Electronic Supplementary Material (ESI) for CrystEngComm.

Unravelling Supramolecular Features and Opto-electronic Properties of Binary Charge Transfer Cocrystal of Blue Fluorescent Di-carbazole and TFT

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Table S1. Crystallographic and refinement parameters of cocrystal CBP:$(TFT)_2$

	CBP:$(TFT)_2$
chemical formula	$C_{52}H_{24}N_6F_8$
formula weight	884.77
temp (K)	100(2)
CCDC Number	2058993
crystal system	Triclinic
space group	*P* -1
a (Å)	11.6287(12)
b (Å)	12.9682(14)
c (Å)	15.0674(14)
α (°)	98.887(5)
β(°)	106.858(5)
γ(°)	108.238(4)
V (Å^3)	1988.7(4)
Z	2
F_{000}	900
ρ_{calcd}(g cm^{-3})	1.478
no. of unique reflection	10049
no. of reflection ($I \geq 2\sigma(I)$)	6718
R_1[a], R_1[b] (all data, $I \geq 2\sigma(I)$)	0.0803, 0.0440
wR_2[a], wR_2[b] (all data, $I \geq 2\sigma(I)$)	0.1134, 0.0956
goodness of fit (F^2)	1.020
largest peak/hole (e Å^{-3})	0.260/ -0.290

Table S2. Energy decomposition analysis for π··π stacking in CBP:$(TFT)_2$

Interaction	**E_{ele}(kJ/mol)**	**E_{pol}(kJ/mol)**	**E_{dis}(kJ/mol)**	**E_{rep}(kJ/mol)**	**E_{tot}(kJ/mol)**
π··π Stacking	-23.6	-8.5	-65.9	36.6	-59.3

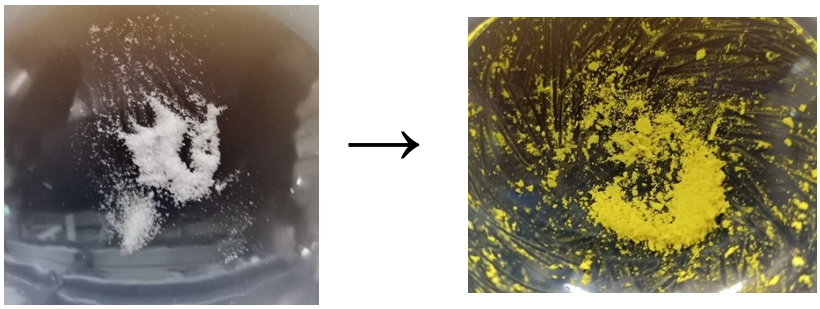


Fig. S1 Instantaneous colour change during formation of cocrystal CBP:$(TFT)_2$.

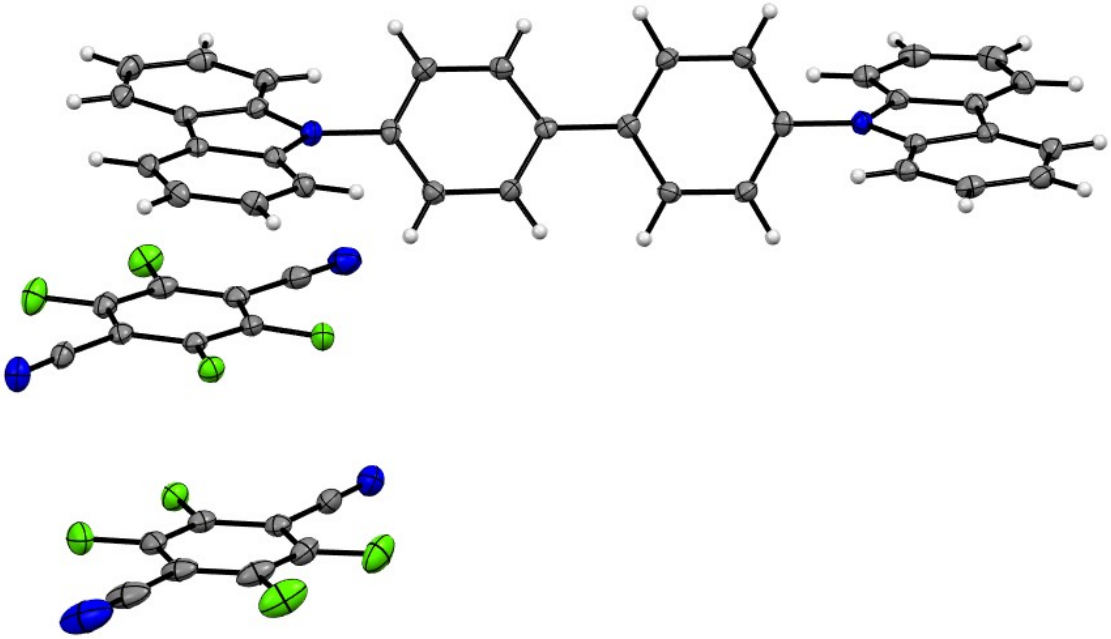


Fig. S2 *ORTEP* diagram (45% probability) of cocrystalCBP:$(TFT)_2$.

