

Supporting Information

Polymorphism in the 1:1 Charge-Transfer Complex DBTTF-TCNQ and its effects on optical and electronic properties

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SI.1. Crystal Growth Procedure

The physical vapor transport (PVT) process was used to grow crystals of the DBTTF-TCNQ polymorphs. Two furnaces, shown in SI Fig. 1, were used to grow each polymorph. A ~30 in (~76 cm) fused quartz tube with a 22 mm inner diameter was used to contain the growth. This was cleaned with Alconox detergent and hot water, followed by a rinse with de-ionized water, a ten minute soak in acetone, and a ten minute soak in isopropanol. The tube was dried and placed on the PVT furnace at 350 °C with 50 mL/min of argon flowing for 24 hours. Several 10 cm tubes,

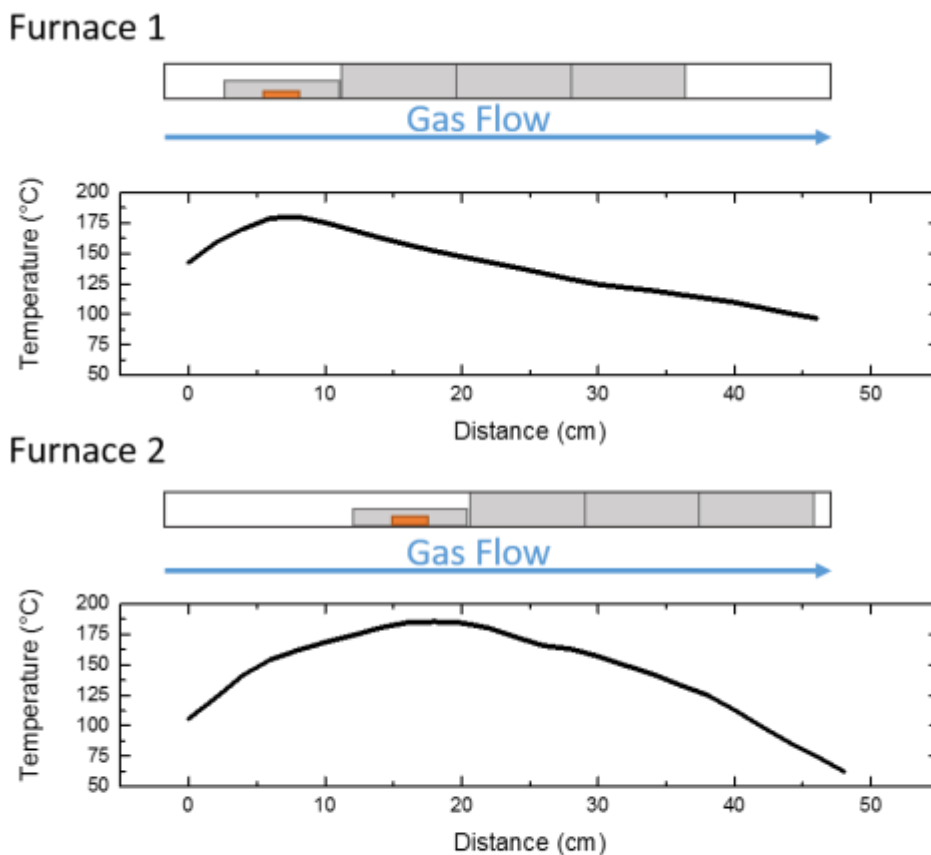


Figure S1. Diagrams of the two PVT furnaces used to grow DBTTF-TCNQ polymorphs. Furnace 2 has a steeper temperature gradient than furnace 1.

(17 mm inner diameter, 20 mm outer diameter) were cleaned by a similar method and placed inside the larger tube during this heating process. The furnace was cooled to room temperature and the DBTTF-TCNQ powder was placed in the hottest zone of the furnace. The powder was kept at room temperature with 50 mL/min argon flow for one day. Following this, the temperature was adjusted so that the interior of the tube was slightly above 100 °C for two hours. This step facilitates the removal of any water adsorbed into the powder. Following this, the powder was heated to the conditions described in the article text, resulting in the growth of both crystal polymorphs.

