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Supporting Information

Colour–Tunable Aggregation Induced Emission of Trifunctional *o*-Carborane Dye

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Contents

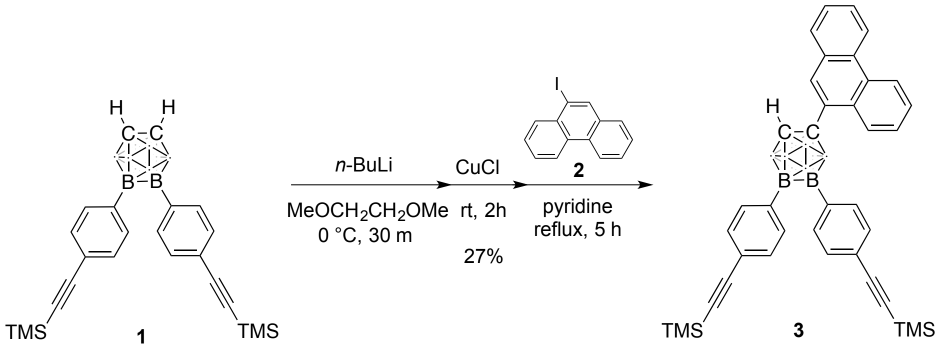
General

^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400, 100, and 128 MHz, respectively. The ^{1}H and ^{13}C chemical shift values were expressed relative to Me_4Si as an internal standard. The ^{11}B chemical shift values were expressed relative to $BF_3 \cdot Et_2O$ as an external standard. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE for electron spray ionization (ESI) and atomic pressure chemical ionization (APCI). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-300 silica gel. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel G3000HXL column) instrument using $CHCl_3$ as an eluent after calibration with standard polystyrene samples. Recyclable preparative high-performance liquid chromatography (HPLC) was performed on a Japan Analytical Industry LC-918R (JAIGEL-1H and 2H columns) or LC-9204 (JAIGEL-2.5H and 3H columns) using $CHCl_3$ as an eluent (flow rate: 3.80 mL/min). UV-vis absorption spectra were obtained on a SHIMADZU UV3600 spectrophotometer. Photoluminescence (PL) spectra were obtained on a Horiba FluoroMax-4 luminescence spectrometer; absolute PL quantum efficiencies (Φ_{PL}) were determined using a Horiba FL-3018 Integrating Sphere. Elemental analyses were performed at Organic Elemental Analysis Research Center, Kyoto University; samples were treated with WO_3 as an additive.

Materials

All synthetic procedures were performed under Ar atmosphere. Tetrahydrofuran (THF) and triethylamine (NEt_3) were purified by passage through purification column under Ar pressure.[1] 1,2-Dimethoxyethane (DME) was purified by distillation under Ar pressure. Pyridine, CuCl, *n*-BuLi in hexane (1.6 M), K_2CO_3, MeOH, $Pd(PPh_3)_4$, and CuI were obtained commercially and used without purification. 9,12-Bis[4-(trimethylsilylethynyl)phenyl]-*o*-carborane (**1**),[2] 9-iodophenanthrene (**2**),[3] 1-phenanthrenyl-*o*-carborane (**6**),[4] and 9,12-bis(4-ethynylphenyl)-*o*-carborane (**S1**)[2] were synthesized and characterized according to the literature.

Synthetic procedures, characterizations, and NMR spectra



n-BuLi hexane solution (2.60 mL, 4.26 mmol) was added dropwise to a solution of **1** (0.98 g, 2.00 mmol) in 6.0 mL of DME at 0 °C under Ar atmosphere. The mixture was stirred for 30 min; then, CuCl (0.51 g, 5.20 mmol) was added in one portion, and the mixture was stirred at room temperature for 2 h. Pyridine (1.21 mL, 15.0 mmol) and **2** (0.70 g, 2.30 mmol) were added in one portion, and the resulting mixture was refluxed for 5 h. After cooling, insoluble materials were removed by filtration through Celite. The filtrate was washed with a 1 N HCl solution, water, and brine. The filtrate was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. The residue was purified by silica gel column chromatography with hexane/AcOEt (v/v =10/1, R_f = 0.31) as an eluent and by HPLC with $CHCl_3$ as an eluent to give compound **3** as a white solid (0.37 g, 0.55 mmol, 27%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.81-8.79 (2H, m, Ar-*H*), 8.66 (1H, d, *J* = 8.31 Hz, Ar-*H*), 8.22 (1H, s, Ar-*H*), 7.92 (1H, d, *J* = 7.09 Hz, Ar-*H*), 7.83-7.62 (4H, m, Ar-*H*), 7.32-7.22 (8H, m, Ar-*H*), 4.95 (1H, s, carborane_C-*H*), 4.31-1.80 (8H, br, B-*H*), 0.26 (9H, s, Si-CH_3) , 0.25 (9H, s, Si-CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 133.2, 131.8, 131.3, 131.2, 130.9, 130.9, 130.2, 129.6, 129.2, 128.5, 127.9, 127.4, 127.2, 126.7, 125.5, 124.2, 122.7, 122.2, 105.7, 94.4, 73.2, 57.6, 0.1. ^{11}B NMR (128 MHz, CD_2Cl_2): δ (ppm) 6.1 –10.6. HRMS (APCI): Calcd. for $C_{38}H_{44}B_{10}Si_2Cl$ $[M+Cl]^-$ m/z 700.3666, found m/z 700.3660. Anal. calcd. for $C_{38}H_{44}B_{10}Si_2$: C 68.63 H 6.67, found: C 68.66 H 6.69.

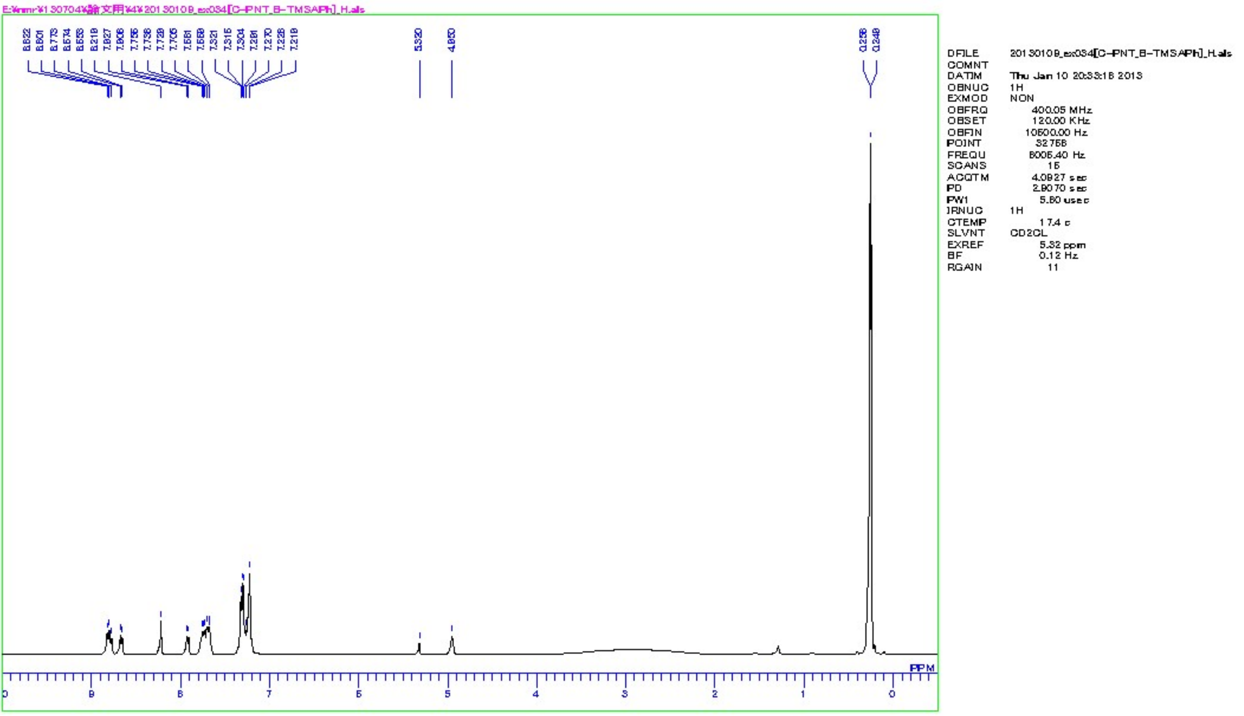


Figure S1. ^{1}H NMR spectra of **3**, 400 MHz, CD_2Cl_2.

