Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting Information

Gold(I) Template Catenane and Rotaxane Synthesis

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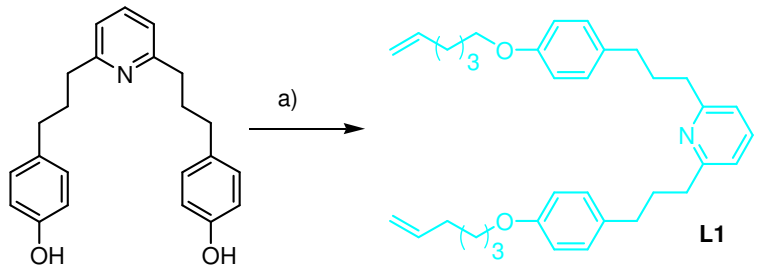
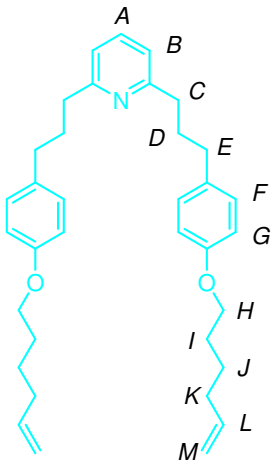
General Experimental Section

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification, tetrahydrofuran, dichloromethane, chloroform, acetonitrile and *N*,*N*-dimethylformamide were dried using a solvent purification system manufactured by Innovative Technology, Newburyport, MA, USA. 2,6-Bis(3-(4-hydroxyphenyl)-propyl)-pyridine and 1-(bis(4-*tert*-butylphenyl) (4-(pent-4-ynyloxy)phenyl)methyl)-4-*tert*-butylbenzene were prepared according to literature procedures.[1] Unless stated otherwise, all reactions were carried out under an atmosphere of nitrogen. Column chromatography was carried out using Silica 60A (particle size 35-70 μm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany) and observed under UV light. By petrol is meant the fraction of petroleum ether boiling between 40 ºC - 60 ºC. All chemical reactions involving gold(I) complexes were carried out in the absence of light whenever possible. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br = broad. Melting points (m.p.) were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. FAB mass spectrometry was carried out by the services at the University of Edinburgh. Accurate mass data were obtained from the EPSRC National Mass Spectrometry Service Centre (Swansea, U.K.).



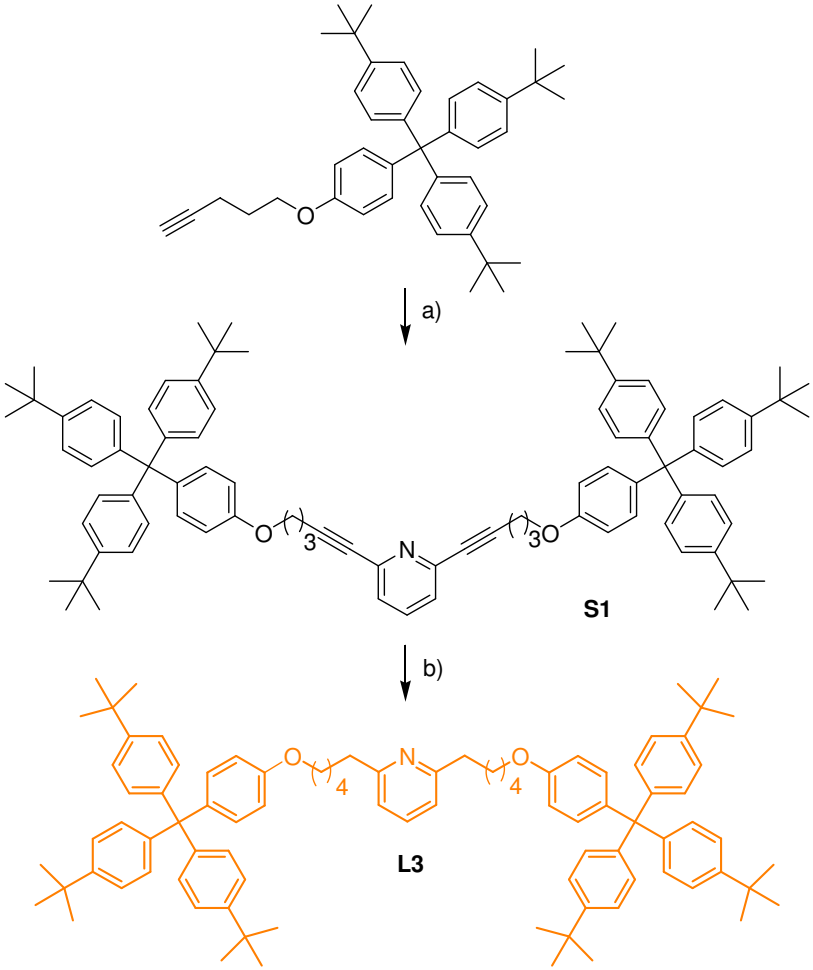
Scheme S1. Synthesis of ligand **L1** from 2,6-bis(3-(4-hydroxyphenyl)-propyl)-pyridine.[1] Reagents and conditions: a) 2,6-bis(3-(4-hydroxyphenyl)-propyl)-pyridine, 6-bromohex-1-ene, K_2CO_3, DMF, 48 h, 80%.



