Supplemental Material

Mobility relaxation and electron trapping in a donor/acceptor-type copolymer

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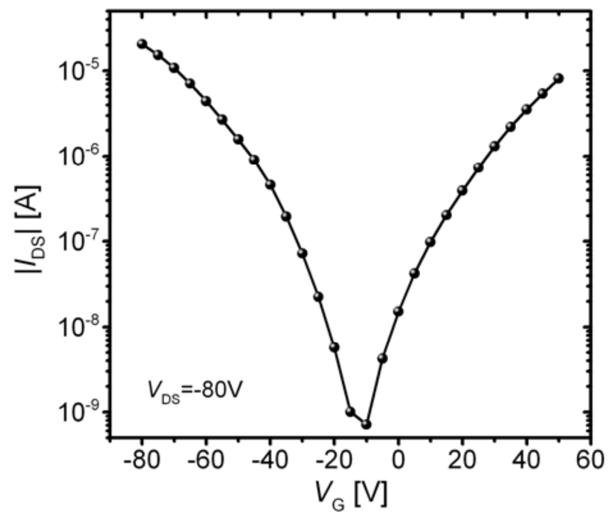
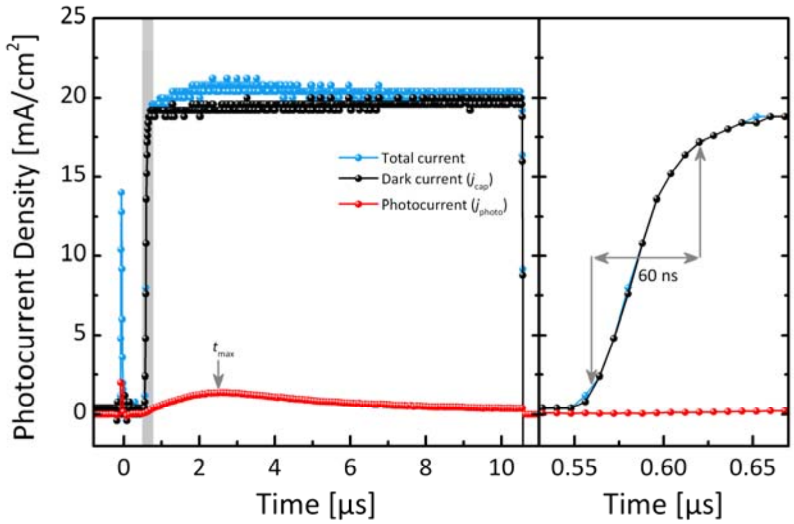
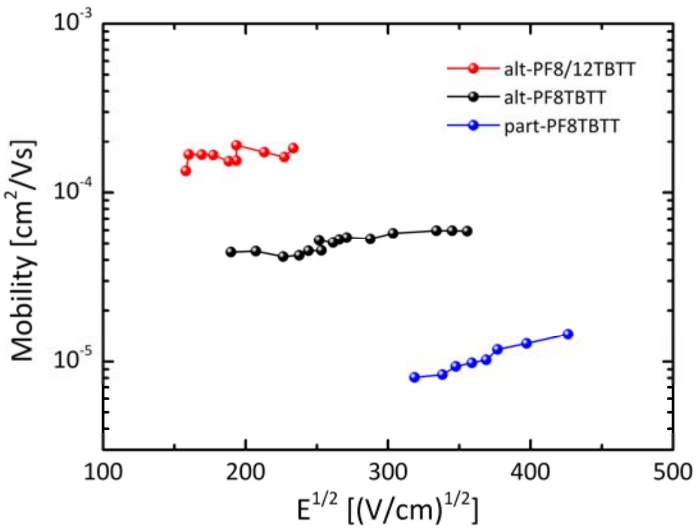


