Supplementary information

Iron(II) Spin Cross-Over (SCO) Materials Based On 2,2'-Dipyridyl-*N*-Alkylamine

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1 - Syntheses.

a - General Considerations. All the starting reagents were purchased from commercial sources (Sigma-Aldrich, Acros and Alfa Aesar) and used without further purification. Deuterated solvents were purchased from Sigma-Aldrich and Cambridge Isotope Laboratories.

b - Synthesis of the 2,2'-dipyridyl-*N*-alkylamine ligands.

2,2'-Dipyridyl-*N*-ethylamine (dpea) has been prepared according to the procedure described in the reference [1]. Yield (1.777 g, 77 %).

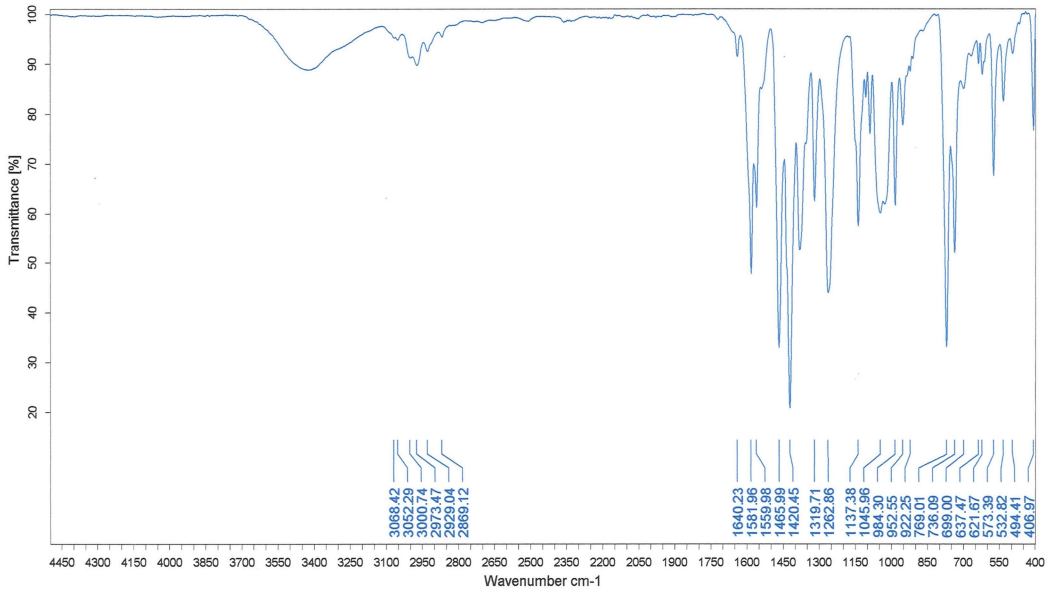

Figure S1. IR data (ν/cm^{-1}) for dpea: 3068w, 3052w, 3001w, 2973w, 2929w, 2869w, 1640w, 1582s, 1560m, 1466s, 1420s, 1320m, 1263s, 1137m, 1046w, 984m, 953m, 922w, 769s, 736m, 699w, 637w, 622w, 573m, 533w, 494w, 406w.

