SUPPORTING INFORMATION

Enhancement of Anion Recognition exhibited by a Halogen Bonding Rotaxane Host System

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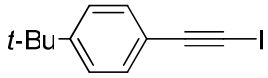
PART I: Synthesis

General Information

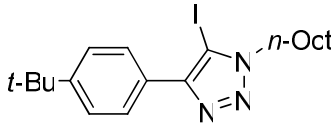
Routine NMR spectra were recorded on a Varian Mercury 300 spectrometer with ^{1}H NMR operating at 300 MHz, ^{13}C (all proton decoupled) at 75.5 MHz, with NMR titrations recorded on a Varian Unity Plus 500 spectrometer with ^{1}H operating at 500 MHz. Mass spectra were recorded on a Bruker micrOTOF spectrometer. Melting points were recorded on a Gallenkamp capillary melting point apparatus and are uncorrected. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was de-ionised and microfiltered using a Milli-Q ® Millipore machine. All tetrabutylammonium salts were stored in a vacuum desiccator over silica prior to use. 1-*n*-Octylazide,[1] tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl] amine (TBTA),[2] macrocycle **3**,[3] and macrocycle precursor **5**[4] were prepared by literature methods. All other solvents and commercial grade reagents were used without further purification.

1-(*tert*-Butyl)-4-(iodoethynyl)benzene



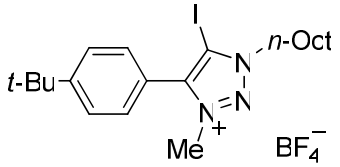
To a solution of 4-*tert*-butylphenylacetylene (351 mg, 2.22 mmol) in acetone (6 mL) were added *N*-iodosuccinimide (1.00 g, 4.44 mmol) and silver nitrate (49.0 mg, 0.29 mmol). The reaction mixture was left to stir for 2 h at RT in the dark under N_2, after which a yellow suspension formed. The suspension was filtered through a silica pad, the pad washed with hexane (5 x 50 mL) and the pale pink filtrate collected. All volatile components were removed in vacuo to give yellow crystals. Yield: 592 mg (94%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.26 (2H, d, Ar*H*, $^{3}J_{HH}$ = 14.5 Hz), 7.07 (2H, d, Ar*H*, $^{3}J_{HH}$ = 14.5 Hz), 1.28 (9H, s, –C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 152.3, 132.8, 125.9, 121.5, 95.1, 35.0, 31.4, 6.8; HRMS (EI) *m/z* calc. for $[M]^+$ 284.0062, found 284.0058; mp 88 °C.

4-(4-(*tert*-Butyl)phenyl)-5-iodo-1-*n*-octyl-1*H*-1,2,3-triazole – 1



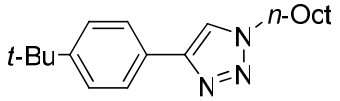
The 5-iodo-1,2,3-triazole **1** was prepared by a modified literature procedure.[5] Copper iodide (10.26 mg, 0.054 mmol) and TBTA (28.36 mg, 0.054 mmol) were stirred in dry THF (1 mL) at RT for 20 min. The catalyst solution was added to a solution of 1-(*tert*-butyl)-4-(iodoethynyl)benzene (303.8 mg, 1.069 mmol) and 1-*n*-octylazide (165.9 mg, 1.07 mmol) in dry THF (10 mL). The reaction mixture was left to stir overnight, quenched with 10 % ammonium hydroxide solution (2 mL) and the THF removed in vacuo. Water (20 mL) was added and the aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated to dryness on a rotary evaporator to give a yellow solid. The crude product was purified by silica gel column chromatography (eluent 10 % methanol in dichloromethane) giving a colorless crystalline solid. Yield: 101 mg (87 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (2H, d, Ar*H*, $^3J_{HH}$ = 8.10 Hz), 7.48 (2H, d, Ar*H*, $^3J_{HH}$ = 8.22 Hz), 4.42 (2H, t, –NCH_2, $^3J_{HH}$ = 7.35 Hz), 1.94 (2H, m, –NCH$_2$CH_2), 1.36–1.28 (20H, m, –CH_2–, –C(CH_3)$_3$), 0.88 (3H, t, –CH$_2$CH_3, $^3J_{HH}$ = 6.54 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.5, 129.0, 127.4, 127.1, 125.4, 110.0, 75.7, 31.7, 31.3, 29.9, 29.1, 29.0, 28.9, 26.4, 22.6, 14.1; HRMS (ESI): *m/z* calc. for $[M + Na]^+$ 462.1377, found 462.1370; mp 55–58 °C.

4-(4-(*tert*-Butyl)phenyl)-5-iodo-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate – 2.BF$_4$



A solution of 4-(4-(*tert*-butyl)phenyl)-5-iodo-1-*n*-octyl-1*H*-1,2,3-triazole **1** (101.0 mg, 0.230 mmol) in dry dichloromethane (15 mL) was treated with trimethyloxonium tetrafluoroborate (68.0 mg, 0.400 mmol) and the reaction mixture left to stir under N_2 for 48 h at RT. Methanol (2 mL) was added and all volatile components were removed in vacuo to give a yellow oil, which was purified by silica gel column chromatography (eluent 2 % methanol in dichloromethane) to give an off-white solid. Yield: 117 mg (94 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (2H, d, Ar*H*, $^3J_{HH}$ = 8.58 Hz), 7.50 (2H, d, Ar*H*, $^3J_{HH}$ = 8.58 Hz), 4.56 (2H, t, –NCH_2CH$_2$–, $^3J_{HH}$ = 7.77 Hz), 4.19 (3H, s, –NCH_3), 1.65–1.27 (20H, –CH_2–, –C(CH_3)$_3$), 0.87 (3H, t, –CH$_2$CH_3, $^3J_{HH}$ = 6.96 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.6, 147.2, 129.8, 126.7, 119.2, 86.9, 55.2, 39.1, 35.1, 31.7, 31.1, 29.0, 28.8, 28.6, 26.3, 22.6, 14.1; HRMS (ESI): *m/z* calc. for $[M – BF_4]^+$ 454.1714, found 454.1705; mp 123–124°C.

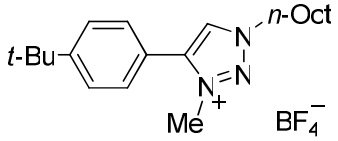
4-(4-(*tert*-Butyl)phenyl)-1-*n*-octyl-1*H*-1,2,3-triazole



Tetrakisacetonitrilecopper(I) hexafluorophosphate (80 mg 0.214 mmol) and TBTA (114 mg, 0.214 mmol) were dissolved in dry dichloromethane (5 mL) and added to a solution of 4-*tert*-butylphenylacetylene (194 µL, 170 mg, 1.07 mmol) and 1-*n*-octylazide (166 mg, 1.07 mmol) in dry dichloromethane (25 mL). *N*,*N*-Diisopropylethylamine (0.192 mL, 142 mg, 1.10 mmol) was added and the reaction left to stir in the dark for 48h at RT. Volatile components were removed in vacuo and the resulting solid purified by silica gel column chromatography (eluent 5 % dichloromethane in methanol) to give a pale yellow solid (292 mg, 87 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (^{1}H, s, –NC*H*), 7.42 (2H, d, Ar*H*, $^3J_{HH}$ = 8.49 Hz), 7.43

(2H, d, Ar*H*, $^3J_{HH}$ = 8.46 Hz), 4.36 (2H, t, –NC*H*$_2$, $^3J_{HH}$ = 7.23 Hz), 1.92 (2H, m, –NCH$_2$C*H*$_2$), 1.35–1.24 (22H, m, –C*H*$_2$–, –C(C*H*$_3$)$_3$), 0.85 (3H, t, –CH$_2$C*H*$_3$, $^3J_{HH}$ = 6.42 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.5, 129.4, 128.2, 126.1, 125.7, 119.4, 50.7, 35.0, 32.0, 31.6, 30.7, 29.4, 29.3, 26.8, 22.9, 14.4; HRMS (ESI): *m/z* calc. for $[M + H]^+$ 314.2591, found 314.2593; mp 50–54°C

