

SUPPORTING INFORMATION

Impact of Structural Polymorphs on Charge Collection and Non-Geminate Recombination in Organic Photovoltaic Devices

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Methods

Materials: All materials in this study were commercially available and used as purchased without any further purifications. PCBM[60] was purchased from Solenne BV. Both batches of high- M_n P3HT (batch EE101702) and low- M_n P3HT (batch EE97802) were purchased from Merck.

Film preparation: Two types of photoactive layers were prepared based on P3HT:PCBM[60] composites (1:1) with different molecular weight of P3HT. The films were developed by spin-coating of the corresponding P3HT:PCBM[60] solutions, as prepared in chlorobenzene solvent with a concentration of 13 mg/mL in respect to P3HT mass. Thin films of high and low M_n -based P3HT:PCBM[60] were deposited onto solvent cleaned Quartz (Spectrosil 2000, UQG Ltd) or glass/ITO/PEDOT:PSS substrates. Thermal annealing of the films was at 140°C for 15'. A KLA Tencor P-6 profilometer was used for determining the film thickness of the high M_n -based and the low M_n -based P3HT:PCBM[60] blend films to be 89 nm and 92 nm respectively.

Device fabrication and characterization: Solar cell devices were fabricated on commercially available indium tin oxide (ITO) substrates (sheet resistance $\sim 15 \Omega/\text{square}$). The ITO substrates were thoroughly cleaned by subsequent ultrasonication in acetone and in isopropanol baths, for 15 minutes each. Then they were ultrasonically cleaned with Hellmanex III surfactant to remove contaminants and residues from the ITO surface. The surfactant was washed away by deionised water, and the substrates were once more cleaned by subsequent ultrasonication in acetone and in isopropanol baths for 15 minutes each. A film of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) was spun over the ITO substrate after 20 minutes of UV-Ozone treatment. Glass/ITO/PEDOT:PSS electrodes were annealed at 140°C for 30 minutes, and then were inserted in a N_2 -filled glove box for completing the deposition

of the P3HT:PCBM[60] layers by spin-coating. A metallic Ca/Al electrode was deposited on the P3HT:PCBM[60] layers by thermal evaporation in vacuum (1×10^{-6} mbar), thereby yielding complete OPV devices with the glass/ITO/PEDOT:PSS/P3HT:PCBM[60]/Ca (5 nm)/Al (100 nm) configuration. The evaporation mask used enabled a device active area of 0.1 cm^2 . The obtained OPV devices were tested electrically by means of current density-voltage (J-V) under simulated solar illumination. A computer-controlled Keithley 2400 source-measure unit was employed for registering the device J-V metrics. During the voltage scans, an Oriel Sol3A (class AAA) solar simulator was used for illuminating the devices with the simulated Air Mass 1.5 Global (AM 1.5G) irradiance. The incident illumination intensity was 1 Sun as verified by using a silicon reference cell (spectral mismatch factor ~ 0.99). On the basis of the obtained J-V characteristics, the PCE parameter of the devices was determined. For each system studied, 4 – 5 devices were characterized in order to confirm the reproducibility of the obtained results.

Raman spectroscopy with 488 nm photoexcitation: An InVia Raman microscope (Renishaw plc) incorporating Argon-ion laser source (Modu-Laser 150) for 488 nm excitation was used to acquire Raman spectra of the samples in a backscattering configuration by in-built CCD detector. Thin films of high and low M_n -based P3HT:PCBM[60] were deposited onto solvent cleaned Quartz (Spectrosil 2000, UQG Ltd) or glass/ITO/PEDOT:PSS substrates. Rayleigh filter and gratings' calibration was performed against well-defined Si-reference peak at 520 cm^{-1} . Samples were measured inside Linkam stage (THMS600) under N_2 purging and low power (defocused laser, $<0.2 \text{ mW}$) to avoid photo-oxidation/degradation. Spectra of 4 different positions of each sample was taken to ensure spectrum reliability whilst peak-position and full width half maximum (FWHM) errors were estimated via instrumental resolution.

