Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Ambipolar Charge Transport in a Bis-Diketopyrrolopyrrole Small Molecule Semiconductor with Tunable Energetic Disorder

Jiyu Zhou, Shiqing Bi, Yang Shuo, Huiqiong Zhou, and Yuan Zhang**

Experimental methods

Materials: BTDPP2 was obtained via lab synthesis. All other materials are purchased without further purification. Detailed synthetic procedures for BTDPP2 are described in ref 22.

Device fabrication and characterization. OFETs were fabricated in a nitrogen purged glove box. The active layers were deposited by spin-coating the BTDPP2 solution from chloroform (6 mg/mL) on pre-cleaned Si/SiO_2 substrates (oxide layer of 150 nm) followed by thermal evaporation of 100 nm Au top contact through shadow masks, yielding a channel width of 2 mm and a channel length of 40 μm. The finished devices were thermally annealed on a hot plate at selected temperatures and immediately cooled down at ambient glove box temperature before testing. The thickness of BTDPP2 active layers was around 40 nm determined by a profilometer.

BTDPP2 electron-only (EO) diodes were fabricated as follows: First, patterned bottom Al anode (30 nm) was constructed by thermal evaporation on pre-cleaned glass substrates. BTDPP2 was spun-coat from the chloroform solution (18 mg/mL) on top of the glass substrate containing Al anode, leading to a film thickness of ~150 nm. Prior to depositing the top electrode, the cast films were thermally annealed at 150 °C for 10 min and cooled in the glove box. Finally, 5 nm of Ba cathode was thermally evaporated on top of the BTDPP2 active layer capped with 100 nm of Al protection layer. The evaporation was performed under a chamber pressure < 1×10^{-7} Torr. Similarly, the OFETs were pre-annealed at the same temperatures prior to depositing the Ba/Al electrode. Completed OFET and diode devices were transferred in a LakeShore vacuum probe station (pressure <10^{-6} Torr) without exposure to air. The electronic characteristics were registered by a Keithley 4200 SC semiconductor parameter analyzer. Low temperature was achieved by purging with liquid nitrogen in a cryosystem controlled by a LakeShore temperature controller.

Data simulation. Data analysis and modeling of OFETs characteristics were performed by using OriginPro (version 8.5) data analysis software embedded with customized programing codes.

Mobility calculation and OFET characteristics simulation

Based on the classical metal-oxide-semiconductor (MOS) theories, the OFET mobility in the linear and saturation regimes can be calculated by,

$$\mu_{lin}(FET) = \frac{L}{WC_iV_d}\frac{\partial I_d}{\partial V_g}\bigg|_{V_g - V_{th} >> V_d} \tag{S1}$$

$$\mu_{sat}(FET) = \frac{2L}{WC_i}\left(\frac{\partial\sqrt{I_d}}{\partial V_g}\right)^2\Bigg|_{V_g - V_{th} << V_d} \tag{S2}$$

where *W*, *L*, C_i is the FET channel width, length and area capacitance of the oxide layer, respectively.

With the charge transport in BTDPP2 characteristic of the phonon-assisted hopping process, the carrier mobility follows the general Arrhenius temperature (*T*) dependence from which the activation energy $\Delta_{mobility}$ can be calculated as,

$$\mu(e,h) = \mu_0(e,h)\exp\left(-\frac{\Delta_{mobility}}{T}\right) \tag{S3}$$

where $\mu_0(e,h)$ is the zero-field mobility with "*e*" and "*h*" in the parenthesis denoting for the electron and hole.

Based on the VRH model, the I_{ds} of OFETs operated in the saturation regime can be analytically described by,

$$I_{ds} = \frac{W}{L}\left(\gamma_e \frac{T}{2T_{0,e}}\frac{T}{2T_{0,e}-T}\left(V_g - V_t\right)^{2T_{0,e}/T} + \gamma_h \frac{T}{2T_{0,h}}\frac{T}{2T_{0,h}-T}\left(-V_g + V_t + V_d\right)^{2T_{0,h}/T}\right) \tag{S4a}$$

where the subscripts "*e*" and "*h*" denote for the electron or hole, and *γ* equals,

$$\gamma = \frac{\sigma_0}{q}\left(\frac{\left(\frac{T_0}{T}\right)^4 \sin\left(\pi\frac{T}{T_0}\right)}{\left(2\alpha\right)^3 B_c}\right)^{T_0/T}\left(\frac{1}{2k_B T_0 \varepsilon_0 \varepsilon_r}\right)^{(T_0/T)-1} C_i^{(2T_0/T-1)} \tag{S4b}$$

with σ_0 standing for the conductivity prefactor, α^{-1} for the overlap between localized states, B_c for the critical number of the onset of percolation, and $\varepsilon_0\varepsilon_r$ for the dielectric constant of the semiconductor.

