Supporting Information

# Modulation of single-molecule magnet behaviour via photochemical [2+2] cycloaddition

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# **1.** Experiment section

## **General Remarks:**

All chemicals were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The thermogravimetric (TG) analyses were performed on a Perkin-Elmer TGA7 thermogravimetric analyzer in flowing N<sub>2</sub> with a heating rate of 10 K/min. The corresponding thermogravimetric curves for complex **1** and **2** are presented in Fig. S2. X-ray powder diffraction (XRPD) intensities for polycrystalline samples were measured at 293 K on a Bruker D8 Advance Diffractometer (Cu $K_{\alpha}$ ,  $\lambda = 1.54056$  Å, Fig. S1). The inductively-coupled plasma atomic emission spectra were analyzed using a TJA IRIS(HR) spectrometer.



Fig. S1 Calculated and experimental X-ray powder diffraction patterns for 1 and 1' (a); for 2 and 2' (b).



Fig. S2 Thermogravimetry curves for 1 (green) and 2 (red) under N<sub>2</sub> atmosphere.

#### Synthesis:

 $[Dy(bpe)(H_2O)_4(NO_3)_2](NO_3)\cdot 2bpe$  (1) and  $[Dy_2(tpcb)(H_2O)_8(NO_3)_4](NO_3)_2\cdot 2bpe\cdot tpcb$  (2). A mixture of bpe (54.6 mg, 0.3 mmol) and  $Dy(NO_3)_3\cdot 6H_2O$  (46.0 mg, 0.1 mmol) was dissolved in 10 ml solution of EtOH/MeCN (V:V = 2:1). The resulting colourless solution was left stand for evaporation at room temperature. Colourless rod-like crystals of 1 available for single crystal diffraction were obtained after 1-2 days. Yield: 89% based on bpe.

2 was obtained as single crystals when the single crystals of 1 were subjected to UV irradiation for 10 hours under an ultra-high pressure mercury lamp with P = 300 W.

Anal. Calc. (%) for 1: N, 13.03; C, 44.70; H, 3.96; for 2, N, 13.03; C, 44.70; H, 3.96. Found (%) for 1: N, 13.07; C, 45.06; H, 3.89; for 2, N, 13.09; C, 44.91; H, 3.95.

 $[Dy_{0.055}Y_{0.945}(bpe)(H_2O)_4(NO_3)_2](NO_3)\cdot 2bpe$  (1') and  $[Dy_{0.11}Y_{1.89}(tpcb)(H_2O)_8(NO_3)_4]$ (NO<sub>3</sub>)<sub>2</sub>·2bpe·tpcb (2'). A mixture of bpe (540 mg, 3 mmol), Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (22.5 mg, 0.05 mmol) and Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (365 mg, 0.95 mmol) was dissolved in 10 ml solution of EtOH/MeCN (V:V = 2:1). The resulting colourless solution was left stand for evaporation at room temperature. Colourless rod-like crystals of 1' available for single crystal diffraction were obtained after 1-2 days. Yield: 92% based on bpe.

2' was obtained as single crystals when the single crystals of 1' were subjected to UV irradiation for 10 hours under an ultra-high pressure mercury lamp with P = 300W.

The amount of Dy(III) in **2'** was assumed to be the same with **1'**, because the single-crystal-to-single-crystal transformation from **1'** to **2'** through [2+2] reaction doesn't change the ratio of elements in complexes. For **1'**, the amount of Dy(III) was confirmed by the inductively coupled plasma (ICP) measurements.

Anal. Calc. (%) for **1**': N, 14.04; C, 48.17; H, 4.27; for **2'**, N, 14.04; C, 48.17; H, 4.27. Found (%) for **1'**: N, 13.94; C, 48.10; H, 4.21; for **2'**, N, 13.66; C, 48.19; H, 4.18.

