Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Polyaromatic Molecular Tubes with a Subnanometer Pore and the Guest-Induced Emission Enhancement Behavior

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Contents

Materials and methods

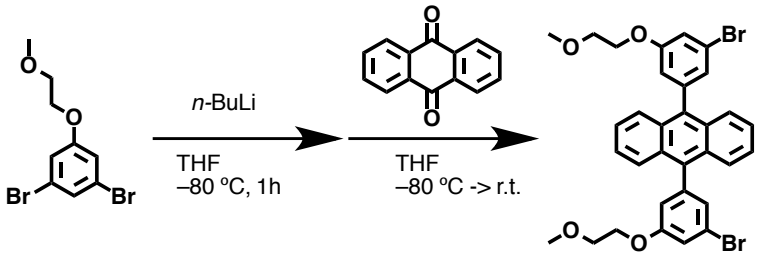
NMR: Bruker AVANCE III 400 (400 MHz) and AVANCE III HD 500 (500 MHz), MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, FT IR: JASCO FT/IR-4200, UV-vis: JASCO V-670DS, Fluorescence: Hitachi F-7000, Elemental analysis: LECO CHNS-932 VTF-900, Absolute PL quantum yield: Hamamatsu C9920-02G with an integration sphere, Recycled GPC: JAI LC-9225NEXT, DFT calculation: Spartan'10 (Wavefunction, Inc.).

Solvents and reagents: TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO CHEMICAL CO., INC., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. 2,3,6,7-Tetramethoxy-9,10-anthraquinone[1] was synthesized according to previously published procedures.

References:

[1] (a) Q. Mao, T.-Q. Nguyen, T. Someya, G. B. Blanchet, C. Nucholls, *J. Am. Chem. Soc.*, **2003**, *125*, 10284–10287; (b) Y. V. Shklyaev, Y. V. Nifontov, *Russ. Chem. Bull. Int. Ed.*, **2002**, *51*, 844–849.

Synthesis of 2a MO-90, (2, 10, 21, 53)



1,3-Dibromo-5-(methoxymethoxy)benzene (0.943 g, 3.04 mmol) and dry THF (50 mL) were added to a 2-necked 200 mL glass flask filled with N_2. A hexane solution (2.65 M) of *n*-butyllithium (1.0 mL, 2.7 mmol) was added dropwise to the flask at –80 ºC under N_2. After the mixture was stirred at –80 ºC for 1 h, a dry THF solution (25 mL) of 9,10-anthraquinone (0.211 g, 1.01 mmol) was added to the solution. The resultant mixture was further stirred at –80 ºC for 1 h and then warmed to r.t. for 12 h. After the obtained solution was concentrated under reduced pressure, acetic acid (20 mL), $NaH_2PO_2 \bullet H_2O$ (0.322 g, 3.04 mmol), and NaI (0.456 g, 3.04 mmol) were added to the solids. The mixture was stirred at 70 ºC for 12 h. The resultant solution was poured into water and then the products were extracted with CH_2Cl_2. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give **2a** as a white solid (0.601 g, 9.44 mmol, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 7.68 (dd, J = 3.5 Hz, 4H), 7.37 (dd, J = 3.3 Hz, 4H), 7.30 (t, J = 2 Hz, 2H), 7.22 (t, J = 1.5 Hz, 2H), 6.99-6.99 (m, 2H), 4.17 (t, J = 4.5 Hz, 4H), 3.77 (t, J = 4.5 Hz, 4H), 3.46 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, r.t.): δ 159.6 (C_q), 141.9 (C_q), 135.8 (C_q), 129.6 (C_q), 126.9 (CH), 126.8 (CH), 123.0 (C_q), 117.4 (CH), 116.6 (CH), 71.0 (CH_2), 67.9 (CH_3), 59.5 (CH_2). FT-IR (KBr, cm^{-1}): 3064, 2981, 2927, 2876, 2815, 2360, 2343, 1590, 1571, 1424, 1381, 1365, 1259, 1236, 1180, 1126, 1060, 1032, 934, 855, 777, 689, 669. MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{32}H_{28}Br_2O_4$ 636.38, Found 636.13 $[M]^+$. HR MS (ESI): *m/z* Calcd. for $C_{32}H_{28}O_4Br_2$ $[M + Na]^+$ 659.0229, Found 659.0230.

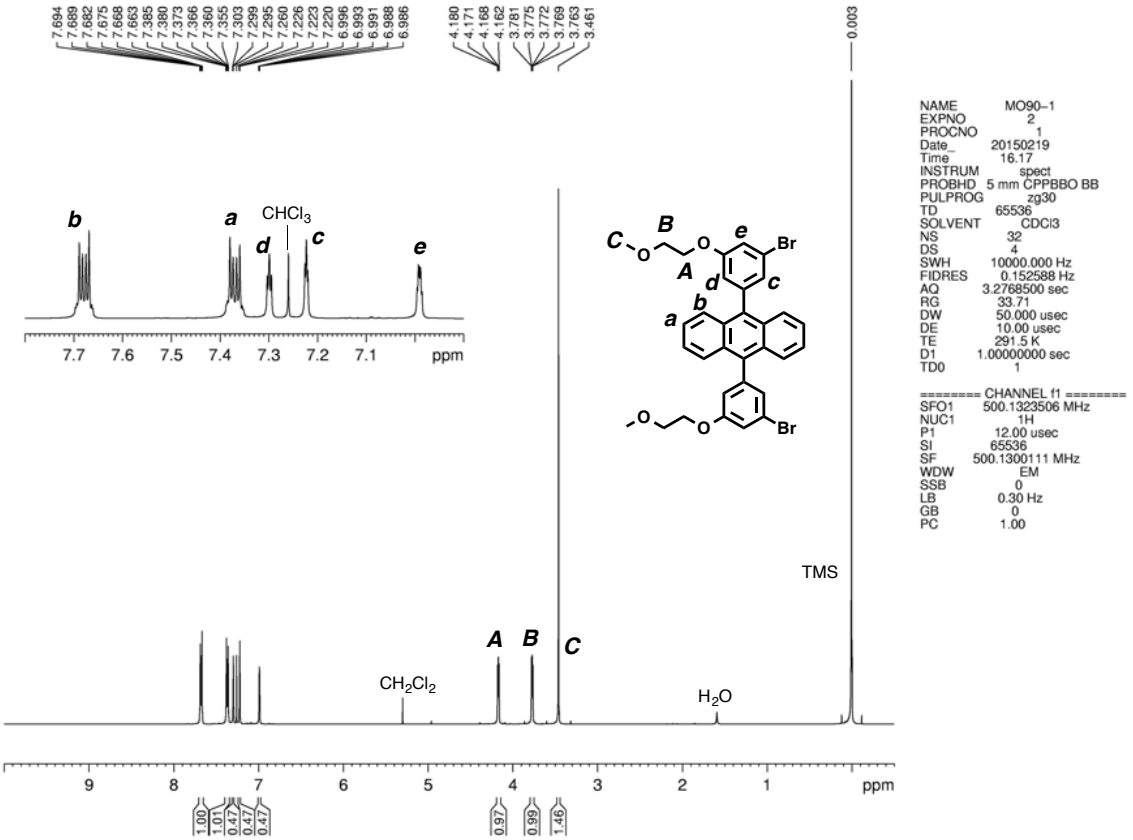


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **2a**.

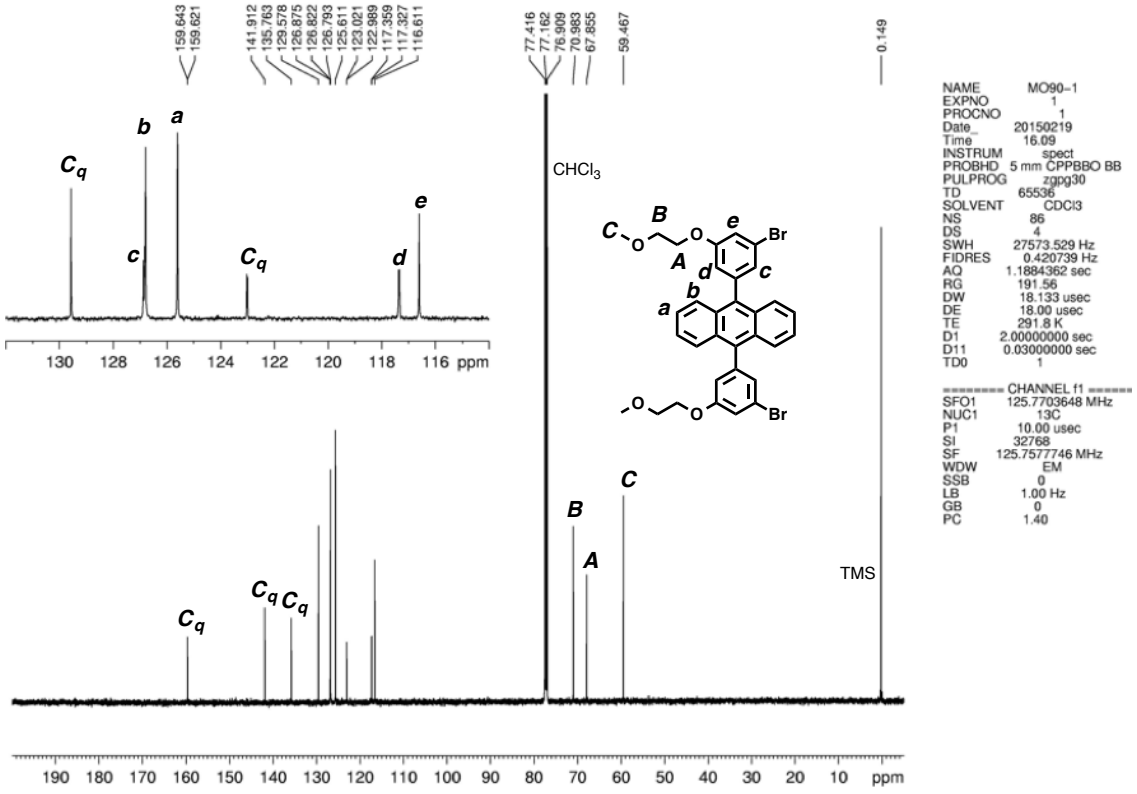


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, r.t.) of **2a**.

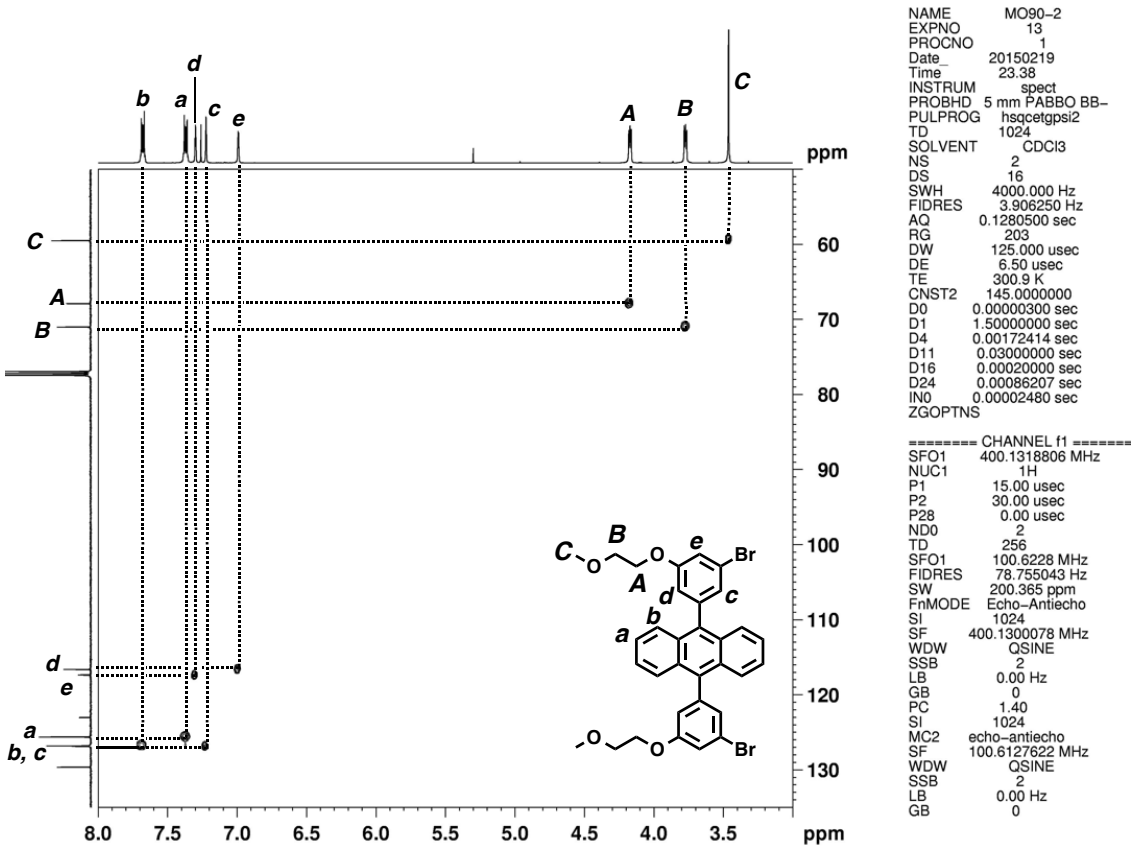


Figure S3. HSQC spectrum (400 MHz, $CDCl_3$, r.t.) of **2a**.

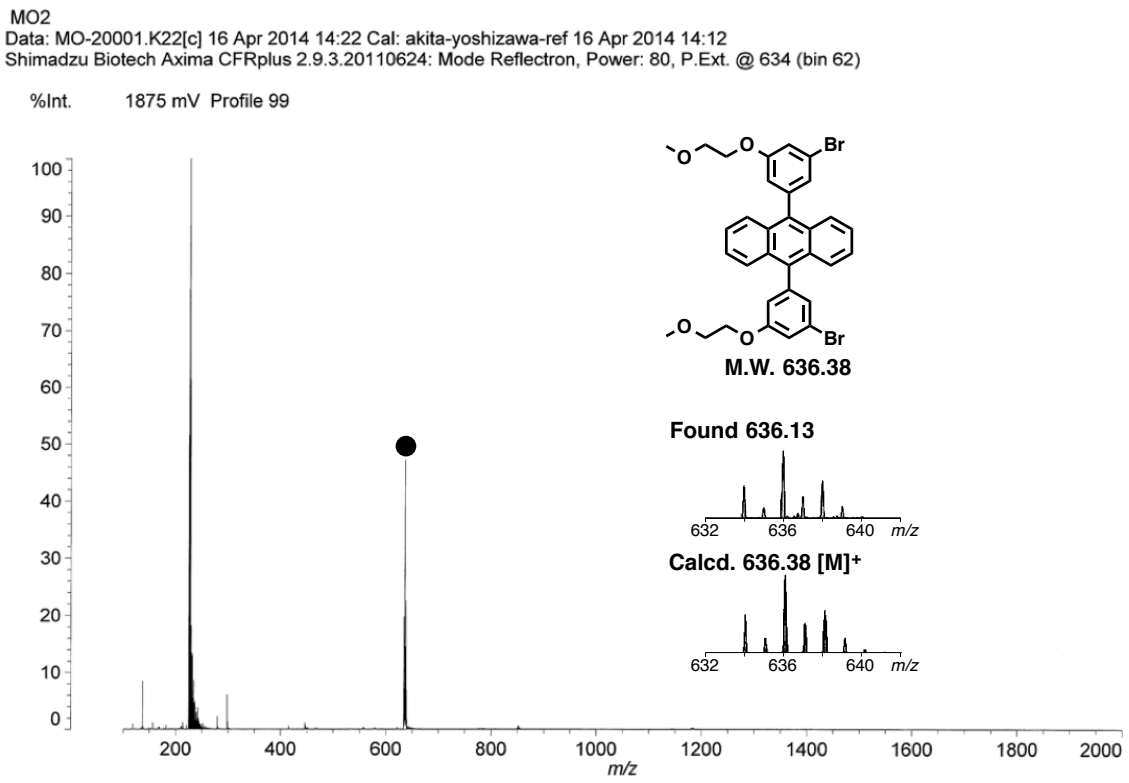
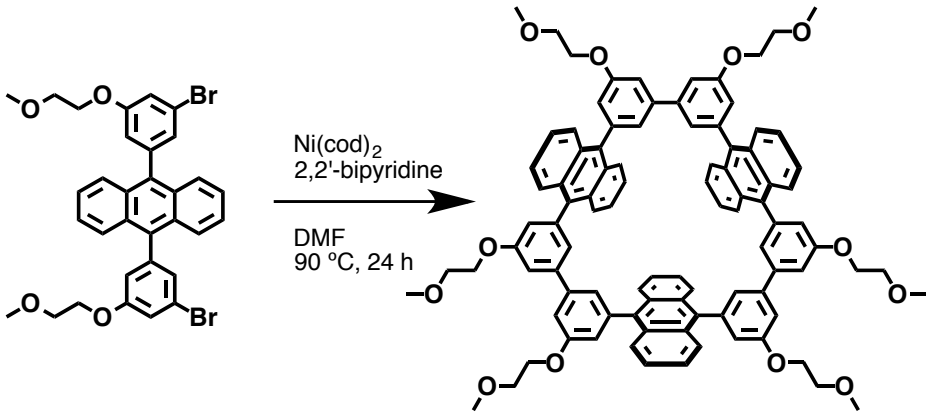


Figure S4. MALDI-TOF MS spectrum (dithranol) of **2a**.

