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Authors: Francis L Buguis, Ryan R Maar, Viktor N Staroverov, and Joe B. Gilroy

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Near-Infrared Boron Difluoride Formazanate Dyes

Francis L. Buguis,^[a] Ryan R. Maar,^[a] Viktor N. Staroverov,^[a] and Joe B. Gilroy*^[a]

F. L. Buguis, Dr. R. R. Maar, Prof. Dr. V. N. Staroverov, Prof. Dr. J. B. Gilroy

Department of Chemistry and The Centre for Advanced Materials and Biomaterials Research (CAMBR) The University of Western Ontario

1151 Richmond Street North, London, Ontario N6A 5B7 (Canada)

E-mail: joe.gilroy@uwo.ca

[a]

Abstract: Near-infrared (NIR) dyes are sought after for their utility in light harvesting, bioimaging, and light-mediated therapies. Since long-wavelength photoluminescence typically involves extensive π -conjugated systems of double bonds and aromatic rings, it is often assumed that NIR dyes have to be large molecules that require complex syntheses. We challenge this assumption by demonstrating that facile incorporation of tertiary amine groups into readily available 3-cyanoformazans affords efficient production of relatively simple NIR-active BF₂ formazanate dyes ($\lambda_{abs} = 691-760$ nm, $\lambda_{PL} = 834-904$ nm in toluene). Cyclic voltammetry experiments on these compounds reveal multiple reversible redox waves linked to the interplay between the tertiary amine and BF₂ formazanate moieties. Density-functional calculations indicate that the NIR electronic transitions in BF₂ formazanates are of $\pi \rightarrow \pi^*$ -type, but do not always involve strong charge transfer.

Introduction

Synthetic dyes that absorb and photoluminesce in the nearinfrared (NIR) spectral region have attracted tremendous interest due to their emerging utility in light harvesting,^[1] bioimaging,^[2] and biomedical^[3] applications. When used for light harvesting (e.g., in photovoltaic cells), NIR dyes harness those regions of the solar energy spectrum that are untapped by conventional dyes, thereby increasing the efficiency of energy conversion.^[4] In the bioimaging arena, dyes that photoluminesce in the NIR-I (700-950 nm) and NIR-II (1000-1700 nm) regions enable deeper tissue penetration, improve signal-to-noise ratios, and enhance imaging capabilities.^[5] State-of-the-art imaging techniques that rely on NIR dyes include fluorescence microscopy,^[6] two-photon excitation microscopy,^[7] photoacoustic imaging, and tomography.^[8] The deep-tissue penetration offered by NIR dyes is also well-suited for light-mediated therapies, [5a, 9] where controlled and localized doses of thermal energy are used for tumor treatment.[3d, 10]

The utility of NIR dyes in many active research areas provides motivation for designing readily accessible, high-performance molecular architectures. Several strategies for the production of NIR dyes have been proposed so far: i) extension of π -electron conjugation;^{[11],[12]} ii) tuning of electron donor-acceptor interactions to induce charge transfer;^[6b, 13] and iii) modulation of properties via controlled aggregation.^[14] The first approach, while seemingly fail-safe, involves complex molecules with extended syntheses.^[11, 12e] Due to the inherent

rigidity of large π -electron systems, this strategy often results in dyes with small Stokes shifts and poor solubility, as in the case of cyanines (*e.g.*, **I**), the most common candidates for bioimaging applications.^[15] The second strategy aims to promote twisted intramolecular charge transfer to enhance NIR photoluminescence.^[13a, 14e, 16] Dyes of this type, exemplified by compound **II**, have found utility in biomedical applications.^[6b, 13b] Molecular integration involving noncovalent interactions (as in **III**) is another effective strategy for the realization of NIR-I and NIR-II photoluminescence.^[13b, 16-17]

The purpose of this work is to call attention to a novel strategy of creating NIR dyes. This strategy involves formazans 1, redox-active nitrogen-rich analogs of β -diketimines, which have already gained prominence in the area of functional molecular materials.^[18] BF₂ complexes 2 derived from formazans 1 are readily accessible, easily tunable dyes^[18-19] that show promise as cell-imaging agents,^[20] electrochemiluminescent light-emitters,^[21] and electron acceptors in photovoltaic cells.^[22]





Recently, we discovered that a BF_2 formazanate 2 with $Ar^1 =$ Ar⁵ = $p-C_6H_4NMe_2$ and R^3 = CN exhibits both NIR photoluminescence 888 (λ_{PL}) = nm) and electrochemiluminescence (λ_{ECL} = 910 nm) despite its relatively simple structure (MW = 383.21 g mol⁻¹) and small π -electron system.^[21c] Given that these properties are extraordinary for such a small molecule, we and others have wondered about their chemical underpinnings. To address this question, we have devised a novel synthetic route leading to amine-substituted BF2 formazanates 2, which enabled us to perform a detailed experimental and theoretical investigation of the optoelectronic properties of these compounds. We will show here that the observed NIR photoluminescence of these complexes arises from the interplay between the formazanate core and tertiary amine substituents.

