Electronic Supplementary Information

Oxacalix[4]arene-bridged pillar[5]arene dimers: syntheses, planar chirality and construction of chiral rotaxanes

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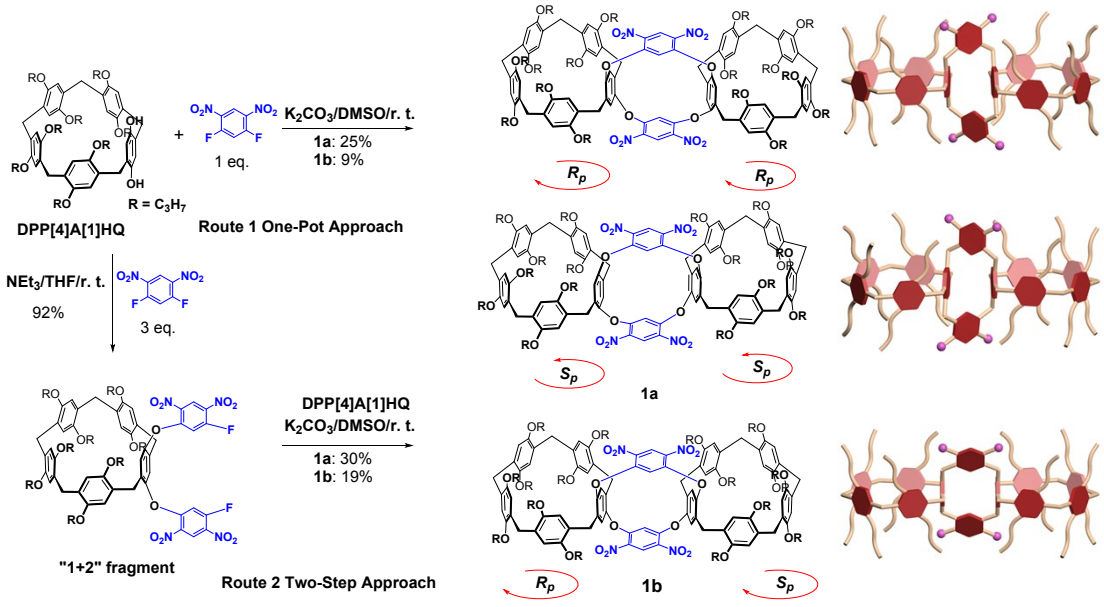
1. Materials and methods

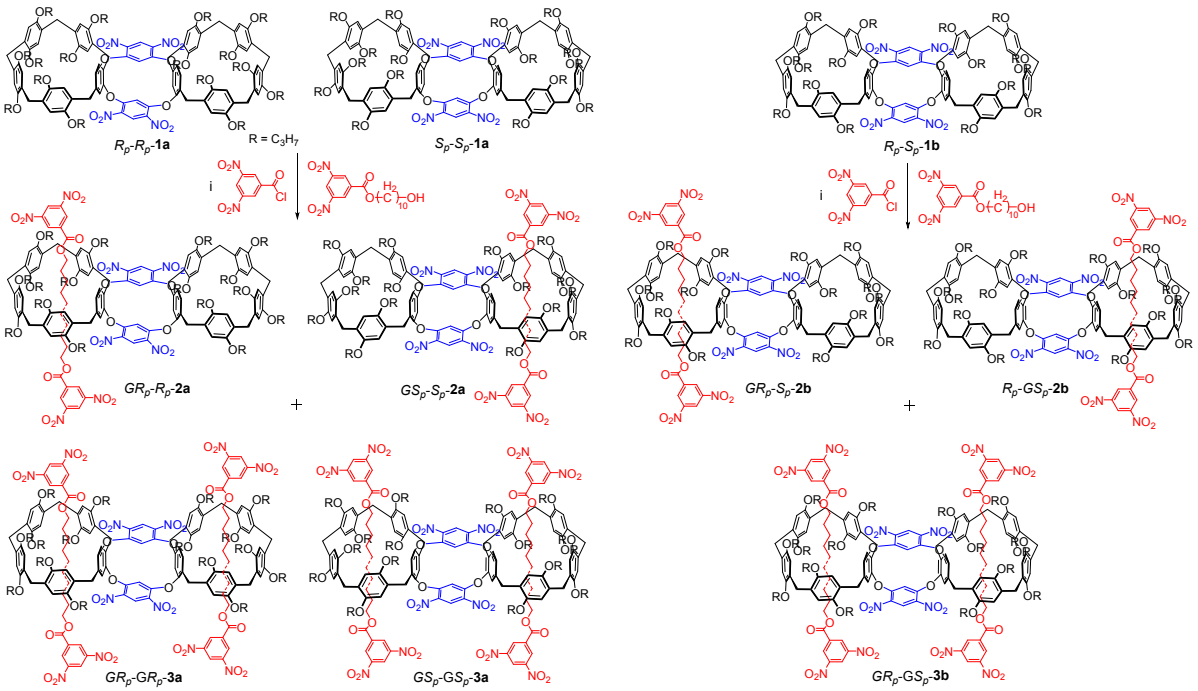
All reagents and solvents were commercially available and used as supplied without further purification. NMR spectra were recorded with a Bruker Advance Ⅱ DMX 400 spectrometer. Chemical shifts were expressed in parts per million (δ: ppm) using residual solvent protons or TMS as internal standards. Chloroform (δ = 7.26 ppm) was used as an internal standard for chloroform-*d*. DMSO (δ = 2.50 ppm) was used as an internal standard for DMSO-d_6. Coupling constants (*J* values) were given in hertz (Hz). High resolution mass spectra (HRMS) analysis was performed with a Waters Xevo G2-S Q-TOF mass spectrometer or with a Agilent 1290–6530 Q-TOF mass spectrometer. The single crystal X-ray diffraction data were collected on an Oxford Diffraction Xcalibur Atlas Gemini Ultra instrument. High performance liquid chromatography (HPLC) analysis was performed with Agilent 1260 Infinity instrument. A preparative Chiralpak ID column was used for the separation of enantiomers. UV-vis spectra and circular dichroism spectra were obtained on Olis DSM 172 spectrometer.

The starting material **DPP[4]A[1]Q** was synthesized according to a literature procedure.[S1]

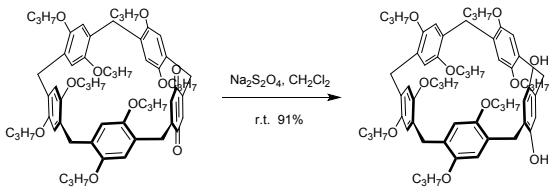
2. Syntheses and characterization for new compounds



Scheme S1 Synthetic routes of P[5]D **1a** and **1b** and representation of three isomers of oxacalix[4]arene-linked pillar[5]arene dimers.



Scheme S2 Synthetic route of [2]rotaxanes **2a** and **2b**, and [3]rotaxanes **3a** and **3b**. i: Et_3N, $CHCl_3$, 0 °C to r.t. Yields: **2a**, 29%, **3a**, 50%; **2b**, 27%, **3b**, 4%.



A solution of **DPP[4]A[1]Q** (0.90 g, 0.95 mmol) in CH_2Cl_2 (50 mL) was stirred in a 100 mL round bottom flask, while an aqueous solution of $Na_2S_2O_4$ (3.31 g, 19 mmol) was added. The mixture was stirred vigorously at r. t. for 4 h. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic phase was washed with water (50 mL) and saturated NaCl solution (50 mL), and dried with anhydrous Na_2SO_4. After flitration and concentration, **DPP[4]A[1]HQ** (0.82 g, 91%) was obtained as a white solid.

m. p.: 195.4-195.8 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 7.18 (br, 2H, ArO**H**), 6.88 (s, 2H, Ar**H**), 6.75 (s, 4H, Ar**H**), 6.52 (s, 2H, Ar**H**), 6.51 (s, 2H, Ar**H**), 3.87 (br, 4H, ArC**H**$_2$), 3.77–3.70 (m, 22H, ArC**H**$_2$, OC**H**$_2$), 1.82–1.62 (m, 16H, OCH$_2$C**H**$_2$), 1.04 (t, J = 7.4 Hz, 6H, C**H**$_3$), 1.00–0.91 (m, 18H C**H**$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 150.2, 148.9, 148.6, 146.5, 146.2, 128.4, 127.4, 126.6, 126.3, 125.8, 117.1, 115.1, 114.1, 113.6, 112.8, 70.5, 69.0, 68.9, 68.8, 29.8, 28.6, 28.3, 22.0, 22.0, 21.3, 9.8, 9.7, 9.4.

HRMS (ESI-TOF): *m*/*z* calcd. for $[C_{59}H_{78}O_{10}+H]^+$, 947.5668, found 947.5640, error 3.0 ppm.

UV-vis ([**DPP[4]A[1]HQ**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 296 nm, *Abs* = 0.584, ε = 1.95 × 10^4 L·mol^{-1}·cm^{-1}.

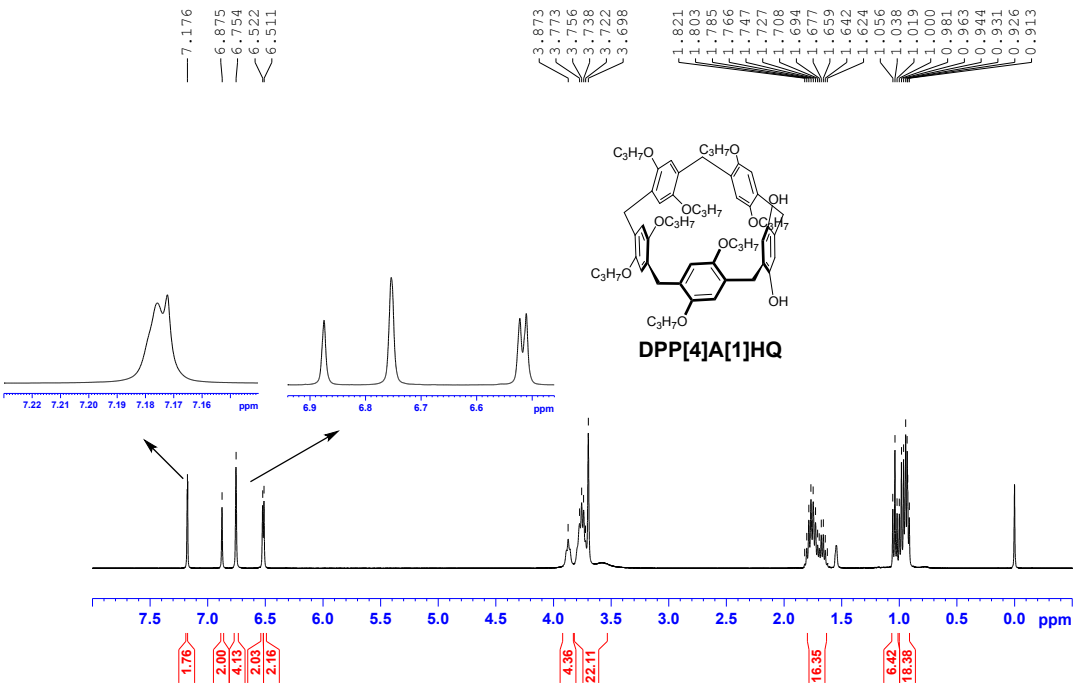


Fig. S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **DPP[4]A[1]HQ**.

