Supporting Information—Experimental

1,5-Bis-[2-(2-(2-(*p*-toluensulfonylethoxy)ethoxy)ethoxy)naphthalene 2NP
Triethylamine (12.4 ml, 9.44 x 10^{-2} mol) and dimethylaminopyridine (DMAP) (0.58g, 4.72 x 10^{-3} mol) were added to a solution of the naphthalene diol **2** (10 g, 2.36 x 10^{-2} mol) and tosyl chloride (13.5 g, 7.09 x 10^{-2} mol) in CH_2Cl_2 (100 ml) . The reaction was stirred for 24 h and worked up by diluting with CH_2Cl_2 (500 ml) and washing with water (3 x 200 ml). The solvent was removed and the resulting pale yellow oil was purified by column chromatography hexane / diethyl ether (100:0, 90:10,...0:100) to yield a pale yellow oil **3** (15.2 g, 88 %). ^{1}H NMR ($CDCl_3$, 400 MHz) 7.84 (d, *J* = 8 Hz, 2H), 7.75 (d, *J* = 8 Hz, 4H), 7.32 (t, *J* = 8 Hz, 2H), 7.25 (d, *J* = 8 Hz, 4H), 6.81 (d, *J* = 8 Hz, 2H), 4.23 (m, 4H), 4.12 (m, 4H), 3.91 (m, 4H), 3.64-3.70 (m, 8H), 3.58 (m, 4H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 154.3 (s), 144.8 (s), 132.9 (s), 129.8 (d), 127.9 (d), 126.8 (s), 125.2 (d), 114.6 (d), 105.7 (d), 70.9 (t), 70.8 (t), 69.8 (t), 69.4(t), 68.7 (t), 67.9 (t), 21.6 (q). MS (FAB) 732 M^+.

1,5-Bis-[2-(2-(2-((2methylhydroxyphenoxy)ethoxy)ethoxy)ethoxy)naphthalene 3NP
K_2CO_3 (6.5 g, 4.7 x 10^{-2} mol) and 2-hydroxybenzyl alcohol (5.8 g, 4.7 x 10^{-2} mol) were added to a solution of the naphthalene bistosylate **3** (11.5 g, 1.57 x 10^{-2} mol) in acetonitrile (500 ml). The solution was then refluxed for 3 days and the resulting mixture worked up by removal of the acetonitrile, addition of water (500 ml) and extraction with CH_2Cl_2 (3 x 200 ml). The resulting dark brown oil was purified by column chromatography dichloromethane / methanol (100:0, 99:1,..., 80:20) to yield a pale yellow oil **4** (9 g, 90 %). ^{1}H NMR ($CDCl_3$, 200 MHz) 7.85 (d, *J* = 8 Hz, 2H), 7.17-7.34 (m, 6H), 6.78-6.95 (m, 6H), 4.65 (m, 4H), 4.26 (m, 4H), 4.15 (m, 4H), 3.96 (m, 4H), 3.86 (m, 4H), 3.72-3.82 (m, 8H). MS (FAB) 636 M^+.

1,5-Bis-[2-(2-(2-((2-formylphenoxy)ethoxy)ethoxy)ethoxy)naphthalene 4NP
A solution of pyridinium chlorochromate PCC (11 g, 5.1 x 10^{-2} mol) and NaOAc (0.745 g, 9.1 x 10^{-3} mol) in CH_2Cl_2 (81 ml) were added to a solution of the naphthalene bis(benzyl alcohol) **4** (6.5 g, 1 x 10^{-2} mol) in CH_2Cl_2 (100 ml). The reaction was stirred for 15 h and worked up by diluting with CH_2Cl_2 (300 ml) and washing with 2N HCl (3 x 200 ml). The solvent was removed and the resulting pale yellow oil was purified by column chromatography dichloromethane / methanol (100:0, 99:1,..., 80:20) to yield a white solid **5** (4.5 g, 70 %). ^{1}H NMR ($CDCl_3$, 400 MHz) 10.51 (s, 2H), 7.88 (d, *J* = 8 Hz, 2H), 7.79 (d, *J* = 8 Hz, 2H), 7.45 (m, 2H), 7.30 (t, *J* = 8 Hz, 2H), 6.97 (d, *J* = 8 Hz, 2H), 6.88 (d, *J* = 8 Hz, 2H), 6.80 (d, *J* = 8 Hz, 2H), 4.25 (m, 4H), 4.15 (m, 4H), 3.95 (m, 4H), 3.87 (m, 4H), 3.72-3.75 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) 189.8 (d), 161.3 (s), 154.3 (s), 135.9 (d), 128.2 (d), 126.8 (s), 125.1 (d), 125.0 (s), 120.9 (d), 114.6 (d), 112.9 (d), 105.7 (d), 71.1 (t), 71.0 (t), 69.9 (t), 69.6 (t), 68.2 (t), 67.9 (t). MS (FAB) 632.2621 (M^+) ($C_{36}H_{40}O_{10}$ requires 632.2622).

