Supplementary Information for:

**Dual stimuli-induced formation of a µ-hydroxido bridged [Zn₉L₅(µ-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 \(^1\). Acetonitrile (CH\(_3\)CN) was supplied by Fisher Scientific and diethyl ether (Et\(_2\)O) 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 (\(\delta\)) 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 CD\(_3\)CN 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 \(^1\)H resonances were assigned using standard 2D NMR techniques, such as \(^1\)H-\(^1\)H COSY, \(^1\)H-\(^1\)H NOESY and 1D selective TOCSY experiments. The solubility of many of the complexes precluded the acquisition of \(^13\)C 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 \(\mu\)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 Zn(NTf₂)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 Zn(NTf₂)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 Zn(NTf₂)₂ (70.9 mg, 112.0 μmol, 2 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 clear yellow solution was filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et₂O (30 mL) precipitated out 2 as a yellow solid that was isolated by centrifugation.

¹H NMR (400 MHz, CD₃CN) δ 9.21 (d, J = 1.7 Hz, 1H, H₁₀), 9.08 (d, J = 1.7 Hz, 1H, H₇), 9.00 (s, 1H, H₄), 8.94 (d, J = 8.3 Hz, 1H, H₂), 8.79 (dd, J = 8.2, 1.8 Hz, 1H, H₈), 8.73 (dd, J = 7.9, 1.9 Hz, 1H, H₆), 8.42 (d, J = 7.9 Hz, 1H, H₅), 7.18 (d, J = 8.9 Hz, 1H, H₃), 6.83 (d, J = 8.9 Hz, 1H, H₂), 3.80 (s, 3H, H₁).

¹³C NMR (176 MHz; CD₃CN) 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

¹⁹F NMR: (376 MHz; CD₃CN, reference C₆F₆): δ -80.49

LR-ESI-MS: m/z: 620.68 (620.83) [Zn₃L₃](NTf₂)₂ ⁴⁺, 921.40 (921.07) [Zn₃L₃](NTf₂)₃ ³⁺, 1522.42 (1521.57) [Zn₃L₃](NTf₂)₄ ²⁺
Figure S1: $^1$H NMR spectrum (400 MHz, 298 K, CD$_3$CN) of $[2](\text{NTf}_2)_6$.

Figure S2: COSY NMR spectrum (400 MHz, 298 K, CD$_3$CN) of $[2](\text{NTf}_2)_6$. 

Figure S3: HSQC NMR spectrum (400 MHz, 298 K, CD$_3$CN) of [2](NTf$_2$)$_6$
Figure S4: NOESY NMR spectrum (400 MHz, 298 K, CD$_3$CN) of [2](NTf$_2$)$_6$. 
Figure S5: LR-ESI-mass spectrum of product [2](NTf₂)₆. Calculated values are in brackets.
Figure S6: (a) HR-ESI-mass spectrum of the $[2](\text{NTf}_2)^{4+}$ ion. (b) Calculated isotopic distribution of $[2](\text{NTf}_2)^{4+}$. 
1:1 ratio of Zn(NTf$_2$)$_2$ 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(NTf$_2$)$_2$ (40.2 mg, 64.3 μmol, 1 equiv.) were suspended in reagent grade CH$_3$CN (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 Et$_2$O (30 mL) precipitated out a yellow solid that was isolated by centrifugation.

Figure S7: $^1$H NMR spectrum (400 MHz, 298 K, CD$_3$CN) of (a) the reaction mixture containing a 1:1:2 ratio of Zn(NTf$_2$)$_2$: 1 : 4-methoxyaniline (b) the reaction mixture containing a 1:2:2 ratio of Zn(NTf$_2$)$_2$: 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 $[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{ClO}_4)_2$ half-pipe 3

$[3,3'6',2''5'',3'''-\text{quaterpyridine}]-6,6''-\text{dicarbaldehyde}$ 1 (4.3 mg, 11.7 μmol, 5 equiv.), 4-methoxyaniline (4.8 mg, 37.39 μmol, 16 equiv.), and Zn(ClO$_4$)$_2$·6H$_2$O (8.0 mg, 21.0 μmol, 9 equiv.) were suspended in reagent grade CH$_3$CN (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 Et$_2$O (30 mL) precipitated out 3 as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et$_2$O 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.

