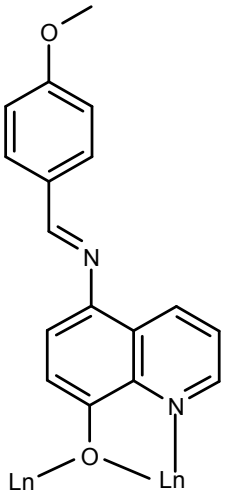
Electronic Supplementary Material (ESI) for RSC Advances.

A series of planar tetranuclear lanthanide complexes: axial ligand modulated magnetic dynamics in Dy_4 species

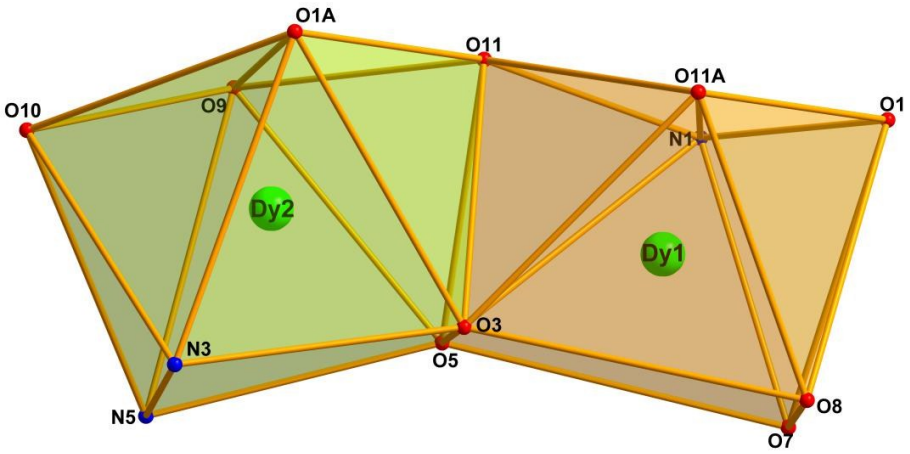
Ya-Xin Zhang,[a] Meng Li,[a] Bi-Ying Liu,[a] Zhi-Lei Wu,[*a] Hai-Ying Wei,[*a] Wen-Min Wang[*b]

[a] *College of Chemistry and Environmental Science, Hebei University, Baoding, 071002, P. R. China.*

[b] *Department of Chemistry, Tianjin University, Tianjin, 300072, China.*



Scheme S1. The μ_2-$\eta^2\eta^1$ bonding mode of L^-.