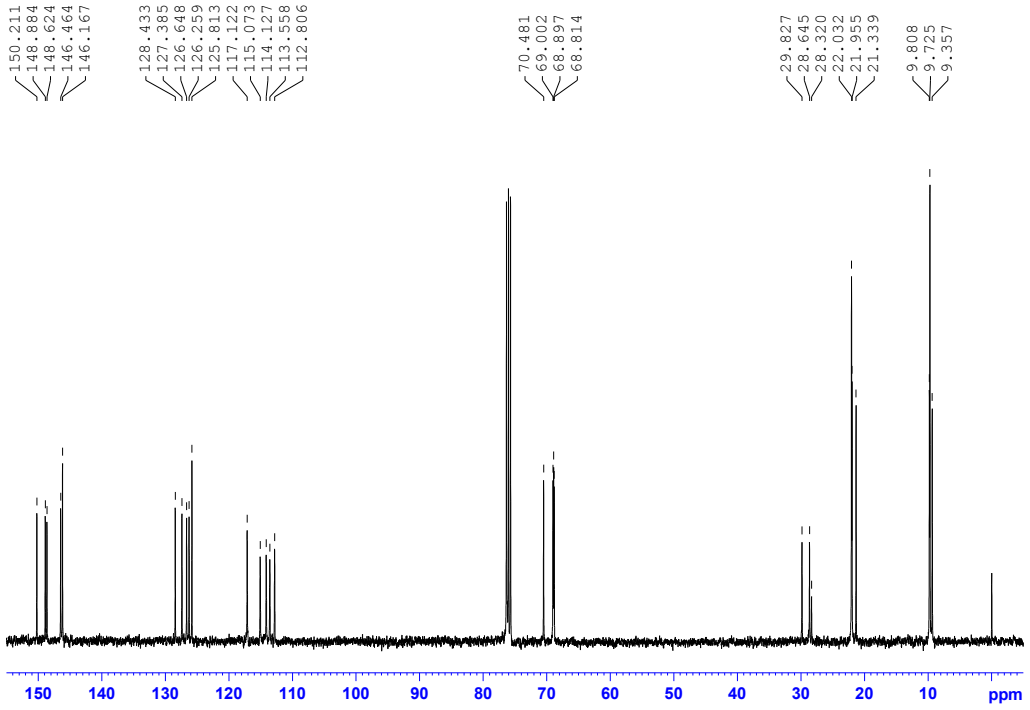
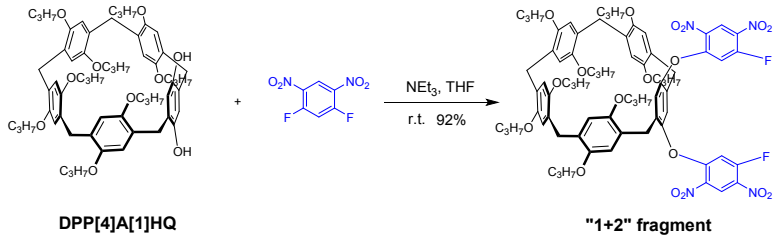


Fig. S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **DPP[4]A[1]HQ**.



To a solution of **DPP[4]A[1]HQ** (1.40 g, 1.48 mmol) and 1,5-difluoro-2,4-dinitroben-zene (0.91 g, 4.44 mmol) in THF (150 mL) was added NEt_3 (0.45 g, 4.44 mmol). The reaction mixture was stirred for 3 days under nitrogen atmosphere at room temperature, and then concentrated and chromatographed on a silica gel column (petroleum ether/CH_2Cl_2, 3:1→ 1:1 v/v) to give pure **"1+2" fragment** (1.80 g, 92%) as a yellow solid.

m. p.: 165.4-166.7 ℃.

^1H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.84 (d, J = 7.32 Hz, 2H, Ar**H**), 7.28 (s, 2H, Ar**H**), 6.96 (s, 2H, Ar**H**), 6.94 (s, 2H, Ar**H**), 6.71 (s, 2H, Ar**H**), 6.56 (s, 2H, Ar**H**), 6.31 (d, J = 11.40 Hz, 2H, Ar**H**), 3.99 (dt, J = 8.9 Hz, 6.4 Hz, 2H, ArC$\mathbf{H}_2$), 3.86–3.63 (m, 20H, ArC$\mathbf{H}_2$, OC$\mathbf{H}_2$), 3.53 (dd, J = 16.9 Hz, 10.4 Hz, 4H, ArC$\mathbf{H}_2$), 1.92–1.73 (m, 12H, $OCH_2C\mathbf{H}_2$), 1.52–1.40 (m, 4H, $OCH_2C\mathbf{H}_2$), 1.13–1.04 (m, 18H, C$\mathbf{H}_3$), 0.80 (t, J = 7.4 Hz, 6H, C$\mathbf{H}_3$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 149.2, 146.5, 146.5, 146.4, 139.5, 139.4, 139.3, 138.1, 124.9, 123.8, 120.3, 120.2, 120.1, 118.5, 117.4, 114.1, 114.0, 113.6, 104.4, 104.2, 103.9, 103.3, 97.5, 97.2, 66.9, 66.6, 66.3, 59.5, 59.4, 59.3, 39.6, 19.9, 19.3, 18.7, 18.4, 12.8, 12.8, 12.7, 12.3.

HRMS (ESI-TOF): m/z calcd. for $[C_{71}H_{80}F_2N_4O_{18}+Na]^+$, 1337.5328, found 1337.5344, error 1.2 ppm.

UV-vis ([**"1+2" fragment**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 297 nm, Abs = 0.881, ε = 2.94 × 10^4 L·mol^{-1}·cm^{-1}.

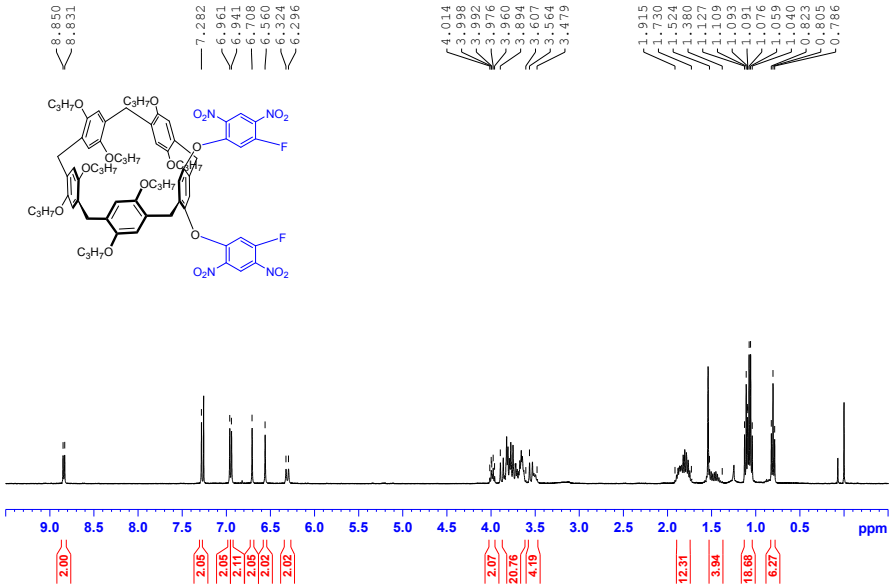


Fig. S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for "1+2" fragment .

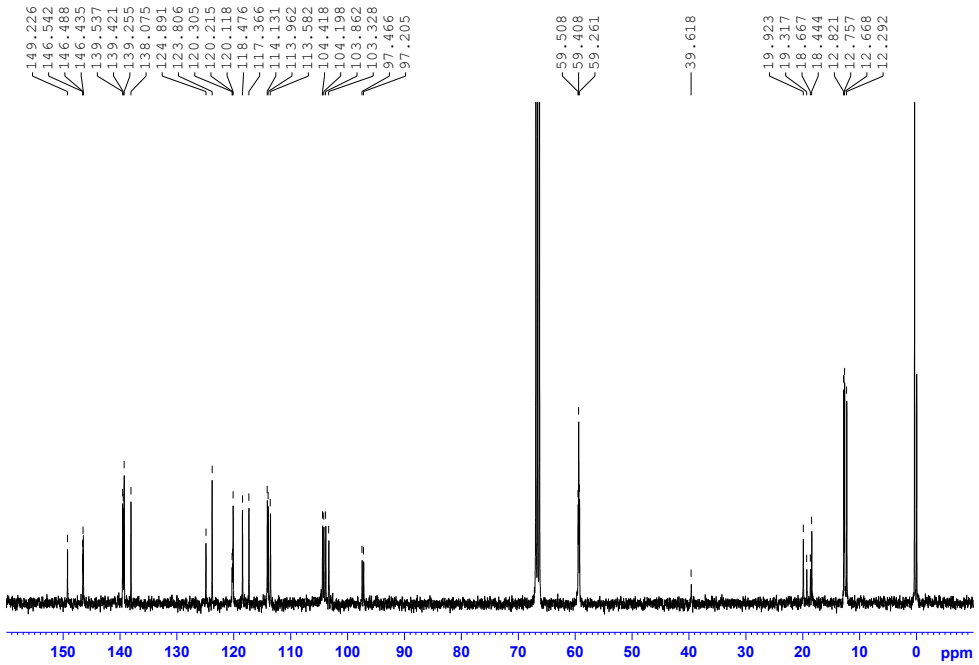
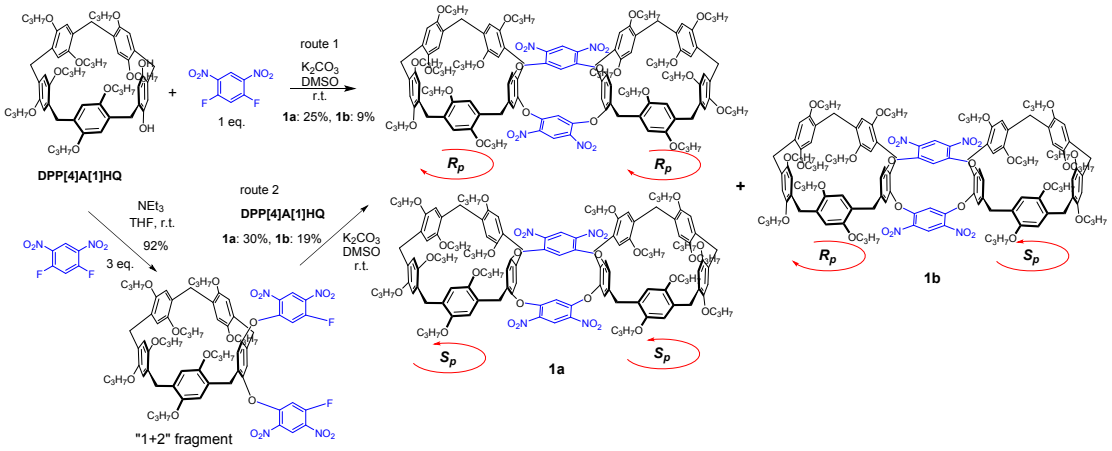


Fig. S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for "1+2" fragment.



Route 1 :

DPP[4]A[1]HQ (0.92 g, 0.97 mmol), 1,5-difluoro-2,4-dinitrobenzene (0.20 g, 0.97 mmol) and K_2CO_3 (0.81 g, 5.88 mmol) were added to a double-mouth round bottom flask. Then DMSO (65 mL) was added to the flask. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 5 days. CH_2Cl_2 (100 mL) and water (100 mL) were added to the solution. Then the organic solvent was collected, and the water layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (3 × 50 mL), and dried with anhydrous Na_2SO_4, and then concentrated and chromatographed on a silica gel column (petroleum ether/CH_2Cl_2, 2:1→ 4:3 v/v) to give pure yellow solid **1a** (0.27 g, 25%) and **1b** (0.10 g, 9%).

Route 2 :

"1+2" Fragment (0.58 g, 0.44 mmol), **DPP[4]A[1]HQ** (0.42 g, 0.44 mmol) and K_2CO_3 (0.37 g, 2.66 mmol) were added to the double-mouth round bottom flask, and then DMSO (40 mL) was added to the flask. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 5 days. CH_2Cl_2 (100 mL) and water (100 mL) were added to the solution. Then the organic solvent was collected, and the water layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (3 × 50 mL), and dried with anhydrous Na_2SO_4, and then concentrated and chromatographed on a silica gel column (petroleum ether/CH_2Cl_2, 2:1 → 4:3 → 1:1 v/v) to give pure yellow solid **1a** (0.29 g, 30%) and **1b** (0.19 g, 19%).

