Supporting Information

π-Extended Planarized Triphenylboranes with Thiophene Spacers

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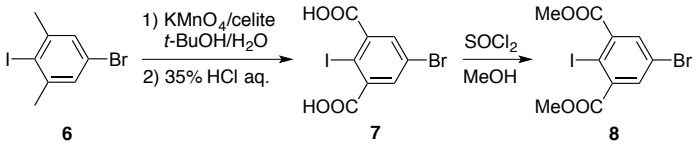
1. Experimental Details

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. ^{1}H, ^{13}C, and ^{11}B NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 128 MHz for ^{11}B) and a JEOL EX-270 spectrometer (270 MHz for ^{1}H) in $CDCl_3$, CD_2Cl_2, or DMSO-d_6. Chemical shifts are reported in δ ppm. ^{1}H NMR spectra are referenced to residual protons in the deuterated solvent as an internal standard. ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent as an internal standard. ^{11}B NMR spectra are referenced to $BF_3{\cdot}OEt_2$ as an external standard. Mass spectrometry was performed with a Bruker Daltonics micrOTOF Focus with the APCI ionization method. Elemental analysis was performed by Chemical Instrumentation Facility, Research Center for Materials Science, Nagoya University. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60 F_{254} (Merck). Column chromatography was performed using silica gel PSQ 100B (Fuji Silysia Chemical). Dry THF, ether, and toluene were purchased from Kanto Chemical. THF/H_2O for the coupling reactions were degassed by bubbling of argon for 30 min before use. Dry 1,2-dichloroethane was purchased from Aldrich. Commercially available solvents and reagents were used as received. 5-Bromo-2-iodo-1,3-dimethylbenzene (**6**),[1] 9-bromo-9,10-dihydro-9-boraanthracene,[2] Pd complex **11**,[3] 5,5′-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene,[4] and $Pd_2(dba)_3{\cdot}CHCl_3$[5] were prepared as described in the literature. All reactions were carried out under an argon atmosphere unless otherwise mentioned.

Dimethyl 5-bromo-2-iodoisophthalate (8)

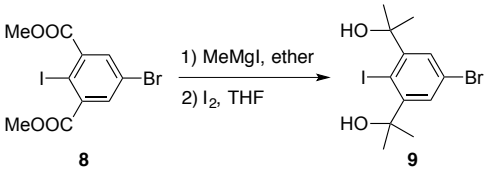


6 **7** **8**

$KMnO_4$ (99.6 g, 630 mmol) and ca. 80 g of Celite was added to the mixture of 5-bromo-2-iodo-1,3-dimethylbenzene (**6**) (37.7 g, 121 mmol) in *t*-BuOH/H_2O (1:1, 410 mL). The mixture was refluxed with stirring for 16.5 h. After cooling to room temperature, the reaction mixture was filtered over Celite and washed with methanol. The filtrate was concentrated to a ca. 1/3 volume under reduced pressure. A 35% aqueous solution of HCl was then carefully added until a white solid precipitated. The solid was collected by filtration and dried under reduced pressure yielding 38.6 g of crude product. The crude 5-bromo-2-iodoisophthalic acid (**7**) was not further purified and was used directly in the next step. ^{1}H NMR (270 MHz, DMSO-d_6) δ 7.78 (s, 2H).

The crude **7** was added to 192 mL of methanol at 0 °C. Thionyl chloride (23 mL, 315 mmol) was added dropwise and the reaction mixture was refluxed for 12 h. After cooling to room temperature, the mixture was diluted with 125 mL of water and extracted with dichloromethane three times. The organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ and brine, and dried over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate as an eluent to give 37.2 g (93.2 mmol) of **8** in 77% yield (overall for the two steps) as a white solid: mp 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H), 3.96 (s, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 166.8, 141.1, 134.4, 122.3, 90.3, 53.2; HRMS (APCI, positive) *m/z* calcd for $C_{10}H_8{}^{79}BrIO_4$ 397.8651, found: 397.8654.

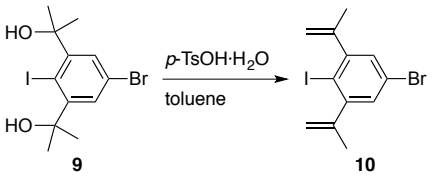
5-Bromo-1,3-bis(2-hydroxypropan-2-yl)-2-iodobenzene (9)



8 **9**

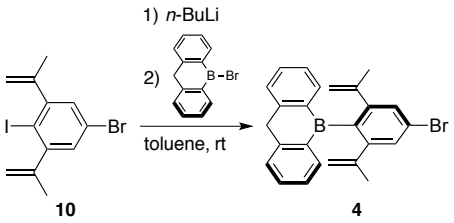
To a solution of **8** (24.7 g, 61.9 mmol) in THF (170 mL) was added slowly a Grignard reagent which was generated by CH_3I (21 mL, 340 mmol) and Mg (8.36 g, 344 mmol) in ether (200 mL). The mixture was refluxed with stirring for 17 h. After I_2 (24 g, 95 mmol) in THF (100 mL) was slowly added, the mixture was stirred at room temperature for 3 h. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl and a saturated aqueous solution of Na_2SO_3. The organic layer was extracted with dichloromethane three times. The organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ and brine, and then dried over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. The crude product was purified by recrystallization from dichloromethane to give 9.43 g (23.6 mmol) of **9** in 38% yield as a white solid: mp 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 2H), 1.84 (s, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 152.2, 129.5, 123.4, 92.4, 75.4, 30.8; HRMS (APCI, positive) *m/z* calcd for $C_{12}H_{16}{}^{79}BrIO_2$ 397.9378, found: 397.9366.

5-Bromo-2-iodo -1,3-di(propen-2-yl) benzene (10)



A solution of **9** (3.84 g, 9.63 mmol) and *p*-toluenesulfonic acid monohydrate (0.372 g, 1.95 mmol) in toluene (50 mL) was refluxed for 1 h in the air. After cooling to room temperature, a saturated aqueous solution of $NaHCO_3$ was added to the reaction mixture. The organic layer was extracted with diethyl ether three times. The organic extracts were washed with brine and dried over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane as an eluent to give 3.39 g (9.34 mmol) of **10** in 97% yield as a white solid: mp 47–48 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 5.22 (m, 2H), 4.90 (m, 2H), 2.06 (s, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 151.8, 148.5, 129.5, 122.2, 116.7, 98.2, 24.0; HRMS (APCI, positive) *m/z* calcd for $C_{12}H_{12}{}^{79}BrI$ 361.9167, found: 361.9168.

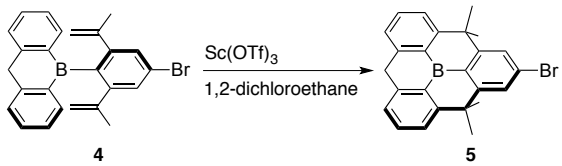
9-[4-Bromo-2,6-di(propen-2-yl)phenyl]-9,10-dihydro-9-boraanthracene (4)



A solution of *n*-BuLi in hexane (1.6 M, 7.3 mL, 12 mmol) was added dropwise to a solution of **10** (4.24 g, 11.7 mmol) in toluene (50 mL) at 0 °C. The mixture was allowed to warm to room temperature, and then stirred for 2.5 h. A solution of 9-bromo-9,10-dihydro-9-boraanthracene (3.01g, 11.7 mmol) in toluene (40 mL) was added dropwise to the reaction mixture at 0 °C. After stirred for 6 h at room temperature, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with diethyl ether three times. The organic extracts were washed with brine and dried over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using 4/1 hexane/dichloromethane as an eluent to give 4.01 g (9.71 mmol) of **4** in 83% yield as a white solid: mp 167–168 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.61 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.49–7.51 (m, 6H), 7.24–7.27 (m, 2H), 4.64–4.65 (m, 2H), 4.49–4.50 (m, 2H), 4.44 (s, 2H), 1.89 (s, 6H); ^{13}C{H} NMR (100 MHz, CD_2Cl_2) δ 149.1,

146.9, 146.8, 137.2, 132.2, 128.5, 128.4, 125.9, 121.7, 117.8, 38.5, 24.1, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CD_2Cl_2) δ 59.1; HRMS (APCI, positive) *m*/*z* calcd for $C_{25}H_{22}{}^{11}B^{79}Br$ 412.0998, found: 412.1001.

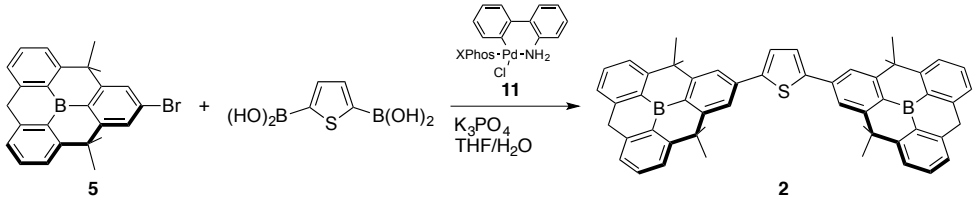
Bromo-substituted planarized triphenylborane 5



4 **5**

This reaction was carried out in a dilute condition (4×10^{-3} M). A mixture of **4** (1.01 g, 2.43 mmol) and $Sc(OTf)_3$ (2.38 g, 4.84 mmol) in 1,2-dichloroethane (600 mL) was refluxed with stirring for 54 h. After cooling to room temperature, a saturated aqueous solution of $NaHCO_3$ was added to the mixture. The organic layer was extracted with dichloromethane three times. The organic extracts were washed with brine and dried over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using 4/1 hexane/dichloromethane as an eluent to give 586 mg (1.42 mmol) of **5** in 58% yield as a white solid: mp 234–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.63–7.69 (m, 4H), 7.43 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 4.59 (s, 2H), 1.78 (s, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 158.4, 155.8, 146.3, 132.7, 128.5, 127.7, 125.4, 124.1, 43.1, 37.5, 34.4, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 45.1; HRMS (APCI, positive) *m*/*z* calcd for $C_{25}H_{22}{}^{11}B^{79}Br$ 412.0998, found: 412.1002.