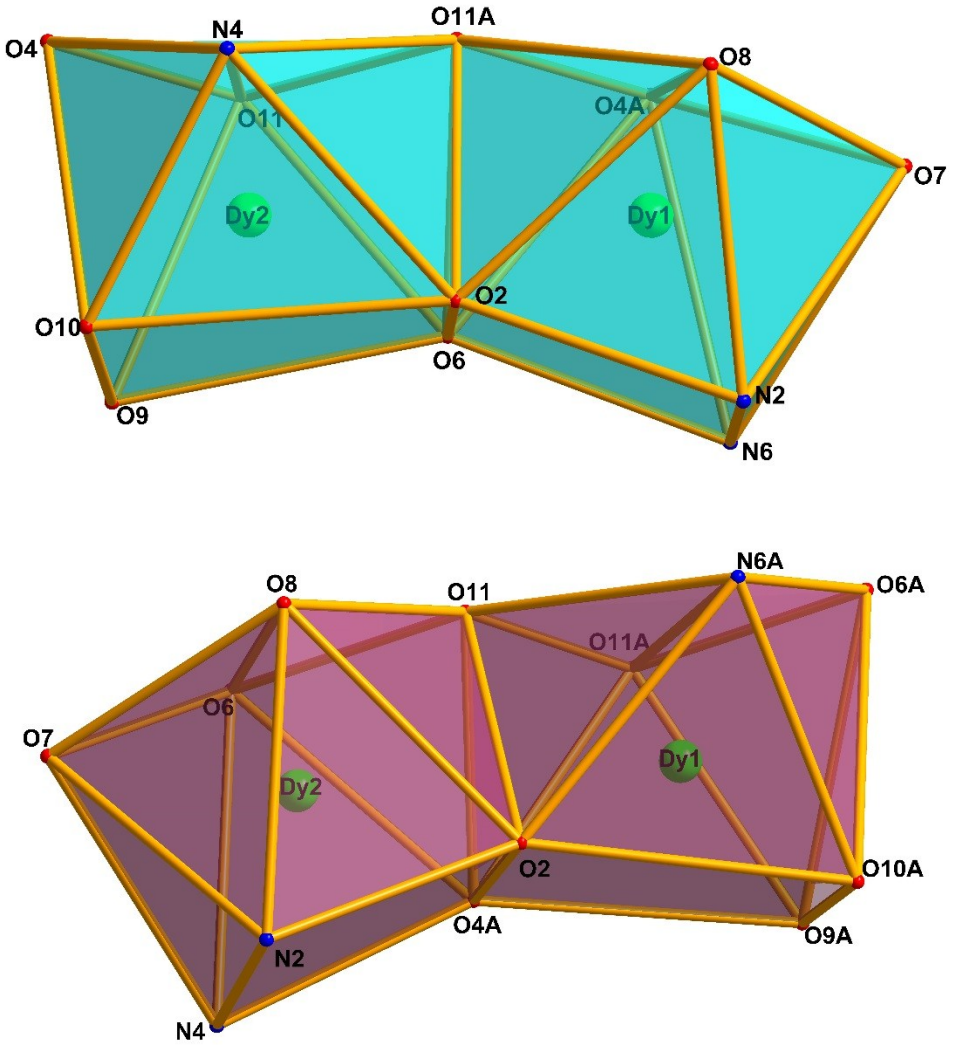
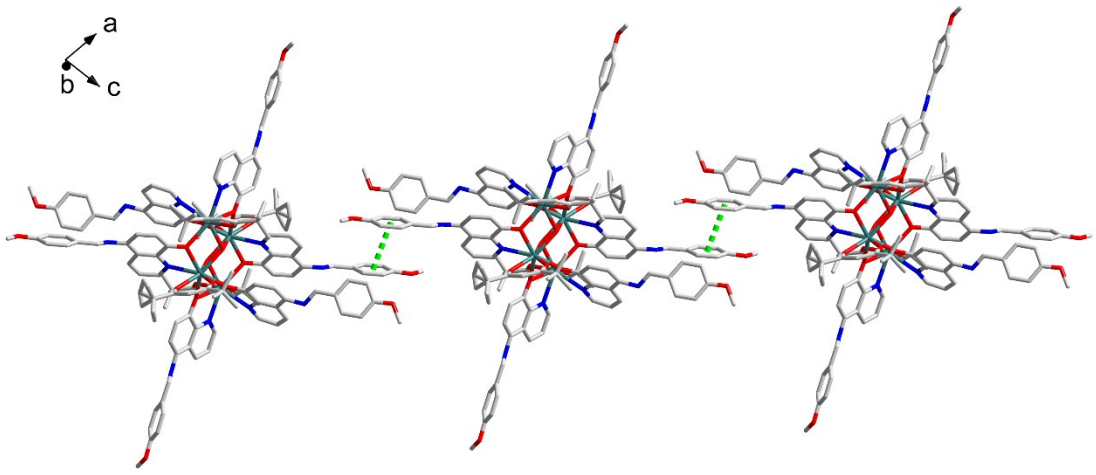


Fig. S1. The eight coordinated environment of Dy^{3+} in compounds **3** (top), **9** (middle) and **10** (bottom), respectively.