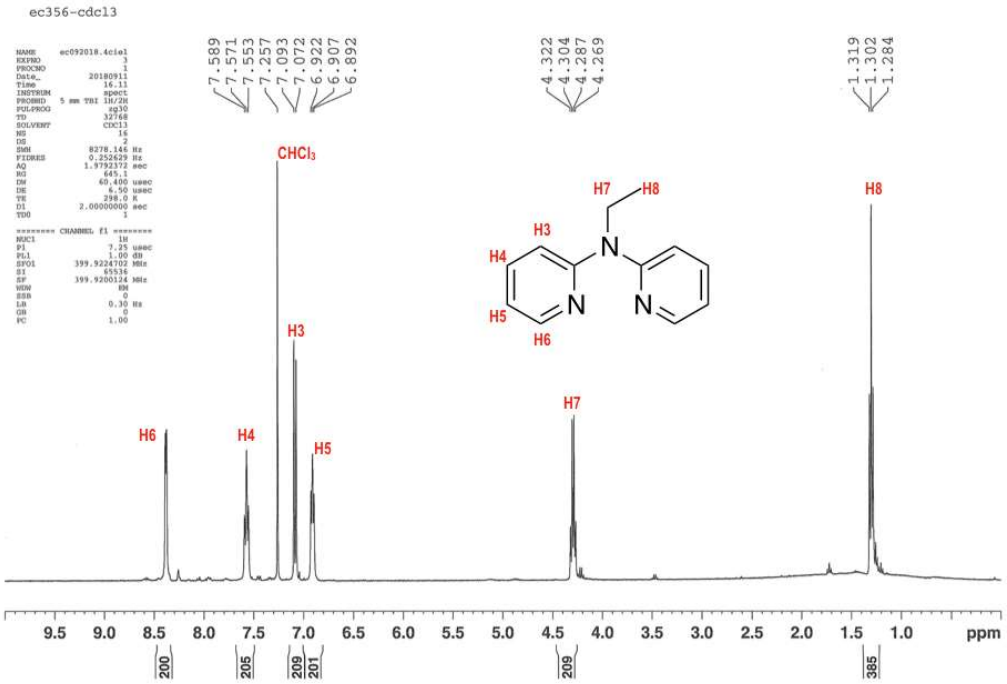

Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$ δ (ppm) for dpea: 1.30 (3H, t, $^{3}J_{H\text{-}H}$ = 6.8 Hz); 4.30 (2H, q, $^{3}J_{H\text{-}H}$ = 7.2 Hz); 6.90 (2H, t, $^{3}J_{H\text{-}H}$ = 6 Hz); 7.08 (2H, d, $^{3}J_{H\text{-}H}$ = 8.4 Hz); 7.57 (2H, t, $^{3}J_{H\text{-}H}$ = 7.2 Hz); 8.37 (2H, d, $^{3}J_{H\text{-}H}$ = 4.3 Hz).

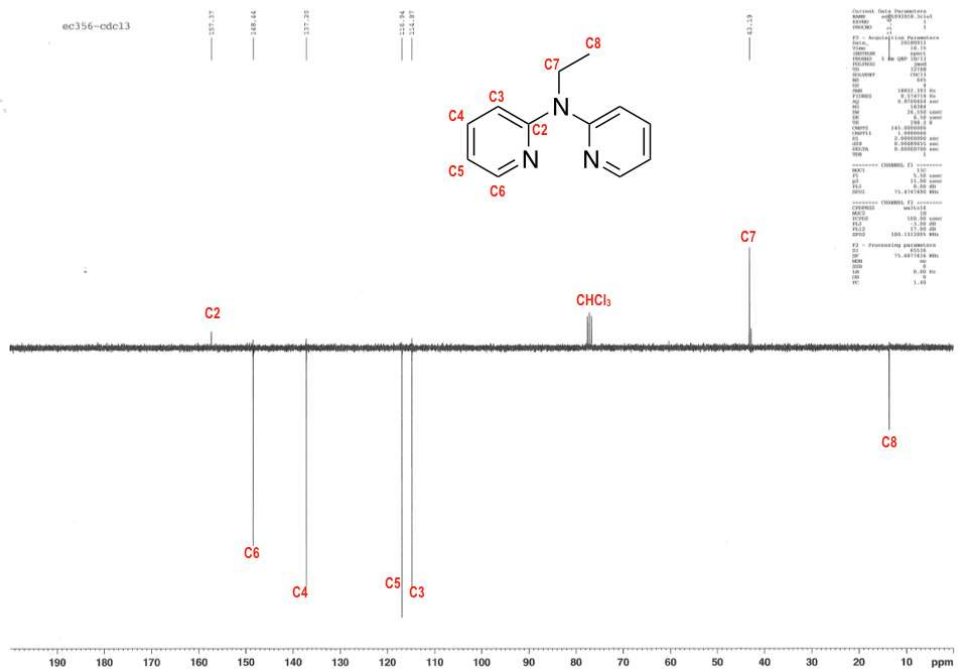

Figure S3. ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) for dpea: 13.66 (-CH_3, ethyl); 43.19 (N-CH_2-, ethyl); 114.87(C=C, aromatic); 116.94 (C=C, aromatic); 137.20 (C=C, aromatic); 148.44 (N=C, aromatic); 157.37 (C=C, aromatic, quat).

