Supplementary Information

Spin Cross-Over (SCO) Anionic Fe(II) Complexes Based on the Tripodal Ligand Tris(2-pyridyl)ethoxymethane

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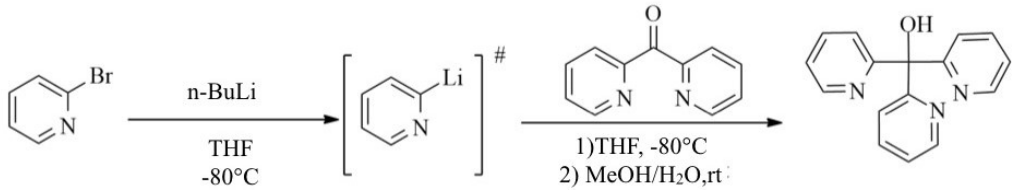
1 - Chemical syntheses and spectroscopic characterisations



Scheme S1. Synthesis of tris(pyridin-2-yl)methanol (py_3C-OH)

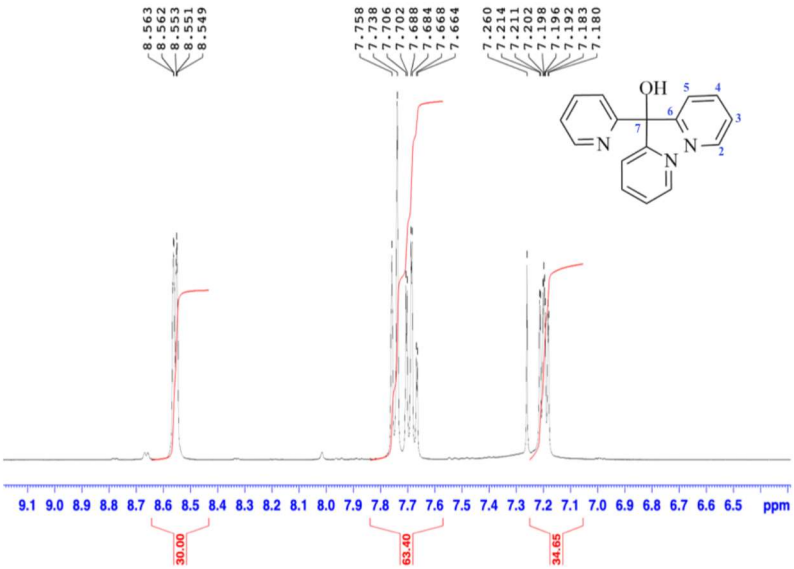


Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)) of py_3C-OH at 25 °C: 7.20 (3H, CH aromatic, q, 3JH-H= 5 Hz, H3), 7.68 (3H, CH aromatic, td, H4), 7.75 (3H, CH aromatic, q, 3JH-H= 8 Hz, H5), 8.46 (3H, CH aromatic, 3JH-H= 5 Hz, td, H2).

