Supporting Information

Anion-driven supramolecular modulation of Spin-Crossover properties in mononuclear Iron(III) Schiff-base Complexes

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Table S1. Hydrogen bond distances and parameters for the complexes of **1**-**4** (Å,°)

1-PF_6									
100K					**300K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N2-H9…F8	0.83(3)	2.22(3)	3.027(3)	164(3)	N2-H9…F4	0.90(7)	2.26(7)	3.073(7)	150(6)
N3-H14…F3^{i}	0.85(5)	2.29(5)	3.052(4)	149(5)	N3-H23…F5^{i}	0.78(5)	2.36(5)	3.081(5)	154(5)
2-ClO_4									
100K					**300K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N2-H9…O10^{ii}	0.89(4)	2.14(4)	2.938(5)	149(4)	N2-H9…O9	0.99(5)	2.24(6)	3.063(6)	139(5)
N3-H14…O7	0.80(5)	2.43(5)	3.138(5)	148(6)	N6-H31…O12	0.90(6)	2.33(6)	3.076(10)	140(6)
N6-H31…O5^{iii}	0.91(7)	2.47(8)	3.164(8)	134(5)	N7-H36…O10	0.80(6)	2.49(6)	3.099(10)	134(3)
N6-H31…O8^{iii}	0.91(7)	2.58(6)	3.305(6)	1.38(5)	N6-H31…O6	0.897	2.618	3.357	140
N7-H36…O9^{iv}	0.84(4)	2.33(4)	3.048(6)	143(3)					
3-I									

100K					**300K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N2-H9…I2	0.89(5)	2.80(5)	3.624(6)	155(4)	N2-H9…I2[v]	0.91	2.96	3.776(8)	150
N3-H14…I1	0.86(5)	3.11	3.832	143	N3-H14…I1	0.91	2.78	3.636(7)	157
N6-H31…I1	0.88(6)	2.88(6)	3.678(6)	152(4)	N6-H31…I1	0.91	2.99	3.771(10)	144
N7-H36…I2[iv]	0.86(6)	3.05(6)	3.773(6)	143(4)	N7-H36…I2	0.91	2.81	3.663(10)	156
4-NO_3									
100K					**300K**				
D-H…A	D-H	H…A	D…A	D-H…A	D-H…A	D-H	H…A	D…A	D-H…A
N2-H9…O7	0.95(5)	2.02(5)	2.932(6)	162(5)	N2-H9…O5[vii]	0.80(4)	2.19(4)	2.963(5)	163(4)
N3-H14…O8[vi]	0.89(7)	2.44(8)	3.072(6)	128(6)	N3-H12…O9[viii]	0.80(5)	2.51(6)	3.108(6)	133(5)
N6-H31…O6	0.92(6)	2.38(5)	3.092(8)	134(3)	N6-H29…O7	0.81(6)	2.56(6)	3.097(8)	125(5)
N7-H36…O8	0.78(6)	2.27(6)	3.021(7)	164(6)	N7-H34…O9	0.80(6)	2.29(6)	3.048(7)	159(5)

Symmetry codes:(i)-1/2+x,1/2-y, z; (ii) x, y,1+z; (iii)-1+x, y, z; (iv)-1/2+x,1/2-y,1/2+z; (v)1/2+x,1/2-y,1/2+z; (vi)1/2+x,1/2-y,-1/2+z; (vii)x,y,-1+z; (viii)-1/2+x,3/2-y,-1/2+z

Table S2. The variations of octahedral distortion parameters (°) for complexes **1-4**

°	**1- PF_6** **295 K→ 100 K**	**2-ClO_4** **295 K→ 100 K**	**3-I** **295 K→ 100 K**	**4-NO_3** **273 K→ 100 K**
$\Delta\Sigma$[a]	34.7	22 5	12.5 -13	0.9 -5
$\Delta\Theta$[a]	111	109 30	81 -67	4 -28

[a] for complex **1,** $\Delta\Sigma = \Sigma_{HS}-\Sigma_{LS}$, $\Delta\Theta = \Theta_{HS}-\Theta_{LS}$

Table S3. Distances between the intrachain and the planes (d_{plane}) at different temperatures.

Compound	100K			300K		
	Intrachain(Å)		d_{plane}(Å)	Intrachain(Å)		d_{plane}(Å)
	Fe1—Fe1	Fe2—Fe2		Fe1—Fe1	Fe2—Fe2	
1-PF_6	6.668		8.635	6.674		8.928
2-ClO_4	6.790	6.605	8.673	6.886	6.699	8.867
3-I	6.894	6.682	8.472	6.947	6.770	8.661
4-NO_3	6.851	6.659	8.409	6.944	6.756	8.517

Table S4. The shortest distances between the centroids of the aromatic fragments of the ligands (d_{cent}), the distances between the centroids and the average plane in the closest neighbor (d_{CP}), shift in the overlap (d_{shift}), tilt angle (Φ).

Compound	1		2				3				4			
T/K	100	300	100		300		100		300		100		300	
Chain	Fe	Fe	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2
*d*cent (Å)	4.540	4.573	4.486	4.759	4.524	4.446	4.582	4.477	4.608	4.565	4.481	4.592	4.558	4.663
*d*CP(Å)	3.632	3.702	3.229	3.453	3.219	3.532	3.733	3.299	3.735	3.387	3.034	3.326	3.633	3.412
*d*shift(Å)	2.724	2.658	3.144	3.275	3.179	2.71	2.657	3.026	2.699	3.061	3.298	3.166	2.753	3.178
Φ (°)	25.6	24.	16.8	22.64	14.3	24.82	16.69	28.40	15.81	28.27	12	24.90	13.4	26.31

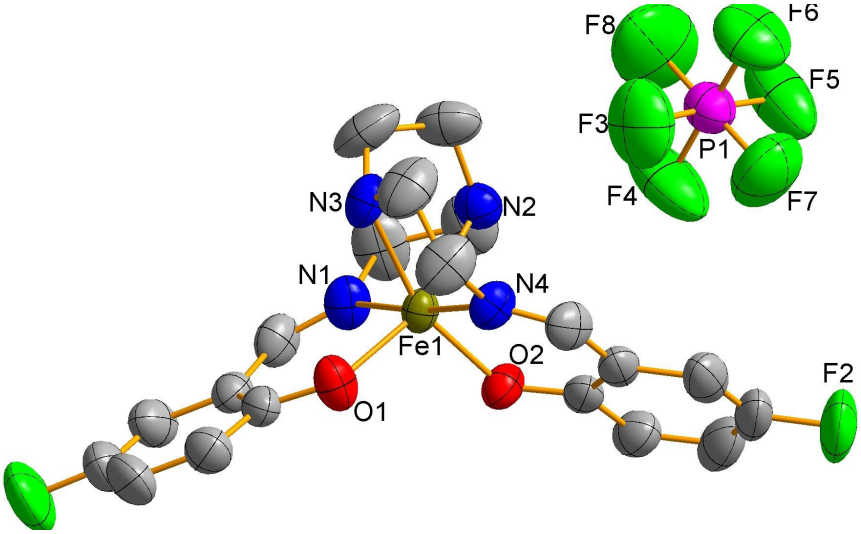


Figure S1. The molecular structure for complex **1** at 300 K, hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% atomic probability.

