Supporting Information for

Barrier-Less Slow Dissociation of Photogenerated Charge Pairs in High-Performance Polymer-Fullerene Solar Cells

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Transient absorption kinetics with different excitation wavelengths

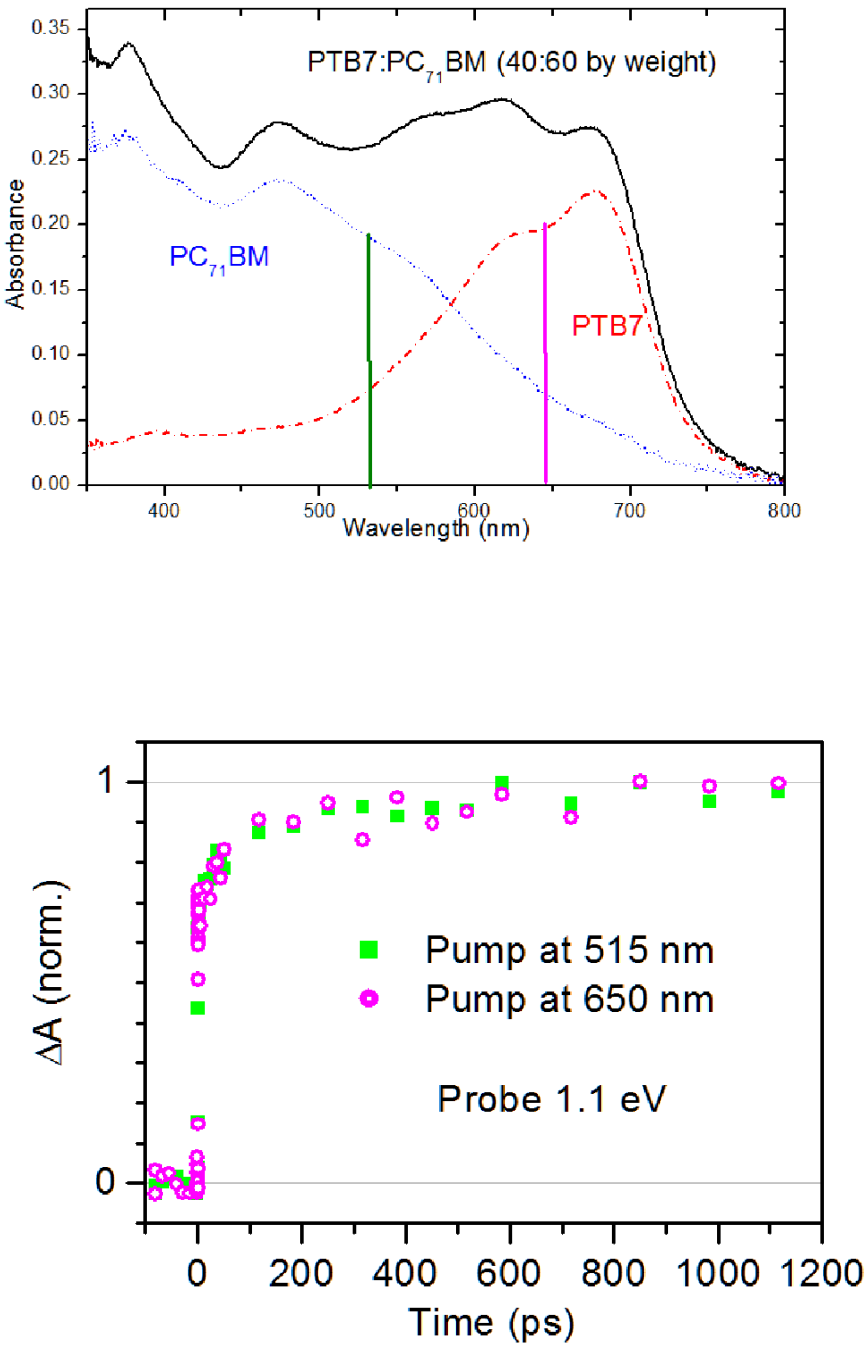

Figure S1. (Top) Absorption spectrum of the optimized blend with the 1:1.5 ratio of PTB7 and $PC_{71}BM$ by weight and contributions from each material. Solid vertical lines indicate the excitation wavelengths used in TA measurements. (Bottom) Normalized transient absorption kinetics at 1.1 eV after excitation with different wavelengths but with similar excitation densities.

