Supporting Information

Switching Charge-Transfer Characteristic from *p*-Type to *n*-Type through Molecule "Doping" (Co-crystallization)

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Scheme S1. Synthetic route to DTPTP





¹H NMR (300 MHz, CDCl₃) δ 9.95 (d, J = 1.8 Hz, 2H), 9.15 (d, J = 3.6 Hz, 2H), 8.30 (d, J = 1.7 Hz, 2H), 8.02 (s, 2H), 7.84 (d, J = 5.2 Hz, 2H), 7.50 – 7.38 (m, 2H), 1.27 (s, 18H).





HR-MS, calcd for C₃₈H₃₁N₄S₃, 639.1711; found, 639.1694.





The thermal property of compound DTPTP was evaluated by TGA under nitrogen atmosphere. As we can see, compound DTPTP exhibited very good thermal stability with an onset decomposition temperature of ~ $385 \text{ }^{\circ}\text{C}$ (considering the 5% weight loss temperature).



Fig. S4 Cyclic voltammogram curves of compound DTPTP

Cyclic voltammetry was carried out with CHI 604E Electrochemical Analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm²) was used as working electrode, platinum wires were used as counter electrode and reference electrode, respectively. Potentials were recorded versus Pt in a solution of anhydrous DCM with 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) as supporting electrolyte at a scan rate of 100 mV s⁻¹. Fc⁺/Fc was used as an internal standard, which has a HOMO energy level of -4.80 eV.



Fig. S5 The bond lengths of TCNQ based on DTPTP₂-TCNQ complex indicate that degree of charge transfer in this complex is about 0.1 (c/(b+d) = 1.375/(1.444+1.434) = 0.478).



Fig. S6 Short contacts in DTPTP₂-TCNQ complex in stacking or neighboring columns



Fig. S7 (a)TEM images and (b) SEAD patterns of DTPTP crystal ribbon. No change of the SAED pattern was observed for the different parts of the same crystal, indicating that the whole ribbon was a single crystal. The SAED pattern of the disk was indexed with the bulk crystal lattice constants.



Fig. S8 (a) Perpendicular and (b) tilted X-ray diffraction (XRD) signals from the DTPTP₂-TCNQ single-crystalline. We note that the angle of facets at the crystal front end in the optical image (Figure 2c, $\theta \approx 84^\circ$) corresponds to the angle between the crystal plane (010) and (001) ($\phi = 84.4^\circ$), which implies that the crystal growth orientation is along the stacking direction [100].



Fig. S9 Hoping routes in the crystal. In (a) and (b), DTPTP is the central molecule, in (c) and (d), TCNQ is the central molecule.

pathway	center-center/Å	V_h/meV	V _e /meV
1	4.75	-0.21	-8.36
2	3.22	18.95	-19.58
3	14.48	0.43	0.24
4	14.89	0.00	0.00
5	14.77	1.54	-0.26
6	13.74	-6.11	-3.04
7	13.77	4.33	0.95
8	11.64	2.38	14.74
9	11.54	1.63	2.81
10	12.34	0.00	-0.57
11	14.40	-2.35	25.76
12	15.14	0.00	0.00
13	13.84	0.01	0.01
14	11.64	0.00	0.00

Table S1. The electronic couplings (V) for all the hopping pathways of compound DTPTP₂-TCNQ.

All of the DFT calculations were performed with the Gaussian 09 program package.