Supplementary Information (SI) for Physical Chemistry Chemical Physics.

DFT insights into opto-electronic properties of near infra-red absorber 1:1 perylene:TCNQ cocrystal towards photovoltaic application

Arkalekha Mandal,[a*] Chris Erik Mohn[a], Yusuf Chanchangi,[b] Carl Henrik Görbitz[a]

[a] Department of Chemistry, Blindern Campus, University of Oslo, Oslo 0371, Norway

[b] Environmental and Sustainability Institute, Faculty of Environment, Science and Economy, University of Exeter, Exeter, Penryn Campus, Cornwall TR10 9FE, United Kingdom

Email address: arkalekha.mandal@kjemi.uio.no

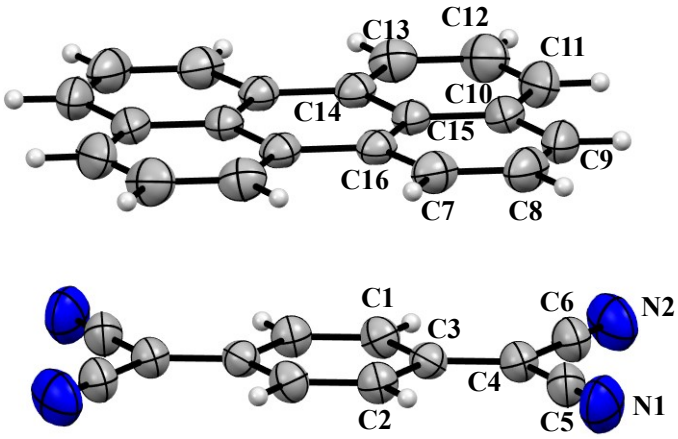

Figure S1. The *ORTEP* diagram of 1:1 perylene:TCNQ cocrystal of the literature reported structure, thermal ellipsoids are drawn with 50 % probability.

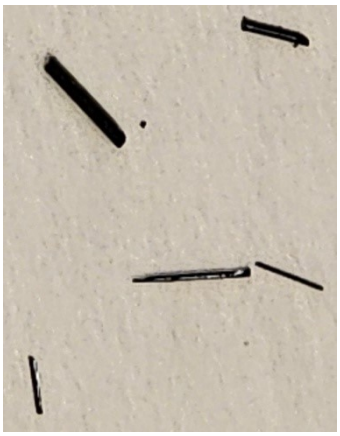

Figure S2. Needle shaped black crystals of 1:1 perylene:TCNQ.

Table S1. Crystallographic and refinement parameters for perylene:TCNQ cocrystal

chemical formula	$C_{32}H_{16}N_4$
formula weight	456.49
temp (K)	290(2)
crystal system	Monoclinic
space group	$P2_1/c$
a (Å)	7.2988(2)
b (Å)	10.8741(2)
c (Å)	14.5519(3)
α (°)	90
β (°)	90.254(2)
γ (°)	90
V (Å^3)	1154.94(4)
Z	2
F_{000}	472
ρ_{calcd} (g cm^{-3})	1.313
R_1[a], R_1[b] (all data, $I \geq 2\sigma(I)$)	0.0476, 0.0423
wR_2[a], wR_2[b] (all data, $I \geq 2\sigma(I)$)	0.1228, 0.1178
goodness of fit (F^2)	1.033
largest peak/hole (e Å^{-3})	0.195/-0.213

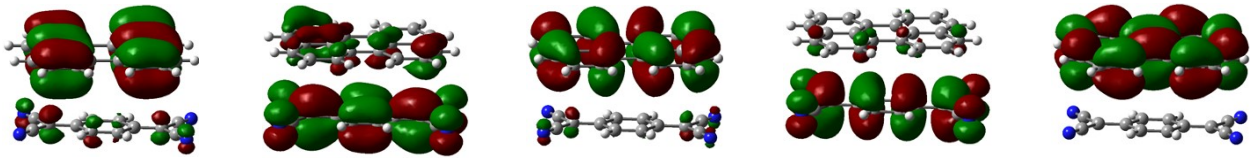

Figure S3. Frontier molecular orbitals of π-stacked D–A dimer calculated at CAM-B3LYP/6-31G(d,p) level of theory.