Formation of the 3,5-Di-*t*-Butyl Bis-imine Dumbbell 5NP
3,5-Di-*t*-butylaniline (180 mg, 9.18 x 10^{-4} mol) was added to a solution of naphthalene dialdehyde **5** (290 mg, 4.59 x 10^{-4} mol) in acetonitrile or CH_2Cl_2 (23 ml) containing powdered 4Å molecular sieves (or $MgSO_4$). The reaction was left to stir for 15 h at room

temperature and the resulting solution was filtered and the solvent removed. The remaining residue was dissolve in CH_2Cl_2 / toluene and the solvent removed *in vacuo* and dried on a vacuum line to leave a pale yellow oil **6** (417 mg, 90 %). ^{1}H NMR (CD_3CN, 400 MHz) 8.90 (s, 2H), 8.01 (dd, *J* = 1.7, 8 Hz, 2H), 7.70 (d, *J* = 8 Hz, 2H), 7.39 (td, *J* = 1.7, 8 Hz, 2H), 7.31 (m, 2H), 7.23 (t, *J* = 8 Hz, 2H), 6.99-7.04 (m, 8H), 6.80 (d, *J* = 8 Hz, 2H), 4.36 (s, 4H), 4.28 (m, 4H), 4.18 (m, 4H), 3.98 (m, 4H), 3.92 (m, 4H), 3. 81 (s, 4H), 1.26 (s, 36 H). MS (FAB) 1007 ($M+H^+$)

Formation of the *p*-Methyl Bis-imine Thread 7NP

As before (91 %). ^{1}H NMR ($CDCl_3$, 400 MHz) 8.90 (s, 2H), 8.01 (dd, *J* = 1.7, 8 Hz, 2H), 7.72 (d, *J* = 8 Hz, 2H), 7.42 (td, *J* = 1.7, 8 Hz, 2H), 7.26 (t, *J* = 8 Hz, 2H), 6.99-7.04 (m, 12H), 6.81 (d, *J* = 8 Hz, 2H), 4.14 (s, 8H), 3.82 (m, 8H), 3.66 (m, 8H), 2.25 (s, 6 H). ^{13}C NMR ($CDCl_3$, 50 MHz) 158.8 (s), 155.8 (d), 154.4 (s), 150.4 (s), 135.5 (s), 132.6 (d), 129.7 (d), 127.6 (d), 126.8 (s), 125.2 (s), 125.1 (d), 121.3 (d), 121.0 (d), 114.6 (d), 112.6 (d), 105.7 (d), 71.1 (t), 71.0 (t), 69.9 (t), 69.7 (t), 68.3 (t), 67.9 (t), 21.0 (q). MS (FAB) 811.394405 ($M+H^+$) ($C_{50}H_{55}N_2O_8$ requires 811.395842).

