Electronic Supporting File

Quantitative Investigation of Weak Intermolecular Interactions of –F and –CF_3 Substituted *In Situ* Cryocrystallized Benzaldehydes

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List of Content:

A- ***2-fluorobenzaldehyde;***
B- ***2-(trifluoromethyl)benzaldehyde;***
C- ***4-(trifluoromethyl)benzaldehyde;***
D- ***2-fluoro-3-(trifluoromethyl)benzaldehyde;***
E- ***2-fluoro-4-(trifluoromethyl)benzaldehyde;***
F- ***4-fluoro-2-(trifluoromethyl)benzaldehyde;***
G- ***3-fluoro-5-(trifluoromethyl)benzaldehyde.***

S.1. Crystallization procedure and details of diffraction experiments

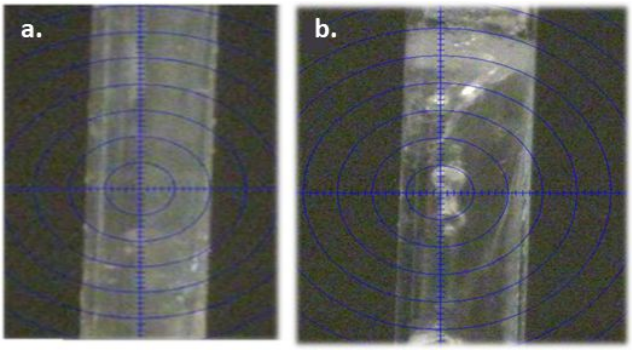

Fig. S1. Crystallization of a) **F** at -7°C and b)**C** at -9°C in a Lindemann capillary.

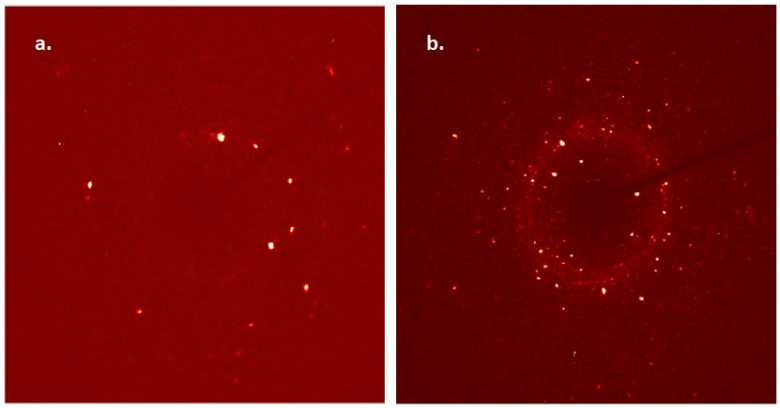

Fig. S2. Still image of a diffraction experiment for crystals obtained *via insitu*cryocrystallized liquids of **F** and **C.**

Table S1. Intra- and Intermolecular Interactions along with Interaction Energies (I.E) obtained from Energy Frameworks (*CrystalExplorer17.5.*)[a].

Motif	Interactions involved	Symmetry code	R^b	E_{ele}	E_{pol}	E_{disp}	E_{rep}	E_{tot}	Geometric parameters
				A					
I	C13…C13(Rg2 -Rg2)	-x, -y+1, -z+1	3.76	-6.7	-0.8	-27.3	12.8	-21.9	3.3881(2)Å
II	C17…C2 (Rg3-Rg1)	x-1, y, z	3.59	-5.2	-0.6	-28.7	12.8	-21.7	3.4221(1) Å
III	C6…C15,	x, y, z	4.15	-4.0	-0.2	-21.8	8.4	-17.6	3.4346(1)Å;

	O3…C7 (Rg1-Rg3)								3.3959(1) Å, 95°
IV	C6-H6…π, O1…C14	x, y, z	5.05	-5.9	-1.7	-13.9	7.4	-14.1	3.0718(1) Å, 152°; 2.9307(1) Å, 134°
V	C3-H3…O3 C21-H21…F1	-x, -y, -z+1	6.81	-8.5	-0.8	-6.7	4.5	-12.0	2.57 Å, 165°; 2.61 Å, 144°
VI	C4-H4…O2	x+1/2,-y+1/2,z+1/2	7.65	-8.9	-1.2	-6.4	5.4	-11.1	2.40 Å, 149°
VII	C10-H10…O3	x+1/2, -y+1/2, z+1/2	8.48	-7.3	-0.9	-2.9	2.2	-9.0	2.56 Å, 162°
VIII	C9-H9…O2	x+1, y, z	7.68	-8.0	-1.5	-4.1	5.8	-8.0	2.30 Å, 165°
IX	C17-H17…O1	x+1/2, -y+1/2, z+1/2	7.59	-5.5	-1.2	-4.70	3.5	-7.9	2.55 Å, 125°
X	C12-H12…O3	x-1/2, -y+1/2, z+1/2	6.31	-1.2	-0.9	-8.1	3.2	-7.0	2.58 Å, 140°
XI	C11-H11…F1	x+1/2, -y+1/2, z+1/2	6.92	-2.5	-0.2	-8.3	4.2	-6.8	2.54 Å, 134°
XII	C5-H5…O1	x+1/2, -y+1/2, z+1/2	7.89	-2.2	-0.5	-3.9	1.6	-5.1	2.80 Å, 146°
XIII	C17-H17…F2	x+1/2, -y+1/2, z+1/2	6.68	-0.9	-0.2	-5.2	1.3	-5.0	2.82 Å, 149°
B									
I	C1…C4, C3-H3…F1, F1…F2	x-1, y, z	4.86	-0.7	-0.7	-23.2	6.9	-17.7	3.6349(8) Å; 2.88 Å, 110°; 3.0562(8) Å, 168°, 102°
II	C5-H5…O1	x+1, y, z	8.28	-7.3	-1.2	-9.0	3.8	-13.7	3.1 Å, 160°
III	C3…C7 (π -π), C6-H6…F2, F1…O1	x, -y+1/2, z+1/2	5.81	-1.7	-0.6	-13.9	4.0	-12.1	3.4801(7) Å; 2.88 Å, 128°; 3.3229(5) Å, 144°, 90°
IV	C3-H3…O1	x+1, -y+1/2, z-1/2	8.07	-8.5	-1.5	-5.6	5.2	-10.3	2.39 Å, 142°
V	F1…F3, F3…F3	-x+1, -y, -z+1	6.45	-0.2	-0.1	-7.7	1.1	-6.9	3.1772(4) Å, 144°, 109°; 3.2619(6) Å, 105°
VI	C4-H4…F2, C5-H5…F2	-x+2, y+1/2, -z+1/2	8.53	-1.6	-0.2	-5.1	1.6	-5.4	2.57 Å, 130°; 2.91 Å, 116°
C									
I	(Rg3…Rg3) F9…O3, F9…C18 (F -π)	-x+2, -y, -z+1	4.62	-0.7	-0.7	-30.3	9.3	-22.5	2.9741(12) Å, 162°, 87°; 3.4313(10) Å
II	(Rg1…Rg3) C7…C24(π -π), F1…F8	-x +5/2, y-1/2, -z+1/2	4.12	-1.1	-0.8	-30.3	11.3	-20.9	3.6869(14) Å; 3.2180(10) Å, 117°, 110°
III	(Rg1…Rg2) C2…C11(π -π), F4…C8 (F -π), F3…F4	x, y, z	4.05	0.1	-0.8	-31.5	11.7	-20.5	3.5002(14) Å, 3.2833(11) Å, 3.0717(11) Å, 159°, 93°
IV	C4-H4…O1	x, y+1, z	7.08	-9.2	-1.6	-9.8	4.9	-15.5	2.56 Å, 140°
V	C24-H24…O3 C19-H19…F8	x, y+1, z	7.08	-8.5	-1.3	-9.1	4.0	-14.7	2.80 Å, 132°; 2.56 Å, 134°
VI	C12-H12…O2, C15-H15…F6	x, y+1, z	7.08	-8.1	-1.3	-8.9	3.9	-14.5	2.63 Å, 135°; 2.74 Å, 131°
VII	C11…C15(π -π), F5…O2	-x+2, -y, -z	4.36	2.3	-0.4	-21.8	5.8	-14.1	3.6571(14) Å, 3.2692(11) Å, 94°
VIII	C23-H23…O2, C17-H17…O2	-x+5/2, y-1/2, -z+1/2	9.28	-5.6	-1.6	-7.3	6.1	-8.4	2.77 Å, 151°; 2.54 Å, 166°
IX	C3-H3…O1, C1-H1…O1	-x+5/2, y-1/2, -z+1/2	9.18	-5.6	-1.6	-7.8	6.8	-8.1	2.71 Å, 150°; 2.54 Å, 162°

