Donor-and-Acceptor Substituted Truxenes as Multifunctional Fluorescent Probes

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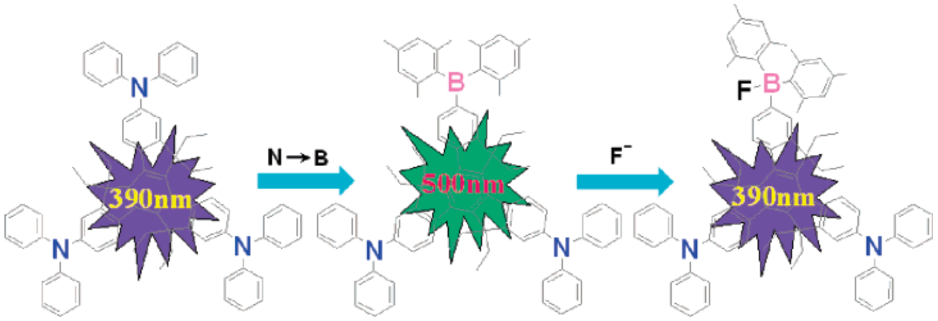

A series of dimesitylboryl acceptor (mesityl = 2,4,6-trimethylphenyl) and/or diphenylamino donor (−N(Ph)$_2$)-substituted truxene derivatives, classified as D-or-A substituted compounds and D-and-A substituted charge-transfer compounds, have been synthesized. Two D-and-A substituted truxene compounds, namely, 2-dimesitylboryl-7,12-di(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (**BN2**) and 2,7-di(dimesitylboryl)-12-(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (**B2N**), exhibit extraordinarily large solvatochromism ranging from 420 nm (in hexane) to 580 nm (in acetonitrile) in aprotic solvents, which can be used to probe the polarity of the solution environment. Due to proton−donor interactions, the solvatochromic red shift of **BN2** and **B2N** in protic solvents has been significantly decreased, and this effect can be used to identify local protic and aprotic environment. Furthermore, because of the interaction between F$^-$ and acceptor, **BN2** and **B2N** show sharp spectral response to fluoride ion concentration. The simultaneous "turn-off" at 500 nm and "turn-on" at 380 nm of the fluorescence signal have provided a good example of a fluorescent ratiometric method, which can greatly enhance the sensitivity of the fluoride ion probe. Underlying these interesting spectral phenomena and multifunctional probe properties is the charge-transfer strategy of grafting donor and acceptor moieties, as A-π-D$_2$ or A$_2$-π-D style, to the triangular truxene.

Introduction

Organic fluorescent probes have been extensively used in biological, medical, and supramolecular systems in recent years[1] since interactions of fluorescent probes with analytes can have a significant influence on emission peak wavelength, intensity, steady-state and transient profiles, or lifetime. Typical fluorescent probes are characterized by a π-conjugated skeleton and a functional group (such as donor or acceptor), and these can serve as sensors for particular ions or small molecules[2−5] or show specific recognition of a property of a microenvironment, such as polarity,[6−8] acidity (pH value),[7,9] fluidity,[10] molecular mobility,[11] or electric potential.[12] Highly sensitive and multifunctional

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fluorescence probes are currently in great demand for fundamental study and practical applications.[13] The general strategy in designing new fluorescence probes is no other than considering two electronic aspects of the molecules: the π-conjugation and the charge-transfer (CT) characters.

Truxene (namely, 10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene) is a planar heptacyclic polyarene. Its various derivatives have been designed for liquid crystals and fullerene precursors.[14] It can be formally regarded as a derivative of 1,3,5-triphenylbenzene with three $-CH_2-$ "clips" added and accordingly three five-membered rings formed to keep the four phenyls in a planar rigid structure. Recently, a variety of dendritic truxene derivatives have been synthesized to extend the π-conjugation.[15] However, both donor (D) and acceptor (A) substituted polar truxene compounds, which may be promising for fluorescent probes, have not been reported hitherto. Owing to the electron-deficient nature of the boron atom, the dimesitylboryl group $-B(Mes)_2$ (Mes = mesityl = 2,4,6-trimethylphenyl) behaves as an electronic "trap" and some of its compounds exhibit interesting optoelectronic properties.[16] Similarly, the diphenylamino donor group $-N(Ph)_2$, with its lone pair of electrons, has been used in designing hole transport materials and organic light-emitting diodes.

In this work, we connect both diphenylamino donor and dimesitylboryl acceptor to the three para-positions (2-, 7-, 12-positions) of truxene, that is, to three terminals of the equilateral triangle truxene skeleton, forming polar A-π-D_2 or A_2-π-D kinds of D-and-A substituted molecules: 2-dimesitylboryl-7,12-di(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (**BN2**) and 2,7-di(dimesitylboryl)-12-(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (**B2N**). **BN2** and **B2N** show large and anomalous solvatochromism, which is very sensitive to aprotic or protic polarity. For comparison, six D-or-A substituted truxene derivatives, namely, **B1**, **B2**, **B3**, **N1**, **N2**, and **N3** (see Scheme 1), have also been synthesized.

Organoboron compounds as fluorescent fluoride ion probes have been investigated by several groups, and the $F^- \rightarrow B$ coordination has been verified by ^{11}B, ^{19}F NMR, and by X-ray structure determination.[17−22] Many fluorescent probes belong to the turn-off or turn-on types, that is, fluorescence is thus quenched or enhanced in the presence of fluoride ions. In fact, our compounds **B1**, **B2**, and **B3** are just the turn-off type, while **BN2** and **B2N** simultaneously exhibit turn-off and turn-on effects, which make them much more sensitive as fluoride ion probes. The syntheses and the novel multifunctional fluorescent probe properties of the **BN2** and **B2N**, together with those of other related compounds, will be reported herein.

