Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting information

Construction of Aromatic-Ring-Layered Structures Using the Terphenylene-layered Polymer as the Scaffold

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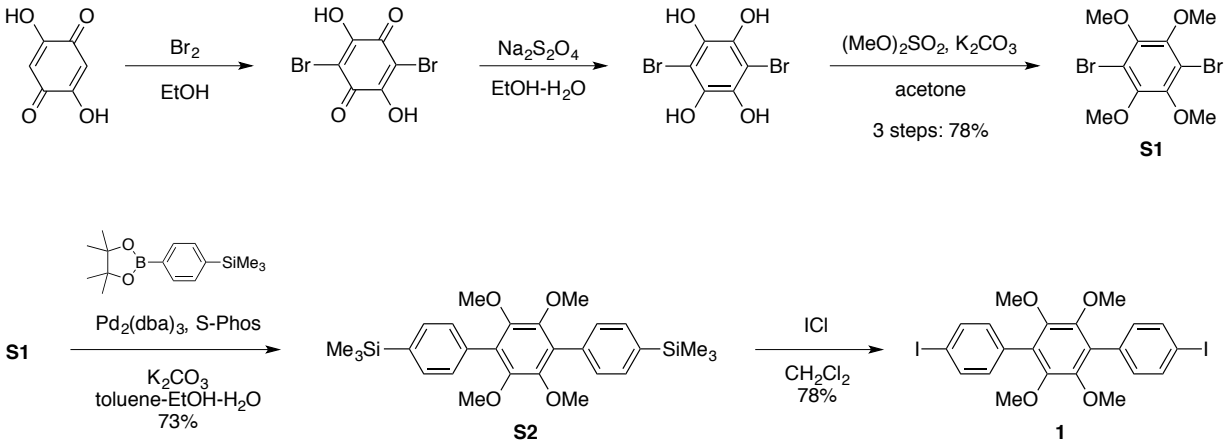
Synthesis of monomer **1**



1,4-Dibromo-2,3,5,6-tetramethoxybenzene (S1).

1,4-Dihydroxy-*p*-benzoquinone (7.79 g, 55.6 mmol) was suspended in EtOH (200 mL), and Br_2 (5.66 mL, 111.2 mmol) was added dropwise to the suspension. The mixture was stirred at room temperature overnight. Red precipitation was formed, which was collected by filtration. The crude product was washed with $CHCl_3$, and then, it was dried in vacuo. The product was dissolved in EtOAc (400 mL). Aqueous $Na_2S_2O_4$ (1 M, 200 mL) was added dropwise to the solution, and the mixture was stirred at room temperature overnight. The organic layer was extracted with EtOAc (100 mL × 2), and the combined organic layer was dried over Na_2SO_4. After Na_2SO_4 was removed, the solution was concentrated in vacuo. The crude product was dissolved in acetone (50 mL). $(MeO)_2SO_2$ (21 mL, 222.4 mmol) and K_2CO_3 (30.7 g, 222.4 mmol) were added to the solution, and the mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into H_2O (200 mL) to precipitate the product. The precipitation was collected by filtration, and it was dried in vacuo. The crude product was purified by recrystallization from $CHCl_3$/MeOH to afford **S1** as a white crystal (15.51 g, 43.6 mmol, 78% for 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.88 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.0, 112.9, 61.0.

1,4-Bis(4'-trimethylphenyl)-2,3,5,6-tetramethoxybenzene (S2).

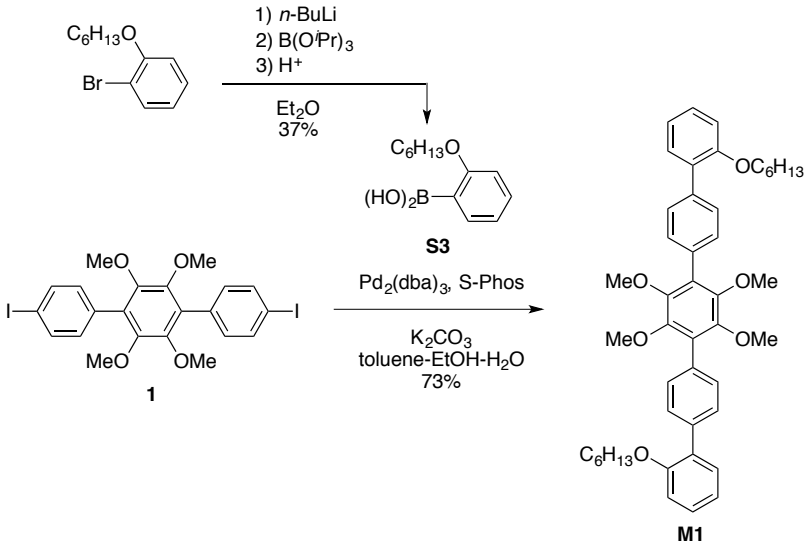
A mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)trimethylsilylbenzene (6.63 g, 24.0 mmol), **S1** (3.56 g, 10.0 mmol), $Pd_2(dba)_3$ (230 mg, 0.25 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-phos) (410 mg, 1.0 mmol), and K_2CO_3 (4.15 g, 30.0 mmol) was dissolved in toluene (50 mL), EtOH (20 mL), and H_2O (30 mL). The solution was refluxed for 24 h. H_2O (50

mL) was added, and the organic layer was extracted with $CHCl_3$ (30 mL × 3). The combined organic layer was dried over $MgSO_4$. After removal of $MgSO_4$, the solution was concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/$CHCl_3$ = 1:1, R_f = 0.2) and by recrystallization from $CHCl_3$/MeOH to afford 1,4-bis(4'-trimethylphenyl)-2,3,5,6-tetramethoxybenzene (**S2**) as a white crystal (3.61 g, 7.29 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (d, J = 8.0 Hz, 4 H), 7.39 (d, J = 8.0 Hz, 4 H), 3.62 (s, 12 H), 0.31 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.0, 139.0, 134.3, 132.9, 130.2, 129.3, 60.9, –1.0. MS (APCI) *m/z*: 495.2378 (calcd for $C_{28}H_{38}O_4Si_2$, $[M + H]^+$ 495.2381). Anal. calcd. for $C_{28}H_{38}O_4Si_2$: C 67.97, H 7.74; found: C 67.71, H 7.81.

1,4-Bis(4'-iodophenyl)-2,3,5,6-tetramethoxybenzene (1).

ICl in CH_2Cl_2 solution (1 M, 4 mL) was added dropwise to the solution of **S2** (825 mg, 1.67 mmol) in CH_2Cl_2 (20 mL) at room temperature. The mixture was stirred at room temperature overnight to form precipitation. The precipitation was collected by filtration, and it was washed with hexane. The crude product was purified by recrystallization from $CHCl_3$/MeOH to afford **1** as a white crystal (781 mg, 1.30 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, J = 8.3 Hz, 4 H), 7.18 (d, J = 8.3 Hz, 4 H), 3.57 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.2, 137.3, 133.4, 132.5, 129.5, 93.5, 61.2. MS (APCI) *m/z*: 602.9519 (calcd for $C_{22}H_{20}O_4I_2$, $[M + H]^+$ 602.9524). Anal. calcd. for $C_{22}H_{20}O_4I_2$: C 43.88, H 3.35, O 10.63, I 42.15; found: C 43.79, H 3.37, O 10.79, I 41.58.

Synthesis of compound **M1**



2-Hexyloxybenzeneboronic acid (S3).

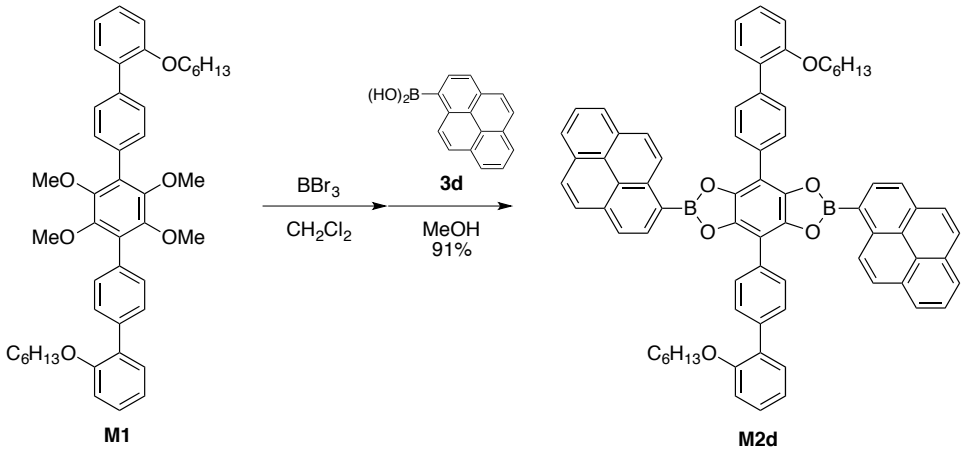
^{n}BuLi (24 mL, 1.6 M hexane solution) was added dropwise to a solution of 2-hexyloxybromobenzene (6.2 g, 24 mmol) in Et_2O (70 mL) at –78 C°. After stirring for 2 h, $B(O^{i}Pr)_3$ (9.2 mL, 40 mmol) was added dropwise to the solution at –78 C°, and it was stirred at room temperature overnight. 1 N HCl was added to the solution to quench the reaction, and then, the organic layer was extracted with Et_2O three times. The organic layer was dried over $MgSO_4$. After removal of $MgSO_4$, the solution was dried in vacuo. The crude product was purified by recrystallization from $CHCl_3$/hexane to afford 2-hexyloxybenzeneboronic acid (**S3**) as a white crystal (1.96 g, 8.8 mmol, 37%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.66 (s, 2 H), 7.57 (d, J = 7.0 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 6.96 (d, J = 8.5 Hz, 1 H), 6.91 (t, J = 7.2 Hz, 1 H), 4.01 (t, J = 6.4 Hz, 2 H), 1.73 (m, 2 H), 1.40 (m, 2 H), 1.30 (m, 4 H), 0.86 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 162.9, 135.4, 131.6, 120.3, 111.2, 67.7, 34.8, 30.9, 28.6, 25.2, 22.0, 13.9.

1,4-Bis([2'-hexyloxy-1,1'-biphenyl]-4-yl)-2,3,5,6-tetramethoxybenzene (M1).

A mixture of **1** (150 mg, 0.25 mmol), **S3** (222 mg, 1.0 mmol), $Pd_2(dba)_3$ (10 mg, 0.012 mmol), S-Phos (21 mg, 0.05 mmol), and K_2CO_3 (138 mg, 1.0 mmol) was dissolved in toluene (5 mL), EtOH (2 mL), and H_2O (3 mL). The solution was refluxed overnight. H_2O (20 mL) was added to the solution, and the product was extracted with $CHCl_3$ (20 mL × 3). The organic layer was dried over

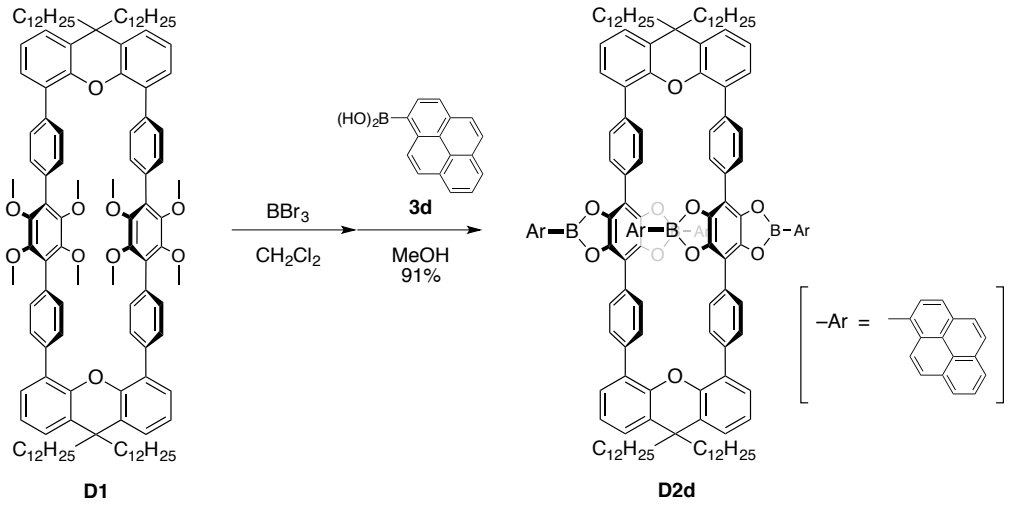
$MgSO_4$. After removal of $MgSO_4$, the solution was concentrated in vacuo. The residue was plugged through short silica gel column ($CHCl_3$, R_f = 0.5), and the product was purified by recrystallization from $CHCl_3$/MeOH to give **M1** (73%, 129 mg, 0.18 mmol) as a white crystal. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (d, J = 8.2 Hz, 4 H), 7.48 (d, J = 8.2 Hz, 4 H), 7.44 (d, J = 7.6 Hz, 2 H), 7.29 (t, J = 7.8 Hz, 2 H), 7.00 (m, 4 H), 3.99 (t, J = 6.4 Hz, 4 H), 3.64 (s, 12 H), 1.75 (m, 4 H), 1.43 (m, 4 H), 1.30 (m, 8 H), 0.88 (t, J = 6.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.1, 147.1, 137.3, 132.1, 130.8, 129.9, 129.6, 129.0, 128.4, 120.7, 112.6, 68.4, 60.9, 31.5, 29.3, 25.8, 22.6, 14.1. MS (APCI) *m/z*: 703.3973 (calcd for $C_{46}H_{54}O_6$, $[M + H]^+$ 703.3993). Anal. calcd. for C 78.60, H 7.74, O 13.66; found: C 78.65, H 7.81, O 13.89.

Synthesis of compound **M2d**



BBr_3 in CH_2Cl_2 solution (1 M, 0.25 mL) was added dropwise to the solution of **M1** (28 mg, 0.04 mmol) in CH_2Cl_2, and the mixture was stirred at room temperature for 2 h. 1-Pyreneboronic acid (**3d**) (0.5 mmol) in CH_2Cl_2/MeOH (v/v = 1:1) was added to the solution and stirred overnight. Excess MeOH was added to the mixture to precipitate the product. The precipitation was collected by filtration, and it was washed with MeOH and hexane. The product was dried in vacuo to obtain **M2d** as a white powder (39 mg, 0.036 mmol, 91%). MS (APCI) *m/z*: 1089.4452 (calcd for $C_{74}H_{60}B_2O_6$, $[M + Na]^+$ 1089.4468).

