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–Supporting Information –
TABLE OF CONTENTS

Experimental Section........................................................................................................ S3

NMR spectra.................................................................................................................. S16

Ortep X-ray structures.................................................................................................. S66

UV-Vis and fluorescence spectra................................................................................. S68

Determination of binding constant for pseudorotaxane.......................................... S70
General Methods

2,7-diazapyrene,\(^1\) ligand 1\(-\)2PF\(_6\),\(^2\) Pd and Pt complexes,\(^3\) 4-(4’-chloromethylphenyl)pyridine,\(^4\) metallocycle 3\(-\)2PF\(_6\),\(^2\) cyclophanes BPPC34C10 (8)\(^5\) and DN38C10 (9)\(^6\) and guests 11,\(^7\) 13,\(^8\) 15,\(^9\) 17,\(^10\) 19\(^10\) and 21\(^11\) were prepared according to literature procedures. All other reagents used were commercial grade chemicals from freshly opened containers. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F\(_{254}\) foils were used for thin layer chromatography, and Merck 60 (230-400 mesh) silica gel was used for flash chromatography. Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 or a Bruker Avance 500 spectrometer equipped with a dual cryoprobe for \(^1\)H and \(^13\)C, using the deuterated solvent as lock and the residual protiated solvent as internal standard. DOSY experiments were referenced using the value 1.92\(\times\)10\(^{-9}\) m\(^2\) s\(^{-1}\) for the DHO signal in D\(_2\)O at 298 K\(^{12}\) and the value 1.97\(\times\)10\(^{-9}\) m\(^2\) s\(^{-1}\) for the CHD\(_2\)NO\(_2\) signal in CD\(_3\)NO\(_2\) at 298 K.\(^{13}\) Mass spectrometry experiments were carried out in a LCQ-q-TOF Applied Biosystems QSTAR Elite spectrometer for low- and high-resolution ESI. UV-Vis spectra were recorded on a Perkin Elmer Lambda 900 spectrometer. Fluorescence spectra were recorded at room temperature on a Perkin Elmer LS 50B fluorescence spectrometer using a 1% T filter and a slit width of 8 nm. Melting points were measured using Stuart Scientific SMP3 apparatus. Microanalyses for C, H and N were performed by the elemental analyses general service of the University of A Coruña.

Crystal structure analysis

The structure was solved by direct methods and refined with the full-matrix least-squares procedure (SHELX-97)\(^{14}\) against \(F^2\). The X-ray diffraction data were collected on a Bruker X8 ApexII. Non-Solvent hydrogen atoms were placed in idealized positions with \(U_{eq}(H) = 1.2U_{eq}(C)\) and were allowed to ride on their parent atoms. Solvent hydrogen atoms were placed in idealized positions with \(U_{eq}(H) = 1.5U_{eq}(C)\) and were allowed to ride on their parent atoms.

**Ligand 4-PF\(_6\)**

To a solution of 2,7-diazapyrene (1.44 g, 7.00 mmol) and a catalytic amount of KI in refluxing CH\(_3\)CN (90 mL) was slowly added a solution of 4-(4’-chloromethylphenyl)pyridine
(0.95 g, 4.66 mmol) cooled to 0 °C in CH$_3$CN (70 mL). The reaction was refluxed for 72 h; after cooling, the solvent was evaporated in vacuo to give a crude product which was purified by column chromatography (SiO$_2$, acetone/NH$_4$Cl 1.5M/MeOH 5:4:1). The product-containing fractions were combined and the solvents were removed in vacuo. The residue was dissolved in H$_2$O/CH$_3$OH (50/30, 800 mL) and an excess of KPF$_6$ was added until no further precipitation was observed. The solid was filtered and washed with water to give 4·PF$_6$ (0.76 g, 31%) as a yellow solid. Mp: 189-191 ºC (dec.). $^1$H NMR (500 MHz, CD$_3$NO$_2$) δ: 6.45 (2H, s); 7.84 (2H, d, J = 8.5 Hz); 8.00 (2H, d, J = 6.4 Hz); 8.03 (2H, d, J = 6.4 Hz); 8.61 (2H, d, J = 9.1 Hz); 8.77 (4H, m); 9.83 (2H, s); 9.88 (2H, s); $^{13}$C NMR (125 MHz, CD$_3$NO$_2$) δ: 67.1 (CH$_2$); 124.6 (CH); 125.5 (C); 127.2 (CH); 127.5 (C); 130.0 (CH); 130.4 (C); 130.9 (C); 131.5 (CH); 132.8 (CH); 137.2 (C); 139.2 (C); 139.5 (CH); 147.4 (CH); 149.8 (CH); 153.7 (C). MS-ESI (m/z): 372.2 [M – PF$_6$]$^+$.

Ligand 4·NO$_3$

To a solution of 4·PF$_6$ (197.0 mg, 0.38 mmol) in CH$_3$CN (90 mL) Bu$_4$NNO$_3$ was added until no further precipitation is observed. The mixture was stirred at rt for 6h and the precipitate was filtered and washed with CH$_3$CN to yield 4·NO$_3$ (130.1 mg, 79 %) as a yellow solid. Mp: 161-163 ºC. $^1$H NMR (500 MHz, D$_2$O) δ: 6.20 (2H, s); 7.69 (4H, m); 7.80 (2H, d, J = 8.3 Hz); 8.31 (2H, d, J = 9.1 Hz); 8.44 (4H, m); 9.51 (2H, s); 9.75 (2H, s); $^{13}$C NMR (125 MHz, D$_2$O) δ: 65.9 (CH$_2$); 123.2 (CH); 124.6 (C); 126.5 (CH); 126.7 (C); 128.6 (C); 129.0 (CH); 129.7 (C); 130.6 (CH); 131.7 (CH); 135.9 (C); 138.5 (C); 138.8 (CH); 147.3 (CH); 147.6 (CH); 150.9 (C). MS-ESI (m/z): 372.2 [M – NO$_3$]$^+$. Anal. Calcd. C, 71.88; H, 4.18; N, 12.90. Found. C, 71.99; H, 4.10; N, 12.72.

Metallocycles 6a,b·6NO$_3$

A solution of 4·NO$_3$ (8.7 mg; 0.020 mmol) and (en)Pd(NO$_3$)$_2$ (5a) (5.8 mg, 0.020 mmol) in D$_2$O (4.0 mL) was stirred at 60 ºC for 1 h. $^1$H NMR (500 MHz, D$_2$O) δ: 3.00 (8H, m); 6.28 (4H, s); 7.59-7.69 (12H, m); 8.50 (4H, m); 8.55-8.61 (6H, m); 8.77 (2H, d, J = 6.8 Hz); 9.95 (4H, s); 9.98 (2H, s); 10.15 (2H, s); $^{13}$C NMR (125 MHz, D$_2$O) δ: 46.8 (CH$_2$); 46.9 (CH$_2$);
47.1 (CH$_2$); 47.2 (CH$_2$); 65.9 (CH$_2$); 124.1 (CH); 124.2 (CH); 125.0 (C); 125.1 (C); 127.4 (C); 127.4 (C); 127.9 (CH); 128.0 (CH); 128.1 (CH); 128.4 (C); 128.5 (C); 129.5 (C); 129.5 (C); 129.7 (CH); 129.7 (CH); 129.9 (CH); 129.9 (CH); 136.1 (C); 136.1 (C); 136.4 (C); 136.6 (C); 139.4 (CH); 139.5 (CH); 148.1 (CH); 148.1 (CH); 150.6 (C); 150.7 (C); 151.0 (CH); 151.0 (CH).

