Hierarchical lithographic patterning of two abrupt spin cross-over Fe(II) complexes into micro-cross-stripes

UPPARI VENKATARAMUDU[✉], SUPRATIM BASAK, MAHAMAD A MOHIDDON and RAJADURAI CHANDRASEKAR*

Functional Molecular Nano/Micro Solids Laboratory, School of Chemistry, University of Hyderabad, Prof. C R Rao Road, Gachibowli, Hyderabad, Telangana 500 046, India
E-mail: r.chandrasekar@uohyd.ac.in

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Abstract. We have fabricated high-resolution microscale cross-patterns from two different Fe(II) spin crossover (SCO) complexes having transition temperatures ($T_{1/2}$) 259 K and 323 K, through lithographic techniques. We hope that our original approach will be useful to create futuristic multi-component SCO devices.

Keywords. Spin cross-over; lithography; Fe(II) complexes; microscale patterns.

1. Introduction

Spin crossover (SCO) compounds are known to act as magnetic switches between high-spin (HS) and low-spin (LS) states depending upon temperature, light, pressure, magnetic field and electric field.^{1–6} SCO compounds displaying sharp transition temperature ($T_{1/2}$) in a narrow temperature range are promising logical materials (1 or 0) for information storage application down to nano/microscale. Kahn *et al.*, have reported the first example of an SCO thermochromic device composed of polymeric one-dimensional complexes of Fe(II) and 4-substituted triazole ligands.³ SCO compounds which consist of Fe(II) metal center, normally show a temperature-dependent HS ($S = 2$; paramagnetic) and LS ($S = 0$; diamagnetic) reversible spin transitions. Hence, the exploitation of these Fe(II) SCO complexes to fabricate high-resolution thin film patterns down to nano/microdomain are of great interest for miniaturized spintronic device applications.

Recently, soft lithographic techniques have emerged as simple and cost-effective solutions to achieve high-resolution SCO device structures.^{7–10} SCO micro-arrays from Fe(II) complexes were fabricated *via* a lithographic technique using polydimethylsiloxane (PDMS) stamps.^{7,8} In this context, we have used SCO complexes

containing Fe(II) metal center and coordination polymers to produce micro-structures of various shapes such as rectangular, wedge and squares.^{9,10} To the best of our knowledge, all of the reported SCO micro-device structures are based on a single SCO complex. Till date, these lithography techniques have not been employed to incorporate two different SCO complexes in a single micro-device structure in a hierarchical fashion.

In this communication we present two unique methodologies to hierarchically¹² create high-resolution micro scale cross-patterns composed of two different abrupt SCO complexes (Scheme 1). One of the SCO complexes is $[\text{Fe}^{\text{II}}(\text{L1})_2](\text{BF}_4)_2$ (**1**), where **L1** is 2,6-di(pyrazol-1-yl)pyridine.¹¹ It shows a very abrupt $T_{1/2}$ at 259 K with a hysteresis loop width, $\Delta T_{1/2} = 3$ K. We have prepared the second complex, $[\text{Fe}^{\text{II}}(\text{L2})_2](\text{BF}_4)_2$ (**2**), where **L2** is 4'-iodo-2,6-di(pyrazol-1-yl)pyridine.¹³ Remarkably, complex **2** exhibited a very abrupt transition with a high $T_{1/2}$ value of 328 K and $\Delta T_{1/2} = 12$ K. Using lithographically controlled wetting techniques, both **1** and **2** were cross-patterned down to micro scale in two ways: (i) on both side and (ii) on the same side of the polystyrene (PS) film to form a double layered flexible SCO devices. The chemical composition and structure of the aforesaid complexes were investigated by single crystal x-ray diffraction and magnetometry techniques. The chemical composition and

*For correspondence

Scheme 1. Graphical representation of hierarchical contact printing processes leading to device structures with two different SCO temperatures.

dimensions of the micro cross-patterns were examined by confocal Raman spectroscopy/microscopy, atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) studies.

2. Experimental

2.1 Materials

HPLC grade solvents were purchased from Merck Chemicals, Hyderabad. The solvents were distilled and dried before reactions, and for extraction purposes. Spectroscopic grade solvents were used for stamping.

2.2 Instrumental methods

IR spectra were recorded on a JASCO FT/IR-5300 or Nicolet 5700 FT-IR instrument equipped with ATR attachment. Elemental analysis was recorded on a C H N analysis Thermo Finnigan Flash EA 1112 analyzer instrument. The temperature dependent magnetic susceptibility of complexes **1** and **2** in the powder state was measured on a Quantum Design vibrating sample magnetometer (VSM-SQUID) setup in the temperature range of 360 $\leftrightarrow$ 4 K at continuous cooling ($\downarrow$) and heating ($\uparrow$) cycles with an applied direct current (DC) magnetic field of 0.1 T. Heating and cooling rate of the sample was kept at a 3 K interval in sweep mode.

