Supporting Information *for "Thermal induced spin crossover in Fe(PyrDer)2[Fe(CN)5NO] with PyrDer = 4-substituted pyridine derivatives,"* by Y. Avila, P. M. Crespo, Y. Plasencia, H. R. Mojica, J. Rodríguez-Hernández, E. Reguera

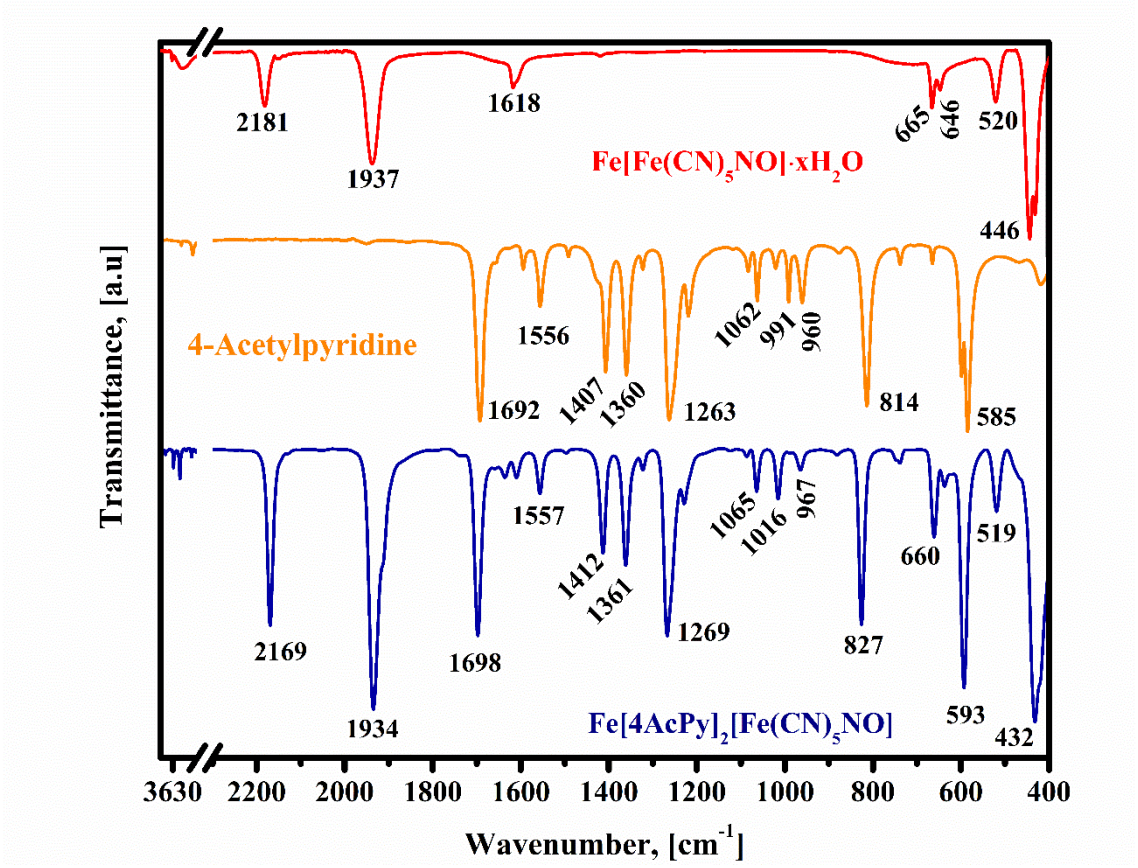

Figure S1: IR spectra for: ferrous nitroprusside, $Fe[Fe(CN)_5NO].2H_2O$ (3D orthorhombic phase); 4-acetylpyridine; and 2D ferrous nitroprusside with 4-acetylpyridine molecules intercalated between neighboring layers, $Fe(4AcPy)_2[Fe(CN)_5NO]$. The 4-acetylpyridine molecule coordination to the axial positions of the iron (2+) atom is appreciated as a frequency shift for the ν(CN), ν(NO) stretching vibrations, absence of water molecule ν(OH) and δ(HOH) bands, and changes in the IR spectra for the intercalated molecule (4-acetylpyridine) relative to the one recorded for the non-intercalated molecule.

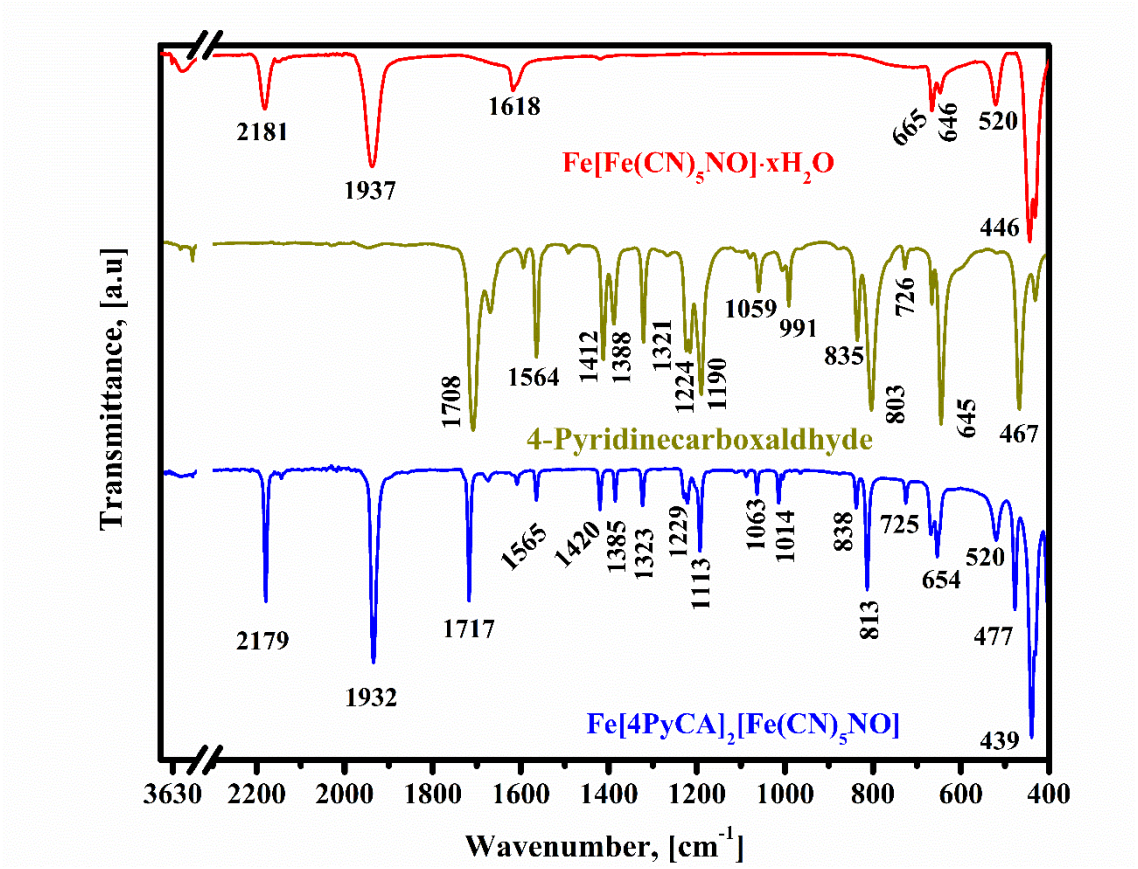

Figure S2: IR spectra for: ferrous nitroprusside, $Fe[Fe(CN)_5NO].2H_2O$ (3D orthorhombic phase); 4-pyridinecarboxaldehyde; and 2D ferrous nitroprusside with 4-pyridinecarboxaldehyde molecules intercalated between neighboring layers, $Fe(4PyCA)_2[Fe(CN)_5NO]$. The 4-pyrinecarboxaldehyde molecule coordination to the axial positions of the iron (2+) atom is appreciated as a frequency shift for the ν(CN), ν(NO) vibrations, absence of water molecule ν(OH) and δ(HOH) bands, and changes in the IR spectra for the intercalated molecule (4-pyrinecarboxaldehyde) relative to the one recorded for the non-intercalated molecule.

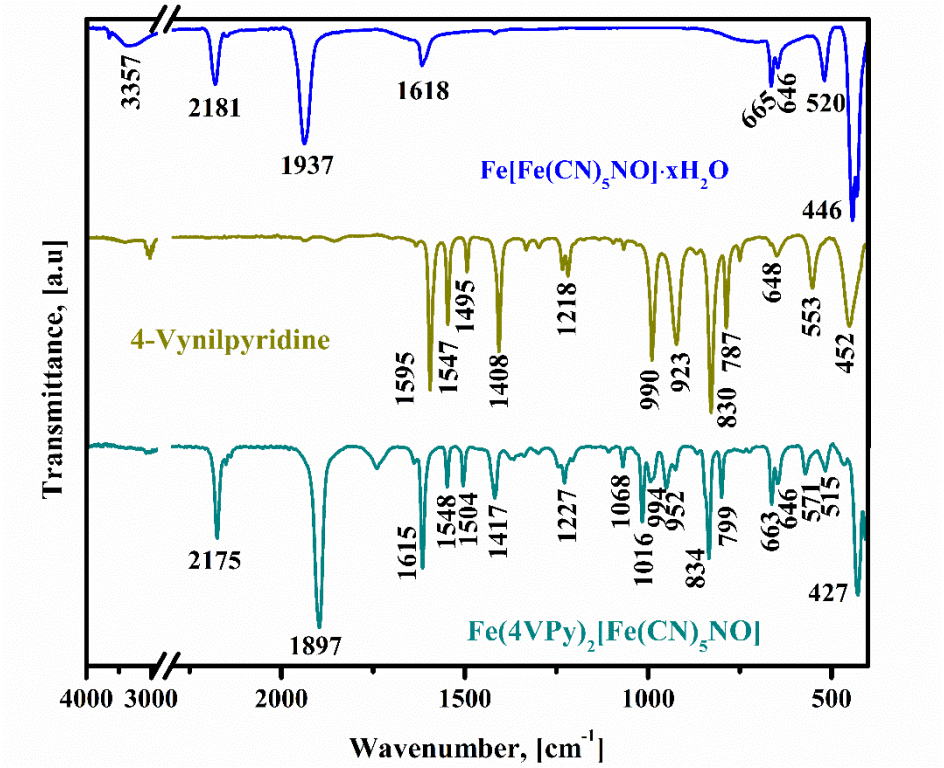

Figure S3: IR spectra for: ferrous nitroprusside, $Fe[Fe(CN)_5NO].2H_2O$ (3D orthorhombic phase); 4-vinylpyridine; and 2D ferrous nitroprusside with 4-vinylpyridine molecules intercalated between neighboring layers, $Fe(4VPy)_2[Fe(CN)_5NO]$. The 4-vinylpyridine molecule coordination to the axial positions of the iron (2+) atom is appreciated as a frequency shift for the ν(CN), ν(NO) vibrations, absence of water molecule ν(OH) and δ(HOH) bands, and changes in the IR spectra for the intercalated molecule (4-Vinylpyridine) relative to the one recorded for the non-intercalated molecule.

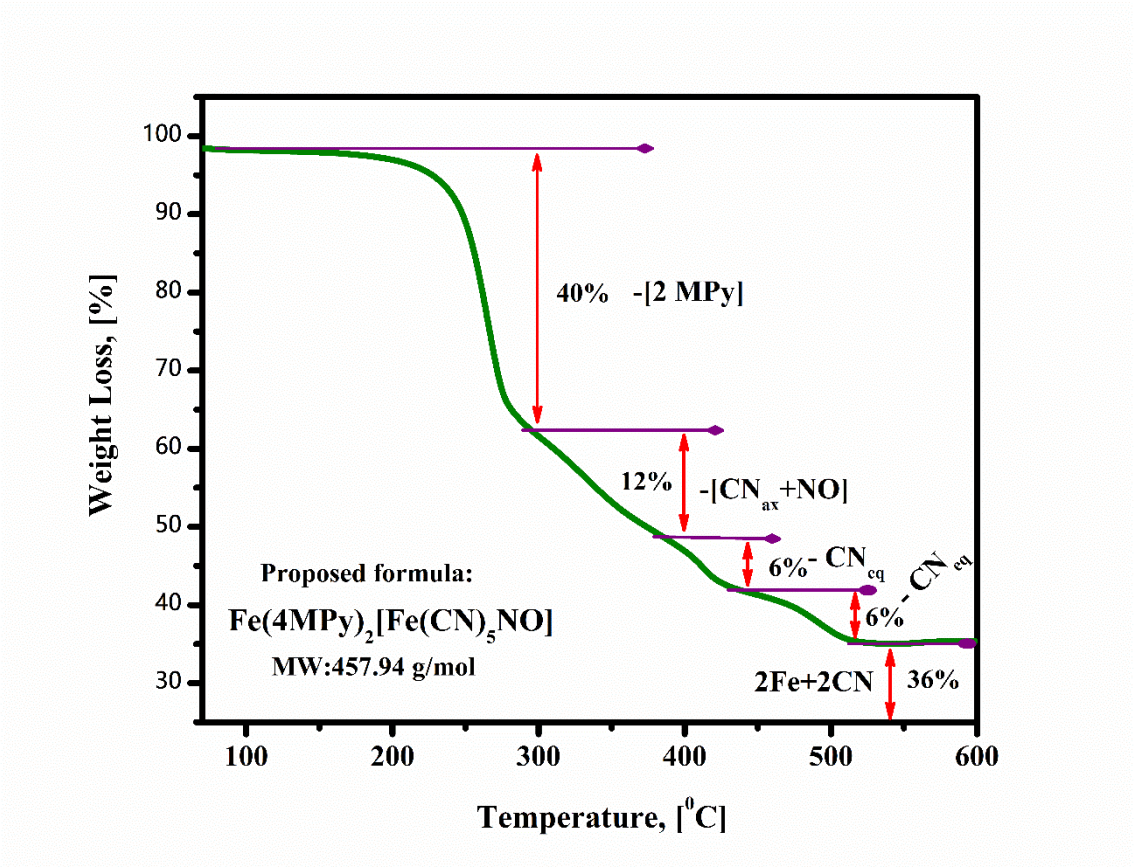

Figure S4: TG curve for 2D ferrous nitroprusside with 4-methylpyridine molecules intercalated between neighboring layers. The weight loss on heating for the 2D solid corresponds to a material with two 4-methylpyridine molecules per formula unit, $Fe(4MPy)_2[Fe(CN)_5NO]$, where 4MPy = 4-methylpyridine.

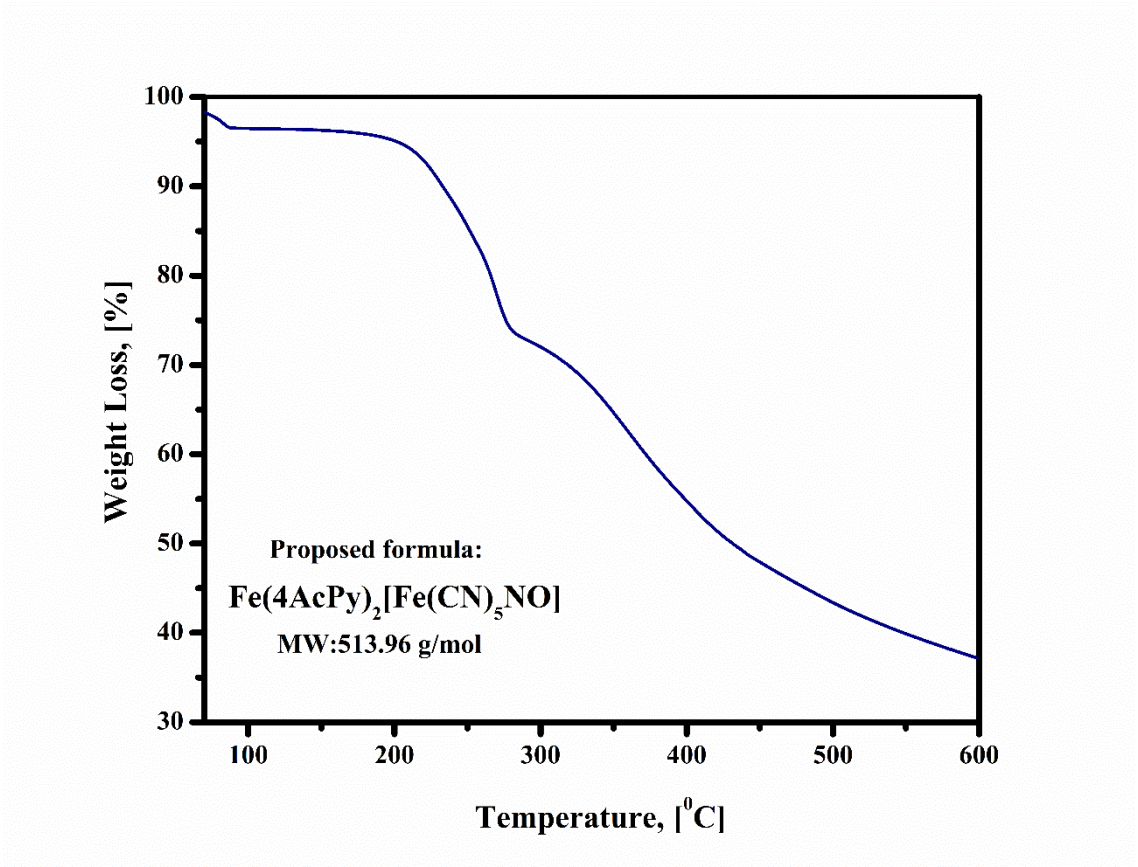

Figure S5: TG curve for 2D ferrous nitroprusside with 4-acetylpyridine molecules intercalated between neighboring layers. The weight loss on heating for the 2D solid corresponds to a material with two 4-acetylpyridine molecules per formula unit, $Fe(4AcPy)_2[Fe(CN)_5NO]$, where 4AcPy = 4-acetylpyridine.

