CHEMISTRY OF MATERIALS

Flexible and Optically Transparent Polymer Embedded Nano/Micro Scale Spin Crossover Fe(II) Complex Patterns/Arrays

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Supporting Information

ABSTRACT: A novel highly soluble spin-crossover (SCO) $[Fe^{II}(L)_2](BF_4)_2$ complex (*I*) was prepared, where L = 4,4''-dioctylated 2',6'-bispyrazolylpyrine. Complex *I* shows reversible temperature dependent SCO behavior with a $T_{1/2}$ centered around 270 K. Exploiting the high solubility and hence superior processability of complex *I* nano/micro scale arrays and square patterns were fabricated on a glass substrate. Additionally, for the first time, for the possible *flexible* technological applications, the SCO arrays (area: 2 mm²) were successfully embedded within an optically transparent



thin polystyrene film and studied using Raman spectroscopy/imaging technique. Variable temperature Raman spectroscopy studies further confirmed the SCO behavior of complex I.

KEYWORDS: spin-crossover, logical structures, soft lithography, 2,6-bis(pyrazolyl)pyridine, memory storage device

1. INTRODUCTION

Spin-crossover (SCO) compounds, are efficient spin state switchable inorganic materials (high-spin, HS \leftrightarrow low-spin, LS) proposed for several technological applications such as in molecular memory devices, sensors, and displays.^{1–3} Many octahedral Fe^(II) complexes are known to show reversible SCO between two different spin states (HS \leftrightarrow LS) with respect to external stimulus such as pressure,³ temperature,^{3,4} magnetic field,^{5a} electric field,^{1d} and light irradiation.^{5b} Among the other applications, one of the uses of these SCO compounds is possible exploitation as logical structures (0 or 1) for information storage.^{1c} For potential technological applications, fabrication of diverse nano/micro scale SCO domains having various dimensions and shapes are an essential step.

Great amounts of effort have been taken toward the development of novel procedures to fabricate thin deposits, films, and patterned nanostructures composed of SCO compounds preserving the magnetic bistability. The first fabrication of SCO thin films was reported by Kahn et al. using Langmuir–Blodgett (LB) techniques⁶ and then later developed by many other groups.⁷ Patterning of SCO compounds was carried out previously by electron beam lithography,^{8,9} polymeric masks,¹⁰ and also by soft lithographic techniques^{11a} such as micro molding in capillaries^{11b} and micro transfer molding.^{10a} Earlier, Cavallini and Ruben et al. have reported the fabrication of one-dimensional (1D) SCO micro arrays using PDMS (polydimethylsiloxane) stamps on a glass substrate.¹² Recently, we have fabricated 1D micro arrays composed of highly soluble Zn(II) coordination polymers prepared from a *back-to-back* coupled tetraoctylated-2,6-bispyrazolylpyrine ligand and Zn(II) ions.¹³ Till now all of

the existing SCO based nano/micro molding was performed on nonflexible solid substrates. To improve the existing *stiff* SCO patterns/array technology into the next stage *flexible smart devices*, it is necessary to organize (implant) these nano/micro SCO patterns within an optically transparent polymer substrate.

In this Article, we report a new synthetic protocol for the preparation of novel 4,4"-dioctylated 2,6-bispyrazolylpyrine (Oct-BPP) ligand *L* and its SCO $[Fe^{II}(L)_2](BF_4)_2$ complex (*I*). We also present the utilization of compound *I* to pattern nano/micro scale (i) 1D wedge stripes, (ii) 1D rectangular stripes, and (iii) 0D square pillars using the LCW (lithographically controlled weighting) technique. Additionally by keeping the *flexible* device fabrication in mind, for the first time, a 1D SCO arrays was successfully implanted in an optically transparent polymer film (Chart 1). All fabricated nano/micro SCO





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structures were thoroughly characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), optical microscopy, and confocal Raman imaging techniques. The SCO phenomenon was also studied by variable temperature bulk magnetic susceptibility measurements and Raman spectroscopic studies.

