Supporting Information for

Tuning the dynamic magnetic behaviour and proton conductivity via water-induced reversible single-crystal to single-crystal structural transformation †

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Table S1. Crystallographic data and Structure Refinement for complexes **1** and **1′**.

Name	**1**	**1′**
Formula	$C_{15}H_{14}DyN_5O_4ClF$	$C_{12}H_{13}DyN_4O_6ClF$
Mr	545.26	526.21
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
T(K)	100 K	100 K
a(Å)	11.0804(3)	11.3360(8)
b(Å)	9.9562(3)	10.1810(4)
c(Å)	16.3993(4)	13.7684(10)
α(°)	90	90
β(°)	96.098(2)	101.143(7)
γ(°)	90	90
V (Å^3)	1798.90(8)	1559.08(17)
Z	4	4
μ (mm^{-1})	4.345	5.016

F(000)	1052	1012
GOF	1.042	1.093
Data collected	9022	7307
Unique	4256	3689
R_{int}	0.0422	0.0423
$R1, wR2[I > 2\sigma(I)]$	0.0350, 0.0652	0.0506, 0.0828
R1, wR2 [all data]	0.0457, 0.0716	0.0824, 0.0941

Table S2. Selected Bond Distances (Å) in complexes **1** and **1′**.

1		**1′**	
Dy-O1	2.158(3)	Dy-O1	2.196(5)
Dy-O2	2.376(3)	Dy-O2	2.319(4)
Dy-O2A	2.339(3)	Dy-O2A	2.442(5)
Dy-N1	2.458(4)	Dy-O5	2.464(5)
Dy-N3	2.604(4)	Dy-N1	2.493(6)
Dy-Cl1	2.7482(11)	Dy-N3	2.574(6)
Dy-O3	2.412(3)	Dy-O3	2.509(5)
Dy-O4	2.397(3)	Dy-O4	2.448(5)
O1-Dy-O2	134.08(10)	Dy-O6	2.494(5)
O1-Dy-O2A	149.22(11)	O1-Dy-O2	134.75(17)
		O1-Dy-O2A	134.76(17)
		O1-Dy-O5	139.98(18)

Table S3. Weak Interaction in **1**.

D-H	d(D-H) (Å)	<DHA(°)	d(D…A) (Å)	d(H…A) (Å)	A
C13-H13b	0.961	119.28	3.197	2.617	F1(0.5-x,0.5+y,0.5-z)
C13-H13c	0.960	162.49	3.618	2.691	F1(0.5-x,0.5+y,0.5-z)

Table S4. Hydrogen Bonds in **1′**.

D-H	d(D-H) (Å)	<DHA(°)	d(D…A) (Å)	d(H…A) (Å)	A
O4-H4b	0.867	146.76	3.167	2.407	Cl1(-0.5+x,0.5-y,0.5+z)
O5-H5a	0.875	167.92	3.098	2.237	Cl1(-0.5+x,0.5-y,0.5+z)
O6-H6a	0.855	113.02	2.978	2.538	O6(1.5-x,0.5+y,1.5-z)
O6-H6b	0.855	156.64	3.147	2.344	Cl1(-0.5+x,0.5-y,0.5+z)

Table S5. Relaxation fitting parameters from Least-Squares Fitting of χ(f) data under zero dc field of **1**.

T (K)	χ_T	χ_S	α	τ''(s)
6	4.32	0.017	0.11	1.31
6.5	3.41	0.016	0.10	0.72
7	2.79	0.016	0.089	0.41
7.5	2.35	0.016	0.076	0.25
8	2.13	0.016	0.068	0.17
8.5	1.91	0.016	0.060	0.11
9	1.76	0.015	0.059	0.079
9.5	1.66	0.015	0.060	0.059
10	1.53	0.016	0.046	0.043
10.5	1.44	0.016	0.041	0.032
11	1.35	0.017	0.036	0.025
11.5	1.29	0.016	0.038	0.019
12	1.22	0.018	0.030	0.015
12.5	1.16	0.018	0.026	0.012
13	1.11	0.019	0.027	0.0094
13.5	1.07	0.020	0.020	0.0075
14	1.02	0.020	0.020	0.0060
14.5	0.98	0.021	0.013	0.0048
15	0.94	0.022	0.010	0.0039
15.5	0.91	0.019	0.025	0.0032
16	0.88	0.022	0.014	0.0026
16.5	0.85	0.022	0.011	0.0021
17	0.82	0.020	0.020	0.0017
17.5	0.80	0.025	0.0079	0.0014
18	0.77	0.022	0.016	0.0011
18.5	0.75	0.023	0.011	9.25E-4
19	0.73	0.026	0.013	7.56E-4
19.5	0.71	0.019	0.027	6.15E-4
20	0.69	0.021	0.024	5.03E-4
20.5	0.67	0.023	0.025	4.11E-4
21	0.66	0.027	0.020	3.38E-4
21.5	0.64	0.015	0.037	2.68E-4
22	0.62	0.014	0.038	2.17E-4
22.5	0.61	0.029	0.029	1.70E-4
23	0.60	0.016	0.040	1.53E-4
23.5	0.53	0.020	0.0093	1.19E-4
24	0.52	0.017	0.019	9.79E-5
24.5	0.51	0.0080	0.052	7.80E-5
25	0.50	0.0058	0.054	6.35E-5
25.5	0.49	0.0077	0.046	5.22E-5

26	0.48	0.0063	0.044	4.19E-5
26.5	0.47	0.012	0.029	3.50E-5
27	0.46	1E-4	0.053	2.77E-5

Table S6. Relaxation fitting parameters from Least-Squares Fitting of χ(f) data under zero dc field of **1′**.

