Developing Carbon Quantum Dots as a Luminescent Material and Revisiting ECL and LED Absolute Measurement Methods

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry
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Abstract

Luminescent materials play increasingly important roles in our lives. Improvements in these materials’ quantum efficiencies (QEs), costs and toxicity can greatly reduce the power consumption, price and environmental damage to the planet, respectively. Carbon quantum dots (CQDs) and luminescent materials exhibiting thermally activated delayed fluorescence (TADF) are two interesting materials in these aspects. Furthermore, measurements on electro-chemiluminescence (ECL) and electroluminescence of these luminescent materials can quickly evaluate their performance for many applications.

In this thesis, controlled CQD syntheses are revealed beneficial to luminescent materials applications. Their film ECL demonstrated relatively stable anionic and cationic radicals leading to high emission at solid/solution interfaces. It has been found that small sizes of CQDs produce efficient bright white film emissions. It has been discovered that film ECL is similar to the light emitting layer in an LED and can be used to find surface states in these CQDs that are predominantly excited to generate a wavelength-potential applied relationship. Combining this knowledge, small emitting CQDs have been analyzed using synchrotron spectroscopy, where thiophene states were uniquely found and likely caused the solid-state emissions and high cationic radical stability, both through cation-π interactions. For the first time, CQD light emitting devices have been constructed to achieve 1 cd/m² blue emissions for 3 h at a constant potential of 7.0 V. Electrochemical impedance spectroscopy has been utilized to display the possibility that device failure is due to small ions reacting at the highest energy interface. Organic long-persistent ECL has been observed for the first time with several TADF molecules. This phenomenon has occurred likely because of an exciplex being formed with a compound that had a small singlet-triplet energy gap. Two simple methods have been developed in this thesis to determine the absolute ECL QE of compounds along with the common commercial emitter Ru(bpy)³⁺. Finally, an analytical strategy has been established for measuring QEs of indicator and lighting LEDs in high accuracy and precision.

Keywords: Carbon Quantum Dots · Light Emitting Electrochemical Cell · Synchrotron · Electrochemiluminescence · Electroluminescence · Aggregation-Induced Emission · Aggregation-Caused Quenching · Quantum Efficiency · Spectroscopy
Summary for Lay Audience

Luminescent materials play increasingly important roles in our lives. Improvements in these materials’ efficiencies, costs and toxicity can greatly reduce the power consumption, price and environmental damage to the planet, respectively. Carbon quantum dots (CQDs) and luminescent materials exhibiting thermally activated delayed fluorescence (TADF) are two of the interesting materials in these aspects. Furthermore, measurements on electrochemiluminescence (ECL) and electroluminescence of these luminescent materials can quickly evaluate their performance for many applications.

This thesis explores an organic light emitter that can be used in the applications described above with a small organic nanoparticle called a carbon quantum dot (CQD). CQDs were chosen because of low toxicity, simple syntheses and tunable optoelectronic properties. This thesis has an emphasis on the CQDs emission in the solid state and understanding how to increase this solid state emission. This thesis also investigated the best ways to measure absolute emissions to provide comparisons between CQDs and other luminescent material standards.

The results of this thesis found high yield and simple CQD syntheses and CQD purification techniques. The CQD syntheses can also be tailored to achieve unique emission properties such as specific colors, stable radicals or solid state emissions. The nature of these emission properties were also investigated to find chemical moieties that are likely responsible for these emission properties. Finally, combining all previous knowledge, the CQDs were successfully incorporated into a bright blue lighting device that emitted visibly for 3 hours. The work presented here contributed to the knowledge of organic and nanoparticle luminescent materials. This thesis also found novel absolute measurement methods that allows researchers to easily compare research results and raise the impact of their research.
Co-Authorship Statement

This thesis includes material from seven published manuscripts and 2 more planned manuscripts that are presented in Chapters 1, 2, 3, 4, 5, and 6. All manuscripts were and will be finalized and submitted by ZD, except for chapter 4 which was finalized and submitted by Dr. Eli Zysman-Colman.

Section 1.1 and 1.2 were written by J. Adsetts.

Section 1.3 was authored by J. Adsetts and Z. Ding. JA and ZD organized manuscript (ChemPlusChem, 908: 85-94, 2020). JA wrote the manuscript.

Section 2.1 was authored by J. Adsetts, S. Hoesterey, C. Gao, D. Love, and Z. Ding (Langmuir, 36: 14432-14442, 2020). JA and CG synthesized 20 % and 80 % of carbon quantum dots, respectively. JA and SH performed 20 % and 80 % of electrochemiluminescence experiments, respectively. LY, RZ, KC, JW, and DL discussed the results. DL provided industrial insight. JA, RZ, and ZD organized the manuscript. JA wrote the manuscript.

Section 2.2 was authored by J. Adsetts, R. Zhang, L. Yang, K. Chu, J. Wong, D. Love and Z. Ding (Frontiers in Chemistry, 8: 580022, 2020). JA performed all experiments. LY, RZ, KC, JW, and DL discussed the results. DL provided industrial insight. JA, RZ, and ZD organized the manuscript. JA wrote the manuscript.

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Chapter 3 was attributed first co-authorship to J. Adsetts and Z. Whitworth. The manuscript was also authored by K. Chu, L. Yang, C. Zhang, and Z. Ding (ChemElectroChem, 9(5): e202101512, 2022). JA and ZW performed 20 % and 80 % of experiments respectively. JA, ZW, KC, LY, CZ, and ZD discussed the results of the manuscript. JA and ZD organized the manuscript. JA wrote the manuscript.

Chapter 4 was attributed first co-authorship to S. Kumar, P. Tourneur, and J. Adsetts. The manuscript was also authored by M. Wong, P. Rajamalli, D. Chen, R. Lazzaroni, P. Viville, D. Cordes, A. Slawin, Y. Olivier, J. Cornil, Z. Ding and E. Zysman-Colman (Journal of Materials Chemistry C, 10: 4646-4667, 2022). SK, MW, and EZC designed and synthesized the materials. SK, PR and PT carried out the photophysical study. JA performed the electrochemical and ECL studies. DC and AS solved the structure of the single crystals. PO, JC, RL, and PV carried out the theoretical modelling. All electrochemical and electrochemiluminescence writing (some of section ”Electrochemical and Photophysical Properties”, all of sections ”Electrochemiluminescence via the Annihilation Pathway” and onward including some of the
conclusions and some of the supplementary information) was done by JA and ZD. All other writing was done by other authors. SK, JA, DC, YO, JC, ZD and EZC edited manuscript. EZC submitted the final manuscript.

Section 5.1 was authored by J. Adsetts, K. Chu, M. Hesari, J. Ma, and Z. Ding (Analytical Chemistry, 93(33): 11626-11633, 2021). JA and ZD outlined idea for manuscripts. All authors contributed to the creation of the analytical setup and experiments. JA and ZD organized the manuscript. JA wrote the manuscript.

Section 5.2 will be co-authored by J. Adsetts and K. Chu. This section will also be authored by M. Hesari, Z. Whitworth, X. Qin, Z. Zhan and Z. Ding. MH synthesized samples. JA, KC, ZW and ZD planned experiments. JA and MH performed all measurements except for the data in Table 5.2.2 which was performed by XQ and ZZ. JA and KC performed all calculations in duplicate. JA, MH and ZD organized manuscript. JA wrote the manuscript.

Chapter 6 will be co-authored by J. Adsetts and K. Chu. This section will also be authored by D. Love and Z. Ding. JA performed all measurements. JA and KC performed all calculations in duplicate. JA and ZD organized manuscript. JA and DL wrote the manuscript.

Chapter 7 was written by J. Adsetts.
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<td>ACN/MeCN</td>
<td>Acetonitrile</td>
</tr>
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<td>ACQ</td>
<td>Aggregation Caused Quenching</td>
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<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride Reference Electrode</td>
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<td>AIE</td>
<td>Aggregation Induced Emission</td>
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<td>AIECL</td>
<td>Aggregation-Induced Electrochemiluminescence</td>
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<td>ALD</td>
<td>Atomic Layer Deposition</td>
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<td>BODIPY</td>
<td>Boron Dipyrrromethene</td>
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<td>BPO</td>
<td>Benzoyl Peroxide</td>
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<td>CCD</td>
<td>Charged Couple Device</td>
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<td>CCT</td>
<td>Correlated Color Temperature</td>
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<td>CE</td>
<td>Counter Electrode</td>
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<td>CIBS</td>
<td>Crystallization Induced Blue-Shift</td>
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<td>CIE</td>
<td>International Commission on Illumination</td>
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<td>CIECL</td>
<td>Crystallization-Induced Electrochemiluminescence</td>
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<td>Canadian Light Source</td>
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<td>CQD</td>
<td>Carbon Quantum Dots</td>
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<td>CT</td>
<td>Charge Transfer</td>
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<td>Cyclic Voltammetry</td>
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<td>DCM</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<td>DMF</td>
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<td>Differential Pulse Voltammetry</td>
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<td>E\textsubscript{g}</td>
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<td>EIS</td>
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<td>\Delta E\textsubscript{ST}</td>
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<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
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<td>iTMC</td>
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<td>MOF</td>
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<td>OLECL</td>
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<td>OLED</td>
<td>Organic Light Emitting Diode</td>
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<td>OLPL</td>
<td>Organic Long-Persistent Photoluminescence</td>
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<td>PBS</td>
<td>Phosphate Buffer Saline</td>
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<td>PCH</td>
<td>Photon Counting Head</td>
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<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)</td>
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<td>PFY</td>
<td>Partial Fluorescence Yield</td>
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<td>RIM</td>
<td>Restricted Intramolecular Motion</td>
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<td>Restricted Intramolecular Rotation</td>
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<td>Spherical Grating Monochromator</td>
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<td>TADF</td>
<td>Thermally Activated Delayed Fluorescence</td>
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<td>TBAP</td>
<td>Tetrabutylammonium perchlorate</td>
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<td>TBAPF$_6$</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
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<td>TEM</td>
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<td>Total Electron Yield</td>
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<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>TLC</td>
<td>Thin Layer Chromatography</td>
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<td>TPE</td>
<td>Tetraphenylethylene</td>
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<tr>
<td>TPrA</td>
<td>Tri-$n$-propylamine</td>
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<tr>
<td>TTA</td>
<td>Triplet-Triplet Annihilation</td>
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<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
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UV    Ultraviolet

XAS   X-ray Absorption Spectroscopy

XEOL  X-ray Excited Optical Luminescence

XPS   X-ray Photoelectron Spectroscopy

XRD   X-ray Diffraction
Chapter 1

Introduction
Section 1.1

Novel Luminescent Materials

Luminescent materials have gained research interest because of the wide range of possible applications such as light emitting diodes (LEDs),[4,9] plasma displays,[5] and immunoassays.[6,13] Luminescent materials can be excited by many types of energy and will relax this excited energy radiatively in the form of a photon.

There are a wide range of applications that use luminescent materials but excite them using different processes. Photoluminescence (PL) is a photon-in, photon-out process. For example, PL excitation is commonly used in phosphor coatings on high-pressure Hg lamps to remove harmful UV radiation.[17] Another method of excitation is to electrogenerate cationic and anionic radicals that can react together to produce an excited state which can emit light, which is termed electrochemiluminescence (ECL). ECL is commonly used in immunoassays. For instance, Roche Diagnostics has commercially employed ECL in a Ru(bpy)$_3^{2+}$/TPrA system to detect cancer antigens,[13] and has recently developed a sensitive ECL method to detect SARS-COV-2 antigen.[12] Another common method of exciting luminescent materials is to apply direct current to luminescent material films, leading to electroluminescence (EL), commonly used in LEDs.

The most important aspect of any luminescent material is its quantum efficiency (QE) for the desired excitation pathway. A QE is defined differently in every application, but generally the QE is a ratio of the input energy divided by the photon energy output and ideally this QE should be as close to 1 as possible. Non-emissive states, solid emission phenomena and side reactions inside applications all reduce the QE. Generally, these aspects are optimized to increase QE as much as possible to benefit applications. For example, LEDs with higher QEs would have lower power consumption, and immunoassays with higher QEs will achieve higher antigen detection limits. Therefore, when developing a luminescent material researching ways to enhance QE should be a priority.

Another consideration for the QE of luminescent materials is solid film phenomena. For
example, aggregation caused quenching (ACQ) can be debilitating for the QE of luminescent materials. ACQ is caused by the interaction of the excited state with adjacent molecules in a film and these interactions can non-radiatively relax the excited state. Unfortunately, many luminescent materials have reduced QE from this phenomenon preventing implementation for many efficient luminescent materials. Conversely, a phenomenon known as aggregation induced emission (AIE) increases luminescent materials QE in films by restricting intramolecular movement that normally would non-radiatively relax the excited state. Ideally, AIE is enhanced in luminescent materials while ACQ is avoided to maximize the QE of the material. Section 1.3 will cover many more solid film phenomena that have implications in luminescent materials QE for lighting applications.

Another emission phenomenon that increases QE is thermally-activated delayed fluorescence (TADF). Normally, luminescent materials excited states are dictated by spin statistics where 75 and 25 % of excitations are triplet and singlet, respectively. Furthermore, organic materials generally do not emit from triplet states limiting their QE to a maximum of 25 %. However, in TADF luminescent materials the triplet to singlet energy gap is low enough that ambient heat can promote electrons from a triplet to a singlet excited state to theoretically achieve 100 % QE. Therefore, TADF luminescent materials’ have the highest theoretical QE of any luminescent materials.

Luminescent materials can be divided into three categories, namely inorganic, organic and nanomaterials. Inorganic luminescent materials generally have high stability and high efficiency but low tunability. Some examples are Y$_3$Al$_5$O$_{12}$, LaMgB$_3$O$_{10}$ and WS$_2$. Organic luminescent materials are generally tunable and efficient but lack stability and some examples are rubrene, indacenodithieno[3,2-b] thiophene-based copolymer, and MEH-PPV. Nanomaterials are highly tunable, efficient and can be stable and examples include CsPbCl$_3$, CuInS$_2$ and carbon quantum dots (CQDs). Luminescent nanomaterials generally have sizes between 1 and 100 nm with controllable size-property relationships.

CQDs have been gaining research interest because they are simple to synthesize, are nontoxic and have tunable optoelectronic properties. These attractive emission qualities, biocompatibility and optoelectronic tunability raise the question of how CQDs will perform in luminescent material applications.

References


Section 1.2

Thesis Scope

The goal of this thesis is to find and optimize the PL QE, ECL QE and EL QE of CQDs as a luminescent material. This goal involves researching luminescent phenomenon that can change the wavelength and QE of CQDs in each of these applications. Additionally, the absolute ECL QE and absolute EL QE instrumental techniques that benefit and simplify the analyses of luminescent materials are developed.

Chapter 2 focuses on the synthesis of suitable CQDs as a luminescent material. Section 2.1 investigated synthetic pathways to discover AIE and ACQ phenomena in CQDs. Section 2.2 investigated the synthetic relationship between the volume used in hydrothermal syntheses and the resulting size of the CQDs. Then a size-ECL QE relationship will be investigated. Section 2.3 investigated the source of AIE phenomena in the CQDs to guide future synthesis of luminescent materials.

Chapter 3 will build a CQD optoelectronic device. The EL of the CQDs in an optoelectronic device and the performance of the device is compared to literature to understand the CQDs suitability as an EL luminescent material.

Chapter 4 investigates TADF compounds with ECL and highlights how ECL can determine the best ways to implement these TADF compounds into EL luminescent applications.

Chapter 5 revisits the optimal ECL analytical techniques to investigate the ECL QE of luminescent materials. This chapter uses the commercial luminophore Ru(bpy)$_3^{2+}$ to highlight the benefits of these new techniques.

Chapter 6 finds faster ways to analyze the performance of LEC technologies and analyzes state-of-the-art LED technology to highlight the effectiveness of the technique.

Chapter 7 will provide conclusions and perspectives for future work.
Section 1.3

Unique Phenomena in Film
Electrochemiluminescence
1.3.1 Preface

This section reviews recently discovered ECL phenomena for luminescent materials that will impact their applications. These ECL phenomena can change the ECL emission wavelength and QE and thus, must be considered for any new luminescent material.

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1.3.2 Abstract

Electrochemiluminescence (ECL) has proven its analytical powers by its commercial applications of immunoassays and by its interrogation of novel luminophores. This minireview discusses the recent advances in film ECL enhancements controlled by interfacial reactions along with aggregation induced, crystallization induced, matrix coordination induced and nanoparticle surface state emissions. These enhancement phenomena are anticipated to lead to applications toward biological and medical diagnosis. Interfacial ECL enhancements of nanoparticle films and an in-depth analysis of the application of this knowledge into development of optoelectronics will follow. Finally, the novel crystallization induced ECL enhancements and hypochromic shifts made this year are provided. Future analyses of these film ECL enhancement phenomena will provide complementary information for the optimal implementation of next generation luminophores into film lighting applications.

1.3.3 Introduction

Electrogenerated chemiluminescence or electrochemiluminescence (ECL) results from electrogenerated species in an electrolyte solution undergoing electron transfer reactions to produce an excited state that can emit light. First reported in 1964-1965 by Hercules, Bard, and Chandross,[5, 15, 30] ECL has attracted immense scientific attention and has led to the commercial development of sensors,[16, 28, 44] enhanced suitability testing of luminophores in lighting applications,[6] cell imaging,[9] and ultimately produced luminescent optoelectronics.[27] From this discovery, Bard and his colleagues pioneered new ECL systems and mechanis-
tic studies over the last half century. ECL can be produced through the annihilation pathway (where radical anions and cations of a luminophore recombine, scheme provided in Figure 1.3.8) or the coreactant pathway (where an electrochemical reaction between a radical luminophore and an appropriate coreactant occurs, scheme provided in Scheme 1.3.3).

ECL is by no means limited to solution species and can be applied to solid systems by casting luminophore films on electrode surfaces. In fact, ECL film testing yields complementary information to photon-in/photon-out and electrochemical techniques to better gauge a luminophore’s suitability for solid lighting and optoelectronics. This complementary information is represented as relative radical stabilities of luminophores and light enhancement factors, like aggregation induced emission (AIE), crystallization induced emission (CIE), matrix coordination induced emissions (MCIE) and interfacial reactions. Interestingly, these factors can provide orders of magnitude light intensity enhancements if developed properly. In fact, Tang and coworkers in 2001 noticed a 333 times photoluminescent (PL) enhancement between solution and solid state organic silole compounds, and coined the term AIE. Since then this phenomenon has been thoroughly studied and incorporated into most luminophore research.

To summarize, AIE provides PL enhancements when brought from a solution to a solid by the restriction of intramolecular motion (RIM) that can cause non-radiative relaxations of excited states. Furthermore, CIE works by the same principles as AIE, but has exhibited even stronger PL enhancements than AIE by restricting or conforming luminophores in favorable radiative recombination configurations. In opposition, aggregation caused quenching (ACQ) PL effects can problematically quench luminescence when brought from a solution to a solid, typically by short-range molecular interactions such as π-π stacking. ACQ is common in many organic planar luminophores such as benzosiloles, boron dipyrromethene (BODIPY) derivatives, carbazole derivatives, and even carbon quantum dots (CQDs) and must be prevented for efficient solid lighting applications. Until recently, many of these phenomena have not been viewed in ECL film spectroscopy techniques.

This minireview will summarize recent progresses in ECL of films and provide ECL perspectives since the 2005 chapter on semiconductor nanocrystal dispersions and films by Bard, Ding and Myung. Each subsection will focus on one example of ECL film development and phenomenon observation, although some phenomena have been demonstrated in literature multiple times. This singular focus will provide thorough knowledge of each phenomenon and how it can be applied to future systems followed by a discussion of potential applications.
1.3.4 Electrochemiluminescence of Films

This section will review film aggregation induced electrochemiluminescence (AIECL) of films and matrix coordination induced electrochemiluminescence (MCIECL) of films.

AIECL of Carboranyl Carbazole Derivative Films

A strong electron donor that is commonly used in luminophores for light emission enhancement, is carbazole as shown in Scheme 1.3.1. Additionally, carborane and carboranyl compounds are candidates for medical imaging and are used as strong electron acceptors for a donor-acceptor luminophore design. Combining carbazoles with carboranes should remove some inter and intra-molecular interactions that can quench excited states through ACQ mechanisms, thus, producing a strong luminophore.

Yan, Lu and Xu et al. synthesized a series of carbazolyl and carboranyl derivatives with various electron withdrawing groups on both the carbazolyl and carboranyl moieties seen in Scheme 1.3.1.[35] This molecular design provided a platform to elucidate electron donating and electron withdrawing groups and their effects on both the carboranyl and carbazolyl moieties in a film. A T-3 THF solution was dropcasted on a glassy carbon electrode (GCE) and dried in a vacuum oven to produce a T-3 filmed electrode. These films were then studied in different water/THF fractions to see the effects of the interfacial reactions with the coreactants. Water was chosen as a solvent due to all compound’s insolubility in water, which was confirmed by TEM studies (Figure 1.3.1c). Furthermore, water will cause aggregation of the film interface, whereas THF will cause the interfacial luminophores to protrude or even dissolve into solution.

Strong ECL was observed when a 50 mM K$_2$S$_2$O$_8$ coreactant in a 95 % water/THF with a T-3 filmed GCE was brought to a negative potential seen in Figure 1.3.1a (purple trace). Under these conditions, the bulk film can be studied because of the inability of T-3 to dissolve or even protrude into the solution. However, when decreasing the water/THF fraction, the ECL intensity is slowly quenched demonstrating the previously discussed AIECL effect in T-3. Furthermore, in 95 % water/THF with 50 mM K$_2$S$_2$O$_8$, T-2 and T-3 had the only notable ECL emissions indicating AIECL in these compounds. In fact, T-2 and T-3 compounds were the only ones that displayed solid PLQY enhancements over solution PQLY values at 1.8 and 1.2 % respectively. The benzene attached to the carboranyl moiety in T-3 must have aided in the film formation to promote AIECL and solid AIE better than the other moieties studied. Moieties on the carbazolyl moiety seem to only harm solid PL and ECL emissions for T-4, T-5 and T-6. Interestingly, a small bathochromic shift occurred from solid PL to the ECL spectra for T-3 in Figure 1.3.1d, indicating a slightly different emission mechanism. This emission was likely from the surface states of the film, where the surface energy of the aggregates is highest.
Scheme 1.3.1: Synthesized carboranyl carbazole sample series with a specific element guide for the carborabyl moieties of the compounds displayed at the bottom of the figure. Reprinted from ref. [35] with permission from Wiley-VCH.
1.3.4. **Electrochemiluminescence of Films**

Figure 1.3.1: a. ECL-voltage curves of T-3 in 20 %, 60 %, 85 %, and 95 % H2O/THF mixtures and 50 mM K2S2O8. Inset is T-3 dispersed in THF and 95 % water/THF. b. ECL and PL trends with different water fractions for T-3. c. TEM image of T-3 in 95 % water/THF. d. PL spectrum (black) of 10 µM T-3 in 95 % H2O. ECL spectrum (red) of T-3 in 95 % water/THF with 50 mM K2S2O8 as a coreactant. Reprinted from ref. [35] with permission from the Wiley-VCH.

The unique carboranyl carbazoles showed intense AIECL film emissions and provided a great example of film AIECL with purely organic molecules. Modifying carboranyl with carbon moieties proved to be effective in AIECL and AIE PL enhancements and could be the focus of future studies as well.

Interested readers should also be directed to Yan, Lu and Xu et al.’s review on solution and film AIECL for further reading,[36] which covers AIECL advancements of polymer dots,[34] Ir complexes,[12] organic dots,[21] and Pt complexes.[4] It should be noted, that De Cola, Hogan, Aliprandi and coworker discovered 20 times ECL enhancements of square planar Pt(II) complexes comparing solution to solid ECL in late 2017 and to the best of our knowledge, was the first to assign AIECL.[4]

**MCIECL of MOF-Rigidified AIE Luminophores in Films**

Tetraphylethylene (TPE) have been shown to give strong luminescence where some of its derivatives displayed AIE PL phenomenon.[29] TPE derivatives present themselves as strong AIECL candidates. Recently Yuan and Xiao et al. produced a novel way of enhancing film ECL from TPE derivatives by incorporating TPE derivatives as linkers in a metal organic framework (MOF).[18] This rigidification of potential luminophores for PLQY enhancements has been displayed in MOFs previously,[20, 24, 37] but has not been demonstrated in ECL films before.

and can produce a bathochromic shift.
Yuan and Xiao et al. provided a term for this film ECL luminophore rigidification strategy as matrix coordination induced electrochemiluminescence (MCIECL). Furthermore, they highlighted how this material can be used as an ECL quencher replacement strategy for sensitive detection of a breast cancer tumor marker, MUC1.

MOF Hf-TCPBE was synthesized following the steps in Scheme 1.3.2a and had confirmed average particle sizes between 1 and 2 µm. Nafion and the as-synthesized Hf-TCPBE were coated on a GCE with 10 µL of triethylamine (TEA) coreactant being added to a phosphate buffer solution (PBS). The MOF coated electrode attained a high ECL efficiency of 22 % relative to Ru(bpy)$_3^{2+}$ in the same conditions. PBS was chosen as a solvent due to the insolubility of Hf-TCPBE, allowing aggregation effects to be studied. In fact, when analyzing H4TCPBE monomers in PBS with 10 µL of TEA, a relative ECL efficiency of 10 % was gained. The filmed Hf-TCPBE showed a more than two times ECL efficiency enhancement when the luminophore monomers were coordinated in a matrix relative to aggregation. Furthermore, when H4TCPBE monomers were completely dissolved in THF with 10 µL of TEA coreactant, a relative ECL efficiency of $<1$ % was observed. This more than 20 times MCIECL enhancement
from the dissolved monomers to the matrix coordination is ascribed to RIM mechanism occurring in the matrix, thereby enhancing relative ECL performance.

An ECL probe was created from the H4TCPBE material described in Scheme 1.3.2b and 1.3.2c. The probe functioned by a replacement mechanism, where a known ECL quencher, ferrocene (Fc), would be replaced by the molecule of interest to yield concentration related ECL intensities. The probe was found to function effectively in detection of MUC1, a breast cancer tumor marker, through this replacement mechanism. Furthermore, it could detect 0.001-1000 pg/mL of a MUC1 solution and even functioned when tested in human serum samples demonstrating sensitivity and selectivity, respectively.

Film MCIECL seems to be a promising technique for testing potential matrix coordinated luminophores. Further investigations into matrix coordination mechanisms are warranted for their potentials in solid lighting applications. This MCIECL target molecule replacement mechanism also provides a platform for sensitive and selective ECL detection of biological markers.

1.3.5 ECL of Carbon Quantum Dot Films

This section focuses on CQD film ECL insights leading to the implementation of CQDs in optoelectronics.

**ECL of AIE and ACQ CQD Films**

Adsetts and Ding et al. discovered a synthetic route to a CQD sample series that exhibited both ACQ and AIE PL effects seen in Figure 1.3.2a and 1.3.2b which will be referred to as CQD1 and CQD2, respectively.[1] Interestingly, the only compositional difference was found in XPS where CQD1 and CQD2 had sulfur contents above 3.0 % and below 1.5 %, respectively. When analyzing both CQDs in 0.1 g/L CQD solutions with 25 mM K$_2$S$_2$O$_8$ as a coreactant, CQD2 had double the emissions compared to CQD1. In fact, the AIE PL effects were predicted to be responsible for the CQD2 solution ECL enhancement resulting in an AIECL mechanism for solution CQD2 studies. All PL phenomena viewed for the CQD samples transferred to the film and solution ECL studies in these CQD systems and produced drastic interfacial ECL efficiency enhancements.

A CQD film on a GCE was created by casting 10 µg of CQDs, then 1 µg of carboxymethyl chitosan and was tested in PBS, an aqueous solution with 25 mM K$_2$S$_2$O$_8$ as a coreactant. Surprisingly, CQD1 performed better in film coreactant ECL pathways than CQD2 did, where relative ECL efficiencies of 26 and 1 % were observed in Figure 1.3.3b and 1.3.3d, respectively. This drastic efficiency difference was rationalized by luminophores that protrude into the solution from the film|solution interface being primarily responsible for light emissions, instead of
Figure 1.3.2: a. PL excitation spectrum of CQD1 with a detection wavelength of 480 nm (red) and PL emission spectrum excited at a wavelength of 385 nm (blue). b. PL excitation spectrum of solid CQD2 with a detection wavelength of 455 nm (black) and color-coded emission spectra with various excitation wavelengths as labelled. All spectra in both panels are normalized to the highest emission peak in Figure 1.3.4b. Insets are photographs (top) under ambient light and luminescence photographs (bottom) upon irradiation with a 265 nm UV lamp. Reprinted from ref. [1] with permission from the American Chemical Society.

luminophores from inside the film. This interfacial enhancement provided a 26 times efficiency enhancement over CQD films that do not exhibit ACQ PL mechanisms.

Spooling ECL spectroscopy allowed tracking the film coreactant ECL as a function of voltage seen in Figure 1.3.3. For both CQD films, a voltage dependence on the emission is seen where a hypsochromic shift occurs with increasing voltage. The maximum film ECL from CQD1 and CQD2 achieved a red correlated color temperature (CCT) of 2000 K at -2.0 V and a CCT of 2900 K at -1.8 V seen in Figure 1.3.3a and 1.3.3c, respectively. A CCT between 2000-3000 K is akin to an incandescent lightbulb or light emitted from a fire. The CQD2 film ECL (Figure 1.3.3b) displayed a drastic bathochromic shift from the solid PL spectra (Figure 1.3.2b) which is attributed to edge state emission mechanisms of nanoparticles where the potential energy is highest on the surface of the nanoparticles.[31] This higher surface energy can lead to drastic bathochromic shifts and also varies with the nanoparticle size. In fact, the hypsochromic shift seen in spooling ECL spectroscopy is attributed to the size distribution of the particles where different sizes have different energy surface states thereby emitting different wavelengths of light in ECL.

CQD Film ECL, LED Half Cells

Adsetts and Ding et al. performed a CQD size dependent study on the CQD film AIECL and interfacial properties to understand CQD emission mechanisms.[2] The CQD sample series featured a range of sizes from 1.5 to 23.8 nm where the smallest (1.5 nm) and largest (23.8 nm)
Figure 1.3.3: Spooling ECL spectroscopy where light is accumulated over 4 s increments by an Andor SOLIS CCD camera between 0 and -2.00 V over 400 s for CQD1 film a. and between 0 and -1.80 V over 360 s for CQD2 film c. during cyclic voltammograms, respectively. Significant light contributions are colored with their corresponding CIE coordinates and background emission contributions were set to white. b/d. An ECL peak height-voltage curve recorded using a CCD camera with the same system described in Figure 1.3.5a and Figure 1.3.5c, respectively. Reprinted from ref. [1] with permission from the American Chemical Society.
Figure 1.3.4: Spooling ECL spectra from a film of CQD3 with 50 mM K₂S₂O₈ taken with an exposure time of 2 s, a scan rate of 12.5 mV/s, yielding 120 spectra over a 240 s cyclic voltammogram. Color of individual spectra correspond to the RGB coordinates found by converting spectra using CIE coordinates. Spectra that show negligible light are displayed as gray. Insets show the wavelength of light emitted from a. the forward scanning starting at -2.0 V vs. Ag/AgCl and b. the reverse scan starting at -3.0 V vs. Ag/AgCl. Reprinted from ref. [2] with permission from Frontiers in Chemistry.

CQDs were covered in detail and referred to as CQD3 and CQD4 in this subsection.

These CQD film studies were performed the same as section 3.1 but used 50 mM K₂S₂O₈ as a coreactant. Notably, the CQD3 and CQD4 films displayed relative ECL efficiencies of 96 and 3 %, respectively compared to a commercial ECL emitter, Ru(bpy)₃²⁺ in the same conditions. A 32 times ECL efficiency enhancement from the largest to smallest CQDs indicates a size dependency on the ECL efficiency at the interface seen in Figure 1.3.4. A smaller CQD size also provides a higher surface area:bulk ratio providing more opportunities for ECL surface reactions. Interestingly, no correlation between the size of the particles and the solution PLQY was observed, indicating the ECL emissions were through a different mechanism.

The same film systems were tested again with tripropylamine (TPrA) as a coreactant, where the electron accepting nature of the CQD films are tested. However, CQD3 and CQD4 films did not exhibit film ECL emissions in the TPrA coreactant system indicating that the cationic stability or reactivity of the film must be improved. Interestingly, until now in this review, the electron donating nature of films has been exclusively observed. By testing both the electron donating and the electron accepting natures of filmed luminophores with different coreactants in ECL, a greater understanding of a filmed luminophore’s implementation in optoelectronics...
can be gained, Scheme 1.3.3. Furthermore, TPrA and K$_2$S$_2$O$_8$ solutions each form half-light emitting cells with a luminophore film when biased at positive and negative potentials respectively. Charge transfers, interfacial reactions, enhancement phenomena and reactivity can all be studied for potential luminophore films during film ECL.

**ECL and EL of CQD Films**

The CQD interfacial ECL film mechanisms and half-cell investigations so far allowed Chu and Ding et al. to implement the CQD films into an optimized optoelectronic device. Coreactant solution ECL with 5 mM BPO as a coreactant and 0.3 g/L of CQDs revealed a voltage independent emission state with a peak wavelength of 660 nm and an ECL efficiency of 0.01% relative to Ru(bpy)$_3^{2+}$ in the same conditions. The CQDs were then incorporated into the light emitting layer of a light emitting electrochemical cell (LEC) as well as trimethylolpropane ethoxylate (TMPE) and LiTf as a polymer electrolyte where a device schematic is seen in the inset of Figure 1.3.5a. Upon an external bias, holes and electrons are injected at the anode and cathode respectively forming a p-n junction starting at 3 V seen in Figure 1.3.5a. When the injected charges develop a p-n junction around 7 V, the injected charges can radiatively recombine emitting light seen in Figure 1.3.5a. This emission increased until 12.5 V where it steadily declined. This device had a luminous efficiency of 0.14% relative to Ru(bpy)$_3^{2+}$ ECL.
in an annihilation pathway.

The electroluminescence (EL) and solution PL had very different maximum peak wavelengths at 610 and 450 nm. However, the ECL emitted from a CQD solution with 5 mM of BPO had a max wavelength of 660 nm, resembling more closely the EL emissions. This difference in solution ECL coreactant emission and the EL emissions may be the aggregation of particles in a film. In fact, the annihilation ECL mechanism and EL mechanisms are very similar where electrogenerated radicals must interact and undergo an electron transfer between each other to produce an excited state. This excited state can then relax to produce light. This indicates how valuable ECL can be in predicting emissive behaviours of novel luminophores in LECs and other optoelectronic devices.

1.3.6 Crystallization Induced ECL

Although CIE phenomena have been thoroughly studied, most studies are limited to photon in and photon out techniques.[26] ECL complements these techniques by providing a glimpse into the implementation of these materials into solid lighting applications by analyzing and comparing film and solution ECL emissions of materials exhibiting CIE phenomenon. This section will review all recent advances achieved for the film ECL analysis of materials exhibiting CIE effects.

**CIECL of Benzosiloles**

As identified in the introduction, benzosiloles have exhibited CIE PL effects previously, but have not displayed CIECL effects. Yang, Ding and Pagenkopf et al. sought to find CIECL for the first time with a \( \pi \)-conjugated benzosilole complex (BSC).[40] The structures of the studied BSC is displayed in Figure 1.3.6a.

Annihilation ECL was performed on 0.5 mM BSC in DCM with a bare GCE. Weak ECL was found for the solution annihilation with an ECL efficiency of 2 % relative to Ru(bpy)\(_3\)\(^{2+}\) in the same conditions. Furthermore, 5 mM benzoyl peroxide (BPO) was added as a coreactant to enhance the measured ECL. The solution ECL increased, however, the solution ECL efficiency decreased to 0.4 % relative to Ru(bpy)\(_3\)\(^{2+}\) in the same conditions. This coreactant solution emission state at a peak wavelength of 660 nm was thought to be a dimer formed by two BSC molecules reacting together after sufficient redox reactions had occurred, profoundly reducing the ECL efficiency.

The ECL annihilation mechanism was then investigated for the crystalline BSC states by dropcasting BSC on a bare GCE in a 1:1 ACN:water mixture, which was chosen to prevent the film from dissolving off the surface of a GCE. The crystalline state of the BSC on the GCE could be confirmed by simple observation seen in the right inset of Figure 1.3.7, where
Figure 1.3.5: a. A linear voltage sweep of the CQD light emitting electrochemical cell (LEC). Inset is an illustration of the CQD LEC device. b. A 1 mA constant current experiment of the CQD LEC device. c. A 120 s accumulated electroluminescent spectrum of the CQD LEC device. Inset is a color photograph of the CQD device operating. Reprinted from ref. [8] with permission from Wiley-VCH.
Figure 1.3.6: a. Molecular structure of BSC studied. BSC crystals under b. day light and c. under 254 nm irradiation. d. Amorphous BSC on TLC plate (left) and crystalline BSC on quartz (right). Amorphous BSC under e. daylight and f. under 254 nm irradiation. g. Amorphous BSC in silica gel matrix (left) and crystalline BSC on quartz (right). h. PL spectra of amorphous (yellow) and crystalline (orange) BSC along with ECL spectrum of a crystal film electrode in a water/ACN electrolyte solution with 5 mM benzoyl peroxide as a coreactant. Reprinted from ref. [40] with permission from Wiley-VCH.
Figure 1.3.7: Spooling ECL spectra of BSC filmed glassy carbon electrode in the presence of 5 mM benzoyl peroxide coreactant at a scan rate of 0.02 V s⁻¹ with a CCD camera exposure time of 2 s. The left inset displays the PL spectra in solution (gray) and solid state (black). The right inset displays a photo of the electrochemical cell used for the ECL experiments under 265 nm irradiation with an apparent yellow film on the glassy carbon electrode. Reprinted from ref. [40] with permission from Wiley-VCH.
the strong yellow color present in the crystalline PL spectra observed in Figure 1.3.6e-g is also seen here. ECL was not viewed for the filmed annihilation mechanism. The radical species interaction needed for annihilation pathway ECL could not happen in this rigid crystal structure. However, after adding 5 mM benzoyl peroxide (BPO) coreactant, the ECL was greatly enhanced to an ECL efficiency of 7 % relative to Ru(bpy)$_3^{2+}$ in the same conditions producing the spooling ECL spectra seen in Figure 1.3.7. The ECL emission matched that of the crystalline BSC PL seen in Figure 1.3.6h, confirming that the emission occurred from the crystalline state and not an amorphous or solution state allowing the bestowment of the title CIECL. Surprisingly, the BSC film coreactant system was almost four times more efficient than the solution coreactant system, marking a dramatic CIECL film efficiency enhancement. In fact, BSC had a relative PLQY in solution and crystalline states of 2 and 6 %, identifying a CIE PL enhancement effect, mirroring the CIECL enhancements seen.

To the best of our knowledge, this is the first report where CIE enhancement was found for ECL studies. DFT calculations of BSC aimed at investigating this novel observation found that for BSC, a large dihedral angle of 98° existed between intersecting benzosilole planes, indicating J-aggregation resulting in a bathochromic shift of roughly 80 nm. This BSC shows favorable electronic and optical properties as a light emitter in optoelectronic applications.

**CIECL of a Di-Boron Complex**

Understanding and converting common ACQ luminophores, like the previously mentioned BODIPY compounds, through sophisticated synthetic design to AIE luminophores provides more potential luminophores for solid lighting applications. Wong, Wang and Ding et al. explored a newly designed di-boron complex (DBC) seen in Figure 8 for its AIECL and CIECL properties hoping to uncover mechanisms by which solid luminescence could be enhanced.[38]

First the ECL annihilation mechanism was investigated for both the crystalline and solution DBC states by loading 40 µg of DBC on a bare GCE in 2:1 ACN:water and with 0.25 mM DBC in ACN respectively. The 2:1 ACN:water mixture was chosen to prevent the film from dissolving off the surface of the bare GCE. No observable ECL was found for the solution DBC, most likely from non-radiative decay pathways. However, the DBC film had an ECL efficiency of 8.5 % relative to Ru(bpy)$_3^{2+}$ in the same conditions. Next, 5 mM BPO coreactant was added to the same two systems described previously to enhance the ECL seen. Interestingly, the film DBC performed better still than the solution DBC with ECL efficiencies of 4.7 and 0.9 % respectively. Clearly the DBC film showed enhanced ECL relative to the solution ECL, even when considering the increased charge needed for redox reactions in a film due to the film’s inherent resistance relative to the electrolyte solution. Figure 1.3.8 displays the DBC film’s annihilation and coreactant pathways ECL emissions, where ECL peak emissions were found at 570 and 630 nm respectively. These annihilation and coreactant emissions are the same wave-
Figure 1.3.8: Accumulated spectra obtained from the di-boron complex film annihilation pathway (blue trace) with corresponding curve fitting (dashed line) and the spectra obtained from the di-boron complex film coreactant pathway with 5 mM benzoyl peroxide coreactant added in a 2:1 ACN:water solution (black trace). Insets display the mechanisms of ECL emissions for both cases. Reprinted from ref. [38] with permission from Wiley-VCH.
lengths as the crystalline PL (570 nm) and solution PL (627 nm) emissions respectively seen in Figure 1.3.9a. Therefore, the film annihilation ECL seen can be attributed to the emission from the crystalline state of the DBC compound. Interestingly, a rare 57-nm hypsochromic PL shift is seen from the solution to crystalline states of the DBC, which was also observed in the ECL studies, marking the first crystallization induced blue shift (CIBS)-ECL ever reported. CIBS has been viewed before in (4-biphenylyl) phenol dibenzofulvene and organic aromatic acids and esters.[10, 13] It is caused by a gradual RIM due to the spacing of the molecules in a crystal. The coreactant mechanism therefore had emissions at the film|solution interface where luminophores are not in a crystalline structure and emit as if they were in solution. This interfacial ECL reaction mechanism theory was shared by the CQD studies mentioned earlier and is again, caused by higher potential energies on the surface of crystals, nanoparticles or films. Similar to the CQD interfacial enhancement mechanism, a five times ECL efficiency enhancement occurred when comparing film to solution species in the same conditions.

To corroborate these novel findings, DFT calculations were performed on the crystal and gas phase DBC molecules. As predicted, a 0.21 eV excitation energy difference was found between the crystal and gas phase DBC. Interestingly, the culprit for the energy difference was a twisting of the central biphenyl seen in Figure 1.3.9a, disrupting the π-conjugation between the two boron moieties. This disruption provides a more locally excited character for the crystal state while preventing intense π-stacking that could quench emissions, resulting in a rare hypsochromic shift that also enhanced emissions. This DBC has favorable solid electronic and optical properties as well as CIECL enhancements and should be considered for future optoelectronic applications.

1.3.7 Summary and Outlook

In conclusion, we have summarized the recent progress made in developing film ECL techniques for identifying solid state phenomena. This film ECL provides optical, electronic and radical stability information for potential luminophores, thereby complementing photon-in and photon-out techniques and assisting in the implementation of luminophores in solid lighting applications. Recently, film ECL identified MOF-rigidified tetraphenylethylene linkers and carbonayl carbazole compounds exhibiting matrix coordinated and aggregation induced ECL enhancements respectively. CQD films exhibited surface state emissions that significantly enhanced interfacial ECL where this information can be ultimately implemented in an efficient optoelectronic device. A benzosilole and a di-boron complex exhibited crystallization induced ECL enhancement effects where DFT and crystallography identified the causes. Furthermore, discovering and enhancing molecules exhibiting crystallization induced ECL enhancements
Figure 1.3.9: a. PL spectra of the crystalline di-boron complex film (blue trace, excited at 532 nm) and a 0.25 mM di-boron complex ACN solution (black, excited at 254 nm). Inset shows the di-boron complex of interest. b. PL images of di-boron complex after recrystallization (left), gradual mechanical grinding (middle three images from left to right), and after exposure to acetone vapors for 24 hours (right). Reprinted from ref. [38] with permission from Wiley-VCH.
lowers the processing needed to incorporate these crystalline materials into filmed luminophore applications. In fact, ECL has countlessly demonstrated its value as a tool in screening series of compounds for their crystalline and film behaviours and can guide synthetic design for the next generation of solid state luminophore materials. Future luminophore crystalline and film analyses should incorporate ECL as a complementary technique to provide radical stability and enhancement/quenching information.

1.3.8 Acknowledgements

We would like to thank the research support from Natural Sciences and Engineering Research Council Canada (NSERC, DG RGPIN-2013-201697, DG RGPIN-2018-06556, and SPG STPGP-2016-493924), Canada Foundation of Innovation, Ontario Innovation Trust (CFI/OIT, 9040) and Western University. J.R.A. appreciates the support from Ontario graduate scholarships (2018-2021).

References


Chapter 2

Carbon Quantum Dot Synthesis, Characterization and Emission Origins
Section 2.1

ECL of Carbon Quantum Dots Exhibiting Solid State Phenomena
2.1.1 Preface

This section investigates a unique set of synthesized CQDs that fluoresce in the solid state. These solid fluorescing CQDs are compared to an almost identically synthesized CQD that do not emit in the solid state to understand this emission difference. The films were characterized in solution and solid state using electrochemistry, ECL, FTIR, UV-Visible spectroscopy, and PL spectroscopy. Results displayed that solid-state emitting CQDs did not emit as well as non-solid-state emitting CQDs when investigated in ECL emission pathways.

This study highlights the differences between PL and ECL emissions in uniquely emitting CQDs with the end goal of understanding how to achieve the best emissions in PL and ECL luminescent material applications. This study also explores the synthesis-physical property relationships of CQDs as well as identifying their radical stability for EL luminescent material applications.

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2.1.2 Abstract

Carbon quantum dots (CQDs) are anticipated to be a great light emitter candidate in optoelectronic devices such as light-emitting diodes and light-emitting electrochemical cells (LECs). However, studies are scarce on CQD light emission mechanisms including very interesting aspects such as aggregation caused quenching (ACQ) and aggregation induced emission (AIE) in their film bulk and especially interfaces. Here we report CQD synthesis using a one-step hydrothermal synthesis with citric acid and varying concentrations of thiourea as precursors at low costs. Photoluminescence (PL), electrochemistry and electrochemiluminescence (ECL) were utilized to investigate the highest and lowest thiourea concentration samples, or sample 1 and sample 2. It was found that the aqueous dispersion of sample 1 had a quantum yield over 100 times than that of sample 2. Samples 1 and 2 showed ACQ and AIE PL effects in the solid state, respectively. Controlling thiourea concentrations yielded CQDs with different photophysical properties. Sample 2 emitted ECL more intensely than sample 1 in a homogenous solution with S$_2$O$_8^{2-}$ as a coreactant, due to aggregation and interactions of CQD species in solution. Very interestingly, sample 1’s CQD film|S$_2$O$_8^{2-}$ system achieved an ECL efficiency of 26% and emitted roughly 26 times more efficiently than sample 1. Predominant interfacial reactions and surface state emission produced intense white light with a correlated color temperature of 2000 K. Sample 2’s film|S$_2$O$_8^{2-}$ ECL emission was weak due to interfacial quenching. Spooling ECL spectroscopy was utilized to investigate emission mechanisms. However, sample 2’s CQD film|TPrA system had four times higher ECL intensity than that of sample 1, most likely due to π-cation interactions leading to a strong CQD·$^+$ stability. ECL along with PL is a great analytical tool for the CQD emitting layer and its interfaces in future LEC devices.

