Synthesis of Crystalline Fluoro-Functionalized Imines, Single Crystal Investigation, Hirshfeld Surface Analysis and Theoretical Exploration

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Table S1. SC-XRD experimental details of **MFIP** and **FPIN**

Crystal data	**MFIP**	**FPIN**
CCDC	2091268	2091269
Chemical formula	$C_{15}H_{12}F_3NO_2$	$C_{17}H_{12}FNO_2$
M_r	295.26	265.28
Crystal system, space group	Orthorhombic, *Aba*2	Monoclinic, $P2_1$
Temperature (K)	296	296
a, b, *c* (Å)	26.638 (3), 13.754 (2), 7.5085 (9)	7.1922 (18), 7.5334 (16), 12.289 (3)
α, β, γ°	90, 90, 90	90, 100.816 (11), 90
V (Å^3)	2751.0 (6)	654.0 (3)
Z	8	2
Density (calculated)g/cm^{-3}	1.426	1.347
F(000)	1216	276
Radiation type	Mo *K*α	Mo *K*α
Wavelength (λ)	0.71073 Å	0.71073 Å
μ (mm^{-1})	0.122	0.094
Crystal size (mm)	0.40 × 0.24 × 0.16	0.36 × 0.26 × 0.17
Data Collection		
Diffractometer	Bruker APEXII CCD diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	multi-scan (SADABS; Bruker, 2007)	multi-scan (SADABS; Bruker, 2007)

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6467, 2412, 1827	5583, 2376, 1587
R_{int}	0.032	0.039
Theta range for data collection (°)	2.962 to 26.991	2.883 to 27.243
Index ranges	-34≤ h ≤22, -16≤ k ≤17, -9 ≤ l ≤5	-9≤ h ≤9, -6≤ k ≤9, -15 ≤ l ≤15
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.639	0.644
Data Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.084, 1.02	0.045, 0.114, 1.00
No. of reflections	2412	2376
No. of parameters	249	182
No. of restraints	137	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.10, −0.16	0.15, −0.14

Table S2. Enrichment ratio for pair of chemical species (X, X) and (X, Y) in compound **MFIP**. Enrichment ratio for a pair of chemical species (X, Y) is obtained by dividing the proportion of actual contacts in the crystal and theoretical proportion of random contacts. Enrichment ratio is not calculated for those contacts having random contact is less than 0.9%.

Contact %	**Atom**	**H**	**C**	**N**	**O**	**F**
	H	25.1	20	1.3	11.1	33.3
	C	20	4.6	1.5	1.8	0.6
	N	1.3	1.5	0	0.1	0
	O	11.1	1.8	0.1	0	0.6
	F	33.3	0.6	0	0.6	0
Surface% S_X		57.95	16.55	1.45	6.8	17.25
Random Contacts % R_{XY}	**Atom**	**H**	**C**	**N**	**O**	**F**
	H	33.58	-	-	-	-
	C	19.18	2.74	-	-	-
	N	1.68	0.48	0.02	-	-
	O	7.88	2.25	0.20	0.46	-
	F	19.99	5.71	0.50	2.35	2.98
Enrichment ratio E_{CH}	**Atom**	**H**	**C**	**N**	**O**	**F**
	H	0.75	-	-	-	-
	C	1.04	1.68	-	-	-
	N	0.77	3.13	-	-	-
	O	1.41	0.80	0.51	0.00	
	F	1.67	0.11	0.00	0.26	0.00

Table S3. Enrichment ratio for pair of chemical species (X, X) and (X, Y) in compound **FPIN**.

Contact %	**Atom**	**H**	**C**	**N**	**O**	**F**
	H	36.1	35.8	2.4	7.5	9.8
	C	35.8	3.5	0.4	0.6	3.8
	N	2.4	0.4	0	0	0
	O	7.5	0.6	0	0	0
	F	9.8	3.8	0	0	0
Surface% S_X		63.85	23.8	1.4	4.05	6.8
Random Contacts % R_{XY}	**Atom**	**H**	**C**	**N**	**O**	**F**
	H	40.77	-	-	-	-
	C	30.39	5.66	-	-	-
	N	1.79	0.67	0.02	-	-
	O	5.17	1.93	0.11	0.16	-
	F	8.68	3.24	0.19	0.55	0.46
Enrichment ratio E_{CH}	**Atom**	**H**	**C**	**N**	**O**	**F**
	H	0.89	-	-	-	-
	C	1.18	0.62	-	-	-
	N	1.34	-	-	-	-
	O	1.45	0.31	-	-	-
	F	1.13	1.17	-	-	-

