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The synthesis, photophysical properties and fluoride anion recognition of a novel branched organoboron compound

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ABSTRACT

A novel two-branched organoboron compound, *N*,*N*-bis(7-dimesitylboryl-9,9-diethyl-9*H*-fluorene-2-yl)aniline, containing a phenylamino group as a π-electron donor, fluorene groups as π-bridges and dimesitylboryl groups as electron acceptors, was synthesized and its photophysical properties in various solvents as well as its fluoride anion recognition properties were investigated. The synthesised compound exhibited strong fluorescence in all solvents with the fluorescence changing from blue to orange on going from solvents of low polarity to those of high polarity. The compound was able to recognize fluoride anions in high sensitivity owing to strong interactions between boron atoms and fluoride anions.

1. Introduction

The heteroatom boron, especially three-coordinate boron, exhibits special effects in many organic functional materials. Owing to its vacant *p*-orbital, trivalent boron is capable of accepting electron density from electron-donating groups through conjugated systems. Thus, trivalent boron-containing groups should be strong π-electron acceptors. Many materials containing three-coordinate organoboron groups exhibit interesting fluorescence emission, nonlinear optical [1], electron-transporting [2], and anion sensing properties [3–5]. Among these, the detection of fluoride anion is an important application of such organoboron species [2].

In recent years, our group has developed a series of dimesitylboryl-containing dipolar donor-π-acceptor type compounds and examined their two-photon excited fluorescence properties [6,7] and utility as chemosensors for fluoride anions with high selectivity and sensitivity [5]. For an ideal two-photon sensor, a large two-photon absorption cross-section, high fluorescence quantum yield and high photo and thermal stability are necessary factors. Over the past ten years, extensive research has established that multi-branched systems show larger two-photon absorption cross-section than their linear analogues, because of the inter-branch coupling effect [8–12]. In particular, three-coordinate nitrogen cored three-branched systems show this effect markedly [13]. However, V-shaped two-branched systems have not been adequately examined.

In this paper, the synthesis, photophysical properties and fluoride anion recognition properties of a novel V-shaped two-branched compound with phenylamino as a terminal electron-donor group and dimesitylboryl groups as electron-acceptor groups are reported.

As shown in Fig. 1, our basic idea was to build a branched system by combining two typical D-π-A systems. In view of its perfect planarity, π-conjugation, thermal and photochemical stabilities, the fluorenyl group, which confers excellent stability to the molecules in both the solid state and in solution [14,15], was chosen as the π-electron bridge. Dimesitylboryl groups were selected as the electron-acceptors. The mesityl group is used to protect the boron from attack by nucleophiles such as water, and to stabilize the charge in the excited state. Furthermore, the steric hindrance of the mesityl group will decrease the possibility of complexation of any other anion larger than fluoride with the boron atom [16].

2. Experimental section

2.1. *Synthesis of* N,N-*bis(7-dimesitylboryl-9,9-diethyl-9*H-*fluorene-2-yl)aniline (**B$_2$N**)*

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer. MALDI-TOF experiments were

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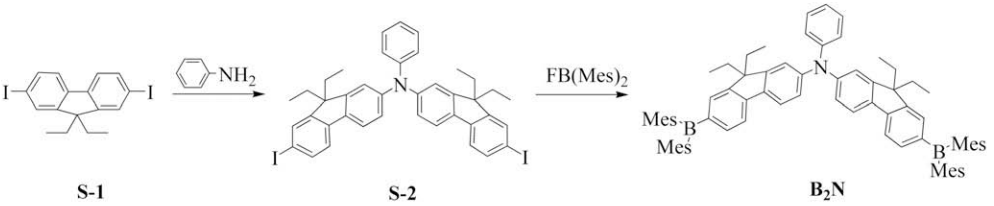


Fig. 1. Synthetic routes of the title compound **B$_2$N** (Mes = 2,4,6-trimethylphenyl).

carried out using a Shimadzu AXIMA-CFRTM plus time-of-flight mass spectrometer (Kratos Analytical, Manchester, U.K.). The melting point was measured on a Mettler-Toledo DSC822e differential scanning calorimeter at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. Elemental analyses were carried out on a PE 2400 autoanalyzer.