2.1.3 Introduction

Light emitting diodes (LEDs) are the most popular conventional lighting devices due to their high electrical efficiency.[22, 26, 30, 46] LEDs require several layers cast in an inert atmosphere, each under specific environmental conditions, potentially raising manufacturing costs. Light emitting electrochemical cells (LECs) have received scientific attention recently as a new class of optoelectronic devices since its invention in 1995 by Pei, Heeger and coworkers.[37] LECs can have a single light emitting layer sandwiched between two air-stable electrodes, drastically reducing the manufacturing processes, and also lowering the potential needed to operate the device.[8, 14] Due to the reduced number of layers, LECs show applications in thin stretchable optoelectronics and as a possible alternative to LEDs.[58] LECs operate by organizing a
p-n junction under external voltage bias, where the salt incorporated separates into p-type and n-type regions. After this p-n junction is formed, radiative recombination occurs in the center of these junctions, which requires a certain turn-on time. Due to the reduced number of layers and the movement of ions, the interfaces between these layers are of the utmost importance. With poor electron transportation or side chemical reactions occurring at any interface, an LEC device will not perform well. This light emitting layer is therefore the most important part of the optoelectronic device. Various materials can be used in the light-emitting layer, such as ionic transition metal complexes (iTMCs), host-guest systems, conjugated polymers, and quantum dots (QDs), where carbon quantum dots (CQDs) gain interest in many aspects.

CQDs have simple syntheses, high photoluminescent quantum yields (QY), and strong biocompatibility, making them a great candidate for optoelectronics. As a potential light emitter, CQD emission mechanisms are not fully understood. Surface states that contribute to light emission are loosely defined as functional groups, oxygen-related disorder-induced localized states and surface defects in carbon structures. Aggregation induced emission (AIE) photoluminescence (PL) effects have also been observed in CQDs, which are created when freely rotating ligands release energy non-radioactively in solution but have enhanced emissions when aggregated. Xu, Lu, Yan and their coworkers reported aggregation-induced electrochemiluminescence (ECL) of carboranyl carbazoles organic dots in aqueous media was for the first time. AIE behavior of tetraphenylethylene derivatives and their supramolecular aggregates at interfaces were only reported recently and only with PL studies. To the best of our knowledge, CQD AIE behavior at interfaces was never analyzed using ECL spectroscopy. Understanding these mysterious mechanisms for CQD light emission in solutions, solids and at interfaces will assist in the optimal implementation of CQDs in optoelectronic and sensing applications. To this end, ECL attracts interest, where redox properties are exploited to yield light from iTMCs, QDs, polymer systems, and organic molecules, all in solution and/or film|solution interfaces. Additionally, the electrode can be either a cathode or an anode, allowing emissions originating from the anionic or cationic radicals of luminophores, respectively, to mimic the operations of cathodic and anodic regions in optoelectronics.

Herein, a controlled synthesis method is revealed toward an avenue to AIE CQDs with citric acid and thiourea precursors. PL effects are reported in solution and films to understand these phenomena. Electrochemistry and ECL are found very useful to identify states and reactions responsible for emissions in both CQD dispersions and CQD film systems. ECL studies of CQD film|solution systems reveal interfacial behaviour that can be exploited to gain physical insight into operation reactions and mechanisms in optoelectronic and sensing devices.
2.1.4 Materials and Methods

Chemicals and Materials

Citric acid [(C₆H₈O₇), 99 %], tris (2,2-bipyridyl)-dichlororuthenium (II) hexahydrate [(Ru(bpy)₃Cl₂·6 H₂O), 97 %], potassium persulfate [(K₂S₂O₈), 99.99 %], quinine sulfate (2:1) dihydrate [((C₂₀H₂₄N₂O₄S·0.5H₂O) · H₂O), 99 %], tripropylamine [(C₉H₂₁N), >98 %], and disodium phosphate [(Na₂HPO₄), >99 %]) were all purchased from Sigma Aldrich (Missisauga, ON). Potassium chloride [(KCl), >99 %] was supplied Alfa Aesar (Ward Hill, MA). Carboxymethyl chitosan [(C₂₀H₃₇N₃O₁₄), 99 %] was obtained from Santa Cruz Biotechnology, Inc. (Dallas, TX). Monosodium phosphate [(NaH₂PO₄), >99 %] and thiourea [(CH₄N₂S), 99.5 %] were purchased from Caledon Laboratory Chemicals (Georgetown, ON).

Synthesis of CQDs

CQDs were prepared via the hydrothermal method using citric acid and varying amounts of thiourea as precursors. Briefly, 1.0 g of citric acid and 1.5 g of thiourea were combined with 20 mL of water in a Teflon-lined autoclave. This autoclave was placed into an oven and held at a constant temperature of 160 °C for 12 hours. The obtained products were blue or colourless depending on the sample. After cooling to room temperature, the CQD solution was dialyzed for 8 hours to remove impurities and obtain greater particle size uniformity. A dialysis bag with a molecular cut-off weight of 1000 Daltons and Milli-Q water were used, which was replaced at least 6 times over at least an 8 h period. The purified solution was subjected to lyophilization to remove water and to obtain a powdered form of the CQDs. For optimization purposes, the same procedure was repeated varying the amount of thiourea added (1 g, 0.5 g, 0.25 g and 0.1 g) whilst keeping all other parameters constant to produce five CQD samples in total.

Material Characterizations

A Varian Cary 50 spectrophotometer (Varian Inc., Cary, North Carolina) with Cary WinUV software (Varian Inc., Cary, North Carolina) was used for UV-visible spectroscopy. The photoluminescence spectra were collected using a Fluorolog spectrometer (QM-7/2005, Photon Technology International (PTI), London, ON) and PTI FelixGX software (PTI). An excitation slit width and an emission slit width of 0.25 mm and 0.1 mm were set, respectively. UV-visible and PL spectra were both collected using the same transparent, quartz cuvette with a 1 cm path length for all experiments. The PL quantum yield (QY) was calculated using the following equation:

\[
\Phi_{PL} = \frac{I_x \cdot A_{st}}{I_{st} \cdot A_x \cdot \left(\frac{n_x}{n_{st}}\right)^2} \cdot 100\% \tag{2.1.1}
\]
where $I$ is the integrated PL emission intensity of an emission spectra excited at 350 nm, $A$ is the absorbance value measured at 350 nm from the UV-Vis spectra, $\eta$ is the refractive index of the solvent, $x$ and $st$ refer to the CQDs and the PL standard quinine sulfate in 0.1 M HCl, respectively.

In the collection of the solid PL, CQD powder was adhered to 2-sided Scotch tape (410B, 3M, Saint Paul, MN) on a custom-made platform with a 45-degree angle between the excitation beam and emission collection. The emission and excitation slit widths were optimized for the signal strength. The 2-sided tape was chosen from many brands to have a very low PL signal. The CQDs were spread over the tape to prevent the excitation beam from exciting the tape.

**Electrochemistry and ECL Setup**

All electrochemistry and electrochemiluminescence experiments were carried out in an electrochemical cell with a three-electrode configuration consisting of a glassy carbon working electrode, a custom Ag/AgCl reference electrode and a Pt coil counter electrode. A buffer solution containing a supporting electrolyte to ensure conductivity of the solution ($0.1 \text{ M phosphate buffer solution} + 0.1 \text{ M KCl, pH} = 7.4$), was used to disperse CQDs in a Pyrex cylindrical tube.

Prior to each experiment, the Pyrex cell was soaked in an isopropanol/KOH bath, then an HCl acid bath to remove previous residual chemicals, then rinsed with ultrapure water and dried in an oven at 120 °C. The Pt counter electrode was sonicated in ultrapure water and dried in the same oven. The Ag/AgCl reference electrode was stored in dark drawer to prevent photodegradation. To ensure cleanliness of the glassy carbon working electrode (GCE, 7 mm$^2$ disc), the surface was sufficiently polished, first, with a 0.3 $\mu$m alumina slurry, sonicated in ultrapure water, and second, with a 0.05 $\mu$m alumina slurry. To confirm cleanliness, the electrode was tested in a ferricyanide solution to attain a roughly +/- 67 mV difference between the cathodic and anodic peaks of the electrochemical reduction reaction.

All analyzed CQD samples were investigated by depositing a film atop a GCE for creating a modified electrode. To achieve this, a 1 g/L solution of CQDs was prepared by sonicating the CQDs in milli-Q water. Using a micropipette, 10 $\mu$g of CQDs were drop-cast atop the working electrode and left to sit at room temperature. After a drying time of 4 hours, 1 $\mu$g of carboxymethyl chitosan was drop-cast on top of the previously applied layer to ensure that the CQD layer was tightly adhered to the electrode surface and to prevent the CQDs from dispersing into the buffer solution. Chitosan does not dissolve in aqueous solutions in a pH above 6.5 and allows CQD films to interact with the solution. [36, 39–41, 48, 49, 56] The buffer solution was degassed with argon for 30 minutes prior to electrochemical testing.

The three-electrode system, driven by the electrochemical workstation (CHI 610A, CH instruments, Austin TX), was placed inside a dark box and hung over a photomultiplier tube (PMT, R928, Hamamatsu, Japan) where the PMT was held at -750 V with a high-voltage
power supply. A flat Pyrex window at the bottom of the electrochemical cell allowed for collection of most ECL light generated in the vicinity of the working electrode by the PMT as photocurrent. The photocurrent measured by the PMT was transformed into a voltage signal by a picoammeter (Keithley 6487, Cleveland, OH). The voltage signal from the picoammeter, and the voltage and current signal from the electrochemical workstation were all sent through a data acquisition board (DAQ 6036E, National Instruments, Austin TX) in tandem to a computer where experimental data was recorded using a custom LabVIEW (National Instruments) program. The relative efficiency of the ECL emission was calculated by finding the charge input and the photocurrent output for this specific experimental setup and comparing these values to a common commercial ECL emitter system, Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$, by the following equation:

$$\Phi_{ECL} = \frac{\int ECL dt}{\int Current dt} \times 100\%$$

where $st$ and $x$ refer to the standard Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ and the CQD/S$_2$O$_8^{2-}$ systems, respectively.

For ECL spectroscopy, a lens was utilized to collimate ECL light onto the spectrometer (Acton 2300i, Princeton Instruments Inc., Trenton, NJ)/CCD camera (Model DV420-BV, Andor Technology, UK) set, allowing sensitive light detection from CQD films on the electrode surface while filtering out any other potential light sources. Accumulation and spooling ECL spectra were taken by coupling the spectrometer with a CCD camera to the electrochemical workstation. The CCD camera was cooled to -65 °C prior to data acquisition. The exposure time and the number of kinetic series were optimized to produce the clearest ECL spectra. In all experiments, the spectrometer wavelength was calibrated using a mercury-argon lamp (HG-1, Ocean Optics, Largo, FL) at a wavelength of 546.07 nm.

Light was removed as much as possible using blackout curtains from interfering with light accumulation during both the PMT and CCD measurements.

### 2.1.5 Results and Discussion

#### CQD Synthesis

Citric acid was used as a carbon precursor and thiourea was added as a S, N dopant precursor in hydrothermal synthesis with a modified recipe and temperature, based on the facts
of high degree carbonization\cite{10} and PL enhancements\cite{13, 23, 56} via doping, respectively. Five samples were created with varying thiourea concentrations between 5 and 75 g/L during synthesis. Product yields were determined by comparing the precursors and final CQD product weights, being all above 27\%. This hydrothermal synthesis method produced grams of CQDs, which is a requirement for intensive optoelectronic and ECL testing, and a great improvement relative to other CQD synthetic methods. The produced CQDs had visually dramatic differences where samples made with increased thiourea were dark green, and CQDs synthesized with reduced thiourea were bright white, almost translucent. This visual difference suggests chemical or particle interaction differences in the CQDs. In this paper, the samples made with 75 g/L and 5 g/L thiourea were studied and are named from now on as sample 1 and sample 2, respectively.

**Solution Photoluminescence Emissions**

UV-visible absorptions of at least 5 CQD concentrations with absorbance below 0.1 and the corresponding PL emission spectra for the same 5 solutions were used to generate a quantum yield (QY) relative to quinine sulfate for every CQD sample, summarized in Table 2.1.1. Sample 1 had the highest relative QY at 6\%. As the thiourea concentration during synthesis decreased, the QYs decreased to 0.01\% for sample 2. The samples made with higher concentrations of thiourea during synthesis showed a dramatic increase in QY likely due to an increase in S and N incorporation into the bulk structure. This finding corroborates previous studies that increased doping with N and S heteroatoms enhances PL emissions for CQDs made with pyrolysis and hydrothermal methods.\cite{13, 23, 56}

In Figure 2.1.1a, the maximum PL emission (brown trace) and excitation (black trace) wavelengths in aqueous solution for sample 1 were found to be 465 nm and 385 nm, respectively. Another weak peak wavelength at 310 nm was observed for sample 1. Color-coded emission spectra in Figure 2.1.1a also display an excitation wavelength dependence. Gan et al. studied excitation wavelength dependence in CQDs, and concluded that excitation wavelength dependence does not originate from one state, instead coming from many emission centers.\cite{13} A second emission peak is viewed at 640 nm with growing intensity as the excitation wavelength is increased, which indicates lower energy emission states. Figure 2.1.1b displays sample 2 dispersed in water with a weak PL signal. These peaks had a maximum excitation (red trace) and emission (blue trace) wavelength of 310 and 410 nm, respectively. Sample 2 lacks the intense excitation and emission peaks that sample 1 has at 465 and 385 nm, respectively. The absence of the 380 nm excitation pathway left sample 2 with debilitated PL emissions, and yielded an emission that was roughly 20 times less intense than sample 1. CQDs’ most intense emission has been associated with quantum confinement effects (QCE), arising from extended π-electron systems that are finely adjusted by surface states, an effect well-studied by
2.1.5. **Results and Discussion**

Figure 2.1.1: a. PL excitation spectrum of sample 1 solution with a detection wavelength of 465 nm (black) and color-coded emission spectra with various excitation wavelengths as labelled. b. PL excitation spectrum of sample 2 solution with a detection wavelength of 380 nm (red) and PL emission spectrum of sample 2 excited at a wavelength of 310 nm (blue). All spectra in both panels are normalized to the highest emission peak in Figure 2.1.1a.

Liu et. al. [28] The solution PL differences between sample 1 and 2 are attributed to the only difference, thiourea precursor concentration. This lack of emissions may also have been caused by relaxation of excited electrons by intramolecular motion, where an excited electron decays by non-radiative recombination pathways like vibrations, rotations or translations of surface moieties. This synthetic difference could have created different non-radiative recombination pathways leading to a quenching of sample 2’s excited state by intramolecular motions.

**Solid Photoluminescence Emissions**

Figure 2.1.2a displays the solid-state PL spectra from sample 1. An excitation scan seen in red was obtained with maximum excitation peaks centered roughly at 340 and 390 nm, closely resembling those of the solution PL excitation peaks. The emission spectrum seen in blue shows two peaks at 480 nm and 640 nm. These peaks also closely resemble those of the solution, but the relative height of the 640 nm peak in the solid state increased dramatically.

Figure 2.1.2b shows the solid-state emission and excitation spectra from sample 2 in black and yellow respectively. The maximum emission and excitation peaks were found at 380 and 450 nm respectively, similar to those of sample 1 solution. In contrast to sample 1, sample 2 did not have an emission peak above 600 nm, indicating different emission centers as described below. Although contentious, previous studies into CQD PL emission mechanisms have shown origination from surface defects, which in turn is loosely defined as oxygen-related disorder-induced localized states and functional groups. [13] [28] The PL peak differences can be attributed to disparate surface defects arising from divergent thiourea precursor concentra-
Figure 2.1.2: a. PL excitation spectrum of sample 1 solid with a detection wavelength of 480 nm (red) and PL emission spectrum excited at a wavelength of 385 nm (blue). b. PL excitation spectrum of sample 2 solid with a detection wavelength of 455 nm (black) and color-coded emission spectra with various excitation wavelengths as labelled. All spectra in both panels are normalized to the highest emission peak in Figure 2.1.2b.

In summary, sample 1 has more intense solution PL emission and sample 2 has more intense solid emissions. We propose that the PL enhancement seen from the solid sample 2 is due to aggregation-induced emission (AIE). The surface defects that prohibit sample 2’s emissions in solution due to non-radiative relaxation pathways such as rotational or vibrational intramolecular movements, are restricted in a solid allowing emission as a solid. We also propose that the solid PL quenching for sample 1, is caused by fluorophores interactions between particles. Energy transfers, $\pi$-$\pi$ stacking, and charge transfers can result from these interactions, creating aggregation-caused quenching (ACQ) of PL emission pathways. ACQ and AIE effects could be selectively created on CQDs if different surface defects on each CQD contributed differently to the CQD PL mechanism. These varying surface defects could have resulted from the differences in thiourea precursor concentration. The above observations demonstrated control over this AIE and ACQ CQD nature by varying the thiourea concentration during synthesis.

In fact, AIE and ACQ effects have been demonstrated in CQDs: without dopants,[57] synthesized from melamine, dithiosalicylic acid where the AIE nature was attributed to disulfide
2.1.5. Results and Discussion

Figure 2.1.3: a. ECL-voltage curve of CQD sample 1 dispersion and the corresponding cyclic voltammogram. b. Differential pulse voltammograms of Sample 1 dispersion with those of blank solution in dotted black. c. ECL-voltage curve of CQD sample 2 dispersion with the corresponding cyclic voltammogram. d. Differential pulse voltammograms of Sample 2 dispersion with those of blank solution in dotted black.

bonds created during synthesis that can cause non-radiative recombination in solution through intramolecular movements,[50] and in CQDs synthesized from citric acid, cysteine and KCl where KCl was determined to play a vital role in the AIE nature.[27] These effects and their influence on interfacial CQD film interactions will be studied with CQD film|coreactant ECL and dispersed CQD coreactant ECL systems.

Electrochemistry and ECL of CQD Dispersion in Annihilation Pathway

The electrochemistry of the CQD samples at a concentration of 0.1 g/L was explored in a 0.1 M PBS solution at a pH of 7.5, also containing 0.1 M KCl as an electrolyte in Figure 2.1.3, by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). For sample 1, in Figure 2.1.3a, an irreversible reduction can be seen around -1.6 V and an irreversible oxidation can be observed around 1.3 V. These redox reactions can be elucidated better by removal of background current using DPV. In Figure 2.1.3b, the irreversible redox reactions can be shown more clearly at -1.55 V and 1.30 V. Figure 2.1.3c displays a CV curve where a slightly more reversible oxidation and reduction can be seen at 1.30 and -1.60 V respectively.
Figure 2.1.4: a. An ECL-voltage curve with 0.1 g/L of sample 1 and 100 mM K$_2$S$_2$O$_8$ added and the corresponding cyclic voltammogram. b. An ECL-voltage curve with 0.1 g/L of sample 2 and 100 mM K$_2$S$_2$O$_8$ added and the corresponding cyclic voltammogram.

Figure 2.1.3d elucidates this electrochemistry more clearly by DPV where the same peaks are found more evident than in Figure 2.1.3c.

During the CV, ECL-voltage curves were measured as shown by the blue traces in Figure 2.1.3a and 2.1.3c. Light typically is produced by an excited state species (CQD*) that relaxes to the ground state. This CQD* is produced by an electron transfer between the electrogenerated CQD$^+$ and CQD$^-$ in the vicinity of the electrode. Both sample 1 and sample 2 do not produce appreciable photocurrent suggesting poor radical stability and/or reactivity of one or both electrogenerated intermediates.

**ECL of CQD Dispersion in Persulfate Coreactant Systems**

K$_2$S$_2$O$_8$ was added to test the electron donating nature of CQD$^-$ in the so-called coreactant pathway. In this coreactant pathway, the lifetime of the radical poses less of an issue, because both species required to produce CQD* are generated at similar potentials or almost the same time. Figure 2.1.4a and 2.1.4b displays S$_2$O$_8^{2-}$ being reduced, beginning around -0.7 V, which then turns into SO$_4^{2-}$ and SO$_4^{2-}$. When CQD is reduced, the SO$_4^{-}$ can accept an electron from CQD$^-$ to produce SO$_4^{2-}$ and CQD* that can relax and emit light. Photocurrent was detected at an onset potential of -1.3 V from this CQD* species in both Figure 2.1.4a and 2.1.4b. In both cases, the photocurrent as the ECL intensity never reached a maximum before the scan started to reverse. This was to prevent the solvent from degrading and participating in the redox reactions occurring. The max photocurrent of sample 1 and sample 2 dispersed in aqueous electrolyte solution is 38 nA and 77 nA, respectively. The stronger light emission for sample 2 could be due to aggregates forming in the solution or the restriction of movement of the fluorophores that would emit in the solution, producing an AIE effect.
2.1.5. Results and Discussion

Figure 2.1.5: a. ECL-voltage curve of a GCE modified with 10 µg of sample 1 in 50 mM K$_2$S$_2$O$_8$ and the corresponding cyclic voltammogram. b. ECL-voltage curve of a GCE modified with 10 µg of sample 2 in 50 mM K$_2$S$_2$O$_8$ and the corresponding cyclic voltammogram.

<table>
<thead>
<tr>
<th>Persulfate Concentration (mM)</th>
<th>Sample 1 Film Relative ECL Efficiency (%)</th>
<th>Sample 2 Film Relative ECL Efficiency (%)</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>2</td>
<td>0</td>
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<tr>
<td>25</td>
<td>26</td>
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<td>4</td>
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<tr>
<td>75</td>
<td>13</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2.1.1: ECL Efficiency data from ECL-voltage curves of CQD film|S$_2$O$_8^{2-}$ systems determined and with eq. 2.1.2, relative to a Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ system.

ECL of Interfacial CQD Films|Persulfate Coreactant Systems

Figure 2.1.5a and 2.1.5b exhibits sample 1 and 2, respectively, cast as films and interacting with a solution of S$_2$O$_8^{2-}$. Following similar mechanism as CQD dispersion/S$_2$O$_8^{2-}$ coreactant systems in section 2.2.4, sample 1 showed much higher ECL intensity than sample 2. Photocurrent initiation started around -1.3 V in both cases, coinciding with the CQD$^-$ generation onset potential. Like before, sample 2 photocurrent generation did not reach a maximum before solvent reduction occurred. Sample 1 reached a photocurrent maximum at -1.7 V, most likely due to the consumption of SO$_4^{2-}$ species near the electrode surface. The photocurrent decreased from this point forward, due to the higher consumption of these species relative to the production of these species.

Further, ECL efficiencies of the CQD films were determined relative to a common ECL emitter with the same coreactant, Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ with eq. 2.1.2. The charge input and
integrated photocurrent from both systems was measured according to eq. 2.1.2 and the concentration of \( S_2O_8^{2-} \) was optimized in terms of ECL efficiency, where these results are summarized in Table 2.1.1. With 25 mM persulafate coreactant, sample 1 film has an ECL efficiency of 26% while that of sample 2 film reaches only to 1%. This ECL efficiency difference was more than 25 times, most likely caused by reaction of the \( SO_4^{2-} \) with the surface of the CQD film, and CQD* relaxation occurring at the CQD film|solution interface, instead of the bulk film. This interaction with sample 1 caused stronger emissions compared to sample 2’s, that may primarily emit from luminophores that have restricted intramolecular relaxation pathways (rotational and vibrational). Further evidence is provided by the relatively weak ECL emission from sample 2 compared to sample 1, that mirrors the solution state photoluminescence differences between sample 2 and sample 1 observed in Figure 2.1.1. One of our previous studies has shown that doping CQD’s and testing their film ECL can cause a roughly 10 times increase in the ECL emissions.[56] The difference here is much greater than 10 times, and the CQDs was doped, but possibly to a lesser extent. Decreased heteroatom doping may contribute to this difference, but the chief difference in ECL efficiency is likely the AIE and ACQ effects at the film|solution interface for each CQD sample.

With potentials below -1.55 V for a CQD Film|\( S_2O_8^{2-} \) system, CQD\(^{−} \) and \( SO_4^{2−} \) are produced and CQD\(^{−} \) can donate an electron to \( SO_4^{−} \) to create CQD* and \( SO_4^{2−} \), where CQD* can emit light. The CQD Film|\( S_2O_8^{2−} \) system is similar to testing the n-type behaviors of optoelectronic materials and mirror the emissions typically seen in optoelectronic mechanisms, where the light emitter donates an electron to an electron acceptor, creating an excited state that emits light. The ECL testing of films provides a superior analytical method in finding the applicability of potential light emitters in optoelectronics. Specifically, the ECL testing of films demonstrates where the light emitter is lacking in stability to guide future synthesis strategies for potential light emitters or to guide manufacturing strategies for optoelectronic device construction.

**Spooling ECL Spectroscopy of CQD Films|Persulfate**

The sample 1-modified GCE system previously used was analyzed by accumulating light every 4 s, yielding 100 spectra over a 400 s scan seen in Figure 2.1.6a and 2.1.6b.

The colors of individual spectra were created by converting emitted light to perceived RGB values using a CIE calculator, from which this color was applied to the individual spectrum. Figure 2.1.6a illustrates the center wavelength of each spectrum with a vertical line. The first emission at -1.33 V is centered at 890 nm and as the potential is increased, the emission wavelength reaches a maximum at 740 nm at -2.0 V (Figure 2.1.6), similar to other reported CQD ECL studies.[7, 9, 42] This wavelength variability has been attributed to multiple emissive states that are accessed when increasing the overpotential applied to the CQD
Figure 2.1.6: Spooling ECL spectroscopy, using the same electrochemical systems described in Figure 2.1.5a and Figure 2.1.5b, except light is accumulated over 4 s increments by an Andor SOLIS CCD camera between 0 and -2.00 V over 400 s for sample 1 film (a) and between 0 and -1.80 V over 360 s for sample 2 film (c) during a cyclic voltammogram, respectively. Significant light contributions are colored with their corresponding CIE coordinates and background emission contributions were set to white. b/d. An ECL peak height-voltage curve recorded using a CCD camera with the same system described in Figure 2.1.6a and Figure 2.1.6c, respectively.
After the maximum ECL intensity at -2.0 V, the maximum wavelength red shifts back until the emission stops around -1.6 V. The lowest and highest light emissions are seen in Figure 2.1.6a in the CIE inset figure. For ECL emissions at an onset potential of -1.33 V and for the ECL maximum at -2.0 V, the CIE (x,y) coordinates are (0.36, 0.35) and (0.50, 0.39), respectively. These two emissions correspond closely to correlated color temperatures (CCT) of 5000 and 2000 K. These CCT are appropriate for indoor lighting settings and are tunable depending on the potential applied to the system. This voltage dependent wavelength emission is attractive for optoelectronic applications. Figure 2.1.6b shows the peak ECL intensity acquired from all the spectra in Figure 2.1.6a and displayed versus voltage. The initial emissions at -1.33 V match well with the emissions seen when capturing light with the PMT, and the reverse scan shows a fast decay, most likely due to the continuous consumption and then depletion of the persulfate radicals that were produced before the CQDs were reduced.

Figures 2.1.6c and 2.1.6d display the electrochemical system described in Figure 2.1.5b, but with light accumulated over 4 s increments with a CCD camera during a 360 s cyclic voltammogram between 0 and -1.8 V. Unlike sample 1, the emission color was much more yellow in character. At -1.33 V and -1.80 V, the CIE (x,y) coordinates are (0.44, 0.41) and (0.42, 0.38) respectively. These two emissions correspond closely to correlated color temperatures (CCT) of 3500 and 2900 K. These CCTs are also appropriate for indoor lighting settings and are slightly less tunable than sample 1, depending on the potential applied to the system. The first emissions at -1.33 V are centered at 770 nm and as the potential is increased, the emission wavelength reaches a maximum at 710 nm at -1.8 V. Figure 2.1.6d shows the maximum intensity of the ECL for every spectrum accumulated, which matches the one seen in Figure 2.1.5b. Again, emissions are seen starting at -1.33 V, correlating to the reduction of CQDs, and the ECL intensity drops when returning from -1.8 V.

These ECL emissions are red shifted 300 nm relative to the PL spectra. This CQD-specific phenomenon is well-documented and reported elsewhere, where essentially PL is emitted from core states and ECL is emitted from surface states. The wavelength maximum variability in sample 2 was significantly reduced compared to sample 1 observed in Figure 2.1.6a and c. In fact, sample 2 and sample 1 films had a wavelength maximum range covering 60 nm between 710-770 nm and 150 nm between 740-890 nm, respectively. This difference may have arisen from the availability of the CQD film interface to interact with SO$_4$\(^{-}\) species in solution, to produce light. The luminophores for the sample 1 film emit strongly when their excited states are not influenced by inter- or intra-molecular forces, which can happen at the CQD film|solution interface where CQD luminophores can protrude into solution and interact with solution species. This allows for a wide range of emission states available, creating a highly tunable color from the applied potential relative to the AIE emitting sample 2. This wavelength
variability observation also supports the 26 times lower ECL efficiency from sample 2 compared to sample 1. The higher intensity and efficiency from the ACQ CQD sample 1 could have been caused by the enhanced radiative recombination of excited species created between interactions of the protruding luminophores at the CQD film/solution interface.

**ECL of Interfacial CQD Film/TPrA Coreactant Pathways**

Figure 2.1.7a and b shows the same sample 1 modified and sample 2 modified electrode system as Figure 2.1.4a and b, respectively, but with 100 mM of TPrA added to the system. TPrA oxidation is seen roughly at 0.70 V in each case, which creates TPrA$^+$, that further loses a proton to form TPrA$^-$. TPrA$^-$ can reduce electrogenerated CQD$^+$ to create CQD*, that may relax to emit light. Weak ECL intensity was observed in the deep blue trace of Figure 2.1.7a or b after CQD$^+$ and TPrA$^-$ were being generated in solution. The CQD$^+$ of sample 1 and 2 are not very stable or reactive upon meeting with TPrA$^-$ to produce CQD* and subsequently light. For future studies of CQDs as a light emitter for optoelectronics, CQD$^+$ must be stabilized. It appears that the emission from sample 2 film is slightly stronger than that from sample 1’s film, with photocurrent maxima of 4 nA and 1 nA, respectively. A reason for the emission differences between sample 1 and 2 film/solution systems containing TPrA could be AIE effects. Aggregated CQD$^+$ could be stabilized by π-stacking between aromatic constituents in sample 2 film, allowing a longer lifetime radical compared to sample 1 film, much the same mechanism as AIE emission principles. Stabilizing a CQD$^+$ allows more interactions with TPrA$^-$ to produce CQD* and subsequently light. Future optoelectronic devices made with AIE-active materials and low cationic radical stability may benefit from cation-π interactions to enhance the stability of the cationic radical effectively increasing emission efficiencies. This effect has been viewed before in AIE optoelectronic applications, but the culprit was not assumed to be radical stabilization, but rather general stabilization achieved by through-space charge transfer
between non-covalent $\pi-\pi$ interactions. \[20\]

A CQD Film|$T\text{PrA}$ at a potential of 1.3 V system is similar to the CQD Film|$S_2\text{O}_8^{2-}$, but CQD$^+$ and $T\text{PrA}^-$ are generated instead of CQD$^-$ and $S\text{O}_4^{2-}$. This system also probes the p-type behaviors of optoelectronic materials and mirror the emissions typically seen in optoelectronic mechanisms. An optoelectronic p-type material would have an oxidized light emitter accept an electron from an electron donor in a way that creates an excited state, which can ultimately emit light, the same as the ECL system described above.

### 2.1.6 Conclusion

CQDs were synthesized using a one-step hydrothermal synthesis with citric acid and varying concentrations of thiourea as precursors. The highest and lowest thiourea concentration samples, or sample 1 and sample 2, showed ACQ and AIE PL effects in the solid state, respectively, while sample 1 aqueous dispersion demonstrated a much higher PL emission than that of sample 2. These different emission centers are attributed to the sole divergence of the samples, the thiourea concentration during synthesis. Solution ECL investigations of these CQDs displayed that sample 2 emitted twice stronger than sample 1, most likely due to aggregation of the CQDs in dispersion. Very interestingly, the CQD film|$S_2\text{O}_8^{2-}$ coreactant system revealed that sample 1’s ECL was 26 times more efficient than that of sample 2, resulting from the dominant reaction of electrogenerated surface monolayer CQD radical anions with $S\text{O}_4^{2-}$ electroproduced in solution. The sample 1 CQD film|$S_2\text{O}_8^{2-}$ system also displayed extreme wavelength variability (+/- 150 nm) versus potential due to exposed, non-aggregated surface states being accessed at higher potentials, ultimately emitting reddish white with a correlated color temperature of roughly 2000 K. The high ECL efficiency of sample 1 film indicates great promise for optoelectronic devices such as LECs. Interfacial ECL studies of CQD films have identified ECL enhancements from non-aggregated surface defects of the CQD’s in the film. Interfacial emission mechanisms were revealed by means of spooling ECL spectroscopy was utilized to investigate. Sample 2’s CQD film|$T\text{PrA}$ coreactant system generated four times the maximum ECL compared to sample 1 in the same conditions, likely due to cation-$\pi$ interface interactions between CQD$^+$ and $\pi$-electrons in the carbon core. These cation-$\pi$ interactions can stabilize a luminophore’s cationic radical in optoelectronic applications, thereby increasing lighting efficiencies.

The above investigations illustrate well that ECL along with PL is a great tool to obtain physical insight into AIE and ACQ mechanisms, as well as interfacial reaction processes.
2.1.7 Acknowledgements

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References


Section 2.2

White Electrochemiluminescence From Carbon Quantum Dot Films
2.2.1 Preface

This section synthesizes and characterizes the PL and ECL emission properties of a large number of CQDs to understand which CQDs emit the strongest PL and ECL and why. The CQD emission pathway is mysterious and poorly understood where no consensus existed for CQD synthesis techniques, CQD emission origins or CQD properties.

The main purpose of this chapter is to discover CQDs with ideal properties for PL and ECL luminescent material applications.

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2.2.2 Abstract

Carbon quantum dots (CQDs) were manufactured from citric acid and urea in a gram-scale synthesis with a controlled size range between 1.5 - 23.8 nm. The size control was realized by varying volume of the precursor solution in a hydrothermal synthesis method. The prepared CQDs were investigated using electrochemiluminescence (ECL) spectroscopy at interfaces of their electrode films and electrolyte solution containing coreactants rather than conventional optoelectronic tests, providing an in-depth analysis of light-emission mechanisms of the so-called half-cells. ECL from the CQD films with TPrA and K$_2$S$_2$O$_8$ as coreactants provided information on the stability of the CQD radicals in the films. It was discovered that CQD\textsuperscript{−} has a powerful electron donating nature to sulfate radical to generate ECL at a relative efficiency of 96 % to the Ru(bpy)$_3$Cl$_2$/K$_2$S$_2$O$_8$ coreactant system, indicating a strong performance in light emitting applications. The smaller the CQD particle sizes, the higher the ECL efficiency of the film interface, most likely due to the increased presence of surface states per mass of CQDs. Spooling ECL spectroscopy of the system revealed a potential-dependent light emission starting from a deep red color to blue-shifted intensity maximum, cool bright white emission with a correlated color temperature of 3200 K. This color temperature is appropriate for most indoor lighting applications. The above ECL results provide information on the performance of CQD light emitters in films, permitting preliminary screening for light emitting candidates in optoelectronic applications. This screening has revealed CQD films as a powerful and cost-effective light emitting layer toward lighting devices for indoor applications.

2.2.3 Introduction

Light emitting diodes (LEDs) have been at the forefront of lighting technology recently due to their decreased energy consumption over compact fluorescent and incandescent lighting technologies. LEDs are conventionally created by depositing many subsequent layers on a substrate in an inert atmosphere.[13, 21, 41, 44] Reducing the number of layers and removing the need for an inert atmosphere can drastically reduce manufacturing costs and operating voltages. To this end, light emitting electrochemical cells (LEC or LEEC) have gained interest. LECs conventionally comprise of two electrodes sandwiching a light-emitting layer that is responsible for both charge transport and light emission.[10] The light-emitting layer typically consists of a polymer and a salt with an incorporated light emitter which organizes itself into a p-i-n junction when an external bias is applied.[13] The polymer electrolyte reduces bulk and contact resistance over LEDs, allowing for air-stable and thicker electrodes. The reduced potentials and simpler device structure allow for cost-effective manufacturing of energy efficient
lighting sources.

Developing LEC technology as a consumer product requires research efforts into analyzing the light emitting layer for its polymer consistency, ion rearrangement efficiency, and electron and hole transportation for radiative recombination. Preeminent, a light emitter with poor electron and hole accepting properties will not efficiently radiatively recombine in an LEC, thus not producing substantial light. To understand the solid-state electron and hole transport mechanisms in light emitters, we propose using electrochemiluminescence (ECL) spectroscopy. ECL spectroscopy effectively allows electron and hole transport mechanisms to be studied independently in a light emitting material, as well as the efficiency and characteristics of the resulting radiative recombination for both electron and hole mechanisms. Studying these processes separately allows for a more fundamental understanding of the overall process of light emission from LECs, which allows the light emission to be improved upon.

An attractive light emitting material for use in LECs is carbon quantum dots (CQDs) due to efficient visible light emissions with tunable band gaps.[2, 4, 42] First discovered in 2004,[37] CQDs are small sp² and sp³ containing carbon particles that have been defined as having sizes below 20 nm, low toxicity, strong chemical stability and a resistance to photobleaching.[3, 12, 17] This study will use ECL spectroscopy to evaluate CQD’s electron and hole transport mechanisms and the efficiency of radiative recombination for applications in optoelectronic. Further, light emission characteristics are reported and the suitability for indoor lighting applications will be assessed.

2.2.4 Materials and Methods

Chemicals and Materials

Citric acid (C₆H₈O₇, 99 %), urea (OCN₂H₄, 99 %), potassium persulfate (K₉S₃O₈, 99.99 %), sodium phosphate monobasic dehydrate (NaH₂PO₄·2 H₂O, ≥ 99 %) and tris(2,2’-bipyridyl)-dichlororuthenium(II) hexahydrate [Ru(bpy)₃Cl₂·6 H₂O, 97 %] were purchased from Sigma-Aldrich (Mississauga, ON). Sodium phosphate (Na₂HPO₄, anhydrous, ≥ 99 %) was obtained from Caledon Laboratory Chemicals (Georgetown, ON). Potassium chloride (KCl, 99 %) was purchased from Alfa Aesar (Ward Hill, MA). Carboxymethylchitosan [(C₁₀H₁₉NO₆)n, 99 %] was obtained from Santa Cruz Biotechnology, Inc. (Dallas, TX). Ultrapurewater (18.2 MΩ cm, Milli-Q, Millipore) was used to prepare solutions. All chemical reagents were used as received and stored at room temperature with exception of carboxymethylchitosan stored at 4 °C.

CQD Synthesis Procedure

The following synthesis procedure was for CQD20, but all syntheses follow the same general format. 1.0 g citric acid and 2.0 g of urea were combined in 20 mL of Milli-Q water and
sonicated for 10 minutes inside a 100 mL Teflon-lined autoclave were acquired from Shanghai Yuhua Instruments Equipment Co. Ltd, China. The steel autoclave used supports pressures up to 3 MPa. A VWR oven was set to warm up to and hold 160 °C for 6 h, then cool down. After returning to room temperature, the autoclaves were removed from the oven and the solution was transferred directly into dialysis bags (Shanghai Yuanye Bio-Technology Co. Ltd, China) with a molecular weight cut-off (MWCO) of 1000 Da. The solution was left to dialyze for at least 8 h, with the water being changed at least 6 times. The solutions were transferred to 50 mL Falcon tubes (VWR Canada), where a Kimwipe was attached to the top with an elastic band. This Falcon tube containing solution was frozen in liquid nitrogen and placed in a Labconco Lyophilizer at -84 °C for at 48 h. The obtained product was light and fluffy and ranged from dark green to brown in color. These CQDs were stored in a refrigerator, sealed with Parafilm, and wrapped in tinfoil to prevent any degradation until use.

**CQD Characterization**

High resolution transmission electron microscopy (HRTEM) images were obtained using a FEI Tecnai G2 F20 microscope. CQD powders were pressed in a sample holder of a FTIR spectrometer (VERTEX 70 FTIR) and measured. Background and blank measurements were taken before spectra acquisition to better identify peaks. UV-visible measurements were taken from 900-200 nm using a Varian Cary 50 Spectrophotometer (Varian Inc., North Carolina) where background and blank measurements were taken before for more accurate results. Photoluminescence (PL) measurements were taken with a Fluorolog spectrophotometer (QM-7/2005, Photon Technology International, London. ON) with excitation and emission slit widths of 0.25 and 0.1 mm respectively. All UV-Visible and PL measurements were done in a 10 mm quartz cuvette. The PL quantum yield (QY) was calculated using the following equation:

\[ \Phi_{PL} = \frac{I_x}{I_{st}} \cdot \frac{A_{st}}{A_x} \cdot \left( \frac{\eta_x}{\eta_{st}} \right)^2 \cdot 100\% \]  \hspace{1cm} (2.2.1)

where I is the integrated PL emission intensity of an emission spectra excited at 350 nm, A is the absorbance value measured at 350 nm from the UV-Vis spectra, \( \eta \) is the refractive index of the solvent, \( x \) and \( st \) refer to the CQDs and the PL standard quinine sulfate in 0.1 M HCl, respectively. \[8\]

**Electrochemical and ECL Experiments**

A custom photovoltaic cell, with a flat Pyrex window at the bottom to allow the detection of light generated at the working electrode, was used for all electrochemical and ECL tests. A three-electrode electrochemical system, where a glassy carbon electrode (GCE, 3 mm diameter) was used as the working electrode, a platinum wire was used as the counter electrode
2.2.4. Materials and Methods

and a custom Ag/AgCl electrode calibrated to an industrial standard Ag/AgCl electrode before operation. All solutions used were 0.1 M phosphate buffer solution (PBS) (pH = 7.5) with 0.1 M KCl as the supporting electrolyte. Dissolved oxygen in the system had a quenching effect for CQD ECL systems seen previously, so all solutions were purged for 15 minutes with argon gas before use. For ECL film studies, 3 mg of GQDs were dispersed in 3 mL of Milli-Q water and were sonicated for ten minutes before use. 10 µL of this solution was dropcasted onto the surface of the GCE and dried at room temperature. To prevent the GQDs dispersing in solution, a thin layer of Chitosan (0.2 mg mL⁻¹ in Milli-Q water, 5 µL) was dropcasted on top of the GQD layer.

The voltammetric ECL curves were obtained using an electrochemical workstation (CHI 610A, CH Instruments, Austin TX) coupled with a photomultiplier tube (PMT, R928, Hamamatsu, Japan) held at -750 V with a high-voltage power supply. The ECL generated at the working electrode was collected by the PMT under the Pyrex window at the bottom of the electrochemical cell. The photocurrent from the PMT was transferred into a voltage signal by a picoammeter (Keithley 6487, Cleveland, OH). This signal, along with the potential and current signals from the electrochemical workstation were simultaneously sent through a data acquisition board (DAQ 6036E, National Instruments, Austin TX) to the computer where the entire data was recorded by a homemade LabVIEW (National Instruments) program. Spooling ECL spectra were acquired by placing the electrochemical cell into a holder on a spectrograph (Cornerstone 260 M, Newport, Irvine, CA) with a CCD camera (Andor 420BV, Andor Technology, UK) cooled to -55 °C. The exposure time and the number of kinetic series were optimized to produce the clearest ECL spectra. A carefully measured lens system which collimated light produced from the entire electrode surface (7 mm² circle) onto the spectrometer/CCD camera set, permitting sensitive detection of light emitted from CQD films on the electrode surface while ignoring any other potential light sources. During all experiments, lights in the experimentation room were turned off to reduce the background interference from ambient light. Blackout curtains were also positioned at the entryways to the lab and surrounding the electrochemical cell setup to prevent possible interference. Wavelength calibration was conducted using a mercury-argon source (HG-1, Ocean Optics, Largo, FL). The relative efficiency of the ECL emission was calculated by finding the charge input and the photocurrent output for this specific experimental setup and comparing these values to the gold standard ECL emitter systems, Ru(bpy)₃²⁺ for annihilation systems and Ru(bpy)₃²⁺/S₂O₈²⁻ for CQD/S₂O₈²⁻ systems by the following equation:
\[ \Phi_{ECL} = \left( \frac{\int ECL \, dt}{\int Current \, dt} \right) \times 100\% \]

(2.2.2)

where \( s_t \) and \( x \) refer to the standard \( \text{Ru(bpy)}_3^{2+}/\text{S}_2\text{O}_8^{2-} \) and the CQD/\( \text{S}_2\text{O}_8^{2-} \) systems, respectively, for example.

2.2.5 Results and Discussion

Carbon Quantum Dot Synthesis

Citric acid was used as the carbon precursor for a hydrothermal synthesis owing to the efficient carbonization as reported by Chen et al.[7] Urea was added as a nitrogen-dopant (N-doped) following our previous studies that report photoluminescence (PL) and ECL enhancements of nitrogen- and sulfur-doped graphene quantum dots.[43] Typical hydrothermal procedures were used as following: 50.0 g/L of citric acid and 100.0 g/L of urea in varying volumes of ultrapure water in a 100 mL Teflon-lined autoclave and heated at 160 °C for 6 h. The volumes of the starting precursor solution were 10 mL (CQD10), 20 mL (CQD20), 30 mL (CQD30), and 40 mL (CQD40), respectively, as seen in Scheme 2.1.1. The obtained product was dark purple in color with no solid precipitate produced. This solution was packed into dialysis bags with molecular weight cutoffs of 1000 Da and placed into 2 L beakers full of Milli-Q water stirred for 8 h. Water was replaced at least every 90 minutes. This technique has been shown to remove all unreacted precursors.[43] The dialyzed solution was then freeze-dried using a lyophilizer for at least three days to fully dehydrate product. Yields of synthesis were measured by comparing the weight of starting precursors to the weight of the final CQD product and were found to be between 27 and 35 %. An important factor for light emitting materials is the bulk low-cost synthesis of the product.[19] This synthesis procedure created gram-scale CQDs with constant oven settings and constant starting solutions providing ideal conditions for scaling up synthesis of CQDs with tunable light emitting properties. A simple and gram-scaled synthesis is always required for optimization and testing of the CQDs’ PL, ECL, and EL emission properties for future device testing. The cost and simplicity of CQDs described above make them an attractive light emitting material for future LEC devices over single molecules (such as highly luminescent carbozolyl derivatives),[22] copolymers (e.g., commercially available PPV copolymer PDY-132),[11] and ionic transition metal complexes (such as Ru, Ir and Cd derivatives)[10] typically used for LECs and optoelectronics. Using
2.2.5. Results and Discussion

Scheme 2.2.1: A schematic representation of CQD synthesis from precursors (a). HRTEM images of the created CQDs with carbon arrangements identified, synthesized with autoclave volumes of 10, 20 mL (b) and 30, 40 mL (c).

100 mL volume autoclaves allows gram scale syntheses of CQDs instead of smaller laboratory amounts.

