Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Spin-crossover in the Fe(4X-pyridine)$_2$[Fe(CN)$_5$NO] series with X = Cl, Br, and I. Role of the distortion for the iron atom coordination environment.

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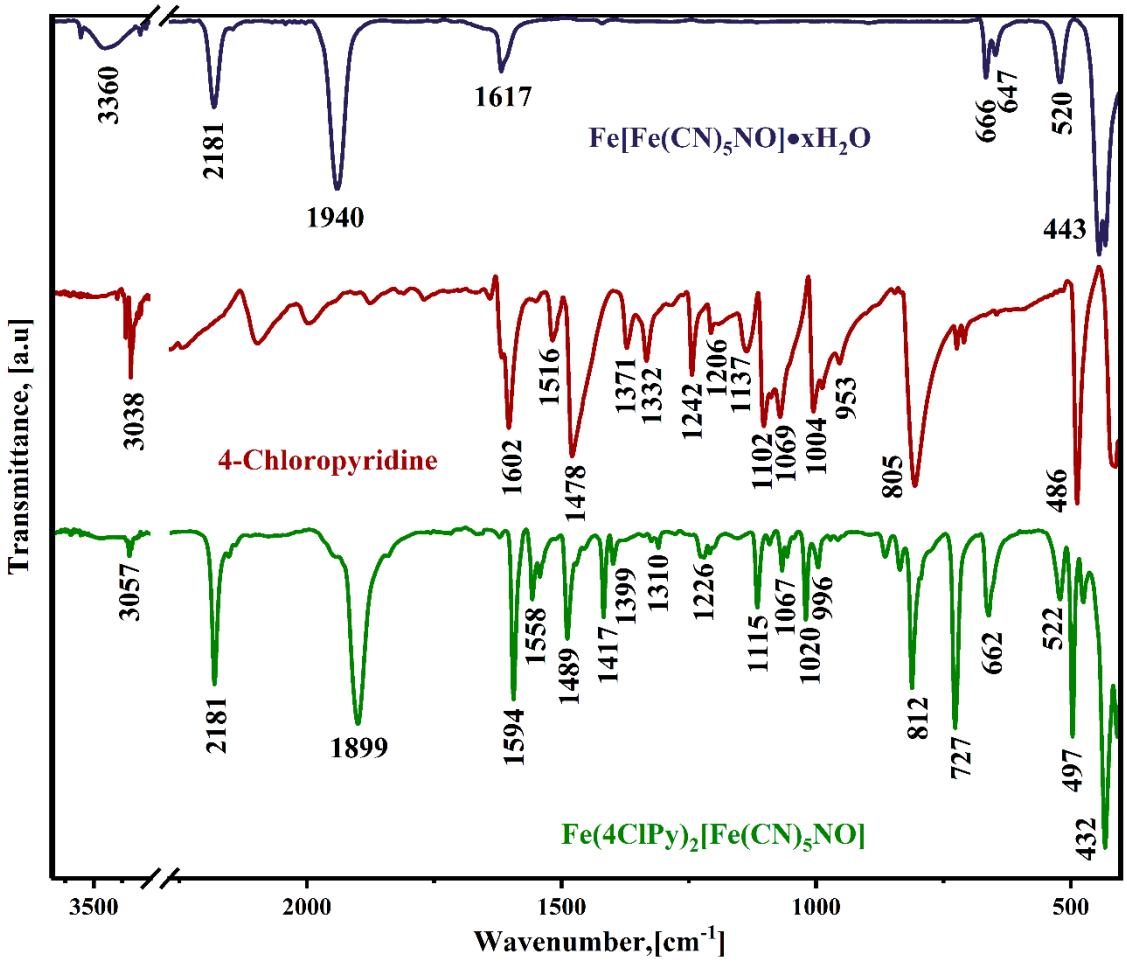

Figure S1. IR spectra for ferrous nitroprussides (cubic phase), 4-Chloropyridine, and the solid formed by the precipitation reaction of sodium nitroprusside, ferrous ammonium sulfate, and this organic ligand.

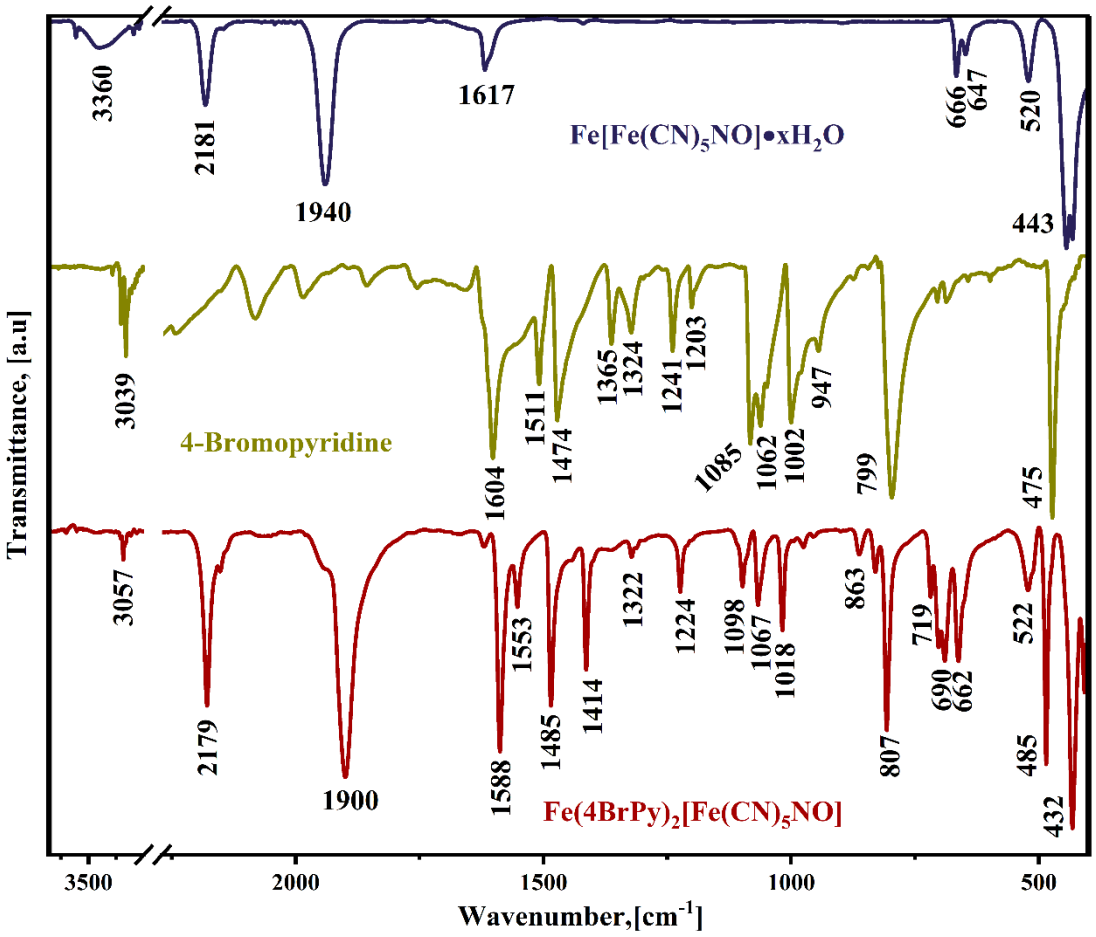

Figure S2. IR spectra for ferrous nitroprussides (cubic phase), 4-Bromopyridine, and the solid formed by the precipitation reaction of sodium nitroprusside, ferrous ammonium sulfate, and this organic ligand.

