Isomeric Boron–Fluorine Complexes with Donor–Acceptor Architecture: Strong Solid/Liquid Fluorescence and Large Stokes Shift

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ABSTRACT
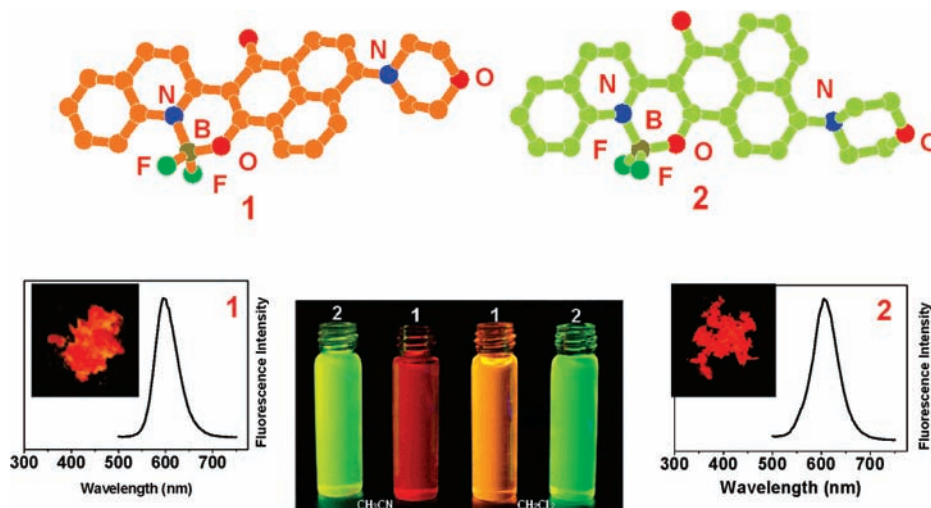
Novel isomeric fluorine–boron complexes with donor–acceptor architecture have been efficiently synthesized and well characterized. Significant features, such as strong solid and liquid fluorescence, unusual large Stokes shifts, and lower LUMO levels and higher HOMO levels, are observed in these potential multifunctional molecules.

Development of high-efficiency fluorophores is essential for the field of molecular sensors[1] and organic light-emitting devices (OLED).[2] Among many conventional fluorophores, dipyrro-boradiazaindacenes (BODIPY) comprise one of the most intriguing families because of their significant optical properties.[3] However, most BODIPYs have the disadvantage of very small Stokes shifts, which can lead to self-quenching and measurement error by excitation light and scattering

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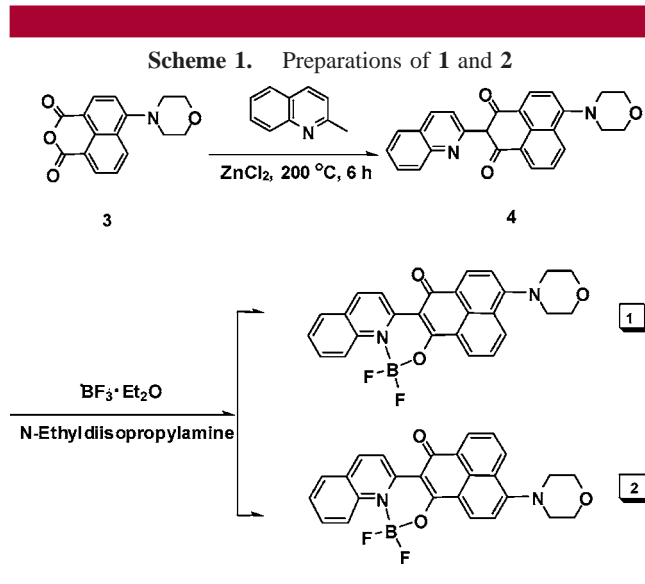
light. The serious self-quenching can also result in weak solid fluorescence, which might partly explain why BODIPYs are rarely applied as electroluminescence materials.[4] Although some efforts have been made to induce larger Stokes shifts in BODIPYs,[5] the problem along with large Stokes shifts, that more energy will be lost via nonradiative decay of the excited fluorophores, is inherent in many other cases. Thus, it is challenging to obtain BODIPY derivatives/analogues with both relatively high fluorescence quantum yields and large Stokes shifts.

