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The synthesis and single and two-photon excited fluorescence of a new quasi-quadrupolar organoborane compound

Ying Chen [a], Duxia Cao [b,*], Shasha Wang [a], Changqiao Zhang [a], Zhiqiang Liu [a,*]

[a] State Key Laboratory of Crystal Materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China
[b] School of Material Science and Engineering, University of Jinan, Jinan 250022, China

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ABSTRACT

A new acceptor-π-acceptor quadrupolar compound with a dimesitylboryl as acceptor and 2,7-dithienylfluorene as the conjugated bridge has been synthesized using the Suzuki–Miyaura coupling reaction. Its single and two-photon related photo-physical properties were experimentally examined. The combination of a large two-photon cross-section ($\delta = 1150$ GM at 730 nm in hexane), high emission quantum yield ($\Phi = 0.81$ in hexane) and a strong binding constant with fluoride anions ($K_1 = 3.0 \times 10^5\ \mathrm{mol^{-1}\ L}$) make this compound attractive for application as a two-photon excited fluorescent chemosensor for fluoride anions.

1. Introduction

Organic boron compounds play important roles in modern optoelectronic materials. Generally, these compounds can be classified into two types. The organic boronic acid/boronate ester act as key intermediates for the further building of conjugated systems [1] and triarylboranes act as functional materials [2,3]. For the latter, physical stability is necessary. Trivalent boron is inherently electron-deficient and isoelectronic with a carbocation. When connected with a π system, trivalent boron will behave as a strong π acceptor through *p*-π* conjugation. However, the *p* orbital is readily attacked by nucleophiles such as water, which results in poor stability of normal trivalent organoboranes. It was found that the addition of two bulky groups (normally mesityl, mesityl = 2,4,6-trimethylphenyl) offered enough steric hindrance to protect the boron center from nucleophilic attack [2–4]. Lots of new boron-containing materials have exhibited interesting photoluminescence and electroluminescence properties in the past decades [2–5].

Since the 1990s, two-photon absorption (TPA) and emission organic materials have attracted much attention due to potential applications, such as 3D optical data storage [6] and laser scanning microscopy [7]. Experimental and theoretical research indicated that quadrupolar and octupolar molecular structure are successful strategies for increasing the TPA and two-photon excited fluorescence (TPEF) properties [8–12]. Contrary to works focusing on the D–π–D system containing diarylamino moieties, some molecules containing $B(Mes)_2$ made by Marder et al. [13–15] and our group [16,17] during the past few years have exhibited large TPA cross-sections with remarkable high quantum yields, which are comparable with the D–π–D analogues.

However, more and more research indicated that the photochemical stability are also very important factor for the application of TPA dyes. Although vinyl connected aromatic systems are one of the best option for TPA materials, their relative poor stability is an important drawback. For example, the one- and two-photon photochemical stability of two vinyl-containing fluorene derivatives had been investigated using both absorption and fluorescence methods by Belfield and coworkers [18]. Photochemical reactions involve the olefinic C=C double bonds, especially cyclo-addition reaction of oxygen with olefinic C=C double bonds were believed to be one main photo-degradation process [18]. We have reported compound **1** (see Scheme 1) possesses strong TPEF and large TPA cross-section up to 1340 GM [16] and can be used as a TPEF active chemosensor for fluoride anions with high sensitivity and selectivity [17]. However, the intrinsic *cis–trans* isomerization of the vinyl moiety and the possible photobleaching processes as mentioned above certainly would limit its usefulness. To overcome this shortcoming, many researchers would like use other rigid and stable groups to build conjugated system in their design of TPA materials [13–15]. Herein, we present details of the synthesis and single and two-photon excited fluorescence properties of new A–π–A compound (**2**) with fluorene instead of divinylbenzene as the conjugating core, namely, 2,7-bis(2′-dimesitylborylthienyl)-9,9-diethylfluorene.