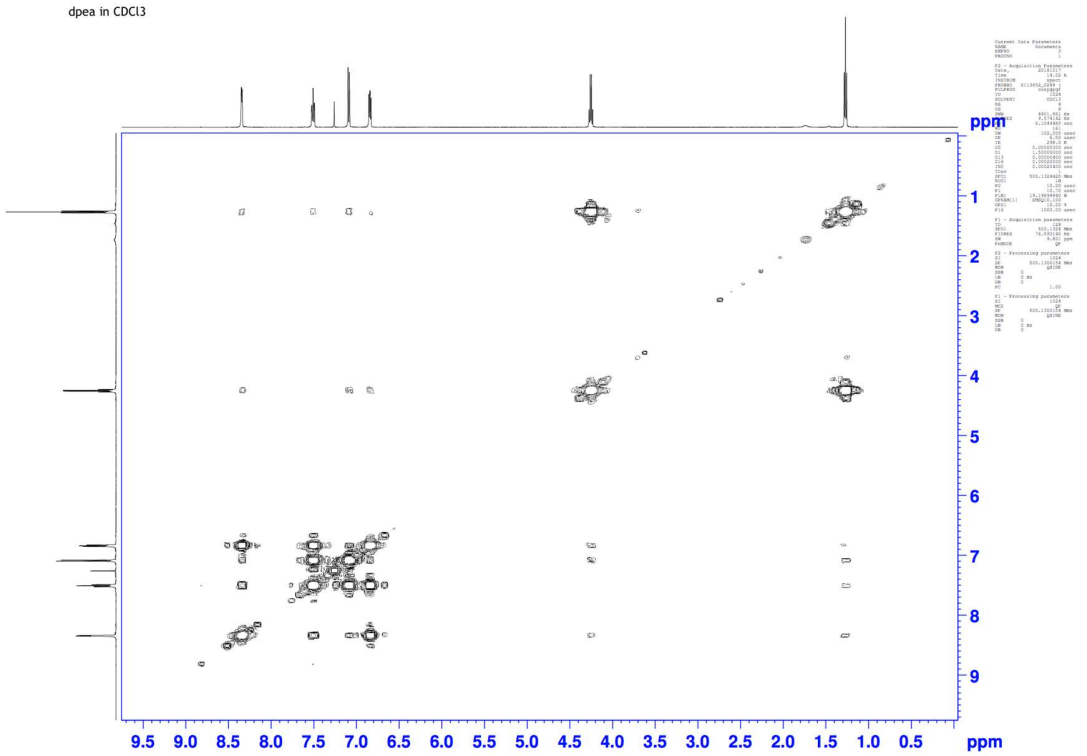

Figure S4. ^{1}H-^{1}H COSY, NMR (500 MHz, $CDCl_3$) δ (ppm) for dpea.

2,2'-Dipyridyl-*N*-propylamine (dppa) has been prepared by using similar procedure reported for 2,2'-dipyridyl-*N*-ethylamine (dpea) by replacing the ethyl iodide by the propyl iodide [1]. Yield (0.935 g, 73 %).

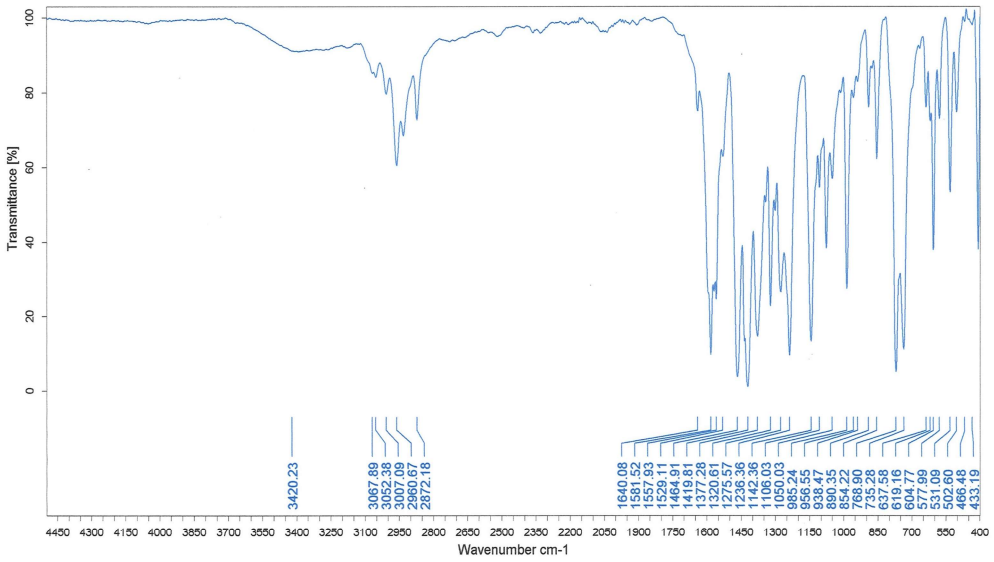

Figure S5. IR data (ν/cm^{-1}) for dppa: 3420br, 3068w, 3052w, 3007m, 2961m, 2872m, 1640w, 1582s, 1558s, 1529m, 1465s, 1419s,1377s, 1321m, 1276s, 1236m, 1142m, 1106m, 1050m, 985f, 957m, 938m, 890s, 854w, 768s, 735s, 638w, 619m, 605m, 578m, 531m, 503m, 466w, 433m.

