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Supporting information for article:

Characterization of fluorine-centered `F···O' σ-hole interactions in the solid-state

Abhishek Sirohiwal, Venkatesha R. Hathwar, Dhananjay Dey, Roshni Regunathan and Deepak Chopra

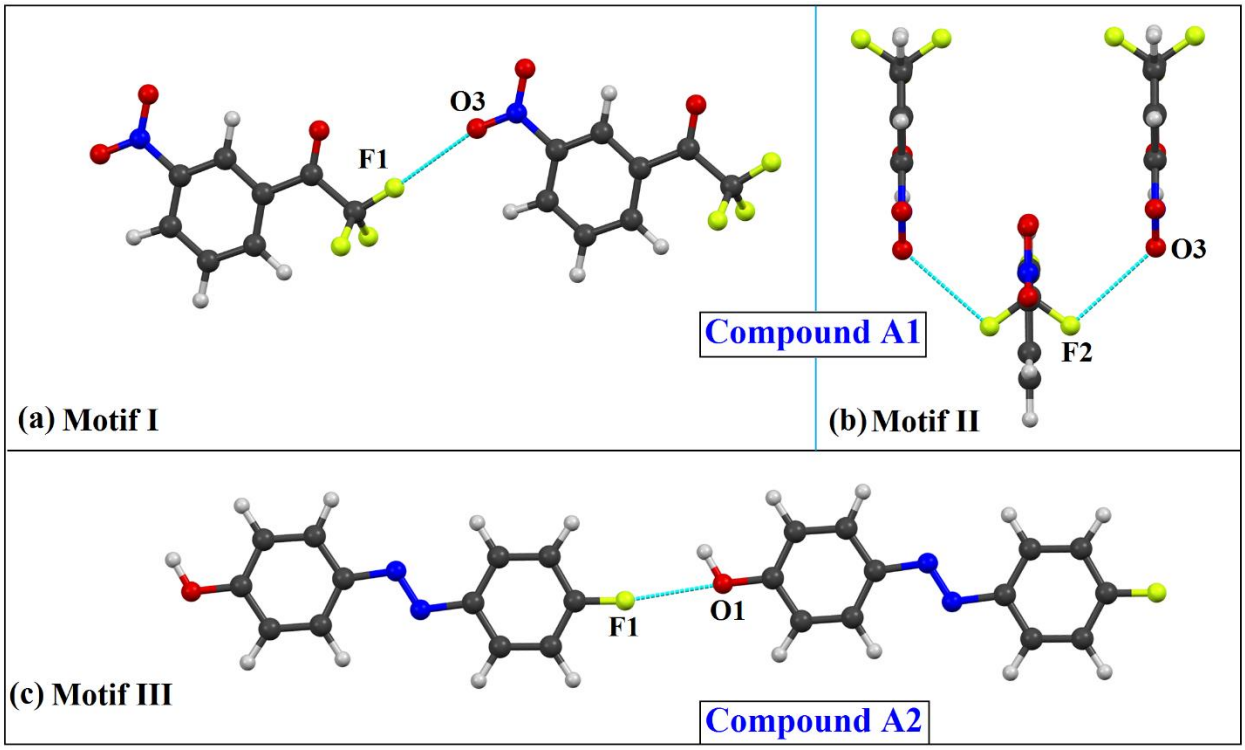

Figure S1 Motifs I and II in compound A1 and motif III in compound A2.

S1. Synthetic procedure of (*E*)-4-((4-fluorophenyl) diazenyl) phenol (A2)

4-fluoroaniline (0.47 ml) was dissolved in a solution of 2 M HCl (16 mL) and the resulting solution was cooled at 0°C. Sodium nitrite dissolved in water was added dropwise into the solution to produce the corresponding diazonium salt. A mixture phenol (0.36 g, 0.003 mol) and 5 ml 7% NaOH dissolved in 10 ml water was added slowly at 0°C, and then a yellow solid was obtained as a precipitate. The reaction mixture was stirred at room temperature for 2 hours. 20% HCl solution was added to the reaction mixture to ensure that the pH=3 was maintained. The precipitated solid was collected and purified by column chromatography. Furthermore, the synthesized compounds were characterized using ^{1}H-NMR, FTIR, Differential Scanning Calorimetry (DSC) and Powder X-ray diffraction (PXRD) and Single Crystal X-Ray Diffraction (SCXRD) techniques.

(*E*)-4-((4-fluorophenyl) diazenyl) phenol (A2): Yield = 79%: FTIR (KBr pellet, cm^{-1}): 3165, M.P. = 154˚C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.86 (m, 4H), 7.16 (t, *J* = 8.65 Hz, 2H), 6.92 (d, *J* = 8.85 Hz, 2H), 5.35 (s, 1H).

