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Two-photon excited fluorescence properties and anions recognition of a trivalent organoboron compound

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ABSTRACT

A trivalent organoboron compound with diethylamino as an electron donor group and dimesitylboryl as an electron acceptor group has been synthesized. Its single- and two-photon excited fluorescence properties have been examined. Pumped by 820 nm laser pulses in femtosecond regime, it showed strong two-photon excited fluorescence at 527 nm in toluene with two-photon absorption cross-section being 859GM. The compound has been found to be a sensitive chemosensor for fluoride and cyanide anions in THF solutions.

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1. Introduction

Two-photon absorption (TPA) is a nonlinear process, in which a molecule simultaneously absorbs two photons to access an excited state. In recent years, a considerable interest has been devoted to the research into organic molecules with strong TPA and two-photon excited fluorescence (TPEF) due to their potential use in advanced photonic applications such as three-dimensional optical data storage [1], up-converted lasing [2], two-photon fluorescence excitation microscopy [3,4], lithographic microfabrication, laser device fabrication [5] and photodynamic therapy [6]. Series of compounds with strong TPEF have been reported, which promoted both the theory and application research of TPA and TPEF [7–10].

From the viewpoint of molecular engineering, structural features such as electron donor or acceptor terminal group and the length of conjugated bridge all play an important role in tuning nonlinear optical properties of materials. A number of studies found that nonlinear optical effect increases with the increase of the length of conjugated bridge and molecular planarity [11,12]. Boron atom has an empty p-orbital and this p-orbital can form p-π type orbital charge transfer with the π-orbital of the conjugated system connecting with boron atoms. It has strong electronic affinity. So, groups with trivalent boron atoms can serve as a good electron acceptor. After decades of exploration, people have synthesized a large number of stable organoboron compounds, which displayed great potentials in fields of nonlinear optical, luminescent materials and electronic transmission [13–15]. Another important role of organoboron compounds is as Lewis acid-based fluoride [16–24] or cyanide [23–29] anions sensors. So, organoboron compounds combine TPEF, fluoride and cyanide anions together very well.

Our group has been interested in fluoride sensors and TPEF based on organoboron compounds for several years [30–32]. We herein report the synthesis of a D-π-A motif organoboron compound with long conjugated bridge. We have measured its linear and two-photon photophysical properties and examined its potential for fluoride and cyanide anions sensors.

2. Experimental

2.1. Chemicals and instruments

Nuclear magnetic resonance spectra were recorded on a MercuryPlus-400 spectrometer. Elemental analyse was carried out on a PE 2400 autoanalyzer. Mass spectrum was obtained on an Agilent 5973N MSD spectrometer. *n*-Butyllithium in hexane solution was obtained from Aldrich Ltd. Dimesitylboron fluoride ($BF(Mes)_2$, Mes = 2,4,6-trimethylphenyl) was purchased from Aldrich Ltd. Other reagents were purchased from Shanghai Reagents and were used as received directly without further purification. All of the solvents were freshly distilled before using.

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2.2. Synthesis

The synthetic strategy of the title compound **1** is outlined in Scheme 1 [33]. 4-[4-(N,N-diethylamino)styryl]aldehyde (**S-1**) and the phosphonium salt (**S-2**) were synthesized according to procedures described in the literatures [34,35]. Then 4-(4-(4-bromostyryl)styryl)-N,N-diethylbenzenamine (**1**′) was prepared by Wittig reactions using **S-1** and one equivalent **S-2**. Finally, the title compound **1** was obtained by substitution of the Br atom of **S-3** using dimesitylboryl group.

2.2.1. 4-(4-(4-Bromostyryl)styryl)-N,N-diethylbenzenamine (1′)

By reaction of **S-1** with one equivalent **S-2** via Wittig reaction, **1**′ was obtained as a green solid with a yield of 50%. ^{1}H NMR(CDC1$_3$, 400 MHz), δ_H (ppm): 1.11(t, J = 7.2 Hz, 6H), 3.31(q, J = 7.1 Hz, 4H), 6.40(d, J = 12.4, 1H), 6.52(d, J = 12.4, 1H), 6.58 (d, J = 8.4, 2H), 6.76 (d, J = 16.4, 1H), 6.95(d, J = 16.4, 1H), 7.10(t, J = 9.0, 3H), 7.25–7.35(m, 6H), 7.41(s, 1H). MS: m/z (%) 431(M$^+$, 100), 416([M-CH$_3$]$^+$, 100). Anal. calcd for $C_{26}H_{26}BrN$: C, 72.22; H, 6.06; N, 3.24. Found: C, 72.38; H, 6.03; N, 3.28.