Planarized triphenylborane-substituted thiophene 2

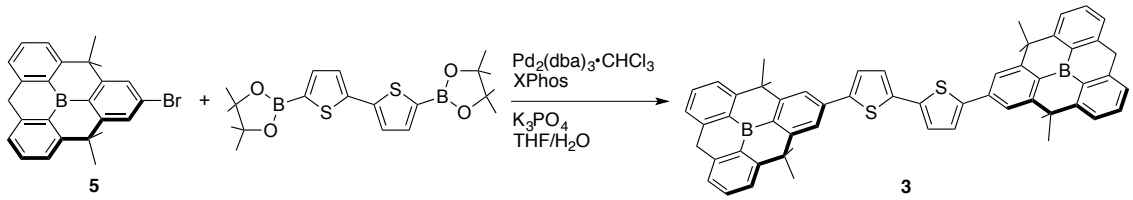


5 **2**

A mixture of **5** (554.6 mg, 1.34 mmol), 2,5-thiophenediboronic acid (115.8 mg, 0.674 mmol), Pd complex **11** (22.4 mg, 28.5 μmol), and K_3PO_4 (422.5 mg, 2.00 mmol) in THF (4.5 mL)/H_2O (2.8 mL) was stirred for 21 h at room temperature. After addition of water, the organic layer was extracted with dichloromethane three times. The organic extracts were washed with brine and dried

over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using 4/1 hexane/dichloromethane as an eluent to give 420 mg (0.561 mmol) of **2** in 84% yield as a yellow solid. Further purification was performed by sublimation (320 °C, 4 × 10^{-2} mmHg) two times for the device fabrication: mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 4H), 7.66–7.71 (m, 8H), 7.59 (s, 2H), 7.45 (d, $^3J_{HH}$ = 6.8 Hz, 4H), 4.62 (s, 4H), 1.90 (s, 24H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 157.2, 156.3, 146.3, 145.5, 138.3, 132.5, 125.3, 125.1, 124.1, 121.9, 43.2, 37.6, 34.7, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 46.0; HRMS (APCI, positive) *m/z* calcd for $C_{54}H_{47}{}^{11}B_2S$ $[M+H]^+$ 749.3596, found: 746.3592.

Planarized triphenylborane-substituted 2,2′-bithiophene 3



5 **3**

A mixture of **5** (1.32 g, 3.19 mmol), 5,5′-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (668 mg, 1.60 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (66.5 mg, 64.4 μmol), XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) (123 mg, 257 μmol), K_3PO_4 (1.37 g, 6.48 mmol) in THF (26 mL)/H_2O (13 mL) was refluxed for 3.5 h. After cooling to room temperature, water was added to the reaction mixture. The organic layer was extracted with dichloromethane three times. The organic extracts were washed with brine and dried over $MgSO_4$. After filtration, volatiles were evaporated under reduced pressure. Washing of the crude product with dichloromethane afforded 1.02 g (1.23 mmol) of **3** in 77% yield as a yellow solid. Further purification was performed by sublimation (350 °C, 4 × 10^{-2} mmHg) two times for the device fabrication: mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 4H), 7.65–7.70 (m, 8H), 7.50 (d, $^3J_{HH}$ = 4.0 Hz, 2H), 7.44–7.45 (m, 4H), 7.34 (d, $^3J_{HH}$ = 4.0 Hz, 2H), 4.62 (s, 4H), 1.87 (s, 24H); ^{13}C and ^{11}B NMR spectra of **3** could not be measured due to its poor solubility in common solvents; Anal Calcd for $C_{58}H_{48}B_2S_2$: C, 83.85; H, 5.82. Found: C, 83.93; H, 5.72; HRMS (APCI, positive) *m/z* calcd for $C_{58}H_{49}{}^{11}B_2S_2$ $[M+H]^+$ 831.3474, found: 831.3481.

2. NMR Spectra

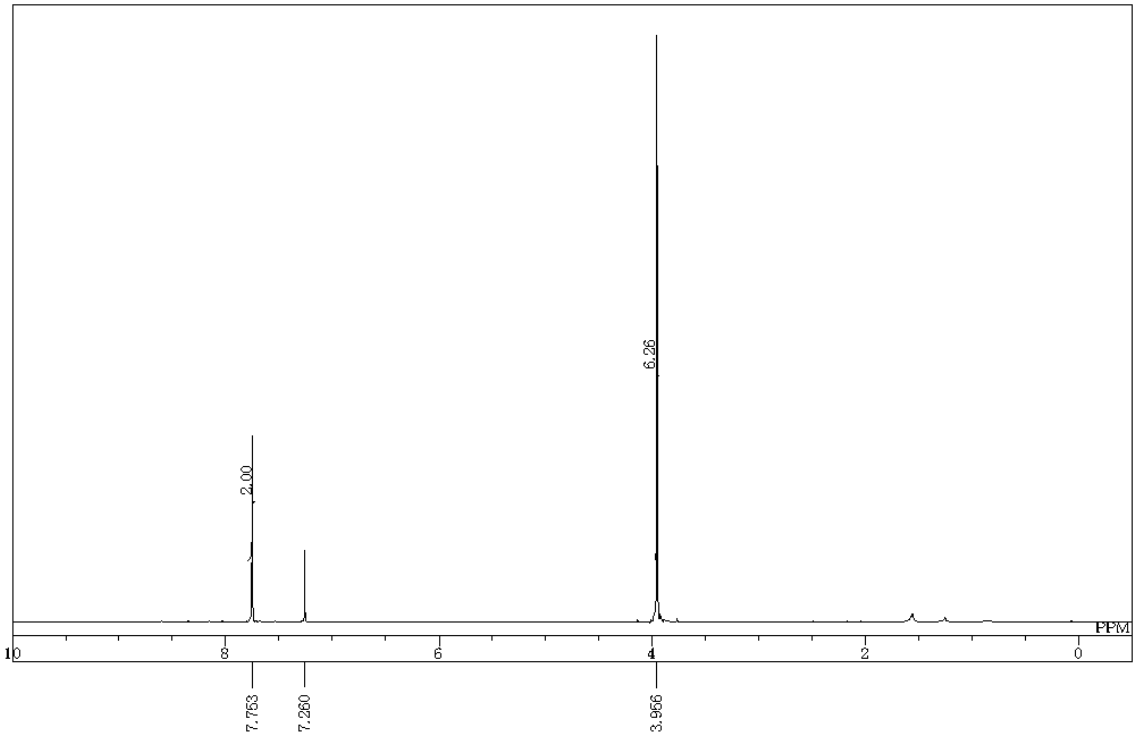


Figure S1. ^{1}H NMR spectrum of **8** in $CDCl_3$.

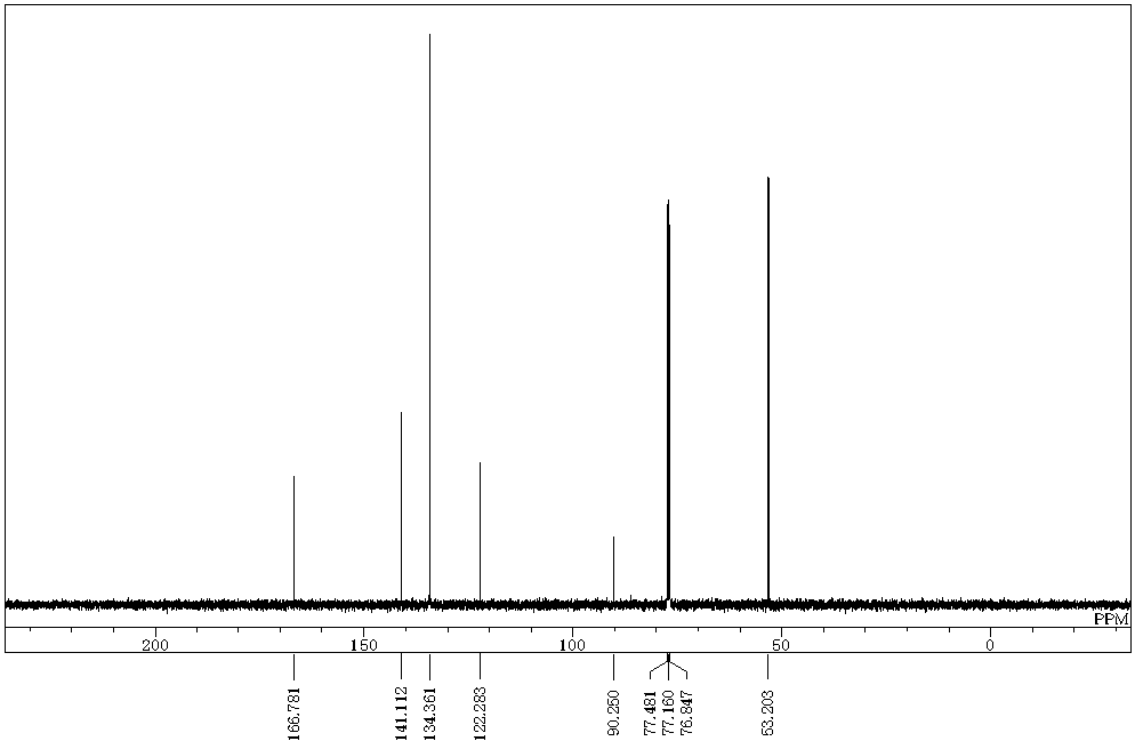


Figure S2. ^{13}C NMR spectrum of **8** in $CDCl_3$.

