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Supplementary Information

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

E. Bartolomé,[a*] A. Arauzo,[b*] J. Luzón,[c] L. Gasque[d]

[a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193-Bellaterra, Barcelona, Spain; ebartolome@icmab.es

[b] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, and Departamento de Física de la Materia Condensada, 50009 Zaragoza, Spain; aarauzo@unizar.es

[c] Centro Universitario de Defensa (CUD), Universidad de Zaragoza, Spain.

[d] Facultad de Química, Universidad Nacional Autónoma de México, Avenida Universidad 3000, CDMX 04510, México.

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

Table S1. Crystal data for **Tb-batho** compound.[92]

	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	*P*-1
a (Å)	11.6630(4)
b (Å)	13.2469(6)
c (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-*K*α
T (K)	295(1)
Density (g.cm^{-3})	1.480
Abs. coef. (mm^{-1})	0.786
Transmission fact.	0.4071 -1.0000
Refl. collected	73159
Senθ/λ (Å^{-1})	0.68
R_{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

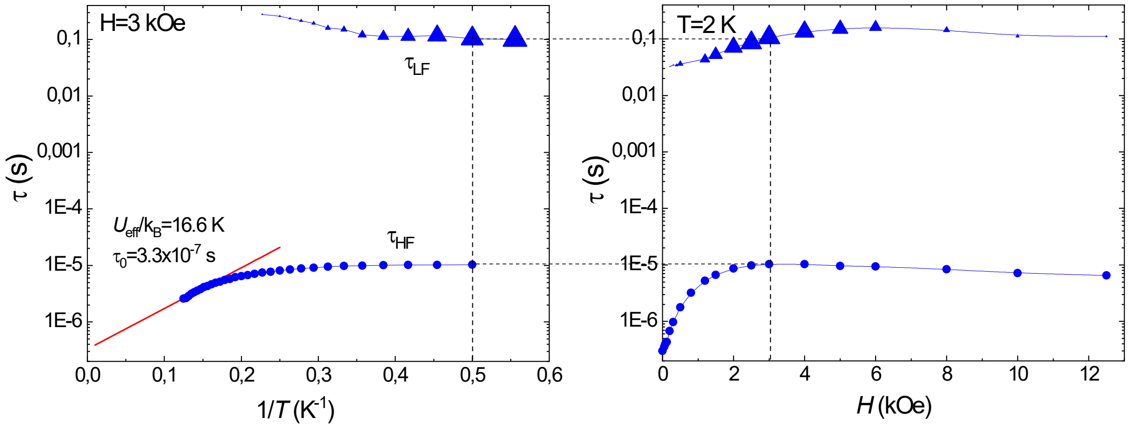

Figure S1. Relaxation time as a function of the inverse temperature, τ(1/*T*), at 3 kOe (a), and as a function of the magnetic field at 2 K.

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} μ_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

