

# A Flexible Polymer-Nanoparticle Hybrid Material Containing Triazole-Based Fe(II) with Spin Crossover Properties for Magneto-Optical Applications

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## Supplementary Information

### 1. Experimentals

#### Step 1. Synthesis of the Si-SCO composite

##### **Silica nanoparticles functionalized by sulfonate groups.**

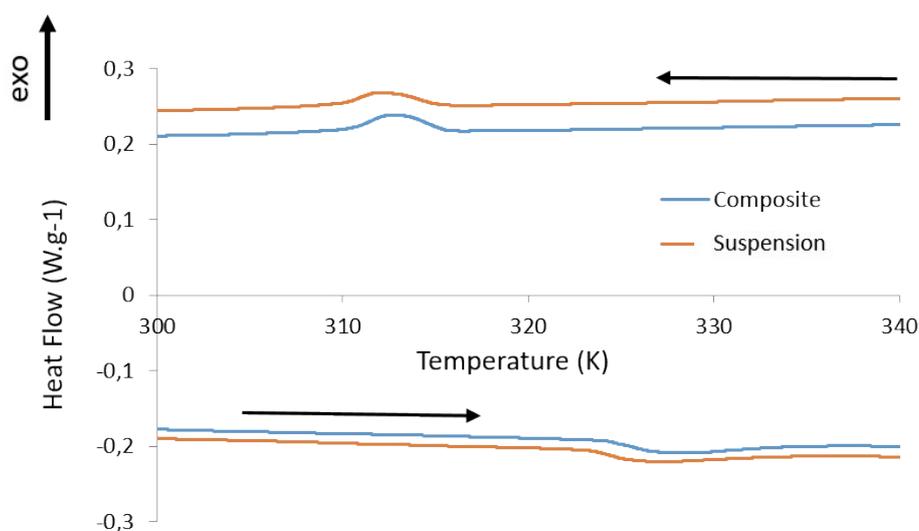
Silica NPs were synthesized following the Stöber process. Sulfonate functionalization of the surface proceeded through a two-steps procedure. Stöber particles were first functionalized with thiol groups by silylation with 3-mercaptopropyltrimethoxysilane (MPTMOS 95%, Aldrich). Typically, 4.12 g of silica NPs were redispersed in a mixture of 410 ml ethanol and 9 ml ammonium hydroxide solution before addition of 4 ml MPTMOS (5 mmol.g<sup>-1</sup> silica). The mixture was stirred for 40 min at room temperature (RT). Subsequently, the reaction mixture was heated to 80°C and the total volume was reduced to approximately two-thirds by distillation of ethanol and ammonia at ambient pressure. The mixture was left to cool down to RT and was subsequently washed three times with ethanol (by centrifugation at 12,000 rpm for 15 min). Finally, oxidation of thiol groups leads to sulfonic acid functionalized particles. In a typical reaction, 3.6 g of thiol-modified particles were suspended in 150 ml sulfuric acid (H<sub>2</sub>SO<sub>4</sub> 30 % (w/w) in H<sub>2</sub>O, Sigma Aldrich) and stirred for 2 hours at RT. Washing with ethanol and water by centrifugation was used to recover SO<sub>3</sub><sup>-</sup> modified particles before drying under vacuum. Zeta potential and size distribution measurements were carried out using a Malvern Zetasizer Nano ZS90 instrument giving a strongly negative zeta potential of *ca.* -53 mV in acetic acid 0.5 M (pH 2.5) and a hydrodynamic diameter of *ca.* 200 nm. The evaluation of the sulfonate density available at the surface of each particle was performed by the titration of thiol grafted prior to

their oxidization through Ellman reaction, taking into account a silica density of  $2 \text{ g/cm}^3$ . The sulfonate density could be evaluated as  $3.5 \text{ mol.mg}^{-1}$ , *i.e.* about 105 groups per particle.