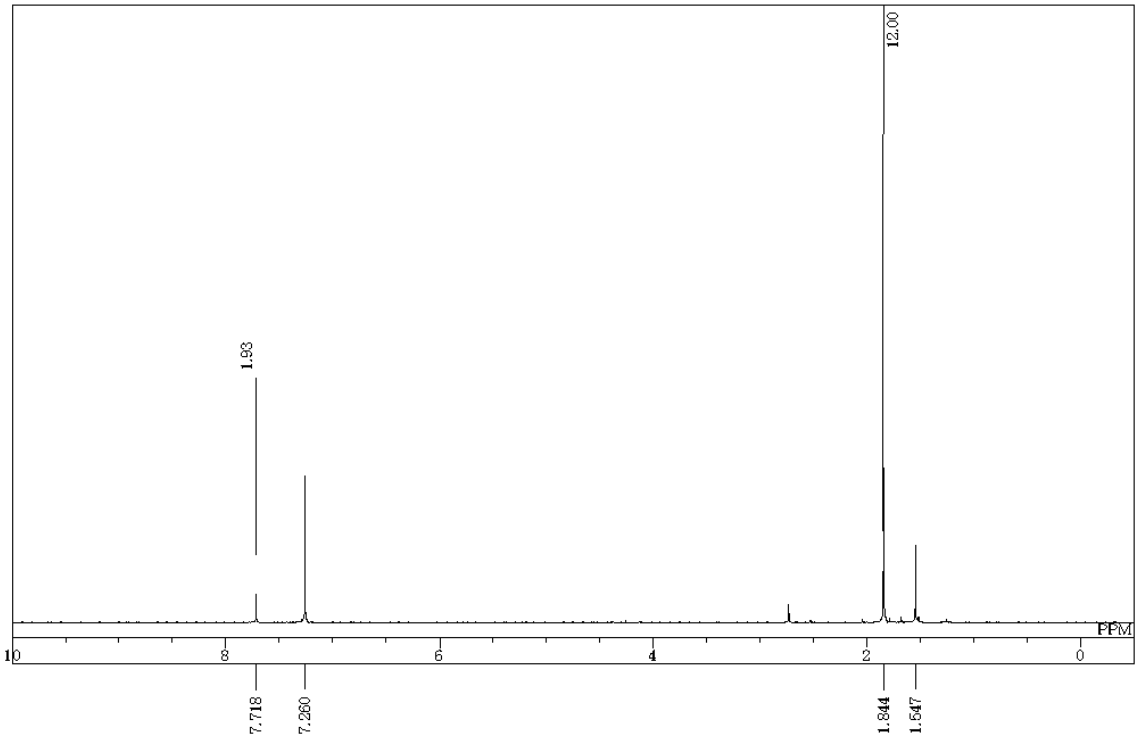


Figure S3. ^{1}H NMR spectrum of **9** in $CDCl_3$.

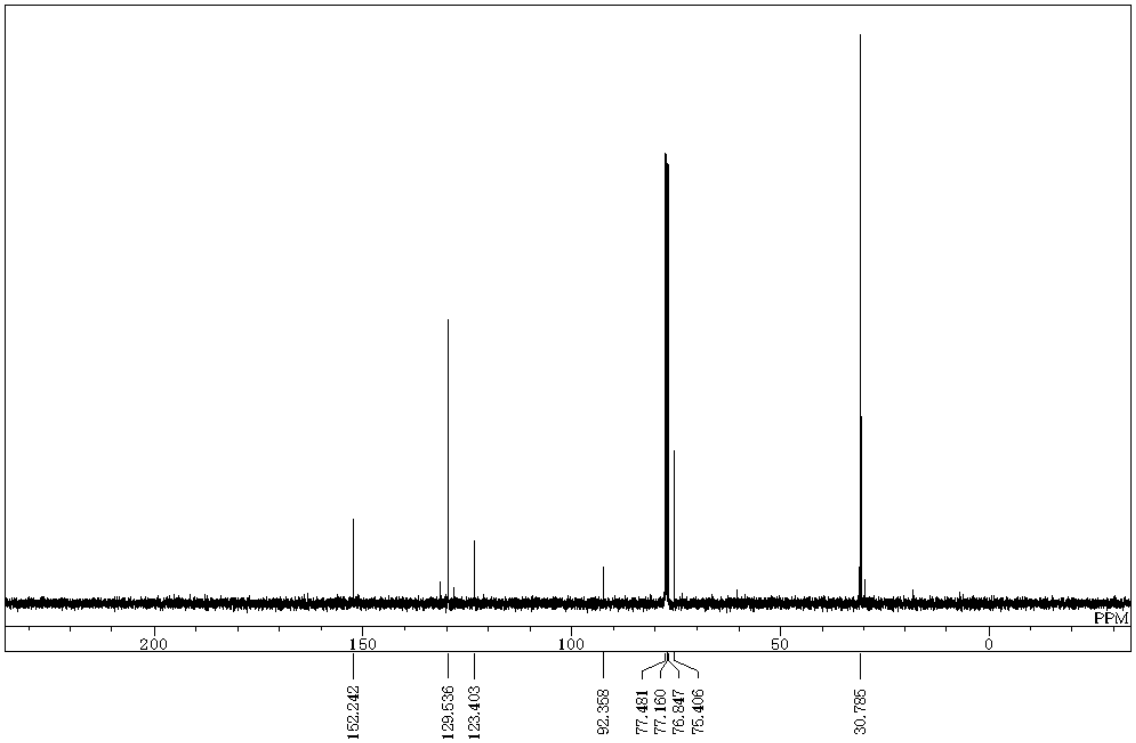


Figure S4. ^{13}C NMR spectrum of **9** in $CDCl_3$.

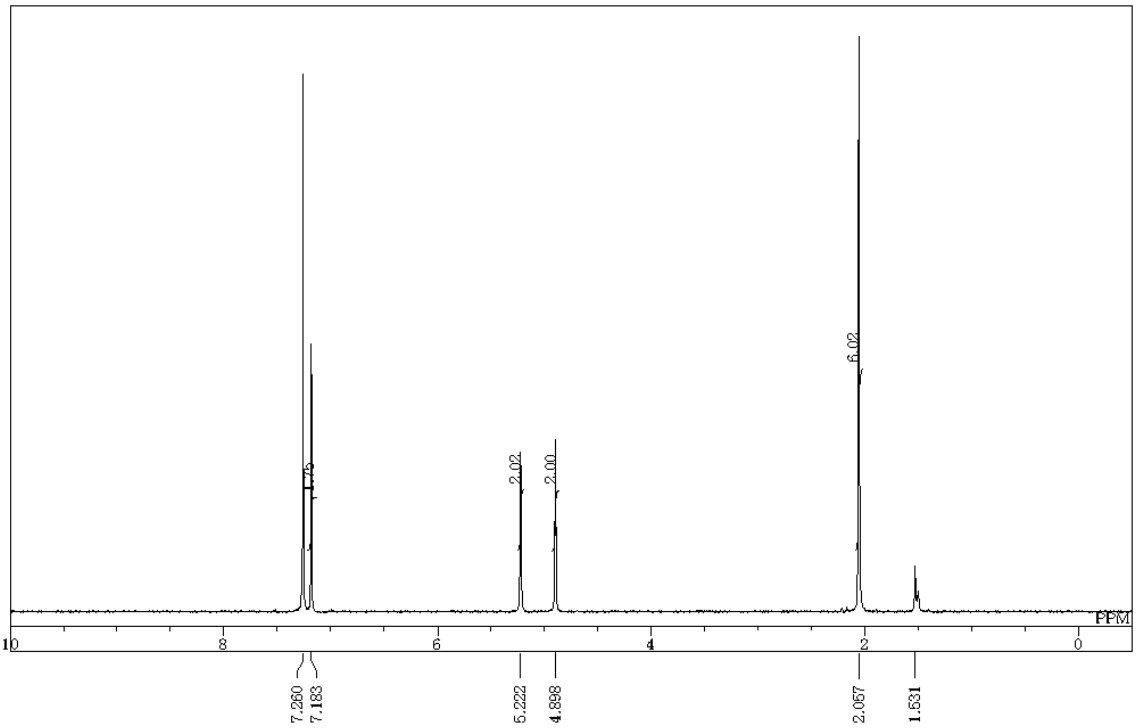


Figure S5. ^{1}H NMR spectrum of **10** in $CDCl_3$.

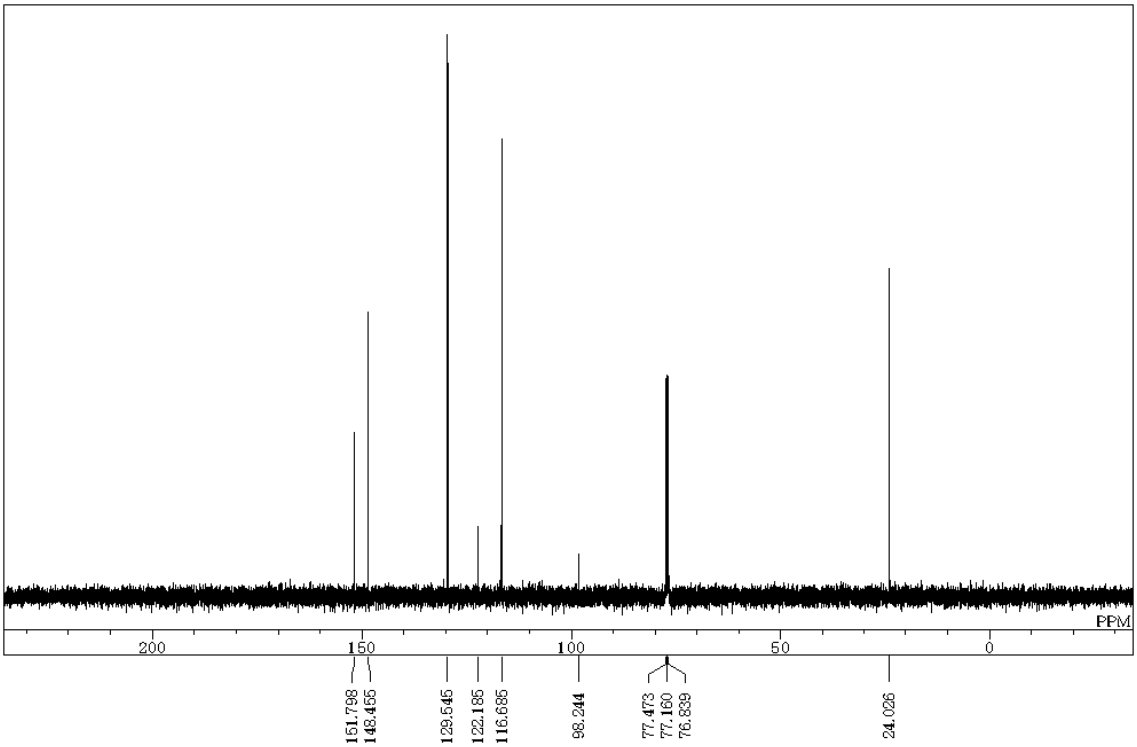


Figure S6. ^{13}C NMR spectrum of **10** in $CDCl_3$.

