# Realization of Toroidal Magnetic Moments in Heterometallic 3d-4f System

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## **Experimental Section**

General Synthetic Considerations. All chemicals and solvents were commercially obtained and used as received without any further purification. FTIR spectra were measured using a Nicolet 6700 Flex FTIR spectrometer equipped with smart iTR<sup>TM</sup> attenuated total reflectance (ATR) sampling accessory in the range from 500 to 4000 cm<sup>-1</sup>. Elemental analysis for C, H and N were carried out on a Perkin-Elmer 2400 analyzer. Ligand H<sub>4</sub>L' (2,6-bis[(6-hydroxymethyl-2-pyridylmethylene)hydrazinecarbonyl]-pyridine) was synthesized by the similar procedure as reported in the previous literature.<sup>1</sup>

Synthesis of  $1 \cdot Tb_6Cu_6$ . Tb(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1 mmol) was added to a solution of H<sub>4</sub>L' (0.1 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.1 mmol) in 15 mL methanol/dichloromethane (v:v = 1:2), and then triethylamine (0.2 mmol) was added. The resultant green solution was stirred for 3 h and subsequently filtered. The filtrate was exposed to air to allow the slow evaporation of the solvent. Green crystals of  $1 \cdot Tb_6Cu_6$  suitable for X-ray diffraction analysis were collected after 1 week. Yield in ~65%. Selected IR (cm<sup>-1</sup>): 3409.31(br), 1572.49(vs), 1426.47(m), 1392.17(s), 1374.49(s), 1288.02(m), 1234.78(w), 1217.61(w), 1196.17(w), 1166.62(w), 1070.57(br), 1016.28(s), 940.95(w), 837.15(w), 794.51(w), 772.42(w), 681.03(w), 619.40(m). Anal. Calcd. for [Tb<sub>6</sub>Cu<sub>6</sub>(H<sub>2</sub>L')<sub>6</sub>Cl<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>]·5ClO<sub>4</sub>·OH (C<sub>126</sub>H<sub>115</sub>N<sub>42</sub>O<sub>51</sub>Cl<sub>17</sub>Cu<sub>6</sub>Tb<sub>6</sub>, MW = 4971): C, 30.44%; H, 2.33%; N, 11.83%. Found: C, 29.01%; H, 2.42%; N, 11.16%.

Synthesis of  $2 \cdot Tb_6 Zn_6$ . Complex  $2 \cdot Tb_6 Zn_6$  was synthesized by the similar procedure as  $1 \cdot Tb_6 Cu_6$  with the replacement of CuCl<sub>2</sub>·2H<sub>2</sub>O by ZnCl<sub>2</sub>. Yield in ~57%. Selected IR (cm<sup>-1</sup>): 3412.19(br), 1607.14(w), 1572.39(s), 1545.40(vs), 1452.94(w), 1421.04(m), 1388.09(m), 1370.04(s), 1283.64(m), 1232.38(w), 1218.37(w), 1191.36(w), 1165.33(w), 1071.74(br), 1015.13(m), 977.00(w), 935.58(w), 841.30(w), 795.21(w), 771.00(w), 694.65(w), 673.54(w), 621.62(m). Anal. Calcd. for [Tb<sub>6</sub>Zn<sub>6</sub>(H<sub>2</sub>L')<sub>6</sub>Cl<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>]·5ClO<sub>4</sub>·OH·30H<sub>2</sub>O (C<sub>126</sub>H<sub>175</sub>N<sub>42</sub>O<sub>81</sub>Zn<sub>6</sub>Tb<sub>6</sub>Cl<sub>17</sub>, MW = 5532.97): C, 27.35%; H, 3.19%; N, 10.63%. Found: C, 27.14%; H, 2.93%; N, 10.51%.

Synthesis of  $4 \cdot Dy_6 Zn_6$ . Complex  $4 \cdot Dy_6 Zn_6$  was synthesized by the similar procedure as  $2 \cdot Tb_6 Zn_6$  with the replacement of Tb(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O by Dy(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O. Yield in ~69%. Selected IR (cm<sup>-1</sup>): 3568.13(br), 3067.52(br), 2953.19(w), 1624.22(w), 1571.54(m), 1541.46(vs), 1420.93(s), 1400.16(w), 1370.00(s), 1282.80(m), 1231.22(w), 1218.44(w), 1190.91(w), 1165.06(w), 1097.39(m), 1072.55(s), 1015.53(m), 976.14(w), 938.19(w), 841.38(w), 794.38(w), 770.98(m), 694.88(w), 671.15(w), 621.42(w). Anal. Calcd. for [Dy<sub>6</sub>Zn<sub>6</sub>(H<sub>2</sub>L')<sub>6</sub>Cl<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>]·5ClO<sub>4</sub>·OH·30H<sub>2</sub>O (C<sub>126</sub>H<sub>175</sub>N<sub>42</sub>O<sub>81</sub>Zn<sub>6</sub>Dy<sub>6</sub>Cl<sub>17</sub>, MW = 5543.94): C, 27.30%; H, 3.18%; N, 10.61%. Found: C, 27.03%; H, 3.05%; N, 10.38%.

