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

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**[Fe(Htrz)<sub>2</sub>(trz)]BF<sub>4</sub>@SiO<sub>2</sub> nanorods were synthesized using a reverse emulsion technique and a Tb<sup>3+</sup> complex was chemically bounded to the silica surface. This Tb-spin crossover nanocomposite demonstrates high luminescence stability under continuous thermal cycling. A reabsorption mechanism is determined to be responsible for the luminescence intensity variation during the spin state switching of the iron complex.**

Spin crossover compounds (SCO) are coordination complexes of 3d<sup>4</sup>–3d<sup>7</sup> transition metals in which low spin (LS) and high spin (HS) states exist and a reversible switching between them can be achieved using different external stimuli like temperature change, light irradiation, magnetic field and others<sup>1,2</sup>. SCO compounds attract scientific attention not only from a fundamental point of view, but also as promising materials for sensors, memory and display devices<sup>3</sup>. In terms of practical application, one of the most promising family of Fe(II) coordination polymers is based on the 4R-1,2,4-triazole ligand<sup>4,5</sup>. Several compounds of this family possess wide thermal hysteresis loops around room temperature and show significant color change upon spin state switching. Probably one of the most studied SCO compound from this family is the [Fe(Htrz)<sub>2</sub>(trz)]BF<sub>4</sub> (Htrz = 1,2,4-triazole and trz = 1,2,4-triazolato) 1-D coordination network possessing stable, reproducible and wide thermal hysteresis above room temperature<sup>6–8</sup>.

Nowadays, manipulations with SCO materials are more and more developed at the nanoscale: nanoparticles<sup>9–16</sup> and thin films<sup>17</sup>. Therefore, an efficient and sensitive method for the spin state monitoring becomes crucial<sup>18,19</sup>. This is one of the reasons of particular interest in hybrid luminescent SCO materials<sup>20</sup>. The possibility of the spin state monitoring by luminescence intensity arises from a radiative or non-radiative process involving the overlap of the SCO absorption in only one of the spin states with

the luminophore emission. To date, this effect is known mainly for 1,2,4-triazole based compounds associated only with organic dyes. These later can be introduced whether as a doping agent<sup>21–23</sup> or as a part of a hybrid core-shell structure<sup>24–26</sup>. Despite the successful developing of luminescent SCO materials with organic dyes their drawback is the high photo-bleaching rate leading to signal loss.

This problem can be overcome by using more stable luminescent rare earth compounds. It is known that the rare earth emission signal possesses high photostability under UV/blue irradiation<sup>27</sup>. This is due to the specific nature of the widely used emission signal originating from f-f transitions<sup>28</sup>. Other advantages of the lanthanide luminescence are characteristic line-like emission spectra, large Stokes shifts and long-lived luminescence excited states. Therefore lanthanide complexes are widely used in numerous applications as sensors, components of display devices and others<sup>29,30</sup>. Combination of lanthanides with Fe<sup>II</sup> complex has been achieved in heterodimetallic helicates, in which the iron ion could be stabilized either in the LS or HS state depending on the ligand used<sup>31,32</sup>. Förster energy transfer was evidenced in the Eu(III)-Fe<sub>HS</sub> helicate. Nevertheless, the detection of the SCO by the modulation of lanthanide emission has not yet been reported.

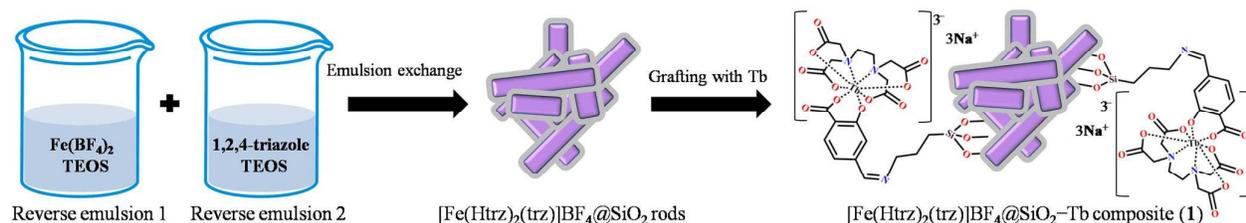
Here we report a new luminescent SCO composite based on the [Fe(Htrz)<sub>2</sub>(trz)]BF<sub>4</sub> complex with a terbium complex grafted on the intermediate silica surface. First, [Fe(Htrz)<sub>2</sub>(trz)]BF<sub>4</sub>@SiO<sub>2</sub> nanoparticles were synthesized using a reverse emulsion technique by mixing two reverse emulsions as shown in fig.1. Triton X-100 was used as a surfactant and 1-hexanol was used as a co-surfactant. Silica shell on the periphery of nanoparticles was obtained by adding triethoxysilane (TEOS) to the reaction mixture. A terbium complex bearing trimethoxysilane moiety was synthesized according to a previously described method<sup>33</sup>. The grafting process was accomplished by refluxing a mixture of silica covered SCO nanorods with the Tb complex in isopropanol. See the Supporting Information (SI) for more details concerning the synthetic procedure.