Similar to Equation S4, the output and transfer characteristics in the linear regime is described by,

$$I_{SD} = \gamma \frac{W}{L} \frac{T}{2T_0} \frac{T}{2T_0 - T} \left[\left(V_g - V_t \right)^{2T_0/T} - \left(V_g - V_t - V_d \right)^{2T_0/T} \right] \tag{S5a}$$

$$\gamma = \frac{\sigma_0}{q} \left(\frac{\left(\frac{T_0}{T} \right)^4 \sin\left(\pi \frac{T}{T_0} \right)}{\left(2\alpha \right)^3 B_c} \right)^{T_0/T} \left(\frac{1}{2k_B T_0 \varepsilon_0 \varepsilon_r} \right)^{(T_0/T)-1} C_i^{(2T_0/T-1)} \tag{S5b}$$

By re-writing Equation S4, the density dependent FET mobility as a function of *V_g* is given by,

$$\mu_{FET}(V_{eff}) = \frac{\sigma_0}{q} \left(\frac{\left(\frac{T_0}{T} \right)^4 \sin\left(\pi \frac{T}{T_0} \right)}{\left(2\alpha \right)^3 B_c} \right)^{T_0/T} \left(\frac{\left(C_i V_{eff} \right)^2}{2k_B T_0 \varepsilon_0 \varepsilon_r} \right)^{(T_0/T)-1} = \frac{\gamma}{C_i} \left(V_{eff} \right)^{2T_0/T-2} \tag{S6}$$

