Supporting Information

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The Impact of Donor-Acceptor Phase Separation on the Charge Carrier Dynamics in pBTTT:PCBM Photovoltaic Blends

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Materials. pBTTT-C14 was provided by Martin Heeney and coworkers. The synthesis was described earlier in the literature.[1] $PC_{70}BM$ was used as received.

Sample preparation. For the preparation of solar cells ITO-coated glass substrates were patterned by wet etching and cleaned by successive ultrasonication in detergent, acetone then *iso*-propanol. Subsequently, the samples were treated with an argon plasma for 15 min prior to spin-coating of a ~40 nm thick poly(3,4-ethylene-dioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) layer. The substrates were transferred into a nitrogen-filled glovebox and heated to 120 °C for 30 min. For the active layer deposition, pBTTT-C14 and $PC_{70}BM$ were dissolved in 1,2-dichlorobenzene at a total concentration of 12.5 mg mL^{-1} in a 1:1 molar ratio (4:6 by weight) or at a total concentration of 25 mg mL^{-1} with a 1:4 ratio by weight. Solutions were stirred overnight at 60 °C. Samples were spun at 60 °C at 800 rpm for 45 s and then placed into a closed petri dish to dry slowly in a solvent rich atmosphere. After drying overnight, the 1:1 molar samples were annealed at 180 °C for 10 min. The 1:4 samples were not annealed. As a top-electrode, a bilayer of 7 nm calcium and 150 nm aluminum was evaporated through a shadow mask. Spectroscopic samples were fabricated in the same way except that quartz substrates were used and no top-electrode was evaporated.

Steady-State Spectroscopy. Steady state absorption spectra were measured with a Perkin Elmer Lambda 25 spectrometer. The layer thickness was determined with a Tencor P10 surface profilometer.

Transient Absorption Spectroscopy. Transient absorption (TA) measurements were performed with a home-built pump-probe setup. To measure in the time range of 1-4 ns with a resolution of ~100 fs, the output of a commercial titanium:sapphire amplifier (Coherent LIBRA-HE, 3.5 mJ, 1 kHz, 100 fs) was split into two beams that pumped two independent commercial optical parametric amplifiers (Coherent OPerA Solo). One optical parametric amplifier (OPA) was used to generate the tunable excitation pulses in the visible, while the second OPA was used to generate the pump beam for white-light generation. For measurements in the spectral range between 550-1100 nm a 1300 nm pump of a few μJ was focused into a c-cut 3 mm thick sapphire window for white-light generation. The variable delay of up to 4 ns between pump and probe was introduced by a broadband retroreflector mounted on a mechanical delay stage. Mostly reflective elements were used to guide the probe beam to the sample to minimize chirp. The excitation pulse was chopped at 500 Hz, while the white-light pulses were dispersed onto a linear silicon photodiode array, which was read out at 1 kHz by home-built electronics. Adjacent diode readings corresponding to the transmission of the sample after an excitation pulse and without an excitation pulse were used to calculate $\Delta T/T$.

For measurements in the time range between 1 ns to 1 ms with a resolution of ~1 ns, the excitation pulse was provided by an actively Q-switched Nd:YVO_4 laser (AOT Ltd. MOPA) at 532 nm. In this case the delay between pump and probe was controlled by an electronic delay generator (Stanford Research Systems DG535). TA measurements were performed at room temperature under a dynamic vacuum of $<10^{-5}$ mbar.

For TA measurements in the NIR spectral range covering 1100-2000 nm a 2100 nm pump was used to generate white-light in an yttrium vanadate window. Furthermore, a dichroic mirror was used to separate the residual pump beam (idler of the OPA at 2100 nm) from the broadband NIR supercontinuum. The NIR pulses were dispersed onto a Peltier-cooled 512 pixel long linear extended InGaAs array (Entwicklungsbüro Stresing) and read out as described above.