### **Preparation of the Si-SCO composite**

140 mg of silica NPs were suspended in 0.75 mL of ethylene glycol: water mixture (v/v 9 : 1) under sonication for 45 minutes. 27.8 mg of iron sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.1 mmol) (Sigma-Aldrich, 99%) were added to the suspension heated at  $50^\circ\text{C}$  for 30 minutes with 20 mg of ascorbic acid. In parallel, 50.4 mg (0.6 mmol) of 4-amino-1,2,4 triazole (ATrz,  $\text{C}_2\text{H}_4\text{N}_4$ , Alfa-Aesar, 99%) was separately dissolved in 0.25 mL of the same ethylene glycol:water mixture at room temperature. After completion of the dissolution of the iron salt, the ATrz solution was placed in an ice bath and the NPs- $\text{FeSO}_4$  solution was added dropwise under stirring

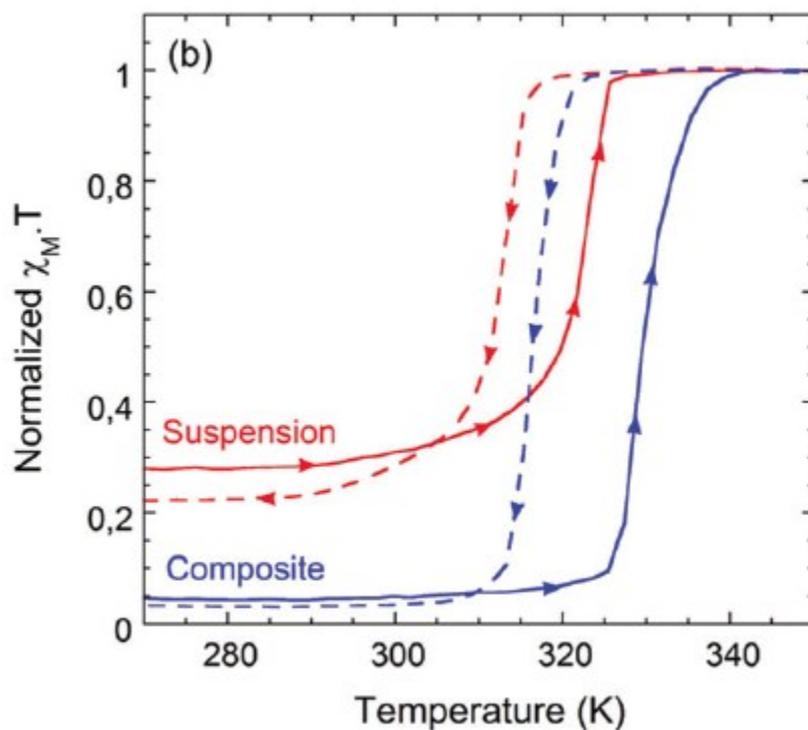
## 2. DSC of Si-SCO composite SCO system



**Figure S1.** DSC profiles for Si-SCO composite (in blue) and SCO suspension without silica NP (in red) aged for 9 days in a mixture of water/glycerol at scan rate of 5 K.min<sup>-1</sup> upon a second thermal cycle.

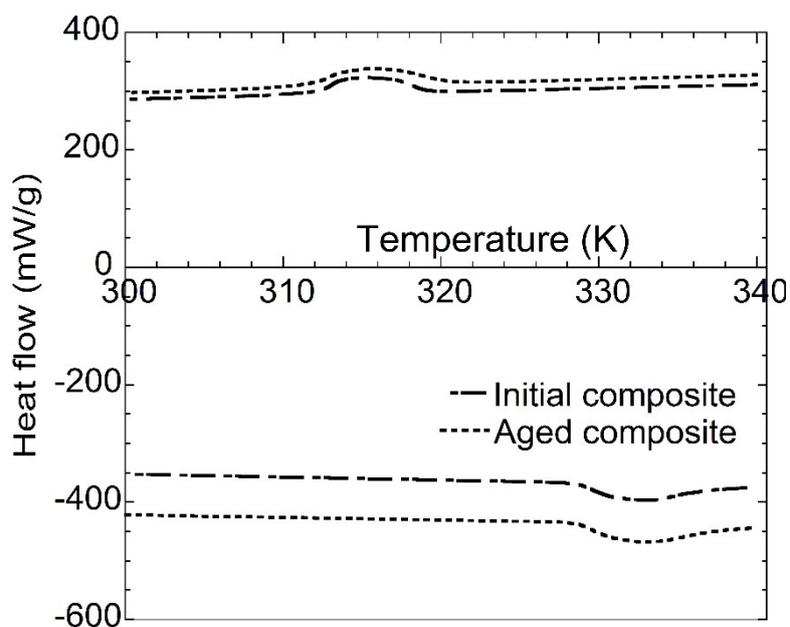
## 3. Magnetic behaviors of Si-SCO composite SCO system