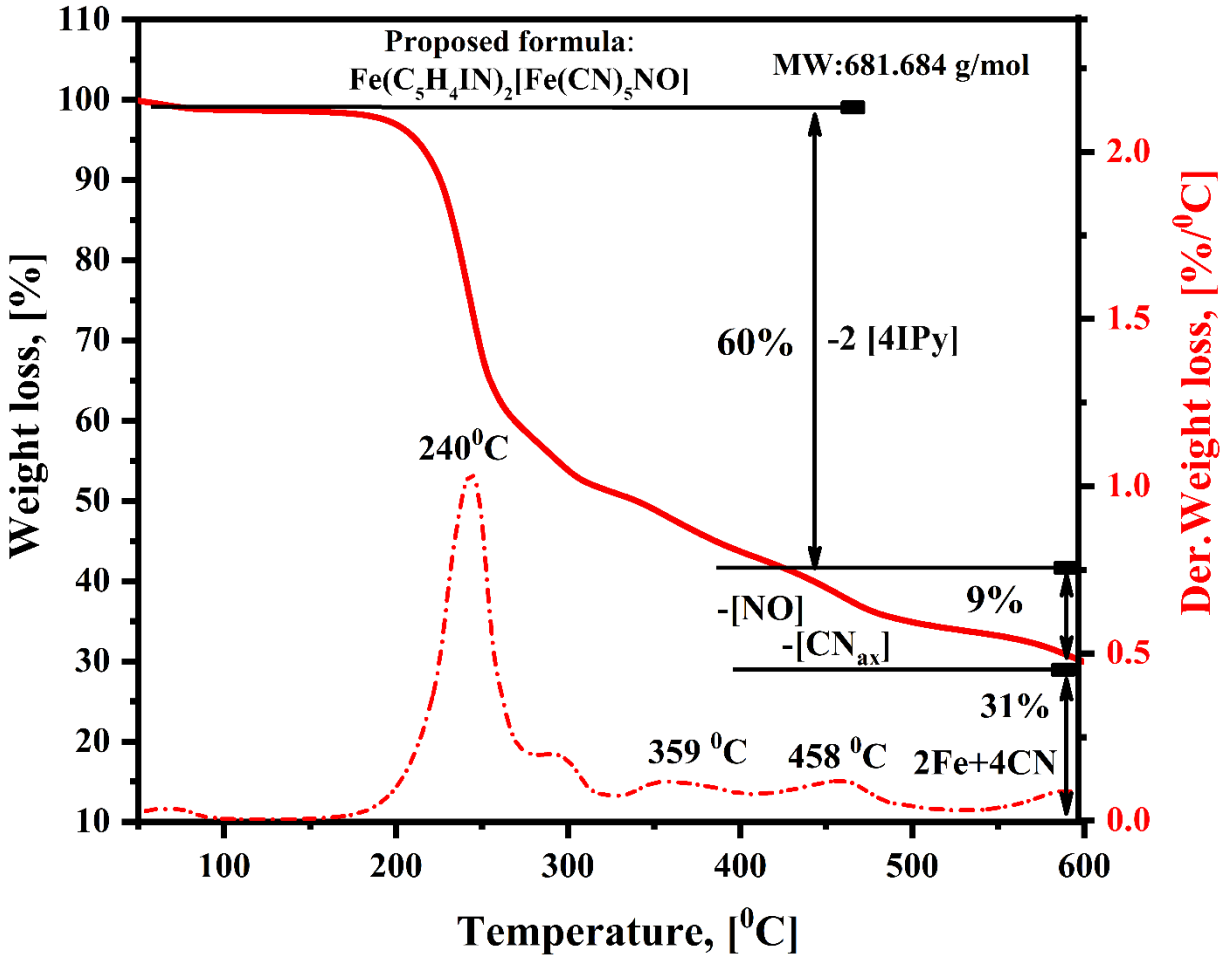

Figure S3. TG curve for the solid formed from the precipitation reaction of aqueous solutions of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, Mohr salt, $Fe(NH_4)_2Fe(SO_4)_2(H_2O)_6$, and the organic ligand (4IPy = 4-Iodopyridine).

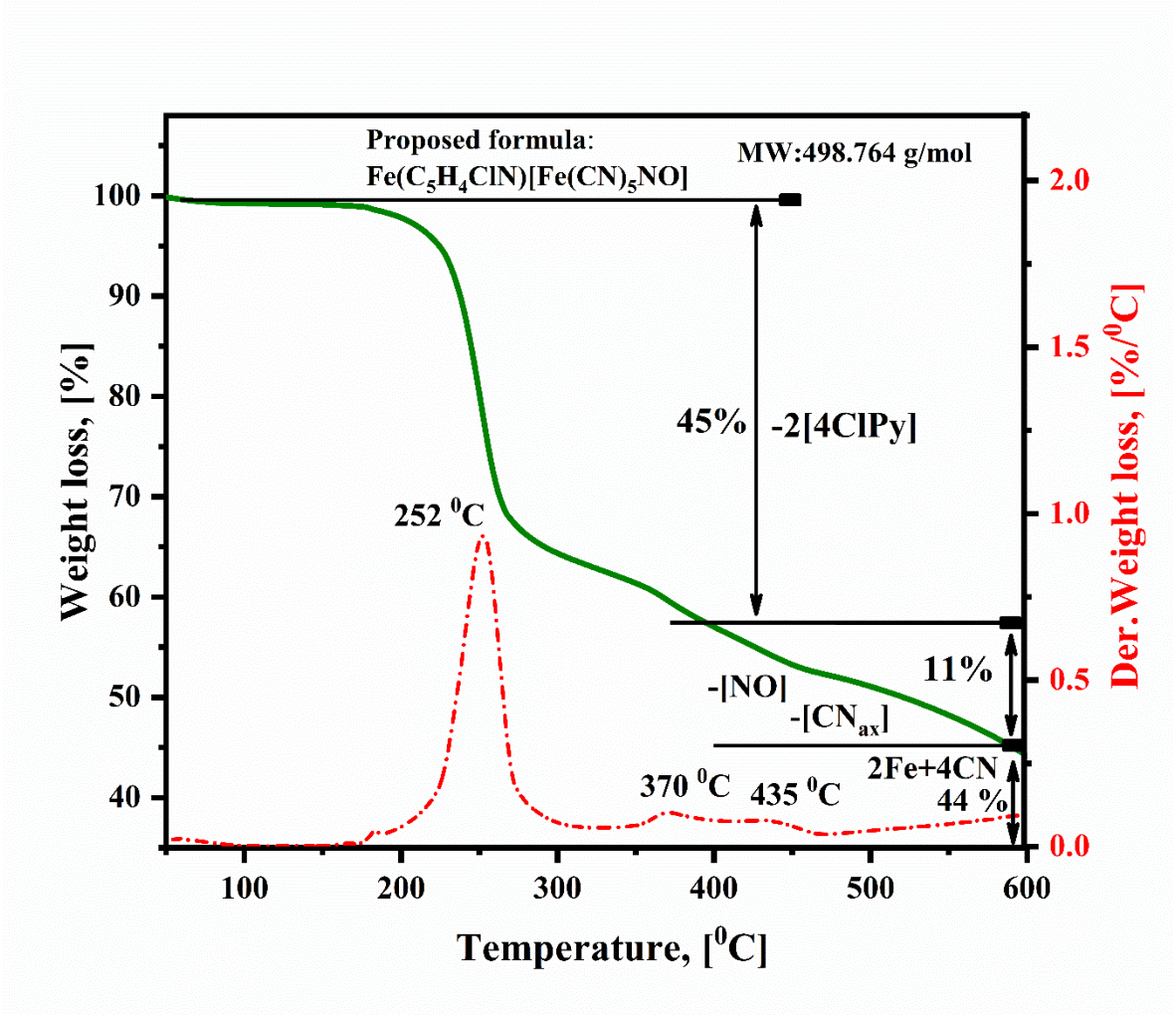

Figure S4. T.G. curve for the solid formed from the precipitation reaction of aqueous solutions of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, Mohr salt, $Fe(NH_4)_2Fe(SO_4)_2(H_2O)_6$, and the organic ligand (4ClPy = 4 Chloropyridine).

