Supporting Information

[2+2] Photochemical Modulation of the Dy(III) Single-Molecule Magnet: Opposite influence on Energy barrier and relaxation time

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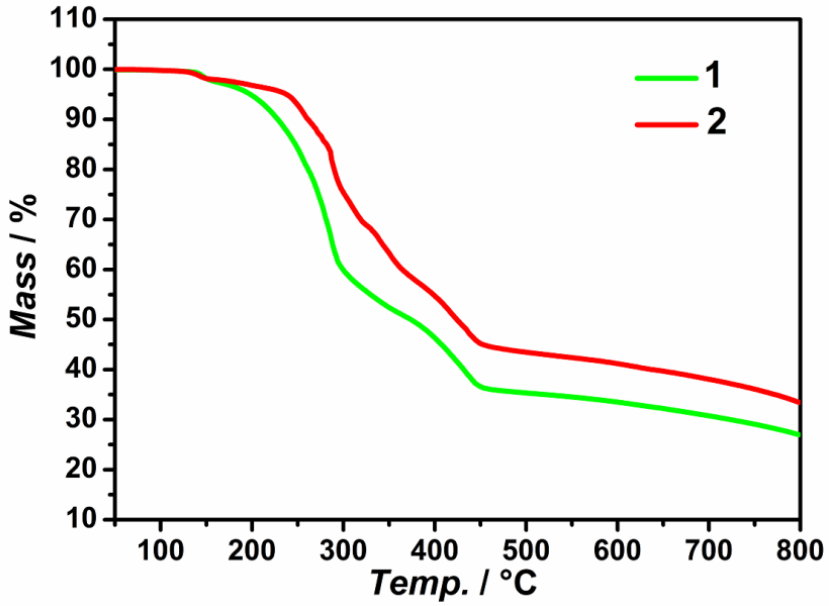

Fig. S1. Thermogravimetry (TG) curves for **1** (green) and **2** (red) under N_2 atmosphere.

