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Mahdi Hesari

Stephanie M. Barbon

Rayner B. Mendes

Viktor N. Staroverov

Zhifeng Ding

See next page for additional authors

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Authors

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Structural Tuning of Boron Difluoride Formazanate Electrochemiluminescence Mediated by Tri-*n*- propylamine

Mahdi Hesari,[¶] Stephanie M. Barbon, Rayner B. Mendes, Viktor N. Staroverov, Zhifeng Ding*
and Joe B. Gilroy*

Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research
(CAMBR), The University of Western Ontario, London, Ontario, Canada, N6A 5B7

[¶]Current address: Department of Chemistry and Chemical Biology, Cornell University, Ithaca,
New York, 14853, USA

ABSTRACT

Electrochemistry and electrogenerated chemiluminescence (ECL) of boron difluoride formazanate complexes bearing *p*-methoxyphenyl *N*-substituents were studied experimentally and computationally. It was shown that the substituents at the 3-position (R^3) of the formazanate backbone play a critical role in the electrochemistry and ECL of the complexes in the presence of tri-*n*-propylamine (TPrA). The ECL emission of **1a** (R^3 = cyano), **1b** (R^3 = phenyl), and **1c** (R^3 = *p*-C₆H₄OMe) occurred at peak wavelengths of 724 nm (1.71 eV), 704 nm (1.76 eV), and 723 nm (1.71 eV), consistent with their photoluminescence maxima. The maximum ECL quantum yields, determined relative to the [Ru(bpy)₃]²⁺/TPrA system, were 450% for **1a**, 244% for **1b**, and 94% for **1c**, respectively. The relatively large Stokes shifts of **1a–1c** were linked to the flattening of these molecules which accompanies their electronic excitation. Through the use of spooling ECL spectroscopy, it was demonstrated that the intensity and relative energies of ECL emission from boron difluoride formazanate complexes can be readily tuned *via* structure modification, variation in applied potential, and/or scan rate.

INTRODUCTION

Electrochemiluminescence or electrogenerated chemiluminescence (ECL) has been used as a versatile electrochemical tool in both analytical and physical studies of photoelectrochemical processes.¹⁻⁴ In the course of an ECL process, light-emitting excited states are produced via interactions of electrogenerated radicals. ECL processes can be driven by scanning or pulsing the applied potential in a range where the luminophore undergoes electrochemical oxidation and reduction to produce reactive radical cations and/or anions that lead to the formation of the excited states through electron transfer. Issues surrounding the short lifetime of the

electrogenerated species can be circumvented by changing the potential/scan rate or selecting an appropriate coreactant.^{2-3,5} Ideally, a coreactant is chosen to be oxidized or reduced at a potential similar to that of the luminophore, further enhancing the probability that the reactive species meet and react upon generation in the vicinity of the working electrode.

Among a wide range of compounds⁶⁻¹³ and materials¹⁴⁻¹⁹ that have shown utility as ECL emitters are boron difluoride (BF₂) formazanate complexes such as **1a–c**, which can be prepared from formazans **2**²⁰⁻²¹ using straightforward and cost-effective syntheses. This makes BF₂ formazanate complexes attractive alternatives to the more commonly studied BODIPY complexes for ECL application.^{8,22} Crucially, the spectroscopic and electrochemical properties of BF₂ formazanate complexes and related metal complexes have been shown to vary widely with their structure.²³⁻³⁸

We have previously reported that BF₂ complex **1a** (R³ = CN) is an efficient ECL emitter in the presence of tri-*n*-propylamine (TPrA).³⁹ In this work, we study the ECL properties of BF₂ formazanate complexes with two other carbon-bound substituents (**1b**: R³ = C₆H₅; **1c**: R³ = *p*-C₆H₄OMe) in the presence of TPrA. We have specifically targeted electron-rich BF₂ formazanate complexes as we assume that a decrease in oxidation potential may lead to an improved match between the oxidation potential of TPrA and the complexes employed, potentially enhancing ECL intensity. The detailed ECL studies presented are complemented by density-functional theory calculations.

