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SUPPLEMENTARY INFORMATION

Enhanced luminescence stability with a Tb–spin crossover nanocomposite for spin state monitoring

Iurii Suleimanov,[a,b] Olena Kraieva[a,] Gábor Molnár[a], Lionel Salmon,[a]* and Azzedine Bousseksou[a]*

[a]Laboratoire de la Chimie de Coordination, CNRS & Université de Toulouse (INPT, UPS), 205 route de Narbonne, 31077 Toulouse Cedex 4, France

[b]Department of Chemistry, National Taras Shevchenko University, 62a Volodymyrska street, 01601 Kyiv, Ukraine

Experimental section

Reagents

All chemicals were purchased from commercial sources and used without purification. $Fe(BF_4)_2 \cdot 6H_2O$, tetraethoxysilane (TEOS), 3-aminopropyltrimethoxysilane (APTMS), Triton X-100, sodium hydroxide and cyclohexane were purchased from Sigma-Aldrich. Terbium(III) nitrate, 1-hexanol and ethylenediamine tetraacetate dihydrate (EDTA) were purchased from Alfa Aesar. 5-formylsalicylic acid (FSA) was purchased from TCI.

Instruments

Variable temperature magnetic moment was recorded with a Quantum Design MPMS2 magnetometer under a magnetic field of 0.1 T at a rate of 2 K/min. Transmission electron microscopy images were obtained with a JEOL JEM-1400 instrument. High Resolution TEM images and EDX spectrum were obtained with a JEOL JSM 2100F microscope. CHN elemental analysis was performed using a Flash EA1112 (Thermo Finnigan) apparatus. ICP-AES analysis was conducted using ICAP 6300 Thermo Hotblock Digestion System. Infrared absorption spectra were recorded with a Perkin Elmer Spectrum 100 spectrometer in ATR mode between 650 and 4000 cm^{-1} with 2 cm^{-1} resolution. Diffuse reflectance spectra were recorded with a Lambda 35 UV/Vis spectrophotometer equipped with a Labsphere RSA-PE-20 integrating sphere. Luminescence excitation and emission spectra and variable temperature lifetime measurements were recorded using a Cary Eclipse (Varian) fluorescence spectrophotometer and a THMS600 liquid nitrogen cryostat (Linkam Scientific Instruments). Variable temperature fluorescence intensity measurements were conducted using an Olympus BX51 microscope equipped with an iKon-M DU934N- BV (Andor Technology) charge-coupled device detector. An objective with a ×5 magnification (numerical aperture, NA = 0.1) was used. A dichroic mirror (cutting edge at 510 nm) was used to separate the excitation and collected light beams. Two band-pass filters were used, one for the excitation, centered at 450 nm (full width at half maximum, FWHM = 45 nm) and another one for the emitted light at 550 nm (FWHM = 50 nm). ^{57}Fe Mössbauer spectrum was recorded using a conventional constant-acceleration type spectrometer equipped with a 50 mCi ^{57}Co source and a flow-type, liquid nitrogen cryostat. Least square fittings of the Mössbauer spectra have been applied with the assumption of Lorentzian line shapes using the Recoil software package.

Synthesis of $[Fe(Htrz)_2(trz)]BF_4@SiO_2$

Silica covered nanorods were prepared according to the method described in ref. 24 with slight modifications. Two emulsions were prepared. The first one contained an aqueous solution of $Fe(BF_4)_2 \cdot 6H_2O$ (422 mg, 1.25 mmol in 1 mL H_2O), 0.2 mL of tetraethoxysilane (TEOS), 3.6 mL of Triton X-100, 3.6 mL of 1-hexanol and 7.5 mL of cyclohexane. The second one contained an aqueous solution of 1,2,4-triazole (262 mg, 3.75 mmol in 1 mL H_2O) and the same composition of TEOS – Triton – hexanol – cyclohexane mixture. The two emulsions were mixed together and left to stir for 24 hours. Then 0.2 ml of TEOS and 0.6 ml of H_2O was added. The resulting mixture was stirred for another 24 h, followed by addition of ethanol to destroy the structure of the emulsion. The nanoparticles were separated by centrifugation, washed three times with ethanol and dried at 70 °C in air.

