Turning the Dielectric Response by Co-crystallisation of Sumanene and Its Fluorinated Derivative

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Contents

1. General experimental information

All chemicals were reagent grade and used as received if not mentioned. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 NMR spectrometer (400 MHz). Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^{1}H ($CDCl_3$: $^1H(\delta) = 7.26$ ppm). TG-DTA was carried out using a Rigaku Thermo Plus TG8120 thermal analysis station with Al_2O_3 reference under N_2. Differential scanning calorimetry (DSC) analysis was performed on a Mettler thermal analysis DSC1-TS station using an Al_2O_3 reference under N_2. Temperature-dependent powder X-ray diffraction patterns were collected on a Rigaku MiniFlex 600 diffractometer using Cu Kα radiation at $\lambda = 0.154187$ nm. Temperature-dependent dielectric constants were measured using the two-probe AC impedance method between 1000 and 1000 × 103 Hz (HP 4194A impedance/gain-phase analyzer, Hewlett-Packard). Electrical contacts were prepared using gold paste (Tokuriki 8560) to attach the 25 μm ϕ gold wires to the 3 mm ϕ compressed pellet. Temperature control between 298 and 423 K was carried out using a Linkam LTS350 hot stage.

2. Co-crystallization experiment

Table S1. Cell parameters of sumanene, difluorosumanene and hexafluorosumanene from single crystal X-ray data.

Compound	**Cell parameter (Å)**		**Cell volume (Å^3)**
	a and *b*	*c*	
Sumanene	16.575	7.580	1803.45
Difluorosumanene	16.735	7.889	1913.49
Hexafluorosumanene	17.064	8.333	2101.33

Co-crystallization of F6-Sum and Sum

Both **F6-Sum** (5.0 mg) in chloroform (1 mL) and **Sum** (3.5 mg) in chloroform (1 mL) were prepared (0.0134 mmol/mL each). They were mixed in various loading ratios (v/v) shown below and were left stand for 24 h.

Table S2. Co-crystallization trials composed of **F6-Sum** and **Sum**

Loading ratio (F6-Sum:Sum)	**Result**
75:25[a]	Only **Sum** crystal
80:20[a]	Only **Sum** crystal
83:17[a]	No single crystal
50:50[b]	No single crystal

[a] Prepared by slow diffusion method with hexane at 25 °C.

[b] Prepared by slow evaporation method at 25 °C.

Co-crystallization of F2-Sum and Sum

Both **F2-Sum** (5.0 mg) in chloroform (2 mL) and **Sum** (4.4 mg) in chloroform (2 mL) were prepared (0.0166 mmol/mL each). They were mixed in various loading ratios (v/v) shown below and were left stand for 24 h at 25 °C to generate the co-crystals by slow evaporation of the solvent. The same procedure was applied for the scale up preparation with using 15 mg of **F2-Sum** in chloroform (6 mL) and 13.2 mg **Sum** in chloroform (6 mL) and mix them in various loading ratios (v/v) shown below and were left stand for 48 h at 25 °C to generate the co-crystals by slow evaporation of the solvent.

Table S3. Structural parameters of the co-crystals composed of **F2-Sum** and **Sum** prepared in small scale.

Loading ratio (F2-Sum:Sum)	**^{1}H NMR Ratio**[a]	**Cell parameter (Å)**		**X-ray ratio**	**Bowl Depth (Å)**	**Bowl to bowl distance (Å)**	**Crystal No.**
		a and *b*	*c*				
87:13[b]	83:17	16.7155(6)	7.8787(3)	81:19	1.161	3.939	1
		16.7139(6)	7.8744(3)	83:17	1.160	3.937	2
75:25[b]	75:25	16.7002(5)	7.8414(3)	71:29	1.153	3.921	3
		16.7127(9)	7.8468(5)	70:30	1.155	3.923	4
50:50	50:50	16.6500(6)	7.7389(3)	40:60	1.138	3.869	5
25:75	10:90	16.6137(8)	7.6344(6)	0:100	1.120	3.812	6
13:87[b]	4:96	16.5929(7)	7.6175(3)	0:100	1.118	3.809	7
		16.5959(7)	7.6226(3)	0:100	1.119	3.811	8

[a] Based on several single crystals prepared in the same batch. The NMR charts are shown in later page.

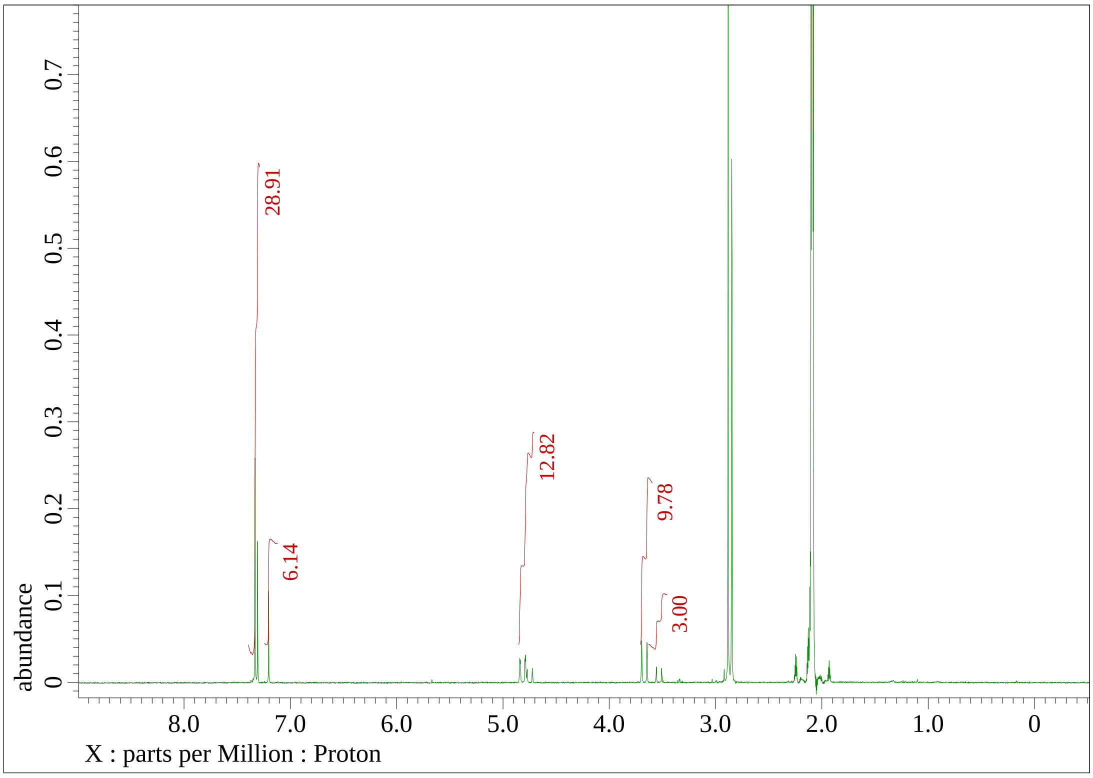
[b] Checked two different single crystals obtained from the same crystallization vial.

Table S4. Structural parameters of the co-crystals composed of **F2-Sum** and **Sum** prepared in a large scale.

