Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Aggregation induced ratiometric fluorescence change for a novel boron-based carbazole derivative

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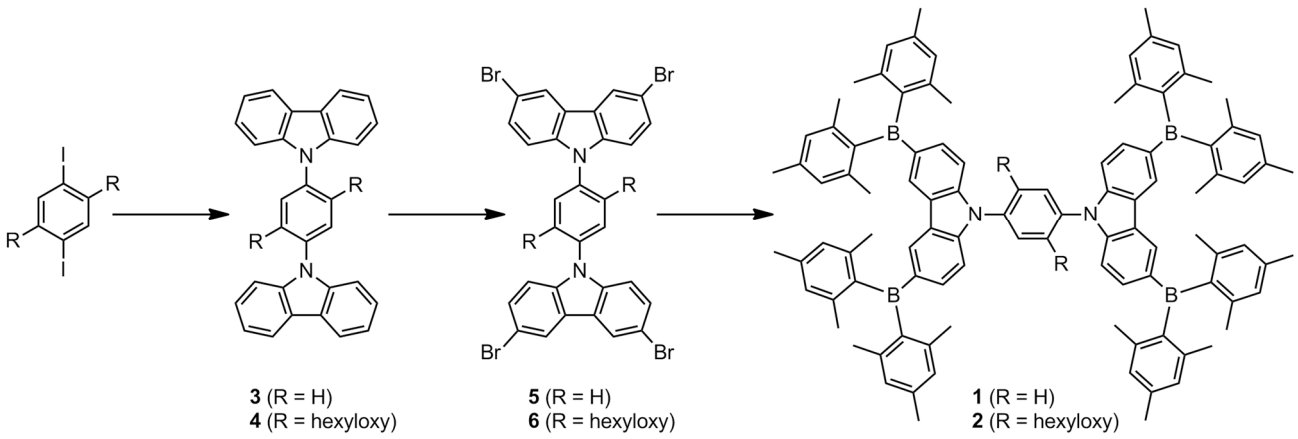
Experimental section

Materials and general methods. All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. All reagents were used as received from commercial sources without further purification except for the following. Tetrahydrofuran (THF) was freshly distilled according to standard procedures.

Melting points were recorded on a WRS-1B melting point detector. All NMR spectra were obtained on a Bruker Avance 600 MHz NMR spectrometer with $CDCl_3$ as solvent. Absorption spectra and fluorescence spectra (5 μM) were performed on a Shimadzu UV-2450 spectrophotometer and a Shimadzu RF-5301PC fluorescence spectrometer (excited at 350 nm), respectively. 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 (excited at 350 nm). FE-SEM images were studied by a JEOL JSM-67010F field emission scanning electron microscope. TEM images were studied by a Hitachi H-8100 transmission electron microscopy. All measurements were performed at RT.

Synthesis of compounds 1 and 2. **1** and **2** were synthesized as shown in Scheme S1. 1,4-bis(carbazol-9yl)benzene (**3**),[S1] 4-bis(carbazol-9yl)-2,5-bis(hexyloxy)benzene (**4**) and 1,4-bis(3,6-dibromocarbazol-9-yl)-2,5-bis(hexyloxy)benzene (**6**)[S2] were synthesized according to literature procedures.

Scheme S1. Synthetic routes for compounds **1** and **2**.



Synthesis of compound 1.

1,4-bis(carbazol-9yl)benzene (**3**). A mixture of carbazole (5.02 g, 30 mmol), 1,4-diiodobenzene (3.30 g, 10 mmol), 18-crown-6 (0.40 g, 1.5 mmol), K_2CO_3 (8.29 g, 60 mmol) and CuI (0.57 g, 3 mmol) was dissolved in DMPU. The reaction mixture was heated at 170 ^{o}C under a nitrogen atmosphere for 18 h. After cooling to room temperature, ice water (200 mL) was added. The mixture was stirred for a further 0.5 h and filtered. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane) to afford the desired product as a white solid (2.08 g, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 (d, J = 7.8 Hz, 4H), 7.82 (s, 4H), 7.57 (d, J = 8.1 Hz, 4H), 7.48 (t, J = 7.6 Hz, 4H), 7.34 (t, J = 7.4 Hz, 4H).