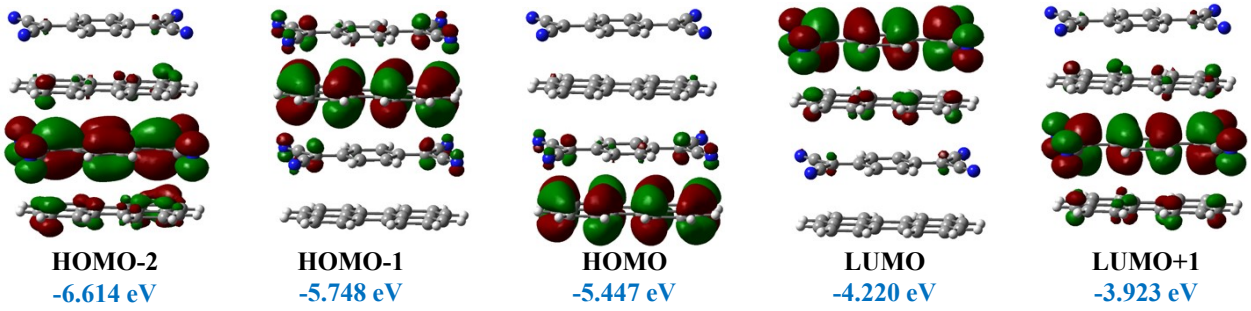

Figure 4. Frontier molecular orbitals of π-stacked D–A–D–A tetramer calculated at B3LYP-D3-BJ/6-31G(d,p) level of theory.

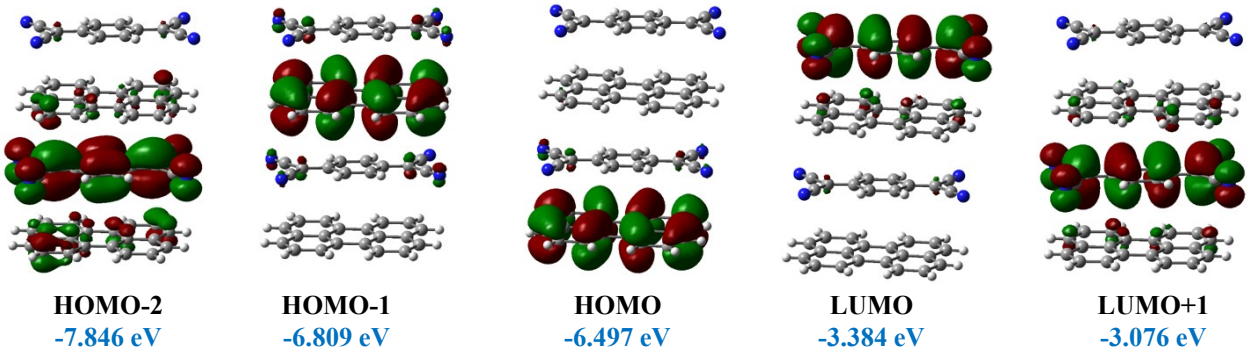

Figure S5. Frontier molecular orbitals of the π-stacked D–A–D–A tetramer calculated at CAM-B3LYP/6-31G(d,p) level of theory.

