Electronic Supplementary Material (ESI) for Chemical Science

Supplementary Information

Fluorescent sensing of ^{99}Tc pertechnetate in water.

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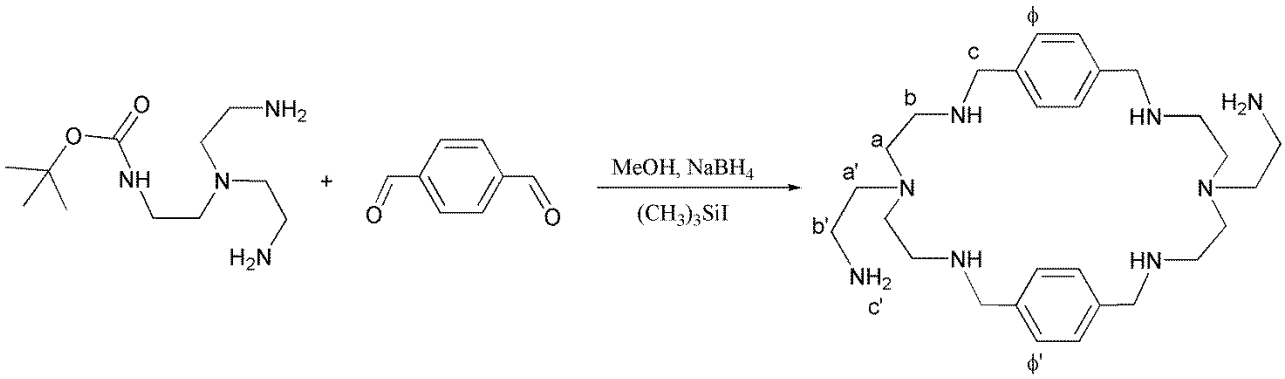
Supplementary Section 1: Syntheses

For the synthesis of **1**, we modified the procedure reported in the literature.[1]

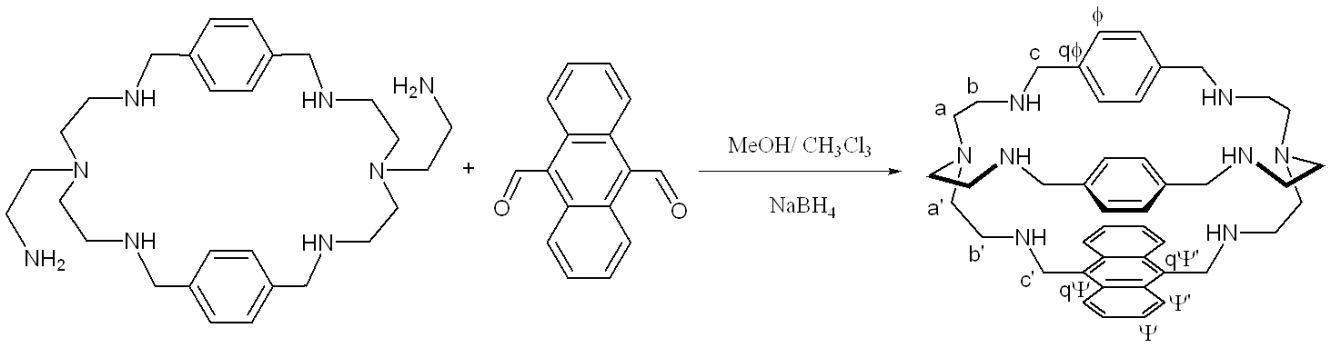
A. Synthesis of the macrocyclic intermediate



N,N-Bis(2-aminoethyl)-N-[2-(tert-butylcarbamoyl)ethyl]-amine[2] (0.85 g, 3.45 mmol) was dissolved in 30 mL of MeOH. Under stirring, a solution of terephthalaldehyde (0.46g, 3.45 mmol) in MeOH 150 mL was added dropwise over 3h at RT. After 20 h stirring, the solution was heated to 50 °C and hydrogenated with $NaBH_4$ (2.76g, 69 mmol). When the addition was complete, the reaction mixture was stirred at 50 °C overnight. The solvent was then removed and the residue was dissolved in basic water (20 mL, pH=9) and extracted with 15 ml CH_2Cl_2 (× 7). The collected organic phases were dried over Na_2SO_4. Iodotrimethylsilane (1.2 mL, 8.28 mmol) was added to the organic solution under stirring and N_2. The mixture was refluxed in inert atmosphere overnight; then 10 mL of MeOH was added. The solvent was removed in vacuo and the residue was dissolved in acid water (20 mL, 1:1=H_2O : HCl) and then extracted with $CHCl_3$ 5x20ml. NaOH was added to water phase to obtain a basic solution (pH=10) and then extracted with 20 ml CH_2Cl_2 (× 7). The collected organic phases were dried over Na_2SO_4 and evaporated to dryness. A light yellow oil was obtained (0.52 g, 1.05mmol 61%).

MS (ESI, MeOH, pos.): *m/z* 250 $[M + 2H]^{2+}$, 498 $[M + H]^+$. ^1H NMR (400 MHz, d_6-DMSO, ppm): δ 2.5 (20*H*, m, $H_{a'}$, H_a, H_b), 3.5 (4*H*, s br, $H_{c'}$), 3.6 (4*H*, t br, $H_{b'}$), 4.49 (8*H*, s, H_c), 7.25 (4*H*, s, H_ϕ), 7.3 (4*H*, s, $H_{\phi'}$).

B. Synthesis of 1.



A solution of 9,10-anthracenedicarboxaldehyde (0.13 g, 0.56 mmol) in 100 ml of MeOH:$CHCl_3$ 1:1 mixture was added dropwise to a stirred solution of the intermediate macrocycle (0.28 g, 0.56 mmol) in 350 mL of the same mixture over 3 h at room temperature. After 24 h stirring, $CHCl_3$ was removed in vacuum. Then, 200 ml of MeOH was added to the reaction mixture, heated to 50 °C and hydrogenated with $NaBH_4$ (0.5 g). When the addition was complete, the reaction was stirred and refluxed for 2 h, then cooled at RT and stirred overnight. The solvent was removed and the residue was dissolved in basic water (20 mL, 3 M NaOH) and extracted with CH_2Cl_2. The collected organic phases were dried over Na_2SO_4 and evaporated to dryness. A yellow solid was obtained (0.37 g, 0.53 mmol, 94%).

MS (ESI, MeOH, pos.): *m/z* 699.5 $[M + H]^+$, 350.6 $[M + 2H]^{2+}$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.8-2.6 (20*H*, m, $H_{a'}$, H_a, H_b), 3.19 (4*H*, *br* t, $H_{b'}$), 3.40 (8*H*, dd, H_c), 4.72 (4*H*, s, $H_{c'}$), 6.20 (8*H*, s, H_Φ), 7.40 (4*H*, m, H_Ψ), 8.49 (4*H*, m, $H_{\Psi'}$). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 47.30 (br, C_b), 47.79 ($C_{b'}$, $C_{c'}$), 52.86 (br, C_a, C_c), 54.73 ($C_{a'}$), 125.04 ($C_{\Psi'}$), 125.73 (C_Ψ), 127.06 (C_ϕ), 130.11 ($C_{q\Psi'}$), 131.86 ($C_{q\Psi}$), 137.8 ($C_{q\phi}$). Calculated for $C_{44}H_{58}N_8$: %C 75.61; %H 8.36; %N 16.03. Experimental: %C 75.40; %H 8.55; %N 15.83

C. Synthesis of $[1H_6(ReO_4)](CF_3SO_3)_5 \cdot 7H_2O$

1 (12 mg, 0.0172 mmol) was dissolved in water (1.5 ml) and methanol (2 ml), in the presence of excess CF_3SO_3H (20 equiv., 0.344 mmol), The solution was stirred at room temperature and $NaReO_4$ (1 equiv., 0.0172 mmol) was dissolved. By slow evaporation of the reaction mixture (1 day), colourless crystal suitable for X-ray diffraction studies were obtained. The residual solvent was evaporated under a slow nitrogen stream, yielding further microcrystalline solid.

^{1}H NMR (400 MHz, CD_3OD, ppm): δ 2.76 (8*H*, m, H_a), 2.87 (4*H*, t, $H_{a'}$), 3.01 (8*H*, m, H_b), 3.5 (4*H*, t *br*, $H_{b'}$), 4.2 (8*H*, dd,H_c), 5.3 (4*H*, s, $H_{c'}$), 7.3 (8H, s, H_ϕ), 7.90 (4*H*, m, $H_{\Psi'}$), 8.49 (4*H*, m, $H_{\Psi'}$). ^{13}C NMR (400 MHz, CD_3OD, ppm): δ 45.22 ($C_{c'}$), 45.86 (C_b), 47.24 ($C_{b'}$), 51.94 (C_a), 52.2 ($C_{a'}$), 52.36 (C_c), 125.75 (C_Ψ), 126.24 ($C_{q\Psi'}$), 129.32 ($C_{\Psi'}$), 131.88 (C_ϕ), 132.4 ($C_{q\Psi'}$), 132.98 ($C_{q\phi}$). IR-ATR, cm^{-1}: ν 3455 (m), 3059 (m), 2838 (m), 1594 (w), 1469 (w), 1446 (w), 1278 (s), 1236 (s), 1220 (s), 1158 (s), 1082 (w), 1024 (s), 899 (s), 819 (w), 761 (s).

D. Synthesis of $[1H_6(TcO_4)](CF_3SO_3)_5 \cdot nH_2O$

1 (12 mg, 0.0172 mmol) was dissolved in water (1.5 ml) and methanol (2 ml), in the presence of excess CF_3SO_3H (20 equiv., 0.344 mmol), The solution was stirred at room temperature and $NaTcO_4$ (1 equiv., 0.0172 mmol) was dissolved. By slow evaporation of the reaction mixture (1 day), colourless crystal were obtained. The residual solvent was evaporated under a slow nitrogen stream, yielding further microcrystalline solid.

^{1}H NMR (400 MHz, CD_3OD, ppm): δ 2.72 (8*H*, m, H_a), 2.82 (4*H*, t, $H_{a'}$), 2.99 (8*H*, m, H_b), 3.41 (4*H*, *br* t, $H_{b'}$), 4.11 (8*H*, dd,H_c), 5.21 (4*H*, s, $H_{c'}$), 7.23 (8H, s, H_ϕ), 7.81 (4*H*, m, $H_{\Psi'}$), 8.36 (4*H*, m, $H_{\Psi'}$). ^{13}C NMR (400 MHz, CD_3OD, ppm): δ 43.67 ($C_{c'}$), 44.29 (C_b), 45.54 ($C_{b'}$), 50.09 (C_a), 50.28 ($C_{a'}$), 50.90 (C_c), 124.03 (C_Ψ), 124.59 ($C_{q\Psi'}$), 127.70 ($C_{\Psi'}$), 130.18 (C_ϕ), 130.61 ($C_{q\Psi'}$), 131.37 ($C_{q\phi}$). ^{99}Tc NMR (400 MHz, CD_3OD, ppm): δ 2.5 (*br* s, $\Delta\nu_{1/2} \cong 500$ Hz).

Supplementary Section 2: Experimental procedures

A. Potentiometric titrations. All measurements were performed at 25°C in aqueous solution (0.1M CF_3SO_3Na). Titrations were performed under nitrogen atmosphere, in the presence of a double junction pH reference electrode (SCE) filled with aqueous CF_3SO_3Na 0.1M. In a typical experiment, 15 mL of a 3.0×10^{-4} M solution of receptor **1** was treated with an excess of a 1.0 M CF_3SO_3H standard solution. Titrations were run by addition of 10 μL portions of standard 0.1 M NaOH, collecting 80-100 points for each titration. Prior to each potentiometric titration, the standard electrochemical potential (E°) of the glass electrode was determined in CF_3SO_3Na 0.1M, by a titration experiment according to the Gran method. Titration data (emf *vs.* mL of NaOH) were processed with the Hyperquad® package[3] to determine the equilibrium constants.

B. ITC experiments. All binding experiments were performed at 30°C. Blank titrations were performed and subtracted from the corresponding titrations to remove the effect of dilution. For perrhenate and pertechnetate (Figures S2, S3), ITC experiments were performed by adding a standard solution of the receptor to the solution of the anion (as the sodium/ammonium salt) in aqueous CF_3SO_3Na 0.1M (placed in the instrument cell). Data were fitted for ligand (i.e. the anion) in the cell, one-site model. In the case of perchlorate, due to the low solubility of the receptor, the association parameters were determined by titrating the standard solution of the receptor with $NaClO_4$ (Figure S4). In this case, data were fitted by ligand in the syringe (one-site model). For the nitrate anion, a competition-based method was applied for the determination of the thermodynamic parameters (reported in Table 1), according the procedure proposed by Z.-Y. Zhang *et al.*.[4] This method is based on the coupling of a high-affinity ligand to the binding of the low-affinity ligand. First of all, the thermodynamic parameters for the interaction with the high-affinity ligand (i.e. perrhenate) have been determined by direct titration (ΔH_{ReO4}, K_{ReO4}). Then, perrhenate was used to titrate the receptor in the presence of excess nitrate ($[NO_3]_0$ = total concentration of sodium nitrate), thus obtaining the apparent ITC parameters (ΔH_{app}, K_{app}) shown in Figure S5. The thermodynamic parameters for nitrate, could be then calculated from apparent parameters, according to equations (1) and (2):[4]

$$K_{NO3} = \left(\frac{KReO4}{Kapp} - 1 \right) \cdot \frac{1}{NO3\ 0} \quad (1)$$

$$\Delta H_{NO3} = (\Delta H_{ReO4} - \Delta H_{app}) \cdot \left(1 + \frac{1}{KNO3 \cdot NO3\ 0}\right) \quad (2)$$

C. Spectrophotometric and spectrofluorimetric titrations. Titrations were performed at 25.0 ± 0.1 °C in aqueous 0.1M CF_3SO_3Na. In a typical experiment, the solution of the receptor was titrated with a 100-fold more concentrated solution of the sodium salt of the envisaged anion. In spectrofluorimetric titrations, the sample was excited at a wavelength corresponding to an isosbestic point in the UV-vis spectra. Titration data were processed with non-linear least-squares procedure (Hyperquad® package),[3] in order to determine the equilibrium constants. Fluorescent spectra at 77K were measured in methanol.

