A folded [2×2] metallosupramolecular grid from a
bis-tridentate (1,2,3-triazol-4-yl)-picolinamide (tzpa)
ligand

Dawn E. Barry, a* Chris S. Hawes, a* Joseph P. Byrne a, Bjørn la Cour Poulsen a, Manuel Ruether b, John E. O’Brien b and Thorfinnur Gunnlaugsson a*

aSchool of Chemistry and Trinity Biomedical Science Institute, The University of Dublin,
Trinity College Dublin, Dublin 2, Ireland.

bSchool of Chemistry, The University of Dublin, Trinity College Dublin, Dublin 2, Ireland

Supporting Information

Additional UV-Visible and Fluorescence Spectra and fitting 2
NMR Titration and VT-NMR Figures 3
T_1 parameters and DOSY NMR Spectra 4
Mass Spectrometry 5
Computational Data 6
^{1}H, ^{13}C, ^{19}F and 2-dimensional NMR spectra 11
References 17
Additional UV-Visible and Fluorescence Spectra and fitting

**Figure S1.** (a) Speciation distribution diagram obtained from UV-visible absorption titration data fit and (b) fit of experimental binding isotherms using the nonlinear regression analysis program ReactLab Equilibria.

**Figure S2.** (a) The overall changes in the fluorescence emission spectra upon titrating 1 (1 x 10^{-5} M) against Zn(ClO₄)₂·6H₂O (0→5equiv.) in CH₃CN at RT and (b) corresponding experimental binding isotherm at λ = 350 nm.
NMR Titration and VT-NMR Figures

Figure S3. $^1$H NMR titration of $\text{1} \ (1 \times 10^{-3} \text{ M})$ with $\text{Zn}^{II}$ from 0 – 5 equiv. in CD$_3$CN.

Figure S4. $^1$H NMR spectrum of $[\text{Zn}_4(\text{I})_4]^{8+}$ (assembled in situ in CD$_3$CN) at 25 °C, 20 °C, 0 °C, -10 °C and -20 °C.
T₁ Data Table and DOSY Spectra

Table S1. $^1$H NMR assignment for 1 and re-dissolved [Zn₄(1)₄]$^{8+}$ in CD₃CN and associated $T₁$ relaxation times. Uncertainties presented at 95% confidence level.

<table>
<thead>
<tr>
<th>Proton label</th>
<th>Ligand 1 ppm</th>
<th>$T₁$ (s)</th>
<th>[Zn₄(1)₄] complex ppm</th>
<th>$T₁$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.83</td>
<td>0.56(1)</td>
<td>3.86</td>
<td>1.4(2)</td>
</tr>
<tr>
<td>b</td>
<td>7.97</td>
<td>2.55(4)</td>
<td>7.94</td>
<td>2.83(9)</td>
</tr>
<tr>
<td>c</td>
<td>7.41</td>
<td>2.24(3)</td>
<td>7.30</td>
<td>2.26(7)</td>
</tr>
<tr>
<td>d</td>
<td>5.65</td>
<td>1.1(2)</td>
<td>5.61</td>
<td>0.64(3)</td>
</tr>
<tr>
<td>e</td>
<td>8.40</td>
<td>1.79(4)</td>
<td>8.72</td>
<td>2.07(13)</td>
</tr>
<tr>
<td>f</td>
<td>8.13</td>
<td>2.24(4)</td>
<td>8.29</td>
<td>1.60(7)</td>
</tr>
<tr>
<td>g</td>
<td>7.86</td>
<td>2.01(3)</td>
<td>8.54</td>
<td>1.33(5)</td>
</tr>
<tr>
<td>h</td>
<td>7.86</td>
<td>2.01(3)</td>
<td>8.24</td>
<td>0.96(4)</td>
</tr>
<tr>
<td>i</td>
<td>8.74</td>
<td>0.59(3)</td>
<td>9.22</td>
<td>0.49(2)</td>
</tr>
<tr>
<td>j</td>
<td>4.56</td>
<td>0.57(1)</td>
<td>4.59</td>
<td>0.37(4)</td>
</tr>
<tr>
<td>k</td>
<td>7.27</td>
<td>1.30(5)</td>
<td>7.60</td>
<td>1.83(10)</td>
</tr>
<tr>
<td>l</td>
<td>7.27</td>
<td>1.30(5)</td>
<td>7.30</td>
<td>2.26(8)</td>
</tr>
<tr>
<td>m</td>
<td>7.20</td>
<td>1.68(2)</td>
<td>7.21</td>
<td>1.68(4)</td>
</tr>
</tbody>
</table>