Product **1a**

m. p.: 195.4-195.8 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.98 (s, 2H, Ar**H**), 7.16 (s, 4H, Ar**H**), 6.87 (s, 4H, Ar**H**), 6.83 (s, 4H, Ar**H**), 6.80 (s, 4H, Ar**H**), 6.78 (s, 4H, Ar**H**), 5.78 (s, 2H, Ar**H**), 4.10 (dt, J = 9.2 Hz, 6.3 Hz, 4H, ArC**H**$_2$), 3.91–3.66 (m, 44H, ArC**H**$_2$, OC**H**$_2$), 3.23 (d, J = 12.9 Hz, 4H, ArC**H**$_2$), 1.90–1.59 (m, 32H, OCH$_2$C**H**$_2$), 1.11 (t, J = 7.4 Hz, 12H, C**H**$_3$), 1.05 (t, J = 7.4 Hz, 12H, C**H**$_3$), 0.96 (t, J = 7.4 Hz, 12H, C**H**$_3$), 0.83 (t, J = 7.4 Hz, 12H, C**H**$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 157.3, 150.6, 150.0, 149.7, 149.2, 147.6, 134.5, 131.6, 129.6, 128.9, 127.7, 126.3, 125.4, 124.4, 115.2, 115.1, 113.8, 103.1, 70.0, 69.8, 30.3, 29.5, 23.1, 22.9, 22.8, 10.8, 10.7, 10.6.

HRMS (ESI): *m*/*z* calcd. for $[C_{130}H_{156}N_4O_{28}+Na]^+$, 2244.0798, found 2244.0813, error 0.67 ppm.

UV-vis ([**1a**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 297 nm, *Abs* = 1.50, ε = 5.00 × 10^4 L·mol^{-1}·cm^{-1}.

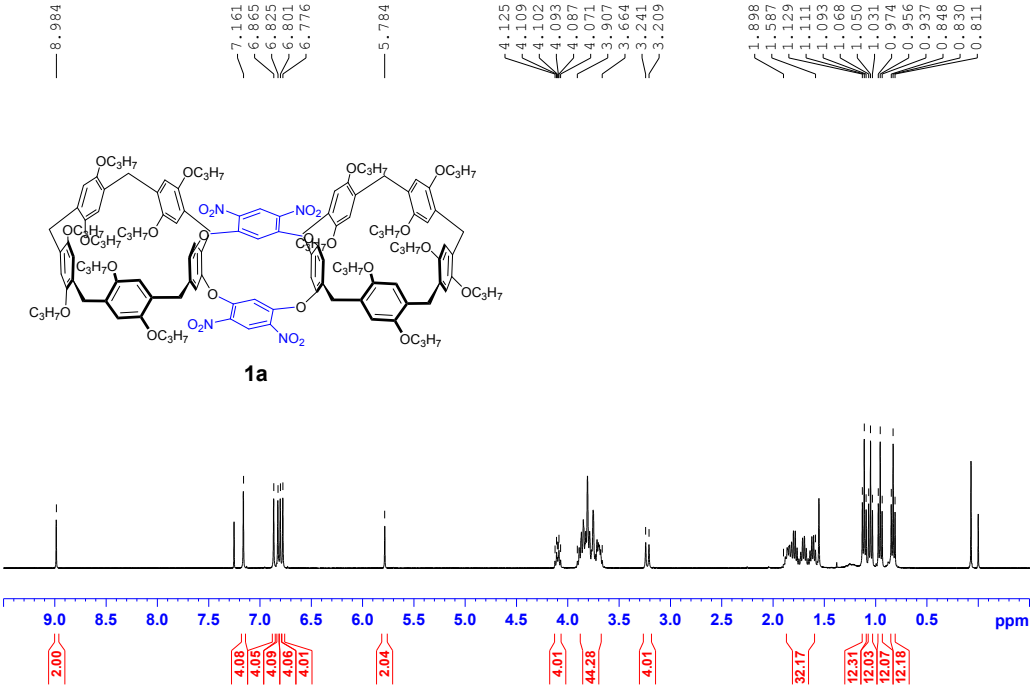


Fig. S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **1a**.

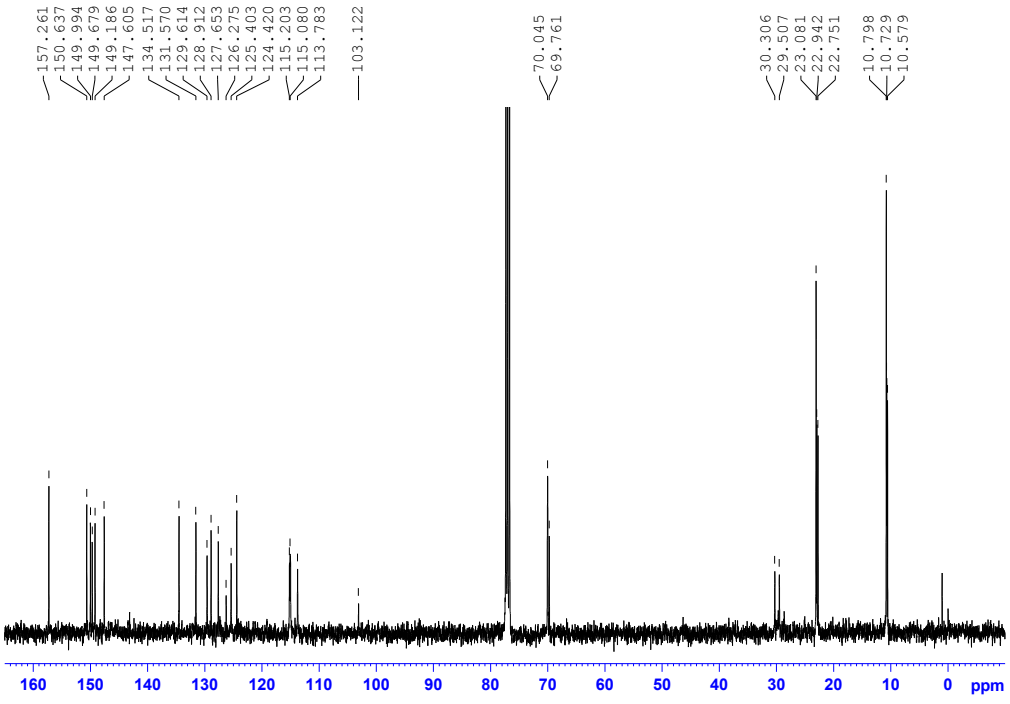


Fig. S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **1a**.

Product **1b**

m. p. 275.2-275.8 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 8.97 (s, 2H, Ar**H**), 7.20 (s, 4H, Ar**H**), 6.89 (s, 4H, Ar**H**), 6.87 (s, 4H, Ar**H**), 6.86 (s, 4H, Ar**H**), 6.75 (s, 4H, Ar**H**), 5.69 (s, 2H, Ar**H**), 4.14–4.09 (m, 4H, ArC$\mathbf{H}_2$), 3.94–3.71 (m, 44H, ArC$\mathbf{H}_2$, OC$\mathbf{H}_2$), 3.13 (d, J = 6.5 Hz, 4H, ArC$\mathbf{H}_2$), 1.93–1.67 (m, 32H, $OCH_2C\mathbf{H}_2$), 1.14 (t, J = 7.4 Hz, 12H, C$\mathbf{H}_3$), 1.09 (t, J = 7.4 Hz, 12H, C$\mathbf{H}_3$), 1.04 (t, J = 7.4 Hz, 12H, C$\mathbf{H}_3$), 0.93 (t, J = 7.4 Hz, 12H, C$\mathbf{H}_3$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 157.1, 150.3, 149.7, 149.6, 149.1, 147.8, 135.0, 131.7, 129.8, 128.6, 127.7, 126.1, 125.2, 124.1, 114.5, 113.5, 103.1, 69.8, 69.7, 31.5, 30.8, 29.6, 23.1, 23.1, 22.8, 10.8, 10.7, 10.7, 10.6.

HRMS (ESI): *m/z* calcd for $[C_{130}H_{156}N_4O_{28}+Na]^+$, 2244.0798, found 2244.0796, error 0.09 ppm.

UV-vis ([**1b**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 297 nm, *Abs* = 1.38, ε = 4.60 × 10^4 L·mol^{-1}·cm^{-1}.

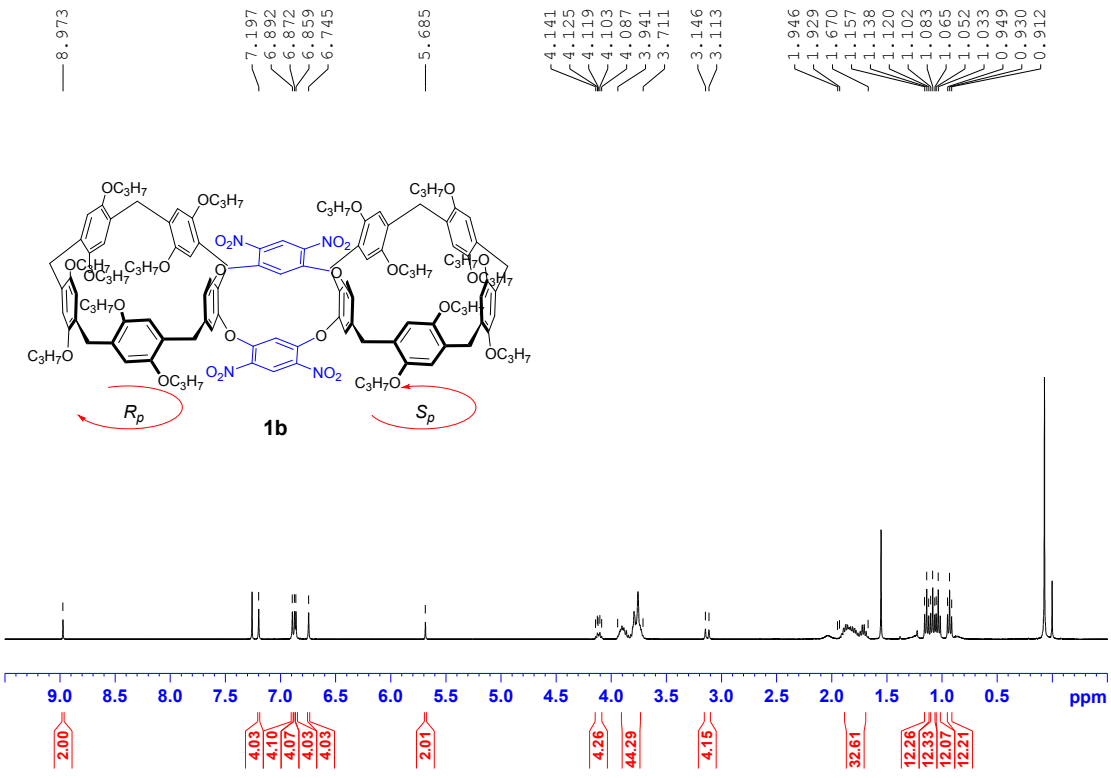


Fig. S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **1b**.

