Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Information

Organic Single Crystals of Charge-Transfer Complexes: Model Systems for the Study of Donor/Acceptor Interactions

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1. Field-effect transistors of DBTTF-TCNQ Polymorphs

Additional current-voltage characteristics for the DBTTF-TCNQ polymorphs are included.

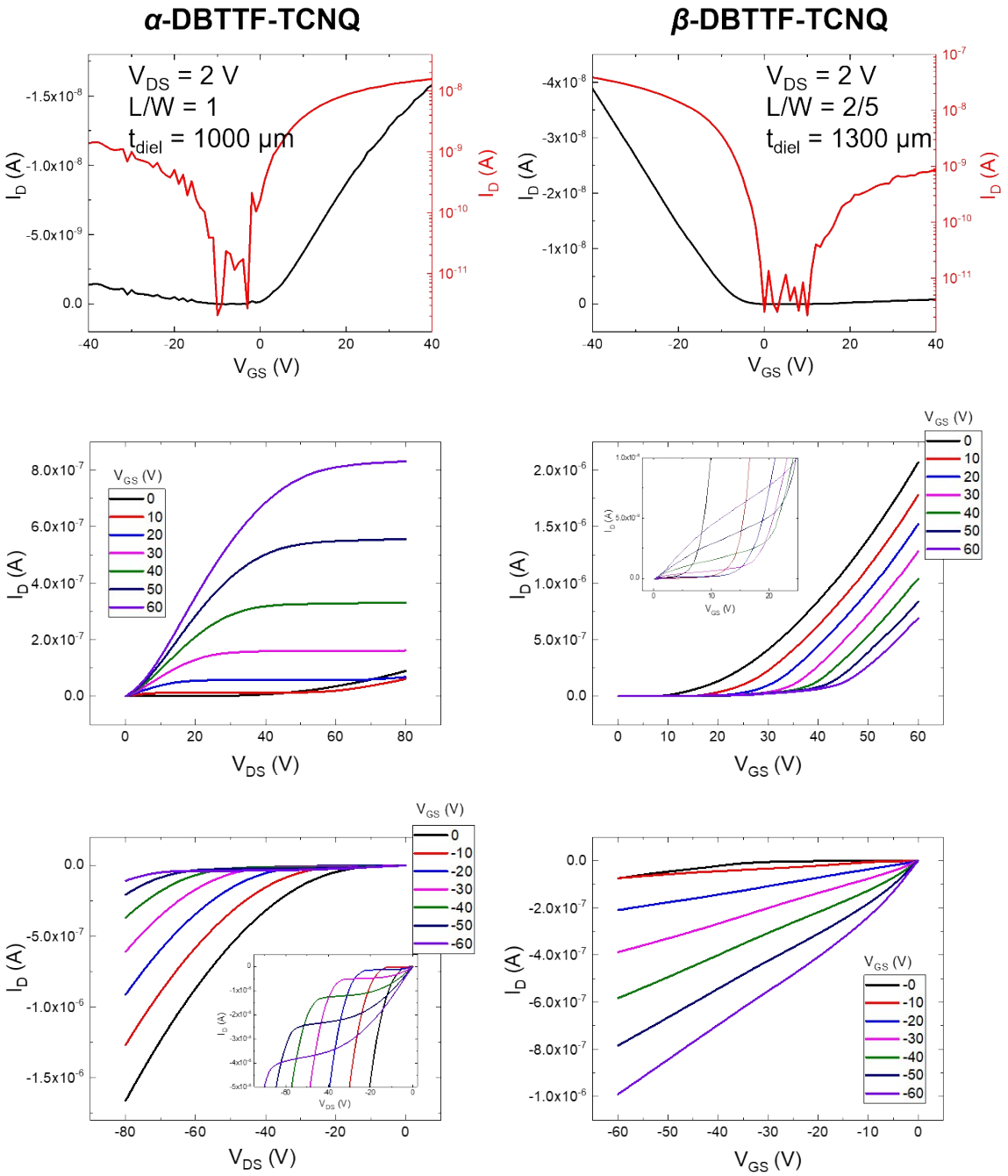

Figure S1. Transfer characteristics for V_{DS} = -2 V, and output characteristics for the α-polymorph (left) the β-polymorph DBTTF-TCNQ (right).