Figure S5 Comparison of DOSY NMR spectra for ligand 1 (left) and [Zn₄(1)₄]$^{8+}$ (right)
Mass Spectrometry

**Figure S6** Electrospray mass spectrum (positive ionisation mode) for $[\text{Zn}_4(1)_4]^{8+}$

**Figure S7** Enlarged regions corresponding to the identified complex fragments listed in Figure S9, comparing measured data (black) to simulated isotopic distribution (red, or red/blue in the case of two overlapping fragments for $[\text{M+L+ClO}_4]^+/[2\text{M+2L+2ClO}_4]^{2+}$).\textsuperscript{S1}
Computational Data and Figures

Geometry optimized structures of \([\text{Zn}_4(\text{I})_4]^{8+}\) were calculated from the crystal structure with the semiempirical method PM3 using Gaussian Software.\(^{S2}\) The optimization in acetonitrile was carried out with polarizable continuum model (PCM).

Figure S8 Comparison of the X-ray crystal structure (left), energy-minimized structure in MeCN (middle) and energy-minimized structure in vacuum (right). All structures are presented without pendant benzyl groups for clarity and/or to simply geometry optimization calculation.

Table S2: Coordinates for \([\text{Zn}_4(\text{I})_4]^{8+}\) in vacuum; PM3

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-1.266</td>
<td>-13.559</td>
<td>-3.299</td>
<td>H</td>
<td>8.175</td>
<td>3.769</td>
<td>1.832</td>
<td>N</td>
<td>-13.602</td>
<td>1.987</td>
<td>1.161</td>
</tr>
<tr>
<td>C</td>
<td>11.668</td>
<td>0.494</td>
<td>2.866</td>
<td>H</td>
<td>-3.732</td>
<td>-8.192</td>
<td>1.832</td>
<td>N</td>
<td>1.065</td>
<td>12.694</td>
<td>-1.229</td>
</tr>
<tr>
<td>C</td>
<td>-11.668</td>
<td>-0.494</td>
<td>2.866</td>
<td>H</td>
<td>13.823</td>
<td>-1.182</td>
<td>4.361</td>
<td>N</td>
<td>-1.065</td>
<td>-12.694</td>
<td>-1.229</td>
</tr>
<tr>
<td>C</td>
<td>-0.494</td>
<td>11.668</td>
<td>-2.866</td>
<td>H</td>
<td>-13.823</td>
<td>1.182</td>
<td>4.361</td>
<td>N</td>
<td>-0.940</td>
<td>10.899</td>
<td>-1.816</td>
</tr>
<tr>
<td>C</td>
<td>0.494</td>
<td>-11.668</td>
<td>-2.866</td>
<td>H</td>
<td>1.182</td>
<td>13.823</td>
<td>-4.361</td>
<td>N</td>
<td>0.940</td>
<td>-10.899</td>
<td>-1.816</td>
</tr>
<tr>
<td>C</td>
<td>-11.535</td>
<td>-1.051</td>
<td>4.145</td>
<td>H</td>
<td>12.158</td>
<td>0.686</td>
<td>4.975</td>
<td>N</td>
<td>-10.899</td>
<td>-0.940</td>
<td>1.816</td>
</tr>
<tr>
<td>C</td>
<td>-1.051</td>
<td>11.535</td>
<td>-4.145</td>
<td>H</td>
<td>-12.158</td>
<td>-0.686</td>
<td>4.975</td>
<td>N</td>
<td>-3.272</td>
<td>8.170</td>
<td>-0.963</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-2.076</td>
<td>10.612</td>
<td>-4.342</td>
<td>H</td>
<td>0.686</td>
<td>-12.158</td>
<td>-4.975</td>
<td>N</td>
<td>8.170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>10.612</td>
<td>2.076</td>
<td>4.342</td>
<td>H</td>
<td>2.531</td>
<td>-10.499</td>
<td>-5.336</td>
<td>N</td>
<td>-8.185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-10.612</td>
<td>-2.076</td>
<td>4.342</td>
<td>H</td>
<td>10.499</td>
<td>2.531</td>
<td>5.336</td>
<td>N</td>
<td>8.185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-1.943</td>
<td>9.995</td>
<td>-2.009</td>
<td>H</td>
<td>-9.112</td>
<td>-3.342</td>
<td>3.414</td>
<td>N</td>
<td>0.891</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.943</td>
<td>-9.995</td>
<td>-2.009</td>
<td>H</td>
<td>-2.500</td>
<td>5.520</td>
<td>-1.083</td>
<td>N</td>
<td>-0.891</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>9.995</td>
<td>1.943</td>
<td>2.009</td>
<td>H</td>
<td>2.500</td>
<td>-5.520</td>
<td>-1.083</td>
<td>N</td>
<td>-12.690</td>
<td>-1.122</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-9.995</td>
<td>-1.943</td>