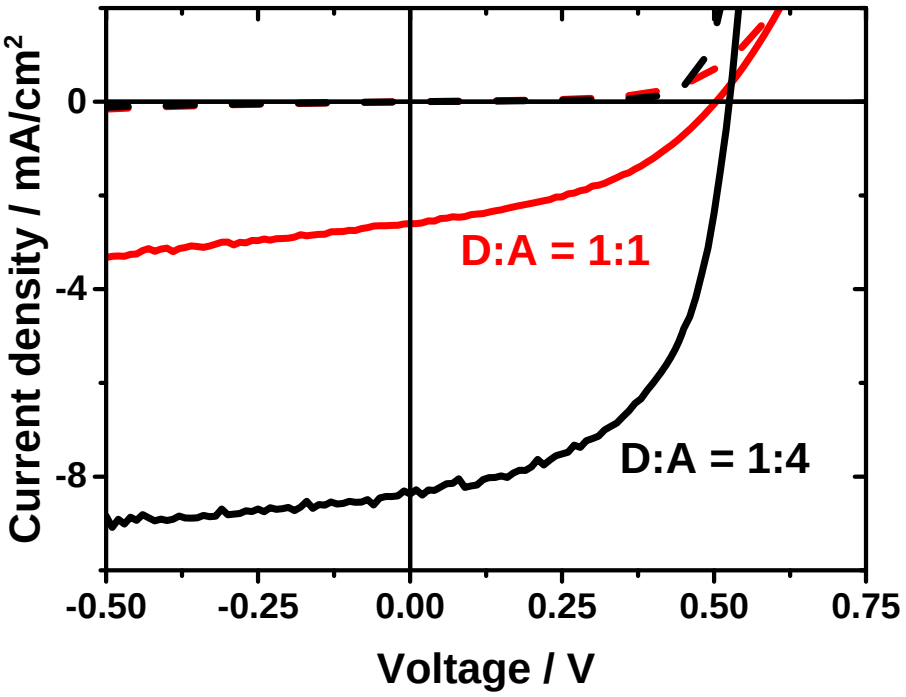
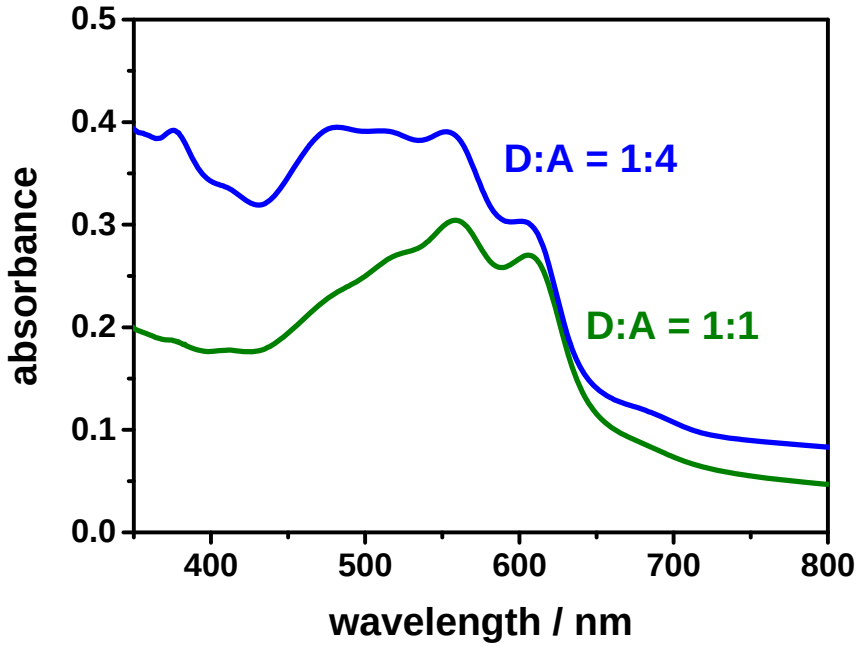
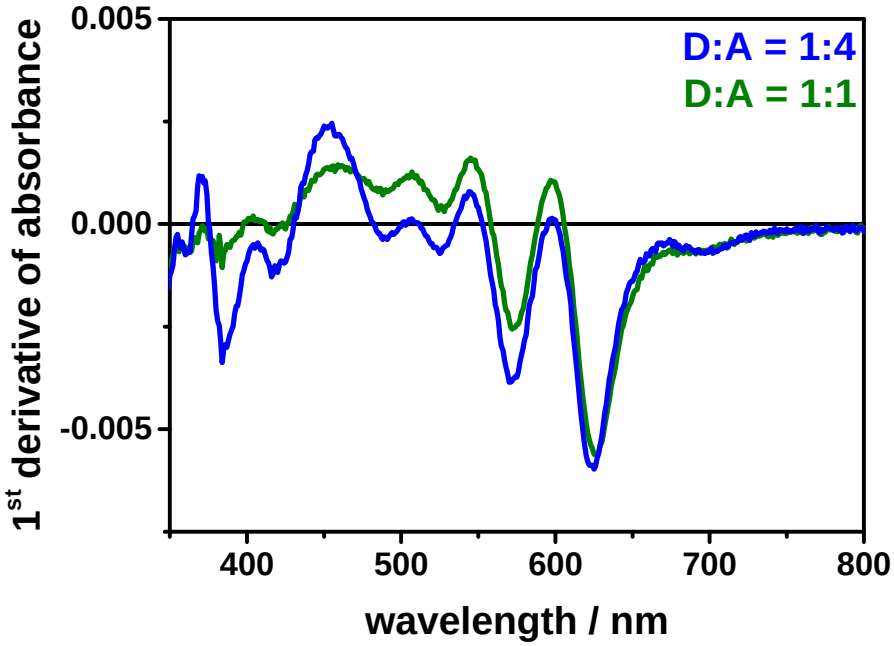