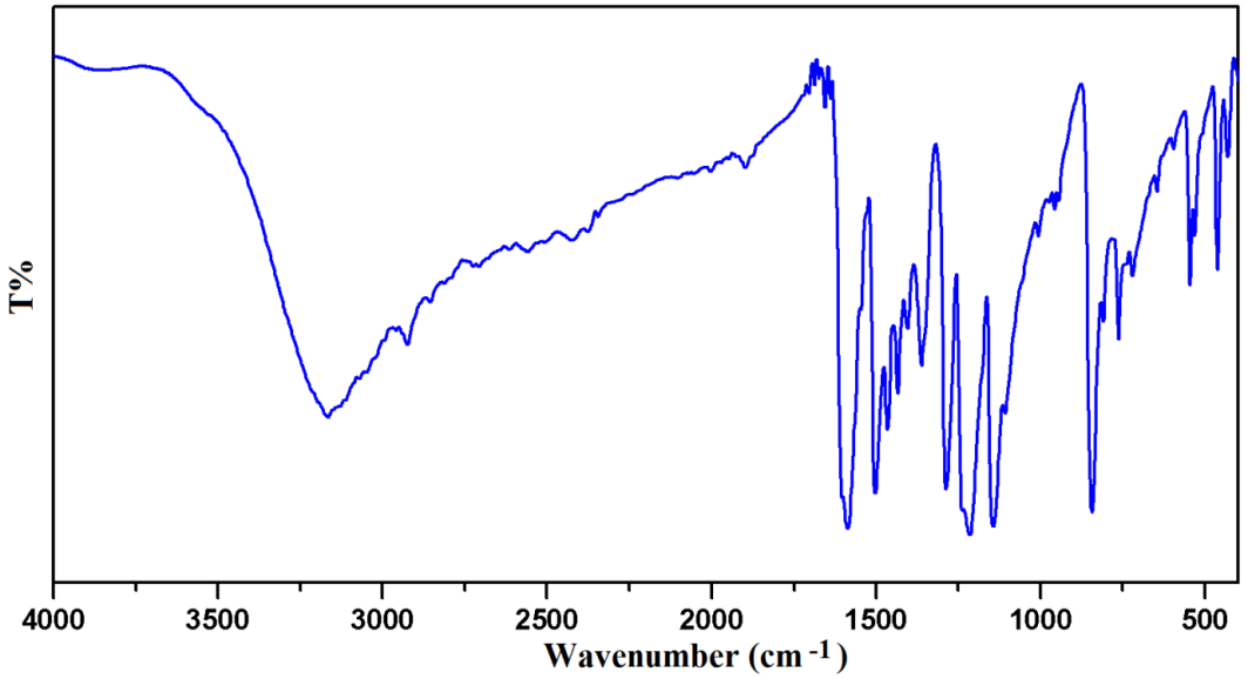

Figure S2 FTIR spectra of the synthesized compound **A2**.

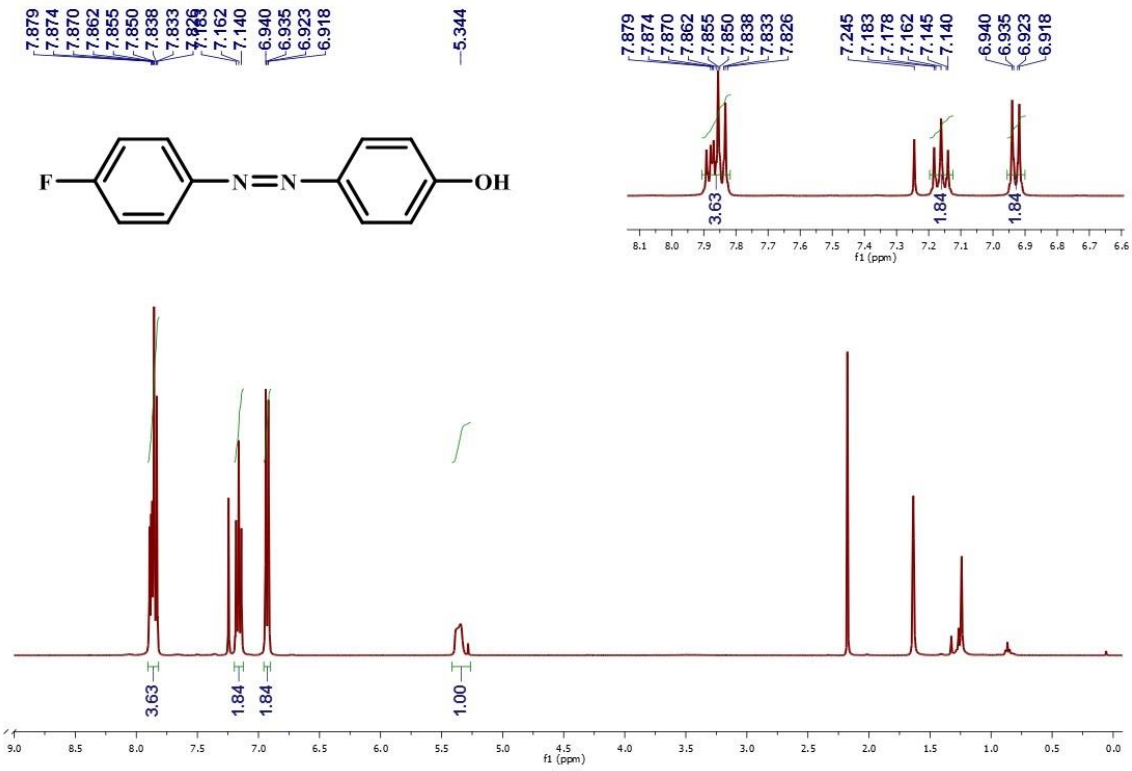

Figure S3 ^{1}H-NMR spectra of the synthesized compound **A2**in $CDCl_3$ (400 MHz).

