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ARTICLE

Synthesis and Characterization of Novel Spin Crossover-Polymeric Composite with Iron(II)-4-amino-1,2,4-triazole Groups

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ABSTRACT

A novel 1-dimensional spin-crossover complex {[Fe(MPEG-trz)₃](BF₄)₂} where polymer chain is attached by chemical modification has already been successively synthesized by self-assembly reaction between methoxy polyethylene glycol (MPEG) grafted 4-amino-1,2,4-triazole (MPEG-trz) and Fe(BF₄)₂·6H₂O. The structure information could be obtained through FT-IR, XRD and ¹H NMR measurements, while spin-crossover behaviour of complex is inspected by super-conducting quantum interference device (SQUID) and DSC. The new metallo-organic polymer not only shows mechanical behaviour particularly the malleability of the material but also exhibit an abrupt spin crossover behaviour with a slender hysteresis loop of 1 K.

KEYWORDS

Iron(II)-4-amino-1,2,4-triazole, Spin crossover, Polymeric composite, Malleable, Cooperative formation mechanism.

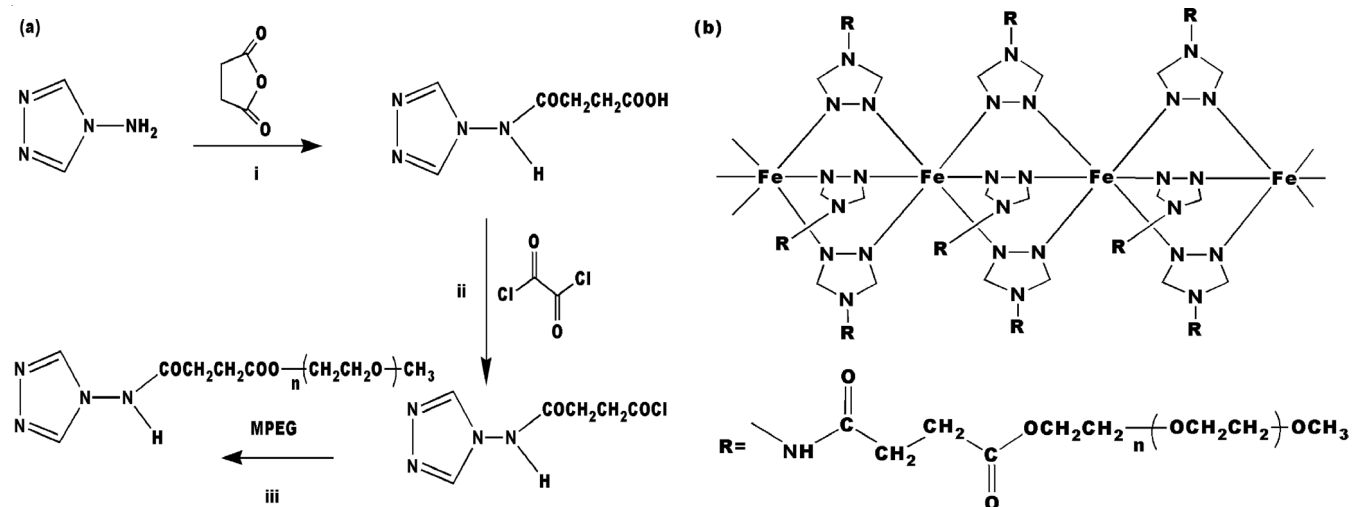
INTRODUCTION

Spin crossover (SCO) complex, an interesting bistable system containing $3d^{4-7}$ metal ions, could exhibit spin transition phenomenon between the low-spin state and the high-spin state under relatively minor external stimuli such as temperature, pressure and light [1-5]. In particular, the iron(II) complexes coordinated by triazole molecule are of vital importance because of their large thermal hysteresis loop around room temperature [6] which is one of the essential factors [7] for potential applications as molecular sensors, molecular switches, data storage and other electronic devices [8].