D. ^{1}H NMR titrations. All measurements were performed at 25°C in D_2O,. pH = 2.0 (as read by the pH electrode) was adjusted before titration, by adding standard CF_3SO_3H in D_2O. For the determination of binding constants, receptor was titrated with a 100-fold more concentrate solution of $NaReO_4$. After each addition of sub-stoichiometric amount of anion, the ^{1}H-NMR spectrum was recorded. After titration, pH was checked again with a glass pH microelectrode. Titration data were processed with the Hyperquad® package[3] to determine the equilibrium constants.

E. Crystal structure analysis. Crystal data of studied compounds are reported in Table S2. Diffraction data for pertechnetate single crystal were collected at 183(2) K with Cu-*K*α X-radiation (λ = 1.54184 Å) on an Agilent SuperNova, Dual source diffractometer, with an Atlas CCD-detector. A suitable crystal (~ 0.29 x 0.22 x 0.19 mm) was covered with the minimal amount of oil (Infineum V8512, formerly known as Paratone N), placed on a nylon loop that is mounted in a CrystalCap Magnetic™ (Hampton Research) and immediately transferred to the diffractometer. Data were corrected for Lorentz and polarisation effects as well as for absorption. The program suite CrysAlisPro was used for data collection, data reduction and multi-scan absorption correction (0.422 and 0.548 min and max transmission factors).[5] Crystal structure was solved by direct methods (SIR 97)[6] and refined by full-matrix least-squares procedures on F^2 using all reflections (SHELXL 97).[7]

Diffraction data for perrhenate single crystal were collected at room temperature with Mo-*K*α X-radiation (λ = 0.71073 Å) on a Bruker-AXS diffractometer, with an APEX CCD-detector. Data reduction was performed with the SAINT software.[8] Intensities were corrected for Lorentz and polarization effects; absorption effects were empirically evaluated by the SADABS software[9] and multi-scan absorption correction was applied to the data (0.548 and 0.835 min and max transmission factors for ReO_4^- crystal). Crystal structure was solved by direct methods (SIR 97)[6] and refined by full-matrix least-squares procedures on F^2 using all reflections (SHELXL 97).[7]

For both structures, anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogens have been placed at calculated positions and their positions refined accordingly to a riding model. Positions of hydrogens belonging to water solvent molecules remained undetermined. The conventional monoclinic unit cell for the crystal containing the TcO_4^- oxo-anion has a = 13.010(1), b =

17.557(1), c = 32.933(1) Å, β = 90.77(1)°. This unit cell has been transformed into a not standard setting with a = 13.010(1), b = 17.557(1), c = 32.933(1) Å, β = 89.23(1)°, by applying the transformation matrix (1 0 0, 0 -1 0, 0 0 -1), in order to make clear the isomorphism with the crystal structure containing the ReO_4^- oxo-anion. With this orientation, all independent atom sites except O(7w) correspond in the two crystal structures. Selected single crystals of both TcO_4^- and ReO_4^- oxo-anions showed a poor X-ray diffraction quality, mainly related to an unresolved disorder affecting the triflate counterions. Crystallographic results for the ReO_4^- crystal were better than those obtained for the TcO_4^- crystal, as evidenced by the final agreement indexes (Table S2). However, the accuracy of the geometrical details of the hexa-protonated cages and of the enclosed oxo-anions and water molecules are similar for both crystal structures. The crystallographic results are considered suitable to the aims of this work, considering also the isomorphism between the two crystal structures. Clearly, the poor X-ray diffraction quality of the data imposed the use of soft restraints (ISOR and DELU instructions) on the least-square procedures involving the U_{ij} values of several atoms belonging to triflate counterions. Also the molecular geometries of several triflate counterion were restrained, using the SAME instruction, to be the same of the best characterized triflate in the crystal structure.

As described in the text, both O(2) and O(3) oxygens of $^{99}TcO_4^-$ and ReO_4^- tetrahedra are placed below the middle of the two C-C bonds shared between the fused benzene rings of anthracene and the resulting C-O distances are in the range 3.19(1)-3.30(1) Å. In addition, the distances between the centroid of the two lateral rings, named r(1) and r(3), of the tricyclic group and the pertinent O atom in the $^{99}TcO_4^-$ complex are: $r(1)_{centroid}$-O(2) 3.50(1) Å, $r(3)_{centroid}$-O(3) 3.22(1) Å; whereas the distances between the centroid of the intermediate ring, named r(2), and the two O atoms are: $r(2)_{centroid}$-O(2) 3.38 Å, $r(2)_{centroid}$-O(3) 3.49 (1) Å. The same distances in the ReO_4^- complex are: 3.47(1), 3.22(1), 3.39(1), 3.48(1) Å. These features suggest the formation of weak anion-π interactions between the anthracenyl moiety of the cage and the O(2) and O(3) atoms of the enclosed oxo-anion.

Supplementary Section 3: Potentiometric measurements

Table S1. Protonation constants, determined by potentiometric titration of 1 in 0.1M CF_3SO_3Na, T = 25°C.

logK_{11}	10.59(3)
logK_{12}	9.6(1)
logK_{13}	8.4(1)
log K_{14}	7.1(1)
logK_{15}	5.3(1)
logK_{16}	5.2(1)
Logβ_{16}	46.2(1)

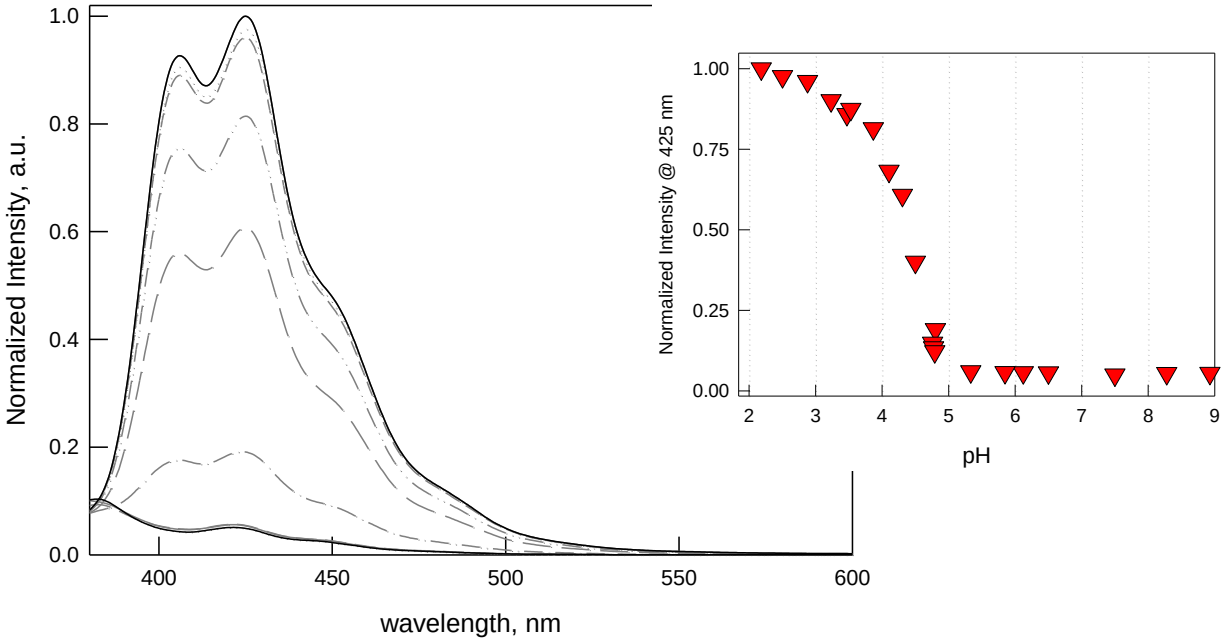


Figure S1. pH-spectrofluorimetric titration of 1 in aqueous solution (0.1M CF_3SO_3Na, T = 25°C). On the left: family of spectra taken over the course of the titration; on the right: profile of Normalised Intensity (i.e. I/I_0 at 425 nm) *vs.* pH.

Supplementary Section 4: ITC measurements in 0.1M CF_3SO_3Na, at pH 2.0

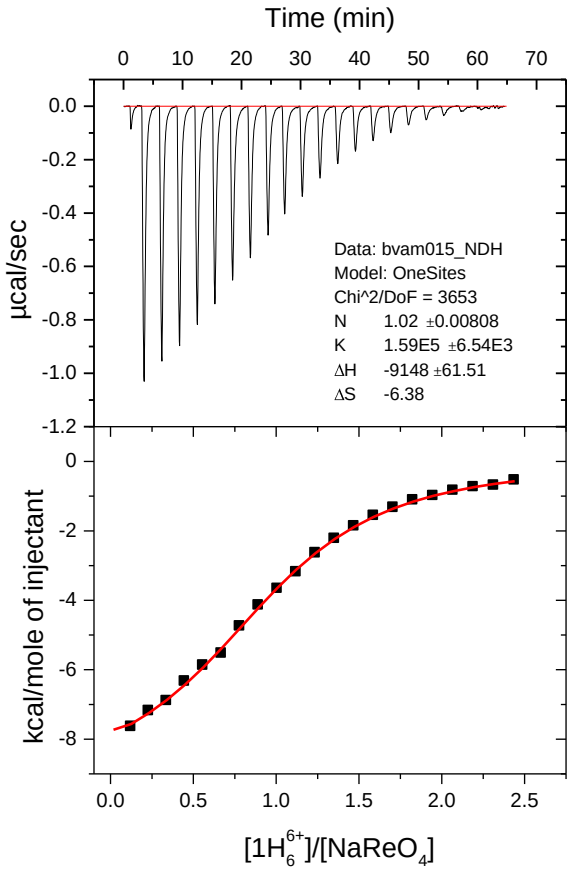


Figure S2. ITC titration of $NaReO_4$ with $\mathbf{1H_6^{6+}}$ ([$NaReO_4$]= 30µM; [$\mathbf{1}H_6^{6+}$]=0.31 mM), T =30°C. Fitting (red curve, bottom figure) for ligand in the cell, one-site model.

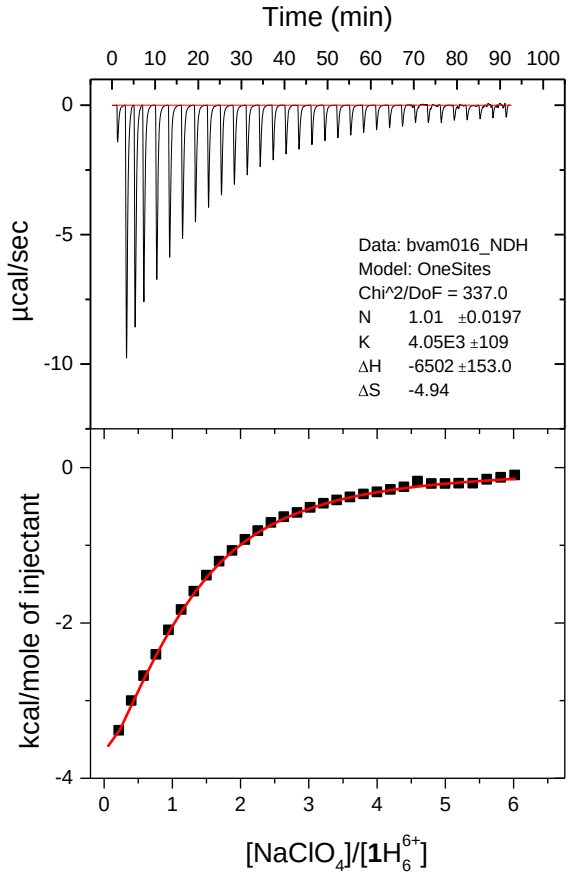


Figure S3. ITC titration of $\mathbf{1H_6^{6+}}$ with $NaClO_4$ ([$\mathbf{1}H_6^{6+}$]=0.31 mM; [$NaClO_4$]= 12 mM;), T =30°C. Fitting (red curve, bottom figure) for ligand in the syringe, one-site model.

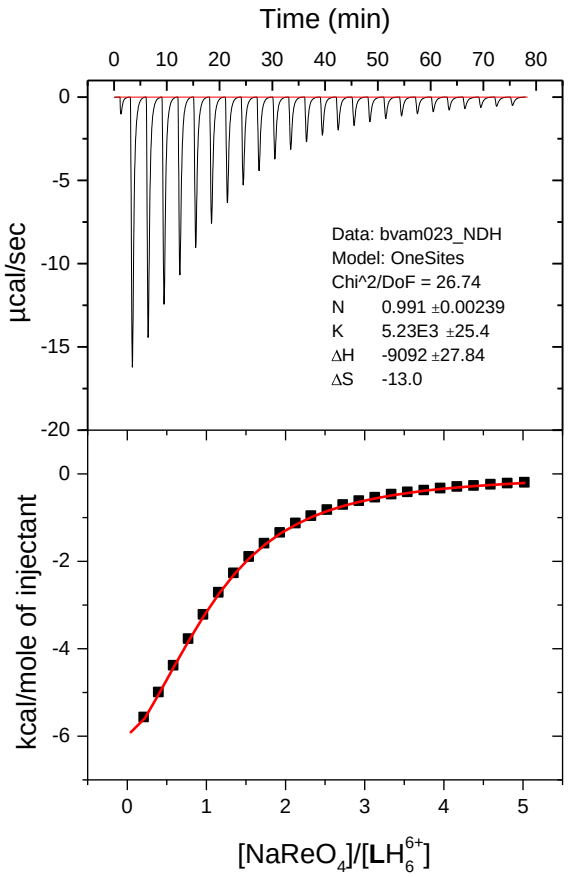


Figure S4. ITC competition experiment: titration of $1H_6^{6+}$ with $NaReO_4$ (in the presence of excess $NaNO_3$). The experiment is based on the competition method by Z.-Y. Zhang *et al.*.[4] A solution 0.37mM in $\mathbf{1}H_6^{6+}$ and 25 mM in $NaNO_3$ (cell) was titrated with $NaReO_4$ (9.9 mM, syringe). T =30°C. Fitting (black curve, bottom figure) for ligand in the syringe, one-site model. The apparent ITC parameters obtained by competition have been then elaborated, by considering $\log_{K11NaReO4}$=5.20(2) and $\Delta H°_{NaReO4}$ = – 9.15(1) Kcal/mol. The thermodynamic parameters for nitrate are reported in Table 1, main text.