Table S4. Natural bond orbital (NBO) analysis of investigated compound **MFIP**

Donor(i)	**Type**	**Acceptor(j)**	**Type**	**E(2)[a] [kcal/mol]**	**E(J)E(i)[b](a.u)**	**F(I,j)[e](a.u)**
C26-C28	π	C30-C31	π*	23.1	0.30	0.074
C8-C9	π	N7-C21	π*	22.62	0.29	0.076
C23-C24	π	C30-C31	π*	21.97	0.30	0.073
C8-C9	π	C13-C15	π*	21.30	0.31	0.074
C30-C31	π	C26-C28	π*	20.83	0.31	0.072
C30-C31	π	C23-C24	π*	19.87	0.31	0.071
C10-C11	π	C13-C15	π*	18.71	0.32	0.069
C13-C15	π	C8-C9	π*	17.23	0.29	0.066
N7-C21	π	C23-C24	π*	10.33	0.39	0.061
C23-C24	π	N7-C21	π*	7.86	0.29	0.045
N7-C21	π	C8-C9	π*	6.19	0.39	0.048
C8-C9	π	C8-C9	π*	1.82	0.29	0.021

C30-C31	σ	C28-C30	σ*	5.96	1.30	0.079
C28-C30	σ	C30-C31	σ*	5.83	1.31	0.078
O4-H5	σ	C9-C10	σ*	5.55	1.29	0.076
C8-C21	σ	N7-C23	σ*	4.99	1.14	0.067
C31-H32	σ	C23-C24	σ*	4.48	1.10	0.063
C15-H16	σ	C11-C13	σ*	4.09	1.10	0.060
C28-H29	σ	C24-C26	σ*	3.87	1.11	0.059
C13-C15	σ	C11-C13	σ*	3.48	1.30	0.06
C9-C10	σ	C8-C21	σ*	3.15	1.22	0.055
N7-C21	σ	C8-C21	σ*	2.73	1.41	0.056
C30-C33	σ	C23-C31	σ*	2.48	1.28	0.050
C23-C31	σ	N7-C23	σ*	1.99	1.16	0.043
O6-C10	σ	C10-C11	σ*	1.69	1.51	0.045
C30-C31	σ	C31-H32	σ*	1.47	1.14	0.037
C15-H16	σ	C13-C15	σ*	1.09	1.14	0.031
C28-H29	σ	C26-C28	σ*	0.99	1.12	0.03
C15-H16	σ	C8-C15	σ*	0.71	1.08	0.025
F2-C33	σ	F3-C33	σ*	0.68	1.33	0.027
O4	LP(2)	C8-C9	π*	39.52	0.36	0.113
O6	LP(2)	C10-C11	π*	32.25	0.36	0.102
N7	LP(1)	O4-H5	σ*	19.06	0.80	0.113
N7	LP(1)	C21-H22	σ*	11.81	0.74	0.086
F1	LP(3)	F2-C33	σ*	10.99	0.72	0.08
O6	LP(1)	C10-C11	σ*	7.41	1.15	0.083
F1	LP(2)	C30-C33	σ*	6.55	0.84	0.067
N7	LP(1)	C23-C24	σ*	5.91	0.95	0.069
F1	LP(2)	F2-C33	σ*	4.84	0.72	0.053
O6	LP(1)	C17-H19	σ*	3.37	0.94	0.051
N7	LP(1)	C8-C21	σ*	2.55	0.89	0.044
O6	LP(1)	C17-H18	σ*	0.81	0.92	0.025
N7	LP(1)	C23-C31	σ*	0.66	0.95	0.023
F1	LP(1)	C30-C33	σ*	0.52	1.49	0.025

Table S5. Natural bond orbital (NBO) analysis of investigated compound **FPIN**

Donor(i)	**Type**	**Acceptor(j)**	**Type**	**E(2)[a] [kcal/mol]**	**E(J)E(i)[b](a.u)**	**F(I,j)[e](a.u)**
C5-C20	π	N4-C21	π*	26.35	0.29	0.08
C27-C29	π	C23-C31	π*	23.15	0.29	0.074
C23-C31	π	C24-C25	π*	22.83	0.30	0.074
C6-C8	π	C5-C20	π*	22.43	0.30	0.076
C27-C29	π	C24-C25	π*	21.85	0.29	0.071
C24-C25	π	C23-C31	π*	20.39	0.31	0.072
C10-C19	π	C11-C13	π*	19.44	0.30	0.071
C15-C17	π	C11-C13	π*	17.78	0.31	0.067