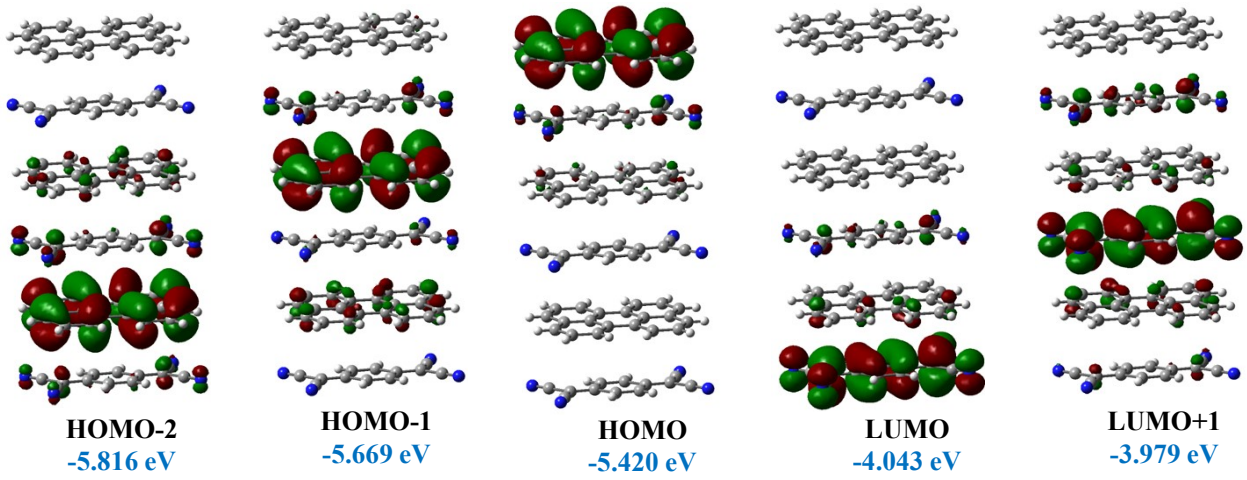

Figure S6. Frontier molecular orbitals of π-stacked D–A–D–A–D–A hexamer calculated at B3LYP-D3-BJ/6-31G(d,p) level of theory.

Table S2. Calculate wavelength, transition energy, oscillator strength and orbital contributions for $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions in π-stacked D–A dimer at ω97X-D/6-31G(d,p) level

Transitions	Wavelength (nm)	Energy (eV)	Oscillator strength	Orbital contribution
$S_0 \rightarrow S_1$	784	1.59	0.0717	HOMO→LUMO, 100%
$S_0 \rightarrow S_2$	420	2.95	0.1654	HOMO-1→LUMO, 75.66% HOMO→LUMO+1, 24.34%
$S_0 \rightarrow S_3$	380	3.26	0.0548	HOMO-6→LUMO, 4.82% HOMO-3→LUMO, 50.49% HOMO-2→LUMO, 32.96% HOMO→LUMO+1, 11.73%