Up to now, a good number of iron(II) spin-crossover complexes (mono- and multi-nuclear) have been synthesized and characterized as bulk (powder or single crystal) or diluted (solid or liquid) materials [9-11]. However, one of the key difficulties in using these materials is their poor processability. It is obvious that polymer could be designed and constructed into any structures and morphologies we need according to their admirable processability and ductility, so introducing macromolecular chain into spin-crossover system by chemical modification would provide a promising route to prepare new kinds of malleable spin-crossover materials [12].

Rubio *et al.* [13] prepared a gel phase iron(II) complex with octadecyl chain which not only exhibited spin-crossover behaviour but also gelation behaviour and when been heated above the melting temperature the gel could be turned into homogeneous solution. Kitchen *et al.* [14] attached hexadecyl into spin-crossover system so as to get a malleable spin-crossover material. However, the author didn't provide corresponding data supporting for the mechanical behaviour especially the malleability of the material. Meanwhile, according to the previous reports the introduction of these groups would alter or weaken the spin-crossover behaviour [15] because of the reduction of the intermolecular interactions between spin-crossover molecules which act as an important factor to control the abruptness of the spin transition along with hysteresis loop [16]. In order to improve this problem, Davidson *et al.* [10] attached polyphosphazene into the spin-crossover system to obtain a malleable spin-crossover material for its regular and order structure unit similar to that of cyclotriphosphazene analogues and possibly it's just the special structure that made the effect upon intermolecular interactions as little as possible. Unfortunately, the rigid structure of cyclotriphosphazene analogues hindered the realization of promised processability. However, it provided a probably route to keep a balance between processability and spin-crossover behaviour when macro-molecular substituents were attached into the spin-crossover system.

In our previous work poly(glycidyl methacrylate) (PGMA) with pendant iron(II) triazole groups was synthesized through the combination of ATRP polymerization and ring-opening reaction, which displayed not only an evident spin crossover performance, but also excellent processability [17]. In a continuous effort, we attached the methoxy polyethylene glycol (MPEG) chain into the spin-crossover system for its flexible chain structure characteristics with repeating and regular unit of ether bond so as to prepare spin-crossover materials with excellent processability [18,19]. In the present work, we have already got one novel polymeric composite with not only mechanical property but also an abrupt spin crossover behaviour by self-assembly reaction between $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and MPEG-trz. The process detail is exhibited schematically in **Scheme-I**.



Scheme-I: (a) Schematic diagram of polymer-based ligand: (i) TEA, acetonitrile, 40 °C, 6 h; (ii) DCM, 0 °C, 6 h; (iii) TEA, DCM/DMF, 25 °C, 12 h; (b) Structural formula of spin-crossover complex

EXPERIMENTAL

Succinic anhydride (Aladdin, China) and 4-amino-1,2,4-triazole (Aladdin, China) were recrystallized from acetic anhydride and acetonitrile respectively and then washing with diethyl ether, finally dried in a vacuum. Methoxy polyethylene glycol with $M_n = 1$ K denoted as MPEG 1K (Fluka, USA) was dried by azeotropic distillation in the presence of toluene. $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and oxalyl chloride were purchased from Aldrich Chemical Co. Trimethylamine (TEA), N,N-dimethylformamide (DMF), dichloromethane (DCM), acetonitrile, were stirred overnight over CaH_2 and distilled under reduced pressure prior to use. Other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and were used as received without any purification.

Fourier transform infrared data was collected on a Bruker VECTOR-22 FT-IR spectrometer, using spectroscopic grade KBr pellet at room temperature. The ^1H NMR spectra were measured on a Bruker AVAN300 CE nuclear magnetic resonance instrument, using D_2O as solvent and tetramethylsilane (TMS) as internal reference. The magnetic measurements were performed on a superconducting quantum interference device (SQUID) magnetometer ($10 \text{ K} \leq T \leq 300 \text{ K}$, $0 \leq H \leq 50 \text{ kOe}$) in external field 1 T. Differential scanning calorimetry (DSC) experiments were performed on a Mettler DSC 822 calorimeter under N_2 atmosphere within temperature from -80 to -0 °C, at heating rate 5 K/min. XRD spectra were collected on an M18XHF-SPA X-ray diffraction instrument, purchased from Mac Science Co. (Japan) with $\text{Cu K}\alpha$ radiation ($k = 1.5406 \text{ \AA}$) at the scanning rate of 0.1 °/s between $2\theta = 5\text{--}50^\circ$.

