

## Fluorescence and Semiconductor Properties of New Polymorph of Coronene:TCNB Charge Transfer Cocrystal

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## **Synthesis of cocrystal I**

Equi-molar amount of coronene (70 mg, 2 mmol) and tetracyanobenzene (52 mg, 2 mmol) were taken together and grinded for two minutes in an agate mortar and pestle. The grinding was continued with addition of few drops of acetonitrile in a 4/5 minutes interval. The resulting mixture turned bright red with addition of acetonitrile. It is pertinent to mention that addition of other solvents including toluene or methanol does not result in change of colour. The resulting red powder was dissolved in chloroform to make a clear solution. The solution was subjected to diffusion of hexane vapour at 5°C to produce red colour, needle shaped crystals after a day.

## **Single crystal X-ray diffraction**

Single crystal X-ray diffraction (XRD) data of cocrystal **I** was collected on a Bruker APEX II diffractometer equipped with a monochromator in the Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). A crystal was mounted on a silicon loop, and the data were collected at 100 K. The CCD data were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELX-2014. All hydrogen atoms were placed in the calculated positions. The crystallographic data are listed in Table S1. Structural information was deposited at the Cambridge Crystallographic Data Centre and the CCDC reference number is 2084814.

## **Spectroscopic measurements**

The absorption spectra of coronene, TCNB and cocrystal **I** were recorded in solid state on a JASCO V-770 spectrofluorometer. Barium sulphate (BaSO<sub>4</sub>) was used as the reference material. Photoluminescence spectra of coronene, TCNB and cocrystal **I** were recorded on a JASCO FP-8500 spectrofluorometer. The photoluminescence quantum yield (PLQY) was measured using an integrating sphere connected to the FP-8500 spectrofluorometer with a Xe light source, excitation

wavelength 365 nm was used for all measurements. All measurements were done by using drop-cast thin films (*conc* = 10 mg/ mL) in poly(methyl methacrylate) *i.e.* PMMA/ toluene matrix.

### Computational methods

Gaussian 16 program package was used for all quantum-mechanical calculations. The HOMO/LUMO energy and molecular electrostatic potential (MEP) of the donor and acceptor molecules were calculated at B3LYP/6-31G(d,p) level using optimized geometries. The HOMO/LUMO of large supramolecular clusters were calculated at CAM-B3LYP/6-31G(d,p) level on crystal coordinates. The D–A dimer extracted from infinite stack in crystal packing diagram was used for calculation. The hybrid exchange–correlation CAM-B3LYP functional comprises of 19% Hartree–Fock (HF) exchange interaction at short-range and 65% HF at long-range, thus takes better account of electron–electron interaction at long range than pure DFT functional B3LYP. Natural bond orbital (NBO) analysis of the  $\pi$ -stacked D–A pairs was performed using dispersion corrected DFT method using BJ damping at B3LYP/6-31G(d,p) level with ultrafine grid to account for dispersion effect of  $\pi \cdots \pi$  stacking interaction. Energy decomposition analysis (EDA) of  $\pi \cdots \pi$  stacking interaction in D–A pair and  $\pi$ -stacked coronene dimers were performed at B3LYP/6-31G(d,p) level using CrystalExplorer (version 17.5). Contribution of different intermolecular interactions including  $\pi \cdots \pi$  stacking, C–H $\cdots$ N/ C–H $\cdots$  $\pi$  hydrogen bonds in crystal packing were estimated by Hirshfeld surface analysis as well curvedness and shape index plots.

Non-adiabatic internal reorganization energy ( $\lambda_{\text{int}}$ ) of hole and electron were calculated at B3LYP/6-31G(d,p) level by summing up the reorganization energy at ground ( $\lambda_i$ ) and excited ( $\lambda_f$ ) states of cation/anion. Following method was used to obtain internal reorganization energy ( $\lambda_{\text{int}}$ )

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

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

In this expression, energy terms  $E_{neutral}$  and  $E_{cation/anion}^*$  indicate the energy of optimized geometry of neutral molecule and energy of cation/anion with optimized neutral molecule respectively. The energy terms  $E_{cation/anion}$  and  $E_{cation/anion}^{**}$  indicates energy of optimized geometry of cation/anion and energy of neutral molecule possessing optimized geometry of the neutral state of molecule. TD-DFT calculation was performed using CAM-B3LYP and 6-31G(d,p) basis set to verify excitation energy, oscillator strength of charge transfer transition. Super-exchange and direct electron transfer integrals were calculated at CAM-B3LYP/6-31+G(d,p) level. We verified excitation energy, oscillator strength of charge transfer transition at CAM-B3LYP/6-31G(d,p) level using donor-acceptor dimer obtained from infinite  $\cdots$ DADADA $\cdots$  stack.

