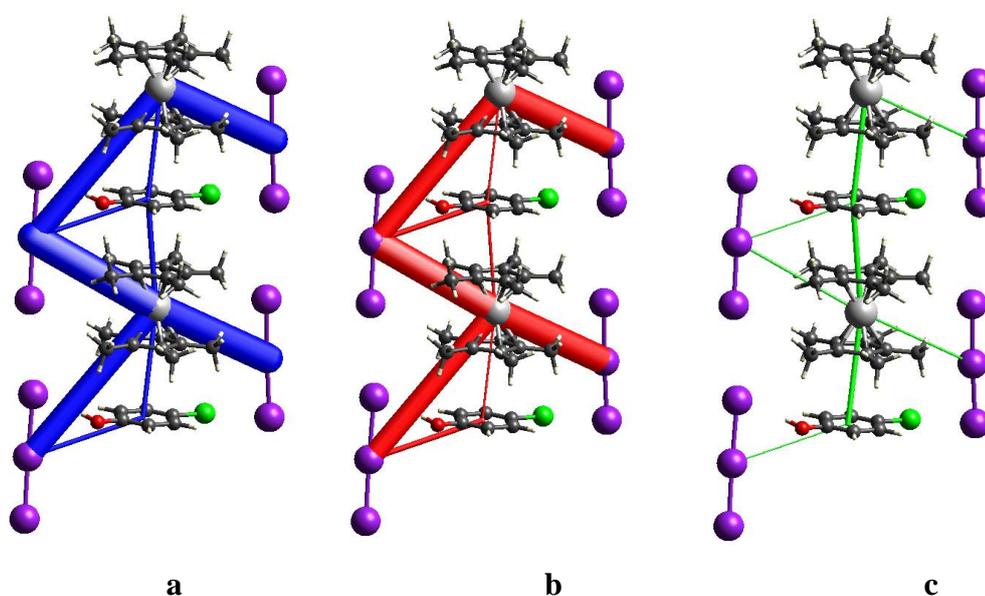


**Structure-defining interactions in the salt cocrystals of [(Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Fe]<sup>+</sup>I<sub>3</sub><sup>-</sup>-XC<sub>6</sub>H<sub>4</sub>OH (X= Cl , I): weak noncovalent vs. strong ionic bonding**

Yury V. Torubaev, Ivan V. Skabitsky and Konstantin A. Lyssenko

*CrystalExplorer energy frameworks.* Energies between molecular pairs are represented as cylinders joining the centroids of pairs of molecules, with the cylinder radius proportional to the magnitude of the interaction energy. Frameworks can be constructed for E<sub>ele</sub> (electrostatic, red cylinders), E<sub>dis</sub> (dispersion, green) and E<sub>tot</sub> (total, blue). The cylinders that make up the framework represent the relative strengths of molecular packing in different directions.<sup>S1</sup>



**Figure S1.** Energy frameworks in **1**. a) total energy , b) electrostatic c) dispersion.

Note that total energy is the sum of the four energy components, scaled using the scale factors below