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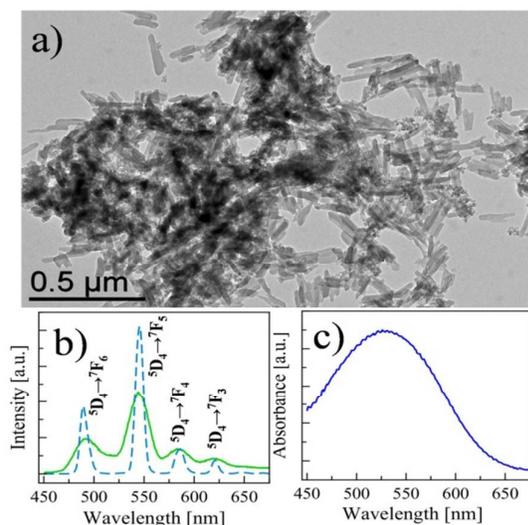
Electronic Supplementary Information (ESI) available: Synthesis and characterization of the composite, experimental details. See DOI: 10.1039/x0xx00000x



**Fig 1.** Synthetic route for the SCO-Tb nanocomposite

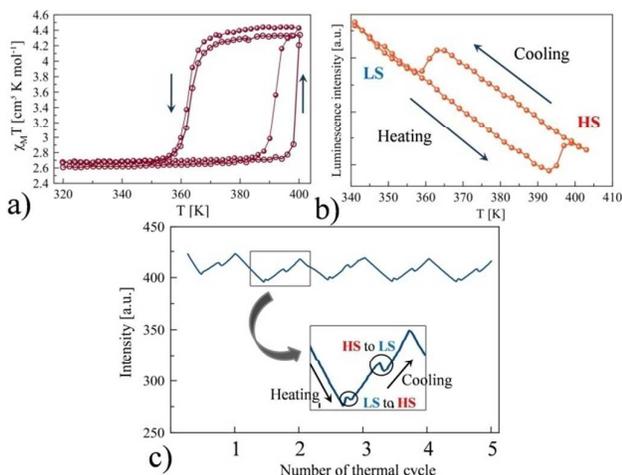
The Tb-SCO nanocomposite (**1**) consists of elongated, aggregated nanoparticles (nanorods) (fig.2a). Their average length and width are 120 and 30 nm, respectively (fig. S1). The energy-dispersive X-ray analysis (EDX) of an ensemble of nanoparticles revealed 14% (atomic) of Tb relative to the iron atomic percentage (fig. S2). The results of the elemental analysis of **1** are listed in Table S1 (SI). Obviously, it is difficult to determine the exact formula of such a complex material, so we have drawn only an approximate composition. The quantities of Tb and Fe found using inductively coupled plasma atomic emission spectroscopy (ICP-AES) of 13.5% and 86.5% (atomic) are in very good agreement with EDX analysis. The SiO<sub>2</sub> content was estimated according to the