2. EXPERIMENTAL SECTION

2.1. Synthesis. 2,6-Bis(4-(oct-1-ynyl)-1H-pyrazol-1-yl)pyridine (1). A Schlenk flask was charged with 2,6-bis(4-iodo-1H-pyrazol-1yl)pyridine 2 (500 mg, 1.07 mmol) together with Pd(PPh₃)₂Cl₂ (37.89 mg, 0.053 mmol), triphenylphosphene (50 mg, 0.19 mmol) and CuI (200 mg, 0.262 mmol). Freshly distilled anhydrous triethylamine (Et₃N, 20 mL) and 1,4-dioxane (10 mL) were added to it. The flask was carefully degassed by freeze-and-thaw cycles several times. 1octyne (0.5 mL; d = 0.746 g/mL, 3.24 mmol) was injected into the flask under argon atmosphere, and the resulting mixture was heated to 80 °C for 48 h. It was then cooled to room temperature and left for stirring for an additional 1 h. The mixture was filtered through filter paper and washed with tetrahydrofuran (THF), and the filtrate was evaporated to get a dark brown solid which was column chromatographed on silica (100-200 mesh) using initially (60:40) DCM/ Hexane and finally (80:20) DCM/Hexane to get a white solid of 1. Yield 350 mg (76%). mp 86–87 °C. ¹H NMR (400 MHz, $CDCl_3$) δ : 8.6 (s, 2H), 7.92-7.90 (t, 1H), 7.82-7.81 (d, 2H), 7.74 (s, 2H), 2.43-2.39 (t, 4H), 1.66–1.58 (m, 4H), 1.48–1.45 (m, 4H), 1.34 (s, 8H), 0.93–0.90 (m, 6H) ppm. $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃) δ : 149.5, 144.6, 141.5, 129.0, 109.6, 106.6, 92.7, 70.6, 31.4, 28.7, 28.6, 22.6, 19.5, 14.1 ppm. FTIR (KBr disc; ν in cm⁻¹): 3146 (-C=C-), 2926, 2848, 2361, 1599, 1464, 1026, 953, 800, 656. LC-MS m/z calcd 427.27, found 428.10. ESIMS: m/z calcd 427.27, found 428.2714 [M⁺+H]. Anal. Calcd for C27H33N5: C, 75.84; H, 7.78; N, 16.38%. Found: C, 75.92; H, 7.85; N, 16.27%.

2,6-Bis(4-octyl-1H-pyrazol-1-yl)pyridine (L). To a degassed solution of 1 (0.3 g, 00.7 mmol) in EtOAc (60 mL) was added 10% Pd/C (0.073 g, 0.07 mmol), the mixture was stirred under H_2 atmosphere (at ambient pressure), and monitored by TLC. After 1 h the mixture was filtered through a Celite plug to remove activated Pd/C. Afterward the plug was washed with 100 mL of EtOAc, and the collected fraction was concentrated in vacuum to get compound L as viscous oil. Yield 0.302 g (>99%) ¹H NMR (400 MHz, CDCl₃) δ : 8.33 (s, 2H), 7.90– 7.86 (t, 1H), 7.77-7.75 (d, 2H), 7.59 (s, 2H), 2.58-2.54 (t, 4H), 1.67-1.64 (m, 4H), 1.36-1.29 (m, 20H), 0.89-0.87 (m, 6H) ppm.¹³C NMR (100 MHz, CDCl₃) δ: 150.1, 142.5, 141.1, 124.8, 124.4, 108.5, 31.9, 30.8, 29.7, 29.4, 29.3, 24.3, 22.7, 14.1 ppm. FTIR (KBr disc; ν in cm⁻¹): 2958, 2918, 2848, 1604, 1585, 1475, 1390, 970, 800, 648, 607, 536, 480, 467. LCMS analysis: m/z calcd 435.34, found 436.25 (positive mode). ESIMS: m/z calcd 435.34, found 436.3403 $[M^{+} + H]$. Anal. Calcd for $C_{27}H_{41}N_5$: C, 74.44; H, 9.49; N, 16.08%. Found: C, 74.28; H, 9.41; N, 16.21%.