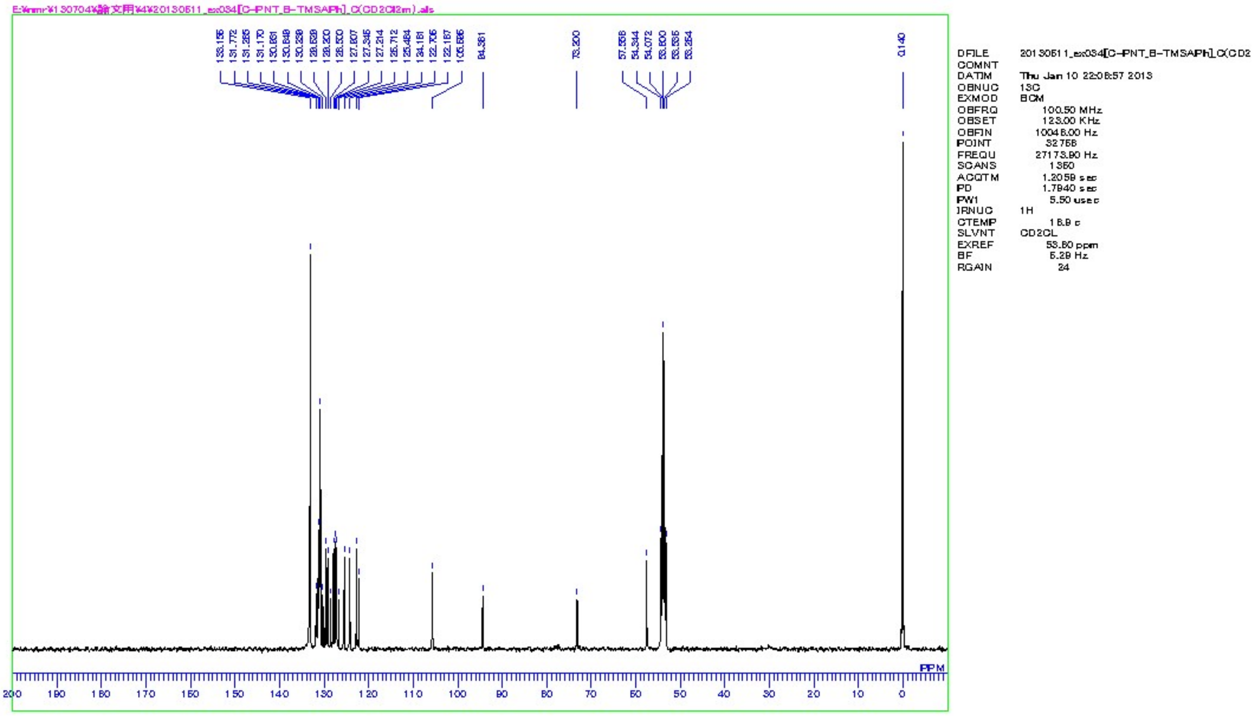


Figure S2. ^{13}C NMR spectra of **3**, 100 MHz, CD_2Cl_2.

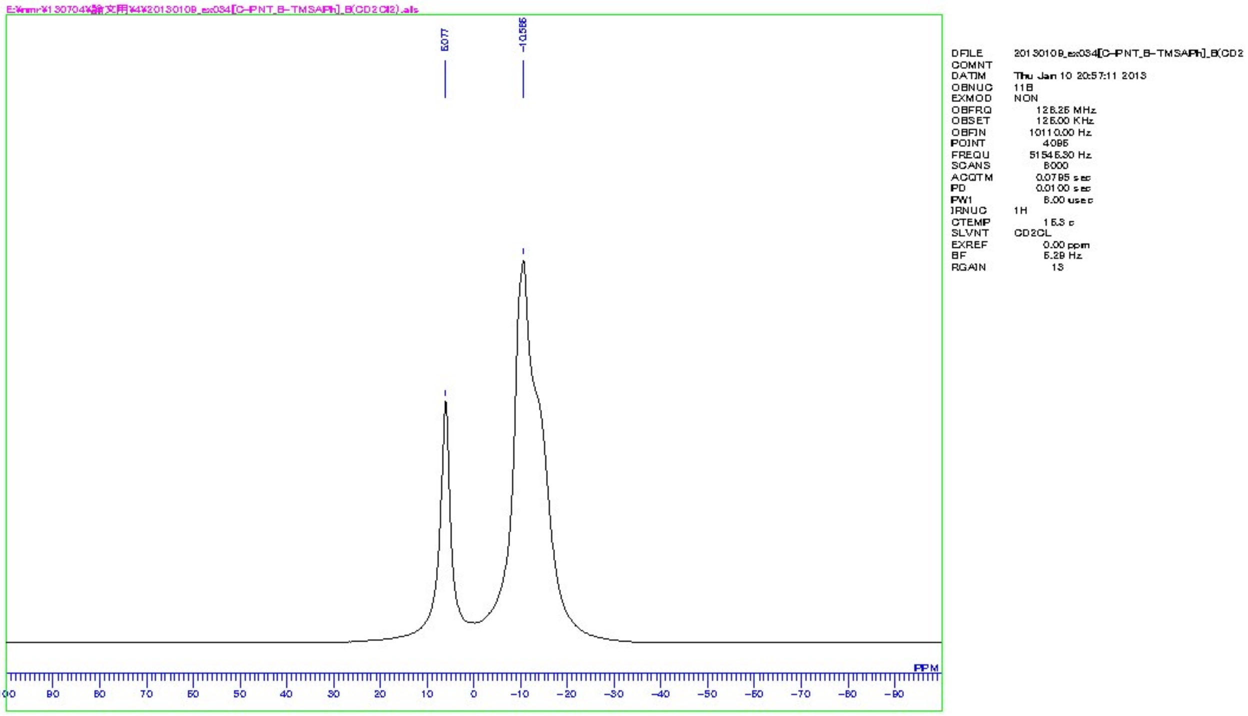


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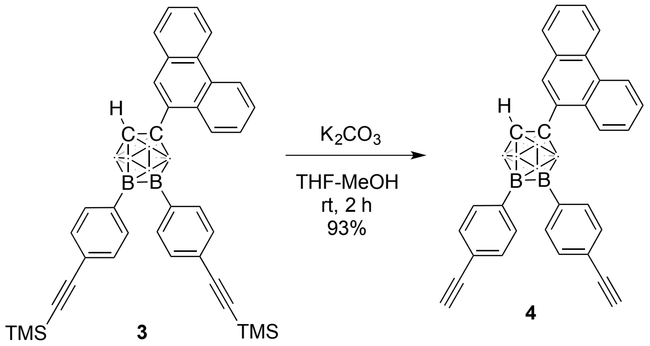
Figure S3. ^{11}B NMR spectra of **3**, 128 MHz, CD_2Cl_2.



To the mixture of compound **3** (0.15 g, 0.23 mmol) and K_2CO_3 (0.093 mg, 0.68 mmol) were added dry THF (2.2 mL) and MeOH (2.2 mL) at room temperature under Ar atmosphere. After stirring at room temperature for 2 h, the reaction was quenched by the addition of aqueous HCl (1.0 N) and extracted with CH_2Cl_2 three times. The CH_2Cl_2 solution was washed with H_2O and brine; then, it was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. The residue was subjected to silica gel column chromatography with hexane/CH_2Cl_2 (v/v= 3/2, R_f = 0.44) as an eluent to obtain compound **4** as a yellow solid (0.11 g, 0.21 mmol, 93%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.83 (1H, d, J = 6.84 Hz, Ar-H), 8.77 (1H, d, J = 8.31 Hz, Ar-H), 8.68 (1H, d, J = 8.06 Hz, Ar-H), 8.22 (1H, s, Ar-H), 7.92 (1H, d, J = 6.84 Hz, Ar-H), 7.78-7.65 (4H, m, Ar-H), 7.32-7.21 (8H, m, Ar-H), 4.98 (1H, s, carborane_C-H), 3.93-1.88 (8H, br, B-H), 3.10 (1H, s, -CC-H) , 3.08 (1H, s, -CC-H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 133.2, 131.7, 131.3, 131.2, 131.1, 130.2, 129.6, 129.2, 128.5, 127.9, 127.3, 127.2, 126.6, 125.4, 124.2, 122.7, 121.1, 121.1, 84.2, 77.4, 73.3, 57.6. ^{11}B NMR (128 MHz, CD_2Cl_2): δ (ppm) 5.9, –9.7, –10.8, –13.9. HRMS (ESI): Calcd. for $C_{32}H_{28}B_{10}Cl\,[M+Cl]^-$ m/z 557.2852, Found m/z 557.2857. Anal. calcd. for $C_{32}H_{28}B_{10}$: C 73.82 H 5.42, found: C 72.72 H 5.64.

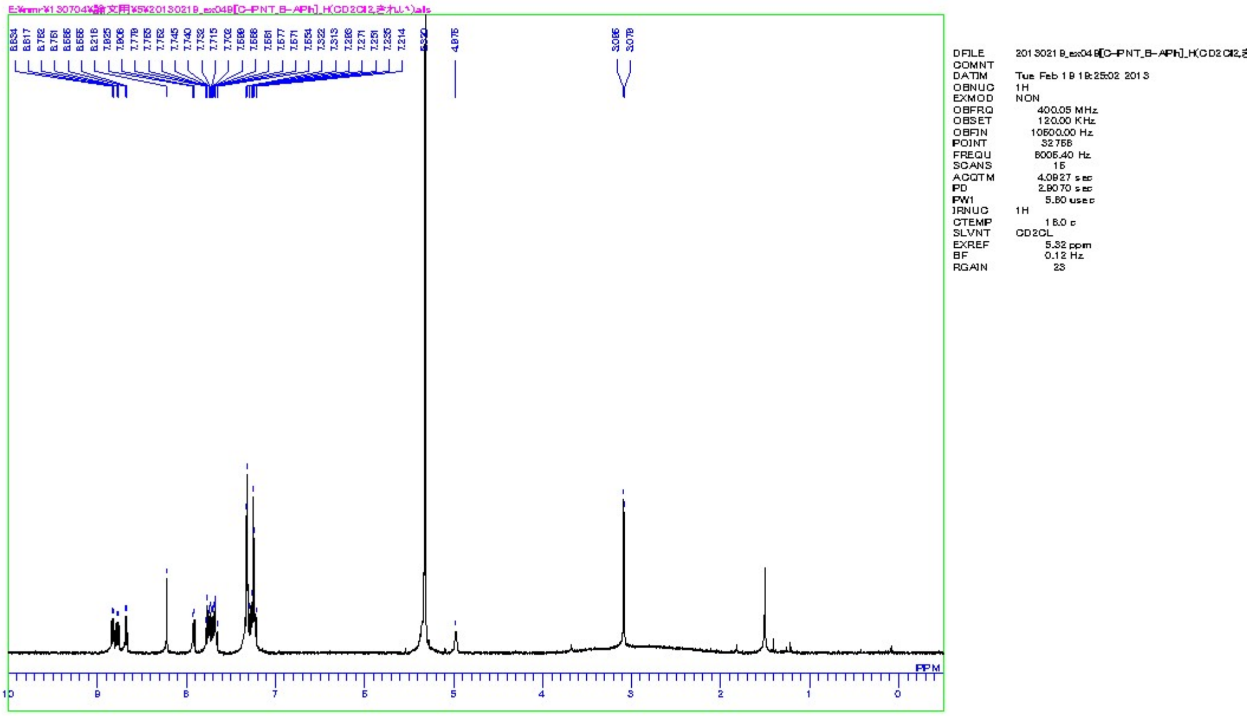


Figure S4. ^{1}H NMR spectra of **4**, 400 MHz, CD_2Cl_2.

