Supporting Information

Modulation of the magnetic properties of mononuclear Dy(III) complexes by tuning the coordination geometry and local symmetry

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Table S1. Crystal data and structure refinement details for **1-3**.

complex	1	2	3
Empirical formula	$C_{51}H_{54}BCl_2DyN_6O_4$	$C_{68}H_{69}Cl_8Dy_2F_{12}N_{16}O_{17}P_2$	$C_{60}H_{54}BCl_8DyN_8O_6$
Formula weight	1059.23	2280.93	1440.02
Temperature	296.0 K	150.0 K	296.0 K
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.4067(5)	12.6622(7)	12.429(5)
b (Å)	14.5674(7)	18.6466(12)	16.344(6)
c (Å)	16.9951(9)	19.8147(13)	30.943(10)
α (°)	75.868(2)	105.480(2)	90
β (°)	81.870(2)	91.339(2)	93.964(12)
γ (°)	79.324(2)	103.205(2)	90
V (Å³)	2442.7(2)	4371.7(5)	6271(4)
Z	2	2	4
D (g/cm³)	1.418	1.733	1.525
Mu (mm⁻¹)	1.614	2.075	1.589
$F(0\,0\,0)$	1063.0	2262.0	2900.0
Completeness	99.7	99.3	98.8
Unique reflections lections	11235	14798	14346
Observed reflections	61817	68773	132829
R_{int}	0.0540	0.0441	0.0355
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0348$ $wR_2 = 0.0700$	$R_1 = 0.0398$ $wR_2 = 0.0988$	$R_1 = 0.0417$ $wR_2 = 0.1101$
R indices (all data)	$R_1 = 0.0475$ $wR_2 = 0.0749$	$R_1 = 0.0507$ $wR_2 = 0.1056$	$R_1 = 0.0467$ $wR_2 = 0.1131$
Goodness-of-fit on F^2	1.060	1.078	1.131

Table S2. Selected bond lengths (Å) and bond angles (°) for **1-3**.

Complex **1**			
Dy(1)-N(1)	2.678(2)	N(5)-Dy(1)-N(3)	120.35(9)
Dy(1)-N(2)	2.588(2)	N(5)-Dy(1)-N(4)	60.37(8)
Dy(1)-N(3)	2.610(3)	N(5)-Dy(1)-N(6)	64.97(9)
Dy(1)-N(4)	2.669(2)	N(6)-Dy(1)-N(1)	59.47(8)
Dy(1)-N(5)	2.587(3)	N(6)-Dy(1)-N(4)	118.92(8)
Dy(1)-N(6)	2.619(3)	O(1)-Dy(1)-N(1)	103.36(8)
Dy(1)-O(1)	2.495(2)	O(1)-Dy(1)-N(2)	128.24(8)
Dy(1)-O(2)	2.424(3)	O(1)-Dy(1)-N(3)	89.40(9)
Dy(1)-O(3)	2.426(2)	O(1)-Dy(1)-N(4)	69.03(8)
Dy(1)-O(4)	2.392(2)	O(1)-Dy(1)-N(5)	73.91(9)
N(2)-Dy(1)-N(1)	59.94(8)	O(1)-Dy(1)-N(6)	71.71(9)
N(2)-Dy(1)-N(3)	64.76(8)	O(2)-Dy(1)-N(1)	68.59(9)
N(2)-Dy(1)-N(4)	121.81(8)	O(2)-Dy(1)-N(2)	77.11(9)
N(2)-Dy(1)-N(6)	119.16(8)	O(2)-Dy(1)-N(3)	73.89(10)
N(3)-Dy(1)-N(1)	117.93(8)	O(2)-Dy(1)-N(4)	103.53(9)
N(3)-Dy(1)-N(4)	60.16(8)	O(2)-Dy(1)-N(5)	124.90(9)
N(3)-Dy(1)-N(6)	158.56(10)	O(2)-Dy(1)-N(6)	86.25(10)
N(4)-Dy(1)-N(1)	171.75(8)	O(2)-Dy(1)-O(1)	52.13(8)
N(5)-Dy(1)-N(1)	121.58(8)	O(2)-Dy(1)-O(3)	146.02(10)
N(5)-Dy(1)-N(2)	157.80(9)	O(3)-Dy(1)-N(1)	116.39(8)
O(3)-Dy(1)-N(2)	77.81(9)	O(4)-Dy(1)-N(2)	83.58(8)
O(3)-Dy(1)-N(3)	74.85(9)	O(4)-Dy(1)-N(3)	124.50(9)
O(3)-Dy(1)-N(4)	71.41(8)	O(4)-Dy(1)-N(4)	112.95(8)
O(3)-Dy(1)-N(5)	82.87(9)	O(4)-Dy(1)-N(5)	76.18(9)
O(3)-Dy(1)-N(6)	126.26(9)	O(4)-Dy(1)-N(6)	76.53(9)
O(3)-Dy(1)-O(1)	140.17(8)	O(4)-Dy(1)-O(1)	143.21(8)
O(4)-Dy(1)-N(1)	74.97(8)	O(4)-Dy(1)-O(2)	143.52(9)
N(3)-Dy(1)-C(30)	81.31(11)	O(4)-Dy(1)-O(3)	53.77(8)

Complex **2**			
Dy(1)-N(1)	2.564(4)	Dy(2)-N(8)	2.613(4)
Dy(1)-N(2)	2.498(4)	Dy(2)-N(9)	2.625(4)
Dy(1)-N(3)	2.610(4)	Dy(2)-N(10)	2.501(4)
Dy(1)-N(4)	2.591(4)	Dy(2)-N(11)	2.574(5)
Dy(1)-N(5)	2.521(4)	Dy(2)-N(12)	2.598(5)
Dy(1)-N(6)	2.576(4)	Dy(2)-N(13)	2.529(5)
Dy(1)-O(1)	2.215(4)	Dy(2)-O(6)	2.221(3)
Dy(1)-O(4)	2.423(4)	Dy(2)-O(9)	2.364(4)
Dy(1)-O(5)	2.378(4)	Dy(2)-O(10)	2.478(4)
N(1)-Dy(1)-N(3)	113.14(15)	N(2)-Dy(1)-N(4)	122.66(15)
N(1)-Dy(1)-N(4)	143.97(14)	N(2)-Dy(1)-N(5)	164.35(15)
N(1)-Dy(1)-N(6)	61.50(15)	N(2)-Dy(1)-N(6)	121.55(15)