C10-C19	π	C5-C20	π*	14.58	0.28	0.057
C6-C8	π	C10-C19	π*	13.9	0.31	0.062
C5-C20	π	C6-C8	π*	12.08	0.31	0.057
N4-C21	π	C23-C31	π*	11.24	0.38	0.064
C23-C31	π	N4-C21	π*	9.09	0.29	0.047
N4-C21	π	C5-C20	π*	6.02	0.38	0.046
C5-C20	π	C5-C20	π*	3.48	0.29	0.029
C11-H12	σ	C10-C19	σ*	5.20	1.08	0.067
C15-H16	σ	C17-C19	σ*	5.02	1.08	0.066
C24-C25	σ	C23-C24	σ*	4.99	1.29	0.072
C17-C19	σ	C19-C20	σ*	4.15	1.23	0.064
C21-H22	σ	C5-C20	σ*	3.96	1.11	0.059
C25-H26	σ	C27-C29	σ*	3.69	1.12	0.058
C6-C8	σ	C10-C11	σ*	3.02	1.31	0.056
C5-C20	σ	C17-C19	σ*	2.95	1.28	0.055
C10-C19	σ	C17-H18	σ*	2.51	1.11	0.047
C8-C10	σ	C11-C13	σ*	1.99	1.31	0.046
C27-C29	σ	C27-H28	σ*	1.27	1.14	0.034
C25-H26	σ	C25-C27	σ*	1.07	1.11	0.031
C17-H18	σ	C15-H16	σ*	0.88	0.94	0.026
N4-C21	σ	C21-H22	σ*	0.64	1.27	0.026
C15-H16	σ	C13-C15	σ*	0.52	1.09	0.021
O2	LP(2)	C5-C20	π*	44.37	0.36	0.118
F1	LP(3)	C24-C25	π*	19.75	0.46	0.092
N4	LP(1)	C21-H22	σ*	11.29	0.75	0.084
O2	LP(1)	C5-C20	σ*	8.33	1.15	0.088
F1	LP(2)	C23-C24	σ*	7.01	1.00	0.075
N4	LP(1)	C23-C31	σ*	6.52	0.94	0.072
O2	LP(3)	C5-C6	σ*	5.26	1.02	0.073
N4	LP(1)	C23-C31	π*	4.70	0.4	0.041
N4	LP(1)	C20-C21	σ*	2.58	0.89	0.044
O2	LP(3)	O2-C5	σ*	1.39	0.88	0.035
N4	LP(1)	C23-C24	σ*	1.20	0.93	0.031
O2	LP(1)	C5-C6	σ*	0.73	1.14	0.026

Table S6. Dipole polarizability, Polarizability, second order hyperpolarizability and their major contributing tensor (a.u) of the entitled compound

Dipole moment			**Polarizability**			**second order hyperpolarizabilities**		
	MFIP	**FPIN**		**MFIP**	**FPIN**		**MFIP**	**FPIN**
μ_x	1.56	-0.30	α_{xx}	392.63	457.07	γ_{xx}	1.90×10^5	2.95×10^5
μ_y	1.73	-1.48	α_{yy}	237.95	308.85	γ_{yy}	1.24×10^4	3.26×10^4
μ_z	0.06	-0.13	α_{zz}	126.69	113.26	γ_{zz}	5.67×10^3	2.50×10^3
μ_{total}	2.35	1.52	$\langle\alpha\rangle$	252.42	293.06	$\langle\gamma\rangle$	2.08×10^5	3.31×10^5

Table S7: Wavelength (λ_{max}), energy and oscillator strength of **MFIP**

E(eV)	λ_{max} (nm)	*f*	MO contributions
3.49	355.35	0.127	H→L (98%)
3.97	312.00	0.572	H-1→L (88%), H-4→L (3%), H-2→L (7%)
4.53	273.89	0.19	H-4→L (14%), H-2→L (73%), H-1→L (9%)
4.71	263.12	0.003	H-3→L (23%), H-1→L+1 (26%), H→L+1 (44%), H-3→L+2 (3%), H-2→L+1 (3%)
4.91	252.41	0.001	H-3→L (23%), H-1→L+1 (16%), HOMO→L+1 (54%), H-2→L+1 (4%)
5.26	235.93	0.032	H→L+2 (85%) H-1→L+3 (7%)