Figure S1. Current-Voltage (J-V) characteristics of pBTTT:$PC_{70}BM$ solar cells at a donor-acceptor ratio of 1:1 (solid red line) and 1:4 (solid black line) and respective dark currents (dashed lines).

a)


absorbance
0.5
0.4
0.3
0.2
0.1
0.0
400
500
600
700
800
wavelength / nm
D:A = 1:4
D:A = 1:1

b)


1st derivative of absorbance
0.005
0.000
-0.005
400
500
600
700
800
wavelength / nm
D:A = 1:4
D:A = 1:1

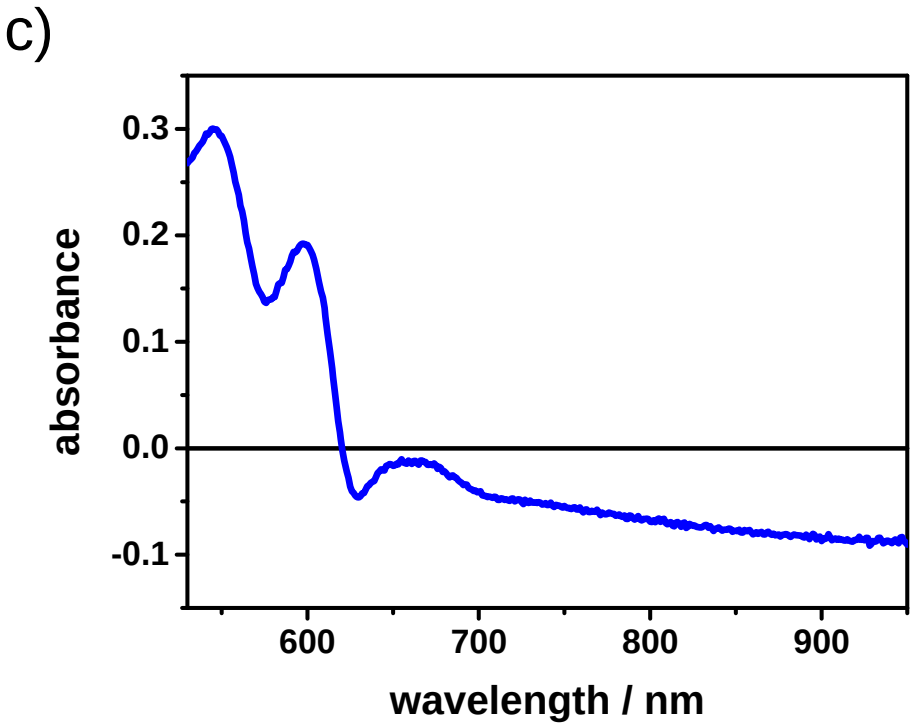


*Figure S2***.** (a) Thin film absorption of pBTTT:$PC_{70}BM$ at a donor-acceptor ratio of 1:1 (green line) and 1:4 (blue line). (b) First derivative of the absorption of a 1:1 (green line) and 1:4 (blue line) blend of pBTTT:$PC_{70}BM$. This signal is equivalent to the electro-absorption. (c) Superposition of the ground state absorption spectrum of a pBTTT:$PC_{70}BM$ (1:4) blend and the first derivative of the absorption spectrum plus a Gaussian-shape photoinduced absorption profile the former accounting for the electroabsorption (EA) and the latter for the photo-induced absorption of charges, respectively.