N(2)-Dy(1)-N(1)	62.48(16)	N(4)-Dy(1)-N(3)	60.03(14)
N(2)-Dy(1)-N(3)	62.65(15)	N(5)-Dy(1)-N(1)	124.37(15)
N(5)-Dy(1)-N(3)	118.89(14)	N(5)-Dy(1)-N(4)	61.67(13)
N(5)-Dy(1)-N(6)	62.88(14)	N(6)-Dy(1)-N(3)	160.56(15)
N(6)-Dy(1)-N(4)	112.06(13)	O(1)-Dy(1)-N(1)	69.89(14)
O(1)-Dy(1)-N(2)	92.08(15)	O(1)-Dy(1)-N(3)	77.00(16)
O(1)-Dy(1)-N(4)	74.21(15)	O(1)-Dy(1)-N(5)	103.49(14)
O(1)-Dy(1)-N(6)	83.77(15)	O(1)-Dy(1)-O(4)	142.97(15)
O(1)-Dy(1)-O(5)	146.13(15)	O(4)-Dy (1)-N(1)	74.06(14)
O(4)-Dy(1)-N(2)	78.43(14)	O(4)-Dy(1)-N(3)	126.34(15)
O(4)-Dy(1)-N(4)	140.52(14)	O(4)-Dy(1)-N(5)	89.83(14)
O(4)-Dy(1)-N(6)	71.75(13)	O(5)-Dy(1)-N(1)	136.65(14)
O(5)-Dy(1)-N(2)	87.12(15)	O(5)-Dy(1)-N(3)	72.62(15)
O(5)-Dy(1)-N(4)	77.84(14)	O(5)-Dy(1)-N(5)	79.06(14)
O(5)-Dy(1)-N(6)	124.93(14)	O(5)-Dy(1)-O(4)	69.83(14)
N(8)-Dy(2)-N(9)	60.34(13)	N(10)-Dy(2)-N(8)	123.47(14)
N(10)-Dy(2)-N(9)	63.13(13)	N(10)-Dy(2)-N(11)	62.39(14)
N(10)-Dy(2)-N(12)	121.02(15)	N(10)-Dy(2)-N(13)	162.74(15)
N(11)-Dy(2)-N(8)	145.96(13)	N(11)-Dy(2)-N(9)	113.91(13)
N(11)-Dy(2)-N(12)	61.51(15)	N(12)-Dy(2)-N(8)	112.89(14)
N(12)-Dy(2)-N(9)	162.51(14)	N(13)-Dy(2)-N(8)	61.01(15)
N(13)-Dy(2)-N(9)	118.39(15)	N(13)-Dy(2)-N(11)	124.87(15)
N(13)-Dy(2)-N(12)	63.36(16)	O(6)-Dy(2)-N(8)	74.07(14)
O(6)-Dy(2)-N(9)	80.67(13)	O(6)-Dy(2)-N(10)	97.07(14)
O(6)-Dy(2)-N(11)	71.89(13)	O(6)-Dy(2)-N(12)	81.92(14)
O(6)-Dy(2)-N(13)	100.14(14)	O(6)-Dy(2)-O(9)	151.01(14)
O(6)-Dy(2)-O(10)	141.35(15)	O(9)-Dy(2)-N(8)	81.38(14)
O(9)-Dy(2)-N(9)	73.81(14)	O(9)-Dy(2)-N(10)	83.64(14)
O(9)-Dy(2)-N(11)	131.33(14)	O(9)-Dy(2)-N(12)	122.56(15)
O(9)-Dy(2)-N(13)	80.65(15)	O(9)-Dy(2)-O(10)	67.05(15)
O(10)-Dy(2)-N(8)	141.54(15)	O(10)-Dy(2)-N(9)	125.31(14)
O(10)-Dy(2)-N(10)	75.69(14)	O(10)-Dy(2)-N(11)	71.23(14)
O(10)-Dy(2)-N(12)	70.68(15)	O(10)-Dy(2)-N(13)	91.55(15)

Complex 3			
Dy(1)-O(1)	2.223(3)	N(4)-Dy(1)-N(3)	61.49(11)
Dy(1)-O(4)	2.166(3)	N(4)-Dy(1)-N(5)	64.19(13)
Dy(1)-N(8)	2.580(3)	N(4)-Dy(1)-N(7)	117.56(11)
Dy(1)-N(3)	2.578(3)	N(5)-Dy(1)-N(8)	61.35(12)
Dy(1)-N(4)	2.537(3)	N(5)-Dy(1)-N(3)	117.18(11)
Dy(1)-N(5)	2.575(4)	N(5)-Dy(1)-N(7)	171.04(11)
Dy(1)-N(6)	2.518(3)	N(6)-Dy(1)-N(8)	61.68(12)
Dy(1)-N(7)	2.637(3)	N(6)-Dy(1)-N(7)	62.70(10)

O(1)-Dy(1)-N(8)	74.02(10)	N(6)-Dy(1)-N(3)	122.94(11)
O(1)-Dy(1)-N(3)	76.91(9)	N(6)-Dy(1)-N(4)	160.04(11)
O(1)-Dy(1)-N(4)	100.51(11)	N(6)-Dy(1)-N(5)	119.04(12)
O(1)-Dy(1)-N(5)	84.38(11)	O(4)-Dy(1)-N(5)	90.10(12)
O(1)-Dy(1)-N(6)	99.43(11)	O(4)-Dy(1)-N(6)	80.23(11)
O(1)-Dy(1)-N(7)	86.66(9)	O(4)-Dy(1)-N(7)	98.85(11)
O(4)-Dy(1)-O(1)	173.49(11)	N(8)-Dy(1)-N(7)	116.13(10)
O(4)-Dy(1)-N(8)	100.30(11)	N(3)-Dy(1)-N(8)	150.90(9)
O(4)-Dy(1)-N(3)	108.80(11)	N(3)-Dy(1)-N(7)	60.25(9)
O(4)-Dy(1)-N(4)	80.07(11)	N(4)-Dy(1)-N(8)	125.54(12)

Table S3. Hydrogen-bonded parameters (Å, °) for **2**.

Complex	D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
	O4-H4A...O14[1]	0.88	2.02	2.887(7)	173.0
	O4-H4B...O11	0.88	1.88	2.732(6)	163.7
	O5-H5D...O11	0.90	1.83	2.680(7)	157.3
	O5-H5E...O14A	0.90	1.94	2.753(9)	150.2
2	O9-H9A...O13[2]	0.91	1.79	2.605(6)	148.3
	O9-H9B...O16[2]	0.91	2.02	2.836(8)	149.8
	O11-H11A...O13	0.87	1.86	2.721(7)	172.9
	O11-H11B...O16	0.87	2.05	2.876(9)	157.7

[1]-1+X,+Y,+Z; [2]+X,1+Y,+Z

Table S4. Continuous Shape Measurements (CShMs) for Dy(III) ions in **1-3** by SHAPE 2.1.