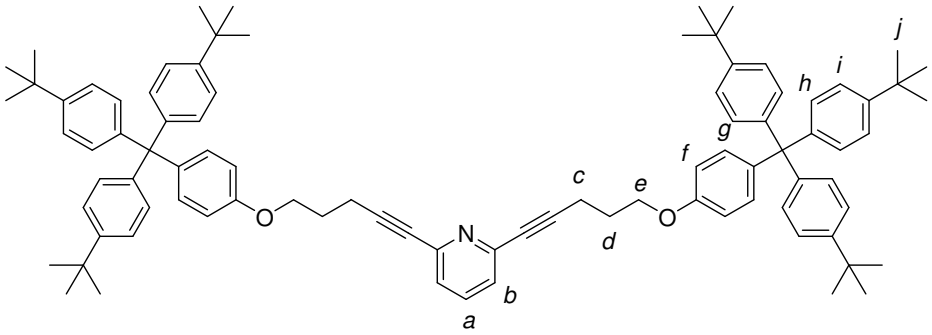
2,6-Bis(3-(4-(hex-5-enyloxy)phenyl)propyl)pyridine - L1

To a solution of 2,6-bis(3-(4-hydroxyphenyl)propyl)pyridine[1] (1.01 g, 2.92 mmol) and 6-bromohex-1-ene (1.20 ml, 8.75 mmol) in DMF (30 ml) was added K_2CO_3 (4.04 g, 29.2 mmol). The suspension was heated at 80 ˚C for 48 h. The reaction mixture was diluted with CH_2Cl_2 (100 ml) and washed with H_2O (50 ml), the organic layer was dried ($MgSO_4$), then purified by column chromatography (CH_2Cl_2: PE 1:1 then CH_2Cl_2) to yield the title compound as a colorless waxy solid (1.19 g, 80%). m.p. 45 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.56 (m, 4H, H_J), 1.79 (m, 4H, H_I), 2.00 (m, 4H, H_D), 2.12 (m, 4H, H_K), 2.61 (m, 4H, H_E), 2.79 (m, 4H, H_C), 3.93 (t, J = 6.5 Hz, 4H, H_H), 5.00 (m, 4H, H_M), 5.83 (m, 2H, H_L), 6.80 (d, J = 8.5 Hz, 4H, H_G), 6.93 (d, J = 7.7 Hz, 2H, H_B),

7.09 (d, J = 8.5 Hz, 4H, H_F), 7.48 (t, J = 7.7 Hz, 1H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.3, 28.8, 32.1, 33.5, 34.7, 38.0, 67.7, 114.3, 114.7, 119.8, 129.3, 134.2, 136.5, 138.6, 157.2, 161.5; LRFAB-MS (3-NOBA matrix): m/z = 512 $[MH]^+$; HRFAB-MS (3-NOBA matrix): m/z = 512.3506 (calcd. $C_{35}H_{46}NO_2$ 512.3523).