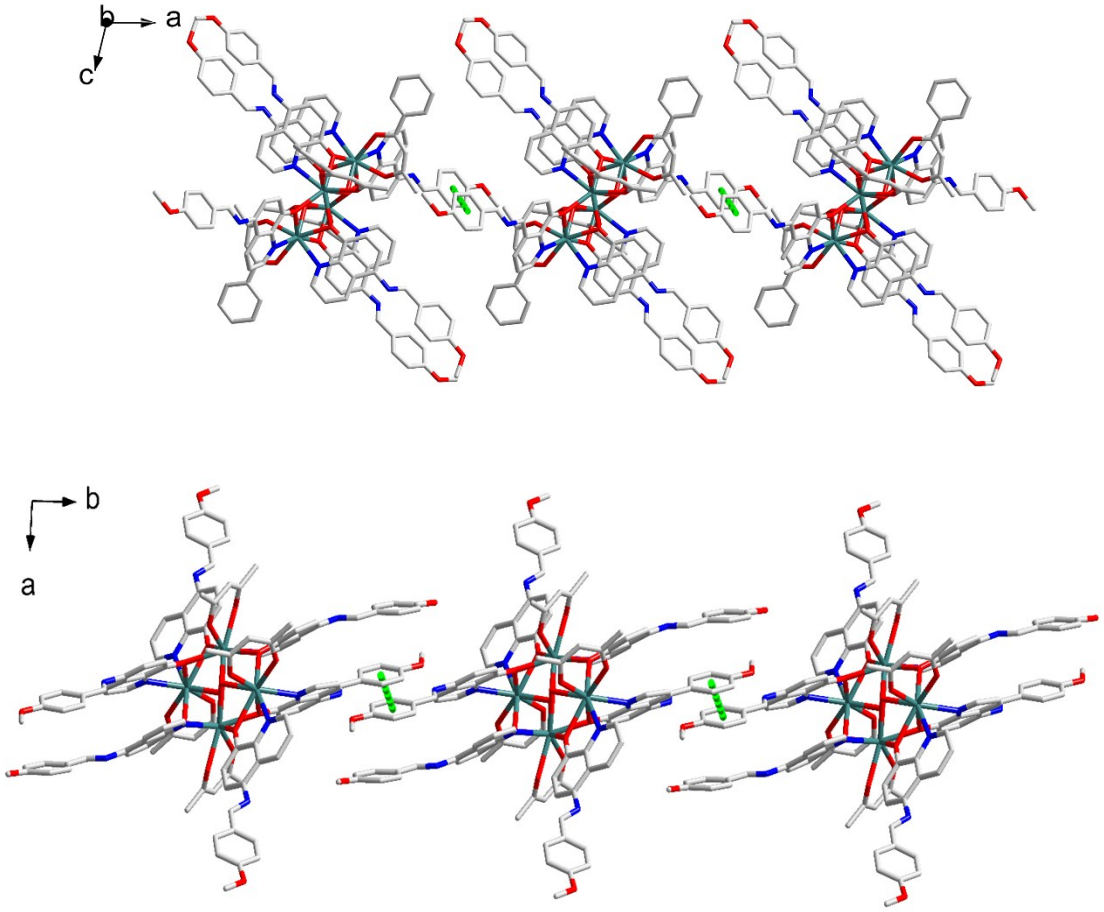
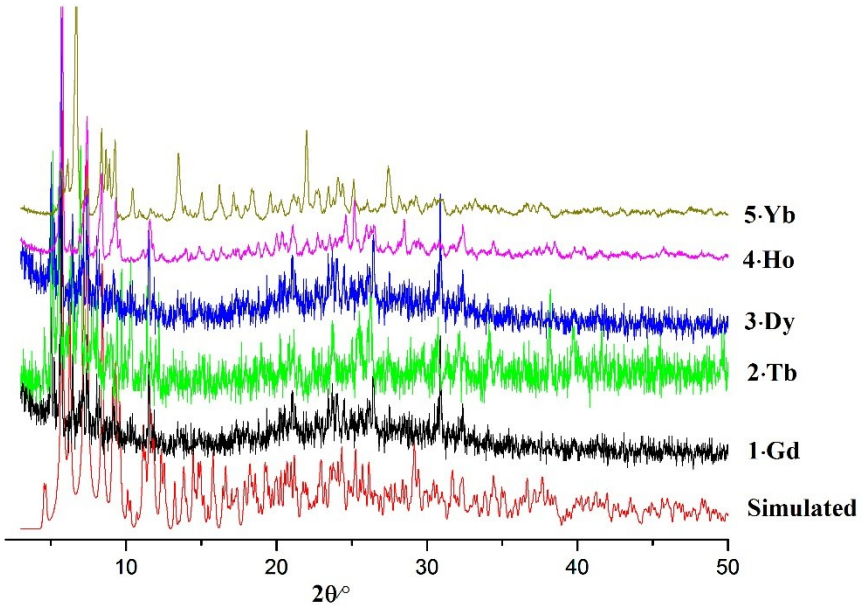


Fig. S2. The crystal packing of compounds **3** (top), **9** (middle) and **10** (bottom) showing the interactions between the molecules in them.