Recently, considerable attention has been paid toward the exploration of multifunctional fluorophores with donor—acceptor (D—A) architectures.[6] Some emissive D—A small molecules have been reported for their ambipolar charge-transport property and high luminescence efficiency.[7] However, for the published, unsymmetrically substituted D—A-type BODIPY dyes, the considerable fluorescence quenching in polar solvents (due to their strong intramolecular charge transfer (ICT) characteristics) remains unchanged.[8] Thus, we launched an investigation to explore novel D—A-type F—B complexes to substitute BODIPYs as multifunctional fluorophores for broader applications, with bipolar characters and excellent emitting properties.

In the present work, the new D—A structures (Scheme 1) were fabricated. Quinoline and phenalene-1,3-dione, groups with low electron density, had been chosen as the ligands, which could coordinate with BF_3 to form the strong electron-acceptor moieties with deep LUMO levels. Amino-type electron-donor moieties (morpholine) were introduced in order to elevate the HOMO level to facilitate the hole transport. The naphthalene ring worked as a π spacer to link the donor and the acceptor, which extended the conjugation systems to favor the emission and charge transport.

The preparations of compounds **1** and **2** are summarized in Scheme 1. When the intermediate compound **4**[9] and $BF_3 \cdot OEt_2$ were heated in toluene at 60 °C for 4 h, a mixture containing two products with totally different fluorescence was formed. The ratio of the orange fluorescence product to the yellow-green fluorescence product was about 2:1. Results showed the ratio could change to 1:2, when the coordination was carried out at room temperature in dichloromethane.

1 and **2** were separated by their polarity distinctions and were fully characterized. These two isomers were finally

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Scheme 1. Preparations of **1** and **2**

confirmed by single-crystal X-ray diffraction studies, which successfully provided the most convincing evidence for their molecular structures and conformational features.

The crystal structures of the two isomers are illustrated in Figure 1, and some relevant structural data of these isomeric
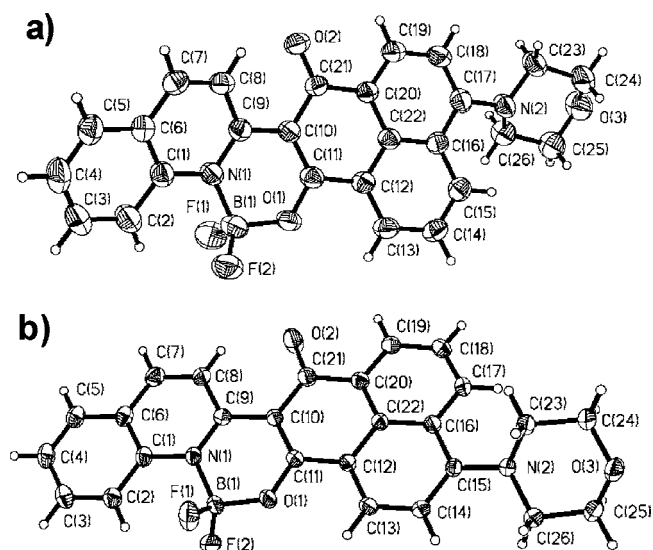

Figure 1. Crystal structures of **1** (a) and **2** (b) with displacement ellipsoids shown at the 50% probability level.

complexes are summarized in Table S1 (Supporting Information). The molecular structures unambiguously show the geometry distinctions for these isomers, i.e., the morpholine ring in **1** is on the opposite side toward the F—B center, while the morpholine ring in **2** is on the same side as the F—B center.

Distinct differences are observed in their molecular planarity. For **1**, the quinoline plane twisted with the phenalene-1,3-dione plane for 27.4°, resulting in an obvious angle along

the molecular plane seen at the side view down the *c*-axis (Supporting Information). However, the phenalene-1,3-dione plane in **2** shows good planarity with the mean deviation of 0.012 Å. The torsion angle of the quinoline plane and the phenalene-1,3-dione plane was only 3.8°.

