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Optoelectronic Tuning of Organoborylazadipyrromethenes via Effective Electronegativity at the Metalloid Center

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S *Supporting Information*

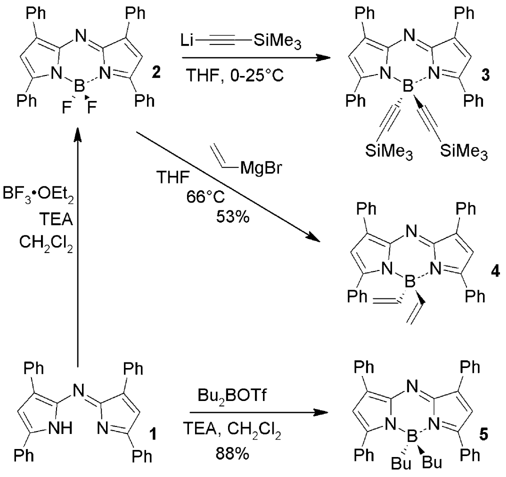
ABSTRACT: Organoborylazadipyrromethenes were synthesized from free base and fluoroborylazadipyrromethenes and characterized with regard to their structural and electronic properties. B−N bond lengths, along with photophysical and redox behavior, appear dependent on the effective electronegativity at the boron atom as tuned by its substituents, with stronger electronegativity correlating to a shorter B−N bond length, red-shifted absorbance, enhanced fluorescence lifetime and yield, and positively shifted redox potentials.

Azadipyrromethenes are a class of dipyrrinoid dyes[1] of interest for their coordination chemistry[2−4] and applications in chemosensing,[5] bioimaging,[6] photodynamic therapy,[7] chemiluminescence,[8] and solar energy.[9−11] The optoelectronic properties of azadipyrrins are sensitive to their coordination environment. Difluoroborylazadipyrrins have nanosecond-lifetime singlet excited states and strong fluorescence, but the free base azadipyrrin is almost nonemissive ($\Phi_F \ll 1\%$).[1,12] Among known metal chelates (Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, Zn^{II}, Ag^{I}, Re^{I}, Au^{I}, Hg^{II}), only certain heteroleptic monovalent coinage metal complexes are luminescent and are only weakly emissive ($\Phi_F < 1\%$).[3,4] Metal chelation shifts the first reduction potential of azadipyrrins to less positive potential compared to the free base, whereas difluoroboryl chelation shifts the reduction potential to more positive potential.[4,8]

The utility of azadipyrrins as electron-accepting sensitizers in excitonic solar cells would be enhanced by a coordination environment that could provide both a stable singlet excited state and an elevated first reduction potential.[11,13] For that purpose, we prepared and characterized a series of organoboron-chelated azadipyrrins. We have found trends in singlet emission intensity, fluorescence lifetime, and redox potentials that correlate to the effective electronegativity at the boron atom: Stronger electronegativity in boryl chelation leads to Lewis acidic modulation of the redox behavior to more positive potentials and stabilizes the excited state. The more electron-poor character of azadipyrrins relative to *meso*-carbon dipyrrins may be the cause of this sensitivity.

The syntheses of azadipyrrin **1** and difluoroboryl chelate **2** followed conditions reported by O'Shea et al.[14] **2** served as starting material in preparing divinylboryl **3** and dialkynylboryl **4** by nucleophilic displacement of fluorine with organometallic reagents.[15] Dibutylboryl **5** was formed by treating **1** with dibutylborontriflate/triethylamine in CH_2Cl_2 (Scheme 1).[16]