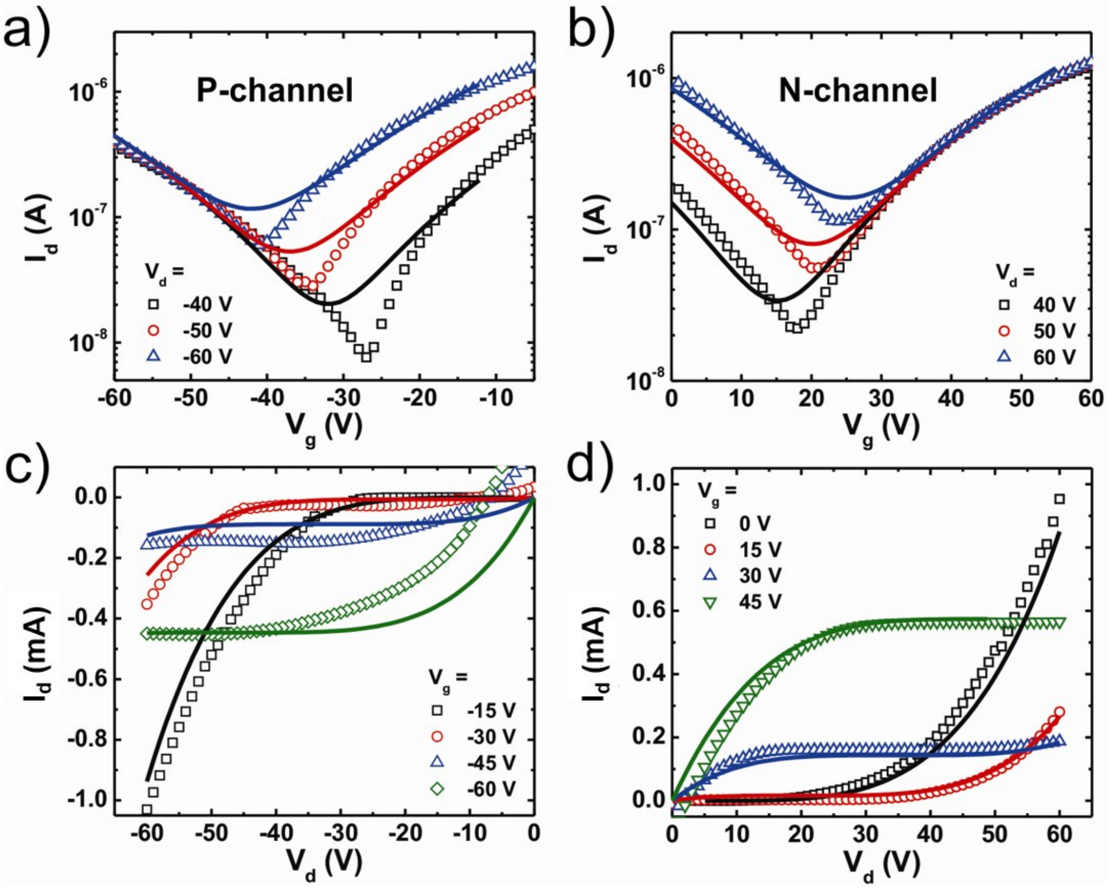

Figure S1. (a), (b) Transfer, and (c), (d) output characteristics of BTDPP2 OFETs with Au source-drain electrodes at room temperature when operated in the *p*-type (a, c) and *n*-type (b, d) modes, respectively. Also shown by lines are the simulations based the VRH model using Equations S4-S5 (SI) with taking into account the density-dependent mobility.

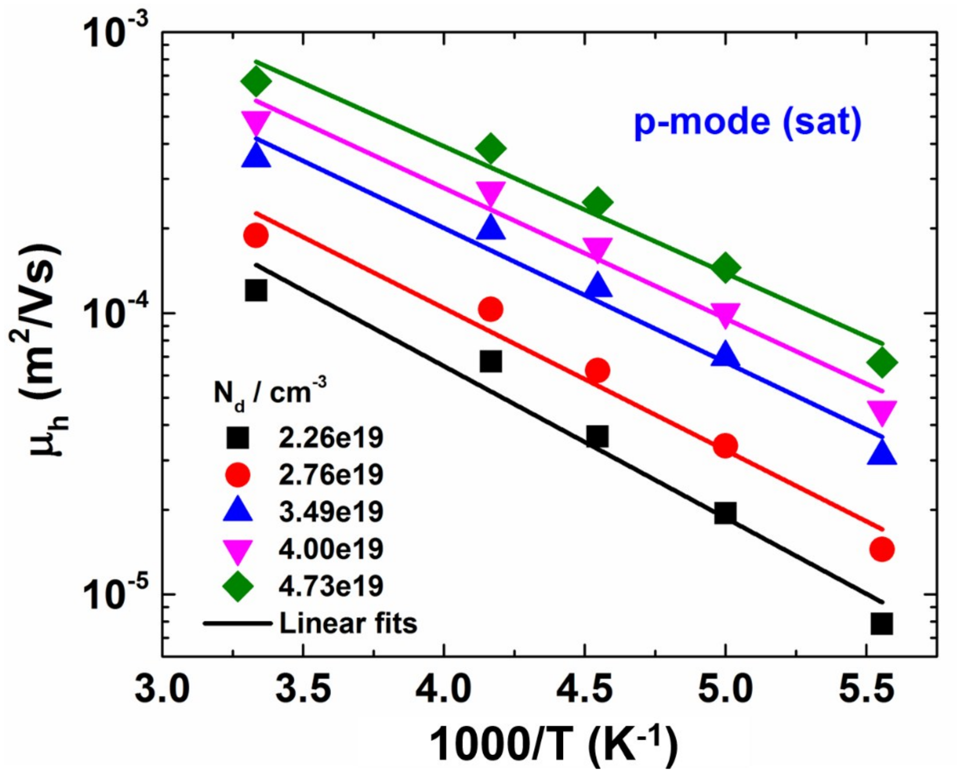

Figure S2. Temperature (*T*)-dependent hole mobility in BTDPP2 OFETs with Au source-drain electrodes at various carrier densities calculated in the saturation regime. Lines are the linear fittings to calculations.