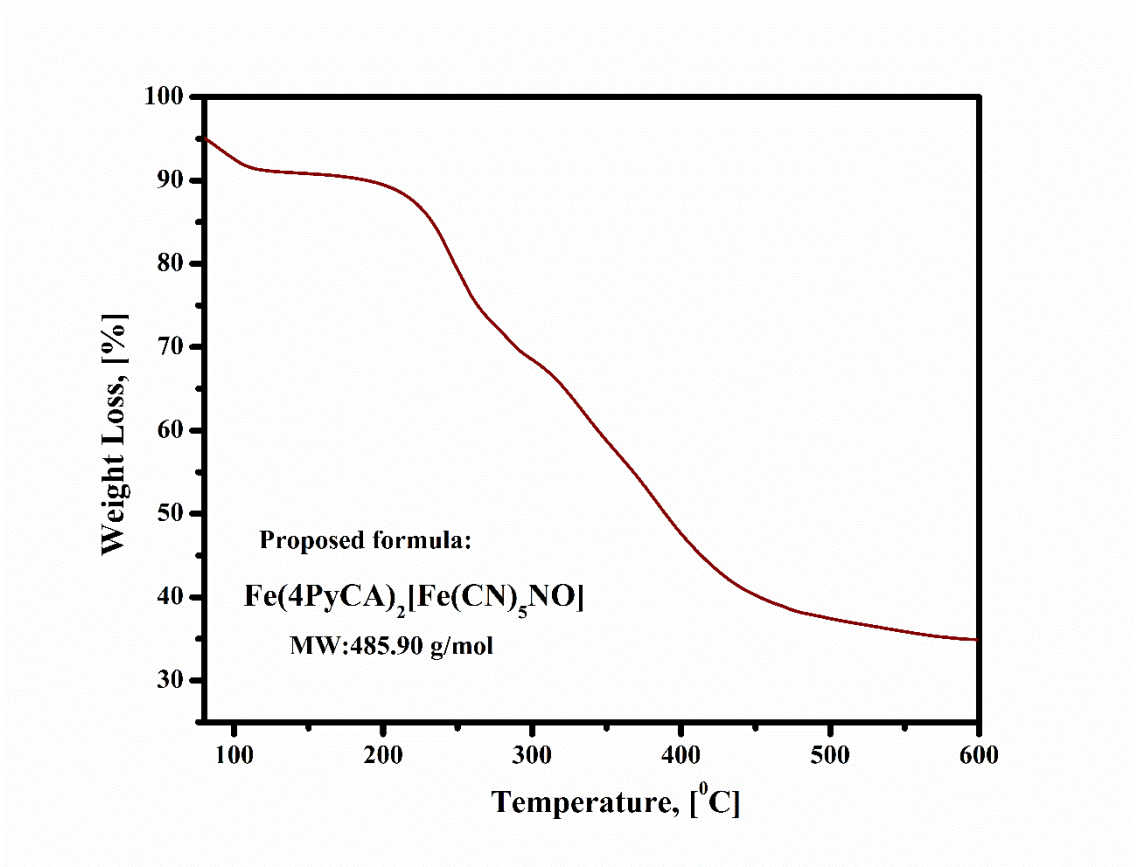

Figure S6: TG curve for 2D ferrous nitroprusside with 4-pyridinecarboxaldheyde molecules intercalated between neighboring layers. The weight loss on heating for the 2D solid corresponds to a material with two 4-pyridinecarboxaldheyde molecules per formula unit, $Fe(4PyCA)_2[Fe(CN)_5NO]$, where 4PyCA = 4-pyridinecarboxaldheyde.

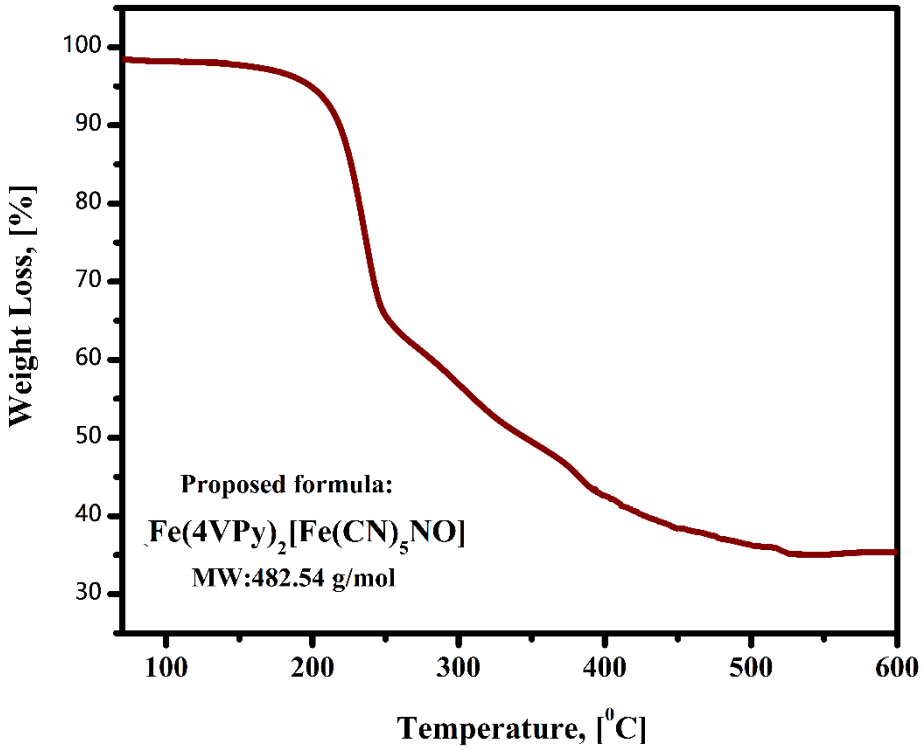

Figure S7: TG curve for 2D ferrous nitroprusside with 4-vinylpyridine molecules intercalated between neighboring layers. The weight loss on heating for the 2D solid corresponds to a material with two 4-vnylpyridine molecules per formula unit, $Fe(4VPy)_2[Fe(CN)_5NO]$, where 4VPy = 4-vinylpyridine.

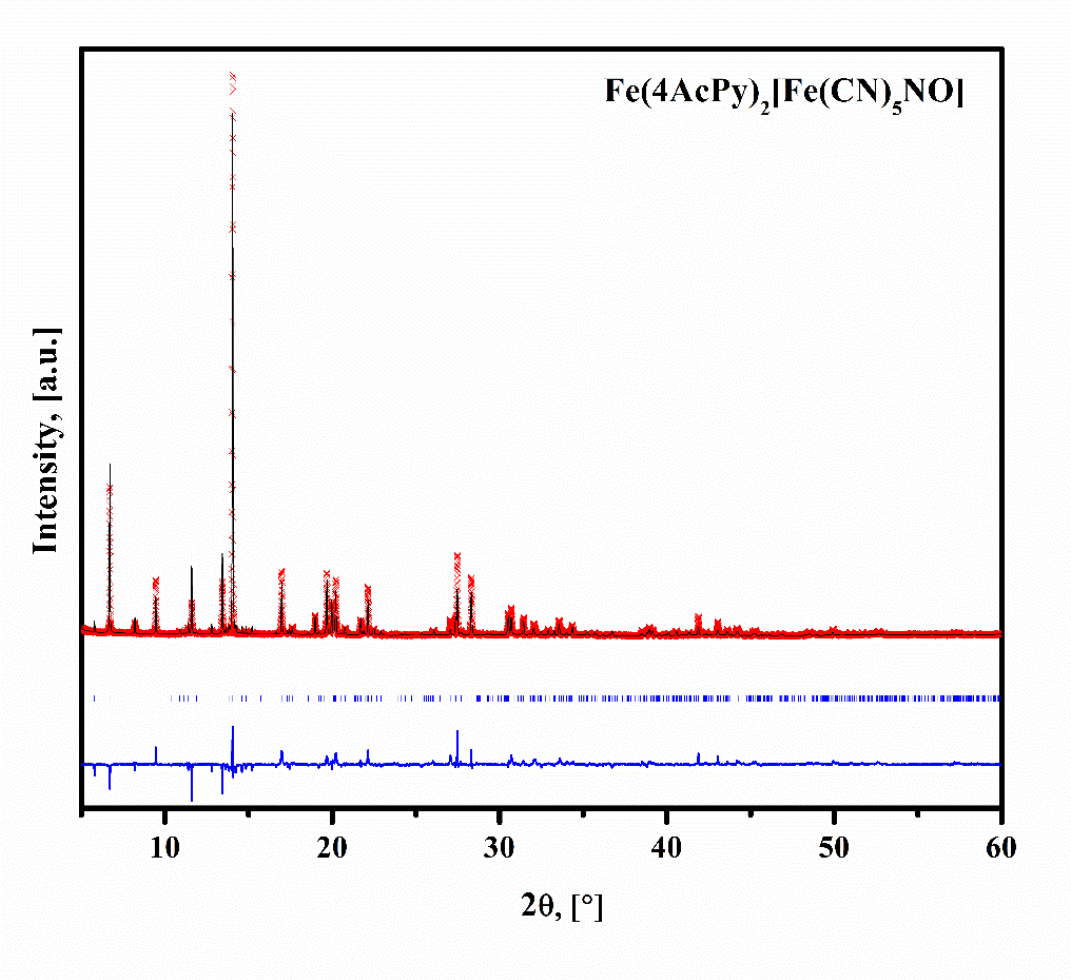

Figure S8: XRD powder pattern for $Fe(4AcPy)_2[Fe(CN)_5NO]$ (black), its fitting (red) according to the refined crystal structure, and the difference(blue) with 4AcPy= 4-acetylpyridine. This solid crystallizes in an orthorhombic unit cell, in the $P2_12_12_1$ space group, with four formula units per cell (Z=4).

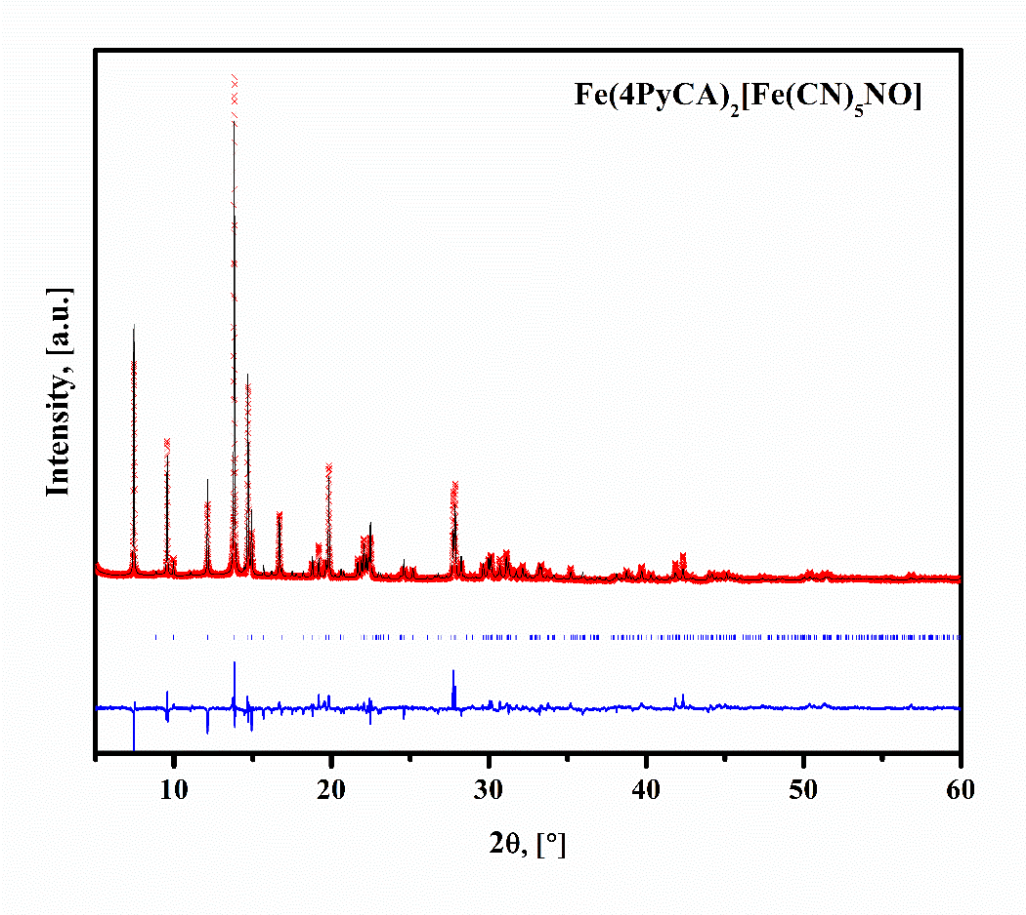

Figure S9: XRD powder pattern for $Fe(4PyCA)_2[Fe(CN)_5NO]$ (black), its fitting (red) according to the refined crystal structure, and the difference(blue) with 4PyCA= 4-pyridinecarboxaldehyde. This solid crystallizes in a monoclinic unit cell in the $P2_1$ space group, with two formula units per cell (Z = 2).

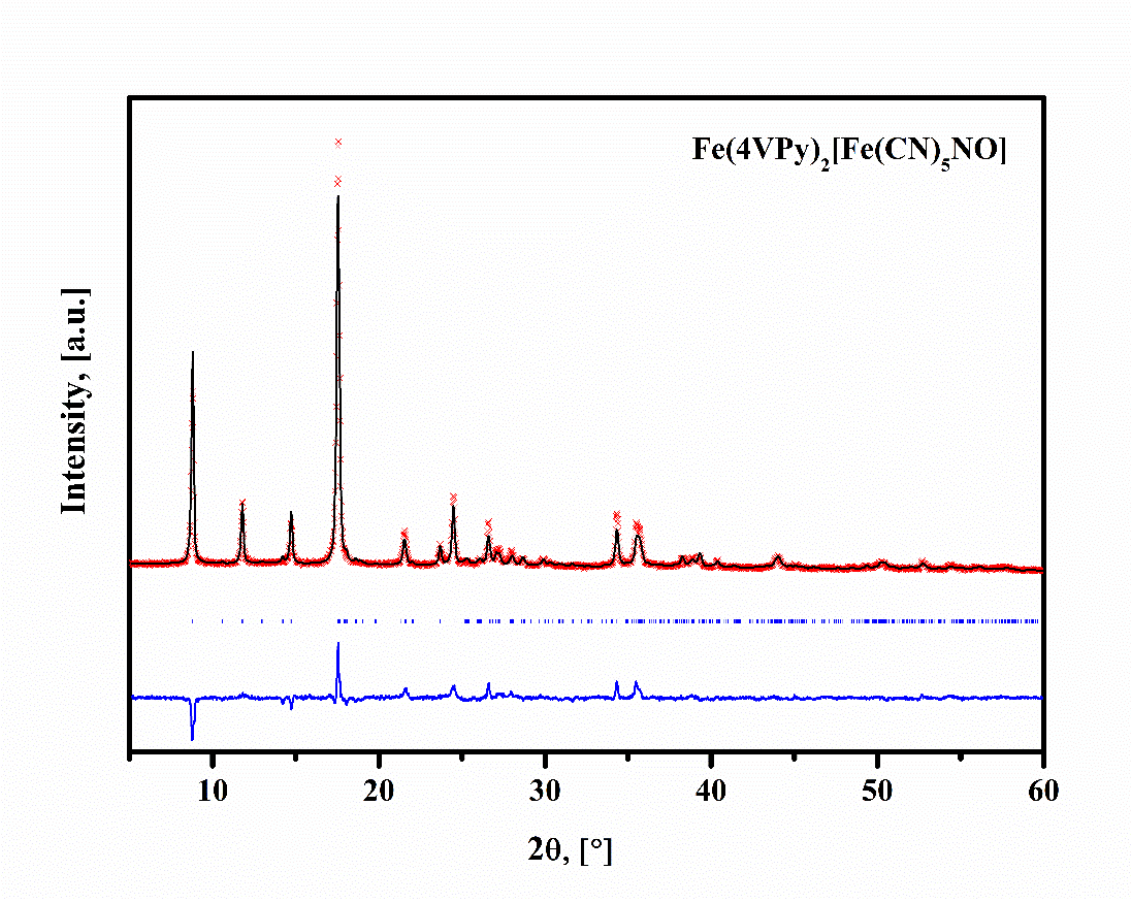

Figure S10: XRD powder pattern for $Fe(4VPy)_2[Fe(CN)_5NO]$ (black), its fitting (red) according to the refined crystal structure, and the difference (blue) with 4VPy= 4-vinylpyridine. This solid crystallizes in a monoclinic unit cell in the $P2_1$ space group, with two formula units per cell (Z = 2).

