

A Dual-Functional Tetrakis-Imidazolium Macrocyclic for Supramolecular Assembly – Supplementary Information

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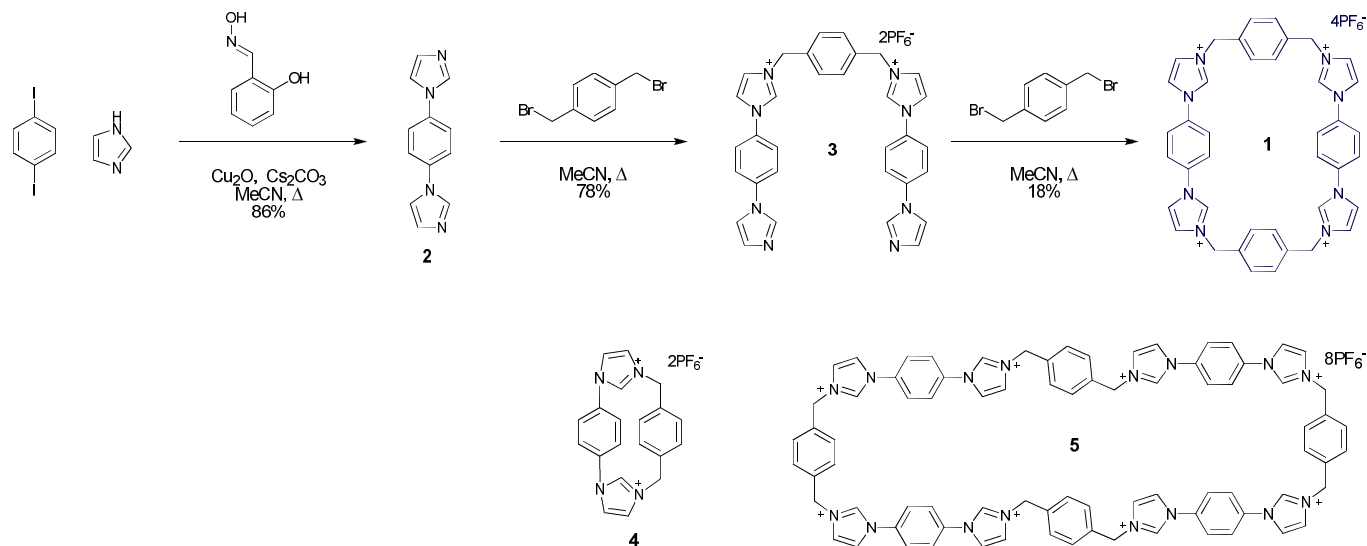
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Synthesis and Characterisation

General Information:

NMR spectra were recorded on a Varian Mercury 300 spectrometer with ^1H NMR operating at 300 MHz, and ^{13}C at 75.5 MHz. Mass spectra were recorded on a Bruker microTOF spectrometer. H_2O was de-ionised and microfiltered using a Milli-Q[®] Millipore machine. 5 All other solvents and commercial grade reagents were used without further purification.



Scheme S1 – Synthesis of macrocycle 1

10

1,4-Di(1H-imidazol-1-yl)benzene (2).¹

1,4-Diiodobenzene (6.60 g, 20 mmol), imidazole (3.41 g, 50 mmol), Cs_2CO_3 (19.55 g, 60 mmol), Cu_2O (0.29 g, 2.0 mmol), and salicylaldehyde (1.10 g, 8.0 mmol) were added to dry, degassed acetonitrile (250 ml) and heated to reflux under a nitrogen atmosphere for two nights. After cooling, CH_2Cl_2 (200 ml) was added and, after vigorous stirring, the mixture was filtered through celite. The filtrate was retained and its solvent evaporated *in vacuo*. The resultant residue was triturated three times with diethyl ether (100 ml), giving **61** as a pale orange powder (3.61 g, 86 %). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.34 (2H, br, *ImH*), 7.83 (2H, br, *ImH*), 7.82 (4H, s, *ArH*), 7.13 (2H, br, *ImH*); ESMS: m/z calc. for $[\text{M} + \text{H}]^+$ 211.09 found 211.09; mp 178 °C.

Bis-imidazolium macrocycle precursor 3.