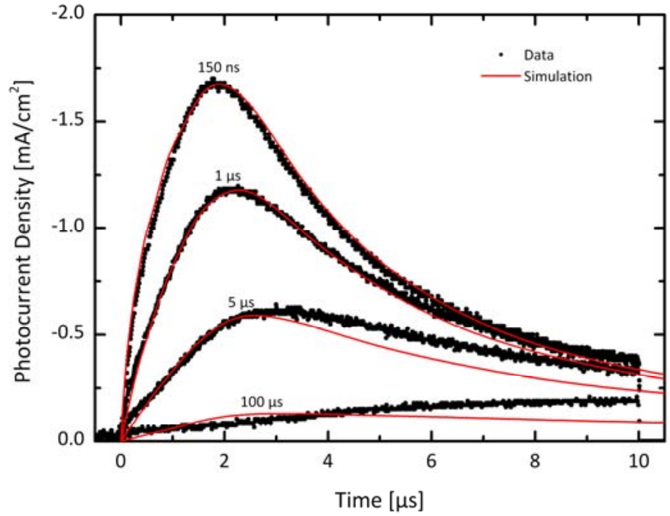
S1. Transfer characteristic of a alt-PF8TBTT bottom gate field effect transistor at a source-drain voltage of -80 V. Thermally grown and HMDS treated SiO_2 on top of a Si substrate served as the gate dielectric, while 100 nm gold was used for the source and drain electrode. It has been shown that n-type transport in bottom-gate OFET structures can be realized for a wide variety of conjugated polymers if the surface of the widely used SiO_2 gate dielectric, which contains a high number of intrinsic electron traps, is treated in a proper way.[37] As the measurements of Inganäs and co-workers were carried out on bare SiO_2,[26, 43] electron transport along the semiconductor/insulator interface might have been disturbed by these traps. We note that the electron mobility may be even higher with optimized gate dielectrics.



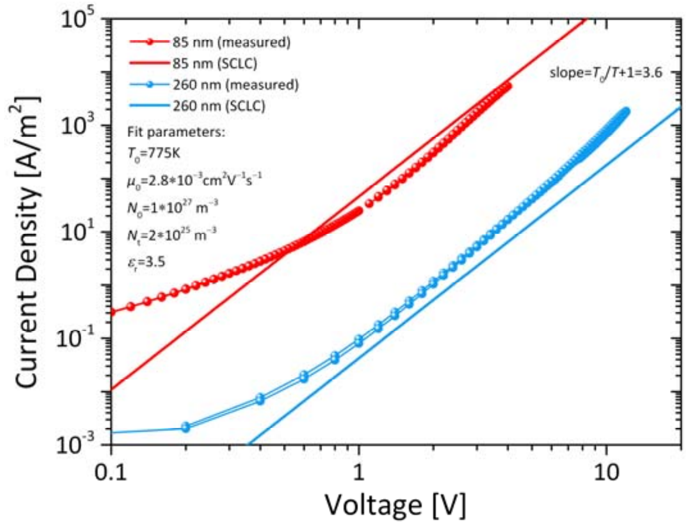
S2. (left) Typical Photo-CELIV transients in the dark (black) and 550 ns after illumination (blue) with a 6 ns laser pulse. The difference between total and dark current is denoted as photocurrent (red). The arrival of the laser pulse at t=0 is visible but no current is flowing during the delay time which demonstrates the accurate setting of the built in voltage. The rectangular shape of the capacitive loading current also demonstrates that injection of charge carriers is negligible even at very high extraction voltages. (right) Zoom into the beginning of the voltage pulse (gray area in the left figure). Time to go from 10% to 90% of the capacitive current is approximately 60 ns, while fastest observed t_{max} is about 1.8 µs. The low resolution of the dark and total current originates from data processing. The oscilloscope digitizes the signals with 8 bit vertical resolution for the full display scale. Further internal calculations such as averaging and subtraction of traces are performed with 12 bit resolution. In order to improve data quality, first the dark current gets measured several times and averaged internally. After that the light current (total current) is measured and the photocurrent is calculated by subtracting the averaged dark current from the light transients. The photocurrent is then displayed at screen filling vertical resolution before transfer (at 8 bit resolution). Effectively, the photocurrent gets digitized at a much higher resolution, thus it shows markedly less conversion artefacts compared to the raw light and dark transients.



S3. Field-dependence of the electron mobility for the three copolymers investigated here, determined with Photo-CELIV. The devices were the same as described in the main text and measurements were performed with a short delay time of 0.5 µs. A weak field-dependence is observed only for part-PF8TBTT.