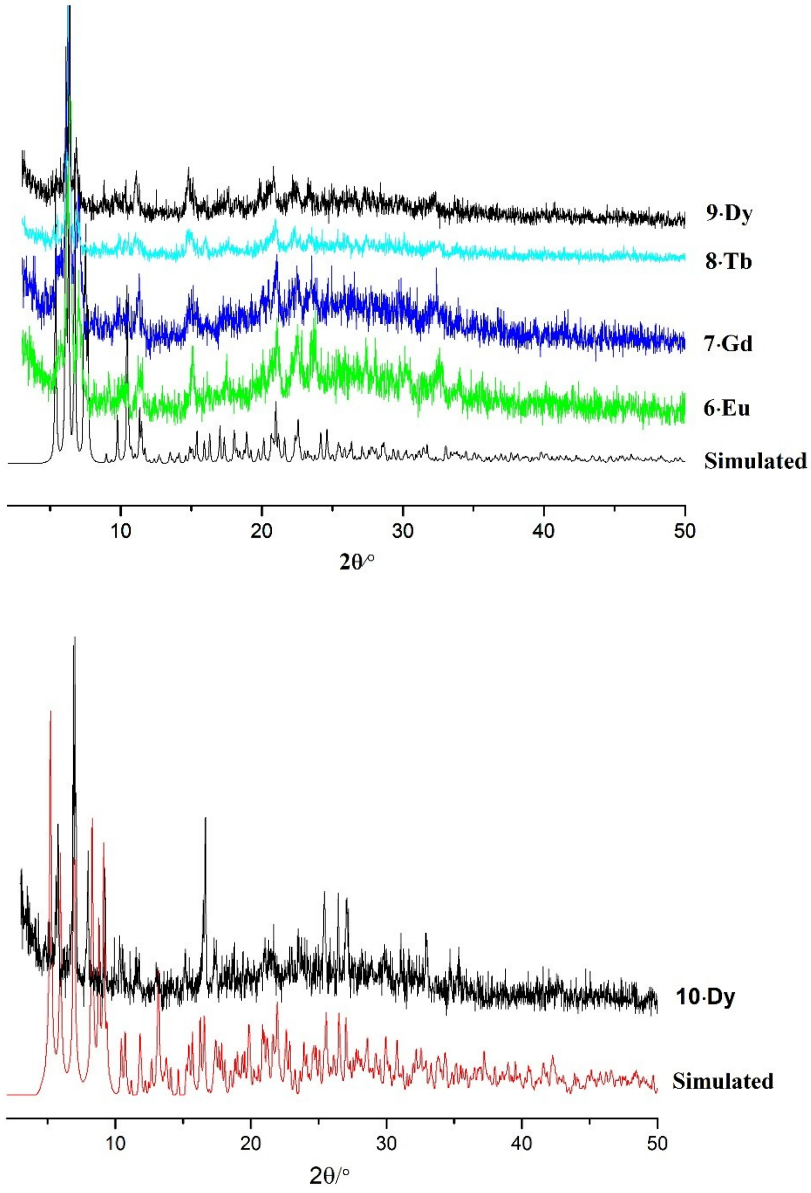
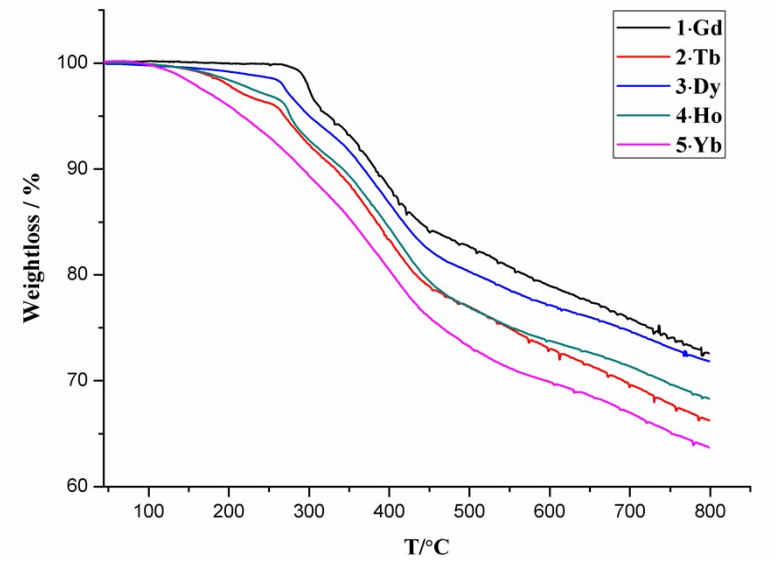


Fig. S3. Simulated and experimental PXRD patterns of compounds **1-5** (top), **6-9** (middle) and **10** (bottom).



