Electronic Supplementary Material (ESI) for CrystEngComm.

Probing distinct nanomechanical behaviour of a new co-crystal and a known solvate of 5-fluoroisatin and identification of a new polymorph

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Table S1: Crystallography and refinement details

DATA	Form-1	Form-2	FIDMSO	FIPICO
Moiety formula	$C_8H_4FNO_2$	$C_8H_4FNO_2$	$C_8H_4FNO_2$, C_2H_6OS	$C_8H_4FNO_2$, $C_6H_5NO_2$
CCDC	1880343	1880341	1880342	1880344
Solvent	Methanol, Ethyl acetate, Acetonitrile, 2-propanol, Acetone + hexane, DCM +Hexane, Chloroform	2-propanol	DMSO	Methanol, Ethyl acetate, Acetonitrile, 2-propanol, Acetone + hexane, DCM +Hexane
Formula weight	165.12	165.12	243.25	288.23
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group, Z	$P2_1/c$, 4	$P2_1/n$, 4	P-1, 2	$P2_1/n$, 4
a(Å)	3.7104(4)	4.8425(7)	8.2627(6)	12.8358(7)
b(Å)	12.1407(15)	24.450(4)	8.3350(6)	6.1720(3)
c(Å)	14.7660(15)	5.7818(9)	8.7473(6)	15.5627(8)
α(˚), β(˚), γ(˚)	90, 93.397(4), 90	90, 99.096(5), 90	91.177(2), 117.067(2), 97.410(3)	90,96.692(2), 90
Volume (Å^3), Density (g/cm^3)	663.99(13), 1.652	675.95(18), 1.623	529.82(7), 1.525	1224.52(11), 1.563
F(000), μ(mm^{-1})	336, 0.139	336, 0.136	252, 0.310	592, 0.127
Θ(min, max)	2.76, 29.563	3.93, 29.75	2.474, 29.125	2.636, 30.035
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	(-5, 4), (-16, 15), (-20, 20)	(-5, 5), (-29, 30), (-7, 7)	(-11, 11), (-11, 11), (-11, 10)	(-18, 17), (-8, 8), (-21, 21)
Treatment of Hydrogens	Fixed	Fixed	Fixed	Fixed

No. unique ref./ obs. Ref.	1851/1235	1314/906	2844/ 2572	3561/2767
No of parameters	109	119	147	193
R_all, R_obs	0.1060, 0.0599	0.1125, 0.0675	0.0386, 0.0342	0.0674, 0.0469
wR_2_all, wR_2_obs	0.1236, 0.1089	0.1328, 0.1210	0.0874, 0.0850	0.1164, 0.1072
$\Delta\rho_{min,\ max}(eÅ^{-3})$	-0.338, 0.355	-0.342, 0.285	-0.524, 0.436	-0.301, 0.343
G.o.F	1.058	1.125	1.084	1.064