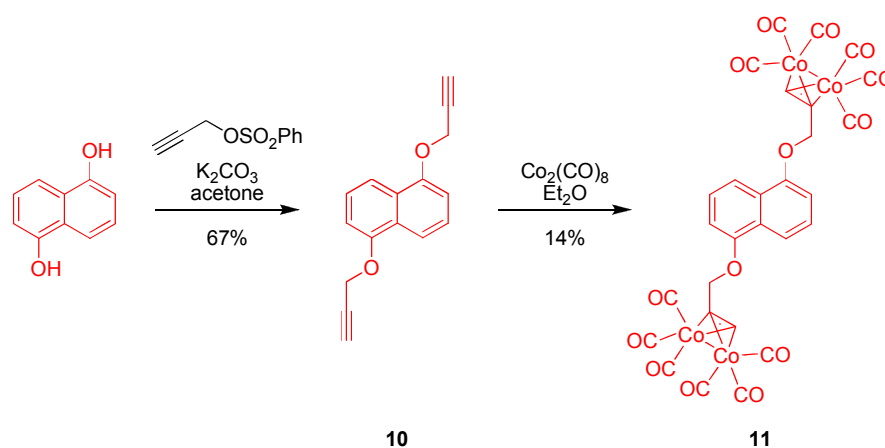
20 Compound **61** (2.00 g, 9.51 mmol) was dissolved in dry acetonitrile (50 ml) and brought to reflux under a nitrogen atmosphere. α,α' -Dibromoxylene (0.50 g, 1.89 mmol) dissolved in dry acetonitrile (100 ml) was added dropwise over the course of an hour to the refluxing solution, which was heated for a further hour. A precipitate formed which was collected (after cooling the solution to room temperature) and washed with acetonitrile (evaporation of the filtrate recovered excess **61**). The solid was dissolved in hot water (100 ml), and NH_4PF_6 (aq, sat.) was added to precipitate **62** as a yellow-orange powder (1.20 g, 78 %). ^1H NMR (300 MHz, acetone- d_6) δ 9.81 (2H, br, *ImH*), 8.31 (4H, m, *ImH*), 8.15 (2H, s, *ImH*), 8.03 (6H, m, *ArH*, *ImH*), 7.80 (2H, br, *ImH*), 7.74 (4H, m, *ArH*), 7.25 (2H, br, *ImH*), 5.78 (4H, s, CH_2); ^{13}C NMR (125 MHz, acetonitrile- d_3) δ 136.0, 135.4, 130.6, 125.4, 125.2, 124.1, 123.7, 123.4, 118.3, 53.7; HR-ESMS: m/z calc. for $[\text{M} - \text{PF}_6]^+$ 669.2073 found 669.2075; mp 228 °C.

Tetrakis-imidazolium macrocycle 1.

30 Compound **62** (2.40 g, 2.95 mmol) was dissolved in dry acetonitrile (600 ml) and brought to reflux under a nitrogen atmosphere. α,α' -Dibromoxylene (0.77 g, 2.95 mmol) dissolved in dry acetonitrile (600 ml) was added via a dropping funnel over three hours. The reaction mixture was then refluxed for a further three nights. A precipitate developed, which was collected by filtration after cooling, and consisted primarily of the side product **63**. The solvent was removed from the filtrate *in vacuo*, and acetone (200 ml) was used to triturate the remaining pale yellow residue, resulting in a white suspension. The solids were collected by filtration (the acetone filtrate contained 35 more side products) and dissolved in hot water (50 ml) before being precipitated by the addition of NH_4PF_6 (aq, sat.), giving pure **60** as a white powder (0.63 g, 18 %). ^1H NMR (300 MHz, acetone- d_6) δ 9.13 (4H, br, *ImH*), 8.31 (8H, m, *ImH*), 7.93 (8H, s, *ArH*), 7.72 (8H, s, *ArH*), 5.75 (8H, s, CH_2); ^{13}C NMR (75 MHz, acetonitrile- d_3) δ 137.3, 135.8, 132.3, 126.1, 123.4, 118.9, 55.0; HR-ESMS: m/z calc. for $[\text{M} - \text{PF}_6]^+$ 1063.1983 found 1063.1989; mp > 300 °C.

Bis-imidazolium side product 4.