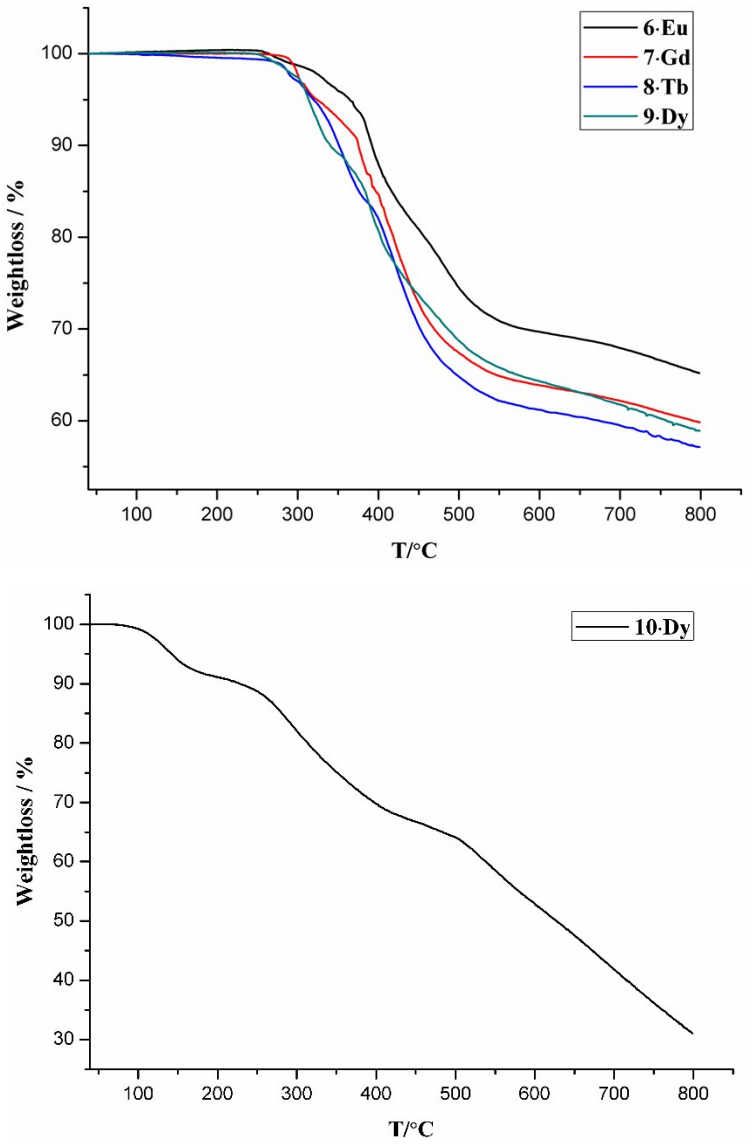


Fig. S4. TGA curses of compounds **1-5**, **6-9** and **10**, respectively.

