Supporting information

Synthesis, Crystal Structure and Study of Magnetocaloric Effect and Single Molecular Magnetic Behaviour in Discrete Lanthanide Complexes

Amit Adhikary, Javeed Ahmad Sheikh, Soumava Biswas and Sanjit Konar*

Department of Chemistry, IISER Bhopal, Bhopal- 462066, India, Fax: (+91) 7556692392.

Table S1. Selected hydrogen bonding distances (Å) and angles (deg) for the complex 1

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C7-H7….O2</td>
<td>x,y,z</td>
<td>0.930</td>
<td>2.607</td>
<td>3.179</td>
<td>120</td>
</tr>
<tr>
<td>O1-H1A-…Cl2</td>
<td>x,y,z</td>
<td>0.851</td>
<td>2.258</td>
<td>2.934</td>
<td>136</td>
</tr>
<tr>
<td>O9-H9A-…Cl2</td>
<td>x,y,z</td>
<td>0.850</td>
<td>2.154</td>
<td>2.845</td>
<td>138</td>
</tr>
<tr>
<td>O3-H3A-…Cl3</td>
<td>-x,+y,-z+1/2 +1</td>
<td>0.850</td>
<td>2.631</td>
<td>3.202</td>
<td>126</td>
</tr>
<tr>
<td>O11-H11A-…N3</td>
<td>-x,-y+1,-z+1</td>
<td>0.930</td>
<td>2.355</td>
<td>2.881</td>
<td>120</td>
</tr>
</tbody>
</table>

Table S2. Selected hydrogen bonding distances (Å) and angles (deg) for the complex 2

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O21- H21B-…Cl3</td>
<td>x,y,z</td>
<td>0.901</td>
<td>2.319</td>
<td>3.077</td>
<td>141</td>
</tr>
<tr>
<td>O9 -H9A ...O6</td>
<td>x,y,z</td>
<td>0.880</td>
<td>2.157</td>
<td>2.776</td>
<td>129</td>
</tr>
<tr>
<td>C18-H18…O10</td>
<td>x,y,z</td>
<td>0.930</td>
<td>2.576</td>
<td>3.158</td>
<td>121</td>
</tr>
<tr>
<td>O3w-H3wA…Cl2</td>
<td>x,y,z</td>
<td>0.850</td>
<td>2.517</td>
<td>3.057</td>
<td>122</td>
</tr>
<tr>
<td>O1-H1B…Cl5</td>
<td>x-1,+y,+z</td>
<td>0.873</td>
<td>2.314</td>
<td>3.012</td>
<td>137</td>
</tr>
<tr>
<td>C30-H30…O10</td>
<td>-x,-y,-z+1</td>
<td>0.930</td>
<td>2.649</td>
<td>3.261</td>
<td>124</td>
</tr>
</tbody>
</table>
Fig. S1. Thermogravimetric analysis plot for complex 1.

Fig. S2. Thermogravimetric analysis plot for complex 2.

Fig. S3. Thermogravimetric analysis plot for complex 3.
Fig. S4. Thermogravimetric analysis plot for complex 4.

Fig. S5. Tri-capped trigonal prismatic geometry around Gd$^{3+}$ with N$_2$O$_6$Cl coordination (left) and N$_4$O$_5$ coordination (right) in complex 1.

Fig. S6. Intra-molecular H-bonding of complex 1
Fig. S7. Inter-molecular H-bonding of complex 1 along a-axis

Fig. S8. Tri-capped trigonal prismatic geometry around Dy$^{3+}$ with N$_6$O$_7$ (left) and N$_4$O$_5$ coordination (right) in complex 2.

Fig. S9. Intra-molecular H-bonding of complex 2
Fig. S10. Inter-molecular H-bonding of complex 2 along a-axis.

Fig. S11. π-π stacking between pyridine ring of complex 2.

Fig. S12. Square antiprismatic geometry around Ln³⁺ (Ln³⁺ = Gd³⁺, Dy³⁺) in complexes 3 and 4.
Fig. S13. Packing diagram of complex 3 (isostcural complex 4) showing zig-zag like arrangement along c-axis.

Fig. S14. M/N\(\mu\)B vs H/T plots for complex 2 at 2-6 K.

Fig. S15. M/N\(\mu\)B vs H/T plots for complex 4 from at 2-6 K.
Fig. S16. Cole–Cole plots for complex 2 (left) and 4 (right) using the ac susceptibility data at zero field. The solid lines are to guide the eye.

Fig. S17. Frequency dependence of the out of phase ($\chi''$) ac susceptibility for complex 2 under a field of 1200 Oe (left) and 1600 Oe (right).

Fig. S18. Frequency dependence of the out of phase ($\chi''$) ac susceptibility for complex 4 under a field of 1400 Oe (left) and 1600 Oe (right).
Fig. S19. Frequency dependence of the in phase ($\chi'$) ac susceptibility for complex 2 (left) and complex 4 (right) under optimized dc fields.