4-(4-(*tert*-Butyl)phenyl)-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate – 4.BF$_4$



A solution of 4-(4-(*tert*-butyl)phenyl)-1-*n*-octyl-1*H*-1,2,3-triazole (350 mg, 1.12 mmol) in dry dichloromethane was treated with trimethyloxonium tetrafluoroborate (333 mg, 2.25 mmol) and left to stir under N_2 for 48 h at RT. Methanol (10 mL) was added and the mixture concentrated to dryness on a rotary evaporator to give a white solid, which was purified by silica gel column chromatography (eluent 5% methanol in dichloromethane) to give a white solid (372 mg, 80 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (1H, s, –NC*H*), 7.56 (2H, d, Ar*H*, $^3J_{HH}$ = 8.79 Hz), 7.54 (2H, d, Ar*H*, $^3J_{HH}$ = 8.82 Hz), 4.57 (2H, t, –NC*H*$_2$, $^3J_{HH}$ = 7.50 Hz), 4.23 (3H, s, –NC*H*$_3$), 2.00 (2H, m, –NCH$_2$C*H*$_3$), 1.40 – 1.24 (21H, m, –C*H*$_2$–, –C(C*H*$_3$)$_3$), 0.85 (3H, t, –CH$_2$C*H*$_3$, $^3J_{HH}$ = 6.27); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.8, 143.7, 129.3, 128.7, 127.0, 119.1, 54.5, 38.6, 35.3, 31.9, 31.3, 29.4, 29.2, 29.0, 26.4, 22.8, 14.3; HRMS (ESI): *m/z* calc. for $[M – BF_4]^+$ 328.2747, found 328.2752; mp 112–113°C.

Anion Exchange General Procedure

A solution of **2**.BF$_4$ or **4**.BF$_4$ (0.06 mmol) in dichloromethane (1.0 mL) was vigorously extracted with a 1M aqueous solution of the ammonium halide salt (5 x 2.0 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated in vacuo to give the product as a colorless solid in quantitative yield.

4-(4-(*tert*-Butyl)phenyl)-5-iodo-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium chloride – 2.Cl

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (4H, s, Ar*H*), 4.42 (2H, t, –NC*H*$_2$–, $^3J_{HH}$ = 7.82 Hz), 4.24 (3H, s, –NC*H*$_3$), 1.93 (2H, m, –NCH$_2$C*H*$_2$), 1.43–1.24 (19H, br m, –C*H*$_2$–, –C(C*H*$_3$)$_3$), 0.89 (3H, t, –CH$_2$C*H*$_3$, $^3J_{HH}$ = 6.30 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.4, 146.5, 130.2, 126.8, 120.0, 99.8, 54.7, 39.2, 35.3, 31.9, 31.3, 29.2 (two superimposed), 29.1, 26.8, 23.2, 14.7; LRMS (ESI) $[M – Cl]^+$ *m/z* = 454.15.

4-(4-(*tert*-Butyl)phenyl)-5-iodo-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium bromide – 2.Br

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (2H, d, Ar*H*, $^3J_{HH}$ = 8.70 Hz), 7.61 (2H, d, Ar*H*, $^3J_{HH}$ = 9.00 Hz), 4.32 (2H, t, –NC*H*$_2$, $^3J_{HH}$ = 6.90 Hz), 4.28 (3H, s, –NC*H*$_3$), 1.86 (2H, m, –NCH$_2$C*H*$_2$), 1.40 (9H, s, –C(C*H*$_3$)$_3$) 1.37–1.25 (10H, br m, –C*H*$_2$–), 0.90 (3H, t, –CH$_2$C*H*$_3$, $^3J_{HH}$ = 6.30 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.2, 145.8, 130.1, 126.6, 119.9, 103.5, 54.3, 39.3, 35.1, 31.7, 31.1, 29.0 (two superimposed), 28.8, 26.1, 22.6, 14.1; LRMS (ESI) $[M – Br]^+$ *m/z* = 454.18.

4-(4-(*tert*-Butyl)phenyl)-5-iodo-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium iodide – 2.I

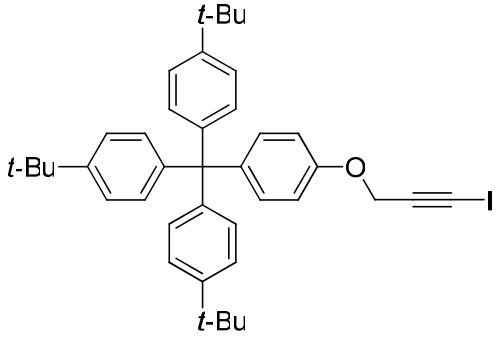
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (2H, d, Ar*H*, $^3J_{HH}$ = 8.10 Hz), 7.61 (2H, d, Ar*H*, $^3J_{HH}$ = 9.00 Hz), 4.35 (2H, t, –NCH_2, $^3J_{HH}$ = 7.50 Hz), 4.25 (3H, s, –NCH_3), 1.89 (2H, m, –NCH$_2$CH_2), 1.40 (9H, s, –C(CH_3)$_3$) 1.39–1.25 (12H, br m, –CH_2–), 0.90 (3H, t, –CH$_2$CH_3, $^3J_{HH}$ = 6.60 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.2, 145.5, 130.2, 126.6, 119.8, 104.4, 54.4, 39.6, 35.1, 31.7, 31.1, 29.0, 28.9, 28.8, 26.2 ,22.6, 14.1; LRMS (ESI) [M – I]$^+$ *m/z* = 454.12.

4-(4-(*tert*-Butyl)phenyl)-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium chloride – 4.Cl
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.65 (1H, s, –NC*H*), 7.60-7.53 (4H, m, Ar*H*), 4.72 (2H, t, $^3J_{HH}$ = 7.41 Hz, –NCH_2), 4.26 (3H, s, –NCH_3), 2.02 (2H, m, –NCH$_2$CH_2), 1.31–1.22 (19H, m, –CH_2–, C(CH_3)$_3$), 0.84 (3H, t, $^3J_{HH}$ = 6.51 Hz, –CH$_2$CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm) 155.7, 143.3, 129.9, 129.3, 127.0, 119.1, 54.5, 38.8, 35.3, 31.9, 31.2, 29.7, 29.2, 29.0, 26.4, 22.8, 14.3; LRMS (ESI) [M – Cl$^-$]$^+$ *m/z* = 328.24

4-(4-(*tert*-Butyl)phenyl)-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium bromide – 4.Br
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (1H, s, –NC*H*), 7.62 (2H, d, Ar*H*, $^3J_{HH}$ = 8.55 Hz), 7.56 (2H, d, Ar*H*, $^3J_{HH}$ = 8.52 Hz), 4.81 (2H, t, –NCH_2, $^3J_{HH}$ = 7.44 Hz), 4.30 (3H, s, –NCH_3), 2.04 (2H, m, –NCH$_2$CH_2), 1.32 – 1.21 (19H, m, –CH_2–, –C(CH_3)$_3$), 0.84 (3H, t, –CH$_2$CH_3, $^3J_{HH}$ = 6.84 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.9, 143.2, 130.4, 129.4, 127.0, 119.0, 54.6, 39.0, 35.3, 31.9, 31.2, 29.8, 29.2, 29.1, 26.4, 22.8, 14.3; LRMS (ESI) [M – Br]$^+$ *m/z* = 328.30.