2.3 Atomic force microscopy (AFM)

AFM imaging was carried out on NT-MDT Model Solver Pro M microscope using a class 2R laser of 650 nm wavelength having a maximum output of 1 mW. All the calculations and image processing were carried out by a software NOVA

1.0.26.1443 provided by the manufacturer. The images were recorded in a semi-contact mode using a noncontact silicon cantilever (NSG10-DLC) tip purchased from NT-MDT, Moscow. The dimensions of the tip are as follows: cantilever length = 100 ($\pm$ 5) μ m, cantilever width 35 ($\pm$ 5) μ m, and cantilever thickness = 1.7–2.3 μ m, resonance frequency = 190–325 kHz, force constant = 5.5–22.5 N/m, chip size = 3.6 $\times$ 1.6 $\times$ 0.4 mm, reflective side = Au, tip height = 10–20 μ m, tip curvature radius = 1–3 nm, and aspect ratio 3:1–5:1.

2.4 Confocal Raman micro-spectroscopy studies

Raman imaging was carried out using backscattering (reflected mode) mode laser confocal optical microscope (B-LCOM) facility of the WiTec alpha 200 SNOM instrument. The Nd:YAG laser operating at 532 nm (maximum output power is 40 mW) was used for the Raman Scan and the bright-field images were captured using a color eyepiece video camera. In the backscattering mode experiment, a 100 $\times$ objective lens was used for the Raman imaging and spectrum collection. The collected Raman signal was sent to a CCD detector through a multimode optical fiber of diameter 25/125 μ m (core/cladding). The Raman spectrum was recorded using a 532 nm long pass edge filter (LPEF) and a 300 grooves/mm grating BLZ = 500 nm, with a 5 s integration time. Four accumulations were performed to acquire a single spectrum and the spectral resolution maximum was 0.1 nm. All the measurements were carried out under ambient conditions.

2.5 Variable temperature Raman spectroscopy studies

Raman spectra of the samples were recorded on a WI-Tec confocal Raman spectrometer equipped with a Peltier-cooled CCD detector. Using a 600 grooves/mm grating BLZ = 500 nm, the accumulation time was typically 10 s and integration time was typically 2.0 s. Ten accumulations were performed for acquiring a single spectrum. An Ar⁺ ion 488 nm laser was used as the excitation source for the Raman scattering.

2.6 Electron microscopy studies

Size and morphology of the microstructures were examined by using a Carl-Zeiss merlin field emission scanning electron microscope (FESEM) using a beam voltage of 3 kV.

2.7 Stamps for lithography

Elastomeric poly-(dimethylsiloxane) (Sylgard 184 Down Corning) stamp was prepared by replica molding of a series of the structured master. The curing process was carried out for 6 h at 60 $^{\circ}$ C. Once cured, the replica was carefully peeled off from the master and used as-is for nano/micropatterning techniques. Test gratings TGZ3 was purchased from NT-MDT and used as masters.

Figure 1. (a) ORTEP plot (50% probability) of LS state complex **2**. The dianions and the hydrogens are omitted for clarity. Bond distances: Fe-N(1): 1.974 Å; Fe-N(2): 1.909 Å; Fe-N(3): 1.976 Å. The inset shows the microcrystals of **2**. (b) A plot of χT versus T of compound **2** measured in the temperature range of 4–360 K in cooling, and heating mode cycles with an applied DC magnetic field of 0.1 T.

2.8 Synthesis

Complex **1** was prepared by following the reported procedure.¹¹

Synthesis of complex 2: 84.5 mg (0.25 mmol) of 2,6-bis-pyrazolyl-4-iodopyridine was dissolved in 30 mL of deaerated acetonitrile. $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (41.93 mg, 0.125 mmol) was added to the above solution. The color of the solution immediately turned orange-red. The solution was kept under reflux accompanied by stirring for overnight under nitrogen atmosphere. After completion of the reaction, the orange-red color solution was filtered and to the filtrate 250 mL of di-isopropyl ether was added to precipitate out the orange-red color complex. The precipitated complex was washed with di-isopropyl ether (3×30 mL) to get a red color powder in 68% yield (77 mg). FTIR (KBr, in cm^{-1}): $\nu = 1605, 1562, 1468, 1337, 1260$ (aromatic C=C), 1036 (broad, Cl-O), 772; Raman (488 nm Ar^+ laser, rt): 1019, 1367, 1412, 1497, 1568, 1610 cm^{-1} ; Bulk Magnetic Data (360 K): $\chi_m T = 3.88 \text{ emu K mol}^{-1}$; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{B}_2\text{F}_8\text{FeI}_2\text{N}_{10}$: C 29.24, H 1.78, N 15.5%. Found: C 29.32, H 1.72, N 15.65%. CCDC No. 1059649.

