

*Supporting Information for*

**Iron(II)-triazole core-shell nanocomposites: toward multistep spin  
crossover materials**

*Yu-Xia Wang<sup>a</sup>, Dan Qiu<sup>a</sup>, Sai-Fei Xi<sup>a</sup>, Zheng-Dong Ding<sup>a</sup>, Zaijun Li<sup>a</sup>,  
Yunxing Li<sup>a</sup>, Xuehong Ren<sup>b</sup> and Zhi-Guo Gu<sup>\*a</sup>*

<sup>a</sup> *The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education,  
School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122,  
P.R. China*

<sup>b</sup> *The Key Laboratory of Eco-textiles of Ministry of Education, College of Textiles and  
Clothing, Jiangnan University, Wuxi 214122, P.R. China*

E-mail: [zhiguogu@jiangnan.edu.cn](mailto:zhiguogu@jiangnan.edu.cn)

## **1. Experimental Section**

### **1.1 Materials and physical measurements**

Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Htrz, NH<sub>2</sub>-trz, Triton X-100, n-pentanol, hexamethylene, acetone and ethanol were all reagent grade and purchased from Sigma-Aldrich and used without further purification. Ultrapure milli-Q water (18.2 MΩ·cm) was used in all experiments.

The Fourier transform infrared (FT-IR) spectra were recorded by FALA2000 FT-IR spectrometer (ABB Bomen Canada) (KBr disk). Powder X-ray diffraction (PXRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker AXS Germany) with Cu Kα radiation in a 2θ range from 5° to 60° at the speed of 2°·min<sup>-1</sup> at room temperature. SEM images were operated by S4800 scanning electron microscope (SEM) (Rili Japan) at an operating voltage of 2 kV. TEM images were obtained by JEM-2100 (HR) transmission electron microscopy (TEM) (JEOL Japan) at 200 kV. The three kinds of nanocomposites were dispersed in alcohol by sonication, then dropped onto carbon reinforced copper grids (200 mesh) and dried in air for at least 12 h to make sure that the nanoparticles (NPs) were monodisperse homogeneous and well defined. The Differential scanning calorimeters (DSC) curves were operated on

(PE) DSC-8000 (PE US) at the temperature range of 220 K-300 K for SCO1 NPs, 300 K-400 K for SCO2 NPs and 200 K-400 K for SCO@SCO NPs. Magnetic measurements were carried out using a MPMS-XL-7 super strong quantum interference magnetometer (Quantum Design US). The samples were testing at two temperature stages with a heating and cooling sweep rate of 3 K·min<sup>-1</sup>. The SCO phenomenon of each samples were clearly displayed by HS fraction vs T curves, in which HS fraction refers to the ratio of iron(II) at high spin state. The scanning temperature of SCO1, SCO2 and SCO@SCO NPs ranged from 220 K to 300 K, 300 K to 400 K and 200 K to 400 K respectively. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

### **1.2 Synthesis of SCO1 and SCO2 nanoparticles**

0.9 mL of Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution (405.1 mg, 1.2 mmol) was added into the microemulsion of TX-100 (12 mL), n-pentanol (12 mL) and cyclohexane (24 mL). Then 0.9 mL of NH<sub>2</sub>-trz aqueous solution (302.7 mg, 3.6 mmol) was added dropwise to the microemulsion under stirring. The water-in-oil microemulsion was stirred under the nitrogen atmosphere in dark at room temperature. 8 mL of the reaction microemulsion with the reaction time of 15 min, 30 min, 1 h, 3 h, 5 h and 8 h respectively were prepared and break the microemulsion with 5 mL acetone, then centrifuged and washed third times with 8 mL ethanol. The SCO1 NPs were obtained by centrifuged under 7000 rpm for 2 min and dried at 60 °C in vacuum for 12 h.

The SCO2 NPs were synthesized by a similar method to that of SCO1 NPs except substituting 0.36 mmol Htrz for 0.36 mmol NH<sub>2</sub>-trz.

