Supporting Information for

Control over the macrocyclisation pathway and product topology in a copper-templated catenane synthesis

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1. Synthesis

General. All reagents were purchased from commercial suppliers (Aldrich, Acros, Dkmchem and J&K) and used without further purification. All the solvents for synthesis were of analytical grade (ACI Labscan and DUKSAN Pure Chemicals). MeCN, CHCl$_3$ and MeOH were distilled over CaH$_2$ before use. DN$_1$, DN$_2$, DN$_3$, L, Phen-OTs, S$_1$-OTs and cucurbit[6]uril (CB[6]) were synthesized according to literature procedures. Microwave-assisted reactions were carried out using a Discover SP microwave synthesizer (CEM, USA) in the closed vessel mode. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck, Germany, Aluminium sheet) and column chromatography was carried out on silica gel 60F (Silicycle, Canada). HPLC analyses were carried out using a Waters-Alliance e2695 system coupled to a 2489 UV/Vis detector. ESI-MS were carried out using a Waters-Acquity UPLC H-Class system coupled with a QDa MS detector. NMR spectra were recorded on Bruker DPX spectrometers with working frequencies of 300 MHz, 400 MHz, 500 or 600 MHz for $^1$H, and 75 MHz, 100 MHz, 125 MHz or 150 MHz for $^{13}$C, respectively. Chemical shifts are reported in ppm and referenced to solvent residues (For $^1$H: CDCl$_3$: $\delta =$ 7.26 ppm, $d_6$-DMSO: $\delta =$ 2.50 ppm, D$_2$O: $\delta =$ 4.79 ppm, CD$_3$CN: $\delta =$ 1.94 ppm; For $^{13}$C: CDCl$_3$: $\delta =$ 77.16 ppm, $d_6$-DMSO: $\delta =$ 39.52 ppm, CD$_3$CN: $\delta =$ 118.26 ppm).

A. Building blocks synthesis

![Scheme S1. Synthesis of DN4 and DN5.](image-url)
**4-OTs.** A mixture of pentaethylene glycol (1.00 g, 4.2 mmol) and NaOH (0.20 g, 5.0 mmol) in THF/H₂O (v:v 5:1, 30 mL) was stirred at room temperature for 10 min. The mixture was then cooled to 0 °C in an ice bath and a solution of TsCl (0.80 g, 4.2 mmol) in THF (30 mL) was added dropwisely over 2 hr and stirred for overnight at room temperature. The solvent was removed by a rotary evaporator and the residue was dissolved in CH₂Cl₂ (50 mL), washed with water and brine, dried over MgSO₄, filtered and concentrated to afford a light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 3:2) to afford the product. Yield = 1.27 g, 77%. ¹H NMR (300 MHz, CDCl₃, 298 K) δ = 7.80 (d, J = 7.5 Hz, 2 H), 7.34 (d, J = 7.5 Hz, 2 H), 4.16 (t, J = 6.0 Hz, 2 H), 3.75–3.51 (m, 18 H), 2.44 (s, 3 H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) δ = 144.9, 133.0, 129.9, 128.0, 72.7, 70.5, 69.3, 68.7, 61.7, 21.6. ESI-MS: 393.5 [M+H]^+.

**5-OTs.** A mixture of hexaethylene glycol (2.50 g, 8.9 mmol) and NaOH (0.43 g, 10.7 mmol) in THF/H₂O (v:v 5:1, 60 mL) was stirred at room temperature for 10 min. The mixture was then cooled to 0 °C in an ice bath and a solution of TsCl (1.70 g, 8.9 mmol) in THF (60 mL) was added dropwisely over 2 hr and stirred for overnight at room temperature. The solvent was removed by a rotary evaporator and the residue was dissolved in CH₂Cl₂ (50 mL), washed with water and brine, dried over MgSO₄, filtered and concentrated to afford a light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 3:2) to afford the product. Yield = 1.67 g, 43%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.79 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 4.15 (t, J = 6.0 Hz, 2 H), 3.75–3.50 (m, 22 H), 2.44 (s, 3 H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) δ = 144.3, 132.4, 129.4, 127.3, 72.0, 70.0, 69.9, 68.9, 68.0, 60.9, 21.0. ESI-MS: 436.5 [M+H]^+.

**DN4-OH.** A mixture of 1,5-dihydroxynaphthalene (0.18 g, 1.2 mmol), 4-OTs (1.00 g, 2.6 mmol), K₂CO₃ (0.67 g, 4.8 mmol) and KI (40 mg, 0.24 mmol) in dry DMF (20 mL) was heated at 100 °C for overnight. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CHCl₃ (50 mL) and 0.5 M NaOH (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl₃ (2 x 50 mL). The organic fractions were combined, washed by brine, dried over MgSO₄, filtered and concentrated to afford a dark oil which was used in the next step.
without further purification. Yield = 0.51 g, 70%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.85 (d, J = 8.0 Hz, 2 H), 7.34 (t, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.0 Hz, 2 H), 4.29 (t, J = 4.0 Hz, 4 H), 3.99 (t, J = 4.0 Hz, 4 H), 3.80 (t, J = 4.0 Hz, 4 H), 3.71–3.65 (m, 24 H), 3.57 (t, J = 4.0 Hz, 4 H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) δ = 154.0, 126.5, 124.9, 114.3, 105.5, 72.5, 71.0, 70.6, 70.3, 70.2, 70.1, 69.8, 69.5, 67.6, 61.2. ESI-MS: 601.3 [M+H]$^+$, 623.1 [M+Na]$^+$.

**DN5-OH.** A mixture of 1,5-dihydroxynaphthalene (0.18 g, 1.2 mmol), 5-OTs (1.10 g, 2.5 mmol), K$_2$CO$_3$ (0.67 g, 4.8 mmol) and KI (0.04 g, 0.24 mmol) in dry DMF (20 mL) was heated at 100 °C for overnight. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CHCl$_3$ (50 mL) and 0.5 M NaOH (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl$_3$ (2 x 50 mL). The organic fractions were combined, washed by brine, dried over MgSO$_4$, filtered and concentrated to afford a dark oil which was used in the next step without further purification. Yield = 0.69 g, 84%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.85 (d, J = 8.0 Hz, 2 H), 7.33 (t, J = 8.0 Hz, 2 H), 6.83 (d, J = 8.0 Hz, 2 H), 4.28 (t, J = 4.0 Hz, 4 H), 3.99 (t, J = 4.0 Hz, 4 H), 3.79 (t, J = 4.0 Hz, 4 H), 3.70–3.67 (m, 8 H), 3.66–3.63 (m, 24 H), 3.57 (t, J = 4.0 Hz, 4 H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) δ = 154.3, 126.7, 125.1, 114.6, 105.6, 77.4, 72.5, 71.3, 70.9, 70.7, 70.6, 70.5, 70.3, 69.8, 67.9, 61.6. ESI-MS: 688.4 [M+H]$^+$, 710.4 [M+Na]$^+$.

**DN4-OTs.** A mixture of DN4-OH (0.50 g, 0.8 mmol), Et$_3$N (0.18 g, 1.8 mmol), 4-(dimethylamino)pyridine (5 mg, 0.04 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at 0 °C. A solution of TsCl (0.33 g, 1.8 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwisely over 2 hr at 0 °C. The reaction mixture was stirred for overnight at room temperature. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CH$_2$Cl$_2$ (50 mL) and H$_2$O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated to afford light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product. Yield = 0.26 g, 34%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.83 (d, J = 8.0 Hz, 2 H), 7.75 (d, J = 8.0 Hz), 7.30–7.28 (m, 6 H), 6.81 (d, J = 8.0 Hz, 2 H), 4.26 (t, J = 4.0 Hz, 4 H),
4.11 (t, J = 4.0 Hz, 4 H), 3.96 (t, J = 4.0 Hz, 4 H), 3.77 (t, J = 4.0 Hz, 4 H), 3.66 (t, J = 4.0 Hz, 4 H), 3.63–3.61 (m, 8 H), 3.59 (t, J = 4.0 Hz, 4 H), 3.58–3.52 (m, 8 H), 2.39 (s, 6 H).

