Supporting Information

Nitronyl nitroxide based 2p-3d-4f chains with magnetocaloric effect and slow magnetic relaxation

Xiufeng Wang, Cun Li, Juan Sun, Licun Li*

Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry and Tianjin Key Laboratory of Metal and Molecule-based Material Chemistry, Nankai University, Tianjin 300071, China

Figure S1. Crystal structure of complex 2. All hydrogen and fluorine atoms are omitted for clarity

Figure S2. Crystal structure of complex 3. All hydrogen and fluorine atoms are omitted for clarity
**Figure S3.** Crystal structure of complex 4. All hydrogen and fluorine atoms are omitted for clarity.

**Figure S4.** Packing diagram of complex 2. All hydrogen and fluorine atoms are not shown for the sake of clarity.
**Figure S5.** Packing diagram of complex 3. All hydrogen and fluorine atoms are not shown for the sake of clarity.

**Figure S6.** Packing diagram of complex 4. All hydrogen and fluorine atoms are not shown for the sake of clarity.
Table S1. Crystallographic data and structure refinement summary for 1–4.

<table>
<thead>
<tr>
<th></th>
<th>1Gd</th>
<th>2 Tb</th>
<th>3 Dy</th>
<th>4 Er</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C\textsubscript{115}H\textsubscript{95}CuF\textsubscript{66}Ln\textsubscript{3}N\textsubscript{8}O\textsubscript{38}</td>
<td>C\textsubscript{115}H\textsubscript{95}CuF\textsubscript{66}Ln\textsubscript{3}N\textsubscript{8}O\textsubscript{38}</td>
<td>C\textsubscript{115}H\textsubscript{95}CuF\textsubscript{66}Ln\textsubscript{3}N\textsubscript{8}O\textsubscript{38}</td>
<td>C\textsubscript{115}H\textsubscript{95}CuF\textsubscript{66}Ln\textsubscript{3}N\textsubscript{8}O\textsubscript{38}</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>3986.29</td>
<td>3991.29</td>
<td>4002.03</td>
<td>4016.31</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>(P_2_1_2_1)</td>
<td>(P_2_1_2_1)</td>
<td>(P_2_1_2_1)</td>
<td>(P_2_1_2_1)</td>
</tr>
<tr>
<td><strong>(a/\text{Å})</strong></td>
<td>19.808(2)</td>
<td>19.8010(14)</td>
<td>19.771(2)</td>
<td>19.7419(18)</td>
</tr>
<tr>
<td><strong>(b/\text{Å})</strong></td>
<td>22.168(3)</td>
<td>22.1604(16)</td>
<td>22.179(2)</td>
<td>22.174(2)</td>
</tr>
<tr>
<td><strong>(c/\text{Å})</strong></td>
<td>33.918(4)</td>
<td>33.851(3)</td>
<td>33.842(4)</td>
<td>33.727(3)</td>
</tr>
<tr>
<td><strong>(\alpha, \text{deg})</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>(\beta, \text{deg})</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>(\gamma, \text{deg})</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>(V/\text{Å}^3)</strong></td>
<td>14894(3)</td>
<td>14853.6(19)</td>
<td>14840(3)</td>
<td>14764(2)</td>
</tr>
<tr>
<td><strong>(Z)</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>(\rho_{\text{calc}}/\text{g cm}^{-3})</strong></td>
<td>1.778</td>
<td>1.785</td>
<td>1.791</td>
<td>1.807</td>
</tr>
<tr>
<td><strong>(F(000))</strong></td>
<td>7839</td>
<td>7852</td>
<td>7864</td>
<td>7888</td>
</tr>
<tr>
<td><strong>(\theta_{\text{min}}, \theta_{\text{max}}, \text{deg})</strong></td>
<td>1.38, 25.01</td>
<td>1.38, 27.88</td>
<td>1.38, 25.01</td>
<td>1.10, 25.01</td>
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<tr>
<td><strong>Reflections collected</strong></td>
<td>118846</td>
<td>152963</td>
<td>109275</td>
<td>124405</td>
</tr>
<tr>
<td><strong>Unique reflns/(R_{\text{int}})</strong></td>
<td>26236/0.0595</td>
<td>35392/0.0449</td>
<td>26082/0.0623</td>
<td>26033/0.0506</td>
</tr>
<tr>
<td><strong>GOF ((F^2))</strong></td>
<td>0.999</td>
<td>1.038</td>
<td>0.992</td>
<td>1.012</td>
</tr>
<tr>
<td><strong>(R_1/wR_2 [I &gt; 2\sigma(I)]^a)</strong></td>
<td>0.0449/0.1151</td>
<td>0.0357/0.0784</td>
<td>0.0517/0.1362</td>
<td>0.0376/0.0984</td>
</tr>
<tr>
<td><strong>(R_1/wR_2 (\text{all data})^a)</strong></td>
<td>0.0473/0.1168</td>
<td>0.0385/0.0799</td>
<td>0.0563/0.1396</td>
<td>0.0396/0.0998</td>
</tr>
</tbody>
</table>

\(^a R_1 = \Sigma(||Fo| - |Fc||)/\Sigma|Fo|, wR_2 = [\Sigma w(||Fo||^2 - ||Fc||^2)]^{1/2}\Sigma w||Fo||^2\)\(^{1/2}\).

Table S2 SHAPE analysis for complexes 1-4.

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<tr>
<th>complex</th>
<th>Ln</th>
<th>SAPR-8</th>
<th>TDD-8</th>
<th>BTPR-8</th>
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<tbody>
<tr>
<td>1</td>
<td>Gd1</td>
<td>2.250</td>
<td>0.116</td>
<td>2.310</td>
</tr>
<tr>
<td></td>
<td>Gd2</td>
<td>2.025</td>
<td>0.135</td>
<td>1.978</td>
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<tr>
<td></td>
<td>Gd3</td>
<td>1.871</td>
<td>0.205</td>
<td>1.866</td>
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<tr>
<td></td>
<td>Tb1</td>
<td>2.165</td>
<td>0.119</td>
<td>2.277</td>
</tr>
<tr>
<td></td>
<td>Tb2</td>
<td>1.937</td>
<td>0.174</td>
<td>1.957</td>
</tr>
<tr>
<td></td>
<td>Tb3</td>
<td>2.069</td>
<td>0.117</td>
<td>2.030</td>
</tr>
<tr>
<td></td>
<td>Dy1</td>
<td>2.224</td>
<td>0.105</td>
<td>2.366</td>
</tr>
<tr>
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<td>Tb2</td>
<td>1.937</td>
<td>0.174</td>
<td>1.957</td>
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<td>Tb3</td>
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<td>0.117</td>
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<td></td>
<td>Dy2</td>
<td>2.054</td>
<td>0.111</td>
<td>2.028</td>
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<tr>
<td></td>
<td>Dy3</td>
<td>1.928</td>
<td>0.175</td>
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<tr>
<td></td>
<td>Er1</td>
<td>1.935</td>
<td>0.168</td>
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<td>Dy2</td>
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<td></td>
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<tr>
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<td>Er3</td>
<td>2.178</td>
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</table>
Figure S7. $M$ versus $H$ plots for 2 at 2 K

Figure S8. $M$ versus $H$ plots for 3 at 2 K
Figure S9. $M$ versus $H$ plots for 4 at 2 K

Figure S10. Temperature dependence of the out-of-phase signals of the ac susceptibility under different frequency (Hz) for 3 ($H_{ac} = 3$ Oe, $H_{dc} = 0$).