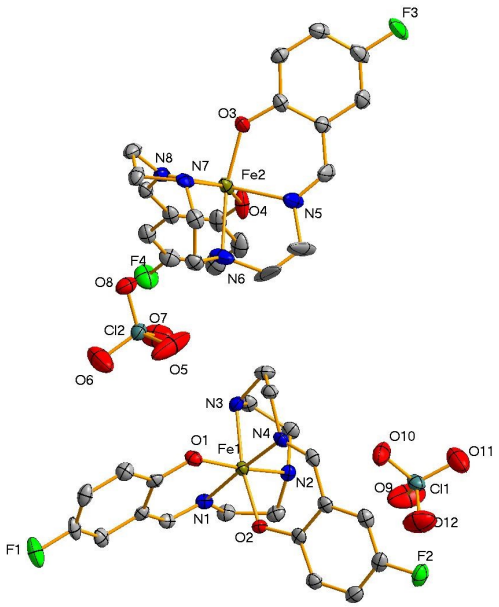


Figure S2. The molecular structure for complex **2** at 100 K, hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% atomic probability.

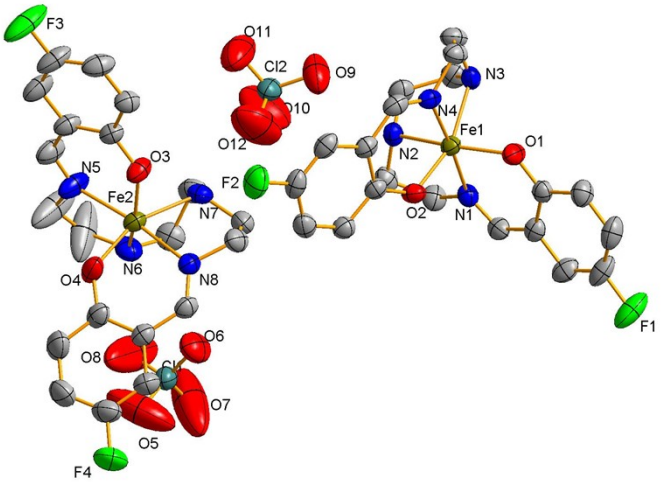


Figure S3. The molecular structure for complex **2** at 300 K, hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% atomic probability.

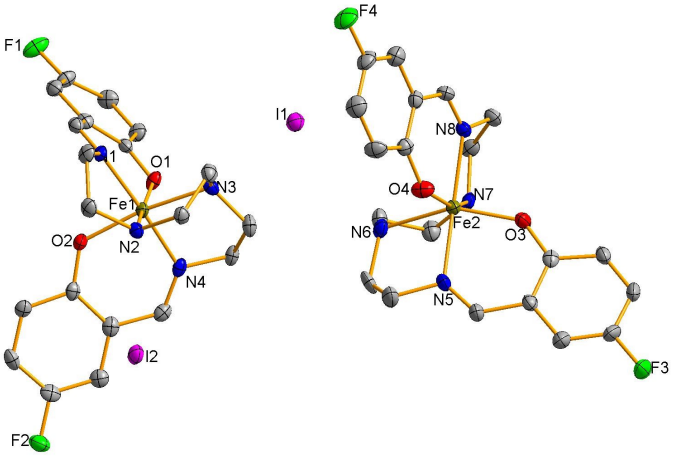


Figure S4. The molecular structure for complex **3** at 100 K, hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% atomic probability.