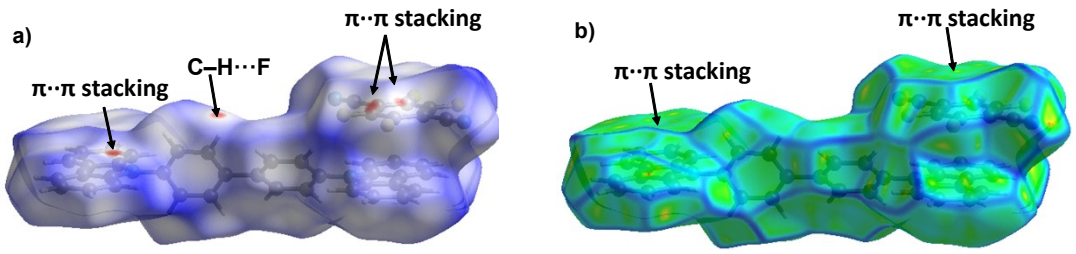


Fig. S3a (a) Hirshfeld surface analysis: d_{norm} plot; (b) Curvedness plot for D–A dimer.

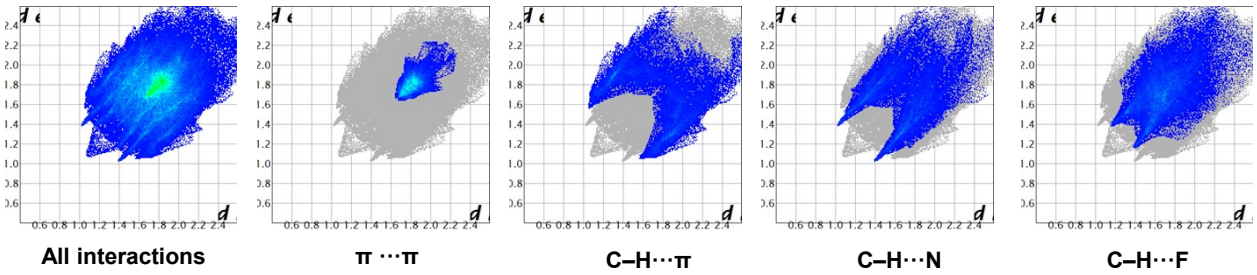


Fig. S3b Fingerprint plots of CBP:$(TFT)_2$cocrystal.

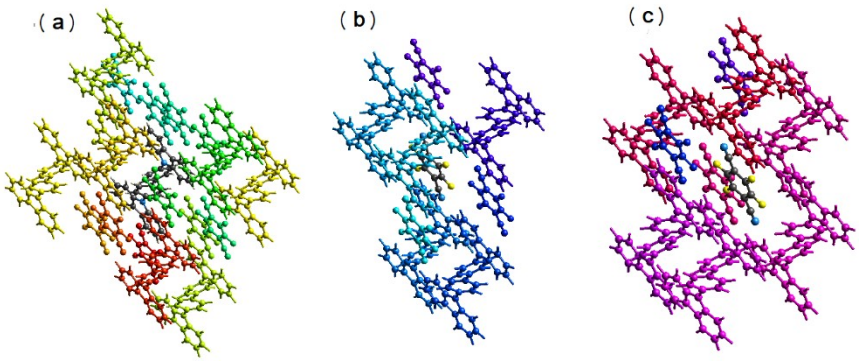


Fig. S4a Colour coding for the neighbouring molecules around (a) CBP; (b) TFT-1 and (c) TFT-2 molecules in CBP:$(TFT)_2$ cocrystal.

Table S3: Interaction energies (kJ/mole) obtained from energy framework calculation for the cocrystal.

Energy Profile for "Residue 1"

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	14.77	B3LYP/6-31G(d,p)	-3.7	-1.3	-7.6	0.0	-11.4
	1	-x, -y, -z	10.60	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	1	-	7.91	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	1	-x, -y, -z	8.93	B3LYP/6-31G(d,p)	0.0	0.0	0.0	0.0	0.0
	1	-	14.43	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	1	-x, -y, -z	9.07	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5
	2	x, y, z	16.14	B3LYP/6-31G(d,p)	-4.7	-0.1	-7.2	0.0	-11.4
	1	-	6.69	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	2	x, y, z	18.30	B3LYP/6-31G(d,p)	-4.9	-0.1	-7.5	0.0	-11.9
	1	-	6.84	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	1	-x, -y, -z	8.71	B3LYP/6-31G(d,p)	-15.6	-3.6	-53.2	36.3	-43.1
	1	-	8.04	B3LYP/6-31G(d,p)	-17.8	-6.2	-65.9	45.2	-52.8
	1	-x, -y, -z	20.76	B3LYP/6-31G(d,p)	0.7	-0.1	-4.5	0.0	-3.3
	1	-	7.46	B3LYP/6-31G(d,p)	-13.7	-4.9	-50.0	31.2	-42.4
	1	-	14.16	B3LYP/6-31G(d,p)	-0.5	-0.3	-7.9	0.0	-7.7
	1	-	10.68	B3LYP/6-31G(d,p)	-4.6	-0.1	-7.2	0.0	-11.3
	1	-	9.00	B3LYP/6-31G(d,p)	1.2	-0.1	-2.7	0.0	-1.1
	1	-	14.46	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5
	1	-	12.21	B3LYP/6-31G(d,p)	-7.9	-0.5	-8.8	0.0	-16.4
	0	-x, -y, -z	7.88	B3LYP/6-31G(d,p)	-10.8	-1.6	-11.8	9.4	-17.0
	0	-	8.04	B3LYP/6-31G(d,p)	-17.8	-6.2	-65.9	45.2	-52.8
	0	-	6.69	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	-	14.77	B3LYP/6-31G(d,p)	-2.9	-1.3	-7.6	0.0	-10.5
	0	-	12.21	B3LYP/6-31G(d,p)	-7.8	-0.5	-8.8	0.0	-16.2