### **1.3 Synthesis of SCO@SCO core-shell nanoparticles**

0.9 mL Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (405.1 mg, 1.2 mmol) aqueous solution was added to the mixture of TX-100 (12 mL), n-pentanol (12 mL) and cyclohexane (24 mL) under stirring. Then 0.9 mL of NH<sub>2</sub>-trz aqueous solution (302.7 mg, 3.6 mmol) was injected into the microemulsion and kept stirring for 30 min. 0.9 mL Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (405.1 mg, 1.2 mmol) aqueous solution and 0.9 mL of Htrz aqueous solution (248.7 mg, 3.6 mmol) were added to the resulting microemulsion respectively. The SCO@SCO core-

shell nanoparticles with reaction time of 15 min, 30 min, 1 h, 3 h, 5 h and 8 h were obtained by demulsification (acetone, 5 mL), centrifugation and washed three times with ethanol (8 mL), then dried at 60 °C for 12 h.

## 2. AAS Analysis

Atom absorption spectroscopy (AAS) was conducted with a TAS-990NFG atom absorption spectroscopy instrument (flame AAS, acetylene/air as firing gas) The concentrations of standard solutions were 0  $\mu\text{g}\cdot\text{mL}^{-1}$ , 1  $\mu\text{g}\cdot\text{mL}^{-1}$ , 2  $\mu\text{g}\cdot\text{mL}^{-1}$ , 3  $\mu\text{g}\cdot\text{mL}^{-1}$ , 4  $\mu\text{g}\cdot\text{mL}^{-1}$ , 5  $\mu\text{g}\cdot\text{mL}^{-1}$  respectively.

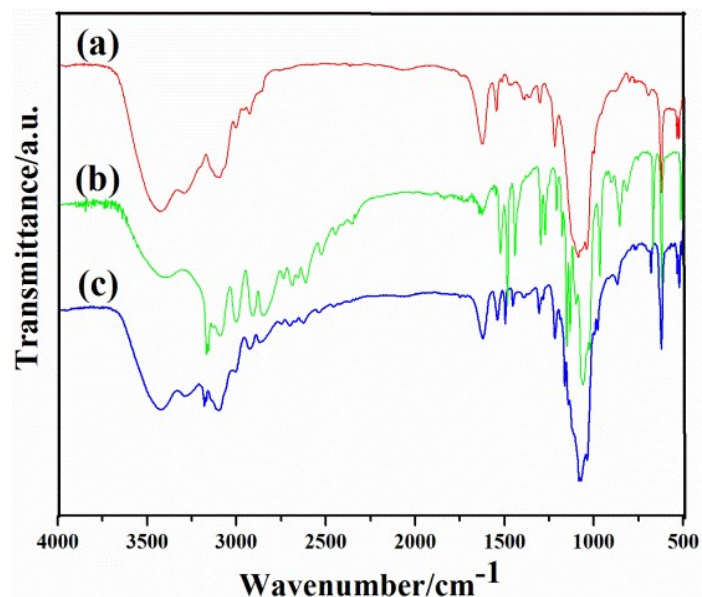
About 5 mg SCO1, SCO2 and SCO@SCO were weighted carefully, following the addition of 3 mL 65% HNO<sub>3</sub> and 2 mL 13% HCl successively. These solutions were diluted to 200 mL ready for AAS analysis. Weight details and direct data are listed in in Table S1. The data obtained by AAS analysis is given in Table S2.

**Table S1** Weight of the samples and AAS analysis results (Fe)

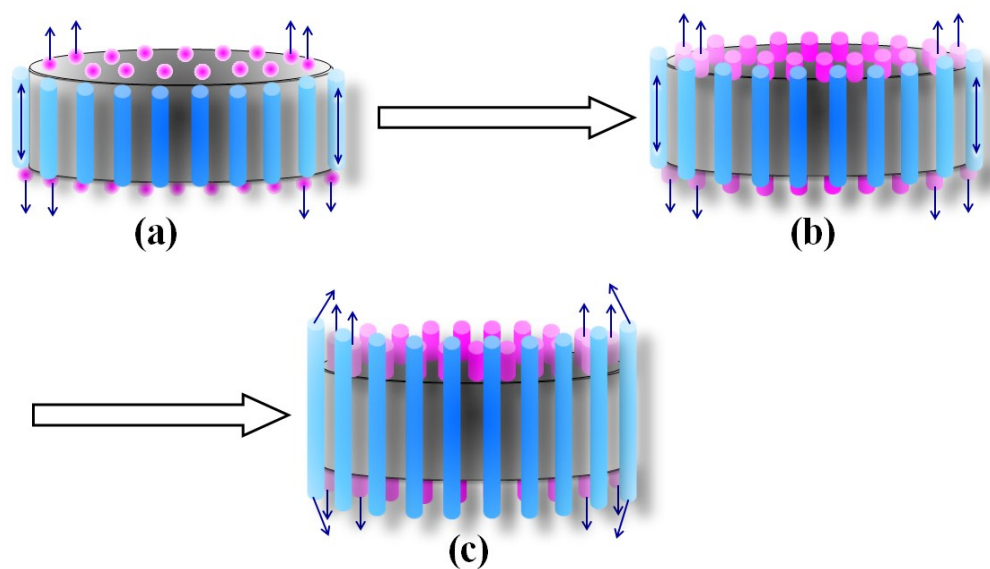
sample	weight (mg)	c(Fe), $\mu\text{g}/\text{ml}$	c(Fe)-c(HNO <sub>3</sub> /HCl), $\mu\text{g}/\text{ml}$
Control group	0.0	-0.113	0.000
SCO1	5.2	2.817	2.930
SCO2	5.4	4.093	4.206
SCO@SCO	5.2	3.131	3.244