Configuration	ABOXIY, **1**	Configuration	ABOXIY, **2**		Configuration	ABOXIY, **3**
TD-10	**2.109**	MFF-9	**3.472**	3.922	HBPY-8	**2.967**
OBPY-10	15.997	HBPY-9	15.015	14.197	CU-8	11.348
PPR-10	11.076	JTC-9	13.524	14.078	SAPR-8	15.328
PAPR-10	11.438	JCCU-9	6.264	6.119	TDD-8	13.946
JBCCU-10	8.742	CCU-9	5.250	5.093	JGBF-8	4.301
JBCSAPR-10	3.927	JCSAPR-9	6.178	6.526	JETBPY-8	22.513
JMBIC-10	6.804	CSAPR-9	4.957	5.288	JBTPR-8	14.115
JATDI-10	18.459	JTCTPR-9	5.828	6.452	BTPR-8	13.933
JSPC-10	2.550	TCTPR-9	6.093	6.301	JSD-8	13.437
SDD-10	2.671	JTDIC-9	11.462	11.813	TT-8	11.954
HD-10	6.366	HH-9	4.051	3.697	ETBPY-8	19.926

Table S5. Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 1000 Oe dc field of **1**.

T(K)	χ_T	χ_S	α
3	1.197	0.358	0.515
3.5	0.985	0.380	0.376
4	0.854	0.366	0.275
4.5	0.761	0.343	0.225
5	0.687	0.331	0.197
5.5	0.626	0.320	0.189
6	0.575	0.280	0.212
6.5	0.535	3.16×10^{-08}	0.322
7	0.497	5.03×10^{-08}	0.342
7.5	0.466	3.85×10^{-08}	0.438
8	0.438	7.44×10^{-08}	0.559

Table S6. Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 1000 Oe dc field of **2**.

T(K)	χ_T	χ_S	α
5	2.149	0.957	0.367
5.5	1.949	0.923	0.329
6	1.787	0.870	0.308
6.5	1.650	0.814	0.293
7	1.531	0.709	0.319
8	1.342	0.652	0.284
9	1.197	0.538	0.281
10	1.071	0.388	0.262

Table S7. Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 500 Oe dc field of **3**.

T(K)	χ_T	χ_S	α
2	2.613	0.106	0.309
2.5	2.151	0.090	0.217
3	1.841	0.074	0.169
3.5	1.598	0.062	0.143
4	1.405	0.051	0.126
4.5	1.255	0.041	0.118
5	1.132	0.033	0.116
5.5	1.030	0.030	0.114
6	0.947	0.039	0.113
6.5	0.875	0.067	0.104

Table S8. Calculated energy levels (cm^{-1}) and g (g_x, g_y, g_z) tensors and τ_{QTM} (s) of the lowest eight Kramers doublets (KDs) of **1**, **1a, 2a, 2b** and **3** using CASSCF/RASSI-SO with ORCA.

	KDs	E/cm^{-1}	g_x	g_y	g_z	g_z Angle/°	τ_{QTM}/s
1	KD$_0$	0.000	0.0086	0.0300	19.8911	--	7.728×10^{-5}
	KD$_1$	135.381	0.3403	0.4595	16.8836	101.00	1.846×10^{-7}
	KD$_2$	172.720	1.1244	2.1609	11.8082	104.89	7.259×10^{-9}
	KD$_3$	198.838	9.3681	6.6819	1.7220	87.79	3.139×10^{-10}
	KD$_4$	249.730	1.9616	2.6386	14.4972	55.38	4.912×10^{-9}
	KD$_5$	302.777	0.2839	2.2431	16.6458	89.59	1.174×10^{-8}
	KD$_6$	334.879	0.0214	1.3888	12.7757	84.46	2.379×10^{-8}
	KD$_7$	363.346	0.3024	3.9791	15.1564	87.99	3.516×10^{-9}
1a	KD$_0$	0.000	0.0000	0.0000	19.9828	--	9.792×10^{5}
	KD$_1$	452.728	0.0000	0.0000	17.0576	1.51	3.842×10^{3}
	KD$_2$	773.849	0.0001	0.0001	14.3403	0.61	1.324
	KD$_3$	1026.546	0.0027	0.0029	11.6860	3.31	2.616×10^{-3}
	KD$_4$	1249.325	0.0332	0.0379	9.0535	7.34	1.274×10^{-5}
	KD$_5$	1447.014	0.3208	0.3837	6.4078	9.92	9.177×10^{-8}
	KD$_6$	1601.640	2.5461	3.0726	3.8224	27.72	1.240×10^{-9}
	KD$_7$	1692.073	13.39237	7.6377	1.1692	2.14	2.324×10^{-10}
2a	KD$_0$	0.000	0.0315	0.1340	19.4796	--	7.620×10^{-5}
	KD$_1$	82.844	0.0745	0.2004	18.6284	63.77	1.456×10^{-6}
	KD$_2$	132.402	0.2838	0.9402	16.9403	132.41	6.284×10^{-8}
	KD$_3$	170.564	1.5215	1.9508	16.4952	98.86	9.735×10^{-9}
	KD$_4$	225.652	1.5268	2.0777	14.9452	37.88	8.150×10^{-9}
	KD$_5$	258.999	4.6775	6.0662	8.5471	122.22	6.988×10^{-10}
	KD$_6$	332.885	0.9674	1.0154	17.3019	115.89	3.153×10^{-8}
	KD$_7$	395.283	0.1497	0.1774	18.9796	113.62	1.258×10^{-6}
2b	KD$_0$	0.000	0.1316	0.1398	19.5184	--	1.892×10^{-6}
	KD$_1$	92.678	0.1860	0.2914	19.1371	121.10	5.721×10^{-7}
	KD$_2$	162.085	1.2929	2.8965	14.9207	41.31	5.416×10^{-9}
	KD$_3$	193.599	0.9151	3.2440	15.4659	103.21	4.977×10^{-9}
	KD$_4$	236.840	1.4818	4.8019	11.1230	135.31	1.727×10^{-9}
	KD$_5$	296.235	1.9574	5.2631	9.7676	84.52	1.276×10^{-9}
	KD$_6$	355.129	1.5686	2.7542	15.9311	57.95	5.776×10^{-9}
	KD$_7$	453.361	0.1594	0.2672	19.1980	71.29	7.087×10^{-7}
3	KD$_0$	0.000	0.0181	0.0280	19.9138	--	6.417×10^{-5}
	KD$_1$	291.753	1.3189	2.2459	15.6436	2.01	8.352×10^{-9}
	KD$_2$	416.542	1.0787	2.9242	13.8248	93.39	5.211×10^{-9}
	KD$_3$	505.181	3.1951	4.2268	11.6370	82.12	1.627×10^{-9}