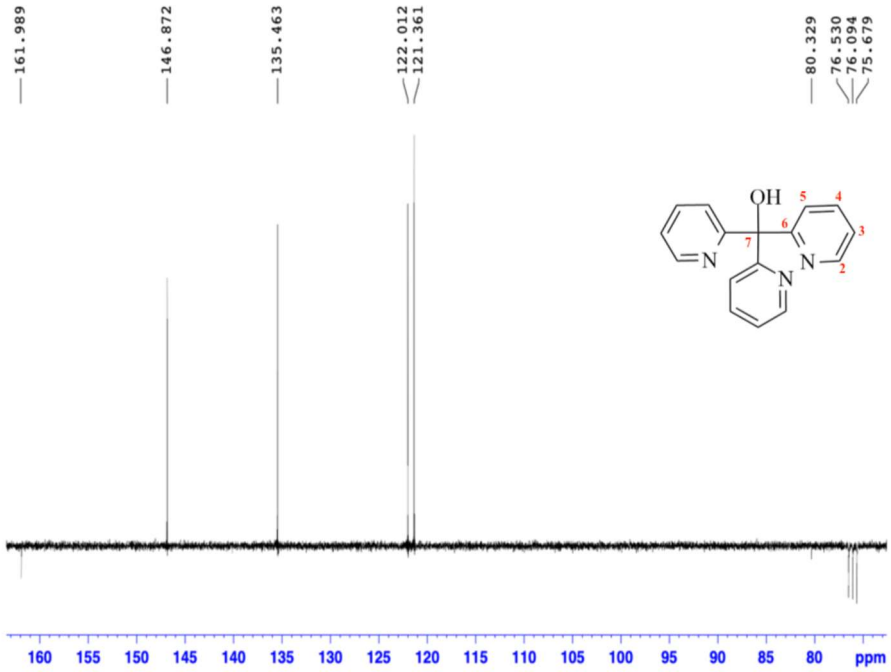


Figure S2. ^{13}C NMR ($CDCl_3$, 75 MHz, δ (ppm)) of py_3C-OH at 25 °C: 81.27 (C7), 121.36 (C3), 122.01 (C5) 135.46 (C4), 146.87 (C2), 161.99 (C6).

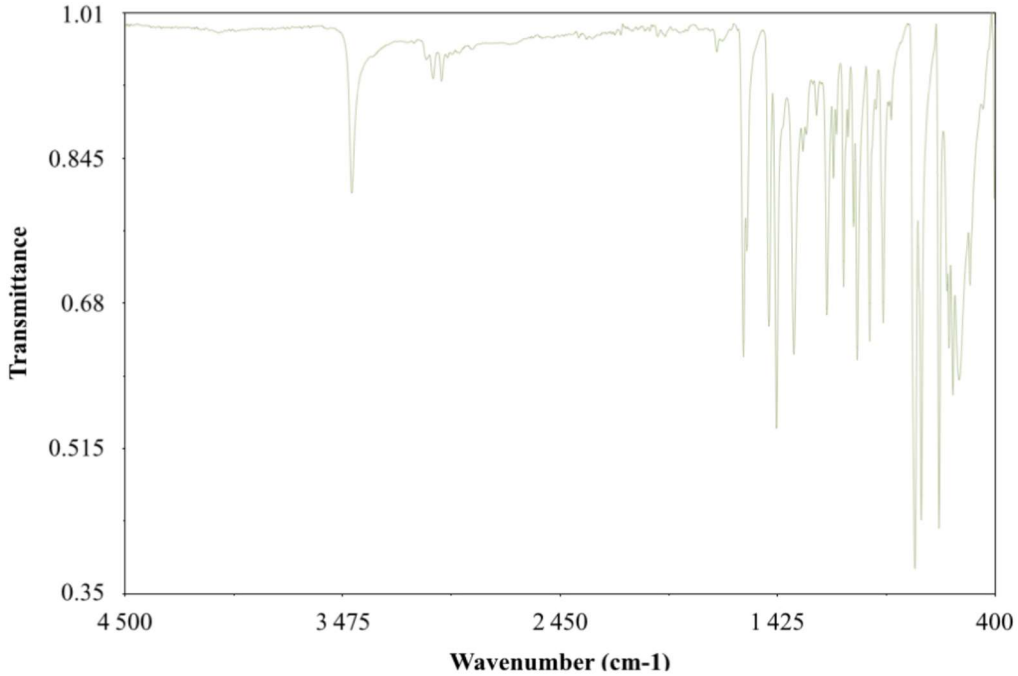
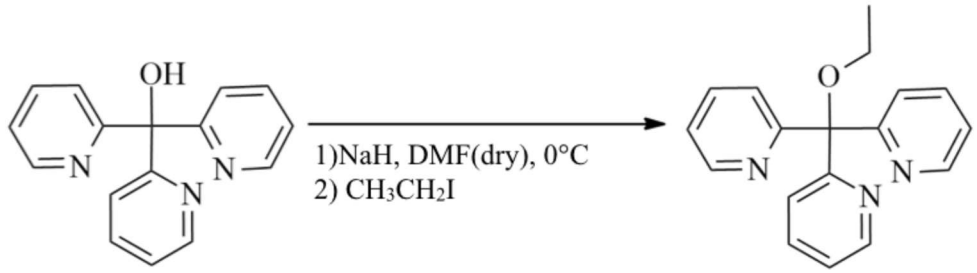


Figure S3. IR spectrum of py_3C-OH at 25 °C (cm^{-1}): 456 (w), 517 (m); 569 (s); 598 (m) 627 (w), 663 (s); 748 (s), 778 (s), 891 (w) 928 (m), 962 (w), 996 (m), 1051 (m),1115 (m), 1193 (m), 1242 (w),1290 (w), 1306 (w), 1349 (s), 1430 (s), 1465 (m), 1570 (m), 1585 (s), 1743 (w), 2979 (w), 3008 (w), 3047 (w), 3432 (m).