Characterization

High-resolution transmission electron microscopy (HRTEM) images of CQD10 (Figure 2.2.1a), CQD20 (Figure 2.2.1b), CQD30 (Figure 2.2.1c), and CQD40 (Figure 2.2.1d) were measured (ca. 120 individual CQDs per synthesis method) and statistical distributions were calculated and fitted to the size distributions. These CQDs displayed average sizes of 1.5 ± 0.3, 2.9 ± 1.2, 7.6 ± 3.1, and 23.8 ± 15.2 nm, respectively. The HRTEM results have revealed a gradual increase in the particle size with augmented volume of the starting solution for the hydrothermal synthesis. The increased carbon precursor appears to increase both the size distribution and particle size, Figure 2.2.1a to d. Reaction temperature, time and concentration were all kept constant in this study yielding unique CQDs. The above results revealed a relationship between volume of CQD precursors (i.e. precursor availability) and size of CQDs produced, leading to a simple way to control the size of particles during hydrothermal syntheses. While using different volumes of the same starting solution, higher volumes created larger CQDs. This may be due to increased autoclave pressure increasing energy available during synthesis or availability of reagents available for CQD synthesis. This finding would be significant, because varying CQD sizes has been shown to change physical and electronic properties.[24, 32] This control is highly attractive for light emitting materials of future LEC devices.
Figure 2.2.1: HRTEM analysis of a. CQD10, b. CQD20, c. CQD30, and d. CQD40, each containing a high-resolution image of a single CQD and a histogram of particle sizes fitted with a Gaussian distribution.
2.2.5. Results and Discussion

Figure 2.2.2: FTIR spectra of CQD10 (black), CQD20 (blue), CQD30 (green), and CQD40 (red).

The HRTEM insets of each panel in Figures 2.2.1 are higher-resolution images of individual CQDs. The insets of Figures 2.2.1a and 2.2.1b show 0.23 nm graphene lattice spacing corresponding to a (1120) graphene lattice plane.[5] We observed this graphitic nature in CQD10 and CQD20, while the larger CQD30 and CQD40 do not. This could be due to increased availability of carbon precursor favoring a disordered carbon sp$^3$ structure, or a heterogeneous mixture of different carbon bonding states. The differences in the carbon bonding of the CQDs has been shown to affect the emission of CQDs.[24, 33] Increased graphene nature can cause greater electron delocalization and stabilize the CQDs. The differences in core states observed by HRTEM should provide changes in the emissions of these CQDs, allowing for a platform to optimize the CQDs for electrogenerated chemiluminescence (ECL) for use in optoelectronics. Also, for optoelectronic devices, consistency and packing of CQD films are of the upmost importance since film quality and properties often rely on particle sizes and how they interact.[34] For this reason, the size and crystallinity of CQDs are paramount and should greatly affect the optoelectronic performance of the films.

FTIR of CQDs

Absorptions between 3000-3300 cm$^{-1}$ correspond to O-H and N-H vibrations as demonstrated in Figure 2.2.2. The broadness of these peaks indicates that the O-H and N-H are involved in extensive hydrogen bonding between the CQDs. Prolonged freeze-drying at temperatures below 200 K ensure all water was sublimated out from these CQDs, leaving these broad peak identities to be exclusively from hydrogen bonding between CQDs. A broad band
at 2800 cm\(^{-1}\) shows C-H stretching characteristic of carbon structures. The bands at 1700 and 1600 cm\(^{-1}\) were attributed to the vibrational absorption bands of -COOH and C=C, respectively. All FTIR peak assignments agree well with those previously reported studies for CQDs prepared differently.\[6, 30, 43\] No obvious functional group differences between CQDs are demonstrated in Figure 2.2.2, which suggests synthesis mechanism is similar, if not the same, between all samples. Although contentious, studies demonstrate evidence for PL and ECL emissions from CQDs originating from surface defects, which are loosely defined as functional groups, oxygen-related disorder-induced localized states and surface defects in carbon structures.\[12, 20\] Smaller CQDs have more functional groups per mass compared to larger CQD particles due to the increased surface area per mass. The variation in functional group density might lead to differences in the PL, ECL, and EL emissions of CQD films.

**Tauc Plot**

Figure 2.2.3a. displays a Tauc plot generated from the UV-Vis spectrum of a CQD10 water dispersion at a concentration of 5 g/L. The Tauc plot displays \( (ah\nu)^{1/r} \) versus \( h\nu \), where \( a \), \( h \), and \( \nu \) are absorption coefficients and \( r \) is the power factor used as a fit for the set of data. The best fit found from Figure 2.2.3b is \( r = \frac{1}{2} \) indicating a direct band gap transformations for the CQD dispersion, aligning well with previously found results on CQDs prepared with hydrothermal methods.\[15, 23, 39\] This direct band gap will favor radiative recombination benefitting electrochemiluminescence quantum yield and electroluminescent device efficiencies, as well as achieving strong PL efficiencies. Linear extrapolations to the x-intercept from the low energy side of peaks in the Tauc plots yields specific absorption energies. Tauc plots were constructed
for all CQDs, where information gained is summarized in Table 2.2.1. The lowest energy absorption in the visible range is due to the band gap of the CQDs. No large deviations from the optical band gap are observed indicating that the state responsible for emission, is shared among all CQDs, despite carbon core state differences. An intrinsic semiconductor $E_g$ is illustrated at 3.19 eV corresponding to a blue wavelength absorption. The second peak, common in every Tauc plot generated around 4.60 eV, corresponds to non-bonding electrons in oxygen and nitrogen dopant atoms in the carbon sp$^2$ or sp$^3$ matrix. [15] A significant 0.3 eV shift is noticed comparing the $E_{n\pi^*}$ between CQD10 and the other CQDs in this study. CQD20, CQD30 and CQD40’s $E_{n\pi^*}$ is more pronounced indicating a larger number of dopants in the carbon sp$^2$ or sp$^3$ matrix. As noticed above, the IR spectra showed no significant variations in functional groups between the synthesized CQDs, thus, following this, the difference in absorptions between the CQDs could be from nitrogen and oxygen dopants in the carbon matrix. The small average size of the CQD10 could prevent the development of more complex types of non-bonding electron containing nitrogen moieties (i.e. pyridinic, and pyrrolic moieties). The subtle differences between syntheses parameters may yield more complex nitrogen doping, leading to different absorptions between some CQDs. This absorption difference may be attributed to a higher presence of non-bonding electron moieties found in larger carbon matrices. The third absorption, which was common to all CQDs, was the $E_{\pi\pi^*}$ transition attributed to the sp$^2$ electrons in the carbon matrix. [20]

**Excitation Wavelength Dependence of Photoluminescence**

By tracking the maximum emission wavelength at 440 nm while varying the excitation wavelength, the black trace in Figure 2.2.3b is attained for a 5 g/L CQDs dispersion in Milli-Q water. There appears to be two excitation peaks where the maximum PL emission was achieved by using a 360 nm excitation wavelength. Excitations from 330 to 400 nm and their resulting emissions color-coded are shown in Figure 2.2.3b, where excitation wavelengths outside this range were omitted due to negligible light emission. The same emission maximum wavelength was achieved from all excitation wavelengths tested within a reasonable error. This excitation wavelength independence suggests that one emission pathway is responsible for almost all band gap emissions from the CQDs. Despite the size distribution of the CQDs, no large differences were noticed in the PL emission, suggesting a common emission state. Liu et al. has demonstrated that short wavelength emissions originate from core states and long wavelength emissions emit from surface states. [24] Gan et al. has also summarized recent findings, describing a common hypothesis that CQDs have an emission resulting from 1-5 nm sp$^2$ carbon centers in all CQD sizes. [12] Despite large size differences, common emission states existed between all CQDs providing evidence for small sp$^2$ light emitting sites dominating PL emissions in these CQDs. It is plausible that the emissions seen in Figure 2.2.3b do not resemble
surface state emissions or are dominated solely by one surface state emission due to their excitation wavelength independent emissions.

The peak emission wavelength is seen at 440 nm for CQD10 in Figure 2.2.3b. Other maximum wavelengths obtained from PL are summarized in Table 2.2.1 for all CQDs in this study. The maximum emission wavelengths from all CQDs are similar with small variation centered around 440 nm. Using the International Commission on Illumination (CIE) standards for relating color to light through red, green and blue (RGB) contributions, the PL emission from all CQDs corresponds to a deep blue emission with CIE coordinates of (0.15, 0.09). This shows that large size differences of the CQDs has little effect on the PL wavelength emitted.

PL quantum yields ($\Phi_{PL}$) of all CQDs were determined relative to a quinine sulfate standard ($\text{C}_4\text{H}_5\text{N}_4\text{O}_8\text{S}$), chosen for its similar emission wavelength to CQDs at 450 nm. The most efficient emission is from CQD20 with a relative quantum yield $\Phi_{PL}$ of 34 %. There was no obvious trend in the emission efficiency of the four prepared CQDs. This shows that large size differences of the CQDs have little effect on the PL efficiency. The intensity of the emission and direct band gap nature of the CQDs, show favorable properties for efficient emission in optoelectronic devices.

### Electrochemistry of CQD Dispersions

The electrochemistry of dispersed CQD10 in solution was explored in a supporting electrolyte solution of 0.1 M phosphate buffer solution (PBS) at a pH of 7.5 containing 0.1 M KCl by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) as shown in Figure 2.2.4a and b, respectively with a glassy carbon electrode (GCE) as the working electrode. All potentials are referred to vs. Ag/AgCl. In Figure 2.2.4a, a small irreversible peak at -1.7 V and a small slightly more reversible peak can be seen at 1.3 V. To better illustrate these peaks, DPV is shown in Figure 2.2.4b where background current is suppressed more than in CV. Comparing the red and black traces, representing a solution with and without dispersed CQD10s, respectively, the redox reaction features of the CQDs are well displayed in Figure

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$E_g$ (eV)</th>
<th>$E_{n-\pi^*}$ (eV)</th>
<th>$E_{\pi-\pi^*}$ (eV)</th>
<th>Emission $\lambda_{PL}$ (nm)</th>
<th>$\Phi$ (% vs. Quinine Sulfate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQD10</td>
<td>3.18</td>
<td>4.60</td>
<td>5.10</td>
<td>440</td>
<td>18</td>
</tr>
<tr>
<td>CQD20</td>
<td>3.26</td>
<td>4.93</td>
<td>5.60</td>
<td>435</td>
<td>34</td>
</tr>
<tr>
<td>CQD30</td>
<td>3.25</td>
<td>4.90</td>
<td>5.63</td>
<td>435</td>
<td>18</td>
</tr>
<tr>
<td>CQD40</td>
<td>3.16</td>
<td>4.90</td>
<td>5.60</td>
<td>435</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 2.2.1: Electronic information on all CQDs samples.
Figure 2.2.4: a. Cyclic voltammogram ECL-voltage curve and b. differential pulse voltammograms of 0.1 g/L CQD10 in 0.1 M phosphate buffer solution at pH of 7.5 with 0.1 M KCl as the supporting electrolyte. Cyclic voltammograms (red) and voltammetric ECL curves (blue) of a CQD-modified glassy carbon electrode in the same solution without (c) and with (d) 100 mM K$_2$S$_2$O$_8$ where “*” denotes the onset of photocurrent. ECL intensity is represented by the photocurrent measured with a photomultiplier tube biased at -750 V.
The cathodic scan shows two irreversible reductions at formal potentials -1.4 V and -1.7 V. All redox reactions, which may be hidden in the charging current seen in the CV in Figure 2.2.4a, are very evident in the DPV in Figure 2.2.4b. The anodic scan illustrates a slightly more reversible oxidation at a formal potential of 1.3 V. Finding these CQD redox reactions allows for the testing of ECL emission.

The electrochemical gap (EE\textsubscript{g}) between the first reduction peak and the first oxidation peak for CQD10 is found to be 2.65 V. In fact, EE\textsubscript{g} was determined from converting the peak difference in volts to electron volts (eV) using an elementary charge of 1 for an electron. DPV was performed on all CQDs in this study and the corresponding EE\textsubscript{g} data is summarized in Table 2.2.2. The larger CQDs (CQD30 and CQD40) had larger EE\textsubscript{g}’s likely due to the difference in carbon core. The larger and unordered carbon nature may increase the energy needed for redox reactions in solution due to significant electron transfer barriers between differently ordered states.

To understand the electrochemical behaviour of a CQD film, GCEs were modified by casting 10 µg of CQDs, followed by 1 µg of chitosan to prevent CQDs dispersing in electrolyte solution. Chitosan was used to allow the CQD film to interact with solution species, and for its stability in neutral solution pH (pH > 6.5).[9, 14, 25–29, 35, 36, 38, 40] CV scans show a strong reduction centered at -1.7 V and a slight oxidation peak at 1.3 V in Figure 2.2.4c. The reduction and oxidation peaks match those in the CQD dispersion with larger values probably due to the overall film resistivity increase from chitosan at the solid/electrolyte interface. In polymer films, and more specifically chitosan films, the width of the electrochemical peaks in CVs increases and the current sensitivity towards analytes in the film decreases.[26] The position of the reduction and oxidation peaks shifts to higher energies relative to analyte in dispersion, owing to the hydrophobic regions of the polymer matrix interacting with the solution and complexing with analytes.[18] Despite these matrix effects when using chitosan, analytical responses typically improve for analyte detection and electrochemical stability improves for films, all relative to solution. The above redox peak positions would guide us to perform and understand ECL experiments.

**ECL in Annihilation Pathway**

The light produced during the CV tests involving both the CQDs dispersion and its film are shown by the voltammetric ECL curves in blue in Figure 2.2.4a and 2.2.4c. This light typically comes from the relaxation of CQD*, which is produced via the reaction between CQD\textsuperscript{+} and CQD\textsuperscript{-} at the working electrode surface. Negligible ECL as photocurrent was seen in both CQD dispersion (Figure 2.2.4a) and film cases (Figure 2.2.4c) possibly indicating poor electron transfers between CQD radical cations and anions in the film and solution or the poor stability of one or both these electrogenerated intermediates.
### Results and Discussion

#### Table 2.2.2: Electrochemical information from differential pulse voltammetry of all CQDs in solution and electrochemiluminescence testing of CQD films in the presence of potassium persulfate.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Electrochemical Gap (EE&lt;sub&gt;e&lt;/sub&gt;) (eV)</th>
<th>Maximum Emission λ&lt;sub&gt;ECL&lt;/sub&gt; (nm)</th>
<th>Φ&lt;sub&gt;ECL&lt;/sub&gt; (% vs. Ru(bpy)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt; with 50 mM K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQD10</td>
<td>2.65</td>
<td>680</td>
<td>96 ± 27</td>
</tr>
<tr>
<td>CQD20</td>
<td>2.71</td>
<td>670</td>
<td>23 ± 15</td>
</tr>
<tr>
<td>CQD30</td>
<td>3.01</td>
<td>750</td>
<td>2 ± 0.2</td>
</tr>
<tr>
<td>CQD40</td>
<td>2.90</td>
<td>750</td>
<td>3 ± 0.2</td>
</tr>
</tbody>
</table>

**Two Half Light-Emitting Electrochemical Cells**

To test if the CQD film ECL could be enhanced, coreactants were added. Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was added to produce sulfate radical anions that can interact with CQD<sup>-</sup> for ECL generation (Figure 2.2.4d) while tripropylamine (TPrA) was used to electrogenerate TPrA radicals which can interact with CQD<sup>+</sup> for ECL production. These two coreactants are easily transferred into radicals at close redox potentials to CQDs, producing both highly oxidizing (sulfate radical anion) or reducing (TPrA radical) intermediates in the vicinity of the working electrode for further reactions for light emission. Here, the two coreactants are newly utilized to form two half light-emitting electrochemical cells for testing CQD films as potential lighting layers.

**ECL of CQD Film/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Interface as the First Half Light-Emitting Electrochemical Cell**

K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is added to solution to test the stability and electron donating nature of CQD<sup>-</sup> in film that is formed at -1.70 V, Figure 2.2.4d. When biasing potentials more negative than -1.50 V, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is electrochemically reduced, then S<sub>2</sub>O<sub>8</sub><sup>2-</sup> loses SO<sub>4</sub><sup>2-</sup> to become SO<sub>4</sub><sup>-</sup> (Figure 2.2.4d). SO<sub>4</sub><sup>-</sup> may react with a CQD<sup>-</sup> upon generation at -1.70 V to create CQD* that may release energy in the form of light (Scheme 2.2.2a). Significant photocurrent as ECL intensity was seen starting at -1.8 V, due to the formation of CQD* as illustrated by the blue trace in Figure 2.2.4d. The maximum ECL intensity reaches 530 nA at -2.7 V due to a buildup of both CQD<sup>-</sup> and SO<sub>4</sub><sup>-</sup> reacting to produce CQD*. When the potential was scanned in the reverse direction, the ECL intensity continues to decrease due to the depletion of SO<sub>4</sub><sup>-</sup> at the CQD film/solution interface. A blank sample containing only the coreactant and solvent showed negligible amounts of light at the same potentials allowing the light emission to be attributed to the CQD<sup>-</sup> reaction with SO<sub>4</sub><sup>-</sup> to produce CQD*, then giving off light.

Further, the relative efficiency of the ECL emission from the half-cell was determined by
finding the charge input and the ECL output for the specific experimental setup and comparing these values to a common commercial ECL emitter system, Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$. ECL efficiency tests on this half-cell were performed from solutions with varying concentrations of K$_2$S$_2$O$_8$ yielding an optimized ECL efficiency at a concentration of 50 mM. Other three CQDs were also used to make film electrodes as above and their half-cells were tested. ECL efficiencies were calculated for all CQDs at many S$_2$O$_8^{2-}$ concentrations but only the optimized 50 mM concentration results were summarized in Table 2.2.2. The smallest CQDs (CQD10) showed the best efficiency and the highest maximum ECL emission. The highest emission from CQD10 is roughly the same as the commercially available ECL emitter Ru(bpy)$_3^{2+}$ (96 %).[31] This half light-emitting electrochemical cell confirms the suitability as the cathodic lighting layer.

For each CQD film electrode, the film thickness is consistent, thus in the smaller CQD10 sample more particles exist on the electrode surface and certainly more functional groups that may produce surface state emissions. Further, only the smaller CQDs (CQD10 and CQD20) showed non-negligible ECL emissions, providing further evidence for a surface state ECL emission. CQD10 should be considered for optoelectronics based on its high ECL emitting efficiency.

**ECL of CQD Film/TPrA System as the Second Half Light-Emitting Electrochemical Cell**

A CQD-modified electrode system with 50 mM TPrA coreactant was tested as well. The onset of oxidation for the TPrA is roughly at 0.7 V, generating TPrA$^+$, then TPrA$^-$ through deprotonation. This TPrA$^-$ can react with the electrogenerated CQD$^+$ created at 1.4 V, to produce an iminium and an excited state CQD*, that can further relax to produce light, Scheme 2.2.2b. Despite the highly oxidizing nature of TPrA$^-$, negligible photocurrent was observed, indicating CQD$^+$ might not stable enough to react in accepting an electron from TPrA$^-$. Furthermore, the electrochemical potentials to generate TPrA$^-$ and CQD$^+$ are discrete greatly, which is unfavourable for the CQD* generation, probably due to the instability of both radicals. This half-cell suggests that CQD$^+$ stability and reactivity improvement is required for optoelectronic applications.

**Comparison of Half-LECs to Full LECs**

A simplified illustration of the CQD/S$_2$O$_8^{2-}$ and the CQD/TPrA systems are included in Scheme 2.2.2a and 2.2.2b, respectively. These individual systems can be thought of as LEC half-cells, where the cathode is Scheme 2.2.2a and the anode is Scheme 2.2.2b. This similarity between the electrochemical setups and a functioning LEC device are seen in Scheme 2.2.2c. The setup in Scheme 2.2.2 has CQDs in a film in contact with an electrolyte solution and an electrode. LEC devices are similar, where light emitters are dispersed in a film with electrolyte but are between two electrodes instead of in contact with a solution and an electrode. In fact, ECL provides details about the stability of both ions that are electrogenerated, as well as rel-
2.2.5. Results and Discussion

Scheme 2.2.2: Simplified illustration of reactions occurring at the surface of a CQD film coated on a glassy carbon electrode containing: a. $S_2O_8^{2-}$ at a potential below -1.5 V vs. Ag/AgCl and b. TPrA at a potential above 1.4 V vs. Ag/AgCl. c. Illustration of the electron flow within a theoretical, fully constructed LEC device.

ative light emission efficiencies, by allowing the testing of multiple coreactants with different reductive and oxidative strengths.

**Spooling ECL Spectroscopy of the Film/Persulfate Half-cell**

A potential scanning cycle from 0 to -3.0 V was performed on the CQD film shown in Figure 2.2.4, where individual spectra were taken during this potential scan every 2 s. Capturing spectrum during the scan (otherwise known as spooling spectroscopy), enables tracking the evolution/devolution of light emission processes during CV scans. Noticeable light is produced at -2.0 V indicating that at this potential, the electrogenerated $SO_4^{-}$ and CQD$^{-}$ react to create CQD*, emitting light. The PMT is generally more sensitive than a CCD camera and was able to detect light emitted from CQD* at an earlier potential than the CCD camera as illustrated in Figure 2.2.4d. Throughout the cathodic potential scan, the wavelength of ECL light slowly blue shifts from a center of 770 nm at -2.0 V, to 650 nm at -3.0 V. This wavelength variation may be due to the coexistence of different oxygen (-OH, -COOH, and -C=O) and nitrogen (-NH$_2$, -NRH, and -CONH$_2$) functional groups on the CQDs. These functional groups on the surface of the CQDs can contribute to many different surface states, all potentially acting as emissive traps at different potentials, thus changing the wavelength of emission.

An increase in the overpotential or driving energy to the CQD films, allows accessing these different energy surface states and may lead to a shorter wavelength or higher energy ECL emission.
Figure 2.2.5: ECL spooling spectra from a film of CQD10 with 50 mM K$_2$S$_2$O$_8$ taken with an exposure time of 2 s, a scan rate of 12.5 mV/s, yielding 120 spectra over a 240 s cyclic voltammogram. Color of individual spectra correspond to the RGB coordinates found by converting spectra using CIE coordinates. Spectra that show negligible light are displayed as grey. Insets show the wavelength of light emitted from a. the forward scanning starting at -2.0 V vs. Ag/AgCl and b. the reverse scan starting at -3.0 V vs. Ag/AgCl.

The color of each spectrum in Figure 2.2.5 illustrates its emission color based on RGB coordinates calculated by a custom MATLAB code produced by our group that uses conventions adopted from the CIE xy chromaticity diagram. By tuning the potential applied to the film, a specific color of light can be achieved between -2.0 and -3.0 V. A wavelength variation is seen during the scan with a slow blue-shift from an emission centered at 790 nm for -2.2 V, to an emission centered at 660 nm for -3.0 V. This wavelength dependency on voltage yields a simple way to achieve multiple colors from one light emitter, providing an attractive emission characteristic for optoelectronic applications.

**Accumulation ECL Spectra**

Figure 2.2.6 illustrates an accumulation ECL spectrum during the potential scan shown in Figure 2.2.4 over 30 s. The color emitted by the CQD film according to CIE color coordinates is a white light (0.42, 0.41) with a correlated color temperature (CCT) of 3200 K estimated from the CIE diagram in Figure 2.2.6. This CCT value corresponds to a cool, bright and vibrant white and is generally used for most indoor lighting applications. Small CQD films yield relatively strong and efficient white light most likely due to efficient recombination of CQD* generated from CQD⁻.
2.2.6 Conclusion

Herein, a protocol to prepare CQDs with controlled size was created from cost effective and readily available precursors. Smaller sized CQDs showed ordered graphitic nature observable in HRTEM but had roughly the same blue PL emission efficiency as the larger CQDs. This shows the PL emissions arising from all CQD particles in this study are similar. As a CQD film, the smallest CQDs had strong white light emission when reacted with 50 mM of the core-actant $\text{S}_2\text{O}_8^{2-}$. This emission was as efficient as a typical ECL standard in the same conditions, $\text{Ru(bpy)}_3^{2+}$. This ECL emission was centered at 650 nm and gave CIE co-ordinates of $(0.42, 0.41)$ with a CCT of 3200 K corresponding to a cool bright white light emission. This color of light is ideal for all indoor lighting conditions. The strong efficiency of light conversion, the ease of synthesis and the color temperature of the white light make CQD films a suitable light emitter candidate for LEC applications. Increased surface states per mass of CQDs for small CQDs may capture more holes from $\text{SO}_4^{2-}$, allowing a higher ECL efficiency. These ECL tests serve as a simulated LEC half-cells where the stability of each electrogenerated ion can be probed using coreactants and the efficiency of light emission can be simply probed using comparisons to commercial light emitters. Future tests will focus on the implementation of CQDs in LEC devices with improved stability and electron accepting nature of CQD$^+$. 

Figure 2.2.6: a. A background-subtracted accumulation of all light emitted during the same cyclic voltammogram of the system described in figure 2.2.4. Full-width half maximum is displayed as well as the main emission wavelength. b. The corresponding CIE color space co-ordinates and correlated color temperature.
2.2.7 Conflicts of Interest

Author David A. Love was employed by the company Rosstech Signal Inc. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

2.2.8 Acknowledgements

A special thank is owed to Prof. Honggang Liao’s group at Xiamen University in China for the TEM characterization. The quality service from the Western Electronic Shop, Glass Shop and ChemBio Store is very much acknowledged. We thank Dr. Ryan Maar and Daniela Cappello in Prof. Joe B. Gilroy’s group for their assistance in utilizing their glovebox. We thank Dr. Rebecca Yardley in Prof. Elizabeth Gillies’ lab for the assistance in utilizing their freeze-dryer.

References


Section 2.3

Structural Origin of Carbon Quantum Dot Luminescence
2.3.1 Preface

This section investigates the same set of CQDs as Section 2.1 but with synchrotron X-ray spectroscopy with the end goal of identifying unique organic moieties that cause the difference in solid state emissions. X-ray excited optical luminescence also characterized the unique AIE and ACQ CQDs to determine if a chemical moiety-luminescence relationship could be found.

Currently, some ACQ and AIE luminogens are known but it is not known what chemical moiety causes AIE in CQDs. Multiple AIE CQDs have been reported in literature but none have explored why or how the AIE CQDs emit in the solid state, to the best of our knowledge.

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2.3.2 Abstract

A carbon quantum dot (CQD) sample series was synthesized from citric acid and varying concentrations of thiourea. The highest (sample 1) and lowest (sample 2) concentrations of thiourea exhibited unique visual effects and electronic structures. X-ray excited optical luminescence (XEOL) along with UV-visible spectroscopy provided unique insight into the absorption and emission mechanisms of samples 1 and 2, where only sample 2 emitted XEOL. Sample 1 exhibited the commonly observed aggregation caused quenching (ACQ) effects in the solid state. while sample 2 displayed unique aggregation induced emissions (AIE) effects upon exciting the sample above the C K edge. The AIE and ACQ sample differences were suspected to be from S moiety differences arising from the varying thiourea concentrations during synthesis. Furthermore, X-ray absorption spectroscopy (XAS) in modes of total electron yields and partial fluorescence yields allowed the identification of specific core and surface states of the CQDs. It was discovered that thiophene moieties were uniquely formed in the AIE sample’s surface and not anywhere in the ACQ CQD sample. The thiophene surface functionality is believed to be a significant contributor to the AIE effects seen in the XEOL studies. Understanding and preventing the common CQD ACQ mechanism allows the application of CQDs in solid lighting applications.

2.3.3 Introduction

Light emitting diodes (LEDs) have become widespread throughout the world due to low power consumption, long operational lifetime and quick response times. However, achieving white LED light at low cost is difficult. Phosphors made from solid luminophores permits down converting some lower wavelength LED light into higher wavelengths. Tuning these phosphor concentrations yields white light and allows achieving specific correlated color temperature (CCT), color rendering index (CRI) and luminous efficiencies. Perovskites or similar rare earth metal luminophores are applied in phosphors, but suffer from complicated syntheses, expensive rare earth elements and toxicity to human life.[4, 40, 43, 44]

Carbon quantum dots (CQDs) have shown great promise for future optoelectronic applications due to simple syntheses, tunable emissions and high photoluminescent quantum yields (PLQYs). However, these CQDs often suffer from aggregation caused quenching (ACQ), and with the exact structures of the CQDs unknown, understanding and preventing this phenomenon is currently very challenging.[42] In fact, CQD emission mechanisms are not exactly known, due to the complex origin of the two emission channels: surface states and core structures. Surface structures are loosely defined, mainly due to their diversity and uncertainty
of the possible structures arising from the different synthetic methods. Surface states have been defined as functional groups, oxygen-related disorders and surface defects, covering just about anything other than sp\(^2\) hybridized carbon.\(^8\) The core states are then the sp\(^2\) hybridized carbon which are affected by the size of the nanoparticles by typical nanoparticle quantum confinement mechanisms. Turning the common ACQ effects of CQDs into aggregation induced emissions (AIE) effects permits higher luminous efficiencies, allowing the benefits of CQDs to be realized in phosphors. This tuning cannot be completed without knowing CQD electronic structures by means of proper investigative techniques.

Investigations of electronic structures using synchrotron spectroscopy have developed better mechanistic understandings of light emission in luminophores.\(^{13, 16, 22, 30, 33, 38, 46}\) These understandings have been developed by the tuning of X-ray energies to yield element specific excitations in luminophores. X-ray excited optical luminescence (XEOL) spectroscopy monitors how luminophores convert X-rays into visible light allowing element-specific investigations into the light emitting processes.\(^{29}\) XEOL and X-ray absorption spectroscopy (XAS) can provide insight into AIE and ACQ emission mechanisms of CQD samples. XAS also allows the measuring of total electron yields (TEY) and partial fluorescence yields (PFY) providing information on the surface and bulk of materials. Combining these measurements for analyses of CQDs permits the understanding of core structures, surface states and their contribution to the light emission mechanisms. Herein, we employ XEOL and XAS to understand element-specific contributions to the light emission mechanisms and correlate structures to AIE/ACQ effects.

### 2.3.4 Materials and Methods

#### Chemicals and Materials

Dibenzothiophene [(C\(_{12}\)H\(_8\)S), \(\geq 99 \%\)], citric acid [(C\(_6\)H\(_8\)O\(_7\)), 99 %], thiourea [(H\(_2\)NCSNH\(_2\), \(\geq 99.0 \%\)], poly(1,4-phenylene sulfide) (PPS) [(C\(_6\)H\(_4\)S-\(n\)], D-methionine [(C\(_5\)H\(_11\)NO\(_2\)S), \(\geq 98 \%\)], L-cysteine [(C\(_3\)H\(_7\)O\(_2\)NS), 97 %], sphalerite [(ZnS), 99.99 %] and 2-thienylboronic acid (TBA) [(C\(_4\)H\(_5\)BO\(_2\)S), \(\geq 95.0 \%\)] were acquired from Sigma-Aldrich (Mississauga, ON). 2-mercapto-5-n-propylpyrimidine (MPP) [(C\(_7\)H\(_{10}\)S), 98 %] was purchased from Alfa Aeser (Ward Hill, MA). 8 mm double-sided conductive carbon tape (77816, Electron Microscopy Sciences, Hatfield, PA) was used for CQD samples for X-ray energies below 285 eV. Above 285 eV, 0.1 mm indium foil (7440-74-6, Sigma Aldrich, Mississauga, ON) was used.

#### Synthesis of CQDs

The CQD synthesis is through hydrothermal method as reported for nitrogen-doped CQDs elsewhere.\(^2\) In brief, citric acid (2.0 g) and of thiourea (1.5 or 0.1 g) were combined in Milli-
Q water in a teflon-lined autoclave, for samples 1 and 2, respectively. The autoclave was heated at 160 °C for 8 hours, then dialyzed in 1 kDa molecular weight cut-off bags for 12 hours to remove unreacted starting reagents or small CQD materials. The purified solution was freeze-dried to sublimate all water from the sample. Sample was sealed and refrigerated until use.

**Identification of Surface Functional Groups by FTIR**

CQD powders were pressed in a sample holder and measured on a FTIR spectrometer (VERTEX 70 FTIR, Bruker, Billerica, MA). Background and blank measurements were taken before spectra acquisition to better identify peaks.

**UV-Visible Measurements of CQD Solutions**

UV-Visible measurements were performed on dilute samples to avoid self-absorption. A Varian Cary 50 UV-Vis Spectrometer (Agilent, Santa Clara, CA) was used for all UV-Vis experiments. Tauc plot transformations were performed using the relationship $\alpha h\nu^{1/r}$ versus $h\nu$. $\alpha$, $h$, $\nu$ and $r$ are absorption coefficients, Planck constant, light frequency and $r=1/2$ for indirect band gaps and $r=2$ for direct band gaps. Based on previous studies,[11] $r=2$ was used for all Tauc plot transformations because of the strong linear fit.

**Synchrotron Spectroscopy Measurements**

The XEOL spectra of the CQD samples with excitation energies at the C, N, and O K-edges were recorded with the Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source (CLS). An optical spectrometer (QE6500, Ocean Optics) was used to collect visible light. All X-ray energies used are normalized to the incident photon flux monitored with a gold mesh except for the C K-edge results, which is normalized to a photodiode which removes carbon contribution from any beamline optic contributions to signal.

$S_{L_{2,3}}$-edge XANES spectra were acquired in the energy range of 158-190 eV at the variable line spacing-plane grating monochromator (VLS-PGM) beamline (E/$\Delta E > 10 000$) at CLS, SK. The samples were mounted in a UHV chamber at a pressure of 1 x $10^{-8}$ Torr. The XANES spectra were measured using the high-energy grating of the beamline yielding a spectral resolution of 0.1 eV with entrance and exit slit widths of 100 $\mu$m. A microchannel plate detector was used to collect the partial fluorescence yield (PFY) signal. Total electron yield spectra were collected by measuring a drain current. All spectra recorded were normalized to the intensity of the photon beam as measured by the drain current of a Ni mesh (transmission 90 %) situated upstream of the sample. All spectra were also calibrated to the $S_{L_{2,3}}$ edge of sphalerite.[17][25]

Synchrotron data treatment and linear combination fitting was performed with Athena 0.9.26.[26] All synchrotron spectra are combinations of at least two spectra, were energy corrected and were normalized. All LCF analysis was also performed with the Athena software.
2.3.5 Results and Discussion

FTIR Analysis of CQDs

Carbon quantum dots (CQDs) were synthesized from citric acid and varying amounts of thiourea in a hydrothermal synthesis. These CQDs exhibited visual differences where the highest and lowest concentrations of thiourea produced were dark green (sample 1) and white (sample 2), respectively. These samples differed only in the thiourea concentration during synthesis, where every other aspect of the hydrothermal syntheses was kept the same. The resulting CQDs have different visual and optoelectronic properties. These CQDs have been analyzed previously where XPS of the same CQDs revealed S contents of 3.2 % (Sample 1) and 1.3 % (Sample 2) where conventional XPS could not distinguish the identities of the contributing S moieties.\[1\] Interestingly though, electrochemiluminescence (ECL) of CQD films and CQD solutions elucidated unique emissions, further suggesting differences in luminescent centers and emission mechanisms. The difference in emission mechanisms is most likely due to thiourea incorporation into the sample, or the effects of thiourea during synthesis. Exploring S chemical environments may provide insight into these unique CQD samples.

Figure 2.3.1 shows an FTIR of the samples and the precursors used to synthesize them both. Many peaks between 1050 and 1250 cm\(^{-1}\) correspond to various C-N, C-S and C-O...
2.3.5. Results and Discussion

Figure 2.3.2: Average XEOL spectra for (a-c) sample 2 and (d-f) sample 1 excited at energies between (a and d insets) 270-285 eV or below the C K edge (285 eV), (a and d) 285-350 eV or above the C K edge, (b and e) 410-460 eV or above the N K edge (400 eV) and (c and f) 535-560 eV or above the O K edge (530 eV).

absorptions and are present in the samples and some of the precursors. The peak at 1600 cm\(^{-1}\) corresponds to C=C bonding, indicating the samples contain conjugated carbon structures common in CQDs. The peak at 1700 cm\(^{-1}\) is attributed to vibrational absorptions by -COOH, seen in both samples, citric acid and not thiourea. The absorption band at 2600 cm\(^{-1}\) has been attributed to a stretching vibration of -SH, and is obvious in sample 2, suggesting sulfur moiety differences in the samples. These differences in sulfur moieties could contribute to differences in solid and solution PL emissions. In fact, sulfur moieties, specifically disulfides, have been linked to the production of AIE in CQDs prepared solvothermally using melamine, dithiosalicylic acid and acetic acid as precursors.\(^{[37]}\) The disulfide bonds were identified as single bonds that could be restricted when brought to a solid state to yield AIE, but the luminophore or mechanism of emission was not identified. Furthermore, disulfide bonds (450-500 cm\(^{-1}\)) were not identified in the FTIR spectra of the samples in this study. The absorptions at 3100 and 3300 cm\(^{-1}\) are commonly attributed to -NH and -OH vibrations. The broadness of the peaks indicates extensive hydrogen bonding in the samples. Substantial sublimation at temperatures below 200 K ensures all water has been removed, allowing the attribution of these peaks to -OH and -NH groups in the CQD samples.

XEOL Spectra

Figure 2.3.2 shows average XEOL spectra for sample 1 and 2 collected over a range of different excitation energies. The XEOL spectra were acquired at a time interval of 0.05 s or at
a frequency of 20 Hz, and then averaged. The fast data acquisition was performed to minimize spectrometer artifacts and determine accurately peak positions and full width half maxima. However, it yields a lower signal to noise ratio. The above acquisition rate allows averaging hundreds of spectra for a single XEOL spectrum. Figure 2.3.2a and 2.3.2d insets show the average XEOL spectra with an excited energy between 270-285 eV for sample 2 and sample 1, respectively, from which no XEOL emissions are seen for either sample. The C K edge is located at 285 eV,[3] and C core electrons were not excited for the XEOL spectra seen in the insets. The S L$_{2,3}$ edge with an energy at 164.7 eV was excited in this range, but no XEOL emissions were observed. This means that S contributes insignificantly to the XEOL emissions. At excitation energies above the C K edge of 285 eV in Figure 2.3.2a and 2.3.2d, sample 2 emitted light while sample 1 did not. In fact, sample 1 never emitted light (Figure 2.3.2d-f), and sample 2 consistently emitted light (Figure 2.3.2a-c) for all the different excitation energies used. In fact, this observation is contrary to expectations. Sample 1 was synthesized with higher concentrations of thiourea as the precursor of heteroatom dopants. Subsequently, CQDs with elevated heteroatom doping levels are expected to show enhanced luminescence.[19, 41] An uncommon phenomenon seen in CQD samples is AIE where certain non-radiative decay pathways for luminophores are restricted in the solid state, allowing radiative decay pathways to be expressed more. This so-called AIE effect results in luminescent enhancements in the solid state. The XEOL observations for sample 2 seem to follow this luminescence mechanism, where only CQDs that display AIE effects emit XEOL. Also, sample 1 seems to exhibit the common CQD ACQ effects where light is not emitted in the solid state. The drastic visual and spectroscopic FTIR (Figure 2.3.1) differences seen between the two CQD samples earlier are further evidence for the AIE and ACQ effects. The functional groups available for non-radiative or radiative decay pathways, and their interactions between CQDs will enhance or quench luminescence. From here on, sample 1 and sample 2 will be referred to by ACQ CQDs and AIE CQDs, respectively. In fact, the same conclusions were found for the same CQDs in PL studies, hinting at similar structural origins of XEOL.[1]

These AIE XEOL effects have been observed in Au nanocluster luminophores previously but the emission mechanism could not be confirmed.[24] However, to the best of our knowledge luminophores that exhibit ACQ effects have not been studied by XEOL spectroscopy. This CQD sample series, which exhibits synthesis controlled AIE and ACQ effects, provides an ideal platform for mechanistic understanding of XEOL emissions. With a small variation in a hydrothermal synthesis, the XEOL emission mechanism can be controlled in CQD samples. The thermal stability of this emission and the CQDs is likely high based on a study by Zhou et al. that found thermal annealing of CQDs hydrothermally synthesized from citric acid and urea drastically improved the PLQY.[23]
2.3.5. Results and Discussion

The XEOL spectra in Figure 2.3.2a-c can be fit with four peaks: two broad emissions centered at 516 and 680 nm; then two sharp emissions at 558 nm and 620 nm. The two broad emissions can be attributed to the two common CQD emission centers: core and surface states.\cite{8, 20} The core and surface state emissions match well with typical CQD width and peaks at emissions of 516 and 680 nm.\cite{20, 41} The sharper peaks at 558 and 620 nm only appear when XEOL is observed, eliminating the possibility of instrument related sensitivities or noise. The characteristic peak positions and sharpness matches well with phonon related emissions. From an emission peak wavelength of 516 nm, the first sharp peak at 558 nm is 42 nm or 1465 cm\textsuperscript{-1} away. This places the relative peak positions directly between the G (1595 cm\textsuperscript{-1}) and D (1330 cm\textsuperscript{-1}) Raman bands typically seen for CQDs.\cite{32} In fact, previous azimuthally polarized laser studies have identified electron-phonon coupling contributing to photoluminescent spectra.\cite{10} To the best of our knowledge, this is the first time electron-phonon coupling has been observed in CQD XEOL studies though. Fitting this seemingly single emission peak with the energies associated with the D and G bands of CQDs results in a strong matching for the data (Figure 2.3.2a-c). Furthermore, a second sharp peak appears at 620 nm, which is 94 nm or 3251 cm\textsuperscript{-1} away from the core emissions of CQDs. Many sp\textsuperscript{2} C materials exhibit a strong peak at 3240 cm\textsuperscript{-1} in Raman spectroscopy corresponding to a 2D’ overtone that involves two longitudinally optical phonon interactions.\cite{35}

Excitation in the energy range of 410 and 460 eV or above the N K edge at 409.9 eV \cite{2} (Figure 2.3.2b), only increased the relative peak height at 680 nm. This CQD surface state peak seems to be contributed to by N K edge excitations. This finding matches the above FTIR observations where many amine functional groups were found to decorate the surface of the CQDs (Figure 2.3.1). Comparing the 516 nm peak between Figure 2.3.2a and 2.3.2b, the peak did not grow indicating N does not contribute significantly to the core state emissions. However, in the energy range of 545 and 560 eV or above the O K edge at 543.1 eV \cite{2} (Figure 2.3.2c), both broad emissions centered at 516 and 680 nm doubled in intensity. It appears O is significantly involved in both the core and surface state emissions of CQDs.

To understand the elemental contributions to the surface and core state emissions seen in CQD XEOL studies (Figure 2.3.2a-c), a study of common electronic transitions for CQDs can be performed by viewing the absorption spectra of the CQDs. Figure 2.3.3a shows the UV-Visible absorption for the ACQ CQDs, with a peak at 325 nm corresponding to \( \pi-\pi^* \) transitions from the C sp\textsuperscript{2} electrons in the graphene structure. A peak at 405 nm is associated with a n-\( \pi^* \) transition from non-bonding electrons in dopant atoms (N, O, and S).\cite{11} Finally, a unique peak at 600 nm, is believed to be surface states in the ACQ CQD samples. Figure 2.3.3c shows the UV-Visible absorption spectra for the AIE CQDs with peaks at 330, 415 and 600 nm and the same assignment of the peaks as the ACQ CQDs. From the Tauc plot transformation, both
Figure 2.3.3: a. Absorption spectra and b. Tauc plot transformations with important energies marked for sample 1. c. Absorption spectra and d. Tauc plot transformations with important energies marked for sample 2.
Figure 2.3.4: PFY spectra for six standards and both CQD samples while scanning X-ray energies across the sulfur L\textsubscript{2,3} edge. LCF for the sample spectra is seen in blue.

samples show two linear extrapolations from the rising edge of the Tauc plots after applying the energy transformations (Figure 2.3.3b and 2.3.3d). Both samples share an absorption at 3.3 eV and a stronger absorption at 4.15 and 4.34 for the ACQ and AIE CQDs respectively. The peaks shared between the samples are almost identical, indicating similar excitation pathways for the CQDs. The CQD samples emitted XEOL after the C K edge excitation indicating that the XEOL emissions are accessible from exciting C and that a π*-π transition most likely yielded a peak at 516 nm. As mentioned above, electron-phonon interactions are responsible for the two sharp peaks at 558 and 620 nm, most likely from another π*-π transitions after the phonon interaction(s) occurred. The n-π* transition is heavily dependent on the incorporation of dopant atoms, where any difference could tailor the emissions seen in CQDs.\textsuperscript{[11, 19]} It appears O and N excitations contributed significantly to the surface state emissions peak at 680 nm seen in the XEOL spectra (Figure 2.3.2a-c). This observation follows the FTIR studies (Figure 2.3.1) where many O and N containing surface functional groups were observed.

**Sulfur L\textsubscript{2,3}-Edge PFY Study**
Figure 2.3.4 shows the partial fluorescence yield (PFY) for solid S standards and solid states of the ACQ and AIE CQDs while a collimated X-ray beam scans across the S L\textsubscript{2,3} edge. As the X-ray energy is scanned, many photons are detected from the sample when reaching 164 eV, or the S L\textsubscript{2,3} edge at 164.7 eV.[3] The S L\textsubscript{2,3} edge represents transitions from the occupied S 2p core-level to unoccupied S 3s $\sigma^*$ orbital. Without hybridization, the S L edge is split into two electron transitions separated in energy by 1.2 eV from S 2p$^{1/2}$ $\Rightarrow$ S 3s $\sigma^*$ and S 2p$^{3/2}$ $\Rightarrow$ S 3s $\sigma^*$. These excitations should result in a relative L\textsubscript{2}:L\textsubscript{3} absorption ratio of 1:2. Six standards are displayed in Figure 2.3.4 and were compared to the CQD samples. Peak assignments were assisted from previous studies into the S L\textsubscript{2,3} edge for methanethiol gases.[5, 7, 34] The ACQ and AIE CQD’s PFY spectra look almost identical with a characteristic 2p$^{3/2}$ $\Rightarrow$ 3s $\sigma^*$ transition at 164.6 eV assigned to S-C bonds. A peak at 165.6 eV has been attributed to a 2p$^{3/2}$ $\Rightarrow$ 3s $\sigma^*$ transition which can be assigned to a S-H bond. Finally, a peak at 166.5 eV is assigned to a 2p$^{1/2}$ $\Rightarrow$ 3s $\sigma^*$ transition assigned to S-C bonds again. Most standards had dissimilar PFY spectra with pre- and post-edge features that did not resemble the samples tested. Methionine was the only sample considered for further linear combination fitting (LCF) from these standards, due to PFY spectra similarity.

LCF is applied to the S L\textsubscript{2,3} edge to provide an understanding of S’s electronic contribution to the luminescence mechanism in the ACQ and AIE CQDs. When performing LCF with methionine and the samples (Figure 2.3.4 blue curves), they are almost identical in PFY spectral information. Calculating an $R^2$ between methionine and CQD spectra between the range of interest (162-170 eV) yields intense correlations of 0.999 and 0.975 for the ACQ and AIE CQDs respectively. These nearly identical PFY spectra indicate that the chemical environment of S in the CQDs is probably in a sulfur ether (RSR from methionine) configuration. The dissimilarity between the other standards tested suggest that the chemical environment of sulfur in the bulk of the CQD samples is not in thiols (RSH from cysteine), thioketones (RC(=S)R’ from thiourea), thiophenes (from 2-thienylboronic acid (TBA)), thiols in conjugated environments (Ar-SH from 2-mercapto-5-n-propylpyrimidine (MPP)) or sulfur ethers in conjugated environments (Ar-S-Ar from poly(1,4-phenylene sulfide) (PPS)).

