# Unravelling Semiconductor Properties of Mixed Stack Donor Acceptor Cocrystals of Pyrene Derivatives and TCNQ: Effect of Crystal Packing *versus* Super-exchange Mechanism

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## Computational methods

Gaussian 16 program package have been used for calculations. The energies of the HOMO/ LUMO of the donor and acceptor have been calculated at B3LYP/6-31G(d,p) level. Natural bond orbital (NBO) analysis on the mixed π··π stacked donor acceptor pairs have been performed at M06-2X/6-31G(d,p) level to take account of the considerable dispersion contribution of π···π stacking interaction. The HOMO/LUMO of the cocrystal were calculated at CAM-B3LYP/6-31G(d,p) level using the crystal coordinates of π-stacked DDA trimer. Similarly, static dipole moment and Mulliken charge analyses of D–A dimers have been performed at CAM-B3LYP/6-31G(d,p) level on the crystal coordinates. Time dependent DFT (TD-DFT) calculations have been performed with the hybrid exchange-correlation CAM-B3LYP functional, which comprises of 19% Hartree–Fock (HF) exchange interaction at the short-range, and 65% HF at the long-range to account for electron-electron repulsion effect in π-stacked molecules. Internal reorganization energy (λ) was calculated at B3LYP/6-31G(d,p) level by summing up the reorganization energies at ground ($\lambda_i$) and excited ($\lambda_f$) state of cation/anion (Fig. S8). Following parameters were calculated for reorganization energy ($\lambda_{int}$).

$\lambda = \lambda_i + \lambda_f = (E^{**}_{cation/anion} - E_{neutral}) + (E^{*}_{cation/anion} - E_{cation/anion})$; while $\lambda_i = (E^{**}_{cation/anion} - E_{neutral})$, and $\lambda_f = (E^{*}_{cation/anion} - E_{cation/anion})$. The $E_{neutral}$ and $E^{*}_{cation/anion}$ indicate the energies of the optimized geometry of neutral molecule and cation/ anion with optimized neutral molecule coordinates, respectively. Similarly, $E_{cation/anion}$ and $E^{**}_{cation/anion}$ denote the energies of optimized geometry of the cation/ anion and neutral molecule with coordinates of optimized geometry of the neutral state.

**Table S1. Calculated wavelength, oscillator strength, transition energy and orbital contributions at CAM-B3LYP/6-31G(d,p) level for selected states in the cocrystal dimer/ tetramer**

| Cocrystal | Electronic Transition | Calculated wavelength (nm) | Oscillator strength | Energy of transition (eV) | Molecular Orbital contributions |
|---|---|---|---|---|---|
| **$(PPA)_2$:TCNQ** | $S_0 \rightarrow S_2$ | 401 | 0.0565 | 3.092 | HOMO-3→LUMO, 21%<br>HOMO-2→LUMO, 15%<br>HOMO-1→LUMO, 64% |
| | $S_0 \rightarrow S_3$ | 363 | 0.3669 | 3.413 | HOMO-3→LUMO, 29%<br>HOMO-2→LUMO, 54%<br>HOMO-5→LUMO, 17% |
| **NPPO:TCNQ** | $S_0 \rightarrow S_2$ | 585 | 0.0117 | 1.121 | HOMO-4→LUMO+1, 11%<br>HOMO-3→LUMO+1, 27%<br>HOMO→LUMO+1, 62% |
| | $S_0 \rightarrow S_3$ | 540 | 0.0141 | 2.296 | HOMO-4→LUMO+1, 30%<br>HOMO-3→LUMO+1, 46%<br>HOMO-1→LUMO+1, 14%<br>HOMO→LUMO+1, 24% |
| | $S_0 \rightarrow S_4$ | 498 | 0.0014 | 2.491 | HOMO-5→LUMO, 31%<br>HOMO-1→LUMO, 69% |