Raman spectroscopy with 473 nm photoexcitation: a CW diode laser (Ultralasers, 50 mW OEM DPSS Laser) was used for photoexciting the samples and measurements were conducted under vacuum, employing low excitation powers ($<0.8\text{ mW}$) to avoid photodegradation. Sample cooling (down to 50 K) was achieved by a sample-in-vacuum closed-cycle cryostat (CCS-150, JANIS), where the samples were placed on a copper cold finger. The Raman scattered light was collected in a 135° backscattering geometry and delivered to a 0.75 m focal-length Czerny–Turner spectrograph (SpectraPro, SP2760i, Princeton Instruments), equipped with a 1200-grooves/mm UV-enhanced holographic grating. The slit width was set to $100\text{ }\mu\text{m}$ providing for 5 cm^{-1} spectral resolution. The scattered light was detected by a LN_2 -cooled 2048×512 pixel, back-illuminated UV-enhanced CCD detector (Spec10:2 KBUV/LN, Princeton Instruments). Cyclohexane was employed for frequency calibration of the spectra.

Atomic force microscopy imaging: AFM measurements were performed in an intermittent contact regime using an NT-MDT Ntegra Prima scanning probe microscope. The NSG10 probe with a nominal tip radius of 6 nm and cantilever stiffness of 11.8 N/m was used in all experiments. $5 \times 5\text{ }\mu\text{m}$, $500 \times 500\text{ nm}$ and $100 \times 100\text{ nm}$ images were collected at a scanning speed of 1 Hz and a resolution of 512 points per scan line for 512 lines. The data was subsequently subjected to levelling using polynomial quadratic equation such as to exclude any background tilt and compensate for any curvature effects. Images were subsequently software analysed using the open source Gwydion platform [D. Nečas and P. Klapetek, Open Physics, 10, 181, 2012] such as to extract the height frequencies of the collected images, a measure of material clustering at the nanoscale.

Time-delayed collection field characterization: Our custom-built TDCF setup uses the second harmonic (532 nm) of an actively Q-switched sub-ns Nd:YVO₄ laser (INNOLAS piccolo AOT)

operating at 5 kHz as excitation. To minimize the RC response time, a small device area of 1 mm² is used. The samples were measured under dynamic vacuum conditions to avoid any degradation. A Keysight S1160A functional generator was used to provide the pre-bias and extraction bias, while a Keysight four channel digital oscilloscope was used to measure the current response of the device.

Transient absorption spectroscopy: The TA spectra were acquired using a home-built setup comprised of a Coherent Legend Duo regenerative amplifier delivering 100 fs pulses of 4.2 mJ at 3 kHz repetition rate at a central wavelength of 800 nm. The fundamental output from the oscillator was decomposed into two beams and applied to a couple of TOPAS prime, an optical parametric amplifier, in order to generate the broad spectral tunability. TOPAS 1 served as the excitation pulse beam and was routed through a retroreflector mounted on a mechanical delay stage, passing twice to obtain a delay line of approximately 10 ns and was focused onto the sample. In parallel to this, a white light continuum was generated by pumping a sapphire crystal with 1300 nm from the second TOPAS. The delayed white light acted as probe beam and was focused on the sample so a spatial overlap between the pump and probe beam was obtained. The transmitted light through the sample was collected, collimated and focused onto a detector, and consequently further processed on a computer to record the acquired transient spectra and the associated charge carrier dynamics. Long delay measurements, in the μ s time range were also performed, by employing the electronic delay provided by a delay generator (Stanford Research Systems DG535) to cover a range of 300 μ s and by using a Q-switched Nd:YVO₄ Innolas piccolo AOT sub nano second amplifier, frequency doubled, with an output of 532 nm. The actual excitation was executed at 532 nm for both the long and short delay. Furthermore, the pump fluence was varied from 1.3, 3, 6, 9 and 19 μ J cm⁻² for the short delay measurements. For the latter the laser fluence varied between 0.8 – 12 μ J cm⁻² in order

to discriminate geminate and non-geminate charge recombination processes. All measurements were performed at room temperature and the samples were kept under dynamic vacuum with pressure lower than 10^{-4} mbar.