Results and Discussion

Synthesis. As shown in Scheme 1, the acceptor substituted compounds **B1**, **B2**, and **B3** or their donor substituted counterparts **N1**, **N2**, and **N3** can be obtained synchronously by boronation or amination to 2,7,12-tribromohexaethyltruxene (**8**) or 2,7,12-triiodohexaethyltruxene (**9**).

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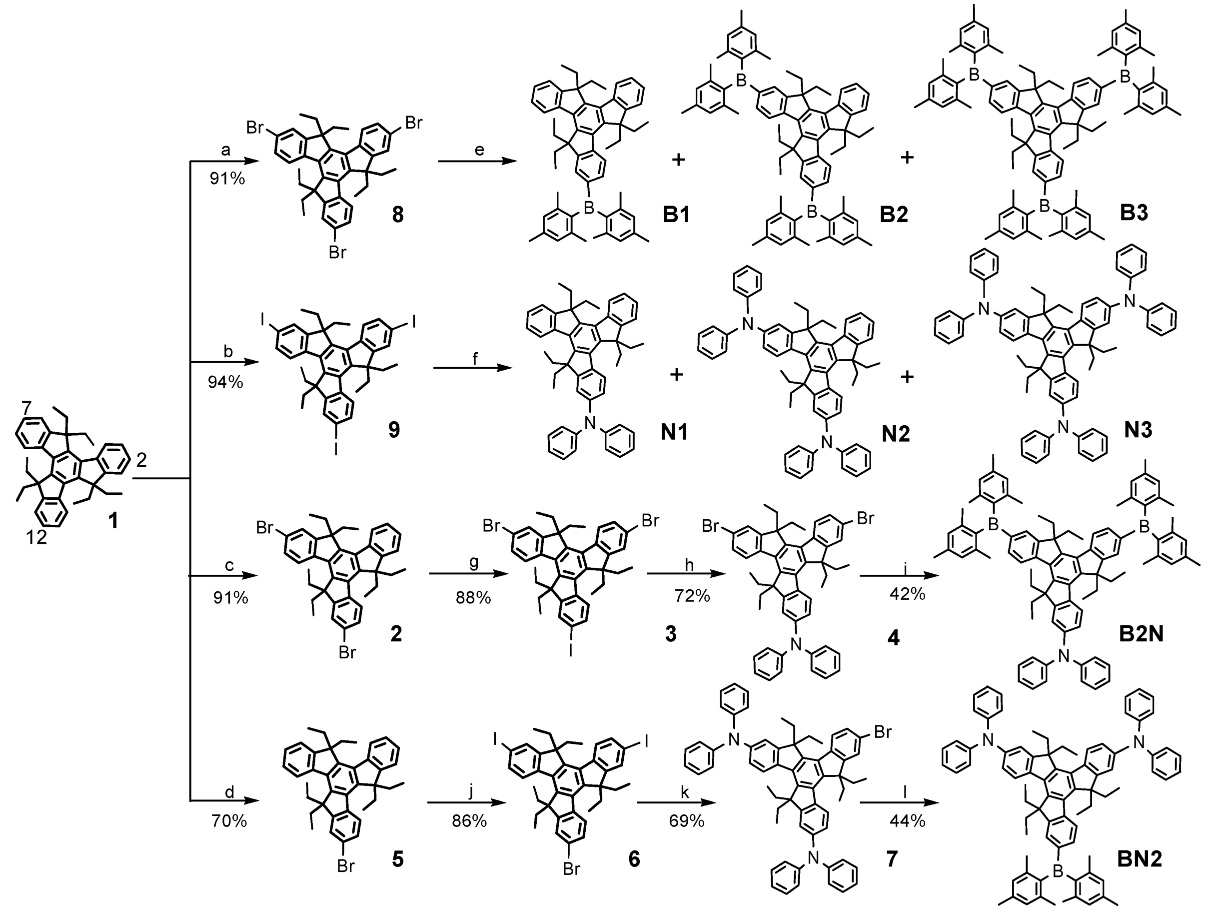
SCHEME 1. Synthesis of Title Compounds[a]



[a] Reaction conditions: (a) bromine, CH_2Cl_2, 25 °C, 12 h; (b) (g) and (j) HIO_3, I_2, $CH_3COOH-H_2SO_4-H_2O-CCl_4$, 80 °C, 4 h; (c) and (d) 1,2-propanediol carbonate, NBS, 60 °C, 2 h; (f), (h), and (k) diphenylamine, K_2CO_3, Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h; (e) (i) and (l) dimesitylboron fluoride, *n*-BuLi, THF, −78 °C, 2 days.

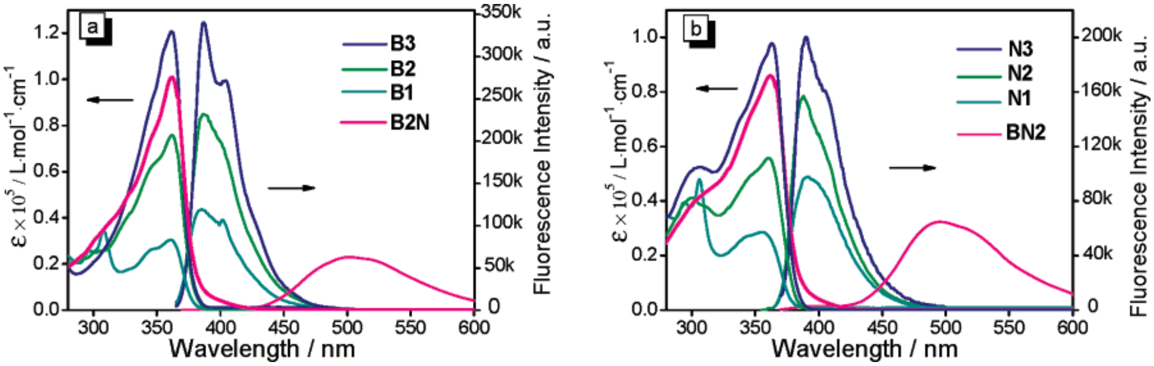


FIGURE 1. (a) Absorption and fluorescence spectra ($\lambda_{ex} = 360$ nm) of **B1**, **B2**, **B3**, and **B2N** in THF with $c = 1.0 \times 10^{-5}$ mol/L; (b) of **N1**, **N2**, **N3**, and **BN2**.