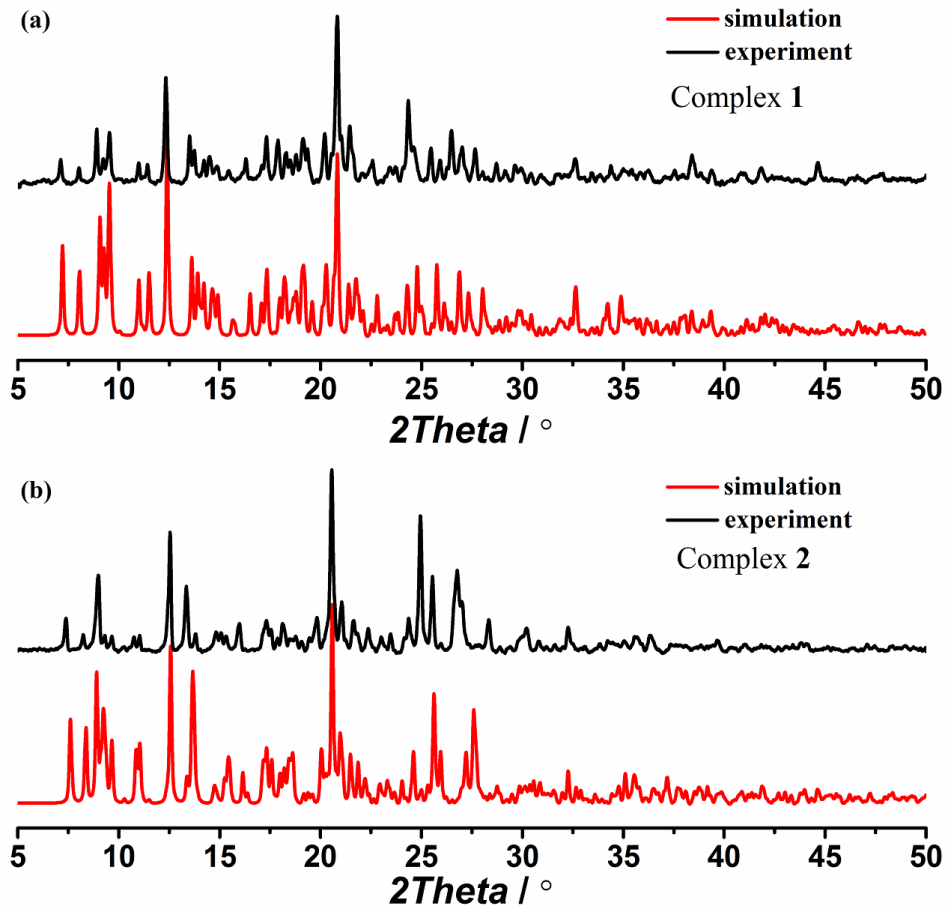

Fig. S2. Simulated and experimental X-ray powder diffraction patterns for **1** and **2**.

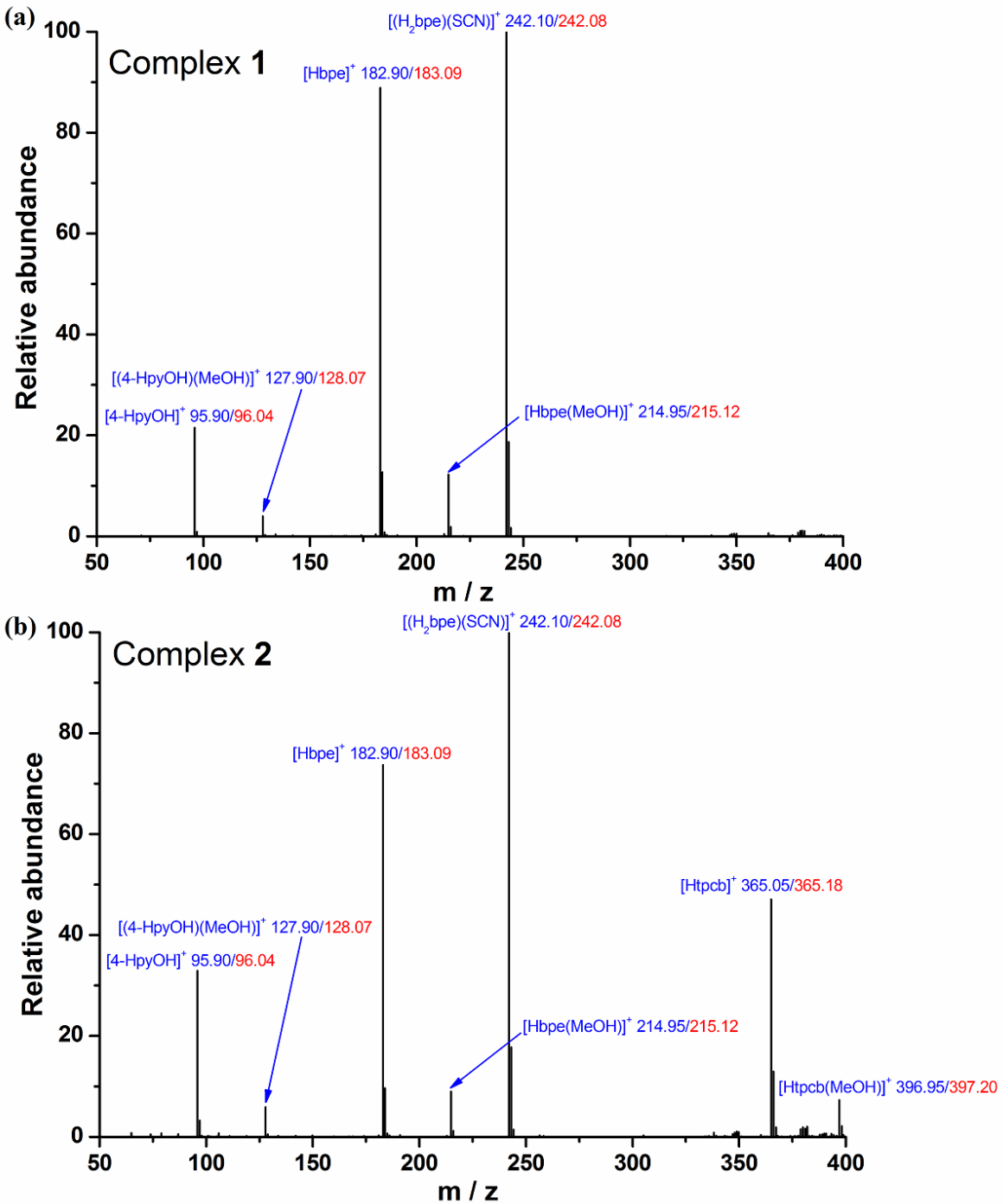

Fig. S3. The LC-MS spectrum for **1** (a) and **2** (b) in MeOH solution. The blue and red labels correspond to the measured and the calculated *m*/*z*, respectively.