T (K)	χ_T	χ_S	α	τ''(s)
2	10.83	0.029	0.15	0.089
2.5	7.88	0.032	0.14	0.072
3	6.18	0.032	0.14	0.063
3.5	5.05	0.033	0.14	0.057
4	4.29	0.033	0.14	0.052
4.5	3.70	0.034	0.14	0.047
5	3.24	0.035	0.13	0.041
5.5	2.88	0.036	0.11	0.034
6	2.58	0.037	0.098	0.026
6.5	2.33	0.037	0.082	0.020
7	2.14	0.038	0.070	0.014
7.5	1.97	0.037	0.062	0.0099
8	1.82	0.039	0.052	0.0069
8.5	1.71	0.036	0.058	0.0048
9	1.60	0.036	0.053	0.0034
9.5	1.51	0.033	0.057	0.0024
10	1.42	0.033	0.054	0.0017
10.5	1.35	0.032	0.058	0.0013
11	1.28	0.022	0.072	9.19E-4
11.5	1.22	0.015	0.081	6.75E-4
12	1.16	0.043	0.052	5.06E-4
12.5	1.11	0.034	0.067	3.70E-4
13	1.068	0.032	0.074	2.70E-4
13.5	1.025	0.043	0.074	1.99E-4
14	0.99	0.013	0.11	1.49E-4
14.5	0.86	0.022	0.059	1.03E-4
15	0.77	0.0080	0.088	7.40E-5
15.5	0.73	0.027	0.044	5.63E-5
16	0.72	1.01E-5	0.10	3.94E-5
16.5	0.70	1.00E-5	0.11	2.91E-5
17	0.67	1.01E-5	0.096	2.18E-5
17.5	0.65	1.00E-5	0.12	1.62E-5
18	0.63	1.01E-5	0.093	1.22E-5

Table S7. Calculated energy levels (cm^{-1}), $\boldsymbol{g}$ (g_x, g_y, g_z) tensors and m_J values of the lowest Kramers doublets (KDs) of the individual Dy fragments of complexes **1** and **1′**.

KDs	**1**			**1′**		
	E/cm^{-1}	g	m_J	E/cm^{-1}	g	m_J
1	0.0	0.003 0.005 19.600	±15/2	0.0	0.011 0.016 19.464	±15/2
2	180.0	0.062 0.076 16.743	±13/2	169.1	0.079 0.100 16.604	±13/2
3	319.2	1.362 1.721 18.113	±9/2	309.1	2.221 3.708 12.395	±9/2
4	344.9	0.628 4.366 10.834	±5/2	368.4	2.217 5.562 11.767	±5/2
5	418.9	8.631 6.450 2.408	±11/2	405.5	2.086 2.592 13.086	±11/2
6	489.9	2.096 2.944 10.980	±7/2	467.8	0.035 0.268 16.119	±7/2
7	534.2	0.460 1.348 14.355	±1/2	531.6	0.103 0.224 16.946	±1/2
8	571.1	0.693 0.893 18.032	±3/2	616.5	0.035 0.099 18.853	±3/2

Table S8. Wavefunction composition for the eight Kramer doublets of the $^6H_{15/2}$ ground multiplet of complexes **1** and **1′**.

	wave functions
1	96%|±15/2>
	91%|±13/2>+5%|±9/2>+2%|±7/2>
	14%|±11/2>+16%|±7/2>+22%|±5/2>+21%|±3/2>+21%|±1/2>
1′	93%|±15/2>
	84%|±13/2>+4%|±11/2>+11%|±9/2>
	4%|±13/2>+58%|±11/2>+5%|±9/2>+19%|±7/2>+5%|±1/2>

Table S9. The $\chi_M T$ values in **1** and **1′** based on experiments and ab initio calculations.

	1		**1′**	
Temperature (K)	Experimental $\chi_M T$ values ($cm^3mol^{-1}K$)	Calculated $\chi_M T$ values ($cm^3mol^{-1}K$)	Experimental $\chi_M T$ values ($cm^3mol^{-1}K$)	Calculated $\chi_M T$ values ($cm^3mol^{-1}K$)
2	20.16	19.59	18.52	16.76
3	18.68	17.54	16.73	15.28
4	17.23	16.33	15.56	14.50
5	16.25	15.55	14.80	14.03
6	15.57	15.01	14.29	13.72
7	15.09	14.63	13.93	13.49
8	14.73	14.34	13.67	13.33
9	14.44	14.11	13.46	13.20
10	14.20	13.93	13.29	13.11
11	14.00	13.79	13.15	13.03
12	13.85	13.67	13.04	12.97
13	13.73	13.57	12.96	12.92
14	13.61	13.49	12.89	12.87
15	13.51	13.42	12.82	12.84
16	13.44	13.36	12.78	12.81
17	13.36	13.31	12.73	12.79
18	13.30	13.27	12.70	12.77
19.	13.25	13.23	12.67	12.75
20	13.21	13.20	12.65	12.74
22	13.14	13.15	12.62	12.72
24	13.09	13.11	12.59	12.71
26	13.04	13.09	12.58	12.71
28	13.01	13.07	12.58	12.71
30	12.99	13.06	12.58	12.71
32	12.97	13.05	12.59	12.72
34	12.96	13.04	12.60	12.73
36	12.95	13.04	12.61	12.74
38	12.95	13.05	12.62	12.75
40	12.95	13.05	12.64	12.77
42	12.95	13.06	12.66	12.78
44	12.96	13.07	12.68	12.80
46	12.96	13.08	12.69	12.81
48	12.97	13.09	12.71	12.83
50	12.98	13.10	12.73	12.85
55	13.01	13.13	12.78	12.89
60	13.06	13.16	12.83	12.93
65	13.11	13.20	12.88	12.98
70	13.14	13.23	12.92	13.02

