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PAPER

A boron-containing carbazole dimer: synthesis, photophysical properties and sensing properties†

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A novel boron-containing π-conjugated compound **BCCB** has been synthesized by the introduction of electron-acceptors (dimesitylboron groups) at the 3,3′-positions of a carbazole dimer (electron-donor). The compound **BCCB** possesses excellent electrochemical properties and high fluorescence quantum yields. In addition, **BCCB** is a sensitive fluorescence sensor with remarkable colour changes and the results could be confirmed through theoretical calculations of the compounds **BCCB** and **$[^n\mathrm{Bu_4N}]^+{}_2[\mathrm{BCCB{\cdot}(F)_2}]^{2-}$**. Our studies indicate that **BCCB** could be used as an excellent optoelectronic material in OLED devices and a ratiometric fluorescent chemosensor.

Introduction

In recent years, π-conjugated derivatives containing boron atoms have attracted a great deal of attention because of their excellent potential applications.[1,2] Their outstanding photophysical properties, such as remarkable solvatochromism of emission spectra and high fluorescence quantum yields, arise from the p_π–π conjugation between the vacant p-orbital on the boron centre with the π-orbital of the π-conjugated molecular system.[3] In addition, three coordinated boron groups can be used as Lewis acids to coordinate with Lewis bases, such as fluoride ions which has attracted great attention because it is highly relevant to human health and environmental issues.[4] The complexation of the boron groups with Lewis bases interrupts the p_π–π conjugation, causing significant changes in photophysical properties.[5] Therefore, boron-containing π-conjugated derivatives have potential applications as two-photon emission materials, nonlinear optical materials and transporting and emissive materials in organic light-emitting devices (OLEDs) as well as selective chemosensors for the detection of fluoride ions.[6–8] Therefore, organoboron compounds have received worldwide interest and an increasing number of studies have focused on utilizing donor–acceptor structures to enhance the photophysical or sensing properties.[9,10]

In view of this situation, we became interested in boron-containing π-conjugated compounds bearing boron groups as electron-acceptors and amine moieties (diphenylamine and carbazole) as electron-donors. Carbazole dimers have an electron-rich structure, high thermal stability and unique electrical and optical properties.[11,12] Chen *et al.* have prepared a series of derivatives by incorporating diarylamines at the peripheries of a carbazole dimer, which were fluorescent in the blue to yellow region with moderate to good quantum yields.[12] Although carbazole dimers have been widely studied, to the best of our knowledge, investigations focused on functionalization of the carbazole dimer *via* connecting electron-acceptors to the 3-,3′-positions have never been reported.

For this reason, in this paper, we designed and synthesized a novel A-π-D-π-A compound containing a large π-conjugated system and two diaryl boron groups as side chains (electron-acceptors) as well as a carbazole dimer as the core (electron-donor), named (*E*)-1,2-bis(3-dimesitylboryl-9-ethylcarbazol-6-yl)ethene (**BCCB**). The structure of compound **BCCB** was characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry and elemental analysis. In addition, its photophysical, electrochemical and sensing properties were investigated by experimental methods and theoretical calculations. We anticipate that the results will increase knowledge of the design and synthesis of novel boron-containing π-conjugated compounds with excellent photophysical and sensing properties.

Results and discussion

Synthesis of BCCB

BCCB was synthesized in four steps as shown in Scheme 1. The first step began with ethylation of carbazole followed by treating the resulting 9-ethylcarbazole with $POCl_3$ and DMF *via* Vilsmeier–Haack reaction to achieve 9-ethylcarbazole-3-carbaldehyde (**1**) in 65% yield. Secondly, 6-bromo-9-ethylcarbazole-3-carbaldehyde (**2**) was prepared in high yield by the reaction of