4-(4-(*tert*-Butyl)phenyl)-3-methyl-1-*n*-octyl-1*H*-1,2,3-triazol-3-ium iodide – 4.I
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.50 (1H, s, –NC*H*), 7.65 (2H, d, $^3J_{HH}$ = 8.64 Hz, Ar*H*), 7.55 (2H, d, $^3J_{HH}$ = 8.61 Hz, Ar*H*), 4.76 (2H, t, $^3J_{HH}$ = 7.47, –NCH_2), 4.30 (3H, s, –NCH_3), 2.06 (2H, m, –NCH$_2$CH_2), 1.33–1.22 (19H, m, , –CH_2–, C(CH_3)$_3$), 0.83 (3H, t, $^3J_{HH}$ = 6.99 Hz, –CH$_2$CH_3); ^{13}C{^{1}H} (75 MHz,, $CDCl_3$) δ (ppm) 155.9, 143.3, 129.7, 129.5, 127.0, 118.9, 54.7, 39.3, 35.3, 31.8, 31.2, 29.7, 29.1, 29.0, 26.4, 22.7, 14.2; LRMS (ESI) [M – I]$^+$ *m/z* = 328.24.

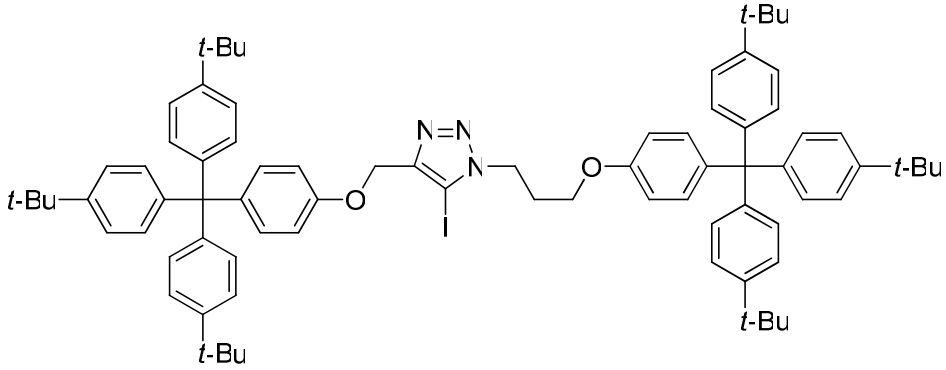
3-(4-(Tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)-1-iodoprop-1-yne)



A solution of 3-(4-(tris(4-(tert-butyl)phenyl)methyl)phenoxy)-prop-1-yne[6] (200 mg, 0.368 mmol) in dry THF was treated with *N*-iodomorpholine (251 mg, 0.736 mmol) and copper(I) iodide (7.00 mg, 0.0368 mmol) and left to stir overnight. The reaction mixture was poured onto a silica pad and washed through with a solution of 5% benzene in cyclohexane (200 mL). The solution was concentrated to dryness on a rotary evaporator to give a white solid (230 mg, 93%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (6H, d, Ar*H*, $^3J_{HH}$ = 8.64 Hz), 7.10–7.04 (8H, m, Ar*H*), 6.80 (2H, d, Ar*H*, $^3J_{HH}$ =

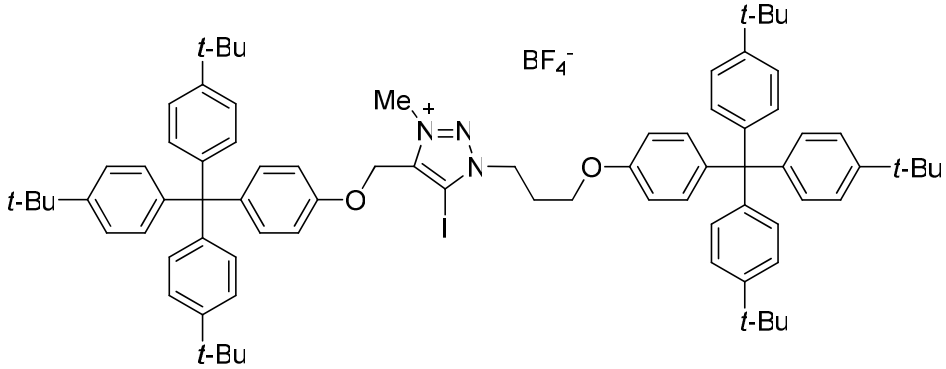
8.97), 4.78 (2H, s, –OCH_2–), 1.28 (27H, s, –C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.7, 148.6, 144.2, 140.8, 132.5, 130.9, 124.3, 113.5, 89.6, 63.3, 57.6, 34.5, 31.6; HRMS (ESI): *m/z* calc. for [M + Na]$^+$ 691.2407, found 691.2387.

5-Iodo-4-((4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)methyl)-1-(3-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)propyl)-1*H*-1,2,3-triazole



Copper iodide (3.0 mg, 0.0155 mmol) and TBTA (8.0 mg, 0.0155 mmol) were stirred in dry THF (1 mL) at RT for 20 min. The catalyst solution was added to a solution of 3-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)-1-iodoprop-1-yne) (200 mg, 0.299 mmol) and ((4-(tris(4-(tert-butyl)phenyl)methyl)phenoxy)propyl)azide[7] (175 mg, 0.299 mmol) in dry THF (10 mL). The reaction mixture was left to stir overnight, quenched with 10 % ammonium hydroxide solution (2 mL) and volatile components removed in vacuo. Water (20 mL) was added and the aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated to dryness on a rotary evaporator to give a pale yellow solid. The crude product was purified by silica gel column chromatography (eluent 2 % methanol in dichloromethane) giving a pale yellow microcrystalline solid. Yield: 230 mg (61 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (12H, d, Ar*H*, $^3J_{HH}$ = 8.55 Hz), 7.10 – 7.04 (16H, m, Ar*H*), 6.87 (2H, d, Ar*H*, $^3J_{HH}$ = 8.91 Hz), 6.73 (2H, d, Ar*H*, $^3J_{HH}$ = 8.88 Hz), 5.06 (2H, s, –OCH_2–), 4.48 (2H, t, –NCH_2–, $^3J_{HH}$ = 7.08 Hz), 3.98 (2H, t, –OCH_2CH$_2$–, $^3J_{HH}$ = 5.73), 2.38 (2H, m, –OCH$_2$CH_2CH$_2$N–), 1.28 (54H, s, –C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.4, 156.3, 148.5, 147.6, 144.3, 140.5, 140.3, 132.5, 132.4, 131.0, 130.9, 124.3, 113.9, 113.3, 81.0, 64.1, 63.3, 63.2, 61.9, 48.1, 34.5, 31.6, 29.9; HRMS (ESI): *m/z* calc. for [M + Na]$^+$ 1278.6283, found 1278.6297;