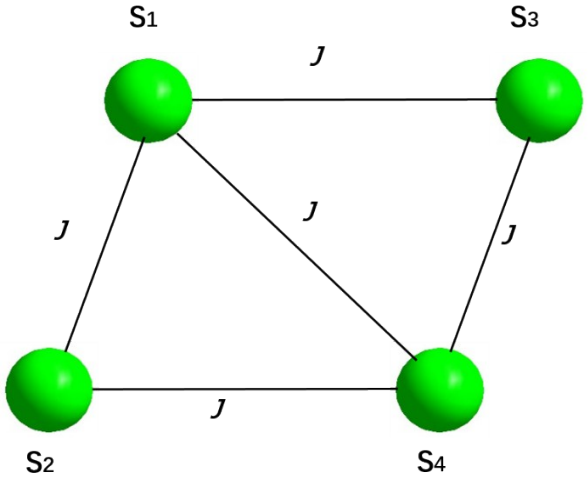
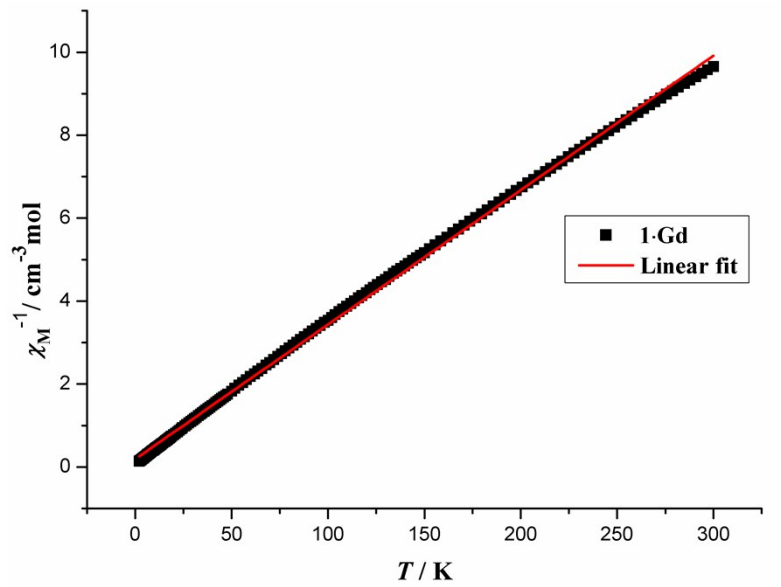
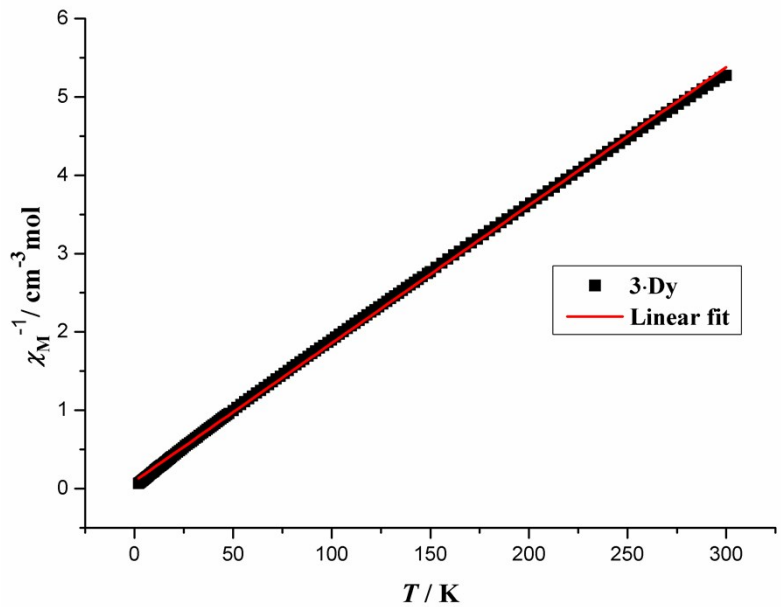
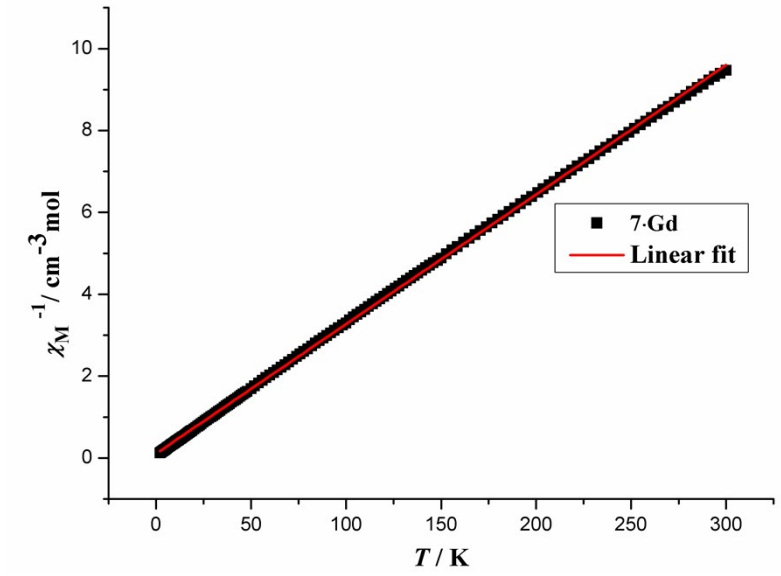


Fig. S5. The model used to fit the $\chi_M T$~T plots for **1**·Gd and **7**·Gd.