2. ARPES Measurements

a. Photoemission data plotted in false color. Here, we present figure 3d (upper portion) in the main paper using false color "copper" look-up table scheme.

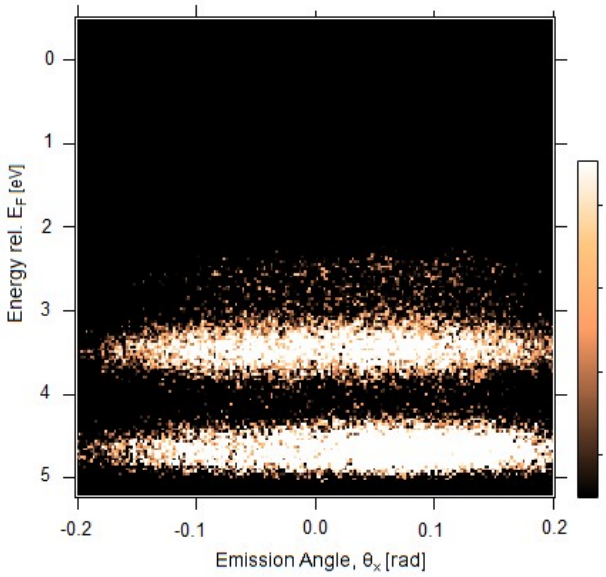

Figure S2. The same data shown in figure 3d of the main paper using the copper look up table.

b. Ionization energy determination of parent compounds from thin-film UV photoelectron spectroscopy (UPS) measurements. Thin-films (~20 nm) of DBTTF and TCNQ were sublimed onto Au substrates, and both films were measured by UPS to determine the work function (by the secondary electron cut-off region) and HOMO center position. The results are tabulated below, and are consistent with results in the literature.[1,2] We note that DBTTF parent compound can exist in different polymorphs.[3,4] Only one was studied in this manuscript.

Table S1. Ionization energy of the DBTTF and TCNQ thin films.

Thin film	**HOMO center wrt E_F [eV]**	**Work Function [eV]**	**Ionization Energy [eV]**
DBTTF	0.87 ± 0.05	4.9 ± 0.05	5.77 ± 0.07
TCNQ	3.4 ± 0.05	4.95 ± 0.05	8.35 ± 0.07

c. We determined the surface work function of air-exposed Au and Ag substrates to be 5.0 eV and 4.9 eV, respectively. This results in the 0.1 eV uncertainty in identifying the HOMO levels of the crystals which accounts for the contact potential differences between using Au and Ag substrates.