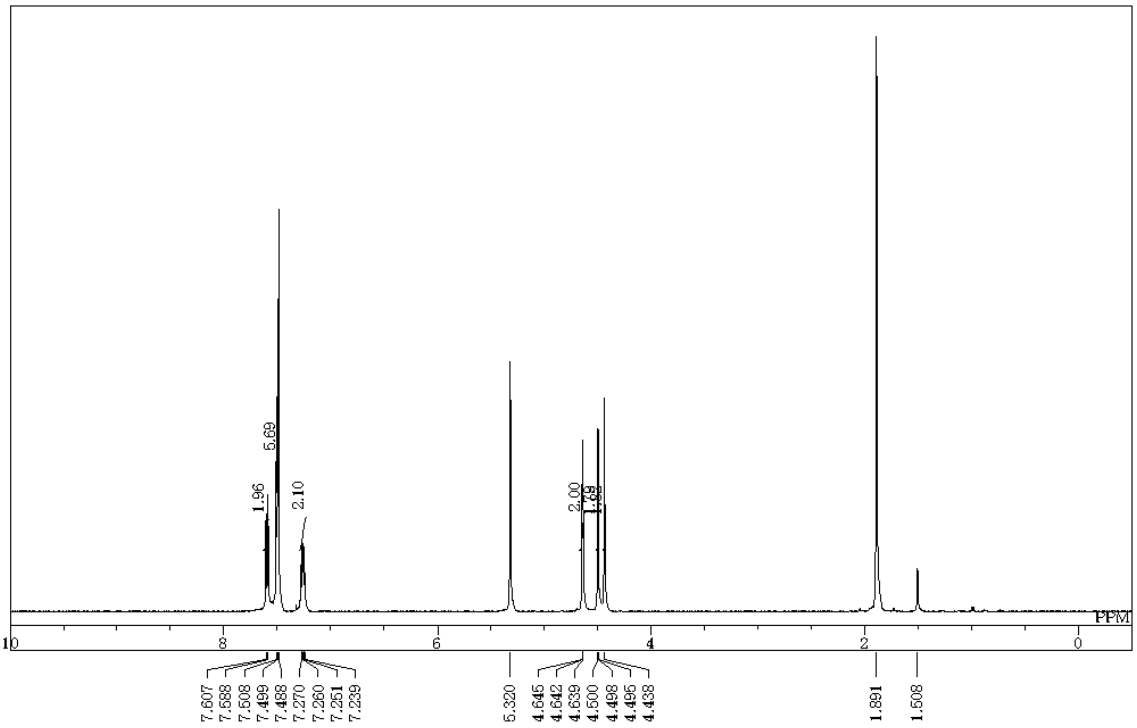


Figure S7. ^{1}H NMR spectrum of **4** in CD_2Cl_2.

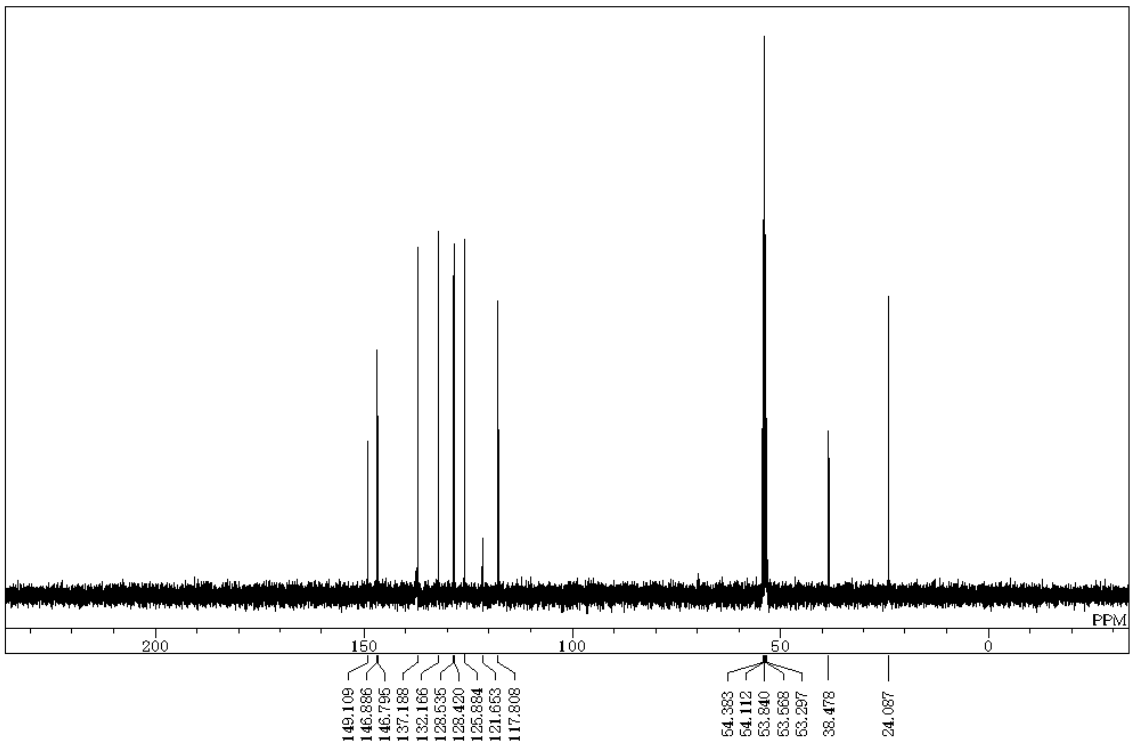


Figure S8. ^{13}C NMR spectrum of **4** in CD_2Cl_2.

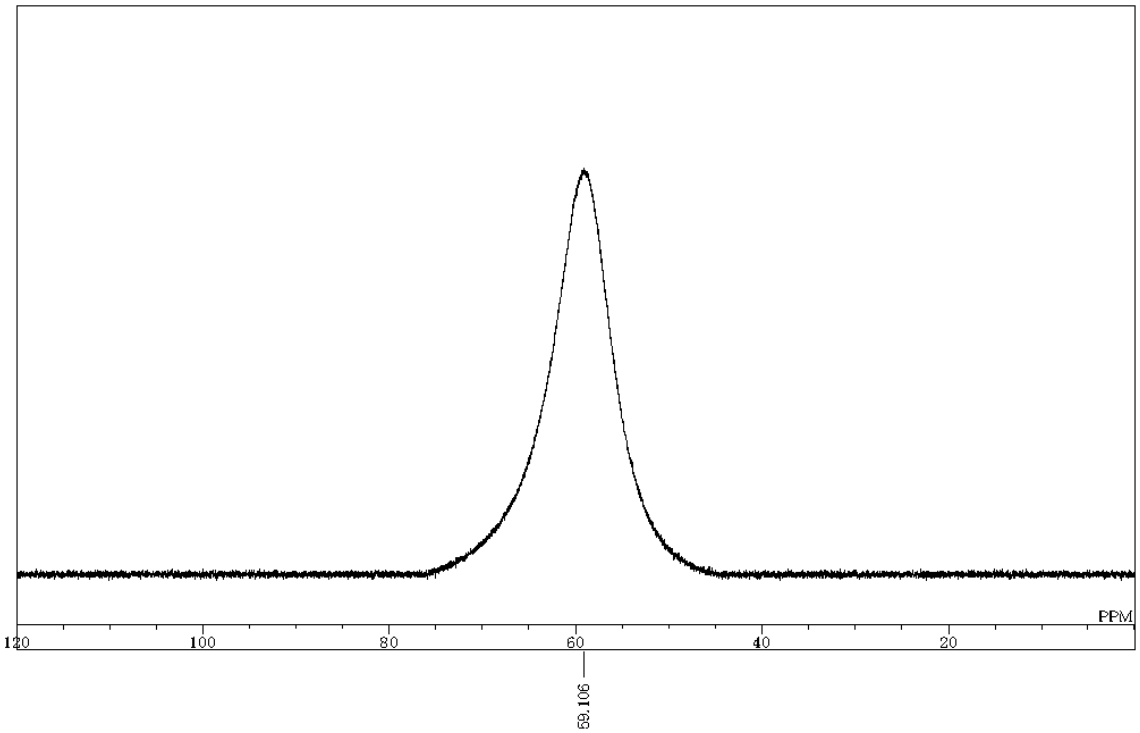


Figure S9. ^{11}B NMR spectrum of **4** in CD_2Cl_2.

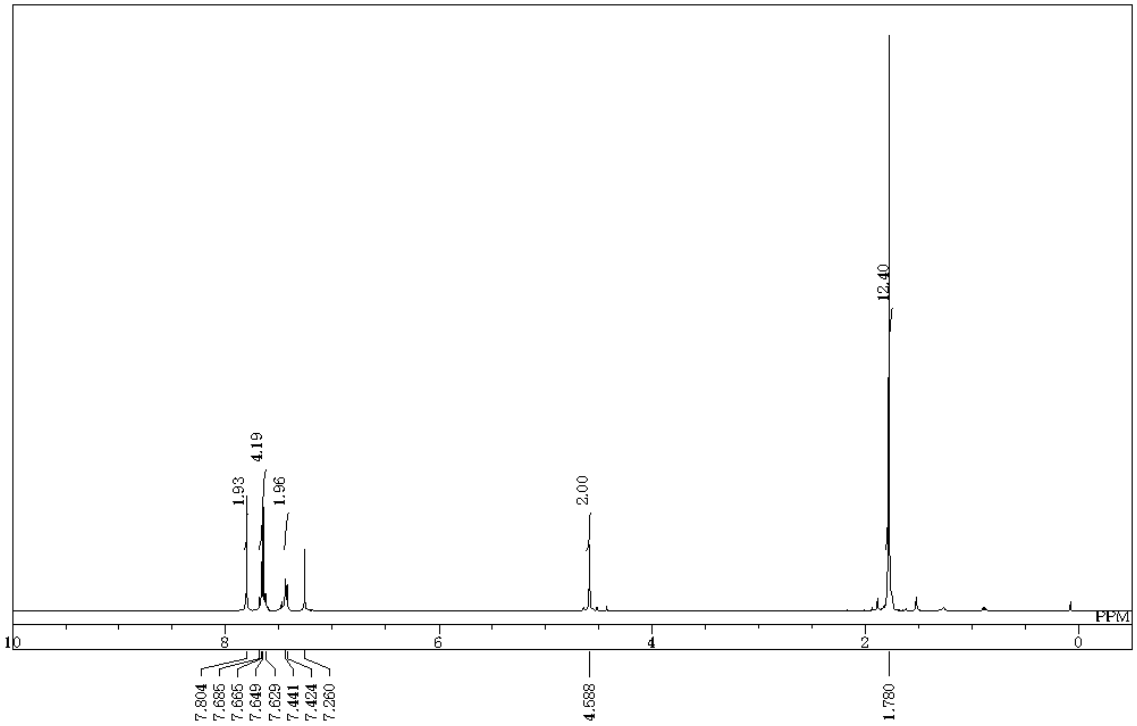


Figure S10. ^{1}H NMR spectrum of **5** in $CDCl_3$.