Synthesis of compound **D2d**



BBr_3 in CH_2Cl_2 solution (1 M, 0.25 mL) was added dropwise to the solution of **D1** (10 mg, 5.7 mmol) in CH_2Cl_2, and the mixture was stirred at room temperature for 2 h. Compound **3d** (1.0 mmol) in CH_2Cl_2/MeOH (v/v = 1:1) was added to the solution and stirred overnight. Excess MeOH was added to the mixture to precipitate the polymer, which was collected by centrifugation. After filtration, the product was washed with MeOH and hexane. It was purified by silica gel column chromatography (hexane/$CHCl_3$ = 1:1, R_f = 0.5) to afford **D2d** as a yellow powder (13 mg, 5.2 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.56 (d, J = 9.0 Hz, 4 H), 8.22 (d, J = 8.0 Hz, 8 H), 7.98 (d, J = 7.6 Hz, 4 H), 7.80 (d, J = 7.3 Hz, 4 H), 7.70 (d, J = 9.0 Hz, 4 H), 7.65 (d, J = 8.0 Hz, 8 H), 7.59 (t, J = 7.5 Hz, 4 H) , 7.52 (d, J = 7.6 Hz, 4 H), 7.47 (d, J = 7.6 Hz, 4 H), 7.37 (d, J = 7.0 Hz, 4 H), 7.21 (t, J = 8.4 Hz, 8 H), 7.00 (d, J = 8.8 Hz, 4 H), 2.19 (m, 8 H), 1.36 (m, 80 H), 0.88 (t, J = 6.7 Hz, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.1, 141.1, 137.6, 135.5, 133.2, 130.4, 130.2, 130.0, 129.6, 129.2, 127.8, 126.5, 126.0, 125.0, 124.8, 123.5, 123.2, 122.9, 111.2, 44.9, 43.0, 32.0, 31.6, 30.3, 29.9, 29.8, 29.5, 25.0, 22.7, 14.2. MS (APCI) *m/z*: 2480.2561 (calcd for $C_{174}H_{164}B_4O_{10}$, $[M + Na]^+$ 2480.2594).

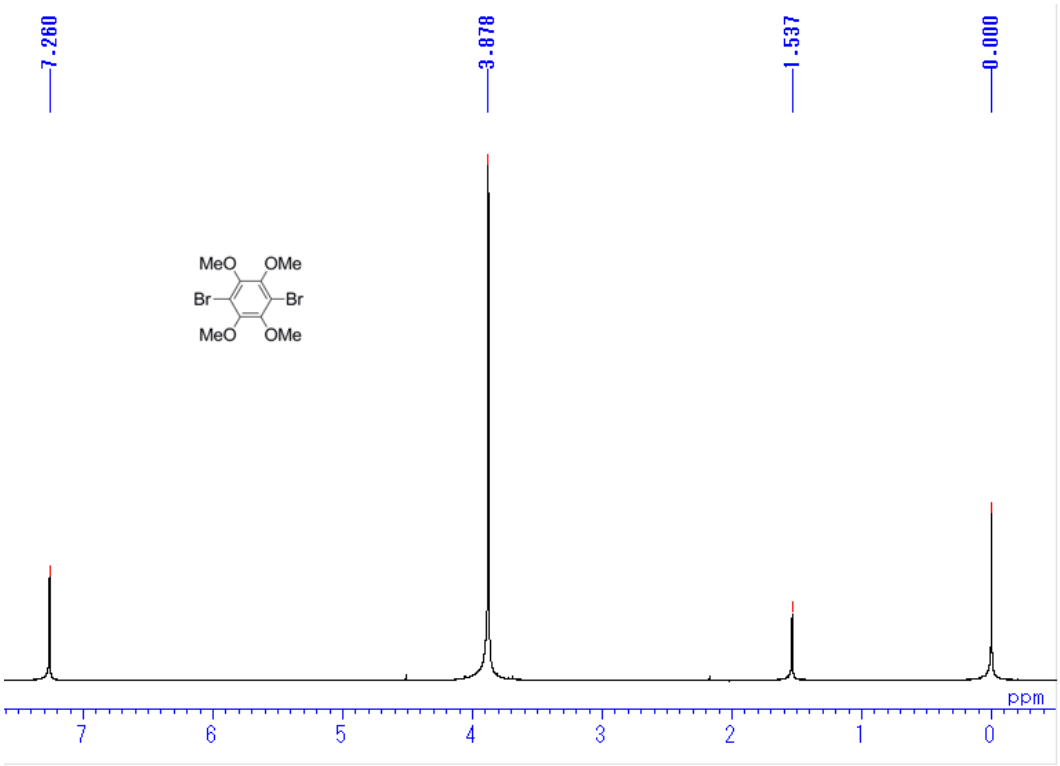


Figure S1. ^{1}H NMR spectrum of **S1**, 400 MHz, $CDCl_3$.

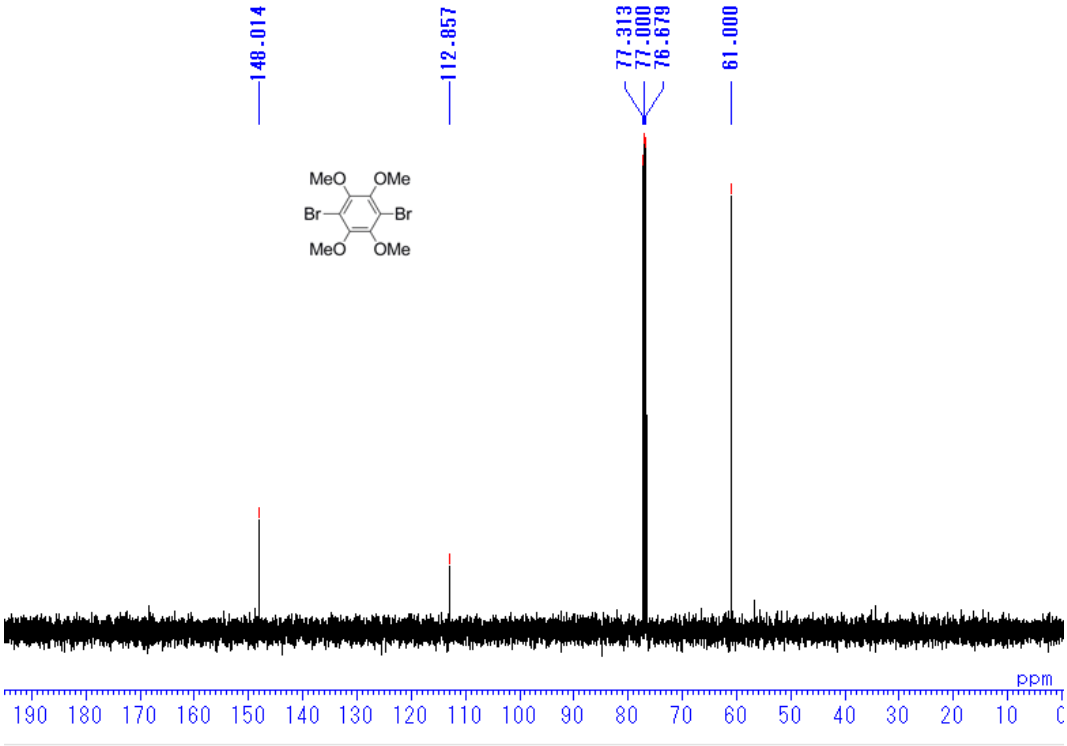


Figure S2. ^{13}C NMR spectrum of **S1**, 100 MHz, $CDCl_3$.

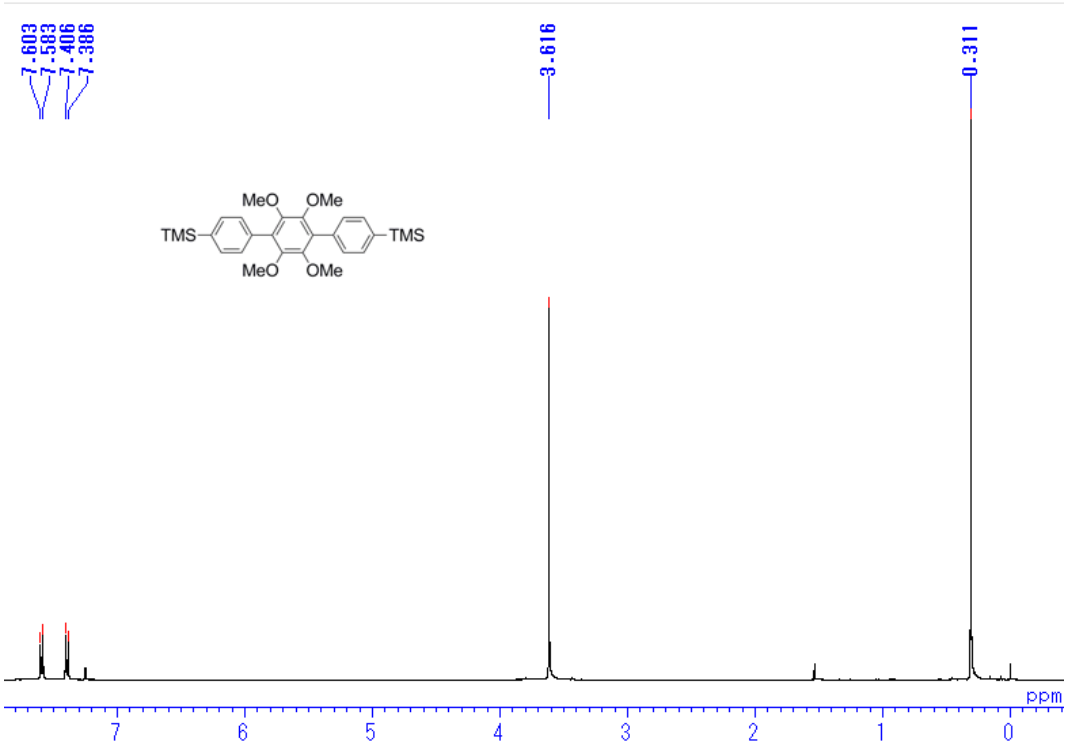


Figure S3. ^{1}H NMR spectrum of **S2**, 400 MHz, $CDCl_3$.

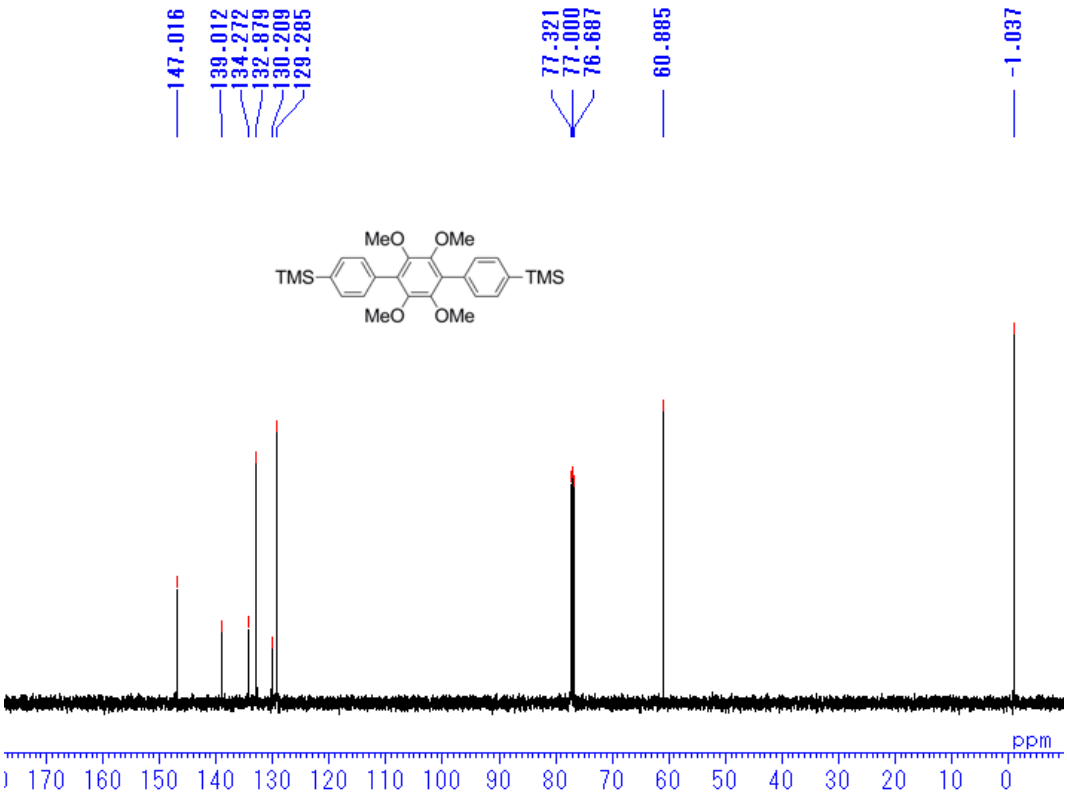


Figure S4. ^{13}C NMR spectrum of **S2**, 100 MHz, $CDCl_3$.

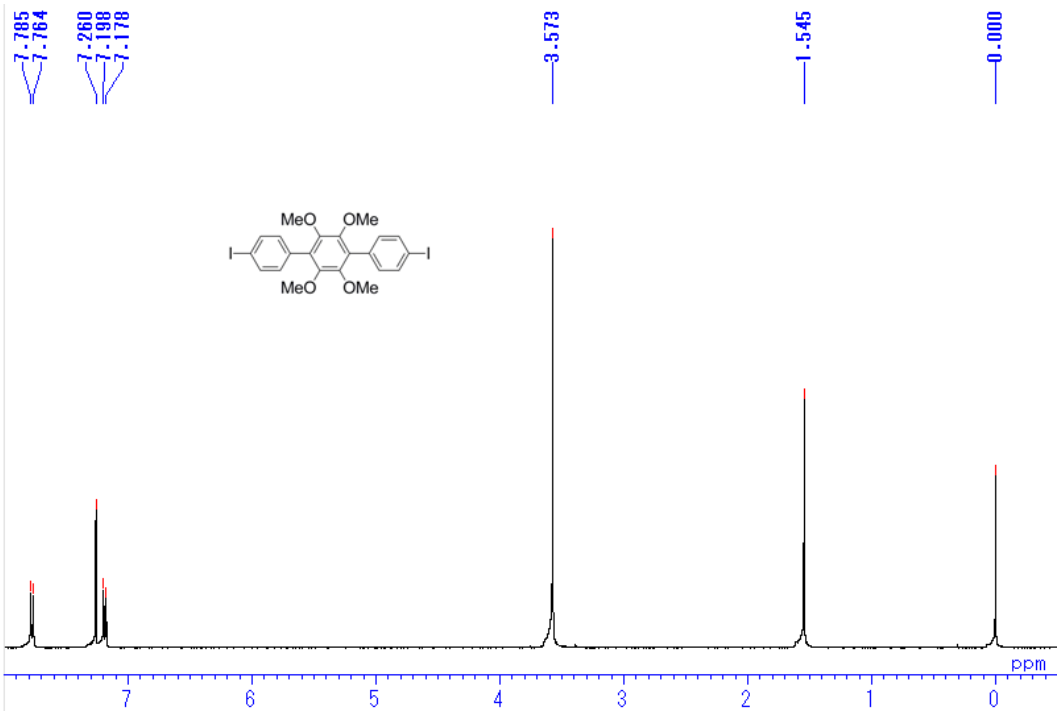


Figure S5. ^{1}H NMR spectrum of **1**, 400 MHz, $CDCl_3$.