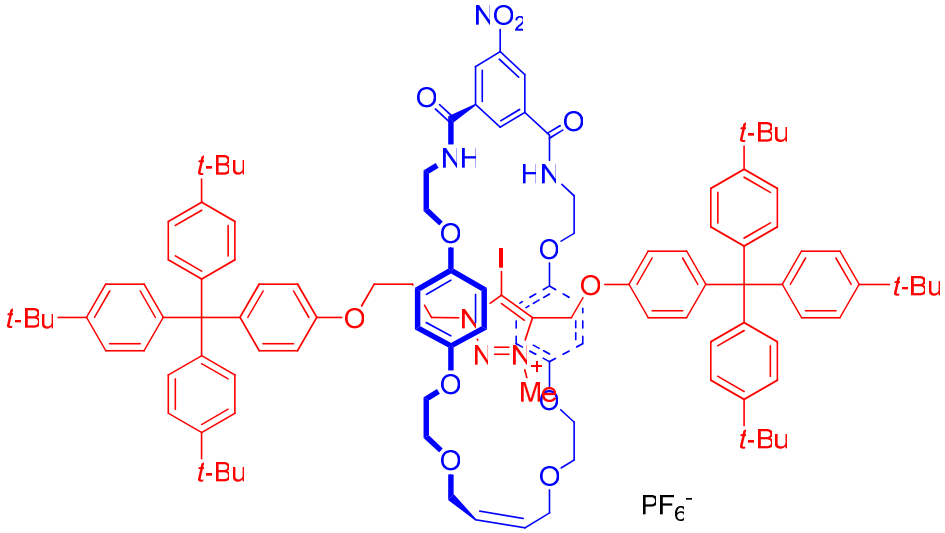
5-iodotriazolium axle – 6.BF_4



A solution of 5-iodo-4-((4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)methyl)-1-(3-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)propyl)-1*H*-1,2,3-triazole (100 mg, 0.0796 mmol) in dry dichloromethane (15 mL) was treated with trimethyloxonium

tetrafluoroborate (30.0 mg, 0.203 mmol) and the reaction mixture left to stir under N_2 for 48 h at RT. Methanol (2 mL) was added and all volatile components were removed in vacuo to give a yellow oil, which was purified by silica gel column chromatography (eluent 2 % methanol in dichloromethane) to give an off-white solid (104 mg, 96 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 7.30–7.24 (12H, m, Ar*H*), 7.08–6.92 (18H, m, Ar*H*), 6.68 (2H, d, Ar*H*, $^3J_{HH}$ = 8.91 Hz), 5.31 (2H, s, –OCH_2N–), 4.80 (2H, t, –NCH_2CH$_2$–, $^3J_{HH}$ = 6.21 Hz), 4.25 (3H, s, –NCH_3), 4.08 (2H, t, –OCH_2CH$_2$–, $^3J_{HH}$ = 5.28 Hz), 2.39 (2H, m, –NCH$_2$CH_2CH$_2$O–), 1.25–1.23 (54H, s, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ (ppm) 155.5, 154.8, 147.9, 147.8, 143.9, 143.8, 140.9, 139.3, 138.2, 131.7, 131.5, 130.0, 124.5, 124.4, 119.5,113.9, 113.2, 73.9, 62.7, 62.6, 55.0, 34.1, 34.0, 31.2; HRMS (ESI): *m/z* calc. for [M – BF_4]$^+$ 1270.6620, found 1270.6593.

5-iodotriazolium rotaxane – 7.PF_6



A solution of **6**.BF_4 (50 mg, 0.0398 mmol) in dichloromethane (1.0 mL) was repeatedly washed with a 2M aqueous solution of ammonium bromide (10 x 2.0 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo* to give **6**.Br, which was dissolved in dry dichloromethane (15 mL). The bis-vinyl macrocycle precursor **5** (25 mg, 0.0370 mmol) was added and the solution left to stir for 15 minutes under N_2 before addition of Grubbs' 2nd generation catalyst (10% by weight, 2.5 mg). The reaction mixture left to stir for 48h under N_2. After this time volatile components were removed *in vacuo* and the crude product purified by preparative TLC (eluent 5% methanol in dichloromethane) to give an off-white solid (10.9 mg, 15%); ^{1}H NMR (500 MHz, $CDCl_3$); δ (ppm) 8.91 (2H, s, Ar*H*), 8.80 (1H, s, Ar*H*), 7.34–7.26 (14H, m, Ar*H*), 7.17–7.11 (14H, m, Ar*H*), 6.84 (2H, d, Ar*H*, $^3J_{HH}$ = 5.04 Hz), 6.66 (2H, d, Ar*H*, $^3J_{HH}$ = 5.07 Hz), 6.54 (2H, d, Ar*H*, $^3J_{HH}$ = 5.16 Hz), 6.43 (2H, d, Ar*H*, $^3J_{HH}$ = 5.16 Hz), 5.50 (2H, m, –C*H*C*H*–), 4.78 (2H, s, –OCH_2N–), 4.15 (3H, s, –NCH_3), 4.10 (2H, t, –OCH_2CH$_2$CH$_2$N–, $^3J_{HH}$ = 4.32 Hz), 4.01 (2H, t, –OCH$_2$CH$_2$CH_2N–, $^3J_{HH}$ = 4.14 Hz), 3.94–3.66 (20H, m, –OCH_2CH_2O–), 1.86 (2H, m, –OCH$_2$CH_2CH$_2$N–), 1.30–1.29 (54H, d, –C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 164.7, 155.7, 154.7, 152.7, 152.2, 150.0, 148.5, 148.3, 144.0, 143.8, 142.2, 136.3, 132.6, 132.3, 130.7, 130.6, 130.5, 129.8, 124.2, 124.1, 114.9, 114.6, 113.2, 113.0, 34.3, 34.2, 31.4, 29.7, 29.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -72.8 (d, *J* = 704.0^{19}F NMR (470 MHz, d^6-acetone) δ (ppm) -73.0 (d, *J* = 707.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) -143.2 (septet, *J* = 702.9 Hz); ^{31}P NMR (202 MHz,

$CDCl_3$) δ (ppm) -144.6 (septet, J = 703.7 Hz) HRMS (ESI): *m/z* calc. for $[M - Br]^-$ 1892.8975, found 1892.8968.

PART II: Crystallography

General information

Single crystal X-ray diffraction data for **2**.Cl, **2**.Br and **2**.I were collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N_2 open-flow cooling device,[8] and the data were collected at 150(2) K. Series of ω-scans were performed to a maximum resolution of 0.77 Å. Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package.[9]

Twinning of the crystal was observed in **2**.I, and analysis with ROTAX[10] in CRYSTALS[11] indicated that the two components were related by a rotation of 180/% about the direct *a* axis. Optimisation of the overlap tolerance and full-matrix refinement gave scale factors of 0.699(2) and 0.301(2).

Data for **7**.Br were collected on Beamline I19 (EH1) at the Diamond Light Source, Didcot, Oxfordshire, where raw frame data were processed (including unit cell refinement, multiscan absorption correction and inter-frame scaling) using CrystalClear.[12] Unfortunately, several attempts demonstrated that the crystals suffered severe radiation damage so data were collected with a single φ scan and scaled accordingly. This strategy meant there was a severe shortage of data, so although the structure solved, it failed to refine. Thus, copious restraints were necessary to try to ensure that the refinement remained stable and maintained sensible geometric and thermal parameters.

The structures were solved by direct methods using SIR92,[13] Superflip,[14] or SHELXS[15] and refined using full-matrix least-squares on F or F^2 within the CRYSTALS suite.[11] Non-hydrogen atoms were refined with anisotropic displacement parameters. Molecular graphics were produced with CrystalMaker. Further details available in the CIF.