Synthesis of carboxyl-terminated 4-amino-1,2,4-triazole ($\text{NH}_2\text{-trz-COOH}$): A typical example is given below. The 4-amino-1,2,4-triazole (0.2520 g, 3 mmol), succinic anhydride (0.450 g, 4.5 mmol) and triethylamine (0.300 g, 3 mmol) were dissolved in 40 mL of anhydrous acetonitrile and the reaction was carried out at 40 °C for 6 h under vigorous stirring. When the reaction finished the solvent was evaporated completely using a rotary evaporator and subsequently precipitated in ethyl acetate. The $\text{NH}_2\text{-trz-COOH}$ was collected by filtration and dried at 40 °C *in vacuo* until constant weight. The $\text{NH}_2\text{-trz-}$

COOH was obtained in 73 %. $^1\text{H NMR}$ (600 MHz, D_2O): δ (ppm) 8.57 (s, $\text{N}=\text{C}-\text{H}$), 2.75 (m, $-\text{COCH}_2\text{CH}_2\text{CO}-$); FT-IR (KBr, cm^{-1}): 3310-3123 ($-\text{NH}$ stretching), 1538 ($\text{C}=\text{N}$ stretching), 1713 ($\text{C}=\text{O}$ stretching), 1670 ($-\text{CONH}-$ stretching).

Synthesis of polymer-based ligand MPEG-trz: A typical example was as follows. A mixture of $\text{NH}_2\text{-trz-COOH}$ (0.9200 g, 5 mmol), oxalyl chloride (5 mL), catalyst DMF and DCM (solvent, 25 mL) was refluxed at 0°C for 6 h under nitrogen atmosphere. The excess oxalyl chloride was evaporated completely using a rotary evaporator. Then the residue was dissolved in 10 mL DMF and was dropped into a mixture of MPEG (6.000 g, 6 mmol), DCM (20 mL) and TEA (0.600 g, 6 mmol), then the reaction was performed at 25°C for 12 h under nitrogen atmosphere. The reaction byproduct triethylamine hydrochloride was removed by filtration and the filtered solution was evaporated to dryness. The solid was dissolved in chloroform and the solution was extracted with a diluted HCl solution (pH 5.0), followed by water and then dried over anhydrous Na_2SO_4 . After evaporation of solvent, the resultant product was purified by precipitating from diethyl ether. The MPEG-trz was collected in 84 %. $^1\text{H NMR}$ (600 MHz, D_2O): δ (ppm) 8.50 (s, $-\text{N}=\text{C}-\text{H}$), 4.27 (t, $-\text{COOCH}_2$), 3.69 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.38 (s, $\text{CH}_3\text{O}-$), 2.68 (m, $-\text{COCH}_2\text{CH}_2\text{CO}-$); FT-IR (KBr, cm^{-1}): 3123-3310 ($-\text{NH}$ stretching), 1563 ($\text{C}=\text{N}$ stretching), 1735 ($-\text{COO}-$ stretching), 1650 ($-\text{CONH}-$ stretching).

Synthesis of Fe(II) complex via $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and MPEG-trz: $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.3375 g, 1 mmol), antioxidants ascorbic acid, methanol (5 mL) and acetone (5 mL) were first added into the bottom of flask and then the solution (5 mL of methanol and 5 mL of acetone) of MPEG-trz (0.3498 g, 3 mmol) was slowly dropped for 20 min. After reacting for 30 min, white precipitate was found on the bottom of flask and then was collected by filtration. Before drying at 40°C *in vacuo* the solid was washed with methanol adequately in order to exclude the influence of 4-amino-1,2,4-triazole to the spin transformation. Fe(II) complexes was obtained in 85 %. FT-IR (KBr, cm^{-1}): 3418 ($-\text{NH}_2$), 1735 ($\text{C}=\text{O}$ stretching), 1558 ($\text{C}=\text{N}$ stretching).

