Electronic Supplementary Material (ESI) for CrystEngComm.

Exploring Semiconductor Property in Charge Transfer Cocrystal of 1-Aminopyrene and TCNQ

Arkalekha Mandal,[a*] Anwesha Choudhury,[c] Rahul Kumar,[a] Parameswar Krishnan Iyer,[b,c*] Prasenjit Mal[a*]

[a]School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, PO Bhimpur-Padanpur, Via Jatni, District Khurda, Odisha 752050, India

[b]Centre of Nanotechnology, Indian Institute of Technology Guwahati, Guwahati, Assam, India, 781039.

[c]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam, India, 781039.

Corresponding Authors Email: arkalekha@niser.ac.in (AM); pmal@niser.ac.in (PM); pki@iitg.ac.in (PKI)

Experimental Section

Materials and methods

1-Aminopyrene, TCNQ and the solvents were used as received from commercial sources without further purification. The cocrystal was characterized using single crystal XRD, UV-Vis, FT-IR and EPR spectra as well as powder XRD, thermo-gravimetric (TGA) analyses of the powdered sample. The structure was solved by direct method using SHELXL-97.[1] Non hydrogen atoms were refined anisotropically by full matrix least-squares on F^2, using SHEXL while both C–H and N–H hydrogen atoms were added at the calculated positions ('constr' method of hydrogen atom addition) and were refined isotropically using a riding model. The parameters of intermolecular interactions were derived using PARST[2] programme and the crystal packing diagrams were obtained by Mercury 3.10.

Synthesis of cocrystal

Equi-molar amounts of 1-aminopyrene (21 mg, 0.1 mmol) and TCNQ (20 mg, 0.1 mmol) were grinded with adding few drops of MeOH for 1 h to produce brownish red powder. Dark red crystals suitable of cocrystal **1** (CCDC: **1915543**) for X-ray study were grown by slow evaporation of toluene solution after four days. Melting point: 192 °C.

Computational methods

The HOMO, LUMO energies and static dipole moment (SDM) were calculated on crystal geometry employing DFT calculations at M06-2X/6-311G(d,p) level of theory to take account of the dispersive nature of π··π stacking interaction.[3] The electron and hole transfer integrals were calculated using frontier molecular orbital energies of AA/ DD dimers and ADA/ DAD trimers obtained from crystal geometries. Coulomb attenuated version of B3LYP (CAM-B3LYP) functional was used for accounting long range correction (LRC) in calculating transfer integrals.[4] Wavelength, oscillator strength and orbital contributions for

vertical electronic excitation were calculated by TD-DFT method using B3LYP/6-31G(d,p) level of theory on crystal coordinates. The interaction energy of dimeric D−A pairs were calculated at M06-2X/6-31G(d,p) level following basis set superposition error corrected (BSSE) method of Boys and Bernerdi.[5] Natural bond orbital (NBO) calculations were performed at M06-2X/6-31G(d,p) level of theory using NBO 3.1.[6] Intermolecular interactions in crystal packing were analysed quantitatively using analysis of the Hirshfeld surface (d_{norm} surface) with 2D fingerprint plots. Analysis of d_{norm} surface with 2D fingerprint plots provides concise description of all weak intermolecular interactions present in crystal packing. The red, white and blue regions on the d_{norm} surface of cocrystal respectively indicate short range contacts, contacts at van der Waals separation and the longer contacts.[7] Interaction energy of π-stacked D−A dimer was analysed with energy decomposition analysis[8] to determine the contribution of electrostatic, polarization, dispersion and repulsion energies ($E_{total} = E_{electric}+E_{polarization}+E_{dispersion}+E_{repulsion}$). Electrostatic, polarization, dispersion and repulsion energy values were obtained with B3LYP-D2/6-31G(d,p) level of theory using Grimme's dispersion correction method. CrystalExplorer 17.5 version was used for all calculations.[8]