1·Gd
Linear fit
χ_M^{-1} / cm^{-3}mol
T / K


3·Dy
Linear fit
χ_M^{-1} / cm^{-3}mol
T / K


7·Gd
Linear fit
χ_M^{-1} / cm^{-3}mol
T / K

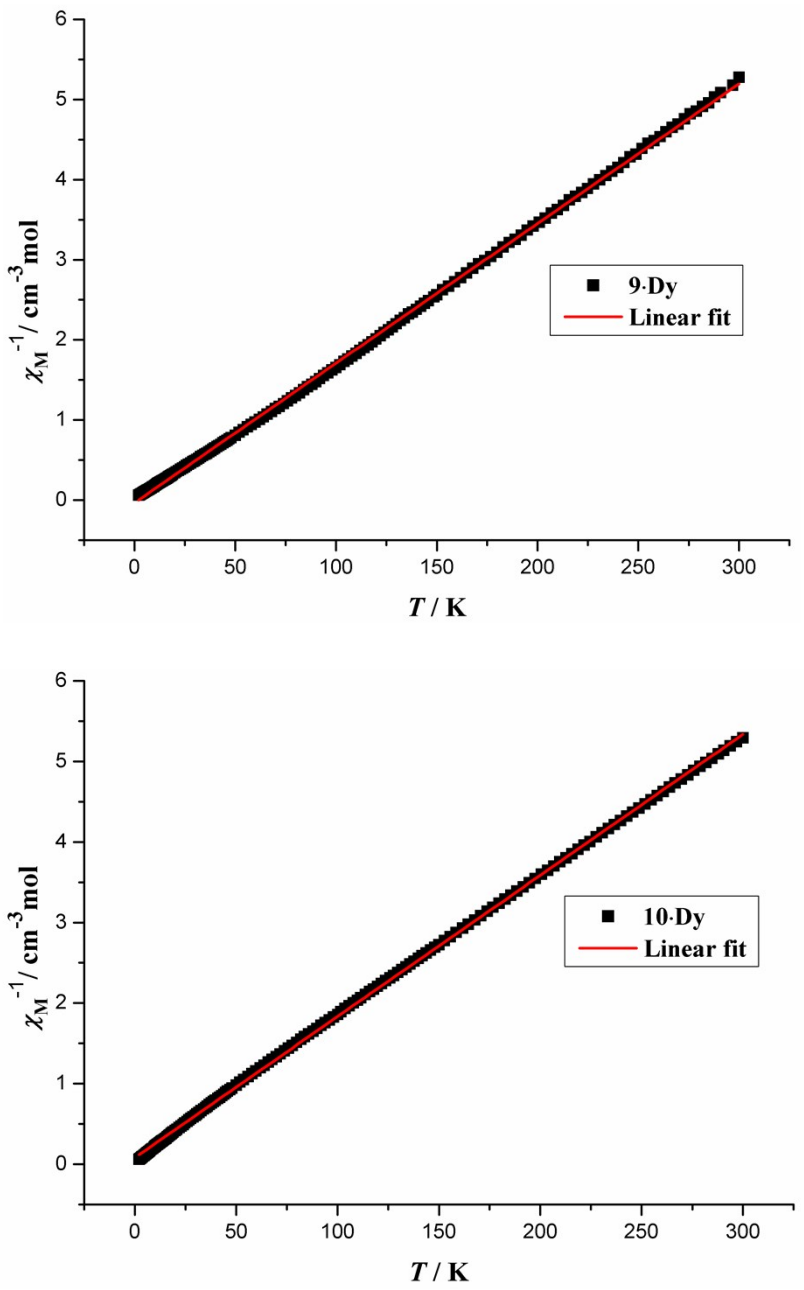


Fig. S6. The χ_M^{-1} versus T and the Curie-Weiss fit for **1**·Gd, **3**·Dy, **7**·Gd, **9**·Dy and **10**·Dy.

Table S1. Crystal data and structure refinements for compounds **1-5**.