X	C9-H9…O3, C11-H11…O3	-x+5/2, y-1/2, -z+1/2	9.20	-4.8	-1.4	-6.9	5.3	-7.7	2.60 Å, 153°; 2.83 Å, 146°
XI	C16-H16…F7, F5…F8	-x+3/2, y-1/2, -z+1/2	7.23	-1.6	-0.2	-7.4	1.6	-7.6	2.59 Å, 165°; 3.1733(9) Å, 130°, 116°
XII	C8-H8…F3, F1…F3, F2…F3	-x+3/2, y-1/2, -z+1/2	7.33	-1.9	-0.2	-7.8	2.8	-7.1	2.47 Å, 165°; 3.1972(9) Å, 151°, 95°; 3.0297(8) Å, 156°, 102°
XIII	C20-H20…F4, C20-H20…F5	-x+3/2, y-1/2, -z+1/2	7.33	-1.4	-0.2	-6.8	1.7	-6.6	2.70 Å, 157°; 2.82 Å, 157°
D									
I	C6…C10 (Rg1-Rg2)	x, y, z	4.23	-0.5	-0.8	-32.8	8.0	-26.0	3.6244(4) Å
II	F7…C18, F5…F11(Rg2-Rg3)	x, y, z	3.85	-0.5	-0.6	-31.1	7.9	-24.3	3.1203(3) Å, 2.9128(4) Å, 131°, 91°
III	C6-H6…O3, C23-H23…O1	-x, -y+1, -z	9.41	-13.3	-1.6	-6.4	5.9	-15.4	2.52 Å, 173°; 2.56 Å, 130°
IV	C15-H15…O2, C14-H14…O2	-x, y+1/2, -z+1/2	9.22	-13.7	-1.7	-7.0	7.0	-15.4	2.43 Å, 137°; 2.54 Å, 175°
V	F1…C6(Rg1-Rg1)	-x-1/2, y-1/2, z	4.95	0.1	-0.4	-17.3	3.5	-14.2	3.5805(4) Å
VI	C7-H7…O3, C22-H22…O1	-x, -y, -z	8.97	-12.5	-1.5	-7.8	7.6	-14.2	2.46 Å, 134°; 2.56 Å, 141°
VII	F12…C20 (Rg3-Rg3)	-x+1/2, y+1/2, z	4.93	-0.1	-0.4	-16.6	3.4	-13.7	3.3794(3) Å
VIII	C4-H4…O2	-x, y+1/2, -z+1/2	8.08	-4.6	-0.7	-5.6	1.4	-9.5	2.78 Å, 119°
IX	C4-H4…F10	-x, y+1/2, -z+1/2	7.76	-3.1	-0.2	-6.2	1.7	-7.8	2.60 Å, 153°
X	C5-H5…F1, C5-H5…F4	x, y+1, z	7.12	-3.7	-0.4	-7.1	3.7	-7.6	2.61 Å, 131°; 2.80 Å, 137°
XI	C13-H13…F5	x, y-1, z	7.12	-3.5	-0.6	-8.1	5.9	-7.6	2.41 Å, 138°
XII	F7…F8	-x, 1-y, -z	7.82	1.1	-0.1	-8.8	1.3	-6.6	3.1160(3) Å, 101°, 103°
XIII	C12-H12…F8	-x, -y, -z	7.91	-2.2	-0.2	-4.2	0.4	-6.2	2.38 Å, 96°
XIV	C21-H21…F9	x, y-1, z	7.12	-0.8	-0.3	-5.4	1.1	-5.5	2.74 Å, 128°
XV	C21-H21…F7	x, y-1, z	7.65	-1.6	-0.2	-3.7	0.7	-4.8	2.70 Å, 158°
XVI	F3…F12	x-1/2, y, -z+1/2	7.84	-0.4	-0.0	-4.6	0.3	-4.8	3.2376(3) Å, 143°, 108°
XVII	F3…F11	-x, y-1/2, -z+1/2	8.04	0.9	-0.1	-5.7	0.4	-4.5	3.0856(3) Å, 133°, 103°
E									
I	C4…C6 (π- π), F4…O1, F4…C8	-x+1, -y+2, -z+2	3.96	0.1	-0.4	-29.4	5.8	-23.8	3.7184(3) Å; 2.8492(2) Å, 161°, 2.8997(2) Å
II	C6-H6…O1	-x+2, -y+2, -z+2	8.46	-15.2	-1.9	-7.7	7.2	-17.7	2.44 Å, 151°
III	C8-H8…O1	-x+2, -y+1, -z+2	10.34	-11.3	-1.3	-7.1	7.2	-12.5	2.52 Å, 129°
IV	F1…F1, C8-H8…F1, F1…C2	-x+1, -y+1, -z+2	6.37	-2.3	-0.3	-10.9	4.7	-8.8	2.9091(2) Å, 94°, 94°; 2.37 Å, 102°; 3.2976(2) Å
V	C3-H3…F2, F2…F2 (Type I)	-x, -y+1, -z+1	6.81	-5.8	-0.3	-9.1	7.3	-8.0	2.23 Å, 173°; 2.9981(2) Å, 139°, 139°
VI	F3…F4 (Type I)	-x, -y+2, -z+1	8.81	0.2	0	-6.2	0.6	-5.4	3.1464(2) Å, 113°, 106°