Device fabrication

Keithley 4200SCS semiconductor parameter analyser was used for performing the Current-Voltage measurements. The measurements were done at room temperature and at the ambient atmosphere conditions. To check ability of the cocrystal to transport electrons, OFET was prepared with the cocrystal acting as the active layer. On cleaned glass substrates ≈ 100 nm thick aluminum gate was deposited by thermal evaporation which was followed by spin coating and annealing with PMMA solution at 100 ºC for 30 min to form a layer of 1 μm. On this layer cocrystal **1** in toluene solution (concentration of 30 mg/mL) were spin coated on separate substrates to form a layer of thickness ~100 nm. Al source and drain contacts of

thickness ~80 nm were deposited on the active layer with channel length and width of 40 μm and 1000 μm, respectively. The field-effect mobility (μ) was calculated using the following equation, $\mu = \frac{L}{WC_i V_{DS}} \frac{\partial I_D}{\partial V_G}$ where, W and L respectively indicate width and length of channel, *Ci* (50 nF/cm^2) is the capacitance per unit area of the gate dielectric layer, while the V_G, V_{th} and V_{DS} are the gate, threshold and source-drain voltages, respectively. The $\frac{\partial I_D}{\partial V_G}$ value is extracted from the slope of the transfer characteristic curve.

Reference

1. G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3.
2. M. Nardelli, *J. Appl. Cryst.*, 1995, **28**, 659.
3. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.,* 2007, **120**, 215.
4. A. Pedone, *J. Chem. Theory Comput.,* 2013, **9**, 4087.
5. S. F. Boys and F. Bernardi, *Mol. Phys.,* 1970, **19**, 553.
6. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F, Weinhold.
7. M. A. Spackman and J.J. McKinnon, *CrystEngComm*, 2002, **4** ,378.
8. J. J. McKinnon and D. Jayatilaka, M.A. Spackman, *Chem Commun.*, 2007, 3814.

Table S1. Crystallographic and refinement parameters for cocrystal **1**

Parameters	Cocrystal **1**
chem formula	$C_{28}H_{15}N_5$
formula wt	421.45
temp (K)	296
Radiation wavelength	1.54184 Å
CCDC Number	1915543
crystal system	Triclinic
space group	*P* -1
a (Å)	6.7858(2)
b (Å)	8.7123(2)
c (Å)	18.1329(4)
α (°)	99.099(2)
β (°)	91.152(2)
γ (°)	97.907(2)
V (Å^3)	1047.50(5)
Z	2
ρ_{calcd} (g cm^{-3})	1.336
no. of unique rflns	4215
no. of rflns ($I \geq 2\sigma(I)$)	3240
R_1[a], R_1[b] (all data, $I \geq 2\sigma(I)$)	0.1352, 0.1199
wR_2[a], wR_2[b] (all data, $I \geq 2\sigma(I)$)	0.2819, 0.2771
goodness of fit (F^2)	1.021
largest peak/hole (e Å^{-3})	0.375/ -0.270

Table S2. Parameters of hydrogen bonding interactions in cocrystal **1**.

Interaction	**D···A (Å)**	**H···A (Å)**	**D−H···A (º)**	**Symmetry**
N1−H1B···N2	3.429(9)	2.58	168	-x+1, -y, -z
N1−H1A···N3	3.472(9)	2.64	163	-x+1, -y+1, -z
C18−H18···N4	3.604(8)	2.80	146	x, y+1, z
C21−H21···N3	3.589(7)	2.77	148	x, y-1, z
C13−H13···N2	3.592(8)	2.66	178	-x+1,-y,-z
C6−H6···N5	3.477(9)	2.83	128	-x+1,-y+1,-z+1
C21−H21···N4	3.580(9)	3.00	122	x, y, z

Table S3. Calculation of super-exchange transfer integrals (meV) from ADA/ DAD triads and energy difference between bridge orbitals in super-exchange pathway (meV) in reported 1:1 pyrene:TCNQ charge transfer cocrystal, crystal coordinates used for calculation

Parameters	1:1 Pyrene: TCNQ
t_e^{super} (meV)	29.4
t_h^{super} (meV)	11.3
D−A−D or A−D−A trimer	
t [(HOMO-1)/LUMO] (meV)	129.3
t [HOMO/LUMO] (meV)	205.6
ΔE[(HOMO-1)/LUMO] (meV)	1439
ΔE[HOMO/LUMO] (meV)	569

Table S4. TD-DFT calculation for cocrystal **1** at M06-2/6-311G(d,p) level of theory