	0	-	6.53	B3LYP/6-31G(d,p)	0.1	-0.1	-1.6	0.0	-1.3
	0	-	7.46	B3LYP/6-31G(d,p)	-13.7	-4.9	-50.0	31.2	-42.4
	0	-	14.16	B3LYP/6-31G(d,p)	-1.2	-0.3	-7.9	0.0	-8.4
	0	-	10.29	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	-	12.73	B3LYP/6-31G(d,p)	0.2	-0.0	-0.2	0.0	0.0
	0	-	9.19	B3LYP/6-31G(d,p)	-0.2	-0.0	-0.2	0.0	-0.4
	0	-	14.43	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	0	-	9.00	B3LYP/6-31G(d,p)	1.2	-0.1	-2.7	0.0	-1.1
	0	-	6.84	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	0	-	7.91	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	0	-x, -y, -z	7.65	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	0	-	10.68	B3LYP/6-31G(d,p)	-4.7	-0.1	-7.2	0.0	-11.4
	0	-	14.46	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5

Energy Profile for "Residue 2"

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	-	14.77	B3LYP/6-31G(d,p)	-3.7	-1.3	-7.6	0.0	-11.4
	0	-x, -y, -z	10.60	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	0	-	7.91	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	0	-x, -y, -z	8.93	B3LYP/6-31G(d,p)	0.0	0.0	0.0	0.0	0.0
	0	-	14.43	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	0	-x, -y, -z	9.07	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5
	0	x, y, z	16.14	B3LYP/6-31G(d,p)	-4.7	-0.1	-7.2	0.0	-11.4
	0	-	6.69	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	x, y, z	18.30	B3LYP/6-31G(d,p)	-4.9	-0.1	-7.5	0.0	-11.9
	0	-	6.84	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	0	-x, -y, -z	8.71	B3LYP/6-31G(d,p)	-15.6	-3.6	-53.2	36.3	-43.1
	0	-	8.04	B3LYP/6-31G(d,p)	-17.8	-6.2	-65.9	45.2	-52.8

	0	-x, -y, -z	20.76	B3LYP/6-31G(d,p)	0.7	-0.1	-4.5	0.0	-3.3
	0	-	7.46	B3LYP/6-31G(d,p)	-13.7	-4.9	-50.0	31.2	-42.4
	0	-	14.16	B3LYP/6-31G(d,p)	-0.5	-0.3	-7.9	0.0	-7.7
	0	-	10.68	B3LYP/6-31G(d,p)	-4.6	-0.1	-7.2	0.0	-11.3
	0	-	9.00	B3LYP/6-31G(d,p)	1.2	-0.1	-2.7	0.0	-1.1
	0	-	14.46	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5
	0	-	12.21	B3LYP/6-31G(d,p)	-7.9	-0.5	-8.8	0.0	-16.4
	1	-x, -y, -z	7.88	B3LYP/6-31G(d,p)	-10.8	-1.6	-11.8	9.4	-17.0
	1	-	8.04	B3LYP/6-31G(d,p)	-17.8	-6.2	-65.9	45.2	-52.8
	1	-	6.69	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	1	-	14.77	B3LYP/6-31G(d,p)	-2.9	-1.3	-7.6	0.0	-10.5
	1	-	12.21	B3LYP/6-31G(d,p)	-7.8	-0.5	-8.8	0.0	-16.2
	1	-	6.53	B3LYP/6-31G(d,p)	0.1	-0.1	-1.6	0.0	-1.3
	1	-	7.46	B3LYP/6-31G(d,p)	-13.7	-4.9	-50.0	31.2	-42.4
	1	-	14.16	B3LYP/6-31G(d,p)	-1.2	-0.3	-7.9	0.0	-8.4
	1	-	10.29	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	-	12.73	B3LYP/6-31G(d,p)	0.2	-0.0	-0.2	0.0	0.0
	0	-	9.19	B3LYP/6-31G(d,p)	-0.2	-0.0	-0.2	0.0	-0.4
	0	-	14.43	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	0	-	9.00	B3LYP/6-31G(d,p)	1.2	-0.1	-2.7	0.0	-1.1
	0	-	6.84	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	0	-	7.91	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	0	-x, -y, -z	7.65	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	0	-	10.68	B3LYP/6-31G(d,p)	-4.7	-0.1	-7.2	0.0	-11.4
	0	-	14.46	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5