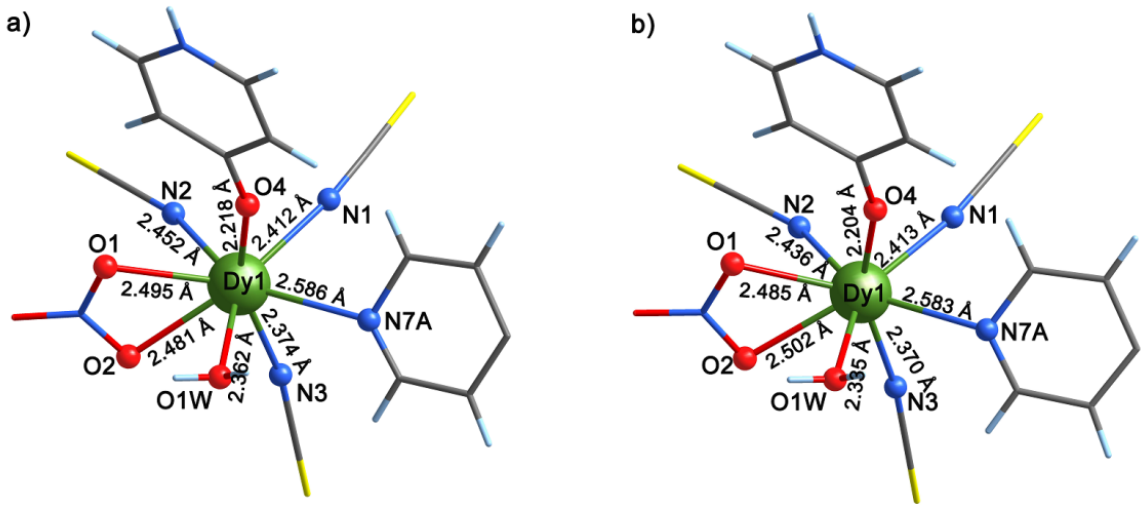

Fig. S4 The coordination environment for Dy(III) ions with marked bond lengths for **1** (a) and **2** (b). Colour Codes: Dy, cyan; S, yellow; N, blue; O, red; C, gray; H, pale blue.

