Supporting information

Photo-Induced Intramolecular Charge Transfer in an Ambipolar Field-Effect Transistor Based on a π-Conjugated Donor–Acceptor Dyad

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Experimental

OFET preparation and characterization:

TTF-PDI was synthesized as reported earlier.[1] All the device fabrication and characterization of the experiments reported here were carried out within a nitrogen glove-box with H_2O and O_2 below 10 ppm. Before dissolving TTF-PDI in dichloromethane (c = 1 mg/ml) the compound was stored under vacuum for about 1 h to remove residual oxygen and humidity; after that the solution was prepared within a nitrogen glove-box. All vials were protected with Al foil to minimize the exposure of the TTF-PDI solution to light.

Highly n-doped Si/SiO_2 substrates with 230 nm of thermally grown SiO_2 and interdigitated gold electrodes in a bottom-gate bottom-contact geometry, purchased from Fraunhofer, were used. A series of devices was prepared by drop casting the solution of TTF-PDI (V = 40 µl) on the SiO_2 with the gold electrodes leading to a film thickness of about $30-40$ nm measured by AFM. To reduce the exposure to ambient light, both the solution vials and the substrates, immediately after dropcasting, were protected or covered with Al foil. For the annealing of the samples a hotplate was used. Electrical characterization was performed by using a

Keithley 2612 SourceMeter. For the characterization of the inverter circuit, an additional Keithely 2400 SourceMeter was connected. Samples were stored in inert N_2 atmosphere for 3 months, and the electrical performance did not exhibit significant changes.

Photoconductivity measurements:

The TTF-PDI OFETs were exposed to the full solar spectrum using a Solar Generator (A class AM1.5 standard reference spectrum solar simulator Model SS-50AAA, Photo Emission Tech. Inc.) with an Intensity of 100 mW/cm^2 and the electrical characteristics were measured with a Keithley 2612 SourceMeter. With the aim to determine the wavelength dependent photoconductivity of the films, the dissolved TTF-PDI was drop cast on a silanized and bare sapphire surface. A pair of coplanar 100 nm thick Al electrodes was thermally evaporated through a shadow mask. The separation between electrodes was 100 μm and 150 μm. The TTF-PDI layer was illuminated in the direction perpendicular to the topmost surface with a pulsed tunable-wavelength laser having a pulse duration of 3 ns (Ekspla NT-342). The pulse repetition was 10 Hz. During the illumination, a bias voltage of 600 V was applied between electrodes in order to collect the photogenerated charge (q). The laser pulse energy (E_{laser}) at varying photon energy – wavelength was measured and reported in Figure S4. Each point of Figure 3b represents an average ratio of 100 laser pulses. The observed noise in the measurement comes mainly from the laser pulse energy variation. We note that due to the employed experimental setup the measurement had to be done in two steps : first in the range from 720 to 1100 nm and then between 420 and 710 nm.

Electrical characterization of TTF-PDI OFETs:

Typical output characteristics for a solution-processed TTF-PDI thin-film OFET with gold

source and drain electrodes measured as prepared in the dark under inert conditions.

a)   b)
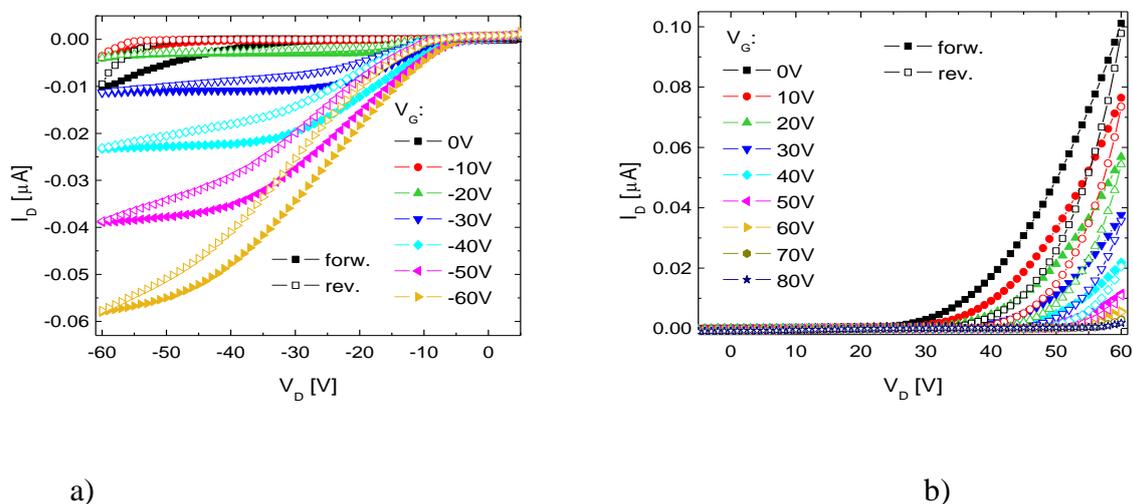
Figure S1. Output characteristics measured for a solution-processed TTF-PDI OFET measured as prepared in the dark under inert conditions. a) hole transport and b) electron transport.