RESULTS AND DISCUSSION

Preparation of polymer-based ligands MPEG-trz. The $\text{NH}_2\text{-trz-COOH}$ used in the following esterification reaction with MPEG-OH which were synthesized by amidation reaction of 4-amino-1,2,4-triazole with succinic anhydride. The synthesized product has been fully characterized by FT-IR and $^1\text{H NMR}$ spectroscopy and the spectra were shown in Figs. 1 and 2, respectively. The characteristic absorption band of amide carbonyl at $\nu = 1670\text{ cm}^{-1}$, acid carbonyl at $\nu = 1713\text{ cm}^{-1}$ and carbon-nitrogen double bond in triazole ring at $\nu = 1538\text{ cm}^{-1}$ shown in Fig. 1(a), combined chemical shift of $-\text{CH}=\text{N}-$ in triazole ring at $\delta = 8.57\text{ ppm}$, $-\text{COCH}_2\text{CH}_2\text{CO}-$ at $\delta = 2.75\text{ ppm}$ shown in Fig. 2(a) indicating that $\text{NH}_2\text{-trz-COOH}$ has been synthesized successfully. The esterification reaction of $\text{NH}_2\text{-trz-COCl}$ with a slight excess of MPEG was carried out at 25°C in the presence of trimethylamine. The characteristic absorption band of ester carbonyl at $\nu = 1735\text{ cm}^{-1}$, amide carbonyl at $\nu = 1650\text{ cm}^{-1}$ and carbon-nitrogen double bond in triazole ring at $\nu = 1563\text{ cm}^{-1}$ shown in Fig. 1(b), combined the new signals at $\delta = 4.27, 3.69$ and 3.38 ppm assigned to

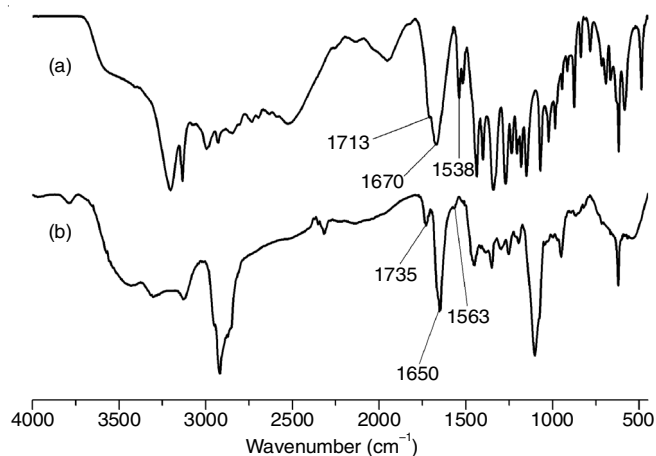


Fig. 1. FT-IR spectra of (a) carboxyl-terminated $\text{NH}_2\text{-trz-COOH}$, (b) polymer-based ligand MPEG-trz

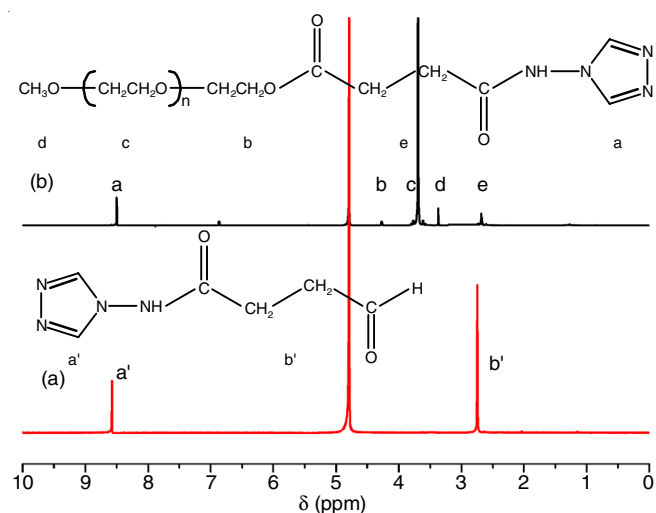


Fig. 2. $^1\text{H NMR}$ spectra of (a) carboxyl-terminated $\text{NH}_2\text{-trz-COOH}$, (b) polymer-based ligand MPEG-trz

$-\text{COOCH}_2-$, $-\text{OCH}_2\text{CH}_2\text{O}-$ and $\text{CH}_3\text{O}-$ observed in Fig. 2(b), indicating that MPEG-trz have been synthesized successfully.