**Table S1. Crystallographic and refinement parameters of cocrystal I**

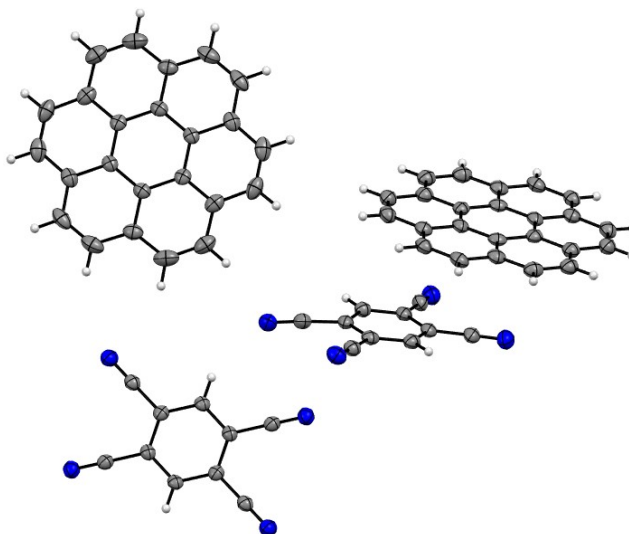
<b>Cocrystal I (COR:TCNB)</b>	
Empirical formula	$C_{26}H_{10}N_4$
Formula weight	378.38
Temperature (K)	100(2)
Crystal system	Triclinic
Space group	$P-1$
$a$ (Å)	7.3212(14)
$b$ (Å)	9.9861(19)
$c$ (Å)	19.292(3)
$\alpha$ (°)	78.231(12)
$\beta$ (°)	89.490(13)
$\gamma$ (°)	77.581(13)
$V$ (Å <sup>3</sup> )	1347.5(4)
$Z$	3
$F_{000}$	582
Density (g cm <sup>-3</sup> )	1.399
Independent reflections	6812 [R(int) = 0.1593]
Data / restraints / parameters	6812 / 0 / 407
Final R indices ( $I \geq 2\sigma(I)$ )	$R_1 = 0.0663$ , $wR_2 = 0.1465$ ,
R indices (all data)	$R_1 = 0.1582$ , $wR_2 = 0.1955$ ,
Goodness-of-fit ( $F^2$ )	0.985
largest diff. peak/hole (e Å <sup>-3</sup> )	0.343/ -0.284
CCDC Number	2084814

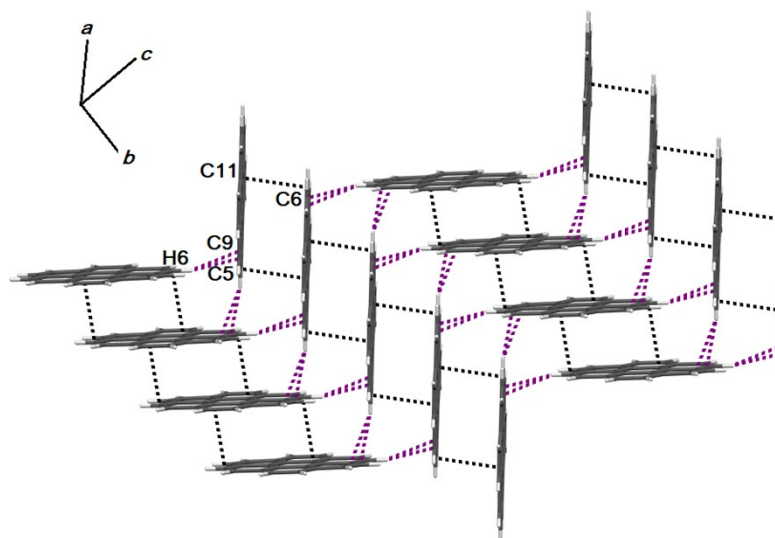
**Table S2. Parameters of intermolecular interactions in Coronene and cocrystal I**

System	Interaction	D···A (Å)	H···A (Å)	D–H···A (°)
Coronene	C11···C6	3.422(2)	-	-
	C6–H6···C9	3.729(3)	2.83	159.1
	C6–H6···C1	3.672(3)	2.82	150.3
Cocrystal I	C36–H36···N1	3.453(3)	2.61	147.7
	C29–H29···N3 <sup>#1</sup>	3.480(4)	2.53	176.0
	C26–H26···N6 <sup>#2</sup>	3.460(4)	2.57	156.6
	C16–H16···N1	3.313(4)	2.40	161.5
	C2–H2···N4 <sup>#3</sup>	3.530(4)	2.58	176.9