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ = 154.3, 144.8, 133.0, 129.8, 128.0, 126.8, 125.1, 114.6, 105.7, 71.0, 70.7, 70.6, 70.5, 69.8, 69.3, 68.6, 67.9, 21.6. ESI-MS: 909.3 [M+H]$^+$, 931.3 [M+Na]$^+$.

DN5-OTs. A mixture of DN5-OH (0.69 g, 1.0 mmol), Et$_3$N (0.21 g, 2.1 mmol), 4-(dimethylamino)pyridine (5 mg, 0.04 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at 0 °C. A solution of TsCl (0.40 g, 2.1 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise over 2 hr at 0 °C. The reaction mixture was stirred for overnight at room temperature. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CH$_2$Cl$_2$ (50 mL) and H$_2$O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated to afford light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product. Yield = 0.24 g, 24%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.82 (d, J = 8.0 Hz, 2 H), 7.75 (d, J = 8.0 Hz, 4 H), 7.33–7.28 (m, 6 H), 6.80 (d, J = 8.0 Hz, 2 H), 4.25 (t, J = 4.0 Hz, 4 H), 4.11 (t, J = 4.0 Hz, 4 H), 3.96 (t, J = 4.0 Hz, 4 H), 3.78 (t, J = 4.0 Hz, 4 H), 3.75–3.55 (m, 32 H), 2.39 (s, 6 H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ = 154.3, 144.7, 132.9, 129.8, 127.9, 126.7, 125.1, 114.6, 105.6, 71.0, 70.7, 70.6, 70.5, 69.8, 69.3, 68.6, 67.9, 21.6. ESI-MS: 996.3 [M+H]$^+$, 1018.3 [M+Na]$^+$.

DN4-Pht. A mixture of DN4-OTs (0.26 g, 0.3 mmol), potassium phthalimide (0.13 g, 0.7 mmol) in dry DMF (10 mL) was heated to 100 °C for overnight. Solvent was removed by a rotary evaporator. The residue was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated to afford a deep yellow oil. The deep yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product as a light-yellow oil. Yield = 0.20 g, 84%. $^1$HNMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.83 (d, J = 8.0 Hz, 2 H), 7.80 (d, J = 8.0 Hz, 4 H), 7.68 (d, J = 8.0 Hz, 4 H), 7.32 (t, J = 8.0 Hz, 2 H), 6.82 (d, J = 8.0 Hz, 2 H), 4.27 (t, J = 4.0 Hz, 4 H), 3.97 (t, J = 4.0 Hz, 4 H), 3.87 (t, J = 4.0 Hz, 4 H), 3.77 (t, J = 4.0 Hz, 4 H), 3.71 (t, J = 4.0 Hz, 4 H), 3.63–3.61 (m, 8 H), 3.59 (t, J = 4.0 Hz, 4 H), 3.58–3.52 (m, 8 H), 2.39 (s, 6 H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ = 154.3, 144.8, 133.0, 129.8, 128.0, 126.8, 125.1, 114.6, 105.7, 71.0, 70.7, 70.6, 70.5, 69.8, 69.3, 68.6, 67.9, 21.6. ESI-MS: 996.3 [M+H]$^+$, 1018.3 [M+Na]$^+$.
3.67 (t, J = 4.0 Hz, 4 H), 3.64–3.59 (m, 16 H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K) δ = 168.3, 154.4, 134.0, 132.2, 126.8, 125.1, 123.3, 114.7, 105.7, 71.0, 70.7, 70.6, 70.1, 69.9, 68.0, 37.3. ESI-MS: 881.7 [M+Na]$^+$. 

**DN5-Pht.** A mixture of DN5-OTs (0.29 g, 0.3 mmol), potassium phthalimide (0.13 g 0.7 mmol) in dry DMF (10 mL) was heated to 100 °C for overnight. Solvent was removed by a rotary evaporator. The residue was partitioned between CH$_2$Cl$_2$ (50 mL) and H$_2$O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated to afford a deep yellow oil. The deep yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product as a light-yellow oil. Yield = 0.17 g, 60%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.39 (d, J = 8.0 Hz, 2 H), 7.77 (d, J = 8.0 Hz, 4 H), 7.63 (d, J = 8.0 Hz, 4 H), 7.28 (t, J = 8.0 Hz, 2 H), 6.78 (d, J = 8.0 Hz, 2 H), 4.24 (t, J = 4.0 Hz, 4 H), 3.95 (t, J = 4.0 Hz, 4 H), 3.83 (t, J = 4.0 Hz, 4 H), 3.75 (t, J = 4.0 Hz, 4 H), 3.69–3.52 (m, 32 H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K) δ = 168.2, 154.2, 133.7, 132.2, 126.7, 125.1, 123.1, 114.5, 105.6, 70.9, 70.6, 70.5, 70.0, 69.8, 67.8, 37.2. ESI-MS: 969.6 [M+Na]$^+$. 

**DN4.** A mixture of DN4-Pht (0.58 g, 0.7 mmol) and hydrazine hydrate (1 mL) in EtOH (50 mL) was heated to reflux for 4 hr. Insoluble materials were removed by filtration and solvent was removed by a rotary evaporator. The residue was dissolved in CH$_2$Cl$_2$ (50 mL), filtered, and the organic solvent was removed by a rotary evaporator to afford the product. Yield = 0.34 g, 85%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.83 (d, J = 8.0 Hz, 2 H), 7.32 (t, J = 8.0 Hz, 2 H), 6.82 (d, J = 8.0 Hz, 2 H), 4.27 (t, J = 4.0 Hz, 4 H), 3.97 (t, J = 4.0 Hz, 4 H), 3.78 (t, J = 4.0 Hz, 4 H), 3.67 (t, J = 4.0 Hz, 4 H), 3.66–3.62 (m, 8 H), 3.60 (t, J = 4.0 Hz, 4 H), 3.58 (t, J = 4.0 Hz, 4 H), 3.45 (t, J = 4.0 Hz, 4 H), 2.81 (t, J = 4.0 Hz, 4 H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K) δ = 154.4, 126.8, 125.2, 114.7, 105.7, 73.3, 71.2, 70.8, 70.7, 70.6, 70.3, 69.9, 68.0, 41.7. ESI-MS: 300.2 [M+2H]$^{2+}$, 599.2 [M+H]$^+$. 

**DN5.** A mixture of DN5-Pht (0.70 g, 0.7 mmol) and hydrazine hydrate (1 mL) in EtOH (50 mL) was heated to reflux for 4 hr. Insoluble materials were removed by filtration and solvent
was removed by a rotary evaporator. The residue was dissolved in CH₂Cl₂ (50 mL), filtered, and the organic solvent was removed by a rotary evaporator to afford the product. Yield = 0.43 g, 84%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.80 (d, J = 8.0 Hz, 2 H), 7.29 (t, J = 8.0 Hz, 2 H), 6.78 (d, J = 8.0 Hz, 2 H), 4.23 (t, J = 4.0 Hz, 4 H), 3.93 (t, J = 4.0 Hz, 4 H), 3.74 (t, J = 4.0 Hz, 4 H), 3.64 (t, J = 4.0 Hz, 4 H), 3.60–3.50 (m, 24 H), 3.42 (t, J = 4.0 Hz, 4 H), 2.78 (t, J = 4.0 Hz, 4 H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) δ = 153.7, 126.3, 124.7, 114.3, 105.4, 73.2, 71.0, 70.7, 70.6, 70.5, 70.2, 69.8, 67.9, 53.7, 41.9, 30.0. ESI-MS: 344.2 [M+2H]²⁺, 687.4 [M+H]⁺.

Scheme S2. Synthesis of L2.