1,4-bis(3,6-dibromocarbazol-9-yl)benzene (**5**). NBS (0.89 g, 5 mmol) in DMF (20 mL) was added dropwise to a

solution of **3** (2.04 g, 5 mmol) in DMF (50 mL) at 0 ^{o}C. The reaction mixture was stirred for 12 h at room temperature. Then, the mixture poured into ice water, and the white precipitate was collected by filtration. The obtained white solid was purified by flash silica-gel column chromatography using petroleum ether as eluent to afford **3** as a white solid (3.11g, 86% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 1.9 Hz, 4H), 7.81 (s, 4H), 7.58 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.43 (d, *J* = 8.6 Hz, 4H).

1,4-bis(3,6-bis(dimesitylboryl)carbazol-9-yl)benzene (**1**). To a solution of **5** (0.33 g, 0.46 mmol) in anhydrous THF (40 mL), t-BuLi (1.6 M solution) in hexane (1.71 mL, 2.74 mmol) was injected at -78 ^{o}C under a dry atmosphere of nitrogen. After stirring for 6 h at room temperature, the reaction mixture was cooled to -78 ^{o}C again, and dimesitylboron fluoride (0.98 g, 3.63 mmol) in THF (20 mL) was added dropwise. The temperature was allowed to rise to room temperature and the mixture was stirred overnight. After the solvent had been removed, residue was dissolved in dichloromethane and precipitate was filtered off. Filtrate was evaporated to dryness, and the crude product was purified by silica-gel column chromatography (CH_2Cl_2/hexane) to give **1** as a pale yellow solid (0.17 g, 26% yield). M.p. > 300 °C; MS (m/z): 1400.8 (M^+). Anal. Calcd for $C_{102}H_{104}B_4N_2$: C, 87.43% ; H, 7.48%; N, 2.00%. Found: C, 87.32%; H, 7.47%; N, 1.97%; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 4H), 7.84 (s, 4H), 7.59 (d, *J* = 8.1 Hz, 4H), 7.48 (d, *J* = 8.1 Hz, 4H), 6.72 (s, 16H), 2.27 (s, 24H), 2.02 (s, 48H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.78, 141.82, 141.35, 139.49, 131.28, 131.18, 131.01, 129.05, 123.35, 123.19, 112.65, 25.16, 24.08.

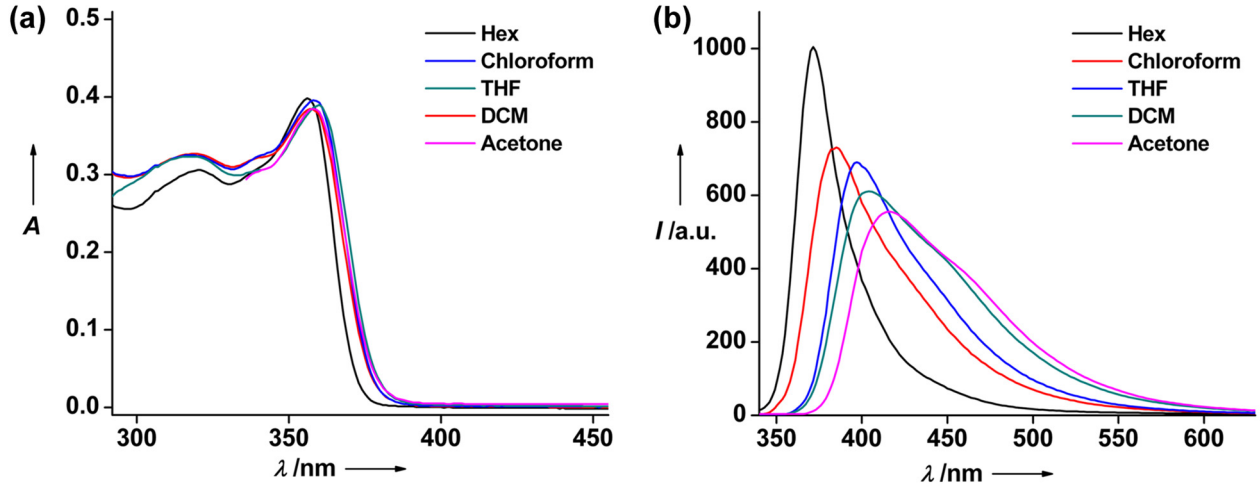
Synthesis of compound 2. 1,4-bis(3,6-bis(dimesitylboryl)carbazol-9-yl)-2,5-bis(hexyloxy)benzene (**2**) was synthesized by a similar procedure as described for **1**.