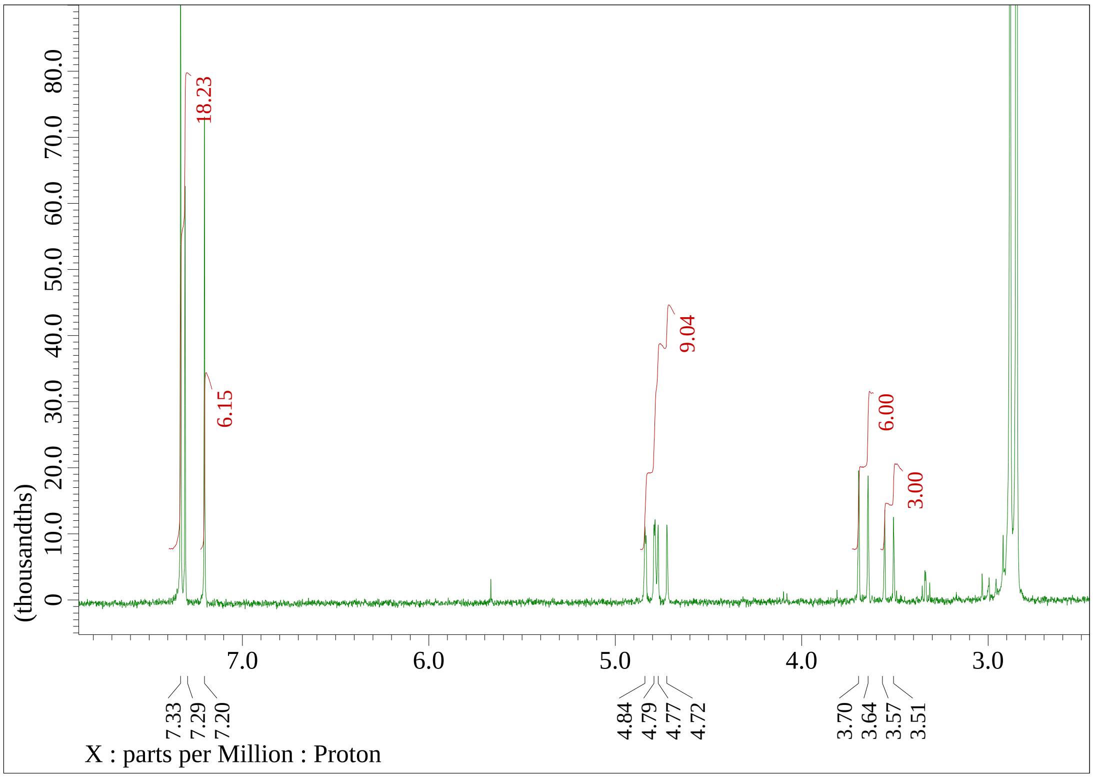
Loading ratio (F2-Sum:Sum)	**Cell parameter (Å)**		**X-ray ratio**[a] **(F2-Sum:Sum)**	**Bowl depth (Å)**	**Bowl-to-bowl Distance (Å)**	**Crystal No.**
	a and *b*	*c*				
100:0	16.735(2)	7.889(2)	100:0	1.160	3.945	Ref. S1
87:13	16.755(1)	7.9305(7)	78:22	1.147	3.966	9
	16.723(1)	7.8675(7)	63:37	1.148	3.934	10
	16.740(2)	7.9040(8)	75:25	1.156	3.952	11
50:50	16.6665(3)	7.7333(2)	38:62	1.136	3.867	12
	16.6836(6)	7.7867(3)	46:54	1.143	3.894	13
	16.6650(5)	7.7508(3)	40:60	1.137	3.876	14
35:65	16.6264(4)	7.6483(2)	11:89	1.117	3.827	15
	16.6293(5)	7.6551(2)	11:89	1.122	3.828	16
	16.6267(4)	7.6522(2)	11:89	1.121	3.825	17
0:100	16.5754(5)	7.5796(5)	0:100	1.114	3.790	Ref. S2

[a] Checked three different single crystals obtained from the same crystallization vial.

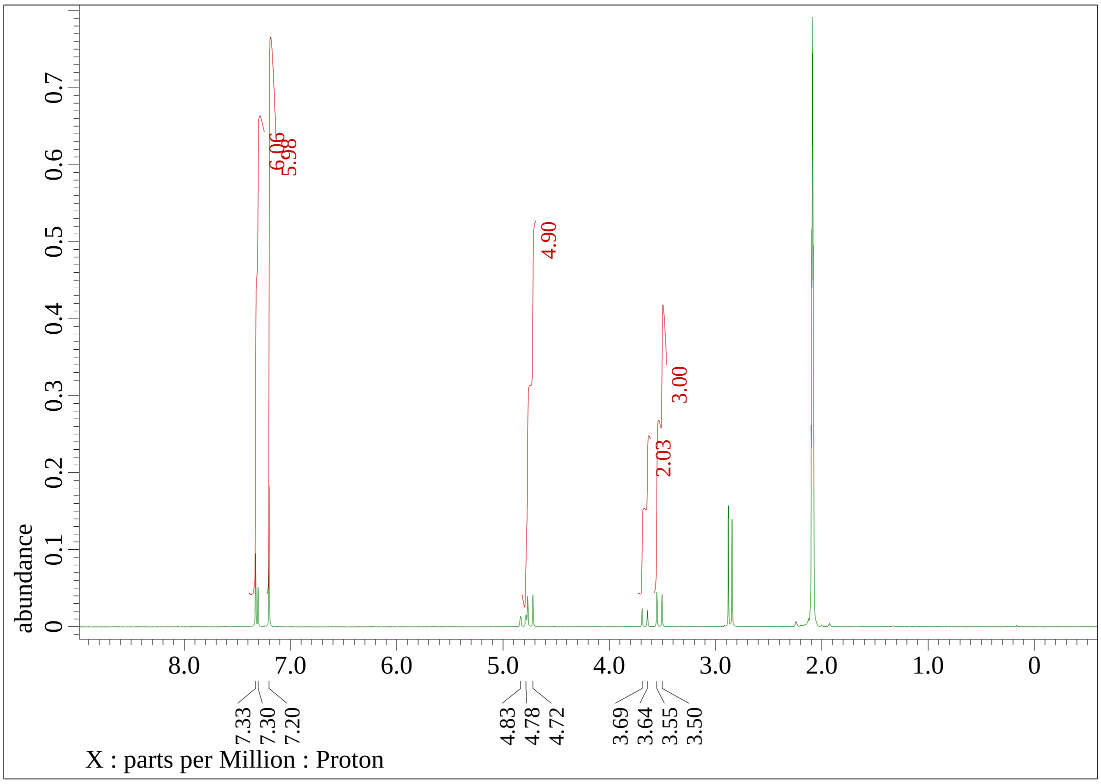
^{1}H-NMR of the co-crystal of **F2-Sum**:**Sum** = 87:13 (loading ratio):



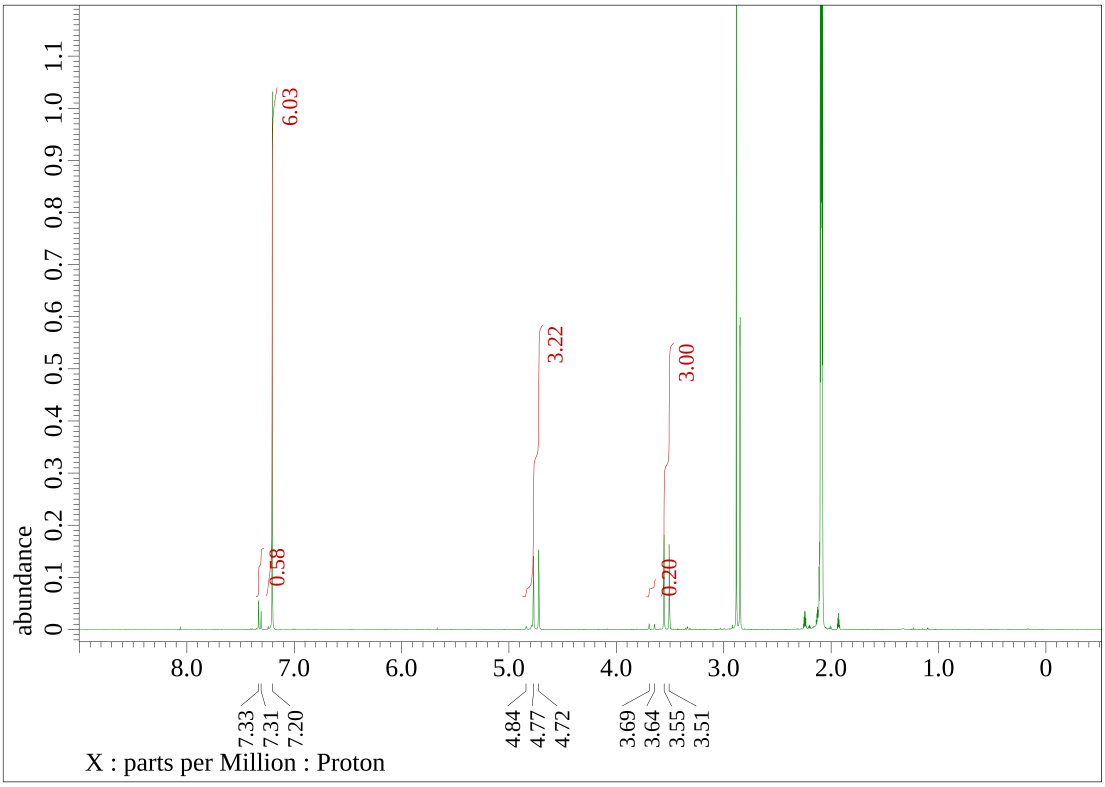
^{1}H-NMR of the co-crystal of **F2-Sum**:**Sum** = 75:25 (loading ratio):