Synthesis of molecular tube 1a MO-94, (60, 77)



Compound **2a** (0.448 g, 0.703 mmol), $Ni(cod)_2$ (0.287 g, 1.04 mmol), 2,2'-bipyridyl (0.179 g, 1.14 mmol), and dry DMF (300 mL) were added to a 2-necked 500 mL glass flask filled with N_2 and then the mixture was stirred at 90 ºC for 24 h. After the reaction was quenched with H_2O, the mixture was concentrated under reduced pressure. The obtained residue was extracted with CH_2Cl_2. The crude product was purified by silica-gel column chromatography ($CHCl_3$:acetone = 10:1) and GPC to give **1a** as a yellow solid (0.050 g, 0.035 mmol, 15% yield).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 7.64 (dd, J = 3.3 Hz, 4H), 7.61 (s, 2H), 7.21 (dd, J = 3.3 Hz, 4H), 7.17 (s, 2H), 7.05 (s, 2H), 4.28 (t, J = 4.5 Hz, 4H), 3.85 (t, J = 4.5 Hz, 4H), 3.52 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, r.t.): δ 159.4 (C_q), 140.9 (C_q), 140.6 (C_q), 136.5 (C_q), 129.5 (C_q), 126.9(CH), 125.1 (CH), 122.5 (CH), 116.5 (CH), 112.0 (CH), 71.3 (CH_2), 67.7 (CH_2), 59.5 (CH_3). FT-IR (KBr, cm^{-1}): 3061, 2923, 2874, 2359, 2341, 1585, 1390, 1365, 1327, 1236, 1126, 1067, 1032, 1029, 845, 768. MALDI-TOF MS (dithranol): m/z Calcd. for $C_{96}H_{84}O_{12}$ 1428.60, Found 1429.25 $[M]^+$. HR MS (ESI): m/z Calcd. for $C_{96}H_{84}O_{12}$ $[M + Na]^+$ 1452.5889, Found 1452.5890.

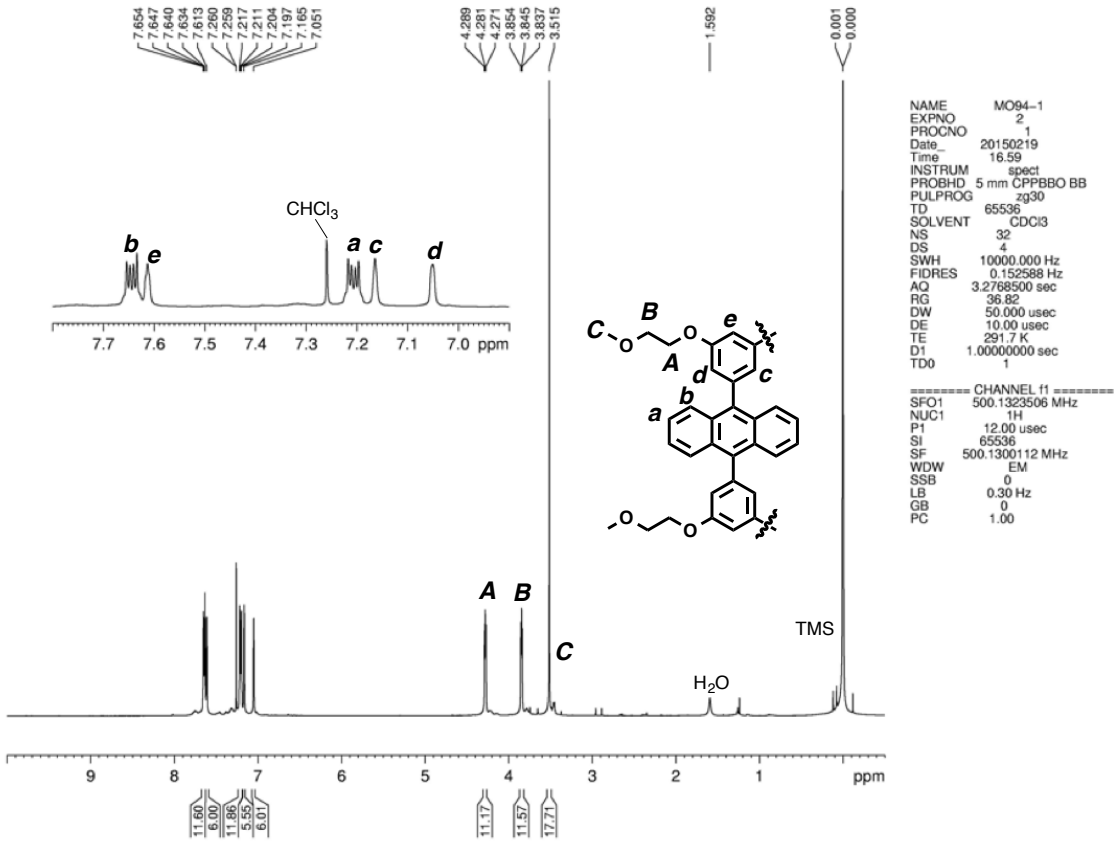


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **1a**.

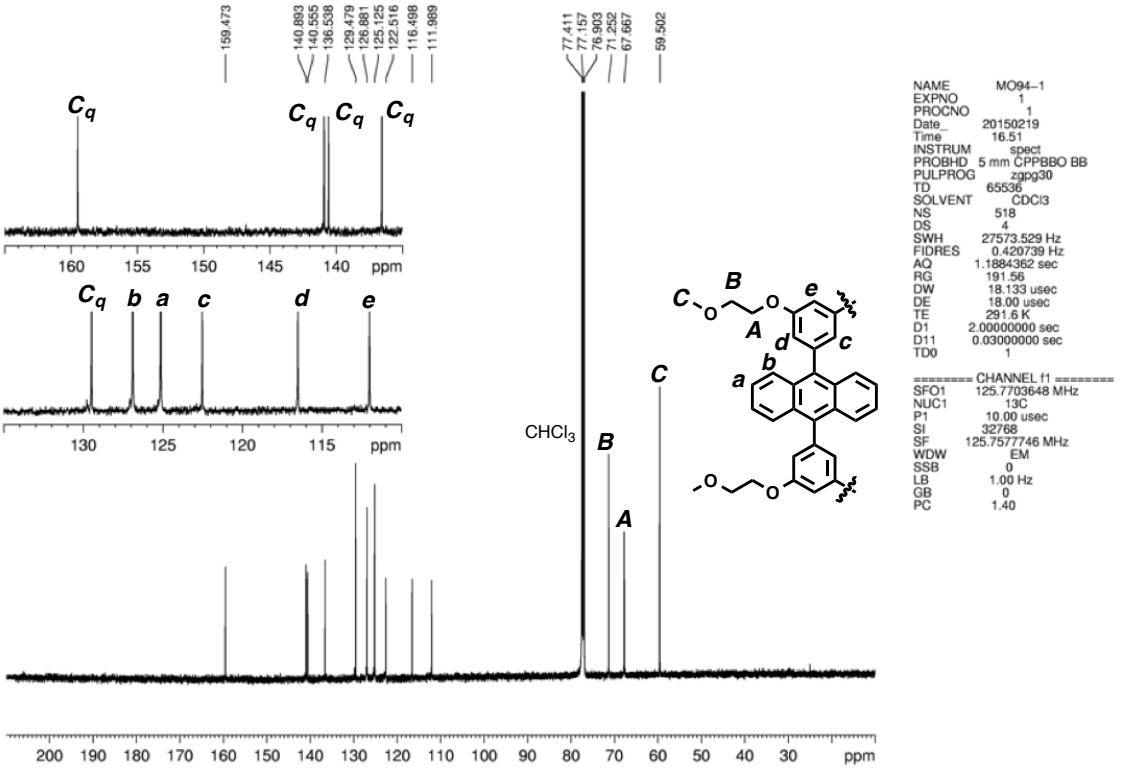


Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, r.t.) of **1a**.

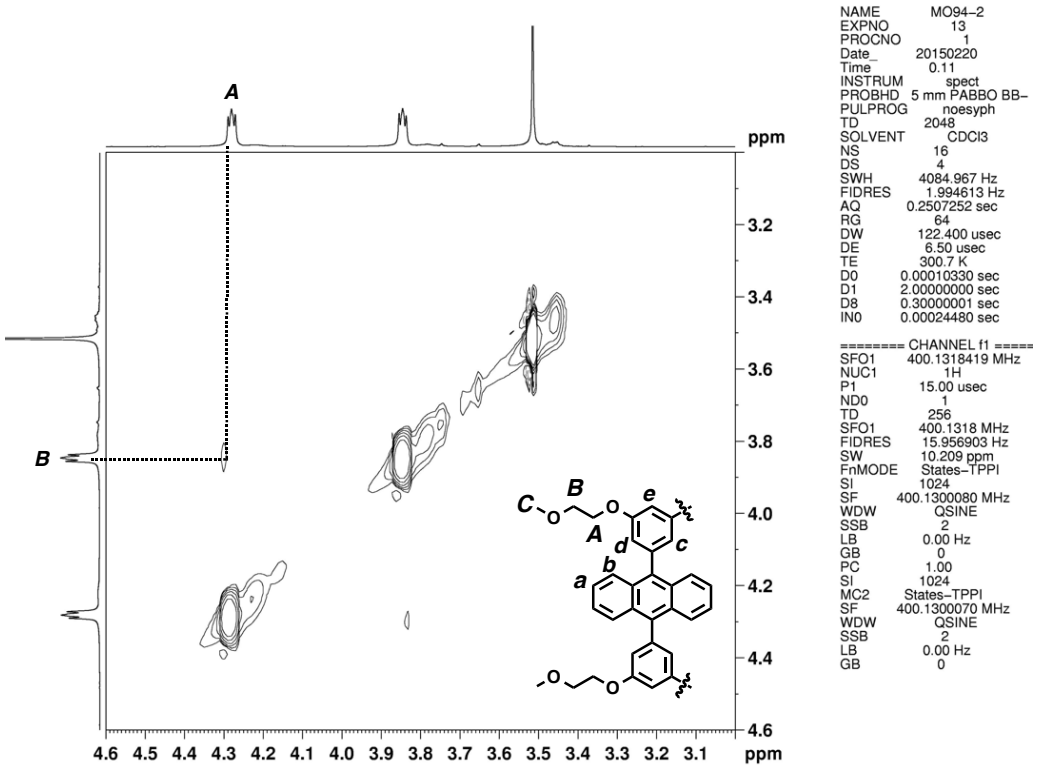


Figure S7a. NOESY spectrum (400 MHz, $CDCl_3$, r.t.) of **1a** (aliphatic region).

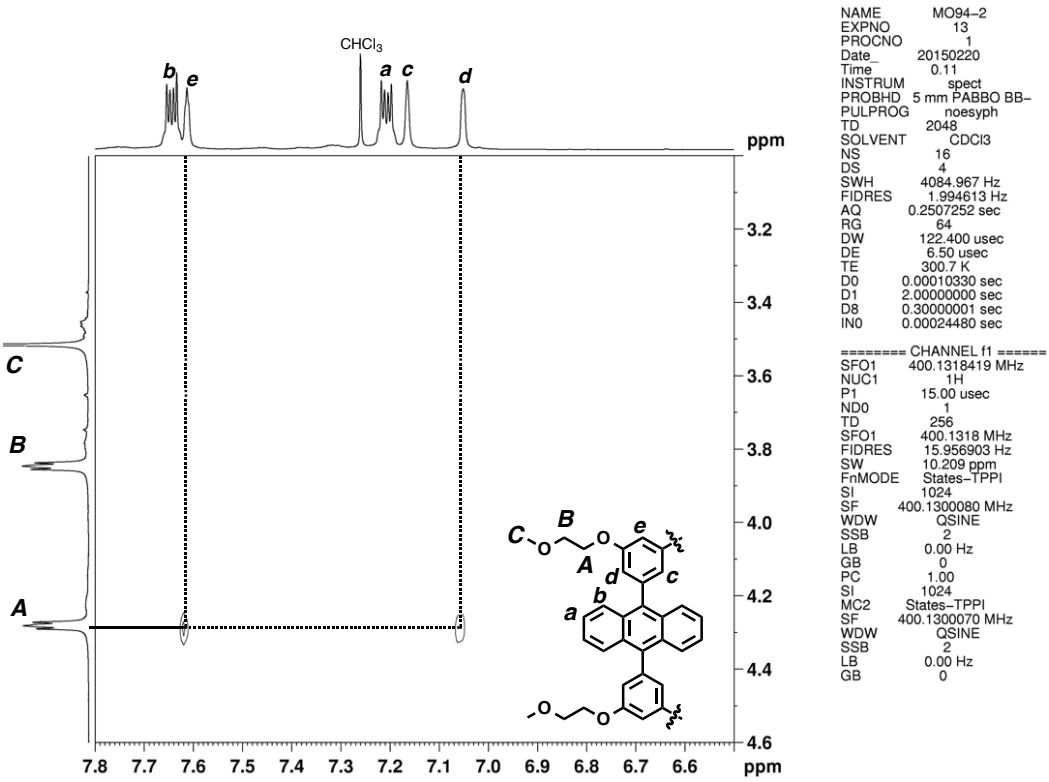


Figure S7b. NOESY spectrum (400 MHz, $CDCl_3$, r.t.) of **1a**.