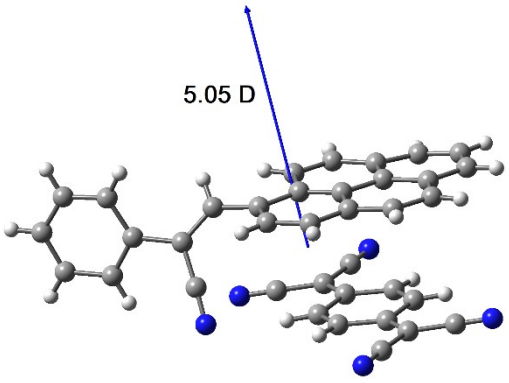


**Fig. S1** Static dipole moment in $(PPA)_2$:TCNQ cocrystal.

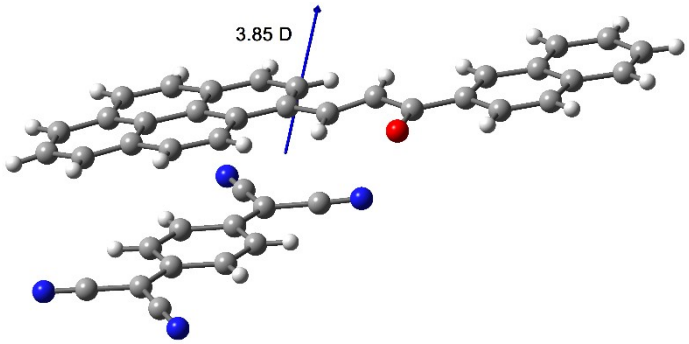


**Fig. S2a** Static dipole moment in pair I (pyrene–TCNQ) in cocrystal NPPO:TCNQ.

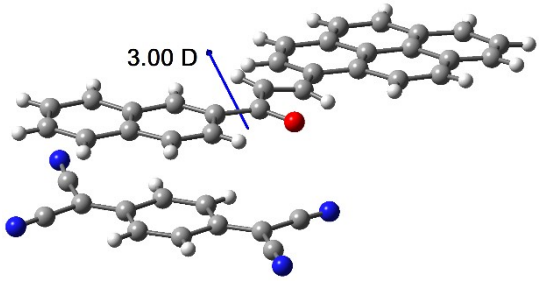


**Fig. S2b** Static dipole moment in pair II (naphthalene–TCNQ) in cocrystal NPPO:TCNQ.

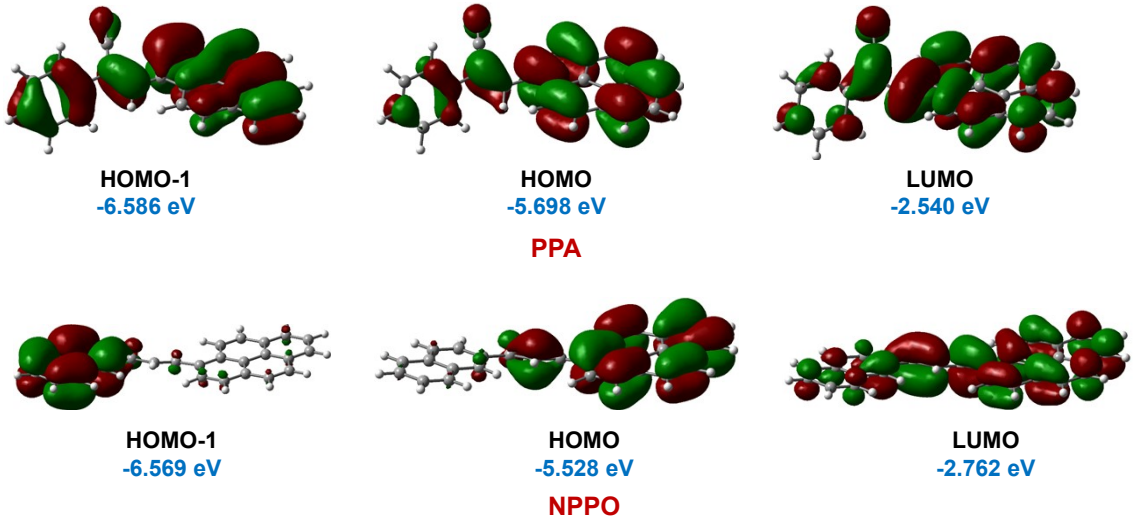