## X-ray Crystallographic Study:

Diffraction data for complex **1** and **2** were collected on a Rigaku R-AXISSPIDER IP diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 150 K. Complex **1'** and **2'** were recorded on an Oxford Diffraction Gemini R CCD diffractometer with Cu $K_a$ ,  $\lambda = 1.54056$  Å at 150 K. The site occupancies of Dy(III) and Y(III) for **1'** and **2'** were determined by the inductively coupled plasma (ICP) measurements. The structures of all complexes were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares methods on  $F^2$  using the SHELXTL program.<sup>1</sup> Hydrogen atoms on organic ligands were generated by the riding mode. CCDC reference numbers are 1051853 (**1**), 1051854 (**2**), 1401223 (**1'**) and 1401224 (**2'**).

1 SHELXTL 6.10, Bruker Analytical Instrumentation, Madison, Wisconsin (USA), 2000.

#### Magnetic measurements:

The magnetic measurements were performed on the polycrystalline samples using a Quantum Design MPMS XL-7 SQUID magnetometer with experimental diamagnetic correction. The samples were mixed with Vaseline to prevent the orientation in magnetic fields.

# 2. Structure and Crystallographic Data

Complex	1	2	1'	2'
Formula	C <sub>36</sub> H <sub>38</sub> N <sub>9</sub> O <sub>13</sub> Dy	C <sub>72</sub> H <sub>76</sub> N <sub>18</sub> O <sub>26</sub> Dy <sub>2</sub>	C <sub>36</sub> H <sub>38</sub> N <sub>9</sub> O <sub>13</sub> Dy <sub>0.06</sub> Y <sub>0.94</sub>	C <sub>72</sub> H <sub>76</sub> N <sub>18</sub> O <sub>26</sub> Dy <sub>0.11</sub> Y <sub>1.89</sub>
$M_{ m r}$	967.25	1934.51	898.08	1795.42
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
<i>a</i> [Å]	11.0970(7)	11.0390(3)	11.0672(2)	11.0563(5)
b[Å]	22.1612(16)	21.8260(4)	22.1008(5)	21.8263(10)
c[Å]	16.3266(11)	16.5559(3)	16.3215(4)	16.5576(10)
α[°]	90	90	90	90
$\beta[\circ]$	90.525(2)	93.732(1)	90.754(2)	93.631(4)
γ[°]	90	90	90	90
V[Å <sup>3</sup> ]	4014.9(5)	3980.47(15)	3991.80(15)	3987.6(4)
Z	4	2	4	2
$\rho_{calcd}$ [mg mm <sup>-3</sup> ]	1.600	1.614	1.494	1.496
<i>T</i> [K]	150	150	150	150
Goof on $F^2$	1.094	1.038	1.184	1.102
$R_1[I > 2\sigma(I)]^{[a]}$	0.0489	0.0324	0.0565	0.0593
wR <sub>2</sub> [all data] <sup>[b]</sup>	0.1175	0.0783	0.1012	0.1106

Table S1. Crystallographic Data and Structural Refinements for 1, 2, 1' and 2'.

<sup>[a]</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, [b] w R_2 = [\sum w (F_o^2 - F_c^2)^2 / w (F_o^2)^2]^{1/2}.$ 

bond lengths (Å)	1	2
Dy1-N1	2.5483(2)	2.5332(0)
Dy1-O1W	2.3880(1)	2.3967(1)
Dy1-O2W	2.3512(1)	2.3468(0)
Dy1-O3W	2.3861(1)	2.4366(1)
Dy1-O4W	2.3331(1)	2.3302(0)
bond angles (°)		
N1-Dy1-O1W	79.006(2)	76.788(1)
N1-Dy1-O3W	82.897(2)	84.652(1)
O4W-Dy1-O4	75.938(2)	74.365(1)
O1W-Dy1-O2	68.019(2)	69.035(1)
O2W-Dy1-O2	70.600(2)	71.374(1)
O4W-Dy1-O5	98.446(3)	94.321(1)
N1-Dy1-O2W	86.373(3)	85.817(1)
N1-Dy1-O4W	79.951(3)	82.262(1)
O3W-Dy1-O4W	71.502(2)	70.891(1)
O3W-Dy1-O2W	70.498(2)	68.484(1)
O2W-Dy1-O5	78.451(3)	80.664(1)
O1W-Dy1-O1	79.969(2)	83.906(1)

Table S2. Selected bond lengths (Å) and bond angles (°) for 1 and 2.