According to previous reports, the spin-crossover behaviour could be triggered by external stimuli such as temperature pressure magnetic field or light irradiation, meanwhile the process is always accompanied with colour change, which the white for high-spin and the purple for low-spin. Consequently, we can estimate whether the spin transformation happens or not qualitatively just according to the colour change of the complex under different temperature. Meanwhile in order to characterize its mechanical behaviour especially the malleability we made the spin-crossover complex into a film for about $40\text{ }\mu\text{m}$ thickness by solution salivate method at room temperature. Firstly 5 % (mass) methylene chloride solution of poly (lactic acid) (PLA) was prepared and then the complex was evenly dispersed in, after evaporation of solvent the film of modified complex was prepared. In Fig. 1 we can clearly observe that the Fe(II) complex is white at room temperature [300 K Fig. 3(a)] while its colour become purple as temperature decreases [77 K Fig. 3(b)], which is the characteristic of *d-d* electronic transitions of low-spin Fe(II) species. This thermochromism indicating that the Fe(II) complex modified by MPEG has the property of the spin-state transition.

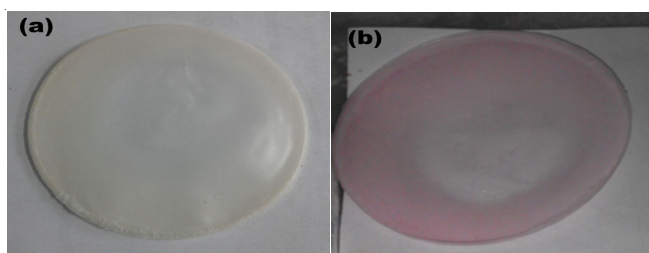


Fig. 3. Demonstration of the thermochromism due to the spin crossover phenomenon for Fe(II) complex: (a) colourless in the high-spin state ($T = 300$ K) and (b) purple in the low-spin state ($T = 77$ K)

In order to test the spin-crossover behaviour of present product quantitatively, we applied the superconducting quantum interference device (SQUID) to record the $\chi_M T$ of the Fe(II) complexes modified by MPEG as the temperature of system increases or decreases (in external field 1 T). The result is shown in Fig. 4. We can observe a notable increase in molar magnetic susceptibility $\chi_M T$ up to $3.2 \text{ cm}^3 \text{ K mol}^{-1}$ between 50 and 300 K. Fig. 4 showed that the T_c (temperature at which one-half of the spin crossover is completed) is 205 K which mainly depending on the coordination environments around the metal centers. The $\chi_M T$ value of low-spin Fe(II) species before the spin crossover was not zero. It is because that the $\chi_M T$ values of coordination polymers of low-spin Fe(II) species most likely originate from the steric effect of polymers and the chain end Fe(II) sites, which always adopt a high spin state and are hydrated, so the polymer/complexes have a shorter-chain increasing number of chain end Fe(II) sites. Therefore, the introduction of MPEG has a huge impact on the spin crossover system.

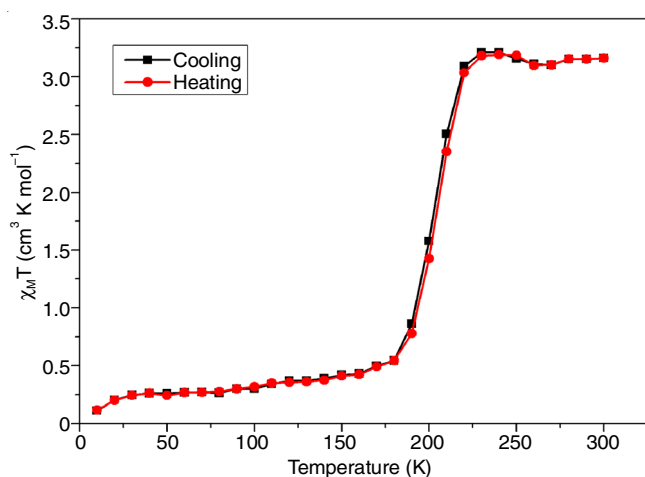


Fig. 4. Magnetic susceptibility profile of spin crossover (SCO) coordination complex