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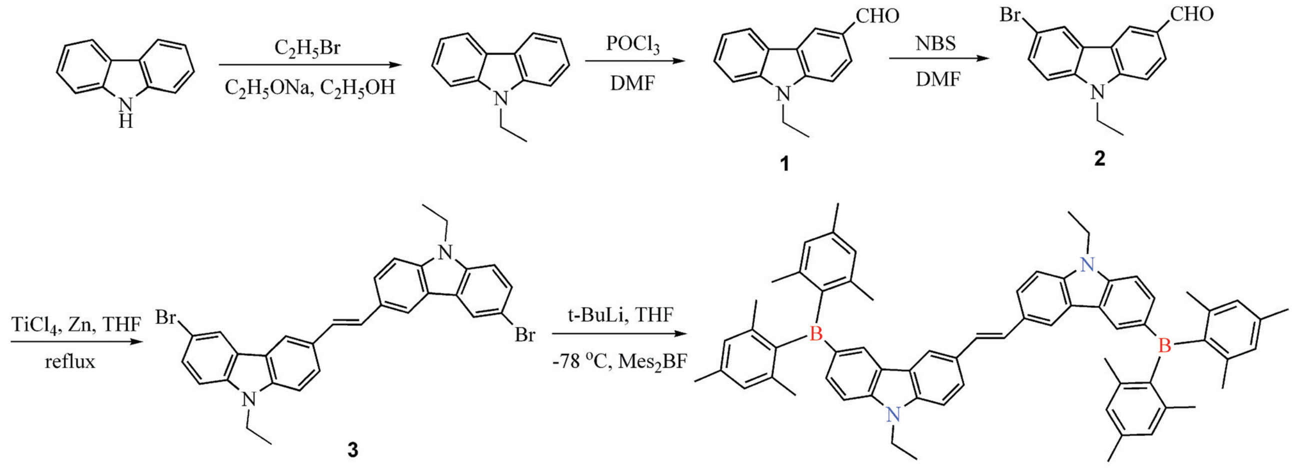
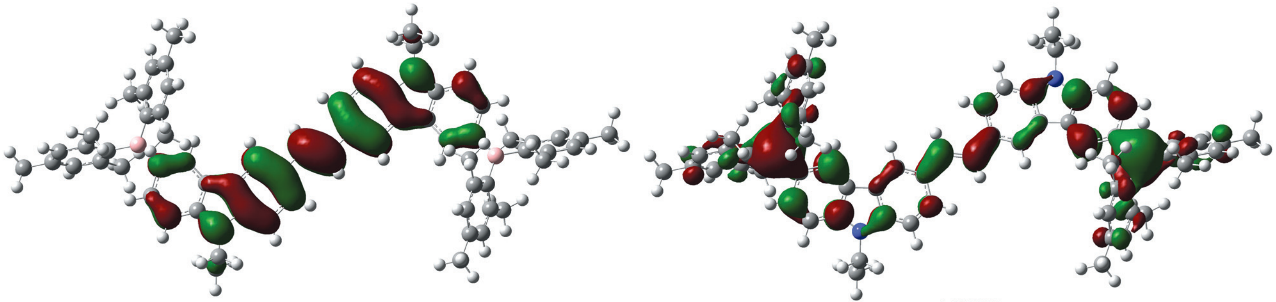
† Electronic supplementary information (ESI) available: ^{1}H NMR, ^{13}C NMR, detailed titration spectra and additional data. See DOI: 10.1039/c2ob00024e



BCCB

Scheme 1 The synthetic route to compound **BCCB**.



HOMO LUMO

Fig. 1 HOMO and LUMO diagrams of compound **BCCB**

compound **1** with NBS. Thirdly, compound **2** was subjected to a McMurry coupling reaction under nitrogen in the presence of titanium(IV) chloride and Zn powder as a catalytic system to furnish (*E*)-1,2-bis(3-bromo-9-ethylcarbazol-6-yl)ethene (**3**) in 75% yield. The final product **BCCB** was obtained in 56% yield by treatment of compound **3** with *t*-BuLi followed by addition of dimesitylboron fluoride. Further details are given in the Experimental section.

