Electronic supplementary information

Photoresponsive self-assembled hexameric capsules based on calix[4]resorcinarenes bearing azobenzene dendron conjugates as side chains

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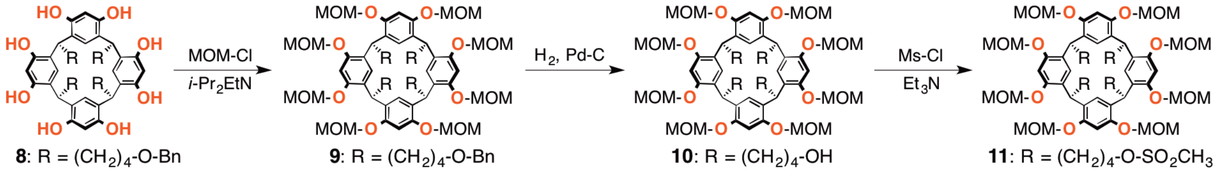
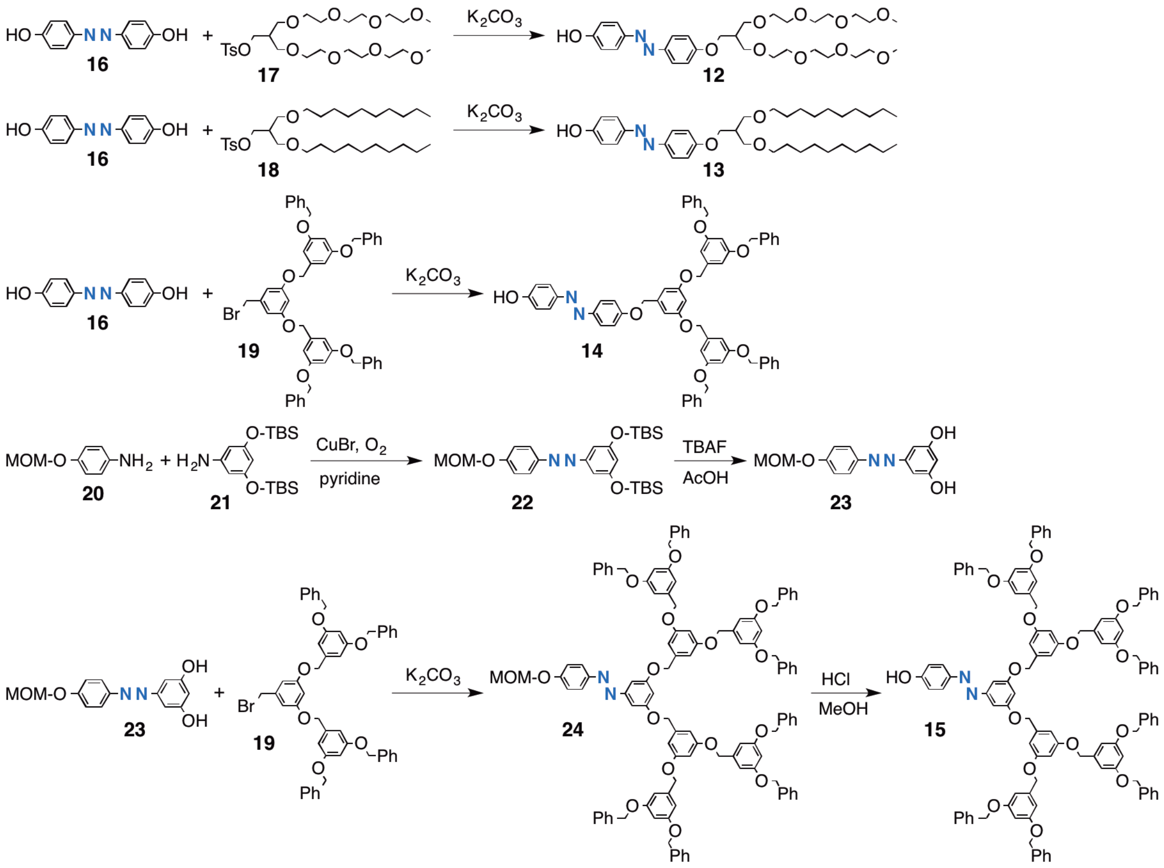
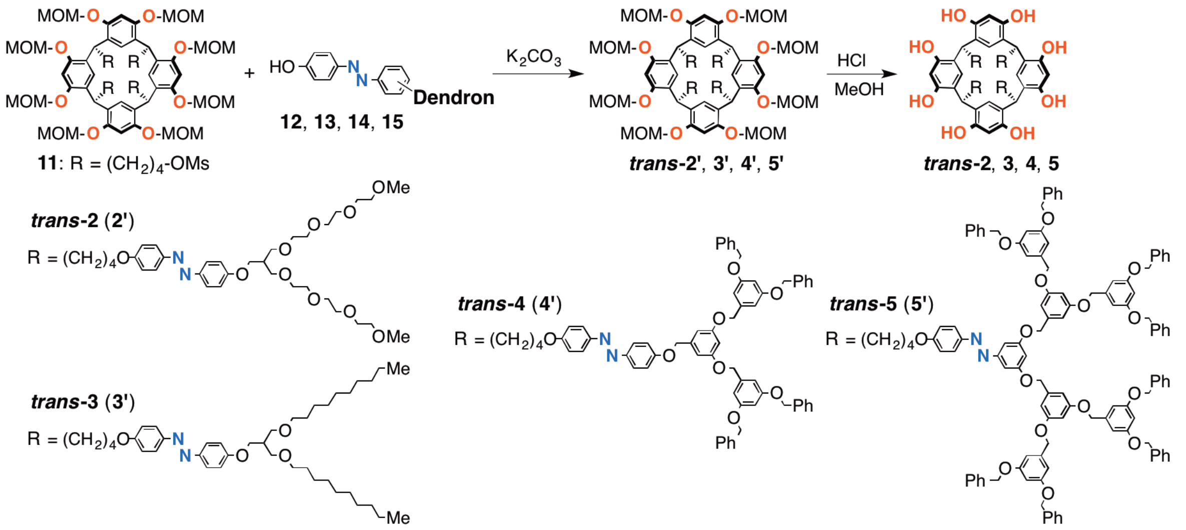


Scheme S1 Synthesis of MOM-protected calix[4]resorcinarene **11**.



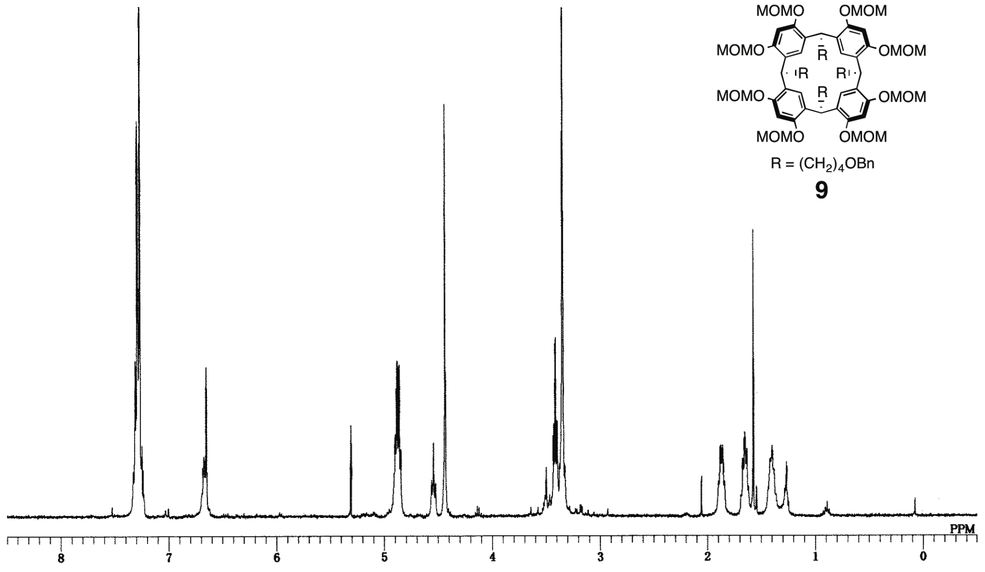
Scheme S2 Synthesis of hydroxyazobenzene dendron conjugates **12**–**15**.

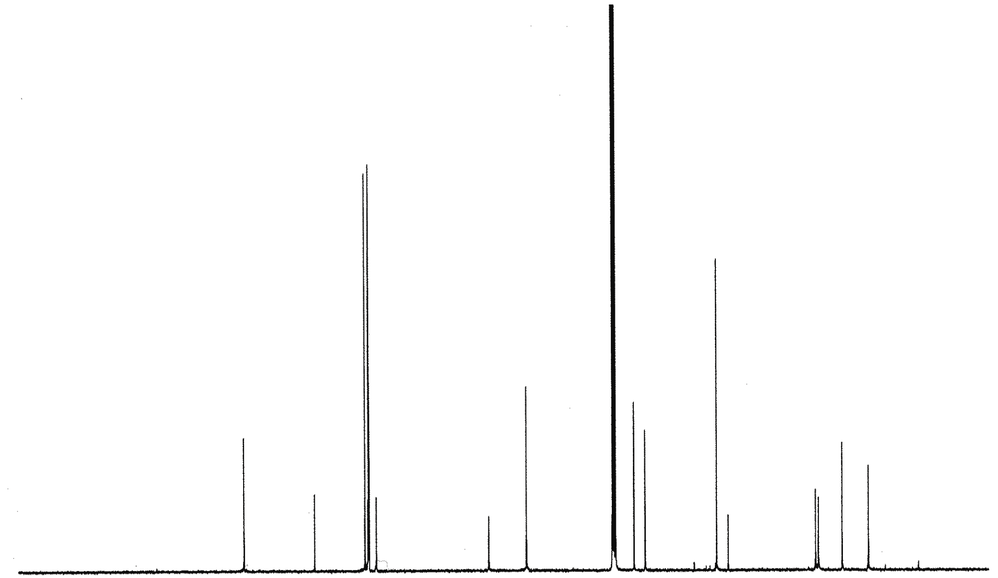


Scheme S3 Synthesis of calix[4]resorcinarenes bearing azobenzene dendron side chains (host molecules) *trans*-**2**–**5**.

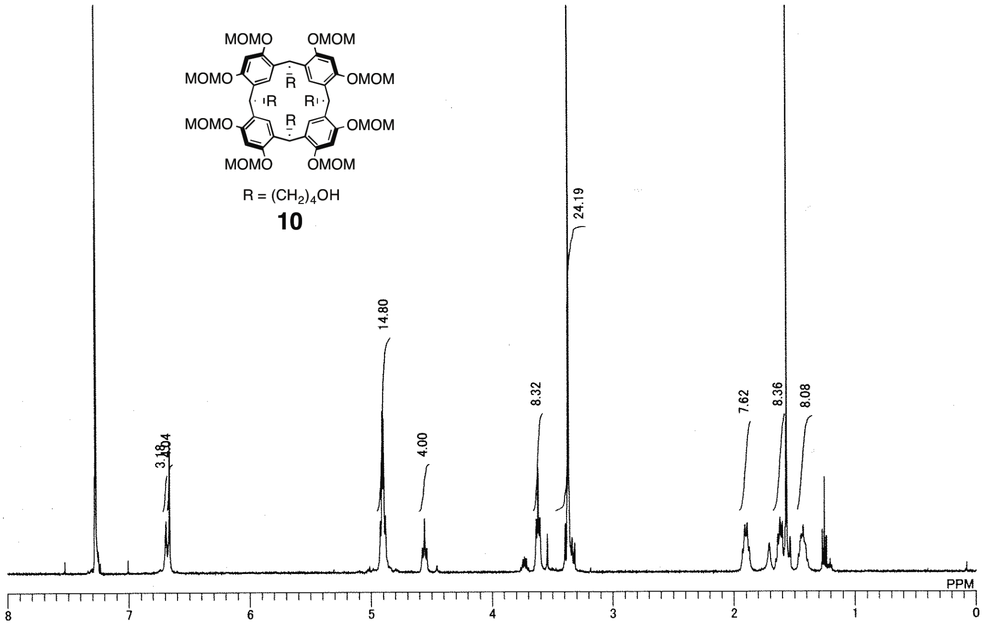
General. THF was distilled from sodium-benzophenone ketyl, and CH_2Cl_2, DMF, Et_3N, and *i*-Pr_2EtN were distilled from CaH_2 under an argon atmosphere. The other solvents and all commercially available reagents were used without any purification. Recycling preparative HPLC was performed on a Japan Analytical Industry LC-9204 using polystyrene gel columns (JAIGEL 1H and 2H) with $CHCl_3$ as an eluent. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a JEOL JNM-AL400 spectrometer. High resolution FD-TOF-MS, ESI-TOF-MS, and MALDI-TOF-MS were performed on a JEOL JMS-T100GCV, a JEOL JMS-T100LP, and a JEOL JMS-S3000, respectively. UV–vis absorption spectra were measured on a Shimadzu UV-2450. Photoirradiation was conducted with a 300 W Xe lamp through a color filter for 350 nm or 450 nm light with ASAHI SPECTRA MAX-302.

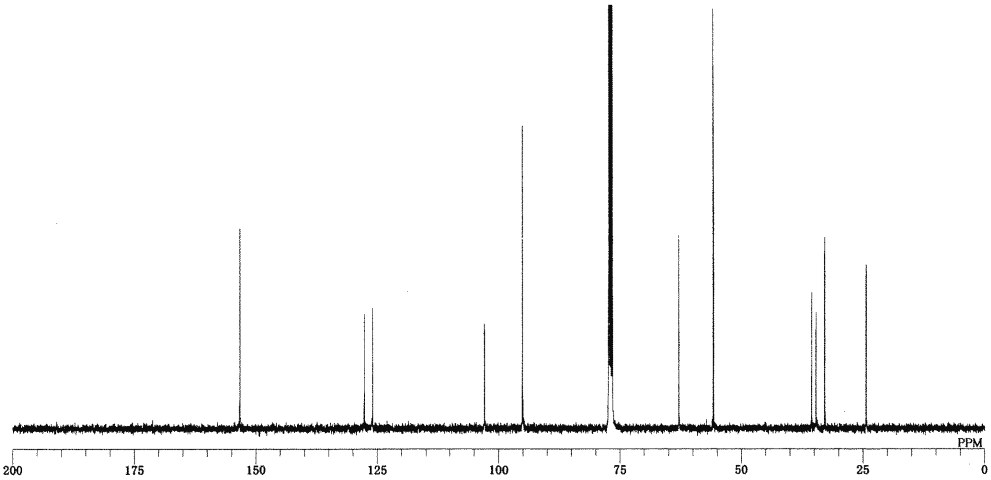
Compound 9. To a solution of **8**[1] (3.38 g, 2.97 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C under Ar were added dry *i*-Pr_2EtN (20 mL, 115 mmol) and chloromethyl methyl ether (7.1 mL, 93 mmol).[2] The reaction mixture was stirred at room temperature for 24 h and then at 40 °C for 24 h. After evaporation of solvents, the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (1:1) to give **9** as a pale yellow viscous oil (3.60 g, 81% yield). ^{1}H NMR ($CDCl_3$) δ 7.31-7.24 (m, 20H), 6.68 (s, 4H), 6.66 (s, 4H), 4.90-4.85 (m, 16H), 4.55 (t, J = 7.3 Hz, 4H), 4.44 (s, 8H), 3.43-3.40 (m, 8H), 3.35 (s, 24H), 1.89-1.86 (m, 8H), 1.67-1.63 (m, 8H), 1.42-1.40 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 153.59, 138.99, 128.61, 128.01, 127.86, 127.72, 126.28, 103.07, 95.35, 73.16, 70.86, 56.20, 35.64, 35.04, 30.16, 24.49; FD-TOF-MS *m*/*z* calcd for $C_{88}H_{112}O_{20}$: 1488.7747 [M]$^+$, found: 1488.7772.



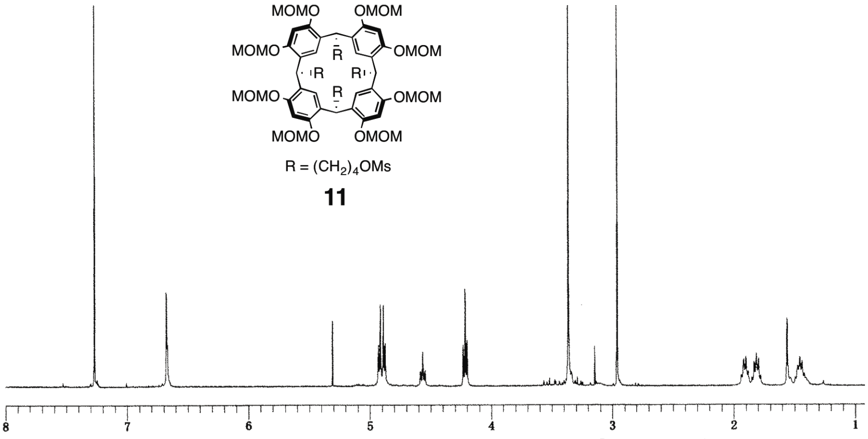


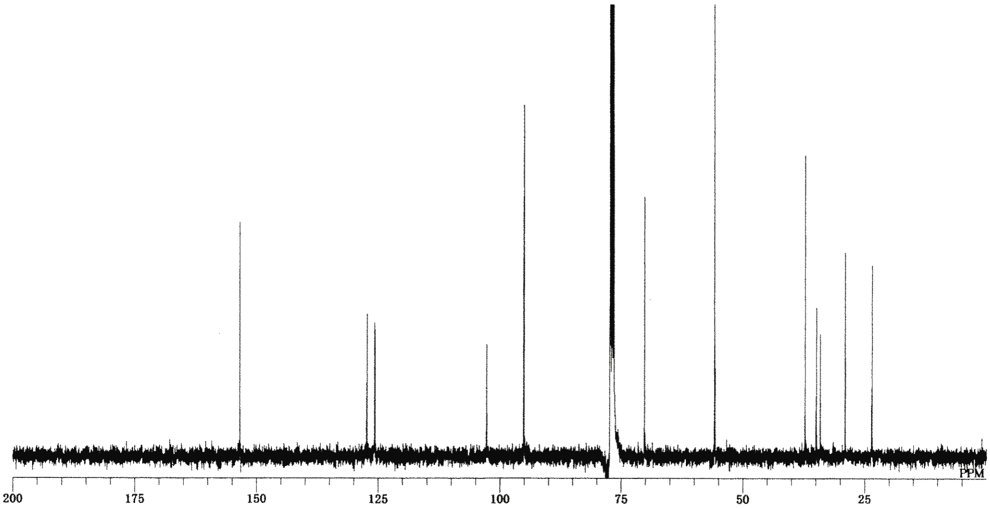
Compound 10. A mixture of **9** (3.60 g, 2.42 mmol) and 10% Pd/C (515 mg) in EtOAc (300 mL) was stirred under H_2 at room temperature for 48 h. The reaction mixture was filtered through Celite pad. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel eluted with EtOH–CH_2Cl_2 (1:12) to give **10** as an off-white solid (1.53 g, 56% yield). Mp. 125-126 °C; ^{1}H NMR ($CDCl_3$) δ 6.69 (s, 4H), 6.66 (s, 4H), 4.92-4.88 (m, 16H), 4.56 (t, *J* = 7.3 Hz, 4H), 3.62 (t, *J* = 6.3 Hz, 8H), 3.37 (s, 24H), 1.91-1.87 (m, 8H), 1.70 (s, 4H), 1.64-1.60 (m, 8H), 1.46-1.42 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 153.29, 127.66, 125.94, 102.92, 95.11, 62.92, 55.83, 35.57, 34.66, 32.89, 24.35; FD-TOF-MS *m*/*z* calcd for $C_{60}H_{88}O_{20}$: 1128.5869 $[M]^+$, found: 1128.5887.



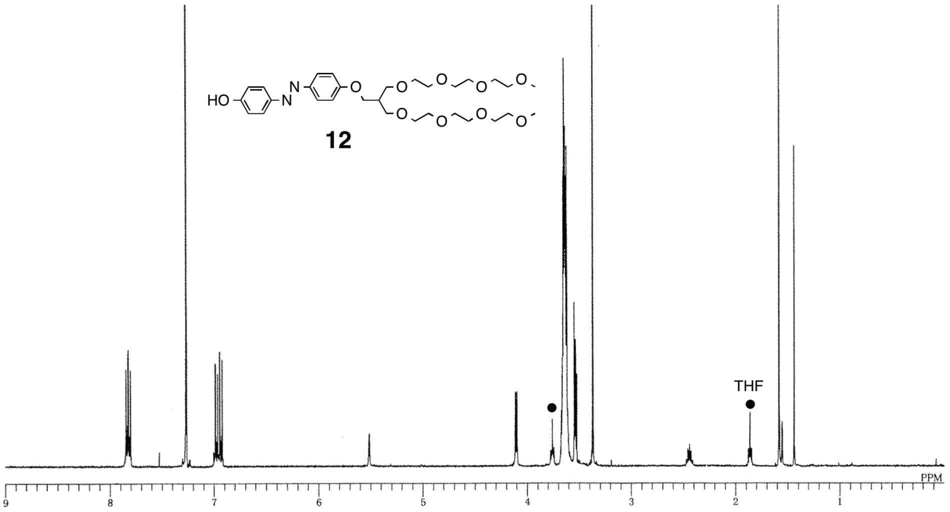


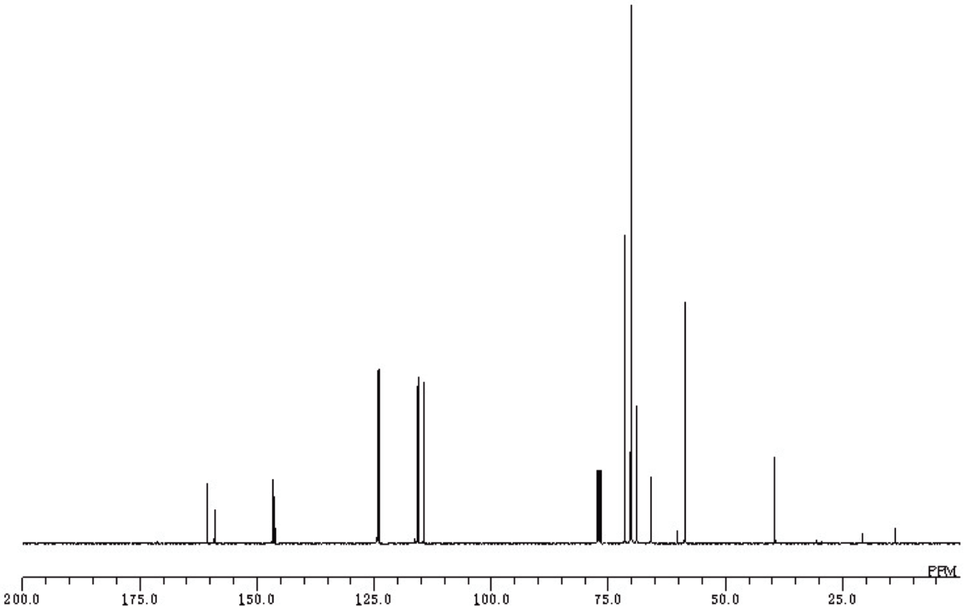
Compound 11. To a solution of **10** (601 mg, 0.532 mmol) in dry CH_2Cl_2 (50 mL) at 0 °C under Ar were added dry Et_3N (1.50 mL, 10.8 mmol) and methanesulfonyl chloride (0.25 mL, 3.2 mmol).[3] The reaction mixture was stirred at room temperature for 3 h, and then quenched and acidified (pH = 3~4) with 1 M HCl at 0 °C and extracted with CH_2Cl_2. The organic layer was washed with sat. aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was dried in vacuo to give **11** as a pale yellow viscous solid (863 mg, quant), which was used to the next reaction without further purification. ^{1}H NMR ($CDCl_3$) δ 6.68 (s, 4H), 6.67 (s, 4H), 4.92 (d, J = 6.3 Hz, 8H), 4.88 (d, J = 6.3 Hz, 8H), 4.57 (t, J = 7.3 Hz, 4H), 4.22 (t, J = 6.8 Hz, 4H), 3.37 (s, 24H), 2.96 (s, 12H), 1.94-1.88 (m, 8H), 1.85-1.78 (m, 8H), 1.50-1.42 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 153.43, 127.30, 125.71, 102.73, 95.07, 70.27, 55.86, 37.27, 34.96, 34.16, 29.07, 23.57; FD-TOF-MS m/z calcd for $C_{64}H_{96}O_{28}S_4$: 1440.4971 $[M]^+$, found: 1440.4999.