75	13.16	13.26	12.97	13.06
80	13.19	13.29	13.01	13.10
85	13.21	13.32	13.05	13.14
90	13.25	13.35	13.09	13.18
95	13.28	13.38	13.13	13.21
100	13.31	13.41	13.16	13.25
110	13.36	13.46	13.22	13.31
120	13.42	13.50	13.29	13.37
130	13.47	13.54	13.35	13.42
140	13.52	13.58	13.40	13.46
150	13.56	13.62	13.44	13.51
160	13.60	13.65	13.49	13.55
170	13.63	13.68	13.53	13.58
180	13.67	13.70	13.56	13.62
190	13.70	13.73	13.59	13.64
200	13.73	13.75	13.62	13.67
210	13.76	13.77	13.65	13.70
220	13.79	13.79	13.67	13.72
230	13.82	13.80	13.69	13.74
240	13.84	13.82	13.71	13.76
250	13.87	13.83	13.73	13.77
260	13.89	13.84	13.74	13.79
270	13.91	13.85	13.76	13.80
280	13.94	13.87	13.77	13.82
290	13.98	13.87	13.80	13.83
300	14.09	13.88	13.85	13.84

Table S10. Fitted exchange coupling constant J_{exch}, the calculated dipole-dipole interaction $J_{dipolar}$ and the total J between Dy^{3+} ions in **1** and **1′** (cm^{-1}).

		1	**1′**
J	$J_{dipolar}$	4.60	3.76
	J_{exch}	-0.50	-1.50
	J	4.10	2.26

Table S11. Proton conductivity of **1′** at 25°C under variable relative humidity (RH).

RH / %	σ (S cm^{-1})
90	2.96×10^{-9}
95	8.00×10^{-9}
98	1.83×10^{-6}

Table S12. Proton conductivity of **1′** at 98% RH under variable temperature.

T (°C)	σ (S cm^{-1})
25	1.83×10^{-6}
30	2.26×10^{-6}
40	4.12×10^{-6}
50	5.49×10^{-6}
60	7.8×10^{-6}
70	1.01×10^{-5}

Table S13. Some typical examples of lanthanide coordination complexes behaving as conducting nanomagnets.

	Structure	**DC field (Oe)**	**U_{eff} (K)**	**σ (S cm^{-1})**	**RH %**	**T (°C)**	**Ref**
$\{[DyL(H_2O)_3]Cl\}_n$	2D	0	197	1.01×10^{-5}	98	70	This work
$[Dy(H_2bim)_2(H_2O)_2(NO_3)_2](NO_3)$	0D	2000	71.6/74.4	1.16×10^{-3}	100	35	3b
$[Dy_{72}(mda)_{24}(mdaH)_8(OH)_{120}(O)_8(NO_3)_{16}](NO_3)_8\cdot 16CH_3OH\cdot 168H_2O$	0D	0	6.5	1.20×10^{-2}	95	95	10c
$\{[Dy(L)(O_x)(H_2O)]_n\cdot 1.5H_2O\}$	3D	2000	36.5	9.06×10^{-5}	95	75	10d
$\{[Dy_4(OH)_4(L)_2(H_2O)_8]\cdot 4.6H_2O\cdot 1.4CH_3CN\}_n$	3D	2000	30.4	2.96×10^{-6}	95	80	10e
$[YbZn_2(SS/RR\text{-}L)_2(H_2O)_4](ClO_4)_3\cdot 5H_2O$	0D	1000	8.9	3.33×10^{-4}	100	45	10f
$(H_5O_2)_2(H)[Yb^{III}(hmpa)_4][Co^{III}(CN)_6]_2\cdot 0.2H_2O$	3D	1000	31.2	1.70×10^{-4}	97	27	10g

Abbreviations: H_2bim=2,2′-biimidazole; $mdaH_2$ = *N*-methyldiethanolamine; H_2L= mucicacid, O_xH_2=oxalicacid; Na_2H_2L = disodium-2,2′-disulfonate-4,4′-oxydibenzoic acid; H_2L = (SS/RR)-cyclohexane-1,2-diylbis(azanediyl)-bis(methylene)-bis(2-methoxyphenol); hmpa = hexamethyl-phosphoramide;

Table S14. Some typical examples of lanthanide coordination complexes based on similar ligand.

	Structure	**U_{eff} (K)**	**Ref**
$\{[DyL(Cl)(CH_3OH)]\cdot CH_3CN\}_n$	2D	316	This work
$\{[DyL(H_2O)_3]Cl\}_n$	2D	197	This work
$[Dy(L)Cl(CH_3OH)]_n$	1D	556	20c
$[Dy_2(L)_2Cl_2(CH_3OH)_3]_n\cdot nCH_3OH$	1D	195	22c
$[Dy(L)Cl(DMF)]_n$	1D	399	22c
H_2L = N′-(5-bromo-2-hydroxybenzylidene)pyrazine-N-oxide-carbohydrazide) [20c,22c].			

