

Communication



The Nano-Confinement Effect on the SCO Behavior of [Fe(NH₂trz)₃](NO₃)₂ 1D Chains in MCM-41

Tian Zhao *^(D), Hexin Zhu and Ming Dong

Key Laboratory of Advanced Packaging Materials and Technology of Hunan Province, School of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou 412007, China; culaisett@126.com (H.Z.); dongming666@126.com (M.D.)

* Correspondence: Correspondence: tian_zhao@hut.edu.cn

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Abstract: A polymeric chain spin-crossover (SCO) compound $[Fe(NH_2trz)_3](NO_3)_2$ was embedded in the pores of mesoporous silica MCM-41, which yielded an M@S composite. The obtained material was characterized by infrared spectrometry, powder X-ray diffractometry, gas sorption studies, electron microscopy, and atomic absorption. The temperature-induced SCO behavior of the composite was monitored by temperature-variable magnetic measurement. The results indicate that the spin transition curve of the composite was evidently shifted to a higher temperature in comparison to bulk $[Fe(NH_2trz)_3](NO_3)_2$. The shift in the transition temperature for M@S [versus bulk $[Fe(NH_2trz)_3](NO_3)_2$] amounted to $T_c^{\uparrow} = 362$ K [347 K] and $T_c^{\downarrow} = 327$ K [314 K] (magnetic data). The significant difference in the SCO behavior of $[Fe(NH_2trz)_3](NO_3)_2$ when embedded in the MCM-41 matrix may be attributed to the strengthened cooperativity of compound **S** and the nano-confinement pressure of SiO₂ walls.

Keywords: spin-crossover; MCM-41; [Fe(NH₂trz)₃](NO₃)₂; matrix effect

1. Introduction

The magnetic properties of spin-crossover (SCO) compounds [1–3] are affected by physical and chemical conditions, such as light, heat, pressure, magnetic field, or solvent (guest) molecules [4–6]. Under the perturbation of a persistent external field, a substance with this property can change from one stable state to another, thus achieving the function of information storage [7–9] and switching [10,11].

The Fe(II) spin-crossover complexes, with the transition temperature near room temperature and the obvious color change, are more suitable for applications in information storage and sensors [12–15]. One interesting direction in this area focuses on the composites that involve a given SCO complex and a given regular matrix [16,17]. Several Fe(II) SCO compounds were synthesized or embedded in matrices, such as MOFs [18], SiO₂ [19], and Ni [20]. These investigations indicated that the spin transition behavior of an SCO compound is not only dependent on its own natural character, but is also influenced by the matrix surrounding the particles. For instance, Mallah and coworkers reported that embedding Fe(pyrazine)Pt(CN)₄ in different matrices would cause a significant effect on the spin transition behavior, achieving a hysteresis of 15 K [21]. Some SCO compounds can be induced from LS to HS by encapsulation of the suitable matrix, including Fe(II) [22], Ni(II), and Co(II) SCO compounds [23]. Recently, it was shown that the spin transition behavior of SCO complexes shifted to a lower temperature through the encapsulation of MIL-101 [18] or C₇₀ [24].

In the previous work, two 1D Fe(II) SCO compounds, $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ and $[Fe(Htrz)_2trz]BF_4$ (Htrz = 4*H*-1,2,4-triazole and trz = 1,2,4-triazolato), were confined in the pores of mesoporous silica MCM-41 [19]. Both of the spin transition temperatures shifted to a higher value. Furthermore, the presence of crystal H₂O strongly influenced the confinement effect of MCM-41, and the dehydration of trapped $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ in the MCM-41 pores would largely raise the spin transition temperature. However, whether this matrix effect is applicable to other SCO compounds still need more investigations.

In the work, another 1D Fe(II) SCO complex, $[Fe(NH_2trz)_3](NO_3)_2$ (Scheme 1), was encapsulated in the pores of mesostructured silica MCM-41. The chosen material has been known to display a reversible hysteresis loop of ~35 K and has attracted keen interest [25–28]. Herein, the "matrix effect" on the SCO behavior of $[Fe(NH_2trz)_3](NO_3)_2$ was investigated by temperature flexible magnetic measurements.



Scheme 1. Schematic drawings of 1D [Fe(NH₂trz)₃](NO₃)₂ (S).