N,*N*-bis(7-dimesitylboryl-9,9-diethyl-9*H*-fluorene-2-yl)aniline was synthesized via two key steps (Fig. 1). Firstly, aniline was reacted with 2 equiv of 2,7-diiodo-9,9-diethyl-9*H*-fluorene (**S-1**) via a Cu-mediated Ullmann reaction at high temperature to afford **S-2** in 83% yield. *N*,*N*-Bis(7-dimesitylboryl-9,9-diethyl-9*H*-fluorene-2-yl)aniline was prepared in 45% yield by lithium/halogen exchange of the iodine atoms on **S-2** with *n*-butyllithium, followed by substitution with dimesitylboron fluoride, at low temperature (−78 °C). This compound was fully characterized by NMR, mass spectroscopy and elemental analysis.

2.1.1. N,N-Bis(7-iodo-9,9-diethyl-9H-fluorene-2-yl)aniline (S-2)

A mixture of aniline (0.34 g, 3.7 mmol), 2,7-diiodo-9,9-diethyl-9*H*-fluorene (4.3 g, 9.1 mmol), potassium carbonate (5.1 g, 37 mmol), copper bronze (0.47 g, 7.4 mmol), 18-crown-6 (0.16 g, 0.6 mmol), and 1,2-dichlorobenzene (80 mL) was heated under reflux for 8 h. After cooling to room temperature, the precipitate was filtered off and the filtrate was purified by column chromatography on silica gel using chloroform/petroleum ether (1:10) as the eluent to give **S-2** as a yellow-green powder (2.4 g, 83%). ^{1}H NMR, δ ($CDCl_3$, 400 MHz): 0.34 (t, *J* = 7.0 Hz, 12H, CH_3, ethyl), 1.79 ~ 1.88 (m, 4H, CH_2, ethyl), 1.89 ~ 2.00 (m, 4H, CH_2, ethyl), 7.02 ~ 7.06 (m, 3H, CH, Ar), 7.09 (s, 2H, CH, Ar), 7.14 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.28 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.36 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.42 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.54 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.61 (d, 2H, *J* = 8.0 Hz, CH, Ar).

2.1.2. N,N-Bis(7-dimesitylboryl-9,9-diethyl-9H-fluorene-2-yl)aniline (B$_2$N)

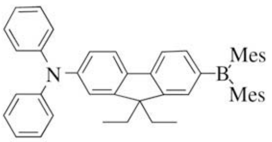
A sample of 1.8 g (2.3 mmol) of **S-2** and 60 mL of freshly distilled THF were added into a three-necked flask under the cover of N_2. The flask was then cooled to −78 °C in a dry ice-acetone bath for about 30 min, and 3 mL of 3.2 M *n*-butyllithium in hexane solution was added dropwise. The mixture was stirred at −78 °C for about 1 h, and then allowed to warm to room temperature. The mixture was cooled to −78 °C again, and 1.3 g (4.8 mmol) of dimesitylboron fluoride in 10 mL freshly distilled THF, was injected quickly via a dry syringe. The mixture was stirred overnight, and then was poured into 200 mL of distilled water and extracted with dichloromethane. The organic solvent was removed using a rotary evaporator and the product was purified by column chromatography on silica gel using chloroform–petroleum ether (1:4) as the eluent to give the product as a yellow powder (1.0 g, 45%). M.p 232–233 °C, ^{1}H NMR, δ ($CDCl_3$, 400 MHz,): 0.30 (t, 12H, *J* = 7.0 Hz, CH_3, ethyl), 1.77 ~ 1.84 (m, 4H, CH_2, ethyl), 1.87 ~ 1.94 (m, 4H, CH_2, ethyl), 2.02 (s, 24H, CH_3, Mes), 2.32 (s, 12H, CH_3, Mes), 6.82 (s, 8H, CH, Mes), 7.03 (d, 1H, *J* = 7.0 Hz, CH, Ar), 7.05(s, 1H, CH, Ar), 7.07 (s, 1H, CH, Ar), 7.11 (s, 2H, CH, Ar), 7.15 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.28 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.43 (s, 2H, CH, Ar), 7.48 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.58 (d, 2H, *J* = 8.0 Hz, CH, Ar), 7.61 (d, 2H, *J* = 8.0 Hz, CH, Ar). ^{13}C NMR, δ ($CDCl_3$, 100 MHz,): (ppm) 152.5, 149.0, 148.1, 147.9, 145.3, 144.3, 142.1, 140.9, 138.4, 136.3, 136.1, 130.5, 129.3, 128.1, 124.3, 123.1, 122.9, 121.1, 118.7, 118.6, 56.1, 32.6, 23.5, 21.2, 8.5. MALDI-TOF MS *m*/*z* = 1029.32. Anal. Calc. for $C_{76}H_{81}B_2N$ (1030.11): C 88.62; H 7.93; N 1.36. Found: C 88.50; H 7.96; N 1.38.

