Elucidating the role of charge transfer on semiconductor properties in a new donor acceptor cocrystal 1,5-dihydroxynaphthalene:TCNQ

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Figure S1. Colour change from brown to dark green with addition of solvent indicating DHN:TCNQ cocrystal formation by solvent assisted mechanochemical grinding.



Figure S2. PXRD pattern of TCNQ, DHN and DHN:TCNQ; showing formation of a new crystalline phase.



Figure S3. *ORTEP* diagram of DHN:TCNQ cocrystal; thermal ellipsoids are drawn at 50% probability.



Figure S4. Aromatic stacking of DHN and TCNQ molecules. Slip distances (in red), centroid – centroid distances, and the perpendicular distance of Cg(1) and Cg(2) on the adjacent ring plane are given in Å, while angles between the Cg(1)-Cg(2) vector and each plane normal are given in ° (deg). Note that for perfectly parallel planes, pairs of slip distances, perpendicular distances and angles would have been similar. The small differences seen here are the result of a 1.62° angle between ring planes.



Figure S5. Four point energy model for reorganization energy calculation.

chemical formula	$C_{22}H_{12}N_4O_2$
formula weight	364.36
temp (K)	298(2)
CCDC Number	2402657
crystal system	Monoclinic
space group	$P2_1/n$
<i>a</i> (Å)	7.126(2)
<i>b</i> (Å)	18.086(5)
<i>c</i> (Å)	7.382(2)
α (°)	90.00
$\beta(^{\circ})$	113.671(7)
γ(°)	90
$V(Å^3)$	871.3(5)
Ζ	2
F_{000}	376
$ ho_{calcd}$ (g cm ⁻³)	1.389
no. of unique reflection	936
no. of reflection $(I \ge 2\sigma(I))$	719
R_1^a, R_1^b (all data, $I \ge 2\sigma(I)$)	0.0694, 0.0509
$\mathrm{wR}_{2^{\mathrm{a}}}, \mathrm{wR}_{2^{\mathrm{b}}}$ (all data, $I \ge 2\sigma(I)$)	0.1263, 0.1163
goodness of fit (F^2)	1.099
largest peak/hole (e Å-3)	0.161/ -0.176

Table S1. Crystallographic and refinement parameters of cocrystal DHN:TCNQ

Table S2. Parameters of optimized and experimental geometries of DHN:TCNQ cocrystal

Geometry	<i>a</i> (Å)	b (Å)	c (Å)	Cg∵Cg (Å)	Inter-planar angle (°)
Optimized	7.125	18.104	6.680	3.6	1.31
Experimental	7.126	18.086	7.382	3.4	1.62

*Centroids and planes of naphthalene ring of DHN and quinonoid ring of TCNQ are considered.

Table S3. Parameters of hydrogen bonding interactions in cocrystal DHN:TCNQ

Interaction	D…A (Å)	H…A (Å)	D-H…A (°)	Symmetry
O1–H1…N1	2.925(4)	1.88(4)	174.0(3)	x, y, z-1
C10–H10…O1	3.432(5)	2.63	145.1	x, y, z+1
C5–H5…N2	3.538(4)	2.68	154.4	x, y, z+1

Table S4. C–C, C=C, C=N bond-lengths in neutral TCNQ and DHN:TCNQ cocrystal



Resonance structures of TCNQ⁻ radical anion indicate variation in C–C (*a*), C=C (*b*) and C=N (*c*) bond lengths upon ionization from neutral TCNQ.

	C–C (a, Å)	C=C (b, Å)	C≡N (c, Å)
Neutral TCNQ	1.433	1.379	1.149
DHN:TCNQ	1.434	1.373	1.140

Table S5.	Coordinates	of high	symmetry	points	in	first	Brillouin	zone	for	DHN:TC	NQ
cocrystal											

High symmetry point	Coordinates
Γ	0, 0, 0
Ζ	0. 0.5, 0
D	0, 0.5, 0.5
В	0, 0, 0.5

А	-0.5, 0. 0.5
E	-0.5, 0.5, 0.5
С	-0.5, 0.5, 0
Y	-0.5, 0, 0

Table S6. Coordinates of high symmetry points in first Brillouin zone for DAN:TCNQ cocrystal

High symmetry point	Coordinates
Γ	0, 0, 0
Z	0. 0.5, 0
D	0, 0.5, 0.5
В	0, 0, 0.5
А	-0.5, 0. 0.5
Е	-0.5, 0.5, 0.5
С	-0.5, 0.5, 0
Y	-0.5, 0, 0



Figure S6. (a) Fingerprint plots for major intermolecular attractive interactions in DHN:TCNQ cocrystal. (b) Hirshfeld surfaces of TCNQ and DHN, only hydrogen bonding interactions are shown. Surfaces are drawn from -0.52 to +1.13 a.u range.



Figure S7. Frontier molecular orbitals in π -stacked tetramer in DHN:TCNQ cocrystal.



Figure S8. Frontier molecular orbitals in π -stacked hexamer in DHN:TCNQ cocrystal.



Figure S9. Frontier molecular orbitals in DAN:TCNQ cocrystal.



Figure S10A. Molecular orbitals involved in $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions in DHN:TCNQ.



Figure S10B. Molecular orbitals involved in $S_0 \rightarrow S_5$ transition in DHN:TCNQ cocrystal.



Figure S10C. Molecular orbitals involved in $S_0 \rightarrow S_6$ transition in DHN:TCNQ cocrystal.



Figure S11. Electron and hole super-exchange integrals in DAN:TCNQ cocrystal.



Figure S12. Direct electron and hole transfer integrals in DHN:TCNQ cocrystal along the crystallographic *c* axis calculated from D–D and A–A dimers.



Figure S13. Band structure of DHN:TCNQ cocrystal calculated with dispersion corrected PBE (PBE-D3) functional with Monkhorst pack 8×3×7 mesh.



Figure S14. (a) Band structure of DHN:TCNQ cocrystal calculated with hybrid HSE06 functional and Γ -centered 4×1×4 mesh at optimized geometry; (b) two highest valence bands and two lowest conduction bands are shown, calculated at hybrid HSE06 functional with Γ -centered 4×1×4 mesh.



Figure S15. (a) Band structure of DAN:TCNQ cocrystal calculated with meta-GGA modified Becke Johnson (MBJ) functional and Γ -centered 4×1×4 mesh at experimental geometry; (b) two highest valence bands and the lowest conduction band are shown, calculated at MBJ functional with Γ -centered 4×1×4 mesh.



Figure S16. (a) Band structure of DAN:TCNQ cocrystal calculated with hybrid HSE06 functional and Γ -centered 4×1×4 mesh at experimental geometry; (b) two highest valence bands and the lowest conduction band are shown, calculated with hybrid HSE06 functional with Γ -centered 4×1×4 mesh.