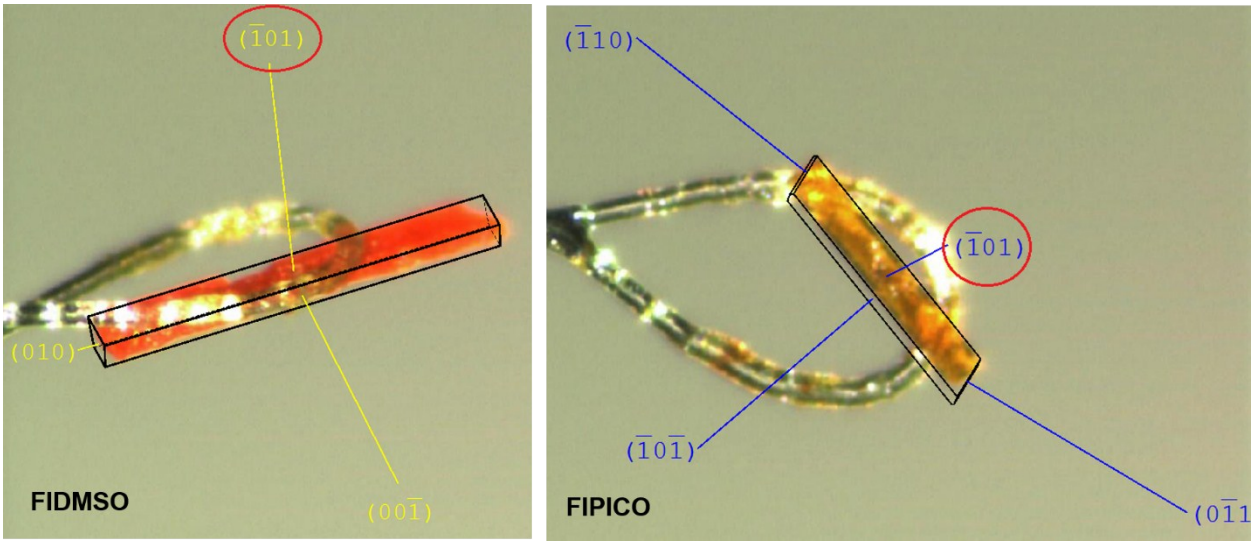

Figure S1. Experimental face indices by SCXRD for FIDMSO and FIPICO crystals. Major faces are circled in red.

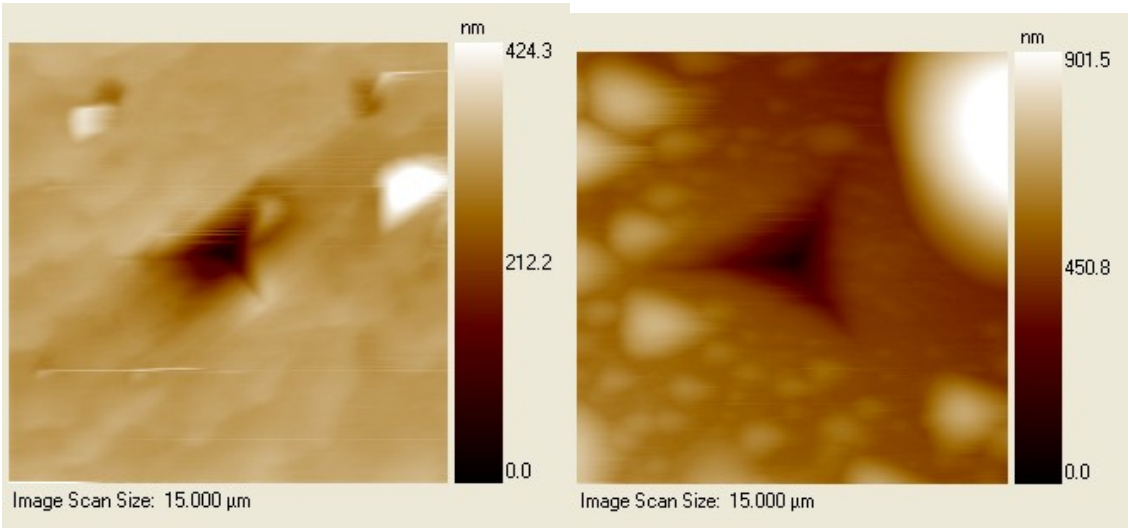

Figure S2.An AFM images of the residual indent of FIDMSO (left) andFIPICO (right)crystals.

Table S2: Intermolecular interactions and interaction energy (kJ/mol) obtain from PIXELC method**.**

Motifs	Symmetry code	Centroid-centroid distance (Å)	E_{coul}	E_{pol}	E_{disp}	E_{rep}	E_{tot}	Possible involved interactions	Geometry (Å/deg)
FIFORM-1									
I	-x+1,-y+1,-z+2	7.668	-84.3	-29.0	-19.2	68.7	-63.8	N1-H1···O1	1.89, 161
II	x-1,-y+1/2,z-1/2	8.142	-19.6	-5.6	-10.5	16.9	-18.8	C6-H6···O1	2.21, 162
III	-x+2,-y,-z+2	6.492	-8.9	-2.6	-8.2	5.9	-13.8	C8-H8···O2	2.57, 153
IV	-x+1,y-1/2,-z+1.5	7.715	-4.4	-1.8	-8.1	6.8	-7.5	C5-H5···F1	2.50, 108
V	x-1,y,z	3.710	0.2	-5.1	-37.1	35.0	-7.1	π(C2-C3-C8)··· π(C4-C5-C6-C7)	3.368
VI	-x,y-1/2,-z+1.5	8.547	-1.1	-1.1	-4.3	2.0	-4.5	C5-H5···F1	2.55, 151
FIFORM-2									
I	x-1/2,-y+1.5,z+1/2	7.125	-46.4	-21.8	-15.2	58.0	-25.3	N1-H1···O1	1.76, 165
II	x-1,y,z	4.843	-8.8	-5.8	-27.2	27.1	-14.8	π(C1*A*-C2*A*)··· π(C5-C6)	3.227
III	x+1,y,z-1	8.108	-9.9	-1.7	-4.2	3.2	-12.6	C5-H5···O2*A*	2.54, 154
IV	-x+2,-y+1,-z+1	9.086	-8.4	-1.9	-8.1	7.1	-11.4	C6-H6···F1	2.41, 172
V	-x+1,-y+1,-z+2	7.496	-5.4	-1.4	-8.5	5.9	-9.5	C8-H8···F1	2.45, 165
VI	x-1/2,-y+1.5,z-1/2	6.807	3.3	-3.3	-8.1	6.7	-1.4	C2*A*···O1	3.011(1)
FIDMSO									
I	-x+2,-y+1,-z+1	5.784	-62.8	-24.1	-16.6	50.7	-52.8	N1-H1···O3	1.82, 164
II	x,y,z	3.860	-15.2	-8.4	-22.9	21.0	-25.6	O3···π(C1-C2)	3.014