The evolution of the field-effect mobility extracted in the saturation regime was analyzed and

plotted in Figure S2. The maximum field-effect mobility was extracted in the saturation

regime ($|V_D|>|V_G - V_{TH}|$) at:

V_D=-60V, V_G=-60V, V_{TH} = -31V: μ_{h+}=0.5*10^{-3}cm^2/Vs.

V_D=+60V, V_G=+60V, V_{TH} = +32V: μ_{e-}=1.5*10^{-3}cm^2/Vs.

for holes and electrons, respectively.

a)   b)
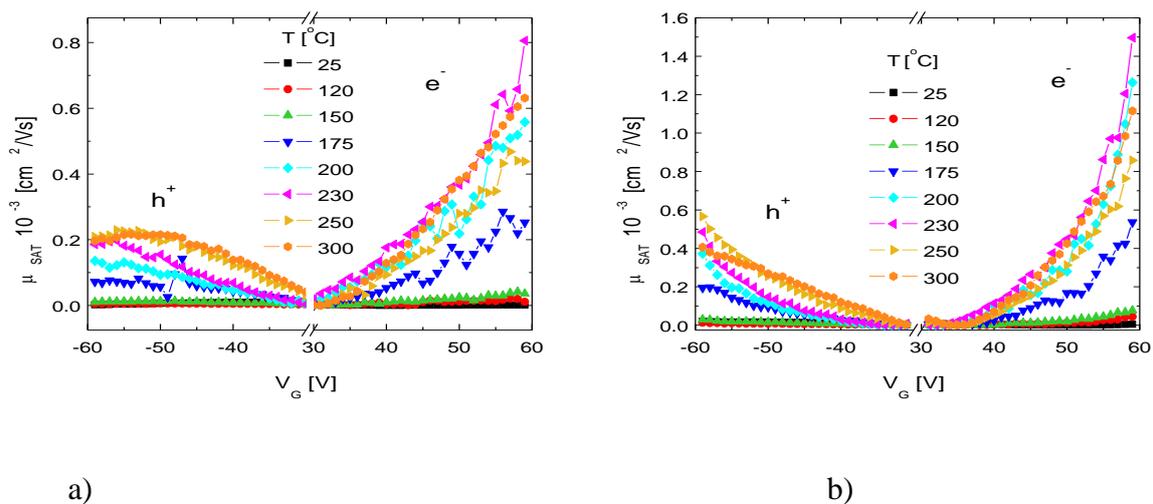
Figure S2. Evolution of the field-effect mobility extracted in the saturation regime, a) forward and b) reverse sweep V_G, for both hole and electron channel operation as a function of annealing temperature. All electrical measurements were carried out at T = 25 ^{o}C.

Evolution of V_{th} for holes (h$^+$) and electrons (e$^-$):
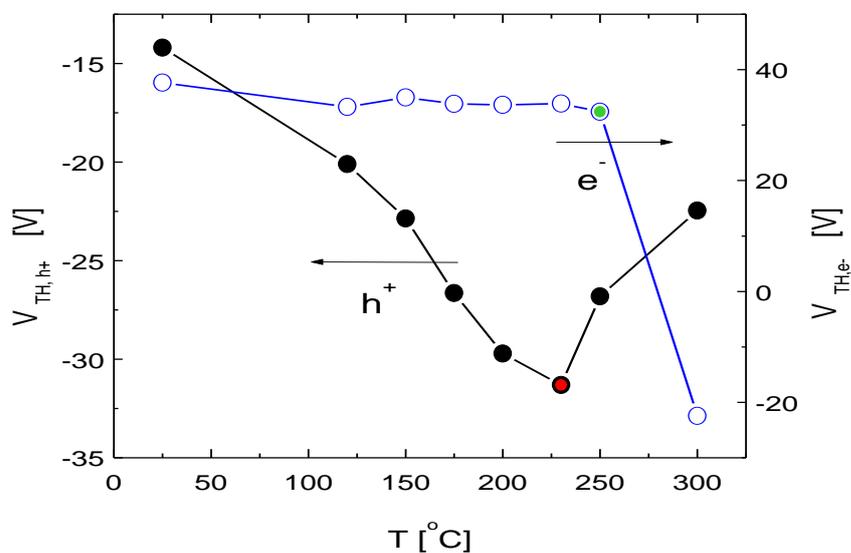
Figure S3. Evolution of the threshold voltage, for holes and electrons, after annealing at different temperatures.