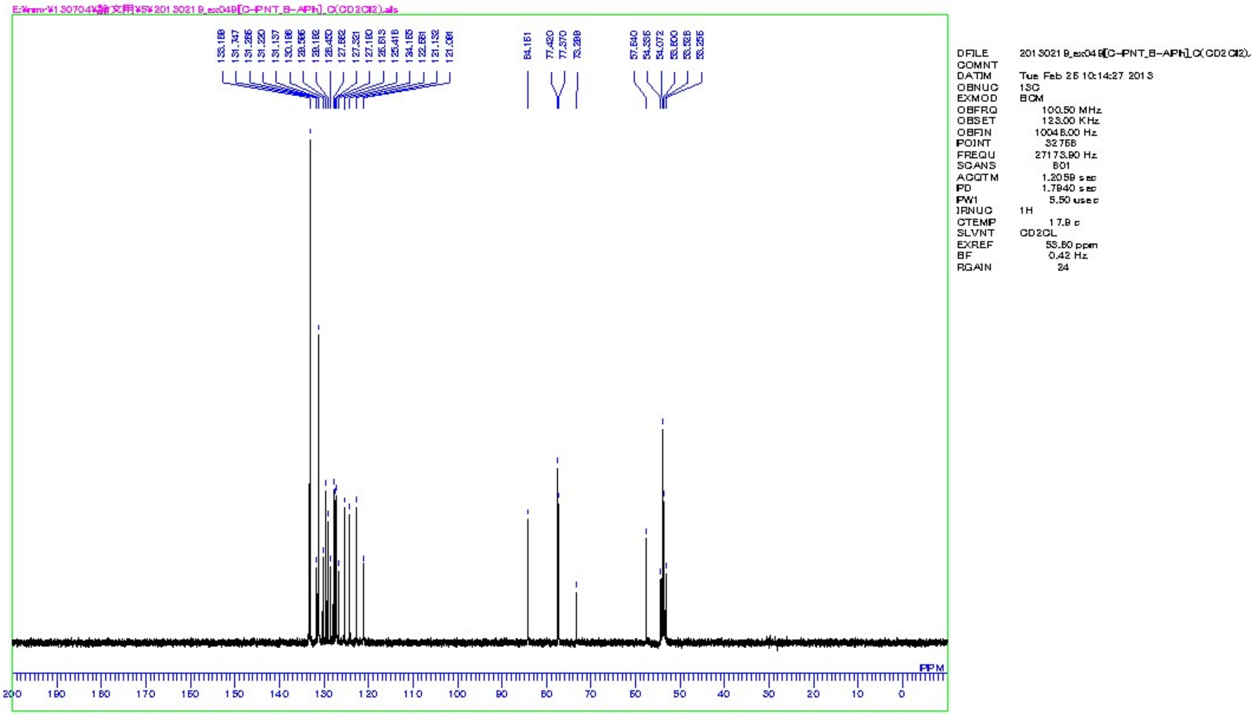


Figure S5. ^{13}C NMR spectra of **4**, 100 MHz, CD_2Cl_2.

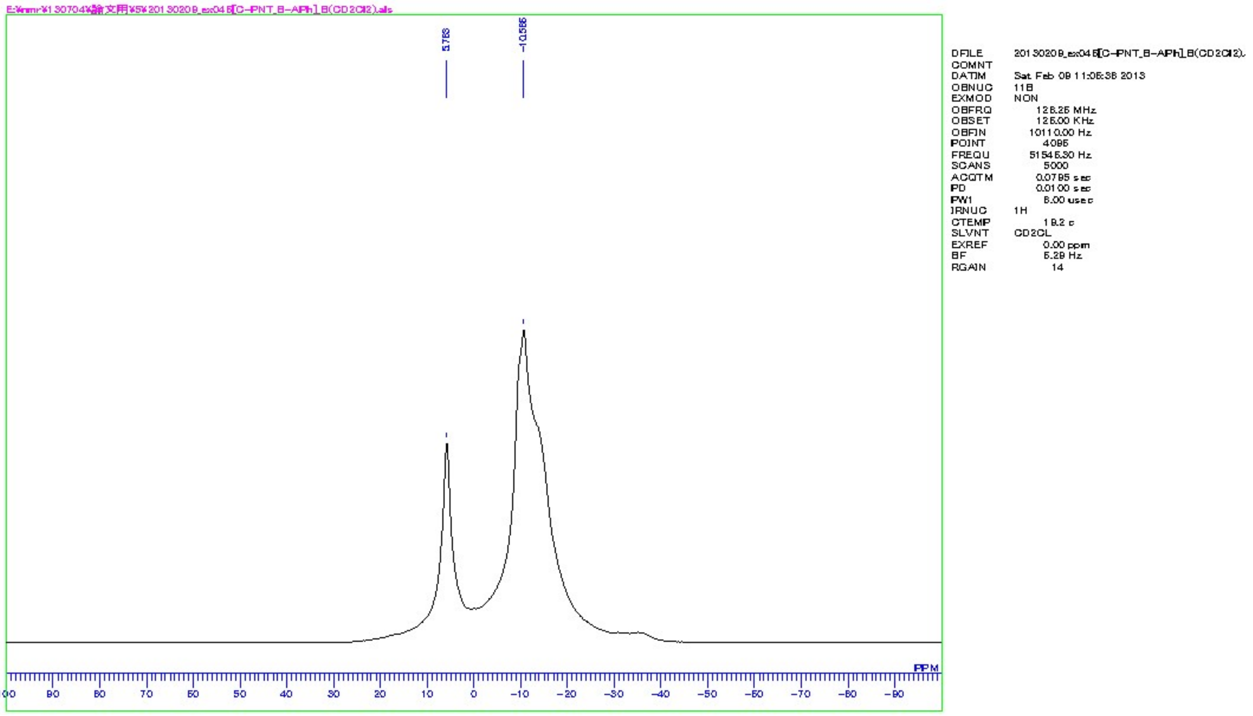
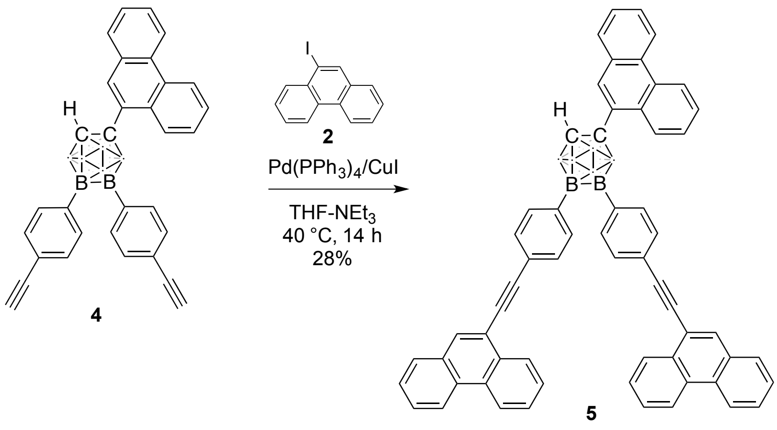


Figure S6. ^{11}B NMR spectra of **4**, 128 MHz, CD_2Cl_2.



The mixture of $Pd(PPh_3)_4$ (5.0 mg, 4.3 μmol), CuI (8.5 mg, 45 μmol), and compound **4** (47 mg, 90 μmol) was dissolved in dry THF (0.9 mL) and NEt_3 (0.9 mL) at room temperature under Ar atmosphere. To the reaction mixture was added compound **2** (69.7 mg, 229 μmol) in one portion. The reaction mixture was stirred at 40 °C under Ar atmosphere for 14 h. After cooling to room temperature, the reaction was quenched by the addition of aqueous NH_4Cl. To the mixture $CHCl_3$ was added, and the organic layer was washed with H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. The residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (v/v = 4/1, R_f= 0.33) as an eluent and by HPLC with $CHCl_3$ as an eluent to give compound **5** as a white solid (22.1 mg, 25.3 μmol, 28%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.83 (2H, d, J = 8.31 Hz, Ar-*H*), 8.71-8.66 (5H, m, Ar-*H*), 8.55-8.53 (2H, m, Ar-*H*), 8.26 (1H, s, Ar-*H*), 8.07 (2H, d, J = 5.38 Hz, Ar-*H*), 7.94 (1H, d, J = 7.82 Hz, Ar-*H*), 7.88 (2H, d, J = 7.82 Hz, Ar-*H*), 7.79-7.48 (18H, m, Ar-*H*), 7.39 (2H, d, J = 8.06 Hz, Ar-*H*), 5.01 (1H, s, carborane_C-*H*), 3.80-2.20 (8H, br, B-*H*). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 133.4, 131.9, 131.9, 131.8, 131.6, 131.4, 131.4, 131.2, 130.9, 130.8, 130.5, 130.4, 130.3, 129.7, 129.2, 128.8, 128.5, 127.9, 127.8, 127.4, 127.4, 127.3, 127.2, 126.7, 125.5, 124.2, 123.1, 122.9, 122.7, 122.4, 122.3, 120.1, 94.7, 88.0, 73.3, 57.6. ^{11}B NMR (128 MHz, CD_2Cl_2): δ (ppm) 6.0, −10.5. HRMS (APCI): Calcd. for $C_{60}H_{45}B_{10}$ $[M+H]^+$ m/z 874.4553, Found m/z 874.4504. Anal. calcd. for $C_{60}H_{44}B_{10}$: C 82.54 H 5.08, found: C 82.36 H 5.14.