## Crystallography

Single-crystal X-ray data of the titled complexes were collected on a Bruker Apex II CCD diffractometer equipped with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 153(2) K. The structure was solved by direct

methods and refined by the full-matrix least-squares method based on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms by using the SHELXS (direct methods) and refined by ShelXL (full matrix leastsquares techniques) in the Olex2 package.<sup>2</sup> Due to the highly disordered solvent molecules in lattice, we use mask command to remove the contributions of the highly disorder. The masked electron density of each complex was attached in the crystallography data. All non-hydrogen atoms in the whole structure were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Crystallographic data of are listed in Table S1. CCDC 1534868-1534870 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

### **Magnetic Measurements**

Magnetic susceptibility measurements were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. Direct current (dc) magnetic susceptibility measurements were performed on a polycrystalline sample of  $1 \cdot Tb_6Cu_6$ ,  $2 \cdot Tb_6Zn_6$  and  $4 \cdot Dy_6Zn_6$  in the temperature range 2–300 K, in an applied field of 1000 Oe. The variable-temperature magnetization was measured in the temperature range of 1.9-300 K with an external magnetic field of 1000 Oe. The dynamics of the magnetization were investigated from the ac susceptibility measurements in the zero static fields and a 3.0 Oe ac oscillating field. Diamagnetic corrections were made with the Pascal's constants<sup>3</sup> for all the constituent atoms as well as the contributions of the sample holder.

	1∙Tb <sub>6</sub> Cu <sub>6</sub>	2·Tb <sub>6</sub> Zn <sub>6</sub>	4·Dy <sub>6</sub> Zn <sub>6</sub>
Formula	C <sub>126</sub> H <sub>115</sub> N <sub>42</sub> O <sub>51</sub> Cl <sub>17</sub> Cu <sub>6</sub> Tb <sub>6</sub>	$C_{126}H_{175}N_{42}O_{81}Zn_6Tb_6Cl_{17}$	$C_{126}H_{175}N_{42}O_{81}Zn_6Dy_6Cl_{17}$
FW, g∙mol <sup>-1</sup>	4971.00	5532.97	5543.94
crystal system	Trigonal	Trigonal	Trigonal
space group	P-3c1	P-3c1	P-3c1
<i>Т</i> , К	296.15	296.15	296.15
λ, Å	0.71073	0.71073	0.71073
<i>a</i> , Å	28.1810(11)	28.4167(7)	28.4167(7)
b, Å	28.1810(11)	28.4167(7)	28.4167(7)
<i>c</i> , Å	20.0915(15)	19.3922(10)	19.3922(10)
α, °	90	90	90
β, °	90	90	90
γ, °	120	120	120
<i>V</i> , Å <sup>3</sup>	13818.3(15)	13561.4(10)	13561.4(10)
Ζ	2	2	2
$\rho_{\rm calcd}, {\rm g} \cdot {\rm cm}^{-3}$	1.195	1.352	1.358
reflns collected	87453	78703	85888
unique reflns	9146	8023	8955
Rint	0.1216	0.1403	0.0863
GOF on $F^2$	1.028	1.029	1.032
$R_1 (\mathbf{I} \ge 2 \sigma (\mathbf{I}))$	0.0714	0.0832	0.0709
$wR_2$ (all data)	0.2606	0.2881	0.2432
CCDC number	1534869	1534868	1534870

Table S1. Crystallographic data for complexes 1. Tb<sub>6</sub>Cu<sub>6</sub>, 2. Tb<sub>6</sub>Zn<sub>6</sub> and 4. Dy<sub>6</sub>Zn<sub>6</sub>.