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* Corresponding authors. Tel./fax: +86 531 8836 2782 (Z. Liu).
E-mail addresses: duxiacao@ujn.edu.cn (D. Cao), zqliu@sdu.edu.cn (Z. Liu).

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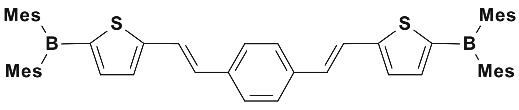

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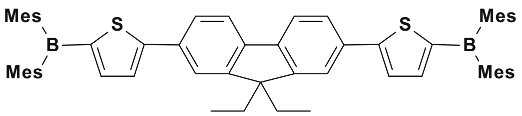

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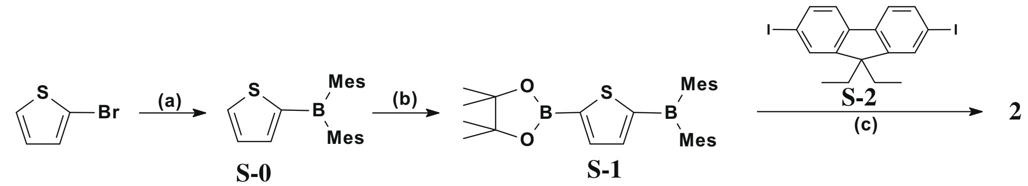

Scheme 1. Synthesis of compound **2**. Reagents and conditions: (a) *n*-BuLi, FB(Mes)$_2$, THF, −78 °C to rt; (b) B$_2$pin$_2$, [Ir(COD)Cl]$_2$, dtbpy, hexane, 80 °C; (c) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, toluene, 80 °C.

2. Experimental

2.1. Chemicals and instruments

Nuclear magnetic resonance spectra were recorded on a Bruker Avance-400 spectrometer. Mass spectrum was recorded on an Applied Biosystems Voyager DE STR (MALDI-TOF) spectrometer. Elemental analysis was carried out on a PE 2400 autoanalyzer. *n*-Butyllithium in hexane solution was obtained from Acros Ltd. Dimesitylboron fluoride (BF(Mes)$_2$) was purchased from Aldrich Ltd. Other reagents, such as fluorene and 2-bromothiophene were purchased from Shanghai Reagents and were used as received directly without further purification. All solvents were freshly distilled before using.

2.2. Synthesis

Compound **2** was prepared via a typical Suzuki–Miyaura cross-coupling reaction (Scheme 1). The boronate ester **S-1** was prepared via Ir-catalysed borylation of 2-dimesitylthiophene [19]. Halo-fluorene **S-2** was prepared via direct halogenations of fluorene at 2, 7 positions [20].

2.2.1. 2-Dimesitylborylthiophene (*S-0*)

To a Schlenk flask charged with 1-bromo-thiophene (2.45 g, 15 mmol) in 50 mL of dry Et$_2$O and a stirrer bar, 1.6 M *n*-BuLi in hexane (10 mL, 16 mmol) was added dropwise via a syringe at −78 °C. The reaction was allowed to warm to room temperature for 1 h and was cooled to −78 °C again and a solution of dimesitylboryl fluoride (4.0 g, 15 mmol) in 20 mL of Et$_2$O was added. The reaction was allowed to warm to room temperature with stirring overnight, then quenched with 10 mL of 1 M HCl, extracted into DCM, dried over Mg$_2$SO$_4$, and concentrated in vacuo. The residue was purified by recrystallization from hexane to give 4.5 g white solid (90% yield). ^{1}H NMR (CDCl$_3$, 400 MHz), $\delta = 7.80$ (q, 1H), 7.37 (q, 1H), 7.12 (m, 1H), 6.73 (s, 4H), 2.21 (s, 6H), 2.01 (s, 12H); ^{13}C{H} NMR (CDCl$_3$, 100 MHz): $\delta = 140.85$, 140.43, 138.55, 138.16, 129.15, 128.21, 23.45, 21.25. Elemental analysis calcd. (%) for $C_{22}H_{25}BS$: C, 79.51; H, 7.58; found: C, 79.47; H, 7.60.