2.2.2. 4-(4-(4-Dimesitylborylstyryl)styryl)-N,N-diethylbenzenamine (1)

2.0 g (4.6 mmol) **1**′ in freshly distilled THF was injected into a three-necked flask under the cover of N_2. Then the flask was cooled to −78 °C by dry ice-acetone bath and then 15 mmol *n*-Butyllithium in hexane solution was dropped. The flask was kept at −78 °C for about 1 h, then warmed naturally to room temperature and stirred for 2 h to get the lithium salt. Then the mixture was cooled to −78 °C again and 1.25 g (4.6 mmol) dimesitylboron fluoride, which had been resolved in 5 mL freshly distilled THF, was injected quickly via a dried injector. The mixture was continuously stirred overnight and then was poured into 200 mL distilled water and extracted with dichloromethane. After a rotary evaporator removed the organic solvent, the product was purified through column chromatography on silica gel using chloroform–petroleum ether (1:9) as eluent. Red powders with yield 45% were obtained. ^{1}H NMR(CDC1$_3$, 400 MHz), δ_H (ppm): 1.11(t, J = 7.0 Hz, 6H), 1.96(s, 12H), 2.23(s, 6H), 3.31(q, J = 7.0 Hz, 4H), 6.52(d, J = 12.4 Hz, 1H), 6.59(d, J = 8.6 Hz, 2H), 6.74(s, 4H), 6.77(d, J = 12.4 Hz, 1H), 6.93(d, J = 16.0 Hz, 1H), 7.05(d, J = 16.4 Hz, 1H), 7.12(d, J = 8.0 Hz, 1H), 7.16–7.24(m, 2H), 7.32(t, J = 8.6 Hz, 3H), 7.38–7.45(m, 4H). MS: m/z (%) 601(M$^+$, 100). Anal. calcd for $C_{44}H_{48}BN$: C, 87.83; H, 8.04; N, 2.33. Found: C, 87.68; H, 8.06; N, 2.37.