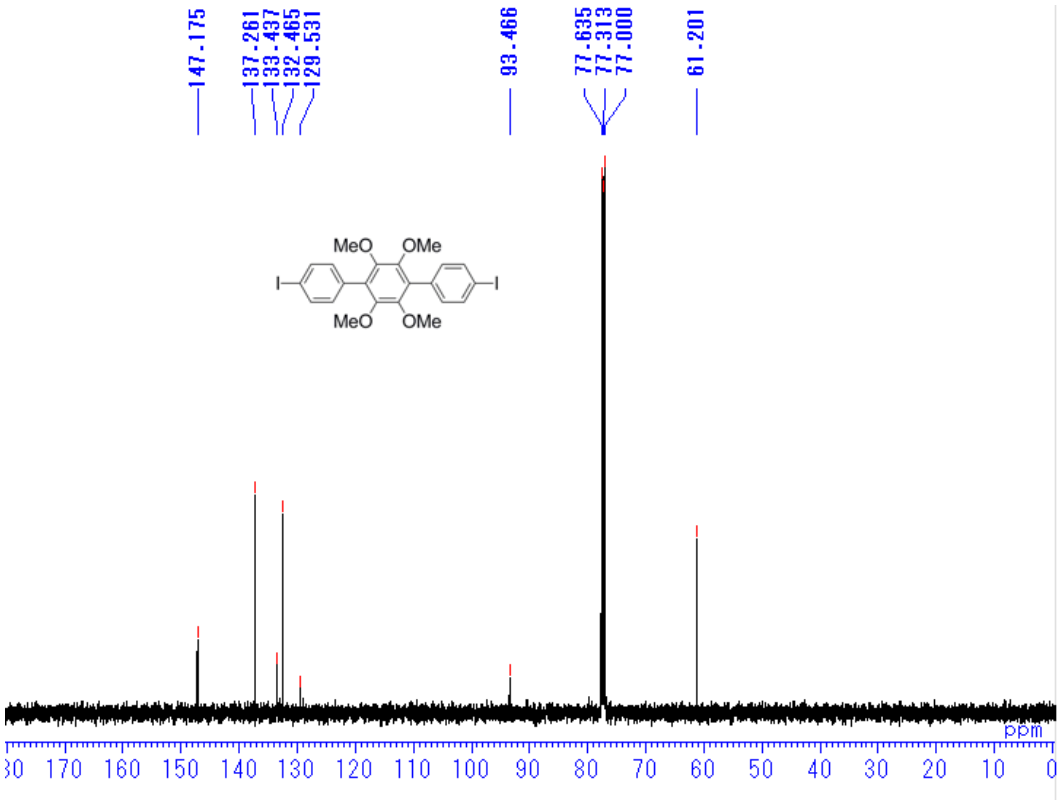


Figure S6. ^{13}C NMR spectrum of **1**, 100 MHz, $CDCl_3$.

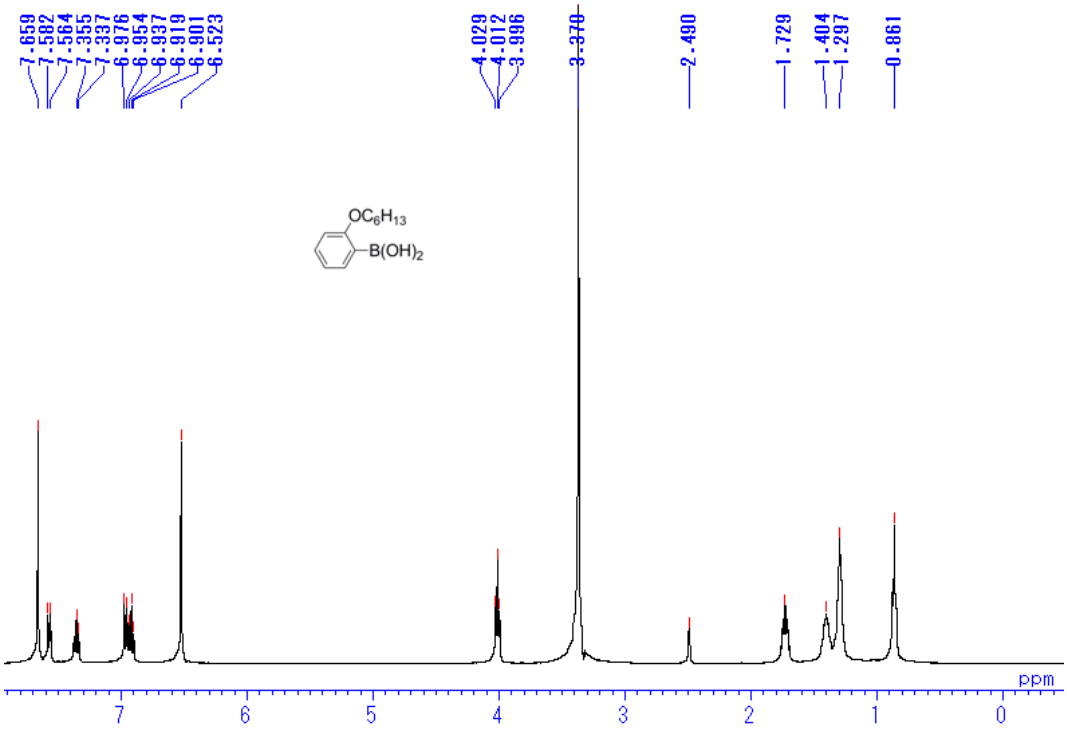


Figure S7. ^{1}H NMR spectrum of **S3**, 400 MHz, DMSO-d_6.

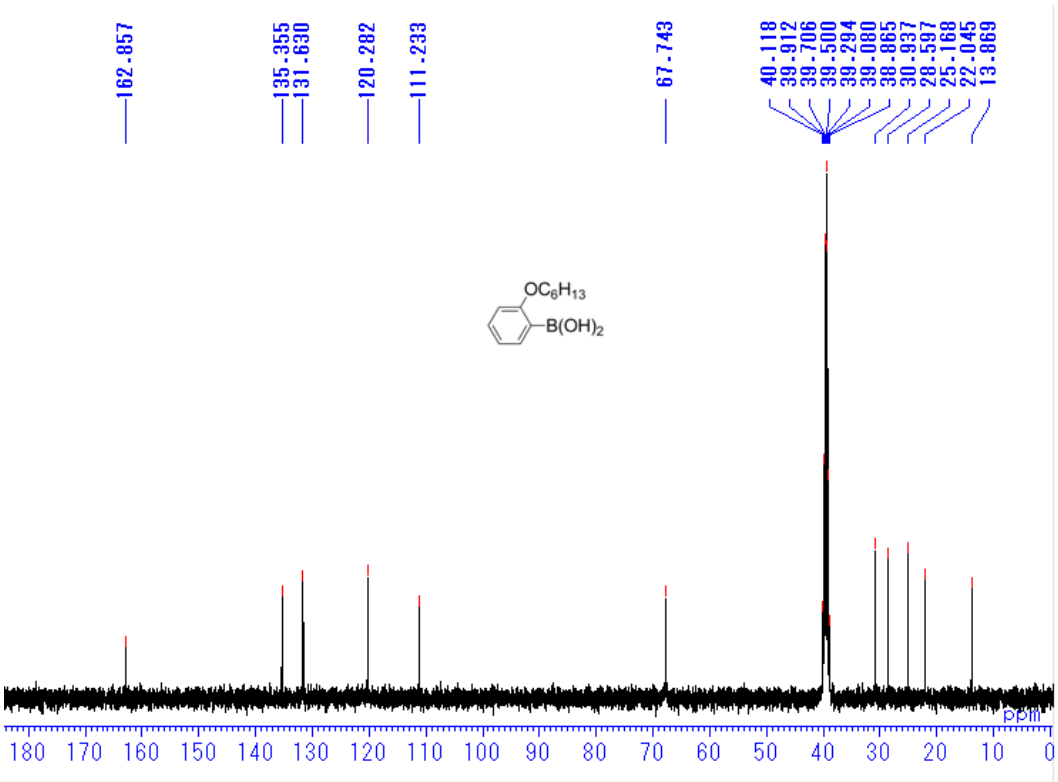


Figure S8. ^{13}C NMR spectrum of **S3**, 100 MHz, DMSO-d_6.

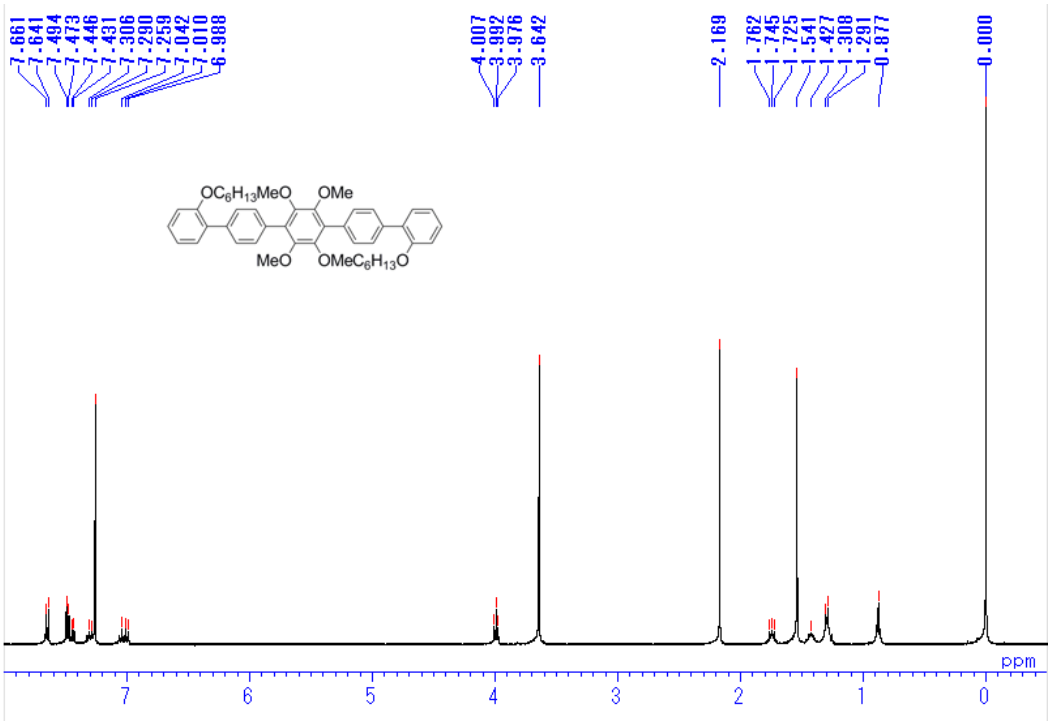


Figure S9. ^{1}H NMR spectrum of **M1**, 400 MHz, $CDCl_3$.

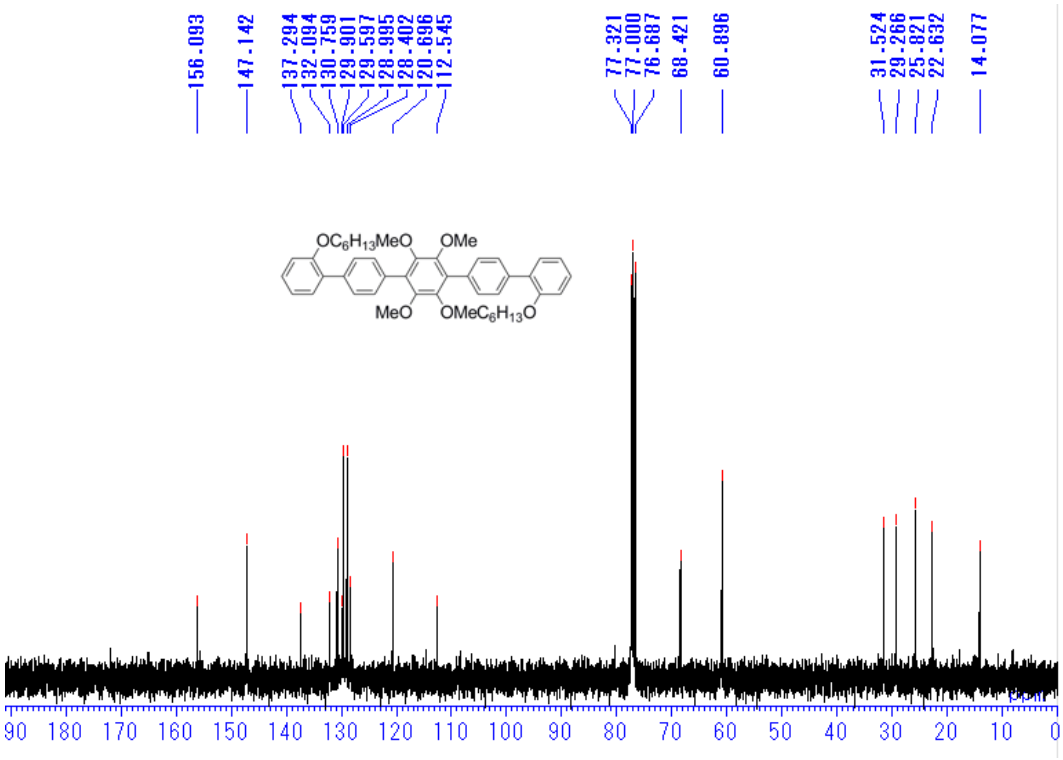


Figure S10. ^{13}C NMR spectrum of **M1**, 100 MHz, $CDCl_3$.