Supplementary Section 5: Crystallographic studies.

Table S2. Crystal data for investigated compounds.

	[**1**H$_6$·ReO$_4$](CF$_3$SO$_3$)$_5$ ·7(H$_2$O)	[**1**H$_6$·TcO$_4$](CF$_3$SO$_3$)$_5$ ·7(H$_2$O)
formula	$C_{49}H_{78}F_{15}N_8O_{26}ReS_5$	$C_{49}H_{78}F_{15}N_8O_{26}S_5Tc$
M	1826.64	1738.49
crystal color	colourless	colourless
dimension [mm]	0.30 x 0.15 x 0.10	0.29 x 0.22 x 0.19
X-radiation	Mo-*K*α	Cu-*K*α
λ [Å]	0.71073	1.54184
T [K]	298	183
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	12.949(2)	13.010(1)
b [Å]	17.658(3)	17.557(1)
c [Å]	32.897(5)	32.933(1)
β [°]	90.081(5)	89.226(1)
V [Å^3]	7522(2)	7522(1)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.613	1.535
μ Mo$_{K\alpha}$ [mm-1]	1.896	3.885
scan type	ω scans	ω scans
θ range [°]	2-25	2-67
measured refl.	50398	46828
unique refl.	13198	12810
R_{int}	0.062	0.039
strong data [$I_O > 2\sigma(I_O)$]	8964	10772
refined parameters	937	937
*R*1, *wR*2 (strong data)	0.0595, 0.1547	0.1125, 0.1240
*R*1, *wR*2 (all data)	0.0930, 0.1786	0.3608, 0.3800
GoF	1.024	1.723
max/min residuals [e Å^{-3}]	0.92/-0.49	2.60/-1.35

Table S3. Features of the H-bond interactions involving the hexa-protonated cage, the oxo-anion and the water molecules inside the cage. The first line refers to TcO_4^- crystal, the second line to the ReO_4^- crystal.

Donor group D	D···A (Å)	H···A(Å)	D-H···A (°)	Acceptor atom A
N(2)-H(2D)	2.97(1)	2.50(1)	113.2(4)	O(1)
	3.03(1)	2.53(1)	115.6(4)	
N(2)-H(2D)	2.75(1)	1.95(1)	147.1(4)	O(2w)
	2.79(1)	2.00(1)	145.5(5)	
N(3)-H(3D)	3.07(1)	2.58(1)	114.4(4)	O(4)
	3.06(1)	2.58(1)	114.1(4)	
N(3)-H(3D)	2.78(1)	1.97(1)	150.0(4)	O(3w)
	2.80(1)	1.99(1)	149.1(4)	
N(4)-H(4A)	2.86(1)	1.98(1)	164.4(5)	O(1w)
	2.87(1)	1.99(1)	164.8(5)	
N(4)-H(4B)	2.95(1)	2.17(1)	143.3(5)	O(1)
	2.90(1)	2.15(1)	140.7(5)	
N(5)-H(5A)	2.82(1)	1.94(1)	165.8(5)	O(4w)
	2.89(1)	2.02(1)	162.3(5)	
N(5)-H(5B)	2.99(1)	2.27(1)	136.4(5)	O(4)
	2.96(1)	2.21(1)	141.2(4)	
N(6)-H(6A)	2.84(1)	1.95(1)	173.2(5)	O(2w)
	2.88(1)	1.98(1)	173.0(5)	
N(6)-H(6B)	2.90(1)	2.02(1)	165.5(5)	O(1w)
	2.94(1)	2.06(1)	165.2(5)	
N(7)-H(7A)	2.83(1)	1.94(1)	168.9(5)	O(3w)
	2.89(1)	2.01(1)	166.8(4)	
N(7)-H(7B)	2.88(1)	1.99(1)	166.3(5)	O(4w)
	2.88(1)	2.02(1)	161.0(4)	
O(1w)	2.81(1)	n.d.	n.d.	O(2)
	2.83(1)			
O(2w)	2.75(1)	n.d.	n.d.	O(3)
	2.78(1)			
O(3w)	2.76(1)	n.d.	n.d.	O(3)
	2.77(1)			
O(4w)	2.85(1)	n.d.	n.d.	O(2)
	2.84(1)			

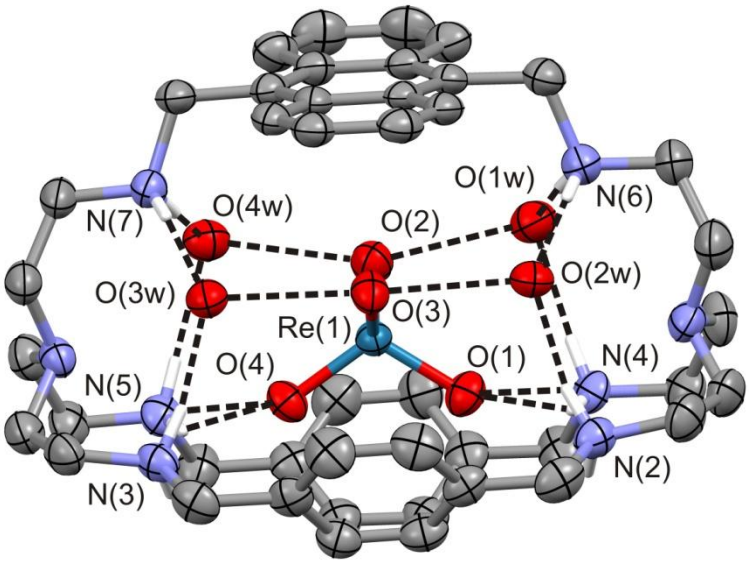


Figure S5. Plot showing thermal ellipsoids of the $[1H_6(ReO_4)]^{5+}$ molecular cation occurring in the $[\mathbf{1}H_6(ReO_4)]$ $(CF_3SO_3)_5 \cdot 7H_2O$ crystal. Ellipsoids are drawn at the 30% probability level, additional water solvent molecules and triflate counter-ions are omitted for clarity. Dashed lines indicate direct and water-mediated H-bonds between the hexa-protonated cage and the perrhenate oxo-anion.

Supplementary Section 6: ^{1}H NMR studies with anions.

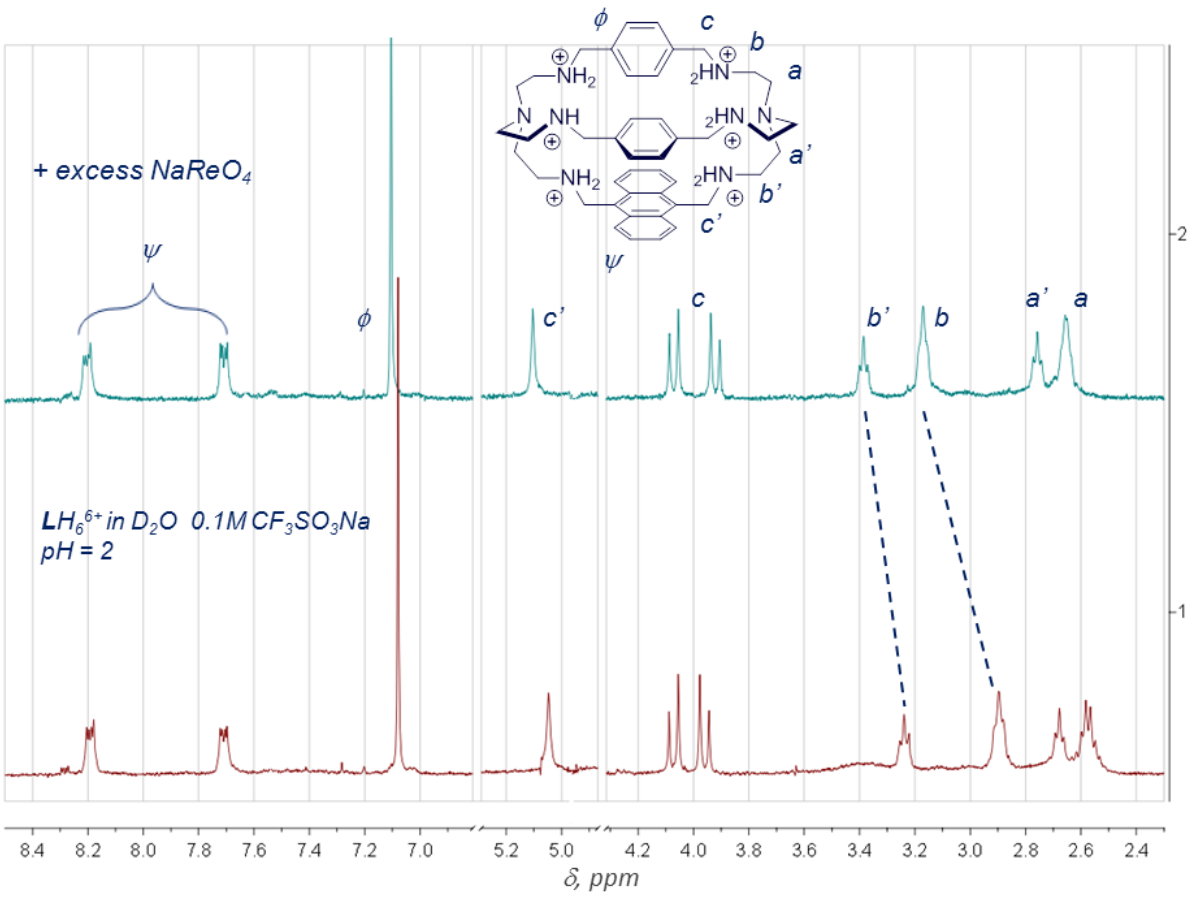


Figure S6. ^{1}H NMR studies in the presence of perrhenate. ^{1}H NMR spectra of **1**H_6^{6+} in D_2O at pH 2, taken before (red line) and after (light blue line) the addition of excess $NaReO_4$, T =25°C. For the titration with $NaReO_4$, the curvature of the titration profile was too steep to allow a safe determination of the binding constant, evaluated as logK_{11} >5.

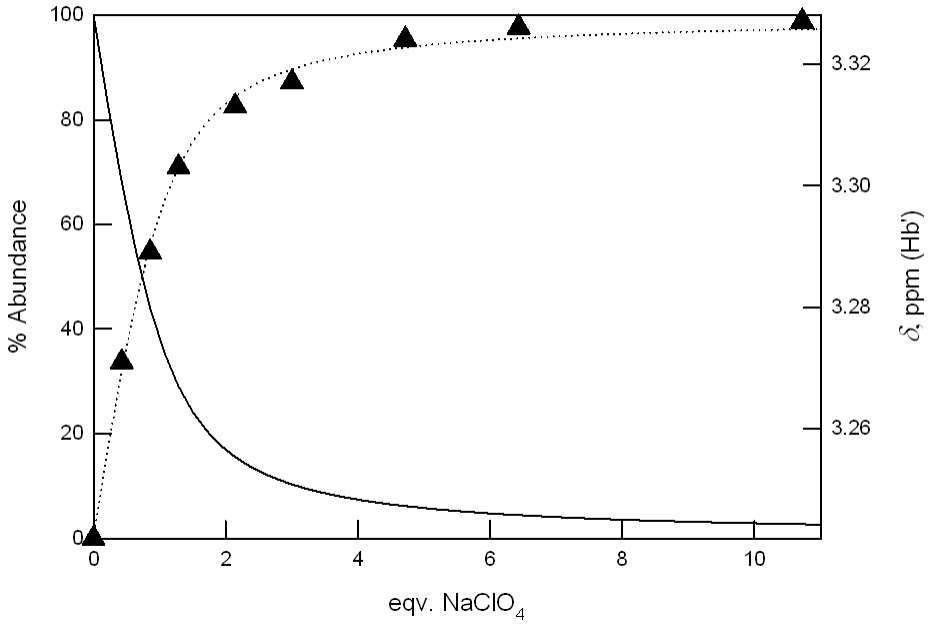


Figure S7. ^{1}H NMR titration profile of $1H_6^{6+}$ with $NaClO_4$ (in D_2O, 0.1M CF_3SO_3Na at pH 2). The fitting of the titration data gave logK_{11}=3.71(1), T =25°C.

