Tuning *p*-type to *n*-type Semiconductor Nature by Charge Transfer Cocrystallization: Effect of Transfer Integral vs. Reorganization Energy

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17. PXRD patterns of cocrystal

Syntheses of cocrystal CBP:(TCNQ)$_2$

Equi-molar amounts of CBP (48 mg, 0.1 mmol) and TCNQ (20 mg, 0.1 mmol) were grinded together for one hour with addition of 2-3 drops of methanol at five minutes interval. Instantaneous colour change to black was observed with addition of methanol. Black, needle shaped crystals suitable for XRD study was obtained after three days by diffusion of hexane to chloroform solution of the grinded black powder. It is pertinent to mention that grinding CBP and TCNQ in 1:1 and 1:2 stoichiometry yielded the same cocrystal.

Single crystal X-ray diffraction

Single crystal X-ray diffraction (XRD) data was collected on a Brucker Apex II diffractometer using φ and ω scan-mode employing a graphite monochromator Mo Kα radiation. The structures were solved by direct methods using SHELX. Non-hydrogen atoms were refined anisotropically with full matrix least squares on F^2. Hydrogen atoms were added at calculated positions and refined isotropically. Corresponding crystallographic and refinement parameters were summarized in Table S1 and the cocrystal was assigned to CCDC code 2058993.

Spectroscopic studies

The absorption spectra of CBP, TCNQ, and cocrystal CBP:(TCNQ)$_2$ were recorded in solid state on a JASCO V-770 spectrofluorometer, equipped with a 60 mm BaSO$_4$-coated integrating sphere. Thin films were prepared by dissolving powdered samples in polystyrene/toluene (1 mg/ ml) solution, and drop-casting the solution on a quartz substrate at 55°C. For all measurements, base-line corrections for the transmittance of a polystyrene substrate were made prior to each measurement. FTIR spectra of TCNQ and corystal CBP:(TCNQ)$_2$ was collected using pellets of powder sample and KBr.

Computational methods

Gaussian 16 program package was used for all calculations. The HOMO/ LUMO energy of the donor and acceptor coformers were calculated at B3LYP/6-31G(d,p) level. The HOMO/LUMO of the cocrystal was calculated at CAM-B3LYP/6-31G(d,p) level on crystal coordinates. Natural bond orbital (NBO) analysis of the π-stacked donor acceptor pair was performed at M06-2X/6-31G(d,p) level with ultrafine grid to account for dispersion effect of π⋯π stacking interaction. Energy decomposition analysis was performed at B3LYP/6-31G(d,p) level using CrystalExplorer (version 17.5). Contribution of different intermolecular interactions on crystal packing were estimated by 2D fingerprint plots on Hirshfeld surface. Potential energy scan with dihedral angle changes (phenyl/phenyl and phenyl/carbazole) were performed at B3LYP/6-31G(d,p) level. The phenyl/carbazole dihedral angle was scanned with removing the molecular symmetry.

Internal reorganization (non-adiabatic) energy (λ) of hole and electron were calculated at B3LYP/6-31G(d,p) level by adding up the reorganization energy at ground (λ_i) and excited (λ_f) state of cation/anion (Fig. S1). Following method was used to obtain reorganization energy (λ)

$$\lambda = \lambda_i + \lambda_f = (E^{**}_{cation/anion} - E_{neutral}) + (E^{*}_{cation/anion} - E_{cation/anion}),$$

$$\lambda_i = (E^{**}_{cation/anion} - E_{neutral}), \text{ and } \lambda_f = (E^{*}_{cation/anion} - E_{cation/anion}).$$

$E_{neutral}$ and $E^{*}_{cation/anion}$ indicate the energy of optimized geometry of neutral molecule and energy of cation/anion with optimized neutral molecule respectively. $E_{cation/anion}$ and $E^{**}_{cation/anion}$ refer to energy of optimized geometry of cation/anion and energy of neutral molecule bearing optimized geometry of neutral state. Free energy of electron transfer Δ^{G^o} is given by $[(E_A+E_B{}^*)-(E_A{}^*+E_B)]$, while E_A and E_B denote energies of neutral state, $E_A{}^*$ and $E_B{}^*$ denote energies of charged species for electron transfer from A to B species.