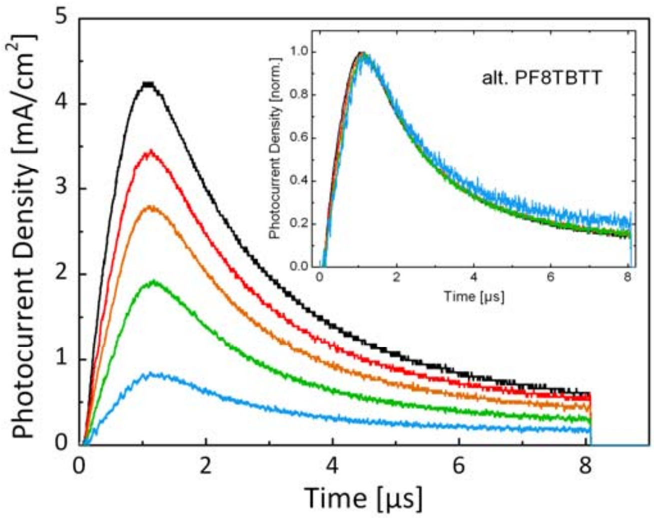
S4. Experimental Photo-CELIV transients of the 170 nm thick alt-PF8TBTT device as displayed in Fig. 2, Fig. 4 and Fig.6 of the main text. Here, the simulation was performed without field-dependent detrapping, while all trapping parameters were identical to those used in the simulation presented in Fig. 4 of the main text. Only the free carrier mobility was slightly varied ($2.5 \cdot 10^{-3}$ $cm^2 V^{-1} s^{-1}$). It is obvious that detrapping of charge carriers is of crucial importance to describe the transients after a long delay time and at the end of the extraction pulse, and that this detrapping must be field-assisted.



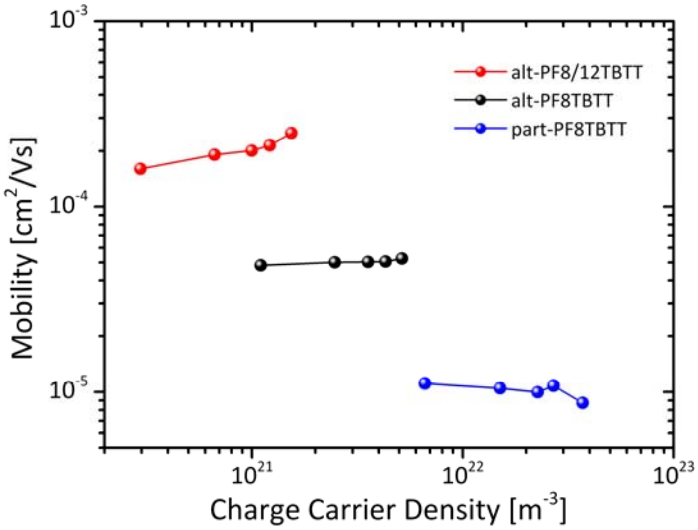
S5. Electron-only currents as function of applied voltage (red and blue spheres). The structure of the single carrier devices was ITO/PEDOT/Al/alt-PF8TBTT/Sm/Al. Injection was from the samarium (Sm) top-electrode, while the aluminium (Al) bottom-contact served as hole-blocking contact. Solid lines correspond to solutions of Eq. 1 with the parameters indicated in the graph. Space charge limited conductance in the presence of an exponential trap state distribution has been treated by Mark and Hellfrich and was experimentally observed for a variety of conjugated polymers. Within this model, the current is given by:[55]

$$J = eN_0\mu_0\left(\frac{l}{l+1}\frac{\varepsilon_0\varepsilon_r}{eN_\mathrm{t}}\right)^l\left(\frac{2l+1}{l+1}\right)^{l+1}\frac{V^{l+1}}{d^{2l+1}} \qquad \left(l = T_0/T\right), \tag{1}$$

where V is the applied voltage, ε_0 the permittivity of free space and ε_r the dielectric constant. The other parameters have the same meaning as described above. Despite small deviations between the model and the measured current, the current-voltage characteristics can be well described by Eq. 1, when similar parameters as for the simulation of the current transients were used. Especially, the slope of the current versus voltage, which only depends on the trap temperature (slope = $T_0/T+1$), is rather well reproduced by the value T_0 = 775K (corresponding to E_0 = 67 meV) derived from the transient experiments.



S6. Room temperature photo-CELIV transients at various excitation intensities measured for an alt-PF8TBTT CGL device. The capacitive loading current j_{cap} was subtracted to visualize photocurrents only. The inset shows normalized transients to demonstrate the intensity-independent shape of the photocurrents.



S7. Charge carrier density-dependence of the electron mobility for the three copolymers investigated here, extracted from intensity modulated Photo-CELIV experiments. Again, measurements were performed with a very short delay of 0.5 µs.

References

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