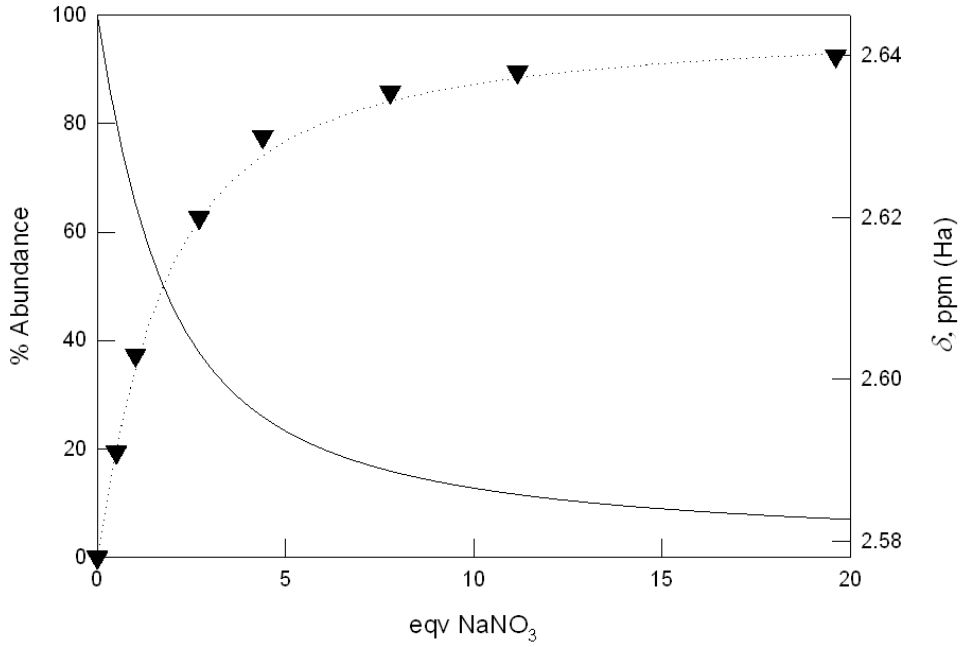


Figure S8. ^{1}H NMR titration profile of $1H_6^{6+}$ with $NaNO_3$ (in D_2O, 0.1M CF_3SO_3Na at pH 2). The fitting of the titration data gave logK_{11}=3.2(1), T =25°C.

Supplementary Section 7: UV/Vis. study with $NaReO_4$.

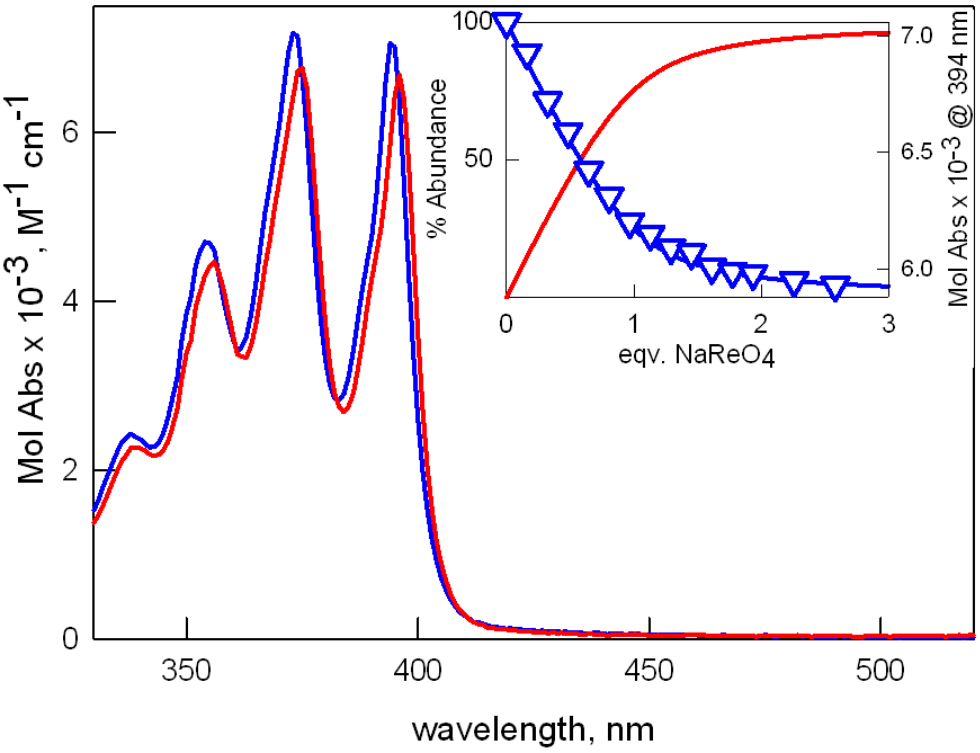


Figure S9. UV/Vis spectra taken upon addition of $NaReO_4$ to a solution of $\mathbf{1}H_6^{6+}$ (0.3 mM in in 0.1M CF_3SO_3Na, pH 2). Initial and final spectra, corresponding to $\mathbf{1}H_6^{6+}$ and $[\mathbf{1}H_6(ReO_4)]^{5+}$ species, are in blue and red, respectively. The inset shows the experimental titration curve (triangles), with the superimposed distribution diagram calculated for $\log K_{11}$ =5.3(1).

Supplementary Section 8: Spectrofluorimetric study on $1H_6^{6+}$ with NaI.

The parabolic behaviour of the plot shown in Figure S11 (i.e. I_0/I vs. concentration of iodide, [I⁻]) indicates that the quenching by iodide is due to both the formation of a 1:1 adduct and to occasional collisions. The profile can be fitted by equation (3):[10]

$$I_0/I = (1+K_{SV}[I^-])\,(1+K_{11}[I^-]) \qquad (3)$$

Pertinent K_{SV} and K_{11} values, obtained through non-linear fitting on equation (3), are reported in Table 2 (main text).

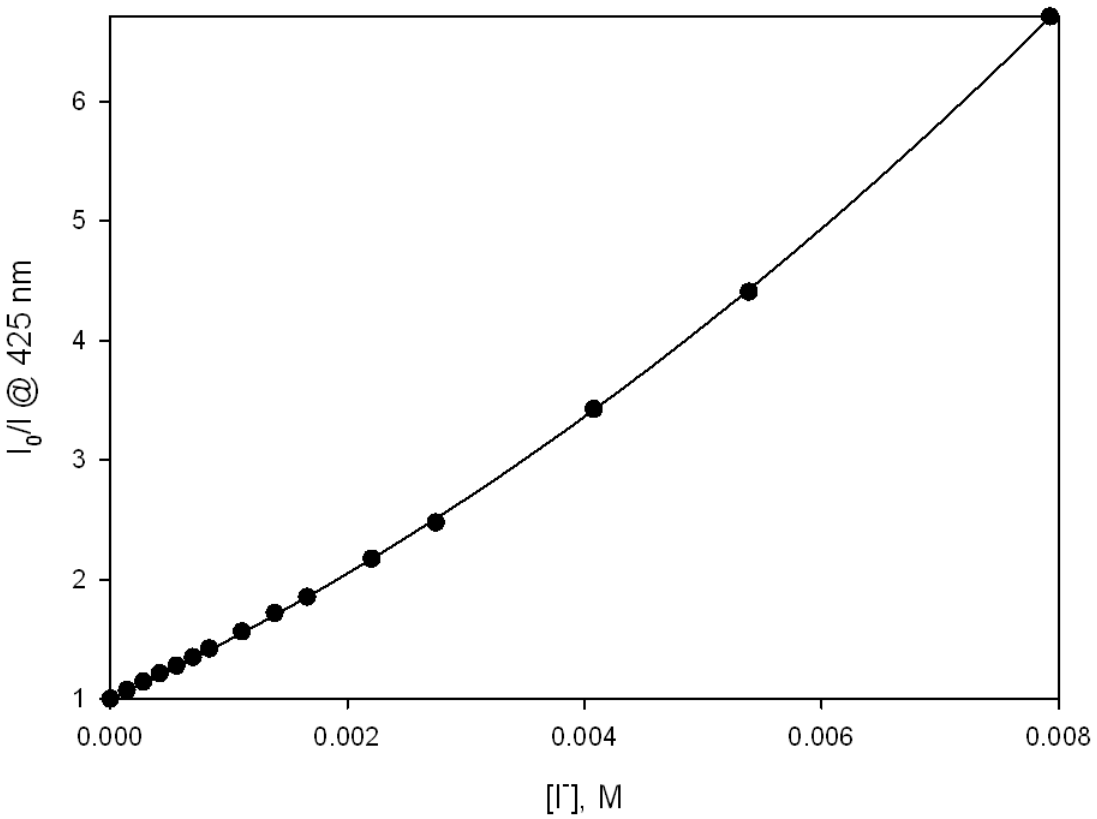


Figure S10. I_0/I profile for the titration of $1H_6^{6+}$ with NaI in aqueous solution (pH 2, 0.1M CF_3SO_3Na, T =25°C). Circles: experimental data; black line: fitting curve.

Supplementary Section 9: Emission spectra at 77K.

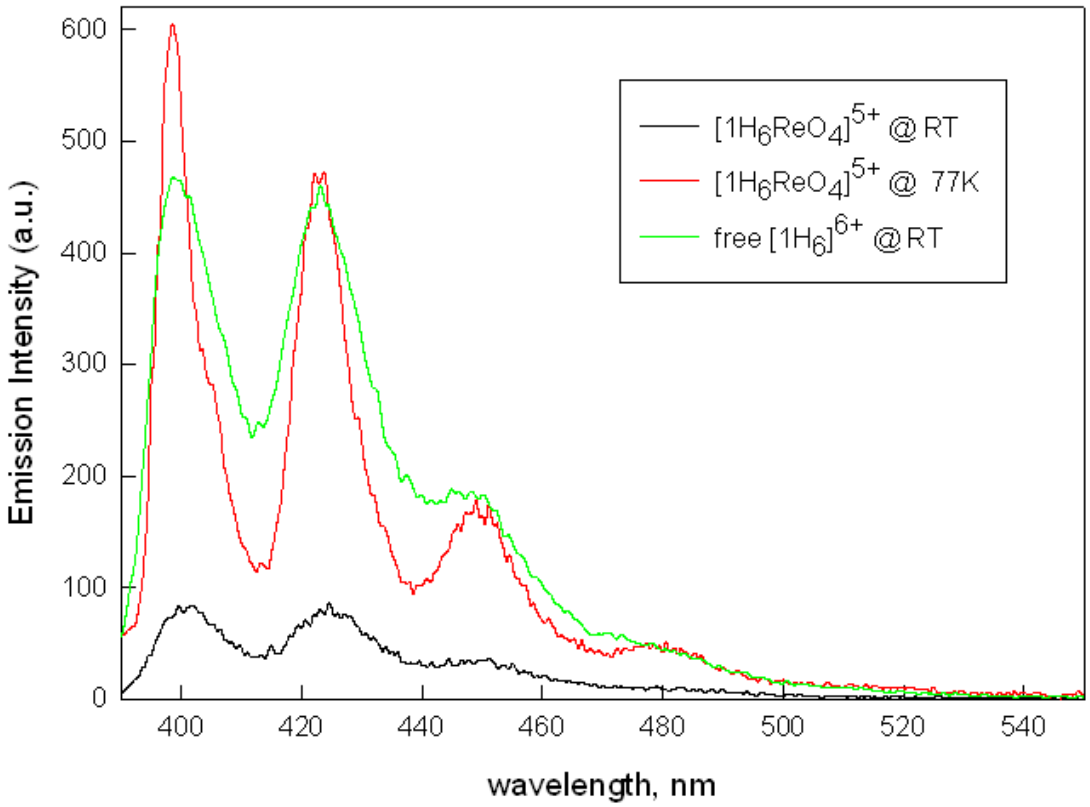


Figure S11. Emission spectra of $1H_6^{6+}$ at 77K. Green line: emission spectrum of $\mathbf{1}H_6^{6+}$ (0.1 mM) in methanol at room temperature (25°C). Black and red lines: emission spectra of the 1:1 complex of $\mathbf{1}H_6^{6+}$ with perrhenate in methanol, before and after freezing in liquid nitrogen (λ_{exc} = 377 nm).

Supplementary Section 11: Spectrofluorimetric competition experiments.

The competition experiments were performed by spectrofluorimetric titration of the receptor (R, 10 μM) with $NaReO_4$ (A), in the presence of a large excess of competing anion (X^-, 50 mM), as the sodium salt, in 0.1M CF_3SO_3Na at pH 2. The experimental data of fluorescence intensity (I_f) vs. concentration of $NaReO_4$ (A_{tot}) were fitted according to equation **(m)**, see below. It has to be noted that, for the chosen competitors (X^- = Cl^-, ClO_4^-, NO_3^-), the fluorescence emission of R and RX have similar intensities (variation < 10%). On the contrary, for perrhenate (A), the fluorescence of the complex RA is about 17% of the pure receptor's emission. This value, as well as the affinity constant (K_{RA} =$10^{5.2}$), result from the spectrofluorimetric titration of R with perrhenate in the absence of X^-.