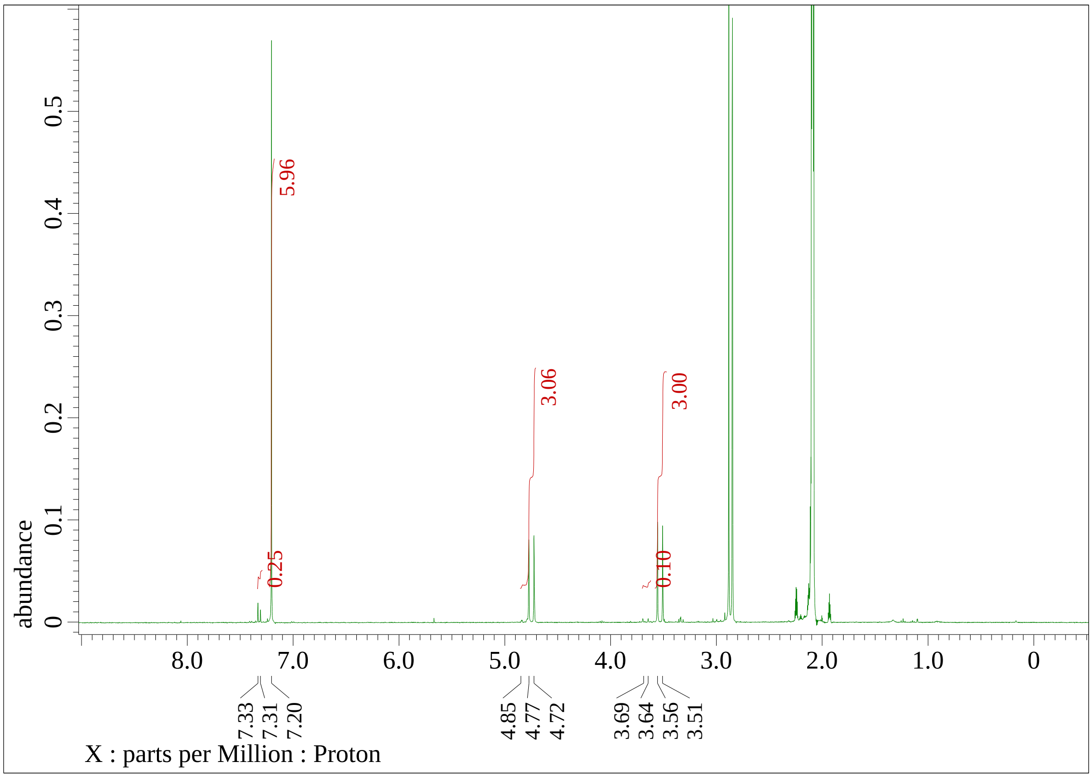
^{1}H-NMR of the co-crystal of **F2-Sum**:**Sum** = 50:50 (loading ratio):



^{1}H-NMR of the co-crystal of **F2-Sum**:**Sum** = 25:75 (loading ratio):



^{1}H-NMR of the co-crsytal of **F2-Sum**:**Sum** = 13:87 (loading ratio):



3. X-ray Crystal Structure Analysis

The diffraction data for crystal No. 1 to 8 were recorded on a XtaLAB Synergy with a Mo-target (λ = 0.71073 Å) equipped with a Rigaku HyPix-6000HE as the detector at 123 K in house.

The diffraction data for crystal No. 9 to 17 were recorded on a XtaLAB Synergy with a Cu-target (λ = 1.54184 Å) equipped with a Rigaku HyPix-6000HE as the detector at 123 K in house.

All the diffraction images were processed by using CrysAlisPro.[S3] All the structures were solved by direct methods (SHELXT-2015, 2018/2)[S4] and refined by full-matrix least squares calculations on F^2 (SHELXL-2018/3)[S5] using the Olex2[S6] program package.

1: $C_{21}H_{10.37}F_{1.63}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.7155(6) Å, c = 7.8787(3) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1906.4(2) Å^3, Z = 6, ρ_{calcd} = 1.534 g cm^{-1}. 1114 unique reflections out of 1139 with $I>2\sigma(I)$, 83 parameters, $2.437° < \theta < 31.013°$, R_1= 0.0330, wR_2= 0.0920, GOF = 1.074. CCDC 2172504.

2: $C_7H_{3.45}F_{0.55}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.7139(6) Å, c = 7.8744(3) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1905.0(2) Å^3, Z = 18, ρ_{calcd} = 1.538 g cm^{-1}. 1118 unique reflections out of 1134 with $I>2\sigma(I)$, 83 parameters, $2.437° < \theta < 30.744°$, R_1= 0.0336, wR_2= 0.0930, GOF = 1.043. CCDC 2172505.

3: $C_7H_{3.53}F_{0.47}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.7002(5) Å, c = 7.8414(3) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1894.0(1) Å^3, Z = 18, ρ_{calcd} = 1.525 g cm^{-1}. 1084 unique reflections out of 1113 with $I>2\sigma(I)$, 83 parameters, $2.439° < \theta < 30.767°$, R_1= 0.0342, wR_2= 0.0936, GOF = 1.035. CCDC 2172509.

4: $C_7H_{3.53}F_{0.47}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.7127(9) Å, c = 7.8468(5) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1898.1(2) Å^3, Z = 18, ρ_{calcd} = 1.520 g cm^{-1}. 944 unique reflections out of 973 with $I>2\sigma(I)$, 83 parameters, $2.437° < \theta < 30.793°$, R_1= 0.0355, wR_2= 0.0973, GOF = 1.059. CCDC 2172508.

5: $C_{21}H_{11.19}F_{0.81}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.6500(6) Å, c = 7.7389(3) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1858.0(2) Å^3, Z = 6, ρ_{calcd} = 1.495 g cm^{-1}. 1073 unique reflections out of 1081 with $I>2\sigma(I)$, 83 parameters, $2.446° < \theta < 30.744°$, R_1= 0.0333, wR_2= 0.0933, GOF = 1.067. CCDC 2172518.

6: $C_{21}H_{11.86}F_{0.14}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.5968(5) Å, c = 7.6249(3) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1818.9(1) Å^3, Z = 6, ρ_{calcd} = 1.461 g cm^{-1}. 1070 unique reflections out of 1080 with $I>2\sigma(I)$, 73 parameters, $2.454° < \theta < 30.692°$, R_1= 0.0344, wR_2= 0.0958, GOF = 1.121. CCDC 2172515.

7: $C_{21}H_{12}$, hexagonal, space group = $R3c$ (No. 161), $a = b$ = 16.5929(7) Å, c = 7.6175(3) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ V = 1816.3(2) Å^3, Z = 6, ρ_{calcd} = 1.450 g cm^{-1}. 1073 unique reflections out of 1086 with $I>2\sigma(I)$, 64 parameters, $2.455° < \theta < 30.873°$, R_1= 0.0360, wR_2= 0.1000, GOF = 1.096. CCDC 2172506.

8: $C_{21}H_{12}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.5959(7)$ Å, $c = 7.6226(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1818.2(2)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.448$ g cm^{-1}. 1083 unique reflections out of 1097 with $I>2\sigma(I)$, 64 parameters, 2.454°<θ<30.840°, R_1= 0.0362, wR_2= 0.1021, GOF = 1.071. CCDC 2172507.

9: $C_{21}H_{10.42}F_{1.58}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.755(1)$ Å, $c = 7.9305(7)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1928.1(3)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.513$ g cm^{-1}. 753 unique reflections out of 802 with $I>2\sigma(I)$, 83 parameters, 5.280°<θ<75.048°, R_1= 0.0762, wR_2= 0.2157, GOF = 1.142. CCDC 2172516.

10: $C_{21}H_{10.79}F_{1.21}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.723(1)$ Å, $c = 7.8675(7)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1905.4(3)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.469$ g cm^{-1}. 705 unique reflections out of 746 with $I>2\sigma(I)$, 83 parameters, 5.290°<θ<75.814°, R_1= 0.0627, wR_2= 0.1685, GOF = 1.078. CCDC 2172512.

11: $C_{21}H_{10.47}F_{1.53}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.740(2)$ Å, $c = 7.9040(8)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1918.2(4)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.515$ g cm^{-1}. 754 unique reflections out of 811 with $I>2\sigma(I)$, 83 parameters, 5.285°<θ<75.377°, R_1= 0.0772, wR_2= 0.1976, GOF = 1.096. CCDC 2172510

12: $C_{21}H_{11.24}F_{0.76}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.6665(3)$ Å, $c = 7.7333(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1860.30(8)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.489$ g cm^{-1}. 604 unique reflections out of 609 with $I>2\sigma(I)$, 83 parameters, 5.308°<θ<76.051°, R_1= 0.036, wR_2 = 0.0901, GOF = 1.151. CCDC 2172511.

13: $C_{21}H_{11.07}F_{0.93}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.6836(6)$ Å, $c = 7.7867(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1877.0(2)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.492$ g cm^{-1}. 559 unique reflections out of 563 with $I>2\sigma(I)$, 83 parameters, 5.303°<θ<75.236°, R_1= 0.0366, wR_2= 0.0972, GOF = 1.107. CCDC 2172517.

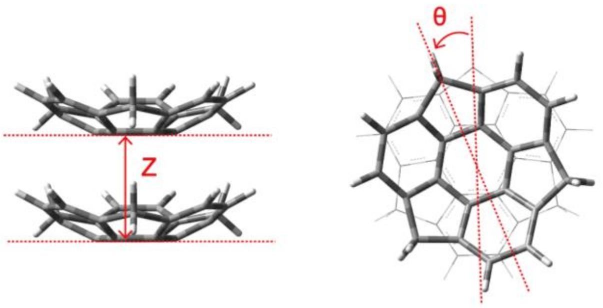
14: $C_{21}H_{11.19}F_{0.81}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.6650(5)$ Å, $c = 7.7508(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1864.18(3)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.489$ g cm^{-1}. 596 unique reflections out of 596 with $I>2\sigma(I)$, 83 parameters, 5.309°<θ<75.489°, R_1= 0.0327, wR_2 = 0.0857, GOF = 1.061. CCDC 2172513.