Synthesis of the Tb complex

The synthesis of the Tb complex is divided into two parts. Initially, the Tb complex is formed from fully deprotonated EDTA, doubly deprotonated FSA and Tb^{3+} ion. The negatively charged complex anion is compensated by three sodium cations which gives a formula $Na_3[Tb(EDTA)(FSA)]$. The second part includes the functionalization of the complex with trimethoxysilane group by mixing with APTMS in methanolic solution. These synthetic procedures were taken from ref 33 without modification except the Tb (III) acetate was changed to Tb (III) nitrate.

Synthesis of $[Fe(Htrz)_2(trz)]BF_4$ – Tb nanocomposite 1

To a suspension of 200 mg of $[Fe(Htrz)_2(trz)]BF_4@SiO_2$ nanoparticles in 40 ml of isopropanol, 0.5 ml of an aqueous solution of 20 mg of Tb complex bearing trimethoxysilane group was added. The mixture was stirred overnight and then refluxed for 3 hours. The composite was separated by centrifugation and washed three times with isopropanol.

Table S1. Elemental analysis of the composite **1**. (The proposed formula was derived from the elemental analysis (C, H, N) and ICP-AES analysis for the Tb and Fe content. Molecular weight was calculated and used to determine molar magnetic susceptibilities)

Compoud		C / %	H / %	N / %	Fe / %	Tb / %	Calculated Formula
Composite 1	calcd	18.83	1.93	22.69	9.6	4.09	$[Fe(Htrz)_2(trz)]BF_4(SiO_2)_{0.9}$ $(TbSiC_{21}H_{22}N_3O_{14}Na_3)_{0.15}$ MW = 583 g·mol^{-1}
	exptl	20.79	2.48	19.76	9.49	4.19	