$^1$H-NMR spectroscopy and LR-ESI MS were consistent with the formation of $[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{ClO}_4)_2$

$^1$H NMR (700 MHz, CD$_3$CN) δ 9.61 (m, 2H, L$_{II}$H$_7$), 9.03 (d, J = 1.5 Hz, 2H), 9.02 (s, 1H), 9.00 (m, 2H, L$_{III}$H$_7$L$_{IV}$H$_4$), 8.95 (d, J = 1.5 Hz, 1H, L$_{I}$H$_7$), 8.88 (dd, J = 2.2, 7.8 Hz, 1H, L$_{V}$H$_6$), 8.86 (dd, J = 2.2, 8.2 Hz, 1H, L$_{II}$H$_4$), 8.84 (m, 2H, L$_{II}$H$_4$), 8.82 (d, J = 6.2 Hz 1H, L$_{I}$H$_6$), 8.80 (d, J = 5.9 Hz, 1H), 8.78 - 8.76 (m, 2H, L$_{II}$H$_6$, L$_{IV}$H$_6$), 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$_{II}$H$_4$, L$_{III}$H$_6$), 8.55 (s, 1H, L$_{V}$H$_3$), 8.49 (dd, J = 5.6, 1.6 Hz, 1H), 8.45-7 (m, 2H), 8.43 (d, J = 5.3 Hz, 1H, L$_{V}$H$_3$), 8.41 (dd, J = 5.6, 1.6 Hz, 1H, L$_{III}$H$_6$), 8.40 - 8.37 (m, 4H, L$_{IV}$H$_5$, L$_{III}$H$_4$), 8.31 (d, J = 5.9 Hz, 1H) 8.26 (d, J = 5.3 Hz, 1H, L$_{III}$H$_5$), 8.15 (d, J = 5.6 Hz, 1H, L$_{III}$H$_5$), 8.06 (d, J = 5.6 Hz, 1H), 7.50 (d, J = 8.5 Hz, 2H, L$_{V}$H$_3$), 7.38 (d, J = 6.2 Hz, 2H, L$_{IV}$H$_3$), 7.17 (d, J = 5.9 Hz, 2H, L$_{I}$H$_3$), 7.12 (d, J = 8.5 Hz, 2H, L$_{IV}$H$_2$), 6.93 (d, J = 6.2 Hz, 2H, L$_{IV}$H$_2$), 6.90 (d, J = 8.6 Hz, 2H, L$_{I}$H$_2$), 6.56 (d, J = 8.5 Hz, 2H, L$_{II}$H$_2$), 6.34 (d, J = 5.9 Hz, 2H, L$_{I}$H$_2$), 6.32 (d, J = 5.9 Hz, 2H, L$_{II}$H$_2$), 5.99 (d, J = 5.9 Hz, 2H, L$_{III}$H$_2$), 4.03 (s, 3H, L$_{V}$H$_1$), 3.91 (s, 3H, L$_{IV}$H$_1$), 3.67 (s, 3H, L$_{III}$H$_1$), 3.60 (s, 3H, L$_{II}$H$_1$), 3.59 (s, 3H, L$_{I}$H$_1$).

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) $[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{ClO}_4)_2$,$^6^+$, 853.88 (854.00) $[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{ClO}_4)_2$,$^5^+$, 1092.18 (1092.36) $[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{ClO}_4)_2$,$^4^+$, 1489.98 (1489.68) $[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{ClO}_4)_2$,$^3^+$.
Figure S9: $^1$H NMR spectrum (700 MHz, 298 K, CD$_3$CN) of [3](ClO$_4$)$_2$ in the region 1 – 5.5 ppm.

Figure S10: $^1$H NMR (700 MHz, 298 K, CD$_3$CN) of [Zn$_9$L$_5$(μ-OH)$_6$](ClO$_4$)$_9$ in the region 5.8 - 9.8 ppm. Peaks for protons 2 and 3 for the five ligand environments L$^1$ - L$^5$ are labeled.
Figure S11: COSY NMR spectrum (700 MHz, 298 K, CD$_3$CN) of [3](ClO$_4$)$_{12}$ in the region 5 – 10 ppm.
Figure S12: NOESY NMR spectrum (700 MHz, 298 K, CD$_3$CN) of [3](ClO$_4$)$_{12}$ in the region 5 – 10 ppm.
Figure S13: LR-ESI-mass spectrum of product [3](ClO₄)₁₂. Calculated values are in brackets.
Figure S14: (a) HR-ESI-mass spectrum of the \([3](\text{ClO}_4)_n^{4+}\) ion. (b) Calculated isotopic distribution of \([3](\text{ClO}_4)_n^{4+}\).
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.), NBu$_4$ClO$_4$ (2.1 mg, 7.25 μmol 4 equiv.) and Zn(NTf$_2$)$_2$ (8.8 mg, 14.1 μmol, 9 equiv.) were suspended in reagent grade CH$_3$CN (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 Et$_2$O (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 Et$_2$O to an acetonitrile solution of the mixture. Although the $^1$H NMR spectrum was broadly consistent with that of 3 synthesised from Zn(ClO$_4$)$_2$, 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.