<td>2.009</td>
<td>H</td>
<td>5.520</td>
<td>2.500</td>
<td>1.083</td>
<td>N</td>
<td>12.690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-2.361</td>
<td>9.216</td>
<td>-0.789</td>
<td>H</td>
<td>-5.520</td>
<td>-2.500</td>
<td>1.083</td>
<td>N</td>
<td>-1.122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.361</td>
<td>-9.216</td>
<td>-0.789</td>
<td>H</td>
<td>-3.245</td>
<td>3.231</td>
<td>-1.658</td>
<td>N</td>
<td>1.122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>9.216</td>
<td>2.361</td>
<td>0.789</td>
<td>H</td>
<td>3.245</td>
<td>-3.231</td>
<td>-1.658</td>
<td>N</td>
<td>-13.593</td>
<td>-2.049</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-9.216</td>
<td>-2.361</td>
<td>0.789</td>
<td>H</td>
<td>3.231</td>
<td>3.245</td>
<td>1.657</td>
<td>N</td>
<td>13.593</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-3.946</td>
<td>7.472</td>
<td>0.163</td>
<td>H</td>
<td>-3.231</td>
<td>-3.245</td>
<td>1.658</td>
<td>N</td>
<td>-2.049</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.946</td>
<td>-7.472</td>
<td>0.163</td>
<td>H</td>
<td>5.531</td>
<td>2.475</td>
<td>-1.083</td>
<td>N</td>
<td>2.049</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>7.472</td>
<td>3.946</td>
<td>-0.163</td>
<td>H</td>
<td>5.531</td>
<td>-2.475</td>
<td>-1.083</td>
<td>N</td>
<td>-14.141</td>
<td>-2.205</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-7.472</td>
<td>-3.946</td>
<td>-0.163</td>
<td>H</td>
<td>2.475</td>
<td>5.531</td>
<td>1.083</td>
<td>N</td>
<td>14.141</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-4.412</td>
<td>6.104</td>
<td>-0.248</td>
<td>H</td>
<td>-2.475</td>
<td>-5.531</td>
<td>1.083</td>
<td>N</td>
<td>-2.205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>4.412</td>
<td>-6.104</td>
<td>-0.248</td>
<td>H</td>
<td>-6.414</td>
<td>6.385</td>
<td>0.527</td>
<td>N</td>
<td>2.205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>6.104</td>
<td>4.412</td>
<td>0.248</td>
<td>H</td>
<td>6.414</td>
<td>-6.385</td>
<td>0.527</td>
<td>O</td>
<td>-1.858</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-6.104</td>
<td>-4.412</td>
<td>0.248</td>
<td>H</td>
<td>6.385</td>
<td>6.414</td>
<td>-0.527</td>
<td>O</td>
<td>1.858</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-3.528</td>
<td>5.213</td>
<td>-0.859</td>
<td>H</td>
<td>-6.385</td>
<td>-6.414</td>
<td>-0.527</td>
<td>O</td>
<td>9.454</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.528</td>
<td>-5.213</td>
<td>-0.859</td>
<td>H</td>
<td>-9.126</td>
<td>3.300</td>
<td>-3.413</td>
<td>O</td>
<td>-9.454</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.213</td>
<td>3.528</td>
<td>0.858</td>
<td>H</td>
<td>9.126</td>
<td>-3.300</td>
<td>-3.413</td>
<td>O</td>
<td>-9.463</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-5.213</td>
<td>-3.528</td>
<td>0.858</td>
<td>H</td>
<td>3.300</td>
<td>9.126</td>
<td>3.413</td>
<td>O</td>
<td>9.463</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.941</td>
<td>-3.924</td>
<td>-1.172</td>
<td>H</td>
<td>-10.510</td>
<td>2.484</td>
<td>-5.336</td>
<td>O</td>
<td>-1.815</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.924</td>
<td>3.941</td>
<td>1.172</td>
<td>H</td>
<td>10.510</td>
<td>-2.484</td>
<td>-5.336</td>
<td>Zn</td>
<td>11.376</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-3.924</td>
<td>-3.941</td>
<td>1.172</td>
<td>H</td>
<td>-2.484</td>
<td>-10.510</td>
<td>5.336</td>
<td>Zn</td>
<td>-11.376</td>
<td>-0.026</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-5.229</td>
<td>3.504</td>
<td>-0.858</td>
<td>H</td>
<td>2.484</td>
<td>10.510</td>
<td>5.336</td>
<td>Zn</td>