The key procedure of synthesizing **BN2** and **B2N** is quantitative bromination and iodination of compound **1**. We can change the ratio of NBS and **1** to make the main product mono- or disubstituted. The resultant mixture of **2** and **5** was very difficult to separate by column chromatography, and they were separated by repetitive recrystallizations in 1,2-propanediol carbonate. Compound **4** or **7** was obtained via Cu-mediated Ullmann condensation of **3** or **6**. Schlenk techniques were used to obtain **BN2** or **B2N** by reacting **4** or **7** with dimesitylboron fluoride in the presence of *n*-BuLi. The C_3 symmetric compounds **B3** and **N3** have been reported in our previous work,[16l] and all of the other polar compounds (**B1**, **B2**, **N1**, **N2**, **BN2**, **B2N** as well as precursors **2**, **3**, **4**, **5**, **6**, **7**) are reported herein for the first time.

Bathochromic Emission and CT Properties. As shown in Figure 1 and Table 1, with increasing substituent (**B1**(**N1**) → **B2**(**N2**) → **B3**(**N3**)), the intensity of the absorption band at 360 nm increased. The molar extinction coefficient ϵ_{max} of this band of all eight compounds (**B1**, **B2**, **B3**, **N1**, **N2**, **N3**, **B2N**, and **BN2**) is approximately proportional to the number of branches, but the absorption maximum λ_{abs} is basically invariant, despite the number and the nature of the substituent group. The absorption maximum λ_{abs} of **N3** has a ~20 nm red shift relative

TABLE 1. Photophysical Data (in THF) of the Subject Compounds

	λ_{abs}[a] (nm)	ϵ_{max} (10^4 M^{-1} cm^{-1})	λ_F[a] (nm)	$\Delta\tilde{\nu}$[b] (10^3 cm^{-1})	$\Delta\tilde{\nu}/\Delta f$[c] ($10^3$ cm^{-1})	Φ[d]	$\Phi\epsilon_{max}$[e] (10^4 M^{-1} cm^{-1})	τ[f] (ns)	τ_0[g] (ns)	μ_g[h] (Debye)
B1	358 (358)	3.0	385	1.96	6.7	0.56	1.7	3.2	5.7	0.55
B2	362 (361)	7.6	387	1.78	5.2	0.40	3.0	4.2	10.5	0.48
B3	362 (360)	12.1	386	1.72	4.3	0.34	4.1	4.4	12.9	0.046
N1	356 (356)	2.9	392	2.58	5.9	0.49	1.4	1.6	3.3	0.22
N2	360 (360)	5.6	390	2.14	5.0	0.36	2.0	1.9	5.3	0.20
N3	364 (363)	9.8	390	1.83	4.7	0.27	2.6	2.1	7.8	0.021
BN2	362 (361, 450)	8.6	496	7.46	19.9	0.21	1.8	14.4	68.6	0.89
B2N	362 (362, 448)	10.1	500	7.62	19.7	0.20	2.0	18.1	90.5	0.87

[a] Absorption and fluorescence maxima with $c = 1.0 \times 10^{-5}$ mol/L; the values in parentheses are calculated by TD-DFT method (for simplicity, ethyl groups in truxene and methyl groups in mesityl have been replaced by a H atom). [b] Stokes shift. [c] The slope of plot of $\Delta\tilde{\nu}$ versus Δf in aprotic solvents based on the Lippert−Mataga equation, where $\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$. [d] Fluorescence quantum yield determined using coumarin 307 as standard. [e] Scaled for fluorescence intensity. [f] Fluorescence lifetime. [g] Radiative lifetime defined by $\tau_0 = \tau/\Phi$. [h] The calculated ground state dipole moment by DFT method (see SI).

to that of 1,3,5-($NPh_2-C_6H_4)_3(C_6H_3)$ in the same solvent,[23] indicating that the planarity and π-conjugation of truxene are better than those of 1,3,5-triphenylbenzene.

When considering the emission and solvatochromic properties, the title compounds can be divided into two groups. The first group consists of D-or-A substituted compounds (**B1**, **B2**, **B3**, **N1**, **N2**, **N3**), which emit blue fluorescence at about 390 nm in THF with a short lifetime (τ < 5 ns) and show moderate Stokes shift (ca. 2000 cm^{-1}; see Table 1). The second group consists of D-and-A substituted **B2N** and **BN2**, which emit green light around 500 nm in THF with much longer lifetime (τ > 10 ns) and show extremely large Stokes shift ($\Delta\tilde{\nu}$ > 7000 cm^{-1}). Comparing **N3** with **BN2**, or **B3** with **B2N**, we can see that the substitution of an N (B) for a B (N) atom results in more than a 100 nm red shift of the fluorescence, whereas a large chemical diversity among the D-or-A substituted compounds did not result in a significant spectral difference.

In order to understand the spectral behaviors, we carried out a TD-DFT (time-dependent density functional theory) calculation at the B3LYP/6-31G* level (see Supporting Information (SI hereafter) for details). For the D-or-A substituted compounds, the lowest-lying allowed transition is located at 360 nm, and there are no (allowed or forbidden) transitions longer than this wavelength. For D-and-A substituted **BN2** and **B2N**, the most allowed transition is also at 360 nm, but another weak transition (with the oscillator strength being $f = 0.02$) appears at 450 nm. Figure 1 indeed shows relatively strong absorption of **BN2** and **B2N** in the right-hand tails of the absorption profiles.