**Table S3.** The CShM values calculated by SHAPE 2.1 for 1 and 2.

	CN	Coordination Geometry	1 2
Dy(III)	9	Spherical capped square antiprism( $C_{4v}$ )	1.26154 1.52945



Fig. S3 The coordination environments of Dy(III) ions in mononuclear [Dy] and dinuclear  $[Dy_2]$  unit of complex 1 (a) and 2 (b), respectively.



**Fig. S4** The hydrogen bonded 1D chain in **1** constructed by mononuclear  $[Dy(bpe)(H_2O)_4(NO_3)_2]^+$  units and guest NO<sup>3-</sup> ions, the parallel and criss-cross packed bpe ligands are marked by blue and red circles respectively. For clarity, the other repetitive bpe ligands are omitted.



**Fig. S5** The group of three criss-cross packed free bpe ligands in complex 1 (a) and the corresponding UV-irradiated product containing a bpe and a *rctt*-tpcb ligand in 2 (b,c). Due to the equidistance of the C=C bonds from two other bpe ligands on both sides, the middle bpe ligand could take place [2+2] dimerization with the either one.

## 3. Plots of Magnetic Data



**Fig. S6** Temperature dependent in-phase  $(\chi_M')$  and out-of-phase  $(\chi_M'')$  signals for 1 (a) and 2 (b) under zero dc field.



Fig. S7 Frequency (1-1488 Hz) dependent ac measurement for 1 (a) and 2 (b) in the absent of dc field at 2, 3 and 5 K.



**Fig. S8** Frequency dependence of  $\chi_{M}'$  and  $\chi_{M}''$  signals at various fields at 2K for 1 (a) and for 2 (b), and their corresponding diluted samples, 1' (c) and 2' (d).



**Fig. S9** The Argand plot deduced from the ac susceptibility of **1** (a), **2** (b), **1'** (c) and **2'** (d) against frequency at 2 K (0-2000 Oe), the solid lines are guided by eyes.



**Fig. S10** The temperature dependence of ac susceptibility for diluted samples 1' under zero (a) and its optimal field (300 Oe) (b).



Fig. S11 The Cole-Cole plots of 1' under zero (a) and 300 Oe (b) dc field with the generalized Debye model.

<i>Temp</i> . [K]	$\tau$ [s]	$\tau_{\rm std.dev.}$ [s]	α	$\alpha_{\rm std.dev}$
7.00	2.17E-5	2.55E-6	0.06616	0.01006
6.60	4.50E-5	2.11E-6	0.04927	0.00737
6.20	7.32E-5	1.62E-6	0.05479	0.00506
5.80	1.15E-4	1.57E-6	0.05905	0.00431
5.40	1.75E-4	1.82E-6	0.07016	0.00411
5.00	2.63E-4	2.56E-6	0.08341	0.00448
4.60	3.93E-4	3.75E-6	0.10015	0.00476
4.19	5.89E-4	5.91E-6	0.11992	0.00517
3.80	8.95E-4	1.00E-5	0.14622	0.00573
3.40	0.00139	1.82E-5	0.1811	0.00651
3.00	0.00221	3.49E-5	0.22749	0.00732
2.60	0.00367	7.15E-5	0.29454	0.00805
2.16	0.00662	1.62E-4	0.38921	0.00803
1.79	0.01127	3.42E-4	0.48692	0.00695

Table S4. Selected parameters from the fitting results of the Cole–Cole plots for 1' under zero field