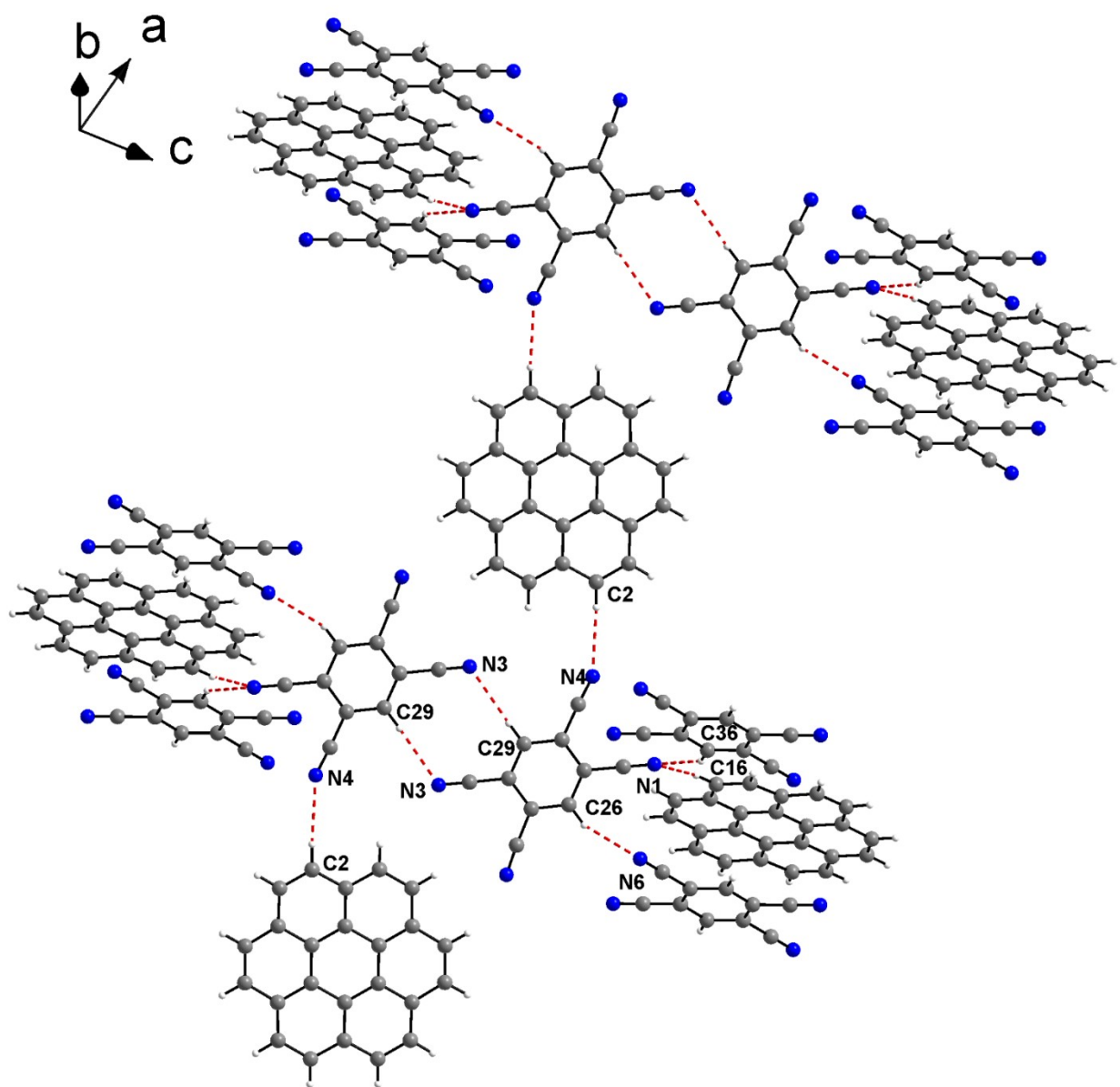
Symmetry transformations used to generate equivalent atoms:

#1 :  $-x+2, -y, -z+1$ ; #2 :  $-x+1, -y+1, -z$ ; #3 :  $-x+1, -y, -z+1$ ;

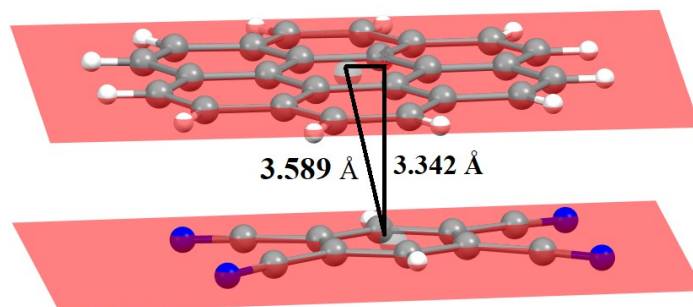
**Fig. S1** ORTEP diagram (50% probability) of cocrystal I showing the asymmetric unit.