15: $C_{12}H_{11.78}F_{0.22}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.6264(4)$ Å, $c = 7.6483(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1831.0(1)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.460$ g cm^{-1}. 761 unique reflections out of 765 with $I>2\sigma(I)$, 73 parameters, 5.321°<θ<76.056°, R_1= 0.0401, wR_2 = 0.1131, GOF = 1.153. CCDC 2172514.

16: $C_{12}H_{11.79}F_{0.21}$, hexagonal, space group = *R*3*c* (No. 161), $a = b = 16.6293(5)$ Å, $c = 7.6551(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1833.3(1)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.457$ g cm^{-1}. 632 unique reflections out of 635 with $I>2\sigma(I)$, 73 parameters, 5.320°<θ<75.681°, R_1= 0.0337, wR_2 = 0.0897, GOF = 1.102. CCDC 2172519.

17: $C_{12}H_{11.79}F_{0.22}$, hexagonal, space group = $R3c$ (No. 161), $a = b = 16.6267(4)$ Å, $c = 7.6522(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ $V = 1832.0(1)$ Å^3, $Z = 6$, $\rho_{\mathrm{calcd}} = 1.458$ g cm^{-1}. 644 unique reflections out of 645 with $I>2\sigma(I)$, 73 parameters, $5.321° < \theta < 75.725°$, $R_1 = 0.0366$, $wR_2 = 0.1063$, GOF = 1.153. CCDC 2172520.

4. Interaction Energy Discussion within Stacking Dimers



All the calculations were done at ωb97xd/6-311+g(d,p) level of theory using Gaussian09 package.[S7] For the simulation, the suitable models were built by making the stacking dimers with each monomer unit optimised under vacuum at at the B3LYP/6-31G(d,p) level of theory (the coordinates are shown in later part). The vertical distance (Z) and the rotation angle (θ) of the two molecules defined by the right figure were changed from 3.7 Å to 4.0 Å and 0° to 120°, respectively. In case of **Sum/F2-Sum** and **Sum/F6-Sum** systems, we also considered the up and down position differences. The name on the front denotes that the corresponding molecule is locating on the upper position: e.g. **F2-Sum/Sum** means **F2-Sum** is on the upper side and **Sum** is on the down side.

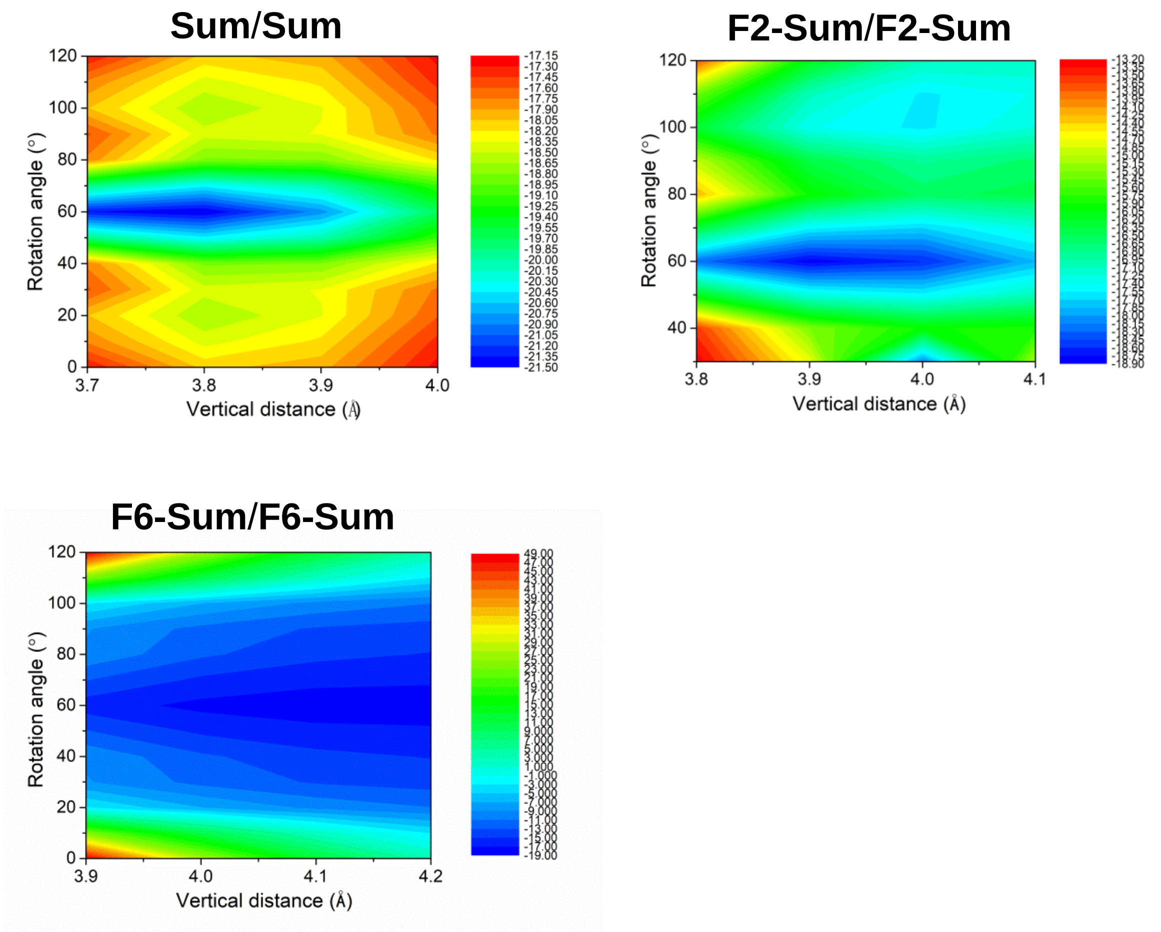


Figure S1. Interaction energy surface of **Sum/Sum**, **F2-Sum/F2-Sum**, **F6-Sum/F6-Sum** pairs.

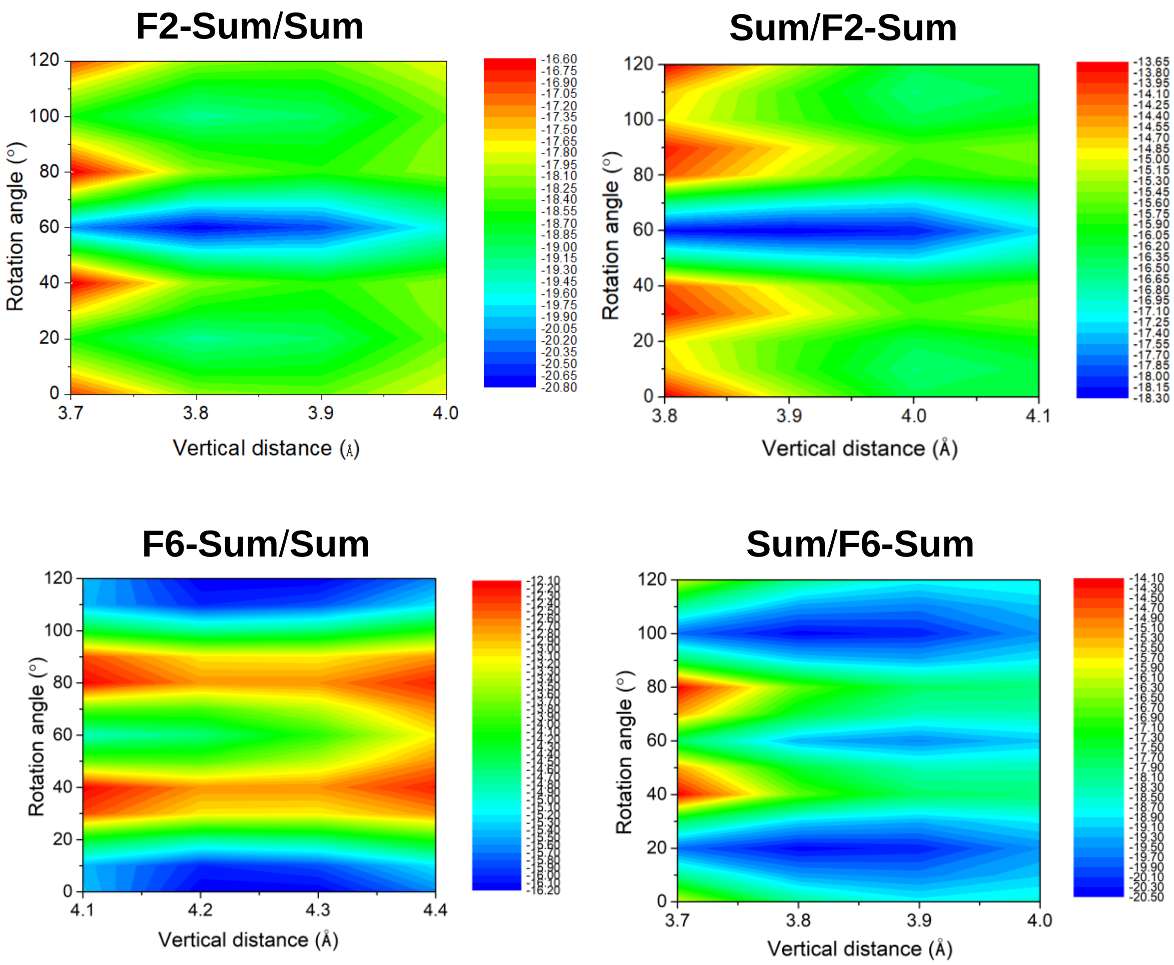


Figure S2. Interaction energy surface of **F2-Sum/Sum**, **Sum/F2-Sum**, and **F6-Sum/Sum**, **Sum/F6-Sum** pair.