PFY is commonly used to discuss the core state of samples containing nanostructures because photons escape materials relatively easily when compared to electrons.[18, 28] Therefore, the sulfur ether environment for both ACQ and AIE CQDs elucidated through LCF most likely comprises the CQD core states. These S core states can donate electron density into the extended C structure, adding electrons and effectively lowering the energy of the $\pi^*$ level and red shifting the emissions from the core state considerably.

This LCF for the S L\textsubscript{2,3} edge absorptions had particularly strong correlations ($R^2 = 0.999$) because of the short core-hole lifetimes (CHL) for low atomic number elements. This short
2.3.5. Results and Discussion

Figure 2.3.5: TEY spectra for seven standards and both CQD samples while scanning X-ray energies across the sulfur L$_{2,3}$ edge. LCF for the sample spectra is seen in blue.

CHL results in sharp spectral information around the absorption energy and poor spectral information away from this absorption energy. This enhanced resolution around the so-called white line region for the S L$_{2,3}$ edge permits simple comparisons between standards to gain accurate chemical environmental information from samples by LCF of standards and sample spectra.[7, 29] Furthermore, the local atomic arrangement may be better elucidated in S K edge studies, but may lack sufficient resolution to distinguish the bond lengths of thiophenes, sulfur ethers and thiols in R-space and the coordination number differences in K-space. These S L$_{2,3}$ investigations will assist in elucidating AIE and ACQ mechanisms in CQDs, allowing future CQD synthetic pathways to be tailored to yield AIE PL effects. Stronger AIE PL effects in CQDs permits widespread applications in solid optoelectronics.

Sulfur L$_{2,3}$-Edge TEY Study

TEY data for the samples was collected at the same time as PFY data for seven standards and the CQD samples (Figure 2.3.5). For comparison, ACQ and AIE CQDs will be analyzed. Both CQDs had a pre-edge peak at 164.6 eV from a characteristic 2p$_{3/2}$ $\rightarrow$ 3s $\sigma^*$ transition assigned to S-C bonds. A peak at 165.6 eV has been attributed to a 2p$_{3/2}$ $\rightarrow$ 3s $\sigma^*$ transition
which can be assigned to a S-H bond. Finally, a peak at 166.5 eV is assigned to a \( 2p_{1/2} \Rightarrow 3s \) \( \sigma^* \) transition assigned to S-C bonds again, identical to the PFY spectra. As a defining feature of the TEY spectra, the ratio of the peak height at 165.6 eV (S-H) to the peak height at 166.5 eV (S-C) will be discussed and referred to as the (S-H)/(S-C) ratio. ACQ and AIE CQDs had (S-H)/(S-C) ratios of 0.92 and 0.90 respectively. Thiourea, MPP, dibenzothiophene, PPS had unique pre- and post-edge features dissimilar from the CQD sample’s TEY spectra. Methionine has two post-edge peaks at 165.6 and 166.5 eV with a (S-H)/(S-C) ratio of 0.85, as well as a pre-edge peak at 164.5 eV. TBA has the same features as methionine, but with a (S-H)/(S-C) ratio of 1.05. Cysteine shares all the same peaks as methionine and TBA, with a (S-H)/(S-C) ratio of 0.96.

Standards and samples were then considered for LCF of the TEY spectra (Figure 2.3.5 blue curves). Both CQD samples had a (S-H)/(S-C) ratio somewhere between methionine (0.85) and cysteine (0.96) or TBA (1.05). These three standards were selected for LCF based on these peak and ratio similarities. The ACQ CQD’s TEY spectra was fit with TEY spectra of cysteine (90 % weight) and methionine (10 % weight) and achieved an \( R^2 \) of 0.998 when considering the energy range of interest (162-170 eV). AIE CQD’s TEY spectra was fit with TEY spectra of cysteine (40 % weight), methionine (40 % weight) and TBA (20 % weight) and achieved an \( R^2 \) of 0.997 when considering the energy range of interest (162-170 eV). Fitting for the AIE CQDs was attempted without TBA’s TEY spectra and the fitting is visibly and statistically worse (\( R^2 \) of 0.970) without incorporation.

The TEY LCF results were drastically different from the PFY LCF results (Figure 2.3.4). This difference highlights the surface and bulk sensitivity of the TEY and PFY techniques. TEY is typically used to discuss the surface states of nanostructures because electrons cannot escape from the bulk material as easily.\[18, 28\] In fact, electrons with energies between 160 and 170 eV have an inelastic mean free path of less than a nanometer exhibiting surface sensitivity.\( \text{(Seah and Dench, 1979)} \) The surface of the ACQ and AIE CQDs contains thiols, which can be confirmed by FTIR as well (Figure 2.3.1). Another contribution to surface groups in both CQD samples is sulfur ethers, similar to the bulk information achieved through PFY LCF (Figure 2.3.4). Other contributor to the surface functional groups in the AIE CQD is surprisingly thiophene environments. AIE CQDs seems to have a unique surface S moiety, created when less thiourea was available during synthesis. The summation of surface and core S chemical environments for the AIE CQDs is included in the simplified Scheme 2.3.1.

Many studies investigate S’s role in AIE PL effects in ideal situations for a variety of samples. Yang et al. noted disulfide bonds as a likely candidate for AIE in CQDs due to the restriction of intramolecular motion (RIM) possible around a disulfide bond, but did not comment on the luminophores that would create this emission.\[37\] Riebe et al. found that
alylated thioethers yielded enantiotropic mesomorphism with soft-crystalline behaviour when these alkyl chains are in a plane, which was also controllable by varying the lengths of alkyl chains.\textsuperscript{[27]} The AIE nature of the AIE CQDs could be due to alkylated thioethers that follow this RIM mechanism. However, the ACQ CQDs also contain these alkylated thioethers and does not exhibit AIE PL effects. It is unlikely that alkylated thioether chains are the origination of the AIE PL effects in the AIE CQDs but not the ACQ CQDs based on the TEY LCF results.

Some studies have reported using thiophene as a building block for AIE-active luminophores in small molecules, but not in materials. Thiophene’s planar aromatic nature and singly-bonded constituents allows RIM from $\pi$-stacking interactions and the enantiotropic mesomorphism mentioned previously.\textsuperscript{[6, 9, 12, 14, 15, 21, 24, 31, 36, 39, 45]} In general, thiophene is proven to act as a donor for a fluorescent charge transfer state in many AIE-active luminophores, but never for CQDs or any materials.\textsuperscript{[9, 12, 14]} Additionally, in the three cases just mentioned, the acceptor in the fluorescent charge transfer was a conjugated aromatic system where two of the systems had nitrogen doping in this acceptor. The presence of thiophene surface states in the AIE CQD seen in the TEY LCF (Figure 2.3.5) could result in its AIE effects. Sufficient charge transfer could occur from the thiophene donor moieties to the N-doped conjugated aromatic structures commonly present in CQDs. These thiophene groups were not found in the ACQ CQDs and the ACQ CQDs do not exhibit AIE effects providing further evidence for thiophene donors in AIE-gens in the AIE CQDs. The production of the unique S thiophene moiety resulted from reducing the thiourea concentration during hydrothermal synthesis of the CQDs. An electronic understanding of the AIE mechanisms occurring in relatively simple CQD materials reduces the barriers preventing the widespread applications of these simple CQD materials in solid optoelectronics.
2.3.6 Conclusion

A CQD sample series was synthesized from citric acid and varying concentrations of thiourea. The highest (sample 1) and lowest (sample 2) concentrations of thiourea exhibited unique visual and electronic effects. XEOL emissions were found only in sample 2, otherwise known as AIE effects. Despite similar chemical functionality, sample 1 exhibited ACQ effects, which is believed to be from unique S moieties introduced with a surplus of available S during synthesis. XEOL core emissions at 515 nm were contributed to greatly by exciting the C K edge. When excited at the N and O K edges, surface state emissions were enhanced with intense emissions at 680 nm. S L_{2,3} edge PFY and TEY data of the CQD samples yielded surface and core state information on the CQD samples. After comparing the standards to the samples, unique thiophene moieties were identified in the AIE CQDs. Thiophenes are commonly used in the design of AIE luminophores due to the planar aromatic constituents and the available functionality on the thiophene ring. Thiophenes typically function as a donor in a donor-acceptor pair combined with N-doped aromatic groups, all of which were found in the AIE CQDs and were likely culprits for the AIE effects seen in the CQD samples. The reduction of S availability during CQD synthesis yielded thiophene functional groups that could be the origination of the AIE PL effects seen in the sample. CQDs typically suffering from ACQ effects are not suitable for applications of CQDs in solid state emissions. XEOL and XAS spectroscopy provided insight into AIE and ACQ mechanisms in CQDs, guiding us to the avenue of CQD applications in solid state optoelectronics.

2.3.7 Acknowledgements

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References


Chapter 3

Carbon Quantum Dot Light Emitting Device
3.1 Preface

This section incorporates the highest ECL-emitting CQDs in Section 2.2 into an LEC. The failure mechanism of this CQD LEC was investigated to find small ions were likely reacting at the highest energy interface in the device.

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\textsuperscript{||} represents first co-authorship.
3.2 Abstract

Light-emitting electrochemical cells (LECs) have presented themselves as an alternative to light emitting diodes (LEDs) because of the simple device design which is accompanied by a lower driving power. LECs operate by rearranging ion and electron transfers that create a p-n junction at a sufficient voltage, permitting LEC emissions. However, this rearrangement is not well understood. Therefore, the ion and electron transfer processes of the device during ion rearrangement, operation and at excessive overpotentials must be characterized for LEC devices. This paper reports on investigation of these LEC processes using electrochemical impedance spectroscopy (EIS). All processes were successfully characterized with simple equivalent circuits. To the best of our knowledge, an inductive low frequency loop was observed in an LEC for the first time. We propose that this inductivity was due to the p-n junction resistance to low frequency potential changes. Consistent observations and inverse proportionality between overpotential and inductance provided additional evidence for our proposal. This p-n junction at low frequency opposition combined with LEC operational stability data can provide a basis for judging the chemical resistance to deterioration and charge storage capacity of p-n junctions in the future. Furthermore, the techniques and equivalent circuits presented here will help to identify failure mechanisms and increasing LEC operational lifetimes.

3.3 Introduction

Light-emitting electrochemical cells (LECs) are electroluminescent devices whose operations require ion and electron transfers.\[22, 25, 56\] The light-emitting layer of an LEC typically contains a light emitter, an ionic species and a polymer that facilitates ion and electron transfers.\[34, 39\] The application of an external electric field to this light-emitting layer causes the ions from the salt/emitter to rearrange into p- and n-doped regions with the ion transfer through the polymer.\[64, 69\] Many types of light emitters have been studied for LECs such as emissive polymers,\[7, 15, 33, 44, 48, 61, 68\] ionic transition metal complexes (iTMCs),\[17, 38, 41, 57\] quantum dots,\[3, 4, 19, 23, 24, 30, 31, 51\] perovskites,\[43, 50\] and small organic compounds.\[54, 62\] One of the least studied of these emitters are quantum dots among which graphene quantum dots (GQDs) are presented to be a great organic alternative to expensive iTMC and emissive polymers.\[2\] However, the electrical characteristics of a device as well as the common device failure mechanisms are not well understood. “Black spots” are sometimes a reversible indicator of heavy ion doping promoted by a stoichiometrically dynamic cathodelpolymer and are attributed to device deterioration over long LEC operation times.\[5, 59\] The investigation and understanding of ion transfer and electron transfer pro-
cesses occurring in LECs will contribute to a better understanding and implementation of LEC technology in the future.

Electrochemical impedance spectroscopy (EIS) is an electrochemical technique commonly used for finding electron and ion transfer processes by varying the frequency over many decades of an AC potential. [9, 18, 35] The first reported EIS experiments were in 1947 by Dr. J. E. B. Randles where he studied a micro-Hg drop amalgam in a NH₄Cl solution while measuring the electron transfer and ion transfer kinetics. [52] Since then, the technique has commonly used to find electrical characteristics of stable systems and can be used on LEC technologies. [28, 66] Some LEC EIS experiments have been performed on emissive polymer LECs, [40, 43, 44, 55, 60, 65] small molecules, [21] and iTMC LECs. [10, 11, 63] To the best of our knowledge, none have been performed on quantum dot LECs.

Herein, this study implemented GQDs as a light emitter into a simple LEC and its device performance and fundamental EIS characteristics were investigated. Equivalent circuits were created for the dynamic stages of LEC operation. Unique and repeatable LEC EIS phenomena were observed for the first time. Ion migration mechanisms necessary for device operation were revealed from these developed equivalent circuits.

3.4 Experimental

Chemicals and Materials

Citric acid (HOC(COOH)(CH₂COOH)₂, ≥99.5%), L-cysteine (HSCH₂CH(NH₂)COOH, 97%), potassium iodide (KI, ≥99.0%), sodium hydroxide (NaOH, ≥97.0%), tetraoctylammonium bromide (TOAB) (CH₃(CH₂)₇)₄NBr, 98%), 2.8 wt % poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) dispersion in H₂O with low-conductivity grade (average Mn = 2,500), anhydrous chlorobenzene (C₅H₆Cl, 99.8%), poly(9-vinylcarbazole) (PVK) (average Mn = 25,000-50,000), diethyl zinc [Zn(CH₂CH₃)₂] were purchased from Sigma Aldrich (St. Louis, MO). Aluminum (Al, 99.99%) was provided from Laurand Associates, Inc. (Bota Raton, FL). A Milli-Q® Type 1 Ultrapure Water System (Millipore Sigma, Burlington, MA) supplied all Milli-Q water (18.2 MΩ cm).

GQD Synthesis

The syntheses of these GQDs followed the procedure reported elsewhere by our group. [70] Briefly, citric acid (1.0 g) and L-cysteine (0.3 g) were mixed in a 25 mL round bottom flask and heated at 240 °C on a heating mantle. Roughly 240 s later, the round bottom flask was removed from the heat and 10 mL of Milli-Q water was added. The resulting water-soluble nitrogen- and sulfur-doped GQDs were dialyzed (1000 Da molecular weight cut-off) in Milli-Q water and freeze-dried at -84 °C in a Labconco lyophilizer (Kansas City, MO) to obtain a solid
product.

**GQD Phase Transfer**

This phase transfer of the hydrophilic GQDs to an organic solvent such as chlorobenzene or dichlorobenzene is roughly based on a previous report by Subir et al.\textsuperscript{47} Briefly, 4.0 mg of GQDs was dispersed in 2.0 mL of Milli-Q water in contact with 2.0 mL of chlorobenzene. The chlorobenzene and water phases were completely separated where the water was completely opaque from GQDs and the chlorobenzene was completely translucent indicating no GQDs had dispersed in the chlorobenzene. TOAB was then added to the liquid mixture, which was vigorously shaken for at least 5 min and then left to settle for 10 min. The water was then separated from the chlorobenzene using a pipette. The water had become less opaque and the chlorobenzene was drastically more colored than before. It is plausible that the TOAB formed a micelle around the GQD allowing the GQDs to become dispersible in chlorobenzene. However, upon irradiating the chlorobenzene dispersion with 240 nm light, there was no emission. Adding 4.0 mg of KI to the GQD chlorobenzene dispersion and vigorously shaking allowed the emission to return but left the GQDs dispersed in solution. The dispersion was used as the stock for spin-coating in the device making.

**LEC Device Preparation**

10.0 mm × 10.0 mm glass with a 3.0 mm band of 140 nm thick ITO glass (Jinghui Electronic Technology, China) was submerged in 2 % Hellmanex II solution (Hellma, Zürich, Switzerland) and left in an Heratherm Advanced Protocol Oven (Sigma-Aldrich, St. Louis, MO) at 35 °C for 0.5 h. The ITO glass was then sonicated for 10 minutes successively in solutions following the order below: water, isopropanol, acetone and then a 10 wt % NaOH solution. The ITO glass was thoroughly rinsed with Milli-Q water to remove any solvent and NaOH. The ITO glass was then heated at 120 °C to remove any remaining solvent.

A PEDOT:PSS solution was prepared using 1:1 ratio of the 2.8 wt % PEDOT:PSS solution to isopropanol for enhancing the solution’s wettability. This solution was then filtered using a 0.22 μm poly(tetrafluoroethylene) (PTFE) hydrophobic filter (Sigma-Aldrich, St. Louis, MO). 50 μL of the above solution was dynamically spincoated using a Laurel Technologies (North Wales, PA) spincoater (Model WS-400B-6NPP/LITE) on the ITO glass at 2500 rpm for 60 s to form a film with 120 nm thickness. This layer was then dried at 70 °C in an oven for 1 h.

After the GQD chlorobenzene phase transfer, we obtained a roughly 2 g/L GQD chlorobenzene dispersion with 2.0 g/L TOAB and 4.0 g/L KI also dissolved in the dispersion. 5.0 mg of PVK was added to this 1.00 mL dispersion which was then left to stir for 48 h. A 100 μL light emitting dispersion was dynamically spin-coated on top of the PEDOT:PSS layer at 3000 rpm for 90 s to form a 100 nm film. This layer was then heated at 70 °C in an oven for 1 h. The devices were then placed in an atomic layer deposition (ALD) instrument (Savannah
3.4. Experimental

200, Cambridge Technologies, Cambridge, MA) controlled by Savannah software and held at 150 °C and 0.01 Torr. The ALD temperature was optimized to be low but still efficiently deposit according to previous studies to not destroy the previous film progress.[16] Alternating pulses of gaseous diethyl zinc and gaseous water were released over the devices to create a 10 nm electron-transporting/hole-blocking interlayer zinc oxide over the film as reported by us elsewhere for a Ru(bpy)$_3^{2+}$ LEC device.[17]

The devices were then placed in a Plasmionique physical vapor deposition (PVD) instrument (Varennes, QC) and an ultra-high vacuum reduced the pressure to $1 \times 10^{-6}$ Torr. The devices were suspended above a fresh Plasmionique tungsten boat (Varennes, QC) in a custom-made brass shadow mask with a pattern on it. The tungsten boat was then heated using high current to melt then evaporate 0.30 g of Al. The shadow mask created a 120 nm Al pattern of five Al band electrodes on a single ITO band glass substrate, which have dimensions of 1.8 mm × 8.0 mm. The devices were immediately transferred into a Nexus II glovebox (Vacuum Atmospheres Company (VAC), Hawthorne, CA) under a medical nitrogen atmosphere to protect the LEC devices as much as possible. All deposited layers except for the ITO pattern were scraped off in a small position permitting a metal connection to be made to the ITO and the Al bands on the device.

LEC Device Characterization

Device testing was conducted immediately after device preparation. A custom 3D printed device holder electrically connected one Al pin and the exposed ITO surface to allow powering the device. These devices were powered through these contacts by a Keithley 2400 Source meter (Solon, OH) controlled by a computer via a NI (Austin, TX) GPIB-USB cable. Device emission was collected by a Hamamatsu Photonics R3896 photomultiplier tube (Japan) held at -750 V by a high voltage power supply (Newport Technology Inc., Irvine, CA), which corresponded to a gain factor of $1.3 \times 10^6$.[1] The PMT response was input into a Keithley Model 6487 picoammeter (Solon, OH) held at an appropriate sensitivity. The picoammeter signal was fed into the computer with a NI data acquisition board (DAQ 6036E). Both the voltage application from Keithley 2400 and the PMT signal were controlled and acquired simultaneously using a custom designed 2019 LabVIEW (Austin, TX) code. Luminance-current-voltage data transformations were performed according to our previous reports.[1, 8] Briefly, photocurrent in nA measured from the PMT was transformed to luminance in cd/m$^2$ using three other measured values: a background-subtracted, normalized GQD LEC emission spectrum, a precisely measured, calibrated experimental setup and the photopic luminous efficiency function representing the visual sensitivity of the human eye to light.

Spectroscopic information was obtained using an Acton SP2300i spectrometer (Acton, MI) coupled to an Andor iDUs 401A-BR-DD-353 charge coupled device (CCD) camera (Belfast,
UK) held at -70 °C. Before measurements, the spectroscopic system was calibrated using the intense 546.07 nm emission from an HG-1 Hg-Ar calibration source (Ocean Optics, Dunedin, FL). Any electrical driving force required during spectroscopic analysis was also applied by the Keithley 2400.

**Electrochemical Impedance Spectroscopy**

A Solartron Analytical 1286 electrochemical interface (Farnborough, NH) was used to provide a potential bias and a Solartron Analytical 1260A impedance analyzer (Farnborough, NH) applied a 30-50 mV sine wave in addition to the potential bias for all impedance testing. Data was recorded at 10 steps/frequency decade with 3 samples measured/frequency. The instruments were controlled, and the data was recorded using Corrware, and ZPlot software (Scribner Associates Inc, Southern Pines, NC). The LEC devices were placed in a custom-designed copper Faraday cage and the cage was grounded using our building’s available ground. All impedance simulations were performed using ZView software (Scribner Associates Inc, Southern Pines, NC). All fitting was performed on both real and imaginary parts of the impedance from $10^5$ to $10^{-1}$ Hz.

EIS tests were performed by holding a constant potential for 90 seconds, then applying a sinusoidal potential perturbation. This process was repeated twice back-to-back to make sure device deterioration did not occur. All device absolute values and EIS values are averages of at least 8 tests across 3 different devices, except for the 12.70 V which contained an average of 4 devices across 2 devices.

**3.5 Results and Discussion**

**Device Characterization**

A GQD LEC was prepared according to the inset of Figure 3.1. PEDOT:PSS was employed as a hole injection layer and a 10 nm ZnO layer was used as an electron injection layer. For the light emitting layer, two salts were required for the efficient phase transfer of the emitter, GQDs, from aqueous to organic solvents. PVK was employed as a matrix to facilitate the necessary ion rearrangement for the LEC to operate efficiently. GQDs also have two excitation modes: a surface and core state[3, 4, 67] which have been characterized previously to be 2.70 eV and 3.87 eV respectively with resulting emissions of 660 nm and 440 nm.[70] The concentrations for the components of the light emitting layer were all optimized for a low turn-on voltage and a high luminance.

Figure 3.1 displays a luminance-current-voltage (LIV) graph recorded from a GQD LEC where the voltage was slowly increased from 0.00 V to 10.00 V at a scan rate of 0.05 V/s and the luminance and current were measured. The current is negligible until the onset potential at 2.50
3.5. Results and Discussion

Figure 3.1: a. A luminance-current-voltage (LIV) graph of a GQD LEC. The inset is an illustrative LEC structure with the ITO-PEDOT:PSS electrode connected as the anode, and the aluminum electrode connected as the cathode. b. A 1 s accumulation of electroluminescence from a device held at a constant current of 2 mA (33.33 mA/cm²). The inset shows the resulting CIE co-ordinates (x,y) of the emission (0.44,0.39).

V and a maximum current is located at 3.50 V. After this local maximum, a decrease in current is seen to a local minimum of 4.00 V. This observation is common in LECs where this negative resistance, or the decrease in current as voltage increases is an indication of the formation of p-n junctions. This phenomenon is related to the electrochemical doping (ECD) model of LEC operation where a p-n junction is formed by the movement of ionic species in the light emitting layer, or in this case the TOAB/KI,PVK and GQD layer. The ionic species (TOAB/KI) separate into cationic sections (TOA⁺ and K⁺) and anionic sections (Br⁻ and I⁻) by doping the PVK polymer to create respective p- and n-doped sections within the light emitting layer. Electrons and holes that are transported by the n- and p-doped sections respectively can recombine in the center of the p-n junction to emit light. However, injected electrons and holes during ion movement can still recombine radiatively like an LED. Following this LEC theory, Figure 3.1 displays this behaviour where the device begins emitting at 4.00 V around the time this p-n junction is formed. This device’s electroluminescence has a peak maximum at 660 nm (Figure 3.1b) corresponding to the GQD surface states investigated previously. Additionally, a shoulder at 430 nm corresponds to the GQDs core states which are traditionally accessed by photoluminescent excitations. These emissions produce a yellowish-white color with (x, y) CIE co-ordinates of (0.44, 0.39) seen in the inset of Figure 3.1b. Then at 4.0 V the current and luminance begin to increase linearly. The luminance deviates from this relationship and peaks at 7.00 V then decreases to a minimum at 8.20 V likely because the overpotential is too great and previously energetically unfavorable side reactions are now contributing to the current consumption. Increasing the potential further augments luminance at a significantly lower efficiency compared to the 7.00 V emission maximum. The power required at the 7.00 V
Figure 3.2: Constant voltage of 7.00 V applied to the device for 1200 s.

<table>
<thead>
<tr>
<th>Voltage Applied (V)</th>
<th>$R_{\text{ext}}$ (Ω)</th>
<th>$R_{\text{int}}$ (MΩ)</th>
<th>C (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>35.1 ± 9.1</td>
<td>4.50 ± 1.61</td>
<td>14.1 ± 1.1</td>
</tr>
</tbody>
</table>

Table 3.1: Average variables used to fit the experimental data from at least 3 devices with two tests each at a bias potential of 0.00 V using the equivalent circuit in inset of Figure 3.3.

...local luminance maxima is 84 mW, whereas the powers at 8.20 and 9.00 V generate the same or lower luminance were 200 mW and 300 mW, respectively.

A constant potential of 7.00 V was held for the device to achieve a constant emission of 0.1 cd/m² for over 1200 s seen in Figure 3.2. As the potential is initially applied, it takes the device 2 s to react to the applied potential before raising to a high maximum. The current decreases in the first 5 s to a minimum, at which point the current begins increasing until the scan ended. This behaviour is typical of an LEC where a p-n junction formation is required for efficient device operation. The emission appeared to be uniform with little degradation at longer times observed as a darkening grey spot.

**Electrical Characteristics of Non-Operating Device (0 V)**

EIS is performed by holding a constant voltage and applying a low amplitude perturbation to the device. The current is measured following the AC potential. If we plot one cycle of the sinusoidal function of potential and the corresponding current, they may differ by an angle...
3.5. Results and Discussion

Figure 3.3: Impedance spectroscopy of a LEC device held at 0.00 V overlapped with a sinusoidal potential with an amplitude of 30 mV over a frequency range of 100,000 to 0.1 Hz. A Nyquist plot (left) and Bode plots (right) show the collected data as circles connected with dotted lines, along with simulated data as a solid black line created using the equivalent circuit in the inset of the Bode plots.

called the phase angle (θ [°]). A phase angle of 0° describes a current that reacts immediately to the sinusoidal potential whereas a phase angle of 90° describes a delay in the current response to the applied potential. Impedance (Z) of a simple system (just a resistor) is found by the simple following relation:

\[ Z(\omega) = \frac{V(\omega)}{i(\omega)} \]  

where \( V(\omega) \) and \( i(\omega) \) are voltage and current as functions of frequency respectively.

Understanding Z is often easier when expressing it in cartesian coordinates by plotting the real (\( Z' \)) and imaginary (\( Z'' \)) part of the impedance as an abscissa (x) and ordinate (y). The magnitude of this line is the total impedance (|Z|) and the \( \theta \) is the angle from the normal. Only out-of-phase components can create -Z" values and only in-phase components can create Z' values. Combination of the -Z" and Z' values provides Z.

The GQD LECs were first biased at a DC potential of 0.00 V and a sinusoidal voltage with an amplitude of 30 mV was applied over six decades of frequencies (from \( 10^5 \) to \( 10^{-1} \) Hz). The current response to this AC potential was measured to understand the electrical characteristics of the device. From this current, some important variables can be analyzed such as the |Z|, phase angle or the angular difference between the potential applied and current response, Z", and the Z'. Figure 3.3 displays Nyquist plots (left) and Bode plots (right) resulting from data transformations of the current and potential time-dependent data measured from the mentioned system. Between \( 10^5 \)-\( 10^1 \) Hz in all plots most variables remain constant or have consistent
Table 3.2: Average variables used to fit the experimental data from at least 3 devices with two tests each at a bias potential of 4.00 V using the equivalent circuit in inset of Figure 3.4. $C_{eff}$ was found using Eq. 3.2.

<table>
<thead>
<tr>
<th>Voltage Applied (V)</th>
<th>$R_{ext}$ (Ω)</th>
<th>$R_{int}$ (kΩ)</th>
<th>$Q$</th>
<th>$\alpha$</th>
<th>$C_{eff}$ (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>62.9 ± 43.3</td>
<td>1.40 ± 0.56</td>
<td>86.7 ± 45.5 e$^{-9}$</td>
<td>0.86 ± 0.03</td>
<td>20.7</td>
</tr>
</tbody>
</table>

$Z'$ and $\theta$ remain constant at 0 Ω and 90° respectively. $-Z''$ and $|Z|$ slowly increase at the same time. The current response lags the potential applied by a phase angle of 90° which is a direct indicator of a capacitor because of the charge storage that occurs with incoming electrons. In other words, this 90° phase angle necessitates that at a maximum potential there is no current measured and at maximum current there is no sinusoidal potential applied. As the frequency continues to decrease past $10^1$ Hz, a real impedance appears and the phase angle approaches 180° at $10^1$ Hz. Since the current at 0.00 V is slightly negative, the $\theta$ enters the second quadrant of a plot of $Z'$ vs. $-Z''$. The development of a real impedance in the Nyquist plot and the removal of the imaginary component (0 ordinate value in cartesian coordinates) at higher frequencies indicates a resistor that follows Ohm’s law. Resistors do not have a frequency dependency and therefore, have no phase angle (either 0 or 180°). Also, looking at the first point (at $10^5$ Hz) a non-zero $Z'$ component can be seen. This $Z'$ component is another resistor that always exists, is frequency-independent, and therefore, would be in series with the other components discussed here.

From these impedance observations, an equivalent circuit is displayed in Figure 3.3 for the GQD LECs held at 0.00 V. This suggested equivalent circuit resembles previous LEC EIS studies that use the polymer Superyellow® as the light emitter in LECs.[40, 44] Fitting the experimental data with this equivalent circuit produces the variables seen in Table 3.1. The small initial resistance (35.1 Ω) is from the small resistance required to transport electrons through the electrodes and to the light emitting layer, which we will assign external resistance ($R_{ext}$). An extremely large resistance (4.50 MΩ) is seen in the device which also has a capacitive (C) nature (14.1 nF). This resistance is much greater than any resistance seen for ITO, PEDOT:PSS, ZnO and Al. Therefore, this resistance is likely associated with ionic transport in the light emitting layer which will be designated as the internal resistance ($R_{int}$). C is due to the geometric capacitance of the system, or the dielectric constants of the media between the electrodes.

**Electrical Characteristics and P-N Junction Formation at 4 V**
3.5. RESULTS AND DISCUSSION

Figure 3.4: Impedance spectroscopy of a GQD LEC device held at 4.00 V overlapped with a sinusoidal potential with an amplitude of 30 mV over a frequency range of 100,000 to 0.1 Hz. A Nyquist plot (left) and Bode plots (right) show the collected data as circles connected with dotted lines, along with simulated data as a solid black line created using the equivalent circuit in the inset of the Bode plots.

Figure 3.4 displays the impedance spectra of a GQD LEC held at 4.00 V with the same 30 mV sinusoidal potential varying frequency perturbation applied as in Figure 3.3. Starting at $10^5$ Hz, a large $Z'$ component exists, likely indicating the same $R_{ext}$ seen earlier. With a positive applied potential and a positive current flowing through the device, the phase angle now falls between 0 and $90^\circ$ instead of the 90-180$^\circ$ range seen in Figure 3.3. A small semicircle is created between $10^5$ to $10^3$ Hz as the -$Z''$ component increases to $10^4$ Hz then decreases as the frequency decreases. Over the same time the $Z'$ component slowly increases. Interestingly, the frequencies at which the same components are seen are drastically different from Figure 3.3. By $10^3$ Hz in Figure 3.4, the semicircle has finished forming whereas in Figure 3.3 the semicircle was just beginning highlighting the dynamic GQD LEC’s electrical characteristics. Lower frequencies than $10^5$ Hz are unremarkable producing almost the same equivalent circuit as Figure 3.3. However, when the Bode plot in Figure 3.3 is compared to the one in Figure 3.3, it is obvious that the semi-circle in Figure 3.4 is relatively depressed. This means a capacitor cannot be used in the equivalent circuit and a constant phase element (CPE) designated as Q1 must be used instead (inset of Figure 3.4). CPE’s are typically used over capacitors in non-homogeneous solid systems because electrons can choose between multiple pathways to pass through a film which all have different capacitances and resistances. This CPE is a summation of all these pathways where $\alpha$ describes whether the average pathway is a pure resistor ($\alpha = 0$) or a pure capacitor ($\alpha = 1$) or anywhere between. The heterogeneity in the light emitting layer is likely caused by the movements of ions and the stoichiometry of the light emitting layer gradually changing. When the GQD LEC is held at 4.00 V, $\alpha$ is 0.86 which means the average electron pathway is characteristic of a capacitor but has some characteristics of
Figure 3.5: Impedance spectroscopy of a GQD LEC device held at 7.00 V overlapped with a sinusoidal potential with an amplitude of 30 mV over a frequency range of 100,000 to 0.1 Hz. A Nyquist plot (left) and Bode plots (right) show the collected data as circles connected with dotted lines, along with simulated data as a solid black line created using the equivalent circuit in the inset of the Bode plots.

Table 3.3: Average variables used to fit the experimental data from at least 3 devices with two tests each at bias potentials of 7.00 V, 9.00 V and 12.70 V, using the equivalent circuit in inset of Figure 3.5. $C_{eff}$ values were found using Eq. 3.2.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>$R_{ext}$ (Ω)</th>
<th>$R_{int}$ (Ω)</th>
<th>$Q = C_{eff}$ (nF)</th>
<th>$\alpha$</th>
<th>$R_{inductor}$ (Ω)</th>
<th>$L_{ion}$ (H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00</td>
<td>39.4 ± 3.2</td>
<td>116.5 ± 60.0</td>
<td>270 ± 71</td>
<td>1.00 ± 0.01</td>
<td>703 ± 60</td>
<td>97.1 ± 11.0</td>
</tr>
<tr>
<td>9.00</td>
<td>34.2 ± 9.5</td>
<td>60.5 ± 17.7</td>
<td>350 ± 57</td>
<td>1.00 ± 0.01</td>
<td>369 ± 131</td>
<td>37.3 ± 18.6</td>
</tr>
<tr>
<td>12.70</td>
<td>37.5 ± 16.5</td>
<td>74.3 ± 5.2</td>
<td>901 ± 608</td>
<td>1.00 ± 0.01</td>
<td>203 ± 9</td>
<td>33.4 ± 22.5</td>
</tr>
</tbody>
</table>

where $C_{eff}$ was found to be 20.7 nF for a GQD LEC held at 4.00 V. The device is storing twice the charge after the p-n junction has formed compared to the 0.00 V. This stage is also characterized by the absence of device emission.

**GQD LEC Emission ($> 4$ V)**

The Bode and Nyquist plots seen in Figure 3.5 are from a GQD LEC held at 7.00 V. Subsequently 9.00 V and 12.70 V EIS experiments were also performed. Starting at $10^5$ Hz to
10^1 Hz, there is virtually no difference between the EIS spectra in Figures 3.4 and 3.5 and the same equivalent circuit can be used. In all cases, the R\text{ext} remains consistent signifying that the electrodes remain air stable. For the CPE, this fitting yields an α value equal to 1, which represents a pure capacitor providing Q units of nF and allows circumventing the use of Eq. 3.2. The fully formed p-n junction of the GQD LEC held at 7.00 V is now emitting strongly from Figure 3.1 which is electrically characterized by an order of magnitude increase in charge storage from 20.7 nF to 270 nF and another order of magnitude decrease in R\text{int} from 1400 Ω to 116.5 Ω. This decrease in R\text{int} and the significant charge storage signifies that the formed p-n junction is now emitting efficiently still following the ECD model of LEC operation. This trend continues to an optimal 9.00 V where C\text{eff} doubles again and the R\text{int} decreases again to almost match the R\text{ext}. At 12.70 V, R\text{int} increases back to the 7.00 V levels signifying the device has had side reactions or “black spots” occur, and the device is deteriorating. The C\text{eff} at 12.70 V more than doubled from 9.00 V again highlighting the ability for charge storage in the light emitting layer. This is the end of the simple EIS device analysis where all stages of device operation have successfully been characterized.

Next a rare observation was made from the EIS plots in Figure 3.5. Interestingly, at frequencies lower than 10^2 Hz the |Z| decreases with contributions from a shrinking Z’ and an increasingly negative -Z”. This trend continues and reaches a minimum peak at 100 Hz where the -Z” increases to 0 and the Z’ continues shrinking. Interestingly, a positive θ that is created by a negative -Z” describes a current that reacts before the applied potential, which is uncommon at low frequencies. An example of a positive θ electrical component is an inductor, which creates an opposing current when a potential is applied due to a large magnetic field governed by Lenz’s Law. Inductors are commonly observed in EIS at high frequencies at which AC does not give a magnetic field time to change direction thereby opposing the current flow. However, an inductor seen at such low frequencies is unlikely because of a slowly changing current permitting the magnetic field time to fully change with the current. An equivalent circuit can be developed from this information. This circuit contains an inductor (L) and a Z’ component which we will designate as a resistor (R\text{inductor}) that are in series. L and R\text{inductor} must be parallel to C\text{eff} and parallel to R\text{int}. Otherwise, the R\text{inductor} and L would not be seen at low frequencies since inductors behave as shorts at long times (the voltage across them is 0.00 V at t=∞) and two or more resistors in series appear as one resistor. The resulting equivalent circuit is seen in the inset of Figure 3.5. In fact, this equivalent circuit happens to match one of the two recommended circuits in the positive θ review paper. Interestingly, our proposed equivalent circuit resembles a commonly proposed equivalent circuit for LECs. These mentioned LEC EIS studies encompassed many light emitters such as quantum dots, emissive polymers and iTMC with conventional
device structures of ITO/PEDOT:PSS/light emitting layer/Al. The equivalent circuit fits very well with $\chi^2$ less than 0.001, indicating strong reproducibility and accuracy. All results are summarized in Table 3.3. Both $L$ and $R_{\text{inductor}}$ start at 97.1 H and 703 $\Omega$ respectively, and steadily decrease as the potential is increased to a minimum of approximately a third of their original values. This indicates that whatever this physical process is, it only appears when the p-n junction is fully formed in the LEC and then steadily decreases with potential.

This inductive effect can be caused by heating where high enough currents decrease resistance and increase inductive effects. However, we do not believe that temperature effects caused this artefact in our studies. We also investigated literature for self-heating insights. In 300 $\mu$m pixel size InGaN LEDs, Gong et al. found at current densities higher than 100,000 mA/cm$^2$, minor heating was produced. Klotz et al. studied heating effects in hydrogen fuel cells where the conversion of hydrogen and oxygen to water is an exothermic process and found up to 10 K increase in temperature when the cell was held at 2,500 mA/cm$^2$. The current densities used in our studies were never higher than 200 mA/cm$^2$ (Figure 3.1) and calculated EIS values were reproducible and constant when tested back-to-back. From literature, our personal experience, and our own data, it is plausible that device self-heating did not contribute to this inductive EIS response.

Interestingly and to the best of our knowledge, this is the first time this positive $\theta$ has been observed in LEC EIS where we will propose a physical interpretation for this observation. The low frequency inductor-like response may describe a larger charge carrier that requires greater times or lower frequencies to react to an AC stimulation. Likely the ions responsible for electron flow in the light emitting layer (TOA$^+$, K$^+$, Br$^-$ and I$^-$) once the p-n junction is formed create a small magnetic field which slowly reacts to the AC at low frequencies. As the overpotential above the emission maximum increases e.g. above 7.00 V, $L$ and $R_{\text{inductor}}$ decrease possibly indicating that the magnetic field created by the ions in the light emitting layer is decreasing and resisting the current flow less. This could be due to side reactions occurring like the mentioned “black spots” earlier which are common with extended usage or high overpotentials. Another interpretation of this positive $\theta$ could be a charge buildup at a layer interface (such as ZnO/[PVK/TOAB:KI/GQDs]) that opposes electron flow. However, this theory would likely see an increasing $L$ and $R_{\text{inductor}}$ with an increasing overpotential above the emission maximum which does not occur. For these reasons we believe that the positive $\theta$ belongs to an inductor-like response from current opposition of the formed p-n junction.

A recent review of this uncommon positive $\theta$ in electrochemical systems that are similar to LECs describes two common physical interpretations. The first, is an ion movement process which is caused by dynamic stoichiometry of a mixed conducting material. This physical interpretation matches our proposed theory where our system necessarily contains ion and
electron movement through a mixed conductor. The second physical interpretation in the electrochemical system positive $\theta$ review is a two-step electrochemical mechanism where a specific site is absorbing and reacting species. In fact, the review’s second physical interpretation may also apply here where $\Gamma$ (which has the lowest standard reduction potential out of $K^+$, Br$^-$ and $\Gamma$) may be absorbing, reacting, and desorbing off a surface in the LEC. However, the increasing potential decreases the quantitative value of $L$ and $R_{\text{inductor}}$, which we believe would be the opposite occurrence if this second physical interpretation applied. Generally, if the overpotential of an electrochemical reaction is increased, the current also increases if migration of the species is not limiting the reaction. Even a diffusion limited process would reach a consistent value instead of decreasing over time or decreasing with an increasing potential. For these reasons, we still believe that the ions in the light emitting layer have created a small magnetic field that opposes a low AC frequency and provides an inductor-like response creating a positive $\theta$.

Polymer light emitting diode (PLED) research groups have also seen negative capacitance at low frequencies which is similar to a positive $\theta$ because of the corresponding large negative $-Z''$ produced from the out-of-phase negative capacitance.[12][13][20][26][29][45][49] The polymers in PLEDs are hole transporting layers or light emitters which resemble LECs. The key difference between LECs and PLEDs is the presence of electrochemical dopants in the light emitting layer. In the field of PLED EIS research, there are two prevailing theories for this positive $\theta$. The first theory is an equilibrium is developed between high energy electrons and holes at a metal|polymer. This first PLED EIS theory is almost the same as our second proposed theory which we believe is unlikely in our system because of the decrease of $L$ and $R_{\text{inductor}}$ with increasing potential. The second PLED EIS theory for the positive $\theta$ is that a recombination current is created when the PLED is emitting light. Strong recombination currents in PLEDs that start at device turn-on voltages unfortunately mimics the device turn-on processes necessary for an LEC. Unlike LEDs, LECs require a p-n junction to be formed before emission making it difficult to separate a recombination current from ion movement processes at turn-on voltages in an LEC. Due to this difficulty, it is hard to apply and assess this recombination current theory for LECs. Also, a strong recombination current or an electron transfer process observed at low frequencies is puzzling. Typically, electron transfer processes are viewed at high frequencies and mass/ion transfer processes are viewed at low frequencies because of the time constants associated with the processes. Therefore, ion movement is more likely to be seen on longer than one second or one Hz time scales and is likely the culprit for the positive $\theta$ at low frequency. We believe that small magnetic fields established by ion rearrangements forming a p-n junction are responsible for the observed positive $\theta$ and $L$ at low frequencies.
### 3.6 Conclusion

A phase-transferred GQD light emitting layer in an LEC displayed three distinct potential-dependent equivalent circuits under operation, forming p-n junction and emitting electroluminescence. All electrical natures of the GQD LEC were found to follow the ECD model. Interestingly, when the device was emitting light, a positive phase angle was seen. This inductor-like response and corresponding resistance also decreased with overpotential signifying an inverse relationship or the presence of side reactions. This positive phase angle only occurred at low frequencies, which was observed for the first time in LECs. We propose that a minor magnetic field created by the p-n junction in an LEC was opposing the changing AC potential at low frequencies creating this inductor-like response. This study provides an electrochemical insight into this positive phase angle in LECs. These observations and equivalent circuits are anticipated to be used in judging the chemical stability of p-n junctions to excessive doping and in increasing the operational lifetimes of all LECs.

### 3.7 Acknowledgements

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### References


REFERENCES


Chapter 4

ECL Analysis of TADF Luminescent Materials
4.1 Preface

This chapter investigates a series of compounds that exhibit thermally activated delayed fluorescence (TADF). TADF allows achieving a theoretical 100 % QY making compounds that exhibit TADF theoretically the most efficient emitters. Therefore, TADF compounds are of great research interest.

This Chapter evaluates the radical stability, emission efficiency, and emission mechanism of this TADF compound series to understand their suitability for implementation in ECL applications.

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4.2 Abstract

Aiming to develop efficient blue-emitting thermally activated delayed fluorescence (TADF) compounds, we have designed and synthesized derivatives of the well-known sky-blue emitter 2CzPN that contain electron-accepting phosphine chalcogenide groups to stabilize the HOMO level relative to the pristine compound, thus increasing the HOMO-LUMO gap and blue-shifting the emission wavelength. By cyclic voltammetry, photophysical data and quantum-chemical calculations, it was found that polar solvents and matrices validated the proposed concept, but these trends were not recovered in non-polar media. The suitability of these 2CzPN derivatives in polar matrices for optoelectronic applications was explored with electrochemiluminescence (ECL) by measuring emission delays, radical stability, emission stabilities, emission efficiencies and emission spectra. Some of the 2CzPN derivatives showed an unprecedented delayed onset of the ECL, and delayed rising time to the ECL maximum, as well as long ECL emission decay. All of these mentioned delay times suggest that these luminophores primarily emit via organic long-persistent electrochemiluminescence (OLECL) mechanisms. The derivatization of the donor groups of the emitters affected both the radical stability and the predominant emission mechanism, providing important insight into their potential as emitters in solid-state electroluminescent devices.

4.3 Introduction

Developing strategies to harvest triplet states in organic light-emitting diodes (OLEDs) based on small molecules has been the focus of considerable effort because, according to spin statistics, they constitute 75 % of the excitons generated in the device. While phosphorescent heavy-metal-based organometallic complexes have successfully achieved 100 % internal quantum efficiency (IQE) thanks to their large spin-orbit coupling (SOC) and hence rapid intersystem crossing (ISC) rates, the use of scare elements such as iridium and platinum is a detracting feature that will ultimately impact large-scale application of OLED technology. Moreover, the inherent instability of blue-emitting heavy metal phosphorescent OLEDs has meant this class of materials is a non-starter in commercial devices.

Materials showing thermally activated delayed fluorescence (TADF), which typically take the form of donor-acceptor organic compounds, have attracted tremendous recent attention as they are capable of efficiently harvesting triplet excitons. For the TADF mechanism to be operational, there must exist a suitably small splitting energy ($\Delta E_{ST}$) between the lowest excited singlet ($S_1$) and triplet ($T_1$) states. When this criterion is met, efficient reverse intersystem crossing (RISC) processes become feasible such that non-emissive triplet...
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Excitons are thermally up-converted to emissive singlet excitons. In order to maintain a small $\Delta E_{ST}$, the exchange integral between the HOMO and LUMO must be minimized, and is commonly achieved by the spatial separation of these orbitals. In general, there are three main molecular designs that respond to this criterion: (1) compounds with twisted conformations between donor and acceptor moieties that emit via an intramolecular charge-transfer state (ICT); (2) compounds that promote through-space charge-transfer interactions between adjacent donor and acceptor units (TSCT); and (3) compounds that are both p- and n-doped nanographenes that emit via multi-resonance TADF (MR-TADF).

