

A New Highly Fluorescent and Symmetric Pyrrole–BF₂ Chromophore: BOPHY

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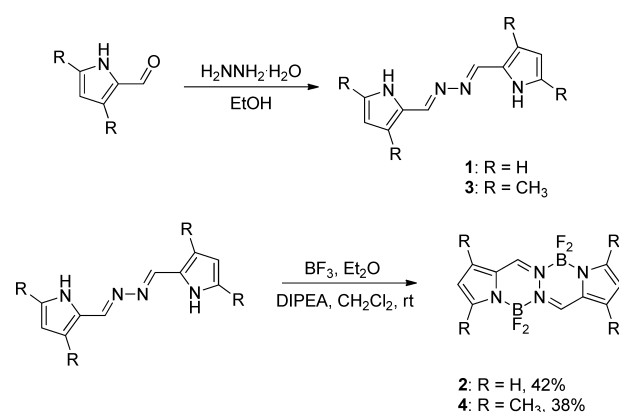
S Supporting Information

ABSTRACT: The new fluorescent chromophore BOPHY can be readily synthesized in two steps from commercially available reagents via the coupling of pyrrole-2-carboxaldehyde with hydrazine followed by reaction with BF₃. The resultant symmetric and dimeric tetracycle is composed of two BF₂ units in six-membered chelate rings appended with pyrrole units on the periphery. The quantum yields of fluorescence for the unmodified compound and the tetramethyl variant are near unity, with values of 95 and 92%, respectively, in CH₂Cl₂. We have probed the electronic structure of this compound via cyclic voltammetry and density functional theory analysis.

Fluorescent chromophores have become essential to modern chemical investigations. Chromophores with high quantum yields of emission, such as fluorescein, coumarin, and arylmethine dyes, have been used in applications ranging from biological imaging and sensing to light harvesting.¹ Some of the more successful fluorophores in the literature belong to the boron dipyrromethene (BODIPY) family of compounds.² These dyes, which are composed of a dipyrromethene bound to a central BF₂ unit, have several optimal characteristics, including large molar absorptivities, high quantum yields of emission, and reasonably sized Stokes shifts. The success of the BODIPY dyes and related compounds has spurred investigations into similar systems, such as the nitrogen-substituted aza-BODIPY variants.^{2a–d,3} Herein we present the new pyrrole-BF₂-based fluorophore bis(difluoroboron)1,2-bis((1*H*-pyrrol-2-yl)methylene)hydrazine (BOPHY), which can be produced via a simple two-step procedure. The resulting chromophore is a symmetric, highly fluorescent compound with two BF₂ units bridged by a coupled pair of Schiff bases.

For several years, we have been investigating the chemistry of Schiff base chelates as part of our work on the chemistry of Re(CO)₃ compounds.⁴ We have also been working with hydrazine as a reagent for the synthesis of phthalazines and phthalazine chelates.⁵ The reaction of aldehydes with hydrazine results in dimeric Schiff base structures, and pyrrole-2-carboxaldehyde readily reacts with hydrazine to form the pyrrole–imine dimeric chelate **1**, shown in Scheme 1.⁶ This compound readily reacts with BF₃ to form the BOPHY chromophore **2**. We can also produce the tetramethyl-substituted BOPHY analogue (Me₄BOPHY, **4**) via the same two-step procedure starting with dimethyl-substituted pyrrole-

Scheme 1



2-carboxylaldehyde via intermediate **3**. Compounds **2** and **4** can be readily purified via column chromatography using silica as the solid phase and methylene chloride as the eluent. Subsequent evaporation of the solvent affords pure crystals of **2** and **4**.

We elucidated the structure of BOPHY and Me₄BOPHY via single-crystal X-ray diffraction, and the structures of the two compounds are shown in Figure 1. The structure of the free ligands (as seen in the case of the tetramethyl variant **3**, also shown in Figure 1) led us to expect a five-membered chelate ring with BF₂, which has been seen upon metal ion coordination.⁷ However, we observed six-membered-ring chelate formation, resulting in a molecule that has an inversion center (C_{2h} symmetry). The chromophore is thus composed of four rings, with two pyrrole units at the periphery and two six-membered rings, each incorporating a BF₂ group. In the solid state, both **2** and **4** are rigidly planar, with only the fluorine atoms and the methyl hydrogen atoms in **4** deviating from the plane of the tetracycle. In **2** and **4**, the bond lengths in the pyrrole units are similar to those seen in BODIPY-type compounds and are indicative of aromaticity of the peripheral pyrrole units at the edge.⁸ The hydrazine Schiff base moieties retain double- and single-bond character, although the C–N double bonds are slightly longer in **2** and **4** by approximately 0.016 and 0.03 Å, respectively, versus the free ligands. This indicates that these compounds do not have aromaticity