TD-DFT calculation was performed with natural transition orbital (NTO) formalism to evaluate major electron-hole pair combination, transition energy, oscillator strength and respective weight of transitions. Natural transition orbital (NTO) analysis gives localized interpretation of particular excitation, hence demonstrates more accurate presentation of charge transfer in donor acceptor system. Super-exchange and direct electron transfer integrals were calculated at CAM-B3LYP/6-31G(d,p) level. The hybrid exchange-correlation CAM-B3LYP functional comprises of 19% Hartree–Fock (HF) exchange interaction at short-range, and 65% HF at long-range to account of long electron-electron distance. Thus, this functional gives reliable values of transfer integrals compared to B3LYP functional in π-stacked donor acceptor systems.

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

	1 [CBP:(TCNQ)$_2$]
chem formula	$C_{60} H_{32} N_{10}$
formula wt	892.95
temp (K)	293(2)
CCDC Number	2058993
crystal system	Triclinic
space group	P -1
a (Å)	6.7820(13)
b (Å)	9.3889(17)
c (Å)	17.885(3)
α (°)	94.958(13)
β (°)	96.022(13)
γ (°)	92.421(13)
V (Å³)	1126.8(4)
Z	1
F_{000}	462
ρ_{calcd} (g cm^{-3})	1.316
no. of unique reflection	38535
no. of reflection ($I \geq 2\sigma (I)$)	5824
R_1[a], R_1[b] (all data, $I \geq 2\sigma(I)$)	0.1601, 0.0688
wR_2[a], wR_2[b] (all data, $I \geq 2\sigma(I)$)	0.2286, 0.1811
goodness of fit (F^2)	1.025
largest peak/hole (e Å^{-3})	0.556/ -0.501

Table S2. C–C, C=C bond-lengths, and C≡N stretching frequencies in neutral TCNQ, TCNQ·- radical and cocrystal

	C–C (Å)	C=C (Å)	C≡N stretching
Neutral TCNQ	1.441	1.374	2225
TCNQ–· radical	1.416	1.420	2186
CBP:TCNQ	1.432	1.372	2220

Table S3. Parameters of intermolecular interactions in CBP and cocrystal CBP:(TCNQ)$_2$

Cocrystal	Interaction	D···A (Å)	H···A (Å)	D–H···A (°)
CBP	C5–H5···C17	3.814	2.93	155.21
	C5–H5···C16	3.698	2.93	139.21
	C10–H10···C15	3.811	2.87	171.25
	C14–H14···C3	3.806	2.83	160.50
	C15–H15···C4	3.831	2.97	152.07
	C18–H18···C12	3.645	2.74	159.46
	C15–H15···C3	3.831	2.97	152.07
	C17–H17···C2	3.829	2.97	151.30
	C18–H18···C6	3.479	2.97	114.98
	C18–H18···C7	3.483	2.80	129.94
CBP:(TCNQ)$_2$	π ···π	3.446	-	-
	C24–H24···N2	3.349	2.74	123.59
	C16–H16···C10	4.151	3.56	124.02

Fig. S1 Colour change during formation of cocrystal CBP:(TCNQ)$_2$ (**1**).
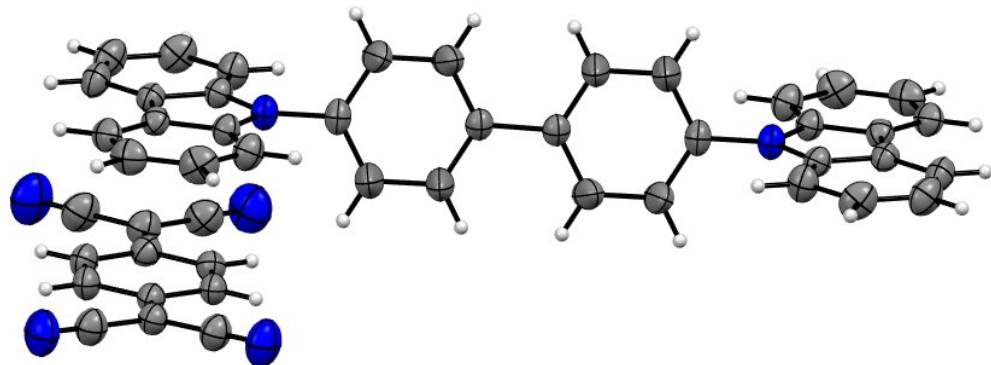
**Fig. S2** *ORTEP* diagram (45% probability) of cocrystal CBP:(TCNQ)$_2$ (**1**).
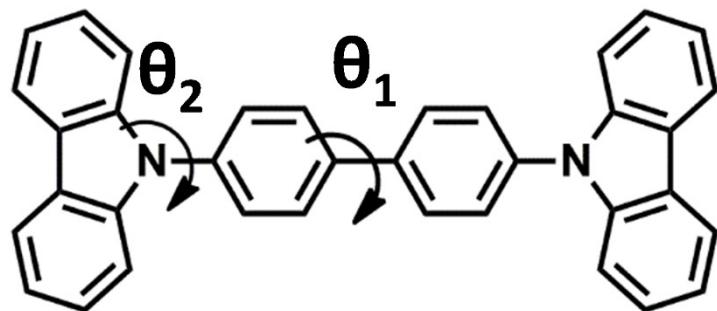
Fig. S3 Phenyl/phenyl (θ_1) and phenyl/carbazole (θ_2) dihedral angles in cocrystal CBP:(TCNQ)$_2$.