Table S5. Summary of the interaction energies of the molecular pairs.

Dimer[a]	**Vertical distance Z (Å)**	**Rotation angle θ (°)**	***E*** **(kcal/mol)**
Sum/Sum	3.8	60	−21.50
F2-Sum/F2-Sum	3.9	60	−18.84
	3.9	180	−18.34
F6-Sum/F6-Sum	4.1	60	−18.01
F2-Sum/Sum	3.9	60	−18.52
Sum/F2-Sum	3.8	60	−20.77
F6-Sum/Sum	4.1	60	−14.90
Sum/F6-Sum	3.9	60	−19.55

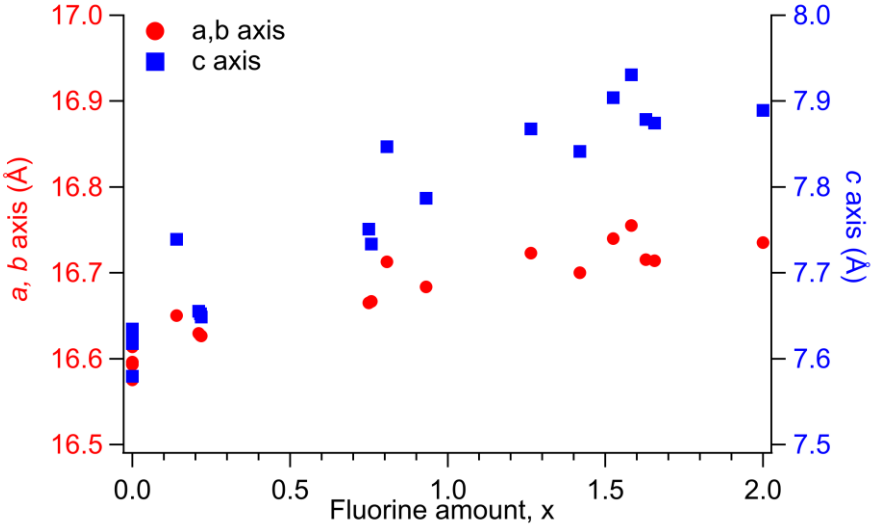


Figure S3 Relationship between fluorine amount in the formula and the cell parameters in each co-crystal. The plot reflects all the crystals obtained by large scale setting. Here, fluorine amount is defined as the value of “x” in the formula of co-crystals $C_{21}H_{12-x}F_x$.

5. Thermal Analysis and Dielectric Measurement Results

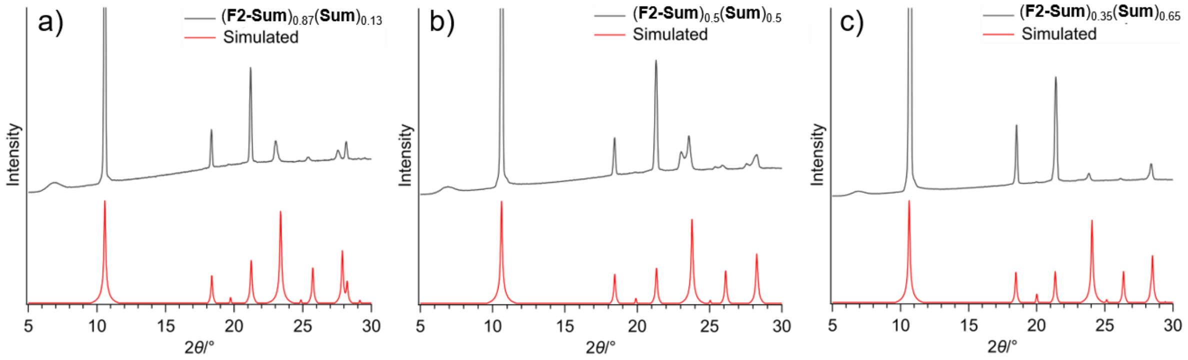


Figure S4 PXRD patterns of a) **(F2-Sum)**$_{0.87}$**(Sum)**$_{0.13}$, b) **(F2-Sum)**$_{0.5}$**(Sum)**$_{0.5}$, and c) **(F2-Sum)**$_{0.35}$**(Sum)**$_{0.65}$ together with their simulated patterns from single crystal data (Crystal 1, 5 and 15).

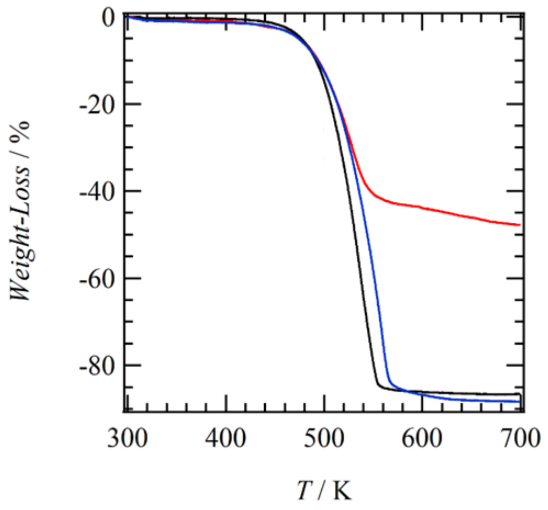


Figure S5 Thermo-gravimetry (TG) experiments of the cocrystals composed of **(F2-Sum)**$_{0.35}$**(Sum)**$_{0.65}$ (blue line), **(F2-Sum)**$_{0.5}$**(Sum)**$_{0.5}$ (red line), **(F2-Sum)**$_{0.87}$**(Sum)**$_{0.13}$ (black line).

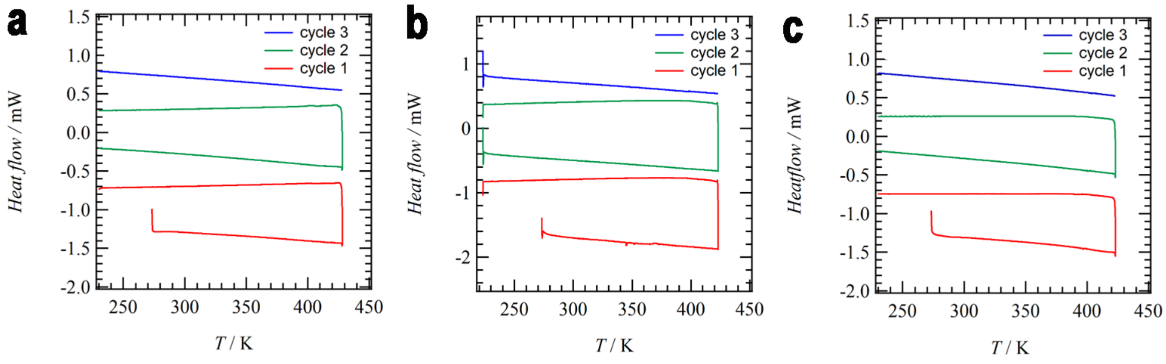


Figure S6 Differential scanning calorimetry (DSC) experiments of the cocrystals of (a) **(F2-Sum)**$_{0.35}$**(Sum)**$_{0.65}$, (b) **(F2-Sum)**$_{0.5}$**(Sum)**$_{0.5}$, and (c) **(F2-Sum)**$_{0.87}$**(Sum)**$_{0.13}$.

