

Electrically controllable molecular spin crossover switching in $\text{Fe}(\text{phen})_2(\text{NCS})_2$ thin film

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Abstract. Spin crossover molecular complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$ in thin film form (20–300 nm) is obtained by simple dip-coating technique on glass substrates. The growth of the molecular films is confirmed by optical and X-ray diffraction data. The morphology of the samples shows distributed nanocrystals with an average size ca. 12 nm. We measure the current (I)-voltage (V) characteristics of a device with 300 nm film thickness and show that application of electric field can induce spin state switching. The electric field experienced by individual nanocrystals separated by nanometric gap is supposed to be quite high and is plausibly playing the crucial role in instigating switching in molecular nanocrystals. The result is quite significant towards developing room temperature molecular spin cross-over switching devices in the nanoscale limit.

1 Introduction

The subject of spin-crossover (SCO) (or spin-equilibrium or spin-transition (ST)) in d-block metal complexes is one of the fascinating and attractive research area of research in the area of magneto-chemistry [1]. Octahedrally-coordinated transition metals with electron configurations of $[\text{Ar}] 3d^4\text{--}3d^7$ can exist in two different electronic states depending on the ligand field strength of the ligand, namely a high spin or a low spin configuration. The SCO centres show electronic configurations switchable between the high-spin (HS) and low-spin (LS) states leading to characteristic changes in color, magnetic moment, electrical resistance, magnetic susceptibility, thermal and electric conductivity, dielectric constant and mechanical properties [2–7], which may be driven by external stimuli such as temperature [8] and/or pressure [9,10], by light irradiation [11–13] or an influence of a magnetic field [14]. Various applications of spin-crossover materials have been confirmed including sensors, display and memory devices [5–7, 15–17], electronic [18] and optoelectronic devices [19]. The molecular magnetic material evolves now as a strong candidate for future spintronic devices where the control of spins in specific environments is needed with novel functionalities. However, despite a large number of studies in this field, still an electronically addressable molecular switch at room temperature is lacking. To address this issue, two important things needs to be explored, namely spin state switching in molecular nanocrystals to obtain

molecular nanodevices, and electrical control of change of molecular spin states which is much more viable than any other external stimuli. The issue has recently been the subject of intense study for various researchers and ushered the possibility of obtaining electrically controlled molecular spin switches in the nanoscale limit [20,21]. The idea stems from the fact the SCO molecules in its high spin and low spin states have different polarizabilities and permanent electric dipole moments. Under external electric field (E), Stark effect comes into play and the change in energy of the molecules is given by $\Delta\text{energy} = \vec{p} \cdot \vec{E} + \frac{1}{2} \sum_{ij} E_i \alpha_{ij} E_j$ where \vec{p} is the dipole moment and α_{ij} is polarizability tensor, E_i and E_j are the components of the electric field corresponding to different molecular states respectively. The linear Stark effect is therefore going to play a significant role in spin state switching of the molecules, particularly in the nanoscale. In this report, we grow SCO molecular nanocrystals and attempt to see how the external applied field instigates spin state switching in nanocrystals.

2 Experimental details

To date, a large variety of spin cross over molecular complexes have been studied and amongst them, the most simplest one largely studied over decades is $\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2$ complex (phen = 1,10-phenanthroline) composed of two phenanthroline groups and two thiocyanate groups [22,23]. Despite various reports, mostly

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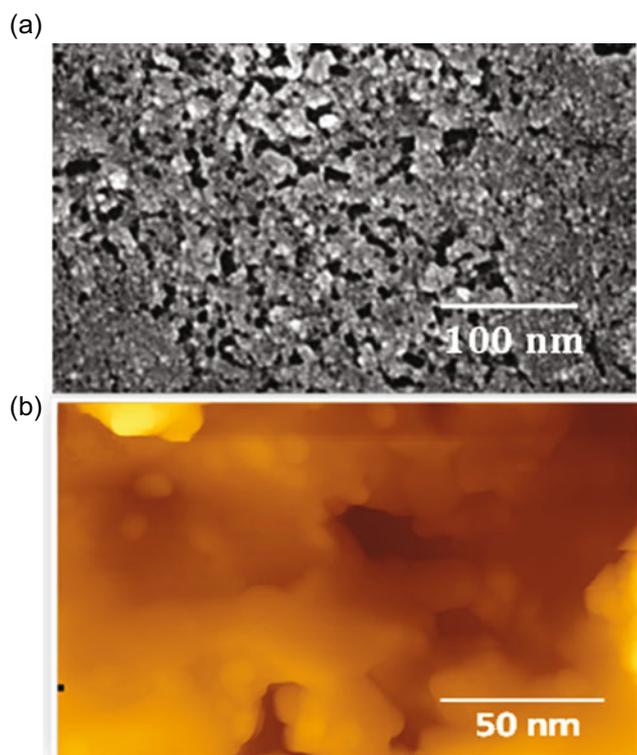