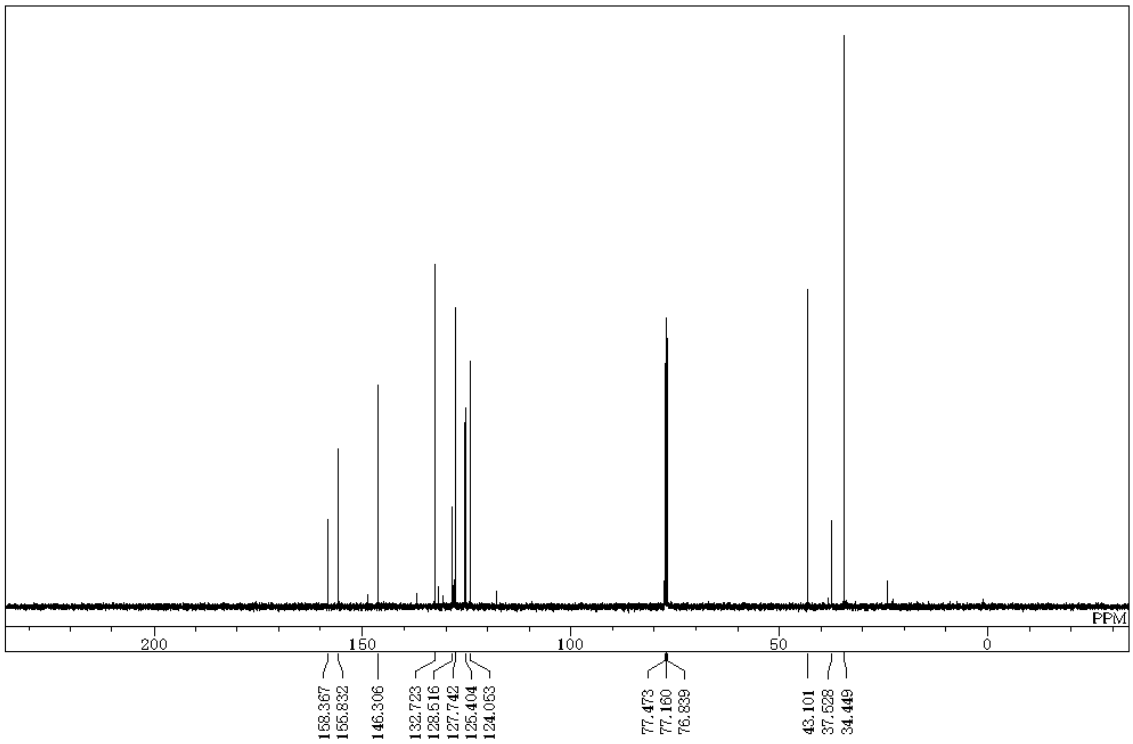


Figure S11. ^{13}C NMR spectrum of **5** in $CDCl_3$.

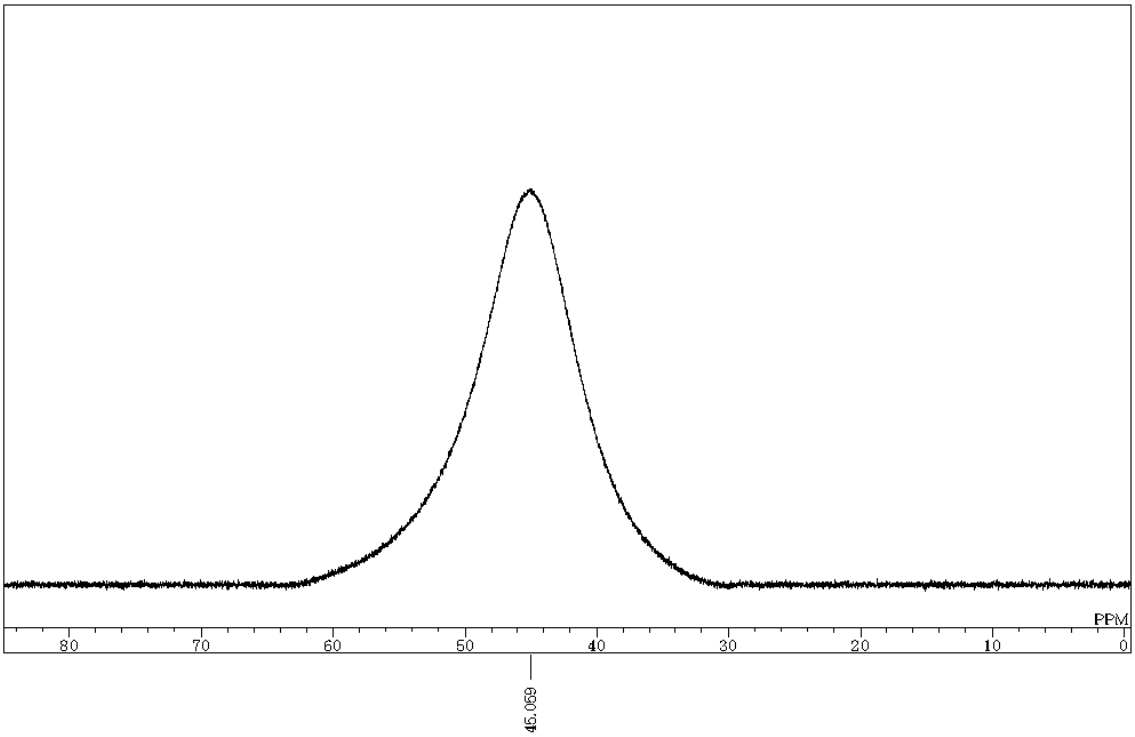


Figure S12. ^{11}B NMR spectrum of **5** in $CDCl_3$.

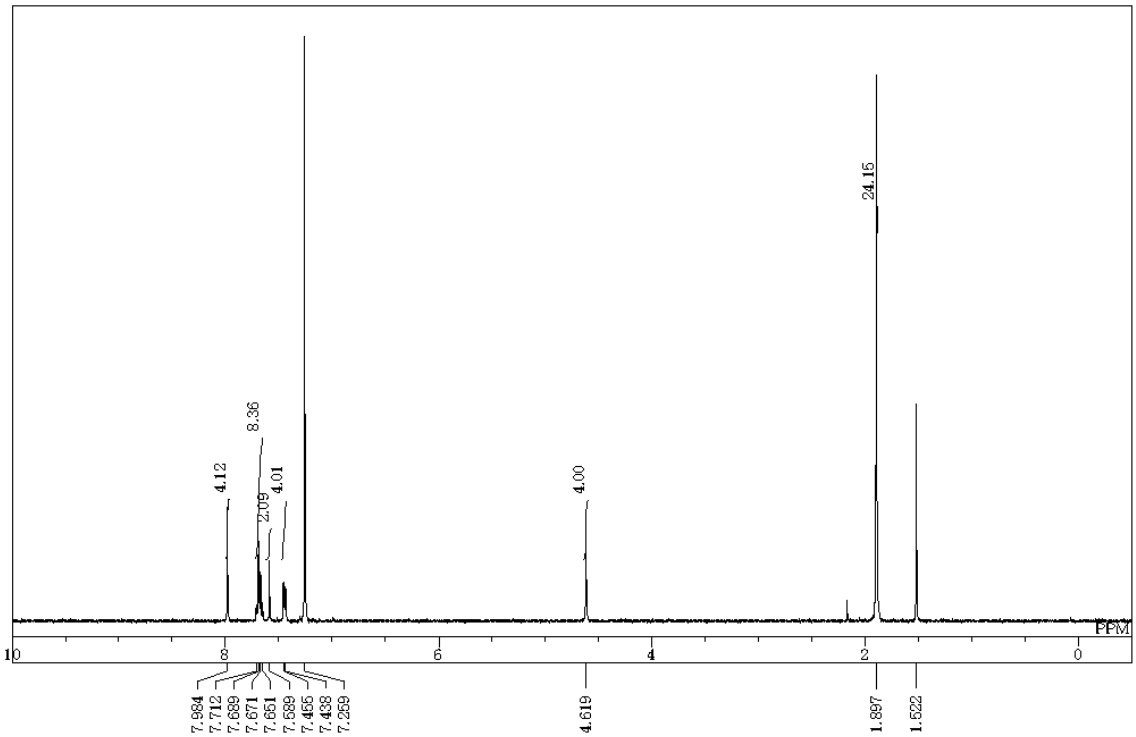


Figure S13. ^{1}H NMR spectrum of **2** in $CDCl_3$.