L2. A mixture of Phen-OTs (2.20 g, 4.0 mmol), 2,4-dihydroxybenzaldehyde (1.16 g, 8.4 mmol), K₂CO₃ (1.64 g, 12.0 mmol) and KI (67 mg, 0.4 mmol) in dry DMF (40 mL) was heated at 100 °C for overnight. Solvent was removed using a rotary evaporator and the residue was partitioned between CHCl₃ (60 mL) and water (30 mL). The aqueous layer was extracted with CHCl₃ (2 x 50 mL). The organic fractions were combined and washed with brine, dried over MgSO₄, concentrated and purified on a silica column (CHCl₃/MeOH/Et₃N = 97:3:0.5 to 90:10:0.5) to afford the product as a white solid. Yield = 1.36 g, 71%. ¹H NMR (300 MHz, CD₃SO, 298 K) δ = 11.02 (s, 2 H), 10.03 (s, 2 H), 8.57 (d, J = 8.2 Hz, 2 H), 8.02 (s, 2 H), 7.89 (d, J = 8.2 Hz, 2 H), 7.67 (d, J = 8.7 Hz, 2 H), 6.76 (dd, J = 8.7, 2.0 Hz, 2 H), 6.66 (d, J = 2.0 Hz, 2 H), 5.60 (s, 4 H). ¹³C{¹H} NMR (75 MHz, CD₃SO, 298 K) δ = 191.0, 164.7, 163.0, 156.5, 144.6, 137.5, 132.2, 128.1, 126.6, 121.2, 116.7, 108.0, 102.0, 71.3. ESI-MS: 481.6 [M+H]⁺.
Scheme S3. Synthesis of Hex.

**S1.** A mixture of S1-OTs (4.05 g, 8.5 mmol), 4-hydroxybenzaldehyde (1.14 g, 9.4 mmol) and K$_2$CO$_3$ (1.76 g, 12.8 mmol) in dried MeCN (50 mL) was heated to reflux for overnight. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CH$_2$Cl$_2$ (50 mL) and H$_2$O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The organic fractions were combined, washed by brine, dried over MgSO$_4$, filtered and concentrated to afford a dark oil. The dark oil was purified on a silica column (EtOAc/hexane = 3:2) to afford the product as a light-yellow oil. Yield = 3.02 g, 84%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 9.88 (s, 1 H), 7.84–7.79 (m, 4 H), 7.72–7.69 (m, 2 H), 7.01 (d, $J = 8.7$ Hz, 2 H), 4.19 (t, $J = 4.0$ Hz, 2 H), 3.89 (t, $J = 5.9$ Hz, 2 H), 3.86 (t, $J = 4.0$ Hz, 2 H), 3.74 (t, $J = 4.0$ Hz, 2 H), 3.68–3.59 (m, 8 H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ = 191.0, 168.4, 164.0, 134.1, 132.3, 132.1, 123.4, 115.0, 71.0, 70.8, 70.7, 70.3, 69.6, 68.1, 67.9, 37.4. ESI-MS: 428.1 [M+H]$^+$.

**Hex-Pht.** A mixture of S1 (3.02 g, 7.1 mmol), 1,6-hexanediamine (0.39 g, 3.4 mmol) and NaBH(OAc)$_3$ (4.50 g, 21.2 mmol) in 1,2-dichloroethane (70 mL) was heated at 80°C for 2 hr. The reaction mixture was diluted with MeOH (40 mL) and cooled at 0°C. NaBH$_4$ (0.52 g, 14.1 mmol) was added in portions. The resulting solution was stirred at room temperature for 2 h. The solvent was removed by a rotary evaporator. The residue was partitioned between CH$_2$Cl$_2$ (75 mL) and H$_2$O (75 mL). The organic layer was separated and the aqueous layer was
extracted with CH$_2$Cl$_2$ (2 x 75 mL). The organic fractions were combined, washed with brine, dried over MgSO$_4$, filtered and concentrated to afford a dark oil. The dark oil was purified on a silica column (CH$_2$Cl$_2$/MeOH/Et$_3$N, 95:5:0.5) to afford the product as a light-yellow oil. Yield = 1.48 g, 47%. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ = 7.84–7.82 (m, 4 H), 7.71–7.69 (m, 4 H), 7.43 (d, $J = 8.6$ Hz, 4 H), 6.88 (d, $J = 8.7$ Hz, 4 H), 4.07 (t, $J = 5.9$ Hz, 4 H), 3.94 (s, 4 H), 3.89 (t, $J = 5.9$ Hz, 4 H), 3.80 (t, $J = 5.9$ Hz, 4 H), 3.73 (t, $J = 5.8$ Hz, 4 H), 3.67–3.58 (m, 16 H), 2.70 (t, $J = 7.2$ Hz, 4 H), 1.70 (t, $J = 7.5$ Hz, 4 H), 1.37 (t, $J = 4.2$ Hz, 4 H). 13C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ = 157.1, 132.1, 128.6, 113.8, 72.6, 70.1, 69.9, 69.6, 69.1, 66.8, 52.7, 48.6, 41.0, 29.3, 26.6. ESI-MS: 940.1 [M+H]$^+$. 

**Hex.** A mixture of Hex-Pht (1.48 g, 1.6 mmol) and hydrazine hydrate (2 mL) in EtOH (50 mL) was heated to reflux for 4 hr. Insoluble materials were removed by filtration and solvent was removed by a rotary evaporator. The residue was dissolved in CH$_2$Cl$_2$ (50 mL), filtered, and the organic solvent was removed by a rotary evaporator to afford the product as a yellow oil. Yield = 887 mg, 83%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 6.93 (d, $J = 8.7$ Hz, 4 H), 6.58 (d, $J = 8.7$ Hz, 4 H), 3.86–3.78 (m, 4 H), 3.59–3.51 (m, 4 H), 3.47–3.27 (m, 24 H), 3.25–3.16 (m, 4 H), 2.33–2.27 (m, 4 H), 1.28–1.13 (m, 4 H), 1.10–0.96 (m, 4 H). 13C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ = 157.1, 132.1, 128.6, 113.8, 72.6, 70.1, 69.9, 69.6, 69.1, 66.8, 52.7, 48.6, 41.0, 29.3, 26.6. ESI-MS: 679.6 [M+H]$^+$. 

**Scheme S4.** Synthesis of Hex-CB[6]

**Hex-CB[6].** A mixture of Hex (68 mg, 0.1 mmol) and CB[6] (100 mg, 0.1 mmol) in 0.2 M HCl (50 mL) was heated to 80 °C for 4 hr. Insoluble materials were removed by filtration. The
filtrate was treated with saturated NH$_4$PF$_6$ (2 mL) to yield a white precipitate. The product was collected by filtration, washed with water and dried under vacuum as a white solid. Yield = 140 mg, 83%. $^1$H NMR (500 MHz, CD$_3$CN, 298 K) $\delta$ = 7.59 (d, $J$ = 8.4 Hz, 4H), 7.00 (d, $J$ = 8.4 Hz, 4H), 6.79 (s, 2H), 5.71 (d, $J$ = 15.3 Hz, 12H), 5.35 (s, 12H), 4.21–4.12 (m, 20H), 3.82 (t, $J$ = 4.5 Hz, 4H), 3.72–3.55 (m, 20H), 3.09 (t, $J$ = 5.2 Hz, 4H), 3.00 (t, $J$ = 7.1 Hz, 4H), 0.74 (d, $J$ = 7.9 Hz, 4H), 0.45 (dt, $J$ = 8.4, 3.7 Hz, 4H). ESI-MS: 838.4 [M+2H]$^+$, 559.2 [M+3H]$^+$.

B. Imine assembly:

General procedure for imine assembly using dioxynaphthalene-derived diamines: A mixture of L1 (45 mg, 0.10 mmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (19 mg, 0.05 mmol) in CHCl$_3$/MeCN (v/v 7:3, 25 mL) was stirred for 30 min under argon. A solution of DNn ($n$ = 1–5, 0.11 mmol) in CHCl$_3$/MeCN (v/v 7:3, 25 mL) was added to reaction mixture. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and NaBH$_4$ (10 mg, 0.25 mmol) was added in portions. The resulting solution was stirred at room temperature for 2 hr. Solvents were removed by a rotary evaporator and the residue was partitioned between CHCl$_3$ (30 mL) and a saturated K$_2$CO$_3$ solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with CHCl$_3$ (3 × 20 mL). The organic fractions were combined, dried over MgSO$_4$ and filtered. The solution was concentrated and re-dissolved in 8 mL CHCl$_3$/CH$_3$CN (v/v 1:1). Pure samples of the products were obtained by preparative HPLC.