Calculated wavelength λ (nm)	**Oscillator strength *f***	**Transition electric moment (D)**	**Transition energy (eV)**	**Orbital contributions**
1162	0.0088	0.210	1.07	HOMO→LUMO, 100%
476	0.0566	0.173	2.62	HOMO-1→LUMO, 100%
390	0.3720	1.965	3.18	HOMO-2→LUMO, 75% HOMO→LUMO+1, 75%

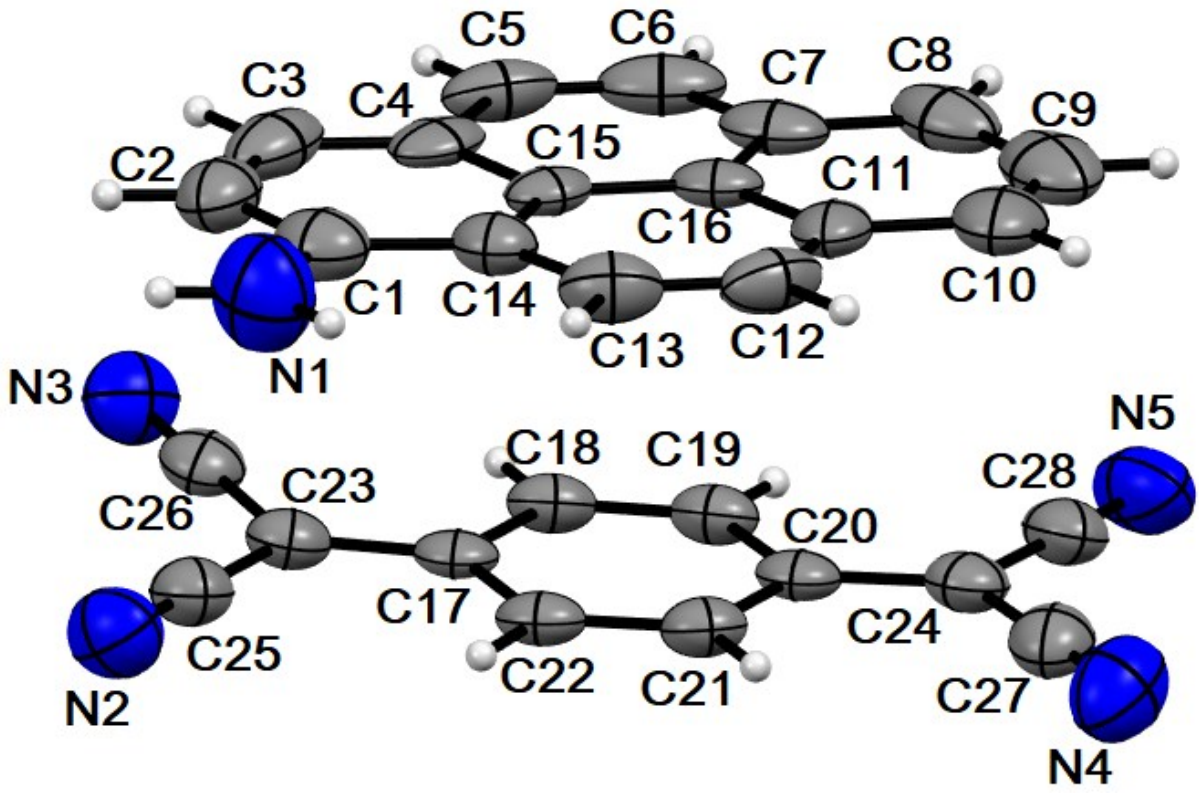

Fig. S1 *ORTEP* diagram (50% thermal probability of ellipsoids) of cocrystal **1**.

