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Synthesis and blue-violet two-photon excited fluorescence of a new organoboron compound

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Abstract

A new A- π -D- π -A type organoboron compound, 3,6-bis(dimesitylboryl)-*N*-butyl-carbazole (abbreviated as **BBC**), with trivalent boron as electron acceptor and carbazole as electron donor and π -conjugated core, has been synthesized and its single and two-photon related photophysical properties experimentally investigated. Pumped by 720 nm laser pulses in femtosecond regime, it showed strong two-photon excited blue-violet fluorescence at 393 nm in toluene and 403 nm in THF. The measured two-photon absorption cross-section by two-photon fluorescence method in toluene and THF is 34 GM and 38 GM, respectively. © 2007 Elsevier B.V. All rights reserved.

Keywords: Two-photon excited fluorescence; Organoboron compound; Blue-violet fluorescence; Carbazole

1. Introduction

In recent years, a considerable interest has been devoted to research into organic molecules with strong 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] and twophoton fluorescence excitation microscopy [3,4]. The further development of these applications greatly benefit from the synthesis of new organic molecules exhibiting strong TPEF in desirable wavelength regions. But most of the molecules reported recently mainly emit TPEF in yellowto-red light region and the molecules emitting TPEF in blue-violet light region are fairly lacking.

Boron atom, especially three-coordinated boron, with its vacant p-orbital, is a useful π electron acceptor in conjugated organic molecular materials. These materials exhibit interesting fluorescence emission, first- and second order nonlinear optical properties, and fluoride ion sensing ability

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[5], and can serve as emissive and/or electron-transport layers in OLEDs [6]. In the past years, we firstly presented the application of trivalent organoboron compounds for TPEF [7–9]. Experiments demonstrated the trivalent organoboron compounds synthesized by our group possess strong TPEF properties and large two-photon absorption (TPA) crosssection. Recently, we designed and synthesized a new A- π -D- π -A type compound basing on trivalent boron atom electron acceptor and aromatic heterocycle conjugated bridge. The introduction of the aromatic heterocycle carbazole as a π -conjugated bridge are based on this aromatic system is much richer in electronic density with a pair of alone electrons on nitrogen atom compared to a benzene and fluorene and has perfect coplanar conformation. In this paper, we report single and two-photon related photophysical properties of this A- π -D- π -A type compound.

2. Experimental

2.1. Chemicals and instruments

Nuclear magnetic resonance spectra were recorded on a MercuryPlus-400 spectrometer. Mass spectrum was

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obtained on an Agilent 5973N MSD spectrometer. Elemental analyse was carried out on a PE 2400 autoanalyzer. *n*-Butyllithium in hexane solution was obtained from Acros Ltd. Dimesitylboron fluoride (BF(Mes)₂, Mes = 2,4,6trimethylphenyl) was purchased from Aldrich Ltd. Other reagents, such as carbazole and 1-bromobutane were purchased from Shanghai Reagents and were used as received directly without further purification. All of the solvents were freshly distilled before using.

2.2. Synthesis

The synthetic strategy is outlined in Scheme 1. The title compound was prepared in three steps via butylation, bromination and boronation reaction. Substitution of 9-hydrogen atom on carbazole using butyl group afforded *N*-butyl-carbazole (S-1) [10]. 3,6-dibromo-*N*-butyl-carbazole (S-2) can be prepared from S-1 and two equivalent Br_2 in acetic acid. Finally, the title compound **BBC** was obtained by substitution of two Br atoms on the 3,6-position of S-2 using dimesitylboryl group.

2.2.1. 3,6-Dibromo-N-butyl-carbazole (S-2)

7.4 g (0.033 mol) *N*-butyl-carbazole was dissolved in 50 mL acetic acid, and then 3.4 mL (0.066 mol) Br₂ in 50 mL acetic acid was added dropwise during 1 h. The mixture was continuously stirred at room temperature for further 2 h. A great deal of white precipitate formed and the separated precipitate was repeatedly washed with ethanol to give white needle-like crystals with a yield 70%. ¹H NMR (CDCl₃, 400 MHz), $\delta_{\rm H}$ (ppm): 0.89 (t, J = 7.3 Hz, 3H), 1.14–1.46 (m, 2H), 1.54–1.92 (m, 2H), 4.56 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.99 (s, 2H).

2.2.2. 3,6-Bis(dimesitylboryl)-N-butyl-carbazole (BBC)

Under the cover of N_2 , 1.6 g (4.2 mmol) S-2 in 50 mL freshly distilled THF was injected into a three-necked flask. Then the flask was cooled to -78 °C for about 30 min, until 14 mmol *n*-butyllithium in hexane solution was dropped. The flask was kept at -78 °C by dry ice-acetone bath for about one hour then warmed naturally to room temperature to get the lithium salt. The mixture was cooled to -78 °C again, and 2.5 g (9.3 mmol) dimesitylboron fluoride, which had been resolved in 10 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. White powders with yield 35% were obtained. ¹H NMR (CDCl₃, 400 MHz), $\delta_{\rm H}$ (ppm): 0.90 (t, J = 7.3 Hz, 3H), 1.09–1.42 (m, 4H), 1.94 (s, 24H), 2.24 (s, 12H), 4.23 (t, J = 7.8 Hz, 2H), 6.75 (s, 8H), 7.23 (d, J = 9.3 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 8.23 (s, 2H). Anal. calcd for C₅₂H₅₉B₂N: C, 86.79; H, 8.26; N, 1.95. Found: C, 86.55; H, 8.18; N, 1.97. MS: *m*/*z* (%) 719 (M⁺, 100).