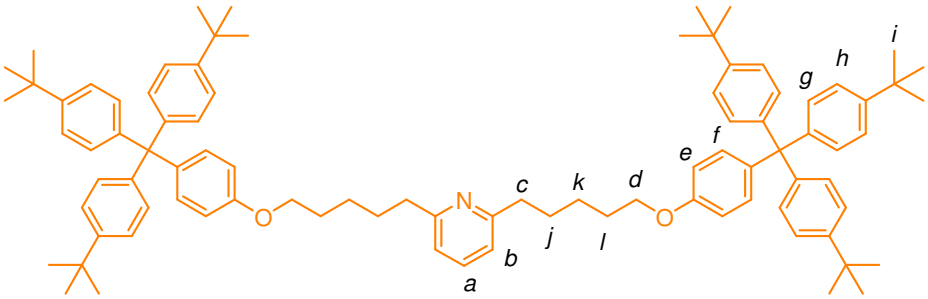


Scheme S2. Synthesis of thread **L3** from 1-(bis(4-*tert*-butylphenyl)(4-(pent-4-ynyloxy)phenyl)methyl)-4-*tert*-butylbenzene.[1] Reagents and conditions: a) 2,6-dibromopyridine, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 85% ; b) Pd/C, THF, EtOH, 18 h, 77%.



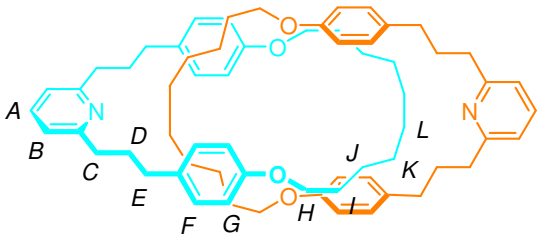
2,6-Bis(5-(4-(tris(4-*tert*-butylphenyl)methyl)phenoxy)pent-1-ynyl)pyridine – S1

To a solution of 1-(bis(4-*tert*-butylphenyl)(4-(pent-4-ynyloxy)phenyl)methyl)-4-*tert*-butylbenzene[1] (2.1 g, 3.7 mmol) and 2,6-dibromopyridine (0.29 g, 1.2 mmol) in THF (15 ml) and Et_3N (15 ml) was added copper(I) iodide (0.046 g, 0.12 mmol) and $PdCl_2(PPh_3)_2$ (0.084 g, 0.12 mmol). The resulting mixture was stirred at RT for 18 h. The solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (100 mL) and washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL) and brine (100 mL). The organic layer was dried ($MgSO_4$), the solvent removed under reduced pressure and the crude residue purified by column chromatography on silica (CH_2Cl_2) to yield the title product as a yellowish solid (1.27 g, 85%). m.p. 159 ˚C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.30 (s, 54H, H_j), 2.08 (m, 4H, H_d), 2.63 (t, J = 7.0 Hz, 4H, H_c), 4.06 (t, J = 6.0 Hz, 4H, H_e), 6.79 (d, J = 8.9 Hz, 4H, H_f), 7.08 (d, J = 8.6 Hz, 16H, H_{g+h}), 7.23 (m, 14H, H_{b+i}), 7.52 (t, J = 7.8 Hz, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 16.2, 28.2, 31.4, 34.3, 63.0, 66.1, 80.5, 90.2, 113.0, 124.0, 125.6, 130.7, 132.2, 136.3, 139.6, 143.8, 144.1, 148.3, 156.6; LRFAB-MS (3-NOBA matrix): *m/z* = 1217 $[MH]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 1216.791 (calcd. $C_{89}H_{102}NO_2$, 1216.791).



Thread – L3

After the addition of 10% w/w Pd/C (0.310 g) to a solution of **S1** (1.55 g, 1.27 mmol) in THF (15 ml), the mixture was repeatedly degassed and purged, first with N_2 and then with H_2, before being stirred for 18 h at rt under a constant atmosphere of H_2. The reaction mixture was then filtered through celite, the solvent removed under reduced pressure and the crude residue purified by column chromatography to yield the title compound as a colorless solid (1.19 g, 77%). m.p. 127 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.32 (s, 54H, H_i), 1.55 (m, 4H, H_k), 1.82 (m, 8H, H_{j+l}), 2.81 (m, 4H, H_c), 3.93 (t, J = 6.4 Hz, 4H, H_d), 6.75 (d, J = 8.9 Hz, 4H, H_e), 6.96 (d, J = 7.7 Hz, 2H, H_b), 7.10 (m, 16H, H_{f+g}), 7.24 (d, J = 8.6 Hz, 12H, H_h), 7.48 (t, J = 7.7 Hz, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.2, 28.8, 29.4, 31.2, 34.1, 39.3, 63.1, 67.7, 113.0, 119.8, 124.0, 130.8, 132.2, 136.5, 139.4, 144.2, 148.2, 156.9, 161.6; LRFAB-MS (3-NOBA matrix): *m/z* = 1225 [M]; HRFAB-MS (3-NOBA matrix): *m/z* = 1224.853 (calcd. $C_{88}{}^{13}CH_{109}NO_2$, 1224.849).