[$Fe^{ll}(L)_2$](BF_4)₂ (I). A 100 mL flask was charged with L (80 mg, 0.183 mmol) and 10 mL of DCM was added to it. A solution of $Fe(BF_4)_2$ 6H₂O (31 mg, 0.091 mmol) in MeOH (10 mL) was added to the above solution. The mixture was heated to reflux for 12 h at nitrogen atmosphere. After cooling, the solvent was evaporated on a rotary evaporator in air. The residue was washed with diisopropyl ether (20 mL × 1) and dried in vacuum to get a yellow color powder of I. Yield 74 mg (73%). The crystals of the complex were obtained by slow evaporation from acetonitrile solution. Anal. Calcd for C₅₄H₈₂B₂F₈FeN₁₀: C, 58.92; H, 7.51; N, 12.72%. Found: C, 58.83; H, 7.61; N, 12.52%. FTIR (KBr disc; ν in cm⁻¹): 3118, 2958, 2927, 2856, 1620, 1572, 1491, 1400, 1321, 1103 (*broad*, *B*–*F*), 1014, 991, 796, 725, 625. M.p.: ~80 °C.

2.2. Bulk Magnetic Studies. The temperature dependent magnetic susceptibility of complex *I* in the powder state was measured on a Quantum Design vibrating sample magnetometer (VSM-SQUID) setup in the temperature range of $340 \leftrightarrow 2$ K at continuous cooling (\downarrow) and heating (\uparrow) cycles with an applied direct current (DC) magnetic

field of 0.5 T. Heating and cooling rate of the sample was kept at a 10 K interval in sweep mode.

2.3. Electron Spin Resonance Spectroscopy (EPR) Studies. Xband EPR spectra were recorded on a Bruker-ER073 spectrometer equipped with an EMX microX source. For data analysis Xenon 1.1b.60 software provided by the manufacturer was used. During the liquid helium measurement the temperature was controlled by a temperature controller supplied by Oxford instruments (ITC 503S).

2.4. Method for Patterning. Micro patterning of complex *I* was carried out by drop casting 20 μ L of a 2 mg/mL solution of complex *I* in acetonitrile (Aldrich, \geq 99% purity) on glass substrate. The substrate was cleaned by sonication for 2 min in electronic-grade water (Milli-Q-pure quality), 2 min in acetone (Aldrich chromatography quality), and then with 2-propanol (Aldrich spectroscopic-grade quality). Before micro patterning the solution of compound *I* was filtered through a Whatman filter paper.

2.5. Stamps for Lithography..^{12,13} Elastomeric poly-(dimethylsiloxane) (Sylgard 184 Down Corning) stamps were prepared by replica molding of a series of structured masters. The curing process was carried out for 6 h at 60 °C. Once cured, the replica was carefully peeled off from the master and used as such for nano/ micro patterning techniques. Test gratings TGQ1, TGZ3 and TGG1 were purchased from NT-MDT and used as masters.

2.6. 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 maximum output of 1 mW. All calculations and image processing was carried out by a software NOVA 1.0.26.1443 provided by the manufacturer. The images were recorded in a semicontact mode using a noncontact silicon cantilever (NSG10-DLC) tip purchased from NT-MDT, Moscow. The dimension of the tip is as follows: cantilever length = $100 (\pm 5) \mu m$, cantilever width 35 $(\pm 5) \mu m$, and cantilever thickness = $1.7-2.3 \mu m$, resonate frequency = 190-325 kHz, force constant = 5.5-22.5 N/m, chip size = $3.6 \times 1.6 \times 0.4 \text{ mm}$, reflective side = Au, tip height = $10-20 \mu m$, tip curvature radius = 1-3 nm, and aspect ratio 3:1-5:1.

2.7. Confocal Raman Micro 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 2.0000 s. Ten accumulations was performed for acquiring a single spectrum. For imaging the integration time was typically 2.000 s, keeping in mind that the *x* or *y* resolution is ~250 nm four points per line and four line per image was taken for imaging of a 1 μ m × 1 μ m area. A He–Ne 633 nm laser was used as an excitation source for the Raman scattering. All measurements were done at ambient conditions.

2.8. Electron Microscopy Studies. Size and morphology of the micro structures were examined by using a Philips XL30 ESEM Scanning Electron Microscope using a beam voltage of 20 kV. TEM measurement was carried out on Tecnai G2 FEI F12 instrument at an accelerating voltage of 120 kV. Carbon coated TEM grids (200 Mesh Type B) were purchased from Ted Pella Inc. U.S.A.

