

Supplementary Information for:

Dual stimuli-induced formation of a μ -hydroxido bridged $[\text{Zn}_9\text{L}_5(\mu\text{-OH})_6]^{12+}$ half-pipe

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1.1 General methods

All chemicals and solvents, unless otherwise stated, were purchased from commercial suppliers and used as received. A previously published procedure was followed to prepare [3,3',6',2''5'',3'''-quaterpyridine]-6,6''-dicarbaldehyde **1**.^[1] Acetonitrile (CH₃CN) was supplied by Fisher Scientific and diethyl ether (Et₂O) was supplied by Sigma Aldrich.

NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer, a Bruker Avance 400 MHz QNP Ultrashield spectrometer, a Bruker Avance III 400 MHz QNP Ultrashield Plus Cryo spectrometer, a Bruker Avance 500 MHz Cryo Ultrashield spectrometer, Bruker Avance 500 MHz BroadBand, and a 700 MHz TXO Cryoprobe Spectrometer spectrometer using residual non-deuterated solvent as the internal standard. All chemical shifts (δ) are quoted in ppm and coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used in reporting the multiplicity for NMR resonances: s = singlet, d = doublet, t = triplet, and m = multiplet. Samples were prepared CD₃CN purchased from EurisoTop or Sigma-Aldrich. The NMR data was processed using Bruker Topspin 3.2. Although the complexity of the spectra precluded full assignment, characteristic ¹H resonances were assigned using standard 2D NMR techniques, such as ¹H-¹H COSY, ¹H-¹H NOESY and 1D selective TOCSY experiments. The solubility of many of the complexes precluded the acquisition of ¹³C NMR data.

For the cationic metal organic complexes: low resolution electrospray ionization mass spectrometry (LR-ESI-MS) was performed on a Micromass Quattro LC mass spectrometer (cone voltage 20 eV; desolvation temp. 313 K; ionization temp. 313 K) infused from a Harvard syringe pump at a rate of 10 μ L min⁻¹. High resolution electrospray ionization mass spectrometry (HR-ESI-MS) was performed on a Thermofisher LTQ Orbitrap XL hybrid ion trap mass spectrometer (capillary temp. 30 °C; tube lens 40 V).

1.2 Synthesis of **2**

When **1** was reacted with in a 1:1 ratio with $\text{Zn}(\text{NTf}_2)_2$ a turbid yellow solution was produced (The insoluble material was hypothesized to be undissolved **1**). In contrast, a 1:2 ratio of **1** to $\text{Zn}(\text{NTf}_2)_2$ led to a clear yellow solution which was used for all subsequent transformation studies. Both methods are reported below.

[3,3'6',2"5",3"-quaterpyridine]-6,6"-dicarbaldehyde **1** (20.5 mg, 56.0 μmol , 1 equiv.), 4-methoxyaniline (13.8 mg, 112.0 μmol , 2 equiv.), and $\text{Zn}(\text{NTf}_2)_2$ (70.9 mg, 112.0 μmol , 2 equiv.) were suspended in reagent grade CH_3CN (3 mL) in a PTFE stoppered Schlenk tube. The reaction mixture was stirred at 70 °C for 12 hours. The resulting clear yellow solution was filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et_2O (30 mL) precipitated out **2** as a yellow solid that was isolated by centrifugation.

^1H NMR (400 MHz, CD_3CN) δ 9.21 (d, $J = 1.7$ Hz, 1H, H_{10}), 9.08 (d, $J = 1.7$ Hz, 1H, H_7), 9.00 (s, 1H, H_4), 8.94 (d, $J = 8.3$ Hz, 1H, H_9), 8.79 (dd, $J = 8.2, 1.8$ Hz, 1H, H_8), 8.73 (dd, $J = 7.9, 1.9$ Hz, 1H, H_6), 8.42 (d, $J = 7.9$ Hz, 1H, H_5), 7.18 (d, $J = 8.9$ Hz, 1H, H_3), 6.83 (d, $J = 8.9$ Hz, 1H, H_2), 3.80 (s, 3H, H_1).

^{13}C NMR (176 MHz; CD_3CN) δ 161.5, 161.2, 149.9, 149.6, 148.1, 143.0, 142.9, 139.6, 138.8, 137.4, 130.9, 125.1, 122.0, 119.5, 115.6, 56.4

^{19}F NMR: (376 MHz; CD_3CN , reference C_6F_6): δ -80.49

LR-ESI-MS: m/z : 620.68 (620.83) $\{[\text{Zn}_3\text{L}_3](\text{NTf}_2)_2\}^{4+}$, 921.40 (921.07) $\{[\text{Zn}_3\text{L}_3](\text{NTf}_2)_3\}^{3+}$, 1522.42 (1521.57) $\{[\text{Zn}_3\text{L}_3](\text{NTf}_2)_4\}^{2+}$

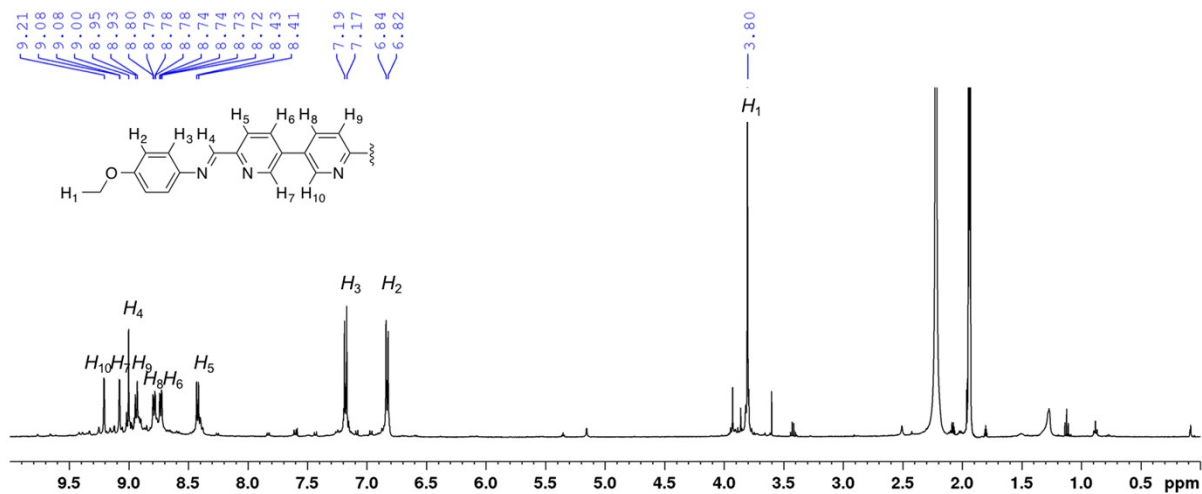


Figure S1: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) of [2](NTf₂)₆

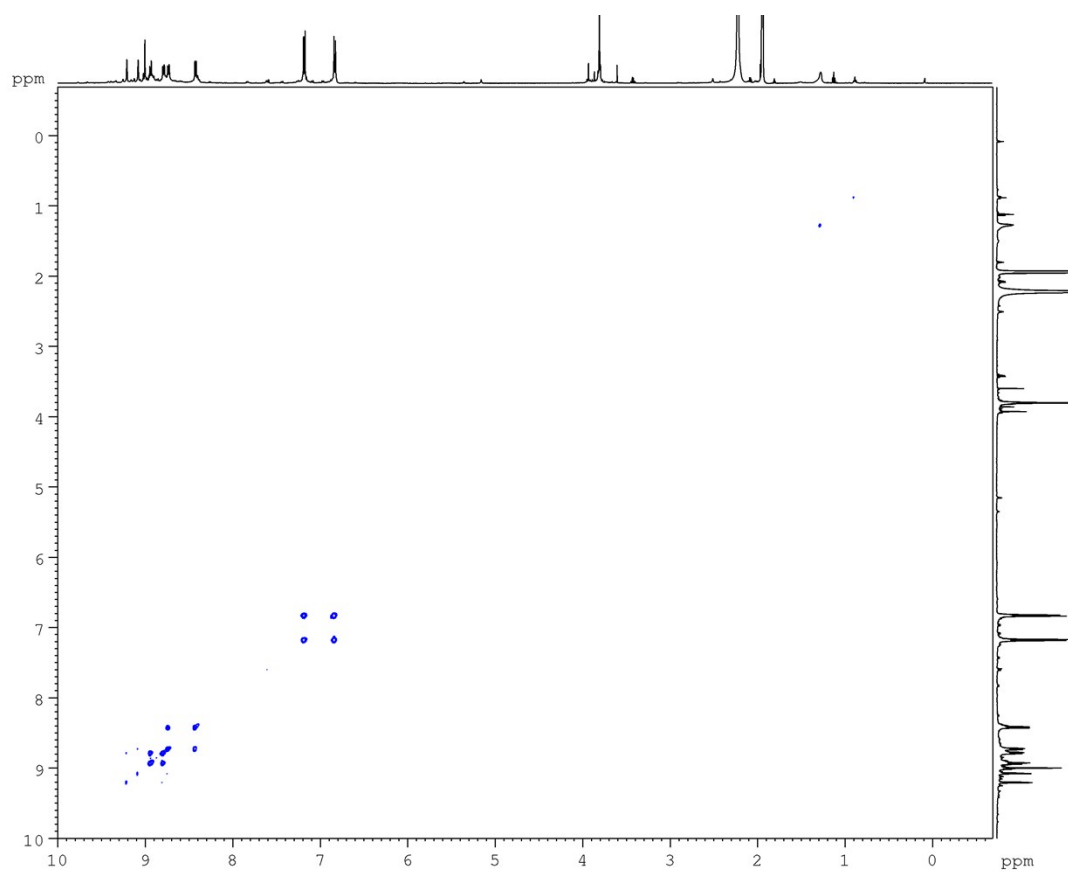


Figure S2: COSY NMR spectrum (400 MHz, 298 K, CD₃CN) of [2](NTf₂)₆

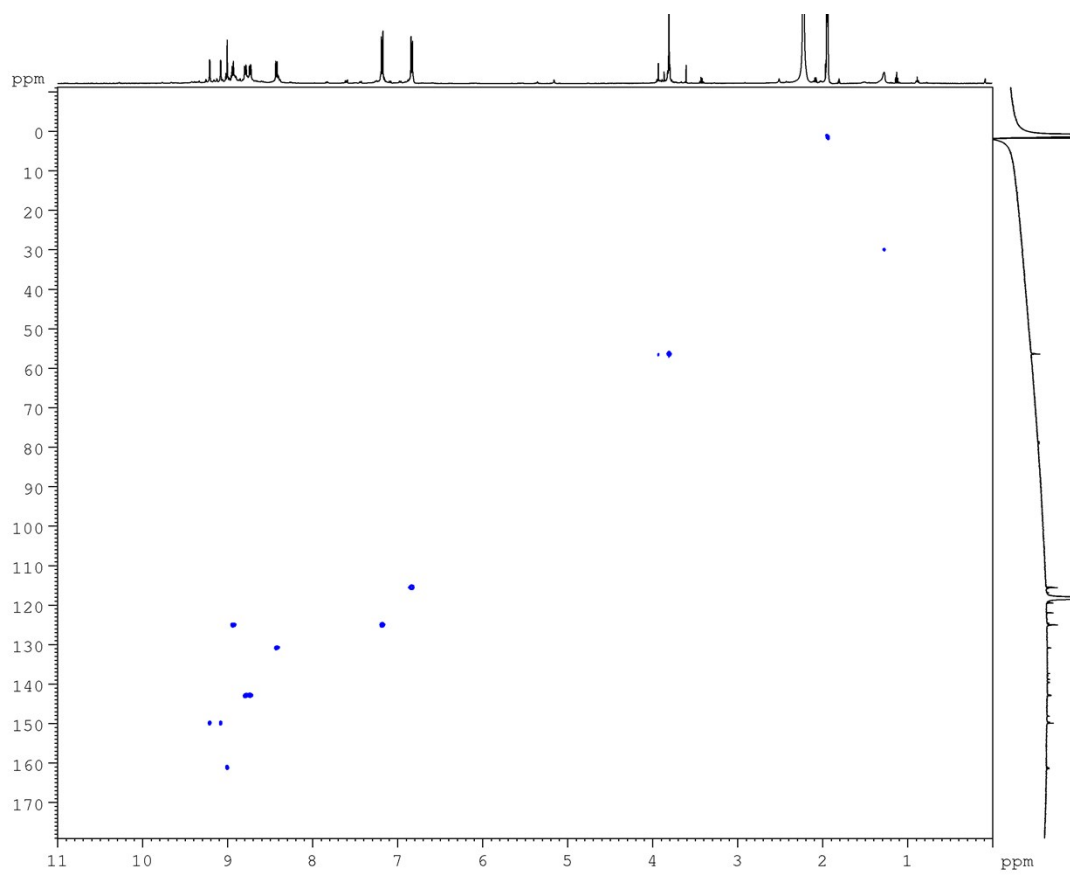


Figure S3: HSQC NMR spectrum (400 MHz, 298 K, CD_3CN) of $[\mathbf{2}](\text{NTf}_2)_6$

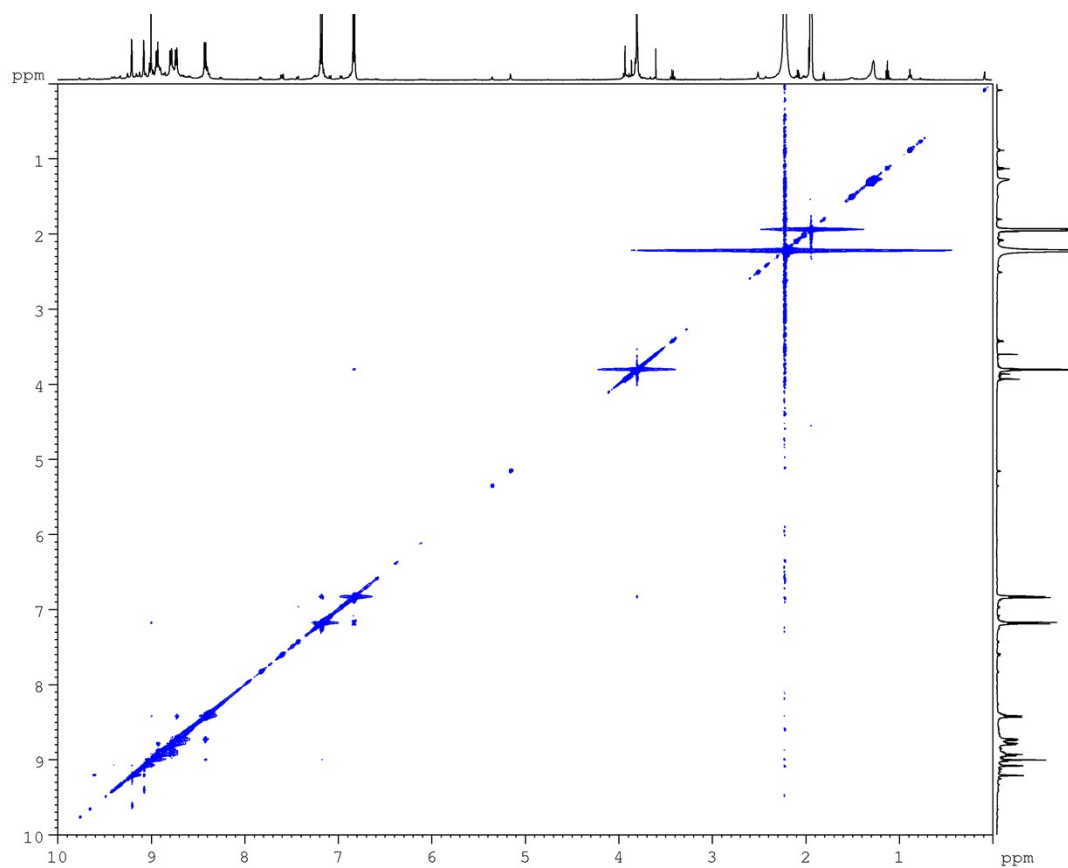


Figure S4: NOESY NMR spectrum (400 MHz, 298 K, CD₃CN) of [2](NTf₂)₆

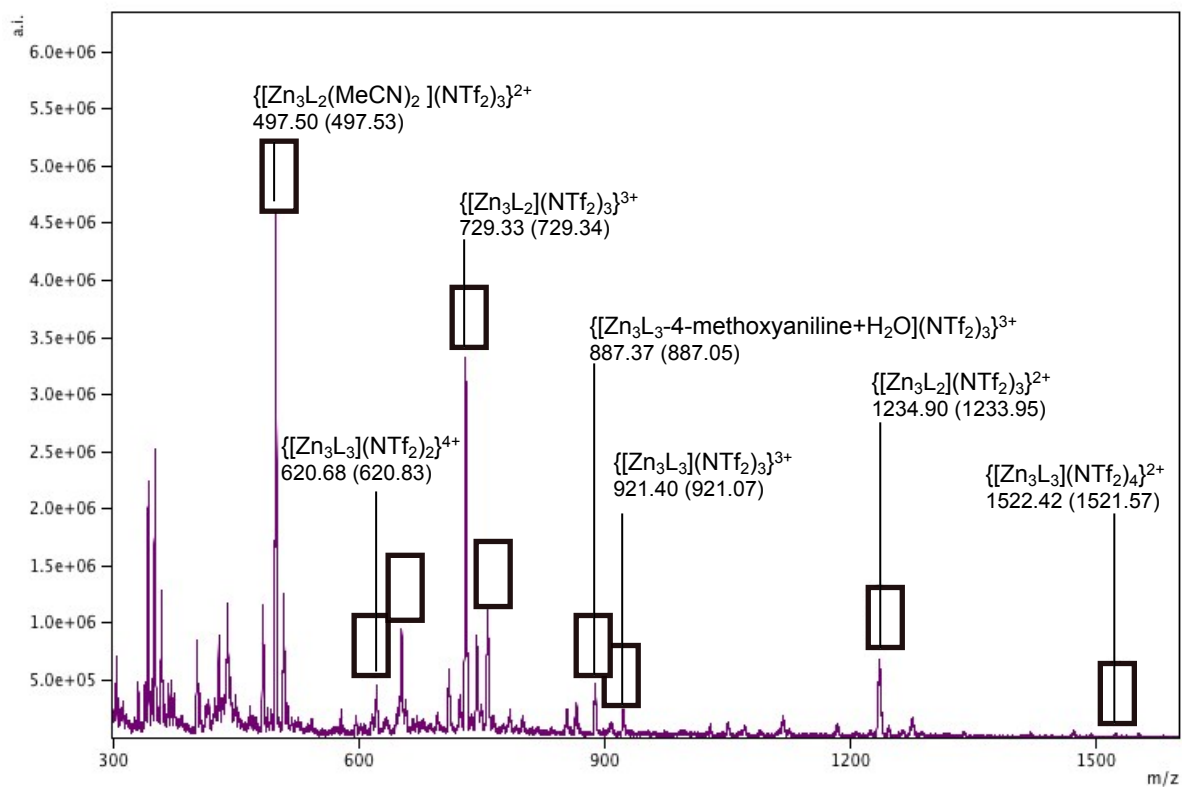


Figure S5: LR-ESI-mass spectrum of product $[2](NTf_2)_6$. Calculated values are in brackets.

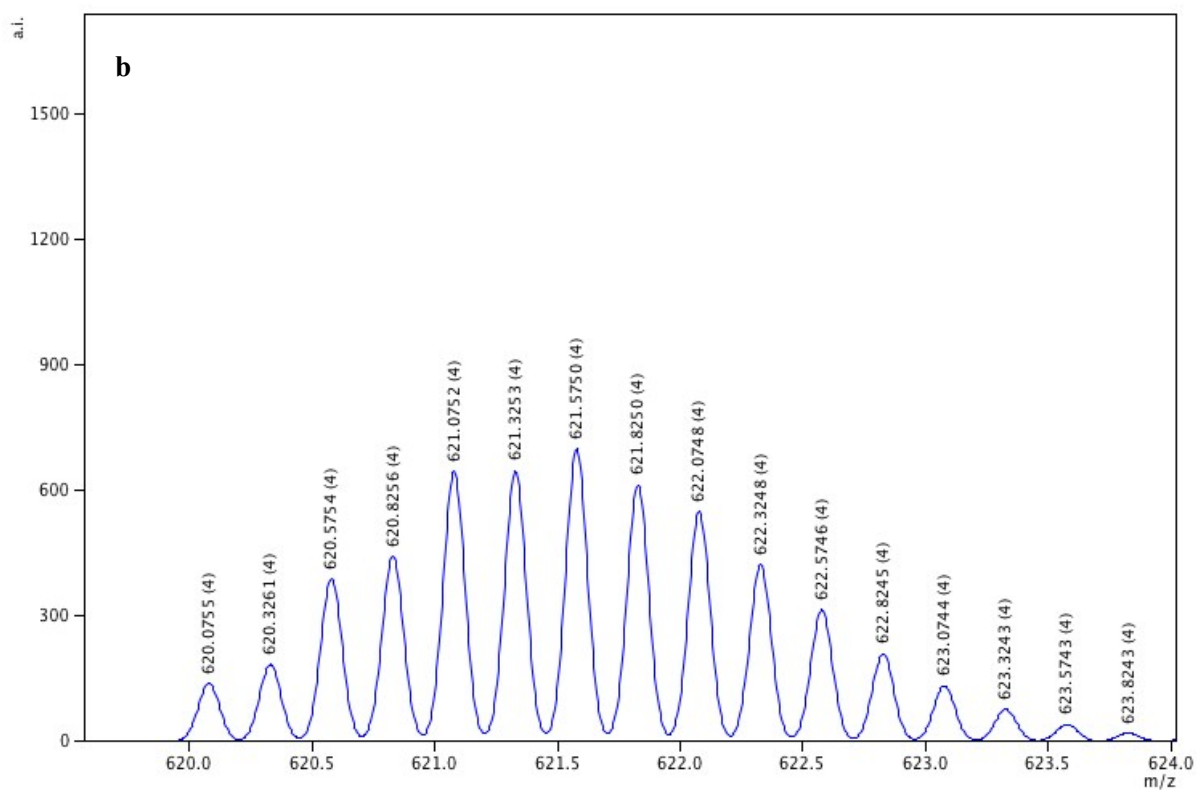
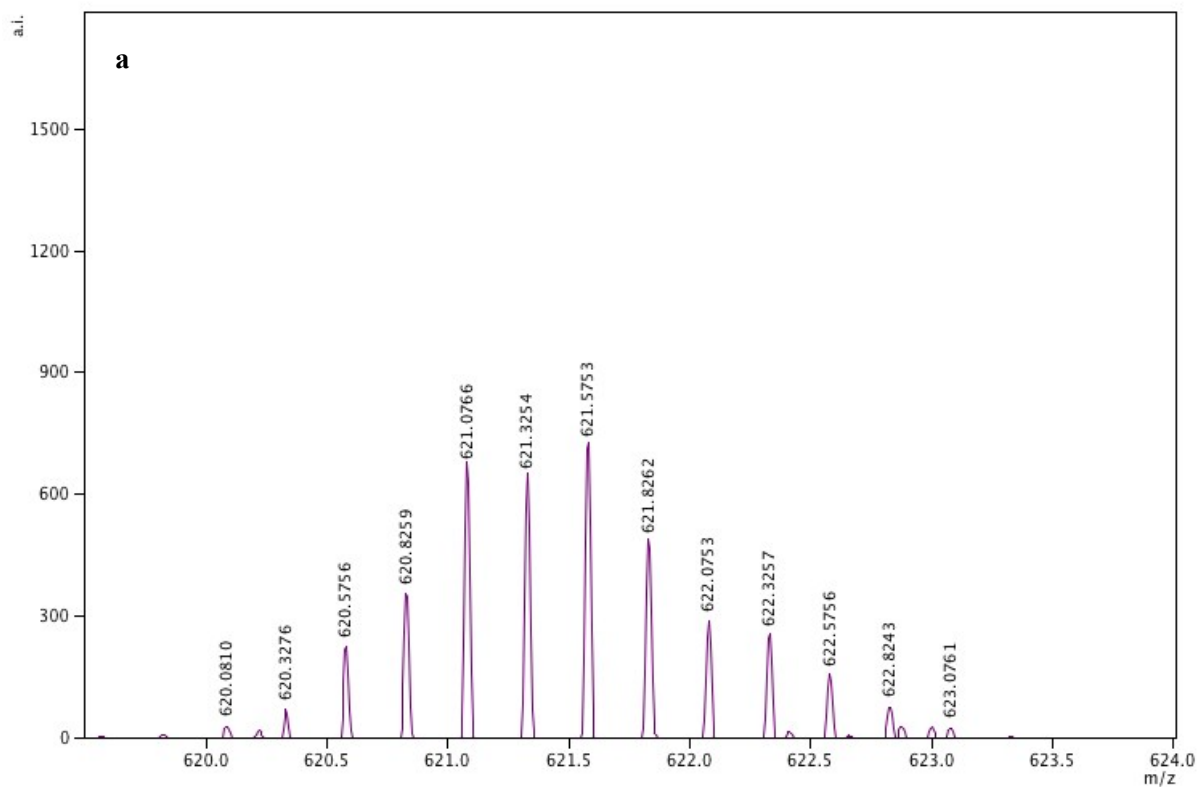


Figure S6: **(a)** HR-ESI-mass spectrum of the $[2](NTf_2)_2^{4+}$ ion. **(b)** Calculated isotopic distribution of $[2](NTf_2)_2^{4+}$.

1:1 ratio of Zn(NTf₂)₂ to **1**

[3,3'6',2"5",3"-quaterpyridine]-6,6"-dicarbaldehyde **1** (23.5 mg, 64.3 μmol, 1 equiv.), 4-methoxyaniline (15.8 mg, 128.5 μmol, 2 equiv.), and Zn(NTf₂)₂ (40.2 mg, 64.3 μmol, 1 equiv.) were suspended in reagent grade CH₃CN (8 mL) in a PTFE stoppered Schlenk tube. The reaction mixture was stirred at 70 °C for 12 hours. The resulting turbid yellow solution was centrifuged and then filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et₂O (30 mL) precipitated out a yellow solid that was isolated by centrifugation.