KD₄	553.397	0.1087	1.8287	9.2537	93.11	1.004×10^{-8}
KD₅	579.551	4.3609	5.2768	8.7172	109.40	8.449×10^{-10}
KD₆	677.018	5.0112	5.1992	10.0056	92.32	8.453×10^{-10}
KD₇	739.008	0.3545	1.0256	16.3616	77.66	4.957×10^{-8}

Table S9. Wave functions with definite projection of the total moment | m_J > for the lowest eight KDs of **1**, **1a, 2a, 2b** and **3** using CASSCF/RASSI-SO with ORCA.

	E/cm⁻¹	wave functions
1	0.000	99.4% |±15/2>
	135.381	6.4% |±13/2> + 20.9% |±9/2> + 32.2% |±7/2> + 25.7% |±5/2> + 10.5% |±3/2>
	172.720	26.1% |±13/2> + 24.4% |±11/2> + 18.7% |±9/2> + 10.8% |±7/2> + 4.2% |±5/2> + 5.1% |±3/2> + 10.8%
	198.838	49.0% |±13/2> + 6.4% |±11/2> + 22.6% |±9/2> + 11.9% |±7/2> + 4.9% |±5/2> + 4.1% |±3/2>
	249.730	17.9% |±13/2> + 45.1% |±11/2> + 12.6% |±9/2> + 6.4% |±7/2> + 5.7% |±5/2> + 5.4% |±3/2> + 6.7% |±1/2>
	302.777	23.3% |±7/2> + 43.6% |±5/2> + 22.2% |±3/2> +7.0% |±1/2>
	334.879	3.0% |±11/2> + 18.0% |±9/2> + 13.8% |±7/2> + 10.3% |±5/2> + 35.5% |±3/2> +18.6% |±1/2>
	363.346	3.6% |±13/2> + 13.3% |±11/2> + 5.1% |±9/2> + 5.7% |±5/2> + 16.9% |±3/2> + 53.8% |±1/2>
1a	0.000	100.0% |±15/2>
	452.728	99.8% |±13/2>
	773.849	99.5% |±11/2>
	1026.546	99.3% |±9/2>
	1249.325	99.0% |±7/2>
	1447.014	97.5% |±5/2>
	1601.640	94.0% |±3/2> + 4.4% |±1/2>
	1692.073	4.2% |±3/2> + 95.2% |±1/2>
2a	0.000	95.2% |±15/2> + 2.8% |±9/2>
	82.844	7.9% |±11/2> + 19.7% |±9/2> + 32.5% |±7/2> + 27.5% |±5/2> + 8.9% |±3/2>
	132.402	33.3% |±13/2> + 18.2% |±11/2> + 8.3% |±9/2> + 16.6% |±7/2> + 16.5% |±5/2> + 7.4% |±3/2>
	170.564	20.3% |±11/2> + 11.8%|±7/2> + 6.0% |±5/2> + 29.0% |±3/2> + 26.4% |±1/2>
	225.652	29.7% |±13/2> + 37.6% |±11/2> +14.3% |±5/2> + 6.8% |±3/2> + 10.0% |±1/2>
	258.999	19.7% |±13/2> + 4.1% |±11/2> + 26.9% |±9/2> + 3.7% |±7/2> + 4.2% |±5/2> + 14.2% |±3/2> + 26.1% |±1/2>
	332.885	9.2% |±13/2> + 15.2% |±11/2> + 8.0% |±9/2> + 19.2% |±7/2> +11.7% |±5/2> + 15.1% |±3/2> +20.6% |±1/2>
	395.283	4.8% |±13/2> + 14.8% |±11/2> + 12.6% |±9/2> + 14.6% |±7/2> + 19.6% |±5/2> + 18.6% |±3/2> + 14.6% |±1/2>
2b	0.000	95.9% |±15/2> + 2.6% |±7/2>
	92.678	5.9% |±13/2> + 12.4% |±11/2> + 27.1% |±9/2> + 24.5% |±7/2> + 21.6% |±5/2> + 5.7% |±3/2>
	162.085	38.9% |±13/2> + 13.7% |±11/2> + 18.3% |±7/2> + 18.0% |±5/2> + 11.3% |±3/2> + 4.3% |±1/2>

	193.599	3.9% |±13/2> + 8.4% |±11/2> + 19.4%|±9/2> + 11.1% |±7/2> + 7.7% |±5/2> + 29.9% |±3/2> + 18.8% |±1/2>
	236.840	20.8% |±13/2> + 28.9% |±11/2> + 3.4% |±9/2> + 17.5% |±5/2> + 23.3% |±1/2>
	296.235	15.6% |±13/2> + 24.9% |±9/2> + 7.7% |±7/2> + 8.8% |±5/2> + 25.5% |±3/2> + 15.1% |±1/2>
	355.129	10.5% |±13/2> + 23.4% |±11/2> + 12.0% |±9/2> + 19.0% |±7/2> + 9.8% |±5/2> + 6.0% |±3/2> + 18.6% |±1/2>
	453.361	4.4% |±13/2> + 11.4% |±11/2> + 10.0% |±9/2> + 12.5% |±7/2> + 18.4% |±5/2> + 21.5% |±3/2> + 21.4% |±1/2>
	0.000	99.6% |±15/2>
	291.753	90.3% |±13/2> + 6.6% |±1/2>
	416.542	7.8% |±13/2> + 17.8% |±11/2> + 3.0% |±9/2> + 3.9% |±7/2> + 6.3% |±5/2> + 20.1% |±3/2> + 40.9% |±1/2>
3	505.181	21.7% |±11/2> + 12.4% |±9/2> + 3.0%|±7/2> + 46.1% |±3/2> + 14.8% |±1/2>
	553.397	20.1% |±11/2> +15.1% |±7/2> + 52.7% |±5/2> + 8.3% |±3/2>
	579.551	35.4% |±11/2> + 6.4% |±9/2> + 15.0% |±7/2> + 6.2% |±5/2> + 4.9% |±3/2> + 31.3% |±1/2>
	677.018	3.3% |±11/2> + 58.4% |±9/2> + 15.3% |±7/2> + 5.7% |±5/2> +13.2% |±3/2> + 3.6% |±1/2>
	739.008	17.5% |±9/2> + 47.4% |±7/2> + 26.8% |±5/2> + 6.5% |±3/2>

Table S10. Mulliken atomic charge on the metal atoms and donor atoms in the ground state of **1**, **1a, 2a, 2b** and **3** calculated within B3LYP-D3/DKH-def2-TZVP level.