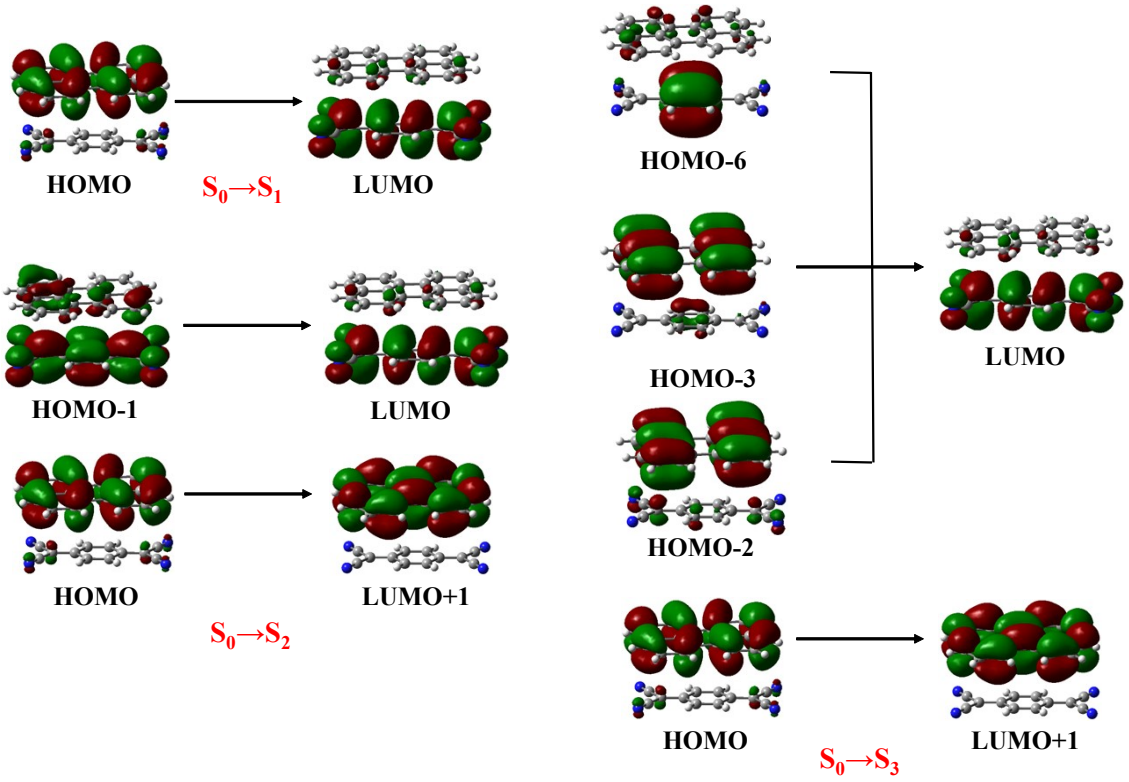

Figure S7. Molecular orbitals taking part in the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions of π-stacked D–A dimer, time dependent DFT analysis was carried out ω97X-D/6-31G(d,p) level.

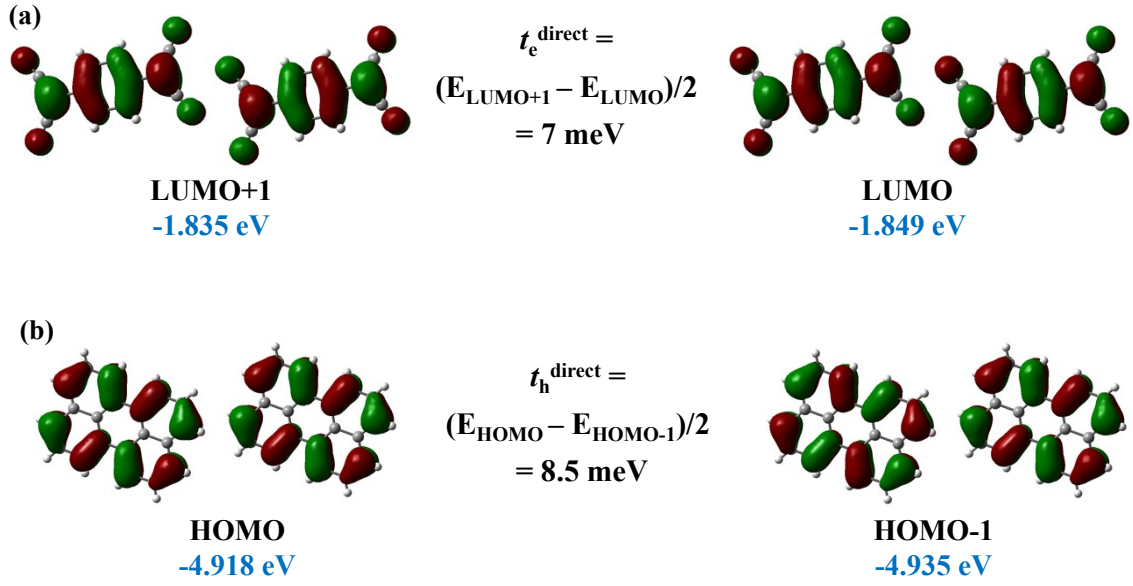

Figure S8. (a) Direct electron transfer integral calculated from nearest acceptor A–A dimer; (b) direct hole transfer integral calculated from nearest donor D–D dimer.

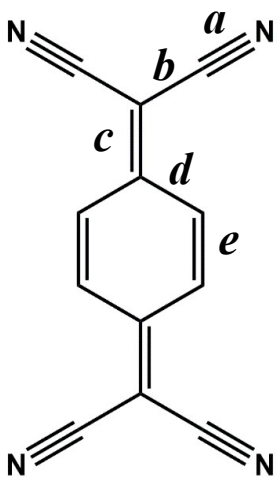

Table S3. Bond-lengths in optimized neutral and anionic geometries of TCNQ

Bond-length	Neutral (Å)	Anion (Å)
a	1.165	1.170
b	1.427	1.416
c	1.390	1.432
d	1.447	1.425
e	1.355	1.375

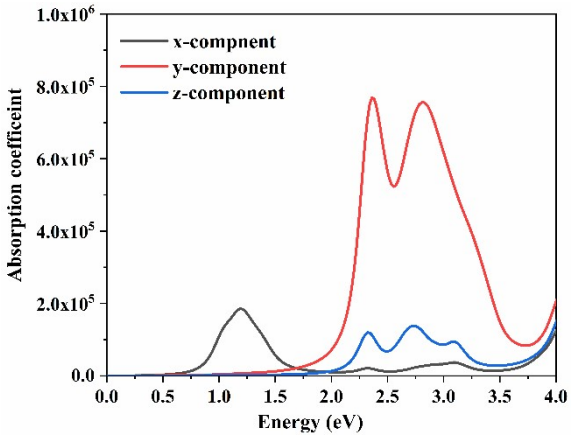

Figure S9. Calculated absorption spectrum from periodic DFT calculation using HSE06 functional on the unit cell experimental geometry with Monkhorst pack 5×3×2 mesh k-points, energy cut-off 500 eV and Gaussian smearing.