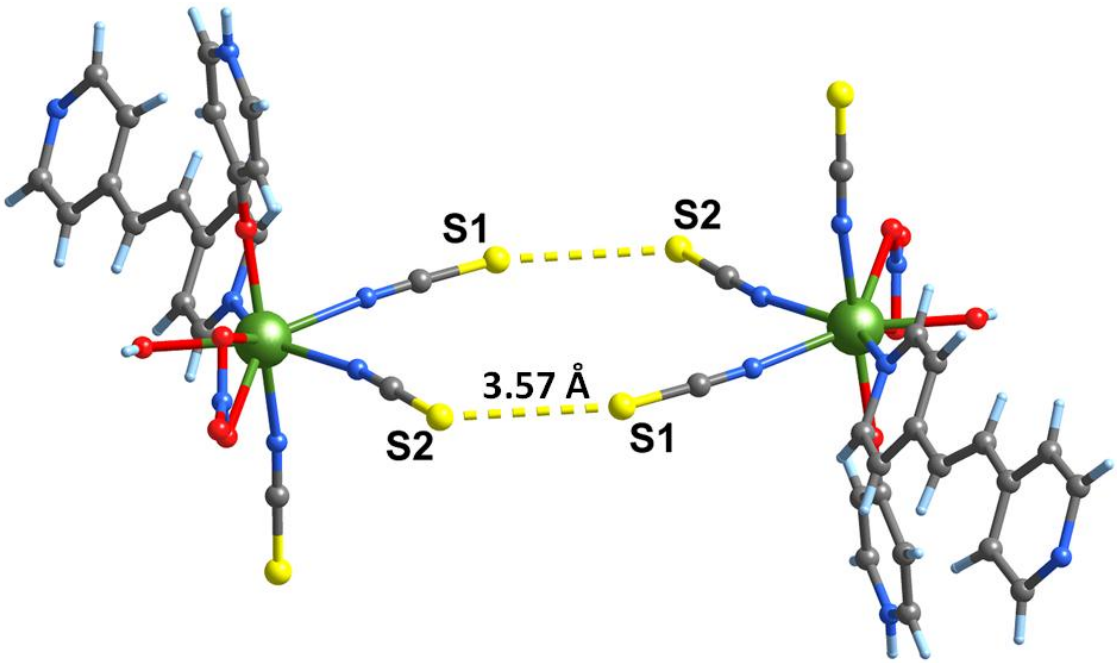

Fig. S5 The S…S interaction between two mononuclear {Dy} units.

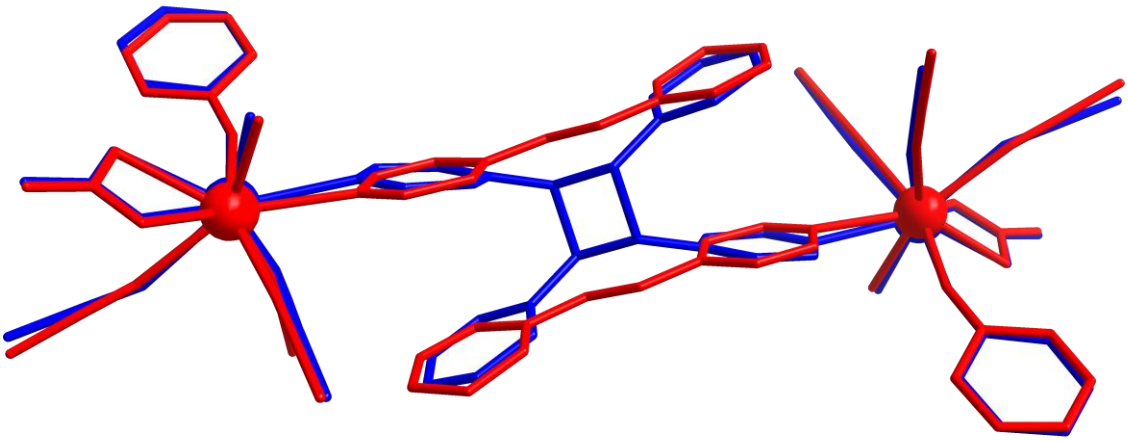

Fig. S6 Overlay diagram of structure differences before (red) and after (blue) [2+2] photodimerization.

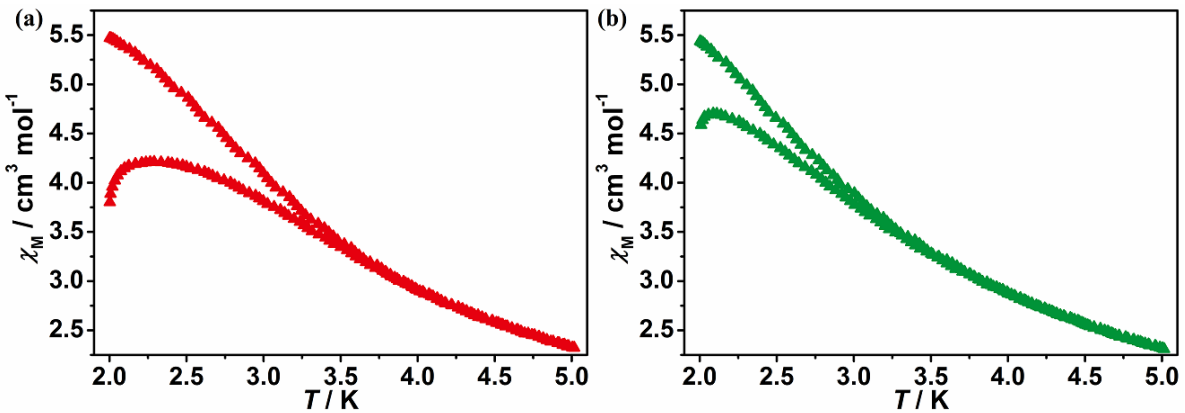

Fig. S7. The ZFC-FC magnetic susceptibilities under a 1 kOe dc field in warm mode for **1** (a) and **2** (b).