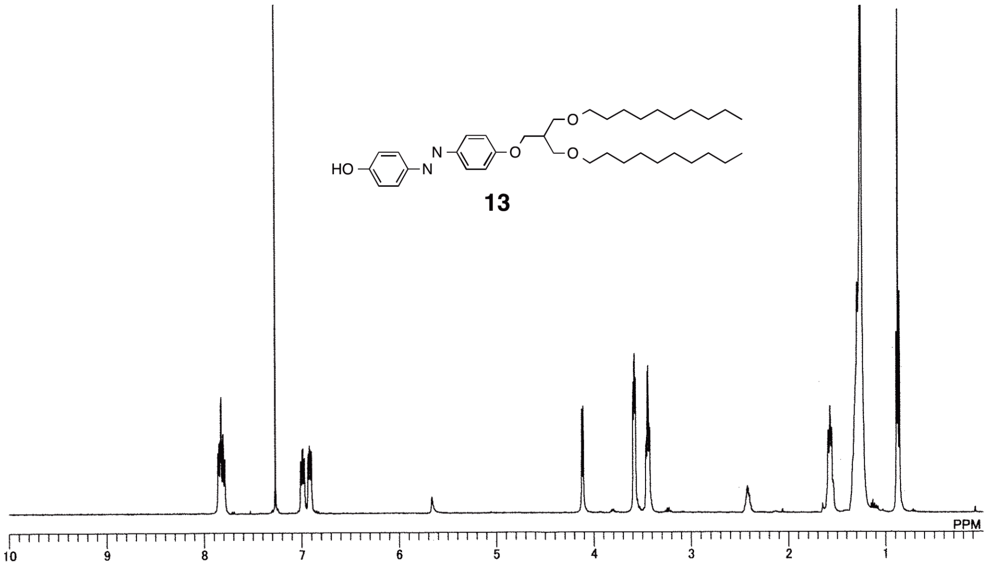


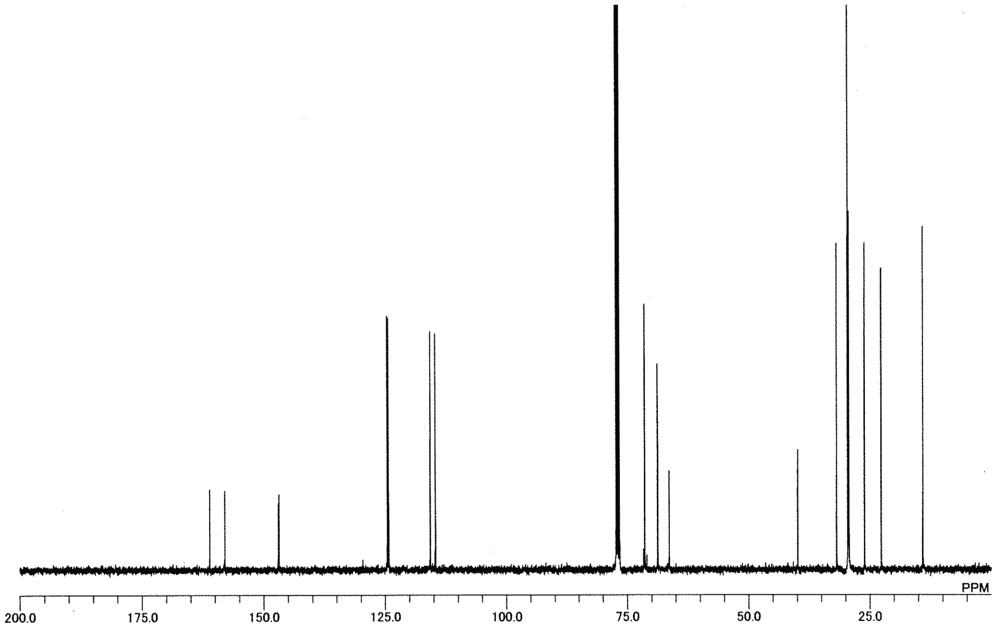
Compound 12. A mixture of **16**[4] (2.67 g, 12.5 mmol), **17**[5] (2.30 g, 4.16 mmol), and K_2CO_3 (1.73 g, 12.5 mmol) in dry DMF (30 mL) under Ar was stirred at 90 °C for 14 h. The reaction mixture was acidified (pH = 3~4) with 2 M HCl at 0 °C and extracted with EtOAc. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane = 1:1, subsequently EtOAc, and finally EtOAc–EtOH = 1:1 to give **12** as an orange oil (1.89 g, 76% yield). ^{1}H NMR ($CDCl_3$) δ 7.85-7.80 (m, 4H), 6.99 (d, J = 9.3 Hz, 2H), 6.94 (d, J = 9.3 Hz, 2H), 5.52 (s, 1H), 4.11 (d, J = 5.7 Hz, 2H), 3.67-3.62 (m, 24H), 3.55-3.53 (m, 4H), 3.37 (s, 6H), 2.44 (sept, J = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 161.13, 157.89, 147.15, 146.90, 124.52, 124.30, 115.72, 114.70, 71.90, 70.61, 70.51, 70.49, 69.28, 66.31, 60.03, 59.01, 39.89; FD-TOF-MS m/z calcd for $C_{30}H_{46}N_2O_{10}$: 594.3152 [M]$^+$, found: 594.3169.



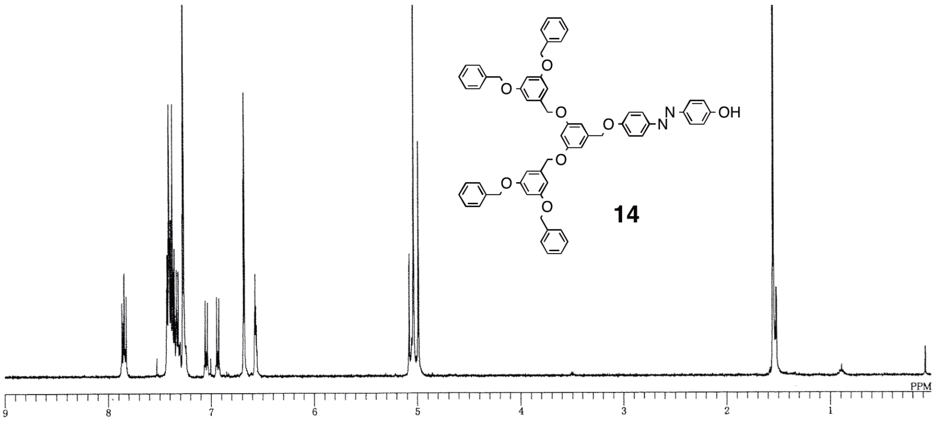


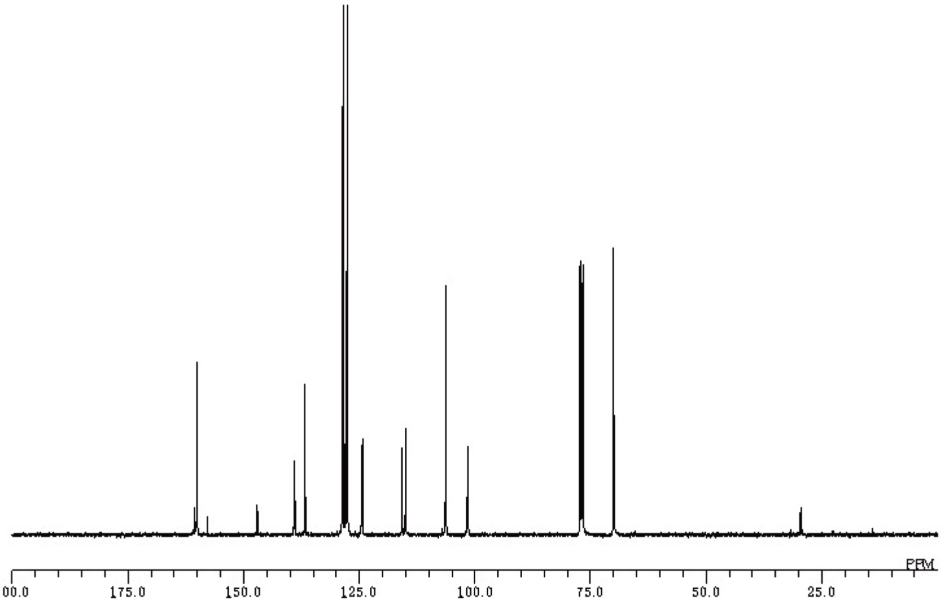
Compound 13. A mixture of **16**[4] (3.21 g, 15.0 mmol), **18**[5] (2.70 g, 5.00 mmol), and K_2CO_3 (2.07 g, 15.0 mmol) in dry DMF (30 mL) under Ar was stirred at 90 °C for 14 h. The reaction mixture was acidified (pH = 3~4) with 2 M HCl at 0 °C and extracted with EtOAc. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (1:9) to give **13** as an orange solid (1.96 g, 67% yield). Mp. 63-64 °C; ^{1}H NMR ($CDCl_3$) δ 7.86-7.79 (m, 4H), 6.99 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.67 (s, 1H), 4.12 (d, J = 5.9 Hz, 2H), 3.59 (d, J = 5.9 Hz, 4H), 3.44 (t, J = 6.8 Hz, 4H), 2.42 (sept, J = 5.9 Hz, 1H), 1.57 (quint, J = 6.8 Hz, 4H), 1.36-1.21 (m, 28H), 0.88 (t, J = 6.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 161.08, 157.99, 146.99, 146.84, 124.51, 124.26, 115.69, 114.65, 77.21, 71.46, 68.76, 66.42, 39.90, 31.88, 29.62, 29.57, 29.46, 29.32, 26.13, 22.66, 14.11; FD-TOF-MS m/z calcd for $C_{36}H_{58}N_2O_4$: 582.4397 [M]$^+$, found: 582.4411.





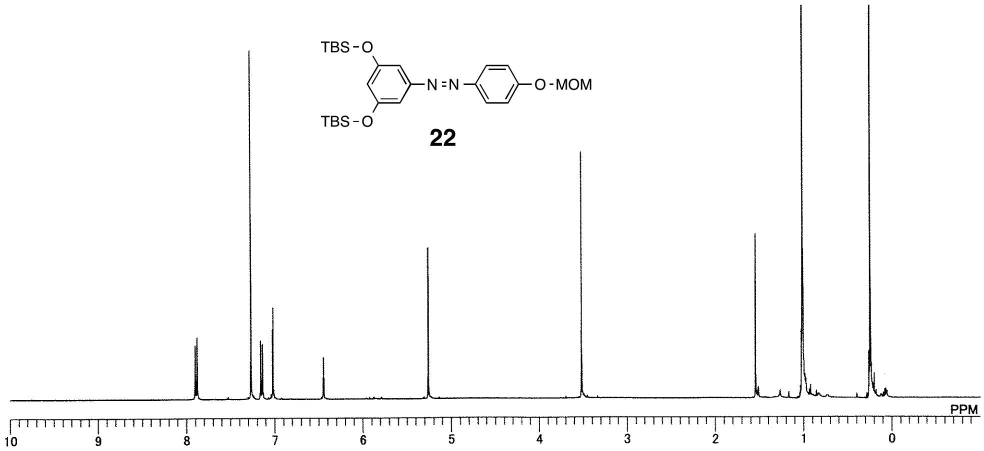
Compound 14. A mixture of **16**[4] (233 mg, 1.09 mmol), **19**[6] (439 mg, 0.543 mmol), and K_2CO_3 (151 mg, 1.09 mmol) in dry DMF (10 mL) under Ar was stirred at 50 °C for 24 h. The reaction mixture was acidified (pH = 3~4) with 2 M HCl at 0 °C and extracted with CH_2Cl_2. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane = 1:3 and then EtOAc to give **14** as an orange solid (300 mg, 59% yield). Mp. 56-57 °C; ^{1}H NMR ($CDCl_3$) δ 7.87-7.83 (m, 4H), 7.43-7.32 (m, 20H), 7.06 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.69 (s, 2H), 6.68 (s, 4H), 6.56 (s, 3H), 5.08 (s, 2H), 5.04 (s, 8H), 4.99 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 163.67, 160.13, 153.98, 147.15, 139.12, 138.98, 136.95, 136.70, 128.59, 128.02, 127.57, 127.00, 124.59, 124.35, 118.55, 115.71, 115.07, 103.72, 106.32, 101.51, 70.07, 69.98; FD-TOF-MS m/z calcd for $C_{61}H_{52}N_2O_8$: 940.3724 [M]$^+$, found: 940.3744.

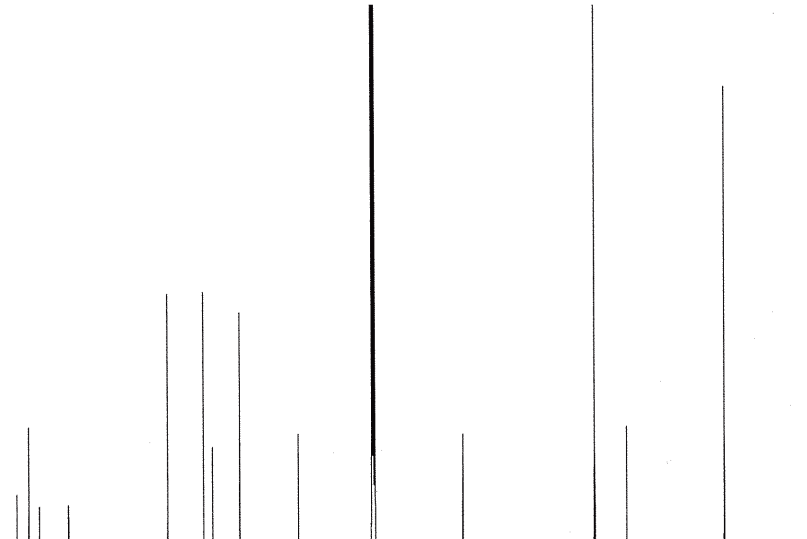




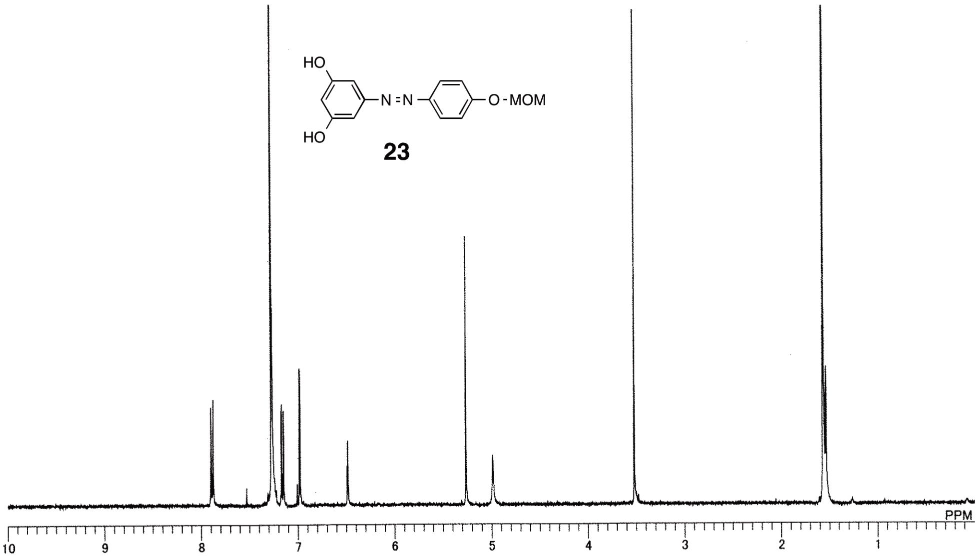
Compound 21. To a solution of 3,5-dihydroxyaniline hydrochloride[7] (3.33 g, 20.6 mmol) and imidazole (11.2 g, 165 mmol) in dry THF (75 mL) under Ar was added a solution of *t*-BuMe$_2$SiCl (12.4 g, 82.4 mmol) in dry THF (75 mL). The resulting mixture was stirred at room temperature for 48 h. After evaporation of solvent, the residue was partitioned between CH$_2$Cl$_2$ and H$_2$O. The organic layer was washed with H$_2$O and brine and dried over Na$_2$SO$_4$. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with hexane and then CH$_2$Cl$_2$–hexane (1:3) to give **21** as a pale brown solid. ^{1}H NMR (CDCl$_3$) δ 5.84 (d, J = 2.0 Hz, 2H), 5.79 (t, J = 2.0 Hz, 1H), 3.54 (s, 2H), 0.97 (s, 18H), 0.18 (s, 12H); FD-TOF-MS *m*/*z* calcd for C$_{18}$H$_{35}$NO$_2$Si$_2$: 353.2206 [M]$^+$, found: 353.2227.

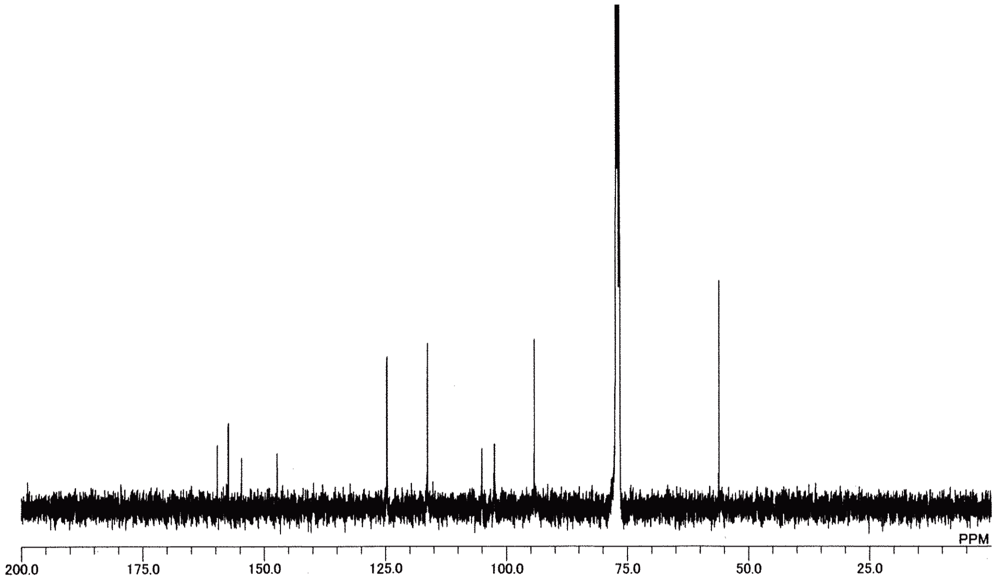
Compound 22. To a mixture of **20** (1.28 g, 8.36 mmol), **21** (14.8 g, 41.8 mmol), and CuBr (0.600 g, 4.18 mmol) were added toluene (100 mL) and pyridine (1.0 mL, 12.5 mmol).[8] The resulting mixture was stirred at 60 °C for 24 h under O$_2$. After cooling to room temperature, the reaction mixture was filtered through Celite pad. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel eluted with CH$_2$Cl$_2$–hexane (1:5 to 1:2.5) to give **22** as an orange viscous solid (1.16 g, 28% yield). ^{1}H NMR (CDCl$_3$) δ 7.89 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.02 (s, 2H), 6.45 (s, 1H), 5.26 (s, 2H), 3.52 (s, 3H), 1.01 (s, 18H), 0.25 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 159.58, 156.83, 154.40, 147.59, 124.62, 116.29, 114.22, 107.92, 94.32, 56.15, 25.73, 25.65, 25.46, 18.19, –4.27; FD-TOF-MS *m*/*z* calcd for C$_{26}$H$_{42}$N$_2$O$_4$Si$_2$: 502.2683 [M]$^+$, found: 502.2701.