Results and Discussion

A new synthetic pathway was developed for the production of amine-substituted formazans 1 in appreciable yields. Addition of the appropriate aryl diazonium tetrafluoroborate salt(s) (Scheme S1) to THF solutions containing CH₃CN and nBuLi at -78 °C produced 3-cyanoformazans 1a-1c in yields ranging from 23 to 66% (Scheme 1, Figures S1-S4). The relatively low yield of 1b (23%) is due to the use of a 50:50 mixture of two aryldiazonium salts (implying a 50% maximum theoretical yield). For comparison, the previously reported synthesis of compound 1a under conditions typical for the production of 3-cyanoformazans had a yield of just 11%, [21c] while 1b and 1c could not be produced at all under similar conditions. Formazan 3 was prepared by adapting an existing procedure (Figure S5 and S6).^[23]

BF2 formazanate complexes 2a-2c and 4 were obtained in yields ranging from 52 to 86% by stirring the corresponding 3cyanoformazans in toluene solutions containing excess NEt₃ and BF₃•OEt₂ (Scheme 1, Figures S7–S12). This transformation was accompanied by a distinctive loss of the diagnostic NH signal in

the ¹H NMR spectra between 12.01 and 12.70 ppm (depending on the formazan), as well as the appearance of a quartet in the ¹⁹F NMR spectra (δ : –132.3 to –137.4) and triplet in the ¹¹B NMR spectra (δ : -0.4 to -0.8). A Stille reaction was used to produce BF2 formazanate 2d in a 65% yield (Scheme 1, Figures S13 and S14). This particular compound was prepared in an effort to electronically isolate the NPh₂ units from the BF₂ formazanate framework and promote charge transfer.

Analysis of the bond lengths in the X-ray structures of 2a^[21c] and 2c (Figure 1 and Table 1) suggests a significant quinoidal character at the N-aryl-substituents: the N6-C6 [1.3689(17) Å] and N7-C12 [1.3656(17) Å] bonds in 2a and N6-C6 [1.3739(12) Å] and N7-C12 [1.4027(11) Å] bonds in 2c are shorter than a typical $N_{(sp^3)}$ - $C_{(Ar)}$ bond [~1.425 Å]^[24] and the N-C bond [1.418(4) Å] in triphenylamine.[25] This observation is consistent with the planar nature of the amine nitrogen atoms and the fact that the sums of the bond angles around nitrogen are 359.7(1)° for 2a and 360.03(8)° for 2c. The boron atoms are four-coordinate in each structure, adopting slightly distorted tetrahedral geometries, and are displaced from the planes defined by the N-aryl substituent and the four nitrogen atoms in the formazanate backbone (N1, N2, N3, and N4), with average dihedral angles of 18.63° and 15.61° for 2a and 2c, respectively. The NNCNN backbone of the formazanate complex is delocalized with the N-C [1.3315(16)-1.3356(17) Å] and N-N [1.3134(14) - 1.3143(14)]for and Å] 2a N-C [1.3371(11)-1.3384(11) Å] and N-N [1.3061(11)-1.3108(11) Å] for 2c bond lengths intermediate of single and double bonds for the respective atoms involved (Table 1),^[24] suggesting an efficient electronic delocalization.

When probed by cyclic voltammetry, amine-substituted BF₂ formazanates 2a-2d display multiple reversible redox events. Each of compounds 2a-2d exhibits two one-electron reduction waves (Figure 2 and Table 2) typical of BF₂ formazanates^[19b] at half-wave potentials $E_{red1} = -0.67$ to -1.03 V and $E_{red2} = -1.65$ V to -1.99 V relative to the ferrocene/ferrocenium redox couple in CH₂Cl₂. The observed trend in the reduction potentials of 2a-2d correlates well with the electron-donating ability of the R¹ and R⁵ substituents ($NMe_2 > NPh_2 > C_6H_4NPh_2$). In most cases the values are significantly more negative than the reduction potentials found for the analogous BF2 formazanate with simple phenyl substituents (R¹ = R⁵ = H; E_{red1} = -0.53 V and E_{red2} = -1.68 V).^[19b]



Scheme 1. Synthesis of amine-substituted BF2 formazanates 2a-2d.