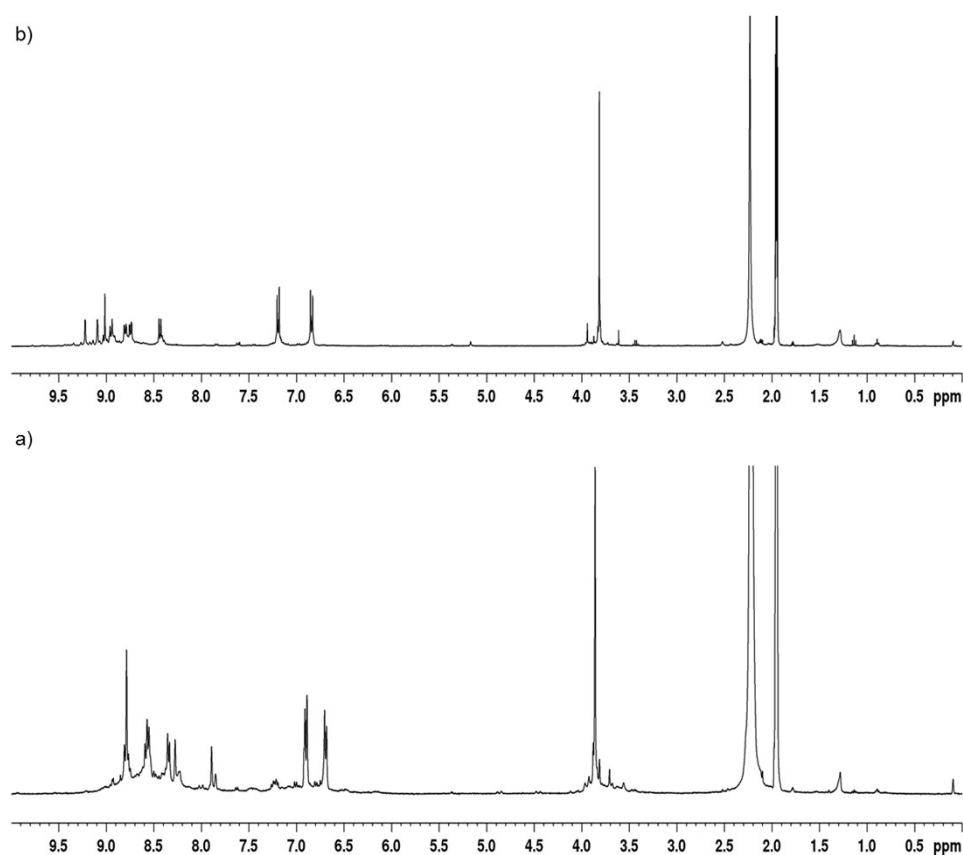


Figure S7: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) of (a) the reaction mixture containing a 1:1:2 ratio of Zn(NTf₂)₂ : **1** : 4-methoxyaniline (b) the reaction mixture containing a 1:2:2 ratio of Zn(NTf₂)₂ : **1** : 4-methoxyaniline for comparison.

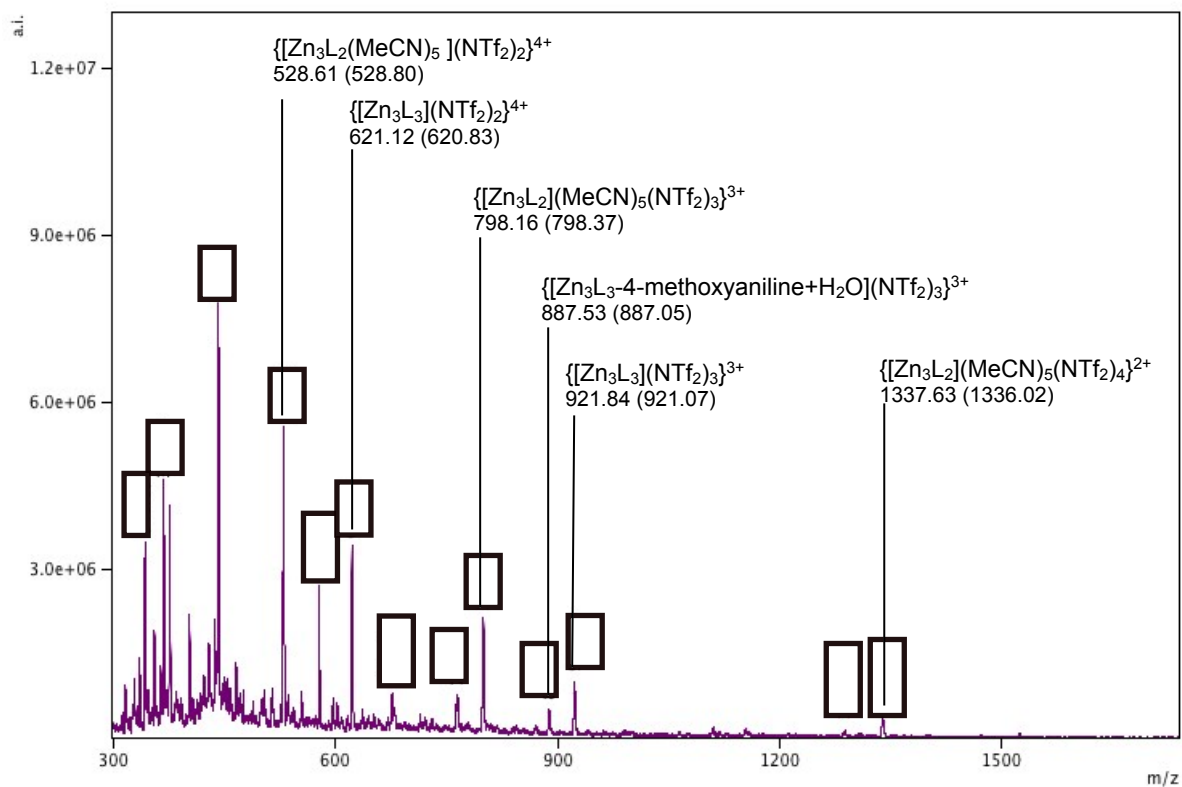


Figure S8: LR-ESI-mass spectrum of product the reaction mixture containing a 1:1:2 ratio of $Zn(NTf_2)_2$: 1 : 4-methoxyaniline. Calculated values are in brackets.

1.3 [Zn₉L₅(μ-OH)₆](ClO₄)₁₂ half-pipe **3**

[3,3'6',2''5'',3'''-quaterpyridine]-6,6'''-dicarbaldehyde **1** (4.3 mg, 11.7 μmol, 5 equiv.), 4-methoxyaniline (4.8 mg, 37.39 μmol, 16 equiv.), and Zn(ClO₄)₂·6H₂O (8.0 mg, 21.0 μmol, 9 equiv.) were suspended in reagent grade CH₃CN (3 mL) in a PTFE stoppered Schlenk tube. The reaction mixture was stirred at 70 °C for 12 hours. The resulting turbid solution was centrifuged and then filtered through a PTFE syringe filter (4.5 μm pore size). Subsequent addition of Et₂O (30 mL) precipitated out **3** as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et₂O into an acetonitrile solution of **3** yielded crystals suitable for analysis by X-ray crystallography.

The above reaction can be performed using 10 equiv. of 4-methoxyaniline and 6 equiv. of triethylamine as the base under conditions described above. ¹H-NMR spectroscopy and LR-ESI MS were consistent with the formation of [Zn₉L₅(μ-OH)₆](ClO₄)₁₂ “**3**(ClO₄)₁₂”

¹H NMR (700 MHz, CD₃CN) δ 9.61 (m, 2H, L^{II}H₇), 9.03 (d, J = 1.5 Hz, 2H), 9.02 (s, 1H), 9.00 (m, 2H, L^{III}H₇ L^VH₄), 8.95 (d, J = 1.5 Hz, 1H, L^IH₇), 8.88 (dd, J = 2.2, 7.8 Hz, 1H, L^VH₆), 8.86 (dd, J = 2.2, 8.2 Hz, 1H), 8.84 (m, 2H, L^{II}H₄), 8.82 (d, J = 6.2 Hz 1H, L^IH₆), 8.80 (d, J = 5.9 Hz, 1H), 8.78 - 8.76 (m, 2H, L^IH₅, L^VH₆), 8.69 (d, J = 5.9 Hz, 1H), 8.67 (dd, J = 1.6, 5.9 Hz, 1H), 8.59 - 8.58 (m, 2H, L^IH₄, L^{II}H₆), 8.55 (s, 1H, L^VH₄), 8.49 (dd, J = 5.6, 1.6 Hz, 1H), 8.45-7 (m, 2H), 8.43 (d, J = 5.3 Hz, 1H, L^VH₅), 8.41 (dd, J = 5.6, 1.6 Hz, 1H, L^{III}H₆), 8.40 - 8.37 (m, 4H, L^VH₅, L^{III}H₄), 8.31 (d, J = 5.9 Hz, 1H) 8.26 (d, J = 5.3 Hz, 1H, L^{II}H₅), 8.15 (d, J = 5.6 Hz, 1H, L^{III}H₅), 8.06 (d, J = 5.6 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H, L^VH₃), 7.38 (d, J = 6.2 Hz, 2H, L^VH₃), 7.17 (d, J = 5.9 Hz, 2H, L^IH₃), 7.12 (d, J = 8.5 Hz, 2H, L^VH₂), 6.93 (d, J = 6.2 Hz, 2H, L^VH₂), 6.90 (d, J = 8.6 Hz, 2H, L^{II}H₃), 6.56 (d, J = 8.5 Hz, 2H, L^{II}H₂), 6.34 (d, J = 5.9 Hz, 2H, L^IH₂), 6.32 (d, J = 5.9 Hz, 2H, L^{III}H₂), 5.99 (d, J = 5.9 Hz, 2H, L^{III}H₃), 4.03 (s, 3H, L^VH₁), 3.91 (s, 3H, L^VH₁), 3.67 (s, 3H, L^{III}H₁), 3.60 (s, 3H, L^{II}H₁), 3.59 (s, 3H, L^IH₁).

Further assignments were hampered by the overlap of signals in the 8.00 to 9.10 ppm region

LR-ESI-MS: *m/z*: 694.85 (694.53) {[Zn₉L₅(μ-OH)₆](ClO₄)₈}⁶⁺, 853.88 (854.00) {[Zn₉L₅(μ-OH)₆](ClO₄)₇}⁵⁺, 1092.18 (1092.36) {[Zn₉L₅(μ-OH)₆](ClO₄)₆}⁴⁺, 1489.98 (1489.68) {[Zn₉L₅(μ-OH)₆](ClO₄)₉}³⁺

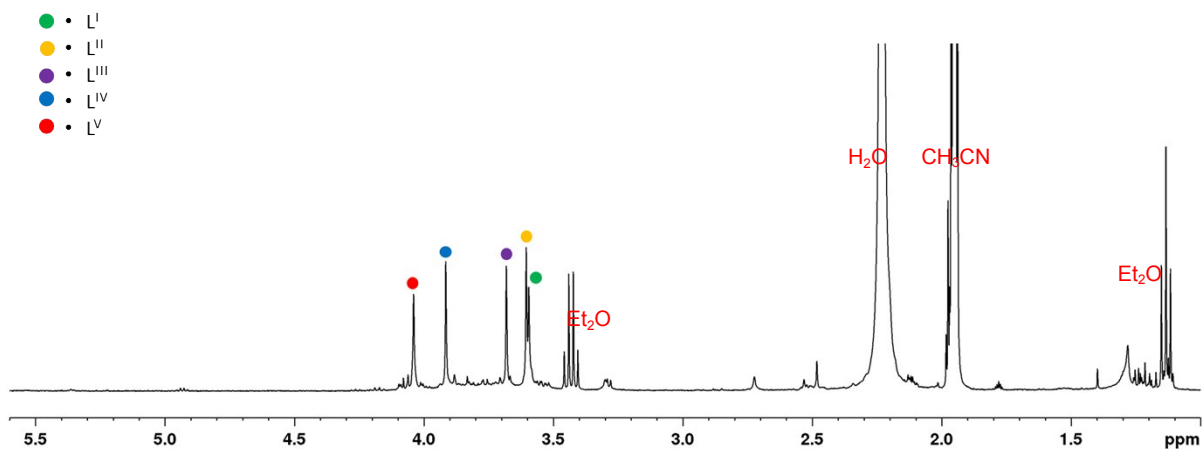


Figure S9: ¹H NMR spectrum (700 MHz, 298 K, CD₃CN) of [3](ClO₄)₁₂ in the region 1 – 5.5 ppm.

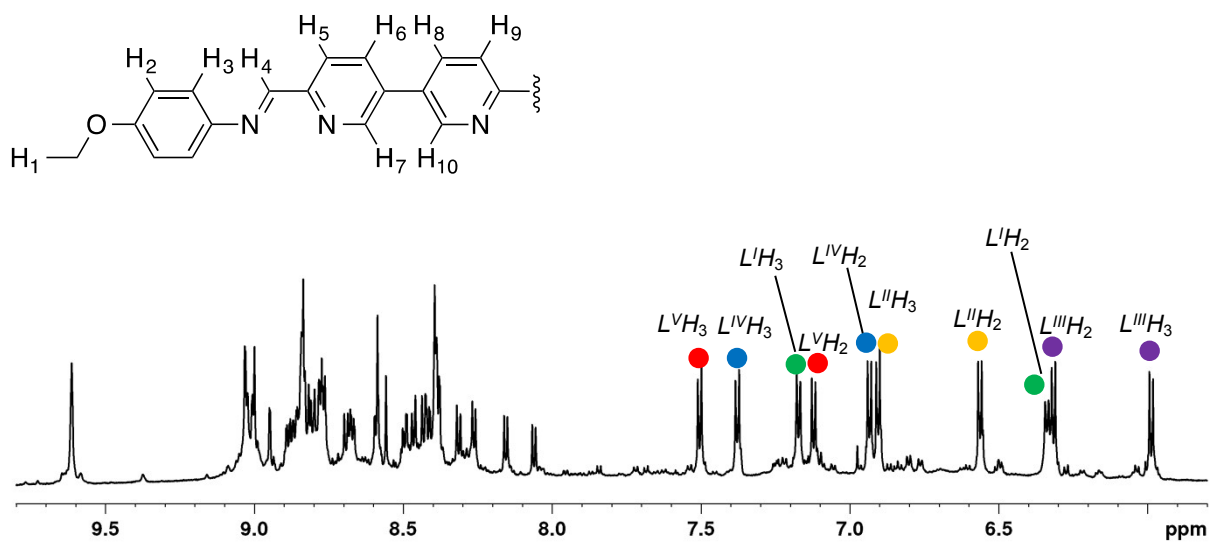


Figure S10: ¹H NMR (700 MHz, 298 K, CD₃CN) of [Zn₉L₅(μ-OH)₆](ClO₄)₁₄ **9** in the region 5.8 - 9.8 ppm. Peaks for protons 2 and 3 for the five ligand environments L^I - L^V are labeled.

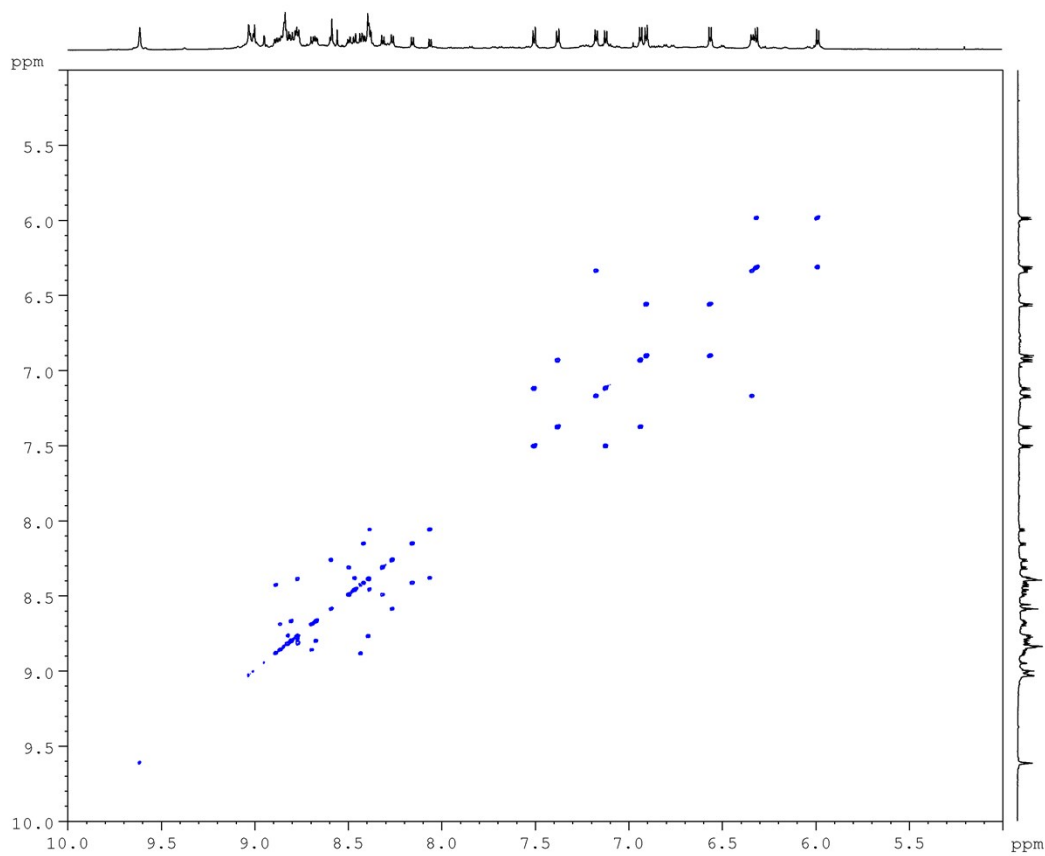


Figure S11: COSY NMR spectrum (700 MHz, 298 K, CD₃CN) of [3](ClO₄)₁₂ in the region 5 – 10 ppm.

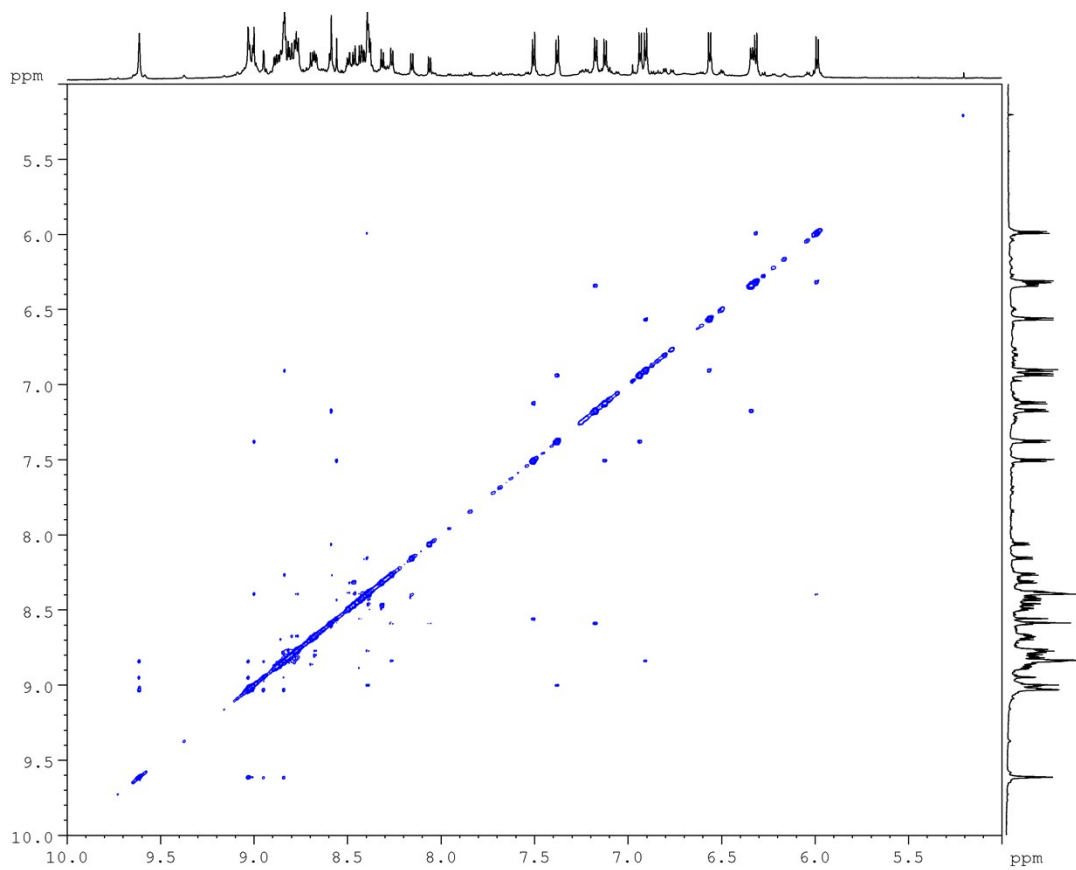


Figure S12: NOESY NMR spectrum (700 MHz, 298 K, CD_3CN) of $[3](ClO_4)_{12}$ in the region 5 – 10 ppm.

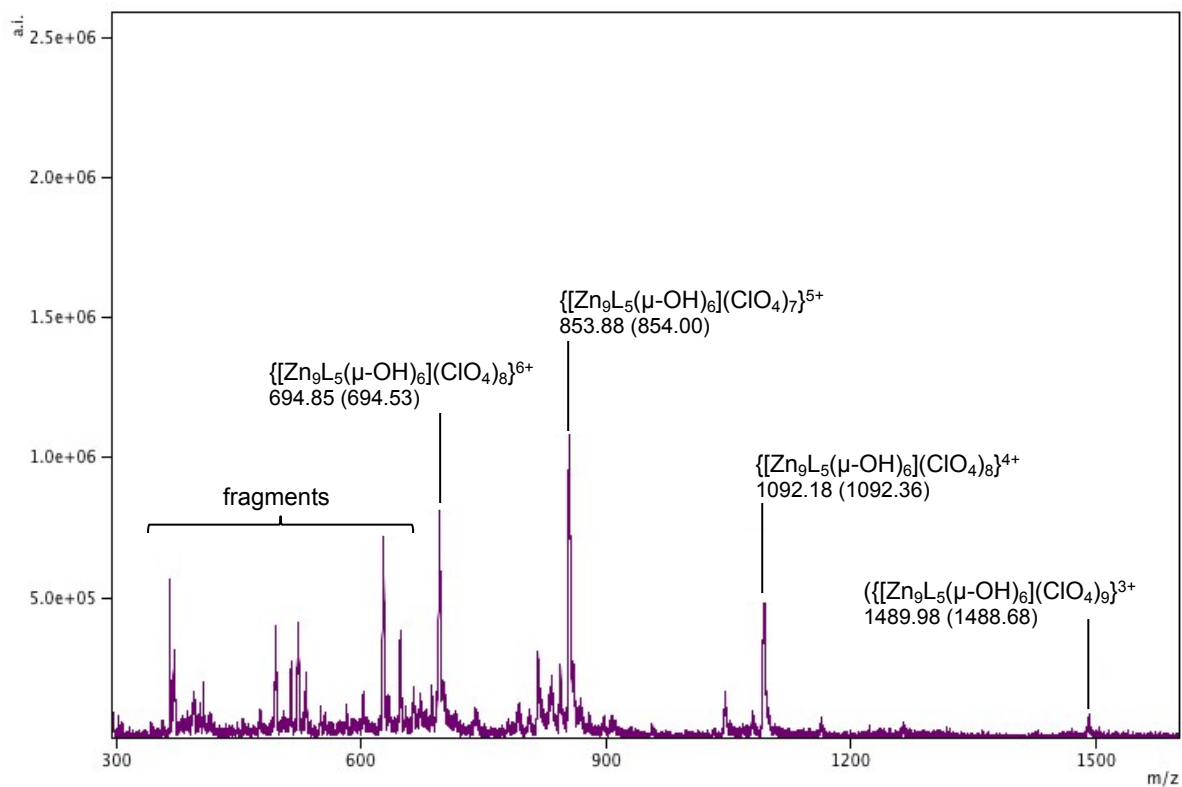


Figure S13: LR-ESI-mass spectrum of product $[3](\text{ClO}_4)_{12}$. Calculated values are in brackets.

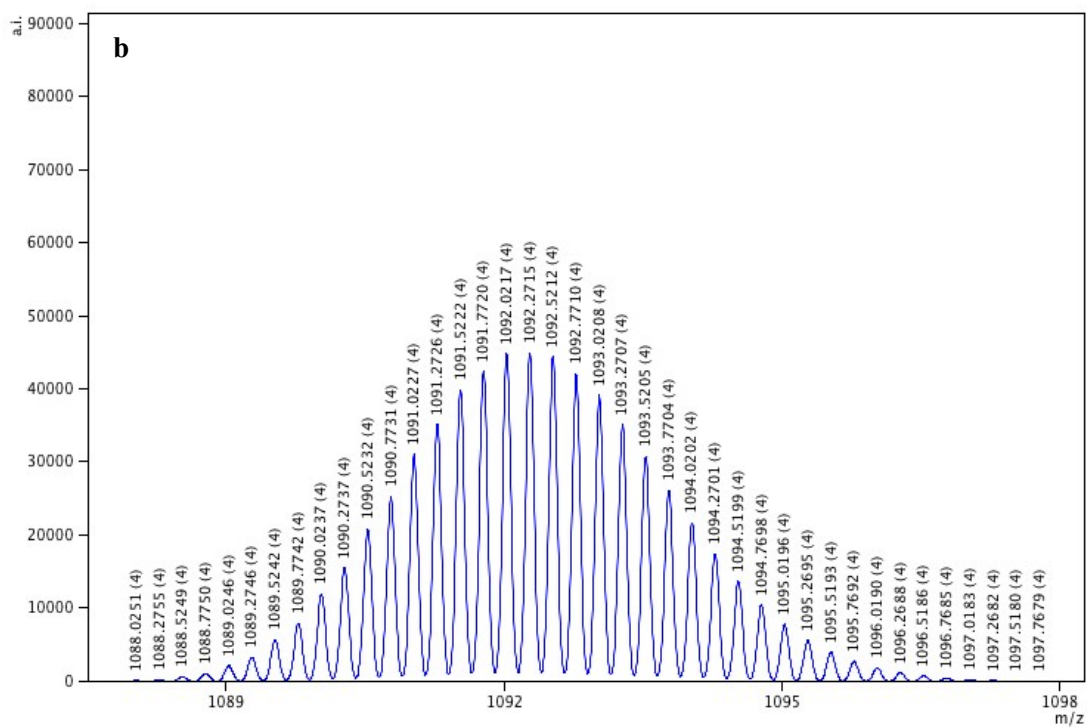
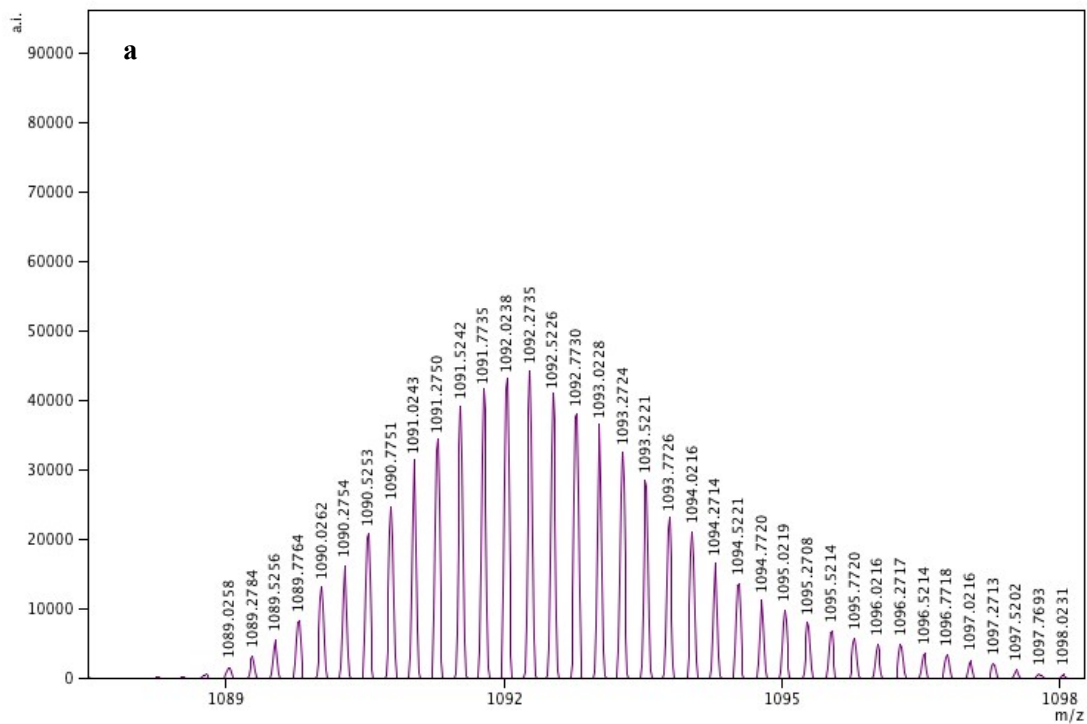


Figure S14: (a) HR-ESI-mass spectrum of the $[3](ClO_4)_8^{4+}$ ion. (b) Calculated isotopic distribution of $[3](ClO_4)_8^{4+}$

1.4 Synthesis of **3** from Zn(NTf₂)₂

[3,3'6',2"5",3"-quaterpyridine]-6,6"-dicarbaldehyde **1** (2.9 mg, 7.9 μmol, 5 equiv.), 4-methoxyaniline (3.1 mg 25.1 μmol, 16 equiv.), NBu₄ClO₄ (2.1 mg, 7.25 μmol 4 equiv.) and Zn(NTf₂)₂ (8.8 mg, 14.1 μmol, 9 equiv.) were suspended in reagent grade CH₃CN (3 mL) in a PTFE stoppered Schlenk tube. The reaction mixture was stirred at 70 °C for 12 hours. The resulting yellow solution was filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et₂O (30 mL) precipitated out a mixture of **3** and **2** as a yellow solid that was isolated by centrifugation. The concentration of **3** could be increased relative to **2** by crystallisation via slow diffusion of Et₂O to an acetonitrile solution of the mixture. Although the ¹H NMR spectrum was broadly consistent with that of **3** synthesised from Zn(ClO₄)₂, resonances were shifted due to the different concentration of perchlorate anions in the solution. This lead to some overlap of resonances. In order to assign these a series of Selective 1D TOCSY experiments were performed. ESI-MS data were consistent with the formation of **3** with a mix of perchlorate and triflimide counter anions.