	1		**1a**		**2a**		**2b**		**3**
Dy	1.9499	Dy	1.7250	Dy1	1.7571	Dy2	1.6794	Dy	1.9386
N1	-0.2872	O1	-0.4669	N1	-0.4084	N8	-0.4347	N3	-0.3326
N2	-0.3082	O2	-0.4839	N2	-0.3905	N9	-0.3679	N4	-0.3268
N3	-0.2988	O3	-0.4715	N3	-0.3473	N10	-0.4024	N5	-0.2934
N4	-0.2933	O4	-0.4736	N4	-0.4276	N11	-0.3907	N6	-0.3175
N5	-0.3227			N5	-0.3893	N12	-0.4251	N7	-0.3092
N6	-0.3040			N6	-0.3321	N13	-0.3778	N8	-0.3055
O1	-0.4997			O1	-0.6430	O6	-0.6464	O1	-0.7185
O2	-0.5274			O4	-0.5217	O9	-0.5806	O4	-0.6931
O3	-0.5157			O5	-0.5787	O10	-0.5765		
O4	-0.5237								

Table S11. Mulliken spin density of **1, 1a, 2a, 2b** and **3**.

	1		1a		2a		2b		3	
Atoms	Spin density	Atoms	Spin density	Atoms	Spin density	Atoms	Spin density	Atoms	Spin density	
Dy	5.0218	Dy	4.9766	Dy	5.0178	Dy	5.0124	Dy	5.0022	
N1	-0.0016	O1	0.0084	N1	-0.2816	N1	-0.2859	N1	-0.0031	
N2	-0.0038	O2	0.0068	N2	-0.1506	N2	-0.0830	N2	-0.0024	
N3	-0.0040	O3	-0.0023	N3	0.0966	N3	0.0970	N3	-0.0027	
N4	-0.0018	O4	0.0135	N4	0.2717	N4	0.2922	N4	-0.0026	
N5	-0.0039			N5	0.0981	N5	0.1067	N5	-0.0016	
N6	-0.0033			N6	-0.0629	N6	-0.1266	N6	-0.0027	
O7	-0.0034			O7	-0.0051	O7	-0.0019	O7	0.0024	
O8	-0.0021			O8	0.0075	O8	-0.0061	O8	0.0011	
O9	-0.0020			O9	0.0025	O9	0.0029			
O10	-0.0025									

Table S12. Calculated crystal field parameters B (k, q) for **1**, **1a, 2a, 2b** and **3** using CASSCF/RASSI-SO with ORCA.

k	q	B_k^q				
		1	1a	2a	2b	3
2	-2	1.55	-1.65	-2.03	-1.37	-1.47×10^{-1}
2	-1	9.51×10^{-1}	4.48×10^{-2}	5.45	4.67	-1.71×10^{-1}
2	0	-3.21	-22.50	-2.01	-2.39	-2.87
2	1	3.61×10^{-1}	-1.88×10^{-1}	8.52×10^{-1}	5.67	-7.48×10^{-1}
2	2	5.25×10^{-2}	5.58×10^{-1}	8.91×10^{-1}	-3.14	1.24
4	-4	-8.09×10^{-3}	-3.17×10^{-3}	1.39×10^{-1}	-6.18×10^{-2}	-2.18×10^{-4}
4	-3	4.06×10^{-3}	2.62×10^{-3}	2.58×10^{-1}	-3.08×10^{-1}	-3.61×10^{-3}
4	-2	-2.37×10^{-4}	-2.31×10^{-2}	-4.34×10^{-2}	-1.01×10^{-1}	-1.35×10^{-3}
4	-1	-6.39×10^{-3}	-1.94×10^{-2}	-8.46×10^{-2}	-3.70×10^{-2}	3.43×10^{-3}
4	0	-1.76×10^{-2}	-4.06×10^{-3}	-2.39×10^{-2}	-2.48×10^{-2}	-1.18×10^{-2}
4	1	1.07×10^{-2}	3.95×10^{-2}	4.58×10^{-2}	-4.09×10^{-2}	5.01×10^{-3}
4	2	-7.82×10^{-3}	1.39×10^{-02}	8.29×10^{-2}	-1.26×10^{-2}	-3.02×10^{-4}
4	3	-3.47×10^{-3}	-2.82×10^{-2}	2.24×10^{-1}	3.48×10^{-2}	-7.83×10^{-4}
4	4	-3.32×10^{-2}	6.61×10^{-3}	-3.84×10^{-2}	1.61×10^{-1}	-8.45×10^{-3}
6	-6	1.45×10^{-2}	1.88×10^{-05}	4.30×10^{-3}	-4.37×10^{-3}	-7.29×10^{-4}
6	-5	-5.60×10^{-4}	-3.92×10^{-5}	-2.61×10^{-3}	-2.73×10^{-4}	-1.97×10^{-4}
6	-4	-4.73×10^{-4}	-1.64×10^{-4}	2.90×10^{-3}	-1.43×10^{-3}	-1.28×10^{-5}
6	-3	4.73×10^{-4}	-1.09×10^{-4}	5.26×10^{-3}	-8.78×10^{-3}	1.58×10^{-5}
6	-2	-1.73×10^{-3}	9.99×10^{-4}	2.19×10^{-3}	3.99×10^{-3}	-7.13×10^{-5}
6	-1	-4.76×10^{-3}	1.16×10^{-3}	9.98×10^{-3}	5.71×10^{-3}	-4.08×10^{-5}
6	0	-8.67×10^{-4}	-7.71×10^{-4}	-5.27×10^{-4}	-7.56×10^{-4}	2.99×10^{-5}
6	1	-7.66×10^{-4}	-2.23×10^{-3}	4.15×10^{-3}	5.69×10^{-3}	-1.31×10^{-6}
6	2	1.36×10^{-3}	-6.50×10^{-4}	-3.54×10^{-3}	1.83×10^{-3}	1.30×10^{-5}
6	3	9.06×10^{-4}	9.46×10^{-4}	9.26×10^{-3}	4.60×10^{-3}	-3.17×10^{-5}
6	4	1.67×10^{-3}	2.01×10^{-4}	-1.28×10^{-3}	4.46×10^{-3}	-8.05×10^{-5}