$^1$H NMR (500 MHz, CD$_3$CN) 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$^V$H$_3$), 7.38 (d, J = 8.9 Hz, 2H, L$^V$H$_3$), 7.13 (d, J = 8.5 Hz, 4H, L$^V$H$_2$, L$^I$H$_3$), 6.91 (d, J = 8.9 Hz, 2H, L$^V$H$_2$), 6.87 (d, J = 8.8 Hz, 2H, L$^V$H$_3$), 6.56 (d, J = 8.8 Hz, 2H, L$^V$H$_3$), 6.33 (d, J = 8.8 Hz, 4H, L$^V$H$_2$, L$^III$H$_2$), 6.08 (d, J = 8.7 Hz, 2H, L$^V$H$_3$), 4.05 (s, 3H, L$^V$H$_1$), 3.91 (s, 3H, L$^V$H$_1$), 3.68 (s, 3H, L$^III$H$_1$), 3.60 (s, 2H, L$^III$H$_1$, L$^I$H$_1$).

$^{19}$F NMR (376 MHz; CD$_3$CN, reference C$_6$F$_6$): δ -80.48 (NTf$_2^-$)

ESI-MS: m/z: 925.69 (925.82) $\{[\text{Zn}_3\text{L}_3(\mu-\text{OH})_6](\text{ClO}_4)_3(\text{NTf}_2)_2]\}^{5+}$, 1181.65 (1181.76) $\{[\text{Zn}_3\text{L}_3(\mu-\text{OH})_6](\text{ClO}_4)_3(\text{NTf}_2)_2]\}^{5+}$
Figure S15: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) of perchlorate templated 3 in the region 1 – 5.5 ppm, showing the resonances for $H_1$.

Figure S16: $^1$H NMR (500 MHz, 298 K, CD$_3$CN) of perchlorate templated 3 in the region 5.8 - 9.8 ppm.
Figure S17: Selective 1D TOCSY spectra (500 MHz, 298 K, CD$_3$CN; $T_{\text{mix}} = 80$ 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$_3$CN; $T_{\text{mix}} = 80$ 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](NTf₂)₃(ClO₄)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$_3$CN in a PTFE stoppered J-Young NMR tube. A $^1$H-NMR spectrum was acquired and a 0.73 mM solution of 4-methoxyaniline in CD$_3$CN (6.2 μL, 6 equiv.) and of H$_2$O (1 μL, 74 equiv.) were added. The reaction mixture was heated at 70 °C for 12 hours and the solution monitored by $^1$H-NMR spectroscopy.

![Figure S20: $^1$H NMR spectra (400 MHz, 298 K, CD$_3$CN) of (a) 2(NTf$_2$)$_6$ and (b) after 12 hours at 70 °C in the presence of 6 equiv. of 4-methoxyaniline and 1 μL of H$_2$O.](image)
1.6 Stability of 2 to tetrabutylammonium perchlorate

2 (4.3 mg, 0.75 μmol, 1 equiv.) was dissolved in 0.5 mL CD$_3$CN in a PTFE stoppered J-Young NMR tube. A 0.19 mM solution of tetrabutylammonium perchlorate in CD$_3$CN (16.6 μL, 4 equiv.) was added. The reaction mixture was heated at 70 °C for 12 hours and the stability of the complex monitored by $^1$H-NMR spectroscopy.