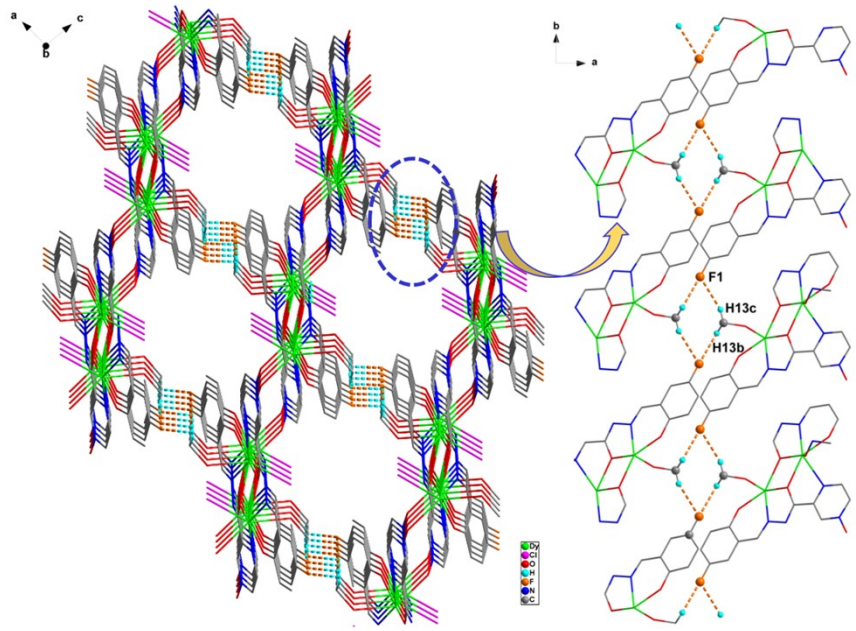


Fig. S1 3D supramolecular structure of **1** connected by hydrogen bonds.

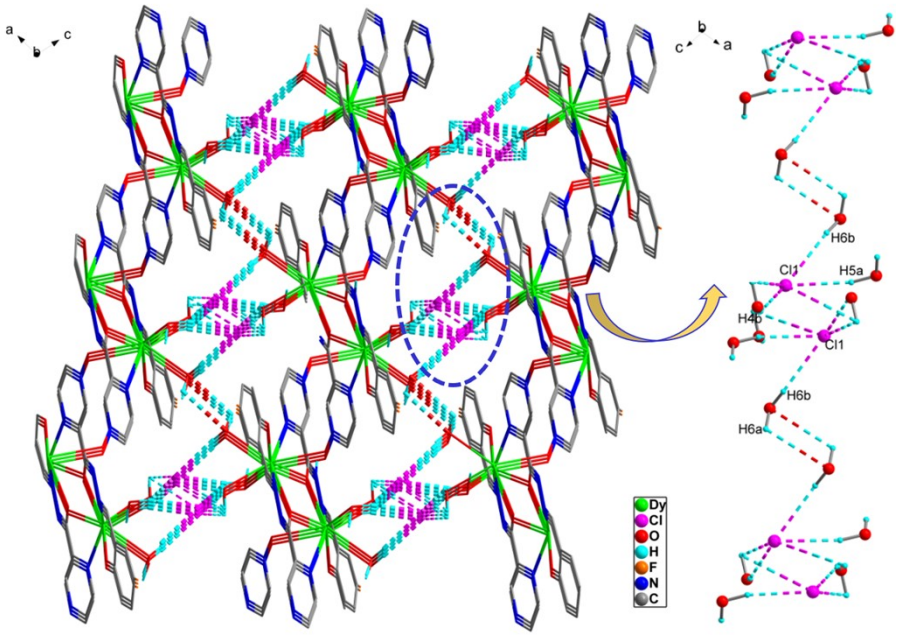


Fig. S2 3D supramolecular structure of **1′** connected by hydrogen bonds.

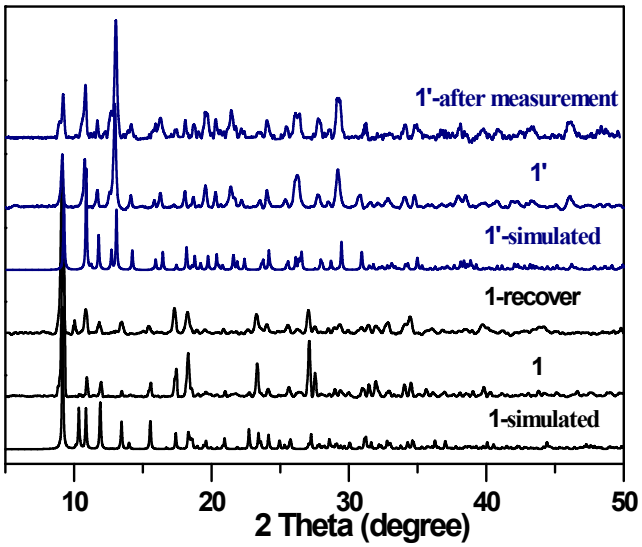


Fig. S3 Powder X-ray diffraction profiles of **1**, **1′** and **1-recover** together with a simulation from the single crystal data. (When **1′** was placed in a mixed solvent of the same proportion as the mother liquor for 2 h at 80 °C, it reabsorbed the solvent molecules and converted to **1** with a notable color change from dark-red to orange. PXRD study revealed that the structure of **1-recover** was identical to that of **1**)

