# Supporting Information 

# Tuning the solid-state emission by co-crystallization through $\boldsymbol{\sigma}$ - and $\boldsymbol{\pi}$-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 $4^{\circ} \mathrm{C}$ 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 $4^{\circ} \mathrm{C}$ 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 plateshaped light-yellow coloured crystals were obtained by slow evaporation in Toluene solvent at $4^{\circ} \mathrm{C}$ 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 $4^{\circ} \mathrm{C}$ 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 $4^{\circ} \mathrm{C}$ 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 + <br> Hexane | Aggregates | Aggregates | Aggregates | Aggregates |
| :---: | :---: | :---: | :---: | :---: |
| Acetone + <br> Chloroform | Aggregates | Aggregates | Aggregates | Block |
| 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 $\mathrm{Cu} \mathrm{K} \alpha$ radiation ( $\lambda=1.54060 \AA$ ). The bulk powder of each sample was placed in a silica sample holder and measured by a continuous scan between $5-40^{\circ}$ with a step size of $0.013103^{\circ}$. 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 $\left(4^{\circ} \mathrm{C}\right)$. Single Crystal X-ray Diffraction data were collected on Bruker AXS Kappa APEXII diffractometer using monochromated Mo K $\alpha$ radiation ( $\lambda=0.71073 \AA$ ) 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. ${ }^{1}$ Data reduction was carried out with Bruker SAINT suite. ${ }^{2}$ Absorption correction was performed by multi-scan method implemented in SADABS. ${ }^{3}$ All the crystal structures were solved by direct methods using SIR 2014. ${ }^{4}$ The crystal structure refinements were done in the program package $\operatorname{Win} G X,{ }^{5}$ and all non-hydrogen atoms were refined anisotropically by full matrix least-squares calculations based on $\mathrm{F}^{2}$ with $S H E L X L-2016 .{ }^{6}$ 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 $P L A T O N^{7}$ and $M E R C U R Y^{8}$ 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 $3{ }^{\circ} \mathrm{C} / \mathrm{min}$ under a dry nitrogen purge ( $20 \mathrm{~mL} / \mathrm{min}$ ).

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 $\mathrm{BaSO}_{4}$ 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 $300 \mu \mathrm{~s}$ 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 $300 \mu \mathrm{~s}, 1 \mathrm{~ms}$ and 150 ms respectively.

## Computational methods

All calculations were carried out using GAUSSIAN09 package ${ }^{9}$ 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 ${ }^{10}$ The basis set $6-311 \mathrm{G}(\mathrm{d}, \mathrm{p})$ was used to describe $\mathrm{C}, \mathrm{H}, \mathrm{N}$ and F atoms and LANL2DZdp ECP was used for I atoms. The interaction energy ( $\Delta \mathrm{E}$ ) of each interaction unit was calculated as the difference between the energy of interaction unit and the sum of the total energies of monomers $\Delta \mathrm{E}_{\text {total }}=\mathrm{E}_{\mathrm{AB}}$ $-\left(E_{A}+E_{B}\right)$. The basis set superposition error (BSSE) was estimated using Boys-Bernardi counterpoise (CP) method. ${ }^{11}$

(a)

(b)

(d)

(e)

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 1,4DITFB.


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.