Figure S21: $^1$H NMR spectra (400 MHz, 298 K, CD$_3$CN) of (a) 2(NTf$_2$)$_6$ and (b) after 12 hours at 70 °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$_3$CN in a PTFE stoppered J-Young NMR tube. A 0.73 mM solution of 4-methoxyaniline in CD$_3$CN (9.6 μL, 6 equiv.) and H$_2$O (1 μL, 56 equiv.) were added and the solution heated at 70 °C for 15 min and a ¹H-NMR spectrum acquired. Subsequently a 0.19 mM solution of tetrabutylammonium perchlorate in CD$_3$CN (24.6 μL, 4 equiv.) was added and the reaction mixture was heated at 70 °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$_3$CN) of: (a) 2(NTf$_2$)$_6$, 6 equiv. of 4-methoxyaniline and 1 μL of H$_2$O, (b) 2 mins at 25 °C after the addition of 4 equiv. of tetrabutylammonium perchlorate, (c) 12 hours at 70 °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)₆(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$_3$CN in a PTFE stoppered J-Young NMR tube. A 0.19 mM solution of tetrabutylammonium perchlorate in CD$_3$CN (24.6 μl, 4 equiv.) was added. The solution was heated at 70 °C for 15 mins and a $^1$H-NMR spectrum acquired. A 0.73 mM solution of 4-methoxyaniline in CD$_3$CN (9.6 μL, 6 equiv.) and H$_2$O (1 μL, 56 equiv.) were added. The reaction mixture was heated at 70 °C for 12 hours and the conversion monitored by $^1$H-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: $^1$H NMR spectra (400 MHz, 298 K, CD$_3$CN) of: (a) [2](NTf$_2$)$_6$ and 4 equiv. of tetrabutylammonium perchlorate, (b) 2 mins at 25 °C after the addition of 6 equiv. of 4-methoxyaniline and 1 μL of H$_2$O, (c) 12 hours at 70 °C after the addition of 6 equiv. of 4-methoxyaniline and 1 μL of H$_2$O.
Figure S25: LR-ESI-mass spectrum of the product of the transformation of [2](NTf₂)₆ to [3](NTf₂)₄(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-Napthalenesulfonate-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-napthalenesulfonate sodium salt (2.1 mg, 9.2 μmol 4 equiv.) and Zn(NTf₂)₂ (12.6 mg, 20.1 μmol, 9 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 filtered through a PTFE syringe filter (4.5 μm pore size) and subsequent addition of Et₂O (30 mL) precipitated out a mixture of 2 and 2-napthalenesulfonate templated 3 as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et₂O into an acetonitrile solution of 2-napthalenesulfonate templated 3 yielded crystals suitable for analysis.

¹H NMR (500 MHz, CD₃CN) 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, L¹H₄), 8.78 (dd, J = 8.0 2.2 Hz, 1H), 8.71 (dd, J = 8.7, 1.9 Hz, 1H), 8.61 (s, 1H, L⁴H₄), 8.59 (dd, J = 8.2, 2.1 Hz, 1H), 8.51 (d, J = 7.3 Hz, 1H), 8.50 (s, 1H, L¹H₄), 8.36 (s, 1H, L⁴H₄), 8.35- 8.31 (m, 2H), 8.30 - 8.28 (m, 2H), 8.25- 8.18(m, 3H, L⁵H₄), 8.15 - 8.04 (m, 4H, L¹H₅), 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] H₃) 7.55 (d, J = 8.5 Hz, 1H, L⁵H₅), 7.29 (d, J = 8.6 Hz, 2H, L⁵H₂), 7.28 (d, J = 8.6 Hz, 2H, L⁴H₅), 7.17 (d, J = 8.2 Hz, 2H, L¹H₅), 6.93 (d, J = 9.0 Hz, 2 H, L¹H₄), 6.84 (d, J = 8.8 Hz, [2] H₂), 6.80 (d, J = 8.8 Hz, 2H, L⁴H₂), 6.63(d, J = 8.7 Hz, 2H, L¹H₂), 6.38 (d, J = 8.9 Hz, 2H, L¹H₂), 6.34 (d, J = 8.7 Hz, 2H, L¹H₂), 6.08 (d, J = 8.7 Hz, 2H, L⁴H₃), 6.10 (s, 3H, L⁵H₁), 3.88 (s, [2] H₁), 3.86 (s, 3H, L⁴H₁), 3.65 (s, 3H, L¹H₃), 3.64 (s, 3H, L¹H₃), 3.54 (s, 3H, L¹H₁).

¹⁹F NMR (376 MHz; CD₃CN, reference C₆F₆): δ -80.55 (NTf₂⁻)

LR-ESI-MS: m/z: 851.54 (851.37) {[Zn₉L₃(μ-OH)₆](NTf₂)₆(NapthSO₃)₂}⁶⁺, 1077.63 (1077.22) {[Zn₉L₃(μ-OH)₆](NTf₂)₅(NapthSO₃)₂}⁵⁺, 1417.26 (1417.51) {[Zn₉L₃(μ-OH)₆](NTf₂)₄(NapthSO₃)₂}⁴⁺
Figure S26: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of 2-napthalenesulfonate templated 3 in the region 1 – 5.5 ppm.