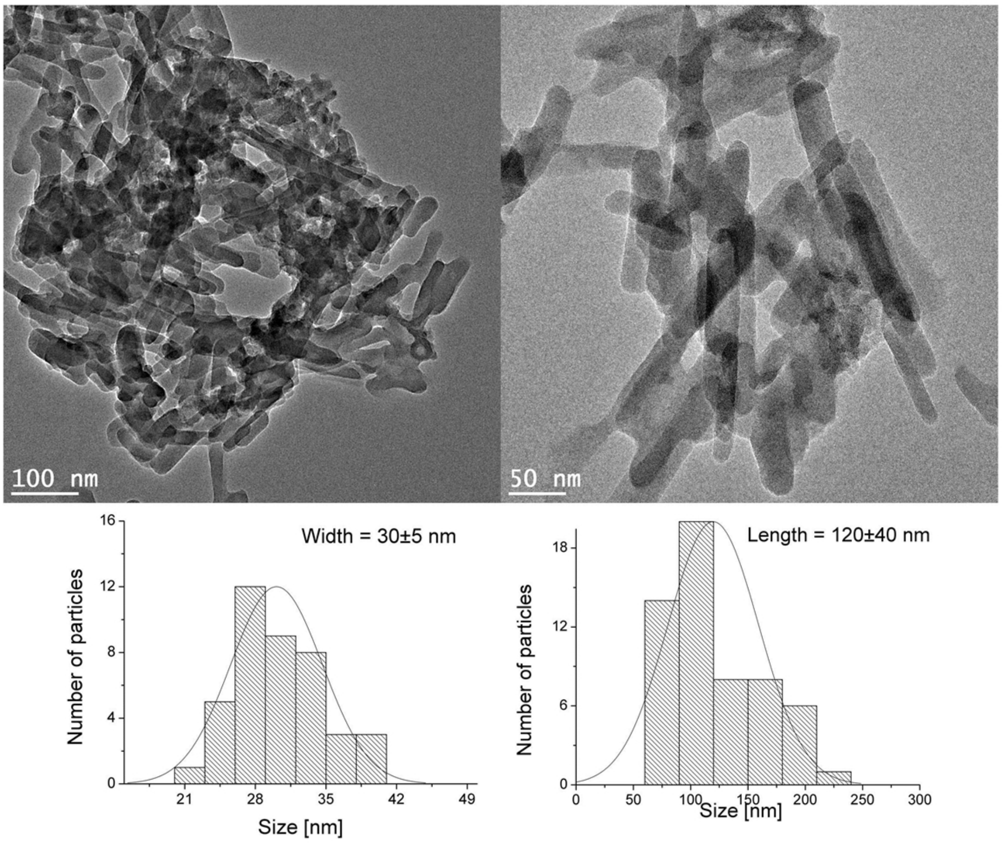
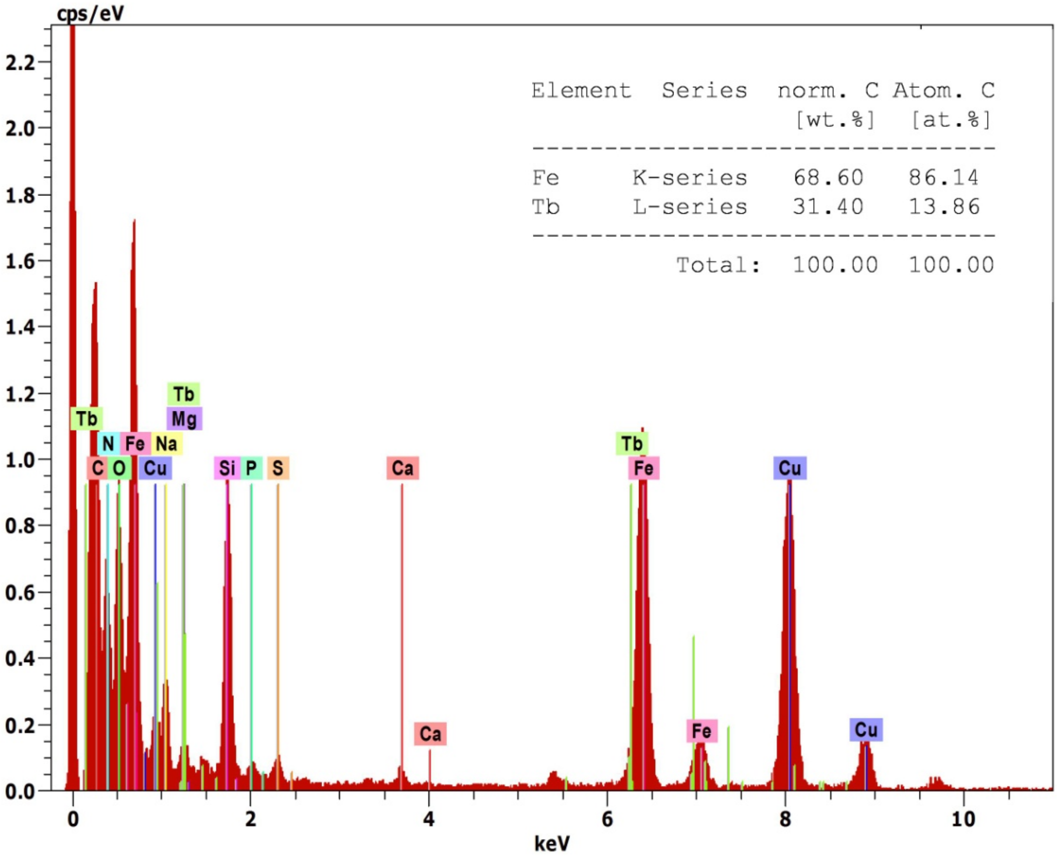