2.3. Measurements

Linear absorption spectra with $C = 1.0 \times 10^{-5}$ mol L⁻¹ were recorded on a PE Lambda 35 UV/VIS spectrometer. Single-photon excited fluorescence (SPEF) spectra with $C = 1.0 \times 10^{-5}$ 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 [11] using a standard method [12]. TPEF exper-



Scheme 1. Synthetic strategy of the title compound.

iments with $C = 1.0 \times 10^{-3}$ mol L⁻¹ were performed with a femtosecond Ti: sapphire laser (76 MHz, 200 fs pulse width, Coherent Mira 900) as pump source and a streak camera (Hamamatsu, model: C5680) in conjunction with an imaging spectrograph (Hamamatsu, model: C5094) as recorder. The TPA and TPEF cross-sections of **BBC** in toluene and THF solutions were measured by using TPEF measurement technique and coumarin 307 as standard solution [13].

2.4. Theory calculation

We performed DFT (density functional theory) quantum chemical calculations on the compound by using Gaussian 03 [14]. The functional used includes Becke's three parameter hybride functional [15] in conjunction with the Lee–Yang–Parr correlation functional [16], which is abbreviated as B3LYP. The basis set is taken as 6-31G. HOMO and LUMO of the compound studied are obtained using the visualization package Gauss View [17].

3. Results and discussion

3.1. Linear absorption and single-photon excited fluorescence properties

The data of linear absorption and SPEF properties of **BBC** in four solvents with different polarity are summarized in Table 1. From Table 1, Figs. 1 and 2, one can see that absorption peak position and absorbance show little dependence on solvent polarity, but SPEF properties are obviously influenced by solvent polarity. The peak positions of SPEF are red-shifted and the fluorescence quantum yields increased. The bathochromic phenomena indicate that the polarity of the compound in excited state is much larger than that in ground state. The difference in dipole moment between excited state and ground state ($\Delta \mu_{ge}$) can be estimated by Lippert–Mataga equation [18]:

$$\Delta \overline{v} = \overline{v}_{abs} - \overline{v}_{SPEF} = 2\Delta \mu_{ge}^2 \Delta f / hca^3 + \text{const}$$
(1)

with $\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)].$

In this equation, h is Planck's constant, c is the speed of light, a is the cavity radius of the molecule, Δf is orientation polarizability reflecting the polarity of solvent, ε and n is the dielectric constant and the refractive index of solvent,

Table 1		
Photophysical	properties	of BBC



Fig. 1. Linear absorption spectra of BBC in various solvents.



Fig. 2. Single-photon excited fluorescence spectra of **BBC** in various solvents.

respectively. From Fig. 3, Stokes' shifts are basically proportional to the orientational polarizability Δf . The slope m of the fitted line is 3.11×10^3 cm⁻¹. The theory geometry optimization procedure gives the total volume of a molecule and its equivalent *a* value (8.0 Å) was obtained by assuming the molecule to be a sphere having this volume. Then the difference in dipole moment between the ground and excited states in solution $\Delta \mu_{ge}$ is 12.5 D. The dependence of fluorescence quantum yield on solvent polarity is unusual because a general trend for the D–A systems is

λ_{abs}^{max} (nm)	$\epsilon_{\rm max}~(10^4~{\rm cm}^{-1}~{\rm M}^{-1})$	$\lambda_{\text{SPEF}}^{\max}$ (nm)	$\Delta \overline{v} \ (cm^{-1})$	$arPhi^{\mathrm{a}}$	$\lambda_{\text{TPEF}}^{\max}$ (nm)	$\sigma_e^{\ b}(GM)^c$	$\sigma^{\rm b}({ m GM})^{\rm c}$		
364	3.9	374, 392	1294	0.52					
366	3.6	385	1348	0.68	393	23	34		
368	3.5	394	1793	0.73	403	28	38		
366	3.4	400	2322	0.74					
	λ_{abs}^{max} (nm) 364 366 368 368 366	$\begin{array}{c c} \lambda_{abs}^{max} (nm) & \varepsilon_{max} (10^4 cm^{-1} M^{-1}) \\ \hline 364 & 3.9 \\ 366 & 3.6 \\ 368 & 3.5 \\ 366 & 3.4 \\ \end{array}$	$\begin{array}{c cccc} \lambda_{abs}^{max} (nm) & \varepsilon_{max} \left(10^4 cm^{-1} M^{-1}\right) & \lambda_{SPEF}^{max} (nm) \\ \hline 364 & 3.9 & 374, 392 \\ 366 & 3.6 & 385 \\ 368 & 3.5 & 394 \\ 366 & 3.4 & 400 \\ \hline \end{array}$	$\begin{array}{c cccc} \lambda_{abs}^{max} (nm) & \hat{v}_{max} (10^4 {\rm cm}^{-1} {\rm M}^{-1}) & \lambda_{\rm SPEF}^{max} (nm) & \Delta \overline{\nu} ({\rm cm}^{-1}) \\ \hline 364 & 3.9 & 374, 392 & 1294 \\ 366 & 3.6 & 385 & 1348 \\ 368 & 3.5 & 394 & 1793 \\ 366 & 3.4 & 400 & 2322 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $		

^a Fluorescence quantum yields determined using coumarin 307 as standard.