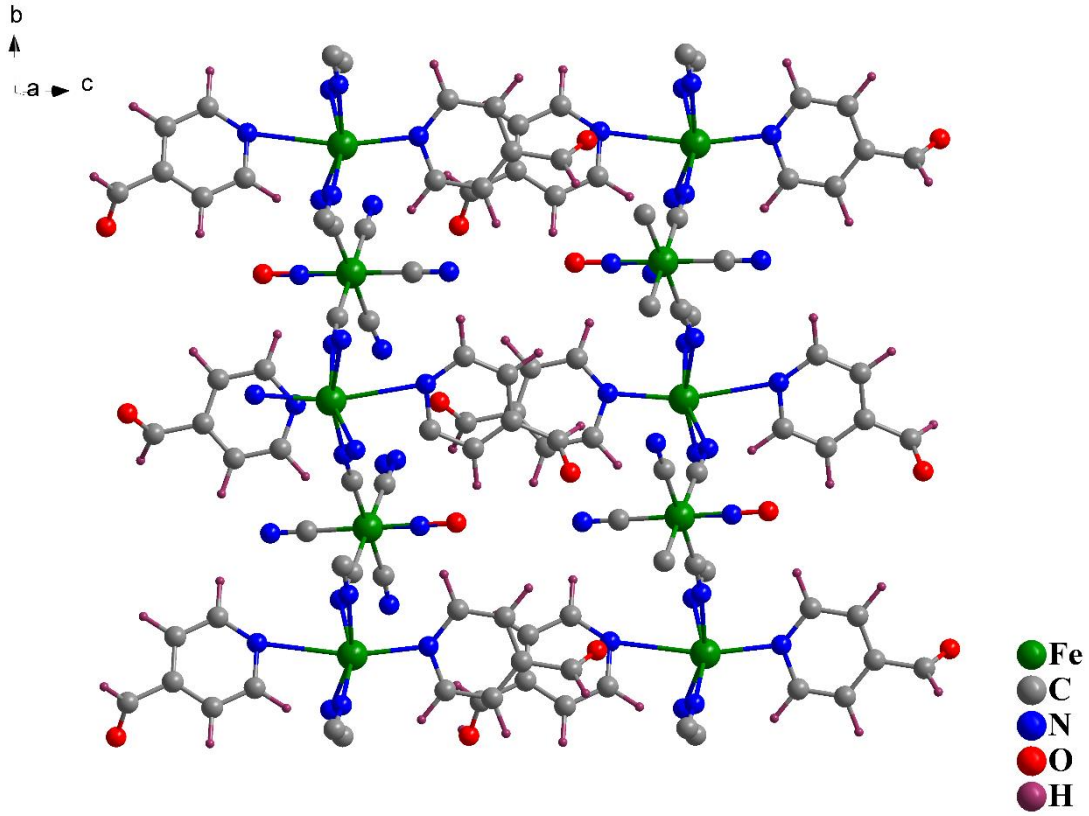

Figure S11: Atomic packing for $Fe(4PyCA)_2[Fe(CN)_5NO]$ wit 4PyCA= 4-pyridinecarboxaldehyde.

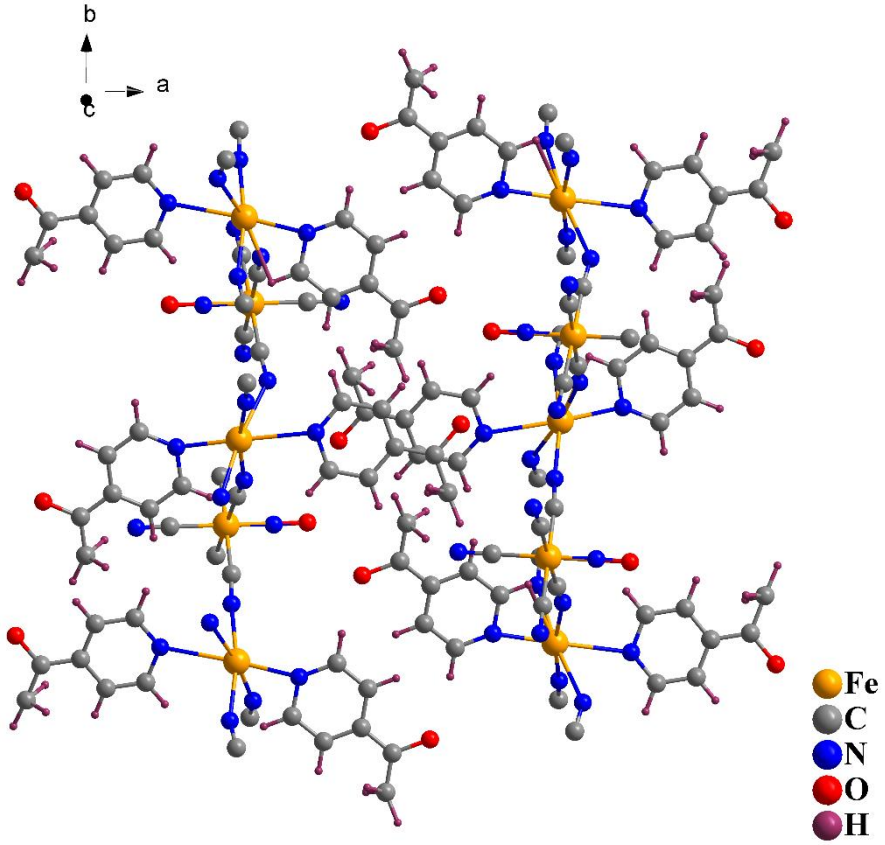

Figure S12: Atomic packing for $Fe(4AcPy)_2[Fe(CN)_5NO]$ wit 4AcPy= 4-acetylpyridine.

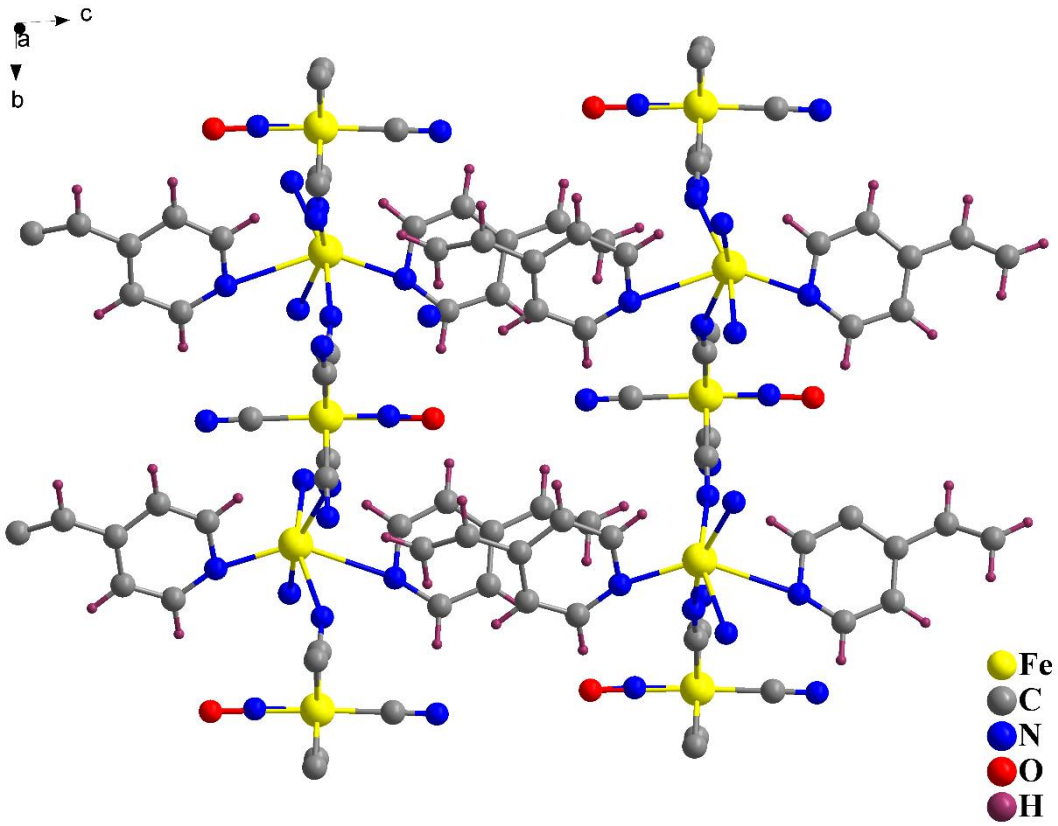

Figure S13: Atomic packing for $Fe(4VPy)_2[Fe(CN)_5NO]$ wit 4VPy= 4-vinylpyridine.

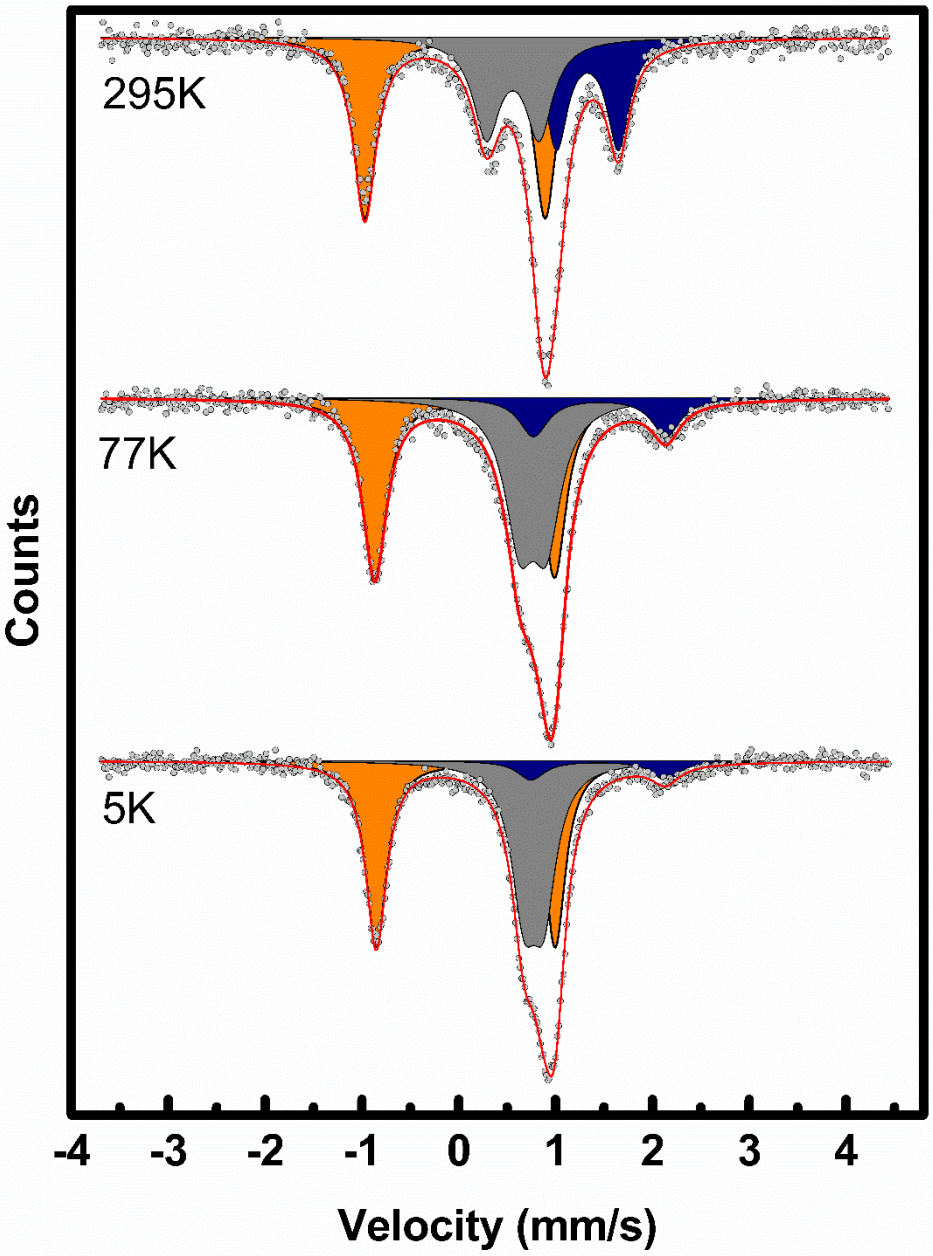

Figure S14: Mössbauer spectra for $Fe(4VPy)_2[Fe(CN)_5NO]$ recorded at 298, 77 and 5 K.

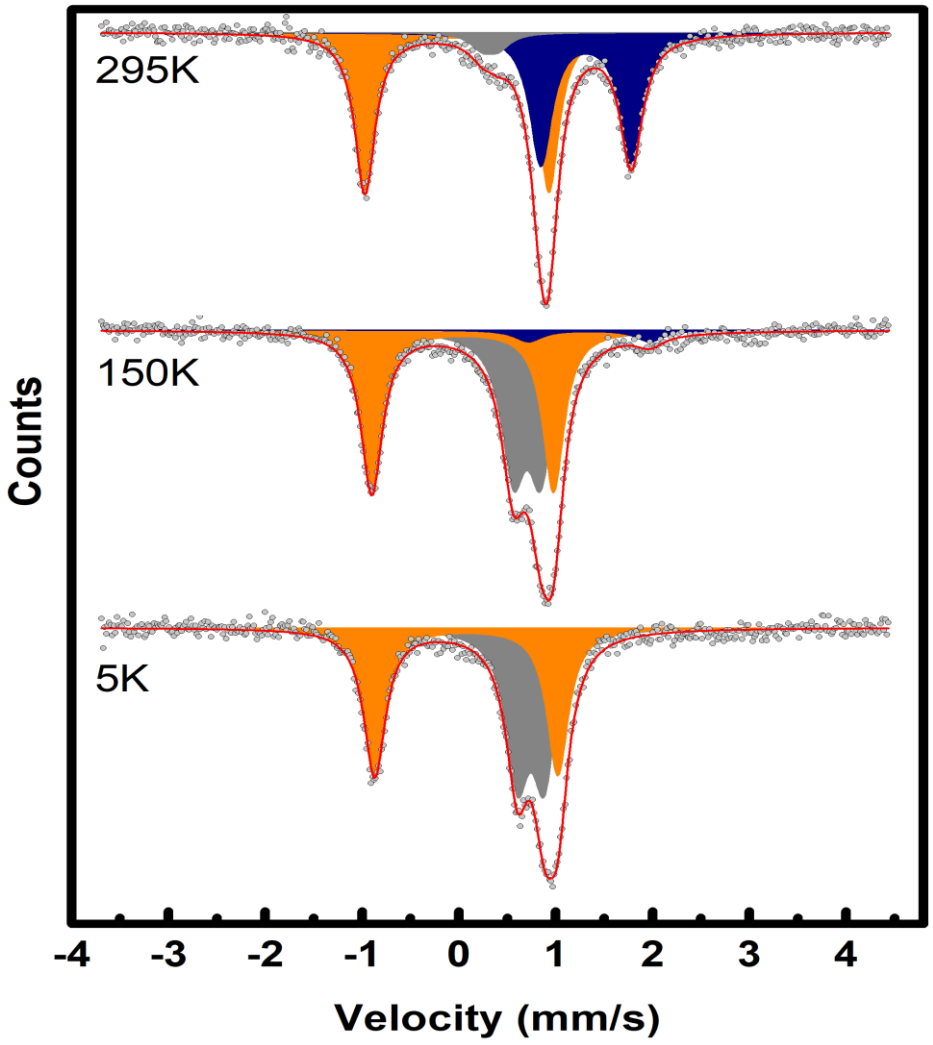

Figure S15: Mössbauer spectra for $Fe(4PyCA)_2[Fe(CN)_5NO]$ recorded at 298, 150 and 5 K.