Time-resolved fluorescence

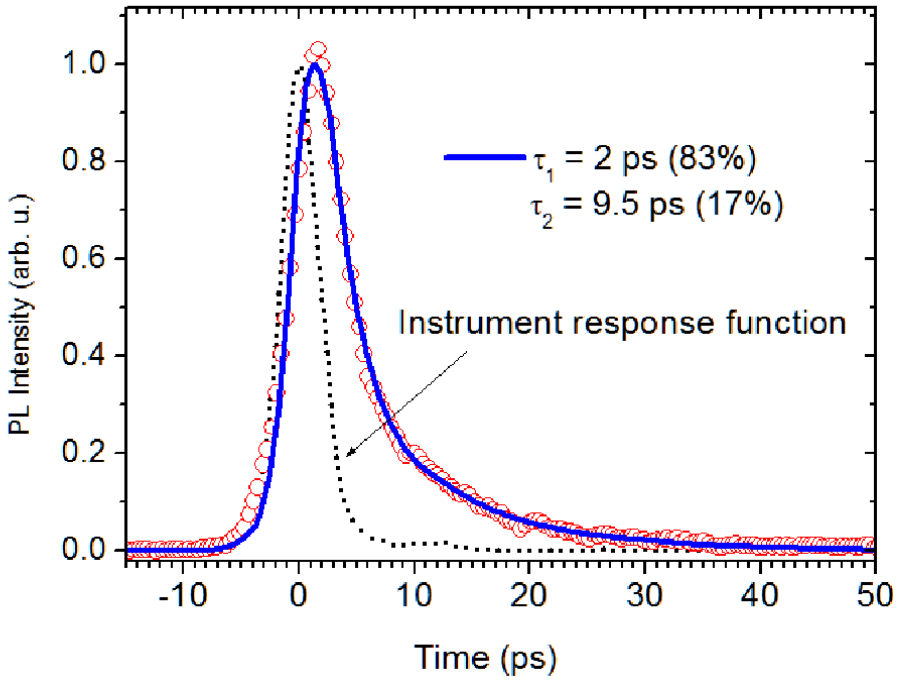

Figure S2. Fluorescence decay in the optimized blend measured in the detection window of 730-880 nm with a Hamamatsu synchroscan streak camera C10910-05 with S-20ER photocathode. The excitation is at 660 nm with 180 fs pulses at 5 kHz repetition rate. The solid line is a fit to the two-exponential decay function with given time constants and amplitudes. The 2 ps decay component is limited by the response time of the streak camera.

Transient absorption set-up

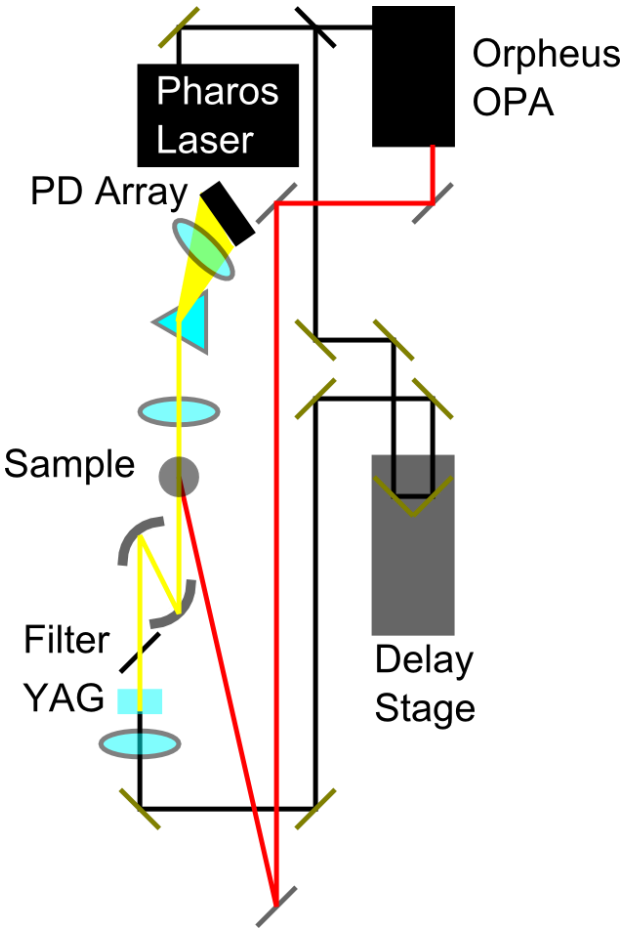

Figure S3. Schematic of transient absorption setup. Excitation was by 180 fs light pulses from an optical parametric amplifier (from Light Conversion) at 2.5 kHz. Optically delayed pulses of white light continuum generated in YAG crystal are used for the probe. The probe light was optically filtered to make a smooth spectral profile, dispersed by a prism after the sample and detected with a photodiode array. The sample was kept in vacuum during measurements and the excitation energy density was 0.5 μJcm^{-2}.