H1. A pure sample of H1 was obtained by preparative HPLC using Method 1. From 1 mL of the 8 mL CHCl$_3$/CH$_3$CN solution, 7.2 mg of H1 was isolated. Isolated yield = 67%. $^1$H NMR (500 MHz, D$_2$O, 298 K) $\delta$ = 8.18 (d, $J$ = 8.5 Hz, 4 H), 7.82–7.74 (m, 12 H), 7.35 (d, $J$ = 7.7 Hz, 4 H), 6.46–6.39 (m, 12 H), 5.78 (d, $J$ = 8.3 Hz, 8 H), 4.47 (t, $J$ = 3.9 Hz, 2 H), 4.10 (d, $J$ = 4.0 Hz, 2 H), 4.02 (s, 2 H), 3.98 (t, $J$ = 5.0 Hz, 2 H), 3.06 (t, $J$ = 4.9 Hz, 2 H). $^{13}$C($^1$H) NMR (150 MHz, D$_2$O, 298 K) $\delta$ = 157.3, 154.2, 152.6, 142.3, 137.3, 130.6, 128.2, 126.3, 126.2, 125.5, 125.4, 121.8, 114.5, 112.6, 106.8, 70.3, 69.3, 68.0, 65.9, 48.9, 46.4, 43.2. ESI-MS: 1563.6 [M]$^+$.
**H1b.** The copper containing H1 was demetallated to give H1b by treating the assembly mixture in CHCl3/MeCN (v/v 1:1, 25mL) with an aqueous solution of NaCN (49 mg, 1.0 mmol, 5 mL) and stirred at room temperature for 4 hr. Volatiles was removed from the mixture and the residue was partitioned between CHCl3 (30 mL) and a saturated K2CO3 solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with CHCl3 (3 × 20 mL). The organic fractions were combined, dried over MgSO4 and filtered. The solution was concentrated and re-dissolved in 8 mL CHCl3/CH3CN (v/v 1:1) by using rotary evaporator. A pure sample of H1b was obtained by preparative HPLC using Method 1. From 1 mL of the 8 mL CHCl3/CH3CN solution, 5.0 mg of H1b was isolated, isolated yield = 54%. 1H NMR (500 MHz, D2O, 298 K) δ = 7.68 (d, J = 8.3 Hz, 4H), 7.54 (s, 4H), 7.31 (d, J = 8.3 Hz, 8H), 7.26 (d, J = 8.4 Hz, 4H), 7.11 (d, J = 8.2 Hz, 4H), 6.88 (t, J = 8.0 Hz, 4H), 6.60 (d, J = 8.2 Hz, 8H), 6.25 (d, J = 7.5 Hz, 4H), 4.23 (d, J = 8.8 Hz, 16H), 3.81 (s, 8H), 3.77 (d, J = 5.1 Hz, 8H), 3.16 (t, J = 4.9 Hz, 4H). ESI-MS: 1523.6 [M+Na]+, 751.6 [M+2H]2+.

**F2.** A pure sample of F2 was obtained by preparative HPLC using Method 1. From 1 mL of the 8 mL CHCl3/CH3CN solution, 4.2 mg of F2 was isolated, isolated yield = 35%. 1H NMR (500 MHz, D2O, 298 K) δ = 8.45 (d, J = 8.1 Hz, 4H), 7.87 (s, 4H), 7.69–7.61 (m, 8H), 7.25 (t, J = 8.0 Hz, 4H), 6.88 (d, J = 7.6 Hz, 4H), 6.55 (d, J = 8.2 Hz, 4H), 5.67 (d, J = 8.2 Hz, 8H), 4.52 (d, J = 10.0 Hz, 4H), 4.38 (d, J = 10.0 Hz, 4H), 4.12 (t, J = 4.2 Hz, 8H), 3.96 (s, 8H), 3.82–3.72 (m, 32H), 3.14–3.11 (m, 8H). ESI-MS: 1739.5 [M]+, 870.5 [M+H]2+.

**H2.** A pure sample of H2 was obtained by preparative HPLC using Method 1. From 1 mL of the 8 mL CHCl3/CH3CN solution, 4.4 mg of H2 was isolated, isolated yield = 37%. 1H NMR δ 8.13 (d, J = 8.2 Hz, 4H), 7.80 (d, J = 8.2 Hz, 4H), 7.68 (d, J = 8.3 Hz, 4H), 7.38 (s, 4H), 7.28 (t, J = 8.0 Hz, 4H), 6.91 (d, J = 7.8 Hz, 4H), 6.74 (d, J = 8.3 Hz, 8H), 6.09 (d, J = 8.2 Hz, 8H), 4.89 (s, 8H), 4.29–4.25 (m, 8H), 4.01–3.96 (m, 8H), 3.92 (s, 8H), 3.85–3.82 (m, 8H), 3.78–3.75 (m, 8H), 3.74–3.70 (m, 8H), 3.08 (t, J = 4.9 Hz, 8H). ESI-MS: 1739.5 [M]+, 870.5 [M+H]2+.

**F3.** A pure sample of F3 was obtained by preparative HPLC using Method 1. From 2 mL of the 8 mL CHCl3/CH3CN solution, 10.8 mg of F3 was isolated, isolated yield = 45%. 1H NMR
(500 MHz, D₂O, 298 K) δ = 8.43 (d, J = 8.1 Hz, 4H), 7.86 (s, 4H), 7.66 (d, J = 8.2 Hz, 8H), 7.24 (t, J = 8.0 Hz, 4H), 6.83 (d, J = 7.5 Hz, 4H), 6.53 (d, J = 8.2 Hz, 8H), 5.68 (d, J = 8.4 Hz, 8H), 4.50–4.40 (m, 8H), 4.10–4.04 (m, 8H), 3.94–3.87 (m, 8H), 3.81–3.74 (m, 16H), 3.70–3.64 (m, 32H), 3.15–3.11 (m, 8H). ¹³C{¹H} NMR (150 MHz, D₂O, 298 K) δ = 157.5, 153.7, 152.9, 142.5, 137.8, 130.5, 128.6, 126.5, 126.2, 125.7, 125.5, 122.4, 114.4, 112.8, 106.7, 70.2, 69.8, 69.6, 69.6, 69.5, 69.1, 67.6, 65.1, 49.8, 45.9. ESI-MS: 1916.2 [M]+, 958.6 [M+H]²⁺.

**H₃.** A pure sample of H₃ was obtained by preparative HPLC using Method 1. From 2 mL of the 8 mL CHCl₃/CH₃CN solution, 5.2 mg of H₃ was isolated. Isolated yield = 20%. ¹H NMR (500 MHz, D₂O, 298 K) δ = 8.28 (d, J = 8.1 Hz, 4H), 7.83 (d, J = 8.1 Hz, 4H), 7.75 (d, J = 8.4 Hz, 4H), 7.59 (s, 4H), 7.32 (t, J = 8.1 Hz, 4H), 6.93 (d, J = 7.7 Hz, 4H), 6.54 (d, J = 8.2 Hz, 8H), 5.95 (d, J = 8.2 Hz, 8H), 4.83 (s, 8H), 4.25–4.22 (m, 8H), 3.95–3.90 (m, 8H), 3.82–3.78 (m, 8H), 3.10–3.05 (m, 8H). ¹³C{¹H} NMR (150 MHz, D₂O, 298 K) δ = 157.6, 153.8, 153.3, 142.5, 137.9, 130.7, 128.6, 126.3, 126.2, 125.7, 125.3, 122.7, 114.4, 113.3, 106.8, 70.7, 69.8, 69.6, 69.5, 69.9, 69.1, 67.8, 65.2, 49.6, 45.6. ESI-MS: 1916.2 [M]+, 958.6 [M+H]²⁺.

