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Through-Space Charge-Transfer Emitting Biphenyls Containing a Boryl and an Amino Group at the *o*,*o*′-Positions

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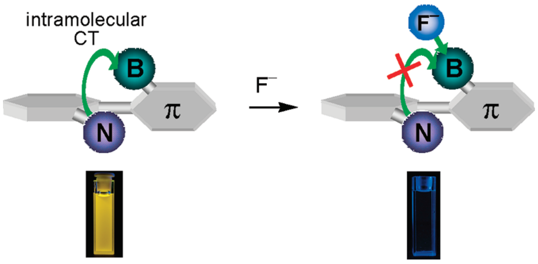
ABSTRACT



A new class of organoboron compounds containing a boryl and an amino group at the *o*,*o*′-positions of biphenyls display bright through-space intramolecular charge transfer fluorescence owing to the close contact between the boryl and the amino groups. Binding of the fluoride ions results in the remarkable blue shift and color change of the fluorescence, enabling colorimetric and ratiometric fluoride ion sensing.

Tricoordinate boron-containing π-conjugated materials have attracted increasing attention due to their intriguing electronic and photophysical properties, which arise from their unique ability to accept electrons through the $p_\pi-\pi^*$ conjugation between the vacant p orbital on the boron atom and the π^* orbital of the π-conjugated framework.[1] When an appropriate electron donor is present, the electron-accepting ability of the boron center makes organoboron compounds display intense intramolecular charge transfer (CT) transitions, which have been exploited extensively in a wide range of applications, such as nonlinear optical materials,[2,3] two-photon absorption and emission materials,[4,5] organic

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light-emitting diodes,[6−8] and chemical sensors for fluoride and cyanide anions.[9−13]

The majority of organoboron compounds exhibiting intramolecular CT transition generally have a linear geometry, in which the donor and the acceptor are attached at the terminal positions of the conjugated spacer. We and others have recently disclosed a class of charge-transfer emitting organoboron materials, in which the electron-accepting boryl groups were introduced at the lateral positions instead.[14] These organoboron materials exhibit extremely intense fluorescence even in the solid state owing to the suppressed fluorescence quenching as a result of the steric bulkiness of the boryl groups and the large Stokes shift induced by the intramolecular CT transition. In the above-mentioned systems, the intramolecular CT transition takes place through the corresponding aromatic linker. In contrast, when the donor and acceptor are connected by a rigid bridge in the U-shaped system,[11] the rigidity of the linker forces the π-systems of the chromophores out of coplanarity with that of the linker. As a consequence, the charge transfer occurs through space rather than through bond, promoting the through-space intramolecular CT fluorescence, which is switchable to $\pi-\pi^*$ fluorescence by the addition of fluoride. Encouraged by the unusual photophysical properties and the various potential applications of the intramolecular CT emitting organoboron materials, here we now disclose a new class of tricoordinate organoboron compounds **1** and **2**, in which a boryl group and an amino group are incorporated at *o*- and *o′*-positions of the biphenyl framework (Figure 1). We envisioned the steric effect of the lateral boryl and amino groups would make the biphenyl moiety exhibit a very twisted structure and permit a very close contact between them. The special molecular structure and the electronic interaction between the boryl and the amino groups would lead to unique properties. In fact, we found that such molecules display intense fluorescence in both solution and the solid state with much longer emission wavelength compared to those of the regioisomers. Binding of **1** with fluoride ions can lead to a 165 nm blue shift of the fluorescence and a significant emission color change, enabling colorimetric and ratiometric fluoride ion sensing.

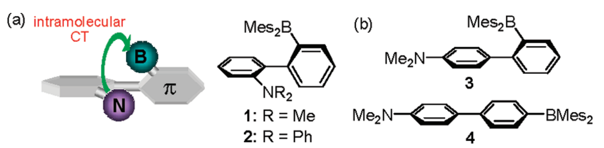

Figure 1. (a) Schematic representation and structures of biphenyls **1**, **2** containing a boryl group and an amino group at *o*,*o′*-positions and (b) structures of the related compounds **3**, **4**.

The syntheses of the boryl-substituted biphenyls **1**−**2** were accomplished via the lithiation of the corresponding bromo-substituted biphenyls with *n*-BuLi followed by treatment with dimesitylfluoroborane (see Supporting Information, SI). These two compounds are stable to air and water and can be purified by flash column chromatography. The structure of **1** was determined by X-ray crystallography. As shown in Figure 2, the biphenyl unit is significantly twisted with a torsion angle of 70.7° between two benzene rings. This nonplanar structure apparently arises from the steric hindrance of the lateral boryl and amino groups. It is worth noting that despite the remarkable steric congestion between the boryl and the amino groups and the rotation flexibility of single bond in the biphenyl framework, the biphenyl moiety is arranged in the geometry with a B···N distance of 3.59 Å, much shorter than those of the through-space CT emitting organoboron compounds reported so far.[11]