Each TADF emitter design principle has its own advantages and disadvantages in terms of emission color, color purity, photoluminescence quantum yield ($\Phi_{PL}$), and RISC efficiency, the latter of which is correlated strongly with device stability. For example, ICT- and TSCT-based TADF emitters have been reported to be both high emissive; their color is easily tunable but their broad emission profiles lead to poor color purity. In contrast, MR-TADF emitters exhibit excellent color purity and $\Phi_{PL}$ but generally possess much lower RISC rates. Regardless of emitter design, the stability of TADF OLEDs remains sub-optimal.

In the pantheon of ICT emitter design, the majority of the research focus has been devoted to new acceptors while the selection of donor moieties has remained rather limited; with carbazole, triphenylamine, acridan, phenoixazine, phenothiazine and dihydrophenazine accounting for more than 98% of all reported donors. This library of donors has been enriched through their chemical substitution that serves to tune the photophysical properties of the emitter. The majority of examples revolve around substituted carbazole derivatives and can be broadly categorized into two families: (i) substituents that enhance the electron-donating strength of carbazole and promote a red-shift in the emission, and; (ii) substituents that reduce the electron-donating strength of the carbazole and promote a blue-shift in the emission. Electron-rich carbazole derivatives used within TADF emitter design include 3,6-dimethylcarbazole, 3,6-dimethoxycarbazole, 3,6-di-t-butylcarbazole, fluorene-fused carbazole, benzofuran-fused carbazole, donor-dendronized carbazole, benzothiophene-fused carbazole, and paracyclophane-fused carbazole. In contrast, 3,6-diphenylcarbazole, 9-phenylcarbazole, $\alpha-\beta-\delta$-carboline, indolocarbazole, diphenylphosphine oxide-substituted carbazole derivatives, triaryl and diarylboronate-substituted carbazole derivatives, and cyanocarbazoles represent examples of electron-poor carbazole derivatives reported in the TADF literature. In the context of blue TADF emitters employing functionalized carbazole donors, Adachi et al. have reported several examples of blue TADF emitters. In 2012, Adachi et al. reported the first example of a deep blue emitter, DTC-
DPS ($\lambda_{PL} = 423$ nm, $\Phi_{PL} = 80\%$, $\Delta E_{ST} = 0.32$ eV in 10 wt % in DPEPO), based on 3,6-di-( tert-butyl)carbazole as the donor and diphenylsulfone as the acceptor. The OLED employing this emitter showed a maximum external quantum efficiency ($\text{EQE}_{\text{max}}$) of 9.9 % and CIE coordinates of (0.15, 0.17).\textsuperscript{[114]} In a following report, an improved $\text{EQE}_{\text{max}}$ of 14.5 % and CIE coordinates of (0.16, 0.16) were reported for the emitter, DMOC-DPS ($\lambda_{PL} = 455$ nm, $\Phi_{PL} = 80\%$, $\Delta E_{ST} = 0.21$ eV in 10 wt % in DPEPO) in which 3,6-di-( tert-butyl)carbazole (DTC) was replaced by 3,6-dimethoxycarbazole (DMOC) as the donor.\textsuperscript{[107]} In another example, a sky-blue emitter BDPCC-TRZ ($\lambda_{PL} = 480$ nm, $\Phi_{PL} = 100\%$, $\Delta E_{ST} = 0.11$ eV in 6 wt % in DPEPO), composed of bis(3,6-diphenylcarbazolyl)carbazole (BDPCC) as the donor and triphenyl-1,3,5-triazine (TRZ) as the acceptor, was reported. The OLED with this emitter achieved an $\text{EQE}_{\text{max}}$ of 20.6 % with $\lambda_{EL}$ at 487 nm and CIE coordinates of (0.19, 0.25).\textsuperscript{[45]} Lee et al. reported 5,11-di(9H-carbazol-9-yl)indolo[3,2,1-jk]carbazole-2-carbonitrile (CNICCz, $\lambda_{PL} = 445$ nm, $\Phi_{PL} = 46\%$, $\Delta E_{ST} = 0.27$ eV) as a deep blue emitter, with a CN-modified indolocarbazole as the acceptor core and carbazole as the donor. Here, deep-blue OLEDs ($\lambda_{EL} = 449$ nm, CIE: (0.15, 0.08)) were realized with an $\text{EQE}_{\text{max}}$ of 12.4 %.\textsuperscript{[21]}

In the seminal paper published in 2012, Adachi et al. reported one of the earliest sky-blue TADF emitters, 4,5-dicarbazolylphthalonitrile (2CzPN, $\lambda_{PL} = 473$ nm, $\Phi_{PL} = 47\%$ in toluene).\textsuperscript{[100]} An OLED device employing this emitter produced a sky-blue emission ($\lambda_{EL} = 475$ nm in 5 wt % PPT doped emitting layer) with an $\text{EQE}_{\text{max}}$ of 8.0 %. An improved OLED device performance ($\lambda_{EL} = 483$ nm, CIE: (0.17, 0.30), $\text{EQE}_{\text{max}} = 13.6 \%$) was achieved when the same emitter was used in a mCP host ($\lambda_{PL} = 477$ nm, $\Phi_{PL} = 89\%$ in 6 wt % mCP doped film, $\Delta E_{ST} = 0.09$ eV).\textsuperscript{[72]} By optimizing the device architecture, Sun et al. were able to achieve an $\text{EQE}_{\text{max}}$ of 21.8 % [CIE: (0.17, 0.27), $\lambda_{EL} = 480$ nm] while using the same emitter in the OLED, by adopting a mixed co-host system (mCP:PO15 = 1:1). However, such a high EQE was only achieved at a very low current density of ca. 0.01 mA cm$^{-2}$, and the device suffered from severe efficiency roll-off at high current density.\textsuperscript{[21]} In pursuit of a deeper blue color using the same general structural motif as 2CzPN, Gyeong et al. reported $\alpha$-CbPN ($\lambda_{PL} = 445$ nm, $\Phi_{PL} = 37\%$, $\Delta E_{ST} = 0.28$ eV in 20 wt % mCP doped film) and $\delta$-CbPN ($\lambda_{PL} = 480$ nm, $\Phi_{PL} = 93\%$, $\Delta E_{ST} = 0.13$ eV in 20 wt % mCP doped film), employing $\alpha/\delta$-carboline donors in lieu of carbazole.\textsuperscript{[41]} A maximum EQE of 22.5 % for a sky-blue OLED with $\lambda_{EL} = 486$ nm and CIE: (0.19, 0.34) was achieved using 20 wt % $\delta$-CbPN in mCP as the light-emitting layer. The same group also reported a triazine-based emitter 5,5-(2-(9H-carbazol-9-yl)-5-(4,6-diphenyl-1,3,5-triazin-2-yl)-1,3-phenylene)bis(5H-pyrido[3,2-b]indole) (CzDCbTrz) containing a $\delta$-carboline donor, and produced an OLED with an $\text{EQE}_{\text{max}}$ of 23.4 % and $\lambda_{EL} = 471$ nm with CIE: 0.16, 0.19 using 6 wt % emitter in 2,8-bis(diphenylphosphineoxide)-dibenzofuran (DBFPO) host. The chemical structures of blue TADF emitters discussed above are shown in Figure 4.1.
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Figure 4.1: Chemical structures of discussed blue TADF emitters.
Electrochemiluminescence (ECL) or electrogenerated chemiluminescence is emitted when electron transfer between electrochemically-generated radicals results in an exciton formation in the proximity of a working electrode, which relaxes radiatively.[4, 5, 18, 19] In fact, this combination of charge recombination, radical generation, exciplex formation,[38] and possibilities of host-guest systems,[111] TADF,[49] triplet-triplet annihilation[33] and phosphorescent emissions via ECL mirrors photophysical processes that can occur in OLEDs. Furthermore, high luminophore concentrations, and film electrodes[3] in ECL studies can mimic bulk and interfacial molecular conditions in OLEDs, allowing predictions of molecular performance before full device manufacturing. ECL finds additional applications in discovering luminophore film enhancement phenomena,[3, 104, 110] and in commercial applications for antigen sensing.[30] Since the early studies on ECL in the 1960s,[13, 42, 88] various types of emissive compounds have been studied.[70] However, the design of commercial ECL luminophores has been mainly limited to noble-metal complexes such as those of Ru, due to their efficient and electrochemically-stable conversion of excitons to light, regardless of the total spin. Analogously to their popular use as emitters in OLEDs, TADF molecules are likewise expected to give high ECL efficiency. Despite the thousands of reports of TADF emitters used in OLEDs, there are only a small number of examples of TADF compounds employed in ECL studies. Imato et al. studied the annihilation ECL properties of carbazole-decorated phthalonitrile based TADF emitters in both DCM and MeCN.[49] Of the compounds investigated, the ECL emission maxima, $\lambda_{ECL}$, for 2CzPN were modestly red-shifted ($\lambda_{ECL} = 550$ and 585 nm in DCM and MeCN, respectively) compared to the photoluminescence maxima, $\lambda_{PL}$, ($\lambda_{PL} = 533$ and 560 nm in DCM and MeCN, respectively) regardless of solvent. Further, the low $\Phi_{PL}$ ($\Phi_{PL} = 34$ and 10 % in DCM and MeCN, respectively) translated into low relative ECL efficiencies, $\Phi_{ECL}$, of 90 and 22 %, respectively, in DCM and MeCN, in comparison to [Ru(bpy)$_3$]$^{2+}$ which showed $\Phi_{ECL} = 100$ % under the same conditions. No discussion concerning the kinetics of exciton decay was provided. Most recently, Niu et al. reported the first example of a solid-state ECL study of a TADF polymer containing a backbone acridan-based donor and pendant triazine-containing acceptor, PCzAPT10.[31] The polymer showed significantly enhanced $\Phi_{ECL}$ of 194 % relative to [Ru(bpy)$_3$]$^{2+}$ when using tri-n-propylamine (TPA) as a co-reactant, compared to the $\Phi_{PL}$ of 21 %. The $\lambda_{ECL}$ was also significantly red-shifted, at 587 nm, compared to the $\lambda_{PL}$ (542 nm) for a neat film of PCzAPT10 immersed in 0.1 M TBAP:MeCN electrolyte solution. Furthermore, Niu et al. made water-soluble 4CzIPN nanoparticles which achieved a relative $\Phi_{ECL} = 0.7$ %, marking the first water-soluble TADF nanoparticle tested.[113]

Using the same 2CzPN scaffold as a starting point, we hypothesized that adding strong electron-withdrawing group such as phosphine-chalcogenides onto the carbazole donor moieties would promote the desired blue-shift in the emission. In this regard, we designed and
synthesized three 2CzPN derivatives and thoroughly investigated their physical, photophysical, electrochemical properties, further supporting these optoelectronic studies with density functional theory (DFT) calculations (Scheme 4.1). ECL was then used to gauge the suitability of these derivatives for optoelectronic applications in the desirable polar media. Assessing the potential of the three 2CzPN derivatives as OLED materials was possible without the time-intensive and costly task of constructing full OLEDs, since ECL provides a tool to simulate charge imbalances, judge relative stabilities of electrically generated radical cations and anions (holes and electrons, respectively), evaluate relative emission efficiencies and understand emission mechanisms of luminophores.[48, 49, 55] Although our reference compound, 2CzPN is a well-studied TADF emitter in the literature, we have redetermined its optoelectronic properties under the same conditions as the three new emitters, as well as calculating its properties, to allow the most accurate comparison.

4.4 Experimental Section

General Synthetic Procedure

All commercially available chemicals and reagent grade solvents were used as received. 3-Bromocarbazole, 3,6-dibromocarbazole, N-TBDMS-3-bromocarbazole and N-TBDMS-3,6-dibromocarbazole were prepared according to the literature.[105] Air-sensitive reactions were performed using standard Schlenk techniques under a nitrogen atmosphere. Anhydrous THF was obtained from a solvent purification system. Flash column chromatography was carried out using silica gel (60 Å, 40-63 µm). Analytical thin-layer-chromatography (TLC) was performed using silica plates with aluminium backings (250 µm with F-254 indicator), and were visualized using a 254/365 nm UV lamp. $^1$H, $^{13}$C and $^{31}$P NMR spectra in CDCl$_3$ or DMSO-d$_6$ were recorded on an NMR spectrometer (400 MHz for $^1$H, 101 MHz for $^{13}$C and 162 MHz for $^{31}$P). The NMR signal is described as follows: s = singlet, d = doublet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublets of doublets, and m = multiplets. Melting points were measured using open-ended capillaries on Electrothermal Mel-Temp melting point apparatus and are uncorrected. High-resolution mass spectrometry (HRMS) was performed by the EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea University. Elemental analyses were performed by Mr. Stephen Boyer, London Metropolitan University. High performance liquid chromatography (HPLC) analysis was conducted on a Shimadzu Prominence Modular HPLC system. HPLC traces were performed using an ACE Excel 2 C18 analytical (3 × 150 mm) column. Gas chromatography mass spectrometry (GCMS) analysis was carried out on a Shimadzu GCMS-QP2010 SE instrument, an advanced standard gas chromatograph mass spectrometer coupled with automated AOC-5000 sample injection system using a Shimadzu-
SH RTX-1 column (fused silica) (length = 25 m, thickness = 0.25 mm, oven temp.: 40 °C to 250 °C; detector: MS; detection temp.: 250 °C; Carrier gas: helium).

**Photophysical Measurements**

Optically dilute solutions of concentrations on the order of $10^{-5}$ or $10^{-6}$ M were prepared in HPLC grade acetonitrile for absorption and emission analyses. Absorption spectra were recorded at room temperature on a Shimadzu UV-1800 double beam spectrophotometer. The molar absorptivity values were determined by linear regression analysis of four solutions of different concentrations within the range of $10^{-4}$ to $10^{-5}$ M prepared by dilution of stock solution ($10^{-3}$ M). Aerated solutions were prepared by using aerated solvents with prior air bubbling for 5 min. whereas degassed solutions were prepared via five freeze-pump-thaw cycles prior to emission analysis using a home-made cuvette with extended solvent bulb designed for cryogenic degassing. Steady-state emission and time-resolved emission spectra were recorded at 298 K using Edinburgh Instruments FLS980 fluorometer. Samples were excited at 360 nm using a Xenon lamp for steady-state measurements and at 378 nm using a PicoQuant pulsed diode laser for time-resolved measurements. Photoluminescence quantum yields for solutions were determined using the optically dilute method\[27\] in which four sample solutions with absorbance at 360 nm being ca. 0.10, 0.080, 0.060 and 0.040 were used. Their emission intensities were compared with those of a reference, quinine sulfate, whose quantum yield ($\Phi_r$) in 1 M H$_2$SO$_4$ was taken as 54.6 %.\[75\] The photoluminescence quantum yield of a sample, $\Phi_s$, can be determined using the equation $\Phi_s = \Phi_r(A_r/A_s)((I_s/I_r)(n_s/n_r)^2$, where $A$ stands for the absorbance at the excitation wavelength ($\lambda_{exc}$: 360 nm), $I$ is the integrated area under the corrected emission curve and $n$ is the refractive index of the solvent, with the subscripts “s” and “r” representing sample and reference respectively. 10 wt % doped poly(methyl methacrylate) (PMMA)/1,3-bis(N-carbazolyl)benzene (mCP) thin films were prepared by spin-coating a chlorobenzene solution of the desired sample on a quartz and sapphire substrate. Solid-state $\Phi_{PL}$ measurements of thin films were performed in an integrating sphere under a nitrogen atmosphere or air using a Hamamatsu C9920-02 luminescence measurement system. For temperature-dependent measurements, samples prepared on sapphire substrates were cooled down to 77 K in a cryostat (Oxford Instruments). Time-resolved spectra (prompt fluorescence and phosphorescence) were obtained in 10 wt % doped mCP or 10 wt % doped PMMA thin films at 77 K using a gated intensified charge coupled device (iCCD camera) from Stanford Computer Optics and under laser excitation at 360 nm.

**Electrochemical Measurements**

All electrochemical experiments were carried out in 3 mL of DCM with a luminophore and with TBAP as the electrolyte, at concentrations of 0.7 mM and 0.1 M, respectively. A Pt electrode with an active diameter of 2 mm was used as the working electrode and was polished
with 1, 0.3 and 0.05 µm aluminum oxide nanoparticles before every use. An electrochemical polish was subsequently performed in 0.1 M H₂SO₄ scanning between -0.9 and 0.9 V vs. Pt wire at a scan rate of 0.5 V/s for 20 minutes. The quality of the polish was verified with cyclic voltammetry of a [Ru(bpy)₃]²⁺ solution at a scan rate of 0.1 V/s by seeing the 60 mV difference between the cathodic and anodic peaks for the [Ru(bpy)₃]²⁺ oxidation and the same peak height. Pt coil counter and reference electrodes were used for all measurements, and calibration of the potential was performed with ferrocene as a reference. All ECL cells were constructed in an inert atmosphere glove box and were sealed to prevent oxygen from entering the cell during experiments.

ECL was measured by a photomultiplier tube (R928 PMT, Hamamatsu Photonics, Japan) held at -750 V. The voltage signal from the PMT was transduced by a Keithley ammeter (6487, Keithley Instruments, Cleveland, OH) into so-called photocurrent measured in nanoamperes (nA).

The spectroscopic measurement methods were reported elsewhere,[4] with a spectrograph (Acton 2300i, Princeton Instruments Inc., Trenton NJ) coupled with a CCD camera (Model DV420-BV, Andor Technology, UK) cooled to -55 °C.

The relative efficiency of the ECL emission was determined by finding the charge input and the ECL output for the specific experimental setup and comparing these values to the commercial standard of ECL emitter systems, [Ru(bpy)₃]²⁺ for annihilation systems and [Ru(bpy)₃]²⁺/BPO or [Ru(bpy)₃]²⁺/TPrA for co-reactant systems, by the following equation:

$$\Phi_{ECL} = \left( \frac{\int \nu_{\text{photons}} dt}{\int \nu_{\text{electrons}} dt} \right) \times 100\% \quad (4.1)$$

where st and x refer to the standard [Ru(bpy)₃]²⁺ and compounds of interest, respectively. Pulsing annihilation efficiencies were measured from 25 pulses using Eq. 4.1.

Reaction enthalpies were calculated by the following equation:[32]

$$-\Delta H^o = E^o \left( \frac{R \cdot \cdot \cdot}{R'} \right) - E^o \left( \frac{R}{R \cdot \cdot \cdot} \right) - T \Delta S^o \quad (4.2)$$

where $E^o$ values are the standard reduction potentials for two half reactions and $T \Delta S^o$ is equal to 0.1 eV when considering the temperature dependence on half reaction potentials. This measurement has an uncertainty of 0.1 eV.
4.5 Results and Discussion

Synthesis and Characterization

The synthesis of the phosphine chalcogenide-modified 2CzPN emitters is shown in Scheme 4.1. Nitrogen-protected precursors 9-(tert-butyldimethylsilyl)-3-bromo-9H-carbazole, TBDMS-BrCz and 9-(tert-butyldimethylsilyl)-3,6-dibromo-9H-carbazole, TBDMS-DBrCz were prepared from their respective bromo- or dibromo-9H-carbazole derivatives. The key intermediates, the phosphine chalcogenide-substituted carbazoles (PPOCz, PPSCz, DiPPOCz), were prepared by lithiation of TBDMS-BrCz and TBDMS-DBrCz followed by diphenylphosphination (TBDMS-PPCz and TBDMS-DiPPCz), and finally oxidation/sulfuration. Removal of the TBDMS group afforded the desired phosphine chalcogenide-substituted carbazole derivatives in moderate-to-excellent yield (40-95%). The respective emitters PPOCzPN, PPSCzPN and DiPPOCzPN were likewise obtained in moderate-to-excellent yield (52-96%) through a nucleophilic aromatic substitution reaction of 4,5-difluorophthalonitrile with PPOCz, PPSCz or DiPPOCz. All the emitters were characterized by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy and high-resolution mass spectrometry (HRMS), and their purity was demonstrated by HPLC and elemental analysis. The emitters PPOCzPN and PPSCzPN were each found to exist as a mixture of rotamers at room temperature in a ratio of 58:42 and 70:30, respectively, which was observed by both HPLC and $^{31}$P,H NMR spectroscopy. This was further substantiated by obtaining single crystals of both rotamers for PPSCzPN.

The molecular structures of PPOCzPN, PPSCzPN, and DiPPOCzPN were determined by single crystal X-ray diffraction analysis (Figure 4.2). Single crystals were grown from a binary solvent system by the vapour diffusion method: chloroform/acetonitrile and DCM/hexane for PPOCzPN; DCM/hexane and chloroform/methanol for PPSCzPN; and DCM/hexane for DiPPOCzPN. On initial analysis of the structure of PPOCzPN (obtained from chloroform/acetonitrile), partial-occupancy chlorine atoms were identified on both the carbazoles, forming PPOCICzPN. This likely arose from chlorination during crystallization from the chloroform solvent. A later crystallisation from DCM/hexane gave rise to a structure of PPOCzPN not showing any chlo-

Scheme 4.1: Chemical structure of 2CzPN and the three phosphine chalcogenide derivatives.
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Scheme 4.2: Synthetic routes for the synthesis of PPXcZPN and DiPPOcZPN. Reaction conditions: (i) n-BuLi (1.6M), THF, -78 °C, 30 min., (ii) PPh₂Cl, -78 °C - rt, 30 min, (iii) H₂O₂ or S₈, THF, rt, 18 h, (iv) TBAF (1.0 M), THF, rt, 1 h, (v) NaH, THF, 30 min., (vi) 4,5-difluorophthalonitrile, rt, 6 h.

Figure 4.2: Thermal ellipsoid plots of the crystal structures of (a) PPOcZPN, (b) PPScZPN-1, (c) PPScZPN-2 and (d) DiPPOcZPN. Ellipsoids are drawn at the 50 % probability level and hydrogen atoms and solvent molecules are omitted for clarity.
Crystallisation of PPSCzPN from the two different solvent combinations gave rise to crystals showing substantially different unit cells. Analysis of these revealed the presence of a different rotamer in each structure, with form 2 also showing included solvent. Only a single rotamer could be crystallised for PPOCzPN. In all the emitters, the interplanar angles between the donor carbazole derivatives and phthalonitrile moiety ranged between $50.71^\circ$ and $59.91^\circ$ and were mostly close to identical within an individual molecule [PPOCzPN $58.12(6)^\circ$ and $59.36(6)^\circ$, PPSCzPN-1 $50.7(3)^\circ$ and $50.9(3)^\circ$, PPSCzPN-2 $52.8(8)^\circ$ and $53.9(8)^\circ$, and $51.5(7)^\circ$ and $59.7(7)^\circ$, and DiPPOCzPN $56.82(8)^\circ$ and $57.69(8)^\circ$]. By contrast, a larger interplanar angle range is computed in the optimized ground-state geometries of the isolated emitters with all compounds showing one torsion angle around $45^\circ$ and the other around $70^\circ$.

The four structures show a number of intermolecular interactions. In both PPOCzPN and DiPPOCzPN a three-dimensional network of weak C-H···O and C-H···N hydrogen bonded molecules is formed [PPOCzPN H···A distances 2.39-2.60 Å, C···A separations 3.120(2)-3.529(3) Å; DiPPOCzPN H···A distances 2.26-2.54 Å, C···A separations 3.018(3)-3.529(3) Å] (where A is the acceptor atom). The networks are reinforced by C-H···π interactions in both structures [PPOCzPN H···centroid distances 2.79-2.90 Å, C···centroid separations 3.549(3)-3.719(2) Å; DiPPOCzPN H···centroid distances 2.74 Å, C···centroid separations 3.546(3) Å], π···π interactions in PPOCzPN [centroid···centroid distances 3.7287(9) Å], and by conventional hydrogen bonds to the water solvent molecule in DiPPOCzPN [H···O distances 1.83(3) and 1.87(4) Å, O···O separations 2.811(3) and 2.858(4) Å].

Both PPSCzPN structures show a different pattern of interactions where weak interactions of specific types give rise to multiple one-dimensional chain structures, these being linked into two-dimensional sheets when they are combined. In PPSCzPN-1, C-H···π interactions [H···centroid distances 2.70 and 2.89 Å, C···centroid separations 3.623(12) and 3.799(15) Å] form chains along the ac-diagonal axis, and weak C-H···N hydrogen bonds [H···N distances 2.45 Å, C···N separations 3.322(16) Å] form chains along the b-axis. The combination of these leads to sheets in the (1 0 -1) plane. In PPSCzPN-2, π···π interactions [centroid···centroid distances 3.668(10)-3.803(10) Å] form chains along the b-axis, and C-H···π interactions [H···centroid distances 2.78 Å, C···centroid separations 3.63(3) Å] form chains along the bc-diagonal axis. The combination of these leads to sheets in the (1 0 0) plane, which are further reinforced by weak C-H···S hydrogen bonds [H···S distances 2.71 Å, C···S separations 3.56(2) Å]. The chloroform solvent molecules in PPSCzPN-2 are held within the lattice by weak hydrogen bonds [H···N distances 2.54 Å, C···N separations 3.41(4) Å; H···S distances 2.62 Å, C···S separations 3.59(2) Å].

None of these structures show a matching pattern of interactions to that shown in the structure of 2CzPN, where multiple sets of C-H···π interactions form sheets in the (0 0 1) plane,
which are reinforced by weak C-H⋯N hydrogen bonds. This is closest to what is seen in PPSCzPN-1, in that sheets are formed by combinations of C-H⋯π and C-H⋯N interactions; however, in 2CzPN, the C-H⋯π interactions form sheets directly, whereas in PPSCzPN-1 both the C-H⋯π interactions and the weak hydrogen bonds are required to form the sheets.

**Electrochemical and Photophysical Properties**

The three emitters PPOCzPN, PPSCzPN and DiPPOCzPN show irreversible oxidation waves and reversible reduction waves in their cyclic voltammograms (CV), recorded in DCM with 0.1 M tetrabutylammonium perchlorate (TBAP) (red curves in Figure 4.3a-c). The values of the HOMO and LUMO energy levels were estimated from the peaks observed in the CV and verified from the differential pulse voltammograms. The HOMO/LUMO levels of the reference compound 2CzPN, as well as PPOCzPN, PPSCzPN and DiPPOCzPN are determined to be -6.28/-3.50, -6.39/-3.56, -6.56/-3.48 and -6.86/-3.56 eV, respectively. As expected, it is easier to reduce and harder to oxidize DiPPOCzPN than PPOCzPN due to the presence of the second electron-withdrawing diphenylphosphine oxide moiety on each carbazole. PPOCzPN is the easiest to oxidize and has the least stable HOMO. Similar electrochemical trends were seen in MeCN.

The optical absorption study of PPOCzPN, PPSCzPN, DiPPOCzPN and the reference emitter 2CzPN was carried out in acetonitrile (polar) and toluene (nonpolar) solvents. Table 4.1 summarizes the photophysical and electrochemical properties of PPOCzPN, PPSCzPN, DiPPOCzPN and the reference emitter 2CzPN in polar solutions and doped films in PMMA (polymethyl methacrylate) as a polar host matrix, leading to the following observations. The phosphine chalcogenide-substituted emitters exhibited similar UV-visible absorption spectra to that of 2CzPN with three major bands observed at around 265 nm, 325 nm, and 360 nm in both solvents (Figure 4.4a and 4.4d). The high-energy band near 265 nm is attributed to a LE transition of the carbazole moiety while the lowest energy bands near 325 nm and 360 nm are ascribed to ICT transitions in view of their low intensity. The ICT bands of the phosphine chalcogenide-substituted emitters are modestly blue-shifted by 380-1020 cm⁻¹ (30-65 nm) compared to the reference emitter 2CzPN due to the presence of the electron-withdrawing substituents. The presence of the second diphenylphosphine oxide group in DiPPOCzPN produced both a more intense absorption of the π-π* band at around 270 nm and the most blue-shifted ICT band. The absorption spectra did not appreciably change between toluene and acetonitrile (see Figure 4.4a versus 4.4d).

The photoluminescence properties of PPOCzPN, PPSCzPN, DiPPOCzPN and 2CzPN were investigated in DCM and toluene, as neat films and as 10 wt % doped PMMA and mCP (1,3-bis(N-carbazolyl)benzene) films, the latter matrix identified as a suitably high triplet-energy host that had previously been used with 2CzPN. The photophysical properties are summarized
Figure 4.3: (a-c) CVs (red) along with ECL-voltage curves (blue) and (d-f) ECL-time curves (red) along with voltage-time curves (blue) during potential pulsing at a pulsing frequency of 10 Hz for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively. Scans were recorded in DCM. CVs were all performed at a scan rate of 0.1 V/s and the second cycle is shown in every case. Pulsing experiments were carried out between 0.1 V above the first oxidation and below the first reduction potentials of the compounds.
4.5. Results and Discussion

Figure 4.4: a. Absorption (solid line) and emission (dashed line) spectra of PPOCzPN, PPSCzPN, DiPPOCzPN and 2CzPN recorded at room temperature in MeCN and DCM solution ($\lambda_{\text{exc}} = 358$ nm), respectively. b. Steady-state photoluminescence spectra of 10 wt % PMMA films of PPOCzPN, PPSCzPN, DiPPOCzPN, 2CzPN ($\lambda_{\text{exc}} = 358$ nm). c. Time-resolved photoluminescence decay profiles of 10 wt % PMMA films of PPOCzPN, PPSCzPN, DiPPOCzPN, 2CzPN ($\lambda_{\text{exc}} = 378$ nm). d. Absorption and emission spectra of PPOCzPN, PPSCzPN, DiPPOCzPN and 2CzPN recorded at room temperature in toluene solution ($\lambda_{\text{exc}} = 370$ nm). e. Steady-state photoluminescence spectra of 10 wt % mCP films of PPOCzPN, PPSCzPN, DiPPOCzPN, 2CzPN ($\lambda_{\text{exc}} = 358$ nm). f. Time-resolved photoluminescence decay profiles of 10 wt % mCP films of PPOCzPN, PPSCzPN, DiPPOCzPN, 2CzPN ($\lambda_{\text{exc}} = 378$ nm).
<table>
<thead>
<tr>
<th>Emitter</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; / nm (ε × 10&lt;sup&gt;-4&lt;/sup&gt; / M&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; / nm</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; / %</th>
<th>λ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; / nm</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt; / %</th>
<th>E&lt;sub&gt;ox&lt;/sub&gt; / V (HOMO&lt;sup&gt;f&lt;/sup&gt; / eV)</th>
<th>E&lt;sub&gt;red&lt;/sub&gt; / V (LUMO&lt;sup&gt;f&lt;/sup&gt; / eV)</th>
<th>ΔE&lt;sup&gt;g&lt;/sup&gt; / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPOCzPN</td>
<td>356 (1.24)</td>
<td>498</td>
<td>51</td>
<td>465</td>
<td>56</td>
<td>1.59 (-6.39)</td>
<td>-1.24 (-3.56)</td>
<td>2.83</td>
</tr>
<tr>
<td>PPSCzPN</td>
<td>358 (1.49)</td>
<td>501</td>
<td>47</td>
<td>465</td>
<td>59</td>
<td>1.76 (-6.56)</td>
<td>-1.32 (-3.48)</td>
<td>3.08</td>
</tr>
<tr>
<td>DiPPOCzPN</td>
<td>351 (1.51)</td>
<td>465</td>
<td>61</td>
<td>428</td>
<td>28</td>
<td>2.06 (-6.86)</td>
<td>-1.24 (-3.56)</td>
<td>2.78</td>
</tr>
<tr>
<td>2CzPN</td>
<td>366 (1.33)</td>
<td>515</td>
<td>29</td>
<td>494</td>
<td>77</td>
<td>1.48 (-6.28)</td>
<td>-1.30 (-3.50)</td>
<td>2.92</td>
</tr>
<tr>
<td>2CzPN&lt;sup&gt;h&lt;/sup&gt;</td>
<td>364 (1.14)</td>
<td>532</td>
<td>29</td>
<td>492</td>
<td>76</td>
<td>1.50 (-6.30)&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-1.42 (-3.38)&lt;sup&gt;i&lt;/sup&gt;</td>
<td>2.92&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> ICT band measured in MeCN at 298 K. <sup>b</sup> In degassed DCM (λ<sub>exc</sub> = 358 nm). <sup>c</sup> Solution Φ<sub>PL</sub> values were determined by the relative method using 0.5 M quinine sulfate in H<sub>2</sub>SO<sub>4</sub> (aq) as the reference (Φ<sub>PL</sub>: 54.6 %).<sup>[75]</sup> <sup>d</sup> 10 wt % doped PMMA thin films (λ<sub>exc</sub> = 360 nm). <sup>e</sup> Absolute Φ<sub>PL</sub> values in 10 wt % doped PMMA thin films under N<sub>2</sub>. <sup>f</sup> In DCM with 0.1 M [n-Bu<sub>4</sub>N]ClO<sub>4</sub> as the supporting electrolyte and SCE as the reference unless otherwise noted.<sup>[22]</sup> The HOMO and LUMO energies were calculated using the relation E<sub>HOMO</sub>/E<sub>LUMO</sub> = -(E<sub>ox</sub>/E<sub>red</sub> + 4.8) eV, where the E<sub>ox</sub> and E<sub>red</sub> are anodic and cathodic formal potentials, respectively, obtained from CV.<sup>[12]</sup> <sup>g</sup> ΔE = |E<sub>HOMO</sub>-E<sub>LUMO</sub>|. <sup>h</sup> Values from ref 77. <sup>i</sup> Determined in MeCN. NA = not available.

Table 4.1: Summary of photophysical and electrochemical properties of PPOCzPN, PPSCzPN, DiPPOCzPN and 2CzPN in apolar media and in the solid state in a mCP matrix and as neat films.
<table>
<thead>
<tr>
<th>Emitter</th>
<th>Toluene</th>
<th>10 wt % doped mCP film</th>
<th>Neat film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$ / nm</td>
<td>$\lambda_{\text{PL}}$ / nm</td>
<td>$\Delta E_{\text{ST}}$ / eV</td>
</tr>
<tr>
<td>PPOCzPN</td>
<td>321, 331, 367</td>
<td>460</td>
<td>0.20</td>
</tr>
<tr>
<td>PPSCzPN</td>
<td>321, 332, 369</td>
<td>460</td>
<td>0.42</td>
</tr>
<tr>
<td>DiPPOCzPN</td>
<td>319, 332, 361</td>
<td>443</td>
<td>0.43</td>
</tr>
<tr>
<td>2CzPN</td>
<td>317, 329, 375</td>
<td>476</td>
<td>0.36</td>
</tr>
<tr>
<td>2CzPN</td>
<td>317, 329, 375$^b$</td>
<td>484$^b$</td>
<td>0.31$^b$</td>
</tr>
</tbody>
</table>

$^a$ ICT band measured in toluene at 298 K. $^b$ In toluene ($\lambda_{\text{exc}} = 370$ nm). $^c$ In 10 wt % doped mCP thin films. $^d$ Absolute quantum yield in 10 wt % doped mCP thin films. $^e$ In neat thin films. $^f$ Absolute quantum yield in neat thin films. $^g$ Measured as the energy difference between the prompt fluorescence onset (at 77 K, $\lambda_{\text{exc}} = 378$ nm, time delay = 1 ns, integration time: 1-100 ns) and the phosphorescence onset (at 77 K, $\lambda_{\text{exc}} = 378$ nm, time delay = 1 ms, integration time = 1-10 ms). $^h$ Values from ref [106]. $^i$ Values from ref [73], measured in 6 wt % doped mCP film, $\Delta E_{\text{ST}}$ was estimated from the fluorescence (300 K) and phosphorescence (5 K) peaks. NA = not available.

Table 4.2: Summary of photophysical and electrochemical properties of PPOCzPN, PPSCzPN, DiPPOCzPN and 2CzPN in apolar media and in the solid state in a mCP matrix and as neat films.
in Tables 4.1 and 4.5 and the emission spectra and decay profiles of the emitters doped in PMMA and mCP thin films are shown in Figures 4.4c and 4.4f. In DCM, the emission maxima shift to progressively higher energy across the series from 2CzPN to PPOCzPN, PPSCzPN, and DiPPOCzPN, at 532 nm, 498 nm, 501 nm, and 465 nm, respectively, reflecting the weakening of the donor. On the other hand, owing to its lower polarity, the emission maxima of these emitters are further blue-shifted in toluene compared to DCM, a reflection of their CT character. In 10 wt % doped PMMA films, the $\lambda_{PL}$ values are all blue-shifted compared to those in DCM solution at 492 nm, 465 nm, 465 nm, and 428 nm, due the less polar nature of this medium (Figure 4.4b). In 10 wt % doped mCP films, the $\lambda_{PL}$ values are surprisingly red-shifted and clustered closer to each other at 496 nm, 474 nm, 474 nm, and 490 nm for 2CzPN, PPOCzPN, PPSCzPN, and DiPPOCzPN, respectively, in full consistency with the trends observed in toluene (Figure 4.4d). The photoluminescence quantum yields, $\Phi_{PL}$ in DCM of PPOCzPN, PPSCzPN and DiPPOCzPN (47-61 %) are higher than that of 2CzPN (29 %).[106] The $\Phi_{PL}$ values of the emitters are somewhat lower in PMMA doped films (ranging from 28-59 %), and are lower than that of 2CzPN (76 %) in the same medium. In mCP, the $\Phi_{PL}$ is recovered with values of 72 %, 73 % and 56 % for PPOCzPN, PPSCzPN and DiPPOCzPN, while that of 2CzPN is very similar to that seen in PMMA (77 %). A slightly higher $\Phi_{PL}$ (89 %) has been reported for 6 wt % 2CzPN in co-evaporated mCP thin film.[73]

Figure 4.4c shows the time-resolved decay traces of the emitters in a PMMA matrix. The emission decay consisted of both prompt ($\tau_p$) nanosecond and delayed ($\tau_d$) microsecond fluorescence components. The prompt fluorescence decays of PPOCzPN, PPSCzPN and DiPPOCzPN were found to be bi-exponential with lifetimes, $\tau_p$, ranging from 13-20 ns, similar to that of 2CzPN ($\tau_p = 8, 21$ ns). The delayed fluorescence decay of the three emitters is tri-exponential in nature with average lifetime of 393 $\mu$s, 416 $\mu$s, and 513 $\mu$s for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively, significantly longer than that of 2CzPN ($\tau_d = 270$ $\mu$s). Figure 4.4f shows the emission decays in mCP, which are similar to the decay profiles in the PMMA matrix. In this medium, the $\tau_p$ ranges from 8-37 ns, longer than those measured in PMMA, and also longer than that of 2CzPN ($\tau_p = 9, 23$ ns). The $\tau_d$ values, on the other hand, for PPOCzPN, PPSCzPN and DiPPOCzPN in 10 wt % mCP thin films were found to be 210 $\mu$s, 206 $\mu$s, and 54 $\mu$s, respectively, which are significantly shorter than those in PMMA and are also shorter than that of 2CzPN ($\tau_d = 277$ $\mu$s). An average $\tau_d$ of 273 $\mu$s has been reported previously for 6 wt % 2CzPN in mCP thin film.[73] The excited state lifetime of the emitters doped in PMMA and mCP films are summarized in Table 4.3. Altogether, in contrast to 2CzPN, the present data for PPOCzPN, PPSCzPN and DiPPOCzPN emitters clearly demonstrate the high sensitivity of the emitter decay dynamics and emission energy towards the nature of the host medium.
### 4.5. Results and Discussion

<table>
<thead>
<tr>
<th>Emitter</th>
<th>( \tau_p (%)/\text{ns}; \tau_d (%)/\mu\text{s} )</th>
<th>( \tau_p (%)/\text{ns}; \tau_d (%)/\mu\text{s} )</th>
<th>( S_1/\text{eV} )</th>
<th>( T_1/\text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPOCzPN</td>
<td>6.1 (43), 20.0 (57); 9 (3), 146 (22), 1024 (75)</td>
<td>10.0 (12), 37.2 (88); 20 (4), 90 (18), 522 (78)</td>
<td>2.96</td>
<td>2.77</td>
</tr>
<tr>
<td>PPSCzPN</td>
<td>5.8 (44), 13.6 (56); 5 (0.5), 174 (10), 1361 (90)</td>
<td>8.6, (44), 31.6 (56); 23 (4), 175 (33), 422 (62)</td>
<td>2.97</td>
<td>2.73</td>
</tr>
<tr>
<td>DiPPOCzPN</td>
<td>6.7 (40), 14.1 (60); 5 (2), 69 (6), 1176 (92)</td>
<td>8.1 (58), 26.4 (42); 0.5 (76), 28 (18), 136 (6)</td>
<td>2.96</td>
<td>2.81</td>
</tr>
<tr>
<td>2CzPN</td>
<td>8.3 (15), 21.1 (85); 6 (4), 124 (22), 680 (72)</td>
<td>9.9 (29), 23.2 (71); 7 (3), 134 (23), 690 (73)</td>
<td>2.90</td>
<td>2.67</td>
</tr>
</tbody>
</table>

\( S_1 \) = singlet state energy obtained from the onset of prompt fluorescence spectra measured at 77 K (\( \lambda_{\text{exc}} = 360 \text{ nm} \), delay time: 1 ns, time window: 1–100 ns).

\( T_1 \) = triplet state energy obtained from the onset of the phosphorescence spectra measured at 77 K (\( \lambda_{\text{exc}} = 360 \text{ nm} \), delay time: 1 ms, time window: 1–10 ms).

Table 4.3: Excited state lifetimes of the emitters doped in PMMA and mCP films.
Temperature-dependent time-resolved emission decay measurements in 10 wt % doped mCP thin films were also tested. There is a clear thermal activation of the delayed fluorescence that is consistent with compounds emitting via a TADF mechanism, despite the different trends in comparison to the PMMA matrix.

The singlet-triplet energy gaps ($\Delta E_{ST}$) were determined from the difference in energy of the onset of the prompt fluorescence and phosphorescence spectra in 10 wt % doped mCP films measured at 77 K (Figure 4.5). The $\Delta E_{ST}$ values for PPOCzPN, PPSCzPN DiPPOCzPN and 2CzPN were found to be 0.19 eV, 0.24 eV, 0.15 eV and 0.23 eV, respectively. The experimentally determined $\Delta E_{ST}$ value for 2CzPN in 10 wt % doped mCP film is in good agreement with the reported value of 0.21 in a 6 wt % doped mCP thin film.[73, 106] The smallest $\Delta E_{ST}$ value (0.15 eV for DiPPOCzPN) is consistent with the observed $\tau_d$, value of 54 µs, which is the shortest among these emitters. It is noteworthy that the TD-DFT calculated $\Delta E_{ST}$ values in the gas phase are consistent with those experimentally determined in the apolar matrix, vide infra, Table 4.4. The $\Delta E_{ST}$ values determined for these chalcogenide-substituted 2CzPN derivatives are of similar magnitude to literature 2CzPN derivatives such as $\alpha$-2CbPN ($\Delta E_{ST} = 0.28$) and $\delta$-2CbPN ($\Delta E_{ST} = 0.13$) in 20 wt % mCP thin film, where $\alpha$/$\delta$-carboline was used as carbazole replacement to blue-shift the emission.[41]

**Theoretical Modelling**

To better understand the differences between the PL behaviors observed in the polar DCM solvent or PMMA matrix versus the apolar toluene solvent or mCP matrix, our study has been complemented by quantum-chemical calculations. In line with our previous theoretical studies on TADF emitters,[77, 106] we have first optimized the ground-state geometry of the 2CzPN and its three derivatives in the gas phase at the Density Functional Theory (DFT) level using the PBE0 functional[2] and a 6-31G(d,p) basis set.[28] In a second step, we have analyzed the nature of the frontier electronic levels of the compounds. Finally, we have described the lowest

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### Table 4.4: Calculated HOMO and LUMO energies of PPOCzPN, PPSCzPN, DiPPOCzPN and 2CzPN in gas phase versus MeCN.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>HOMO / eV</th>
<th>LUMO / eV</th>
<th>$\Delta E$ / eV</th>
<th>HOMO / eV</th>
<th>LUMO / eV</th>
<th>$\Delta E$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPOCzPN</td>
<td>-6.05</td>
<td>-2.52</td>
<td>3.53</td>
<td>-6.06</td>
<td>-2.48</td>
<td>3.58</td>
</tr>
<tr>
<td>PPSCzPN</td>
<td>-5.98</td>
<td>-2.58</td>
<td>3.40</td>
<td>-6.13</td>
<td>-2.50</td>
<td>3.63</td>
</tr>
<tr>
<td>DiPPOCzPN</td>
<td>-6.42</td>
<td>-2.73</td>
<td>3.69</td>
<td>-6.37</td>
<td>-2.57</td>
<td>3.80</td>
</tr>
<tr>
<td>2CzPN</td>
<td>-6.11</td>
<td>-2.41</td>
<td>3.70</td>
<td>-6.04</td>
<td>-2.39</td>
<td>3.65</td>
</tr>
</tbody>
</table>
Figure 4.5: Prompt fluorescence (at 77 K) and phosphorescence spectra (at 77 K) of a. PPOCzPN, b. PPSCzPN, c. DiPPOCzPN, and d. 2CzPN, in 10 wt % doped mCP thin films ($\lambda_{\text{exc}} = 360$ nm).
singlet and triplet excited states of the emitters by performing TD-DFT calculations within the Tamm-Dancoff approximation,[44] employing the same functional and basis set.

In the case of the isolated PPOCzPN and PPSCzPN compounds, we have obtained two different low-energy conformers varying by the amplitude of the torsion angles $\phi$ between the carbazole and phthalonitrile units. For PPOCzPN, rotamer 2 with $\phi_1 = 134.3^\circ$ and $\phi_2 = -69.2^\circ$ is more stable by 0.29 eV compared to the other rotamer with $\phi_1 = -64.8^\circ$ and $\phi_2 = -65.9^\circ$; in the case of PPSCzPN, there is a much larger difference of 1.33 eV between the most stable rotamer (with $\phi_1 = 133.2^\circ$ and $\phi_2 = -69.5^\circ$) compared to the second rotamer (with $\phi_1 = -65.8^\circ$ and $\phi_2 = -64.6^\circ$). In view of the large energy difference between the two rotamers (compared to the thermal energy, $kT$), their co-existence in solution most probably arises from their synthesis, rather than from thermal conversion following synthesis. We will discuss hereafter the properties of the most stable rotamer; for sake of completeness, the very similar properties computed for the second rotamer in the gas phase were collected. In contrast, we only found a single stable conformer for 2CzPN and DiPPOCzPN with the same torsion angles for both carbazole substituents ($\phi_1 = \phi_2 = 58.9^\circ$ for 2CzPN and $\phi_1 = \phi_2 = 65.7^\circ$ for DiPPOCzPN).