III	x,y,z-1	6.936	-11.5	-3.0	-7.3	7.0	-14.8	C9-H9*B*···O1 C10-H10*B*···O1	2.43, 153 2.58, 147
IV	-x+1,-y,-z	6.303	-4.7	-1.6	-7.5	6.2	-7.5	C10-H10*A*···O2	2.62, 114
V	x,y+1,z	6.302	-1.5	-1.4	-6.4	2.9	-6.4	C9-H9*C*···F1	2.62, 164
VI	-x+1,-y+1,-z	4.012	-32.0	-8.9	-19.3	14.1	-46.1	C10-H10*C*···O3	2.54, 161
VII	-x+2,-y,-z+1	3.528	-8.7	-3.9	-36.1	27.9	-20.8	π (Cg)··· π (Cg)	3.474
VIII	x-1,y,z	8.263	-13.7	-3.8	-9.4	10.2	-16.7	C6-H6···O2	2.37, 147
IX	-x+2,-y,-z	7.460	-2.9	-0.7	-9.0	5.4	-7.2	F1···C7	3.154(1)
FIPICO									
I	x,y-1,z	6.686	-65.1	-25.0	-16.9	52.6	-54.3	N1-H1···O3 C5-H5···O3	1.91, 138 2.34, 125
II	-x+1.5,y-1/2,-z+1/2	6.626	-20.2	-5.5	-8.3	10.2	-23.7	C14-H14···O1	2.26, 161
III	x-1/2,-y+1/2,z-1/2	7.943	-17.8	-4.0	-6.3	9.6	-18.5	C12-H12···O2	2.28, 173
IV	x-1/2,-y-1/2,z-1/2	8.837	-16.3	-3.6	-5.6	8.0	-17.6	C13-H13···O1	2.30, 162
V	x,y,z	3.487	3.9	-15.0	-34.5	35.5	-10.1	C1···O4	2.948(1)
VI	-x+1/2,y+1/2,-z+1/2	8.228	-3.7	-1.9	-7.2	8.2	-4.6	F1···π(C12-C13)	2.888
VII	-x+1,-y,-z+1	3.488	-6.9	-4.4	-33.4	25.7	-19.0	C3···C3	3.375(1)
VIII	-x+1,-y+1,-z+1	6.388	-5.6	-2.8	-9.8	5.9	-12.3	C8-H8···O2	2.62, 146
IX	-x+1/2,y-1/2,-z+1/2	8.469	-0.1	-1.1	-7.1	3.8	-4.4	C6-H6···F1	2.52, 124
X	-x+1.5,y-1/2,-z+1/2	6.006	-57.5	-35.9	-16.5	63.2	-46.7	N2-H2···O4	1.72, 153

Table S3: Intermolecular interactions and interaction energy (kJ/mol) obtain from energy frameworks analysis.

Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the
four energy components, scaled appropriately (see the scale factor table below)

FIDMSO:

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	-	3.86	B3LYP/6-31G(d,p)	-13.6	-6.0	-22.6	20.0	-26.1
	1	-	5.78	B3LYP/6-31G(d,p)	-59.3	-14.5	-8.7	51.7	-49.1
	2	x, y, z	8.26	B3LYP/6-31G(d,p)	-14.2	-3.3	-8.6	11.4	-18.0
	1	-x, -y, -z	6.96	B3LYP/6-31G(d,p)	-6.2	-1.2	-4.4	1.1	-10.6
	1	-x, -y, -z	7.46	B3LYP/6-31G(d,p)	-2.9	-0.2	-11.7	6.0	-9.6
	1	-	6.30	B3LYP/6-31G(d,p)	-2.2	-0.8	-6.3	3.1	-6.5
	1	-x, -y, -z	3.53	B3LYP/6-31G(d,p)	-7.1	-1.8	-47.5	27.8	-33.0
	1	-	6.30	B3LYP/6-31G(d,p)	-5.1	-1.6	-7.8	7.3	-8.8
	1	-	3.86	B3LYP/6-31G(d,p)	-13.6	-6.0	-22.6	20.0	-26.1
	1	-x, -y, -z	6.02	B3LYP/6-31G(d,p)	-6.8	-4.5	-19.5	12.6	-19.7
	1	-	6.94	B3LYP/6-31G(d,p)	-13.4	-3.1	-7.3	10.8	-16.1
	1	-	6.29	B3LYP/6-31G(d,p)	-5.3	-1.6	-6.8	3.9	-10.3
	1	-	7.37	B3LYP/6-31G(d,p)	-0.2	-0.4	-5.5	2.9	-3.4
	1	-x, -y, -z	9.51	B3LYP/6-31G(d,p)	0.5	-0.3	-1.9	0.1	-1.4
	1	-	6.58	B3LYP/6-31G(d,p)	5.0	-1.5	-9.0	8.0	1.3
	1	-	6.03	B3LYP/6-31G(d,p)	2.1	-0.7	-10.0	8.3	-1.9
	0	-x, -y, -z	4.01	B3LYP/6-31G(d,p)	-28.7	-7.9	-15.7	18.6	-38.3
	0	-	6.30	B3LYP/6-31G(d,p)	-5.1	-1.6	-7.8	7.3	-8.8
	0	-	7.37	B3LYP/6-31G(d,p)	-0.2	-0.4	-5.5	2.9	-3.4
	0	-x, -y, -z	7.80	B3LYP/6-31G(d,p)	-1.2	-0.1	-0.8	0.0	-2.1
	0	-	6.94	B3LYP/6-31G(d,p)	-13.4	-3.1	-7.3	10.8	-16.1
	0	-	6.29	B3LYP/6-31G(d,p)	-5.3	-1.6	-6.8	3.9	-10.3
	0	-	6.58	B3LYP/6-31G(d,p)	5.0	-1.5	-9.0	8.0	1.3
	0	-	6.03	B3LYP/6-31G(d,p)	2.1	-0.7	-10.0	8.3	-1.9

	0	-	5.78	B3LYP/6-31G(d,p)	-59.3	-14.5	-8.7	51.7	-49.1
	0	-	6.30	B3LYP/6-31G(d,p)	-2.2	-0.8	-6.3	3.1	-6.5
	0	-x, -y, -z	4.48	B3LYP/6-31G(d,p)	-8.6	-0.8	-8.4	9.5	-11.1

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

FIPICO:

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	3.49	B3LYP/6-31G(d,p)	8.1	-13.0	-41.7	33.6	-16.6
	1	-x, -y, -z	3.49	B3LYP/6-31G(d,p)	-5.9	-2.4	-44.6	26.6	-30.5
	1	x, y, z	6.17	B3LYP/6-31G(d,p)	3.3	-1.7	-9.9	2.6	-4.8
	1	-x+1/2, y+1/2, -z+1/2	8.47	B3LYP/6-31G(d,p)	0.6	-0.8	-7.6	4.3	-3.9
	0	-	6.69	B3LYP/6-31G(d,p)	-61.0	-20.3	-11.2	53.2	-56.4
	0	-	6.19	B3LYP/6-31G(d,p)	-10.6	-7.2	-12.6	7.6	-22.8
	0	-	7.88	B3LYP/6-31G(d,p)	3.9	-1.3	-4.6	0.8	-0.4
	0	-	8.84	B3LYP/6-31G(d,p)	-16.1	-3.0	-4.6	9.0	-17.6
	1	-x, -y, -z	6.39	B3LYP/6-31G(d,p)	-6.5	-2.5	-9.8	7.4	-12.7
	1	-	6.63	B3LYP/6-31G(d,p)	-21.1	-4.8	-7.6	11.4	-25.4
	1	-	8.23	B3LYP/6-31G(d,p)	-2.7	-1.1	-8.2	8.6	-5.5
	1	-	7.94	B3LYP/6-31G(d,p)	-18.3	-3.4	-5.4	10.6	-20.0
	0	-	8.84	B3LYP/6-31G(d,p)	-16.1	-3.0	-4.6	9.0	-17.6
	0	-x, -y, -z	5.81	B3LYP/6-31G(d,p)	5.0	-4.5	-21.9	20.5	-4.4
	0	-x, -y, -z	9.61	B3LYP/6-31G(d,p)	15.2	-1.5	-1.7	0.1	13.5
	0	-	8.23	B3LYP/6-31G(d,p)	-2.7	-1.1	-8.2	8.6	-5.5
	0	-	3.49	B3LYP/6-31G(d,p)	8.1	-13.0	-41.7	33.6	-16.6
	0	-	6.63	B3LYP/6-31G(d,p)	-21.1	-4.8	-7.6	11.4	-25.4
	0	x, y, z	6.17	B3LYP/6-31G(d,p)	-8.3	-8.8	-11.6	10.5	-18.9
	0	-x+1/2, y+1/2, -z+1/2	6.01	B3LYP/6-31G(d,p)	-53.7	-25.3	-11.2	62.1	-47.0