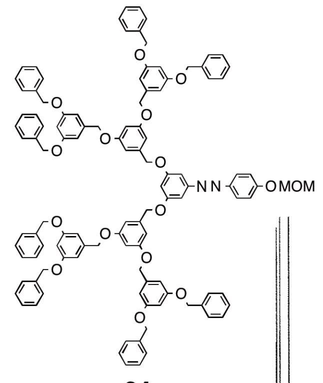


Compound 23. To a solution of **22** (1.16 g, 2.31 mmol) in THF (20 mL) at 0 °C under Ar were added AcOH (0.40 mL, 7.0 mmol) and 1 M *n*-Bu_4NF in THF (6.9 mL, 6.9 mmol). The reaction mixture was stirred at 0 °C for 30 min, and then poured into sat. aqueous NH_4Cl at 0 °C and extracted with EtOAc. The organic layer was washed with sat. aqueous $NaHCO_3$, H_2O, and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (1:2) to give **23** as an orange solid (429 mg, 68% yield). Mp. 136-137 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 6.99 (s, 2H), 6.49 (s, 1H), 5.26 (s, 2H), 4.99 (s, 2H), 3.52 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.68, 157.41, 154.68, 147.35, 124.70, 116.31, 105.02, 102.44, 94.27, 56.17; FD-TOF-MS *m/z* calcd for $C_{14}H_{14}N_2O_4$: 274.0954 [M]$^+$, found: 274.0974.





Compound 24. A mixture of **19**^{6} (2.06 g, 2.51 mmol), **23** (230 mg, 0.839 mmol), and K_2CO_3 (462 mg, 3.35 mmol) in dry DMF (15 mL) under Ar was stirred at 50 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2 and filtered, and the filtrate was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (3:1) to give **24** as an orange solid (1.38 g, 95% yield). Mp. 123-124 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, J = 8.8 Hz, 2H), 7.41-7.30 (m, 40H), 7.20 (d, J = 2.0 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 6.73 (s, 1H), 6.70-6.68 (m, 12H), 6.57-6.55 (m, 6H), 5.24 (s, 2H), 5.05 (s, 4H), 5.02 (s, 16H), 4.98 (s, 8H), 3.51 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.15, 160.06, 159.75, 154.50, 147.45, 139.21, 139.07, 136.77, 128.54, 128.32, 127.96, 127.53, 124.74, 116.35, 106.49, 106.37, 104.79, 101.95, 101.70, 101.63, 94.30, 70.16, 70.08, 70.00, 56.20; FD-TOF-MS m/z calcd for $C_{112}H_{98}N_2O_{16}$: 1727.6950 $[M]^+$, found: 1727.6980.



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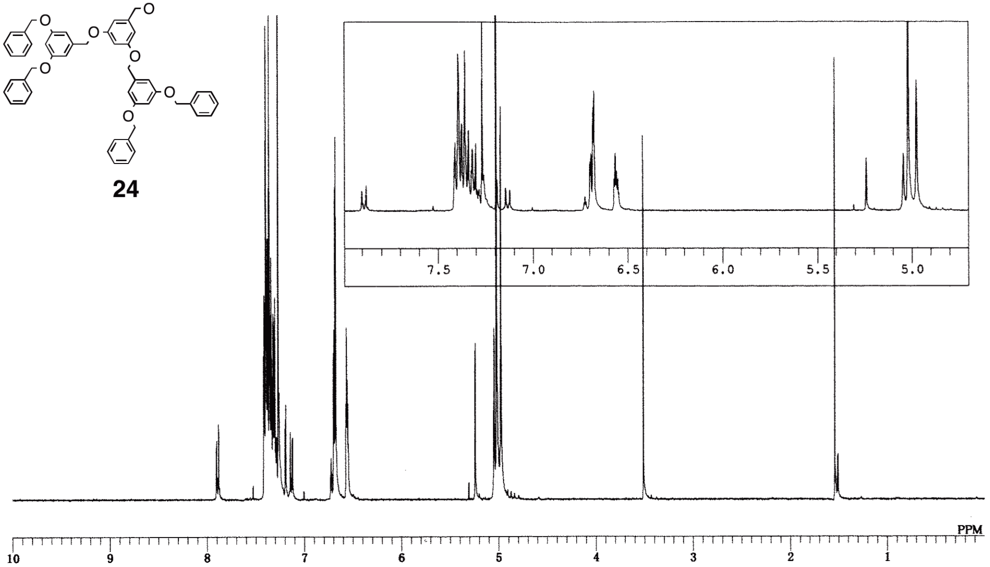
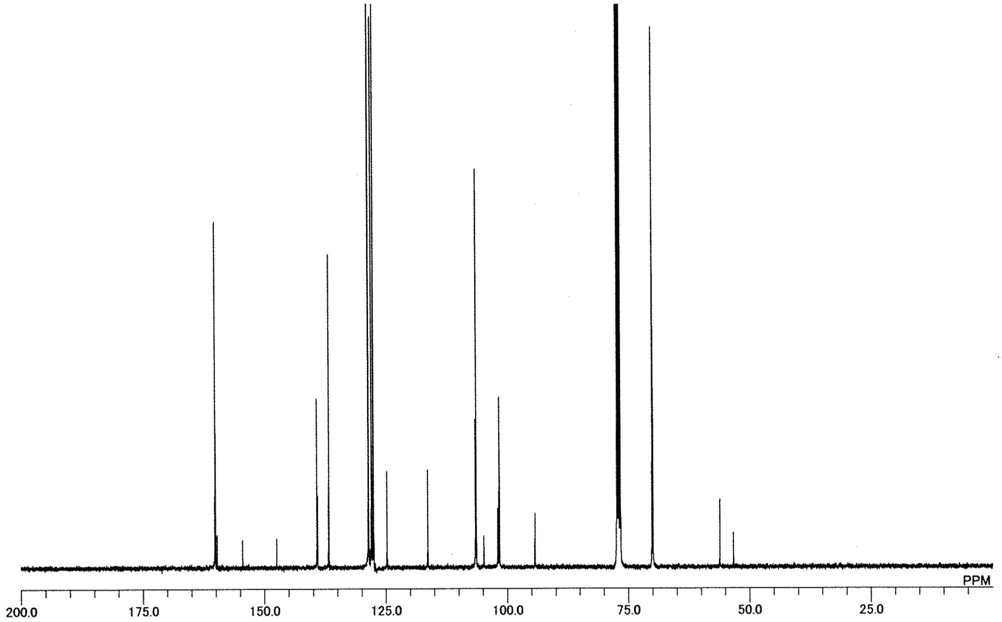
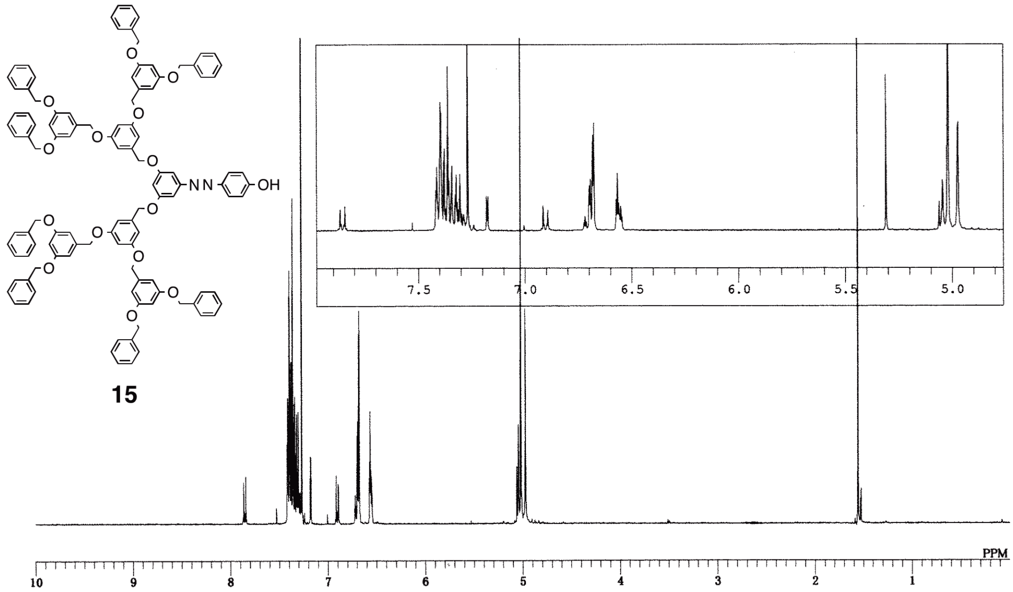




Compound 15. To a solution of **24** (1.38 g, 0.799 mmol) in MeOH (4 mL) and $CHCl_3$ (12 mL) was added a few drops of conc. HCl. The resulting mixture was stirred at 65 °C for 30 min under Ar. After evaporation of solvents, the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with CH_2Cl_2 to give **15** as an orange solid (1.28 g, 95% yield). Mp. 60-61 °C; ^1H NMR ($CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 7.41-7.29 (m, 40H), 7.18 (d, J = 2.4 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.72 (s, 1H), 6.70 (s, 4H), 6.68 (s, 8H), 6.57 (t, J = 2.4 Hz, 4H), 6.55 (s, 2H), 5.06 (s, 1H), 5.04 (s, 4H), 5.02 (s, 16H), 4.97(s, 8H); ^{13}C NMR ($CDCl_3$) δ 160.12, 160.04, 158.45, 154.45, 146.82, 139.18, 139.09, 136.74, 128.54, 127.96, 127.53, 125.07, 115.78, 106.49, 106.37, 104.75, 101.89, 101.62, 70.07, 69.98; FD-TOF-MS m/z calcd for $C_{110}H_{94}N_2O_{15}$: 1683.6688 $[M]^+$, found: 1683.6717.



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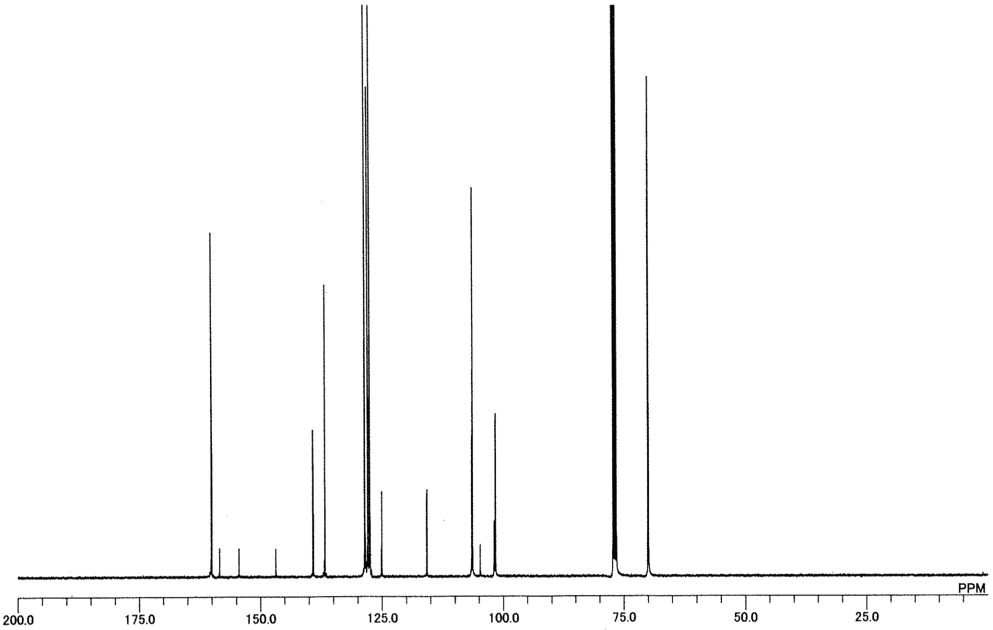
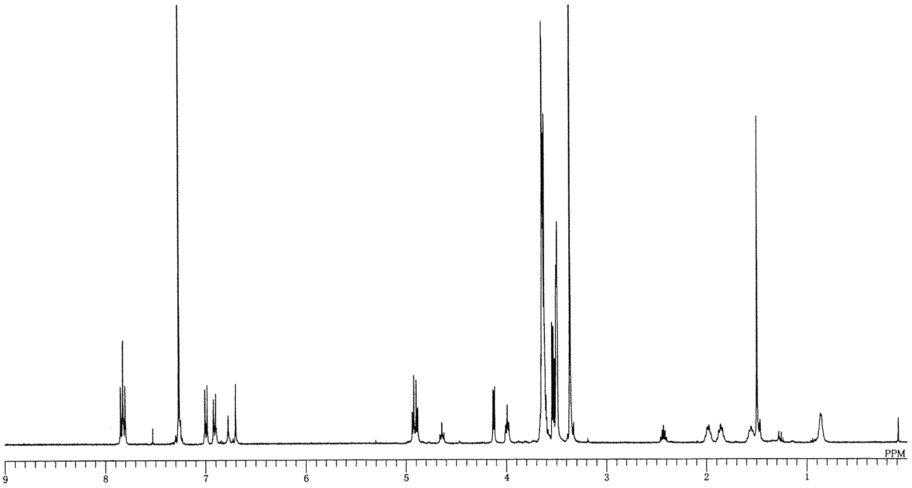
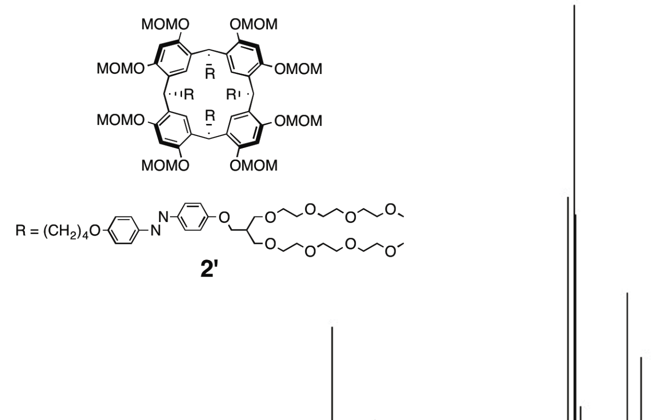


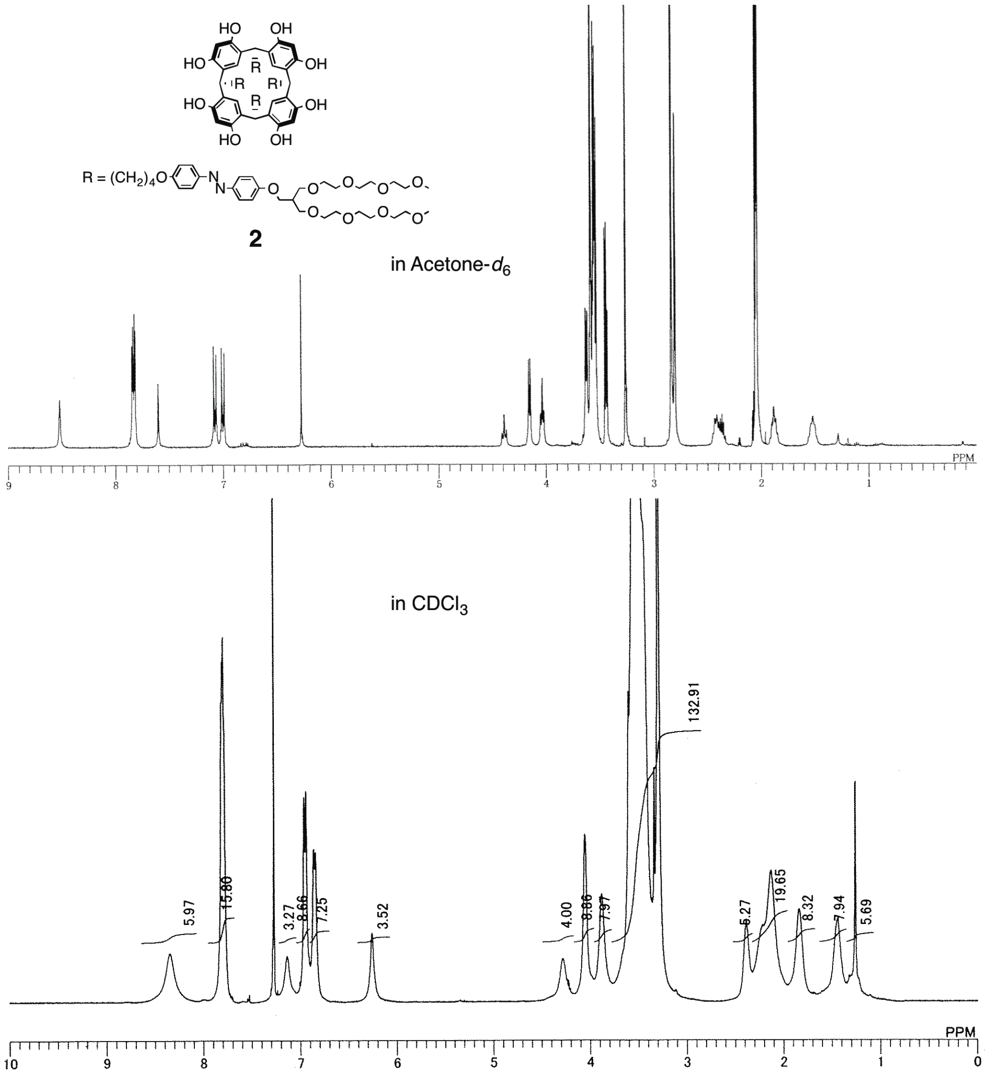
Compound 2'. A mixture of **11** (574 mg, 0.398 mmol), **12** (1.89 g, 3.18 mmol), and K_2CO_3 (879 mg, 6.36 mmol) in dry DMF (20 mL) under Ar was stirred at 90 °C for 72 h. The reaction mixture was diluted with EtOAc and filtered, and the filtrate was partitioned between EtOAc and H_2O. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–EtOH (4:1 to 3:1) to give **2'** as an orange viscous oil (931 mg, 68% yield). ^1H NMR ($CDCl_3$) δ 7.85-7.80 (m, 16H), 7.01 (d, J = 8.8 Hz, 8H), 6.92 (d, J = 8.8 Hz, 8H), 6.78 (s, 4H), 6.70 (s, 4H), 4.94-4.88 (m, 16H), 4.65 (t, J = 7.3 Hz, 4H), 4.14 (d, J = 5.6 Hz, 8H), 3.99 (t, J = 6.8 Hz, 8H), 3.65-3.62 (m, 96H), 3.54-3.51 (m, 16H), 3.37 (s, 48H), 2.43 (sept, J = 5.6 Hz, 4H), 1.98-1.93 (m, 8H), 1.88-1.83 (m, 8H), 1.58-1.53 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 161.19, 161.10, 153.40, 148.26, 146.90, 146.48, 125.96, 124.28, 119.78, 115.71, 114.60, 102.57, 95.07, 71.93, 70.65, 70.62, 70.52, 70.49, 69.28, 66.31, 59.01, 55.83, 53.85, 39.94, 34.96, 34.16, 29.25, 23.65; ESI-TOF-MS *m/z* calcd for $C_{180}H_{264}N_8O_{56}Na_2$: 1740.3943 $[M + 2Na]^{2+}$, found: 1740.3964.

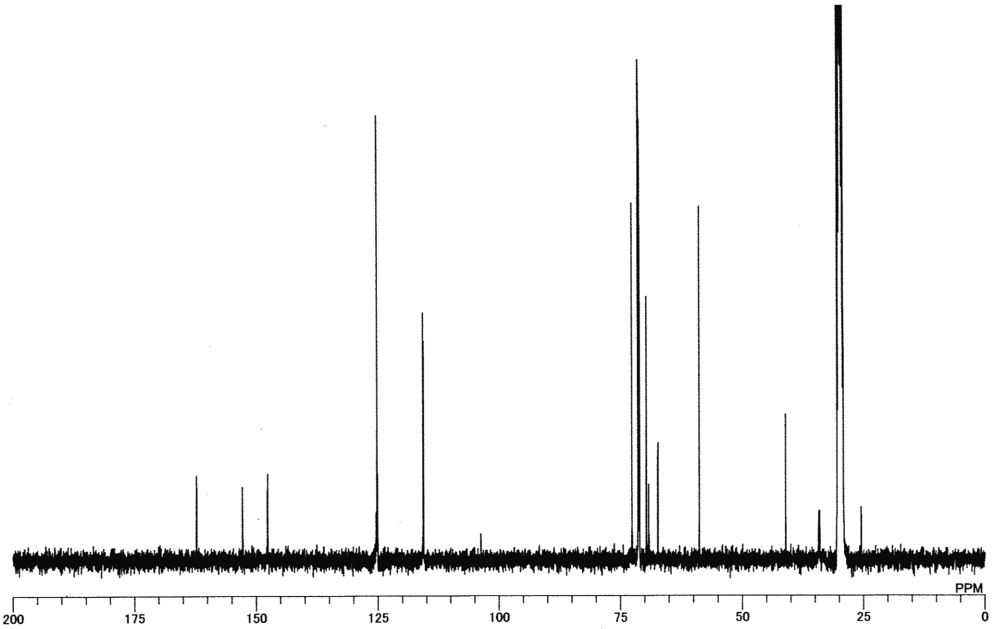




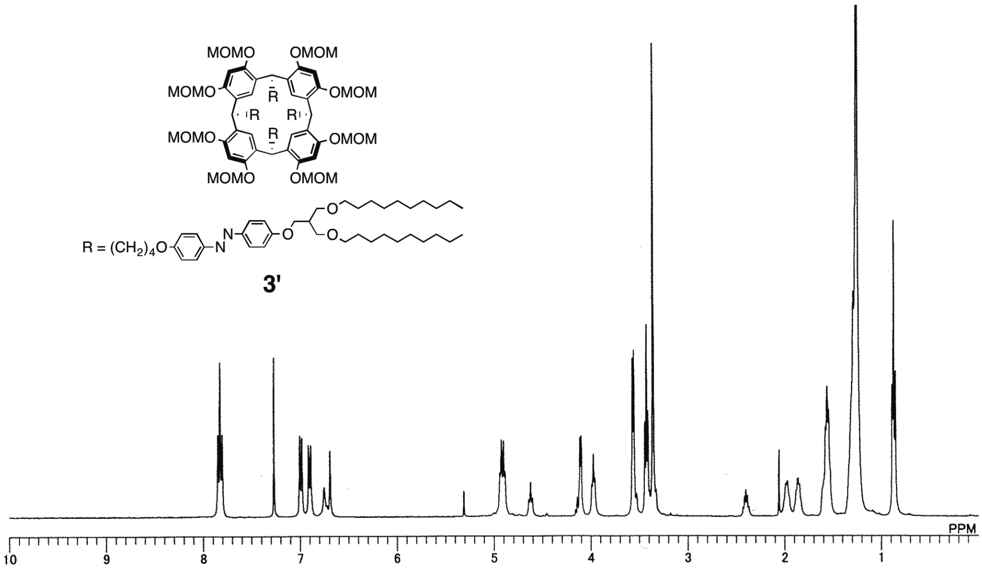
2'

