Flexible and Optically Transparent Polymer Embedded Nano/Micro Scale Spin Cross-Over Fe(II) Complex Patterns/Arrays
3.1 Abstract

A novel spin-crossover (SCO) \([\text{Fe}^{II}(L4)_2](BF_4)_2\) complex (C2) was prepared, where \(L4\) is 4,4''-dioctylated 2',6'-bispyrazolylpyridine. Complex C2 shows reversible temperature dependent SCO behaviour with a \(T_{1/2}\) centred around 270 K together with a ~2 K wide hysteresis loop. Exploiting the high solubility and hence superior processability of SCO complex C2, nano/micro scale arrays and square patterns were fabricated on a glass substrate. Additionally, for the first time, for possible flexible technological applications, the SCO arrays (area \(2 \times 2 \text{ mm}^2\)) 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 behaviour of complex C2.

3.2 Introduction

SCO or spin transition compounds, are an efficient spin-state switchable (high-spin; HS ↔ low-spin; LS) bistable inorganic materials 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; \(S = 2\); paramagnetic ↔ LS; \(S = 0\); diamagnetic) with respect to external stimulus such as pressure,\(^3\) temperature,\(^3,\)\(^4\) magnetic field,\(^5\) electric field\(^1\)\(^d\) and light irradiation.\(^5\)\(^b\) Among the other applications, one of the uses of these SCO compounds is possible exploitation as logical structures (0 or 1) for information storage.\(^1\)\(^c\) For potential technological applications, fabrication of diverse nano/micro scale SCO domains having various dimensions and shapes are an essential step.

Great amount of efforts have been taken towards 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 ST thin films was reported by Kahn et al. using Langmuir–Blodgett (LB) techniques\(^6\) and then later developed by many other groups.\(^7\) Patterning of spin crossover compounds was carried out previously by electron beam lithography,\(^8,\)\(^9\) polymeric masks\(^10\) and also by soft lithographic techniques\(^11\)\(^a\) such as micro molding in capillaries\(^11\)\(^b\) and micro transfer molding.\(^10\)\(^a\) Earlier, Cavallini and Ruben et al. have reported the fabrication of one dimensional (1D) ST micro arrays using PDMS (polydimethylsiloxane) stamps on a glass
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-bispyrazolylpyridine ligand and Zn\(^{II}\) ions (discussed in chapter 2).\(^{13}\) Till now all of the existing SCO based nano/micro molding was performed on non-flexible solid substrate. 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 with in an optically transparent polymer substrate.

In this chapter, we present a new synthetic protocol for the preparation of novel 4,4″-dioctylated 2,6-bispyrazolylpyridine (Oct-BPP) ligand \(L_4\) and its SCO complex \([\text{Fe}^{II}(L_4)_2](\text{BF}_4)_2\) (C2). We also present the utilization of model compound C2 to pattern nano/micro scale i) 1D wedge stripes, ii) 1D rectangular stripes and iii) 0D square pillars using LCW (lithographically controlled wetting) technique. Additionally by keeping the flexible device fabrication in mind, for the first time, linear SCO arrays were successfully implanted within an optically transparent polymer film. All fabricated nano/micro SCO 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 property of the bulk materials was studied by using variable temperature magnetic susceptibility and Raman spectroscopy.

**3.3. EXPERIMENTAL SECTION**

**3.3.1 Synthesis:**

Compounds 23 and 24 were prepared according to literature procedure.\(^{14,15a}\)