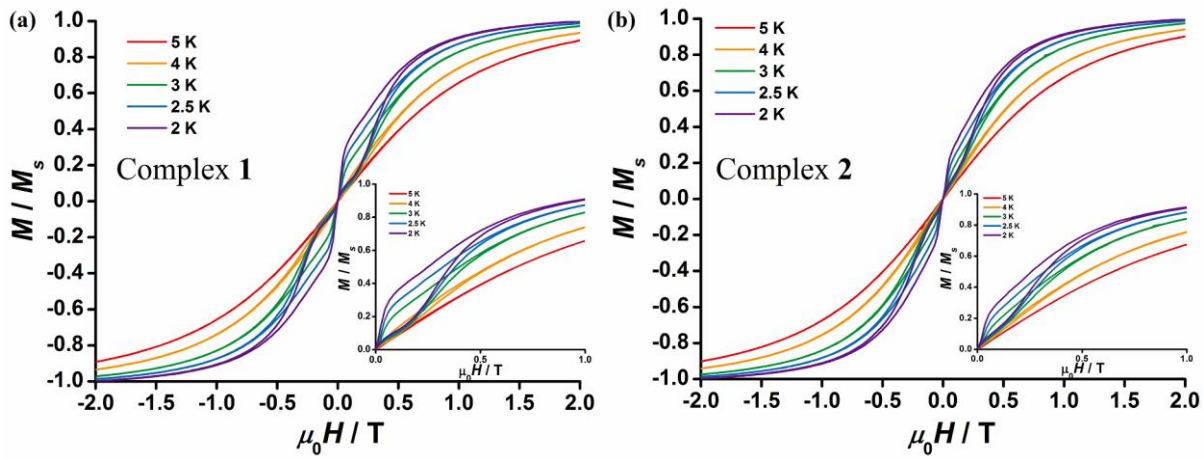

Fig. S8. The magnetic hysteresis for **1** (a) and **2** (b) at 2-5 K.