Formation of the 3,5-Di-t-Butyl Bis-amine Dumbbell 6NP

Sodium borohydride (60 mg, 1.58 x 10^{-4} mol) was added to a solution of the diimine **6** (250 mg, 2.49 x 10^{-4} mol) in methanol / CH_2Cl_2 (2 ml : 1 ml). The reaction was allowed to stir for 3 h and worked up by removal of the solvent, addition of water (100 ml) and extraction with CH_2Cl_2. The oil was purified by column chromatography hexane / diethyl ether (100:0, 9:10,...,0:100) to yield a clear oil **7** (0.208 mg, 76 %). ^{1}H NMR ($CDCl_3$, 400 MHz) 7.88 (d, *J* = 8 Hz, 2H), 7.25-7.73 (m, 4H), 7.21 (m, 2H), 6.93 (m, 2H), 6.87 (d, *J* = 8 Hz, 2H), 6.80-6.85 (m, 4H), 6.55 (m, 4H), 4.36 (s, 4H), 4.28 (m, 4H), 4.18 (m, 4H), 3.98 (m, 4H), 3.92 (m, 4H), 3. 81 (s, 4H), 1.26 (s, 36 H). MS (FAB) 1011.6459 ($M+H^+$) ($C_{64}H_{87}N_2O_8$ requires 1011.6462).

Formation of the *p*-Methyl Bis-amine Thread 8NP

As before (66 %). ^{1}H NMR (CD_3CN, 400 MHz) 7.77 (d, *J* = 8 Hz, 2H), 7.30 (t, *J* = 8 Hz, 2H), 7.21 (m, 2H), 7.15 (td, *J* = 1.7, 8 Hz, 2H), 6.82-6.98 (m, 10H), 6.50 (m, 4H), 4.71 (brs, 2H), 4.18-4.23 (m, 8 H), 4.10 (m, 4 H), 3.89 (m, 4 H), 3. 82 (m, 4 H), 3. 71 (m, 8 H), 2.10 (s, 6 H). ^{13}C NMR ($CDCl_3$, 50 MHz) 156.8 (s), 154.4 (s), 146.2 (s), 129.7 (d), 129.3 (d), 128.2 (d), 128.1 (s), 126.9 (d), 124.4 (s), 125.2 (s), 120.8 (d), 114.7 (d), 113.5 (d), 111.7 (d), 105.8 (d), 71.1 (t), 71.0 (t), 69.9 (t), 67.9 (t), 67.8 (t), 44.3 (t), 20.5 (q). MS (FAB) 815.427195 ($M+H^+$) ($C_{50}H_{59}N_2O_8$ requires 815.427142).

1,4-Bis-[2-(2-(2-((2-formylphenoxy)ethoxy)ethoxy)ethoxy)benzene 4BZ

K_2CO_3 (1.7 g, 1.23 x 10^{-2} mol) and 2-hydroxybenzaldehyde (1.5 g, 1.23 x 10^{-2} mol) were added to a solution of 1,5-bis-[2-(2-(2-(*p*-toluenesulfonylethoxy)-ethoxy)ethoxy)benzene (3.76g, 5.51 x 10^{-3} mol) in DMF (100 ml). The solution was then heated at 80 °C for 3 days and the resulting mixture worked up by addition of water (500 ml) and extraction with CH_2Cl_2 (3 x 200 ml). After removal of the organic solvent, the resulting dark brown oil was purified by column chromatography hexane / ethyl acetate (100:0, 95:5,..., 80:20) to yield a pale yellow oil **11** (1.5 g, 46 %). ^{1}H NMR ($CDCl_3$, 200 MHz) 10.42 (s, 2H), 7.70 (dd, *J* = 1.75, 8 Hz, 2H), 7.30 (td, *J* =1.75, 8 Hz, 2H), 6.84-6.93 (m, 4H), 6.73 (s,

4H), 4.11 (m, 4H), 3.95 (m, 4H), 3.78 (m, 4H), 3.70 (m, 4H), 3.63 (s, 8H). ^{13}C NMR ($CDCl_3$, 50 MHz) 189.6 (d), 161.2 (s), 153.0 (s), 135.9 (d), 128.0 (d), 125.0 (s), 120.8 (d), 115.5 (d), 113.0 (d), 70.9 (t), 70.7 (t), 69.8 (t), 69.4 (t), 68.2 (t), 68.0 (t). MS (FAB) 582.2472 (M^+) ($C_{32}H_{38}O_{10}$ requires 582.2465).