¹H NMR (500 MHz, CD₃CN) 9.61 (s, 1H), 9.59 (s, 1H), 9.03 - 8.98 (m, 5H), 8.94 (d, J = 1.8 Hz, 1H), 8.86 - 8.82 (m, 4H), 8.81-8.75 (m, 4H), 8.68 - 8.64 (m, 2H), 8.60 (dd, J = 7.5, 2.0 Hz, 1H), 8.56 (s, 1H), 8.54 (s, 1H), 8.47(dd, J = 8.5, 2.4 Hz, 1H) 8.44 - 8.34 (m, 6H), 8.33 (dd J = 8.0, 1.9 Hz, 1H), 8.30 - 8.27 (m, 2H), 8.14 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H, L^VH₃), 7.38 (d, J = 8.9 Hz, 2H, L^VH₃), 7.13 (d, J = 8.5 Hz, 4H, L^VH₂, L^IH₃), 6.91 (d, J = 8.9 Hz, 2H, L^VH₂), 6.87 (d, J = 8.8 Hz, 2H, L^IH₃), 6.56 (d, J = 8.8 Hz, 2H, L^IH₂), 6.33 (d, J = 8.8 Hz, 4H, L^IH₂, L^{III}H₂), 6.08 (d, J = 8.7 Hz, 2H, L^{III}H₃), 4.05 (s, 3H, L^VH₁), 3.91 (s, 3H, L^VH₁), 3.68 (s, 3H, L^{III}H₁), 3.60 (s, 6H, L^IH₁, L^IH₁).

¹⁹F NMR (376 MHz; CD₃CN, reference C₆F₆): δ -80.48 (NTf₂⁻)

ESI-MS: *m/z*: 925.69 (925.82) {[Zn₉L₃(μ-OH)₆](ClO₄)₅(NTf₂)₂}⁵⁺, 1181.65 (1181.76) {[Zn₉L₃(μ-OH)₆](ClO)₆(NTf₂)₂}⁵⁺

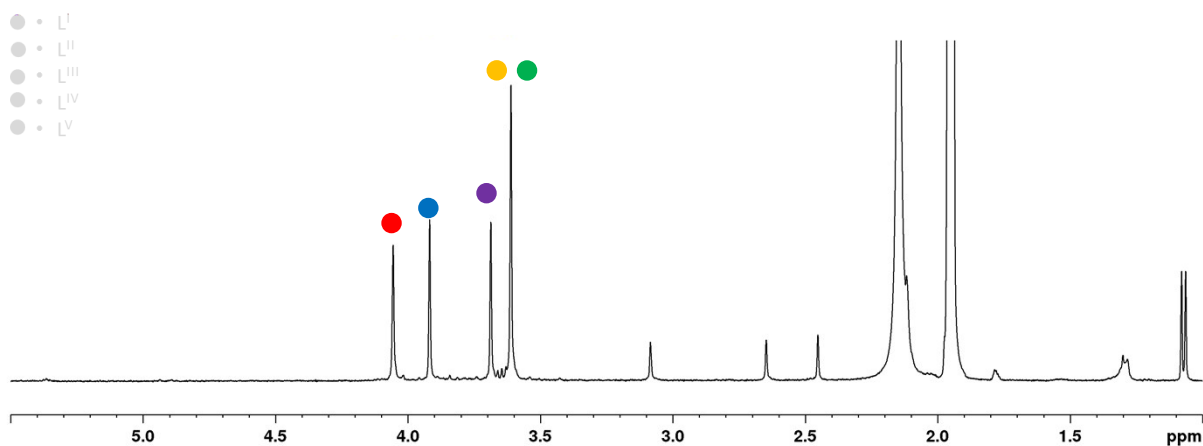


Figure S15: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) of perchlorate templated **3** in the region 1 – 5.5 ppm, showing the resonances for H_1 .

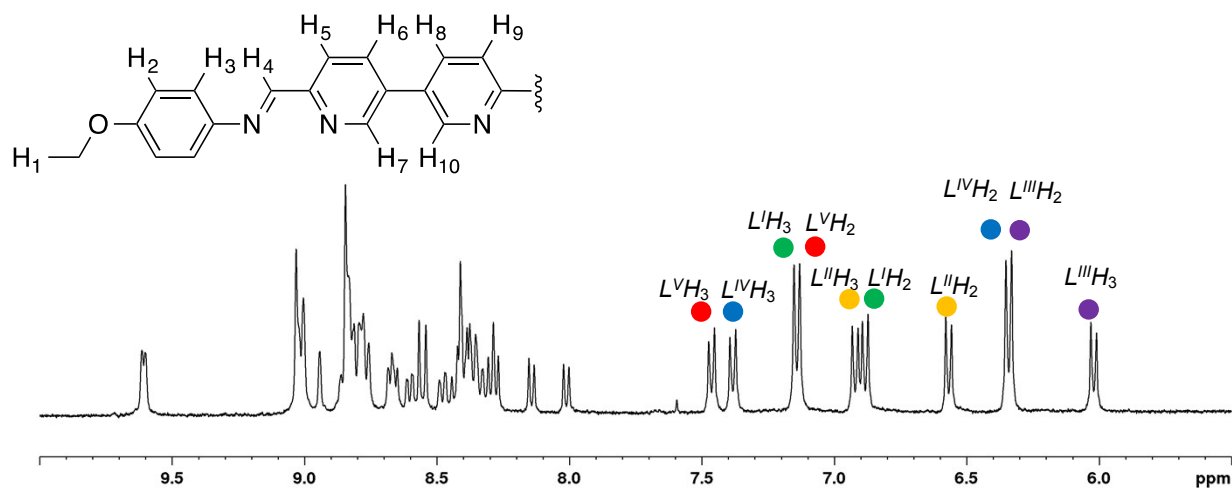


Figure S16: ^1H NMR (500 MHz, 298 K, CD_3CN) of perchlorate templated **3** in the region 5.8 - 9.8 ppm.

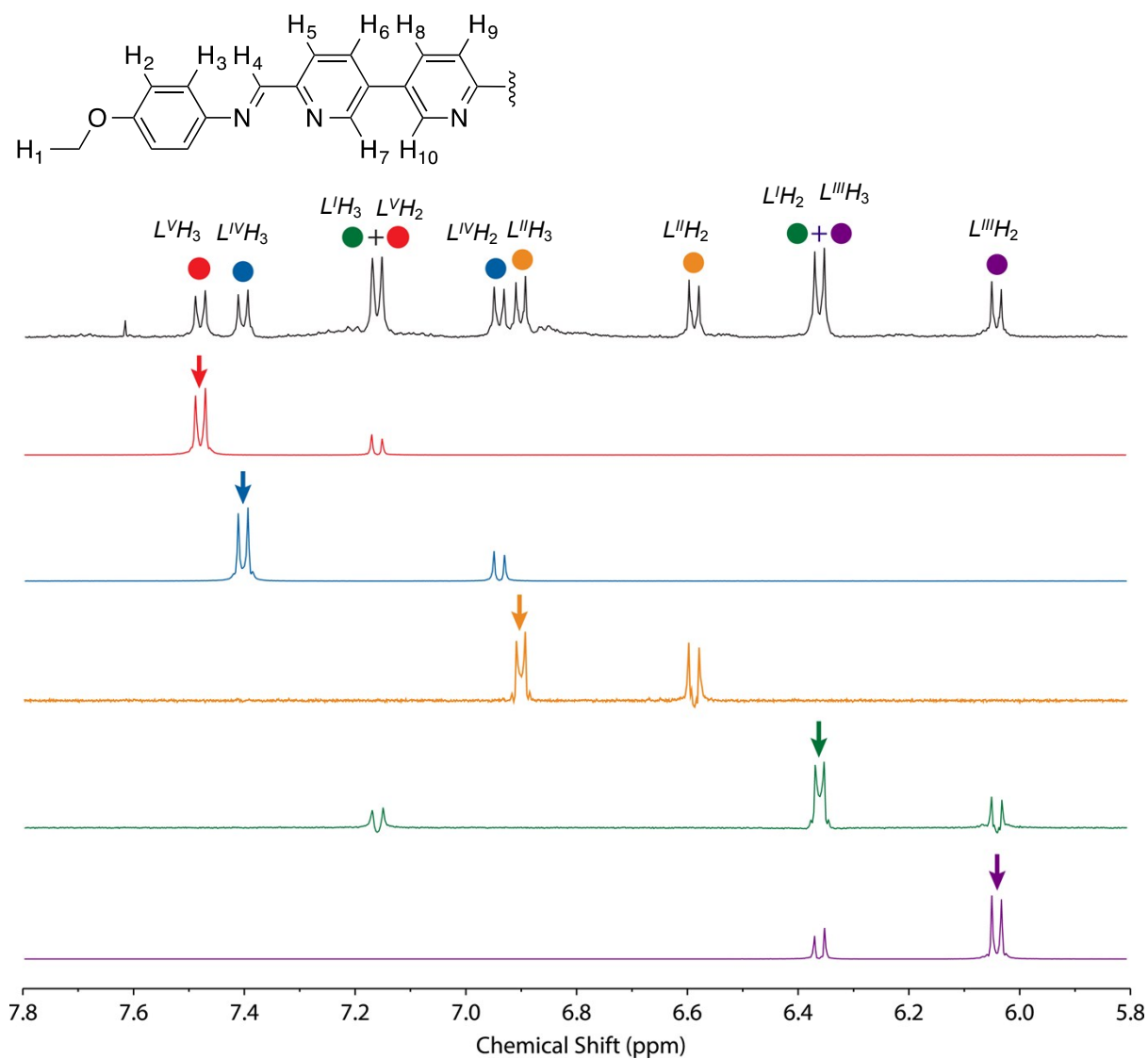


Figure S17: Selective 1D TOCSY spectra (500 MHz, 298 K, CD₃CN; $T_{\text{mix}} = 80$ ms) of perchlorate templated **3**, highlighting the 5 total aniline spin systems within the structure. Pairs of coloured circles denote J -coupled spins.

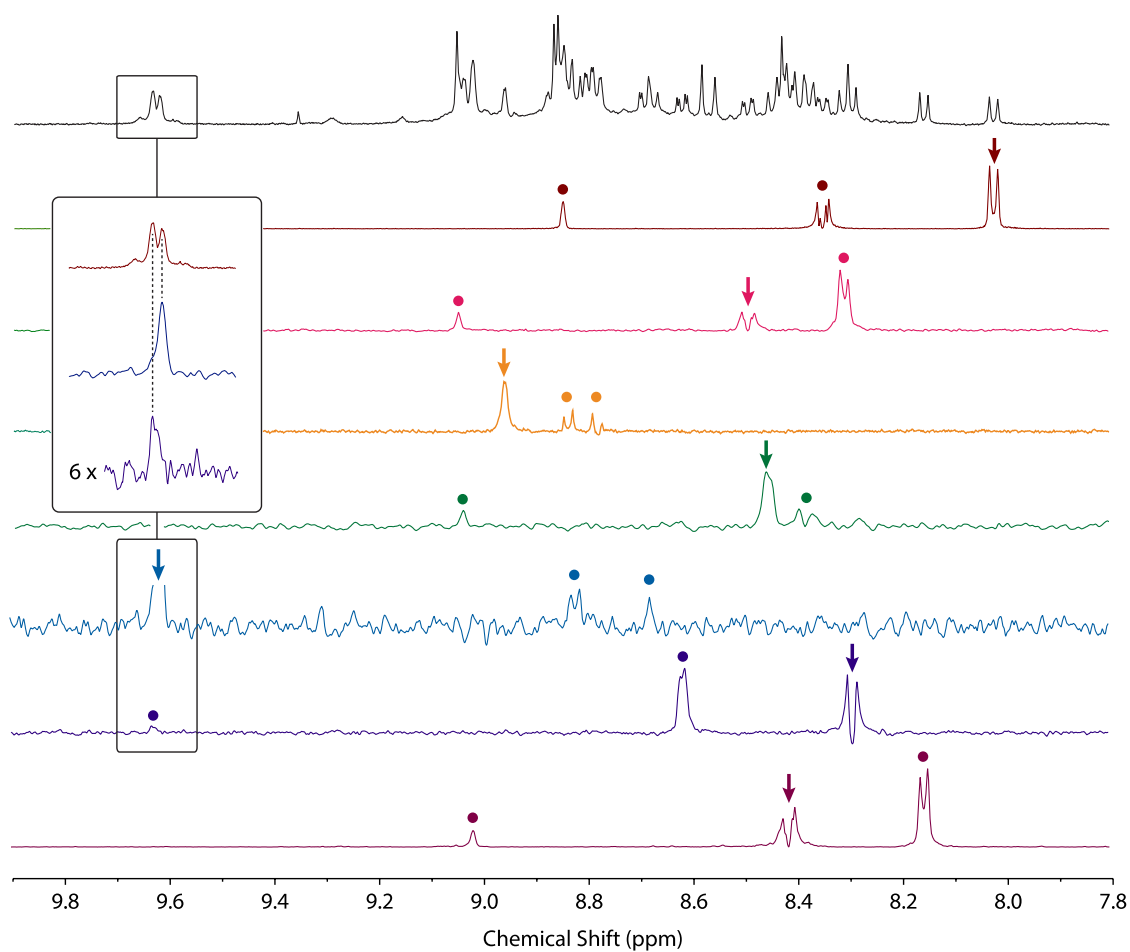


Figure S18: Selective 1D TOCSY spectra (500 MHz, 298 K, CD_3CN ; $T_{\text{mix}} = 80$ ms) of perchlorate templated **3**, highlighting 7 of the 10 total pyridyl spin systems within the structure. Isolated protons could not be identified for the final three spin systems, which precluded selective irradiation.

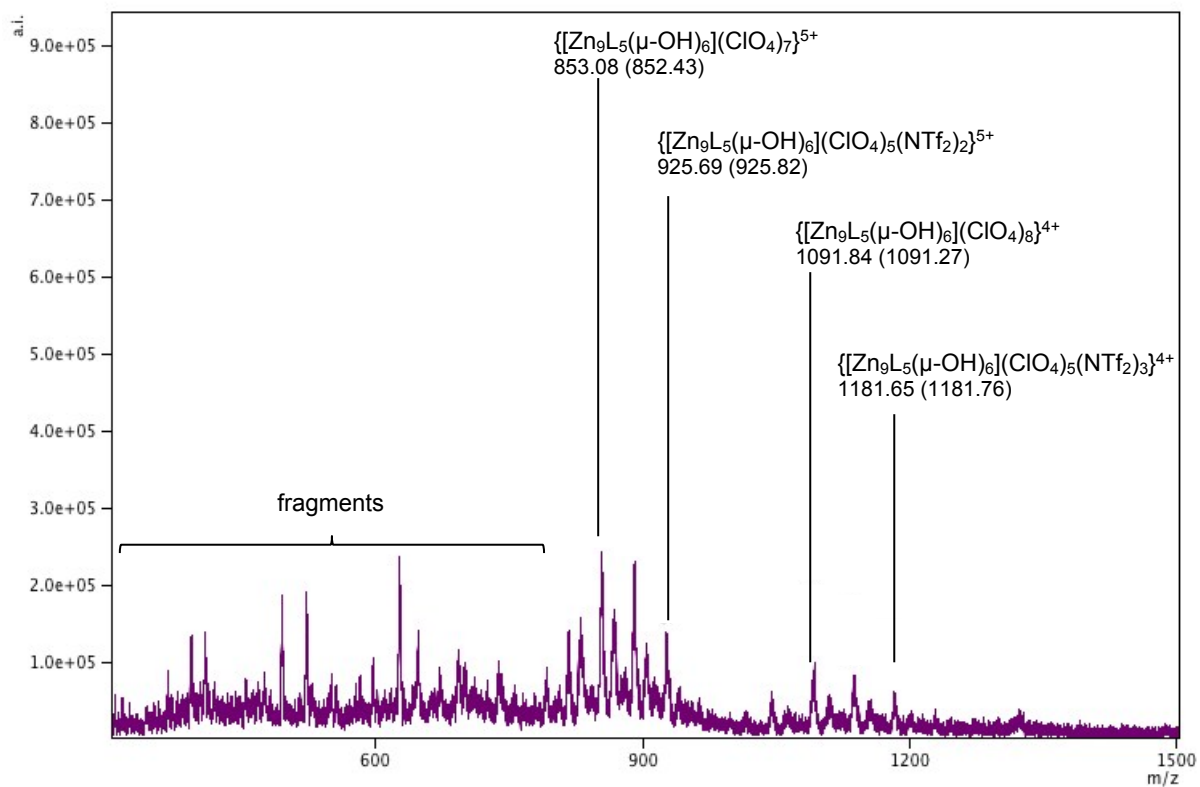


Figure S19: LR-ESI-mass spectrum of product $[3](NTf_2)_8(ClO_4)_4$. Calculated values are in brackets.

1.5 Stability of **2** to 4-methoxyaniline

2 (4.1 mg, 0.75 μmol , 1 equiv.) was dissolved in 0.5 mL CD_3CN in a PTFE stoppered J-Young NMR tube. A ^1H -NMR spectrum was acquired and a 0.73 mM solution of 4-methoxyaniline in CD_3CN (6.2 μL , 6 equiv.) and of H_2O (1 μL , 74 equiv.) were added. The reaction mixture was heated at 70 $^\circ\text{C}$ for 12 hours and the solution monitored by ^1H -NMR spectroscopy.

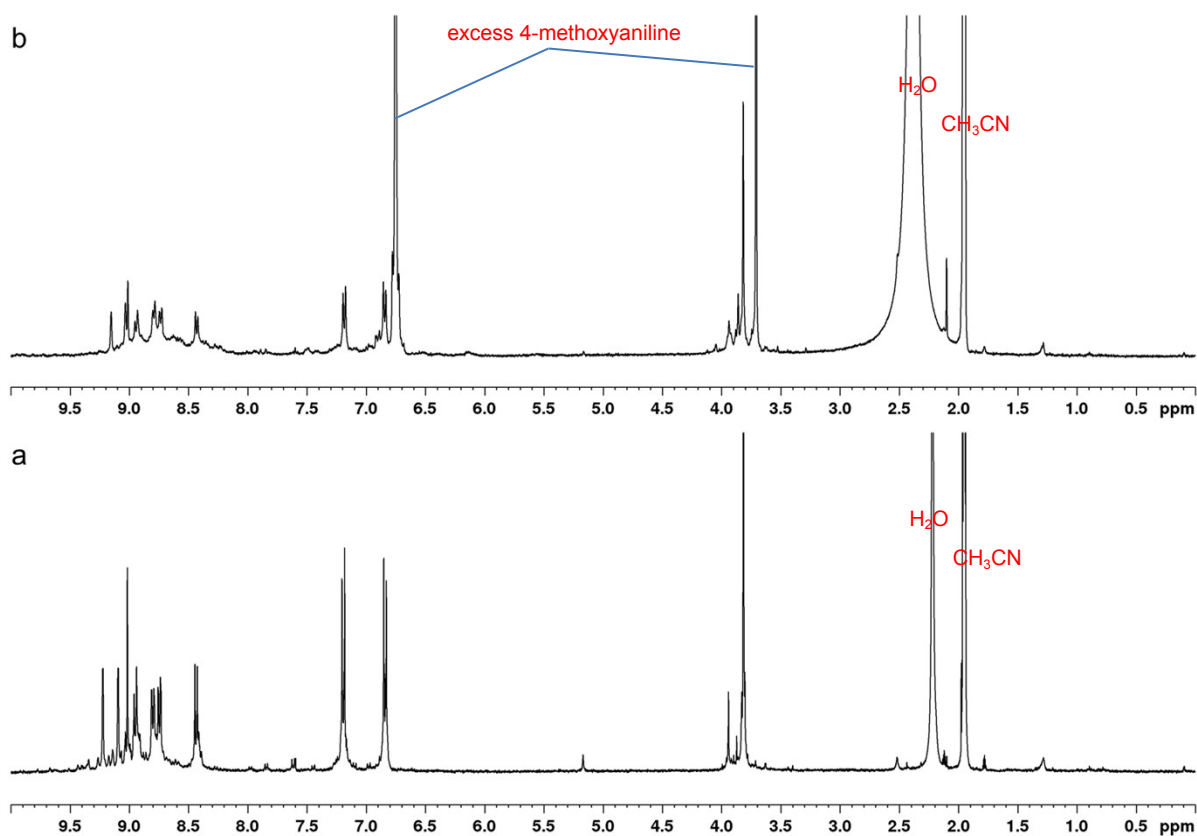


Figure S20: ^1H NMR spectra (400 MHz, 298 K, CD_3CN) of (a) **2**(NTf_2)₆ and (b) after 12 hours at 70 $^\circ\text{C}$ in the presence of 6 equiv. of 4-methoxyaniline and 1 μL of H_2O .

1.6 Stability of **2** to tetrabutylammonium perchlorate

2 (4.3 mg, 0.75 μmol , 1 equiv.) was dissolved in 0.5 mL CD_3CN in a PTFE stoppered J-Young NMR tube. A 0.19 mM solution of tetrabutylammonium perchlorate in CD_3CN (16.6 μL , 4 equiv.) was added. The reaction mixture was heated at 70 $^\circ\text{C}$ for 12 hours and the stability of the complex monitored by ^1H -NMR spectroscopy.

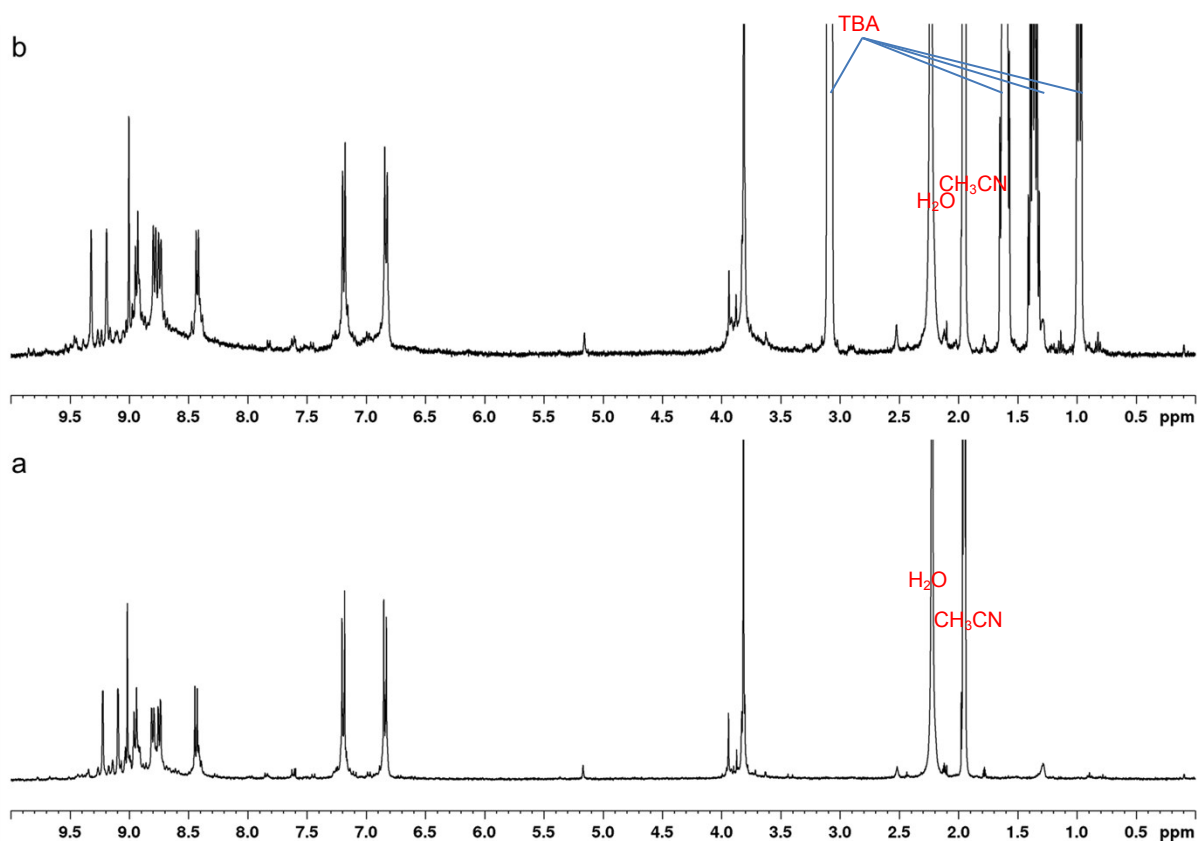


Figure S21: ^1H NMR spectra (400 MHz, 298 K, CD_3CN) of (a) **2**(NTf_2)₆ and (b) after 12 hours at 70 $^\circ\text{C}$ in the presence of 4 equiv. of tetrabutylammonium perchlorate.

1.7 Conversion of **2** into **3** through the addition of perchlorate

2 (6.4 mg, 1.2 μmol , 1 equiv.) was dissolved in 0.5 mL CD_3CN in a PTFE stoppered J-Young NMR tube. A 0.73 mM solution of 4-methoxyaniline in CD_3CN (9.6 μL , 6 equiv.) and H_2O (1 μL , 56 equiv.) were added and the solution heated at 70 $^\circ\text{C}$ for 15 min and a ^1H -NMR spectrum acquired. Subsequently a 0.19 mM solution of tetrabutylammonium perchlorate in CD_3CN (24.6 μL , 4 equiv.) was added and the reaction mixture was heated at 70 $^\circ\text{C}$ for 12 hours whilst the conversion was monitored by ^1H -NMR spectroscopy. LR-ESI-MS of the final solution contained signals corresponding to **3** and a library of ClO_4^- and NTf_2^- anions.