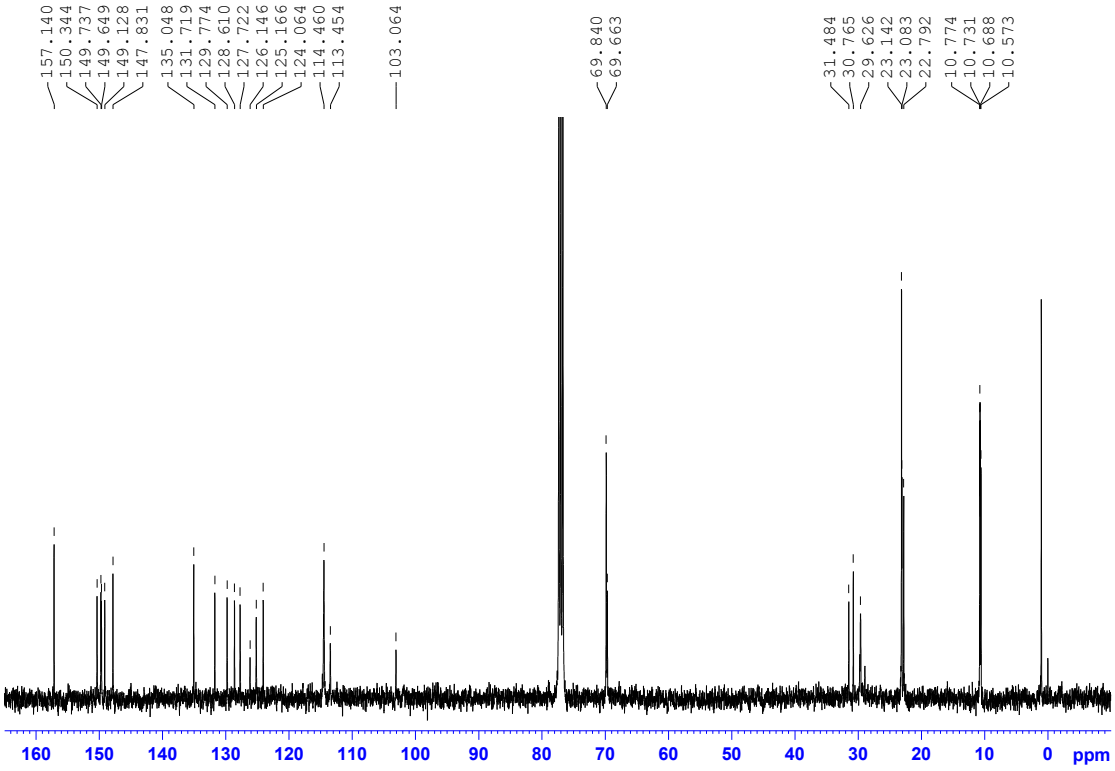
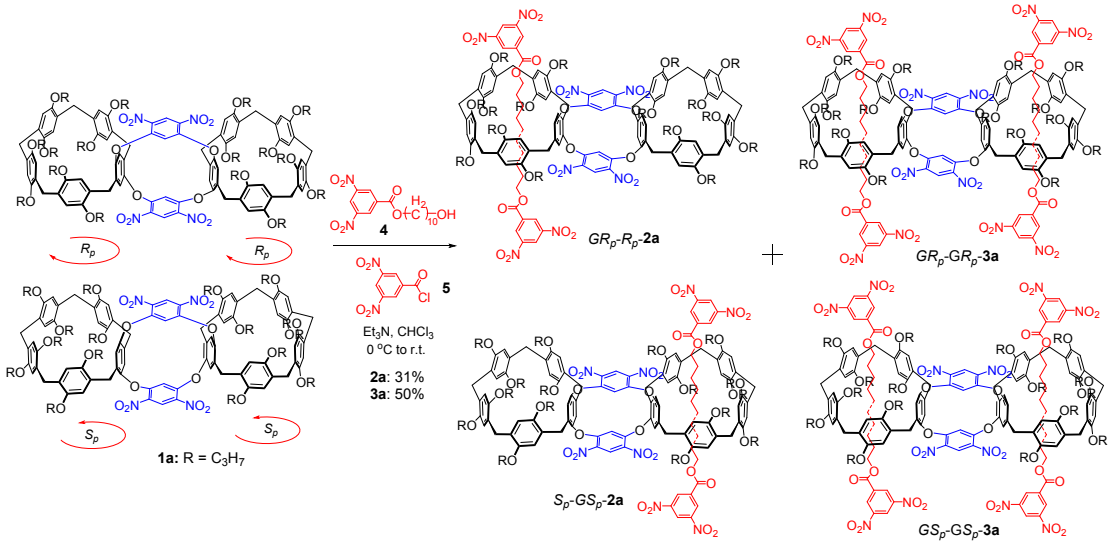


Fig. S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **1b**.



A mixture of **1a** (0.22 g, 0.10 mmol) and **4** (0.30 g, 0.80 mmol) in anhydrous $CHCl_3$ (0.6 mL) was stirred at 0 °C for 1 h, following by addition of Et_3N (0.13 g, 1.20 mmol). Then a solution of 3,5-dinitrobenzoyl chloride **5** (0.28 g, 1.20 mmol) in anhydrous $CHCl_3$ was added dropwise within 5 min. After 10 min, the mixture was allowed to warm slowly to room temperature and stirred for 24 h. Then the mixture was concentrated and chromatographed on a silica gel column (petroleum ether/CH_2Cl_2, 2:1→ 1:1→1:2 v/v) to give yellow solids **2a** (0.08 g, 29%) and **3a** (0.17 g, 50%).

Product **2a**

m. p.: 178.1–179.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 9.25 (t, J = 2.1 Hz, 2H, Ar**H**), 9.18 (d, J = 2.1 Hz, 4H, Ar**H**), 8.84 (s, 2H, Ar**H**), 7.40 (s, 2H, Ar**H**), 7.18 (s, 2H, Ar**H**), 7.00 (s, 2H, Ar**H**), 6.95 (s, 2H, Ar**H**), 6.88 (s, 4H, Ar**H**), 6.87 (s, 2H, Ar**H**), 6.84 (s, 2H, Ar**H**), 6.83 (s, 2H, Ar**H**), 6.79 (s, 2H, Ar**H**), 5.81 (s, 2H, Ar**H**), 4.15–4.10 (m, 2H, *G*COOC**H**$_2$), 4.08–4.03 (m, 4H, ArC**H**$_2$), 3.93–3.64 (m, 46H, ArC**H**$_2$, OC**H**$_2$, *G*COOC**H**$_2$), 3.32 (d, J = 12.9 Hz, 4H, ArC**H**$_2$), 3.20 (d, J = 12.7 Hz, 4H, ArC**H**$_2$), 2.00–1.62 (m, 32H, $OCH_2C\mathbf{H}_2$), 1.18 (t, J = 7.4 Hz, 6H, C**H**$_3$), 1.13 (t, J = 7.4 Hz, 6H, C**H**$_3$), 1.11–1.04 (m, 12H, C**H**$_3$), 1.01 (t, J = 7.4 Hz, 6H, C**H**$_3$), 0.97 (t, J = 7.4 Hz, 6H, C**H**$_3$), 0.89–0.72 (m, 20H, C**H**$_3$, *G*C**H**$_2$), –0.24 (br, 8H, *G*C**H**$_2$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 162.3, 157.4, 157.1, 150.8, 150.6, 149.9, 149.7, 149.2, 148.7, 147.8, 147.6, 135.0, 134.6, 134.4, 131.7, 131.3, 130.2, 129.6, 129.3, 128.9, 128.8, 127.7, 126.2, 125.4, 125.3, 124.7, 124.4, 122.2, 115.5, 115.0, 114.1, 113.8, 113.6, 103.0, 70.2, 70.1, 70.0, 69.7, 67.5, 30.2, 30.1, 29.7, 29.5, 28.2, 24.7, 23.3, 23.3, 23.1, 23.0, 22.8, 22.7, 10.8, 10.7, 10.6, 10.5.

HRMS (ESI): *m*/*z* calcd. for $[C_{154}H_{182}N_8O_{40}+Na]^+$, 2806.2346, found 2806.2287, error 2.1 ppm.

UV-vis ([**2a**] = 3 × 10^{-5} M, 25 ^{o}C): λ_{max} = 296 nm, *Abs* = 1.41, ε = 4.70 × 10^4 L·mol^{-1}·cm^{-1}.

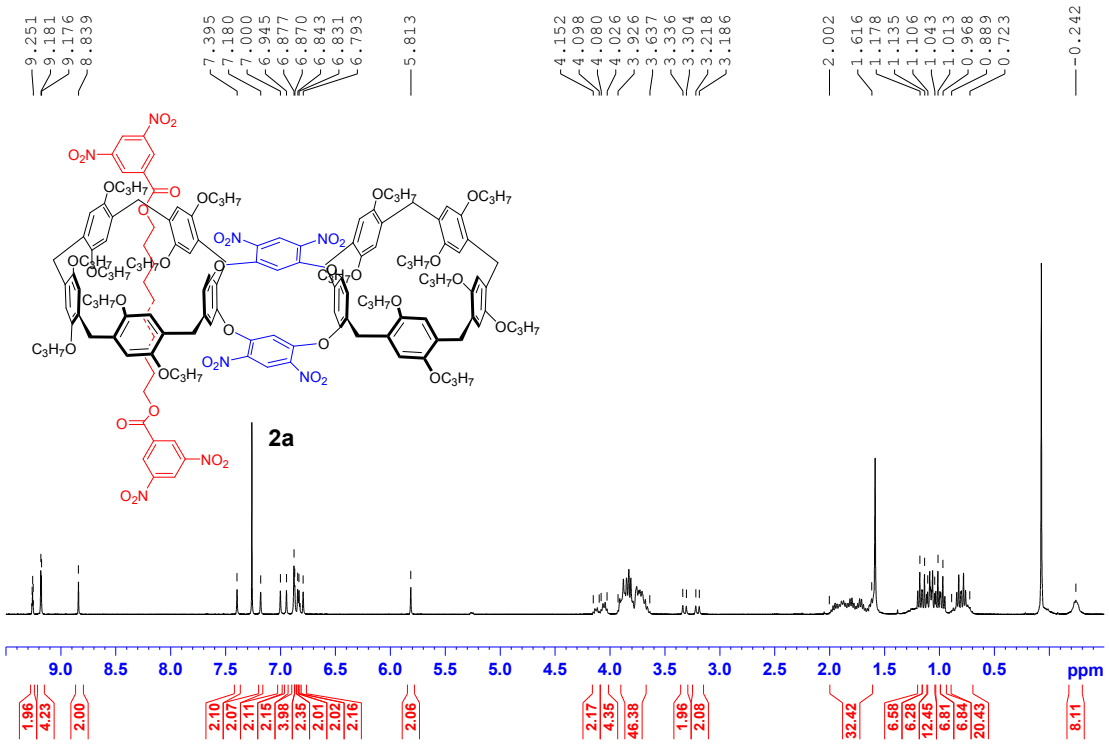


Fig. S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **2a**.

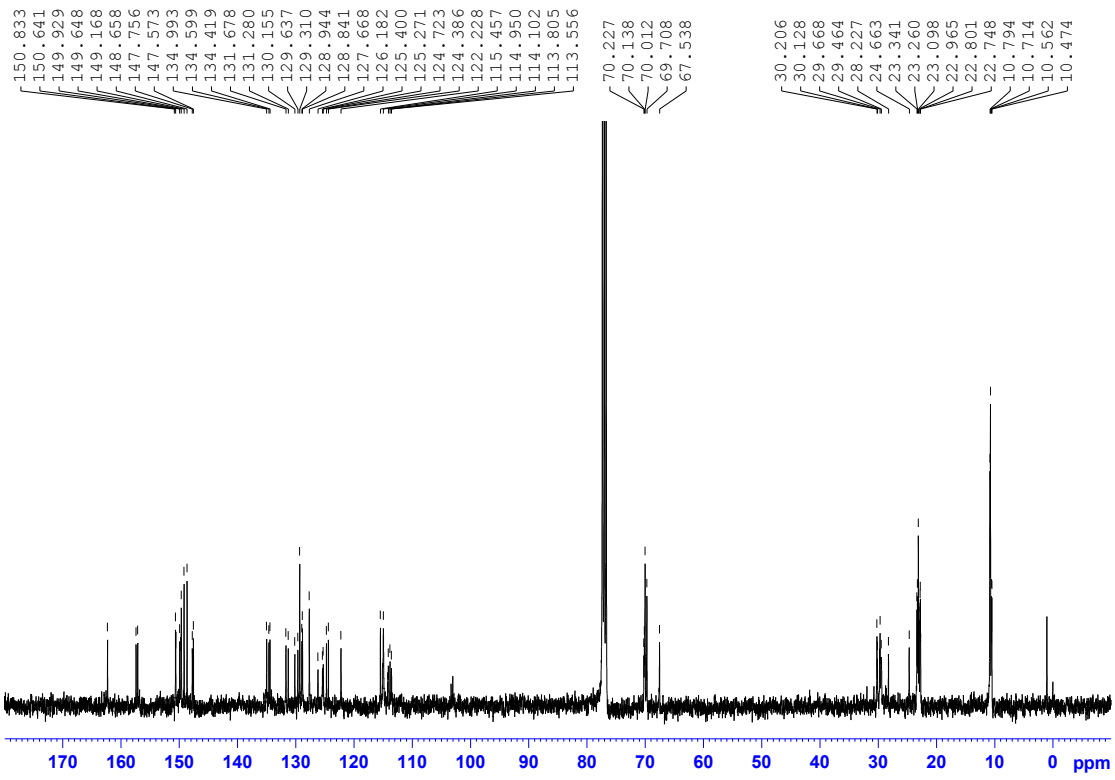


Fig. S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **2a**.