Figure S27: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of 2-napthalenesulfonate templated 3 in the region 5.5 – 10 ppm.
Figure S28: COSY NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O 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, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O 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-napthalenesulfonate. However, the $^1$H–$^1$H 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-napthalenesulfonate.

Figure S30: Partial 2D $^1$H–$^1$H NOESY spectrum (500 MHz, 298 K, CD$_3$CN; $T_{\text{mix}} = 600$ ms) of 2-napthalenesulfonate 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-napthalenesulfonate 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-napthalenesulfonate templated 3. Calculated values are in brackets.
Figure S32: (a) HR-ESI-mass spectrum of the $[3](\text{NapthSO}_3)_2(\text{NTf}_2)_3^{5+}$ ion. (b) Calculated isotopic distribution of $[3](\text{NapthSO}_3)_2(\text{NTf}_2)_3^{5+}$.
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.), NBu₄ReO₄ (3.62 mg, 7.25 μmol, 4 equiv.) and Zn(NTf₂)₂ (40.2 mg, 64.3 μmol, 1 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 2 and Perrhenate templated 3 as a yellow solid that was isolated by centrifugation. Slow diffusion (> 1 week) of Et₂O into an acetonitrile solution of perrhenate templated 3 yielded crystals suitable for analysis.

1H NMR (500 MHz, CD₃CN) 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, L⁴H₄), 8.98 (s, [2] H₂), 8.94 - 8.87 (m), 8.83 (s, 1H, L¹H₄), 8.81 - 8.68 (m, 10H), 8.66 - 8.63 (m, 4H), 8.62 (s, 1H, L⁵H₄), 8.59 (s, 2H, L⁴H₄), 8.58 - 8.54 (m, 1H), 8.51 (m, 1H), 8.45 - 8.43 (m, 1H), 8.42 (s, 1H, L⁶H₄), 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, L⁵H₄), 16 (d, J = 8.7 Hz, [2] H₃), 7.12 (d, J = 9.2 Hz, 2H, L⁴H₂), 7.28 (d, J = 8.6 Hz, 2H, L⁴H₃), 7.13 (d, J = 9.0 Hz, 2H, L⁵H₃), 6.93 (d, J = 9.0 Hz, 2H, L⁴H₂), 6.85 (d, J = 8.7 Hz, 2H, L⁴H₃), 6.84 (d, J = 8.7 Hz, [2] H₂), 6.55 (d, J = 8.7 Hz, 2H, L⁵H₃), 6.34 (d, J = 8.7 Hz, 2H, L⁴H₂), 6.33 (d, J = 8.6 Hz, 2H, L⁵H₄), 6.02 (d, J = 8.8 Hz, 2H, L⁴H₃), 4.06 (s, 3H, L⁵H₄), 3.91 (s, 3H, L⁴H₄), 3.81 (s, [2] H₁), 3.68 (s, 3H, L⁵H₄), 3.65 (s, 3H, L⁴H₃), 3.62 (s, 3H, L⁵H₃).

19F NMR (376 MHz; CD₃CN, reference C₆F₆): δ -80.10 (NTf₂⁻)

ESI-MS: m/z: 844.79 (845.18) {[Zn₉L₃(μ-OH)₆](ReO₄)₆}⁺, 1089.07 (1088.60) {[Zn₉L₃(μ-OH)₆](ReO₄)₄(NTf₂)₄}⁺, 1438.55 (1437.97) {[Zn₉L₃(μ-OH)₆](ReO₄)₄(NTf₂)₆}⁺
Figure S33: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of perrhenate templated 3 in the region 1 – 5.5 ppm.

Figure S34: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) $^1$H NMR spectrum of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of perrhenate templated 3 in the region 5.5 – 11 ppm.
Figure S35: COSY NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of perrhenate templated 3 in the region 5.5 – 10 ppm.
Figure S36: NOESY NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O 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.

\[
\left[ \text{Zn}_9L_5(\mu-\text{OH})_6\right](\text{ReO}_4)_3(\text{NTf}_2)_4 \quad 1089.07 \ (1088.60)
\]

\[
\left[ \text{Zn}_9L_5(\mu-\text{OH})_6\right](\text{ReO}_4)_3 \quad 844.79 \ (845.18)
\]

\[
\left[ \text{Zn}_9L_5(\mu-\text{OH})_6\right](\text{ReO}_4)_2 \quad 1438.55 \ (1437.97)
\]
Figure S38: (a) HR-ESI-mass spectrum of the $[3]$(ReO$_4$)$_3$(NTf$_2$)$_4^{5+}$ ion. (b) Calculated isotopic distribution of $[3]$(ReO$_4$)$_3$(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 Zn(NTf₂)₂ (26.0 mg, 41.4 μmol, 9 equiv.) were suspended in reagent grade CH₃CN (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 Et₂O (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 Et₂O into an acetonitrile solution of triflate templated 3 yielded crystals suitable for analysis.