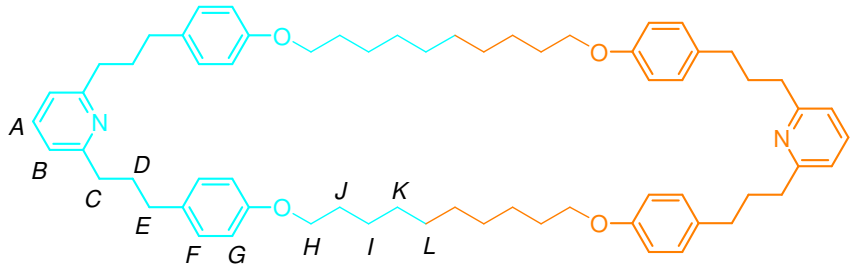


Catenane - L2

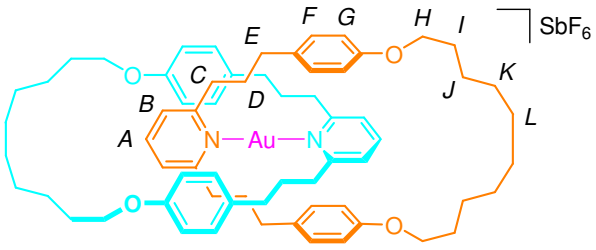
To a solution of **L1** (0.178 g, 0.348 mmol) in acetone (5 ml) was added $AuCl(SMe_2)$ (0.0513 g, 0.174 mmol), the solution was stirred. After 5 min $AgSbF_6$ (0.0598 g, 0.174 mmol) was added and the grey-blue suspension was stirred for a further 5 min before filtration through a pad of celite and removal of the solvent under reduced pressure. The crude residue was redissolved in CH_2Cl_2 (100 ml) and Grubbs' 1st generation olefin metathesis catalyst (0.058 g, 0.070 mmol) was added and the purple solution was stirred for 2 d with a stream of nitrogen bubbled directly through the solution. The solvent was removed under reduced pressure, the crude residue was redissolved in CH_2Cl_2 (10 ml) to which was added 1M HCl(aq) (10 ml) followed by heating at 40 ˚C for 18 h. The reaction mixture was neutralized with saturated aqueous sodium bicarbonate (100 ml) then extracted with CH_2Cl_2 (3 × 100 ml). The combined organic layers were washed with brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was dissolved in THF (5 ml) and EtOH (5 ml) then 10% w/w Pd/C (0.070 g) was added. The reaction vessel was repeatedly degassed and purged with N_2, then repeatedly degassed and purged with H_2 and left to stir for 18 h under an atmosphere of H_2. The reaction mixture was filtered through a pad of celite, concentrated under reduced pressure and then purified by column chromatography (0% to 10% EtOAc in CH_2Cl_2 gradient elution) to yield catenane **L2** (0.069 g, 41%) as a colorless oil which solidified on standing, mono-pyridine macrocycle (0.034 g, 40% w.r.t. **L1**) and bis-pyridine

macrocycle (0.030 g, 18 % w.r.t. **L1**) as a colorless solid. The ^{1}H NMR and ^{13}C NMR spectra of the mono-pyridine macrocycle were consistent with the published data.[1]

L2: m.p. 66 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 0.91 (br, 16H, H_{K+L}), 1.11 (br, 8H, H_J), 1.50 (m, 8H, H_I), 1.78 (m, 8H, H_D), 2.49 (m, 8H, H_E), 2.65 (m, 8H, H_C), 3.71 (t, J = 6.4 Hz, 8H, H_H), 6.61 (d, J = 8.5 Hz, 8H, H_G), 6.86 (d, J = 8.5 Hz, 8H, H_F), 6.92 (d, J = 7.7 Hz, 4H, H_B), 7.47 (t, J = 7.7 Hz, 2H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.6, 28.4, 28.7, 29.6, 32.7, 35.4, 38.4, 67.1, 114.5, 119.6, 129.2, 134.0, 136.4, 157.0, 161.6; LRFAB-MS (3-NOBA matrix): m/z = 486 $[MH_2]^{2+}$; HRFAB-MS (3-NOBA matrix): m/z = 486.3387 (calcd. $C_{66}H_{88}N_2O_4$ 486.3367).