Energy Profile for “Residue 3”

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	-	14.77	B3LYP/6-31G(d,p)	-3.7	-1.3	-7.6	0.0	-11.4
	0	-x, -y, -z	10.60	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	0	-	7.91	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	0	-x, -y, -z	8.93	B3LYP/6-31G(d,p)	0.0	0.0	0.0	0.0	0.0
	0	-	14.43	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	0	-x, -y, -z	9.07	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5
	0	x, y, z	16.14	B3LYP/6-31G(d,p)	-4.7	-0.1	-7.2	0.0	-11.4
	0	-	6.69	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	x, y, z	18.30	B3LYP/6-31G(d,p)	-4.9	-0.1	-7.5	0.0	-11.9
	0	-	6.84	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	0	-x, -y, -z	8.71	B3LYP/6-31G(d,p)	-15.6	-3.6	-53.2	36.3	-43.1
	0	-	8.04	B3LYP/6-31G(d,p)	-17.8	-6.2	-65.9	45.2	-52.8
	0	-x, -y, -z	20.76	B3LYP/6-31G(d,p)	0.7	-0.1	-4.5	0.0	-3.3
	0	-	7.46	B3LYP/6-31G(d,p)	-13.7	-4.9	-50.0	31.2	-42.4
	0	-	14.16	B3LYP/6-31G(d,p)	-0.5	-0.3	-7.9	0.0	-7.7
	0	-	10.68	B3LYP/6-31G(d,p)	-4.6	-0.1	-7.2	0.0	-11.3
	0	-	9.00	B3LYP/6-31G(d,p)	1.2	-0.1	-2.7	0.0	-1.1
	0	-	14.46	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5
	0	-	12.21	B3LYP/6-31G(d,p)	-7.9	-0.5	-8.8	0.0	-16.4
	0	-x, -y, -z	7.88	B3LYP/6-31G(d,p)	-10.8	-1.6	-11.8	9.4	-17.0
	0	-	8.04	B3LYP/6-31G(d,p)	-17.8	-6.2	-65.9	45.2	-52.8
	0	-	6.69	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	-	14.77	B3LYP/6-31G(d,p)	-2.9	-1.3	-7.6	0.0	-10.5
	0	-	12.21	B3LYP/6-31G(d,p)	-7.8	-0.5	-8.8	0.0	-16.2
	1	-	6.53	B3LYP/6-31G(d,p)	0.1	-0.1	-1.6	0.0	-1.3
	0	-	7.46	B3LYP/6-31G(d,p)	-13.7	-4.9	-50.0	31.2	-42.4

	0	-	14.16	B3LYP/6-31G(d,p)	-1.2	-0.3	-7.9	0.0	-8.4
	1	-	10.29	B3LYP/6-31G(d,p)	-4.0	-1.5	-18.3	8.6	-16.0
	0	-	12.73	B3LYP/6-31G(d,p)	0.2	-0.0	-0.2	0.0	0.0
	0	-	9.19	B3LYP/6-31G(d,p)	-0.2	-0.0	-0.2	0.0	-0.4
	1	-	14.43	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	1	-	9.00	B3LYP/6-31G(d,p)	1.2	-0.1	-2.7	0.0	-1.1
	1	-	6.84	B3LYP/6-31G(d,p)	-10.3	-1.0	-55.0	38.0	-36.1
	1	-	7.91	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	1	-x, -y, -z	7.65	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.8	0.0	-0.8
	1	-	10.68	B3LYP/6-31G(d,p)	-4.7	-0.1	-7.2	0.0	-11.4
	1	-	14.46	B3LYP/6-31G(d,p)	-16.1	-3.7	-54.4	38.1	-43.5