Fig. S1 High resolution TEM images of the composite **1** and its size distribution



Element	Series	norm. C [wt.%]	Atom. C [at.%]
Fe	K-series	68.60	86.14
Tb	L-series	31.40	13.86
	Total:	100.00	100.00

Fig. S2 EDX spectrum of the composite **1** representing Tb and Fe content

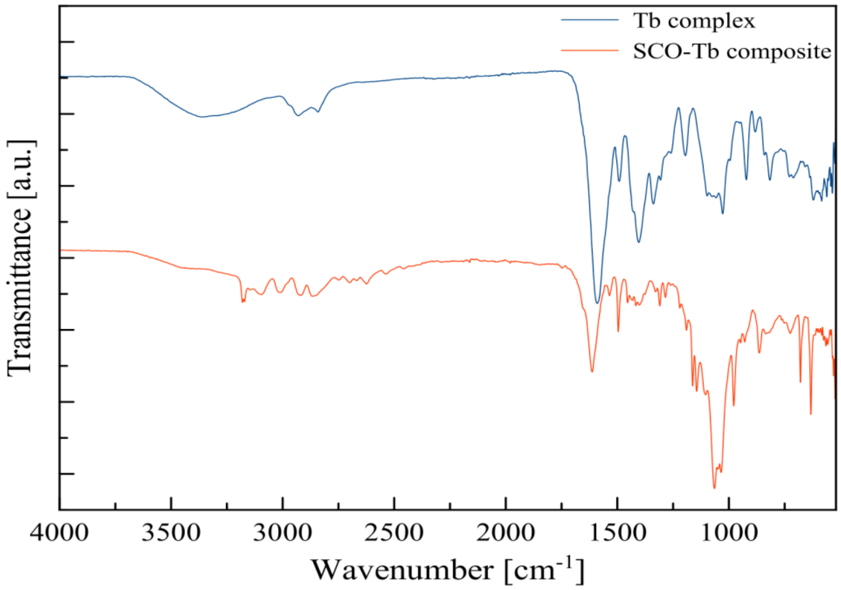


Fig. S3 FTIR spectra of the free Tb complex and composite **1**

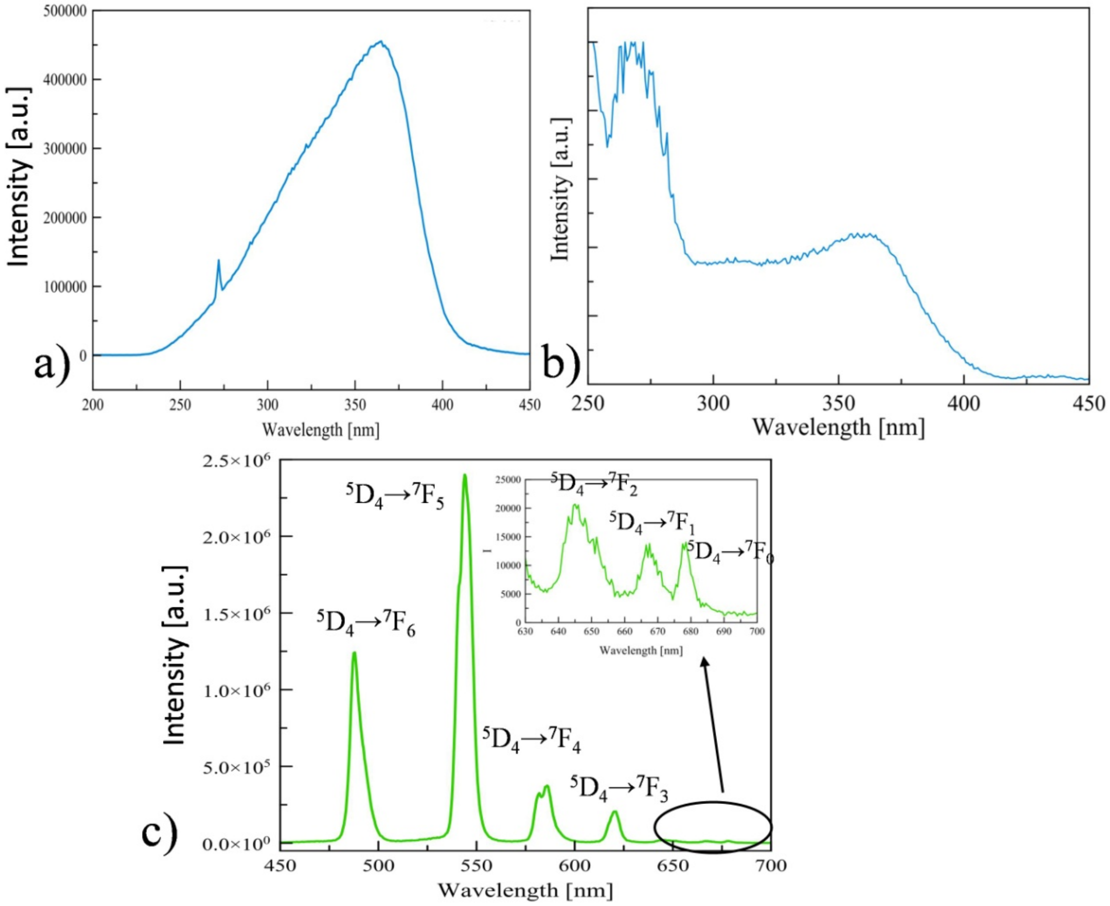


Fig. S4 a) Excitation spectrum of the free Tb complex in the solid state monitored at 