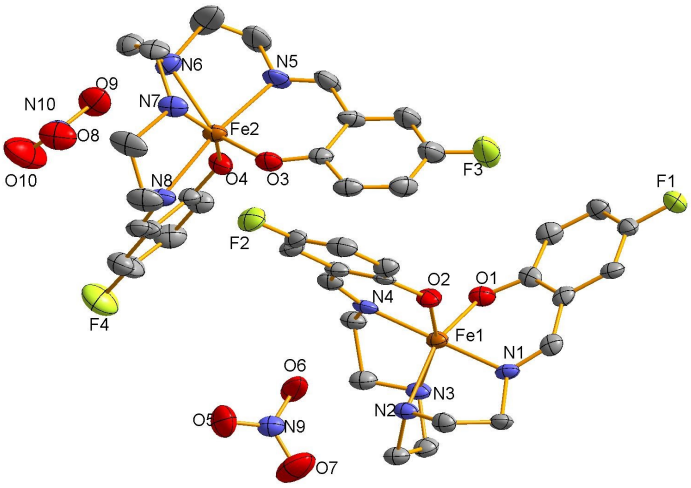
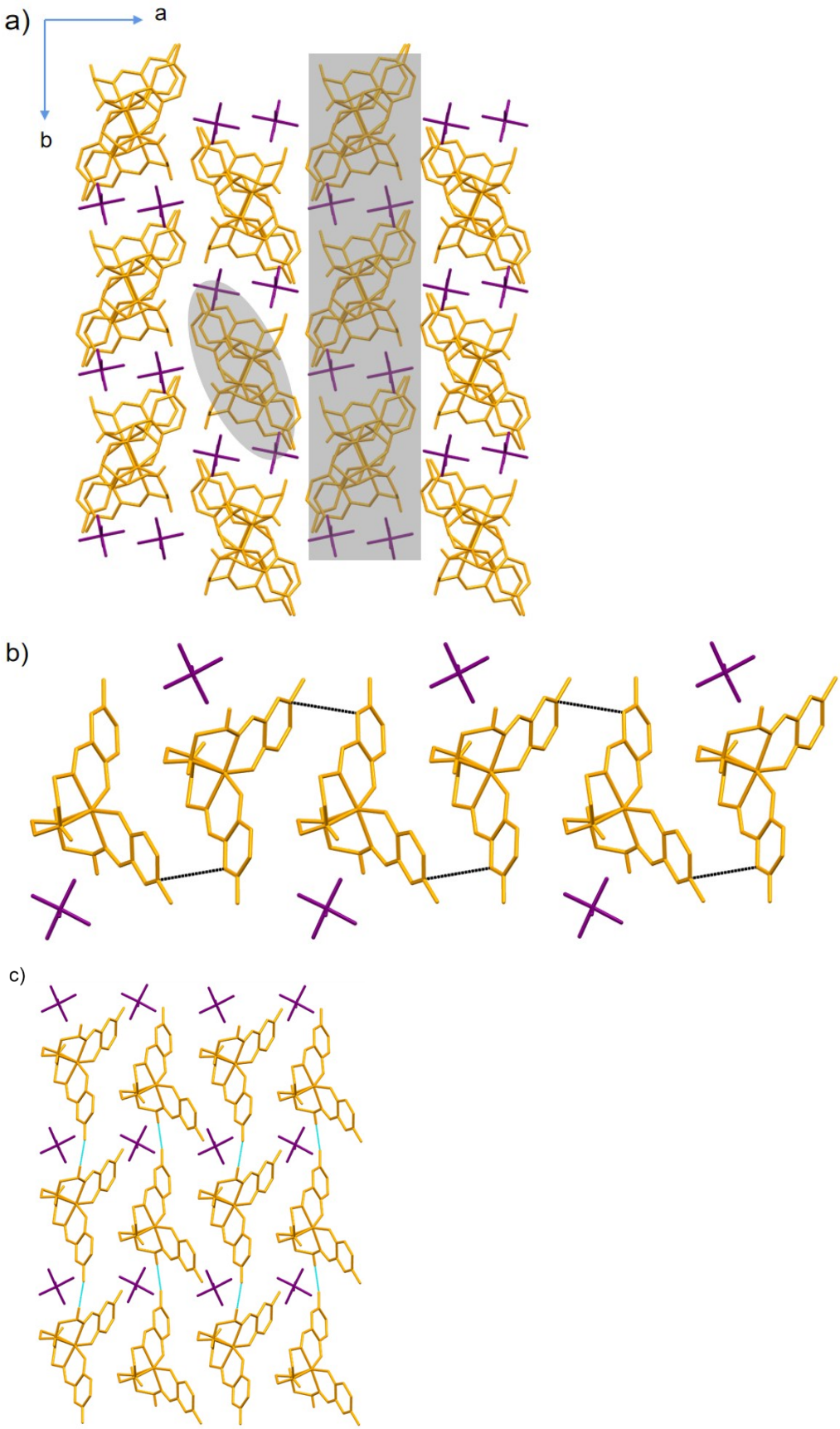


Figure S5. The molecular structure for complex **4** at 100 K, hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% atomic probability.


a)
a
b
b)
c)

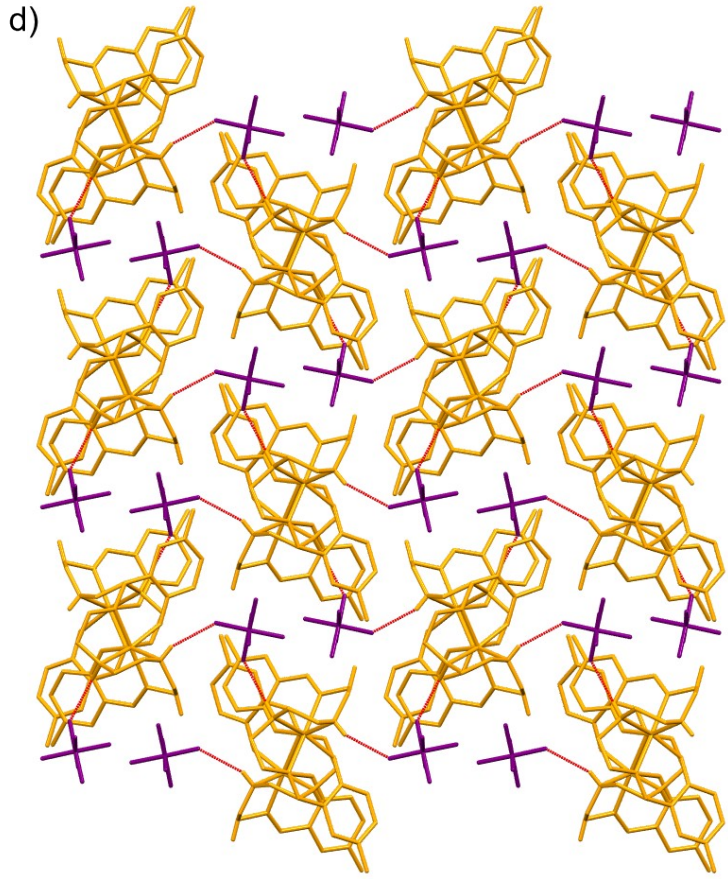
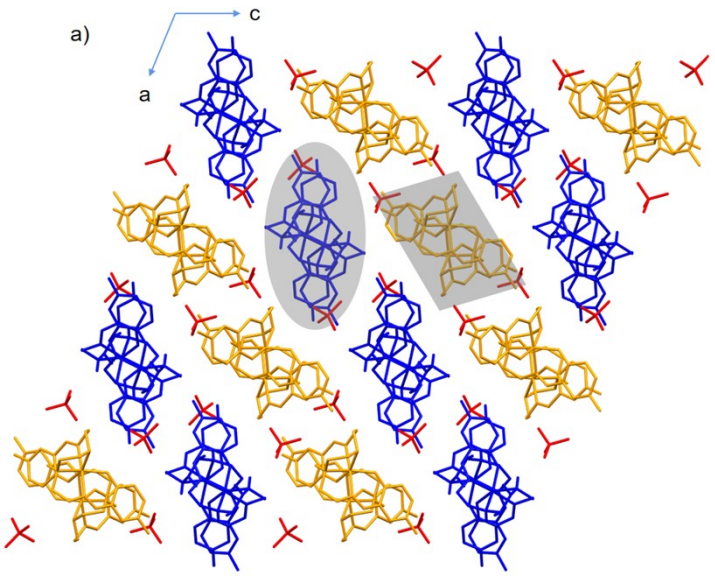


Figure S6. (a) Crystal packing of complex **1** at 300 K, viewed along the *c* axis, the 1D chain is shown in the light grey (ellipse) background and the layer-like unit is shown in the light grey (rectangle) background. (b) The chain viewed along the *a* axis, showing the C···C short contacts (black dotted line) between arene. (c) The C–H···F interactions (cyan dotted line) in **1** linking the chains into a plane. (d) The N–H···F hydrogen bonds (red dotted line) between the [Fe(5-F-sal-N-1,4,7,10)]$^{+}$ cations and PF_6^- anions in **1** linking the plane into 3D network.