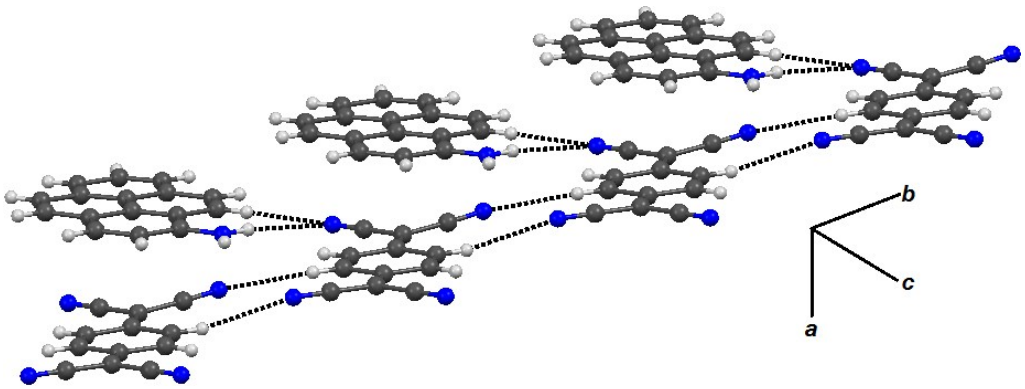

Fig. S2 Multiple C−H···N hydrogen bonds forming a two dimensional array in crystal packing of cocrystal **1**.

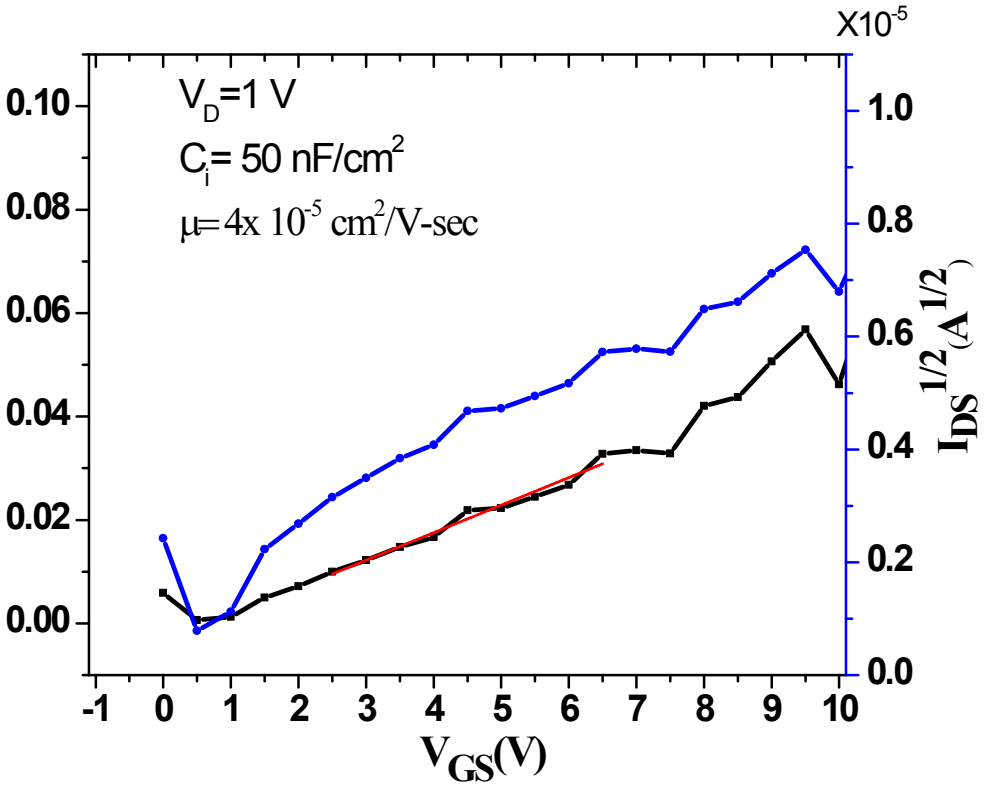

Fig S3. Electron transfer characteristic of cocrystal **1**.