**2,6-bis(4-(oct-1-ynyl)-1H-pyrazol-1-yl)pyridine (25):** A Schlenk flask was charged with 2,6-bis(4-iodo-1H-pyrazol-1-yl)pyridine 24 (500 mg, 1.07 mmol) together with Pd(PPh\(_3\))\(_2\)Cl\(_2\) (37.89 mg, 0.053 mmol), triphenylphosphene (50 mg, 0.19 mmol) and CuI (200 mg, 0.262 mmol). Freshly distilled anhydrous triethylamine (Et\(_3\)N, 20 mL) and 1,4-dioxane (10 mL) were added to it. The flask was carefully degassed by freeze-and-thaw cycles several times. 1-octyne (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 hour. 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 white solid of 25. Yield 350 mg (76%). mp 86-87 °C. $^1$H 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. $^{13}$C NMR (100 MHz, CDCl$_3$) 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. Raman Shift (powder, RT, $\lambda_{ex}$ = 633 line of He-Ne laser): 954, 997, 1076, 1260, 1405, 1442, 1487, 1569, 1588, 2241 (-C≡C-) cm$^{-1}$. LC-MS $m/z$ calc 427.27, found 428.10. ESI-MS: $m/z$ calc 427.27, found 428.2714 [M$^+$+H]. Anal. Calcd for C$_{27}$H$_{33}$N$_5$: C, 75.84; H, 7.78; N, 16.38%. Found: C, 75.92; H, 7.85; N, 16.27%.

Scheme 3.1 Reagents and conditions: (a) K/Diglyme, 5 days; (b) I$_2$/HIO$_3$; (c) 1-octyne, Cul, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, dioxane/TEA; (d) Pd/C, H$_2$, 1 h; (e) DCM/MeOH, Fe(BF$_4$)$_2$·6H$_2$O.

2,6-bis(4-octyl-1H-pyrazol-1-yl)pyridine (L4): To a degassed solution of 25 (0.3 g, 0.07 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 hour the mixture was filtered through a celite plug to remove activated Pd/C and subsequently washed with 100 mL of EtOAc. The collected fractions were combined and concentrated in vacuum to get compound L4 as viscous oil. Yield 0.302 g ( $>$99%) $^1$H NMR (400 MHz, CDCl$_3$) 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. $^{13}$C NMR (100 MHz, CDCl$_3$) 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. Raman Shift (powder, RT, $\lambda_{ex}$ = 633 line of He-Ne laser): 954, 997, 1076, 1439, 1469, 1591, 1609 cm$^{-1}$. LCMS analysis: $m/z$ calc 427.27.
3.3.2 Method for pattering. Micro patterning of \( C_2 \) was carried out by drop casting 20 \( \mu L \) acetonitrile solution of \( C_2 \) (2 mg/mL) on a glass substrate. Before use, the substrate was cleaned by sonication using electronic-grade water (Milli-Q-pure quality), acetone (Aldrich chromatography quality) and 2-propanol (Aldrich spectroscopic-grade quality) for 2 min each. Before micro patterning, an acetonitrile (Aldrich, ≥ 99% purity) solution of \( C_2 \) was filtered through a Whatman filter paper.

3.3.3 Stamps for lithograph:\(^{12,13}\) Elastomeric PDMS (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 (Fig. 3.1) 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.

3.3.4 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 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 for a 100X objective having NA 0.95, four points per line and four line per image was taken for imaging of a 1\( \mu m \) x 1\( \mu m \) area. A He-Ne 633 nm laser was
used as an excitation source for the Raman scattering. All measurements were done at ambient conditions.

3.4 RESULT AND DISCUSSION

3.4.1 Synthesis:

Ligand $L_4$ was synthesized from a commercially available 2,6-dibromopyridine in four steps in good yields (Scheme 3.1). Conversion of 2,6-dibromopyridine into 2,6-bispyrazolylpyridine $23$ was carried out as per the reported procedure. Compound $23$ was successfully converted to its diiodinated derivative $24$ as per our earlier procedure in 74% yield. Transformation of compound $24$ into $25$ was achieved via Sonogashira coupling reaction conditions by using 1-octyne in Et$_3$N/THF solvents using Pd(PPh$_3$)$_2$Cl$_2$ catalyst in 78% yield. The alkynes groups in $25$ was reduced using Pd/C under H$_2$ atmosphere to obtain highly soluble 2,6-dioctylated bispyrazolylpyridine $L_4$ in a quantitative 99% yield. The reduction of compound $25$ was confirmed by disappearance of $-C≡C-$ peak in $^{13}$C NMR at 92.7 and 70.6 ppm and appears below 40 ppm i.e. aliphatic region. The progress of the reaction can also be confirmed by Raman spectroscopic measurement. The $-C≡C-$ Raman shift which appears at 2241 cm$^{-1}$, disappears for $L_4$ (Fig. A2). An yellowish mononuclear iron(II) complex $[\text{Fe}^{	ext{II}}(L_4)_2](\text{BF}_4)_2$ ($C_2$), was synthesized from $L_4$ by using the respective Fe(II) salt in 2:1 DCM/MeOH solvent mixture. Attempts to crystallize the complex $C_2$ in various solvents were unsuccessful as it formed single crystals not suitable for X-ray diffraction.