Formation of the 3,5-Di-*t*-Butyl Bis-diimine Dumbbell 5BZ

Procedure as described for naphthalene derivative **5NP**.

^{1}H NMR (CD_3CN, 400 MHz) 8.90 (s, 2H), 8.02 (m, 2H), 7.42 (m, 2H), 7.32 (m, 2H), 7.01-7.17 (m, 6H), 6.51 (s, 4H), 4.17 (m, 4H), 3.95 (m, 4H), 3.86 (m, 4H), 3.61 (m, 8H), 3.55 (m, 8H), 1.29 (s, 18H). ^{13}C NMR ($CDCl_3$, 50 MHz) 158.8 (s), 156.1 (d), 153.1 (s), 152.3 (s), 151.7 (s), 132.6 (d), 127.7 (d), 125.3 (s), 121.3 (d), 119.8 (d), 115.6 (d), 115.4 (d), 1125 (d), 71.0 (t), 70.9 (t), 69.9 (t), 69.8 (t), 68.3 (t), 68.0 (t), 35.0 (s), 31.6 (q). MS (FAB) 957 ($M+H^+$)

Dynamic [2]Rotaxane 9NP·$4PF_6$

Powdered 4 Å molecular sieves and 3,5-di-*t*-butylaniline (11.2 mg, 5.4 x 10^{-5} mol) were added to a solution of **4NP** (17.2 mg, 2.7 x 10^{-5} mol) and **CBPQT**·$4PF_6$ (30 mg, 2.7 x 10^{-5} mol) in MeCN (2.73 ml, 10 mM). The reaction mixture was left to stir for 15 h at room temperature and then filtered before removing the solvent to leave a purple solid of **9NP**·$4PF_6$. ^{1}H NMR (CD_3CN, 400 MHz) 8.94 (brs, 4H), 8.77 (s, 2H), 8.46 (brs, 4H), 7.78-7.90 (m, 10H), 7.36 (m, 2H), 6.95-7.25 (m, 14H), 6.89 (t, J = 8 Hz, 2H), 6.76 (d, J = 8 Hz, 2H), 6.16 (d, J = 8 Hz, 2H), 5.86 (t, J = 8 Hz, 2H), 5.50-5.65 (m, 8H), 3.95-4.21 (m, 24H), 2.28 (d, J = 8 Hz, 2H), 1.34 (s, 18H). ES MS 838 $[M - 3PF_6 + 2H]^{2+}$.

Fixed [2]Rotaxane 10NP·$4PF_6$

BH_3·2,6-lutidine (13 mg, 1.1 x 10^{-4} mol) was added to a solution of **9NP**·$4PF_6$ (75mg, 5.6 x 10^{-5} mol) in MeCN (3.6 ml). After stirring at rt for 15h, Et_2O was added to the reaction mixture and the resulting purple solid collected and redissolved in MeCN (3.6 ml). NH_4PF_6/H_2O was then added to the reaction mixture, which was stirred for a further 2 h. On removal of the organic solvent, the resulting solid was filtered, washed (H_2O) and purified by column chromatography on silica gel (MeOH : [MeOH(7)/2M $NH_4Cl_{(aq)}$(2)/$MeNO_2$(1)] {1:1}), resulting in a purple solid of **10NP**·$4PF_6$ (22mg, 40%). ^{1}H NMR (CD_3CN, 400 MHz, 313 K) 8.81 (brs, 8H), 7.96 (brs, 8H), 7.13-7.20 (m , 12H), 6.73-6.78 (m, 8H), 6.43 (m, 4H), 5.93 (d, J = 8 Hz, 2H), 5.66 (d, J = 8 Hz, 2H), 5.66 (brs, 8H), 3.98-4.31 (m, 32H), 2.35 (d, J = 8 Hz, 2H), 1.21 (s, 36H). FAB MS 1820 $[M-2PF_6]^+$.