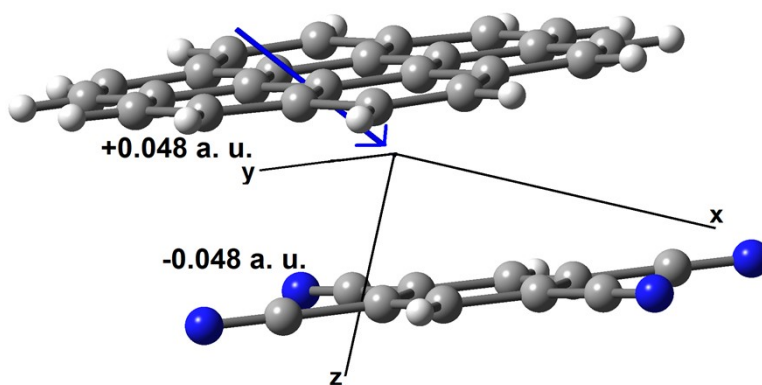
**Fig. S2** Crystal packing of  $\gamma$ -polymorphic form of coronene (CCDC reference no: 2024483).



**Fig. S3** Hydrogen bonding interactions in cocrystal I.

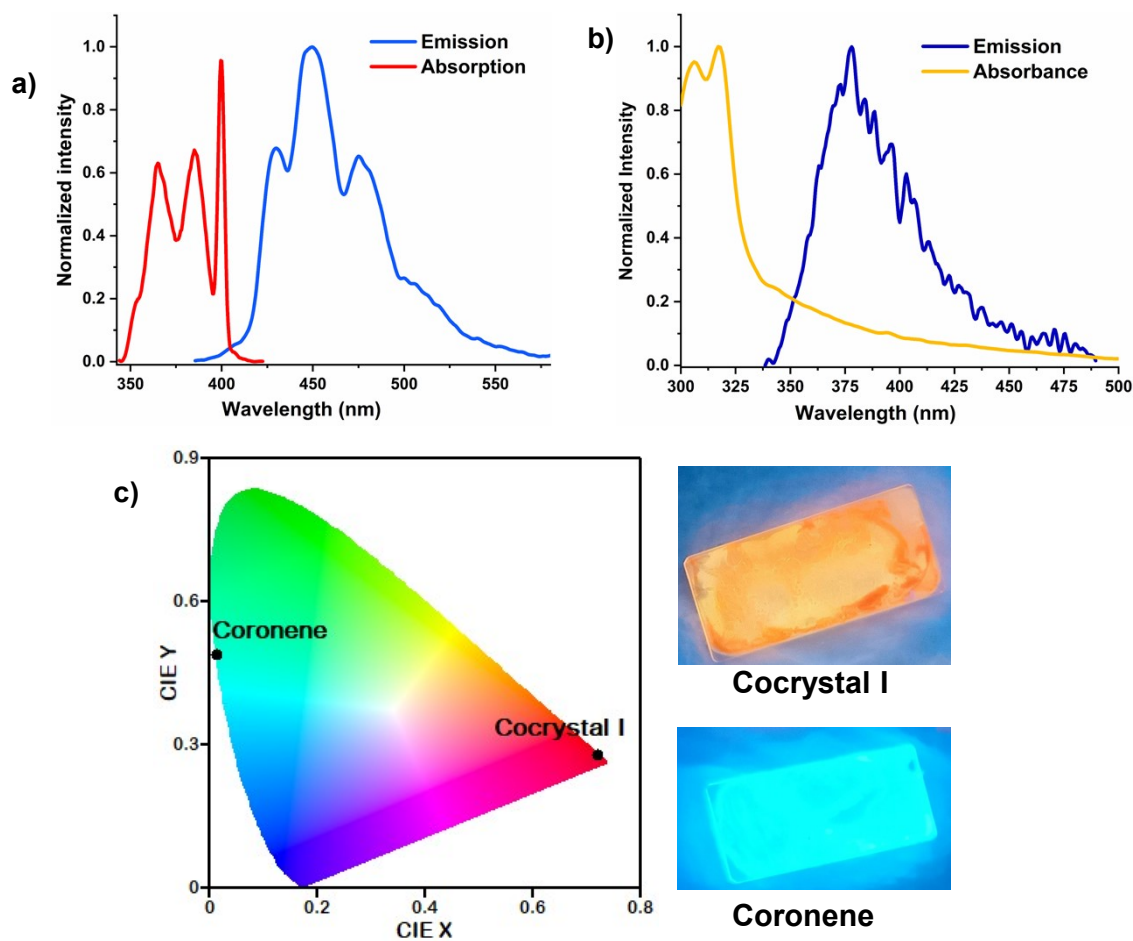


**Fig. S4** Displacement of donor and acceptor molecules in reported 1:1 polymorph of coronene:TCNB.

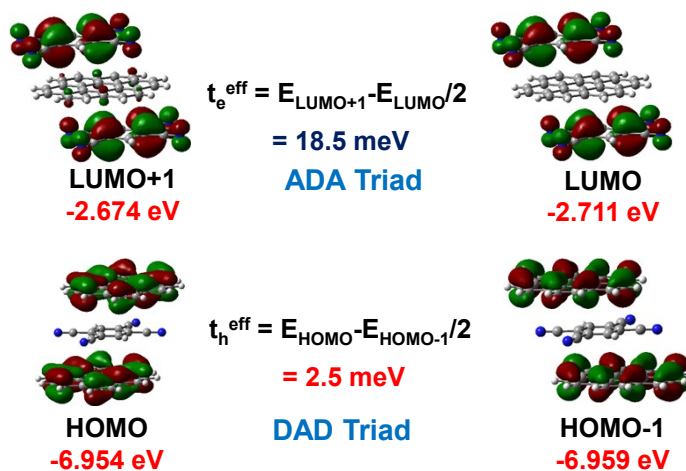


**Fig. S5** Dipole moment in D-A dimer in ground state.

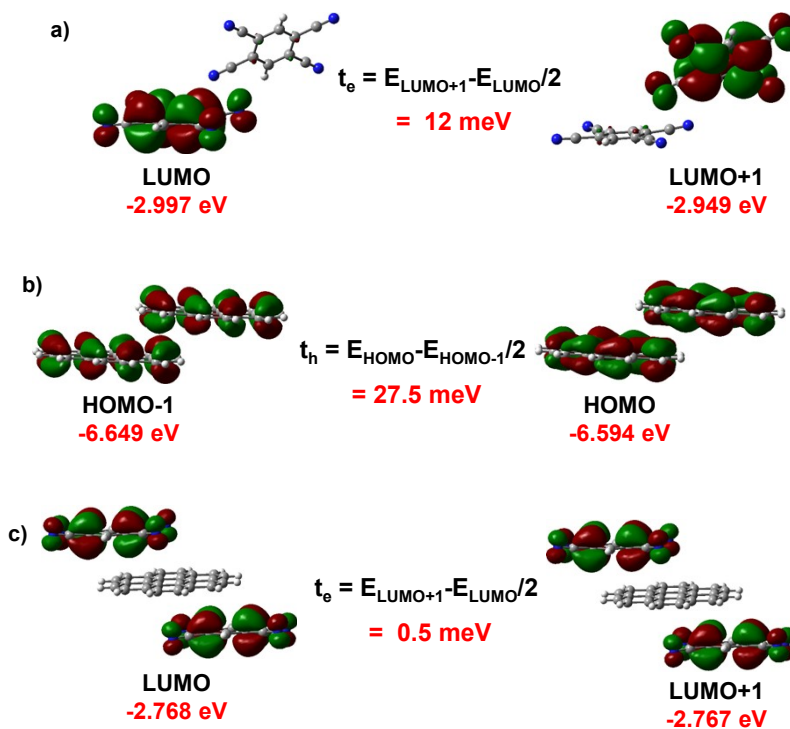




**Fig. S6** a) Absorption and emission (excitation at 350 nm) spectra of coronene in THF solution; b) Absorption and emission (excitation at 300 nm) spectra of TCNB using drop-cast thin film in PMMA/ toluene matrix; c) CIE colour coordinates for coronene and cocrystal I; thin films coated with coronene and cocrystal I solution in PMMA/toluene, excited with 365 nm UV lamp.



**Fig. S7** Super-exchange transfer integrals along mixed D–A stack in 2:3 polymorph of coronene:TCNB.



**Fig. S8** Charge transfer integral calculation; a) Direct electron transfer integral; b) Direct hole transfer integral; c) Super-exchange electron transfer integral via A–D–A trimer.