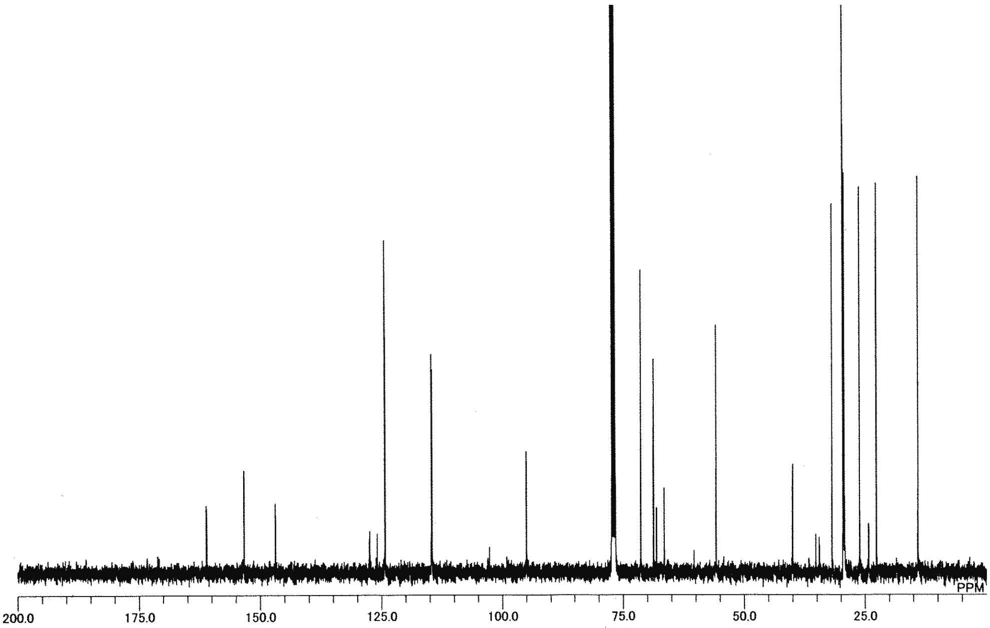
Compound 2. To a solution of **2'** (135 mg, 0.0395 mmol) in MeOH (5 mL) was added a drop of conc. HCl. The resulting mixture was stirred at 65 °C for 30 min under Ar. After evaporation of solvent, the residue was partitioned between EtOAc and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with EtOAc–EtOH (1:1 to 1:2) to give **2** as an orange viscous solid (75.0 mg, 62% yield). ^{1}H NMR (acetone-d_6) δ 8.52 (s, 8H), 7.85-7.82 (m, 16H), 7.61 (s, 4H), 7.09 (d, J = 9.3 Hz, 8H), 7.02 (d, J = 9.3 Hz, 8H), 6.28 (s, 4H), 4.39 (t, J = 7.3 Hz, 4H), 4.16 (d, J = 5.6 Hz, 8H), 4.03 (t, J = 6.8 Hz, 8H), 3.63-3.54 (m, 96H), 3.46-3.43 (m, 16H), 3.37 (s, 24H), 2.46-2.36 (m, 12H), 1.90-1.88 (m, 8H), 1.54-1.51 (m, 8H); ^{1}H NMR ($CDCl_3$) δ 8.35 (brs, 8H), 7.79 (brs, 16H), 7.14 (brs, 4H), 6.95 (d, J = 8.3 Hz, 8H), 6.85 (d, J = 8.3 Hz, 8H), 6.26 (brs, 4H), 4.28 (brs, 4H), 4.06 (brs, 8H), 3.88 (brs, 8H), 3.82-3.25 (m, 136H), 2.39 (brs, 4H), 2.14 (brs, 8H), 1.84 (brs, 8H), 1.44 (brs, 8H); ^{13}C NMR (acetone-d_6) δ 162.25, 162.17, 152.81, 147.67, 147.58, 125.34, 125.13, 115.72, 115.60, 103.78、 72.64, 71.42, 71.30, 71.24, 71.11, 71.07, 69.67, 69.18, 67.29, 58.80, 41.08, 34.27, 34.08, 25.53; ESI-TOF-MS m/z calcd for $C_{164}H_{232}N_8O_{48}Na_2$: 1564.7911 [M + 2Na]$^{2+}$, found: 1564.7928.



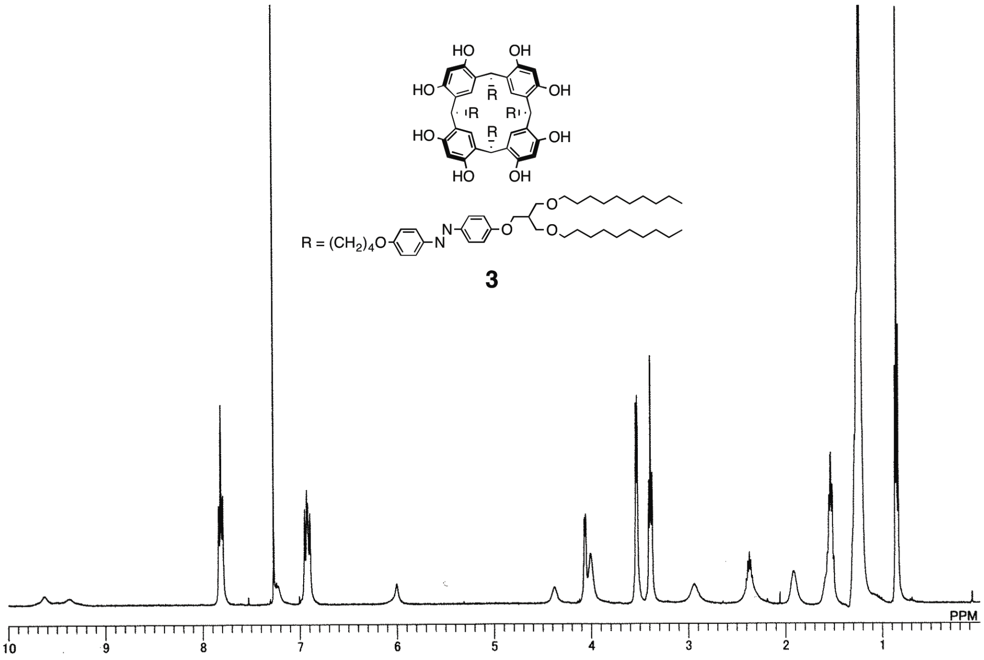

PPM
200
175
150
125
100
75
50
25
0

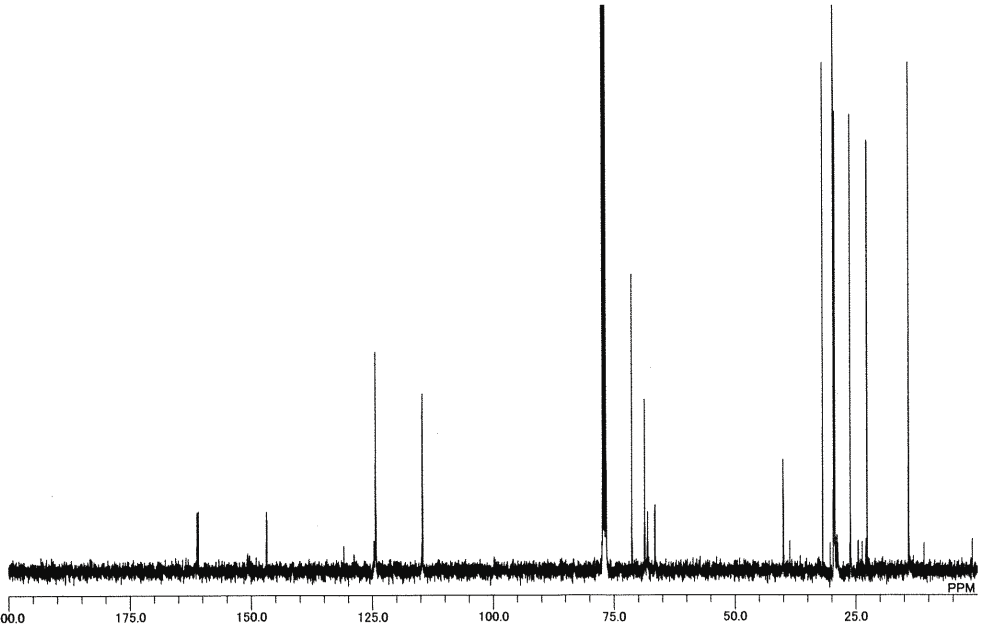
Compound 3’. A mixture of **11** (346 mg, 0.240 mmol), **13** (1.13 g, 1.92 mmol), and K_2CO_3 (530 mg, 3.84 mmol) in dry DMF (15 mL) under Ar was stirred at 90 °C for 72 h. The reaction mixture was diluted with EtOAc and filtered, and the filtrate was partitioned between EtOAc and H_2O. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (1:9 to 1:5 to 1:1) and finally EtOAc to give **3’** as an orange solid (617 mg, 74% yield). Mp. 55-56 °C; ^{1}H NMR ($CDCl_3$) δ 7.83 (t, J = 8.8 Hz, 16H), 6.99 (d, J = 8.8 Hz, 8H), 6.90 (d, J = 8.8 Hz, 8H), 6.75 (s, 4H), 6.69 (s, 4H), 4.94-4.89 (m, 16H), 4.62 (t, J = 7.3 Hz, 4H), 4.12 (d, J = 5.9 Hz, 8H), 3.98 (t, J = 6.3 Hz, 8H), 3.56 (d, J = 5.9 Hz, 16H), 3.43 (t, J = 6.6 Hz, 16H), 3.36 (s, 24H), 2.40 (sept, J = 5.9 Hz, 4H), 1.97 (brs, 8H), 1.86 (brs, 8H), 1.60-1.55 (m, 24H), 1.35-1.21 (m, 112H), 0.87 (t, J = 6.6 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 161.12, 161.03, 153.34, 146.90, 146.85, 127.47, 125.92, 124.26, 114.66, 114.52, 102.67, 95.00, 71.37, 68.75, 68.15, 66.57, 55.83, 40.06, 35.25, 34.54, 31.88, 29.63, 26.58, 29.48, 29.33, 29.25, 26.16, 24.29, 22.66, 14.11; ESI-TOF-MS *m/z* calcd for $C_{204}H_{312}N_8O_{32}Na_2$: 1717.1448 $[M + 2Na]^{2+}$, found: 1717.1489.



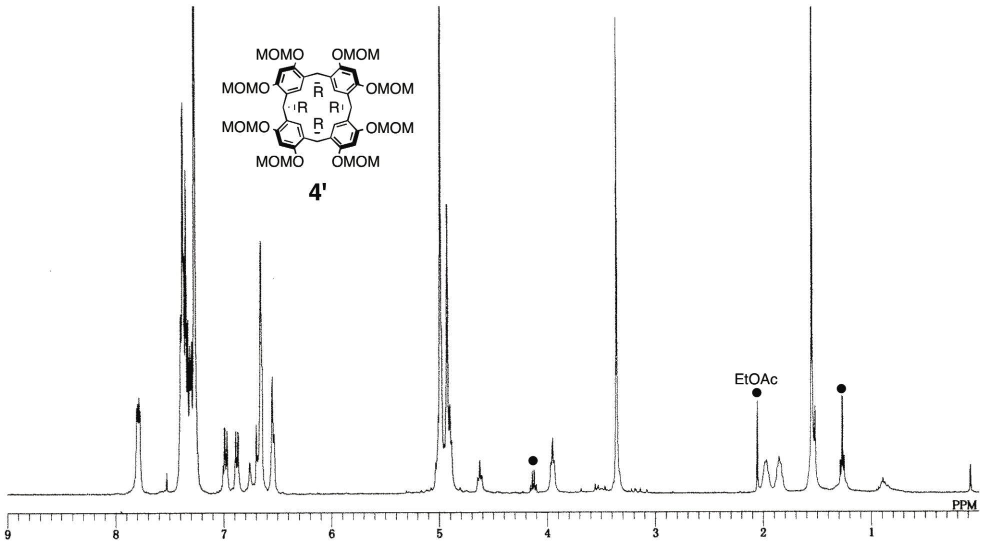


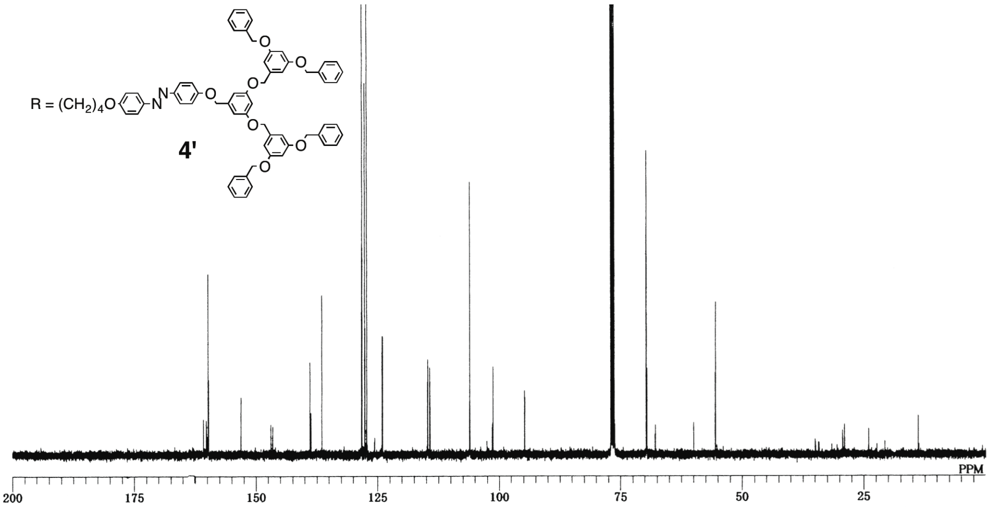
Compound 3. To a solution of **3'** (100 mg, 0.0296 mmol) in 1:1 (v/v) MeOH–$CHCl_3$ (5 mL) was added a drop of conc. HCl. The resulting mixture was stirred at 65 °C for 30 min under Ar. After evaporation of solvents, the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (1:1) and then EtOAc to give **3** as an orange solid (76.1 mg, 85% yield). Mp. 212-213 °C; ^1H NMR ($CDCl_3$) δ 9.63 (brs, 4H), 9.38 (brs, 4H), 7.84-7.80 (m, 16H), 7.22 (s, 4H), 6.95-6.90 (m, 16H), 6.00 (s, 4H), 4.38 (brs, 4H), 4.06 (d, J = 5.9 Hz, 8H), 4.01 (brs, 8H), 3.53 (d, J = 5.9 Hz, 16H), 3.39 (t, J = 6.8 Hz, 16H), 2.44-2.31 (m, 12H), 1.92 (brs, 8H), 1.62-1.48 (m, 24H), 1.35-1.21 (m, 112H), 0.85 (t, J = 6.8 Hz, 24H); ^{13}C NMR ($CDCl_3$) δ 161.16, 160.86, 146.84, 130.88, 124.63, 124.28, 114.62, 71.35, 68.73, 68.13, 66.60, 40.08, 31.89, 29.65, 29.60, 29.49, 29.34, 28.90, 28.81, 26.17, 24.52, 23.71, 22.98, 22.67, 14.12; ESI-TOF-MS m/z calcd for $C_{188}H_{280}N_8O_{24}Na_2$: 1541.0399 $[M + 2Na]^{2+}$, found: 1541.0468.



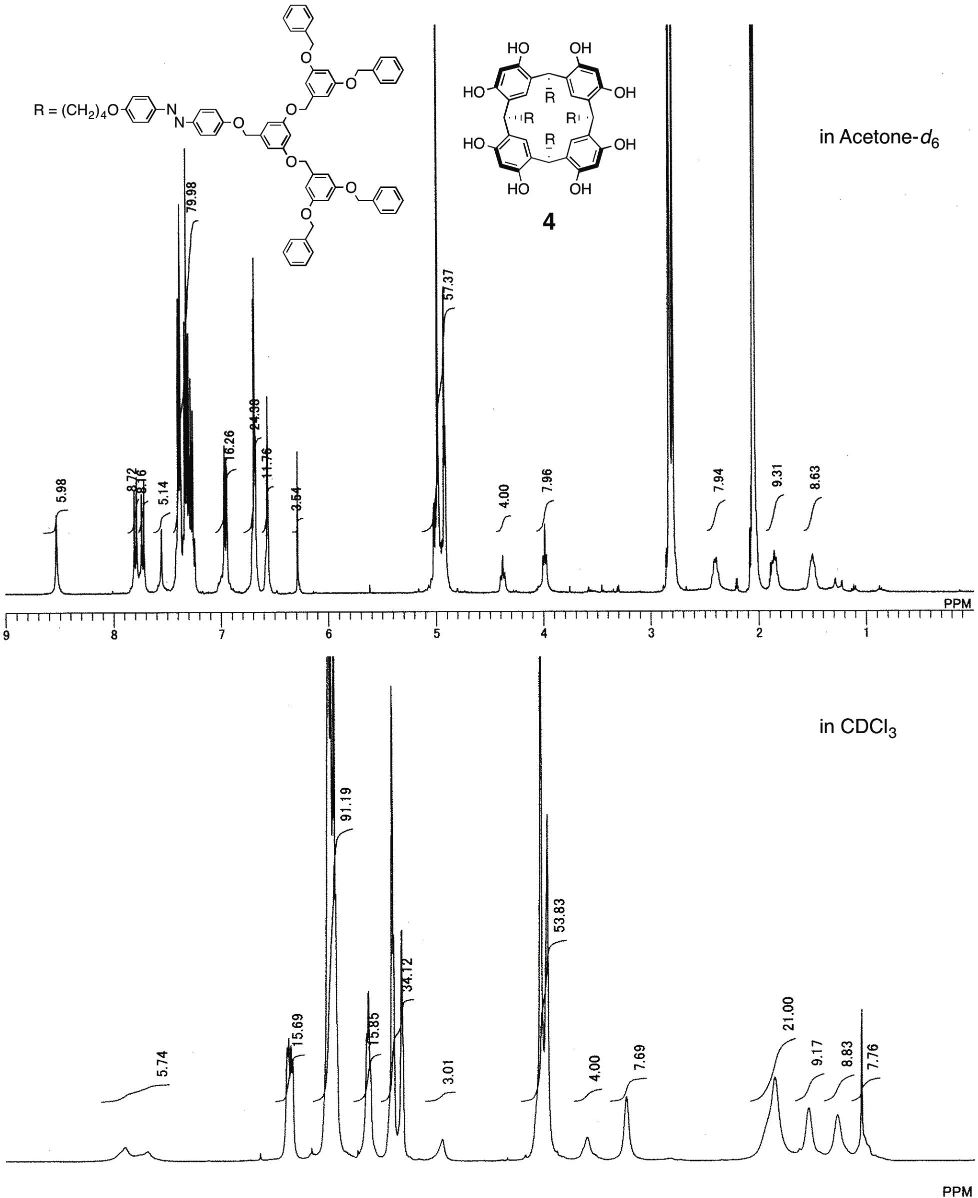


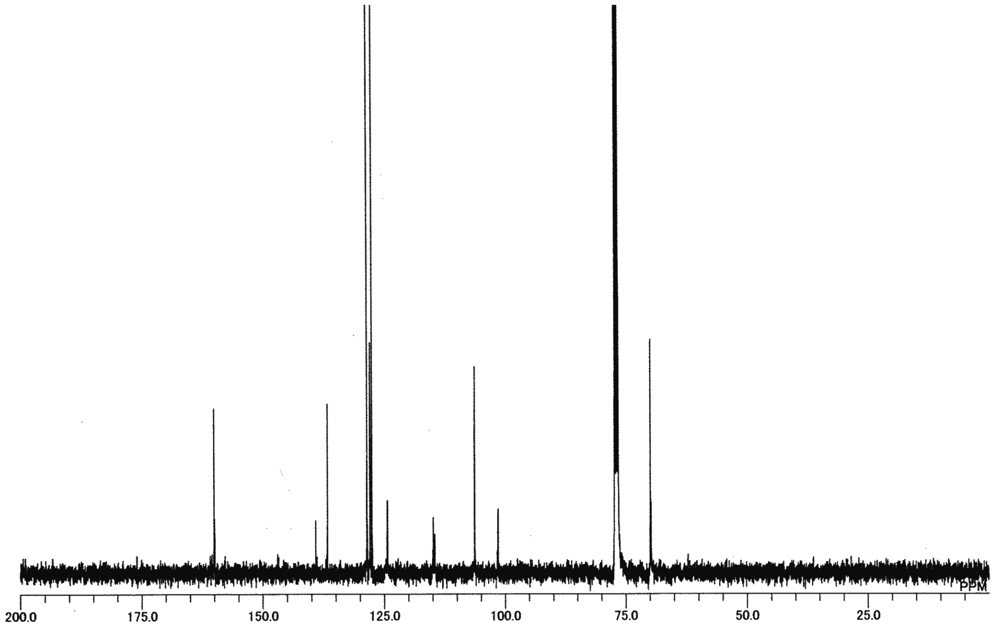
Compound 4'. A mixture of **11** (76.6 mg, 0.0532 mmol), **14** (300 mg, 0.319 mmol), and K_2CO_3 (66.2 mg, 0.479 mmol) in dry DMF (7 mL) under Ar was stirred at 50 °C for 24 h and then at 80 °C for 72 h. The reaction mixture was diluted with EtOAc and filtered, and the filtrate was partitioned between EtOAc and H_2O. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–hexane (11:9) to give **4'** as an orange solid (160 mg, 63% yield). Mp. 63-64 °C; ^{1}H NMR ($CDCl_3$) δ 7.80-7.78 (m, 16H), 7.40-7.30 (m, 80H), 6.99 (d, J = 8.8 Hz, 8H), 6.89 (d, J = 8.8 Hz, 8H), 6.76 (s, 4H), 6.70 (s, 4H), 6.66 (s, 24H), 6.55 (s, 8H), 6.53 (s, 4H), 4.99-4.90 (m, 72H), 4.63 (t, J = 7.3 Hz, 4H), 3.95 (t, J = 6.8 Hz, 8H), 3.36 (s, 24H), 1.97-1.95 (m, 8H), 1.86-1.84 (m, 8H), 1.58-1.54 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 160.83, 160.18, 159.84, 159.76, 153.09, 146.90, 146.56, 138.88, 138.69, 136.46, 131.91, 128.23, 127.65, 125.62, 127.22, 124.03, 123.99, 114.70, 114.25, 106.06, 106.02, 102.51, 101.38, 101.28, 94.77, 69.76, 69.66, 67.91, 55.52, 35.01, 34.28, 28.03, 24.03 MALDI-TOF-MS m/z calcd for $C_{304}H_{288}N_8O_{48}Na$: 4844.0339 [M + Na]$^+$, found: 4844.0550.