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Figure 1. Solid-state structure of BF_2 formazanate 2c. Thermal displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths, bond angles, and additional structural metrics for BF_2 formazanates $2a^{[21c]}$ and 2c. Additional structural refinement data for 2c are reported in Table S1.

Metric		2a ^[21c]	2c
Bond lengths (Å)	N1-N2	1.3134(14)	1.3061(11)
	N3-N4	1.3143(14)	1.3108(11)
	N2-C1	1.3315(16)	1.3384(11)
	N4-C1	1.3356(17)	1.3371(11)
	N1-C3	1.4143(16)	1.4107(11)
	N4-C9	1.4140(16)	1.4214(11)
	N6-C6	1.3689(17)	1.3739(12)
	N7-C12	1.3656(17)	1.4027(11)
	N1-B1	1.5670(17)	1.5754(12)
	N4-B1	1.5703(17)	1.5628(12)
Bond angles (°)	N2-N1-B1	124.35(10)	124.48(7)
6 ()	N3-N4-B1	123.83(10)	123.87(7)
	N2-C1-N3	130.32(11)	130.03(8)
	N1-B1-N4	106.71(10)	106.83(7)
Boron displacement (Å) ^[a]		0.136	0.116
Twist angle α_1 (°) ^[b]		18.51	15.57
Twist angle α_2 (°) ^[b]		18.74	15.65

^[a]Distance between the B atom and the plane defined by the NNCNN backbone. ^[b]Angles between the planes defined by the *N*-aryl substituents and the NNCNN backbone.

BF2 formazanates 2a-2d also exhibit reversible oxidation events (Figure 2). Similar oxidation events are not typically observed within the stability window of common electrochemistry solvents for other BF2 formazanates. In compounds 2a-2c, oxidation occurs in two one-electron steps ($E_{ox1} = 0.25$ to 0.47 V and E_{ox2} = 0.66 V to 0.79 V) and follows the same trend as the reduction waves (Figure 2). We attribute these features to the stepwise oxidation of the amine substituents to radical cations, by drawing an analogy with other electron-rich amines.^[26] The stepwise oxidation is indicative of the electronic communication between the terminal NR₂ groups through a molecule-wide π conjugated system. In 2d, however, only one oxidation wave corresponding to two electrons was observed at $E_{ox1} = 0.54$ V, indicating that the NPh₂ groups are electronically isolated from each other and provide a platform for significant charge transfer. This oxidation process likely results in the production of a diradical dication (Scheme 2). Our attempts to chemically oxidize dyes 2a-2d have not yielded clean reaction products, perhaps due to competing decomposition pathways associated with amine-derived radical cations.^[27] Nonetheless, amine substituents at the N-aryl rings create an electronic environment that is qualitatively different from that of BF2 formazanates and related compounds.

Given the relatively simple molecular structures of BF_2 formazanates **2a-2d**, their low-energy absorption and photoluminescence bands are unexpected. In general, BF_2 formazanates absorb and emit in the red region of the



Figure 2. Cyclic voltammograms recorded for dry, degassed 0.05 mM solutions of BF₂ formazanates **2a–2d** in CH₂Cl₂ containing 0.1 M [*n*Bu₄N][PF₆] as supporting electrolyte at a scan rate of 100 mV s⁻¹. The arrows denote the initial scan direction.

Table 2. Cyclic voltammetry data recorded for BF_2 formazanates 2a-2d in CH_2Cl_2 reported relative to the ferrocene/ferrocenium redox couple.