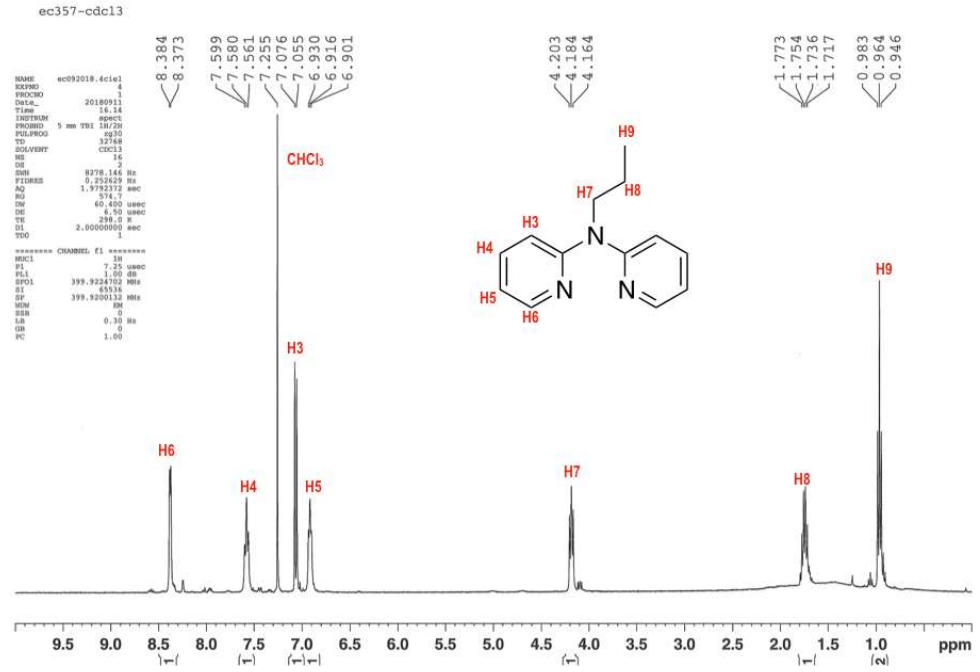

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) for dppa: 0.96 (3H, t, $^{3}J_{H\text{-}H}$ = 7.6 Hz), 1.74 (3H, q, $^{3}J_{H\text{-}H}$ = 7.6 Hz, $^{3}J_{H\text{-}H}$ = 7.9 Hz); 4.18 (2H, t, $^{3}J_{H\text{-}H}$ = 8 Hz); 6.91 (2H, t , $^{3}J_{H\text{-}H}$ = 5.6 Hz); 7.06 (2H, d, $^{3}J_{H\text{-}H}$ = 8.4 Hz); 7.58 (2H, t, $^{3}J_{H\text{-}H}$ = 7.6 Hz); 8.37 (2H, d, $^{3}J_{H\text{-}H}$ = 4.4 Hz).