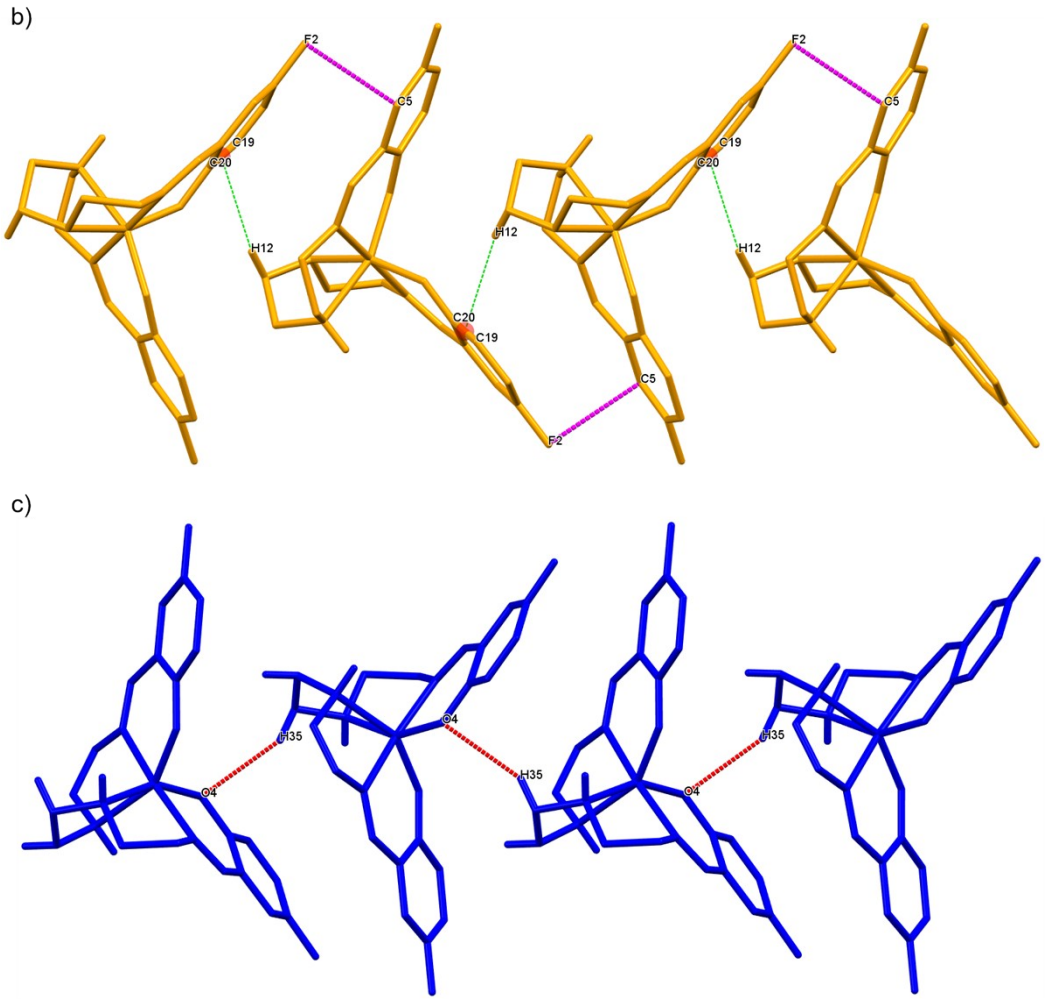


Figure S7. (a) Crystal packing of complex **2** at 300 K, viewed along the *b* axis. The Fe1 and Fe2 units are shown in orange and blue, respectively. (b) The formation of 1D Fe1 chain (rhombus background) by means of p-π interactions (magenta dotted line) and C–H···π (green dotted line) interactions. (c) The formation of 1D Fe2 chain (ellipse background) by means of C-H···O (red dotted line) interactions.

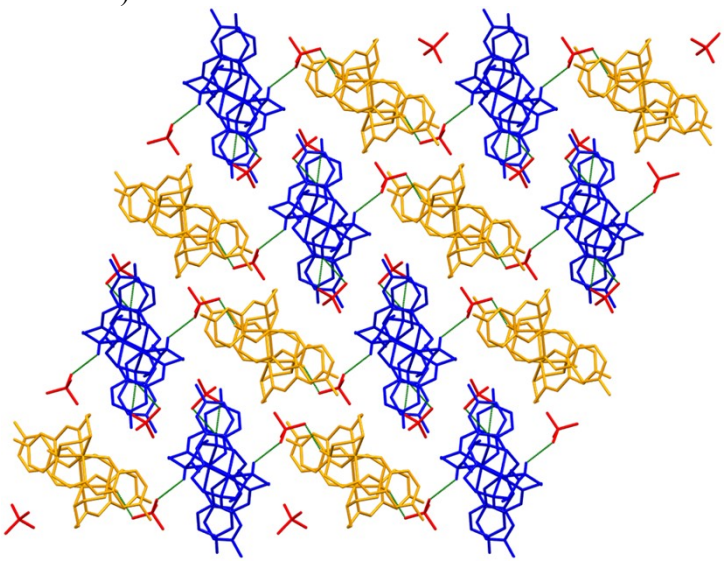


Figure S8. At 300K, N–H···O interactions (bottle green dotted line) linking the Fe1 and Fe2 centers in complex **2**. The Fe1 and Fe2 units are shown in orange and blue, respectively.