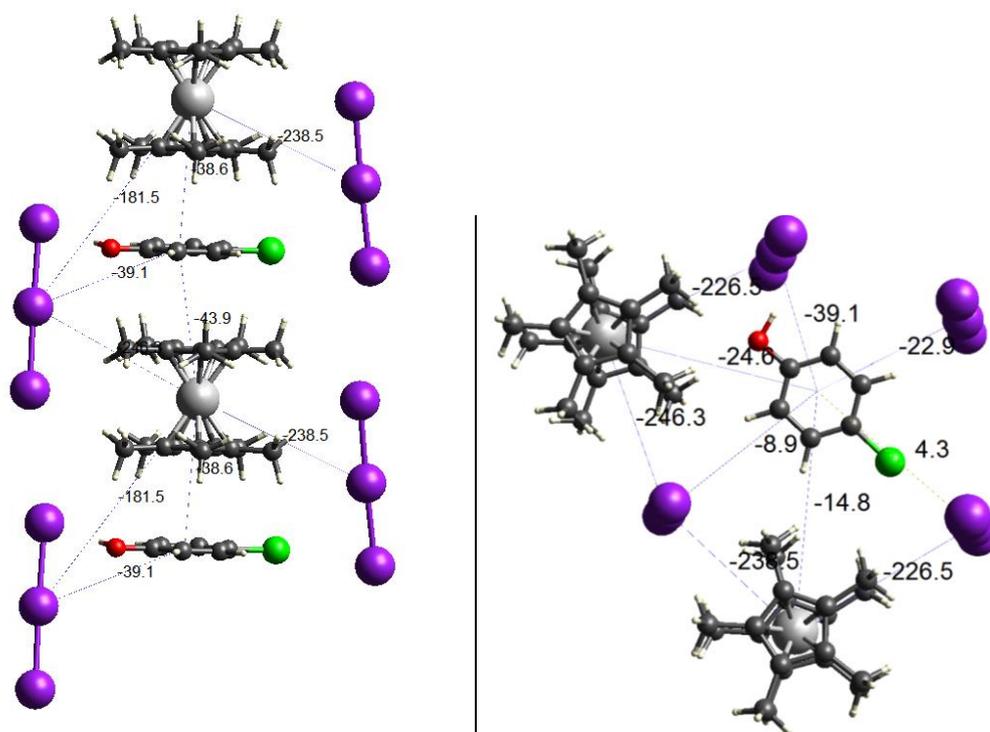
Scale factors for benchmarked energy models

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ...	1.057	0.740	0.871	0.618

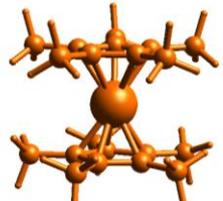
S1 a) [http://crystalexplorer.scb.uwa.edu.au/wiki/index.php/Energy\\_Frameworks](http://crystalexplorer.scb.uwa.edu.au/wiki/index.php/Energy_Frameworks) ;

b) M.J. Turner, S.P. Thomas, M.W. Shi, D. Jayatilaka, M.A. Spackman, *Chem. Commun.*, 2015, 51 ,3735-3738:

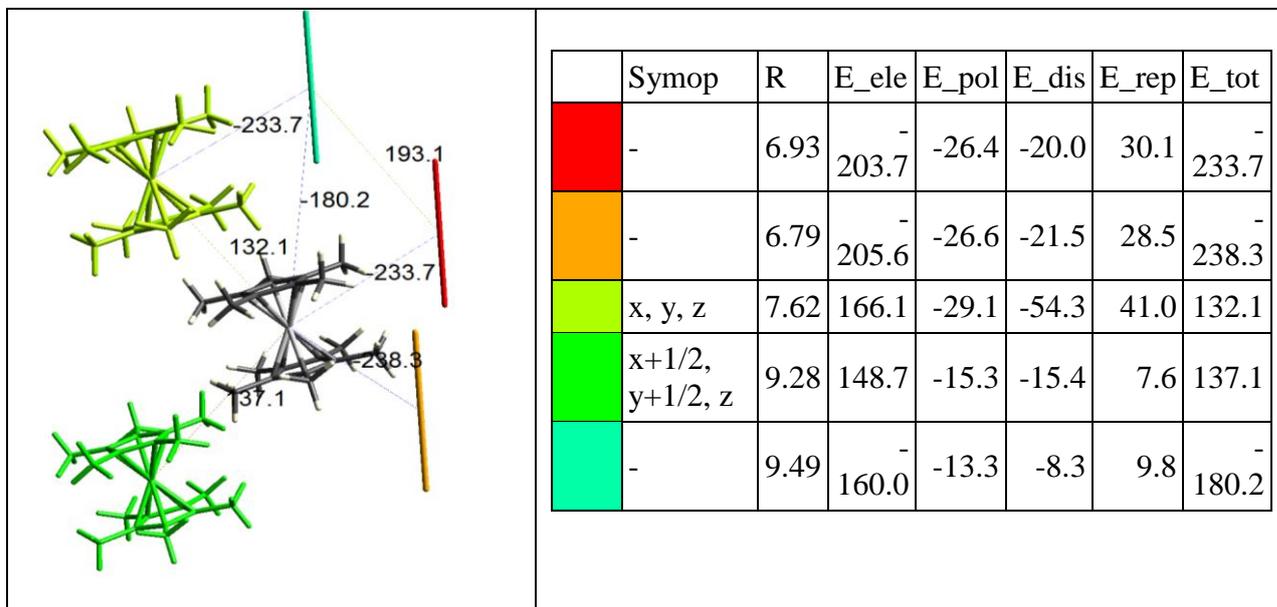
c) C.F. Mackenzie, P.R. Spackman, D. Jayatilaka, M.A. Spackman, *IUCrJ*, 2017, 4 ,575-587:.