Fig. 1. (a) SEM morphology and (b) AFM surface morphology of a representative SCO film with thickness 300 nm showing the growth of molecular nanocrystals.

on powder samples, a suitable technique to grow the molecular complex in thin film form is still lacking which is urgently required for device application of the SCO materials [24–29]. Interestingly, the electronic structure of the molecules is found to be similar to that of bulk at room temperature giving rise to hope of developing devices capable of functioning at room temperature.

Starting materials for the film synthesis are ferrous ammonium sulfate hexahydrate (Mohr's Salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), 1,10-phenanthroline monohydrate, sodium thiocyanate (NaSCN). All the chemicals are analytical grade purity and used as received without further purification. The $\text{Fe}(\text{phen})_2(\text{NCS})_2$ film is deposited on glass substrate by dip coating technique using a home-made dip-coater. We prepared the complex $\text{Fe}(\text{phen})_3(\text{NCS})_2$ following a wet chemical method. First, 1,10-phenanthroline monohydrate and ferrous ammonium sulfate hexahydrate solution in deionized water is prepared separately. Then, both the solution is mixed properly resulting into a dark red solution. The volume ratio of the two solutions is maintained 3:1 throughout to prepare the dark red solution. In the next step, proper amount of saturated solution of sodium thiocyanate was added to the above solution for the formation of the complex $\text{Fe}(\text{phen})_3(\text{NCS})_2$. Thin films of $\text{Fe}(\text{phen})_3(\text{NCS})_2$ were deposited on thoroughly cleaned glass substrates by a dip-coater. The glass substrates is cleaned sequentially in ultrasonic baths of acetone and 2-propanol and dried up properly in vacuum before film deposition. The films are

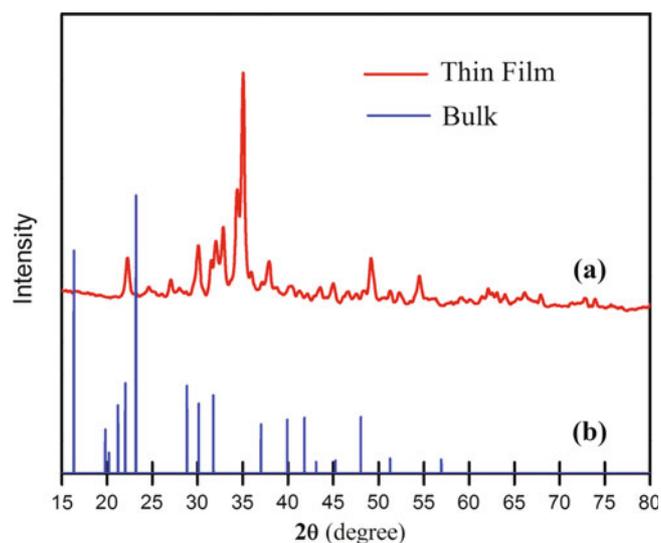


Fig. 2. (a) XRD pattern showing sharp reflections of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ thin film (thickness ~ 300 nm) on glass substrate. (b) The XRD data has been compared with that of bulk sample [33].

deposited at a slow dipping rate ~ 0.1 mm/s. Films of different thicknesses are deposited by varying number of dipping times. Then the films are annealed further at 190°C in vacuum to obtain the desired $\text{Fe}(\text{phen})_2(\text{NCS})_2$ complex films. We obtained films of thicknesses ranging from 20 to 300 nm and used for further characterizations.