¹H NMR (500 MHz, CD₃CN) δ 9.72 (s), 9.68 (s), 9.33 (s), 9.23 (s), 9.05 (s, 2H, L⁴H₄), 9.03-9.01 (m), 8.98 (s, 1H, [2] H₄), 8.93-8.85 (m), 8.81-8.71 (m, L⁵H₄), 8.66-8.50 (m, L¹H₄), 8.43-8.36 (m, L¹⁴H₄, L⁵H₄), 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, L⁵H₃), 7.30 (d, J = 8.6 Hz, 2H, L⁴H₃), 7.20 (d, J = 9.2 Hz, 2H, L⁴H₂), 7.16 (d, J = 8.7 Hz, [2] H₃), 7.10 (d, J = 9.0 Hz, 2 H, L¹H₂), 6.86 (d, J = 9.0 Hz, 2H, L⁴H₂), 6.85 (d, J = 8.7 Hz, 2H, L⁴H₂), 6.84 (d, J = 8.7 Hz, [2] H₂), 6.31 (d, J = 8.7 Hz, 2H, L²H₂), 6.56 (d, J = 8.7 Hz, 2H, L²H₂), 6.33 (d, J = 8.6 Hz, 2H, L¹⁴H₂), 6.02 (d, J = 8.8 Hz, 2H, L¹⁴H₂), 4.08 (s, 3H, L⁵H₁), 3.91 (s, 3H, L¹⁴H₁), 3.81 (s, [2] H₁), 3.67 (s, 3H, L¹⁴H₁), 3.60 (s, 3H, L¹¹H₁), 3.58 (s, 3H, L¹¹H₁).

¹⁹F NMR (376 MHz; CD₃CN, reference C₆F₆): δ -80.50 (NTf₂⁻) -79.69 br (OTf⁻)

ESI-MS: m/z: 809.85 (809.85) {[Zn₉L₃(μ-OH)₆](OTf)₃(NTf₂)₃]⁺⁺⁺, 1028.28 (1027.41) {[Zn₉L₃(μ-OH)₆](OTf)₃(NTf₂)₄]⁵⁺, 1354.89 (1354.74) {[Zn₉L₃(μ-OH)₆](OTf)₃(NTf₂)₅]⁴⁺.}
Figure S39: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of triflate templated 3 in the region 1 – 5.5 ppm.

Figure S40: $^1$H NMR spectrum (500 MHz, 298 K, CD$_3$CN) $^1$H NMR spectrum of redissolved crystals generated by the slow diffusion of Et$_2$O into an acetonitrile solution of triflate templated 3 in the region 5.5 – 11 ppm.
Figure S41: COSY NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by
the slow diffusion of Et$_2$O into an acetonitrile solution of triflate templated 3 in the region 5.5–10 ppm.
Figure S42: NOESY NMR spectrum (500 MHz, 298 K, CD$_3$CN) of redissolved crystals generated by the slow diffusion of Et$_2$O 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.

\[ \{[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{OTf})_3(\text{NTf}_2)_3\}^{6+} \]

809.85 (809.85)

\[ \{[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{OTf})_3(\text{NTf}_2)_2\}^{5+} \]

975.66 (975.42)

\[ \{[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{OTf})_2(\text{NTf}_2)_2\}^{4+} \]

1028.28 (1027.41)

\[ \{[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{OTf})_2(\text{NTf}_2)_1\}^{3+} \]

1354.89 (1354.74)

\[ \{[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{OTf})_1(\text{NTf}_2)_2\}^{2+} \]

1290.38 (1298.75)

\[ \{[\text{Zn}_9\text{L}_5(\mu-\text{OH})_6](\text{OTf})_1(\text{NTf}_2)_1\}^{1+} \]

975.66 (975.42)
Figure S44: (a) HR-ESI-mass spectrum of the [3](OTf)₄(NTf₂)₃⁺ ion. (b) Calculated isotopic distribution of [3](OTf)₄(NTf₂)₃⁺ ion.
1.12 Anion displacement reactions

The slow diffusion (> 1 week) of Et$_2$O into an acetonitrile solution of 3 synthesised from Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$ClO$_4$, NBu$_4$OTf or, NBu$_4$ReO$_4$ yielded high purity 3 suitable for template displacement studies. Analysis was limited to $^1$H 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-napthalenesulfonate

Crystals of 3 (2.0 mg, 0.3 µmol, 1 equiv.) synthesised from Zn(NTf₂)₂ and 4 equiv. of NBu₄ClO₄ were dissolved in CD₃CN and a ¹H-NMR spectrum was acquired. Aliquots of a 0.15 mM solution of sodium 2-napthalenesulfonate (2.1 µL, 0.3 µmol, 1 equiv.) in 1:2 D₂O/CD₃CN were added and the reaction followed by ¹H-NMR spectroscopy.