VII	C5-H5…F1	x, y+1, z	7.47	-1.3	-0.2	-6.0	2.2	-5.3	2.46 Å, 155°
F									
I	C1...C1, C6…C7(π- π), C6-H6…F1	x+1/2, -y, -z+2	4.73	-9.7	-1.1	-34.2	16.6	-28.5	3.4754(1) Å; 3.2820(1) Å; 2.65 Å, 121°
II	C3-H3…O1	x, y+1, z	7.94	-12.7	-1.7	-5.4	8.1	-11.7	2.20 Å, 163°
III	C3…C3, F2…F3	x-1/2, -y+1, -z+2	5.82	1.0	-0.3	-13.5	2.0	-9.7	3.8237(1) Å; 3.3444(1) Å, 102°, 101°
IV	C7-H7…F2, F1…F2	-x+1/2, y-1/2, -z+3/2	7.30	-0.4	-0.1	-7.8	1.9	-6.3	2.66 Å, 173°; 3.0689(1) Å, 146°, 106°
V	C5-H5…F3	-x+1/2, y+1/2, -z+5/2	9.20	-3.3	-0.4	-5.0	3.2	-5.6	2.35 Å, 146°
VI	C5-H5…F1	-x, -y+1/2, z+1/2	7.95	-1.0	-0.1	-5.1	1.2	-5.0	2.73 Å, 116°
G									
I	C3…C4 (π-π), F3…C7	-x+1/4, y+1/4, z+1/4	3.94	-3.2	-0.5	-34.4	11.6	-26.4	3.4657(1)Å, 3.2584(1) Å
II	C2-H2…O1	-x+1, -y, -z	8.71	-14.3	-1.9	-8.8	10.6	-14.5	2.34 Å, 148°
III	C7-H7…O1	-x+1, -y-1/2, z	9.75	-11.7	-1.2	-6.0	4.9	-14.1	2.65 Å, 124°
IV	C4-H4…F3	-x, -y, -z	7.03	-4.1	-0.4	-9.6	2.6	-11.4	2.65 Å, 150°
V	C7…O1	-x+1/4, y+3/4, z+3/4	7.50	-4.4	-1.0	-8.2	4.06	-9.6	3.0650(1) Å, 115°
VI	C6-H6…F1, C7-H7…F1	x, y+1/2, -z	7.48	-3.7	-0.4	-6.0	3.06	-7.1	2.42 Å, 160°; 2.87 Å, 154°
VII	F4…F4	-x, -y+1/2, z	8.29	-0.2	-0.1	-6.5	1.66	-5.1	2.7965 Å, 107°, 107°

[a]The values of E_{ele}, E_{pol}, E_{disp}, E_{rep}(in kJ/mol) are scaled according to the scaling parameter (discussed in S.4.1.) as mentioned in Mackenzie *et al.,* 2017 [reference 48 in main manuscript]; The % contribution of individual component is calculated through $(E_{comp}/(E_{stab}))*100$ where $E_{stab}= E_{ele}+ E_{disp}+ E_{pol}$; [b] R= centroid-centroid distance for respective dimer.

S.2. Cambridge Structural Database:

A database search for benzaldehydes gave a total of 1814 hits, out of which only 19 hits matched with our criteria of halogenated benzaldehydes. The condition for search were as follows: 3D coordinates determined, no errors, not polymeric, only single crystal structures, only organics structures. The detail of crystallographic study is discussed in the main manuscript. Rest of the studies primarily discusses the role of halogenated benzaldehydes in synthesis, bio-organic molecular action/inhibition, and their function as conducting polymers. The REFCODES are AREHEM[1], AREHIQ[1], BETMET[2], IBUYOW[3], IBUYUC[3], KEYKAD [4], LABRIQ[5], PADHUY[6], SOYYAI[7], UWUVAL[8], YUMVOS[9].

S.3. Differential Scanning Calorimetry:

DSC data for 5 benzaldehydes were recorded on a Perkin Elmer DSC 6000 instrument under nitrogen gas atmosphere at a flow rate of 20 mL/min. Each liquid sample was placed in an open aluminium pan at a scan rate of 5°C/min and solidification/freezingoccurred in the range of −45 °C to 30 °C (Table 2). Two of the liquids namely, **A** and **B** had freezing point beyond the range of the measuring instrument. The freezing points of the same are mentioned based on *in situ*cryocrystallization experiments.

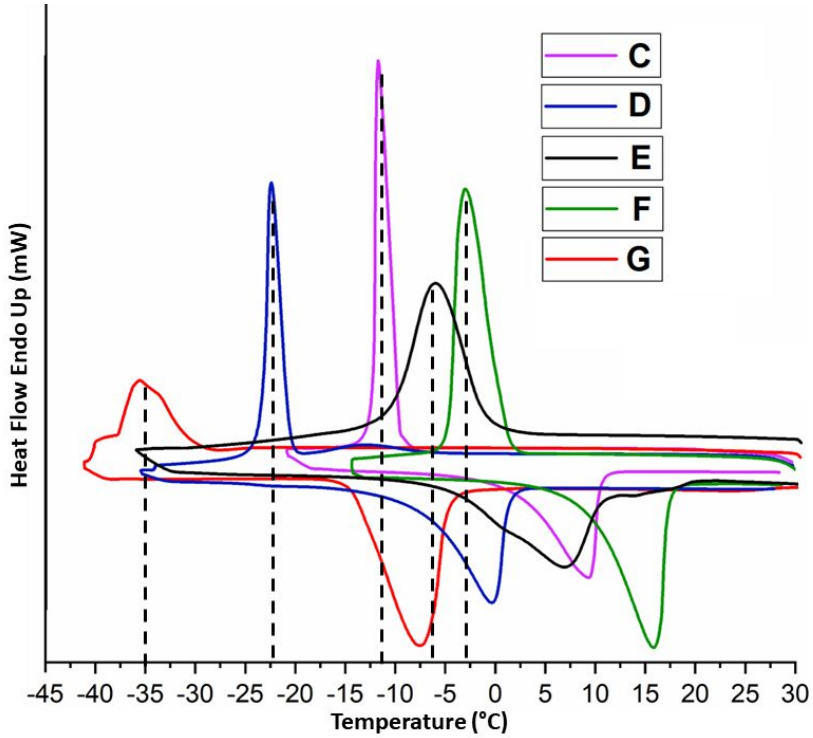

Fig S3. DSC traces of **C**, **D**, **E**, **F**and**G**at a scan rate of 5°C/min.

S.4. Computational Details:

All the calculations were carried out using *CrystalExplorer 17.5* (references in main manuscript). All the computations were carried out using accurate method with CE-B3LYP/6-31G(d,p).10

S.4.1. Energy Frameworks:

In order to visualize the interaction topology in these crystal structures, energy framework analysis has been performed using *CrystalExplorer 17.5*. The input file used for calculation is .cif file. A 3.8Å cluster is drawn around the selected molecule and the incomplete molecules are completed. The interaction energy is calculated by accurate energy model which includes CE-B3LYP/6-31G (d, p).The calculation of the interaction energies is inclusive of normalization of C-H bond lengths to neutron distances[10].In this method, the values of interaction energies are used to construct the three-dimensional topology of interactions that are termed as energy frameworks. The pairwise intermolecular interaction energies in the crystal structures are represented as cylinders joining the molecules. The radii of these cylinders are proportional to the strength of the intermolecular interaction. The tube size was set at the default value of 80, with an energy cut-off of 4 kJ mol^{-1}. The values are scaled factors for benchmarked energy models usingk_ele=1.057, k_pol=0.740, k_disp=0.871, k_rep=0.618 [Reference 49 in main article].[11]

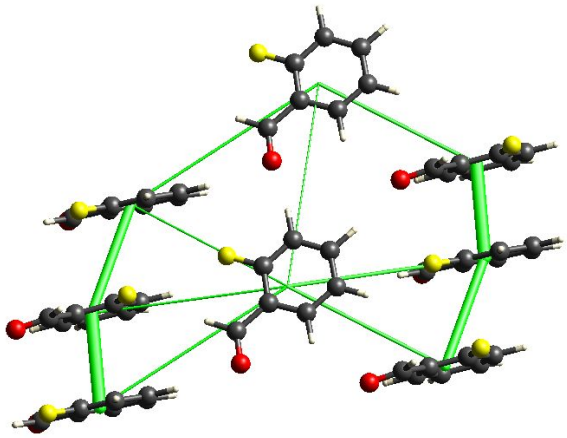

Fig S4. Dispersion component stabilizing the molecular stacks in the crystal structure of **A** shown by energyframeworks in green.