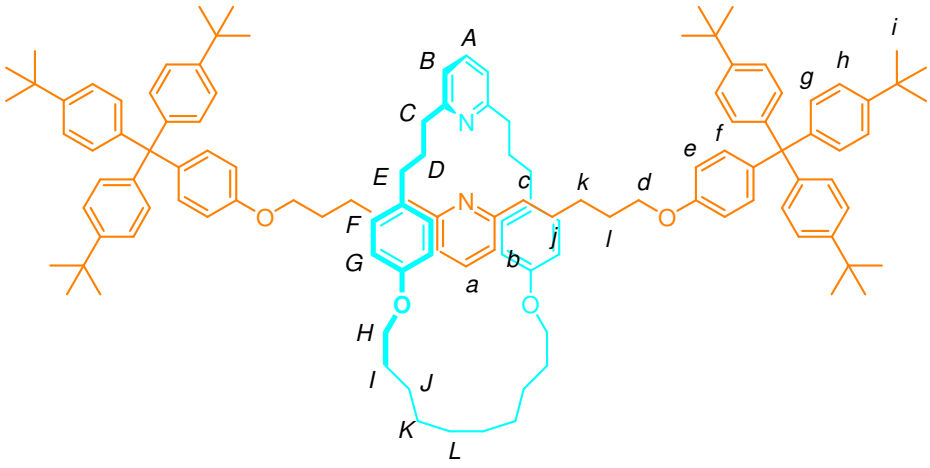


Bis-pyridine macrocycle: m.p. 69 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ =1.33 (br, 16H, H_{K+L}), 1.45 (br, 8H, H_J), 1.76 (m, 8H, H_I), 2.01 (m, 8H, H_D), 2.62 (m, 8H, H_E), 2.79 (m, 8H, H_C), 3.92 (t, J = 6.5 Hz, 8H, H_H), 6.81 (d, J = 8.5 Hz, 8H, H_G), 6.93 (d, J = 7.7 Hz, 4H, H_B), 7.09 (d, J = 8.5 Hz, 8H, H_F), 7.48 (t, J = 7.7 Hz, 2H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 22.6, 25.8, 29.4, 31.6, 32.1, 34.7, 38.0, 68.0, 114.3, 119.8, 129.3, 134.2, 136.4, 157.3, 161.5; LRFAB-MS (3-NOBA matrix): m/z = 486 $[MH_2]^{2+}$; HRFAB-MS (3-NOBA matrix): m/z = 486.3371 (calcd. $C_{66}H_{88}N_2O_4$ 486.3367).



Catenate - [(**L2**)Au]SbF_6

To a solution of **L2** (0.157 g, 0.162 mmol) in acetone (2 ml) was added $AuCl(SMe_2)$ (0.0476 g, 0.162 mmol), the solution was stirred for 5 min to give [(**L2**)AuCl] [from which an aliquot was taken for analysis: ^{1}H NMR (400 MHz, $CDCl_3$, 300K): 1.09 (br, 8H, H_{k+l}), 1.09 (br, 4H, H_j), 1.44 (m, 12 H, H_{i+K+L}), 1.60 (br, 4H, H_J), 1.76 (m 12H, $H_{d+D+ I}$), 2.57 (m, 16H, $H_{c+C+e+E}$), 3.70 (m, 8H, H_{h+H}), 6.27 (br, 4H, H_G), 6.60 (d, J = 8.5 Hz, 4H, H_g), 6.72 (br, 4H, H_F), 6.85 (d, J = 8.5 Hz, 4H, H_f), 6.91 (d, J = 7.7 Hz, 2H, H_b), 7.47 (m, 3H, H_{a+B}), 8.06 (br, 1H, H_A)]. $AgSbF_6$ (0.0557 g, 0.162 mmol) was added and the resulting grey-blue suspension was stirred for 5 min before being filtered through a pad of celite. The solvent was removed under reduced pressure to yield the title compound as a colorless solid (0.225 g, 99%). Single crystals suitable for investigation by X-ray crystallography were grown by vapor diffusion of diisopropyl ether into a solution of [(**L2**)Au]SbF_6 in acetone. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.47 (br, 16H, H_{K+L}), 1.55 (m, 8H, H_J), 1.73 (m, 16H, H_{D+I}), 2.47 (m, 8H, H_C), 2.55 (m, 8H, H_E), 3.69 (t, J = 5.9 Hz, 8H, H_H), 6.21 (d, J = 8.5 Hz, 8H, H_G), 6.67 (d, J = 8.5 Hz, 8H, H_f), 7.42 (d, J = 7.8 Hz, 4H, H_B), 8.04 (t, J = 7.8 Hz, 2H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 26.4, 28.9, 29.0, 29.5, 32.0, 34.2, 39.5, 67.0, 113.5, 123.3, 129.6, 132.3, 141.0, 157.1, 162.6.



