# Supporting Information

## Unique Y-shaped Lanthanide Aggregates and Single-molecule Magnets Behaviour for the $Dy_4$ Analogue

**Shufang Xue,[a, b] Yun-Nan Guo, [a, b] Lang Zhao,[a] Peng Zhang, [a, b] and Jinkui Tang*[a]**

Table S1. Selected Bond Distances (Å ) and Angles (deg) in Complexes **1-3**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Complex 1** | | | | | | | |
| Tb(1)-N(1) | 2.546(12) | Tb(2)-O(1) | 2.343(9) | Tb(3)-O(2) | 2.427(10) | Tb(4)-N(6) | 2.640(13) |
| Tb(1)-N(4) | 2.491(12) | Tb(2)-O(2) | 2.289(10) | Tb(3)-O(3) | 2.527(9) | Tb(4)-N(9) | 2.457(13) |
| Tb(1)-N(16) | 2.633(14) | Tb(2)-O(7) | 2.331(9) | Tb(3)-O(4) | 2.343(10) | Tb(4)-N(11) | 2.568(14) |
| Tb(1)-N(19) | 2.457(11) | Tb(2)-O(8) | 2.380(10) | Tb(3)-O(5) | 2.182(12) | Tb(4)-N(14) | 2.447(13) |
| Tb(1)-O(1) | 2.351(9) | Tb(2)-O(10) | 2.259(10) | Tb(3)-O(11) | 2.468(9) | Tb(4)-O(4) | 2.361(10) |
| Tb(1)-O(8) | 2.421(10) | Tb(2)-O(11) | 2.526(10) | Tb(3)-O(12) | 2.746(11) | Tb(4)-O(7) | 2.368(10) |
| Tb(1)-O(10) | 2.436(9) | Tb(2)-O(15) | 2.392(13) | Tb(3)-O(16) | 2.545(13) | Tb(4)-O(11) | 2.535(10) |
| Tb(1)-O(13) | 2.398(10) | Tb(2)-O(19) | 2.320(10) | Tb(3)-O(17) | 2.423(13) | Tb(4)-O(18) | 2.441(11) |
| Tb(1)-O(14) | 2.486(10) | Tb(2)-Tb(3) | 3.5992(11) | Tb(3)-O(19) | 2.378(11) | Tb(4)-O(19) | 2.395(9) |
| Tb(1)-Tb(2) | 3.5307(11) | Tb(2)-Tb(4) | 3.6208(11) | Tb(3)-Tb(4) | 3.6304(11) | | |
| Tb(1)-O(1)-Tb(2) | 97.6(3) | Tb(1)-O(8)-Tb(2) | 94.7(3) | Tb(1)-O(10)-Tb(2) | 97.5(3) | | |
| Tb(2)-O(2)-Tb(3) | 99.4(4) | Tb(2)-O(11)-Tb(3) | 92.2(3) | Tb(2)-O(19)-Tb(3) | 100.0(4) | | |
| Tb(3)-O(4)-Tb(4) | 101.0(4) | Tb(3)-O(11)-Tb(4) | 93.0(3) | Tb(3)-O(19)-Tb(4) | 99.0(4) | | |
| Tb(2)-O(7)-Tb(4) | 100.8(4) | Tb(2)-O(11)-Tb(4) | 91.4(3) | Tb(2)-O(19)-Tb(4) | 100.3(4) | | |
| **Complex 2** | | | | | | | |
| Dy(1)-O(1) | 2.349(5) | Dy(2)-O(10) | 2.251(6) | Dy(3)-O(5) | 2.170(6) | Dy(4)-O(4) | 2.359(6) |
| Dy(1)-O(13) | 2.379(6) | Dy(2)-O(19) | 2.288(5) | Dy(3)-O(4) | 2.324(6) | Dy(4)-O(7) | 2.367(5) |
| Dy(1)-O(8) | 2.404(6) | Dy(2)-O(2) | 2.291(6) | Dy(3)-O(19) | 2.346(6) | Dy(4)-O(19) | 2.393(6) |
| Dy(1)-O(10) | 2.419(5) | Dy(2)-O(7) | 2.306(6) | Dy(3)-O(16) | 2.394(7) | Dy(4)-O(18) | 2.430(6) |
| Dy(1)-N(19) | 2.442(7) | Dy(2)-O(1) | 2.330(5) | Dy(3)-O(2) | 2.416(6) | Dy(4)-N(14) | 2.445(7) |
