## **Supporting Information**

# Tuning the solid-state emission by co-crystallization through $\sigma$ - and $\pi$ -hole directed intermolecular interactions

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#### **Experimental Section**

**Reagents.** 1,4-Diiodotetrafluorobenzene (1,4-DITFB, 98%) was purchased from Sigma-Aldrich, Benzo[c]cinnolene (BCC, 99%) was purchased from Alfa-Aesar, 4,4'-Bis(2,2-diphenyl vinyl)-biphenyl (BDVB, >99%) was purchased from TCI Chemicals, 9-Benzhydrylidenefluorene (BHF, >98%) was purchased from Alfa-Aesar and 9,9-Bis(4-aminophenyl)fluorine (BAF, >98%) was purchased from TCI Chemicals.

#### **Preparation of Single Crystals**

**Co-crystal 1.** Equal equivalents of BCC and 1,4-DITFB were taken in a mortar and ground with a pestle for 75 minutes with the addition of a drop of methanol during every 15-minute interval. The resulting light-yellow powder mixture was dissolved in a variety of solvents and solvent mixtures and kept for crystallization at a low temperature. Rod-shaped colourless crystals of Form I were obtained by slow evaporation from Chloroform solvent at 4°C for two days (Figure S1a) and crystals of similar shape and colour belonging to Form II were obtained by slow evaporation from Acetonitrile solvent at 4°C for nearly a week (Figure S1b).

**Co-crystal 2.** 1 equivalent of BDVB and 2 equivalents of 1,4-DITFB were ground in a mortar with a pestle for 75 minutes with the simultaneous addition of a drop of methanol every 15 minutes. The resulting light-yellow powder was dissolved in a variety of solvents and kept for crystallization at a low temperature. Hexagonal plate-shaped light-yellow coloured crystals were obtained by slow evaporation in Toluene solvent at 4°C for nearly three weeks (Figure S1c).

**Co-crystal 3.** 1 equivalent of BHF and 2 equivalents of 1,4-DITFB were ground in a mortar with a pestle for 75 minutes with the simultaneous addition of a drop of methanol every 15 minutes. The resulting light-yellow powder was dissolved in a variety of solvents and kept for crystallization at a low temperature. Block-shaped light-yellow coloured crystals were obtained by slow evaporation in a 1:1 Dichloromethane : Hexane solvent kept at 4°C for about one week (Figure S1d).

**Co-crystal 4.** 1 equivalent of BAF and 2 equivalents of 1,4-DITFB were ground in a mortar with a pestle for 75 minutes with the simultaneous addition of a drop of methanol every 15 minutes. The resulting colourless powder was dissolved in a variety of solvents and kept for crystallization at a low temperature. Block-shaped colourless crystals were obtained by slow evaporation in a 1:1 Acetone : Chloroform solvent kept at 4°C for a few days (Figure S1e).

The following table contains the list of solvents used for crystallizing the co-crystal powders.

Solvent / Cocrystal	Co-crystal 1	Co-crystal 2	Co-crystal 3	Co-crystal 4
DCM+ Hexane	Aggregates	Aggregates	Block	Aggregates
Acetone + Hexane	Aggregates	Aggregates	Aggregates	Aggregates
Chloroform	Needle (Form I)	Fibrous	Aggregates	Aggregates

Ethyl acetate +	Aggregates	Aggregates	Aggregates	Aggregates
Hexane				
Acetone +	Aggregates	Aggregates	Aggregates	Block
Chloroform				
Acetonitrile	Needle (Form II)	Aggregates	Fibrous	Aggregates
DCM + Methanol	Aggregates	Aggregates	Aggregates	Aggregates
Methanol	Fibrous	Aggregates	Aggregates	Aggregates
Ethanol	Aggregates	Aggregates	Fibrous	Aggregates
Isopropanol	Aggregates	Fibrous	Aggregates	Aggregates
Toluene	Aggregates	Hexagonal Plates	Aggregates	Fibrous
DMSO	Aggregates	Aggregates	Aggregates	Aggregates
THF	Aggregates	Aggregates	Aggregates	Aggregates

**PXRD.** Powder X-Ray Diffraction Patterns of all the co-crystals were obtained at 298 K on PANalytical Empyrean X-Ray Diffractometer with a Cu K $\alpha$  radiation ( $\lambda$ =1.54060Å). The bulk powder of each sample was placed in a silica sample holder and measured by a continuous scan between 5–40° with a step size of 0.013103°. The simulated pattern was generated from the single crystal structure using Mercury3.10. Chemical and structural identity between bulk materials and single crystals were always verified by comparing the experimental and simulated powder diffraction patterns.