			-	-
	1·Tb <sub>6</sub> Cu <sub>6</sub>	$2 \cdot Tb_6 Zn_6$	3·Dy <sub>6</sub> Cu <sub>6</sub>	$4 \cdot Dy_6Zn_6$
Tb/Dy(1)-O(1)	2.412(7)	2.417(9)	2.366(16)	2.402(6)
Tb/Dy(1)-O(2)	2.390(6)	2.372(10)	2.38(2)	2.381(8)
Tb/Dy(1)-O(3)	2.443(7)	2.383(9)	2.359(13)	2.378(7)
Tb/Dy(1)-O(4)	2.405(7)	2.401(10)	2.385(19)	2.397(7)
Tb/Dy(1)-O(5)	2.467(9)	2.400(11)	2.42(2)	2.388(8)
Tb/Dy(1)-N(1)	2.475(5)	2.485(11)	2.474(10)	2.481(8)
Tb/Dy(1)-N(2)	2.513(8)	2.478(10)	2.491(17)	2.482(7)
Tb/Dy(1)-N(6)	2.501(8)	2.469(11)	2.456(15)	2.474(8)
Tb/Dy(1)-N(7)	2.480(5)	2.479(10)	2.441(9)	2.479(7)
Cu/Zn(1)-Cl(1)	2.385(3)	2.263(5)	2.308(9)	2.255(4)
Cu/Zn(1)-Cl(2)	2.313(4)	2.266(4)	2.413(8)	2.268(3)

 $\label{eq:complexes} \mbox{Table S2. Selected bond distances (Å) for complexes $1 \cdot Tb_6Cu_6, $2 \cdot Tb_6Zn_6, $3 \cdot Dy_6Cu_6$ and $4 \cdot Dy_6Zn_6$.}$ 



Fig. S1 Structure view of complexes  $1 \cdot Tb_6Cu_6$  (left) and  $2 \cdot Tb_6Zn_6$  (right) along *c* axis (top) and *b* axis (bottom) with parameter labels. The purple, azure, orange, green, blue, dark, red and grey spheres representing Tb, Cu, Zn, Cl, N, C, O and H, respectively; solvents have been omitted for clarity.



Fig. S2 Structure view of complexes  $3 \cdot Dy_6Cu_6$  (left) and  $4 \cdot Dy_6Zn_6$  (right) along *c* axis (top) and *b* axis (bottom) with parameter labels. The pink, azure, orange, green, blue, dark, red and grey spheres representing Dy, Cu, Zn, Cl, N, C, O and H, respectively; solvents have been omitted for clarity.



Fig. S3 Top views along *c* axis (left) and packing models along *b* axis (right) with parameter labels for complexes  $1 \cdot Tb_6Cu_6$  (top) and  $2 \cdot Tb_6Zn_6$  (bottom); solvents have been omitted for clarity.



Fig. S4 Top views along *c* axis (left) and packing models along *b* axis (right) with parameter labels for complexes  $3 \cdot Dy_6Cu_6$  (top) and  $4 \cdot Dy_6Zn_6$  (bottom); solvents have been omitted for clarity.



Fig. S5 Packing models of complexes  $1 \cdot Tb_6Cu_6$  (left) and  $2 \cdot Tb_6Zn_6$  (right) along *c* axis.



Fig. S6 Packing models of complexes  $3 \cdot Dy_6 Cu_6$  (left) and  $4 \cdot Dy_6 Zn_6$  (right) along c axis.

Table S3. The CShM values calculated by SHAPE 2.1 for  $1 \cdot Tb_6Cu_6$ ,  $2 \cdot Tb_6Zn_6$ ,  $3 \cdot Dy_6Cu_6$  and  $4 \cdot Dy_6Zn_6$ .

Coordination Geometry	Atom	1·Tb <sub>6</sub> Cu <sub>6</sub>	2·Tb <sub>6</sub> Zn <sub>6</sub>	Atom	3·Dy <sub>6</sub> Cu <sub>6</sub>	4·Dy <sub>6</sub> Zn <sub>6</sub>
Johnson triangular cupola J3 ( $C_{3\nu}$ )		15.123	14.908		15.044	15.021
Capped cube J8 ( $C_{4\nu}$ )		9.852	9.842		10.191	9.989
Spherical-relaxed capped cube $(C_{4\nu})$		8.215	8.276		8.568	8.426
Capped square antiprism J10 ( $C_{4\nu}$ )	Tb	3.004	2.901	Dy	2.749	2.793
Spherical capped square antiprism $(C_{4\nu})$		2.126	2.051		1.910	1.911
Tricapped trigonal prism J51 $(D_{3h})$		4.514	4.424		4.265	4.312
Spherical tricapped trigonal prism $(D_{3h})$		2.303	2.145		2.089	2.039



Fig. S7 Temperature dependent  $\chi_M T$  products at 1 kOe between 2 and 300 K for  $1 \cdot Tb_6Cu_6$  (red),  $2 \cdot Tb_6Zn_6$  (green),  $3 \cdot Dy_6Cu_6$  (pink) and  $4 \cdot Dy_6Zn_6$  (blue).