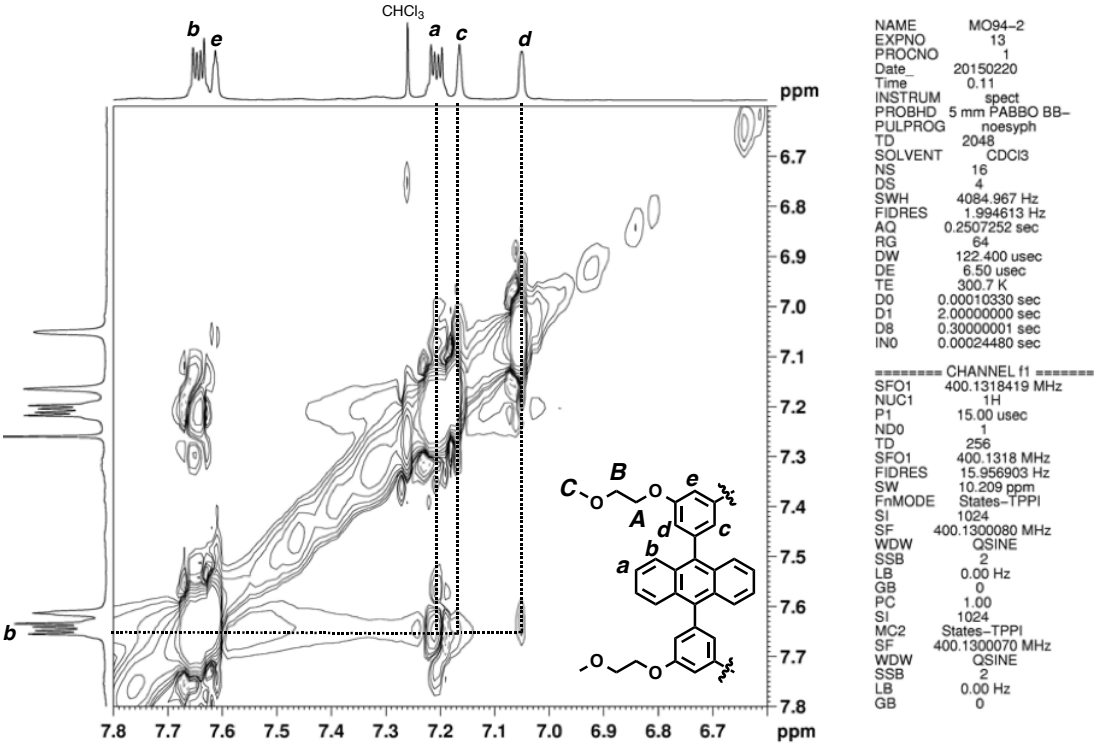


Figure S7c. NOESY spectrum (400 MHz, $CDCl_3$, r.t.) of **1a** (aromatic region).

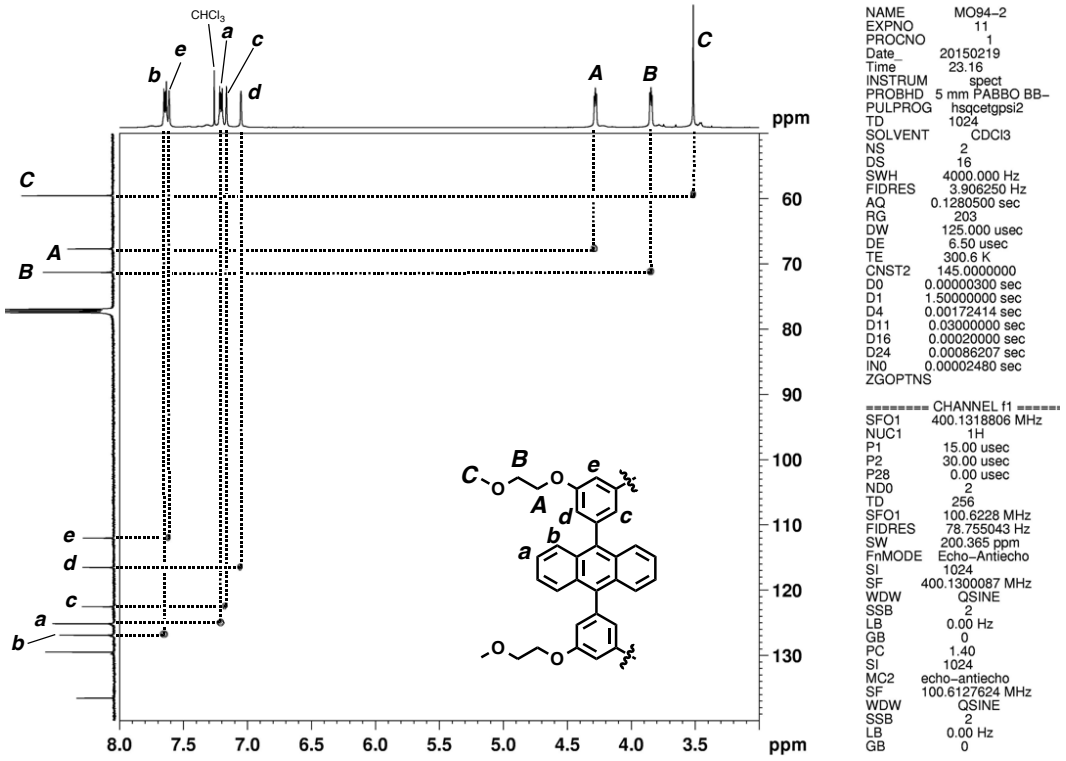


Figure S8. HSQC spectrum (400 MHz, $CDCl_3$, r.t.) of **1a**.

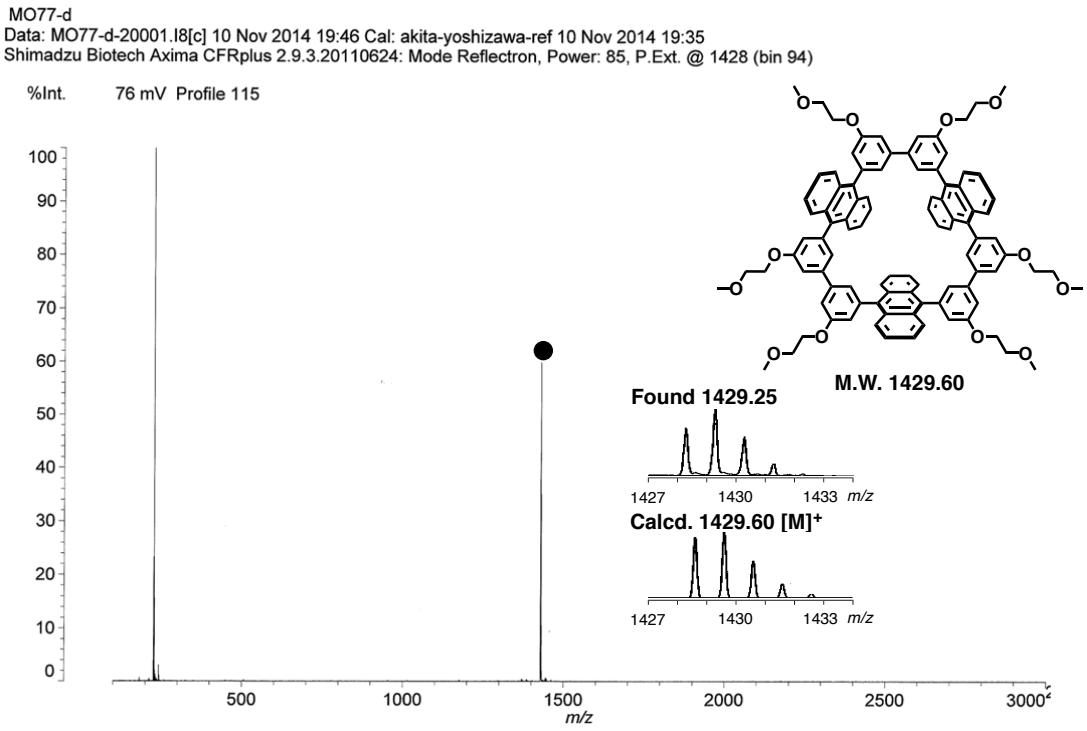
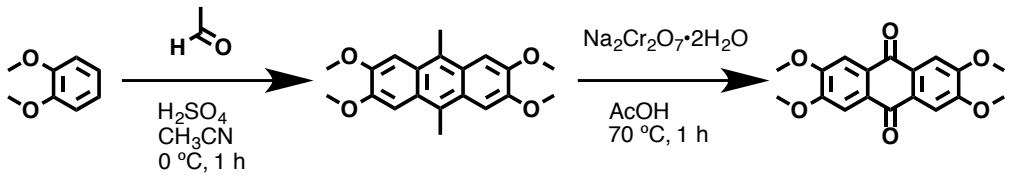


Figure S9. MALDI-TOF MS spectrum (dithranol) of **1a**.

Synthesis of 2,3,6,7-tetramethoxy-9,10-anthraquinone KH-368 (382)



A CH_3CN solution (2.1 mL) of 1,2-dimethoxybenzene (4.244 g, 30.71 mmol) and acetaldehyde (1.708 g, 38.78 mmol) was added dropwised to a 2-necked 200 mL glass flask containing concentrated sulfuric acid (15 mL) at 0 ºC. After the mixture was stirred at 0 ºC for 1 h, water was added to the solution. After the neutralization by a NaOH aqueous solution, the resultant mixture was filtered and washed with water, CH_3OH, and hexane to afford 2,3,6,7-tetramethoxy-9,10-dimethylanthracene as a white solid (2.620 g, 8.027 mmol). The white solid, $Na_2Cr_2O_7•2H_2O$ (6.028 g, 33.56 mmol), and AcOH (40 mL) were added to a 2-necked 200 mL glass flask filled with N_2. After the mixture stirred at 70 ºC for 1 h, water was added to the flask at r.t. The crude product was filtered and washed with water, CH_3OH, and hexane to afford 2,3,6,7-tetramethoxy-9,10-anthraquinone as a yellow solid (1.569 g, 4.778 mmol, 31% yield).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 7.68 (s, 4H), 4.07 (s, 12H). MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{18}H_{16}O_6$ 328.09, Found 328.07 $[M]^+$.

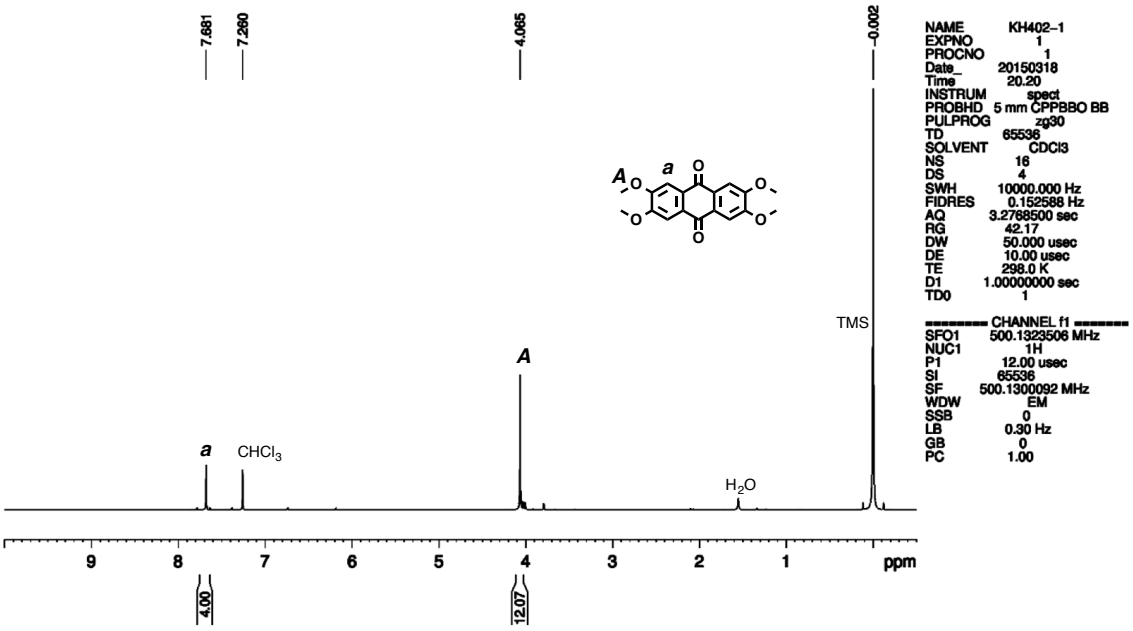
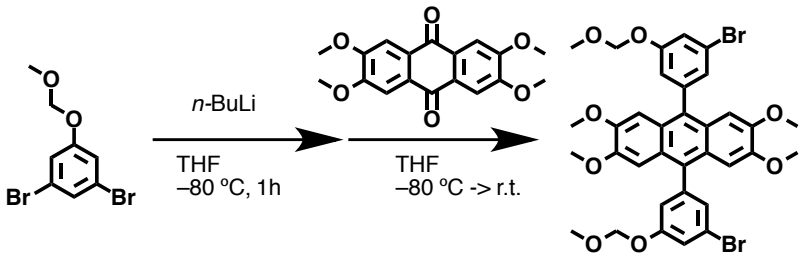


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of 2,3,6,7-tetramethoxy-9,10-anthraquinone.

Synthesis of 2b KH-388, (362, 369, 379, 383)



1,3-Dibromo-5-(methoxymethoxy)benzene (4.097 g, 13.84 mmol) and dry THF (70 mL) were added to a 2-necked 200 mL glass flask filled with N_2. A hexane solution (2.69 M) of *n*-butyllithium (5.0 mL, 13 mmol) was then added dropwise to the flask at –80 ºC under N_2. After the mixture was stirred at –80 ºC for 1 h, a dry THF solution (100 mL) of 2,3,6,7-tetramethoxy-9,10-anthraquinone (2.048 g, 6.237 mmol) was added to the solution. The resultant mixture was further stirred at –80 ºC for 1 h and then warmed to r.t. for 12 h. After the obtained solution was concentrated under reduced pressure,

acetic acid (50 mL), $NaH_2PO_2•H_2O$ (0.743 g, 7.01 mmol), and NaI (0.995 g, 6.86 mmol) were added to the solids. The mixture was stirred at 70 ºC for 12 h. The resultant solution was poured into water and then the products were extracted with CH_2Cl_2. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give **2b** as a white solid (1.559 g, 2.140 mmol, 34% yield).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 7.39 (dd, J = 2.0 Hz, 2H), 7.31-7.29 (m, 2H), 7.13-7.11 (m, 2H), 6.83 (s, 14H), 5.23-5.23 (m, 4H), 3.80 (s, 12H), 3.51-3.50 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, r.t.): δ 158.3 (C_q), 149.3 (C_q), 142.7 (C_q), 131.6 (C_q), 127.8 (CH), 125.6 (C_q), 123.1 (C_q), 119.1 (CH), 118.1 (CH), 103.7 (CH), 94.7 (CH_2), 56.4 (CH_3), 55.8 (CH_3). FT-IR (KBr, cm^{-1}): 3441, 3067, 2998, 2953, 2826, 1596, 1563, 1530, 1493, 1464, 1429, 1245, 1206, 1150, 1121, 1080, 1030, 999, 849, 753. MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{34}H_{32}Br_2O_8$ 728.04, Found 727.99 $[M]^+$. E.A.: Calcd. for $C_{34}H_{32}O_8Br_2•(C_6H_{14})_{0.14}$: C, 56.51; H, 4.62; Br, 21.58. Found: C, 56.28; H, 4.33; Br, 21.32.