Our subject molecules are all rigid, and we can assume that the molecular conformations do not undergo large changes in the course of relaxation from the Frank−Condon state to the fluorescent state. Therefore the LUMO of (**BN2** and **B2N**) shown in Figure 2 may be close to their fluorescent state. The calculated weak transition ($f = 0.02$) between the LUMO and HOMO is consistent with the much longer radiative lifetime τ_0 (shown in Table 1), and the corresponding transition wavelength (450 nm) is in agreement with the dramatically red-shifted emission. One can notice that LUMOs of **BN2** and **B2N** are of the CT state (Figure 2).

Solvatochromism and Polarity Sensing. The absorption spectral properties of all these compounds are basically independent of the solvent. However, their emission spectra exhibit positive solvatochromism. As shown in Figures 3, 4, and Table 3 (in SI), the solvatochromism is moderate for the D-or-A substituted compounds and extraordinarily large for the D-and-A substituted ones. The emission maxima of **BN2** and **B2N** extend from about 420 nm (blue-violet in hexane) to about 580 nm (salmon pink in acetonitrile), spanning 160 nm of the spectral region. This broad region offers real possibility to enhance their sensitivity as polarity probes. They show distinct color changes in different aprotic solvents under UV light excitation (Figure 3).

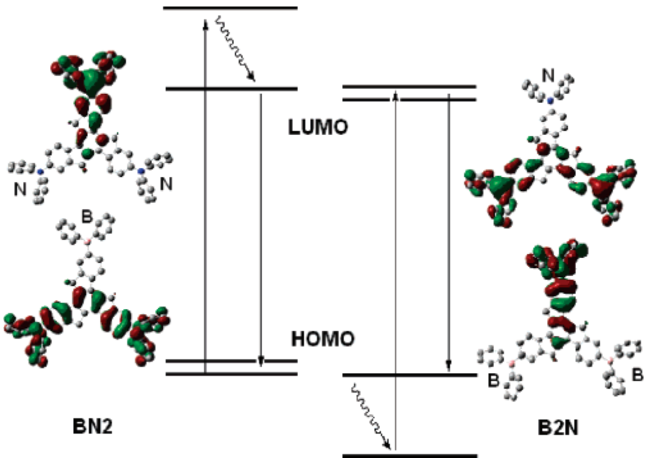


FIGURE 2. Schematic of the frontier molecular orbitals, energy levels, and transitions of **BN2** and **B2N** based on TD-DFT calculation. Due to the large molecular size, the ethyl and methyl groups have been replaced by a H atom, and the reduced structures have been further optimized by DFT methods.

It is known that solvatochromic effect is associated with the CT of a molecule and that the degree of CT can be estimated by the Lippert equation:[24]

$$\Delta\tilde{\nu}_{st} = 2\Delta\mu_{eg}{}^2\Delta f/hca^3 + \text{const}$$

where $\Delta\tilde{\nu}_{st}$ is the Stokes shift, $\Delta\mu_{eg}$ is the dipole moment difference between the excited state and the ground state, Δf is the orientation polarizability expressed as $\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$, ϵ and n are the dielectric constant and refractive index of the solvent, and a is the cavity radius of the molecule. By the Lippert equation, the slope of the $\Delta\tilde{\nu}_{st} - \Delta f$ plot, symbolized as $\Delta\tilde{\nu}/\Delta f$, can be a measure of $\Delta\mu_{eg}$.

As shown in Figure 4 and Table 1, the $\Delta\tilde{\nu}/\Delta f$ values of the six D-or-A compounds are almost the same. The $\Delta\tilde{\nu}/\Delta f$ values of the D-and-A compounds **BN2** or **B2N** are also virtually identical and 4 times that of the D-or-A compounds. On the basis of the similar molecular dimensions among **B3**, **N3**, **BN2**,

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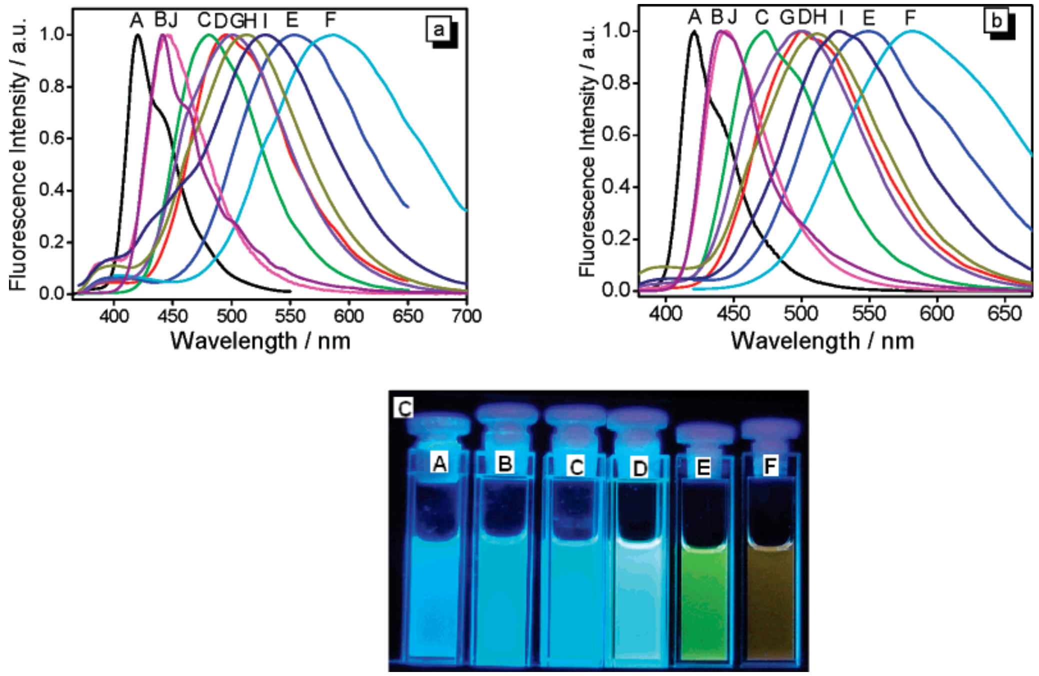