Scheme 1. Synthesis of Organoborylazadipyrrins



The dialkynyl- and divinylborylazadipyrrins **3** and **4** gave single crystals suitable for X-ray diffraction, and their structures are shown in Figure 1. The unit cell for **4** includes two azadipyrrin molecules that differ slightly in the dihedral angles of the phenyl substituents (see the Supporting Information, SI). The *meso*-nitrogen (N2) induces shortened bond lengths (N2−C4 and N2−C8) compared to the corresponding C−C bonds of *meso*-carbon dipyrromethenes (BODIPYs),[15] causing a slight puckering of the azaboraindacene core (C1−C8, N1, and B1) and an out-of-plane distortion at the N−B bonds that is consistent with the known crystal structure of **2**,[17] whereas the free base azadipyrrin core is planar.[4] The puckering results in axial/equatorial positioning of the boron substituents; however, the ^{1}H NMR resonances for the silyl and vinyl groups of **3** and **4** (respectively) indicate equivalence for each pair of substituents, implying rapid ring flipping at the N−B−N end of the center ring (see the SI). The butyl groups of **5** are also equivalent in the ^{1}H NMR and exhibit ring-current shielding by the nearby phenyl rings. N−B bond lengths increase in the series **2** < **3** < **4** (1.55/1.56, 1.56/1.57, and 1.58/1.60 Å, respectively).

UV−vis absorbance and fluorescence spectra of **1**−**5** are shown in Figure 2. When fluorine is replaced by alkyne substituents, the absorption maximum blue-shifts from 655 to 649 nm. Further blue shifting to as far as 592 nm occurs as hybridization of the carbon substituents at boron changes (sp →

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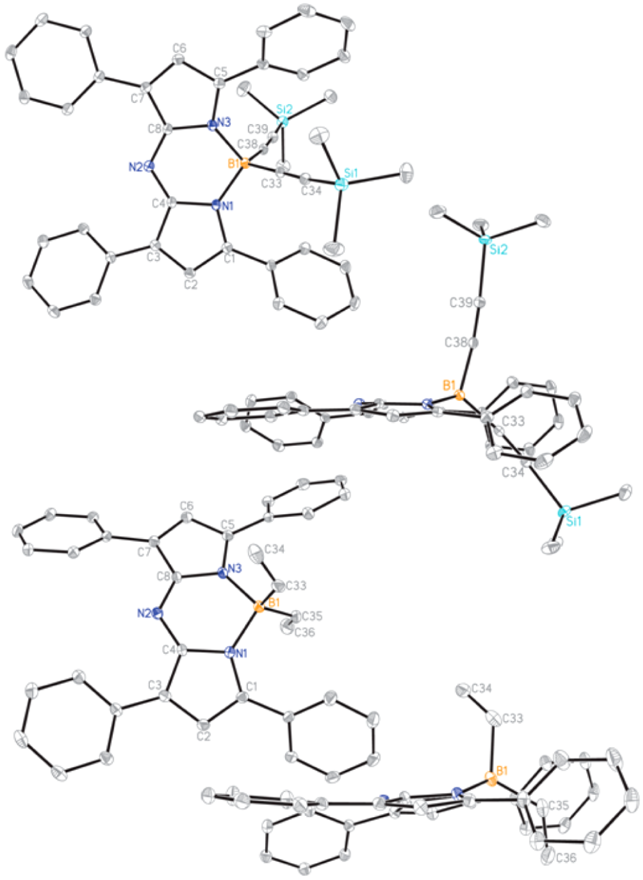

Figure 1. Crystal structures of **3** (upper half) and **4** (lower half).[18] Hydrogen atoms are removed for visual clarity.

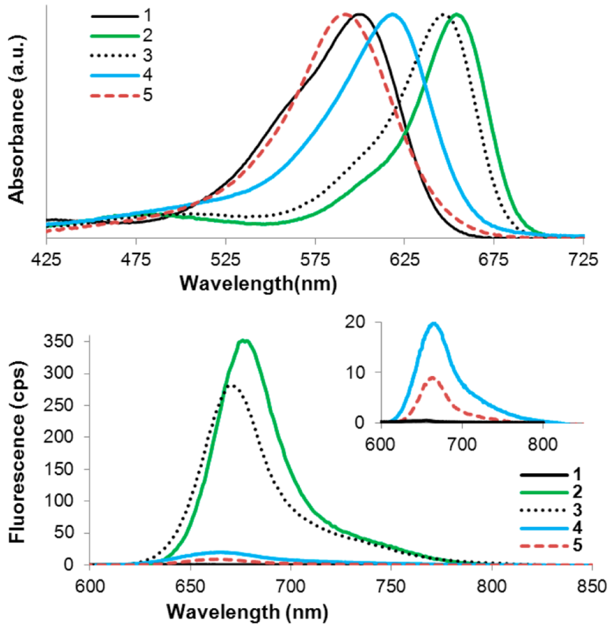

Figure 2. Absorption (upper) and fluorescence spectra (lower) of **1**−**5** in toluene at room temperature.