Table S1. Crystal Data and Structure Refinement

| Sample Code | Co-crystal 1 |  | Co-crystal 2 | Co-crystal 3 | Co-crystal 4 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Stoichiometric <br> Ratio | Form I <br> $(2 * 0.5 \mathrm{D}: 1 \mathrm{~A})$ | Form II <br> $(1 \mathrm{D}: 2 \mathrm{~A})$ | $1 \mathrm{D}: 1 \mathrm{~A}$ | $2 * 0.5 \mathrm{D}: 1 \mathrm{~A}$ | $1 \mathrm{D}: 1 \mathrm{~A}$ |
| Formula | $\mathrm{C}_{18} \mathrm{H}_{8} \mathrm{~F}_{4} \mathrm{I}_{2} \mathrm{~N}_{2}$ | $\mathrm{C}_{30} \mathrm{H}_{16} \mathrm{~F}_{4} \mathrm{I}_{2} \mathrm{~N}_{4}$ | $\mathrm{C}_{46} \mathrm{H}_{30} \mathrm{~F}_{4} \mathrm{I}_{2}$ | $\mathrm{C}_{32} \mathrm{H}_{18} \mathrm{~F}_{4} \mathrm{I}_{2}$ | $\mathrm{C}_{31} \mathrm{H}_{20} \mathrm{~F}_{4} \mathrm{I}_{2} \mathrm{~N}_{2}$ |
| Solvent | Dichloromethane | Acetonitrile | Toluene | Dichloromethane <br> $:$ Hexane | Acetone : <br> Chloroform |
| Crystal Size (mm) | 0.36 X 0.12 X <br> 0.08 | 0.20 X 0.02 X 0.02 | 0.21 X 0.13 X <br> 0.08 | 0.30 X 0.20 X <br> 0.10 | 0.24 X 0.11 X <br> 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 |


| Crystal System | Monoclinic | Monoclinic | Monoclinic | Triclinic | Triclinic |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Space Group | $P 2{ }_{1} / c$ | $P 2{ }_{1} / c$ | $P 2{ }_{1} / c$ | $P-1$ | $P-1$ |
| Z | 4 | 4 | 4 | 2 | 2 |
| $a(\AA)$ | 4.4893 (3) | 26.714 (9) | 13.9639(5) | $9.3655(4)$ | 11.5700(4) |
| $\boldsymbol{b}(\AA)$ | 15.5665 (5) | 13.423 (4) | $9.2151(3)$ | 11.0244(4) | 11.6762(4) |
| $c(\AA)$ | 24.4653 (9) | 7.556 (3) | 28.0322(9) | 13.4310(5) | 11.7522(4) |
| $\alpha\left({ }^{\circ}\right)$ | 90 | 90 | 90 | 89.844(2) | 70.484(2) |
| $\beta\left({ }^{\circ}\right)$ | 92.894 (2) | 97.82 (2) | 98.6600(10) | 74.129(2) | 63.812(2) |
| $\gamma\left({ }^{\circ}\right)$ | 90 | 90 | 90 | 73.241 | 73.849(2) |
| Volume ( $\mathrm{A}^{\text {3 }}$ ) | 1707.52 (11) | 2684.1 (15) | 3566.0(2) | 1272.85(9) | 1326.69(8) |
| Density ( $\mathrm{g} \mathrm{cm}^{-3}$ ) | 2.264 | 2.399 | 1.700 | 1.911 | 1.878 |
| F (000) , $\mu\left(\mathrm{mm}^{-1}\right)$ | 1088, 3.729 | 1464, 2.399 | 1792, 1.819 | 704, 2.521 | 724, 2.423 |
| $\theta(\min , \max )\left(^{\circ}\right.$ ) | $1.551,30.185$ | $2.161,30.421$ | 2.234, 27.878 | 1.936, 28.699 | 1.992, 30.259 |
| $\underset{\text { min,max }, \mathbf{k}_{\text {min }, \text { max }},}{\mathbf{l}_{\text {min }, \text { max }}}$ | $\begin{gathered} (-6,6),(-21,21),(- \\ 34,27) \end{gathered}$ | $\begin{gathered} (-37,37),(-19,19) \\ (-10,10) \end{gathered}$ | $\begin{gathered} (-16,18),(-12,12), \\ (-34,36) \end{gathered}$ | $\begin{gathered} (-12,12),(-14,14) \\ (-17,18) \end{gathered}$ | $\begin{gathered} (-16,16),(-16,16), \\ (-16,16) \end{gathered}$ |
| 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 | $0.0453,0.0337$ |
| $\mathbf{w R}_{2}$ _all, $\mathrm{wR}_{\mathbf{2} \text { _obs }}$ | 0.1107, 0.1074 | 0.2157, 0.1611 | 0.0670, 0.0642 | 0.0820, 0.0804 | 0.0796, 0.0753 |
| $\Delta \rho_{\text {min,max }}\left(\mathrm{e} \AA^{-3}\right)$ | -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 | $\mathbf{D}-\mathbf{H} \cdots \mathbf{A}(\AA)$ | $\mathbf{D} \cdots \mathbf{A}(\AA)$ | $\angle \mathbf{D}-\mathbf{H} \cdots \mathbf{A}(\AA) /$ <br> $\angle \mathbf{D} \cdots \mathbf{A}(\AA)$ |
| :--- | :---: | :---: | :---: | :---: |
| Co-crystal 1 ( Form I ) <br> $\mathrm{C} 8-\mathrm{H} 8 \cdots \mathrm{~F} 1$ |  |  |  |  |
| $\mathrm{C} 9-\mathrm{H} 9 \cdots \mathrm{~F} 3$ | $\mathrm{x}+1, \mathrm{y}-1 / 2,-\mathrm{z}+3 / 2$ | 2.546 | 3.342 | 144 |
| $\mathrm{C} 10-\mathrm{H} 10 \cdots \mathrm{~F} 3$ | $\mathrm{x}+1,-\mathrm{y}+3 / 2, \mathrm{z}-1 / 2$ | 2.459 | 3.096 | 126 |