<td>-0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.229</td>
<td>-3.504</td>
<td>-0.858</td>
<td>H</td>
<td>-12.161</td>
<td>0.631</td>
<td>-4.975</td>
<td>Zn</td>
<td>0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3.504</td>
<td>5.229</td>
<td>0.858</td>
<td>H</td>
<td>12.161</td>
<td>-0.631</td>
<td>-4.975</td>
<td>H</td>
<td>8.108</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-3.504</td>
<td>-5.229</td>
<td>0.858</td>
<td>H</td>
<td>0.631</td>
<td>12.161</td>
<td>4.975</td>
<td>H</td>
<td>8.108</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-6.124</td>
<td>4.384</td>
<td>-0.248</td>
<td>H</td>
<td>-0.631</td>
<td>-12.161</td>
<td>4.975</td>
<td>H</td>
<td>4.758</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>6.124</td>
<td>-4.384</td>
<td>-0.248</td>
<td>H</td>
<td>-13.818</td>
<td>-1.244</td>
<td>-4.360</td>
<td>H</td>
<td>-4.758</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-4.385</td>
<td>-6.124</td>
<td>0.248</td>
<td>H</td>
<td>-1.244</td>
<td>13.818</td>
<td>4.360</td>
<td>H</td>
<td>14.952</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-5.715</td>
<td>5.689</td>
<td>0.045</td>
<td>H</td>
<td>1.244</td>
<td>-13.818</td>
<td>4.360</td>
<td>H</td>
<td>-4.178</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.715</td>
<td>-5.689</td>
<td>0.045</td>
<td>H</td>
<td>16.163</td>
<td>-2.808</td>
<td>2.155</td>
<td>H</td>
<td>4.179</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.689</td>
<td>5.715</td>
<td>-0.045</td>
<td>H</td>
<td>-16.163</td>
<td>2.808</td>
<td>2.156</td>
<td>H</td>
<td>-16.154</td>
<td>-2.872</td>
<td>-2.165</td>
</tr>
<tr>
<td>Atom</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>Atom</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>Atom</td>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
<td>--------</td>
<td>-------</td>
<td>------</td>
<td>-------</td>
<td>--------</td>
<td>-------</td>
<td>------</td>
<td>-------</td>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>C</td>
<td>3.030</td>
<td>-0.685</td>
<td>10.695</td>
<td>C</td>
<td>4.002</td>
<td>-8.787</td>
<td>7.441</td>
<td>H</td>
<td>13.759</td>
<td>0.581</td>
<td>-2.626</td>
</tr>
<tr>
<td>C</td>
<td>3.835</td>
<td>-0.779</td>
<td>8.270</td>
<td>H</td>
<td>-5.393</td>
<td>-3.252</td>
<td>1.456</td>
<td>N</td>
<td>8.098</td>
<td>-0.295</td>
<td>-8.452</td>
</tr>
<tr>
<td>C</td>
<td>-6.675</td>
<td>-6.457</td>
<td>-5.211</td>
<td>H</td>
<td>4.661</td>
<td>2.484</td>
<td>-1.303</td>
<td>N</td>
<td>-1.839</td>
<td>8.805</td>
<td>4.453</td>
</tr>
<tr>
<td>C</td>
<td>7.238</td>
<td>0.750</td>
<td>-8.135</td>
<td>H</td>
<td>-3.933</td>
<td>3.784</td>
<td>-1.316</td>
<td>N</td>
<td>2.235</td>
<td>-2.237</td>
<td>8.920</td>
</tr>
<tr>
<td>C</td>
<td>3.474</td>
<td>-1.598</td>
<td>7.197</td>
<td>H</td>
<td>-3.035</td>
<td>-2.205</td>
<td>5.331</td>
<td>N</td>
<td>8.484</td>
<td>-0.955</td>
<td>-7.328</td>
</tr>
<tr>
<td>C</td>
<td>-6.809</td>
<td>-5.520</td>
<td>-4.183</td>
<td>H</td>
<td>2.969</td>
<td>5.063</td>
<td>2.243</td>
<td>N</td>
<td>-2.168</td>
<td>8.017</td>
<td>3.479</td>
</tr>
<tr>
<td>C</td>
<td>7.119</td>
<td>0.691</td>
<td>-6.745</td>
<td>H</td>
<td>-5.565</td>
<td>1.175</td>
<td>-5.049</td>
<td>N</td>
<td>2.479</td>
<td>-2.475</td>
<td>7.670</td>
</tr>
<tr>
<td>C</td>
<td>3.917</td>
<td>-1.665</td>
<td>5.810</td>
<td>H</td>
<td>-4.491</td>
<td>7.317</td>
<td>5.760</td>
<td>N</td>
<td>7.916</td>
<td>-0.386</td>
<td>-6.312</td>
</tr>
<tr>
<td>C</td>
<td>-6.248</td>
<td>-5.439</td>
<td>-2.840</td>
<td>H</td>
<td>4.570</td>
<td>0.032</td>
<td>8.326</td>
<td>N</td>
<td>-6.597</td>
<td>-4.321</td>
<td>-2.122</td>
</tr>
</tbody>
</table>