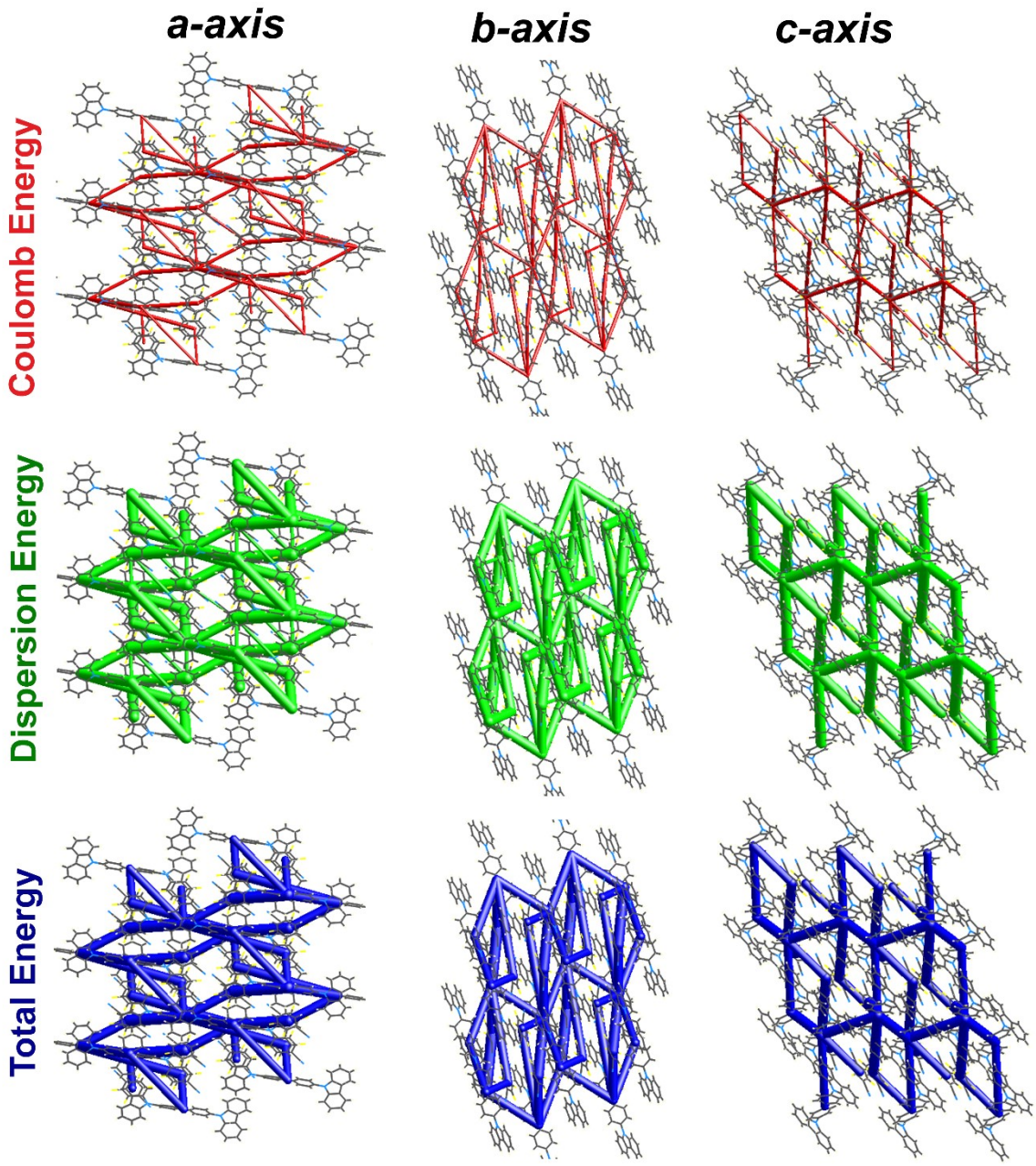


Fig. S4b Energy framework analyses; a) Total energy along crystallographic *a*, *b* and *c* axes; b) Electrostatic energy along crystallographic *a*, *b* and *c* axes; c) Dispersion energy along crystallographic *a*, *b* and *c* axes.

Table S4: Interaction Energies as obtained from CrystalExplorer

E_{elec}	E_{pol}	E_{dis}	$E_{repl.}$	E_{tot}	*Average* E_{tot} (kJ/mole)
-55.71	-9.03	-160.84	66.92	-158.66	-158.66

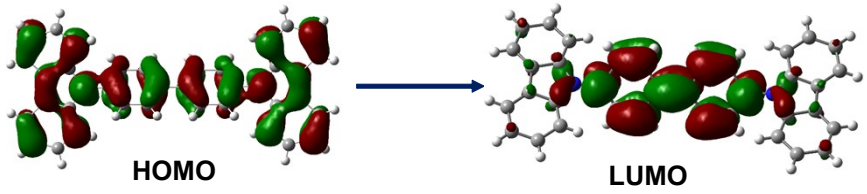


Fig. S5 Molecular orbitals taking part in electronic transition in pristine CBP, calculated at NTO/CAM-B3YP/6-31G(d,p) level.

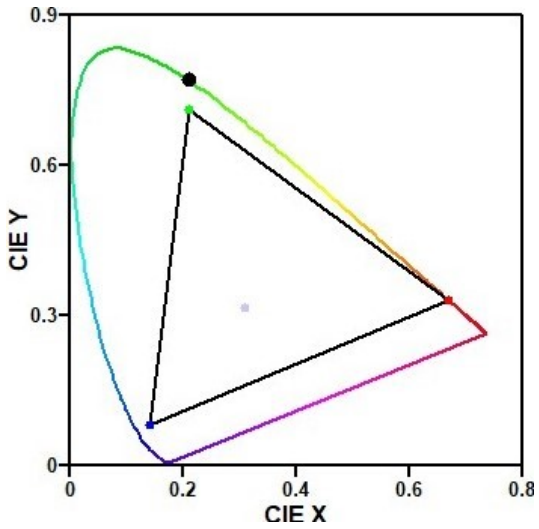


Fig. S6 Colour coordinates for CBP:$(TFT)_2$cocrystal (black circle).