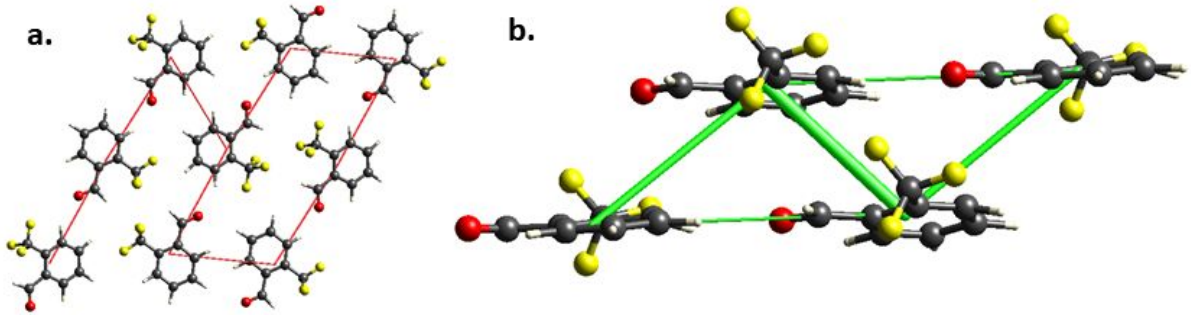

Fig. S5 a. Electrostatic component depicting the stabilization of the 2-D sheet of **B** shown *via* energyframeworks in red; **b.** Dispersive components stabilize the molecular stack in **B** shown by energyframeworks in green.

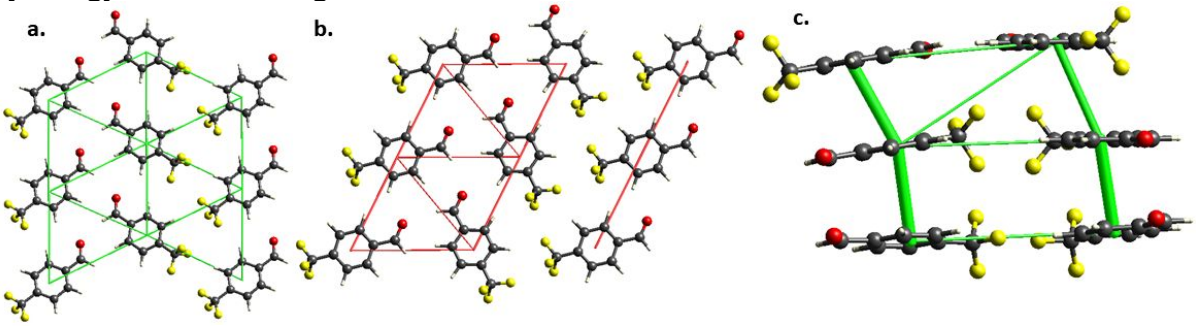

Fig S6 a. 2-D layer stabilized via C-H…O and C-H…F with dispersive contribution from C-H…F hydrogen bonds stabilizing crystal structure of **C** shown by energyframeworks in green; **b.**Stabilization of 2D sheet via electrostatic contribution from C-H…O hydrogen bond in crystal structure of **C**shown by energyframeworks in red; **c.** Major dispersion contribution stabilizing the molecular stacks in **C** shown by energyframeworks in green.

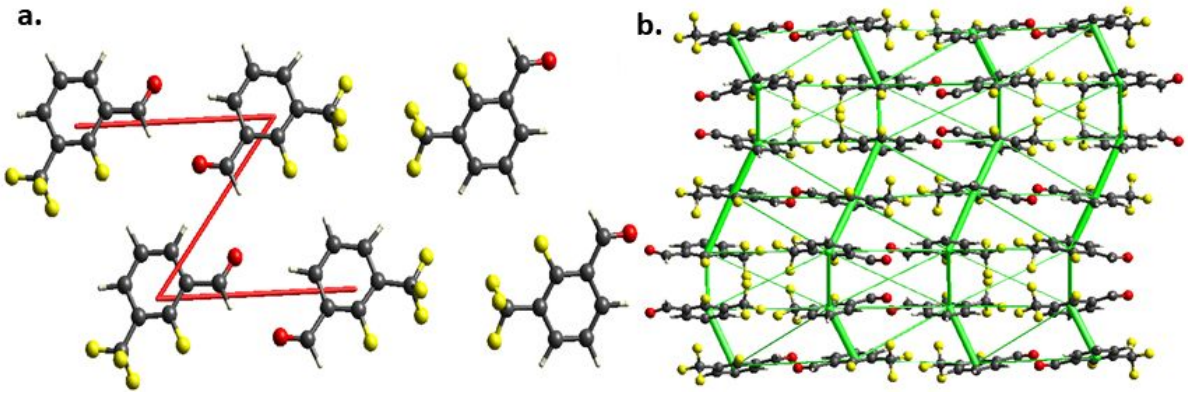

Fig. S7. a. Electrostatic component stabilizing the 2-D sheet in crystal structure of **D** shown by energyframeworks in red; **b.** Dispersive components stabilizing the molecular stack present in crystal structure of **D** shown by energyframeworks in green.

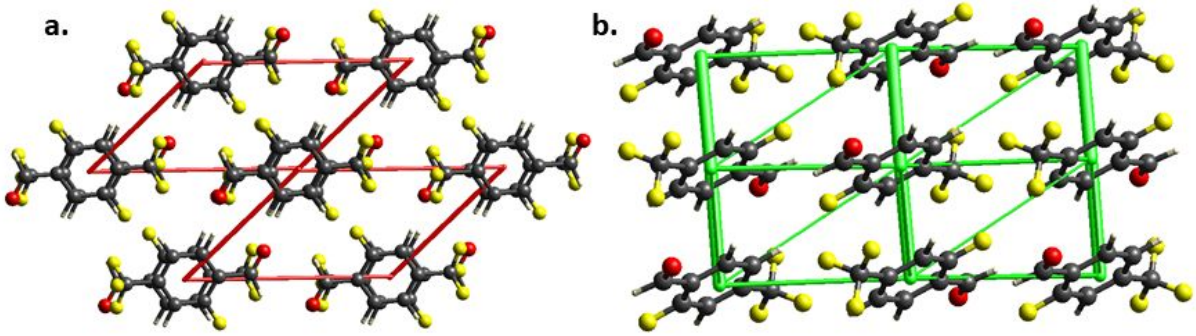

Fig. S8. a. Electrostatic component stabilizing the 2-D sheet in crystal structure of **E**shown through energy frameworks in red; **b.** Dispersive components stabilizing the molecular stack in crystal structure of **E** shown by energyframeworks in green.