3.4.2 UV-Vis Spectroscopy Studies:

![Figure 3.2](a) Absorption and emission spectra of ligand $L_4$ and compound $25$ recorded at RT. (b) Absorption spectra of complex $C_2$ in DCM recorded at RT.
Compounds 25 and L4 in dichloromethane (DCM) displayed absorption/emission maxima ($\lambda_{\text{max}}$) centered at 318/343 and 310/337 nm, respectively. Whereas the UV–Vis absorption studies of $\sim 10^{-5}$ M DCM solution of complex C2 showed an absorption maximum ($\lambda_{\text{max}}$) at 314 nm, (Fig. 3.2 b) which is 4 nm red shifted compared to ligand L4. The broad band in Fig. 3.2b at around 400-500 region can be assigned to metal to ligand charge transfer.\textsuperscript{17}

\subsection*{3.4.3 Magnetic Susceptibility Studies:}

The temperature dependent magnetic susceptibility of complex C2 showed a reversible SCO behavior at multiple heating and cooling cycles (Fig. 3.3). The heating mode measurement was performed only up to 340 K to avoid sample melting. At 340 K the product of the molar magnetic susceptibility and temperature ($\chi T$) is 3.56 emu K mol\textsuperscript{-1}, which is almost close to an expected value for a HS iron(II) ion ($S = 2$). Upon cooling the $\chi T$ value decreased sharply and reached a minimum value of 1.03 emu K mol\textsuperscript{-1} down to ~ 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 microcrystalline powder sample. Below, 210 K the $\chi T$ value decreased in a sluggish manner and reached 0.34 emu K mol\textsuperscript{-1} at 16 K. Upon subsequent cooling the $\chi T$ value dropped down abruptly to the minimum value of 0.07 emu K mol\textsuperscript{-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 ca. 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 (Fig. A3).

### 3.4.4 Raman Spectroscopy Studies:

Furthermore in Fe–N\(_6\) type SCO compounds; the difference in the average Fe–N bond distances between HS and LS states is ~ 0.2 Å. This is due to the population of the anti-bonding e\(_g^*\) orbitals in the HS state. Hence Raman spectroscopy at variable temperature is a very sensitive technique to probe the Raman active vibration modes associated with HS↔LS state structural transformation in Fe(II) complexes. Confocal Raman spectroscopy investigations of complex \(\mathbf{C2}\) at 77 K (HS 14%; LS 86%), 298 K (HS 88%; LS 12%) and 323 K (99% ~ 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 observation supports the operating SCO phenomenon in \(\mathbf{C2}\). 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 \(\mathbf{C2}\) in both spin states (Fig. 3.4).

### 3.4.5 Micro/Nano Fabrication

The octahedral SCO complex \(\mathbf{C2}\) 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 \(\mathbf{C2}\) into several geometrical shapes embedded within an optically transparent flexible polymer film was envisaged. Hence,
several new PDMS stamps consists of i) 1D wedge stripes, ii) 1D rectangular stripes and iii) 0D square pillars from several commercially available AFM test gratings, were prepared (Fig. 3.5 and 3.6).