2.2.2. 2-Dimesitylboryl-5-Bpin-thiophene (*S-1*)

In a dry N$_2$ filled Schlenk tube, the pre-catalyst [Ir(COD)Cl]$_2$ (7 mg, 1% mol), ligand dtbpy (12 mg, 1% mol), and a little scale of B$_2$pin$_2$ (~20 mg) were mixed in 2 mL hexane and stirred vigorously until the solution turned brown. Then 2-dimesitylboryl-thiophene (3.32 g, 10 mmol), B$_2$pin$_2$ (2.54 g, 10 mmol) and 15 mL hexane was added to the tube. The tube was sealed with a Teflon cap and stirred at 80 °C for 16 h. The mixture passed through a short silica pad to remove the Ir-containing catalyst, then concentrated and recrystallized from hexane at −20 °C to get 3.87 g white crystalline product with acceptable purity (86% yield). ^{1}H NMR (CDCl$_3$, 400 MHz), $\delta = 7.61$ (d, $J = 3.6$ Hz, 1H), 7.40 (d, $J = 3.6$ Hz, 1H), 6.73 (s, 4H), 2.21 (s, 6H), 2.00 (s, 12H), 1.25 (s, 12H). ^{13}C{H} NMR (CDCl$_3$, 100 MHz): $\delta = 140.79$, 140.29, 138.61, 138.16, 128.15, 84.28, 24.82, 23.41, 21.20. Elemental analysis calcd. (%) for $C_{28}H_{36}B_2O_2S$: C, 73.39; H, 7.92; found: C, 73.27; H, 7.90.

2.2.3. 2,7-Bis(2′-dimesitylthienyl)-9,9-diethylfluorene (*2*)

2-Dimesitylboryl-5-Bpin-thiophene (**S-1**, 0.46 g, 1.0 mmol) and 2,7-diiodo-9,9-diethylfluorene (**S-2**, 0.24 g, 0.5 mmol) were placed in a 100 mL Schlenk tube, which was evacuated and purged with nitrogen gas three times. Pd(PPh$_3$)$_4$ (12 mg, 0.01 mmol), toluene (~10 mL) and saturated aquaues solution of Na$_2$CO$_3$ (~0.5 mL) were added under nitrogen. The tube was sealed with a Teflon cap and stirred at 80 °C for 16 h before it was quenched. This mixture was extracted with dichloromethane, dried over MgSO$_4$, concentrated in vacuo. Purification by column chromatography (silica gel using chloroform–petroleum ether (1:6) gave a bright yellow powder with yield 64%. ^{1}H NMR (CDCl$_3$, 400 MHz), $\delta = 7.67$ (s, 4H), 7.60 (s, 2H), 7.53 (d, $J = 3.6$ Hz, 2H), 7.45 (d, $J = 3.6$ Hz, 2H), 6.86 (s, 8H), 2.33 (s, 12H), 2.17 (s, 24H); ^{13}C {H} NMR (CDCl$_3$, 100 MHz), $\delta = 157.70$, 151.05, 141.89, 141.48, 141.16, 140.89, 138.52, 133.18, 128.20, 125.37, 120.49, 120.24, 56.56, 32.84, 23.55, 21.28, 8.54. MS (MALDI-TOF) *m*/*z* calcd for $C_{61}H_{64}B_2S_2$: 883; found 883; elemental analysis calcd. (%) for $C_{61}H_{64}B_2S_2$: C, 82.98; H, 7.31; S, 7.26; found: C, 82.88; H, 7.30; S, 7.33.