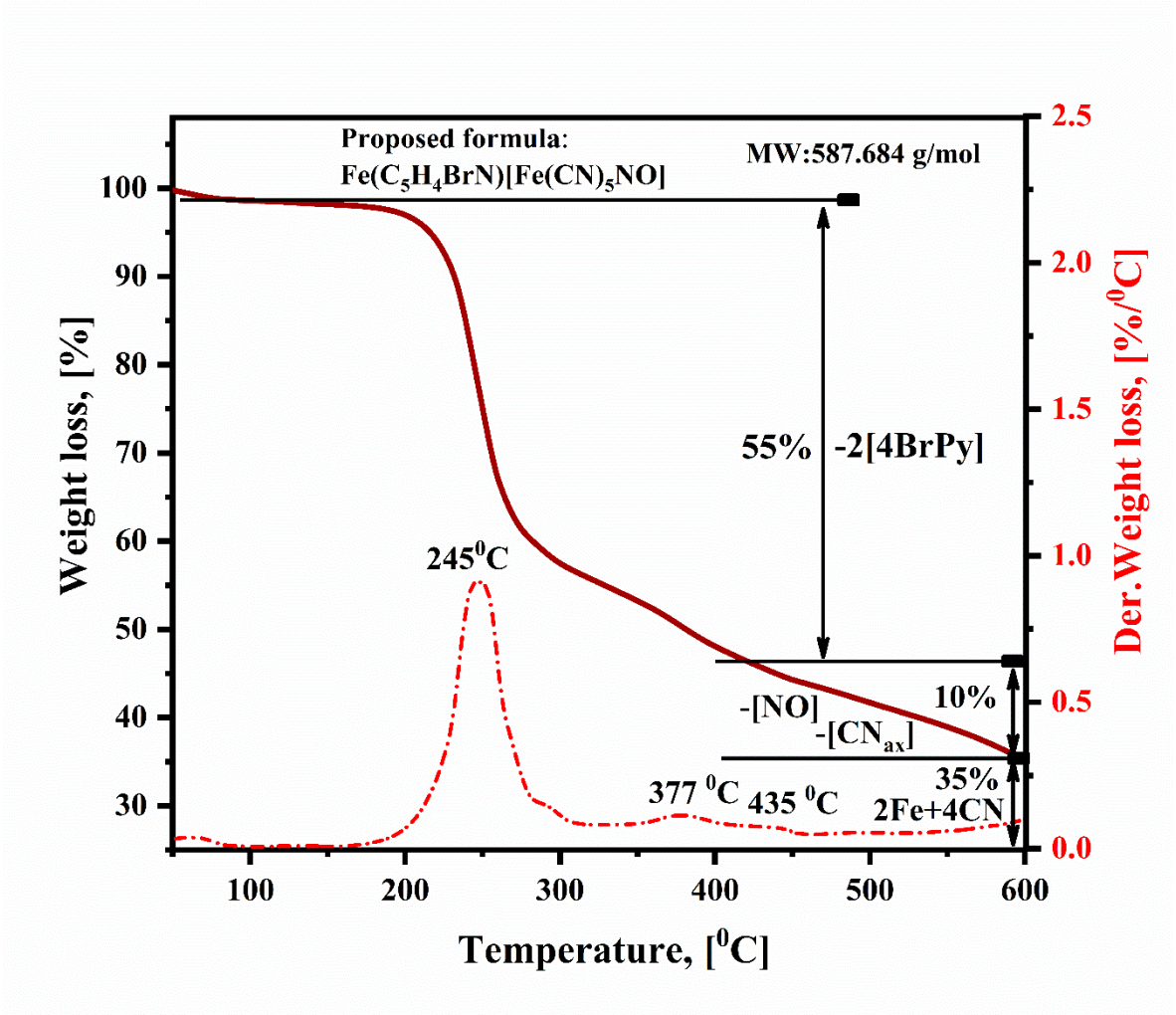

Figure S5. T.G. curve for the solid formed from the precipitation reaction of aqueous solutions of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, Mohr salt, $Fe(NH_4)_2Fe(SO_4)_2(H_2O)_6$, and the organic ligand (4BrPy = 4 Bromopyridine).

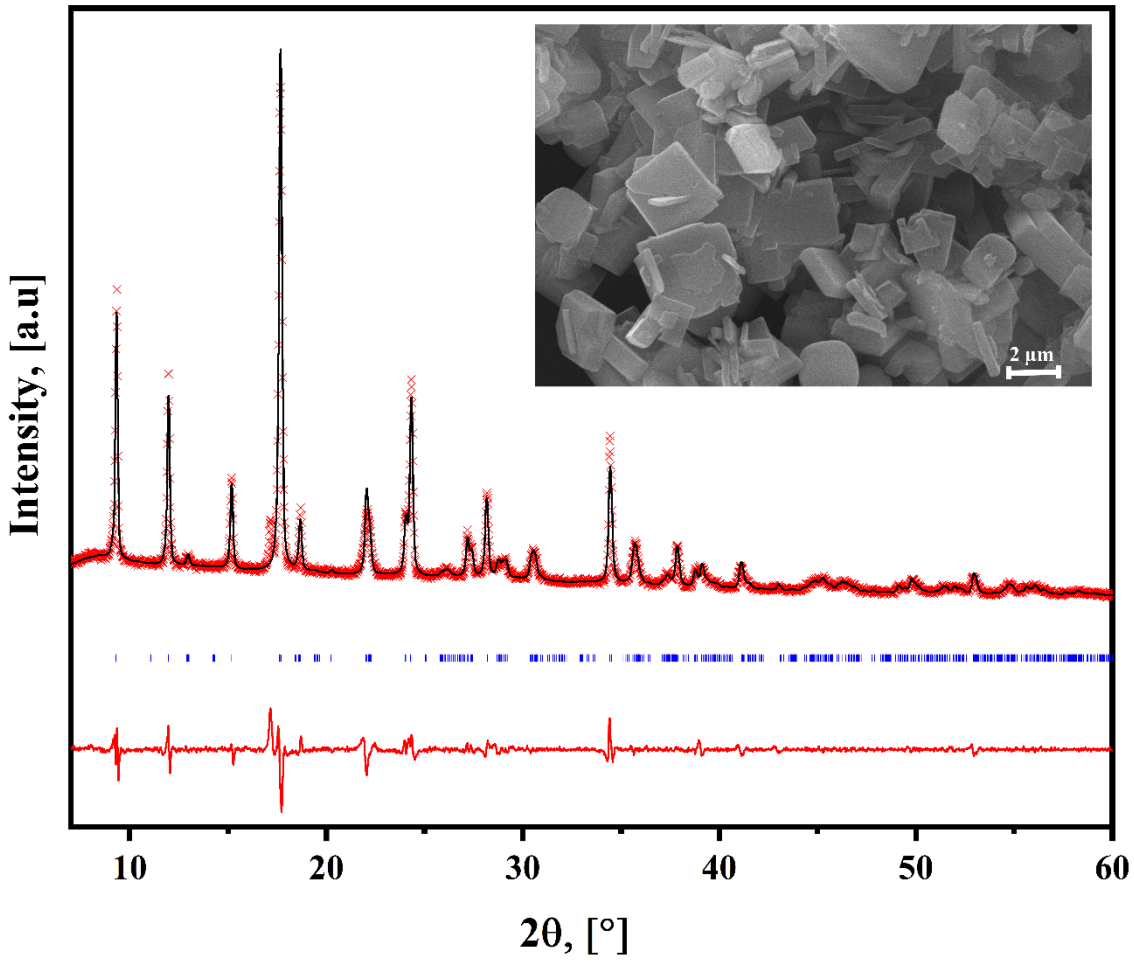

Figure S6. Experimental and fitted XRD powder patterns and their difference for $Fe(4ClPy)_2[Fe(CN)_5NO]$. Inset: Morphology for the crystallites of the obtained solid.