**SCXRD.** Good quality single crystals of all the co-crystals suitable for X-Ray Single crystal analysis were obtained by slow evaporation method at low temperature (4°C). Single Crystal X-ray Diffraction data were collected on Bruker *AXS* Kappa *APEXII* diffractometer using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K using an Oxford Cryostream low-temperature device. Unit cell measurements, data integration, scaling and absorption corrections for the crystals were done with Bruker *APEXII* software.<sup>1</sup> Data reduction was carried out with Bruker *SAINT* suite.<sup>2</sup> Absorption correction was performed by multi-scan method implemented in *SADABS*.<sup>3</sup> All the crystal structures were solved by direct methods using *SIR* 2014.<sup>4</sup> The crystal structure refinements were done in the program package *WinGX*,<sup>5</sup> and all non-hydrogen atoms were refined anisotropically by full matrix least-squares calculations based on F<sup>2</sup> with *SHELXL*-2016.<sup>6</sup> hydrogen atoms were included in calculated positions as riding atoms, while some hydrogen atoms were located from the difference Fourier Map. Details of crystal data, data collection, and refinement details are given in Table S1. The *PLATON*<sup>7</sup> and *MERCURY*<sup>8</sup> programs were used for structure analysis and also molecular and crystal structure drawings preparation.

**Differential Scanning Calorimetry (DSC).** The DSC traces of all the co-crystal components and their respective co-crystals were recorded with a PerkinElmer DSC 6000 instrument where approximately 1.0 mg of each compound were successively placed in hermetically sealed aluminium pan in vacuum and subsequently scanned at a rate of 3 °C/min under a dry nitrogen purge (20 mL/min).

**UV-vis. absorption spectroscopy.** Diffuse reflectance UV-Vis.-NIR spectra of solid powdered co-crystals and their aromatic counterparts were collected under ambient conditions on a Cary 5000 UV-Vis.-NIR (Agilent) equipped with diffuse reflectance accessory by using reflectance standard disk and BaSO<sub>4</sub> as a standard.

**Emission Spectroscopy.** The Photoluminescence emission spectra of the co-crystals and their respective individual precursors were collected using HORIBA-JOBINYVON spectrofluorometer equipped with a 450 W Xenon CW lamp as the excitation source.

**Emission Lifetime.** The emission lifetime of all the co-crystals were measured in solid-state using HORIBA Delta-Flex TCSPC system using 410 nm LEASER as excitation source.

**Fluorescence Microscopy Images.** Fluorescence microscopy imaging of all the crystals and their co-crystals were performed in OLYMPUS IX-83-inverted fluorescence microscope using OLYMPUS cellsens dimension 1.1 software. For Co-crystal 1 and 2 we have used DAPI channel with excitation wavelength of 455 nm and

exposure times of 40 ms and 300  $\mu$ s respectively. For Co-crystal 3 and 4 we have used FITC channel with excitation wavelength of 518 nm and exposure times of 100 ms and 130 ms respectively. For BCC crystals we have used FITC channel with emission wavelength of 518 nm and exposure time of 30 ms, while for crystals of BDVB, BHF and BAF we have used DAPI channel with emission wavelength of 455 nm and exposure times of 300  $\mu$ s, 1 ms and 150 ms respectively.