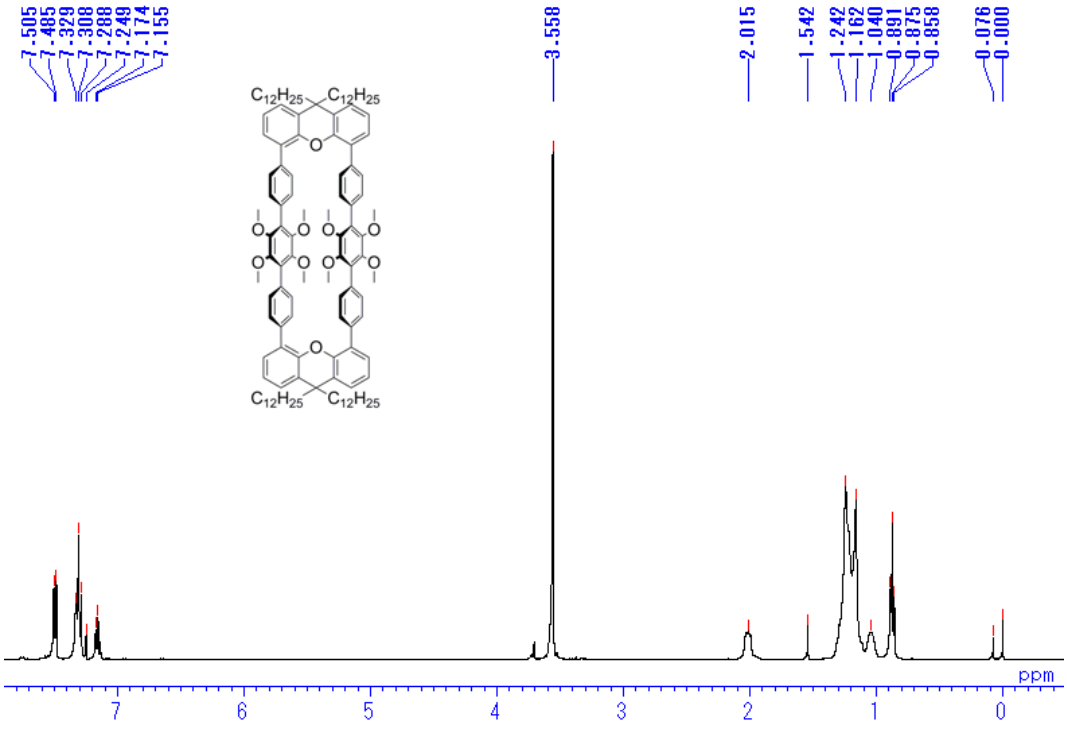


Figure S11. ^{1}H NMR spectrum of **D1**, 400 MHz, $CDCl_3$.

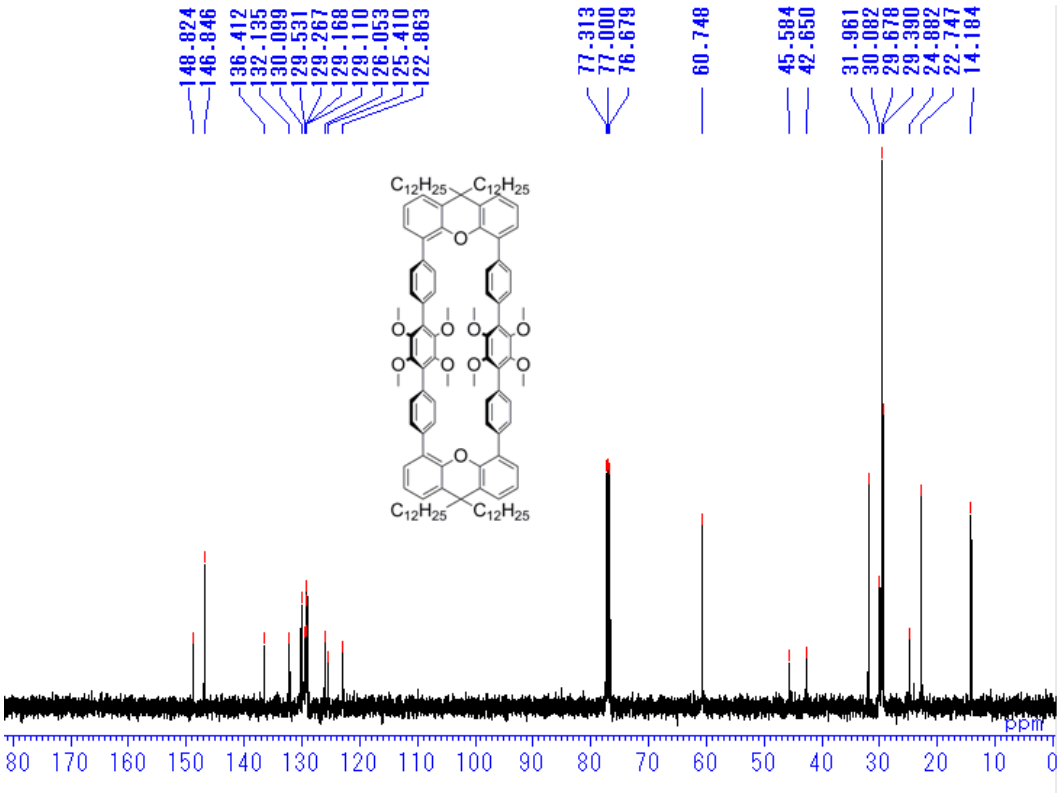


Figure S12. ^{13}C NMR spectrum of **D1**, 100 MHz, $CDCl_3$.

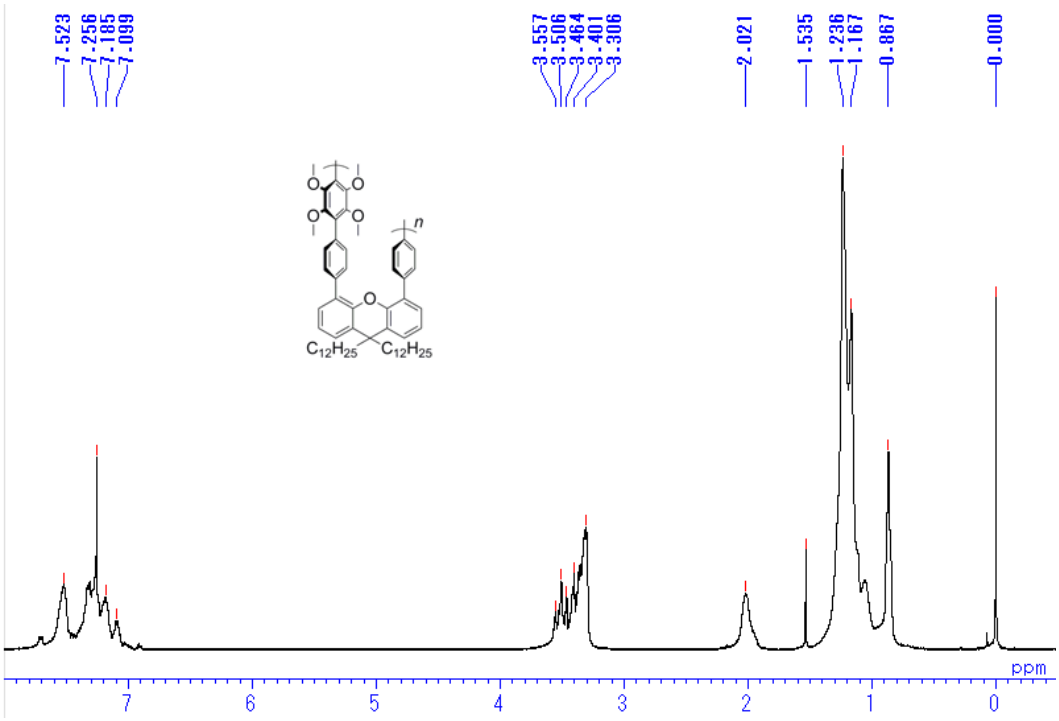


Figure S13. ^{1}H NMR spectrum of **P1**, 400 MHz, $CDCl_3$.

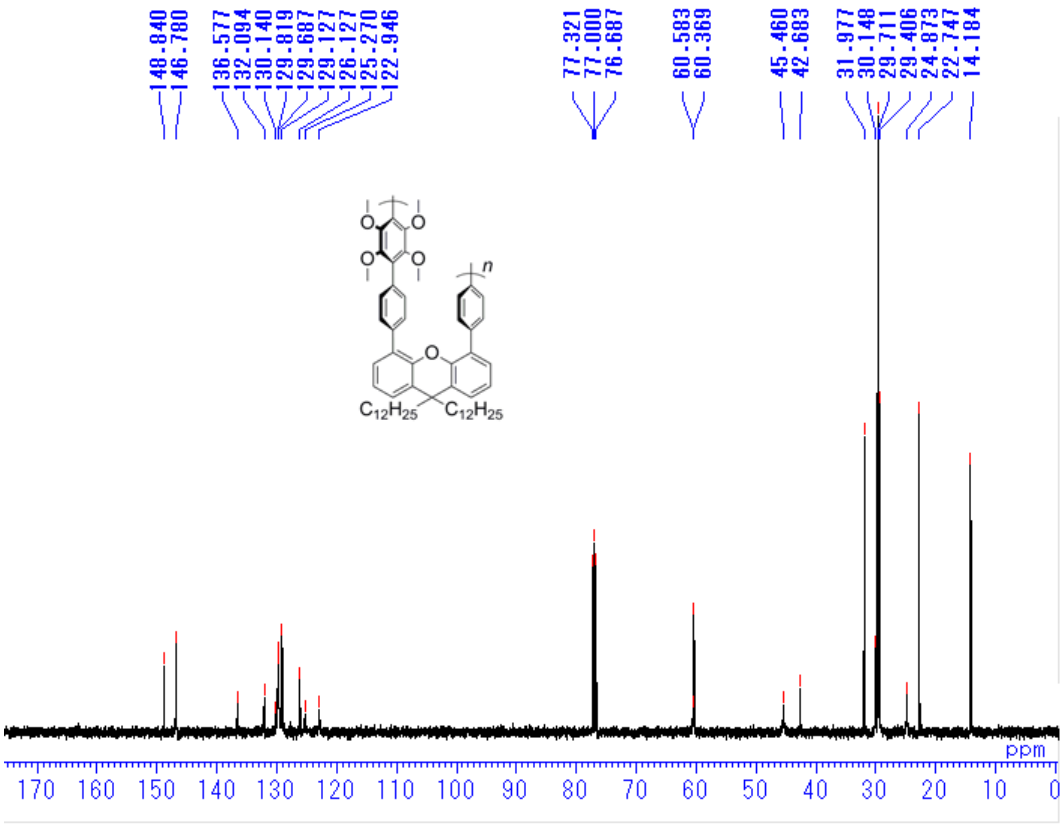


Figure S14. ^{13}C NMR spectrum of **P1**, 100 MHz, $CDCl_3$.

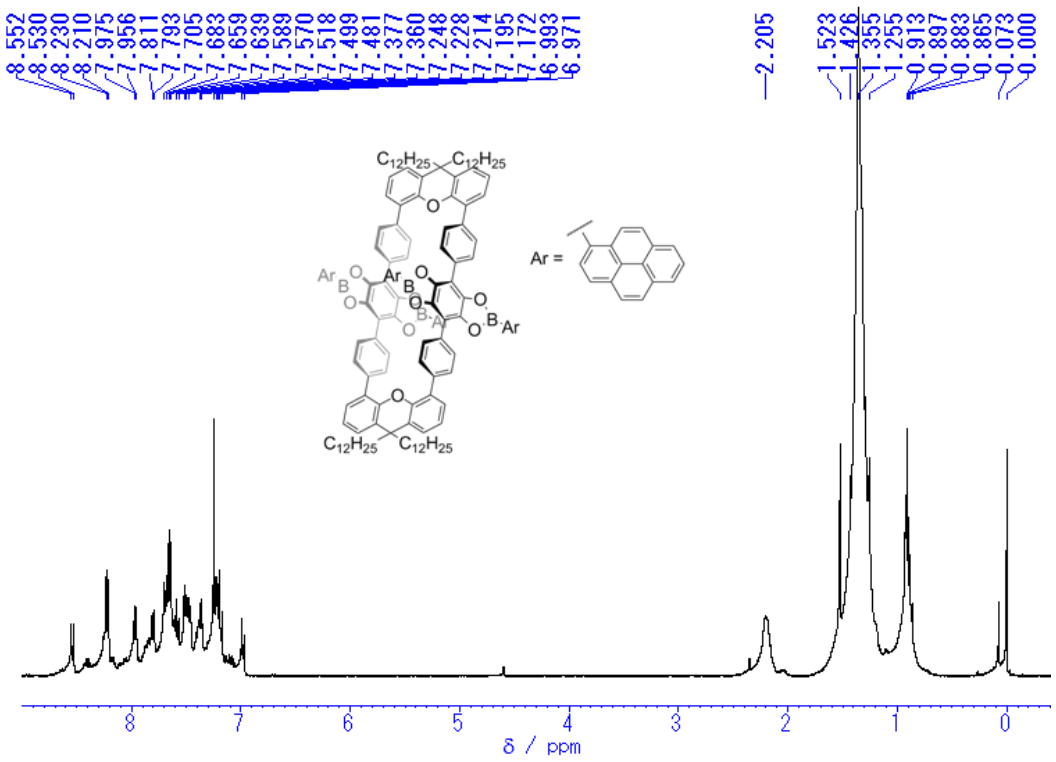


Figure S15. ^{1}H NMR spectrum of **D2d**, 400 MHz, $CDCl_3$.