The suspension (SCO system) sample presents a non-overlapping region below 310 K, in contrary to the composite system (Si-SCO), which is thermo-reversible, as detailed in our previous paper [36]. This should result from changes in the interactions between the crystals due to some modifications in their environments. In particular, depending on the rigidity of the host, long-range elastic interactions can be mediated or dampened, leading to a stabilization of the low spin species. Other parameters, such as distance between objects or the strength of their interactions with the matrix also play a role in the modification of their behavior. **In the composite system, the percolation of the amorphous phase due to the presence of nanoparticles increases the stabilization of the low spin species, leading to a better reversibility.**



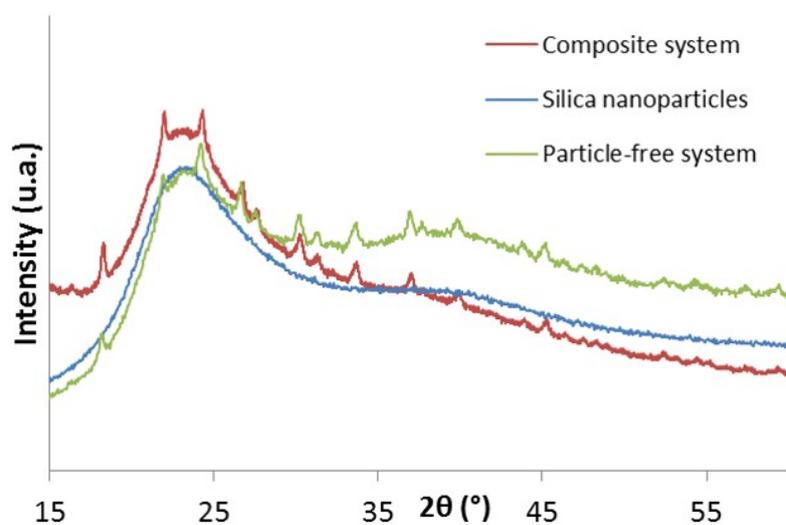
**Figure S2.** Thermal dependence of normalized  $\chi_M T$  product of Si-SCO composite (in blue) and SCO suspension without silica NP (in red) aged for 9 days in a mixture of water/glycerol at scan rate of  $5 \text{ K}\cdot\text{min}^{-1}$  cycle.