**Metallocycles 6a,b·6PF$_6$**

A solution of 4·NO$_3$ (21.7 mg; 0.050 mmol) and 5a (14.5 mg, 0.050 mmol) in H$_2$O (10.0 mL) was stirred at 60 ºC for 1h. An excess of KPF$_6$ was added until no further precipitation was observed. The solid was filtered and washed with water to obtain 6a,b·6PF$_6$ (32.0 mg, 66%) as a pale brown solid. Mp: 195-197 ºC.

$^1$H NMR (500 MHz, CD$_3$NO$_2$) δ: 3.22 (8H, m); 4.59 (2H, m); 4.76 (2H, m); 6.34 (4H, s); 7.66 (12H, m); 8.58 (4H, m); 8.63 (4H, m); 8.69 (2H, d, $J = 6.4$ Hz); 8.83 (2H, d, $J = 6.5$ Hz); 9.84 (4H, m); 10.00 (2H, s); 10.18 (2H, s).

$^{13}$C NMR (125 MHz, CD$_3$NO$_2$) δ: 48.5 (CH$_2$); 48.6 (CH$_2$); 48.7 (CH$_2$); 48.9 (CH$_2$); 67.6 (CH$_2$); 125.4 (CH); 125.5 (CH); 126.5 (C); 129.0 (C); 129.1 (C); 129.5 (CH); 129.6 (CH); 129.9 (C); 130.0 (C); 131.0 (CH); 131.1 (C); 131.1 (CH); 131.6 (CH); 131.6 (CH); 137.7 (C); 137.8 (C); 137.9 (C); 141.0 (CH); 141.0 (CH); 150.1 (CH); 150.2 (CH); 152.0 (C); 152.0 (C); 152.9 (CH); 153.0 (CH).

**Metallocycles 7a,b·6PF$_6$**

A solution of ligand 4·NO$_3$ (39.0 mg, 0.090 mmol) and (en)Pt(NO$_3$)$_2$ (5b) (34.0 mg, 0.090 mmol) in H$_2$O (24.0 mL) was stirred at 100 ºC for 8d. Upon cooling to room temperature, an excess of KPF$_6$ was added until no further precipitation was observed. The solid was filtered to yield 7a,b·6PF$_6$ (88.1 mg, 92%) as a pale brown solid. Mp: 243-245 ºC (dec.).

$^1$H NMR (500 MHz, CD$_3$NO$_2$) δ: 3.17 (8H, m); 4.93 (2H, m); 5.13 (4H, m); 5.33 (2H, m); 6.34 (4H, s); 7.67 (12H, m); 8.62 (8H, m); 8.71 (2H, d, $J = 5.6$ Hz); 8.86 (2H, d, $J = 5.7$ Hz); 9.85 (4H, m); 10.01 (2H, s); 10.19 (2H, s). $^{13}$C NMR (125 MHz, CD$_3$NO$_2$) δ: 49.6 (CH$_2$); 49.7 (CH$_2$); 49.8 (CH$_2$); 49.9 (CH$_2$); 67.6 (CH$_2$); 67.6 (CH$_2$); 125.7 (CH); 125.8 (CH); 126.4 (C); 126.4 (C); 128.9 (C); 129.0 (C); 129.2 (CH); 129.3 (CH); 129.5 (CH); 130.4 (C); 130.4 (C); 131.0 (CH); 131.1 (C); 131.1 (C); 131.1 (CH); 131.5 (CH); 131.6.
(CH); 137.5 (C); 137.7 (C); 137.8 (C); 137.9 (C); 141.0 (CH); 151.1 (CH); 151.1 (CH); 151.9 (C); 153.6 (CH); 153.7 (CH). HRMS-ESI (m/z): Calcd para [M – 2PF\(_6\)-]\(^{2+}\) 917-1114, found 917.1085; calcd. for [M – 3PF\(_6\)-]\(^{3+}\) 563.0860, found 563.0843; calcd. for [M – 4PF\(_6\)-]\(^{4+}\) 386.0733, found. 386.0726; calcd. for [M – 5PF\(_6\)-]\(^{5+}\) 289.8657, found 279.8645.

**Metallocycles 7a,b·6NO\(_3\)**

To a solution of 7a,b·6PF\(_6\) (55.0 mg, 0.026 mmol) in CH\(_3\)CN (4 mL) Bu\(_4\)NNO\(_3\) was added until no further precipitation is observed. The precipitate was filtered and washed with CH\(_3\)CN to yield 7a,b·6NO\(_3\) (31.1 mg, 74 %) as a pale brown solid.

**1H NMR (500 MHz, D\(_2\)O)** δ: 2.92 (8H, m); 6.28 (4H, s); 7.61-7.69 (12H, m); 8.50-8.58 (8H, m); 8.63 (2H, d, J = 6.9 Hz); 8.80 (2H, d, J = 6.9 Hz); 9.96 (4H, s); 9.99 (2H, s); 10.17 (2H, s);

**13C NMR (125 MHz, D\(_2\)O)** δ: 47.4 (CH\(_2\)); 47.6 (CH\(_2\)); 47.6 (CH\(_2\)); 47.8 (CH\(_2\)); 65.8 (CH\(_2\)); 65.9 (CH\(_2\)); 124.4 (CH); 124.4 (CH); 124.8 (C); 124.9 (C); 127.2 (C); 127.3 (C); 128.0 (CH); 128.0 (CH); 128.1 (CH); 128.9 (C); 128.9 (C); 129.5 (C); 129.5 (C); 129.7 (CH); 129.7 (CH); 136.1 (C); 136.1 (C); 136.2 (C); 136.3 (C); 139.4 (CH); 139.4 (CH); 149.0 (CH); 149.0 (CH); 150.3 (C); 150.5 (C); 151.6 (CH); 151.7 (CH).

