Electronic Supplementary Information

Ultrafast Polaron-Pair Dynamics in a Poly(3-hexylthiophene-2,5-diyl) Device Influenced by a Static Electric Field: Insights into Electric-Field-Related Charge Loss

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IV Characteristics of P3HT Diode

Fig. S1 shows the current-voltage (I-V) characteristics of the P3HT device measured in both dark and light. An illumination with an air mass 1.5 sun spectrum which is equivalent to a power density of 100 mW cm⁻² was used for the measurement under light.



Fig. S1 IV-characteristics of P3HT device in dark and under illumination.

UV-Vis Absorption Spectroscopy

The UV-Vis absorption spectrum of the neat P3HT thin film has been taken in the spectral range 200 to 1100 nm using a UV-Vis absorption spectrometer (Lamda 12, PerkinElmer, USA).



Fig. S2 UV-Vis absorption spectrum of the neat P3HT thin film.

Transient Absorption of Neat P3HT Thin Film (Long-Time Behaviour)

Even for relatively long delay times (here, up to 300 ps) the very slow decay part of the transient can only be recognized as constant offset.



Fig. S3 shows the normalized differential transmission measured at 650 nm in a neat P3HT thin film with 24 μ J/cm² initial pump excitation at 520 nm. The transient has been taken averaging just three loops.

Anisotropy Measurement for Neat P3HT Film and P3HT Device in Presence of an External Electric Field

Table S1 Anisotropy values r(t) calculated for t = 0 ps for the P3HT diode in presence of different external electric fields at an excitation fluence of 24 μ J/cm².

Compare to panels of Fig. 7	External Voltage	r(t) for $t = 0$ ps
(a)	Neat P3HT Thin film (No Field)	0.43 ± 0.01
(b)	0 V (built-in-potential present)	0.08 ± 0.01
(c)	-1 V (in reverse Bias)	0.08 ± 0.01
(d)	-2 V (in reverse Bias)	0.08 ± 0.01
(e)	0.8 V(in forward bias)	0.18 ± 0.01