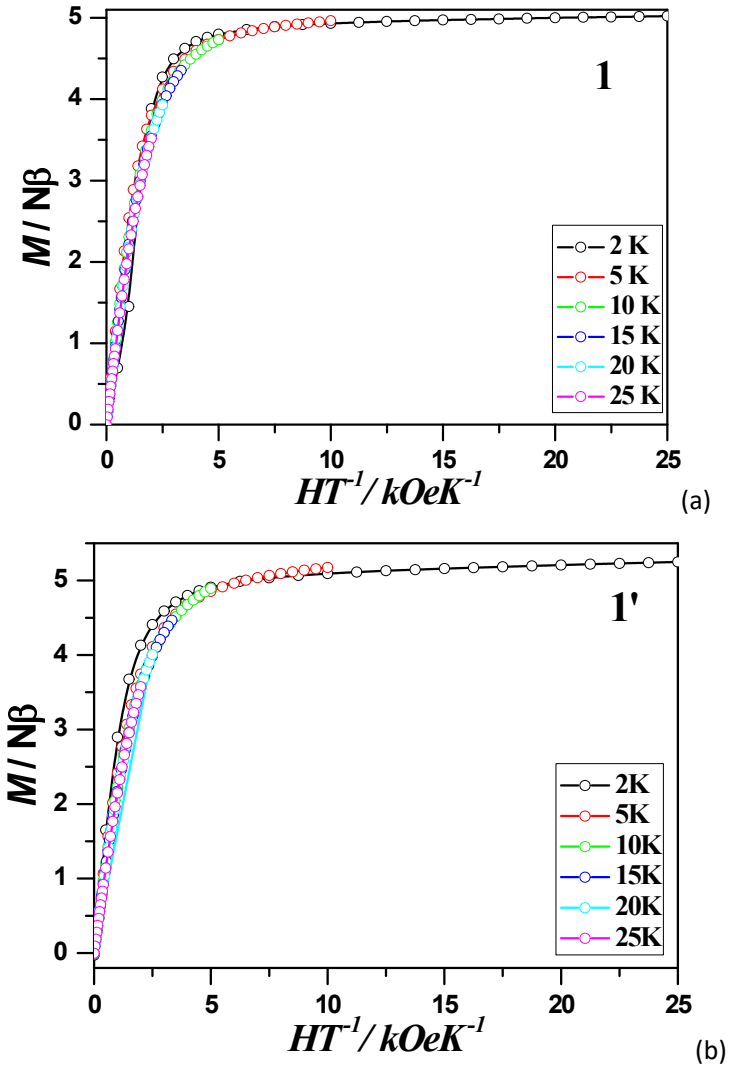


Fig. S4 Plots of *M*-*H* for **1** (a) and **1′** (b).

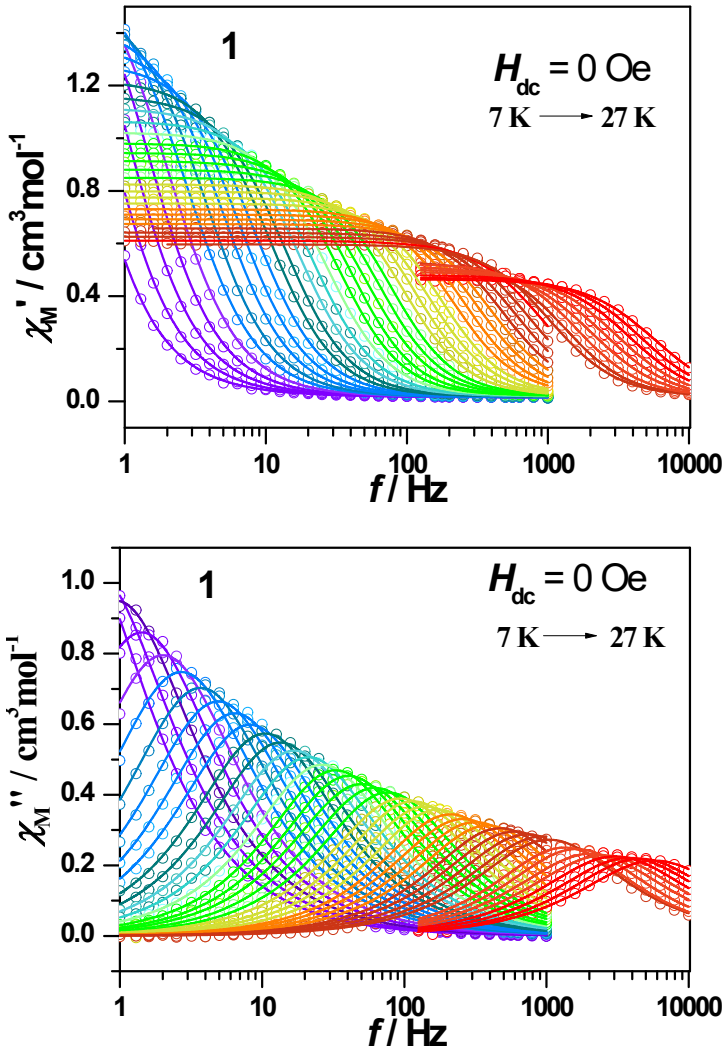


Fig. S5 *Ac-f* curves measured under zero *dc* fields for **1**. Solid lines were fitted using a generalized Debye relaxation model, simultaneously to $\chi'(f)$ and $\chi''(f)$ curves.