Theoretical calculations

Theoretical calculations can provide a reasonable qualitative indication of the excitation and emission properties.[13] Herein, the frontier molecular orbitals of **BCCB**, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were investigated at the DFT/B3LYP/6-31G (d, p) level. Molecular orbital calculations revealed that the HOMO of compound **BCCB** is localized mainly on the carbazole dimer, whereas the LUMO includes the two boron side chains and the carbazole dimer (Fig. 1). Thus, the electronic transition from the ground state to the first excited state mainly involves the intramolecular charge transfer (ICT) from the carbazole dimer to the peripheral boron groups.[14] The calculated HOMO and LUMO energy levels are −4.85 eV and −1.46 eV. Although the calculated LUMO level is higher than the experimental value, the calculated HOMO level and HOMO–LUMO gap (3.39 eV) are in good agreement with experimental data.

Photophysical properties

The UV-vis absorption spectra (Fig. 2) and fluorescence spectra (Fig. 3) of compound **BCCB** were measured in various solvents (1.0×10^{-5} M) of different polarity. As shown in Fig. 2, the absorption spectra of **BCCB** display almost identical maxima in the different solvents, indicating only slight solvent-dependence. This indicates that the structural and electronic characteristics of the ground and Franck–Condon (FC) excited states[15] do not differ much with a change in solvent polarity. Compound **BCCB** exhibits an absorption band at 340–350 nm which is assigned to the π–π^* transition of the carbazole dimer core[12] and a low-energy broad band at 390–420 nm which is assigned to the overlapping ICT band from the electron-donor (carbazole dimer) to the electron-acceptors (diaryl boron groups).

To further elucidate the absorption spectra of compound **BCCB** observed experimentally, we computed a singlet–singlet electronic transition based on the optimized geometry of the ground state of **BCCB**, using time-dependent density functional theory (TD-DFT) method at the B3LYP/6-31G (d, p) level. The excitation energies, oscillator strengths and main configurations for the most relevant absorption bands were listed in Table S1,

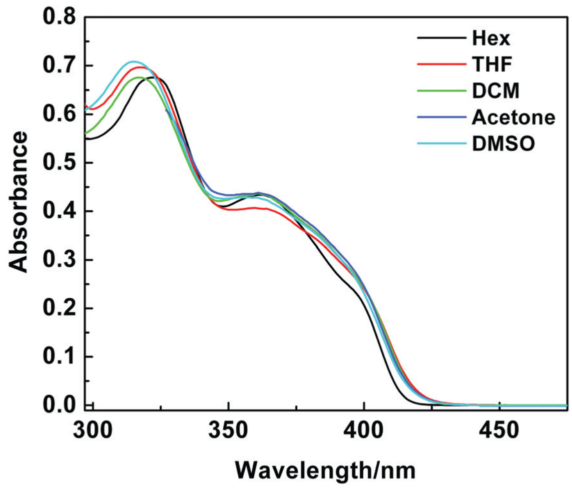


Fig. 2 UV-vis absorption spectra of compound **BCCB** in different solvents.

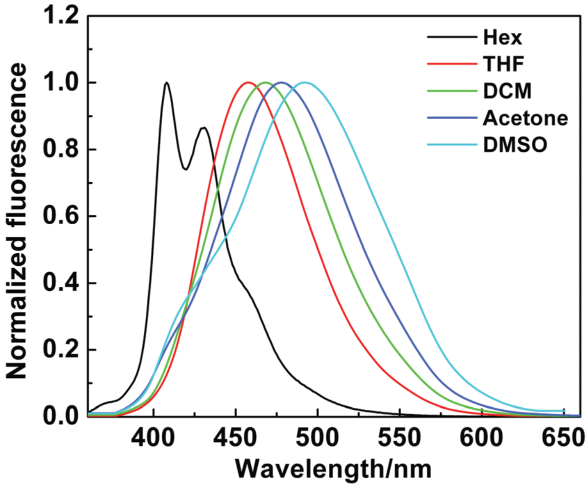


Fig. 3 Fluorescence spectra of compound **BCCB** in different solvents. Excited at 380 nm.

ESI.† Owing to the lowest-energy electronic transition, HOMO → LUMO, which mostly consists of the intramolecular charge transfer, a weak absorption band occurs around 410 nm. Another absorption band of the carbazole dimer occurs around 340 nm, mainly consisting of a HOMO → LUMO + 3 vertical transition (Fig. S1, ESI†).[15,16] The calculated results are in good agreement with the experimental absorption spectra.