EXPERIMENTAL SECTION

General Considerations

Reactions were carried out under nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Solvents used for synthetic procedures were purchased from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under inert (nitrogen) atmosphere over 4 Å molecular sieves. The synthesis and characterization of 1,5-(*p*-methoxyphenyl)-3-phenyl formazan,³⁰ 1,3,5-(*p*-methoxyphenyl)formazan,³⁴ and BF₂ formazanate complex **1b**³⁰ have been reported previously. NMR spectra were recorded on 400 MHz (¹H: 399.8 MHz, ¹¹B: 128.3 MHz, ¹⁹F: 376.1MHz) or 600 MHz (¹H: 599.5 MHz, ¹³C: 150.8 MHz) Varian INOVA spectrometers. ¹H NMR spectra were referenced to residual CHCl₃ (7.27 ppm) and ¹³C{¹H} NMR spectra were referenced to CDCl₃ (77.0 ppm). ¹¹B NMR spectra were referenced to BF₃·OEt₂ at 0 ppm, and ¹⁹F NMR spectra were referenced to CFC₃ at 0 ppm. Mass spectrometry data was recorded in positive-ion mode using a high-resolution Finnigan MAT 8200 spectrometer using electron impact ionization. UV-vis absorption spectra were recorded using a Cary 300 scan instrument. Molar extinction coefficients were determined from the slope of a plot of absorbance against concentration using four solutions with known concentrations ranging between 10 and 100 μM. FT-IR spectra were recorded on a KBr disk using a Bruker Vector 33 FT-IR spectrometer.

1,3,5-(*p*-methoxyphenyl)formazanate BF₂ complex **1c**

1,3,5-(*p*-methoxyphenyl)formazan (1.00 g, 2.60 mmol) was dissolved in dry toluene (100 mL). NEt₃ (0.79 g, 1.1 mL, 7.8 mmol) was then added slowly and the solution was stirred for 10 min. BF₃·OEt₂ (1.85 g, 1.60 mL, 13.0 mmol) was then added, and the solution was heated with

stirring at 80 °C for 18 h. The solution gradually turned from dark red to dark purple during this time. After cooling to 20 °C, deionized H₂O (10 mL) was added to quench any excess reactive boron-containing compounds. The purple toluene solution was then washed with deionized water (3 × 50 mL), dried over MgSO₄, gravity-filtered and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (CH₂Cl₂, neutral alumina) to yield **1c** as a dark purple microcrystalline solid. Yield = 0.75 g, 66%. ¹H NMR (399.8 MHz, CDCl₃) δ 8.03 (d, ³J_{HH} = 9 Hz, 2H, aryl CH), 7.85 (d, ³J_{HH} = 9 Hz, 4H, aryl CH), 7.00–6.95 (m, 6H, aryl CH), 3.87 (s, 3H, OCH₃), 3.86 (s, 6H, OCH₃) ppm. ¹³C NMR (100.5 MHz, CDCl₃): δ 160.8, 160.7, 137.9, 137.8, 127.1, 127.0, 125.2 (t, ⁴J_{CF} = 3 Hz), 114.6, 114.3, 55.9, 55.7 ppm. ¹¹B NMR (128.3 MHz, CDCl₃): δ -0.5 (t, ¹J_{BF} = 29 Hz) ppm. ¹⁹F NMR (376.1 MHz, CDCl₃) δ -146.3 (q, ¹J_{BF} = 28 Hz) ppm. FT-IR (KBr): 2997 (m), 2911 (s), 2832 (m), 1656 (s), 1594 (m), 1499 (s), 1455 (m), 1413 (m), 1238 (s), 1156 (s) cm⁻¹. UV-vis (CH₃CN): λ_{max} = 550 nm (ε = 24,300 M⁻¹ cm⁻¹). Mass Spec. (EI, +ve mode): exact mass calculated for [C₂₂H₂₁N₄O₂BF₂]⁺: 438.1675; exact mass found: 438.1662; difference: -2.8 ppm. Anal. Calcd. (%) for C₂₂H₂₁N₄O₃BF₂: C, 60.30; H, 4.83; N, 12.78. Found: C, 60.37; H, 4.82; N, 12.73. See Figures S1 and S2 for ¹H and ¹³C NMR spectra.