Figure S45: (a) ¹H-NMR of crystals of 3 synthesised from Zn(NTf₂)₂ and 4 equiv. of NBu₄ClO₄. (b) after the addition of 1 equiv. of sodium 2-napthalenesulfonate (c) after the addition of 2 equiv. of sodium 2-napthalenesulfonate. The appearance of resonances corresponding to 2-napthalene sulfonate templated 3 can be observed in (c).
Addition of trifluoromethanesulfonate to perchlorate templated 3

Crystals of 3 synthesised from Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$ClO$_4$ (0.8 mg, 0.13 μmol, 1 equiv.) were dissolved in CD$_3$CN and a $^1$H-NMR spectrum was acquired. Aliquots of a 0.045 M solution of tetrabutylammonium trifluoromethanesulfonate (2.8 μL, 0.13 μmol, 1equiv.) in CD$_3$CN were added and the reaction followed by $^1$H-NMR spectroscopy.

Figure S46: (a) $^1$H-NMR of crystals of 3 synthesised from Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$ClO$_4$. (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 Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$ClO$_4$ (0.8 mg, 0.13 μmol, 1 equiv.) were dissolved in CD$_3$CN and a $^1$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$_3$CN were added and the reaction followed by $^1$H-NMR spectroscopy.

Figure S47: (a) $^1$H-NMR of crystals of 3 synthesised from Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$ClO$_4$. (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 Zn(NTf₂)₂ and 4 equiv. of NBu₄OTf (1.94 mg, 0.3 µmol, 1 equiv.) were dissolved in CD₃CN 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.) CD₃CN were added and the reaction followed by ¹H NMR spectroscopy.

Figure S48: (a) ¹H NMR of crystals of 3 synthesised from Zn(NTf₂)₂ and 4 equiv. of NBu₄OTf. (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, 1 equiv.) in 1:2 D$_2$O/CD$_3$CN were added to the solution from the perchlorate displacement of trifluoromethanesulfonate and the reaction followed by $^1$H NMR spectroscopy.

Figure S49: (a) $^1$H NMR of crystals of 3 synthesised from Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$OTf (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-napthalene sulfonate templated 3 can be observed in (c).
Addition of perrhenate to trifluoromethanesulfonate templated 3

Crystals of 3 synthesised from Zn(NTf₂)₂ and 4 equiv. of NBu₄OTf (3.78 mg, 0.5 μmol, 1 equiv.) were dissolved in CD₃CN 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.) CD₃CN were added and the reaction followed by ¹H NMR spectroscopy.

Figure S50: (a) ¹H NMR of crystals of 3 synthesised from Zn(NTf₂)₂ and 4 equiv. of NBu₄ReO₄. (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-napthalenesulfonate to a mixture of perrhenate and trifluoromethanesulfonate templated 3

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

Figure S51: (a) $^1$H NMR of crystals of 3 synthesised from Zn(NTf$_2$)$_2$ and 4 equiv. of NBu$_4$ReO$_4$. (b) after addition of 4 equiv. of tetrabutylammonium perchlorate (c) after the further addition of 2 equiv. of sodium 2-napthalenesulfonate. Although the resonances corresponding to 2-napthalene 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$_\alpha$ radiation generated from a sealed tube (0.71073 Å) with $\omega$ and $\psi$ scans at 180(2) K; a Bruker D8 VENTURE equipped with high-brilliance IμS Cu Kα radiation ($\lambda = 1.54178$ Å), with $\omega$ and $\psi$ scans at 100(2) K or at Beamline I19 of Diamond Light Source employing silicon double crystal monochromated synchrotron radiation (0.6889 Å) with $\omega$ 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, Dₐ 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(MoKα) 0.71073 Å, μ(MoKα) 1.112 mm⁻¹, T(SORTAV)min,max 0.849, 0.991, 2θmax 40.78, hkl range -19 19, -21 21, -28 28, N 120107, Nind 23478(Rmerge 0.1287), Nobs 14941(I > 2σ(I)), Nvar 2984, residuals * R1(F) 0.0749, wR2(F²) 0.2256, GoF(all) 1.029, Δρmin,max -0.923, 1.023 e⁻ Å⁻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.