In contrast to the slight solvatochromism in the UV-vis absorption spectra, the differences in the corresponding fluorescence spectra are dependent on solvent polarity; compound **BCCB** displayed remarkable solvatochromism. As shown in Fig. 3, with increasing polarity of the solvents, a bathochromic shift of 90 nm ranging from 405 nm (in hexane) to 495 nm (in DMSO) was observed. Because polar solvents are propitious to the ICT process,[17] such a distinct solvatochromism indicated that intramolecular charge transfer from the carbazole dimer to the dimesitylboron groups takes place during the excitation process.

The fluorescence quantum yields and the fluorescence decay behaviours of compound **BCCB** were measured in different polar solvents at room temperature. The fluorescence quantum yield was calculated from eqn (1).[18]

Table 1 The fluorescence quantum yields (Φ) and lifetimes (τ, ns) of compound **BCCB** in different solvents

Solvents	Hex	THF	DCM	Acetone	DMSO
Quantum yields	0.81	0.73	0.62	0.58	0.54(0.95[a])
Lifetimes (ns)	4.97	4.29	4.18	4.23	4.15(3.01[a])

[a] Recorded in DMSO solution with saturated fluoride ions.

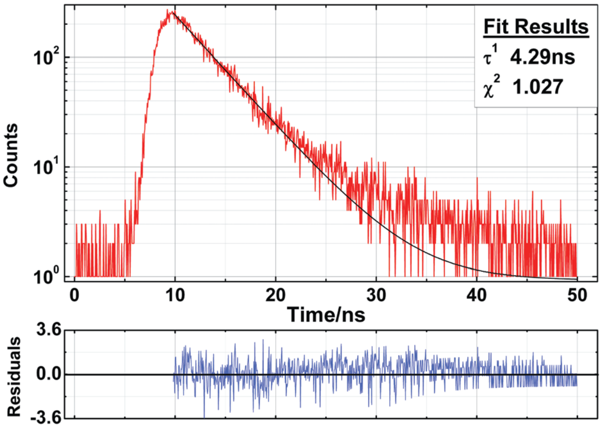


Fig. 4 The fluorescence decay profile of compound **BCCB** in THF.

$$\Phi_s = \Phi_r \frac{F_s A_r}{F_r A_s}\left(\frac{n_r}{n_s}\right)^2 \tag{1}$$

where Φ is the fluorescence quantum yield, F is the integration of the emission intensities, A is the absorbance at the excitation wavelength, n is the refractive index of the solution and the subscripts "r" and "s" denote reference and sample, respectively. The fluorescence quantum yields (Φ) and fluorescence lifetimes (τ, ns) are collected in Table 1. A typical fluorescence decay curve of **BCCB** is shown in Fig. 4. As shown in Table 1, compound **BCCB** exhibited high fluorescence quantum yields (Φ_{max} = 0.81), indicating that it could be used as an excellent optoelectronic material in organic light-emitting diode devices.

Electrochemical properties

The electrochemical properties of compound **BCCB** were studied by cyclic voltammetry measurements (Fig. S4, ESI†). The measurement was performed with 1.0×10^{-5} M MeCN solution of **BCCB** under argon using 1.0×10^{-3} M tetrabutylammonium perchlorate in anhydrous MeCN as the supporting electrolyte. The HOMO energy level can be calculated by using the empirical equation HOMO = $-(E_{ox} + 4.40)$ eV, where E_{ox} stands for the onset potentials for oxidation. Therefore, the HOMO energy level of **BCCB** was estimated by using the onset potentials for oxidation (0.93 V) and was found to be −5.33 eV. From the absorption edges of the UV-vis spectra, the optical band gap (E_g) was estimated as 3.05 eV. The LUMO energy level, which was derived from the relationship E_g = HOMO −