Table S4. Coordinates of high symmetry points along the first Brillouin zone in 1:1 perylene:TCNQ cocrystal system

High symmetry point	Coordinates
Γ	0, 0, 0
Z	0, 0.5, 0
D	0, 0.5, 0.5
B	0, 0, 0.5
A	-0.5, 0, 0.5
E	-0.5, 0.5, 0.5
Z	0, 0.5, 0
C	-0.5, 0.5, 0
Y	-0.5, 0, 0

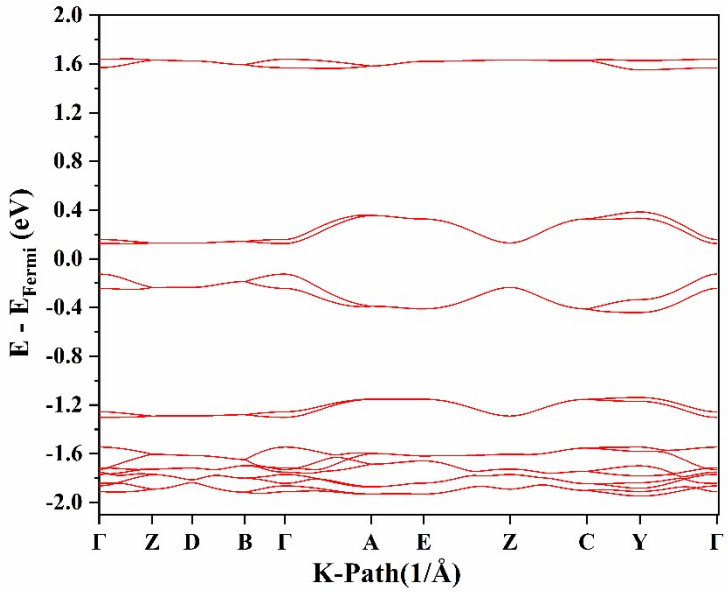

Figure S10. Band structure of 1:1 perylene:TCNQ cocrystal calculated on experimental geometry with GGA functional PBE using line mode k-points, 600 eV energy cut-off, and Gaussian smearing.

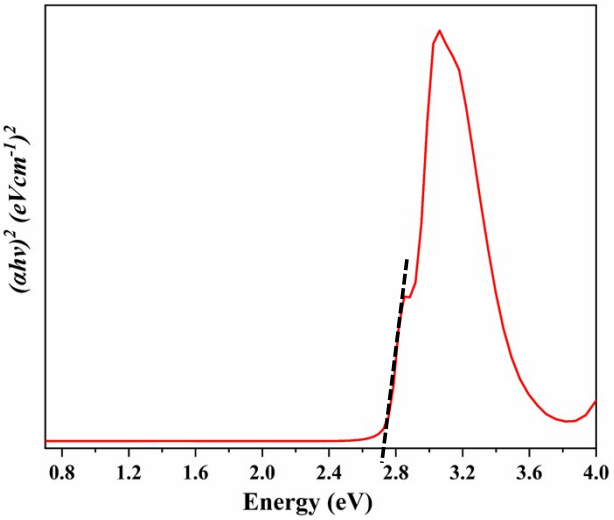

Figure S11. Tauc plot for 1:1 perylene:TCNQ cocrystal by fitting the direct bandgap equation: $(\alpha h\nu)^2 = h\nu - E_g$, while α = absorbance, $h\nu$ = energy and Eg = bandgap.