Scheme S2. Synthesis of tris(pyridin-2-yl)ethoxymethane (py$_3$C-OEt).

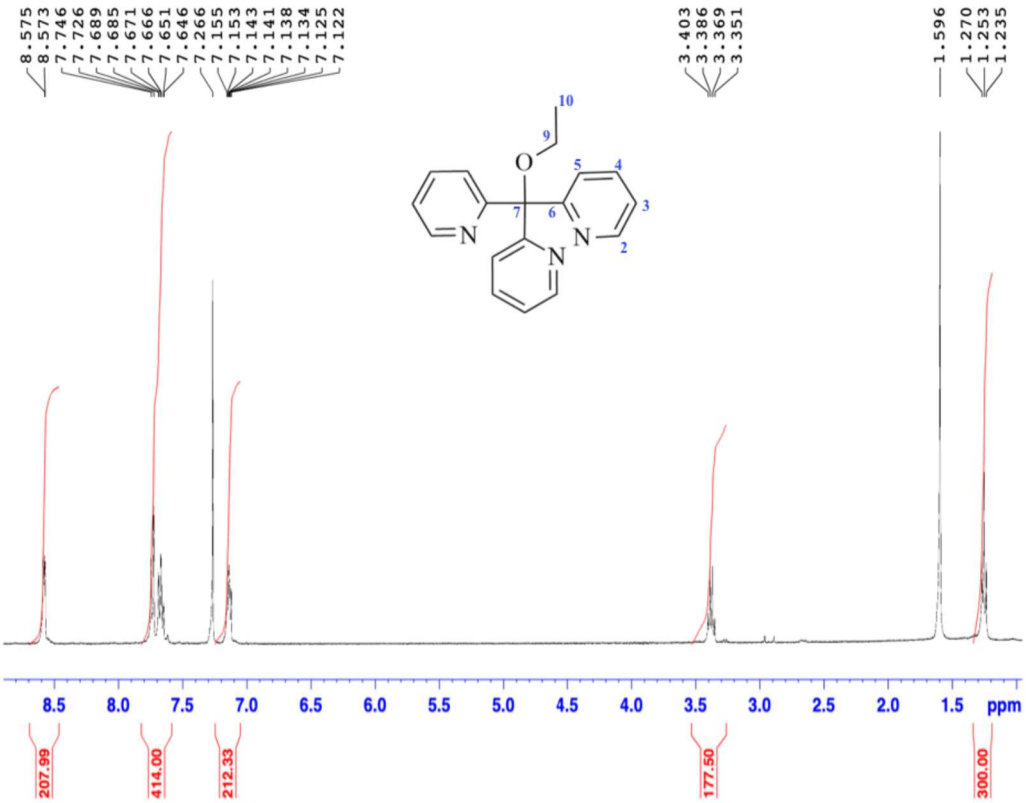


Figure S4. ^{1}H NMR (CDCl3, 400 MHz, δ (ppm)) of py$_3$C-OEt at 25 C: 1. 24 (3H, CH3, t, 3JH-H= 7,2 Hz, H10), 3.37 (2H, CH2, q, 3JH-H= 7,2Hz, H9), 7.13 (3H, CH aromatic ring, q, 3JH-H= 8 Hz, H3), 7.65 (3H, CH aromatic ring, q, 3JH-H= 8 Hz, H5), 7.73 (3H, CH aromatic ring, d, 3JH-H= 8 Hz, H4), 8.57 (2H, CH aromatic ring, d, 3JH-H= 4,8 Hz, H2).