Product **3a**

m. p. > 300 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 9.23 (t, J = 2.1 Hz, 4H, Ar**H**), 9.16 (d, J = 2.1 Hz 8H, Ar**H**), 8.67 (s, 2H, Ar**H**), 7.41 (s, 4H, Ar**H**), 7.01 (s, 4H, Ar**H**), 6.95 (s, 4H, Ar**H**), 6.91 (s, 4H, Ar**H**), 6.87 (s, 4H, Ar**H**), 5.84 (s, 2H, Ar**H**), 4.09–4.03 (m, 8H, ArC**H**$_2$, *G*COOC**H**$_2$), 3.93–3.63 (m, 48H, ArC**H**$_2$, OC**H**$_2$, *G*COOC**H**$_2$), 3.31 (d, J = 12.8 Hz, 4H, ArC**H**$_2$), 2.01–1.58 (m, 32H, OCH$_2$C**H**$_2$), 1.18 (t, J = 7.4 Hz, 12H, C**H**$_3$), 1.10 (t, J = 7.4 Hz, 12H, C**H**$_3$), 1.01 (t, J = 7.4 Hz, 12H, C**H**$_3$), 0.88–0.83 (m, 6H, *G*C**H**$_2$) 0.78–0.73 (m, 22H, C**H**$_3$, *G*C**H**$_2$), –0.24 (br, 16H, *G*CH$_2$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 162.3, 157.3, 150.7, 149.7, 149.7, 149.2, 148.6, 147.7, 135.1, 134.4, 131.4, 130.2, 129.3, 128.94, 127.7, 126.1, 125.3, 124.8, 122.2, 115.0, 114.1, 113.6, 103.0, 70.1, 69.7, 67.5, 37.4, 37.1, 34.4, 32.8, 32.0, 31.5, 30.2, 30.1, 29.7, 29.7, 29.4, 28.6, 28.2, 28.00, 27.1, 26.8, 26.4, 25.9, 25.5, 24.7, 24.5, 23.4, 23.3, 22.8, 22.7, 19.8, 14.1, 10.8, 10.7, 10.5.

MALDI-TOF-MS: *m*/*z* calculated for $[C_{178}H_{208}N_{12}O_{52}+H]^+$, 3346.407 found 3347.495, error 0.33‰. X-ray single crystal analysis of **3a** was further carried out.

UV-vis ([**3a**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 295 nm, *Abs* = 1.69, ε = 5.63 × 10^4 L·mol^{-1}·cm^{-1}.

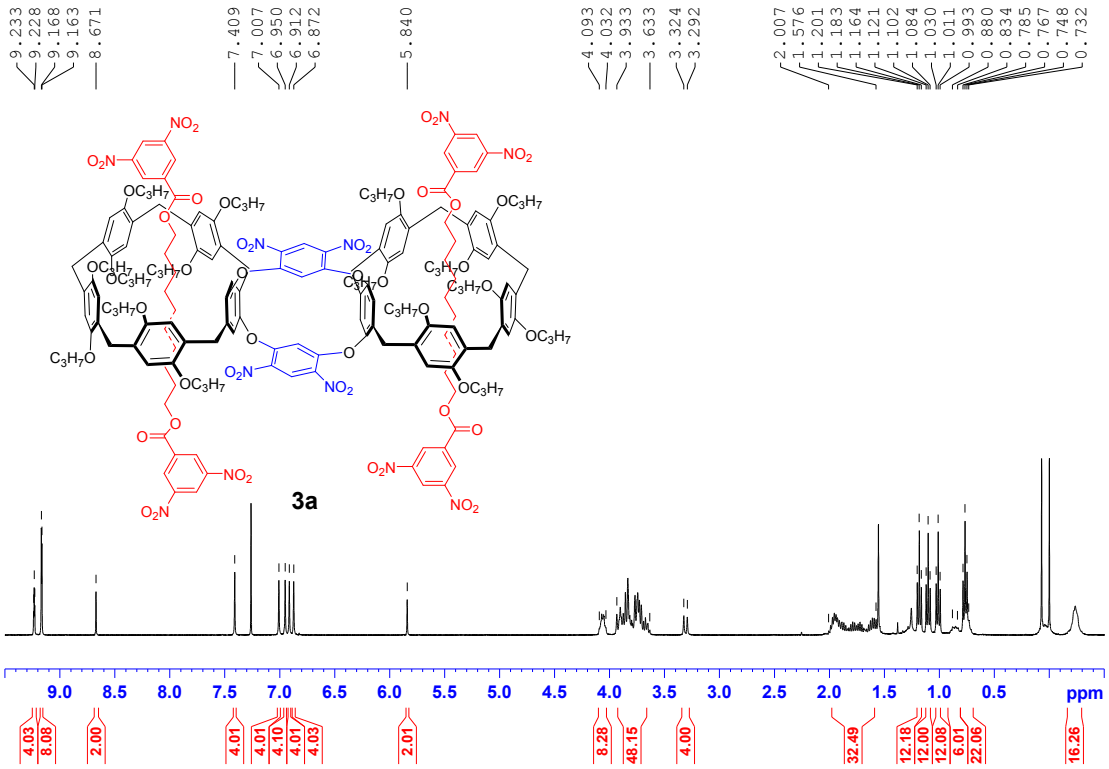


Fig. S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **3a**.

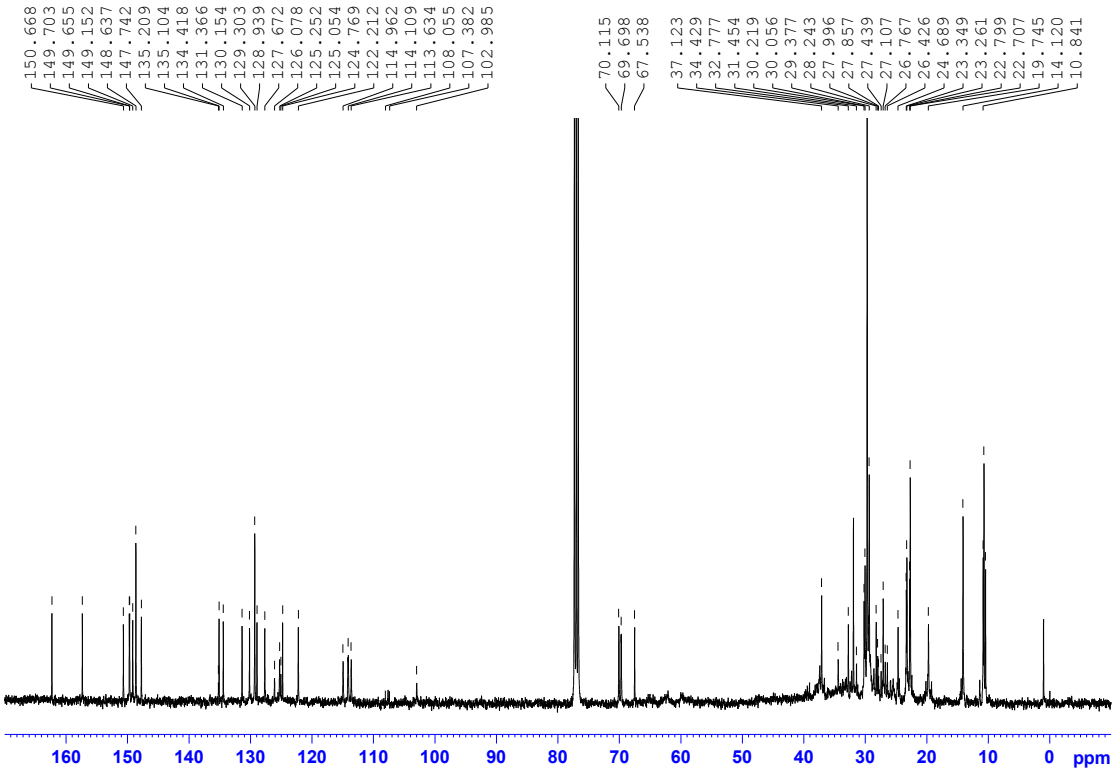
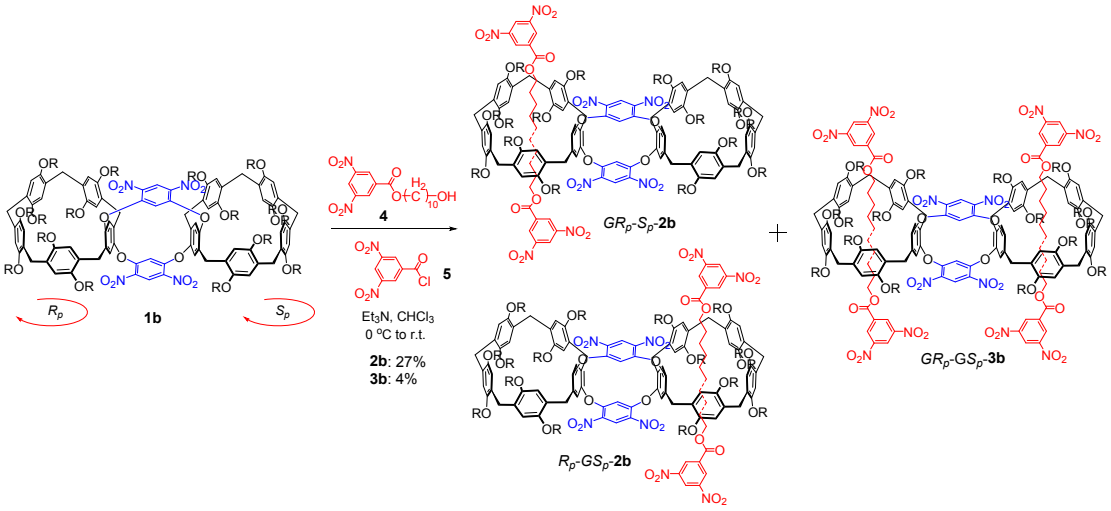


Fig. S12. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **3a**.



A mixture of **1b** (0.22 g, 0.10 mmol) and **4** (0.30 g, 0.60 mmol) in anhydrous $CHCl_3$ (1.5 mL) was stirred at 0 °C for 1 h, following by addition of Et_3N (0.15 g, 1.50 mmol). Then a solution of 3,5-dinitrobenzoyl chloride **5** (0.35 g, 1.50 mmol) in anhydrous $CHCl_3$ was added dropwise within 5 min. After 10 min, the mixture was allowed to warm slowly to room temperature and stirred for 24 h. Then the mixture was concentrated and chromatographed on a silica gel column (petroleum ether/CH_2Cl_2, 2:1→ 1:1→1:2 v/v) to give yellow solids **2b** (0.08 g, 27%) and **3b** (0.01 g, 4%).