**Pseudorotaxane 1·2PF\(_6\)⊂8**

To a solution of 1·2PF\(_6\) (2.1 mg; 3.0 × 10\(^{-3}\) mmol) in CD\(_3\)NO\(_2\) (0.6 mL) 8 (1.6 mg, 3.0 × 10\(^{-3}\) mmol) was added. **1H NMR (500 MHz, CD\(_3\)NO\(_2\))** δ: 10.14 (4H, s), 9.98 (4H, s), 8.80 (4H, d, J = 9.1 Hz), 8.58 (4H, d, J = 9.1 Hz), 8.41 (2H, s), 5.90 (8H, s), 3.93–3.72 (24H, m), 3.64 (8H, m). **13C NMR (125 MHz, CD\(_3\)NO\(_2\))** δ: 153.0 (C), 150.8 (CH), 139.0 (CH), 134.3 (CH), 131.2 (C), 131.1 (C), 127.3 (C), 126.9 (CH), 125.1 (C), 115.1 (CH), 82.0 (CH\(_2\)), 71.8 (CH\(_2\)), 71.6 (CH\(_2\)), 71.0 (CH\(_2\)), 68.9 (CH\(_2\)).
**Pseudorotaxane 1·2PF₆⊂9**

To a solution of 1·2PF₆ (2.1 mg; 3.0 × 10⁻³ mmol) in CD₃NO₂ (0.6 mL) 9 (1.9 mg, 3.0 × 10⁻³ mmol) was added. \(^1\)H NMR \((500 MHz, CD₃NO₂)\): 10.10 (4H, s), 9.88 (4H, s), 8.70 (4H, d, J = 9.1 Hz), 8.42 (4H, d, J = 9.1 Hz), 8.26 (2H, s), 6.43 (8H, m), 6.15 (4H, d, J = 7.1 Hz), 4.06 (8H, m), 4.02 (8H, m), 3.95 (16H, m). \(^{13}\)C NMR \((125 MHz, CD₃NO₂)\): 154.3 (C), 150.5 (CH), 138.4 (CH), 134.1 (CH), 130.7 (C), 130.3 (C), 127.3 (C), 126.7 (C), 125.9 (C), 125.9 (CH), 124.3 (C), 113.9 (CH), 106.0 (CH), 82.2 (CH₂), 72.3 (CH₂), 72.2 (CH₂), 71.2 (CH₂), 69.2 (CH₂).

**Catenane 3(8)₂·4OTf·4PF₆**

To a solution of 1·2PF₆ (7.1 mg; 0.010 mmol) and 2 (5.6 mg, 0.024 mmol) in CD₃NO₂ (4.0 mL) 8 (5.4 mg, 0.010 mmol) was added. \(^1\)H NMR \((500 MHz, CD₃NO₂)\): 3.11 (4H, m); 3.32 (8H, br s); 3.83 (58H, m); 4.09 (4H, m); 4.64 (2H, m); 5.00 (4H, br s); 5.30 (4H, br s); 5.50 (8H, s); 8.26 (4H, s); 8.33 (4H, d, J = 9.2 Hz); 8.48 (4H, d, J = 9.3 Hz); 8.82 (4H, d, J = 9.4 Hz); 8.89 (4H, d, J = 9.4 Hz); 10.11 (4H, s); 10.36 (4H, s); 10.53 (4H, s); 10.61 (4H, s); \(^{13}\)C NMR \((125 MHz, CD₃NO₂)\): 49.1 (CH₂); 49.4 (CH₂); 66.9 (CH₂); 69.2 (CH₂); 70.5 (CH₂); 71.0 (CH₂); 71.2 (CH₂); 71.7 (CH₂); 72.1 (CH₂); 82.6 (CH₂); 115.0 (CH); 119.1 (C); 121.0 (C); 123.5 (C); 124.7 (C); 125.6 (C); 128.6 (C); 128.8 (CH); 129.2 (C); 129.7 (C); 129.9 (CH); 130.1 (C); 130.4 (C); 131.4 (C); 132.6 (CH); 133.0 (CH); 140.4 (C); 141.6 (C); 151.4 (CH); 152.3 (C).
To a solution of 1·2PF₆ (7.1 mg, 0.010 mmol) and (en)Pd(OTf)₂ (2) (5.6 mg, 0.024 mmol) in CD₃NO₂ (4.0 mL) DNP34C10 (9) (6.4 mg, 0.010 mmol) was added. ¹H NMR (500 MHz, CD₃NO₂): The complexity of the spectrum precluded its analysis (Figure S46).

X-ray diffraction quality single crystals of the catenane were grown by slow diffusion of diethyl ether into a solution of 1·2PF₆, (en)Pd(OTf)₂ (2) and 9 in acetonitrile.

Regioselective catenation

To a solution of 6a,b·6PF₆ (5.8 mg, 3.0 × 10⁻³ mmol) in CD₃NO₂ (0.6 mL) 8 (3.2 mg, 6.0 × 10⁻³ mmol) was added. ¹H NMR (500 MHz, CD₃NO₂) δ: 3.23 (16H, m); 3.44 (12H, m); 3.59-4.19

S8
(52H, m); 4.60 (4H, m); 4.85 (4H, m); 5.11 (4H, s); 5.39 (8H, s); 6.24 (4H, s); 7.73 (4H, d, \(J = 8.4\) Hz); 7.83 (4H, d, \(J = 6.7\) Hz); 7.92 (4H, d, \(J = 8.4\) Hz); 8.27 (8H, m); 9.19 (4H, d, \(J = 6.6\) Hz); 9.77 (4H, s); 9.87 (4H, s); \(^{13}\)C NMR (500 MHz, \(CD_3NO_2\)) \(\delta\): 48.6 (CH\(_2\)); 49.2 (CH\(_2\)); 66.7 (CH\(_2\)); 67.2 (CH\(_2\)); 68.8 (CH\(_2\)); 69.2 (CH\(_2\)); 70.7 (CH\(_2\)); 70.8 (CH\(_2\)); 71.0 (CH\(_2\)); 71.4 (CH\(_2\)); 71.6 (CH\(_2\)); 71.7 (CH\(_2\)); 71.8 (CH\(_2\)); 112.1 (CH); 114.4 (CH); 125.1 (C); 126.2 (CH); 127.9 (C); 129.2 (CH); 129.3 (CH); 129.5 (C); 129.9 (C); 131.0 (CH); 132.0 (CH); 137.8 (C); 138.1 (C); 141.0 (CH); 149.6 (CH); 152.1 (C); 153.6 (CH).

Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a solution of 1·PF\(_6\), (en)Pd(OTf)\(_2\) (2) and 8 in nitromethane.

**Catenane 6a(9)\(_2\)·6PF\(_6\)**

To a solution of 6a,b·6PF\(_6\) (5.8 mg, 3.0 \(\times\) 10\(^{-3}\) mmol) in \(CD_3NO_2\) (0.6 mL) 9 (3.8 mg, 6.0 \(\times\) 10\(^{-3}\) mmol) was added. \(^1\)H NMR (500 MHz, \(CD_3NO_2\)). The complexity of the spectrum precluded its analysis (Figure S55).