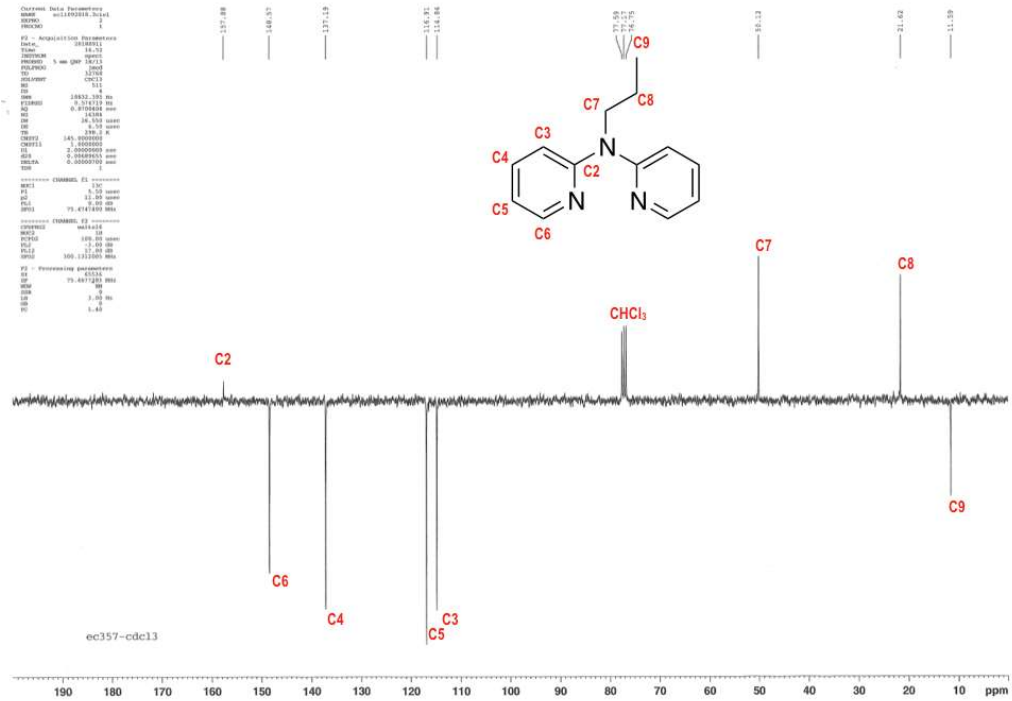

Figure S7. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) for dppa: 21.62 (CH_3-CH_2-); 50.12 (N-CH_2-); 114.84 (C=C, aromatic); 116.91 (C=C, aromatic); 137.19 (C=C, aromatic); 148.57 (N=C, aromatic); 157.88 (C=C, aromatic, quat).

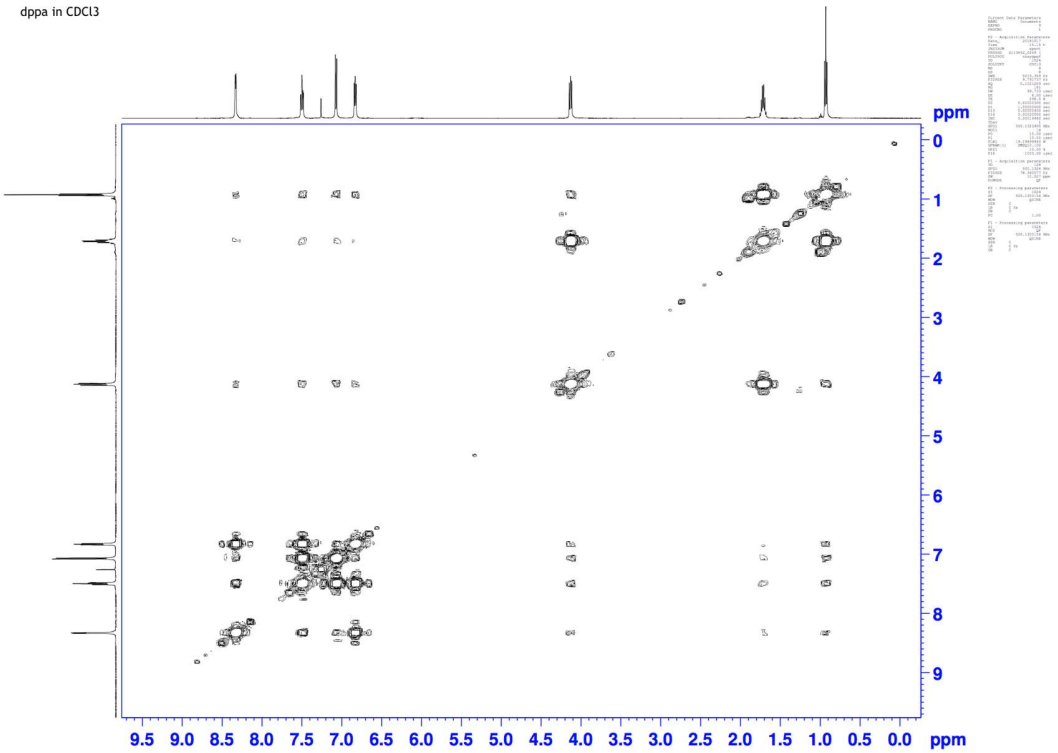

Figure S8. ^{1}H-^{1}H COSY, NMR (500 MHz, $CDCl_3$) δ (ppm) for dppa

c - Preparation of the Fe(II) complexes.