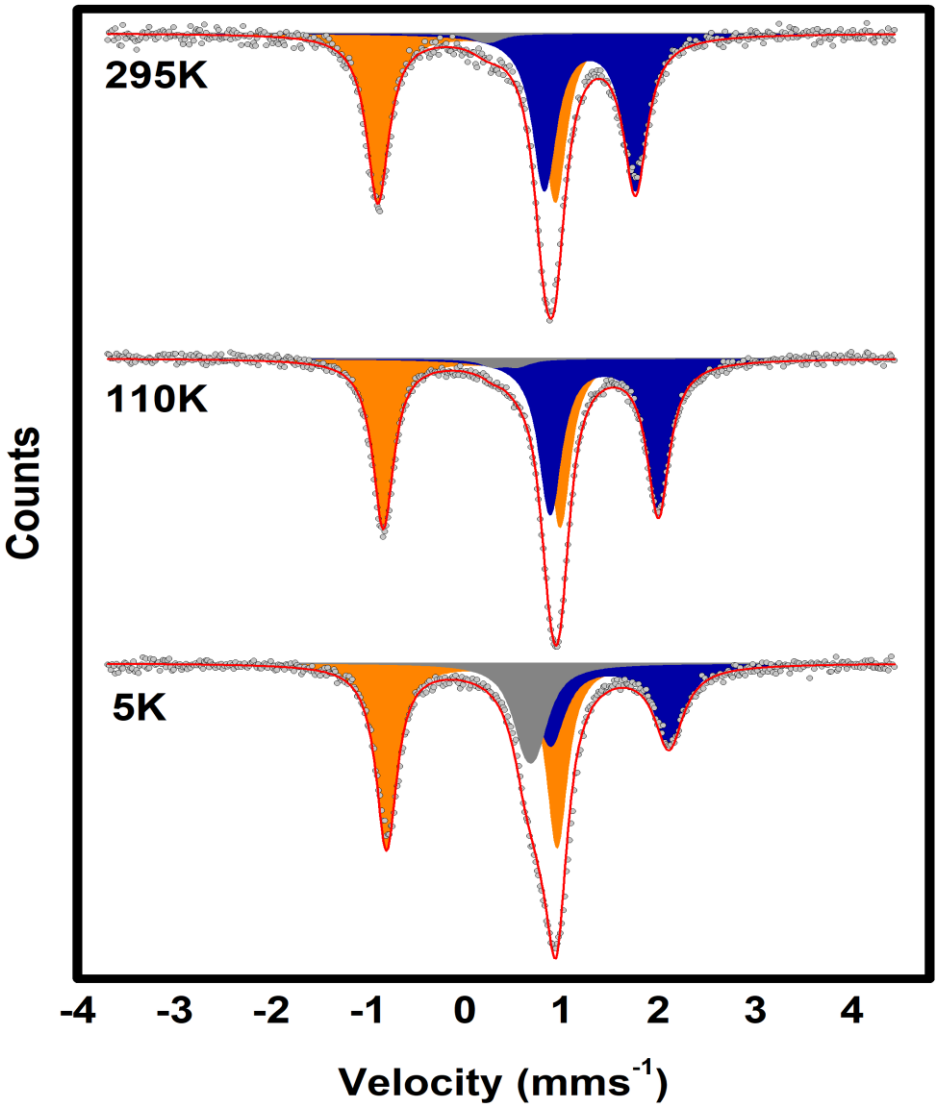

Figure S16: Mössbauer spectra for $Fe(4AcPy)_2[Fe(CN)_5NO]$ recorded at 298, 110 and 5 K.

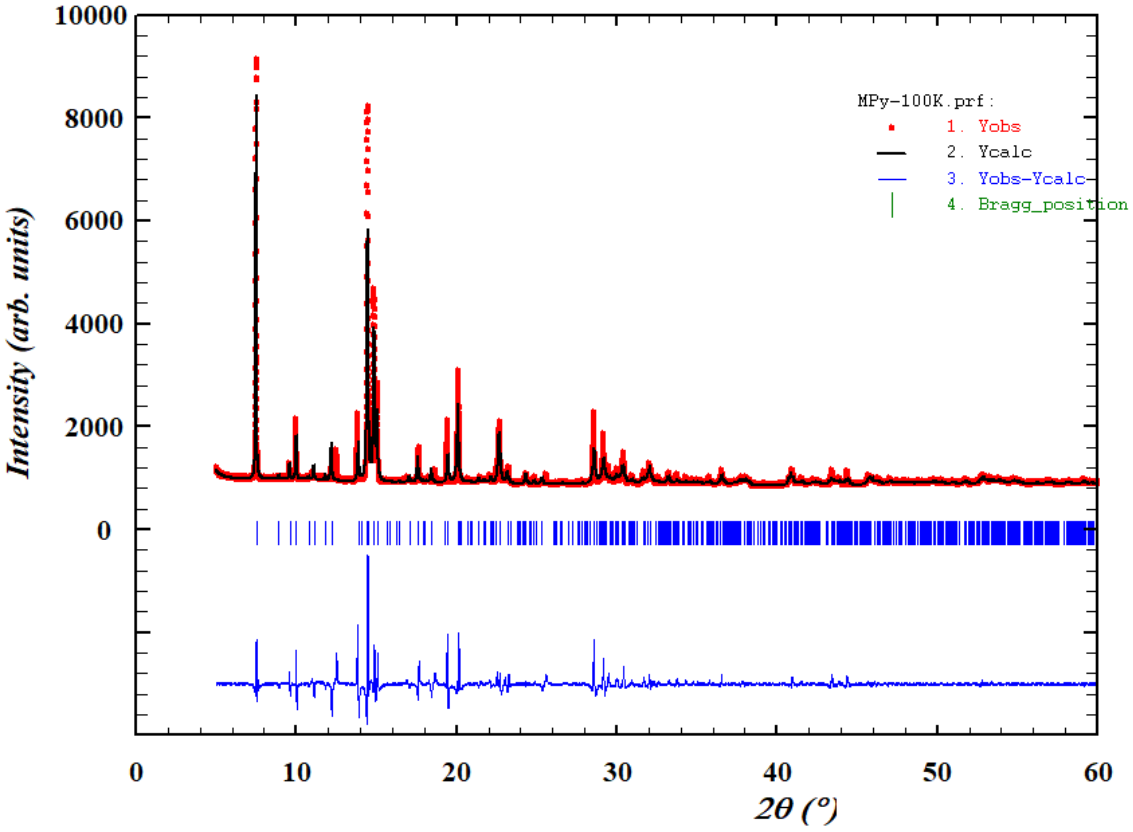

Figure S17: XRD powder pattern recorded at 100 K for $Fe(4MPy)_2[Fe(CN)_5NO]$. This pattern corresponds to a monoclinic unit cell with cell parameters: **a** = 9.821 Å; **b** = 14.805 Å; **c** = 7.372 Å; β =105.58 °, and unit cell volume of 1032.6 $Å^3$. The unit cell volume at 300 K is 1042.56 $Å^3$. The unit cell contraction related to the spin transition results 1.05 %.

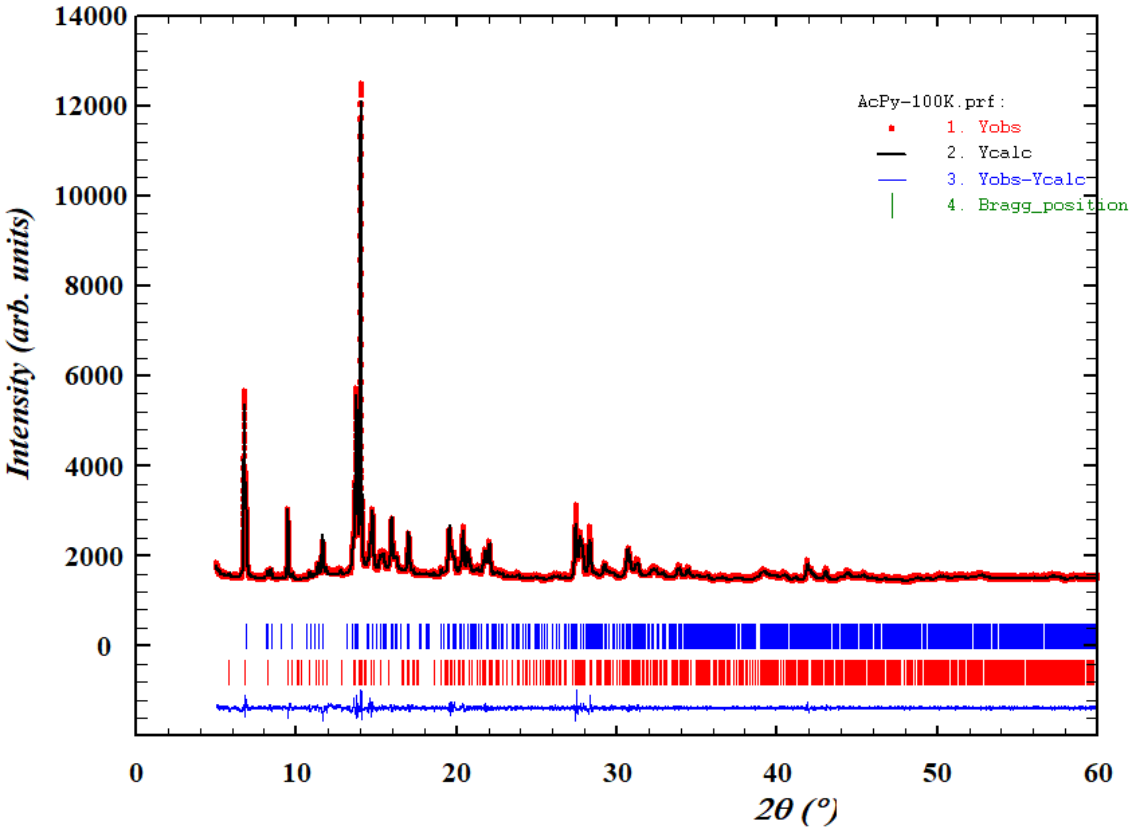

Figure S18: XRD powder pattern recorded at 100 K for $Fe(4CAPy)_2[Fe(CN)_5NO]$. This pattern corresponds to a monoclinic unit cell with cell parameters: **a** = 7.306 Å; **b** = 14.836 Å; **c** = 9.648 Å; β =101.96 °, and unit cell volume of 1023.2 Å3. The unit cell volume at 300 K is 1035.96 $Å^3$. The unit cell contraction related to spin transition results 1.23 %.

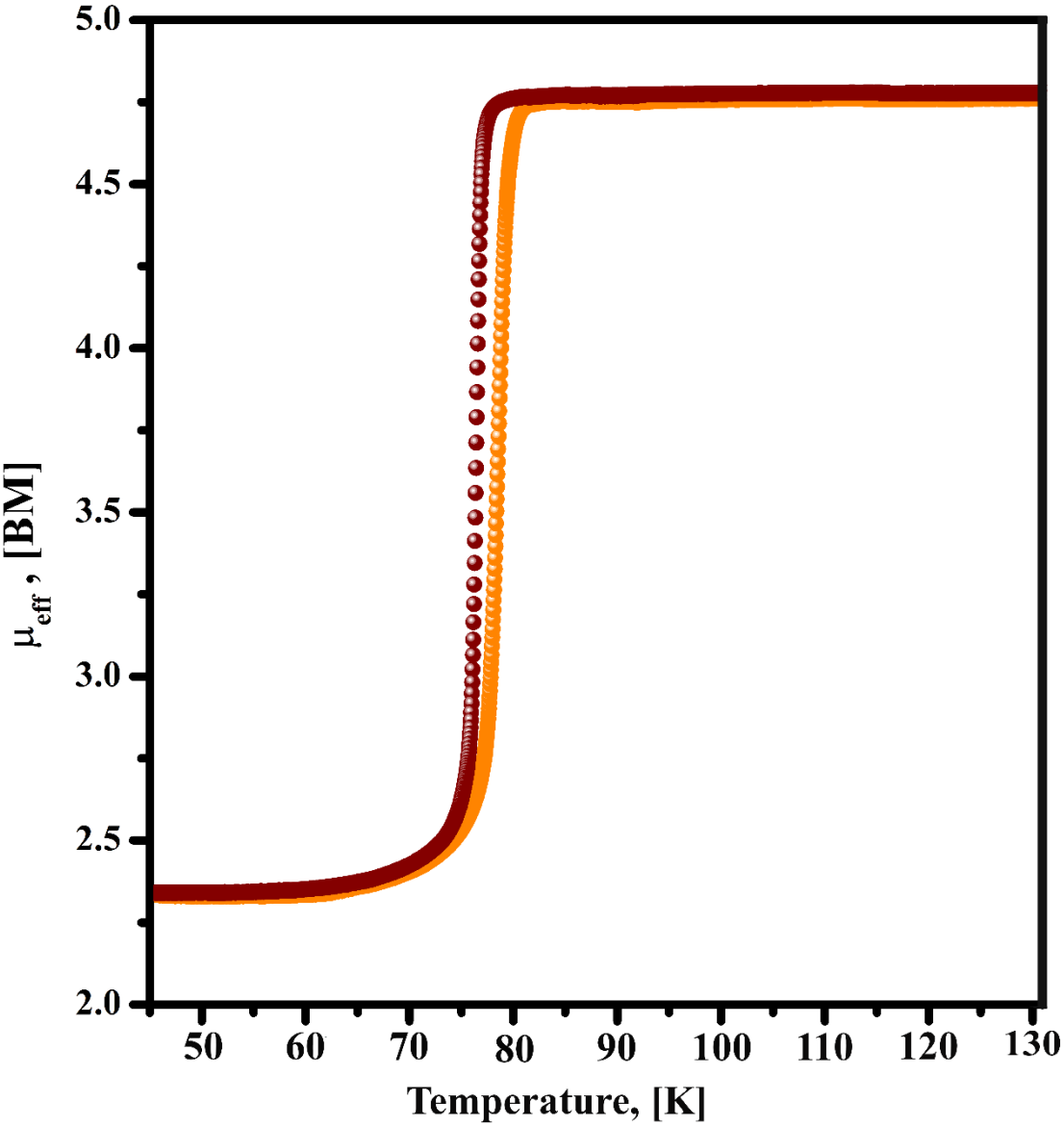

Figure S19: Effective magnetic moment (μe_{ff}) versus temperature curve for $Fe(4VPy)_2[Fe(CN)_5NO]$.

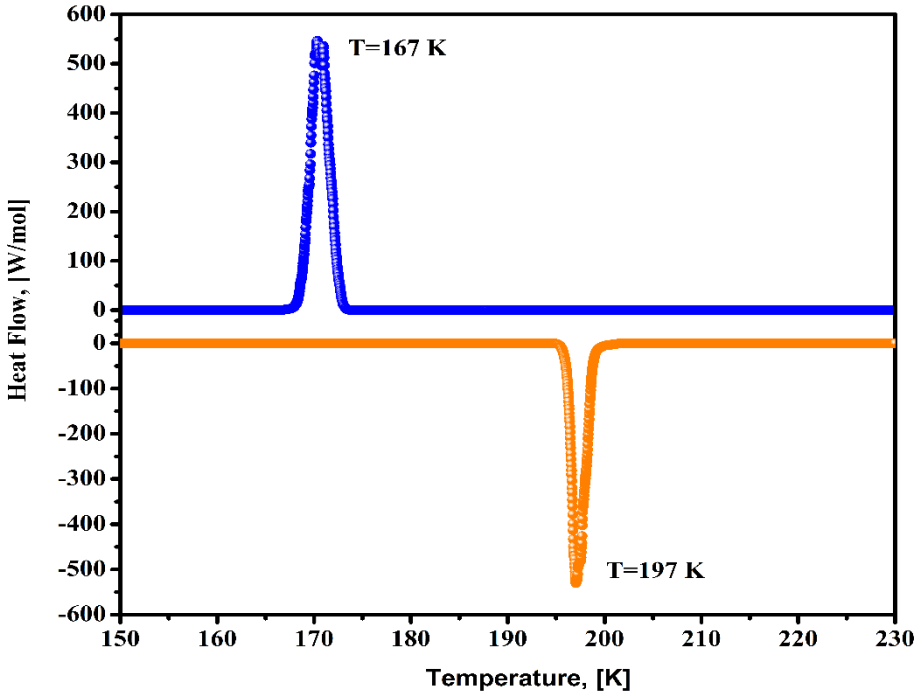

Figure S20: DSC curves on the sample cooling and then on heating for $Fe(4MPy)_2[Fe(CN)_5NO]$.