Table S5. Coordinates of the high symmetry points along the first Brillouin zone in 1-aminopyrene:TCNQ cocrystal system

High symmetry point	Coordinates
Γ	0, 0, 0
Z	0, 0, 0.5
X	0.5, 0, 0
Y	0, 0.5, 0
R	0.5, 0.5, 0.5
T	0, 0.5, 0.5
U	0.5, 0, 0.5
V	0.5, 0, 0

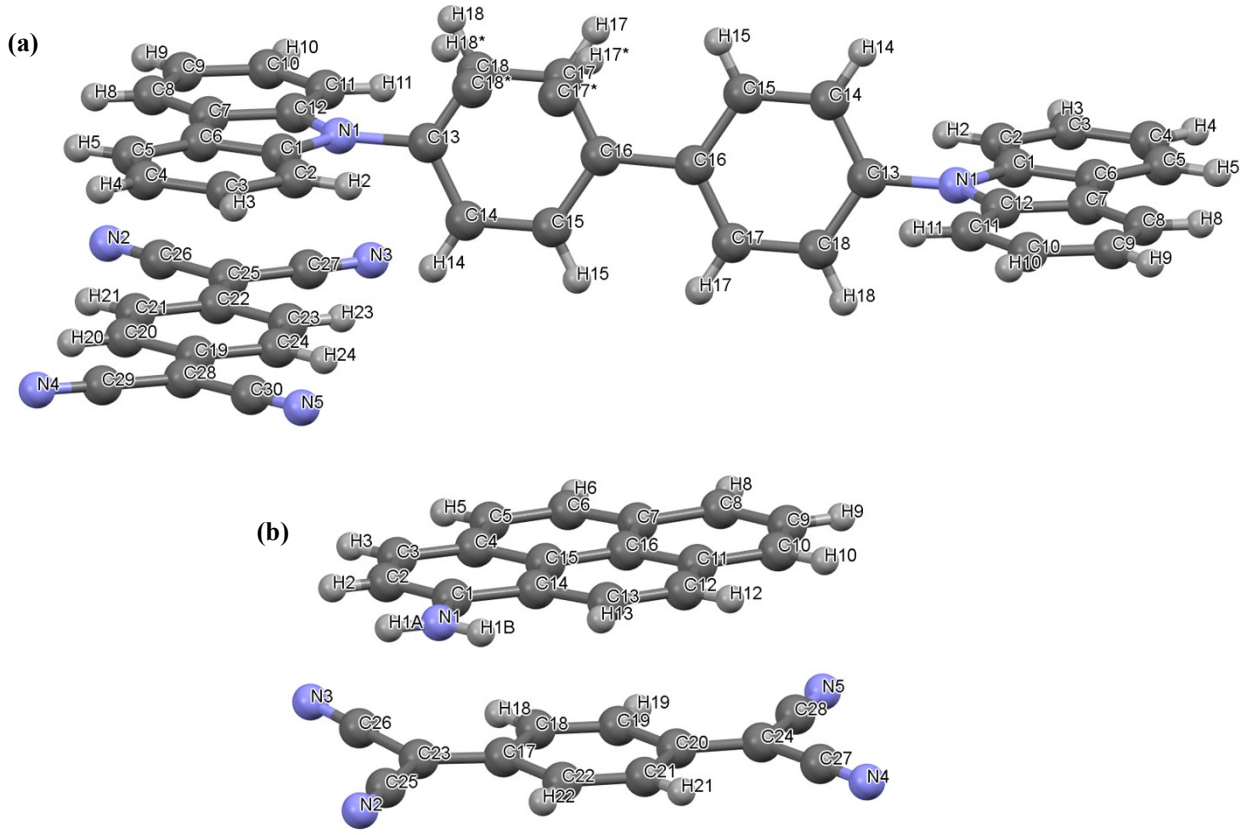

Figure S12. (a) Asymmetric unit of the CBP:$(TCNQ)_2$ cocrystal; (b) asymmetric unit of the 1-aminopyrene:TCNQ cocrystal.