In order to study the spin crossover behaviour further, we applied differential scanning calorimetry (DSC) to study the change of ΔH during the heating and cooling procedure. Although in the range of 200–290 K the Fe(II) complex modified by MPEG (Fig. 5) doesn't display an abrupt endothermic or exothermic curve, connecting with the SQUID the spin crossover phenomenon still existed and occurred.

Additionally, we had examined the crystal structure of Fe(II) complex modified by MPEG through XRD (Fig. 6). An intense diffraction peak of 6.5° appeared, which is related to

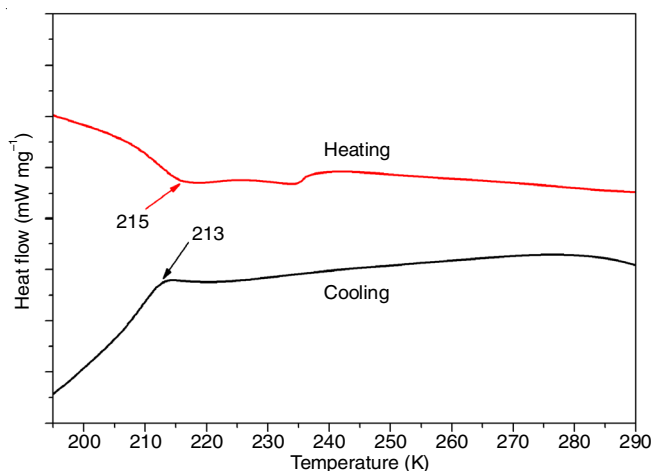


Fig. 5. DSC spectrum of spin crossover complex

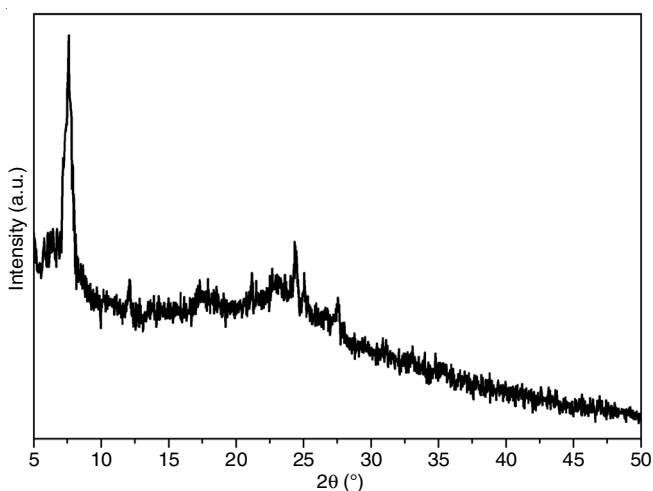


Fig. 6. X-ray diffraction (XRD) profile of spin crossover (SCO) coordination complex at 296 K

the coordination bond between organic ligand and central metal ion. In another word, the value most likely suggests an interdigitation of the polymer to give irregular polynuclear Fe(II) chain. From 18° to 28° there is a wide diffraction peak, which is attributed to the appearance of amorphous MPEG.

Conclusion

In summary, we have prepared a novel Fe(II) complex by self-assembly reaction between polymer-based MPEG-trz and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$. According to the results of ^1H NMR, FT-IR, the complex has been synthesized successfully. The SQUID and DSC measurements showing that Fe(II) complex modified by MPEG chain displayed an evident spin crossover performance, meanwhile, the crystal structure of the modified spin-crossover complex is characterized by XRD. However, what will happen to spin crossover behaviour when the various molecular weight MPEG are introduced into the spin crossover system? *i.e.*, how the various molecular weight MPEG influence the spin transformation in mechanism? We will keep introducing macromolecular chain into this system, further studies are in progress.

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