^1H NMR (300 MHz, acetone- d_6) δ 9.83 (2H, br, *ImH*), 8.33 (2H, br, *ImH*), 8.16 (4H, s, *ArH*), 8.02 (2H, br, *ImH*), 7.72 (4H, s, *ArH*), 5.77 (4H, s, CH_2); ^{13}C NMR (125 MHz, acetonitrile- d_3) δ 136.2, 135.3, 130.6, 125.4, 124.3, 123.4, 118.3, 53.8; HR-ESMS: m/z calc. for $[\text{M} - \text{H} - 2\text{PF}_6]^+$ 313.1453 found 313.1443; mp 257 °C (decomp.).



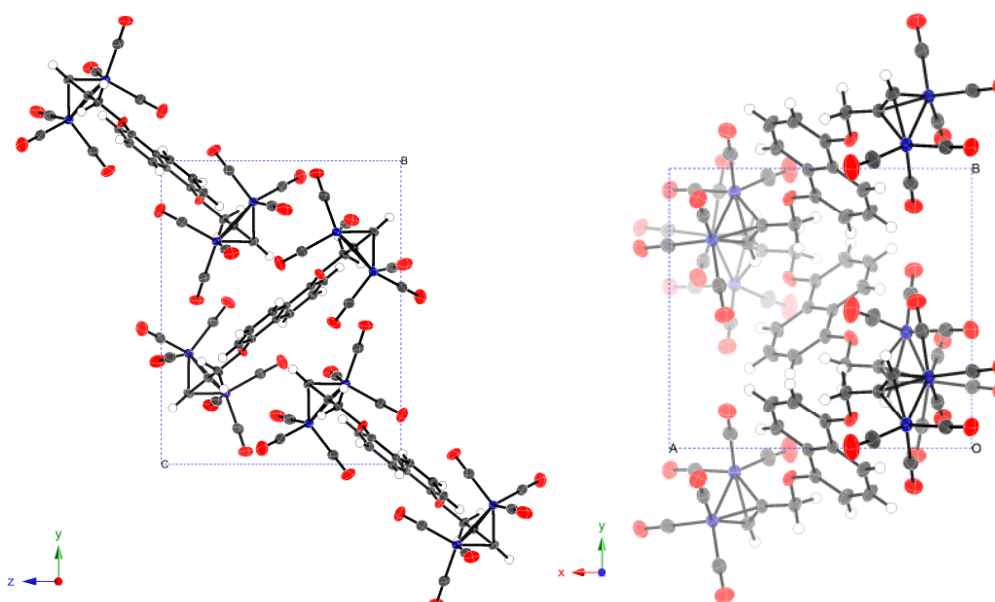
Scheme S2 – Synthesis of 11

1,5-Dihydroxynaphthalene bis(propargyl) ether (10).

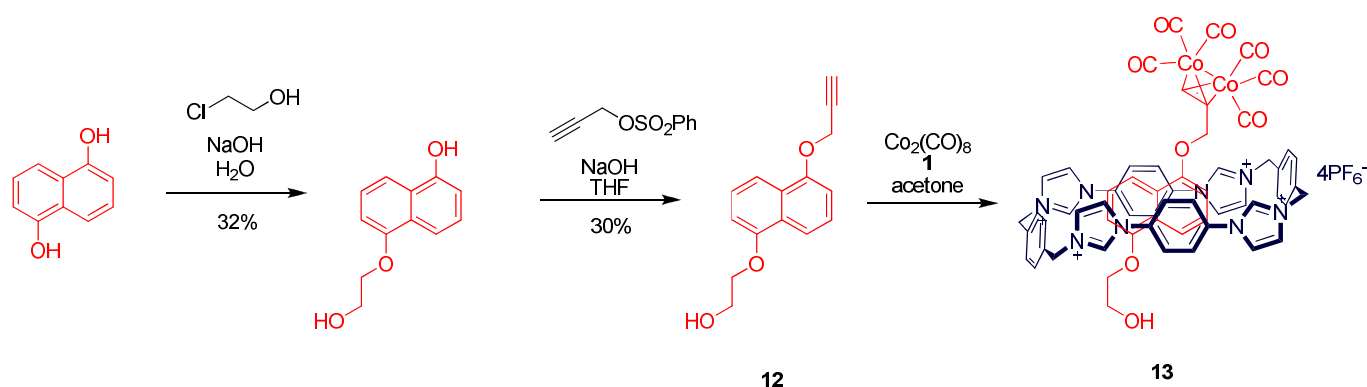
5 1,5-Dihydroxynaphthalene (0.53 g, 3.3 mmol), propargyl benzenesulphonate (1.62 g, 8.3 mmol), and K_2CO_3 (1.14 g, 8.3 mmol) were added to acetone (50 ml) and the mixture was refluxed overnight. After cooling, the solids were removed by filtration and washed with acetone (20 ml). The solvent was removed and the residue purified by silica gel column chromatography eluted with 9:1 hexane/ethyl acetate, giving pure **70** as a beige powder (0.52 g, 67 %). 1H NMR (300 MHz, acetone- d_6) δ (ppm) 7.91 (2H, d, $^3J = 8.5$ Hz, ArH), 7.40 (2H, dd, $^3J = 8.5$, 7.6 Hz, ArH), 6.99 (2H, d, $^3J = 7.6$ Hz, ArH), 4.90 (4H, d, $^4J = 2.3$ Hz, CH_2), 2.55 (2H, t, $^4J = 2.3$ Hz, $C\equiv CH$); ^{13}C NMR (75 MHz, acetone- d_6) δ (ppm) 206.6, 128.3, 126.4, 115.9, 107.7, 80.0, 77.5, 57.1; ESMS: m/z calc. for $[M + H]^+$ 237.09, found 237.09; mp 108 °C.