TEOS quantity added<sup>34</sup>. However, we could not reach sufficiently good match with the C,H,N analysis. This could be explained by a partial destruction of the Tb complex during the grafting and/or remaining traces of solvents. Infrared spectrum of **1** contains the characteristic stretching mode at 1615 cm<sup>-1</sup> shifted by 24 cm<sup>-1</sup> in comparison with the unattached Tb complex (1591 cm<sup>-1</sup>) belonging to coordinated carboxylic groups (fig. S3). This confirms the presence of the Tb complex on the silica surface. Emission spectra of the SCO-Tb composite and free Tb complex acquired from powder samples at room temperature are shown in fig. 2b. The samples were excited at 360 nm wavelength which corresponds to the maximum of the excitation spectra (fig. S4). Both emission spectra contain four characteristic Tb<sup>3+</sup> <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>J</sub> (J=6-3) transitions at 489, 545, 585 and 620 nm respectively. The other three <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>J</sub> (J=2-0) transitions can be detected only for the free Tb complex at 646, 667 and 678 nm (fig. S2c), while for the SCO-Tb composite these transitions are not visible because of the significant peak broadening and reduced emission intensity. An important point here is an almost complete overlapping of several Tb emission peaks with the [Fe(Htrz)<sub>2</sub>(trz)]BF<sub>4</sub> absorption band in the LS state (fig. 2c) while in the HS state the complex does not absorb in that region. As the most intense <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> transition (545 nm) is situated very close to the absorption maximum (530 nm) of the complex, good pre-conditions for the emission intensity modulation are reached. Indeed, luminescence intensity investigations evidenced its dependence of the sample temperature which is clearly related to the spin state of the complex. As was expected, luminescence intensity rises drastically while switching from the LS to the HS state and reaches its initial value while switching in the opposite direction (fig. 3b). It should be noted that the high rate of thermal quenching for the Tb complex makes the luminescence intensity curve monotonously decrease when the temperature is increasing. This inconvenience can be easily overcome by subtracting the thermal quenching component (see fig.S5). From the resulting curve the spin transition temperatures can be easily determined. Thereby,



**Fig. 2** a) TEM image of **1** b) Luminescence emission spectra of **1** (green solid line) and of the free Tb complex (blue dashed line) at  $\lambda_{\text{ex}}=360$  nm c) Absorbance spectrum of [Fe(Htrz)<sub>2</sub>(trz)]BF<sub>4</sub> in the LS state.

$T_{1/2}\uparrow$  equal to 395 K and  $T_{1/2}\downarrow$  equal to 361 K are in good agreement with SQUID measurements. Magnetic susceptibility measurements confirm also the presence of  $Tb^{3+}$  reflected by the high molar magnetic susceptibility when the SCO complex is in the LS state (fig. 3a). The quantity of Tb should contribute  $1.5\text{ cm}^3\text{Kmol}^{-1}$  to the  $\chi_M T$  value.

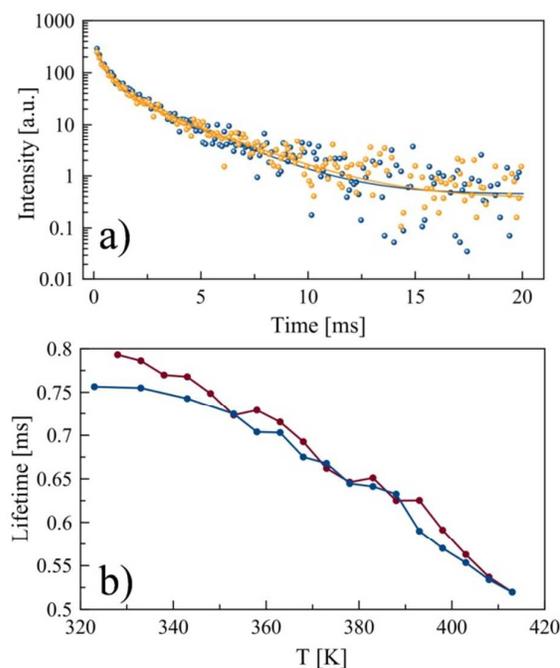


**Fig. 3** a) Magnetic susceptibility vs temperature curves of **1** in the first (open circles) and second (filled circles) consecutive cycles b) Temperature dependent luminescence intensity variation of **1** c) Luminescence intensity changes of **1** during five consecutive heating-cooling cycles.