$sp^2 \rightarrow sp^3$). Fluorescence maxima blue-shift in the same trend but with smaller increments, resulting in increasing Stokes shifts. The fluorescence intensity decreases as λ_{max} blue-shifts, and only **2** and **3** exhibited fluorescence lifetimes in the nanosecond regime (Table 1). It seems that there is a minimum boryl electronegativity that is required to stabilize the azaboraindacene core. The decline in the fluorescence quantum yield from **2** to **3** is different from the trend for *meso*-carbon dialkynyldipyrrins, for which fluorescence quantum yields actually increase slightly.[15,19] Additionally, Kee et al. reported that dialkylboryldipyrrins are blue-shifted by only 6−7 nm compared to difluoroboryldipyrrins, with a 3-fold decrease in Φ_F (0.33 vs 0.93, respectively),[16] whereas **5** is blue-shifted by 62 nm relative to **2** and shows a 50-fold drop in the fluorescence quantum yield.

Cyclic voltammetry showed less positive redox potentials for the organoborylazadipyrromethenes relative to **2** (−0.82 V vs Fc/Fc^+), and the degree of redox shift follows the increase in the p character of the s/p hybridization of the organic substituent (Table 1). Oxidation potentials shifted less than reduction potentials, which increases the electrochemical potential gap in the order **2** < **3** < **4** = **5**. The shift in the redox potentials from **2** to **3** is similar to that seen for *meso*-carbon difluoroboryl- versus dialkynyldipyrrin compounds.[15,19] The relative sizes of the photochemical versus electrochemical energy gaps for **1**−**5** tune the energetic ordering of their radical anion and neutral (singlet) photoexcited states. **2**, like the free base **1**, has a less positive potential for its excited-state oxidation potential than for its reduction potential (Table 1). Dialkynylboryl **3** has nearly isoenergetic values for these states, while divinylboryl **4** and dibutylboryl **5** each have a less positive redox potential for their reduced state than for their excited-state oxidation potential.

Kohn−Sham orbitals for **1**−**5** generated by density functional theory are remarkably similar across the compounds in this study, and they indicate no frontier orbital density at boron (see the SI), leaving only the inductive effect of the boryl subsituents to explain the above-mentioned trends. Group electronegativity values for carbon in different hybridizations, along with many other functional groups, have been calculated and/or correlated to empirical data to yield sets of values on the Pauling scale that do not agree on absolute values but do agree on qualitative trends: increasing s character in carbon hybridization leads to increased electronegativity, and the values for the alkyl (2.2−2.5), alkenyl (2.3−2.8), and alkynyl (2.5−3.1) groups are all far below that of fluorine (4.0).[20] Alkynyl group electronegativity is also well below the elemental electronegativity of oxygen (3.5) but is near that of nitrogen (3.0−3.2).

The effect of a chelation center's electronegativity on the azadipyrrin optoelectronic properties can also be correlated to data for previously reported complexes: While this manuscript was in progress, Jiang and co-workers reported the synthesis of dialkynylboryl- and diarylborylazadipyrromethenes and they noted significant differences in absorbance maxima and fluorescence yields between the two types, with their diarylborylazadipyrromethenes having depressed fluorescence similar to our divinylboryl **4**.[21] Leblebici et al. reported an aryloxyborylazadipyrromethene that exhibited fluorescence yields and redox behavior quite similar to those of difluoroborylazadipyrromethenes, which can be explained by the strong electronegativity of oxygen (χ = 3.61).[10,22] Among some reported homoleptic bis(azadipyrrin)metal chelates, a shift toward less positive reduction potential correlates to decreasing the metal electronegativity in the order Ni > Co > Zn (χ = 1.88, 1.84, and 1.59, respectively).[4,23] All of the investigated metals are less electronegative than boron (χ = 2.05),[22] and the metal complexes are nonemissive. The corresponding copper complexes do not follow the redox trend because of their facile $Cu^{II}-Cu^{I}$ reduction process.[4] On the basis of the electronegavity trends observed in