Raman spectroscopy

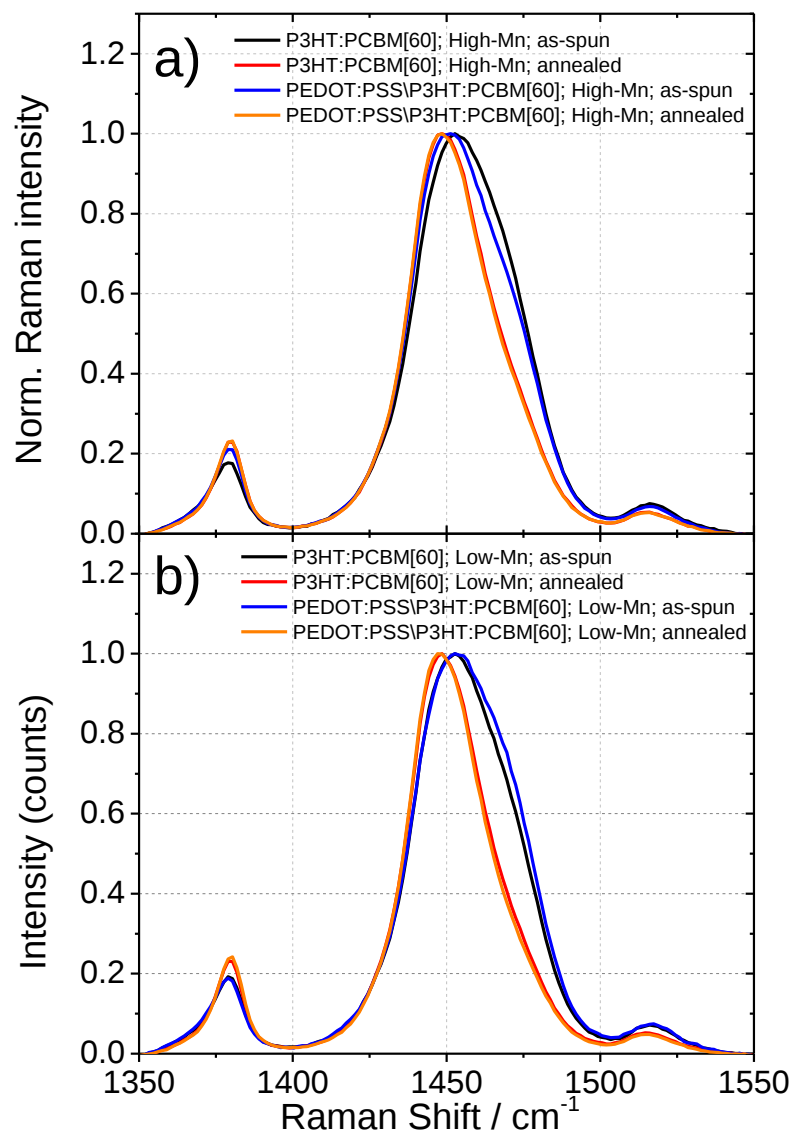


Figure S1: Room temperature resonance Raman spectra of as-spun and annealed P3HT:PCBM[60] blend films after photoexcitation at 488 nm, deposited on plain quartz and glass/ITO/PEDOT:PSS substrates. Films were prepared based on a) on high- M_n P3HT and b) on low- M_n P3HT.