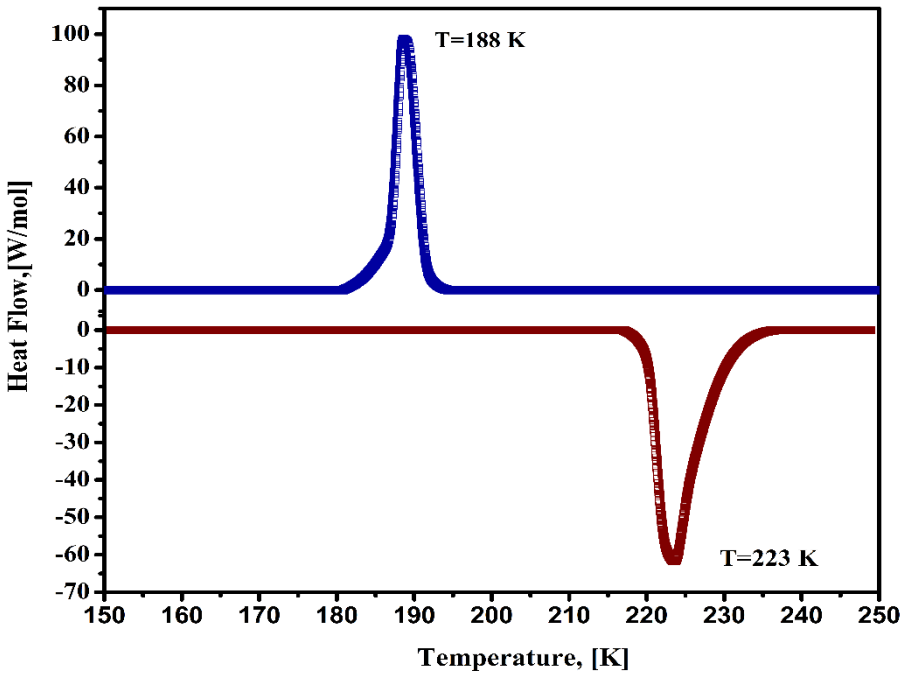

Figure S21: DSC curves on the sample cooling and then on heating for $Fe(4PyCA)_2[Fe(CN)_5NO]$.

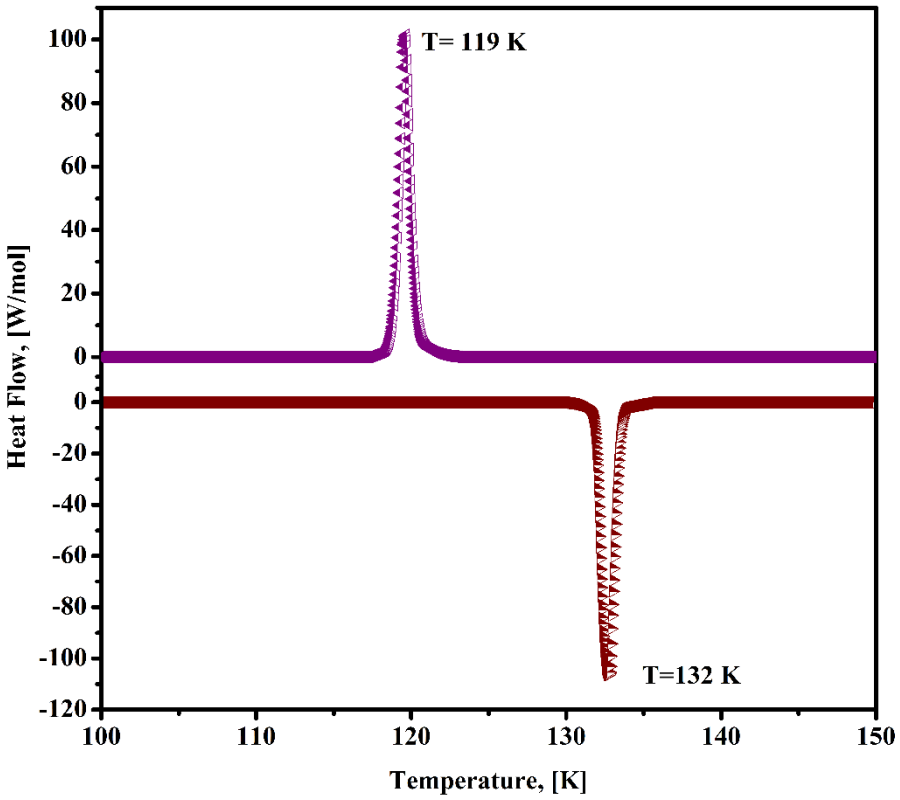

Figure S22: DSC curves on the sample cooling and then on heating for $Fe(4AcPy)_2[Fe(CN)_5NO]$.

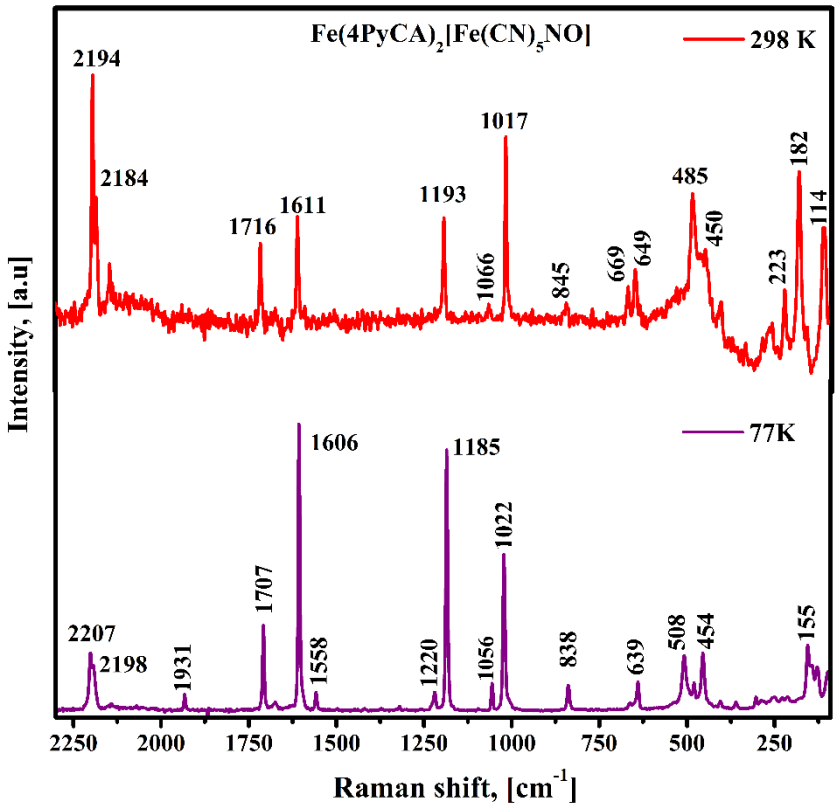

Figure S23: Raman spectra for $Fe(4PyCA)_2[Fe(CN)_5NO]$ recorded at 298 and 77 K.

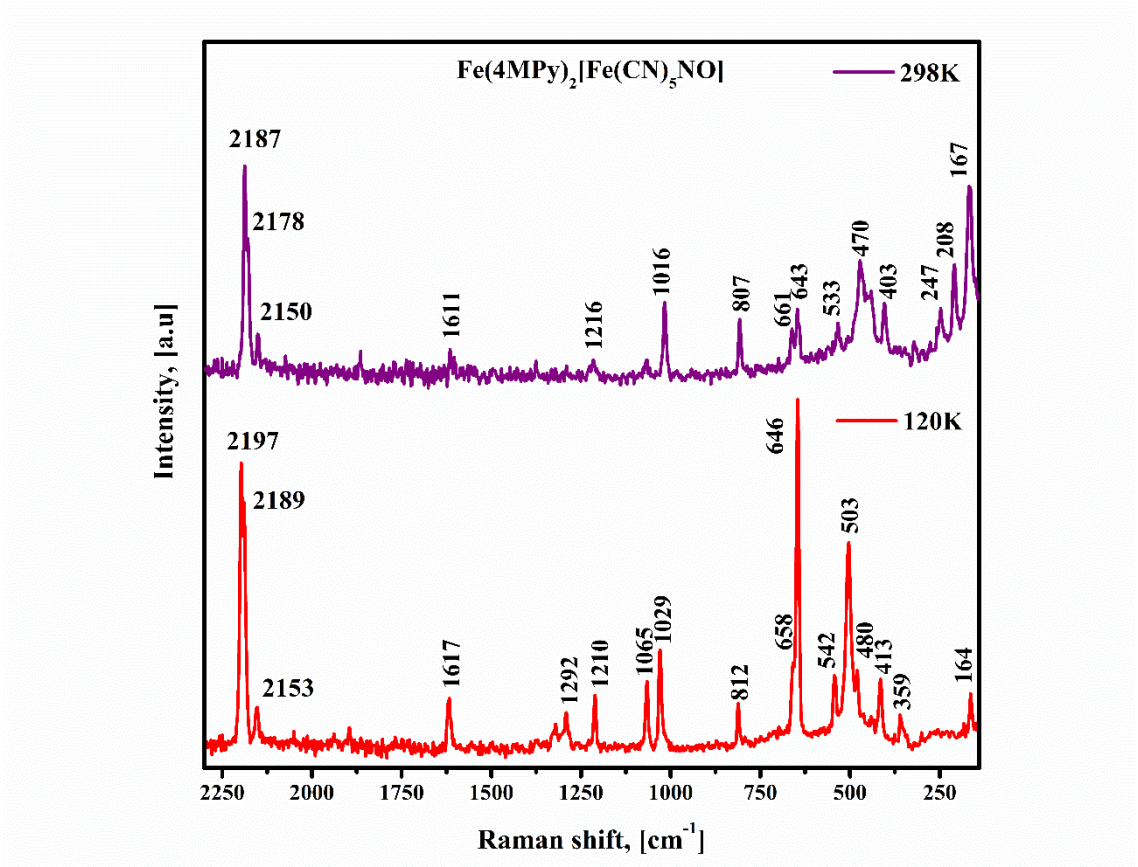

Figure S24: Raman spectra for $Fe(4MPy)_2[Fe(CN)_5NO]$ recorded at 298 and 77 K.

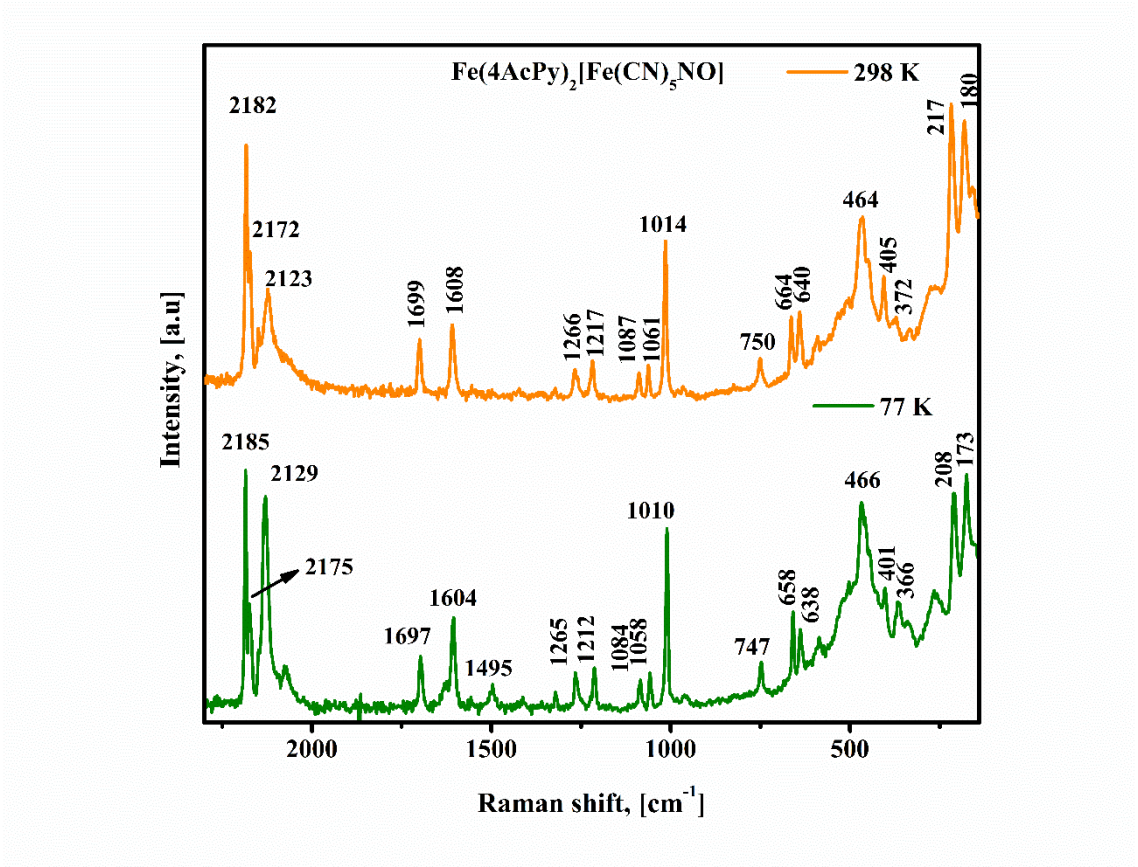

Figure S25: Raman spectra for $Fe(4AcPy)_2[Fe(CN)_5NO]$ recorded at 298 and 77 K.

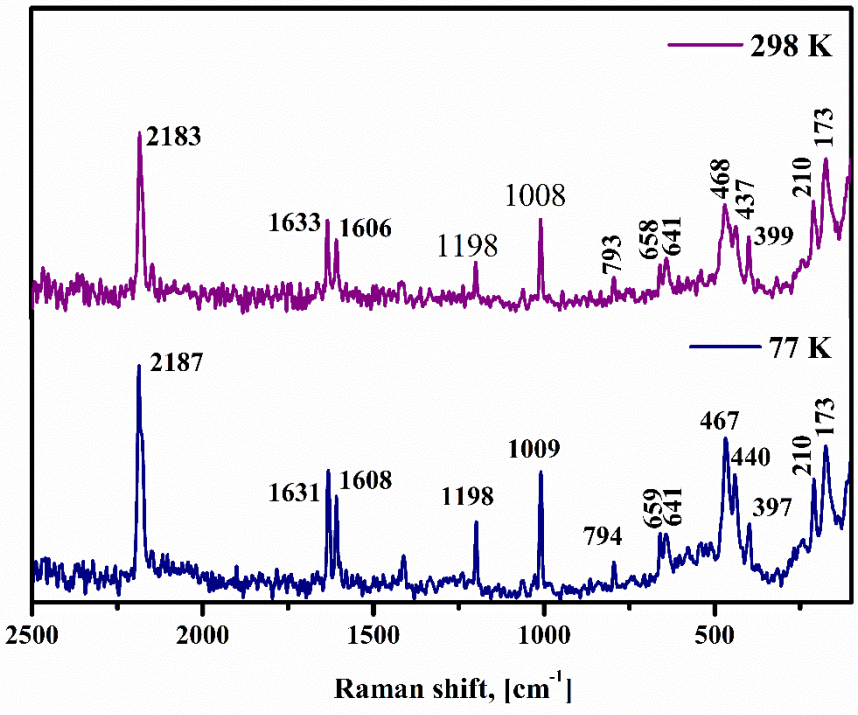

Figure S26: Raman spectra for $Fe(4VPy)_2[Fe(CN)_5NO]$ recorded at 298 and 77 K.