Table 1 Crystallographic Data and Experimental Parameters for the X-ray Structural Analysis

	2.Cl	**2**.Br	**2**.I	**7**
Formula	$C_{21}H_{33}ClIN_3$	$C_{21}H_{33}BrIN_3$	$C_{21}H_{33}I_2N_3$	$C_{113}H_{132}BrIN_6O_{12}$
Formula weight	489.87	534.32	581.32	1973.13
Crystal habit, color	Plate, colorless	Plate, colorless	Plate, colorless	Needle, colorless
Crystal size, mm	0.37 x 0.14 x 0.02	0.17 x 0.16 x 0.04	0.39 x 0.24 x 0.02	0.01 x 0.01 x 0.06
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/a$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	14.0380(17)	32.4278(12)	11.1796(4)	14.684(4)
b, Å	10.9503(17)	11.0563(5)	14.7396(5)	14.875(3)
c, Å	15.929(3)	14.1912(5)	15.5956(6)	30.286(10)
α, °			81.4488(12)	76.35(5)
β, °	101.329(11)	109.461(2)	80.4591(12)	77.67(5)
γ, °			89.9085(16)	62.34(4)

Volume, Å^3	2400.8(6)	4797.3(3)	2505.47(16)	5652(4)
Z	4	8	4	2
D_{calcd}, g cm^{-3}	1.355	1.480	1.541	1.159
μ, mm^{-1}	1.45	3.01	2.52	0.694
GoF	1.12	1.03	1.06	1.0063
Independent reflns	4613 (R_{int} = 0.071)	5328 (R_{int} = 0.046)	11419 (R_{int} = 0.072)	7298 (R_{int} = 0.181)
Obs. reflns ($I > 2.0\sigma(I)$)	2328	4303	8147	7749
θ range, °	2.85–26.34	3.31–27.42	5.09–27.80°	1.35-20.09
Temperature, K	150	150	150	120
Final R, wR ($I > 2.0\sigma(I)$)	0.1482, 0.1734	0.0370, 0.0425	0.0720, 0.0805	0.1501, 0.3494
R, wR (all data)	0.1773, 0.2109	0.0525, 0.0540	0.1062, 0.1090	0.2130, 0.4124
Largest diff. peak and hole, e Å^{-3}	5.97, –1.29	0.98, –1.12	2.19, –1.68	0.83, –0.63

Figure S1: X-ray structure of **2**.Cl. Ellipsoids are shown at 50%. Hydrogen Atoms have been removed for clarity. Halogen bonding interactions: I(15)–Cl(16) 2.950(6) Å (r_{obs}/r_{vdW}[16] = 0.79); C(13)–I(15)–Cl(16) 176.9(5)°.

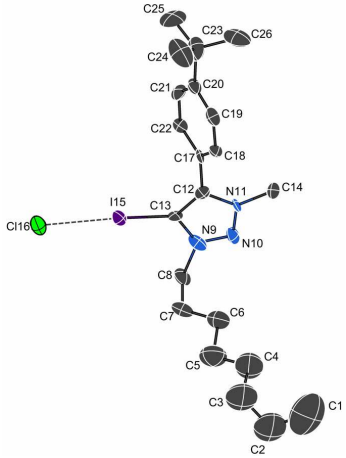


Figure S2: X-ray structure of **2**.Br. Ellipsoids are shown at 50%. Hydrogen Atoms have been removed for clarity. Halogen bonding interactions: I(15)–Br(16) 3.0927(4) Å (r_{obs}/r_{vdW}[16] = 0.81); C(13)–I(15)–Br(16) 177.74(9)°.

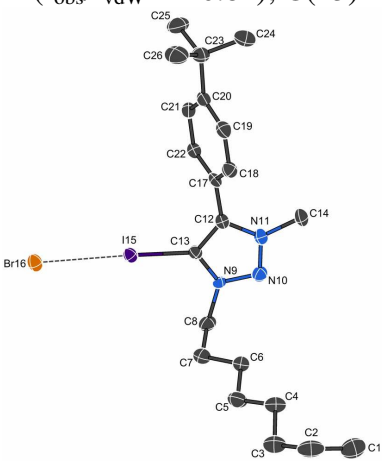


Figure S3: X-ray structure of **2**.I. Ellipsoids are shown at 50%. Hydrogen atoms have been removed for clarity. Halogen bonding interactions: I(115)–Br(116) 3.2833(8) Å (r_{obs}/r_{vdW}[16] = 0.83); I(215)–Br(216) 3. 2818(8) Å (r_{obs}/r_{vdW}[16] = 0.83); C(113)–I(115)–Br(116) 179.2(2)°; C(213)–I(215)–Br(216) 179.1(2)°.

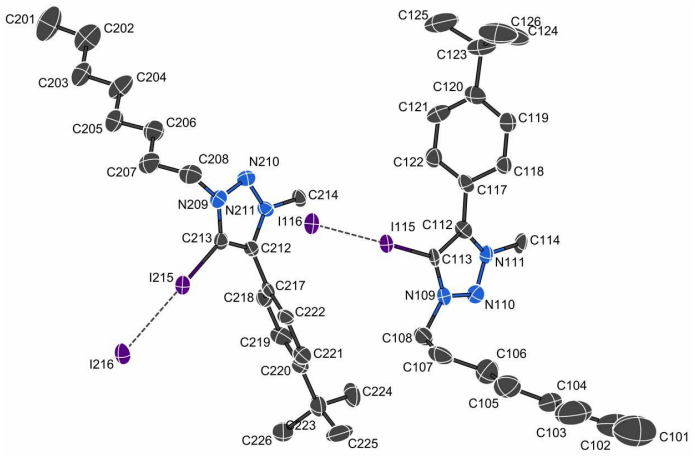
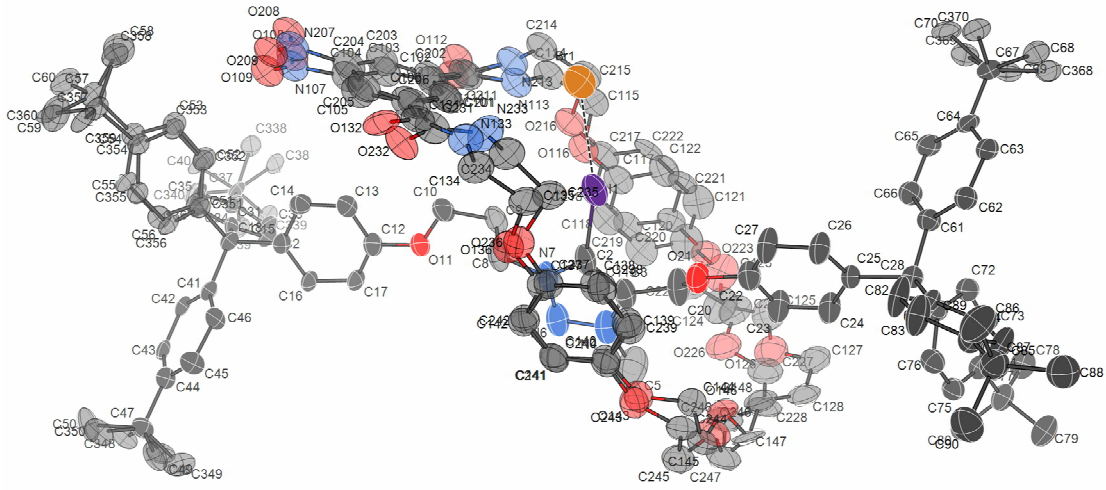


Figure S4: X-ray structure of **7**.Br. Ellipsoids are shown at 20%. Hydrogen atoms have been removed for clarity. Halogen bonding interactions: I(1)–Br(1) 3.127(4) Å (r_{obs}/r_{vdW}[16] = 0.81); C(2)–I(1)–Br(1) 165.07(15)°.