FIGURE 3. Normalized emission spectra of **BN2** (a) and **B2N** (b) in different solvents ($c = 1.0 \times 10^{-5}$ mol/L, $\lambda_{ex} = 360$ nm; A, hexane; B, toluene; C, $CHCl_3$; D, THF; E, acetone; F, CH_3CN; G, *n*-PrOH; H, EtOH; I, MeOH; J, H_2O). (c) Fluorescence of **B2N** in various aprotic solvents under UV light.

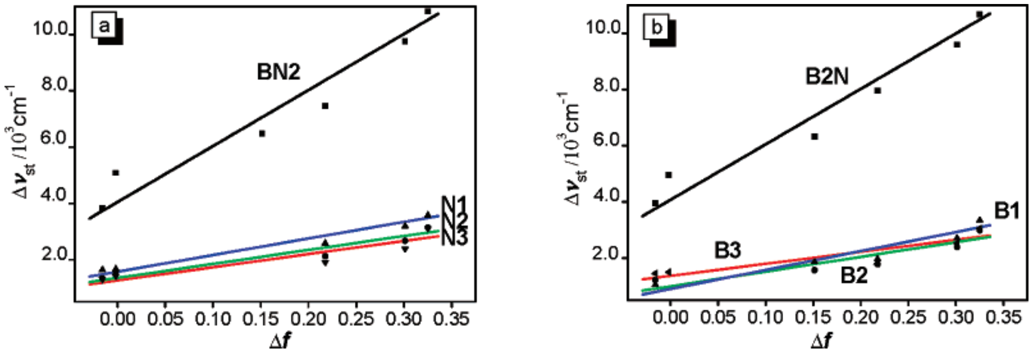

FIGURE 4. Stokes shift $\Delta\tilde{\nu}_{st}$ versus orientation polarizability Δf of the aprotic solvents (the detailed solvents can be found in Figure 5b): (a) for **BN2**, **N1**, **N2**, and **N3**; (b) for **B2N**, **B1**, **B2**, and **B3**.

and **B2N** and on the calculated ground dipole moment μ_g in Table 1, we conservatively estimate that the excited dipole moment μ_e of **BN2** or **B2N** is at least twice the μ_e of **N3** or **B3**:

$$\mu_e\ (\mathbf{BN2}\ \text{or}\ \mathbf{B2N}) > 2\mu_e\ (\mathbf{N3}\ \text{or}\ \mathbf{B3})$$

This indicates that the polarity of the **BN2** and **B2N** in the excited state has been greatly enhanced.

Protic versus Aprotic Response. Compounds **BN2** and **B2N** show anomalous solvatochromism compared with other reported solvatochromic fluorescent probes. As shown in Figure 5a, common solvatochromic probes such as methyl 2-[6-(dimethylamino)-2,3-naphthalimido] acetate (**6DMN-GlyOMe**) usually produce relatively smaller Stokes shifts in aprotic solvents than in protic solvents.[2,3,5−8] The points in protic solvents in the $\Delta\tilde{\nu} - \Delta f$ graph are generally above the line describing the aprotic solvents. However, for the case of **BN2** and **B2N**, it is the opposite. Their emission maxima are located at a relatively shorter wavelength in the protic solvents, which means, in protic solvents, the points lie under the $\Delta\tilde{\nu} - \Delta f$ line of aprotic solvents (see Figure 5b).

As shown in Figure 5, by combining the normal probes and the anomalous **BN2** or **B2N**, we can acquire the aprotic-or-protic information of a polar environment, and this selectivity may be useful in biological and environmental research. For example, the emission maxima of **6DMN-GlyOMe** are $\lambda = 549$ nm in CH_3CN and 589 nm in MeOH,[6] those of **B2N** are $\lambda = 582$ nm in CH_3CN and 528 nm in MeOH. In an unknown environment, if the emission maximum of **B2N** is at about 580 nm, this may be a highly polar aprotic environment; if the emission maximum of **B2N** is at about 530 nm and that of **6DMN-GlyOMe** is at about 580 nm, we know this is a protic environment.

The unique solvatochromism of (hydroxyl-based) protic versus aprotic solvents may be partly attributed to the interactions between the nitrogen donor and the acidic hydrogen of the hydroxyl group (N···H−OR hydrogen bonding), which

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(24) (a) Von Lippert, E. *Z. Naturforsch A: Phys. Sci.* **1955**, *10*, 541. (b) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690. (c) Von Lippert, E. *Z. Electrochem.* **1957**, *61*, 962.