|					
6	5	-7.76×10^{-3}	1.27×10^{-5}	1.37×10^{-3}	2.41×10^{-3}	-2.96×10^{-5}
6	6	-3.00×10^{-3}	1.09×10^{-5}	4.09×10^{-3}	-3.76×10^{-3}	1.06×10^{-4}
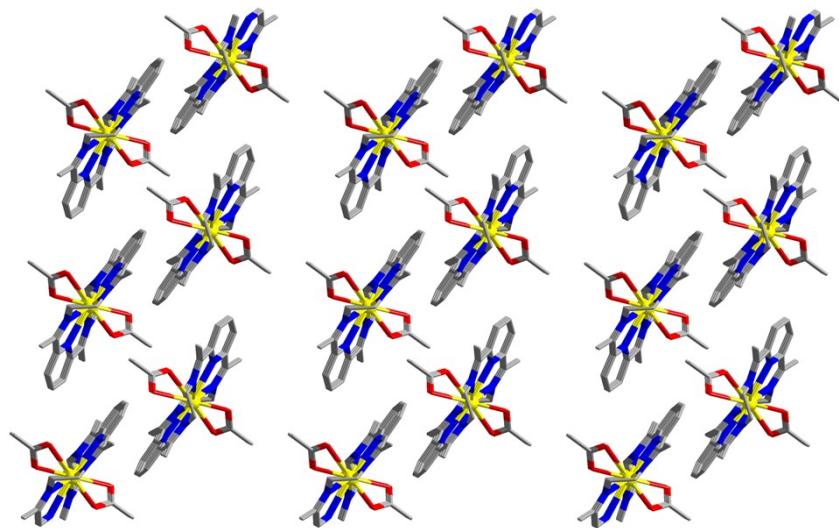
Fig. S1 Crystal packing diagram for complex **1**. All hydrogen atoms, solvent molecules, and the counter ion [BPh$_4$]$^+$ for **1** are omitted for clarity.

(a)