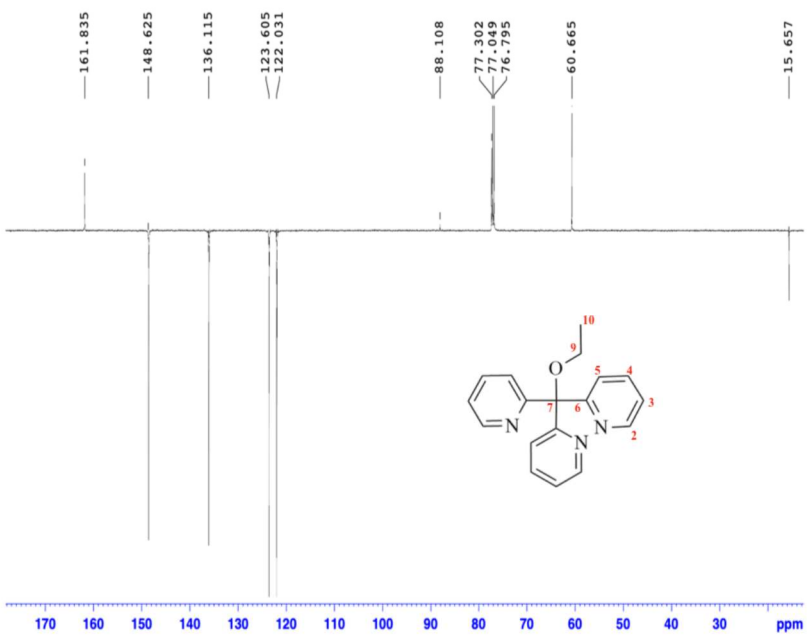


Figure S5. ^{13}C NMR (CDCl3, 125 MHz, δ (ppm)) of py$_3$C-OEt at 25°C: 15.56 (C10), 60.67 (C9), 88.11 (C7), 122.03 (C3), 123.61 (C5) 136.16 (C4), 148.63 (C2), 161.84 (C6).

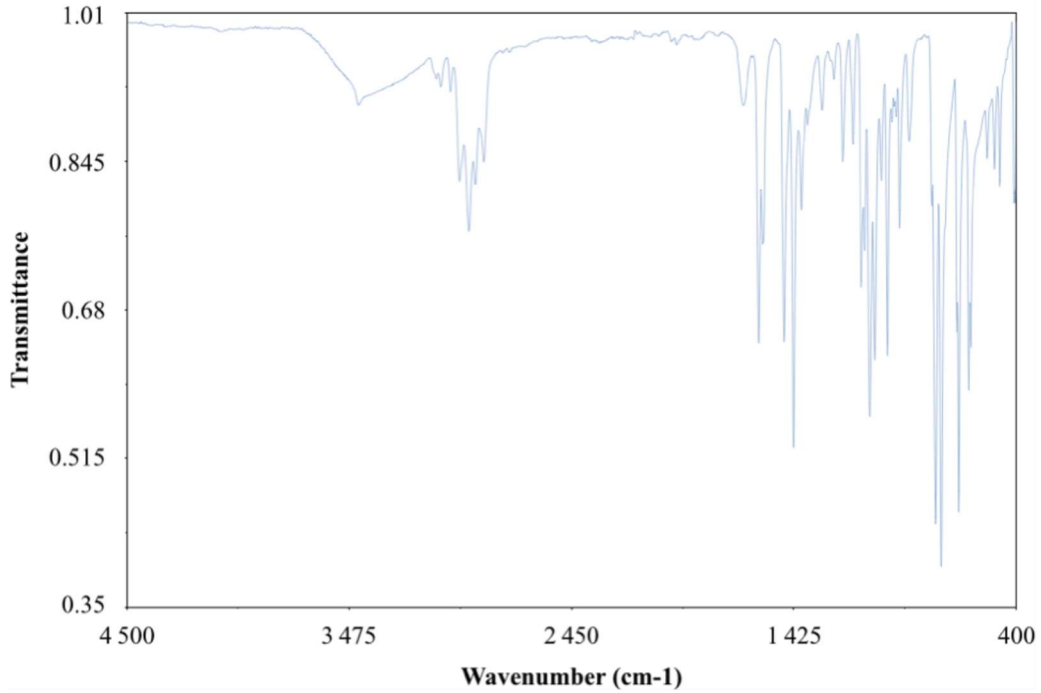


Figure S6. IR of py$_3$C-OEt at 25 °C (cm^{-1}): 476 (w), 500 (w), 534 (w), 610 (m), 619 (s), 665 (s), 673 (m), 745 (s), 771 (s), 789 (w), 893 (w & l), 937 (m), 953 (w), 993 (s), 1021 (m), 1051 (s), 1074 (s), 1098 (m), 1114 (m), 1152 (w), 1199 (w), 1240 (w), 1293 (w), 1361 (w), 1390 (m), 1426 (s), 1469 (s), 1567 (m), 1586 (s), 1658 (br), 2854 (w), 2893 (w), 2922 (m), 2967 (w), 3009 (w), 3053 (w).

