Electronic Supplementary Information

Ditopic binding of perchlorate anion to hexaazamacroyclic hosts

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Synthesis

L1. Diethylenetriamine (1.00 g, 9.70 mmol) and 2,5-thiophenedicarboxaldehyde (1.35 g, 9.70 mmol) were separately dissolved in CH3OH (200 cm3). Both solutions were added simultaneously dropwise over 4 h to a stirred CH3OH (400 cm3) at 0° C. The mixture was kept at room temperature under stirring for another 24 h, after which the solvent was evaporated. The resulting Schiff base was reduced to amine with NaBH4 (1.73 g, 45.7 mmol) in CH3OH (100 cm3) at room temperature for 12 h. The solvent was evaporated under reduced pressure and the residue was dissolved in water ((100 cm3). The aqueous phase was extracted by CH2Cl2 (3x100 cm3). The organic layers were combined and dried with MgSO4. The product was purified by column chromatography on neutral Al2O3 using an eluent of CH2Cl2 containing 2% CH3OH to give the hexaazamacrocycle L1 as a white powder. Yield 1.23 g, 65%. Found: C, 56.6; H, 8.2; N, 20.1. C20H34N6S2 requires C, 56.8; H, 8.1; N, 19.9. 1H NMR (300 MHz, CDCl3, TMS): δ 6.73 (s, 4H, ArH), 3.87 (s, 8H, ArCH2), 3.77 (t, 8H, CH2).

[H6L1]6+·6TsO−. The tosylate salt of L1 was obtained by titrating the macrocycle L1 (0.05 g, 0.118 mmol) dissolved in CH3OH (2 cm3) with TsOH. The addition of diethyl
ether (2 cm\(^3\)) yielded a white precipitate that was filtered and dried. Yield 0.135 g, 80%. Found: C, 51.6; H, 5.8; N, 5.7. C\(_{62}\)H\(_{62}\)N\(_6\)O\(_{18}\)S\(_8\) requires C, 51.1; H, 5.7; N, 5.8. \(^1\)H NMR (300 MHz, D\(_2\)O, TSP): \(\delta\) 7.69 (d, 12H, ArH), 7.38 (d, 12H, ArH), 7.22 (s, 4H, ArH), 4.48 (s, 8H, ArCH\(_2\)), 3.51 (t, 8H, CH\(_2\)), 2.99 (t, 8H, CH\(_2\)), 2.42 (s, 12H, CH\(_3\)).

\([H_6L1]^{6+}\cdot6\text{ClO}_4^-\). To a solution of L\(_1\) (50 mg, 0.118 mmol) in CH\(_3\)OH (2 cm\(^3\)) was added perchloric acid (ca. 0.05 cm\(^3\)). The white precipitate formed immediately was filtered and washed with diethyl ether. Yield 0.05 g, 80%. Found: C, 23.1; H, 4.0; N, 8.1. C\(_{20}\)H\(_{40}\)Cl\(_6\)N\(_6\)O\(_{24}\)S\(_2\) requires C, 23.4; H, 3.9; N, 8.2. \(^1\)H NMR (300 MHz, D\(_2\)O, TSP): \(\delta\) 7.23 (s, 4H, ArH), 4.46 (t, 8H, CH\(_2\)), 3.32 (t, 8H, CH\(_2\)), 2.95 (s, 12H, CH\(_3\)).

L\(_2\). This ligand was prepared from the reaction of diethylenetriamine (1.00 g, 9.70 mmol) and terephthalaldehyde (1.30 g, 9.70 mmol) following the similar method as described for L\(_1\). Yield 1.20 g, 60%. Found: C, 69.7; H, 9.1; N, 20.7. C\(_{24}\)H\(_{38}\)N\(_6\) requires C, 70.2; H, 9.3; N, 20.5. \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS): \(\delta\) 7.29 (s, 8H, ArH), 3.80 (s, 8H, ArCH\(_2\)), 2.85 (t, 8H, CH\(_2\)), 2.83 (t, 8H, CH\(_2\)).