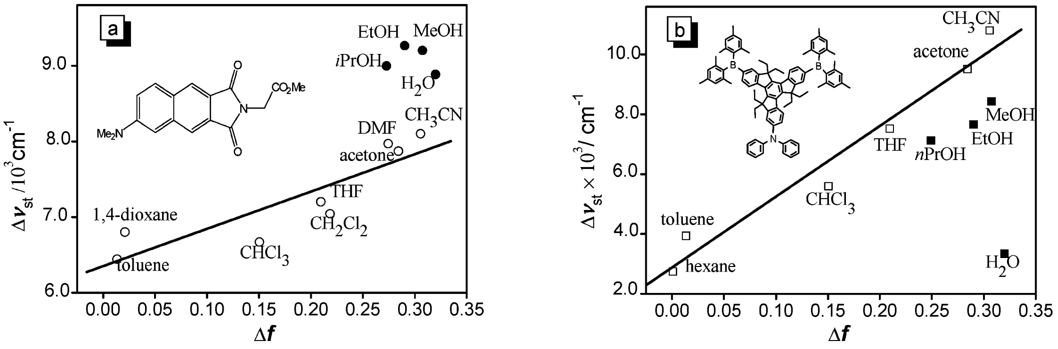

FIGURE 5. Stokes shift $\Delta\tilde{\nu}_{st}$ versus orientation polarizability Δf of the solvents: (a) for **6DMN-GlyOMe** (○, aprotic solvents; ●, protic solvents)[6] and (b) for **B2N** (□, aprotic solvents; ■, protic solvents).

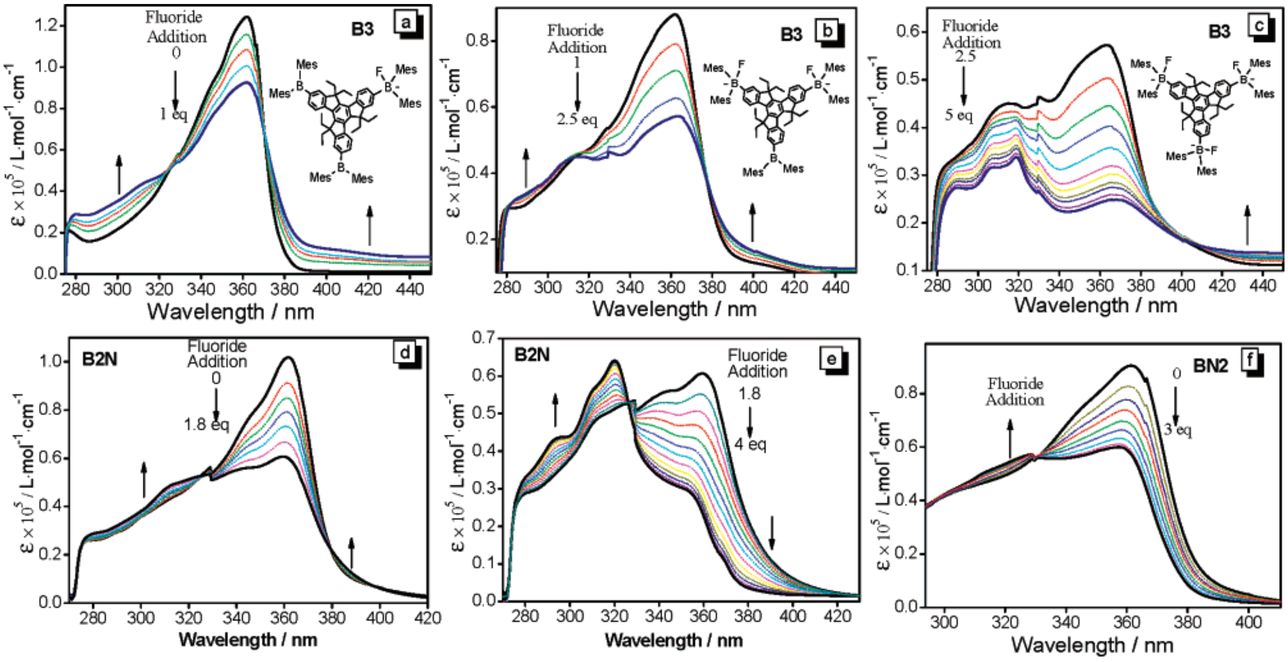

FIGURE 6. Absorption spectra for the titration of **B3**, **B2N**, and **BN2** ($c = 1.0 \times 10^{-5}$ mol/L in THF) with *n*-Bu$_4$NF solution of THF: (a), (b), and (c) of **B3**; (d) and (e) of **B2N**; (f) of **BN2**.

reduce the donor capability and truncate the π-delocalization. The much blue-located emission in water shows the extreme case, where the donating function of $-NPh_2$ in **BN2** and **B2N** has been greatly extinguished by $N \rightarrow H^+$ or $N\cdots H-O-H$ interactions.

Fluoride Ion Sensing and $F^- \rightarrow B$ Coordination. Compounds **B1**, **B2**, **B3**, **BN2**, and **B2N** are sensitive to the fluoride ion. As shown in Figure 6 and in SI, on addition of *n*-Bu$_4$NF to a THF solution of **B3**, a gradual decease in intensity of the 360 nm absorption band was observed, and the 280−330 nm band emerges and grows. The evolution of the absorption curves of **BN2** or **B2N** with the titration of the F^- are similar, but not as sharp as that of **B3**. The binding constants of the five compounds with fluoride ion have been determined based on the absorption titrations (Table 2).

TABLE 2. The Binding Constants of F^- to B1, B2, B3, BN2, and B2N

	K_1 (M^{-1})	K_2 (M^{-1})	K_3 (M^{-1})
B1	3.1×10^5		
B2	2.9×10^5	2.8×10^4	
B3	3.9×10^5	2.5×10^4	1.6×10^4
BN2	2.5×10^5		
B2N	3.1×10^5	2.2×10^4	

As shown in Figure 7a, the blue emission band of **B3** has been gradually quenched in the course of F^- titration. This turn-off type of spectral signal change is not very sensitive, for the quenching may be caused by other external factors. Recently, Wang and co-workers have reported the turn-on type of fluorescence sensor which made progress compared with the turn-off type of fluoride ion probe.[20a] As shown in Figure 7b, with the decreasing of the green emission peak at 500 nm, a new blue peak at 380 nm progressively develops in the course of F^- titration. This means that the evolution of the emission spectra of **BN2** and **B2N** shows both the turn-off and turn-on characters. Similar spectral behaviors have been observed with other molecular or polymeric systems,[18,20−22] whereas the "off-and-on" character of the emission spectra of **BN2** and **B2N** is more significant because their two strong peaks are well-separated by a spacing of 120 nm.