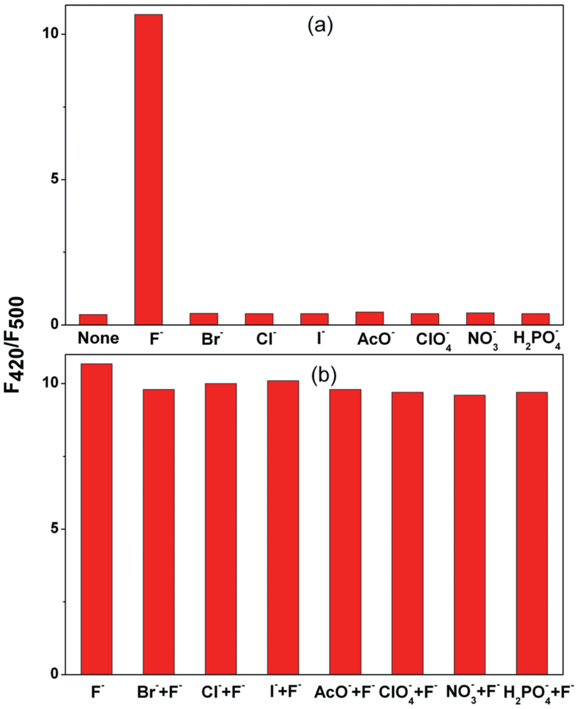


Fig. 5 (a) Fluorescence responses of **BCCB** upon addition of 20 equiv. of various anions in DMSO solution. (b) Fluorescence responses of **BCCB** to **F**$^-$ (20 equiv.) containing 20 equiv. of various other anions.

LUMO, was calculated to be −2.28 eV. The low HOMO energy level suggests that compound **BCCB** has high oxidative stability.

Sensing properties

As a general adapted method, excess amounts (*ca.* 20 equiv.) of various tetrabutylammonium anion salts were added to 1.0 × 10^{-5} M DMSO solutions of **BCCB**. Compound **BCCB** shows weak complexation with other halide anions (Br^-, Cl^-, I^-), AcO^-, ClO_4^-, NO_3^-, $H_2PO_4^-$, but not for F^- and CN^- (Fig. 5a). In addition, competition experiments were also performed by addition of 20 equiv. of F^- to the DMSO solutions of compound **BCCB** in the presence of 20 equiv. of miscellaneous anion salts (Fig. 5b). The competitive anions had no obvious interference with the detection of F^-, indicating the system was hardly affected by these coexistent anions.

In view of specific interaction between F^- and the boron centre, the response of compound **BCCB** (1.0 × 10^{-5} M) to F^- was investigated through absorption spectra (Fig. S2, ESI†) and fluorescence spectra. As shown in Fig. 6a, with the stepwise addition of F^-, the green ICT emission band centered at 500 nm underwent gradual "turn-off", along with the blue emission band of local excitation[19] at 420 nm displaying a rapid "turn-on", due to the inhibition of the intramolecular charge transfer from the carbazole dimer to the boron side chains. The changes in the fluorescence spectrum stopped and the ratio of the emission intensities at 420 nm and 500 nm (I_{420}/I_{500}) became constant when the amount of F^- added reached 4 equiv. (Fig. 6b); notably, the complexation with fluoride ions caused an obvious increase in fluorescence efficiency (Φ = 0.54 for **BCCB**; Φ = 0.95 for **BCCB·F$_2$$^{2-}$**). The fluorescence quantum yields (Φ) and lifetimes (τ, ns) of compound **BCCB·F$_2$$^{2-}$** in DMSO were also listed in Table 1. Upon stepwise addition of F^-, a clear isosbestic point at 460 nm could be observed; upon further addition of F^-, the isosbestic point shifted from 460 to 485 nm. Such a similar shift of more than 15 nm has already been reported.[20] The two different isosbestic points of the emission spectra are obviously due to the formation of the monoanion **BCCB·F**$^-$ and the dianion **BCCB·F$_2$$^{2-}$**, respectively. According to the 1 : 2 Benesi–Hildebrand equation (Fig. S5, ESI†), the plot of $1/(I - I_0)$ against $1/[F^-]^2$ shows a linear relationship ($R^2 = 0.9978$), indicating that **BCCB** indeed associates with F^- in a 1 : 2 stoichiometry.[21] The association constant, K, is determined from the slope to be 3.98 × 10^8 M^{-2}. When examining the emission changes at 410 nm upon gradual addition of F^-, a good linear working range from 0.25–3.25 equiv. was observed (Fig. 6c). The detection limit was measured to be 3.81 × 10^{-7} M, which suggests that compound **BCCB** is highly sensitive for the monitoring of fluoride ions.