Dimer I   **Dimer II**   **Dimer III**
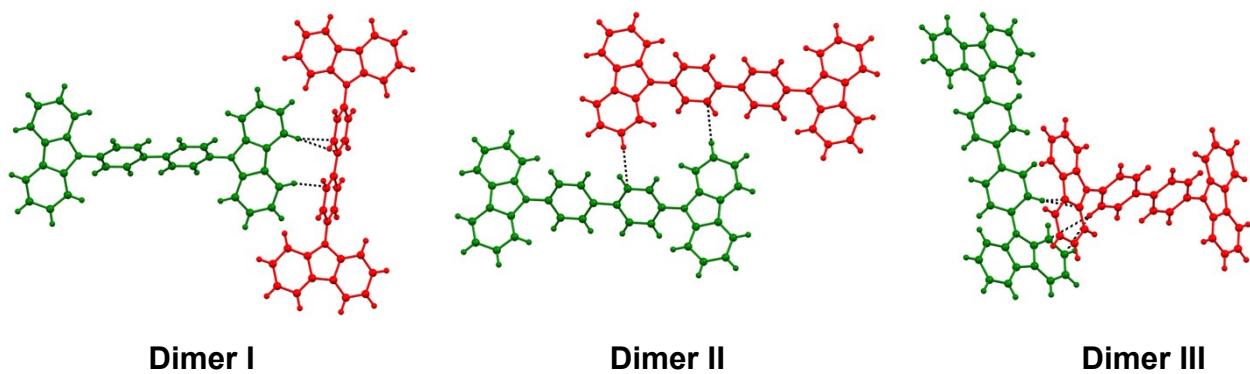
Fig. S4 Multiple C–H···π hydrogen bonded molecular pairs in crystal packing of CBP.

| HOMO-2 | HOMO-1 | HOMO | LUMO | LUMO+1 |
| | | ADA | | |

| HOMO-2 | HOMO-1 | HOMO | LUMO | LUMO+1 |
| | | DAD | | |
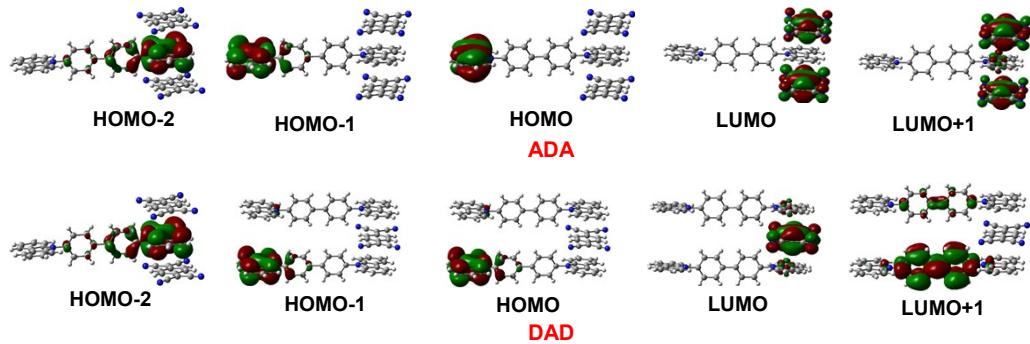
Fig. S5 Frontier molecular orbitals in ADA and DAD molecular fragments in CBP:(TCNQ)$_2$, MO offset is observed in all cases except LUMO+1 of DAD.