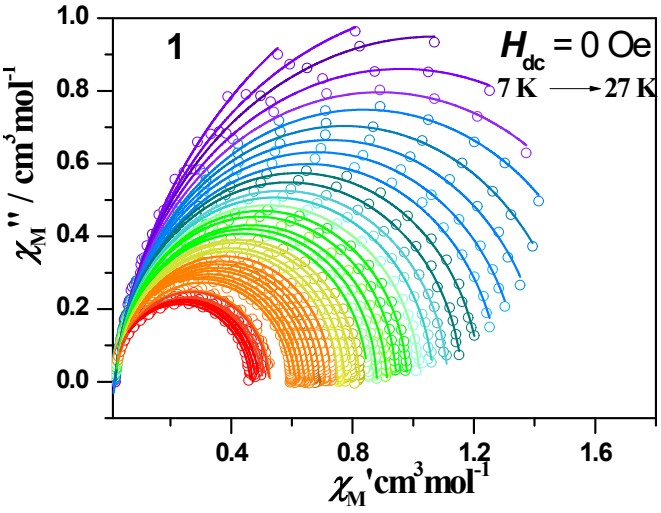


Fig. S6 Cole-cole plots of **1** under zero *dc* field.

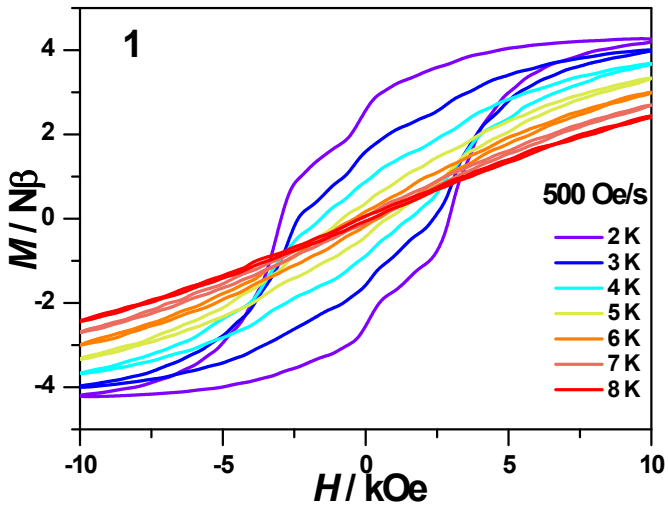


Fig. S7 Hysteresis loop for **1** at different temperatures with sweep rates of 500 Oe/s.

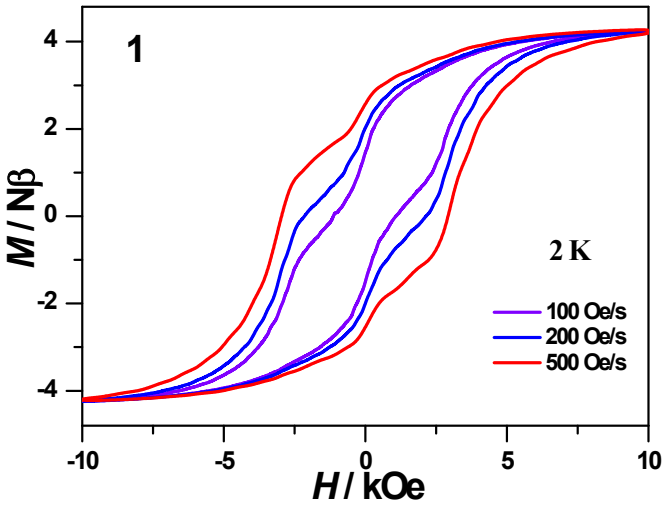


Fig. S8 Hysteresis loop for **1** measured with different sweep rates at 2 K.