	E _{red2} (V)	E _{red1} (V)	E _{ox1} (V)	E _{0x2} (V)		
$2a^{[21c]}$ (R ¹ = R ⁵ = NMe ₂)	-1.99	-1.03	0.25	0.66 ^[a]		
2b ($R^1 = NPh_2, R^5 = NMe_2$)	-1.83	-0.92	0.38	0.73		
2c $(R^1 = R^5 = NPh_2)$	-1.72	-0.83	0.47	0.79		
2d $(R^1 = R^5 = C_6H_4NPh_2)$	-1.65	-0.67	0.54			
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^{la}Irreversible peak. Potential at maximum anodic current is reported.

electromagnetic spectrum and exhibit modest photoluminescence quantum yields.[19b, 28] For example, the phenyl derivative ($R^1 = R^5 = H$) has $\lambda_{abs} = 502$ nm, $\lambda_{PL} = 586$ nm, and $\Phi_{PL} = 15\%$ in toluene.^[19b] By contrast, dyes **2a–2d** have λ_{abs} values ranging from 691 to 760 nm, λ_{PL} values from 834 to 904 nm, and quantum yields of 2-7% in toluene (Figure 3, Table 3). It is evident from these numbers that the introduction of tertiary amine groups at the N-aryl substituents dramatically alters the electronic structure of BF₂ formazanates. First, the maximum absorption wavelengths for 2a-2c increase with the size of the π -electron system as expected. The largest complex 2d, however, has the shortest λ_{abs} of the four. This suggests that the NPh₂ groups of 2d are electronically isolated from the BF₂ formazanate scaffold in the ground state. Second, dyes 2a-2c exhibit normal photoluminescence solvatochromism: their λ_{PI} values increase with solvent polarity. The opposite trend is observed for 2d, which has λ_{PL} = 904 nm in toluene and λ_{PL} = 881 nm in THF (no detectable photoluminescence in CH₃CN).

The quantum yields for NIR dyes **2a–2d** are lower than those of BF₂ formazanate dyes that photoluminesce at shorter wavelengths because non-radiative decay is enhanced by the narrowed optical bandgap according to the energy-gap law.^[29] It is noteworthy that a related BF₂ formazanate dye bearing methoxy substituents (R¹ = R⁵ = OMe; λ_{abs} = 572 nm, λ_{PL} = 656 nm, Φ_{PL} = 77%) does not exhibit NIR bands and shows limited sensitivity to solvent polarity ($\Delta\lambda_{PL}$ = 6 nm across a similar range of solvents).^[19b] To understand these unusual photophysical properties of amine-substituted BF₂ formazanates, we turned to electronic structure calculations.

Time-dependent density-functional theory (TDDFT) calculations implicate the highest occupied molecular orbital (HOMO, π type) and lowest unoccupied molecular orbital (LUMO, π^* type) as the orbital pair that makes the dominant contribution

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to the observed absorption and photoluminescence maxima for each of dyes **2a–2d**. Figures 4 and S15 show that the HOMO and LUMO of **2a–2c**, both at the ground- and excited-state geometries, span at least a dozen common atoms, whereas the HOMO and LUMO of **2d** are localized on different parts of the molecule. This strongly suggests that the HOMO \rightarrow LUMO transition in **2d** involves significant charge transfer. Another telltale sign of strong charge transfer^[30] in **2d** is that standard density functionals such as PBE0^[31] grossly underestimate the lowest absorption energy for this particular dye but not for **2a–2c** (Table S2). It is known that the charge-transfer error of standard functionals can be remedied by using tunable range-separated hybrid density functionals,^[32] e.g., LC- ω hPBE.^[33] When we optimized the solvated structures of **2a–2d** and calculated their excitation energies using the LC- ω hPBE/DGDZVP2 method with a tuned range-separation parameter ω =0.14, the maximum absorption wavelengths of **2a–2c** changed little, whereas the λ_{abs} of **2d** improved dramatically and all results were now within 6–52 nm of the experimental values (Tables 3 and S3). Photoluminescence wavelengths of **2a–2d** computed using the LC- ω hPBE functional (Table 3) are in equally good agreement with experiment (errors of 2–77 nm). The experimentally observed trends in the wavelengths of absorption maxima (**2c** > **2b** > **2a** > **2d**) and photoluminescence maxima



Figure 3. Normalized UV-vis absorption (black lines) and photoluminescence (red lines) spectra of dyes 2a-2d in 3-6 µM dry, degassed toluene solutions.

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Table 3. Experimental and calculated solution-state characterization data for BF ₂	formazanates 2a-2d.	The theoretical values were	obtained using	TDDFT at the
LC- ω hPBE($\omega = 0.14$)/DGDZVP2 SCRF=PCM level with <i>equilibrium</i> solvation.				