Table 4.4 collects the HOMO and LUMO energies of the four emitters calculated in the gas phase as well as in acetonitrile by modelling the solvent as a dielectric continuum using the Polarizable Continuum Model (PCM)[36], as implemented in Gaussian 16-A03;[34] in the latter case, the geometry is fully reoptimized within the PCM model, although this hardly changes the gas phase geometry. In acetonitrile, the HOMO is progressively stabilized going from 2CzPN to PPOCzPN to PPSCzPN and DiPPOCzPN, which is generally consistent with the trends observed in the experimental electrochemistry data in DCM (Table 4.1) and acetonitrile. On the other hand, the calculated LUMO energies vary to a lesser extent both according to the calculations and electrochemical measurements, as expected by the fact that the LUMO is localized on the phthalonitrile acceptor while the varying substituents are added on the donor fragment. Strikingly, the trends appear to be quite different when computing the frontier orbital energies in the gas phase, which is expected to reflect the properties in a non-polar medium such as toluene or the mCP matrix. The major difference is that the HOMO is not stabilized but in fact slightly destabilized when going from 2CzPN to PPOCzPN or PPSCzPN, although it is stabilized going from 2CzPN to DiPPOCzPN.

The shape and energies of the orbitals in acetonitrile are displayed in Figure 4.6. As expected, the HOMOs are mainly localized on the carbazole moieties, and the LUMOs are strongly localized on the phthalonitrile. In the monosubstituted compounds, the HOMO displays a small amount of electron density on the phosphine chalcogenide units, thus limiting the role played by mesomeric effects in defining the actual HOMO energies. The HOMO level is both the most delocalized in DiPPOCzPN and the most stabilized, which is also evidenced
4.5. Results and Discussion

Figure 4.6: HOMO and LUMO energies of the four compounds in their most stable geometries together with the energy of the lowest singlet and triplet excited states, as calculated in acetonitrile.

by its electrochemistry (Figures 4.3 and 4.9). The shift of the HOMO among the compounds is a subtle interplay mostly between the inductively electron-withdrawing effects associated with the phosphine chalcogenide groups and electrostatic interactions between the polar phosphine chalcogenide and cyano moieties, which are expected to be further tuned by changes in the medium polarity. Altogether, the HOMO-LUMO gap in the gas phase is red shifted by 0.2-0.3 eV going from 2CzPN to PPOCzPN and PPSCzPN while it remains unchanged for DiPPOCzPN. In contrast, the electronic bandgaps of 2CzPN, PPOCzPN, PPSCzPN are quite similar in MeCN and larger by 0.2 eV for DiPPOCzPN, thus demonstrating the strong impact of the medium polarity on the electronic structure of the compounds and by extension on the charge-transfer state energies, as evidenced at the experimental level.

When coupled to a time-dependent (TD) formalism, DFT calculations can also give access to the excited-state photophysical properties of the emitters. We will describe below the excited state energies and associated oscillator strength ($f$) calculated in acetonitrile as well as the energy difference between $T_1$ and $S_1$ (Table 4.5) for vertical excitation processes (i.e. in the ground-state geometry). We will not address here at the theoretical level the changes in the emission properties as a function of the medium polarity evidenced experimentally, since a proper analysis would require a time-consuming optimization of the $S_1$ state (both in gas
phase and in a polar medium described with PCM) which is often impeded by convergence problems and might require the use of another functional.\(^\text{[2]}\) PPOCzPN and PPSCzPN exhibit a slightly red-shifted \(S_1\) state compared to 2CzPN (blue-shifted in the case of DiPPOCzPN), accompanied by a reduction in the oscillator strength, as well as slightly smaller \(\Delta E_{ST}\) values. The calculated \(\Delta E_{ST}\) values of the emitters in the toluene are all around or above 0.2 eV, in good consistency with those experimentally obtained in toluene (Table 4.5); there is a very good quantitative agreement for 2CzPN (0.31 eV in theory versus 0.36 eV in toluene). These energies are marginally affected when performing the calculations in toluene or in acetonitrile. Strikingly, the experimental \(\Delta E_{ST}\) values are systematically reduced in the mCP matrix, most likely due in part to changes in the conformations of the emitters in these thin films. Both 2CzPN and DiPPOCzPN have a second triplet excited state \(T_2\) that lies below \(S_1\), thus providing a conduit to facilitate reverse intersystem crossing process.\(^\text{[31, 81]}\) The \(T_1\) and \(S_1\) excited states are predominantly characterized by a HOMO-LUMO transition and hence both display a significant ICT character.

The absorption spectra simulated in the gas phase predict similar energy for the lowest absorption peaks (around 350 nm and 400 nm) for the four compounds; the same trends are also observed for the experimental spectra recorded both in MeCN and toluene (Figures 4.4a and 4.4d). Note that the lowest absorption peak around 400 nm is systematically associated with higher-lying excited states while the lowest excited state \(S_1\) gives rise to the shoulder on the low energy side. This state is mostly described by a HOMO to LUMO excitation. Analysis of the hole and electron densities obtained within the attachment/detachment formalism points to a similar charge transfer character in the \(S_1\) state of the four compounds in acetonitrile or in gas phase (Table 4.5); the overlap index \(\phi_S\), ranging from 1 for a pure locally excited state (LE) to 0 for a pure charge-transfer (CT) state, is around 0.4 in all cases, i.e., an indication of a hybrid state with significant LE and CT character. The \(T_1\) state exhibits systematically a higher \(\phi_S\) index pointing to a more local excited state. This change in character between the \(S_1\) and \(T_1\) (\(T_2\)) states ensures non-vanishing spin-orbit coupling based on El Sayed’s rules and opens up the RISC channel.

**Electrochemiluminescence via the Annihilation Pathway**

ECL is luminescence generated when electrochemically-generated radical cations (hole) and radical anions (electron) undergo an electron transfer to create an excited state (exciton), which can release its energy as light (Figure 4.7a). The behavior of this luminescence can describe radical stability, reactivity and general emission mechanisms of luminophores at concentrations that are typically greater than that in solutions used in photoluminescence studies. Radical cations and anions are produced in solution when the species are oxidized and reduced, respectively in the vicinity of the same working electrode. If these two species collide, an ele-
<table>
<thead>
<tr>
<th>Compound</th>
<th>States</th>
<th>Energy / eV</th>
<th>$f$</th>
<th>Main Component of Excitation</th>
<th>$\phi_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPOCzPN</td>
<td>$T_1$</td>
<td>2.65</td>
<td></td>
<td>HOMO$\rightarrow$LUMO (76.5 %)</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>2.65</td>
<td>0.028</td>
<td>HOMO$\rightarrow$LUMO (97.7 %)</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_{ST}$</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPSCzPN</td>
<td>$T_1$</td>
<td>2.68</td>
<td></td>
<td>HOMO$\rightarrow$LUMO (80.5 %)</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>2.90</td>
<td>0.032</td>
<td>HOMO$\rightarrow$LUMO (97.9 %)</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_{ST}$</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DiPPOCzPN</td>
<td>$T_1$</td>
<td>2.80</td>
<td></td>
<td>HOMO$\rightarrow$LUMO (82.1 %)</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>$T_2$</td>
<td>3.06</td>
<td></td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>3.07</td>
<td>0.045</td>
<td>HOMO$\rightarrow$LUMO (98.3 %)</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_{ST}$</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2CzPN</td>
<td>$T_1$</td>
<td>2.63</td>
<td></td>
<td>HOMO$\rightarrow$LUMO (87.8 %)</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>$T_2$</td>
<td>2.86</td>
<td></td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>2.95</td>
<td>0.100</td>
<td>HOMO$\rightarrow$LUMO (98.4 %)</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_{ST}$</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Excitation energies, $\Delta E_{ST}$, oscillator strengths, and main component of the excitations in terms of one-electron transitions, as calculated in acetonitrile.
Figure 4.7: a. Annihilation and c. benzoyl peroxide (BPO) co-reactant mechanisms for ECL emission. L, benzoic acid (Bz) and BPO stand for luminophore, benzoate and benzoyl peroxide, respectively. This scheme is illustrative and not energy accurate. Both triplet and singlet energy states can be accessed from either co-reactant or annihilation mechanisms. b. Diagram illustrating excimer formation and the equilibrium established between anionic and cationic radicals.

electron transfer can happen from the HOMO (or LUMO) of a radical anion to the HOMO (or LUMO) of a radical cation, potentially creating an exciton that can subsequently emit light in the form of ECL. This mechanism is not limited to the generation of triplets as illustrated in Figure 4.7a, but also can form systematically singlets in the case of an annihilation mechanism, in an analogous manner to exciton generation in an organic light-emitting diode. We note that it is unlikely for radicals to undergo further redox reactions at an electrode surface to create excited state species as described in the literature.[58] In fact, the electrode surface might quench the radical or excited species.

To electrogenerate an excited state, the electronic gap of the redox reactions (EEg) must be greater than the photoluminescence emission peak energy (Eg) as defined by Eq. 4.2. For an ECL annihilation system, R’ and R are the same species. However, R’ can become a radical while R remains the luminophore in an oxidative-reduction ECL co-reactant system or R can become an oxidant while R’ remains a luminophore in a reductive-oxidation ECL co-reactant system. Using Eq. 4.2, the electronic gap for PPOCzPN, PPSCzPN and DiPPOCzPN in DCM are measured to be 2.73, 2.98 and 3.19 eV, respectively, from the redox potentials in differential pulse voltammograms. From the prompt fluorescence spectra in DCM, the optical gap for PPOCzPN, PPSCzPN and DiPPOCzPN are 2.49, 2.47 and 2.66 eV, respectively. As expected, the energy provided by the redox reactions for all compounds is sufficient to generate both singlet and triplet excited states. The blue curves in Figure 4.3a-c demonstrate ECL
generated during scan cycles between redox reaction potentials for PPOCzPN, PPSCzPN and DiPPOCzPN. DiPPOCzPN shows a maximum ECL intensity of 60 nA, while PPOCzPN and PPSCzPN display weak emissions up to 1 nA. This indicates that the radical cation is sufficiently stable to survive in solution until the radical anion is created, and the two species collide. DiPPOCzPN$^+$ is the most stable radical ion because it produced the highest ECL emission in the annihilation pathway. It also appears that the radical anion is not as stable as the radical cation for all species, because no ECL is seen upon first reduction of the species followed by compound oxidation, even after multiple cycles.

Figure 4.3d-f shows ECL-time curves during pulsing between 0.1 V more anodic than the oxidation and 0.1 V more cathodic than reduction peak potentials, respectively. PPOCzPN, PPSCzPN and DiPPOCzPN yielded annihilation ECL maxima at 700, 1100 and 17500 nA, respectively. In pulsing experiments, the time between the generation of both radical species in solution is shorter than that in potential cycling, allowing the lifetime of the radical not to be a significant issue and the annihilation ECL to be enhanced. The pulsing annihilation efficiency was determined by Eq. 4.1 where $x$ and $st$ stand for the luminophore and [Ru(bpy)$_3$]$^{2+}$ under the same conditions, respectively. These ECL efficiencies were determined to be 1, 1 and 10 % relative to [Ru(bpy)$_3$]$^{2+}$, for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively (Table 4.6). Interestingly, 2CzPN showed no emissions in the annihilation pathway. DiPPOCzPN continued to have the highest ECL maxima and also had the most efficient emission; interestingly, the structurally similar PPOCzPN had the lowest efficiency. Most emission was observed when a negative potential was applied, further providing evidence for the higher stability of the radical cation over the radical anion. In fact, PPOCzPN is the only species to display emission when a positive potential was applied or when radical cations were actively being produced in pulsing experiments (Figure 4.3d-f), indicating a relatively high radical anion reactivity, or a relatively lower radical cation reactivity than the other compounds. For optoelectronic applications, ECL efficiency, ECL maxima, radical stability and radical reactivity are all important parameters to consider. Inequalities between radical cation and radical anion stabilities and reactivities can cause excess charge buildup in OLEDs, leading to fast device degradation. High ECL maxima and efficiencies indicate efficient charge transfers as well as limited non-radiative decay pathways. Therefore, PPOCzPN appears desirable for optoelectronic applications because of relatively more stable and reactive radical ion species, although it has low ECL maxima and efficiency.

After several pulses, the emission intensity of DiPPOCzPN decreases by over 75 %, whereas PPOCzPN and PPSCzPN remain relatively stable over the same time (Figure 4.8). It appears that DiPPOCzPN may form side products during the annihilation pulsed ECL experiment that influence the generation of excited species. This fast decay may also be caused by a charge
### Table 4.6: Summary of ECL data.

<table>
<thead>
<tr>
<th></th>
<th>PPOCzPN</th>
<th>PPSCzPN</th>
<th>DiPPOCzPN</th>
<th>Ru(bpy)$_3^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EE$_g$ (eV)$^a$</td>
<td>2.73</td>
<td>2.98</td>
<td>3.19</td>
<td>2.55</td>
</tr>
<tr>
<td>Pulsing ECL$_{onset}$ delay (ms)$^b$</td>
<td>7</td>
<td>14</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Pulsing ECL$_{max}$ delay (ms)$^b$</td>
<td>11</td>
<td>19</td>
<td>24</td>
<td>4</td>
</tr>
<tr>
<td>Pulsing ECL Efficiency (%)$^c$</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Max pulsing ECL (nA)</td>
<td>700</td>
<td>1,150</td>
<td>17,500</td>
<td>70,000</td>
</tr>
<tr>
<td>Annihilation ECL $\lambda_{max}$ (nm)</td>
<td>520</td>
<td>500</td>
<td>475</td>
<td>620</td>
</tr>
<tr>
<td>EE$_g$ BPO (eV)$^d$</td>
<td>3.01</td>
<td>3.48</td>
<td>3.39</td>
<td>3.04</td>
</tr>
<tr>
<td>BPO ECL Efficiency (%)$^c$</td>
<td>17</td>
<td>6</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Max BPO ECL (nA)</td>
<td>3,200</td>
<td>1,280</td>
<td>80</td>
<td>26,500</td>
</tr>
<tr>
<td>BPO ECL $\lambda_{max}$ (nm)</td>
<td>520</td>
<td>500</td>
<td>545</td>
<td>620</td>
</tr>
</tbody>
</table>

$^a$ Electronic gaps (EE$_g$) were obtained using Eq. 4.2 and the differential pulse voltammograms of the compounds. $^b$ These values are averages from at least 40 pulses with individual conditions described in Figure 4.3. $^c$ Obtained from Eq. 4.1 relative to [Ru(bpy)$_3^{2+}$ at the same concentration, electrolyte and concentration of co-reactant if applicable. $^d$ Obtained from Eq. 4.2 but with substituting $E'(R^+/R'^{-})$ with the oxidative power of BPO from ref. (Chandross and Sonntag, 1966)
Figure 4.8: Extended annihilation pulsing spectra of PPOCzPN, PPSCzPN and DiPPOCzPN in degassed DCM with 0.1 M of TBAP.
imbalance where negatively or positively charged species that accumulate over time interfere with the exciton states, similar to exciton-polaron quenching of excited states.[20]

**Average ECL Onset Times**

These experiments reveal for the first time (Figure 4.3d-f) that there is a delay in the ECL onset times ($ECL_{onset}$) from donor-acceptor TADF compounds; PPOCzPN, PPSCzPN and DiPPOCzPN had 7 (26 pulses measured), 14 (36 pulses measured) and 11 ms (37 pulses measured) initial ECL delays, respectively. The data are summarized in Table 4.6 and zoom-in ECL-time curves of a single pulse of each compound are shown in Figure 4.9. The slow kinetics of the formation of an excimer between the radical cation and radical anion of these compounds may cause this delay as illustrated in Figure 4.6.

We first considered phosphorescence as the origin of these long ECL onset times. For time comparisons of diffusion properties and emissions, the well-studied commercial phosphorescent ECL emitter $[\text{Ru}(\text{bpy})_3]^2+$,[71][97][98][101] was tested under the same conditions (Figure 4.10) and showed no observed delay (47 pulses measured). A well-studied organic compound with a known diffusion coefficient is diphenylanthracene (DPA) ($DACN = 0.20 \times 10^{-6}$ cm$^2$ s$^{-1}$),[87] which shows an order of magnitude difference between its diffusion coefficient and

Figure 4.9: Zoomed annihilation pulsing spectra of PPOCzPN, PPSCzPN and DiPPOCzPN in degassed DCM with 0.1 M of TBAP.
4.5. Results and Discussion

Figure 4.10: Annihilation pulsing for 0.7 mM Ru(bpy)$_3$(PF$_6$)$_2$ in degassed DCM with 0.1 M TBAP as an electrolyte.

that of [Ru(bpy)$_3$]$^{2+}$ (DACN = 5.8 × 10$^{-6}$ cm$^2$ s$^{-1}$). If we assume that DPA and these 2CzPN derivatives have similar magnitudes of diffusion coefficient in DCM, from a comparison of their initial emission delays (7 and 0 ms for PPOCzPN and [Ru(bpy)$_3$]$^{2+}$, respectively), differences in diffusion rates can be ruled out as a cause of emission delays in the 2CzPN derivatives. We believe diffusion delays are on the time scale of microseconds and cannot explain the observed time delay shown in Figure 4.3d-f.

We next considered triplet-triplet annihilation as the origin for the long ECL onset times. A TTA mechanism has been used to explain millisecond photoluminescence lifetimes for phenanthrene and may explain the delay of the onset of the ECL seen here.[84] Also, the competition for triplet exciton depopulation by TTA, RISC and non-radiative pathways has been studied by Grüne et al. in a m-MTDATA:3TPYMB exciplex TADF OLED to estimate that TTA was responsible for 50 % of triplet depopulation, which effectively extended the emission decay time.[39] However, Grüne et al. excited their sample for 4 ms at a specific current density and did not see any delay in the onset of emission. TTA has been observed in carbazolyl phthalonitrile derivatives where there is an observed blue-shifting in the solid-state PL as well as serious efficiency roll-off in the OLEDs,[72, 79] but to the best of our knowledge it has not been demonstrated before by ECL in 2CzPN derivatives. Mechanistically, TTA can be simplified to two triplet excitons (T$_1$) combining to form a singlet exciton (S$_n$) seen in Figure 4.7b. The system in the S$_n$ state then relaxes to the S$_1$ state by internal conversion according to Kasha’s law, which can then emit light. TTA is also a common tetramolecular process in ECL where the radical cation of N,N,N’,N’-tetramethyl-p-phenylenediamine (TMPD$^+$) and the radical anion of DPA (DPA$^-$) reside as a well-studied purely TTA-emitting ECL system.[13, 23, 33, 76] This TMPD$^+$/DPA$^-$ system can only generate T$_1$ from charge transfer reactions and not S$_1$ as dic-
tated by Eq. 4.2. However, this TTA mechanism has never been accompanied by an observed induction time either in ECL or OLED prior to observed emission.

To the best of our knowledge, there has only been one study of emission delay after excitation in an ECL system, where the ECL of DPA was found to have a delay on the order of 100 µs. This delay was attributed to uncompensated solution resistance. In comparison, our experiment also has a platinum working electrode with the same electrolyte (TBAP) at a similar concentration, but the delay we determined is a few orders of magnitude larger than what Rosenmund et al. observed. Thus, neither uncompensated solution resistance, nor triplet-triplet annihilation (TTA), nor phosphorescence is responsible and that this ECL emission delay is currently unexplained in the literature.

Interestingly, an organic long-persistent photoluminescence (OLPL) phenomenon was recently discovered by Kabe et al. in a system comprising a phosphine oxide-containing TADF acceptor (2,8-bis(diphenylphosphoryl)dibenzo-[b,d]thiophene) (PPT)) and N,N,N’,N’-tetramethylbenzidine (TMB) as a donor molecule. More recently, this OLPL system has been used in an OLED to achieve organic long-persistent electroluminescence (OLEL). Unfortunately, solution and solid state emission delays of the system were not investigated on time scales smaller than 1 s, thereby limiting comparisons with the 2CzPN derivatives. However, OLPL and OLEL are both emitted from an exciplex state and therefore the emission was found to be both concentration dependent and layer-thickness dependent. This exciplex emission was also found to have thermal activation processes and thermoluminescence in films. Li et al. reported that the TADF emitter, CzPhAP, did not show any delay in the onset of emission but did show 900 s of persistent emission after 60 s of laser excitation, when cast in a PMMA film. These unusually long emission times were ascribed to slow charge recombination rates of the luminophore in the thick film, leading to organic long-persistent photoluminescence (OLPL) because of an established equilibrium between exciplex formation with radicals and the subsequent radical disassociation. We thus contend that the delay in the onset of the ECL emission seen in Figure 4.3d-f may be best explained by a heretofore previously unreported organic long-persistent electrochemiluminescence (OLECL), analogous to the works of Kabe et al. We hypothesize that an equilibrium exists between the emissive excimer and the dissociated constituents and that the slow association kinetics could cause this delay as illustrated in Figure 4.7b.

Average ECL Rising Times to Maximum

The average times from the onset of ECL to the ECL emission maximum after a pulse for PPOCzPN, PPSCzPN and DiPPOCzPN were found to be 11 (78 pulses measured), 19 (37 pulses measured) and 24 ms (77 pulses measured), respectively (Figure 4.3d-f and Table 4.6). Again, for comparison, [Ru(bpy)_3]^{2+} was analyzed using the same ECL pulsing method.
and this compound shows a rise time of 4 ms (158 pulses measured, Figure 4.10). Notably, the magnitude of the delay in reaching the maximum ECL emission intensity (Table 4.6) correlates with the trends in $\Delta E_{ST}$ values in toluene (Table 4.5), where PPOCzPN has the smallest $\Delta E_{ST}$ at 0.20 eV, and PPSCzPN and DiPPOCzPN have the largest $\Delta E_{ST}$ at 0.42 and 0.43 eV, respectively (Figure 4.11). Based on this relationship, we can confidently rule out TTA as a dominant emission mechanism. Interestingly, the OLPL TADF emitter CzPhAP mentioned earlier had a similarly large $\Delta E_{ST}$ of 0.18 compared with PPOCzPN (Table 4.5).

**Average long emission decay time**

The average long emission decay time after switching off pulses was measured to find how long it took ECL emission to return to 0 nA after the potential is switched off (Figures 4.3d-f and 4.10). These long emission decay times were found to be 0, 6, and 6 ms for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively. Expectedly, the same trends for the delay to the onset of ECL and the time required from the ECL onset to reach a maximum ECL intensity were observed. However, the ECL decay times were roughly half the magnitude of the ECL onset times. By contrast, $[\text{Ru(bpy)}_3]^{2+}$ shows instantaneous ECL emission during both cathodic and anodic pulses (Figure 4.10), and rapid decay of the ECL emission, which could not be quantified.

**ECL of BPO Co-reactant Systems**

Benzoyl peroxide (BPO) was added as a co-reactant to the electrochemical systems described in Figure 4.3 and the potential was scanned in the cathodic direction. This co-reactant pathway is described in Figure 4.7c. Around -0.45 V vs. SCE, BPO is reduced and ultimately decomposes into a benzoate radical (Figure 4.7c). When PPOCzPN, PPSCzPN and
Figure 4.12: (a-c) CVs (red) along with ECL-voltage curves (blue) during potential pulsing at a pulsing frequency of 10 Hz for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively, all with 10 mM BPO was added as a co-reactant. (d-f) Spooling ECL spectroscopy of the corresponding systems described in Figures 4.12a-c. Insets of Figures 4.12d-f represent respective stacked spooling ECL spectra. The purple color of these insets was arbitrarily chosen.
DiPPOCzPN are subsequently reduced to form PPOCzPN\(^{\cdot-}\), PPSCzPN\(^{\cdot-}\) and DiPPOCzPN\(^{\cdot-}\), the benzoate radical produced earlier can abstract an electron from the HOMOs of the reduced TADF compounds to produce excited states PPOCzPN*, PPSCzPN* and DiPPOCzPN*, respectively. These excited-state compounds then emit ECL through the so-called co-reactant pathway. Figure 4.12a-c show the reduction waves corresponding to the reduction of BPO (red traces) and the corresponding photocurrent generated (blue traces). ECL intensity maxima of 3000, 1280 and 80 nA were measured for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively. PPOCzPN showed the strongest ECL response, which was almost three-fold stronger than that of PPSCzPN and 38 times that of DiPPOCzPN. From previous theoretical and experimental studies,\(^{[13]}\) benzoate radicals have a redox potential of 1.5 V, which is sufficient to oxidize the three TADF compounds in this study, and for this co-reactant ECL pathway to provide more energy than the annihilation ECL pathway. The difference in emission intensities compared to the annihilation pathway is likely due to this available energy increase.

The BPO co-reactant ECL efficiencies for PPOCzPN, PPSCzPN and DiPPOCzPN were determined to be 17, 6 and 1 %, respectively, using Eq. 4.1 (Table 4.6). Interestingly, this ECL efficiency difference between PPOCzPN and DiPPOCzPN resembles the difference in \(\phi_{PL}\) for the emitters in a PMMA film (56 to 28 %) more than it does the \(\phi_{PL}\) difference in DCM (51 to 61 %). This indicates that the ECL co-reactant pathway for DiPPOCzPN has an additional non-radiative decay pathway. In ECL co-reactant systems, the lifetime of the radical poses less of an issue than in annihilation experiments, since radical reactants are generated almost simultaneously, typically allowing ECL enhancement in solution. Now that radical stability is less of a factor, PPOCzPN\(^{\cdot-}\) appears to have a higher reactivity than DiPPOCzPN\(^{\cdot-}\) and PPSCzPN\(^{\cdot-}\) towards BPO. A higher anion reactivity for PPOCzPN was noted during pulsing experiments (Figure 4.3d-f) and appears to have been observed again in the BPO experiments. With increased available energy, it appears that PPOCzPN is the strongest emitter and maintains its position as the best candidate for optoelectronics.

**ECL Spectroscopy**

Figures 4.12d-f show spooling ECL spectroscopy performed on all co-reactant systems described herein. The ECL spooling spectra add a new data dimension of wavelength to the same spectra seen in Figures 4.12a-c. The BPO co-reactant systems show a light green emission for all species with maximum emission CIE coordinates of (0.29,0.40), (0.31,0.42) and (0.33,0.38) for PPOCzPN, PPSCzPN and DiPPOCzPN, respectively. In contrast to the annihilation pathway and also observed in the PL study, the DiPPOCzPN/BPO co-reactant system has the most red-shifted emission spectrum (Table 4.4 and Figure 4.12f), rather than the most blue-shifted. This large red-shift and relative drop in efficiency indicate that DiPPOCzPN may suffer from exciplex formation under these conditions. Exciplexes are heterodimeric species.
created by intermolecular interactions between a hole on the donor moiety of one molecule and the electron on the acceptor moiety of a second molecule.\cite{24} Exciplexes typically have smaller HOMO-LUMO gaps than either of the constituent components, thereby resulting in an observed red-shifted emission. Exciplex formation in OLEDs with luminophores substituted by diphenyl phosphine oxide substituents have been reported by Tourneur et al., who harnessed this exciplex formation to produce emissions from both intramolecular and intermolecular charge-transfer states yielding white light OLEDs.\cite{99} The exciplex identified during DiPPOCzPN/BPO co-reactant analysis appears not to be affected by an increasing concentration of reduced species in the vicinity of the electrode, since as the cyclic voltammogram progresses, no shift in emission maxima is seen (insets of Figure 4.12d-f). Additionally, there was no identified exciplex formation during the annihilation studies with DiPPOCzPN. The most probable explanation for the observed red-shifted emission is due to the exciplex between DiPPOCzPN$^-$ and Bz$^+$. Newcomb et al. has identified the necessity to screen potential TADF OLED emitters for exciplex formation, as the presence of exciplexes was shown to lower device lifetime.\cite{78} Masui et al. also identified large EQE roll-off in OLEDs caused by charge imbalance in the emissive layer that are exacerbated at higher current densities.\cite{10,72} The exciplex formation in these compounds is characteristic of compounds that also exhibit OLPL, thereby supporting OLECL emission as the dominant mechanism. Interestingly, the longest pulsing ECL onset delay belonged to DiPPOCzPN, which was the only compound to form a very evident exciplex during BPO co-reactant analysis. Interestingly, 2CzPN showed emissions centered at 550 nm, resembling the emissions seen in the DiPPOCzPN/BPO coreactant studies. This center wavelength is also 50 nm red-shifted from the 2CzPN PL studies likely due to a similar exciplex formation.

In a similar manner to the BPO co-reactant, 5 mM tripropylamine (TPrA) was added as an alternative co-reactant (Figure 4.13). The PPSCzPN/TPrA system behaved in the exact same manner as the DiPPOCzPN/BPO system, likely indicating a similar exciplex formation. There were no excimers identified in the PPSCzPN annihilation mechanism, indicating that the interactions between PPSCzPN$^+$ and NPr$_3$ may be responsible for the exciplex formation. The PPSCzPN/TPrA system also seems to be concentration-dependent where an increasing overpotential that creates more PPSCzPN$^+$ in the vicinity of the electrode gradually causes a red-shift. The compounds with the longest onset to ECL emission, longest time to achieve a maximum ECL intensity, longest ECL decay time, largest $\Delta E_{ST}$ and weakest ECL efficiencies likely form exciplexes under co-reactant conditions. These correlations and relationships all support the putative OLECL emission mechanism.

In Figure 4.14 the normalized accumulation spectra of all ECL processes discussed so far are overlapped, with ECL peak wavelengths summarized in Table 4.6. A slight red-shift is seen
Figure 4.13: Spooling ECL spectroscopy of the same systems described in Figure 4.10. Insets of each figure represent the respective spectra rotated to view a 2D wavelength versus ECL intensity. The color of spectra in the inset are the individual spectrum’s corresponding RGB coordinates.
Figure 4.14: Accumulated ECL spectra during different light generation methods. The annihilation ECL, BPO co-reactant ECL, TPrA co-reactant ECL and photoluminescence emissions are colored in black, blue, red and green traces for a. PPOCzPN, b. PPSCzPN and c. DiPPOCzPN, respectively.
4.6 Conclusions

Herein, we detailed the synthesis and characterization of three new 2CzPN derivatives with phosphine chalcogenide oxide groups substituted on the donor moiety. This strategy successfully stabilized the HOMO level of the donor, confirmed by cyclic voltammetry. By extension, the lowest-lying charge-transfer state was shifted to higher energy, thereby promoting a deeper blue emission, confirmed by photoluminescence studies. Surprisingly, the same trends are not recovered when measuring emissions in apolar media, thus highlighting solvatochromic effects on the TADF properties of the 2CzPN derivatives. Quantum-chemical calculations support these solvatochromic observations. Electrochemiluminescence studies in the desirable polar medium revealed a heretofore undocumented emission mechanism under electrical excitation in solution. Delayed ECL onset times relative to common ECL emitters in annihilation pathway revealed that organic long-persistent emission was operational and that the delay in the onset times correlated with the $\Delta E_{ST}$ of the emitters. PPOCzPN, which has the smallest $\Delta E_{ST}$, yielded the strongest, fastest, and most efficient ECL emissions when using BPO co-reactant. Thus, this compound should be the most suitable for optoelectronic applications after considering radical stability, emission stability, emission efficiency and emission intensity. Studies on ECL spooling spectroscopy and accumulated ECL spectroscopy identified that an exciplex of DiPPOCzPN forms while in the presence of radical anions. Analogous to the OLPL mechanism advanced by Kabe et al. the slow kinetics of exciplex formation and subsequent emission are likely responsible for the OLECL in this case. This work reveals a heretofore unknown ECL emission mechanism, OLECL, that manifests in both very long onset of ECL emission and long ECL lifetimes. Our study also provides significantly more detailed insight into the ECL of TADF compounds, which can be used to guide and screen TADF compound suitability for optoelectronic applications such as OLEDs.
4.7 Acknowledgements

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References


Chapter 5

Designing Absolute ECL Quantum Efficiency Techniques
Section 5.1

ECL Quantum Efficiency Quantification Strategy with a PMT
5.1.1 Preface

This section greatly improves past absolute ECL QE quantification methods that were developed before 1975. Absolute ECL QE has many benefits over the relative ECL QE method and our research group recommends using any absolute ECL QE analytical method to analyse ECL luminescent materials. These methods allow comparing results between labs to increase the applicability and impact of ECL research.

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5.1.2 Abstract

This work presents a thorough guide to procedures for absolute electrochemiluminescence (ECL) quantum efficiency ($\Phi_{\text{ECL}}$) measurements, which if employed effectively should raise the research impact of ECL studies for any luminophore. Absolute measurements are not currently employed in ECL research. Instead, ECL efficiencies have been determined relative to Ru(bpy)$_3^{2+}$ in similar conditions, regardless of whether the conditions are favorable for Ru(bpy)$_3^{2+}$ emissions or not. In fact, the most cited Ru(bpy)$_3^{2+}$ $\Phi_{\text{ECL}}$ is from the pioneering work by the Bard research group in 1973 by means of a rotating ring-disk electrode revolving at 52 rotations per second measured with a silicon photodiode. Our presented technique uses a common disk electrode, spectrometer and photomultiplier tube to measure the $\Phi_{\text{ECL}}$. The more common light detection hardware and electrodes combined with an in-depth calculation walkthrough will provide ECL researchers the necessary tools to implement $\Phi_{\text{ECL}}$ measurement procedures in their own laboratories. Following a facile instrument setup and calculation, a systematic study of Ru(bpy)$_3^{2+}$ $\Phi_{\text{ECL}}$ finds comparable results to those performed by Bard and coworkers.

5.1.3 Introduction

Absolute emission measurements provide unique insight into luminophores allowing for quantum yield (QY, defined as photon in photon out processes) or quantum efficiency (QE, defined as electron in photon out processes) measurements, where these methods are common in research fields such as photoluminescence (PL) and light emitting diodes (LEDs). Electrochemiluminescence or electrogenerated chemiluminescence (ECL) occurs when appropriately electrogenerated radicals undergo an electron transfer to create an excited state emitting light.[35, 43–45] The ECL field has also been steadily growing to quadruple the number of publications with ECL in the title in the last decade.[1, 17, 21, 30, 32] Unlike PL and LED research fields, ECL research does not have a widely accepted equivalent way of measuring QE. Akin to PL and LED studies, QE measurements for ECL research is very important because it predicts how strong emitters can be in practical applications.[15, 16, 25, 36, 47, 49]

LED research typically employs external quantum efficiencies (EQE) to quickly gauge absolute device performance without relying on commonly accepted standard solutions (devices in this case) like PLQY studies do.[3] In these absolute measurements, emission profiles, operational stability, and finely-tuned, finely-calibrated hardware setups are all required. These absolute measurements require little to no context where absolute values can be understood and interpreted immediately, significantly raising the research impact of results. Like the LED
research field, ECL research would also greatly benefit from absolute measurements and will be considered in this technical note.

Currently instead of absolute measurements, ECL research often reports emissions relative to \( \text{Ru(bpy)}_3^{2+} \) in the following equation:

\[
\Phi_{\text{ECL},x} = \Phi_{\text{ECL},st} \times \left( \frac{ECL_x}{ECL_{st}} \right) \times \left( \frac{Q_{st}}{Q_x} \right)
\]  

(5.1.1)

with integrated ECL emissions (ECL) and integrated current or charge (Q) that flows into the cell. Single values instead of calibration plots are generally reported for \( \Phi_{\text{ECL}} \). Unlike PLQY measurements, these so-called relative ECL efficiencies do not have standard solutions, standard concentrations, or standard coreactant concentrations. \( \Phi_{\text{ECL},st} \) is almost always \( \text{Ru(bpy)}_3^{2+} \) ECL emissions taken as 5 %, regardless of variations in concentrations, differences in testing conditions or discrepancies in solution polarity. This 5 % QE value measured in 1973 by the Bard research group also used a rotating ring-disk electrode (RRDE) at 52 revolutions per second in a concentration of 1 mM \( \text{Ru(bpy)}_3^{2+} \) ACN solution in annihilation pathway.\(^{[40]} \) Reporting 5 % \( \text{Ru(bpy)}_3^{2+} \) efficiencies that are not in ACN, not with a RRDE, not as the same concentration, or in coreactant systems etc. has created poor comparisons to measured results these almost four decades. The lack of standardization between relative measurements means that reported relative efficiencies have considerable error and mismatching between research results are difficult or not applicable. Mentioned previously, comparing different wavelengths of light can lead to orders of magnitude detector sensitivity differences yielding widely inaccurate relative ECL results. Even the kinetics of a reaction changes drastically when varying \( \text{Ru(bpy)}_3^{2+} \) and coreactant concentrations where extensive research has proved this.\(^{[26]} \) Especially, the relative QE procedure is really tough to use in recently advanced film ECL investigations.\(^{[1]} \) As a consequence of the lack of standards, the reported ECL efficiency experimental conditions are needed to interpret results, which can diminish the impact of ECL research. ECL research can grow faster if absolute measurement procedures are implemented, akin to the NIST methods of PLQY testing.\(^{[10, 18]} \)

Some work to find absolute ECL efficiencies was performed in the 1970s by the pioneering ECL research groups, Bard and Faulkner,\(^{[26, 28, 40]} \) while the Bard research group provided the most quoted 5 % \( \text{Ru(bpy)}_3^{2+} \) \( \Phi_{\text{ECL}} \) value determined at a RRDE.\(^{[40]} \) These \( \Phi_{\text{ECL}} \) measurement techniques used a photodiode along with actinometry. An actinometric solution consisted of iron(III) oxalate to measure or correct for light emissions between 250-500 nm, which is no longer common or used in literature, likely because of the complicated historical hardware or the lack of popularity of ECL measurements at the time. These research group’s pioneering
ideas and conventions are commonly seen in the absolute measurement methods currently em-
ployed in PL and LED research fields, such as calibrating light sensitive hardware, finding solid
angles of emissions, accounting for light detector sensitivities including many unique ECL cor-
rection factors. Despite the lack of adoption of these absolute ECL measurement techniques,
the 5 % Ru(bpy)$_3^{2+}$ $\Phi_{ECL}$ value has still been quoted and becomes a “gold standard” in recent
research. Most researchers including us use this value matched to experimental conditions that
the 5 % Ru(bpy)$_3^{2+}$ $\Phi_{ECL}$ value was originally measured in, but always forego the intricate
group in the mid-70s did use potential pulsing at a stationary disk electrode to determine ECL
efficiencies of diphenylanthracene and rubrene systems.[27] With the increase in popularity of
the ECL analytical technique and modern optical tools such as highly sensitive photomultiplier
tubes, well-calibrated photodiodes in a wide wavelength range, fast digital data acquisition and
advanced computer software for data treatments, there is much room for improvement on the
past $\Phi_{ECL}$ techniques that will provide increased ECL research impact.

Herein, this report presents an ECL measurement method for the absolute efficiency of a
well studied ECL emitter, Ru(bpy)$_3^{2+}$, by combining many past and recent scientific advances.
This $\Phi_{ECL}$ measurement setup employs a PMT at a fixed distance from the electrode surface
to have the best chance for appropriate ECL detection during transient or non-transient experi-
ments.

5.1.4 Materials and Methods

**Chemicals**

Tetrabutylammonium hexafluorphosphate (TBAPF$_6$) ([CH$_3$CH$_2$CH$_2$CH$_2$]$_4$N)PF$_6$, ≥99.0
%), ruthenium-tris(2,2’-bipyridyl) dihexafluorophosphate ([Ru(bpy)$_3$](PF$_6$)$_2$, 97 %), anhydrous
acetonitrile (ACN) (CH$_3$CN, 99.8 %), bis(cyclopentadienyl)iron (Fc) (Fe(C$_5$H$_5$)$_2$, 98 %) and
concentrated sulfuric acid (H$_2$SO$_4$, 95-97 %) were purchased from Sigma Aldrich (Missis-
sauga, ON). All dry chemicals were stored in a desiccator.

**Electrochemistry Preparations**

A 2 mm diameter platinum disc electrode and platinum wire coils were used as the working
and reference/counter electrodes, respectively. Prior to experiments, the platinum disk elec-
trode was mechanically polished with 1, 0.3 and 0.05 $\mu$m alumina particles and then treated
electrochemically in a 0.1 M H$_2$SO$_4$ solution by cycling the applied potential between -0.30
and 1.25 V vs. Ag/AgCl at a scan rate of 0.5 V/s for 20 minutes as this has been proven the
most effective platinum electrode polishing method.[29] This electrochemical polishing poten-
tial window must ensure that the hydrogen adsorption and desorption peaks (at ca. -0.1 V vs.
Ag/AgCl) and the reduction and oxidation of platinum (at ca. 0.46 and 1.00 V vs. Ag/AgCl respectively) are observed. The quality of the electrode treatment was verified with a CV of a Ru(bpy)$_3^{2+}$ solution at a scan rate of 0.1 V/s by viewing a 60 mV difference between the cathodic and anodic peaks for the Ru(bpy)$_3^{2+}$ oxidation. Due to the oxygen reactivity to quench excited states leading to lower emission efficiencies, 1 mM Ru(bpy)$_3^{2+}$ solutions in MeCN with 0.1 M TBAPF$_6$ as the supporting electrolyte were prepared and ECL cells were assembled in an inert atmosphere glovebox Nexus II (Vacuum Atmospheres Company (VAC), Hawthorne, CA).\[41\](White and Bard, 1982) Redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple as the internal standard (0.40 V vs SCE in ACN) that was measured promptly after all measurements.\[12\]

**Instrumentation**

Figure 5.1.1 displays the instrumentation required to perform QE measurements. An Autolab PGSTAT30 (Metrohm, Switzerland) was used as the driving force for ECL generation. The electrochemical reactions and light emission took place in the ECL cell that contains a light emitter such as Ru(bpy)$_3^{2+}$. A high voltage (HV) power supply set at -750 V powered a photomultiplier tube (PMT) (R3896, Hamamatsu, Japan) that measured the ECL intensity as photocurrent with a corresponding gain of 4.78×10$^5$, which is simply defined as the ratio of anode output current to the photoelectric current from the photocathode. A picoammeter (Model 6487, Keithley, Cleveland, OH) was utilized to transduce the photocurrent from the PMT to a voltage signal.

For accurate measurements with the PMT, wavelength-specific calibrations should be performed with an individually calibrated photodiode (S120VC, Thorlabs, Newton, NJ) connected to an optical power meter (PM100D, Thorlabs, Newton, NJ) as a reference. The calibration procedure used a red LED (TLHK46Q1R2, Vishay Intertechnology, Malvern, PA) with a center wavelength of 633 nm and Lambertian emission profile as the calibration light source. This calibration involved measuring light emitted from the LED at fixed potentials over 60 s on both the uncalibrated PMT and individually calibrated photodiode. These 60 s measurements were averaged and a plot of average calibrated total photon emission rate measured on the calibrated photodiode versus average uncalibrated total photon emission rate measured on the PMT from the LED was created in Figure 5.1.1. Exact total photon emission rate calculations will be discussed later. The slope of this graph yields a Calibration Correction Factor that will be used to correct the uncalibrated PMT signal. This graph had an almost perfect linear relationship between the two variables when completed with an $R^2$ of 0.9997.

A custom light tight box was built to house the ECL cell and PMT during measurements. The transduced ECL signal was fed into one of the two analog input channels on the potentiostat and measured along with the applied potential profile and electrochemical current on a
Figure 5.1.1: PMT calibration curve. Each point is an average of 60 s of measurement of an LED held at a fixed voltage on both the PMT and calibrated photodiode (PD). The voltages used for the LED were 1.45, 1.50, 1.55, 1.60 and 1.65 V and the calculations of the photon emission rate are included in the main text. The calibration correction factor 480,378 came from the slope of this graph and had relative units of uncalibrated PMT signal per calibrated PD signal. This calibration curve has an $R^2=0.9997$.

Figure 5.1.2: Example instrumentation for quantum efficiency measurements with an inset of solid angle descriptions.
computer controlling the Autolab via NOVA software. All electrochemical measurements were performed in the inert atmosphere glovebox. All instruments were kept outside of the glovebox, except for the PMT as illustrated by Figure 5.1.2. These exterior instruments had air-tight Bayonet Neill-Concelman (BNC) connectors that passed through the wall of the glovebox, permitting electrochemical and light-sensitive measurements inside an inert atmosphere.

Since the setup in Figure 5.1.2 captures a small percentage of the total ECL emission, corrections are required to find the total light emitted in the ECL process. Therefore, the distance from the electrode surface to the PMT surface (d_{PMT}) and the surface area of the PMT (A_{PMT}) must be measured, as shown by the inset of Figure 5.1.2. Also, d_{PMT} must be five times greater than and less than 50 times of the electrode diameter. This minimum distance requirement is known as the “five times rule” and allows for less than 1 % in the error calculations of the solid angle. For example, if an electrode surface has a 2 mm diameter, the light source must be at least 10 mm away and roughly up to 100 mm away.[34]

The spectroscopic measurement methods were reported elsewhere,[2, 3] with a spectrograph (Acton sp2300i, Princeton Instruments Inc., Trenton NJ) coupled with a CCD camera (Model DU401a-BR-DD, Andor Technology, UK) cooled to -65 °C. Since the CCD camera has its own wavelength-dependent quantum efficiency, all measured spectra in this report were corrected by the quantum efficiency of the CCD camera provided by the manufacturer to get a true emission spectrum.

Finally, total \( \Phi_{ECL} \) is determined by finding total photons emitted from the ECL source, and total incoming electrons injected into the ECL cell by the following equation:

\[
\Phi_{ECL} = \left( \frac{\int \nu_{\text{photons}} \, dt}{\int \nu_{\text{electrons}} \, dt} \right) \times 100\% 
\]  

(5.1.2)

where \( \nu_{\text{photons}} \) is the total ECL photon emission rate and \( \nu_{\text{electrons}} \) is the total Faradaic electron rate flowing into the electrochemical cell yielding total \( \Phi_{ECL} \) in a percentage of photons per electron.

### 5.1.5 Results and Discussion

To convert signal from a PMT (Figure 5.1.3a-b) into total photon emission rate (Figure 5.1.3d), the following checklist must be completed seen in Table 5.1.1. Included in the calculation procedure described in step 5 of the checklist, are photon and electron correction factors to adjust the typically unavoidable self-absorption of ECL by the solution and remove non-Faradaic current that indirectly contributes to the electrogeneration of radicals, respectively.
Figure 5.1.3: Cyclic voltammogram (black) and ECL-voltage curve (blue for cathodic and red for anodic) of a 1 mM Ru(bpy)$_3^{2+}$ solution containing 0.1 M TBAPF$_6$ with platinum wire coils for the counter and reference electrodes and a 2 mm diameter platinum for the working electrode. b. Current-time (black) and ECL-time (red) curves during a potential pulsing experiment at a frequency of 100 Hz, where the potentials used were 0.1 V above the oxidation and below the first reduction of the solution as indicated with dashed black lines in Figure 5.1.3a. c. Absorption spectrum (red) and background subtracted and normalized ECL spectrum (S($\lambda$)) (black) of the same Ru(bpy)$_3^{2+}$ electrolyte solution. d. Total photon emission rate created from calculations of ECL-time curve (red) in Figure 5.1.3b using Eqs. 5.1.5 and 5.1.6.
1. Cyclic Voltammograms (CVs) and ECL photocurrent-voltage curves (Figure 5.1.3a).

2. Electrochemiluminescence-time curve (red trace in Figure 5.1.3b) and the corresponding current-time curve (black trace in Figure 5.1.3b) in a potential pulsing procedure containing a minimum of 10 pulse pairs for a repeatable value.

