

Electronic Supplementary Information

Solvent-tuned magnetic exchange interaction in Dy₂ system ligated by μ -phenolato heptadentate Schiff base

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1. X-ray crystallographic data

Table S1. Crystallographic Data for compounds **1-4**.

Compound ^a	1	2	3	4
Empirical formula	C ₅₄ H ₅₄ Dy ₂ N ₈ O ₆	C ₅₆ H ₅₈ Cl ₄ Dy ₂ N ₈ O ₆	C ₆₂ H ₆₄ Cl ₆ Dy ₂ N ₈ O ₈	C ₆₀ H ₆₀ Cl ₆ Dy ₂ N ₈ O ₈
Formula weight	1236.05	1405.90	1586.91	1558.86
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₍₁₎ / <i>n</i>	<i>P</i> 2 ₍₁₎ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₍₁₎ / <i>n</i>
<i>a</i> (Å)	11.211(3)	12.399(3)	11.675(2)	12.540(2)
<i>b</i> (Å)	18.586(5)	12.348(3)	12.589(2)	13.764(2)
<i>c</i> (Å)	11.571(3)	18.779(4)	13.298(2)	18.544(3)
<i>α</i> (°)	90.00	90.00	64.222(3)	90.00
<i>β</i> (°)	96.437(5)	98.274(4)	84.541(3)	98.178(3)
<i>γ</i> (°)	90.00	90.00	65.307(3)	90.00
<i>V</i> (Å ³)	2395.8(11)	2845.3(11)	1590.1(4)	3168.1(9)
<i>Z</i>	2	2	1	2
<i>F</i> (000)	1228	1396	790	1548
<i>R</i> 1 ^[a] , [<i>I</i> > 2σ(<i>I</i>)]	0.0792	0.0539	0.0502	0.0517
w <i>R</i> 2 ^[b] , [<i>I</i> > 2σ(<i>I</i>)]	0.1834	0.1279	0.1184	0.0889
<i>R</i> 1 ^a , (all data)	0.1139	0.1064	0.0666	0.1042
w <i>R</i> 2 ^b , (all data)	0.2021	0.1622	0.1411	0.1056
GOF on <i>F</i> ²	1.107	1.004	1.041	0.980

$${}^aR_1 = \Sigma(F_o - F_c)/\Sigma F_o, {}^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$$

Table S2. Selected bond lengths and angles for compounds **1-4**.

1					
Dy(1)-O(1)	2.226(7)	O(2) ⁱ -Dy(1)-N(1)	143.5(3)	O(2)-Dy(1)-N(1)	113.2(3)
Dy(1)-O(2)	2.349(7)	O(1)-Dy(1)-N(4) ⁱ	75.6(3)	N(4) ⁱ -Dy(1)-N(3) ⁱ	66.0(3)
Dy(1)-N(1)	2.485(9)	O(3) ⁱ -Dy(1)-N(4) ⁱ	72.3(3)	O(1)-Dy(1)-N(2)	110.6(3)
Dy(1)-N(2)	2.784(8)	O(2) ⁱ -Dy(1)-N(4) ⁱ	115.5(3)	O(3) ⁱ -Dy(1)-N(2)	81.3(3)
Dy(1)-O(3) ⁱ	2.239(8)	O(2)-Dy(1)-N(4) ⁱ	142.7(3)	O(2) ⁱ -Dy(1)-N(2)	83.0(2)
Dy(1)-O(2) ⁱ	2.332(7)	N(1)-Dy(1)-N(4) ⁱ	85.1(3)	O(2)-Dy(1)-N(2)	71.1(2)
Dy(1)-N(4) ⁱ	2.483(9)	O(1)-Dy(1)-N(3) ⁱ	80.9(3)	N(1)-Dy(1)-N(2)	65.2(3)
Dy(1)-N(3) ⁱ	2.771(8)	O(3) ⁱ -Dy(1)-N(3) ⁱ	111.2(3)	N(4) ⁱ -Dy(1)-N(2)	144.3(3)
O(1)-Dy(1)-O(3) ⁱ	136.3(3)	O(2) ⁱ -Dy(1)-N(3) ⁱ	71.0(2)	N(3) ⁱ -Dy(1)-N(2)	148.5(2)
O(1)-Dy(1)-O(2) ⁱ	139.9(2)	O(2)-Dy(1)-N(3) ⁱ	82.9(2)	O(1)-Dy(1)-N(1)	72.0(3)
O(3) ⁱ -Dy(1)-O(2) ⁱ	81.7(3)	N(1)-Dy(1)-N(3) ⁱ	144.5(3)	O(3) ⁱ -Dy(1)-N(1)	76.4(3)
O(1)-Dy(1)-O(2)	79.7(3)	O(3) ⁱ -Dy(1)-O(2)	141.6(3)	O(2) ⁱ -Dy(1)-O(2)	69.2(3)
ⁱ -x,-y,-z					
2					

Dy(1)-O(1)	2.307(6)	O(3)-Dy(1)-O(1) ⁱ	139.1(2)	O(3)-Dy(1)-N(2)	80.1(2)
Dy(1)-O(2)	2.233(7)	O(1)-Dy(1)-O(1) ⁱ	69.4(3)	O(1)-Dy(1)-N(2)	83.0(2)
Dy(1)-O(3)	2.224(7)	O(3)-Dy(1)-N(1)	77.6(3)	O(1) ⁱ -Dy(1)-N(2)	71.1(2)
Dy(1)-O(1) ⁱ	2.322(6)	O(2)-Dy(1)-N(1)	72.2(3)	N(1)-Dy(1)-N(2)	66.5(3)
Dy(1)-N(1)	2.479(8)	O(1)-Dy(1)-N(1)	144.2(3)	N(4)-Dy(1)-N(2)	143.3(3)
Dy(1)-N(4)	2.501(9)	O(1) ⁱ -Dy(1)-N(1)	114.4(2)	O(3)-Dy(1)-N(3)	111.0(2)
Dy(1)-N(2)	2.754(8)	O(3)-Dy(1)-N(4)	72.3(3)	O(2)-Dy(1)-N(3)	80.5(2)
Dy(1)-N(3)	2.773(8)	O(2)-Dy(1)-N(4)	77.6(3)	O(1)-Dy(1)-N(3)	70.7(2)
O(3)-Dy(1)-O(2)	139.0(2)	O(1)-Dy(1)-N(4)	113.8(2)	O(1) ⁱ -Dy(1)-N(3)	82.8(2)
O(3)-Dy(1)-O(1)	79.0(2)	O(1) ⁱ -Dy(1)-N(4)	144.4(3)	N(1)-Dy(1)-N(3)	143.7(3)
O(2)-Dy(1)-O(1)	139.8(2)	N(1)-Dy(1)-N(4)	84.1(3)	N(4)-Dy(1)-N(3)	66.7(3)
O(2)-Dy(1)-O(1) ⁱ	79.8(2)	O(2)-Dy(1)-N(2)	111.2(2)	N(2)-Dy(1)-N(3)	148.1(2)
ⁱ -x,-y+2,-z					
3					
Dy(1)-O(1) ⁱ	2.227(5)	O(3)-Dy(1)-O(2) ⁱ	140.29(19)	O(3)-Dy(1)-N(2)	110.2(2)
Dy(1)-O(3)	2.226(6)	O(2)-Dy(1)-O(2) ⁱ	69.5(2)	O(2)-Dy(1)-N(2)	71.25(18)
Dy(1)-O(2)	2.311(5)	O(1) ⁱ -Dy(1)-N(1)	75.4(2)	O(2) ⁱ -Dy(1)-N(2)	83.43(19)
Dy(1)-O(2) ⁱ	2.347(6)	O(3)-Dy(1)-N(1)	72.2(2)	N(1)-Dy(1)-N(2)	66.8(2)
Dy(1)-N(1)	2.466(7)	O(2)-Dy(1)-N(1)	115.8(2)	N(4) ⁱ -Dy(1)-N(2)	144.0(2)
Dy(1)-N(4) ⁱ	2.488(7)	O(2) ⁱ -Dy(1)-N(1)	144.0(2)	O(1) ⁱ -Dy(1)-N(3) ⁱ	112.0(2)
Dy(1)-N(2)	2.729(7)	O(1) ⁱ -Dy(1)-N(4) ⁱ	71.5(2)	O(3)-Dy(1)-N(3) ⁱ	80.7(2)
Dy(1)-N(3) ⁱ	2.763(7)	O(3)-Dy(1)-N(4) ⁱ	78.4(2)	O(2)-Dy(1)-N(3) ⁱ	82.36(19)
O(1) ⁱ -Dy(1)-O(3)	137.4(2)	O(2)-Dy(1)-N(4) ⁱ	143.8(2)	O(2) ⁱ -Dy(1)-N(3) ⁱ	71.09(19)
O(1) ⁱ -Dy(1)-O(2)	140.3(2)	O(2) ⁱ -Dy(1)-N(4) ⁱ	112.8(2)	N(1)-Dy(1)-N(3) ⁱ	143.1(2)
O(3)-Dy(1)-O(2)	79.7(2)	N(1)-Dy(1)-N(4) ⁱ	84.1(2)	N(4) ⁱ -Dy(1)-N(3) ⁱ	65.9(2)
O(1) ⁱ -Dy(1)-O(2) ⁱ	80.32(19)	O(1) ⁱ -Dy(1)-N(2)	80.5(2)	N(2)-Dy(1)-N(3) ⁱ	148.5(2)
ⁱ -x,-y+2,-z					
4					
Dy(1)-O(3)	2.214(5)	O(1)-Dy(1)-O(2) ⁱ	138.80(16)	O(1)-Dy(1)-N(1)	111.50(18)
Dy(1)-O(1)	2.228(5)	O(2)-Dy(1)-O(2) ⁱ	69.4(2)	O(2)-Dy(1)-N(1)	71.23(17)
Dy(1)-O(2)	2.316(5)	O(3)-Dy(1)-N(2)	78.02(19)	O(2) ⁱ -Dy(1)-N(1)	83.36(17)
Dy(1)-O(2) ⁱ	2.322(5)	O(1)-Dy(1)-N(2)	71.84(19)	N(2)-Dy(1)-N(1)	66.37(19)
Dy(1)-N(2)	2.496(6)	O(2)-Dy(1)-N(2)	113.31(19)	N(3)-Dy(1)-N(1)	142.60(19)
Dy(1)-N(3)	2.496(6)	O(2) ⁱ -Dy(1)-N(2)	145.16(19)	O(3)-Dy(1)-N(4)	112.11(19)
Dy(1)-N(1)	2.751(6)	O(3)-Dy(1)-N(3)	71.6(2)	O(1)-Dy(1)-N(4)	79.65(18)
Dy(1)-N(4)	2.789(6)	O(1)-Dy(1)-N(3)	79.22(19)	O(2)-Dy(1)-N(4)	83.07(17)
O(3)-Dy(1)-O(1)	139.42(17)	O(2)-Dy(1)-N(3)	145.35(19)	O(2) ⁱ -Dy(1)-N(4)	70.88(17)
O(3)-Dy(1)-O(2)	138.89(17)	O(2) ⁱ -Dy(1)-N(3)	112.71(18)	N(2)-Dy(1)-N(4)	142.98(19)
O(1)-Dy(1)-O(2)	79.23(17)	N(2)-Dy(1)-N(3)	85.0(2)	N(3)-Dy(1)-N(4)	66.56(19)
O(3)-Dy(1)-O(2) ⁱ	79.71(17)	O(3)-Dy(1)-N(1)	79.06(19)	N(1)-Dy(1)-N(4)	148.75(17)

$i-x+1,-y+2,-z+1$

Table S3. The calculated results for Dy^{III} ions configuration of compounds **1-4** by SHAPE 2.1 software.

Configuration	ABOXIY, 1	ABOXIY, 2	ABOXIY, 3	ABOXIY, 4
Hexagonal bipyramid (D_{6h})	16.243	15.848	16.139	15.883
Cube (O_h)	11.002	10.334	10.570	9.962
Square antiprism (D_{4d})	1.423	1.318	1.268	1.389
Triangulardodecahedron (D_{2d})	3.353	3.449	3.252	3.357
Johnson gyrobifastigium J26 (D_{2d})	17.223	17.710	17.043	17.539
Johnson elongated triangular bipyramid J14 (D_{3h})	25.811	25.929	25.832	25.479
Biaugmented trigonal prism J50 (C_{2v})	4.109	4.011	3.885	3.933
Biaugmented trigonal prism (C_{2v})	3.402	3.338	3.101	3.486
Snub sphenoid J84 (D_{2d})	6.584	6.499	6.202	6.408

2. The ¹H NMR and ¹³C NMR spectra of Ligand

2.1 The ¹H NMR and ¹³C{¹H} spectra of ligand H₃api

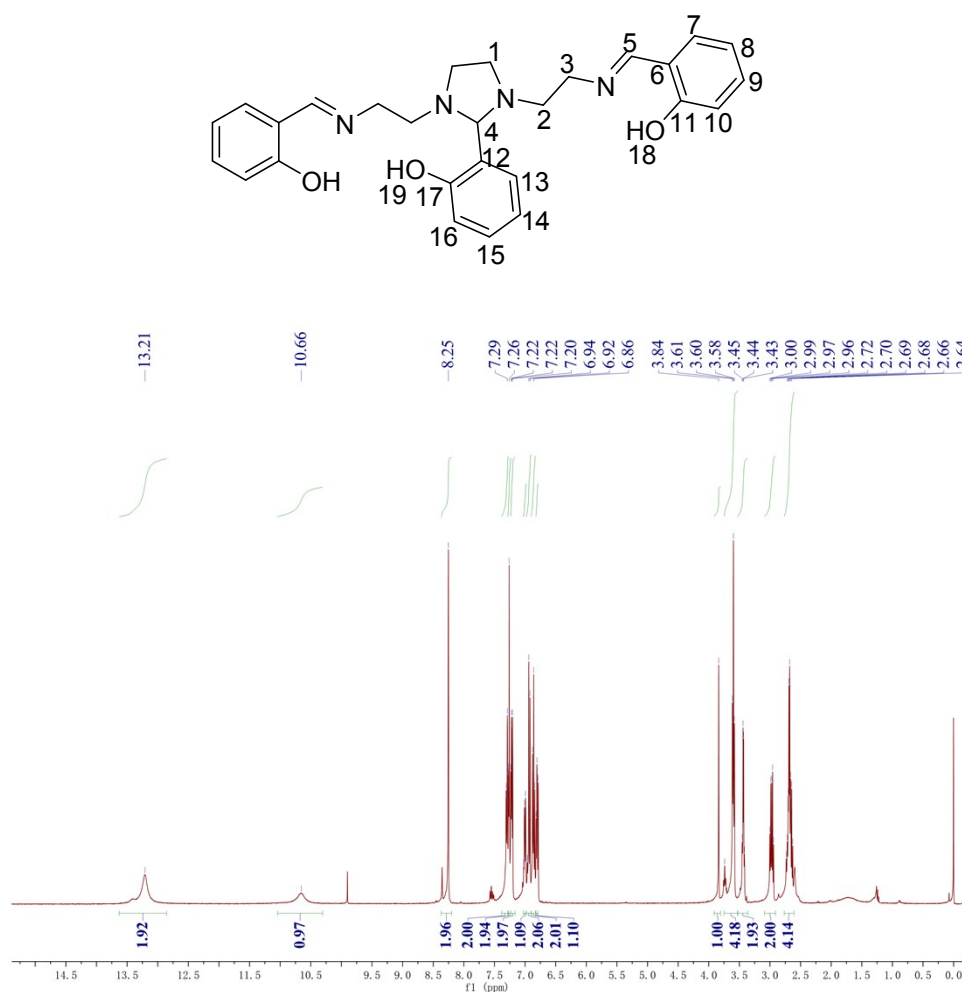


Fig. S1 ^1H -NMR spectra of ligand H_3api .

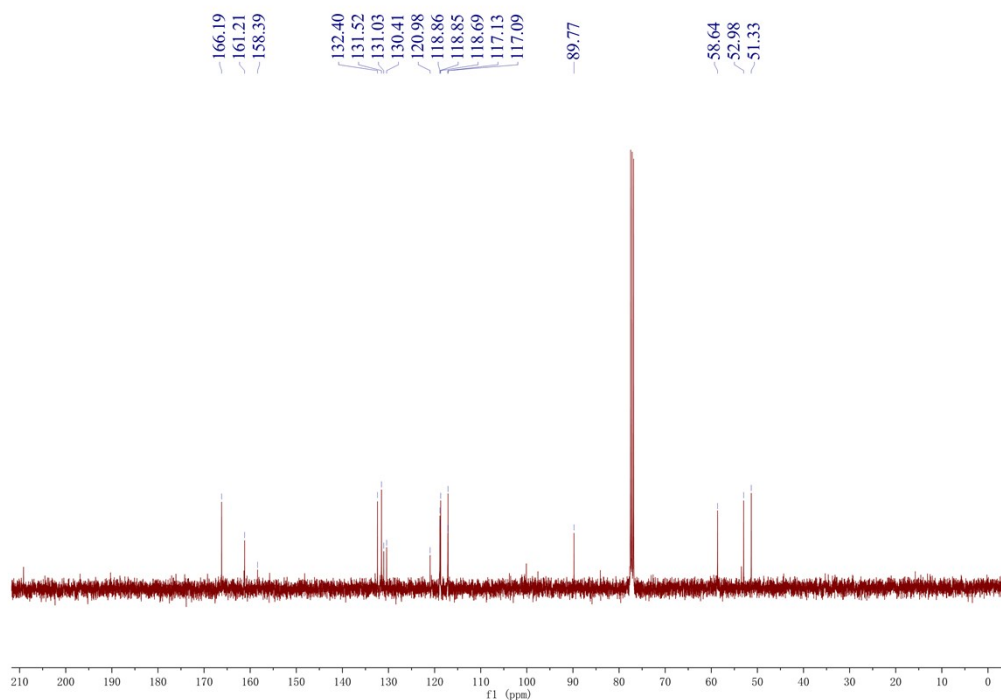
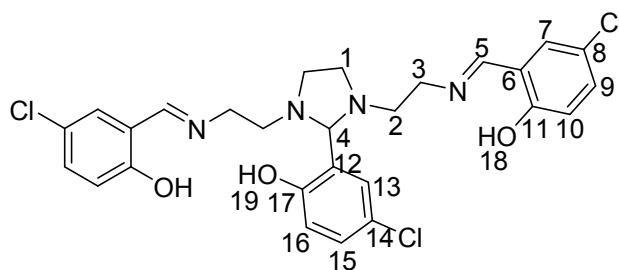


Fig. S2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of ligand H_3api .

2.2 The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ spectra of ligand H_3Clapi



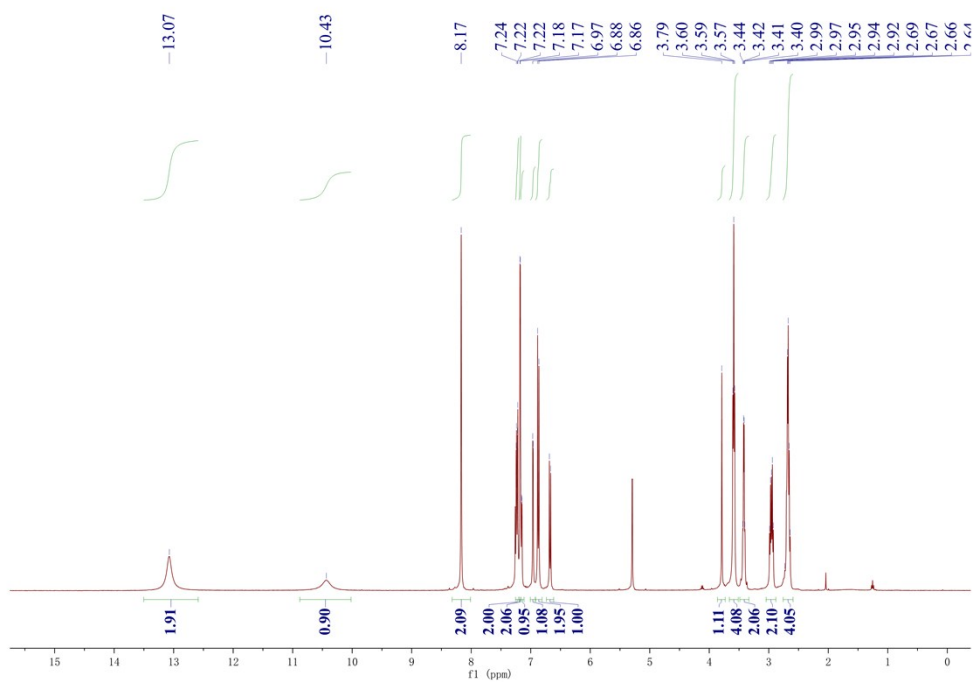


Fig. S3 ^1H -NMR spectra of ligand H_3Clapi .

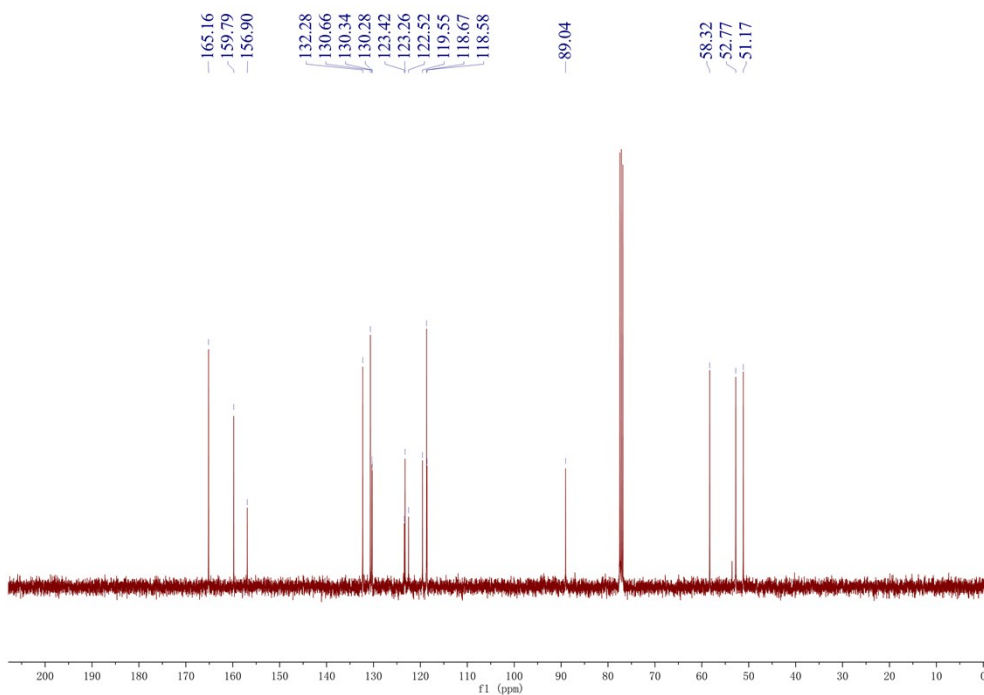


Fig. S4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of ligand H_3api .

3. X-Ray Powder Diffraction

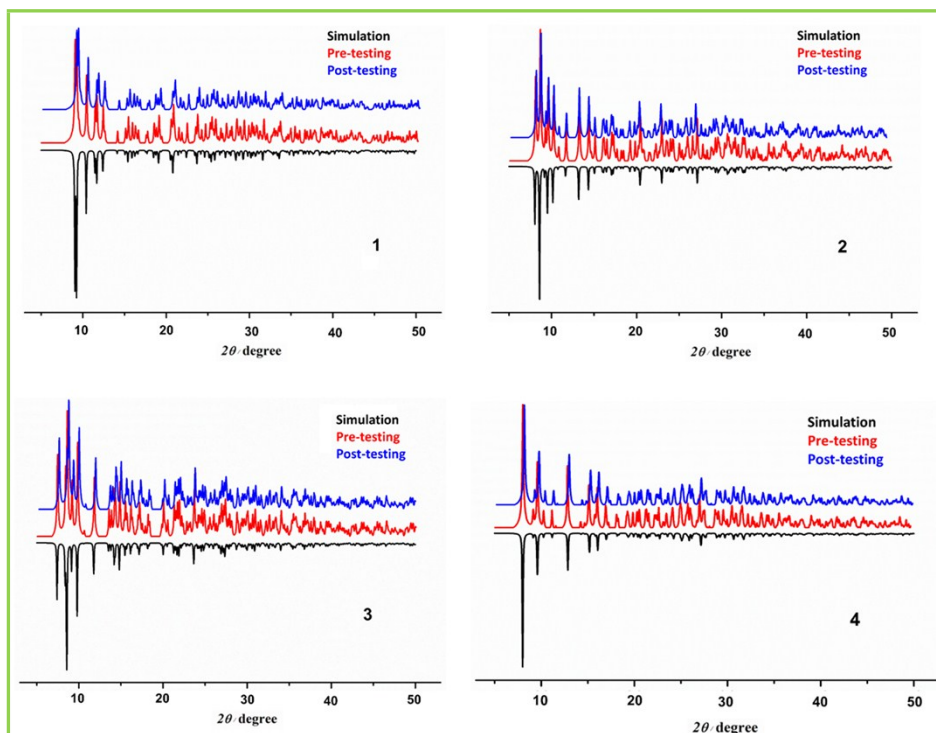


Fig. S5 Experimental and simulated PXRD of compounds 1-4.

4. Thermogravimetric analyses

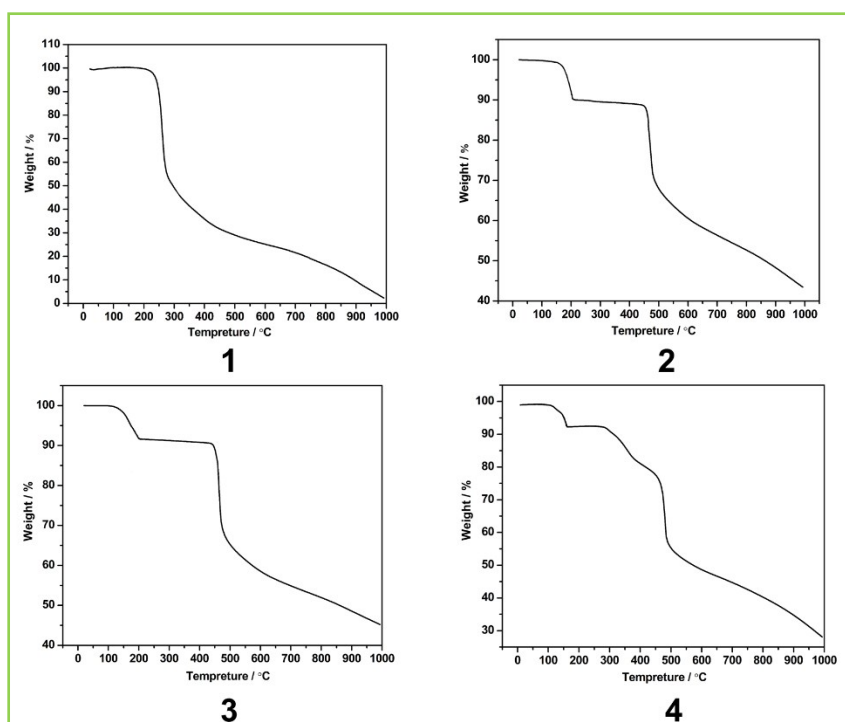


Fig. S6 Thermogravimetric analyses curve of compounds 1-4.

5. Crystal Structure

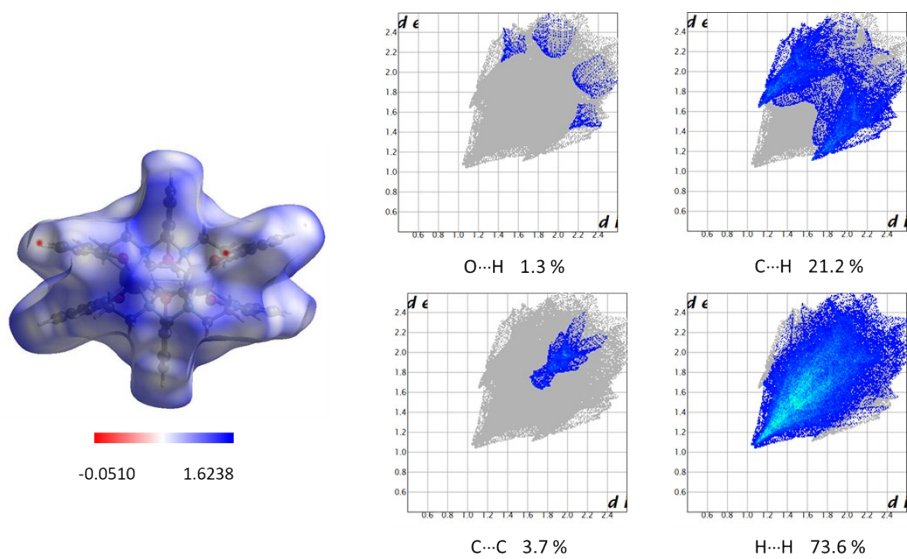


Fig. S7 The 3D Hirshfeld surface analysis and 2D fingerprint plot of compound 1.

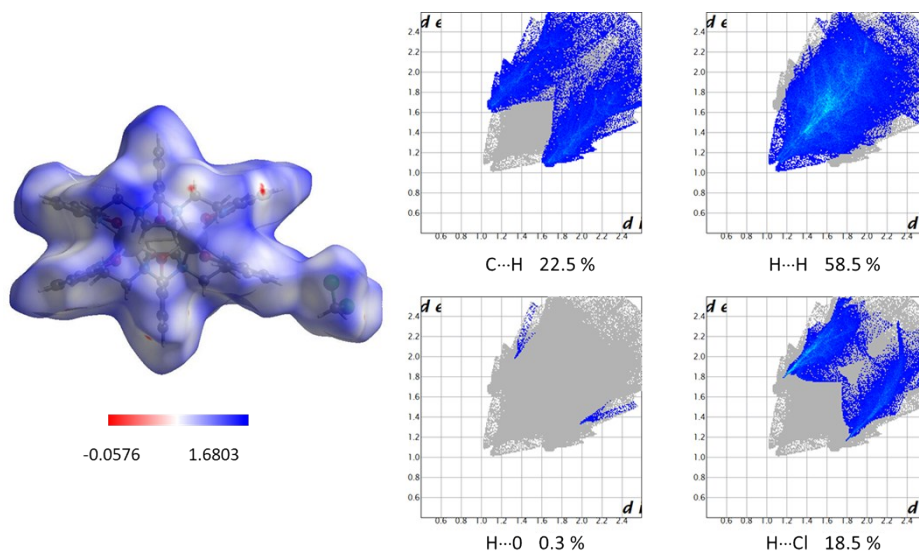


Fig. S8 The 3D Hirshfeld surface analysis and 2D fingerprint plot of compound 2.

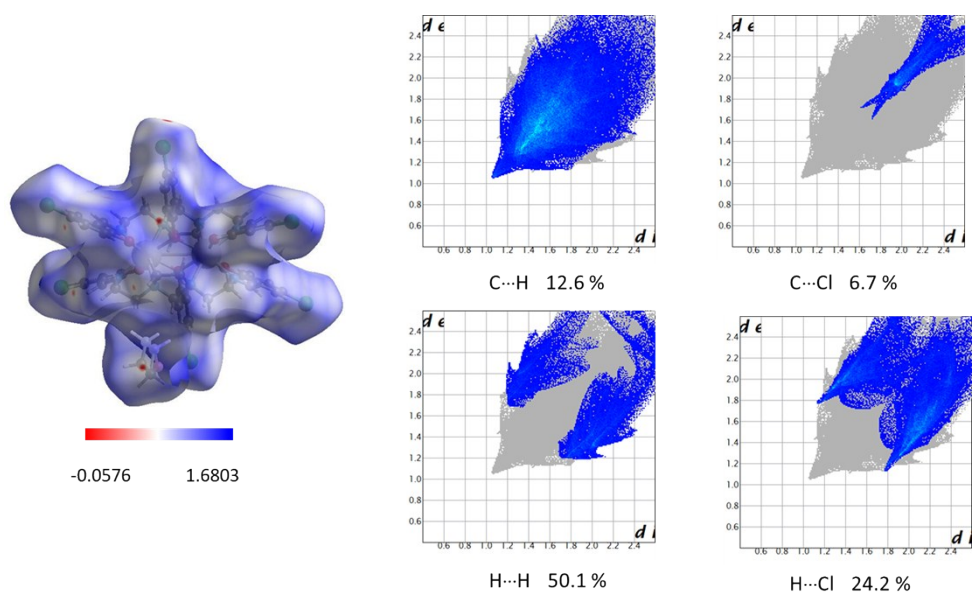


Fig. S9 The 3D Hirshfeld surface analysis and 2D fingerprint plot of compound 3.

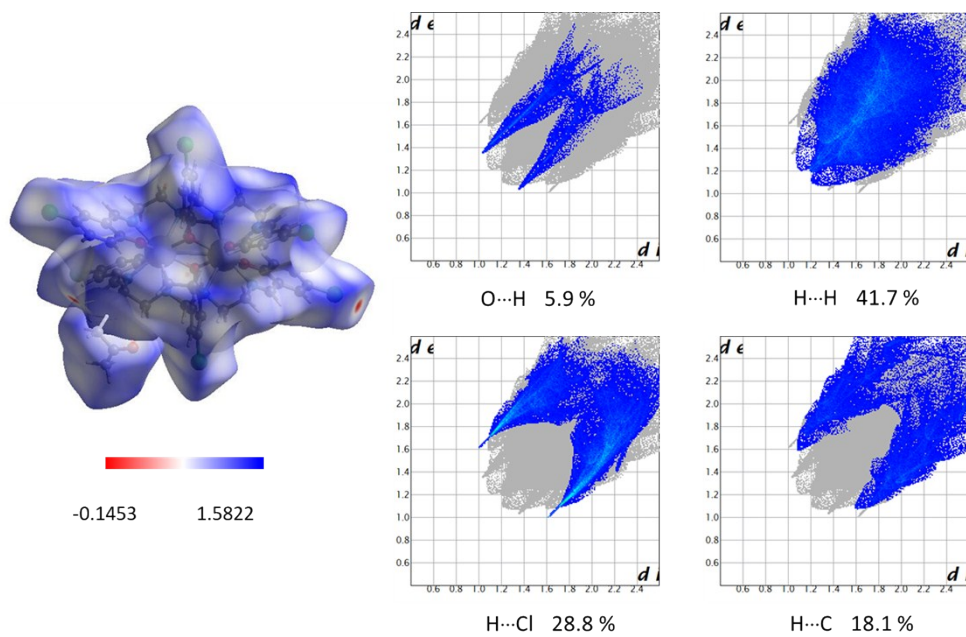


Fig. S10 The 3D Hirshfeld surface analysis and 2D fingerprint plot of compound 4.

6. Magnetic Measurements

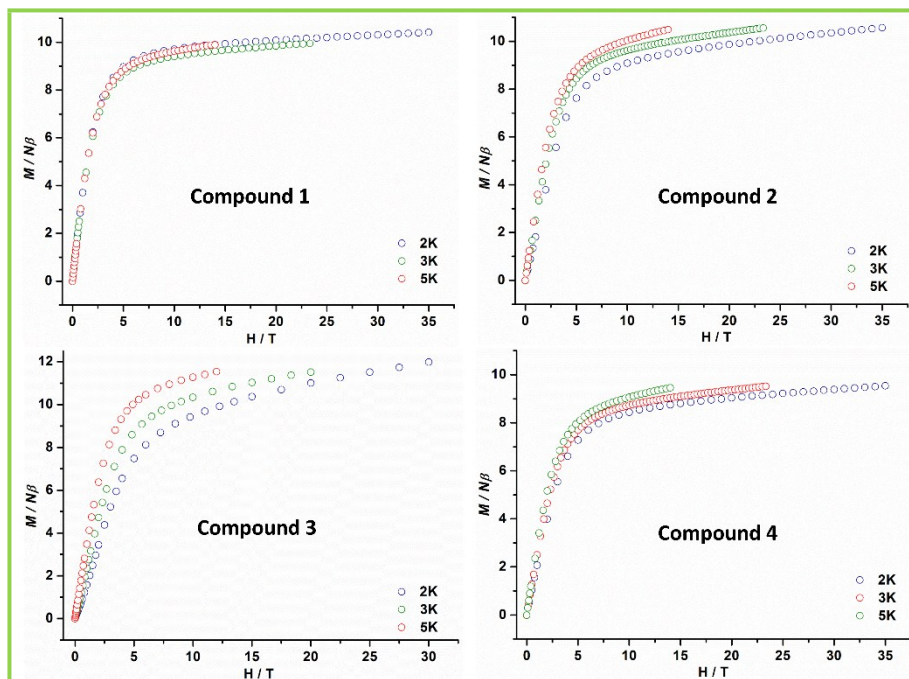


Fig. S11 Experimental M versus H/T plots of compounds **1**, **2**, **3** and **4** measured at 2.0 K, 3.0 K and 5.0 K.

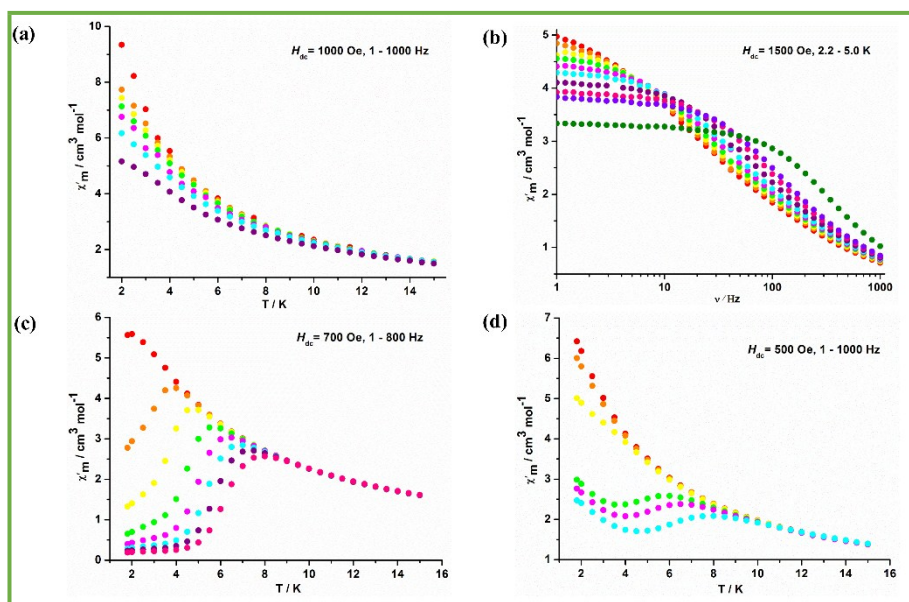


Fig. S12 Temperature dependence of the in-phase ac susceptibility signals under 1000 Oe dc field for **1**, 1500 Oe dc field for **2**, 700 Oe dc field for **3**, 500 Oe dc field for **4**.

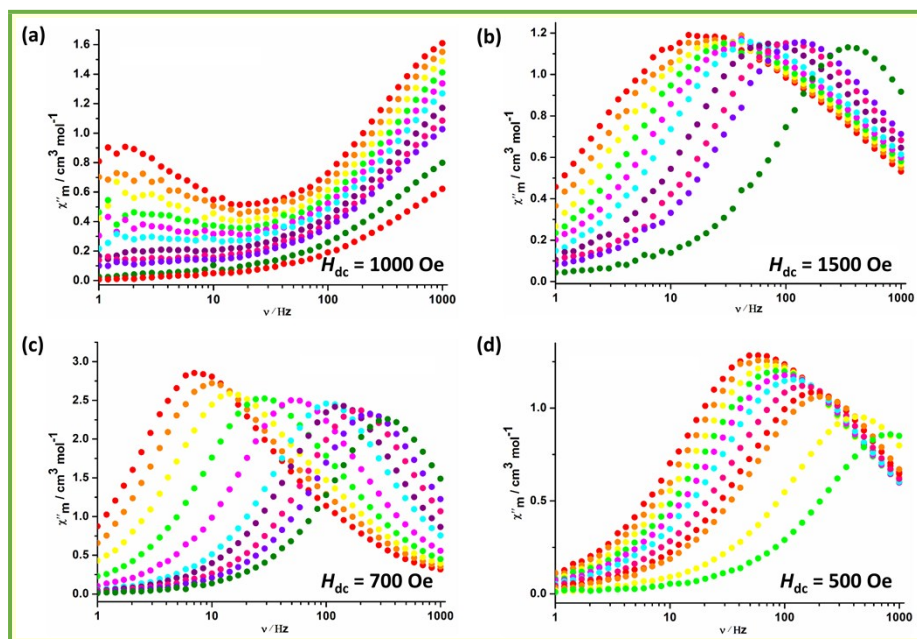


Fig. S13 Frequency dependence of the out-phase ac susceptibility signals under 1000 Oe dc field for **1**, 1500 Oe dc field for **2**, 700 Oe dc field for **3**, 500 Oe dc field for **4**.

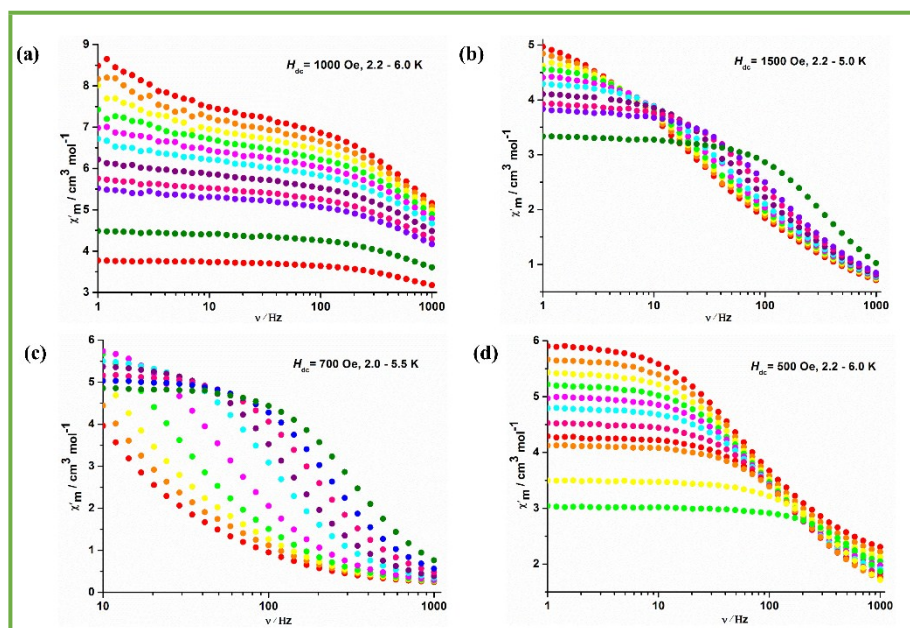


Fig. S14 Frequency dependence of the in-phase ac susceptibility signals under 1000 Oe dc field for **1**, 1500 Oe dc field for **2**, 700 Oe dc field for **3**, 500 Oe dc field for **4**.

Table S4 Selected parameters from the fitting results of the Cole-Cole plots for **2** ($H_{dc} = 1500$ Oe), **3** ($H_{dc} = 700$ Oe) and **4** ($H_{dc} = 500$ Oe).

2, $H_{dc} = 1500$ Oe

T (K)	τ	a	residual
2.2	6.23E-03	0.478	1.03E-01
2.4	5.10E-03	0.460	1.34E-01
2.6	4.13 E-03	0.433	1.78E-01
2.8	3.4E-03	0.407	1.88E-01
3.0	2.73E-03	0.374	1.75E-01
3.2	2.26E-03	0.344	1.68E-01
3.5	1.68E-03	0.303	1.41E-01
3.8	1.25E-03	0.263	8.80E-02
4.0	1.03E-03	0.244	6.20E-02
5.0	4.15E-04	0.180	1.66E-02
3, $H_{dc} = 700$ Oe			
T (K)	τ	a	residual
2.0	1.69E-02	0.230	1.01
2.5	1.26E-02	0.232	1.13
3.0	8.21E-03	0.205	9.37E-01
3.5	4.73E-03	0.150	5.26E-01
4.0	2.61E-03	9.57E-02	2.12E-01
4.5	1.44E-03	5.82E-02	8.03E-02
4.7	1.14E-03	4.88E-02	5.55E-02
5.0	8.05E-04	3.78E-02	3.73E-02
5.2	6.43E-04	3.24E-02	2.55E-02
5.5	4.63E-04	2.59E-02	1.81E-02
4, $H_{dc} = 500$ Oe			
T (K)	τ	a	residual
2.2	2.10E-03	2.84E-01	1.85E-01
2.4	1.94E-03	2.66E-01	1.45E-01
2.6	1.76E-03	2.52E-01	1.10E-01
2.8	1.58E-03	2.40E-01	7.96E-02
3.0	1.41E-03	2.27E-01	6.18E-02
3.2	1.24E-03	2.14E-01	4.55E-02
3.5	1.02E-03	1.98E-01	2.90E-02
3.8	8.31E-04	1.84E-01	1.96E-02
4.0	7.23E-04	1.75E-01	1.41E-02
5.0	3.61E-04	1.45E-01	4.18E-03
6.0	1.82E-04	1.36E-01	3.07E-03

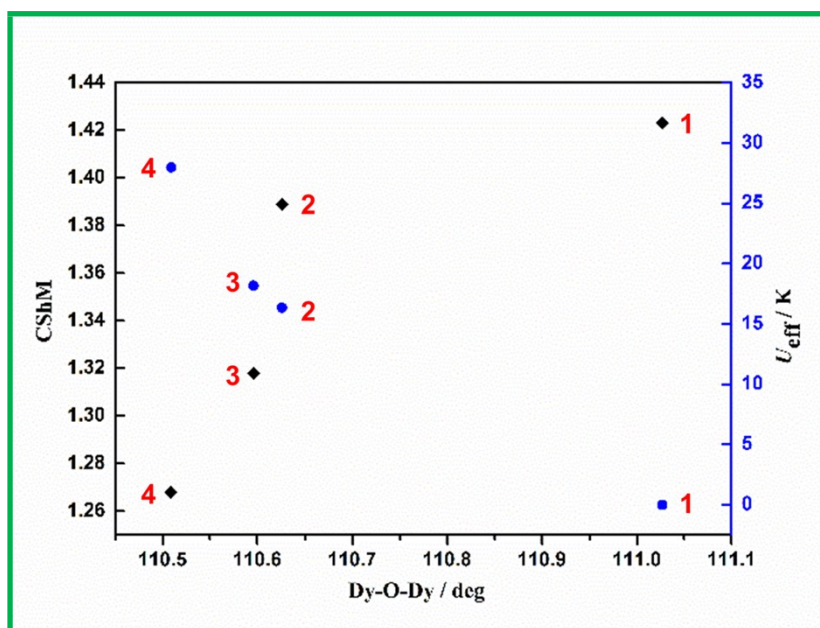


Fig. S15 Dy-O-Dy(deg) vs. CShM, U_{eff} for compounds **1-4**.

7. Computational details

Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{III} fragment of the complete structures (see Figure S21 for the complete structure of compound **1**; see Figure S23 for the other three complete fragments) on the basis of single-crystal X-ray determined geometry have been carried out with MOLCAS 8.0 program package.^{S1} The dinuclear compounds **1-4** have an inversion center, thus only one magnetic center is calculated. During the calculations, the other Dy^{III} ion was replaced by diamagnetic Lu^{III}. The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Dy^{III} ions; VTZ for close O and N; VDZ for distant atoms. 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 couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For the fragment of individual Dy^{III} ion, active electrons in 7 active spaces include all f electrons (CAS (9 in 7)) 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, 130 from 490 doublets for the Dy^{III} fragment).

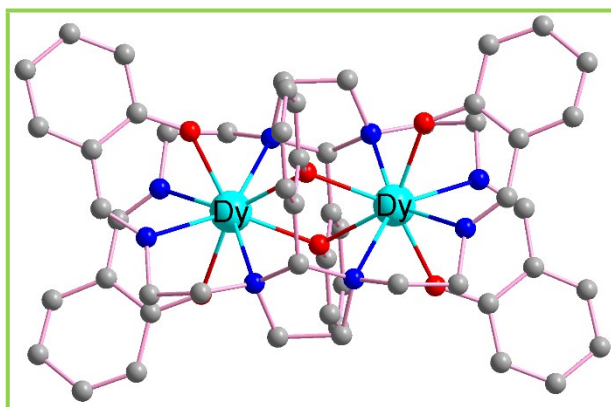


Fig. S16 Calculated complete structures for compound **1**; H atoms are omitted.

To fit the exchange interaction in four compounds, we took two steps to obtain them. Firstly, we calculated one Dy^{III} fragment using CASSCF to obtain the corresponding magnetic properties. And then, the exchange interaction between the magnetic centers is considered within the Lines model,^{S2} while the account of the dipole-dipole magnetic coupling is treated exactly. The Lines model is effective and has been successfully used widely in the research field of f-element single-molecule magnets.^{S3}

For compounds **1-4**, there is only one type of J .

The exchange Hamiltonian is:

$$\hat{H}_{exch} = -J_{total} \hat{S}_{Dy1}^y \hat{S}_{Dy1'}^y \quad (S1)$$

The J_{total} is the parameter of the total magnetic interaction ($J_{total} = J_{dipolar} + J_{exchange}$) between magnetic center ions. The $\hat{S}_{Dy}^y = \pm 1/2$ are the ground pseudospin on the Dy^{III} sites. The dipolar magnetic coupling can be calculated exactly, while the exchange coupling constants were fitted through comparison of the computed and measured magnetic susceptibility and molar magnetization using the POLY_ANISO program.^{S4}

Table S5 Calculated energy levels (cm⁻¹), g (g_x , g_y , g_z) tensors and m_J values of the lowest Kramers doublets (KDs) of one Dy^{III} center for compounds **1-4**.

KDs	m_J	1		2		3		4	
		E/cm^{-1}	g	E/cm^{-1}	g	E/cm^{-1}	g	E/cm^{-1}	g
1	$\pm 15/2$	0.0	0.040	0.0	0.062	0.0	0.079	0.0	0.052
			0.098		0.154		0.209		0.128
			18.743		18.714		18.537		18.775
2	$\pm 13/2$	99.8	0.455	103.6	0.582	91.0	0.661	106.3	0.499

			0.691 14.805		0.834 14.854		0.938 14.541		0.704 14.986
3	$\pm 11/2$	195.3	1.707 1.930 11.853	210.9	2.347 2.476 11.468	188.7	2.274 2.544 11.329	217.7	2.208 2.244 11.655
4	$\pm 9/2$	296.4	4.550 5.352 7.748	317.9	4.976 5.683 7.208	289.3	4.611 5.779 7.391	326.2	5.102 5.739 7.155
5	$\pm 3/2$	386.4	2.277 2.862 10.608	419.2	1.492 1.910 11.123	385.1	1.546 2.158 11.211	425.6	1.699 1.967 11.013
6	$\pm 1/2$	495.4	0.688 1.026 14.620	540.0	0.457 0.660 14.676	500.7	0.476 0.696 14.815	543.6	0.430 0.626 14.649
7	$\pm 5/2$	649.6	0.026 0.049 16.872	701.7	0.013 0.027 16.922	662.3	0.009 0.037 16.861	703.0	0.016 0.025 16.950
8	$\pm 7/2$	745.0	0.017 0.030 19.226	814.0	0.012 0.018 19.319	763.5	0.016 0.029 19.200	816.2	0.009 0.013 19.359

Table S6 Exchange energies (cm^{-1}) and main values of the g_z for the lowest two exchange doublets of compounds **1-4**.

	1		2		3		4	
	E	g_z	E	g_z	E	g_z	E	g_z
1	0.0	0.000	0.0	0.000	0.0	0.000	0.0	0.000
2	0.3	37.484	1.8	37.424	1.4	37.071	1.1	37.548

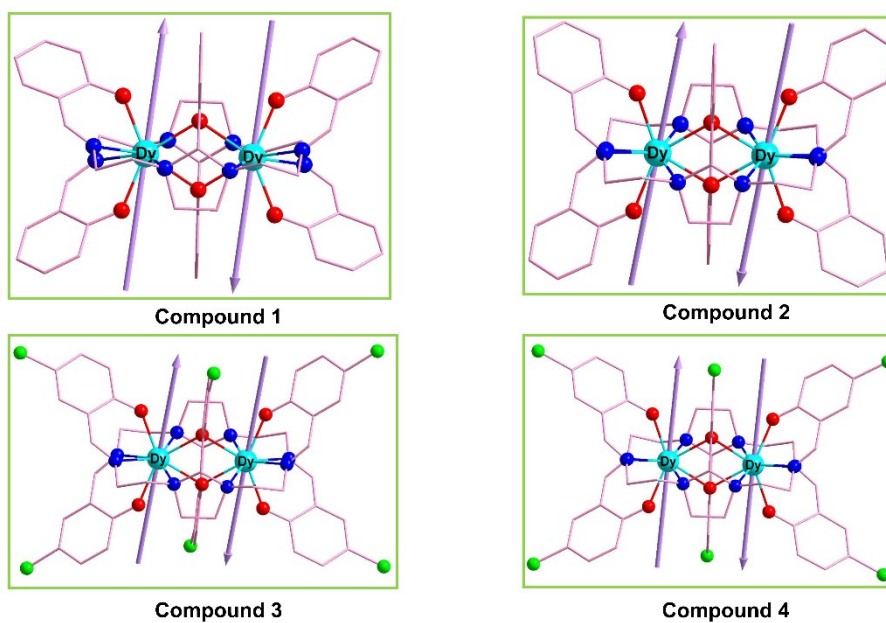


Fig. S17 Orientations of the local main magnetic axes of the ground doublets on Dy^{III} ion of compounds 1-4.

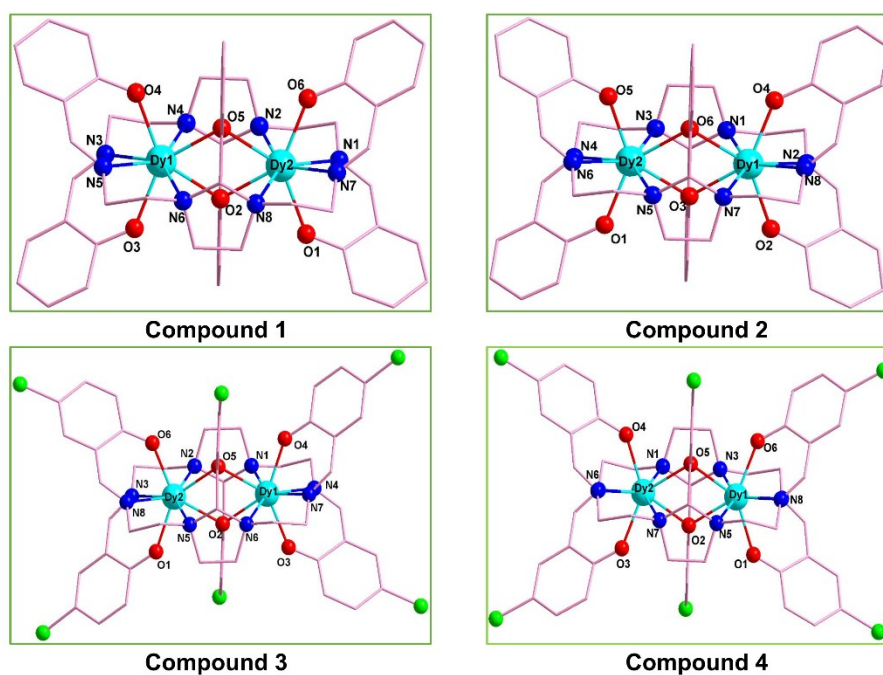


Fig. S18 Labeled molecular structures of compounds 1-4.

Table S7 Natural Bond Order (NBO) charges per atom in the ground state of compounds 1-4 calculated within CASSCF.

Compound	1	2	3	4
Dy1	2.476	2.476	2.477	2.479
O1	-0.813	-0.826	-0.808	-0.815
O1'	-0.817	-0.830	-0.819	-0.816

O2	-0.874	-0.885	-0.867	-0.883
O3	-0.855	-0.848	-0.863	-0.874
N1	-0.314	-0.324	-0.316	-0.319
N2	-0.411	-0.418	-0.430	-0.415
N3	-0.413	-0.426	-0.412	-0.400
N4	-0.314	-0.309	-0.315	-0.316

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