2 – Structural characterisations

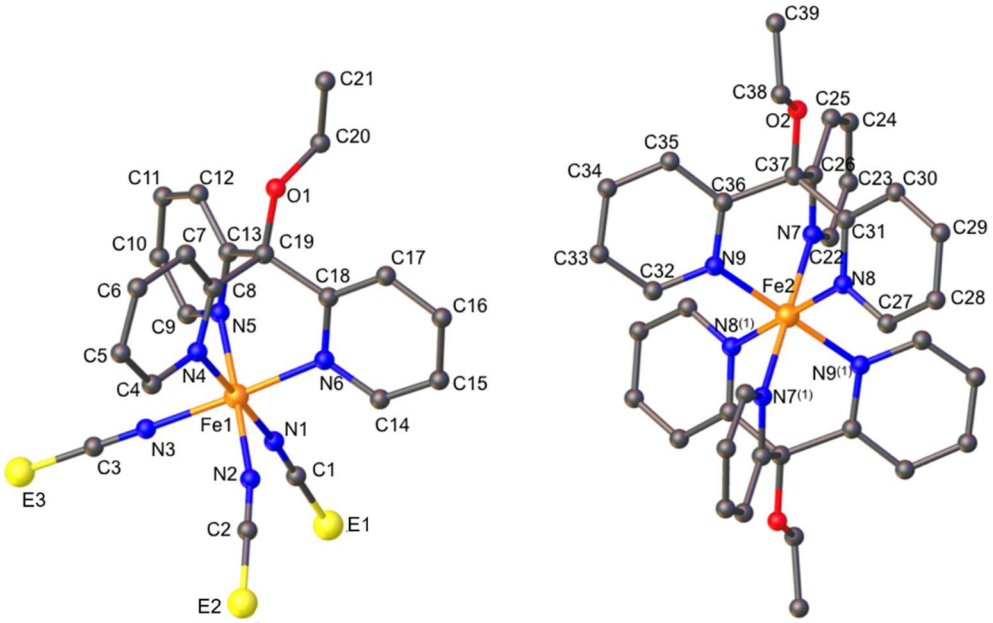


Figure S7. Molecular structure of **1**-**2** showing the asymmetric unit and the Fe(II) environments of the anionic ($[Fe(py_3C\text{-}OEt)(NCE)_3]^-$) and cationic ($[Fe(py_3C\text{-}OEt)_2]^{2+}$) moieties. Hydrogen atoms are omitted for the sake of clarity. Codes of equivalent position: (1) = -x,-y,-z.

Table S1. Crystal data and structural refinement parameters for complexes [Fe(py_3C-OEt)$_2$][Fe(py_3C-OEt)(NCE)$_3$]$_2$·2CH_3CN (E = S (**1**), BH_3 (**2**)).

Complex	**1**		**2**
Temperature (K)	293	100	200
Color	 Orange	 Red	Red
Formula	$C_{82}H_{74}Fe_3N_{20}O_4S_6$		$C_{82}H_{92}Fe_3N_{20}O_4B_6$
Radiation	MoKα (λ = 0.71073)		MoKα (λ = 0.71073)
M (g·mol^{-1})	1763.52		1654.16
Cryst. syst / Space group	Triclinic / *P*-1		Triclinic / *P*-1
a (Å)	11.6683(5)	11.432(5)	11.6827(8)
b (Å)	11.9026(7)	11.829(5)	12.0204(10)
c (Å)	17.1711(9)	16.857(5)	16.9162(11)
α (°)	78.192(5)	78.072(5)	78.389(6)
β (°)	88.279(4)	88.037(5)	87.805(6)
γ (°)	66.544(5)	65.879(5)	65.767(7)
Volume (Å^3)	2137.9(2)	2032.4(14)	2119.3(3)
Z	1		1
ρ_{calc} (g/cm^{-3})	1.370	1.441	1.296
μ (mm^{-1})	0.710	0.747	0.568
F(000)	912.0	912.0	864.0
2Θ range (°)	6.834 - 58.856	6.527 - 58.824	6.508 to 58.484
Reflections collected	18918	26672	15809
Independent reflections / R_{int}	9830 / 0.0458	9534 / 0.0722	9657 / 0.0701
Goodness-of-fit on F^2	1.028	1.066	0.997
R_1 / wR_2	0.0692 / 0.1697	0.0605 / 0.1476	0.0823 / 0.2031
$\Delta\rho$max/min (e·Å^{-3})	0.892/-0.703	2.11/-1.047	1.177/-1.490
Data/restraints/parameters	5988 / 56 / 523	6916 / 58 / 523	5051 / 74 / 550