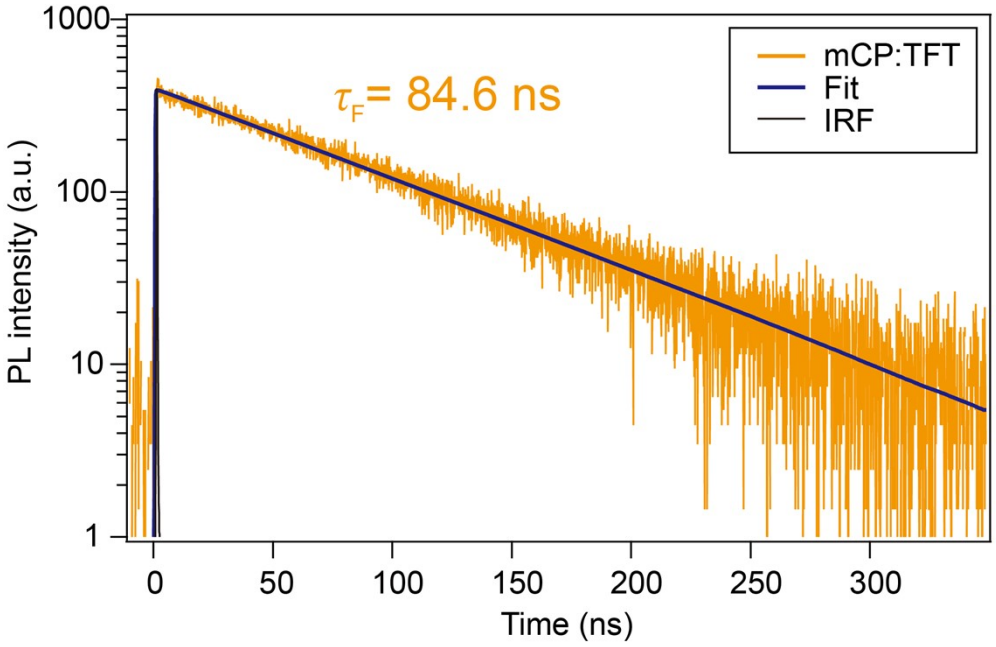


Fig. S7 Time-resolved photoluminescence (PL) decay profile monitored at 535 nm and fitting results with single-exponential decay function in cocrystal CBP:$(TFT)_2$.

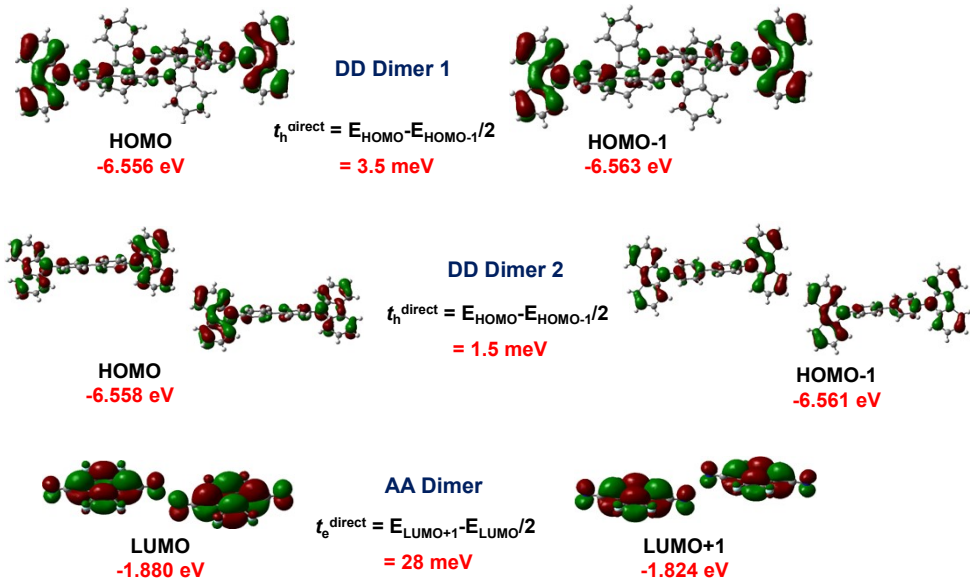


Fig. S8 Direct hole and electron transfer integral in cocrystal CBP:$(TFT)_2$.