Table S8: Wavelength (λ_{max}), energy and oscillator strength of **FPIN**

E(eV)	λ_{max} (nm)	*f*	MO contributions
3.34	371.28	0.578	H→L (98%)
3.945	314.28	0.128	H-1→L (82%), H-4→L (2%), H-2→L (5%), H→L+2 (6%)
4.08	303.98	0.015	H-2→L (79%), H-4→L (5%), H-1→L (6%), H→L+2 (4%)
4.39	282.55	0.042	H→L+1 (91%), H-1→L+2 (3%)
4.53	273.91	0.006	H-3→L (76%),H-4→L (4%), H-3→L+1 (2%), H-2→L (3%), H-2→L+3 (3%), H→L+3
4.76	260.60	0.072	H-4→L (60%), H-1→L+1 (12%),H-3→L (5%), H-2→L (8%), H→L+2 (7%)

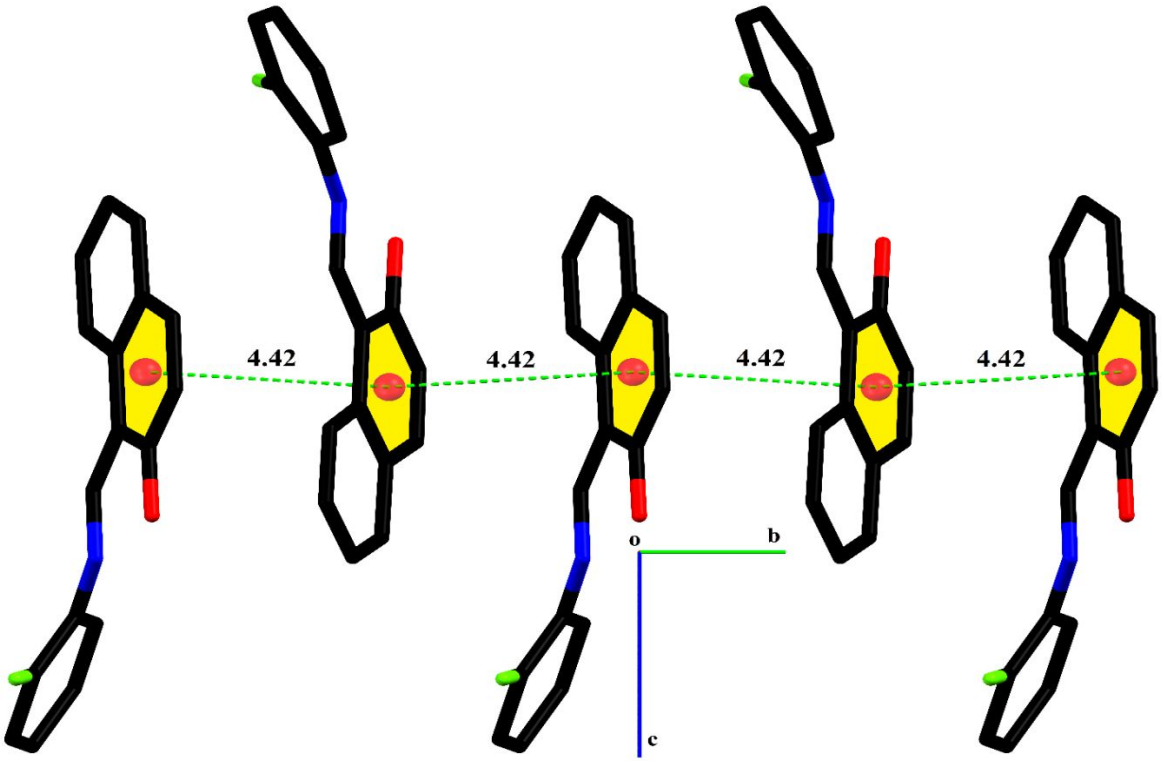


Figure S1. Off-set π···π stacking interaction in the crystal packing of **FPIN**. Distances shown for measured in Å. For clarity, H-atoms are not shown.

