



Supporting Information

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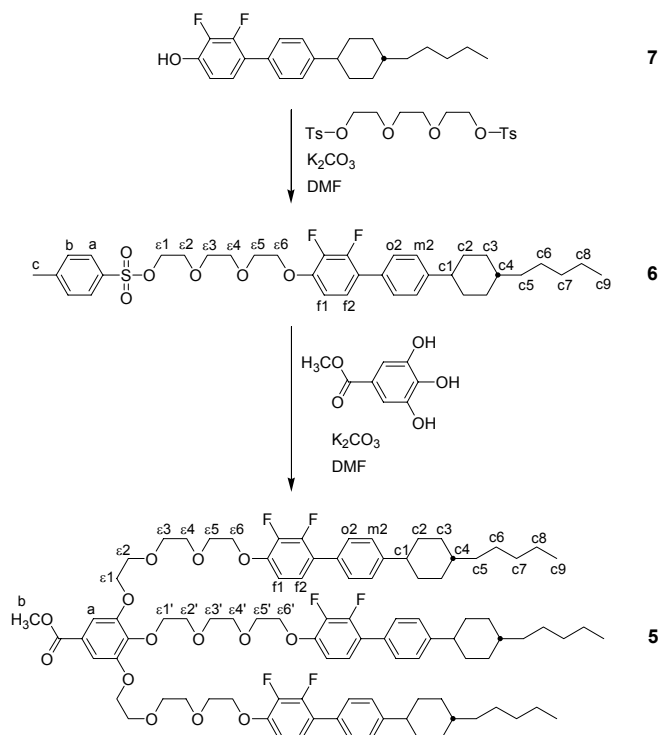
A Liquid-Crystalline [2]Catenane and Its Copper(I) Complex

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General. NMR spectra were recorded using a JEOL JNM-LA400 at 400 MHz for ^1H NMR and at 100 MHz for ^{13}C NMR or a Bruker AVANCE 300 at 300MHz for ^1H NMR in CDCl_3 . Chemical shifts of ^1H and ^{13}C NMR signals were quoted to internal standard Me_4Si ($\delta = 0.00$) and CDCl_3 ($\delta = 77.00$) respectively. Mass spectra were recorded on a JEOL JMS-AX505H spectrometer for MALDI or a Bruker MicroTOF instrument for ESI. Elemental analysis was carried out with a Yanaco MT-6 CHN autocorder. Liquid-crystalline phases were characterized with an Olympus BX51 optical polarizing microscope equipped with a Mettler FP82 HT hot-stage. Differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 Phoenix calorimeter operated at a scanning rate of $5\text{ }^\circ\text{C min}^{-1}$. Gel permeation chromatography was performed with a TOSOH HLC-8220 GPC instrument equipped with two TSKgel G3000HXL columns connected in series, a TOSOH SD-8020 degasser, a RI detector (TOSOH RI-8020), and a TOSOH CO-8020 column oven ($40\text{ }^\circ\text{C}$). X-ray scattering measurements were carried out on a Rigaku RINT-2500 system using $\text{CuK}\alpha$ radiation.

Materials. All reagents of the highest quality were purchased from Aldrich, Kanto, Tokyo Kasei, or Wako, and were used without further purification. Unless otherwise noted, all of the reactions were carried out under an argon atmosphere in dry solvents.

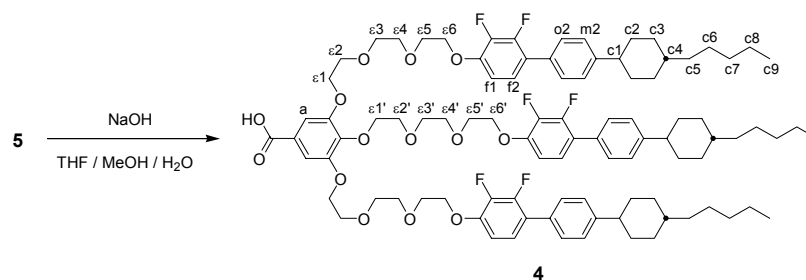


2-[2-(2-{2,3-Difluoro-4-[4-(4-*trans*-pentylcyclohexyl)phenyl]phenoxy}ethoxy)ethoxy]