| HOMO-2 | HOMO-1 | HOMO | LUMO | LUMO+1 |
| -5.471 eV | -5.454 eV | -5.446 eV | -4.510 eV | -4.248 eV |
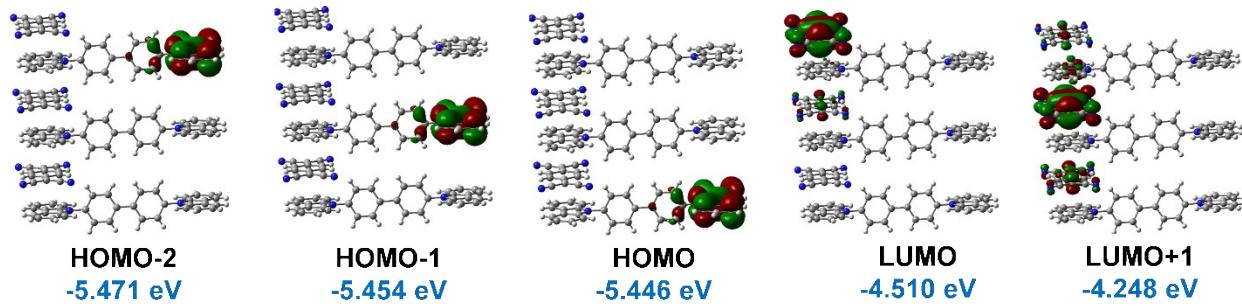
Fig. S6 Frontier molecular orbitals in ADADAD molecular fragment in CBP:(TCNQ)$_2$, MO offset is observed in all cases.
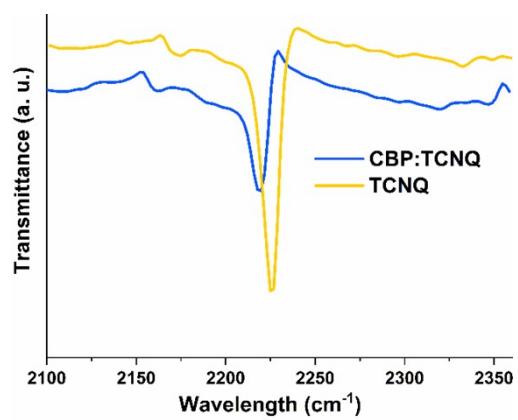
**Fig. S7** Nitrile (C≡N) stretching frequency in CBP:(TCNQ)$_2$ cocrystal and neutral TCNQ.
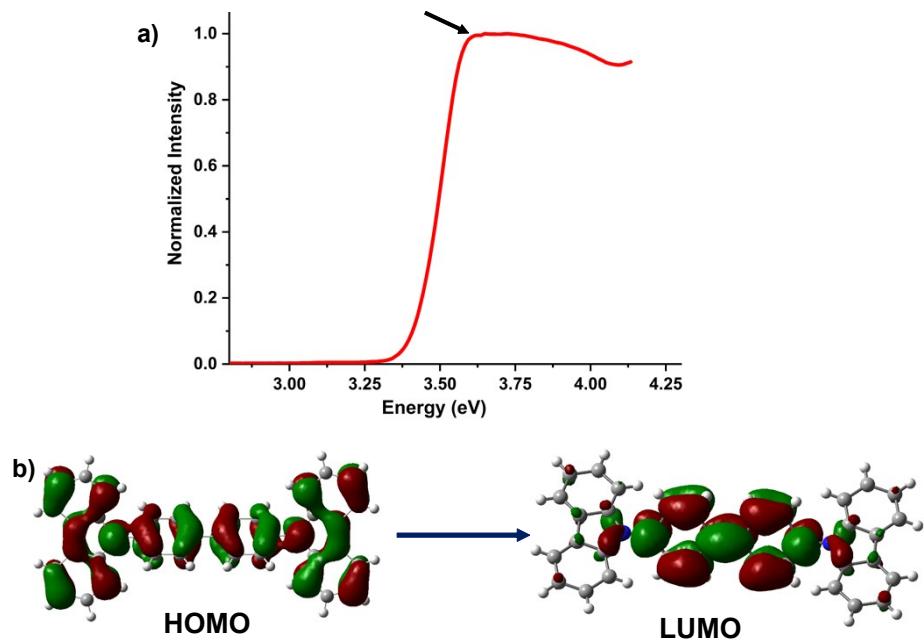