Product 2**b**

m. p.: 250.9–251.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 9.27 (br, 2H, Ar**H**), 9.20 (d, J = 1.9 Hz, 4H, Ar**H**), 8.82 (s, 2H, Ar**H**), 7.36 (s, 2H, Ar**H**), 7.20 (s, 2H, Ar**H**), 6.98 (s, 2H, Ar**H**), 6.95 (s, 2H, Ar**H**), 6.89 (s, 2H, Ar**H**), 6.84 (s, 2H, Ar**H**), 6.83 (s, 4H, Ar**H**), 6.81 (s, 2H, Ar**H**), 6.73 (s, 2H, Ar**H**), 5.73 (s, 2H, Ar**H**), 4.08–4.03 (m, 6H, ArC**H**$_2$ *G*COOC**H**$_2$), 3.91–3.67 (m, 46H, ArC**H**$_2$, OC**H**$_2$, *G*COOC**H**$_2$), 3.15 (d, J = 4.1 Hz, 2H, ArC**H**$_2$), 3.12 (d, J = 3.9 Hz, 4H, ArC**H**$_2$), 1.98–1.64 (m, 32H, OCH$_2$C**H**$_2$), 1.18 (t, J = 7.4 Hz, 6H, C**H**$_3$), 1.12–1.03 (m, 24H, C**H**$_3$), 1.01–0.97 (t, J = 7.8 Hz, 6H, C**H**$_3$), 0.91–0.77 (m, 20H, C**H**$_3$, *G*C**H**$_2$), –0.23 (br, 8H, *G*C**H**$_2$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 161.3, 156.4, 156.1, 149.5, 149.4, 148.8, 148.6, 148.6, 148.1, 148.0, 147.6, 146.9, 146.7, 134.4, 133.9, 133.4, 130.6, 130.2, 129.0, 128.7, 128.3, 127.8, 127.6, 126.7, 126.6, 125.1, 124.3, 124.0, 123.6, 123.1, 121.2, 114.4, 113.9, 113.8, 113.0, 112.6, 112.4, 101.9, 69.1, 68.9, 68.7, 66.5, 29.2, 28.8, 28.6, 28.4, 27.2, 23.7, 22.3, 22.2, 22.2, 22.0, 22.0, 21.8, 21.7, 9.8, 9.8, 9.7, 9.5, 9.4.

HRMS (ESI): *m*/*z* calcd. for $[C_{154}H_{182}N_8O_{40}+H]^+$, 2784.25261, found 2784.23853, error 4.9 ppm.

UV-vis ([**2b**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 296 nm, *Abs* = 1.59, ε = 5.30 × 10^4 L·mol^{-1}·cm^{-1}.

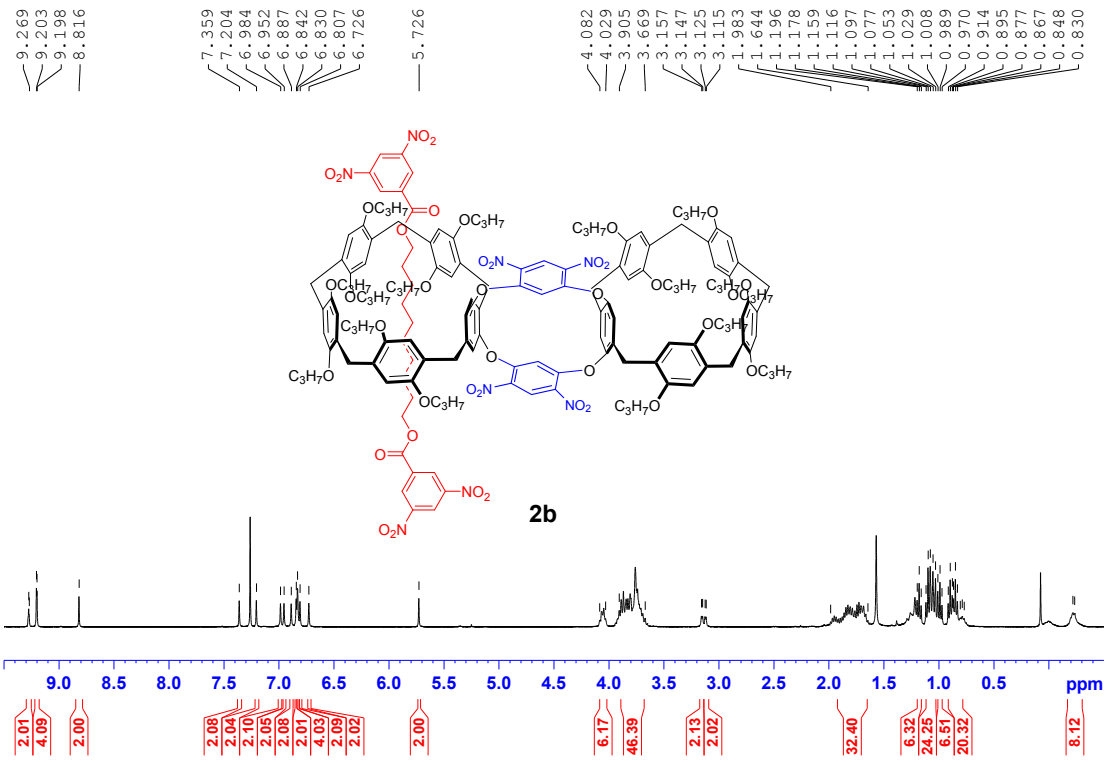


Fig. S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **2b**.

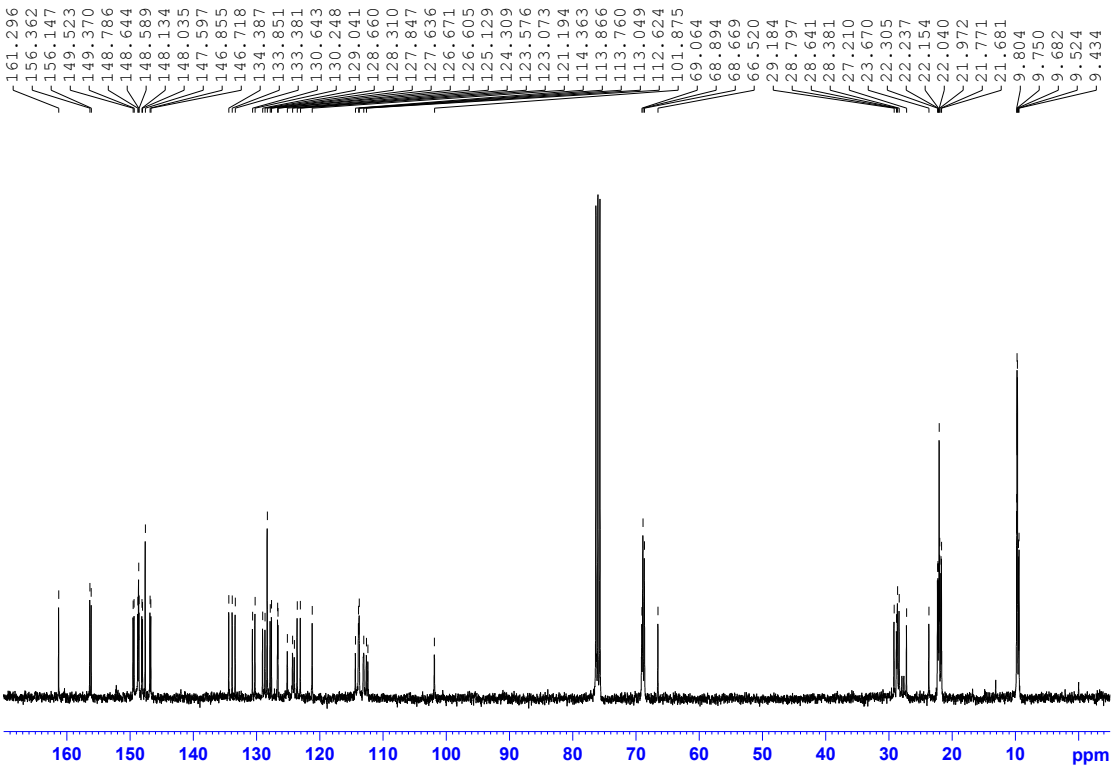


Fig. S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **2b**.

Product **3b**

m. p.: > 300 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 9.27 (t, J = 2.0 Hz, 4H, Ar**H**), 9.21 (d, J = 2.1 Hz 8H, Ar**H**), 8.66 (s, 2H, Ar**H**), 7.42 (s, 4H, Ar**H**), 6.98 (s, 4H, Ar**H**), 6.95 (s, 4H, Ar**H**), 6.89 (s, 4H, Ar**H**), 6.81 (s, 4H, Ar**H**), 5.74 (s, 2H, Ar**H**), 4.07–4.02 (m, 8H, ArC$\mathbf{H}_2$, *G*COOC$\mathbf{H}_2$), 3.92–3.63 (m, 48H, ArC$\mathbf{H}_2$, OC$\mathbf{H}_2$, *G*COOC$\mathbf{H}_2$), 3.11 (d, J = 13.0 Hz, 4H, ArC$\mathbf{H}_2$), 2.00–1.64 (m, 32H, $OCH_2C\mathbf{H}_2$), 1.18 (t, J = 7.4 Hz, 12H, C$\mathbf{H}_3$), 1.19–1.01 (m, 24H, C$\mathbf{H}_3$), 0.87–0.78 (m, 28H, C$\mathbf{H}_3$ *G*C$\mathbf{H}_2$), –0.22 (br, 16H, *G*C$\mathbf{H}_2$).

^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 162.4, 157.4, 150.6, 149.8, 149.2, 148.7, 147.9, 135.5, 134.5, 131.5, 130.2, 129.5, 129.0, 127.7, 125.2, 124.6, 114.2, 113.4, 70.2, 70.0, 69.8, 67.6, 30.2, 29.8, 29.5, 28.3, 24.8, 23.4, 23.3, 22.8, 10.9, 10.8, 10.5.

HRMS (ESI): *m*/*z* calcd for $[C_{178}H_{208}N_{12}O_{52}+H]^+$, 3346.40733, found 3346.38330, error 7.2 ppm.

UV-vis ([**3b**] = 3 × 10^{-5} M, 25 °C): λ_{max} = 296 nm, *Abs* = 1.68, ε = 5.60 × 10^4 L·mol^{-1}·cm^{-1}.

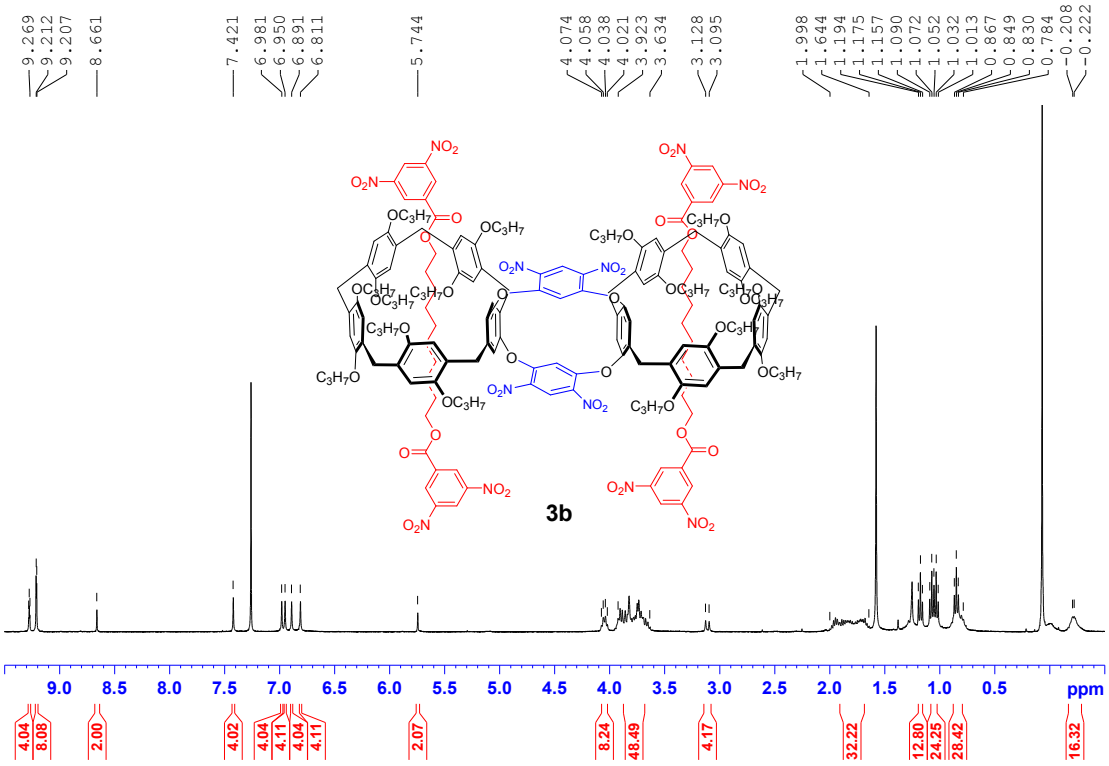


Fig. S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) for **3b**.