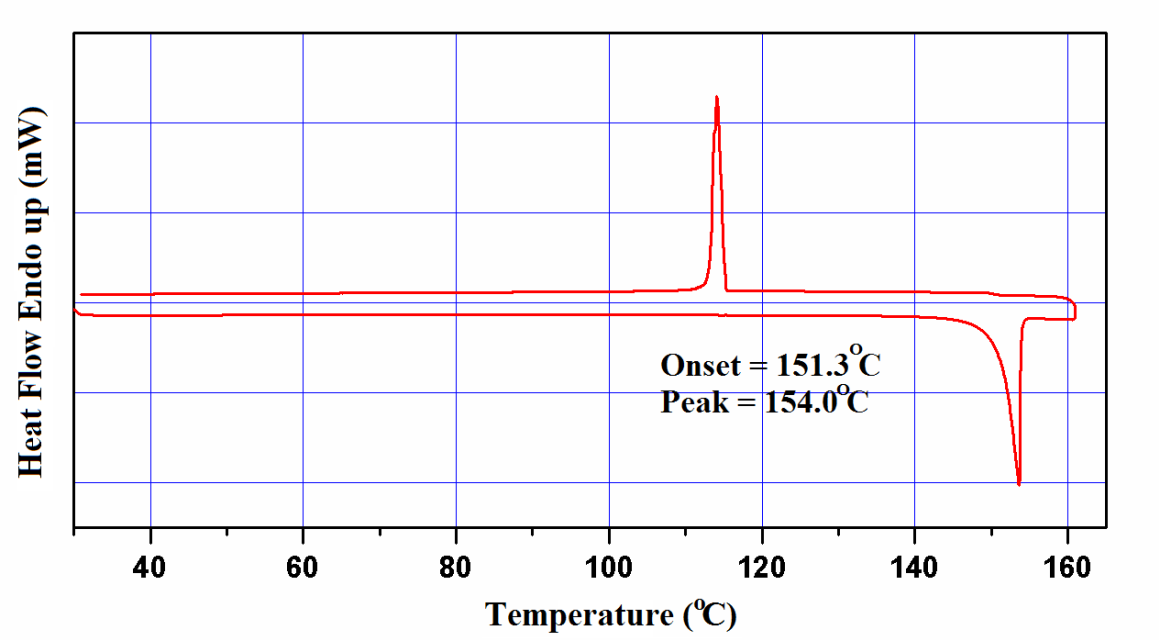

Figure S4 DSC plot for **A2** in the temperature range 30-162°C @ 5°C/min.

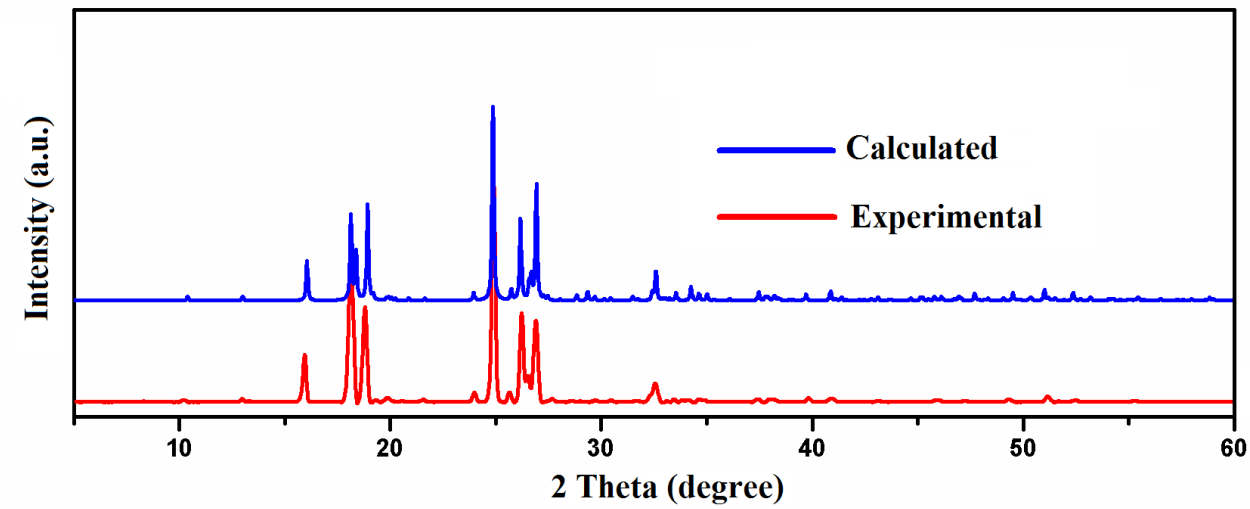

Figure S5 Comparison of the powder diffraction pattern (experimental and calculated) of **A2**.

S2. Data collection and structure refinement

The single crystal diffraction data have been collected using a Bruker AXS CMOS-type PHOTON 100 detector using monochromated Mo Kα radiation (λ = 0.71073 Å) in phi (ϕ) and omega (ω) scan. The unit cell measurement, data collection, integration, scaling and absorption corrections for these forms were done using Bruker Apex II software (Bruker, 2006). The intensity data were processed by using the Bruker SAINT (Siemens, 1995) suite of programs. The crystal structures were solved by direct methods using SIR 92 (Altomare *et al.*, 1994) and refined by the full matrix least squares method using SHELXL 2014 (Sheldrick, 2008) present in the program suite WinGX (version 2014.1) (Farrugia, 1999). Empirical absorption correction was applied using SADABS (Sheldrick, 2007). Then non-hydrogen atoms were refined anisotropically and the hydrogen atoms bonded to C atom, were positioned geometrically and refined using a riding model with U_{iso} (H) =1.2U_{eq}. The crystal packing diagrams were generated using Mercury 3.5.1(CCDC) program (Macrae *et al.*, 2008). Geometrical calculations were done using PARST (Nardelli, 1995) and PLATON (Spek, 2009).