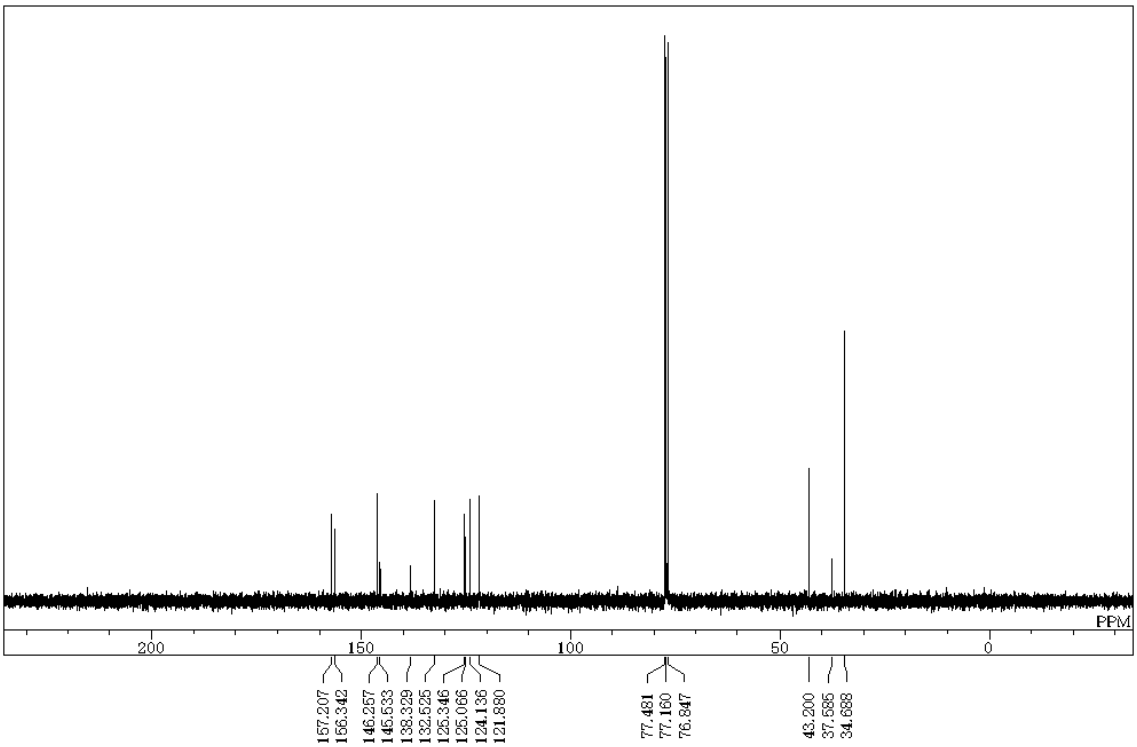


Figure S14. ^{13}C NMR spectrum of **2** in $CDCl_3$.

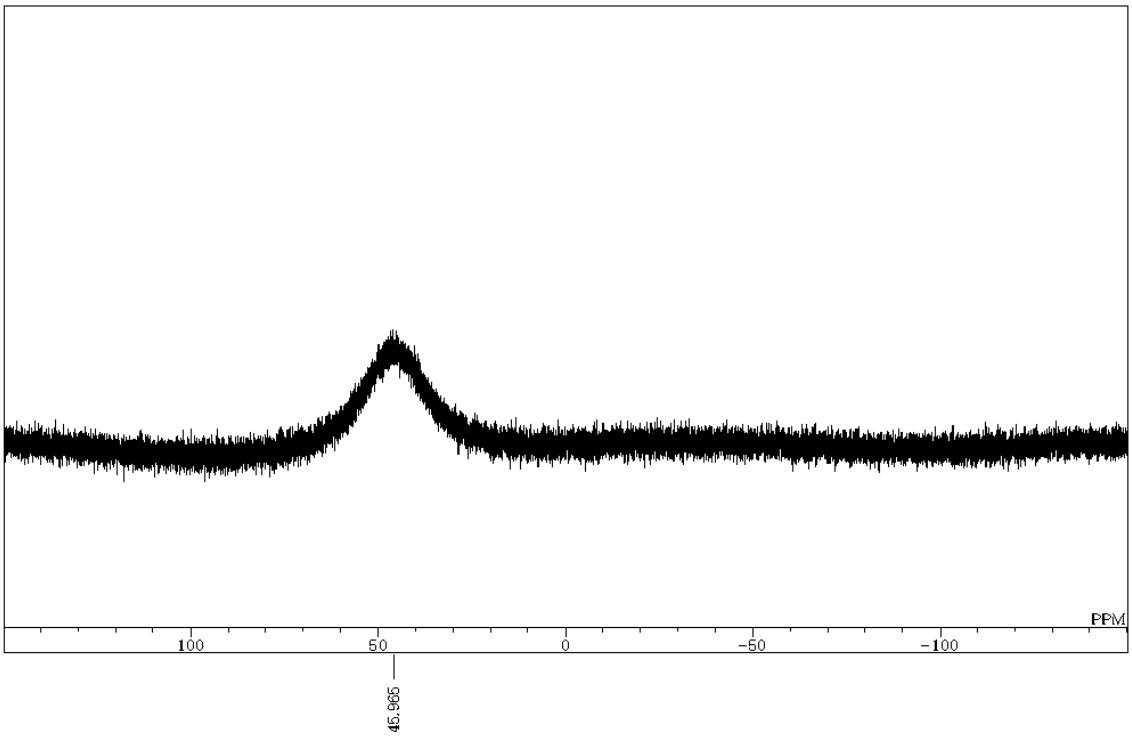


Figure S15. ^{11}B NMR spectrum of **2** in $CDCl_3$.

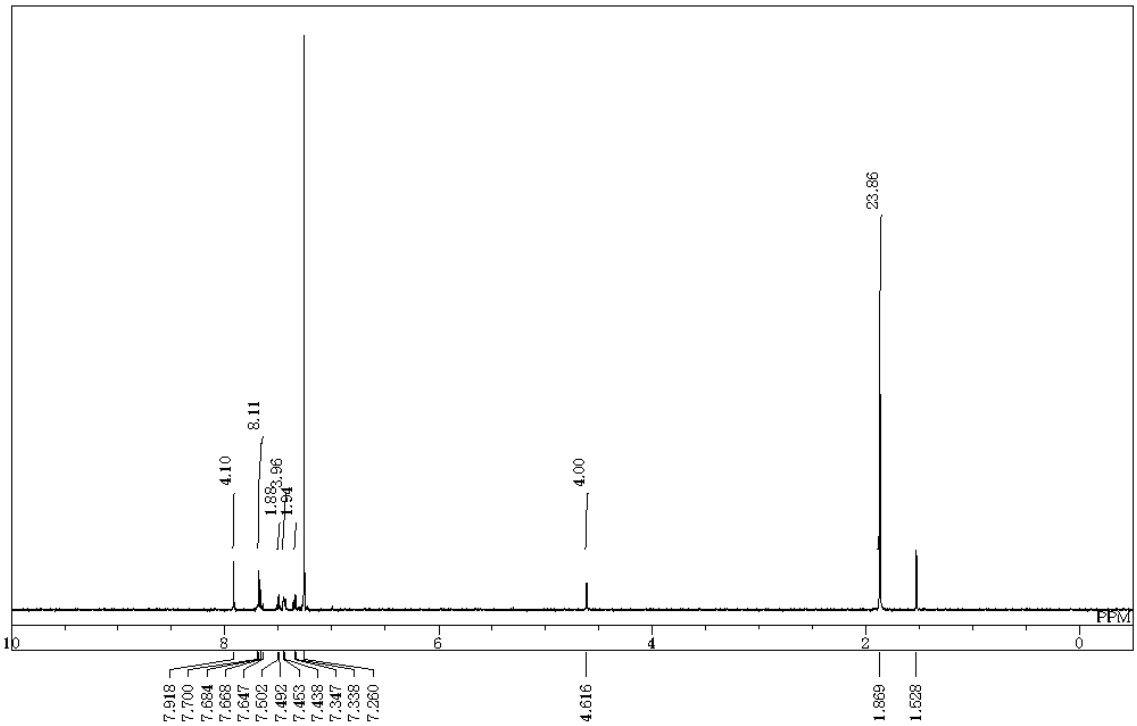


Figure S16. ^{1}H NMR spectrum of **3** in $CDCl_3$.

3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on a SII Exstar 6000 TG/DTA 6200 (Seiko) apparatus at a heating rate of 5 °C/min under a nitrogen atmosphere.

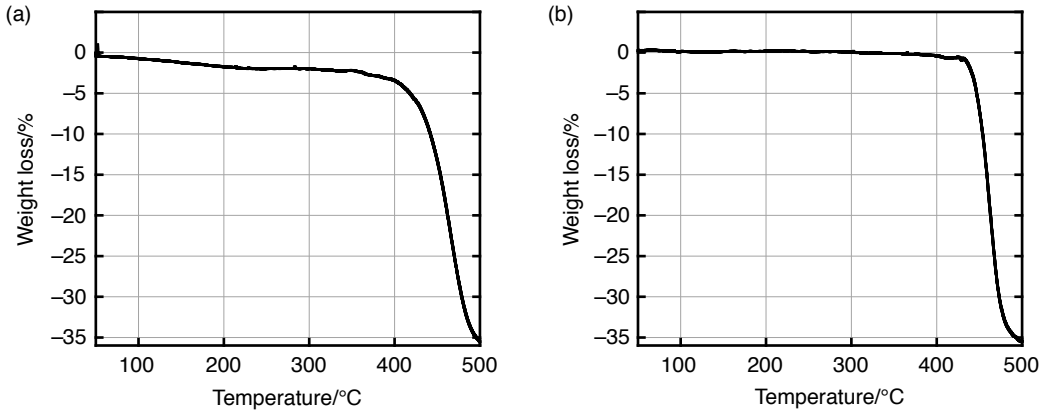


Figure S17. Thermogravimetric analysis of (a) **2** and (b) **3** heating at 5 °C/min under N_2 atmosphere.

4. Photophysical Properties of 2 and 3

UV-vis absorption and fluorescence spectra were measured with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in degassed spectral grade solvents. Fluorescence quantum yields were determined with a Hamamatsu C9920-01 calibrated integrating sphere system within ±3% error. Fluorescence lifetimes were determined with a Hamamatsu C4780 picosecond fluorescence measurement system.