| C3-H3 $\cdots$ F4 | $-\mathrm{x}+2,-\mathrm{y}+2,-\mathrm{z}+1$ | 2.606 | 3.148 | 118 |
| :---: | :---: | :---: | :---: | :---: |
| C14-I1 $\cdots$ N1 | $\mathrm{x}+1, \mathrm{y}, \mathrm{z}$ |  | 2.873 | 176 |
| C14-I1 $\cdots \mathrm{N} 2$ | $\mathrm{x}+1, \mathrm{y}, \mathrm{z}$ |  | 3.508 | 160 |
| C14-I1 $\cdots$ I2-C17 | $\mathrm{x}+1, \mathrm{y}, \mathrm{z}$ |  | 3.762 | 167, 109 |
| Co-crystal 1 ( Form II ) $\mathrm{C} 4-\mathrm{H} 4 \cdots \mathrm{~F} 2$ | $\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ | 2.613 | 3.131 | 116 |
| C16-H16 $\cdots$ F 4 | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}$ | 2.608 | 3.307 | 132 |
| C2-H2 ${ }^{\text {I }}$ I | $\mathrm{x}, \mathrm{y}, \mathrm{z}$ | 3.125 | 3.732 | 124 |
| C25-I1 $\cdots$ N1 | $\mathrm{x}, \mathrm{y}, \mathrm{z}$ |  | 2.875 | 173 |
| C28-I2 $\cdots \mathrm{N} 3$ | $\mathrm{x}, \mathrm{y}, \mathrm{z}$ |  | 2.962 | 178 |
| $\begin{aligned} & \text { Co-crystal } 2 \\ & \text { C15-H15 } \cdots \mathrm{I} 1 \end{aligned}$ | $\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ | 3.141 | 3.905 | 139 |
| C34-H34 $\cdots$ F3 | $\begin{gathered} -\mathrm{x}+2, \mathrm{y}-1 / 2-1,- \\ \mathrm{z}+1 / 2 \end{gathered}$ | 2.620 | 3.395 | 139 |
| C25-H25 $\cdots$ C9 | $x, y+1, z$ | 2.803 | 3.519 | 133 |
| C25-H25 ${ }^{\text {C }}$ C10 | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}$ | 2.752 | 3.596 | 148 |
| C27-H27 $\cdots$ C39 | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}$ | 2.887 | 3.827 | 171 |
| C18-H18 $\cdots$ C34 | $-\mathrm{x}+2, \mathrm{y}-1 / 2,-\mathrm{z}+1 / 2$ | 2.826 | 3.620 | 142 |
| C46-F4 $\cdots$ F4-C46 | 1-x, -3-y, -z |  | 2.755 | 134, 134 |
| C43-I1 $\cdots$ C45 | -x+1, -y-2, -z |  | 3.677 | 84 |
| C43-I1 ${ }^{\text {c }}$ C8 | $\begin{gathered} -\mathrm{x}+1, \mathrm{y}-1 / 2-1,- \\ \mathrm{z}+1 / 2 \end{gathered}$ |  | 3.525 | 158 |
| C43-I1 ${ }^{\text {c }}$ C 9 | $\begin{gathered} -\mathrm{x}+1, \mathrm{y}-1 / 2-1,- \\ \mathrm{z}+1 / 2 \end{gathered}$ |  | 3.407 | 146 |
| C43-I1 $\cdots$ C10 | $\begin{gathered} -\mathrm{x}+1, \mathrm{y}-1 / 2-1,- \\ \mathrm{z}+1 / 2 \end{gathered}$ |  | 3.642 | 144 |
| C46-I2 $\cdots$ C 6 | $\mathrm{x},-\mathrm{y}-1 / 2, \mathrm{z}-1 / 2$ |  | 3.599 | 135 |
| C46 $\cdots$ C22 | $\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ |  | 3.293 |  |
| $\mathrm{Cg} 1 \cdots \mathrm{Cg} 2$ | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}$ |  | 3.697 |  |
| $\mathrm{Cg} 2 \cdots \mathrm{Cg} 2$ | -x+1,-y-2,-z |  | 4.007 |  |
| Co-crystal 3 $\mathrm{C} 11-\mathrm{H} 11 \cdots \mathrm{~F} 2$ | 1-x, 1-y, 1-z | 2.637 | 3.512 | 165 |
| C3-H3 $\cdots$ F 4 | $\mathrm{x}-1, \mathrm{y}, \mathrm{z}$ | 2.522 | 3.398 | 170 |