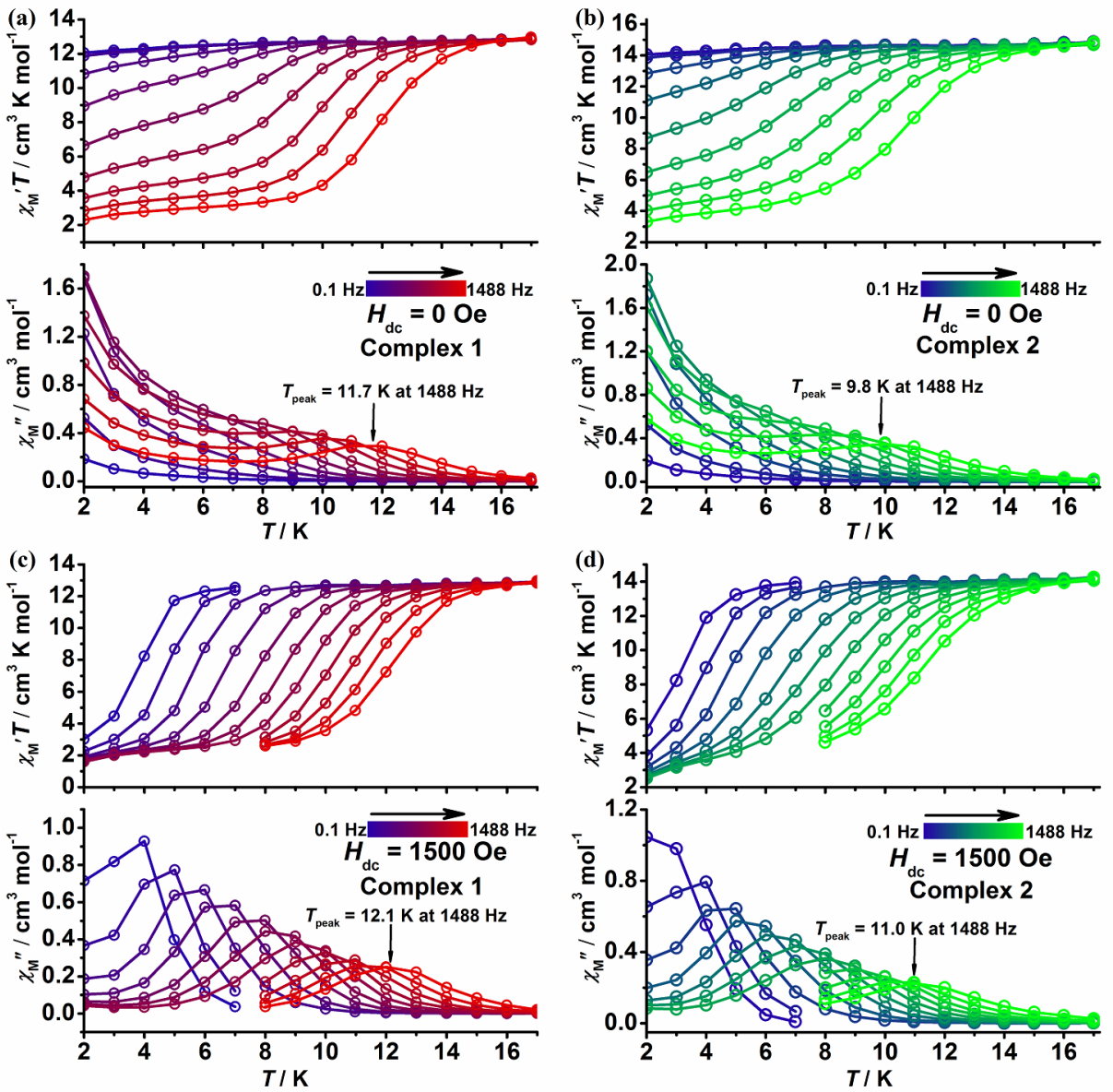

Fig. S9. The temperature dependence of ac susceptibility for **1** under zero (a) and its optimal field (1500 Oe) (b) and **2** under zero (c) and its optimal field (1500 Oe) (d).

