Supplementary Information

Light-induced magnetic switching in a coumarin-based Tb Single Molecule Magnet

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- S1. Crystal structure and magnetic relaxation of Tb-batho
- S2. Additional magneto-optical measurements
- S3. Additional Ab initio calculation results

S1. Crystal structure and magnetic relaxation of Tb-batho

	Tb-batho
CCDC deposition	CCDC-2013258
Formula	$C_{58.4}H_{41.2}N_2O_{12.7}Tb$
fw	1133.05
Crystal size (mm ³)	0.40×0.14×0.03
Colour	colourless
Space group	<i>P</i> -1
a (Å)	11.6630(4)
b (Å)	13.2469(6)
<i>c</i> (Å)	18.3330(8)
α (°)	78.553(3)
β (°)	76.079(3)
γ (°)	68.680(3)
$V(Å^3)$	2541.72(19)
Z, Z'	2, 1
Diffractometer	Stadivari
Radiation	Ag-Kα
$T(\mathbf{K})$	295(1)
Density (g.cm ⁻³)	1.480
Abs. coef. (mm ⁻¹)	0.786
Transmission fact.	0.4071 -1.0000
Refl. collected	73159
$\text{Sen}\theta/\lambda$ (Å ⁻¹)	0.68
$R_{\rm int}$ (%)	10.07
Completeness (%)	99.8
Data/parameters	13480 / 681
Restraints	1
$R_1, wR_2 [I > 2\sigma(I)]$	4.17, 7.50
R_1 , wR_2 [all data]	7.96, 8.24
GOF on F^2	0.795

Table S1. Crystal data for Tb-batho compound.92



Figure S1. Relaxation time as a function of the inverse temperature, $\tau(1/T)$, at 3 kOe (a), and as a function of the magnetic field at 2 K.

S2. Additional magneto-optical measurements

Light-induced dc magnetic switching experiments were performed on two pellets of similar diameter (2.5 mm) but different thicknesses: 0.05 mm (pellet 1) and 0.1 mm (pellet 2). Results for pellet 1 are presented in the main text, while data for pellet 2 are shown here. Qualitatively, both pellets exhibit a similar phenomenology. Magnetization versus time M(t) experiments at T = 1.8 K, H = 1 kOe, with the lamp alternately switched 'Off' and 'On' (Figure S2a), confirm the observed switching effect observed in pellet 1.

The maximum magnetization modulation, ΔM (Off/On), occurs under optimal irradiation at 380 nm (Figure S2a, b), reaching a value of ΔM (Off/On) = 0.024 μ_B /fu (approximately 3% of the magnetization at 1.8 K). This smaller modulation, compared to that of pellet 1, suggests that not all of the sample contributes to the effect in pellet 2. Comparing ΔM (Off/On) to the *ab initio* calculated maximum possible change, ΔM^{max} , indicates that the excited population level in this case may reach, at most, 5%.

The Off/On switching experiments under 275 nm light at H = 1 kOe and temperatures of T = 1.8 K and 300 K are compared in Figure S2d. At room temperature, the light-induced change in magnetization is either not detected or falls below the measurement noise threshold (< 6 x $10^{-4} \mu_{B}/fu$).

To study the influence of the applied dc magnetic field on the light-induced magnetization change, we performed time-dependent magnetization measurements while switching the light "Off" and "On" at 1.8 K under an increased field of 10 kOe (Figure S3a). The magnetization switching is reproduced, with a maximum response observed under 380 nm illumination; however, the magnitude of the change is reduced, reaching



280 nm and 800 nm; (b) Magnetization change between the Uff and Un value as a function of the interesting of the state of the second of the interesting of the second of

 ΔM (Off/On) = 0.018 μ_B /fu. Additionally, we measured the field-dependence of the magnetization, M(H), with the light alternately switched "Off" and "On" (250 nm) at T = 1.8 K (Figure S3b). The difference between the two curves, ΔM (Off/On)(H), is plotted in Fig. S3c. The light-induced magnetization change reaches its peaks at 3 kOe for this wavelength, becoming almost negligible above 25 kOe.