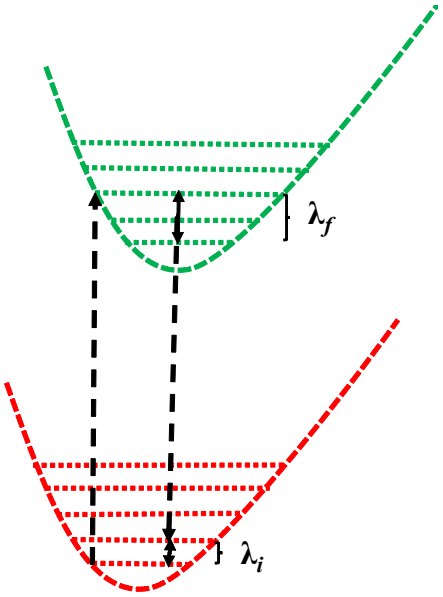
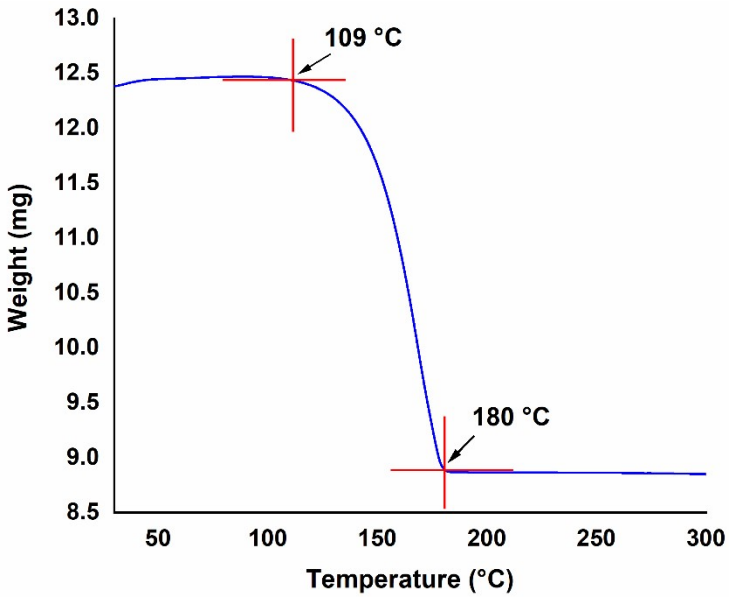


Fig. S9 Four point model for reorganization energy calculation.



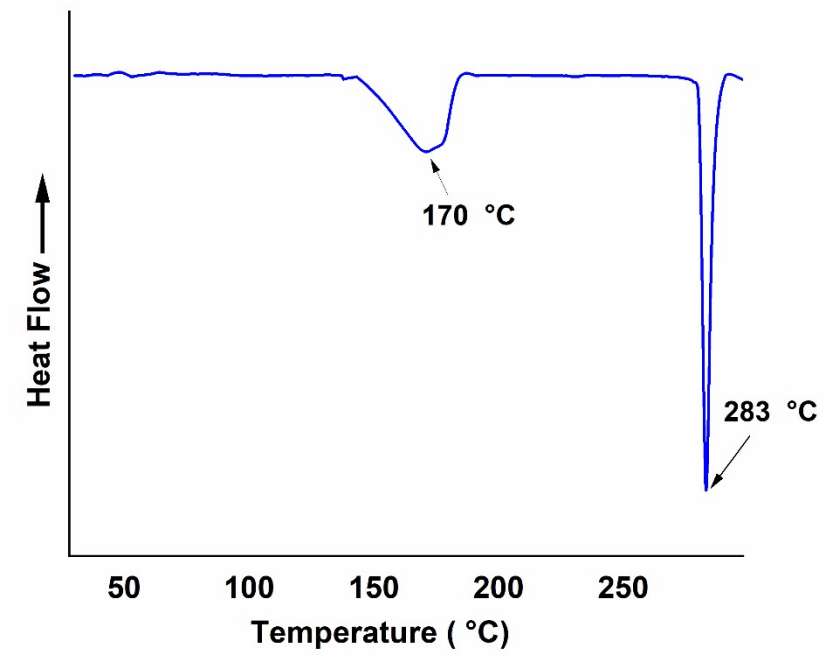


Fig. S10 TGA/ DSC of the grinded solid.

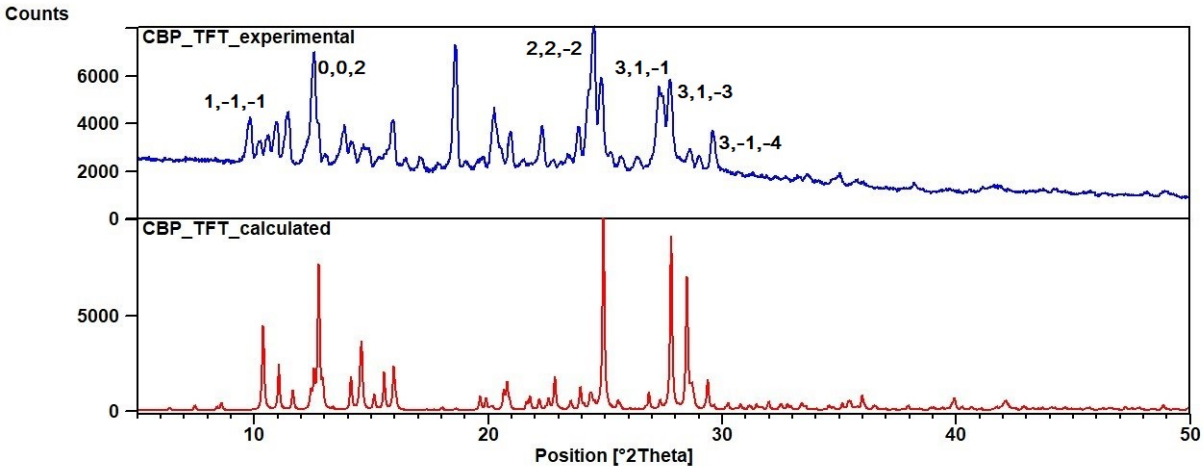


Fig. S11 The PXRD of the grinded solid.