1,5-Dihydroxynaphthalene bis(propargyl) ether dicobalt hexacarbonyl complex (11).

15 Compound **70** (0.040 g, 0.17 mmol) was dissolved in dry, degassed, diethyl ether (25 ml), and $Co_2(CO)_8$ (0.23 g, 0.68 mmol) was added in one portion. The solution was stirred for three hours under a nitrogen atmosphere, after which it was exposed to the air. Slow precipitation of grey, agglomerated bulk cobalt was observed, and the mixture was filtered to eliminate this. The solvent was removed *in vacuo*, giving a $70 \cdot 2[Co_2(CO)_6]$ as a red crystalline solid (0.019 g, 14 %). 1H NMR (300 MHz, acetone- d_6) δ (ppm) 8.01 (2H, d, $^3J = 8.2$ Hz, ArH), 7.40 (2H, dd, $^3J = 8.2$, 7.6 Hz, ArH), 7.13 (2H, d, $^3J = 7.6$ Hz, ArH), 6.65 (2H, s, $C=CH$), 5.54 (4H, s, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 199.3, 153.8, 126.8, 125.0, 115.0, 105.7, 89.2, 72.1, 68.8; ESMS: not, found (decomposition likely); mp 100-20 °C (decomp.). Slow evaporation of an acetone solution of **11** yielded two polymorphic crystal structures.



25 **Figure S1** – X-ray crystal structures of the two polymorphs of **11**. Thermal ellipsoids shown at 50 % probability.



Scheme S3 – Synthesis of pseudorotaxane **13**

5-(2-Hydroxyethoxy)naphthalen-1-ol.

Sodium hydroxide (5.00 g, 0.125 mol) was dissolved in water (50 ml). 1,5-Dihydroxynaphthalene (2.50 g, 15.6 mmol) and 2-chloroethanol (3.75 g, 46.8 mmol) were added, and the solution was refluxed for four hours. After cooling, the mixture was acidified by the addition of 1M HCl (aq), and then extracted with CH₂Cl₂ (3 x 50 ml). The organic layers were combined and concentrated, after which the residue was purified by silica gel column chromatography eluted with 1:1 ethyl acetate/hexane giving **14** as a beige powder (1.03 g, 32 %). ¹H NMR (300 MHz, CDCl₃) δ 7.82 (2H, m, ArH), 7.38 (2H, m, ArH), 6.88 (2H, m, ArH), 4.28 (2H, t, ³J = 4.6 Hz, CH₂), 4.10 (2H, t, ³J = 4.6 Hz, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ: 154.6, 153.0, 127.3, 126.3, 125.8, 125.0, 115.1, 113.6, 109.3, 105.8, 69.9, 61.4; ESMS: *m/z* calc. for [M + H]⁺ 205.08 found 205.12; mp 150 °C.

1,5-Dihydroxynaphthalene 2-hydroxyethyl propargyl ether (**12**).