ethyl *p*-toluenesulfonate (6). To a mixture of tri(ethylene glycol) bis(*p*-toluenesulfonate)^[1] (15.0 g, 32.7 mmol) and K₂CO₃ (3.38 g, 24.5 mmol) in dry DMF (50 mL) was added dropwise a solution of **7**^[2] (2.90 g, 8.1 mmol) in dry DMF (20 mL) with stirring at 80 °C. The reaction mixture was stirred for 6 h at 80 °C. After cooling to room temperature, the mixture was poured into water, and the product was extracted with ethyl acetate three times. The combined organic layers were washed with aqueous ammonium chloride and brine, and dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was purified by column chromatography (silica, hexane/ethyl acetate = 3:1, v/v) and dried under vacuum to afford **6** as a colorless viscous oil (yield = 2.22 g, 43%). ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.4 Hz, 2H, *H_a*), 7.42 (d, *J* = 8.0 Hz, 2H, *H_{o2}*), 7.32 (d, *J* = 8.4 Hz, 2H, *H_b*), 7.27 (d, *J* = 8.0 Hz, 2H, *H_{m2}*), 7.11-7.06 (m, 1H, *H_{f2}*), 6.82-6.77 (m, 1H, *H_{f1}*), 4.22 (t, *J* = 5.2 Hz, 2H, *H_{ε6}*), 4.17 (t, *J* = 5.2 Hz, 2H, *H_{ε1}*), 3.86 (t, *J* = 5.2 Hz, 2H, *H_{ε5}*), 3.72-3.66 (m, 4H, *H_{ε2,ε4}*), 3.61 (t, *J* = 5.2 Hz, 2H, *H_{ε3}*), 2.54-2.47 (m, 1H, *H_{c1}*), 2.42 (s, 3H, *H_c*), 1.94-1.86 (m, 4H, *H_{c2,c3-equatorial}*), 1.53-1.42 (m, 2H, *H_{c2-axial}*), 1.34-1.20 (m, 9H, *H_{c4,c5,c6,c7,c8}*), 1.11-1.01 (m, 2H, *H_{c3-axial}*), 0.90 (t, *J* = 6.8 Hz, 3H, *H_{c9}*). ¹³C NMR (100 MHz, CDCl₃): δ 148.8 (dd, *J* = 248, 11 Hz), 147.5 (s), 147.2 (dd, *J* = 8, 3 Hz), 144.8 (s), 141.9 (dd, *J* = 248, 15 Hz), 133.0 (s), 132.2 (s), 129.8 (s), 128.6 (d, *J* = 3 Hz), 127.9 (s), 127.0 (s), 123.6 (s), 123.5 (dd, *J* = 4, 4 Hz), 110.0 (d, *J* = 3 Hz), 70.9 (s), 70.8 (s), 69.6 (s), 69.5 (s), 69.2 (s), 68.7 (s), 44.3 (s), 37.4 (s), 37.3 (s), 34.3 (s), 33.6

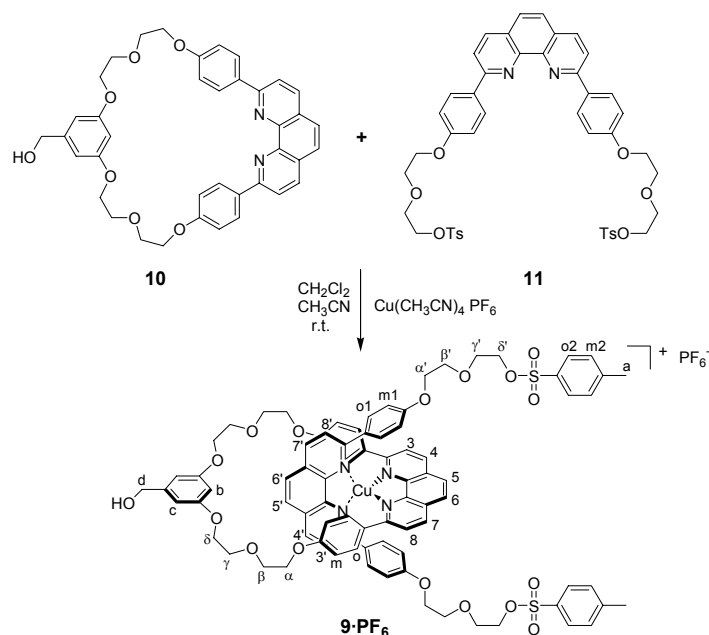
(s), 32.2 (s), 26.6 (s), 22.7 (s), 21.6 (s), 14.1 (s). MS (MALDI): m/z 667.22 (calcd $[M+Na]^+ = 667.29$), 683.20 (calcd $[M+K]^+ = 683.26$).