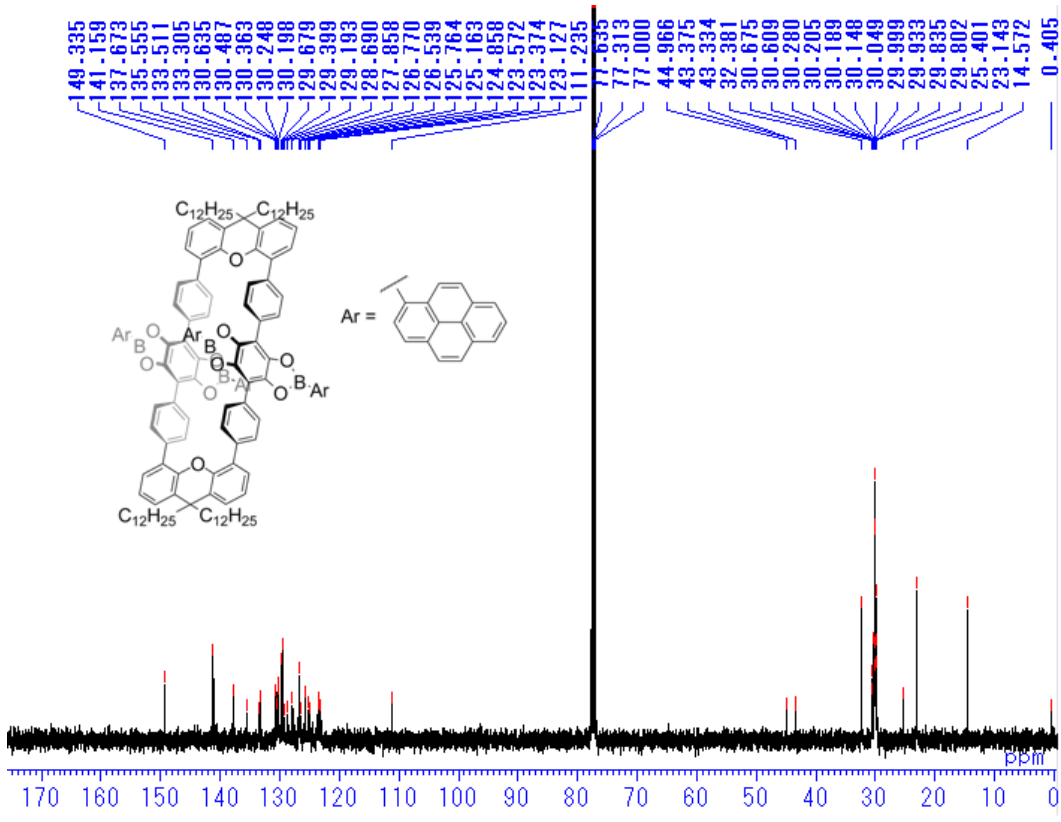


Figure S16. ^{13}C NMR spectrum of **D2d**, 100 MHz, $CDCl_3$.

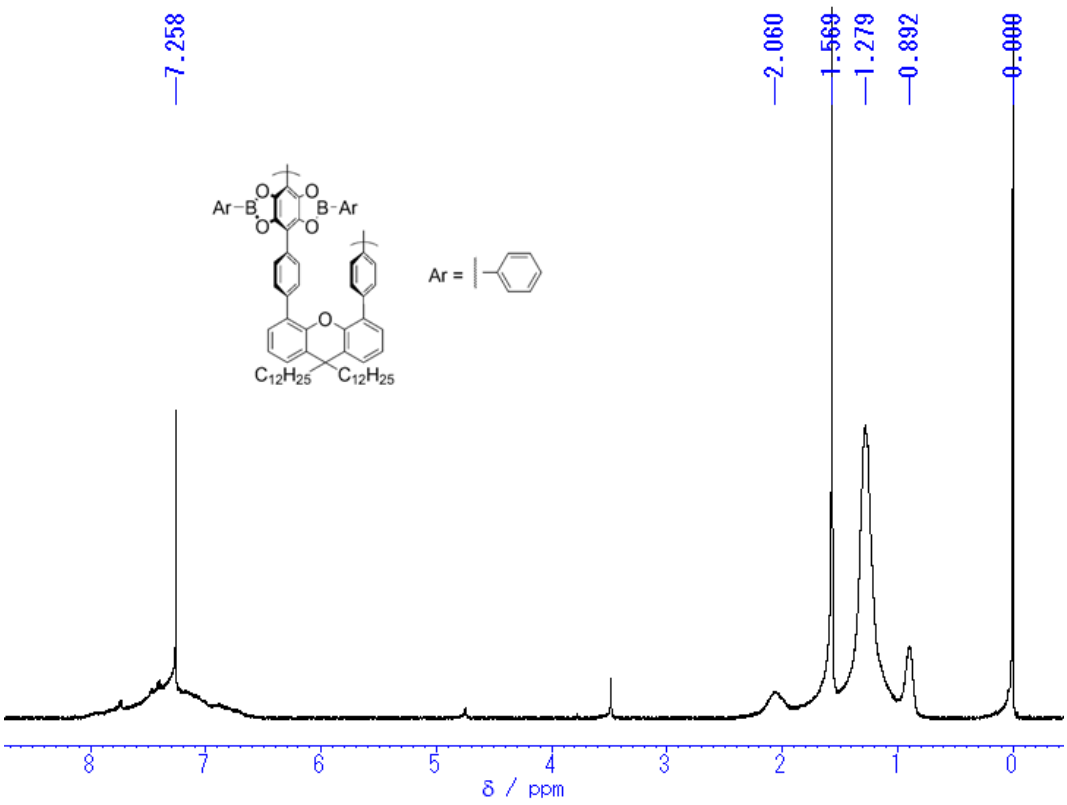


Figure S17. ^{1}H NMR spectrum of **P2a**, 400 MHz, $CDCl_3$.

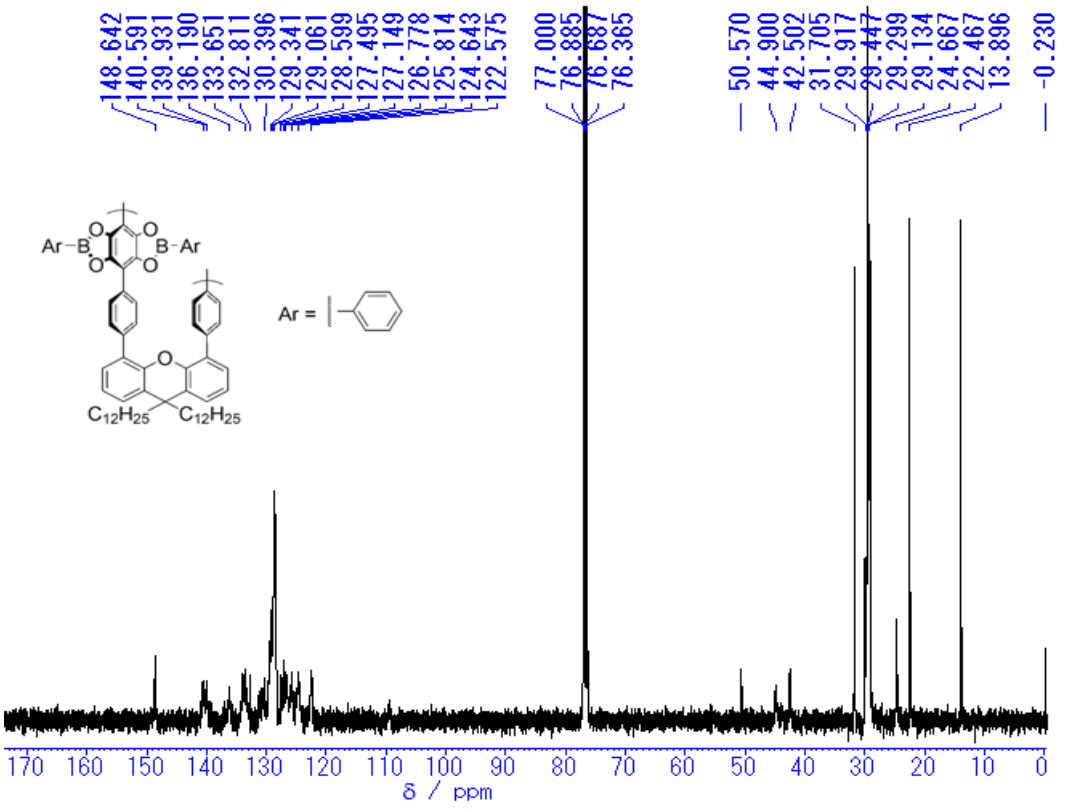


Figure S18. ^{13}C NMR spectrum of **P2a**, 100 MHz, $CDCl_3$.

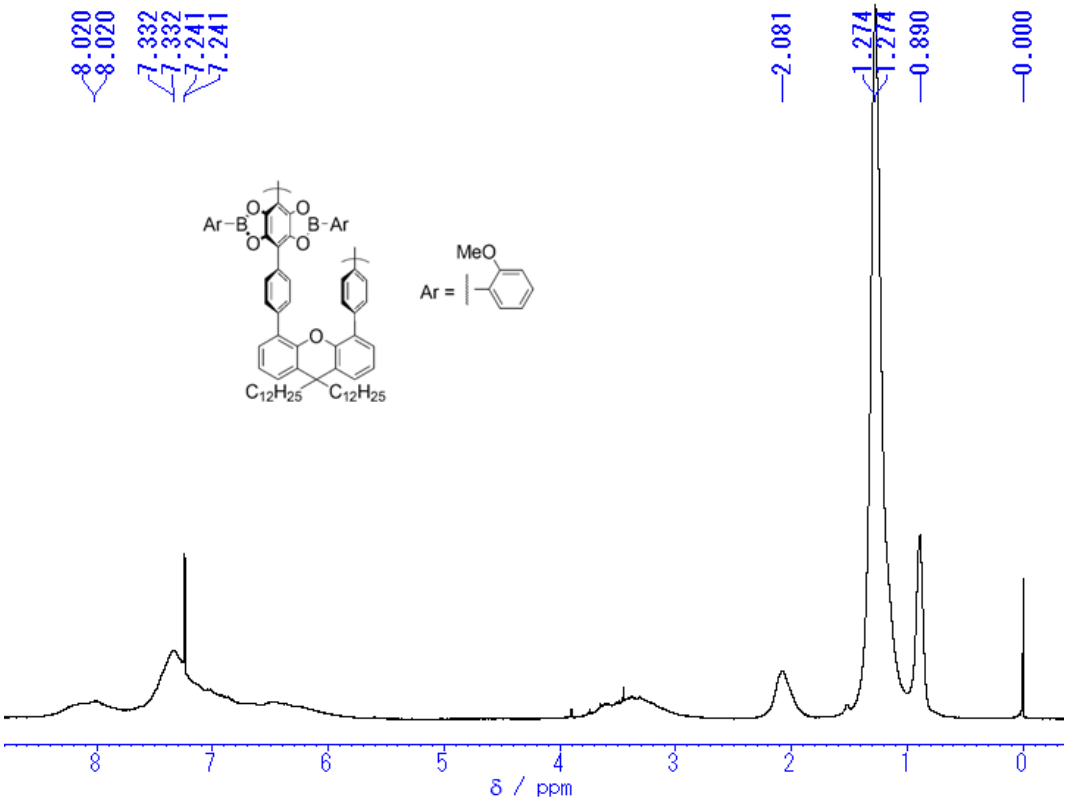


Figure S19. ^{1}H NMR spectrum of **P2b**, 400 MHz, $CDCl_3$.

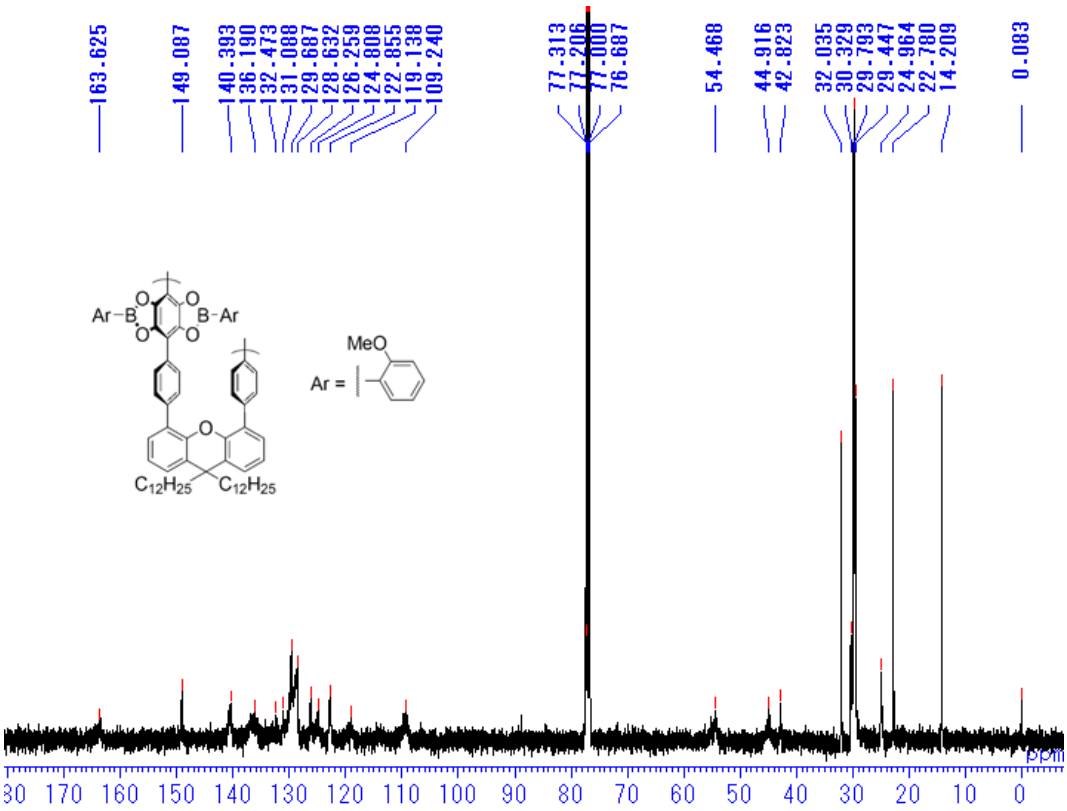


Figure S20. ^{13}C NMR spectrum of **P2b**, 100 MHz, $CDCl_3$.