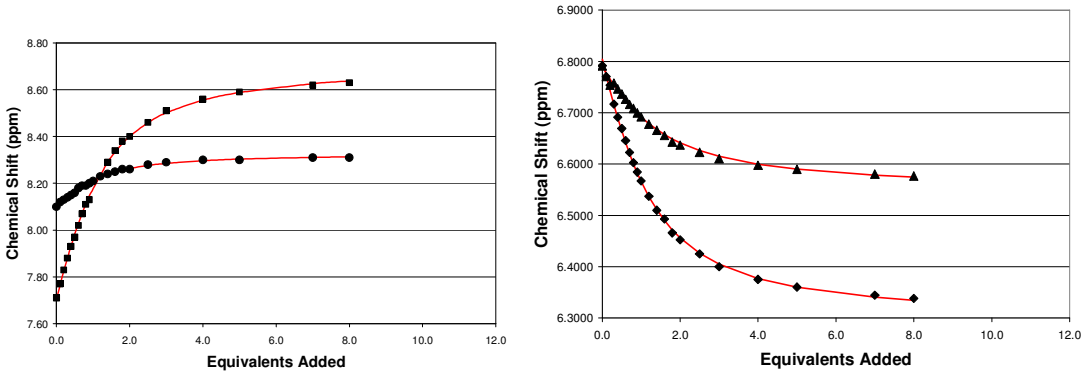


PART III: NMR threading studies

^{1}H NMR titrations were conducted in $CDCl_3$ at 293 K. To 0.5 mL of a 2 x 10^{-3} M solution of the macrocycle were added aliquots of the guests such that upon addition of 100 µl represented administrating ten equivalents. Spectra were recorded at 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents. The resonances of the exterior isophthalamide, interior isophthalamide, and hydroquinone protons were monitored. The resultant curves were analysed as approximations of a Job-plot, and equilibrium constants were obtained through the curve-fitting program WinEQNMR2.[17]

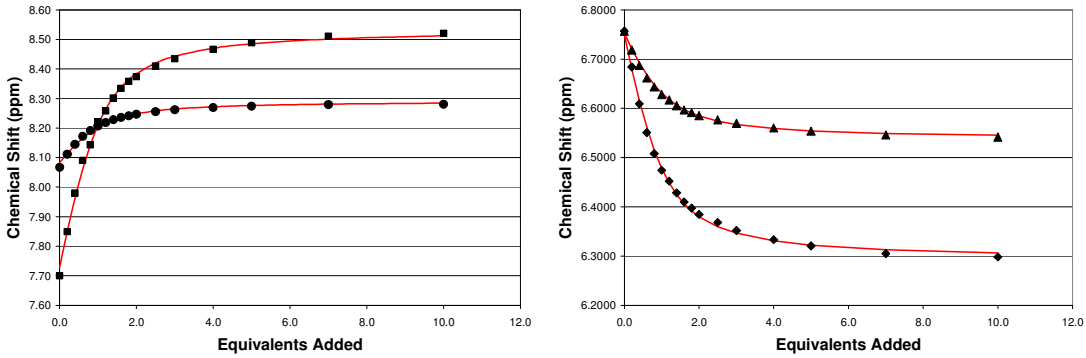
5-Iodo-1,2,3-triazolium threading

Titration of **2**.Cl into a $CDCl_3$ solution of macrocycle **3**



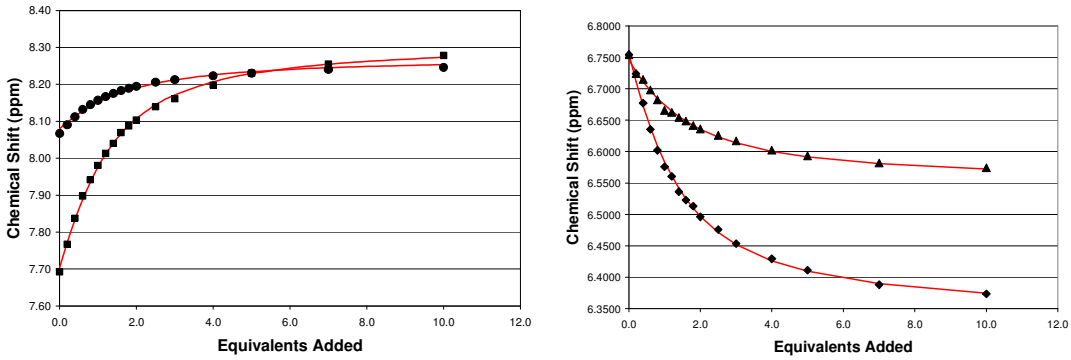
● Exterior isophthalamide protons K_a = 642(47) M^{-1}
■ Interior isophthalamide proton K_a = 555(20) M^{-1}
▲ Hydroquinone K_a = 379(26) M^{-1}
♦ Hydroquinone K_a = 538(17) M^{-1}

Titration of **2**.Br into a $CDCl_3$ solution of macrocycle **3**



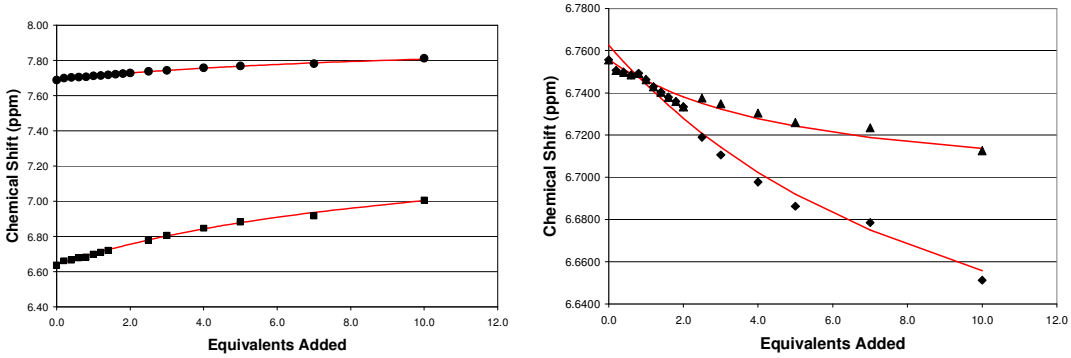
● Exterior isophthalamide protons K_a = 1069(30) M^{-1}
■ Interior isophthalamide proton K_a = 1208(11) M^{-1}
▲ Hydroquinone K_a = 972(26) M^{-1}
♦ Hydroquinone K_a = 1188 (93) M^{-1}

Titration of **2**.I into a $CDCl_3$ solution of macrocycle **3**



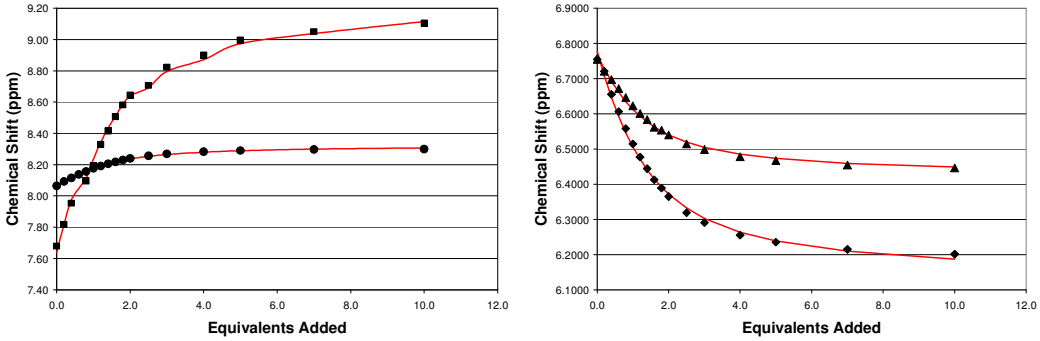
● Exterior isophthalamide protons K_a = 297(21) M^{-1}
■ Interior isophthalamide proton K_a = 470(26) M^{-1}
▲ Hydroquinone K_a = 298(40) M^{-1}
♦ Hydroquinone K_a = 392(24) M^{-1}