**Catenane 7a(8)\(_2\)·6PF\(_6\)**

A solution of 7a,b·6PF\(_6\) (25.0 mg, 0.012 mmol) and BPP34C10 (8) (25.2 mg, 0.047 mmol) in CH\(_3\)NO\(_2\) (2.4 mL) was stirred at 100 °C for 7d. After cooling to rt, the solvent was removed under reduced pressure without heating. The resulting residue was suspended in water (12 mL) and Amberlite\textsuperscript{TM} IRA-402 (0.50 g) was added. The mixture was stirred at rt for 24h. The resin was removed by filtration and the filtrate was concentrated under reduced pressure. The resulting crude was purified by flash chromatography (SiO\(_2\), acetone/NH\(_4\)Cl\(_{aq}\) 1.5M/MeOH 5:4:1).
product containing fractions were combined and the solvent removed under reduced pressure to afford a residue that was dissolved in H₂O (15 mL). An excess of KPF₆ was added until no further precipitation is observed. The solid was filtered and washed with water to yield catenane 7a(8)_2·6PF₆ (24.0 mg, 64 %) as a yellow solid. ¹H NMR (500 MHz, CD$_3$NO$_2$) δ: 3.16 (16H, m); 3.45 (12H, m); 3.59-4.19 (52H, m); 4.88 (4H, m); 5.16 (4H, s); 5.41 (8H, s); 6.25 (4H, s); 7.75 (4H, d, J = 8.6 Hz); 7.81 (4H, d, J = 7.0 Hz); 7.93 (4H, d, J = 8.6 Hz); 8.27 (8H, m); 9.21 (4H, d, J = 6.9 Hz); 9.78 (4H, s); 9.90 (4H, s); ¹³C NMR (125 MHz, CD$_3$NO$_2$) δ: 49.4 (CH$_2$); 50.2 (CH$_2$); 66.7 (CH$_2$); 67.2 (CH$_2$); 68.8 (CH$_2$); 70.7 (CH$_2$); 70.9 (CH$_2$); 71.0 (CH$_2$); 71.5 (CH$_2$); 71.7 (CH$_2$); 71.8 (CH$_2$); 112.1 (CH); 114.5 (CH); 125.0 (C); 126.4 (CH); 127.7 (C); 129.4 (CH); 129.5 (CH); 129.6 (C); 130.0 (C); 131.0 (CH); 132.0 (CH); 137.9 (C); 137.9 (C); 141.1 (CH); 149.8 (CH); 152.1 (C); 153.8 (CH). HRMS-ES (m/z): calc. for [M – 3PF$_6$]⁺ 920.5941, found 920.5905; calc. for [M – 4PF$_6$]⁺ 654.2044, found 654.2035; calc. for [M – 5PF$_6$]⁵⁺ 494.3705, found 494.3700.

Catenane 7a(9)_2·6PF₆

A solution of 7a·6PF₆ (25.0 mg, 0.012 mmol) and 9 (30.0 mg, 0.047 mmol) in CH$_3$NO$_2$ (2.4 mL) was stirred at 100 °C for 7d. After cooling to rt, the solvent was removed under reduced pressure without heating. The resulting residue was suspended in water (12 mL) and Amberlite™ IRA-402 (0.50 g) was added. The mixture was stirred at rt for 24h. The resin was removed by filtration and the filtrate was concentrated under reduce pressure. The resulting crude was purified by flash chromatography (SiO$_2$, acetone/NH$_4$Cl$_aq$ 1.5M/MeOH 5:4:1). The product containing fractions were combined and the solvent removed under reduced pressure to afford a residue that was dissolved in H$_2$O (15 mL). An excess of KPF₆ was added until no further precipitation is observed. The solid was filtered and washed with water to yield catenane 7a(9)_2·6PF₆ (25.3 mg, 63 %) as a yellow solid. ¹H NMR (500 MHz, CD$_3$NO$_2$) The complexity of the spectrum precluded its analysis (Figure S58).

General procedure for the regioselective formation of inclusion complexes

To a solution of $4 \cdot \text{NO}_3$ (4.3 mg; 0.010 mmol) and (en)Pd(NO$_3$)$_2$ (5a) (2.9 mg; 0.010 mmol) in D$_2$O (2.0 mL) guests 15, 17, 19, 20, 21 (0.010 mmol), 11, 13, 16, 18 (0.020 mmol) or 10 (0.070 mmol) were added and the mixture was stirred at 60ºC for 1h.

Inclusion complex (10)$_2 \subset 6a \cdot 6\text{NO}_3$

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 3.01 (8H, s); 6.13 (4H, s); 6.24 (56H, s); 7.74 (4H, d, $J = 8.5$ Hz); 7.84 (8H, m); 8.31 (4H, d, $J = 9.2$ Hz); 8.44 (4H, d, $J = 9.2$ Hz); 9.01 (4H, d, $J = 6.8$ Hz); 9.80 (4H, s); 10.01 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.4 (CH$_2$); 46.5 (CH$_2$); 65.4 (CH$_2$); 115.3 (CH); 123.8 (CH); 124.2 (C); 125.7 (C); 127.5 (CH); 127.7 (C); 127.9 (CH); 128.8 (C); 129.1 (CH); 129.6 (CH); 135.8 (C); 135.9 (C); 138.0 (CH); 147.3 (CH); 148.0 (C); 150.2 (C); 150.8 (CH).

Inclusion complex (11)$_2 \subset 6a \cdot 6\text{NO}_3$

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 3.01 (8H, s); 6.13 (4H, s); 6.24 (56H, s); 7.74 (4H, d, $J = 8.5$ Hz); 7.84 (8H, m); 8.31 (4H, d, $J = 9.2$ Hz); 8.44 (4H, d, $J = 9.2$ Hz); 9.01 (4H, d, $J = 6.8$ Hz); 9.80 (4H, s); 10.01 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.4 (CH$_2$); 46.5 (CH$_2$); 65.4 (CH$_2$); 115.3 (CH); 123.8 (CH); 124.2 (C); 125.7 (C); 127.5 (CH); 127.7 (C); 127.9 (CH); 128.8 (C); 129.1 (CH); 129.6 (CH); 135.8 (C); 135.9 (C); 138.0 (CH); 147.3 (CH); 148.0 (C); 150.2 (C); 150.8 (CH).
$^1$H NMR (500 MHz, D$_2$O) $\delta$: 3.00 (8H, s); 3.72-3.83 (64H, m); 6.18 (4H, s); 7.81 (4H, d, $J = 8.5$ Hz); 7.90 (8H, m); 8.36 (4H, d, $J = 9.2$ Hz); 8.48 (4H, d, $J = 9.2$ Hz); 9.11 (4H, d, $J = 6.8$ Hz); 9.90 (4H, s); 10.08 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.8 (CH$_2$); 46.9 (CH$_2$); 60.5 (CH$_2$); 65.8 (CH$_2$); 67.2 (CH$_2$); 68.9 (CH$_2$); 71.9 (CH$_2$); 114.4 (CH); 124.3 (CH); 126.1 (C); 127.8 (CH); 128.1 (C); 128.3 (CH); 129.1 (C); 129.8 (CH); 130.2 (CH); 136.4 (C); 136.6 (C); 138.7 (CH); 147.9 (CH); 150.4 (C); 151.3 (C); 151.5 (CH).