Fig. S8 a) Molecular orbitals taking part in electronic transition in pristine CBP.
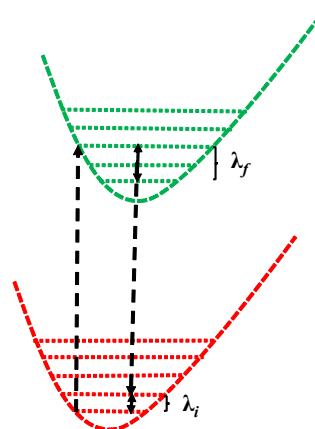
Fig. S9 Four point energy model for calculating internal reorganization energy.
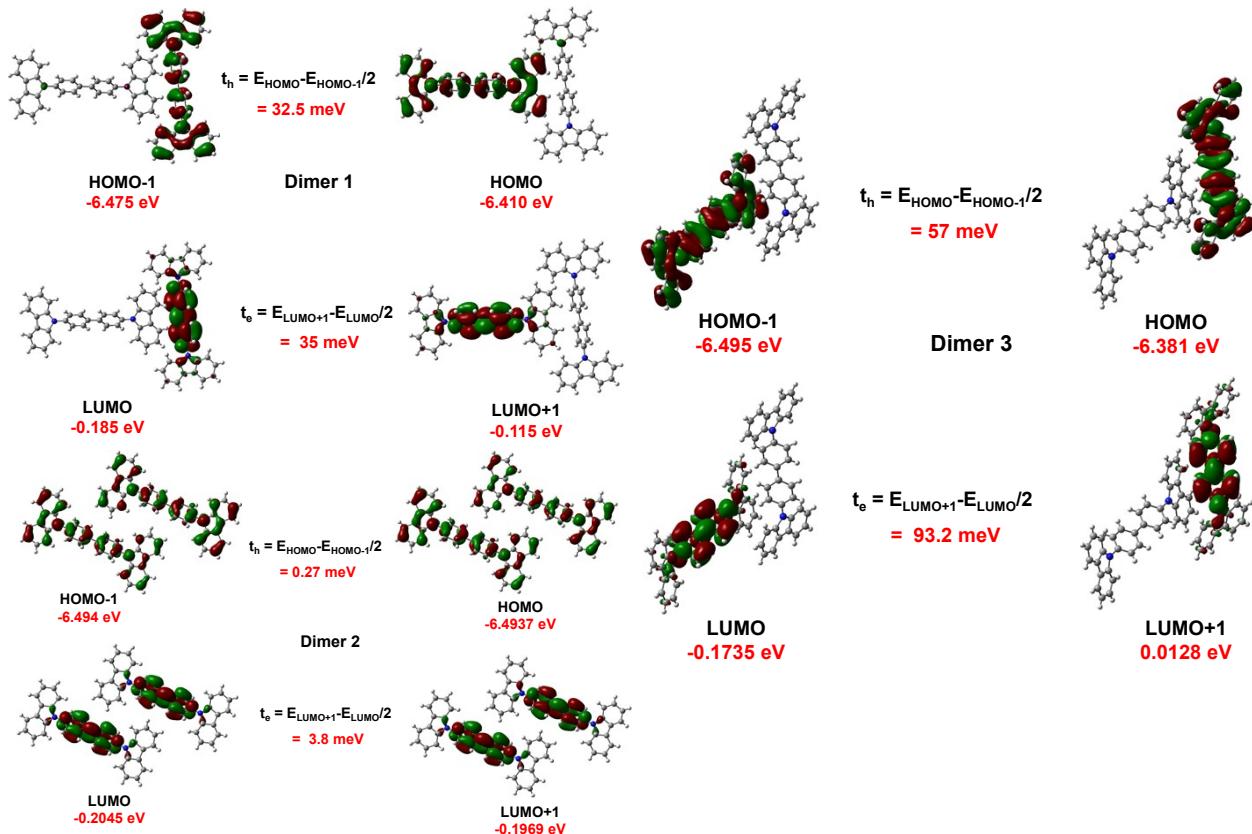
Fig. S10 Hole and electron transfer integrals in CBP calculated from nearest dimer pairs.