3. ECL spectrum (black trace in Figure 5.1.3c).

4. Quantum efficiency curve from manufacturer and then calibration of PMT (Figure 5.1.3a and 5.1.4b) along with the ECL spectrum.

5. Determination of $\Phi_{ECL}$ following the calculation procedure.

Table 5.1.1: Checklist for tabulated data requirements of electrochemiluminescence (ECL) quantum efficiency determinations. Following the checklist will allow changing photocurrent from a PMT seen in Figure 5.1.3a-b to total photon emission rate seen in Figure 5.1.3d.

**Cyclic Voltammograms and ECL-Voltage Curves**

ECL measurements performed with the setup in Figure 5.1.2 are displayed in Figure 5.1.3a-b using a ECL luminophore, Ru(bpy)$_3^{2+}$. The CV of a 1 mM Ru(bpy)$_3$(PF$_6$)$_2$ with 0.1 M TBAPF$_6$ as the supporting electrolyte is displayed in the black trace of Figure 5.1.3a. Upon scanning anodically, Ru(bpy)$_3^{2+}$ undergoes oxidation reaction at a formal potential of 1.37 V vs. SCE. As the potential is scanned in the cathodic direction, Ru(bpy)$_3^{2+}$ is reduced three times at formal potentials of -1.33, -1.58, and -1.78 V vs. SCE and as expected, all redox reactions match previous experiments performed by the Bard group.[40] ECL is depicted in blue in this annihilation pathway, where radicals Ru(bpy)$_3^{+}$ and Ru(bpy)$_3^{3+}$ undergo an electron transfer to generate an excited state, Ru(bpy)$_3^{2+*}$ emitting light upon relaxation to the ground state.[40] The ECL peak obtained in the anodic scan color-coded in red is six times higher than that in the cathodic scan color-coded in blue. The peak heights are an indication of the stability and reactivity of the two radical species.

**Current-Time and ECL-Time Curves During Voltage Pulsing**

Potential pulsing for ECL in annihilation pathway is used to reduce the time between radical generations seen in a CV to better gauge luminophore efficiency and emissions. Figure 5.1.3b displays current-time (black) and ECL-time (red) curves of the same solution during a potential pulsing experiment at a frequency of 100 Hz, where -1.43 and 1.47 V vs. SCE, or 0.1 V below and above the first reduction and oxidation are stepped alternatively, as indicated by black
dashed lines in Figure 5.1.3a. The anodic and cathodic traces reach an ECL maxima of 234 and 150 µA at -1.43 and 1.47 V, respectively. An ECL enhancement of 100,000 times is achieved along with 200 times increase in maximum current when comparing Figure 5.1.3a to 5.1.3b. Obviously, the efficiency of the ECL reaction increased mainly due to the lower time between radical generation. Mentioned previously, radical stability is less of an issue so that ECL evolution significantly increases. Furthermore, the pulsing frequency of applied potential was varied from 0.1 Hz to 1000 Hz in a large time window. In this way, QE at each pulsing frequency will be determined with great statistics through at least 100 cycles and up to 10,000 cycles.

**ECL Spectra**

Collecting the ECL seen in the red trace in Figure 5.1.3b on a CCD camera produces an emission spectrum, black trace in Figure 5.1.3c, where a peak wavelength is found to be 620 nm. Also, in Figure 5.1.3c as a red trace is the absorption spectrum of the same 0.1 M TBAPF₆ and 1 mM Ru(bpy)₃²⁺ solution used in these studies. Obviously, the black and red traces overlap indicating self-absorption, a common phenomenon of concentrated solutions. Unlike PL studies, the concentration of luminophores in ECL studies is typically a few orders of magnitude greater, typically with a deeply colored solution. The loss of this higher energy emitted light will significantly affect the Φₑcl if left unaccounted for. Self-absorption corrections will be discussed later.

With all necessary data collected thus far, Φₑcl calculations can begin. All calculations were performed with custom scripts written in Matlab which are also discussed in the Supporting Information. Specific Matlab codes are available upon request from the corresponding author.

**Detection Area Correction Factor Along With Electrode Reflectivity**

QE measurements necessitate calculating total light emitted from the source which cannot be collected by a PMT as illustrated by the inset of Figure 5.1.2. An important consideration in accounting for this missed light is the light source’s angular emission profile. Unlike most optoelectronics, ECL has been proven to emit in equal intensity in every direction like a perfect sphere,[27] also described as a non-Lambertian emission profile. Some assumptions to simplify the required math will be made here where the ECL emission will be treated as a point source and that the emission occurs at the surface of the electrode. To correct ECL measurements for any missed light, the ratio of light collected by the PMT of the total sphere of random ECL emission (σₑcl,Non-Lambertian) along with the Pt disc reflectivity will be determined in the following equation:[26][27]
\[ \sigma_{\text{PMT, Non-Lambertian}} = \frac{A_{\text{PMT}}}{4 \pi (d_{\text{ECL to PMT}})^2} \times (1 + R_{\text{elec}}) \tag{5.1.3} \]

where \( A_{\text{PMT}} \) is the PMT surface area, \( 4 \pi (d_{\text{ECL to PMT}})^2 \) is the total ECL emission sphere surface area created by the distance the electrode surface is away from the PMT surface \( (d_{\text{ECL to PMT}}) \) and \( R_{\text{elec}} \) is the platinum electrode’s reflectivity at the peak ECL emission of 620 nm \( (R_{\text{elec}} = 0.60) \). Combining the reflection factor with our previous assumptions, 60% of the ECL emitted in the upper hemisphere will be reflected back towards the PMT, inflating the overall emission. Therefore, the observed emitted light should be \( 1 + R_{\text{elec}} \) lower due to the detection of the reflected light. As an example calculation, the \( d_{\text{PMT}} \) for this study is 71.6 mm creating a total emission sphere of 64,422 mm\(^2\). The R3896 Hamamatsu PMT has an effective area \( (A_{\text{PMT}}) \) of 192 mm\(^2\) allowing the collection of 0.00298 spheres or 0.298% of the total emission. Not considering this detection area correction factor for this study results in missing 99.7% of ECL emissions thereby underestimating the QE of the ECL reaction by 99.7%. The above detection area correction matches closely with that used by Bard research group, while omitting the complicated integration sphere hardware utilized by the Faulkner lab. Finally, the total emission should be reduced by \( 1 + R_{\text{elec}} \) providing a \( \sigma_{\text{PMT, Non-Lambertian}} \) of 0.00477 spheres.

**Hardware-Specific, Wavelength-Specific Factor**

Due to differences in hardware sensitivity to specific incoming light seen in Figure 5.1.4, a hardware-specific, wavelength-specific factor (C) is required for all QE measurements in the following equation:

\[ C = \frac{\int Q(\lambda) \times S(\lambda) \times d\lambda}{\int S(\lambda) \times d\lambda} \tag{5.1.4} \]

where, \( S(\lambda) \) is a background subtracted, normalized true emission spectrum of the incoming light (Figure 5.1.3c, black trace) and \( Q(\lambda) \) is the calibrated QE of the PMT in this study (Figure 5.1.4). Unfortunately, as mentioned previously, most PMTs are not individually calibrated, yielding differentiation in wavelength-specific QEs from batch to batch production of PMTs. An average PMT QE curve is provided by the manufacturer as displayed in Figure 5.1.4. Mentioned in the experimental section, an optical power meter with an individually calibrated photodiode was used for calibrating this PMT. Briefly, the integration limits should only include \( S(\lambda) \) where the \( Q(\lambda) \) is non-negligible. For Ru(bpy)\(_3\)^{2+}, the integration limits were set to 450
5.1.5. Results and Discussion

Figure 5.1.4: a. A Hamamatsu photomultiplier tube (Model Number R3896) curve of photoelectrons generated at the photocathode per each incoming photon at individual wavelengths, or quantum efficiency, provided by the manufacturer. b. Calibrated PMT quantum efficiency curve at a biased voltage of -750 V obtained from that in Figure 5.1.4a calibrated with a LED source at wavelength of 633 nm. This calibration is applicable to a small wavelength range around the calibration source’s wavelength (633 ± 50 nm).
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and 900 nm because there are no detectable emissions before 450 nm and the PMT is completely insensitive to wavelengths beyond 900 nm. Furthermore, since \( S(\lambda) \) is on both the numerator and denominator which cancels units and drastically simplifies the measurement process, the units for \( C \) come from the modified \( Q(\lambda) \) yielding units of electrons from the PMT per specific incoming photon. Calculating the \( C \) factor for 1 mM \( \text{Ru(bpy)}_3^{2+} \) emissions on a R3896 Hamamatsu PMT, a value of 64,436 electrons per average \( \text{Ru(bpy)}_3^{2+} \) ECL incoming photon is obtained. This \( C \) factor is commonly accounted for in literature where this method deviates insignificantly from other studies.\[4–6, 14, 27\]

Uncorrected Total Photon Emission Rate Measurements

Initially, the variables necessary to convert the photoelectrons excited from the photocathode of the PMT and enhanced by the photodynodes of the PMT for an unspecific incoming light, or photocurrent (\( PC_{PMT} \)), to an uncorrected total photon emission rate (\( \nu'_{\text{photon}} \)) with units of photons per second have been acquired and can be combined in the following equation:\[4, 26, 27\]

\[
\nu'_{\text{photons}} = \frac{PC_{\text{PMT}} * N_A}{F * \sigma_{\text{PMT}} * C}
\] (5.1.5)

where \( N_A \) is Avogadro’s number and \( F \) is Faraday’s constant. As an example converting the maximum photocurrent height in Figure 5.1.3b (234 \( \mu \)A) to uncorrected total photon emission rate yields a value of \( 1.08 \times 10^{13} \) photons per second emitted by \( \text{Ru(bpy)}_3^{2+} \).

Absorption Correction of Total Photon Emission Rate

Also mentioned previously, the self-absorption of the solution must be considered. When viewing the UV-visible absorption data in Figure 5.1.3c, overlap between the emission in the black trace and absorption in the red trace is occurring as early as 480 nm. Assuming that the ECL emission in Figure 5.1.3c is completely Gaussian and fitting the ECL spectrum peak half that has no self-absorption (fitting the 630-850 nm range) a model emission is gained. Subtracting this model gaussian emission peak from the ECL spectrum, a self-absorbed ECL peak is achieved. Integrating the original ECL spectrum and the self-absorbed peak, then comparing the peaks, the self-absorbed portion is found to be 17 % of the main peak’s area. Self-absorption accounts for roughly 17 % of removed light, requiring an absorption correction factor of 1.17 for the total photon emission rate measurement. This absorption correction factor matches previous studies closely.\[26, 40\] Notably, this absorption correction factor is only applicable for this exact system’s luminophore and electrolyte concentrations.

At this point, the data and calculations needed to convert total uncorrected photon emission rate (\( \nu'_{\text{photon}} \)) to total photon emission rate (\( \nu_{\text{photon}} \)) have been acquired and discussed respectively and can be combined in the following equation:
\[ \nu_{\text{photon}} = \nu'_{\text{photon}} \times AbsorptionCorrectionFactor \] (5.1.6)

When this equation is applied to the original photocurrent data collected in Figure 5.1.3b, Figure 5.1.3d is produced displaying the total photon emission rate during pulsing spectra. Eq. 5.1.6 will adjust the \( \nu'_{\text{photon}} \) pulsing maximum found earlier from \( 1.08 \times 10^{13} \) photons per second to a \( \nu_{\text{photon}} \) of \( 1.27 \times 10^{13} \) photons per second. This corrected total photon emission rate is an essential step in finding a luminophore’s \( \Phi_{\text{ECL}} \). Eq. 5.1.6 must be applied to every data point in the dataset and not just the ECL maximum to get the calculated dataset in Figure 5.1.3d.

**Current Correction Factors**

During pulsing and cyclic voltammetry, there is significant non-Faradaic current that does not directly contribute to the ECL emission which can be corrected for in the following equation:[13, 26, 27]

\[ \text{ChargeCorrectionFactor} = 1 - \frac{\int |i_{BG}| \, dt}{\int |i_x| \, dt} \] (5.1.7)

This equation divides the absolutely integrated background current (\( i_{BG} \)) by the absolute current integration of the pulsing experiment (\( i_x \)) and subtracts this from one. This background current is found in pulsing experiments by performing the same measurement (time period, pulsing width and frequency, current sensitivities, etc.) but with lower applied potentials. In this background experiment, the potentials were set 0.5 V below the oxidation (0.87 V) and 0.5 V above the first reduction (-0.83 V). This ensures that no species in solution are contributing to the current generated but allows all other non-Faradaic processes to occur. This charge correction factor is then multiplied by the current in the QE calculation. The percent of non-Faradaic current during the experiment can be found by removing the 1- from Eq. 5.1.7 and multiplying the fraction left by 100 %. A percentage of non-Faradaic current of 9.0 % or a Charge Correction Factor of 0.91 was found for the 100 Hz 1 mM Ru(bpy)\(_3^{2+}\) annihilation pulsing experiment.

Combining the above discussed current correction factors, the following equation for electron flow rate into the ECL cell (\( \nu_{\text{electrons}} \)) with units electrons per second is produced:

\[ \nu_{\text{electrons}} = \frac{i \times \text{ChargeCorrectionFactor}}{q_e} \] (5.1.8)
Table 5.1.2: ECL quantum efficiency, ECL maxima and non-Faradaic current percentage during measurements for different pulsing frequencies of a 1 mM Ru(bpy)$_3^{2+}$ solution. All values were taken from experiments with at least 1000 pulses (except for 0.1 Hz).

<table>
<thead>
<tr>
<th>Pulsing Frequency (Hz)</th>
<th>$\Phi_{ECL}$ (%)</th>
<th>First 10 Pulses</th>
<th>Last 10 Pulses</th>
<th>Normalized Max ECL Emission</th>
<th>Faradaic Current During Measurements (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.09 ± 0.02</td>
<td>0.07</td>
<td>0.11</td>
<td>0.06</td>
<td>77.1</td>
</tr>
<tr>
<td>1</td>
<td>0.27 ± 0.06</td>
<td>0.19</td>
<td>0.26</td>
<td>0.06</td>
<td>90.7</td>
</tr>
<tr>
<td>10</td>
<td>1.01 ± 0.04</td>
<td>1.07</td>
<td>0.97</td>
<td>0.24</td>
<td>90.4</td>
</tr>
<tr>
<td>100</td>
<td>2.43 ± 0.12</td>
<td>2.26</td>
<td>2.50</td>
<td>1.00</td>
<td>91.0</td>
</tr>
<tr>
<td>1000</td>
<td>0.28 ± 0.05</td>
<td>0.28</td>
<td>0.39</td>
<td>0.22</td>
<td>66.6</td>
</tr>
</tbody>
</table>

where $q_e$ is the elementary charge per electron and $i$ is the current during the pulsing experiment. Eq. 5.1.8 must be applied to every data point in the current data. For example, the maximum current measured in Figure 5.1.3b was -1.76 mA, which is converted to $1.00 \times 10^{19}$ electrons per second injected into the cell at this maximum pulse height.

**Quantum Efficiency Determination**

Then, by integrating both total photon emission rate ($\nu_{photons}$) and electron flow rate ($\nu_{electons}$) over the same amount of time, the total photons and total electrons of the scan are achieved respectively. Dividing these totals and multiplying by 100 provides a total photon per electron ($\Phi_{ECL}$) in percent or $\Phi_{ECL}$ seen in Eq. 5.1.2. This equation was used for calculating the $\Phi_{ECL}$ of Ru(bpy)$_3^{2+}$ during varying pulsing frequencies over at least 1000 pulses (except for 0.1 Hz with 100 pulses) where this data was summarized in Table 5.1.2. Many more absolute data transformations are possible with $\nu_{photons}$ and $C$ collected, such as luminance (cd/m$^2$), current efficacy (cd/A), luminance efficacy (lm/W) and radiance (W/sr/m$^2$) with in-depth data transformations available from other studies.[4]

The $\Phi_{ECL}$ of the CV depicted in Figure 5.1.3b was measured at 0.0019 % of electrons converted to photons, providing an $\Phi_{ECL}$ value far below any pulsing annihilation scans seen in Table 5.1.2. This low $\Phi_{ECL}$ is caused by two factors, large time differences between radical generation and unnecessary reductions of Ru(bpy)$_3^{2+}$. At a scan rate of 0.1 V/s seen in Figure 5.1.3b, the minimum time between radical generation would be 27 s which is 17 s longer than the 0.1 Hz pulsing frequency, drastically lowering the QE due to radical quenching. Ru(bpy)$_3^{2+}$ has been found to generate the most ECL when the Ru(bpy)$_3^{3+}$ and Ru(bpy)$_3^{2+}$ species undergo an electron transfer where Ru(bpy)$_3^{0}$ and Ru(bpy)$_3^{-}$ have been found to hurt
5.1.5. Results and Discussion

Unwanted reductions and long times between radical generations result in lower $\Phi_{\text{ECL}}$ for Ru(bpy)$_3^{2+}$. The maximum total $\Phi_{\text{ECL}}$ received for Ru(bpy)$_3^{2+}$ was found to be 2.43% at 100 Hz pulsing frequency. Previously, Bard et al. measured $\Phi_{\text{ECL}}$ of a 1 mM Ru(bpy)$_3^{2+}$ solution in ACN with a RRDE operating at different rotation frequencies. They discovered that a RRDE rotation rate of 52 revolutions per second with disk and ring potentials of 1.48 V and -1.37 vs. SCE, respectively, in a 1 mM Ru(bpy)$_3^{2+}$ ACN solution yielded a $\Phi_{\text{ECL}}$ maxima just under 5%. Although the experimental setup is vastly different, a RRDE rotating at 52 revolutions per second and 100 Hz pulsing experiments at very similar potentials produced comparable $\Phi_{\text{ECL}}$ values.

As expected, the extra convection mixing during a RRDE testing provides more opportunities for radicals to meet thereby generating a higher $\Phi_{\text{ECL}}$ relative to pulsing experiments. The 2.43% $\Phi_{\text{ECL}}$ is comparable to the highest extended pulsing $\Phi_{\text{ECL}}$ we could find in literature. This maximum $\Phi_{\text{ECL}}$ of 6.2% was also reported by the Bard research group and was found for a 9,10-diphenylanthracene (7.8 mM) / thianthrene (11.1 mM) (DPA/TH) in a solution of 50% ACN:33% benzene:17% toluene by volume with potential pulsing between 1.46 and -2.14 V vs. SCE at a pulsing frequency of 60 Hz over a period of 14 hours.

The lowest Ru(bpy)$_3^{2+}$ $\Phi_{\text{ECL}}$ in Table 5.1.2 occurs at 0.1 Hz and 1000 Hz which also corresponds to the lowest Faradaic current percentages during measurements. It appears that the $\Phi_{\text{ECL}}$ is directly related to the background current during measurements where high background currents produce low $\Phi_{\text{ECL}}$. For a 1000 Hz pulsing frequency, the potential is likely switching too fast for sufficient redox reactions to occur resulting in a third of current contributing to electrical double layer formations. Despite this high non-Faradaic current, the maximum ECL emissions remained high and comparable to the maximum emissions at 10 Hz. The highest Faradaic current percentage of 91.0% during 100 Hz pulsing produced the highest $\Phi_{\text{ECL}}$ and the highest maximum emission as well. 100 Hz pulsing frequency for this specific system had an appropriate balance of non-Faradaic current, redox reactions and optimized pulsing time between radical generation to permit optimized ECL emissions. Previously, the Bard research group also noted an optimal pulsing frequency of 60 Hz for the DPA/TH system which was close to our optimal 100 Hz pulsing frequency.

Interestingly, an ECL emission delay of 250 $\mu$s after the cathodic pulse is seen in the 1000 Hz pulsing frequency scan. This ECL delay has been documented well by previous studies and arises from electrical double layer charging on the surface of the electrode and uncompensated electrolyte resistance between the counter and working electrodes. The authors of this paper described this delay to be tenths of milliseconds or typically 100 $\mu$s.

Figure 5.1.5 depicts a cycle or time dependency on the $\Phi_{\text{ECL}}$ for all pulsing frequencies discussed in this study. Interestingly, in almost every case (excluding 10 Hz) the $\Phi_{\text{ECL}}$ value
increases over time. The current values (Figures 5.1.5a-e) in almost every case start high and slowly decrease over time, whereas the photocurrent values (Figures 5.1.5a-e) start low and steadily increase over time. This was seen previously by the Bard research group [26, 27] and was attributed to the removal of quenching agents (such as dissolved molecular oxygen) by luminophore radicals. The temporary removal of luminophore radicals lowers $\Phi_{ECL}$ until the quenching agents are fully reacted at which point the $\Phi_{ECL}$ can slowly increase over time. Interestingly, the increase in $\Phi_{ECL}$ can be dramatic as is the case for 0.1 Hz pulsing. The first 10 and last 10 pulses have $\Phi_{ECL}$ values of 0.07 % and 0.11 %, respectively, which occurs over 600 s totally. This large variation in $\Phi_{ECL}$ highlights the variability present in these scans.

The other pulse frequencies do not change as drastically as the 0.1 Hz, likely because of the shorter times used, but is still apparent when comparing the values. This variability in $\Phi_{ECL}$ values necessitates the averaging a minimum of 10 pulse pairs of an optimized system for a repeatable $\Phi_{ECL}$ value seen in Table 5.1.2. As evidenced by Figure 5.1.5, selecting one pulse pair from a series of pulses will skew results lowering the repeatability.

From Figure 5.1.5c, the $\Phi_{ECL}$ of each cycle (20 ms) is found for the 10 Hz 200 s scan, there is a 0.06 % variance for the calculated values over the entire scan, indicating low $\Phi_{ECL}$ variability over long times. In fact, this long-term ECL stability is commonly found for some ECL systems where the Bard research group discovered ECL systems that produced stable $\Phi_{ECL}$ values over 14 h. [27] However, this stability seems to be system-dependent where many lu-
minophores form unwanted side products after extended electrochemical testing which should be carefully considered for future studies.\cite{19, 23, 24, 42} Despite the small variances with experiments in a constant cell, large variances were found between different cell preparations. The 10 Hz pulsing frequency 1 mM Ru(bpy)$_3^{2+}$ $\Phi_{ECL}$ experiment was measured three separate times with three separate cells on three separate days and was found to have a 26 % variance between $\Phi_{ECL}$ values. To the best of our knowledge, all other $\Phi_{ECL}$ reports did not comment on error or reproducibility of $\Phi_{ECL}$ values. One report commented on the reproducibility of a lamp/calibration source in their $\Phi_{ECL}$ setup that had ±3 % error,\cite{6} but a lamp’s light generation method is vastly different to ECL generation and serves as a poor comparison. However, comparing this pulsing ECL error to standard PL measurements for even the most well-studied standards (e.g. quinine sulfate), there is a ±4 % error in its reported PLQY value.\cite{10} Assuming researchers can measure this standard and their samples PLQY with a similar accuracy, the sum of the error will be roughly ±10 %.

Some factors in this reported $\Phi_{ECL}$ were not considered that would likely contribute to the error seen in the measurements. Small amounts of dissolved oxygen are hard to completely purge from a system and can scavenge radical states to reduce efficiency greatly. Radical products can quickly decompose into unwanted decomposition products and not contribute to the $\Phi_{ECL}$ as evidenced by the pulsing frequency changes. These unknown decomposition products can absorb light to an unknown extent or interfere with quick electron transfers between appropriate radicals to generate excited states, thereby lowering $\Phi_{ECL}$. Excited states can also be quenched by the platinum electrode surface further lowering the $\Phi_{ECL}$. This study attempted to reduce or eliminate any conditions that lower $\Phi_{ECL}$ all possible known $\Phi_{ECL}$ quenchers. Future studies can discover and then reduce these quenching possibilities. Concentration-dependence on the $\Phi_{ECL}$ was also not investigated in this study.

\subsection{Conclusion}

Herein, a new practical analytical strategy has been described that allows for measurements of absolute $\Phi_{ECL}$, being compared with those in literature. These $\Phi_{ECL}$ measurements are built on the great ideas from Bard and Faulkner research groups in the 1970’s and make them more accessible for all researchers. This procedure will be simply implemented once the usual instrumentation is set up and software programs are developed. As the number of ECL researchers and ECL applications grow, so should the quality of data. Similar to the absolute and standardized measurement methods adapted by most LED and PL studies, implementation of these absolute practices will provide higher impact ECL results and permit their instant understandings. These also invite researchers who are unfamiliar with ECL to understand results.
and their implications clearly.

5.1.7 Acknowledgements

We appreciate very much the financial supports to this research by Natural Sciences and Engineering Research Council Canada (NSERC, DG RGPIN-2018-06556 and SPG STPGP-2016-493924), Canada Foundation of Innovation/Ontario Innovation Trust (CFI/OIT, 9040) and The University of Western Ontario. JRA and KC are grateful to Ontario graduate scholarships. We sincerely thank our Electronic Shop in Chemistry and ChemBio store for the quality service.

References


REFERENCES


Section 5.2

Simplified ECL Quantum Efficiency with CCD Camera
5.2.1 Preface

This section provides a simpler ECL QE analytical method than the one just discussed in Section 5.1. However, this method does not make the method in Section 5.1 obsolete. Section 5.1’s measurement method is more sensitive than the method presented in this section. Therefore, despite the simplicity of this new method, the method presented in Section 5.1 may be required for some luminescent materials.

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Chapter 5.2. Simplified ECL Quantum Efficiency with CCD Camera

5.2.2 Abstract

Currently, the electrochemiluminescence (ECL) efficiency of a luminophore is evaluated by measuring the ratio of ECL intensity generated by a certain number of electrons injected. Then, this ratio is compared to that of the commercial luminophore, Ru(bpy)$_3^{2+}$ under the same test conditions. However, the ECL intensity from a luminophore will be different on every instrumental setup due to wavelength-specific interaction of light with photodetectors. Also, previous absolute ECL techniques require multiple instruments, each of which has its own wavelength-specific light losses leading to complicated hardware and calculation requirements. Herein, this manuscript presents an absolute way to evaluate the ECL quantum efficiency, permitting researchers to quickly compare ECL results and elucidate ECL mechanisms. The accuracy and precision of this new physical strategy is verified with the well-studied Ru(bpy)$_3^{2+}$ to find an ECL QE of 0.64%. The strategy was then exemplified with Au$_{25}^{0}$($SC_2H_4Ph)$_{18}$ to represent a difficult spectroscopic challenge and this ECL QE was found to be 0.0062%. Finally, Ru(bpy)$_3^{2+}$ ECL QE at different TPrA concentrations was evaluated to understand how the TPrA concentration affects the ECL QE of Ru(bpy)$_3^{2+}$. Significant Ru(bpy)$_3^{2+}$ ECL QE decreases were viewed from $3.2 \times 10^{-3}$% at 6.25 mM TPrA to $6.5 \times 10^{-6}$% at 200 mM TPrA likely due to high excited state quenching. Along with our previous publications on Au cluster ECL, discussed are factors influencing the ECL intensity such as the diffusion of electroactive molecules, the stability of radicals, the reactivity of excited states and the analyte’s reactivity. Profound variations were observed on this finding, which has large implications for past, current and future relative ECL efficiencies also discussed in length.

5.2.3 Main Text

In electrochemiluminescence (ECL) of a luminophore in investigations, most quantum efficiency measurements are taken relative to that of conventional standard Ru(bpy)$_3^{2+}$ by comparing their ratios of ECL emission to total charge injected in similar conditions using the following equation:[7]

$$\Phi_{ECL,x} = \Phi_{ECL,st} \left( \frac{ECL_x}{ECL_{st}} \right) \left( \frac{Q_{st}}{Q_x} \right)$$ (5.2.1)

where $\sigma_{ECL}$ is the ECL efficiency, ECL is integrated photodetector signal, $Q$ is the charge in units of Coulombs, and $st$ and $x$ denote the standard Ru(bpy)$_3^{2+}$ and luminophore, respectively. The quantum efficiency of Ru(bpy)$_3^{2+}(QE, \Phi_{ECL,st})$ is commonly referenced as 5%. However,
this result came from the Bard group in 1973 where they used a relatively high concentration of Ru(bpy)$_3^{2+}$ in solution with a rotating ring-disk electrode (RRDE).[22] This RRDE was rotating quickly where a ring electrode generates Ru(bpy)$_3^{2+}$ and the disk electrode generates Ru(bpy)$_3^+$,[22] which undergo an electron transfer to form an excited state emitting ECL. However, most ECL experiments are performed in static solutions and a RRDE is rarely used. Therefore, comparing ECL efficiencies to this landmark study is often inconvenient and inconsistent. Based on the vast research field on ECL fundamentals and applications,[13, 20, 21, 24–28, 32, 34, 35, 40, 42, 44, 45] relative $\Phi_{ECL}$ is not enough for quantitative physical measurements.

Another way to evaluate the ECL QE is through simulations.[8, 10, 11, 19, 36, 41] Electrochemical oxidation rate constants of coreactants and luminophores can be found experimentally and quickly to guide simulations and to predict the ECL QE tendency.[11] These ECL QE calculations are effective in optimizing the 3D space that ECL is emitted for enhancing sensing applications.

Literature exists for researchers to measure their own ECL QE that can refer back to the utilization of a calibrated photodiode prior to charge-coupled device (CCD) cameras.[6, 23] Very recently our group has developed methods by means of a photomultiplier in photocurrent and photon-counting modes.[1, 9] The absolute quantum efficiency ($\Phi_{AQE}$) can be determined through the following simplified equation:[2]

$$\Phi_{AQE} = \int_{t_0}^{t_0 + x} \frac{\sum_{pixel=1}^{pixel=w} \nu_{photons}(t)}{\nu_{electrons}(t)} dt \times 100\% \quad (5.2.2)$$

where $\Phi_{AQE}$ is the percent ratio of photons emitted to electrons injected, $\nu_{photons}(t)$ is the total photon emission rate on a pixel in units of photons s$^{-1}$, $\Sigma \nu_{photons}(t)$ is the sum of all photons in a defined pixel range, $w$ is the width of the pixel array, $\nu_{electrons}(t)$ is the electron input in electrons s$^{-1}$ and $x$ is the desired integration time to find $\Phi_{AQE}$. However, these methods involve multiple calibrated instrument setups, greatly increasing the complexity of measurements.[1, 5] Generally in these methods, a pre-calibrated photodetector (such as a photodiode, photon counting head or photomultiplier tube), and a spectrometer are needed to properly evaluate the $\Phi_{AQE}$ of a compound. The calibrated photodetector such as a photomultiplier tube (PMT) plays a major role, for which commercial and traceable calibration services are not always available, while most calibrated photodiodes are not sensitive enough to measure certain ECL signals. Furthermore, many photodetectors may not be sensitive to certain wavelengths of light in the near-infrared region, which prevents researchers from properly analyzing their samples.
of interest. Having multiple instruments able to collect light over large wavelength windows can therefore be expensive and challenging.

Herein, we present an instrumentally and mathematically simpler method to determine $\Phi_{AQE}$ using only a spectrometer coupled with a spectroscopy CCD camera calibrated against a pre-calibrated photodiode. Generally, this calibration should be carried out for the setup once a year and unless the setup is modified, the calibration should be stable. Commercial calibrations to be provided by the spectroscopy CCD camera will be great help to implement the instrumentation. This technique is exemplified with a near-infrared (NIR) emitter, $\text{Au}_{25}^0(\text{SC}_2\text{H}_4\text{Ph})_{18}$ nanocluster (which will be abbreviated to $\text{Au}_{25}^0$), to demonstrate a relatively difficult spectroscopic challenge.\cite{18}

\section*{5.2.4 Experimental Methods}

\textbf{Materials and reagents}

SureSeal benzene (anhydrous, 99.8 \%) and acetonitrile (anhydrous, 99.8 \%) were purchased from Sigma Aldrich Canada (Mississauga, ON), and stored in an inert atmosphere. These solvents were mixed in a 1:1 ratio to produce the final solvent mixture used in electrochemical experiments. Tetrabutylammonium perchlorate (TBAP, electrochemical grade, >99.0 \%) was obtained from Supelco, and used as received. Tripropylamine (TPrA, >98 \%) was bought from Sigma-Aldrich Canada, and stored at 4 $^\circ$C. $\text{Au}_{25}^0$ was synthesized and characterized following our procedure published elsewhere.\cite{18}

\textbf{Electrochemistry and electrochemiluminescence}

A three-electrode system was used for all electrochemical measurements, where the working electrode was a platinum disc (2 mm diameter) inlaid in a glass tube, and the counter and reference electrodes were coiled platinum wires, Figure [5.2.1]. Electrochemical measurements were conducted inside a cylindrical glass tube with a flat quartz window at the bottom to allow for the detection of ECL light. The potentiostat used was a CH Instruments Model 610a electrochemical workstation (CH Instruments Inc., Austin, TX) or a PAR 263A potentiostat/galvanostat (EG& G Princeton Applied Research, Oak Ridge, TN) to generate the constant potential profile. ECL spectra were recorded using a SP2300i spectrophotograph (Teledyne Princeton Instruments, Trenton, NJ) with an attached CCD camera (Andor DU401-BR-DD-352, Oxford Instruments, UK) cooled to -65 $^\circ$C, Figure [5.2.1] Wavelength calibration was accomplished using a mercury source (HG-1, Ocean Optics, Dunedin, FL) using a center wavelength of 546 nm. Spooling ECL spectra were acquired each at a time interval of 1 s during a cyclic voltammogram; the obtained spectra were combined in a three-dimensional plot using a custom MATLAB program.\cite{16}
Absolute ECL quantum efficiencies (AQEs). AQEs were determined from ECL spectra and chronoamperograms using a MATLAB program developed in our group with equations described below.

5.2.5 Results and Discussion

Instrument setup and measurements

Figure 5.2.1 displays the entire spectroelectrochemical/photoelectrochemical setup required for measuring $\Phi_{AQE}$ with a spectrograph coupled with a CCD camera. Briefly, a potentiostat applies a working potential to an ECL cell with three electrodes immersed in a solution of 1:1 benzene:acetonitrile containing 6.25 mM tri-n-propylamine (TPrA), 0.1 M tetrabutyl ammonium perchlorate (TBAP) and 0.1 mM Au$_{25}^0$. A constant potential of 0.89 V vs. SCE is applied, at which TPrA is oxidized once and Au$_{25}^0$ twice to ultimately produce TPrA$^-$ and Au$_{25}^{2+}$ respectively, seen in the schematic insets of Figure 5.2.2a, as we reported elsewhere. Accordingly, the electrochemical current-time curve (chronoamerogram) is shown in Figure 5.2.2a. The generated TPrA$^-$ and Au$_{25}^{2+}$ species can react to produce Au$_{25}^{+*}$ and an iminium ion (Im$^+$) in the vicinity of the working electrode. This Au$_{25}^{+*}$ can emit light as ECL with the simplified mechanism shown in the inset of Figure 5.2.2b. For more details on Au$_{25}^0$ re-
dox chemistry and Au$_{25}^+$ photoluminescence please refer the Latimer diagram we published elsewhere.[14, 18] For this experimental setup, the emitted ECL then enters the spectrometer through a slit at a controlled width to adjust the light intensity, Figure 5.2.1. It is assumed here that all light entering the slit will hit the first mirror and that the whole spectrometer is optically aligned. The spectrometer will then have the aluminum mirror reflecting the incident light, then a grating separating light by wavelength, finally another mirror directing the light onto a 2D CCD camera sensor array to produce a spectrum. For example, the CCD array used in this report is a 2D pixel array of 1024×127 pixels. This data is then summed by wavelength into a 1D spectrum seen as the red trace in Figure 5.2.2b. This is all the ECL data needed to calculate the $\Phi_{AQE}$ using a CCD camera.

Correction factors in determining the AQE. To determine the $\Phi_{AQE}$, several corrections for the photon and electron counting have been considered for everything the photons and electrons interact with. Some of these factors are not unique to a CCD camera and have been discussed at length elsewhere.[1] The factors specific to this work will be briefly discussed below.

When an ECL photon is initially created, it will pass through the solution it is in and may be self-absorbed. By comparing a UV-visible absorption spectrum to the ECL emission spectrum at the same concentration, any self-absorption is quickly apparent by evaluating the peak overlap. Luckily, for this compound, negligible amounts of light are self-absorbed, meaning that this correction factor (A) is unneeded for this system.
Next, the photons will pass through the Pyrex window on the bottom of our ECL cell. The Pyrex transmits > 90% of the light at 950 nm where a wavelength dependent correction for the Pyrex absorption must be applied seen in Figure 5.2.3. Since the Pyrex window transmission is roughly equal over the entire spectrum range between 200 and 1100 nm, this wavelength independent correction factor of 111% for the Pyrex window should be applied to all data.

After the Pyrex window, the photon will pass through the slit of the spectrometer (Figure 5.2.1). Since only a small percentage of the total ECL emission enters the slit, illustrated as a small part of the yellow light hemisphere in Figure 5.2.1, the total number of photons emitted during the ECL process must be corrected from the light measured on the CCD camera with the solid angle calculation. With a 1.50 mm × 4.25 mm rectangular slit, the surface area of the light collected (A) will be 6.38 mm². If the distance between the electrode surface and the spectrometer slit (d) is 20 mm and the proven randomly emitted ECL is in a perfect sphere centered on the electrode, the surface area of the total sphere is 5027 mm². However, assuming the total upper hemisphere of emitted light hits the electrode surface, a certain percentage of it will be reflected towards the spectrometer slit inflating the photon value. For a Pt electrode and a 950 nm emitter, a platinum surface will reflect 77% of the light which requires a reflectance correction \(R_{elec}\) of 0.77. These discussions are summarized in the following equation:
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Figure 5.2.4: a. The calibration curve for the red LED measured on both the Thorlabs calibrated photodiode and the CCD camera coupled to a spectrometer. Each point corresponds to 3 averaged 60 s scans each at a single potential ranging from 750 mV to 800 mV. b. The manufacturer provided QE of a DU401a-BR-DD Andor CCD camera cooled to -70 °C seen as the red trace. The calibrated QE curve which considers light losses in the spectrometer and the CCD camera (Q(λ)) is seen as the blue trace. c. The blue curve from Figure 5.2.4b multiplied by the GF.

\[
\sigma_{\text{Spherical}} = \frac{A}{4 \pi d^2} (1 + R_{\text{elec}})
\]  

(5.2.3)

where \(\sigma_{\text{Spherical}}\) describes the light collected from a spherically emitting point source with units of spheres. The \(\sigma_{\text{Spherical}}\) for this setup discussed so far will be \(2.24 \times 10^{-3}\) spheres collected which is a very small fraction.

Next, the f number of the spectrometer must be considered that can increase the intensity of light on the CCD camera if considered appropriately. A lens must be used to focus ECL appropriately into the spectrometer for optimal intensity calibrations. If a lens is not used, the calibration source and ECL light should be measured at the exact same position to remove as many errors as possible.

The photon will then travel through the spectrometer which generally contains two Al mirrors and a grating as the schematic in Figure 5.2.1. Here, a wavelength specific intensity correction factor is not considered for the sake of simplicity.

A CCD camera calibration of the setup QE curve using a known, stable and wavelength-relevant light source is now required and is the key in the calibration procedure; the blue trace in Figure 5.2.4b shows the final result of this calibration while the red trace in Figure 5.2.4b is the manufacturer-reported QE of the CCD camera. This has been performed with a calibrated Thorlabs S120VC silicon photodiode connected to a PM100D compact power and energy meter with a bright, stable LED purchased from Vishay Electronics Limited with a center wavelength of 633 nm. This LED wavelength range and stability were verified by the
5.2.5. Results and Discussion

CCD camera. Briefly, this calibration was performed by measuring the LED emission for 60 s using both the CCD/spectrograph setup and calibrated photodiode. In total, five different driving voltages were used (corresponding to the points in Figure 5.2.4a) for the LED, where tests were performed in triplicate and averaged. The unitless calibration value was taken as the slope of the line of best fit for Figure 5.2.4a and was found to be 39.1. This means the LED light measurements on this spectrometer/CCD camera setup should be adjusted 39.1 times higher. Then, this calibration factor was incorporated into the QE of the CCD camera (red trace) to produce a calibrated QE for the entire setup ($Q(\lambda)$) shown as the blue trace in Figure 5.2.4b.

This specific setup’s $Q(\lambda)$ is incorporated into calculations as follows:

$$I_{corr} = \frac{I}{Q(\lambda)} \times 100\%$$  \hspace{1cm} (5.2.4)

where $I$ is the CCD camera’s signal in counts and the corrected signal $I_{corr}$ has units of counts $\times$ photons $\times$ electrons$^{-1}$. For example, 405 counts at 950 nm and a 41% quantum efficiency will yield a $I_{corr}$ value of 988 counts $\times$ photons $\times$ electrons$^{-1}$. In this way, every pixel in the CCD array is treated as a single photodetector. Also, collecting the intensity and corresponding wavelength is important for ECL studies where the emission peak wavelength can shift significantly from their photoluminescence (PL). For example, carbon quantum dots have many accessible surface states where the maximum wavelength of ECL emission can shift up to 150 nm from their PL peak wavelength.[2–4]

It should be noted that the CCD QE from 900-1100 nm drastically drops as seen in Figure 5.2.4b, blue trace, and approaches 0 around 1100 nm. From Eq. 5.2.3 the CCD counts collected around 1100 nm would need to be corrected by dividing near 0 to produce very large $I_{corr}$ as represented in the blue trace in Figure 5.2.5a. In our best judgement, we believe anything below a 3% QE correction would introduce too much error into the absolute ECL determination when considering near infinite correction values and the manufacturer reported error. Therefore, any wavelengths above 1050 nm with this CCD array are not considered in this study.

Previously, setup calibrations and CCD camera QE were accounted for through a weighted photodetector sensitivity factor ($C$). This so-called $C$ factor is found by multiplying the background subtracted and normalized emission spectra ($S(\lambda)$) by the CCD camera’s sensitivity ($Q(\lambda)$) expressed as a ratio as follows:[5, 22, 23, 30]

$$C = \frac{\int Q(\lambda) \ast S(\lambda) \ast d\lambda}{\int S(\lambda) \ast d\lambda}$$  \hspace{1cm} (5.2.5)
However, this $C$ factor requires all experimental data to be performed on both the photodetector and a spectrometer coupled to a CCD camera instead of performing the experiment only on a spectrometer coupled to a CCD camera as presented herein. This $C$ factor method generally increases experimental times or leads to significantly increased experimental complexity relative to the technique presented in this manuscript.

Similar calibration methods are performed commercially. For example, Thorlabs calibrates photodiodes according to National Institute of Standards and Technology (NIST) or Physikalisch-Technische Bundesanstalt (PTB) standards where a S120VC photodiode power sensor that has a wavelength range from 200-1100 nm will have four wavelengths calibrated. The S120VC includes 200-279 nm, 280-439 nm, 440-980 nm, and 981-1100 nm calibrations. However, most importantly the calibrated wavelengths must be as close as possible to the analyte’s wavelengths because of the wavelength-dependent light loss when light interacts with solid materials.

To complete this photon flux calculation, there are some additional corrections to consider. Commonly, a gain factor ($GF$) is used in CCD arrays to amplify the signal from every pixel where the $GF$ typically has units of electrons $\times$ count$^{-1}$. For this camera, a $GF$ of 12.2 electrons $\times$ count$^{-1}$ was provided by the manufacturer.

The CCD array sums the charges produced into a 1D line seen in Figure 5.2.2b by passing the collected charges along the pixels. This pixel-to-pixel charge-transfer efficiency of this CCD camera and most CCD cameras is 99.999% so a correction is not considered in this manuscript.

These corrections so far have only affected the intensity of the emissions, and not the wavelength. This wavelength should be calibrated by an external light source that has an intense and sharp emission peak near the analyte’s emission, such as a Hg lamp for visible light or a Xe lamp for NIR wavelengths. A wavelength-shift is generally applied to the corrected spectrum to align the spectrometer and CCD array appropriately.

Finally, the accumulation time ($t$) that was used for the experiment must be considered which in this case is 2 s. Every correction factor to measure the true number of photons has now been discussed and the photon flux can be calculated as shown in Figure 5.2.5a.

With $I_{corr}$ in unit of counts-photons electron$^{-1}$, all corrections can be applied to convert $I_{corr}$ to $\nu_{photons(t)}$ with unit of photons s$^{-1}$ sphere$^{-1}$ pixel$^{-1}$ in the following equation:

$$\nu_{photons(t)} = I_{corr} \times \frac{GF \times CC}{t \times \sigma_{random}} \tag{5.2.6}$$

The resulting transformation is seen from counts in Figure 5.2.2b to photon flux in Figure 5.2.5a. For example, an $I_{corr}$ of 988 counts-photons electrons$^{-1}$, a $GF$ of 12.2 electrons count$^{-1}$,
5.2.5. **Results and Discussion**

Figure 5.2.5: Data transformations for the data in Figure [5.2.2](#). a. The red trace shows the generated charge carriers in electrons on each pixel of the CCD camera by multiplying the counts generated by the gain factor. The blue trace shows the total photons flux emitted onto each pixel of the CCD camera in the entire 2 s accumulation. b. The total electron flux applied to the ECL cell.

![Data transformations for the data in Figure 5.2.2](#) a. The red trace shows the generated charge carriers in electrons on each pixel of the CCD camera by multiplying the counts generated by the gain factor. The blue trace shows the total photons flux emitted onto each pixel of the CCD camera in the entire 2 s accumulation. b. The total electron flux applied to the ECL cell.

a 39.1 calibration factor (CC), $t$ of 2 s, and a $\sigma_{	ext{spherical}}$ of $2.24 \times 10^{-3}$ spheres, a $\nu_{\text{photons}}(t)$ of $1.1 \times 10^8$ photons s$^{-1}$ sphere$^{-1}$ is determined.

Interestingly, when correcting for CCD array QE, the QE curve (blue trace of Figure [5.2.5a](#)) descends faster than the edge of the emission (red trace of Figure [5.2.2b](#)) meaning the measured maximum wavelength will be red-shifted to the edge of the manufacturer reported QE wavelength range. One may realize that the employed CCD camera was not sensitive to these wavelength peaks (red trace of Figure [5.2.5a](#)), and likely did not capture the true wavelength maxima. In our lab, we attempted to measure ECL spectrum of the same Au$_{25}$/TPrA coreactant system on an InGaAs camera to determine the maximum wavelength emission. However, due to the low InGaAs QE, a well-defined spectrum could not be acquired.

Correcting the measured electrons is much simpler than the photons. When applying a potential, a percentage of the current is not involved in redox reactions but rather other non-redox processes is known as the non-Faradaic current. This non-Faradaic current can easily be measured by performing the same experiment but at a potential where no redox reactions occur. More details on this calculation are reported elsewhere.[1, 9] For this study, the potential was held at 0 V for 2 s and the charge was calculated. For this scan, 99% of the current was Faradaic current which requires a non-Faradaic current correction factor (NFCCF) of 0.99. This NFCCF was likely so low because of the high concentration of TPrA in the solution. Combining the current with this NFCCF and the elementary charge constant ($q_e$) of $1.60 \times 10^{-19}$ C electron$^{-1}$ in the following equation:
Table 5.2.1: The ECL QE calculated values from the test in Figure 5.2.2 and 2 other identical tests.