Fig. S8 Extracted temperature dependence of  $\Delta \chi_M T$  products for  $[Tb_6Cu_6]-[Tb_6Zn_6]$  (blue),  $[Dy_6Cu_6]-[Dy_6Zn_6]$  (red) at 1 kOe between 2 and 300 K.



Fig. S9 Molar magnetization (*M*) vs. magnetic field (*H*) for  $1 \cdot Tb_6Cu_6$  at 1.9, 3.0 and 5.0 K. Inset represents the relevant plots of magnetization *M* versus *H*/*T*.



Fig. S10 Molar magnetization (*M*) vs. magnetic field (*H*) for  $2 \cdot Tb_6 Zn_6$  at 1.9, 3.0 and 5.0 K. Inset represents the relevant plots of magnetization *M* versus *H*/*T*.



Fig. S11 Molar magnetization (*M*) vs. magnetic field (*H*) for  $3 \cdot Dy_6Cu_6$  at 1.9, 3.0 and 5.0 K. Inset represents the relevant plots of magnetization *M* versus *H*/*T*.



Fig. S12 Molar magnetization (*M*) vs. magnetic field (*H*) for  $4 \cdot Dy_6 Zn_6$  at 1.9, 3.0 and 5.0 K. Inset represents the relevant plots of magnetization *M* versus *H*/*T*.



Fig. S13 Molar magnetization (*M*) vs. magnetic field (*H*) for  $1 \cdot Tb_6Cu_6$  at 1.9 K.



Fig. S14 Temperature dependence of ac susceptibility for 1. Tb<sub>6</sub>Cu<sub>6</sub> at indicated frequencies under zero dc field.



Fig. S15 Temperature and frequency dependence of ac susceptibility for  $3 \cdot Dy_6Cu_6$  at indicated frequencies and temperatures under zero dc field.



Fig. S16 Temperature dependence of ac susceptibility for  $4 \cdot Dy_6 Zn_6$  at indicated frequencies under zero dc field.



Fig. S17 Cole-Cole plots for  $1 \cdot Tb_6Cu_6$  at zero field between 1.9 and 5.0 K. The solid lines indicate the best fits to the experiments with the generalized Debye model.



Fig. S18 Plot of  $\tau vs. T^{-1}$  for **1**·**Tb**<sub>6</sub>**Cu**<sub>6</sub>, obtained under zero dc fields over the temperature range 1.9–3 K. The red line represents the Arrhenius fitted result.

## Ab initio calculation on individual lanthanide fragment

Complete-active-space self-consistent field (CASSCF) calculations on individual Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup>) fragments (see Figure S18 for the model structures of complexes  $1 \cdot Tb_6Cu_6$  and  $3 \cdot Dy_6Cu_6$ ; see Figure 4 for the complete molecular structures) of complexes 1. Tb<sub>6</sub>Cu<sub>6</sub> and 3. Dy<sub>6</sub>Cu<sub>6</sub> on the basis of X-ray determined geometry have been carried out with MOLCAS 8.0 program package.<sup>4</sup> Due to their symmetry of 1. Tb<sub>6</sub>Cu<sub>6</sub> and 3. Dy<sub>6</sub>Cu<sub>6</sub>, we only need to calculate one Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup>) fragment for each of them. For CASSCF calculations, the basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for the central Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup>); VTZ for close O and N; VDZ for distant atoms. Considering the influence of the neighboring two Cu ions, we replaced them with the diamagnetic Zn<sup>II</sup> atoms. Besides, the influence of neighboring Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup> ion) was taken into account by the closed-shell La<sup>III</sup> ab initio embedding model potentials (AIMP; La.ECP.deGraaf.0s.0s.0e-La-(LaMnO3.).<sup>5</sup> The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit coupling was handled separately in the restricted active space state interaction (RASSI-SO) procedure. The active electrons in 7 active spaces include all f electrons (CAS(8 in 7) for complex  $1 \cdot Tb_6Cu_6$  and CAS(9 in 7) for complex  $3 \cdot Dy_6 Cu_6$ ) in the CASSCF calculation. To exclude all the doubts we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 21 sextets, 128 from 224 quadruplets and 130 from 490 doublets for Dy<sup>III</sup> fragment; all from 7 septets, all from 140 quintets and 68 from 500 triplets for the Tb<sup>III</sup> fragment). The calculated eight lowest calculated Kramers doublets (KDs) and the *g* tensors of individual Ln<sup>III</sup> ion for complexes  $1 \cdot Tb_6Cu_6$  and  $3 \cdot Dy_6Cu_6$  using CASSCF/RASSI are shown in Table S4.