**Fig. S3** Static dipole moment in pair II (naphthalene–TCNQ) in cocrystal NPPO:TCNQ.

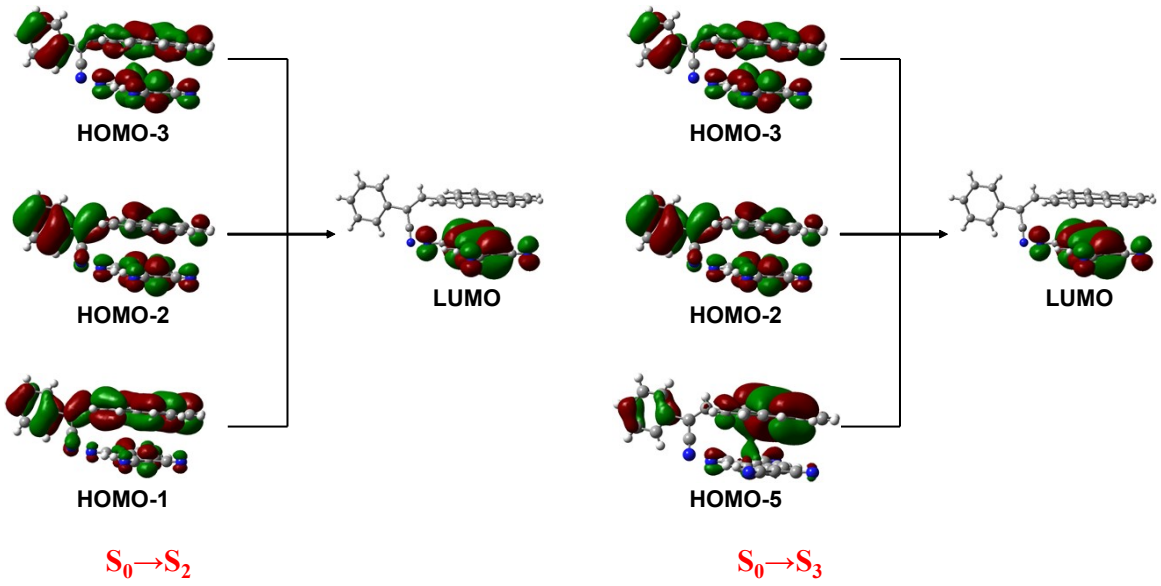


**Fig. S4** Molecular orbitals taking part in selected electronic transitions in $(PPA)_2$:TCNQ.

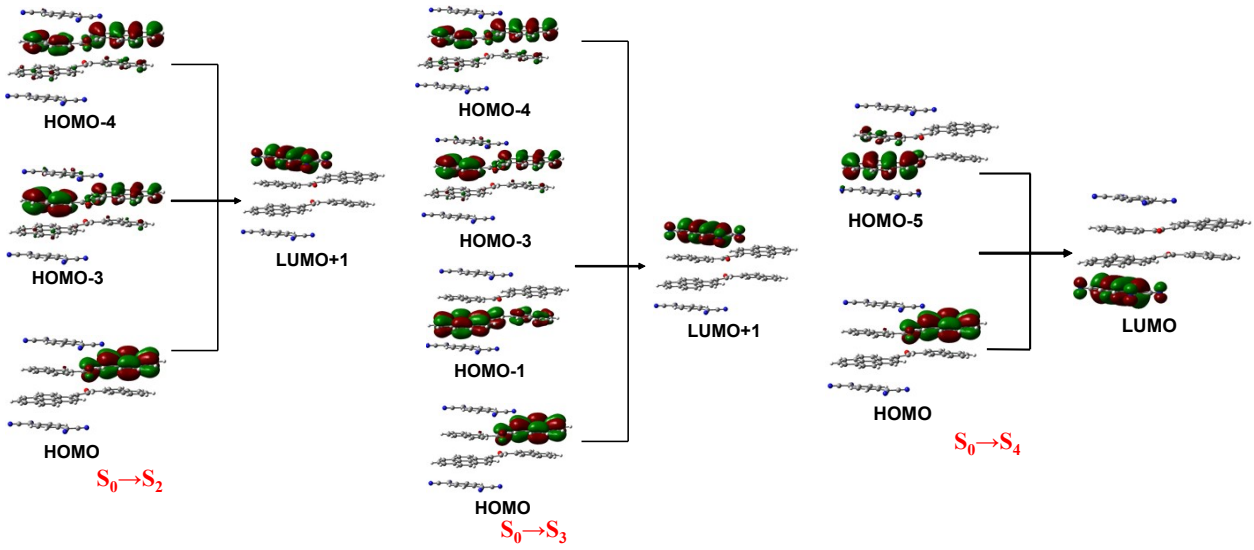


**Fig. S5** Molecular orbitals taking part in selected electronic transitions in NPPO:TCNQ.

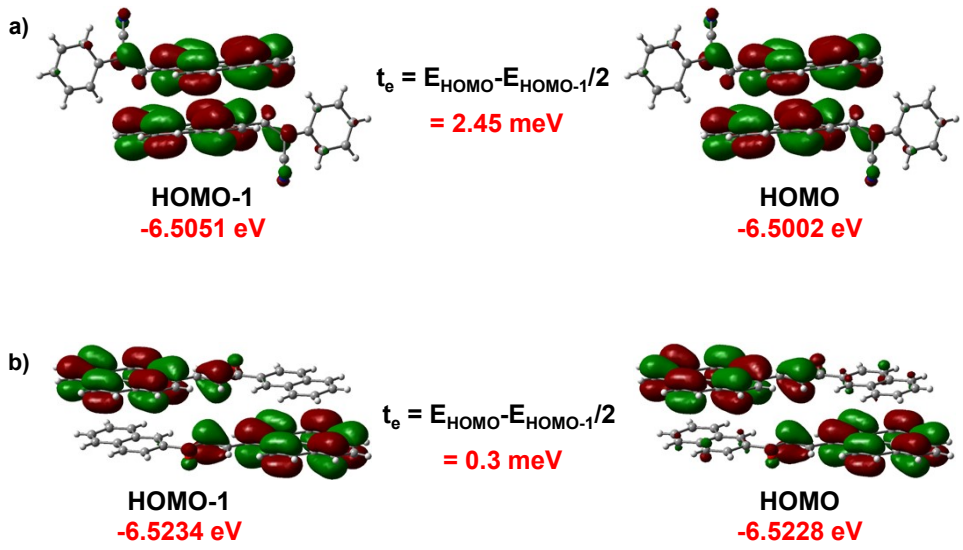


**Fig. S6** (a) Direct hole transfer integral in nearest DD pair along mixed π-stack of cocrystal **1** [$(PPA)_2$:TCNQ]; (b) direct and electron transfer integral in nearest DD pair along mixed π-stack of cocrystal **2** [NPPO:TCNQ]; calculated at CAM-B3LYP/6-31G(d,p).

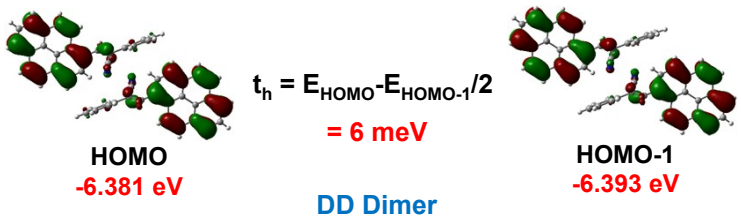


**Fig. S7** Direct hole transfer integral in nearest DD pair of cocrystal **1** [$(PPA)_2$:TCNQ], calculated at CAM-B3LYP/6-31G(d,p).