Propargyl benzenesulfonate (0.79 g, 4.03 mmol), and NaOH (0.16 g, 4.03 mmol) were added to THF (50 ml), and the mixture was heated to reflux. Compound **14** (0.25 g, 1.22 mmol) was added in one portion, and the reaction was refluxed for the further 18 hours. After cooling, the solvent was evaporated and the residue was dissolved in diethyl ether (50 ml) and washed with water (3 x 50 ml). The solvent was removed from the organic portion, and the crude product purified using silica gel column chromatography eluted with 25:1 CH₂Cl₂/MeOH, giving **12** as a beige powder (0.09 g, 30 %). ¹H NMR (300 MHz, CDCl₃) δ 7.90 (2H, m, ArH), 7.40 (2H, m, ArH), 7.00 (1H, d, ³J = 7.0 Hz, ArH), 6.88 (1H, d, ³J = 7.3 Hz, ArH), 4.90 (2H, d, ⁴J = 2.3 Hz, CH₂), 4.28 (2H, t, ³J = 4.6 Hz, CH₂), 4.11 (2H, t, ³J = 4.6 Hz, CH₂), 2.56 (1H, t, ⁴J = 2.3 Hz, C=CH); ¹³C NMR (125 MHz, 20:1 CDCl₃/CD₃OD) δ 154.1, 153.0, 126.6, 125.2, 124.8, 114.9, 114.5, 106.2, 105.7, 78.5, 75.5, 69.5, 61.0, 58.1; ESMS: *m/z* calc. for [M + H]⁺ 243.1 found 243.1; mp 116 °C.

Pseudorotaxane **13**.

Macrocycle **1** (11.0 mg, 9.1 x 10⁻⁶ mol) and compound **12** (2.95 mg, 1.22 x 10⁻⁵ mol) were dissolved in dry, degassed acetone (5 ml). Co₂(CO)₈ (12.4 mg, 3.6 x 10⁻⁵ mol) was added in one portion, and the solution was stirred overnight under a nitrogen atmosphere. Agglomerated cobalt was removed by filtration, and slow evaporation of the solvent yielded crystals suitable for X-ray structural analysis. ¹H NMR (300 MHz, acetone-d₆) δ 9.97 (4H, s, ImH), 9.12 (8H, m, ImH), 8.73 (2H, m, NaphthH), 8.65 (8H, s, ArH), 8.60 (8H, s, ArH), 8.14 (2H, m, NaphthH), 7.88 (2H, m, NaphthH), 7.49 (1H, s, C=CH), 6.60 (8H, s, ImCH₂), 6.37 (2H, s, CH₂C=CH), 5.08 (2H, t, ³J = 4.7 Hz, CH₂), 4.89 (2H, t, ³J = 4.7 Hz, CH₂). **Thread:** ¹H NMR (200 MHz, acetone-d₆) δ 7.95 (2H, br, NaphthH), 7.38 (2H, br, NaphthH), 7.11 (1H, br, NaphthH), 6.99 (1H, br, NaphthH), 6.63 (1H, br, C=CH), 5.51 (2H, br, CH₂C=CH), 4.24 (2H, br, CH₂), 4.03 (2H, br, CH₂); ¹³C NMR (125 MHz, acetone-d₆) δ 208.2, 200.9, 155.5, 154.7, 127.7, 126.1, 125.7, 115.7, 114.9, 106.7, 106.4, 73.6, 71.0, 69.5, 61.4.

Crystallography

35

Single crystal X-ray diffraction data were collected using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer, or in the case of macrocycle **5** using silicon double crystal monochromated synchrotron radiation ($\lambda = 0.68890$ Å) at Diamond Light Source beamline I19 on a custom built Rigaku diffractometer. Both diffractometers were equipped with a Cryostream N₂ open-flow cooling device,² and the data were collected at 150(2) K or 100(2) K.

40 If using the Nonius machine, series of ω -scans were performed in such a way as to collect every independent reflection to a maximum resolution of 0.77 Å, aiming for 99.5 % completeness. Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package.³

When using synchrotron radiation, ω -scans were performed such that a half-sphere of data was collected to a maximum resolution of 0.77 Å. Cell refinement, data reduction, and scaling were performed using the CrystalClear package.⁴

45 The structures were solved by direct methods using the SIR92 software⁵ or by charge flipping using Superflip.⁶ The structures were refined using full-matrix least-squares on F² or F within the CRYSTALS suite.⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters, unless specified otherwise. Disordered portions were modelled using refined partial occupancies. Geometric and vibrational restraints were applied where appropriate to ensure physically reasonable models. The H atoms were usually located in the difference map, but those attached to carbon atoms were repositioned geometrically. Protic H atoms which could not be located in the difference map were positioned to satisfy hydrogen bonding requirements. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C-H in the range 0.93-0.98 Å, N-H in the range 0.86-0.89 Å, and O-H = 0.82 Å and isotropic displacement factors in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

50 In some cases (**5**, **1**.Acetone I, and **11**) the molecular structure within solvent voids could not be resolved in the difference map, and PLATON SQUEEZE^{8,9} was used to account for the residual electron density in the refinement.