| C5-H5 $\cdots$ F3 | $\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ | 2.476 | 3.392 | 161 |
| :---: | :---: | :---: | :---: | :---: |
| C27-I1 $\cdots$ C10 | $\mathrm{x}+1, \mathrm{y}, \mathrm{z}$ |  | 3.580 | 156 |
| C30-I2 $\cdots$ C3 | -x, -y, -z |  | 3.651 | 136 |
| C30-I2 $\cdots$ C 4 | -x, -y, -z |  | 3.359 | 158 |
| C30-I2 $\cdots$ C 5 | -x, -y, -z |  | 3.589 | 162 |
| C27 $\cdots$ C19 | $1+\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ |  | 3.393 |  |
| C29 $\cdots$ C22 | $1+\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ |  | 3.399 |  |
| C31 $\cdots$ C19 | -x, 1-y, -z |  | 3.194 |  |
| C32 $\cdots$ C21 | -x, 1-y, -z |  | 3.354 |  |
| C32 $\cdots$ C 22 | -x, 1-y, -z |  | 3.394 |  |
| $\mathrm{Cg} 3 \cdots \mathrm{Cg} 4$ | $\mathrm{x}-1, \mathrm{y}+1,+\mathrm{z}$ |  | 3.405 |  |
| $\mathrm{Cg} 4 \cdots \mathrm{Cg} 3$ | -x, 1-y,-z |  | 3.495 |  |
| Co-crystal 4 <br> N1-H1A $\cdots$ I1 | 1-x, 2-y, 1-z | 3.128 | 3.723 | 131 |
| C23-H23 $\cdots$ F2 | 1-x, 2-y, 1-z | 2.568 | 3.507 | 170 |
| C24-H24 $\cdots$ F2 | 1-x, 2-y, 1-z | 2.629 | 3.436 | 143 |
| C1-H1 $\cdots$ F1 | $2-\mathrm{x}, 2-\mathrm{y}, 1-\mathrm{z}$ | 2.603 | 3.266 | 127 |
| N2-H2A $\cdots$ N1 | $\mathrm{x}, \mathrm{y}-1, \mathrm{z}$ | 2.351 | 3.201 | 163 |
| N1-H1B $\cdots$ C21 | 1-x, 2-y, 2-z | 2.799 | 3.427 | 154 |
| N1-H1B $\cdots$ C22 | 1-x, 2-y, 2-z | 2.861 | 3.520 | 162 |
| N2-H2B $\cdots$ C1 | $2-\mathrm{x}, 1-\mathrm{y}, 1-\mathrm{z}$ | 2.678 | 3.324 | 151 |
| C1-H1 $\cdots$ C14 | 2-x, 2-y, 1-z | 2.876 | 3.599 | 134 |
| C22-H22 $\cdots$ C25 | 1-x, 1-y, 2-z | 2.827 | 3.662 | 147 |
| C26-I1 $\cdots$ C11 | $\mathrm{x}, \mathrm{y}, \mathrm{z}$ |  | 3.295 | 169 |
| C26-I1 $\cdots$ C12 | $\mathrm{x}, \mathrm{y}, \mathrm{z}$ |  | 3.320 | 165 |
| C29-I2 $\cdots$ C10 | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}-1$ |  | 3.467 | 159 |
| C29-I2 $\cdots$ C11 | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}-1$ |  | 3.324 | 172 |
| C29-I2 $\cdots$ C12 | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}-1$ |  | 3.572 | 160 |
| C27-F4 $\cdots$ C2 | $\mathrm{x}, \mathrm{y}, \mathrm{z}-1$ |  | 3.003 | 144 |
| C27-F4 ${ }^{\text {c }}$ C3 | $\mathrm{x}, \mathrm{y}, \mathrm{z}-1$ |  | 3.126 | 133 |