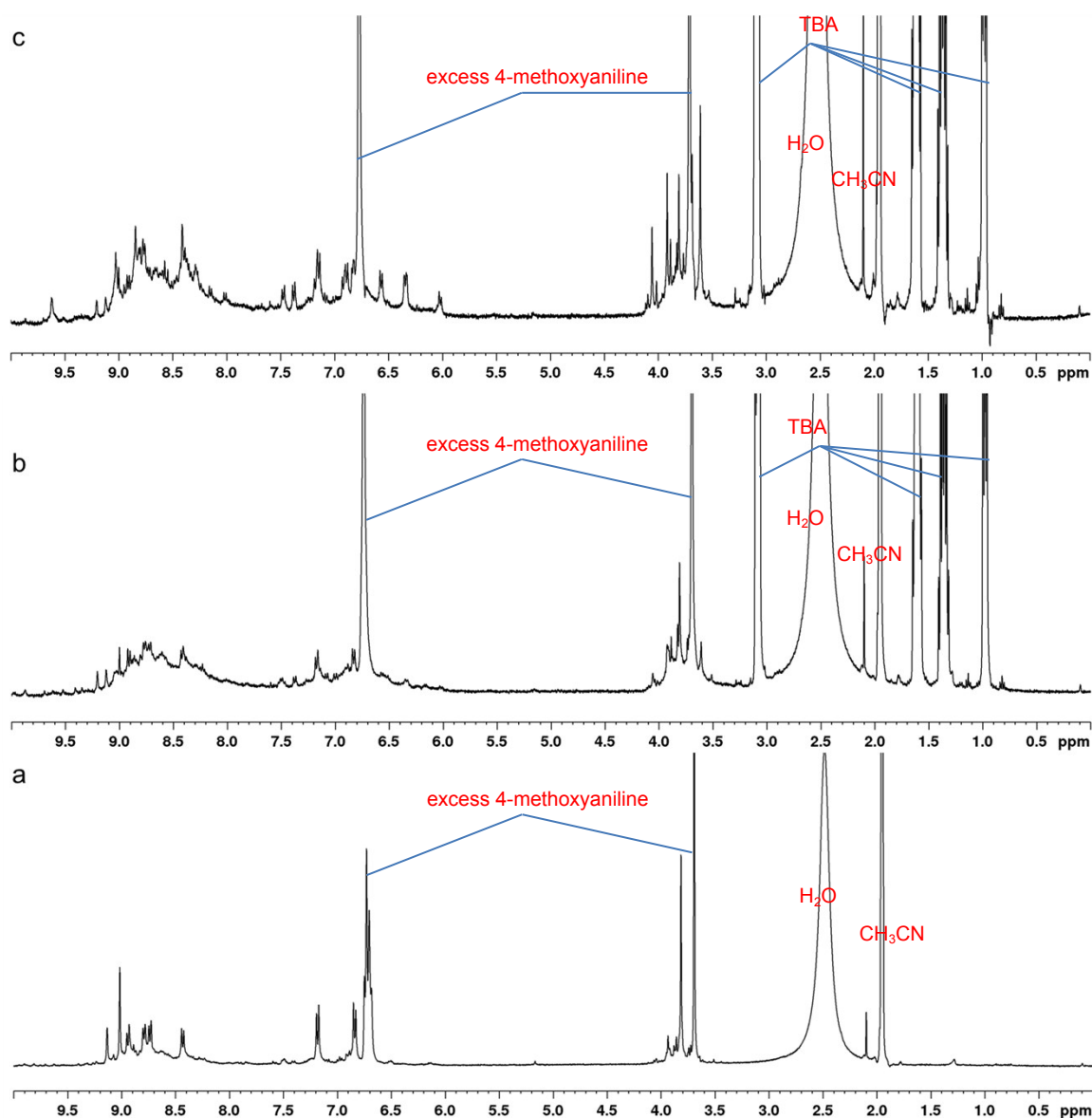


Figure S22: ^1H NMR spectra (400 MHz, 298 K, CD_3CN) of: (a) **2**(NTf_2)₆, 6 equiv. of 4-methoxyaniline and 1 μL of H_2O , (b) 2 mins at 25 $^\circ\text{C}$ after the addition of 4 equiv. of tetrabutylammonium perchlorate, (c) 12 hours at 70 $^\circ\text{C}$ after the addition of tetrabutylammonium perchlorate.

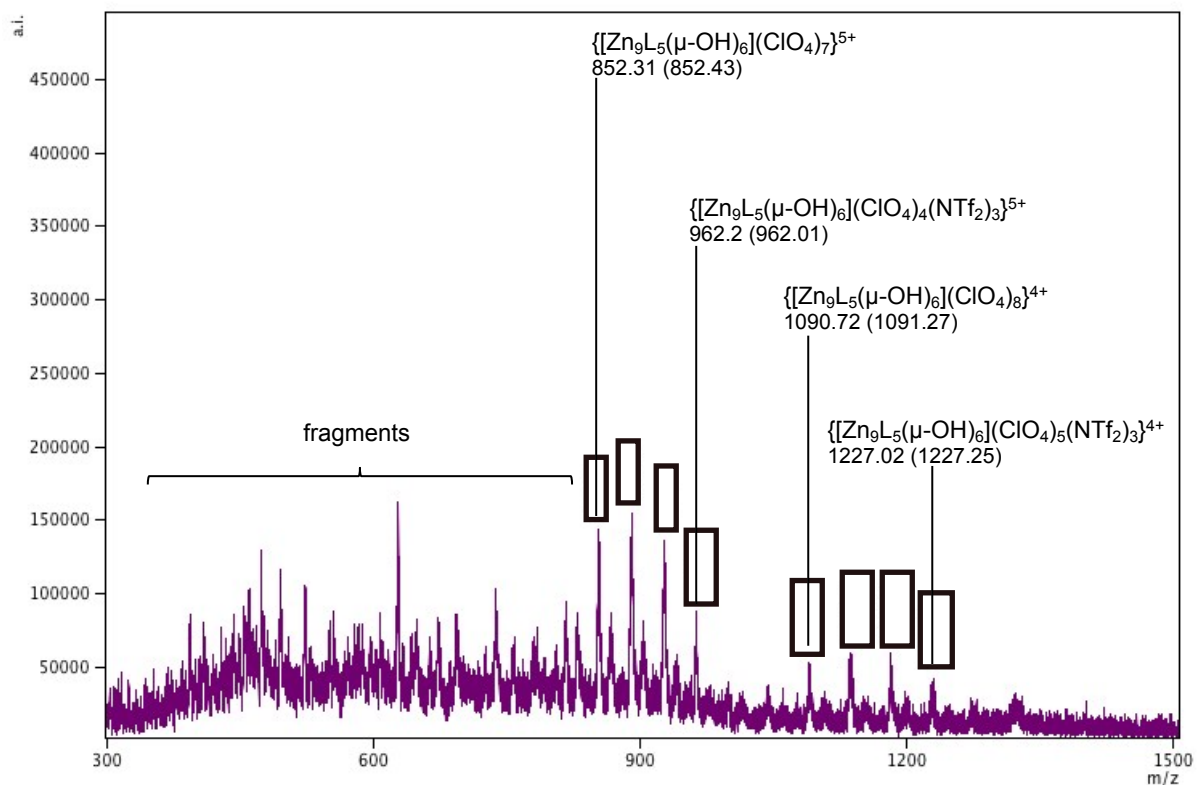


Figure S23: LR-ESI-mass spectrum of the product of the transformation of [2](NTf₂)₆ to [3](NTf₂)₈(ClO₄)₄ through the addition of 4 equiv. of tetrabutylammonium perchlorate to a solution of [2](NTf₂)₆ and 6 equiv. of 4-methoxyaniline and 1 μL of H₂O.

1.8 Conversion of 2 into 3 through the addition of 4-methoxyaniline

2 (6.8 mg, 1.2 μmol , 1 equiv.) was dissolved in 0.5 mL CD_3CN in a PTFE stoppered J-Young NMR tube. A 0.19 mM solution of tetrabutylammonium perchlorate in CD_3CN (24.6 μL , 4 equiv.) was added. The solution was heated at 70 $^\circ\text{C}$ for 15 mins and a ^1H -NMR spectrum acquired. A 0.73 mM solution of 4-methoxyaniline in CD_3CN (9.6 μL , 6 equiv.) and H_2O (1 μL , 56 equiv.) were added. The reaction mixture was heated at 70 $^\circ\text{C}$ for 12 hours and the conversion monitored by ^1H -NMR spectroscopy. LR-ESI-MS of the final solution contained signals corresponding to **3** and a library of ClO_4^- and NTf_2^- anions.

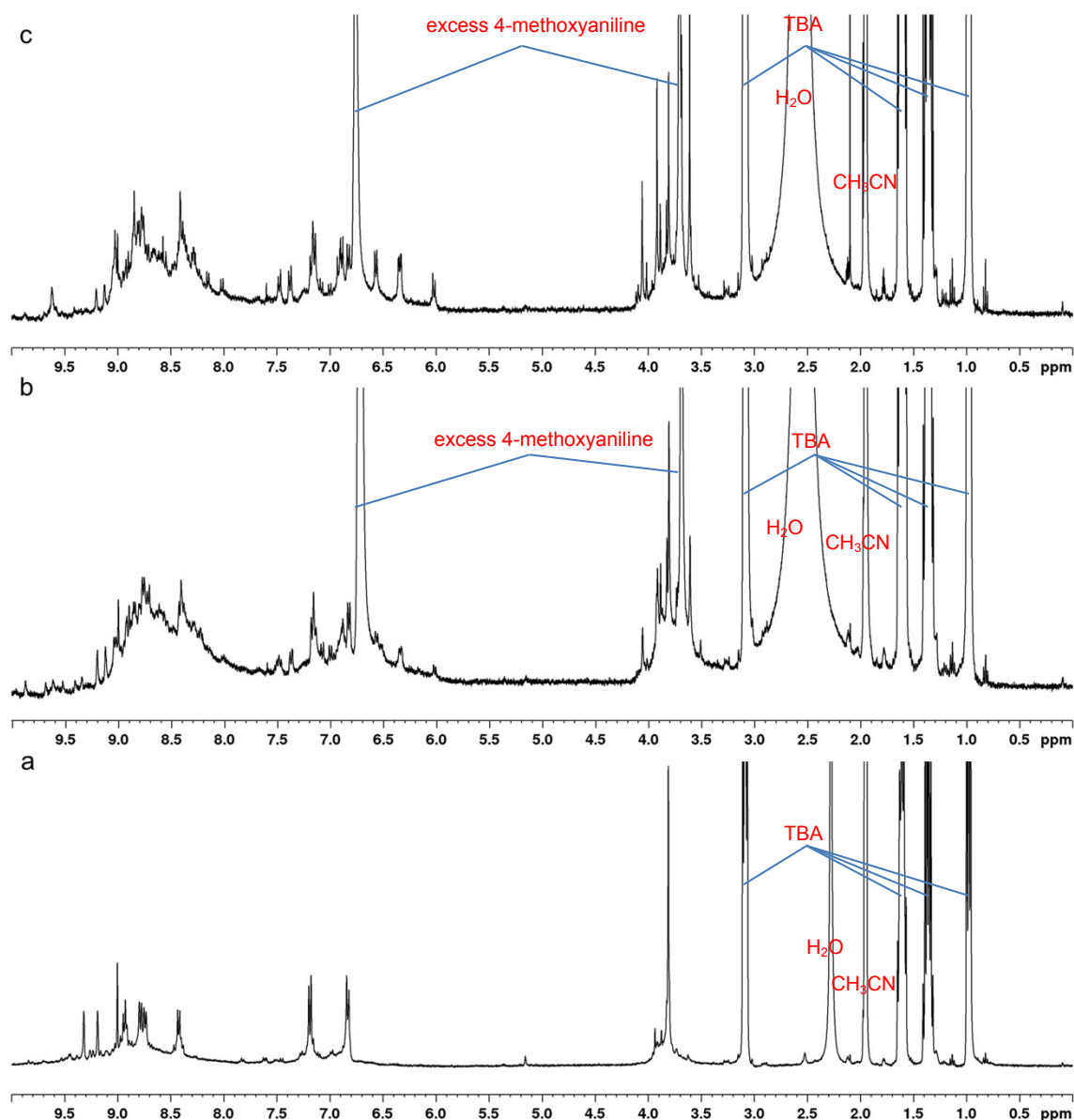


Figure S24: ^1H NMR spectra (400 MHz, 298 K, CD_3CN) of: (a) **2** and 4 equiv. of tetrabutylammonium perchlorate, (b) 2 mins at 25 $^\circ\text{C}$ after the addition of 6 equiv. of 4-methoxyaniline and 1 μL of H_2O , (c) 12 hours at 70 $^\circ\text{C}$ after the addition of 6 equiv. of 4-methoxyaniline and 1 μL of H_2O .

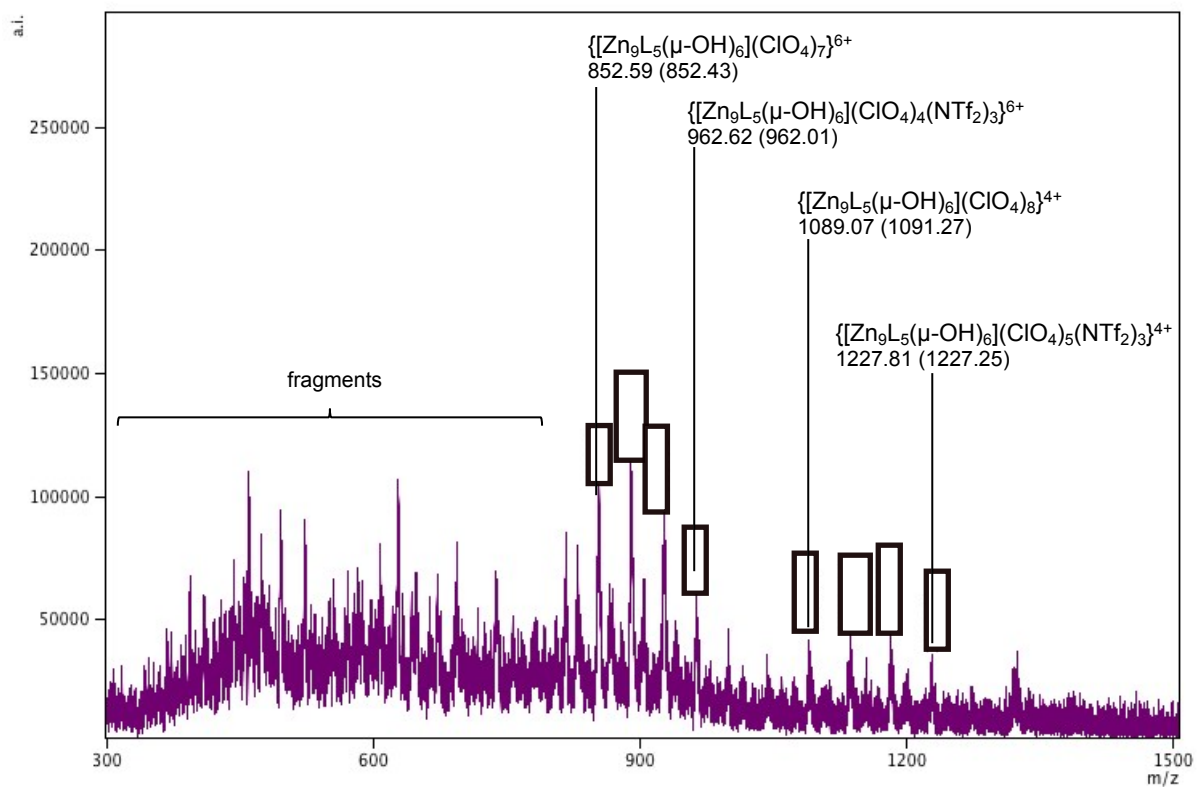


Figure S25: LR-ESI-mass spectrum of the product of the transformation of [2](NTf₂)₆ to [3](NTf₂)₈(ClO₄)₄ through the addition of 6 equiv. of 4-methoxyaniline and 1 μL of H₂O to a solution of [2](NTf₂)₆ and 4 equiv. of tetrabutylammonium perchlorate. Calculated values are in brackets.

1.9 2-Naphthalenesulfonate-templated **3**

[3,3'6',2''5'',3'''-quaterpyridine]-6,6'''-dicarbaldehyde **1** (4.2 mg, 11.5 μmol , 5 equiv.), 4-methoxyaniline (4.5 mg, 36.8 μmol , 16 equiv.), 2-naphthalenesulfonate sodium salt (2.1 mg, 9.2 μmol 4 equiv.) and $\text{Zn}(\text{NTf}_2)_2$ (12.6 mg, 20.1 μmol , 9 equiv.) were suspended in reagent grade CH_3CN (8 mL) in a PTFE stoppered Schlenk tube. The reaction mixture was stirred at 70 °C for 12 hours. The resulting turbid yellow solution was filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et_2O (30 mL) precipitated out a mixture of **2** and 2-naphthalenesulfonate templated **3** as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et_2O into an acetonitrile solution of 2-naphthalenesulfonate templated **3** yielded crystals suitable for analysis.

^1H NMR (500 MHz, CD_3CN) δ 9.91 (s, 1H), 9.87 (s, 1H), 9.51(s, 1H), 9.45 (s, 1H), 9.11 (s, 1H), 9.04 (s, 1H), 8.95 (s, 1H), 8.90 (s, 1H), 8.85 (s, 1H, $\text{L}^{\text{II}}\text{H}_4$), 8.78 (dd, $J = 8.0$ 2.2 Hz, 1H), 8.71 (dd, $J = 8.7$, 1.9 Hz, 1H), 8.61 (s, 1H, $\text{L}^{\text{IV}}\text{H}_4$), 8.59 (dd, $J = 8.2$, 2.1 Hz, 1H), 8.51 (d, $J = 7.3$ Hz, 1H), 8.50 (s, 1H, $\text{L}^{\text{I}}\text{H}_4$), 8.36 (s, 1H, $\text{L}^{\text{III}}\text{H}_4$), 8.35- 8.31 (m, 2H), 8.30 - 8.28 (m, 2H), 8.25- 8.18(m, 3H, $\text{L}^{\text{V}}\text{H}_4$), 8.15 - 8.04 (m, 4H, $\text{L}^{\text{I}}\text{H}_3$), 8.00 (d, $J = 8.4$ Hz, 1H), 7.89- 7.83 (m, [**2**]), 8.79 (m, 2H), 7.60 (d, $J = 8.2$ Hz, [**2**] H_3) 7.55 (d, $J = 8.5$ Hz, 1H, $\text{L}^{\text{V}}\text{H}_3$), 7.29 (d, $J = 8.6$ Hz, 2H, $\text{L}^{\text{V}}\text{H}_2$), 7.28 (d, $J = 8.6$ Hz, 2H, $\text{L}^{\text{IV}}\text{H}_3$), 7.17 (d, $J = 8.2$ Hz, 2H, $\text{L}^{\text{I}}\text{H}_3$), 6.93 (d, $J = 9.0$ Hz, 2 H, $\text{L}^{\text{II}}\text{H}_3$), 6.84 (d, $J = 8.8$ Hz, [**2**] H_2), 6.80 (d, $J = 8.8$ Hz, 2H, $\text{L}^{\text{IV}}\text{H}_2$), 6.63(d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{II}}\text{H}_2$), 6.38 (d, $J = 8.9$ Hz, 2H, $\text{L}^{\text{I}}\text{H}_2$), 6.34 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{III}}\text{H}_2$), 6.08 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{III}}\text{H}_3$), 4.10 (s, 3H, $\text{L}^{\text{V}}\text{H}_1$), 3.88 (s, [**2**] H_1), 3.86 (s, 3H, $\text{L}^{\text{IV}}\text{H}_1$), 3.65 (s, 3H, $\text{L}^{\text{III}}\text{H}_1$), 3.64 (s, 3H, $\text{L}^{\text{II}}\text{H}_1$), 3.54 (s, 3H, $\text{L}^{\text{I}}\text{H}_1$).

^{19}F NMR (376 MHz; CD_3CN , reference C_6F_6): δ -80.55 (NTf_2^-)

LR-ESI-MS: m/z : 851.54 (851.37) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{NTf}_2)_4(\text{NaphSO}_3)_2\}^{6+}$, 1077.63 (1077.22) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{NTf}_2)_5(\text{NaphSO}_3)_2\}^{5+}$, 1417.26 (1417.51) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{NTf}_2)_6(\text{NaphSO}_3)_2\}^{4+}$

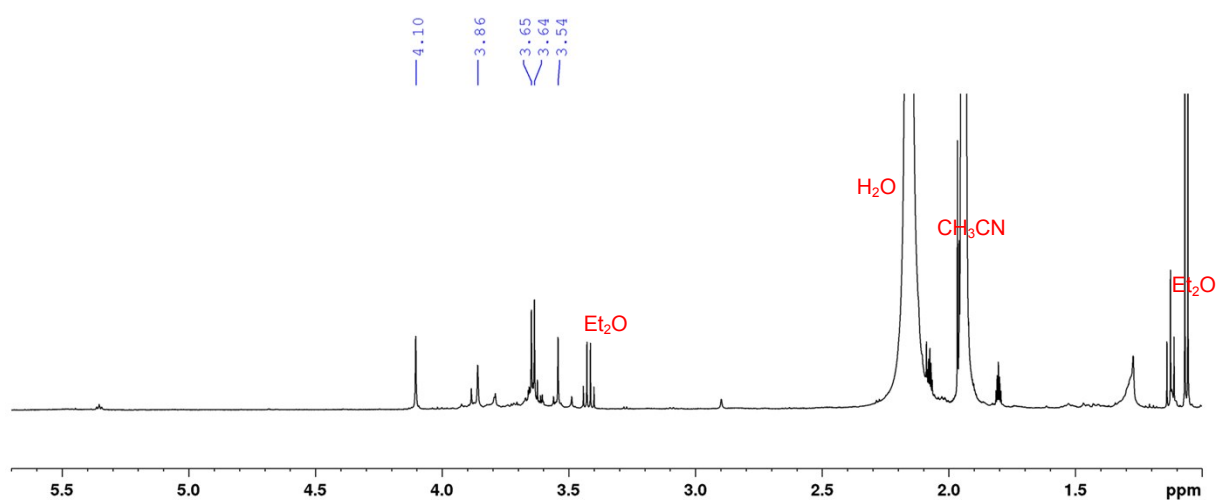


Figure S26: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) of redissolved crystals generated by the slow diffusion of Et_2O into an acetonitrile solution of 2-naphthalenesulfonate templated **3** in the region 1 – 5.5 ppm.

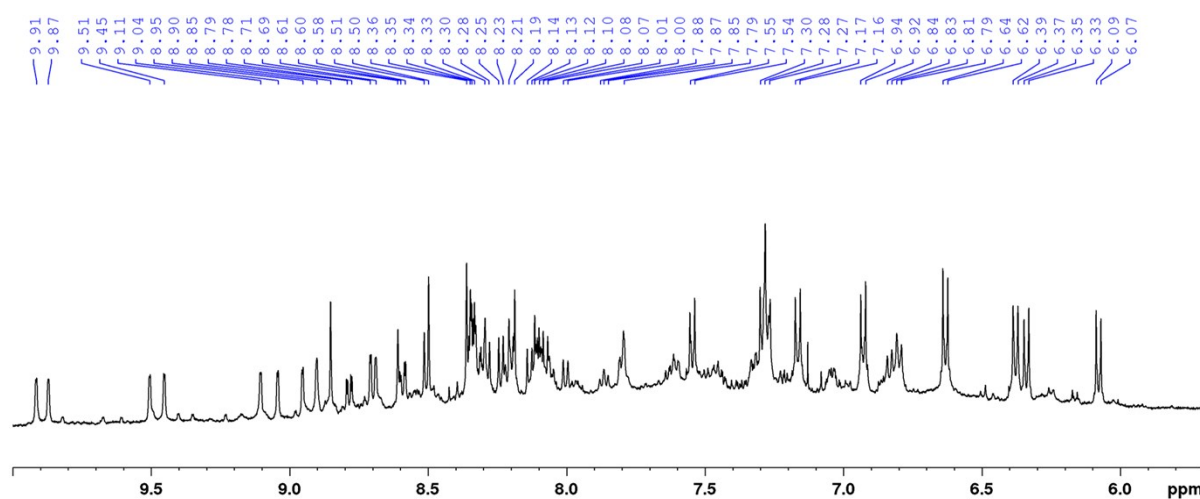


Figure S27: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) of redissolved crystals generated by the slow diffusion of Et_2O into an acetonitrile solution of 2-naphthalenesulfonate templated **3** in the region 5.5 – 10 ppm.

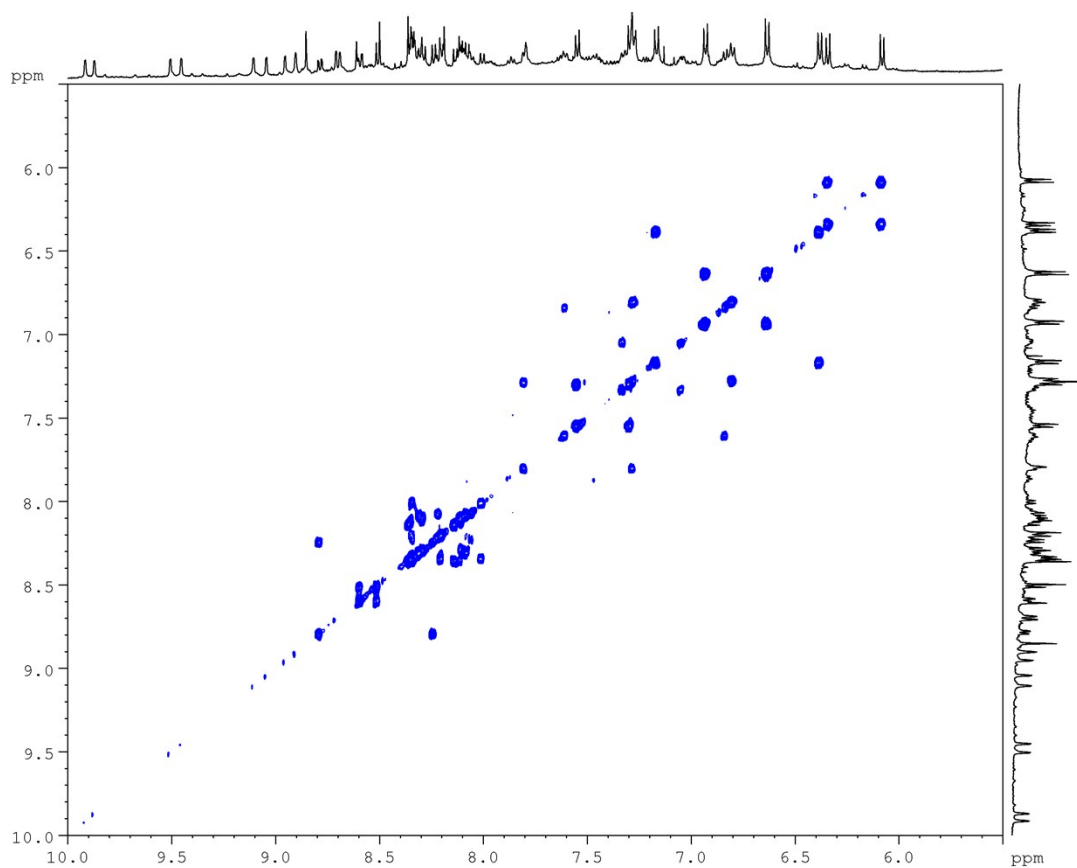


Figure S28: COSY NMR spectrum (500 MHz, 298 K, CD₃CN) of redissolved crystals generated by the slow diffusion of Et₂O into an acetonitrile solution of 2-naphthalenesulfonate templated **3** in the region 5.5 – 10 ppm.