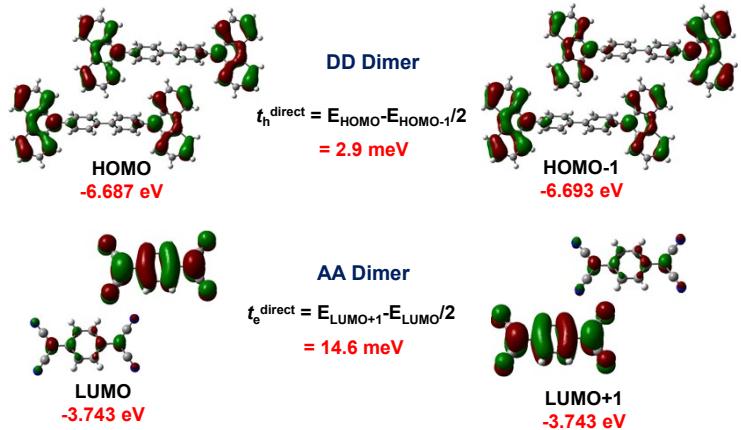
Fig. S11 Direct hole and electron transfer integral in cocrystal CBP:(TCNQ)$_2$.
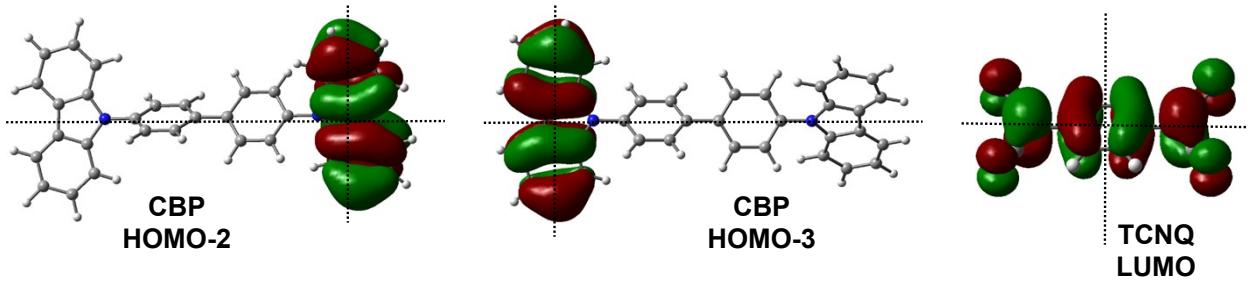
Fig. S12 HOMO-2 and HOMO-3 orbital of CBP, symmetry properties of the orbitals are shown in comparison to LUMO of TCNQ.
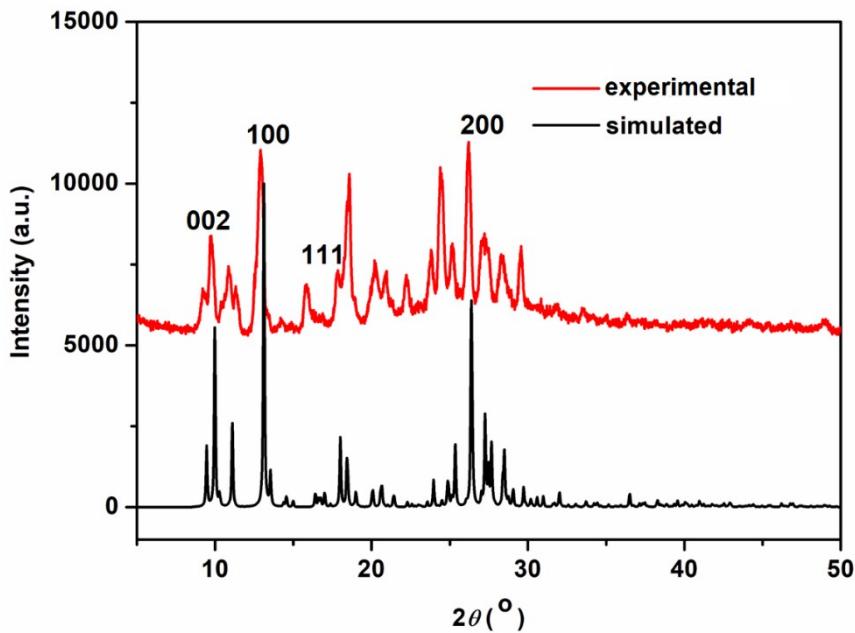
Fig. S13 PXRD pattern of cocrystal **1** [CBP:(TCNQ)$_2$].

