Electronic Supporting Information

Pentanuclear lanthanide pyramids based on thiacalix[4]arene ligand exhibiting slow magnetic relaxation

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Table S1. Selected bond lengths (Å) and angles (°) for 1–3

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Bond angles (°)

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| Ln(3)-O(3)-Ln(4) | 97.6(2)   | 97.69(19) | 97.3(2)   |
| Ln(4)-O(4)-Ln(1) | 98.30(18) | 97.36(17) | 98.04(18) |
| Ln(1)-O(5)-Ln(3) | 169.4(2)  | 168.9(2)  | 168.6(2)  |
| Ln(1)-O(5)-Ln(2) | 89.51(15) | 89.61(14) | 89.57(18) |
| Ln(3)-O(5)-Ln(2) | 90.07(15) | 89.46(14) | 89.97(17) |
| Ln(1)-O(5)-Ln(4) | 89.03(15) | 89.30(14) | 89.10(18) |
| Ln(3)-O(5)-Ln(4) | 89.47(14) | 89.54(13) | 89.18(17) |
| Ln(2)-O(5)-Ln(4) | 169.6(2)  | 169.2(2)  | 168.9(2)  |
| Ln(4)-O(6)-Ln(1) | 99.6(2)   | 99.09(18) | 99.5(2)   |
| Ln(4)-O(6)-Ln(5) | 105.3(2)  | 105.54(18) | 104.7(2) |
| Ln(1)-O(6)-Ln(5) | 104.4(2)  | 104.66(19) | 104.7(2) |
| Ln(1)-O(7)-Ln(2) | 98.50(19) | 98.76(18) | 98.77(19) |
| Ln(1)-O(7)-Ln(5) | 103.9(2)  | 104.51(18) | 105.3(2) |
| Ln(2)-O(7)-Ln(5) | 104.5(2)  | 105.41(18) | 105.6(2) |
| Ln(2)-O(8)-Ln(3) | 99.5(2)   | 99.20(18) | 99.62(19) |</p>
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Table S2. Selected bond lengths (Å) and angles (°) for 4–6
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<td>H···A</td>
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Table S3. Hydrogen-bond distances (Å) and angles (°) for 1 and 4.
Table S4. Shape analysis for the metal centers of 1

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<th>ML8</th>
<th>SAPR-8</th>
<th>TDD-8</th>
<th>JSD-8</th>
<th>JBTPR-8</th>
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<td>Dy1</td>
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SAPR-8 (D4d): Square antiprism
TDD-8 (D2d): Triangular dodecahedron
JSD-8 (D2d): Snub diphenoid J84
JBTPR-8 (C2v): Biaugmented trigonal prism J50
BTPR-8 (C2v): Biaugmented trigonal prism

Table S5. Shape analysis for the metal centers of 4

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<th>JTCTPR-9</th>
<th>TCTPR-9</th>
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<td>2.665</td>
<td>1.446</td>
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JCSAPR-9 (C4v): Capped square antiprism J10
CSAPR-9 (C4v): Spherical capped square antiprism
JTCTPR-9 (D3h): Tricapped trigonal prism J51
TCTPR-9 (D3h): Spherical tricapped trigonal prism
MFF-9 (Cs): Muffin
**Fig. S1.** The XRPD patterns (red lines) obtained from the as-synthesized solids of 1–6 and the simulated XRPD patterns (black lines) from single crystals of 1–6.

**Fig. S2.** The crystal structures of complexes 2 and 3.
**Fig. S3.** (a) The neighbouring \{Dy\}_5 clusters are linked together through several sets of O–H⋯X and C–H⋯X (X = O and Cl) hydrogen bonds (blue dashed lines) between solvent and the framework in 1. (b) Each ⋯Dy\(_5\)⋯Dy\(_5\)⋯Dy\(_5\)⋯ chain stacks together via two sets of C–H⋯π interactions (orange dashed lines) in an ⋯ABAB⋯ fashion. (c) Top view of the layer.

**Fig. S4.** The crystal structures of complexes 5 and 6.
Fig. S5. In 4, two CH₃OH and three acetone molecules exist around the {Dy₃} cluster, and two CH₃OH molecules connect with the framework through several O−H···O hydrogen bonds (dashed lines).

Fig. S6. Temperature-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 1 at the frequency of 999 Hz under 1000 Oe dc field.

Fig. S7. Frequency-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 1 at the temperature of 1.9 K under zero and 1000 Oe dc field, respectively.
Fig. S8. Temperature-dependent in-phase $\chi'$ (right) and out-of-phase $\chi''$ (left) ac susceptibility signals for 4 at the frequency of 999 Hz under 1000 Oe dc field.

Fig. S9. Frequency-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 4 at the temperature of 1.9 K under zero and 1000 Oe dc field, respectively.

Fig. S10. Temperature-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 2 at the frequency of 999 Hz under zero and 1000 Oe dc field, respectively.
Fig. S11. Temperature-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 3 at the frequency of 999 Hz under zero and 1000 Oe dc field, respectively.

Fig. S12. Temperature-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 5 at the frequency of 999 Hz under zero and 1000 Oe dc field, respectively.

Fig. S13. Temperature-dependent in-phase $\chi'$ and out-of-phase $\chi''$ ac susceptibility signals for 6 at the frequency of 999 Hz under zero and 1000 Oe dc field, respectively.