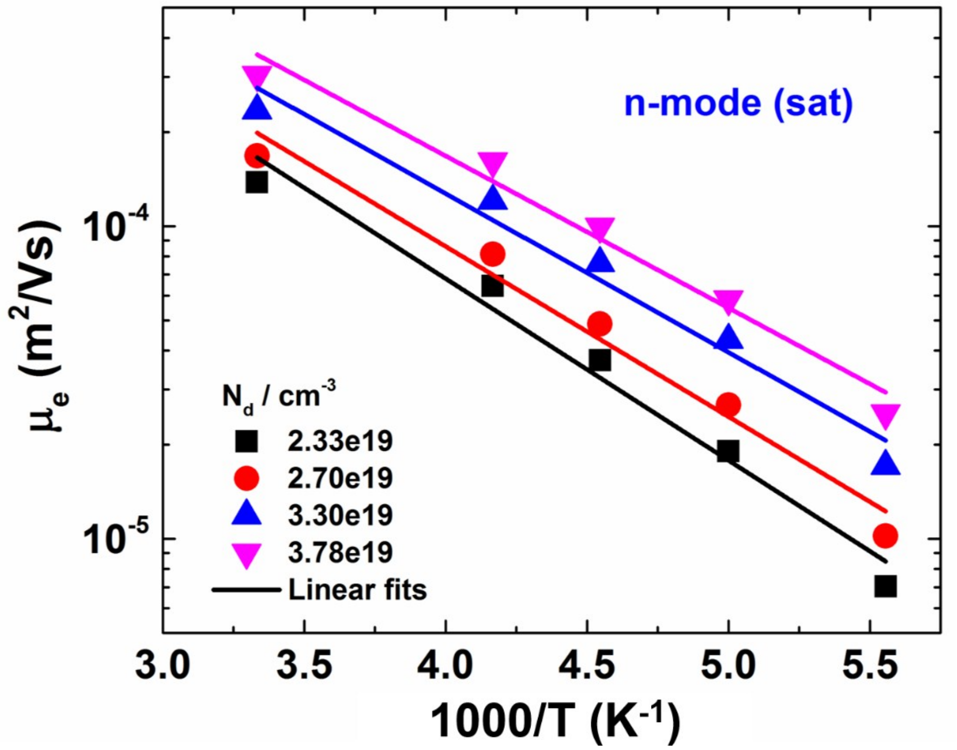

Figure S3. *T*-dependent electron mobility in BTDPP2 OFETs with Au source-drain electrodes at various carrier densities calculated in the saturation regime. Lines are the linear fittings to calculations.

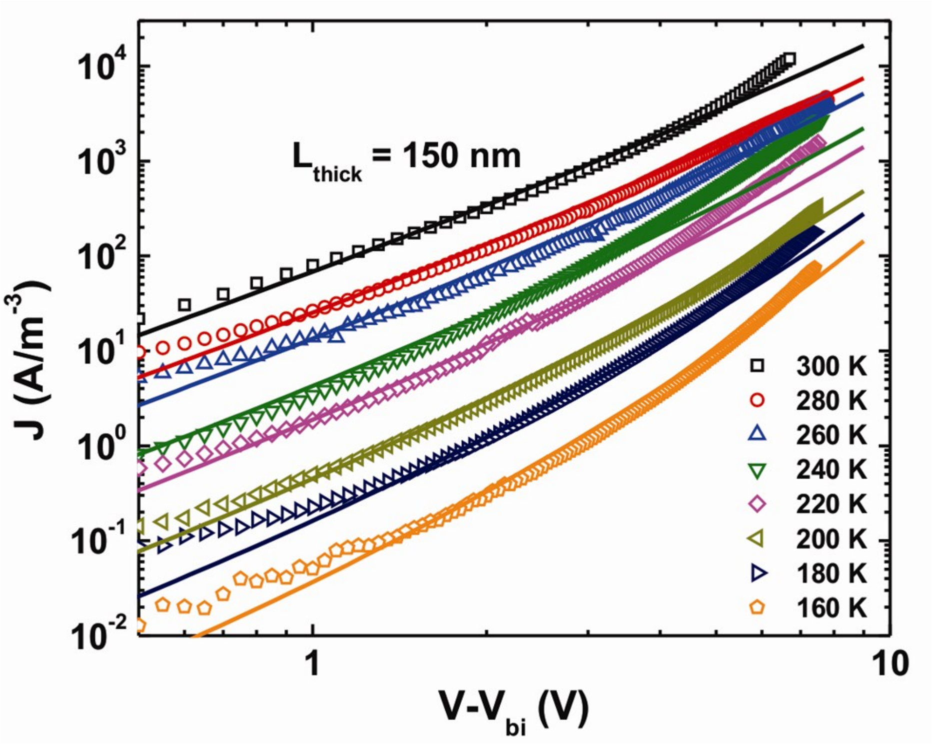

Figure S4. Current density versus voltage characteristics of BTDPP electron-only diodes measured at various temperatures. Lines are the fittings to measurements with the space-charge limited current model (Mott-Gurney Law).