After the construction of a stable, physically reasonable, and complete model, the weights were optimised,^{10, 11} anomalous reflections were omitted, and absent high-angle data (in the case of poorly diffracting samples) was pruned using the Wilson plot. This generally led to convergence of the refinement, giving the final structure.

For the **11** in which the refinement did not converge immediately, initially half-shifts, then restraints, and finally rigid body refinement were used to overcome this problem.

IUCr CheckCIF/PLATON was used to validate the structures, and warnings were dealt with as appropriate or justified using validation reply forms.

Selected crystallographic data are presented in Tables S1-S3, and complete data, including particular refinement details where appropriate are presented in CIF format online.

10 Table S1 Selected crystallographic data

Compound reference	5	1.MeCN	1.Acetone I	1.H₂O
Chemical formula	C ₈₀ H ₇₂ N ₁₆ •8(F ₆ P)•2(CHCl ₃)	C ₄₀ H ₃₆ N ₈ •C ₄ H ₆ N ₂ •4(F ₆ P)	C ₄₀ H ₃₆ N ₈ •2(C ₃ H ₆ O)•4(F ₆ P)	C ₄₀ H ₃₆ N ₈ •4(F ₆ P)•6(H ₂ O)
Formula Mass	2656.01	1290.73	1324.80	1316.72
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
<i>a</i> /Å	10.061(10)	9.8471(2)	23.7695(4)	8.2914(2)
<i>b</i> /Å	10.107(9)	11.4921(2)	11.2232(2)	19.8515(4)
<i>c</i> /Å	30.25(3)	12.2245(2)	24.0588(5)	16.9016(4)
<i>α</i> /°	94.45(3)	68.0681(10)	90	90
<i>β</i> /°	97.31(4)	89.3833(9)	114.5895(9)	97.5218(10)
<i>γ</i> /°	95.24(4)	85.0539(8)	90	90
Unit cell volume/Å ³	3026(5)	1278.13(4)	5836.11(19)	2758.01(11)
Temperature/K	100	150	150	150
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
No. of formula units per unit cell, <i>Z</i>	1	1	4	2
No. of reflections measured	38030	21390	39540	29821
No. of independent reflections	27918	5808	6634	6262
<i>R</i> _{int}	0.075	0.020	0.067	0.048
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.1042	0.0592	0.0766	0.0745
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1993	0.0679	0.1963	0.1946
Final <i>R</i> _{<i>I</i>} values (all data)	0.1182	0.0717	0.1201	0.0936
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.2124	0.0679	0.2254	0.2086

Table S2 Selected crystallographic data

Compound reference	1.Acetone II	1.DMF.H₂O	1.9	11
Chemical formula	C ₄₀ H ₃₆ N ₈ •4(C ₃ H ₆ O)•4(F ₆ P)	C ₄₀ H ₃₆ N ₈ •4(F ₆ P)•2(C ₃ H ₇ NO)•2(H ₂ O)	C ₄₀ H ₃₆ N ₈ •C ₂₀ H ₁₆ N ₂ O ₂ •4(F ₆ P)•2(C ₃ H ₆ O)	0.39(C ₄₁ H ₂₈ Co ₄ O ₁₈)•C ₄₀ H ₃₆ N ₈ •4(F ₆ P)
Formula Mass	1440.96	1390.85	1641.15	1620.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
<i>a</i> /Å	9.58970(10)	16.7324(3)	17.5254(2)	22.9688(10)
<i>b</i> /Å	10.4314(2)	20.1029(3)	12.73450(10)	18.0778(6)
<i>c</i> /Å	32.0723(5)	17.8841(3)	30.6082(4)	21.4031(7)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	97.2039(7)	108.4741(7)	90.6673(6)	90
<i>γ</i> /°	90	90	90	90
Unit cell volume/Å ³	3182.99(9)	5705.67(16)	6830.59(13)	8887.1(6)
Temperature/K	150	150	150	150
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 1 <i>c</i> 1	<i>I</i> <i>b</i> <i>a</i> <i>m</i>
No. of formula units per unit cell, <i>Z</i>	2	4	4	4
No. of reflections measured	27120	85501	20671	8504
No. of independent reflections	5760	13493	15120	4570
<i>R</i> _{int}	0.063	0.080	0.162	0.076
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0622	0.0742	0.0502	0.1542
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1357	0.1933	0.1190	0.1803
Final <i>R</i> _{<i>I</i>} values (all data)	0.0962	0.1162	0.0833	0.1821
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1538	0.2246	0.1591	0.1803