2.2. Photophysical properties measurement

Linear absorption and single-photon fluorescence spectra of the new compound at a concentration of 1.0×10^{-5} M in various solvents were measured on a PE lambda 35 UV–vis spectrometer and an Edinburgh FLS920 fluorescence spectrometer, respectively. All the solvents used for absorption and fluorescence measurements were HPLC grade. Two-photon excited fluorescence spectra of **B$_2$N** and its linear dipolar counterpart **BN** [2-(*N*,*N*-diphenylamino)-7-dimesitylboryl-9,9-diethylfluorene, shown in Fig. 2] in THF at a concentration of 1.0×10^{-4} M were performed with a femtosecond Ti: sapphire laser as pump source. The wavelength, pulse width and repetition rate of the laser radiation were 800 nm, 200 fs and 76 MHz, respectively.

3. Results and discussion

The linear absorption and fluorescence emission spectra of **B$_2$N** in various solvents of differing polarity are shown in Figs. 3 and 4, respectively. The comprehensive photophysical properties are listed in Table 1. The shapes of the spectra show slight changes with increase in solvent polarity. The absorption spectra in low polarity solvents (hexane and toluene) exhibit obvious vibrational structure, which becomes less pronounced with increase in solvent polarity. However, the wavelength of the absorption maximum shows little dependence on solvent polarity, as they all lie in blue region (~420 nm). The fluorescence properties of **B$_2$N** including the emission maximum and quantum yield are obviously influenced by solvent polarity. With increase in solvent polarity, the emission maximum exhibits an obvious bathochromic shift, and there is a decrease in quantum yield, with the exception of that observed in hexane, which is less than those in toluene, chloroform and THF. Upon changing the apolar solvent hexane for the highly polar acetonitrile, the emission maximum of **B$_2$N** is red-shifted from 445 nm to 538 nm, a difference of 93 nm. Thus it can be inferred that the polarity of this compound in the ground state is small, but the polarity in the excited state is greatly increased due to intramolecular charge transfer. This difference also means that



BN

Fig. 2. Molecular structure of compound **BN**.

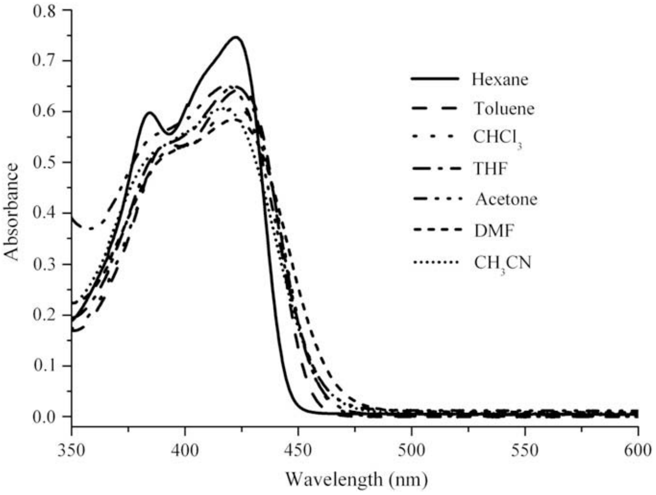


Fig. 3. Linear absorption of the title compound **B_2N** in various solvents with $C = 1.0 \times 10^{-5}$ M.

the boron-containing group acts as a strong π-acceptor in the excited state, but not in the ground state.

To examine the optical properties of this V-shaped branched system in context, a comparison with those of its linear dipolar counterpart **BN** [6] was carried out. It was found that, **B_2N** possesses longer wavelength absorption and fluorescence maxima, and exhibits weaker fluorescence solvatochromism relative to **BN**. Compared with **BN**, the absorption maximum of **B_2N** is obviously red-shifted and the absorbance greatly increases. For example, the $\lambda_{max}^{(abs)}$ of **B_2N** in THF is red-shifted by 22 nm (422 vs 400 nm [6]) and the absorbance increases 51% (64,800 vs 43,000 cm M^{-1}) relative to **BN**. Thus, it appears that there are intramolecular coupling effects between the branches connected by the phenylamino group. The difference between the fluorescence maximum of **B_2N** and that of **BN** decreases with increase in solvent polarity. For example, their solutions in highly polar acetonitrile exhibit fluorescence maxima at the nearly same wavelength. Using the Lippert equation [17], which relates the Stokes shift to the change in the molecular dipole moment between the ground and excited states, and the fact that the ground state dipole moments in related boron-containing compounds are relatively small, we can infer that the excited state dipole moment of **B_2N** is less than that of **BN**. This can be easily explained by regarding the dipole moment of **B_2N** as the sum of the vector addition of two (almost opposing) dipole moments of **BN**.