As shown in Table 1, both compounds exhibit high

Table 1. Optical Properties of **1** and **2**

cmpd	solvent	UV		fluorescence	
		λ abs/nm	$\log\epsilon_{max}$	λ em/nm	$\Phi_F{}^a$
1	CH_2Cl_2	427, 368	4.22	588	0.50
	THF	427, 365	4.25	596	0.53
	CH_3CN	424, 365	4.32	620	0.47
	C_2H_5OH	423, 366	4.01	584	0.45
	CH_3OH	419, 365	3.87	564	0.44
2	CH_2Cl_2	468, 374	4.16	544	0.53
	THF	464, 370	4.31	545	0.55
	CH_3CN	468, 369	4.20	553	0.49
	C_2H_5OH	460, 369	3.90	552	0.46
	CH_3OH	461, 369	3.83	558	0.45

a The fluorescence quantum yields (Φ_F) were estimated with quinine-sulfate (Φ_F = 0.55 in 50 mM H_2SO_4 solution) as a standard.

fluorescence quantum yields (0.45−0.55) in solution. Different from the small Stokes shift and insensitivity to the environment of most BODIPYs, large Stokes shifts and remarkable spectral changes are observed in various solvents. For **1**, in acetonitrile, the emission maximum is at 620 nm, and the Stokes shift was about 7455 cm⁻¹. Compared to the spectra in the non-protic solvents, the emission wavelength of **1** blue-shifts by 56 nm in methanol solvent, with the Stokes shift being 6135 cm⁻¹. For **2**, the emission maximum red-shifts slightly with increasing solvent polarity. It varies from 544 nm in non-ploar dichloromethane to 558 nm in highly polar methanol. The Stokes shift of **2** increases to 3771 cm⁻¹ in methanol. The sensitive emission responses toward media, along with the high fluorescence yields, qualify **1** and **2** as suitable sensor molecules for communicating local environmental properties.

According to previous theoretical results,[10] ICT is the major mechanism responsible for the solvent-reliant emission properties and the large Stokes shifts of **1** and **2**. Interestingly, the two isomers having the same acceptor−spacer−donor units, display quite different fluorescence properties. Compared with **2**, **1** has much longer wavelength emissions, much larger Stokes shifts, and much broader emission bands (Figure 2), which indicate more effective ICT processes. As de Silva et al.[11] have suggested, photoexcitation of a ''push−pull'' π electron system will generate an electric field with the positive pole at the position of the electron donor and the negative pole at the position of the electron acceptor. In

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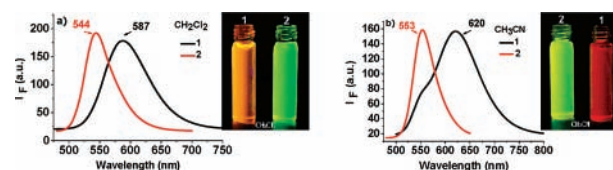
Figure 2. Photos of liquid fluoresence and fluorescent spectra of **1** and **2** in dichloromethane (a) and in acetonitrile (b).

our BF complex isomers, their positive poles are located at the morpholine nitrogen atom, but their negative poles are affected greatly by their geometry distinctions. Crystal studies have already indicated that, for **1**, the quinoline moiety is twisted out of the phenalene-1,3-dione plane considerably, which leads to partial decoupling. For **2** such a twist does not exist, which means better conjugation. For the excited molecule **1**, there is a tendency for the negative pole to localize mainly on quinoline nitrogen because of the non-planarity. But for **2**, the negative pole can be delocalized onto a larger area covering the quinoline and phenalene-1,3-dione. Therefore, **1** has a higher dipolar moment than **2** upon excitation, and thus, ICT processes in **1** are more effective.

For deeper understanding of optical properties displayed by **1** and **2**, calculations were performed with the Gaussian 03 package[12] in Virtual Laboratory for Computational Chemistry, CNIC, CAS at the B3LYP level.[13] The basis sets 6-31G(d,p) was used for all atoms. Geometric parameters from X-ray diffraction analysis were used for the calculation.