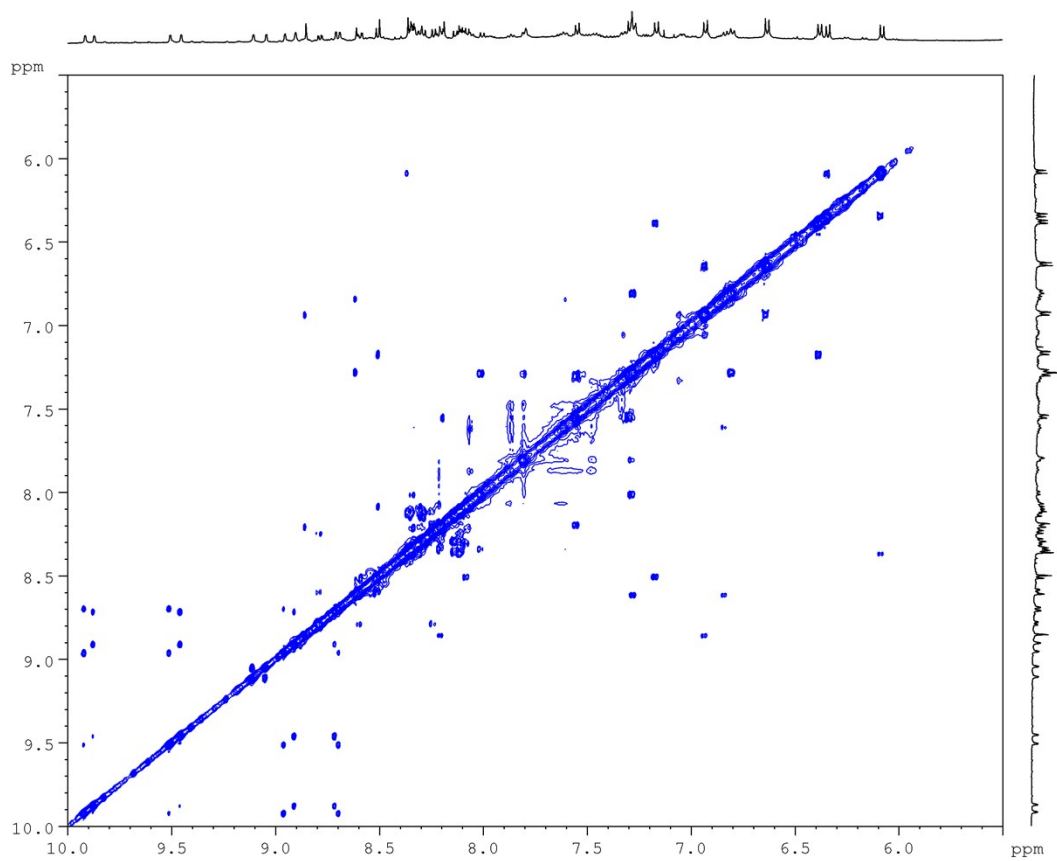


Figure S29: NOESY NMR spectrum (500 MHz, 298 K, CD₃CN) of redissolved crystals generated by the slow diffusion of Et₂O into an acetonitrile solution of 2-naphthalenesulfonate templated **3** in the region 5.5 – 10 ppm.

The overlap of resonances within the 8.0 - 8.5 ppm region precluded a full assignment of the ligands and the identification of the resonances associated with bound or free 2-naphthalenesulfonate. However, the ^1H - ^1H NOESY interactions between the distinctive resonances in the region of 9.0 – 8.0 ppm supported the evidence from the solid state analysis with the observed downfield shifts characteristic of ring current effects from the bound 2-naphthalenesulfonate.

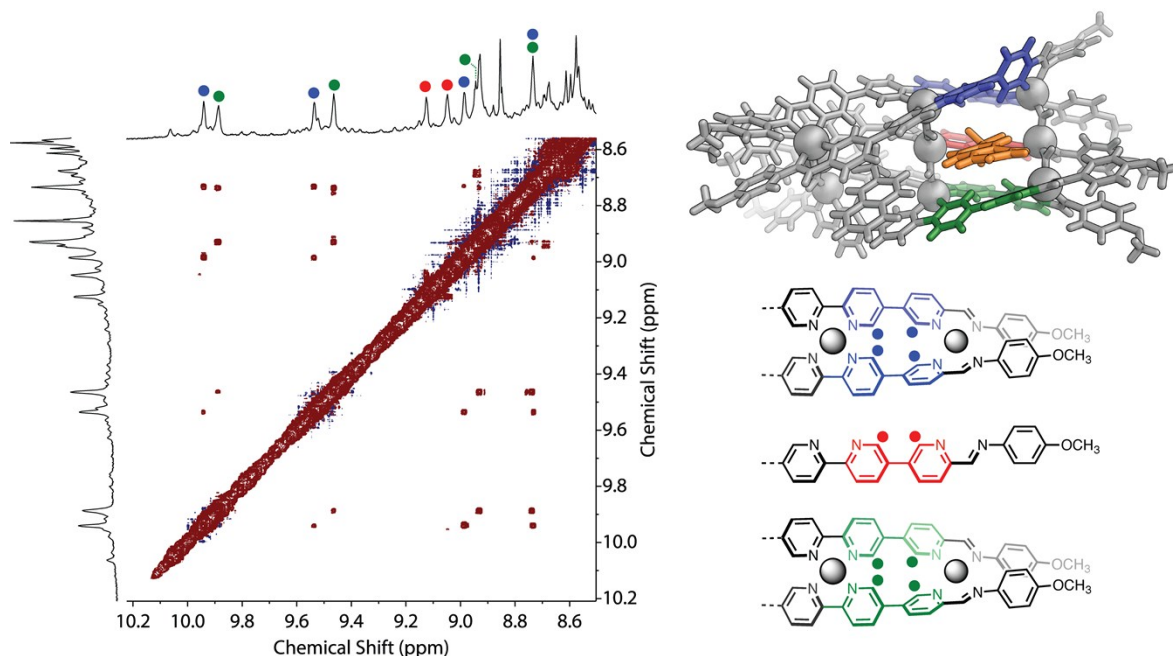


Figure S30: Partial 2D ^1H - ^1H NOESY spectrum (500 MHz, 298 K, CD_3CN ; $T_{\text{mix}} = 600$ ms) of 2-naphthalenesulfonate templated **3**. Peaks marked with coloured circles are assigned to the *H*-2 protons of the 3,3'-bipyridyl moieties. These protons are directed towards sulfonate group of the 2-naphthalenesulfonate guest (orange) bound within the cavity of the half-pipe structure. Three distinct groups of resonances are observed in the crystal structure (blue, red and green moieties), which is consistent with the coupling observed in the NOESY spectrum.

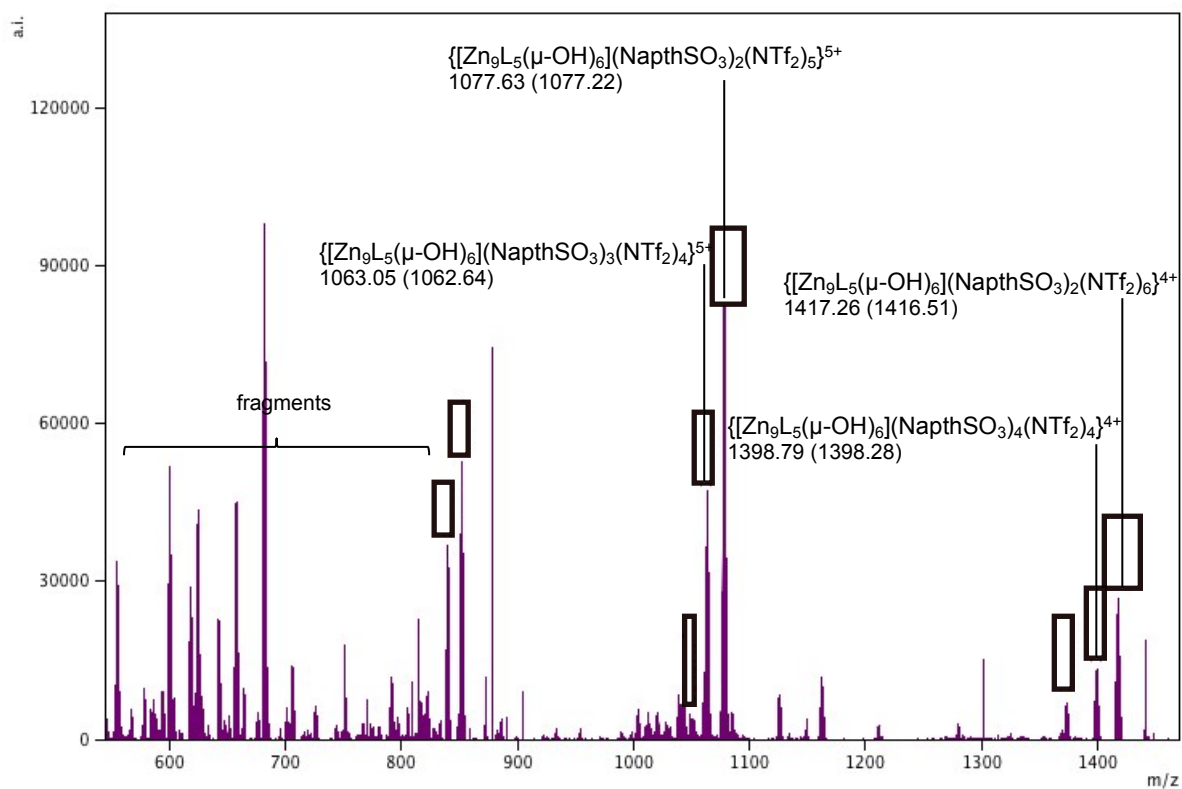


Figure S31: LR-ESI-mass spectrum of product 2-naphthalenesulfonate templated **3**. Calculated values are in brackets.

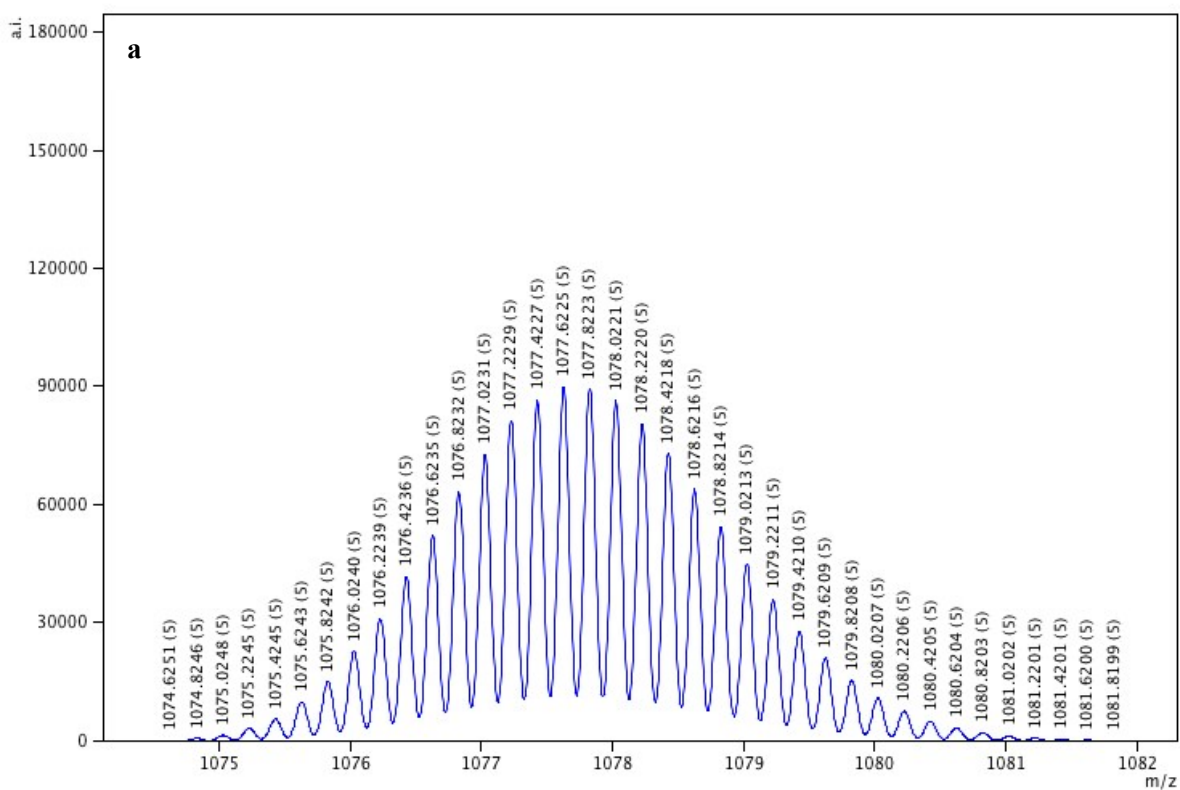
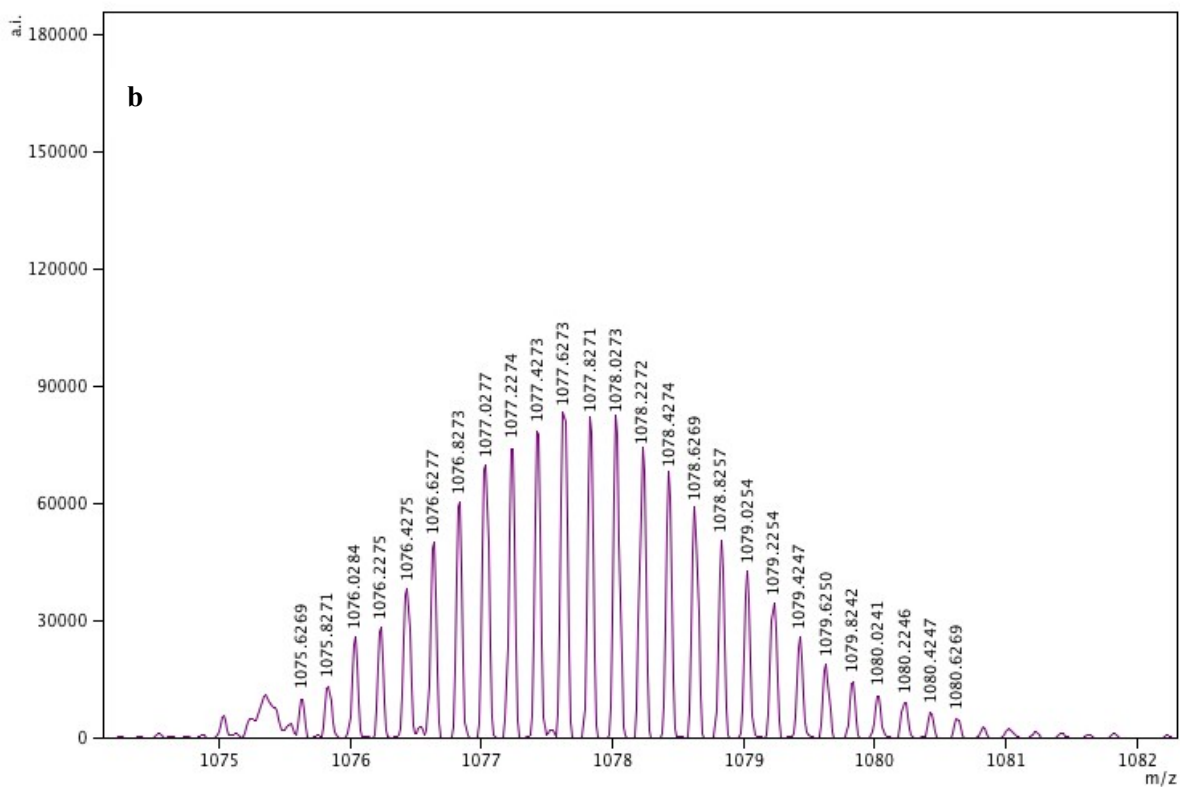


Figure S32: **(a)** HR-ESI-mass spectrum of the $[3](\text{NaphSO}_3)_2(\text{NTf}_2)_5^{5+}$ ion. **(b)** Calculated isotopic distribution of $[3](\text{NaphSO}_3)_2(\text{NTf}_2)_5^{5+}$

1.10 Perrhenate-templated **3**

[3,3'6',2"5",3"-quaterpyridine]-6,6"-dicarbaldehyde **1** (3.32 mg, 9.1 μmol , 5 equiv.), 4-methoxyaniline (3.57 mg, 123.15 μmol , 16 equiv.), NBu_4ReO_4 (3.62 mg, 7.25 μmol 4 equiv.) and $\text{Zn}(\text{NTf}_2)_2$ (40.2 mg, 64.3 μmol , 1 equiv.) were suspended in reagent grade CH_3CN (3 mL) in a PTFE stoppered Schlenk tube. The reaction mixture was stirred at 70 $^\circ\text{C}$ for 12 hours. The resulting yellow solution was filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et_2O (30 mL) precipitated out a mixture of **2** and Perrhenate templated **3** as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et_2O into an acetonitrile solution of perrhenate templated **3** yielded crystals suitable for analysis.

^1H NMR (500 MHz, CD_3CN) δ 9.87 (s, 1H), 9.85 (s, 1H), 9.33 (s, 1H), 9.14 (m, 2H), 9.07 - 9.00 (m, 1H), 9.05 (s, 1H, $\text{L}^{\text{V}}\text{H}_4$), 8.98 (s, [**2**] H_4), 8.94 - 8.87 (m), 8.83 (s, 1H, $\text{L}^{\text{I}}\text{H}_4$), 8.81 - 8.68 (m, 10H), 8.66 - 8.63 (m, 4H), 8.62 (s, 1H, $\text{L}^{\text{V}}\text{H}_4$), 8.59 (s, 2H, $\text{L}^{\text{II}}\text{H}_4$), 8.58 - 8.54 (m, 1H), 8.51 (m, 1H), 8.45 - 8.43 (m, 1H), 8.42 (s, 1H, $\text{L}^{\text{III}}\text{H}_4$), 8.41 - 8.34 (m, 5H), 8.32 - 8.24 (m, 6H), 8.11 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 7.3$ Hz, 1H), 7.43 (d, $J = 8.7$ Hz, 1H, $\text{L}^{\text{V}}\text{H}_3$), 16 (d, $J = 8.7$ Hz, [**2**] H_3), 7.12 (d, $J = 9.2$ Hz, 2H, $\text{L}^{\text{V}}\text{H}_2$), 7.28 (d, $J = 8.6$ Hz, 2H, $\text{L}^{\text{IV}}\text{H}_3$), 7.13 (d, $J = 9.0$ Hz, 2 H, $\text{L}^{\text{II}}\text{H}_3$), 6.93 (d, $J = 9.0$ Hz, 2H, $\text{L}^{\text{IV}}\text{H}_2$), 6.85 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{I}}\text{H}_3$), 6.84 (d, $J = 8.7$ Hz, [**2**] H_2), 6.55 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{I}}\text{H}_2$), 6.34 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{II}}\text{H}_2$), 6.33 (d, $J = 8.6$ Hz, 2H, $\text{L}^{\text{III}}\text{H}_2$), 6.02 (d, $J = 8.8$ Hz, 2H, $\text{L}^{\text{III}}\text{H}_3$), 4.06 (s, 3H, $\text{L}^{\text{V}}\text{H}_1$), 3.91 (s, 3H, $\text{L}^{\text{V}}\text{H}_1$), 3.81 (s, [**2**] H_1), 3.68 (s, 3H, $\text{L}^{\text{III}}\text{H}_1$), 3.65 (s, 3H, $\text{L}^{\text{II}}\text{H}_1$), 3.62 (s, 3H, $\text{L}^{\text{I}}\text{H}_1$).

^{19}F NMR (376 MHz; CD_3CN , reference C_6F_6): δ -80.10 (NTf_2^-)

ESI-MS: m/z : 844.79 (845.18) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{ReO}_4)_6\}^{6+}$, 1089.07 (1088.60) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{ReO}_4)_3(\text{NTf}_2)_4\}^{5+}$, 1438.55 (1437.97) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{ReO}_4)_2(\text{NTf}_2)_6\}^{4+}$

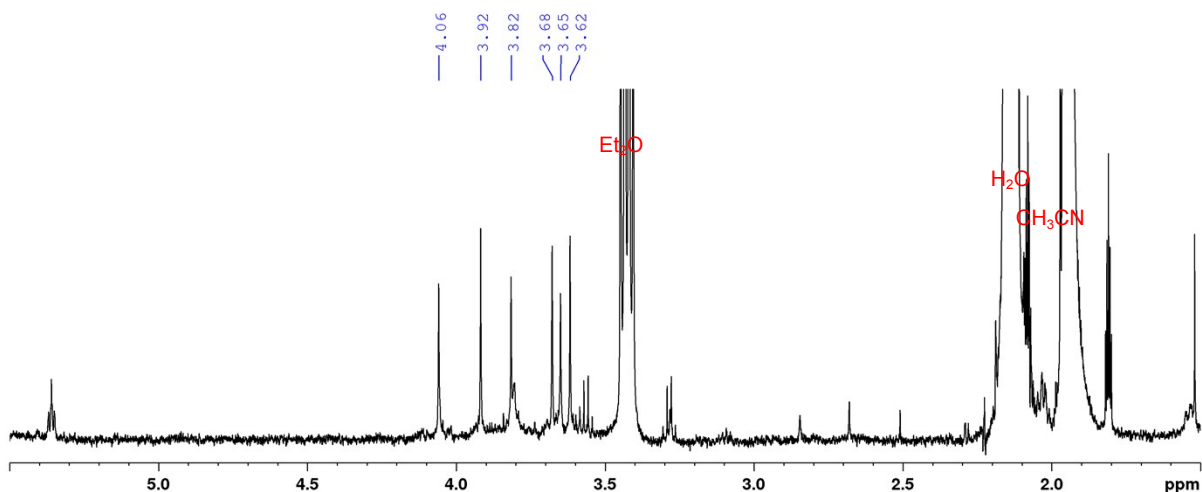


Figure S33: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) of redissolved crystals generated by the slow diffusion of Et_2O into an acetonitrile solution of perhenate templated **3** in the region 1 – 5.5 ppm.

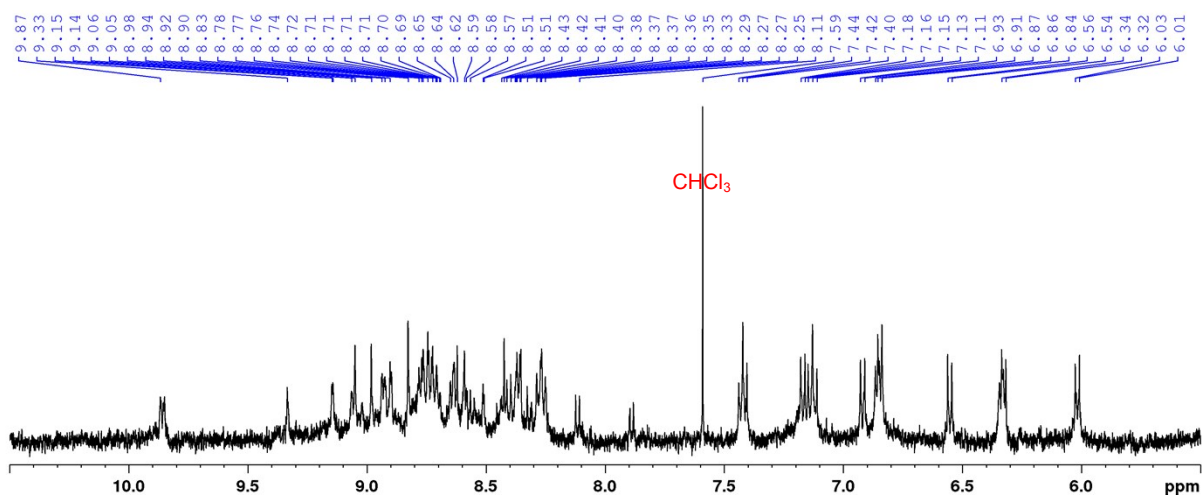


Figure S34: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) ^1H NMR spectrum of redissolved crystals generated by the slow diffusion of Et_2O into an acetonitrile solution of perhenate templated **3** in the region 5.5 – 11 ppm.

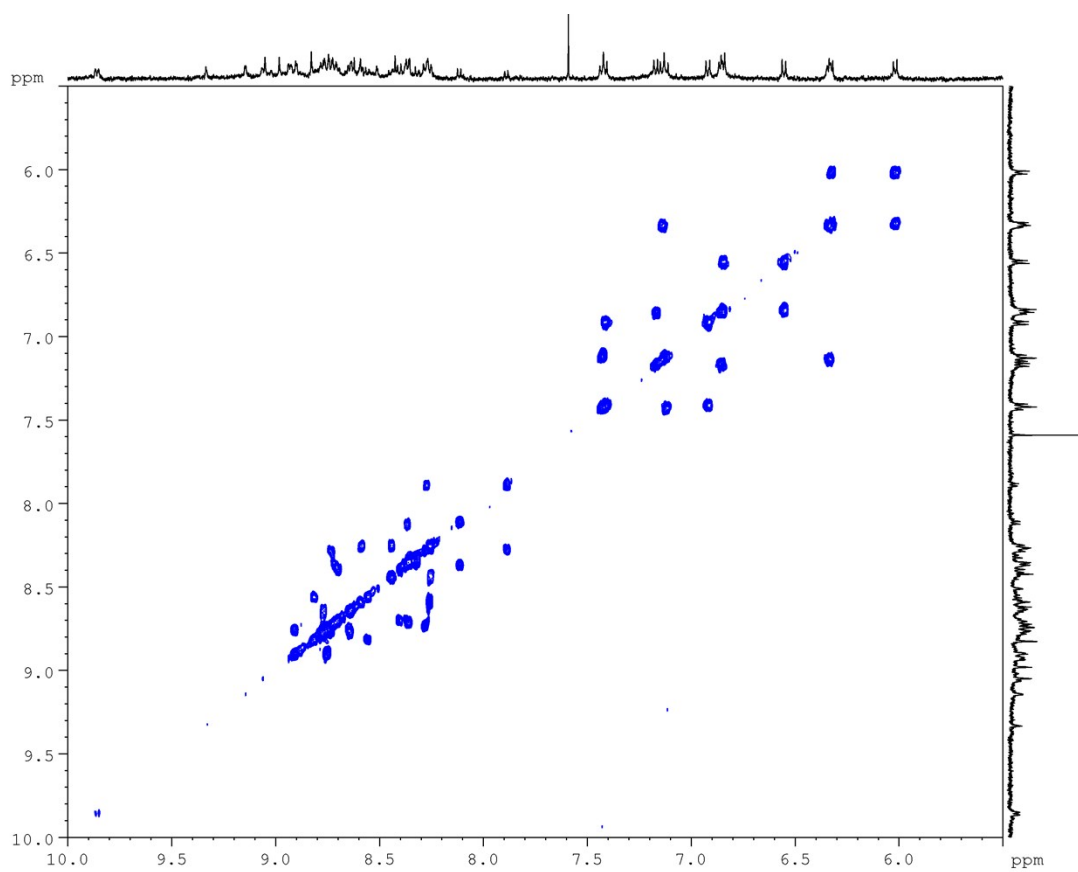


Figure S35: COSY NMR spectrum (500 MHz, 298 K, CD₃CN) of redissolved crystals generated by the slow diffusion of Et₂O into an acetonitrile solution of perrhenate templated **3** in the region 5.5 – 10 ppm.