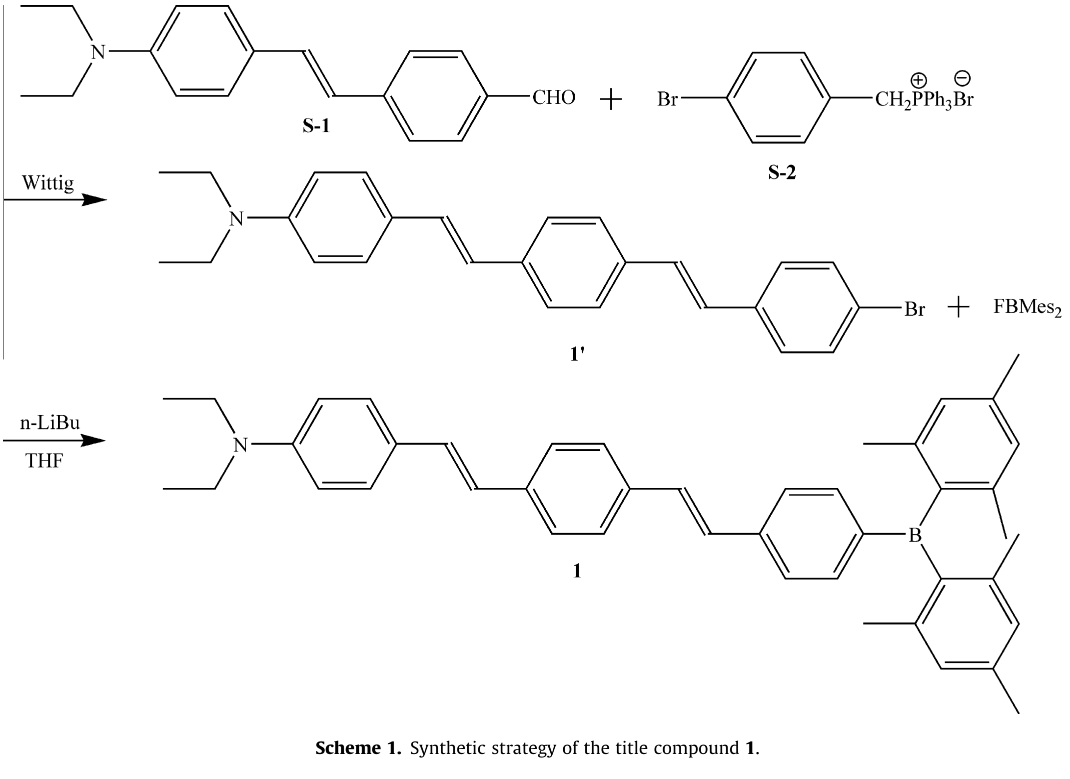
2.3. Measurements

UV/vis absorption and single-photon excited fluorescence (SPEF) spectra with $C = 1.0 \times 10^{-5}$ mol L^{-1} were recorded on Shimadzu UV 2550 and FLS920 fluorescence spectrometer, respectively. The SPEF quantum yields Φ were measured by using a standard method [36] with coumarin 307 [37] as the standard. Two-photon excited fluorescence spectra of the compounds in toluene and THF with $C = 1.0 \times 10^{-4}$ mol L^{-1} were performed with a femtosecond Ti:sapphire laser (80 MHz, 80 fs pulse width, Spectra-Physics Inc., Tsunami 3941-M1 BB) over the range 740–880 nm as pump source. The input laser powder was 150 mW for all measurements, which was carefully monitored to ensure sufficient TPEF intensity.

3. Results and discussion

3.1. Linear absorption and single-photon excited fluorescence properties

Linear photophysical properties of compound **1** in various solvents are shown in Table 1 and Fig. 1. As shown in Table 1 and Fig. 1, one can see that absorption peak position and absorbance show little dependence on polarity of the solvents. In contrast, its emission properties display an obvious solvatochromic effect. With increasing polarity of the solvents, the emission maximum of



Scheme 1. Synthetic strategy of the title compound **1**.

Table 1
Linear photophysical properties of compounds **1'** and **1** in various solvents.

	Solvents	λ^{abs} (nm)	ε ($10^4\ M^{-1}cm^{-1}$)	λ^{fluo} (nm)	Φ	τ (ns)
1	Hexane	414	6.22	468, 503	0.52	1.1
	Toluene	424	5.35	525	0.45	1.5
	THF	422	5.61	602	0.21	2.3
	Acetonitrile	417	5.82	677	0.02	–
1′	Hexane	395	4.7	439, 464	0.38	0.9
	Toluene	401	4.2	470, 496	0.36	1.0
	THF	400	5.1	523	0.32	1.5
	Acetonitrile	395	4.9	566	0.25	2.2

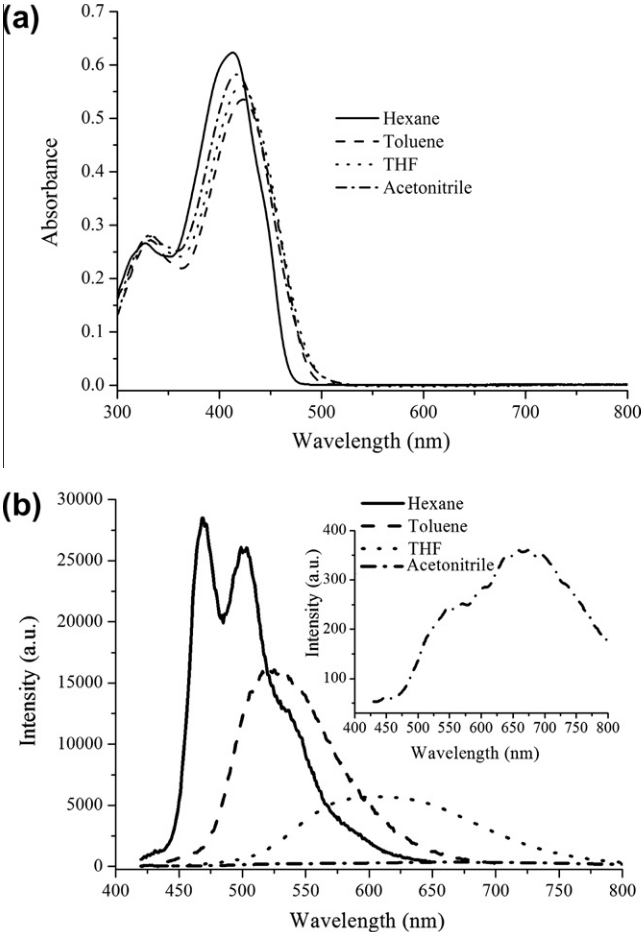


Fig. 1. Linear absorption (a) and single-photon excited fluorescence (b) spectra of compound **1** in various solvents.