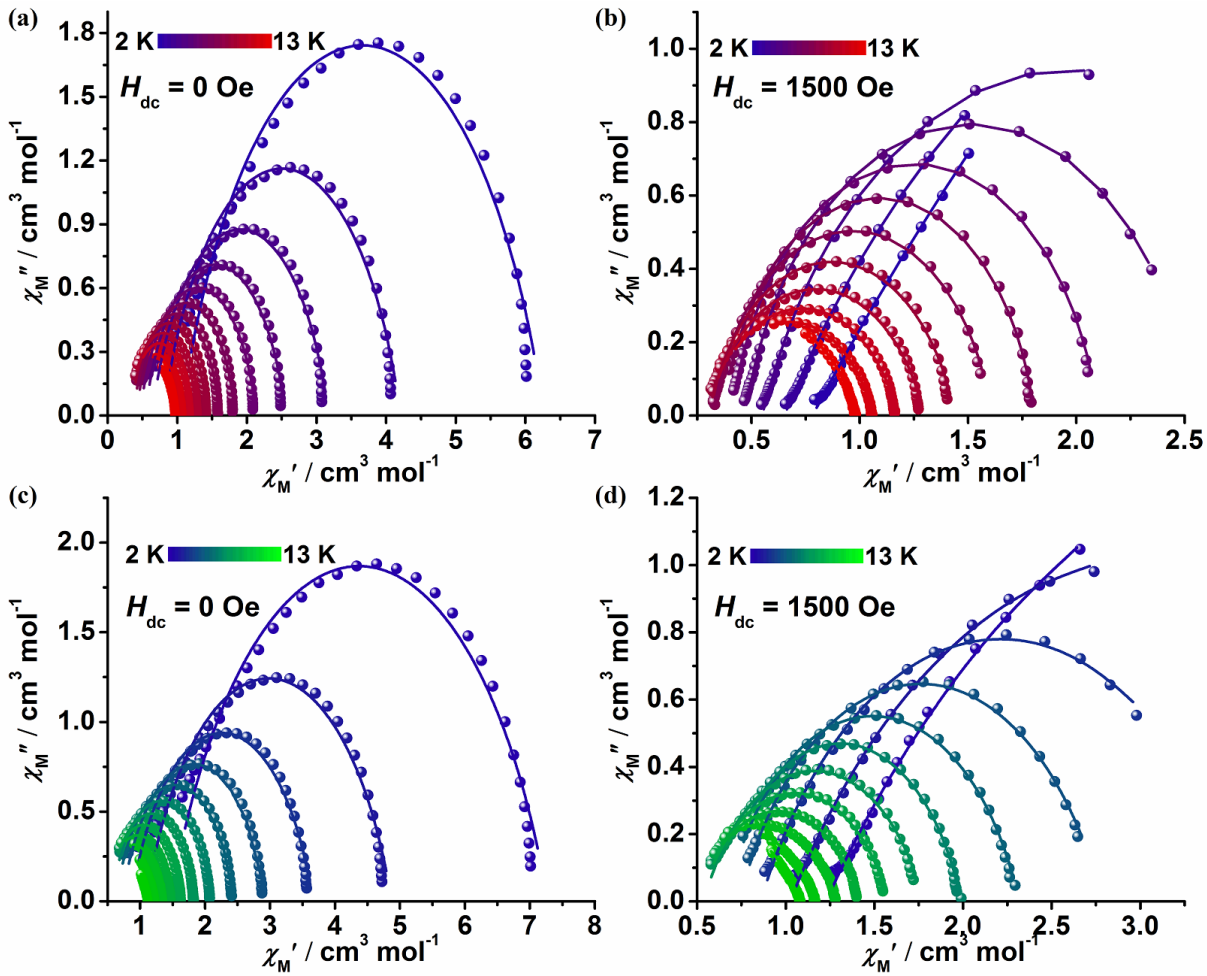

Fig. S10. The Cole-Cole plots of **1** (a,b) and **2** (c,d) under zero (a,c) and 1500 Oe (b,d) dc field with the generalized Debye model.

Table S1. The fitting parameters of the Cole–Cole plots for **1** and **2** under zero and 1500 Oe field.

	Complex **1**				Complex **2**			
H (Oe)	0		1500		0		1500	
Temp. [K]	τ [s]	α	τ [s]	α	τ [s]	α	τ [s]	α
2	0.00406	0.24884	—	—	3.26E-03	0.27115	—	—
3	0.00342	0.23752	—	—	2.84E-03	0.25905	—	—
4	0.00299	0.22944	1.45002	0.2516	2.38E-03	0.24706	0.38632	0.33127
5	0.00268	0.21999	0.29504	0.17066	1.88E-03	0.23054	0.0866	0.28011
6	0.00233	0.20563	0.08414	0.13213	1.35E-03	0.21087	0.02785	0.24809
7	0.0019	0.18275	0.0299	0.11996	9.01E-04	0.19656	0.01116	0.23075
8	0.0014	0.15748	0.01182	0.15397	5.79E-04	0.18921	0.00458	0.28663
9	8.88E-04	0.14054	0.00458	0.19051	3.54E-04	0.18986	0.00189	0.30618
10	4.91E-04	0.13982	0.00165	0.23308	2.01E-04	0.20242	6.86863E-4	0.33557
11	2.56E-04	0.14465	5.5591E-4	0.25551	1.03E-04	0.22492	2.20142E-4	0.36888
12	1.21E-04	0.1449	1.65853E-4	0.24979	3.92E-05	0.26653	4.47679E-5	0.41191
13	5.65E-05	0.15655	5.52647E-5	0.24603	1.27E-05	0.2993	1.2451E-5	0.41618