ECL Studies

Tetra-*n*-butylammonium hexafluorophosphate ([*n*Bu₄N][PF₆]) and CH₃CN (anhydrous) were purchased from Sigma-Aldrich. For all measurements, a three-electrode configuration including a 2 mm diameter Pt disc inlaid in a glass sheath as the working electrode and two Pt coils that served as the quasi-reference and counter electrodes. The electrochemical potential window was calibrated by taking the ferrocenium/ferrocene (Fc⁺/Fc) redox potential of 0.40 V vs. SCE as an internal standard.⁴⁰ A cylindrical electrochemical cell with a flat Pyrex window at the bottom for the detection of ECL was filled and assembled in a glove box. Cyclic voltammetry experiments

were performed using a CHI 610A electrochemical analyzer (CH Instruments, Austin, TX). The general experimental parameters for the cyclic voltammetry experiments were as follows: 0.000 V initial potential on the experimental scale, positive or negative initial scan polarity, 4 sweep segments, 0.001 V sample interval, 2 s quiet time, $1.5 \times 10^{-5} \text{ A V}^{-1}$ sensitivity.

The ECL-voltage curves were obtained using the CHI 610A potentiostat coupled with a photomultiplier tube (PMT, R928, Hamamatsu, Japan) held at -750 V with a high voltage power supply. The ECL was collected using the PMT placed under the flat Pyrex window, and was measured as a photocurrent that was transformed to a voltage signal using a picoammeter/voltage source (Keithley 6487, Cleveland, OH). The potential and current signals from the electrochemical workstation and the photocurrent signal from the picoammeter were sent simultaneously through a DAQ board (DAQ 6052E, National Instruments, Austin, TX) to a computer. The data acquisition system was controlled from a custom-made LabVIEW program (ECL_PMT610a.vi, National Instruments, Austin, TX). The photosensitivity on the picoammeter was set manually in order to avoid signal saturation. ECL spectroscopy was conducted using an Acton 2300i spectrograph (Princeton Instruments, Acton, MA) with a grating of 50 l/mm blazed at 600 nm , and an iDUS charged-coupled device (CCD) camera (Model DU401-BR-DD-352, Andor Technology Ltd., Belfast, UK). The wavelengths of the spectrograph and camera set were calibrated with known emission lines of a mercury lamp each time. The accumulated ECL spectra were recorded during two successive potential scan cycles. The spooling ECL spectra were recorded using the Andor Technology program during a potential scan cycle. The following typical parameters were used for the Andor Technology program under the kinetic parameters option tab: exposure time = 1 s , number of accumulations = 1 , and the spectrometer was centered at 700 nm using the 50 l/mm grating. Photoluminescence (PL) spectra were acquired from a 0.01

mM solution of compounds of **1b** and **1c** using the same camera and spectrograph set with a 532 nm wavelength laser (Coherent Inc., Mississauga, ON). A long-pass edge filter was placed between the sample and the spectrograph entrance to cut the excitation wavelength and harmonic peaks.

RESULTS AND DISCUSSION

Cyclic Voltammetry

The electrochemistry of BF₂ formazanate complexes **1b** and **1c** was investigated at a scan rate of 100 mV s⁻¹ in CH₃CN solutions containing 0.1 M [*n*Bu₄N][PF₆] (Figures 1, S3, and S4, Table 1). In the anodic potential region of the cyclic voltammogram (CV) obtained for **1b** (Figure 1A), the first and second peaks were assigned to two successive one-electron oxidations of BF₂ formazanate complex **1b** to its ligand-centred radical cation (formal potential $E^{\circ'}_{1b^{\bullet+}/1b} = 1.21$ V vs. SCE) and dication ($E^{\circ'}_{1b^{2+}/1b^{\bullet+}} = 1.46$ V vs. SCE) forms. The reverse scan indicates that the electrochemical oxidations were irreversible or quasi-reversible, which in turn suggests that the oxidation products (**1b**^{•+} and **1b**²⁺) are highly reactive. It is probable that the highly reactive character of **1b**^{•+} also contributes to the reduced current response for the second oxidation wave. In the cathodic region, two reversible one-electron reduction waves, corresponding to the **1b** / **1b**^{•-} redox couple at $E^{\circ'}_{1b/1b^{\bullet-}} = -0.56$ V and the **1b**^{•-} / **1b**²⁻ redox couple at $E^{\circ'}_{1b^{\bullet-}/1b^{2-}} = -1.66$ V vs. SCE, were observed.