Table 1
Photophysical properties of **B_2N** in various solvents.

Solvents	λ_{abs} (nm)	ε_{max} (10^4 cm^{-1} mol^{-1} L)	λ_{SPEF} (nm)	Φ
Hexane	422	7.46	445	0.46
Toluene	424	6.44	461	0.53
$CHCl_3$	422	6.07	477	0.48
THF	422	6.48	490	0.48
Acetone	418	6.50	515	0.38
DMF	422	5.84	533	0.37
CH_3CN	417	6.06	538	0.34

Recently, Blanchard-Desce et al. [18] reported that for some multi-branched systems, although each branch makes a similar contribution to the transition from the ground state to the excited state, the transition from the excited state to the ground state is largely localised on one branch. It seems that this assumption can also explain the increased absorbance and decreased quantum yield of **B_2N** relative to those of **BN**. In fact **B_2N** exhibits a stronger fluorescence intensity for the same excitation intensity because of its larger $\Phi\varepsilon_{max}$ term.

The most interesting result is that this coupling enhanced effect also takes place for the two-photon absorption process. Both the compounds (**B_2N** and **BN**) do not absorb linearly in the range from 500 to 1000 nm. Therefore, any emission induced by excitation at this wavelength range should be derived from multiphoton absorption processes. The only reasonable excitation mechanism is a two-photon mechanism, i.e., simultaneous absorption of two photons by a single molecule.

The two-photon excited fluorescence spectra of the compounds excited at 800 nm in THF are recorded using a similar procedure to that previously reported [7]. As shown in Fig. 5, the two-photon excited fluorescence intensity of **B_2N** is nearly double that of **BN**. Considering that these intensities are proportional to the term of $\Phi\sigma_2$, we find that the two-photon absorption cross-section σ_2 of **B_2N** is nearly 3 times that of **BN**.

The possibility of using **B_2N** as a chemosensor for fluoride anion was also examined by titration experiments. Remarkable changes in the UV–vis absorption spectrum of **B_2N** in THF upon the addition of tetrabutylammonium fluoride (n-Bu_4NF, abbreviated as TBAF) are shown in Fig. 6. Upon the addition of TBAF, the characteristic intense charge-transfer absorption band between 350 nm and 450 nm with a maximum at 422 nm becomes weaker, and a new

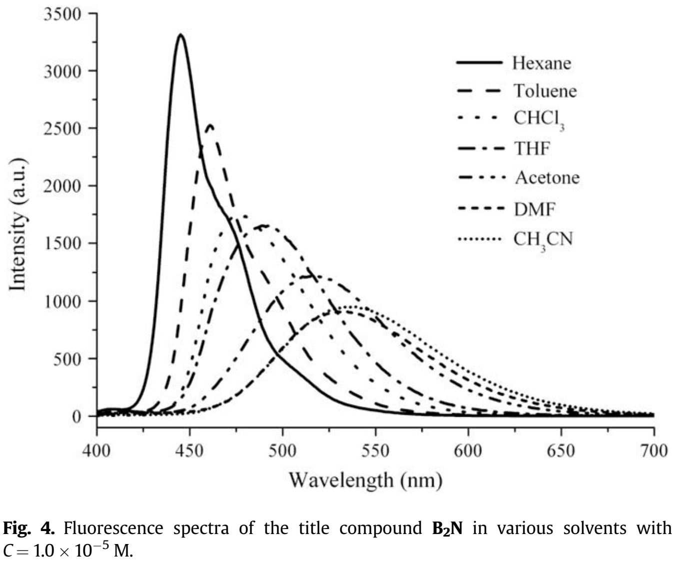


Fig. 4. Fluorescence spectra of the title compound **B_2N** in various solvents with $C = 1.0 \times 10^{-5}$ M.