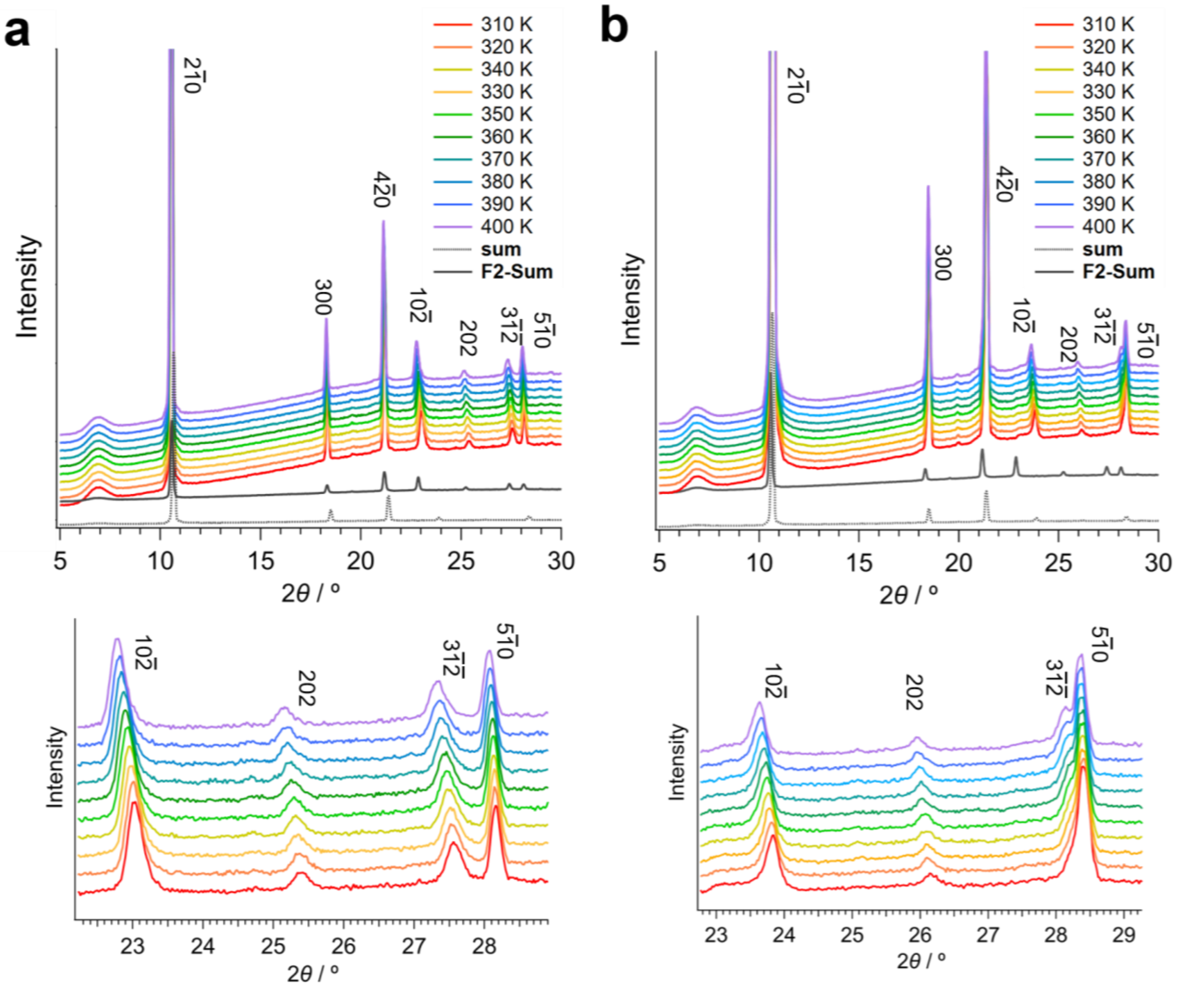


Figure S7. Variable temperature PXRD data. a) The patterns of the co-crystalline powder of (**F2-Sum**)$_{0.87}$(**Sum**)$_{0.13}$. b) The patterns of the co-crystalline powder of (**F2-Sum**)$_{0.35}$(**Sum**)$_{0.65}$. The figures at the bottom of each pattern show the magnified one in 2θ range 23~29°.

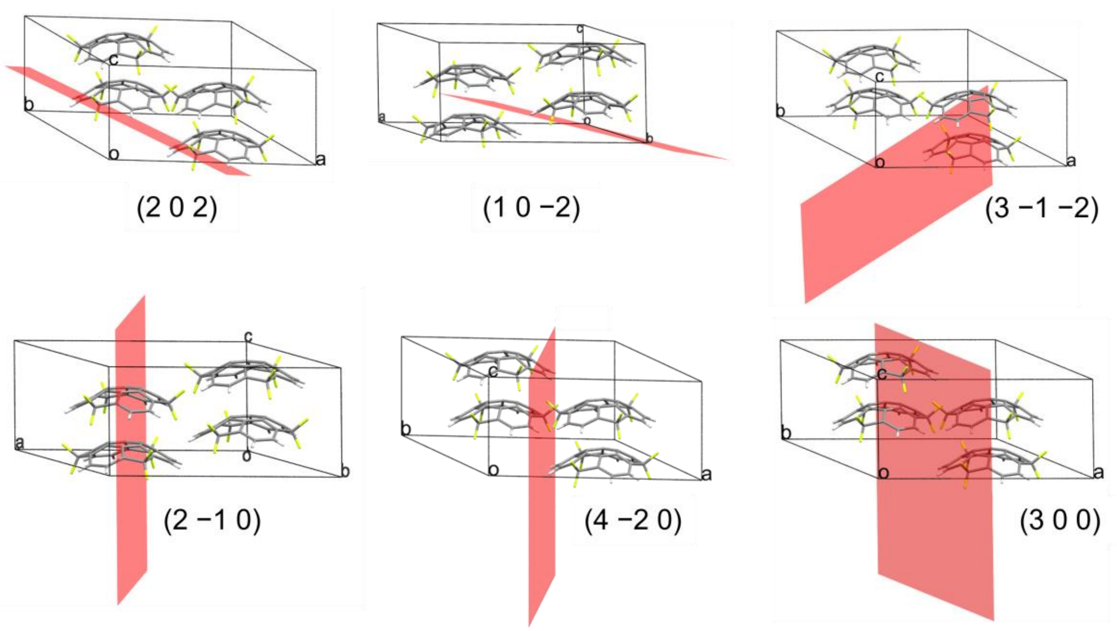


Figure S8. Lattice plane and the structure relationships.

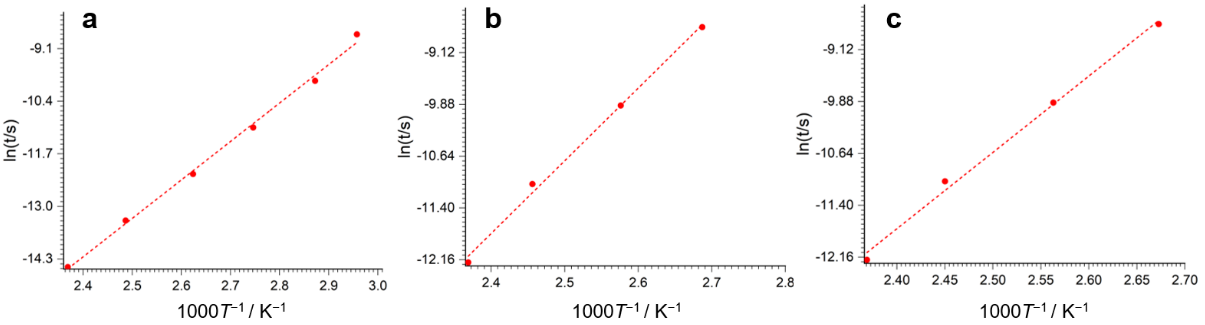


Figure S9. Arrhenius plot of the relaxation time τ as a function of inverse temperature for a) **(F2-Sum)**$_{0.35}$**(Sum)**$_{0.65}$, b) **(F2-Sum)**$_{0.5}$**(Sum)**$_{0.5}$, and c) **(F2-Sum)**$_{0.87}$**(Sum)**$_{0.13}$ powder co-crystalline pellet, where the τ-value is the inverse of measurement f-values of the $\tau = 1/(2*\pi*f)$. The dotted line represents the least-squares fit of the data.

6. Interaction Energy Decomposition Analysis

For the EDA analysis, we used the EDA-FF method which is based on molecular force field by using Multiwfn (version: 3.7).[S8] To make the system simplify, the coordinate of the pair models was extracted from the CIF file of the co-crystal of (**F2-Sum**)$_{0.87}$(**Sum**)$_{0.13}$ (crystal No. 11) and directly applied for the calculation. All the possible structures of the pairs in the co-crystals were considered.

6-1 Intra-columnar interactions

The extracted coordinates of the carbon skeletons were in the orientation as shown in the following figure (pink coloured ones). The name on the front denotes that the corresponding molecule is locating on the upper position: e.g. **F2-Sum**/**Sum** means **F2-Sum** is on the upper side and **Sum** is on the down side.