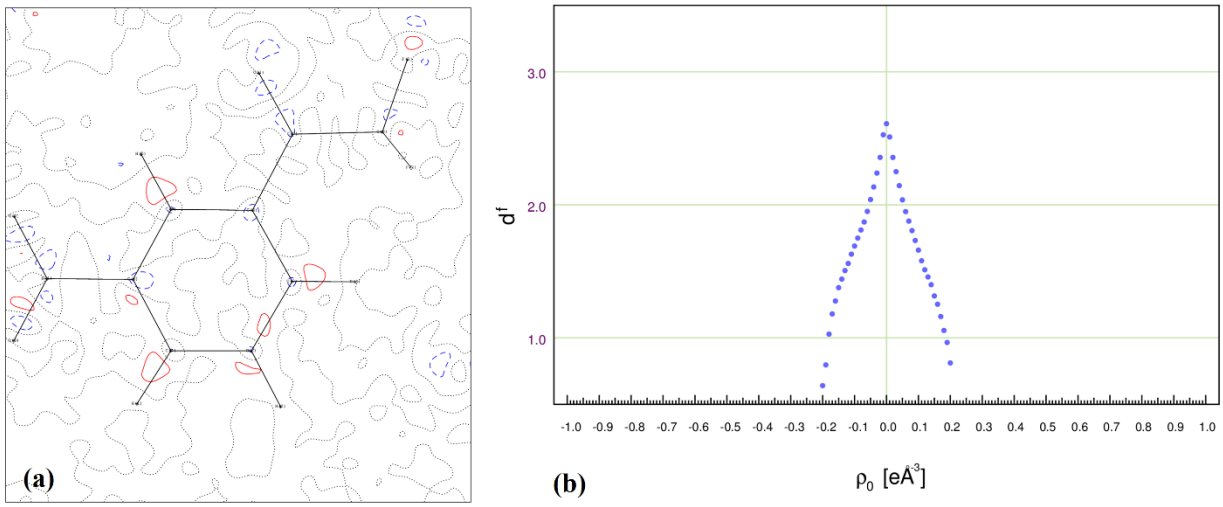

Figure S6 (a) Residual electron density map and (b) The fractal dimension plots for compound **A1**. The contour intervals are drawn at ±0.10 e·Å^{-3}.

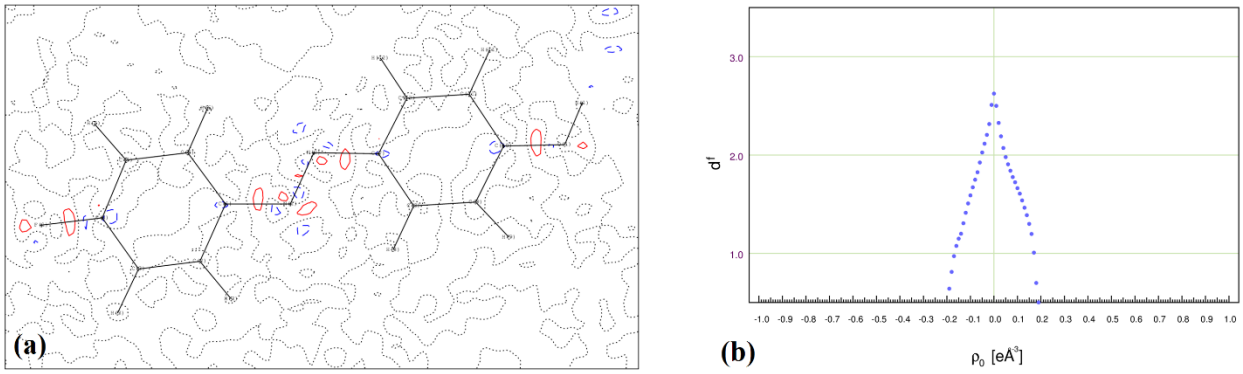

Figure S7 (a) Residual electron density map and (b) The fractal dimension plots for compound **A2**. The contour intervals are drawn at ±0.10 e·Å^{-3}.

Table S1 Possible intermolecular interactions present in the crystal packing of **A2**

D-H···A	D-H(Å)	D···A(Å)	H···A(Å)	∠D-H···A(º)	Symmetry
O1-H1···N2	0.94	2.924(3)	1.99	176	-x+3/2, y-1/2, -z+1/2
C11-H11···N2	1.08	3.542(3)	2.76	129	-x+3/2, y-1/2, -z+1/2
C5-H5···N1	1.08	3.489(3)	2.65	134	x-1/2, -y+3/2, z-1/2
C12-H12···O1	1.08	3.384(3)	2.71	120	-x+3/2, y+1/2, -z+1/2
C6-H6···O1	1.08	3.565(3)	2.71	136	-x+3/2, y+1/2, -z+1/2
C12-H12···F1	1.08	3.493(2)	2.59	140	-x+1/2, y-1/2, -z+1/2
C6-H6···F1	1.08	3.756(3)	2.76	153	-x+1/2, y-1/2, -z+1/2

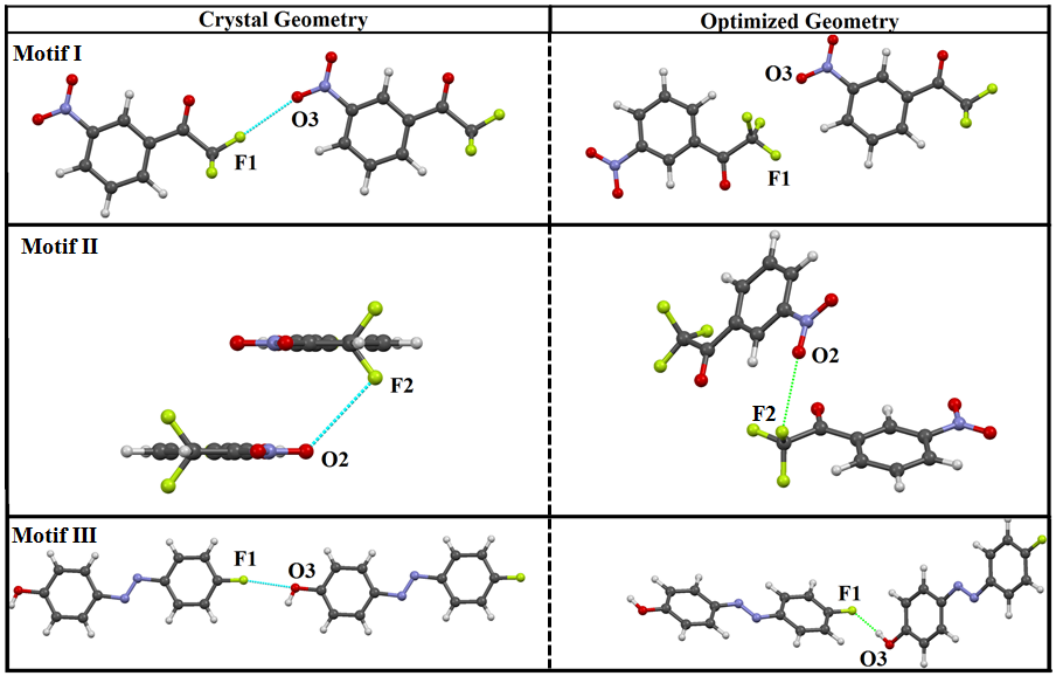

Figure S8 Optimized geometry of Motif **I**, **II** and **III**.