3,4,5-Tris{2-[2-(2-{2,3-difluoro-4-[4-(4-*trans*-pentylcyclohexyl)phenyl]phenoxy}ethoxy)ethoxy]ethoxy}benzoic acid methyl ester (5). A mixture of gallic acid methyl ester (0.18 g, 0.98 mmol), **6** (2.2 g, 3.4 mmol), and K_2CO_3 (0.41 g, 3.0 mmol) in dry DMF (30 mL) was vigorously stirred for 11 h at 80 °C. After cooling to room temperature, the reaction mixture was added into water, and the product was extracted with ethyl acetate three times. The combined organic layers were washed with aqueous ammonium chloride and brine, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography (silica, ethyl acetate), washed with methanol, and dried under vacuum to give **5** as a white waxy solid (yield = 1.47 g, 94%). 1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 6H, H_{o2}), 7.29 (s, 2H, H_a), 7.25 (m, 6H, H_{m2}), 7.07-7.02 (m, 3H, H_{f2}), 6.81-6.75 (m, 3H, H_{f1}), 4.25-4.18 (m, 12H, $H_{\epsilon1,\epsilon1',\epsilon6,\epsilon6'}$), 3.89-3.80 (m, 12H, $H_{\epsilon2,\epsilon2',\epsilon5,\epsilon5'}$), 3.85 (s, 3H, H_b), 3.75-3.72 (m, 12H, $H_{\epsilon3,\epsilon3',\epsilon4,\epsilon4'}$), 2.53-2.46 (m, 3H, H_{c1}), 1.93-1.86 (m, 12H, $H_{c2,c3}$ -equatorial), 1.52-1.42 (m, 6H, H_{c2} -axial), 1.34-1.23 (m, 27H, $H_{c4,c5,c6,c7,c8}$), 1.10-1.01 (m, 6H, H_{c3} -axial), 0.92-0.88 (m, 9H, H_{c9}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (s), 152.3 (s), 148.8 (dd, $J = 246$, 11 Hz), 147.5 (s), 147.2 (d, $J = 8$ Hz), 142.5 (s), 141.8 (dd, $J = 246$ Hz, 16Hz), 132.2 (s), 128.6 (d, $J = 3$ Hz), 127.0 (s), 124.9 (s), 123.5 (s), 123.4 (m), 110.0 (s), 108.9 (s), 72.5 (s), 71.0 (s), 70.9 (s), 70.7 (s), 70.6 (s), 69.7 (s), 69.6 (s), 69.5 (s), 68.9 (s), 52.1 (s), 44.3 (s), 37.4 (s), 37.3 (s), 34.3 (s), 33.6 (s), 32.2 (s), 26.6 (s), 22.7 (s), 14.1 (s). MS (MALDI): m/z 1623.92 (calcd $[M+Na]^+ = 1623.86$), 1638.91 (calcd $[M+K]^+ = 1638.84$).



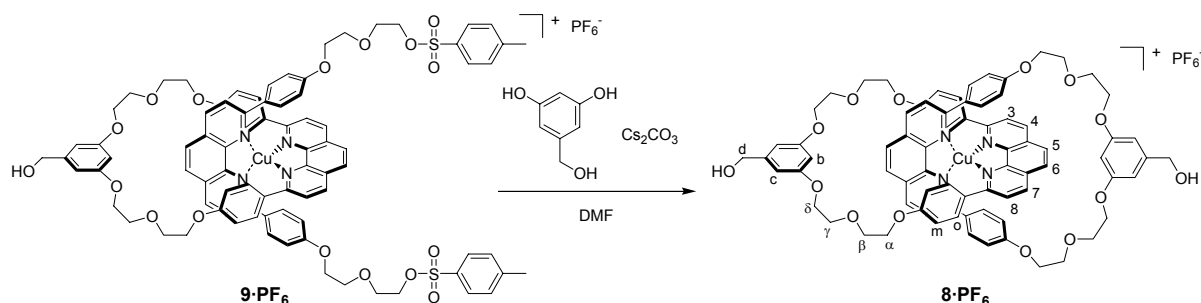
3,4,5-Tris{2-[2-(2-{2,3-difluoro-4-[4-(4-*trans*-pentylcyclohexyl)phenyl]phenoxy}ethoxy)ethoxy]ethoxy}benzoic acid (4). To a stirred solution of **5** (1.31 g, 0.82 mmol) in THF/methanol (20 mL/15 mL) was added aqueous NaOH (ca. 10 M, 5 mL). The mixture was refluxed for 2 h, and then neutralized with an aqueous hydrochloric acid to obtain a precipitate. The precipitate was filtered off and washed with water. The crude product was