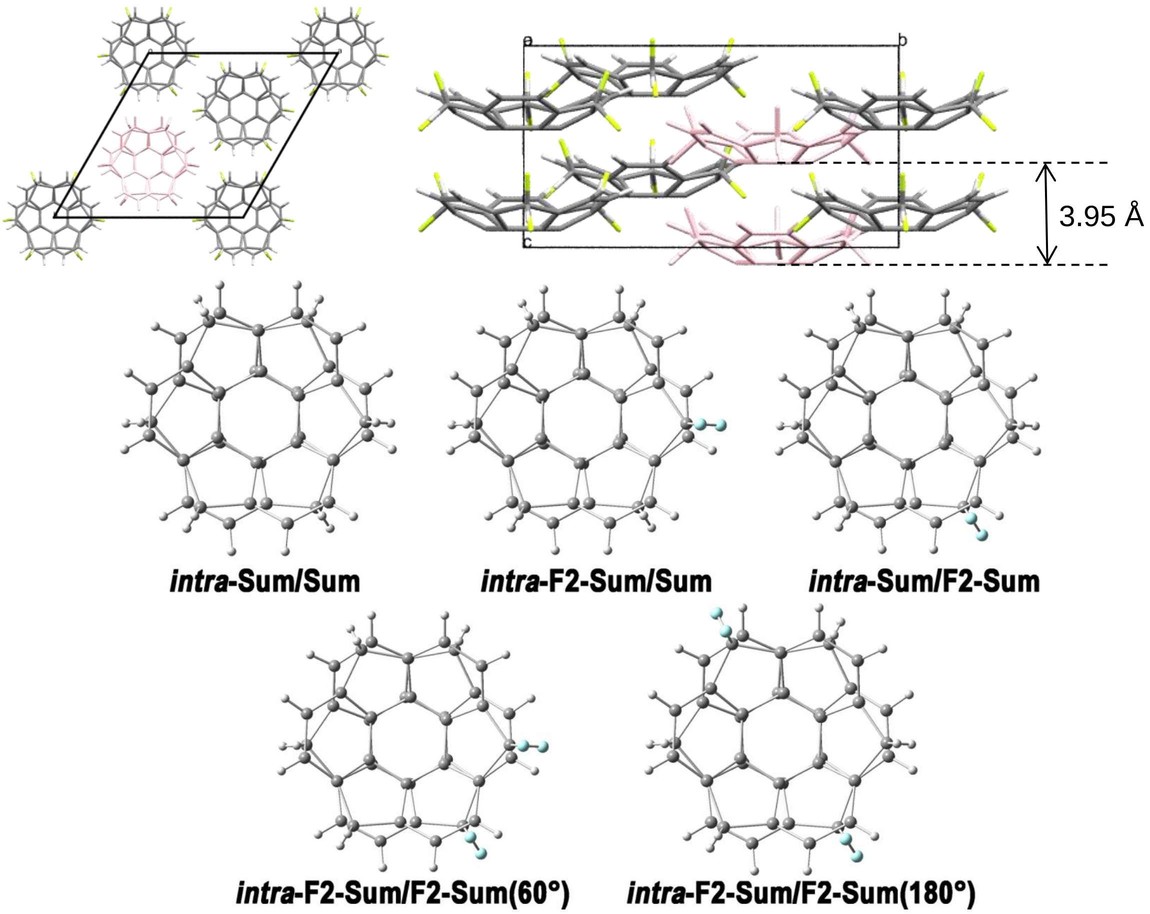


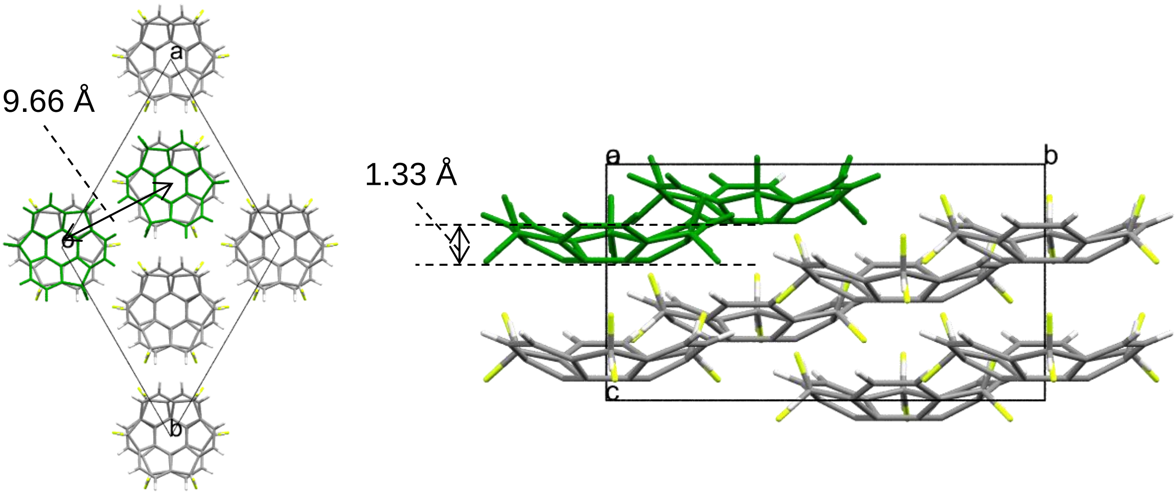
Figure S9. Top view of the molecular pairs for calculating the intra-columnar interactions. 60° and 180° in **F2-Sum**/**F2-Sum** pairs indicates the rotation angles corresponding to the F-attached two benzylic carbons. Gray, carbon; white, hydrogen; pale blue, fluorine.

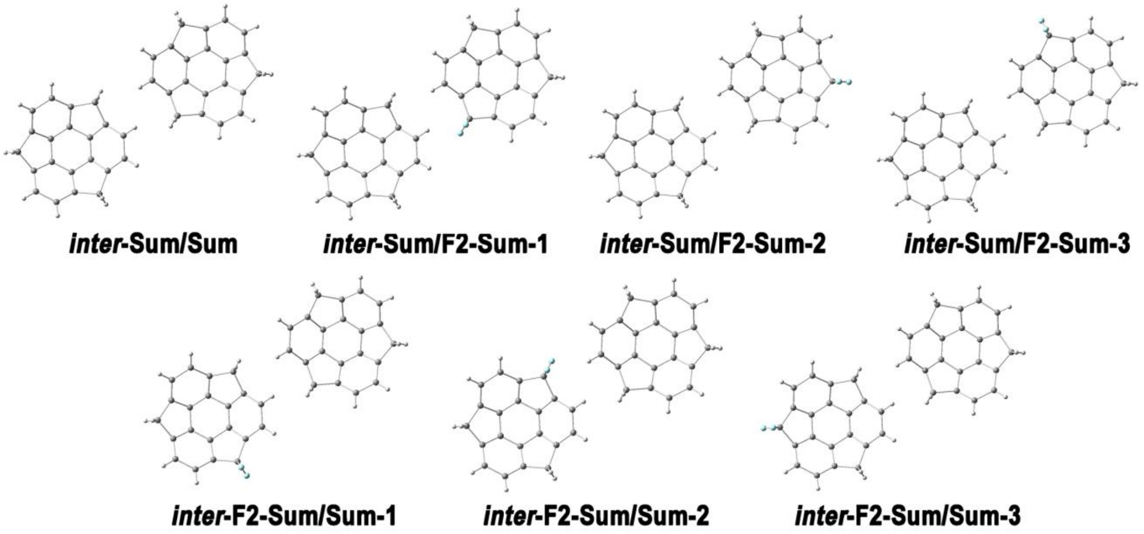
Table S6. Intra-columnar interaction energies of the molecular pairs (**Sum/Sum**, **Sum/F2-Sum** and **F2-Sum/F2-Sum**). D/R means the ratio of the dispersion energy to the repulsion energy.

Molecular pair	Electrostatic (kJ/mol)	Repulsion (kJ/mol)	Dispersion (kJ/mol)	Total energy (kJ/mol)	D/R
***intra*-Sum/Sum**	−0.04	44.38	−116.75	−72.40	−2.63069
***intra*-F2-Sum/Sum**	2.4	56.99	−126.07	−66.67	−2.21214
***intra*-Sum/F2-Sum**	−1.34	49.34	−121.03	−73.03	−2.45298
***intra*-F2-Sum/F2-Sum (60°)**	0.45	61.97	−130.48	−68.05	−2.10553
***intra*-F2-Sum/F2-Sum (180°)**	0.44	61.95	−130.36	−67.97	−2.10428

6-2 Inter-columnar interactions

The extracted coordinates of the carbon skeletons were in the orientation as shown in the following figure (green coloured ones). The name on the front denotes that the corresponding molecule is locating on the left side position (lower position along the *c* axis): e.g. **F2-Sum**/**Sum** means **F2-Sum** is on the left side and **Sum** is on the right side.