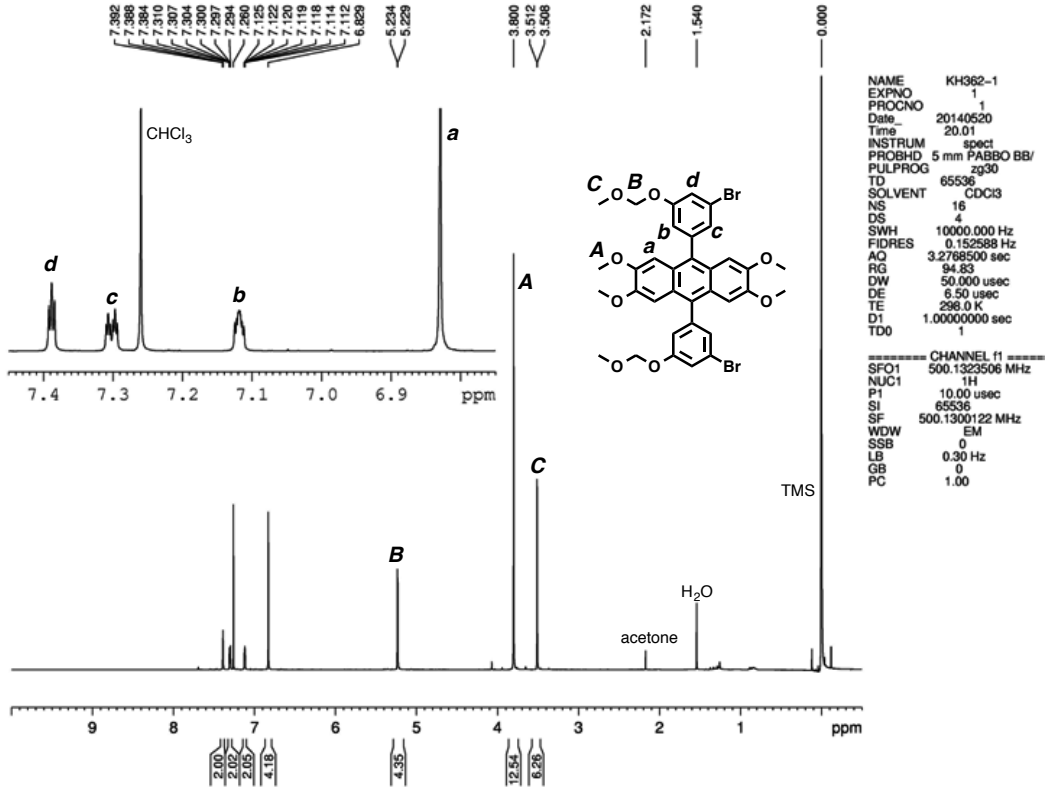


Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **2b**.

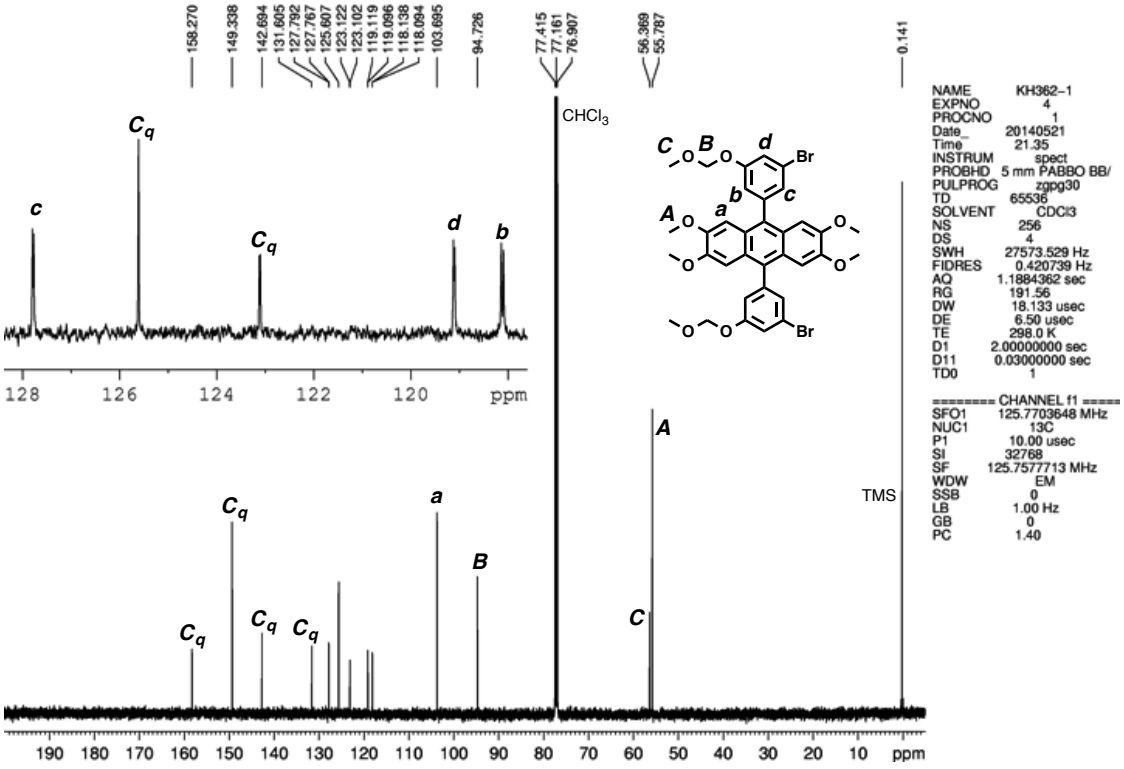


Figure S12. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, r.t.) of **2b**.

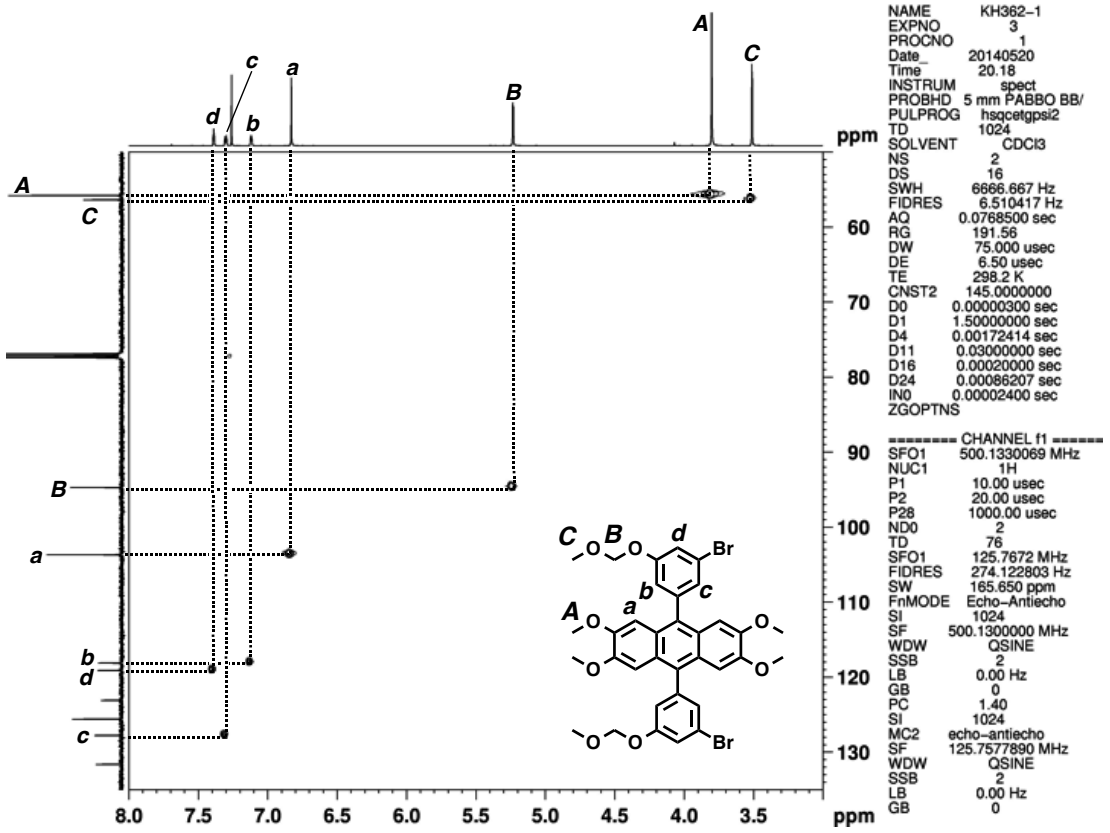


Figure S13. HSQC spectrum (400 MHz, $CDCl_3$, r.t.) of **2b**.

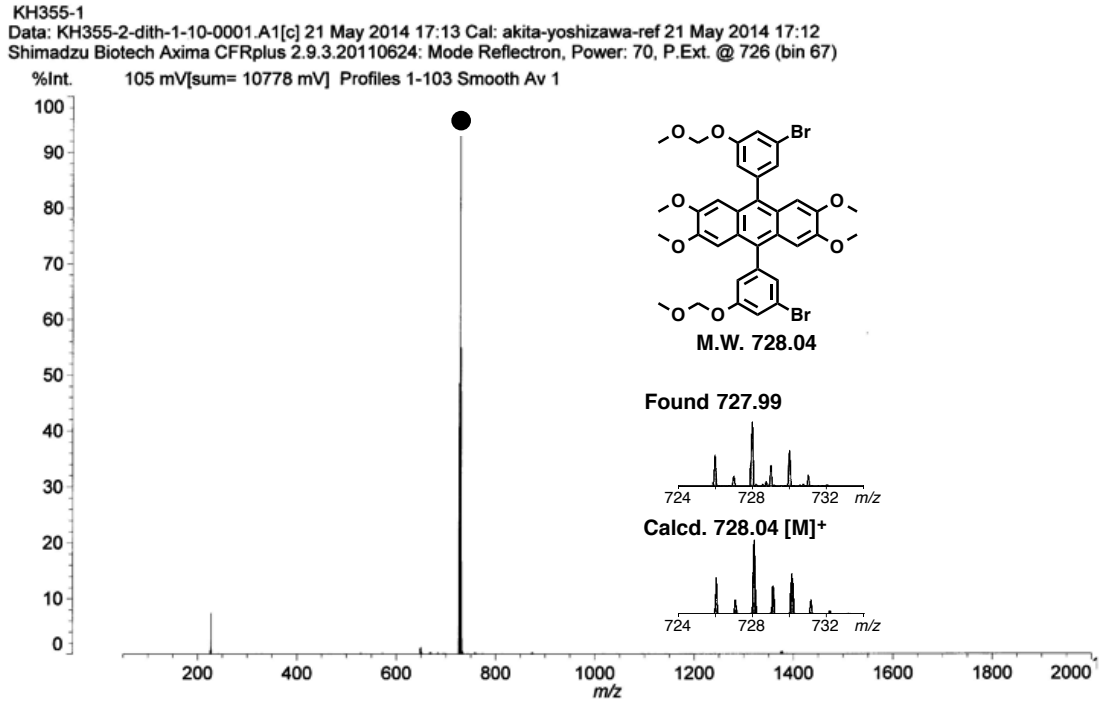
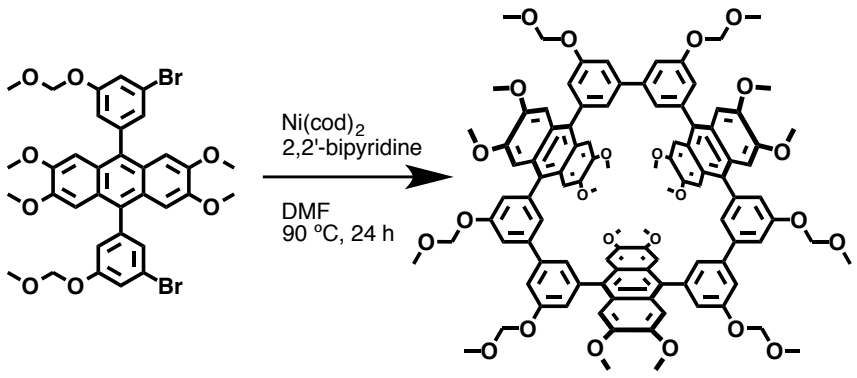


Figure S14. MALDI-TOF MS spectrum (dithranol) of **2b**.

Synthesis of molecular tube 1b' KH-390, (363, 375, 377, 386, 392)



Compound **2b** (0.630 g, 0.865 mmol), $Ni(cod)_2$ (0.493 g, 1.79 mmol), 2,2'-bipyridyl (0.064 g, 0.41 mmol), and dry DMF (450 mL) were added to a 2-necked 500 mL glass flask filled with N_2 and then the mixture was stirred at 90 ºC for 24 h. After the reaction was quenched with water, the mixture was concentrated under reduced pressure and the residue was extracted with CH_2Cl_2. The crude product was purified by silica-gel column chromatography ($CHCl_3$:acetone = 10:1) and GPC to give **1b'** as a yellow solid (0.047 g, 0.028 mmol, 10% yield).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 7.64 (s, 6H), 7.37 (s, 6H), 7.24 (s, 6H), 6.90 (s, 12H), 5.34 (m, 12H), 3.62 (s, 36H), 3.57 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, r.t.): δ 158.2 (C_q), 148.9 (C_q), 141.6 (C_q), 141.4 (C_q), 132.5 (C_q), 125.6 (C_q), 124.1 (CH), 118.2 (CH), 113.9 (CH), 103.9 (CH), 94.8 (CH_2), 56.3 (CH_3), 55.4 (CH_3). FT-IR (KBr, cm^{-1}): 3469, 2949, 2828, 1585, 1493, 1433, 1373, 1241, 1204, 1151, 1126, 1083, 1032, 851, 755. MALDI-TOF MS (dithranol): *m/z* Calcd. for $C_{102}H_{96}O_{24}$ 1705.63, Found 1705.35 $[M]^+$. E.A.: Calcd. for $C_{102}H_{96}O_{24}\bullet(C_6H_{14})_{0.3}$: C, 70.55; H, 5.56. Found: C, 70.22; H, 5.59.

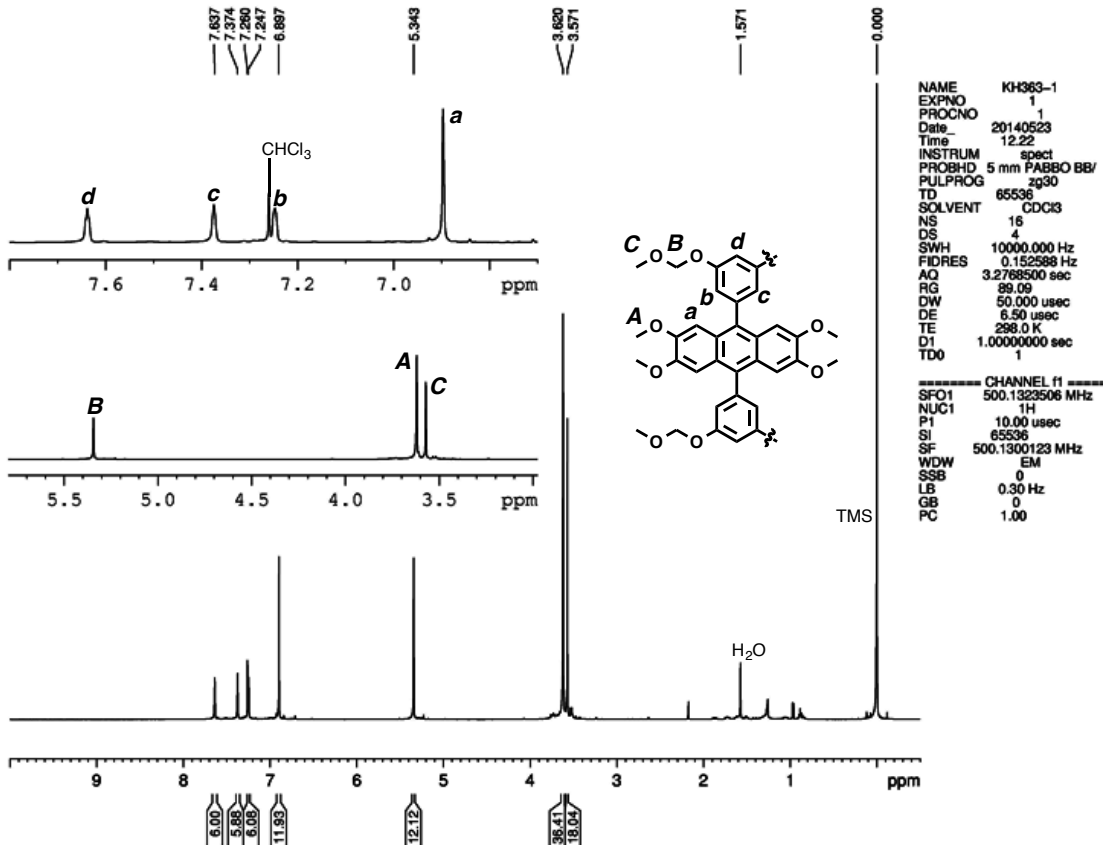


Figure S15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **1b'**.