**Inclusion complex (13)⊂6a·6NO$_3$**

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 2.99 (8H, m); 5.60 (8H, m); 6.01 (4H, s); 7.77 (4H, d, $J = 9.1$ Hz); 7.92 (8H, m); 7.97 (4H, d, $J = 8.6$ Hz); 8.08 (4H, d, $J = 6.8$ Hz); 9.13 (4H, d, $J = 6.9$ Hz); 9.47 (4H, s); 9.72 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.7 (CH$_2$); 46.8 (CH$_2$); 65.8 (CH$_2$); 107.1 (CH); 111.4 (CH); 123.1 (C); 124.5 (CH); 124.9 (C); 126.7 (CH); 127.5 (C); 128.2 (C); 128.4 (CH); 128.8 (CH); 130.5 (CH); 135.4 (C); 136.6 (C); 137.7 (CH); 147.3 (CH); 149.5 (C); 150.7 (C); 151.4 (CH).

**Inclusion complex (14)⊂6a·6NO$_3$**

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 3.00 (8H, s); 3.72-3.83 (64H, m); 6.18 (4H, s); 7.81 (4H, d, $J = 8.5$ Hz); 7.90 (8H, m); 8.36 (4H, d, $J = 9.2$ Hz); 8.48 (4H, d, $J = 9.2$ Hz); 9.11 (4H, d, $J = 6.8$ Hz); 9.90 (4H, s); 10.08 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.8 (CH$_2$); 46.9 (CH$_2$); 60.5 (CH$_2$); 65.8 (CH$_2$); 67.2 (CH$_2$); 68.9 (CH$_2$); 71.9 (CH$_2$); 114.4 (CH); 124.3 (CH); 126.1 (C); 127.8 (CH); 128.1 (C); 128.3 (CH); 129.1 (C); 129.8 (CH); 130.2 (CH); 136.4 (C); 136.6 (C); 138.7 (CH); 147.9 (CH); 150.4 (C); 151.3 (C); 151.5 (CH).
Inclusion complex (15)$_2$$\subset$6a·6NO$_3$

\[
\begin{align*}
\text{R} &= \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \\
(15)_2^{\circ}$ & 6a·6NO$_3$
\end{align*}
\]

$^1$H NMR (500 MHz, D$_2$O, 353 K) $\delta$: 3.40-3.49 (8H, m); 4.06 (8H, m); 4.33 (8H, m); 4.41 (8H, m); 4.50 (8H, m); 5.90-6.07 (6H, m); 6.55 (4H, s); 8.38 (4H, d, $J = 9.1$ Hz); 8.48-8.59 (12H, m); 8.68 (4H, d, $J = 5.7$ Hz); 9.71 (4H, d, $J = 6.7$ Hz); 10.02 (4H, s); 10.21 (4H, s).

Inclusion complex (16)$_2$$\subset$6a·6NO$_3$

\[
\begin{align*}
\text{R} &= \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \\
(16)_2^{\circ}$ & 6a·6NO$_3$
\end{align*}
\]

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 3.01 (8H, s); 6.03 (4H, s); 7.81 (4H, d, $J = 9.2$ Hz); 7.94 (4H, d, $J = 8.7$ Hz); 8.00 (4H, d, $J = 8.7$ Hz); 8.05 (4H, d, $J = 9.2$ Hz); 8.12 (4H, d, $J = 7.0$ Hz); 9.19 (4H, d, $J = 7.0$ Hz); 9.50 (4H, s); 9.87 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.8 (CH$_2$); 46.9 (CH$_2$); 65.7 (CH$_2$); 105.9 (CH); 113.3 (CH); 121.1 (C); 123.5 (C); 124.5 (CH); 124.9 (C); 126.8 (CH); 127.2 (C); 127.8 (C); 128.5 (CH); 128.6 (C); 128.9 (CH); 130.4 (CH); 133.1 (C); 136.4 (C); 136.6 (C); 137.8 (CH); 147.4 (CH); 150.5 (C); 151.6 (CH); 152.0 (C).

Inclusion complex (17)$_2$$\subset$6a·6NO$_3$

\[
\begin{align*}
\text{R} &= \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \\
(17)_2^{\circ}$ & 6a·6NO$_3$
\end{align*}
\]

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 3.00 (8H, s); 3.29 (4H, m); 3.88-4.00 (32H, m); 4.51 (4H, m); 5.46 (m); 6.11 (4H, s); 7.89 (4H, d, $J = 9.2$ Hz); 8.00 (8H, m); 8.11 (4H, d, $J = 9.1$ Hz); 8.16 (4H, d, $J$
= 5.4 Hz); 9.33 (4H, m); 9.69 (4H, s); 9.96 (4H, s); \(^1^3\)C NMR (125 MHz, D\(_2\)O) \(\delta\): 46.8 (CH\(_2\)); 46.9 (CH\(_2\)); 60.7 (CH\(_2\)); 65.7 (CH\(_2\)); 68.8 (CH\(_2\)); 72.3 (CH\(_2\)); 102.8 (CH); 114.2 (CH); 123.3 (C); 124.3 (CH); 125.2 (C); 126.9 (CH); 127.9 (C); 128.3 (CH); 128.7 (C); 129.4 (CH); 130.4 (CH); 136.3 (C); 137.1 (CH); 138.1 (CH); 147.6 (CH); 150.4 (C); 152.0 (CH); 154.1 (C).

**Inclusion complex (18)\(_2\subset\)6a·6NO\(_3\)**

\(\overset{1^H}{\text{NMR (500 MHz, D\(_2\)O)}} \delta:\) 3.00 (8H, m); 4.26 (8H, m); 5.51 (4H, m); 6.05 (4H, s); 7.86 (4H, d, \(J = 9.1\) Hz); 7.95 (4H, d, \(J = 8.5\) Hz); 7.99 (4H, d, \(J = 8.2\) Hz); 8.10 (8H, m); 9.18 (4H, d, \(J = 6.3\) Hz); 9.53 (4H, s); 9.87 (4H, s); \(^1^3\)C NMR (125 MHz, D\(_2\)O) \(\delta\): 46.8 (CH\(_2\)); 46.9 (CH\(_2\)); 65.7 (CH\(_2\)); 108.2 (CH); 121.5 (CH); 122.9 (CH); 123.7 (C); 124.5 (CH); 125.1 (C); 125.9 (C); 126.9 (CH); 127.9 (C); 128.5 (CH); 128.7 (C); 129.0 (CH); 130.5 (CH); 136.5 (C); 136.5 (C); 138.0 (CH); 142.8 (C); 147.4 (CH); 150.6 (C); 151.6 (CH).