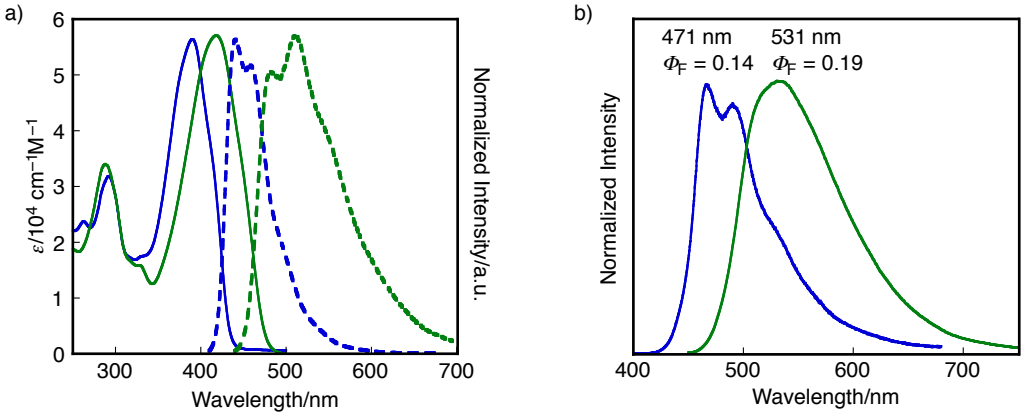


Figure S18. (a) UV-vis absorption (solid lines) and fluorescence (dashed lines) spectra of **2** (blue) and **3** (green) in THF. (b) Fluorescence spectra of **2** (blue) and **3** (green) in the solid state (crystalline powder).

Table S1. Excited-State Dynamics of **2** and **3** in THF

	τ^a [ns]	Φ_F	k_r^b [10^8 s^{-1}]	k_{nr}^c [10^8 s^{-1}]
2	1.36	0.92	6.8	0.59
3	0.32	0.25	7.8	23

[a]Fluorescence lifetime. [b]Radiative decay rate constant ($k_r = \Phi_F/\tau$). [c]Non-radiative decay rate constant ($k_r = (1 - \Phi_F)/\tau$).

5. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out under an argon atmosphere using a THF or CH_2Cl_2 solution of sample with a concentration of 0.1 mM for **2** and 0.01 mM for **3**, and 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) as a supporting electrolyte with a scan rate of 0.1 V/s. The redox potentials were calibrated with ferrocene as an internal standard.

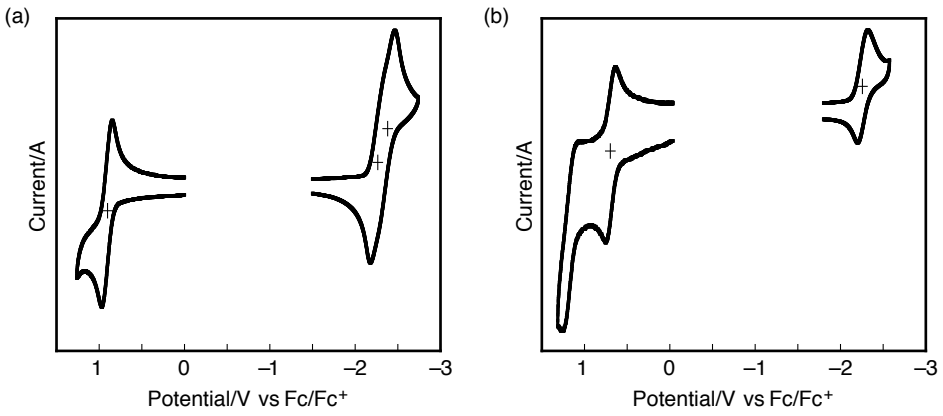


Figure S19. Cyclic voltammograms of (a) **2** and (b) **3** in THF for reduction and in CH_2Cl_2 for oxidation with $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte at a scan rate of 0.1 V/s.

6. X-Ray Crystallographic Analysis

Structural analysis of 2. Needle-shaped yellow single crystals of **2** were grown by vapor diffusion from chloroform/hexane. The intensity data were collected on a Rigaku Saturn CCD diffractometer with Vari Max monochromator MoKα radiation (λ = 0.71070 Å) at 123 K. A total of 64636 reflections were measured at the maximum 2θ angle of 50°, of which 25657 were independent reflections (R_{int} = 0.0480). The structure was solved by direct methods (SHELXS-97)[6] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[6] The complexly dispersed electron densities derived from the solvent molecules that were included in the crystalline lattice were removed by the SQUEESE program in PLATON.[7] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are as follows: $C_{54}H_{46}B_2S$; FW = 748.59, Monoclinic, $P2_1$, a = 14.544(11) Å, b = 26.440(19) Å, c = 25.33(3) Å, β = 93.68(2)°, V = 9719(16) Å^3, Z = 8, D_{calcd} = 1.023 g cm^{-3}. The refinement converged to R_1 [I>2σ(I)] = 0.0880, wR_2 (all data) = 0.2571, GOF = 1.054.

Structural analysis of 3. Prism-shaped yellow single crystals of **3** were grown by vapor diffusion from chloroform/hexane. The intensity data were collected on a Rigaku Saturn CCD diffractometer with Vari Max monochromator MoKα radiation (λ = 0.71070 Å) at 123 K. A total of 13723 reflections were measured at the maximum 2θ angle of 50°, of which 3752 were independent reflections (R_{int} = 0.0606). The structure was solved by direct methods (SHELXS-97)[6] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[6] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are as follows: $C_{58}H_{48}B_2S_2$; FW = 830.70, Monoclinic, $P2_1/c$, a = 15.74(7) Å, b = 8.443(17) Å, c = 16.49(4) Å, β = 101.67(8)°, V = 2146(11) Å^3, Z = 2, D_{calcd} = 1.286 g cm^{-3}. The refinement converged to R_1 [I>2σ(I)] = 0.0708, wR_2 (all data) = 0.2005, GOF = 1.082.

Crystallographic data of **2** and **3** have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-968463 and 968464, respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

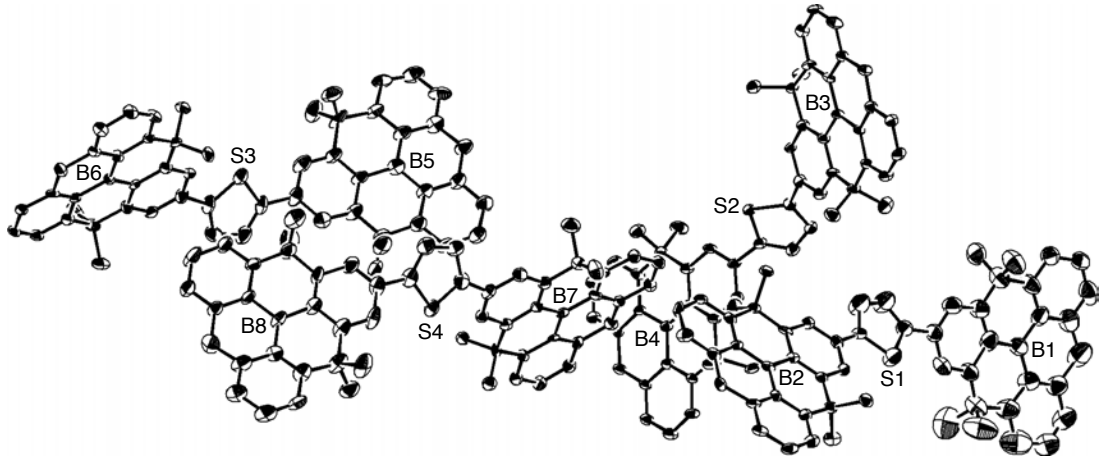


Figure S20. ORTEP drawing of **2** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. The crystal consists of four crystallographycally independent molecules, whose structures are shown.

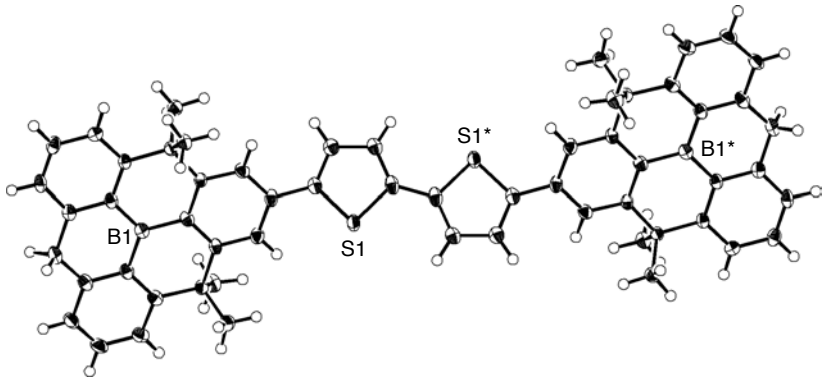


Figure S21. ORTEP drawing of **3** (50% probability for thermal ellipsoids).

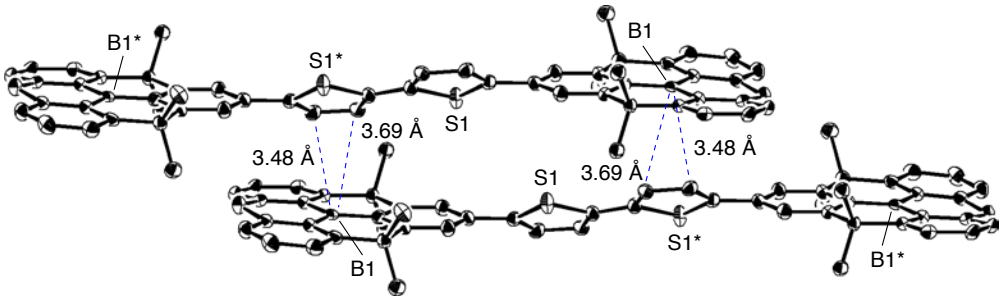


Figure S22. A representative view of the adjacent two molecules **3** in the crystal packing structure (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

7. Theoretical Calculations

Theoretical calculations of **2** and **3** were conducted using the Gaussian 03 program.[8] The geometries optimized at the B3LYP/6-31G(d) level were used for the TD-DFT calculations at the B3LYP/6-31G(d) level. Transfer integrals t_{LUMO} in the crystal packing structures of **2** and **3** were calculated using the Amsterdam Density Functional (ADF) program[9] at the PW91/DZP level of theory.