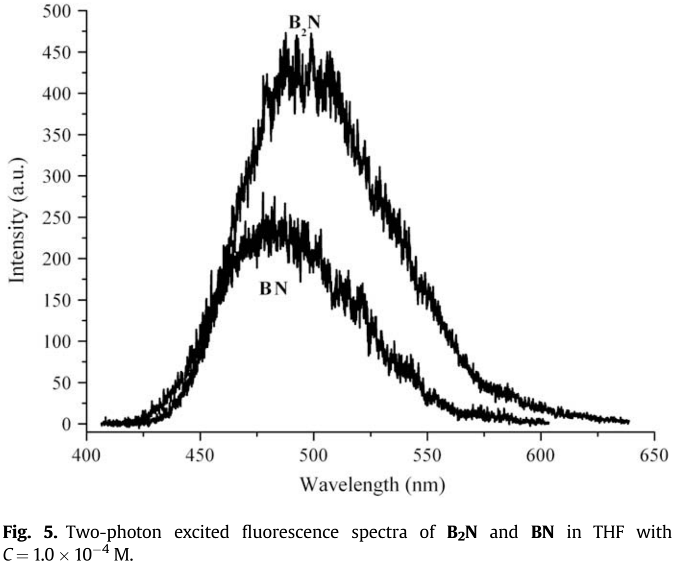


Fig. 5. Two-photon excited fluorescence spectra of **B_2N** and **BN** in THF with $C = 1.0 \times 10^{-4}$ M.

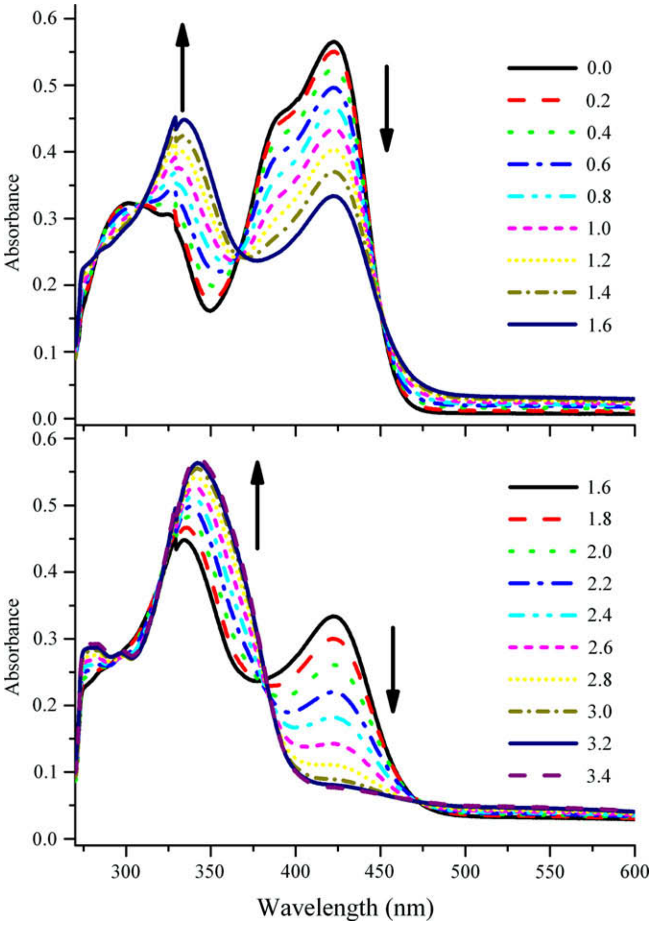


Fig. 6. Changes in UV–vis absorption of **B_2N** (1.0×10^{-5} M) at 20 °C in THF upon the addition of different equivalents of TBAF.

absorption maximum at ca. 334 nm appears, which increases in intensity upon increasing the amount of TBAF, until there are 1.6 equiv with respect to **B_2N** have been added. Two isosbestic points at 367 nm and 450 nm were observed. Molar ratio analysis indicates that these changes can be ascribed to 1:1 complexation of **B_2N** with a fluoride anion [19]. When more than 1.6 equiv of TBAF are added, the primary absorption band decreases further, and two new isosbestic points at 384 nm and 471 nm are observed. These spectral changes can be attributed to the complexation of the sample with the second fluoride anion. The association constants of **B_2N** with fluoride anions were determined as $K_1 = 3.5 \times 10^5$ M^{-1} and $K_2 = 1.1 \times 10^5$ M^{-1}. The results indicate that **B_2N** can recognize fluoride anions with high sensitivity, which can be attributed to strong interactions between the boron atoms and fluoride anions.

4. Conclusions

In summary, a novel two-branched organoboron compound **B_2N** was synthesised. The photophysical properties of the compound in different solvents, and affinity for fluoride anion using UV–vis absorption were investigated. The results indicate that **B_2N** can recognize fluoride anions with high sensitivity. The remarkable TPEF of this compound also suggest its potential as two-photon active chemosensor for fluoride anion.

Acknowledgments

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