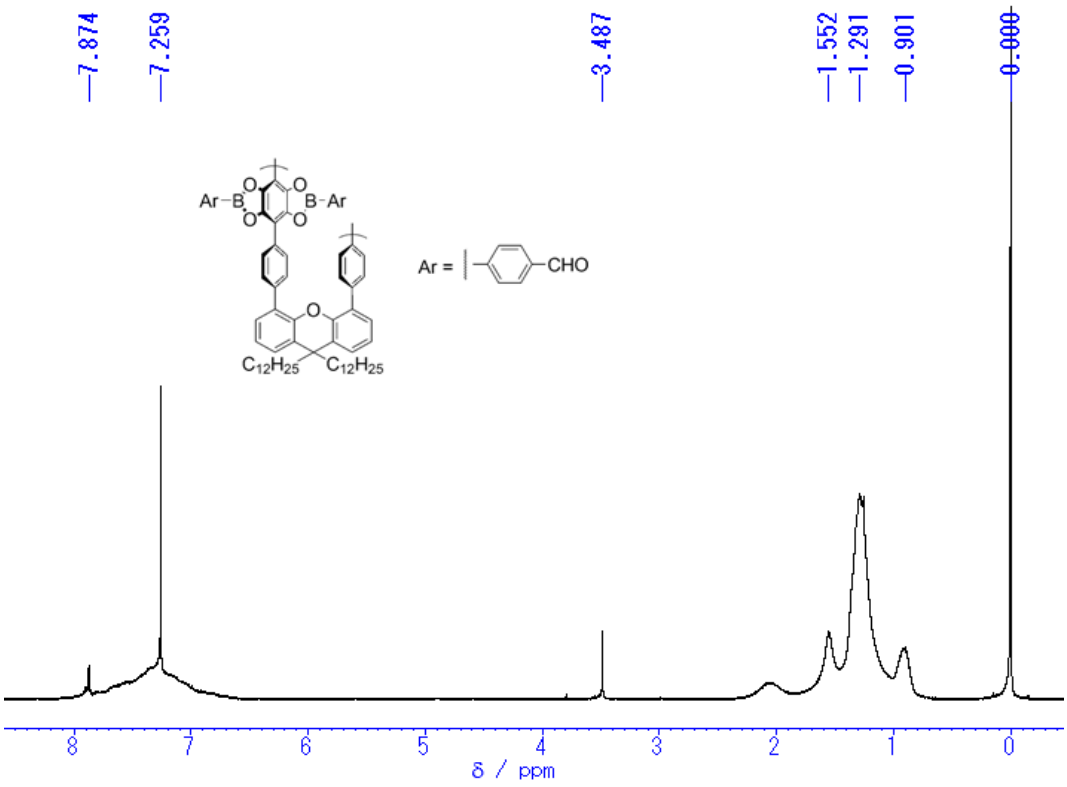


Figure S21. ^{1}H NMR spectrum of **P2c**, 400 MHz, $CDCl_3$.

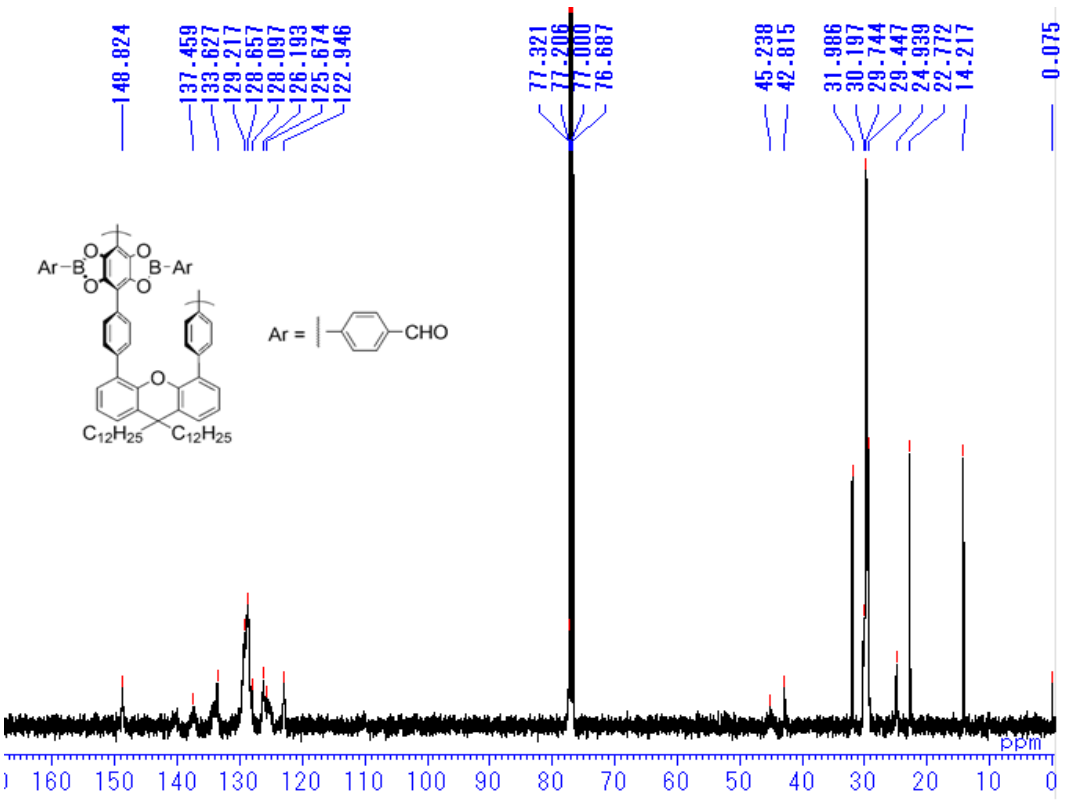


Figure S22. ^{13}C NMR spectrum of **P2c**, 100 MHz, $CDCl_3$.

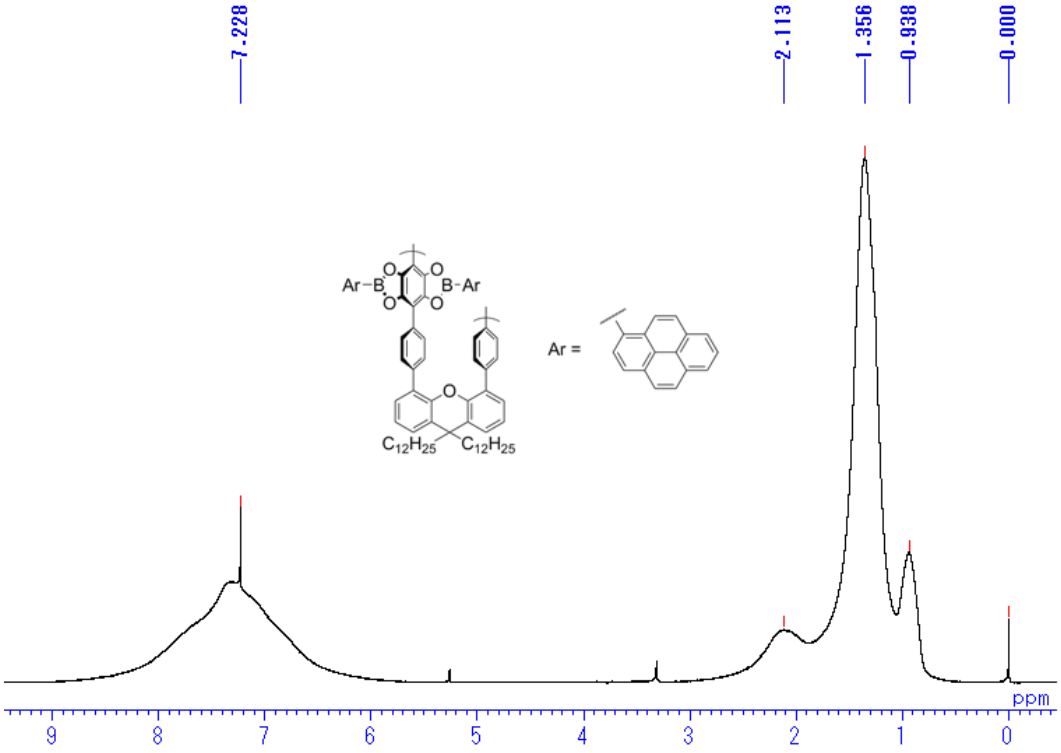


Figure S23. ^{1}H NMR spectrum of **P2d**, 400 MHz, $CDCl_3$.

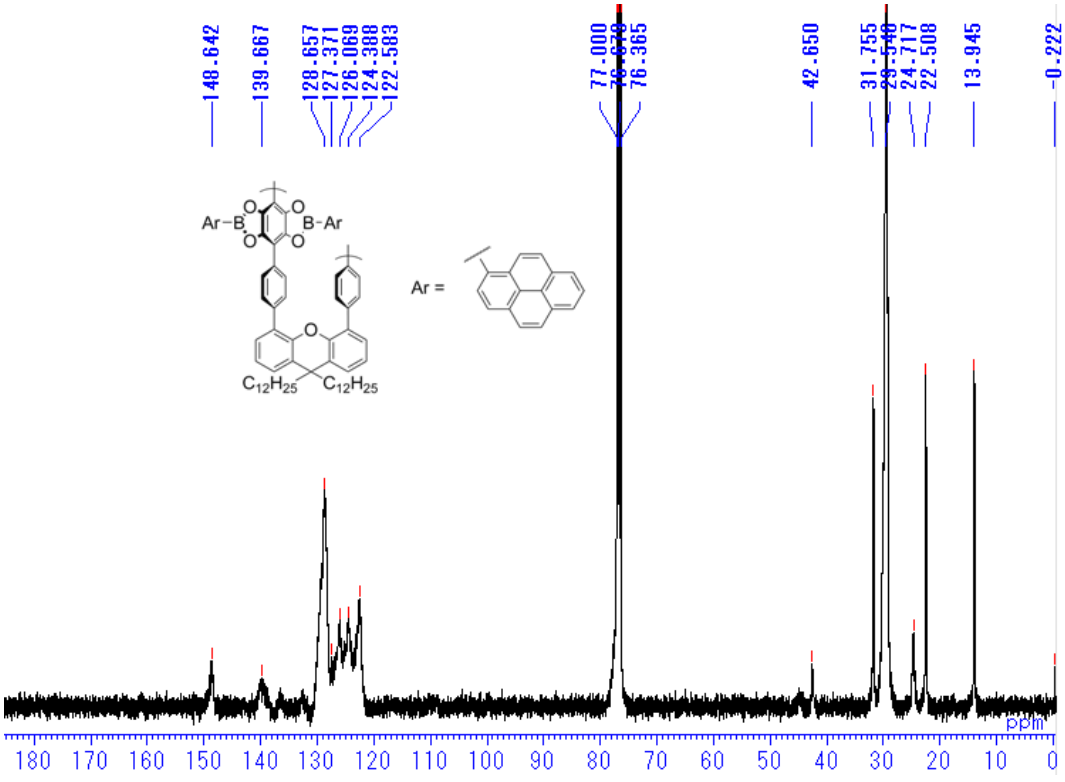


Figure S24. ^{13}C NMR spectrum of **P2d**, 100 MHz, $CDCl_3$.

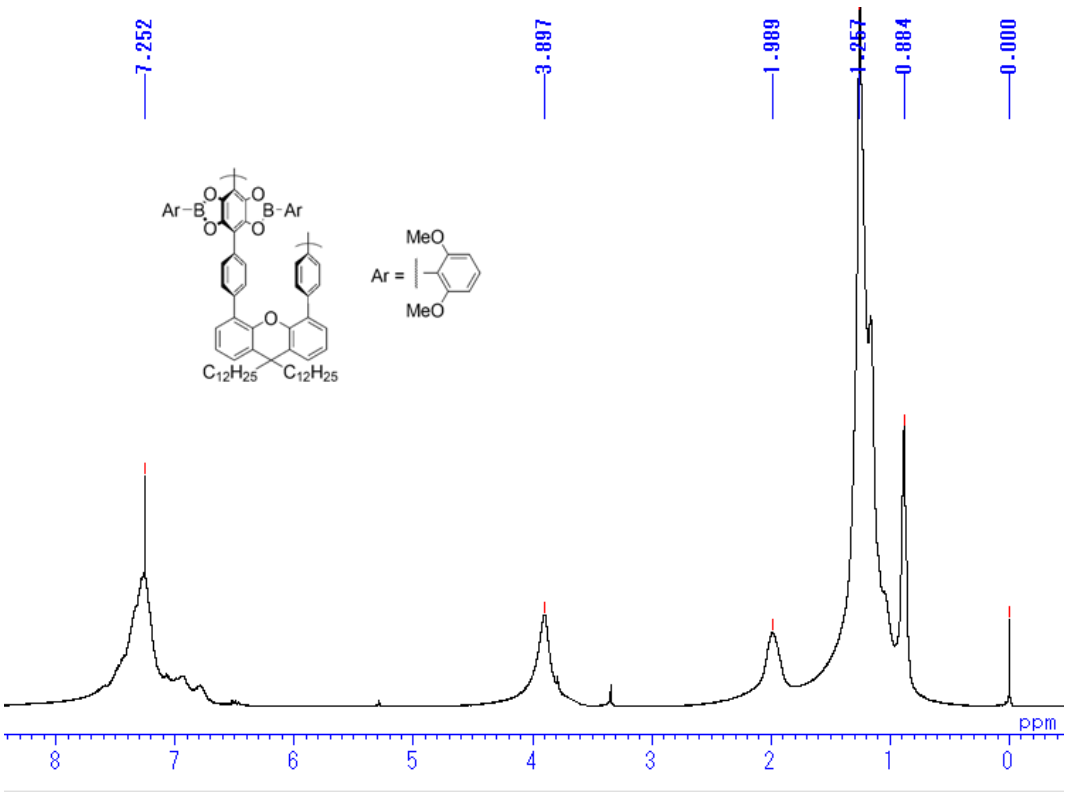


Figure S25. ^{1}H NMR spectrum of **P2e**, 400 MHz, $CDCl_3$.