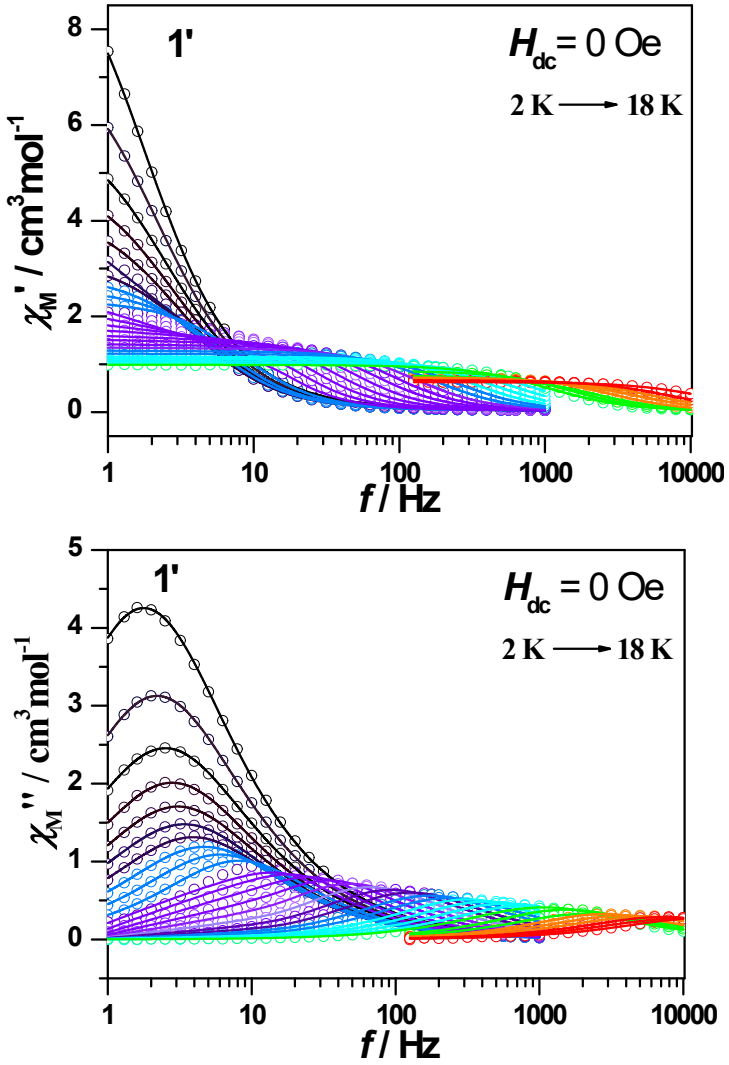


Fig. S9 *Ac-f* curves measured under zero *dc* fields for **1′**. Solid lines were fitted using a generalized Debye relaxation model, simultaneously to χ' (f) and χ'' (f) curves.

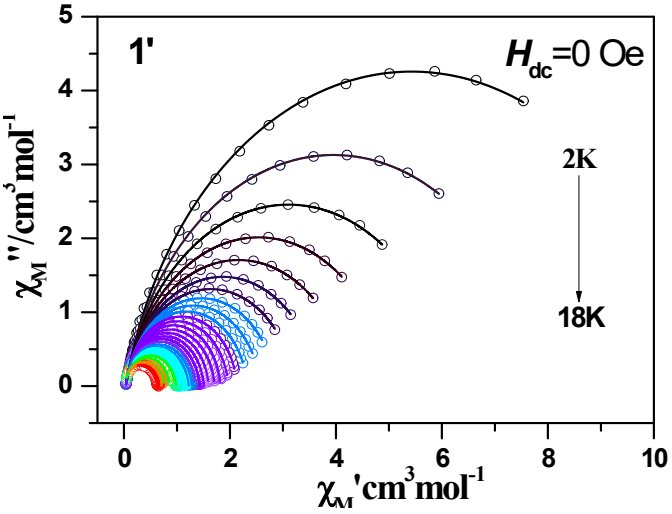


Fig. S10 Cole-cole plots of **1′** under zero *dc* field.

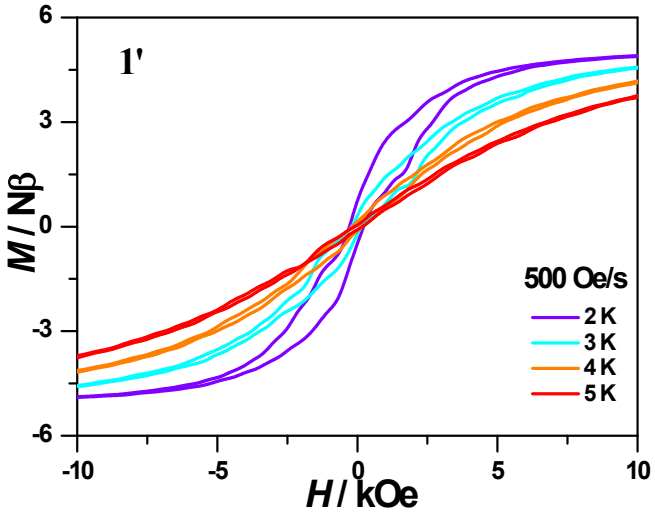


Fig. S11 Hysteresis loop for **1′**at different temperatures with sweep rates of 500 Oe/s.