Fig. S19 Calculated model structures of complexes 1. Tb<sub>6</sub>Cu<sub>6</sub> (left) and 3. Dy<sub>6</sub>Cu<sub>6</sub> (right). H atoms are omitted.

Table S4. Calculated energy levels (cm<sup>-1</sup>),  $g(g_x, g_y, g_z)$  tensors and  $m_J$  values of the lowest Kramers doublets (KDs) of individual Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup>) fragments of complexes 1·Tb<sub>6</sub>Cu<sub>6</sub> and 3·Dy<sub>6</sub>Cu<sub>6</sub>.

KDs	1∙Tb <sub>6</sub> Cu <sub>6</sub>			3·Dy <sub>6</sub> Cu <sub>6</sub>		
	$E/cm^{-1}$	g	m <sub>J</sub>	$E/cm^{-1}$	g	$m_J$
1	0.0	0.000			0.004	
		0.000	±6	0.0	0.025	$\pm 15/2$
	0.4	17.810			19.710	
	76.3	0.000			0.145	
2		0.000	±5	117.8	0.532	$\pm 13/2$
	78.1	14.468			17.450	
	145.7	0.000			0.118	
3		0.000	±4	164.3	0.847	$\pm 9/2$
	169.8	11.003			16.578	
	197.4				0.709	
4			0	213.2	2.083	$\pm 11/2$
					13.174	
	260.5	0.000			9.247	
5	279.8	0.000	±3	271.2	7.169	$\pm 3/2$
		12.510			3.451	
	298.5	0.000			9.088	
6	305.9	0.000	±2	355.3	5.886	$\pm 5/2$
		13.204			2.632	
7	437.5	0.000			2.906	
		0.000	±1	416.0	3.346	$\pm 7/2$
	438.6	17.722			7.716	
8					0.865	
				471.5	4.038	$\pm 1/2$
					14.850	

#### Evaluation of the exchange interactions in two complexes by BS-DFT calculation

To obtain the isotropic exchange coupling constants *J*, Orca 3.0.3 calculations<sup>6</sup> were performed with the popular hybrid functional B3LYP proposed by Becke<sup>7</sup> and Lee et al.<sup>8</sup> Triple- $\zeta$  with one polarization function TZVP<sup>9</sup> basis sets were used for all atoms, and zero order regular approximation (ZORA) was used for the scalar relativistic effect in all calculations. In the model structures (Figure S16), the influence of the Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup> ion) on the two ends was taken into account by the closed-shell La<sup>III</sup> ab initio embedding model potentials. Besides, considering the long distance between adjacent Ln<sup>III</sup> ions, the Ln-Ln interactions were omitted by us. We only calculated two pairs: Ln-Cu and Cu-Cu. Firstly, we used the isotropic Gd<sup>III</sup> ion to replace the central Ln<sup>III</sup> (Tb<sup>III</sup> or Dy<sup>III</sup>), and then we utilized one diamagnetic Zn<sup>II</sup> ions to take place of one of Cu<sup>II</sup> ions for each complex to calculate the Gd<sup>III</sup>-Cu<sup>II</sup> exchange coupling. For the Cu-Cu pair, the central Ln<sup>III</sup> ion was replaced with one diamagnetic Lu<sup>III</sup> ion. The large integration grid (grid = 6) was applied to Gd<sup>III</sup> and Cu<sup>II</sup> ions for ZORA calculations. Tight convergence criteria were selected to ensure the results to be well converged with respect to technical parameters. Through calculating the energies of two spin states: the high spin state ( $S_{HS} = S_{Gd} + S_{Cu}$  for Gd<sup>III</sup>-Cu<sup>II</sup> pair and  $S_{HS} = S_{Cu2} + S_{Cu1}$  for Cu<sup>II</sup>-Cu<sup>II</sup> pair, respectively) and the broken-symmetry state (flip the spin on Cu1<sup>II</sup>;  $S_{BS} = S_{Gd} - S_{Cu1}$  for Gd<sup>III</sup>-Cu<sup>II</sup> pair and  $S_{BS} = S_{Cu2} - S_{Cu1}$  for Cu<sup>II</sup>-Cu<sup>II</sup> pair, respectively), we obtained the isotropic Gd<sup>III</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> pair and  $S_{HS} = S_{Cu2} - S_{Cu1}$  for Cu<sup>II</sup>-Cu<sup>II</sup> pair, respectively), we obtained the isotropic Gd<sup>III</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> pair and  $S_{HS} = S_{Cu2} - S_{Cu1}$  for Cu<sup>II</sup>-Cu<sup>II</sup> pair, respectively), we obtained t

