Supporting Information

Rotational order-disorder and spin crossover behaviour in a neutral iron(II) complex based on asymmetrically substituted large planar ionogenic ligand

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Table S1. Crystal data of **2F**.

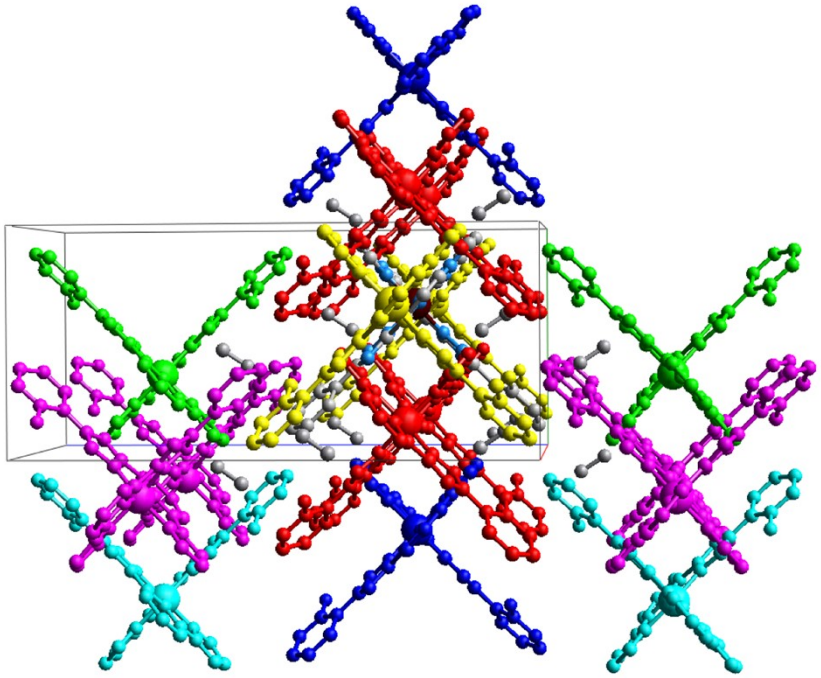
Temperature/K	**220(2)**	**293(2)**
Empirical formula	$C_{34}H_{28}F_2FeN_{12}O_2$	
Formula weight	730.53	
Crystal system	orthorhombic	
Space group	*Pbcn*	
Crystal size/mm^3	0.09 × 0.08 × 0.04	
a/Å	12.7752(8)	13.05(2)
b/Å	10.7048(7)	10.401(18)
c/Å	24.3576(16)	25.06(4)
V/Å^3	3331.0(4)	3402(10)
Z	4	4
ρ_{calc} g/cm^3	1.457	1.426
μ/mm^{-1}	0.517	0.506
F(000)	1504.0	1504.0
2Θ range for data collection/°	4.62 to 50.1	5.008 to 50.024
Index ranges	-15 ≤ h ≤ 15 -12 ≤ k ≤ 12 -26 ≤ l ≤ 29	-15 ≤ h ≤ 15 -12 ≤ k ≤ 12 -29 ≤ l ≤ 29
Reflections collected	22138	23664
Independent reflections	2946 [R_{int} = 0.1270, R_{sigma} = 0.0637]	3001 [R_{int} = 0.2049, R_{sigma} = 0.0917]
Data/restraints/parameters	2946/0/233	3001/0/243
Goodness-of-fit on F^2	1.105	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0703, wR_2 = 0.1626	R_1 = 0.0624, wR_2 = 0.1477
Final R indexes [all data]	R_1 = 0.1149, wR_2 = 0.1929	R_1 = 0.1520, wR_2 = 0.2283
Largest diff. peak/hole / e Å^{-3}	0.91/-0.56	0.59/-0.39

Table S2. Comparison of the cell parameters of indicated phases.

	a, Å	*b*, Å	*c*, Å
2F^{293K}	13.05(2)	10.40(2)	25.06(4)
2F^{des} *	13.40	8.63	26.73

*Evaluated by Expo2014 software[1].