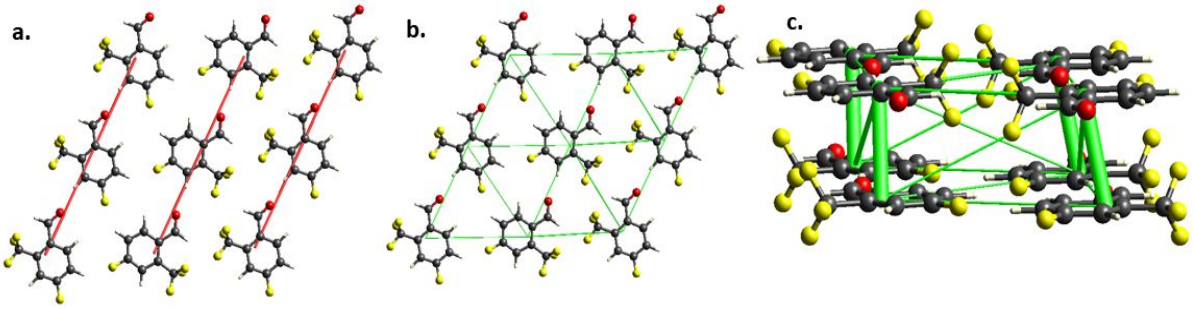

Fig. S9 a. Crystal structure of **F** stabilized primarily *via* electrostatics in the 2-D sheet shown through energy frameworks in red; **b.** Dispersive component stabilizing the 2-D sheets in crystal structure of **F**; **c.** Dispersive force contribution stabilizing the crystal structure of **F** shown by energyframeworks in green.

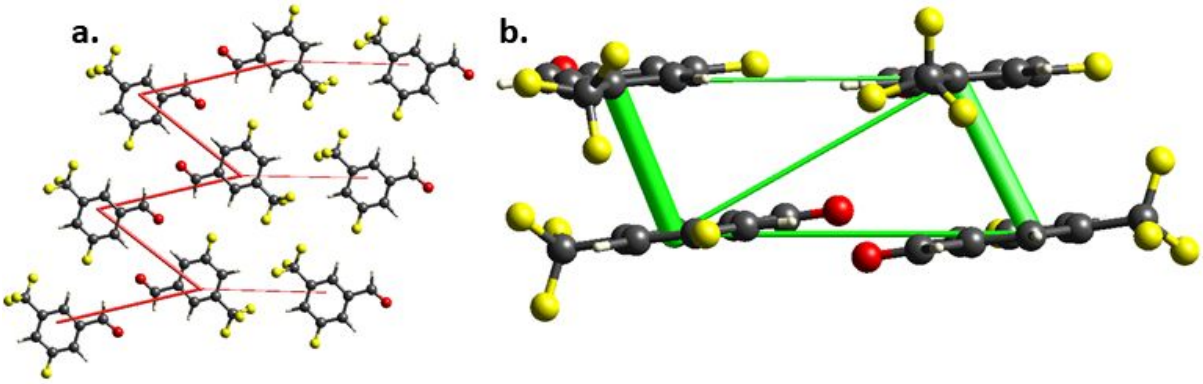

Fig. S10 a. Electrostatic component stabilizing the 2-D sheet of crystal structure of **G**shown by energyframeworks in red; **b.** Dispersive components stabilize the molecular stack in crystal structure of **G** shown by energyframeworks in green**.**

S.4.2. Lattice Energy:

The lattice energy of -F and/or -CF_3 benzaldehydes are computed with the help of *Crystal Explorer 17.5.* For one molecule in the asymmetric unit, a cluster of 20Å is created around the selected molecule and the molecule fragments are completed. Further, the energy is computed for the cluster with the help of accurate method constituting of CE-B3LYP/6-31G(d,p) and the energy is calculated by summing half of the product of N and E_{tot}. For Z'>1 molecule in the asymmetric unit, a cluster of 20Å is created around the selected molecule and the molecule fragments are completed. Accurate method constituting of CE-B3LYP/6-31G(d,p) is utilized for computation of interaction energy as mentioned above and an average of the value obtained for individual molecule selected, is tabulated in Table 2.

S.4.3. Hirshfeld Surface Analysis, 2-D Finger print plots and Enrichment ratios:

With the help of 'Hirshfeld surface generation' option in *Crystal Explorer 17.5.* a surface was generated using accurate method with CE-B3LYP/6-31G(d,p).

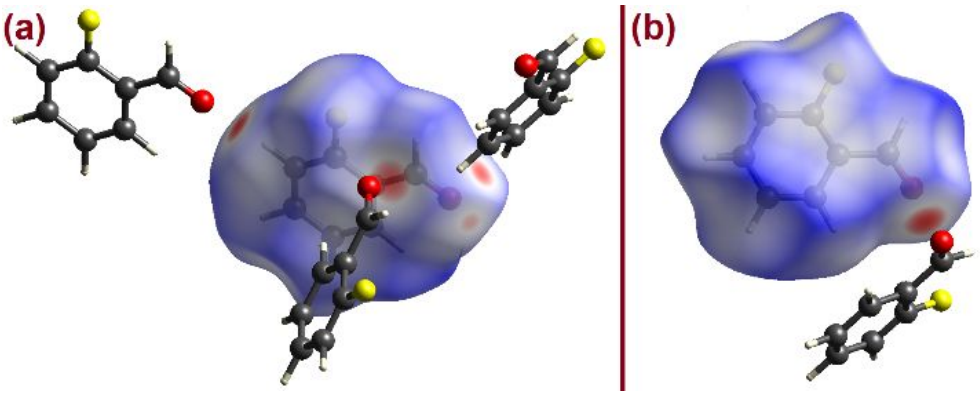

Fig S11. a. &b.d_{norm} surface showing the pairwise O···H interactions for **A**.

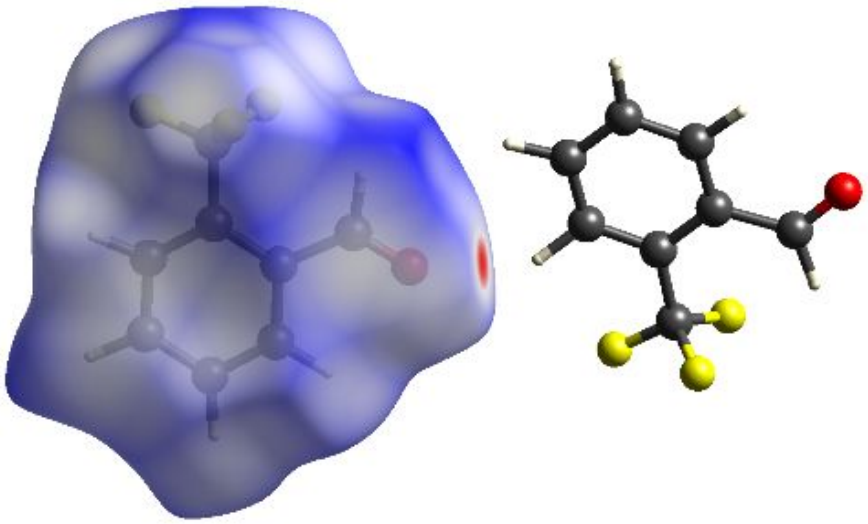

Fig S12. d_{norm} surface showing the pairwise O···H interactions for **B**.