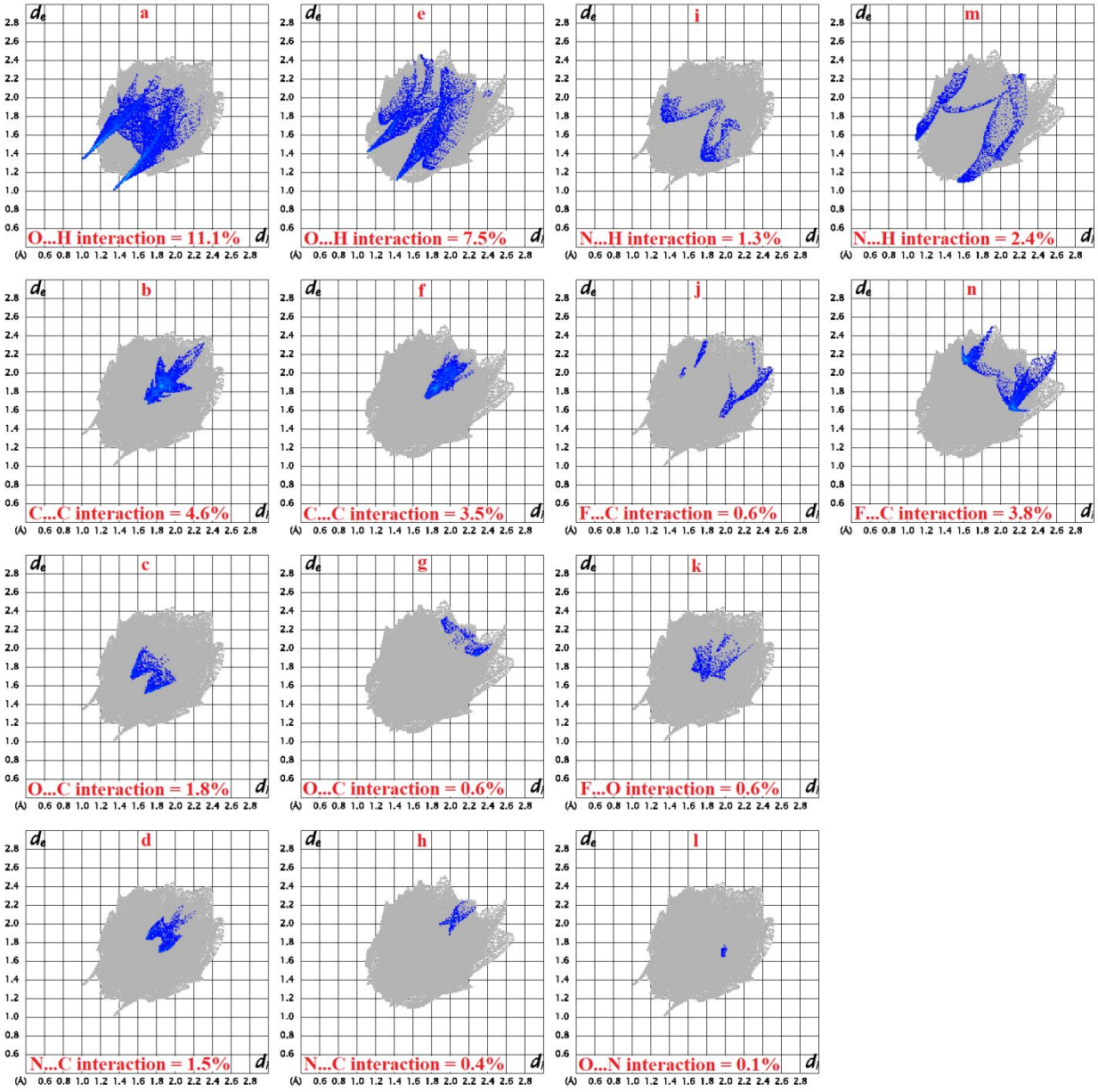


Figure S2. Comparison of the remaining 2D plots of **MFIP (a-d, i-h)** with **FPIN (e-h, m,n)**.