3 Results and discussion

In Figure 1a, we present a representative scanning electron microscope (SEM) image of the molecular film deposited on glass substrate. The image clearly shows the dense growth of molecular film with uniformly distributed grains over the whole substrate. The typical size of the clusters is obtained to be ~ 12 nm. The film is found to be quite stable and adsorbs well in the substrate. The AFM (atomic force microscopy) surface morphology (Fig. 1b) of the sample resembles well to that of SEM image showing the granular growth of the molecular film. The crystal structure of the film as investigated by X-ray diffraction (XRD) pattern shows a series of distinct sharp reflections characteristic to $\text{Fe}(\text{phen})_2(\text{NCS})_2$ in its high spin state at room temperature [23, 30–32] shown in Figure 2a. The XRD data of the sharp peaks of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ thin film has been compared with that of the bulk (Fig. 2b) [33]. The slight displacement in some peak positions of the film arises due to the nanocrystalline growth of the material in the thin film form as well as the strain introduced during the growth of the film.

The growth of the films with increasing thickness can be further monitored with the optical transmission data obtained from UV-vis spectrometer at room temperature. The data shows the thin films exhibit a strong absorbance peak centered at ca. 530 nm for all the films which is characteristic of the ${}^1\text{A}_{1g}$ to ${}^1\text{T}_{1g}$ ligand field absorption

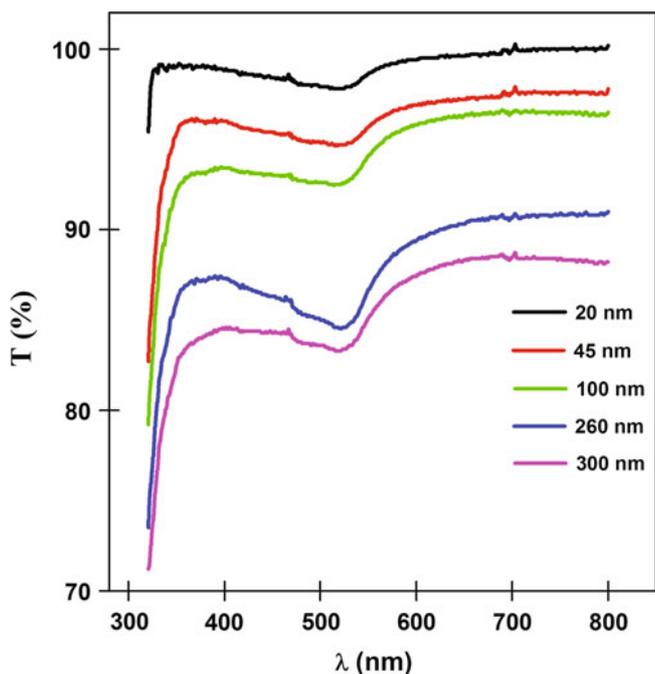


Fig. 3. UV-vis optical absorption spectra of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ thin films with thicknesses 20–300 nm showing the growth of the film on glass substrate.

giving rise to the violet color of the SCO compound [34,35]. The data is obtained for film thicknesses 20–300 nm and the absorption features remains unchanged even for the thinnest films (Fig. 3). This is plausibly indicative of the fact that the electronic structure of the samples remains same irrespective of the film thicknesses.

The as-synthesized samples $\text{Fe}(\text{phen})_3(\text{NCS})_2$ is found to be in a low spin state at all temperatures as confirmed by temperature-dependent Mössbauer spectroscopy [36]. On the other hand, $\text{Fe}(\text{phen})_2(\text{NCS})_2$ is at its high spin at room temperature and switches to low spin state at lower temperature (~ 175 K). At low spin state, the t_{2g} and e_g states are separated by large splitting energy Δ , whereas the high spin state is characterized by reduced crystal field energy. The two configurations may therefore exhibit different electrical resistances and instigate us further to look into the I - V characteristics of the SCO thin films at its LS and HS state.

We measure I - V characteristics of a relatively thicker $\text{Fe}(\text{phen})_2(\text{NCS})_2$ film device of thickness 300 nm by a two probe technique (Fig. 4a) at room temperature. As shown in Figure 4b, in the forward cycle, with the increase in applied bias (0 to 5 V), the current increases in a sub-linear way, while in the reverse cycle (5 to 0 V), when the applied bias is decreased, the current decreases substantially resulting in an electric field dependent hysteresis in the I - V characteristics. This voltage and hence the electric field dependent transition between high and low conductance of the molecular nanocrystals even at room temperature is quite new in the paradigm of spin crossover materials research. The high conductance state can be ascribed to the high spin state and the low conductance