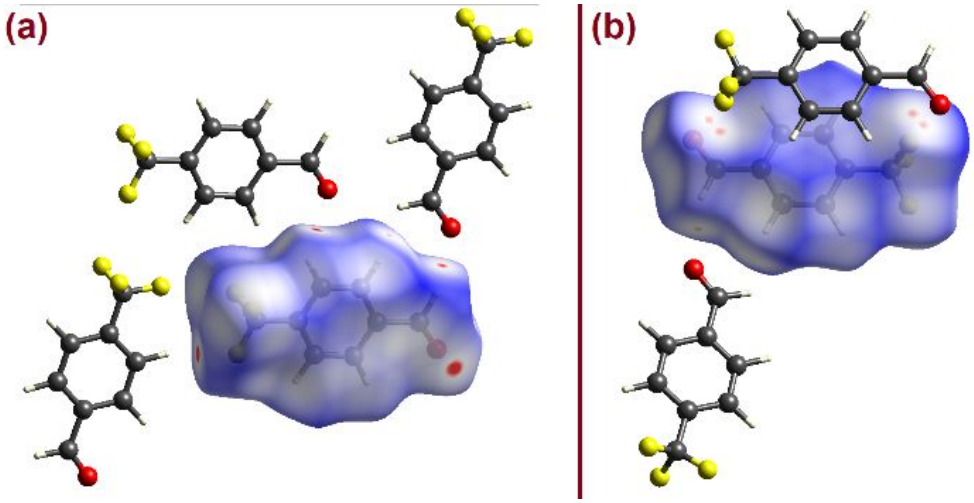

Fig S13. a. d_{norm} surface showing the pairwise O···H and F···H for **C**, **b.** d_{norm} surface showing the pairwise O···H and F···C interactions for **C**.

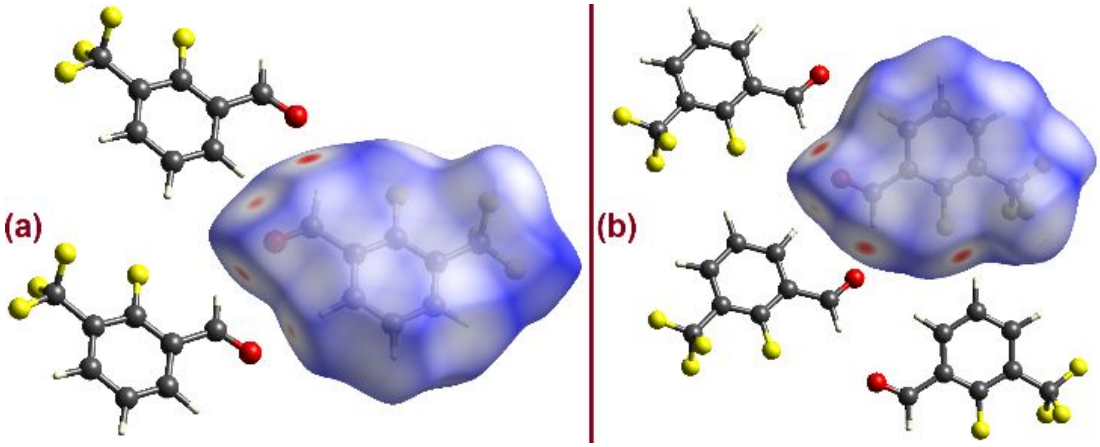

Fig S14. a.d_{norm} surface showing the pairwise O···H interactions for **D**, **b.**d_{norm} surface showing the pairwise O···H contacts and pairwise F···H contacts for **D**.

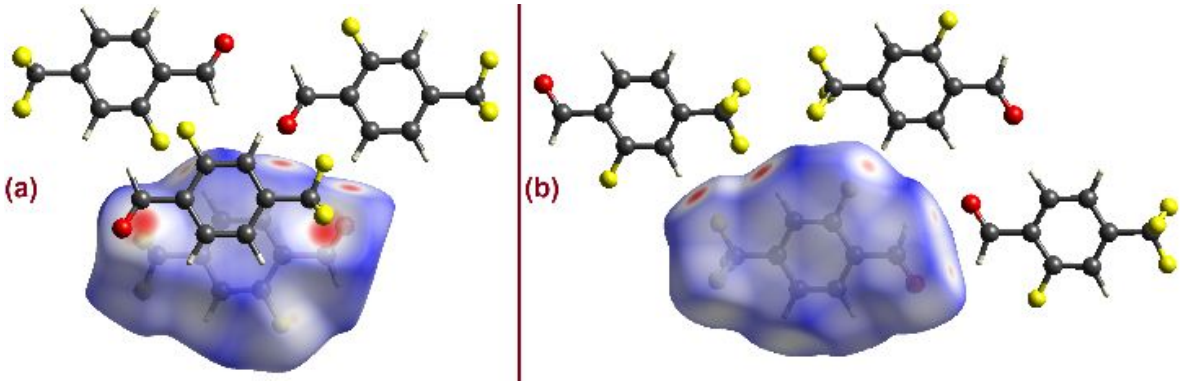

Fig S15. a.d_{norm} surface showing the pairwise O···H, F···H and F···C interactions for **E**, **b.**d_{norm} surface showing the pairwise F···H and O···H interactions for**E**.

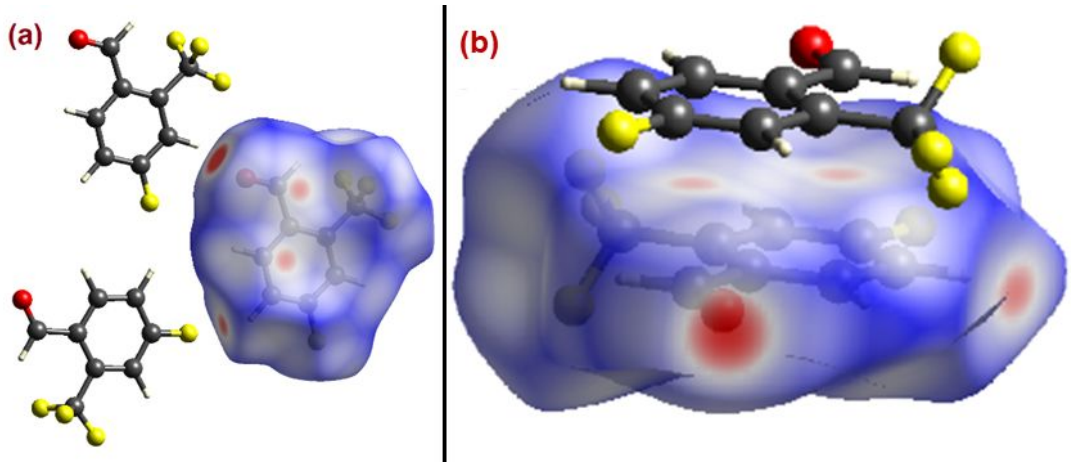

Fig S16. a.d_{norm} surface showing the pairwise O···H and F···H for **F**, **b.**d_{norm} surface showing the pairwise C···C interactions for **F**.