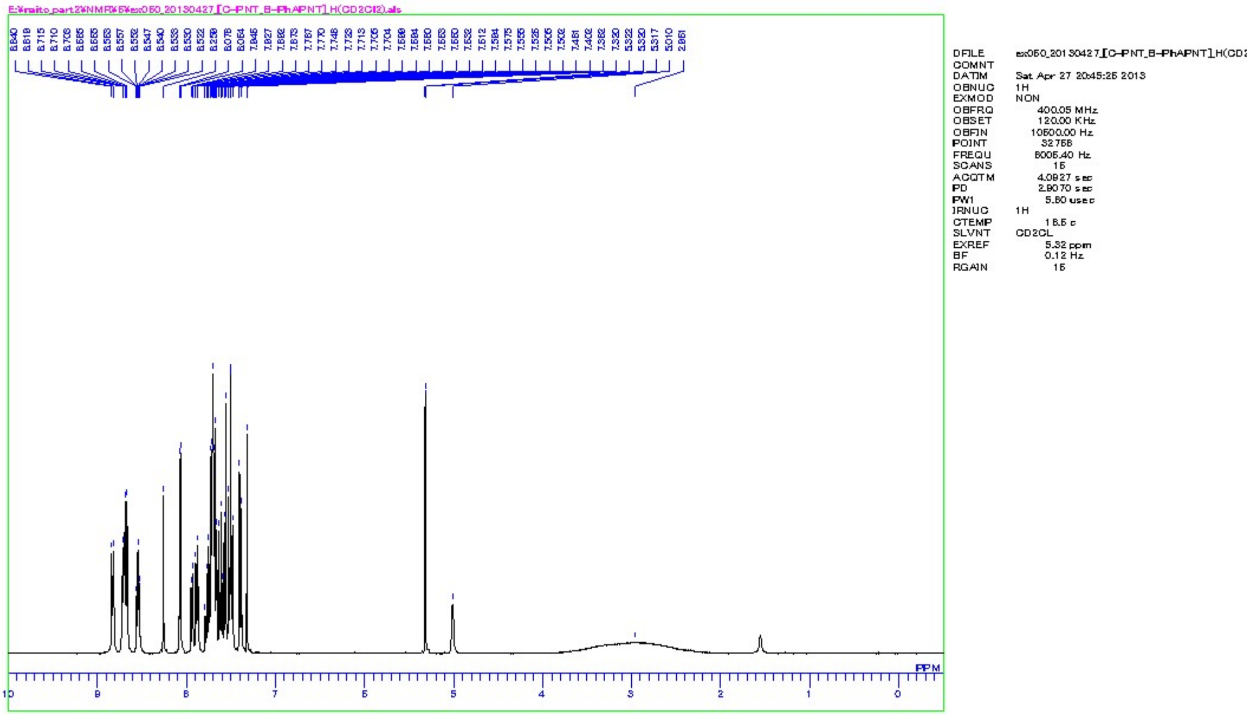


Figure S7. ^{1}H NMR spectra of **5**, 400 MHz, CD_2Cl_2.

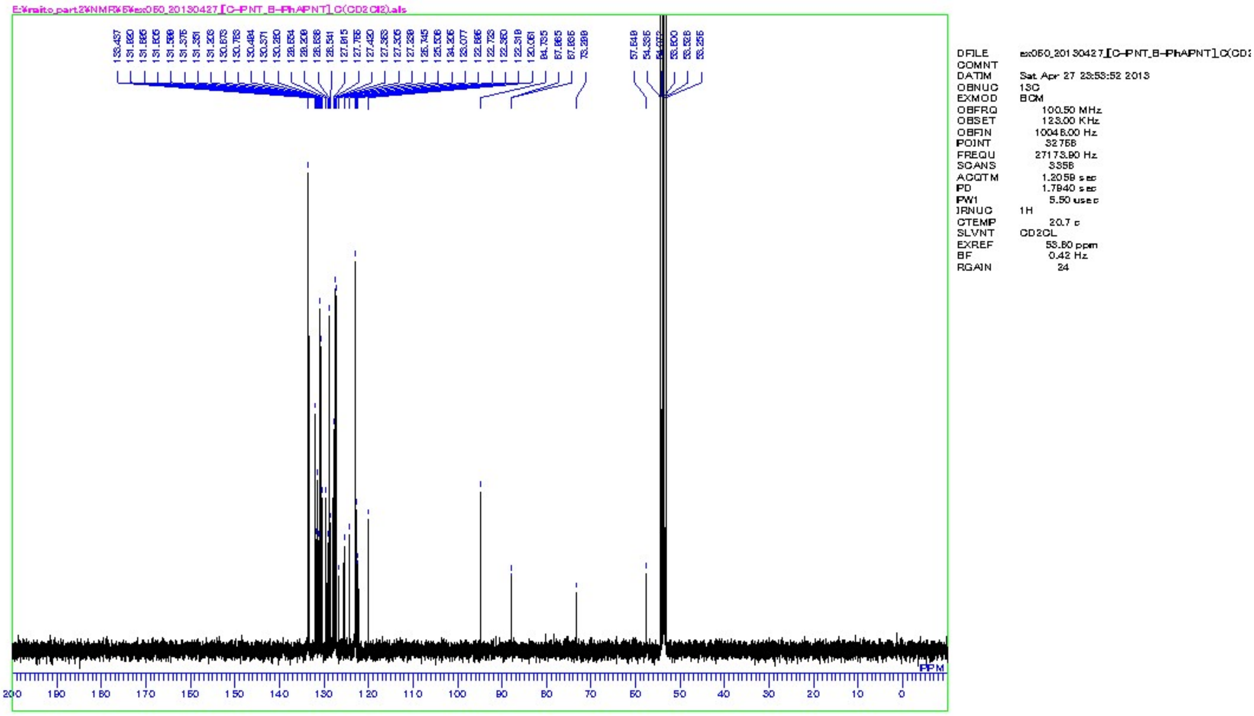


Figure S8. ^{13}C NMR spectra of **5**, 100 MHz, CD_2Cl_2.

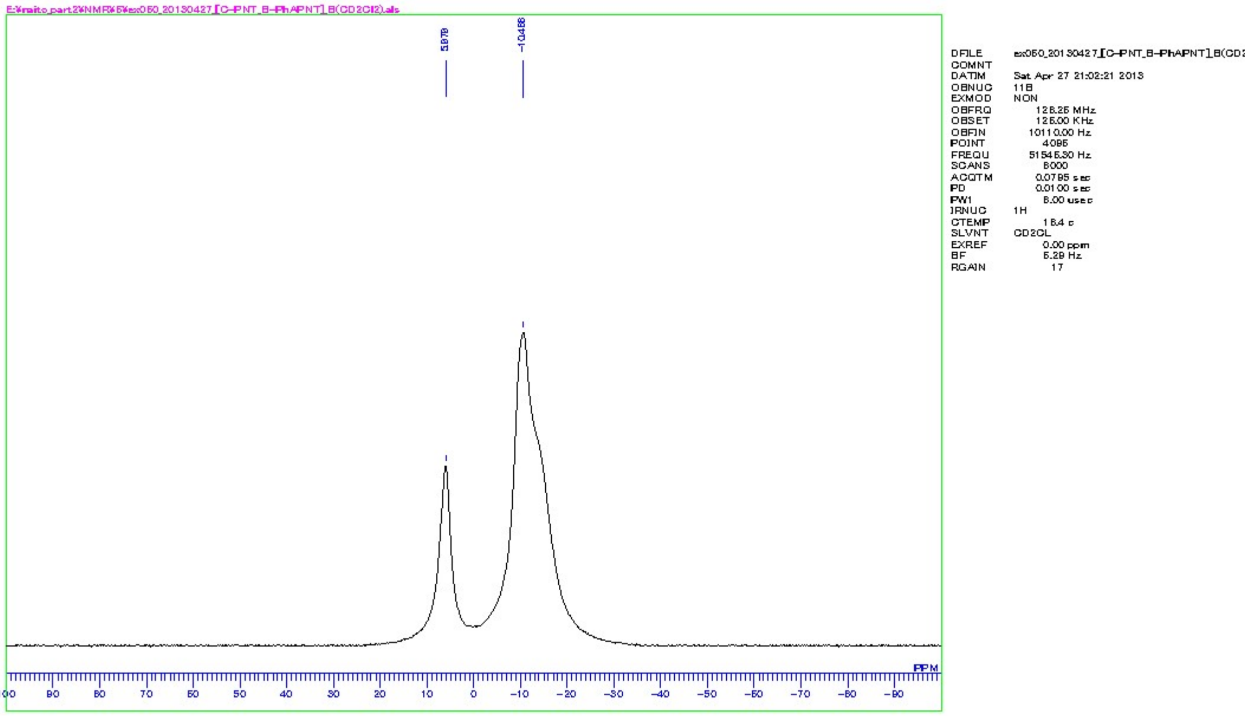


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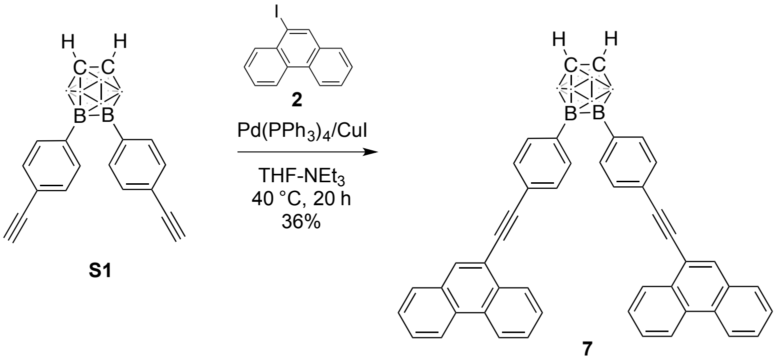
Figure S9. ^{11}B NMR spectra of **5**, 128 MHz, CD_2Cl_2.