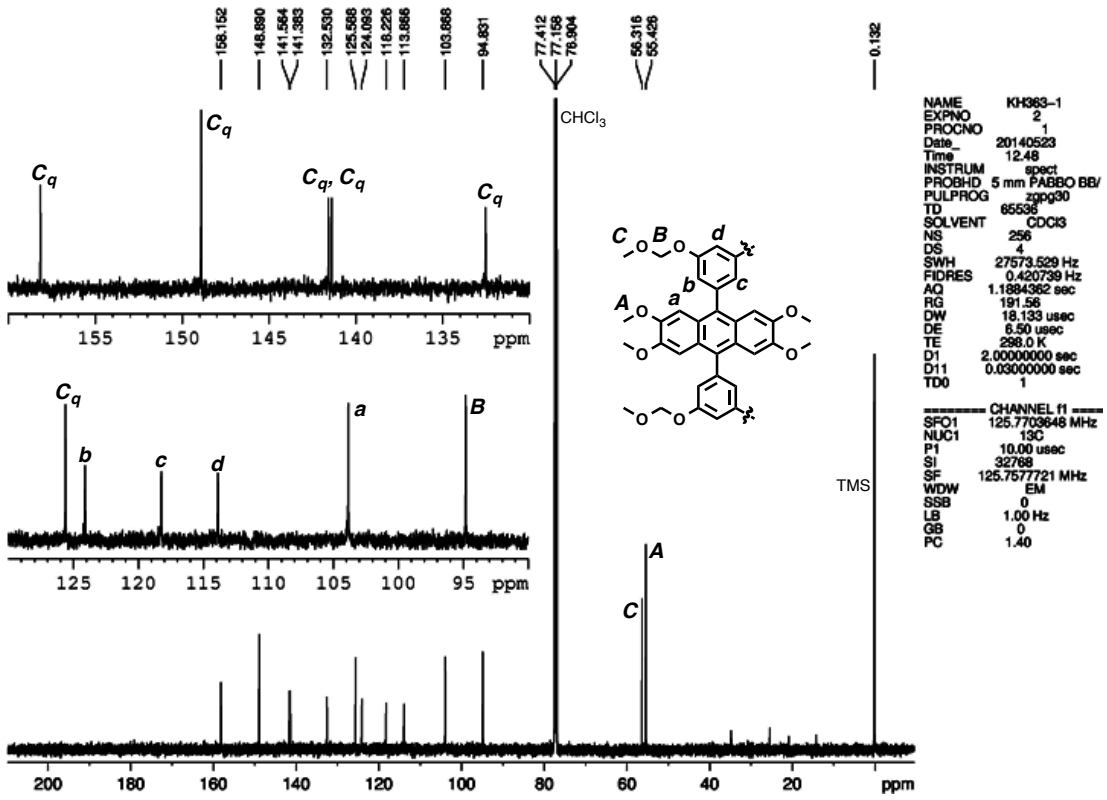


Figure S16. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, r.t.) of **1b'**.

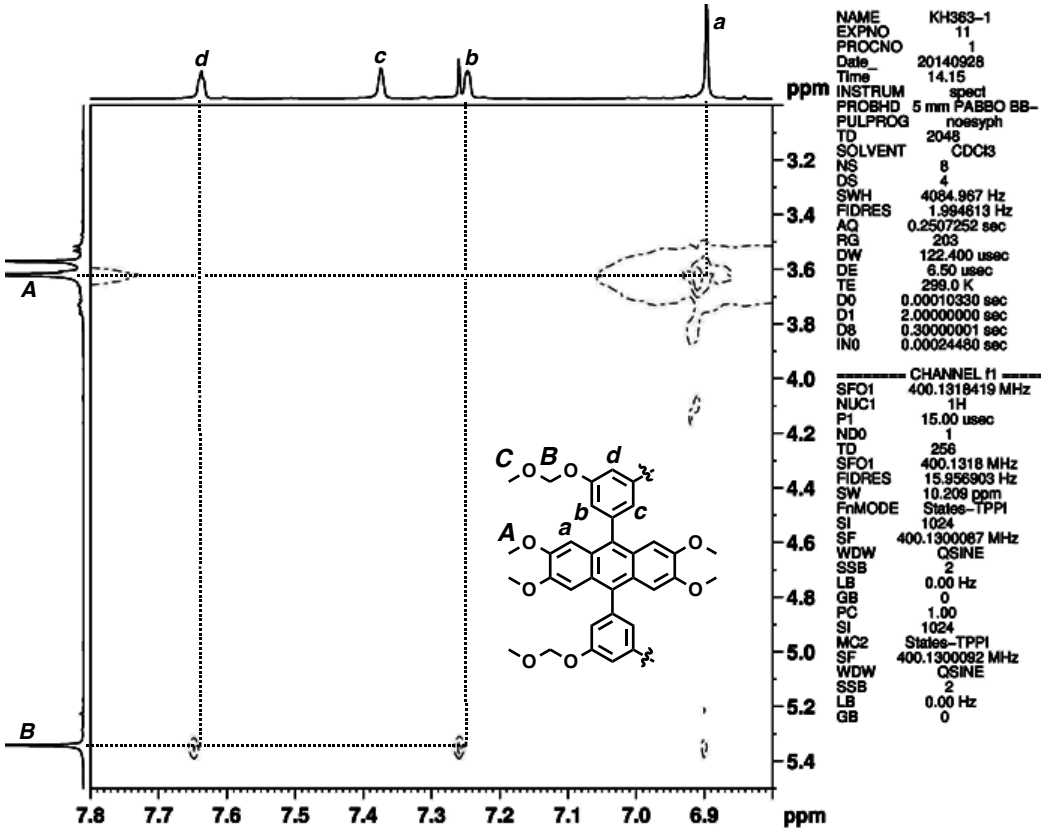


Figure S17a. NOESY spectrum (400 MHz, $CDCl_3$, r.t.) of **1b'**.

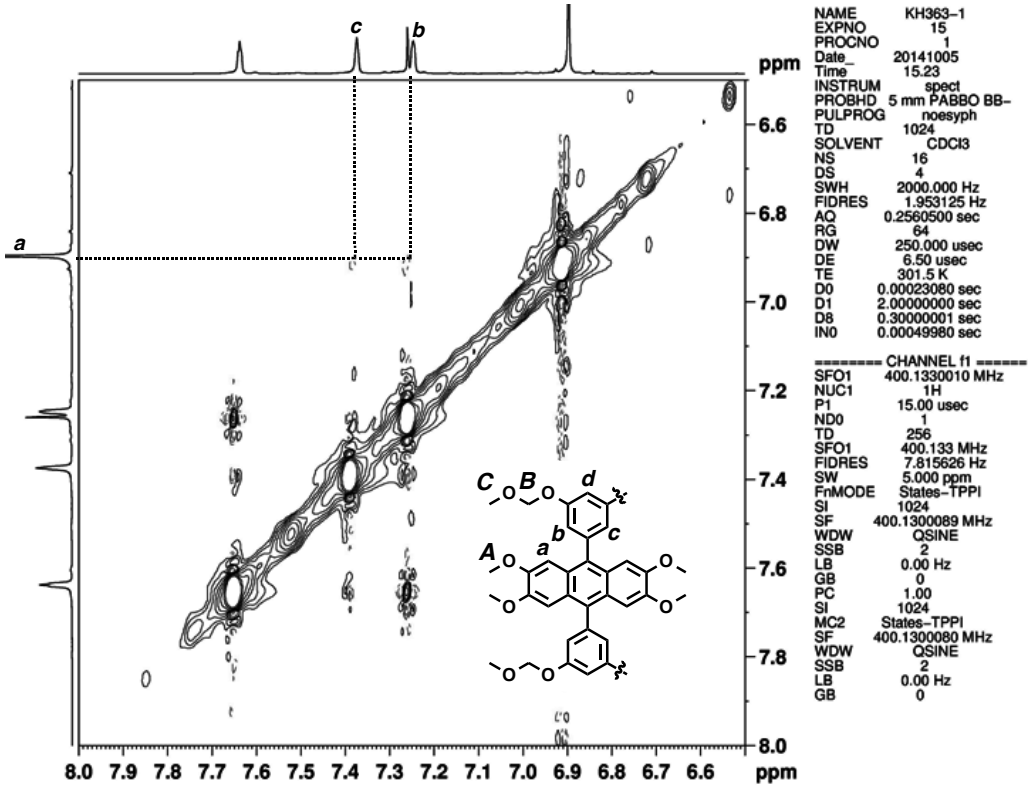


Figure S17b. NOESY spectrum (400 MHz, $CDCl_3$, r.t.) of **1b'** (aromatic region).

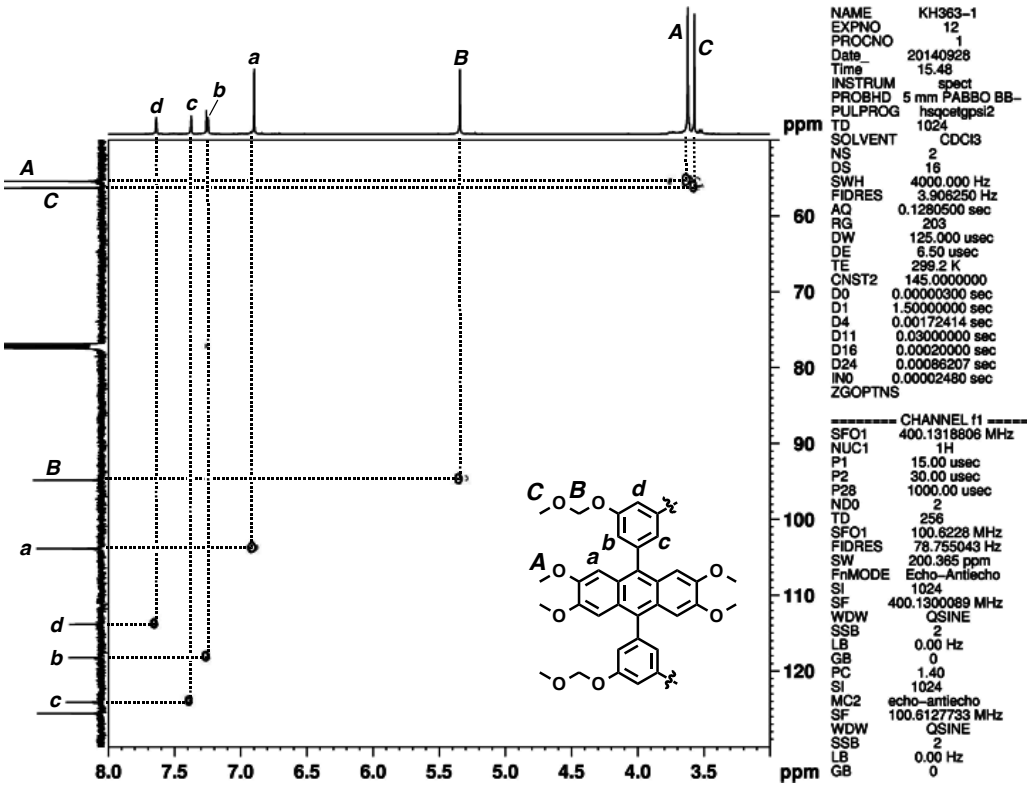


Figure S18. HSQC spectrum (400 MHz, $CDCl_3$, r.t.) of **1b'**.

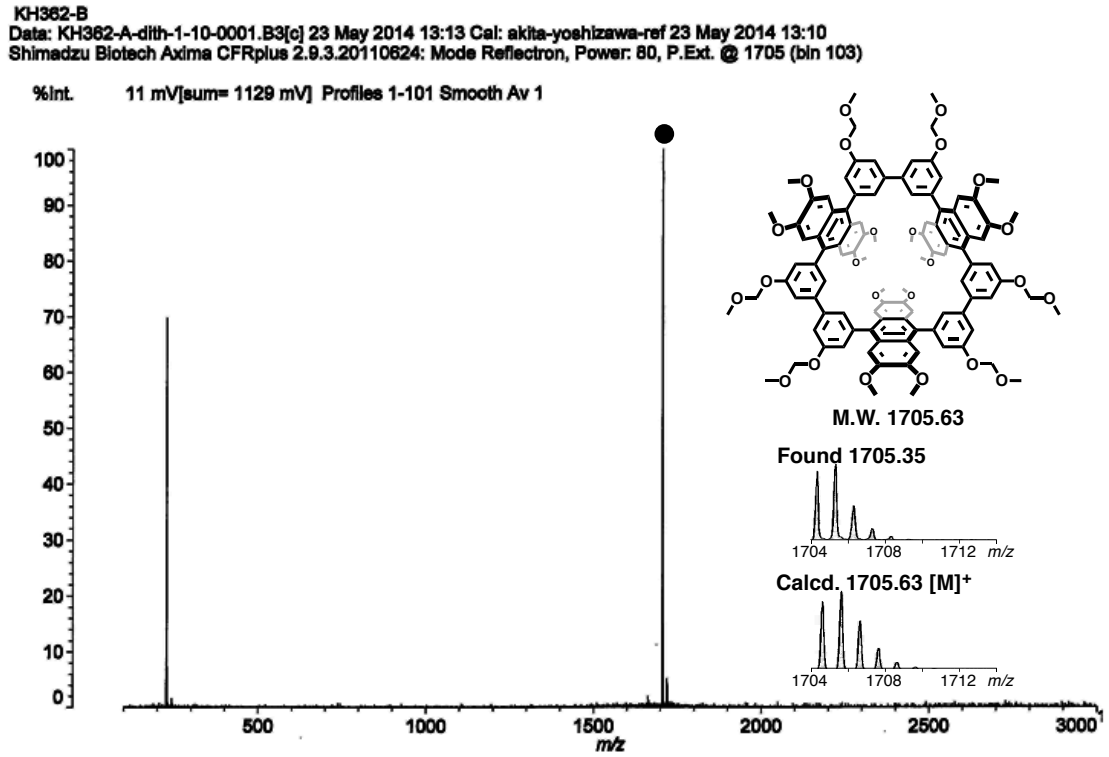
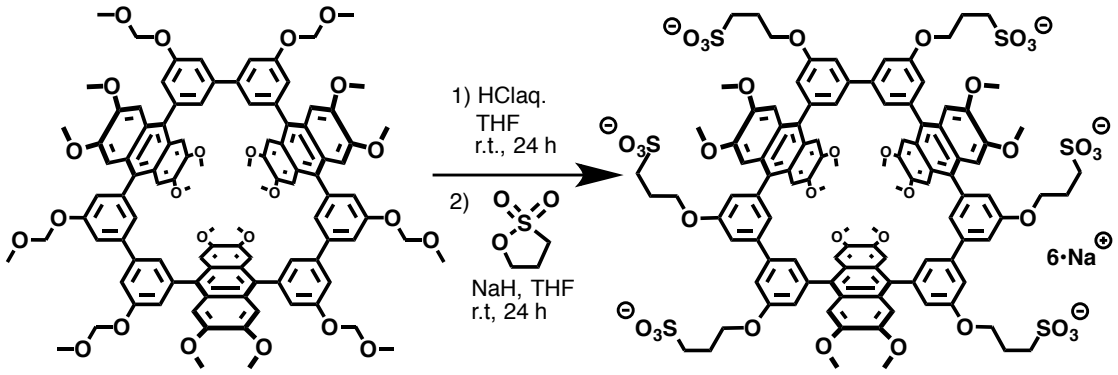


Figure S19. MALDI-TOF MS spectrum (dithranol) of **1b'**.