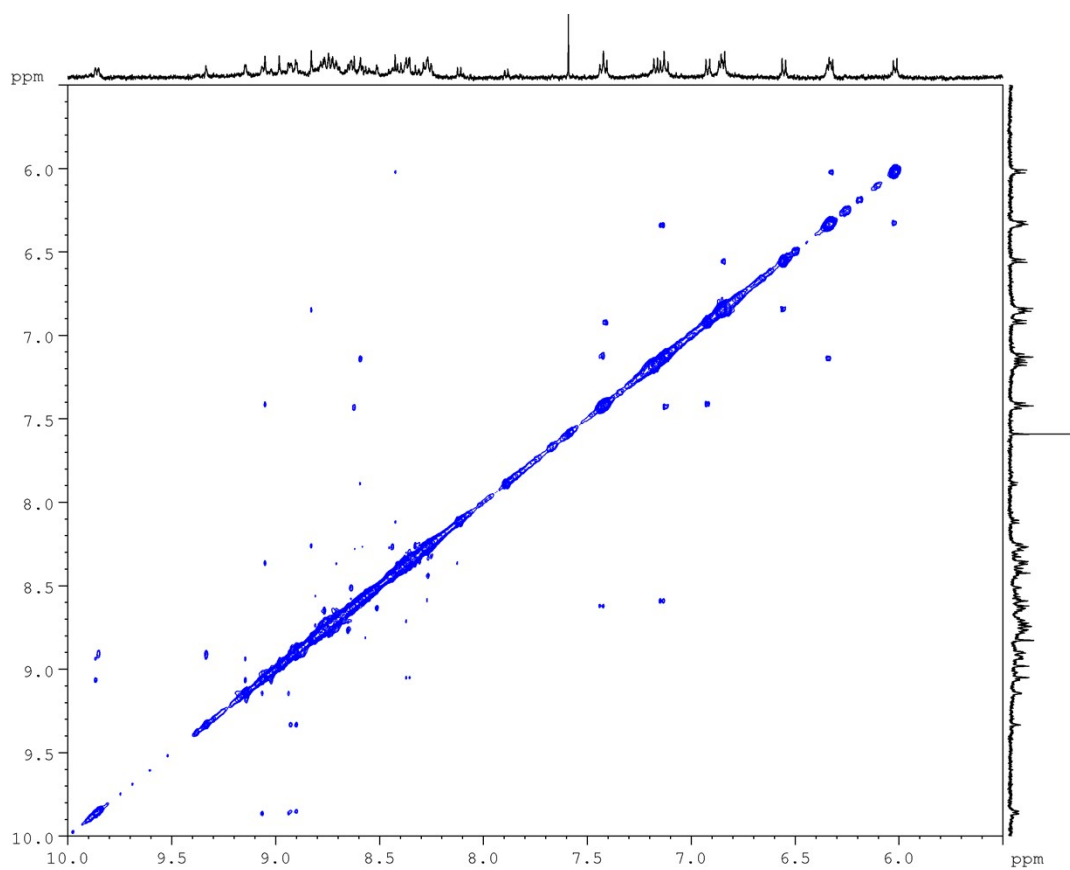


Figure S36: NOESY NMR spectrum (500 MHz, 298 K, CD₃CN) of redissolved crystals generated by the slow diffusion of Et₂O into an acetonitrile solution of perrhenate templated **3** in the region 5.5 – 10 ppm.

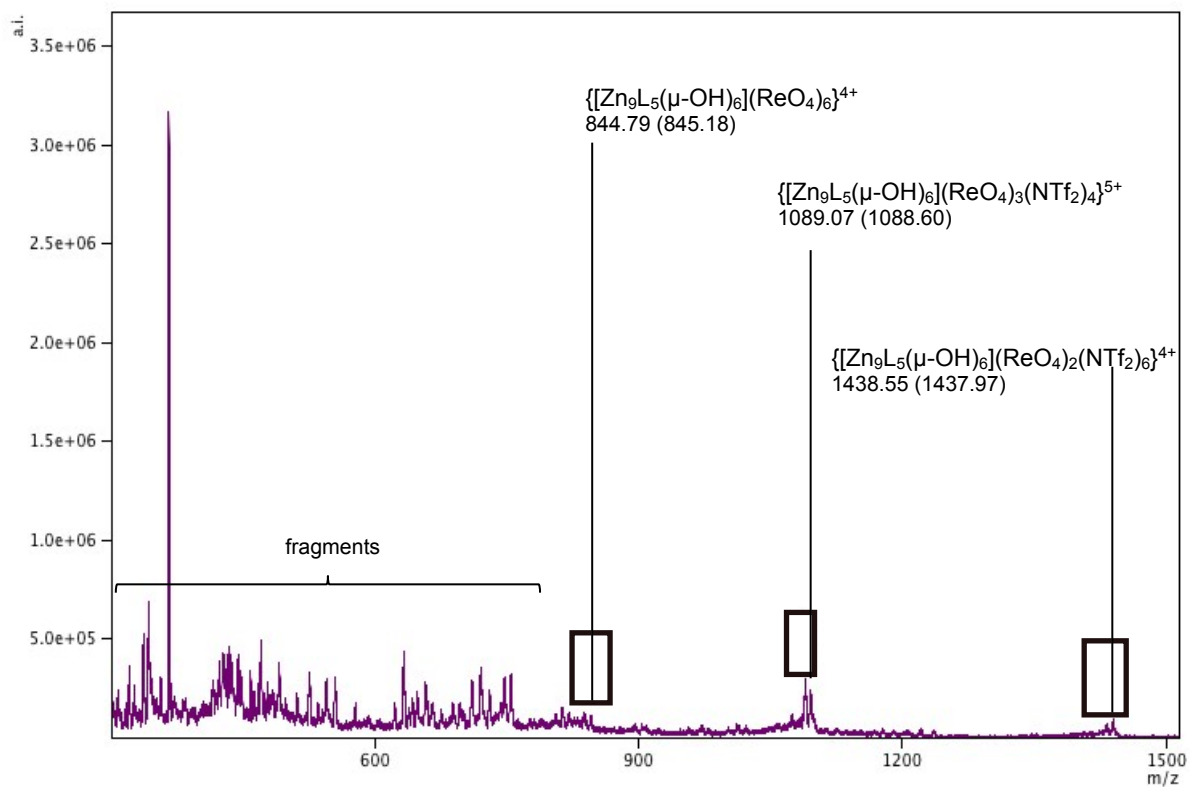


Figure S37: LR-ESI-mass spectrum of perrhenate templated **3**. Calculated values are in brackets.

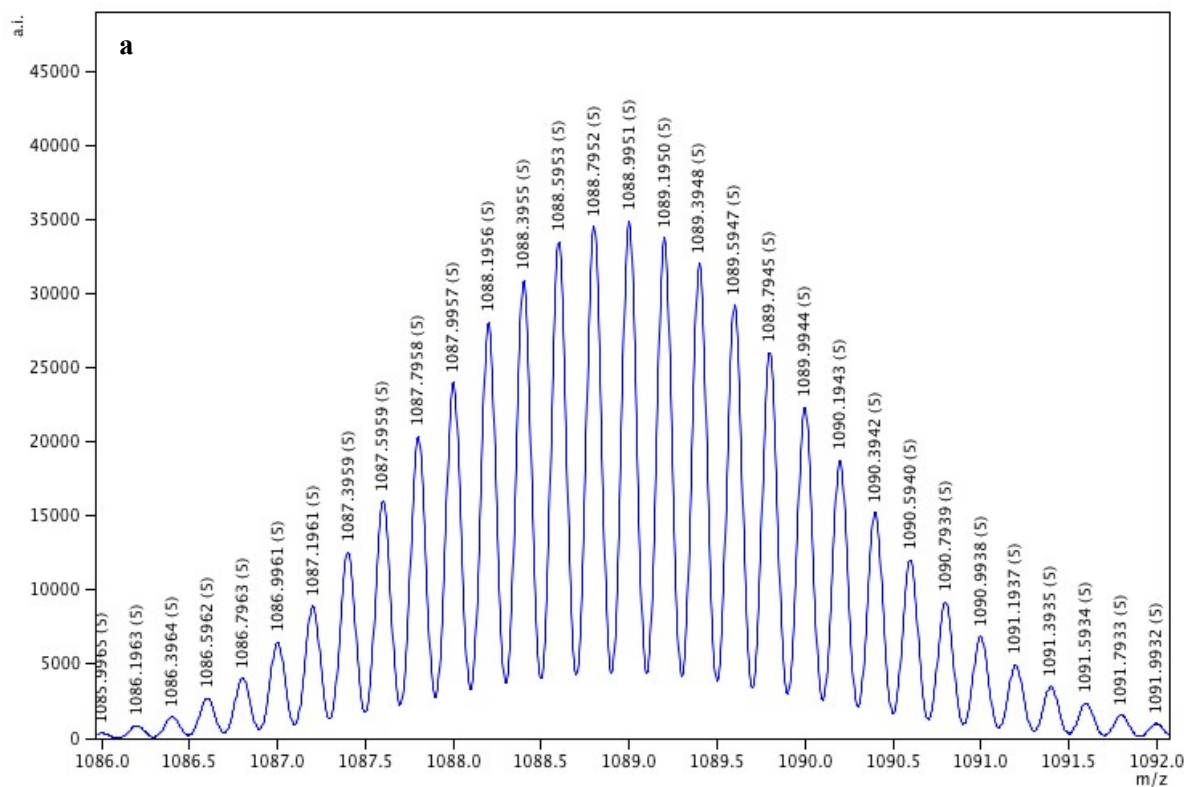
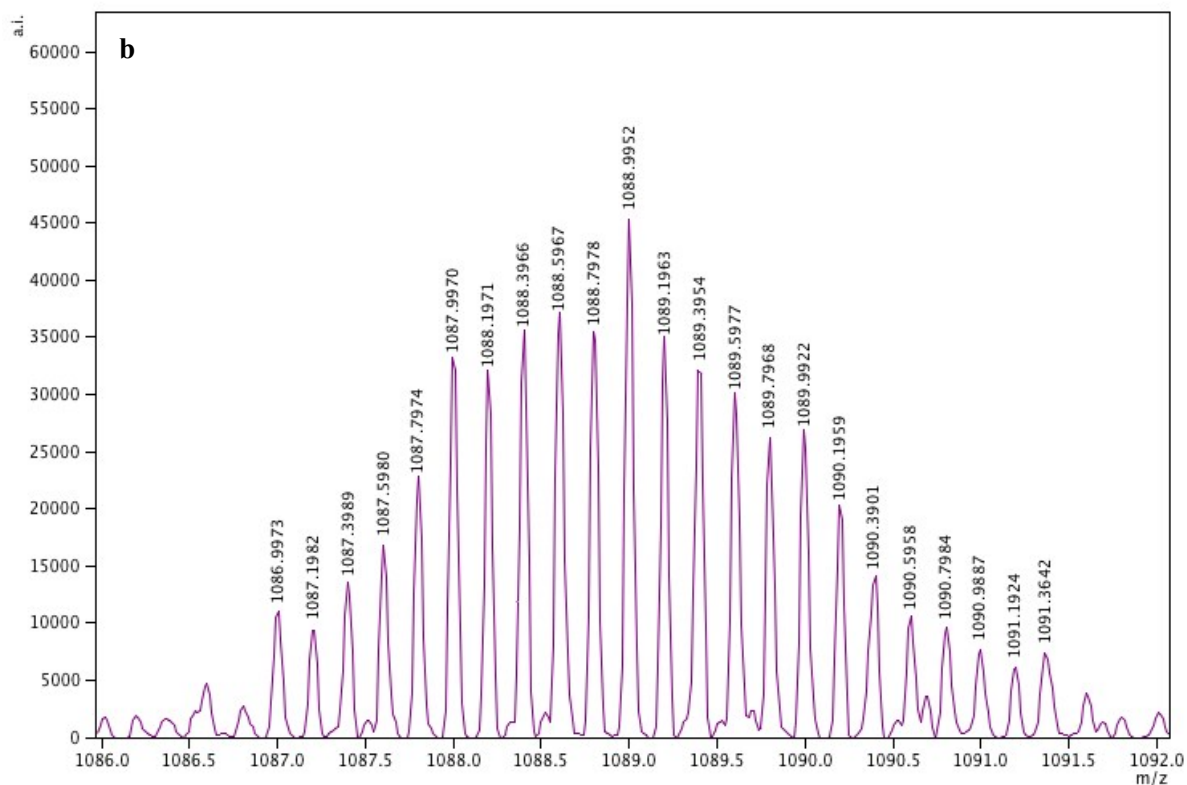


Figure S38: (a) HR-ESI-mass spectrum of the $[3](\text{ReO}_4)_3(\text{NTf}_2)_4^{5+}$ ion. (b) Calculated isotopic distribution of $[3](\text{ReO}_4)_3(\text{NTf}_2)_4^{5+}$

1.11 Trifluoromethanesulfonate templated **3**

[3,3'6',2"5",3"-quaterpyridine]-6,6"-dicarbaldehyde **1** (8.4 mg, 23.0 μmol , 5 equiv.), 4-methoxyaniline (9.4 mg, 73.6 μmol , 16 equiv.), tetrabutylammonium trifluoromethanesulfonate (triflate) (7.7 mg, 18.4 μmol , 4 equiv.) and $\text{Zn}(\text{NTf}_2)_2$ (26.0 mg, 41.4 μmol , 9 equiv.) were suspended in reagent grade CH_3CN (5 mL) and heated at 70 °C in a PTFE stoppered Schlenk tube until all the solids dissolved and a yellow solution was obtained. The reaction mixture was stirred at 70 °C for 12 hours. The solution was filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et_2O (30 mL) precipitated out a mixture of **2** and triflate templated **3** as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et_2O into an acetonitrile solution of triflate templated **3** yielded crystals suitable for analysis.

^1H NMR (500 MHz, CD_3CN) δ 9.72 (s), 9.68 (s), 9.33 (s), 9.23 (s), 9.05 (s, 2H, $\text{L}^{\text{IV}}\text{H}_4$), 9.03-9.01 (m), 8.98 (s, 1H, [**2**] H_4), 8.93-8.85 (m), 8.81-8.71 (m, $\text{L}^{\text{II}}\text{H}_4$), 8.66-8.50 (m, $\text{L}^{\text{I}}\text{H}_4$), 8.43-8.36 (m, $\text{L}^{\text{IV}}\text{H}_4$, $\text{L}^{\text{V}}\text{H}_4$), 8.32-8.26 (m), 8.24 (d, $J = 8.0$ Hz), 8.15 (d, $J = 8.1$ Hz), 8.00 (d, $J = 8.1$ Hz), 7.51 (d, $J = 8.7$ Hz, 1H, $\text{L}^{\text{V}}\text{H}_3$), 7.30 (d, $J = 8.6$ Hz, 2H, $\text{L}^{\text{IV}}\text{H}_3$), 7.20 (d, $J = 9.2$ Hz, 2H, $\text{L}^{\text{V}}\text{H}_2$), 7.16 (d, $J = 8.7$ Hz, [**2**] H_3), 7.10 (d, $J = 9.0$ Hz, 2 H, $\text{L}^{\text{I}}\text{H}_3$), 6.86 (d, $J = 9.0$ Hz, 2H, $\text{L}^{\text{IV}}\text{H}_2$), 6.85 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{II}}\text{H}_3$), 6.84 (d, $J = 8.7$ Hz, [**2**] H_2), 6.31 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{I}}\text{H}_2$), 6.56 (d, $J = 8.7$ Hz, 2H, $\text{L}^{\text{II}}\text{H}_2$), 6.33 (d, $J = 8.6$ Hz, 2H, $\text{L}^{\text{III}}\text{H}_2$), 6.02 (d, $J = 8.8$ Hz, 2H, $\text{L}^{\text{III}}\text{H}_3$), 4.08 (s, 3H, $\text{L}^{\text{V}}\text{H}_1$), 3.91 (s, 3H, $\text{L}^{\text{IV}}\text{H}_1$), 3.81 (s, [**2**] H_1), 3.67 (s, 3H, $\text{L}^{\text{III}}\text{H}_1$), 3.60 (s, 3H, $\text{L}^{\text{II}}\text{H}_1$), 3.58 (s, 3H, $\text{L}^{\text{I}}\text{H}_1$).

^{19}F NMR (376 MHz; CD_3CN , reference C_6F_6): δ -80.50 (NTf_2^-) -79.69 br (OTf)

ESI-MS: m/z : 809.85 (809.85) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{OTf})_3(\text{NTf}_2)_3\}^{6+}$, 1028.28 (1027.41) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{OTf})_3(\text{NTf}_2)_4\}^{5+}$, 1354.89 (1354.74) $\{[\text{Zn}_9\text{L}_3(\mu\text{-OH})_6](\text{OTf})_3(\text{NTf}_2)_5\}^{4+}$.

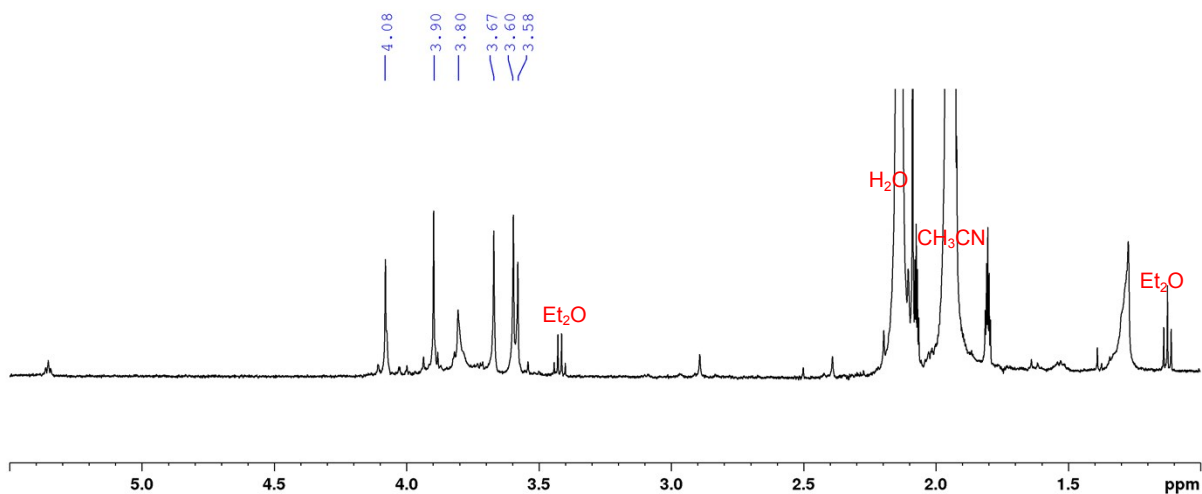


Figure S39: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) of redissolved crystals generated by the slow diffusion of Et_2O into an acetonitrile solution of triflate templated **3** in the region 1 – 5.5 ppm.

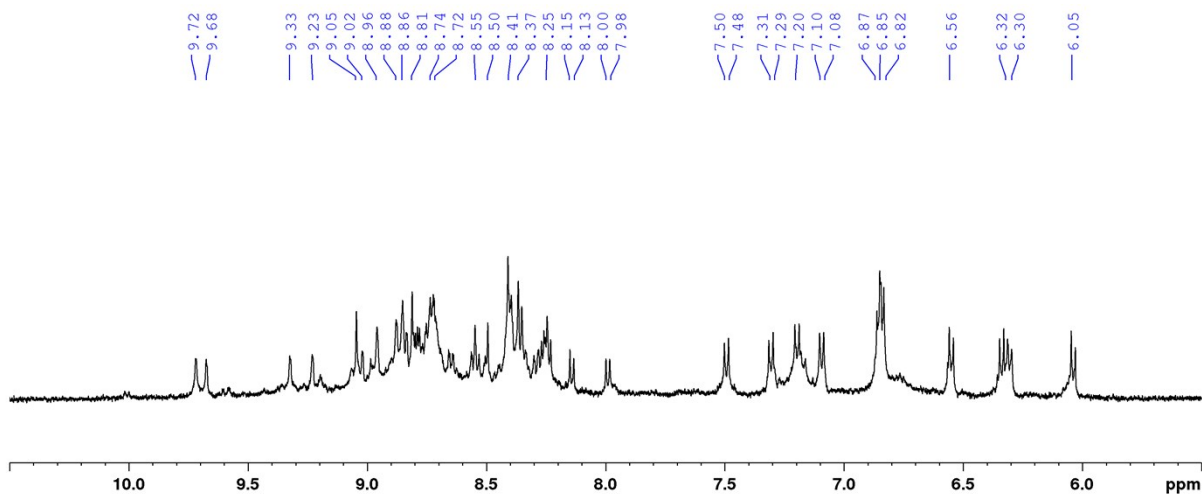


Figure S40: ^1H NMR spectrum (500 MHz, 298 K, CD_3CN) ^1H NMR spectrum of redissolved crystals generated by the slow diffusion of Et_2O into an acetonitrile solution of triflate templated **3** in the region 5.5 – 11 ppm.

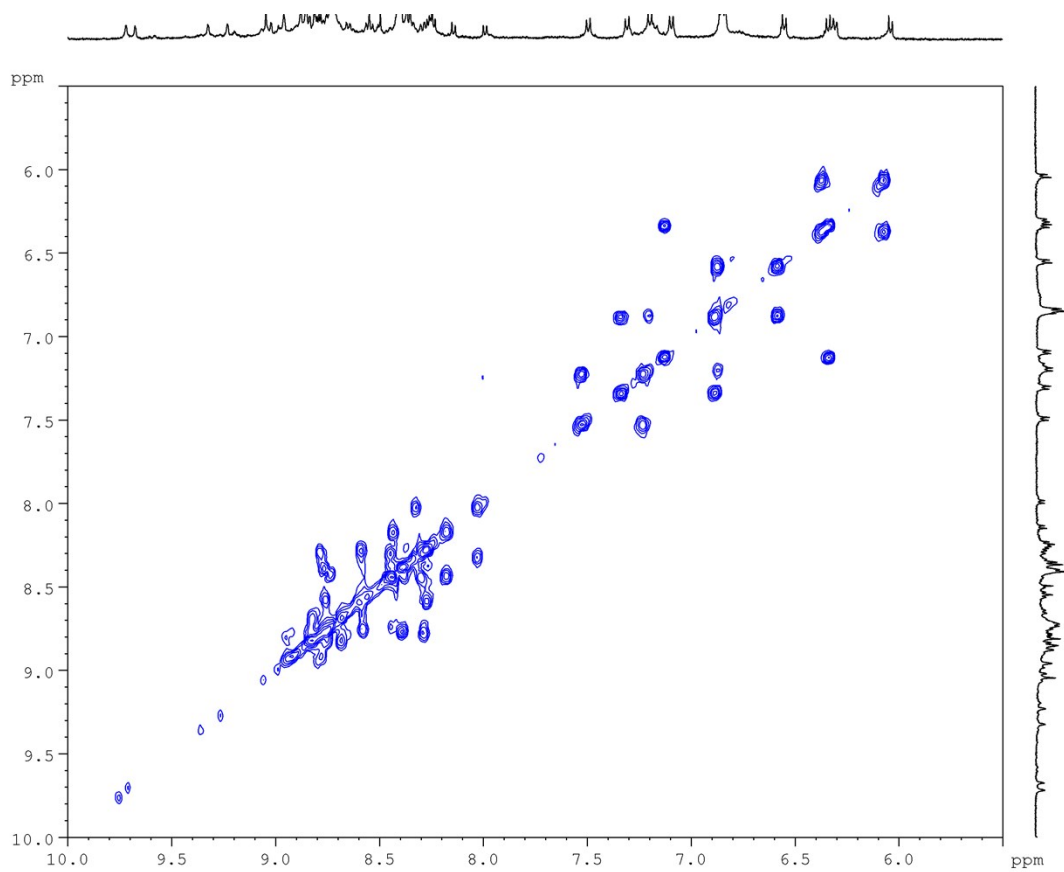


Figure S41: COSY NMR spectrum (500 MHz, 298 K, CD₃CN) of redissolved crystals generated by the slow diffusion of Et₂O into an acetonitrile solution of triflate templated **3** in the region 5.5 – 10 ppm.

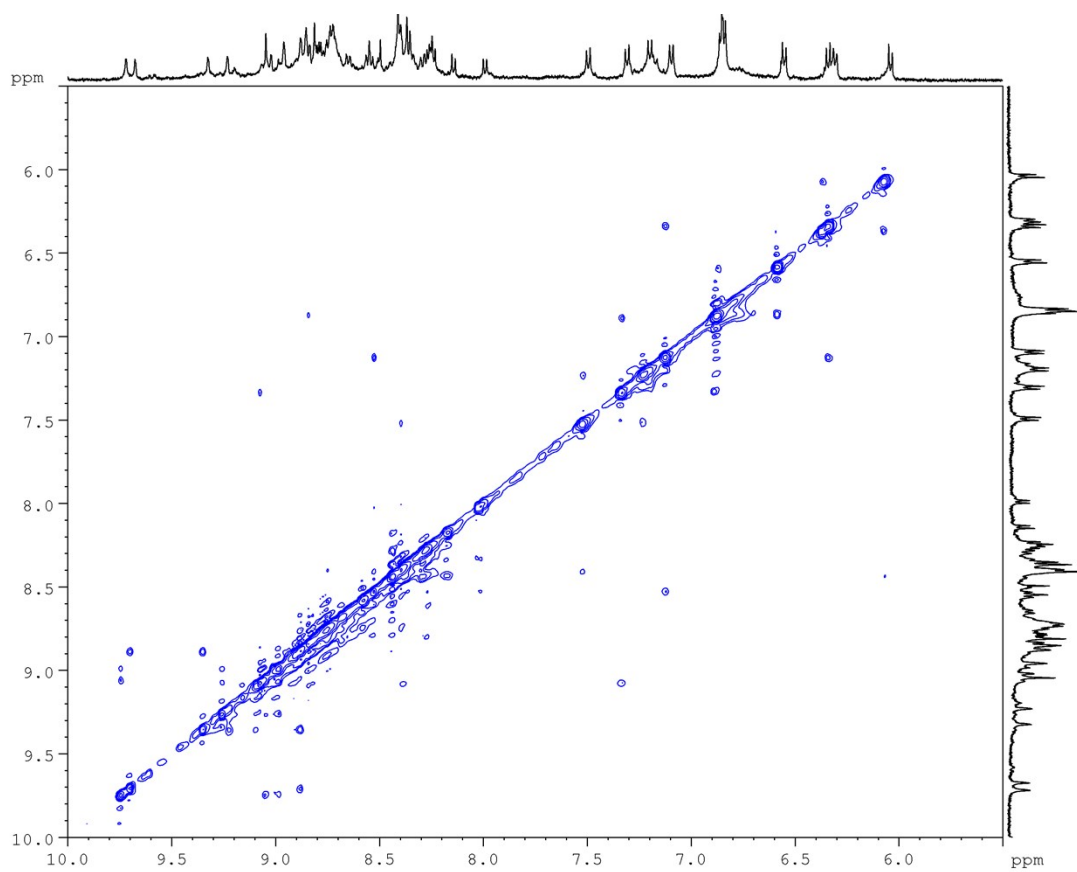


Figure S42: NOESY NMR spectrum (500 MHz, 298 K, CD₃CN) of redissolved crystals generated by the slow diffusion of Et₂O into an acetonitrile solution of triflate templated **3** in the region 5.5 – 10 ppm.