This characteristic color change makes the detection of F^- more convenient and less subject to external factors. Furthermore, the off-and-on property of **BN2** or **B2N** means they can act as highly sensitive and selective (see SI) sensors in the

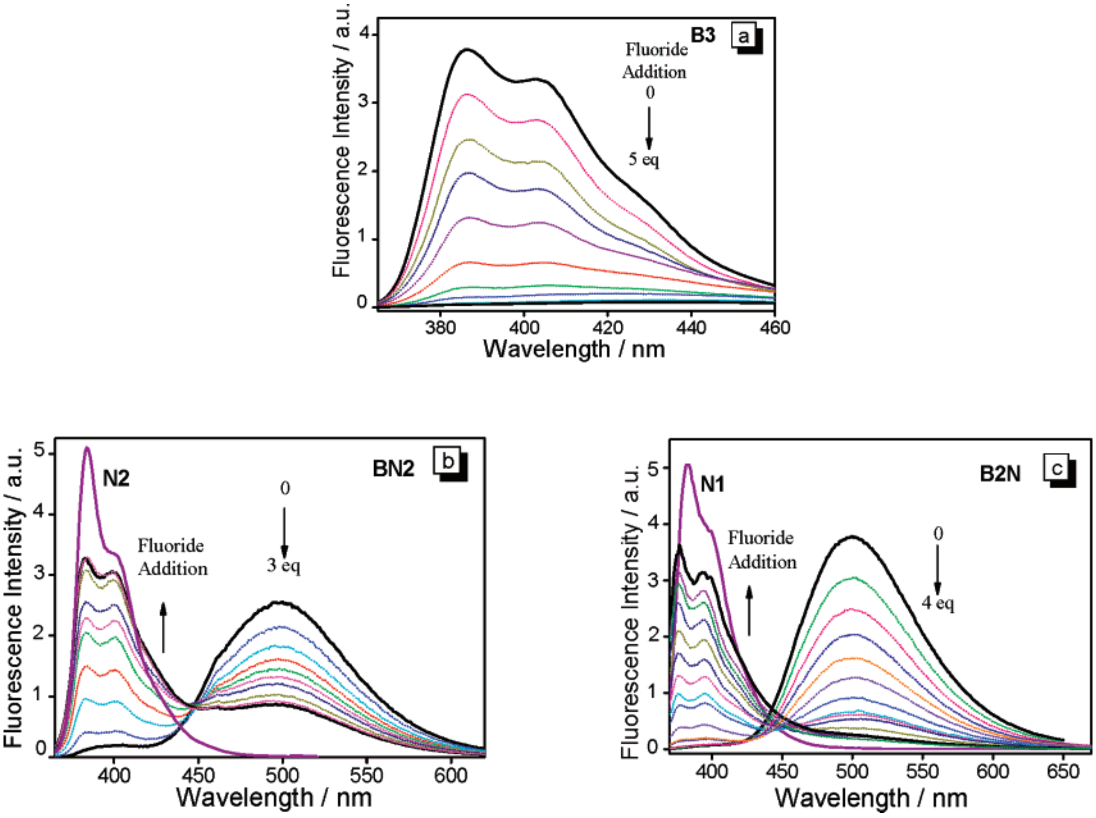

FIGURE 7. Emission spectra for the titrations of **B3** (a), **BN2** (b), and **B2N** (c) ($c = 1.0 \times 10^{-5}$ mol/L in THF, $\lambda_{ex} = 360$ nm, **N1** and **N2** in toluene) with n-Bu$_4$NF solution of THF.

fluorescent ratiometric method.[18,25] The sensitivity can be enhanced by measuring the ratio of the fluorescence intensities at two different wavelengths.

As shown in Figure 7b and c, the emission spectra approach an asymptotic profile in the off-and-on evolution with a total addition of 3 or 4 equiv of the F^- to the **BN2** or **B2N** solution, respectively. It is noteworthy that the asymptotic emission spectra of the F^- coordinate-saturated solution of **BN2** or **B2N** are close to the emission spectra of compounds **N2** or **N1**, respectively, as if the $-B(Mes)_2$ acceptor had been removed or shielded.

This suggests that the $F^- \rightarrow B$ coordination changes the trivalent boron to tetravalent one, saturating the acceptor. The loss of the acceptor greatly reduces the CT, quenches the CT emission band, and the fluorescence spectra appear to be those of no-acceptor compounds. Fortunately, the turn-off of the CT emission band (500 nm) in **BN2** or **B2N** is accompanied by the turn-on of the emission band (380 nm) of **N2** or **N1**. This interesting property of **BN2** and **B2N** enables them to be highly sensitive fluoride ion probes.

Conclusion

Two functional groups ($-N(Ph)_2$ donor and $-B(Mes)_2$ acceptor) have been substituted into the three "corners" of the triangular truxene molecule, resulting in eight compounds: the D-or-A substituted **B1**, **B2**, **B3**, **N1**, **N2**, **N3** and the D-and-A substituted **BN2** and **B2N**. All D-or-A substituted members are quite different in chemical composition but show similar spectral behaviors. On the other hand, larger spectral changes are observed for **BN2** and **B2N**, where effective charge transfer (CT) exists.

The 110 nm red shift of the emission peak of D-and-A compounds (**BN2** and **B2N**) relative to all the D-or-A compounds can be interpreted as the result of nesting a CT state (HOMO or LUMO) between the 360 nm of energy gap of the D-or-A compounds (see Figure 2).