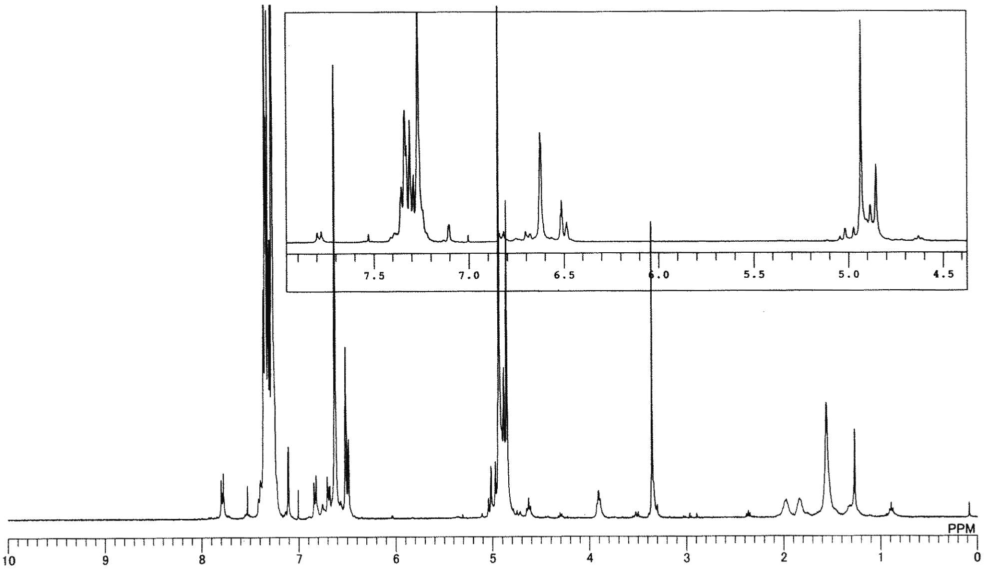


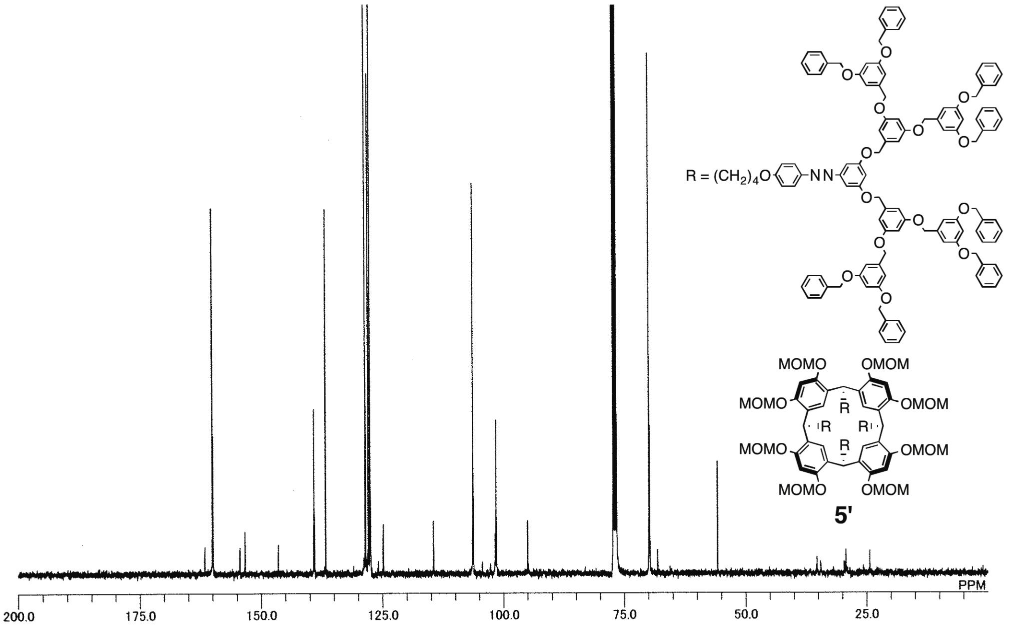
Compound 4. To a solution of **4'** (160 mg, 0.0332 mmol) in 1:2 (v/v) MeOH–$CHCl_3$ (6 mL) was added a drop of conc. HCl. The resulting mixture was stirred at 65 °C for 30 min under Ar. After evaporation of solvents, the residue was partitioned between $CHCl_3$ and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with CH_2Cl_2–acetone-MeOH (10:2:0.25) followed by reprecipitation with $CHCl_3$–hexane to give **4** as an orange solid (87.3 mg, 59% yield). Mp. 95-97 °C; ^{1}H NMR (acetone-d_6) δ 8.53 (s, 8H), 7.80 (d, J = 8.8 Hz, 8H), 7.73 (d, J = 8.8 Hz, 8H), 7.55 (s, 4H), 7.40-7.24 (m, 80H), 6.97-6.95 (m, 16H), 6.69-6.68 (m, 24H), 6.57 (s, 12H), 6.29 (s, 4H), 5.02-4.91 (m, 56H), 4.38 (t, J = 7.3 Hz, 4H), 3.99 (t, J = 6.8 Hz, 8H), 2.42-2.38 (m, 8H), 1.89-1.85 (m, 8H), 1.52-1.48 (m, 8H); ^{1}H NMR ($CDCl_3$) δ 9.65 (brs, 4H), 9.40 (brs, 4H), 7.80 (d, J = 8.8 Hz, 8H), 7.75 (d, J = 8.8 Hz, 8H), 7.41-7.20 (m, 84H), 6.95-6.85 (m, 16H), 6.67-6.56 (m, 24H), 6.51 (brs, 12H), 6.04 (brs, 4H), 4.92-4.85 (m, 56H), 4.40 (brs, 4H), 3.95 (brs, 8H), 2.27 (brs, 8H), 1.88 (brs, 8H), 1.55 (brs, 8H); ^{13}C NMR ($CDCl_3$) δ 160.16, 159.96, 139.12, 136.39, 128.51, 127.94, 127.52, 124.34, 114.89, 114.59, 106.30, 101.47, 69.95, 69.84 (no emergence of resonances in the regions between 0 and 40 ppm); MALDI-TOF-MS m/z calcd for $C_{288}H_{256}N_8O_{40}Na$: 4491.8235 [M + Na]$^+$, found: 4491.8462.



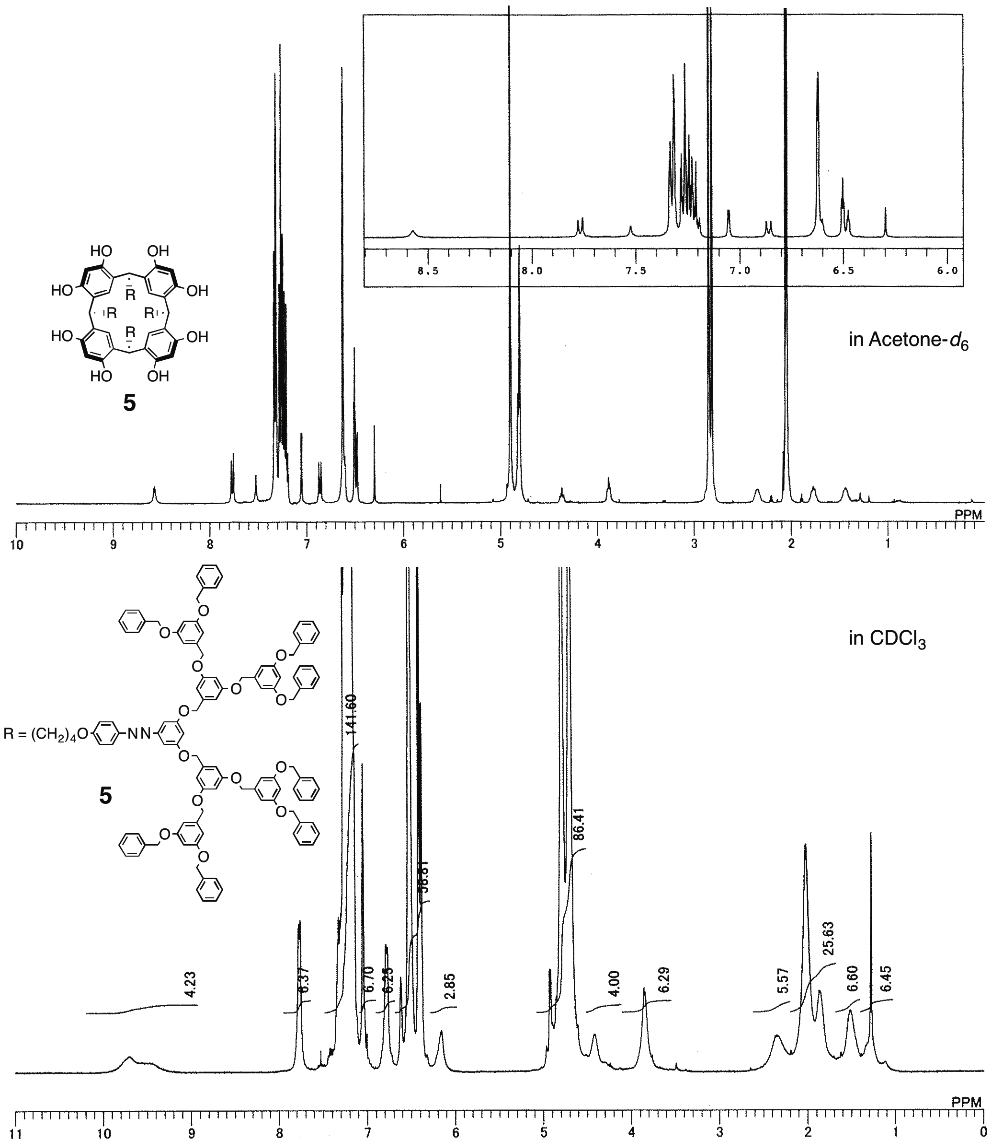

PPM
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0

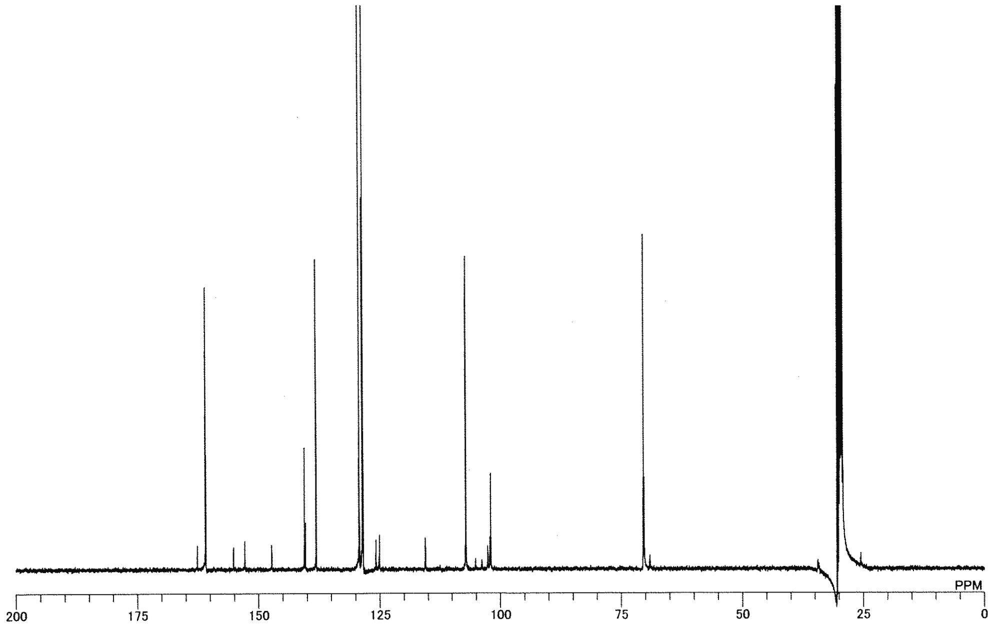
Compound 5'. A mixture of **11** (108 mg, 0.0748 mmol), **15** (1.01 g, 0.598 mmol), and K_2CO_3 (166 mg, 1.20 mmol) in dry DMF (10 mL) under Ar was stirred at 80 °C for 24 h, subsequently at 100 °C for 48 h, and finally at 120 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2 and filtered, and the filtrate was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O (5 times) and brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with EtOAc–$CHCl_3$ (1:15) to give **5'** as an orange solid (287 mg, 49% yield). Mp. 62-63 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 8H), 7.39-7.29 (m, 160H), 7.10 (s, 8H), 6.84 (d, J = 8.8 Hz, 8H), 6.75 (s, 4H), 6.71 (s, 4H), 6.69 (s, 4H), 6.63 (s, 48H), 6.51 (s, 16H), 6.49 (s, 8H), 5.02-4.86 (m, 128H), 4.63 (t, J = 6.8 Hz, 4H), 3.91 (t, J = 6.3 Hz, 8H), 3.36 (s, 24H), 2.00-1.96 (m, 8H), 1.86-1.82 (m, 8H), 1.58-1.54 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 161.63, 160.04, 159.98, 159.93, 154.40, 153.35, 146.48, 139.16, 139.03, 136.71, 128.89, 128.50, 127.91, 127.52, 125.90, 124.85, 114.50, 106.36, 106.27, 104.38, 102.74, 101.73, 101.57, 101.50, 95.00, 69.94, 69.82, 68.17, 55.84, 35.34, 34.54, 29.30, 24.40; MALDI-TOF-MS m/z calcd for $C_{500}H_{456}N_8O_{76}Na$: 7815.2129 [M + Na]$^+$, found: 7815.2661.





Compound 5. To a solution of **5'** (160 mg, 0.0205 mmol) in 1:2 (v/v) MeOH–$CHCl_3$ (6 mL) was added a drop of conc. HCl. The resulting mixture was stirred at 65 °C for 30 min under Ar. After evaporation of solvents, the residue was partitioned between $CHCl_3$ and H_2O. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with CH_2Cl_2–acetone-MeOH (12:2:0.25) followed by reprecipitation with $CHCl_3$–hexane to give **5** as an orange solid (127 mg, 83% yield). Mp. 76-77 °C; ^{1}H NMR (acetone-*d*$_6$) δ 8.57 (s, 8H), 7.78 (d, *J* = 8.8 Hz, 8H), 7.52 (s, 4H), 7.34-7.19 (m, 160H), 7.06 (s, 8H), 6.87 (d, *J* = 8.8 Hz, 8H), 6.63-6.61 (m, 52H), 6.50 (t, *J* = 2.0 Hz, 16H), 6.48 (s, 8H), 6.30 (s, 4H), 4.90 (s, 64H), 4.82-4.80 (m, 48H), 4.37 (t, *J* = 6.8 Hz, 4H), 3.89 (t, *J* = 6.3 Hz, 8H), 2.36-2.32 (m, 8H), 1.79-1.75 (m, 8H), 1.46-1.42(m, 8H); ^{1}H NMR ($CDCl_3$) δ 9.70 (brs, 4H), 9.46 (brs, 4H), 7.78 (d, *J* = 7.3 Hz, 8H), 7.40-7.12 (m, 164H), 7.05 (s, 8H), 6.77 (d, *J* = 7.3 Hz, 8H), 6.62 (s, 4H), 6.55-6.37 (m, 72H), 6.16 (brs, 4H), 4.93-4.60 (m, 112H), 4.42 (brs, 4H), 3.86 (brs, 8H), 2.35 (brs, 8H), 1.87 (brs, 8H), 1.52 (brs, 8H); ^{13}C NMR (acetone-*d*$_6$) δ 162.63, 160. 94, 160.86, 155.17, 152.83, 147.26, 140.53, 140.32, 138.39, 138.10, 129.22, 129.02, 128.57, 128.43, 128.12, 125.76, 125.16, 115.57, 107.15, 105.13, 103.87, 102.64, 102.20, 102.04, 70.41, 70.29, 69.10, 34.44, 34.23, 25.55; MALDI-TOF-MS *m*/*z* calcd for $C_{484}H_{424}N_8O_{68}Na$: 7463.0023 [M + Na]$^+$, found: 7463.0588.





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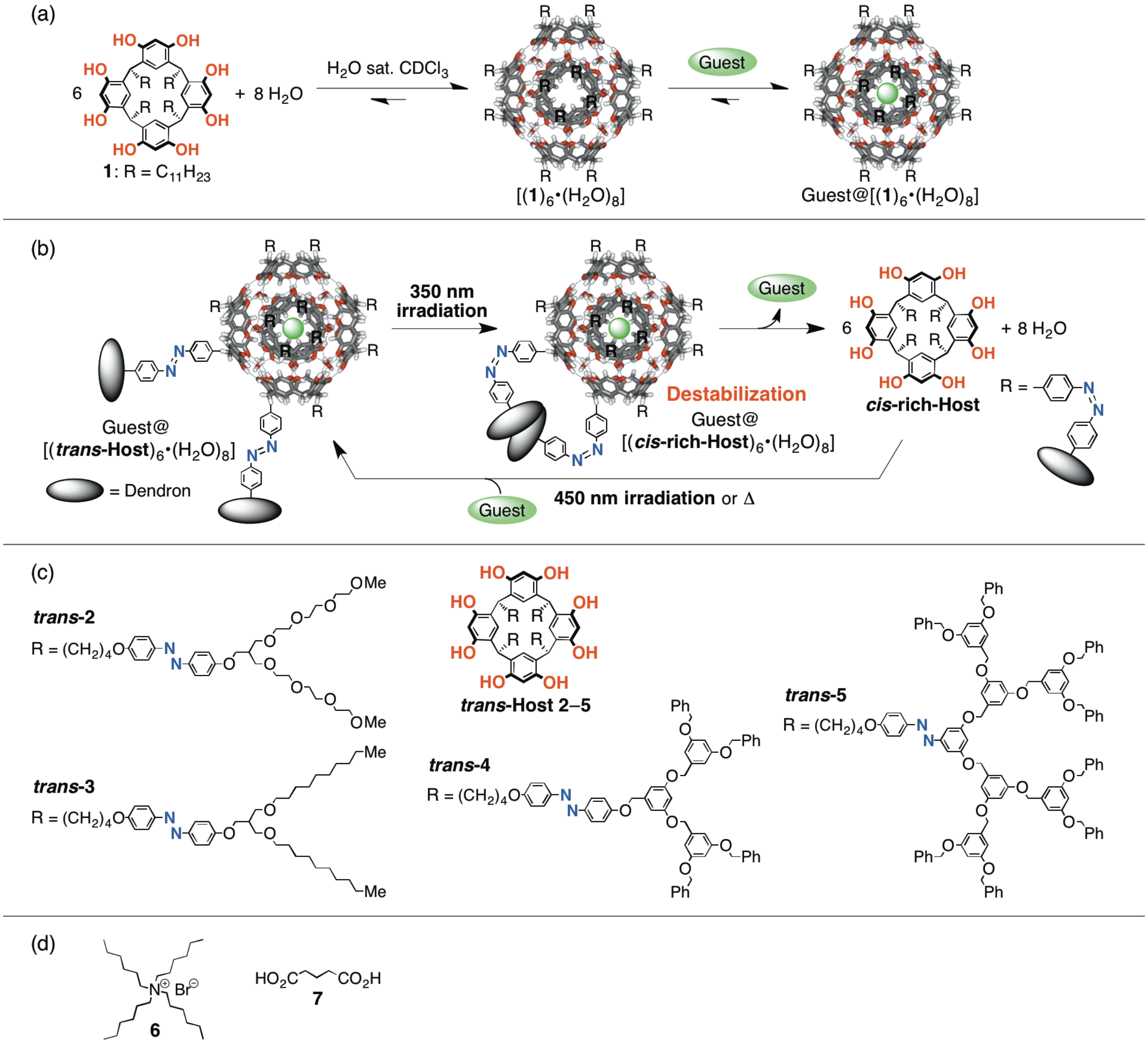


Fig. S1 (a) Self-assembly of **1** and H_2O into a hexameric capsule $[(\mathbf{1})_6•(H_2O)_8]$ and guest encapsulation. (b) Schematic representation of assembly–disassembly–reassembly process of self-assembled hexameric capsules $[(\mathbf{2}–\mathbf{5})_6•(H_2O)_8]$ in conjunction with guest encapsulation–release–reencapsulation by light stimuli. (c) Structures of hosts *trans*-**2**–**5**. (d) Guest structures **6** and **7**.