Table 1. Optical and Electrochemical Data for Compounds 1−5

compound	λ_{abs} (nm)[a]	λ_{em} (nm)	$E_{0,0}$ (eV)	Φ_F[b]	τ_F (ns)	E^{i0}_{ox}	E^{i0}_{red}	$E^{i0}_{ox} - E^{i0}_{red}$	$E^{0}_{S*/S^{\bullet+}}$
H-ADP (**1**)	599	639	1.94	n/a[c]	n/a[d]	0.55[e]	−1.22[e]	1.77	−1.39
F_2B-ADP (**2**)	654	678	1.83	0.34	1.94	0.86	−0.82	1.68	−0.97
$(TMSCC)_2B$-ADP (**3**)	647	671	1.85	0.22	1.48	0.80	−1.01	1.81	−1.05
$(C_2H_3)_2B$-ADP (**4**)	618	667	1.86	0.017	n/a[d]	0.79	−1.13	1.92	−1.07
Bu_2B-ADP (**5**)	592	663	1.87	0.006	n/a[d]	0.67	−1.25	1.92	−1.20

E^{i0}_{ox} = oxidation potential ($E_{1/2}$); E^{i0}_{red} = reduction potential ($E_{1/2}$); $E^{0}_{S*/S^{\bullet+}}$ = excited-state oxidation potential (as $E^{i0}_{ox} - E^{i0}_{red}$). All potentials are V vs Fc/Fc^+. [a] Absorbance and fluorescence data measured under ambient conditions (in $CHCl_3$ and toluene, respectively). [b] Quantum yields calculated using rhodamine B ($\Phi_F = 0.7$ in ethanol; $\lambda_{exc} = 490$ nm). Φ_F are corrected for changes in refractive index. [c] Fluorescence of compound **1** was too weak to quantify accurately. [d] Lifetimes of compounds **3**−**5** were not measurable by the instrument (detection limit ~300 ps). [e] Data from ref 24.

this study, we predict that some additional range in the optoelectronic behavior of emissive azadipyrromethenes may be available in boryl chelates having nitrogen-based substituents, a class that has not yet been explored for either azadipyrrins or their *meso*-carbon analogues. We anticipate that these insights will improve the utility of azadipyrrin dyes for photoelectrochemical cells and related applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, NMR and mass spectral data, individual UV−vis absorbance and fluorescence data, and molecular orbital images for compounds **2**−**5**, additional crystal structure images, and CIF files for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(18) Crystal data for **3** and **4** collected on a Bruker APEX II diffractometer: T = 100 K,; λ(Mo Kα) = 0.71074 Å. For **3**: $C_{42}H_{40}BN_3Si_2$, fw = 653.76, triclinic $P\bar{1}$, Z = 2, a = 10.0268(10) Å, b = 12.5229(12) Å, c = 15.1688(14) Å, α = 81.432(2)°, β = 79.619(2)°, γ = 84.886(2)°, V = 1848.8(3) Å^3, D = 1.174 g cm^{-3}, μ = 0.129 mm^{-1}, R1 = 0.0361, wR2 = 0.0873. For **4**: $C_{36}H_{28}BN_3$, fw = 513.42, triclinic $P\bar{1}$, Z = 4, a = 8.8688(11) Å, b = 18.125(2) Å, c = 19.124(2) Å, α = 62.151(2)°, β = 81.553(2)°, γ = 80.656(2)°, V = 2673.1(6) Å^3, D = 1.276 g cm^{-3}, μ = 0.074 mm^{-1}, R1 = 0.0478, wR2 = 0.0974.

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