Coordinates of DFT optimized structure of CBP

C	-7.82993700	2.80036700	-1.17595400
C	-6.47993100	3.15640600	-1.33498400
C	-5.45195000	2.29097700	-0.96761700
C	-5.80721000	1.05199500	-0.42759500
C	-7.16436300	0.67042900	-0.27350000
C	-8.17743700	1.55961900	-0.65036500
H	-8.60679300	3.49906500	-1.47054400
H	-6.22892800	4.12562600	-1.75572600
H	-4.41279100	2.56925000	-1.10309300

H	-9.22143100	1.28155300	-0.53762400
C	-5.80721500	-1.05199200	0.42759300
C	-5.45196000	-2.29097500	0.96761900
C	-6.47994500	-3.15640100	1.33498000
C	-7.82995000	-2.80036100	1.17594000
C	-8.17744400	-1.55961300	0.65034700
C	-7.16436600	-0.67042400	0.27348900
H	-4.41280300	-2.56925000	1.10310200
H	-6.22894700	-4.12562200	1.75572400
H	-8.60680900	-3.49905700	1.47052500
H	-9.22143700	-1.28154500	0.53759800
N	-4.98763100	0.00000000	0.00000000
C	-3.56835700	-0.00000200	0.00000300
C	-2.85973600	1.01037200	0.66179900
C	-2.85973500	-1.01037600	-0.66179200
C	-1.46817300	1.01199600	0.65042400
H	-3.40427200	1.79063000	1.18299000
C	-1.46817200	-1.01200100	-0.65041200
H	-3.40427000	-1.79063200	-1.18298500
C	-0.74223700	-0.00000300	0.00000700
H	-0.93606000	1.81873200	1.14484400
H	-0.93605800	-1.81873700	-1.14483100
C	0.74104600	-0.00000400	0.00000900
C	1.46751400	-0.40140900	-1.13388700
C	1.46751300	0.40140000	1.13390600
C	2.85887000	-0.39403800	-1.14164000
H	0.93620500	-0.68454100	-2.03731400
C	2.85886900	0.39402800	1.14166000
H	0.93620300	0.68453100	2.03733300

C	3.56827600	-0.00000400	0.00001100
H	3.40245300	-0.67267600	-2.03816900
H	3.40245000	0.67266400	2.03819100
C	5.80667600	-1.08535300	-0.33489400
C	5.80667500	1.08535100	0.33489900
C	5.45277500	-2.38706800	-0.70005800
C	7.16362400	-0.69203300	-0.21277700
C	5.45277400	2.38706600	0.70006500
C	7.16362400	0.69203600	0.21276600
C	6.48141500	-3.28876300	-0.96389000
H	4.41408400	-2.68993200	-0.77003500
C	8.17748900	-1.61794200	-0.48406200
C	6.48141400	3.28876400	0.96388400
H	4.41408300	2.68992700	0.77005500
C	8.17748900	1.61794900	0.48403800
C	7.83111000	-2.91138400	-0.86260100
H	6.23104200	-4.30575900	-1.25101500
H	9.22122100	-1.33031200	-0.39563700
C	7.83110900	2.91139100	0.86257900
H	6.23104100	4.30576000	1.25101000
H	9.22122100	1.33032300	0.39560200
H	8.60850800	-3.63803300	-1.07729000
H	8.60850800	3.63804300	1.07725900
N	4.98659200	-0.00000400	0.00001100

Coordinates of DFT optimized structure of CBP⁺· cation

C	-7.81086000	2.88686100	-0.94373300

C	-6.46615500	3.25800700	-1.08224400
C	-5.43568700	2.36597400	-0.78649200
C	-5.79278900	1.09346700	-0.32986800
C	-7.14709400	0.69575000	-0.21182700
C	-8.15982700	1.60153800	-0.51740500
H	-8.59068600	3.60219900	-1.18294300
H	-6.21868300	4.25409600	-1.43385100
H	-4.40033700	2.65352600	-0.92384600
H	-9.20326200	1.31429000	-0.43613400
C	-5.79278900	-1.09346700	0.32986700
C	-5.43568600	-2.36597400	0.78649200
C	-6.46615500	-3.25800700	1.08224400
C	-7.81086000	-2.88686100	0.94373300
C	-8.15982700	-1.60153800	0.51740500
C	-7.14709400	-0.69575000	0.21182700
H	-4.40033700	-2.65352600	0.92384600
H	-6.21868300	-4.25409600	1.43385100
H	-8.59068500	-3.60219900	1.18294300
H	-9.20326200	-1.31429000	0.43613400
N	-4.97034400	0.00000000	0.00000000
C	-3.56495100	0.00000000	0.00000000
C	-2.85323700	1.05748600	0.59554300
C	-2.85323700	-1.05748600	-0.59554300
C	-1.46788100	1.04868800	0.59704600
H	-3.39288000	1.86215900	1.08119100
C	-1.46788100	-1.04868800	-0.59704600
H	-3.39288000	-1.86215900	-1.08119100
C	-0.73601000	0.00000000	0.00000000
H	-0.94327800	1.87988900	1.05555400