#### **Computational methods**

All calculations were carried out using *GAUSSIAN09* package<sup>9</sup> The single point energies of the structures of all interaction units and the monomers extracted from the crystal structure of the co-crystals were calculated using the density functional M06-2x<sup>10</sup> The basis set 6-311G(d,p) was used to describe C, H, N and F atoms and LANL2DZdp ECP was used for I atoms. The interaction energy ( $\Delta E$ ) of each interaction unit was calculated as the difference between the energy of interaction unit and the sum of the total energies of monomers  $\Delta E_{total} = E_{AB} - (E_A + E_B)$ . The basis set superposition error (BSSE) was estimated using Boys-Bernardi counterpoise (CP) method.<sup>11</sup>



**Figure S1.** Photographs of co-crystals taken under optical microscope showing morphological features of (a) Form I of Co-crystal 1, (b) Form II of Co-crystal 1, (c) Co-crystal 2, (d) Co-crystal 3 and (e) Co-crystal 4.



**Figure S2a.** ORTEP diagram of Form I of Co-crystal 1 with one molecule of BCC and two half molecules of 1,4-DITFB.



**Figure S2b.** ORTEP diagram of Form II of Co-crystal 1 with two molecules of BCC and one molecule of 1,4-DITFB.



Figure S2c. ORTEP diagram of Co-crystal 2 with one molecule of BDVB and one molecule of 1,4-DITFB.



Figure S2d. ORTEP diagram of Co-crystal 3 with one molecule of BHF and two half molecules of 1,4-DITFB.



Figure S2e. ORTEP diagram of Co-crystal 4 with one molecule of BAF and one molecule of 1,4-DITFB.



**Figure S3.** Geometry of BDVB molecule (a) with diphenylvinyl moieties oriented *trans* along the central biphenyl plane in its crystal structure and (b) with diphenylvinyl moieties oriented *cis* along the central biphenyl plane after co-crystallization with 1,4-diiodotetrafluorobenzene.

Sample Code	Со-сі	ystal 1	Co-crystal 2	Co-crystal 3	Co-crystal 4
Stoichiometric Ratio	Form I (2*0.5D : 1A)	Form II (1D : 2A)	1D : 1A	2*0.5D : 1A	1D : 1A
Formula	$C_{18}H_8F_4I_2N_2$	$C_{30}H_{16}F_{4}I_{2}N_{4} \\$	$C_{46}H_{30}F_4I_2$	$C_{32}H_{18}F_4I_2$	$C_{31}H_{20}F_{4}I_{2}N_{2} \\$
Solvent	Dichloromethane	Acetonitrile	Toluene	Dichloromethane : Hexane	Acetone : Chloroform
Crystal Size (mm)	0.36 X 0.12 X 0.08	0.20 X 0.02 X 0.02	0.21 X 0.13 X 0.08	0.30 X 0.20 X 0.10	0.24 X 0.11 X 0.09
Morphology	Rod	Rod	Plate	Block	Block
Formula Weight	582.06	762.27	912.50	732.26	750.29
Temperature (K)	100 (2)	298 (2)	100 (2)	100 (2)	100 (2)
Wavelength (A°)	0.71073	0.71073	0.71073	0.71073	0.71073

Table S1. Crystal Data and Structure Refinement

Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space Group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	<i>P</i> -1	<i>P</i> -1
Z	4	4	4	2	2
a ( Å )	4.4893 (3)	26.714 (9)	13.9639(5)	9.3655(4)	11.5700(4)
b ( Å )	15.5665 (5)	13.423 (4)	9.2151(3)	11.0244(4)	11.6762(4)
c ( Å )	24.4653 (9)	7.556 (3)	28.0322(9)	13.4310(5)	11.7522(4)
α(°)	90	90	90	89.844(2)	70.484(2)
β(°)	92.894 (2)	97.82 (2)	98.6600(10)	74.129(2)	63.812(2)
γ(°)	90	90	90	73.241	73.849(2)
Volume (A°3)	1707.52 (11)	2684.1 (15)	3566.0(2)	1272.85(9)	1326.69(8)
Density (g cm <sup>-3</sup> )	2.264	2.399	1.700	1.911	1.878
F (000),µ(mm <sup>-1</sup> )	1088, 3.729	1464, 2.399	1792, 1.819	704, 2.521	724, 2.423
heta (min, max) (°)	1.551 , 30.185	2.161, 30.421	2.234, 27.878	1.936, 28.699	1.992, 30.259
h <sub>min,max</sub> , k <sub>min,max</sub> , I <sub>min,max</sub>	(-6,6), (-21,21), (- 34,27)	(-37,37), (-19,19), (-10,10)	(-16,18), (-12,12), (-34,36)	(-12,12), (-14,14), (-17,18)	(-16,16), (-16,16), (-16,16)
Treatment of Hydrogens	Fixed	Fixed	Fixed	Located	Fixed, Located
No. unique ref/obs. Ref.	5038, 4509	8066, 3066	8468, 7423	6526, 6117	7799, 6406
No of Parameters	235	361	469	415	368
R_all, R_obs	0.0497, 0.0429	0.2393, 0.0909	0.0367, 0.0298	0.0380, 0.0349	0.0453, 0.0337
wR2_all, wR2_obs	0.1107, 0.1074	0.2157, 0.1611	0.0670, 0.0642	0.0820, 0.0804	0.0796, 0.0753
$\Delta  ho_{min,max}(e \text{\AA}^{-3})$	-1.901, 1.450	-1.098, 0.603	-1.087, 0.818	-2.175, 1.102	-1.779, 1.910
G.o.F	1.109	0.994	1.036	1.126	1.022
CCDC	1880026	1880027	1880028	1880030	1880031