**F₅.** Pure sample of F₅ was obtained by preparative HPLC using Method 1. From 1 mL of the 8 mL CHCl₃/CH₃CN solution, 6.5 mg of H₅ was isolated, isolated yield = 43%. ¹H NMR (500 MHz, D₂O, 298 K) δ = 8.37 (d, J = 8.1 Hz, 4H), 7.77 (s, 4H), 7.73 (d, J = 8.1 Hz, 4H), 7.64 (d, J = 8.5 Hz, 3H), 7.18 (d, J = 7.0 Hz, 4H), 6.77 (d, J = 7.9 Hz, 4H), 6.60 (d, J = 8.3 Hz, 8H), 5.83 (d, J = 8.4 Hz, 8H), 4.58 (d, J = 4.6 Hz, 8H), 4.16–4.10 (m, 8H), 3.93–3.87 (m, 8H), 3.86–3.81 (m, 8H), 3.71–3.67 (m, 8H), 3.63–3.60 (m, 16H), 3.59–3.47 (m, 32H), 3.10–3.05 (m, 8H). ¹³C{¹H} NMR (125 MHz, D₂O, 298 K) δ = 156.1, 153.8, 153.1, 142.6, 137.9, 136.6, 130.7, 129.5, 126.8, 126.5, 126.2, 125.8, 123.1, 113.0, 111.9, 106.7, 70.3, 69.8, 69.5, 69.4, 69.3, 69.3, 69.1, 69.1, 67.8, 67.7, 64.3, 48.7, 45.9. ESI-MS: 1135.6 [M+H]³⁺, 757.4 [M+2H]⁴⁺, 568.3 [M+3H]⁵⁺.

**H₅.** Pure sample of H₅ was obtained by preparative HPLC using Method 1. From 2 mL of the 8 mL CHCl₃/CH₃CN solution, 3.2 mg of H₅ was isolated, isolated yield = 22%. ¹H NMR (500 MHz, D₂O, 298 K) δ = 8.37 (d, J = 8.4 Hz, 4H), 7.82 (d, J = 7.9 Hz, 4H), 7.76 (d, 4H), 7.72 (s, 4H),
$\delta = 156.2, 153.8, 153.3, 142.6, 138.0, 136.6, 131.0, 129.4, 126.8, 126.5, 126.3, 125.8, 123.3, 113.1, 112.0, 106.5, 70.3, 69.8, 69.5, 69.4, 69.3, 69.2, 69.1, 69.0, 67.8, 67.7, 64.4, 48.8, 45.9. \text{ESI-MS: } 1135.6 \ [\text{M+H}]^{2+}, 757.4 \ [\text{M+2H}]^{3+}, 568.3 \ [\text{M+3H}]^{4+}.

**General procedure of imine assembly using α,ω-diamine with 7 to 12 methylene groups:** A mixture of $\text{L1}$ (45 mg, 0.1 mmol) and $\text{[Cu(CH_3CN)_4]PF_6}$ (19 mg, 0.05 mmol) in CHCl$_3$/MeCN (v/v 7:3, 25 mL) was stirred for 30 min under argon. A solution of α,ω-diamine (0.11 mmol) in CHCl$_3$/MeCN (v/v 7:3, 25 mL) was added to reaction mixture. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and NaBH$_4$ (10 mg, 0.25 mmol) was added in portions. The resulting solution was stirred at room temperature for 2 hr. Solvents were removed by a rotary evaporator and the residue was partitioned between CHCl$_3$ (30 mL) and a saturated K$_2$CO$_3$ solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with CHCl$_3$ (3 × 20 mL). The organic fractions were combined, dried over MgSO$_4$ and filtered. The solution was concentrated and re-dissolved in 8 mL CHCl$_3$/CH$_3$CN (v/v 1:1) by using rotary evaporator. Pure samples of assembly products were obtained by preparative HPLC.

**H6.** A pure sample of $\text{H6}$ was obtained by preparative HPLC using Method 2. From 2 mL of the 8 mL CHCl$_3$/CH$_3$CN solution, 11.6 mg of $\text{H6}$ was isolated, isolated yield = 72%. $^1$H NMR (500 MHz, D$_2$O, 298 K) $\delta = 8.55$ (d, $J = 8.1$ Hz, 4H), 8.10 (d, $J = 8.1$ Hz, 4H), 7.80 (s, 4H), 6.70 (d, $J = 8.3$ Hz, 8H), 5.94 (d, $J = 8.4$ Hz, 8H), 4.98 (s, 8H), 3.82 (s, 8H), 2.89 (t, $J = 7.6$ Hz, 8H), 1.78 (s, 8H), 1.51 (d, $J = 9.5$ Hz, 12H). $^{13}$C($^1$H) NMR (100 MHz, D$_2$O, 298 K) $\delta = 157.6, 153.6, 143.2, 137.8, 130.6, 128.5, 126.5, 126.1, 123.7, 113.6, 70.9, 49.9, 46.3, 27.5, 25.9, 25.4. \text{ESI-MS: } 1155.5 \ [\text{M}]^+, 578.0 \ [\text{M+H}]^{2+}.$

**H7.** A pure sample of $\text{H7}$ was obtained by preparative HPLC using Method 2. From 2 mL of the 8 mL CHCl$_3$/CH$_3$CN solution, 13.4 mg of $\text{H7}$ was isolated, isolated yield = 81%. $^1$H NMR
(500 MHz, D2O, 298 K) δ = 8.50 (d, J = 8.2 Hz, 4H), 8.08 (d, J = 8.2 Hz, 4H), 7.71 (s, 4H), 6.70 (d, J = 8.1 Hz, 8H), 5.97 (d, J = 8.2 Hz, 8H), 5.02 (s, 8H), 3.83 (s, 8H), 2.88 (t, J = 7.4 Hz, 8H), 1.78 (t, J = 7.7 Hz, 8H), 1.61–1.48 (m, 16H). 13C{1H} NMR (125 MHz, D2O, 298 K) δ = 157.6, 153.1, 143.1, 137.7, 130.8, 128.3, 126.3, 126.0, 122.7, 113.1, 70.8, 50.0, 46.7, 27.4, 25.9, 25.2. ESI-MS: 1183.6 [M]+, 592.3 [M+H]2+, 395.1 [M+2H]3+.

H8. A pure sample of H8 was obtained by preparative HPLC using Method 2. From 2 mL of the 8 mL CHCl3/CH3CN solution, 12.4 mg of H8 was isolated, isolated yield = 73%. 1H NMR (500 MHz, D2O, 298 K) δ = 8.56 (d, J = 8.1 Hz, 4H), 8.11 (d, J = 8.2 Hz, 4H), 7.83 (s, 4H), 6.68 (d, J = 8.0 Hz, 8H), 6.04 (d, J = 8.1 Hz, 8H), 5.05 (d, J = 8.7 Hz, 8H), 3.82 (s, 8H), 2.89 (t, J = 7.5 Hz, 8H), 1.88–1.79 (m, 8H), 1.61–1.54 (m, 20H). 13C{1H} NMR (100 MHz, D2O, 298 K) δ = 157.6, 153.4, 143.0, 137.9, 130.5, 128.6, 126.3, 126.0, 123.3, 113.2, 71.1, 49.4, 46.1, 28.1, 27.7, 25.9, 25.5. ESI-MS: 1211.6 [M]+, 605.9 [M+H]2+, 404.3 [M+2H]3+.

H9. A pure sample of H9 was obtained by preparative HPLC using Method 2. From 2 mL of the 8 mL CHCl3/CH3CN solution, 13.2 mg of H9 was isolated, isolated yield = 76%. 1H NMR (500 MHz, D2O, 298 K) δ = 8.55 (d, J = 8.1 Hz, 4H), 8.09 (d, J = 8.1 Hz, 4H), 7.82 (s, 4H), 6.69 (d, J = 8.2 Hz, 8H), 6.06 (d, J = 8.3 Hz, 8H), 5.05 (s, 8H), 3.82 (s, 8H), 2.83 (t, J = 7.3 Hz, 8H), 1.80–1.74 (m, 8H), 1.58–1.52 (m, 24H). 13C{1H} NMR (125 MHz, CDCl3, 298 K) δ = 157.5, 153.4, 143.0, 137.9, 130.5, 128.6, 126.3, 123.4, 113.1, 71.1, 49.4, 46.2, 28.0, 27.7, 25.7, 25.5. ESI-MS: 1239.6 [M]+, 620.0 [M+H]2+, 413.9 [M+2H]3+.