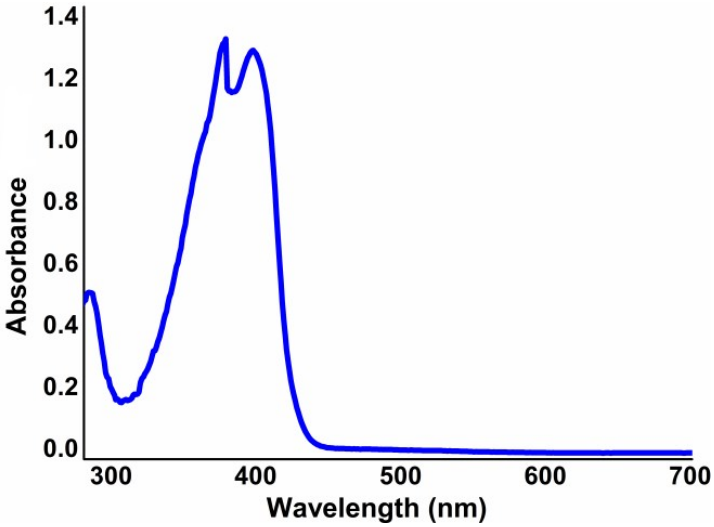

Fig. S4 UV-Vis spectrum of cocrystal **1** in MeCN solution (c = 10^{-5} M) shows no occurrence of charge transfer.

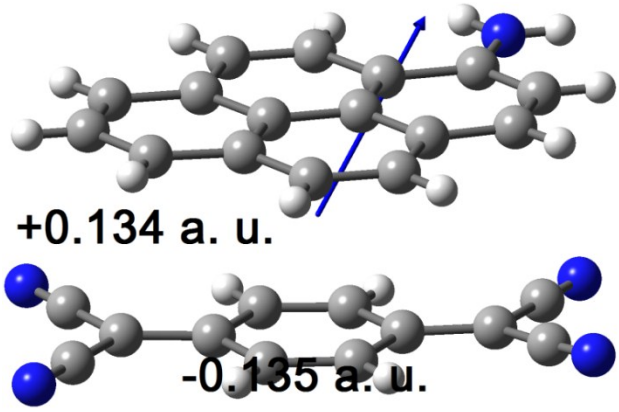

Fig. S5 Mulliken charge distribution in cocrystal **1**.

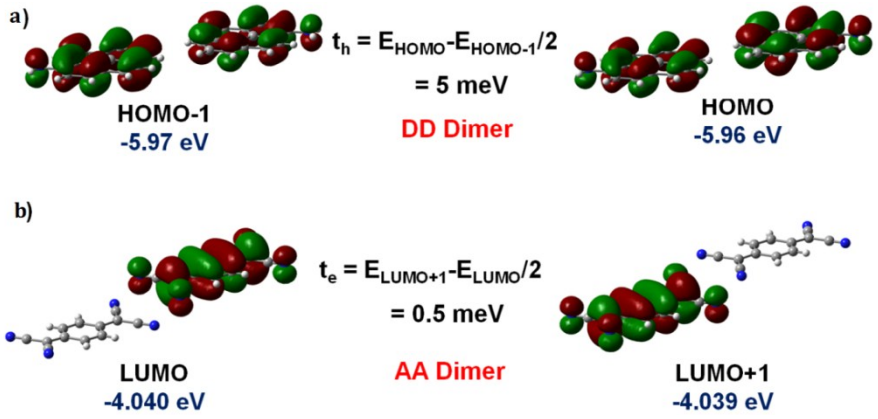

Fig. S6 Direct hole (t_h^{super}) and electron transfer (t_e^{super}) integrals in cocrystal **1**, calculated at CAM-B3LYP/6-311G(d,p) level of theory.

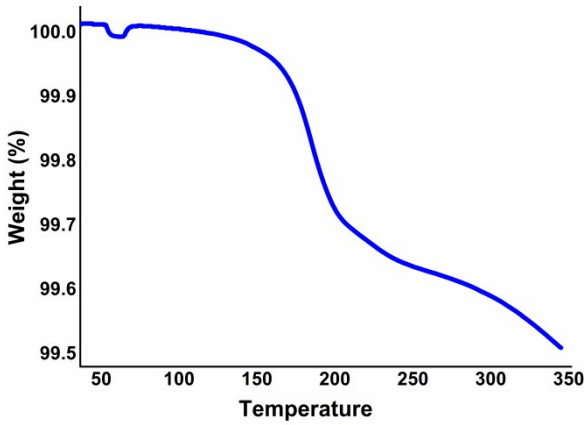

Fig. S7 Thermo-gravimetric analysis of cocrystal **1** shows decay at 200ºC.