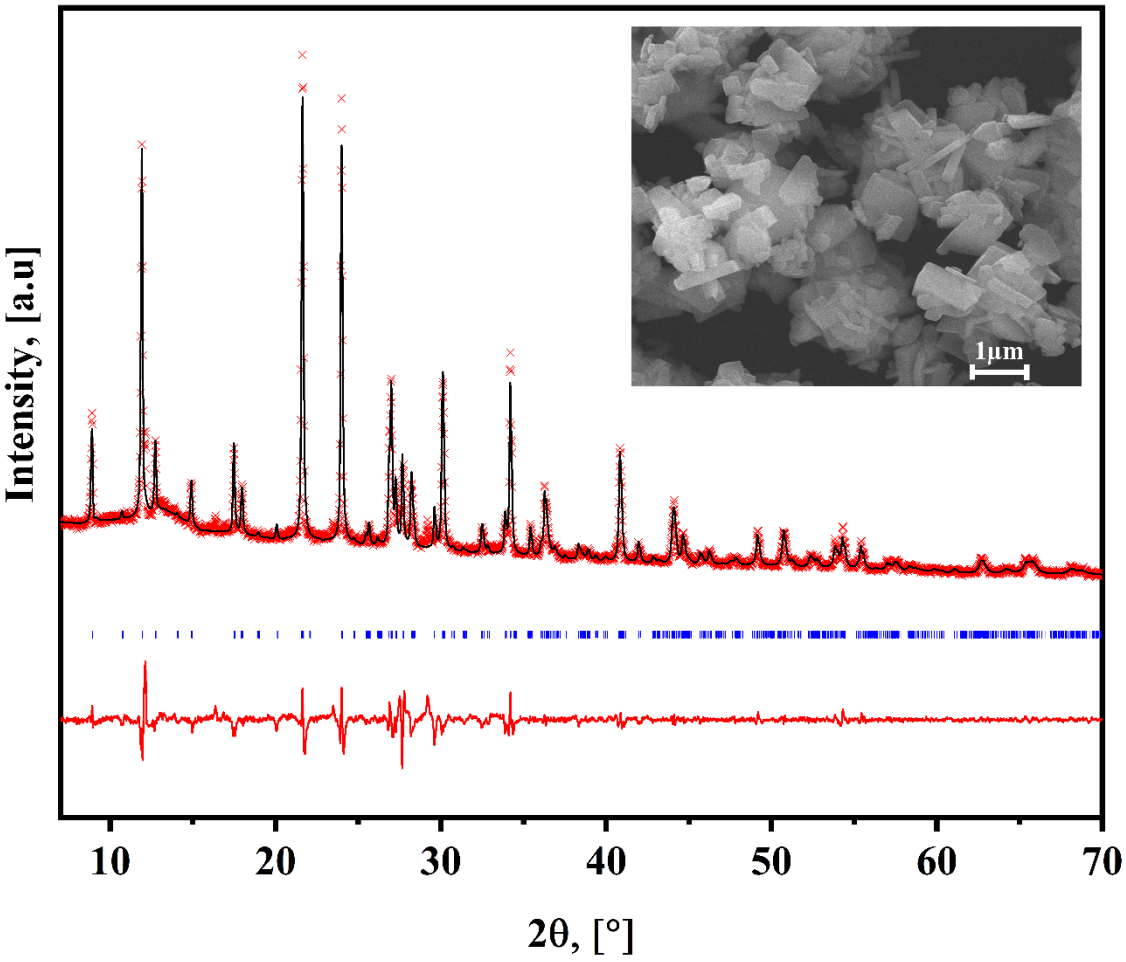

Figure S7. Experimental and fitted XRD powder patterns and their difference for $Fe(4lPy)_2[Fe(CN)_5NO]$. Inset: Morphology for the crystallites of the obtained solid.

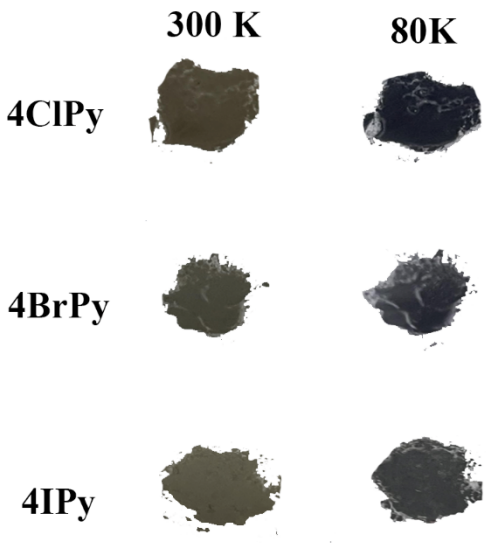

Figure S8. Color change for the $Fe(4XPy)_2[Fe(CN)_5NO]$ series with X = Cl, Br, I.

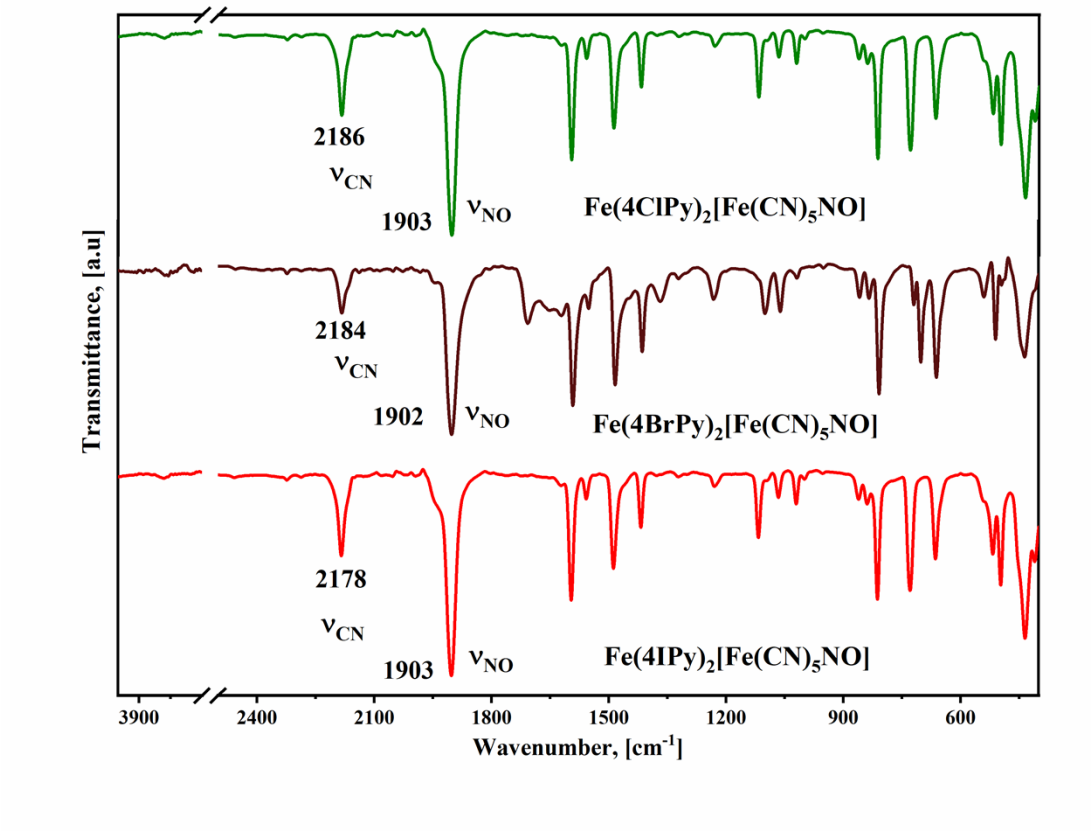

Figure S9. IR spectra at 80 K for the $Fe(4XPy)_2[Fe(CN)_5NO]$ series with X = Cl, Br, I.

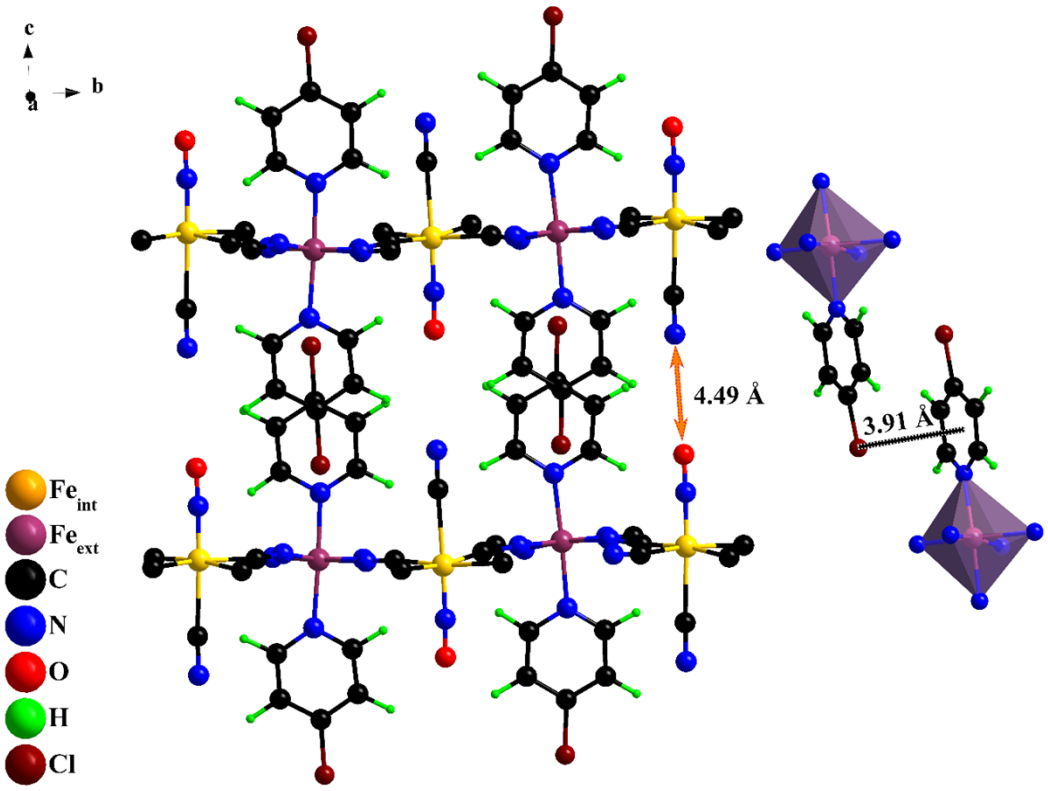

Figure S10. Calculated structure for the LS phase of $Fe(4ClPy)_2[Fe(CN)_5NO]$.