Titration of **2**.BF_4 into a $CDCl_3$ solution of macrocycle **3**



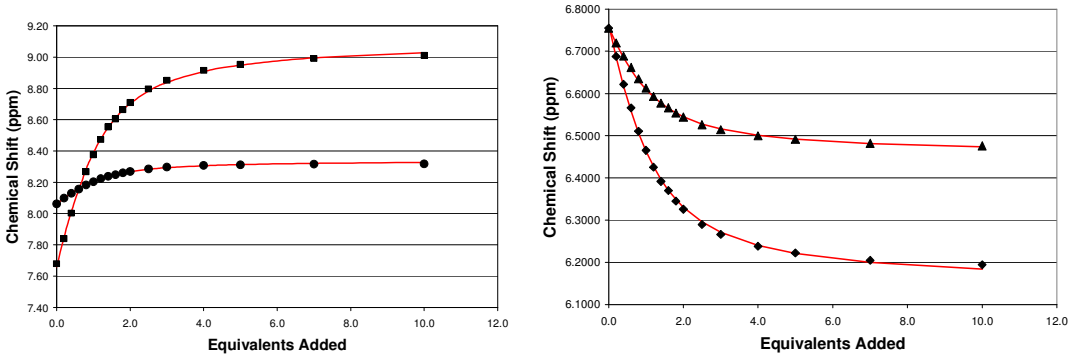
● Exterior isophthalamide protons K_a = 49(20) M^{-1}
■ Interior isophthalamide proton K_a = 23(7) M^{-1}
▲ Hydroquinone K_a = 76(46) M^{-1}
♦ Hydroquinone K_a = 29(19) M^{-1}

Titration of **4**.Cl into a $CDCl_3$ solution of macrocycle **3**



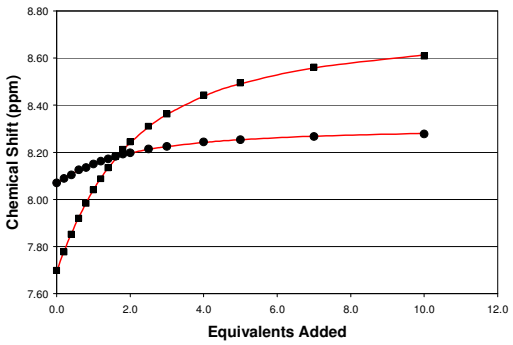
● Exterior isophthalamide protons K_a = 500(41) M^{-1}
■ Interior isophthalamide proton K_a = 411(28) M^{-1}
▲ Hydroquinone K_a = 490(37) M^{-1}
♦ Hydroquinone K_a = 490(38) M^{-1}

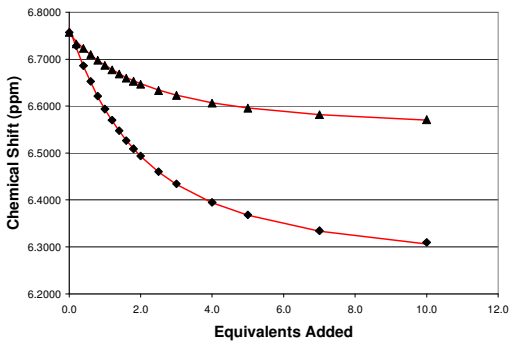
Titration of **4**.Br into a $CDCl_3$ solution of macrocycle **3**



● Exterior isophthalamide protons K_a = 775(59) M^{-1}
■ Interior isophthalamide proton K_a = 680(27) M^{-1}
▲ Hydroquinone K_a = 620(18) M^{-1}
♦ Hydroquinone K_a = 610(31) M^{-1}

Titration of **4**.I into a $CDCl_3$ solution of macrocycle **3**





● Exterior isophthalamide protons K_a = 243(18) M^{-1}
■ Interior isophthalamide proton K_a = 230(4) M^{-1}
▲ Hydroquinone K_a = 215(20) M^{-1}
♦ Hydroquinone K_a = 232(8) M^{-1}

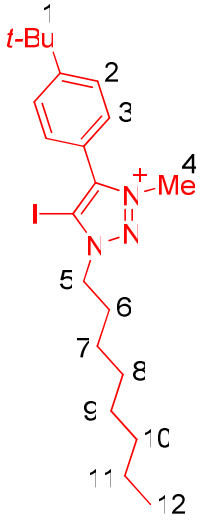
Through-Space NMR Spectroscopy

^{1}H Rotating frame Overhouse Effect Spectroscopy (ROESY) was used to assess through-space dipolar couplings.

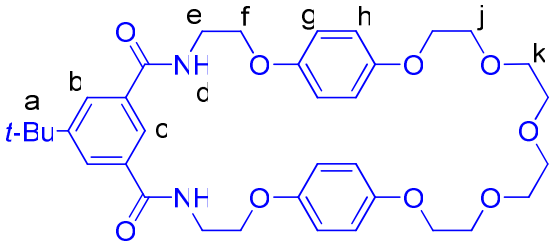
2.Br.3 pseudorotaxane.

The spectrum was recorded for a solution containing **2**.Br (25.0 mg, 0.047 mol) and macrocycle **3** (30.4 mg, 0.047 mmol) dissolved in 0.60 ml $CDCl_3$.

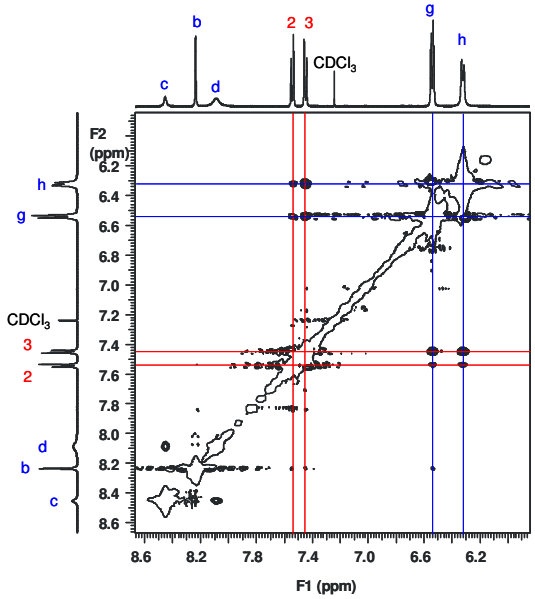
Proton assignments for **2** and **3** are shown below. ROESY figures show selected regions of the spectrum with the accompanying assignment of through-space couplings shown on the right.