Table S3: Coordinates for [Zn(d)₄]⁸⁺ in acetonitrile; PM3/PCM
<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Zn</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.902</td>
<td>-0.833</td>
<td>5.265</td>
<td>-5.506</td>
<td>5.594</td>
<td>4.129</td>
</tr>
<tr>
<td>C</td>
<td>-5.398</td>
<td>-6.409</td>
<td>-2.294</td>
<td>5.401</td>
<td>-0.084</td>
<td>5.895</td>
</tr>
<tr>
<td>C</td>
<td>5.538</td>
<td>2.557</td>
<td>-6.126</td>
<td>-5.134</td>
<td>-7.301</td>
<td>-2.878</td>
</tr>
<tr>
<td>C</td>
<td>-4.901</td>
<td>-6.218</td>
<td>-1.007</td>
<td>5.445</td>
<td>2.865</td>
<td>-7.175</td>
</tr>
<tr>
<td>C</td>
<td>4.843</td>
<td>3.222</td>
<td>-5.117</td>
<td>-4.235</td>
<td>-6.967</td>
<td>-0.559</td>
</tr>
<tr>
<td>C</td>
<td>-5.420</td>
<td>4.600</td>
<td>2.198</td>
<td>4.193</td>
<td>4.071</td>
<td>-5.366</td>
</tr>
<tr>
<td>C</td>
<td>5.231</td>
<td>-0.973</td>
<td>3.918</td>
<td>-6.297</td>
<td>3.969</td>
<td>2.391</td>
</tr>
<tr>
<td>C</td>
<td>-5.245</td>
<td>-5.074</td>
<td>-0.289</td>
<td>5.996</td>
<td>-0.327</td>
<td>3.468</td>
</tr>
<tr>
<td>C</td>
<td>4.967</td>
<td>2.805</td>
<td>-3.793</td>
<td>-4.848</td>
<td>-4.905</td>
<td>0.725</td>
</tr>
<tr>
<td>C</td>
<td>-4.740</td>
<td>4.496</td>
<td>0.986</td>
<td>4.411</td>
<td>3.313</td>
<td>-2.989</td>
</tr>
<tr>
<td>C</td>
<td>4.584</td>
<td>-1.930</td>
<td>3.139</td>
<td>-5.068</td>
<td>3.779</td>
<td>0.217</td>
</tr>
<tr>
<td>C</td>
<td>-6.101</td>
<td>-4.129</td>
<td>-0.867</td>
<td>4.827</td>
<td>-2.041</td>
<td>2.070</td>
</tr>
<tr>
<td>C</td>
<td>5.805</td>
<td>1.726</td>
<td>-3.486</td>
<td>-4.431</td>
<td>-0.227</td>
<td>-0.115</td>
</tr>
<tr>
<td>C</td>
<td>-3.626</td>
<td>5.311</td>
<td>0.750</td>
<td>2.974</td>
<td>-0.270</td>
<td>-0.423</td>
</tr>
<tr>
<td>C</td>
<td>3.611</td>
<td>-2.751</td>
<td>3.722</td>
<td>-0.829</td>
<td>2.305</td>
<td>-1.341</td>
</tr>
<tr>
<td>C</td>
<td>-6.514</td>
<td>-2.850</td>
<td>-0.192</td>
<td>0.787</td>
<td>-2.578</td>
<td>0.255</td>
</tr>
<tr>
<td>C</td>
<td>5.993</td>
<td>1.173</td>
<td>-2.102</td>
<td>-2.126</td>
<td>0.619</td>
<td>0.237</td>
</tr>
<tr>
<td>C</td>
<td>-2.806</td>
<td>5.275</td>
<td>-0.510</td>
<td>0.662</td>
<td>0.011</td>
<td>0.419</td>
</tr>
<tr>