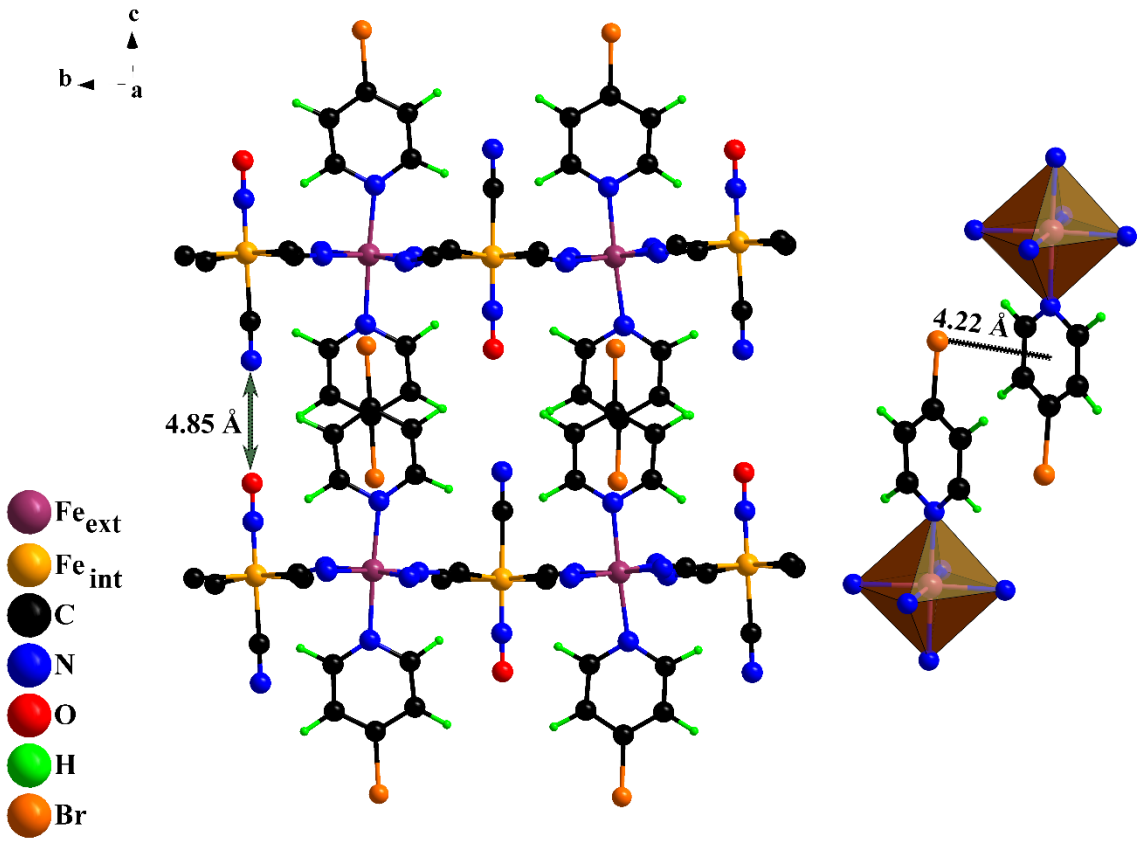

Figure S11. Calculated structure for the LS phase of $Fe(4BrPy)_2[Fe(CN)_5NO]$.

Table S1: Chemical analysis results for the obtained polycrystalline materials

Sample	%Fe		%X		%C		%N		%O		%H	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
4ClPy	22.39	21.89	14.20	13.56	36.11	36.78	22.46	21.78	3.21	3.98	1.62	1.60
4BrPy	19.00	20.98	27.19	27.01	30.65	29.94	19.06	19.89	2.72	2.87	1.37	1.22
4IPy	16.38	15.01	37.22	38.56	26.42	27.97	16.43	15.00	2.34	2.56	1.18	1.20

Table S2: Details of data collection, crystal data, and structure refinement for $Fe(4XPy)_2[Fe(CN)_5NO]$ series with X = Cl, Br and I at 300 K and 0K (calculated).

	$Fe(4BrPy)_2[Fe(CN)_5NO]$	**$Fe(4ClPy)_2[Fe(CN)_5NO]$**	**$Fe(4IPy)_2[Fe(CN)_5NO]$**
Data collection			
Diffractometer	D8 Advance (from Bruker)		
Detector	lynx eye		
Wavelength (Å)	CuK_a: 1.54183		
2θ range (°)	6.0-70.0	6.0-60.0	6.0-70.0
Step size (°)	0.00908	0.01967	0.01967
Time per step (s)	0.01	0.01	0.01

Unit cell			
Space Group	$P2_1$	$P2_1$	$P2_1$
Cell Parameter	a= 7.3553(4)Å	a= 7.3377(5)Å	a= 7.3881(7)Å
	b= 14.8367(6)Å	b= 14.8736(7)Å	b= 14.7798(6)Å
	c= 10.3066(5)Å	c= 10.2039(5)Å	c= 10.5338(7)Å
	β= 110.81(5)°	β= 110.55(3)°	β= 110.40(5)°
V(Å^3)	1051.4(2)	1042.8(2)	1078.1(2)
Z	2	2	2
Refinement			
# of reflections	487	325	502
# of refined parameters			
Structural	120	120	120
Profile	38	38	38
R_{exp}	2.34	2.26	3.40
R_{wp}	4.86	4.82	9.58
R_B	3.10	2.86	7.56
S	2.07	2.13	2.82
	$Fe(4BrPy)_2[Fe(CN)5NO]$-calculated	**$Fe(4ClPy)_2[Fe(CN)5NO]$-calculated**	**$Fe(4IPy)_2[Fe(CN)5NO]$-calculated**
Unit cell			
Space Group	$P2_1$	$P2_1$	$P2_1$
Cell Parameter	a= 7.3036Å	a= 7.0979Å	a= 7.2880Å
	b= 14.7619Å	b= 14.7517Å	b= 14.5611Å
	c= 10.2385Å	c= 10.1774Å	c= 10.6696Å
	β= 110.57°	β= 107.80°	β= 110.06°
V(Å^3)	1033.5	1014.6	1063.5
Z	2	2	2

Table S3. Refined atomic positions and thermal (Biso) and occupation (Occ) factors for the materials under study.

Composition	site	x	y	z	Biso	Occ	x	y	z
		$Fe(4BrPy)_2[Fe(CN)_5NO]$					$Fe(4BrPy)_2[Fe(CN)_5NO]$-calculated		
Fee	2a	0.0262	0.6443	0.0284	2.04	1	-0.0006	0.6323	0.0111
Fei	2a	0.5002	0.8968	0.0117	2.15	1	0.4867	0.8759	0.0140
C1	2a	0.3085	0.8081	0.0144	3.83	1	0.2851	0.7882	0.0125
N1	2a	0.2021	0.7541	0.0195	3.83	1	0.1856	0.7305	0.0290
C2	2a	0.6721	0.7989	0.0126	3.83	1	0.6582	0.7807	0.0057
N2	2a	0.7713	0.7429	0.0028	3.83	1	0.7721	0.7242	0.0066
C3	2a	0.6972	0.9820	0.0109	3.83	1	0.6735	0.9607	-0.0060
N3	2a	0.8107	1.0302	0.0000	3.83	1	0.7850	1.0416	-0.0069
C4	2a	0.3346	0.9980	0.0126	3.83	1	0.3167	0.9996	0.0056
N4	2a	0.2439	1.0590	0.0166	3.83	1	0.2149	1.0572	0.0171
C5	2a	0.4143	0.8957	-0.1870	3.83	1	0.3909	0.8712	-0.2001
N5	2a	0.3633	0.8950	-0.3055	3.83	1	0.3429	0.8707	-0.3227
N	2a	0.5780	0.8977	0.1807	3.83	1	0.5598	0.8785	0.1827
O	2a	0.6243	0.8985	0.2993	3.83	1	0.6046	0.8786	0.3026
N7	2a	-0.0465	0.6604	-0.1929	3.83	1	-0.0926	0.6420	-0.2066
C7	2a	-0.1057	0.7347	-0.2738	3.83	1	-0.1397	0.7175	-0.2806
C8	2a	-0.1864	0.7332	-0.4194	3.83	1	-0.2160	0.7169	-0.4270
C9	2a	-0.2075	0.6499	-0.4863	3.83	1	-0.2370	0.6344	-0.4925
C10	2a	-0.1483	0.5718	-0.4066	3.83	1	-0.1843	0.5533	-0.4193
C11	2a	-0.0694	0.5806	-0.2616	3.83	1	-0.1065	0.5614	-0.2759
Br1	2a	-0.3148	0.6430	-0.6819	3.65	1	-0.3545	0.6300	-0.6896
N8	2a	0.0989	0.6282	0.2497	3.83	1	0.0953	0.6167	0.2282
C12	2a	0.1581	0.5539	0.3306	3.83	1	0.1444	0.5420	0.3087
C13	2a	0.2388	0.5554	0.4762	3.83	1	0.2237	0.5476	0.4520
C14	2a	0.2599	0.6387	0.5431	3.83	1	0.2407	0.6304	0.5208
C15	2a	0.2007	0.7168	0.4634	3.83	1	0.1774	0.7063	0.4401
C16	2a	0.1218	0.7080	0.3184	3.83	1	0.1106	0.6965	0.2972
Br2	2a	0.3672	0.6456	0.7387	3.65	1	0.3573	0.6363	0.7152

Table S4. Refined atomic positions and thermal (Biso) and occupation (Occ) factors for the materials under study.