Set-up to measure ultrafast carrier drift

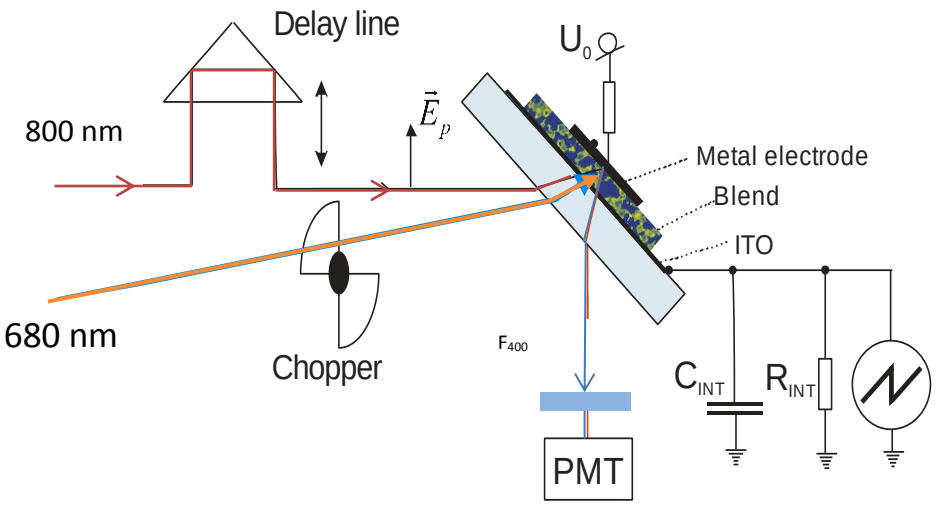

Figure S4. Schematic of the TREFISH setup. A p-polarized probe light pulsed at 1 kHz and 800 nm is shone on a cell at ~45° incidence angle. An applied electric field *F* polarizes the blend and induces optical anisotropy for incident p-polarized light so that the second harmonic of the probe light (SH) is generated and detected by a photomultiplier. Its intensity is proportional to F^2. Pump pulses at 680 nm wavelength are generated by an optical parametric amplifier and chopped at 500 Hz. They overlap spatially with the probe and generate charge pairs which drift in response to electric field and so they screen it. The field screening is found by taking a ratio of SH intensities with and without pump pulse. The time delay between pump and probe pulses is varied by an optical delay line.

EFISH signal dependence on the total electric field and time

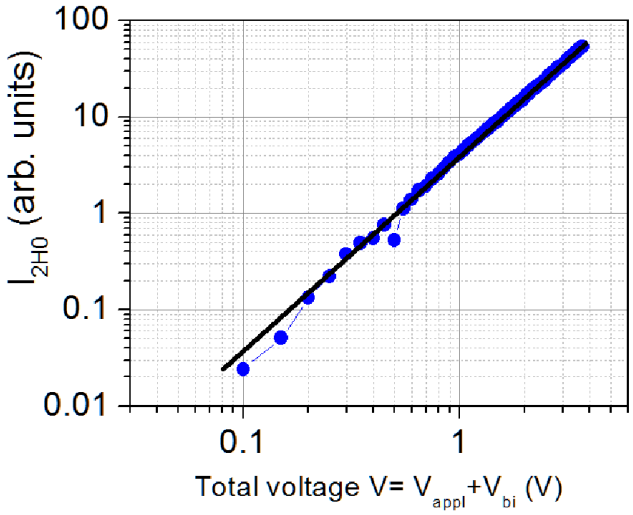

Figure S5. The intensity of the second harmonic in the dark as a function of the total voltage which is a sum of the applied external voltage and the built-in voltage. Solid line represent a function $I_{2H0} = aV^2$ where a is constant.

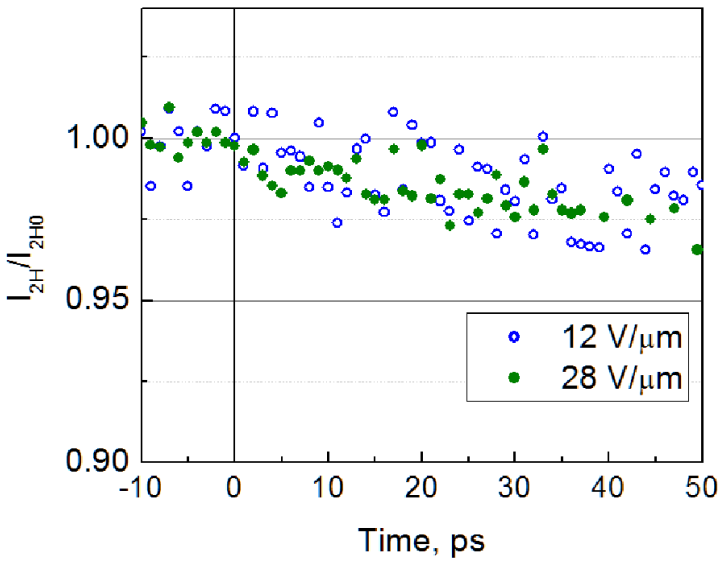

Figure S6. The ratio of the second harmonic intensity with excitation pulse I_{SH} and without excitation I_{SH0} on a short time scale for different values of the total electric field.