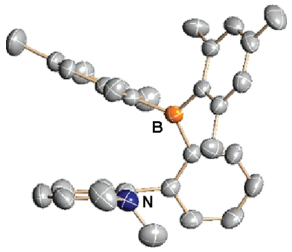

Figure 2. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

In cyclohexane, the UV−vis absorption spectrum of **1** features an intense band at 306 nm (log ε = 4.74) (Figure 3). In the fluorescence spectrum, it displays a strong green emission at 521 nm (Φ_F = 0.47 in cyclohexane). Two notable features are the particularly large Stokes shift ($\Delta\lambda$ = 215 nm, $\Delta\nu$ = 13485 cm^{-1}) and very long emission wavelength for this biphenyl unit with such a limited conjugation length. The TDDFT calculation (B3LYP/6-31G(d)) indicates that the intense absorption band at 306 nm is assignable to the transition from HOMO−1 located on the filled π-orbitals of the mesityl and phenyl rings to the

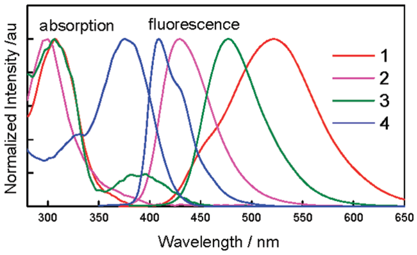

Figure 3. Absorption and fluorescence spectra of **1**−**4** in cyclohexane.

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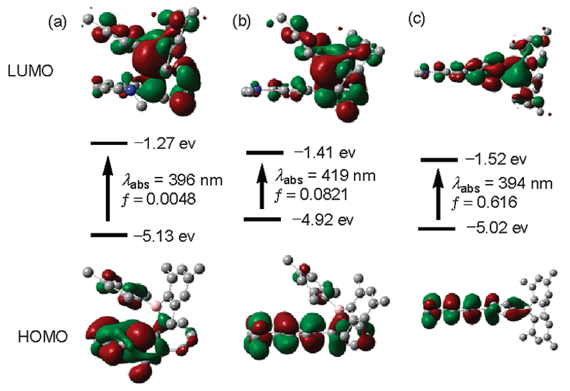

Figure 4. Plot of the Kohn−Sham HOMO and LUMO energy levels and pictorial drawings of the HOMOs and LUMOs for (a) **1**, (b) **3**, and (c) **4**. The transition energies and oscillator strengths were calculated at the B3LYP/6-31G(d) level of theory.

LUMO located on the dimesitylborylphenyl moiety (see SI). The lowest electronic transition in fact mainly consists of a charge transfer from the HOMO localized on the dimethylaminophenyl unit to the LUMO with a quite small oscillator strength (f = 0.0048), which presumably makes the lowest transition band too weak to be distinguished (Figure 4). Since there is almost no overlap between the two frontier orbitals, the charge transfer from the HOMO to the LUMO takes place most likely through space rather than through bond. The through-space CT transition was further supported by a substantial fluorescence solvatochromism, from 521 nm in cyclohexane to 540 nm in benzene, 547 nm in chloroform, 551 in THF, and 580 nm in MeCN (see SI). Another notable feature for **1** is that it shows increased fluorescence intensity in the solid state, similar to other organoboron compounds containing lateral boryl groups.[14c] The quantum yield for its spin-coated film is 0.86, as determined by a calibrated integrating sphere. Such a fluorescence behavior may be ascribed to the easily exchangeable multiple conformations of the nonplanar structure of the main chain, which facilitate the nonradiative decay of the excited state. In the solid state, the exchanges between multiple conformations are greatly suppressed due to the spatial congestion of the molecular stacking in the solid state.[15] The emission spectrum is quite similar to that in cyclohexane, indicative of a comparable environment that has arisen in the solid state and in the dilute cyclohexane solution.

To elucidate the uniqueness of the photophysical properties for the current through-space intramolecular CT organoboron π-system, we compared the photophysical properties of **1** with those of its regioisomers **3** and **4**. In contrast to **1**, **3** and **4** display distinct intramolecular CT absorption bands at 388 and 369 nm respectively, with **4** having the highest absorption intensity (log ε = 3.48 for **3**; 4.50 for **4**). The assignments of the CT absorption bands have been corroborated by the theoretical calculations (Figure 4) and the large solvent dependence of the fluorescence spectra (see SI). Although the calculated first excited energies of these three compounds are not remarkably different, the oscillator strength increases greatly from 0.0048 for **1** to 0.0821 for **3** and 0.616 for **4**, which is in good agreement with the order of the experimentally obtained molecular absorption coefficients for these three molecules. These results suggest that the nature of the transition significantly depends on the geometry of the molecular structure. In compound **1**, the benzene rings of the biphenyl main chain are approximately perpendicular to each other due to the large steric congestion of the lateral boryl and amino groups, which in return results in the poor conjugation of the biphenyl. From **1** to **3** and **4**, with the decrease in the steric congestion of the lateral groups, the biphenyl moiety presumably becomes increasingly planar, which makes the conjugation more efficient. As a result, the HOMO is most delocalized in **4**, facilitating the CT transition from the amino group to the boryl group. It is most noteworthy that **3** and **4** exhibit blue and purple blue fluorescence at much shorter wavelengths compared to that of **1** (λ_{em} = 477 nm for **3**; 409 nm for **4** in cyclohexane). Similarly, the emission wavelength of **1** is the longest among these three compounds for their spin-coated films (λ_{em} = 519 nm for **1**; 507 nm for **3**; and 478 for **4**). Based on the Lippert−Mataga plots (see SI), **1** displays the smallest dipole moment change from the ground state to the excited state. And thus the long emission wavelength of **1** may arise from its extremely twisted structure, which would cause a significant structural relaxation in the excited state and thus substantial structure differences between the twisted structure in the ground state and presumably planar structure in the excited state. The current molecular design may provide a new method to achieve fluorescence at long wavelengths.