	0	-	7.94	B3LYP/6-31G(d,p)	-18.3	-3.4	-5.4	10.6	-20.0
	0	-	7.88	B3LYP/6-31G(d,p)	3.9	-1.3	-4.6	0.8	-0.4
	0	-	6.19	B3LYP/6-31G(d,p)	-10.6	-7.2	-12.6	7.6	-22.8
	0	-	6.69	B3LYP/6-31G(d,p)	-61.0	-20.3	-11.2	53.2	-56.4

Form-1:

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	3.71	B3LYP/6-31G(d,p)	3.5	-2.8	-47.0	34.2	-18.2
	2	-x, y+1/2, -z+1/2	8.55	B3LYP/6-31G(d,p)	-0.7	-1.0	-4.8	2.7	-4.0
	1	-x, -y, -z	8.69	B3LYP/6-31G(d,p)	-5.8	-0.6	-1.6	0.0	-8.0
	2	x, -y+1/2, z+1/2	8.14	B3LYP/6-31G(d,p)	-19.9	-4.3	-8.7	17.9	-20.7
	1	-x, -y, -z	5.60	B3LYP/6-31G(d,p)	1.1	-1.5	-14.6	5.7	-9.1
	2	-x, y+1/2, -z+1/2	7.72	B3LYP/6-31G(d,p)	-3.8	-1.2	-9.4	7.4	-8.5
	1	-x, -y, -z	7.67	B3LYP/6-31G(d,p)	-83.8	-17.1	-12.8	74.5	-66.4
	2	x, -y+1/2, z+1/2	7.47	B3LYP/6-31G(d,p)	-0.0	-1.7	-7.0	2.3	-6.0
	1	-x, -y, -z	6.49	B3LYP/6-31G(d,p)	-9.8	-2.3	-8.4	7.2	-14.9
	1	-x, -y, -z	8.34	B3LYP/6-31G(d,p)	-11.2	-1.2	-3.5	0.2	-15.6

Form-2:

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x+1/2, -y+1/2, z+1/2	6.81	B3LYP/6-31G(d,p)	5.2	-3.2	-10.1	7.2	-1.2
	2	x, y, z	5.78	B3LYP/6-31G(d,p)	0.0	-2.4	-15.3	8.3	-9.9
	2	x, y, z	4.84	B3LYP/6-31G(d,p)	-7.2	-3.1	-33.8	26.2	-23.2
	2	x+1/2, -y+1/2, z+1/2	7.12	B3LYP/6-31G(d,p)	-44.7	-10.9	-11.2	60.5	-27.7
	2	x+1/2, -y+1/2, z+1/2	10.10	B3LYP/6-31G(d,p)	-4.1	-0.3	-0.5	0.0	-5.1
	2	x, y, z	8.11	B3LYP/6-31G(d,p)	-10.4	-1.6	-4.1	3.6	-13.5
	1	-x, -y, -z	6.76	B3LYP/6-31G(d,p)	-1.4	-0.4	-15.2	5.9	-11.3
	1	-x, -y, -z	7.50	B3LYP/6-31G(d,p)	-5.1	-0.5	-9.0	7.6	-8.9