The first oxidation wave corresponding to the conversion of **1c** to **1c**^{•+} occurs at $E^{\circ'}_{1c^{\bullet+}/1c} = 1.00$ V vs. SCE with quasi-reversible characteristics (Figure 1B). At $E^{\circ'}_{1c^{2+}/1c^{\bullet+}} = 1.30$ V vs. SCE the second oxidation from **1c**^{•+} to **1c**²⁺ takes place. Compound **1c** is easier to oxidize than compound **1b**, and the separation between the formal potentials of the two successive oxidation

reactions for **1c** ($\Delta E^{\circ'} = 300$ mV) is larger than that observed for **1b** ($\Delta E^{\circ'} = 250$ mV). The first one-electron reduction wave corresponding to the conversion of **1c** to **1c^{•-}** was observed at $E^{\circ'}_{1c/1c^{\bullet-}} = -0.67$ V vs. SCE, slightly more negative than that observed for **1b**, a result that is consistent with the presence of the electron-rich carbon-bound methoxyphenyl substituent. At more negative potentials, **1c^{•-}** undergoes a second reduction reaction at $E^{\circ'}_{1c^{\bullet-}/1c^{2-}} = -1.80$ V vs. SCE with poor reversibility in comparison to the same process for **1b**. Based on the CV data, the dianionic form of complex **1b** appears to be more stable than the analogous compound formed from **1c**. Compared to compound **1a**, compounds **1b** and **1c** are easier to oxidize and more difficult to reduce (Table 1).³⁹

Table 1. Formal potentials (V vs. SCE) obtained by cyclic voltammetry for BF₂ formazanate complexes (LBF₂) **1a–1c**. L = formazanate ligand.

	LBF ₂ ²⁺ /LBF ₂ ^{•+}	LBF ₂ ^{•+} /LBF ₂	LBF ₂ /LBF ₂ ^{•-}	LBF ₂ ^{•-} /LBF ₂ ²⁻
1a ³⁹	2.17	1.90	−0.02	−1.13
1b	1.46	1.21	−0.56	−1.66
1c	1.30	1.00	−0.67	−1.80

Figure 1. Cyclic voltammograms (left axes) and ECL-voltage curves (right axes) recorded at a scan rate of 100 mV s^{-1} for 0.1 mM solutions of **1b** and **1c** in CH_3CN containing 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$. The arrows and crosses show the direction and starting point of the potential scan. ECL was not observed in the extended potential windows examined.

ECL Studies

The ECL properties of BF_2 formazanate complexes **1b** and **1c** were examined in the presence and absence of tri-*n*-propylamine (TPrA) as a coreactant (Figures 1–3 and S5–S19). First, we probed for an ECL annihilation pathway, where, by means of potential scanning or pulsing, radical anions and cations may be electrogenerated before they react to form excited-state species. The ECL intensities were measured using a PMT during the scan in a potential range of *ca.* -2.25 to 1.75 V (right-hand-side scales in Figures 1A and 1B).¹ Because no appreciable ECL signal was observed for either compound, we concluded that the electrogenerated radical anions/cations and dianions/dications do not react efficiently and/or do not have sufficient lifetimes to allow for their conversion to light-emitting excited states.

Second, we examined the ECL of BF_2 formazanate complexes **1b** and **1c** in the presence of a reductive coreactant, $\text{TPrA}^\bullet$, which was electrogenerated from TPrA. This was accomplished

by collecting CVs, ECL-voltage curves, and spooling ECL spectra (Figure 2). For each data collection, the starting applied potential was set at a value where no electrochemical reactions occur. The spooling spectra (Panels C and D) allow for ECL to be monitored as a function of time and contain data corresponding to both the forward and reverse scans depicted in the CVs and ECL-voltage curves. As is often the case, when compound **1b** was analyzed within an expanded potential window, the ECL spooling spectra reveal two broad features (Figure 2D). The first feature corresponds to the ECL response from -0.15 V to 1.9 V vs. SCE. The second feature corresponds to the reverse scan ($1.9\text{ V} \rightarrow -0.15\text{ V}$). On the reverse scan, the concentration of the electrogenerated species implicated in the ECL process are reduced in the vicinity of the working electrode, and the ECL intensity is attenuated. Similar behavior was observed for complex **1c**.