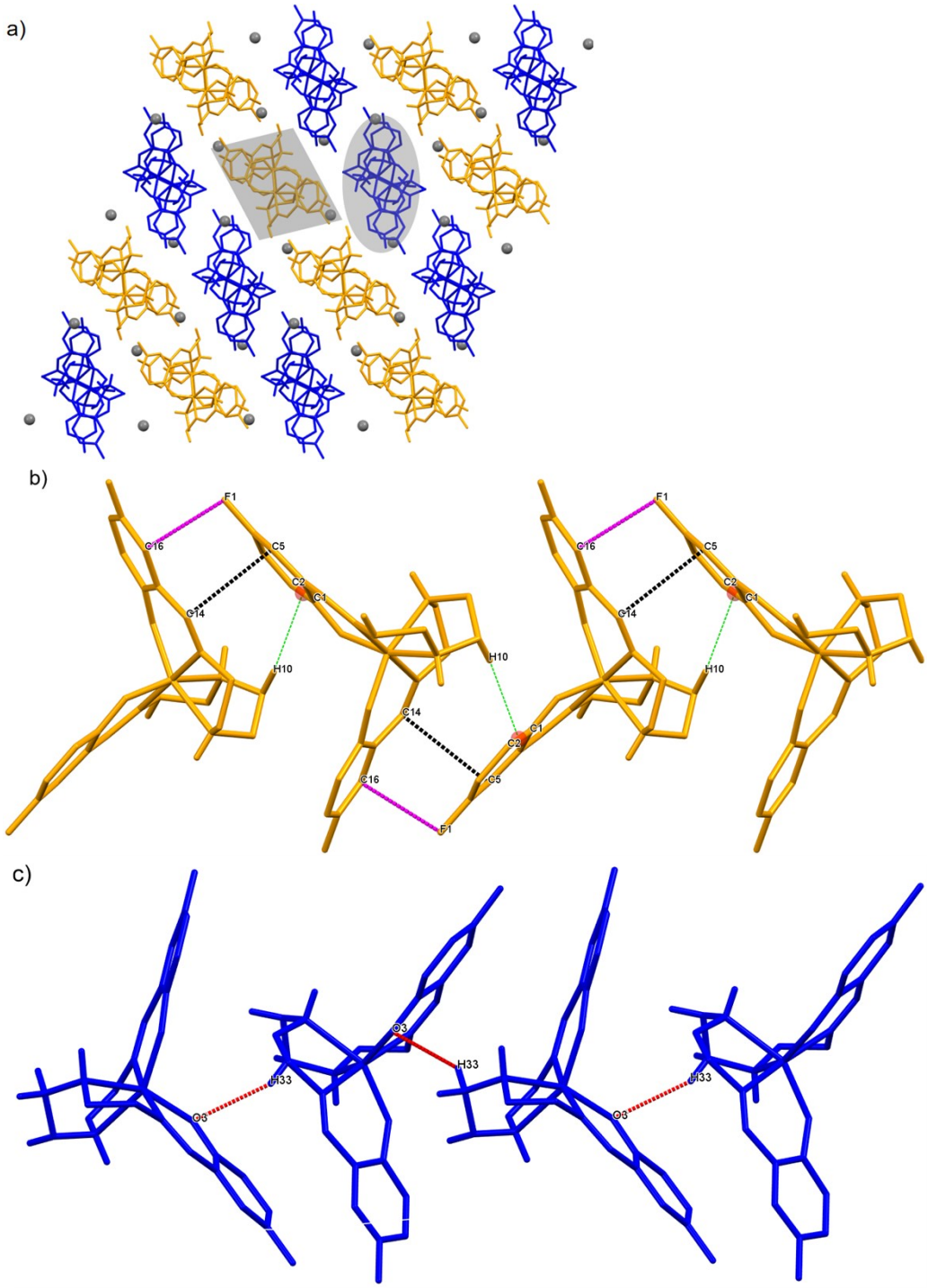


Figure S9. Crystal packing of complex **3** at 300 K, viewed along the *b* axis. The Fe1 and Fe2 units are shown in orange and blue, respectively. (b) The formation of 1D Fe1 chain (rhombus background) by means of C···C short contacts (black dotted line) , p-π (magenta dotted line) and C–H···π (green dotted line) interactions. (c) The formation of 1D Fe2 chain (ellipse background) by means of C-H···O (red dotted line) interactions.

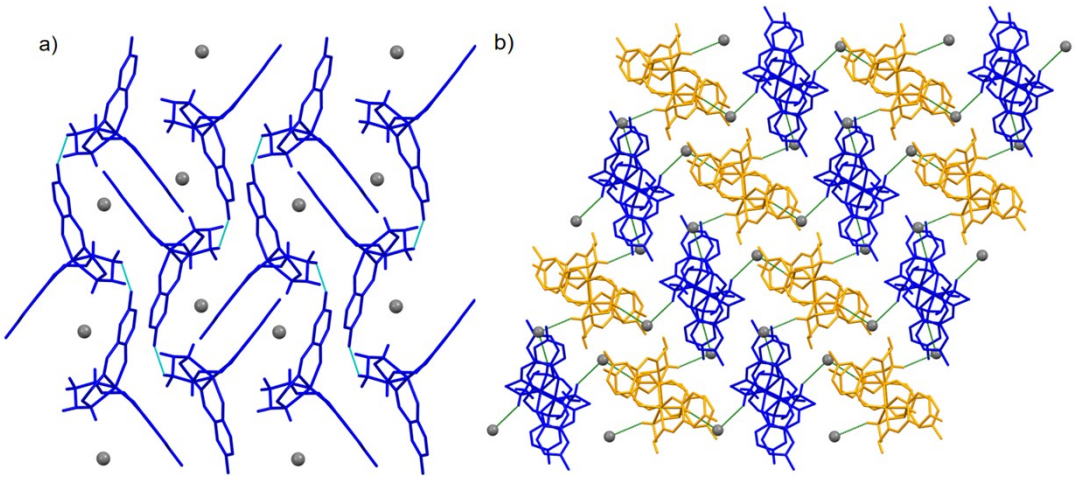
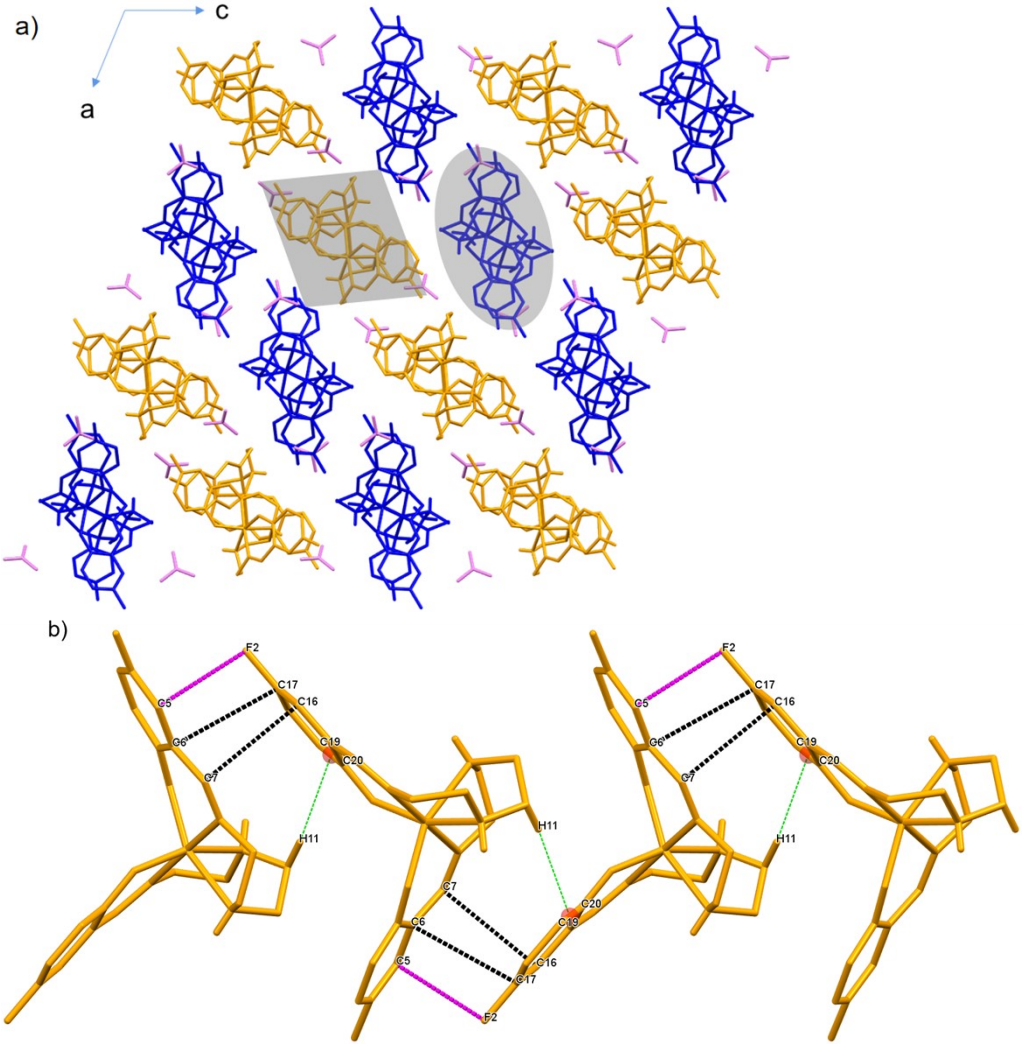