<td>C</td>
<td>2.839</td>
<td>-3.798</td>
<td>2.969</td>
<td>-0.695</td>
<td>-0.147</td>
<td>-1.722</td>
</tr>
<tr>
<td>C</td>
<td>-6.109</td>
<td>-1.286</td>
<td>1.754</td>
<td>0.603</td>
<td>-1.270</td>
<td>-1.842</td>
</tr>
<tr>
<td>C</td>
<td>5.177</td>
<td>1.172</td>
<td>0.287</td>
<td>-1.114</td>
<td>0.597</td>
<td>2.502</td>
</tr>
<tr>
<td>C</td>
<td>-2.357</td>
<td>4.105</td>
<td>-2.704</td>
<td>0.141</td>
<td>1.737</td>
<td>2.118</td>
</tr>
<tr>
<td>C</td>
<td>2.325</td>
<td>-4.784</td>
<td>0.700</td>
<td>-2.106</td>
<td>-1.219</td>
<td>-3.458</td>
</tr>
<tr>
<td>C</td>
<td>-4.716</td>
<td>-0.774</td>
<td>1.961</td>
<td>1.925</td>
<td>-1.927</td>
<td>-3.845</td>
</tr>
<tr>
<td>C</td>
<td>3.773</td>
<td>1.354</td>
<td>0.776</td>
<td>-4.739</td>
<td>-1.170</td>
<td>4.083</td>
</tr>
<tr>
<td>C</td>
<td>-2.299</td>
<td>2.621</td>
<td>-2.903</td>
<td>4.287</td>
<td>2.988</td>
<td>2.094</td>
</tr>
<tr>
<td>C</td>
<td>2.205</td>
<td>-3.996</td>
<td>-0.569</td>
<td>-3.718</td>
<td>2.646</td>
<td>-4.532</td>
</tr>
<tr>
<td>C</td>
<td>-3.987</td>
<td>-0.260</td>
<td>0.886</td>
<td>3.553</td>
<td>-5.283</td>
<td>-1.660</td>
</tr>
<tr>
<td>C</td>
<td>2.756</td>
<td>0.518</td>
<td>0.311</td>
<td>-3.315</td>
<td>-4.033</td>
<td>5.618</td>
</tr>
<tr>
<td>C</td>
<td>-1.450</td>
<td>1.840</td>
<td>-2.117</td>
<td>3.544</td>
<td>6.502</td>
<td>1.186</td>
</tr>
<tr>
<td>C</td>
<td>1.369</td>
<td>-2.880</td>
<td>-0.625</td>
<td>-7.268</td>
<td>1.892</td>
<td>-4.677</td>
</tr>
<tr>
<td>C</td>
<td>-2.699</td>
<td>0.220</td>
<td>1.088</td>
<td>6.982</td>
<td>-5.407</td>
<td>-2.550</td>
</tr>
<tr>
<td>C</td>
<td>1.460</td>
<td>0.670</td>
<td>0.788</td>
<td>-3.361</td>
<td>-6.471</td>
<td>6.186</td>
</tr>
<tr>
<td>C</td>
<td>-1.382</td>
<td>0.468</td>
<td>-2.325</td>
<td>3.977</td>
<td>8.520</td>
<td>-0.231</td>
</tr>
<tr>
<td>C</td>
<td>1.270</td>
<td>-2.147</td>
<td>-1.802</td>
<td>9.281</td>
<td>-5.608</td>
<td>-1.578</td>
</tr>
<tr>
<td>C</td>
<td>-2.132</td>
<td>0.196</td>
<td>2.357</td>
<td>-9.636</td>
<td>2.504</td>
<td>-4.145</td>
</tr>
<tr>
<td>C</td>
<td>1.169</td>
<td>1.651</td>
<td>1.730</td>
<td>-1.216</td>
<td>-7.670</td>
<td>6.689</td>
</tr>
<tr>
<td>C</td>
<td>-2.167</td>
<td>-0.134</td>