Figure 2. Panels A and B: Cyclic voltammograms (left axes) and ECL-voltage curves (right axes) recorded at a scan rate of 20 mV s^{-1} for a 0.1 mM solution of **1b** in CH_3CN containing 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ in the presence of 20 mM TPrA over potential ranges between -0.15 and 1.4 V vs. SCE (A) and between -0.15 and 1.9 V vs. SCE (B). Panels C and D: spooling ECL spectra of the same solution in the same potential ranges, respectively, recorded at 5 s intervals.

The CVs recorded for mixtures of **1b** and TPrA consisted of two oxidation waves (Figure 2A and 2B). The first, centred at *ca.* 1.0 V vs. SCE , corresponded to both the oxidation of TPrA to TPrA^{++} and **1b** to 1b^{*+} , with the former redox couple giving rise to the majority of the current response due to its higher concentration. The second wave corresponded to the oxidation of 1b^{*+} to 1b^{2+} .

The onset ECL spooling spectrum was detected at 0.99 V ($t = 57 \text{ s}$) (Figure 2C) and agreed well with the ECL onset potential obtained in the ECL-voltage curve (Figure 2A). At this

potential, the TPrA coreactant was oxidized to its corresponding radical cation according to the equation

The resulting radical cation deprotonated quickly to form TPrA radical ($\text{TPrA}^\bullet$)⁴¹

$\text{TPrA}^\bullet$ is a highly reactive reducing agent ($E^\circ = -1.7$ eV) that reacted with electrogenerated $\mathbf{1b}^{\bullet+}$ to produce excited state $\mathbf{1b}^*$

This excited state relaxes to the ground state ($\mathbf{1b}$), emitting light at 704 nm (1.76 eV)

At higher applied potentials, larger quantities of the highly reactive radical cation form ($\mathbf{1b}^{\bullet+}$) were formed and electron transfer between $\mathbf{1b}^{\bullet+}$ and $\text{TPrA}^\bullet$ was enhanced (the dark-green spectrum in Figure 2C). The enhanced ECL emission also occurred at the same peak wavelength of 704 nm (1.76 eV) and the ECL intensity reached its first maximum at 1.3 V *vs.* SCE.

When the maximum potential was increased to 1.9 V *vs.* SCE, the dication of the BF_2 formazanate dye ($\mathbf{1b}^{2+}$) can be formed

At this potential, the radical $\mathbf{1b}^{\bullet+}$ can form via the following comproportionation reaction

This reaction is energetically favorable (see Table 4 below), as was previously observed for compound $\mathbf{1a}$.³⁹ It also increases the concentration of $\mathbf{1b}^{\bullet+}$ in addition to that produced by direct electrogeneration and leads to a greater overall ECL intensity and a second ECL maximum at 1.58 V *vs.* SCE.

The ECL data collected for complex **1c** are very similar to those described above for complex **1b**, with an ECL onset potential of 0.96 V ($t = 59$ s) and maximum ECL emission at a wavelength of 723 nm (1.71 eV, Figure 3, S11–S17). The first ECL wave maximum in the ECL-voltage curve (blue curve in Figure 3) was observed at 1.3 V ($t = 75$ s) and the second one at 1.6 V vs. SCE. We therefore conclude that ECL from **1c** is generated via a mechanism similar to that proposed for **1b**. The ECL-voltage curve and spooling patterns collected for **1c** revealed greater separation between the two ECL intensity maxima compared to those observed in the CV collected for **1b**, an observation that is consistent with the difference in oxidation peak potentials observed for **1c** (Figure 1B). The ECL evolution and devolution patterns from the ECL-voltage curves and the spooling ECL spectra for compounds **1b** and **1c** were also qualitatively similar.

Figure 3. Cyclic voltammogram (left axis, Panel A), and ECL-voltage curve (right axis, Panel A), and spooling spectra (panel B) recorded at a scan rate of 20 mV s^{-1} for a 0.1 mM solution of **1c** in CH_3CN containing 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ in the presence of 20 mM TPrA over a potential range of -0.21 to 1.89 V vs. SCE. The spooling ECL spectra were recorded at 5 s time intervals.