The calculations reveal that the electron density in the LUMO of these two compounds is mainly distributed over part A (Figure 3). For **1**, the electron density in the HOMO
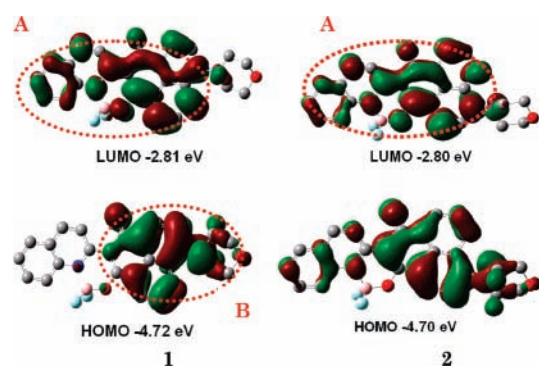

Figure 3. Diagrams showing the HOMO and LUMO levels of **1** and **2**.

is localized on part B, while that for **2** is donated by all atomic orbits in the aromatic rings. A more effective excited-

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state intramolecular charge transfer (ICT) from part B to part A is suggested in **1**, relative to **2**, which is in accordance with the results of spectral studies.

Compared with BODIPYs, **1** and **2** have other significant features. In the solid state, they show strong fluorescence with sharp peaks and large Stokes shifts. As shown in Figure 4, the emission maxima are at 595 nm for **1** (fwhm = 55
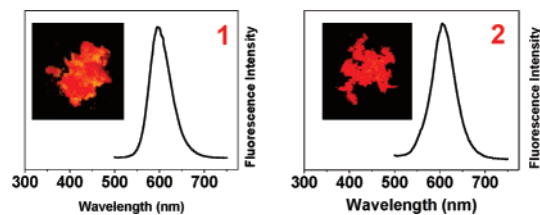

Figure 4. Photos of solid fluoresence and fluorescent spectra in the solid state of **1** and **2**.

nm) and at 605 nm for **2** (fwhm = 57 nm), with the Stokes shifts of 10441 cm^{-1} and 5257 cm^{-1}, respectively.

The narrow solid-state emission bands of **1** and **2** are also unusual and intriguing, as spectral broadening is a very common phenomenon for solid emitting materials. In the present work, the introduction of a morpholine ring increases the steric hindrance, which to some extent, prevents the molecules from packing compactly and thus avoids the spectral broadening. Few intermolecular interactions between molecules, together with large Stokes shifts, provide favorable factors that eliminate self-quenching and enhance their solid fluorescence.

As discussed above, molecules of **2** have good planarity and are regularly parallel with each other, with partial $\pi-\pi$ stacking over the quinoline ring. (Supporting Information). Therefore, the large red-shifts of the solid emission maximum in **2** can be attributed to the increased intermolecular interactions in the solid state compared to those in the solutions.

The electronic states (HOMO/ LUMO levels) of **1** and **2** were investigated by cyclic voltammetry (CV) (Figure 5). The oxidation CVs of these two compounds are both characterized by an irreversible wave. The ionization potential (IP, HOMO level) of compounds **1** and **2** are 5.45
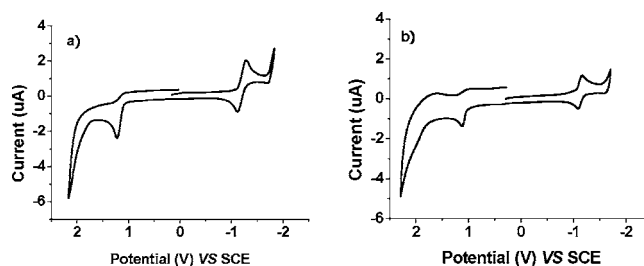

Figure 5. Cyclic voltammograms of **1** (a) and **2** (b) measured in CH$_3$CN solution, containing 0.1 M TBAPF$_6$ at 20 °C.

and 5.40 eV, respectively. **1** and **2** both show reversible reduction waves. The estimated electron affinity (EA, LUMO level) values are 3.28 eV for **1** and 3.34 eV for **2**. The LUMO values of these compounds are lower than that of BODIPY (-3.05 eV) (Supporting Information) and the commonly used current electron-transport materials Alq$_3$ (-3.0 eV).[14] The better electron-accepting features of **1** and **2** make them more promising in practical applications as charge-transport materials.

In summary, novel isomeric D$-$A-type fluorine$-$boron complexes have been efficiently synthesized and well characterized. Significant features, such as strong fluorescence in solution and solid state, unusual large Stokes shifts, and lower LUMO and higher HOMO levels, are observed in these two structural isomers. These properties qualify these novel F$-$B complexes as multifunctional fluorophores that can be employed in light-emitting or -sensing applications.

Supporting Information Available: General experimental methods, compound characterization data, crystallographic information files (CIF), crystallographic analyses, and related optical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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