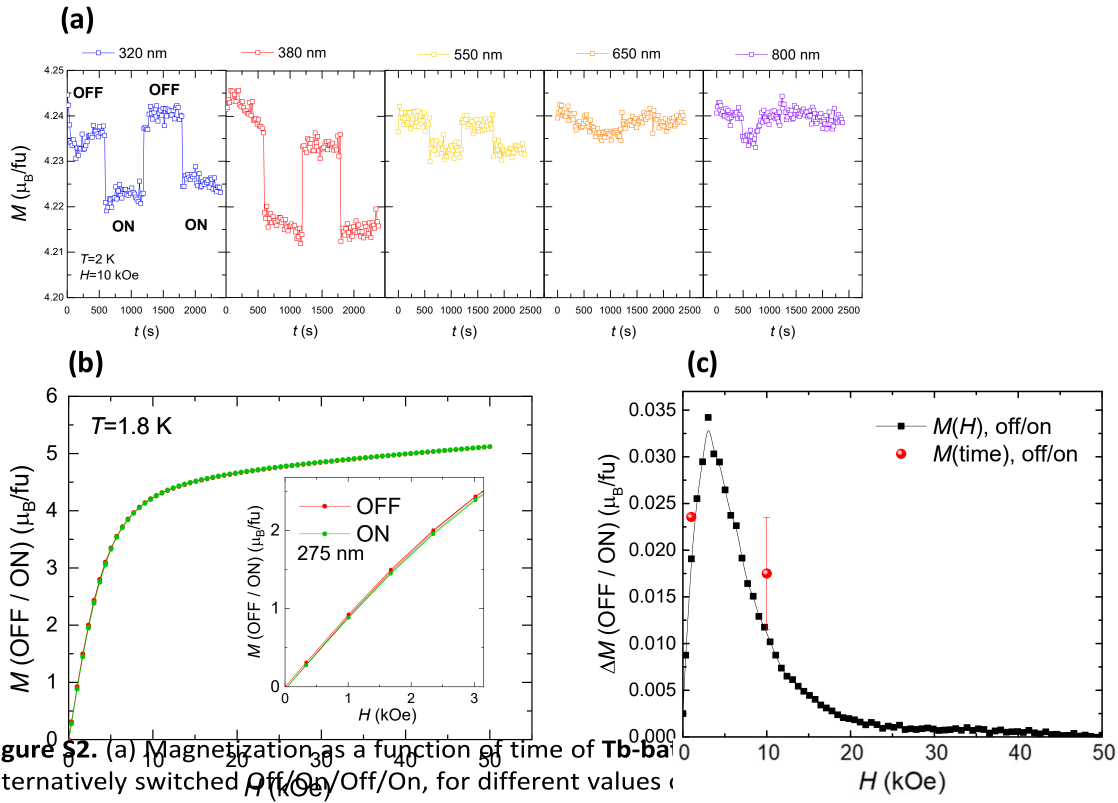

Figure S2. (a) Magnetization as a function of time of **Tb-ba** is alternatively switched Off/On/Off/On, for different values n 280 nm and 800 nm; (b) Magnetization change between the Off and On value as a function of the incident light wavelength, ΔM(Off/On) at 1.8 K, for an applied field of $H = 1$ kOe and 10 kOe; (c) Temperature of the sample monitored during the Off/On experiments (set $T = 1.8$ K, $\lambda = 380$ nm); (d) Switch Off/On experiments (under $\lambda = 275$ nm light) at $H = 1$ kOe, at $T = 1.8$ K and room temperature. Measurements conducted on pellet 2.

Figure S3. (a) Magnetization as a function of time of **Tb-batho** at $T = 2$ K, $H = 10$ kOe, as the lamp is alternatively switched Off/On/Off/On, for different values of the incident light wavelength between 280 nm and 800 nm; (b) Field dependence of the magnetization at $T = 1.8$ K with the lamp switched Off and On ($\lambda = 275$ nm); (c) Magnetization change between Off/On (275 nm) as a function of magnetic field. Measurements conducted on pellet 2.

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

Table S2. *Ab initio* calculated energy levels of Tb(III) in **Tb-batho** for the ^7F_J (J=0-6) multiplets and first excited $^5D_4$. multiplet.

$^{2S+1}L_J$	**Energy (K)**
$^5D_4$	33997.21664
	33989.50949
	33984.35907
	33963.11122
	33948.27776
	33932.73369
	33927.80613
	33869.40983
	33868.74525
$^7F_0$	8826.87077
$^7F_1$	8553.25433
	8542.39797
	8365.71889
$^7F_2$	7980.65479
	7900.79366
	7785.06431
	7754.33385
	7549.2645
$^7F_3$	6785.46106
	6768.35245
	6743.24477
	6701.34501
	6648.12027
	6629.61806
	6612.03206
$^7F_4$	5422.86238
	5376.62511
	5339.97419
	5318.96345
	5209.72806
	5129.38149
	5059.0693
	5049.72553
	5028.79306
$^7F_5$	3472.9261
	3455.85534
	3375.35294
	3354.26062
	3323.40945
	3294.49747
	3278.68693
	3242.05558
	3163.9748
	3062.27088
	3045.41824
$^7F_6$	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

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 $^7F_6$. ground multiplet. The numbers in the table indicate the weight of the $|+M_J\rangle$ and $|-M_J\rangle$ states.

Levels	Energy (K)	|-6>	|-5>	|-4>	|-3>	|-2>	|-1>	|0>	|+1>	|+2>	|+3>	|+4>	|+5>	|+6>
$\|\xi_0\rangle$	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