[a] $R1 = \sum|F_o-F_c|/F_o$. [b] $wR2 = \{w(F_o^2-F_c^2)^2]/ wF_o^2)^2]\}^{1/2}$. [c] $GooF = \{w(F_o^2-F_c^2)^2]/ (N_{obs}-N_{var})\}^{1/2}$

Table S2. Bond lengths and bond angles of compounds **1** and **2.**

Compounds	**1**	**2**	
	293 K	**100 K**	**200 K**
Fe1-N1	2.083(4)	1.949(3)	1.944(4)
Fe1-N2	2.086(4)	1.956(3)	1.954(4)
Fe1-N3	2.110(4)	1.965(3)	1.943(5)
Fe1-N4	2.237(3)	1.987(3)	1.978(4)
Fe1-N5	2.180(3)	1.948(3)	1.943(4)
Fe1-N6	2.191(3)	1.952(3)	1.945(4)
Fe2-N7	2.003(3)	1.989(3)	1.998(4)
Fe2-N8	1.962(3)	1.960(3)	1.947(4)
Fe2-N9	1.957(3)	1.954(3)	1.963(4)
N1-Fe1-N2	93.81(16)	89.10(12)	89.43(17)
N1-Fe1-N3	93.57(16)	89.71(12)	88.76(17)
N1-Fe1-N4	174.87(13)	178.91(11)	179.06(17)
N1-Fe1-N6	93.55(14)	92.32(12)	92.52(17)
N2-Fe1-N3	94.83(15)	89.14(11)	88.69(18)
N2-Fe1-N4	89.62(13)	89.90(11)	89.90(17)
N3-Fe1-N4	89.94(13)	89.84(12)	90.56(17)
N5-Fe1-N1	94.34(14)	92.92(11)	92.47(17)
N5-Fe1-N2	170.20(13)	177.71(12)	177.47(17)
N5-Fe1-N3	90.09(14)	89.79(11)	93.02(18)
N5-Fe1-N4	81.90(11)	88.07(11)	88.22(16)
N5-Fe1-N6	79.16(12)	88.58(11)	88.48(17)
N6-Fe1-N2	94.90(14)	92.41(11)	89.78(17)
N6-Fe1-N3	167.52(13)	177.46(12)	177.99(17)
N6-Fe1-N4	82.34(11)	88.16(11)	88.15(16)