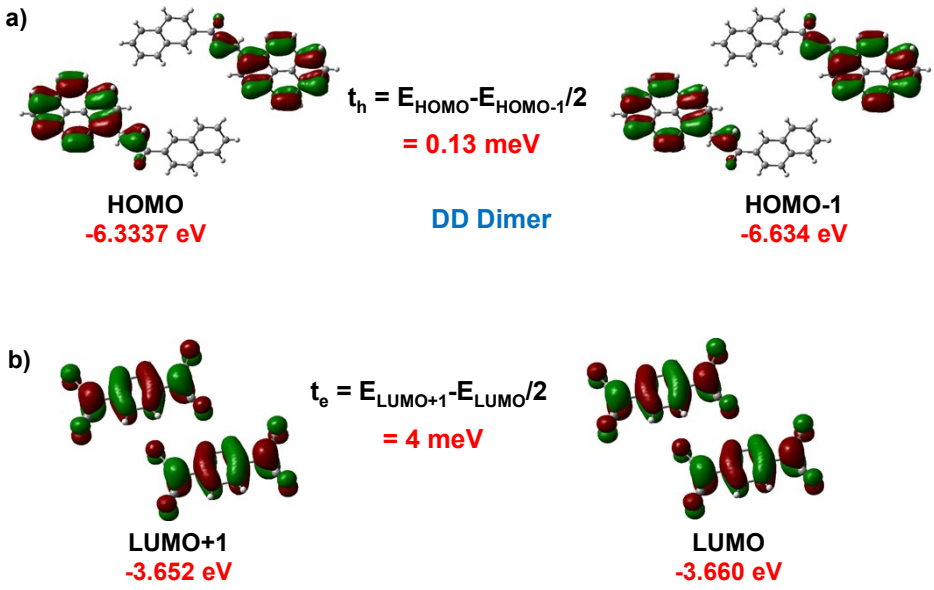


**Fig. S8** (a) Direct hole transfer integral in nearest DD pair of cocrystal **2** (NPPO:TCNQ); (b) direct and electron transfer integral in nearest AA pair of cocrystal **2**; calculated at CAM-B3LYP/6-31G(d,p).

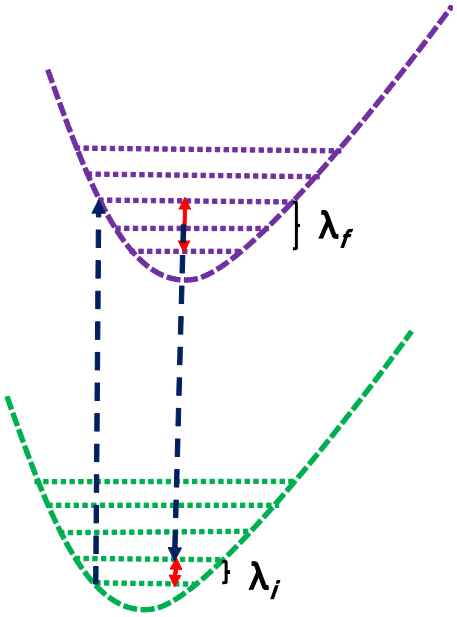


**Fig. S9** Four point model for reorganization energy calculation.

**Table S2** Energy of neutral and ionic donors and acceptor

| Species | Energy (Hartree) |
|---|---|
| Optimized, neutral PPA | -1016.70135532 |
| Cationic, single point PPA | -1016.44493898 |
| Optimized, cationic PPA | -1016.44874178 |
| Neutral, single point PPA | -1016.44493898 |
| | |
| Optimized, neutral NPPO | -1191.47608178 |
| Cationic, single point NPPO | -1191.22480688 |
| Optimized, cationic NPPO | -1191.22220549 |
| Neutral, single point NPPO | -1191.47349118 |
| | |
| Optimized, neutral TCNQ | -678.74325248 |
| Anionic, single point TCNQ | -678.70360799 |
| Optimized, Anionic TCNQ | -678.70845690 |
| Neutral, single point TCNQ | -678.73853315 |