1,4-bis(carbazol-9yl)-2,5-bis(hexyloxy)benzene (**4**). Yield: 37%, a white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.17 (d, *J* = 7.8 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 4H), 7.30 (s, 2H), 3.77 (t, *J* = 6.4 Hz, 4H), 1.38–1.33 (m, 4H), 1.05–0.98 (m, 4H), 0.98–0.88 (m, 8H), 0.69 (t, *J* = 7.2 Hz, 6H).

1,4-bis(3,6-dibromocarbazol-9-yl)-2,5-bis(hexyloxy)benzene (**6**). Yield: 91%, a white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 1.7 Hz, 4H), 7.54 (dd, *J* = 8.6, 1.7 Hz, 4H), 7.24 (s, 2H), 7.18 (d, *J* = 8.6 Hz, 4H), 3.78 (t, *J* = 6.3 Hz, 4H), 1.41–1.31 (m, 4H), 1.09–1.00 (m, 4H), 0.96–0.90 (m, 8H), 0.72 (t, *J* = 7.2 Hz, 6H).

1,4-bis(3,6-bis(dimesitylboryl)carbazol-9-yl)-2,5-bis(hexyloxy)benzene (**2**). Yield: 55%, a pale yellow solid; M.p. 160 °C; MS (m/z): 1602.0 (M^+); Anal. Calcd for $C_{114}H_{128}B_4N_2O_2$: C, 85.50% ; H, 8.06%; N, 1.75%. Found: C, 85.34%; H, 8.00%; N, 1.69%; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.37 (s, 4H), 7.60 (d, *J* = 8.2 Hz, 4H), 7.32 (s, 2H), 7.22 (d, *J* = 8.2 Hz, 4H), 6.83 (s, 16H), 3.79 (t, *J* = 6.4 Hz, 4H), 2.32 (s, 24H), 2.04 (s, 48H), 1.40–1.31 (m, 4H), 1.02–0.96 (m, 8H), 0.67 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 147.06, 143.83, 143.78, 141.34, 141.16, 138.22, 132.98, 131.28, 131.00, 129.80, 126.96, 123.06, 112.90, 72.74, 34.06, 34.02, 31.67, 28.12, 28.08, 26.48, 25.16, 24.11, 24.08, 16.74.

Figure S1. Absorption spectra (a) and fluorescence spectra (b) of compound **1** in different solvents. Excited at 350 nm.



Theoretical calculations

We calculated frontier molecular orbitals (Figure S2) using density functional theory (DFT) method, absorption and fluorescence spectra (Figure S3) in THF solvent using time-dependent density functional theory (TD-DFT) method. All calculations were performed using the B3LYP functional and the 6-31G (d, p) basis set. The excitation energies, oscillator strengths and main configurations for the most relevant singlet excited states were listed in Table S1 and Table S2.

As shown in Figure S2 and Table S1, all the electronic transitions of **1** and **2** are mainly consists of the intramolecular charge transfer from the 1,4-bis(carbazol-9yl)benzene core to the peripheral dimesitylboron groups, and an strong absorption band of **1** and **2** occurs around 353 nm and 349 nm, respectively. On the other hand, as shown in Table S2, the fluorescence peaks with the large oscillator strength of **1** and **2** both originate from S_1, a HOMO→LUMO transition. The calculated wavelength of the fluorescence spectra in THF for **1** and **2** are located at 398 and 392 nm, respectively. The results are in good agreement with the experimental absorption and fluorescence spectra.