Synthesis of molecular tube 1b KH-385, (378, 380, 395)



Tube **1b'** (33.2 mg, 0.0195 mmol), concentrated HCl (3 mL), THF (5 mL), and water (2 mL) were added to a 100 mL glass flask and the mixture was stirred at r.t. for 4 h. After the resultant mixture was concentrated under reduced pressure, the crude product was washed with water and $CHCl_3$ and then purified by silica-gel column chromatography (hexane:acetone = 1:1) to give deprotected tube **1b"** as a white solid (^{1}H NMR (500 MHz, d_6-acetone, r.t.): δ 8.85 (s, 6H), 7.49 (dd, J = 2.0, 2.0 Hz, 6H), 7.25 (s, 6H), 7.02 (dd, J = 2.5, 1.5 Hz, 6H), 3.53 (s, 36H)). NaH (60% in oil; 24.0 mg,

0.600 mmol) was washed with hexane in a 100 mL glass flask under N_2. The obtained tube **1b"** and dry THF (10 mL) were added to the flask and then the mixture was stirred at r.t. for 1 h. 1,3-Propanesultone (0.055 g, 4.5 mmol) was added dropwise to the flask and the resultant mixture was stirred overnight at r.t. The mixture was concentrated under reduced pressure and the crude product was washed with hexane, acetone, and 1-propanol to afford **1b** as a yellow solid (29.6 mg, 0.0128 mmol, 66% yield).

^{1}H NMR (500 MHz, CD_3OD, r.t.): δ 7.63 (s, 6H), 7.23 (s, 6H), 7.08 (s, 6H), 6.87 (s, 12H), 4.35 (t, J = 6.3 Hz, 12H), 3.56 (s, 32H), 3.09 (t, J = 7.5 Hz, 12H), 2.37 (q, J = 6.9 Hz, 12H). ^{13}C NMR (125 MHz, CD_3OD, r.t.): δ 161.2 (C_q), 150.2 (C_q), 142.9 (C_q), 142.9 (C_q), 134.0 (C_q), 126.8 (C_q), 123.6 (CH), 117.5 (CH), 112.9 (CH), 104.9 (CH), 68.1 (CH_2), 55.8 (CH_3), 49.5-48.5 (overlapped with MeOH), 26.5 (CH_2). FT-IR (KBr, cm^{-1}): 3459, 2941, 1637, 1585, 1530, 1493, 1433, 1376, 1239, 1125, 1043, 851, 755, 528. ESI-TOF MS (CH_3OH): m/z 361.2 [**1b** – 6Na$^+$]$^{6-}$, 438.0 [**1b** – 5Na$^+$]$^{5-}$, 553.3 [**1b** – 4Na$^+$]$^{4-}$, 745.4 [**1b** – 3Na$^+$]$^{3-}$.

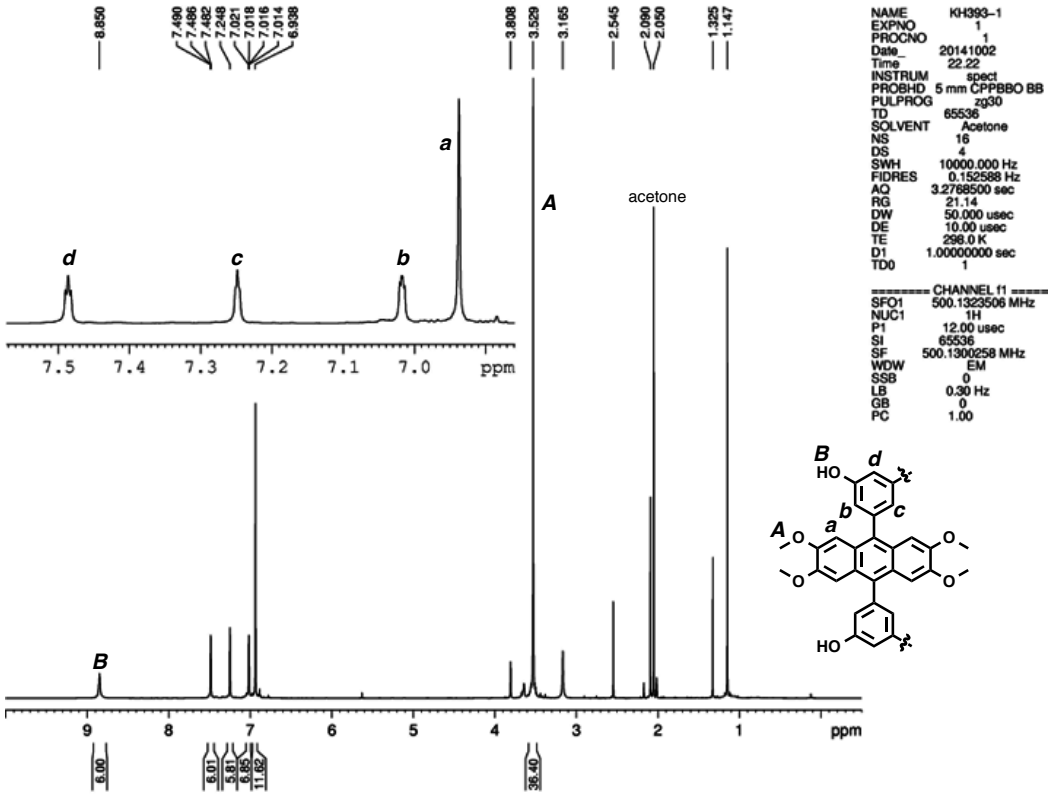


Figure S20. ^{1}H NMR spectrum (500 MHz, d_6-acetone, r.t.) of **1b"**.

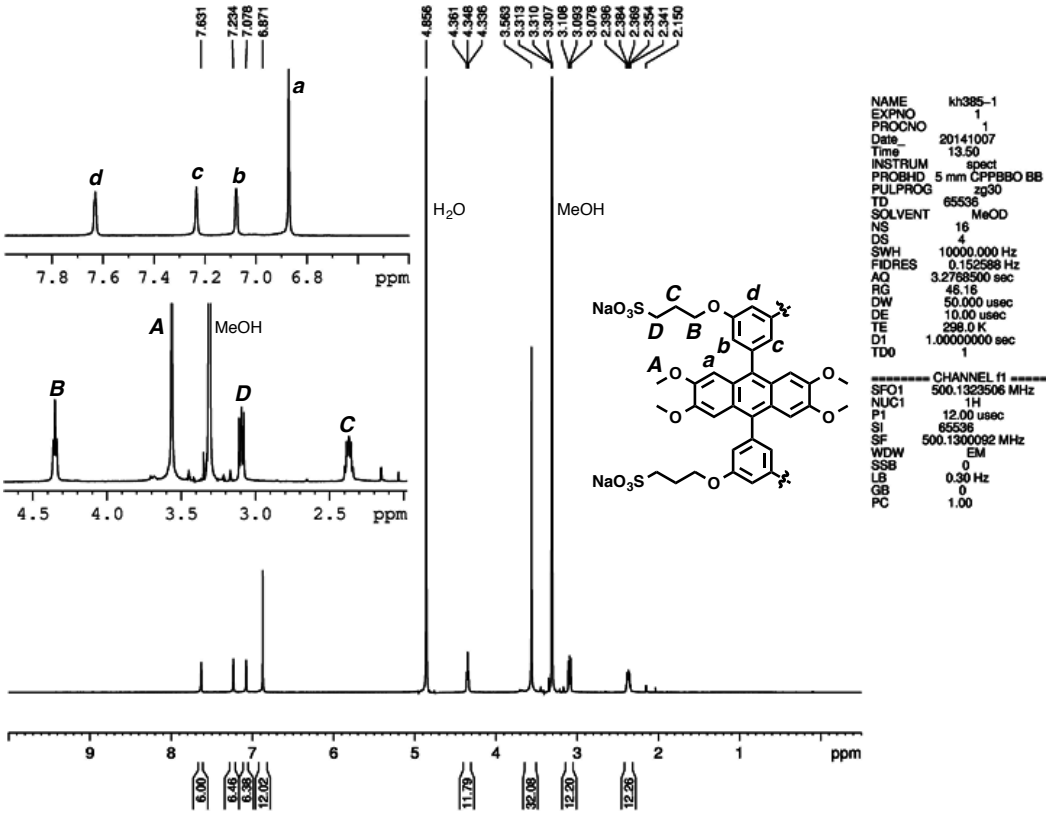


Figure S21. [1]H NMR spectrum (500 MHz, CD_3OD, r.t.) of **1b**.

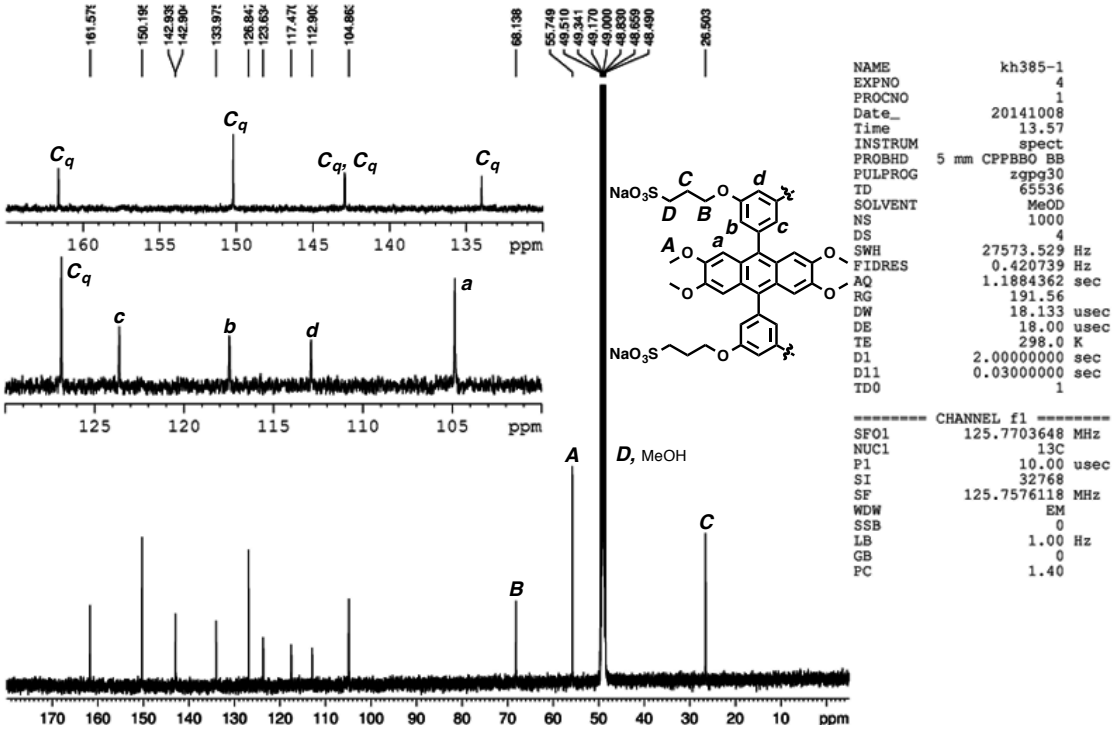


Figure S22. [13]C NMR spectrum (125 MHz, CD_3OD, r.t.) of **1b**.

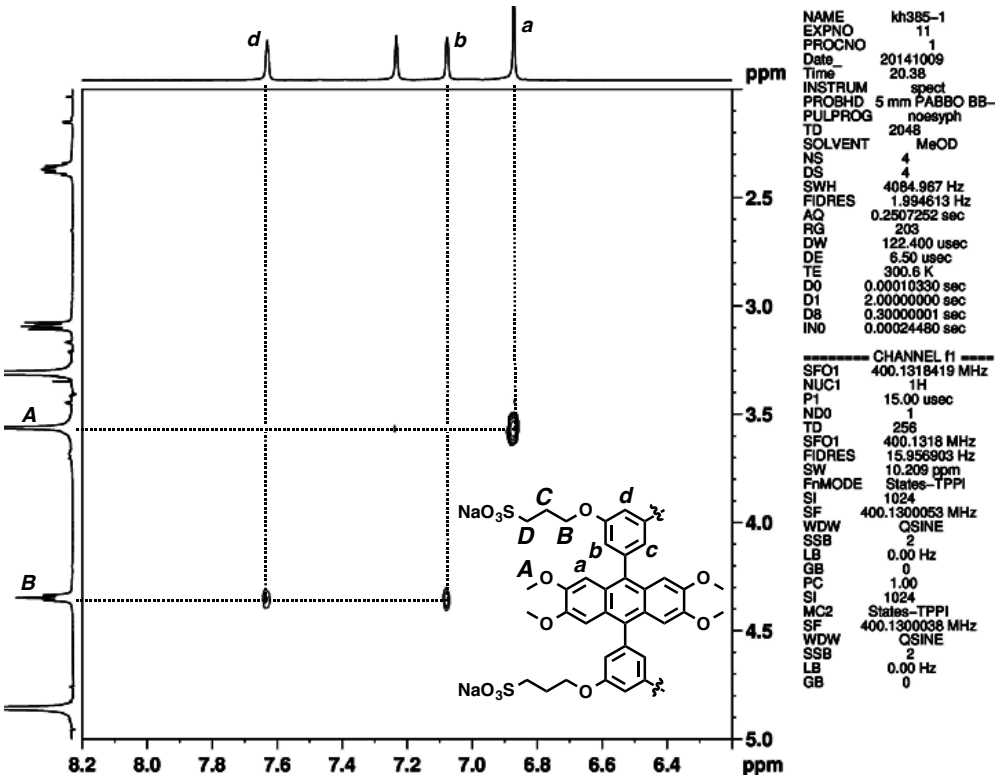


Figure S23a. NOESY spectrum (400 MHz, CD_3OD, r.t.) of **1b**.

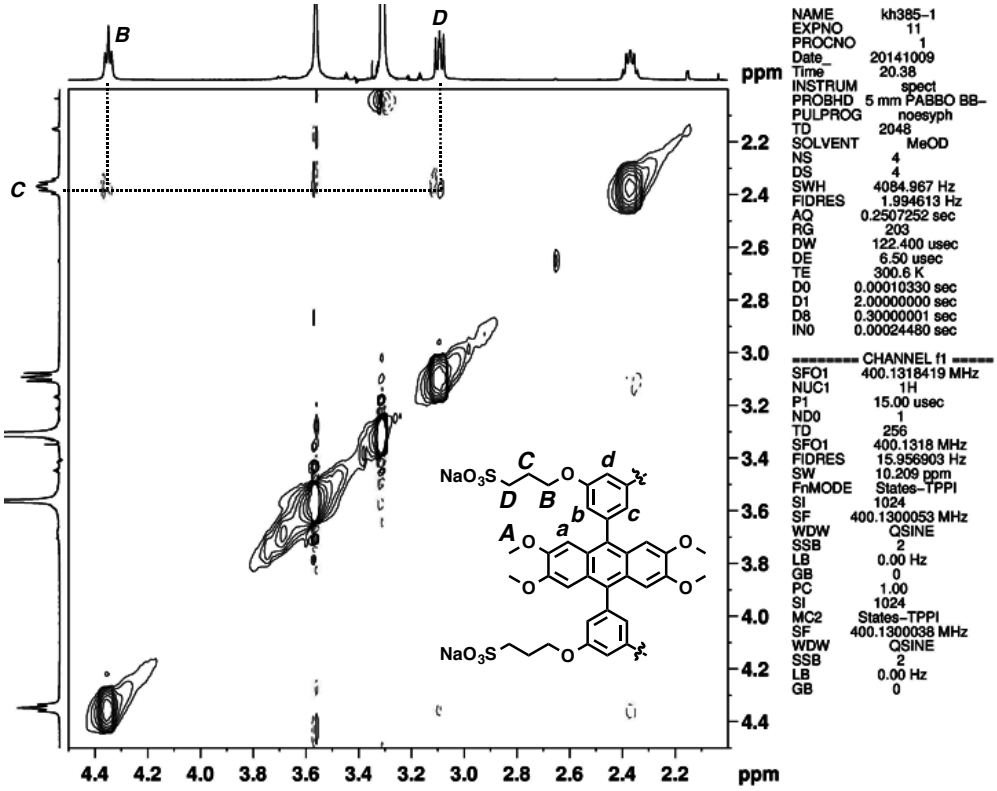


Figure S23b. NOESY spectrum (400 MHz, CD_3OD, r.t.) of **1b** (aliphatic region).