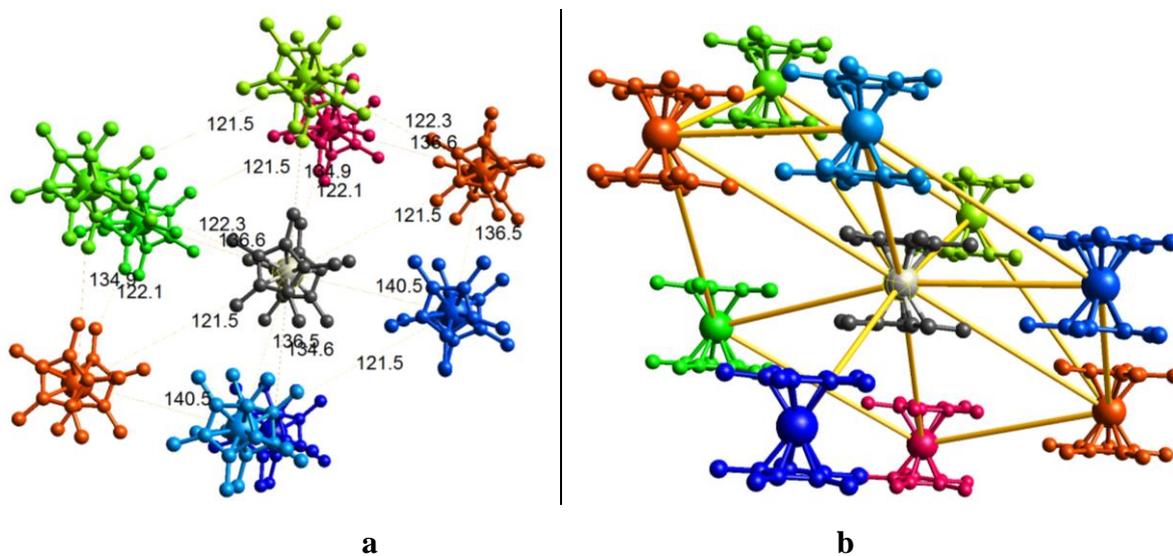
**Figure S2.** Intermolecular interaction energies (TONTTO\CE-B3PYP DGDZVP) in **1** (in kJ/mol).

	R	E_ele	E_pol	E_dis	E_rep	E_tot
	6.07	-18.4	-8.5	-9.7	37.3	-11.1
	5.71	-5.7	-8.8	-39.7	36.6	-24.5
	9.32	-20.4	-5.7	-4.7	6.7	-25.8
	5.77	-22.2	-8.9	-44.6	34.7	-47.5