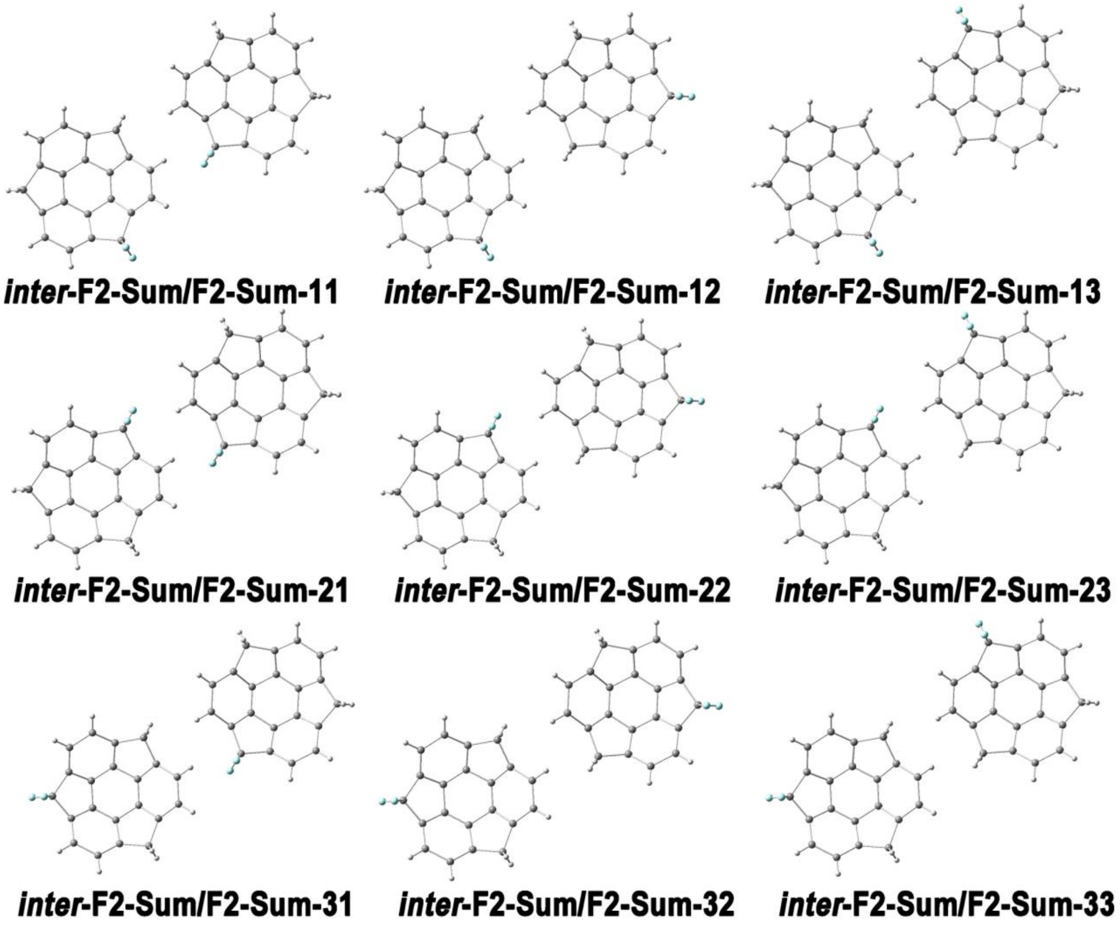

***inter*-Sum/Sum** ***inter*-Sum/F2-Sum-1** ***inter*-Sum/F2-Sum-2** ***inter*-Sum/F2-Sum-3**

***inter*-F2-Sum/Sum-1** ***inter*-F2-Sum/Sum-2** ***inter*-F2-Sum/Sum-3**

Figure S11. Top view of the molecular pairs (**Sum**/**Sum** and **Sum**/**F2-Sum**) for calculating the intra-columnar interactions. Gray, carbon; white, hydrogen; pale blue, fluorine.

Table S7. Inter-columnar interaction energies of the molecular pairs (**Sum**/**Sum** and **Sum**/**F2-Sum**). D/R means the ratio of the dispersion energy to the repulsion energy.

Molecular pair	Electrostatic (kJ/mol)	Repulsion (kJ/mol)	Dispersion (kJ/mol)	Total energy (kJ/mol)	D/R
***inter*-Sum/Sum**	0.16	4.23	−13.62	−9.22	−3.21986
***inter*-Sum/F2-Sum-1**	1.24	8.25	−17.75	−8.26	−2.15152
***inter*-Sum/F2-Sum-2**	0.17	4.23	−13.63	−9.22	−3.22222
***inter*-Sum/F2-Sum-3**	0.13	4.23	−13.67	−9.31	−3.23168
***inter*-F2-Sum/Sum-1**	0.48	4.23	−13.68	−8.97	−3.23404
***inter*-F2-Sum/Sum-2**	0.43	12.92	−18.16	−4.81	−1.40557



inter-F2-Sum/F2-Sum-11 *inter*-F2-Sum/F2-Sum-12 *inter*-F2-Sum/F2-Sum-13

inter-F2-Sum/F2-Sum-21 *inter*-F2-Sum/F2-Sum-22 *inter*-F2-Sum/F2-Sum-23

inter-F2-Sum/F2-Sum-31 *inter*-F2-Sum/F2-Sum-32 *inter*-F2-Sum/F2-Sum-33

Figure S12. Top view of the molecular pairs (**F2-Sum**/**F2-Sum**) for calculating the intra-columnar interactions. Gray, carbon; white, hydrogen; pale blue, fluorine.

Table S8. Inter-columnar interaction energies of the molecular pairs (**F2-Sum**/**F2-Sum**). D/R means the ratio of the dispersion energy to the repulsion energy.

Molecular pair	**Electrostatic (kJ/mol)**	**Repulsion (kJ/mol)**	**Dispersion (kJ/mol)**	**Total energy (kJ/mol)**	**D/R**
***inter*-F2-Sum/F2-Sum-11**	0.98	8.25	−17.84	−8.62	−2.16242
***inter*-F2-Sum/F2-Sum-12**	0.86	4.23	−13.69	−8.61	−3.23641
***inter*-F2-Sum/F2-Sum-13**	0.56	4.23	−13.74	−8.95	−3.24823
***inter*-F2-Sum/F2-Sum-21**	-2.05	16.95	−22.39	−7.49	−1.32094
***inter*-F2-Sum/F2-Sum-22**	-0.36	12.92	−18.17	−5.61	−1.40635
***inter*-F2-Sum/F2-Sum-23**	-0.07	12.92	−18.23	−5.38	−1.41099

7. Cartesian Coordinates of Optimized Structures

a) Optimized cartesian coordinates of **Sum.**

C	1.40971	0.01336	-0.68398	C	-0.69329	-1.22753	-0.68398
C	0.71643	1.21417	-0.68398	C	0.69329	-1.22753	-0.68398
C	1.21479	2.36589	-0.06664	C	1.44152	-2.23498	-0.06664
C	0	3.30365	0.18499	C	2.86105	-1.65183	0.18499
C	-1.21479	2.36589	-0.06664	C	2.65632	-0.13091	-0.06664
C	-2.51709	2.27967	0.43868	C	3.23279	1.04003	0.43868
C	-3.23279	1.04003	0.43868	C	2.51709	2.27967	0.43868
H	0	3.69921	1.20598	H	3.20361	-1.84961	1.20598
H	0	4.17039	-0.48998	H	3.61167	-2.0852	-0.48998
H	-2.97058	3.12003	0.95865	H	4.18732	1.01258	0.95865
H	-4.18732	1.01258	0.95865				

b) Optimized cartesian coordinates of **F2-Sum.**

C	-0.72807	0.42883	1.40845	H	-0.46523	2.50976	3.61095
C	-0.76868	-0.77111	0.71984	H	0.9536	-0.59868	4.15942
C	-0.17103	-1.92834	1.22121	H	0.90317	-2.71028	2.92724
C	0.05695	-2.86406	0	C	-0.76868	-0.77111	-0.71984
C	-0.17103	-1.92834	-1.22121	C	-0.72807	0.42883	-1.40845
C	0.37951	-1.85974	-2.50067	C	-0.08488	0.55525	-2.64801
C	0.41117	-0.62104	-3.21784	C	0.19893	2.06833	-2.85551
H	0.90317	-2.71028	-2.92724	C	-0.04885	2.65898	-1.43994
H	0.9536	-0.59868	-4.15942	C	0.4875	3.72906	-0.71512
C	-0.70008	1.67128	-0.69379	C	0.4875	3.72906	0.71512
C	-0.70008	1.67128	0.69379	H	1.22475	2.24417	-3.19482
C	-0.04885	2.65898	1.43994	H	-0.46523	2.50976	-3.61095
C	0.19893	2.06833	2.85551	H	1.03298	4.52442	-1.21683
C	-0.08488	0.55525	2.64801	H	1.03298	4.52442	1.21683
C	0.41117	-0.62104	3.21784	F	-0.80176	-3.93402	0
C	0.37951	-1.85974	2.50067	F	1.31881	-3.39181	0
H	1.22475	2.24417	3.19482				

c) Optimized cartesian coordinates of **F6-Sum.**

C	1.4119	0.0169	-0.83506	H	2.89439	3.09049	0.9609
C	0.72058	1.21429	-0.83506	C	-0.72058	1.21429	-0.83506
C	1.21908	2.3464	-0.18111	C	-1.4119	0.0169	-0.83506
C	0	3.27868	0.07002	C	-2.64158	-0.11745	-0.18111
C	-1.21908	2.3464	-0.18111	C	-2.83942	-1.63934	0.07002
C	-2.48545	2.26176	0.39111	C	-1.4225	-2.22895	-0.18111
C	-3.20147	1.02158	0.39111	C	-0.71602	-3.28335	0.39111
H	-2.89439	3.09049	0.9609	C	0.71602	-3.28335	0.39111
H	-4.12364	0.96137	0.9609	H	-1.22925	-4.05186	0.9609
C	-0.69132	-1.23119	-0.83506	H	1.22925	-4.05186	0.9609
C	0.69132	-1.23119	-0.83506	F	0	4.36066	-0.76803
C	1.4225	-2.22895	-0.18111	F	0	3.77388	1.34122
C	2.83942	-1.63934	0.07002	F	-3.26827	-1.88694	1.34122
C	2.64158	-0.11745	-0.18111	F	-3.77644	-2.18033	-0.76803
C	3.20147	1.02158	0.39111	F	3.26827	-1.88694	1.34122
C	2.48545	2.26176	0.39111	F	3.77644	-2.18033	-0.76803
H	4.12364	0.96137	0.9609				

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