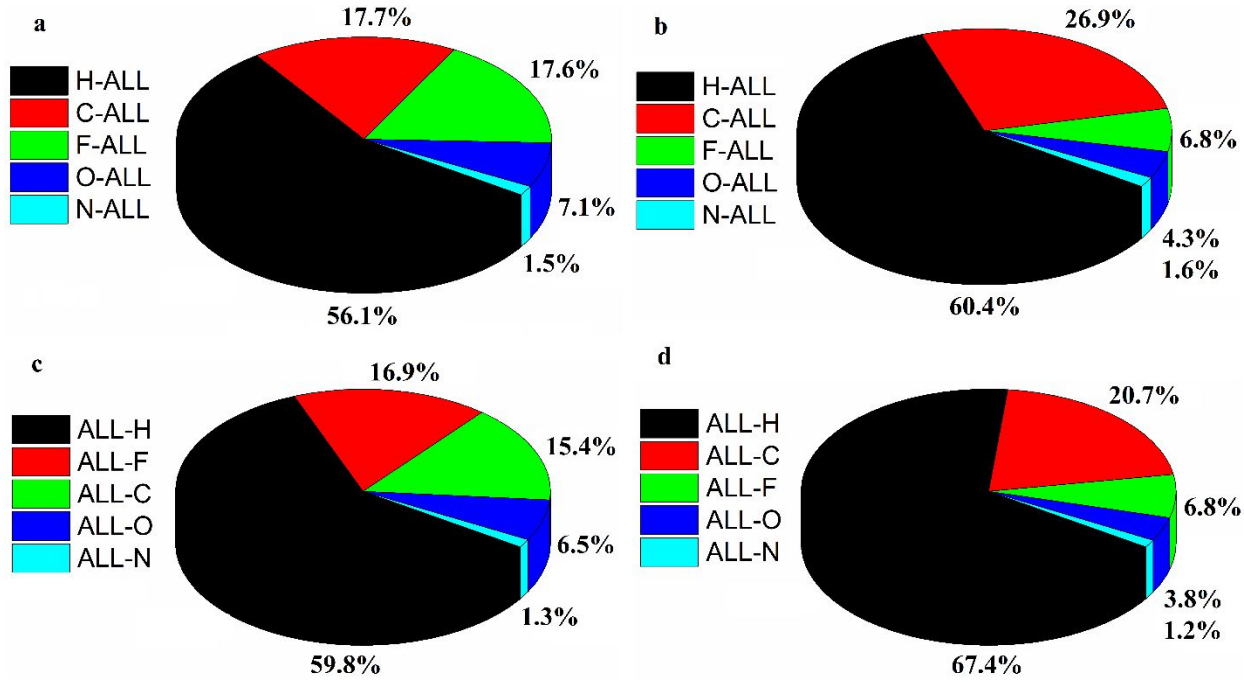


Figure S3. (a-b) Summary of interactions of an atom present inside HS with the neighboring molecules for **MFIP** and **FPIN**, respectively. **(c-d)** Summary of interactions of ALL the atoms present inside HS with an atom of surrounding molecules for **MFIP** and **FPIN**, respectively.