**Table S2** Fe-content and molecular weight based on the AAS analysis

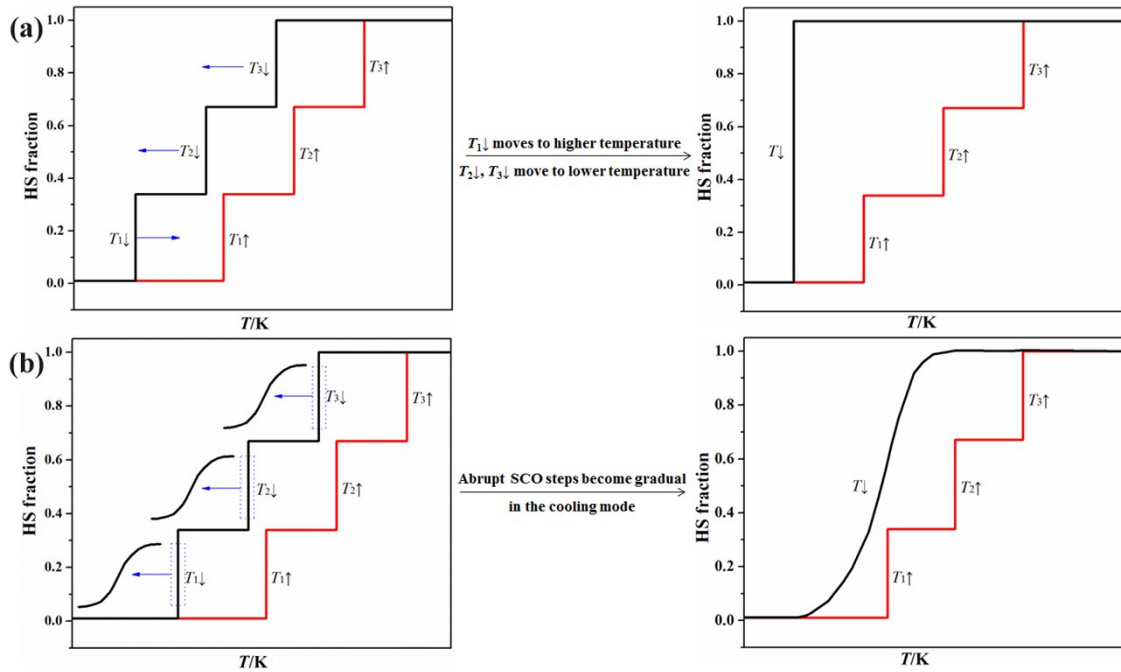
sample	SCO1	SCO2	SCO@SCO
Fe content (wt %)	11.270	15.577	12.477
molecular weight	495.519	358.509	447.584



**Fig. S1** FT-IR spectra of SCO1 (a), SCO2 (b), SCO@SCO (c).



**Fig. S2** The growing mechanism of SCO@SCO NPs: (a) small particles on the top/bottom surface of SCO1 NP and rod arrays on the side surface of the core, (b) rod arrays both on the top/bottom surface and side surface of the core, (c) SCO shell on the side surface of SCO1 growing to the central axis of the cylindrical SCO1 NP.



**Fig. S3** The schematic for unique SCO property of three-step in the warming mode and one step in the cooling mode: (a) the influence of transition temperatures moving; (b) The impact of change in shapes of SCO behavior.