**Inclusion complex (19)\(_2\subset\)6a·6NO\(_3\)**

\(\overset{1^H}{\text{NMR (500 MHz, D\(_2\)O)}} \delta:\) 2.98 (8H, m); 3.90-3.98 (32H, m); 5.99 (4H, m); 6.14 (4H, s); 7.89 (4H, m); 8.05 (4H, d, \(J = 8.6\) Hz); 8.10 (4H, d, \(J = 8.5\) Hz); 8.22 (4H, d, \(J = 6.5\) Hz); 9.32 (4H, d, \(J = 6.7\) Hz); 9.68 (4H, s); 9.94 (4H, s); \(^1^3\)C NMR (125 MHz, D\(_2\)O) \(\delta\): 46.9 (CH\(_2\)); 47.0 (CH\(_2\)); 60.6 (CH\(_2\)); 65.7 (CH\(_2\)); 68.4 (CH\(_2\)); 72.3 (CH\(_2\)); 104.4 (CH); 123.0 (CH); 123.4 (C); 124.2 (CH); 125.1 (C); 127.0 (CH); 128.0 (C); 128.4 (CH); 128.8 (C); 129.2 (CH); 130.7 (CH); 136.1 (C); 137.3 (C); 138.2 (CH); 145.2 (CH); 147.6 (CH); 150.4 (C); 151.1 (CH).
Inclusion complex (20)$_2$⊂6a·6NO$_3$

\[ \text{Inclusion complex (20)$_2$⊂6a·6NO}_3 \]

$^1$H NMR (500 MHz, D$_2$O) $\delta$: 2.98 (8H, m); 5.28 (4H, br m); 5.52 (4H, br m); 6.01 (4H, s); 7.75 (4H, d, $J = 9.1$ Hz); 7.99 (16H, m); 9.06 (4H, d, $J = 7.0$ Hz); 9.45 (4H, s); 9.82 (4H, s); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$: 46.7 (CH$_2$); 46.8 (CH$_2$); 65.8 (CH$_2$); 101.7 (CH); 106.3 (CH); 115.8 (CH); 117.0 (C); 121.6 (CH); 122.5 (C); 123.6 (C); 124.6 (CH); 125.0 (C); 126.5 (CH); 127.0 (C); 127.6 (C); 128.5 (CH); 128.8 (CH); 130.4 (CH); 135.9 (C); 137.0 (C); 137.8 (CH); 147.5 (CH); 148.5 (C); 150.5 (C); 151.2 (CH).

Inclusion complex (21)$_2$⊂6a·6NO$_3$

$^1$H NMR (500 MHz, D$_2$O, 338 K) $\delta$: 3.35-3.42 (8H, m); 4.11-4.29 (24H, m); 4.46 (8H, m); 6.50 (4H, s); 6.78 (8H, m); 7.10 (8H, m); 8.23 (4H, d, $J = 9.5$ Hz); 8.33 (4H, d, $J = 8.3$ Hz); 8.41 (8H, m); 8.49 (4H, d, $J = 6.6$ Hz); 9.60 (4H, d, $J = 6.2$ Hz); 9.95 (4H, s); 10.25 (4H, s).
**Figure S1:** Superposed DOSY (CD$_3$NO$_2$, 500 MHz, 298 K) experiment of: a) 1.25 mM solution of 3·4OTf·4PF$_6$ (blue). b) 2.5 mM solution of ligand 1·2PF$_6$ (yellow).
1-(4-(pyridin-4-yl)benzyl)-2,7-diazapyren-1-ium hexafluorophosphate (4·PF₆)

Figure S2: ¹H NMR (CD₃NO₂, 500 MHz) spectrum of 4·PF₆.

Figure S3: ¹³C NMR (CD₃NO₂, 125 MHz) spectrum of 4·PF₆.
Figure S4: HSQC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 4-PF$_6$.

Figure S5: HMBC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 4-PF$_6$.
Figure S6: COSY (CD$_3$NO$_2$, 500 MHz) spectrum of 4·PF$_6$. 
1-(4-(pyridin-4-yl)benzyl)-2,7-diazapyren-1-ium nitrate (4·NO₃)

Figure S7: $^1$H NMR (D₂O, 500 MHz) spectrum of 4·NO₃

Figure S8: $^{13}$C NMR (D₂O, 125 MHz) spectrum of 4·NO₃.
Figure S9: HSQC (D$_2$O, 500 and 125 MHz) spectrum of 4·NO$_3$.

Figure S10: HMBC (D$_2$O, 500 and 125 MHz) spectrum of 4·NO$_3$. 
Figure S11: COSY (D$_2$O, 500 MHz) spectrum of 4-NO$_3$. 
Metalloycles 6a,b·6NO₃

Figure S12: ¹H NMR (D₂O, 500 MHz) spectrum of 6a,b·6NO₃

Figure S13: ¹³C NMR (D₂O, 125 MHz) spectrum of 6a,b·6NO₃.
Figure S14: HSQC (D$_2$O, 500 and 125 MHz) spectrum of 6a,b·6NO$_3$.

Figure S15: HMBC (D$_2$O, 500 and 125 MHz) spectrum of 6a,b·6NO$_3$. 
**Figure S16**: COSY (D$_2$O, 500 MHz) spectrum of 6a,b·6NO$_3$. 
Figure S17: $^1$H NMR (D$_2$O, 300 MHz) spectra of 6a,b·6NO$_3$ at different concentrations: a) 2.5 mM. b) 1 mM. c) 0.25 mM.

Figure S18: Superposed DOSY (D$_2$O, 500 MHz, 298 K) experiments of: a) 10 mM solution of 4·NO$_3$ and 5a. b) 10 mM solution of 4·NO$_3$. c) 5a.
Metalocycles 6a,b·6PF₆

Figure S19: $^1$H NMR (CD₃NO₂, 500 MHz) spectrum of 6a,b·6PF₆

Figure S20: $^{13}$C NMR (CD₃NO₂, 125 MHz) spectrum of 6a,b·6PF₆
Figure S21: HSQC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 6a,b·6PF$_6$

Figure 22: HMBC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 6a,b·6PF$_6$
Figure S23: COSY (CD$_3$NO$_2$, 500 MHz) spectrum of 6a,b·6PF$_6$. 
Metalocycles 7a,b·6PF₆

Figure S24: $^1$H NMR (CD$_3$NO$_2$, 500 MHz) spectrum of 7a,b·6PF₆.

Figure S25: $^{13}$C NMR (CD$_3$NO$_2$, 125 MHz) spectrum of 7a,b·6PF₆.
Figure S26: HSQC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 7a,b·6PF$_6$.

Figure S27: HMBC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 7a,b·6PF$_6$. 
Figure S28: COSY (CD$_3$NO$_2$, 500 MHz) spectrum of 7a,b·6PF$_6$.

Figure S29: Superposed DOSY (CD$_3$NO$_2$, 500 MHz, 298 K) experiments of: a) metalloycles 7a,b·6PF$_6$ (blue). b) ligand 4 PF$_6$ (yellow).
Figure S30: Observed (top) and theoretical (bottom) isotopic distribution for fragment \([7a,b - 3\text{PF}_6]^{3+}\) (exp. m/z = 563.0843, theoretical m/z = 563.0860).
Metalocycles 7a,b·6NO₃

Figure S31: ¹H NMR (D₂O, 500 MHz) spectrum of 7a,b·6NO₃.

Figure S32: ¹³C NMR (D₂O, 125 MHz) spectrum of 7a,b·6NO₃.
Figure S33: HSQC (D$_2$O, 500 and 125 MHz) spectrum of 7a,b·6NO$_3$.