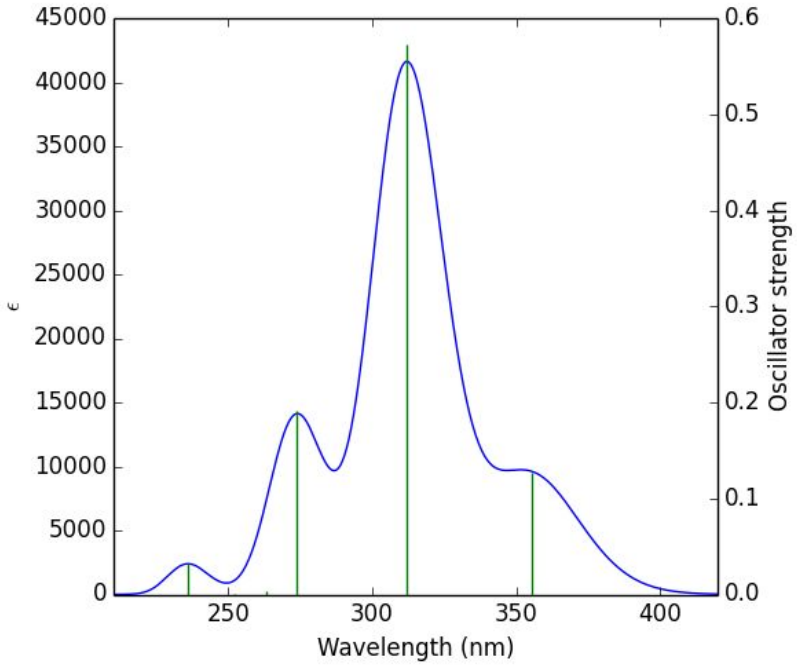


Figure S4: Simulated absorption spectra of **MFIP**

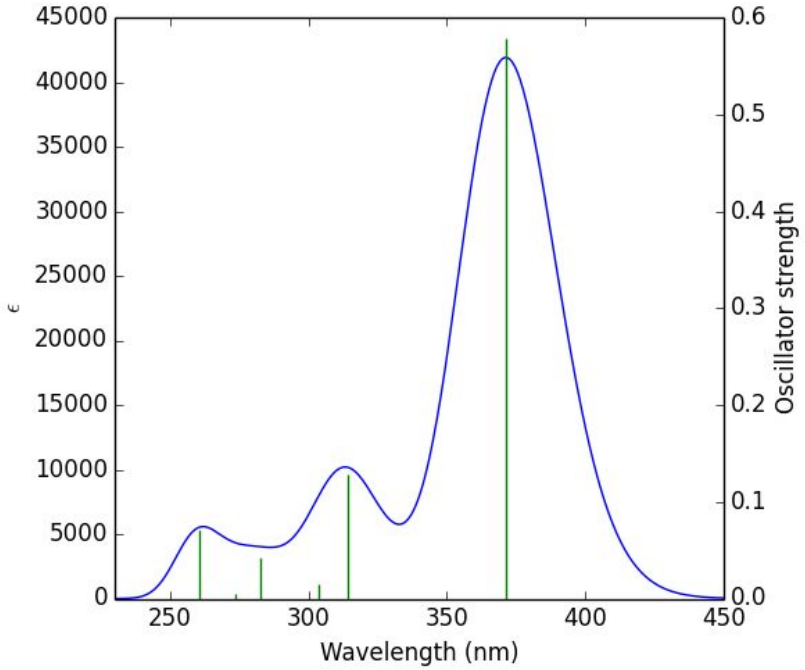
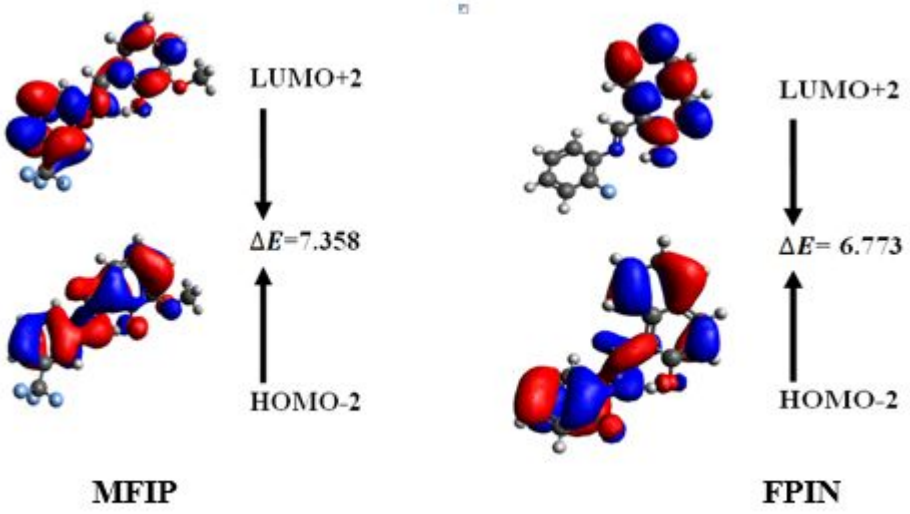


Figure S5: Simulated absorption spectra of **FPIN**



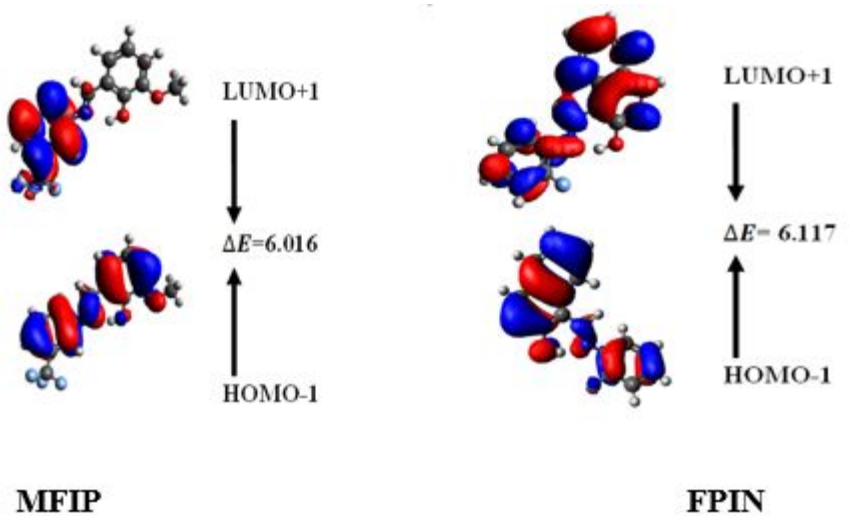


Figure S6. Frontier molecular orbitals of entitled compounds.