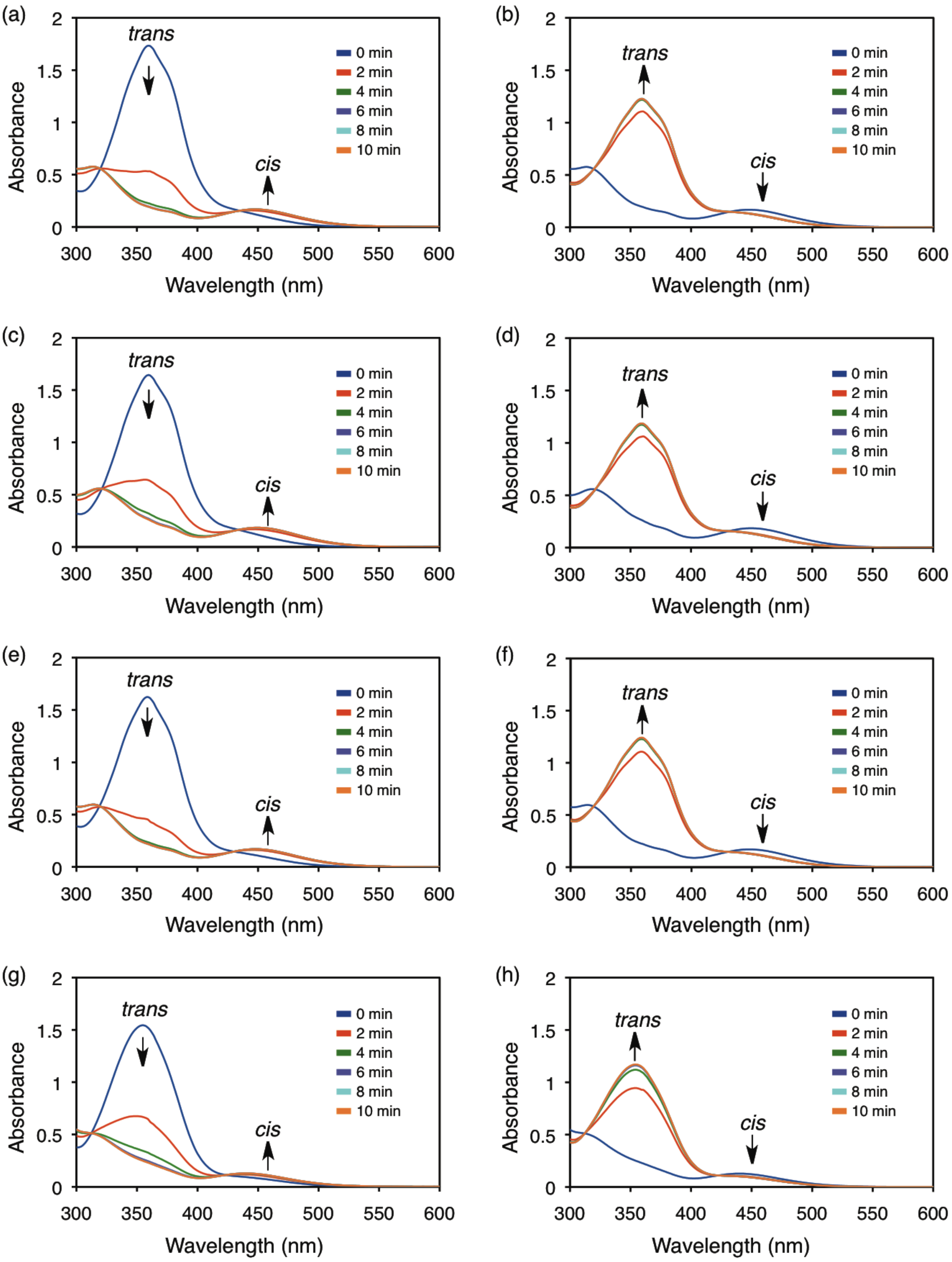


Fig. S2 UV–vis absorption spectral changes of *trans*-**2**–**5** in CH_2Cl_2 (0.015 mM each) upon photoirradiation: *trans*-**2** upon irradiation (a) at 350 nm for 0–10 min and then (b) at 450 nm for 0–10 min; *trans*-**3** upon irradiation (c) at 350 nm for 0–10 min and then (d) at 450 nm for 0–10 min; *trans*-**4** upon irradiation (e) at 350 nm for 0–10 min and then (f) at 450 nm for 0–10 min; *trans*-**5** upon irradiation (g) at 350 nm for 0–10 min and then (h) at 450 nm for 0–10 min.

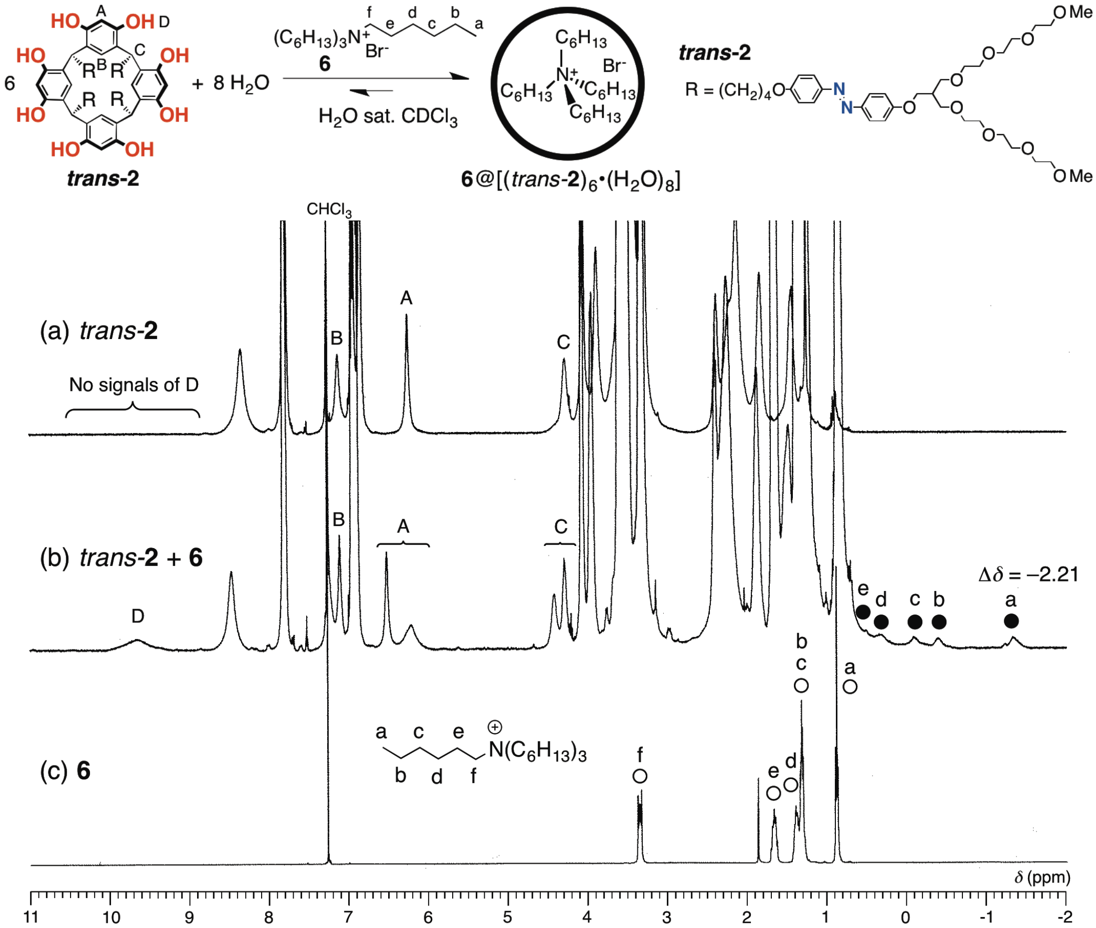


Fig. S3 ^{1}H NMR spectra (H_2O-saturated $CDCl_3$, 298 K): (a) [*trans*-**2**] = 6 mM, (b) [*trans*-**2**] = 6 mM and [**6**] = 3 mM, and (c) [**6**] = 3 mM. Solid and open circles indicate the encapsulated and free **6**, respectively.

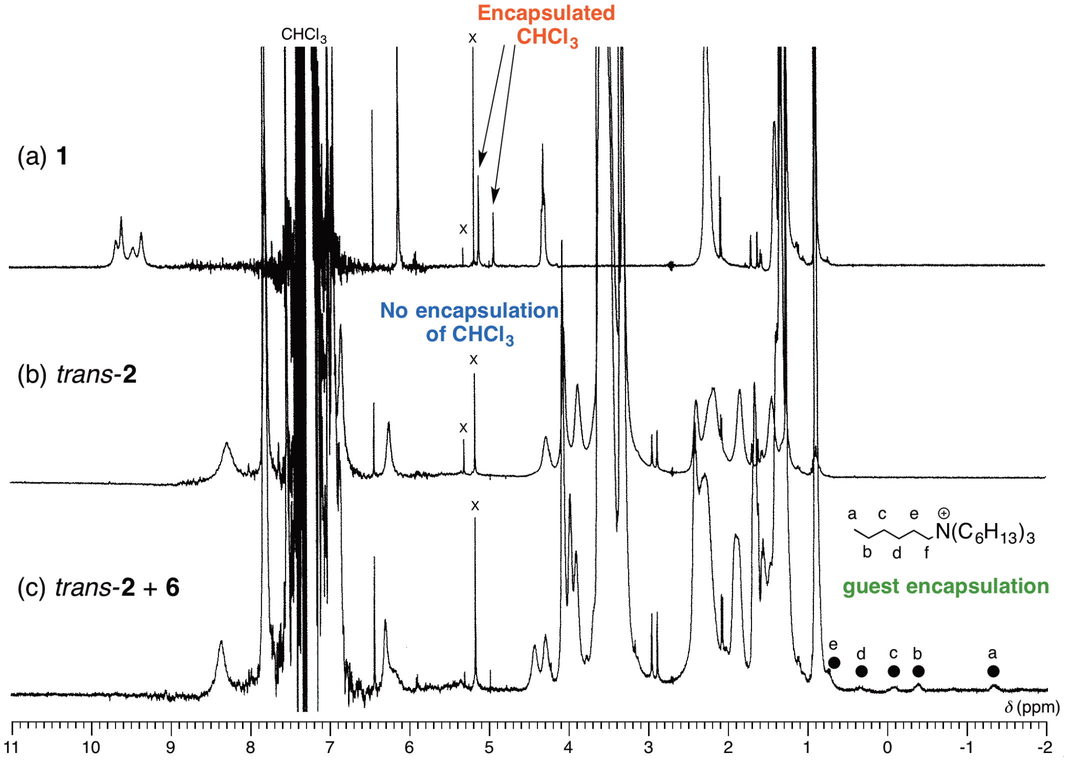


Fig. S4 ^{1}H NMR spectra (H_2O-saturated $CHCl_3$, 298 K): (a) [**1**] = 6 mM,[ref. 9] (b) [*trans*-**2**] = 6 mM, and (c) [*trans*-**2**] = 6 mM and [**6**] = 3 mM. Impurities in $CHCl_3$ are indicated with ×. $CDCl_3$ sealed in capillary was used for NMR lock solvent.

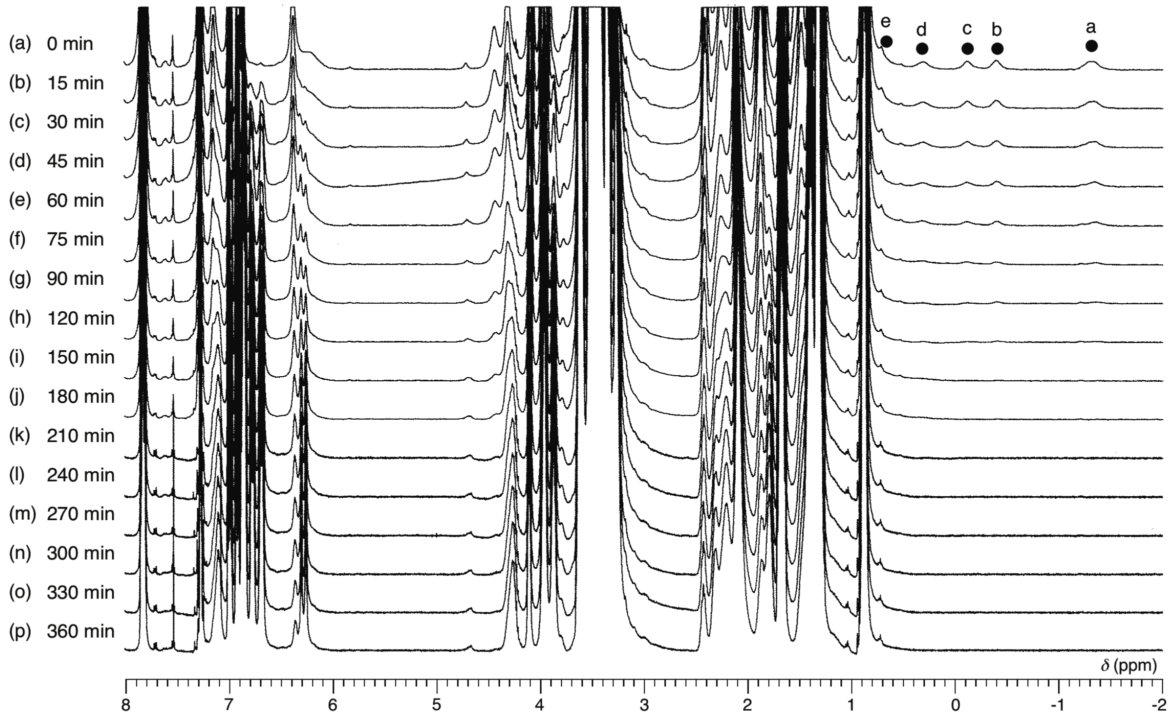


Fig. S5 ^{1}H NMR spectral changes of a mixture of *trans*-**2** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([*trans*-**2**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 9 mM) upon photoirradiation at 350 nm: (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 75 min, (g) 90 min, (h) 120 min, (i) 150 min, (j) 180 min, (k) 210 min, (l) 240 min, (m) 270 min, (n) 300 min, (o) 330 min, and (p) 360 min. The signals marked 'a–e' indicate the encapsulated **6** and are assigned in Fig. S3.

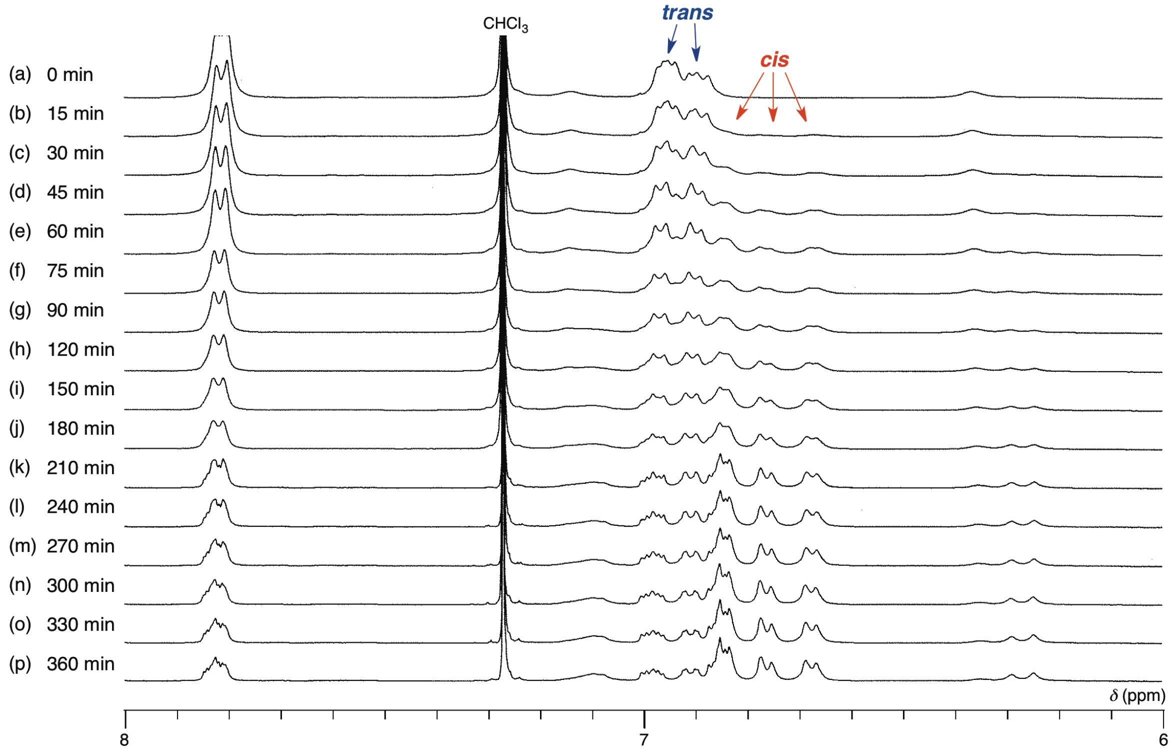


Fig S6 Expanded ^{1}H NMR spectra of Fig. S5 in the region of 6–8 ppm.

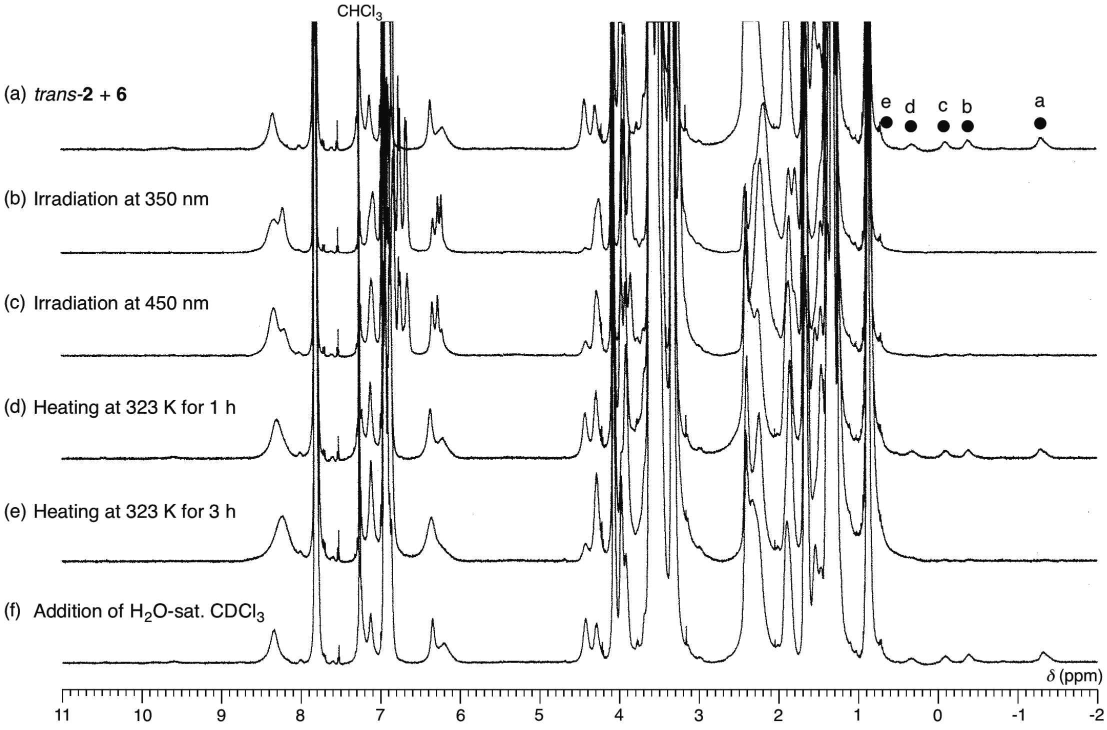
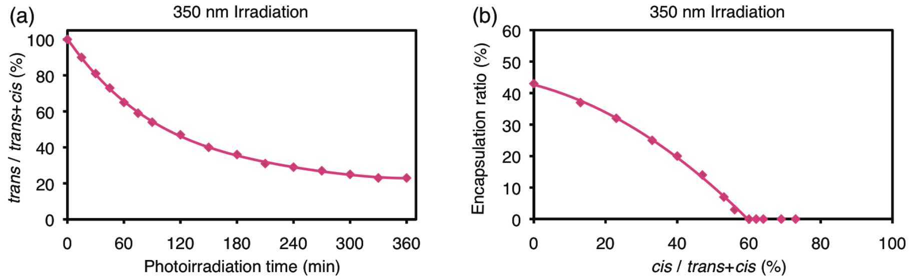


Fig. S7 ^{1}H NMR spectral changes of a mixture of *trans*-**2** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([*trans*-**2**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 9 mM, 600 μL): (a) before photoirradiation and heating, (b) upon photoirradiation at 350 nm for 3 h, (c) after photoirradiation at 450 nm for 3 h, (d) after heating at 323 K for 1 h, (e) after additional heating at 323 K for 2 h (total 3 h), and (f) after addition of 50 μL of H_2O-saturated $CDCl_3$. The signals marked 'a–e' indicate the encapsulated **6** and are assigned in Fig. S3.



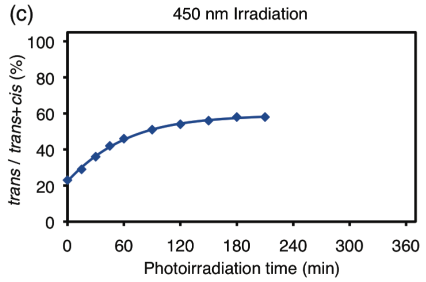


Fig. S8 (a) Plots of *trans*/(*trans* + *cis*) ratio changes (%) of a mixture of *trans*-**2** and **6** in H_2O-saturated $CDCl_3$ at 298 K as a function of 350 nm photoirradiation time ([*trans*-**2**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 9 mM). (b) Plots of guest-encapsulation ratio changes (%) as a function of *cis*/(*trans* + *cis*) ratio changes (%) in Fig. S8a. (c) Plots of *trans*/(*trans* + *cis*) ratio changes (%) of a mixture of *cis-rich*-**2** and **6** (initial = final sample of Fig. S8a) in H_2O-saturated $CDCl_3$ at 298 K as a function of 450 nm photoirradiation time.