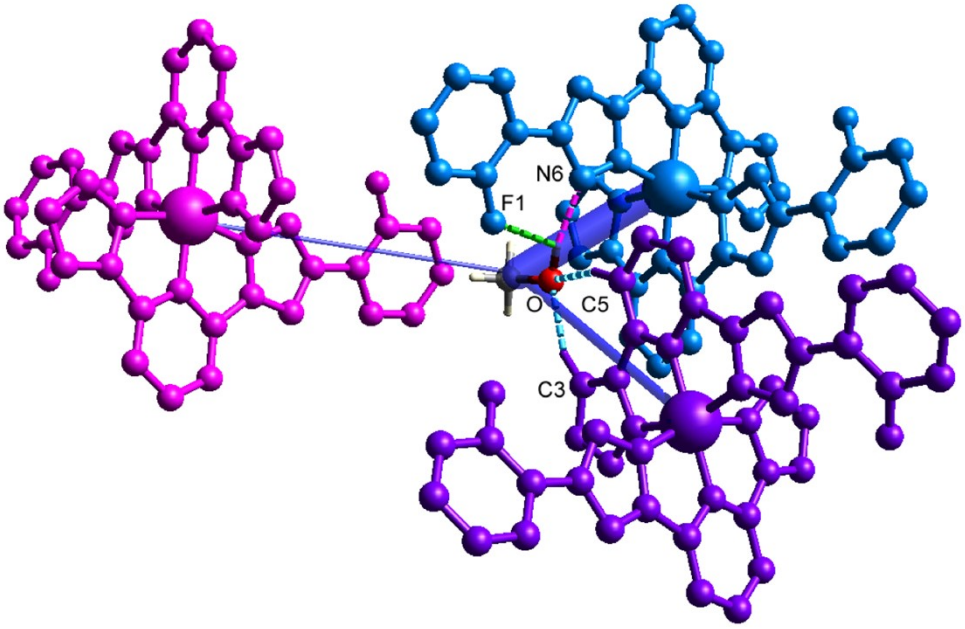
Table S3. Full colour-coded interaction mappings of a central reference molecule with nearest neighbors of **2F** and the contributions to the total energy in both spin states as calculated by DTF-B3LYP/6-31G(d,p) method.



	Symmetry operation	**R, Å**	**F-atom orientation**	**Energy, kJ mol^{-1}**					
				Electrostatic	Polarization	Dispersion	Exchange- repulsion	E(Total)	**ΔE("away"– "towards")**
	x+1/2, y+1/2, -z+1/2	8.34	"towards" "away"	-34.7 -35.7	-18.0 -18.7	-80.1 -84.7	56.6 62.8	-84.8 -86.5	-1.7
	x, y, z	13.05	"towards" "away"	7.1 7.4	-1.9 -1.9	-10.6 -10.6	7.6 7.6	1.6 1.8	0.2
	x, y, z	10.40	"towards" "away"	-22.	-5.2 -5.6	-29.	20.7	-40.	-1.3

				5 - 24. 2		1 - 28. 6	21. 5	1 - 41. 4	
	-x, -y, -z	12.5 4	“towards” “away”	-2.1 -5.0	-2.5 -2.4	- 19. 4 - 19. 0	7.6 7.7	- 16. 3 - 18. 8	-2.5
	-x, -y, -z	16.5 5	“towards” “away”	-0.1 0.6	-0.6 -0.7	-7.9 -7.6	3.0 3.1	-5.6 -4.6	-1.0