R = concentration of the free receptor **A** = concentration of free ReO_4^-

X = concentration of the free competitor; since X^- is in large excess: $\mathbf{X} = \mathbf{X_{tot}}$

RA , **R X** = concentrations of the corresponding complexes

(a) $\mathbf{R + A \leftrightarrows RA}$ $\mathbf{K_A}$, affinity constant for ReO_4^- ($10^{5.2}$)

(b) $\mathbf{R + X \leftrightarrows RX}$ $\mathbf{K_x}$, affinity constant for X^- (to be determined)

From **(a)** and **(b)**, the concentrations of the complexes can be obtained:

(c) $\mathbf{RA = K_A \times A \times R}$

(d) $\mathbf{RX = K_x \times X \times R}$

From the mass balance, the total concentrations of perrhenate and receptor can be calculated:

(e) $\mathbf{A_{tot} = A + RA}$

(f) $\mathbf{R_{tot} = R + RX + RA}$

From **(c)** and **(e)**, the expression for the concentration of free perrhenate can be obtained, **(g):**

$$\mathbf{A_{tot} = A \times (K_A \times R + 1)}$$

(g) $$\mathbf{A} = \frac{\mathbf{Atot}}{(\mathbf{K_A \times R + 1})}$$

From **(d)**, **(f)** and **(g)**, we can write the total concentration of the receptor as:

$$\mathbf{R_{tot}} = \mathbf{R} + \mathbf{K_x \times R \times X} + \mathbf{K_A \times R \times} \left(\frac{\mathbf{Atot}}{\mathbf{K_A \times R + 1}}\right)$$

(h) $$\mathbf{R_{tot}} = \frac{\mathbf{K_A \times R^2 + R + K_x \times R \times X + K_x \times X \times K_A \times R^2 + K_A \times Atot \times R}}{\mathbf{K_A \times R + 1}}$$

From **(h)**, the concentration of the free receptor **R** can be determined, **(i)**:

$$\mathbf{K_A\, R^2\, 1 + K_x \times X + R\, 1 + K_x \times X + K_A \times A_{tot} - K_A \times R_{tot} - R_{tot} = 0}$$

(i) $$\mathbf{R} = \frac{\mathbf{-1 + K_x \times X + K_A \times A_{tot} - K_A \times R_{tot} + \sqrt{[\,1 + K_x \times X + K_A \times A_{tot} - K_A \times R_{tot}\,]^2 + 4 K_A \times R_{tot}\; 1 + K_x \times X\,}}}{\mathbf{2K_A\,(1 + K_x \times X)}}$$

In the course of the competition experiment, the emission intensity $\boldsymbol{I_f}$ is proportional to the concentrations of all emitting species, and can be expressed by the following equation:

(l) $$\boldsymbol{I_f} = \boldsymbol{a}\,\mathbf{R} + \boldsymbol{a'}\,\mathbf{RX} + \boldsymbol{b}\,\mathbf{RA}$$

Since for the chosen competitors X^-, $\boldsymbol{a'} \cong \boldsymbol{a}$

we obtain: $\boldsymbol{I_f} = \boldsymbol{a}\,\mathbf{R} + \mathbf{RX} + \boldsymbol{b}\,\mathbf{RA} = \boldsymbol{a}\,(\mathbf{R_{tot} - RA}) + \boldsymbol{b}\,\mathbf{RA}$

knowing that the residual fluorescence for RA is 17% of both R and RX, we have:

$\boldsymbol{b} \cong \boldsymbol{a} \times \mathbf{0.17}$

Thus, $\boldsymbol{I_f}$ can be written as:

(m) $$\boldsymbol{I_f} = \boldsymbol{a}\,\mathbf{R_{tot}} - \boldsymbol{a} - \mathbf{0.17}\boldsymbol{a}\,\left(1 - \frac{1}{\mathbf{1 + K_A \times R}}\right)\mathbf{A_{tot}}$$

R = given in any point by equation **(i)**

$\boldsymbol{a}$ = (initial fluorescence intensity, I_0)/ $\mathbf{R_{tot}}$

$\mathbf{R_{tot}}$ = total concentration of the receptor (i.e. 10^{-5}M)

$\mathbf{K_A}$ = affinity constant for perrhenate (i.e. $10^{5.2}$, see Table 2 in the main text)

$\mathbf{X} = \mathbf{X_{tot}}$ (i.e. 0.05M)

For every competition experiment, $\boldsymbol{I_f}$ is plotted against $\mathbf{A_{tot}}$ (i.e. the concentration of the added perrhenate), and the obtained profile is fitted for equation **(m).**

In following figures, we report an example of the calculations above for $X^-=ClO_4^-$

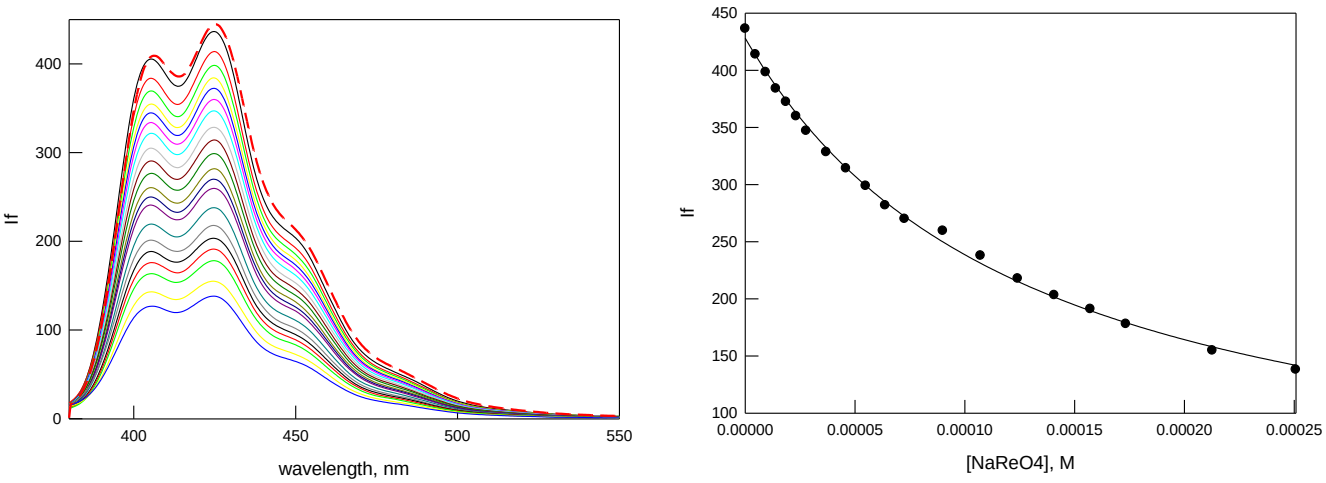


Figure S12. Spectrofluorimetric titration of $1H_6^{6+}$ (10^{-5}M) with $NaReO_4$,in the presence of excess $NaClO_4$ (0.05M), in 0.1M CF_3SO_3Na pH =2 (affinity constant for perrhenate: 5.2(1) logarithmic units) **.** On the left: sequence of emission spectra (λ_{exc}. 377 nm). On the right: titration profile fitted for equation **(m)**. The obtained affinity constant for perchlorate is 3.6(1) logarithmic units perrhenate logK_{11}=5.2)

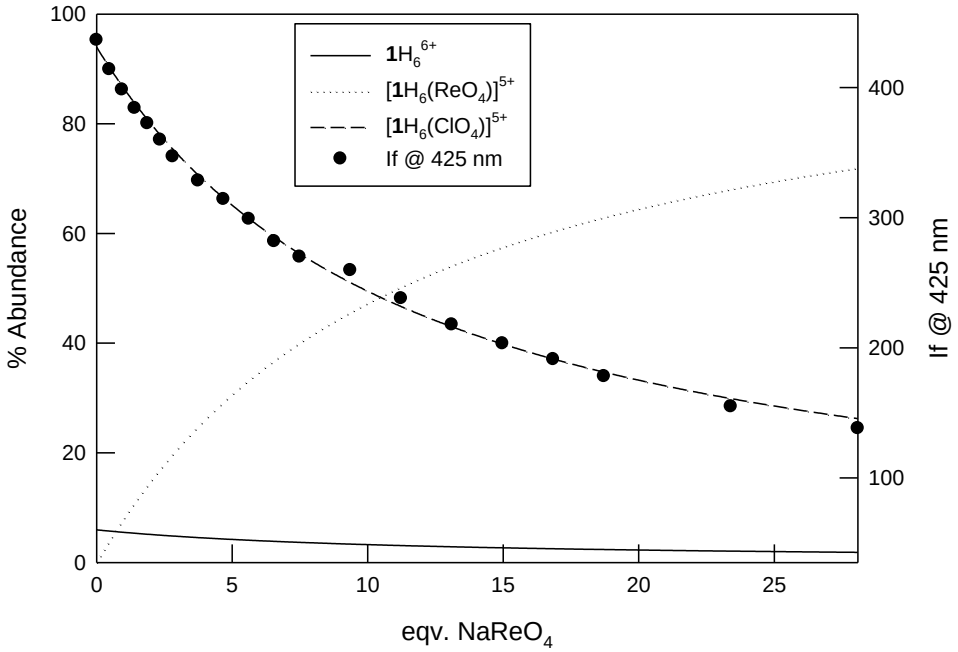


Figure S13. Spectrofluorimetric titration of $1H_6^{6+}$ (10^{-5}M) with $NaReO_4$, in the presence of excess $NaClO_4$ (0.05M), in 0.1M CF_3SO3Na pH =2. Distribution diagram of the species over the course of the competition experiment. logK_{11}: $NaReO_4$=5.2(1); $NaClO_4$=3.6(1).

Supplementary Section 12: Characterisation

A. Characterisation of $[1H_6(ReO_4)](CF_3SO_3)_5 \cdot 7H_2O$

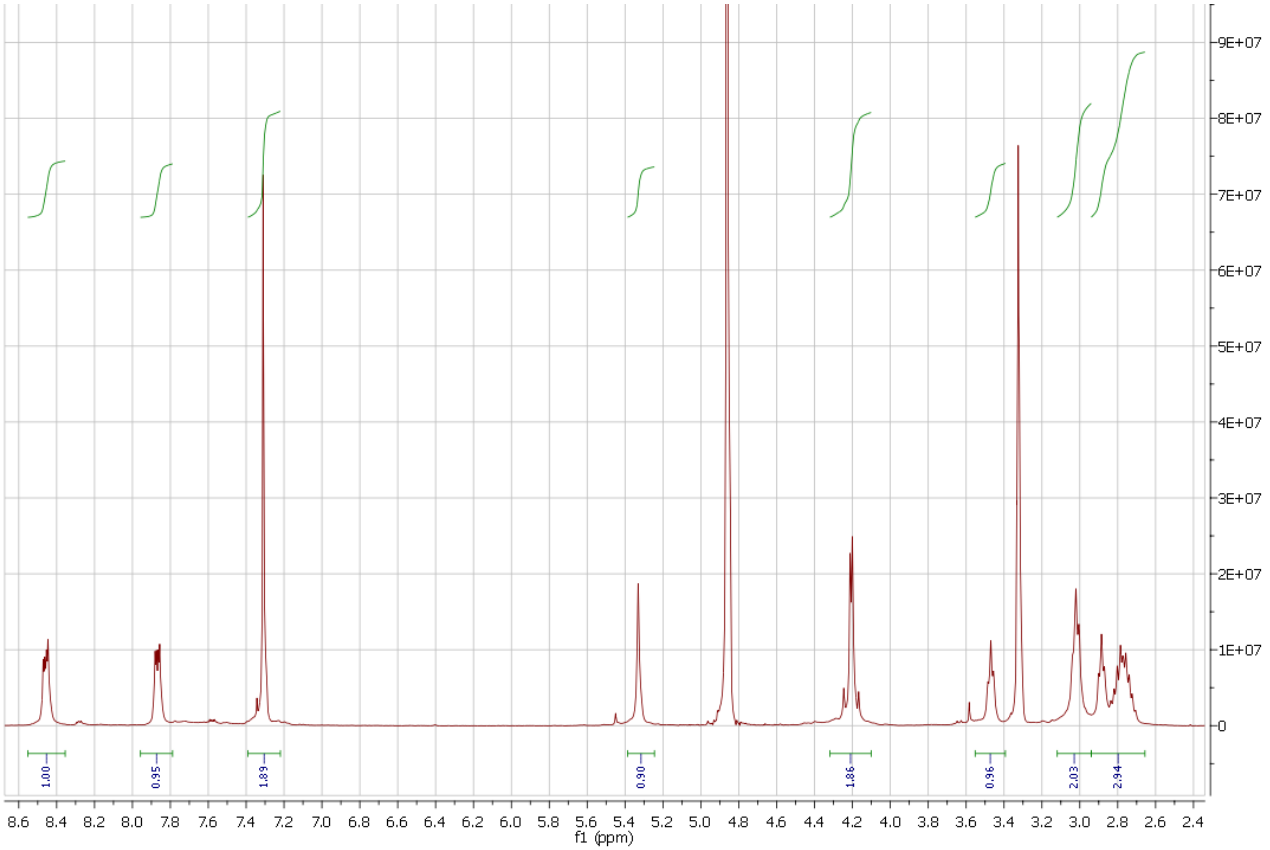


Figure S14. ^{1}H NMR spectrum of $[1H_6(ReO_4)](CF_3SO_3)_5 \cdot 7H_2O$ in CD_3OD (400 MHz)