### Table S2. Intermolecular Hydrogen bonds and Other Interactions in co-crystals

Co-crystal	Symmetry Code	D–H…A (Å)	D…A (Å)	∠D–H…A (Å)/ ∠D…A (Å)
Co-crystal 1 ( Form I )				
C8–H8…F1	-x+1, y-1/2, -z+3/2	2.546	3.342	144
С9–Н9…F3	x+1, -y+3/2, z-1/2	2.459	3.096	126
C10–H10…F3	x+1, -y+3/2, z-1/2	2.599	3.161	119

C3–H3…F4	-x+2, -y+2, -z+1	2.606	3.148	118
C14–I1…N1	x+1, y, z		2.873	176
C14–I1…N2	x+1, y, z		3.508	160
C14–I1…I2–C17	x+1, y, z		3.762	167, 109
Co-crystal 1 ( Form II )				
C4–H4…F2	x, y-1, z	2.613	3.131	116
C16–H16…F4	x, y+1, z	2.608	3.307	132
С2-Н2…I1	x, y, z	3.125	3.732	124
C25–I1…N1	x, y, z		2.875	173
C28–I2…N3	x, y, z		2.962	178
Co-crystal 2				
C15–H15…I1	x, y-1, z	3.141	3.905	139
C34–H34…F3	-x+2, y-1/2-1, - z+1/2	2.620	3.395	139
С25–Н25…С9	x, y+1, z	2.803	3.519	133
С25–Н25…С10	x, y+1, z	2.752	3.596	148
С27–Н27…С39	x, y+1, z	2.887	3.827	171
С18–Н18…С34	-x+2, y-1/2, -z+1/2	2.826	3.620	142
C46–F4…F4–C46	1-x, -3-y, -z		2.755	134, 134
C43–I1····C45	-x+1, -y-2, -z		3.677	84
C43–I1····C8	-x+1, y-1/2-1, - z+1/2		3.525	158
C43–I1····C9	-x+1, y-1/2-1, - z+1/2		3.407	146
C43–I1…C10	-x+1, y-1/2-1, - z+1/2		3.642	144
C46–I2…C6	x, -y-1/2, z-1/2		3.599	135
C46…C22	x, y-1, z		3.293	
Cg1…Cg2	x, y+1, z		3.697	
Cg2…Cg2	-x+1,-y-2,-z		4.007	
Co-crystal 3				
C11–H11…F2	1-x, 1-y, 1-z	2.637	3.512	165
C3–H3…F4	x-1, y, z	2.522	3.398	170