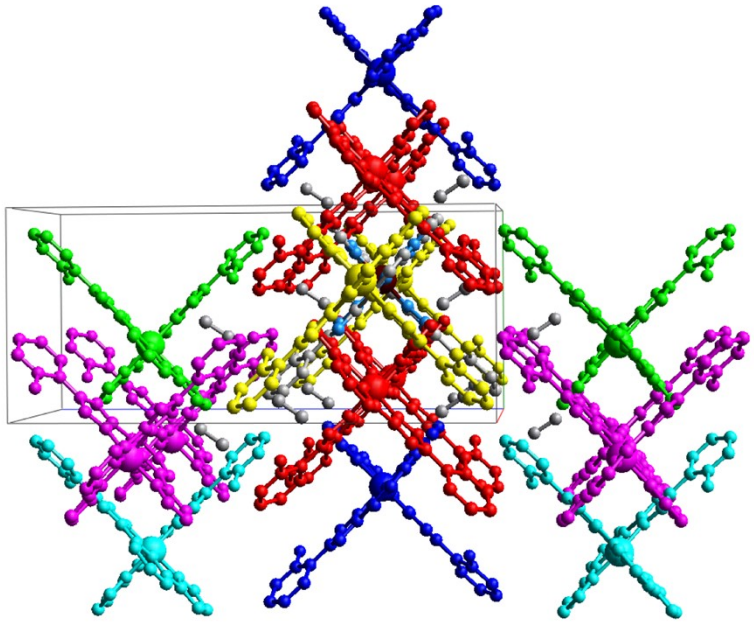
Table S4. Full colour-coded interaction mappings of a methanol molecule with nearest neighbour molecules of **2F** and the contributions to the total energy in both spin states and F-atom orientations calculated by DTF-B3LYP/6-31G(d,p) method. Cut-off is 5.0 kJ mol^{-1}.



Colour code	Symmetry operation of the contact complex molecule	Spin state, F-atom orientation	*R*, Å	Energy, kJ mol^{-1}					
				Electrostatic	Polarization	Dispersion	Exchange- repulsion	E(Total)	ΔE("away"–"towards")
	same	220K, LS	4.38	-59.8	-19.0	-31.4	72.3	-60.0	5.2
		293K, HS, "away"	4.30	-50.9	-16.2	-27.7	59.8	-53.0	
		293K, HS, "towards"	4.30	-54.8	-17.5	-30.2	63.0	-58.2	
	x+1/2, y+1/2, -z+1/2	220K, LS	8.08	-21.1	-5.7	-9.9	26.3	-18.8	0.0
		293K, HS, "away"	8.35	-5.3	-9.7	23.2	-18.7		
		293K, HS,		-	-5.3	-9.7	23.2	-18.7	

		“towards”	8.31	19.6 - 19.6					
	-x, -y, -z	220K, LS 293K, HS, “away” 293K, HS, “towards”	8.71 8.79 8.79	-3.4 -2.4 -2.4	-0.8 -0.9 -0.6	-10.2 -8.5 -8.8	7.0 4.7 4.6	-8.8 -7.6 -7.8	0.2

Table S5. The full colour-coded interaction mappings of a central reference molecule with nearest neighbors of **2F** and the contributions to the total energy in both spin states as calculated by DTF-B3LYP/6-31G(d,p) method. For the HS state phase calculation are for the fluorine atom oriented in the same way as in the LS state (toward the Fe^{II} ion).



Color code	Spin state	Symmetry operation	R, Å	ΔR(LS–HS), Å	Energy, kJ mol^{-1}					
					Electrostatic	Polarization	Dispersion	Exchange - repulsion	E(Total)	ΔE(Total) (LS–HS)
	LS HS	x+1/2, y+1/2, -z+1/2*	8.33 8.34	**-0.01**	-38.4 -34.7	-17.6 -18.0	-74.0 -80.1	58.8 56.6	-81.7 -84.8	**3.1**
	LS HS	-x, -y, -z	12.21 12.54	**-0.33**	-0.4 -2.1	-2.8 -2.5	-21.3 -19.4	9.5 7.6	-15.1 -16.3	**1.2**
	LS HS	x, y, z	12.78 13.05	**-0.27**	7.4 7.1	-1.5 -1.9	-8.8 -10.6	4.8 7.6	2.1 1.6	**0.5**
	LS HS	-x+1/2, -y+1/2, z+1/2	15.11 15.24	**-0.13**	0.5 0.6	-0.7 -0.7	-4.1 -3.5	0.1 0.0	-3.5 -2.8	**-0.7**
	LS HS	-x, -y, -z	16.82 16.63	**0.19**	-1.4 -0.1	-0.7 -0.6	-10.5 -7.9	7.3 3.0	-6.6 -5.6	**-1.0**