2.3. Measurements

Linear absorption spectra with $C = 5.0 \times 10^{-6}$ mol L^{-1} were recorded on a Shimadzu UV 2550 spectrometer. Single-photon excited fluorescence (SPEF) spectra with $C = 5.0 \times 10^{-6}$ mol L^{-1} were measured on an Edinburgh FLS920 fluorescence spectrometer. The SPEF quantum yields Φ for the compound were determined relative to coumarin 307 [21] using a standard method [22]. TPEF experiments with $C = 1.0 \times 10^{-4}$ mol L^{-1} were performed with a femtosecond Ti:sapphire laser (80 MHz, 200 fs pulse width, Spectra Physics) as a pump source and a USB 2000 + Micro Fiber Spectrometer (Ocean optics) as the recorder. The TPA cross-sections of compound **2** in toluene and THF solutions were measured by using a TPEF measurement technique and coumarin 307 as Ref. [23].

3. Results and discussion

3.1. Linear absorption and single-photon excited fluorescence properties

Linear absorption and SPEF properties of **2** in various solvents with different polarity along with compound **1** in toluene (Table 1) are reported. The absorption and emission spectra of **2** showed clear vibronic structures (Fig. 1). Generally, compound **2** displays a broad charge-transfer absorption band with maxima of 404–412 nm and shoulders at higher wavelength. Compound **2** emits strong fluorescence in the blue–green spectral region with a high quantum yield over 70%. Upon increasing the polarity of the solvents, the emission maximum, λ_{max}(em), is gradually shifted toward longer wavelengths by 20 nm. The weak solvatochromism and small stokes-shift relate to the quasi-quadrupolar structural motif of this compound and a rigid backbone. The dipole moment of the molecule is small both in the ground and excited state due to symmetric charge transfer, therefore the dipole–dipole interaction between the solvent and solute should be quite weak, and only small solvatochromism is observed.

Interestingly, compared with the spectral properties of vinylphenylene-bridged compound **1**, both the absorption and emission of the fluorene-bridged compound **2** are significantly blue-shifted by nearly 30 nm. In addition, the extinction coefficients, ε, of **2** are also decreased by 20%, but the quantum yield of **2** is obviously higher than that of **1**. The differences between compounds **1** and **2** can be related to the differences in the structure of their cores. It seems that the fluorine (in **2**) does not provide as effective conjugation as the divinylbenzene (in **1**), as evidenced by the spectral blue-shift of **2**. However, the higher rigidity of the fluorene compared to the isomerizable divinylbenzene means less possibility of a non-radiative transition, and should contribute to the higher quantum yield.

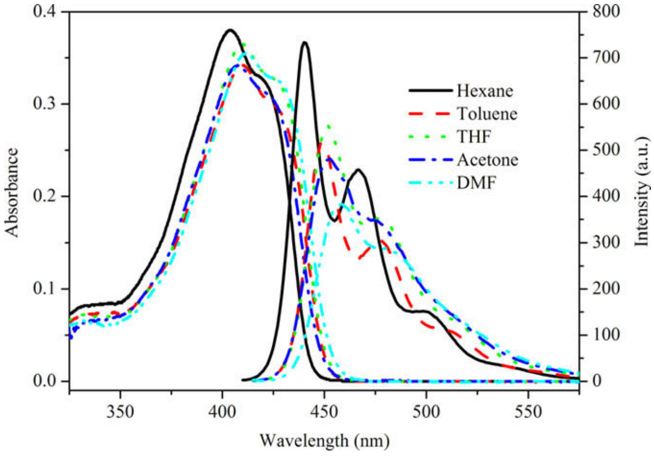

Fig. 1. Linear absorption and single-photon excited fluorescence emission spectra of **2** in various solvents ($C = 5.0 \times 10^{-6}$ mol L^{-1}; $\lambda_{ex} = 400$ nm).

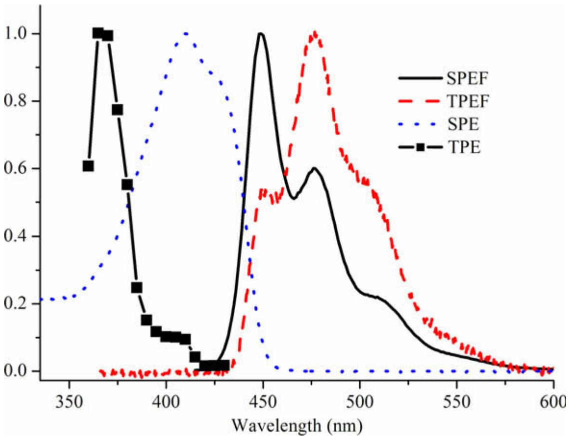

Fig. 2. The normalized single and two-photon excitation and emission spectra of **2** in toluene. The wavelengths for the TPE spectrum have been divided by two.