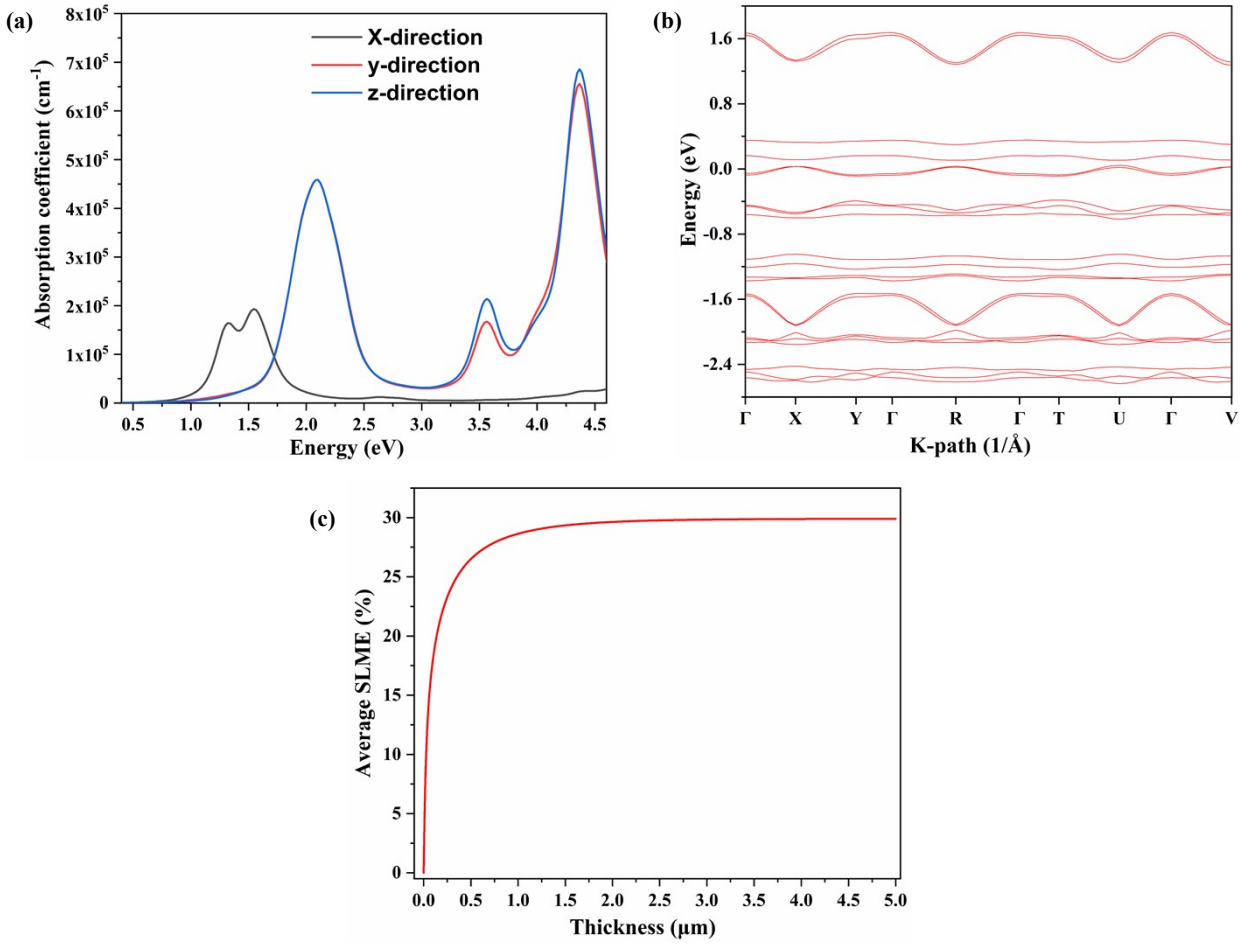

Figure S13. (a) Calculated absorption spectrum of 1:2 CBP:$(TCNQ)_2$ cocrystal from periodic DFT calculation using HSE06 functional on the unit cell experimental geometry with Monkhorst pack 4×3×1 mesh k-points, energy cut-off 500 eV and Gaussian smearing; (b) the band structure of CBP:$(TCNQ)_2$ cocrystal using HSE06 functional on the unit cell experimental geometry with Monkhorst pack 4×3×1 mesh k-points, energy cut-off 500 eV and Gaussian smearing; (c) spectroscopic limited maximal efficiency (SLME) calculated using HSE06 functional.