	LS HS	x, y, z*	10.70 0 10.40 0	**0.30**	-25.7 -22.5	-5.6 -5.2	-32.7 -29.1	24.9 20.7	-44.4 -40.1	**-4.3**

* interactions within the supramolecular layers of stacking molecules

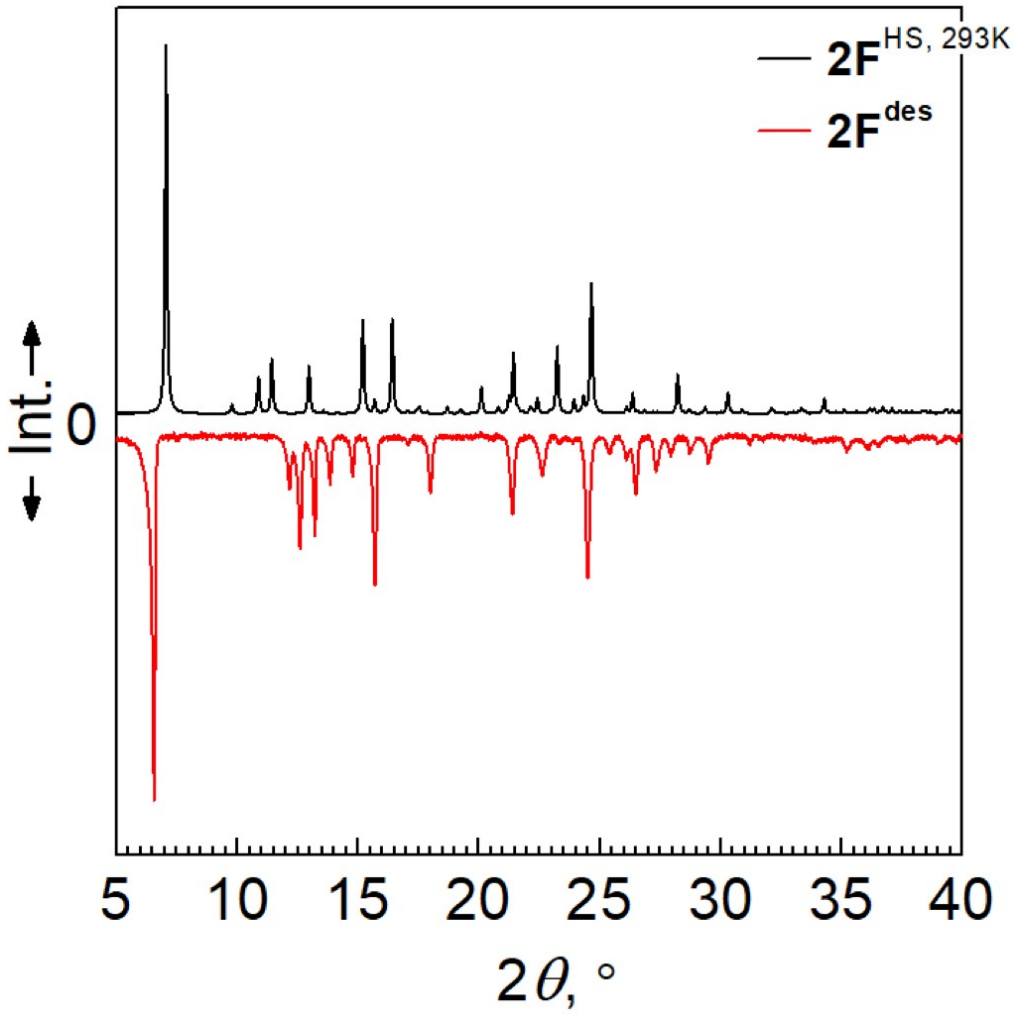


Figure S1. Comparison of calculated X-ray powder diffraction profile of **2F** at 293 K with the experimental one of **2F^{des}** recorded at room temperature.

REFERENCES

1 A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Crystallogr.* **2013**, *46*, 1231-1235.