compound **1** varies from 503 nm in hexane to 677 nm in CH_3CN with a shift of nearly 174 nm. Also, with the increase of solvent polarity, the fluorescence intensity and fluorescent quantum yield show a substantial reduction. Phenomenon above can be explained by twisted intramolecular charge transfer (TICT) [38,39]. All these cases indicate that typical intramolecular charge-transfer takes place during the excitation process, which results in a highly polarized excited state.

A direct comparison of the organoboron compound **1** with its precursor **1'** clearly indicates that the former possesses much improved photophysical properties. Compound **1** exhibits higher fluorescence quantum yields and longer fluorescence lifetime relative to **1'** (shown in Table 1), which indicates that the –B(Mes)$_2$ group acts as a fluorophore. Compound **1** shows longer linear absorption and fluorescence emission wavelength and more obvious solvatochromism relative to **1'** that indicating that compound **1** possesses larger polarity.

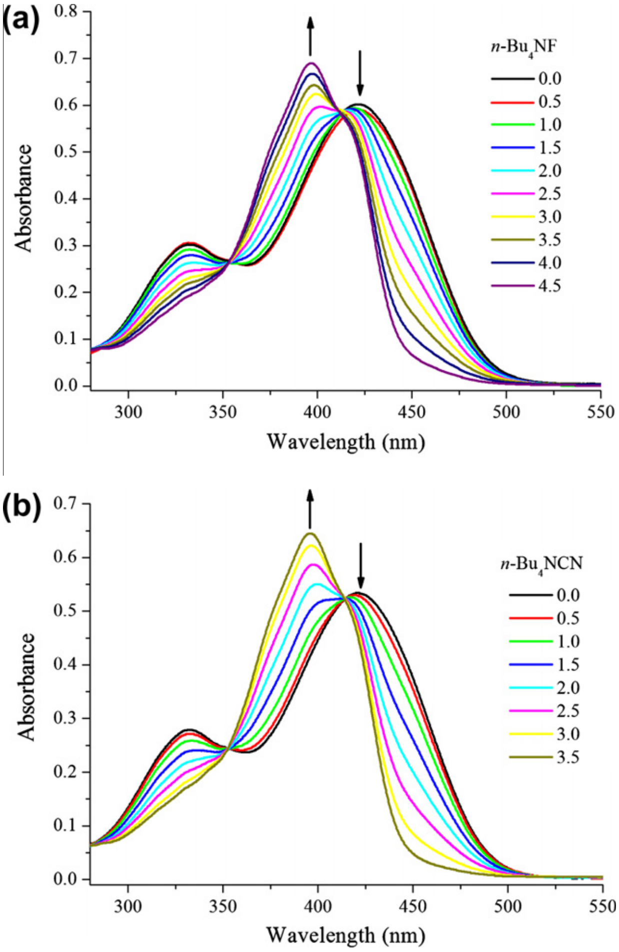


Fig. 2. Changes in UV–vis absorption spectra of compound **1** at 20 °C in THF upon the addition of different equivalents of TBAF (a) or TBACN (b).

3.2. Spectral response to fluoride and cyanide anions

As a general adapted method, *n*-Bu$_4$NF (TBAF) or *n*-Bu$_4$NCN (TBACN) as fluoride or cyanide source was progressively added to a THF solution of compound **1**. The linear absorption and single-photon excited fluorescence emission spectra of solutions containing increasing concentration of fluoride anions or cyanide anions were recorded to examine the complexation between **1** and F^- or CN^-. Compound **1** shows an obvious spectral response to the added TABF and TBACN. As shown in Fig. 2, upon complexation with fluoride or cyanide anions, the characteristic intense charge-transfer absorption at 420 gradually decreases and a new peak at 396 nm appears. When 4.5 equivalents TBAF or 3.5 equivalents TBACN were added, the absorption peak at 420 nm disappeared completely. So **1** can recognize for fluoride and cyanide anions with similar bonding ability. The phenomenon upon is contributed to the formation of the 1:1 adduct **1-F** or **1-CN**.