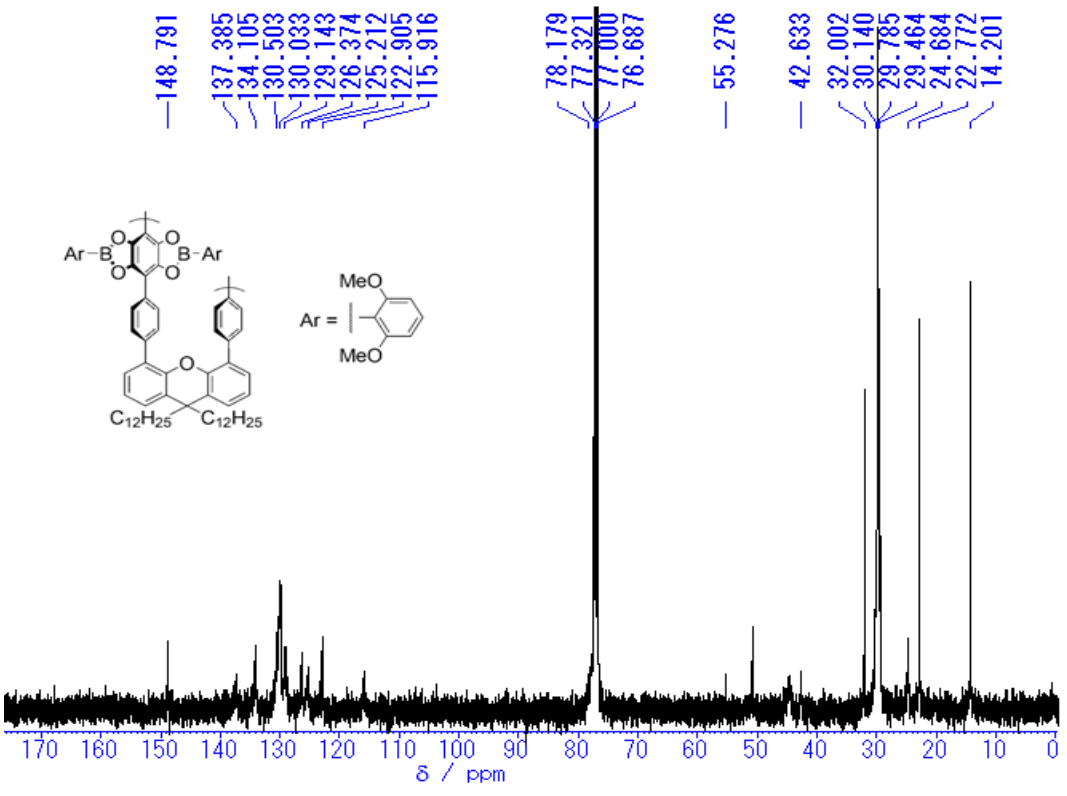


Figure S26. ^{13}C NMR spectrum of **P2e**, 100 MHz, $CDCl_3$.

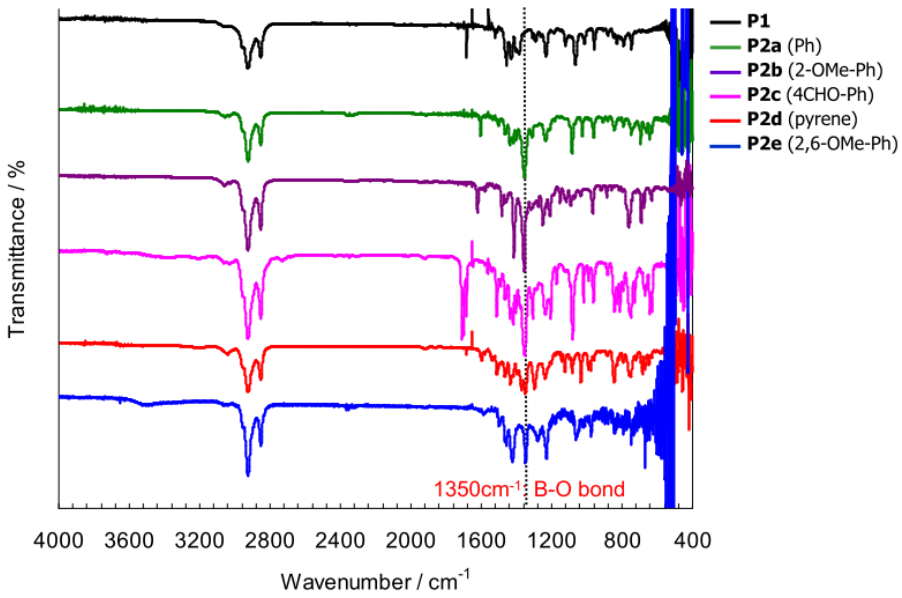


Figure S27. FT-IR spectra of polymers **P1** and **P2a-e** (film on KBr).

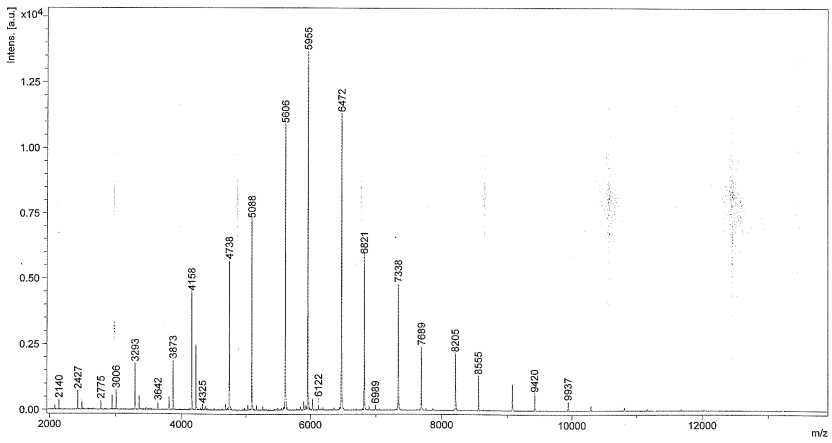


Figure S28. MALDI-TOF-Mass spectrum of **P1** using DCTB as a matrix.

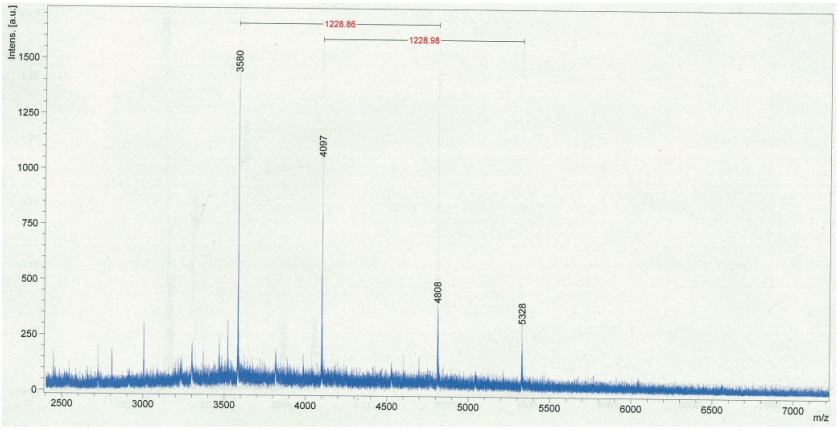


Figure S29. MALDI-TOF-Mass spectrum of **P2d** using DCTB as a matrix.

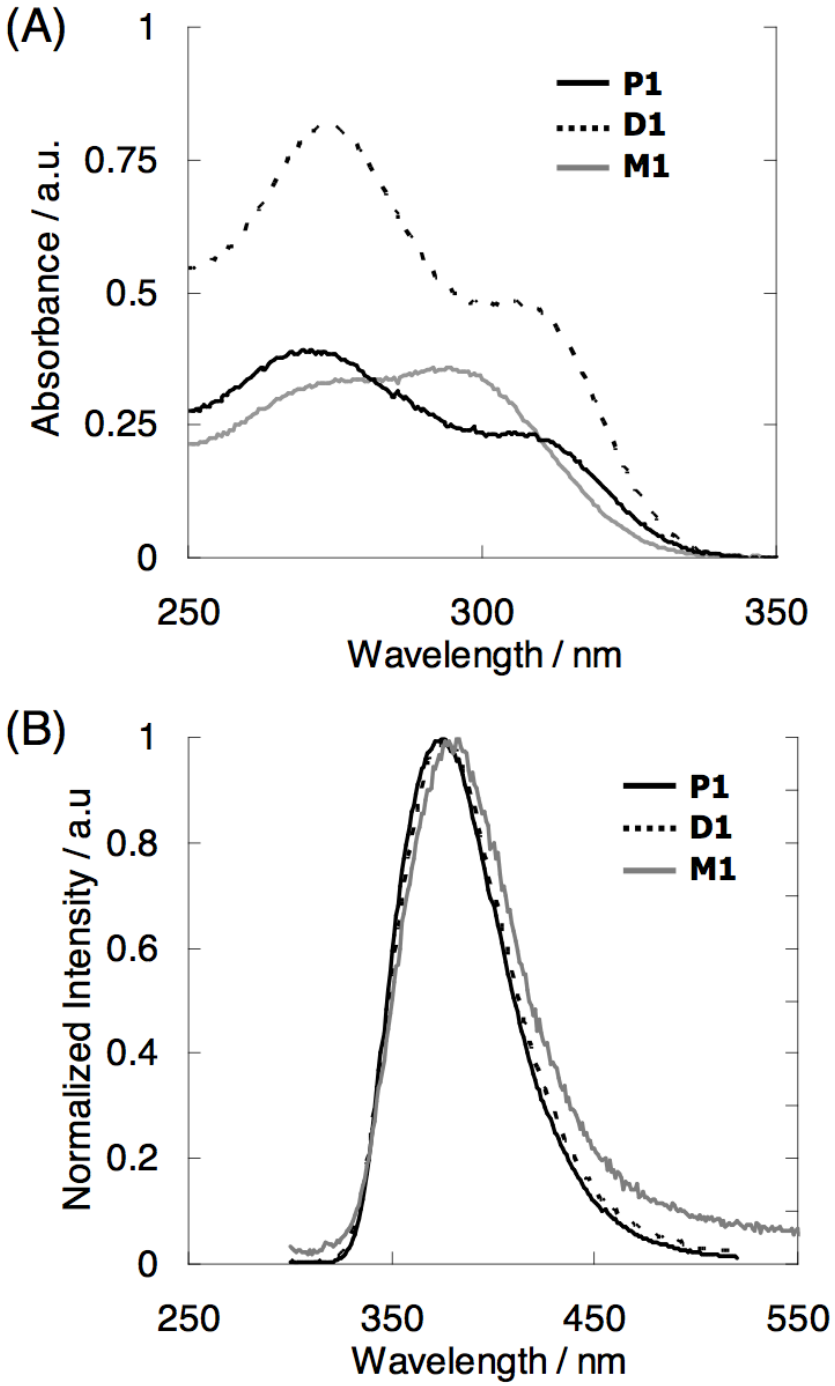


Figure S30. (A) UV-vis absorption spectra of **M1**, **D1,** and **P1** in $CHCl_3$ (1.0×10^{-5} M). (B) Fluorescence emission spectra of **M1**, **D1,** and **P1** in $CHCl_3$ (1.0×10^{-5} M), excited at each absorption maximum.

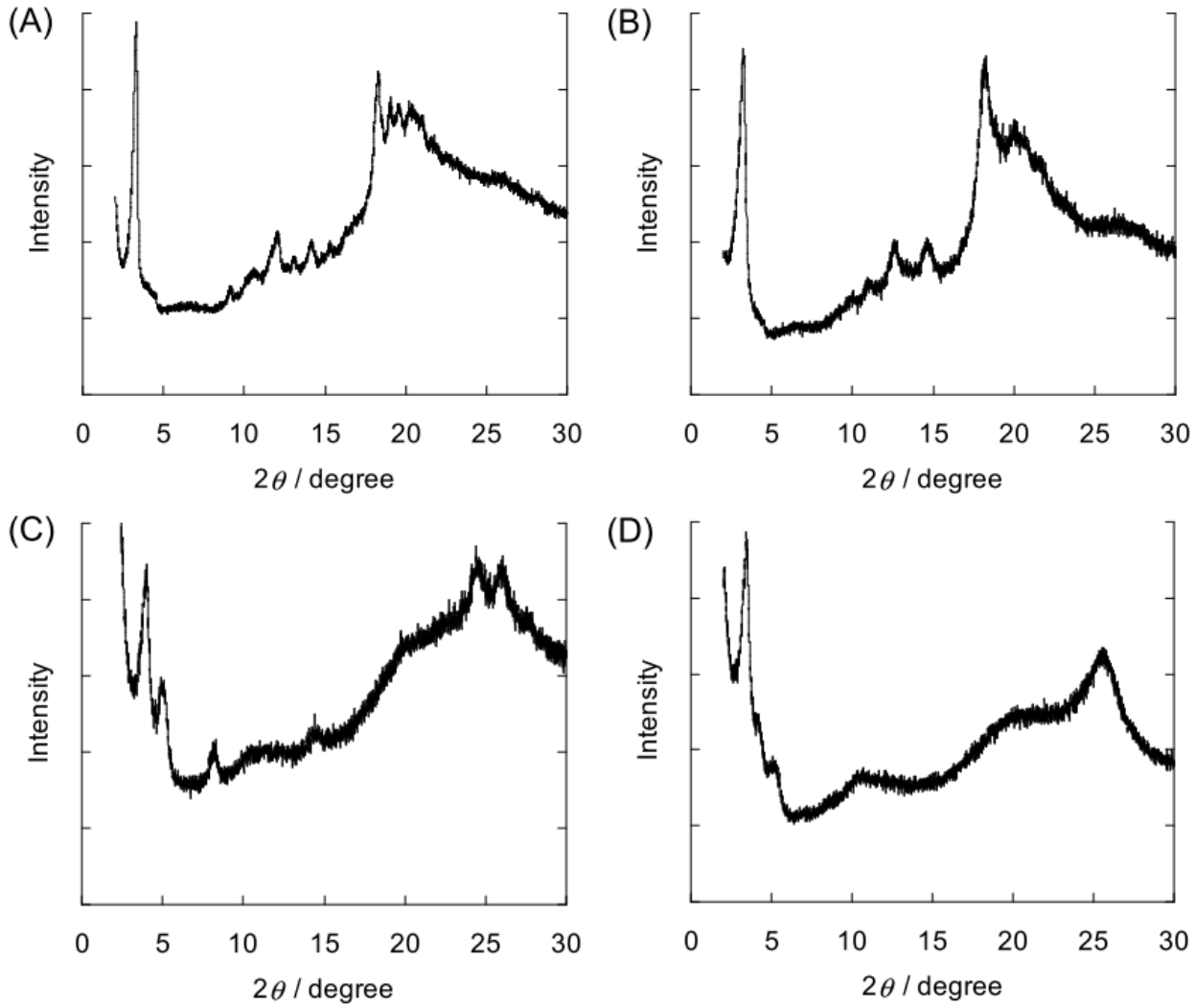


Figure S31. X-ray powder diffraction patterns of (A) **D1**, (B) **P1**, (C) **D2d**, and (D) **P2d**.