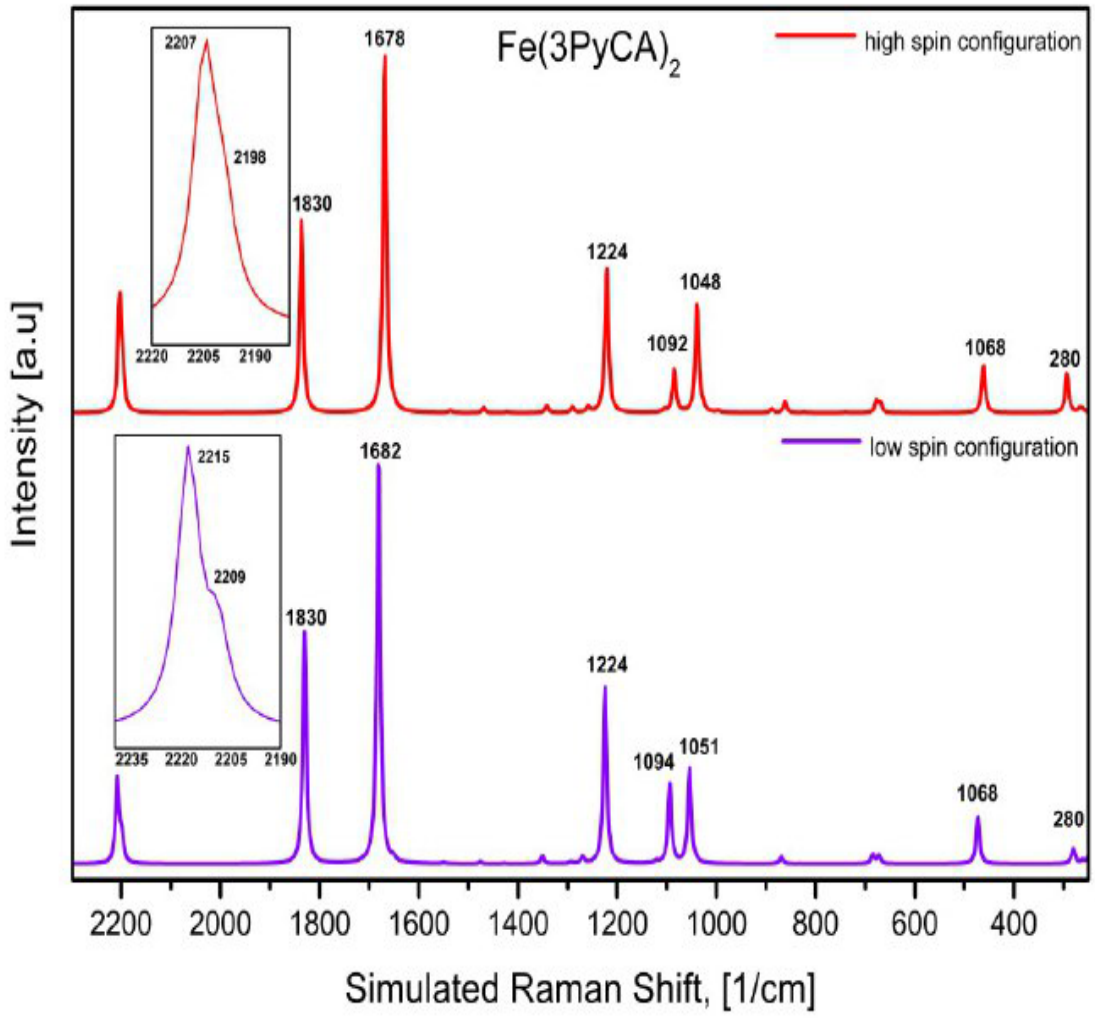

Figure S27: Comparison of the simulated Raman spectra for $Fe(3PyCA)_2[Fe(CN)_5NO$ in High Spin and Low Spin configurations.

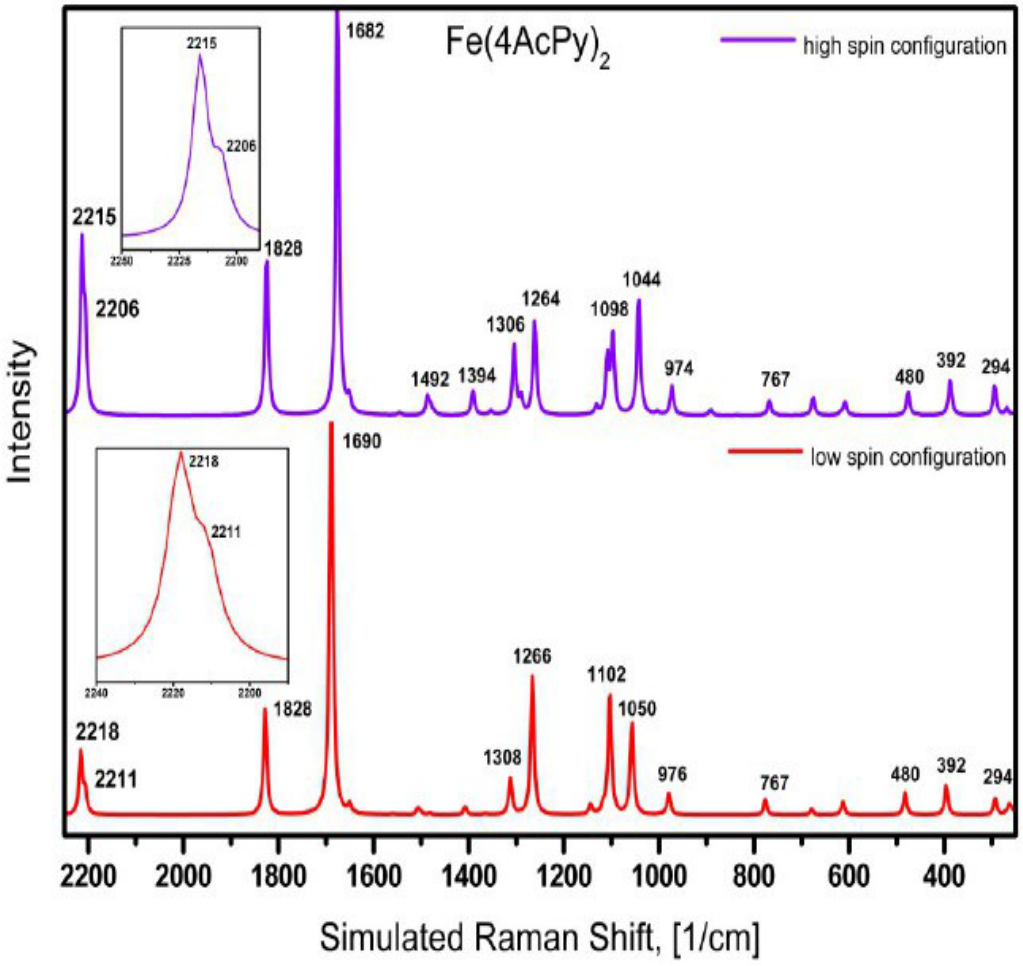

Figure S28: Comparison of the simulated Raman spectra for $Fe(4AcPy)_2[Fe(CN)_5NO$ in High Spin and Low Spin configurations.

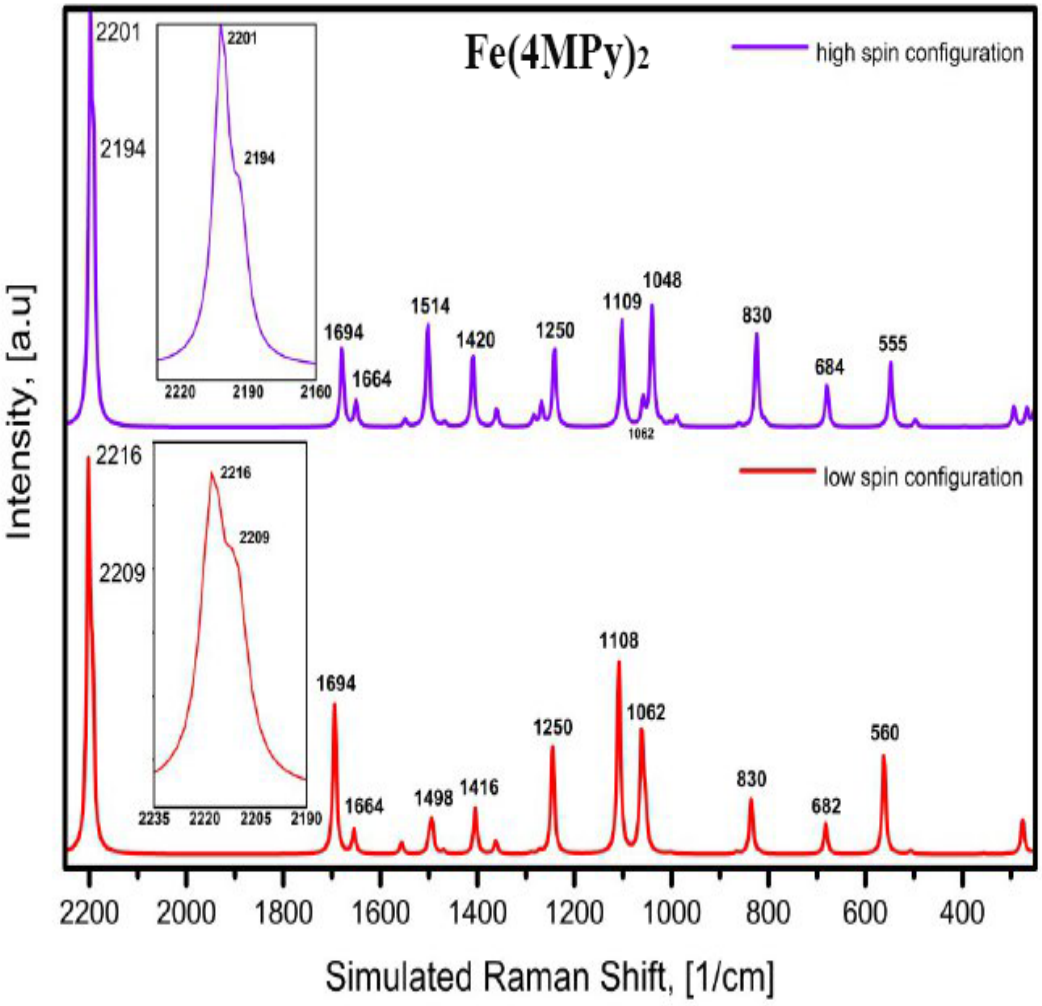

Figure S29: Comparison of the simulated Raman spectra for $Fe(4MPy)_2[Fe(CN)_5NO$ in High Spin and Low Spin configurations.

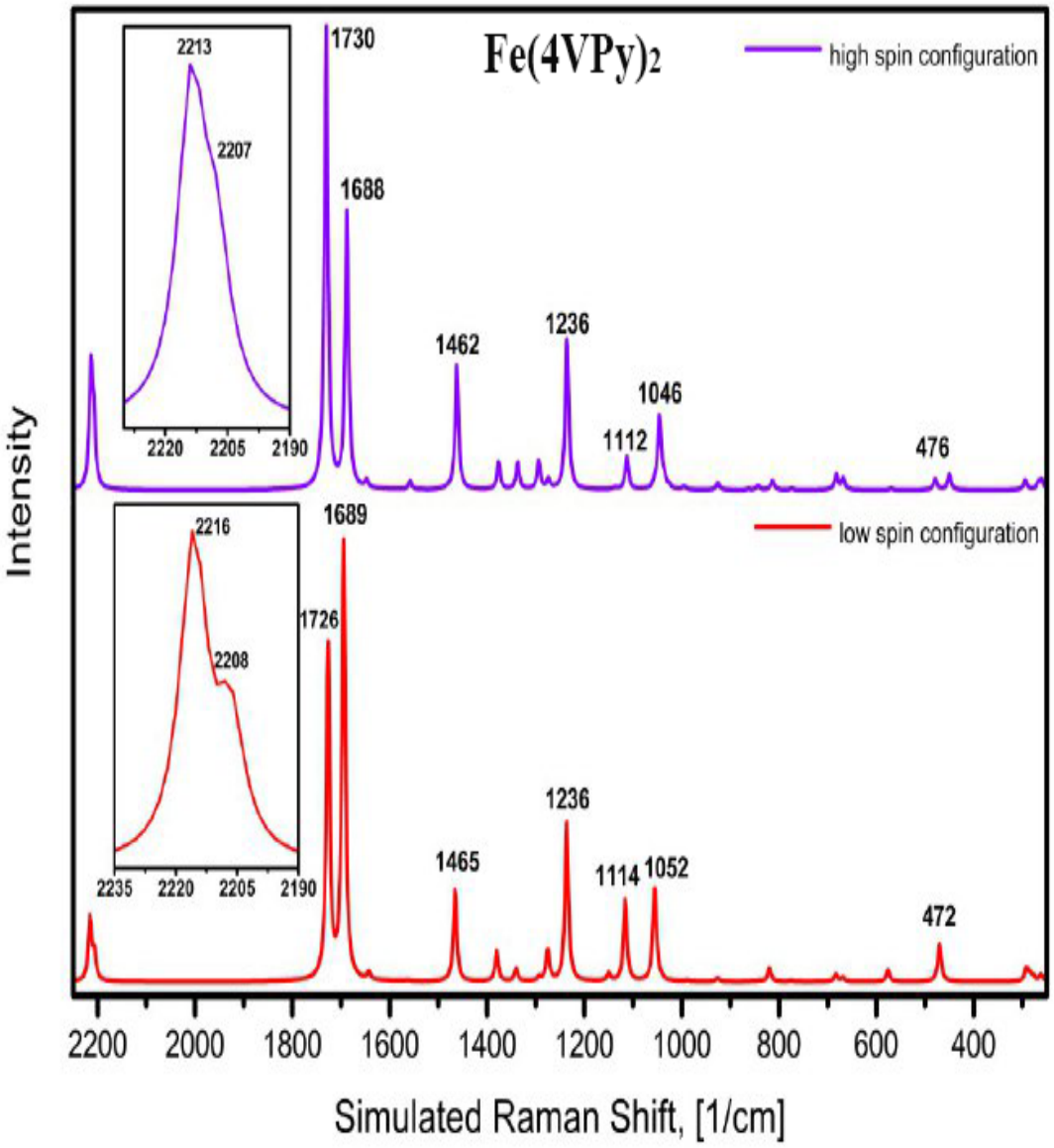

Figure S30: Comparison of the simulated Raman spectra for $Fe(4VPy)_2[Fe(CN)_5NO$ in High Spin and Low Spin configurations.

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Table S1: Details of data collection, crystal data and structure refinement for $Fe(4MPy)_2[Fe(CN)_5NO]$ at 300 K.

	$Fe(4MPy)_2[Fe(CN)_5NO]$
Data collection	
Diffractometer	XPD-10B beamline of the LNLS synchrotron radiation facility
Detector	Ge (111) analyzer crystal
Wavelength (Å)	1.239840
2θ range (°)	5.0-60.0
Step size (°)	0.003
Time per step (s)	5
Unit cell	
Space Group	$P2_1$
Parameters (Å)	a= 9.8979(2)
	b= 14.8359(4)
	c= 7.3795(1)
	β= 105.826(1)
V($Å^3$)	1042.40(2)
Z	2
Refinement	
# of reflections	603
# of refined parameters	
Structural	85
Profile	11
Rexp	1.55
Rwp	3.48
RB	2.28
S	2.24

Table S2: Details of data collection, crystal data and structure refinement for Fe(4AcPy)2$[Fe(CN)_5NO]$ at 300 K.

	$Fe(4AcPy)_2[Fe(CN)_5NO]$
Data collection	
Diffractometer	XPD-10B beamline of the LNLS synchrotron radiation facility
Detector	Ge (111) analyzer crystal
Wavelength (Å)	1.239840
2θ range (°)	5.0-60.0
Step size (°)	0.003
Time per step (s)	5
Unit cell	

Space Group	$P2_12_12_1$
Parameters (Å)	a= 21.2004(2)
	b= 15.0384(2)
	c= 7.2541(1)
V(Å^3)	2312.75(2)
Z	4
Refinement	
# of reflections	788
# of refined parameters	
Structural	45
Profile	12
R_{exp}	1.71
R_{wp}	5.40
R_B	3.68
S	3.15

Table S3: Details of data collection, crystal data and structure refinement for Fe(4PyCA)2[Fe(CN)$_5$NO] at 300 K.

	Fe(4PyCA)$_2$[Fe(CN)$_5$NO]
Data collection	
Diffractometer	XPD-10B beamline of the LNLS synchrotron radiation facility
Detector	Ge (111) analyzer crystal
Wavelength (Å)	1.239840
2θ range (°)	5.0-60.0
Step size (°)	0.003
Time per step (s)	5
Unit cell	
Space Group	$P2_1$
Parameters (Å)	a= 7.3006(1)
	b= 14.8714(2)
	c= 9.7573(2)
	β= 102.062(1)
V(Å^3)	1035.97(2)
Z	2
Refinement	
# of reflections	600
# of refined parameters	
Structural	85
Profile	11
R_{exp}	1.68
R_{wp}	4.17
R_B	2.58
S	2.48

Table S4: Details of data collection, crystal data and structure refinement for $Fe(4VPy)_2[Fe(CN)_5NO]$ at 300 K.