3. Results and Discussion

3.1 Single crystal XRD studies

The orange-red color precipitate of complex **2** was dissolved in acetonitrile and crystallized by slowly diffusing di-isopropyl ether vapor into the solute. Bright red crystals suitable for single-crystal X-ray diffraction (XRD) were found after 7 days. Room temperature single crystal XRD data revealed a pseudo-octahedral

environment of complex **2** in $Pbcn$ space group (Figure 1). The asymmetric units of **2** consisted of the $[\text{Fe}^{\text{II}}(\text{L}2)_2]$ cation, and two corresponding BF_4 anions. The Fe-N bond distances of complex **2** varied from 1.909 Å to 1.979 Å. These bond distances (below 2 Å) clearly indicated the LS state of Fe(II) ion at 293 K (Figure 1a). This result also suggested that the metastable HS state is present above room temperature.

3.2 Temperature dependent magnetic property studies

Further, the temperature-dependent magnetic susceptibility of polycrystalline complex **2** was performed on a VSM-SQUID device in the temperature range of 360 $\leftrightarrow$ 4 K (DC magnetic field of 0.1 T) (Figure 1b). At 360 K the product of the molar magnetic susceptibility and temperature (χT) of the compound was $3.88 \text{ emu K mol}^{-1}$, which was in the range of value expected for a HS state Fe(II) ion ($S = 2$). Upon cooling, the χT value abruptly decreased to $1.22 \text{ emu K mol}^{-1}$ at 300 K and reached a minimum value of ca. $0.01 \text{ emu K mol}^{-1}$ at 4 K. The latter minimum χT value indicated the complete transformation of the bulk of the Fe(II) ion to the LS state. Further measurements performed in both cooling ($T_{1/2} \downarrow = 322 \text{ K}$) and heating ($T_{1/2} \uparrow = 334 \text{ K}$) cycles demonstrated the occurrence of an abrupt SCO effect with ca. 12 K ($\Delta T_{1/2}$) wide hysteresis loop. Notably, the SCO phenomenon occurred above room temperature with a $T_{1/2}$ of 328 K. The presence of hysteresis loop clearly demonstrated the existence of significant intermolecular cooperativity in the solid state.²

Figure 2. (a) and (b) Confocal optical microscopy images of **1** and **2** microarrays formed on both sides of PS film, respectively. (c) and (d) are the corresponding FESEM images. The insets show the Fe EDS mapping. (e, f) are the corresponding Raman intensity profile of microarrays. Insets show the respective Raman images of selected areas. (g) Raman spectra from the micro-arrays formed on surface of PS film.

3.3 Lithography, electron microscopy and atomic force microscopy studies

To construct smart SCO device containing two SCO complexes (**1** and **2**), two types of hierarchical contact printing (CP) technique were employed. In our first approach, with an idea to store information on both sides of the flexible SCO device, we have patterned complexes **1** and **2** on both sides of transparent PS film by means of CP technique. In order to do this, two elastomeric PDMS stamps having arrays of rectangular cross-section were prepared from a hard master (NTMDT AFM test gratings model TGZ3) by following conventional procedures.⁹ The qualities of the PDMS stamps were also examined by AFM technique.⁹ At first, the PS solution was drop-cast on a glass slide to form a homogeneous thin film. Later, the ink of the complex **1** was prepared by dissolving 2 mg of **1** in 1 mL of acetonitrile solution. The PDMS stamp was judiciously wetted with the above ink solution and the extra solution was removed by using a filter paper. Then the stamp coated with ink was printed on the thin PS film and consequently, a weight of 20 g a metal plate was kept on top of the stamp to make an even flat contact between the bottom of the stamp and the polymer substrate. After 4 h, the stamp was lifted off very cautiously to avoid any damage to the patterns.

The prepared micro-structure was examined on a laser confocal Raman microscope (reflection mode) equipped with a 488 nm Ar^+ laser. The obtained optical micrographs clearly revealed the formation of one-dimensional arrays of complex **1** on one of the sides

of the PS substrate (Figure 2a). The FESEM image of the above substrate clearly confirmed the pattern formation and the dimension (width $\sim 1 \mu\text{m}$ and height $\sim 50 \text{ nm}$) of each array (Figure 2c). Further, Raman imaging of a selected area of the SCO pattern formed on PS film confirmed the composition of the patterns (arrays) by displaying characteristic peaks correspond to **1**, while the rest of the area exhibited only Raman signals correspond to PS (Figure 2e, g). The 3D Raman plot showed rather similar intensities from the SCO arrays indicating the uniform distribution of complex **1** in each array (Figure 2e). Afterwards, to make a pattern on the reverse side of the PS film, the PS film containing arrays was carefully peeled-off, and the opposite side was used for further stamping with complex **2**. For this, again a fresh PDMS stamp was coated with compound **2** ink (2 mg of **2** in 1 mL in acetonitrile), rotated by 90° relative to arrays of **1**, and printed, the resultant film was peeled-off after 4 h. FESEM examination confirmed the pattern formation on the other side of PS film (Figure 2d, f) and the composition (**2**) of arrays. Confocal Raman microscopy evidently revealed the distinct Raman spectra of **1** and **2** from both sides of the film together with PS peaks (Figure 2g). Interestingly, Raman spectral mapping with a laser could not resolve the cross-pattern formation (Figure 2g), which indicated the back-to-back usage possibility with lasers.