purified by column chromatography (silica, ethyl acetate) and dried under vacuum to afford **12** as a white waxy solid (yield = 1.12 g, 86%). ^1H NMR (400 MHz, CDCl_3): δ 7.39 (m, 6H, $H_{\text{O}2}$), 7.35 (s, 2H, H_{a}), 7.24 (m, 6H, $H_{\text{m}2}$), 7.07-7.02 (m, 3H, $H_{\text{f}2}$), 6.80-6.75 (m, 3H, $H_{\text{f}1}$), 4.27 (t, $J = 4.8$ Hz, 2H, $H_{\text{e}1'}$), 4.22-4.17 (m, 10 H, $H_{\text{e}1,\text{e}6,\text{e}6'}$), 3.90-3.82 (m, 12H, $H_{\text{e}2,\text{e}2',\text{e}5,\text{e}5'}$), 3.75-3.73 (m, 12H, $H_{\text{e}3,\text{e}3',\text{e}4,\text{e}4'}$), 2.52-2.45 (m, 3H, $H_{\text{c}1}$), 1.93-1.85 (m, 12H, $H_{\text{c}2,\text{c}3\text{-equatorial}}$), 1.50-1.41 (m, 6H, $H_{\text{c}2\text{-axial}}$), 1.34-1.20 (m, 27H, $H_{\text{c}4,\text{c}5,\text{c}6,\text{c}7}$), 1.10-1.02 (m, 6H, $H_{\text{c}3\text{-axial}}$), 0.92-0.88 (m, 9H, $H_{\text{c}9}$). ^{13}C NMR (100 MHz, CDCl_3): δ 170.7 (s), 152.4 (s), 148.8 (dd, $J = 246$, 11 Hz), 147.4 (s), 147.2 (d, $J = 8$ Hz), 143.3 (s), 141.8 (dd, $J = 246$, 16 Hz), 132.2 (s), 128.6 (d, $J = 3$ Hz), 127.0 (s), 123.9 (s), 123.5 (s), 123.4 (m), 109.9 (s), 109.5 (s), 72.5 (s), 71.0 (s), 70.9 (s), 70.7 (s), 70.6 (s), 69.7 (s), 69.6 (s), 69.5 (s), 69.4 (s), 68.9 (s), 44.3 (s), 37.4 (s), 37.3 (s), 34.3 (s), 33.6 (s), 32.2 (s), 26.6 (s), 22.7 (s), 14.1 (s). MS (MALDI): m/z 1610.21 (calcd $[M+\text{Na}]^+ = 1609.85$), 1626.19 (calcd $[M+\text{K}]^+ = 1625.82$). Anal. calcd for $\text{C}_{94}\text{H}_{120}\text{F}_6\text{O}_{14}$: C, 71.10; H, 7.62%; found: C, 70.96; H, 7.86%.

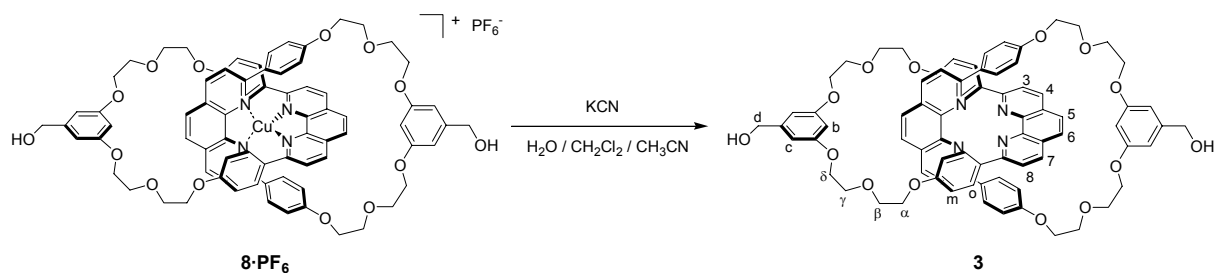


Pre-catenane 9·PF₆. To a solution of **10**^[3] (127 mg, 0.197 mmol) in CH₂Cl₂ (50 mL) was added a degassed solution of Cu(CH₃CN)₄PF₆ (75 mg, 0.20 mmol) in CH₃CN (25 mL). The mixture turned to orange upon stirring 15 min. A degassed solution of **11** (167 mg, 0.197 mmol) in CH₂Cl₂ (20 mL) was introduced into the previous solution, which turned to red. The progress of the reaction was controlled by TLC (CH₂Cl₂/MeOH 94:6). After 2h, the solvents were evaporated to dryness and the crude product was taken up with CH₂Cl₂ (50 mL) and water (50 mL). The aqueous layer was extracted with CH₂Cl₂, and the organic layer was