SI.2. X-Ray Photoelectron Spectroscopy

Spectral fitting was performed to identify the different states in which the S atoms exist. For the β -DBTTF-TCNQ, the S 2p fits were performed by using one pair of Voigt lineshapes for the $2p_{3/2}$ and $2p_{1/2}$, fixing the spin orbit area ratio ($2p_{3/2}:2p_{1/2}$ as 2:1), and coupling the Gaussian widths. Due to the complicated S 2p spectral shape of the α -DBTTF-TCNQ, three pairs of Voigt lineshapes were used while coupling the Gaussian and Lorentzian widths, fixing the area ratio (2:1), and fixing the spin-orbit splitting as 1.14 eV (determined from the fit of β -DBTTF-TCNQ). It was necessary to use three different chemical environments as it was clear that using one or two chemical environments poorly described the spectrum. The N 1s spectrum of both polymorphs were deconvoluted by coupling the Gaussian widths, while the Lorentzian widths were allowed to vary to account for the different electronic states. For quantification purposes, we used the integrated N 1s and S 2s XPS lines to compare the relative sulfur and nitrogen content of the polymorphs as they are energetically closer than N 1s and S 2p, and this helps reduce the disparity of the electron spectrometer efficiency at different kinetic energies. This in turn helps to reduce the uncertainty in the estimated relative sulfur and nitrogen content.

SI.3. Optical Absorbance Measurements

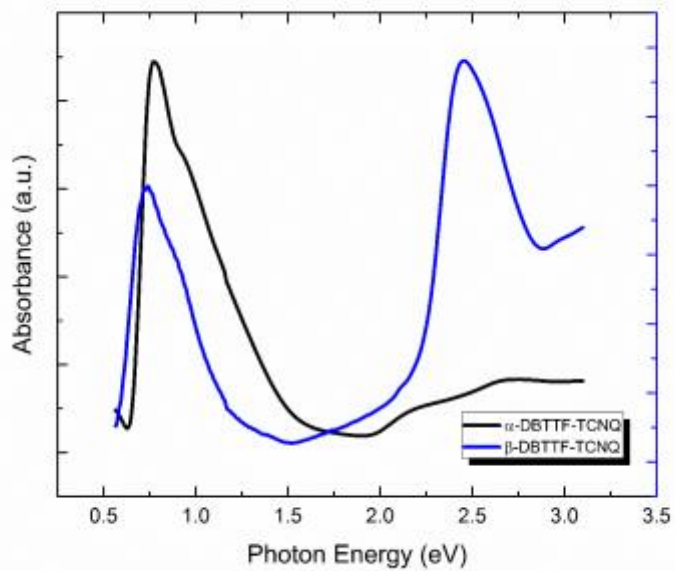


Figure S2. Optical absorbance of α -DBTTF-TCNQ (black) and β -DBTTF-TCNQ (blue). The charge-transfer peak of the former peaks at 0.78 eV while the latter peaks at 0.73 eV.

SI.4. Ultraviolet Photoemission Spectroscopy

UPS measurements were performed in the same XPS vacuum system stated previously by using an He discharge lamp (21.2 eV) as the excitation source and applying a -5 V bias to the sample to clear the work function of the spectrometer. The energy scale was calibrated by measuring the Fermi step in a bare Au sample. The UPS spectrum is shown below in SI Fig. 3. In each spectrum, the background contribution from the Au was removed in order to clearly resolve the HOMO feature (open circles in SI Fig. 3). Finally, one Gaussian lineshape was used to estimate the center of the HOMO (solid red line, SI Fig. 3).