**Preparation of TTF-PDI thin film on quartz for absorption measurements**

To measure the absorption spectra of TTF-PDI in the film, a solution of TTF-PDI in CH_2Cl_2 (c = 1 mg/ml) was drop-cast on top of a quartz slide and stored in vacuum at about 100°C overnight to remove solvent and residual oxygen or humidity. After that the ABS-spectra were recorded in a dark room under ambient conditions.

**Photoconductivity measurements**

The TTF-PDI layer was illuminated in the direction perpendicular to the sample top surface with a pulsed tunable-wavelength laser. The pulse duration was 3 ns. The pulse repetition was 10 Hz. During the illumination, a bias voltage of 600 V was applied between electrodes in order to collect the photogenerated charge (q). In Figure S4 we present the laser pulse energy (E_{laser}) at varying photon energy - wavelength. The laser pulse energy was between 20 and 150 nJ, focused in a region of 100 μm x 5 mm between the electrodes. Therefore, the illumination energy was below 30 μJ/cm^2 per pulse. E_{laser} was used to estimate the number of incident photons Nph.
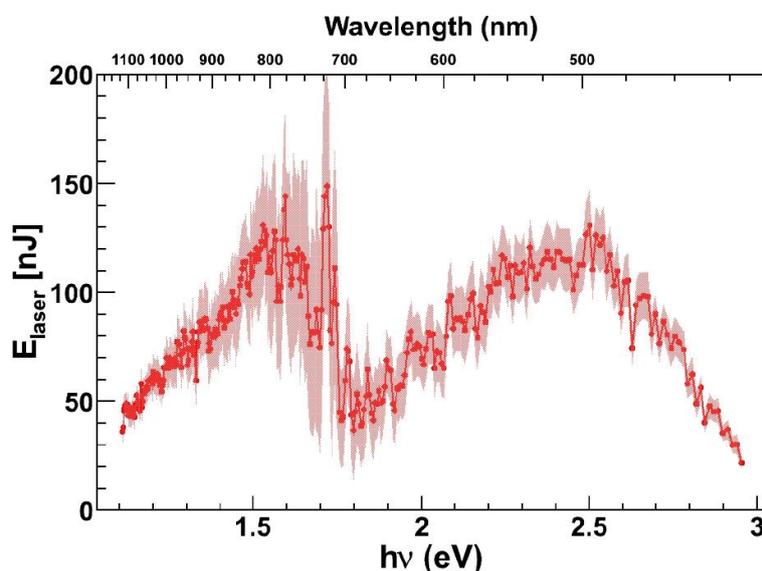
Figure S4. Laser pulse energy as a function of incident photon energy.
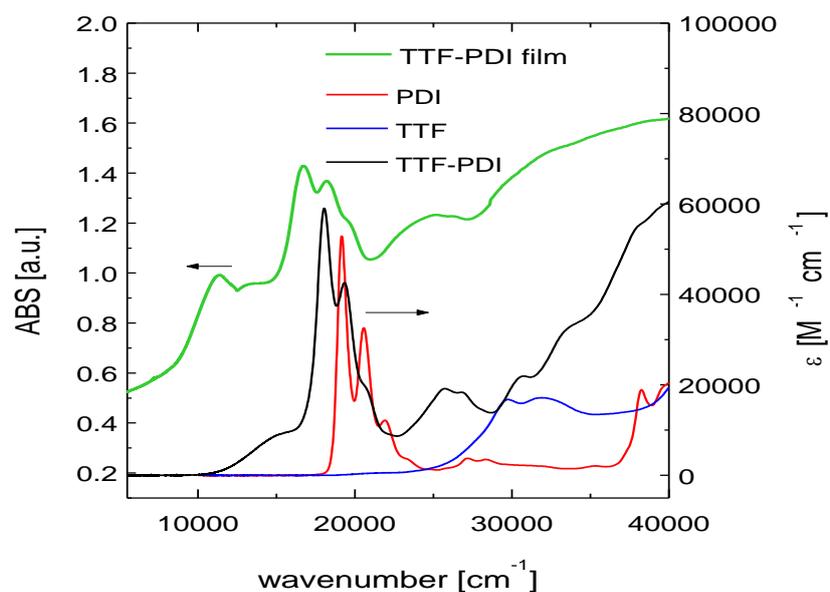
Figure S5. Electronic absorption spectra measured for: TTF-PDI film on top of a quartz slide (green), PDI in solution (red), TTF in solution (blue) and TTF-PDI in solution (black). All solutions were done in CH_2Cl_2 with a concentration of 2×10^{-5} M at room temperature.
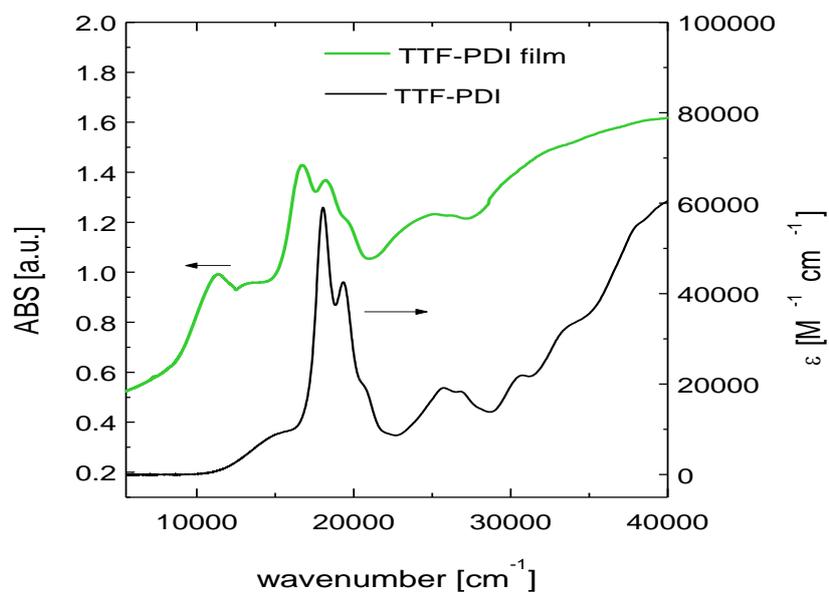
a)