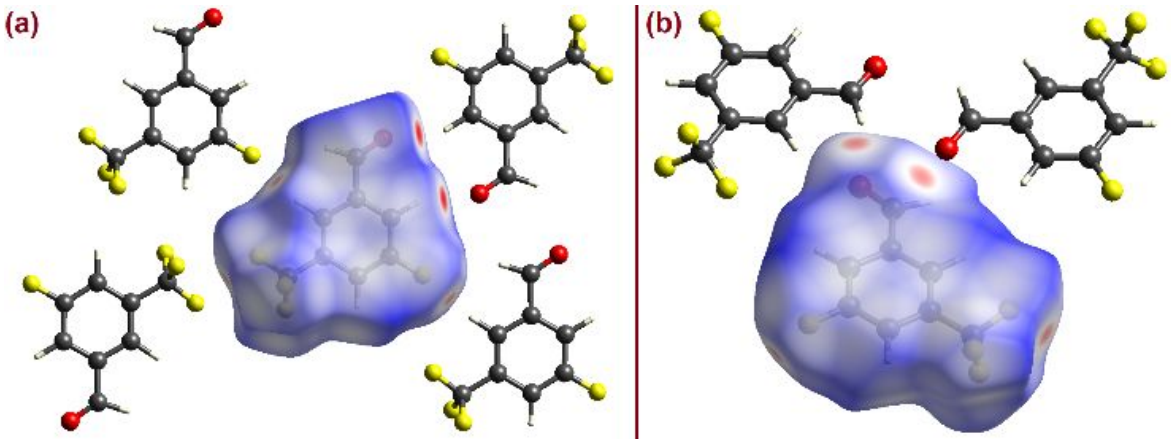

Fig S17. a.d_{norm} surface showing the pairwise O···H, F···H and F···F interactions for**G**, **b.**d_{norm} surface showing the pairwise O···H interactions for **G**.

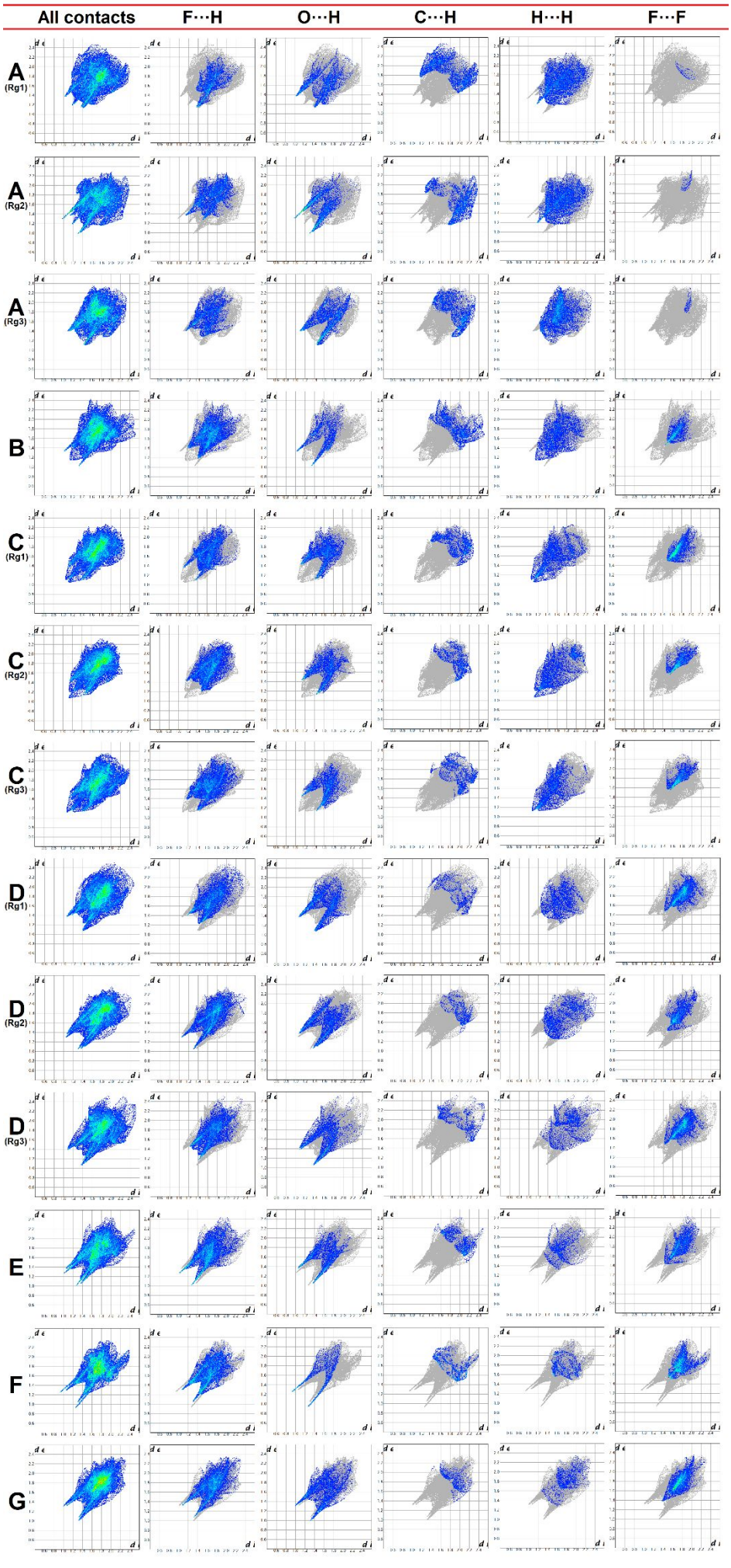
All contacts
F···H
O···H
C···H
H···H
F···F
A (Rg1)
A (Rg2)
A (Rg3)
B
C (Rg1)
C (Rg2)
C (Rg3)
D (Rg1)
D (Rg2)
D (Rg3)
E
F
G

Figure S18. Fingerprint plots of A(I)/(II)/(III), B, C (I)/(II)/(III), D(I)/(II)/(III), E, F and G depicting F···H/H···F, O···H/H···O, C···H/H···C, H···H and F···F contacts.

The Enrichment ratios have been calculated with the help of the method described in the study by Jelsch, *et al.* [reference 54 in the main manuscript].

Table S2: Contact surface, Random contact and Enrichment ratio for fluorinated benzaldehydes.