Composition	site	x		y	z	Biso	Occ	x	y	z
				$Fe(4ClPy)_2[Fe(CN)_5NO]$				$Fe(4ClPy)_2[Fe(CN)_5NO]$-calculated		
Fee	2a	0.0262		0.6443	0.0284	2.44	1	0.0062	0.6320	0.0178
Fei	2a	0.5002		0.8968	0.0117	2.85	1	0.4898	0.8804	0.0177
C1	2a	0.3085		0.8081	0.0144	4.02	1	0.2874	0.7916	0.0162
N1	2a	0.2021		0.7541	0.0195	4.02	1	0.1998	0.7266	0.0304
C2	2a	0.6721		0.7989	0.0126	4.02	1	0.6589	0.7834	0.0073
N2	2a	0.7713		0.7429	0.0028	4.02	1	0.7769	0.7264	0.0152
C3	2a	0.6972		0.9820	0.0109	4.02	1	0.6796	0.9648	-0.0081
N3	2a	0.8107		1.0302	0.0000	4.02	1	0.7929	1.0410	-0.0184
C4	2a	0.3346		0.9980	0.0126	4.02	1	0.3151	0.9999	0.0067
N4	2a	0.2439		1.0590	0.0166	4.02	1	0.2057	1.0572	0.0145
C5	2a	0.4143		0.8957	-0.1870	4.02	1	0.3864	0.8737	-0.2205
N5	2a	0.3633		0.8950	-0.3055	4.02	1	0.3506	0.8735	-0.3413
N	2a	0.5780		0.8977	0.1807	4.02	1	0.5614	0.8818	0.1863
O	2a	0.6243		0.8985	0.2993	4.02	1	0.6023	0.8801	0.3045
N7	2a	-0.0465		0.6604	-0.1929	4.02	1	-0.0810	0.6391	-0.1905
C7	2a	-0.1057		0.7347	-0.2738	4.02	1	-0.1252	0.7150	-0.2639
C8	2a	-0.1864		0.7332	-0.4194	4.02	1	-0.2023	0.7148	-0.4091
C9	2a	-0.2075		0.6499	-0.4863	4.02	1	-0.2235	0.6327	-0.4773
C10	2a	-0.1483		0.5718	-0.4066	4.02	1	-0.1702	0.5522	-0.4006
C11	2a	-0.0694		0.5806	-0.2616	4.02	1	-0.0968	0.5595	-0.2601
Cl1	2a	-0.3065		0.6435	-0.6668	3.24	1	-0.3314	0.6280	-0.6523
N8	2a	0.0989		0.6282	0.2497	4.02	1	0.1025	0.6186	0.2312
C12	2a	0.1581		0.5539	0.3306	4.02	1	0.1496	0.5416	0.3096
C13	2a	0.2388		0.5554	0.4762	4.02	1	0.2250	0.5465	0.4517
C14	2a	0.2599		0.6387	0.5431	4.02	1	0.2450	0.6287	0.5188

C15	2a	0.2007		0.7168	0.4634	4.02	1	0.1812	0.7055	0.4402
C16	2a	0.1218		0.7080	0.3184	4.02	1	0.1173	0.6966	0.2997
Cl2	2a	0.3589		0.6451	0.7236	3.24	1	0.3478	0.6337	0.6940

Table S5. Refined atomic positions and thermal (Biso) and occupation (Occ) factors for the materials under study.

Composition	site	x	y	z	Biso	Occ	x	y	z
		$Fe(4IPy)_2[Fe(CN)_5NO]$					$Fe(4IPy)_2[Fe(CN)_5NO]$-calculated		
Fee	2a	0.4953	0.1360	0.9835	2.39	1	0.4847	0.1319	0.9842
Fei	2a	0.9981	0.3789	1.0000	2.87	1	0.9983	0.3781	1.0013
C1	2a	0.8055	0.2887	0.9846	4.15	1	0.7851	0.2886	0.9750
N1	2a	0.6820	0.2408	0.9733	4.15	1	0.6831	0.2298	0.9864
C2	2a	1.1755	0.2879	0.9838	4.15	1	1.1756	0.2807	0.9857
N2	2a	1.2865	0.2365	0.9795	4.15	1	1.2900	0.2236	0.9859
C3	2a	1.1902	0.4693	1.0091	4.15	1	1.1900	0.4718	1.0086
N3	2a	1.3031	0.5209	1.0098	4.15	1	1.3046	0.5299	1.0170
C4	2a	0.8202	0.4668	1.0127	4.15	1	0.8023	0.4718	1.0097
N4	2a	0.7140	0.5192	1.0202	4.15	1	0.6997	0.5304	1.0211
C5	2a	0.8998	0.3956	0.8076	4.15	1	0.8837	0.3903	0.8084
N5	2a	0.8300	0.4086	0.6954	4.15	1	0.8284	0.4049	0.6932
N	2a	1.0765	0.3618	1.1604	4.15	1	1.0778	0.3632	1.1645
O	2a	1.1302	0.3467	1.2722	4.15	1	1.1371	0.3442	1.2765
N7	2a	0.3963	0.1663	0.7646	4.15	1	0.3871	0.1569	0.7695
C7	2a	0.3562	0.2359	0.6762	4.15	1	0.3563	0.2313	0.6900
C8	2a	0.2826	0.2258	0.5370	4.15	1	0.2916	0.2242	0.5509
C9	2a	0.2479	0.1386	0.4851	4.15	1	0.2453	0.1387	0.4919
C10	2a	0.2874	0.0653	0.5728	4.15	1	0.2847	0.0623	0.5766
C11	2a	0.3607	0.0826	0.7105	4.15	1	0.3552	0.0739	0.7132
I1	2a	0.1380	0.1181	0.2775	3.52	1	0.1345	0.1244	0.2855
N8	2a	0.5943	0.1057	1.2024	4.15	1	0.5874	0.1086	1.2001
C12	2a	0.6344	0.0361	1.2908	4.15	1	0.6206	0.0345	1.2829
C13	2a	0.7080	0.0462	1.4300	4.15	1	0.6912	0.0428	1.4241
C14	2a	0.7427	0.1334	1.4819	4.15	1	0.7306	0.1317	1.4778
C15	2a	0.7032	0.2067	1.3942	4.15	1	0.6968	0.2075	1.3939
C16	2a	0.6299	0.1894	1.2565	4.15	1	0.6206	0.1917	1.2583
I2	2a	0.8526	0.1539	1.6895	3.52	1	0.8431	0.1461	1.6854

Table S6. Calculated inter-atomic distances (in Å) and bond angles (in °) for the materials under study a) Fe(4BrPy)2[Fe(CN)5NO], b) Fe(4BrPy)2[Fe(CN)5NO]-calculated.