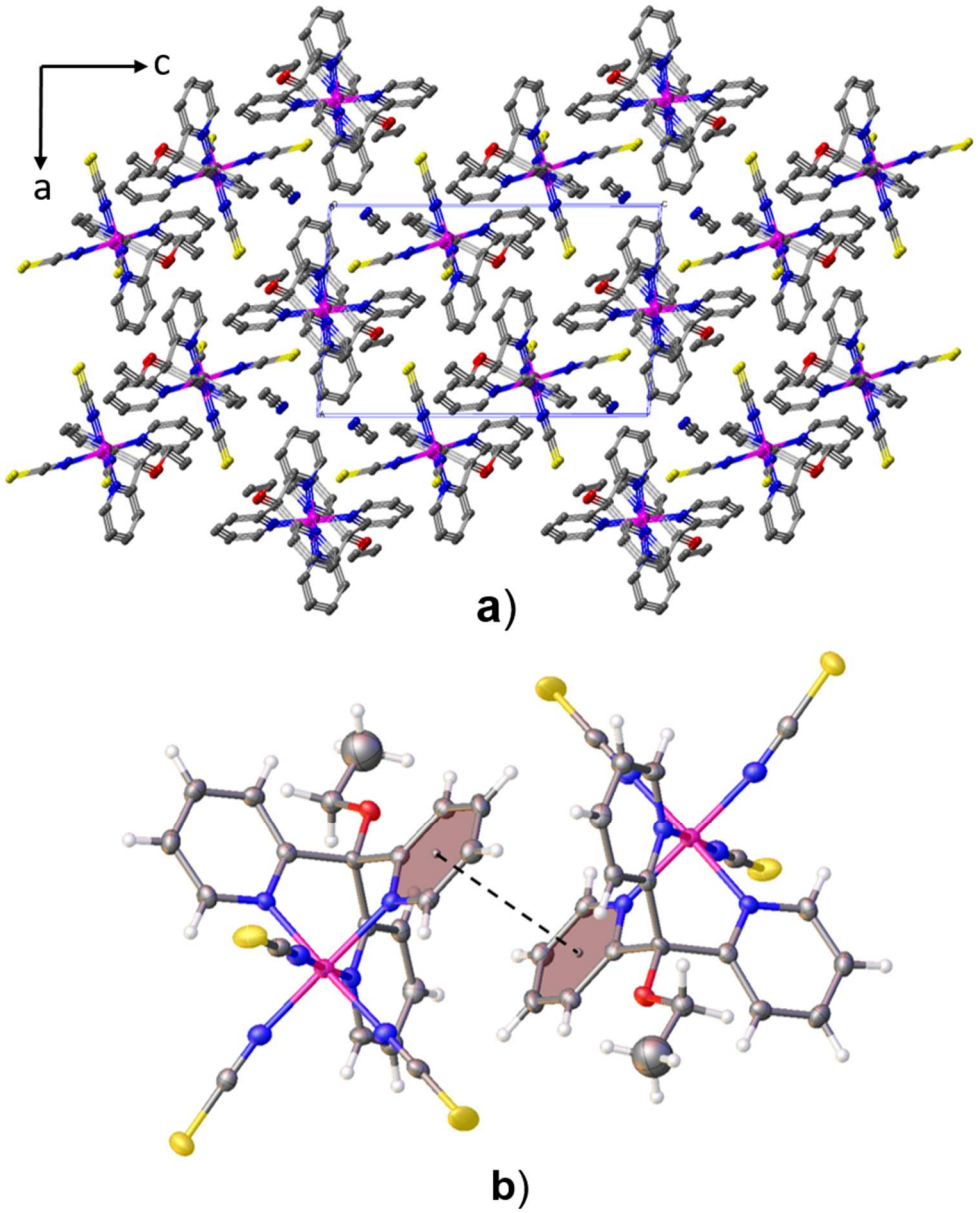


Figure S8. Projection of the crystal packing in the *ac* plane (**a**) and π-π contact motif (**b**) of **1** (similar in **2**)