545 nm b) Excitation spectrum of the composite **1** in the solid state monitored at 545 nm c) Emission spectrum of the free Tb complex in the solid state at room temperature using a 360 nm excitation wavelength.

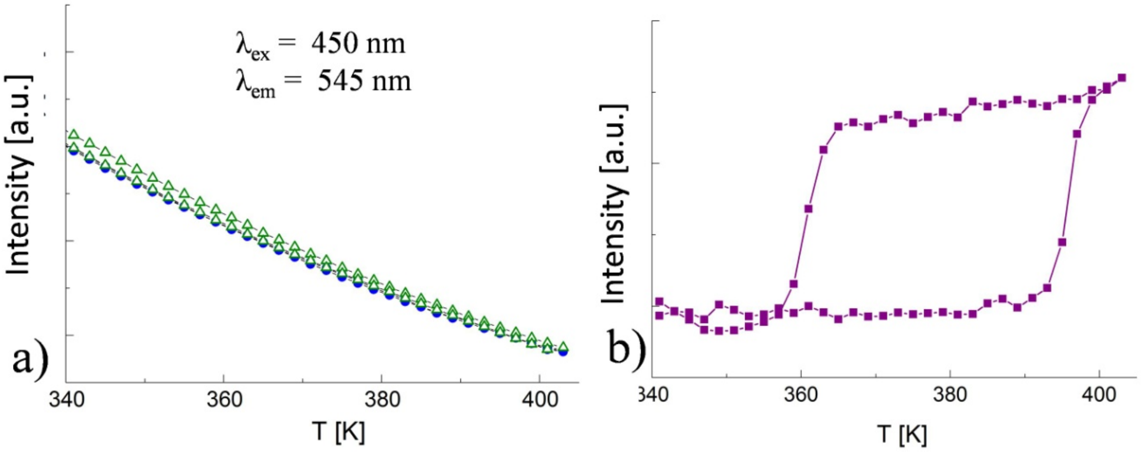


Fig. S5 a) Temperature dependent luminescence intensity variation of the free Tb complex in two consecutive heating-cooling modes b) Luminescence intensity vs temperature of the composite **1** obtained by removing the thermal quenching of the free Tb complex.