The through-space charge transfer is a general feature for the present biphenyl π systems containing a boryl and an amino group at the o,o'-positions. Compound **2** also shows a characteristic through-space emission, which is also highly dependent on the polarity of the solvents (see SI). Due to the lower electron-donating ability of the diphenylamino group relative to that of the dimethylamino group, a significant blue shift in the fluorescence of **2** was observed compared to that of **1**, ca. 90 nm in cyclohexane. Notably, the absorption of **2** is very similar to that of **1**, confirming that the intense absorption band of **1** at 306 nm is assignable to the transition from HOMO−1 to

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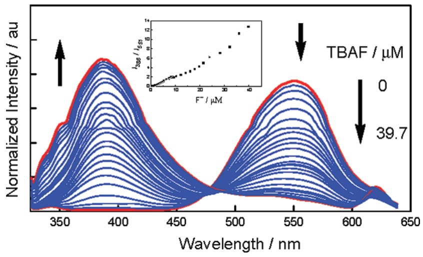

Figure 5. Fluorescence spectra change of **1** (1.08 μM in THF) upon addition TBAF. Inset: Plot of fluorescence intensity ratios beween 386 and 551 nm (I_{386}/I_{551}) versus concentration of F^- in THF.

LUMO, which is independent of the electron-donating ability of the amino group.

Considering the characteristic intramolecular CT emission of the present tricoordinate organoboron π system, we next investigated their fluorescence sensing ability for fluoride ions using **1** as a representative compound. The addition of excess fluoride ions to a THF solution of **1** led to the appearance of a new fluorescence band at 386 nm, blue-shifted by 165 nm. Such a large blue shift is very rare for the tricoordinate compounds when complexed with fluoride. This is accompanied by a blue shift of the absorption to a much shorter wavelength, which is hardly measured and can be assigned to a charge transfer from the HOMO localized on the dimesityl rings to the LUMO delocalized over the biphenyl part (see SI). The corresponding charge-transfer emission presumably tallies with the fluorescence band at 386, with a much higher energy than that of the through-space charge-transfer emission of **1**. Moreover, the complexation of **1** with fluoride resulted in a significant increase in the fluorescence efficiency (Φ_F = 0.27 for **1**; Φ_F = 0.98 for **1•F**$^-$ in THF). The remarkable blue shift and high fluorescence intensity of **1** irrespective of the binding mode prompted us to investigate its ratiometric fluorescence sensing ability for fluoride ions. The titration experiment of **1** with the fluoride ion was carried out using n-Bu_4NF as the fluoride source. The fluorescence spectral change of **1** (1.08 μM) upon addition of TBAF is shown in Figure 5. As the concentration of TBAF increased, the emission band at 551 nm decreased and the blue-shifted band at 386 nm increased gradually. This change became saturated when the concentration of TBAF amounted to 39.7 μM. The binding constant was determined to be 1.55×10^5 M^{-1}, which is comparable to those of other tricoordinate organoboron compounds. It is most noteworthy that the ratios of emission intensities at 386 and 551 nm (I_{386}/I_{551}) exhibit a dramatic change from 0.008:1 to 12.7:1 and increase linearly almost within the whole region. Moreover, a dramatic color change of emission was observed from yellow to blue (see SI), thus enabling colorimetric fluoride ion sensing by the naked eye. While it has been well documented that tricoordinate organoboron compounds can act as efficient fluorescent sensors for fluoride ions, little ratiometric fluorescence sensing has been reported because of the trivial fluorescence spectra changes or the low fluorescence intensity of either organoboron compounds or their complexes with fluoride ions.[13] Our current molecular design may also provide an efficient strategy to obtain organoborons capable of the ratiometric fluorescence sensing of fluoride ions.

In summary, we have disclosed a new class of tricoordinate organoboron compounds, in which the electron-accepting boryl group and the electron-donating amino group are incorporated at the o,o'-positions of the biphenyl framework. The close contact between boryl and amino groups permits a characteristic through-space intramolecular CT fluorescence at long wavelengths. Binding of fluoride ions leads to the remarkable fluorescence spectra and color changes, enabling colorimetric and ratiometric fluoride ion sensing.

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Supporting Information Available. Experimental details, photophysical data, results of theoretical calculations, and crystallographic data in CIF format. These materials are available free of charge via the Internet at http://pubs.acs.org.