Figure S10. (a) C–H···F interactions (cyan dotted line) in **3** linking the chains into Fe2 plane. (b) N–H···I interactions (bottle green dotted line) linking the Fe1 and Fe2 centers in complex **3**. The Fe1 and Fe2 units are shown in orange and blue, respectively.



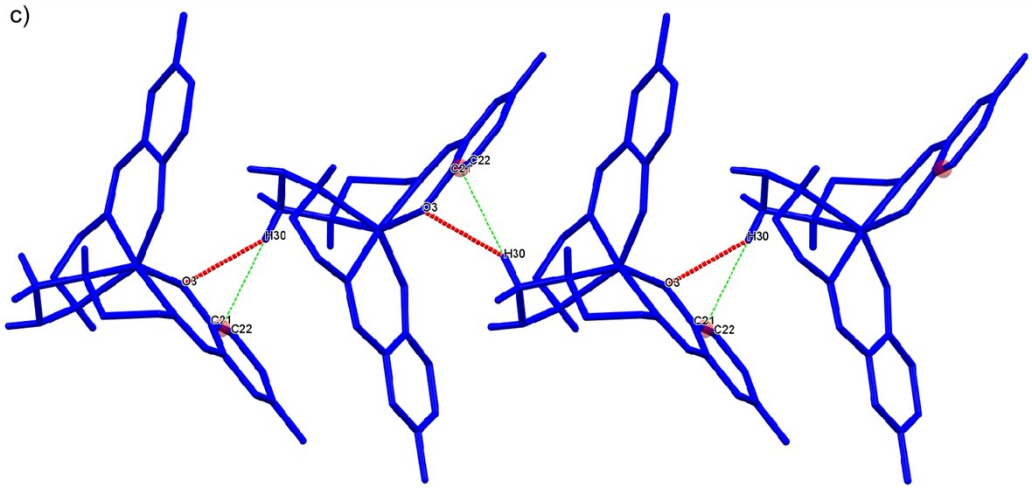


Figure S11. (a) Crystal packing of complex **4** at 300 K, viewed along the *b* axis. The Fe1 and Fe2 units are shown in orange and blue, respectively. (b)The formation of a supramolecular 1D chain (rhombus background) along the crystallographic *a* axis by means of C···C short contacts (black dotted line), p-π (magenta dotted line) and C–H···π (green dotted line) interactions. (c)The formation of a supramolecular 1D chain (ellipse background) along the crystallographic *c* axis by means of C-H···π (green dotted line) and C-H···O (red dotted line) interactions.