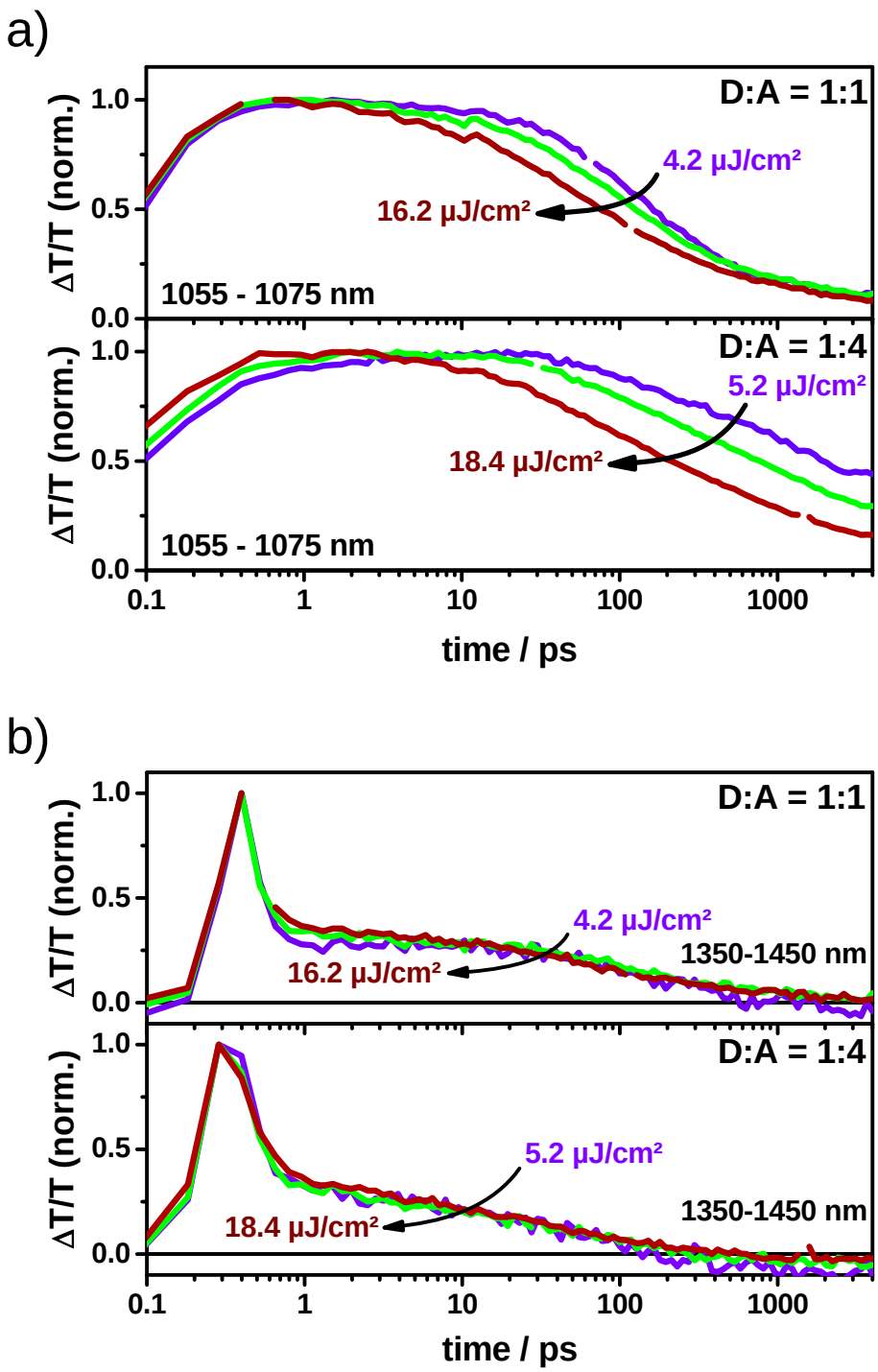


Figure S3. (a) Intensity-dependence of the dynamics of the charge-induced absorption in the spectral range from 1055-1075 nm of a pBTTT:$PC_{70}BM$ blend at ratios of 1:1 (upper panel) and 1:4 (lower panel). (b) Dynamics tracked between 1350-1450 nm, that is the spectral range, in which the pBTTT exciton-induced and charge-induced absorption occur. Note the fast sub-ps signal decay indicating ultrafast polymer exciton dissociation in both blends.

[1] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.***2006**, *5*, 328.