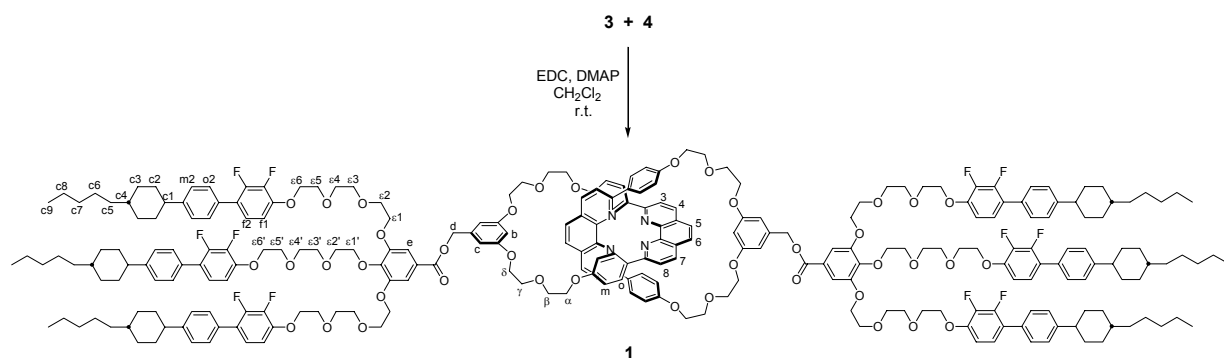
washed with water. The combined organic layers were evaporated to dryness to afford quantitatively **9**·PF₆ as a brown-red solid (yield = 333 mg). It was used for the next step without further purification. ¹H NMR (acetone-*d*₆, 300 MHz): δ 8.66 (d, ³*J* = 8.1 Hz, 2H, *H*_{4,7}), 8.65 (d, ³*J* = 8.4 Hz, 2H, *H*_{4,7}), 8.19 (s, 2H, *H*_{5,6}), 8.15 (s, 2H, *H*_{5,6}), 7.99 (d, ³*J* = 8.4 Hz, 2H, *H*_{3,8}), 7.97 (d, ³*J* = 8.4 Hz, 2H, *H*_{3,8}), 7.84 (d, ³*J* = 8.1 Hz, 4H, *H*₀₁), 7.57 (d, ³*J* = 8.7 Hz, 4H, *H*₀), 7.44 (d, ³*J* = 7.8 Hz, 4H, *H*₀₂), 7.43 (d, ³*J* = 8.7 Hz, 4H, *H*_{m2}), 6.79 (t, ⁴*J* = 2.1 Hz, 1H, *H*_b), 6.73 (d, ⁴*J* = 2.4 Hz, 2H, *H*_c), 6.18 (d, ³*J* = 9.0 Hz, 4H, *H*_{m1}), 6.11 (d, ³*J* = 8.7 Hz, 4H, *H*_m), 4.63 (d, 2H, *H*_d), 4.34 (m, 4H, *H*_α), 4.27 (m, 4H, *H*_{α'}), 3.95 (m, 4H, *H*_β), 3.76 (m, 20H, *H*_{β,γ,γ',δ,δ'}), 2.40 (s, 6H, *H*_a). HRMS (ESI): *m/z* calcd for C₈₅H₈₀N₄O₁₇S₂Cu: 1555.4256; found 1555.4285 [*M*-PF₆]⁺.



Copper(I) [2]catenane 8·PF₆. Compound **9**·PF₆ (400 mg, 0.235 mmol), 3,5-dihydroxybenzyl alcohol (36 mg, 0.259 mmol), Cu(CH₃CN)₄PF₆ (87 mg, 0.235 mmol) and ascorbic acid (29 mg, 0.165 mmol) were dissolved in dry DMF (230 mL). The mixture was degassed and the temperature rose to 45 °C. Then Cs₂CO₃ (383 mg) were added. The progress of the reaction was checked by TLC and when decomplexation of **9**⁺ was observed, 1 equiv. of Cu(I) complex, resorcinol derivative, and compound **11** were added. After 120 h, the solvent was evaporated and the residue was taken up in CH₂Cl₂ (100 mL). A saturated aqueous solution of KPF₆ (20 mL) was added. The resulting mixture was stirred for 1 h. The aqueous layer was extracted six times with CH₂Cl₂ and the organic layer was washed with water. The combined organic layers were evaporated to dryness. The crude product was purified by column chromatography (silica, CH₂Cl₂ containing 0.5 to 2 % MeOH) to afford **8**·PF₆ as a brown-red solid (yield = 108 mg, 31 %). ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.52 (d, ³*J* = 8.4 Hz, 4H, *H*_{4,7}), 8.03 (s, 4H, *H*_{5,6}), 7.75 (d, ³*J* = 8.1 Hz, 4H, *H*_{3,8}), 7.26 (d, ³*J* = 8.7 Hz, 8H, *H*₀), 6.69 (t, ⁴*J* = 2.4 Hz, 2H, *H*_b), 6.65 (d, ⁴*J* = 2.4 Hz, 4H, *H*_c), 6.04 (d, ³*J* = 8.7 Hz, 8H, *H*_m), 4.66 (s, 4H, *H*_d), 4.26 (m, 8H, *H*_α), 3.94 (m, 8H, *H*_β), 3.76 (m, 16H, *H*_{γ,δ}). HRMS (ESI): *m/z* calcd for C₇₈H₇₂N₄O₁₄Cu: 1351.4341; found 1351.4350 [*M*-PF₆]⁺.