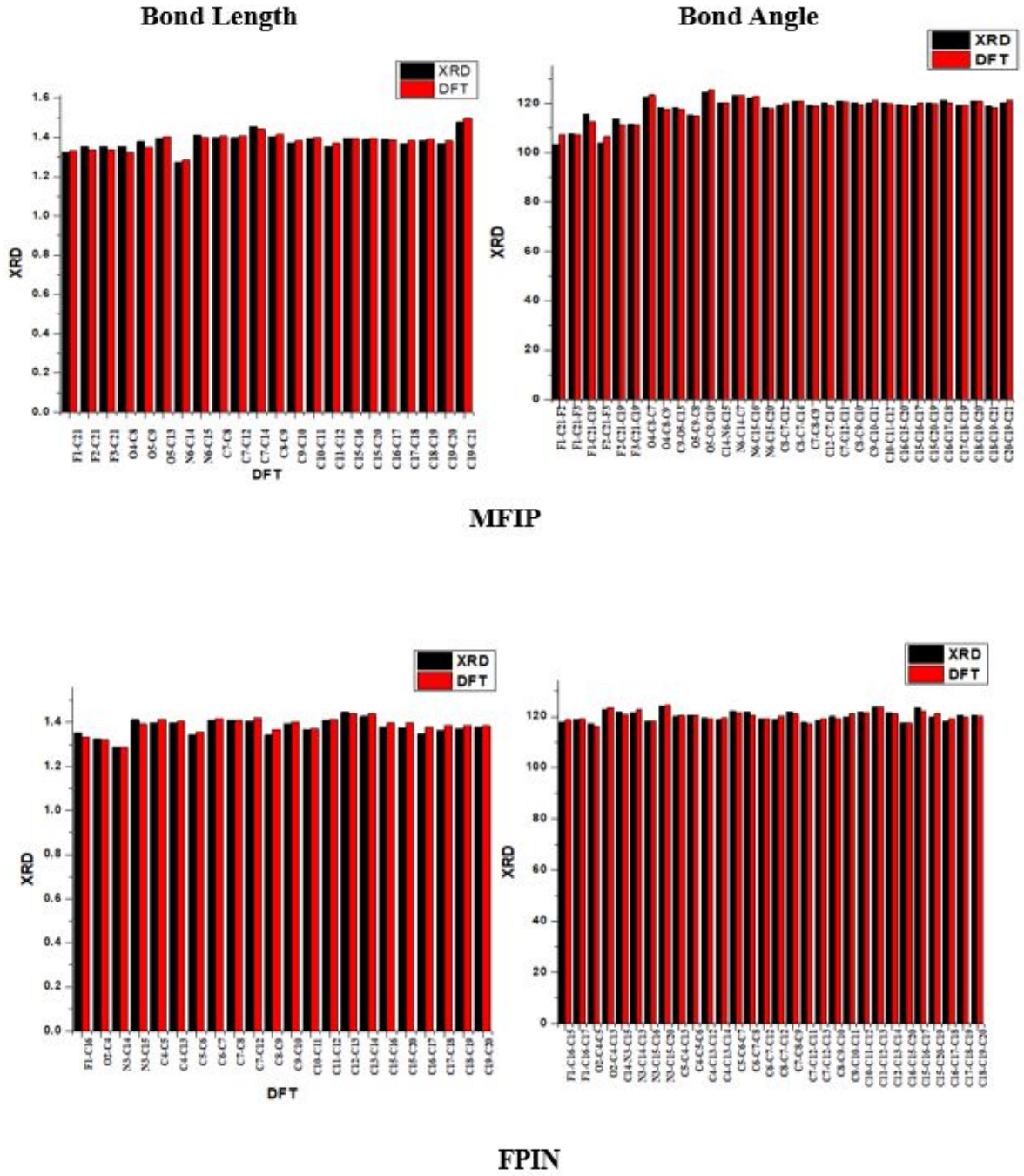


Figure S7. Bond Lengths in Å and Bond Angles in ° for **MFIP** and **FPIN.**