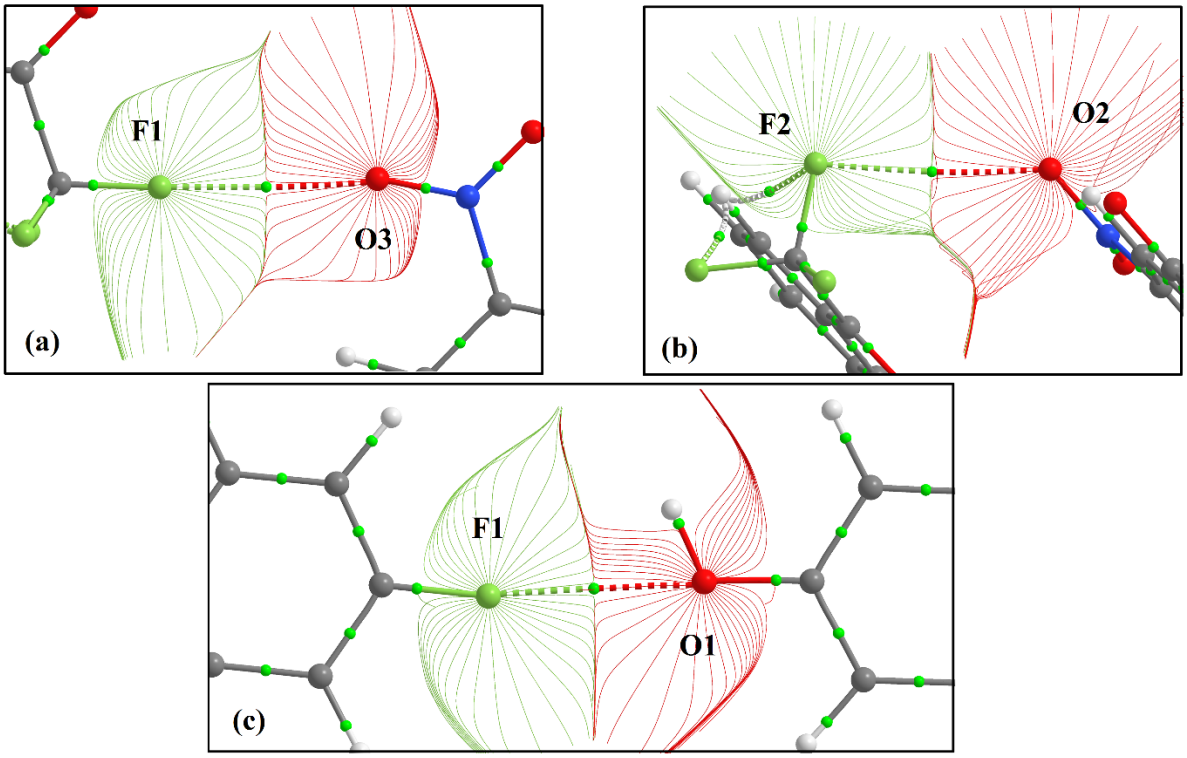

Figure S9 Gradient vector field plot (from AIMALL) of intermolecular region depicting F···O contact in motifs (a) **I**, (b) **II** and (c) **III**.

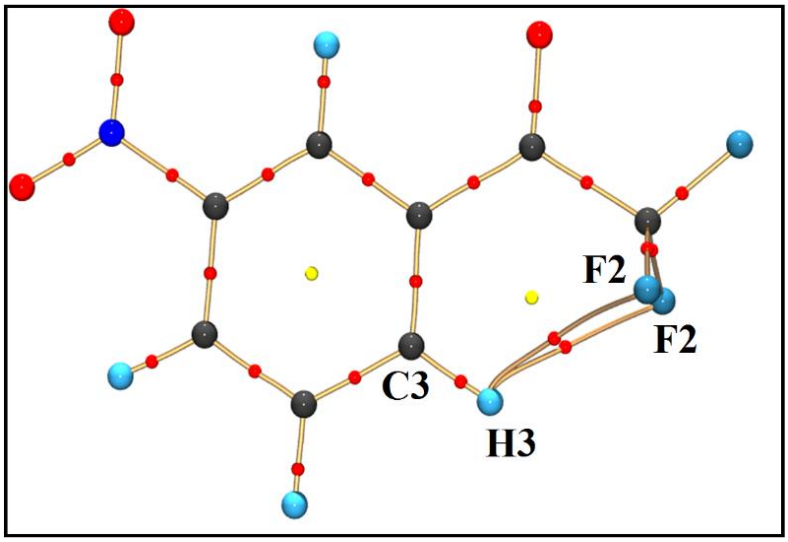

Figure S10 The molecular graph for an isolated molecule of **A1** obtained using XD. (Red and yellow dots represents BCP and RCP respectively).

Table S2 Topological features for intramolecular C-H···F interaction obtained using AIMALL for an isolated molecule of **A1**.