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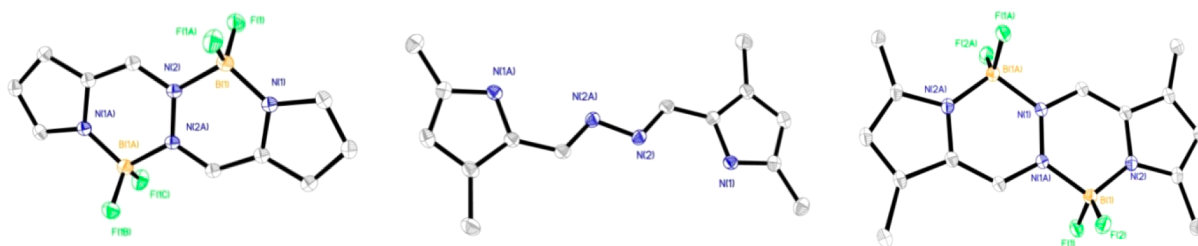


Figure 1. Structures of **2**, **3**, and **4** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

extended across the tetracycles. Several compounds having features similar to **2** and **4** have recently been reported, including a bisnaphthridine BF_2 dimer⁹ and a series of isoindoline-based BF_2 chromophores,¹⁰ but **2** and **4** are the first examples of hydrazine-based pyrrole- BF_2 dimers.

The absorption and emission spectra of **2** and **4** are shown in Figure 2. The unsubstituted BOPHY molecule **2** exhibits

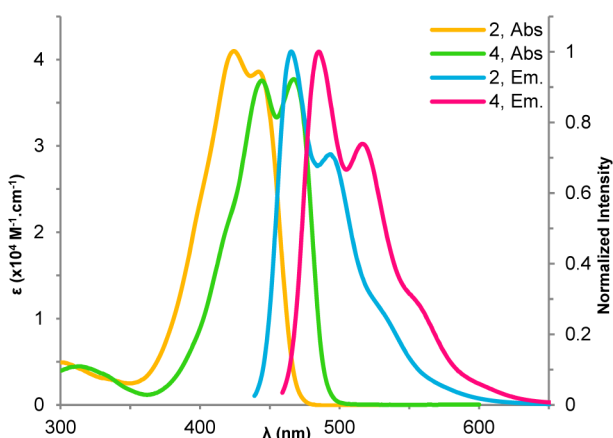


Figure 2. Absorption and emission spectra of **2** and **4** in CH_2Cl_2 .

absorption maxima at 424 and 442 nm, with extinction coefficients of 4.09×10^4 and $3.86 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The tetramethyl-substituted variant **4** exhibits red-shifted absorption bands, with absorptions at 444 nm ($3.75 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 467 nm ($3.74 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Both compounds are strongly emissive, with quantum yields of emission in CH_2Cl_2 close to unity (95 and 92% for **2** and **4**, respectively). Both exhibit two emission bands, at 465 and 493 nm for **2** and 485 and 518 nm for **4**. Like the BODIPY fluorophores,^{2,12} solutions of **2** and **4** are stable toward light and air for days as well as toward extended UV irradiation (365 nm) in the presence of air (see the Supporting Information). There are a couple of notable features in the absorption and emission spectra of the two fluorophores. First, we observed a difference between the relative intensities of the absorption bands of these two compounds, with **2** having more intense absorption in the higher-energy band whereas **4** has nearly equal absorptivities for the two bands. Second, the emission profile is not the mirror image of the absorption profile, and the higher-energy emission is more intense than the lower-energy emission in both **2** and **4**. This is in apparent contradiction to Kasha's rule, as will be discussed below.

We also investigated the cyclic voltammetry of compounds **1–4**, which can be seen in the Supporting Information. Cyclic voltammetry experiments were carried out in THF using tetrabutylammonium hexafluorophosphate as the electrolyte.

The free ligands show irreversible reductions at approximately -0.90 and -0.80 V vs Ag/AgCl for **1** and **3**, respectively. Compound **3** exhibits what appears to be a second irreversible reduction at about -1.05 V vs Ag/AgCl . Upon formation of the BF_2 adducts, the reductions shift to more positive (higher) potentials at approximately -0.5 V vs Ag/AgCl for both **2** and **4**. These shifts to higher potentials were expected on the basis of the binding of the electron-deficient BF_2 unit and correlate well with the red shifts of the absorption bands in going from **1** and **3** to **2** and **4**, respectively.