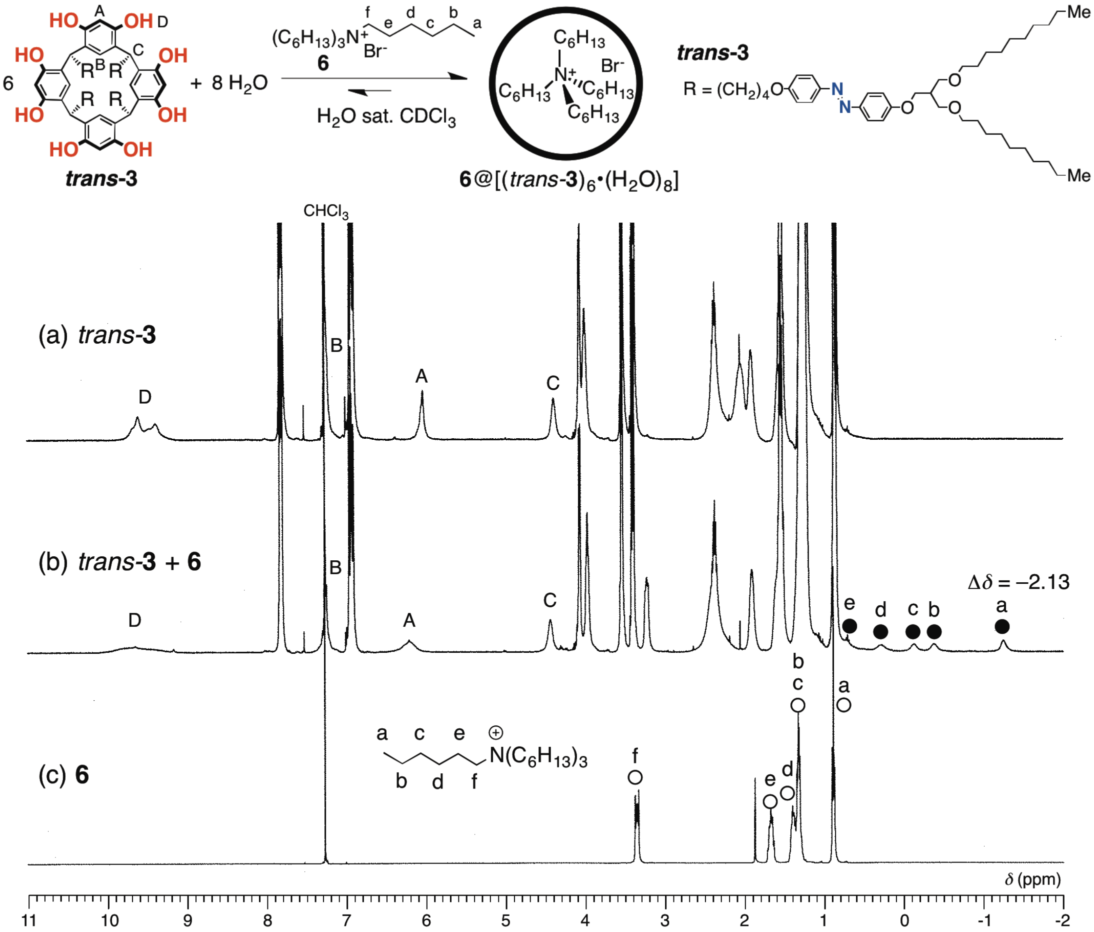


Fig. S9 ^{1}H NMR spectra (H_2O-saturated $CDCl_3$, 298 K): (a) [*trans*-**3**] = 6 mM, (b) [*trans*-**3**] = 6 mM and [**6**] = 3 mM, and (c) [**6**] = 3 mM. Solid and open circles indicate the encapsulated and free **6**, respectively.

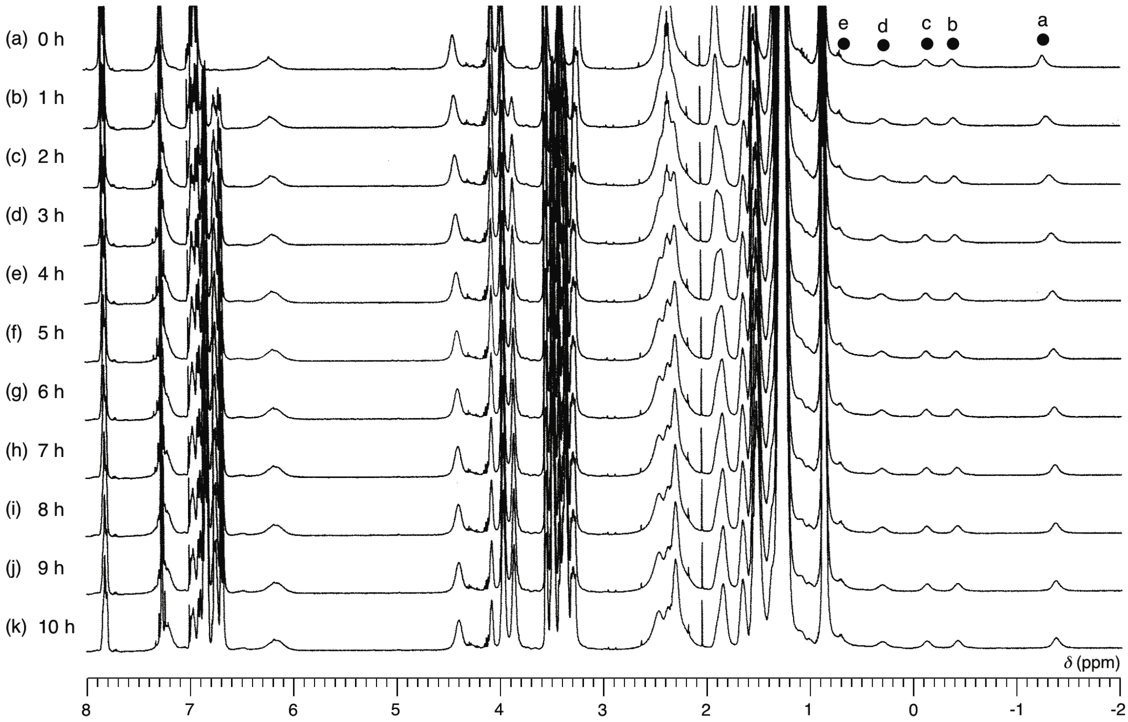


Fig. S10 ^{1}H NMR spectral changes of a mixture of *trans*-**3** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([*trans*-**3**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 3 mM) upon photoirradiation at 350 nm: (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 5 h, (g) 6 h, (h) 7 h, (i) 8 h, (j) 9 h, and (k) 10 h. The signals marked 'a–e' indicate the encapsulated **6** and are assigned in Fig. S9.

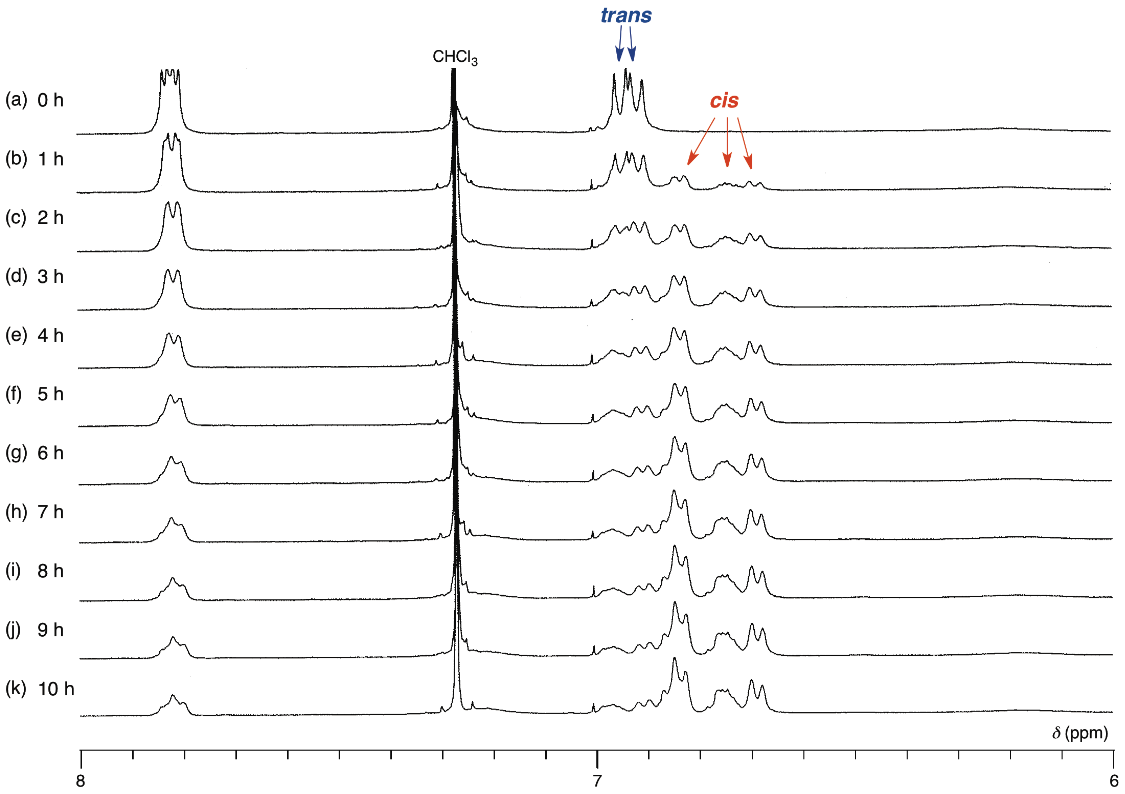


Fig. S11 Expanded ^{1}H NMR spectra of Fig. S10 in the region of 6–8 ppm.

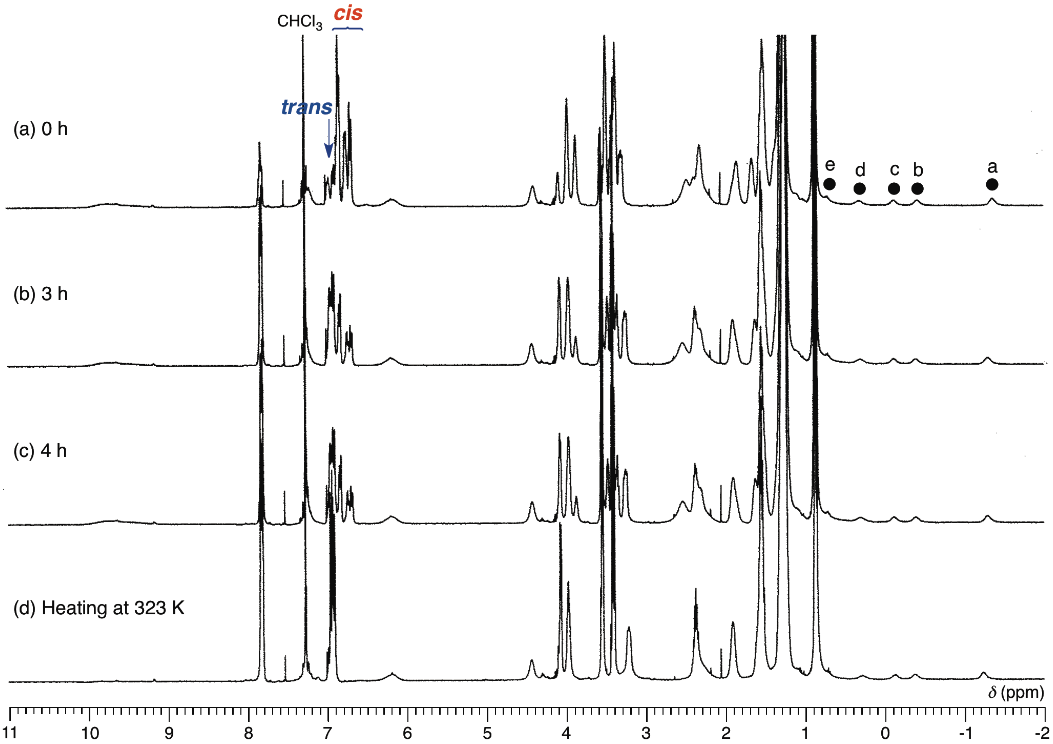


Fig. S12 ^{1}H NMR spectral changes of a mixture of *cis-rich*-**3** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([**3**: average *trans*:*cis* = 29:71]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 3 mM): (a) before photoirradiation and heating, (b) upon photoirradiation at 450 nm for 3 h, (c) after additional photoirradiation at 450 nm for 1 h (total 4 h), and (d) after heating at 323 K for 3 h. The signals marked 'a–e' indicate the encapsulated **6** and are assigned in Fig. S9.

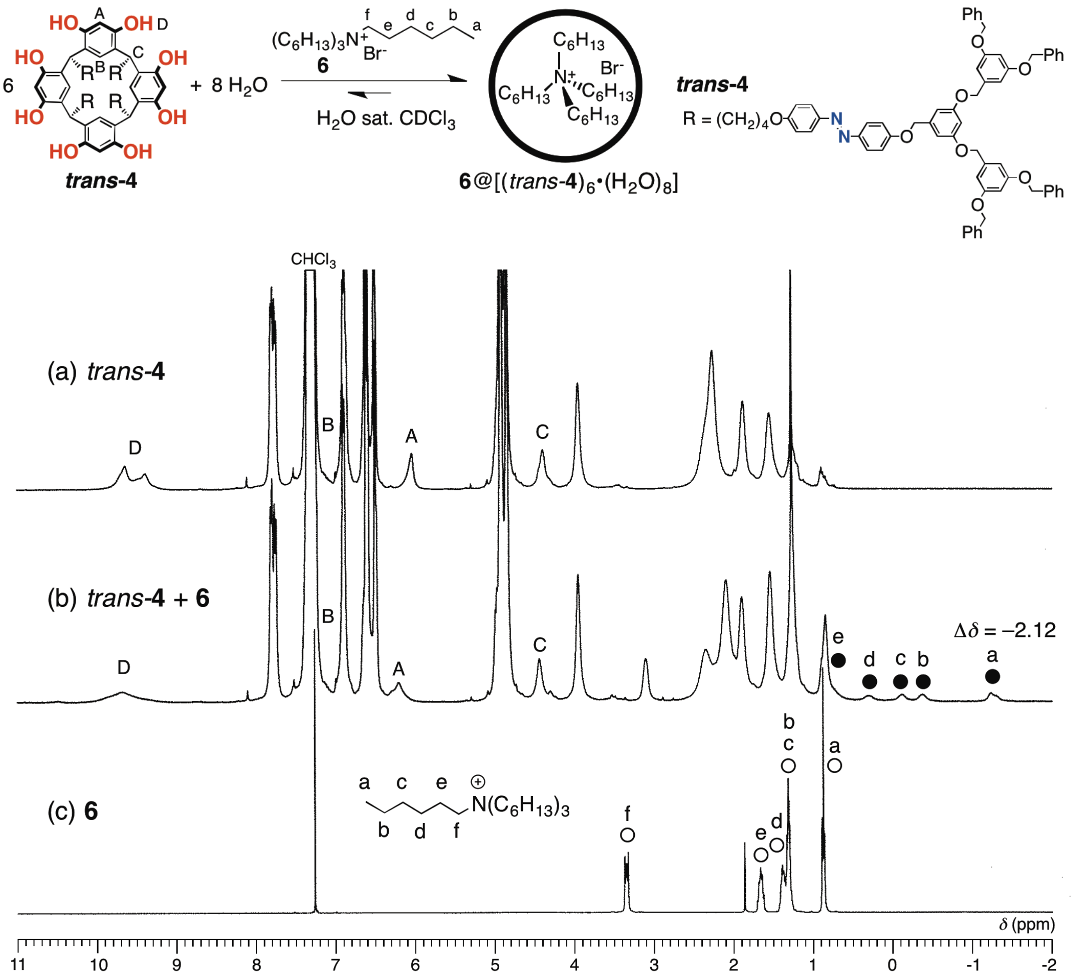


Fig. S13 ^{1}H NMR spectra (H_2O-saturated $CDCl_3$, 298 K): (a) [*trans*-**4**] = 6 mM, (b) [*trans*-**4**] = 6 mM and [**6**] = 3 mM, and (c) [**6**] = 3 mM. Solid and open circles indicate the encapsulated and free **6**, respectively.

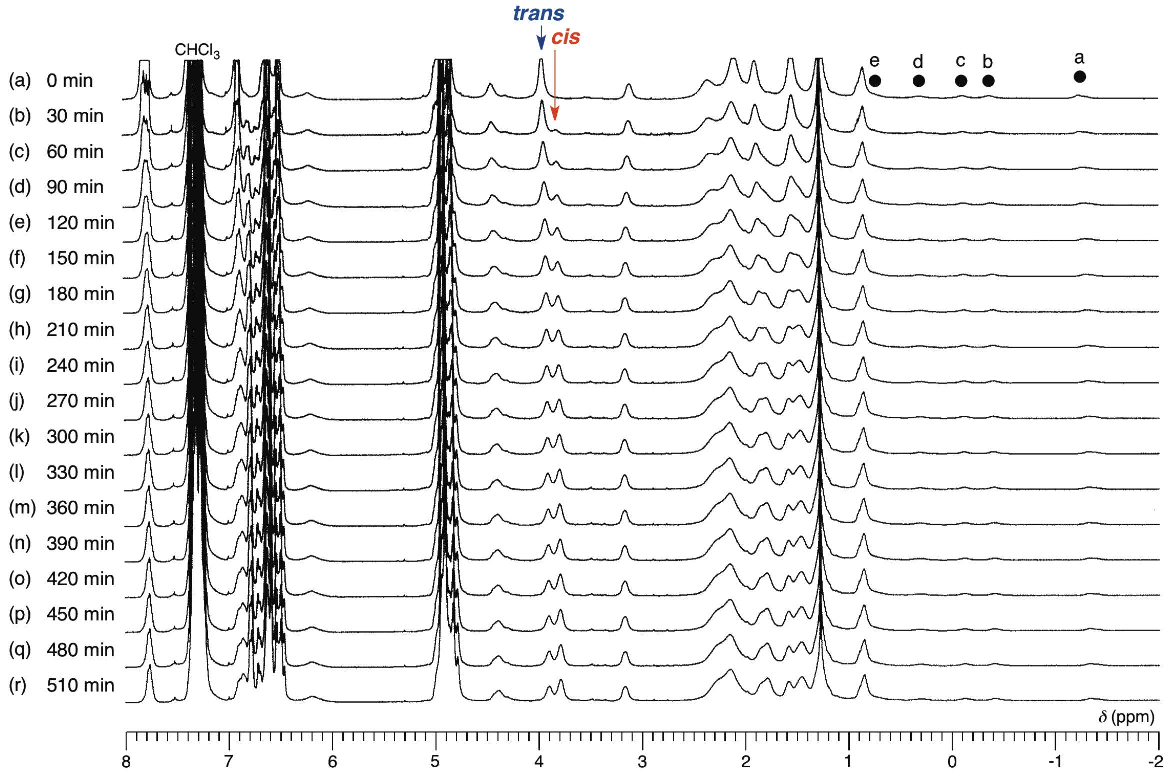


Fig. S14 ^{1}H NMR spectral changes of a mixture of *trans*-**4** and **6** in H_2O-saturated $CDCl_3$ at 298 K ($[\textit{trans}\text{-}\mathbf{4}]_{\text{initial}}$ = 6 mM and $[\mathbf{6}]_{\text{initial}}$ = 3 mM) upon photoirradiation at 350 nm: (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, (g) 180 min, (h) 210 min, (i) 240 min, (j) 270 min, (k) 300 min, (l) 330 min, (m) 360 min, (n) 390 min, (o) 420 min, (p) 450 min, (q) 480 min, and (r) 510 min. The signals marked 'a–e' indicate the encapsulated **6** and are assigned in Fig. S13.

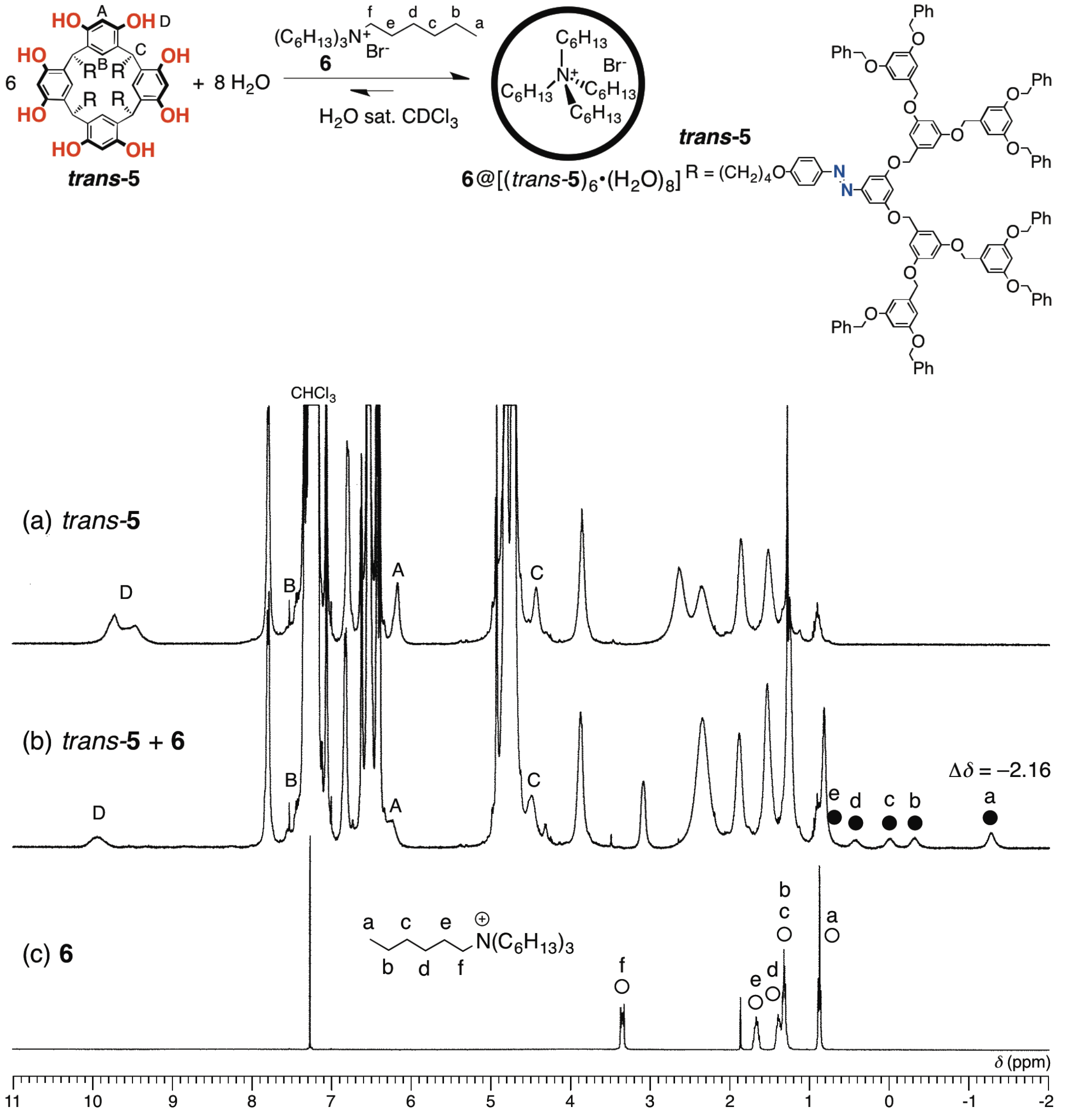


Fig. S15. ^{1}H NMR spectra (H_2O-saturated $CDCl_3$, 298 K): (a) [*trans*-**5**] = 6 mM, (b) [*trans*-**5**] = 6 mM and [**6**] = 3 mM, and (c) [**6**] = 3 mM. Solid and open circles indicate the encapsulated and free **6**, respectively.