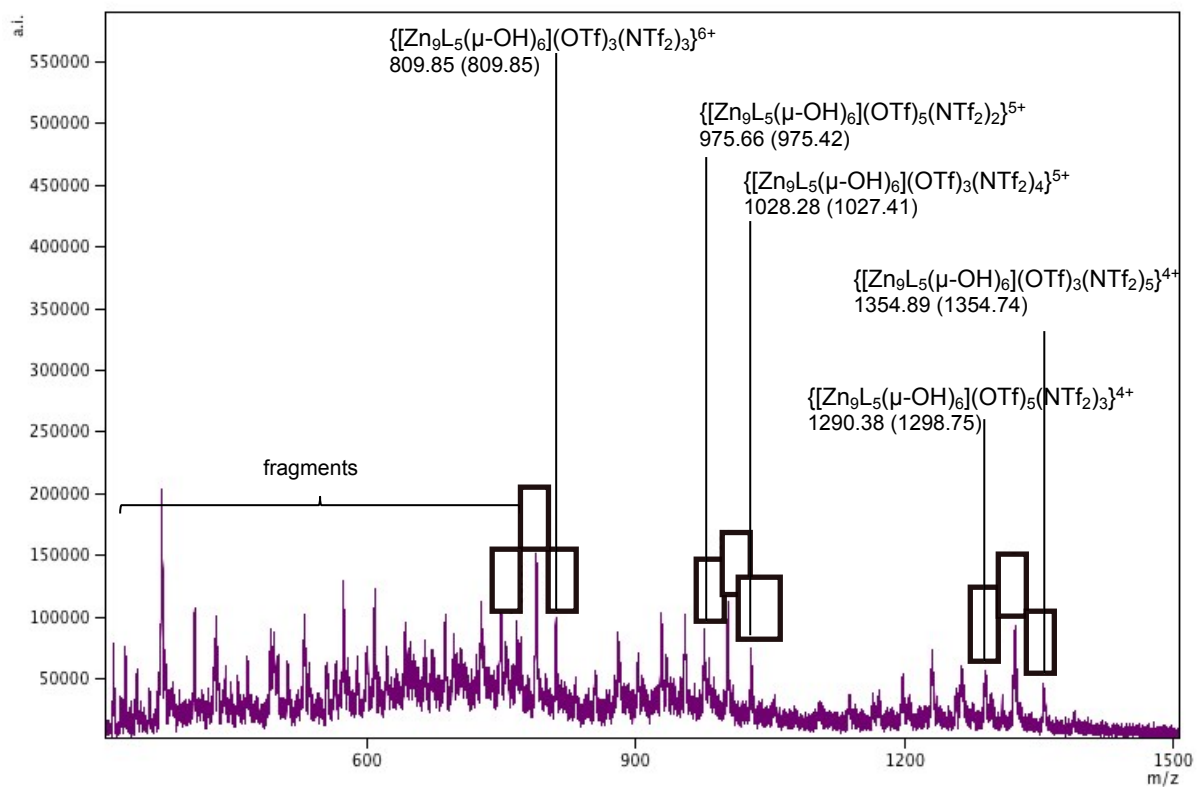


Figure S43: LR-ESI-mass spectrum of triflate templated **3**. Calculated values are in brackets.

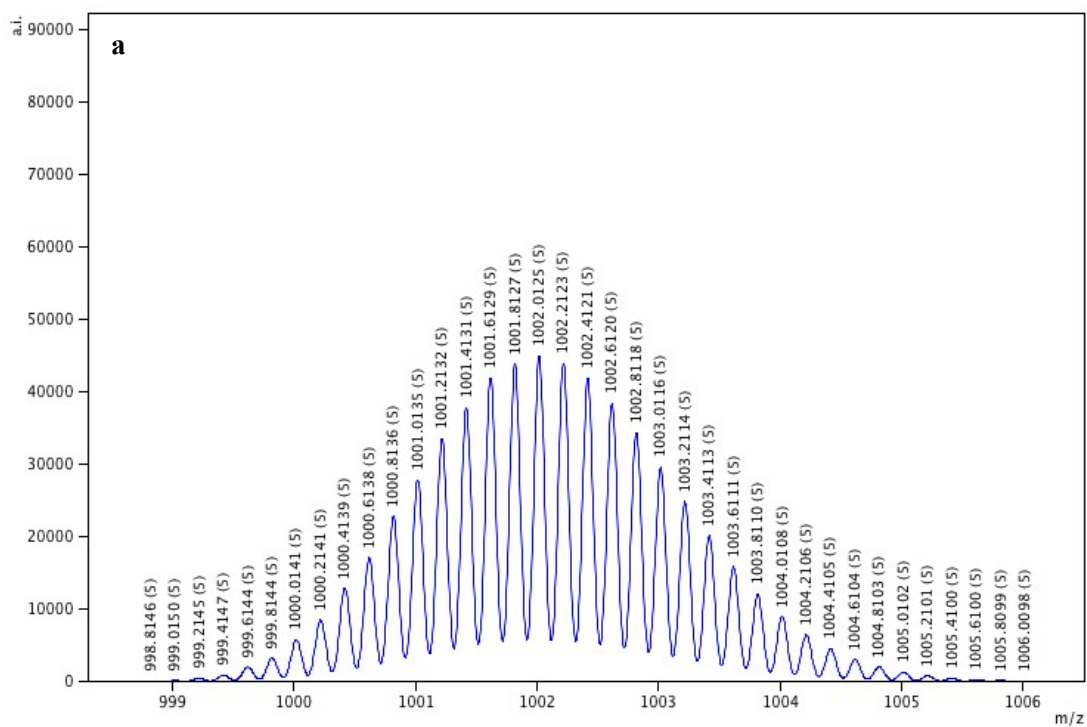
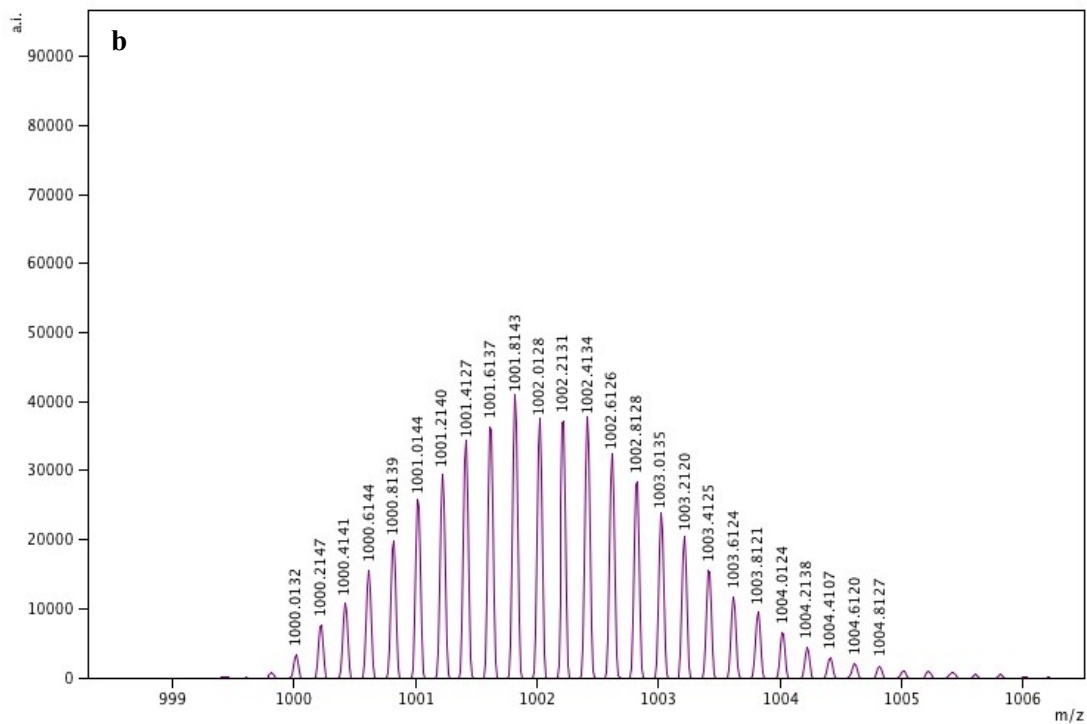


Figure S44: (a) HR-ESI-mass spectrum of the $[3](OTf)_4(NTf_2)_3^{5+}$ ion. (b) Calculated isotopic distribution of $[3](OTf)_4(NTf_2)_3^{5+}$

1.12 Anion displacement reactions

The slow diffusion (> 1 week) of Et₂O into an acetonitrile solution of **3** synthesised from Zn(NTf₂)₂ and 4 equiv. of NBu₄ClO₄, NBu₄OTf or, NBu₄ReO₄ yielded high purity **3** suitable for template displacement studies. Analysis was limited to ¹H NMR spectroscopy as the libraries of anions produced highly complex low intensity ESI-spectra.

Addition of 2 equiv. of 2-naphthalenesulfonate to dissolved crystals of perchlorate templated **3** was found to cleanly displace perchlorate.

Addition of 4 equiv. perrhenate to crystals of perchlorate templated **3** was found to cause a slight change in the NMR spectrum indicative of either a mixed templated species or shifts due to changes in the ionic strength of the solution.

Addition of 4 equiv. of perchlorate to crystals of triflate templated **3** was found to cause a slight change in the NMR spectrum indicative of either a mixed templated species or shifts due to changes in the ionic strength of the solution. Addition of 2 equiv. of 2-naphthalenesulfonate to the resulting solution was found to cleanly form 2-naphthalenesulfonate templated **3**.

Addition of 4 equiv. of perchlorate to crystals of perrhenate templated **3** was found to cause a slight change in the NMR spectrum indicative of either a mixed templated species or shifts due to changes in the ionic strength of the solution. Addition of a further 2 equiv. of 2-naphthalenesulfonate the resulting solution was found generate resonances associated with 2-naphthalenesulfonate templated **3**. However, the resonances were broadened indicating the transformation may not have proceeded as cleanly as the examples above.

Displacement of perchlorate by 2-naphthalenesulfonate

Crystals of **3** (2.0 mg, 0.3 μmol , 1 equiv.) synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ClO_4 were dissolved in CD_3CN and a $^1\text{H-NMR}$ spectrum was acquired. Aliquots of a 0.15 mM solution of sodium 2-naphthalenesulfonate (2.1 μL , 0.3 μmol , 1 equiv.) in 1:2 $\text{D}_2\text{O}/\text{CD}_3\text{CN}$ were added and the reaction followed by $^1\text{H-NMR}$ spectroscopy.

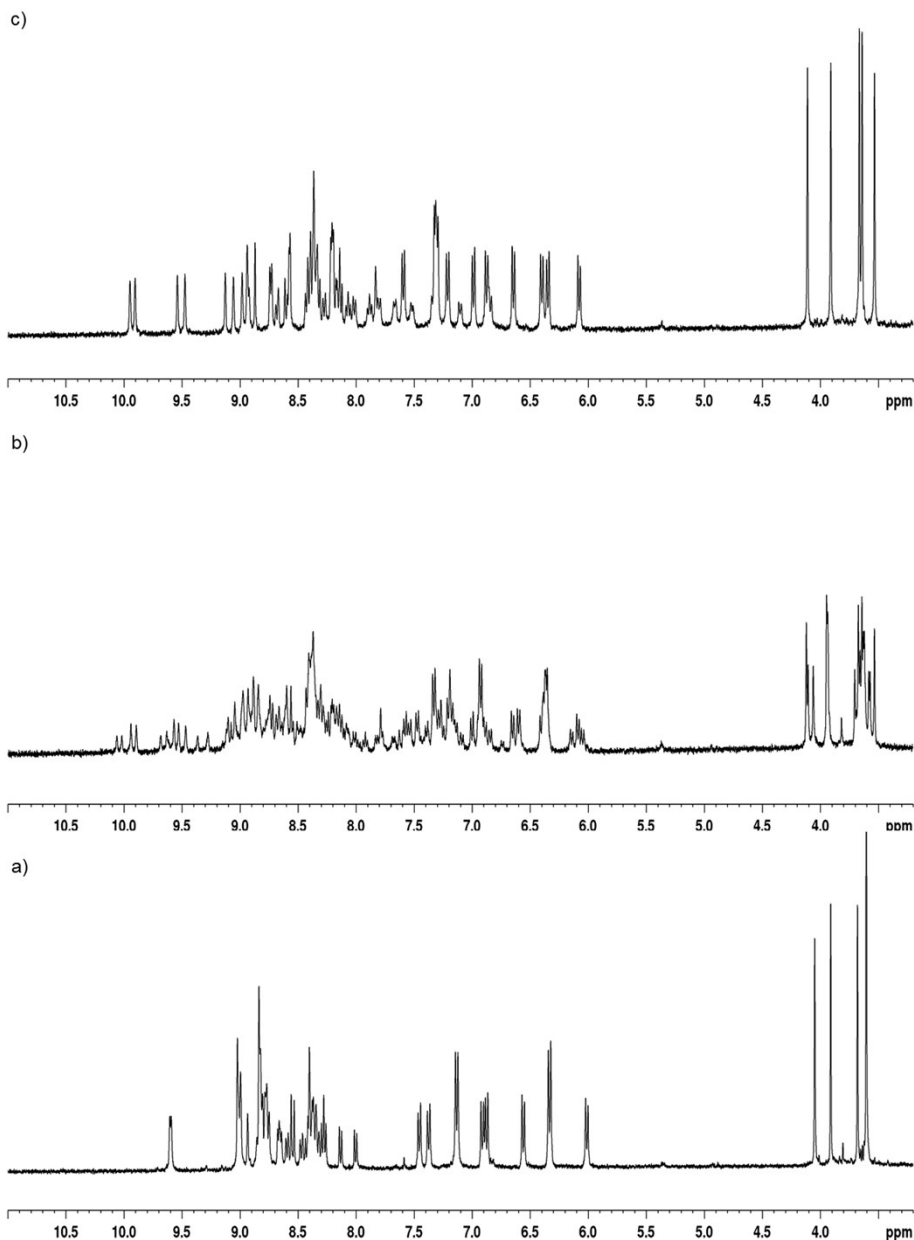


Figure S45: (a) $^1\text{H-NMR}$ of crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ClO_4 . (b) after the addition of 1 equiv. of sodium 2-naphthalenesulfonate (c) after the addition of 2 equiv. of sodium 2-naphthalenesulfonate. The appearance of resonances corresponding to 2-naphthalene sulfonate templated **3** can be observed in (c).

Addition of trifluoromethanesulfonate to perchlorate templated **3**

Crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ClO_4 (0.8 mg, 0.13 μmol , 1 equiv.) were dissolved in CD_3CN and a ^1H -NMR spectrum was acquired. Aliquots of a 0.045 M solution of tetrabutylammonium trifluoromethanesulfonate (2.8 μL , 0.13 μmol , 1equiv.) in CD_3CN were added and the reaction followed by ^1H -NMR spectroscopy.

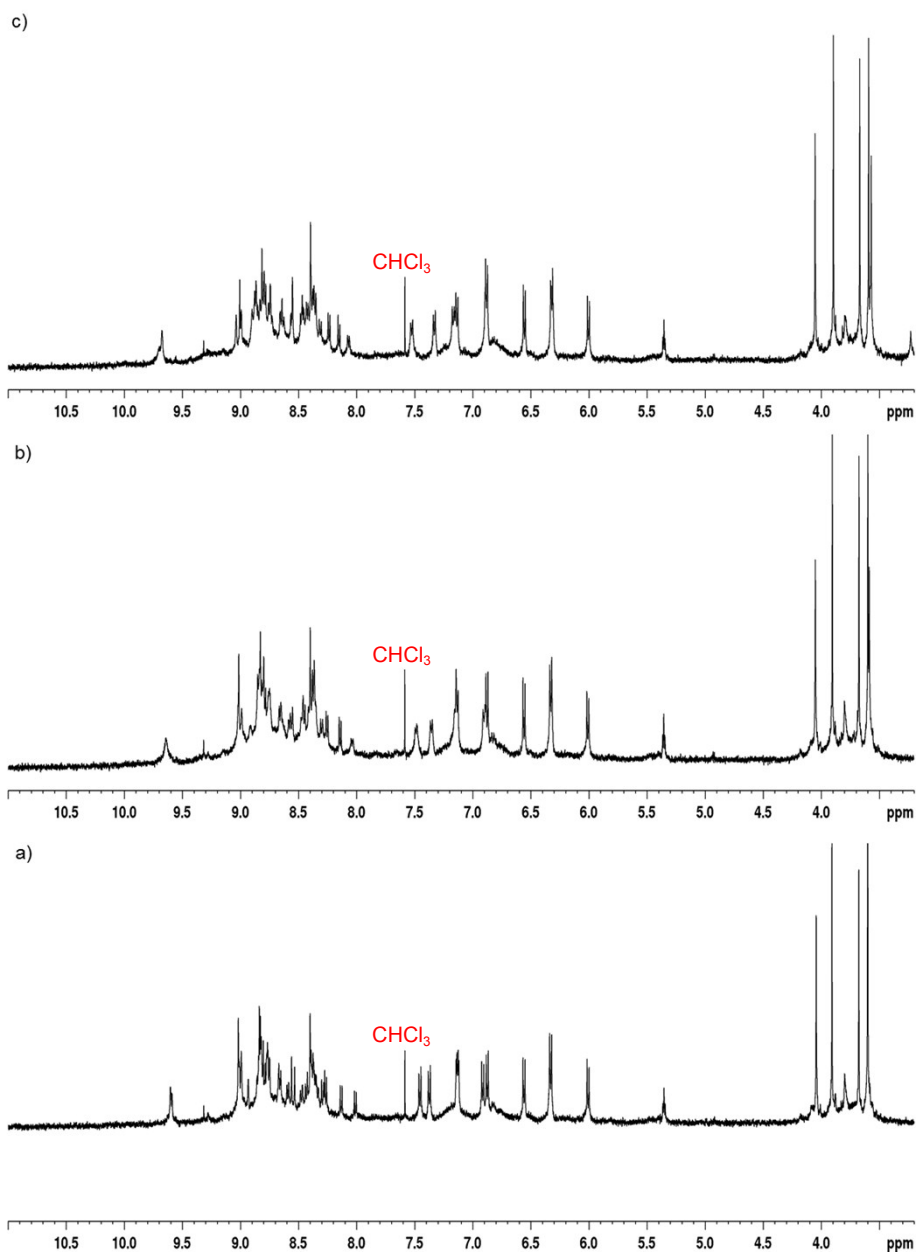
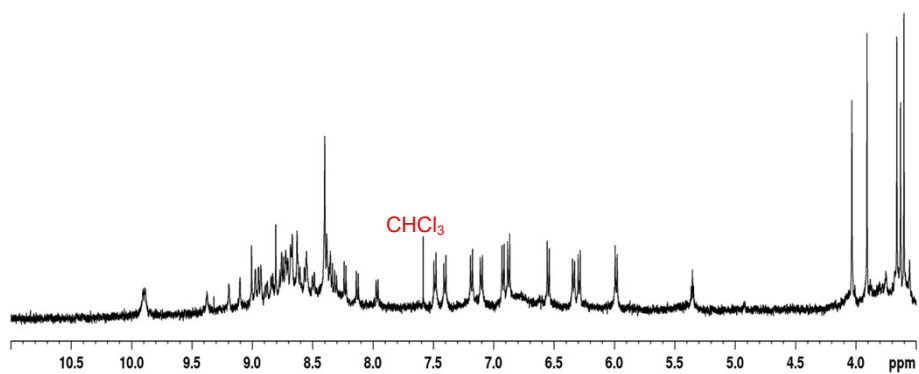


Figure S46: (a) ^1H -NMR of crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ClO_4 . (b) 1 equiv. of tetrabutylammonium trifluoromethanesulfonate (c) 4 equiv. of tetrabutylammonium trifluoromethanesulfonate. The slight changes in the NMR shifts are inconclusive and are either indicative of a mixed templated species or changes in the ionic strength of the solution.

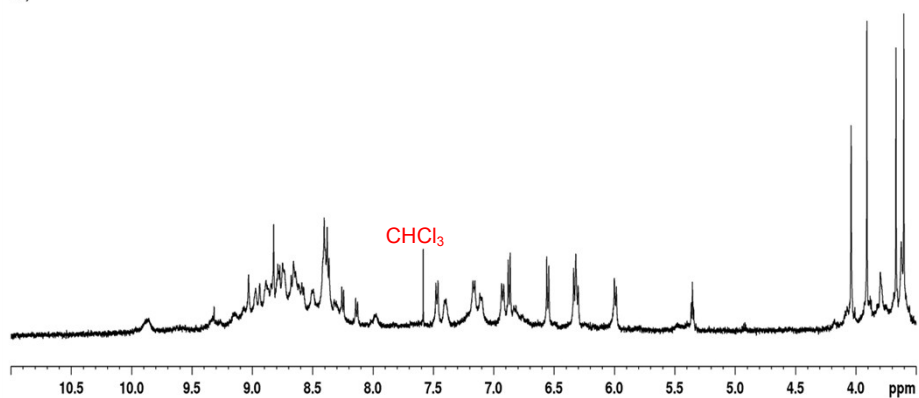
Addition of perrhenate to perchlorate templated **3**

Crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ClO_4 (0.8 mg, 0.13 μmol , 1 equiv.) were dissolved in CD_3CN and a $^1\text{H-NMR}$ spectrum was acquired. Aliquots of a 0.045 M solution of tetrabutylammonium perrhenate (2.8 μL , 0.13 μmol , 1 equiv.) in CD_3CN were added and the reaction followed by $^1\text{H-NMR}$ spectroscopy.

c)



b)



a)

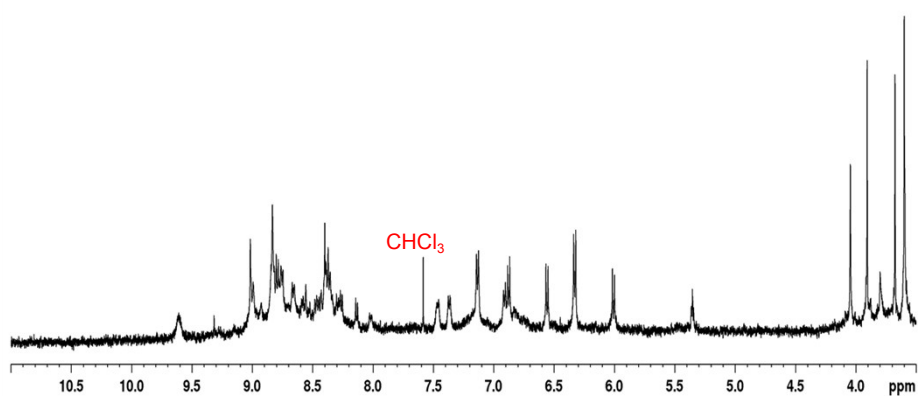


Figure S47: (a) $^1\text{H-NMR}$ of crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ClO_4 . (b) 1 equiv. of tetrabutylammonium perrhenate (c) 4 equiv. of tetrabutylammonium perrhenate. The slight changes in the NMR shifts are inconclusive and are either indicative of a mixed templated species or changes in the ionic strength of the solution.

Addition of perchlorate to trifluoromethanesulfonate templated **3**

Crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4OTf (1.94 mg, 0.3 μmol , 1 equiv.) were dissolved in CD_3CN and a ^1H NMR spectrum was acquired. Aliquots of a 0.04 mM solution of tetrabutylammonium perchlorate (6.81 μL , 0.3 μmol , 1 equiv.) CD_3CN were added and the reaction followed by ^1H NMR spectroscopy.

c)

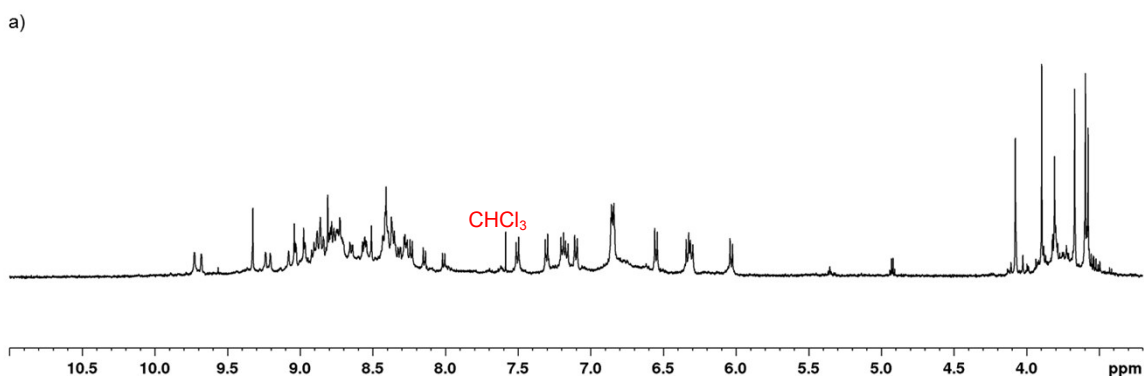
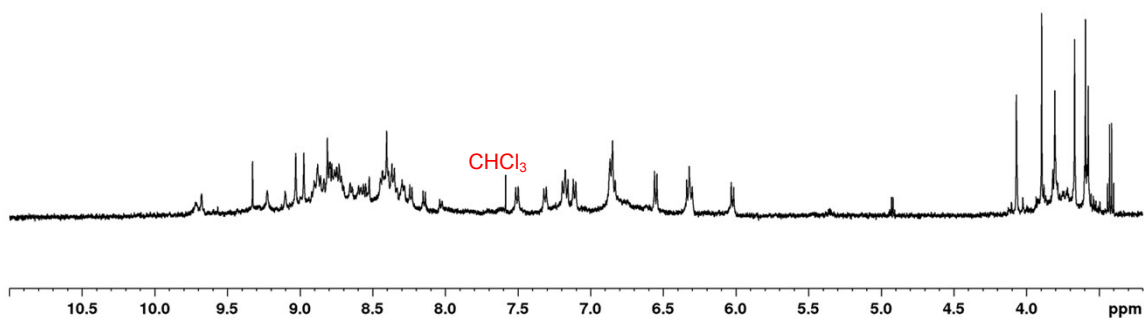
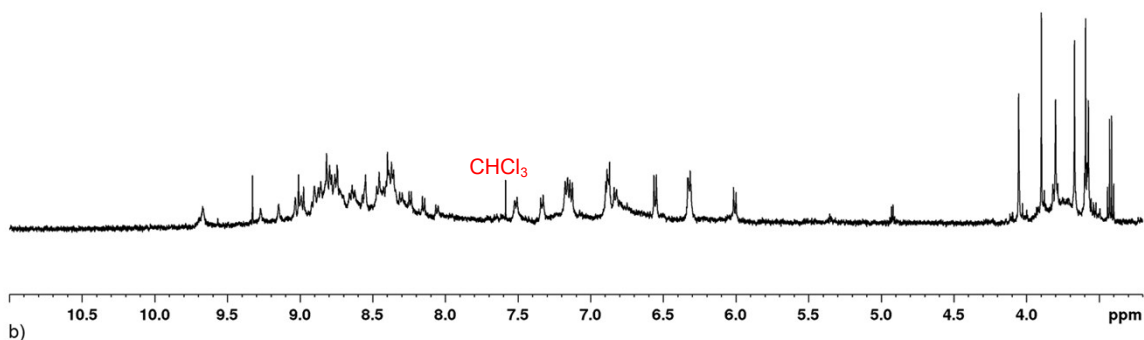
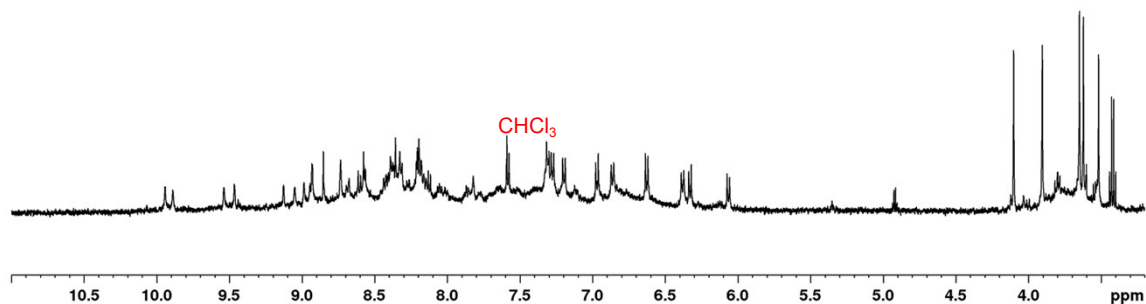


Figure S48: (a) ^1H NMR of crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4OTf . (b) 1 equiv. of tetrabutylammonium perchlorate (c) 4 equiv. of tetrabutylammonium perchlorate. The slight changes in the NMR shifts are inconclusive and are either indicative of a mixed templated species or changes in the ionic strength of the solution.