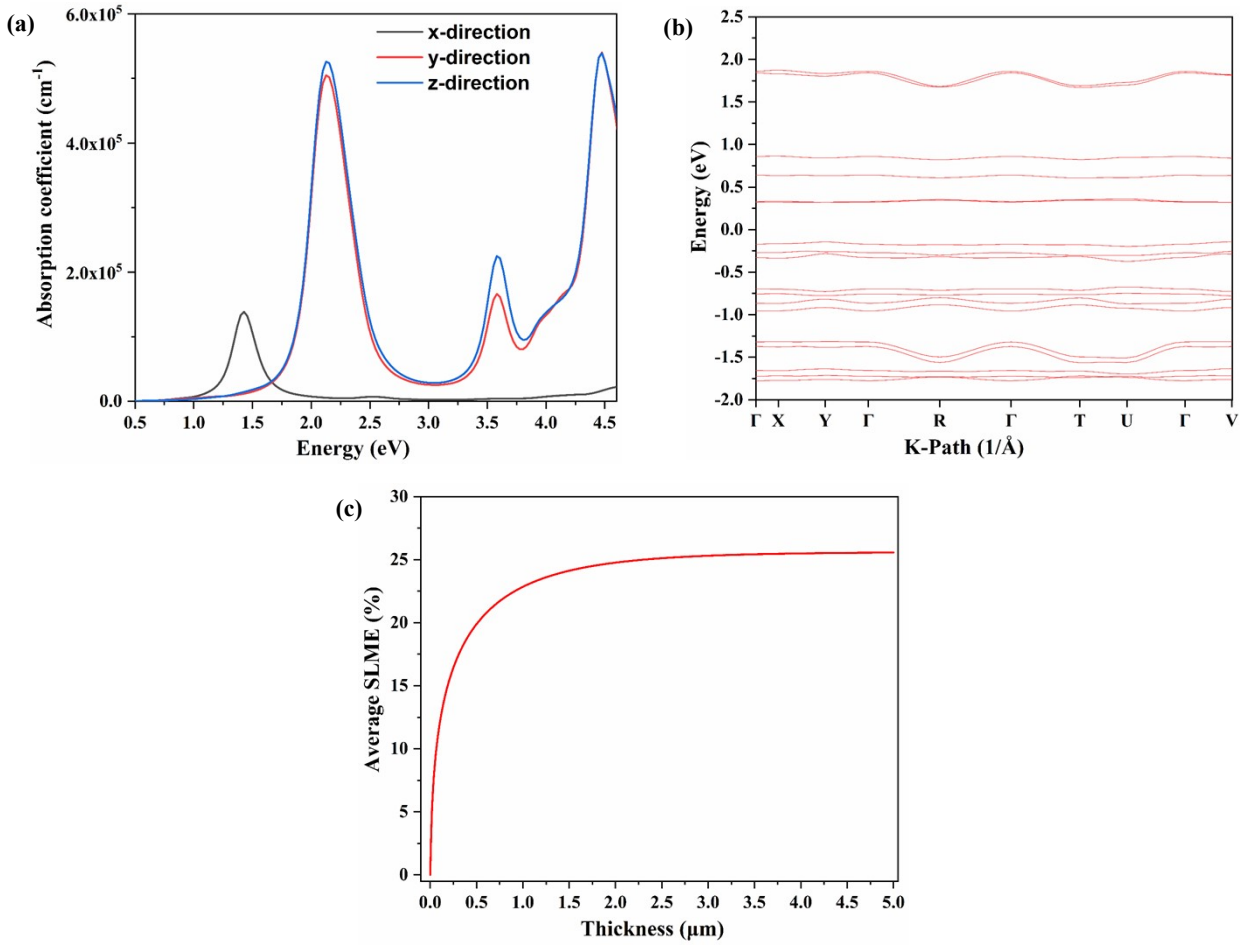

Figure S14. (a) Calculated absorption spectrum of 1:2 CBP:$(TCNQ)_2$ cocrystal from periodic DFT calculation using HSE06 functional on the unit cell experimental geometry with Monkhorst pack 4×3×1 mesh k-points, energy cut-off 500 eV and Gaussian smearing; (b) the band structure of CBP:$(TCNQ)_2$ cocrystal using HSE06 functional on the unit cell experimental geometry with Monkhorst pack 4×3×1 mesh k-points, energy cut-off 500 eV and Gaussian smearing; (c) spectroscopic limited maximal efficiency (SLME) calculated using HSE06 functional.