In order to explain the absorption and emission spectra of **2** and **4**, we conducted density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on these systems.¹¹ DFT calculations suggested that the C_{2h} geometries in **2** and **4** do not represent energy minima (see the Supporting Information for a detailed discussion); instead, C_2 -symmetry (both boron atoms deviating from planarity toward one side) and C_i -symmetry (boron atoms deviating from planarity toward different sides) structures are the stationary points on the potential energy surfaces. The energy differences between the C_2 and C_i geometries are small (1.3–1.6 kcal/mol), and the corresponding orbital energies and compositions are also very similar to each other (see Figure 3 and the Supporting

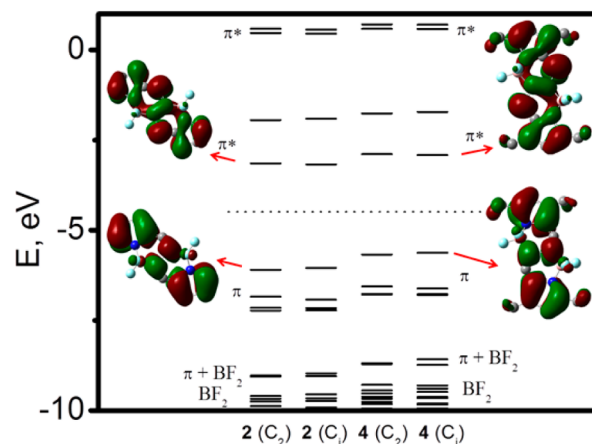


Figure 3. DFT-predicted orbital energies for **2** and **4** with pictorial representations of the frontier MOs.

Information). The highest-occupied molecular orbitals (HOMOs) in **2** and **4** are π -type MOs that are $\sim 70\%$ delocalized between the two pyrrole fragments with $\sim 30\%$ contribution from the N–N bridge, while the lowest-occupied molecular orbitals (LUMOs) are π^* -type MOs having $\sim 90\%$ pyrrolic and $\sim 10\%$ N–N bridge character (Figure 3). Both the HOMO and LUMO in **4** have higher energies than those in **2**, reflecting the electron-donating nature of the methyl groups. The HOMO in **4** undergoes a larger degree of destabilization

(~ 0.4 eV) than the LUMO (~ 0.3 eV), which leads to its smaller HOMO–LUMO gap. The HOMO and HOMO–1 as well as the LUMO and LUMO+1 in **2** and **4** are energetically well-separated from each other (~ 1 eV), which in turn (taking into consideration the nature of the C_{2h} , C_2 , and C_i point groups) should result in the presence of only one low-energy band in their absorption spectra. Indeed, the TDDFT-predicted absorption spectra of **2** and **4** with C_2 and C_i symmetries (Figure 4; also see the Supporting Information) are in excellent

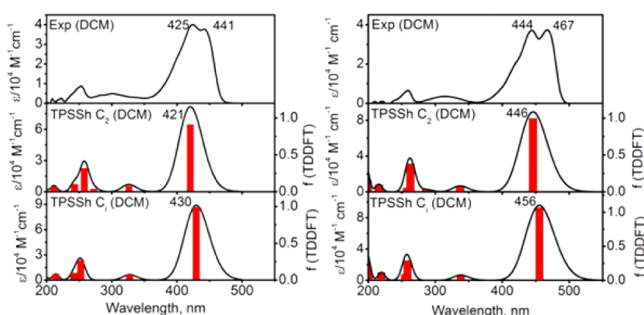


Figure 4. (top) Experimental and (middle, bottom) TDDFT-predicted absorption spectra of (left) **2** and (right) **4** in DCM.

agreement with the experimental data and clearly suggest that the strong band observed in the visible range for **2** and **4** is dominated by HOMO to LUMO excitation. The TDDFT-predicted ~ 25 nm red shift for the first excited state in **4** relative to **2** is in excellent agreement with the experimental data. In agreement with their electronic structures, the TDDFT-predicted energy of the second excited state is ~ 1 eV higher than the first excited state in **2** and **4** and correlates well with their experimentally observed band at ~ 320 nm. Thus, on the basis of their electronic structures and TDDFT calculations, it should be suggested that, similar to the other polycyclic systems, the two low-energy clear bands and the shoulder observed in the absorption spectra of **2** and **4** belong to a vibronic progression of the same excited state rather than to the different excited states. In agreement with this hypothesis, some structural reorganization in the excited state of **2** or **4** can result in a slight change in the displacement (the relative intensities across the main vibronic progression) in the emission spectra of **2** and **4** compared with their absorption spectra (Figure 2).

In conclusion, the BOPHY architecture represents a new structural motif for highly fluorescent compounds. Compounds **2** and **4** have unusual absorption and emission properties that are not intuitive from their orbital configurations; we hypothesize that structural reorganization, such as vibronic coupling, may be involved. Additionally, the BOPHY structural motif is an attractive target for functionalization at a variety of positions on the periphery, and we have investigated the methylated variant. We are continuing our work on characterizing the photophysical properties of **2** and **4** as well as synthesizing structural variants.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details; spectroscopic, crystallographic, electrochemical, and DFT data for target compounds; CIFs for **2–4**; and complete ref 11a (as SI ref S2). 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.

A provisional patent on **2** and **4** has been filed under USPTO serial no. 61/906,443.

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