Table S1. Powder X-ray Diffraction results

Compounds	observed peaks / Å		
D1	26.67	9.64, 8.43, 7.34	6.72, 6.22, 4.84, 4.66, 4.54
P1	27.08	8.09, 7.03	6.05, 4.88, 4.43
D2d	22.02, 17.45, 10.79		6.15, 3.65, 3.42
P2d	25.59, 20.82, 16.79	8.47	3.49

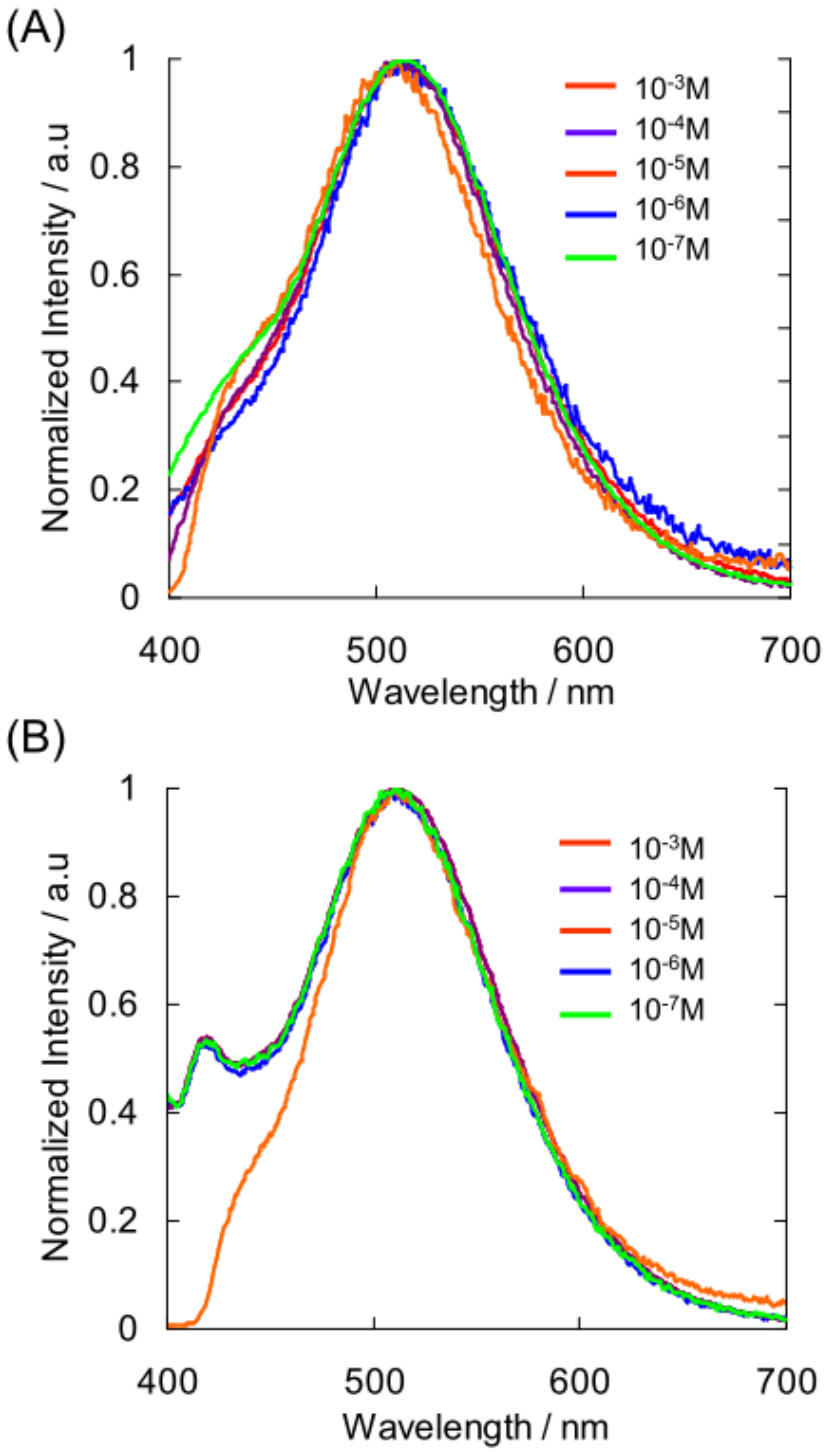


Figure S32. Normalized fluorescence emission spectra of (A) **P2d** and (B) **D2d** in $CHCl_3$ (1.0×10^{-3}, 1.0×10^{-4}, 1.0×10^{-5}, 1.0×10^{-6}, and 1.0×10^{-7} M), excited at each absorption maximum.

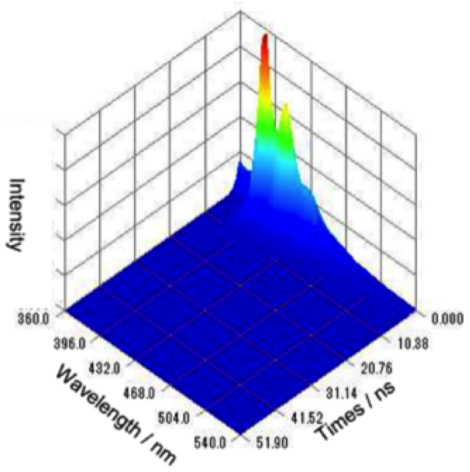


Figure S33. Time-resolved emission spectra of **M2d** in $CHCl_3$ (1.0×10^{-5} M).

(A) (B)

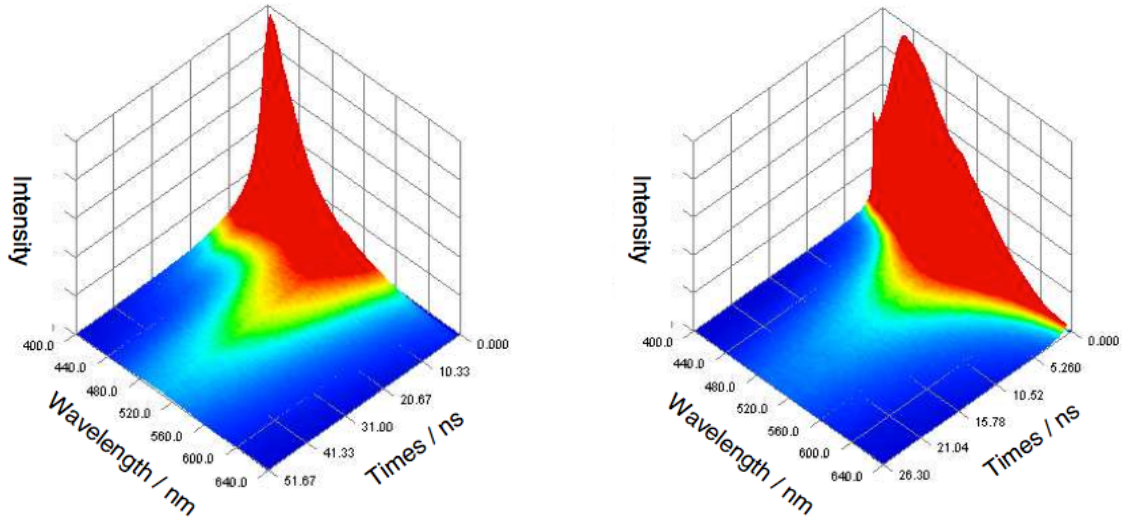


Figure S34. Time-resolved emission spectra of **D2d** (A) in $CHCl_3$ (1.0×10^{-5} M) and (B) the film.

(A) (B)

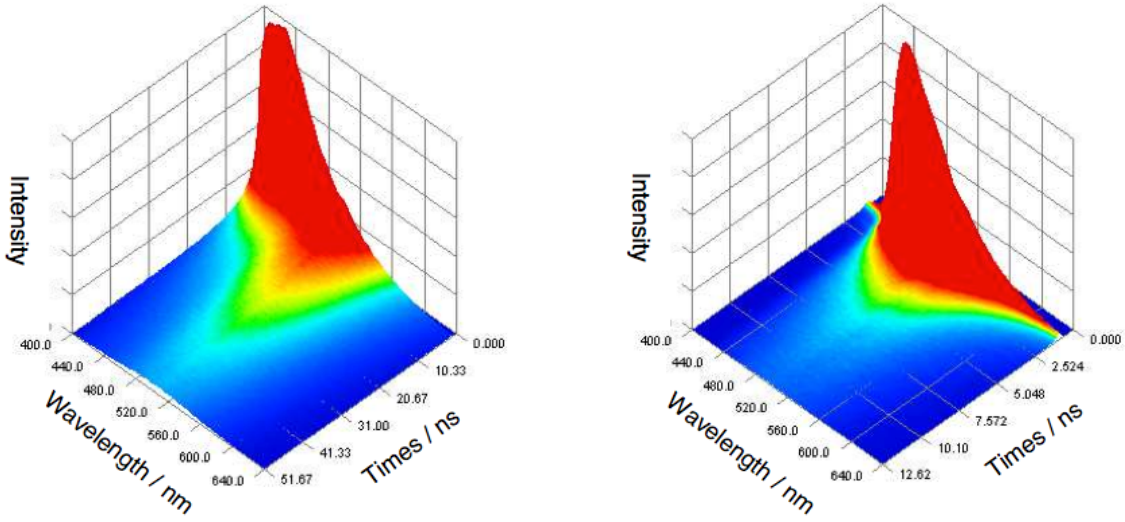


Figure S35. Time-resolved emission spectra of **P2d** (A) in $CHCl_3$ (1.0×10^{-5} M) and (B) the film.

Table S2. Results of fluorescence decay analysis

Compound (observed λ_{em})	τ / ns	χ^2
M2d (410 nm)	2.4	1.24
D2d (415 nm)	τ_1 = 1.9 (28.3%)	1.02
	τ_2 = 7.8 (71.7%)	
D2d (520 nm)	τ_1 = 6.9 (8.0%)	1.18
	τ_2 = 34.5 (92.0%)	
P2d (420 nm)	τ_1 = 1.5 (25.5%)	1.28
	τ_2 = 8.7 (74.5%)	
P2d (520 nm)	τ_1 = 8.1 (7.7%)	1.21
	τ_2 = 34.9 (92.3%)	
P2d film (520 nm)	τ_1 = 2.4 (21.0%)	1.10
	τ_2 = 12.2 (78.9%)	

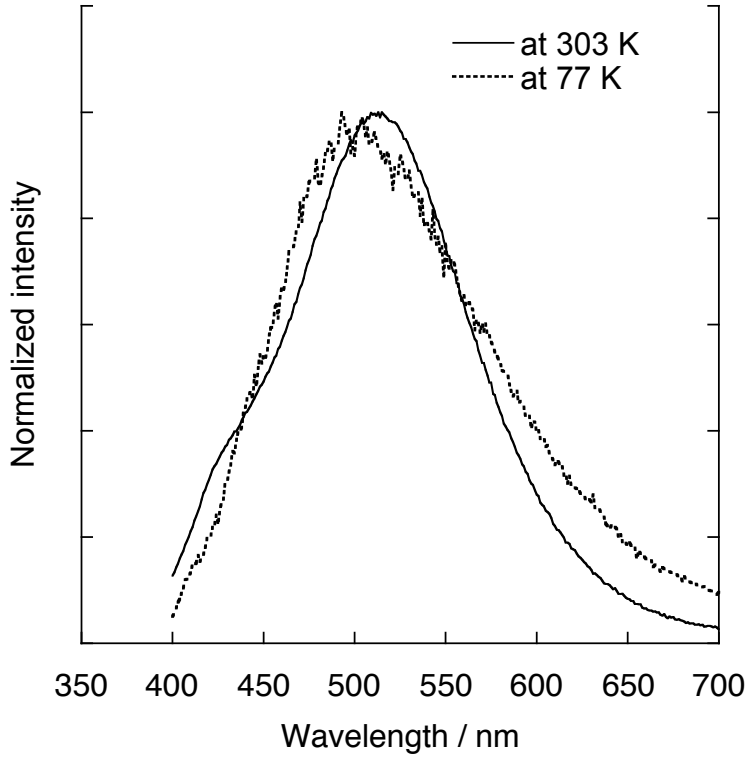


Figure S36. Fluorescence emission spectra of **P2d** in 2-methyltetrahydrofuran (1.0×10^{-5} M) at 303 K and 77 K.

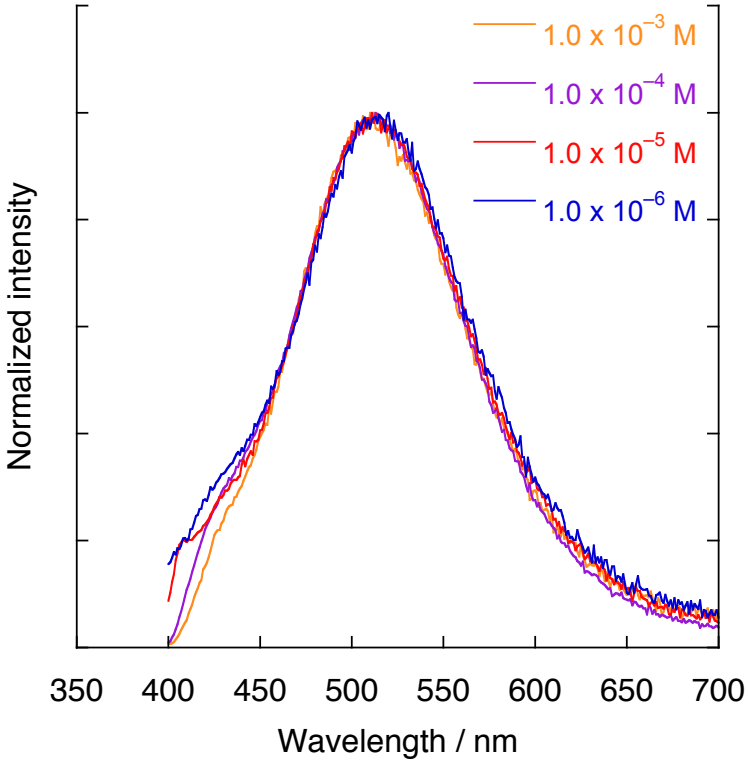


Figure S37. Normalized fluorescence emission spectra of **P2d** in 2-methyltetrahydrofuran (1.0×10^{-3}, 1.0×10^{-4}, 1.0×10^{-5}, and 1.0×10^{-6} M), excited at each absorption maximum.