The 160 nm red shift (420 nm in hexane to 580 nm in acetonitrile) and the proton-dependent solvatochromism of the emission of **BN2** and **B2N** are evidence of their highly polar CT fluorescent state and can be used to probe the polarity of solutions and further to identify protic and aprotic environments.

In the presence of fluoride ion, the fluorescence peak position of **BN2** or **B2N** can be blue shifted to that observed for **N2** or **N1**. Thus **BN2** and **B2N** prove to be promising fluoride ion probes based on their highly sensitive off-and-on spectral response of the fluorescence.

We have shown that the multifunctional probe abilities of **BN2** and **B2N** can be related to their novel CT properties, as well as to their versatile N···H−O hydrogen bonding and $F^- \rightarrow B$ coordination.

Experimental Section

Synthesis of 2-Dimesitylboryl-7,12-di(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (BN2). n-BuLi (2.8 M solution in n-hexane, 0.50 mL, 1.40 mmol) was added to a stirred solution of compound **7** (0.45 g, 0.49 mmol) in THF (15 mL) under nitrogen at −78 °C over 20 min, and followed by warming to room temperature naturally. After reacting for further 4 h, the reactants

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[25] (a) Yang, R. H.; Li, K. A.; Wang, K. M.; Zhao, F. L.; Li, N.; Liu, F. *Anal. Chem.* **2003**, *75*, 612. (b) Xu, Z. C.; Xiao, Y.; Qian, X. H.; Cui, J. N.; Cui, D. W. *Org. Lett.* **2005**, *7*, 889.

were cooled to −78 °C again, and dimesitylboron fluoride (0.38 g, 1.42 mmol) in THF (5 mL) was injected over 20 min. The temperature was allowed to naturally rise to room temperature and the mixture continuously stirred for 2 days. Then the reactants were diluted with ethyl acetate, washed with water, and dried over magnesium sulfate. After removing solvents, the crude product was obtained. After purified by column chromatography on silica gel, eluting with dichloromethane/petroleum ether (1:8), compound **BN2** was obtained (0.23 g, 44%, $R_f = 0.37$) as a white powder: mp 331−333 °C; ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ 0.17−0.29 (m, 18H), 1.90−2.06 (m, 18H), 2.33 (s, 6H), 2.83−2.90 (m, 6H), 6.85 (s, 4H), 7.00−7.58 (m, 26H), 8.08−8.21 (m, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) δ 153.8, 153.7, 151.4, 147.5, 145.9, 144.2, 143.4, 140.5, 138.1, 137.9, 135.0, 134.8, 134.6, 129.4, 128.7, 127.7, 124.9, 123.7, 123.6, 122.2, 121.5, 117.2, 56.2, 56.1, 29.2, 28.8, 28.7, 23.1, 20.8, 8.2, 8.0; UV−vis (THF, 1.0×10^{-5} mol/L) λ/nm (ϵ/dm^3·mol^{-1}·cm^{-1}) 362 (86 000); MALDI-TOF *m*/*z* 1093.7 [M^+], 1064.7 [$M - 29$]$^+$. Anal. Calcd for $C_{81}H_{81}BN_2$: C, 88.98; H, 7.47; N, 2.56. Found: C, 88.81; H, 7.63; N, 2.34.

Synthesis of 2,7-Di(dimesitylboryl)-12-(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (B2N). *n*-BuLi (2.8 M solution in *n*-hexane, 2.00 mL, 5.60 mmol) was added to a stirred solution of compound **3** (1.10 g, 1.32 mmol) in THF (30 mL) under nitrogen at −78 °C over 20 min, and followed by warming to room temperature naturally. After reacting for further 4 h, the reactants were cooled to −78 °C again, and dimesitylboron fluoride (1.34 g, 5.00 mmol) in THF (10 mL) was injected over 30 min. The temperature was allowed to naturally rise to room temperature and the mixture continuously stirred for 2 days. Then the reactants were diluted with ethyl acetate, washed with water, and dried over magnesium sulfate. After removing solvents, the crude product was obtained. After purified by column chromatography on silica gel, eluting with dichloromethane/petroleum ether (1:8), compound **B2N** was obtained (0.65 g, 42%, $R_f = 0.49$) as a white powder: mp >400 °C; ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ 0.16−0.28 (m, 18H), 1.52−2.06 (m, 30H), 2.34 (s, 12H), 2.86−2.92 (m, 6H), 6.85 (s, 8H), 7.02−7.60 (m, 16H), 8.12−8.27 (m, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) δ 153.8, 151.5, 151.3, 147.4, 146.1, 145.1, 144.7, 144.1, 143.9, 141.6, 140.5, 138.3, 138.2, 138.1, 138.0, 134.7, 129.4, 128.8, 127.7, 123.8, 123.7, 123.6, 122.3, 117.1, 56.4, 56.3, 56.2, 29.2, 28.8, 28.6, 23.1, 20.8, 8.2, 8.0; UV−vis (THF, 1.0×10^{-5} mol/L) λ/nm (ϵ/dm^3·mol^{-1}·cm^{-1}) 362 (101000); MALDI-TOF *m*/*z* 1174.8 [M^+], 1145.8 [$M - 29$]$^+$. Anal. Calcd for $C_{87}H_{93}B_2N$: C, 88.98; H, 7.98; N, 1.19. Found: C, 88.71; H, 8.12; N, 1.11.

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Supporting Information Available: Syntheses, relevant spectral graphs, and data of compounds **B1**, **B2**, **B3**, **N1**, **N2**, and **N3**; the calculation of binding constants; the computational work and results of **B3**, **N3**, **BN2**, and **B2N**. This material is available free of charge via the Internet at http://pubs.acs.org.

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