Figure S6. Electronic absorption spectra measured for: TTF-PDI film on top of a quartz slide (green), TTF-PDI in CH_2Cl_2 with a concentration of 2×10^{-5} M at room temperature.

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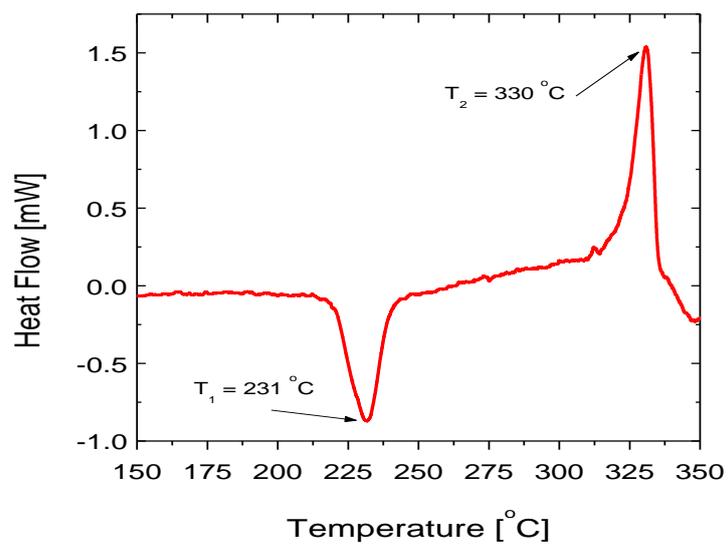
Figure S7. Differential Scanning Calorimeter (DSC) analysis of 3.6 mg TTF-PDI heating at a rate of 10 $^{\circ}$C/min.

References:

[1]   M. Jaggi, C. Blum, N. Dupont, J. Grilj, S.-X. Liu, J. Hauser, S. Decurtins, *Org. Lett.* **2009**, *11*, 3096.