(b)
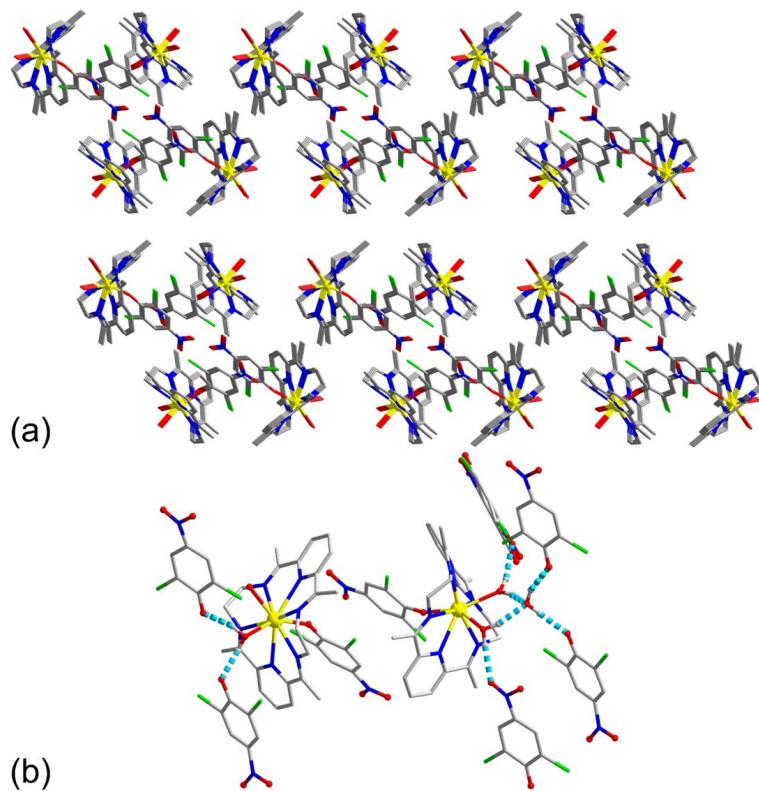
Fig. S2 (a) Crystal packing diagram for complex **2**. All hydrogen atoms (except for the H atoms in the H-bonds), solvent molecules, and the counter ion [PF$_6$]$^+$ for **2** are omitted for clarity. (b) Hydrogen bonding in complex **2** (the dashed line represents the interaction).
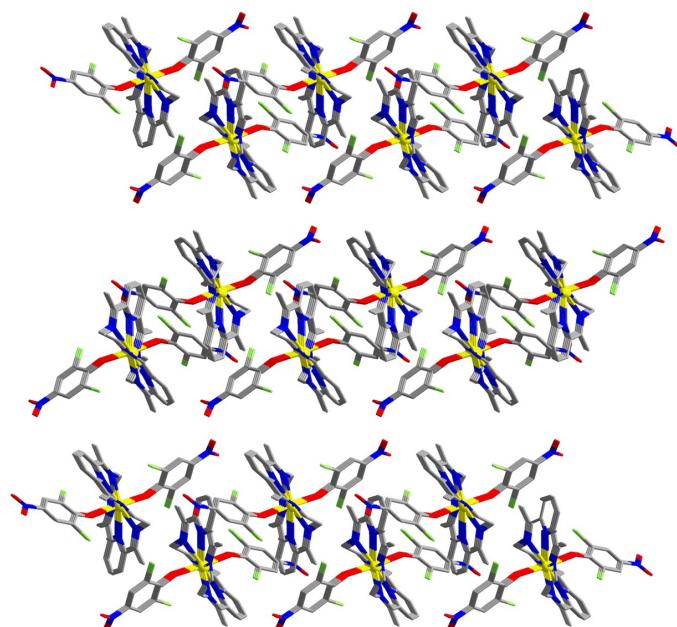
Fig. S3 Crystal packing diagram for complex **3**. All hydrogen atoms, solvent molecules, and the counter ion [BPh$_4$]$^+$ for **3** are omitted for clarity.
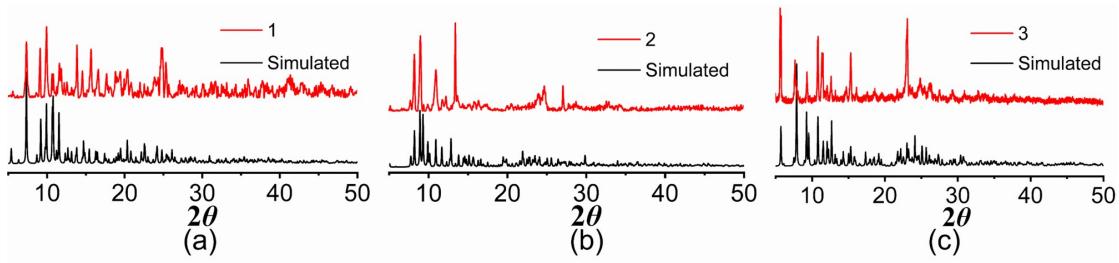
Fig. S4 PXRD curves of **1** (a), **2** (b) and **3** (c).
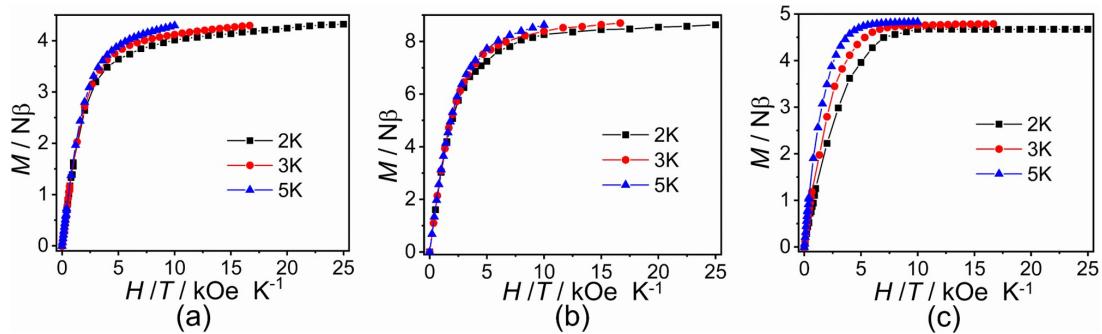
Fig. S5 *M vs H/T* curves for **1** (a), **2** (b) and **3** (c) at indicated temperatures.
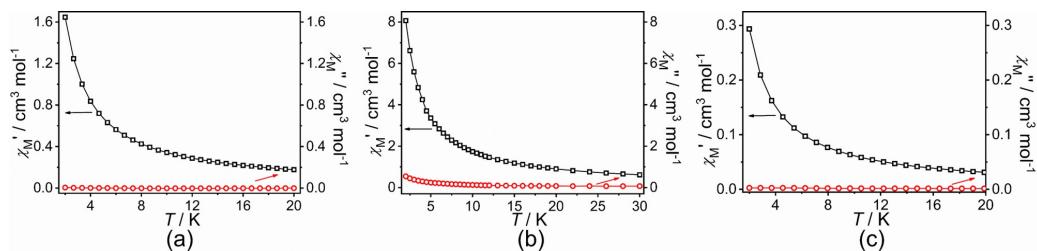
Fig. S6 Ac magnetic susceptibility measurements for **1** (a), **2** (b) and **3** (c) in zero static field.
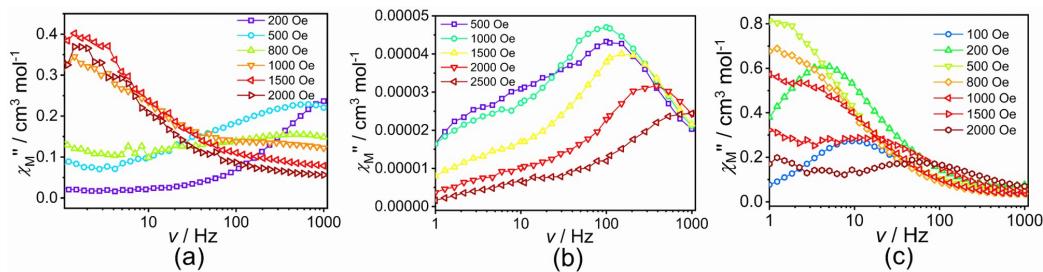
Fig. S7 Frequency dependence of χ''_M susceptibilities for **1** (a), **2** (b) and **3** (c) under different dc fields.
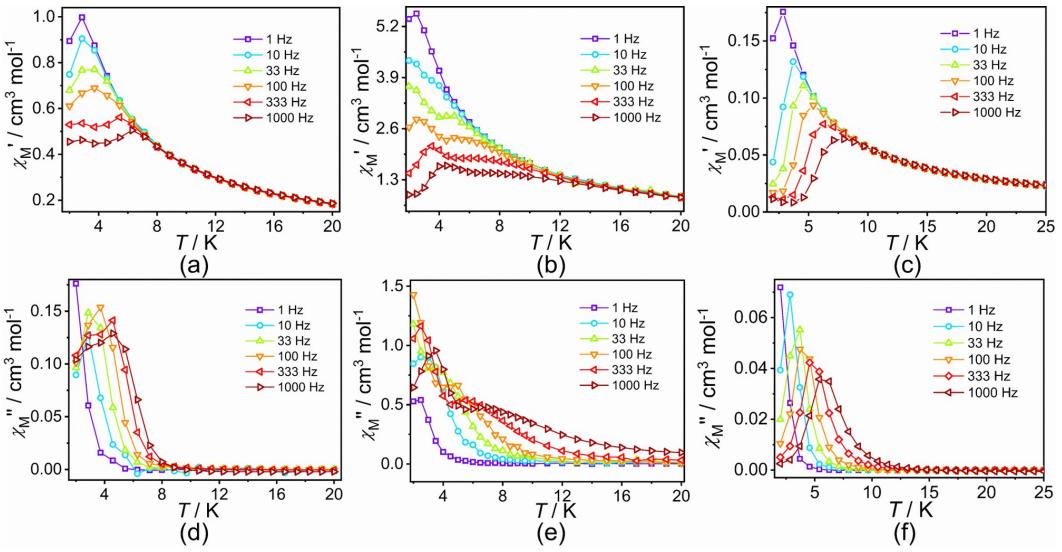
Fig. S8 Temperature dependence of the in-phase (χ'_M, top) and out-of-phase (χ''_M, bottom) ac susceptibilities at different frequencies under the external dc fields for complexes **1** (a, d)**, 2** (b, e) and **3** (c, f).
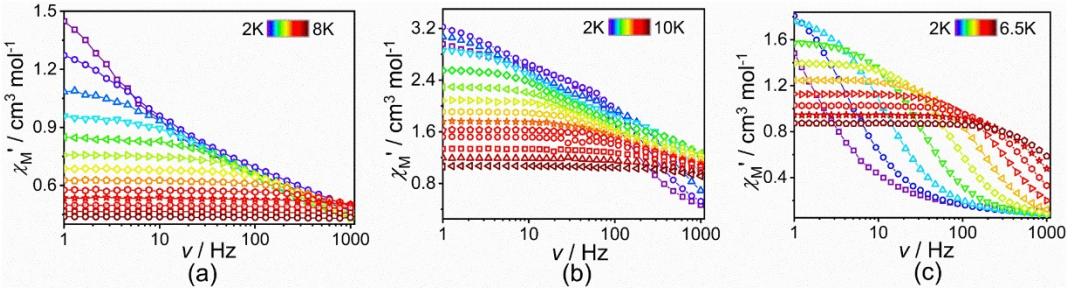
Fig. S9 Frequency dependence of χ'_M susceptibilities for **1** (a), **2** (b) and **3** (c) under the external dc fields.
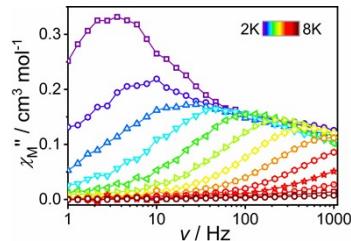