| Dy(1)-O(14) | 2.469(6) | Dy(2)-O(15) | 2.390(7) | Dy(3)-O(11) | 2.451(6) | Dy(4)-N(9) | 2.453(7) |
| Dy(1)-N(4) | 2.487(7) | Dy(2)-O(8) | 2.394(5) | Dy(3)-O(17) | 2.506(7) | Dy(4)-O(11) | 2.535(6) |
| Dy(1)-N(1) | 2.568(7) | Dy(2)-O(11) | 2.529(5) | Dy(3)-O(3) | 2.530(6) | Dy(4)-N(11) | 2.563(7) |
| Dy(1)-N(16) | 2.634(7) | Dy(2)-Dy(3) | 3.5814(5) | Dy(3)-O(12) | 2.756(6) | Dy(4)-N(6) | 2.630(8) |
| Dy(1)-Dy(2) | 3.5183(5) | Dy(3)-Dy(4) | 3.6151(6) | Dy(2)-Dy(4) | 3.6176(5) | | |
| Dy(1)-O(1)-Dy(2) | 97.5(2) | Dy(1)-O(8)-Dy(2) | 94.32(19) | Dy(1)-O(10)-Dy(2) | 97.7(2) | | |
| Dy(2)-O(2)-Dy(3) | 99.1(2) | Dy(2)-O(11)-Dy(3) | 91.96(18) | Dy(2)-O(19)-Dy(3) | 101.2(2) | | |
| Dy(3)-O(4)-Dy(4) | 101.0(2) | Dy(3)-O(11)-Dy(4) | 92.94(19) | Dy(3)-O(19)-Dy(4) | 99.4(2) | | |
| Dy(2)-O(7)-Dy(4) | 101.5(2) | Dy(2)-O(11)-Dy(4) | 91.19(18) | Dy(2)-O(19)-Dy(4) | 101.2(2) | | |
| **Complex 3** | | | | | | | |
| Ho(1)-O(1) | 2.330(6) | Ho(2)-O(10) | 2.249(6) | Ho(3)-O(5) | 2.165(6) | Ho(4)-O(4) | 2.354(6) |
| Ho(1)-O(13) | 2.356(6) | Ho(2)-O(2) | 2.273(6) | Ho(3)-O(4) | 2.318(6) | Ho(4)-O(7) | 2.360(6) |
| Ho(1)-O(8) | 2.383(6) | Ho(2)-O(19) | 2.289(6) | Ho(3)-O(19) | 2.340(6) | Ho(4)-O(19) | 2.373(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ho(1)-O(10) | 2.413(5) | Ho(2)-O(1) | 2.320(5) | Ho(3)-O(16) | 2.373(8) | Ho(4)-O(18) | 2.397(7) |
| Ho(1)-O(14) | 2.439(6) | Ho(2)-O(15) | 2.378(8) | Ho(3)-O(2) | 2.409(6) | Ho(4)-N(14) | 2.421(8) |
| Ho(1)-N(19) | 2.445(7) | Ho(2)-O(7) | 2.295(6) | Ho(3)-O(11) | 2.443(6) | Ho(4)-N(9) | 2.431(7) |
| Ho(1)-N(4) | 2.476(7) | Ho(2)-O(8) | 2.378(6) | Ho(3)-O(17) | 2.511(8) | Ho(4)-O(11) | 2.535(6) |
| Ho(1)-N(1) | 2.550(7) | Ho(2)-O(11) | 2.521(6) | Ho(3)-O(3) | 2.517(6) | Ho(4)-N(11) | 2.565(8) |
| Ho(1)-N(16) | 2.618(7) | Ho(2)-Ho(3) | 3.5646(6) | Ho(3)-O(12) | 2.759(6) | Ho(4)-N(6) | 2.615(8) |
| Ho(1)-Ho(2) | 3.5114(6) | Ho(2)-Ho(4) | 3.5909(6) | Ho(3)-Ho(4) | 3.6054(6) | | |
| Ho(1)-O(1)-Ho(2) | 98.1(2) | Ho(1)-O(8)-Ho(2) | 95.0(2) | Ho(1)-O(10)-Ho(2) | 97.7(2) | | |
| Ho(2)-O(2)-Ho(3) | 99.1(2) | Ho(2)-O(11)-Ho(3) | 91.8(2) | Ho(2)-O(19)-Ho(3) | 100.7(2) | | |
| Ho(3)-O(4)-Ho(4) | 101.0(2) | Ho(3)-O(11)-Ho(4) | 92.8(2) | Ho(3)-O(19)-Ho(4) | 99.8(2) | | |
| Ho(2)-O(7)-Ho(4) | 101.0(2) | Ho(2)-O(11)-Ho(4) | 90.5(2) | Ho(2)-O(19)-Ho(4) | 100.8(2) | | |