H	-0.94327800	-1.87988900	-1.05555400
C	0.73447900	0.00000000	0.00000000
C	1.46763900	-0.63306500	-1.02753100
C	1.46763900	0.63306500	1.02753100
C	2.85242300	-0.63650700	-1.03322900
H	0.94421300	-1.08349400	-1.86373300
C	2.85242300	0.63650700	1.03322900
H	0.94421300	1.08349400	1.86373300
C	3.56548300	0.00000000	0.00000000
H	3.39135700	-1.08291900	-1.86089200
H	3.39135700	1.08291900	1.86089200
C	5.79243700	-1.11254300	-0.25864500
C	5.79243700	1.11254300	0.25864500
C	5.43630600	-2.44376000	-0.49570600
C	7.14664300	-0.70855000	-0.16350800
C	5.43630600	2.44376000	0.49570600
C	7.14664300	0.70855000	0.16350800
C	6.46713600	-3.36382100	-0.68586300
H	4.40136000	-2.76273600	-0.51639100
C	8.15980400	-1.64531200	-0.35164900
C	6.46713600	3.36382100	0.68586300
H	4.40136000	2.76273600	0.51639100
C	8.15980400	1.64531200	0.35164900
C	7.81157300	-2.97212800	-0.62317700
H	6.22003500	-4.40279800	-0.87700800
H	9.20312000	-1.35502900	-0.28022300
C	7.81157300	2.97212800	0.62317700
H	6.22003500	4.40279800	0.87700800
H	9.20312000	1.35503000	0.28022300

H	8.59176100	-3.71080800	-0.77393600
H	8.59176100	3.71080800	0.77393600
N	4.96968200	0.00000000	0.00000000

Coordinates of DFT optimized structure of CBP⁻· anion

C	-7.86426400	3.03498100	-0.23967500
C	-6.50771600	3.41094200	-0.27864600
C	-5.48893700	2.46598700	-0.20498400
C	-5.85463600	1.12023000	-0.08863400
C	-7.21987400	0.72110300	-0.05364100
C	-8.22385100	1.69469600	-0.12922800
H	-8.63481500	3.79896200	-0.29700800
H	-6.24896800	4.46271800	-0.36990600
H	-4.44219800	2.74840100	-0.23475800
H	-9.27196300	1.40613300	-0.10450900
C	-5.85463600	-1.12023000	0.08863400
C	-5.48893700	-2.46598700	0.20498400
C	-6.50771700	-3.41094200	0.27864600
C	-7.86426400	-3.03498100	0.23967500
C	-8.22385100	-1.69469600	0.12922800
C	-7.21987400	-0.72110300	0.05364000
H	-4.44219800	-2.74840100	0.23475800
H	-6.24896800	-4.46271800	0.36990600
H	-8.63481500	-3.79896200	0.29700800
H	-9.27196300	-1.40613300	0.10450900
N	-5.03596700	0.00000000	0.00000000
C	-3.60493700	0.00000000	0.00000000

C	-2.87690200	0.53201200	1.08719700
C	-2.87690200	-0.53201200	-1.08719700
C	-1.49678700	0.53697100	1.08497800
H	-3.41916000	0.94240300	1.93635000
C	-1.49678700	-0.53697100	-1.08497800
H	-3.41916000	-0.94240300	-1.93635000
C	-0.71935200	0.00000000	0.00000000
H	-0.99248100	0.97520900	1.93977800
H	-0.99248000	-0.97520900	-1.93977800
C	0.71933100	0.00000000	0.00000000
C	1.49678800	-0.43123400	-1.13128400
C	1.49678800	0.43123400	1.13128500
C	2.87686800	-0.42538300	-1.13318900
H	0.99261600	-0.75278800	-2.03659600
C	2.87686800	0.42538300	1.13318900
H	0.99261600	0.75278800	2.03659600
C	3.60489500	0.00000000	0.00000000
H	3.41924900	-0.74245500	-2.02137800
H	3.41924900	0.74245500	2.02137800
C	5.85472900	-1.12367100	0.00153000
C	5.85472900	1.12367100	-0.00153000
C	5.48896000	-2.47427700	0.01375300
C	7.21998100	-0.72311500	-0.00249600
C	5.48896000	2.47427700	-0.01375200
C	7.21998100	0.72311500	0.00249600
C	6.50760300	-3.42224500	0.01452600
H	4.44217700	-2.75797100	0.02157500
C	8.22386600	-1.69979100	-0.00276000
C	6.50760300	3.42224500	-0.01452600

H	4.44217700	2.75797100	-0.02157500
C	8.22386600	1.69979100	0.00276000
C	7.86420400	-3.04456400	0.00426000
H	6.24869700	-4.47789500	0.02461600
H	9.27200500	-1.41025600	-0.00578700
C	7.86420400	3.04456400	-0.00426000
H	6.24869700	4.47789500	-0.02461600
H	9.27200500	1.41025600	0.00578700
H	8.63468400	-3.81075600	0.00248000
H	8.63468400	3.81075600	-0.00248100
N	5.03600900	0.00000000	0.00000000