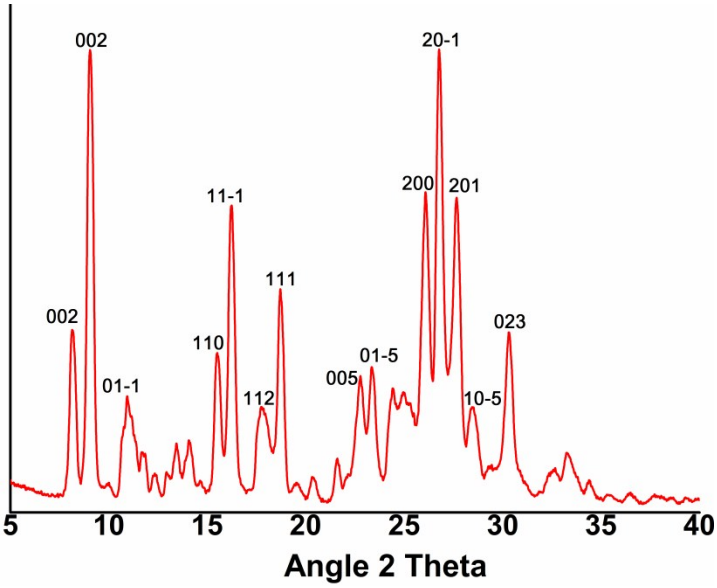

Fig. S8 Powder XRD of cocrystal **1** shows high purity of the bulk phase.

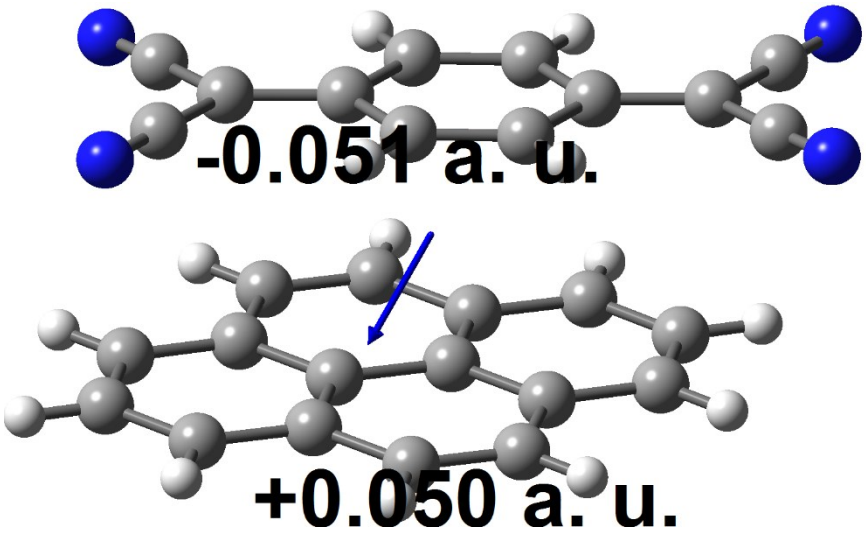

Fig. S9 Mulliken charge distribution in reported 1:1 pyrene:TCNQ cocrystal.

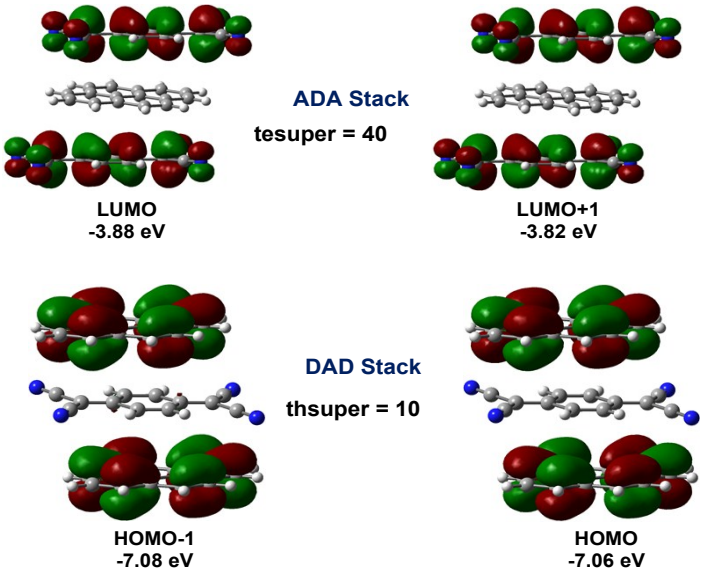

Fig. S10 Super-exchange hole (t_h^{super}) and electron transfer (t_e^{super}) integrals in reported 1:1 pyrene:TCNQ cocrystal, calculated at CAM-B3LYP/6-311G(d,p) level of theory.