[2]Catenane 3. To a solution of **8·PF₆** (150 mg, 0.10 mmol) in CH₃CN/CH₂Cl₂ (15 mL/8 mL) was added a solution of KCN (52 mg, 0.80 mmol) in H₂O (3 mL). After 5 h, the same amount of KCN was added again. After 24h, the solvents were removed in vacuo, and water (100 mL) and CH₂Cl₂ (100 mL) were added. The aqueous layer was extracted three times with CH₂Cl₂, the organic layer was washed with water. The combined organic layers were evaporated to dryness. The crude product was purified by column chromatography (silica, CH₂Cl₂ containing 0.5 to 6 % MeOH) to afford catenane **3** as a yellow solid (yield = 60 mg, 46 %). Macrocycle **10** was also isolated (30 mg) showing that during the course of the demetallation reaction, opening reactions of a macrocycle also occur. ¹H NMR (CDCl₃, 300 MHz): δ 8.29 (m, 12H, *H*_{o,4,7}), 8.02 (d, ³*J* = 8.4 Hz, 4H, *H*_{3,8}), 7.76 (s, 4H, *H*_{5,6}), 7.03 (d, ³*J* = 8.5 Hz, 8H, *H*_m), 6.82 (s, 2H, *H*_b), 6.51 (s, 4H, *H*_c), 4.18 (m, 20H, *H*_{d,α,δ}), 3.86 (m, 16H, *H*_{β,γ}). HRMS (ESI): *m/z* calcd for C₇₈H₇₃N₄O₁₄: 1289.512; found 1289.532 [*M*+H]⁺.



Free [2]catenane 1. To a solution of **4** (42 mg, 0.026 mmol) in CH₂Cl₂/EtOAc (3 mL/0.3 mL) were added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC, 54 mg, 0.28 mmol) and 4-dimethylaminopyridine (DMAP, 136 mg, 1.1 mmol). After stirring at room temperature for 20 minutes, **3** (14.4 mg, 0.011 mmol) was added as a solid, and the suspension was sonicated in an ultra-sound bath until a clear solution is obtained. The solution was stirred for one week at room temperature. A mixture of EDC (54 mg, 0.28 mmol) and DMAP (136 mg, 1.1 mmol) in CH₂Cl₂ (2 mL) was added to the solution and the mixture was stirred for another week at room temperature. A saturated aqueous solution of

NaHCO₃ (30 mL) was added and the product was extracted with CHCl₃. The combined organic layers were dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was purified with recycling GPC to yield **1** as a slightly yellowish amorphous solid (yield = 39 mg, 75 %). ¹H NMR (CDCl₃, 400 MHz): δ 8.32 (d, ³J = 8.4 Hz, 8H, H_o), 8.18 (d, ³J = 8.8 Hz, 4H, H_{4,7}), 7.98 (d, ³J = 8.0 Hz, 4H, H_{3,8}), 7.70 (s, 4H, H_{5,6}), 7.37 (d, ³J = 8.1 Hz, 12H, H_{o2}), 7.23 (d, ³J = 8.3 Hz, 12H, H_{m2}), 7.17 (s, 4H, H_e), 7.06 (d, ³J = 8.8 Hz, 8H, H_m), 7.03-6.98 (m, 6H, H_{f2}), 6.77-6.70 (m, 8H, H_{f1,b}), 6.56 (d, ⁴J = 1.6 Hz, 4H, H_c), 5.12 (s, 4H, H_d), 4.22-4.11 (m, 16H, H_{ε1',ε6,ε6'}), 4.08 (t, ³J = 4.8 Hz, 8H, H_δ), 4.05 (t, ³J = 4.8 Hz, 8H, H_{ε1}), 3.86-3.64 (m, 72H, H_{ε2,ε2',ε3,ε3',ε4,ε4',ε5,ε5',α,β,γ}), 2.51-2.44 (m, 6H, H_{c1}), 1.92-1.84 (m, 24H, H_{c2,c3-equatorial}), 1.50-1.40 (m, 12H, H_{c2-axial}), 1.35-1.19 (m, 54H, H_{c4,c5,c6,c7,c8}), 1.09-0.99 (m, 12H, H_{c3-axial}), 0.92-0.88 (m, 18H, H_{c9}). ¹³C NMR (CDCl₃, 100 MHz): δ 165.8, 160.0, 159.9, 156.6, 152.2, 150.0 (m), 147.4, 147.3 (m), 146.1, 143.0, 142.5, 138.1, 136.5, 132.9, 132.2, 129.2, 128.5 (d), 127.4, 127.0, 125.5, 124.8, 123.5, 123.3 (m), 119.5, 115.3, 109.9, 108.9, 106.6, 102.6, 72.4, 71.0, 70.9, 70.8, 70.6, 70.5, 69.8, 69.6, 69.5, 69.4, 69.1, 68.8, 67.4, 67.3, 44.3, 37.4, 37.3, 34.3, 33.6, 32.2, 26.7, 22.7, 14.1. MS (MALDI): *m/z* 4428.37 (calcd [M+H]⁺ = 4427.21), 4450.25 (calcd [M+Na]⁺ = 4449.19).