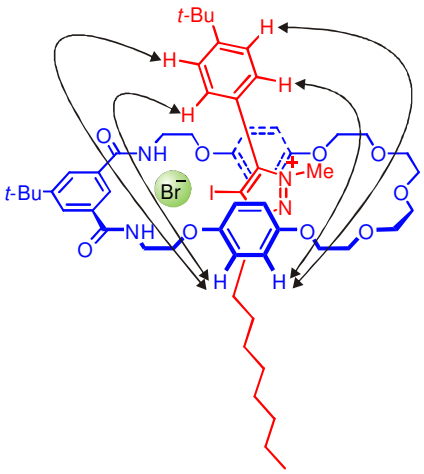


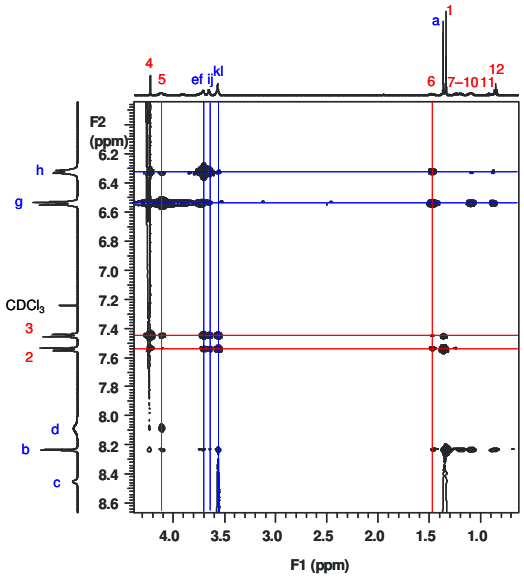
2

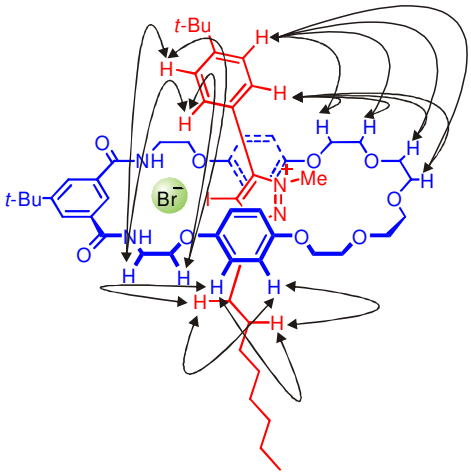


3



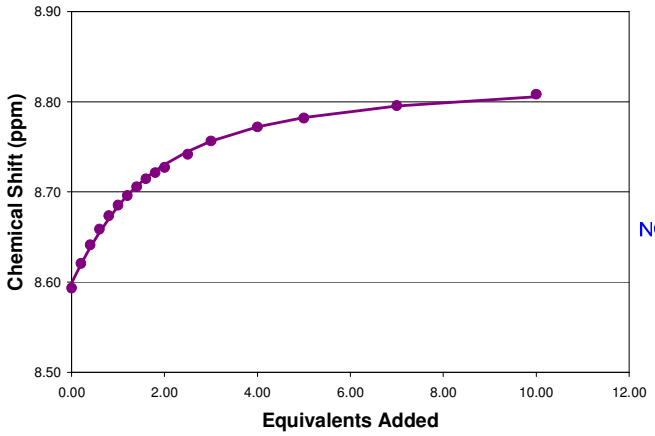


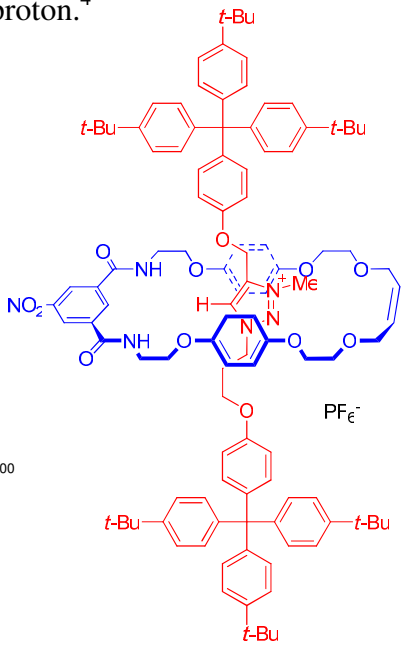




PART IV: NMR rotaxane studies

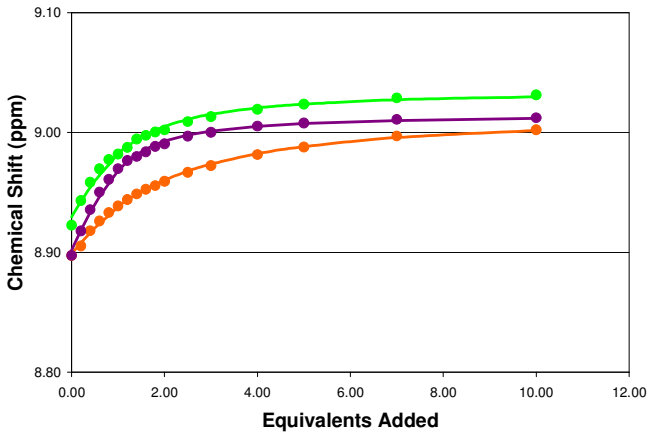
Titration of TBA iodide into a 1:1 $CDCl_3/CD_3OD$ solution of the hydrogen bonding rotaxane, monitoring the internal isophthalamide proton.[4]

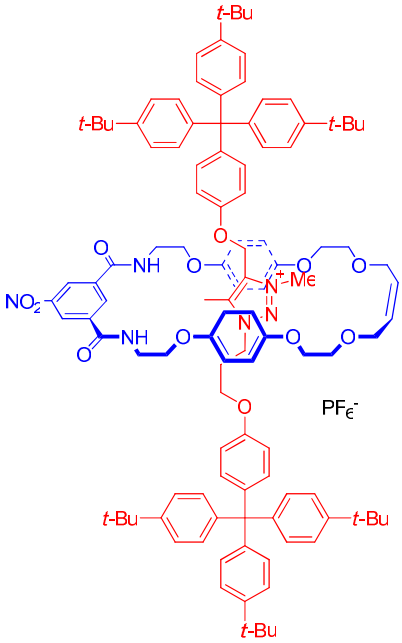




- Iodide K_a = 420 M^{-1}

Titration of TBA halide salts into a 45:45:10 $CDCl_3/CD_3OD/D_2O$ solution of the halogen bonding rotaxane **7**.PF_6.

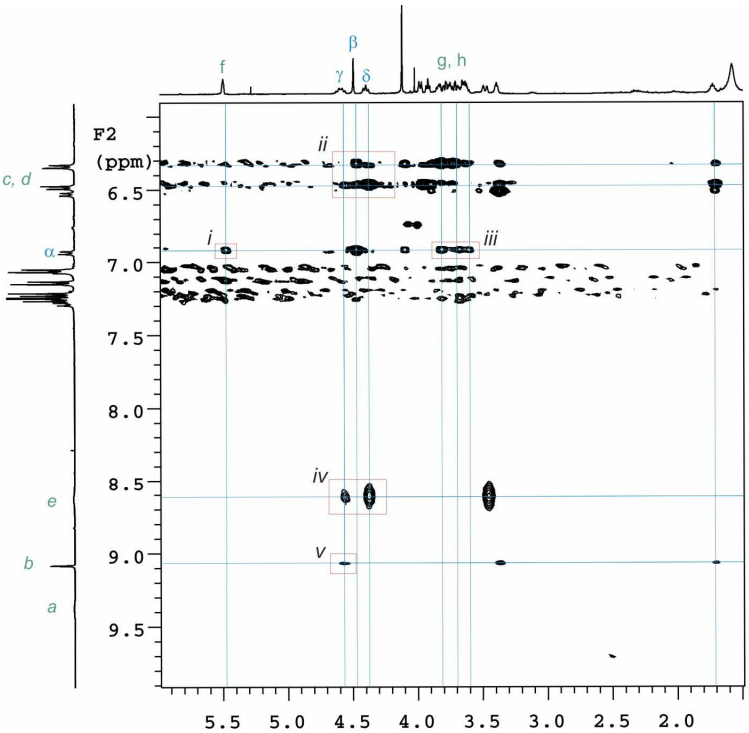


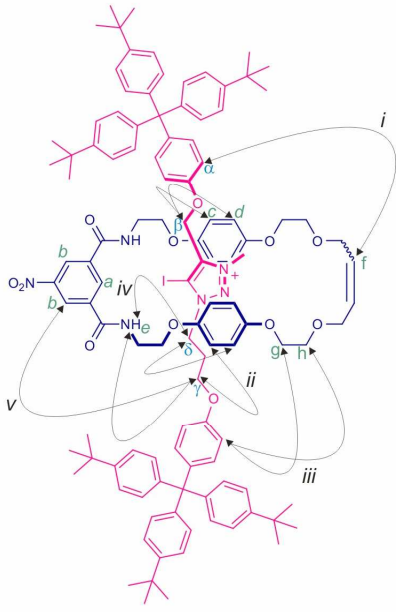


- Chloride K_a = 457(4) M^{-1}
- Bromide K_a = 1251(10) M^{-1}
- Iodide K_a = 2228(171) M^{-1}

Rotaxane 7.Br

The spectrum was recorded for a solution of **7**.Br (10.9 mg, 5.5 x 10^{-6} mol) dissolved in 0.50 ml $CDCl_3$.





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