In our second approach, to create a flexible SCO cross-pattern on the same side of the PS, we have directly printed both **1** and **2** layer-by-layer (one on top of other) at 90° angle. At first, a stamp coated with an ink of compound **2** was contact printed on the PS film as per

Figure 3. (a) Confocal microscopy image of cross-patterned **1** and **2** on the same side of PS film. (b) FESEM image of SCO cross-pattern. (c) and (d) EDS data of two cross stripes confirming their composition.

the above-described procedure. Then, compound **1** ink was prepared by dissolving 2 mg of **1** in 1 mL mixed acetonitrile and ethylene glycol (1:0.1 ratio). To create cross-pattern of two SCO complexes, on top of compound **2** pattern, ink **1** was printed at 90° angle. It is imperative to remove the excess ink from the stamp to get cross-pattern at a large surface area. Further, this would ensure less damage to already existing complex **2** patterns. Laser confocal microscope examination of the sample clearly exhibited the formation of a clear cross-pattern (Figure 3a). FESEM image further confirmed that the cross-stripes were formed one on top of another (Figure 3b). The composition of individual cross stripes was evidently demonstrated by the energy dispersive x-ray (EDS) analyses. As one can see, only

the bottom pattern (composed of **2**) exhibited peaks from iodine atom, in addition to C, N, Fe, and F (Figure 3d).

3.4 Variable temperature Raman spectroscopy studies

Variable temperature Raman spectroscopy is an important tool to probe the vibrational changes associated with HS and LS state structural transformation since the difference in the average Fe–N bond distances between these two states is $\sim 0.2 \text{ \AA}$. To investigate the vibrational frequency changes (due to bond polarization changes) associated with SCO effect, solid-state Raman spectroscopy measurements of complex **1** and complex **2** (thin pellet state) were performed at 77 K and 298 K using a confocal Raman microscope setup equipped with an Ar^+ 488 nm laser (power: 40 mW). Both complexes **1** and **2** showed characteristic Raman spectra (Figure 4). In comparison to room temperature Raman spectrum, at 77 K (LNT) the spectrum of **2** exhibited two new prominent peaks at 495 cm^{-1} and 963 cm^{-1} . The former peak is probably due to Fe–N stretching frequency. Additionally, the intensity of the peaks at 1227 cm^{-1} and 1610 cm^{-1} (C=C) decreased and the HS state peak at 1044 cm^{-1} has shifted to 1069 cm^{-1} in LS state (see # mark in Figure 4). The other all major vibration bands appeared at 1019, 1022, 1367, 1412, 1497, 1568 and 1610 cm^{-1} (C=C) correspond to complex **2** in both spin states (Figure 4). Similarly, for complex **1**, the low-temperature Raman spectrum exhibited three new noticeable peaks at 463 , 678 and 959 cm^{-1} , compared

Figure 4. Variable temperature Raman spectra of SCO complexes **1** and **2**. LNT is liquid nitrogen temperature and RT room temperature. # stands for new peaks.

to the HS state spectrum at 293 K. The intensity of all the other peaks gradually increased in the LS state. The other major vibration bands at 259, 1024, 1372, 1420, 1506 and 1628 cm^{-1} of complex **1** appeared in both spin states (Figure 4, right).

4. Conclusions

In summary, we have shown two innovative methods to print two chemically different abrupt-SCO Fe(II) compounds ($T_{1/2} = 259$ K for **1** and 328 K for **2**) precisely on a transparent poly(styrene) PS film using contact printing techniques. In the first approach, both compounds were cross printed on both sides of the PS film. In the second method, the same side of the PS film was cross-patterned successfully with both SCO compounds. The presented nanotechnology approaches are original and further work in this direction might advance devices based on inorganic spin switches.

Supplementary Information (SI)

Crystallographic data for the structural analyses of complex **2** have been deposited with the Cambridge Crystallographic Data Centre bearing the CCDC Nos. 1059649. Copies of this information are available on request at free of charge from CCDC, Union Road, Cambridge, CB21EZ, UK (fax: +44-1223336-033; e-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>). Spectroscopic analysis of single patterns, cross-patterns and elemental analysis data are available at www.ias.ac.in/chemsci.

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