2. Results and Discussion

The [Fe(NH₂trz)₃](NO₃)₂ (**S**) chains were embedded in the cylindrical pores of MCM-41 and formed a hybrid material M@S (for the synthesis procedure, please see Experimental Section). The obtained M@S material showed a reversible strong color change, which represented its spin transition from LS (pink) to HS (white). The infrared (IR) spectra of **S** and M@S were highly consistent, C-H and N-H stretching vibrations were clearly observed in the range of 3000~3500 cm⁻¹, the peak at 1650 cm⁻¹ indicated the bending modes of -NH₂, and all modes of the triazole ring including coupled C-C and N-N stretching were shown between 600 and 1500 cm⁻¹ (Figure 1a). Comparing powder X-ray diffractograms (PXRD) of M@S and **S** confirmed that the compound **S** formed the same crystalline phase in MCM-41 (Figure 1b). However, several small new peaks arose in the region of 18° ~22° 2 θ compared with pure **S** (Figure 1b). In fact, those new peaks were attributed to the highly loaded [Fe(NH₂trz)₃](NO₃)₂ molecules in the pores of MCM-41. Furthermore, the much wider "full width at half maximum" (FWHM) of M@S implied that the much smaller compound **S** particles exist in composite M@S. Thus, both IR spectra and PXRD characterization confirmed the presence of compound **S** in the composite (Figure 1).



Figure 1. (a) IR spectra and (b) powder X-ray diffractograms (PXRD) patterns of compound **S**, hybrid material M@S, and MCM-41.

The amount of SCO compound **S** was determined from the Fe analysis by atomic absorption spectroscopy (AAS) to 54.95%. The formula of compound **S** is $C_6H_{12}N_{14}O_6Fe$ (432.09 g/mol), Fe: 12.92%.

At present, Fe analysis, IR, and PXRD characterization only confirmed the presence of compound **S** in material M@S, but not inside the pores of MCM-41. Nevertheless, the case of compound **S** occupied the pores of MCM-41, and the porosity of MCM-41 was largely decreased, especially with such a high loading (54.95%). The porosity of M@S and MCM-41 was measured by N₂ physic-sorption studies at 77 K (Figure 2). The blank host MCM-41 possessed Brunauer–Emmett–Teller (BET) and Langmuir surface areas of 860 and 1240 m²/g, respectively, while the M@S material only yielded BET and Langmuir surface areas of 220 and 330 m²/g, respectively. Thus, compared to pure MCM-41, the porosity of M@S material was decreased significantly to less than 30% of MCM-41. The N₂ physic-sorption isotherms of M@S belonged to type-IV(a), with a Type *H2(b)* hysteresis loop, which may be attributed to the pore blocking [29]. Obviously, such a pore structure must be caused by the formation of compound **S** inside the pores of MCM-41. The S-shaped N₂ physic-sorption isotherms of MCM-41 highly agreed with the literature reports [30,31]. All in all, the decrease in porosity of M@S was good evidence that the pores of MCM-41 were filled with compound **S** as expected.



Figure 2. N₂ physic-sorption isotherms of M@S and MCM-41.

The morphologies of MCM-41, compound **S**, and M@S were detected by scanning electron microscopy (SEM) (Figure 3). The pure compound **S** consisted of rod-like crystals, which can be easily distinguished from amorphous MCM-41. Sample M@S showed similar morphology to native MCM-41, and no characteristic compound **S** crystals could be found in M@S. This result also supports the idea that the compound **S** was inside the mesopores of MCM-41, and the residual material outside the pores was removed by washing treatment.



Figure 3. SEM images of MCM-41, compound S, and M@S. The scale bar is 500 nm in all images.

Transmission electron microscopy (TEM) images more intuitively revealed the formation of nanocrystals of compound **S** inside the mesopores of MCM-41 (Figure 4). The black dots in the images represent the compound **S** nanocrystals, which had a diameter of ~2 nm, and this result coincides with mesopores sizes of MCM-41 ($2.1 \sim 2.7$ nm). Under higher resolution (the right image of Figure 4), it can be clearly found that the black dots were composed of lattices planes, which were indicative of crystalline material.



Figure 4. TEM images of M@S with different magnifications.

In this work, the spin-transition (ST) behavior of M@S material and compound S were investigated by DC magnetic measurements. The analysis results are shown in Figure 5. The spin-crossover behavior of compound S was well investigated in the literature [26,27]. It was known for having abrupt spin transitions and a large hysteresis loop of ~35 K, with T_c^{\uparrow} = 348 K and T_{cl} = 313 K [26,27]. However, in our measurement, the spin-transition curves of compound S had slight discrepancies with T_c^{T} = 347 K and $T_{c\downarrow}$ = 314 K, which were within the error range (Figure 5). M@S presented a reversible hysteresis loop of ~35 K, with T_c^{\uparrow} = 362 K and $T_{c\downarrow}$ = 327 K (Figure 5). Compared to pure S, the spin-transition curves of M@S clearly shifted to a higher temperature. As temperature increased, χ^{*T} steadily increased, reaching about 1.08 emuK/molOe, around 356 K, after which χ^{*T} increased sharply at 365 K. Beyond this temperature, χ^*T increased very slightly and showed a plateau of 3.70 emuK/molOe at 380 K, which represented HS Fe(II) ions. In the cooling procedure, as temperature decreased, χ^{*T} followed the same pathway as that detected when heating, except in the range of 333~360 K, which displayed a hysteresis loop of ~35 K, wide centered at ~345 K. Compared to pure S, the whole spin transition hysteresis loop shifted ~15 K at a higher temperature (Figure 5). The hysteresis loop was retained over successive cooling and heating thermal cycles, which confirmed the SCO reversibility of M@S and S.