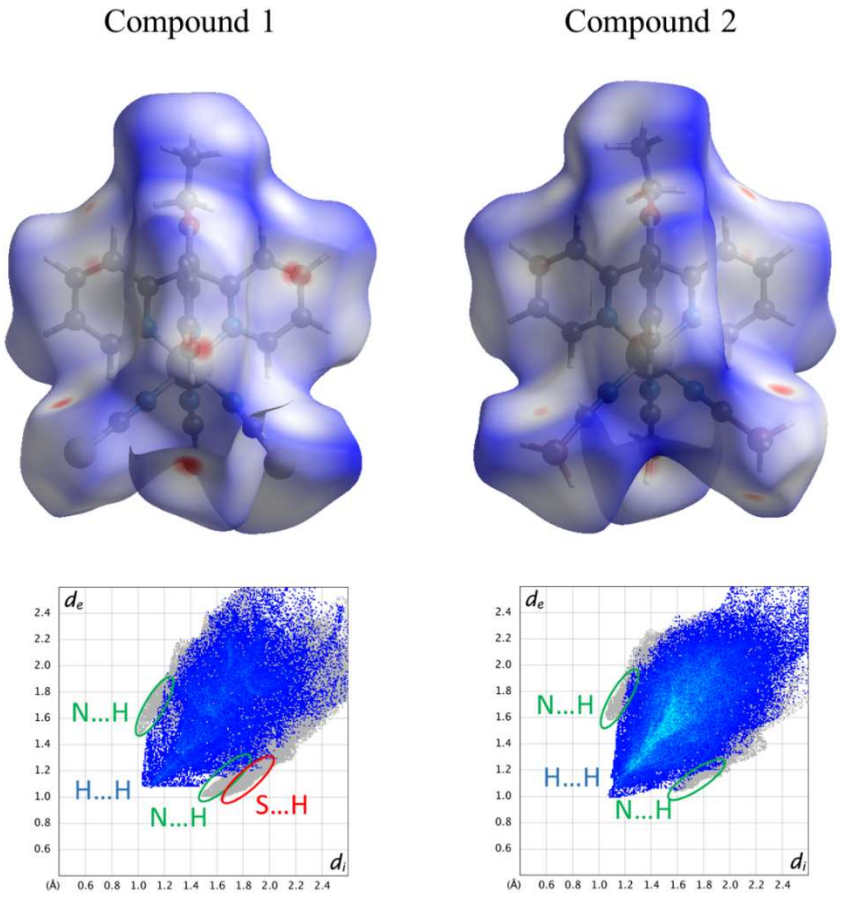


Figure S9. 3D Hirshfeld surface maps and fingerprint plots of the intermolecular interactions around the $[Fe(py_3C\text{-}OEt)(NCE)_3]^-$ anions for compounds **1** and **2**.

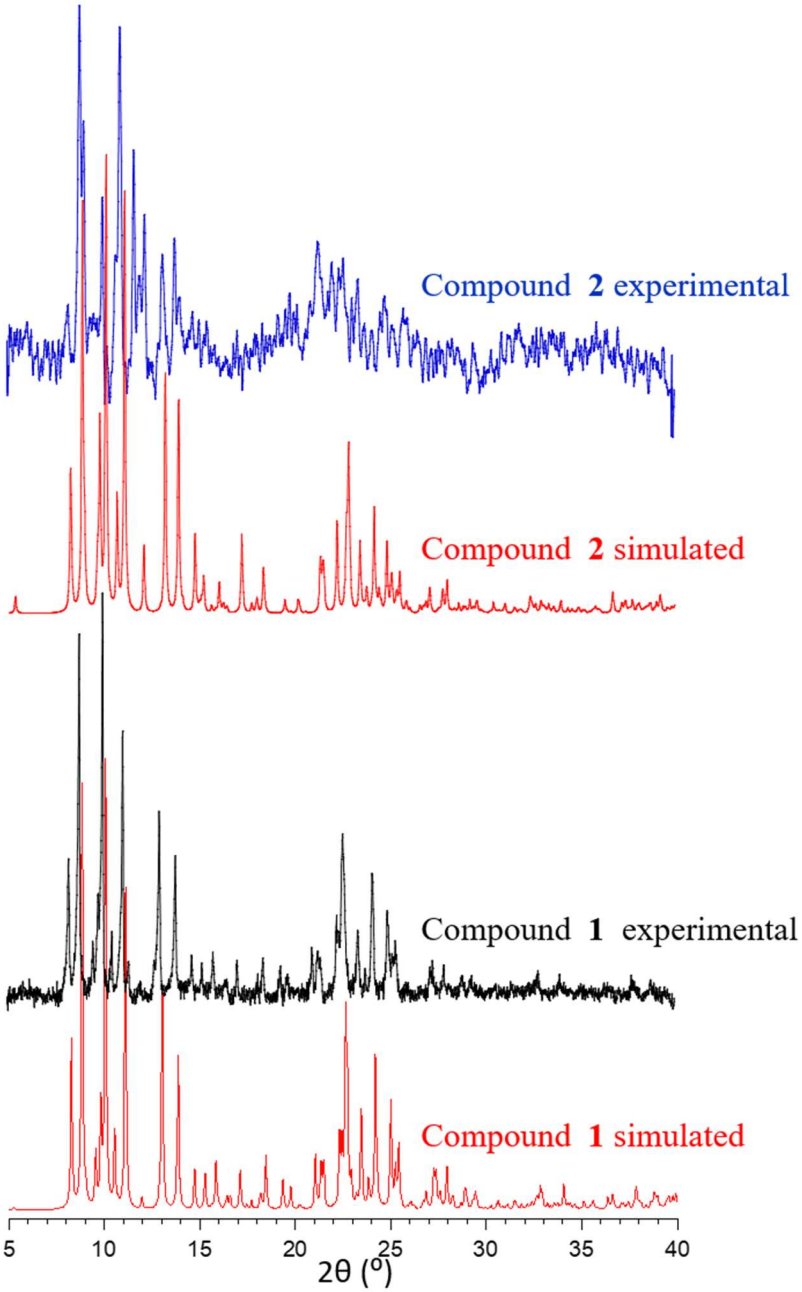


Figure S10. Experimental and simulated XRPD patterns for compounds **1** and **2**.