	$Fe(4VPy)_2[Fe(CN)_5NO]$	
Data collection		
Diffractometer	D8-Advance (Bruker)	
Detector	Lynkeye	
Wavelength (Å)	1.54183	
2θ range (°)	5.0-80.0	
Step size (°)	0.02	
Time per step (s)	10	
Unit cell		
Space Group	$P2_1$	
Parameters (Å)	a= 7.2712(2)	
	b= 15.0207(4)	
	c= 10.7144(2)	
	β= 110.20(1)	
V($Å^3$)	1098.22 (2)	
Z	2	
Refinement		
# of reflections	707	
# of refined parameters	Structural	Profile
	85	11
Rexp	4.59	
Rwp	9.68	
RB	7.46	
S	2.11	

Table S5. Refined atomic positions and thermal (B_{iso}) and occupation (Occ) factors for $Fe_{ext}(4MPy)_2[Fe_{int}(CN)_5NO]$ at 300K

Composition	site	x	y	z	Biso	Occ
$Fe_{ext}(4MPy)_2[Fe_{int}(CN)_5NO]$-300K						
Fe_{ext}	2a	0.9819(1)	0.5453(1)	0.5102(1)	1.51(2)	1
Fe_{int}	2a	0.9934(1)	0.8116(1)	0.9962(1)	1.87(2)	1
C1	2a	0.9824(3)	0.9098(2)	0.8236(3)	2.3(2)	1
N1	2a	0.9725(3)	0.9717(4)	0.7314(4)	2.3(2)	1
C2	2a	0.9948(3)	0.7260(4)	0.8009(3)	2.3(2)	1
N2	2a	1.0010(2)	0.6738(3)	0.6931(5)	2.3(2)	1
C3	2a	0.9889(5)	0.8971(5)	1.1844(5)	2.3(2)	1
N3	2a	0.9861(4)	0.9481(4)	1.2965(3)	2.3(2)	1
C4	2a	0.9982(4)	0.7120(2)	1.1661(4)	2.3(2)	1
N4	2a	0.9964(3)	0.6522(2)	1.2605(2)	2.3(2)	1
C5	2a	0.7924(3)	0.8065(3)	0.9345(2)	2.3(2)	1
N5	2a	0.6743(2)	0.8096(3)	0.9054(3)	2.3(2)	1
N6	2a	1.1612(2)	0.8178(3)	1.0418(1)	2.3(2)	1
O1	2a	1.2789(2)	0.8228(5)	1.0673(5)	2.3(2)	1
N7	2a	1.2216(5)	0.5264(4)	0.6004(3)	3.8(2)	1
C6	2a	1.2849(4)	0.6095(4)	0.5990(3)	3.8(2)	1
C7	2a	1.4290(4)	0.6172(2)	0.6690(3)	3.8(2)	1
C8	2a	1.5082(3)	0.5418(2)	0.7397(4)	3.8(2)	1
C9	2a	1.4448(3)	0.4587(2)	0.7410(4)	3.8(2)	1
C10	2a	1.3007(4)	0.4510(4)	0.6710(5)	3.8(2)	1
C11	2a	1.6655(5)	0.5502(4)	0.8162(3)	3.8(2)	1
N8	2a	0.7426(2)	0.5189(6)	0.3413(2)	3.8(2)	1
C12	2a	0.6600(2)	0.4433(4)	0.3371(2)	3.8(2)	1
C13	2a	0.5151(2)	0.4501(3)	0.2880(3)	3.8(2)	1
C14	2a	0.4521(3)	0.5333(3)	0.2428(4)	3.8(2)	1
C15	2a	0.5348(4)	0.6089(4)	0.2471(5)	3.8(2)	1
C16	2a	0.6797(4)	0.6022(5)	0.2961(3)	3.8(2)	1
C17	2a	0.2941(2)	0.5415(5)	0.1891(3)	3.8(2)	1

Table S6. Calculated inter-atomic distances (in Å) and bond angles (in °) from the refined crystal structure for $Fe_{ext}(MPy)_2[Fe_{int}(CN)_5NO]$ at 300K.

Bond distances (Å)	Bond angles (°)	
$Fe_{ext}(4MPy)_2[Fe_{int}(CN)_5NO]$-300K		
Fe_{ext}-N1 = 2.239(2)	N1-Fe_{ext}-N2 = 149.79(3)	N1-C1-Fe_{int} = 174.70(5)
Fe_{ext}-N2 = 2.314(1)	N1-Fe_{ext}-N3 = 100.95(4)	N2-C2-Fe_{int} = 176.50(5)
Fe_{ext}-N3 = 1.992(1)	N1-Fe_{ext}-N4 = 69.70(3)	N3-C3-Fe_{int} = 179.94(6)
Fe_{ext}-N4 = 2.465(2)	N1-Fe_{ext}-N7 = 75.81(4)	N4-C4-Fe_{int} = 177.21(5)
Fe_{ext}-N7 = 2.299(2)	N1-Fe_{ext}-N8 = 83.75(4)	N5-C5-Fe_{int} = 174.68(9)
Fe_{ext}-N8 = 2.389(2)	N2-Fe_{ext}-N3 = 101.95(2)	O1-N6-Fe_{int} = 177.53(10)
Fe_{int}-C1 = 1.919(1)	N2-Fe_{ext}-N4 = 83.90(3)	C1-N1-Fe_{ext} = 150.65(5)
Fe_{int}-C2 = 1.924(2)	N2-Fe_{ext}-N7 = 91.03(3)	C2-N2-Fe_{ext} = 165.75(5)
Fe_{int}-C3 = 1.890(2)	N2-Fe_{ext}-N8 = 110.56(3)	C3-N3-Fe_{ext} = 168.73(5)
Fe_{int}-C4 = 1.930(1)	N3-Fe_{ext}-N4 = 166.12(3)	C4-N4-Fe_{ext} = 168.23(5)
Fe_{int}-C5 = 1.917(2)	N3-Fe_{ext}-N7 = 75.79(4)	Fe_{ext}-N7-C6 = 108.82(6)
Fe_{int}-N6 = 1.605(2)	N3-Fe_{ext}-N8 = 101.32(4)	N7-C6-C7 = 119.58(6)
C1-N1 = 1.131(1)	N4-Fe_{ext}-N7 = 91.66(3)	C6-C7-C8 = 119.64(7)
C2-N2 = 1.124(1)	N4-Fe_{ext}-N8 = 88.11(3)	C7-C8-C9 = 120.74(4)
C3-N3 = 1.127(1)	N7-Fe_{ext}-N8 = 158.25(5)	C8-C9-C10 = 119.62(6)
C4-N4 = 1.131(1)	C1-Fe_{int}-C2 = 90.84(3)	C9-C10-N7 = 119.61(7)
C5-N5 = 1.130(1)	C1-Fe_{int}-C3 = 88.27(4)	C10-N7-Fe_{ext} = 129.86(5)
N6-O = 1.131(1)	C1-Fe_{int}-C4 = 178.17(4)	C10-N7-C6 = 120.81(4)
N7-C6 = 1.384(1)	C1-Fe_{int}-C5 = 90.28(4)	C7-C8-C11= 119.65(6)
C6-C7 = 1.383(1)	C1-Fe_{int}-N6 = 87.92(4)	C9-C8-C11= 119.61(6)
C7-C8 = 1.384(1)	C2-Fe_{int}-C3 = 178.76(4)	Fe_{ext}-N8-C12 = 129.83(5)
C8-C9 = 1.385(1)	C2-Fe_{int}-C4 = 88.70(4)	N8-C12-C13 = 120.71(7)
C9-C10 = 1.383(1)	C2-Fe_{int}-C5 = 90.86(4)	C12-C13-C14 = 119.70(6)
C10-N7 = 1.383(1)	C2-Fe_{int}-N6 = 88.65(4)	C13-C14-C15 = 119.55(4)
C8-C11 = 1.510(1)	C3-Fe_{int}-C4 = 92.17(3)	C14-C15-C16 = 120.81(7)
N8-C12 = 1.383(1)	C3-Fe_{int}-C5 = 88.29(4)	C15-C16-N8 = 119.57(6)
C12-C13 = 1.384(1)	C3-Fe_{int}-N6 = 92.17(5)	C16-N8-Fe_{ext} = 107.24(6)
C13-C14 = 1.382(1)	C4-Fe_{int}-C5 = 87.95(4)	C16-N8-C12 = 119.65(4)
C14-C15 = 1.384(1)	C4-Fe_{int}-N6 = 93.84(4)	C13-C14-C17 = 120.14(6)
C15-C16 = 1.384(1)	C5-Fe_{int}-N6 = 178.14(7)	C15-C14-C17 = 120.30(6)
C16-N8 = 1.383(1)		
C14-C17 = 1.510(2)		

Table S7. Refined atomic positions and thermal (B_{iso}) and occupation (Occ) factors for $Fe_{ext}(4AcPy)_2[Fe_{int}(CN)_5NO]$ at 300K

Composition	site	x	y	z	Biso	Occ
$Fe_{ext}(AcPy)_2[Fe_{int}(CN)_5NO]$-300K						
Fe_{ext}	4a	0.0012(1)	1.0011(1)	-0.2521(1)	1.5(2)	1
Fe_{int}	4a	0.0165(1)	0.7541(1)	0.2487(1)	1.8(2)	1
C1	4a	0.0303(2)	0.6651(2)	0.4337(4)	3.0(2)	1
N1	4a	0.0428(2)	0.6116(3)	0.5368(3)	3.0(2)	1
C2	4a	0.0015(5)	0.8406(3)	0.0571(3)	3.0(2)	1
N2	4a	-0.0089(3)	0.8890(3)	-0.0580(4)	3.0(2)	1
C3	4a	0.1042(5)	0.7535(4)	0.2028(4)	3.0(2)	1
N3	4a	0.1565(4)	0.7531(4)	0.1755(4)	3.0(2)	1
C4	4a	0.0077(3)	0.6632(4)	0.0650(2)	3.0(2)	1
N4	4a	0.0074(3)	0.6086(2)	-0.0421(3)	3.0(2)	1
C5	4a	0.0249(4)	0.8426(3)	0.4397(4)	3.0(2)	1
N5	4a	0.0287(3)	0.8922(2)	0.5562(3)	3.0(2)	1
N6	4a	-0.0580(2)	0.7523(2)	0.2877(3)	3.0(2)	1
O1	4a	-0.1105(2)	0.7550(2)	0.3150(4)	3.0(2)	1
N7	4a	0.1179(3)	0.5257(3)	0.8037(4)	3.6(2)	1
C6	4a	0.2415(4)	0.4955(4)	0.8117(4)	3.6(2)	1
C7	4a	0.2199(4)	0.5776(3)	0.7877(2)	3.6(2)	1
C8	4a	0.1582(3)	0.5928(4)	0.7836(2)	3.6(2)	1
C9	4a	0.1394(4)	0.4435(4)	0.8277(2)	3.6(2)	1
C10	4a	0.2012(5)	0.4283(3)	0.8318(3)	3.6(2)	1
C11	4a	0.3032(3)	0.4803(3)	0.8157(3)	3.6(2)	1
C12	4a	0.3248(3)	0.3982(3)	0.8398(3)	3.6(2)	1
O2	4a	0.3435(2)	0.5475(2)	0.7956(4)	3.6(2)	1
N8	4a	0.0983(4)	0.9754(2)	0.8124(4)	3.6(2)	1
C13	4a	0.1566(4)	1.0080(3)	0.8170(5)	3.6(2)	1
C14	4a	0.2056(2)	0.9532(4)	0.8302(5)	3.6(2)	1
C15	4a	0.1964(2)	0.8659(5)	0.8388(4)	3.6(2)	1
C16	4a	0.0885(3)	0.8877(5)	0.8210(3)	3.6(2)	1
C17	4a	0.1381(3)	0.8333(3)	0.8343(2)	3.6(2)	1
C18	4a	0.2453(3)	0.8111(2)	0.8519(2)	3.6(2)	1
C19	4a	0.2362(4)	0.7238(2)	0.8606(2)	3.6(2)	1
O3	4a	0.3037(5)	0.8438(3)	0.8565(2)	3.6(2)	1

Table S8. Calculated inter-atomic distances (in Å) and bond angles (in °) from the refined structure for $Fe_{ext}(4AcPy)_2[Fe_{int}(CN)_5NO]$ at 300K.

Bond distances (Å)	Bond angles (°)	
$Fe_{ext}(AcPy)_2[Fe_{int}(CN)_5NO]$-300K		
Fe_{ext}-N1 = 2.464(2)	N5-Fe_{ext}-N2 = 82.07(3)	N3-C3-Fe_{int} = 179.96(3)
Fe_{ext}-N2 = 2.207(2)	N5-Fe_{ext}-N4 = 97.93(3)	N4-C4-Fe_{int} = 174.67(6)
Fe_{ext}-N4 = 2.208(2)	N5-Fe_{ext}-N7 = 105.74(2)	N5-C5-Fe_{int} = 177.31(6)
Fe_{ext}-N5 = 2.226(1)	N5-Fe_{ext}-N1 = 172.42(3)	O1-N6-Fe_{int} = 176.98(3)
Fe_{ext}-N7 = 2.579(2)	N5-Fe_{ext}-N8 = 75.67(2)	C1-N1-Fe_{ext} = 144.19(5)
Fe_{ext}-N8 = 2.146(1)	N2-Fe_{ext}-N4 = 169.31(4)	C2-N2-Fe_{ext} = 160.91(5)
Fe_{int}-C1 = 1.918(1)	N2-Fe_{ext}-N7 = 96.15(2)	C4-N4-Fe_{ext} = 175.53(5)
Fe_{int}-C2 = 1.930(1)	N2-Fe_{ext}-N1 = 94.25(2)	C5-N5-Fe_{ext} = 159.08(5)
Fe_{int}-C3 = 1.889(1)	N2-Fe_{ext}-N8 = 79.42(2)	Fe_{ext}-N7-C8 = 136.19(3)
Fe_{int}-C4 = 1.918(1)	N4-Fe_{ext}-N7 = 73.50(2)	N7-C8-C7 = 119.97(3)
Fe_{int}-C5 = 1.929(2)	N4-Fe_{ext}-N1 = 84.46(3)	C8-C7-C6 = 120.16(3)
Fe_{int}-N6 = 1.605(1)	N4-Fe_{ext}-N8 = 111.01(2)	C7-C6-C10 = 119.91(4)
C1-N1 = 1.130(1)	N7-Fe_{ext}-N1 = 67.95(2)	C6-C10-C9 = 119.94(3)
C2-N2 = 1.129(1)	N7-Fe_{ext}-N8 = 175.19(2)	C10-C9-N7 = 120.04(3)
C3-N3 = 1.126(1)	N1-Fe_{ext}-N8 = 110.27(2)	C9-N7-Fe_{ext} = 102.79(2)
C4-N4 = 1.130(1)	N6-Fe_{int}-C3 = 178.76(3)	C9-N7-C8 = 119.98(4)
C5-N5 = 1.130(1)	N6-Fe_{int}-C1 = 90.86(3)	C7-C6-C11= 120.16(3)
N6-O1 = 1.131(1)	N6-Fe_{int}-C4 = 90.84(3)	C6-C11-C12= 120.15(3)
N7-C9 = 1.329(1)	N6-Fe_{int}-C5 = 88.62(3)	C6-C11-O2= 119.93(3)
C9-C10 = 1.330(1)	N6-Fe_{int}-C2 = 88.63(3)	C10-C6-C11= 119.93(3)
C10-C6 = 1.331(1)	C3-Fe_{int}-C1 = 88.27(3)	Fe_{ext}-N8-C16 = 92.22(3)
C6-C7 = 1.328(1)	C3-Fe_{int}-C4 = 88.27(2)	N8-C16-C17 = 119.03(4)
C7-C8 = 1.328(1)	C3-Fe_{int}-C5 = 92.24(3)	C16-C17-C15 = 120.50(3)
C8-N7 = 1.330(1)	C3-Fei-C2 = 92.20(2)	C17-C15-C14 = 119.96(4)
C6-C11 = 1.328(1)	C1-Fe_{int}-C4 = 90.21(4)	C15-C14-C13 = 120.08(4)
C11-O2 = 1.331(1)	C1-Fe_{int}-C5 = 87.98(3)	C14-C13-N8 = 119.96(3)
C11-C12 = 1.328(1)	C1-Fe_{int}-C2 = 178.07(4)	C13-N8-Fe_{ext} = 146.14(3)
N8-C16 = 1.337(1)	C4-Fe_{int}-C5 = 178.10(4)	C13-N8-C16 = 120.46(4)
C16-C17 = 1.336(1)	C4-Fe_{int}-C2 = 87.94(3)	C17-C15-C18 = 119.90(3)
C17-C15 = 1.330(1)	C5-Fei-C2 = 93.87(4)	C15-C18-C19 = 120.22(4)
C15-C14 = 1.329(1)	N1-C1-Fe_{int} = 174.76(5)	C15-C18-O3 = 119.88(3)
C14-C13 = 1.329(1)	N2-C2-Fe_{int} = 177.33(6)	C14-C15-C18 = 120.13(4)
C13-N8 = 1.330(1)		
C15-C18 = 1.328(1)		
C18-O3 = 1.333(1)		
C18-C19 = 1.328(1)		

Table S9. Refined atomic positions and thermal (B_{iso}) and occupation (Occ) factors for $Fe_{ext}(4PyCA)_2[Fe_{int}(CN)_5NO]$ at 300K