$$J_{i-j} = \frac{2(E_{BS} - E_{HS})}{S_{\max}^2}$$

The corresponding exchange Hamiltonian is:

)  
$$H = -J_{ij} \hat{S}_{i} \hat{S}_{j}$$

The formula to obtain the  $J_{Gd-Cu}$  and  $J_{Cu-Cu}$  can be expressed as following:

$$J_{Gd-Cu} = \frac{E_{BS} - E_{HS}}{8} \qquad \qquad J_{Cu-Cu} = 2(E_{BS} - E_{HS})$$

According to the rescaling equation proposed by Chibotaru and co-workers,<sup>12</sup> the corresponding  $J_{Dy-Cu}$  and  $J_{Tb-Cu}$  is equal to  $7/5J_{Gd-Cu}$  and  $7/6J_{Gd-Cu}$ , respectively. Additionally, we calculated  $Ln^{III}-Cu^{II}$  and  $Ln^{II}-Ln^{II}$  dipole-dipole interactions  $J_{dip}$  with respect to the spin  $\mathscr{K} = 1/2$  for  $Ln^{III}$  and  $Cu^{II}$  of two complexes within the Lines model,<sup>13</sup> which could be calculated exactly based on the calculated orientations of local anisotropy axes.

Table S5. Calculated Ln<sup>III</sup>-Cu<sup>II</sup> and Cu<sup>II</sup>-Cu<sup>II</sup> exchange coupling constants  $J_{\text{Ln-Cu}}$  (cm<sup>-1</sup>) with respect to the real spin ( $^{\mathscr{G}} = 5/2$  for Dy<sup>III</sup>,  $^{\mathscr{G}} = 3$  for Tb<sup>III</sup> and  $^{\mathscr{G}} = 1/2$  for Cu<sup>II</sup>, respectively) of the Ln<sup>III</sup> ions of complexes **1**·**Tb**<sub>6</sub>Cu<sub>6</sub> and **3**·**D**y<sub>6</sub>Cu<sub>6</sub> using BS-DFT method.

	1∙Tb <sub>6</sub> Cu <sub>6</sub>	3·Dy <sub>6</sub> Cu <sub>6</sub>	
$J_{ m Ln-Cu}$	2.01	1.59	
J <sub>Cu-Cu</sub>	6.03	1.41	

Table S6. Calculated  $Ln^{III}$ - $Cu^{II}$  and  $Ln^{II}$ - $Ln^{II}$  dipole-dipole interactions  $J_{dip}$  with respect to the spin  $\mathscr{I} = 1/2$  for  $Ln^{III}$  and  $Cu^{II}$  in  $1 \cdot Tb_6Cu_6$  and  $3 \cdot Dy_6Cu_6$  (cm<sup>-1</sup>).

		1∙Tb <sub>6</sub> Cu <sub>6</sub>	3·Dy <sub>6</sub> Cu <sub>6</sub>
Ln-Cu	$J_{ m dip}$	0.12	0.12
Ln-Ln	$J_{ m dip}$	-0.04	-0.02



Fig. S20 Labeled exchange coupling constants of the calculated model structure for complexes  $1 \cdot Tb_6Cu_6$  and  $3 \cdot Dy_6Cu_6$ .



Fig. S21 Orientations of the local main magnetic axes of the ground Kramers doublet on  $Dy^{III}$  along *c* axis (top) and *b* axis (bottom) of complexes  $1 \cdot Tb_6Cu_6$  (left) and  $3 \cdot Dy_6Cu_6$  (right). The green vectors represent the orientation of the calculated anisotropy axes, and the orange vectors represent the orthogonalized magnetic axes of the system.

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