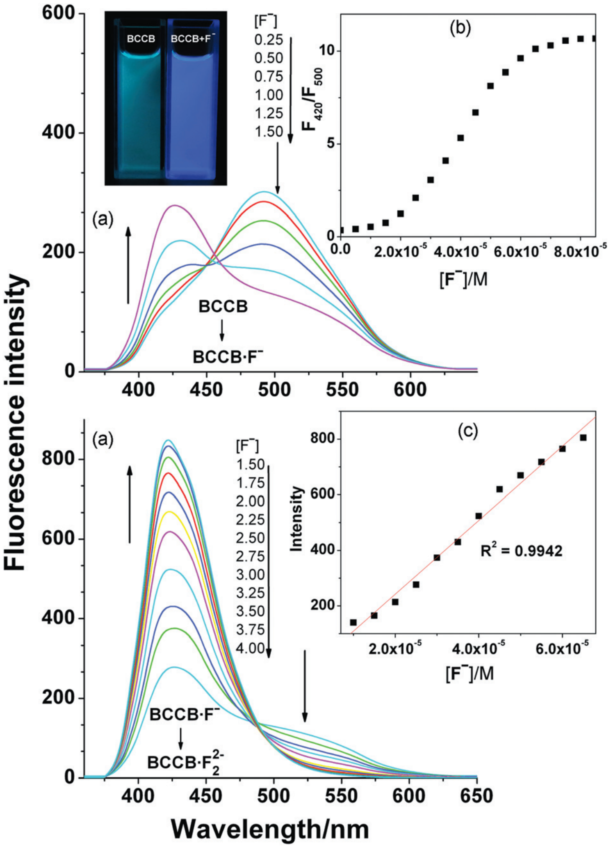


Fig. 6 (a) Fluorescence titration spectra of **BCCB** in DMSO upon gradual addition of **F**$^-$. Excited at 380 nm. (b) Fluorescence intensity ratio changes (I_{420}/I_{500}) of **BCCB** upon gradual addition of **F**$^-$. (c) Fluorescence intensity changes at 420 nm upon gradual addition of **F**$^-$.

The emission spectra of **BCCB·F$_2$$^{2-}$** are quite close to those of (*E*)-1,2-bis(9-ethyl-3,9′-bi(9*H*-carbazol)-6-yl)-ethene, which does not contain the diaryl boron groups.[12] It indicated that the complexation of the boron groups with F^- changed three-coordinated boron to four-coordinated boron and interrupted the p_π–π conjugation, just as the character of the boron centre is changed from electron-acceptor to electron-donor. In order to gain a