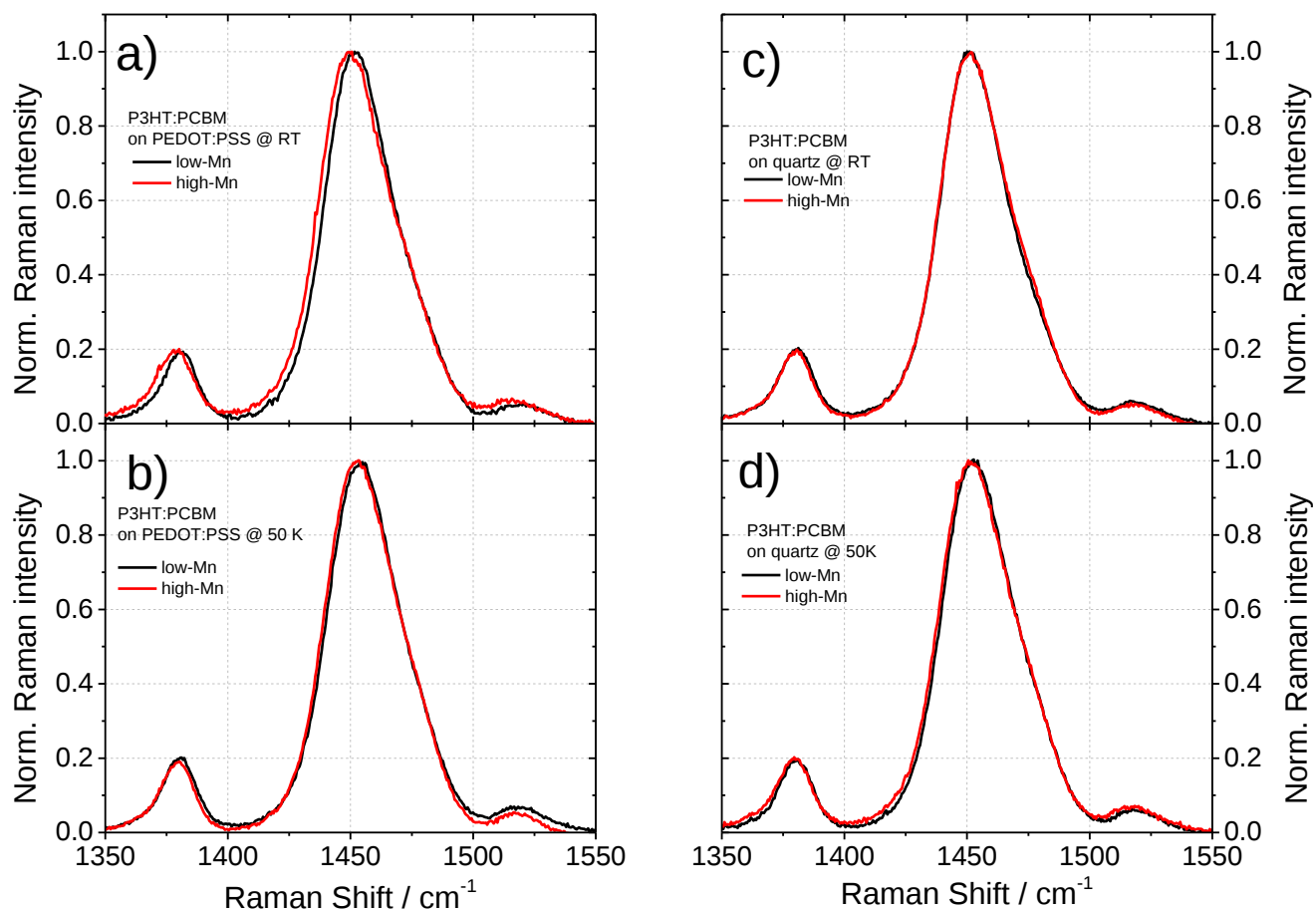


Figure S2: Resonance Raman spectra of semi-complete P3HT:PCBM[60] devices with thermally annealed P3HT:PCBM[60] photoactive layers developed by low- and high- M_n P3HT and acquired at a) room temperature and b) at 50 K. Resonance Raman spectra of thermally annealed P3HT:PCBM[60] films deposited on plain quartz substrates developed by low- and high- M_n P3HT and acquired at c) room temperature and d) at 50 K. In all cases photoexcitation was at 473 nm.

System	Room temperature		50 K	
	C=C centre (cm ⁻¹)	C=C FWHM (cm ⁻¹)	C=C centre (cm ⁻¹)	C=C FWHM (cm ⁻¹)
Annealed high-M _n , quartz	1451.4 ± 0.7	34 ± 1	1451.5 ± 0.7	37 ± 1
Annealed low-M _n , quartz	1451.0 ± 0.7	33 ± 1	1452.4 ± 0.7	36 ± 1
Annealed high-M _n , PEDOT:PSS	1449.5 ± 0.7	35 ± 1	1453.0 ± 0.7	36 ± 1
Annealed low-M _n , PEDOT:PSS	1451.7 ± 0.7	33 ± 1	1454.5 ± 0.7	34 ± 1

Table S1: Overview of the room temperature and low temperature (50 K) Raman results obtained for the annealed P3HT:PCBM[60] films (see Figure S2), after photoexcitation at 473 nm.