H10. A pure sample of H10 was obtained by preparative HPLC using Method 2. From 2 mL of the 8 mL CHCl3/CH3CN solution, 13.0 mg of H10 was isolated, isolated yield = 74%. 1H NMR (500 MHz, D2O, 298 K) δ = 8.55 (d, J = 8.1 Hz, 4H), 8.09 (d, J = 8.1 Hz, 4H), 7.86 (s, 4H), 6.67 (d, J = 8.3 Hz, 8H), 6.08 (d, J = 8.3 Hz, 8H), 5.05 (s, 8H), 3.84 (s, 8H), 2.87 (t, J = 7.8 Hz, 8H), 1.82–1.76 (m, 8H), 1.55–1.50 (m, 28H). 13C{1H} NMR (125 MHz, CDCl3, 298 K) δ = 156.4, 155.2, 143.1, 137.7, 133.0, 128.8, 128.7, 126.6, 125.4, 113.1, 71.3, 53.0, 49.1, 30.1, 29.6, 29.3, 29.0, 27.3. ESI-MS: 1267.1 [M]+, 634.0 [M+H]2+, 423.3 [M+2H]3+. 
**H11.** A pure sample of H11 was obtained by preparative HPLC using *Method 1*. From 2 mL of the 8 mL CHCl₃/CH₃CN solution, 12.8 mg of H11 was isolated, isolated yield = 71%. $^1$H NMR (500 MHz, D2O) δ = 8.55 (d, $J = 8.2$ Hz, 4H), 8.08 (d, $J = 8.1$ Hz, 4H), 7.88 (s, 4H), 6.69 (d, $J = 8.2$ Hz, 8H), 6.08 (d, $J = 8.2$ Hz, 8H), 5.05 (s, 8H), 3.87 (s, 8H), 2.85 (t, $J = 7.6$ Hz, 8H), 1.80–1.74 (m, 8H), 1.51–1.48 (m, 32H). $^{13}$C($^1$H) NMR (100 MHz, D₂O, 298 K) δ = 157.7, 153.5, 143.0, 138.0, 130.6, 128.7, 126.4, 126.1, 122.9, 113.2, 71.1, 49.0, 45.8, 28.2, 27.8, 27.6, 25.5, 24.6. ESI-MS: 1295.1 [M]$^+$, 648.4 [M+H]$^{2+}$, 432.7 [M+2H]$^{3+}$.

**Procedure for imine assembly using Hex:** A mixture of L2 (48 mg, 0.1 mmol) and Cu(CH₃CN)$_4$PF₆ (19 mg, 0.05 mmol) in CHCl₃/MeCN (v/v 7:3, 25 mL) was stirred for 30 min under argon. A solution of Hex (75 mg, 0.11 mmol) in CHCl₃/MeCN (v/v 7:3, 25 mL) was added to reaction mixture. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and NaBH₄ (10 mg, 0.25 mmol) was added in portions. The resulting mixture was stirred at room temperature for 2 hr. Solvents were removed by a rotary evaporator and the residue was partitioned between CHCl₃ (30 mL) and a saturated K₂CO₃ solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with CHCl₃ (3 × 20 mL). The organic fractions were combined, dried over MgSO₄ and filtered. The solvents were removed and re-dissolved in CHCl₃/MeCN (v/v 1:1, 25 mL) and treated with a solution of NaCN (50 mg, 1 mmol) in H₂O (5 mL). The resulting mixture was stirred at room temperature for 4 h and partitioned between CHCl₃ (30 mL) and a saturated K₂CO₃ solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with CHCl₃ (3 × 20 mL). The organic fractions were combined, dried over MgSO₄ and filtered. Pure samples of the assembly products were obtained by preparative HPLC.

**F12b.** Pure sample of F12b was obtained by preparative HPLC using *Method 3*. From 2 mL of the 8 mL CHCl₃/CH₃CN solution, 13.0 mg of F12b was isolated, isolated yield = 46%. $^1$H NMR (500 MHz, D₂O, 298 K) δ = 7.99 (d, $J = 8.3$ Hz, 4H), 7.47 (d, $J = 8.2$ Hz, 4H), 7.42 (s, 4H), 7.14 (d, $J = 8.5$ Hz, 4H), 7.10 (d, $J = 8.2$ Hz, 8H), 6.73 (d, $J = 8.2$ Hz, 8H), 6.59 (s, 4H), 6.49–6.45 (m, 4H), 5.02 (s, 8H), 4.07 (s, 8H), 3.89 (d, $J = 4.9$ Hz, 8H), 3.79 (s, 8H), 3.71 (s, 8H), 3.65 (s, 8H), 3.61–3.58 (m, 32H), 3.18 (t, $J = 4.9$ Hz, 8H), 2.62–2.57 (m, 8H), 1.28 (s, 8H), 0.91 (s, 8H).
$^{13}$C{$^{1}$H} NMR (125 MHz, D$_2$O, 298 K) δ = 163.1, 160.0, 158.6, 156.6, 143.2, 137.8, 132.8, 131.3, 127.8, 122.9, 117.6, 115.2, 114.9, 110.6, 106.8, 102.3, 70.2, 69.7, 69.7, 69.6, 69.6, 69.5, 68.8, 67.0, 65.1, 49.5, 46.2, 45.9, 45.5, 24.9, 24.7. ESI-MS: 1128.1 [M+2H]$^{2+}$, 752.4 [M+3H]$^{3+}$, 564.6 [M+4H]$^{4+}$.

**H12b.** Pure sample of H12b was obtained by preparative HPLC using Method 3. From 2 mL of the 8 mL CHCl$_3$/CH$_3$CN solution, 6.0 mg of H12 was isolated, isolated yield = 21%. $^1$H NMR (500 MHz, D$_2$O, 298 K) δ = 8.41 (d, J = 8.3 Hz, 4H), 7.90 (s, 4H), 7.19 (d, J = 8.4 Hz, 4H), 7.11 (d, J = 8.4 Hz, 8H), 6.71 (d, J = 8.4 Hz, 8H), 6.68–6.63 (m, 8H), 5.42 (s, 8H), 4.84 (s, 8H), 4.11 (s, 8H), 3.90–3.85 (m, 8H), 3.77–3.73 (m, 16H), 3.65–3.61 (m, 32H), 3.23 (t, J = 4.9 Hz, 8H), 2.57–2.52 (m, 8H), 1.25 (s, 8H), 0.87 (s, 8H). $^{13}$C{$^{1}$H} NMR (125 MHz, D$_2$O, 298 K) δ = 163.2, 159.3, 158.8, 156.9, 143.5, 138.0, 133.0, 131.7, 128.0, 123.0, 117.6, 115.4, 115.0, 110.7, 106.9, 102.6, 70.3, 69.9 69.8, 69.7, 69.6, 69.0, 67.2, 65.3, 49.7, 46.5, 46.1 45.7, 25.0, 24.8. ESI-MS: 1128.1 [M+2H]$^{2+}$, 752.4 [M+3H]$^{3+}$, 564.6 [M+4H]$^{4+}$.

**Procedure for imine assembly using Hex-CB[6]:** A mixture of L2 (12 mg, 0.025 mmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (4.5 mg, 0.0125 mmol) in CHCl$_3$/MeCN (v/v 7:3, 12 mL) was stirred for 30 min under argon. A solution of Hex-CB[6] (68 mg, 0.03 mmol) in MeCN (12 mL) was added to the reaction mixture. Piperidine (2.5 μl, 0.025 mmol) was added. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and NaBH$_4$ (4 mg, 0.1 mmol) was added in portions. The resulting mixture was stirred at room temperature for 2 hr and concentrated by a rotary evaporator. The residue was re-dissolved in 4 mL of CHCl$_3$/MeCN (v/v 7:3).