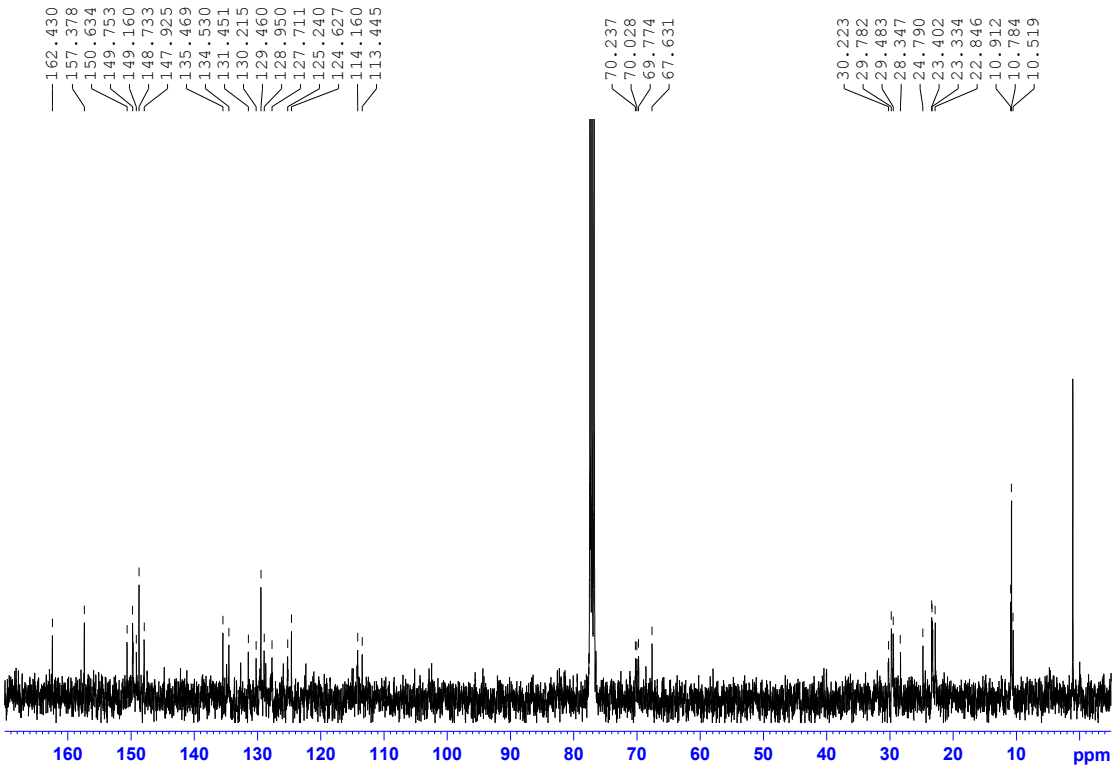


Fig. S16. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) for **3b**.

3. Influence of the yields of [2]rotaxane **2a** and [3]rotaxane **3a**

Table S1 Yields of the products after changing the molar ratio of **1a** and **4**.

Molar ratio	Yield of product	
1a:**4**	**2a**	**3a**
1:1	42%	< 1%
1:2	15%	6%
1:4	14%	21%
1:6	31%	44%
1:8	29%	50%
1:10	31%	19%

4. Comparison of ^{1}H NMR spectra for **1a** & **1b**

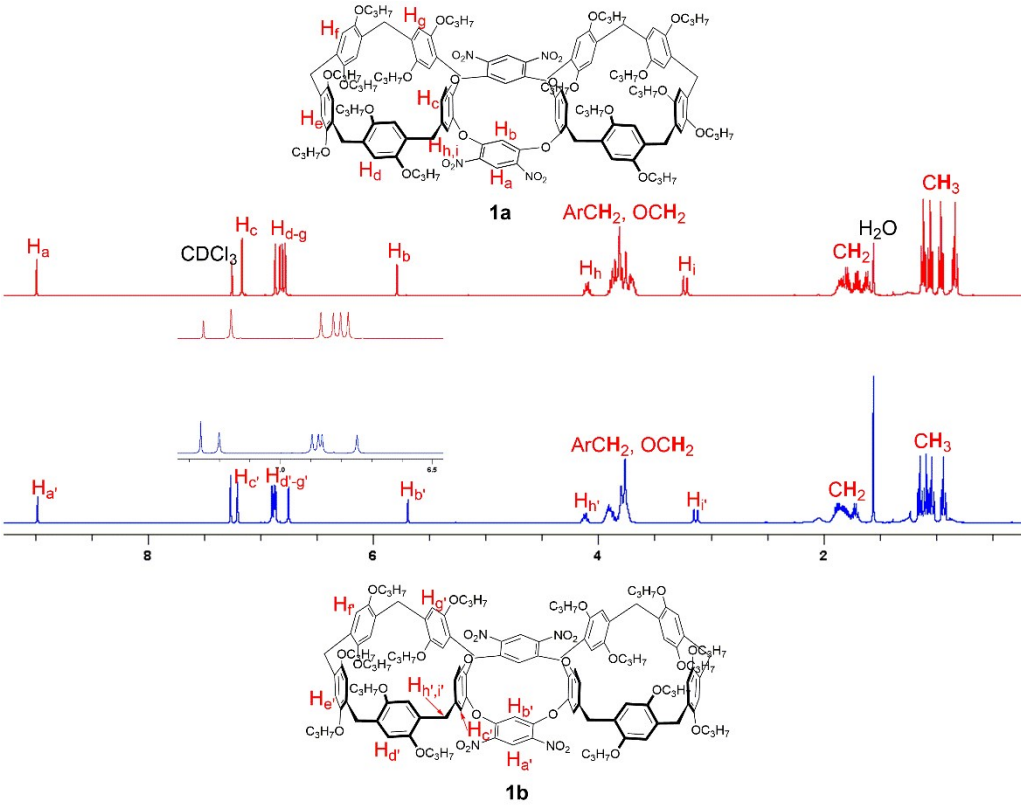


Fig. S17. Stacked ^{1}H NMR for P[5]D **1a** and **1b** in $CDCl_3$, 400 MHz, 298 K.

5. Complexation and Job plot for **1a** and **4**

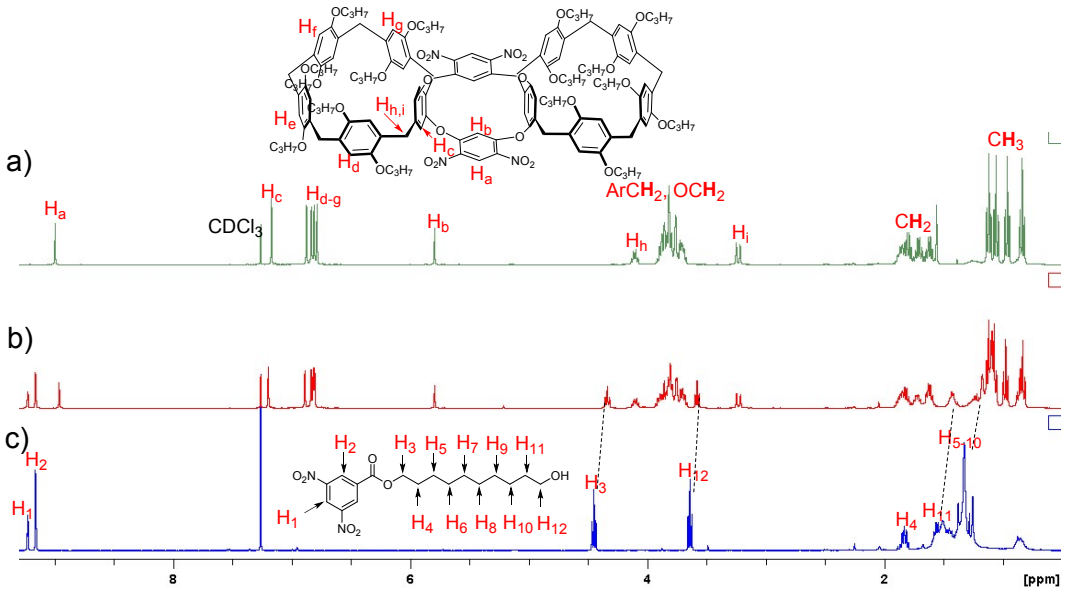


Fig. S18. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of (a) free host **1a**, (b) **1a** and 2.0 equiv. of **4**, (c) free guest **4**. [**1a**] = 10 mM.

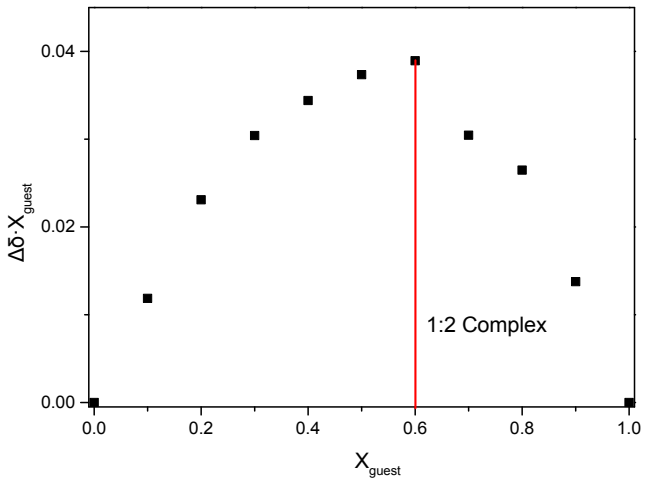


Fig. S19. Job plot of the complexation between **1a** and **4**. The Job plot was conducted by varying the mole fractions of host **1a** and guest **4**. Peak shifts of methylene protons adjacent to the ester group in **4** were utilized. Concentration: [**1a**] + [**4**] = 10 mM.

6. UV/Vis and CD spectra of **1b**

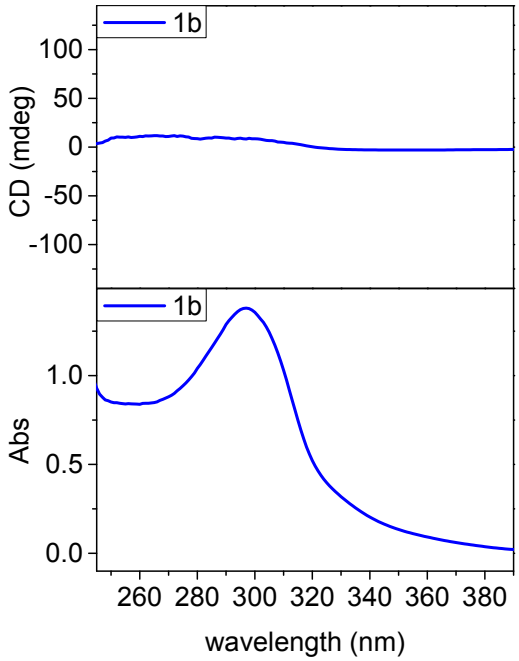


Fig. S20. UV/Vis and CD spectra of **1b** (3×10^{-5} M) in chloroform at 25 °C.

7. X-Ray single crystal parameters, packing diagram for **1b**, and structure for **3a**

Single crystals of **1b** and **3a** suitable for X-ray analysis were both obtained by slow evaporation of hexane into a $CHCl_3$ solution, respectively.