As shown in Fig. 3, the single-photon excited fluorescence emission spectra recorded with excitation at 410 nm also displayed obvious changes when fluoride or cyanide anions were added. The strong emission band of **1** at 602 nm gradually decreased, and a new emission band at 473 nm (F^-) or 475 nm (CN^-) appeared. When 4.8 equivalents TBAF or 4.4 equivalents TBACN were

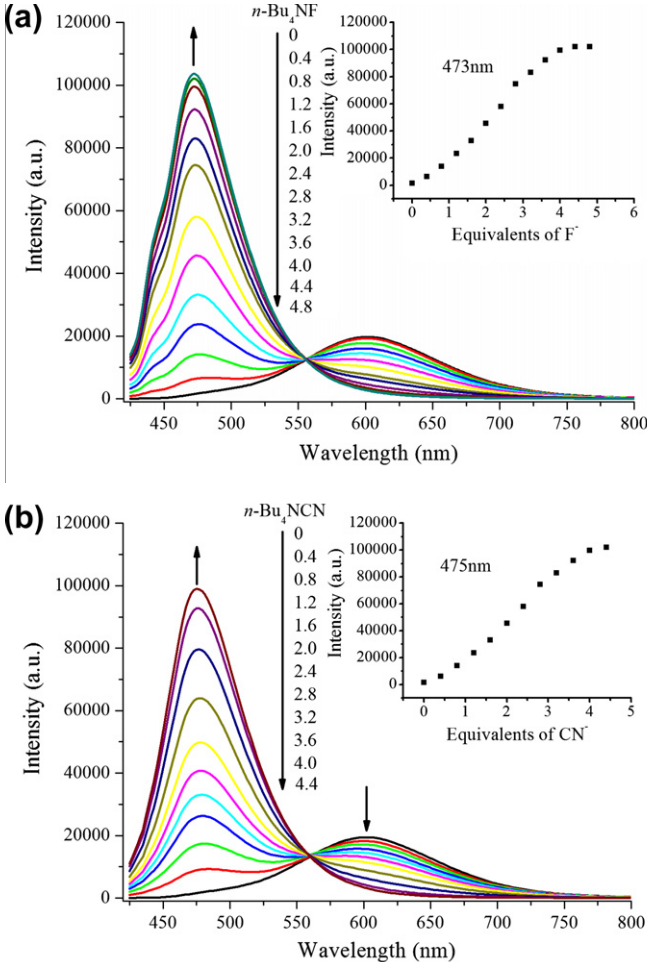


Fig. 3. Changes in single-photon excited fluorescence spectra of compound **1** at 20 °C in THF upon the addition of different equivalents of TBAF or TBACN. *Inset*: Titration curves at 473 nm (TBAF) or 475 nm (TBACN).

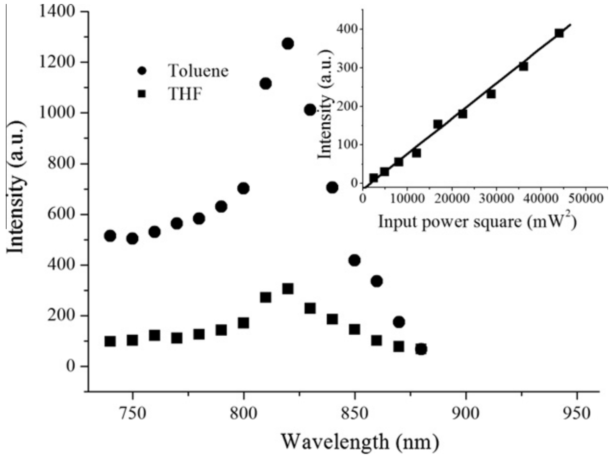


Fig. 4. Two-photon excitation (TPE) spectra of compound **1** in toluene and THF with $C = 1.0 \times 10^{-4}$ mol L^{-1}. *Inset*: The output fluorescence intensity vs. the input power square for **1** in THF.