Table S2. Lanthanide Geometry Analysis by SHAPE Software for Complexes **1-3**

| | Ln1 | Ln2 | Ln3 | Ln4 |
|---|---|---|---|---|
| geometry | mono-capped square antiprism | triangular dodecahedron | mono-capped square antiprism | mono-capped square antiprism |
| | ($C_{4V}$) | ($D_{2d}$) | ($C_{4V}$) | ($C_{4V}$) |
| **1** | 2.021 | 0.942 | 1.345 | 1.622 |
| **2** | 1.916 | 0.929 | 1.312 | 1.636 |
| **3** | 1.934 | 0.985 | 1.308 | 1.551 |

Table S3. Selected Hydrogen Bonds in Complex **2**

| D-H | d(D-H) (Å) | d(H…A) (Å) | <DHA (°) | d(D…A) (Å) | A |
|---|---|---|---|---|---|
| N3-H3A | 0.88 | 2.244 | 156 | 3.0575 | O14[1-*x*, -*y*, 1-*z*] |
| N8-H8B | 0.88 | 2.631 | 149 | 3.4168 | O18[-*x*, 1-*y*, -*z*] |

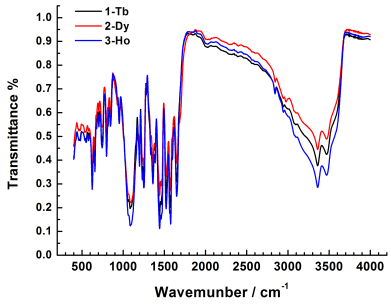


Fig. S1 IR spectra of a crystalline sample of complexes **1-3**.