All calculations were carried out using the Gaussian09 program package (Revision A.02)[S3] and performed using the advanced computing facilities of supercomputing centre of computer network information centre of Chinese Academy of Sciences.

Figure S2. Frontier orbitals of compounds **1** and **2**.

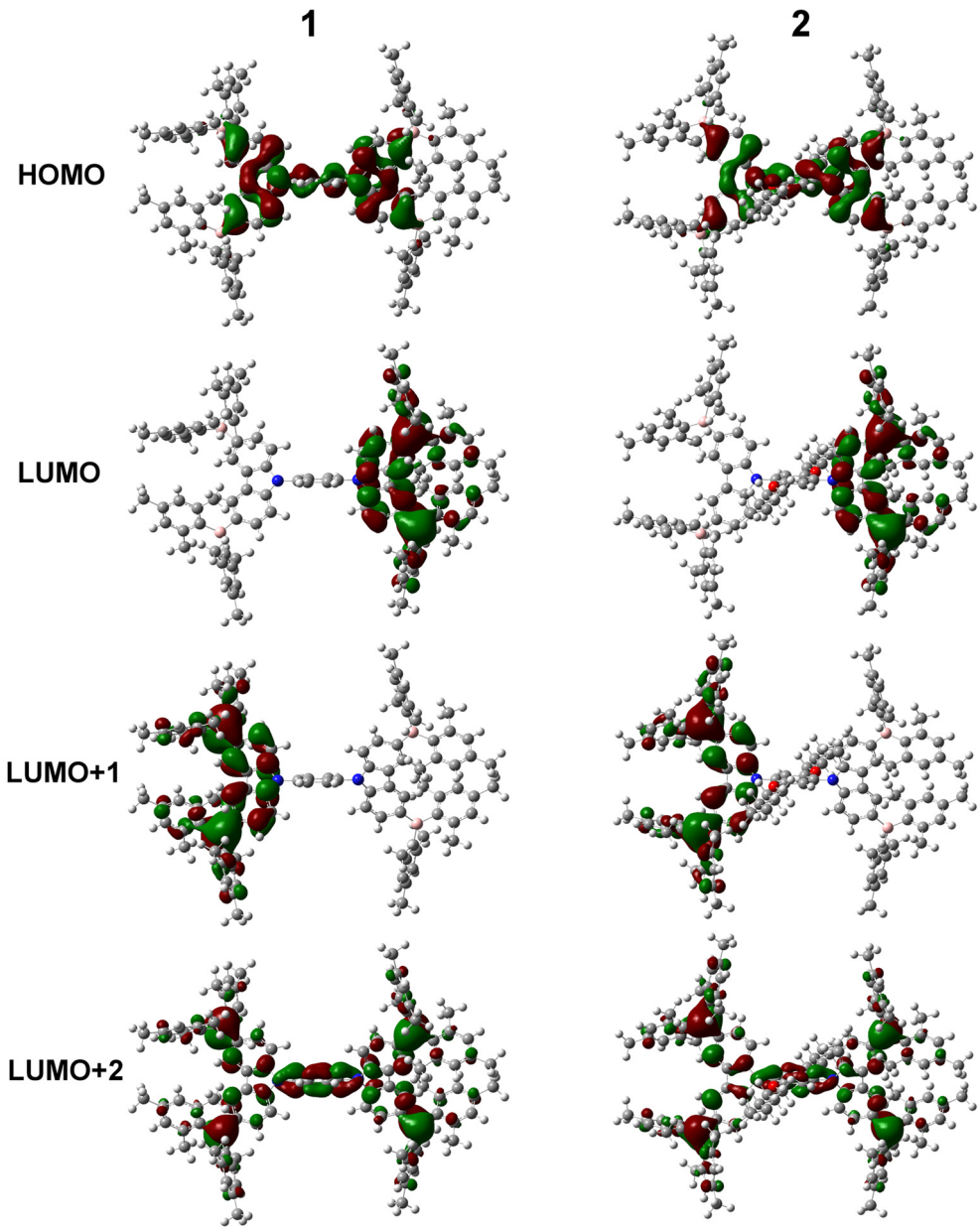


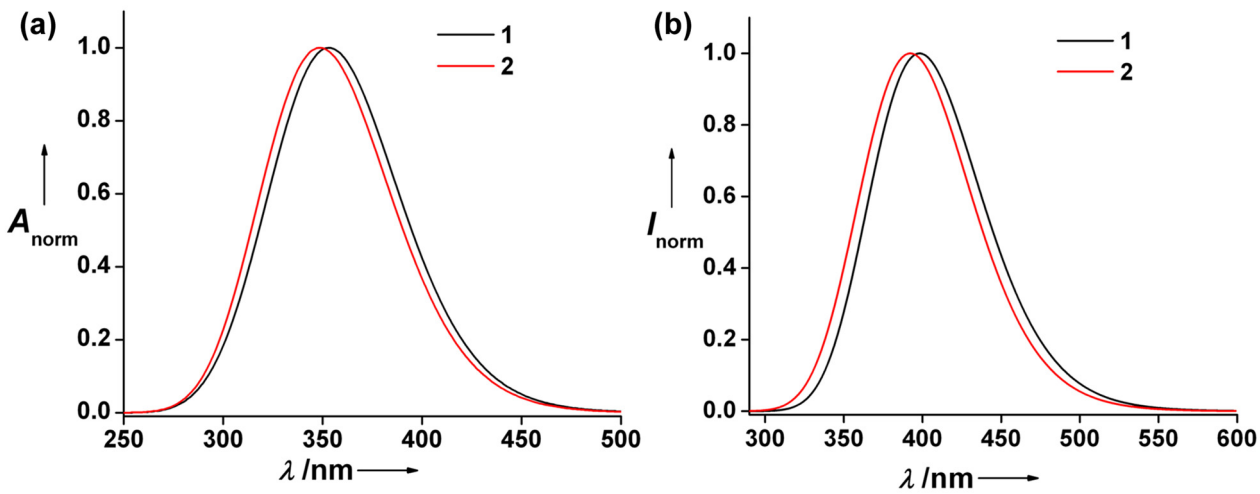
Table S1. Calculated data of absorption spectra for compounds **1** and **2** in THF solvent.

Compound	electron transition	excitation energy (eV)	λ_{abs} (nm)	oscillator strength (f)	main transition configuration
1	$S_0 \rightarrow S_1$	3.365	368.4	0.412	HOMO→LUMO: 0.585
	$S_0 \rightarrow S_2$	3.371	367.8	0.586	HOMO→LUMO+1: 0.585
	$S_0 \rightarrow S_3$	3.544	349.9	0.878	HOMO→LUMO+2: 0.629
2	$S_0 \rightarrow S_1$	3.386	366.1	0.150	HOMO→LUMO: 0.504
	$S_0 \rightarrow S_2$	3.393	365.4	0.847	HOMO→LUMO+1: 0.508
	$S_0 \rightarrow S_3$	3.626	341.9	0.790	HOMO→LUMO+2: 0.513

Table S2. Calculated data of fluorescence spectra for compounds **1** and **2** in THF solvent.

Compound	electron transition	excitation energy (eV)	λ_{em} (nm)	oscillator strength (f)	main transition configuration
1	$S_1 \rightarrow S_0$	3.117	397.8	0.632	HOMO→LUMO: 0.641
2	$S_1 \rightarrow S_0$	3.160	392.2	0.619	HOMO→LUMO: 0.617

Figure S3. Simulated absorption spectra (a) and fluorescence spectra (b) of **1** and **2** in THF.



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