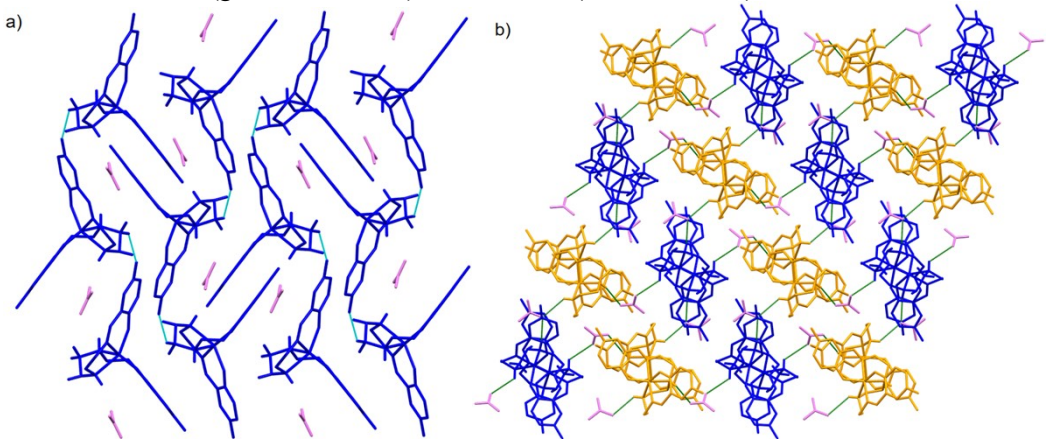
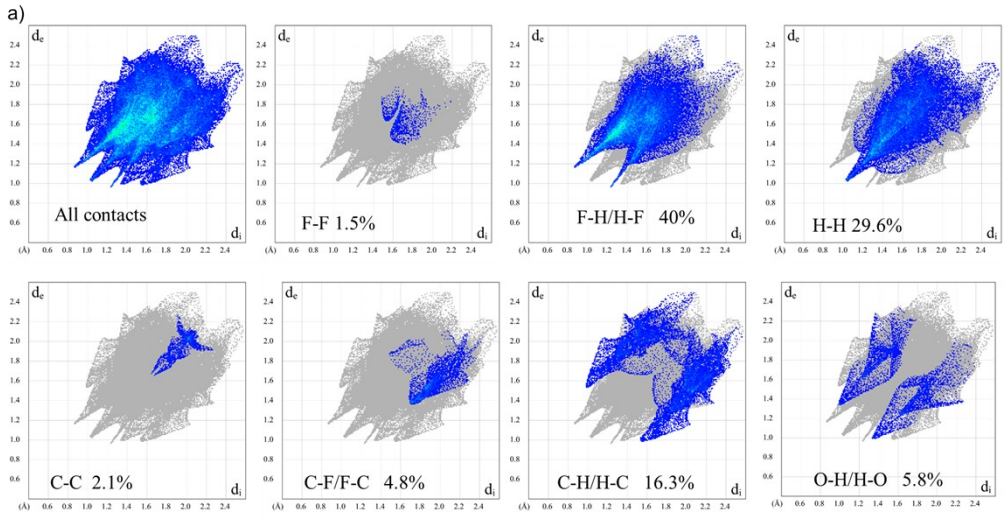
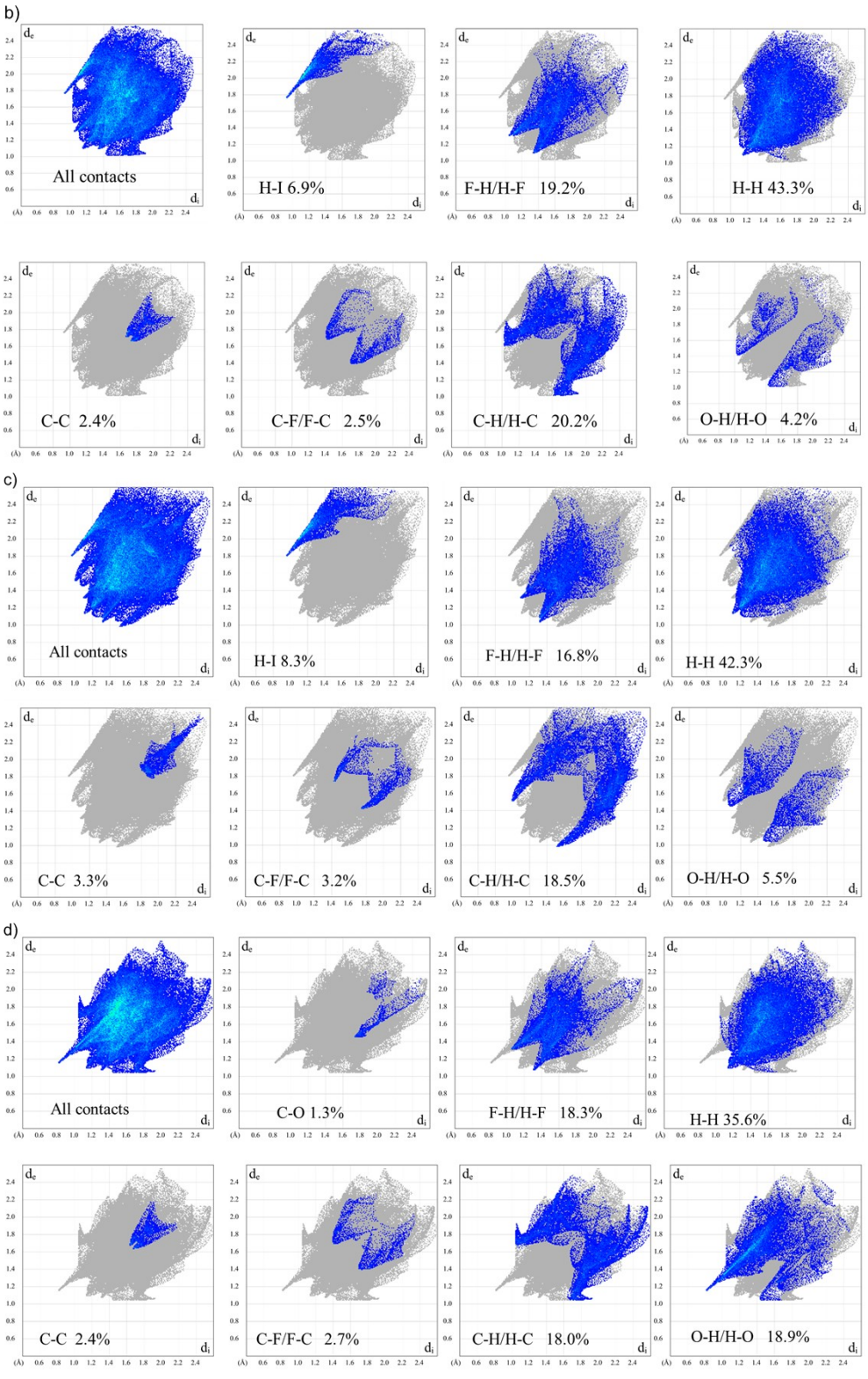


Figure S12. (a)C–H···F interactions (cyan dotted line) in **4** linking the chains into Fe2 plane. (b)N–H···O interactions (bottle green dotted line) linking the Fe1 and Fe2 centers in complex **4**. The Fe1 and Fe2 units are shown in orange and blue, respectively.




b)
All contacts
H-I 6.9%
F-H/H-F 19.2%
H-H 43.3%
C-C 2.4%
C-F/F-C 2.5%
C-H/H-C 20.2%
O-H/H-O 4.2%
c)
All contacts
H-I 8.3%
F-H/H-F 16.8%
H-H 42.3%
C-C 3.3%
C-F/F-C 3.2%
C-H/H-C 18.5%
O-H/H-O 5.5%
d)
All contacts
C-O 1.3%
F-H/H-F 18.3%
H-H 35.6%
C-C 2.4%
C-F/F-C 2.7%
C-H/H-C 18.0%
O-H/H-O 18.9%