Figure S34: HMBC (D$_2$O, 500 and 125 MHz) spectrum of 7a,b·6NO$_3$. 
Figure S35: COSY (D$_2$O, 500 MHz) spectrum of 7a,b·6NO$_3$.

Figure S36: Superposed DOSY (D$_2$O, 500 MHz, 298 K) experiments of: a) metalocycles 7a,b·6NO$_3$ (blue). b) ligand 4·NO$_3$ (yellow).
Pseudorotaxane 1·2PF₆⊂8

Figure S37: $^1$H NMR (CD₃NO₂, 500 MHz) spectrum of 1·2PF₆⊂8.

Figure S38: $^{13}$C NMR (CD₃NO₂, 500 MHz) spectrum of 1·2PF₆⊂8.
Figure S39: $^1$H NMR (CD$_3$NO$_2$, 500 MHz) spectrum of 1·2PF$_6$⊂9.

Figure S40: $^{13}$C NMR (CD$_3$NO$_2$, 500 MHz) spectrum of 1·2PF$_6$⊂9.
Catenane 3(8)$_2$·4OTf·4PF$_6$

**Figure S41**: $^1$H NMR (CD$_3$NO$_2$, 500 MHz) spectrum of 3(8)$_2$·4OTf·4PF$_6$.

**Figure S42**: $^{13}$C NMR (CD$_3$NO$_2$, 125 MHz) spectrum of 3(8)$_2$·4OTf·4PF$_6$. 
Figure S43: HSQC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 3(8)$_2$·4OTf·4PF$_6$.

Figure S44: HMBC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 3(8)$_2$·4OTf·4PF$_6$. 
**Figure S45**: COSY (CD$_3$NO$_2$, 500 MHz) spectrum of $3(8)_2$·4OTf·4PF$_6$. 
Catenane \(3(9)_2\cdot4\text{OTf}\cdot4\text{PF}_6\)

**Figure S46**: \(^1\text{H NMR (CD}_3\text{NO}_2, 500\text{ MHz, }298\text{ K) spectrum of }3(9)_2\cdot4\text{OTf}\cdot4\text{PF}_6.\)**
Catenane $6a(8)_2 \cdot 6PF_6$

**Figure S47:** $^1H$ NMR (CD$_3$NO$_2$, 500 MHz) spectrum of $6a(8)_2 \cdot 6PF_6$.

**Figure S48:** $^{13}C$ NMR (CD$_3$NO$_2$, 500 y 125 MHz) spectrum of $6a(8)_2 \cdot 6PF_6$. 

S43
Figure S49: HSQC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 6a(8)$_2$·6PF$_6$.

Figure S50: HMBC (CD$_3$NO$_2$, 500 and 125 MHz) spectrum of 6a(8)$_2$·6PF$_6$. 
Figure S51: COSY (CD$_3$NO$_2$, 500 MHz) spectrum of 6a(8)$_2$·6PF$_6$.

Figure S52: Partial $^{13}$C NMR (CD$_3$NO$_2$, 125 MHz) spectra of: (a) ligand 4·PF$_6$, (b) metalloccycles 6a,b·6PF$_6$, and (c) catenane 6a(8)$_2$·6PF$_6$. Peak labels are defined in Scheme 1.
**Figure S53:** Superposed DOSY (CD$_3$NO$_2$, 500 MHz, 298 K) experiment of: a) 5 mM solution of 6a(8):6PF$_6$ (blue). b) 5 mM solution of 6a,b·6PF$_6$ (yellow). c) 10 mM solution of ligand 4·PF$_6$ (blue).

**Figure S54:** Partial EXSY (CD$_3$NO$_2$, 500 MHz, 298 K) spectrum showing the correlation between HQ$_{out}$ and HQ$_{in}$.
Catenane 6a(9)$_2$·6PF$_6$

Figure S55: $^1$H NMR (CD$_3$NO$_2$, 500 MHz, 298 K) spectrum of 6a(9)$_2$·6PF$_6$. 
Catenane 7a(8)$_2$·6PF$_6$

**Figure S56:** $^1$H NMR (CD$_3$NO$_2$, 500 MHz) spectrum of 7a(8)$_2$·6PF$_6$.

**Figure S57:** $^{13}$C NMR (CD$_3$NO$_2$, 125 MHz) spectrum of 7a(8)$_2$·6PF$_6$. 
Catenane $7a(9)_2 \cdot 6\text{PF}_6$

Figure S58: $^1$H NMR (CD$_3$NO$_2$, 500 MHz) spectrum of $7a(9)_2 \cdot 6\text{PF}_6$. 
Inclusion complex (10)⊂6a·6NO₃

Figure S59: ^1^H NMR (D₂O, 500 MHz) spectrum of (10)⊂6a·6NO₃

Figure S60: ^1^C NMR (D₂O, 125 MHz) of (10)⊂6a·6NO₃.
Inclusion complex (11)$_2$·6a·6NO$_3$

Figure S61: $^1$H NMR (D$_2$O, 500 MHz) spectrum of (11)$_2$·6a·6NO$_3$.

Figure S62: $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of (11)$_2$·6a·6NO$_3$.  

R = CH$_2$CH$_2$OCH$_2$CH$_2$OH
Figure S63: HSQC (D$_2$O, 500 and 125 MHz) spectrum of (11)$_2$$·$6a·6NO$_3$.

Figure S64: HMBC (D$_2$O, 500 and 125 MHz) spectrum of (11)$_2$$·$6a·6NO$_3$. 
Figure S65: COSY (D$_2$O, 500 MHz) spectrum of (11)$_2$·6a·6NO$_3$. 

R = CH$_2$CH$_2$OCH$_2$CH$_2$OH
Inclusion complex \((13)_2 \subset 6a \cdot 6NO_3\)

\[ R = CH_2CH_2OCH_2CH_2OH \]

**Figure S66:** \(^1\)H NMR (D\(_2\)O, 500 MHz) spectrum of \((13)_2 \subset 6a \cdot 6NO_3\)

**Figure S67:** \(^{13}\)C NMR (D\(_2\)O, 125 MHz) spectrum of \((13)_2 \subset 6a \cdot 6NO_3\)
Inclusion complex (14)$_2$:6a·6NO$_3$

**Figure S68:** $^1$H NMR (D$_2$O, 500 MHz) spectrum of (14)$_2$:6a·6NO$_3$.

**Figure S69:** $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of (14)$_2$:6a·6NO$_3$. 
Figure S70: HSQC (D$_2$O, 500 and 125 MHz) spectrum of (14)$_2$$\subset$6a·6NO$_3$.