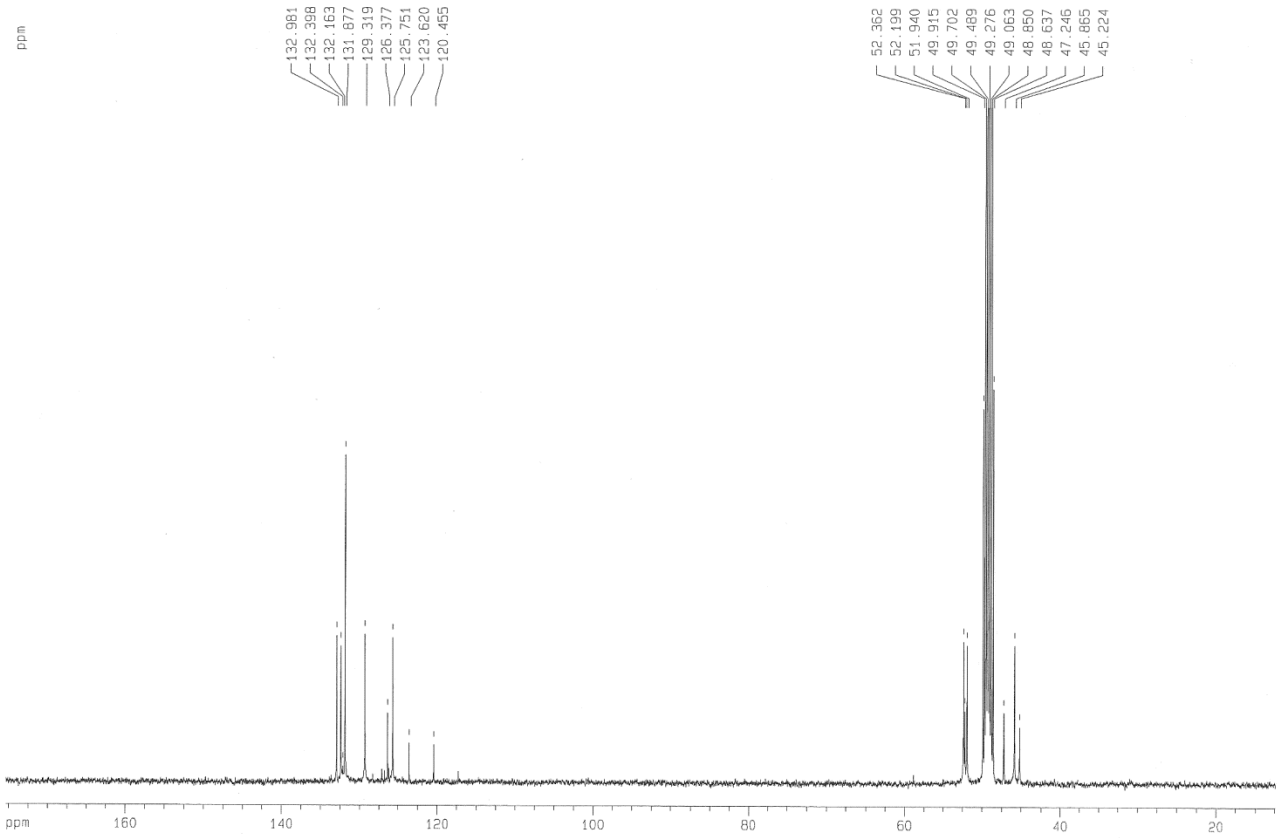


Figure S15. ^{13}C NMR spectrum of $[1H_6(ReO_4)](CF_3SO_3)_5 \cdot 7H_2O$ in CD_3OD (400 MHz)

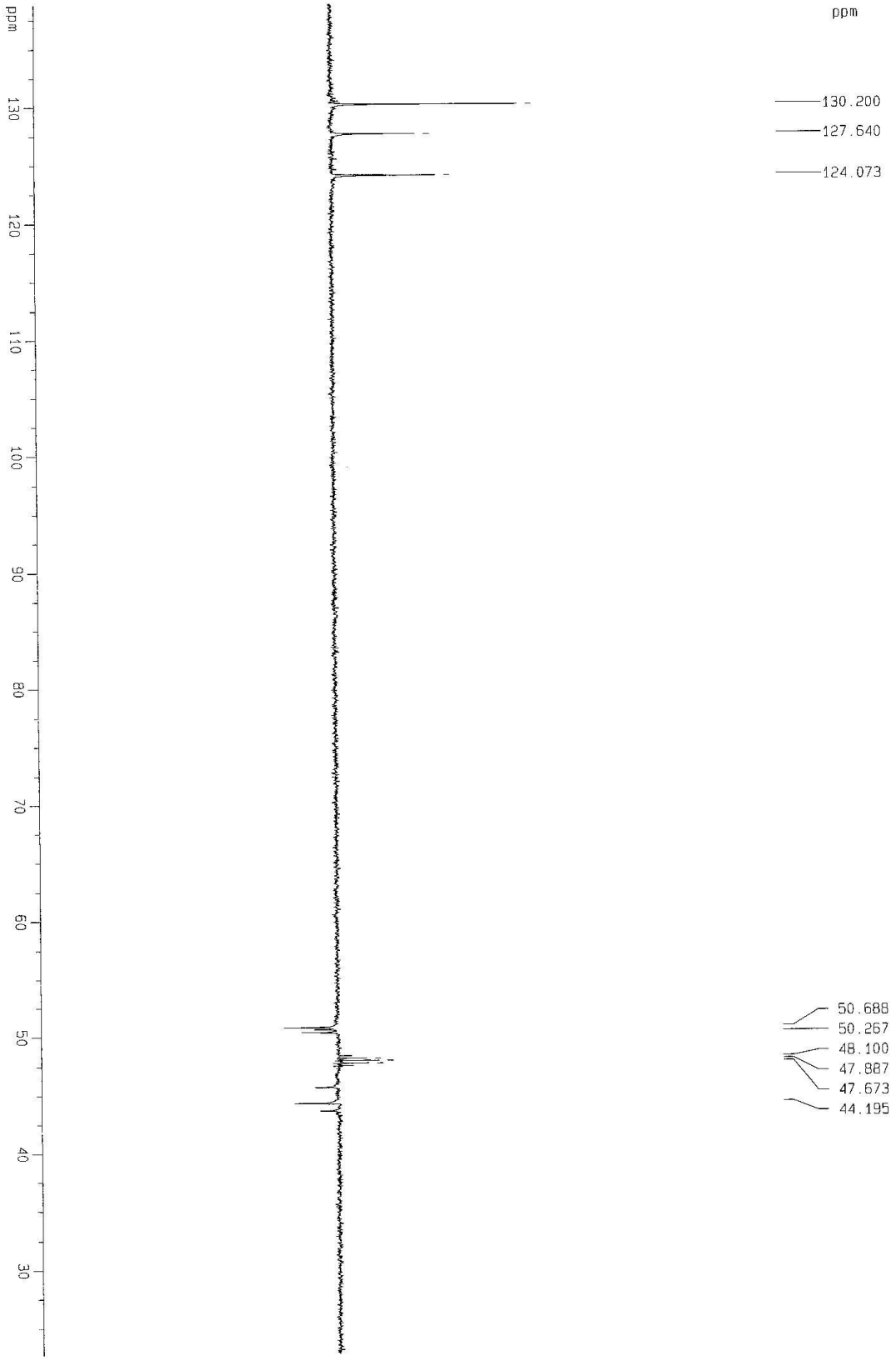


Figure S16. DEPT ^{13}C spectrum of $[1H_6(ReO_4)](CF_3SO_3)_5 \cdot 7H_2O$ in CD_3OD (400 MHz)

B. Characterisation of azacryptand 1

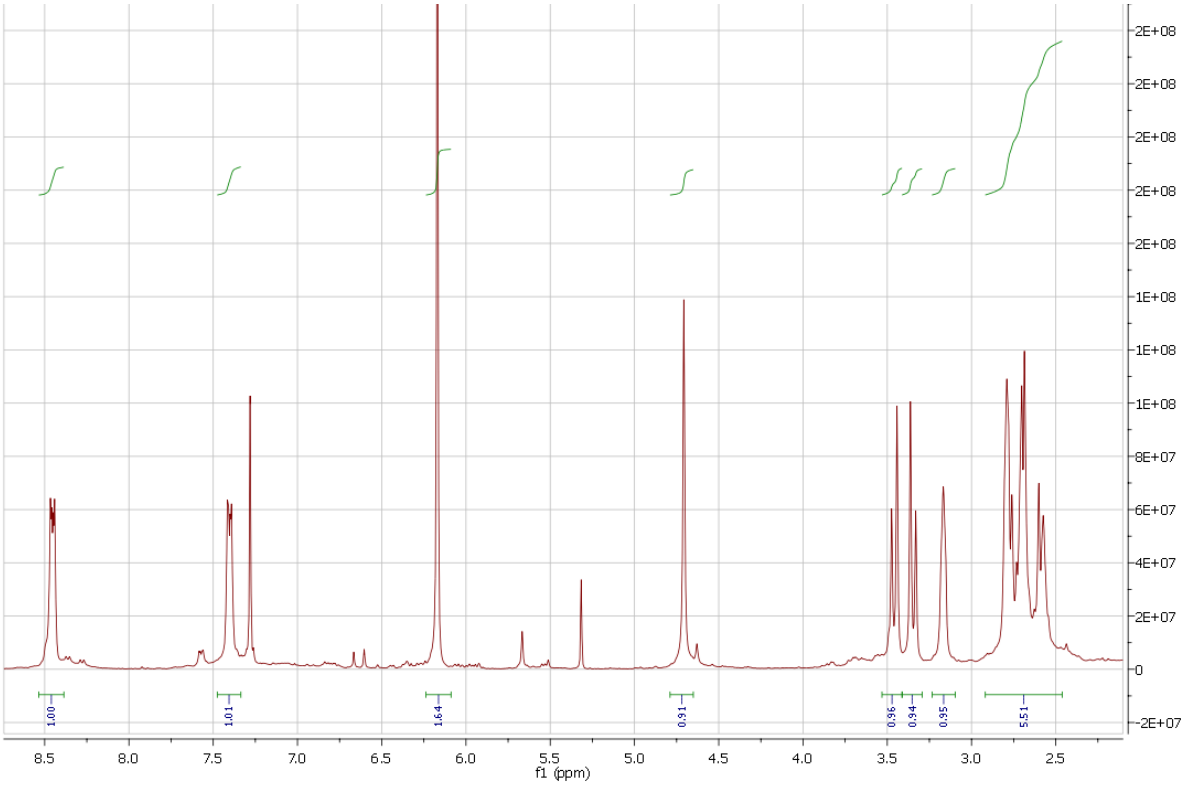


Figure S17. ^{1}H NMR spectrum of 1 in $CDCl_3$ (400 MHz)

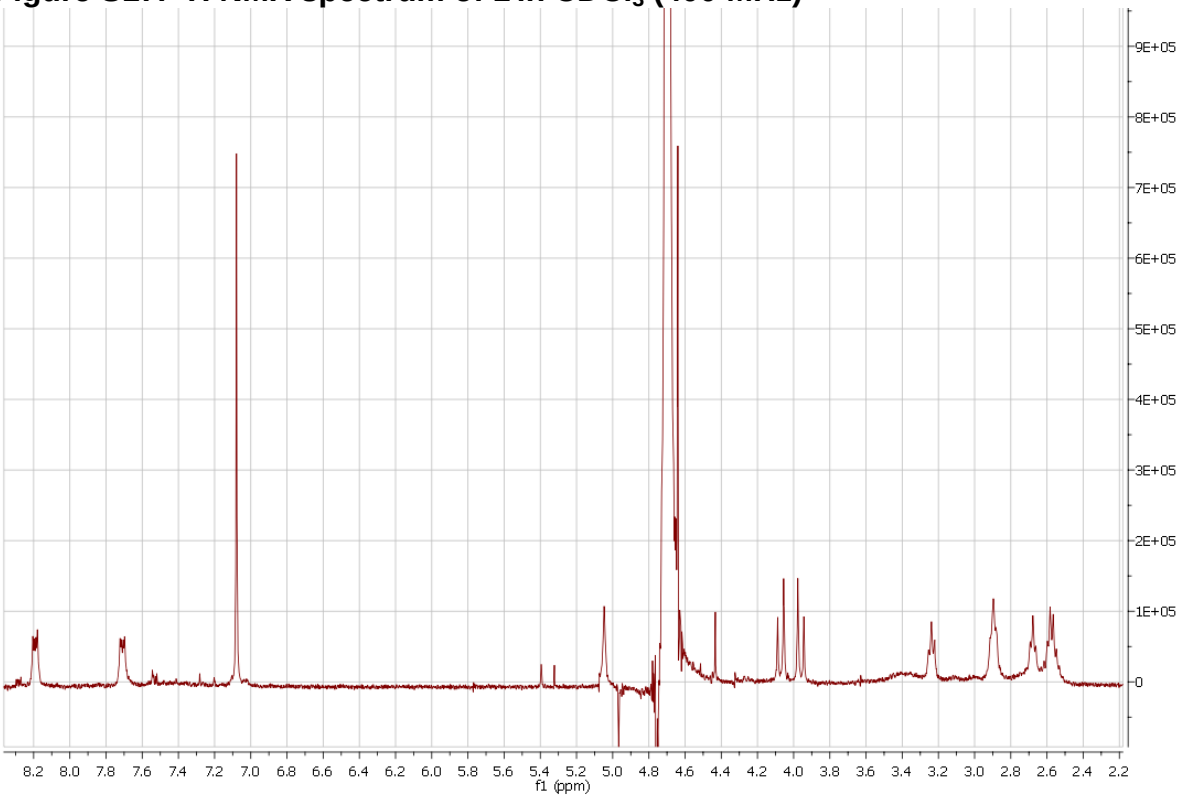


Figure S18. ^{1}H NMR spectrum of $1H_6^{6+}$ in D_2O pD =2 (400 MHz)

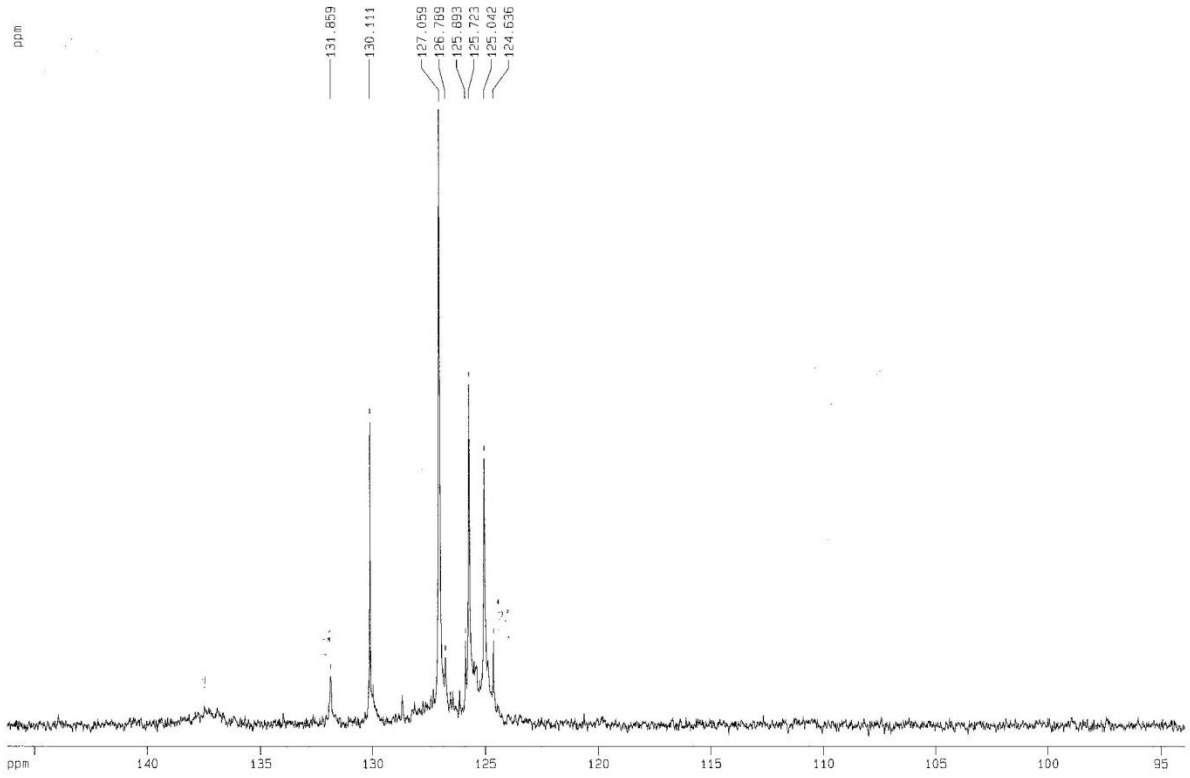


Figure S19a. ^{13}C NMR spectrum of 1 in $CDCl_3$ (400 MHz)