<table>
<thead>
<tr>
<th>Constant Potential Voltage (V)</th>
<th>NFCCF</th>
<th>Total Photons ($\times 10^{12}$)</th>
<th>Total Electrons ($\times 10^{12}$)</th>
<th>Au$<em>{25}^{0}$ / TPrA $\Phi</em>{AQE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>0.99</td>
<td>0.0362</td>
<td>559</td>
<td>0.0066</td>
</tr>
<tr>
<td>0.85</td>
<td>0.99</td>
<td>0.0370</td>
<td>669</td>
<td>0.0055</td>
</tr>
<tr>
<td>0.85</td>
<td>0.99</td>
<td>0.0368</td>
<td>552</td>
<td>0.0067</td>
</tr>
</tbody>
</table>

The ECL QE is calculated using the following equation:

$$
\nu_{electrons} = \frac{i \times NFCCF}{q_e}
$$

(5.2.7)

The electron flux ($\nu_{electrons}$) is generated. Taking a single data point which is the highest current from Figure 5.2.2a of 70 $\mu$A and using Eq. 5.2.7, a $\nu_{electrons}$ of $4.30 \times 10^{14}$ electrons per second is calculated.

The NFCCF remained constant for all tests as predicted. There should not be significant deviation of the non-Faradaic current between tests that use the same potentials and concentrations. However, one test did have slightly different electrons injected. This may be due to small differences in coreactant concentration between tests.

**$\Phi_{AQE}$ of the 0.1 mM Au$_{25}^{0}$/6.25 mM TPrA coreactant system**

The final $\Phi_{AQE}$ determination proceeds as described using Eq. 5.2.2. For example, summing up the red trace of Figure 5.2.5a yields $1.81 \times 10^8$ photons s$^{-1}$ sphere$^{-1}$, then multiplying by the CCD camera accumulation time of 2 s and one whole sphere yields $36.2 \times 10^9$ photons. Integrating the electron flux by time in Figure 5.2.5b yields a total of $5.52 \times 10^{14}$ electrons. Dividing the total photons by total electrons and multiplying by 100 yields a $\Phi_{AQE}$ of 0.0066 %.

Overall, the constant voltage $\Phi_{AQE}$ for the Au$_{25}^{0}$ / 6.25 mM TPrA system was found to be 0.0062 % from an average of 3 separate trials with all data summarized in Table 5.2.1.

For the first time, the $\Phi_{AQE}$ is reported using only a calibrated CCD camera and spectrophotograph setup. In addition, for the first time, the $\Phi_{AQE}$ of a Au nanocluster / TPrA coreactant system is reported. Since the $\Phi_{AQE}$ is rather new, there are very few compounds available for $\Phi_{AQE}$ TPrA coreactant comparisons. There are currently Ru(bpy)$_3^{2+}$ / TPrA coreactant systems tested and Ir(ppy)$_3$ / benzoyl peroxide (BPO) systems tested, but these experiments employed compounds with much different concentrations, and a direct comparison is therefore difficult. [9, 43]
Figure 5.2.6: A 1 mM Ru(bpy)$_3$(PF$_6$)$_2$ and a 0.1 M TBAPF$_6$ solution in acetonitrile pulsed at 10 Hz between -1.6 and 1.0 V vs. Pt wire. The total summed photon flux is calculated from the equations described earlier and are plotted on the left y axis. The electron flux is plotted on the right y axis.

Φ$_{AQE}$ verification with 1 mM Ru(bpy)$_3^{2+}$ in pulsing mode. To verify the accuracy and precision of this new strategy to determine Φ$_{AQE}$ by means of a CCD the conventional standard ECL emitter, Ru(bpy)$_3^{2+}$ that has a known Φ$_{AQE}$ value tested in the annihilation pathway was determined to produce Figure 5.2.7[2] This test is a pulsing experiment in annihilation pathway for a 1 mM Ru(bpy)$_3$(PF$_6$)$_2$ in acetonitrile containing 0.1 TBAPF$_6$ with a pulsed potential range between -1.6 and 1.0 V at a frequency of 10 Hz. The Φ$_{AQE}$ for this 10 Hz pulsing test was determined to be 0.64 %, which was averaged between 5 separate 50 s scans. This Φ$_{AQE}$ value is very close to previous studies, but a PMT and a CCD camera were used to find Φ$_{AQE}$ values of 1.0 %. [1] These similar values again attest to the accuracy of the presented CCD Φ$_{AQE}$ technique.

Figure 5.2.7 is also significant because commonly, researchers test ECL using a photodetector such as a PMT and then perform the exact same scans over a CCD camera and spectrograph setup. Separating testing of Φ$_{AQE}$ and wavelength creates a temporal and instrumental disconnect between intensity and emissions where emissive or spectral instabilities in some luminophores will provide inconsistent Φ$_{AQE}$ results. Collecting both intensity and wavelength data simultaneously directly connects Φ$_{AQE}$ values to wavelength data, eliminating this problem. Furthermore, the emissive stability luminophores can be assessed, where Figure 5.2.7 displays that the Ru(bpy)$_3^{2+}$ annihilation maximum emission of about $3 \times 10^9$ gradually in-
Figure 5.2.7: Spooling ECL spectroscopy of Ru(bpy)$_3$(PF$_6$)$_2$. A solution of 1 mM Ru(bpy)$_3$(PF$_6$)$_2$ and 0.1 M TBAPF$_6$ in acetonitrile pulsed between -1.6 and 1.0 V vs. Pt wire to produce this spooling spectrum which was collected by a spectrometer coupled to a CCD camera. Accumulations were done with 1 s accumulations where 50 accumulations were taken in total. Calculations converting CCD counts to photon flux were done by using Eq. 5.2.6.

The above demonstrates a very high stability of Ru(bpy)$_3^{2+}$ ECL in the annihilation pathway upon potential pulsing.

Φ$_{AQE}$ of 0.1 mM Ru(bpy)$_3^{2+}$ with various TPrA concentrations and discussion on Φ$_{AQE}$ of other Au clusters. One final benefit of the Φ$_{AQE}$ over the relative Φ$_{ECL}$ technique is illustrated in Table 5.2.2 in which the Φ$_{AQE}$ of 0.1 mM Ru(bpy)$_3^{2+}$ in 1:1 acetonitrile:benzene was measured in three replicates using various TPrA coreactant concentrations in a constant potential mode at +1.50 V. Interestingly, the electrochemical current proportionally increased with augmented TPrA concentration as expected but the ECL intensity drastically decreases. This is likely because the excited state Ru(bpy)$_3^{2+*}$ can react with excess TPrA, resulting in quenching of the ECL emission. While increasing the TPrA concentration from 6.25 mM to 200 mM, the Φ$_{AQE}$ of Ru(bpy)$_3^{2+}$ decreased almost 500 times from 3.2 × 10$^{-3}$ % to 6.5 × 10$^{-6}$ %. Ru(bpy)$_3^{2+}$ Φ$_{AQE}$ value therefore drastically changing with the TPrA concentration. These dynamic Φ$_{ECL}$ values are illustrated in our past papers. In our group’s Chem. Eur. J. paper that analyzed Au$_{18}$ the Φ$_{ECL}$ increased 45 times from 5.5 % at 6.25 mM TPrA to 249 % at 200 mM TPrA. [18]
<table>
<thead>
<tr>
<th>TPrA Concentration (mM)</th>
<th>Total Photons ($\times 10^9$)</th>
<th>Total Electrons ($\times 10^{15}$)</th>
<th>Ru(bpy)$<em>3^{2+}$ / TPrA $\Phi</em>{AQE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.25</td>
<td>5.2 ± 0.07</td>
<td>1.5 ± 0.04</td>
<td>3.4 ± 0.1 × 10^{-3}</td>
</tr>
<tr>
<td>12.5</td>
<td>4.5 ± 0.07</td>
<td>2.7 ± 0.3</td>
<td>1.5 ± 0.01 × 10^{-3}</td>
</tr>
<tr>
<td>25</td>
<td>1.6 ± 0.04</td>
<td>5.4 ± 0.06</td>
<td>3.0 ± 0.01 × 10^{-4}</td>
</tr>
<tr>
<td>50</td>
<td>0.42 ± 0.02</td>
<td>11 ± 0.2</td>
<td>4.0 ± 0.2 × 10^{-5}</td>
</tr>
<tr>
<td>100</td>
<td>0.16 ± 0.005</td>
<td>17 ± 0.009</td>
<td>9.1 ± 0.3 × 10^{-5}</td>
</tr>
<tr>
<td>200</td>
<td>0.14 ± 0.006</td>
<td>22 ± 0.001</td>
<td>6.4 ± 0.3 × 10^{-6}</td>
</tr>
</tbody>
</table>

Table 5.2.2: A 0.1 mM Ru(bpy)$_3$(PF$_6$)$_2$ and a 0.1 M TBAPF$_6$ solution in 1:1 benzene:acetonitrile pulsed at 10 Hz between 0.0 and 1.0 V vs. Pt wire. These experiments were performed by Ziying Zhan and Dr. Xiaoli Qin from Dr. Ding’s research group and their contribution is appreciated.

Also, in our group’s paper that analyzed Au$_{38}$, the $\Phi_{ECL}$ increased 65 times from 13 % at 6.25 mM TPrA to 836 % at 200 mM TPrA.[17] Finally, in our report on Au$_{31}$(SR)$_{15}$ the $\Phi_{ECL}$ increased 230 times from 1,010 % at 6.25 mM TPrA to 230,811 % at 100 mM TPrA.[15]

For each of these discussed Au nanocluster $\Phi_{ECL}$ paper, our research group reported a modest $\Phi_{ECL}$ value for each cluster typically around 50 mM TPrA because of the difficulty interpreting the large $\Phi_{ECL}$ values at high TPrA concentrations. However, these $\Phi_{ECL}$ values can be better understood if the newly presented $\Phi_{AQE}$ physical strategy is used. In all cases, it appears the Au nanocluster $\Phi_{AQE}$ values remain constant whereas the Ru(bpy)$_3^{2+}$ $\Phi_{AQE}$ steadily decreases as the TPrA concentration is increased. This reactivity difference is likely due to the higher energy of the Ru(bpy)$_3^{2+}$ excited states with emissions of 660 nm instead of 900 nm from Au nanoclusters. This higher energy excited state may be more reactive, forming non-emissive excimers or exciplexes, which will relatively decrease the $\Phi_{AQE}$ values.

The ECL process can be complicated by factors influencing the ECL intensity such as the diffusion of electroactive molecules, the stability of radicals, the reactivity of excited states (evidenced above) and the analyte’s reactivity between itself in the annihilation pathway or coreactants in the coreactant pathway. Herein, this newly presented $\Phi_{AQE}$ technique allows deconvoluting many of these variables and parameters. Furthermore, wavelength-specific light losses due to unique hardware setups of different researchers must be accounted for because these wavelength specific light losses will modify $\Phi_{ECL}$ and $\Phi_{AQE}$ when measuring luminophore’s that have different maximum wavelengths than the commercial standard Ru(bpy)$_3^{2+}$. 
5.2.6 Conclusion

Herein, a new methodology to determine ECL \( \Phi_{AQE} \) of luminophores was presented which requires less instrumentation and less calculations relative to the ECL photon counting head (PCH) and PMT \( \Phi_{AQE} \) techniques presented by our research group previously.\[1, 9\] The \( \Phi_{AQE} \) of Au\(_{250}^0 \) was determined to be 0.0062 % and our past ECL studies of Au nanoclusters were reconsidered in the context of \( \Phi_{AQE} \) instead of relative \( \Phi_{ECL} \). This method was verified to investigate Ru(bpy)\(_3^{2+} \) in the same conditions as previous \( \Phi_{AQE} \) studies to find very similar \( \Phi_{AQE} \) values reported in those studies.\[1\] This agreement attests to the precision and accuracy of our new technique. This new ECL CCD \( \Phi_{AQE} \) technique permits analysis of the wavelength of the emission during potential scans or extended pulsing. In a pulsing study, Ru(bpy)\(_3^{2+} \)’s max emission wavelength was found to be stable over 50 s whereas the intensity tripled from its origin over this 50 s. Our physical strategy is by no means limited to Au clusters and Ru(bpy)\(_3^{2+} \), which is anticipated to be widely utilized in ECL of vast variety of luminophores.

To consider all factors affecting the ECL efficiency properly and objectively for specific luminophores, it is simpler to consider just the \( \Phi_{AQE} \) (absolute) value instead of both Ru(bpy)\(_3^{2+} \) and the luminophore in \( \Phi_{ECL} \) in a relative measurement. Our research group recommends using the \( \Phi_{AQE} \) method to understand how all discussed ECL factors can affect the ECL performance of specific luminophores. Such an analysis will then closely resemble other well-established research disciplines such as light emitting diode (LED) research, where luminosities and luminous efficiencies for luminophores and devices are paramount.

References


Chapter 6

LED External Quantum Efficiency with a CCD camera
6.1 Preface

This section extends the absolute QE method developed in Section 5.2 to the LED research field. This CCD external quantum efficiency (EQE) technique is commercially available but documentation on setup design or required calculations are not readily available to researchers to the best of our knowledge. Providing all researchers the tools needed to quickly and reliably evaluate optoelectronic devices will ensure uniformity between research results and permits more researchers to contribute to optoelectronic research.

This section will be submitted to an appropriate journal.
6.2 Abstract

This section presents an instrumental setup that can measure an optoelectronic device’s external quantum efficiency (EQE), absolute intensity and color stability using one instrument and in one scan for the first time. All calculations, calibrations and setup design are included within. This technique increases measurement accuracy and preciseness because wavelength specific data and intensity are collected simultaneously. This technique also requires less calculations because only one instrument’s wavelength specificity must be considered instead of having multiple instruments that require multiple calibrations and considerations. To demonstrate this technique, a high quantum efficiency LED is compared to an indicator LED to measure the differences in EQE, color stability and absolute intensity.

6.3 Introduction

Light emitting diodes (LEDs) were commercially produced in 1968 with no practical applications and have evolved to become universally synonymous with lighting. However, many applications have room for performance increases for specific LED types. Therefore, during research of these new LEDs their absolute emission performance is of the upmost performance. Ideally this performance measurement is quick and simple. However, in some proposed absolute measurement techniques there are two spectroscopic techniques that must operate simultaneously. One device measures the wavelength-specific data and the other measures the intensity. However, each instrument has wavelength-specific intensity losses that must be corrected for to understand the devices absolute emission. This dual-instrument measurement system requires proper timing to align data, wavelength-alignment and intensity calibrations and many post-measurement calculations. Ideally, one instrument would measure both intensity and wavelength-specific data to significantly reduce calibrations, calculations, measurement difficulty and increase research output without sacrificing research quality.

Herein, this manuscript presents a single-instrument spectroscopic method for measuring external quantum efficiencies that reduces instrument complexity and increases precision and accuracy relative to other absolute measurement methods. A brief comparison of a red indicator LED (ILED) to a red high QE LED (HQELED) is performed to demonstrate the effectiveness of the new technique.
6.4 Methods

The red XLamp® XP-E LED (Cree, Durham, NC) represents the HQELED used in this study and was used as received from the manufacturer. A TLHK46Q1R2 red LED (Vishay Semiconductors, Malvern, PA) was used as the ILED and was also used as received from the manufacturer. A Keithley 2400 source meter (Solon, OH) was connected to a computer through a GPIB-USB and controlled the power applied to the LEDs. Light was initially collected in an Acton 2300i spectrometer (Acton, MI). The spectrometer had a 50 g/mm grating blazed at 600 nm. After going through the spectrometer, the light hits an Andor iDUS 401A-BR-DD-353 charge coupled device (CCD) camera (Belfast, UK) held at -70 °C. A graphical representation of the system is seen in Figure 6.1, where an example LED with a Lambertian emission matches both the HQE and ILEDs emission angles. The wavelength of the CCD camera was calibrated using an HG-1 HG-AR calibration source (Ocean Optics, Dunedin, FL) using the 546.07 nm wavelength. A range of optical density (OD) filters (Thorlabs, Newton, NJ) between 1-4 OD factor were required to reduce the strength of the emission to a range that was measurable by the CCD camera.

An individually calibrated photodiode (S120VC, Thorlabs, Newton, NJ) coupled to an optical power meter (PM100D, Thorlabs, Newton, NJ) was used to calibrate the CCD setup along with the LEDs described earlier because of their stable constant emission.
6.5 Results and Discussion

**Raw Data**

Figure 6.2a shows data collected from the HQELED during a 1.0-2.0 V scan with a 50 mA current limit and a 0.007 V/s scan rate. A background spectrum collected using the same accumulation time of the CCD camera was subtracted from every collected spectrum in Figure 6.2. Appreciable emission started around 1.20 V or 30 s and quickly reached the set current limit of 50 mA after about 80 s or 1.83 V. A corresponding maximum intensity of 22,660 counts was achieved such that the emission, current and potential remained constant for the remaining 62 s of the scan. Figure 6.2b and 6.2c displays a 10 minute 50 mA constant current scan of the same HQELED that also reached 1.83 V and 22,660 counts. Figures 6.2a and 6.2b represent all the data needed to find the quantitative performance of this LED. Figure 6.2c displays a detailed spectrum profile of Figure 6.2b. Any qualitative variations in the emission wavelength would be clearly seen in this profile during the length of the scan.

**Converting CCD Signal to Photon Flux**

To convert the data from Figure 6.2a into the absolute data seen in Figure 6.3a and then 6.3b, some equations and calculations must be considered. The calculations will be discussed in the order they interact with the light emitted from the LED itself. All corrections will be applied to the signal of every pixel of the CCD camera \( (I/\lambda) \). However, one could sum the signal of each accumulation to produce an image like Figure 6.3b to significantly reduce the complexity of calculations.

Initially, the emitted light will head towards the entrance slit of the spectrometer. If an OD filter was used, it is likely between the LED and the entrance slit. In this study, an OD 2 and OD 4 filter were used to reduce this LEDs intensity. These OD filters were individually calibrated to provide an actual OD of 5.79 at 633 nm. This OD factor will increase the counts by 105.79...
Figure 6.3: Conversion of CCD intensity data from Figure 6.2a to photon flux. a. Full collection of all data. b. The result of summing all rows of CCD pixels from Figure 6.2b.

which increases maximum intensity in Figure 6.2a from 22,660 counts to $1.40 \times 10^{10}$ counts.

Next, the light enters the entrance slit but this is only a fraction of the total light emitted. The solid angle of the Lambertian emission ($\Omega$) must be found by the following equation:[2]

$$\Omega = 2\pi \left(1 - \cos\left(\frac{A}{d}\right)\right)$$  \hspace{1cm} (6.1)

where $A$ is the entrance slit area in m$^2$ and $d$ is the distance from the LED to the entrance slit. In this study, the $\Omega$ was $4.35 \times 10^{-4}$ steradians which is divided by our corrected counts of $1.40 \times 10^{10}$ counts to yield $3.21 \times 10^{13}$ counts per steradian.

The HQELED light passes through the slit and enters the spectrometer, hits a mirror, then a grating, then another mirror and then the CCD array seen in Figure 6.1. Each of these mirrors, the grating and the photosensitive material in the CCD camera has a wavelength-specific QE associated with it and the third is seen in Figure 6.4’s blue trace. The manufacturer-reported QE can be calibrated for wavelength-specific light loss in the entire spectroscopic setup and for the photosensitive material in the CCD camera ($Q(\lambda)$) where the result of such a calibration for the setup in this study is seen in Figure 6.4’s red trace. This calibration procedure is simple in principle where commercial,[7] and research examples exist.[1, 2] For this setup, a calibration factor of 3.91 was achieved where the manufacturer-reported CCD cameras QE ($Q(\lambda)$) (Figure 6.4’s blue trace) was divided by the 3.91 calibration factor to achieve ($Q(\lambda)$) (Figure 6.4’s red trace) which also yields a ($Q(\lambda)$) value of 0.21 photons per electron at 633 nm. Finally, the $3.21 \times 10^{13}$ counts per steradian can be corrected to $1.53 \times 10^{14}$ count photons per steradian per electron.
Figure 6.4: The manufacturer provided QE for the CCD camera used in this study (blue trace) and the same curve calibrated for all light losses encountered in the spectrometer and CCD camera’s photosensitive material (red trace).

The calibration factor of 3.91 was close to the minimum expected calibration value when considering the 633 nm wavelength of light and all potential light losses in the spectrometer. There is a percentage of light that is lost in the spectrometer as zero-order light also known as a reflection off the grating seen at 0 nm in Figure 6.2c. Light is also lost through second generation harmonics (SHG) seen at 1266 nm in Figure 6.2c. However, not every spectrometer has such a wide grating that can measure the exact amount of light intensity lost to zero-order light but in this case roughly 25% of light is lost. Each Al mirror will reduce the light intensity by 8% at 633 nm, the 50 g/mm grating has a 30% light loss at 633 nm, and the CCD camera has a 25% light loss at 633 nm (Figure S1’s blue trace). Considering known light losses, a theoretical calibration factor of 3 is expected for this setup when it is measuring a 633 nm LED light source. The higher measured calibration value of 3.91 is likely from misalignment of the spectroscopic setup, dust or debris on mirrors or gratings or the gradual decay of photosensitive materials in the CCD camera.

As the CCD array reads out the charges that are stored in each pixel, a gain factor (GF) is typically used for CCD cameras where in this study, a gain factor of 12.2 electrons per count was provided by the manufacturer. Correcting the \(1.53 \times 10^{14}\) count photons per steradian per electron for this GF produces \(1.87 \times 10^{15}\) photons per steradian. The charge-transfer efficiency between pixels of most CCD cameras is above 99.995% meaning a correction factor to account for lost charges when reading the pixel’s signal is unnecessary unless high precision is desired.

Finally, the CCD camera accumulation time (\(t\)) is used to provide the time dimension. This
study used an accumulation time of 1 \( \text{s} \) to measure the HQELED in Figure 6.2a and Figure 6.2b. This turns \( 1.87 \times 10^{15} \) photons per steradian into \( 1.87 \times 10^{15} \) photons per second per steradian and produces Figure 6.3a. Every correction factor discussed so far to generate the photon flux \( (\nu_{\text{photons}}) \) can be combined in the following equation:

\[

\nu_{\text{photons}}(\lambda) = \frac{I(\lambda) \ast GF \ast 10^{OD}}{Q(\lambda) \ast t} \ast \frac{1}{2\pi \ast \left(1 - \cos \left(\frac{A}{d}\right)\right)} \quad (6.2)

\]

where \( OD \) is the calibrated OD of the filters used in the study.

Summing the photons emitted in one second and multiplying by the amount of steradians emitted from the light source \( (2\pi) \) yields the data in Figure 6.3b’s blue trace. Many more absolute data transformations are possible from photon flux such as power, radiance, luminance and many more with calculations described elsewhere.[1, 2]

**Converting Current to Electrons Per Second**

Current is much simpler to convert than the CCD camera signal. Briefly, the current must be divided by the elementary charge of an electron \( (C) \) which is \( 1.602 \times 10^{-19} \) coulombs per electron by the following equation:

\[

\nu_{\text{electrons}} = \frac{i}{C} \quad (6.3)

\]

Many more absolute data transformations are possible from photon flux and electron flux into the device such as EQE, luminous efficiency and many more where calculations are reported thoroughly elsewhere.[1, 2]

**Comparing Indicator LEDs to High Power LEDs**

Figure 6.5 displays a constant current test with the ILED tested with the setup in Figure 6.1 at the manufacturer-reported current maximum of 50 mA. This manufacturer-reported current maximum is the same as the current limit imposed on the HQELED discussed earlier. The corresponding potential to the 50 mA current limit was on average 1.93 V which is exactly 0.10 V higher than the HQELED at the same current. A constant emission is achieved after 49 s which was \( 1.27 \times 10^{16} \) photons per second per steradian. All absolute emission data for both the HQELED and ILED are summarized in Table 6.1. The HQELED had 10 times higher EQE at 50 mA than the ILED which corresponds to a slightly lower required power and an almost 10 times increase in emission intensity.

**Converting Photon Flux to CIE Coordinates**
6.5. RESULTS AND DISCUSSION

Figure 6.5: a. The converted data obtained from a 50 mA constant current test over 5 minutes with an ILED. b. The wavelength vs. total photon flux profile of the scan in Figure 6.5a.

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<th>ILED</th>
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<td>$1.20 \times 10^{16}$</td>
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<tr>
<td>Total electrons in 1 s at 50 mA</td>
<td>$3.12 \times 10^{17}$</td>
<td>$3.12 \times 10^{17}$</td>
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<td>EQE at 50 mA (photons / electrons in %)</td>
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<td>$3.84 \pm 1.96$</td>
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<td>$1.93 \pm 0.12$</td>
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<td>Max total photon flux at 50 mA (photons / s /sr)</td>
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<td>$1.27 \times 10^{16}$</td>
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<td>Time until color stabilization (s)</td>
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<td>49</td>
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<tr>
<td>$t = 1$ s CIE coordinates (x,y)</td>
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<td>(0.684,0.315)</td>
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<tr>
<td>$t = 60$ s CIE coordinates (x,y)</td>
<td>(0.661,0.337)</td>
<td>(0.689,0.309)</td>
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Table 6.1: Device statistics of the ILED and HQELED. The first five rows are averages of 3 scans. The last three rows are from Figure 6.3a and Figure 6.5 for the HQELED and ILED respectively using equations 6.4-6.8.
Figure 6.6: The CIE (x,y) co-ordinates as time progresses for the indicator LED (blue circles) vs. the high QE LED (green circles). The inset shows the color change of the LEDs over a long scan where the times are displayed beside each color emitted. The indicator LEDs 1 s and 14-300 s emissions have (x,y) CIE coordinates of (0.684,0.315) and (0.689,0.309), respectively. The high QE LEDs 1 s and 49-300 s emissions have (x,y) CIE coordinates of (0.661,0.338) and (0.661,0.337), respectively.
Figure 6.6's green and blue circles show the corresponding International Commission on Illumination (CIE) 1931 colors in (x,y) coordinates from Figure 6.3a and Figure 6.5 using equations 6.4-6.8. The advantage of this CCD EQE technique is that after finding absolute emission data \( n \text{ photons}(\lambda) \), determining the color stability and CIE (x,y) emission colors of the LEDs is simple. The CIE (x,y) co-ordinates are found by the following equations:

\[
x = \frac{X}{X + Y + Z} \tag{6.4}
\]

\[
y = \frac{Y}{X + Y + Z} \tag{6.5}
\]

where \( X, Y \) and \( Z \) are found by the following equations:

\[
X = \int n \text{ photons}(\lambda) * \bar{x}(\lambda) * d(\lambda) \tag{6.6}
\]

\[
Y = \int n \text{ photons}(\lambda) * \bar{y}(\lambda) * d(\lambda) \tag{6.7}
\]

\[
Z = \int n \text{ photons}(\lambda) * \bar{z}(\lambda) * d(\lambda) \tag{6.8}
\]

and \( \bar{x}, \bar{y}, \) and \( \bar{z} \) are the numerical descriptions of an average human’s photopic vision.[4]

Figure 6.6 shows the calculated CIE (x,y) co-ordinates for Figure 6.5a where the emissions start at (0.684,0.315) and over 49 s eventually redshifts to (0.689,0.309) where it becomes constant for the remaining 251 s in Figure 6.5a. The color stability or constant CIE coordinates is described as a time that neither the x or y CIE co-ordinates changes more than 0.001.

The HQELED started at CIE (x,y) coordinates of (0.661,0.338) and changed to (0.661,0.337) after 14 s where it remained constant for the remaining 586 s of the scan in Figure 6.3a. This slight redshift of the emission is shown in the inset of Figure 6.6 as the green circles. The HQELED color purity remained much more stable than the ILED. Even when viewing the profile emissions of each LED in Figure 6.2c and 6.5b the HQELED clearly shifts color much less than the ILED.
6.6 Conclusion

The presented technique allows measuring absolute performance of LEDs with one instrument. This simple hardware setup uniquely permits tracking color purity during a scan with minimal additional calculations after performing the EQE calculations. This technique is simpler and faster for measuring EQE and other absolute statistics of LEDs than previously reported research techniques permitting faster research output from LED laboratories.

Red HQELEDs and red ILEDs were tested at the same constant current using this experimental setup to find 37.0 % and 3.84 % EQE respectively. The color purity was much higher over a 10 minute period where the HQELED was found to only shift from (x,y) CIE coordinates of (0.661,0.338) to (0.664,0.337) whereas the red ILED shifted (0.005,-0.006) for its (x,y) coordinates. Clearly, there are major performance enhancements with the red HQELED compared to the red ILED that are clearly discernible with this experimental setup.

6.7 Acknowledgements

We would like to acknowledge the financial supports to this research from Natural Sciences and Engineering Research Council Canada (NSERC, DG RGPIN-2018-06556 and SPG STPGP-2016-493924), Canada Foundation of Innovation/Ontario Innovation Trust (CFI/OIT, 9040) and Western University. JRA and KC are thankful to Ontario graduate scholarships. We sincerely thank our Electronic Shop in Chemistry and ChemBio store for the quality service as this research would not be possible without them.

References


Chapter 7

Conclusions and Future Work
7.1 Conclusions and Summary

Chapter 1 outlines the field of luminescent materials where low cost and high QE materials can greatly improve their applications. However, gauging luminescent materials’ suitability is not simple especially because solid state phenomena can unpredictably quench luminescence and electronic properties of molecules or materials are impossible to predict. To this end, this thesis presents research on developing synthetic pathways for efficient CQD luminescent materials, building LECs using the optimized CQDs and developing simpler analytical methods to quickly gauge a luminescent materials’ suitability for specific applications.

Chapter 2 focused on synthesizing CQDs, understanding their emissions and then optimizing their emissions for the light emitting layers of optoelectronics. In Section 2.1, a simple CQD synthesis pathway was discovered that created ACQ and AIE CQDs by varying the thiourea concentration during synthesis. This simple synthetic control over CQD solid emission phenomena allows understanding dopant-solid emission property relationships for CQDs. However, AIE and ACQ properties only describe how the excited state emits where generating the excited state electrically is equally as important for optoelectronic applications. ECL can provide this understanding. Solution ECL studies revealed the AIE CQDs performed two times better than the ACQ CQDs likely through CQD aggregations in solution. Interestingly, the ACQ CQDs performed the best in a film because it is likely that the interface that is reacting with coreactants protrudes into solution and does not suffer ACQ phenomena. The AIE CQDs had a significantly more stable cationic radical which is rare for CQDs. This radical stability could be due to the same mechanism that causes AIE, namely, cation-π interactions can stabilize cationic radicals.

Section 2.2 focused on a slightly different synthetic pathway for CQDs where the thiourea precursor in Section 2.1 was changed to urea. During this study, it was also found that there were 2 emission pathways generally separated into surface (ECL excitations) and core (PL excitations) emission states where the core emissions were significantly blue-shifted. While investigating the size-emission relationship, a clear size-ECL emission relationship was discovered where small CQDs emitted much stronger than large CQDs in oxidative coreactant ECL film emission pathways. The ECL film emission pathway is considered similar to LED emission pathways where the sample is first reduced or oxidized in a film by an electrode, then the complementary redox reaction required to create an excited state is generated from coreactants in solution. In this way, both sides of the half cell, the reduction and oxidation in films by electrodes, can be viewed. Also, cationic instability of all analyzed CQDs supported out hypothesis for cationic radical stability from Section 2.1 that cation-π interactions are required for AIE and high cationic stability.
Finally, the investigations into CQD synthetic and emission mechanisms ended with Section 2.3 where CQDs were analyzed with synchrotron X-ray PFY, XEOL and TEY analytical methods. It was thought that the sulfur incorporation was responsible for the AIE nature since in our lab’s experience and in literature, the only CQDs that emit in AIE pathways contain sulfur. Interestingly, the AIE sample emitted XEOL and the ACQ predictably did not. Furthermore, it was found that when the carbon K edge was excited it contributed significantly to the core state emissions of CQDs. Then, when the nitrogen and oxygen K edges were excited they contributed more to the surface state emissions of CQDs. In this way, XEOL performed similarly to PL studies for CQDs which has not yet been observed. While comparing PFY and TEY CQD samples to different S standards, it became clear that both CQDs contained mainly sulfur ethers and thiols in unconjugated carbon environments in both their core and surface states. Interestingly, the AIE CQDs uniquely contained thiophenes on their surface states. These thiophenes were used as AIE-luminogens in other studies where this S moiety may be responsible for the AIE emissions in CQDs. Any CQDs used as solid luminescent materials should consider focusing on making thiophene moieties in CQDs to achieve the AIE property and higher cationic radical stability.

Ultimately, Chapter 2 quantified the PL QE and ECL QE for optimized CQDs. CQD AIE phenomena was discovered, chemical moieties contributing to AIE were identified and these moieties were synthetically controlled. These contributions allowed better implementation of CQDs in PL and ECL luminescent material applications.

Chapter 3 focused on manufacturing CQD LECs and understanding their emissions processes. To emit efficiently, the device required a transparent ITO bottom electrode on a glass substrate, then a PEDOT:PSS layer used for hole transport and electron blocking, then the light emitting layer which will be discussed in more detail, a ZnO hole blocking electron transport layer and an Al top electrode. The light emitting layer consisted of a polymer, some salts and CQDs. It was observed that water was detrimental to the device function which posed a large hurdle for most of our labs aqueously synthesized CQDs. Recent research from another lab allowed changing the phase of the CQDs to generate an efficient device that had a maximum emission of 1.0 cd/m² and constant blue emission of 0.1 cd/m² that was predicted to be emitting visibly for 3 hours at 7.0 V constant potential. This device is the first published CQD LEC and also rivaled a methylammonium lead bromide perovskite NP LEC device with nearly identical device structure (ITO/PEDOT:PSS/LiTf:TMPE:Perovskite NP/Al) to achieve 2 cd/m² maximum emission at 18.0 V and a constant 0.2 cd/m² green emission at 8.0 V of constant potential. Finally, the electrical characteristics of the LEC device were studied to understand how it could be better. EIS studies revealed that small ions used in the phase transfer were likely causing premature device failure. Ideally, larger ions that are common in LEC de-
7.1. Conclusions and Summary

Vices could be used in the phase transfer process to circumvent this issue to manufacture better CQD lighting. These contributions allow for an efficient implementation of CQDs into an EL luminescent material application.

In Chapter 4, a series of organic TADF compounds were studied using ECL to gauge their suitability in an optoelectronic device. Interestingly, large ECL delays were seen during ECL annihilation pulsing. These delays were larger than any time delays seen in any other emission pathway. For example, TTA can have a large maximum emission delay of up to 1 ms. Interestingly, a new organic phenomenon described as OLECL may be responsible for these long emission times. Briefly, molecules require TADF capability and an exciplex forming nature to exhibit this phenomenon. When an exciplex forms it will stabilize the excited state or electrogenerated radical. When in an exciplex, the excited state or electrogenerated radical can alternate between triplet and singlet excited states which can significantly extend the average lifetime of an emission state. Furthermore, these molecules closely resembled other known film OLPL molecules and this emission delay was directly correlated to the molecule’s $\Delta E_{ST}$. Furthermore, known OLPL and OLECL molecules contain diphenylphosphine oxide moieties which may be the first known OLPL/OLECL-gen when it is added to certain molecules.

This OLECL phenomena will theoretically decrease the maximum ECL intensity. This discovery of OLECL allows better implementation of TADF luminescent materials in ECL applications.

Chapter 5 discusses how the quality and impact of ECL data could be increased. Currently, ECL is measured relative to a commercial standard called Ru(bpy)$_3^{2+}$ without using constant ECL conditions which causes many kinetic and instrumental setup differences. These differences make comparing ECL results between labs and even researchers in the same lab very difficult. To raise the quality of data and utility of results in ECL, I designed two techniques to collect absolute ECL results. After discussing the technique and calculations, the ECL standard Ru(bpy)$_3^{2+}$ had its absolute ECL efficiency in the annihilation pathway found to provide researchers with a standard benchmark for comparison and to verify the accuracy and preciseness of the technique. Section 5.2 focuses on simplifying this instrumental setup even further to permit researchers quick comparisons of work. The main improvement is that instead of performing the measurement on two instruments like Section 5.1, this new technique uses one instrument to measure intensity and wavelength data at the cost of some intensity loss. This single instrument also allows correlating changes in intensity with possible changes in emission states, which was an important theme in Chapter 2 while measuring CQD surface states. Also, this simplified technique lowers the instrumental setup barrier for researchers to begin performing ECL studies allowing more researchers to contribute to ECL studies.

Finally, Chapter 6 presents a way for researchers to perform absolute LED measurements
using a single instrument instead of two instruments. This greatly simplifies measurements and reduces error between measurements and laboratories. All code was supplied for researchers to perform these measurements themselves to reduce measurement setup complexities and allow more researchers to collect precise and accurate LED data. To showcase my new method, I partnered with our industry partner Rosstech Signals Inc. to take state-of-the-art HQELEDs and compare them to a common ILED to highlight the difference in device performance. From my calculations, their claims were precise where a 40% EQE was achieved in the HQELED and an approximately 4% EQE was achieved in ILEDs at the same input power. These measurements were verified by a Taiwanese company to verify this technique's accuracy and preciseness as well as the company's high QE claims.

7.2 Future Work

CQD's synthesis mechanism is still relatively unknown. For example, a synthetic question was how the carbon precursors are reduced to a 0 oxidation state. This has been somewhat explored in a process called hydrothermal carbonization (HTC) where organic wastes are turned into aromatic hydrocarbon fuels. However, to the best of my knowledge this style of study has not been applied to the field of CQDs. This study involves analyzing all species produced in a hydrothermal autoclave after synthesis and before purification occurs. If exact waste products and their relative quantities could be discovered as well as the size and composition of the created CQDs, the precursor identity and concentration can be correlated to the achieved CQDs. Ideally correlations between size of CQDs, precursor concentrations during synthesis, heteroatom doping in CQDs and specific waste products could be determined. I am particularly interested in this study for the CQDs discussed in Section 2.3 to understand how thiophene could have been created in abundance in low S synthetic conditions and not in appreciable quantities in the high S synthetic conditions. Gaining this understanding will help steer future synthetic conditions towards producing specific moieties in CQDs.

The cationic radical stability of CQDs is important in ECL studies and will serve to increase the ECL QE for CQDs. However, the way to achieve this is not clear. This thesis found that CQDs that exhibited AIE also exhibited high cationic radical stability and it was hypothesized that the high stability was due to thiophene in the surface states of the CQDs. Ideally, this theory could be confirmed, and new synthetic techniques could be developed or explored to create a higher stability cationic radical for CQDs.

In this thesis, water was identified to be harmful for LEC device operation. Unfortunately, all CQD syntheses are performed in water. Some CQD phase transfer techniques were found that transferred the CQDs from aqueous to organic phases. However, this phase transfer tech-
7.2. Future Work

technique required small ions which ultimately made it into the LEC device. To the best of our knowledge, these small ions were never incorporated into an LEC device and there is no precedent for them functioning efficiently in an LEC. This thesis also identified that these ions were likely harmful to the LEC device operation. Future research could be performed to use ions that are commonly used in LECs in the phase transfer techniques. An example ion would be bis-(trifluoromethanesulfonyl)-azonide. Future studies into the performance of LECs with CQDs that have been phase transferred using different salts could produce higher efficiency and longer-lasting LEC devices. Furthermore, varying the identity of salts and performing EIS studies could verify the hypotheses in Chapter 3 that small anions were reacting with ZnO at the light emitting layer—ZnO interface due to excessive interface charging. Understanding and preventing this issue should increase the lifetime of devices.

Additionally, the LEC device structure seen in Figure 3.1 and the identity of the layers could be revisited to optimize device performance. For example, the ZnO was suspected to be reactive and contribute to premature device failures and could be exchanged with an equally thick layer of AlO or LiF. Summarily, all layers of the device could be reconsidered to optimize electron flow through low energy interfacial barriers while maintaining high EQEs.

The final aspect of future work could be simplifying the absolute QE procedures discussed in Chapters 5 and 6. Calibrating experimental setups is still the most complicated aspect of absolute QE determination. A simple calibration technique can be established for all experimental setups and researchers. For example, a standard lamp measured with a simple spectrometer can be used to simplify calibrations because intensity correlations can be made between the expected result on the supplied simple spectrometer and the experimenter’s measurement setup. This simple technique removes the burden from researchers to accurately calibrate their setup and automates the process to ensure high quality and precise absolute QE results.
Appendix A

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Film Electrochemiluminescence Controlled by Interfacial Reactions Along with Aggregation, Matrix-Coordination, and Crystallization-Induced Emissions

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Appendix D

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Closely Following Equivalent Circuit Changes during Operation of Graphene Dot Light-Emitting Electrochemical Cells

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Appendix H

Curriculum Vitae
EDUCATION

University of Western Ontario, London, Ontario
PhD. in Physical/Analytical Chemistry  
2017-Present
Thirteen publications with six first author papers

University of Western Ontario, London, Ontario
Specialization in Chemistry (BSc)  
2013-2017
Thesis: Analyzing Proton Conductivity of IL-Soaked Nafion in Fuel Cells Using SECM

Grey Highlands Secondary School, Fleshterton, Ontario
High School Diploma  
2009-2013
Awarded Jack S. Banks Award for outstanding academic and sports achievement

AWARDS

3x Ontario Graduate Scholarship (OGS)  
2018-Present
Western Graduate Research Scholarship (WGRS)  
2017-Present
Dean's Honours List  
2013/14, 2016/17
Western Award of Excellence  
Sept. – Apr. 2013

Publications (* indicates co-first authorship)


EXECUTIVE COMMITTEES
Western University, London, Ontario
Pres. of Western Uni. Student Chapter of the Electrochemical Society 2018-2021
Organizing symposiums every December and summer socials every July
Creating posters and marketing material to encourage participation from different departments
Engaging local electrochemical businesses to deliver talks at symposiums (NWMO, Surface Science Western previously)

Western University, London, Ontario

Student Representative for the Seminar Committee 2019-Present
Organizing scientists and researchers from North America that interest Western University students from chemistry and engineering departments to give talks and spend the day with students.

TEACHING EXPERIENCE
University of Western Ontario
Third Year Analytical Chemistry Teaching Assistant 2018-2021
Taught students how to use a GC-MS instrument to do analytical separations and to improve their scientific writing styles through formal lab write-ups. Also developed computer simulations for virtual classes that modelled GC spectra in Matlab.

University of Western Ontario
First Year Chemistry Teaching Assistant 2017-2018, 2021
Taught students basic analytical/organic chemistry laboratory skills and basic scientific reporting techniques

Tutor for High School Chemistry 2015-2018
Covered syllabus and enriched multiple students in advanced science/chemistry topics

PRESENTATIONS (*indicates presenter)
Structural Origin of Carbon Quantum Dot Luminescence by Synchrotron X-Ray Spectroscopy
IUPAC CCCE 2021 Aug. 2021
Adsetts, J.R.*; Hoesterey, S.; Love, D. A.; Ding, Z.

Next Generation of High-Density Energy Materials
Western University Departmental Seminar Mar. 2020
Adsetts, J.R.*; Ding, Z.

Optimizing Light Emission For Biocompatible Nanomaterials Using Synchrotron Techniques
CANBIC-7 2019 (Parry Sound) May 2019
Adsetts, J.R.*; Chu, K.; Zhang, R.; He, S.; Yang, L.; Ding, Z.

Using Film Electrochemiluminescence to Assess Carbon Quantum Dots for Light-Emitting Electrochemical Cells
SOUSCC (2019) at University of Toronto Scarborough Apr. 2019
Hoesterey, S.*; Adsetts, J.R.; Zhang, R.; Ding, Z.
Luminescent graphene quantum dots for novel light emitting electrochemical cells

**Western University Student Chapter of the Electrochemical Society**

He, S.*, Yang, L.; Adsetts, J.R.; Zhang, R.; Yang, L.; Ding, Z.

Dec. 2018

Electrochemiluminescence of Graphene Carbon Quantum Dots

**101st Canadian Chemistry Conference and Exhibition (Edmonton)**

Adsetts, J.R.*; Zhang, R.; He, S.; Turnbull, M.; Yang, L.; Ly, M.; Ding, Z.

May. 2018

Quasi-Full Device Light Emitting Cells

**Western University Student Chapter of the Electrochemical Society**

Adsetts, J.R.*; Zhang, R.; He, S.; Yang, L.; Ding, Z.

Dec. 2017

Electrochemiluminescence of Nitrogen- and Sulfur-doped Graphene Quantum Dots

**Western University Student Chapter of the Electrochemical Society**

Zhang, R.*; Adsetts, J.R.; He, S.; Yang, L.; Ding, Z.

Dec. 2017

Electrochemiluminescence (ECL) Properties of Carbonaceous Quantum Dots (CQDs) Derived from Renewable Sources

**Western University Student Chapter of the Electrochemical Society**

He, S.*; Yang, L.; Adsetts, J.R.; Zhang, R.; Yang, L.; Ding, Z.

Dec. 2017

Investigating Proton Conductivity of Ionic Liquid Saturated Fuel Cells Using Scanning Electrochemical Microscopy (SECM)

**SOUSCC (2017) at York University**

Adsetts, J.R.*; Filice, F.; Henderson, J.; Ding, Z.

Mar. 2017

A Nafion thickness dependence of H₂O₂ yield during O₂ reduction at Nafion/Pt microelectrode studied by scanning electrochemical microscopy

**4472A Analytical Chemistry Presentation**

Adsetts, J.R.*


A Rapid Method For The Identification of Nitrocellulose in High Explosives and Smokeless Powders Using GC-EI-MS

**3372G Analytical Chemistry Poster Day**

Adsetts, J.R.*; Yunyaeva, O.*

Mar. 2016

Synthesis of Ferrocene and (Mesitylene)Molybdenum Tricarbonyl

**3371F Inorganic Chemistry Presentation**

Adsetts, J.R.*

Nov. 2015

**PREVIOUS EXPERIENCE**

National Research Council – Construction Research Council

**Engineering Student**

- Evaluating Canada’s bridge infrastructure program and developing an engineering review paper as a resource for Canada’s bridge owners
- Developing a research project outline aimed at creating new
University of Western Ontario

**Undergraduate/Graduate Researcher for Professor Ding’s Group**  
Sept. 2016 - Present

- Conducted novel experiments to find physical properties of fuel cells and reported results at conferences, group meetings and in a theses paper.

Canadian Light Source

**Intern**  
July – Aug. 2019

- Designed and implemented a new optics system for light collection for the x-ray excited optical luminescence (XEOL) system which acquired data at the same rate as the current system.
- Tested graphene quantum dot LED devices using the XEOL and x-ray mapping systems to understand light emitting properties of graphene quantum dots and their applications in LED technologies.

The Town of The Blue Mountains

**Environmental Initiatives Assistant**  
May – Aug. 2016

- Created ‘Bottles For BVO’, a bottle return program on municipal property where all proceeds went to a local not-for-profit charity. Wrote Memorandums of Understandings and handled insurance for any liabilities the municipality was exposed to for this operation.
- Conducted energy consumption data analysis per provincial regulations while working with different departments to facilitate future energy reporting.
- Promoted the Town’s phone app at local events and on municipal properties under the alias “Johnny Sunglasses”.
- Operated a hazardous waste return center on municipal property that sorted and shipped hazardous waste products to waste treatment facilities.