For nano/micro fabrication, at first LCW technique on glass slide was adopted. A 20 μL acetonitrile solution of complex C2 was placed on a clean glass slide. After that the PDMS stamp was gently placed on the solution meniscus and the stamp was pressed with a weight of ~10 g. This pressure allowed the solution to stay within the micro channels of the stamp. As the solvent evaporates, the solute precipitates onto the substrate only

Figure 3.5 Non contact mode AFM images, height profile and 3D image of (a, b and c) Rectangular pattern, (d, e and f) Triangle pattern, and (g, h and i) Square pattern of molds.

Figure 3.6 SEM images of (a) Rectangular pattern, (b) Triangle pattern of mold.
below the micro channels, giving rise to a structured pattern that replicates the negative features of the stamp. The confocal microscope (Fig. 3.7a) and SEM image (Fig. 3.7b) of

![Image](image.png)

**Figure 3.7** 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.

the 1D wedge stripes showed that the length of a SCO stripe is extended up to several hundred micrometers with the height within the submicron 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 µm, respectively (Fig. 3.7c, 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 long which are well separated by empty

![Image](image.png)

**Figure 3.8** Micro-Raman image of wedge and rectangular patterns: a) Raman image of a wedge pattern. b) Raman intensity profile along the red line in c. c) Raman 3D image profile. d) Raman image of rectangular pattern. e) Raman 3D profile. f) Raman signal from the empty channel (violet line), Raman signal along the stripes (red line).

channels (Fig. 3.7e, f). AFM topography measurement of the same sample showed that
the rectangular micro stripes width × height × roughness (along the stripe) profiles were about 2 µm × ~ 400 nm × ~ 7 nm, respectively, with a uniform periodicity (Fig. 3.7g, h). The empty channel width between the two adjacent micro stripes was about 1.5 µm. Similarly, arrays of 0D micro square pillars were fabricated, which might be useful as logical structures with photonic properties, if the synergy between the two properties is established. The optical microscope evidently displayed the presence of 0D micro square pillar arrays covering wide surface area (Fig. 3.7i). AFM measurements revealed the formation of nearly perfect squares with the height (H) and width (W) profiles of 25 nm × 1.5 µm, respectively (Fig. 3.7j, k). Here, the height of each square is 27 times smaller than the height of 1D arrays. The top surface area of each square is just 2.25 µm². Confocal Raman spectroscopy (laser: He-Ne 633 nm) studies evidently confirmed the chemical composition of all arrays by displaying characteristic peaks corresponding to complex $C_2 \left[ Fe^{II}(L_4)_2 \right] (BF_4)_2$. Furthermore the empty channel/areas showed no Raman signals indicating the precision and quality of the patterns (Fig. 3.8).

3.4.6 Fabrication of Flexible SCO Device:

Finally to fabricate a flexible, compact and easy to handle nano/micro scale transparent SCO device, as a model, we intended to embed these micro stripes 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 solvent 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 nano/micro patterns. For fabrication, at first a solution of PS in toluene 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 × 1.5 cm) by drop casting of 100 µL of the polymer solut-
Upon evaporation of the solvent, a free standing thin film of thickness around 5-6 µm was obtained (Fig. 3.9). The thickness of a sample film was determined by scratching the film with a scalpel and then measuring the lateral profile by AFM. Subsequently, a 1D rectangular stripe composed of SCO complex C2 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 flexible SCO device of area $2 \times 2 \text{mm}^2$ embedded within an optically transparent polymer film is shown in (Fig. 3.12).