$[Fe(dpea)_2(NCS)_2]$ (**1**). Single-crystals of **1** were prepared using slow diffusion procedure, in a fine glass tube (3.0 mm diameter): a first solution was obtained by a mixture of aqueous solution (1.0 mL) of $FeCl_2.4H_2O$ (13 mg, 0.065 mmol) and ethanolic solution (1.0 mL) containing dpea ligand (25.9 mg, 0.13 mmol). The second solution was prepared by dissolving potassium thiocyanate (12.63 mg, 0.13 mmol) in 1.0 mL of H_2O and placed in the fine glass tube. The first solution (2 mL) was then carefully added. After three days, yellow small prismatic crystals of **1** were formed by slow diffusion at room temperature. Anal. Calcd. for $C_{26}H_{26}FeN_8S_2$ (**1**): C, 54.7; N, 19.6; H, 4.6. Found: C, 54.9; N, 19.9; H, 4.6. $[Fe(dppa)_2(NCS)_2]$ polymorphs (**2** and **2'**)**.** Using similar procedure than that described above for **1**, but by replacing dpea by dppa ligand (27.7 mg, 0.13 mmol), two single crystal phases **2** (orange prisms) and **2'** (yellow prisms) have been formed after two weeks. Anal. Calcd. for $C_{26}H_{26}FeN_8S_2$ (**2** and **2'**): C, 56.2; N, 18.7; H, 5.0. Found for **2**: C, 56.4; N, 19.1; H, 4.9. Found for **2'**: C, 56.5; N, 19.0; H, 4.9.

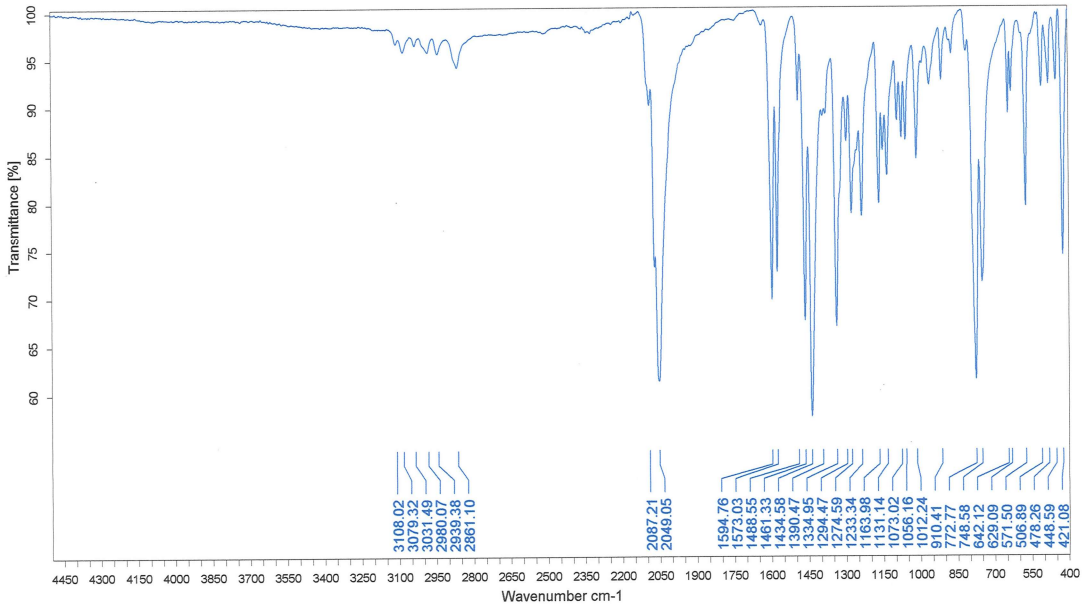

Figure S9. IR data (ν/cm^{-1}) for complex **1**: 3108w, 3079w, 3031w, 2980w, 2939w, 2861w, 2087sh, 2049s, 1595s, 1573s, 1489w, 1461s, 1435s, 1335s, 1294m, 1233m, 1164m, 1073m, 1056m, 1012m, 910w, 773s, 749s, 642w, 629w, 572m, 507m, 478m, 449m, 421s.