The mixture of $Pd(PPh_3)_4$ (6.2 mg, 5.4 μmol), CuI (2.5 mg, 13 μmol), and compound **S1** (45.1 mg, 148 μmol) was dissolved in dry THF (1.5 mL) and NEt_3 (1.5 mL) at room temperature under Ar atmosphere. To the reaction mixture was added compound **2** (117.8 mg, 387 μmol). The reaction mixture was stirred at 40 °C under Ar atmosphere for 20 h. After cooling to room temperature, the reaction was quenched by the addition of aqueous NH_4Cl. To the mixture $CHCl_3$ was added, and the organic layer was washed with H_2O and brine. The organic layer was dried over $MgSO_4$. After $MgSO_4$ was removed, the solvent was evaporated. The residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (v/v = 3/2(gradient), $R_f = 0.28$) as an eluent and by HPLC with $CHCl_3$ as an eluent to give compound **7** as a white solid (38.0 mg, 54.6 μmol, 37%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.72-8.66 (4H, m, Ar-*H*), 8.52 (2H, dt, J = 5.52, 1.89 Hz, Ar-*H*), 8.05 (2H, s, Ar-*H*), 7.88 (2H, t, J = 4.63 Hz, Ar-*H*), 7.72-7.59 (8H, m, Ar-*H*), 7.47 (4H, dd, J = 6.46, 1.83 Hz, Ar-*H*), 7.31 (4H, d, J = 8.28 Hz, Ar-*H*), 3.86 (2H, s, carborane_C-*H*), 3.80-1.40 (8H, br, B-*H*). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 133.4, 133.3, 132.3, 132.0, 131.7, 131.4, 130.8, 130.6, 130.4, 128.9, 127.8, 127.5, 127.5, 127.4, 127.3, 123.1, 123.0, 122.3, 94.7, 87.9, 50.6. ^{11}B NMR (128 MHz, CD_2Cl_2): δ (ppm) 6.2, –10.2, –11.3, –15.6. HRMS (APCI): Calcd. for $C_{46}H_{37}B_{10}$ $[M+H]^+$ m/z 699.3820, Found m/z 699.3851.

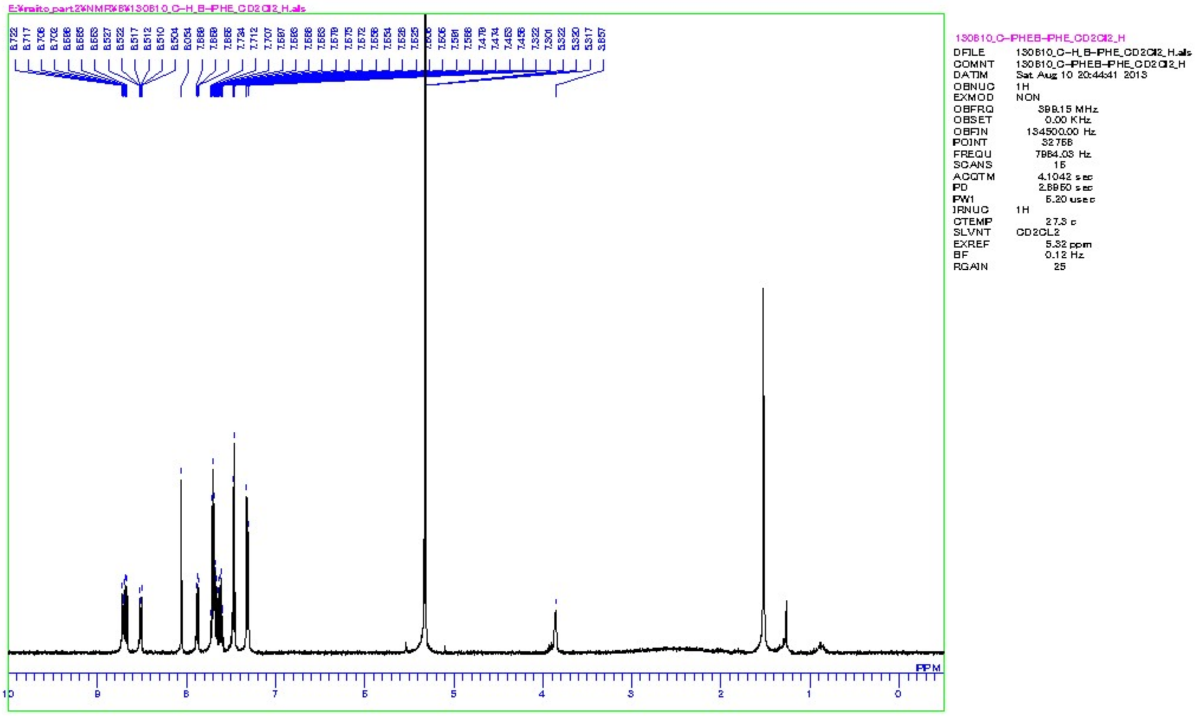


Figure S10. ^{1}H NMR spectra of **7**, 400 MHz, CD_2Cl_2.

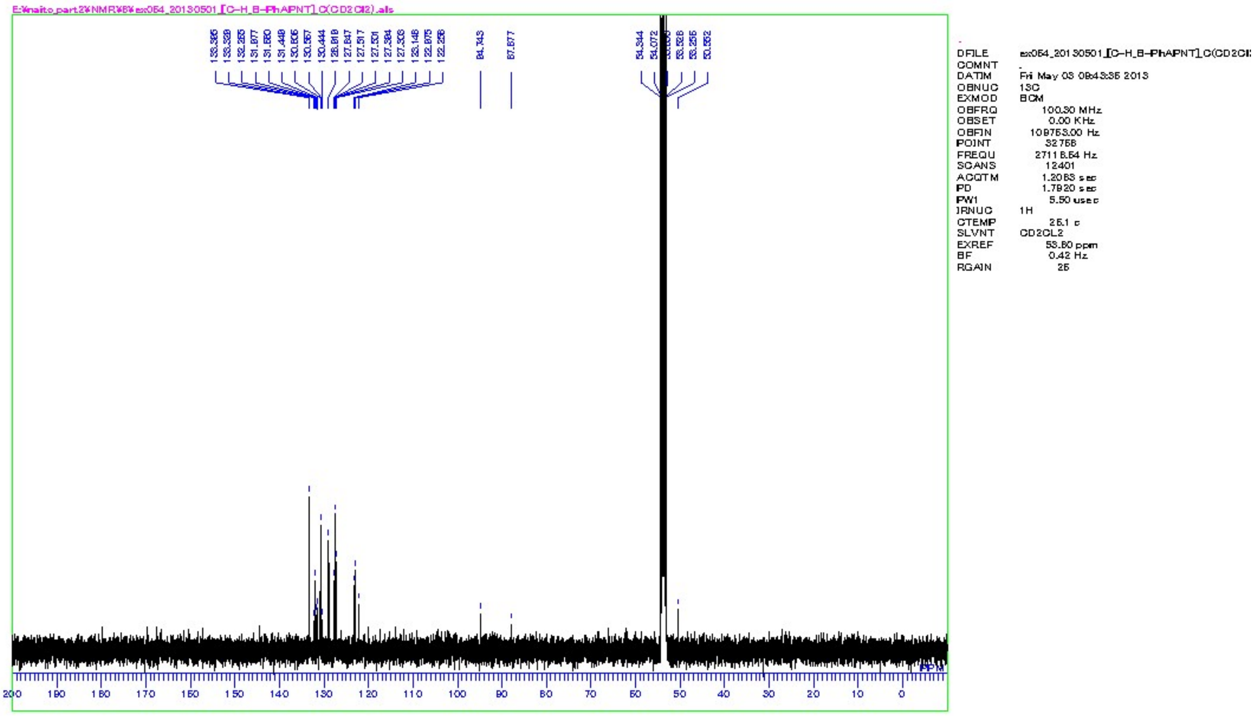


Figure S11. ^{13}C NMR spectra of **7**, 100 MHz, CD_2Cl_2.