\([H_6L2]^{6+}\cdot6\text{TsO}_4^-\). The salt was prepared from the reaction of L\(_2\) (50 mg, 0.122 mmol) with TsOH in CH\(_3\)OH (2 cm\(^3\)). A white precipitate was obtained on the addition of diethyl ether (2 cm\(^3\)). Yield 0.140 g, 80%. Found: C, 54.2; H, 5.8; N, 5.6. C\(_{66}\)H\(_{86}\)N\(_6\)O\(_{18}\)S\(_6\) requires C, 54.9; H, 6.0; N, 5.8. \(^1\)H NMR (300 MHz, D\(_2\)O, TSP): \(\delta\) 7.42 (d, 12H, ArH), 7.26 (s, 8H, ArH), 4.21 (s, 8H, ArCH\(_2\)), 3.27 (t, 8H, CH\(_2\)), 3.01 (t, 8H, CH\(_2\)), 2.43 (s, 12H, CH\(_3\)).

\([H_4L2]^{4+}\cdot4\text{ClO}_4^-\). To a solution of L\(_2\) (50 mg, 0.122 mmol) in CH\(_3\)OH (2 cm\(^3\)) was added perchloric acid (ca. 0.05 cm\(^3\)). The white precipitate formed immediately was filtered and washed with diethyl ether. The white precipitate formed, was filtered and washed with diethyl ether. Yield 0.07 g, 75%. Found: C, 35.8; H, 5.4; N, 10.2. C\(_{24}\)H\(_{42}\)Cl\(_4\)N\(_6\)O\(_{16}\) requires C, 35.5; H, 5.2; N, 10.3. \(^1\)H NMR (300 MHz, D\(_2\)O, TSP): \(\delta\) 7.43 (s, 8H, ArCH\(_2\)), 3.30 (t, 8H, CH\(_2\)), 2.99(t, 8H, CH\(_2\)).
NMR titration studies

Binding studies were carried out by $^1$H NMR titrations of $[\text{H}_6\text{L1}]^{6+}\cdot6\text{TsO}^-$ or $[\text{H}_6\text{L2}]^{6+}\cdot6\text{TsO}^-$ with NaClO$_4$ in D$_2$O at pH 4.0 at room temperature, performed on a 300 MHz Bruker NMR spectrophotometer. Initial concentrations were used as 2 mM and 20 mM for the ligand and anion, respectively, and the pH of the solution was adjusted with a concentrated solution of TsOH and NaOH in D$_2$O. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-$d_4$ acid (TSP) in D$_2$O was used as an external reference in a sealed capillary tube. Each titration was performed by 12 measurements in the range of $R$ ([perchlorate]$_0$/[ligand]$_0$) =0 to 10. The association constant $K$ was calculated from the non-linear regression analysis of the NMR shifts of aliphatic protons with a 1:1 association model using Sigma Plot software, from the equations, 

$$\Delta\delta = ([A]_0 + [L]_0 + 1/K - (([A]_0 + [L]_0 + 1/K)^2 - 4[L]_0[A]_0)^{1/2})\Delta\delta_{\text{max}} / 2[L]_0$$

(where L is ligand and A is anion). Error limit in $K$ was less that 15%.

Job plot

Binding stoichiometry was determined by Job plot analysis of the $^1$H NMR spectra of $[\text{H}_6\text{L1}]^{6+}\cdot6\text{TsO}^-$ or $[\text{H}_6\text{L2}]^{6+}\cdot6\text{TsO}^-$ with varying amount of perchlorate anion in D$_2$O at pH 4.0 to match what was used in the NMR binding studies described above. Stock solutions (10 mM) of ligands and perchlorate anion were prepared separately in D$_2$O and the solution pH was adjusted with a concentrated solution of TsOH and NaOH in D$_2$O. Ten NMR samples were prepared with different proportions of the ligand and anion solution so that the final concentration ([L] + [ClO$_4^-$]) of each sample became 10 mM. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-$d_4$ acid (TSP) in D$_2$O was used as an external reference in a sealed capillary tube. The Job plots were obtained plotting $\Delta\delta ([L]/ ([L] + [\text{ClO}_4^-]))$ with $([L] + [\text{ClO}_4^-])$ as shown in Figure S1 and Figure S2.
Figure S1. Job plot of $\mathbf{L1}$ with $\text{NaClO}_4$ in $\text{D}_2\text{O}$ at pH 4.0 showing a maximum at 0.5 mole fraction of $\mathbf{L1}$.