The scan rate dependence of the **1b**/TPrA coreactant system was initially investigated in the potential window between -0.15 and 1.4 V vs. SCE (Figure 4). The spooling ECL patterns suggest that the maximum resolution and ECL intensity for **1b** in this potential window was achieved at a scan rate of 50 mV s^{-1} . When the maximum potential was increased to 1.9 V vs. SCE (Figure 5), the comproportionation reaction discussed above (equation 7) was implicated in the ECL mechanism and the concentration of **1b**^{•+} was increased. In this potential window, an optimal scan rate of 100 mV s^{-1} revealed three clear evolution/devolution peaks and a maximum single-point ECL intensity. Similar scan-rate dependence was observed for compound **1c** (Figure S18–S19). Together, these data demonstrate that the kinetics associated with the generation of light-emitting excited states **1b**^{*} and **1c**^{*} and their corresponding ECL intensity can be controlled through variation of luminophore structure, applied potential, and scan rate.

Figure 4. Spooling ECL spectra recorded at various scan rates for a 0.1 mM solution of **1b** in CH₃CN in the presence of 20 mM TPrA and 0.1 M [*n*Bu₄N][PF₆] from −0.15 to 1.4 V vs. SCE. The spooling ECL spectra at 20 mV s^{−1} was recorded at 5 s intervals, while those at other scan rates were recorded at 1 s intervals.

Figure 5. Spooling ECL spectra recorded at various scan rates for a 0.1 mM solution of **1b** in CH₃CN in the presence of 20 mM TPrA and 0.1 M [nBu₄N][PF₆] from –0.15 to 1.9 V *vs.* SCE. The spooling spectra at 20 mV s^{–1} was recorded at 5 s intervals, while those at other scan rates were recorded with 1 s intervals.

The ECL emission efficiencies were estimated using the following formula:

$$\Phi_{\text{ECL}} = \frac{\left(\frac{\int \text{ECL } dt}{\int \text{Current } dt} \right)_x}{\left(\frac{\int \text{ECL } dt}{\int \text{Current } dt} \right)_{\text{st}}} \times 100\%$$

where Φ_{ECL} is the quantum yield (%) relative to the [Ru(bpy)₃]²⁺/TPrA coreactant system,⁴² ECL is the light emission intensity in the ECL voltage curves, current is the electrochemical current in the corresponding CVs, st is the standard {[Ru(bpy)₃]²⁺/TPrA} and x is the analyte in question.

The nature of the substituents appended to BODIPYs has been shown to affect the stability and electron-transfer kinetics associated with radical anions and cations involved in electron transfer leading to ECL.⁴³ It is therefore worth comparing ECL efficiencies of BF₂ formazanates **1a–c**. The ECL efficiencies, obtained at various scan rates through relative comparison of ECL responses from **1a–1c** and [Ru(bpy)₃]²⁺/TPrA under identical experimental conditions, are reported in Table 2. At low scan rates, the ECL efficiencies for **1b** and **1c** are larger than those observed for **1a**. At higher scan rates, the ECL behavior becomes more complex and the trend is reversed. It is possible that the non-classical scan-rate dependence observed for **1a** relates to the reduced stability of its radical cation form (**1a**^{•+}) relative to the electron-rich triaryl-substituted analogs (**1b**^{•+} and **1c**^{•+}), which benefit from enhanced delocalization due to the presence of a phenyl substituent at the 3-position of the formazanate framework. In all cases, the maximum ECL intensity exceeds that of the benchmark [Ru(bpy)₃]²⁺/TPrA coreactant system.⁴² These data also show that the ECL performance of BF₂ formazanate complexes can be readily tuned through structural modification, applied potential, and scan rate variation.

Table 2. ECL efficiencies for BF₂ formazanate complexes **1a–c** relative to [Ru(bpy)₃]²⁺/TPrA at various scan rates.