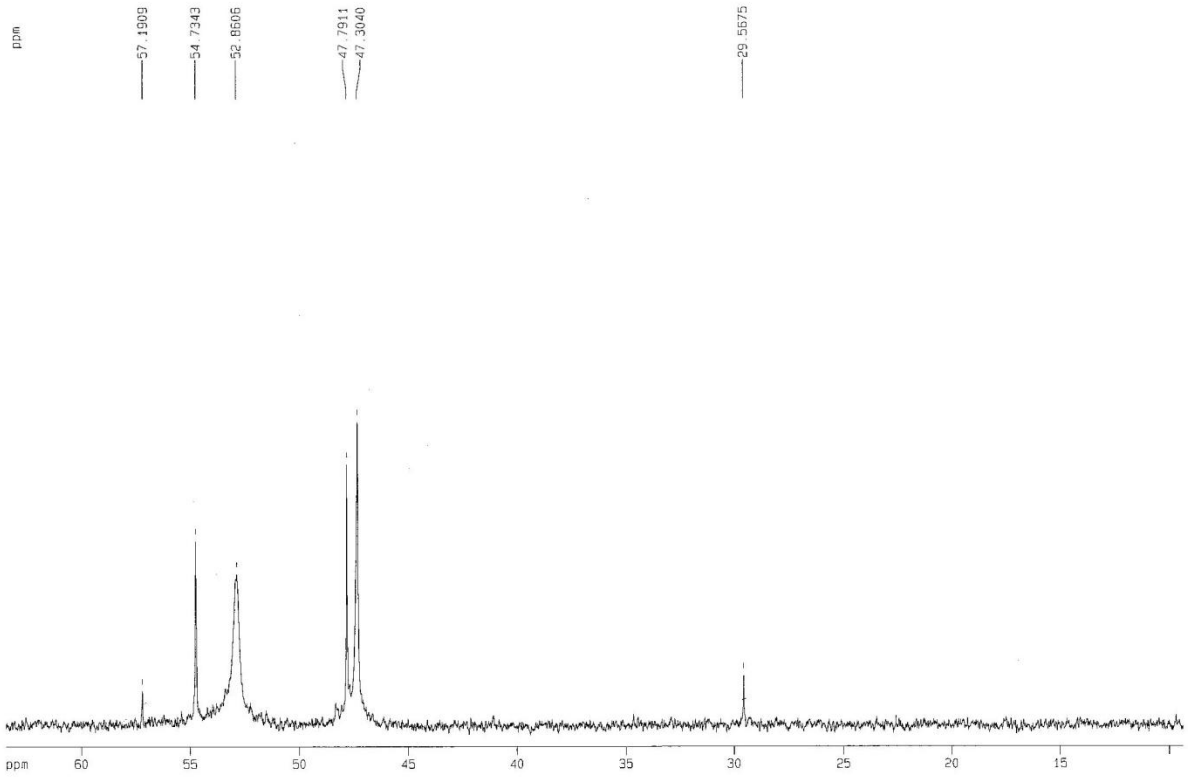


Figure S19b. ^{13}C NMR spectrum of 1 in $CDCl_3$ (400 MHz)

C. Characterisation of $[1H_6(TcO_4)](CF_3SO_3)_5 \cdot nH_2O$

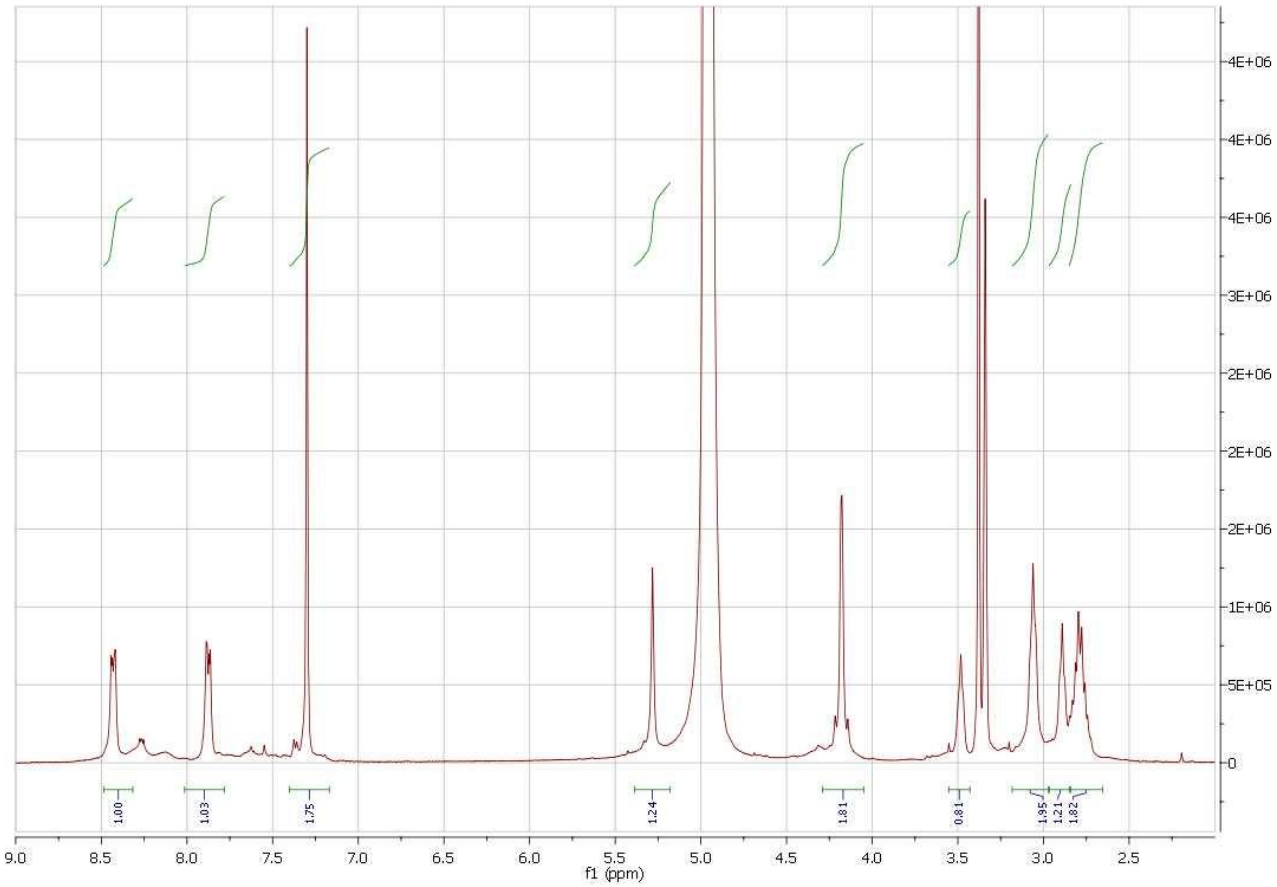


Figure S20. ^{1}H NMR spectrum of $[1H_6(TcO_4)](CF_3SO_3)_5 \cdot nH_2O$ in CD_3OD (400 MHz)

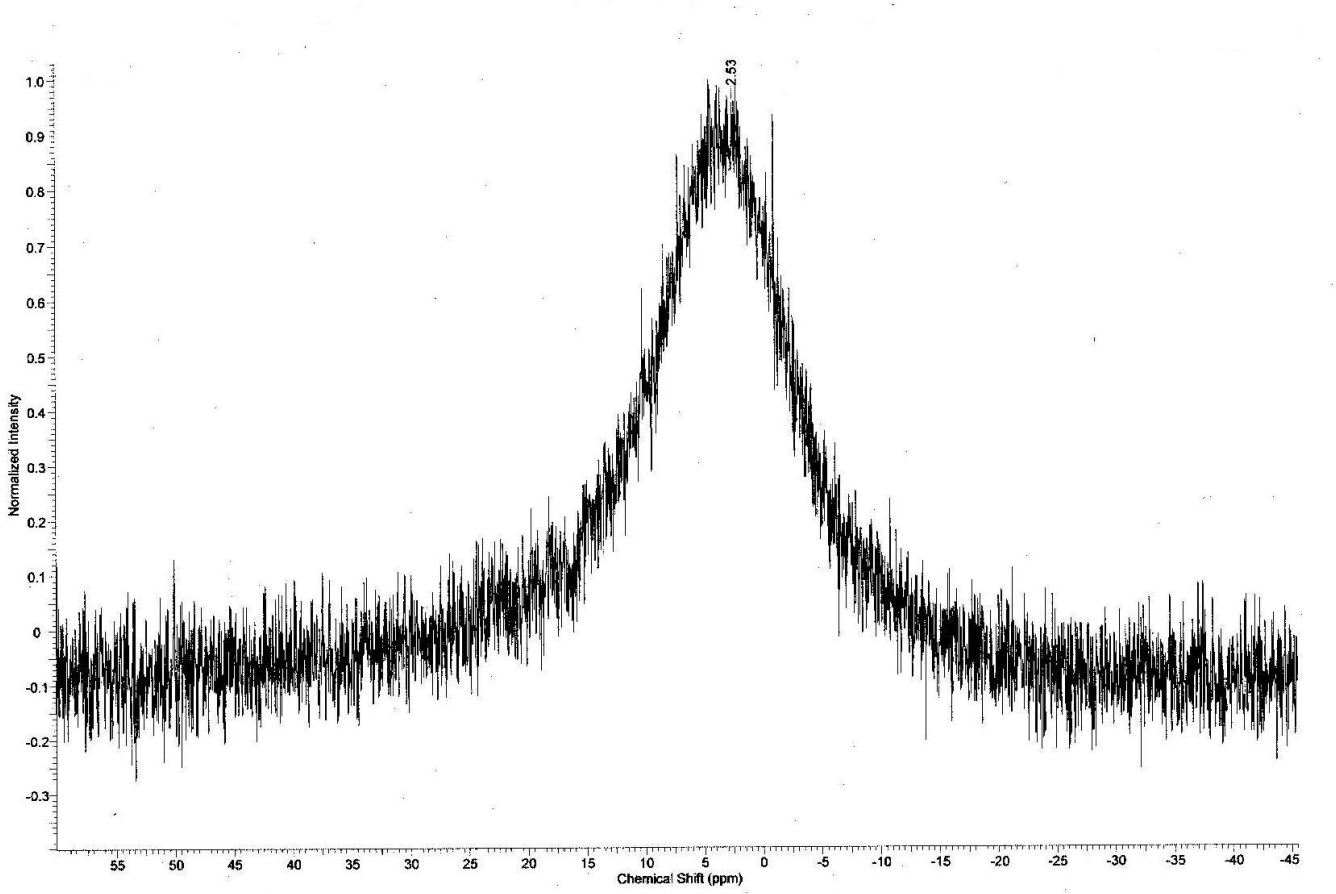


Figure S21. ^{99}Tc NMR spectrum of $[1H_6(TcO_4)](CF_3SO_3)_5 \cdot nH_2O$ in CD_3OD (400 MHz)