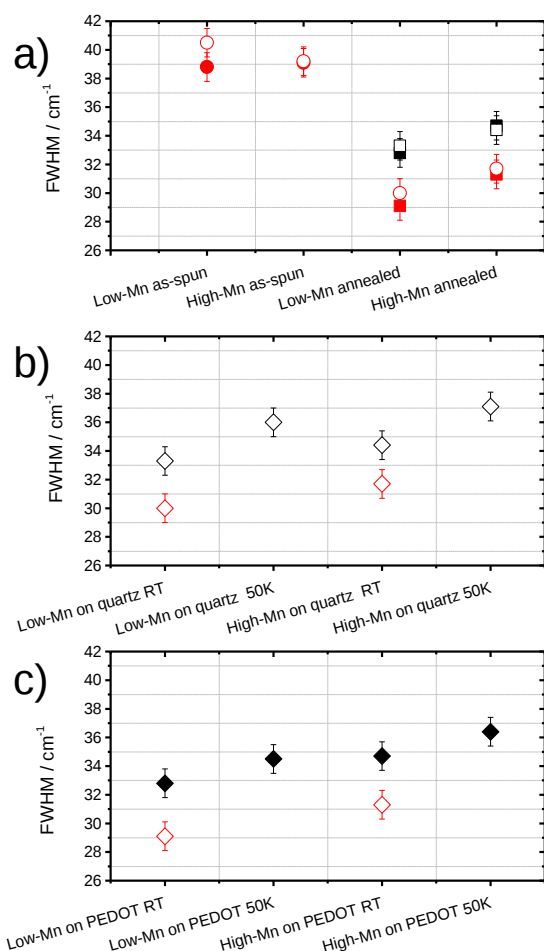


Figure S3: a) Comparative results for the width (FWHM) of the Raman peak that corresponds to the C=C vibrational mode of the thiophene ring in P3HT as obtained a) for the low-M_n and the high-M_n P3HT-based P3HT:PCBM[60] films in their as-spun (circles) and annealed (squares) state, deposited on plain quartz (open symbols) and on glass/ITO/PEDOT:PSS (filled symbol) substrates, after photoexcitation at 473 nm (black-coloured symbol) and 488 nm (red-coloured symbol) at room temperature b) for the low-M_n and the high-M_n P3HT-based P3HT:PCBM[60] annealed films deposited on plain quartz substrates, after photoexcitation at 473 nm (open black diamonds) and 488 nm (open red diamonds) at room temperature (RT) and at 50 K. c) for the low-M_n and the high-M_n P3HT-based P3HT:PCBM[60] annealed films deposited on glass/ITO/PEDOT:PSS substrates, after photoexcitation at 473 nm (filled black diamonds) and 488 nm (open red diamonds) at room temperature (RT) and at 50 K.

Time-delayed-collection field electrical characterization

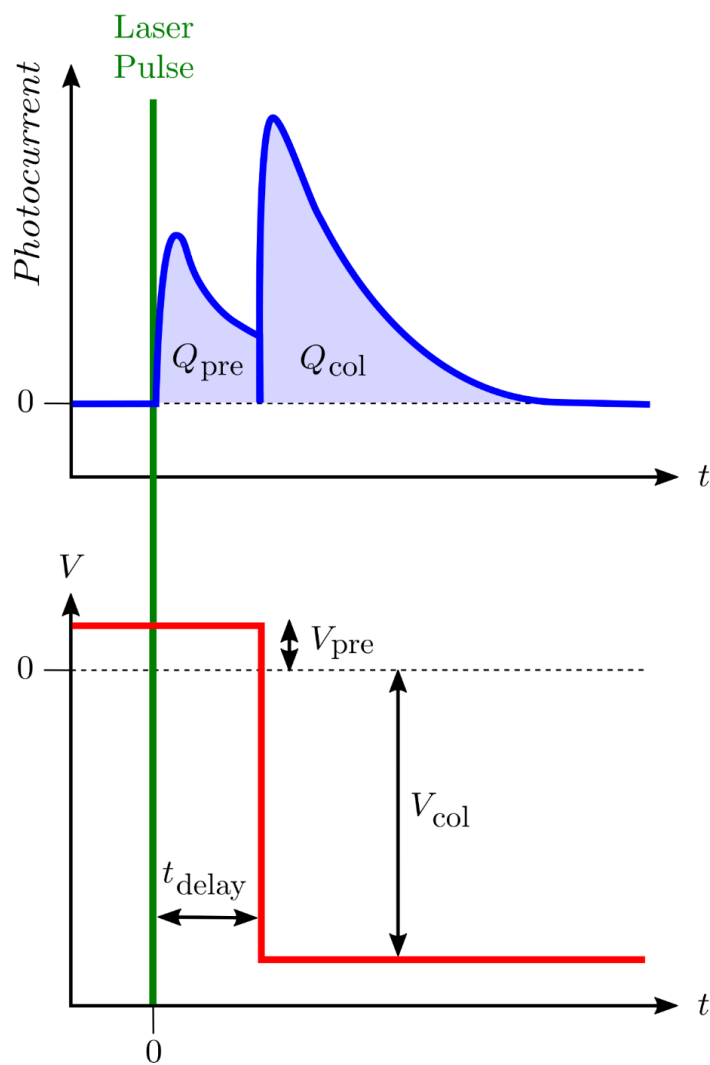


Figure S4: Schematic of the time-delayed-collection field experiment: photocurrent transients, the delay time, and the applied voltage