<td>-3.304</td>
<td>2.072</td>
<td>10.018</td>
<td>-0.087</td>
</tr>
<tr>
<td>C</td>
<td>2.006</td>
<td>-2.516</td>
<td>-2.923</td>
<td>-11.197</td>
<td>0.763</td>
<td>-3.236</td>
</tr>
<tr>
<td>C</td>
<td>-2.853</td>
<td>-0.315</td>
<td>3.436</td>
<td>10.861</td>
<td>-3.664</td>
<td>-1.710</td>
</tr>
<tr>
<td>C</td>
<td>2.178</td>
<td>2.497</td>
<td>2.190</td>
<td>1.101</td>
<td>-8.686</td>
<td>7.148</td>
</tr>
<tr>
<td>C</td>
<td>-3.016</td>
<td>0.641</td>
<td>-4.093</td>
<td>-0.029</td>
<td>11.390</td>
<td>-1.424</td>
</tr>
<tr>
<td>C</td>
<td>-4.151</td>
<td>-0.792</td>
<td>3.235</td>
<td>12.294</td>
<td>-1.541</td>
<td>-1.955</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>3.482</td>
<td>2.341</td>
<td>1.717</td>
<td>H</td>
<td>-2.561</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>---</td>
<td>--------</td>
</tr>
<tr>
<td>C</td>
<td>-3.821</td>
<td>-0.009</td>
<td>-5.179</td>
<td>H</td>
<td>2.002</td>
<td>-0.541</td>
</tr>
<tr>
<td>C</td>
<td>-1.023</td>
<td>-2.430</td>
<td>5.487</td>
<td>H</td>
<td>8.249</td>
<td>-1.707</td>
</tr>
<tr>
<td>C</td>
<td>-6.131</td>
<td>-0.651</td>
<td>-4.364</td>
<td>H</td>
<td>3.550</td>
<td>0.282</td>
</tr>
<tr>
<td>C</td>
<td>-1.160</td>
<td>-3.891</td>
<td>5.821</td>
<td>H</td>
<td>8.117</td>
<td>0.000</td>
</tr>
<tr>
<td>C</td>
<td>1.416</td>
<td>6.902</td>
<td>1.337</td>
<td>H</td>
<td>-6.643</td>
<td>-1.391</td>
</tr>
<tr>
<td>C</td>
<td>-7.529</td>
<td>-0.176</td>
<td>-4.075</td>
<td>H</td>
<td>5.907</td>
<td>1.639</td>
</tr>
<tr>
<td>C</td>
<td>-2.383</td>
<td>-4.572</td>
<td>5.846</td>
<td>H</td>
<td>2.760</td>
<td>-5.787</td>
</tr>
<tr>
<td>C</td>
<td>2.719</td>
<td>7.175</td>
<td>0.902</td>
<td>H</td>
<td>-6.695</td>
<td>-0.568</td>
</tr>
<tr>
<td>C</td>
<td>-7.966</td>
<td>1.138</td>
<td>-4.283</td>
<td>H</td>
<td>5.428</td>
<td>0.090</td>
</tr>
<tr>
<td>C</td>
<td>7.693</td>
<td>-4.568</td>
<td>-2.613</td>
<td>H</td>
<td>-1.334</td>
<td>4.513</td>
</tr>
<tr>
<td>C</td>
<td>2.958</td>
<td>8.297</td>
<td>0.111</td>
<td>H</td>
<td>-1.243</td>
<td>0.147</td>
</tr>
<tr>
<td>C</td>
<td>8.971</td>
<td>-4.676</td>
<td>-2.068</td>
<td>H</td>
<td>-3.617</td>
<td>-1.098</td>
</tr>
</tbody>
</table>
$^1$H, $^{13}$C and $^{19}$F NMR Spectra