Figure 5. The thermal-variable magnetic curves for compound **S** and M@S (two cycles), the solid dots represent heating progress, and the blank dots stand for cooling procedure.

the SCO compound molecules were well isolated and lost their cooperativity, resulting in the ST temperature shift to a lower temperature [22,23]. Nevertheless, in our case, the ST temperature shifted to a higher value. The loading of compound **S** was quite high (nearly up to ~55%), and the distance between **S** molecules was very small (Figure 4); thus, the influence of lost cooperativity was limited. On the contrary, with such a high loading of compound **S** (Figure 6), the cooperativity may have been strengthened during the crystallization procedure [32], which led to a "matrix effect" of ST with a higher temperature [22,23]. The similar "matrix effect" with enhancing cooperativity was also detected by encapsulating the iron SCO complex in various liquid matrices [32]. Additionally, this "matrix effect" may have been due to the rigid media of SiO₂ as well, which led to a stronger nano-confinement pressure and resulted in a higher temperature direction shift [19]. It has been reported that, when Fe(pyrazine)Pt(CN)₄ was encapsulated with a thin SiO₂ shell, its spin–transition curve would occur at higher temperatures [21], which was also consistent with our experimental results. Thus, for 1D SCO chains, the narrow MCM-41 mesopores indeed restricted the SCO behavior.



Figure 6. Schematic presentation of the "matrix effect" from the walls of MCM-41.

3. Experimental Section

3.1. The Preparation of M@S

Two hundred and seventy-eight milligrams of $FeSO_4 \cdot 7H_2O$ (1 mmol) and 40 mg of ascorbic acid were dissolved in 1 mL hot water. A hot solution of 261 mg of $Ba(NO_3)_2$ in 1 mL of water was added to the solution of iron salt dropwise under stirring, maintaining the heating using a water bath. The mixture was allowed to cool down, and after 3 h of stirring, the formed precipitate of $BaSO_4$ was filtered off and washed with water (Solution A).

Two hundred and fifty-two milligrams of 4-amino-1,2,4-triazole (AT) and 100 mg of MCM-41 powder (purchased from Aldrich with the pore size of 2.1–2.7 nm) in 2 mL of ethanol were stirred for 12 h. The formed slurry was added at once to the solution, and the mixture was stirred for 3 h. The precipitate was filtered off, washed twice with water and twice with ethanol, and dried in an evacuated desiccator over silica gel. Yield: ~332 mg of a pink powder.

3.2. Characterization

Powder X-ray diffractograms (PXRD) were measured on a Bruker D2 Phaser instrument using a flat low background sample holder and Cu-Ka radiation (l = 1.54182 Å) at 30 kV covering 2 theta angles 5–80° over a time of 2 h, that is 0.01°/S.

 N_2 adsorption isotherms were acquired on a Quantachrome Nova[®] instrument, with 2 h degassing at a temperature of 120 °C in a vacuum prior to each measurement.

FT-IR spectra were recorded on a Bruker TENSOR 37 IR spectrometer at ambient temperature in the range of 4000 to 500 cm^{-1} with an ATR unit.

Atomic absorption spectrometry (AAS) was carried out with a Perkin Elmer Analyst100 instrument, the iron content of the sample was determined by comparison to standard solution.

Scanning electron microscopy (SEM) measurements were conducted on an ESEM Quanta 400 FEG instrument at 10kV.

Transmission electron microscopy (TEM) measurements were conducted on an FEI Tecnai G2 f20 instrument at 200kV.

DC magnetic measurements were carried out on a Quantum Design MPMS XL-5 SQUID magnetometer in a magnetic field of 1000 Oe, starting from 200 to 400 K (heating), and then cooling back to 200 K.

4. Conclusions

In summary, a composite material M@S comprised of the 1D SCO complex $[Fe(NH_2trz)_3](NO_3)_2$ and MCM-41 was successfully prepared. Its spin transition behavior was identified by DC magnetic measurement. Compared to the pure complex, the spin transition temperature of M@S shifted to a higher value. This phenomenon could be ascribed to the strengthened cooperativity of compound **S** and the nano-confinement of mesopore walls of MCM-41, which indicated a significant "matrix effect" on the spin-crossover transition of $[Fe(NH_2trz)_3](NO_3)_2$.

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Conflicts of Interest: The authors declare that there is no conflict of interest.

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