Interaction	Method	Geometry (Å, °)	R_{ij} (Å)	ρ (e/Å^3)	$\nabla^2\rho$ (e/Å^5)	λ_3 (e/Å^5)	ε	V_b (a.u)	G_b (a.u)	|V|/G	DE^V kcal/mol
C-H···F	XD	2.45, 113	2.466	0.076	1.080	1.58	0.16	-0.0049	0.0080	0.61	1.534
	TOPOND		2.538	0.069	1.025	1.36	0.14	-0.0063	0.0084	0.75	1.985
	AIMALL		2.523	0.071	1.049	1.39	0.18	-0.0082	0.0095	0.86	2.573

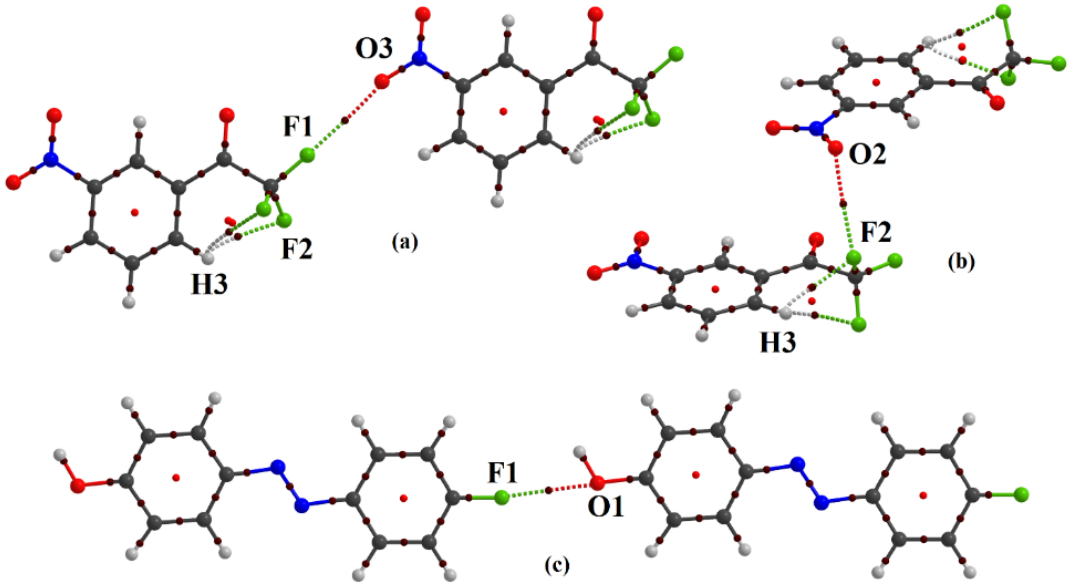

Figure S11 The molecular graph obtained using AIMALL for the motif (a) **I**, (b) **II** and (c) **III** (brown and red dots represents BCP and RCP respectively).

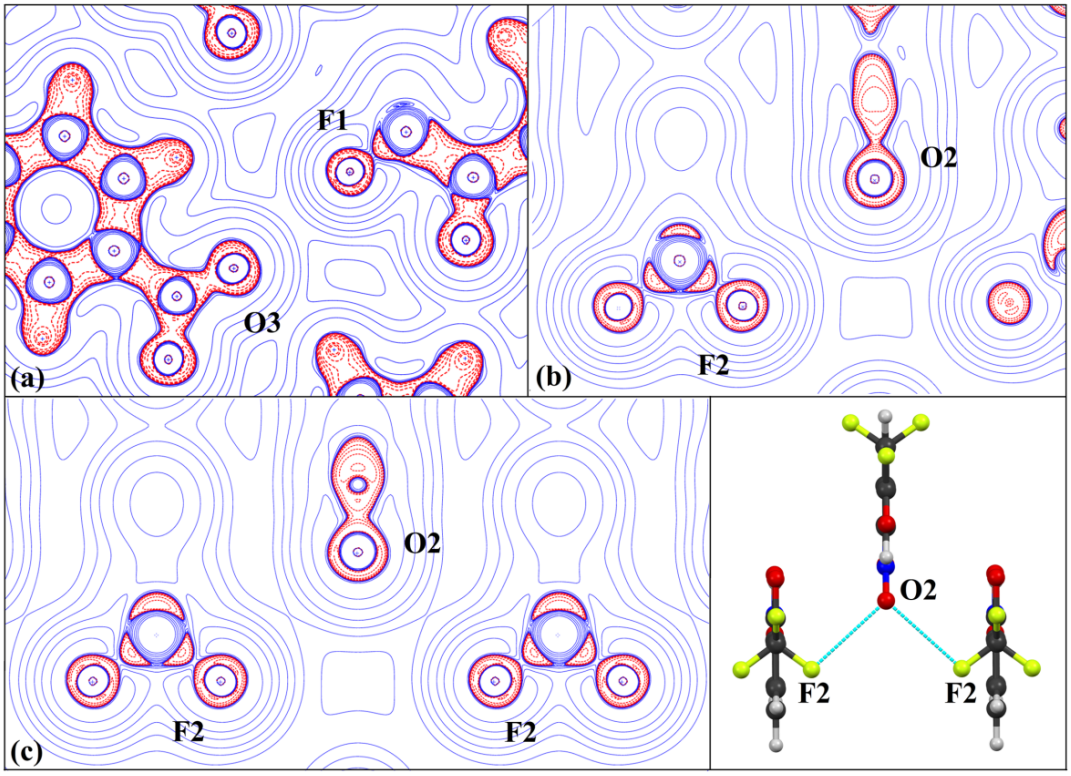

Figure S12 2-D Laplacian diagram plotted with TOPOND98 (B3LYP/6-311G**) where, (a) motif **I** with F1···O3, (b) motif **II** with F2···O2 and (c) alternative view of motif **II** based F···O contact (bifurcated), where F2-O2-F2 are in one plane. Red lines (broken) are charge concentrated (CC) region, whereas blue line (solid) is charge depleted (CD) region.