R1 = Σ||F₀| - |F̄|/Σ|F₀| for F₀ > 2σ(F₀); wR2 = (Σw(F₀² - F̄²)²/Σ(wF₀²)²)¹/² all reflections, w=1/[σ²(F₀²)+(0.1175P)²+51.2610P] where P=(F₀²+2F̄²)/3

* R1(F) = Σ||F₀| - |F̄||/Σ|F₀| for F₀ > 2σ(F₀); wR2 = (Σw(F₀² - F̄²)²/Σ(wF₀²)²)¹/² all reflections, w=1/[σ²(F₀²)+(0.1175P)²+51.2610P] where P=(F₀²+2F̄²)/3
[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, Dc 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, 2θmax 94.88, hkl range -29 36, -21 20, -32 32, N₁₃₁₄₃₃, Nind 23676(Rmerge 0.0537), Nobs 16225(I > 2σ(I)), Nvar 2260, residuals * R1(F) 0.0786, wR2(F²) 0.2483, GoF(all) 1.072, Δρmin,max -0.589, 1.215 e⁻ Å⁻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.

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 6 1 2 2 (#178), a 36.800(17), b 36.800(17), c 35.22(2) Å, γ 120º, V 41306(45) Å³, Dc 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, 2θmax 31.99, hkl range -29 29, -29 29, -28 28, N₁ 122626, Nind 7400(Rmerge 0.1391), Nobs 5698(I > 2σ(I)), Nvar 1267, residuals * R1(F) 0.0937, wR2(F²) 0.2655, GoF(all) 1.071, Δρmin,max -0.318, 0.522 e⁻ Å⁻³.

* R1 = Σ||Fₒ|| - |Fc||Σ|Fₒ|| for Fₒ > 2σ(Fₒ); wR2 = (Σw(Fₒ² - Fc²)²/Σ(wFc²)²)¹/² all reflections, w=1/[σ²(Fₒ²)+(0.2000P)²-0.0400P] where P=(Fₒ²+2Fc²)/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.
\[\text{[Zn}_9\text{L}_5(\mu-\text{OH})_9]\cdot2\text{C}_{10}\text{H}_7\text{SO}_3\cdot10\text{NTf}_2\cdot\text{MeCN}\]

Formula \(\text{C}_{222}\text{H}_{163}\text{F}_60\text{N}_{41}\text{O}_{62}\text{S}_{22}\text{Zn}_9\), \(M = 6830.57\), Monoclinic, space group \(P 21/n\) (#14), \(a = 15.8416(11)\), \(b = 55.356(4)\), \(c = 33.8750(19)\) Å, \(V = 29706(3)\) Å\(^3\), \(D_c = 1.527\) g cm\(^{-3}\), \(Z = 4\), crystal size 0.020 by 0.010 by 0.003 mm, colour yellow, habit block, temperature 100(2) Kelvin, \(\lambda\) (synchrotron) 0.6889 Å, \(\mu\) (synchrotron) 0.815 mm\(^{-1}\), \(T\) (SADABS) \(\min\), \(\max\) 0.5451, 0.7442, 2\(\theta\) \(\max\) 33.36, \(hkl\) range -13 12, -46 45, -28 28, \(N = 141378\), \(N_{\text{ind}} = 17766\) (\(R_{\text{merge}} = 0.1220\)), \(N_{\text{obs}} = 14944\) (\(I > 2\sigma(I)\)), \(N_{\text{var}} = 2665\), residuals * \(R1(F) = 0.1869\), \(wR2(F^2) = 0.4548\), GoF(all) 1.374, \(\Delta\rho_{\text{min,max}} = -0.819, 0.895\) e\(^{-}\) Å\(^{-3}\).

* \(R1 = \Sigma||F_o|| - |F_c||/\Sigma|F_o|\) for \(F_o > 2\sigma(F_o)\); \(wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma (wF_c^2)^2))^{1/2}\) all reflections, \(w=1/[(\sigma^2(F_o^2)+(0.2000P)^2+350.0000P)]\) 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 1.2 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 \(\text{Zn}_9\text{L}_5\) 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-napthalenesulfonate with the 2-napthalenesulfonate anions shown in space-filling mode.
1.14 References

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