Fig. S10 Frequency dependence of χ''_M susceptibilities for **1** under the external dc fields.
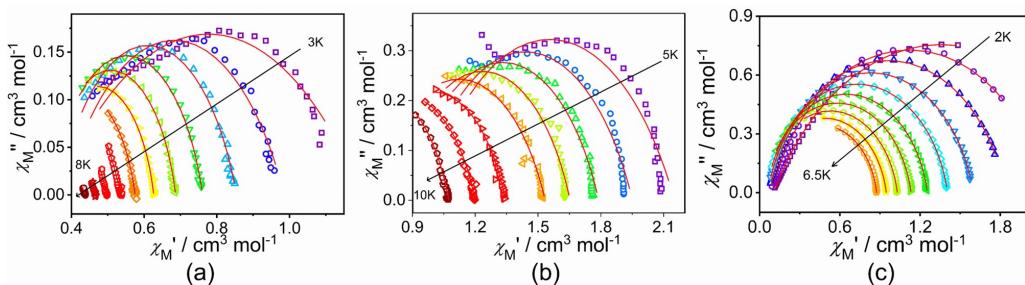

Fig. S11 Cole-Cole plots under the static dc fields for **1** (a), **2** (b) and **3** (c). The solid lines represent the best fit to the measured results.
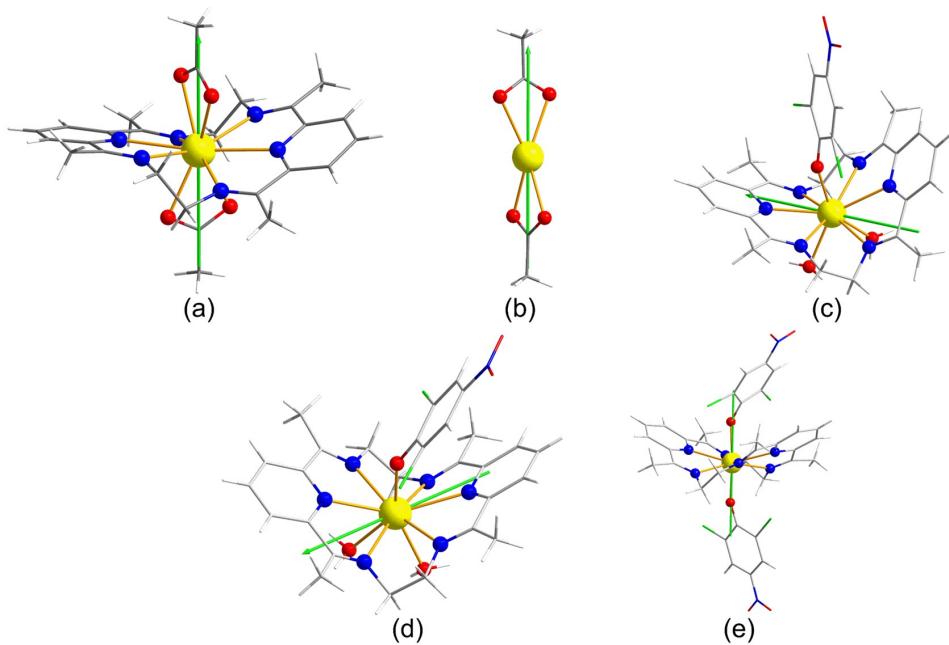
Fig. S12 Calculated orientations of the local main magnetic axes on Dy(III) in the ground KDs of **1** (a), **1a** (b), **2a** (c), **2b** (d) and **3** (e).
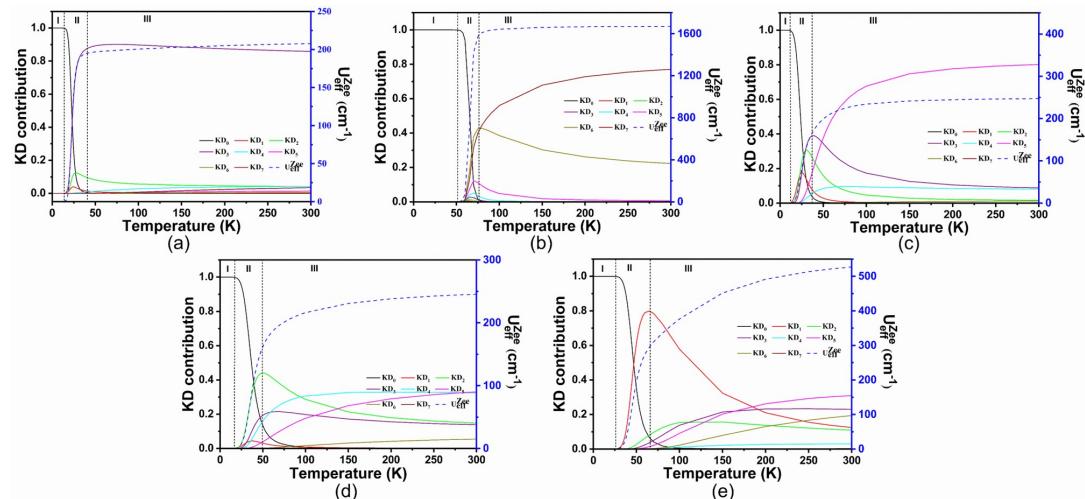

Fig. S13 Predicted effective barrier and relaxation contributions from various KDs of complexes **1** (a), **1a** (b), **2a** (c), **2b** (d) and **3** (e), U_{eff} is represented as a dashed black line, and its value is indicated on the right *y*-axis, the left *y*-axis represents the relative contribution of each KD to relaxation.