Table S3 Selected crystallographic data

Compound reference	1.Cl	1.N₃	1.BzO	1.AuCl₂.2Cl.PF₆
Chemical formula	C ₄₀ H ₃₆ N ₈ •C _{4.40} H _{10.28} N _{1.47} O _{1.47} •4(H ₂ O)•4(Cl)	C ₄₀ H ₃₆ N ₈ •2(H ₂ O)•4(N ₃)•1.29(C ₃ H ₆ O)•0.71(C ₃ H ₇ NO)	C ₄₀ H ₃₆ N ₈ •4(C ₇ H ₅ O ₂)•11.25(H ₂ O)	C ₄₀ H ₃₆ N ₈ •2(C ₃ H ₇ NO)•F ₆ P•AuCl ₂ •2(Cl)
Formula Mass	949.96	959.71	2631.86	1258.71
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
<i>a</i> /Å	10.19200(10)	8.01430(10)	9.1698(2)	34.1635(6)
<i>b</i> /Å	20.0159(3)	22.0345(3)	16.1629(3)	12.0970(2)
<i>c</i> /Å	24.1601(4)	13.2696(2)	23.2751(5)	12.7837(2)
<i>α</i> /°	90	90	101.4334(8)	90
<i>β</i> /°	90	93.0774(5)	93.1531(8)	106.8314(8)
<i>γ</i> /°	90	90	105.6044(9)	90
Unit cell volume/Å ³	4928.71(12)	2339.91(6)	3235.03(12)	5056.87(15)
Temperature/K	150	150	150	150
Space group	<i>Pcmb</i>	<i>P2₁/n</i>	<i>P1</i>	<i>C2/c</i>
No. of formula units per unit cell, <i>Z</i>	4	2	1	4
No. of reflections measured	44344	45230	42347	62641
No. of independent reflections	5738	5343	21249	5738
<i>R</i> _{int}	0.061	0.053	0.074	0.053
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0679	0.0553	0.0532	0.0378
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1932	0.1362	0.1244	0.0857
Final <i>R</i> _{<i>I</i>} values (all data)	0.1013	0.0820	0.0833	0.0508
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.2127	0.1487	0.1551	0.0914

Table S4 Selected crystallographic data

Compound reference	11 form I	11 form II
Chemical formula	C ₂₈ H ₁₂ Co ₄ O ₁₄	C ₂₈ H ₁₂ Co ₄ O ₁₄
Formula Mass	808.1272	808.13
Crystal system	Monoclinic	Monoclinic
<i>a</i> /Å	12.9114(3)	9.6916(2)
<i>b</i> /Å	10.3713(3)	13.8803(3)
<i>c</i> /Å	12.8078(3)	10.9660(3)
<i>α</i> /°	90	90
<i>β</i> /°	119.7800(12)	94.1530(10)
<i>γ</i> /°	90	90
Unit cell volume/Å ³	1488.57(7)	1471.30(6)
Temperature/K	150	150
Space group	<i>P121/c1</i>	<i>P21/n</i>
No. of formula units per unit cell, <i>Z</i>	2	2
No. of reflections measured	23475	15310
No. of independent reflections	3515	3330
<i>R</i> _{int}	0.047	0.030
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0277	0.0229
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.0663	0.0540
Final <i>R</i> _{<i>I</i>} values (all data)	0.0358	0.0278
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0702	0.0565

NMR Titrations

¹H NMR titrations were performed using a Varian Unity Plus 500 spectrometer. A solution of the intended guest species (10⁻⁵ mol in 0.10 ml solvent) was added in a stepwise fashion to a solution of macrocycle **1** (10⁻⁶ mol in 0.50 ml solvent) at 293 K. Spectra were measured and chemical shifts recorded at 22 titration points (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 equivalents of guest to host). Data from the titrations was used in Job plot-type analyses.¹² These plot χ_H against $\chi_H \cdot \Delta\delta$, where $\Delta\delta$ is the difference between the observed chemical shift of a specific proton and the chemical shift of the pure host, and χ_H is the mole fraction. The binding stoichiometry can then be inferred from the position of the maximum. The resulting titration data, along with the binding stoichiometry and estimates of binding constants and final chemical shifts, were entered into the WinEQNMR2¹³ programme to obtain stability constants. Iterations were then performed to provide the most accurate result. The archetypal peak movements for π -complexes and hydrogen bonded complexes are illustrated by the titrations of **1** with DHN (**7**) and TBA chloride respectively (Fig. S1).