3. RESULT AND DISCUSSION

Highly soluble ligand *L* was synthesized from a commercially available 2,6-dibromopyridine in four steps in good yields (Scheme 1). Conversion of 2,6-dibromopyridine into 2,6-bispyrazolylpyridine 3 was carried out as reported.¹⁴ Compound 3 was successfully converted to its diiodinated derivative 2 as per our previously reported procedure in 74% yield.^{15,16} Transformation of compound 2 into 1 was achieved via Sonogashira coupling reaction conditions by using 1-octyne in Et₃N/THF solvents using Pd(PPh₃)₂Cl₂ catalyst in 78% yield. The alkyne groups in 1 were reduced using Pd/C under H₂ atmosphere to obtain highly soluble 2,6-dioctylated bispyrazolylpyridine *L* in a quantitative 99% yield. The ligands were characterized by employing NMR, LC-MS, FTIR, and elemental analysis techniques. The mononuclear iron(II)

Scheme 1. Reagents and Conditions^a



^a(a) K/Diglyme, 5 days; (b) I₂/HIO₃,72%; (c) 1-octyne, CuI, Pd(PPh₃)₂Cl₂, PPh₃, dioxane/TEA, 78%; (d) Pd/C, H₂, 1 h, 99%; (e) DCM/MeOH, Fe(BF₄)₂·6H₂O, 73%.

complex $[Fe^{II}(L)_2](BF_4)_2$ (*I*), was synthesized from *L* by using the respective Fe^{II} salt in 2:1 DCM/MeOH solvent mixture to get a yellowish powder. Attempts to crystallize the complex *I* in various solvents were unsuccessful as it formed single crystals not suitable for X-ray diffraction.

The temperature dependent magnetic susceptibility of complex I showed a reversible SCO behavior at multiple heating and cooling cycles (Figure 1). The heating mode



Figure 1. χT vs *T* plot for the complex *I* measured in the temperature range of 2–340 K in the heating, cooling, and heating mode cycles with an applied DC magnetic field of 0.5 T. Inset shows the multiple cycle measurements of samples obtained from two different batches.

measurement was performed only up to 340 K to avoid sample melting. At 340 K the product of the molar magnetic susceptibility and temperature (χT) is 3.56 emu K mol⁻¹, which is almost close to an expected value for a HS iron(II) ion (S = 2). Upon cooling the χT value decreased sharply and reached a minimum value of 1.03 emu K mol⁻¹ down to \sim 210 K indicating operating SCO behavior. The calculated $T_{1/2}$ value of this regime is 270 K, which remained nearly constant for three heating and cooling cycles. Interestingly, the SCO curve was accompanied by a hysteresis loop ($\Delta T_{1/2}$). In the first measurement cycle the $\Delta T_{1/2}$ was about 5 K, which reduced to 2 K at the end of the third cycle, indicating the evaporation of trapped solvent/moisture from the powder sample. Below 210 K the χT value decreased very sluggishly and reached 0.34 emu K mol⁻¹ at 16 K. Upon subsequent cooling the χT value dropped down abruptly to the minimum value of 0.07 emu K

 mol^{-1} at 2 K because of zero-field splitting of the remaining HS molecules. Calculation of the number fraction (*f*) involved in the SCO event showed that about 70% of the molecules undertake rather sharp SCO in the temperature range of 340 K–210 K, and the remaining fractions show very sluggish SCO below 210 K down to 16 K. The lowest value of about 0.34 emu K mol⁻¹ in the sluggish plateau indicates the presence of paramagnetic impurities in the sample. EPR measurement of the sample down to 4 K confirmed the presence of HS state Fe(III) impurities by displaying characteristic peaks (Supporting Information, Figure S10).