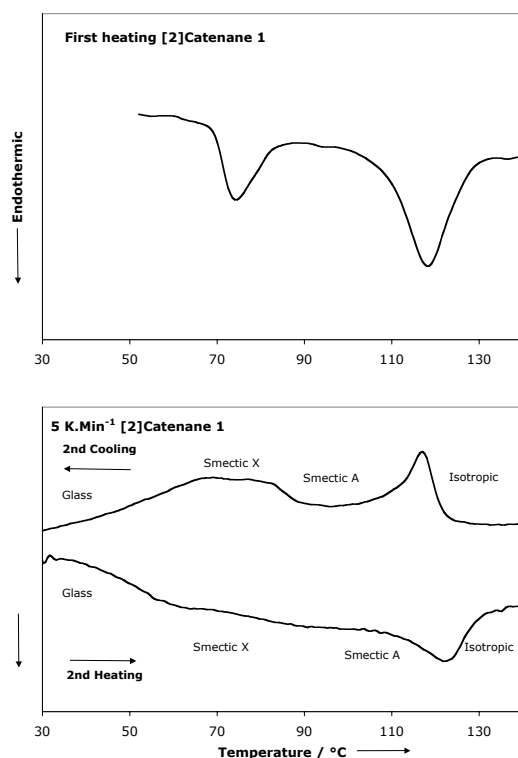
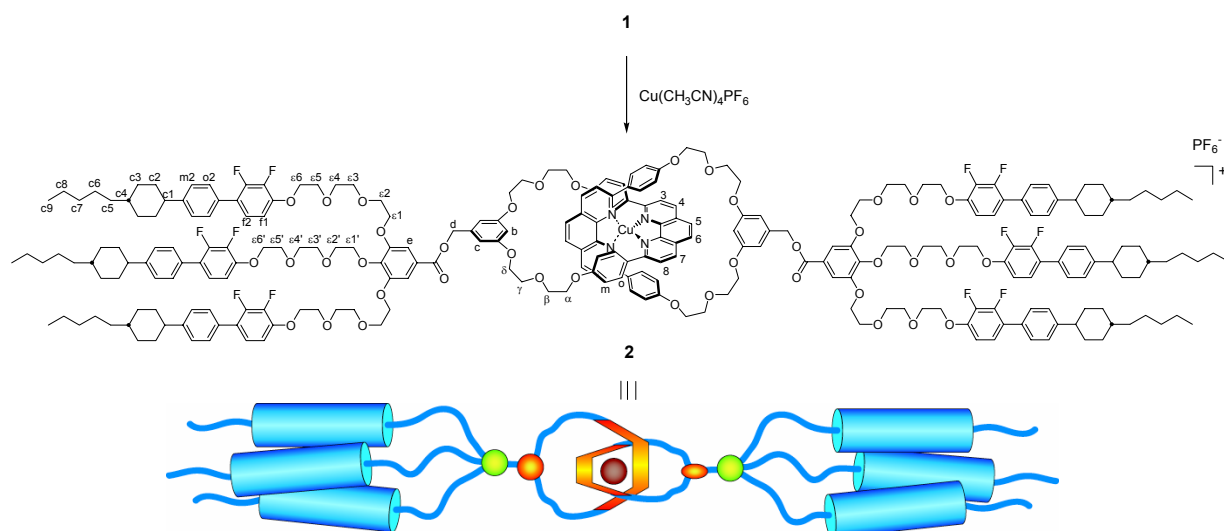


Figure S1. DSC thermograms of free [2]catenane **1** at a scanning rate of 5 °C min⁻¹.