^b TPEF cross-section (σ_e) and TPA cross-section (σ) at $\lambda_{ex} = 720$ nm.

^c 1GM = 10^{-50} cm⁴ s photon⁻¹ molecule⁻¹.



Fig. 3. Stokes shift $\Delta \overline{\nu}$ vs orientational polarizability Δf of the solvents. (The scatter dots are the experimental data and the line is the linearly fitted result.)

that fluorescence quantum yield decreases with increasing solvent polarity. An origin of this unexpected behavior may be a decrease of nonradiative deactivation rate [19].

We also investigated the charge transfer mode of the compound. Fig. 4 illustrates the electron density distribution of the frontier molecular orbitals (HOMO and LUMO). In the HOMO, the electrons are mainly concentrated on the nitrogen atom and carbazole ring, while in the LUMO, the electrons are spread to the boron atoms. The theory calculation indicates that charge transfer from *N*-butyl-carbazole to boron atoms upon excitation from HOMO to LUMO.

3.2. Two-photon excited fluorescence properties

TPEF was collected at a direction perpendicular to the pump beam. During TPEF measurement, volume reabsorption effect occurred because concentrated solutions $(1.0 \times 10^{-3} \text{ mol } \text{L}^{-1})$ were used. To minimize the re-absorption effect, the excitation beam was focused as closely as possible to the quartz cell wall, which faced the slit of imaging spectrograph. From linear absorption spectra (Fig. 1), one can see that the compound is linear optical penetrable in the range from 400 to 1000 nm. Therefore, any emission induced by excitation at this wavelength range should be derived from multiphoton absorption process.

When a Ti: sapphire femtosecond laser output 720 nm laser is used as the pump source, the compound shows strong blue-violet TPEF in toluene (393 nm) and THF (403 nm) solution. TPEF peak positions of the compound in both solvents are obvious red-shifted relative to that of their corresponding SPEF spectra, which may result from re-absorption effect in concentrated solution [20]. In Fig. 5, one can see that the short wavelength side of the SPEF and the long wavelength side of the linear absorption band have a certain extent overlapping. The spectral profiles of the TPEF spectra of the compound are very similar



Fig. 4. The electron density distribution of the frontier molecular orbitals of **BBC**.

to that of SPEF spectra. Just like solvent effect on SPEF, the peak position of TPEF is red-shifted with the increase of solvent polarity from toluene to THF. λ_{max} (TPEF) is



Fig. 5. The UV absorption, single-photon-excited fluorescence (SPEF) spectra with $C = 1.0 \times 10^{-5} \text{ mol L}^{-1}$ and two-photon-excited fluorescence (TPEF) spectrum with $C = 1.0 \times 10^{-3} \text{ mol L}^{-1}$ of **BBC** in THF.

shifted from 393 nm in toluene to 403 nm in THF. All the spectral characters discussed above seems to indicate that either single or two-photon excited initial state may relax to the same fluorescence emission state.

TPA cross-section σ and TPEF cross-section σ_e are important parameters in evaluating materials' TPA and TPEF properties [13,21]. There are many methods to get them such as Z-scan, TPEF measurement technique and so on. In this paper, the latter are used to get σ and σ_e of the compound and coumarin 307 is selected as standard solution. The TPEF cross-sections (σ_e) were obtained referring to the following equation [21]:

$$\sigma_{\rm e} = \sigma_{\rm e,r} \frac{C_{\rm r}}{C} \frac{n_{\rm r}}{n} \frac{F}{F_{\rm r}}$$
(2)

In this equation, r stands for the reference compound, n for the refractive index, C for the concentration and F for the integral fluorescence intensity.

$$\sigma = \sigma_{\rm e}/\Phi' \tag{3}$$

 Φ' is TPEF quantum yield. Up to now, it is difficult to measure Φ' strictly. Here we assumed that Φ' are constant over the entire spectral range and $\Phi' = \Phi$ in our experiment. TPA cross-section at 720 nm in toluene and THF is measured 34 GM and 38 GM in this way, respectively.

4. Conclusion

A new A- π -D- π -A type organoboron compound has been synthesized. The single and two-photon related photophysical properties are reported. The compound exhibits strong two-photon up-converted blue-violet fluorescence with 720 nm laser excitation. DFT quantum chemical calculation indicates that upon excitation to the excited state, charge transfer from *N*-butyl-carbazole to boron atoms takes place.

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