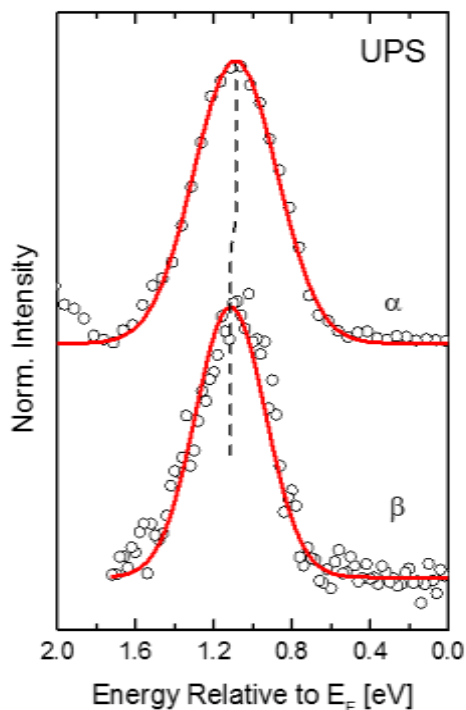


Figure S3. UPS spectra of the HOMO region for the α -polymorph (top) and the β -polymorph (bottom) with respect to the Fermi energy (E_F). The data of the polymorphs (open circles) are shown after subtracting the background contribution from the Au substrate, and a fit of one Gaussian lineshape (red line) is used to estimate the center of the HOMO. The dashed line is a guide to the eye for the small, but measurable shift of the HOMO between the two polymorphs.

SI.5. DFT Calculations

Electronic coupling ($t_{H(D)-L(A)}$) between HOMO of the donor (DBTTF) and LUMO of the acceptor (TCNQ), and the effective transfer integrals for holes (t_h^{eff}) and electrons (t_e^{eff}) calculated at B3LYP/6-31G level.

	$t_{H(D)-L(A)}$ (meV)	t_h^{eff} (meV)	t_e^{eff} (meV)
α -polymorph	379	85	71
β -polymorph	157	8	18

Table S1. Transfer integrals for holes and electrons in each DBTTF-TCNQ polymorph.

The inverse effective mass tensor was calculated by means of Sperling's centered difference method with $dk = 0.014/\text{Bohr}$. The calculation for effective mass of electrons did not converge.

Wave vector		m/m_0	Direction		
(0.0 0.0 0.0)	$m_1(\text{h})$	0.938	1.000	0.809	-0.035
	$m_2(\text{h})$	4.871	0.002	-0.128	1.000

Table S2. Effective mass of holes in β -polymorph of DBTTF-TCNQ.

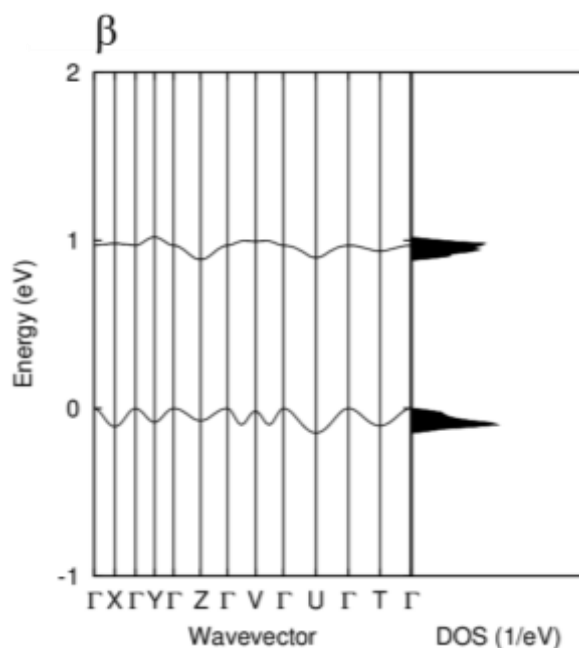


Figure S4. Band structure and density of states of the β -polymorph of DBTTF-TCNQ. The points of high symmetry in the first Brillouin zone are labeled as follows: $\Gamma = (0,0,0)$, $X = (0.5,0,0)$, $Y = (0,0.5,0)$, $Z = (0,0,0.5)$, $V = (0.5,0.5,0)$, $U = (0.5,0,0.5)$, $T = (0,0.5,0.5)$. The conduction band and valence band widths are similar (150 meV and 138 meV respectively).