Figure S2. Job plot of $\mathbf{L2}$ with $\text{NaClO}_4$ in $\text{D}_2\text{O}$ at pH 4.0 showing a maximum at 0.5 mole fraction of $\mathbf{L2}$. 
Crystallographic details

Crystallographic data for \([\text{H}_6\text{L}_1(\text{ClO}_4)_2](\text{ClO}_4)_4\cdot4\text{H}_2\text{O}\)

Figure S3. The molecular structure of \([\text{H}_6\text{L}_1(\text{ClO}_4)_2](\text{ClO}_4)_4\cdot4\text{H}_2\text{O}\) showing the atom-numbering scheme

Instrumentation and software

Data collection: Bruker Apex2; cell refinement: Bruker Apex2; data reduction: Bruker Apex2; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: Bruker SHELXTL.
Data collection

Bruker Kappa Apex-II CCD area detector

diffra toxin 3690 independent reflections

Radiation source: fine-focus sealed tube 3561 reflections with $I > 2\sigma(I)$

Monochromator: graphite $R_{int} = 0.030$

$T = 90$ K $\theta_{max} = 68.7^\circ$

phi and $\omega$ scans $\theta_{min} = 3.6^\circ$

Absorption correction: multi-scan SADABS (Sheldrick, 2002)

$T_{min} = 0.314$, $T_{max} = 0.605$

10176 measured reflections

Refinement

Refinement on $F^2$ Secondary atom site location: difference Fourier map

Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.032$ H atoms treated by a mixture of

independent and constrained refinement $wR(F^2) = 0.087$ $w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.0629P]$

$S = 1.05$ $(\Delta/\sigma)_{max} = 0.002$

3690 reflections $\Delta\rho_{max} = 0.45$ e Å$^{-3}$

345 parameters $\Delta\rho_{min} = -0.37$ e Å$^{-3}$

103 restraints Extinction correction: SHELXL,

$F_c =$ $k F_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{1/4}$ Extinction coefficient: 0.0022 (3)

Primary atom site location:
structure-invariant direct methods

Supplementary Material (ESI) for CrystEngComm

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Crystallographic data for $[\text{H}_4\text{L}_2\text{(ClO}_4)_2\text{(H}_2\text{O})]_2\text{(ClO}_4)_2$:  

**Figure S4.** The molecular structure of $[\text{H}_4\text{L}_2\text{(ClO}_4)_2\text{(H}_2\text{O})]_2\text{(ClO}_4)_2$: showing the atom-numbering scheme

**Instrumentation and software**

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997); program(s) used to solve structure: *SIR97* (Altomare et al., 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**Data collection**

- KappaCCD (with Oxford Cryostream) diffractometer: 7932 independent reflections
- Radiation source: fine-focus sealed tube: 5349 reflections with $I > 2\sigma(I)$
Monochromator: graphite  
\( R_{int} = 0.097 \)

\( T = 90 \text{ K} \)  
\( \theta_{\text{max}} = 27.1^\circ \)  
\( \theta_{\text{min}} = 2.6^\circ \)

Absorption correction: multi-scan

HKL Scalepack (Otwinowski & Minor 1997)

\( h = -15 \rightarrow 15 \)  
\( k = -18 \rightarrow 18 \)  
\( l = -26 \rightarrow 26 \)

61377 measured reflections

Refinement

Refinement on \( F^2 \)

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

independent and constrained refinement

\( R[F^2 > 2\sigma(F^2)] = 0.051 \)

where \( P = (P_{o}^2 + 2F_c^2)/3 \)

\( wR(F^2) = 0.105 \)

(\( \Delta/\sigma \))_{\text{max}} = 0.001

\( S = 1.03 \)

7932 reflections

474 parameters

Extinction correction: SHELXL,

\( F_c^* = kF_c[1 + 0.001xF_c^2\lambda^2/\sin(2\theta)]^{1/4} \)

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Flack parameter: 0.28 (5)

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of \( F2 \) against ALL reflections. The weighted \( R \)-factor \( wR \) and goodness of fit \( S \) are based on \( F2 \), conventional \( R \)-factors \( R \) are based on \( F \), with \( F \) set to
zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors (gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

References: