Structurally modulated single- ion magnets of mononuclear β-diketone dysprosium(III) Complexes

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Scheme S1 Synthesis of intermediate products and target ligands.

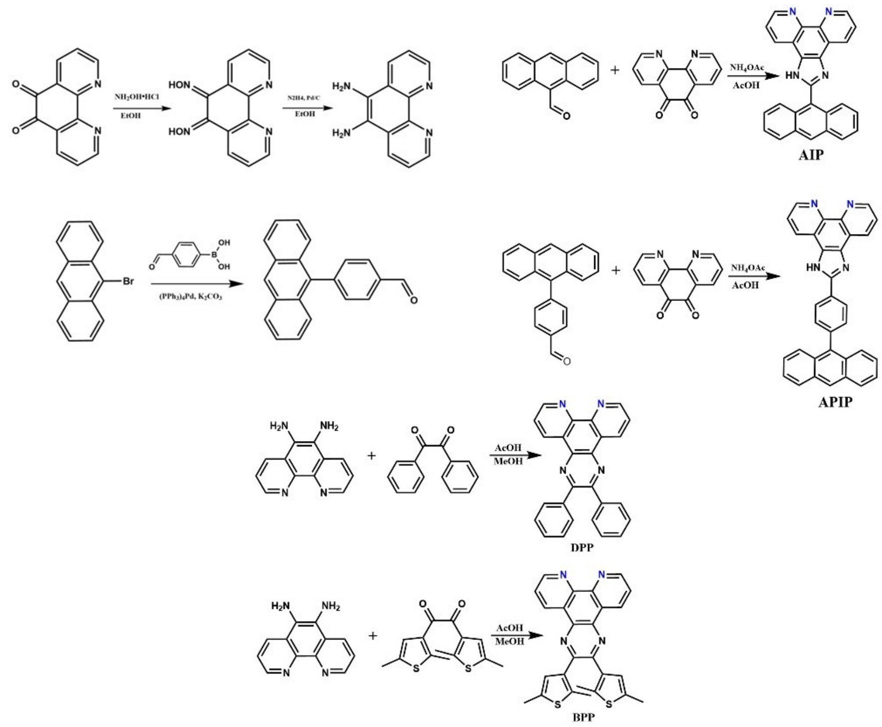


Table S1 Crystal Data and crystallographic refinement parameters for **1**, **2**, **3**, **4** and **5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{52}H_{32}DyF_9N_4O_7S_3$	$C_{59}H_{42}DyF_9N_4O_9S_3$	$C_{50}H_{28}DyF_9N_4O_6S_3$	$C_{51}H_{35}DyF_9N_4O_{6.5}S_5$	$C_{102}H_{60}Dy_2F_{18}N_8O_{15}S_6$
Formula weight	1254.50	1380.65	1210.44	1301.63	2496.94
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic,	Monoclinic
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$C2/c$
T / K	193 K	193 K	193 K	153 K	296
a (Å)	13.6667(12)	10.6671(2)	10.1831(12)	10.5518(11)	13.6952(11)
b (Å)	19.2642(18)	25.8281(6)	22.233(3)	21.069(2)	19.2367(14)
c (Å)	41.493(4)	20.6774(4)	21.689(3)	24.247(2)	41.347(3)
α (º)	90	90	90	90	90
β (º)	91.986(5)	102.3810(10)	101.119(5)	90	92.205(2)
γ (º)	90	90	90	90	90
V (Å^3)	10917.8(17)	5564.4(2)	4818.3(10)	5390.5(9)	10884.8(14)
Z	8	4	4	4	4
F (000)	4984	2764	2396	2592	4952.0
GOF on F^2	1.139	1.056	1.097	1.012	1.099
R_1/WR_2 [$I>2\sigma(I)$]	0.1039/0.2205	0.0656/0.1698	0.0581/0.1601	0.0416/0.1039	0.0921/0.2255
R_1/WR_2 [all data]	0.1580/0.2428	0.1113/0.1850	0.0659/0.1641	0.0504/0.1079	0.1437/0.2376
CCDC	1994052	1994051	1994050	1994048	2033641

Table S2 Selected bond lengths (Å) for **1**, **2**, **3** and **4**.

1 / Å		**2 / Å**		**3 / Å**		**4 / Å**	
Dy(1)-O(1)	2.334(17)	Dy(1)-O(1)	2.321(5)	Dy(1)-O(1)	2.314(5)	Dy(1)-O(1)	2.288(5)
Dy(1)-O(2)	2.339(13)	Dy(1)-O(2)	2.302(5)	Dy(1)-O(2)	2.347(5)	Dy(1)-O(2)	2.353(5)
Dy(1)-O(3)	2.288(13)	Dy(1)-O(3)	2.335(5)	Dy(1)-O(3)	2.326(5)	Dy(1)-O(3)	2.294(5)
Dy(1)-O(4)	2.338(12)	Dy(1)-O(4)	2.328(6)	Dy(1)-O(4)	2.330(5)	Dy(1)-O(4)	2.344(5)
Dy(1)-O(5)	2.326(15)	Dy(1)-O(5)	2.337(5)	Dy(1)-O(5)	2.314(5)	Dy(1)-O(5)	2.335(5)
Dy(1)-O(6)	2.345(19)	Dy(1)-O(6)	2.319(5)	Dy(1)-O(6)	2.323(4)	Dy(1)-O(6)	2.302(5)
Dy(1)-N(3)	2.550(15)	Dy(1)-N(3)	2.571(6)	Dy(1)-N(3)	2.544(6)	Dy(1)-N(3)	2.590(6)
Dy(1)-N(4)	2.584(13)	Dy(1)-N(4)	2.555(6)	Dy(1)-N(4)	2.541(6)	Dy(1)-N(4)	2.569(6)

Table S3 Selected bond angles (°) for **1**, **2**, **3** and **4**.

1 / °		**2 / °**		**3 / °**		**4 / °**	
O(3)-Dy(1)-O(5)	78.1(5)	O(2)-Dy(1)-O(6)	114.3(2)	O(5)-Dy(1)-O(1)	116.10(18)	O(1)-Dy(1)-O(3)	88.80(18)
O(3)-Dy(1)-O(6)	140.5(5)	O(2)-Dy(1)-O(1)	72.3(2)	O(5)-Dy(1)-O(6)	73.06(16)	O(1)-Dy(1)-O(6)	136.31(18)
O(5)-Dy(1)-O(6)	72.3(5)	O(6)-Dy(1)-O(1)	79.28(19)	O(1)-Dy(1)-O(6)	76.37(17)	O(3)-Dy(1)-O(6)	114.98(19)
O(3)-Dy(1)-O(1)	81.6(5)	O(2)-Dy(1)-O(4)	148.43(19)	O(5)-Dy(1)-O(3)	76.88(17)	O(1)-Dy(1)-O(5)	150.64(17)
O(5)-Dy(1)-O(1)	142.2(5)	O(6)-Dy(1)-O(4)	73.4(2)	O(1)-Dy(1)-O(3)	149.78(17)	O(3)-Dy(1)-O(5)	80.48(17)
O(6)-Dy(1)-O(1)	137.1(5)	O(1)-Dy(1)-O(4)	79.8(2)	O(6)-Dy(1)-O(3)	82.43(18)	O(6)-Dy(1)-O(5)	72.44(18)
O(3)-Dy(1)-O(4)	73.3(5)	O(2)-Dy(1)-O(3)	136.85(19)	O(5)-Dy(1)-O(4)	138.96(16)	O(1)-Dy(1)-O(2)	72.21(17)
O(5)-Dy(1)-O(4)	80.3(4)	O(6)-Dy(1)-O(3)	84.69(19)	O(1)-Dy(1)-O(4)	81.45(18)	O(3)-Dy(1)-O(2)	75.86(18)
O(6)-Dy(1)-O(4)	76.5(5)	O(1)-Dy(1)-O(3)	150.85(19)	O(6)-Dy(1)-O(4)	76.21(17)	O(6)-Dy(1)-O(2)	146.33(17)
O(1)-Dy(1)-O(4)	123.4(5)	O(4)-Dy(1)-O(3)	72.34(18)	O(3)-Dy(1)-O(4)	72.67(17)	O(5)-Dy(1)-O(2)	78.66(17)
O(3)-Dy(1)-O(2)	118.4(5)	O(2)-Dy(1)-O(5)	73.28(18)	O(5)-Dy(1)-O(2)	80.72(17)	O(1)-Dy(1)-O(4)	75.52(17)
O(5)-Dy(1)-O(2)	146.0(6)	O(6)-Dy(1)-O(5)	73.36(18)	O(1)-Dy(1)-O(2)	72.43(17)	O(3)-Dy(1)-O(4)	73.48(17)
O(6)-Dy(1)-O(2)	77.9(5)	O(1)-Dy(1)-O(5)	121.0(2)	O(6)-Dy(1)-O(2)	124.09(18)	O(6)-Dy(1)-O(4)	77.13(17)
O(1)-Dy(1)-O(2)	71.8(5)	O(4)-Dy(1)-O(5)	135.80(17)	O(3)-Dy(1)-O(2)	137.79(17)	O(5)-Dy(1)-O(4)	126.02(17)
O(4)-Dy(1)-O(2)	77.2(5)	O(3)-Dy(1)-O(5)	76.33(18)	O(4)-Dy(1)-O(2)	139.92(17)	O(2)-Dy(1)-O(4)	135.40(16)
O(3)-Dy(1)-N(3)	80.5(5)	O(2)-Dy(1)-N(4)	87.9(2)	O(5)-Dy(1)-N(4)	80.09(18)	O(1)-Dy(1)-N(4)	99.28(18)
O(5)-Dy(1)-N(3)	74.1(5)	O(6)-Dy(1)-N(4)	140.6(2)	O(1)-Dy(1)-N(4)	135.01(17)	O(3)-Dy(1)-N(4)	146.47(18)
O(6)-Dy(1)-N(3)	114.6(5)	O(1)-Dy(1)-N(4)	77.3(2)	O(6)-Dy(1)-N(4)	146.37(17)	O(6)-Dy(1)-N(4)	80.96(17)
O(1)-Dy(1)-N(3)	71.3(5)	O(4)-Dy(1)-N(4)	71.6(2)	O(3)-Dy(1)-N(4)	71.89(18)	O(5)-Dy(1)-N(4)	76.68(17)
O(4)-Dy(1)-N(3)	146.5(5)	O(3)-Dy(1)-N(4)	101.23(19)	O(4)-Dy(1)-N(4)	114.64(18)	O(2)-Dy(1)-N(4)	75.82(17)
O(2)-Dy(1)-N(3)	134.9(5)	O(5)-Dy(1)-N(4)	146.0(2)	O(2)-Dy(1)-N(4)	69.30(18)	O(4)-Dy(1)-N(4)	140.06(17)
O(3)-Dy(1)-N(4)	142.7(5)	O(2)-Dy(1)-N(3)	68.79(19)	O(5)-Dy(1)-N(3)	141.68(17)	O(1)-Dy(1)-N(3)	71.09(18)
O(5)-Dy(1)-N(4)	103.1(5)	O(6)-Dy(1)-N(3)	153.03(19)	O(1)-Dy(1)-N(3)	82.94(18)	O(3)-Dy(1)-N(3)	148.68(18)
O(6)-Dy(1)-N(4)	70.9(5)	O(1)-Dy(1)-N(3)	124.82(19)	O(6)-Dy(1)-N(3)	145.24(17)	O(6)-Dy(1)-N(3)	70.44(19)
O(1)-Dy(1)-N(4)	75.3(5)	O(4)-Dy(1)-N(3)	119.0(2)	O(3)-Dy(1)-N(3)	103.69(18)	O(5)-Dy(1)-N(3)	128.21(17)
O(4)-Dy(1)-N(4)	144.1(5)	O(3)-Dy(1)-N(3)	77.66(19)	O(4)-Dy(1)-N(3)	73.29(17)	O(2)-Dy(1)-N(3)	117.83(19)
O(2)-Dy(1)-N(4)	81.6(5)	O(5)-Dy(1)-N(3)	82.69(19)	O(2)-Dy(1)-N(3)	73.76(17)	O(4)-Dy(1)-N(3)	78.26(18)
N(3)-Dy(1)-N(4)	64.6(5)	N(4)-Dy(1)-N(3)	64.0(2)	N(4)-Dy(1)-N(3)	64.46(18)	N(4)-Dy(1)-N(3)	62.99(18)

Table S4 The evaluated local coordination geometry analysis for **1**, **2**, **3** and **4**. by SHAPE software

shape	symmetry	distortion(τ)			
		1	2	3	4
Heptagonal pyramid	C_{7v}	22.662	22.109	21.871	23.371
Hexagonal bipyramid	D_{6h}	16.313	12.777	15.763	15.205
Cube	O_h	10.113	7.098	9.502	8.357
Square antiprism	D_{4d}	0.506	1.358	0.596	1.069
Triangular dodecahedron	D_{2d}	2.202	1.126	2.290	1.026
Johnson gyrobifastigium J26	D_{2d}	15.456	14.431	15.028	15.792
Biaugmented trigonal prism J50	C_{2v}	2.233	2.756	2.432	2.227
Biaugmented trigonal prism	C_{2v}	1.679	2.199	1.802	1.712

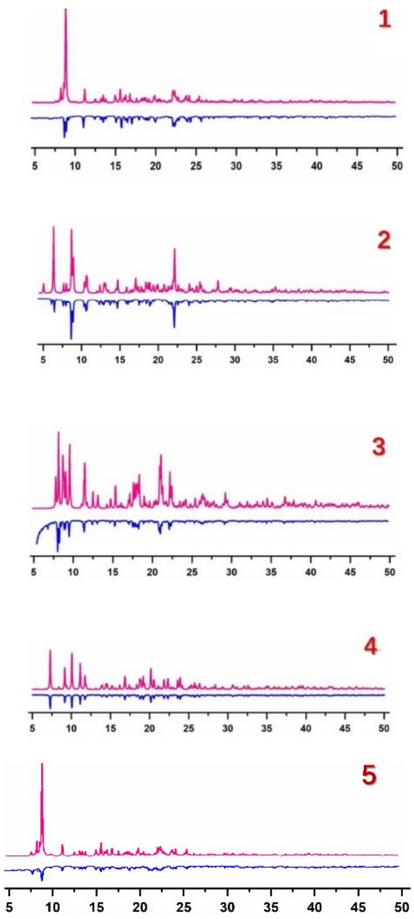


Fig. S1 The powder XRD patterns obtained from synthesized microcrystals (blue lines) and the simulated results (red lines) from single crystal data of **1**, **2**, **3**, **4** and **5**.

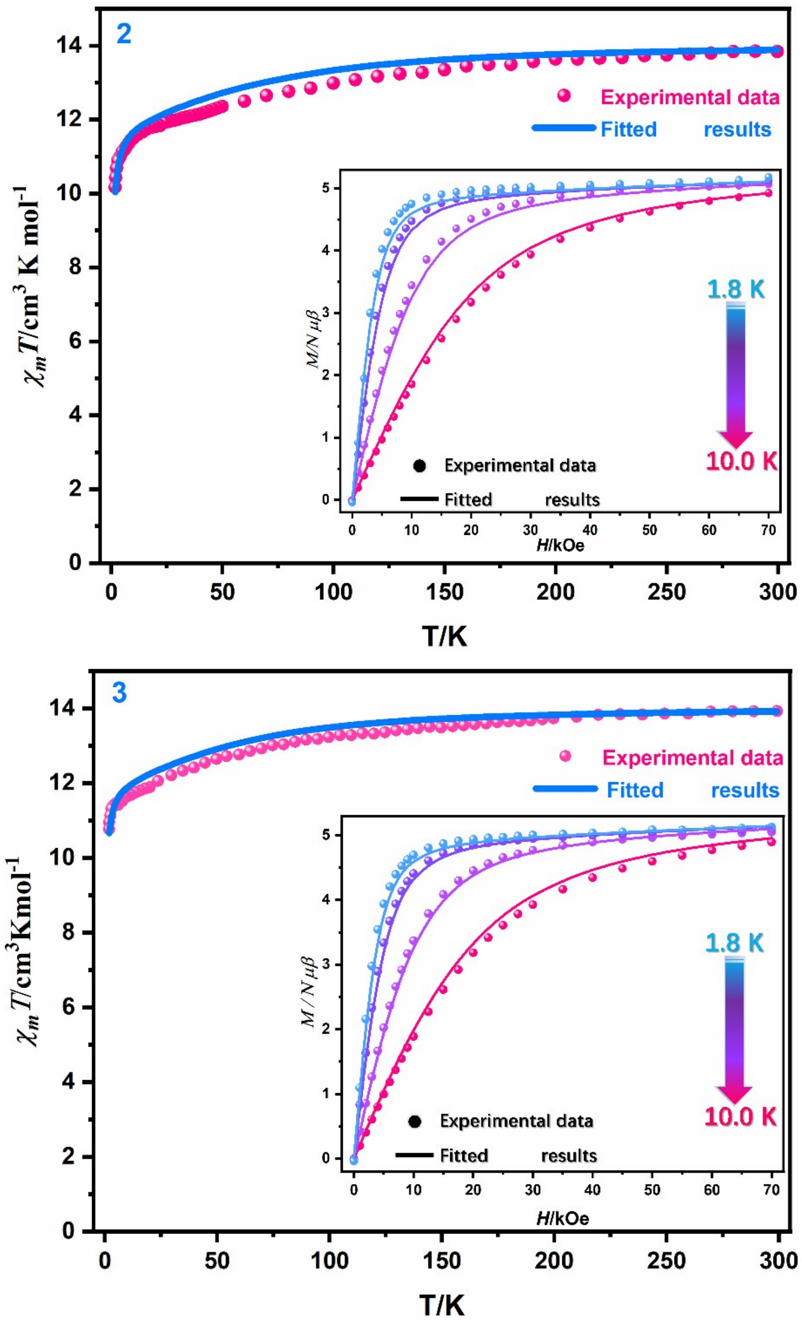


Fig. S2 The variable-temperature magnetic susceptibilities of **2** and **3** under an external field of 1 KOe in the temperature range of 1.8-300 K (top view, insert: field-dependent magnetization at 1.8, 2.5, 5.0 and 10 K. The solid line represents the best fitted results.)

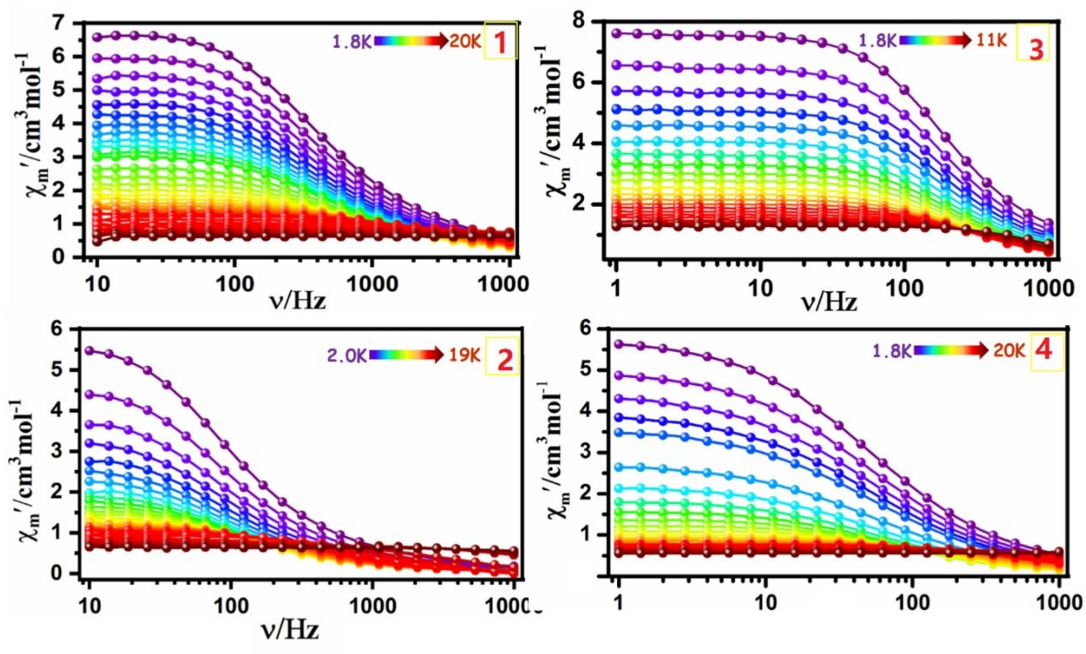
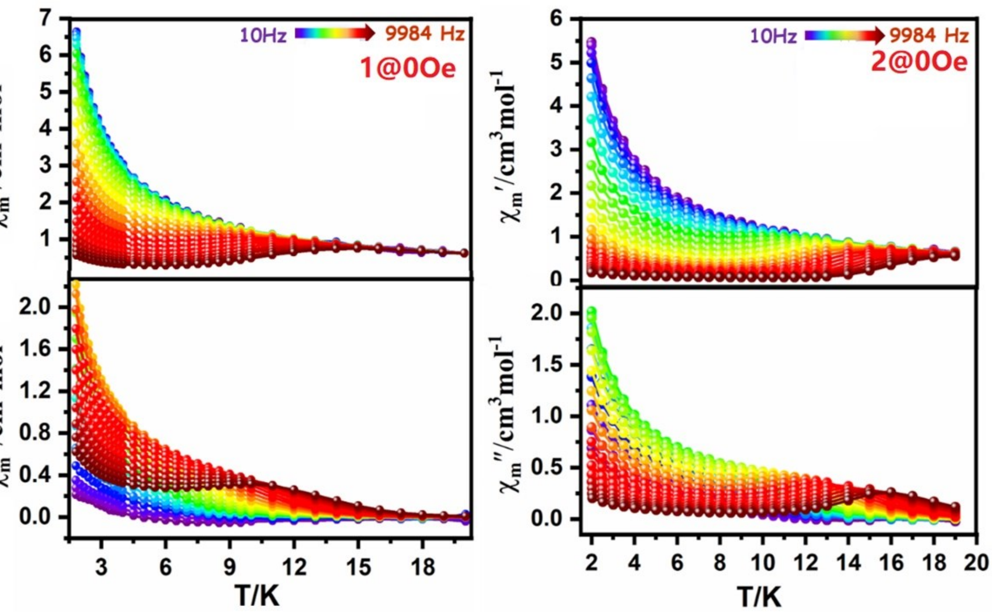


Fig. S3 Frequency dependence of the in-phase (χ') ac susceptibility of **1**, **2**, **3** and **4** in zero dc field.



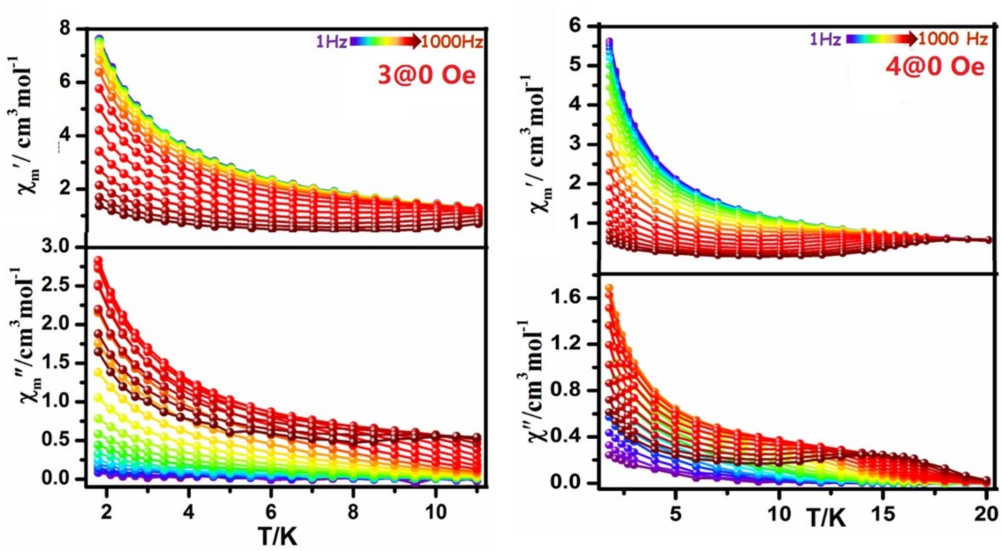
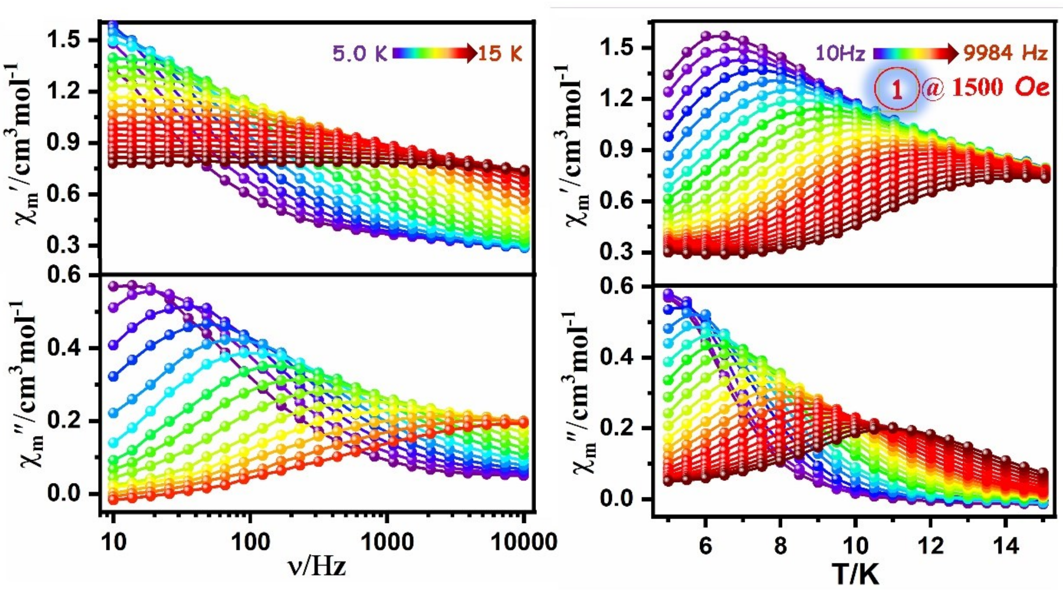
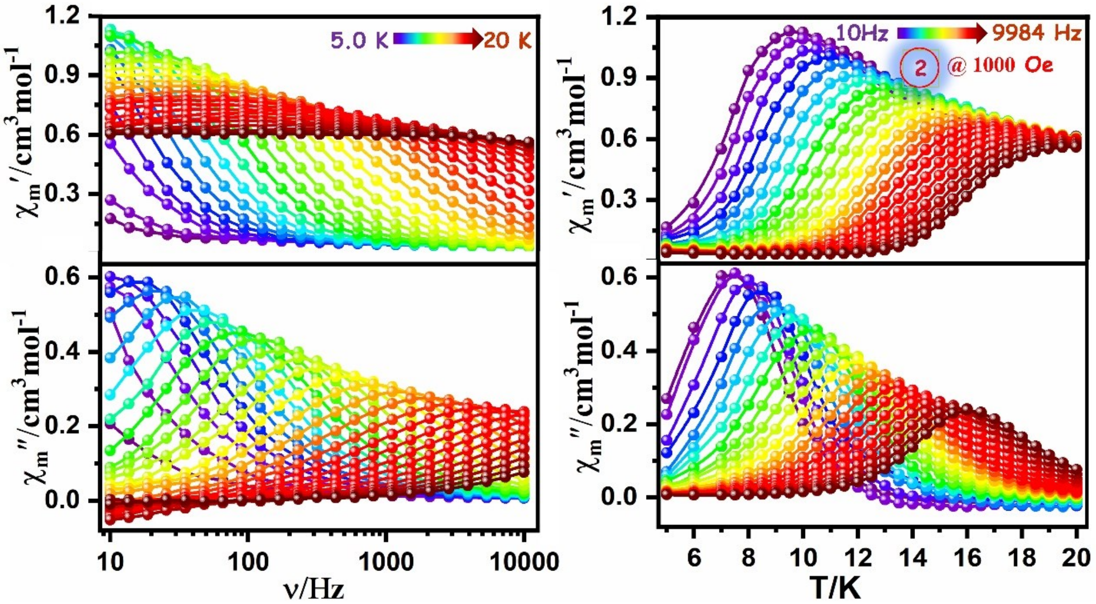
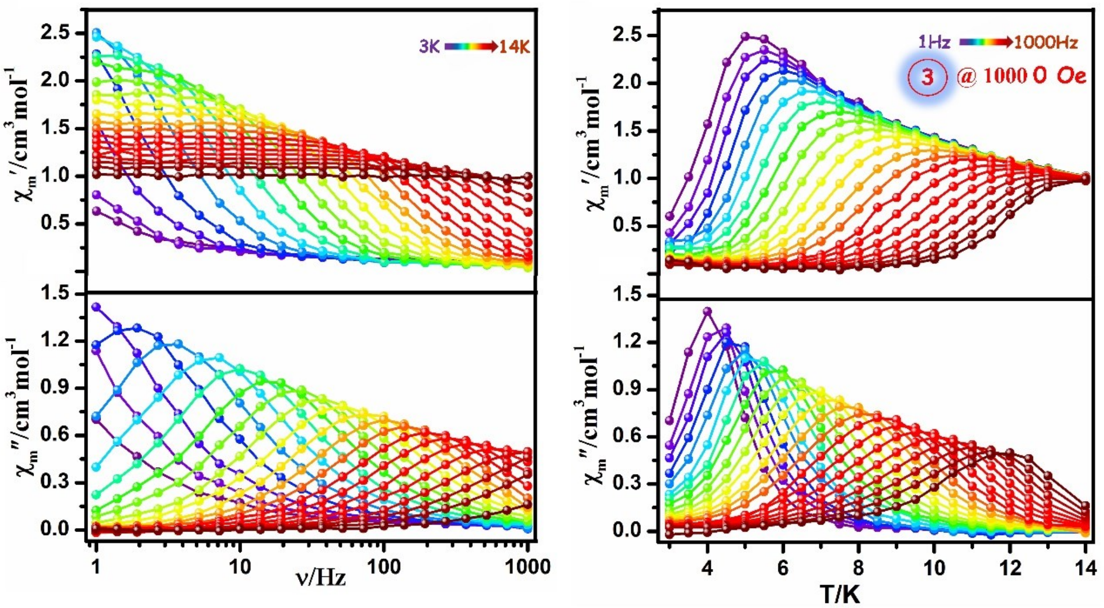
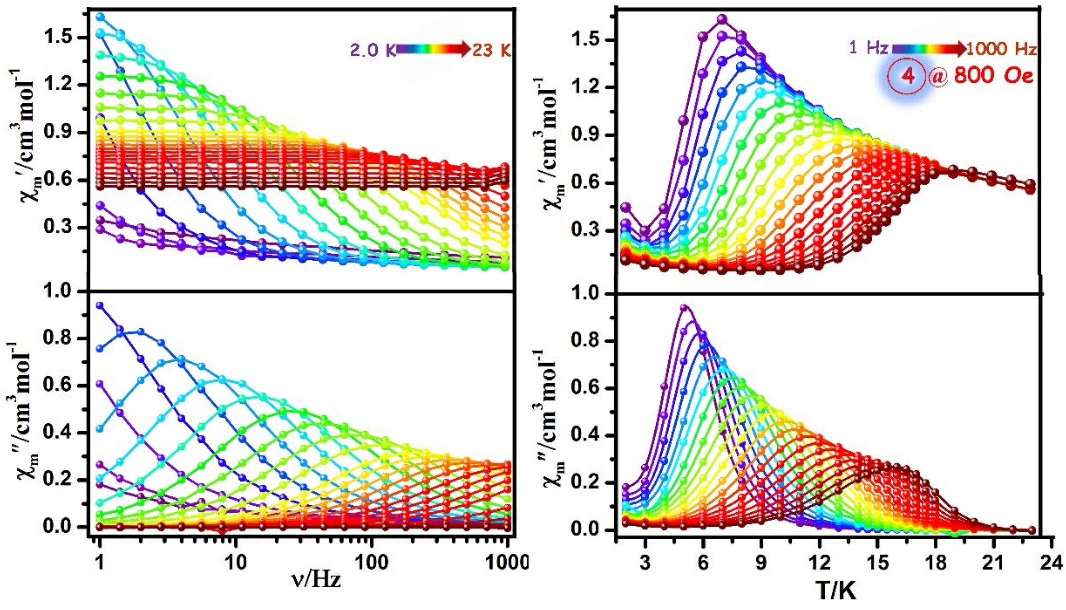


Fig. S4 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility of **1**, **2**, **3** and **4** in zero dc field.




5.0 K → 20 K
10Hz → 9984 Hz
2 @ 1000 Oe
χm'/cm3mol-1
χm''/cm3mol-1
ν/Hz
T/K


3K → 14K
1Hz → 1000Hz
3 @ 1000 0 Oe
χm'/cm3mol-1
χm''/cm3mol-1
ν/Hz
T/K



Fi**g. S5** Frequency and temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility of **1**, **2**, **3** and **4** in optimal dc field.

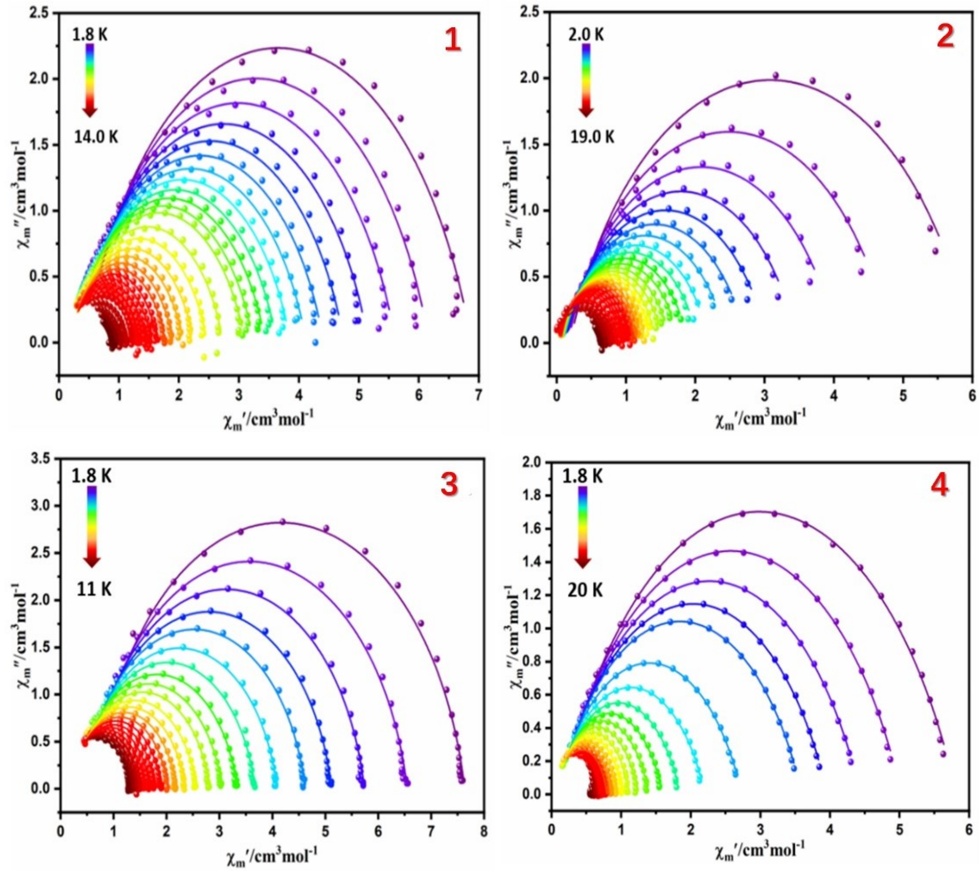
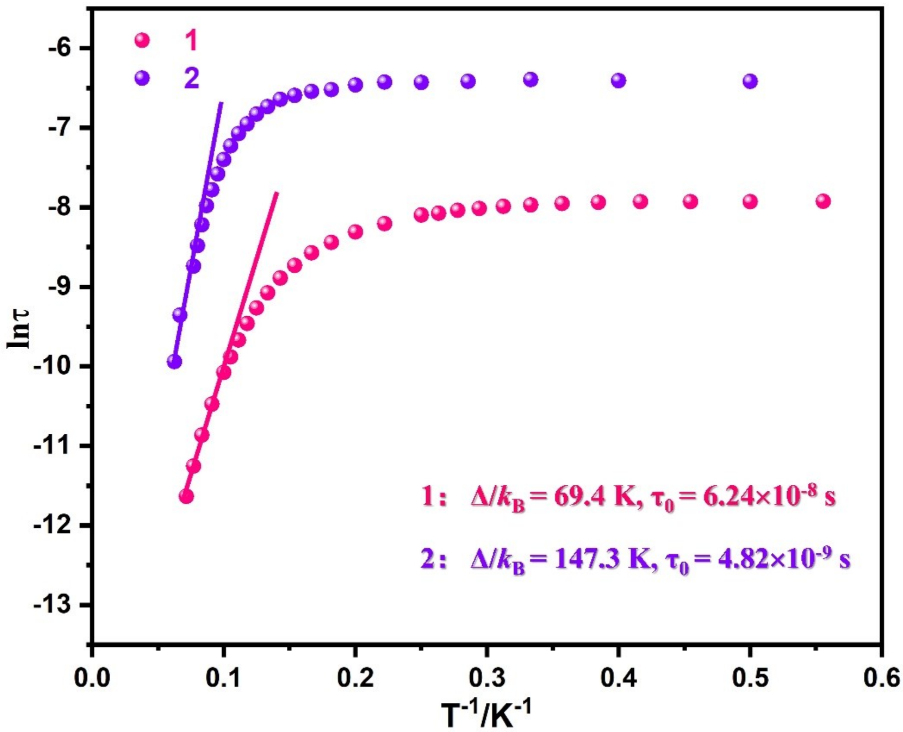


Fig. S6 The Cole-Cole fitted data for **1**, **2**, **3** and **4** in zero dc field by generalized Debye model (the solid lines represent the best results).



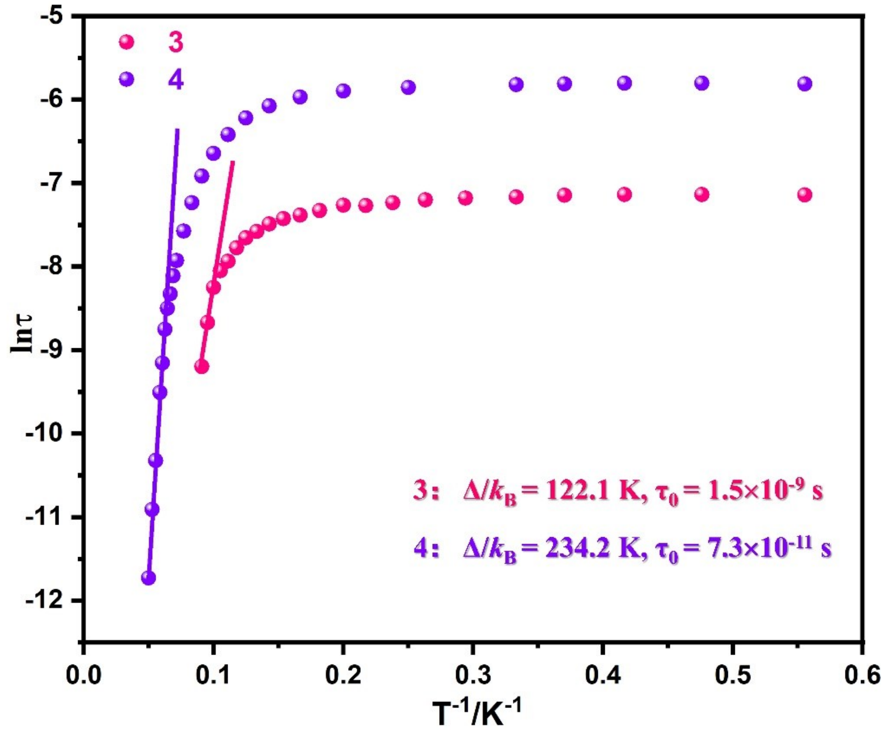


Fig. S7 The extracted magnetic relaxation time τ plot as a function of 1/T of four complexes under zero dc field. The straight lines represent the best fitting based on Arrhenius law.

Table S5 The calculated energy levels (cm^{-1}), g (g_x, g_y, g_z) tensors and m_J values of the minimum KDs of Dy(III) motifs in complex **1**.

<table>
<tr><th rowspan="2">KDs</th><th colspan="3">Complex **1**</th></tr>
<tr><th>*E*</th><th>***g***</th><th>m_J</th></tr>
<tr><td>1</td><td>0.0</td><td>0.025
0.036
19.517</td><td>94.9%|±15/2>+4.1%|±11/2>+0.6%|±7/2>+0.3%|±5/2>+0.1%|±9/2>+0.1%|±1/2></td></tr>
<tr><td>2</td><td>102.9 (148.2 K)</td><td>1.234
4.350
14.004</td><td>46.7%|±13/2>+11.2%|±3/2>+11.1%|±11/2>+10.0%|±1/2>+9.3%|±9/2>+7.8%|±5/2>+3.2%|±7/2>+0.7%|±15/2></td></tr>
<tr><td>3</td><td>125.0</td><td>1.075
3.672
11.753</td><td>29.2%|±1/2>+27.5%|±13/2>+18.0%|±3/2>+9.0%|±7/2>+5.6%|±5/2>+5.5%|±11/2>+5. 1%|±9/2>+0.2%|±15/2></td></tr>
<tr><td>4</td><td>154.8</td><td>1.439
3.731
10.456</td><td>26.9%|±9/2>+26.4%|±11/2>+15.0%|±5/2>+10.4%|±13/2>+9.4%|±1/2>+8.1%|±7/2>+2.3%|±3/2>+1.5%|±15/2></td></tr>
<tr><td>5</td><td>190.5</td><td>2.111
4.644
11.247</td><td>24.2%|±7/2>+22.1%|±3/2>+20.0%|±11/2>+15.8%|±9/2>13.8%|±5/2>+2.0%|±1/2>+1.6%|±13/2>+0.4%|±15/2></td></tr>
<tr><td>6</td><td>227.8</td><td>1.240
1.633
16.087</td><td>31.6%|±7/2>+31.2%|±5/2>+12.2%|±3/2>+10.2%|±9/2>+8.9%|±1/2>+4.7%|±11/2>+1.3%|±13/2>+0.1%|±15/2></td></tr>
<tr><td>7</td><td>299.7</td><td>0.392
0.451
19.200</td><td>40.1%|±1/2>+31.5%|±3/2>+18.5%|±5/2>+4.6%|±7/2>+3.1%|±9/2>+1.7%|±11/2>+0.6%|±13/2>+0.1%|±15/2></td></tr>
<tr><td>8</td><td>437.2</td><td>0.028
0.059
19.692</td><td>29.5%|±9/2>+26.7%|±11/2>+18.6%|±7/2>+12.0%|±13/2>+7.9%|±5/2>+2.6%|±3/2>+2.2%|±15/2>+0.3%|±1/2></td></tr>
</table>

Table S6 The calculated energy levels (cm^{-1}), *g* (g_x, g_y, g_z) tensors and m_J values of the minimum KDs of Dy(III) motifs in complex **2**.

<table>
<tr><th rowspan="2">KDs</th><th colspan="3">Complex **2**</th></tr>
<tr><th>*E*</th><th>***g***</th><th>m_J</th></tr>
<tr><td>1</td><td>0.0</td><td>0.009
0.010
19.458</td><td>93.0%|±15/2>+6.5%|±11/2>+0.2%|±7/2>+0.1%|±9/2>+%|±5/2>+0.1%|±3/2></td></tr>
<tr><td>2</td><td>133.9</td><td>0.354</td><td>58.1%|±13/2>+27.1%|±9/2>+9.4%|±11/2>+2.4%|±7/2>+1.5%|±3/2>+0.5%|±15/2>+0.5%|±5/2>+0.5%|±1/2></td></tr>
</table>

<table>
<tr><td></td><td>(187.5 K)</td><td>0.518
16.387</td><td></td></tr>
<tr><td>3</td><td>192.0</td><td>3.072
4.318
10.601</td><td>30.3%|±7/2>+21.4%|±11/2>+15.8%|±13/2>+12.6%|±5/2>+7.2%|±1/2>+6.2%|±3/2>+5.8%|±9/2>+0.7%|±15/2></td></tr>
<tr><td>4</td><td>227.7</td><td>9.322
7.225
1.996</td><td>26.1%|±1/2>+21.9%|±5/2>+19.2%|±3/2>+14.5%|±11/2>+9.8%|±7/2>+6.3%|±9/2>+1.4%|±15/2>+0.8%|±13/2></td></tr>
<tr><td>5</td><td>280.0</td><td>0.487
3.792
11.803</td><td>28.5%|±3/2>+17.4%|±9/2>+16.8%|±5/2>+14.9%|±7/2>+12.6%|±1/2>+5.8%|±11/2>+3.2%|±13/2>+0.6%|±15/2></td></tr>
<tr><td>6</td><td>323.1</td><td>1.519
2.514
15.822</td><td>29.4%|±5/2>+22.2%|±7/2>+14.5%|±11/2>+13.4%|±9/2>+7.7%|±13/2>+7.3%|±3/2>+4.4%|±1/2>+1.1%|±15/2></td></tr>
<tr><td>7</td><td>395.0</td><td>0.227
0.688
17.843</td><td>47.0%|±1/2>+34.0%|±3/2>+8.3%|±5/2>+3.8%|±9/2>+3.7%|±11/2>+1.8%|±13/2>+1.2%|±7/2>+0.3%|±15/2></td></tr>
<tr><td>8</td><td>476.8</td><td>0.050
0.139
19.239</td><td>26.1%|±9/2>+24.2%|±11/2>+19.2%|±7/2>+12.5%|±13/2>+10.2%|±5/2>+3.2%|±3/2>+2.4%|±1/2>+2.3%|±15/2></td></tr>
</table>

Table S7 The calculated energy levels (cm^{-1}), *g* (g_x, g_y, g_z) tensors and m_J values of the minimum KDs of Dy(III) motifs in complex **3**.

<table>
<tr><th rowspan="2">KDs</th><th colspan="3">Complex **3**</th></tr>
<tr><th>*E*</th><th>***g***</th><th>m_J</th></tr>
<tr><td>1</td><td>0.0</td><td>0.017
0.024
19.561</td><td>95.2%|±15/2>+4.0%|±11/2>+0.3%|±7/2>+0.2%|±9/2>+0.1%|±5/2></td></tr>
<tr><td>2</td><td>115.9 (166.9 K)</td><td>0.646
1.284
16.688</td><td>55.0%|±13/2>+15.8%|±11/2>+13.8%|±9/2>+4.5%|±3/2>+4.1%|±5/2>+3.5%|±7/2>+2.6%|±1/2>+0.5%|±15/2></td></tr>
<tr><td>3</td><td>151.1</td><td>2.048
3.284
12.227</td><td>27.6%|±13/2>+18.7%|±9/2>+17.9%|±7/2>+12.3%|±1/2>+10.8%|±3/2>+7.3%|±11/2>+5.2%|±5/2>+0.3%|±15/2></td></tr>
<tr><td>4</td><td>178.1</td><td>3.482
6.048
8.826</td><td>28.8%|±11/2>+20.9%|±1/2>+20.8%|±5/2>+13.5%|±9/2>+8.4%|±3/2>+3.9%|±7/2>+2.6%|±13/2>+1.2%|±15/2></td></tr>
<tr><td>5</td><td>214.3</td><td>1.794
2.498
11.690</td><td>31.4%|±7/2>+20.3%|±3/2>+15.4%|±11/2>+14.4%|±9/2>+12.9%|±5/2>+3.8%|±1/2>+1.3%|±13/2>+0.3%|±15/2></td></tr>
<tr><td>6</td><td>279.0</td><td>0.073
0.254
16.309</td><td>35.0%|±5/2>+21.3%|±7/2>+19.0%|±3/2>+12.6%|±1/2>+10.2%|±9/2>+1.3%|±11/2>+0.5%|±13/2>+0.1%|±15/2></td></tr>
<tr><td>7</td><td>345.5</td><td>0.156
0.305</td><td>47.5%|±1/2>+33.8%|±3/2>+12.7%|±5/2>+3.2%|±7/2>+1.3%|±9/2>+0.9%|±11/2>+0.6%|±13/2>+0.1%|±15/2></td></tr>
</table>

		18.839	
8	453.7	0.026 0.051 19.626	28.0%|±9/2>+26.4%|±11/2>+18.4%|±7/2>+12.3%|±13/2>+9.1%|±5/2>+3.2%|±3/2>+2.1%|±15/2>+0.4%|±1/2>

Table S8 The calculated energy levels (cm^{-1}), g (g_x, g_y, g_z) tensors and m_J values of the minimum KDs of Dy(III) motifs in complex **4**.

KDs	Complex **4**		
	E	***g***	m_J
1	0.0	0.004 0.007 19.640	95.2%|±15/2>+4.5%|±11/2>+0.1%|±9/2>
2	156.6 (225.5 K)	0.721 1.461 15.382	71.9%|±13/2>+16.0%|±9/2>+3.2%|±5/2>+2.6%|±11/2>+2.3%|±3/2>+2.2%|±1/2>+1.7%|±7/2>+0.1%|±15/2>
3	196.8	0.864 2.429 13.898	20.9%|±3/2>+20.4%|±11/2>+14.6%|±5/2>+14.3%|±7/2>+13.4%|±11/2>+8.8%|±13/2>+7.0%|±9/2>+0.6%|±15/2>
4	249.9	3.499 6.071 9.681	40.8%|±11/2>+14.5%|±1/2>+13.1%|±7/2>+11.3%|±5/2>+10.0|±9/2>+7.1%|±3/2>+1.6%|±1 13/2>+1.6%|±15/2>
5	286.6	0.784 3.64	31.4%|±7/2>+27.1%|±9/2>+11.1%|±11/2>+10.6%|±3/2>+7.8%|±5/2>+6.5%|±13/2>+2.1%|±1/2>+0.4%|±15/2>

<table>
<tr><td></td><td></td><td>6
13.347</td><td></td></tr>
<tr><td>6</td><td>335.7</td><td>1.221
2.627
15.774</td><td>40.4%|±5/2>+18.6%|±3/2>+15.0%|±7/2>+14.5%|±1/2>+8.5%|±9/2>+2.1%|±11/2>+0.7%|±13/2>+0.2%|±15/2></td></tr>
<tr><td>7</td><td>394.2</td><td>0.312
0.525
18.422</td><td>42.1%|±1/2>+19.8%|±3/2>+13.4%|±5/2>+2.0%|±11/2>+1.2%|±9/2>+0.9%|±7/2>+0.5%|±13/2>+0.1%|±15/2></td></tr>
<tr><td>8</td><td>491.6</td><td>0.007
0.025
19.431</td><td>30.1%|±9/2>+23.6%|±11/2>+23.6%|±7/2>+10.0%|±13/2>+9.2%|±5/2>+1.7%|±15/2>+1.2%|±1/2>+0.7%|±3/2></td></tr>
</table>

Table S9 Fitting results of the Cole-Cole plots for **1** with a generalized Debye model under zero dc field.

T/K	χ_S / cm^3· mol^{-1}	χ_T / cm^3 · mol^{-1}	τ	α
1.8	0.43708	6.87291	3.6121E-4	0.22271
2.0	0.39896	6.16952	3.60291E-4	0.22286
2.2	0.36462	5.61235	3.6013E-4	0.22446
2.4	0.32951	5.15717	3.59366E-4	0.2292
2.6	0.31108	4.75257	3.5567E-4	0.22798
2.8	0.29503	4.41126	3.51109E-4	0.22726
3.0	0.27395	4.12107	3.45602E-4	0.23031
3.2	0.26507	3.85689	3.38616E-4	0.22796
3.4	0.24945	3.62811	3.30227E-4	0.23003
3.6	0.2379	3.44052	3.23091E-4	0.23217
3.8	0.2358	3.23962	3.10782E-4	0.2265
4.0	0.22219	3.10294	3.03566E-4	0.23234
4.5	0.22098	2.73482	2.73065E-4	0.21948
5.0	0.20785	2.46985	2.45366E-4	0.21968
5.5	0.19162	2.24483	2.15373E-4	0.22312

6.0	0.18408	2.07008	1.88914E-4	0.22434
6.5	0.18791	1.89898	1.61199E-4	0.21393
7.0	0.18399	1.77138	1.37345E-4	0.2153
7.5	0.19506	1.63682	1.14319E-4	0.20037
8.0	0.19342	1.53911	9.46263E-5	0.20334
8.5	0.19913	1.44965	7.78204E-5	0.20177
9.0	0.21811	1.35419	6.32979E-5	0.18577
9.5	0.21131	1.29635	5.10412E-5	0.2064
10.0	0.25011	1.20927	4.19902E-5	0.1763
11.0	0.27563	1.12168	2.81577E-5	0.20167
12.0	0.32369	1.02094	1.90677E-5	0.19408
13.0	0.37002	0.94837	1.29713E-5	0.20177
14.0	0.41944	0.8835	8.85945E-6	0.19776

Table S10 Fitting results of the Cole-Cole plots for **2** with a generalized Debye model under zero dc field.

T/K	χ_s / cm$^3\cdot$ mol^{-1}	χ_T / cm$^3\cdot$ mol^{-1}	τ	α
2.0	0.19398	5.9675	0.00163	0.22856
2.5	0.16107	4.81135	0.00165	0.23035
3.0	0.13446	4.03939	0.00167	0.23468
3.5	0.12293	3.4615	0.00163	0.23027
4.0	0.10964	3.03486	0.00161	0.23045
4.5	0.09628	2.73685	0.00162	0.23682
5.0	0.09128	2.45474	0.00156	0.23068
5.5	0.08966	2.1946	0.00147	0.21752
6.0	0.08278	2.0372	0.00144	0.21859
6.5	0.07939	1.89023	0.00137	0.21302
7.0	0.07249	1.76399	0.0013	0.21192
7.5	0.07446	1.63013	0.00119	0.19198
8.0	0.0729	1.52722	0.00108	0.18012
8.5	0.07221	1.42834	9.54676E-4	0.1632
9.0	0.06715	1.35917	8.47799E-4	0.1586
9.5	0.06788	1.27275	7.24816E-4	0.13811
10.0	0.06313	1.20492	6.09846E-4	0.13317
10.5	0.06123	1.1472	5.08917E-4	0.12292
11.0	0.05556	1.10405	4.17911E-4	0.12737
11.5	0.05084	1.05195	3.3166E-4	0.12656
12.0	0.05162	0.99753	2.54048E-4	0.1144
12.5	0.04477	0.96284	1.95189E-4	0.12664
13.0	0.04182	0.92811	1.46371E-4	0.13335
14.0	0.00368	0.86243	1.90007E-4	0.16991

15.0	6.69514E-16	0.79959	1.00163E-4	0.16809
16.0	1.0042E-15	0.75477	4.81782E-5	0.21442
17.0	1.61605E-15	0.70803	9.48703E-6	0.23616
18.0	2.22327E-15	0.6745	4.82277E-6	0.26005
19.0	3.39688E-15	0.63915	2.50125E-6	0.25929

Table S11 Fitting results of the Cole-Cole plots for **1** with a generalized Debye model under 1500 Oe dc field.

T/K	χ_S / $cm^3 \cdot mol^{-1}$	χ_T / $cm^3 \cdot mol^{-1}$	τ	α
5.0	0.29501	2.45025	0.01623	0.37045
5.5	0.28389	2.27105	0.00917	0.35892
6.0	0.27827	2.06782	0.00518	0.34144
6.5	0.26834	1.91819	0.00326	0.35101
7.0	0.26923	1.74819	0.00194	0.34309
7.5	0.27156	1.64093	0.00125	0.34626
8.0	0.27611	1.51661	7.62808E-4	0.34453
8.5	0.27031	1.44275	4.93515E-4	0.3693
9.0	0.26894	1.3617	3.00989E-4	0.38316
9.5	0.27305	1.27954	1.78537E-4	0.38833
10.0	0.27876	1.2104	1.08426E-4	0.39412
10.5	0.28508	1.15454	6.75083E-5	0.40148
11.0	0.31239	1.0903	4.35778E-5	0.38342
11.5	0.34195	1.03732	2.98194E-5	0.3656
12.0	0.35511	0.99358	1.99856E-5	0.36125
12.5	0.39993	0.95202	1.56427E-5	0.33186
13.0	0.42381	0.91689	1.17386E-5	0.31946
13.5	0.45776	0.88222	9.50217E-6	0.2934
14.0	0.43909	0.85242	6.12607E-6	0.30261
14.5	0.4864	0.82228	5.76642E-6	0.2625
15.0	0.58598	0.78721	8.78168E-6	0.11846

Table S12 Fitting results of the Cole-Cole plots for **2** with a generalized Debye model under 1000 Oe dc field.

T/K	χ_S / $cm^3 \cdot mol^{-1}$	χ_T / $cm^3 \cdot mol^{-1}$	τ	α
5.0	0.04885	2.39279	0.35532	0.26708
6.00034	0.0456	2.9639	0.11056	0.15481
7.00027	0.0387	1.57657	0.02462	0.12889
7.50009	0.03623	1.50399	0.016	0.11456
8.00026	0.03757	1.423	0.01041	0.09594
8.50022	0.03411	1.39229	0.00768	0.11412
9.00013	0.03353	1.31849	0.00528	0.10981

9.50033	0.03341	1.25489	0.00376	0.10901
10.00012	0.03344	1.20394	0.00266	0.11254
10.49996	0.03383	1.14506	0.00188	0.11625
10.99997	0.03642	1.06845	0.00127	0.10309
11.50014	0.03288	1.03228	9.18921E-4	0.1259
12.00008	0.03187	1.00622	6.38227E-4	0.1448
12.49706	0.02902	0.96829	4.39175E-4	0.16534
13.00126	0.02882	0.92707	2.91576E-4	0.17747
13.50149	0.02401	0.89453	1.93463E-4	0.20071
14.00131	0.01931	0.86655	1.26901E-4	0.2218
14.50119	0.02456	0.82852	8.21591E-5	0.22132
15.00555	0.01735	0.79897	5.34499E-5	0.24214
15.50276	0.01254	0.77923	3.49855E-5	0.2607
16.00393	0.02762	0.75292	2.40178E-5	0.25744
16.50367	0.07205	0.72281	1.8111E-5	0.22871
17.00384	0.11683	0.69763	1.42398E-5	0.20221
17.50645	0.16207	0.67765	1.16073E-5	0.17902
18.00789	0.19195	0.66346	9.24142E-6	0.17675
18.50749	0.25163	0.64115	8.50755E-6	0.12381
19.00957	0.30095	0.6239	7.87827E-6	0.08516
19.50869	0.19506	0.61882	3.56104E-6	0.20049
20.00907	0.11082	0.60508	1.8982E-6	0.22902

Table S13 Fitting results of the Cole-Cole plots for **3** with a generalized Debye model under zero dc field.

T/K	χ_s / cm^3· mol^{-1}	χ_T / cm^3 · mol^{-1}	τ	α
1.79994	0.68247	7.63047	7.90338E-4	0.12425
2.10022	0.58676	6.54591	7.94945E-4	0.12714
2.40007	0.53354	5.73653	7.92531E-4	0.12384
2.6999	0.48532	5.11768	7.86584E-4	0.12589
3.00016	0.4291	4.61752	7.71045E-4	0.12843
3.40002	0.40391	4.08624	7.60955E-4	0.12572
3.80019	0.36708	3.66977	7.44136E-4	0.12516
4.20004	0.30807	3.33485	7.2124E-4	0.13306
4.60014	0.27708	3.04502	6.96964E-4	0.13128
4.99998	0.29762	2.80633	6.9742E-4	0.12139
5.50017	0.24336	2.55688	6.54382E-4	0.12621
6.00003	0.22108	2.34462	6.21008E-4	0.12065

6.50018	0.22217	2.17119	5.94496E-4	0.11116
7.00309	0.21671	2.01487	5.57332E-4	0.09984
7.50015	0.19394	1.89022	5.11109E-4	0.097
7.99992	0.21328	1.76729	4.73046E-4	0.0767
8.50001	0.19632	1.6633	4.1915E-4	0.06697
9.00001	0.1527	1.5764	3.57413E-4	0.07317
9.50003	0.1665	1.48102	3.09846E-4	0.04743
9.99991	0.13689	1.41636	2.54372E-4	0.05919
10.49978	0.12903	1.34954	2.07994E-4	0.05475
10.99992	0.13317	1.28618	1.66203E-4	0.04793

Table S14 Fitting results of the Cole-Cole plots for **4** with a generalized Debye model under zero dc field.

T/K	χ_s / $cm^3 \cdot mol^{-1}$	χ_T / $cm^3 \cdot mol^{-1}$	τ	α
1.8	0.14522	5.81597	0.00299	0.30771
2.1	0.12411	5.02562	0.00301	0.30962
2.4	0.10434	4.43676	0.00301	0.31483
2.7	0.09871	3.96325	0.00299	0.314
3.0	0.09003	3.5968	0.00296	0.31377
4.0	0.07551	2.73329	0.00286	0.31274
5.0	0.07504	2.2048	0.00274	0.30376
6.0	0.07742	1.84746	0.00255	0.28691
7.0	0.07186	1.59254	0.00229	0.27041
8.0	0.07682	1.39387	0.00199	0.24396
9.0	0.07362	1.23598	0.00163	0.22006
10.0	0.07209	1.11034	0.0013	0.19988
11.0	0.06668	1.01382	9.91884E-4	0.19011
12.0	0.05883	0.92996	7.19353E-4	0.1867
13.0	0.06448	0.86113	5.13534E-4	0.18701
14.0	0.09075	0.79482	3.61103E-4	0.16519
14.5	0.10365	0.76822	2.99838E-4	0.15753
15.0	0.11659	0.74272	2.42144E-4	0.14804
15.5	0.14847	0.7183	2.03242E-4	0.12616
16.0	0.15166	0.69636	1.58012E-4	0.11426
16.5	0.11823	0.67627	1.05469E-4	0.12563
17.0	0.11374	0.65689	7.42519E-5	0.13068
18.0	1.25E-10	0.61844	3.28221E-5	0.08639
19.0	2.74E-10	0.58635	1.8314E-5	1.85E-10
20.0	4.22E-10	0.55907	8.06479E-6	2.07E-10

Table S15 Fitting results of the Cole-Cole plots for **3** with a generalized Debye model under 1000 Oe dc field.

T/K	χ_S / $cm^3 \cdot mol^{-1}$	χ_T / $cm^3 \cdot mol^{-1}$	τ	α
3.0	0.10078	3.82858	0.22547	0.15298
3.5	0.08787	3.17963	0.09156	0.10937
4.0	0.08184	2.83316	0.04632	0.09179
4.5	0.07067	2.56755	0.02546	0.07877
5.0	0.06575	2.33941	0.0153	0.06502
5.5	0.06146	2.18756	0.00977	0.06652
6.0	0.05476	2.01936	0.00643	0.06139
6.5	0.05279	1.8749	0.00434	0.05177
7.0	0.05437	1.7675	0.00305	0.05286
7.5	0.05219	1.66253	0.00212	0.05194
8.0	0.06504	1.5653	0.00155	0.04182
8.5	0.06381	1.49139	0.0011	0.04755
9.0	0.06324	1.4181	7.89238E-4	0.05375
9.5	0.06033	1.3509	5.51856E-4	0.05765
10.0	0.07754	1.29044	3.89811E-4	0.05715
10.5	0.07912	1.23335	2.67735E-4	0.05943
11.0	0.09242	1.18298	1.74816E-4	0.06662
11.5	5.5739E-15	1.1379	1.00581E-4	0.09657
12.0	9.04733E-15	1.09324	6.15591E-5	0.09243
12.5	1.65476E-14	1.01105	2.46681E-5	0.05455

Table S16 Fitting results of the Cole-Cole plots for **4** with a generalized Debye model under 800 Oe dc field.

T/K	χ_S / $cm^3 \cdot mol^{-1}$	χ_T / $cm^3 \cdot mol^{-1}$	τ	α
2.0	0.06992	2.69677	0.25706	0.17089
3.0	0.05987	2.17057	0.0891	0.14908
4.0	0.05275	1.84699	0.03921	0.13891
5.0	0.04834	1.61335	0.01949	0.13383
6.0	0.04525	1.42771	0.01034	0.13134
7.0	0.04376	1.28389	0.0058	0.13493
8.0	0.04357	1.16845	0.00337	0.14397
9.0	0.04768	1.07113	0.00199	0.15465
10.0	0.06189	0.99018	0.00119	0.16267
11.0	0.08772	0.91904	6.99264E-4	0.16001

12.0	0.10804	0.88544	5.32615E-4	0.14971
13.0	0.12649	0.85673	4.00895E-4	0.14179
14.0	0.14467	0.82803	3.00291E-4	0.12777
14.5	0.15621	0.80299	2.1742E-4	0.12164
15.0	0.16165	0.77933	1.5263E-4	0.11868
15.5	0.14393	0.75545	1.00507E-4	0.11562
16.0	0.07217	0.73394	5.83136E-5	0.12203
16.5	4.2571E-9	0.71299	3.60278E-5	0.10119
17.0	1.01551E-8	0.67491	2.02916E-5	3.45845E-15
17.5	1.53572E-8	0.64333	9.05365E-6	3.9435E-15

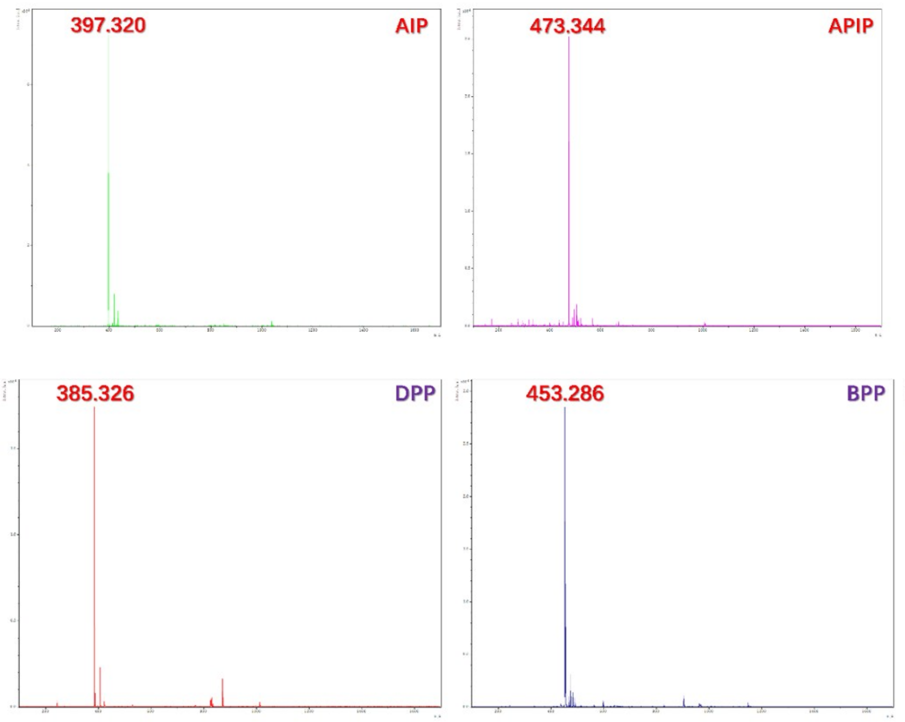


Fig. S8 MALDI-TOF-MS of four ligands.

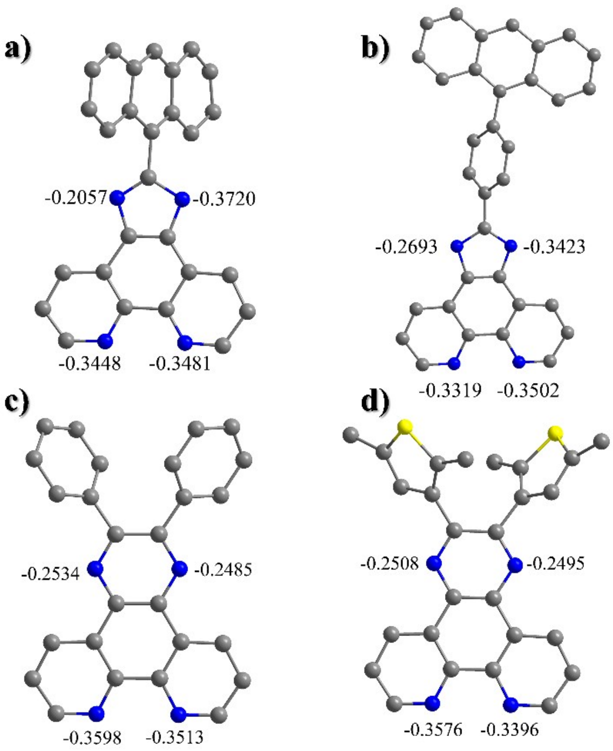


Fig. S9 The preliminary analysis of NBO charge located at N atoms (au) of **1** (a), **2** (b), **3** (c) and **4** (d) (the Dy ions and β-diketone ligands are omitted).

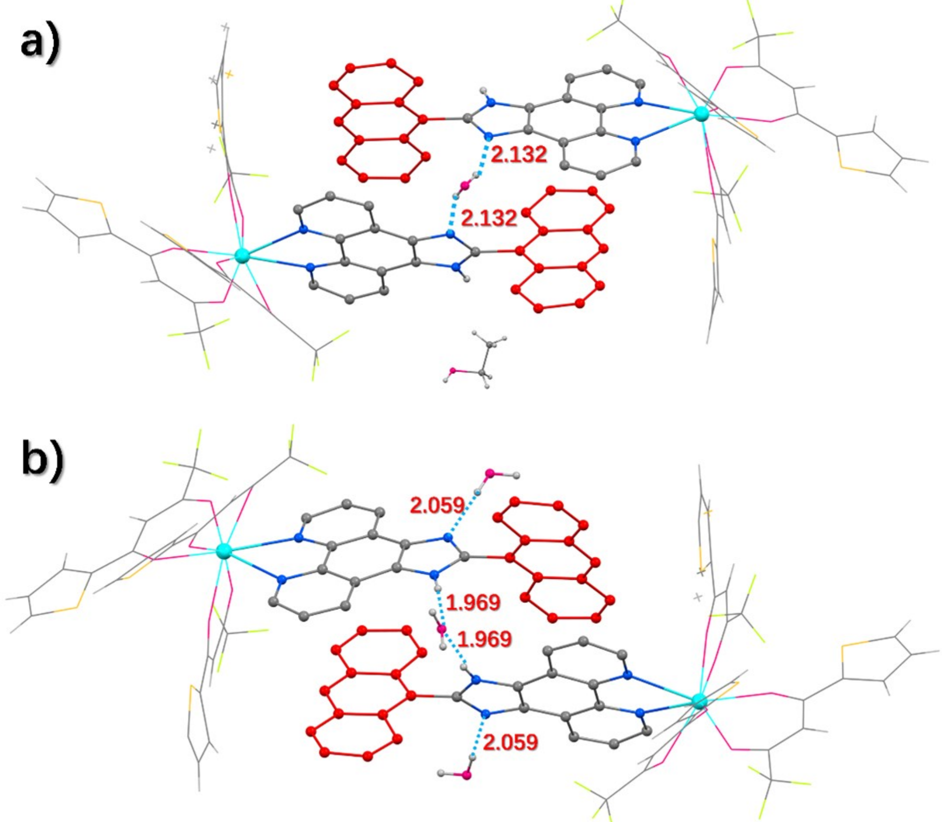


Fig. S10 Crystal structure and hydrogen bonds interaction for **1** (a) and **5** (b). Color code: Dy, light-blue; O, red; N, blue; C, gray; F, green; S, yellow.

Table S17 Comparison of selected bond lengths (Å) for **1** and **5**.

1 / Å		**5 / Å**	
Dy(1)-O(1)	2.334	Dy(1)-O(1)	2.326
Dy(1)-O(2)	2.339	Dy(1)-O(2)	2.293
Dy(1)-O(3)	2.288	Dy(1)-O(3)	2.319
Dy(1)-O(4)	2.338	Dy(1)-O(4)	2.319
Dy(1)-O(5)	2.326	Dy(1)-O(5)	2.318
Dy(1)-O(6)	2.345	Dy(1)-O(6)	2.347
Dy(1)-N(3)	2.550	Dy(1)-N(3)	2.542
Dy(1)-N(4)	2.584	Dy(1)-N(4)	2.526

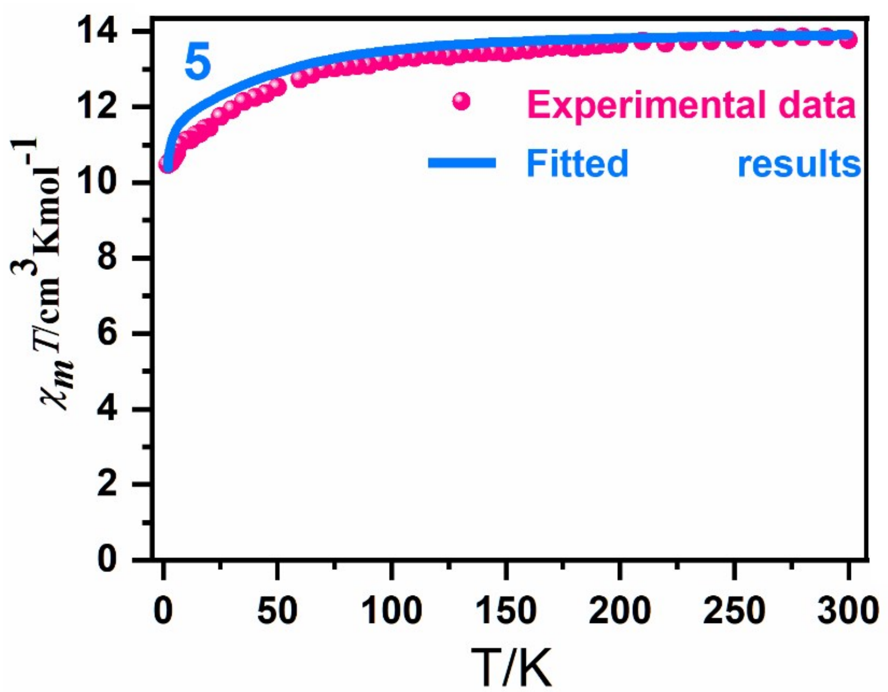


Fig. S11 The variable-temperature magnetic susceptibilities of **5** under an external field of 1 kOe in the temperature range of 1.8-300 K. The solid lines represent the best calculated data with the intermolecular interaction *zJ′* of –0.03, respectively.

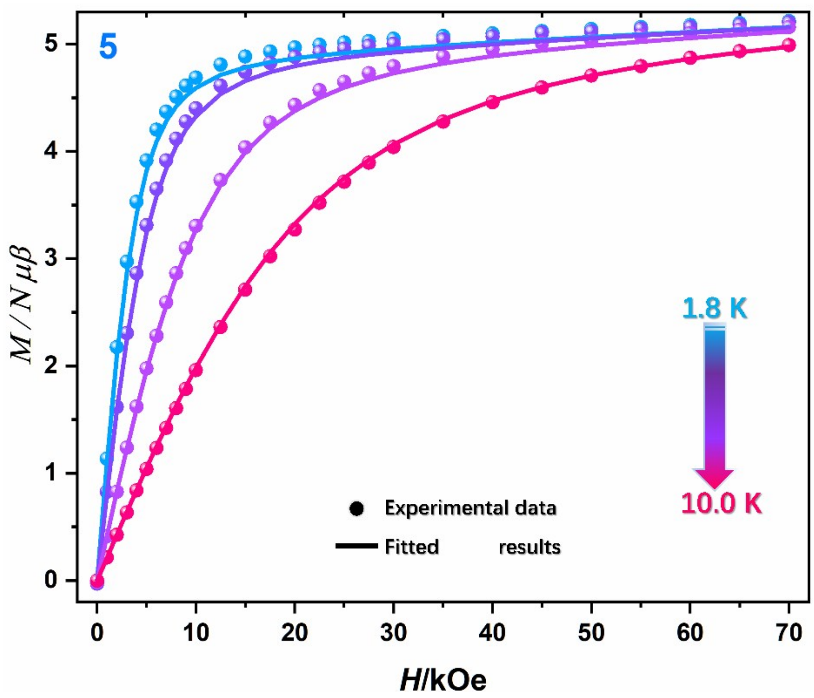


Fig. S12 The field-dependent magnetization at 1.8, 2.5, 5.0 and 10 K of **5**. The solid line represents the best fitted results.

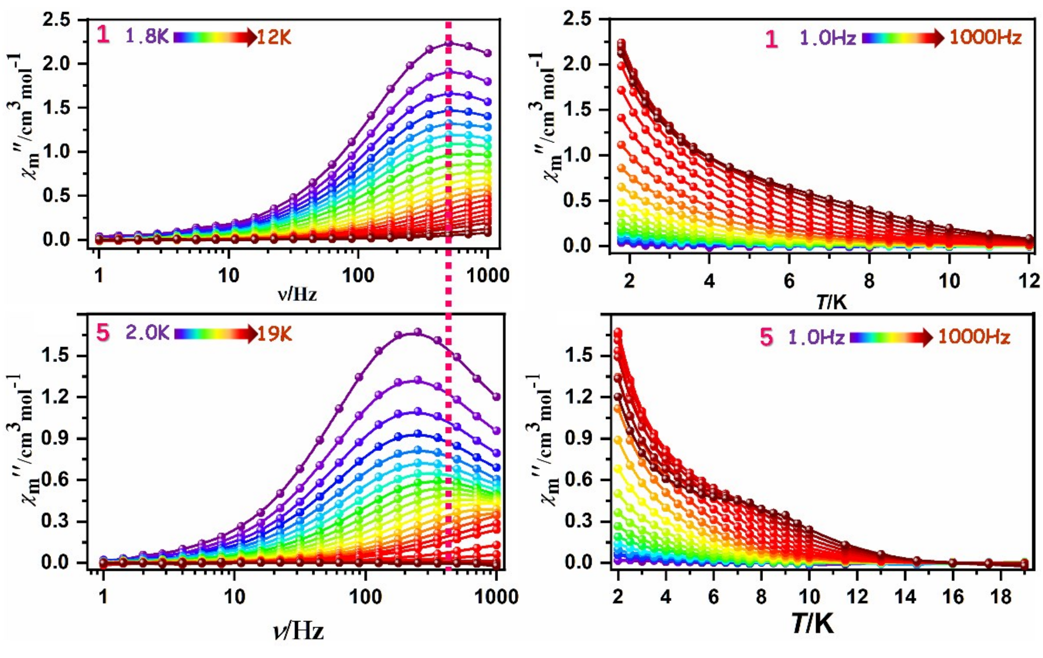


Fig. S13 Frequency and temperature dependence of out-of-phase (χ'') ac susceptibility of **1** and **5** in zero dc field collected using MPMS.

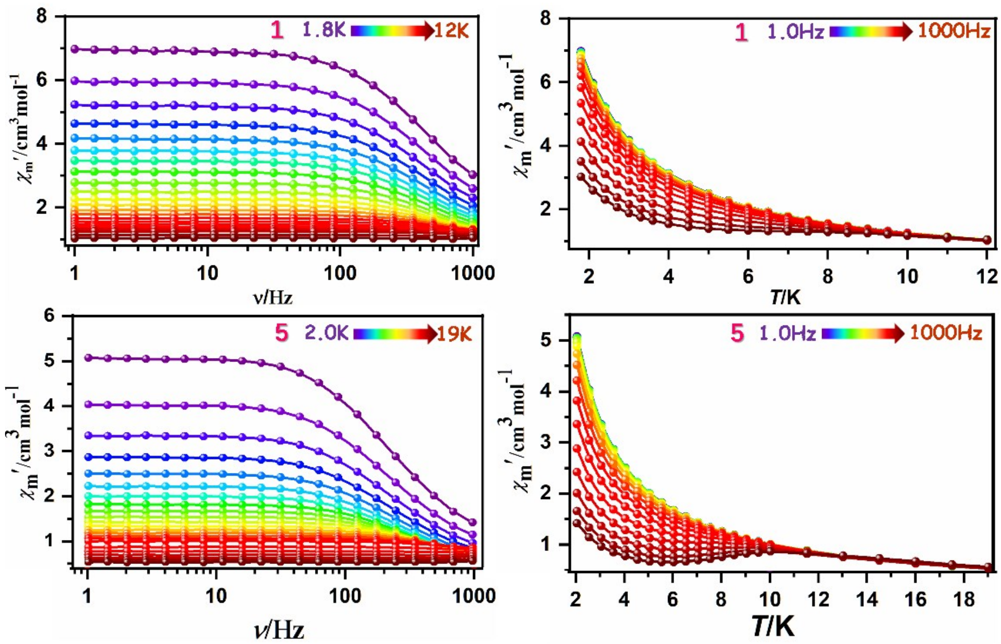


Fig. S14 Frequency and temperature dependence of in-phase (χ') ac susceptibility of **1** and **5** in zero dc field collected using MPMS.

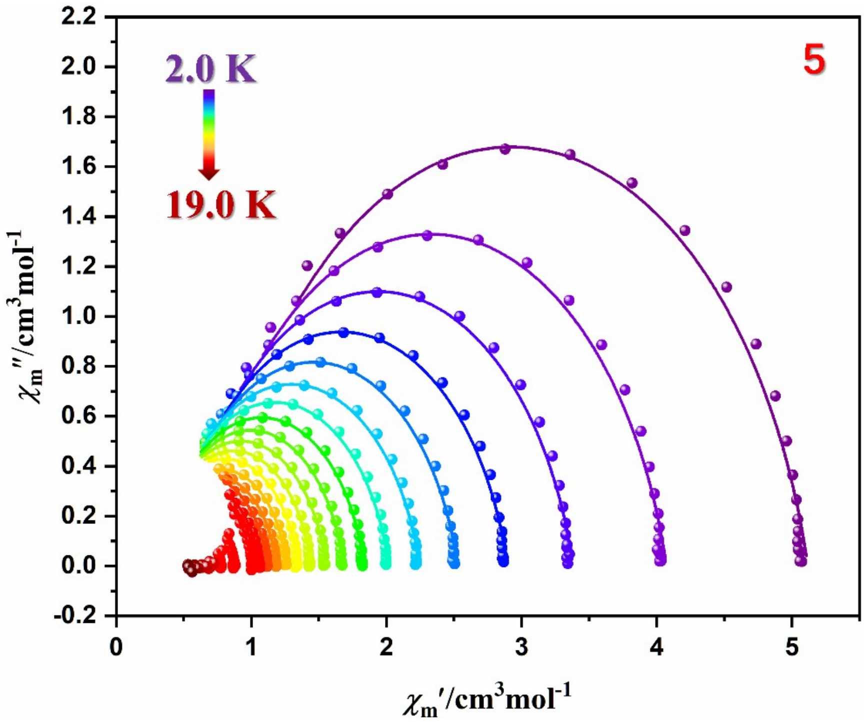


Fig. S15 The Cole-Cole fitted data for **5** in zero dc field by generalized Debye model (the solid lines represent the best results).

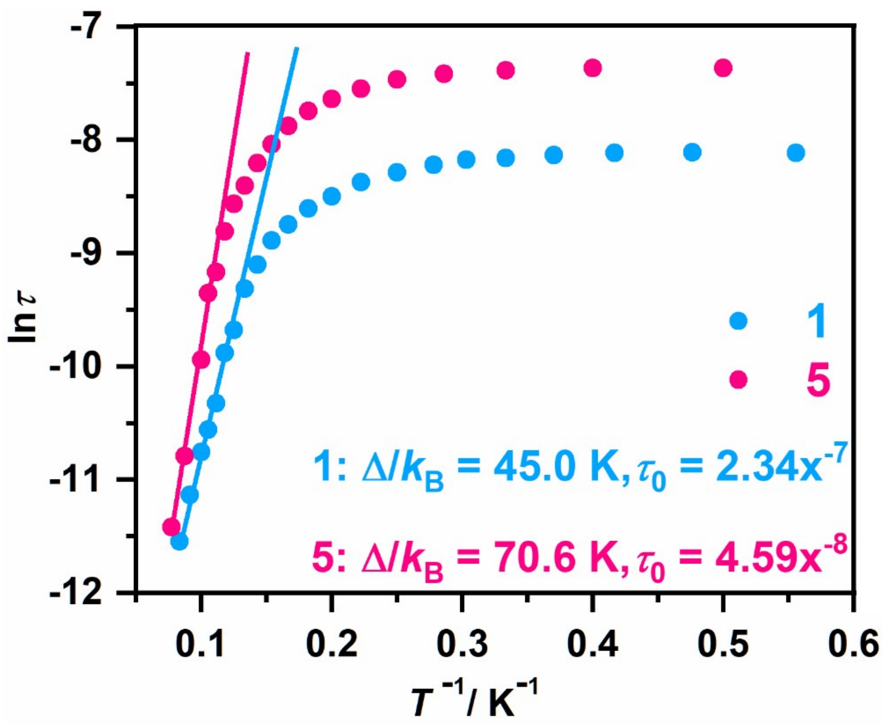


Fig. S16 The extracted magnetic relaxation time τ plot as a function of 1/T of **1** and **5** under zero dc field. The straight lines represent the best fitting based on Arrhenius law.

Table S18 The calculated energy levels (cm^{-1}), g (g_x, g_y, g_z) tensors and major m_J values of the minimum KDs of Dy(III) motifs in complex **5**.

KDs	**5**		
	E/cm^{-1}	g	m_J
1	0.0	0.014 0.028 19.389	±15/2
2	102.4 (147.5 K)	1.396 4.284 13.429	±13/2
3	126.1	1.688 4.366 10.189	±1/2
4	156.9	1.396 3.946 10.238	±9/2
5	189.2	1..668 4.634 11.064	±7/2
6	229.5	1.276 1.700 15.887	±5/2

7	304.0	0.247 0.302 19.003	±3/2
8	455.4	0.018 0.036 19.663	±11/2

Table S19 Wave functions with definite projection of the total moment | m_J > for the lowest two KDs for complexe **5**.

	E/cm^{-1}	wave functions
Complex	0.0	93.2%|±15/2>+5.5%|±11/2>
	102.4 (147.5 K)	57.6%|±13/2>+9.5%|±11/2>+9.0%|±3/2>+7.8%|±9/2 >

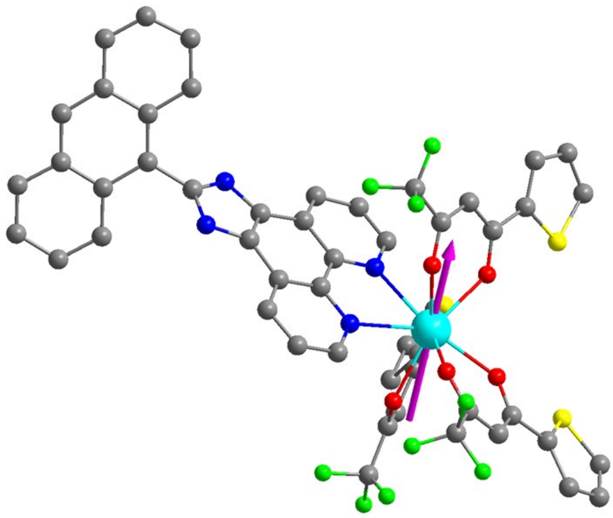


Fig. S17 The *ab initio* calculated orientations of the local main magnetic axes of the ground KDs on Dy(III) ion for complex **5**. Color code: Dy, light-blue; O, red; N, blue; C, gray; F, green; S, yellow.

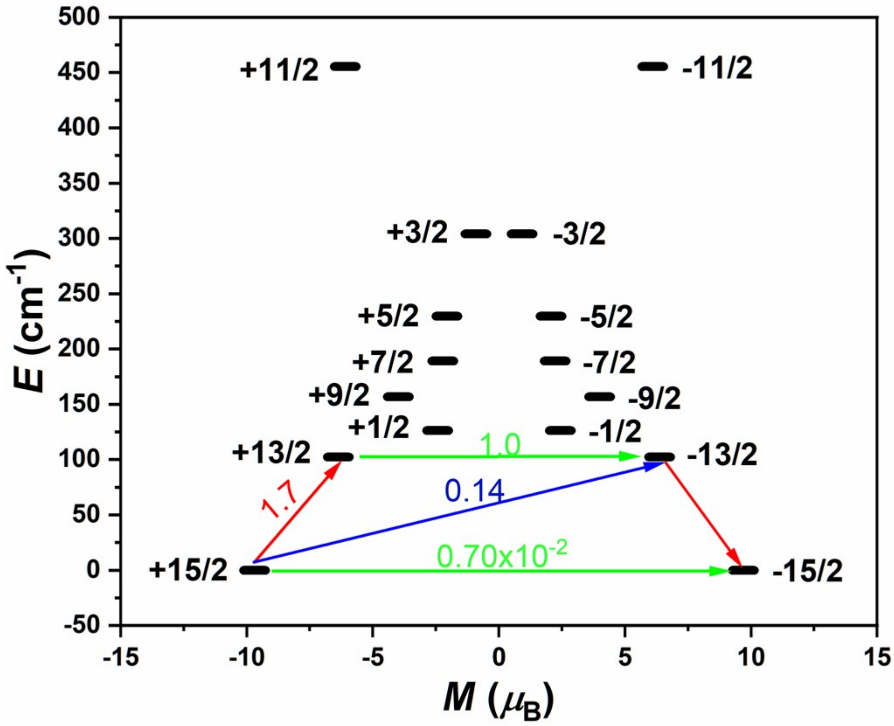


Fig. S18 The Magnetization blocking barriers in **5**. The thick black lines represent the KDs as a function of their magnetic moments along the magnetic axis. The green lines correspond to diagonal QTM, and the blue lines represent Orbach relaxation process. The red arrows represent the most possible path for magnetic relaxation. The numbers at each arrow stand for the mean absolute values of the transversal magnetic moments.

Table S20 Fitting results of the Cole-Cole plots for **1** with a generalized Debye model under zero dc field using MPMS.

T/K	χ_s / cm^3· mol^{-1}	χ_T / cm^3 · mol^{-1}	τ	α
11.99991	1.11384	6.97538	2.98741E-4	0.1643
10.99972	0.97821	5.97589	3.01006E-4	0.164
10.00011	0.86418	5.23558	2.99498E-4	0.16692
9.50025	0.75934	4.65129	2.93648E-4	0.16915
9.00013	0.67409	4.18509	2.85238E-4	0.17043
8.49976	0.65914	3.80356	2.81222E-4	0.16693
8.00074	0.60934	3.48809	2.69293E-4	0.16844
7.50032	0.56215	3.13949	2.51905E-4	0.16762
6.99984	0.53888	2.78718	2.30673E-4	0.16034
6.50012	0.49692	2.50789	2.04138E-4	0.15883
5.99996	0.49958	2.27643	1.83444E-4	0.15012
5.49989	0.47542	2.0892	1.58644E-4	0.15111

5.00007	0.46315	1.92732	1.37876E-4	0.14591
4.49998	0.41712	1.79018	1.11831E-4	0.15265
3.99996	0.36819	1.66927	9.03119E-5	0.15249
3.59993	0.22772	1.56425	6.27508E-5	0.16918
3.29997	0.21079	1.47297	5.10956E-5	0.16744
3.00004	3.72211E-14	1.3929	3.27212E-5	0.17736
2.70012	6.24475E-14	1.32113	2.59517E-5	0.18389
2.40009	7.91085E-14	1.25339	2.13253E-5	0.17398
2.10007	2.40389E-13	1.13945	1.45992E-5	0.14057
1.79995	3.37805E-13	1.04485	9.6935E-6	0.12361

Table S21 Fitting results of the Cole-Cole plots for **5** with a generalized Debye model under zero dc field using MPMS.

T/K	χ_s / $cm^3 \cdot mol^{-1}$	χ_T / $cm^3 \cdot mol^{-1}$	τ	α
2.00003	0.72264	5.11601	6.33375E-4	0.16228
2.49985	0.58717	4.06979	6.30887E-4	0.16313
2.99989	0.49583	3.38002	6.19596E-4	0.16377
3.49996	0.43722	2.89513	6.02513E-4	0.1633
4.00008	0.39778	2.5245	5.71462E-4	0.15948
4.4999	0.34961	2.24335	5.25962E-4	0.15883
4.99974	0.32971	2.01609	4.80472E-4	0.15137
5.50099	0.32073	1.83237	4.33267E-4	0.1439
6.00018	0.30935	1.67947	3.79361E-4	0.13841
6.50041	0.29618	1.54914	3.23505E-4	0.13393
7.00003	0.2961	1.43797	2.7379E-4	0.12749
7.49982	0.28537	1.34124	2.24323E-4	0.12383
7.99996	0.31559	1.25781	1.90674E-4	0.11856
8.49988	0.30053	1.18425	1.49356E-4	0.12473
8.99991	0.21894	1.1183	1.04522E-4	0.13925
9.49985	0.25285	1.05997	8.64712E-5	0.13908
9.99992	0.07841	1.00681	4.80554E-5	0.17275
11.49982	6.91657E-6	0.87448	2.05735E-5	0.15565
12.99992	6.88615E-6	0.77505	1.10103E-5	0.08738
14.49987	4.64575E-14	0.69711	3.59018E-6	0.04776
16.00022	7.11372E-14	0.63522	5.67963E-20	0.06976
17.49993	3.75415E-14	0.58099	8.12071E-20	0.09972
18.99996	3.86223E-14	0.53648	6.81252E-20	0.13548