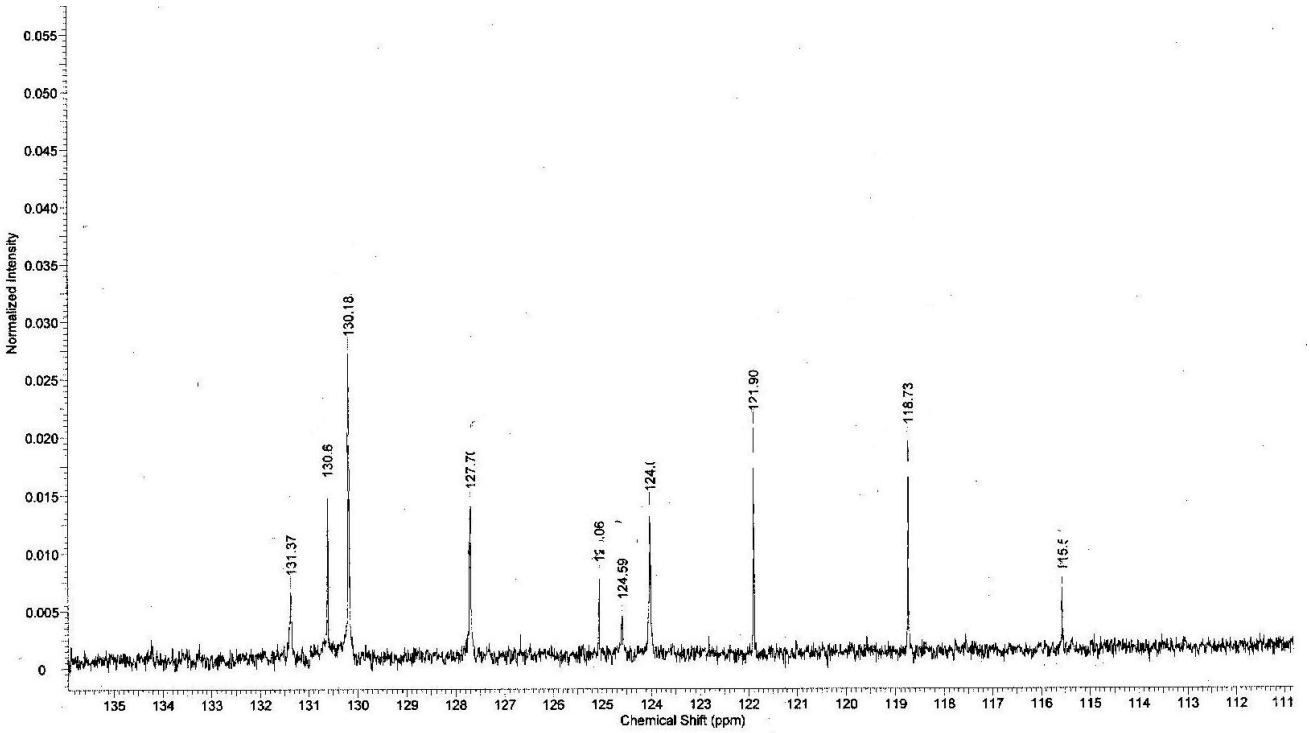


Figure S22a. ^{13}C NMR spectrum of $[1H_6(TcO_4)](CF_3SO_3)_5{\cdot}nH_2O$ in CD_3OD (400 MHz)

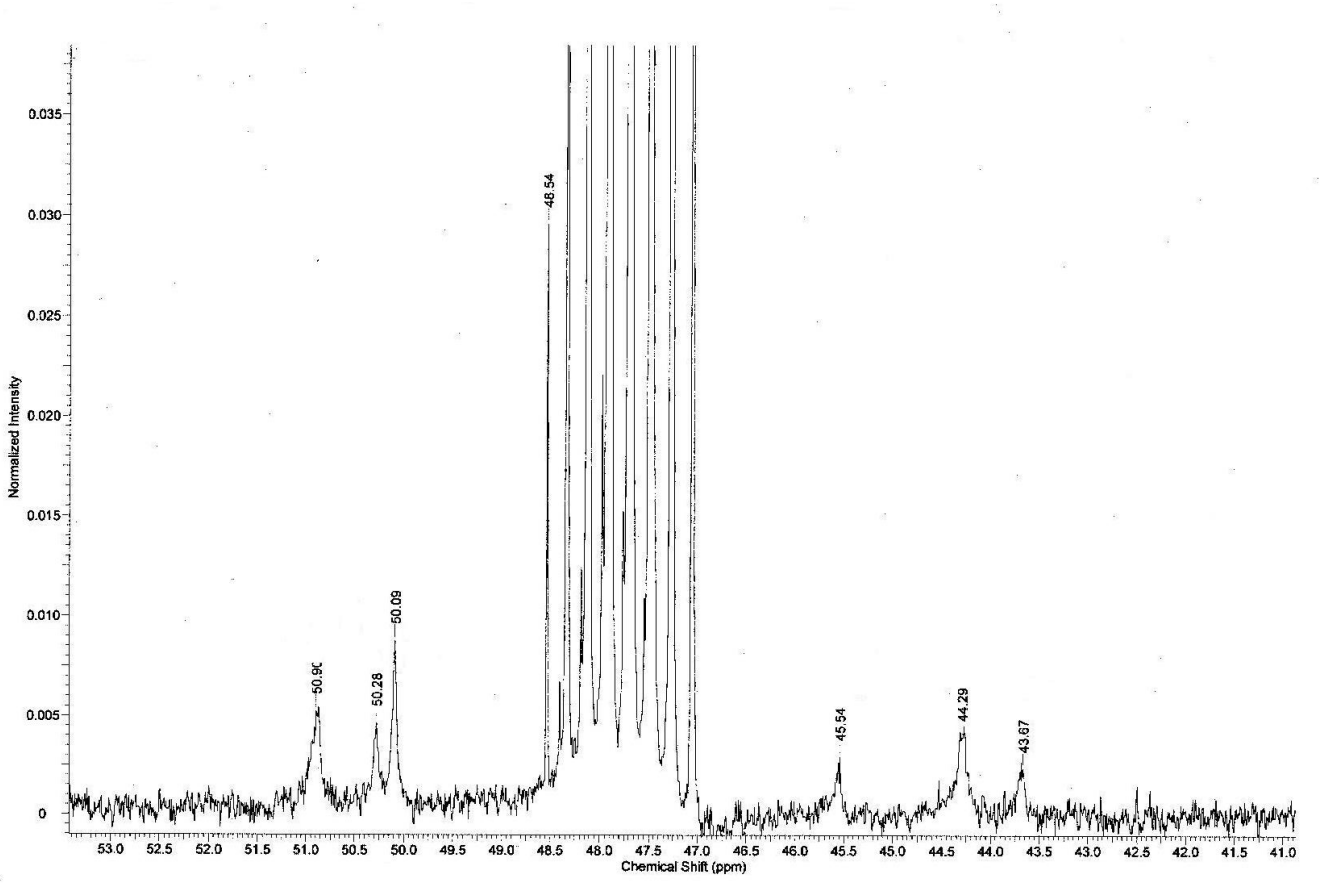


Figure S22b. ^{13}C NMR spectrum of $[1H_6(TcO_4)](CF_3SO_3)_5{\cdot}nH_2O$ in CD_3OD (400 MHz)

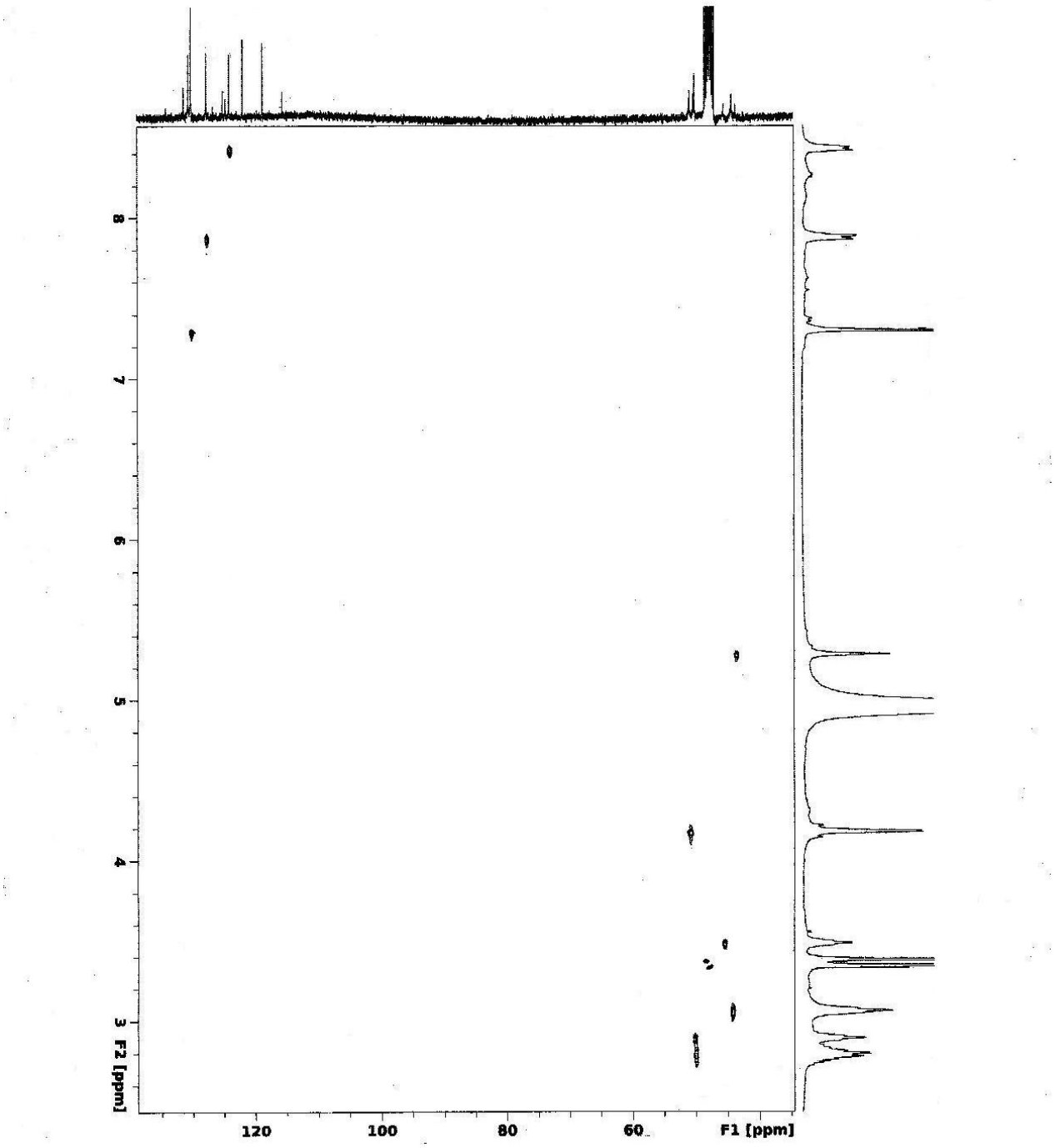


Figure S23. Heterocorrelation (^{1}H-^{13}C) spectrum of $[1H_6(TcO_4)](CF_3SO_3)_5 \cdot nH_2O$ in CD_3OD (400 MHz)

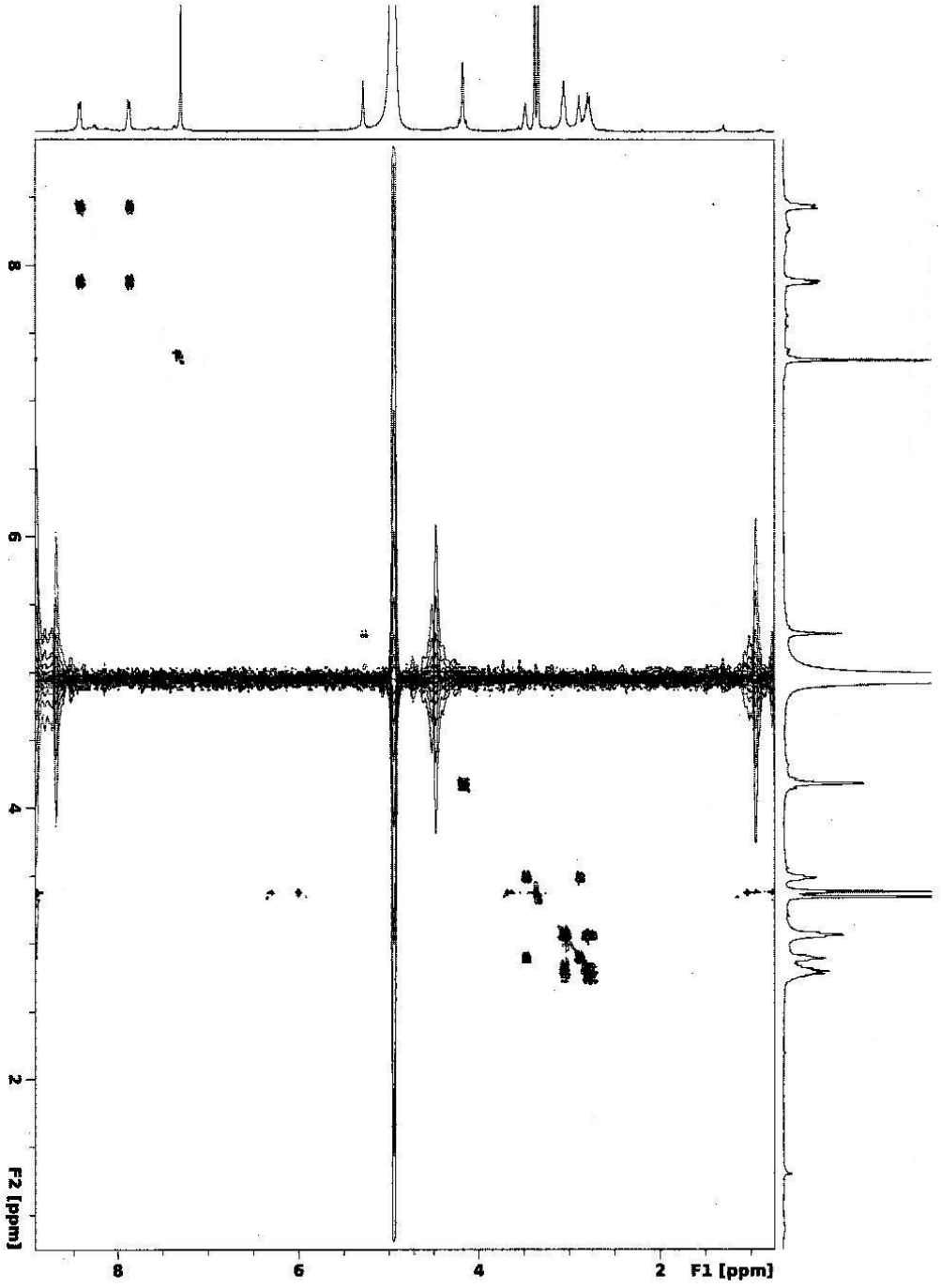


Figure S24. COSY spectrum of $[1H_6(TcO_4)](CF_3SO_3)_5 \cdot nH_2O$ in CD_3OD (400 MHz)

Supplementary References

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