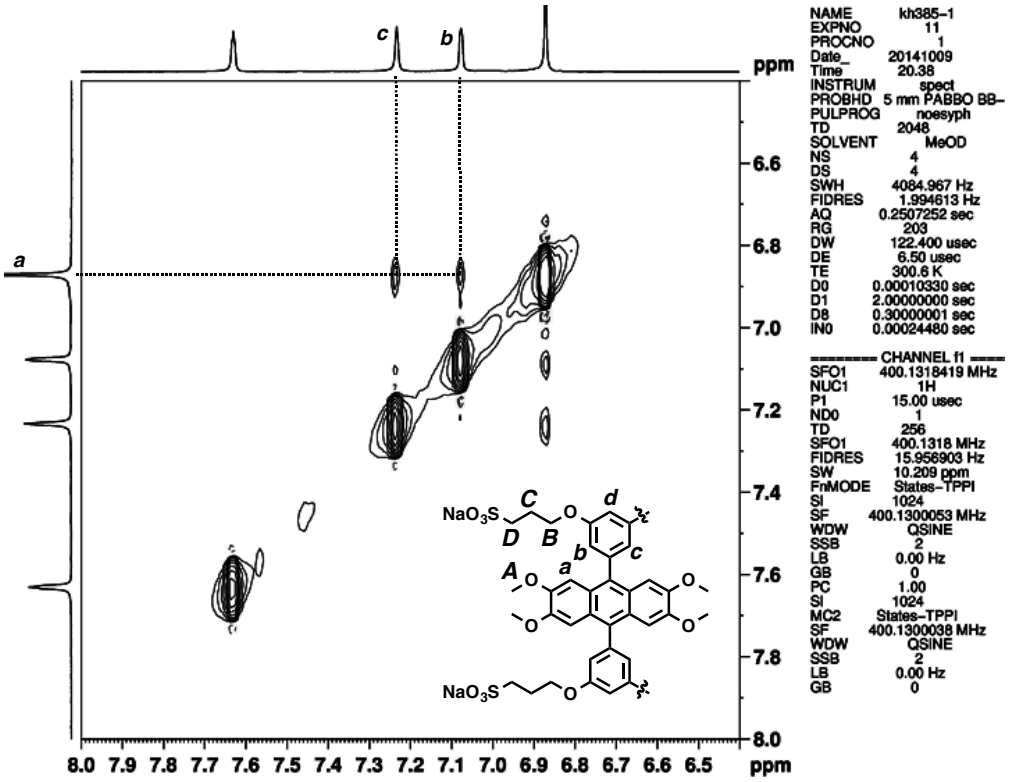


Figure S23c. NOESY spectrum (400 MHz, CD_3OD, r.t.) of **1b** (aromatic region).

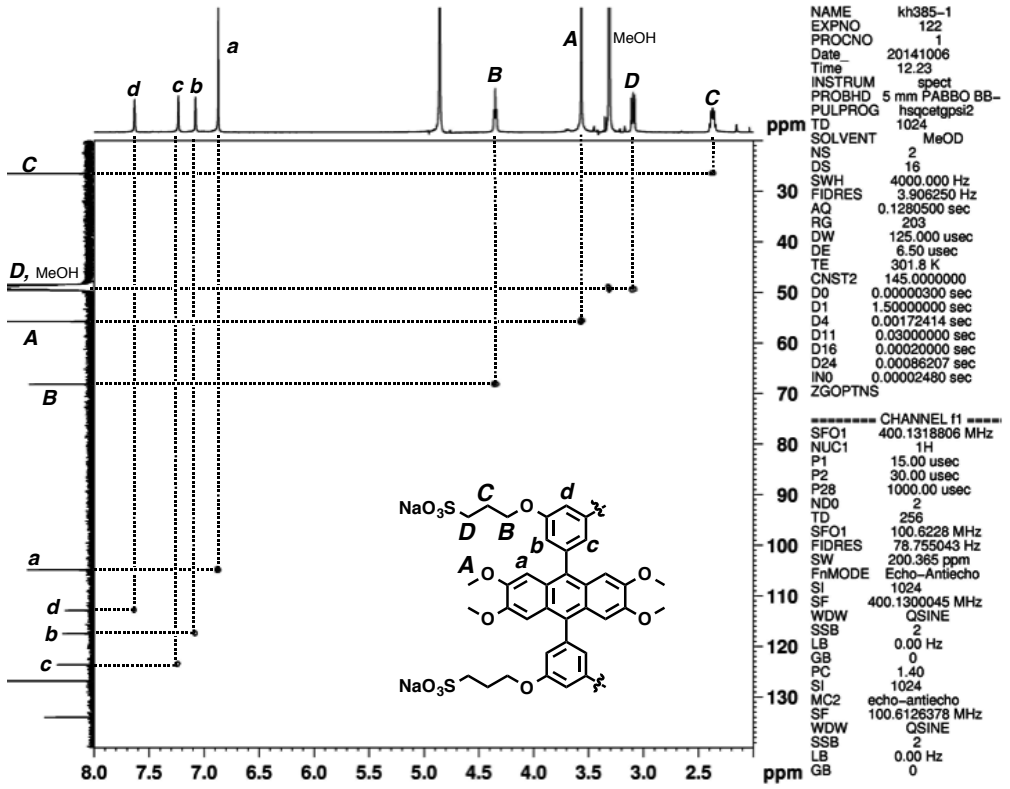


Figure S24. HSQC spectrum (400 MHz, CD_3OD, r.t.) of **1b**.

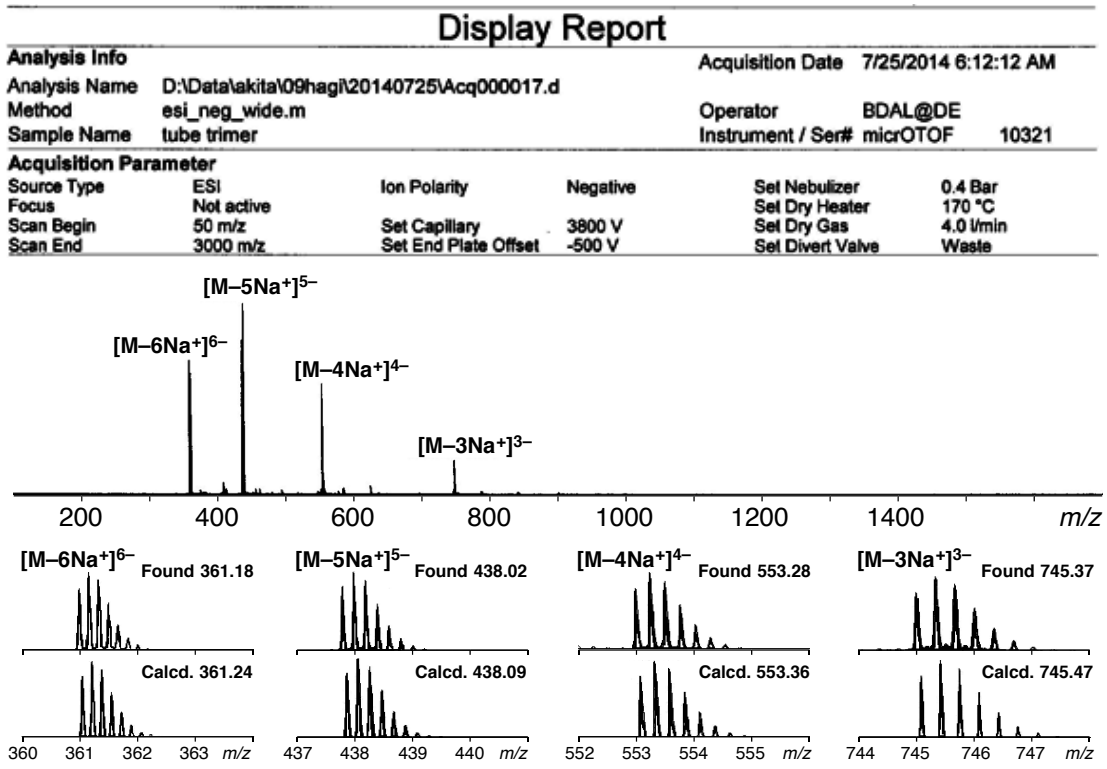


Figure S25. ESI-TOF MS spectrum (CH_3OH) of **1b**.

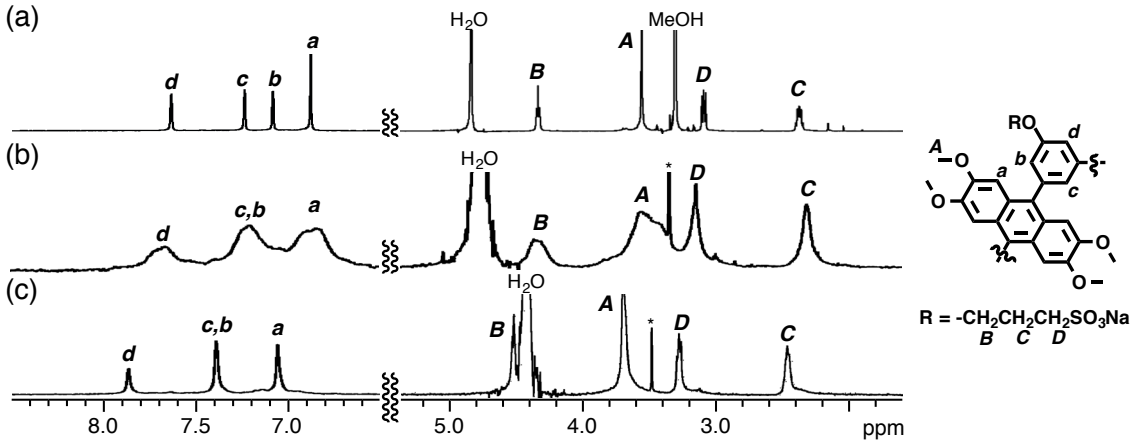


Figure S26. ^{1}H NMR spectra (500 MHz, 0.4 mM) of tube **1b** in (a) CD_3OD at r.t. and in D_2O at (b) r.t. and (c) 70 ºC.

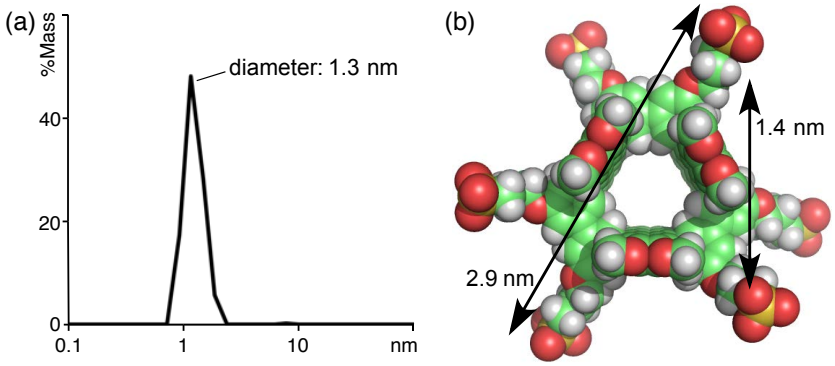


Figure S27. (a) Particle size distribution (H_2O, 0.4 mM, r.t.) of **1b** by DLS analysis and (b) the optimized structure of **1b**.

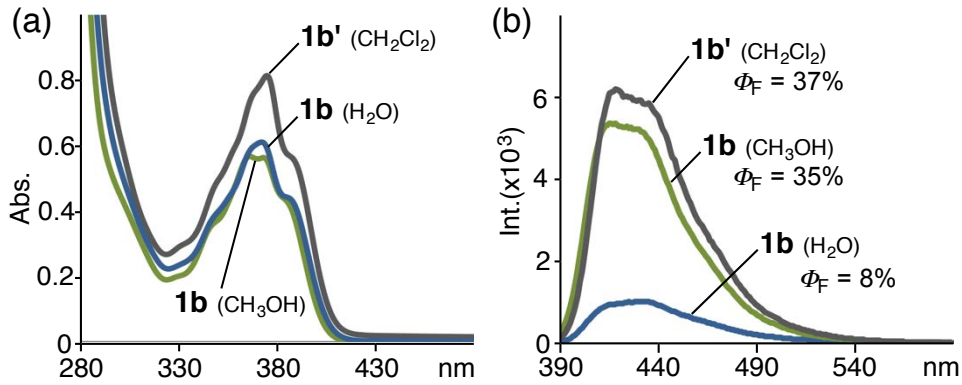
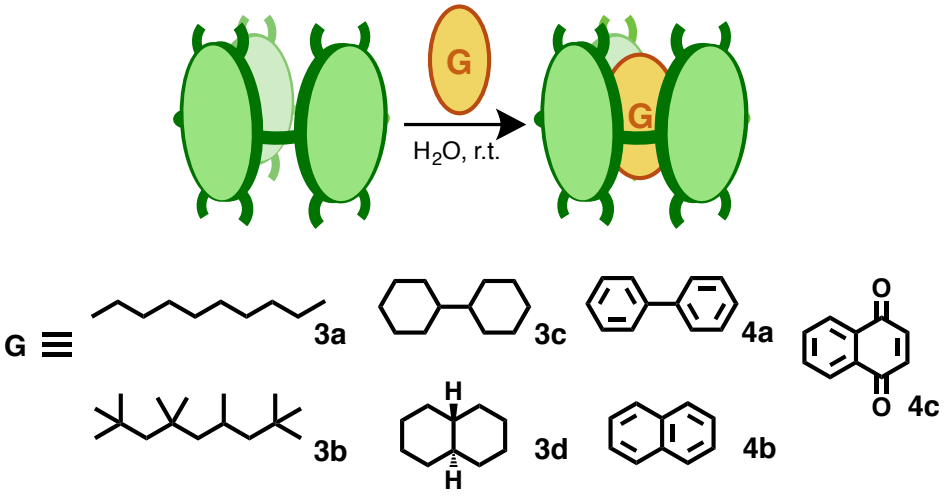


Figure S28. (a) UV-vis (0.2 mM, r.t.) and (b) fluorescence spectra (λ_{ex} = 375 nm, 0.2 mM, r.t.) of **1b'** in CH_2Cl_2 and **1b** in H_2O and CH_3OH.

Synthesis and properties of 1b⊃3a-d and 1b⊃4a-c KH-425 (421)



n-Decane (**3a**; 0.12 mg, 0.84 μmol) was added to an aqueous solution (0.4 mL) of tube **1b** (1.00 mg, 0.43 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h.

After filtration, the formation of 1:1 host-guest complex **1b⊃3a** was confirmed by ^{1}H NMR, UV-vis, fluorescence, and ESI-TOF MS analyses. 1:1 Host-guest complexes **1b⊃3b-d** and **1b⊃4a-c** were also obtained by the same procedure.

1b⊃3a: ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.84 (s, 6H), 7.32-7.31 (m, 12H), 6.95 (s, 12H), 4.45 (br, 12H, overlapped by H_2O), 3.68 (br, 36H), 3.25 (br, 12H), 2.42 (br, 12H), 0.04 (br, 4H), –0.04 (br, 6H), –0.28 (br, 4H), –0.54 (br, 4H), –0.73 (br, 4H). ESI-TOF MS (H_2O): *m/z* 384.9 [**1⊃3a** – $6Na^+]^{6-}$, 466.5 [**1⊃3a** – $5Na^+]^{5-}$, 589.1 [**1⊃3a** – $4Na^+]^{4-}$.

