Supporting Information for Materials Horizons article:

Hole delocalization as a driving force for charge pair dissociation in

organic photovoltaics

Andrew B. Matheson, Arvydas Ruseckas, Scott J. Pearson, Ifor D.W. Samuel

Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife, KY16 9SS, United Kingdom

1. Choice of excitation photon energy



Fig. S1. Ground state absorbance of two blended films with different donor: acceptor load ratios used in transient absorption measurements. Green arrows show the excitation photon energies which were selected to give similar absorbance and hence similar excitation density profiles and average excitation density of $\sim 2.6 \times 10^{17}$ cm⁻³ in both bends.

2. Charge pair generation



Fig. S2. Fluorescence decay in the PTB7:PC₇₁BM blends with different polymer content measured by a streak camera after excitation with 180 fs pulses at 5 kHz repetition rate with given photon energies. The initial decay in \sim 3 ps is resolution-limited with a small component extending to 20 and 40 ps in the 40:60 and 90:10 blends, respectively. They are significantly faster than the decay observed in neat PTB7 films which showed about 200 ps lifetime implying that the majority of primary singlet excitons split into charge pairs within 3 ps in both blends.

3. Discussion on possible triplet state contribution



Fig. S3. TA spectra at different times and a composite spectrum constructed from the 3 ps spectrum assuming that the 30% rise of the signal at 1.1 eV comes from formation of PTB7 triplet excitons. The measured spectrum of the optimized blend at 1 ns shows a narrower peak compared to the composite spectrum and also there is a 0.03 eV difference in the peak position indicating that the observed red-shift is incompatible with recombination to the triplet state.



Fig. S4. TA kinetics of the optimized blend at 1.1 eV measured with different excitation densities. The rise time of the induced absorption at 1.1 eV does not change when the excitation density is decreased by a factor of three. This allows us to rule out non-geminate recombination to the triplet state which would show an excitation density dependence.

4. Comparison of blends prepared with DIO and without



Fig. S5. Transient absorption spectra of PTB7: $PC_{71}BM$ blends prepared (a) with DIO and (b) without DIO at selected time delays. Ground state absorbance (G.S.A.) spectra are also shown. c) Kinetics at 1.1 eV (filled circles) and 1.7 eV (open circles) for blends prepared with (black) and without DIO (green).