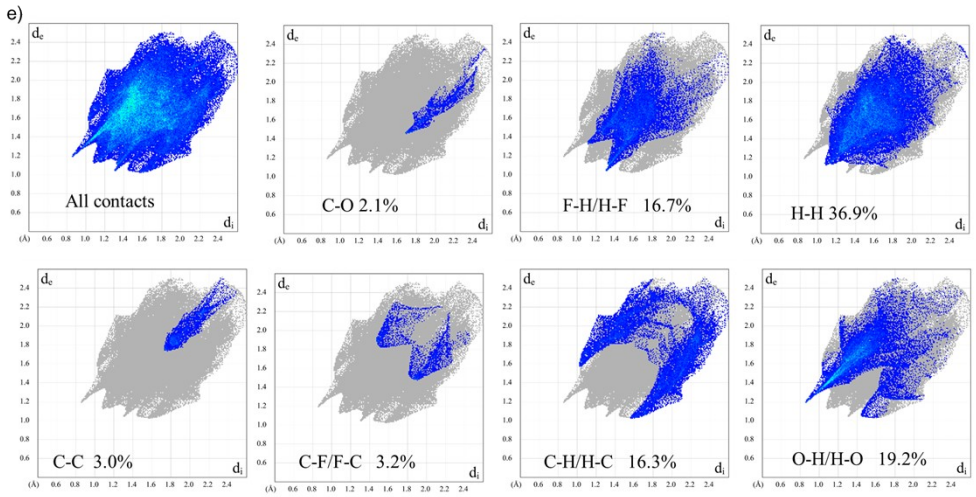


Figure S13. Hirshfeld surface 2D fingerprint plots: all contacts for (a) **1**, (b) Fe1 in **3**, (c) Fe2 in **3**, (d) Fe1 in **4**, (e) Fe2 in **4** at 100K.

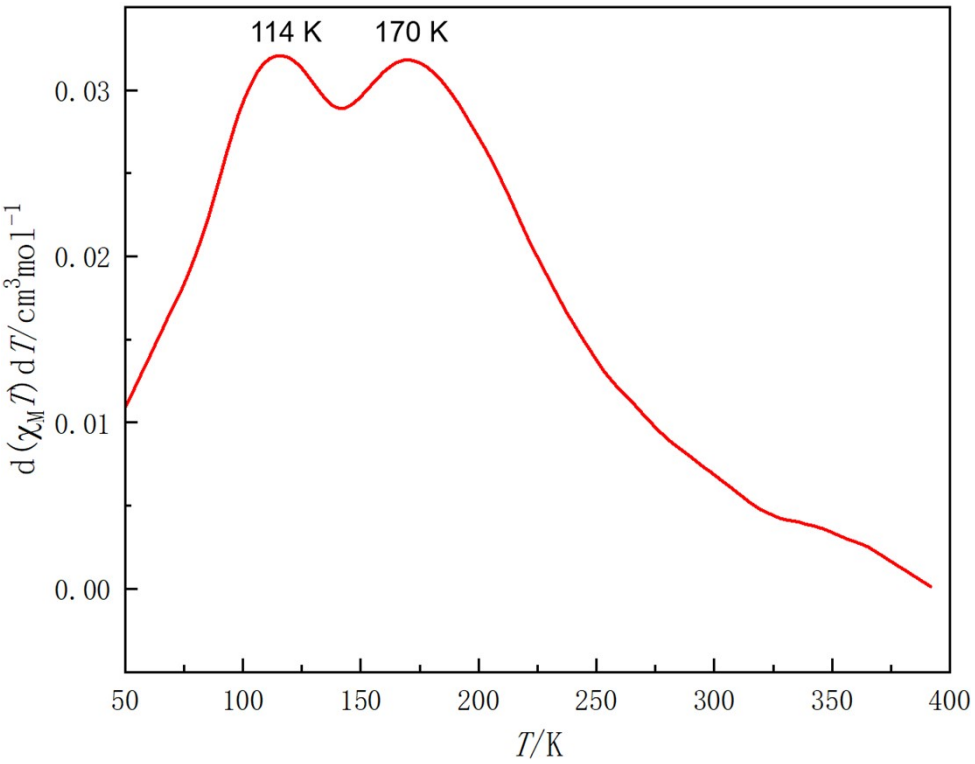


Figure S14. The first derivative of $\chi_M T$ in the 50−400 K range in **2**.

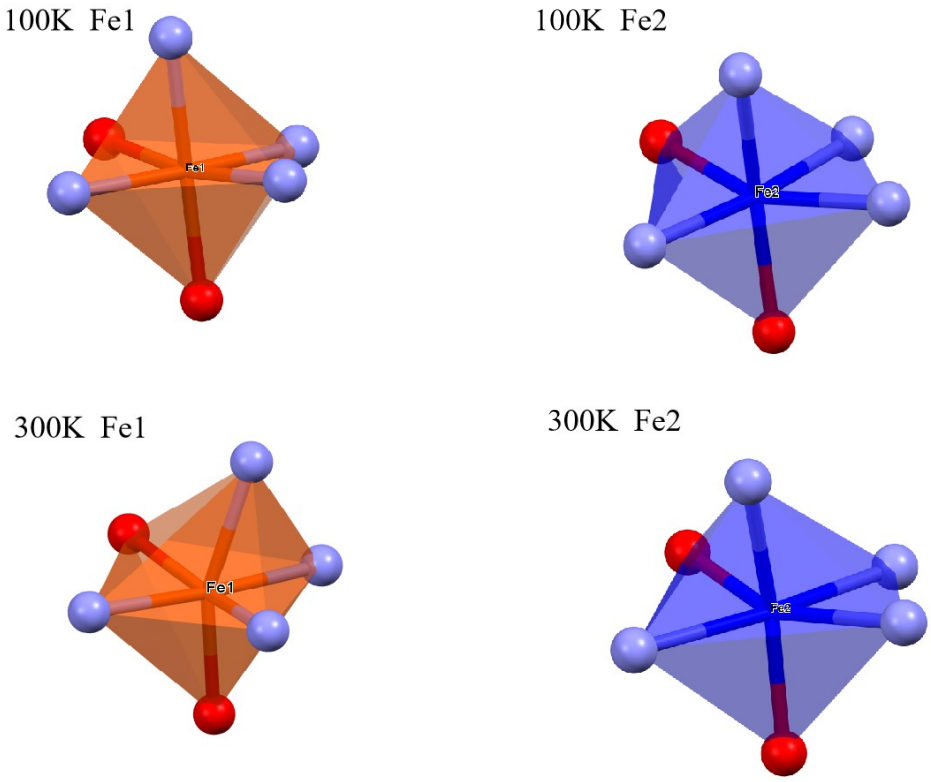


Figure S15. Geometries around Fe1 and Fe2 in **2**.