**H13.** Pure sample of H13 was obtained by preparative HPLC using Method 4. From 1 mL of the 4 mL CHCl$_3$/CH$_3$CN solution, 8.4 mg of H13 was isolated, isolated yield = 52%. $^1$H NMR (500 MHz, D$_2$O, 298 K) δ = 8.48 (d, J = 8.1 Hz, 4H), 8.00 (d, J = 8.2 Hz, 4H), 7.87 (s, 4H), 7.61 (d, J = 8.8 Hz, 8H), 6.96 (d, J = 8.8 Hz, 8H), 6.39 (d, J = 8.5 Hz, 4H), 5.64 (d, J = 15.6 Hz, 24H), 5.50 (s, 4H), 5.42 (d, J = 4.5 Hz, 4H), 5.37 (s, 24H), 4.28–4.27 (m, 8H), 4.21–4.16 (m, 24H), 4.11–4.04 (m, 8H), 3.88 (s, 8H), 3.75–3.67 (m, 48H), 3.11 (s, 8H), 2.94 (s, 8H), 0.81 (s, 8H),
0.40 (s, 8H). $^{13}$C($^{1}$H) NMR (125 MHz, D$_2$O, 298 K) $\delta$ = 159.4, 158.5, 155.9, 142.8, 138.1, 131.4, 128.7, 126.5, 125.7, 124.7, 119.8, 117.5, 115.2, 114.9, 109.9, 109.6, 104.0, 70.2, 70.1, 69.7, 69.6, 69.5, 68.9, 68.8, 67.1, 65.0, 51.6, 51.3, 48.0, 46.0, 45.9, 45.8, 26.7, 26.1. ESI-MS: 1107.2 [M+4H+TFA]$^{4+}$, 863.2 [M+4H]$^{5+}$, 719.5 [M+5H]$^{6+}$.

Procedure for imine assembly using L2 and Hex·CB[6]: To a solution of L2 (12 mg, 0.025 mmol) in CHCl$_3$/MeCN (v/v 7:3, 12 mL) was added Hex·CB[6] (68 mg, 0.03 mmol) in MeCN (12 mL) and stirred at room temperature for 30 min. Piperidine (2.5 µl, 0.025 mmol) was added and the yellow solution was heated at 80 °C for overnight under argon. The solution was cooled to 0 °C and NaBH$_4$ (4 mg, 0.1 mmol) was added in portions. The resulting mixture was stirred at room temperature for 2 hr. Solvents were removed and the residue re-dissolved in 4 mL CHCl$_3$/MeCN (v/v 7:3). Pure sample of M13 was obtained by preparative HPLC using Method 2. From 1 mL of the 4 mL CHCl$_3$/CH$_3$CN solution, 12.4 mg of M13 was isolated, isolated yield = 82%. $^1$H NMR (500 MHz, D$_2$O, 298 K) $\delta$ = 8.38 (s, 4H), 7.84 (d, $J$ = 8.4 Hz, 4H), 7.79 (s, 4H), 7.49 (d, $J$ = 8.8 Hz, 8H), 7.08 (d, $J$ = 8.5 Hz, 4H), 6.97 (d, $J$ = 8.7 Hz, 8H), 6.54 (s, 4H), 6.52 (d, $J$ = 8.4 Hz, 4H), 5.39 (d, $J$ = 15.6 Hz, 24H), 5.13 (s, 24H), 4.12–4.06 (m, 8H), 4.00–3.95 (m, 32H), 3.75 (s, 8H), 3.65–3.59 (m, 24H), 3.57–3.54 (m, 16H), 3.53 (s, 16H), 3.08 (t, $J$ = 4.9 Hz, 8H), 2.73 (t, $J$ = 7.3 Hz, 8H), 0.51 (s, 8H), 0.16 (s, 8H). $^{13}$C($^{1}$H) NMR (125 MHz, D$_2$O, 298 K) $\delta$ = 158.6, 157.1, 155.7, 141.6, 138.6, 131.3, 128.6, 127.0, 124.8, 122.9, 118.6, 117.5, 115.0, 112.1, 111.5, 109.6, 102.6, 70.9, 70.3, 70.0, 69.7, 69.6, 69.5, 69.5, 69.0, 67.3, 65.3, 51.6, 51.2, 48.0, 46.1, 42.9, 39.4, 26.5, 25.8. ESI-MS: 1063.1 [M+2H]$^{2+}$, 709.1 [M+3H]$^{3+}$, 532.1 [M+4H]$^{4+}$. 
2. HPLC Analysis

HPLC analyses were carried out using a Waters-Alliance e2695 system coupled to a 2489 UV/Vis detector. HPLC grade H₂O (Scharlau), MeCN (Arkonic Scientific), formic acid (Merck) and trifluoroacetic acid (J&K) were used as received. C18 SunFire preparative columns (5 μm, 10 × 250 mm or 10 μm, 4.6 × 250 mm) were used with gradient elution described below. UV-Vis absorbance was monitored at 280 nm.

Method 1 (flow rate = 1 mL/min)

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<th>MeCN (with 0.05% formic acid)</th>
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</tr>
<tr>
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<td>0%</td>
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</tr>
<tr>
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</table>

Method 2 (flow rate = 3 mL/min)

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Method 3 (flow rate = 3 mL/min)

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Method 4 (flow rate = 3 mL/min)

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<tr>
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</tbody>
</table>

Figure S1. HPLC chromatograms (Method 1) of the crude assembly mixture from [Cu(L1)₂]+ and (a) DN1 (after demetallation), (b) DN2, (c) DN3, (d) DN4 and (e) DN5.
Figure S2. HPLC chromatograms (Method 2) of the crude assembly mixture from [Cu(L1)₂]⁺ and (a) Alk7, (b) Alk8, (c) Alk9, (d) Alk10, (e) Alk11 and (f) Alk12.

Figure S3. HPLC chromatogram of the crude assembly mixture from L2 and Hex-CB[6]. Separation was achieved using Method 2.
3. NMR

**Figure S4.** $^1$H NMR (300 MHz, CDCl$_3$, 298 K) of 4-OTs.

**Figure S5.** $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of 4-OTs.
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of 5-OTs.

Figure S7. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of 5-OTs.
Figure S8. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN4-OH.

Figure S9. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN4-OH.
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN5-OH.

Figure S11. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN5-OH.
Figure S12. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN4-OTs.

Figure S13. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN4-OTs.
Figure S14. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN5-OTs.

Figure S15. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN5-OTs.
Figure S16. $^1$HNMR (400 MHz, CDCl$_3$, 298 K) of DN4-Pht.

Figure S17. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN4-Pht.
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN5-Pht.

Figure S19. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN5-Pht.
Figure S20. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN4.

Figure S21. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of DN4.
Figure S22. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of DN5.

Figure S23. $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K) of DN5.
Figure S24. $^1$H NMR (300 MHz, (CD$_3$)$_2$SO, 298 K) of L2.

Figure S25. $^{13}$C($^1$H) NMR (75 MHz, (CD$_3$)$_2$SO, 298 K) of L2.
Figure S26. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of S1.

Figure S27. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of S1.
Figure S28. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) of Hex-Pht.

Figure S29. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of Hex-Pht.
Figure S30. $^1\text{H}$ NMR (400 MHz, CDCl$_3$, 298 K) of Hex.

Figure S31. $^{13}$C($^1\text{H}$) NMR (100 MHz, CDCl$_3$, 298 K) of Hex.
Figure S32. $^1$H NMR (500 MHz, CD$_3$CN, 298 K) of Hex-CB[6].

Figure S33. $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$CN = 7/3, 298 K) of (a) L1 and (b) [Cu(L1)$_2$]$^+$. 
Figure S34. \(^1\)H NMR (500 MHz, D\(_2\)O, 298 K) of H1.

Figure S35. \(^{13}\)C\(^{1}(\text{H})\) NMR (150 MHz, D\(_2\)O, 298 K) of H1.
Figure S36. $^1$H NMR (500 MHz, D$_2$O) of H1 at 348 K (top) and 298 K (bottom).

Figure S37. NOESY (500 MHz, D$_2$O, 298 K, d$_8$ = 700ms) of H1.
Figure S38. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H1b.

Figure S39. $^1$H NMR (500 MHz, D$_2$O, 298 K) of F2.
Figure S40. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H2.

Figure S41. $^1$H NMR (500 MHz, D$_2$O, 298 K) of F3.
Figure S42. $^{13}$C(1H) NMR (150 MHz, D$_2$O, 298 K) of F3.

Figure S43. NOESY (500 MHz, D$_2$O, 298 K, $d_6 = 700$ ms) of F3.
**Figure S44.** DOSY (500 MHz, D$_2$O, 298 K) of F3.