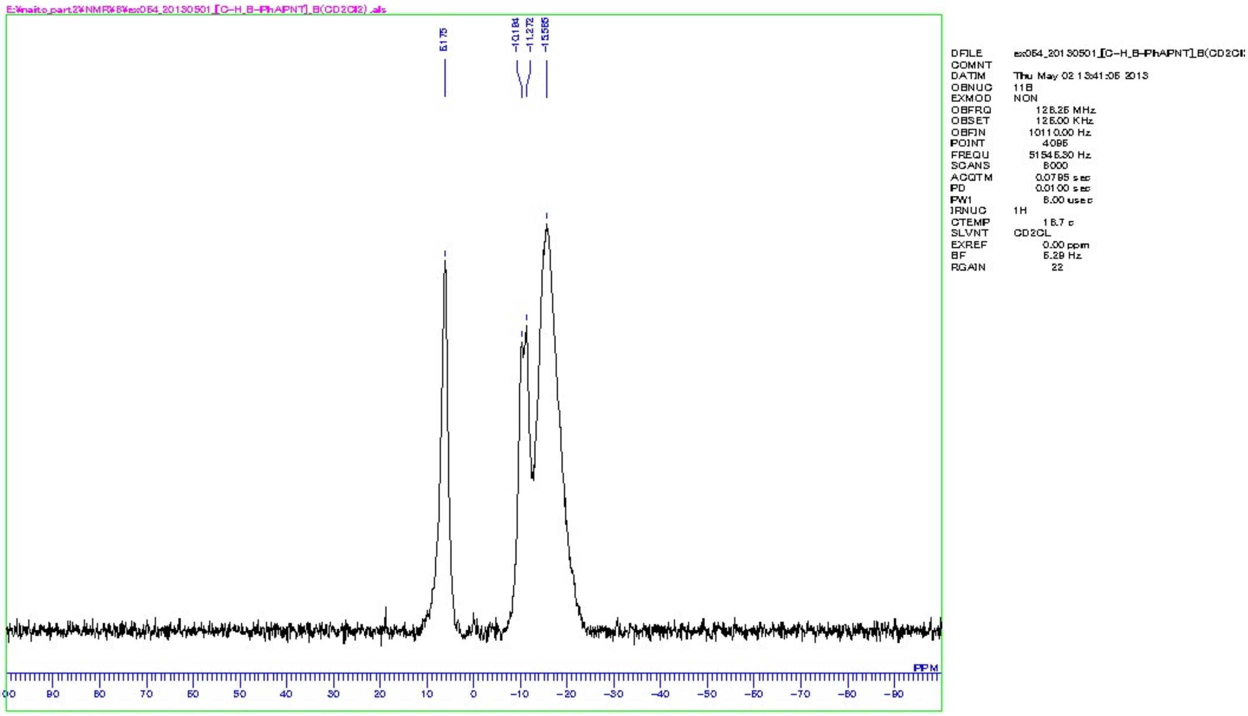


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Figure S12. ^{11}B NMR spectra of **7**, 128 MHz, CD_2Cl_2.

UV-vis absorption and fluorescence spectra **in THF**

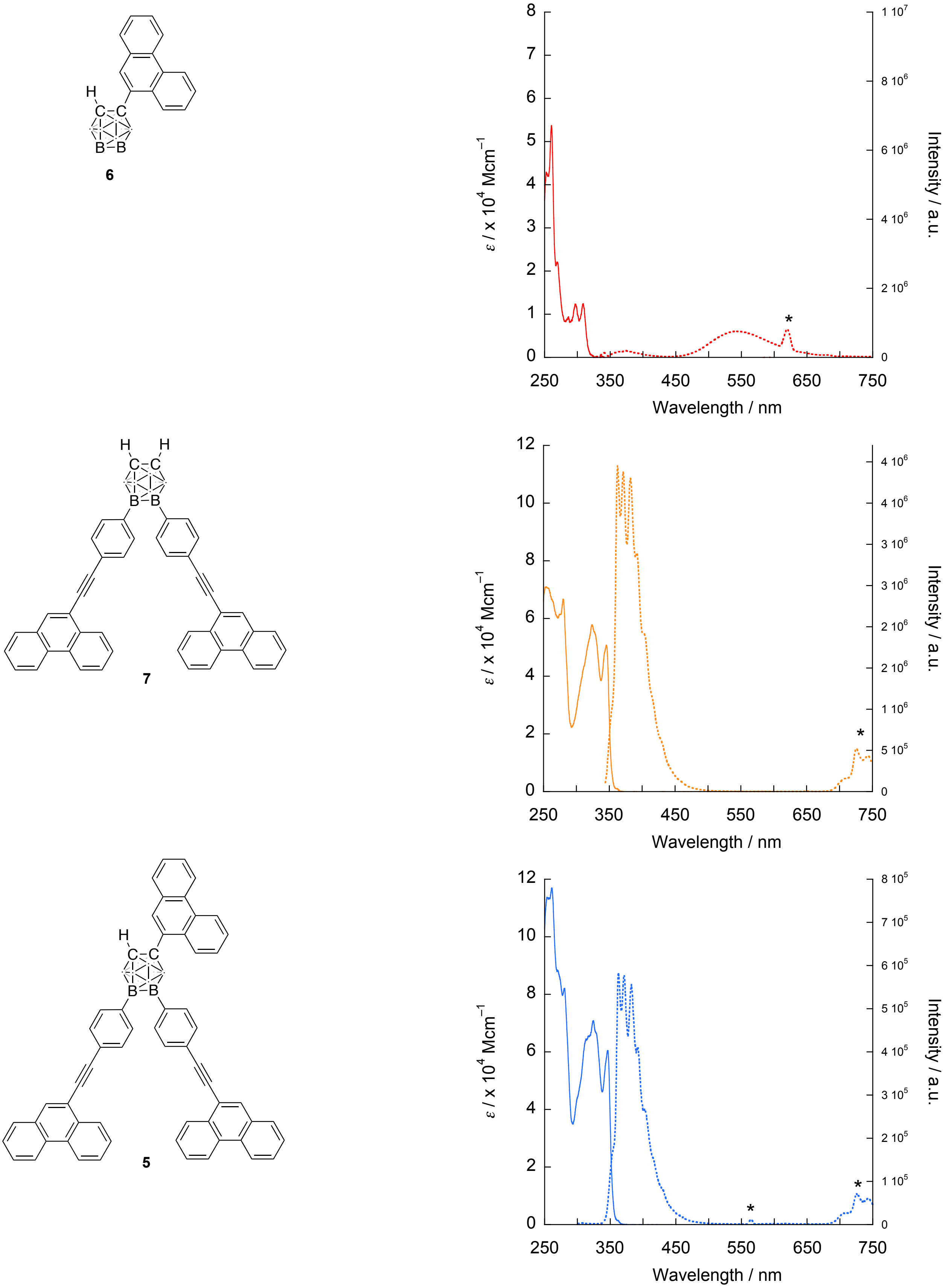
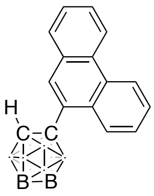


Figure S13. UV-vis absorption and fluorescence spectra of compound **6** (excited at 310 nm), **7** (excited at 324 nm), and **5** (excited at 281 nm) in THF (1.0×10^{-5} M). The asterisks denote scattered light (the overtone peaks of the excitation wavelength) and the overtone peaks of the PL.

UV-vis absorption and fluoresence spectra **in THF/H_2O = 1/99 (v/v)**



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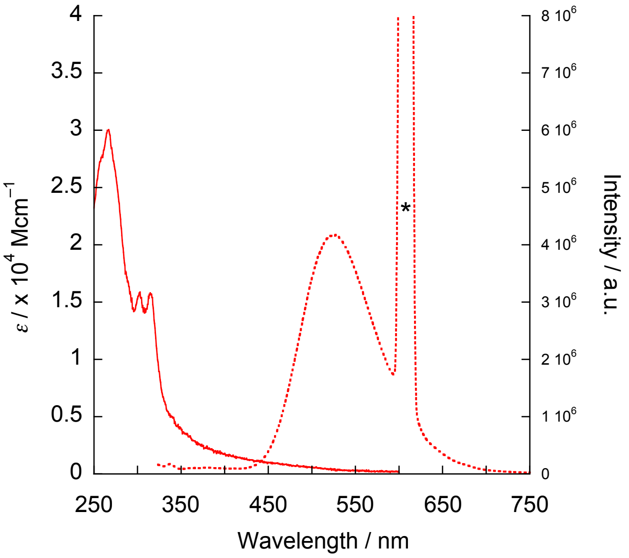

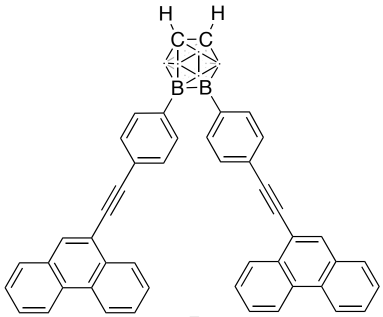

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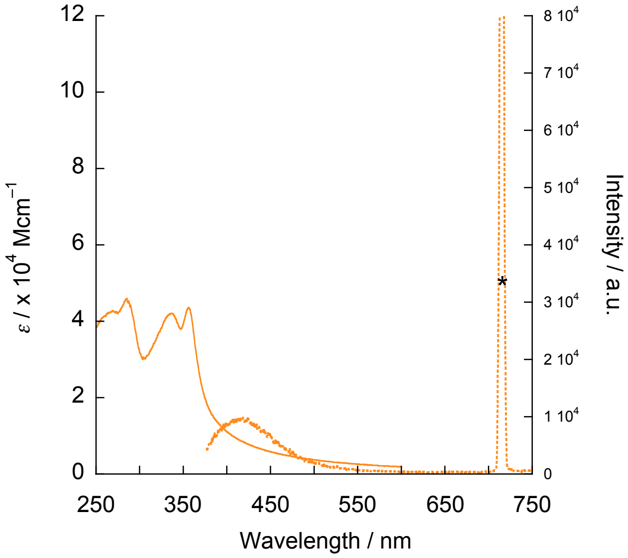

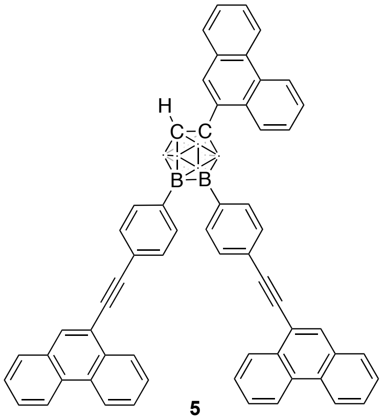

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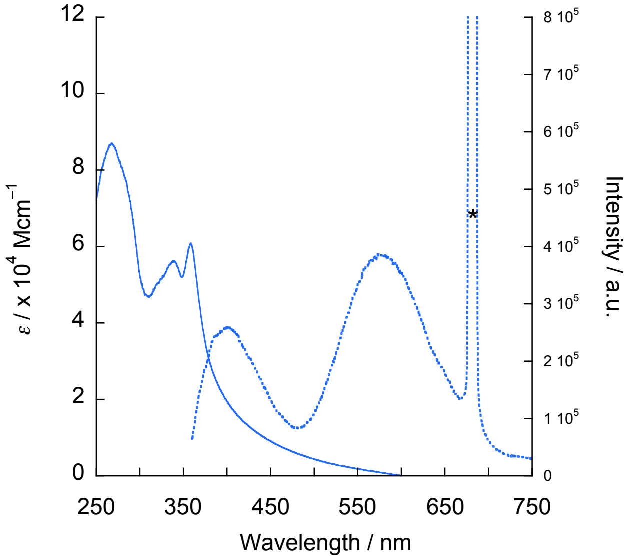
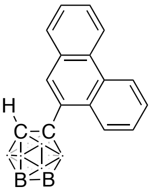


Figure S14. UV-vis absorption and fluorescence spectra of compound **6** (excited at 310 nm), **7** (excited at 357 nm) and **5** (excited at 340 nm) in THF/H_2O (v/v) = 1/99 (1.0×10^{-5} M). The asterisks denote scattered light (the overtone peaks of the excitation wavelength).