Transient absorption kinetics at the isosbestic point

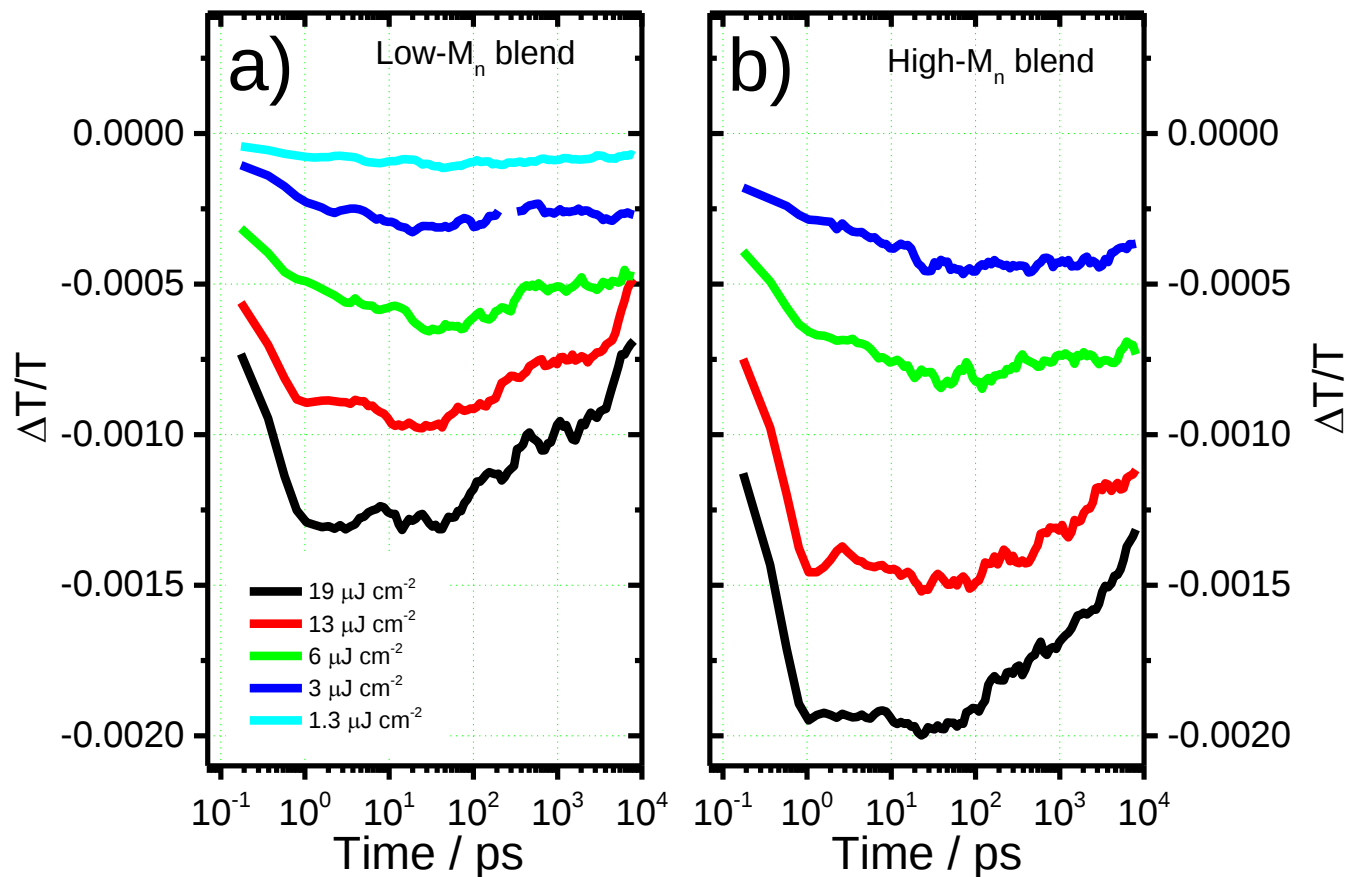


Figure S5: Fluence-dependent charge carrier dynamics at the isosbestic point as measured for annealed P3HT:PCBM[60] blend films prepared by the a) low- M_n P3HT batch and the b) high- M_n P3HT batch. The signature of monomolecular recombination is instant at $1.3 \mu\text{J cm}^{-2}$, whilst at higher fluences the bimolecular recombination is predominant. An annihilation process attributed to exciton-charge interactions is visible at early times.