Copper(I) [2]catenane 2. To a stirred solution of **1** (16 mg, 3.6×10^{-3} mmol) in CH₂Cl₂ (2 mL) was added a solution of Cu(CH₃CN)₄PF₆ (1.35 mg, 3.6×10^{-3} mmol) in MeCN (1 mL). The deep red solution was stirred for 1 h at room temperature. The solvents were removed under reduced pressure, and the product was dried under vacuum. It was used without any further purification. ¹H NMR (CDCl₃, 400 MHz): δ = 8.51 (d, 3J = 8.4 Hz, 4H, H_{4,7}), 8.02 (s, 4H, H_{5,6}), 7.74 (d, 3J = 8.4 Hz, 4H, H_{3,8}), 7.38 (d, 3J = 8.4 Hz, 12H, H₀₂), 7.33 (s, 4H, H_e), 7.29-7.23 (m, H_{0, m2} with solvent), 7.05-7.02 (m, 6H, H_{f2}), 6.79-6.75 (m, 6H, H_{f1}), 6.73 (s, 2H, H_b), 6.68 (s, 4H, H_c), 6.04 (d, 3J = 8.8 Hz, 8H, H_m), 5.29 (s, 4H, H_d), 4.25-3.70 (m, 104H, H _{ϵ 1, ϵ 1', ϵ 2, ϵ 2', ϵ 3, ϵ 3', ϵ 4, ϵ 4', ϵ 5, ϵ 5', ϵ 6, ϵ 6', α , β , γ , δ}), 2.51-2.44 (m, 6H, H_{c1}), 1.92-1.84 (m, 24H, H_{c2eq, c3eq}), 1.50-1.40 (m, 12H, H_{c2ax}), 1.35-1.19 (m, 54H, H_{c4, c5, c6, c7, c8}), 1.09-0.99 (m, 12H, H_{c3ax}), 0.90 (t, 3J = 6.6 Hz, 18H, H_{c9}). MS (MALDI): m/z 4491.23 (calcd [M]⁺ = 4491.14), 4515.94 (calcd [M+Na]⁺ = 4515.13), 4532.05 (calcd [M+K]⁺ = 4531.10).

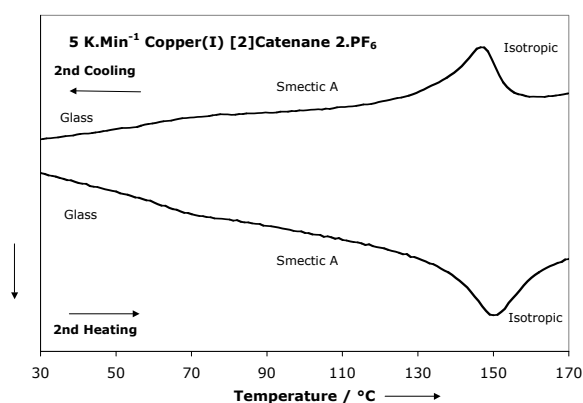


Figure S2. DSC thermograms of copper(I) [2]catenane **2** at a scanning rate of 5 °C min⁻¹.

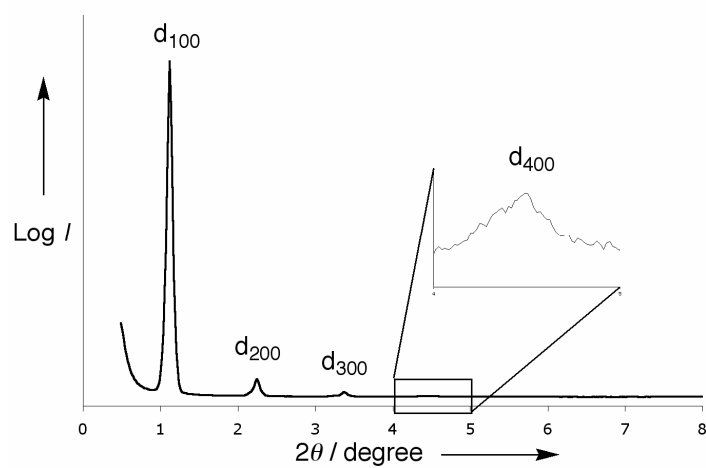


Figure S3. Small-angle X-ray scattering pattern of copper(I) [2]catenane **2** at 100 °C.

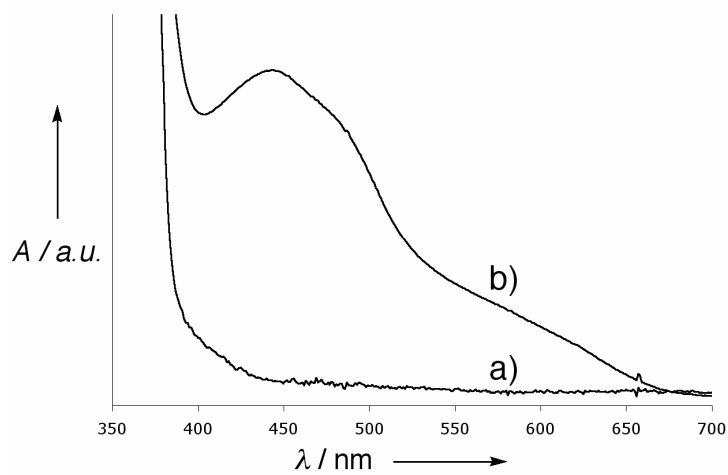


Figure S4. Visible absorption spectra of (a) **1** and (b) **2** in CHCl_3 .

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