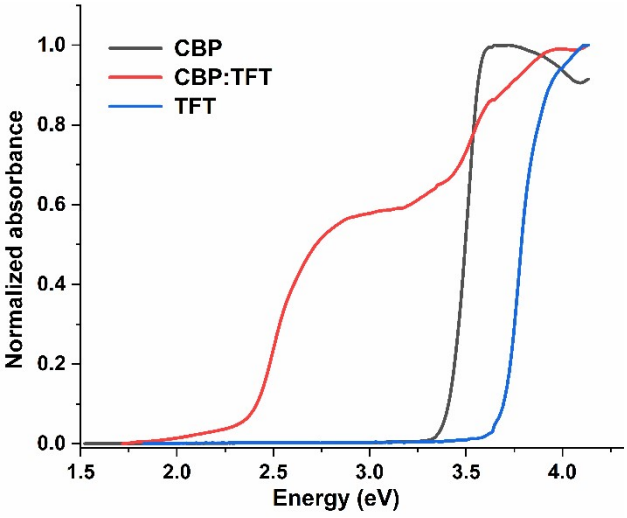


Fig. S12a Absorption spectra of CBP:$(TFT)_2$ cocrystals and coformers in drop-cast thin film.

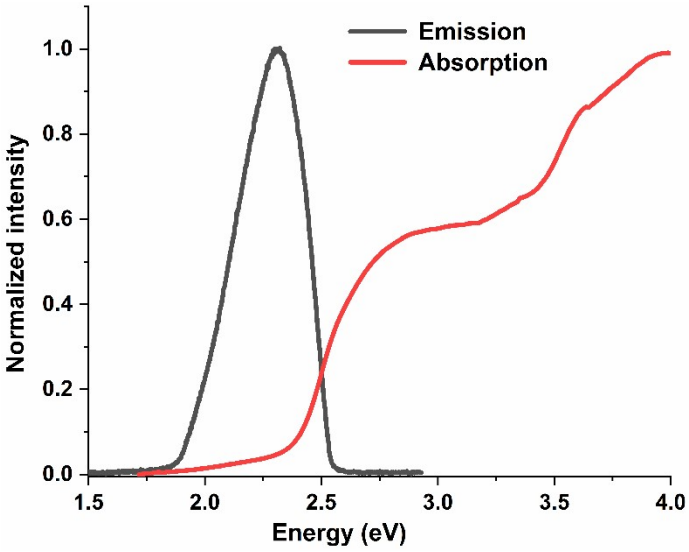


Fig. S12b Absorption and emission spectra of CBP:$(TFT)_2$ spin-coated thin film.

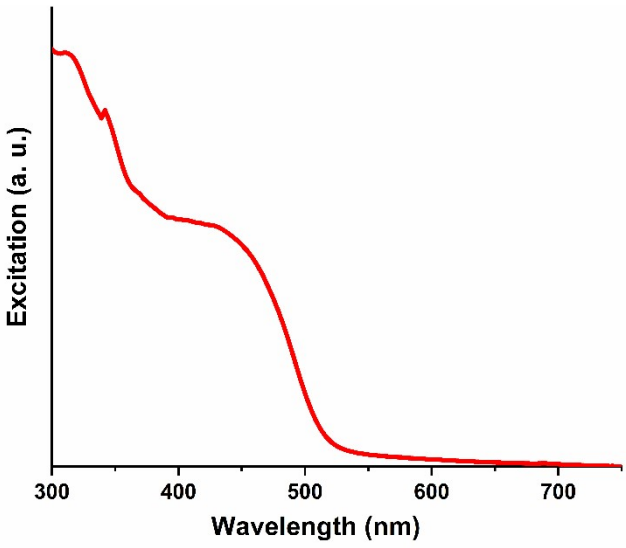


Fig. S13 Excitation spectrum of CBP:$(TFT)_2$ spin-coated thin film, emission at 550 nm.

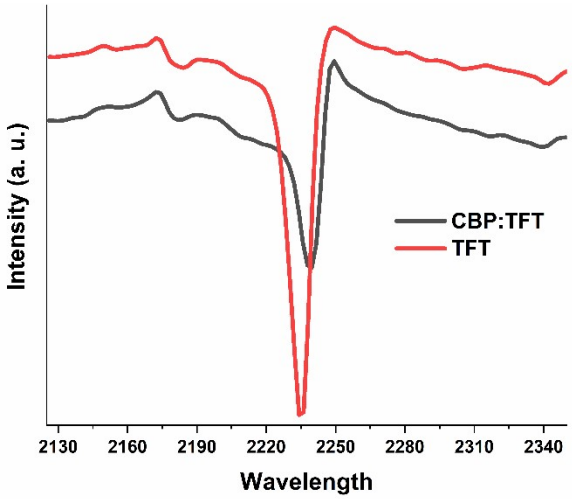


Fig. S14 FTIR spectra of CBP:(TFT)2 and TFT showing C≡N stretching.