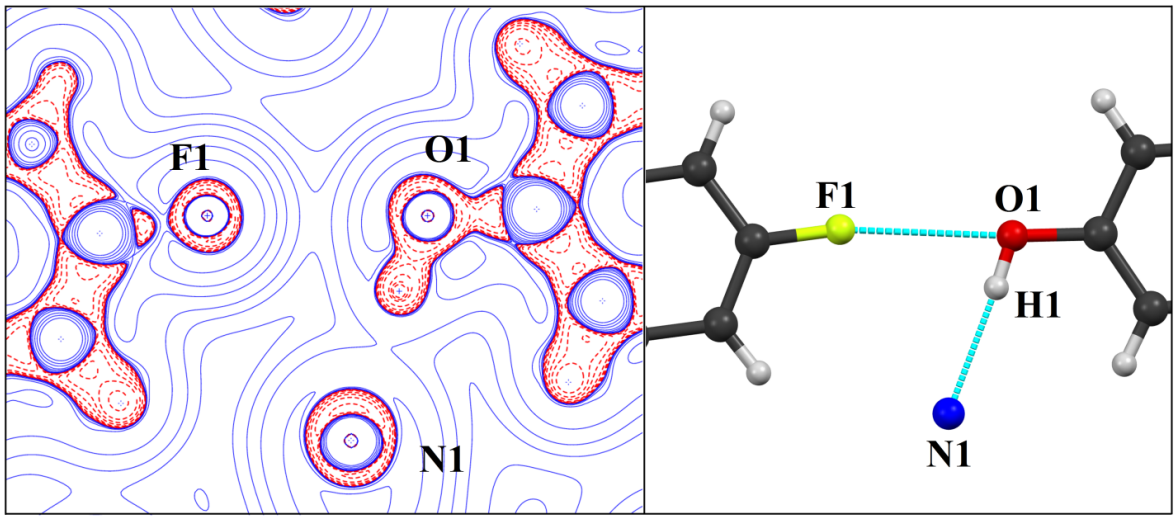

Figure S13 2-D Laplacian diagram plotted with TOPOND98 (B3LYP/6-311G**) representing F1···O1 contact present in motif **III** in **A2** crystal system.

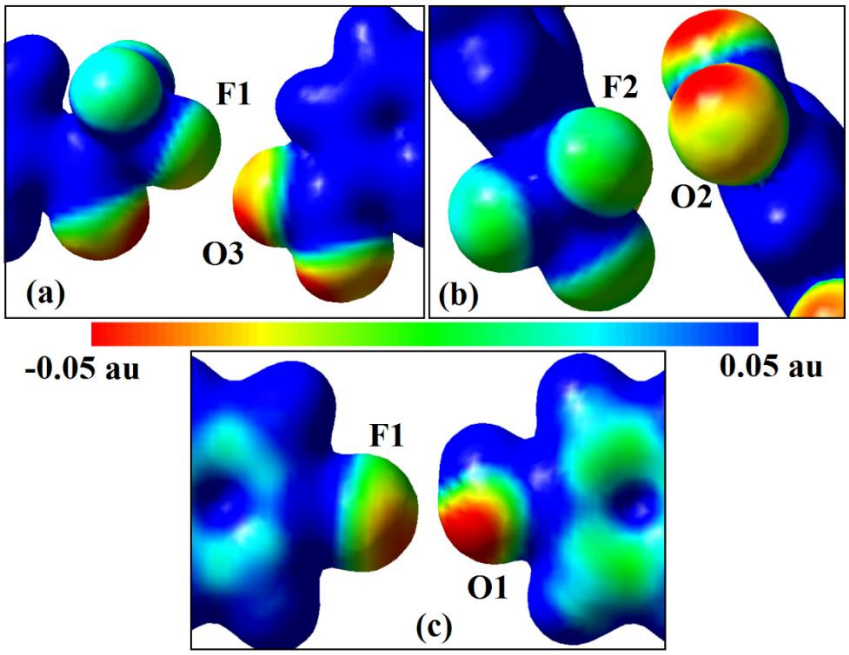

Figure S14 Electrostatic potential for the motif (a) **I**, (b) **II** and (c)**III** mapped on charge density isosurface value of ±0.05 au. (obtained from gas phase calculations at "crystal geometry" at MP2/6-311G++(d,p) level of theory).

S3. Cambridge Structural Database (CSD) Searches:

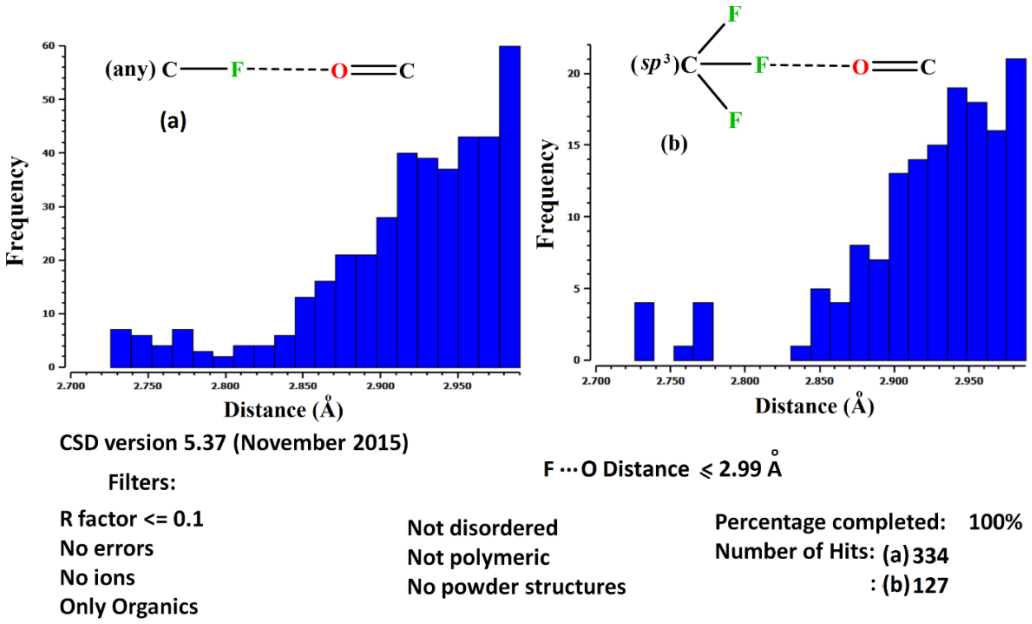

Figure S15 Distribution plot for intermolecular C(any/sp^3)-F···O=C contact obtained from CSD search.