3. Double Exponential Fit of trap Density of States

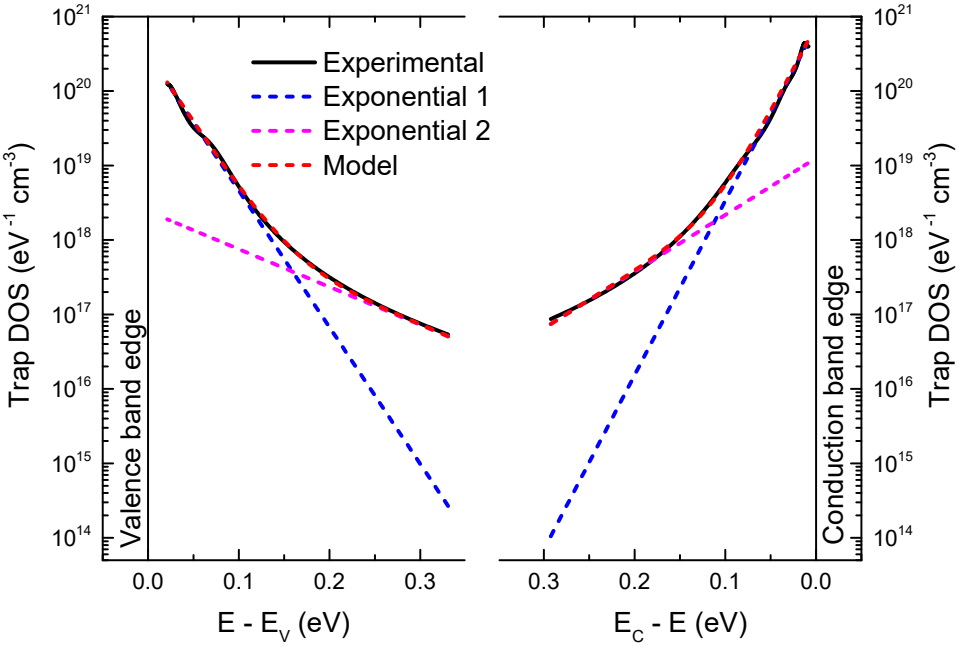

Figure S3. Model fits (broken lines) to experimental *t*-DOS spectra (solid lines) of α-polymorph.

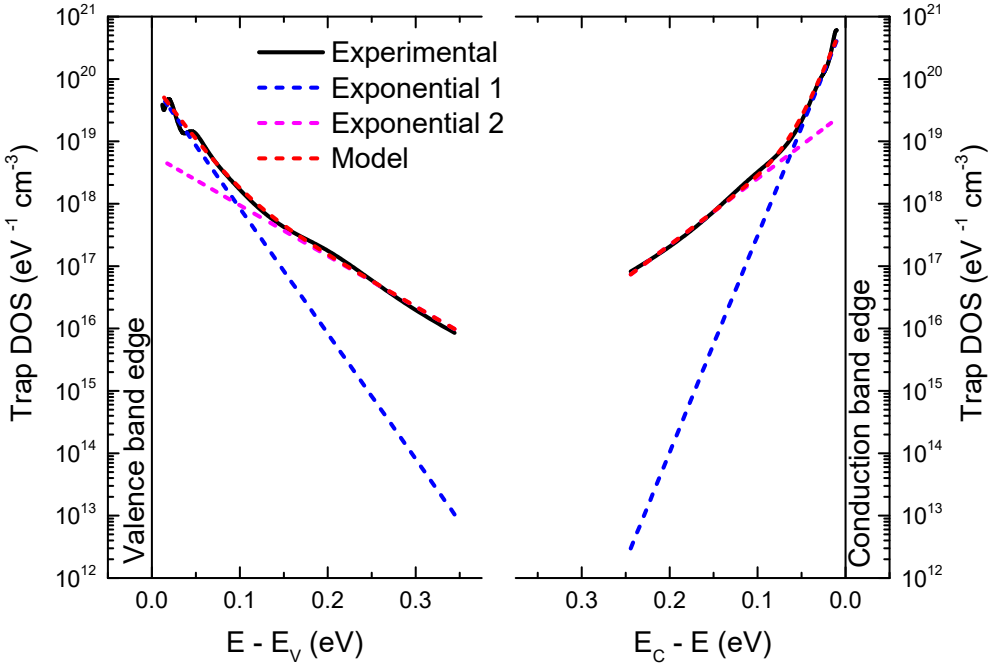

Figure S4. Model fits (broken lines) to experimental *t*-DOS spectra (solid lines) of *β*-polymorph.

References

1. Nielsen, P. Substrate dependent ionization and polarization energies of molecules: Dibenztetrathiafulvalene. *Solid State Commun.* **26**, 835–838 (1978).

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3. Brillante, A. *et al.* The four polymorphic modifications of the semiconductor dibenzo-tetrathiafulvalene. *CrystEngComm* **10**, 1899 (2008).

4. Pfattner, R., Bromley, S. T., Rovira, C. & Mas-Torrent, M. Tuning crystal ordering, electronic structure, and morphology in organic semiconductors: Tetrathiafulvalenes as a model case. *Adv. Funct. Mater.* **26**, 2256–2275 (2016).