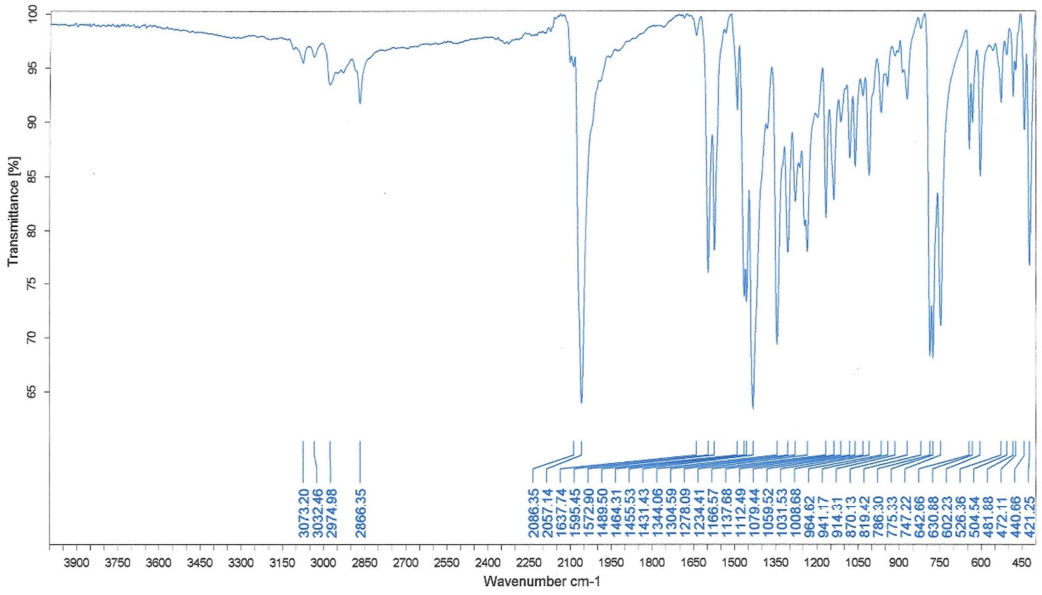

Figure S10. IR data (ν/cm^{-1}) for polymorph I (**2**): 3073w, 3032w, 2974w, 2866w, 2086w, 2057s, 1638m, 1595m, 1489s, 1464m, 1455m, 1431s, 1344s, 1305m, 1278m, 1234m, 1167m, 1138m, 1112w, 1079w, 1060m, 1032m, 1009m, 965w, 941w, 914w, 870w, 819s, 786s, 775s, 747m, 643m, 631m, 602m, 526m, 505m, 482w, 472w, 441m, 421m.

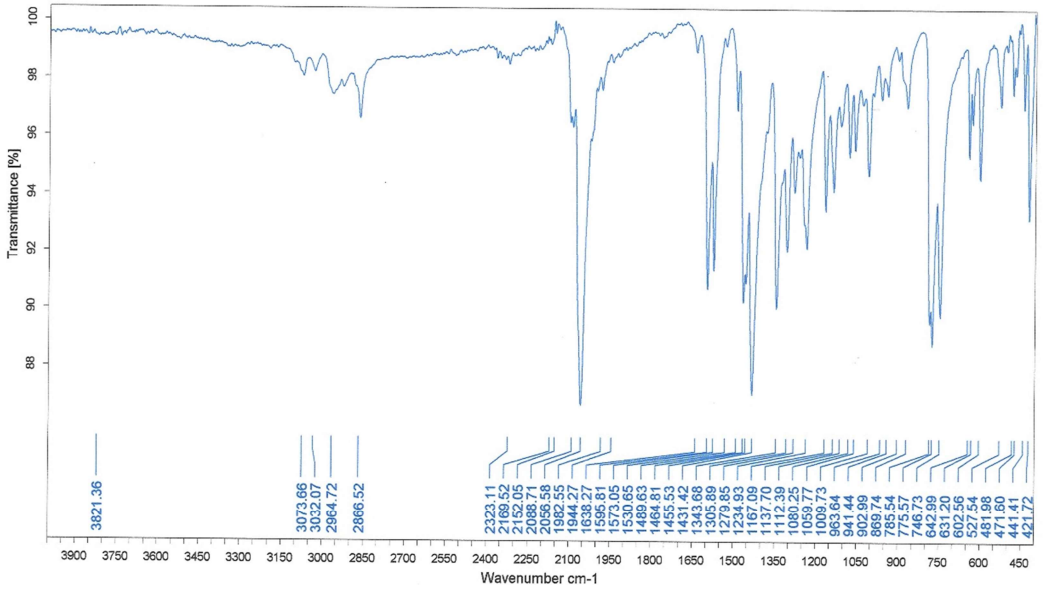

Figure S11. IR data (ν/cm^{-1}) for polymorph II (**2'**): 3073w, 3032w, 2965w, 2867w, 2170w, 2152w, 2089w, 2057s, 1638m, 1596m, 1490s, 1465m, 1456m, 1431s, 1344s, 1306m, 1280m, 1235m, 1167m, 1138m, 1112w, 1080w, 1059m, 1010m, 964w, 941w, 903w, 786s,775s, 746s, 747m, 642m, 631m, 603m, 528m, 482w, 472w, 441m, 422m.

2 - Physical Measurements and characterizations.