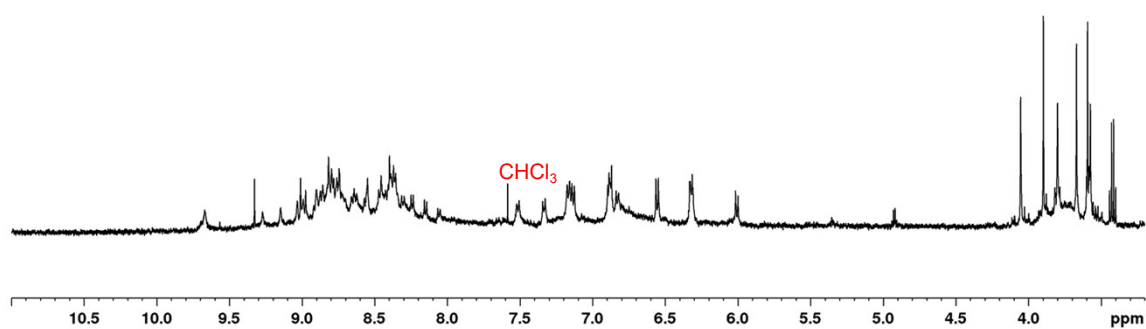
Addition of 2-naphthalenesulfonate to a mixture of perchlorate and trifluoromethanesulfonate templated 3

Aliquots of a 0.07 M solution of sodium 2-naphthalenesulfonate (4.4 μL , 0.3 μmol , 1equiv.) in 1:2 $\text{D}_2\text{O}/\text{CD}_3\text{CN}$ were added to the solution from the perchlorate displacement of trifluoromethanesulfonate and the reaction followed by ^1H NMR spectroscopy.

c)



b)



a)

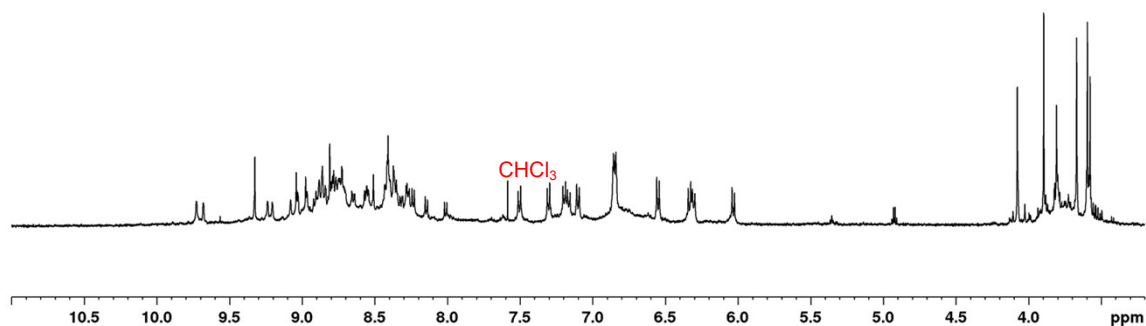


Figure S49: (a) ^1H NMR of crystals of 3 synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4OTf (b) after the addition of 4 equiv. of tetrabutylammonium perchlorate (c) after the further addition of 2 equiv. of sodium 2-naphthalenesulfonate. The appearance of resonances corresponding to 2-naphthalene sulfonate templated 3 can be observed in (c).

Addition of perrhenate to trifluoromethanesulfonate templated **3**

Crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4OTf (3.78 mg, 0.5 μmol , 1 equiv.) were dissolved in CD_3CN and a ^1H NMR spectrum was acquired. Aliquots of a 0.04 mM solution of tetrabutylammonium perchlorate (12.3 μL , 0.5 μmol , 1 equiv.) CD_3CN were added and the reaction followed by ^1H NMR spectroscopy.

c)

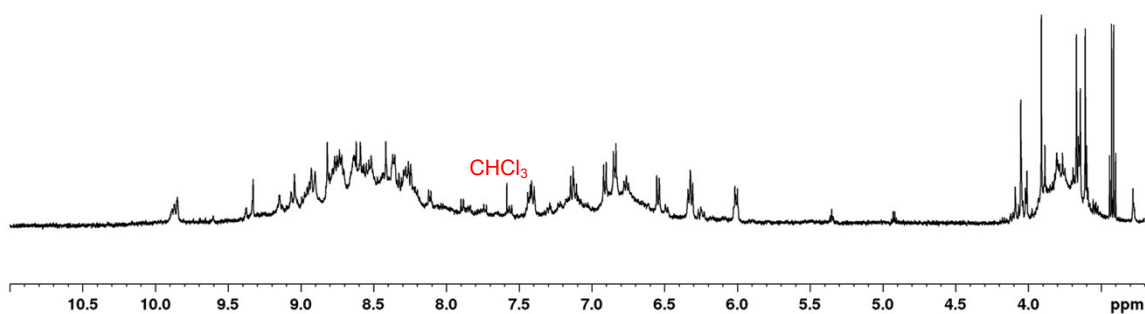
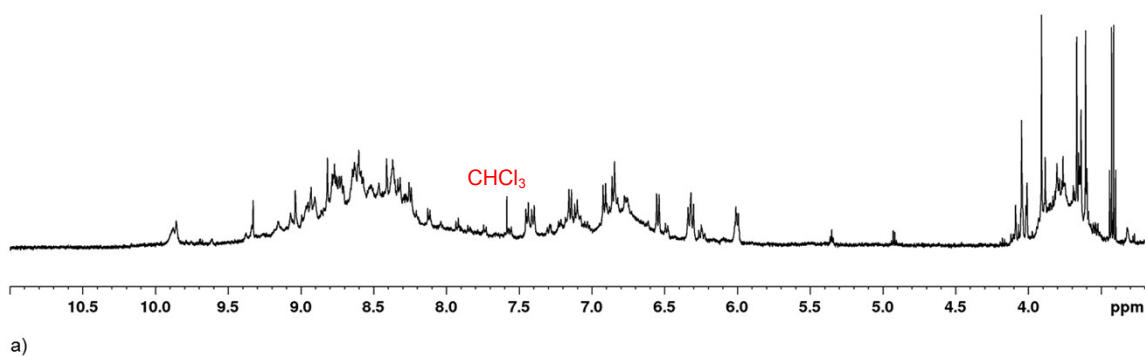
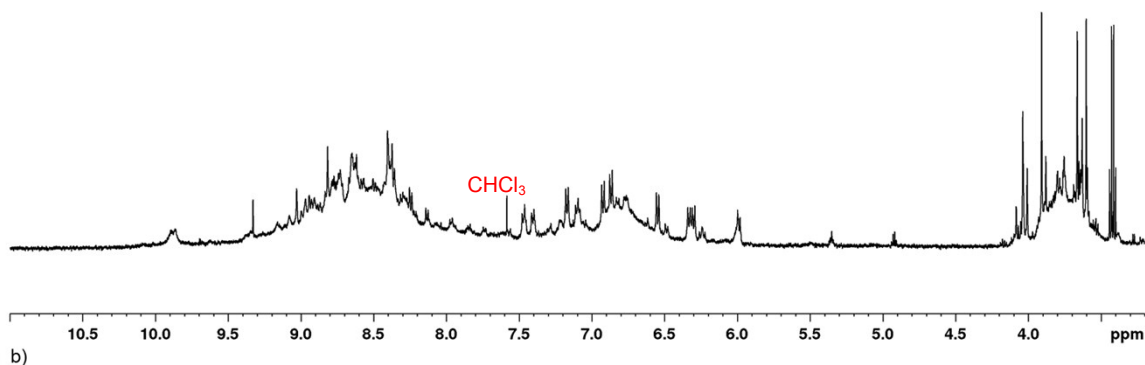
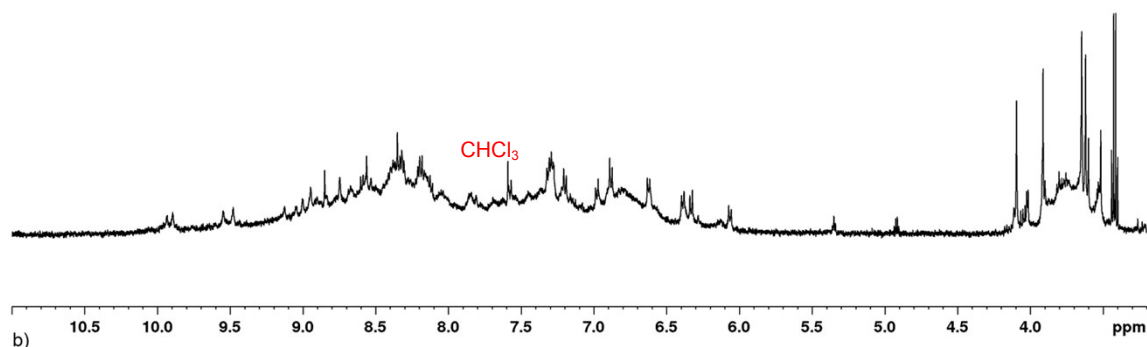


Figure S50: (a) ^1H NMR of crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ReO_4 . (b) 1 equiv. of tetrabutylammonium perchlorate (c) 4 equiv. of tetrabutylammonium perchlorate. The slight changes in the NMR shifts are inconclusive and are either indicative of a mixed templated species or changes in the ionic strength of the solution.

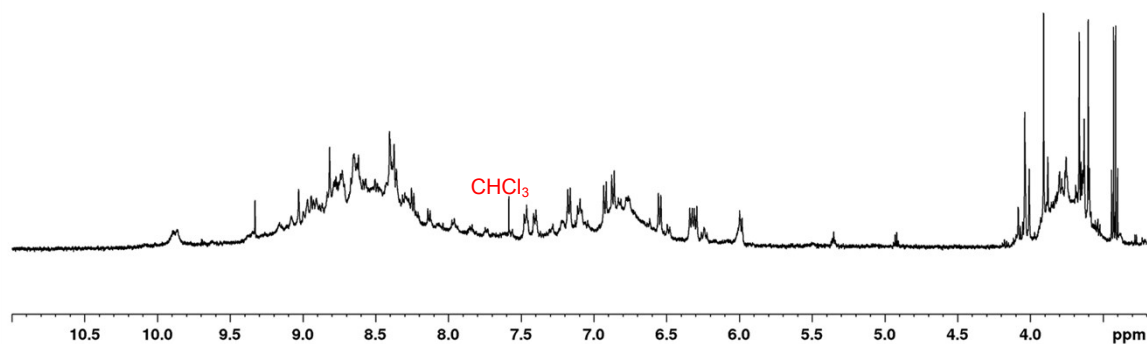
Addition of 2-naphthalenesulfonate to of a mixture of perrhenate and trifluoromethanesulfonate templated **3**

Aliquots of a 0.07 M solution of sodium 2-naphthalenesulfonate (7.9 μl , 0.5 μmol , 1 equiv.) in 1:2 $\text{D}_2\text{O}/\text{CD}_3\text{CN}$ were added to the solution from the perchlorate displacement of trifluoromethanesulfonate and the reaction followed by ^1H NMR spectroscopy.

c)



b)



a)

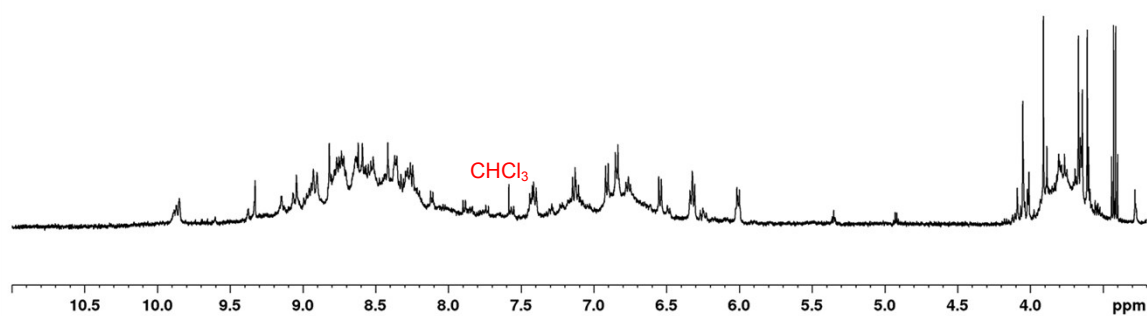


Figure S51: (a) ^1H NMR of crystals of **3** synthesised from $\text{Zn}(\text{NTf}_2)_2$ and 4 equiv. of NBu_4ReO_4 . (b) after addition of 4 equiv. of tetrabutylammonium perchlorate (c) after the further addition of 2 equiv. of sodium 2-naphthalenesulfonate. Although the resonances corresponding to 2-naphthalene sulfonate templated **3** can be observed in (c) the spectrum contains broad poorly resolved peaks indicating the transformation was not as clean as those above.

1.13 Single Crystal X-ray Diffraction

Data were collected with on a Nonius Kappa FR590 diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å) with ω and ψ scans at 180(2) K; a Bruker D8 VENTURE equipped with high-brilliance I μ S Cu K α radiation ($\lambda = 1.54178$ Å), with ω and ψ scans at 100(2) K or at Beamline I19 of Diamond Light Source employing silicon double crystal monochromated synchrotron radiation (0.6889 Å) with ω scans at 100(2) K. Data integration and reduction were undertaken with HKL Denzo and Scalepack^[2] or with SAINT and XPREP.^[3] Multi-scan empirical absorption corrections were applied using SORTAV^[4] or SADABS.^[5] Subsequent computations were carried out using the WinGX-32^[6] graphical user interface. The structures were solved using SHELXS or SUPERFLIP^[7] then refined and extended with SHELXL-2013.^[8] Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. The oxygen-bound hydrogen atoms were first located in the electron density map; their coordinates were allowed to refine and then fixed. The location of these hydroxide hydrogens should be regarded as approximate due to the low resolution of the data and disorder in the anions they are hydrogen-bonded to. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. Crystallographic data along with specific details pertaining to the refinement follow (CCDC 1410155-1410158).

[Zn₉L₅(μ-OH)₆]·12ClO₄·6H₂O·11MeCN

Formula C₂₀₂H₁₉₁Cl₁₂N₄₁O₇₀Zn₉, *M* 5326.68, Triclinic, space group P-1 (#2), *a* 19.431(4), *b* 22.435(5), *c* 28.802(6) Å, α 81.86(3), β 81.60(3), γ 75.35(3)°, *V* 11945(5) Å³, *D_c* 1.481 g cm⁻³, *Z* 2, crystal size 0.230 by 0.140 by 0.020 mm, colour colourless, habit plate, temperature 180(2) Kelvin, λ (MoK α) 0.71073 Å, μ (MoK α) 1.112 mm⁻¹, *T*(SORTAV)_{min,max} 0.849, 0.991, $2\theta_{\max}$ 40.78, *hkl* range -19 19, -21 21, -28 28, *N* 120107, *N*_{ind} 23478(*R*_{merge} 0.1287), *N*_{obs} 14941(*I* > 2σ(*I*)), *N*_{var} 2984, residuals * *R*1(*F*) 0.0749, *wR*2(*F*²) 0.2256, GoF(all) 1.029, $\Delta\rho_{\min,\max}$ -0.923, 1.023 e⁻ Å⁻³.

**R*1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; *wR*2 = $(\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections, $w=1/[\sigma^2(F_o^2)+(0.1175P)^2+51.2610P]$ where $P=(F_o^2+2F_c^2)/3$

Specific refinement details:

The crystals were very susceptible to solvent loss and rapid (<10 seconds) handling prior to quenching in the cryostream was required to collect data. Despite these measures and the use of long exposure times the crystals were weakly diffracting and no reflections were observed at better than 1.00Å resolution. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure. Reflecting the poor diffraction properties the ClO₄⁻ anions show extensive evidence of disorder: seven were modelled as disordered over two locations with a number of bond length and thermal parameter restraints. As a consequence of this disorder there are a number of short contacts between disordered anions and partially occupied solvent molecules. One of the anisidine units was also modelled as disordered over two locations.

[Zn₉L₅(μ-OH)₆]·4ReO₄·8NTf₂·MeCN

Formula C₁₉₈H₁₄₉F₄₈N₃₉O₆₄Re₄S₁₆Zn₉, *M* 6856.64, Monoclinic, space group P 21/c (#14), *a* 38.4811(16), *b* 22.2330(9), *c* 33.8318(14) Å, β 115.6360(10), *V* 26095.5(19) Å³, *D_c* 1.745 g cm⁻³, *Z* 4, crystal size 0.122 by 0.077 by 0.061 mm, colour yellow, habit block, temperature 180(2) Kelvin, λ(CuKα) 1.54178 Å, μ(CuKα) 6.636 mm⁻¹, *T*(SADABS)_{min,max} 0.6123, 0.7493, 2θ_{max} 94.88, *hkl* range -29 36, -21 20, -32 32, *N* 131433, *N*_{ind} 23676(*R*_{merge} 0.0537), *N*_{obs} 16225(*I* > 2σ(*I*)), *N*_{var} 2260, residuals * *R*1(*F*) 0.0786, *wR*2(*F*²) 0.2483, GoF(all) 1.072, Δρ_{min,max} -0.589, 1.215 e⁻ Å⁻³.

**R*1 = Σ||*F*₀| - |*F*_c||/Σ|*F*₀| for *F*₀ > 2σ(*F*₀); *wR*2 = (Σ*w*(*F*₀² - *F*_c²)²/Σ(*wF*_c²)²)^{1/2} all reflections, *w*=1/[σ²(*F*₀²)+(0.1616*P*)²+31.3679*P*] where *P*=(*F*₀²+2*F*_c²)/3

Specific refinement details:

The crystals were very susceptible to solvent loss and rapid (<10 seconds) handling prior to quenching in the cryostream was required to collect data. Despite these measures and the use of a high intensity laboratory source and long exposure times the crystals were weakly diffracting and no reflections were observed at better than 1.05Å resolution. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure.

Two of the anisidine units were modelled as disordered over two locations and several more show evidence of thermal motion resulting from the presence of dynamic disorder in these groups. Consequently there are a number of close contacts between symmetry-generated and/or disordered anisidine units and between these groups and disordered ReO₄⁻ anions. The two outermost ReO₄⁻ anions were modelled as disordered over two locations and with fractional occupancy. Some further electron density peaks close to these disordered ReO₄⁻ anions were modelled as partial occupancy oxygen or rhenium atoms. Apart from the four ReO₄⁻ anions associated with the Zn₉L₅ cation, only one other anion lattice site could be resolved; this anion was modelled as a triflimide with 0.7 occupancy. Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from the remaining anions (assigned to triflimide in the formula) and disordered solvent. This area of diffuse electron density could not be successfully modelled and the SQUEEZE^[9] function of PLATON^[10] was employed.

[Zn₉L₅(μ-OH)₆]·2OTf·10NTf₂

Formula C₂₀₂H₁₄₆F₄₀N₆₂O₆₆S₂₂Zn₉, *M* 6551.45, Hexagonal, space group P 61 2 2 (#178), *a* 36.800(17), *b* 36.800(17), *c* 35.22(2) Å, γ 120°, *V* 41306(45) Å³, *D_c* 1.580 g cm⁻³, *Z* 6, crystal size 0.100 by 0.003 by 0.002 mm, colour yellow, habit needle, temperature 100(2) Kelvin, λ (synchrotron) 0.6889 Å, μ (synchrotron) 0.819 mm⁻¹, *T*(SADABS)_{min,max} 0.5853, 0.7440, $2\theta_{\max}$ 31.99, *hkl* range -29 29, -29 29, -28 28, *N* 122626, *N*_{ind} 7400(*R*_{merge} 0.1391), *N*_{obs} 5698(*I* > 2σ(*I*)), *N*_{var} 1267, residuals* *R*1(*F*) 0.0937, *wR*2(*F*²) 0.2655, GoF(all) 1.071, $\Delta\rho_{\min,\max}$ -0.318, 0.522 e⁻ Å⁻³.

**R*1 = $\sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; *wR*2 = $(\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections, $w=1/[\sigma^2(F_o^2)+(0.2000P)^2-0.0400P]$ where $P=(F_o^2+2F_c^2)/3$

Specific refinement details:

The crystals were very susceptible to solvent loss and rapid (<10 seconds) handling prior to quenching in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation the crystals were very weakly diffracting and no reflections were observed at better than 1.25Å resolution. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure. The asymmetric unit contains half of a [Zn₉L₅(μ-OH)₆] and associated counterions. Due to the less than ideal resolution, extensive restraints were required to facilitate realistic modelling for the organic parts of the structure. The GRADE program^[11] was employed using the GRADE Web Server^[12] to generate a full set of bond distance and angle restraints (DFIX, DANG, FLAT) for the organic ligands, triflate anions and triflimide anions. Similarity (SIMU) and enhanced rigid bond restraints^[13] (RIGU) were applied to all atoms except for zinc to facilitate anisotropic refinement. The disordered anions were modelled isotropically except for the sulfur atoms.

Due to the high levels of thermal motion (or minor unresolved disorder) around the periphery of the molecule there are a number of close contacts between symmetry-generated and/or disordered methyl groups. The triflate anion was modelled as disordered over two locations. Apart from the two triflate anions associated with the Zn₉L₅ cation, only two other anion lattice sites could be resolved; these anions were modelled as partial occupancy triflimide anions. Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from the remaining anions (assigned to triflimide in the formula) and disordered solvent. This area of diffuse electron density could not be successfully modelled and the SQUEEZE^[9] function of PLATON^[10] was employed.

[Zn₉L₅(μ-OH)₆]·2C₁₀H₇SO₃·10NTf₂·MeCN

Formula C₂₂₂H₁₆₃F₆₀N₄₁O₆₂S₂₂Zn₉, *M* 6830.57, Monoclinic, space group P 2₁/n (#14), *a* 15.8416(11), *b* 55.356(4), *c* 33.8750(19) Å, β 90.229(3), *V* 29706(3) Å³, *D_c* 1.527 g cm⁻³, *Z* 4, crystal size 0.020 by 0.010 by 0.003 mm, colour yellow, habit block, temperature 100(2) Kelvin, λ(synchrotron) 0.6889 Å, μ(synchrotron) 0.815 mm⁻¹, *T*(SADABS)_{min,max} 0.5451, 0.7442, 2θ_{max} 33.36, *hkl* range -13 12, -46 45, -28 28, *N* 141378, *N*_{ind} 17766(*R*_{merge} 0.1220), *N*_{obs} 14944(*I* > 2σ(*I*)), *N*_{var} 2665, residuals* *R*1(*F*) 0.1869, *wR*2(*F*²) 0.4548, GoF(all) 1.374, Δρ_{min,max} -0.819, 0.895 e⁻ Å⁻³.

**R*1 = Σ||*F*_o| - |*F*_c||/Σ|*F*_o| for *F*_o > 2σ(*F*_o); *wR*2 = (Σ*w*(*F*_o² - *F*_c²)²/Σ(*wF*_c²)²)^{1/2} all reflections, *w*=1/[σ²(*F*_o²)+(0.2000*P*)²+350.0000*P*] where *P*=(*F*_o²+2*F*_c²)/3

Specific refinement details:

The crystals were very susceptible to solvent loss and rapid (<10 seconds) handling prior to quenching in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation the crystals were very weakly diffracting and no reflections were observed at better than 1.2 Å resolution. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure. Due to the less than ideal resolution, extensive restraints were required to facilitate realistic modelling for the organic parts of the structure. The GRADE program^[11] was employed using the GRADE Web Server^[12] to generate a full set of bond distance and angle restraints (DFIX, DANG, FLAT) for the organic ligands, triflate anions and triflimide anions. Similarity (SIMU) and enhanced rigid bond restraints^[13] (RIGU) were applied to all atoms except for zinc to facilitate anisotropic refinement. Due to very high levels of thermal motion (or minor unresolved disorder) around the periphery of the molecule there are a number of close contacts between anisidine units of neighbouring molecules. The anions showed evidence of high thermal motion and were modelled isotropically except for the sulfur atoms. Apart from the two 2-naphthalenesulfonate anions associated with the Zn₉L₅ cation, six triflimide anions could be resolved. Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from the remaining anions (assigned to triflimide in the formula) and disordered solvent. This area of diffuse electron density could not be successfully modelled and the SQUEEZE^[9] function of PLATON^[10] was employed. Despite the higher than ideal residuals, the final model is in good agreement with experimentally observed electron density.

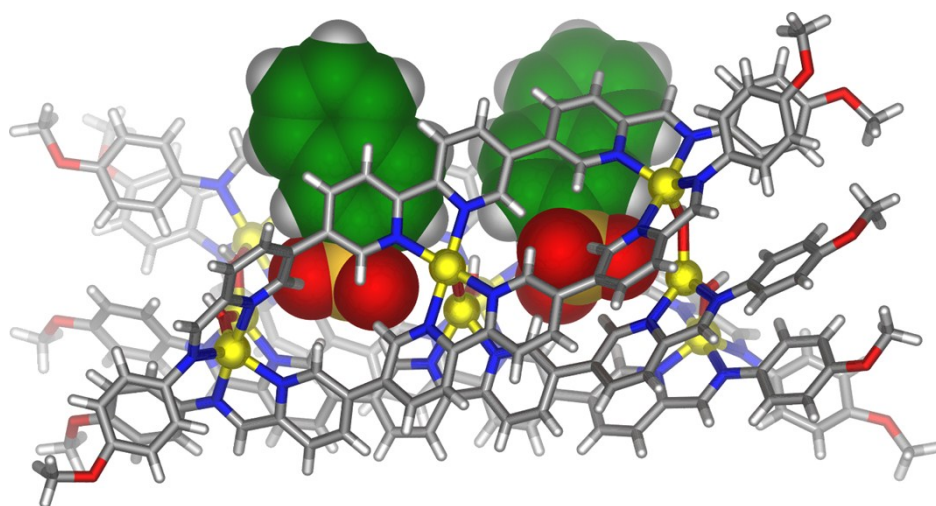


Figure S52: Additional view of the X-ray structure of **3** templated 2-naphthalenesulfonate with the 2-naphthalenesulfonate anions shown in space-filling mode.

1.14 References

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