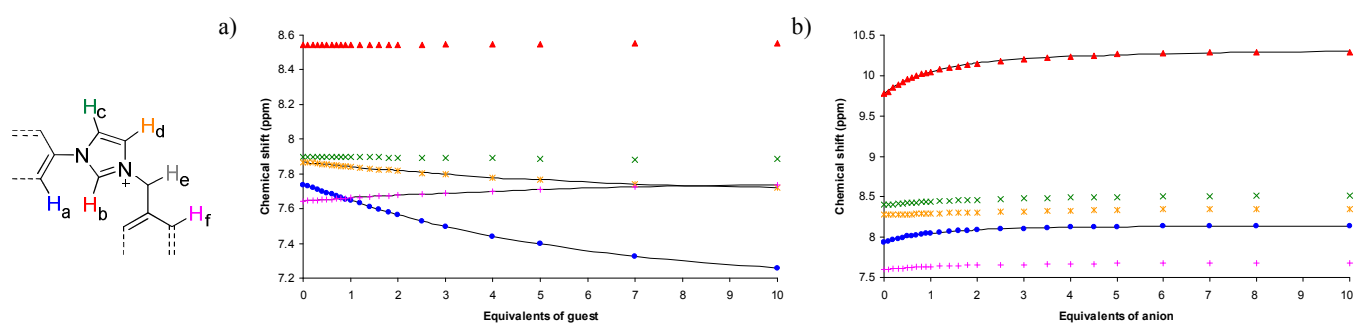


Figure S2 – ^1H NMR peak perturbations of macrocycle **1** for the addition of (a) DHN **7** in acetonitrile- d_3 , and (b) TBA chloride in DMSO-d_6 . Coloured points designate the proton resonances as indicated. Black lines, where present, represent the binding curves fitted using WinEQNMR2.

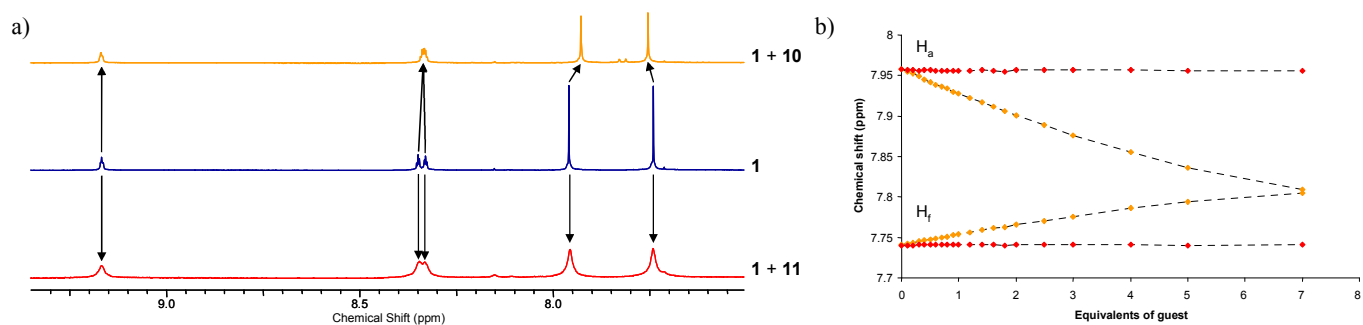


Figure S3 – ^1H NMR peak perturbations of macrocycle **1** for the addition of DHN thread **10** and cobalt carbonyl-stoppered thread **11** in acetone- d_6 (293 K). (a) Spectral shifts upon addition of one equivalent of threads. The broadening of the bottom spectrum is typical of alkyne-cobalt carbonyl complexes. (b) Changes in phenylene (H_a) and xylene (H_f) proton resonances of **1** upon progressive addition of **10** (orange) and **11** (red) in acetone- d_6 . Black dotted lines added for clarity.

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