Scan Rate (mV s ⁻¹)	Relative Quantum Yield, Φ _{ECL} (%)		
	1a ³⁹	1b	1c
20	41	244	94
50	72	180	66
100	282	48	20
200	450	30	11

Comparison of Photoluminescence and ECL Spectra

Photoluminescence (PL) spectroscopy measurements for 0.01 mM solutions of compounds **1b** and **1c** were performed in CH₃CN electrolyte solution (Figure 6 and Table 3 below). The wavelengths of maximum photoluminescence (λ_{PL}) for **1b** and **1c** in CH₃CN were 689 nm (1.80 eV) and 726 nm (1.71 eV). The PL quantum yield (Φ_{PL}) of both compounds calculated by relative comparison⁴⁴ with [Ru(bpy)₃][PF₆]₂⁴⁵ were 5.0% and 4.5% for **1b** and **1c**, respectively. As has previously been observed for analogous systems,²⁴ these values are significantly lower than that determined for **1a** (Φ_{PL} = 42.5%) and other cyano-substituted BF₂ formazanates.²⁵ To facilitate comparison with the accumulated ECL spectra of compounds **1b** and **1c**, the same spectroscopic set-up with a 532 nm laser source was used to measure the PL spectra of both complexes (Figure 6). The accumulated ECL spectra of compounds **1b** and **1c** in the presence of TPrA show a peak wavelength at 704 nm (1.76 eV) and 723 nm (1.71 eV), respectively. These data are consistent with the PL data discussed above, confirming that the excited state involved in both PL and ECL processes is the same. The modest differences between the accumulated ECL and PL spectra may be due to the inner-filter effect (self-absorption) which originates from the difference in the analyte concentration in two experiments.⁴⁶

Figure 6. Photoluminescence (dashed line) and accumulated ECL (solid line) spectra. The accumulated ECL spectra were recorded for 0.1 mM solutions of **1b** and **1c** in CH₃CN containing 0.1 M [*n*Bu₄N][PF₆] and 20 mM TPrA, for 60 s. The PL spectra were recorded for 0.01 mM solutions of **1b** and **1c** in CH₃CN.

The results of UV-Vis absorption, PL, ECL, and electrochemical measurements for compounds **1a–1c** are summarized in Table 3. The relative energies of the absorption and emission maxima observed are consistent with the results of detailed studies of the effect of substituent variation in closely related BF₂ formazanates.²⁴⁻²⁵

Table 3. Lowest electronic transition energies for **1a–1c** (in eV) determined experimentally.

Compound	Absorption	Emission		Electrochemistry ^c
	UV-Vis ^a	PL ^b	ECL ^b	
1a ^e	2.27	1.76	1.71	1.71
1b	2.30	1.80	1.76	1.66
1c	2.25	1.71	1.71	1.69

^aTaken as λ_{max} (Figure S20). ^bTaken as wavelength of maximum photoluminescence/electrochemiluminescence intensity (Figure 6). ^cTaken as the difference between the onset of oxidation and reduction.⁴⁷ ^dFrom reference 39.

Computational Studies

The electronic structure and the thermodynamics of the comproportionation reactions of BF₂ formazanate complexes **1a–1c** were investigated computationally using the M06 density-functional approximation⁴⁸ and the 6-311+G* basis set as implemented in the *Gaussian* program.⁴⁹ The comproportionation reaction is, schematically,

where LBF₂ represents **1a**, **1b**, or **1c** and L represents the respective formazanate ligand. Table 4 shows that this reaction is thermodynamically favorable for all three complexes, both in gas phase and in CH₃CN solution, and supports the proposed ECL mechanism. M06/6-311+G* calculations also show that there is no significant difference between the highest occupied molecular orbitals (HOMO) of **1a**, **1b**, and **1c** or between the lowest unoccupied molecular orbitals (LUMO) of these compounds (Figure 7). This observation is consistent with previous studies^{24,29} which showed that variation of carbon-bound aryl substituents does not significantly alter excitation energies and other properties whose description involves frontier orbitals.

Table 4. Comproportionation reaction energies of **1a–1c** (in kJ mol^{−1}) in gas phase and in CH₃CN solution calculated at the M06/6-311+G* level of theory.

Compound	Gas phase		Solution ^a	
	ΔE_e	ΔG°_{298}	ΔE_e	ΔG°_{298}
1a	−330.4	−337.7	−64.3	−73.0
1b	−304.2	−309.2	−55.0	−59.0
1c	−289.9	−296.4	−47.2	−53.2

^aUsing the polarizable continuum model of implicit solvation.

Figure 7. HOMO and LUMO orbitals for BF₂ formazanate complexes **1a–1c**. Although this is not evident from the plots, the ground-state geometries of these molecules are non-planar.