Bond distance (Å)								
Bond distance (Å)	a)	b)	Angles (°)	a)	b)	Angles (°)	a)	b)
Fee-N1	2.102	1.952	N1-Fee-N2	89.51	92.35	N1-C1-Fei	177.23	169.93
Fee-N2	2.318	2.132	N1-Fee-N3	102.82	88.42	N2-C2-Fei	174.69	176.28
Fee-N3	2.154	2.079	N1-Fee-N4	159.15	168.51	N3-C3-Fei	174.62	164.52
Fee-N4	2.260	1.856	N1-Fee-N7	78.11	90.09	N4-C4-Fei	177.28	168.15
Fee-N7	2.163	2.095	N1-Fee-N8	101.89	91.14	N5-C5-Fei	179.91	177.10
Fee-N8	2.163	2.095	N2-Fee-N3	161.34	177.66	O-N-Fei	176.95	177.11
Fei-C1	1.936	1.957	N2-Fee-N4	73.36	76.64	C1-N1-Fee	174.15	167.15
Fei-C2	1.924	1.904	N2-Fee-N7	85.60	88.70	C2-N2-Fee	166.53	174.30
Fei-C3	1.925	1.915	N2-Fee-N8	94.40	93.46	C3-N3-Fee	166.80	164.48
Fei-C4	1.935	2.193	N3-Fee-N4	91.34	102.45	C4-N4-Fee	157.69	162.87
Fei-C5	1.917	2.055	N3-Fee-N7	83.37	89.09	Fee-N7-C7	129.99	126.05
Fei-N	1.629	1.619	N3-Fee-N8	96.63	88.73	N7-C7-C8	124.42	122.13
C1-N1	1.134	1.170	N4-Fee-N7	88.59	86.42	C7-C8-C9	118.18	117.49
C2-N2	1.134	1.176	N4-Fee-N8	91.41	92.79	C8-C9-C10	119.12	122.50
C3-N3	1.135	1.447	N7-Fee-N8	180.0	177.47	C9-C10-C11	118.25	115.49
C4-N4	1.134	1.162	N-Fei-C1	88.35	89.38	C10-C11-N7	124.30	123.61
C5-N5	1.143	1.179	N-Fei-C2	91.17	95.14	C11-N7-Fee	113.06	115.42
N-O	1.146	1.154	N-Fei-C3	91.15	96.79	C11-N7-C7	115.73	118.53
N7-C7	1.357	1.323	N-Fei-C4	88.35	89.54	C8-C9-Br1	120.39	118.78
C7-C8	1.404	1.404	N-Fei-C5	178.77	179.16	C10-C9-Br1	120.48	118.64
C8-C9	1.397	1.373	C5-Fei-C1	92.53	89.77	Fee-N8-C12	129.99	131.04
C9-C10	1.397	1.393	C5-Fei-C2	88.02	84.85	N8-C12-C13	124.42	121.61
C10-C11	1.404	1.381	C5-Fei-C3	87.94	84.05	C12-C13-C14	118.18	121.34
C11-N7	1.359	1.371	C5-Fei-C4	92.44	90.60	C13-C14-C15	119.12	117.40
C9-Br1	1.889	1.896	C1-Fei-C2	88.14	90.93	C14-C15-C16	118.25	118.19
N8-C12	1.357	1.348	C1-Fei-C3	178.14	173.82	C15-C16-N8	124.30	125.26
C12-C13	1.404	1.378	C1-Fei-C4	93.70	97.85	C16-N8-Fee	113.06	113.10
C13-C14	1.397	1.394	C3-Fei-C2	90.08	88.46	C16-N8-C12	115.73	115.85
C14-C15	1.397	1.372	C3-Fei-C4	88.08	82.32	C13-C14-Br2	120.39	120.30
C15-C16	1.404	1.378	C2-Fei-C4	178.09	170.10	C15-C14-Br2	120.48	122.24
C16-N8	1.359	1.358						
C14-Br2	1.889	1.872						

Table S7. Calculated inter-atomic distances (in Å) and bond angles (in °) for the materials under study a) Fe(4ClPy)2[Fe(CN)5NO], b) Fe(4ClPy)2[Fe(CN)5NO]-calculated.

Bond distance (Å)	a)	b)	Angles (°)	a)	b)	Angles (°)	a)	b)
Fee-N1	2.103	1.935	N1-Fee-N2	89.25	93.07	N1-C1-Fei	177.24	165.39
Fee-N2	2.318	2.136	N1-Fee-N3	103.15	89.57	N2-C2-Fei	174.74	172.45
Fee-N3	2.154	1.957	N1-Fee-N4	159.17	169.77	N3-C3-Fei	174.66	167.33
Fee-N4	2.260	1.813	N1-Fee-N7	78.31	90.90	N4-C4-Fei	177.28	168.80
Fee-N7	2.144	2.021	N1-Fee-N8	101.69	89.96	N5-C5-Fei	179.91	173.80
Fee-N8	2.144	2.077	N2-Fee-N3	161.38	177.33	O-N-Fei	176.93	176.16
Fei-C1	1.936	1.941	N2-Fee-N4	73.56	78.92	C1-N1-Fee	174.15	166.34
Fei-C2	1.924	1.891	N2-Fee-N7	85.30	88.02	C2-N2-Fee	166.57	173.90
Fei-C3	1.924	1.911	N2-Fee-N8	94.70	94.64	C3-N3-Fee	166.78	169.10
Fei-C4	1.936	2.138	N3-Fee-N4	91.11	98.42	C4-N4-Fee	157.70	164.00
Fei-C5	1.900	2.310	N3-Fee-N7	83.73	91.60	Fee-N7-C7	129.81	125.24
Fei-N	1.615	1.634	N3-Fee-N8	96.27	85.70	N7-C7-C8	124.16	122.44
C1-N1	1.134	1.175	N4-Fee-N7	88.42	82.55	C7-C8-C9	117.91	118.44
C2-N2	1.133	1.172	N4-Fee-N8	91.58	96.96	C8-C9-C10	119.65	119.44
C3-N3	1.134	1.405	N7-Fee-N8	180.0	177.16	C9-C10-C11	117.94	117.71
C4-N4	1.134	1.167	N-Fei-C1	88.67	90.49	C10-C11-N7	124.07	123.88
C5-N5	1.133	1.177	N-Fei-C2	90.90	93.98	C11-N7-Fee	112.70	116.88
N-O	1.136	1.148	N-Fei-C3	90.83	97.48	C11-N7-C7	116.27	117.87
N7-C7	1.356	1.329	N-Fei-C4	88.61	91.93	C8-C9-Cl1	120.16	120.25
C7-C8	1.393	1.410	N-Fei-C5	178.77	178.23	C10-C9-Cl1	120.19	120.11
C8-C9	1.397	1.381	C5-Fei-C1	92.22	88.05	Fee-N8-C12	129.81	129.18
C9-C10	1.397	1.408	C5-Fei-C2	88.28	84.97	N8-C12-C13	124.16	120.91
C10-C11	1.393	1.368	C5-Fei-C3	88.25	83.96	C12-C13-C14	117.91	120.87
C11-N7	1.359	1.358	C5-Fei-C4	92.18	89.27	C13-C14-C15	119.65	117.98
C9-Cl1	1.729	1.711	C1-Fei-C2	87.86	88.27	C14-C15-C16	117.94	118.16
N8-C12	1.356	1.369	C1-Fei-C3	178.14	171.94	C15-C16-N8	124.07	125.28
C12-C13	1.393	1.382	C1-Fei-C4	93.98	98.05	C16-N8-Fee	112.70	114.38
C13-C14	1.397	1.377	C3-Fei-C2	90.36	89.95	C16-N8-C12	116.27	116.43
C14-C15	1.397	1.381	C3-Fei-C4	87.80	82.97	C13-C14-Cl2	120.16	120.10
C15-C16	1.393	1.368	C2-Fei-C4	178.09	171.31	C15-C14-Cl2	120.19	121.91
C16-N8	1.359	1.333						
C14-Cl2	1.729	1.709						

Table S8. Calculated inter-atomic distances (in Å) and bond angles (in °) for the materials under study a) Fe(4IPy)2[Fe(CN)5NO], b) Fe(4IPy)2[Fe(CN)5NO]-calculated.