Furthermore in $Fe-N_6$ SCO compounds, the difference in the average Fe-N bond distances between HS and LS states is ~0.2 Å. Hence Raman spectroscopy at variable temperature is a very sensitive technique to probe the Raman active vibration modes associated with HS + LS state structural transformations in ${\rm Fe}^{({\rm II})}$ complexes. Confocal Raman spectroscopy investigations at 77 K (HS 14%; LS 86%), 298 K (HS 88%; LS 12%), and 348 K (99% \sim HS) were performed to monitor the SCO event. In comparison to the Raman spectrum at 348 K, the low temperature spectrum showed two new prominent peaks at 899 cm⁻¹ and 1127 cm⁻¹. Additionally, the intensity of the peaks at 1021 cm⁻¹ and 1398 cm⁻¹ gradually increased in the LS state. This observed result supports the operating SCO phenomenon. The other major vibration bands at 964 cm⁻¹, 998 cm⁻¹, 1021 cm⁻¹, 1398 cm⁻¹, 1441 cm⁻¹, 1445 cm⁻¹, 1590 cm⁻¹, and 1610 cm^{-1} correspond to complex *I* in both spin states (Figure 2).



Figure 2. Variable temperature Raman spectra of complex I in thin pellet state at 77 K, 298 K, and 323 K.

The octahedral SCO complex *I* was highly soluble in common solvents because of the presence of four octyl chains per Fe^(II) complex molecule. Taking advantage of its solubility, lithographic patterning of SCO compound *I* into several geometrical shapes embedded within an optically transparent flexible polymer film was envisaged. Hence, we prepared several new PDMS stamps consists of (i) 1D wedge stripes, (ii) 1D rectangular stripes, and (iii) 0D square pillars from several commercially available AFM standards (Supporting Information, Figures S8, S9). For the nano/micro fabrication, at first a LCW technique on glass slide was adopted. A 20 μ L acetonitrile solution of complex *I* was injected on a clean glass slide. After that the PDMS stamp was pressed with a weight of

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Figure 3. (a,e,i) Optical images of wedge stripes, rectangular stripes, and square pillars, respectively. (b,f) SEM images of wedge and rectangular stripes. (c,g,j) AFM 3D images of wedge stripes, rectangular stripes, and square pillars, respectively. (d, h, k) AFM topographic profile (height and width) of the patterns shown in c,g,j, respectively.

 \sim 10 g. This pressure allowed the solution to stay in the micro channels. As the solvent evaporates, the solute nicely precipitates onto the substrate only below the micro channels, giving rise to a structured pattern that replicates the negative feature of the stamp.

The confocal microscope (Figure 3a) and SEM image (Figure 3b) of the 1D wedge stripes showed that the length of a SCO stripe is extended up to several hundred micrometers with the height within the submicrometer domain. The AFM profile measurements of the wedge stripes showed that the height, fwhm (full width at half maxima), and period/channel parameters were 400 nm, 830 nm, and 3 μ m, respectively (Figure 3c, d). The triangular edge angle of a stripe was about 70°. Investigation of the rectangular stripes by confocal microscopy and SEM studies revealed the formation of periodic micro stripes of several millimeters in length which are well separated by empty channels (Figure 3e, f). AFM topography measurement of the same sample showed that the rectangular micro stripes width \times height \times roughness (along the stripe) profiles were about 2 μ m × ~400 nm × ~7 nm, respectively, with a uniform periodicity (Figure 3g, h). The empty channel width between the two adjacent micro stripes was about 1.5 μ m. Additionally we have fabricated 0D micro square pillars which might be useful as logical structures as well as photonic applications if the synergy between the two is established. The optical microscope clearly exhibited the presence of 0D micro square pillar arrays on a 2D surface (Figure 3i). AFM measurements revealed the formation of nearly perfect squares with the height (H) and width (W) profiles of 25 nm $\times 1.5 \,\mu$ m, respectively (Figure 3 j, k). Here, the height of each square is 27 times smaller than the height of the 1D array. The top surface area of each square is just 2.25 μ m². Confocal Raman spectroscopy (laser: He-Ne 633 nm) studies evidently confirmed the chemical composition of all arrays by displaying characteristic peaks corresponding to complex I [Fe^{II}(L)₂]- $(BF_4)_2$. Furthermore the empty channel/areas showed no Raman signals indicating the precision and quality of the patterns (Supporting Information, Figure S1).