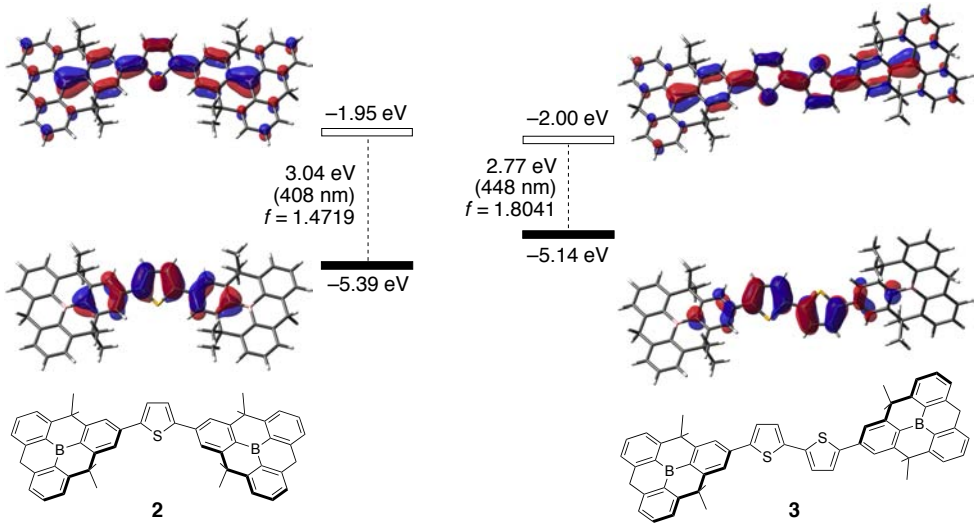


Figure S23. Kohn-Sham plots and energy levels of HOMO and LUMO of **2** and **3**, together with the transition energies calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

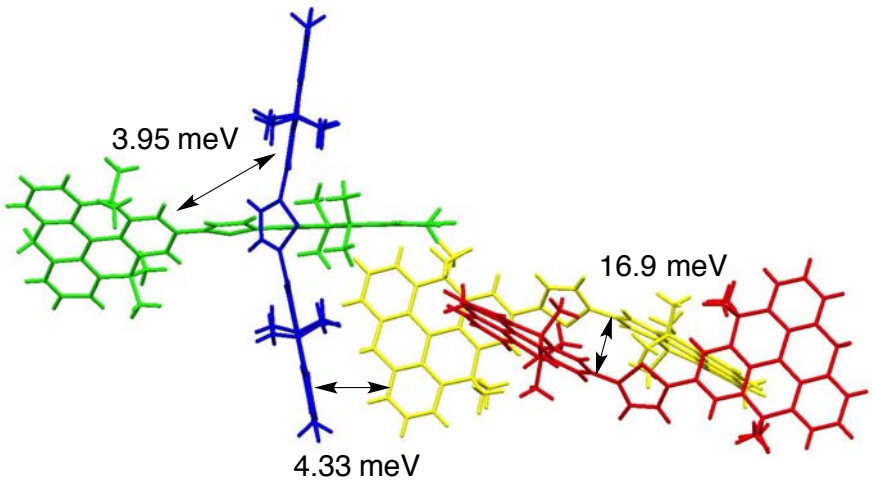


Figure S24. Transfer integrals t_{LUMO} of **2** in the crystal structure calculated with the ADF program at the PW91/DZP level of theory.

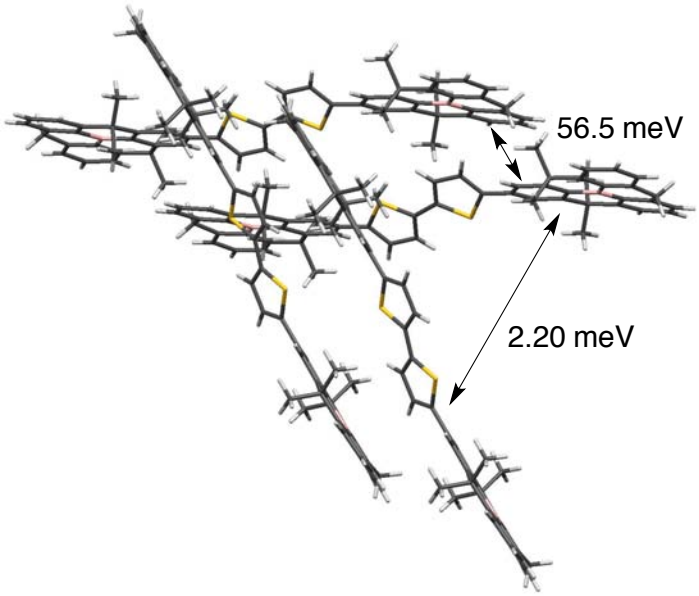


Figure S25. Transfer integrals t_{LUMO} of **3** in the crystal structure calculated with the ADF program at the PW91/DZP level of theory.

8. Details of Electroluminescence Device Fabrication

NPD, Alq_3, and Liq were sublimed grade (Figure S26). The deposition was carried out under 10^{-5} Pa. The deposition rate were 0.2–0.3 nm/s for NPD, Alq_3, compounds **2**, and **3**, 0.01 nm/s for Liq, and 0.1–0.2 nm/s for Al, respectively. The active area was 4 mm^2. Current density–voltage–luminance (*J*–*V*–*L*) of the devices were measured with a source measure unit (Keithley 2400) and spectrometer (Topcon, SR-3). Personal-computer based software for device characterization was provided by Keithley Instruments K. K. Japan. Figure S27 shows the EL characteristics of OLEDs with a device structure of ITO/NPD (50 nm)/Alq_3 (70–*x* nm)/**2** or **3** (*x* nm)/Liq (1 nm)/Al (80 nm). The applied voltage *V* to gain the luminance of 1000 cd/m^2 were 9.4 V for [**2** (*x* = 15)], 11.2 V for [**2** (*x* = 30)], 7.6 V for [**3** (*x* = 15)], and 9.0 V for [**3** (*x* = 30)], respectively.

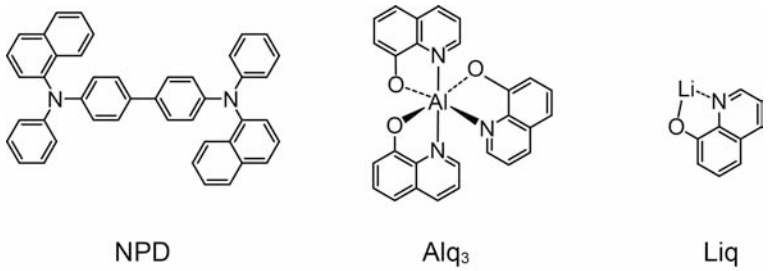


Figure S26. Chemical structures of the materials used for device fabrications.

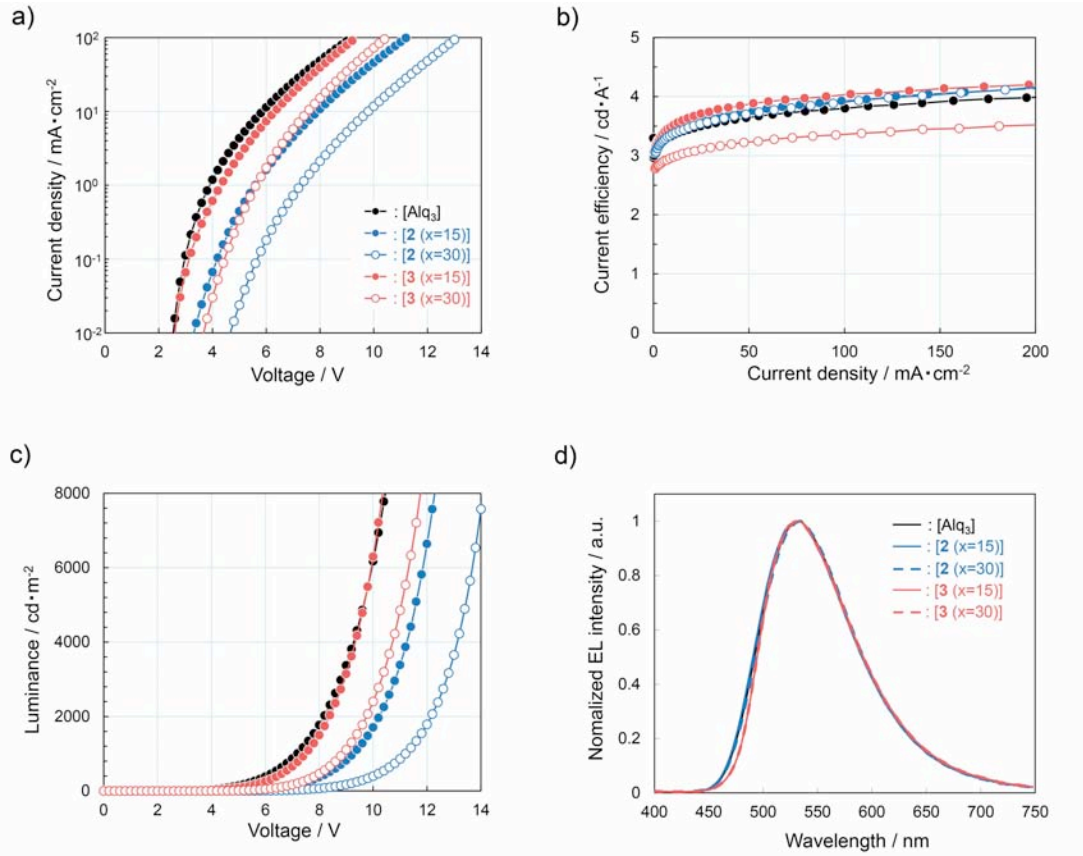


Figure S27. (a) Current density–voltage, (b) current efficiency–current density, and (c) luminance–voltage characteristics are shown. The normalized electroluminescence (EL) spectra measured at a driving current density of 25 mA/cm^2 are shown in (d).

9. References

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