Elemental analyses were performed on a Perkin-Elmer Elemental Analyzer. Infrared (IR) spectra were collected in the range 4000−200 cm^{-1} on a FT-IR BRUKER ATR VERTEX70 Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-400 and AMX-75 spectrometers, and the spectra were referenced internally using residual proton solvent resonances relative to tetramethylsilane (δ = 0 ppm). Magnetic measurements were performed with a Quantum Design MPMS3 SQUID magnetometer in the 2-350 K temperature range at 0.1 T magnetic field. Experimental susceptibility was corrected for the diamagnetism of the constituent atoms of the sample by using Pascal's tables and for the diamagnetism of the sample holder.

3 - X-Ray Crystallography.

a - Crystallographic Data Collection and Refinement. Crystallographic study of compounds **1**, **2** and **2'** were performed at 296 and 170 K. The crystallographic data have been collected on an Oxford Diffraction Xcalibur CCD diffractometer with Mo Kα radiation. For the data collections, except for complex **2'**, similar single crystal was used for both temperatures: 0.20 x 0.18 x 0.13 mm^3 (**1**); 0.38 x 0.30 x 0.23 mm^3 (**2**); 0.14 x 0.12 x 0.10 mm^3 for **2'** at 296 K and 0.25 x 0.23 x 0.16 mm^3 for **2'** at 170 K. All the data collections were performed using 1° ω-scans with different

exposure times (50 s and 40 s per frame for **1** at 296 and 170 K, respectively; 10 s per frame for **2** at 296 and 170 K; 50 s and 13 s per frame for **2'** at 296 and 170 K, respectively). The unit cell determinations and data reductions were performed using the CrysAlis program suite on the full set of data [2]. The crystal structures were solved by direct methods and successive Fourier difference syntheses with the Sir97 program [3] and refined on F^2 by weighted anisotropic full-matrix least-square methods using the SHELXL97 program [4]. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were calculated and therefore included as isotropic fixed contributors to F_c.

Table S1. The pertinent crystallographic data for complexes **1**, **2** and **2'**.

Compound	**1**		**2**		**2′**	
T / K	296	170	296	170	296	170
Spin state	*HS*	*LS*	*HS*	*LS*	*HS*	*LS*
Color	Yellow	Red	Orange	Red	Yellow	Red
[a]Chem. formula	$C_{26}H_{26}FeN_8S_2$		$C_{28}H_{30}FeN_8S_2$		$C_{28}H_{30}FeN_8S_2$	
M g/mol	570.52		598.57		598.57	
Crystal system	Orthorhombic		Orthorhombic		Triclinic	
Space group	$Pna2_1$		Pccn		$P\bar{1}$	
a /Å	18.476(1)	18.8753(4)	11.5110(6)	11.1465(3)	9.1819(4)	9.1603(7)
b /Å	11.7696(5)	11.3230(3)	12.3330(5)	11.9640(4)	9.9566(4)	10.1973(9)
c /Å	12.3397(5)	12.0873(3)	21.684(1)	21.1526(6)	17.2697(5)	16.868(2)
α /°	90	90	90	90	89.758(3)	89.911(6)
β/°	90	90	90	90	89.490(3)	89.874(6)
γ /°	90	90	90	90	68.154(4)	67.590(8)
V./Å^3	2683.4(2)	2583.4(2)	3078.4(2)	2820.8(2)	1465.4(1)	1456.6(2)
Z	4	4	4	4	2	2
ϱ_{calc} g/cm^3	1.412	1.467	1.291	1.409	1.357	1.365
[a]R_1	0.0403	0.0301	0.0535	0.0434	0.0639	0.0580
[b]wR_2	0.0948	0.0704	0.1751	0.1248	0.1716	0.1507
[c]GOF on F^2	1.019	1.038	1.045	1.070	1.012	1.062
CCDC numbers	1866638	1866637	1866640	1866639	1866642	1866641

[a]$R_1 = \Sigma|Fo-Fc|/Fo)$ [$I \geq 2\sigma$ (I)] and [b]$wR_2 = [\Sigma((\omega(Fo^2-Fc^2))^2/(\omega(Fo^2))^2)]^{1/2}$ [all data]. [c]G.O.F = $[(\Sigma(\omega(Fo^2-Fc^2))^2/(Nobs-Nvar)]^{1/2}$.

References

1. Rauterkus, M. J.; Fakih, S.; Mock, C.; Puscasu, I.; Krebs, B. Cisplatin analogues with 2,2-dipyridylamine ligands and their reactions with DNA model nucleobases. *Inorg. Chim. Acta* **2003**, *350*, 355-365.
2. Oxford Diffraction (2006). Xcalibur CCD/RED CrysAlis Software system. Oxford Diffraction Ltd, Abingdon, England.
3. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR*97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **1999**, *32*, 115-119.
4. Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3-8.