Bond distance (Å)	a)	b)	Angles (°)	a)	b)	Angles (°)	a)	b)
Fee-N1	2.102	2.025	N1-Fee-N2	88.21	92.11	N1-C1-Fei	174.71	165.55
Fee-N2	2.131	1.953	N1-Fee-N3	96.89	88.72	N2-C2-Fei	176.59	175.11
Fee-N3	2.246	2.139	N1-Fee-N4	176.25	176.50	N3-C3-Fei	177.27	177.49
Fee-N4	2.309	1.985	N1-Fee-N7	77.38	82.48	N4-C4-Fei	179.95	174.77
Fee-N7	2.208	2.184	N1-Fee-N8	102.61	96.42	N5-C5-Fei	174.73	173.10
Fee-N8	2.208	2.191	N2-Fee-N3	174.88	179.15	O-N-Fei	177.61	173.48
Fei-C1	1.915	1.973	N2-Fee-N4	92.57	91.28	C1-N1-Fee	168.08	173.19
Fei-C2	1.927	1.964	N2-Fee-N7	82.18	85.39	C2-N2-Fee	176.25	178.09
Fei-C3	1.927	1.935	N2-Fee-N8	97.82	94.78	C3-N3-Fee	173.13	174.91
Fei-C4	1.886	1.999	N3-Fee-N4	82.36	87.89	C4-N4-Fee	173.33	172.80
Fei-C5	1.916	1.946	N3-Fee-N7	99.27	94.91	Fee-N7-C7	142.03	135.97
Fei-N	1.604	1.650	N3-Fee-N8	80.73	84.94	N7-C7-C8	124.06	122.12
C1-N1	1.128	1.167	N4-Fee-N7	99.08	96.92	C7-C8-C9	117.91	119.35
C2-N2	1.130	1.177	N4-Fee-N8	80.92	84.17	C8-C9-C10	119.71	117.22
C3-N3	1.128	1.170	N7-Fee-N8	180.0	178.89	C9-C10-C11	117.93	120.29
C4-N4	1.125	1.168	N-Fei-C1	87.96	92.15	C10-C11-N7	124.03	122.06
C5-N5	1.129	1.174	N-Fei-C2	88.64	89.51	C11-N7-Fee	101.54	105.37
N-O	1.126	1.156	N-Fei-C3	93.87	93.61	C11-N7-C7	116.36	118.66
N7-C7	1.349	1.346	N-Fei-C4	92.21	92.29	C8-C9-I1	120.12	121.16
C7-C8	1.383	1.398	N-Fei-C5	178.09	175.01	C10-C9-I1	120.17	121.55
C8-C9	1.388	1.384	C5-Fei-C1	90.20	83.02	Fee-N8-C12	142.03	136.47
C9-C10	1.387	1.399	C5-Fei-C2	90.86	91.86	N8-C12-C13	124.06	122.65
C10-C11	1.384	1.379	C5-Fei-C3	87.96	91.15	C12-C13-C14	117.91	117.39
C11-N7	1.349	1.334	C5-Fei-C4	88.26	86.05	C13-C14-C15	119.71	120.21
C9-I1	2.073	2.080	C1-Fei-C2	90.85	91.14	C14-C15-C16	117.93	117.51
N8-C12	1.349	1.362	C1-Fei-C3	178.09	173.70	C15-C16-N8	124.03	125.36
C12-C13	1.383	1.420	C1-Fei-C4	88.28	85.25	C16-N8-Fee	101.54	106.79
C13-C14	1.388	1.405	C3-Fei-C2	88.65	91.47	C16-N8-C12	116.36	116.73
C14-C15	1.387	1.389	C3-Fei-C4	92.19	91.95	C13-C14-I2	120.12	118.37
C15-C16	1.384	1.380	C2-Fei-C4	178.76	176.02	C15-C14-I2	120.17	121.41
C16-N8	1.349	1.344						
C14-I2	2.073	2.092						

Table S9. Relevant interatomic distances (in Å), distortion indexes $\sum|90-\alpha_i|$ ($\angle$, in ^{o}), and CShM for the $Fe(Py)_2[Fe(CN)_5NO]$, $Fe(3FPy)_2[Fe(CN)_5NO]$, and $Fe(3ClPy)_2[Fe(CN)_5NO]$.

Ligand	Phase	$Fe–N_L$	$Fe–N_{CN}$	$\sum\|90-\alpha_i\|$	$\sum\|60-\Theta_i\|$	CShM
Py	HS (295 K), XRD	Fe1–N5: 2.335(14) Fe1–N6:2.232(1)	Fe1–N1: 2.134(8) Fe1–N2: 2.134(8) Fe1–N3: 2.161(16) Fe1–N4: 2.149(24)	35.52	49.53	0.33
	LS (50 K), XRD	Fe1–N5: 2.252(11) Fe1–N6:2.234(11)	Fe1–N1: 2.092(8) Fe1–N2: 2.209(10) Fe1–N3: 2.092(8) Fe1–N4: 2.209(10)	21.01	33.84	0.13
3FPy	HS (295 K), XRD	Fe1–N6: 2.286(10) Fe1–N5:2.404(15)	Fe1–N1: 2.403(15) Fe1–N2: 2.110(20) Fe1–N3:	55.83	85.91	0.77

	LS (100K), XRD	Fe1–N5: 2.284(11) Fe1–N6:2.393(15)	2.202(16) Fe1–N4: 2.149(24) Fe1–N1: 2.399(25) Fe1–N2: 2.208(20) Fe1–N3: 2.199(10) Fe1–N4: 2.146(12)	49.19	71.15	0.69
3ClPy	HS (295 K), XRD	Fee–N8: 2.406(46) Fee–N7: 2.522(54)	Fee–N1: 2.200(32) Fee–N2: 2.141(24) Fee–N3: 2.391(44) Fee–N4: 2.193(24)	72.25	124.20	1.24

CShM: continuous shape measure was calculated using Shape [41]software

Table S10. Mössbauer parameters (δ, Δ_{QS}, Γ) at 5 and 295 K for the $Fe(3XPy)_2[Fe(CN)_5NO]$ series, according to reference 18.

Ligand	Temp (K)	δ*, mm/s	Δ_{QS}, mm/s	Γ, mm/s	Area (%)
3FPy	295K	-0.064	1.822	0.261	50
		1.260	0.665	0.303	41
		1.136	1.898	0.429	9
	5K	-0.088	1.802	0.266	50
		0.670	0.076	0.292	36
		1.463	2.026	0.384	13
3ClPy	295K	0.036	1.942	0.325	52
		1.216	0.781	0.325	44
		1.344	2.029	0.284	4
	5K	0.076	1.858	0.281	53
		1.446	1.182	0.345	38
		1.438	2.311	0.386	9
3BrPy	295K	0.019	1.884	0.278	51
		1.277	0.829	0.328	46
		1.240	2.231	0.291	3
	5K	0.075	1.851	0.268	51
		1.464	1.135	0.369	39
		1.497	1.617	0.376	10
3IPy	295K	0.022	1.808	0.306	48
		1.305	0.855	0.324	43
		1.376	2.173	0.338	9
	5K	0.065	1.836	0.272	49

		1.365	1.440	0.338	27
		1.558	1.467	0.322	24

*) The value of δ is reported relative to sodium nitroprusside at room temperature.

Table S11. Mössbauer parameters (δ, ΔQS, Γ) at 5 and 295 K for a series of pillared ferrous nitroprussides, according to reference 48.

Ligand	Temp (K)	δ*, mm/s	Δ_{QS}, mm/s	Γ, mm/s	Area (%)
1,3-oxazole	295K	-0.013	1.772	0.26	50
		1.236	1.209	0.31	50
	5K	0.002	1.848	0.27	50
		1.396	2.131	0.28	50
pyridine-3-carbaldehyde	295K	0.061	1.946	0.295	51
		1.199	0.728	0.273	42
		1.213	1.707	0.358	7
	5K	0.083	1.831	0.28	50
		1.459	1.147	0.42	44
		1.551	2.401	0.44	6
1H-pyrazole	295K	-0.014	1.860	0.27	51
		1.344	1.691	0.31	49
	5K	0.088	1.879	0.27	49
		1.499	1.612	0.298	31
		1.492	2.238	0.38	19
Imidazo[1,2-a]pyridine	295K	-0.129	1.789	0.298	51
		1.191	1.434	0.418	42
		1.130	1.822	0.403	7
	5K	-0.003	1.850	0.269	48
		1.383	2.304	0.315	28
		1.388	1.671	0.270	18
		0.919**	----	0.372	6
Pyridazine	295K	-0.098	1.701	0.268	50
		1.224	0.989	0.388	31
		1.334	2.744	0.459	19
	5K	0.012	1.690	0.285	50
		1.461	3.296	0.327	45
		1.529	1.397	0.434	5
4-(2-pyridin-4-ylethyl)pyridine	295K	-0.021	1.885	0.261	51
		1.306	0.847	0.302	43
		1.299	2.008	0.368	6
	5K	0.057	1.903	0.274	51
		1.469	1.405	0.312	43
		1.455	1.631	0.268	6

*) The value of δ is reported relative to sodium nitroprusside at room temperature.

** The apparent two low intensity doublets really correspond to lines 2, 3, 4 and 5 for the sextet of a Goethite impurity (6% of relative area).

Table S12. Mössbauer parameters at different temperatures for $Fe_{ext}(PyrDer)_2[Fe_{int}(CN)_5NO]$ with PyrDer = 4MPy, 4AcPy, 4PyCA, according to reference 20.

Ligand	Temp (K)	δ*, mm/s	Δ_{QS}, mm/s	Γ, mm/s	Area (%)
4AcPy	295K	0.017	1.833	0.28	50
		1.290	0.939	0.29	48
		0.232	0.115	0.29	2
	5K	0.070	1.762	0.26	50
		1.495	1.222	0.36	30
		0.678	0.120	0.33	20
4PyCA	295K	-0.021	1.901	0.26	50
		1.313	0.934	0.28	45
		0.322	0.167	0.30	5
	5K	0.075	1.892	0.27	50
		0.742	0.277	0.29	50
4MPy	295K	-0.047	1.875	0.32	45
		1.308	0.619	0.39	33
		0.593	0.628	0.35	22
	5K	0.059	1.905	0.27	50
		0.758	0.136	0.29	50

*) The value of δ is reported relative to sodium nitroprusside at room temperature. Fitting error in the values of δ and Δ is no higher than 0.001 mm/s. The error in the value of Γ remains below 0.01 mm/s.