**Figure S45.** $^1$H NMR (500 MHz, D$_2$O, 298 K) of H3.
Figure S46. $^{13}$C{${}^1$H} NMR (150 MHz, D$_2$O, 298 K) of H3.

Figure S47. NOESY (500 MHz, D$_2$O, 298 K, $d_8 = 700$ms) of H3.
Figure S48. DOSY (500 MHz, D$_2$O, 298 K) of H3.

Figure S49. $^1$H NMR (500 MHz, D$_2$O, 298 K) of F5.
Figure S50. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of F5.

Figure S51. $^1$H NMR (500 MHz, D$_2$O) of F5 at 338 K (top) and 298 K (bottom).
Figure S52. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H$_5$.

Figure S53. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of H$_5$. 
Figure S54. $^1$H NMR (500 MHz, D$_2$O) of H5 at 338 K (top) and 298 K (bottom).

Figure S55. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H6.
Figure S56. $^{13}$C{^1}H NMR (125 MHz, D$_2$O, 298 K) of H6.

Figure S57. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H7.
Figure S58. $^{13}$C\{$^1$H} NMR (125 MHz, D$_2$O, 298 K) of H7.

Figure S59. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H8.
Figure S60. $^{13}$C(H) NMR (125 MHz, D$_2$O, 298 K) of H8.

Figure S61. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H9.
Figure S62. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of H9.

Figure S63. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H10.
Figure S64. $^{13}$C{[$^1$H]} NMR (125 MHz, CDCl$_3$, 298 K) of H10.

Figure S65. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H11.
Figure S66. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of H11.

Figure S67. $^1$H NMR (500 MHz, D$_2$O, 298 K) of F12b.
Figure S68. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of F12b.

Figure S69. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H12b.
Figure S70. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of H12b.

Figure S71. $^1$H NMR (500 MHz, D$_2$O, 298 K) of M13.
Figure S72. $^1$H NMR (500 MHz, D$_2$O, 298 K) of H13.

Figure S73. $^{13}$C($^1$H) NMR (125 MHz, D$_2$O, 298 K) of H13.
Figure S74. Variable temperature $^1$H NMR (500 MHz, D$_2$O) of H13.

Figure S75. NOESY (500 MHz, D$_2$O, 298 K, d$_8$ = 700ms) of H13.
Figure S76. Variable temperature $^2$H NMR (500 MHz, D$_2$O) of F13.
4. ESI-MS

Mass spectrometry was performed on a Thermo Scientific LTQ FLEET mass spectrometer or a Finnigan LCQ mass spectrometer. HR-ESI-MS were carried out on a Bruker ESI Quadrupole TOF mass spectrometer. MS² experiments were carried out on a Thermo Scientific LTQ FLEET mass spectrometer. Isotopic patterns were simulated using IsoPro, version 3.1.

Figure S77. (a) ESI-MS spectrum of F1b (after demetallation), (b) HRMS of the peak at $m/z = 1524.7$ (left: experimental; right: simulation) (c) MS² spectrum of F1b upon fragmentation of the peak at $m/z = 1524.7$. 

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Figure S78. (a) ESI-MS spectrum of H1b (after demetallation), (b) HRMS of the peak at m/z = 1524.7 (left: experimental; right: simulation) (c) MS² spectrum of H1b upon fragmentation of the peak at m/z = 1524.7.
Figure S79. (a) ESI-MS spectrum of F2, (b) HRMS of the peak at m/z = 870.9 (left: experimental; right: simulation) (c) MS² spectrum of F2 upon fragmentation of the peak at m/z = 870.9.
Figure S80. (a) ESI-MS spectrum of H2, (b) HRMS of the peak at m/z = 870.9 (left: experimental; right: simulation) (c) MS² spectrum of H2 upon fragmentation of the peak at m/z = 870.9.
Figure S81. (a) ESI-MS spectrum of F3b (after demetallation), (b) HRMS of the peak at m/z = 927.7 (left: experimental; right: simulation) (c) MS² spectrum of F3b upon fragmentation of the peak at m/z = 927.7.
Figure S82. (a) ESI-MS spectrum of H3b (after demetallation), (b) HRMS of the peak at m/z = 927.9 (left: experimental; right: simulation) (c) MS² spectrum of H3b upon fragmentation of the peak at m/z = 927.9.
Figure S83. (a) ESI-MS spectrum of F4, (b) HRMS of the peak at $m/z = 1047.5$ (left: experimental; right: simulation) (c) MS$^3$ spectrum of F4 upon fragmentation of the peak at $m/z = 1047.5$. 
Figure S84. (a) ESI-MS spectrum of H4, (b) HRMS of the peak at $m/z = 1047.5$ (left: experimental; right: simulation) (c) MS$^2$ spectrum of H4 upon fragmentation of the peak at $m/z = 1047.5$
Figure S85. (a) ESI-MS spectrum of \( \text{F5} \), (b) HRMS of the peak at \( m/z = 1135.5 \) (left: experimental; right: simulation) (c) MS\(^2\) spectrum of \( \text{F5} \) upon fragmentation of the peak at \( m/z = 1135.5 \).
Figure S86. (a) ESI-MS spectrum of H5, (b) HRMS of the peak at m/z = 1135.6 (left: experimental; right: simulation) (c) MS² spectrum of H5 upon fragmentation of the peak at m/z = 1135.6.
Figure S87. (a) ESI-MS spectrum of H6, (b) HRMS of the peak at m/z = 1155.5 (left: experimental; right: simulation) (c) MS² spectrum of H6 upon fragmentation of the peak at m/z = 1155.5
Figure S88. (a) ESI-MS spectrum of H7, (b) HRMS of the peak at m/z = 1183.6 (left: experimental; right: simulation) (c) MS² spectrum of H7 upon fragmentation of the peak at m/z = 1183.6
Figure S89. (a) ESI-MS spectrum of H8, (b) HRMS of the peak at m/z = 1211.6 (left: experimental; right: simulation) (c) MS² spectrum of H8 upon fragmentation of the peak at m/z = 1211.6
Figure S90. (a) ESI-MS spectrum of H9, (b) HRMS of the peak at $m/z = 1239.6$ (left: experimental; right: simulation) (c) MS$^2$ spectrum of H9 upon fragmentation of the peak at $m/z = 1239.6$
Figure S91. (a) ESI-MS spectrum of H10, (b) HRMS of the peak at $m/z = 1267.1$ (left: experimental; right: simulation) (c) MS$^2$ spectrum of H10 upon fragmentation of the peak at $m/z = 1267.1$
Figure S92. (a) ESI-MS spectrum of H11, (b) HRMS of the peak at m/z = 1295.1 (left: experimental; right: simulation) (c) MS² spectrum of H11 upon fragmentation of the peak at m/z = 1295.1
Figure S93. (a) ESI-MS spectrum of F12b (after demetallation), (b) HRMS of the peak at $m/z = 752.4$ (left: experimental; right: simulation) (c) MS$^2$ spectrum of F12b upon fragmentation of the peak at $m/z = 752.4$. 
Figure S94. (a) ESI-MS spectrum of H12b (after demetallation), (b) HRMS of the peak at $m/z = 752.4$ (left: experimental; right: simulation) (c) MS$^2$ spectrum of H12b upon fragmentation of the peak at $m/z = 752.4$
Figure S95. (a) ESI-MS spectrum of \textbf{F13}, (b) HRMS of the peak at $m/z = 1107.2$ (left: experimental; right: simulation) (c) MS$^2$ spectrum of \textbf{F13} upon fragmentation of the peak at $m/z = 1107.2$
Figure S96. (a) ESI-MS spectrum of H13, (b) HRMS of the peak at m/z = 863.2 (left: experimental; right: simulation) (c) MS² spectrum of H13 upon fragmentation of the peak at m/z = 1107.2
## 5. X-Ray Diffraction Analysis

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The X-ray intensity data were measured on a Bruker D8 Venture X-ray Diffractometer equipped with microfocus μS radiation and Photon100 CMOS detector. The frames were integrated with the
Bruker SAINT software package using a narrow-frame algorithm. The structure was solved and refined using the Bruker SHELXTL Software Package.

**Figure S97.** The complex molecule was shown at 50% probability thermal ellipsoids with the atom numbering scheme (only the major component is shown).
6. References:


