Electronic Supplementary Material (ESI) for CrystEngComm.

Interplay of halogen and hydrogen bonding in a series of heteroleptic iron(III) complexes

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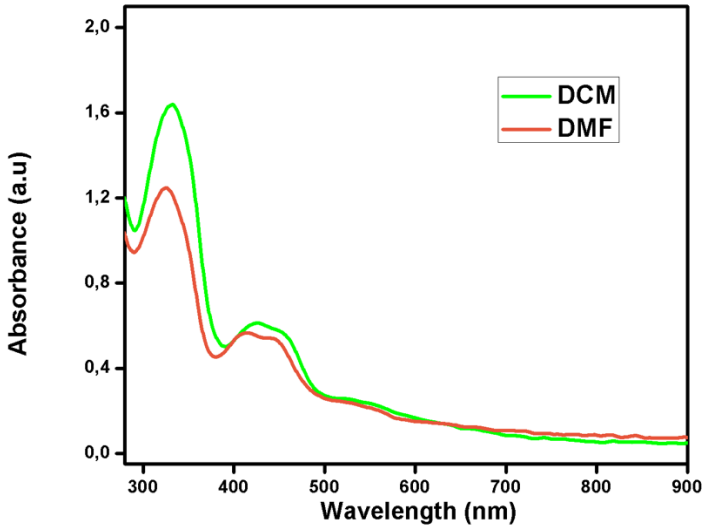
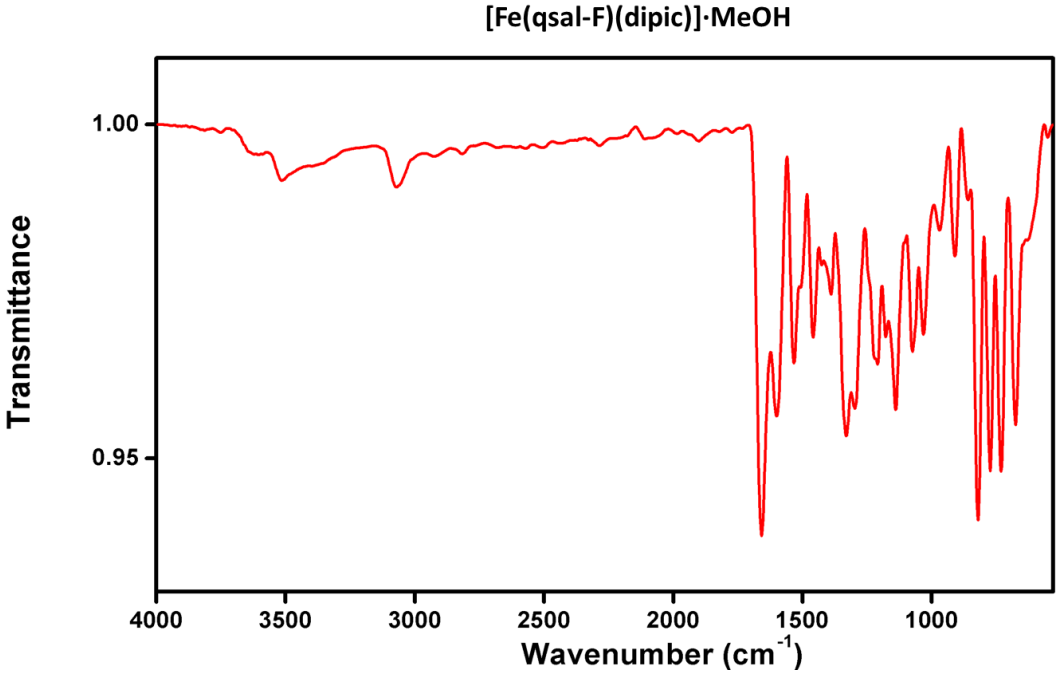
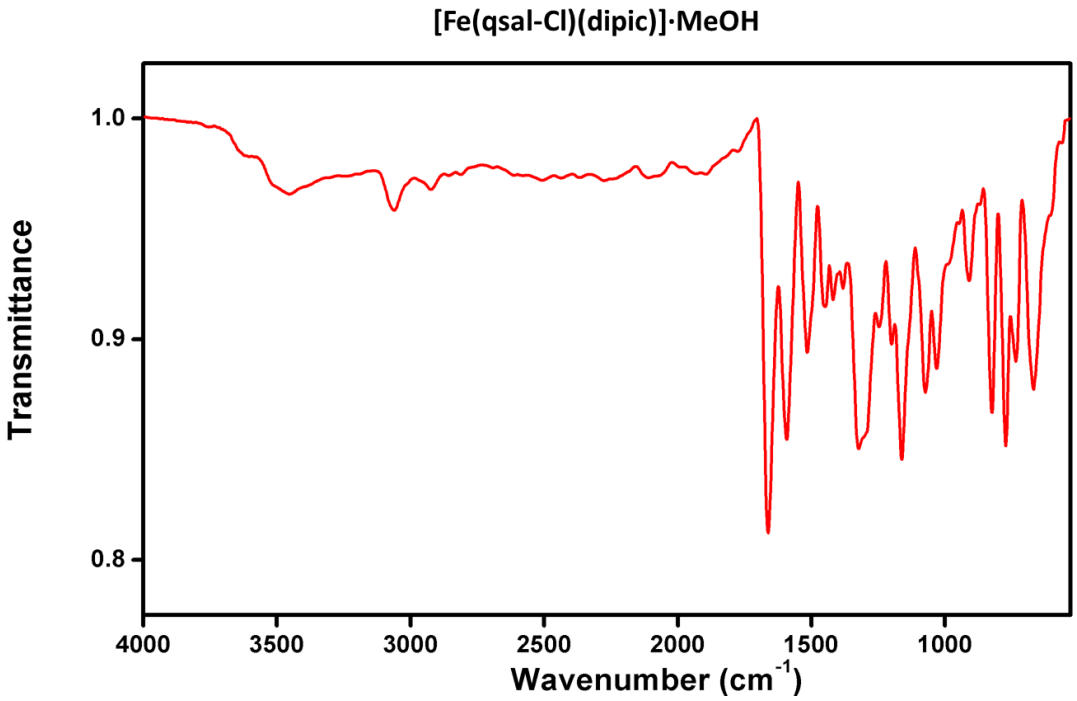
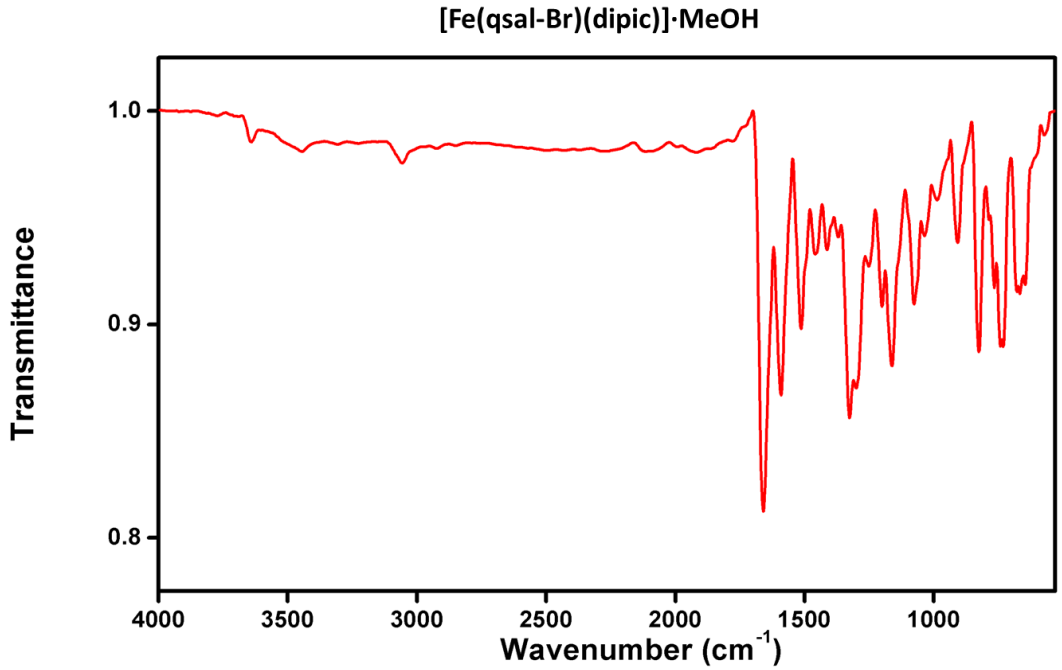


Figure S1 UV-Visible spectra of **4** in DCM (green) and DMF (orange) at 0.001 M.

ATR-IR spectra




[Fe(qsal-Cl)(dipic)]·MeOH
Transmittance
1.0
0.9
0.8
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)


[Fe(qsal-Br)(dipic)]·MeOH
Transmittance
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0.8
4000
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3000
2500
2000
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Wavenumber (cm-1)

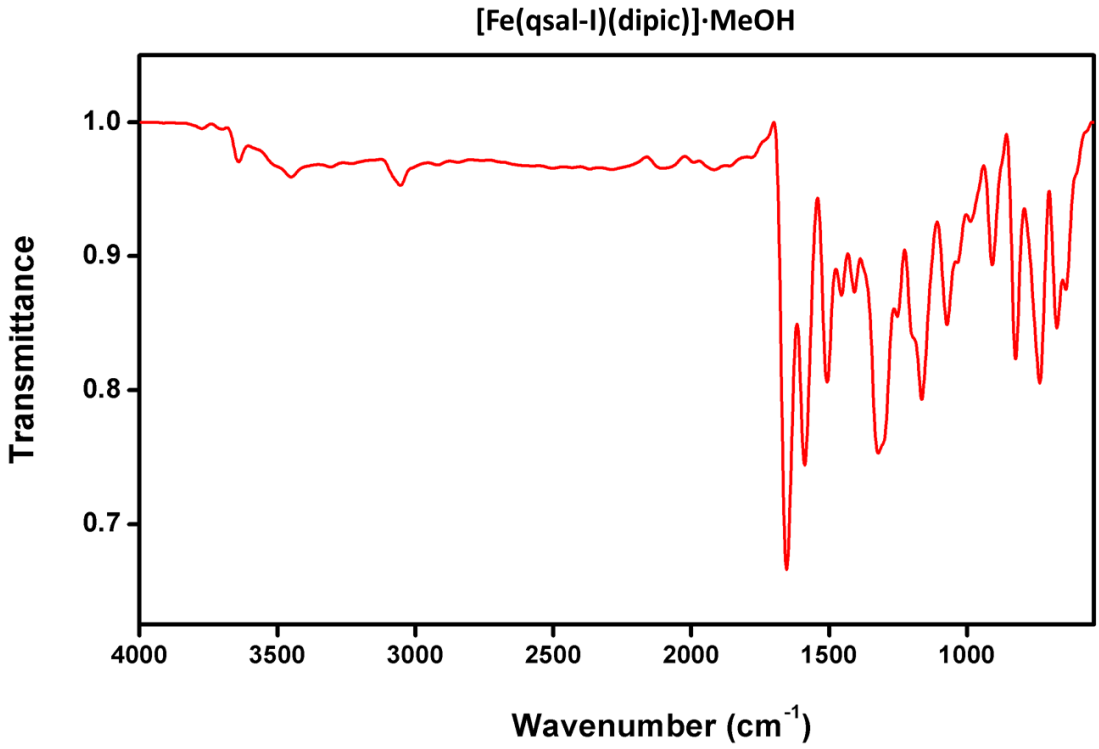


Figure S2 ATR-IR spectra for **1**-**4**.

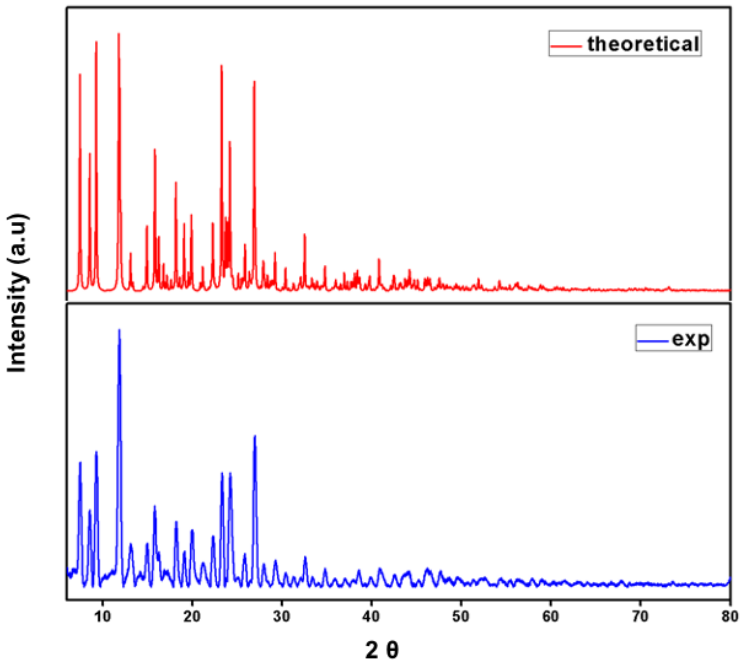
Table S1 Crystallographic data and structure refinement of **1**-**4**.

	[Fe(qsal-X)(dipic)]·MeOH			
	F	**Cl**	**Br**	**I**
Empirical formula	$C_{24}H_{17}FFeN_3O_6$	$C_{24}H_{17}ClFeN_3O_6$	$C_{24}H_{17}BrFeN_3O_6$	$C_{24}H_{17}IFeN_3O_6$
Formula weight/ $gmol^{-1}$	518.26	534.70	579.16	626.15
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a / Å	8.1982(3)	8.2215(2)	12.20560(10)	12.1991(2)
b / Å	11.5358(5)	11.9651(3)	9.30670(10)	9.3756(2)
c / Å	12.9597(6)	12.8982(3)	18.8067(2)	19.0747(4)
α / °	103.868(4)	105.940(2)	90	90
β / °	103.308(4)	105.557(2)	94.8010(10)	95.6028(19)
γ / °	107.779(4)	104.264(2)	90	90
Cell volume / $Å^3$	1070.33(9)	1102.95(5)	2128.83(4)	2171.23(8)
Z	2	2	4	4
Absorption coefficient / mm^{-1}	6.168	7.027	8.326	17.172
Reflections collected	15309	16928	17206	17238
Independent reflections, R_{int}	3880, 0.0798	4030, 0.0546	3905, 0.0782	3969
Max. and min. transmission	0.736 / 0.202	0.743 / 0.397	1.000 / 0.734	0.526 / 0.232
Restrains/parameters	0/ 318	36/ 318	0/ 318	0/ 318
Final R indices [I>=2σ (I)]				
R_1, wR_2	0.0686, 0.1762	0.0813, 0.2119	0.0489, 0.1237	0.0675, 0.1704
CCDC No.	2075294	2075296	2075295	2075297

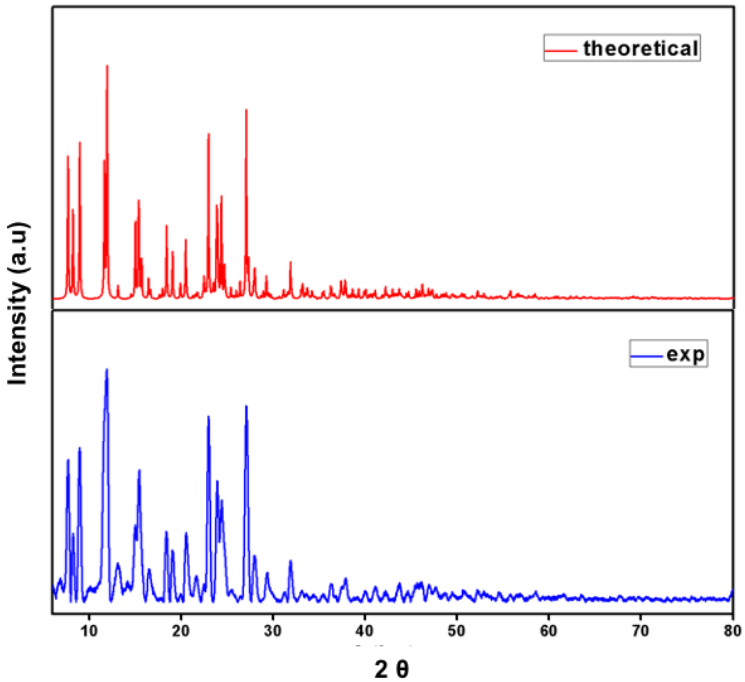
Table S2 Intermolecular interactions of **1**-**4** (Å).

		F	Cl	Br	I
1D chain					
C-H···O					
	O1-H21	2.587	2.582	2.686	2.711
	O2-H10	2.472	2.541	2.643	2.497
π-π					
Quinoline	centroid-centroid	3.794	3.696	3.668	3.710
Dipic	centroid-centroid	-	-	3.553	3.567
C=O···π					
dipic	atom-atom	3.322	3.350	-	-
Fe-Fe					
dipic		7.529	7.466	7.691	7.707
quinoline		6.756	6.769	7.061	7.087
2D and 3D					
π-π					
Quinoline	centroid-centroid	3.771	3.525	3.575	3.585
C-H···O					
dipic-quin	O5-H5	2.662	2.576	2.662	2.675
X···H	X1-H1	2.437	2.844	3.008	3.058
X···π	X1-C21	-	3.422	-	3.632
X···O	X1-O5	-	-	3.166	3.151
OH···CH	H6A-O5	1.930	1.831	2.236	2.261

1


theoretical
exp
Intensity (a.u)
10
20
30
40
50
60
70
80
2 θ

2


theoretical
exp
Intensity (a.u)
10
20
30
40
50
60
70
80
2 θ

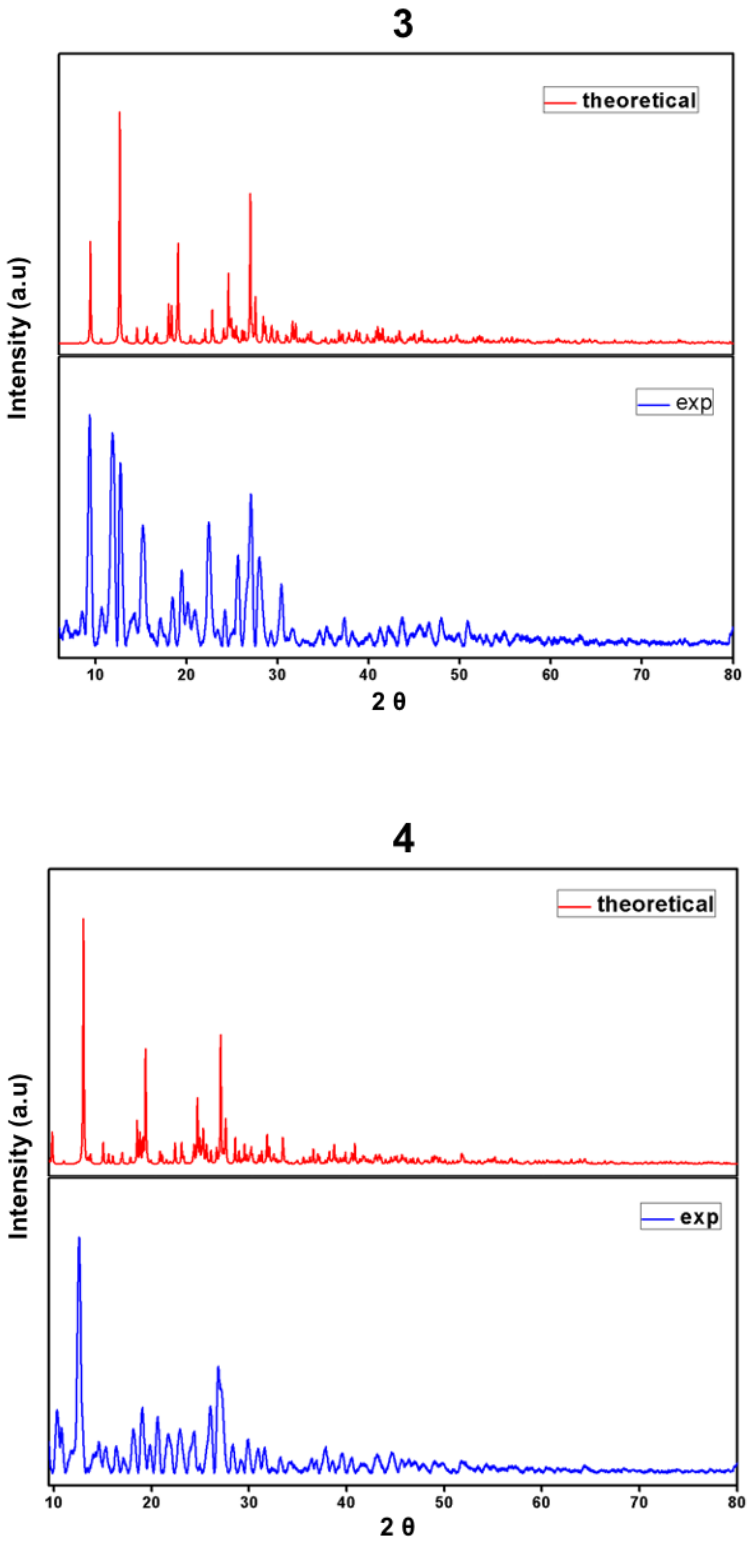


Figure S3 Experimental PXRD diffractograms (blue) and the corresponding simulated patterns (red) for **1-4** at room temperature.

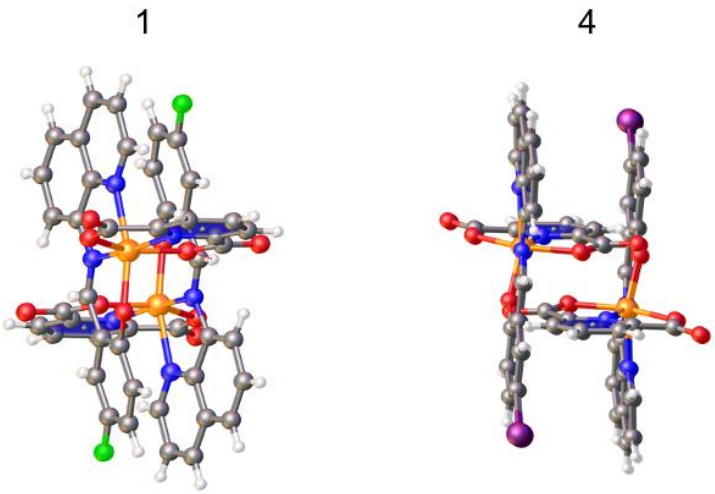


Figure S4 Cross-section of the 1D chain for **1** (square) and **4** (rectangular).

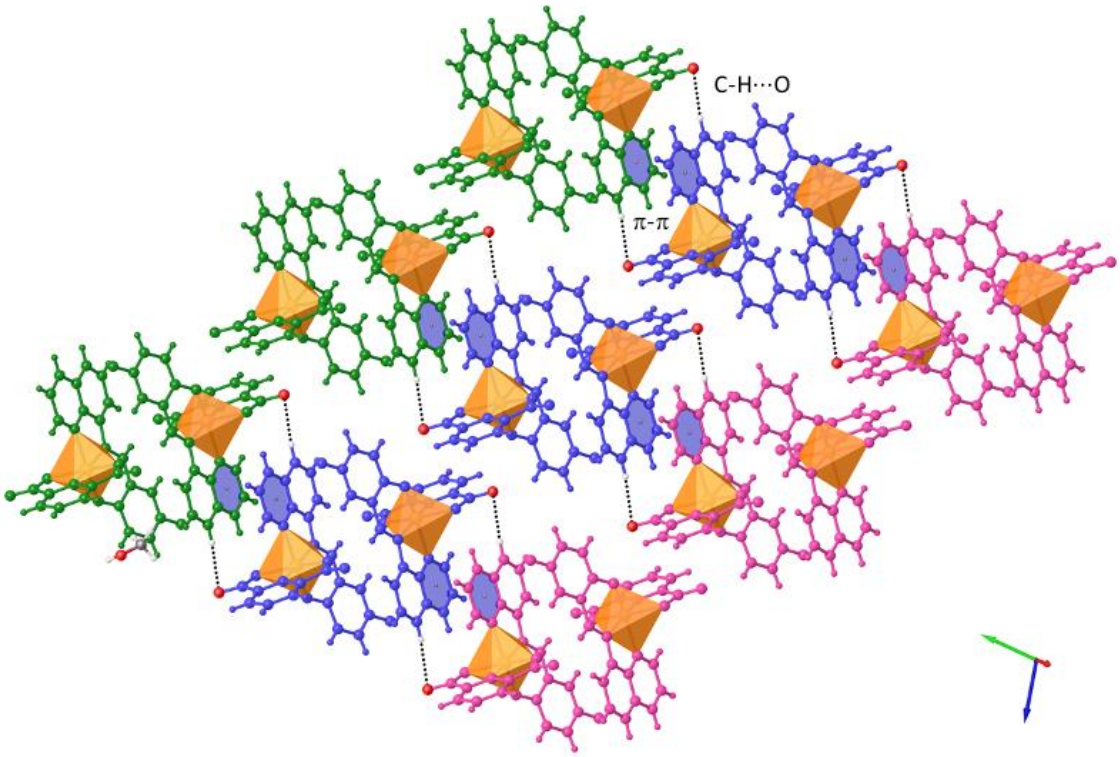


Figure S5 Structural representation of the supramolecular π-π and C-H···O contacts connecting the planes of Fe(III) centers in **1**.

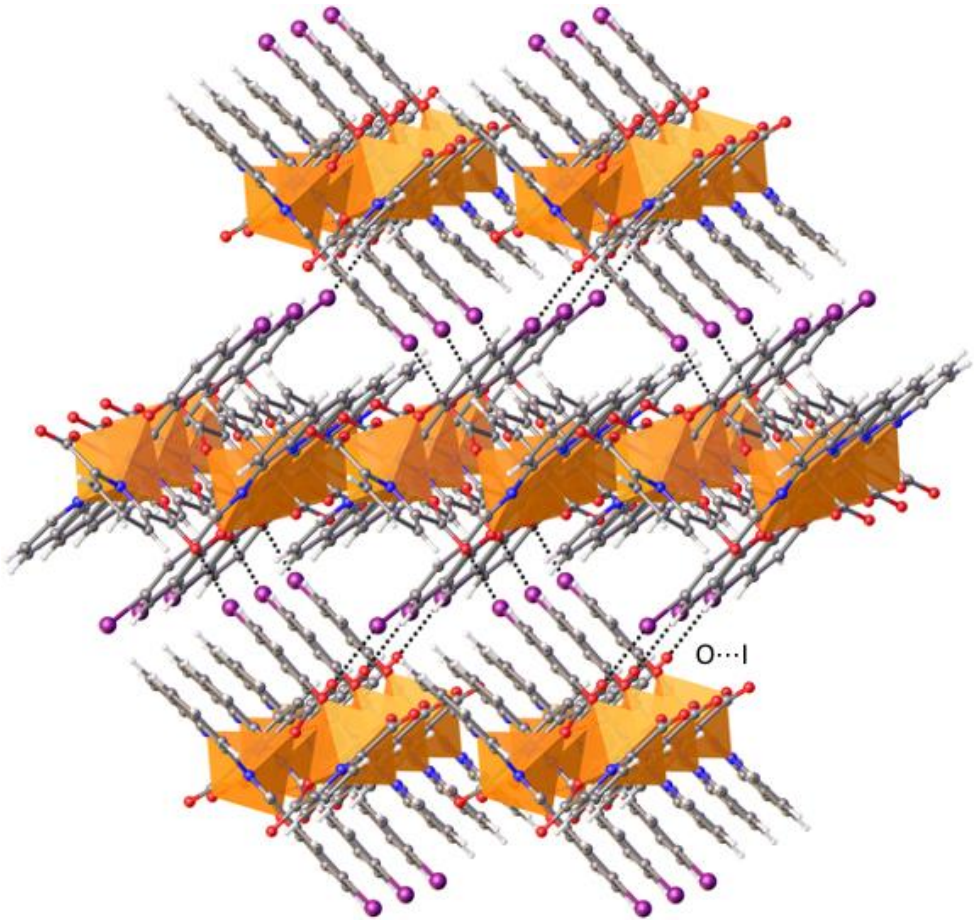


Figure S6 Structural representation of the supramolecular O···I interactions connecting the planes of Fe(III) centers in **4**.

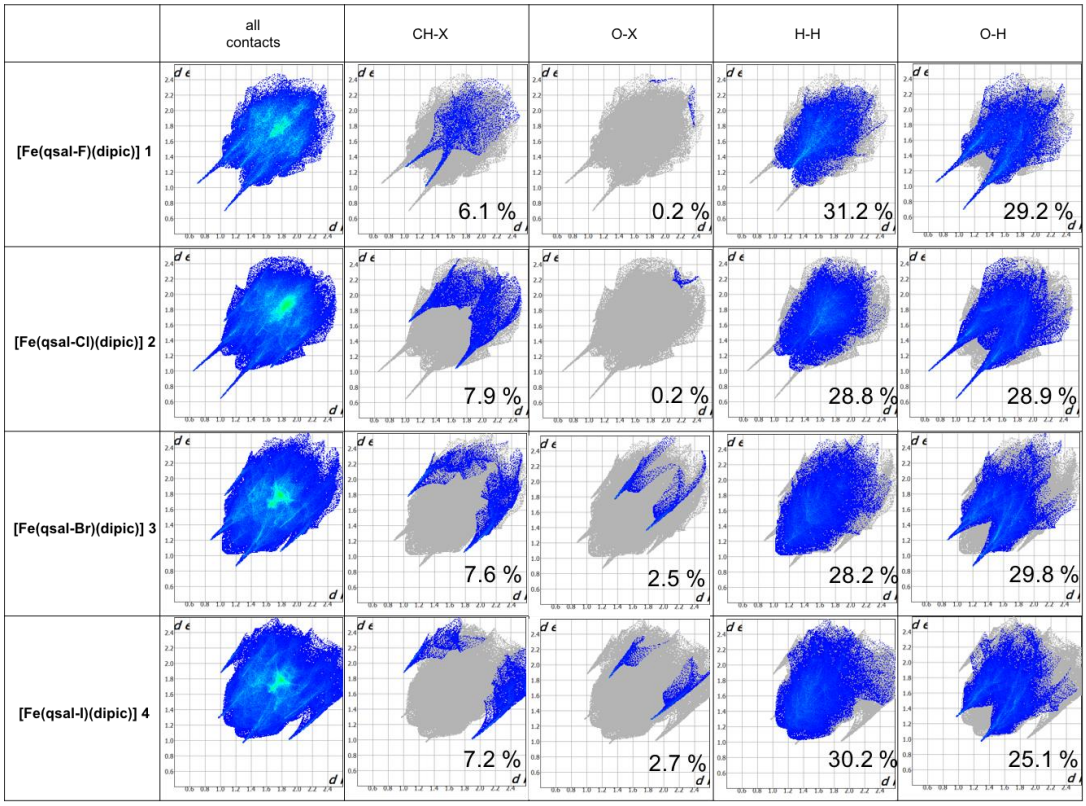


Figure S7 Hirshfeld surface 2D fingerprint plots: all contacts, C-H···X, O···X, H···H and O···H for **1-4.**

Table S3 Intermolecular interactions contributions for **1-4** calculated by Hirshfeld surface.

	H···H	**CH···X**	**H···O**	**H···C**	**O···X**	**C···C**	**C···X**	**H···N**	**Other**
1	31.2	6.1	29.2	14.7	0.2	9.0	3.2	1.6	4.8
2	28.8	7.9	28.9	15.2	0.2	8.2	4.1	1.7	5.0
3	28.2	7.6	29.8	12.0	2.5	9.0	3.2	1.9	5.6
4	30.2	7.2	25.1	16.0	2.7	8.3	3.0	1.9	5.8

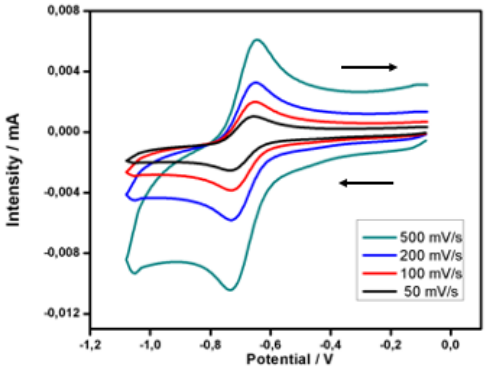
Theoretical Results

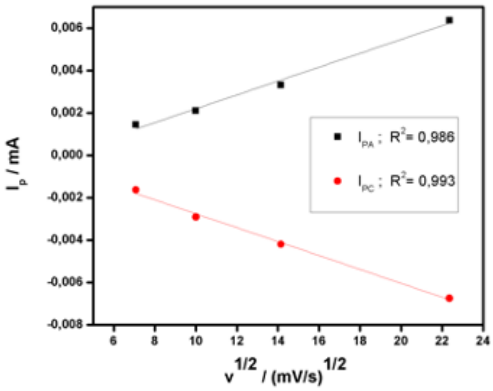
Table S4. QTAIM parameters at the bond critical points for the different dimers in the crystal structures **1**-**4**. All values are given in a.u.

System	X	ρ	$\nabla^2\rho$	V	G	H	$\|V\|/G$	DI(A,B)
1 hydrogen bond	F	0.0069	0.0317	-0.0042	0.0061	0.0019	0.6885	0.0266
1 X···π		0.0044	0.0166	-0.0022	0.0032	0.0010	0.6875	0.0198
1 C=O···π		0.0050	0.0168	-0.0024	0.0033	0.0009	0.7273	0.0081
2 hydrogen bond	Cl	0.0059	0.0215	-0.0030	0.0042	0.0012	0.7143	0.0302
2 X···π		0.0064	0.0198	-0.0029	0.0039	0.0010	0.7436	0.0400
2 C=O···π		0.0055	0.0186	-0.0027	0.0037	0.0010	0.7297	0.0158
3 halogen bond	Br	0.0083	0.0331	-0.0049	0.0066	0.0017	0.7424	0.0773
3 X···H		0.0058	0.0178	-0.0027	0.0036	0.0009	0.7500	0.0371
3 π···π		0.0067	0.0212	-0.0033	0.0043	0.0010	0.7674	0.0147
4 halogen bond	I	0.0109	0.0405	-0.0065	0.0083	0.0018	0.7831	0.1077
4 X···H		0.0071	0.0193	-0.0032	0.0040	0.0008	0.8000	0.0500
4 π···π		0.0067	0.0210	-0.0033	0.0043	0.0010	0.7674	0.0147

Electrochemical Studies

1





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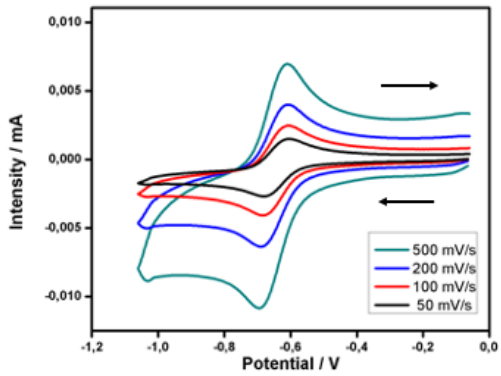

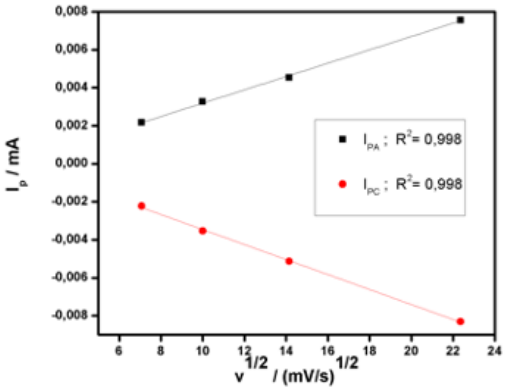

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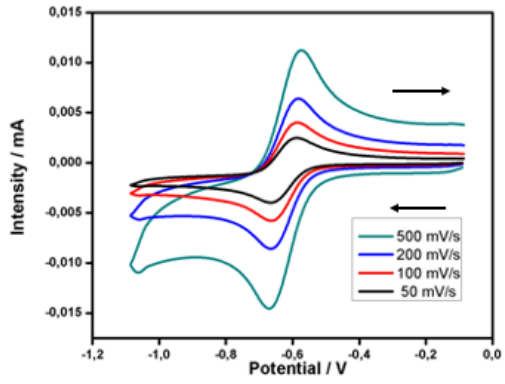

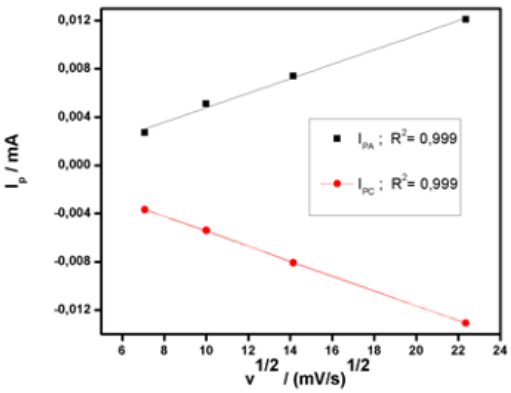

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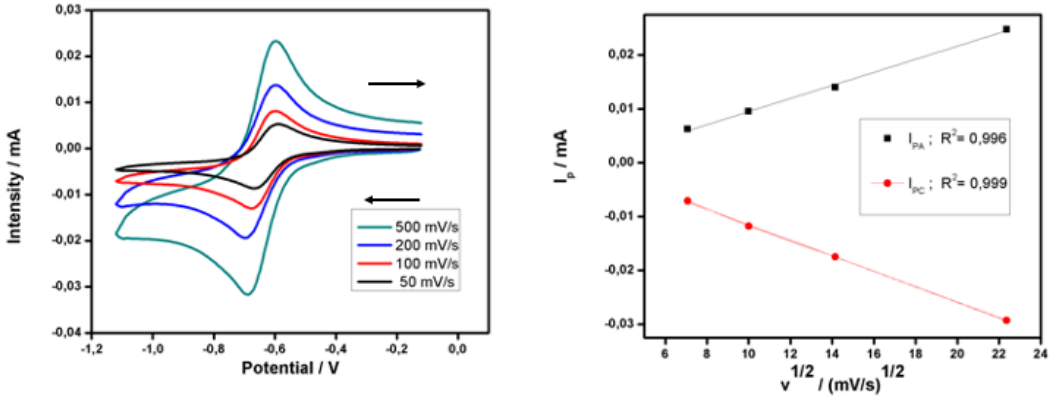

Figure S8 Cyclic voltammogram (Fe^{3+}/Fe^{2+} redox peak) of **1**-**4** at different scan rates (left) and the representation of i_p vs $v^{1/2}$ (right).

Table S4 Electrochemical properties of **1**-**4**.

		i_{pa}/i_{pc}	ΔEp (V)	E°’ (V)	D($cm^2 \cdot s^{-1}$)
1	50 mV/s	0.856	0.063	-0.681	$5.31 \cdot 10^{-6}$
	100 mV/s	0.881	0.065	-0.675	
	200 mV/s	0.905	0.070	-0.683	
	500 mV/s	0.959	0.072	-0.682	
2	50 mV/s	0.967	0.066	-0.621	$6.43 \cdot 10^{-6}$
	100 mV/s	0.931	0.070	-0.622	
	200 mV/s	0.915	0.072	-0.622	
	500 mV/s	0.945	0.071	-0.623	
3	50 mV/s	0.869	0,066	-0.620	$1.68 \cdot 10^{-5}$
	100 mV/s	0.892	0.068	-0.615	
	200 mV/s	0.959	0.072	-0.618	
	500 mV/s	0.959	0.088	-0.619	
4	50 mV/s	0.911	0.068	-0.645	$7.56 \cdot 10^{-5}$
	100 mV/s	0.866	0.071	-0.642	
	200 mV/s	0.917	0.088	-0.644	
	500 mV/s	1.020	0.085	-0.644	

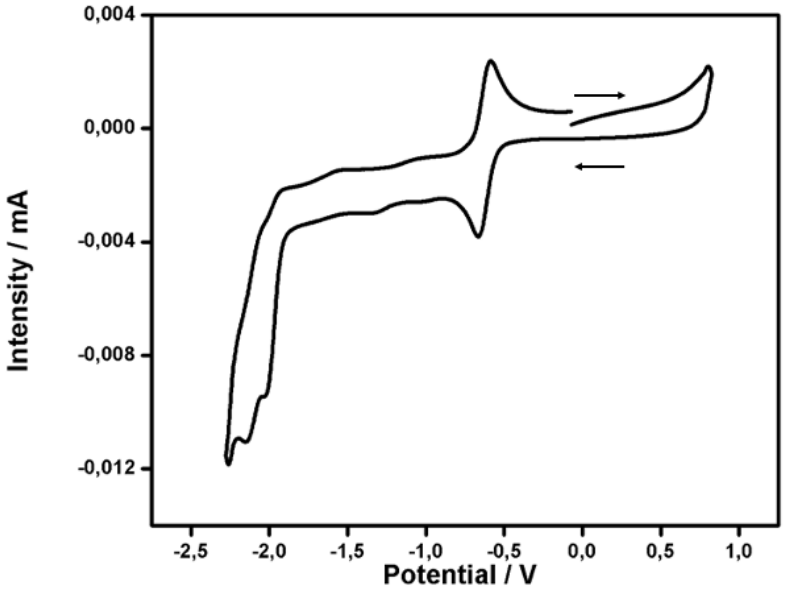

Figure S9 Cyclic voltammogram of **4** in DCM containing 0.1 M of $TBAPF_6$ (scan rate 50 mV/s) vs Fc/Fc^+.

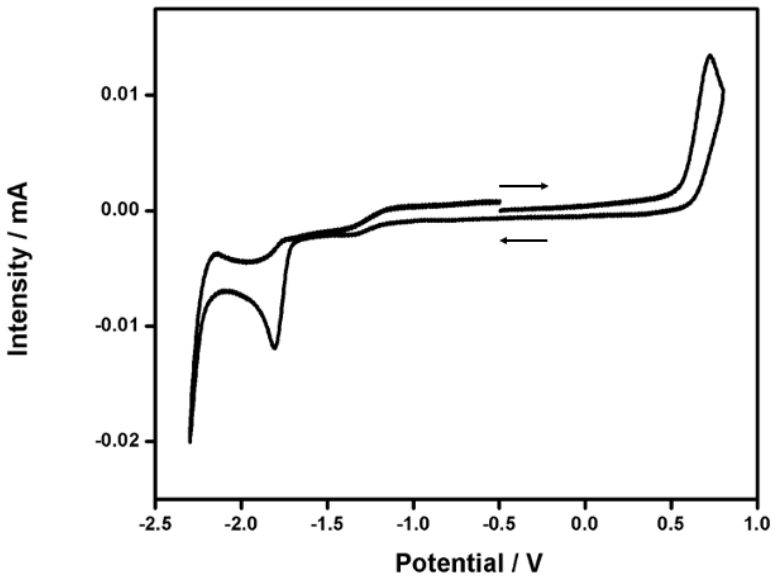

Figure S10 Cyclic voltammogram of Hqsal-I in DCM containing 0.1 M of $TBAPF_6$ (scan rate 50 mV/s) vs Fc/Fc^+.

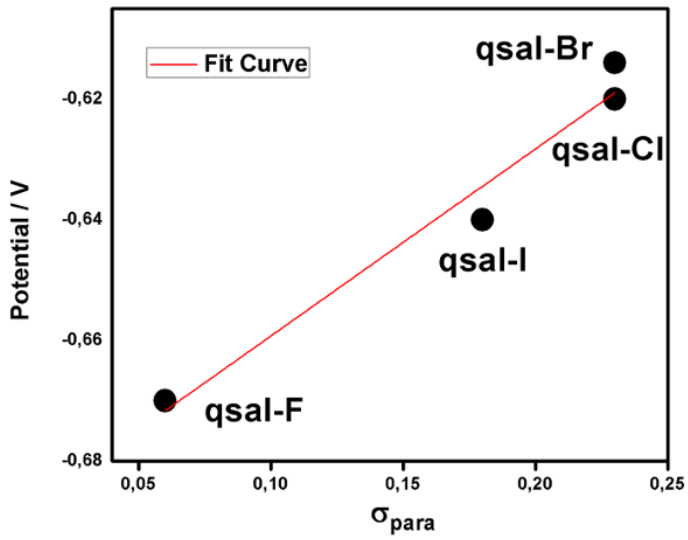

Figure S11 Plot of E′°(V) vs σ_p for **1-4**.