#### 4. DSC characterization of Si@Si-SCO aged for 28 days.



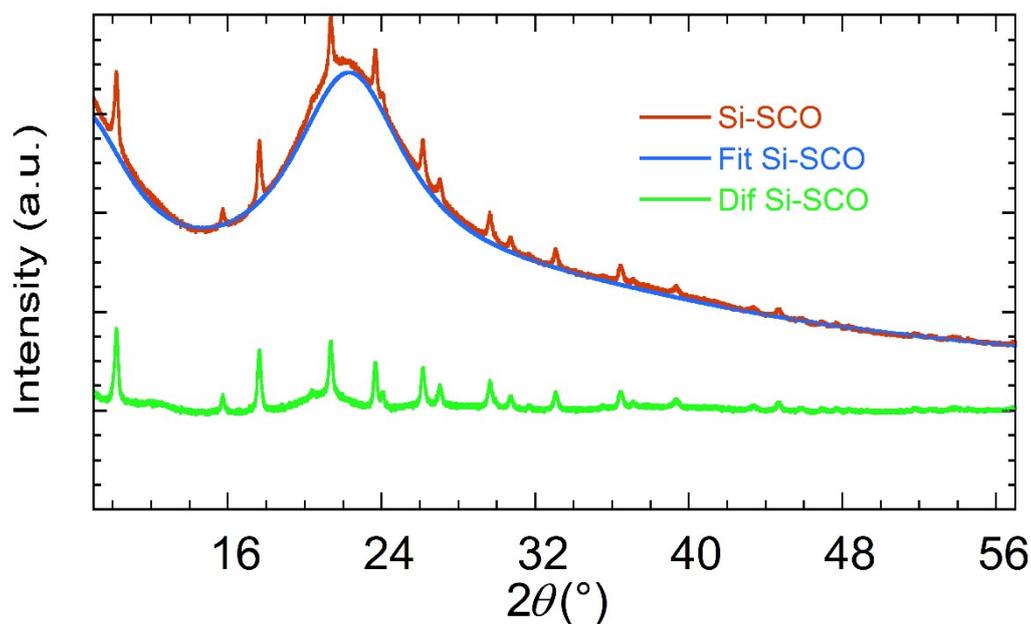
**Figure S3.** DSC characterization at  $5 \text{ K}\cdot\text{min}^{-1}$  of Si@Si-SCO aged for 28 days compared to the freshly prepared. DSC thermographs plotted as “exo up”.

## 5. XRPD of the composite system Si-SCO and of its components



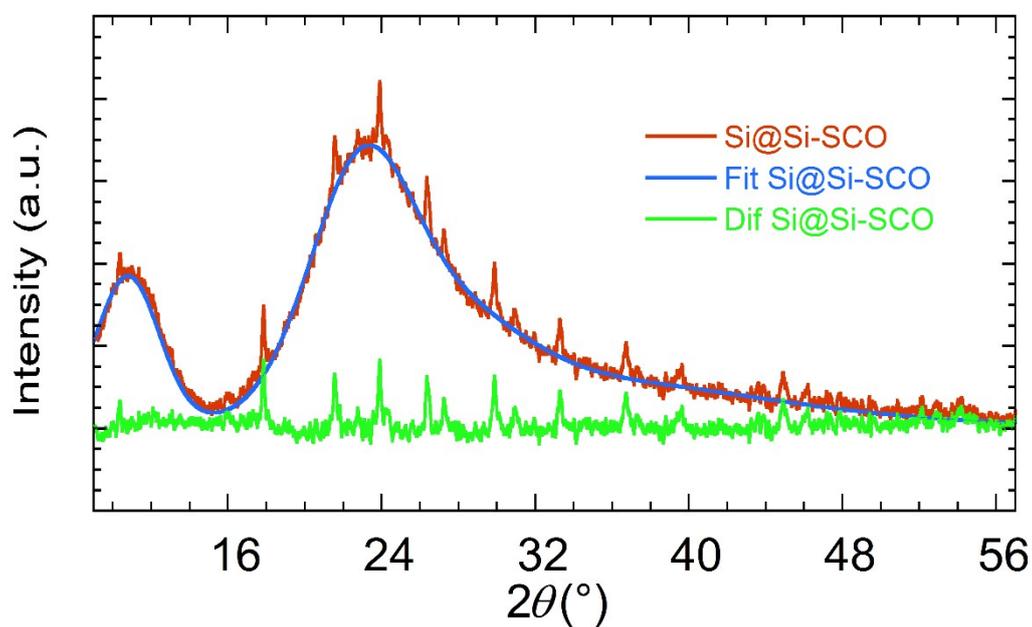
**Figure S4.** XRPD diffractograms of the 9 days-old Si-SCO composite (red), of the NP-SiSO<sub>3</sub> nanoparticles alone (blue) and of the 9 days-old SCO system in absence of silica NP (green)

## 6. XRPD of the Si-SCO composite and subtraction of the amorphous background



**Figure S5.** XRPD Diffractograms of Si-SCO aged for 14 days (raw data in red; amorphous contribution in blue; subtraction in green).

## 7. XRPD of the Si@Si-SCO composite and subtraction of the amorphous background



**Figure S6.** XRPD Diffractograms of Si@Si-SCO aged for 14 days (raw data in red; amorphous contribution in blue; subtraction in green).