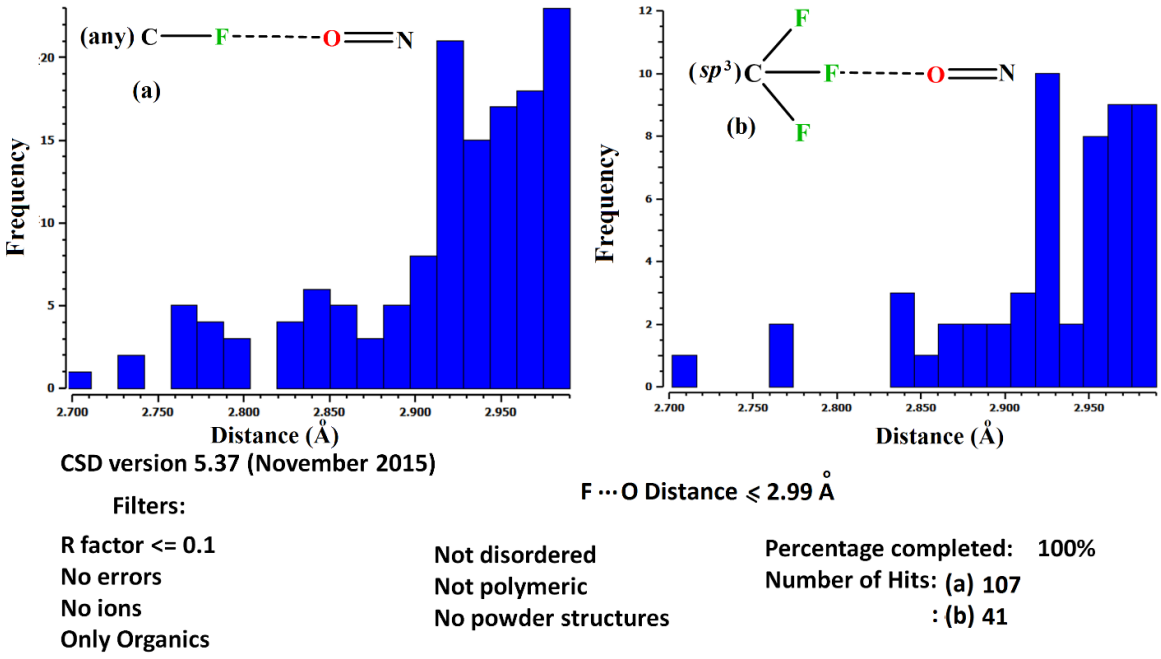

Figure S16 Distribution plot for intermolecular C(any/sp^3)-F···O=N contact obtained from CSD search.

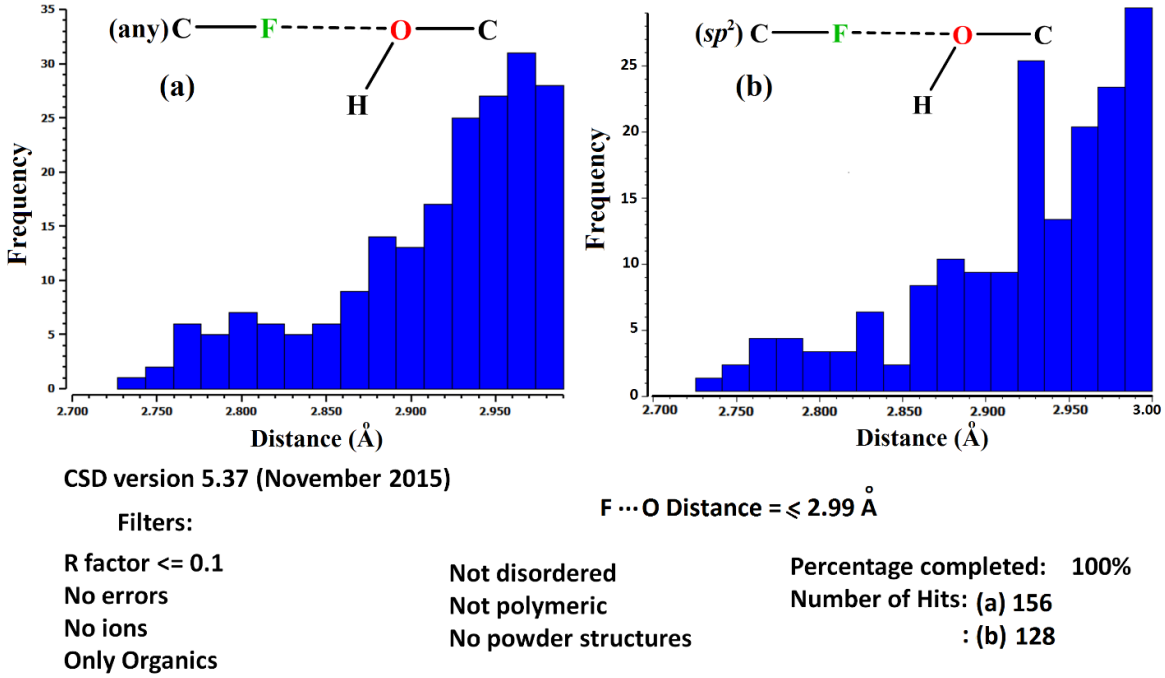

Figure S17 Distribution plot for intermolecular C(*any*/sp^2)-F···OH-C contact obtained from CSD search.

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