1b⊃3b (2,2,4,4,6,8,8-heptamethylnonane): ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.77 (s, 6H), 7.30 (s, 6H), 7.20 (s, 6H), 6.83 (br, 12H), 4.45 (br, 12H, overlapped by H_2O), 3.61 (s, 36H), 3.16 (s, 12H), 2.32 (s, 12H), –0.11 (s, 9H), –0.24 (br, 2H), –0.42 (br, 2H), –0.62 (br, 2H), –0.72 (br, 6H), –1.00 (br, 3H), –1.02-–1.15 (m, 5H). ESI-TOF MS (H_2O): *m/z* 396.9 [**1⊃3b** – $6Na^+]^{6-}$, 480.9 [**1⊃3b** – $5Na^+]^{5-}$, 606.8 [**1⊃3b** – $4Na^+]^{4-}$.

1b⊃3c (bicyclohexyl): ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.86 (s, 6H), 7.35 (s, 6H), 7.30 (s, 6H), 6.93 (br, 12H), 4.45 (br, 12H, overlapped by H_2O), 3.69 (s, 36H), 3.25 (s, 12H), 2.41 (s, 12H), 0.73 (br, 2H), 0.13 (br, 4H), –0.11 (br, 2H), –0.29 (br, 4H), –0.59 (br, 4H), –1.00—1.01 (m, 6H). ESI-TOF MS (H_2O): *m/z* 388.9 [**1⊃3c** – $6Na^+]^{6-}$, 471.3 [**1⊃3c** – $5Na^+]^{5-}$, 595.1 [**1⊃3c** – $4Na^+]^{4-}$.

1b⊃3d (*trans*-decalin): ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.71 (s, 6H), 7.23 (s, 6H), 7.21 (s, 6H), 6.84 (br, 12H), 4.45 (br, 12H, overlapped by H_2O), 3.56 (s, 36H), 3.14 (s, 12H), 2.31 (s, 12H), 0.21 (br, 4H), –0.34-–0.39 (m, 8H), –1.06 (br, 4H), –1.18 (br, 2H). ESI-TOF MS (H_2O): *m/z* 384.2 [**1⊃3d** – $6Na^+]^{6-}$, 465.6 [**1⊃3d** – $5Na^+]^{5-}$, 587.8 [**1⊃3d** – $4Na^+]^{4-}$.

1b⊃4a (biphenyl): ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.76 (s, 6H), 7.31 (s, 6H), 6.93-6.92 (m, 18H), 6.57 (s, 2H), 6.00 (s, 4H), 5.58 (s, 4H), 4.45 (br, 12H, overlapped by H_2O), 3.61 (s, 36H), 3.24 (s, 12H), 2.41 (br, 4H). ESI-TOF MS (H_2O): *m/z* 383.0 [**1⊃4a** – $6Na^+]^{6-}$, 466.1 [**1⊃4a** – $5Na^+]^{5-}$, 585.8 [**1⊃4a** – $4Na^+]^{4-}$.

1b⊃4b (naphthalene): ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.69 (s, 6H), 7.21 (s, 6H), 7.04 (s, 6H), 6.81 (s, 12H), 6.36 (br, 4H), 6.21 (br, 4H), 4.40 (br, 12H), 3.50 (s, 36H), 3.16 (br, 12H), 2.32 (br, 4H). ESI-TOF MS (H_2O): *m/z* 382.6 [**1⊃4b** – $6Na^+]^{6-}$, 463.8 [**1⊃4b** – $5Na^+]^{5-}$, 585.3 [**1⊃4b** – $4Na^+]^{4-}$.

1b⊃4c (1,4-naphthoquinone): ^{1}H NMR (500 MHz, D_2O, 70 ºC): δ 7.69 (s, 6H), 7.37 (br, 4H), 7.20 (s, 6H), 7.13 (s, 6H), 7.08 (br, 4H), 6.83 (s, 12H), 6.59 (br, 4H), 4.45 (br, 12H, overlapped by H_2O), 3.48 (s, 24H), 3.14 (s, 12H), 2.35 (s, 12H).

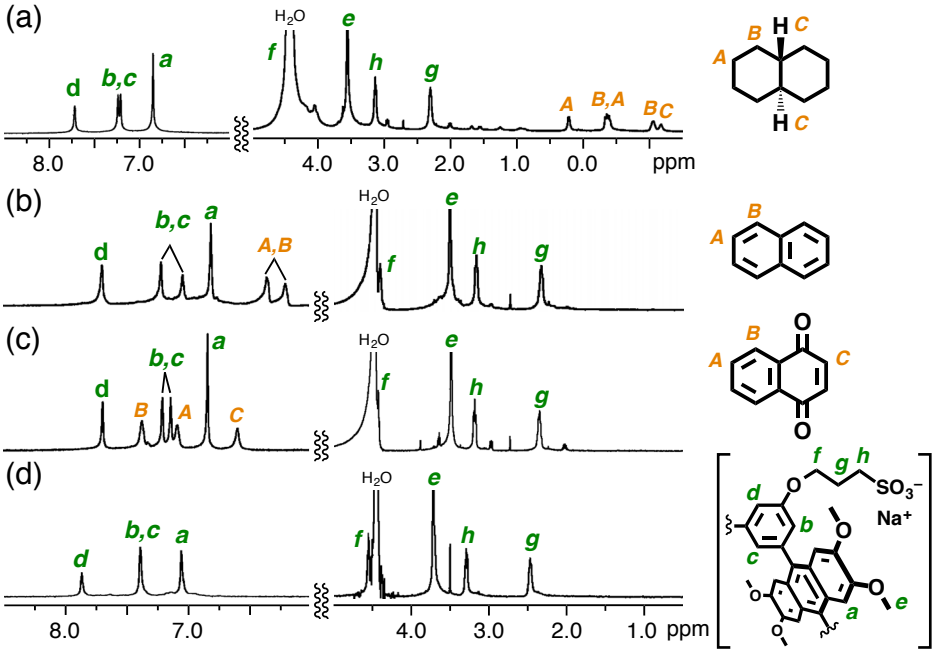


Figure S29. ^{1}H NMR spectra (500 MHz, 1.1 mM, D_2O, 70 ºC) of (a) **1b⊃3d**, (b) **1b⊃4b**, (c) **1b⊃4c**, and (d) **1b**.

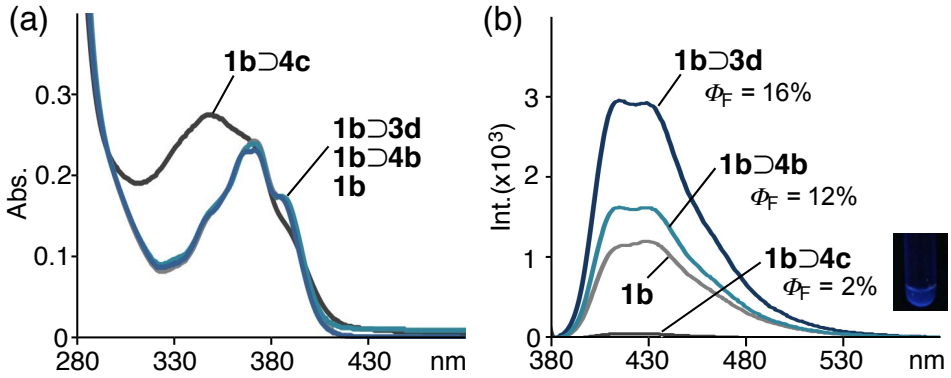
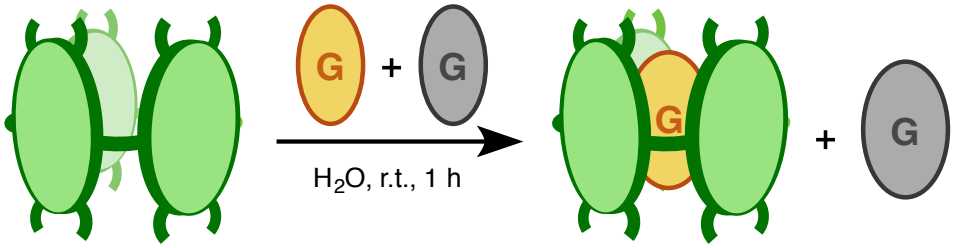


Figure 30. (a) UV-vis (0.1 mM, H_2O, r.t.) and (b) fluorescence spectra (λ_{ex} = 375 nm, 0.1 mM, H_2O, r.t.) of **1b⊃3d**, **1b⊃4b**, **1b⊃4c**, and **1b**.

Competitive binding experiments of 3a-d and 4a-c by 1b KH-417



n-Decane (**3a**; 0.05 mg, 0.4 μmol) and 2,2,4,4,6,8,8-heptamethylnonane (**3b**; 0.08 mg, 0.4 μmol) were added to a D_2O solution (0.5 mL) of tube **1b** (0.50 mg, 0.22 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the formation and ratio of host-guest complexes were confirmed by ^{1}H NMR. Competitive binding experiments of **3a** and **3c**, **3b** and **3c**, **3b** and **3d**, **4a** and **4c**, and **3c** and **4a** by tube **1b** were examined under the similar conditions. Naphthalene (**4b**) shows slight water solubility so that we excluded the competitive binding experiments.

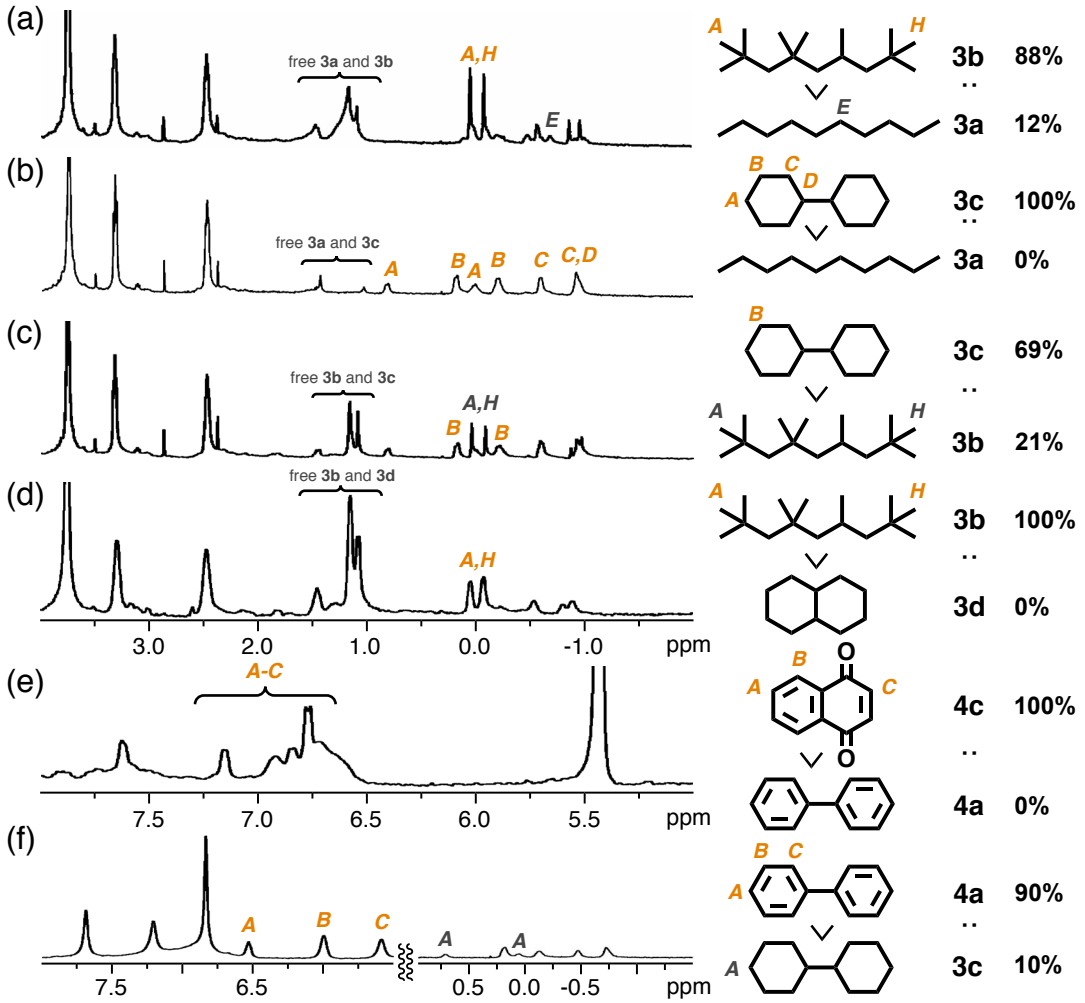
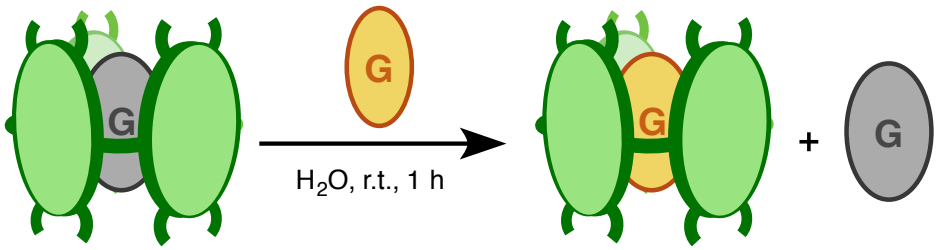


Figure S31. ^{1}H NMR spectra (500 or 400 MHz, 0.5 mM, D_2O, 70 ºC) after the competitive binding experiments of (a) **3a** and **3b**, (b) **3a** and **3c**, (c) **3b** and **3c**, (d) **3b** and **3d**, (e) **4a** and **4c**, and (f) **3c** and **4a** by tube **1b**. The binding rates were determined by the signal integration.

Guest exchange experiment of 1b⊃3a by 4a KH-417-2



Biphenyl (**4a**; 0.06 mg, 0.4 μmol) was added to a D_2O solution of **1b⊃3a** (0.53 mg, 0.22 μmol) in a glass test tube and the solution was stirred at r.t. for 1h. The guest exchange was confirmed by ^{1}H NMR analysis.

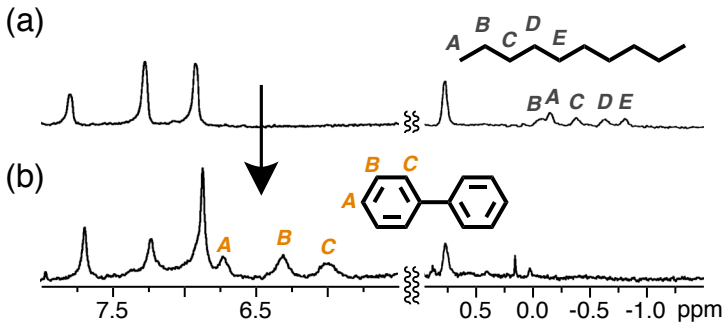
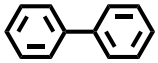
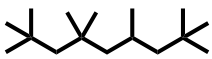
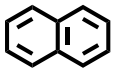
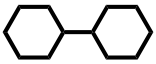
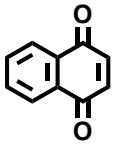
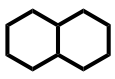


Figure S32. ^{1}H NMR spectra (400 MHz, 0.5 mM, D_2O, 70 ºC) (a) before and (b) after addition of **4a** to **1b⊃3a**.

Table S1. Volume and length of guests **3a-d** and **4a-c** by DFT calculation (B3LYP/6-31G*).

guests		volume / Å^3	length / Å	guests		volume / Å^3	length / Å
	**3a**	199.3	11.6		**4a**	182.9	7.1
	**3b**	305.5	9.5		**4b**	150.7	5.1
	**3c**	208.9	7.2		**4c**	160.5	5.1
	**3d**	171.3	5.2				