Rotaxane - L4

To a solution of **L1** (0.0810 g, 0.158 mmol) in acetone (2 ml) was added $AuCl(SMe_2)$ (0.0467 g, 0.158 mmol), the solution was stirred for 5 min. $AgSbF_6$ (0.0543 g, 0.158 mmol) was added and the grey-blue suspension was stirred for 5 min before filtration through a pad of celite into a receiver flask that contained a solution of **L3** (0.193 g, 0.158 mmol) in acetone (5 ml). The solvent was removed under reduced pressure. The crude residue was redissolved in CH_2Cl_2 (100 ml), Grubbs' 1st generation olefin metathesis catalyst (0.026 g, 0.32 mmol) was added and the purple solution was stirred for 2 d with a stream of nitrogen bubbled directly through the solution. The solvent was removed under reduced pressure, the crude residue was redissolved in CH_2Cl_2 (10 ml) to which was added 1M HCl(aq) (10 ml) followed by heating at 40 ˚C for 18 h. The reaction mixture was neutralized with saturated aqueous sodium bicarbonate (100 ml) then extracted with CH_2Cl_2 (3 × 100 ml). The combined organic layers were washed with brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was redissolved in THF (5 ml) and EtOH (5 ml) then 10% w/w Pd/C (0.055 g) was added. The reaction vessel was repeatedly degassed and purged with N_2, then repeatedly

degassed and purged with H_2 and left to stir for 18 h under an atmosphere of H_2. The reaction mixture was filtered through a pad of celite, concentrated under reduced pressure and then purified by column chromatography (0% to 10% EtOAc in CH_2Cl_2 gradient elution) to yield rotaxane **L4** (0.070 g, 26%) as a colorless solid, and catenane **L2** (0.021 g, 14%) as a colorless solid. Selected analytical data for **L4**: m.p. 100 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.19 (, 12H, H_{k+K+L}), 1.31 (m, 58H, H_{i+J}), 1.42 (m, 4H, H_l), 1.49 (m, 4H, H_j), 1.63 (m, 4H, H_I), 1.80 (m, 4H, H_D), 2.53 (m, 4H, H_E), 2.60 (m, 4H, H_c), 2.68 (m, 4H, H_C), 3.48 (t, J = 6.7 Hz, 4H, H_d), 3.80 (t, J = 6.5 Hz, 4H, H_H), 6.54 (m, 8H, H_{e+G}), 6.79 (d, J = 8.5 Hz, 4H, H_F), 6.84 (m, 4H, H_{b+B}), 6.98 (d, J = 8.9 Hz, 4H, H_f), 7.10 (d, J = 8.6 Hz, 12H, H_g), 7.24 (d, J = 8.6 Hz, 12H, H_h), 7.33 (t, J = 7.7 Hz, 1H, H_A), 7.40 (t, J = 7.6 Hz, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 25.7, 25.8, 28.8, 29.1, 29.6, 29.7, 29.8, 31.4, 32.9, 34.3, 34.3, 35.3, 38.5, 63.0, 67.1, 67.4, 113.0, 114.3, 119.6, 119.6, 124.0, 129.1, 130.7, 132.0, 133.8, 133.9, 136.2, 136.5, 139.0, 144.3, 148.2, 156.8, 156.9, 161.6; LRFAB-MS (3-NOBA matrix): *m/z* = 1710 $[MH]^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 1711.184 (calcd. $C_{120}{}^{13}C_2H_{152}N_2O_4$ 1711.182).

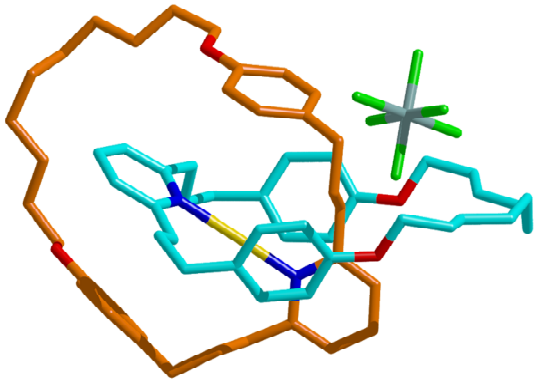


Figure S1. X-ray crystal structure of [(**L2**)Au]SbF_6

Table S1. Crystal data and structure refinement for [(**L2**)Au]SbF_6.