3.2. Two-photon excited fluorescence properties

As shown in Fig. 1, there was not linear absorption over 550 nm for compound **2**. Therefore upon excitation with a laser in the range of 700–900 nm, the frequency up-converted fluorescence can be safely attributed to a multiphoton absorption process. In our measurements, when the solution of **2** was excited with a fs laser at 730 nm, it presented bright fluorescence emission. This emission nearly overlaps the spectra of SPEF and its intensities are linearly dependent on the square of input laser power. All these results indicate a two-photon excitation mechanism for this emission.

Further experiments reveal that the emission spectra of compound **2** is independent of the excitation wavelengths (from 720 to 860 nm), but the intensity of emission is effected by altering the excitation wavelength. By tuning the pump wavelengths incrementally from 720 to 860 nm while keeping the input power constant (100 mW) and then recording the emission intensity, the two-photon excitation spectra of **2** was obtained. As shown in Fig. 2, the peak position of single-photon excitation (SPE) spectrum and two-photon excitation (TPE) spectrum of compound **2** is at 410 and 730 nm, respectively, which indicates that the energy level of the TPE state is about 0.47 eV higher than that of the SPE state. This is consistent with the prediction that the two-photon allowed states for quadrupoles should be located at higher energy than the single-photon allowed states [8–10,14], but fluorescence normally occurs from the same excited state.

The TPEF spectrum of compound **2** in Fig. 2 shows a red shift relative to the SPEF spectrum. The shoulder at higher wavelength is weaker in the TPEF spectrum compared to the SPEF spectrum. This is due to a re-absorption effect, considering the partial overlap of the SPE and SPEF spectra and the higher concentration of the

Table 1
Single and two-photon related photo-physical properties of compound **2**.

	Solvents	Linear absorption		SPEF		TPEF	
		λ_{max} (nm)	$10^{-4}\cdot\varepsilon$	λ_{max} (nm)	Φ	λ_{max} (nm)	δ (GM)
2	DMF	412	7.8	459, 481	0.70	462, 488	780 (730 nm)
	Acetone	407	7.5	452, 475	0.78	456, 488	750 (730 nm)
	THF	409	8.0	451, 477	0.81	453, 486	1080 (730 nm)
	Toluene	410	7.5	449, 477	0.78	451, 477	990 (730 nm)
	Hexane	404	8.4	440, 466	0.87	450, 471	1150 (730 nm)
1	Toluene	435	9.3	482, 515	0.61	491, 514	1340 (775 nm)

samples in TPEF measurements. This re-absorption effect will induce some experimental error in calculating the TPA cross-sections from the generally used comparative TPEF measurement technique.

Generally, the TPA cross-section of **2** is large (~1000 GM) and dependent on solvent. For comparison, the value of **2** is less than that of compound **1** (990 GM vs. 1340 GM in toluene), and the λ_{TPE} of compound **2** is also blue-shifted by 45 nm (730 nm vs. 775 nm). These results seem consistent with the single-photon related properties as discussed above. The relative short electron delocalization range of compound **2** may decrease the quadrupolar charge transfer and influence TPA.

3.3. Spectral response to fluoride complexation

Trivalent organoboron compounds have been studied as chemosensors for fluoride anions with high selectivity and sensitivity [24–30]. The recognition mechanism is attributed to the unique steric structure of bulky dimesitylboryl group (offering selectivity) and the Lewis acid–base interaction between the trivalent boron atom and fluoride anion (offering sensitivity). In the presence of a fluoride anion, the strong B–F interaction is believed to interrupt the extended π-conjugation and thereby causes a change of the related photo-physical properties.