The difference of  $1.1\text{ cm}^3\text{Kmol}^{-1}$  can be attributed to some traces of Fe (III) HS causing an asymmetric Fe (II) LS doublet in the Mössbauer spectrum (fig.S6). At the same time, the  $\chi_M T$  value at 400 K is  $4.45\text{ cm}^3\text{Kmol}^{-1}$  that is quite close to the calculated  $4.5\text{ cm}^3\text{Kmol}^{-1}$ . The spin transition is slightly shifted towards higher temperatures when compared to the  $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4@SiO_2$  rods (fig. S7). The LS to HS transition in **1** occurs at 392 K (second cycle), whereas for the  $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4@SiO_2$  rods the transition temperature is 377 K (second cycle). The same behavior is observed, but to a lesser extent for the transition in the opposite direction. The SCO-Tb composite exhibits the HS to LS transition at 362 K while non-functionalized  $SCO@SiO_2$  rods return to the LS state at 355 K. Thus, the thermal hysteresis for the SCO-Tb composite is 8 K wider when compared to  $SCO@SiO_2$ . This effect is obviously brought by the grafting of the Tb complex, but its origin, at the moment, is not clear.

As it is widely known the main shortcoming of organic luminophores is the loss of their emission intensity upon continuous photo and thermal excitation. The emission intensity of the rare earth ions is known to be much less affected in comparison with organic dyes. We have tested our SCO-Tb composite to photobleaching resistance in five continuous heating-cooling cycles. The excitation was performed at 450 nm (bandpass filter) using a 100 W halogen lamp and the signal was monitored at 550 nm (bandpass filter). The temperature change rate was 4 K/min between 323K and 403 K where the signal was acquired each 30s. The overall exposition time was 200 minutes. The results are shown in fig3c.

The SCO-Tb composite was found to be highly stable towards photo-bleaching. The intensity diminution after the fifth cycle is only 1.4 % of the starting value. In similar conditions typical photobleaching rate with organic dyes is several tens of percents. It is assumed that two mechanisms responsible for the luminescence intensity change upon SCO are possible. The first one, called Förster resonance energy transfer (FRET), includes non-radiative energy transfer between a donor (Tb complex in our case) and an acceptor (SCO complex). The efficiency of this transfer depends strongly on the donor-acceptor distance, spectral overlap, donor quantum yield and acceptor extinction coefficient<sup>35</sup>. The second one is the reabsorption of the emitted photons by the SCO complex. Taking into account a low extinction coefficient of  $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$  due to the forbidden d-d transition in the LS state, the reabsorption mechanism could be dominating. To clarify this point, a series of temperature dependent luminescence lifetime measurements have been performed. The powdered composite was excited with 360 nm wavelength and its temperature was controlled with a cryostat. All decays were



**Fig. 4** a) Lifetime decays and fits of **1** at 373 K in the LS state (blue) and HS state (yellow) b) Lifetime variation of **1** in one thermal cycle (heating in red and cooling in blue).

fitted with a three-exponential function:

$$F(t) = A + B_1 \exp\left(-\frac{t}{T_1}\right) + B_2 \exp\left(-\frac{t}{T_2}\right) + B_3 \exp\left(-\frac{t}{T_3}\right)$$

and then the average lifetime was calculated according to the formula:

$$\tau_{\text{ave}} = B_1^* T_1 + B_2^* T_2 + B_3^* T_3$$

Multieponential decays, probably, signify the presence of several Tb centers with different environment. These centers could be formed during the grafting process. Lifetime decays and their fits at 373 K for the LS and HS states are shown in fig

4a. Lifetime values equal to 0.662 ms and 0.668 ms were found for the LS and HS states respectively. These values are smaller when compared to the free Tb complex lifetime which was found to be 1.285 ms. The lifetime variation for a heating-cooling cycle is presented in fig 4b. As can be seen, there is only ordinary temperature dependence for the lifetime curve and no correlation with the spin state. This result suggests that no non-radiative energy transfer processes occur between the SCO compound and the Tb complex since if it was the case the excited state lifetime should be different in the two spin states. As was expected due to the low extinction coefficient of the  $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$  complex and probably high distances between the SCO and Tb complexes only photon reabsorption is possible.

In summary, we have presented the synthesis of a Tb-spin crossover composite. The SCO and photo-physical properties of this bistable luminescent composite have been fully characterized. For the first time, a successful use of the rare earth luminescence to follow the SCO process is demonstrated here. This nanocomposite shows a reversible increase of the luminescence intensity upon switching from the low spin state to the high spin state. This nanocomposite presents a high resistance to photobleaching and remains stable upon several consecutive thermal cycles. The terbium luminescence lifetime investigations at various temperatures have revealed no lifetime dependence on the spin state of the complex in agreement with the luminescence reabsorption energy transfer.

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