CCDC-680077		
Identification code	[(**L2**)Au]SbF_6	
Empirical formula	$C_{66}H_{86}AuF_6N_2O_4Sb$	
Formula weight	1404.08	
Temperature	93(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.008(2) Å	α= 90°.
	b = 19.798(2) Å	β= 90°.
	c = 36.675(5) Å	γ = 90°.
Volume	12349(3) $Å^3$	
Z	8	
Density (calculated)	1.510 Mg/m^3	
Absorption coefficient	8.418 mm^{-1}	
F(000)	5696	
Crystal size	0.1000 × 0.1000 × 0.0300 mm^3	
Theta range for data collection	2.41 to 68.61°.	
Index ranges	-19≤h≤19, -23≤k≤23, -44≤l≤43	
Reflections collected	159948	
Independent reflections	11303 [R(int) = 0.0996]	
Completeness to theta = 66.50°	99.7%	

Absorption correction	Multiscan
Max. and min. transmission	1.0000 and 0.6555
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11303 / 4 / 722
Goodness-of-fit on F^2	1.213
Final R indices [I>2sigma(I)]	R1 = 0.0794, wR2 = 0.1818
R indices (all data)	R1 = 0.0984, wR2 = 0.1958
Largest diff. peak and hole	0.688 and -1.777 e.Å^{-3}

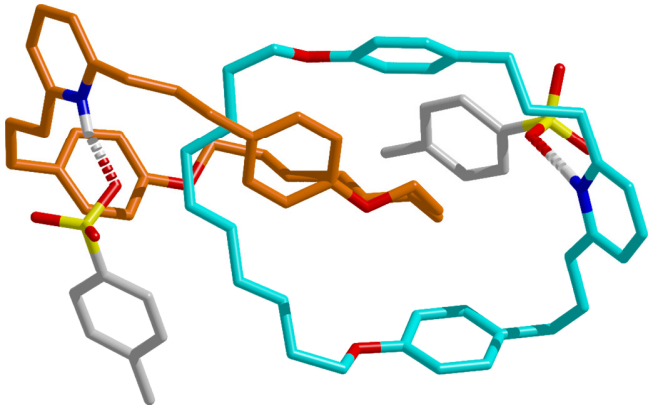


Figure S2. X-ray crystal structure of H_2**L2**$(OTs)_2$

Table S2. Crystal data and structure refinement for H_2**L2**$(OTs)_2$.

CCDC-682689		
Identification code	H_2**L2**$(OTs)_2$	
Empirical formula	$C_{80}H_{106}N_2O_{12}S_2$	
Formula weight	1351.79	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 38.606(5) Å	α= 90°.
	b = 10.9310(13) Å	β= 108.412(8)°.
	c = 19.303(3) Å	γ = 90°.
Volume	7729.0(17) Å^3	
Z	4	

Density (calculated)	1.162 Mg/m^3
Absorption coefficient	0.128 mm^{-1}
F(000)	2912
Crystal size	0.200 × 0.200 × 0.100 mm^3
Theta range for data collection	1.94 to 25.35°.
Index ranges	$-45<h\leq45$, $-13\leq k<13$, $-21\leq l\leq23$
Reflections collected	33273
Independent reflections	6961 [R(int) = 0.1880]
Completeness to theta = 25.00°	98.9%
Absorption correction	Multiscan
Max. and min. transmission	1.0000 and 0.9223
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6961 / 3 / 448
Goodness-of-fit on F^2	1.243
Final R indices [I>2sigma(I)]	R1 = 0.2011, wR2 = 0.3766
R indices (all data)	R1 = 0.2128, wR2 = 0.3831
Extinction coefficient	0.0018(3)
Largest diff. peak and hole	0.586 and -0.533 $e.Å^{-3}$

References:

[1] J. Berna, J. D. Crowley, S. M. Goldup, K. D. Hanni, A. L. Lee, D. A. Leigh, *Angew. Chem. Int. Ed.* **2007**, *46*, 5709-5713.