In our experiments, *n*-Bu$_4$NF (TBAF) as the fluoride source was gradually added to THF solutions of each borane. Fig. 3 shows the spectral change of **2** in THF solution (6.5 μM) upon the addition of TBAF. Perhaps due to the two symmetrical dimesityboryl moieties in molecule **2**, there were two clear stages of sensing the fluoride ion in both absorption and emission spectra. In the first stage, for F-addition from 0 to 2.0 equivalents, the main absorption between 390 and 450 nm of **2** greatly decreased and the absorption edge was red-shifted from 460 to 500 nm. As a result, the whole band degenerated to a broad single band centered at 410 nm. The presence of two distinct isosbestic points at 362 and 443 nm and molar ratio analysis indicate that the spectral change in this concentration range can be ascribed to 1:1 complexation of **2** with fluoride ion with a binding constant $K_1 = 3.0\ (\pm 0.3) \times 10^5\ \mathrm{M}^{-1}\ \mathrm{L}$. Furthermore, the emission intensity also decreased in this process. In the second stage, the further addition of a large excess of TBAF caused subsequent spectral changes with a new absorption peak at 390 nm, and the absorption edge greatly blue-shifted back to around 440 nm. Correspondingly, the emission spectra are also blue-shifted. These changes could be assumed to be complexation with the second fluoride ion. The binding constant for this process is estimated to be $K_2 = 1.8\ (\pm 0.4) \times 10^5\ \mathrm{M}^{-1}\ \mathrm{L}$.

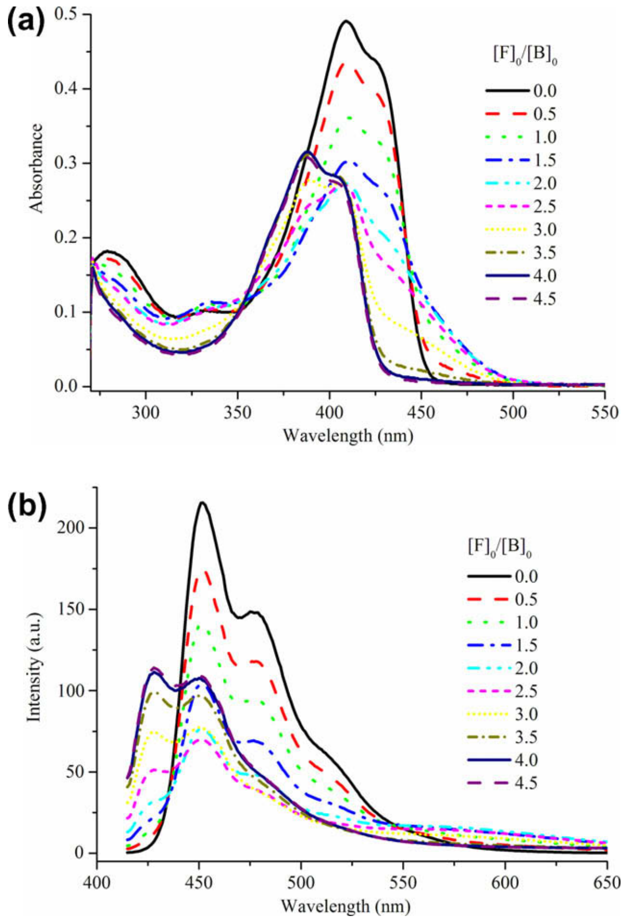

Fig. 3. Absorption (a) and emission (b) spectra of **2** (6.5 μM; λ_{ex} = 400 nm) in THF upon the addition of fluoride anions.

4. Conclusions

A new A–π–A type compound with dimesityl protected trivalent borons as electron acceptors was synthesized. Its single- and two-photon related photo-physical properties and complexation with fluoride anions were examined. The high quantum yield and strong two-photon absorption as well as a strong interaction with fluoride anions make this compound a potential luminescent material and chemosensors.

Acknowledgments

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