**Figure S3.** Intermolecular interaction energies (TONTTO\CE-B3PYP DGDZVP) in **2** (in kJ/mol).

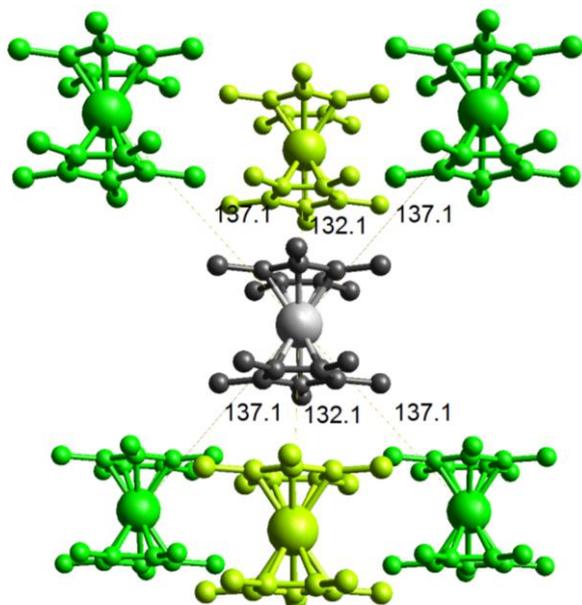


**Figure S4.** Intermolecular interaction energies (TONTO\CE-B3PYP DGDZVP) in [DMFc]I<sub>3</sub> (**3a**) in kJ/mol.



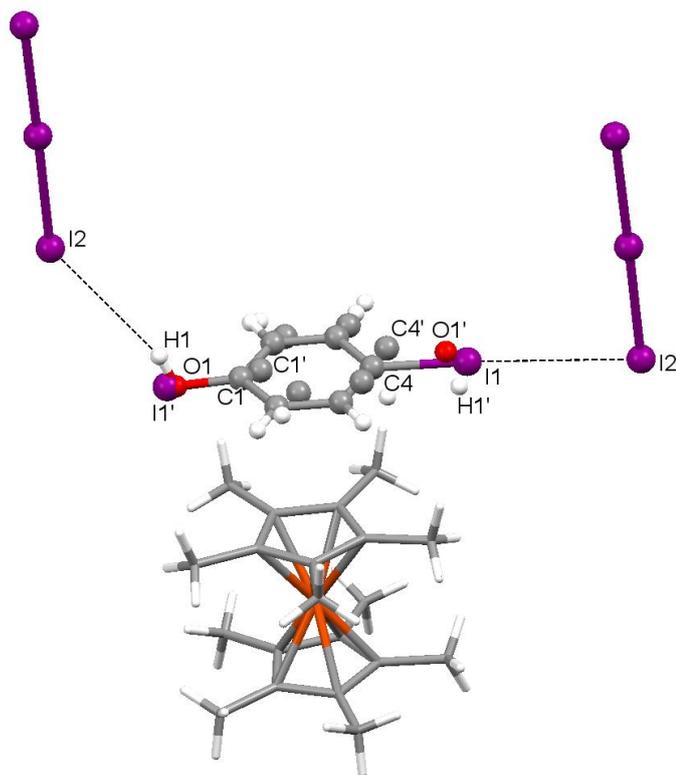
	N	Symop	R	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	11.54	120.4	-5.8	-1.8	0.0	121.5
	1	-x, -y, -z	9.68	142.1	-12.0	-9.9	3.5	134.9
	1	-x, -y, -z	11.46	121.6	-6.2	-2.1	0.0	122.3
	1	-x, -y, -z	9.48	145.2	-12.8	-9.8	2.0	136.6
	1	-x, -y, -z	9.38	147.4	-14.6	-14.3	6.4	136.5
	1	-x, -y, -z	8.40	161.2	-22.1	-24.7	12.8	140.5
	1	-x, -y, -z	9.81	141.9	-12.0	-8.8	1.8	134.6

**Figure S5.** Repulsive Intermolecular interaction (TONTO\CE-B3PYP DGDZVP) between [DMFc] cations in a 5 Å cluster of **2**. **a**) energy of intermolecular interaction (in kJ/mol) **b**) energy framework.



N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x, y, z	7.62	B3LYP/DGDZVP	166.1	-29.1	-54.3	41.0	132.1
4	x+1/2, y+1/2, z	9.28	B3LYP/DGDZVP	148.7	-15.3	-15.4	7.6	137.1

**Figure S6.** Repulsive Intermolecular interaction (TONTO\CE-B3PYP DGDZVP) between [DMFc] cations in a 5 Å cluster of **3a** (in kJ/mol).



**Figure S7.** OH / I disorder in **2**.

Occupancies: O1' (3.5%), I1 (96.5%), I1'(3.5%), O1(96.5%)