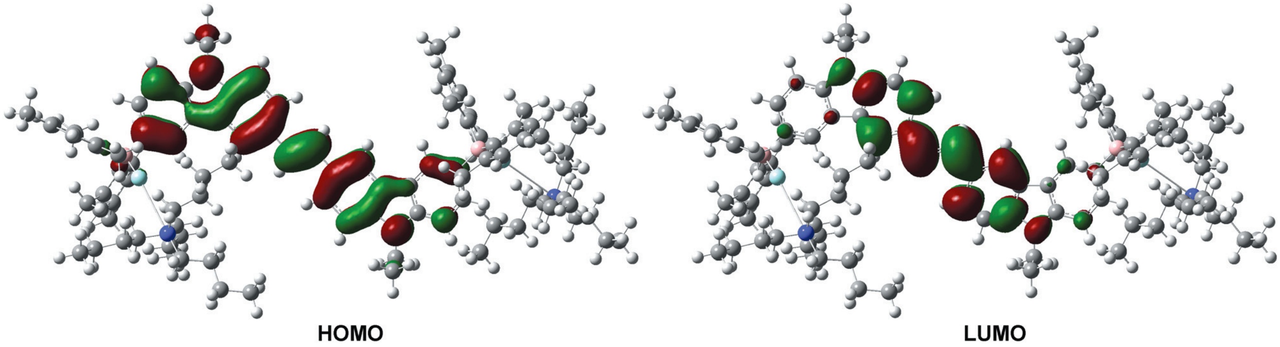


Fig. 7 HOMO and LUMO diagrams of compound **$[^n\mathrm{Bu_4N}]^+{}_2[\mathrm{BCCB}{\cdot}(\mathrm{F})_2]^{2-}$**.

detailed insight into the sensing properties of **BCCB**, we conducted theoretical calculations of compound **$\mathrm{BCCB}{\cdot}\mathrm{F_2}^{2-}$** using DFT/B3LYP/6-31G++ (d, p) method. As shown in Fig. 7, the electron density of the HOMO and LUMO are both localized primarily on the carbazole dimer. Compared with compound **BCCB**, the frontier molecular orbitals of **$\mathrm{BCCB}{\cdot}\mathrm{F_2}^{2-}$** reveals the inhibition of electron flow from the N centre (electron-donor) to the B centre (electron-acceptor), causing the disappearance of the ICT emission band around 500 nm. The result could lead to the understanding of the changes in the fluorescence spectra.

Conclusions

In summary, a novel A-π-D-π-A compound **BCCB** was obtained by the introduction of diaryl boron groups at the 3,3′-positions of carbazole dimer. **BCCB** possesses outstanding oxidative stability and high fluorescence quantum yields, indicating its potential application as an excellent optoelectronic material in OLEDs. The theoretical calculations are in good agreement with the experimental results of the absorption spectra, and can provide useful guidelines to understand the changes in the fluorescence spectra. Moreover, the competition and titration experiments suggest that compound **BCCB** is a highly sensitive ratiometric fluorescence sensory material with remarkable colour changes. Compared with a blank sample, a saturated F^- solution increases the fluorescence efficiency about twofold. Our studies will improve knowledge to facilitate the ongoing exploration in optoelectronic applications and the design of novel boron-containing π-conjugated derivatives with outstanding sensing properties.

Experimental section

Materials and general methods

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were freshly distilled according to standard procedures. All reagents were used as received from commercial sources without further purification. Melting points were determined on a WRS-1B melting point detector. All NMR spectra were recorded on a Bruker Avance 600 MHz NMR spectrometer with $\mathrm{CDCl_3}$ as solvent. Absorption spectra were taken on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were obtained on a Shimadzu RF-5301PC fluorescence spectrometer (excited at 380 nm). Excitation and emission slit widths were both set at 3 nm. Cyclic voltammetry experiments were performed with a CHI-600C electrochemical analyzer, the measurements were carried out with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and an Ag/AgCl reference electrode. The scan speed is 50 mV $\mathrm{s^{-1}}$. The fluorescence decay curves were recorded with Time-Correlated Single Photon Counting (TCSPC) technique using a commercially available Edinburgh Instruments device. Fluorescence quantum yields were determined using a standard actinometry method. Quinine sulphate was used in the actinometer with a known fluorescence quantum yield of 0.55 in 0.1 M sulfuric acid, the samples were excited at 350 nm. All measurements were performed at room temperature. All calculations were carried out using the Gaussian03 program package.[22]

Synthesis of BCCB

The compounds **1**,[23] **2**[24] and **3**[12] were synthesized according to literature procedures.

9-Ethylcarbazole-3-carbaldehyde (1). M.p.: 89.7–90.5 °C. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$) δ (ppm): 10.09 (s, 1H), 8.61 (d, J = 1.5 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 8.01 (dd, J = 8.5, 1.6 Hz, 1H), 7.54 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.47 (t, J = 7.9 Hz, 2H), 7.35–7.31 (m, 1H), 4.41 (q, J = 7.3 Hz, 2H), 1.47 (t, J = 7.3 Hz, 3H).