S3. Additional Ab initio calculation results

<u>**Table S2.** Ab initio calculated energy levels of Tb(III) in **Tb-batho** for the ${}^{7}F_{J}$ (J=0-6) multiplets and first excited ${}^{5}D_{4}$. multiplet.</u>

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3278.68693 3242.05558 3163.9748 3062.27088 3045.41824 ⁷ F ₆ 523.30643 521.34364 396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302		3294.49747
3242.05558 3163.9748 3062.27088 3045.41824 ⁷ F ₆ 523.30643 521.34364 396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302		3278.68693
^{3163.9748} 3062.27088 3045.41824 ⁷ F ₆ ^{523.30643} ^{521.34364} 396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0		3242.05558
^{3062.27088} 3045.41824 ⁷ F ₆ ^{523.30643} 521.34364 396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0		3163.9748
⁷ F ₆ ⁷ F ₆ ⁷ F ₆ ^{523.30643} ^{521.34364} ^{396.99394} ^{386.11542} ^{342.2582} ^{318.6539} ^{307.03196} ^{219.84885} ^{216.61935} ^{122.9253} ^{122.70315} 0.14302 0		3062.27088
 /F₆ 523.30643 521.34364 396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0 	_	3045.41824
521.34364 396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0	′F ₆	523.30643
396.99394 386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0		521.34364
386.11542 342.2582 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0		396.99394
342.2382 318.6539 307.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0		300.11342
317.03196 219.84885 216.61935 122.9253 122.70315 0.14302 0		342.2302
219.84885 216.61935 122.9253 122.70315 0.14302 0		307 03106
215.64663 216.61935 122.9253 122.70315 0.14302 0		219 8/1885
122.9253 122.70315 0.14302 0		215.04005
122.70315 0.14302		122 9253
0.14302		122.70315
0		0.14302
		0

Levels	Energy (V)	-6>	-5>	-4>	-3>	-2>	-1>	0>	+1>	+2>	+3>	+4>	+5>	+6>
	(K)													
$ \xi_0\rangle$	0	0.25	0.17	0.05	0.02	0.01	0.00	0.00	0.00	0.01	0.02	0.05	0.17	0.25
$ \xi_1\rangle$	0.143	0.25	0.17	0.05	0.02	0.01	0.00	0.00	0.00	0.01	0.02	0.05	0.17	0.25
$ \xi_2\rangle$	122.70	0.01	0.06	0.13	0.13	0.07	0.10	0.00	0.10	0.07	0.13	0.13	0.06	0.01
$ \xi_3\rangle$	122.93	0.01	0.06	0.13	0.12	0.12	0.02	0.08	0.02	0.12	0.12	0.13	0.06	0.01
$ \xi_4\rangle$	216.62	0.18	0.10	0.14	0.03	0.02	0.03	0.00	0.03	0.02	0.03	0.14	0.10	0.18
$ \xi_5\rangle$	219.85	0.18	0.09	0.15	0.04	0.02	0.01	0.02	0.01	0.02	0.04	0.15	0.09	0.18
$ \xi_6\rangle$	307.03	0.04	0.13	0.09	0.07	0.08	0.04	0.10	0.04	0.08	0.07	0.09	0.13	0.04
$ \xi_7\rangle$	318.65	0.05	0.14	0.09	0.12	0.05	0.09	0.02	0.09	0.05	0.12	0.09	0.14	0.05
$ \xi_8\rangle$	342.26	0.01	0.03	0.07	0.12	0.11	0.14	0.04	0.14	0.11	0.12	0.07	0.03	0.01
$ \xi_9\rangle$	286.12	0.01	0.02	0.05	0.08	0.09	0.18	0.14	0.18	0.09	0.08	0.05	0.02	0.01
$ \xi_{10}\rangle$	396.99	0.01	0.01	0.02	0.10	0.08	0.11	0.34	0.11	0.08	0.10	0.02	0.01	0.01
$ \xi_{11}\rangle$	521.34	0.00	0.00	0.01	0.11	0.10	0.20	0.16	0.20	0.10	0.11	0.01	0.00	0.00
$ \xi_{12}\rangle$	523.31	0.00	0.00	0.02	0.03	0.25	0.16	0.08	0.16	0.25	0.03	0.02	0.00	0.00

Table S3 *Ab initio* calculated energy levels of **Tb-batho** and eigenstates of Tb(III) in terms of the free ion wave functions, for the ⁷F₆. ground multiplet. The numbers in the table indicate the weight of the $|+M_J\rangle$ and $|-M_J\rangle$ states.