	1·Gd	**2**·Tb	**3**·Dy	**4**·Ho	**5**·Yb
formula	$C_{127}H_{115.5}Gd_4N_{14.5}O_{22}$	$C_{127}H_{115.5}Tb_4N_{14}O_{22}$	$C_{127}H_{115.5}Dy_4N_{14.5}O_{22}$	$C_{127}H_{115.5}Ho_4N_{14.5}O_{22}$	$C_{127}H_{115.5}Yb_4N_{14.5}O_{22}$
fw	2825.85	2832.55	2846.85	2856.57	2888.99
T/K	293(2)h	293(2)	113(2)	293(2)	293(2)
Cryst syst	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	16.0344(2)	16.0380(6)	15.8898(9)	16.0223(6)	15.9945(6)
b/Å	19.862(2)	19.7829(8)	19.6837(1)	19.7955(7)	19.7881(6)
c/Å^3	20.309(2)	20.3633(8)	20.3485(9)	20.3368(7)	20.2867(7)
α/°	76.952(4)	76.7080(1)	76.789(3)	76.8060(1)	76.9190(1)
β/°	72.697(4)	73.0480(1)	73.047(3)	72.9870(1)	72.8040(1)
γ/°	86.957(4)	87.7160(1)	87.924(4)	87.5900(1)	87.3730(1)
Volume/Å	6015.1(1)	6012.0(4)	5923.6(6)	6003.0(4)	5973.0(4)
Z	2	2	2	2	2
ρ_{calc}mg/mm^3	1.504	1.531	1.596	1.580	1.606
μ/mm^{-1}	2.248	2.397	2.570	2.683	3.179
F(000)	2712	2764	2838	2846	2870
2θ range for data collection	2.843 to 25.010	2.891 to 25.009	3.056 to 25.009	2.935 to 28.347	2.897 to 25.010
Reflections collected	114775	255204	65209	91179	76384
Unique reflns	21112	21167	20695	29490	20970
Goodness-of-fit on F^2	1.022	1.034	1.021	1.032	1.028
R_1, wR_2 ($I > 2\sigma(I)$)	0.0647, 0.1339	0.0369, 0.0768	0.0270, 0.0731	0.0516, 0.0904	0.0473, 0.0990
R_1, wR_2 (all data)	0.1229, 0.1562	0.0466, 0.0811	0.0332, 0.0755	0.0956, 0.1102	0.0921, 0.1228
Largest diff. Peak/hole/ e Å^{-3}	1.785/-1.373	1.138/ -0.730	1.174/ -0.799	2.512/ -1.196	1.698/ -1.332

Table S2. Crystal data and structure refinements for compounds **6-10**.

	6·Eu	**7**·Gd	**8**·Tb	**9**·Dy	**10**·Dy
formula	$C_{154}H_{174}Eu_4N_{14}O_{24}$	$C_{154}H_{174}Gd_4N_{14}O_{24}$	$C_{154}H_{174}Tb_4N_{14}O_{24}$	$C_{154}H_{168}Dy_4N_{16}O_{22}$	$C_{150}H_{128}Dy_4N_{16}O_{22}$
fw	3212.90	3234.06	3240.74	3245.03	3156.68
T/K	113(2)	113(2)	113(2)	293(2)	293(2)
Cryst syst	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	$P2_1/c$
a/Å	14.9764(8)	14.9356(1)	14.9673(6)	15.0463(5)	17.423(3)
b/Å	16.0330(8)	15.9841(9)	15.9870(6)	15.9891(6)	13.940(2)
c/Å^3	17.9785(1)	17.9763(1)	17.9639(8)	17.9493(6)	30.573(6)
α/°	67.916(4)	67.916(8)	67.936(4)	68.0810(1)	90
β/°	74.079(5)	74.027(1)	74.001(6)	73.9990(1)	103.736(4)
γ/°	71.793(4)	71.695(9)	71.656(5)	71.2970(1)	90
Volume/Å	3739.1(4)	3714.8(5)	3720.2(3)	3734.3(2)	7213(2)
Z	1	1	1	1	2
ρ_{calc}mg/mm^3	1.427	1.446	1.447	1.443	1.453
μ/mm^{-1}	1.726	1.834	1.950	2.049	2.119
F(000)	1640	1644	1648	1644	3160
2θ range for data collection	3.096 to 27.567	3.100 to 25.019	3.100 to 25.009	2.935 to 25.006	3.002 to 25.010
Reflections collected	47942	40809	41002	45210	60491
Unique reflns	16871	12981	12988	13083	12620
Goodness-of-fit on F^2	1.051	1.080	1.056	1.025	1.039
R_1, wR_2 ($I > 2\sigma(I)$)	0.0277, 0.0687	0.0299, 0.0676	0.0292, 0.0772	0.0362, 0.0949	0.0885, 0.2182
R_1, wR_2 (all data)	0.0316, 0.0710	0.0402, 0.0725	0.0331, 0.0821	0.0452, 0.1025	0.1318, 0.2415
Largest diff. Peak/hole/ e Å^{-3}	1.854/-1.547	1.799/-0.934	2.372/-0.981	2.412/-1.511	2.552/-1.148