Figure S71: HMBC (D$_2$O, 500 and 125 MHz) spectrum of (14)$_3$$\subset$6a·6NO$_3$. 
Figure S72: COSY (D$_2$O, 500 MHz) spectrum of (14)$_2$$\subset$6a$\cdot$6NO$_3$. 
Inclusion complex (15)$_2$·6a·6NO$_3$

**Figure S73:** $^1$H NMR (D$_2$O, 500 MHz, 298 K) spectrum of (15)$_2$·6a·6NO$_3$.

**Figure S74:** $^1$H NMR (D$_2$O, 300 MHz, 353 K) spectrum of (15)$_2$·6a·6NO$_3$. 
Inclusion complex $(16)_2\subset6a\cdot6\text{NO}_3$

Figure S75: $^1\text{H}$ NMR (D$_2$O, 500 MHz) spectrum of $(16)_2\subset6a\cdot6\text{NO}_3$.

Figure S76: $^{13}\text{C}$ NMR (D$_2$O, 125 MHz) spectrum of $(16)_2\subset6a\cdot6\text{NO}_3$. 
Inclusion complex (17)$_2$·6a·6NO$_3$

$R = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$

Figure S77: $^1$H NMR (D$_2$O, 500 MHz) spectrum of de (17)$_2$·6a·6NO$_3$.

Figure S78: $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of (17)$_2$·6a·6NO$_3$. 

S60
Figure S79: DOSY (D$_2$O, 500 MHz, 298 K) experiment of inclusion complex (17)$_2\subset$6a·6NO$_3$. 
Inclusion complex \((18)_2 \subset 6a \cdot 6NO_3\)

**Figure S80:** \(^1H\) NMR (D\(_2\)O, 500 MHz) spectrum of \((18)_2 \subset 6a \cdot 6NO_3\).

**Figure S81:** \(^{13}C\) NMR (D\(_2\)O, 125 MHz) spectrum of \((18)_2 \subset 6a \cdot 6NO_3\).
Inclusion complex (19)$_2$$\subset$6a·6NO$_3$

Figure S82: $^1$H NMR (D$_2$O, 500 MHz) spectrum of (19)$_2$$\subset$6a·6NO$_3$.

Figure S83: $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of (19)$_2$$\subset$6a·6NO$_3$. 
Inclusion complex $(20)_2 \subset 6a \cdot 6\text{NO}_3$

**Figure S84:** $^1\text{H NMR (D}_2\text{O, 500 MHz)}$ spectrum of $(20)_2 \subset 6a \cdot 6\text{NO}_3$.

**Figure S85:** $^{13}\text{C NMR (D}_2\text{O, 125 MHz)}$ spectrum of $(20)_2 \subset 6a \cdot 6\text{NO}_3$. 
Inclusion complex $(21)_2\subset 6a\cdot 6NO_3$

R = OCH₂CH₂OCH₂CH₂OH

**Figure S86**: $^1H$ NMR (D₂O, 300 MHz, 298 K) spectrum of $(21)_2\subset 6a\cdot 6NO_3$.

**Figure S87**: $^1H$ NMR (D₂O, 300 MHz, 338 K) spectrum of $(21)_2\subset 6a\cdot 6NO_3$. 

ORTEP X-ray structures

**Figure S88:** ORTEP drawing of the X-ray structure of ligand 1·2PF$_6$. The displacement ellipsoids are drawn for 50% probability. H atoms, counterions and solvent molecules are omitted for clarity.

**Figure S89:** ORTEP representation of the X-ray structure of 3(9)$_2$·4OTf·4PF$_6$ showing the 50% probability displacement ellipsoids. H atoms, counterions and solvent molecules are omitted for clarity.
Figure S90: ORTEP drawing of the solid state structure of catenane 6a(8)\textsubscript{2}·6PF\textsubscript{6} showing the 50% probability displacement ellipsoids. H atoms, counterions and solvent molecules are omitted for clarity.
UV-Vis and fluorescence spectra

Figure S91: UV-Vis absorption spectra of ligands 1·2PF₆ (1.0×10⁻⁴ mM), 4·PF₆ (1.0×10⁻⁴ M) and 4·NO₃ (1.0×10⁻⁴ mM).

Figure S92: Charge transfer band region of the UV-Vis spectra (CH₃CN) of ligand 1·2PF₆ and pseudorotaxanes 1·2PF₆⊂8 and 1·2PF₆⊂9.

Figure S93: UV-Vis spectra (CH₃NO₂, optical path length 1.0 mm) of metallocycle 3·4OTf·4PF₆ and catenanes 3(8)₂·4OTf·4PF₆ and 3(9)₂·4OTf·4PF₆. Inset: detail of the charge transfer band region (450-650 nm).
**Figure S94:** Fluorescence emission spectra (solid lines) and excitation spectra (dashed lines) (293 K) of ligands $1\cdot2\text{PF}_6$ ($1.0\times10^{-4}$ mM), $4\cdot\text{PF}_6$ ($1.0\times10^{-4}$ mM) and $4\cdot\text{NO}_3$ ($1.0\times10^{-4}$ mM).

**Figure S95:** Fluorescence emission spectra (solid lines) and excitation spectra (dashed lines) ($\text{CH}_3\text{NO}_2$, 293 K) of ligand $1\cdot2\text{PF}_6$ ($1.0\times10^{-4}$ M), metallocycle $3\cdot4\text{OTf}\cdot4\text{PF}_6$ ($5.0\times10^{-5}$ M) and catenanes $3(8)\cdot4\text{OTf}\cdot4\text{PF}_6$ ($5.0\times10^{-5}$ M) and $3(9)\cdot4\text{OTf}\cdot4\text{PF}_6$ ($5.0\times10^{-5}$ M).

**Figure S96:** Fluorescence emission spectra (solid lines) and excitation spectra (dashed lines) ($\text{H}_2\text{O}$, 293 K) of metallocycles $6\mathbf{a,b}\cdot\text{NO}_3$ ($5.0\times10^{-5}$ M) and inclusion complexes $(11)_2\subset6\mathbf{a}\cdot\text{6NO}_3$ ($5.0\times10^{-5}$ mM) and $(15)_2\subset6\mathbf{a}\cdot\text{6NO}_3$ ($5.0\times10^{-5}$ M).
Determination of binding constant ($K_a$) between 1·2PF$_6$ and DN38C10 (9) by UV/Vis titration method.

A 0.5 mM solution of host 9 in acetonitrile and a solution of guest 1·2PF$_6$ (6 mM) and host 9 (0.5 mM) in acetonitrile were separately prepared. Then, aliquots of the guest/host solution (initially 10 µL, then 20 µL; 50 µL and, finally 100 µL) were added to the host solution (2 mL), recording the spectrum of the mixture after each addition (overall 35 points). The association constants were determined by using the nonlinear least squares fitting of the titration curves plotting the corrected $A$ ($\varepsilon_{1·2PF_6} = 101.7$ L mol$^{-1}$ at 470 nm) of the host-guest complex charge-transfer band against the concentration of the corresponding guest. The titration curve fits perfectly to the 1:1 binding isotherm ($R^2 = 0.999$).

Temperature: 298 K

$\lambda_{\text{max}} = 470$ nm

$K_a = 4268 \pm 124$ M$^{-1}$
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13 SHELX-97, Release 97-2; G. M. Sheldrick, University of Göttingen, Germany, 1997.