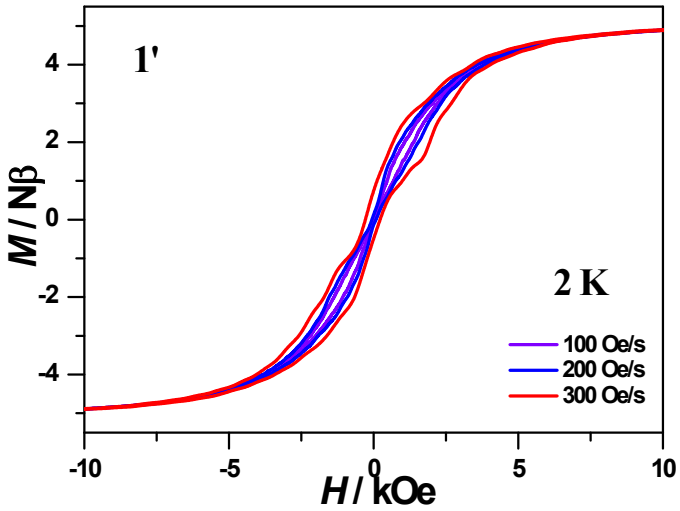
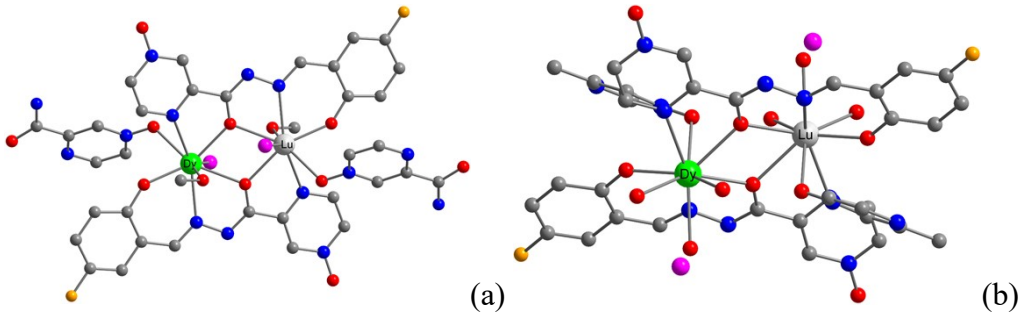
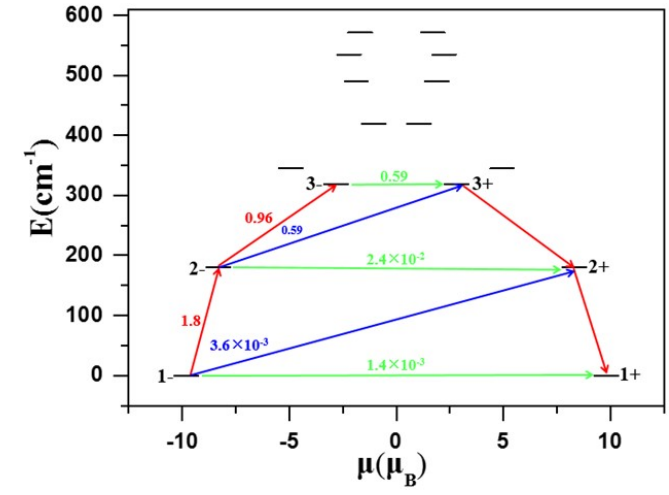


Fig. S12 Hysteresis loop for **1′** measured with different sweep rates at 2 K.

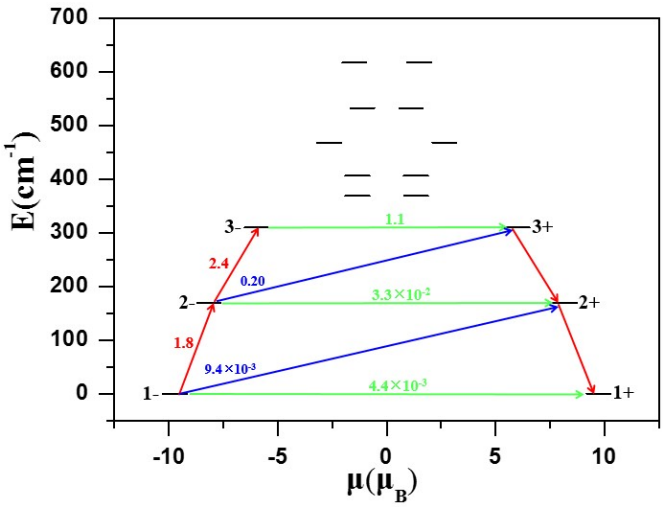


(a) (b)

Fig. S13 Calculated model structure for complexes **1** (a) and **1′** (b); H atoms are omitted.



(a)



(b)

Fig. S14 The magnetization blocking barriers in complexes **1** (a) and **1′** (b). The thick black lines represent the Kramers doublets as a function of their magnetic moment along the magnetic axis. The green lines correspond to diagonal quantum tunneling of magnetization (QTM); the blue line represent off-diagonal relaxation process. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

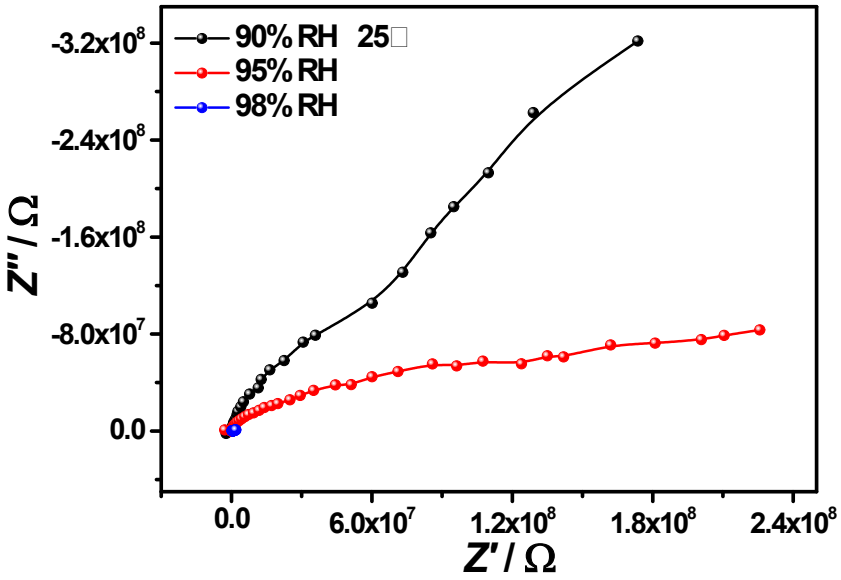


Fig. S15 Nyquist plot for **1′** at 25°C under different RH.