Fluorescence spectra **in the solid state**



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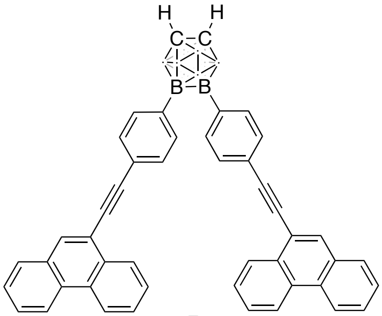

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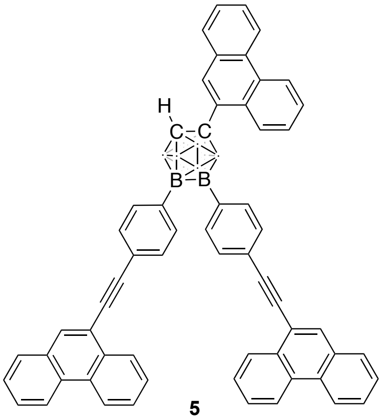

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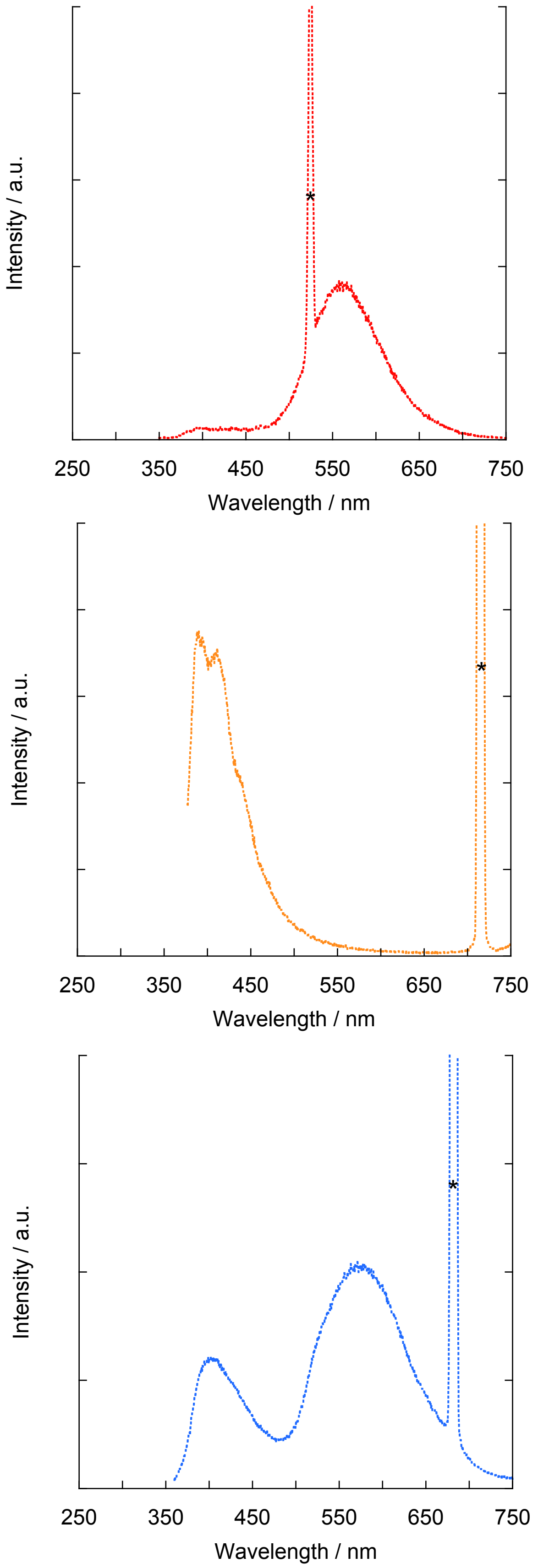
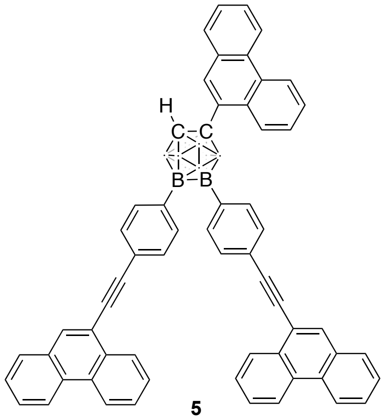


Figure S15. Fluorescence spectra of compound **6** (excited at 261 nm), **7** (excited at 357 nm) and **5** (excited at 340 nm) in their solid state. The asterisks denote scattered light (the overtone peaks of the excitation wavelength).

Fluorescence spectrum **in 2-MeTHF at 77K**



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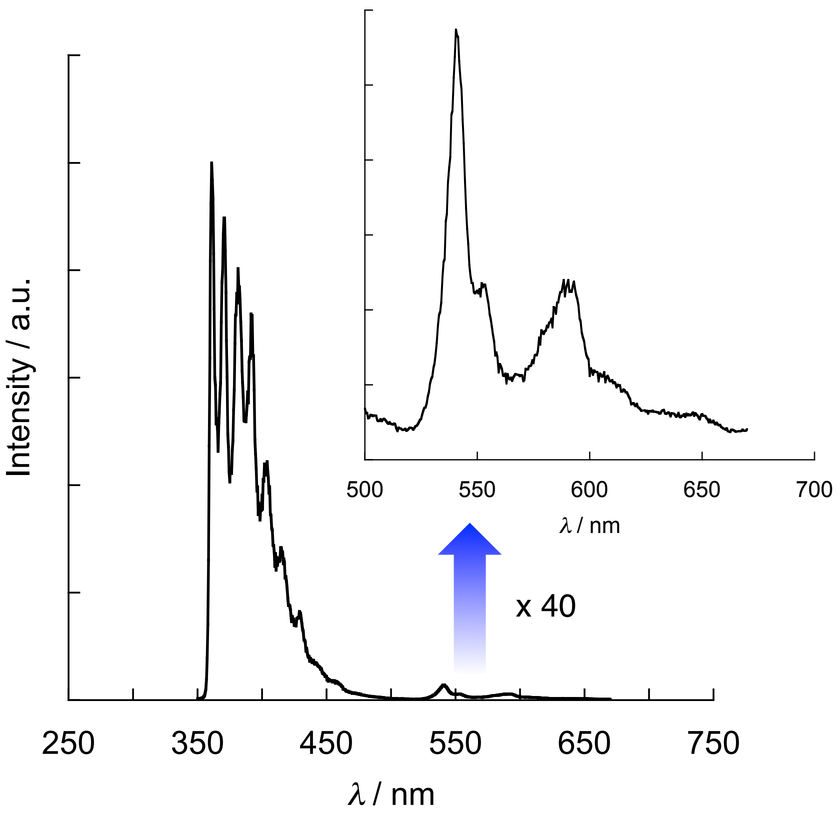


Figure S16. Fluorescence spectrum of **5** (excited at 281 nm) in 2-MeTHF at 77K.