Table S5. Selected parameters from the fitting results of the Cole–Cole plots for 1' under 300 Oe field

<i>Temp</i> . [K]	τ[s]	$\tau_{\rm std.dev.}$ [s]	α	$\alpha_{\rm std.dev}$
7.00	2.63E-5	1.68E-6	0.06998	0.00637
6.60	5.45E-5	1.45E-6	0.05036	0.00487
6.20	9.11E-5	1.16E-6	0.0474	0.00349
5.80	1.45E-4	1.36E-6	0.05334	0.00348
5.40	2.29E-4	1.57E-6	0.06	0.00317
5.00	3.61E-4	2.25E-6	0.06929	0.00329
4.60	5.69E-4	3.61E-6	0.07914	0.00354
4.19	9.06E-4	5.99E-6	0.09201	0.00374
3.80	0.0015	1.01E-5	0.11121	0.00377
3.40	0.0026	1.94E-5	0.1363	0.00404
3.00	0.00486	4.40E-5	0.17048	0.0046
2.60	0.01028	1.28E-4	0.21977	0.00549
2.16	0.02889	5.48E-4	0.29943	0.00572
1.80	0.09215	0.00139	0.32373	0.00635



**Fig. S12** The temperature dependence of ac susceptibility for diluted samples **2'** under zero (a) and its optimal field (400 Oe) (b).



Fig. S13 The Cole-Cole plots of 2' under 400 dc field with the generalized Debye model.

Temp. [K]	$\tau[s]$	$\tau_{\rm std.dev.}$ [S]	α	$\alpha_{\rm std.dev}$
6.20	2.51E-5	3.23E-6	0.17769	0.01154
5.80	4.97E-5	2.85E-6	0.16748	0.00824
5.40	9.68E-5	2.61E-6	0.16024	0.00603
5.00	1.85E-4	2.97E-6	0.16136	0.00514
4.60	3.80E-4	4.58E-6	0.15743	0.00517
4.19	8.23E-4	8.22E-6	0.15675	0.00497
3.80	0.00195	1.96E-5	0.16292	0.00518
3.40	0.00524	7.22E-5	0.18558	0.0068
3.00	0.01665	2.28E-4	0.18622	0.00743
2.60	0.05621	9.92E-4	0.20029	0.00891
2.21	0.23358	0.00636	0.24302	0.01464
1.82	0.68053	0.03996	0.43090	0.01412

Table S6. Selected parameters from the fitting results of the Cole–Cole plots for 2' under 400 Oe field



Fig. S14 Field dependence of the magnetic relaxation time ( $\tau$ ) at 2 K for 1' (a) and 2' (b). The dashed blue and green lines correspond to the contributions to the relaxation time of the QTM and direct relaxation processes. The solid red line corresponds to the weighted sum of the two processes.

Table S7. The fitting parameters of the Raman, direct, QTM and Orbach processes for 1' and 2'

	$A_1$ (s <sup>-1</sup> Oe <sup>-3</sup> )	$A_2$ (K Oe <sup>-1</sup> )	$B_1$ (s <sup>-1</sup> )	$B_2$ (Oe <sup>-2</sup> )	$C (s^{-1} K^{-n})$	п	$ au_{0}\left( \mathrm{s} ight)$
1' - 0 Oe field	-	_	20.52	_	6.24	3.92	3.25E-12
1' - 300 Oe field	1.83E-8	0.0053	20.52	1.09E-4	0.465	5.44	4.56E-12
2' - 400 Oe field	3.00E-9	0.0040	30.08	3.76E-4	2.87E-3	8.94	8.89E-10



**Fig. S15** Arrhenius plot constructed from data obtained under a dc field of 0 Oe (a) and 300 Oe (b) for 1' and 400 Oe (c) for 2'. The solid lines represent data fits to an, Raman (magenta), QTM (orange), Orbach (dark cyan) and Direct (dark yellow) process. The dashed lines represent a data fit to the total processes simultaneously.