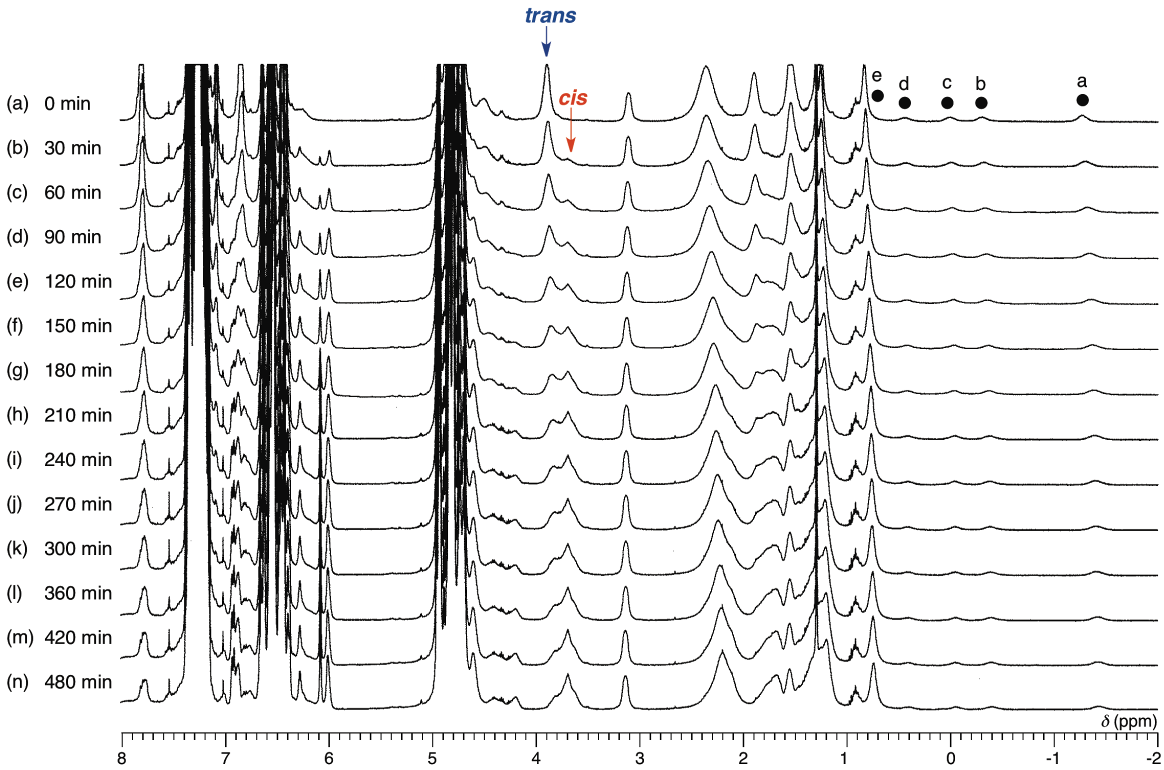


Fig. S16 ^{1}H NMR spectral changes of a mixture of *trans*-**5** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([*trans*-**5**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 3 mM) upon photoirradiation at 350 nm: (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, (g) 180 min, (h) 210 min, (i) 240 min, (j) 270 min, (k) 300 min, (l) 360 min, (m) 420 min, and (n) 480 min. The signals marked ‘a–e’ indicate the encapsulated **6** and are assigned in Fig. S15.

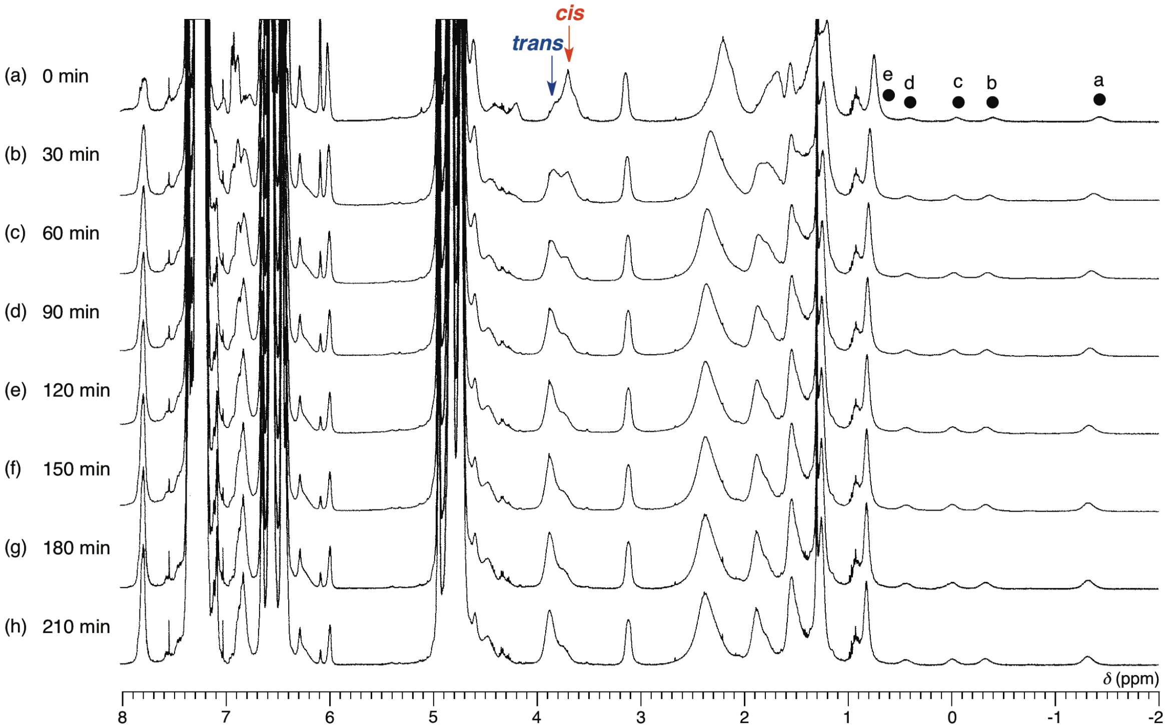


Fig. S17 ^{1}H NMR spectral changes of a mixture of *cis-rich*-**5** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([**3**: average *trans*:*cis* = 27:73]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 3 mM) upon photoirradiation at 450 nm: (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, (g) 180 min, and (h) 210 min. The signals marked ‘a–e’ indicate the encapsulated **6** and are assigned in Fig. S15.

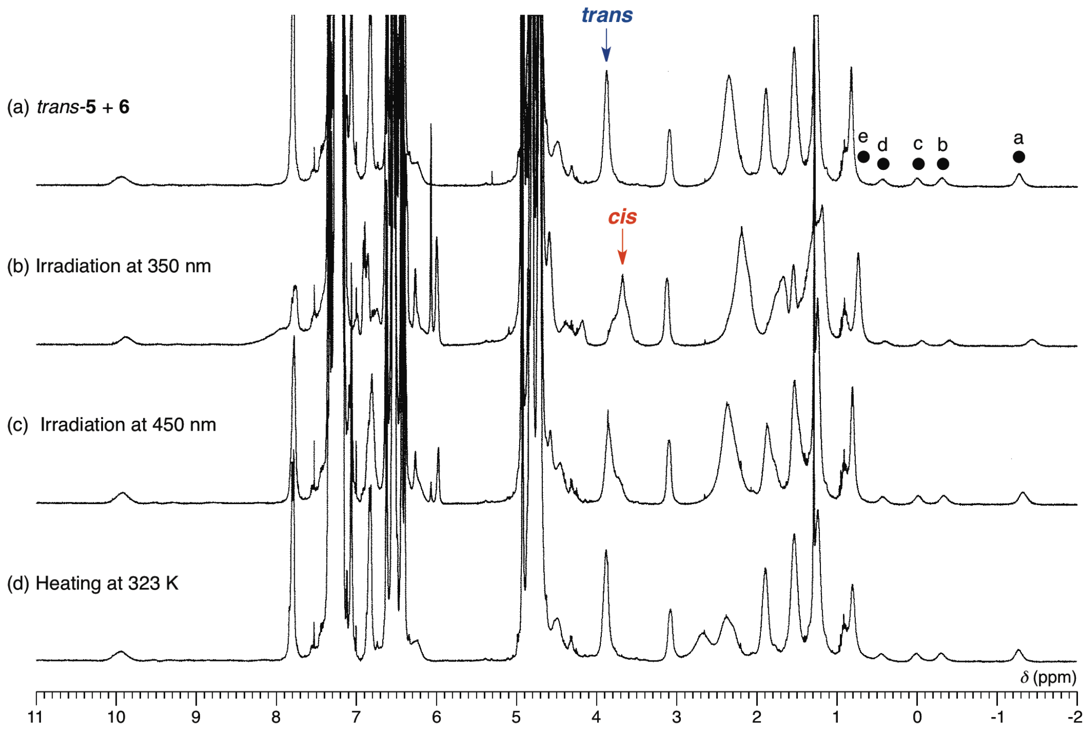


Fig. S18 ^{1}H NMR spectral changes of a mixture of *trans*-**5** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([*trans*-**5**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 3 mM): (a) before photoirradiation and heating, (b) upon photoirradiation at 350 nm for 7 h, (c) after photoirradiation at 450 nm for 3 h, and (d) after heating at 323 K for 3 h. The signals marked 'a–e' indicate the encapsulated **6** and are assigned in Fig. S15.

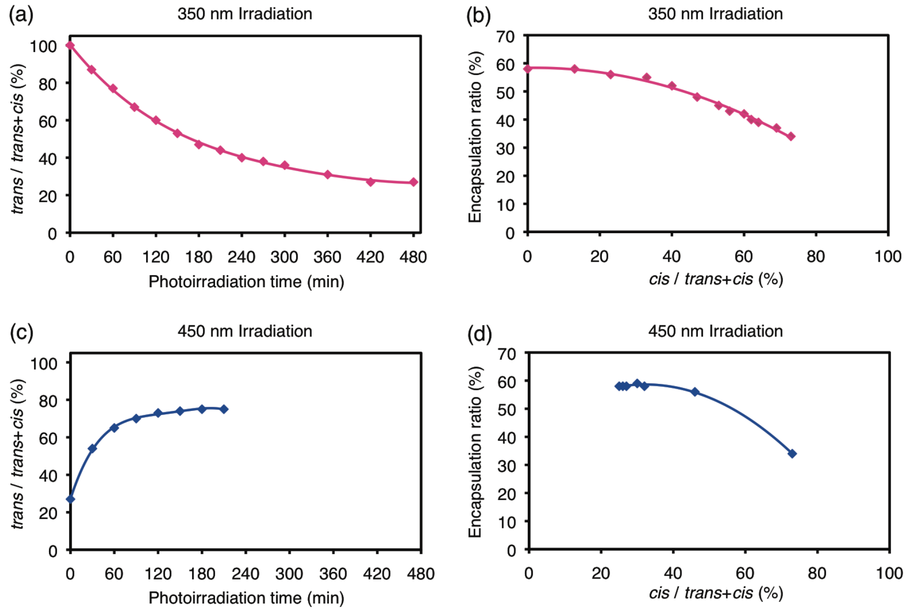


Fig. S19 (a) Plots of *trans*/(*trans* + *cis*) ratio changes (%) of a mixture of *trans*-**5** and **6** in H_2O-saturated $CDCl_3$ at 298 K as a function of 350 nm photoirradiation time ([*trans*-**5**]$_{\text{initial}}$ = 6 mM and [**6**]$_{\text{initial}}$ = 3 mM). (b) Plots of guest-encapsulation ratio changes (%) as a function of *cis*/(*trans* + *cis*) ratio changes (%) in Fig. S19a. (c) Plots of *trans*/(*trans* + *cis*) ratio changes (%) of a mixture of *cis-rich*-**5** and **6** (initial = final sample of Fig. S19a) in H_2O-saturated $CDCl_3$ at 298 K as a function of 450 nm photoirradiation time. (d) Plots of guest-encapsulation ratio changes (%) as a function of *cis*/(*trans* + *cis*) ratio changes (%) in Fig. S19c.

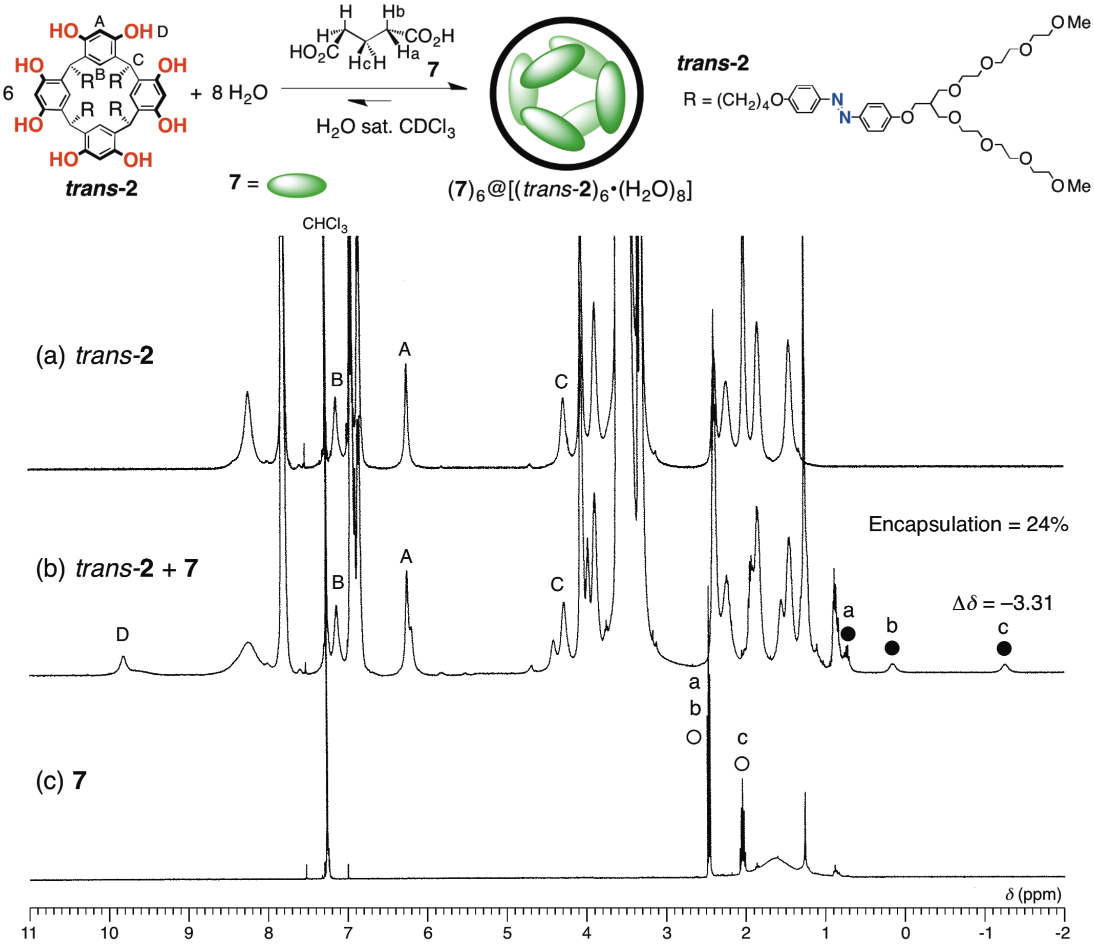


Fig. S20 ^{1}H NMR spectra (H_2O-saturated $CDCl_3$, 298 K): (a) [*trans*-**2**] = 6 mM, (b) [*trans*-**2**] = 6 mM and [**7**] = 9 mM (if completely soluble), and (c) [**7**] = 9 mM (if completely soluble). Solid and open circles indicate the encapsulated and free **7**, respectively.

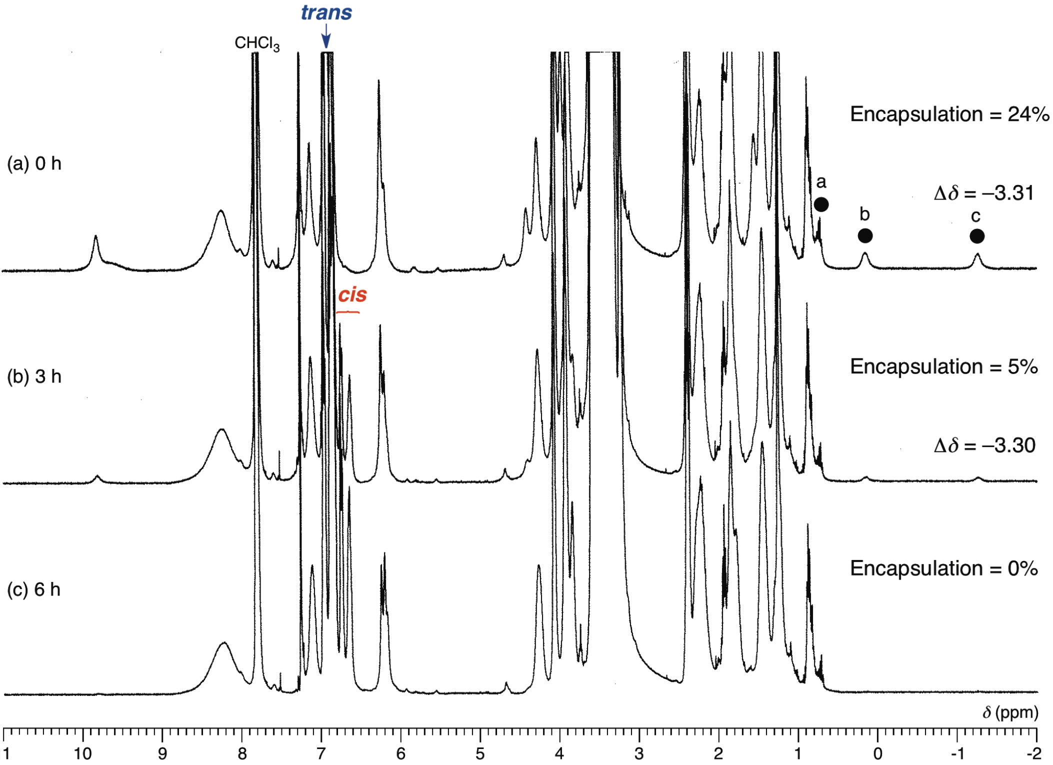


Fig. S21 ^{1}H NMR spectral changes of a mixture of *trans*-**2** and **7** in H_2O-saturated $CDCl_3$ at 298 K ([*trans*-**2**]$_{initial}$ = 6 mM and [**7**]$_{initial}$ = 9 mM) upon photoirradiation at 350 nm: (a) 0 h, (b) 3 h, and (c) 6 h. The signals marked 'a–c' indicate the encapsulated **7** and are assigned in Fig. S20.

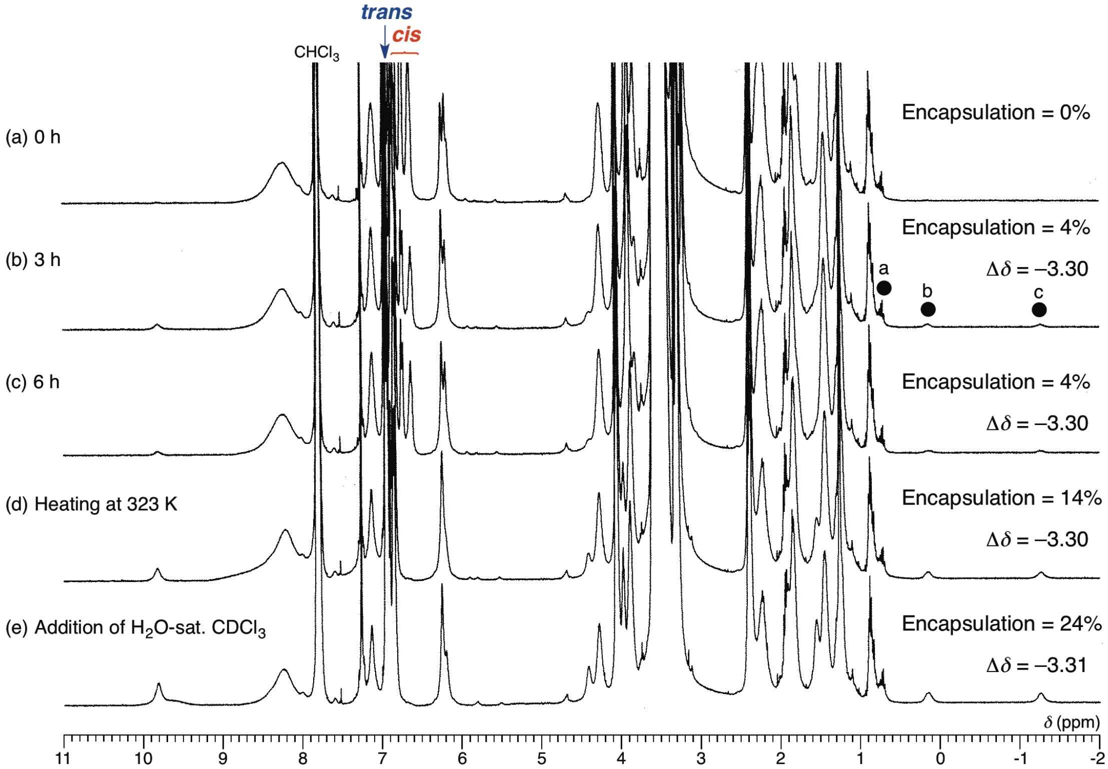


Fig. S22 ^{1}H NMR spectral changes of a mixture of *cis-rich*-**2** and **6** in H_2O-saturated $CDCl_3$ at 298 K ([**2**: average *trans*:*cis* = 47:53]$_{initial}$ = 6 mM and [**7**]$_{initial}$ = 9 mM, 600 μL): (a) before photoirradiation and heating, (b) after 450 nm photoirradiation for 3 h, (c) after 450 nm photoirradiation for 6 h, (d) after heating at 323 K for 3 h, and (e) after addition of 50 μL of H_2O-saturated $CDCl_3$. The signals marked 'a–c' indicate the encapsulated **7** and are assigned in Fig. S20.