0.1	Experiment				т	Theory		
Solvent	λ _{abs} (nm)	ε (M ⁻¹ cm ⁻¹)	λ _{PL} (nm)	Φ _{PL} ^[a] (%)	v _{st} (nm)	v _{st} (cm ⁻¹)	λ _{abs} (nm)	λ _{PL} (nm)
$2a^{[21c]} (R^1 = R^5 = NMe_2)$								
Toluene	728	41300	834	7	106	1746	680	771
CH ₂ Cl ₂	733	41300	866	4	133	2095	732	868
THF	731	38600	855	2	124	1984	726	858
CH ₃ CN	728	43600	888	<1	160	2475	755	925
2b ($R^1 = NPh_2, R^5 = NM$	e ₂)							
Toluene	734	46000	860	4	126	1996	701	815
CH ₂ Cl ₂	741	47500	898	<1	157	2359	749	913
THF	735	46500	880	<1	145	2242	748	903
CH ₃ CN	729	47400	915	<1	186	2788	763	955
2c ($R^1 = R^5 = NPh_2$)								
Toluene	760	47000	902	2	142	2071	731	874
CH ₂ Cl ₂	760	45800	924	<1	164	2335	766	910
THF	745	45500	917	<1	172	2518	774	961
CH ₃ CN	735	45600	935	2	200	2910	783	1012
2d ($R^1 = R^5 = C_6H_4NPh_2$	2)			A				
Toluene	691	25900	904	2	213	3410	667	844
CH ₂ Cl ₂	684	24300	900	<1	216	3509	690	946
THF	665	30100	881	<1	216	3687	688	936
CH ₃ CN ^[b]	643	26100	-	A		-	695	988

^[a]Determined using integrating sphere method. ^[b]Photoluminescence was not detected in CH₃CN.

(2c ≈ 2d > 2b > 2a) are also adequately reproduced by the LCωhPBE(ω=0.14)/DGDZVP2 calculations. Excitation of BF₂ formazanate dyes results in their structural reorganization (planarization).^[21b, 28b, 34] In the case of compounds 2a-2c, our calculations show that the excited states are significantly more sensitive to solvent variation than the ground states (Table 3), which is a common manifestation of solvatochromism. The charge-transfer character of the $\pi \rightarrow \pi^*$ electronic transitions is also responsible for the larger Stokes shifts of **2d** compared to those of **2a**-**2c**.



Figure 4. Frontier molecular orbitals of compounds 2a-2d computed at the ground-state molecular geometries using the LC- ω hPBE($\omega = 0.14$)/DGDZVP2 SCRF=(PCM, Solvent=Toluene) method.

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Conclusion

We have developed a new synthetic route to tertiary aminesubstituted 3-cyanoformazans and used it to carry out a systematic investigation of the unusually low absorption and photoluminescence energies of BF₂ formazanate dyes 2a-2d. Cyclic voltammetry experiments and electronic structure calculations suggest that the NIR transitions in all of these dyes involve the HOMO-LUMO pair, but occur by different mechanisms. Detailed TDDFT and photophysical studies reveal that the electronic transitions of dyes 2a-2c ($\lambda_{abs} = 728-760$ nm and λ_{PL} = 834-902 nm in toluene) are best described as $\pi \rightarrow \pi^*$ with little to no charge transfer. The energies of these transitions exhibit greater sensitivity to solvent variation in the near-planar excited states (photoluminescence solvatochromism) than in the nonplanar ground-state structures. The electronic transitions in dye 2d (λ_{abs} = 691 nm and λ_{PL} = 904 nm in toluene) are also of $\pi \rightarrow \pi^*$ type, but have a strong charge-transfer character and exhibit even larger Stokes shifts.

In summary, this work demonstrates the exciting feasibility of NIR dyes consisting of relatively small π -electron systems and suggests that significant charge transfer is not a prerequisite for their NIR activity. These findings open new strategies for enhancing the functionality of luminescent compounds used in materials chemistry and chemical biology arenas.

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Keywords: Boron formazanates • near-infrared dyes • charge transfer • cyclic voltammetry • range-separated hybrid functionals

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RESEARCH ARTICLE

Entry for the Table of Contents



Simple and readily synthesizable BF₂ complexes of *tert*-amine-substituted 3-cyanoformazans are shown to absorb and emit light at wavelengths that are unusually long for such small molecules (λ_{abs} = 691–760 nm, λ_{PL} = 834–904 nm in toluene). Detailed investigations of several such complexes reveal that strong charge transfer is not a prerequisite for their near-infrared activity.

Institute and/or researcher Twitter usernames: @westernuchem, @gilroygroup