Figure S9. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of 1.

Figure S10. $^{13}$C NMR (100 MHz, CD$_3$CN) spectrum of 1.
Figure S11. HSQC (400 MHz, CD$_3$CN) spectrum of 1.

Figure S12. HMBC (600 MHz, CD$_3$CN) spectrum of 1.
Figure S13. NHCOSY (600 MHz, CD$_3$CN) spectrum of 1.

Figure S14. $^{19}$F NMR spectrum of [Zn$_4$L$_4$]$^{8+}$ assembled in situ from 1 and Zn(BF$_4$)$_2$·xH$_2$O.
Figure S15. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of isolated [Zn$_4$(1)$_4$]$^{8+}$ complex.

Figure S16. $^{13}$C NMR (100 MHz, CD$_3$CN) spectrum of isolated [Zn$_4$(1)$_4$]$^{8+}$ complex.
Figure S17. HSQC (600 MHz, CD$_3$CN) spectrum of isolated [Zn$_4$(1)$_4$]$^{8+}$ complex.

Figure S18. HMBC (600 MHz, CD$_3$CN) spectrum of isolated [Zn$_4$(1)$_4$]$^{8+}$ complex.
Figure S19. NHCOSY (600 MHz, CD$_3$CN) spectrum of isolated [Zn$_4$(1)$_4$]$^{8+}$ complex.
References