Composition	site	x	y	z	Biso	Occ
$Fe_{ext}(CA)_2[Fe_{int}(CN)_5NO]$-300K						
Fe_{ext}	2a	0.0111(1)	0.0195(1)	0.5248(1)	3.8(2)	1
Fe_{int}	2a	0.5095(1)	0.2791(1)	0.5173(1)	3.8(2)	1
C1	2a	0.6995(2)	0.1881(3)	0.5396(3)	6.8(2)	1
N1	2a	0.8073(2)	0.1333(2)	0.5420(3)	6.8(2)	1
C2	2a	0.3123(3)	0.3677(2)	0.4958(4)	6.8(2)	1
N2	2a	0.1932(4)	0.4174(4)	0.4860(5)	6.8(2)	1
C3	2a	0.5010(4)	0.2765(4)	0.3225(5)	6.8(2)	1
N3	2a	0.4960(3)	0.2749(3)	0.2063(4)	6.8(2)	1
C4	2a	0.3190(2)	0.1882(2)	0.4889(4)	6.8(2)	1
N4	2a	0.2100(2)	0.1334(3)	0.4625(3)	6.8(2)	1
C5	2a	0.7071(3)	0.3676(3)	0.5484(3)	6.8(2)	1
N5	2a	0.8270(5)	0.4172(2)	0.5704(3)	6.8(2)	1
N6	2a	0.5166(5)	0.2790(4)	0.6829(2)	6.8(2)	1
O1	2a	0.5216(3)	0.2831(5)	0.7992(3)	6.8(2)	1
N7	2a	0.1239(3)	0.0337(4)	0.7542(2)	6.8(2)	1
C6	2a	0.1721(3)	-0.0530(3)	0.7992(2)	6.8(2)	1
C7	2a	0.2337(2)	-0.0698(4)	0.9406(4)	6.8(2)	1
C8	2a	0.2463(3)	0.0001(3)	1.0356(4)	6.8(2)	1
C9	2a	0.1980(5)	0.0868(3)	0.9905(3)	6.8(2)	1
C10	2a	0.1364(5)	0.1037(2)	0.8490(2)	6.8(2)	1
C11	2a	0.3118(2)	-0.0178(2)	1.1860(2)	6.8(2)	1
O2	2a	0.4478(5)	0.0211(5)	1.2514(2)	6.8(2)	1
N8	2a	-0.0992(3)	0.0475(4)	0.2346(4)	6.8(2)	1
C12	2a	-0.1371(3)	0.0998(4)	0.1148(4)	6.8(2)	1
C13	2a	-0.2302(2)	0.0625(2)	-0.0102(3)	6.8(2)	1
C14	2a	-0.2846(2)	-0.0268(3)	-0.0139(3)	6.8(2)	1
C15	2a	-0.2467(3)	-0.0790(3)	0.1060(4)	6.8(2)	1
C16	2a	-0.1535(4)	-0.0417(4)	0.2310(4)	6.8(2)	1
C17	2a	-0.3835(2)	-0.0665(4)	-0.1468(2)	6.8(2)	1
O3	2a	-0.3191(2)	-0.1316(3)	-0.1941(2)	6.8(2)	1

Table S10. Calculated inter-atomic distances (in Å) and bond angles (in °) from the refined structure for $Fe_{ext}(4PyCA)_2[Fe_{int}(CN)_5NO]$ at 300K.

Bond distances (Å)	Bond angles (°)	
$Fe_{ext}(4PyCA)_2[Fe_{int}CN)_5NO]$-300K		
Fe_{ext}-N1 = 2.283(2)	N5-Fe_{ext}-N2 = 85.391(4)	N5-C5-Fe_{int} = 177.259(6)
Fe_{ext}-N2 = 2.115(2)	N5-Fe_{ext}-N4 = 88.546(2)	O1-N6-Fe_{int} = 176.852(11)
Fe_{ext}-N4 = 2.391(2)	N5-Fe_{ext}-N7 = 111.357(4)	C1-N1-Fe_{ext} = 174.405(5)
Fe_{ext}-N5 = 2.243(1)	N5-Fe_{ext}-N1 = 160.238(3)	C2-N2-Fe_{ext} = 174.722(5)
Fe_{ext}-N7 = 2.228(2)	N5-Fe_{ext}-N8 = 75.401(3)	C4-N4-Fe_{ext} = 152.720(5)
Fe_{ext}-N8 = 2.808(3)	N2-Fe_{ext}-N4 = 162.778(3)	C5-N5-Fe_{ext} = 144.876(5)
Fe_{int}-C1 = 1.917(1)	N2-Fe_{ext}-N7 = 103.111(4)	C6-N7-Fe_{ext} = 104.278(6)
Fe_{int}-C2 = 1.930(2)	N2-Fe_{ext}-N1 = 94.139(2)	Fe_{ext}-N7-C10 = 134.614(6)
Fe_{int}-C3 = 1.889(2)	N2-Fe_{ext}-N8 = 90.319(4)	C10-N7-C6 = 120.821(4)
Fe_{int}-C4 = 1.918(1)	N4-Fe_{ext}-N7 = 94.110(4)	N7-C6-C7 = 119.573(5)
Fe_{int}-C5 = 1.929(2)	N4-Fe_{ext}-N1 = 86.175(4)	C6-C7-C8 = 119.708(8)
Fe_{int}-N6 = 1.606(2)	N4-Fe_{ext}-N8 = 72.543(3)	C7-C8-C9 = 120.682(4)
C1-N1 = 1.130(1)	N7-Fe_{ext}-N1 = 88.030(4)	C8-C9-C10 = 119.661(5)
C2-N2 = 1.130(1)	N7-Fe_{ext}-N8 = 165.229(6)	C9-C10-N7 = 119.556(8)
C3-N3 = 1.127(1)	N1-Fe_{ext}-N8 = 84.850(4)	C12-N8-Fee = 154.179(6)
C4-N4 = 1.130(1)	N6-Fe_{int}-C3 = 178.774(8)	Fe_{ext}-N8-C16 = 84.471(6)
C5-N5 = 1.130(1)	N6-Fe_{int}-C1 = 90.842(5)	C16-N8-C12 = 120.820(4)
N6-O1 = 1.129(1)	N6-Fe_{int}-C4 = 90.842(5)	N8-C12-C13 = 119.652(9)
N7-C6 = 1.384(1)	N6-Fe_{int}-C5 = 88.654(5)	C12-C13-C14 = 119.566(5)
C6-C7 = 1.382(1)	N6-Fe_{int}-C2 = 88.654(5)	C13-C14-C15 = 120.717(4)
C7-C8 = 1.383(1)	C3-Fe_{int}-C1 = 88.316(4)	C14-C15-C16 = 119.713(9)
C8-C9 = 1.384(1)	C3-Fe_{int}-C4 = 88.271(4)	C15-C16-N8 = 119.532(5)
C9-C10 = 1.383(1)	C3-Fe_{int}-C5 = 92.205(5)	C11-C8-C7 = 119.691(8)
C10-N7 = 1.383(1)	C3-Fe_{int}-C2 = 92.160(5)	C11-C8-C9 = 119.627(5)
C8-C11 = 1.470(1)	C1-Fe_{int}-C4 = 90.258(4)	O2-C11-C8 = 120.009(9)
C11-O2 = 1.209(1)	C1-Fe_{int}-C5 = 87.948(3)	C15-C14-C17 = 119.700(9)
N8-C12 = 1.383(1)	C1-Fe_{int}-C2 = 178.093(4)	C13-C14-C17 = 119.584(5)
C12-C13 = 1.382(1)	C4-Fei-C5 = 178.129(4)	O3-C17-C14 = 119.992(5)
C13-C14 = 1.384(1)	C4-Fe_{int}-C2 = 87.911(3)	
C14-C15 = 1.383(1)	C5-Fe_{int}-C2 = 93.879(5)	
C15-C16 = 1.382(1)	N1-C1-Fei = 174.708(5)	
C16-N8 = 1.383(1)	N2-C2-Fe_{int} = 177.320(6)	
C14-C17 = 1.470(1)	N3-C3-Fe_{int} = 179.955(10)	
C17-O3 = 1.209(1)	N4-C4-Fe_{int} = 174.747(5)	

Table S11. Refined atomic positions and thermal (B_{iso}) and occupation (Occ) factors for $Fe_{ext}(4VPy)_2[Fe_{int}(CN)_5NO]$ at 300K

Composition	site	x	y	z	Biso	Occ
$Fe_{ext}(VPy)_2[Fe_{int}(CN)_5NO]$						
Fe_{ext}	2a	0.0023(2)	0.1785(3)	0.0369(1)	1.51(2)	1
Fe_{int}	2a	0.4801(1)	0.4307(2)	0.0104(2)	1.87(2)	1
C1	2a	0.3136(2)	0.3344(1)	0.0254(2)	2.3(2)	1
N1	2a	0.2222(4)	0.2766(1)	0.0381(2)	2.3(2)	1
C2	2a	0.6658(4)	0.3438(1)	-0.0053(3)	2.3(2)	1
N2	2a	0.7663(2)	0.2909(2)	-0.0190(3)	2.3(2)	1
C3	2a	0.6510(2)	0.5258(5)	0.0013(2)	2.3(2)	1
N3	2a	0.7435(5)	0.5861(2)	0.00000	2.3(2)	1
C4	2a	0.3026(1)	0.5174(2)	0.0285(2)	2.3(2)	1
N4	2a	0.1969(2)	0.5690(5)	0.0394(2)	2.3(2)	1
C5	2a	0.3688(2)	0.4348(2)	-0.1812(2)	2.3(2)	1
N5	2a	0.3109(2)	0.4378(2)	-0.2934(3)	2.3(2)	1
N6	2a	0.5786(1)	0.4293(4)	0.1695(3)	2.3(2)	1
O	2a	0.6417(4)	0.4337(4)	0.2817(3)	2.3(2)	1
N7	2a	0.1555(4)	0.2230(2)	0.2369(2)	3.8(2)	1
C6	2a	0.1145(2)	0.1387(5)	0.2632(4)	3.8(2)	1
C7	2a	0.1491(3)	0.1060(2)	0.3900(4)	3.8(2)	1
C8	2a	0.2313(4)	0.1632(1)	0.4967(3)	3.8(2)	1
C9	2a	0.2758(2)	0.2503(1)	0.4736(2)	3.8(2)	1
C10	2a	0.2354(1)	0.2766(3)	0.3431(2)	3.8(2)	1
C11	2a	0.2706(3)	0.1320(4)	0.6319(4)	3.8(2)	1
N8	2a	0.8642(2)	0.2368(4)	0.7841(3)	3.8(2)	1
C12	2a	0.4163(2)	0.1599(3)	0.7414(3)	3.8(2)	1
C13	2a	0.7796(2)	0.2838(1)	0.6712(2)	3.8(2)	1
C14	2a	0.7446(3)	0.2503(1)	0.5447(3)	3.8(2)	1
C15	2a	0.8001(1)	0.1630(2)	0.5333(1)	3.8(2)	1
C16	2a	0.8875(4)	0.1126(1)	0.6472(4)	3.8(2)	1
C17	2a	0.9160(5)	0.1522(2)	0.7691(2)	3.8(2)	1
C18	2a	0.7670(3)	0.1245(3)	0.4029(1)	3.8(2)	1
C19	2a	0.6193(4)	0.1447(4)	0.2896(2)	3.8(2)	1

Table S12. Calculated inter-atomic distances (in Å) and bond angles (in °) from the refined structure for $Fe_{ext}(4VPy)_2[Fe_{int}(CN)_5NO]$ at 300K.

Bond distances (Å)	Bond angles (°)	
$Fe_{ext}(VPy)_2[Fe_{int}(CN)_5NO]$		
Fe_{ext}-N1 = 2.171(2)	N1-Fe_{ext}-N2 = 89.18(3)	N2-C2-Fe_{int} = 176.45(5)
Fe_{ext}-N2 = 2.333(2)	N1-Fe_{ext}-N3 = 77.90(2)	N3-C3-Fe_{int} = 174.65(5)
Fe_{ext}-N3 = 2.450(2)	N1-Fe_{ext}-N4 = 156.40(3)	N4-C4-Fe_{int} = 179.93(5)
Fe_{ext}-N4 = 2.157(1)	N1-Fe_{ext}-N7 = 69.90(3)	N5-C5-Fe_{int} = 177.27(7)
Fe_{ext}-N7 = 2.152(2)	N1-Fee-N8 = 78.64(3)	O-N6-Fe_{int} = 175.28(8)
Fe_{ext}-N8 = 2.690(2)	N2-Fe_{ext}-N3 = 153.82(3)	C1-N1-Fe_{ext} = 169.54(5)
Fe_{int}-C1 = 1.929(1)	N2-Fe_{ext}-N4 = 96.66(2)	C2-N2-Fe_{ext} = 158.84(4)
Fe_{int}-C2 = 1.928(1)	N2-Fe_{ext}-N7 = 96.49(3)	C3-N3-Fe_{ext} = 160.19(4)
Fe_{int}-C3 = 1.918(1)	N2-Fe_{ext}-N8 = 61.31(2)	C4-N4-Fe_{ext} = 151.52(4)
Fe_{int}-C4 = 1.889(1)	N3-Fe_{ext}-N4 = 87.26(3)	Fe_{ext}-N7-C6 = 80.86(4)
Fe_{int}-C5 = 1.930(2)	N3-Fe_{ext}-N7 = 100.17(3)	N7-C6-C7 = 123.99(4)
Fe_{int}-N6 = 1.605(1)	N3-Fe_{ext}-N8 = 93.57(3)	C6-C7-C8 = 117.95(6)
C1-N1 = 1.129(1)	N4-Fe_{ext}-N7 = 131.55(3)	C7-C8-C9 = 119.72(4)
C2-N2 = 1.123(1)	N4-Fe_{ext}-N8 = 84.16(3)	C8-C9-C10 = 117.90(4)
C3-N3 = 1.131(1)	N7-Fe_{ext}-N8 = 141.85(4)	C9-C10-N7 = 124.06(7)
C4-N4 = 1.127(1)	C1-Fe_{int}-C2 = 88.71(4)	C10-N7-Fe_{ext} = 161.46(5)
C5-N5 = 1.129(1)	C1-Fe_{int}-C3 = 178.15(3)	C10-N7-C6 = 116.38(4)
N6-O = 1.131(1)	C1-Fe_{int}-C4 = 92.15(3)	C7-C8-C11= 120.11(6)
N7-C6 = 1.352(1)	C1-Fe_{int}-C5 = 93.86(4)	C9-C8-C11= 120.16(4)
C6-C7 = 1.384(1)	C1-Fe_{int}-N6 = 87.96(4)	C8-C11-C12= 126.33(7)
C7-C8 = 1.389(1)	C2-Fe_{int}-C3 = 90.83(3)	Fe_{ext}-N8-C13 = 165.48(5)
C8-C9 = 1.390(1)	C2-Fe_{int}-C4 = 178.75(4)	N8-C13-C14 = 124.05(7)
C9-C10 = 1.384(1)	C2-Fe_{int}-C5 = 88.71(4)	C13-C14-C15 = 117.92(4)
C10-N7 = 1.351(1)	C2-Fe_{int}-N6 = 90.83(4)	C14-C15-C16 = 119.71(4)
C8-C11 = 1.454(1)	C3-Fe_{int}-C4 = 88.28(4)	C15-C16-C17 = 117.93(7)
C11-C12= 1.347(1)	C3-Fe_{int}-C5 = 87.92(3)	C16-C17-N8 = 124.03(4)
N8-C13 = 1.351(1)	C3-Fe_{int}-N6 = 90.26(4)	C17-N8-Fe_{ext} = 77.92(4)
C13-C14 = 1.384(1)	C4-Fe_{int}-C5 = 92.14(4)	C17-N8-C13 = 116.36(4)
C14-C15 = 1.389(1)	C4-Fe_{int}-N6 = 88.29(4)	C14-C15-C18 = 120.19(4)
C15-C16 = 1.390(1)	C5-Fe_{int}-N6 = 178.11(6)	C16-C15-C18 = 120.09(6)
C16-C17 = 1.384(1)	N1-C1-Fe_{int} = 177.27(5)	C15-C18-C19= 126.31(7)
C17-N8 = 1.352(1)		
C15-C18 = 1.453(1)		
C18-C19= 1.348(1)		

Table S13: Unit cell parameter for $Fe(4MPy)_2[Fe(CN)_5NO]$ and $Fe(4CAPy)_2[Fe(CN)_5NO]$ 100 K

Molecule	Unit cell parameters	Unit cell volume, $Å^3$	Unit cell volume reduction, %
4MPy	**a** = 9.821 Å; **b** = 14.805 Å; **c** = 7.372 Å; β =105.58 °	V (100 K): 1032.6 V (300 K): 1042.56	1.05
4CAPy	**a** = 7.306 Å; **b** = 14.836 Å; **c** = 9.648 Å; β =101.96 °	V (100 K): 1023.2 V (300 K): 1035.96	1.23