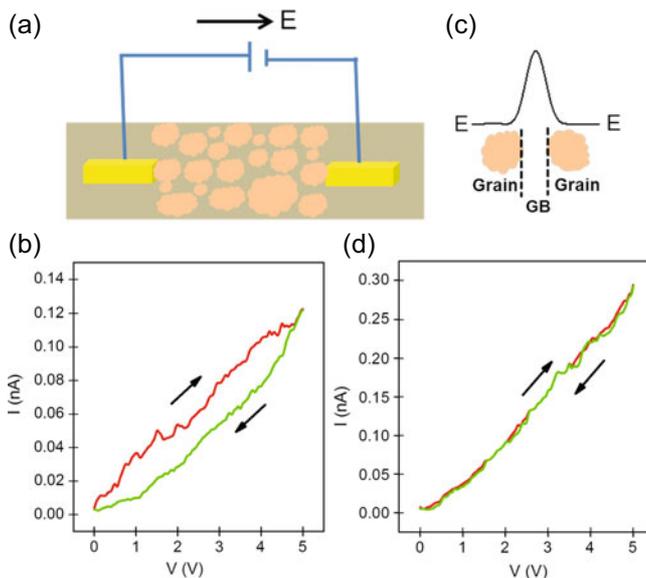


Fig. 4. (a) Schematic diagram for the fabrication of 300 nm $\text{Fe}(\text{phen})_2(\text{NCS})_2$ film device on glass substrate connected with silver electrode for electrical measurement. (b) I - V characteristics of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ thin film with the applied bias between 0 and 5 V, (c) schematic view of the effective electric field (E) at the grain boundary (GB) of two grains separated by a gap of few nm. (d) I - V characteristic of $\text{Fe}(\text{phen})_3(\text{NCS})_2$ thin film with the applied bias between 0 and 5 V. In (b) and (d), red and green curves show the data obtained under forward and reverse cycle respectively.

state to the low spin state. The effect of spin state variation on the conductance has been confirmed by many investigations [37,38]. This spin transition induced by electrical field at a fixed (room) temperature is quite new and never observed before. It also raises the possibility of fabricating spin based devices at room temperature, awaited for long since the development of spin cross over materials. The possibility of electric field induced spin state switching has been explored by many authors recently [39,40]. Lefter et al. [39] reports the observation of spin state switching on micrometric rod shaped particles of $\text{Fe}(\text{Htrz})_2(\text{trz})(\text{BF}_4)$ complex placed between interdigitated electrodes in the thermal hysteresis region at an applied electric field. Prins et al. [40] reports electrically addressable spin cross over on $\text{Fe}(\text{trz})_3(\text{BF}_4)_2$ nanoparticles of size ca. 11 nm placed between 100 nm spaced electrodes at 340 K. In contrast to these, we made similar observation on thin film devices consisting of ca. 12 nm $\text{Fe}(\text{phen})_2(\text{NCS})_2$ SCO particles even with relatively larger electrode separation 0.5 mm at 300 K. It therefore necessitates to discuss the role of electric field in the above spin state switching phenomenon. To be mentioned that such phenomenon is not observed or may not be observed on bulk SCO systems. There exists an electric field gradient within the thin film between the electrodes and the effective field experienced by at the grain boundary of individual nanoparticles separated by nanometric distances is significantly large as shown schematically in Figure 4c. Thus for a nanoparticle system, the influence of

electric field on the metal ligand field is quite high and can induce switching between high and low spins corresponding to high and low conductance respectively. For comparison, we do similar *I-V* measurement on Fe(phen)₃(NCS)₂ film device with similar thickness as shown in Figure 4d, showing no such electric field dependent behavior.

4 Conclusions

In conclusion, we demonstrate that spin crossover molecular thin films with varying thicknesses can be obtained by simple dip-coating technique. The optical spectra exhibit a strong absorbance peak centered at ca. 530 nm for all the films which is characteristic of the ¹A_{1g} to ¹T_{1g} ligand field absorption. The structural characterization show a dense growth of molecular nanocrystals of size 12 nm distributed within the films. The *I-V* characteristics of a device fabricated with 300 nm film show a distinct conductance loop under a voltage cycle. The result is quite important towards the plausibility of electrically addressable spin crossover molecular switching nanoscale devices even at room temperature. The large electric field experienced by the individual nanocrystals at the grain boundary is plausibly playing the crucial role in instigating spin state switching in the molecular thin film complex. Other important factors like surface effects, local joule heating may be further considered to understand fully the switching mechanism upon application of electric field in such molecular nanocrystals.

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