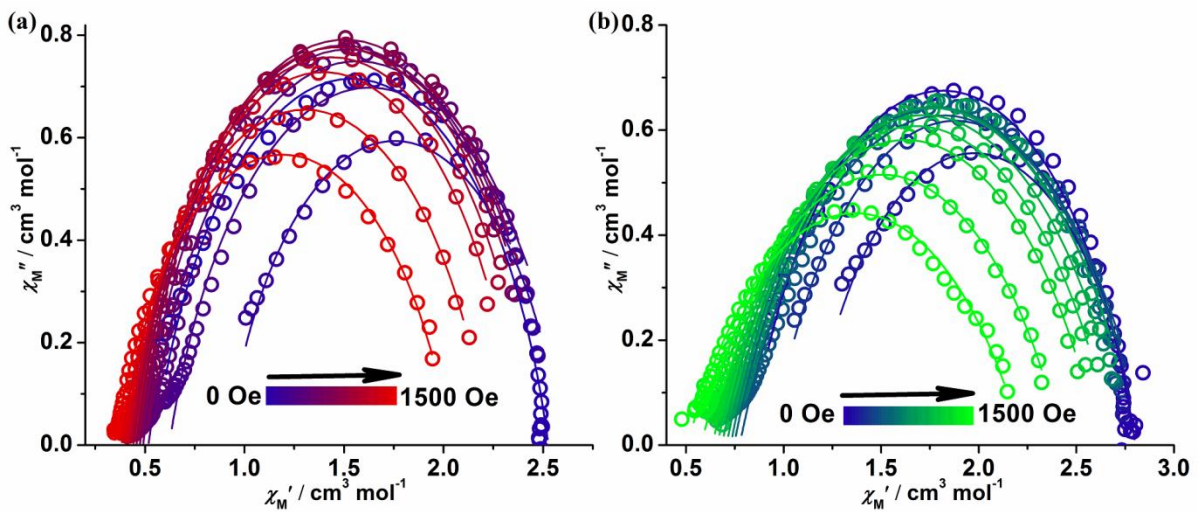

Fig. S11. The Argand plot deduced from the ac susceptibility of **1** (a) and **2** (b) against frequency at 5 K (0-5000 Oe). The Cole-Cole fitting at different fields are corresponding to the solid lines.

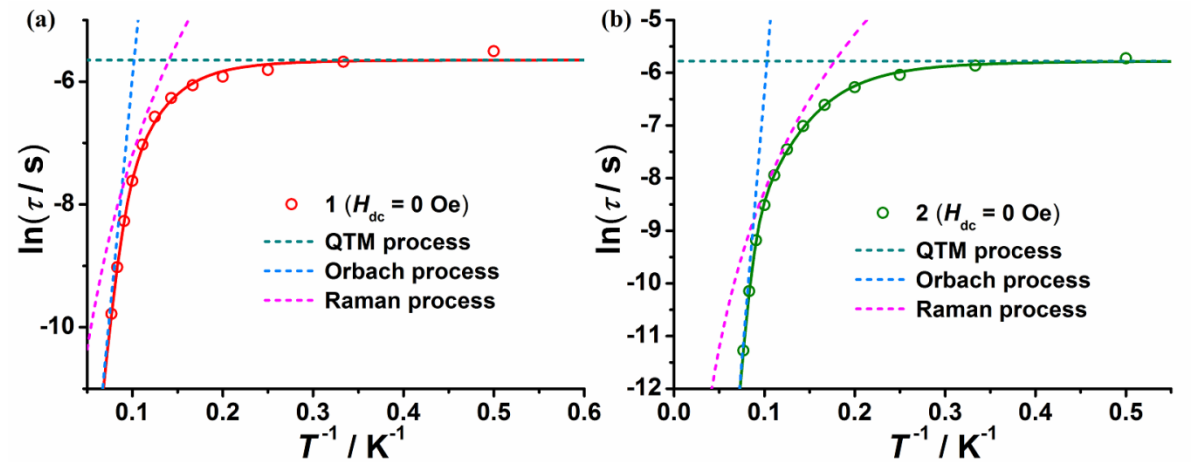

Fig. S12. Arrhenius plot constructed from data obtained under zero dc field for **1** (a) and **2** (b). The dashed lines respectively represent the component to the Raman (purple), QTM (dark cyan) and Orbach (blue) process. The solid lines represent the best fit to the total relaxation process.