For TEM measurement the SCO device was fabricated on a copper-coated TEM grid and the top and bottom PS layers were formed by spin coating of a toluene solution of PS at 1000 rpm for 10s. The total entrenched polystyrene layer thickness is around 6.2 µm. The bottom layer thickness is ~ 5-6 µm and top layer thickness is ~ 200 nm as measured from AFM (Fig. 3.10). However it is possible to change the polymer layer thickness by changing the concentration of PS solution and spin coating speed. TEM investigation of the flexible polymer embedded SCO thin film clearly showed a light and
dark areas from the polymer and SCO pattern, respectively (Fig. 3.11a-c). Additionally, the energy dispersive X-ray analysis (EDAX) evidently confirmed the presence of Fe in the dark SCO patterns, by exhibiting characteristic Fe signals (Fig. 3.11d). Raman spectroscopy/imaging of the embedded film showed collective signals from PS and complex $C_2$. Imaging of Raman signal (at 958 cm$^{-1}$) corresponds to complex $C_2$) established the presence of rectangular stripe at regular intervals within the polymer matrix (see red color, Fig. 3.12a, b). Imaging of the PS signal (1037 cm$^{-1}$) is shown in blue in color, which confirmed the distribution of polymer in the entire area of the film (Fig. 3.12c, d). The combination of the two images (Fig. 3.12b and Fig. 3.12d) is shown in (Fig. 3.12f). Here, the blue area indicates the presence of PS and the pink lines (red + blue color code mixing) correspond to complex $C_2$ stripes as well as PS.

![Figure 3.12](image)

**Figure 3.12** Raman spectroscopy/images of a flexible SCO complex $C_2$ embedded PS film. a) Raman spectrum of complex $C_2$. b) Imaging of the SCO device embedded PS film using complex $C_2$ 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 $C_2$ 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.
Chapter 3
Polymer Embedded Soft Lithographic Fe(II) Complex Pattern

3.5 Conclusions

A highly soluble Fe(II) SCO compound with the \( T_{1/2} \) of 270 K was prepared from a novel 4,4"-dioctylated 2,6-bispyrazolylpyridine ligand. Various nano/microscale geometric patterns composed of the Fe(II) SCO complex was successfully fabricated. Keeping in mind that the SCO pattern can act as future memory based devices, one of the patterns was embedded within an optically transparent and flexible polymer. The embedded film was well characterized to support their fabrication as well as functional behaviour. The presented technology is very simple, unprecedented and promising for potential future development in the SCO-based memory storage devices.

References
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Appendix

FTIR Spectra:

![FTIR spectra](image)

**Figure A1.** FTIR spectra of complexes and ligands.
NOTE (Fig. A1.): Compound 25: 3146 cm\(^{-1}\) (−C≡C−), 1599, 1464, 2361 cm\(^{-1}\) (aromatic −C≡C−). Compound L4: 1475, 1585, 1390 cm\(^{-1}\) (aromatic −C≡C−). Complex C2: 1103 cm\(^{-1}\) (broad, B-F), 1572, 1491, 1400 cm\(^{-1}\) (aromatic −C≡C−).

Figure A2. Confocal Raman micro spectroscopic data of powder sample complex C2 and ligands. Excitation wavelength \(\lambda_{ex} = 633\) nm (He-Ne Laser).

NOTE (Fig. A2.): Confocal Raman micro spectroscopy investigation of bulk powder of complex C2 and ligands have shown clear evidence for the formation of complex from ligand L4. The peaks 1266, 1555 and 1681 cm\(^{-1}\) in complex C2 are newly appeared and 1397 cm\(^{-1}\) peak is disappeared. The doubled peaks of ligand L4 at 1591 and 1609 cm\(^{-1}\) are shifted to 1585 and 1612 cm\(^{-1}\) in complex C2. The −C≡C− stretching frequency is showing at 2241 cm\(^{-1}\) in compound 25. This is disappearing at ligand L4. There are new peaks at 1076 and 1260 cm\(^{-1}\) in compound 25. The 1405 cm\(^{-1}\) peak intensity increased and shifted in ligand L4 than 25.

Figure A3. Liquid He temperature ESR measurement of Fe\(^{II}\)(L4)\(_2\)BF\(_4\)\(_2\). Parameters: frequency 9.388755 GHz, and 100 kHz modulation frequency, 0.3 Gauss modulation amplitude, 21 msec time constant, 42 sec sweep time, 0.998 mW microwave power, 105 gain, 1 scan.

NOTE (Fig. A3.): The ESR measurement of the powder sample of complex C2 at 4 K shows signal due to Fe\(^{III}\) impurities.