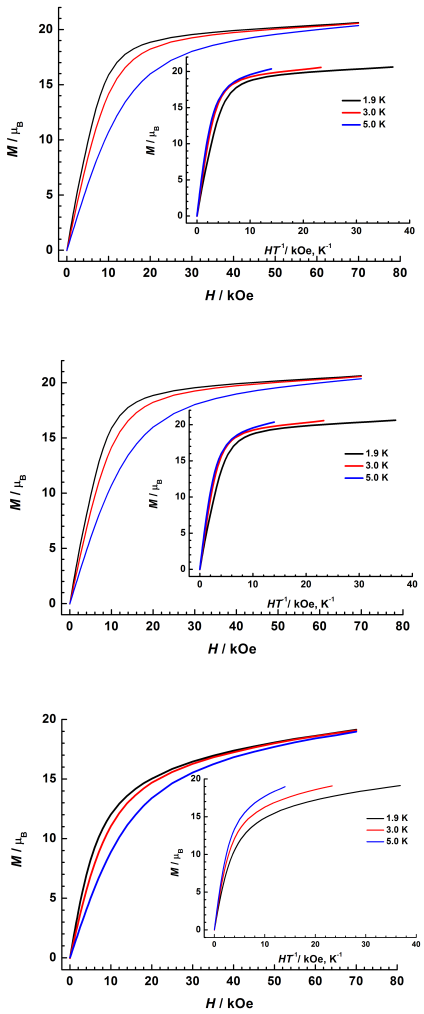


Fig. S2 Field dependences of magnetization in the field range 0−70 kOe and temperature range 1.9−5.0 K. Insets: Plots of the reduced magnetization *M* versus *H/T* (top) for **1**, (middle) for **2** and (bottom) for **3**.

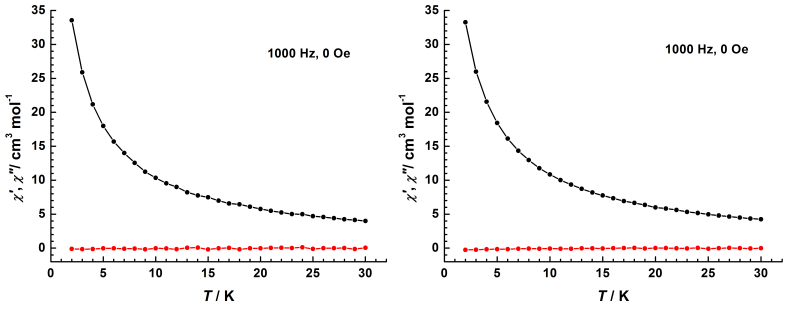


Fig. S3 Temperature dependence of the ac susceptibilities of **1** (left) and **3** (right) measured in zero static field at the indicated frequency.

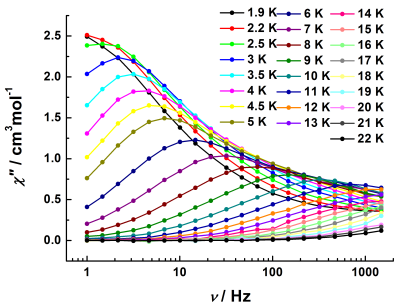


Fig. S4 Frequency dependence of the out-of-phase ac susceptibilities of **2** measured under zero static field.

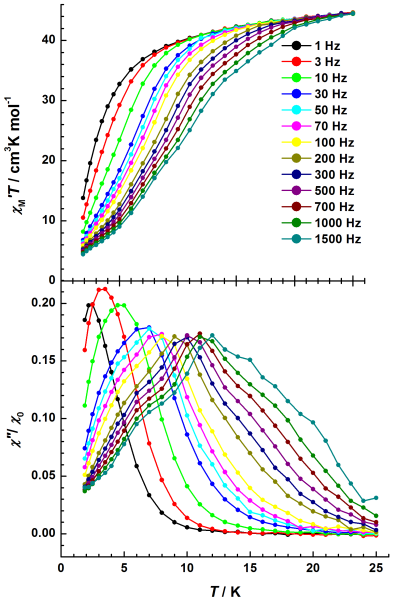


Fig. S5 Temperature dependence of top) $\chi'T$, and bottom) $\chi''/\chi_0$, where $\chi'$, $\chi''$, and $\chi_0$ are in-phase-ac, out-of-phase-ac, and dc molar magnetic susceptibilities, respectively, for **2** under zero static field and oscillating at the indicated frequencies.

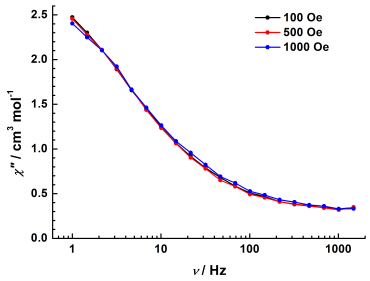


Fig. S6 Frequency-dependent out-of-phase component of the ac susceptibility of **2** under dc fields of 100, 500 and 1000 Oe at 1.9 K.