Fluoresence spectra (not normalized) **in THF/H_2O**

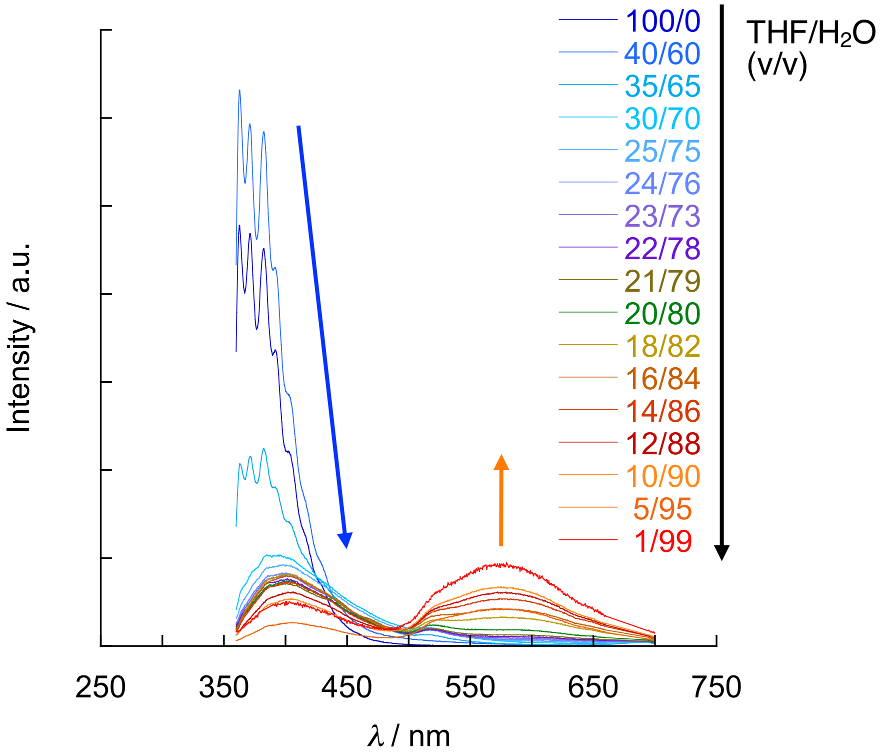
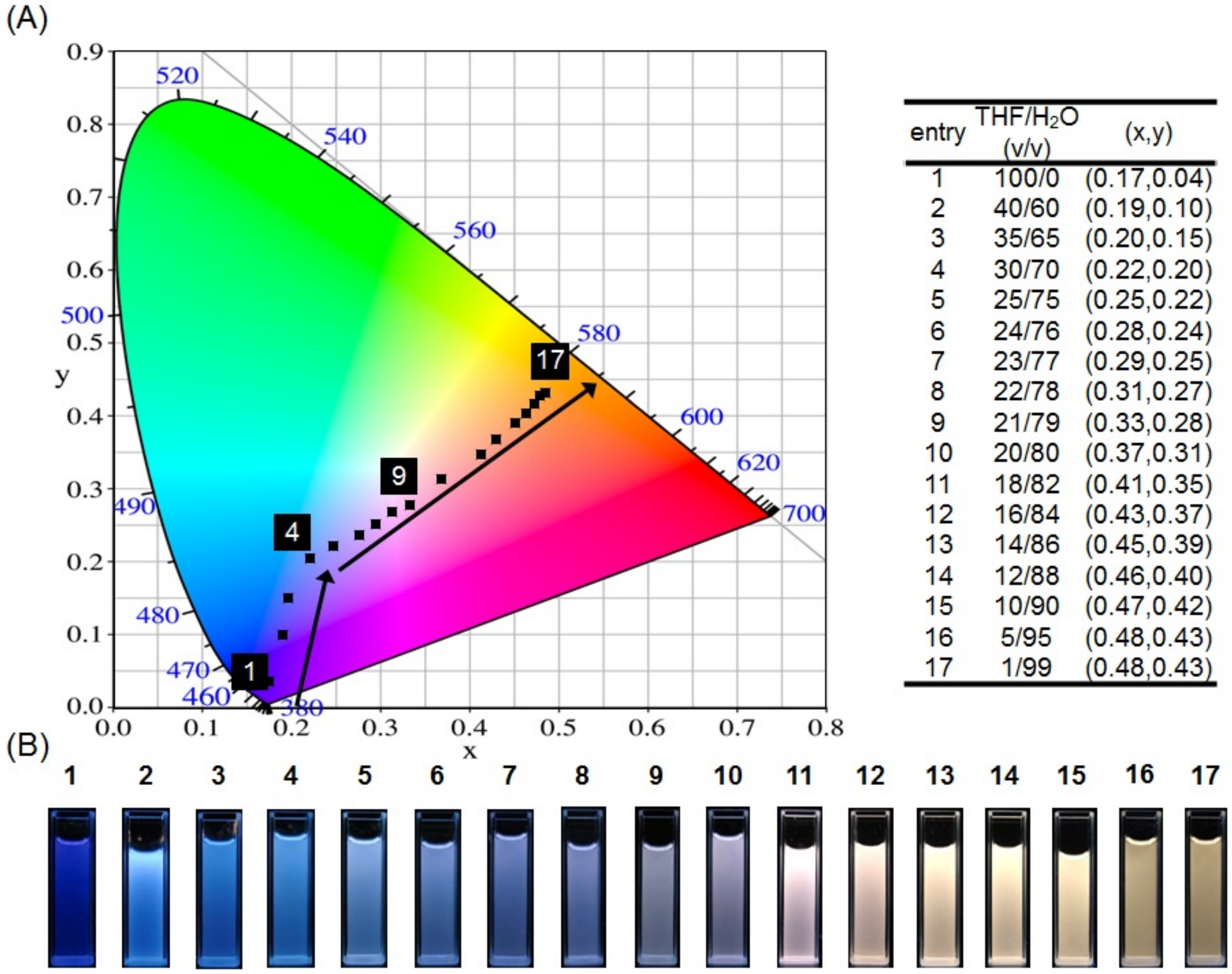


Figure S17. Fluorescence spectra of **5** (excited at 340 nm) in THF/H_2O (1.0×10^{-5} M).



entry	THF/H_2O (v/v)	(x,y)
1	100/0	(0.17,0.04)
2	40/60	(0.19,0.10)
3	35/65	(0.20,0.15)
4	30/70	(0.22,0.20)
5	25/75	(0.25,0.22)
6	24/76	(0.28,0.24)
7	23/77	(0.29,0.25)
8	22/78	(0.31,0.27)
9	21/79	(0.33,0.28)
10	20/80	(0.37,0.31)
11	18/82	(0.41,0.35)
12	16/84	(0.43,0.37)
13	14/86	(0.45,0.39)
14	12/88	(0.46,0.40)
15	10/90	(0.47,0.42)
16	5/95	(0.48,0.43)
17	1/99	(0.48,0.43)

Figure S18. (A) Emission colors of **5** in a CIE 1931 chromaticity diagram; table shows the ratio of THF/H_2O (v/v) (1.0×10^{-5} M) and the spectral chromaticity coordinates. (B) Pictures of emission color change of **5**.

Results of density functional theory (DFT) calculation[5]

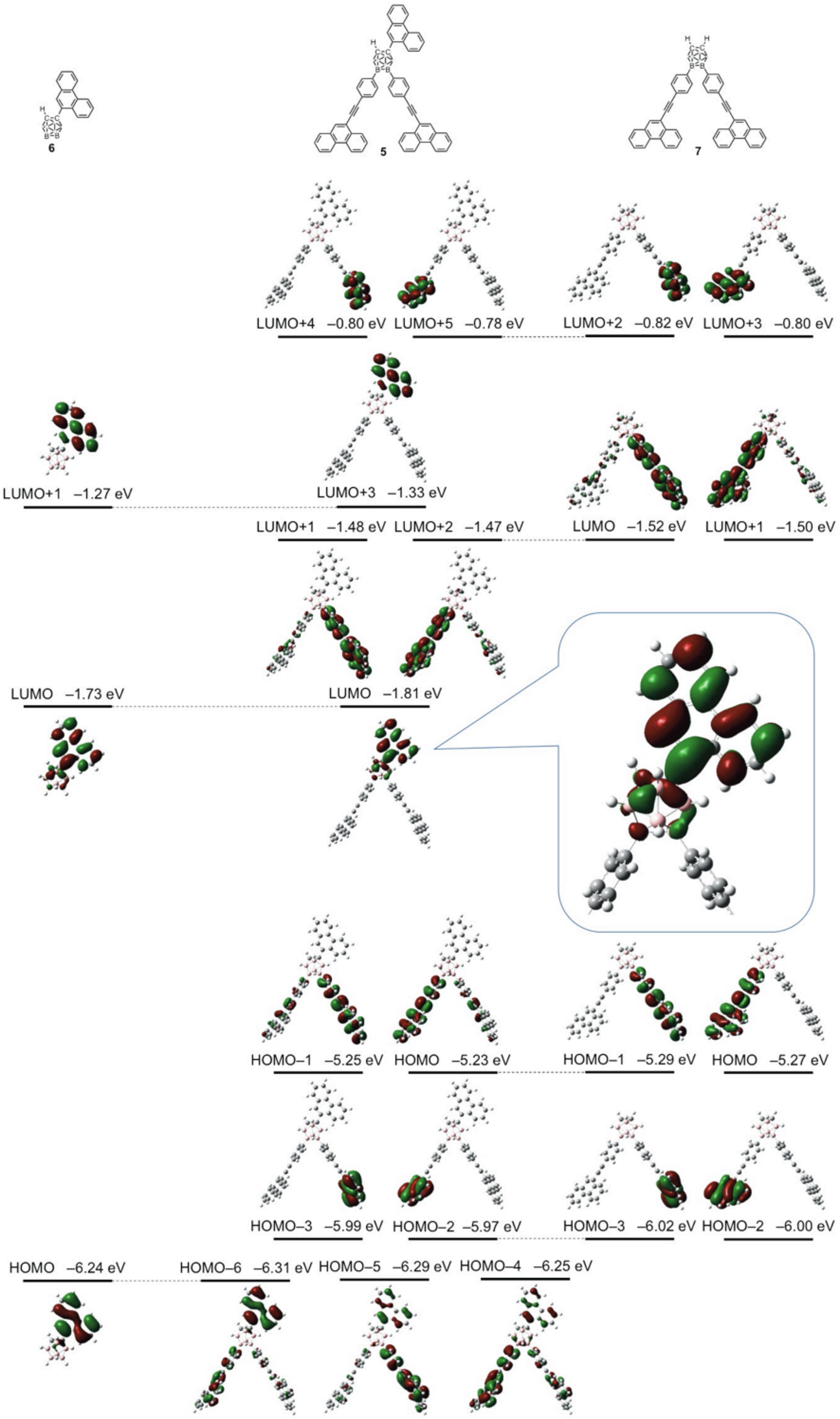


Figure S19. Structures and molecular orbital diagrams for **5**, **6** and **7**. All compounds were optimized by B3LYP/6-31G(d,p) level of theory with charge = 0 and multiplicity = 1.

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