Finally to fabricate a flexible, compact, and easy to handle nano/micro scale transparent SCO device, as a model, we intended to embed the microstripes within a transparent polymer film. In this context, we found polystyrene (PS) quite attractive, since it is easy to handle and dissolves in most of the organic solvents except acetonitrile. The solubility of the polymer plays an important role because the polymer should not dissolve in the solvent which is used for the preparation of SCO complex nano/micro patterns. For fabrication, at first a toluene solution of PS was prepared by dissolving 125 mg of PS in 2 mL of toluene. Then a thin layer of PS was fabricated on a clean and smooth glass substrate of dimension (1.2 cm \times 1.5 cm) by drop casting of 100 μ L of the polymer solution. Upon evaporation of the solvent, a free-standing thin film of thickness around 5-6 μ m was obtained (see Supporting Information, Note on Figure S7). Subsequently, a 1D rectangular stripe composed of SCO complex I was fabricated on the top of the PS layer. The formation of the rectangular stripes was easily observed by confocal optical microscope. Finally, the SCO pattern was concealed by carefully spin coating a PS solution without destroying the lower PS layer. The photograph of a flexible SCO device of area 2 mm² embedded within an optically transparent polymer film is shown in Figure 5. Similarly for TEM measurement the device was fabricated on a copper-coated TEM grid and the PS layers were formed by spin coating of a toluene solution PS at 1000 rpm for 10 s.

TEM investigation of the flexible polymer embedded SCO thin film clearly showed light and dark areas from the polymer and dark 1D SCO pattern, respectively (Figure 4a-c). Additionally, the energy dispersive X-ray analysis (EDAX) evidently confirmed the presence of Fe in the dark SCO patterns, by exhibiting Fe signals (Figure 4d). Raman spectroscopy/imaging of the embedded film showed collective signals from PS and complex I. Imaging of Raman signal (at 958 cm⁻¹ corresponds to complex I) established the presence of a rectangular stripe at regular intervals within the polymer matrix (see red color, Figure 5a,b). Imaging of the PS signal (1037 $\,\mathrm{cm^{-1}})$ is shown in blue color, which confirmed the distribution of polymer in the entire area of the film (Figure 5c,d). The combination of the two images (Figure 5b and Figure 5d) is shown in Figure 5f. Here, the blue area indicates the presence of PS and the pink lines (red+ blue color code mixing) correspond to complex I stripes as well as PS.

4. CONCLUSIONS

A highly soluble $\text{Fe}^{(II)}$ SCO compound with the $T_{1/2}$ of 270 K was prepared from a novel 4,4"-dioctylated 2,6-bispyrazolylpyrine ligand. Various nano/microscale geometric patterns composed of the $\text{Fe}^{(II)}$ SCO complex were successfully fabricated. Keeping in mind that the SCO pattern can act as

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Figure 4. (a) SCO complex (*I*) embedded PS film formed on TEM grid (scale bar is 10 μ m). (b and c) A folded film displaying its optical transparency. (d) EDAX performed on the SCO stripes is marked in white circle displaying Fe signals for K_{av} K_b, and L lines at 6.4, 6.9, and 0.65 KeV, respectively.



Figure 5. Raman spectroscopy/images of a flexible SCO complex I embedded PS film. (a) Raman spectrum of complex I. (b) Imaging of the SCO device embedded PS film using complex I peaks. (c) Raman spectrum of bulk PS film. (d) Imaging of the SCO device embedded PS film using PS peaks. (e) Raman spectrum of SCO complex I embedded film. (f) Combined image of b and d. The bottom photographs show the flexibility of the SCO device embedded within the optically transparent polymer film.

future memory based devices, we have embedded one of the patterns within an optically transparent and flexible polymer. The embedded film was well characterized to support their fabrication as well as functional behavior. The presented technology is very simple, unprecedented, and promising for potential future development in the SCO-based memory storage devices.

ASSOCIATED CONTENT

S Supporting Information

Micro Raman image of fabricated pattern, FTIR spectra, film thickness measurement, AFM images of embedded pattern, AFM and SEM images of PDMS molds and copies of ¹HNMR, ¹³CNMR, DEPT, LC mass and elemental analysis data. This material is available free of charge via the Internet at http:// pubs.acs.org.

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The authors declare no competing financial interest.

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ABBREVIATIONS

SCO, Spin crossover; PS, Polystyrene; BPP, Bispyrazolyl pyridine; TLC, thin layer chromatography

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