Calculations of the absorption and emission energies of **1a–1c** using the time-dependent linear-response adiabatic M06/6-311+G* approximation (Table 5) were in good agreement with experiment (Table 3), consistent with an earlier assessment of M06 as the best-performing functional for valence excited states.⁵⁰

Recent computational studies by the Otten and Jacquemin groups⁵¹⁻⁵² showed that (i) BF₂ formazanate complexes in their electronic ground states have geometries of C_s symmetry with puckered formazanate rings, whereas the first electronically excited states are flattened structures of C_{2v} or nearly C_{2v} symmetry; (ii) this flattening is responsible for the relatively large Stokes shifts. Our M06/6-311+G* calculations (Table 5 and Supporting Information) show the same effects for the structures of the ground and lowest singlet excited states of **1a–1c** and therefore also implicate the geometric reorganization as a key contributor to the roughly 0.5 eV difference between the observed λ_{max} and λ_{PL} values.

Table 5. Vertical absorption and emission energies of **1a–1c** in gas phase and in CH₃CN solution calculated at the M06/6-311+G* level of theory without vibrational zero-point energy corrections. See the Supporting Information for details on the methodology.

Compound	λ_{abs} , nm	λ_{em} , nm	ΔE_{abs} , eV	ΔE_{em} , eV	Stokes shift, eV
Gas phase					
1a	504	597	2.46	2.08	0.38
1b	508	637	2.44	1.95	0.49
1c	543	713	2.28	1.74	0.54
CH ₃ CN solution, PCM with linear response					
1a	536	758	2.32	1.64	0.68
1b	525	779	2.36	1.59	0.77
1c	556	825	2.23	1.50	0.73
CH ₃ CN solution, PCM with state-specific solvation					
1a	534	646	2.32	1.92	0.40
1b	519	686	2.39	1.81	0.58
1c	617	—	2.01	—	—

CONCLUSIONS

The electrochemistry and ECL characteristics of two *p*-methoxyphenyl-substituted BF₂ formazante complexes (**1b** and **1c**) were examined in detail and compared to those previously reported for **1a**. The electrochemical properties of the complexes included well-resolved features at both oxidative and reductive potentials, corresponding to the formation of radical cations/anions and dications/dianions. Studies in the absence of a co-reactant confirmed that complexes **1a–1c** were not ECL-active on their own. When TPrA was added as a coreactant, ECL light generation occurred *via* a series of reactions implicating both the radical cation and dication forms of each BF₂ formazanate complex. The ECL mechanism was investigated by collecting cyclic voltammograms, ECL-voltage curves, and spooling ECL spectra. Based on the obtained electrochemical, optical, and computational data, we proposed an ECL mechanism involving a reaction between TPrA[•] and the radical cation form of each BF₂ formazanate complex. Examination of the PL properties of **1a–1c** revealed photoluminescence maxima that were consistent with the wavelengths of maximum ECL emission [724 nm (1.71 eV) for **1a**, 704 nm (1.76 eV) for **1b**, and 723 nm (1.71 eV) for **1c**]. Additionally, the maximum ECL efficiencies observed for **1b** and **1c** were found to be lower than those observed for **1a** at most scan rates. This trend mirrors that of the PL data collected for the same compounds and likely relates to non-radiative decay pathways associated with the presence of carbon-bound aryl substituents in **1b** and **1c**. The emission maxima observed in this study were drastically red-shifted ($\nu_{ST} > 165$ nm, 4300 cm^{-1}) relative to the respective absorption maxima for each compound, an effect which, according to density-functional calculations, is associated with the flattening of the ground-state molecular geometries of BF₂ formazanate complexes that accompanies electronic excitation. Our future work in this area will focus on exploiting the ECL properties of BF₂ formazanate

complexes via their incorporation into polymer scaffolds, potentially allowing for thin-film properties and device applications to be explored.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI: #####.

NMR spectra for **1c**, additional CV and ECL data, computational details and atomic coordinates of optimized structures.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: joe.gilroy@uwo.ca; zfding@uwo.ca. Tel: +1 (519) 661-2111 ext. 81561 (JBG)/ +1 (519) 661-2111 ext. 86161 (ZD).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval of the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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