| C31-F2 $\cdots \mathrm{C} 22$ | $\mathrm{x}, \mathrm{y}+1, \mathrm{z}-1$ |  | 3.144 | 165 |
| :--- | :---: | :---: | :---: | :---: |

$\mathrm{Cg} 1=$ Centroid of phenyl ring C21-C22-C23-C24-C39-C40 in BDVB molecule; $\mathrm{Cg} 2=$ 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 Cocrystal 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 | Spectra/ $\lambda$, nm |  | Decays/ $\boldsymbol{\tau}$, ns |  |  | $\boldsymbol{\tau}_{\text {average }} / \mathbf{n s}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\lambda_{\text {ex }}$ | $\lambda_{\text {em }}$ | $\tau_{1}\left(f_{1}, \%\right)$ | $\tau_{2}\left(f_{2}, \%\right)$ | $\tau_{3}\left(f_{3}, \%\right)$ |  |
| 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.
Table S4. Comparison of the melting points of the binary co-crystals and their respective components.

| Starting Materials | Melting Point $\left({ }^{\circ} \mathbf{C}\right)$ | Co-crystal | Melting Point $\left({ }^{\circ} \mathbf{C}\right)$ |
| :---: | :---: | :---: | :---: |
| BCC | 156 | Co-crystal 1 (Form I) | 139 |
| 1,4-DITFB | 106 | Co-crystal 1 (Form II) | 147 |
| BDVB | 205 |  | Co-crystal 2 |
| 1,4-DITFB | 106 |  | 154 |
| BHF | 229 |  | 152 |
| Co-crystal 3 |  |  |  |
| BAF | 106 |  | 140 |
| 1,4-DITFB | 234 | 106 |  |





2d


3a



4b


3c


4c

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

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