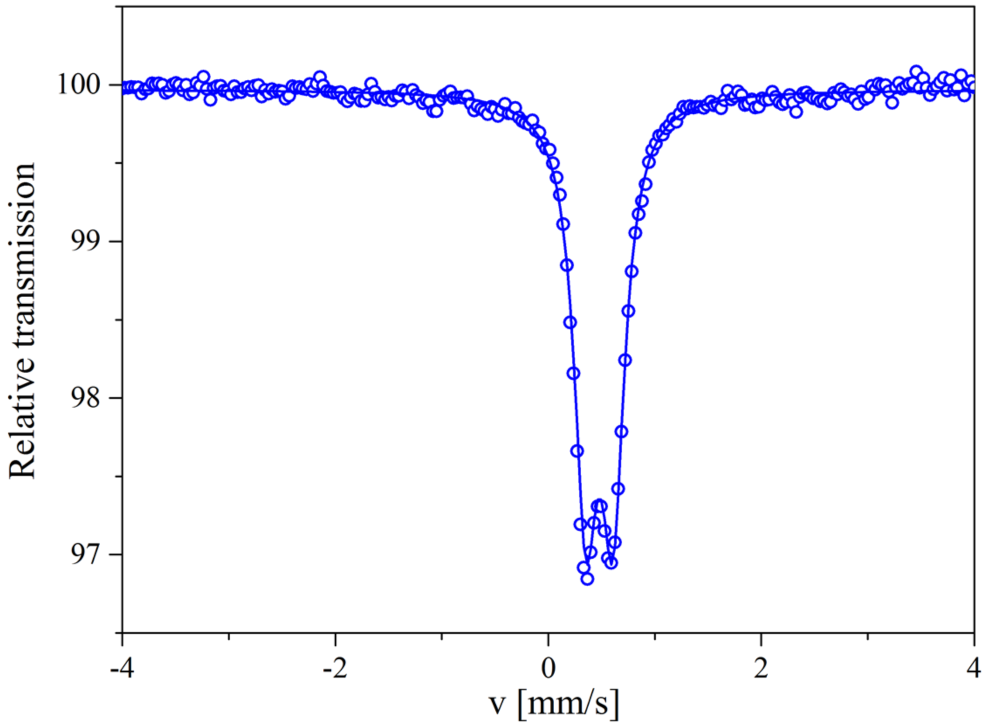


Fig. S6 ^{57}Fe Mössbauer spectrum of the composite **1** at 80K. The spectrum was fitted with a doublet with an isomer shift δ = 0.4798(51) mm/s (relative to α-Fe) and a quadrupole splitting ΔEq = 0.2552(65) mm/s corresponding to an iron(II) LS.

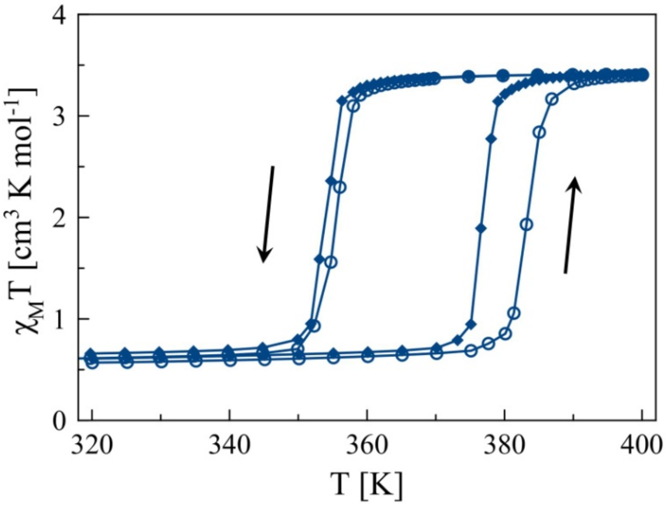


Fig. S7 Magnetic susceptibility measurements of the $[Fe(Htrz)_2(trz)]BF_4@SiO_2$ nanorods in the first (open circles) and second (filled squares) consecutive thermal cycles