C5–H5…F3	x, y-1,z	2.476	3.392	161
C27–I1···C10	x+1, y, z		3.580	156
C30–I2····C3	-x, -y, -z		3.651	136
C30–I2····C4	-x, -y, -z		3.359	158
C30–I2…C5	-x, -y, -z		3.589	162
C27…C19	1+x, y-1, z		3.393	
C29…C22	1+x, y-1, z		3.399	
C31…C19	-x, 1-y, -z		3.194	
C32…C21	-x, 1-y, -z		3.354	
C32…C22	-x, 1-y, -z		3.394	
Cg3…Cg4	x-1, y+1,+z		3.405	
Cg4…Cg3	-x, 1-y,-z		3.495	
Co-crystal 4				
N1–H1A…I1	1-x, 2-y, 1-z	3.128	3.723	131
C23–H23…F2	1-x, 2-y, 1-z	2.568	3.507	170
C24–H24…F2	1-x, 2-y, 1-z	2.629	3.436	143
C1–H1···F1	2-x, 2-y, 1-z	2.603	3.266	127
N2–H2A…N1	x, y-1, z	2.351	3.201	163
N1–H1B…C21	1-x, 2-y, 2-z	2.799	3.427	154
N1–H1B…C22	1-x, 2-y, 2-z	2.861	3.520	162
N2-H2B…C1	2-x, 1-y, 1-z	2.678	3.324	151
C1-H1C14	2-x, 2-y, 1-z	2.876	3.599	134
С22–Н22····С25	1-x, 1-y, 2-z	2.827	3.662	147
C26–I1…C11	x, y, z		3.295	169
C26–I1····C12	x, y, z		3.320	165
C29–I2····C10	x, y+1, z-1		3.467	159
C29–I2…C11	x, y+1, z-1		3.324	172
C29–I2····C12	x, y+1, z-1		3.572	160
C27–F4····C2	x, y, z-1		3.003	144
C27–F4···C3	x, y, z-1		3.126	133

C31–F2…C22	x, y+1, z-1		3.144	165
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Cg1 = Centroid of phenyl ring C21-C22-C23-C24-C39-C40 in BDVB molecule; Cg2 = Centroid of 1,4-Diiodotetrafluorobenzene in Co-crystal 2. Cg3 = Centroid of Fluorene moiety C14-C15-C16-C17-C18-C19-C20-C21-C22-C23-C24-C25-C26 in BHF molecule; Cg4 = Centroid of 1,4-Diiodotetrafluorobenzene in Co-crystal 3.



**Figure S4.** Profile fitting of the experimental powder patterns obtained from the bulk-powders of (a) Co-crystal 1, (b) Co-crystal 2, (c) Co-crystal 3 and (d) Co-crystal 4.



Figure S5. Fluorescence decay profile of (a) Co-crystal 1, (b) Co-crystal 2, (c) Co-crystal 3 and (d) Co-crystal 4.

Table S3. Total luminescent properties of Co-crystals 1-4.

Co-crystal	Spectr	a/λ, nm	Decays/ <b>τ</b> , ns			τ /ns
Co-ci ystai	λ <sub>ex</sub>	λ <sub>em</sub>	$\tau_1(f_1, \%)$	$\tau_2(f_2, \%)$	$\tau_3(f_3, \%)$	t average/ 113
1	375	465	0.810 (14.41)	3.712 (5.64)	0.035 (79.94)	2.46
2	410	465	0.159 (0.39)	0.434 (2.22)	0.005 (97.39)	0.27
3	380	536	0.951 (100)			0.95
4	290	540	2.084 (0.01)	17.871 (0.04)	0.004 (99.95)	10.85



Figure S6. DSC profiles of all the individual components of the co-crystals.

Starting Materials	Melting Point (°C)	Co-crystal	Melting Point (°C)	
BCC	156	Co-crystal 1 (Form I)	139	
1,4-DITFB	106	Co-crystal 1 (Form II)	147	
BDVB	205	Co. americal 2	154	
1,4-DITFB	106	Co-crystal 2		
BHF	229	Co. ametal 2	150	
1,4-DITFB	106	Co-crystal 5	152	
BAF	234	Co. ametal 4	140	
1,4-DITFB	106	Co-crystal 4	140	



**Figure S7.** The  $\sigma$ -hole… $\pi$ ,  $\pi$ -hole… $\pi$  and other halogen bonding units obtained from single co-crystal structure data for calculation of Interaction energies (M06-2X with 6-311G<sup>\*\*</sup> basis set for H, C, N, F atoms and LANL2DZdp ECP basis set for I atoms).

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