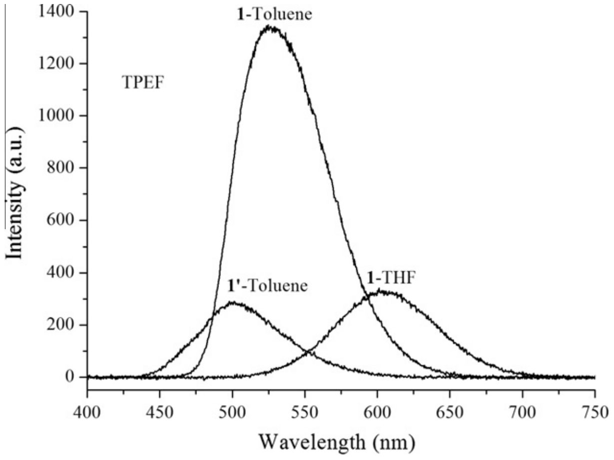
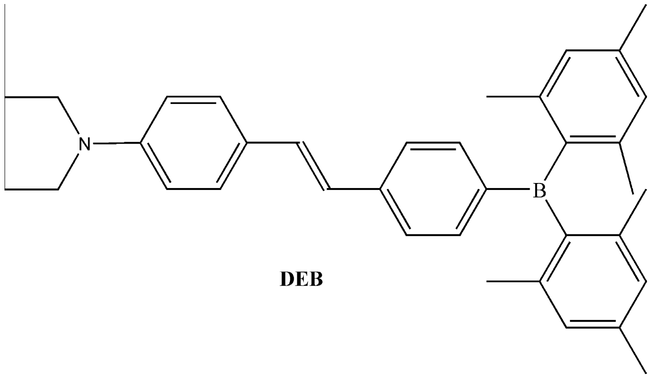


Fig. 5. Two-photon excited fluorescence (TPEF) spectra of **1** in toluene and THF with excitation wavelength 820 nm and $C = 1.0 \times 10^{-4}$ mol L^{-1}.



DEB

Fig. 6. Molecular structure of compound **DEB**.

added, the fluorescence peak at 602 nm disappeared completely. This phenomenon also indicates the recognition of compound **1** for fluoride and cyanide anions. Interestingly, conversion of **1** into **1-F** and **1-CN** is accompanied by the disappearance of orange colour in solution.

3.3. Two-photon excited fluorescence properties

TPEF was collected at a direction perpendicular to the pump beam. From linear absorption spectra (Fig. 1a), one can see that the compound is linear optical penetrable in the range from 500 to 1000 nm. Therefore, any emission induced by excitation at this wavelength range should be derived from multiphoton absorption process. As shown in Fig. 4, TPEF intensity of compound **1** is proportional to the square of the input laser power from 50 mW to 210 mW, which suggests the two-photon excitation mechanism.

Two-photon excitation (TPE) spectra of compound **1** in toluene and THF with excitation wavelength from 740 nm to 880 nm were shown in Fig. 4. From Fig. 4, one can see the optimal excitation wavelengths in both solvents are 820 nm, which are almost twice those of the corresponding linear absorption maxima.

TPEF spectra of the compounds shown in Fig. 5 were taken when they were excited at 820 nm. Compound **1** exhibits strong TPEF emission in toluene (527 nm) and THF (606 nm). TPEF intensity of compound **1** in toluene is almost four times that in THF, which is similar to SPEF. The phenomenon above exhibits that stronger polarity solvent THF induces obvious fluorescence quench of **1**. TPEF intensity of compound **1** in toluene is almost four times that of the precursor **1’**, which indicates the replacement of bromine atom using boron atom is beneficial to TPEF.

TPA cross-sections of **1** in toluene and THF at 820 nm are obtained using two-photon excited fluorescence method with counarin307 as Ref. [40], which are 859GM and 522GM, respectively. TPA cross-section of **1** in toluene is about four times that of **1'** (206GM) in same solvent. TPA cross-section of **1** in THF is almost three times that of the corresponding short-chain analogue (DEB, Fig. 6) with one phenyl-vinyl compound (194GM) in THF solution [35], which indicates that the extending conjugated system is beneficial to nonlinear optical properties of the compounds.

4. Conclusion

In summary, a D-π-A dipolar organoboron compound with long conjugated bridge was synthesized. Its single and two-photon related photophysical properties and the property for fluoride and cyanide bonding are measured. The compound exhibits strong two-photon up-converted yellow fluorescence and large two-photon absorption cross-sections (859GM in toluene and 522GM in THF) with 820 nm laser excitation. The compound can recognize for fluoride anions and cyanide anions.

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