	1	-x, -y, -z	9.09	B3LYP/6-31G(d,p)	-7.6	-0.9	-8.2	8.9	-10.3
	1	-x, -y, -z	9.18	B3LYP/6-31G(d,p)	-0.2	-0.1	-3.0	0.2	-2.7

	1	-	8.23	B3LYP/6-31G(d,p)	2.0	-21.9	-8.2	12.0	-13.9
	1	-	7.94	B3LYP/6-31G(d,p)	9.6	-21.5	-5.4	15.2	-1.0

Table S4: Lattice Energy obtained from the PIXELC method

Form	E_{coul}(kJ/mol)	E_{pol}(kJ/mol)	E_{disp}(kJ/mol)	E_{rep}(kJ/mol)	E_{tot}(kJ/mol)
FIDMSO	-66.6	-25.4	-79.0	79.1	-91.8
FIPICO	-122.7	-48.6	-89.1	117.6	-142.8
Form 1	-77.3	-27.4	-91.6	102.4	-94.0
Form 2	-76.4	-31.5	-87.7	111.7	-84.0

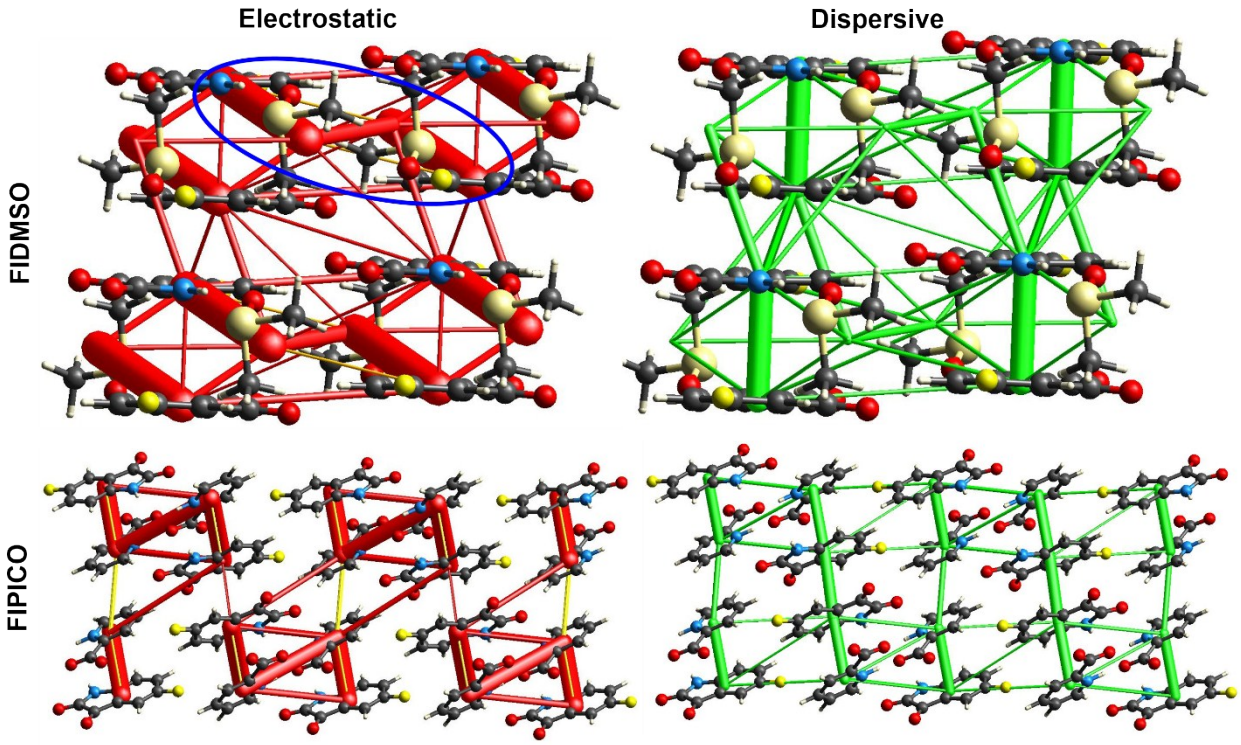

Figure S3. Decomposed electrostatic (red) and dispersive (green) energy frameworks of FIDMSO (above) and FIPICO (below), respectively. Note that in FIDMSO, the extented major electrostatic components (blue circle) is pointing along the direction of indention.