6-Bromo-9-ethylcarbazole-3-carbaldehyde (2). 9-Ethylcarbazole-3-carbaldehyde (**1**) (10 g, 44.8 mmol) was dissolved in DMF (150 mL) and the solution was cooled in an ice bath. A solution of NBS (8.77 g, 49.3 mmol) in DMF (50 mL) was added dropwise. The reaction mixture was allowed to stir for 12 h at room temperature. Then, the mixture was poured into ice water, and the white precipitate was collected by filtration to afford 6-bromo-9-ethylcarbazole-3-carbaldehyde (**2**). Yield: 82%. M.p.: 131.4–132.2 °C. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$) δ (ppm): 10.09 (s, 1H), 8.53 (d, J = 1.2 Hz, 1H), 8.25 (d, J = 1.9 Hz, 1H), 8.03 (dd, J = 8.5, 1.4 Hz, 1H), 7.61 (dd, J = 8.6, 1.9 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 4.38 (q, J = 7.3 Hz, 2H), 1.46 (t, J = 7.3 Hz, 3H).

(*E*)-1,2-Bis(3-bromo-9-ethylcarbazol-6-yl)ethene(3). 6-Bromo-9-ethylcarbazole-3-carbaldehyde (**2**) (10 g, 33.1 mmol) and Zn powder (8.656 g, 132.4 mmol) was suspended in anhydrous THF (200 mL) under N_2. Titanium(IV) chloride (7.28 mL, 66.2 mmol) was added dropwise to the reaction mixture at −78 °C. Then, the cooling bath was removed, and the mixture was refluxed for 10 h. After cooling to room temperature, ice water (200 mL) was added and the reaction mixture was stirred for a further 0.5 h. The mixture was extracted with CH_2Cl_2 and the combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2–hexane) to afford (*E*)-1,2-bis(3-bromo-9-ethylcarbazol-6-yl)ethene (**3**). Yield: 75%. M.p.: 251.2–252.5 °C. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.24 (d, J = 1.9 Hz, 2H), 8.19 (s, 2H), 7.73 (dd, J = 8.5, 1.1 Hz, 2H), 7.54 (dd, J = 8.6, 1.8 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.32 (s, 2H), 7.27 (d, J = 8.6 Hz, 2H), 4.34 (q, J = 7.2 Hz, 4H), 1.44 (t, J = 7.3 Hz, 6H).

(*E*)-1,2-Bis(3-dimesitylboryl-9-ethylcarbazol-6-yl)ethene (BCCB). Under a dry atmosphere of nitrogen, *t*-BuLi (1.6 M solution) in hexane (2.4 mL, 3.84 mmol) was injected into a solution of **3** (1 g, 1.75 mmol) in anhydrous THF (40 mL) at −78 °C, followed by warming to room temperature. After stirring for 6 h, the reaction mixture was cooled to −78 °C again, and dimesitylboron fluoride (1.08 g, 4 mmol) in THF (20 mL) was added dropwise over 30 min. The temperature was allowed to rise to room temperature and the mixture was stirred for a further 12 h. After evaporation of the solvent, the residue was dissolved in dichloromethane and the precipitate was filtered off. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2–hexane) to give **BCCB**. Yield: 56%. M.p.: 135.4–137.1 °C. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.37 (s, 2H), 8.27 (s, 2H), 8.15 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.43–7.37 (m, 4H), 7.33 (s, 2H), 6.71 (s, 8H), 4.38 (q, J = 7.2 Hz, 4H), 2.25 (s, 12H), 2.00 (s, 24H), 1.47 (t, J = 7.1 Hz, 6H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 143.3, 141.0, 140.9, 138.5, 138.0, 128.4, 128.2, 125.8, 124.3, 123.1, 120.5, 119.0, 118.4, 108.9, 108.7, 108.6, 108.0, 37.7, 23.7, 22.3, 14.0. MS (m/z): 910.5611 (M^+). Anal. Calcd for $C_{66}H_{68}B_2N_2$: C, 87.03%; H, 7.52%; N, 3.08%. Found: C, 86.48%; H, 7.22%; N, 2.97%.

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