	Contact Surface				**Random Contact**				**Enrichment ratio**			
A (Rg1)	**F**	**C**	**O**	**H**	**F**	**C**	**O**	**H**	**F**	**C**	**O**	**H**
F	0.5				1.2				0.4			
C	4.0	8.9			5.3	4.9			0.7	1.8		
O	1.2	2.8	0.3		2.4	4.6	0.0		0.5	0.6	0.0	
H	16.6	19.9	16.5	29.2	12.7	24.7	11.7	31.0	1.3	0.8	1.4	0.9
A (Rg2)												
F	0.5				1.5				0.3			
C	0.0	3.8			3.7	2.1			0.0	1.7		
O	0.8	5.2	0.4		3.5	4.0	0.0		0.2	1.2	0.0	
H	23.9	16.7	20.8	27.9	15.0	17.2	16.1	34.3	1.6	0.9	1.2	0.8
A(Rg3)												
F	0.0				0.0				0.0			
C	3.8	8.8			4.6	3.6			0.8	2.4		
O	1.3	1.1	0.0		2.7	4.4	0.0		0.4	0.2	0.0	
H	19.0	15.9	20.8	28.7	1.3	21.0	13.1	31.9	1.4	0.7	1.6	0.9
B												
F	9.2				8.2				1.1			
C	1.7	3.7			8.4	2.2			0.2	1.7		
O	2.2	7.6	0.0		5.8	3.0	0.0		0.4	2.5	0.0	
H	34.7	12.8	10.7	17.3	26.4	13.7	9.5	2.2	1.3	0.9	1.1	0.8
C(Rg1)												
F	15.4				8.4				1.8			
C	2.0	7.4			8.9	2.3			0.2	3.1		
O	0.0	3.8	0.0		0.0	3.4	0.0		0.0	1.1	0.0	
H	25.4	10.3	18.2	17.3	25.7	13.6	9.8	19.6	0.9	0.7	1.8	0.8
C(Rg2)												
F	9.9				8.3				1.2			
C	2.1	9.5			9.0	2.5			0.2	3.8		
O	2.9	3.0	0.0		6.0	3.3	0.0		0.5	0.9	0.0	
H	32.8	7.3	15.2	17.0	25.7	14.0	9.4	19.9	1.3	0.5	1.6	0.8
C(Rg3)												
F	10.2				10.2				1.0			
C	7.6	6.1			9.6	2.2			0.8	2.7		
O	3.1	1.8	0.1		6.3	2.9	0.0		0.5	0.6	0.0	
H	33.0	8.4	14.6	15.1	27.6	12.9	8.5	18.6	1.2	0.6	1.7	0.8
D(Rg1)												
F	13.6				13.3				1.0			
C	13.3	6.2			11.4	2.4			1.1	2.5		
O	3.1	0.9	0.7		8.4	3.5	0.0		0.3	0.2	0.0	
H	29.3	4.7	17.6	10.5	26.4	11.3	8.3	13.2	1.1	0.4	2.1	0.7
D(Rg2)												
F	11.1				12.2				0.9			
C	9.0	8.7			10.8	2.4			0.8	3.6		
O	4.3	0.1	0.0		7.3	0.0	0.0		0.6	0.0	0.0	
H	34.3	4.7	16.6	11.3	27.3	12.1	8.2	15.3	1.2	0.4	2.0	0.7
D(Rg3)												
F	18.5				17.9				1.0			
C	16.7	3.1			12.3	2.1			1.4	1.5		
O	1.2	1.0	0.8		8.2	2.8	2.1		0.1	0.4	0.3	
H	29.7	5.2	15.6	8.2	28.3	9.7	6.4	11.2	1.1	0.5	2.4	0.7
E												
F	12.7				14.9				0.8			

C	9.8	6.6			11.8	2.3			0.8	2.8		
O	5.4	0.3	0.0		8.1	3.2	0.0		0.6	0.0	0.0	
H	36.8	7.3	15.3	5.8	27.5	10.8	7.4	12.6	1.3	3.4	2.0	0.5
F												
F	18.0				15.2				1.2			
C	4.5	5.6			13.6	3.0			0.3	1.8		
O	2.7	10.1	0.0		8.5	3.8	0.0		0.3	2.6	0.0	
H	34.8	9.2	9.0	6.1	25.4	11.4	7.1	10.6	1.4	0.8	1.3	0.5
G												
F	19.3				16.5				1.2			
C	6.1	9.8			12.5	2.3			0.5	4.1		
O	2.9	1.3	0.0		8.7	3.3	0.0		0.1	0.3	0.0	
H	33.8	3.8	17.2	5.8	27.0	10.2	7.1	11.0	1.3	0.3	2.4	0.5

S.4.4. Molecular Electrostatic Surface Potential

In order to gain insights into the electrostatic complementarity of all the involved intermolecular interactions, the molecular electrostatic surface potentials (MESPs) for all the –F and –CF_3 benzaldehydes have been plotted onto their crystal geometry using *CrystalExplorer17.5*. Each and every molecule inside the asymmetric unit generates a unique Hirshfeld surface which assists us for a direct comparison of all the molecules in different crystalline environments. Positive regions (blue) of the electrostatic potential surface always prefer to interact with the complementary negative regions (red) of the surface belonging to neighboring adjacent molecules in the crystal packing. The strength and directionality of all the hydrogen and halogen bonds can be rationalized by a direct comparison of electrostatic potential values mapped over their Hirshfeld surfaces.

Table S3: Electrostatic complementarity between C-H and O/F*/F#

Atom	**$V_{s,max}$ (kJmol^{-1})**	**Atom**	**$V_{s,min}$(kJmol^{-1})**
A (Rg1, Rg2, Rg3)			
C3-H3	+121.3	O3	-122.3
C10-H10	+98.4	O2	-143.1
C11–H11/ C21–H21	+55.7/+64.8	F1*	-39.9
C17–H17	+76.1	F2*	-34.9
B			
C3–H3	+147.5	O1	-177.7
C4–H4/ C5–H5	+76.1/ +78.5	F2#	-40.9
C (Rg1, Rg2, Rg3)			
C17–H17/ C23–H23	+116.6/ +159.4	O2	-129.4
C3–H3/ C1–H1	+159.9/+92.1	O1	-131.8
C9–H9/ C11–H11	+92.2/+132.1	O3	-146.2
C20–H20	+101.8	F4/F5#	-42.0
C15–H15	+50.9	F6#	-48.0
C8–H8	+116.6	F3#	-47.8
D (Rg1, Rg2, Rg3)			
C6–H6/ C7–H7	+110.3/+102.7	O3	-113.7
C23–H23	+99.8	O2	-142.3
C22–H22	+112.6	O1	-136.0
C5–H5	+104.5	F1*	-52.0
C13-H13	+144.4	F5*	-47.3
C21-H21	+101.3	F9*	-38.6
C4–H4	+105.0	F10#	-41.7
C12–H12	+95.6	F8#	-43.6
E			
C8-H8/ C6-H6	+89/+116.3	O1	-136.8
C5-H5/ C8-H8	+132.1/+89.0	F1*	-22.3
C3–H3	+160.2	F2#	-26.2
F			
C3–H3	+203.5	O1	-168.3
C5–H5	+158.6	F3*	-28.9

C7–H7/ C6-H6	+71.4/+26.8	F2/F1[#]	-30.4
G			
C2–H2	+142.3	O1	-132.6
C6–H6/ C7–H7	+159.4/+93.5	F1*	-35.4
C4-H4	+116.8	F3[#]	-26.3

*- fluorine attached to sp^2hybridized aryl carbon; #- fluorine attached to sp^3 carbon.

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