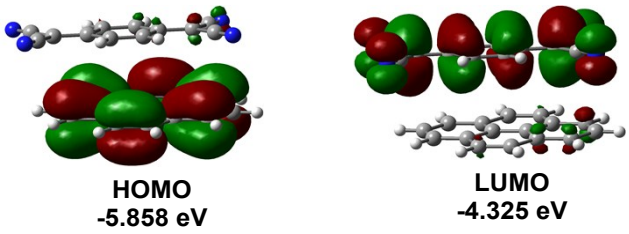

Fig. S11 The HOMO and LUMO distribution in reported 1:1 pyrene:TCNQ cocrystal.

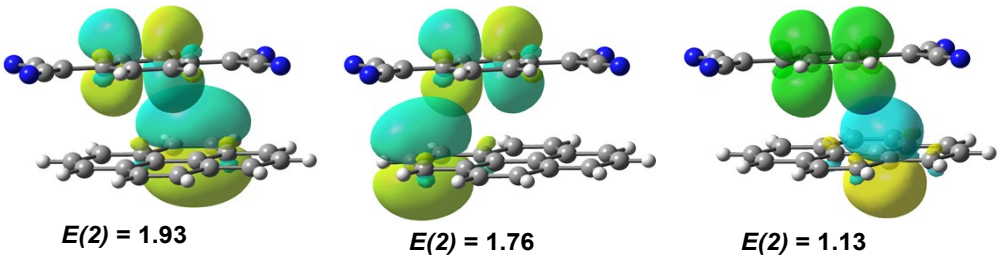

Fig. S12 Natural bond orbital (NBO) analyses in reported 1:1 pyrene:TCNQ cocrystal.

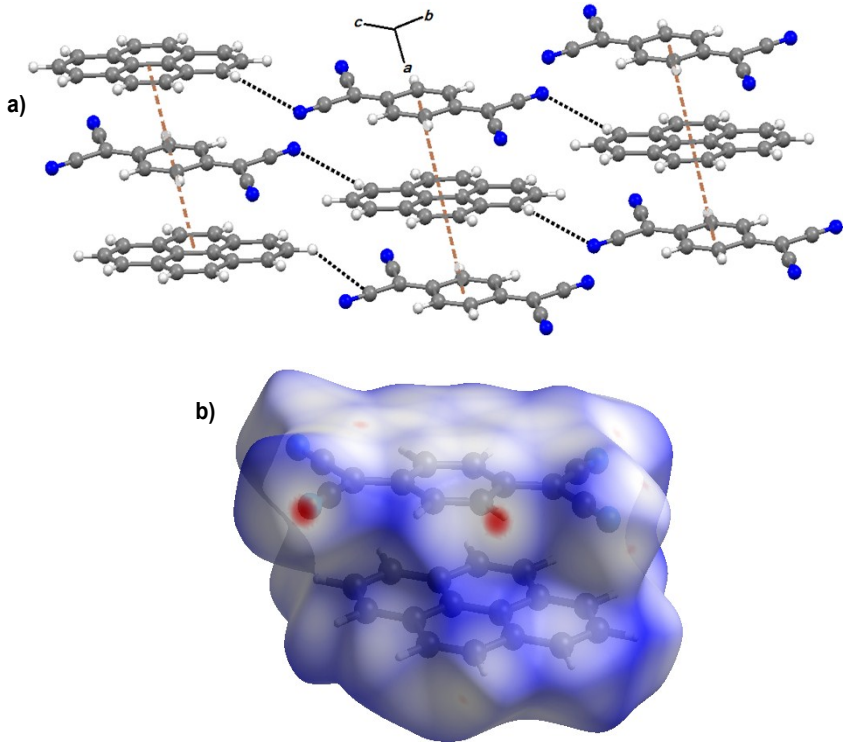

Fig. S13 (a) Crystal packing of reported 1:1 pyrene:TCNQ cocrystal; (b) The d_{norm} surface of pyrene:TCNQ cocrystal.