Crystal data and structure refinement for **1b**	
Identification code	190513_wk_005_2_0m_sq
Empirical formula	$C_{132}H_{158}Cl_6N_4O_{28}$
Moiety formula	$2(CHCl_3)$, $C_{130}H_{156}N_4O_{28}$
Formula Weight	2461.31
Temperature / K	170(2)
Crystal size / mm^3	0.309 × 0.283 × 0.103
Crystal system	triclinic
Space group	P −1 (2)
a / Å	14.4932(11)
b / Å	21.9303(16)
c / Å	24.2711(18)
α / °	85.199(2)
β / °	74.810(2)
γ / °	83.340(2)
Volume U / $Å^3$	7383.1(10)
Z	2
Density Calculated D_c / $g \cdot cm^{-3}$	1.107
μ / mm^{-1}	0.181
F_{000}	2608
Radiation wavelength	λ(Mo-K_α) = 0.71073 Å
2θ range for data collection / °	4.56 ~ 50.68
Index ranges	$-18 \le h \le 18$, $-27 \le k \le 27$, $-29 \le l \le 30$
Reflections collected	106381
Independent reflections	30148 [R_{int} = 0.0541, R_{sigma} = 0.0591]
Data / restraints / parameters	30148 / 1 / 1546
Goodness-of-fit on F^2	1.054
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0898, wR_2 = 0.2653

Final R indexes [all data]	$R_1 = 0.1366$, $wR_2 = 0.3010$
Largest diff. peak / hole / e A^{-3}	1.081 / −0.598
CCDC No	2010288

Crystal data and structure refinement for **3a**	
Identification code	190419_wk_r2_0ma
Empirical formula	$C_{179}H_{209}Cl_3N_{12}O_{52}$
Moiety formula	$CHCl_3$, $C_{130}H_{156}N_4O_{28}$, $2(C_{24}H_{26}N_4O_{12})$
Formula Weight	3466.92
Temperature / K	170(2)
Crystal size / mm^3	0.48 × 0.2 × 0.13
Crystal system	monoclinic
Space group	P 2_1/c (14)
a / Å	23.5752(15)
b / Å	33.8217(17)
c / Å	22.6177(14)
α / º	90.00
β / º	101.290(2)
γ / º	90.00
Volume *U* / $Å^3$	17685.3(18)
Z	4
Density Calculated D_c / $g \cdot cm^{-3}$	1.302
μ / mm^{-1}	0.139
F_{000}	7336
Radiation wavelength	λ(Mo-K_α) = 0.71073 Å
2θ range for data collection / º	4.446 ~ 52.782
Index ranges	$-24 \le h \le 29$, $-41 \le k \le 42$, $-28 \le l \le 27$
Reflections collected	152230
Independent reflections	36072 [$R_{int} = 0.0667$, $R_{sigma} = 0.0660$]
Data / restraints / parameters	36072 / 60 / 2231
Goodness-of-fit on F^2	1.035
Final R indexes [$I \ge 2\sigma(I)$]	$R_1 = 0.0756$, $wR_2 = 0.2027$
Final R indexes [all data]	$R_1 = 0.1179$, $wR_2 = 0.2322$

Largest diff. peak / hole / e A^{-3}	1.135 / −0.778
CCDC No	2010287

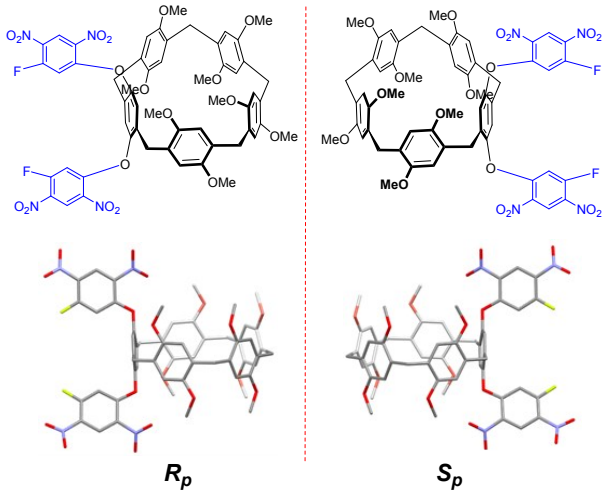


Fig. S21 X-Ray single crystal structure for bis(2,4-dinitro-5-fluoro-phenyl) pillar[5]arene, showing a pair of planar chiral enantiomers. C, black; H, white; O, red; N, blue; F, green.

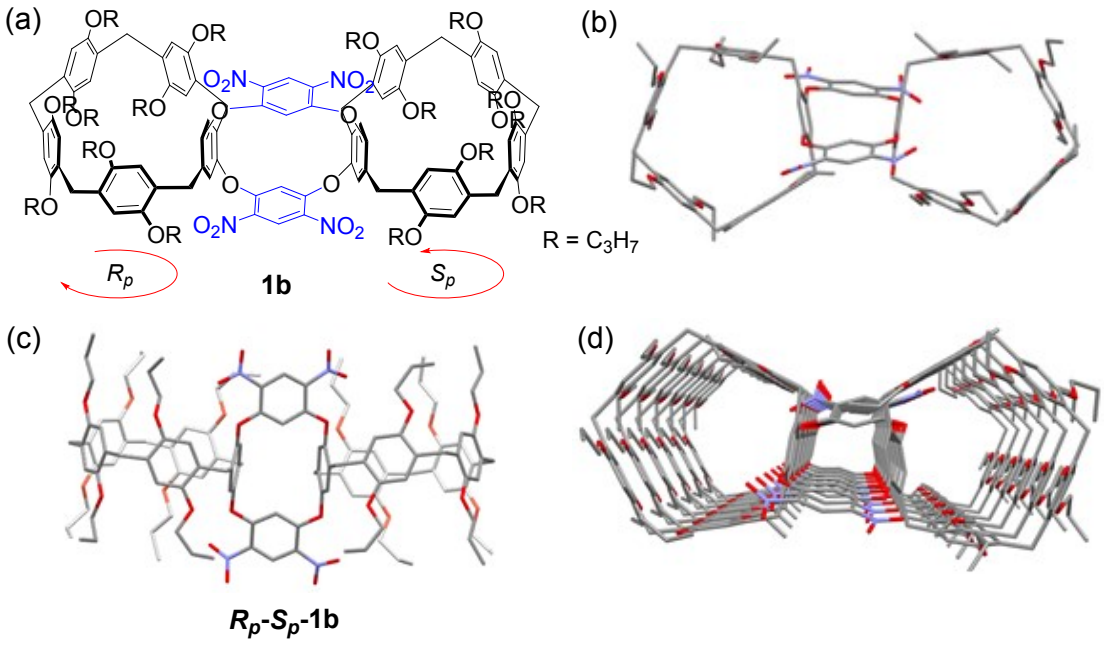


Fig. S22. Chemical structure (a) and crystal structure of **1b**: (b) top view, (c) side view, (d) self-assembled channel, and (e) crystal packing. Solvent molecules and hydrogen atoms are omitted for clarity. C, black; H, white; O, red; N, blue.

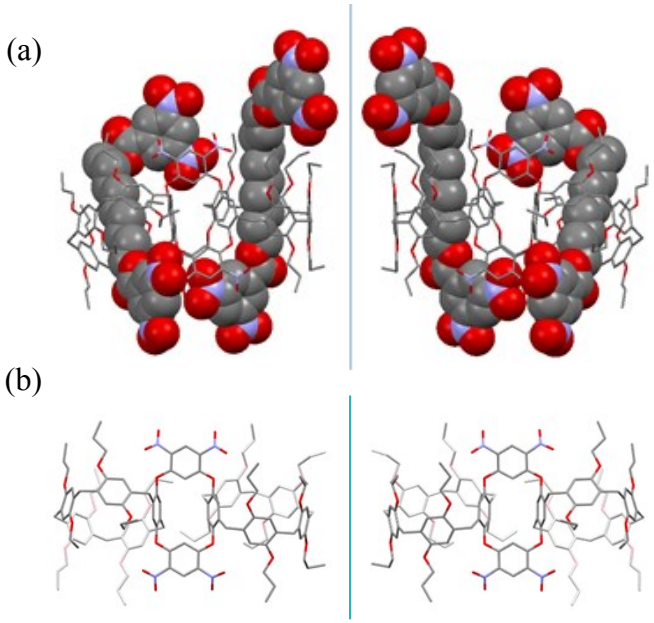


Fig. S23. Crystal structure of GR_p-GR_p-**3a** (left) and GS_p-GS_p-**3a** (right) showing a pair of planar chiral enantiomers: (a) with guest molecules, (b) without guest molecules.

8. HPLC traces of **"1+2" fragment**, **2a**, **3a**, **2b** and **3b**

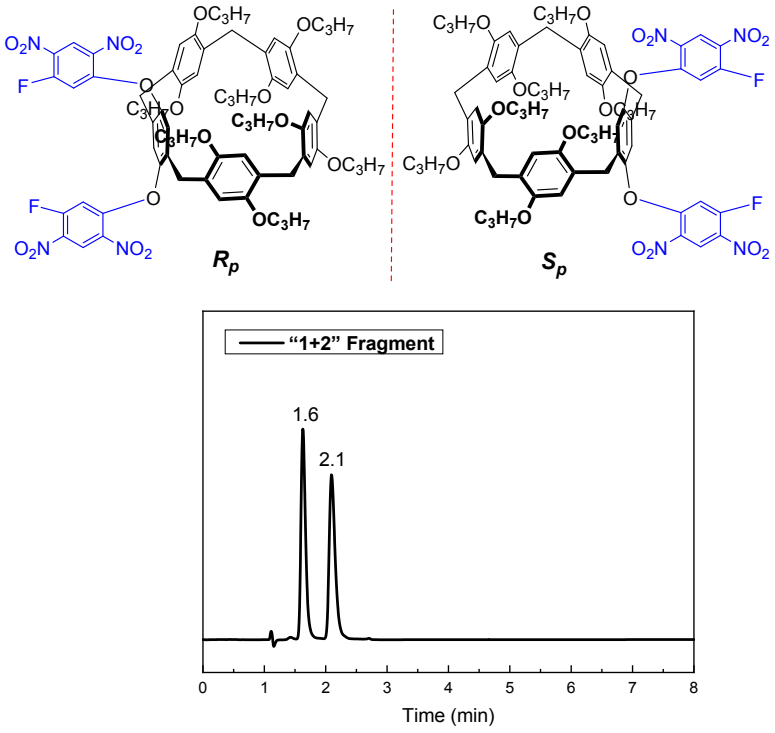


Fig. S24. HPLC traces for **"1+2" fragment**, detected by UV at λ = 254 nm. Conditions: column, DAICEL CHIRALPAK ID; mobile phase, C_6H_{14}:CH_2Cl_2 = 55:45; flow rate = 3.0 mL/min; temperature, 25 ℃.

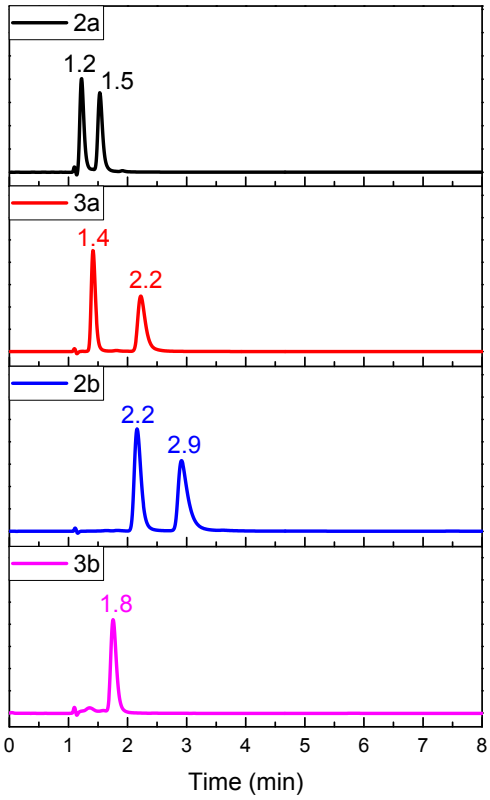


Fig. S25. HPLC traces of **2a**, **3a**, **2b** and **3b**, detected by UV at λ = 254 nm. Conditions: column, DAICEL CHIRALPAK ID; **2a**, **3a** and **3b** were measured by mobile phase, C_6H_{14}:CH_2Cl_2 = 40:60; **2b** was measured by mobile phase, C_6H_{14}:CH_2Cl_2 = 55:45; flow rate = 3.0 mL/min; temperature, 25 ℃.

9. References

S1. C. Han, D. Zhao, H. Li, H. Wang, X. Huang and D. Sun, *ChemistrySelect*, 2018, **3**, 11.