Electronic Supplementary Material (ESI) for Chemical Science
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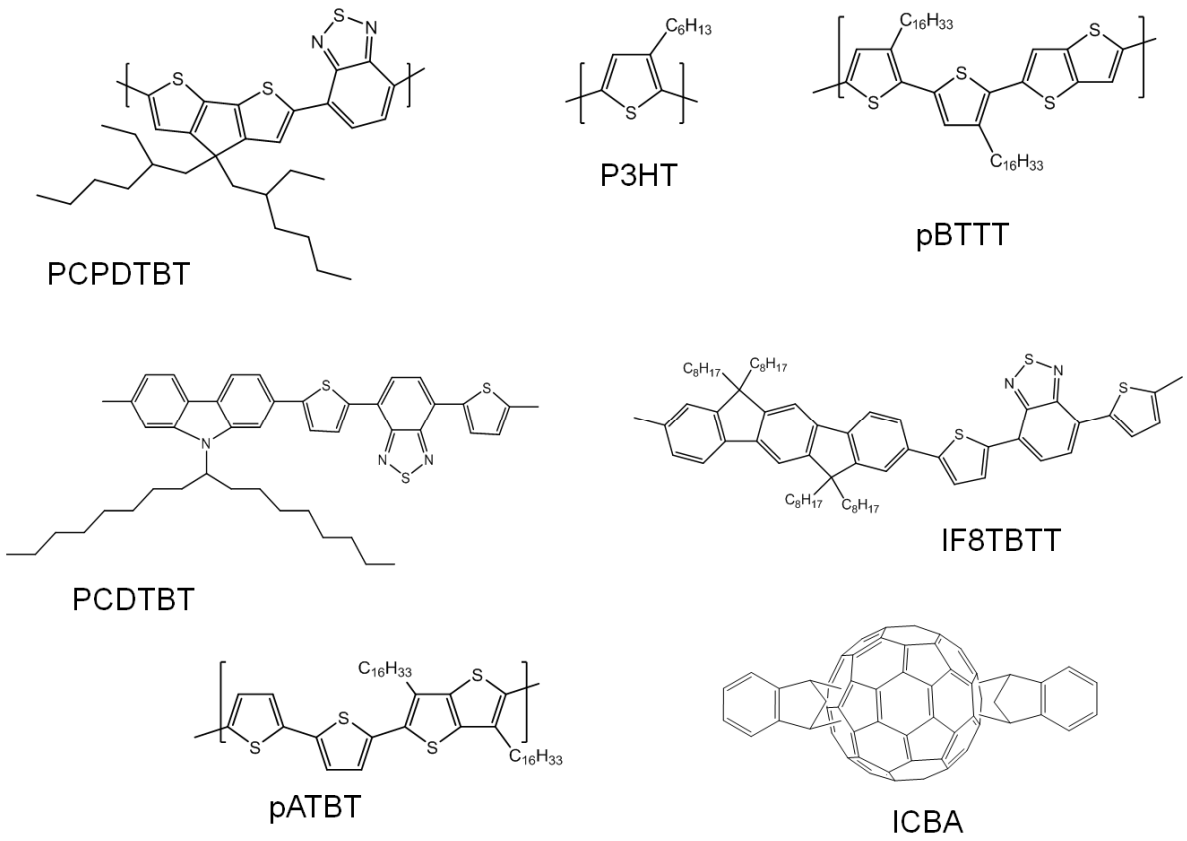
Supporting Information For:

Fullerene aggregation as a key driver of charge separation in polymer / fullerene bulk heterojunction solar cells

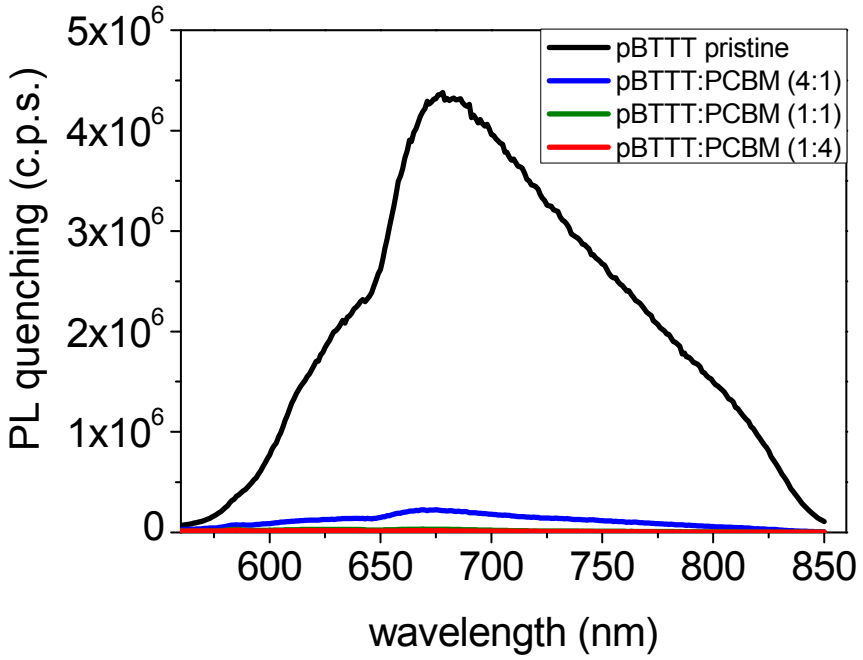
Fiona C. Jamieson,[1] Ester Buchaca Domingo,[2] Thomas MaCarthy-Ward,[1] Martin Heeney,[1,] Natalie Stingelin,[2,3]* James R. Durrant[1,]*

Centre for Plastic Electronics, Departments of Chemistry[1] and Materials,[2] , Imperial College London, Exhibition Road, London, SW7 2AZ, UK. [3]FRIAS, School of Soft Matter Research, University of Freiburg, 79104 Freiburg, Germany.

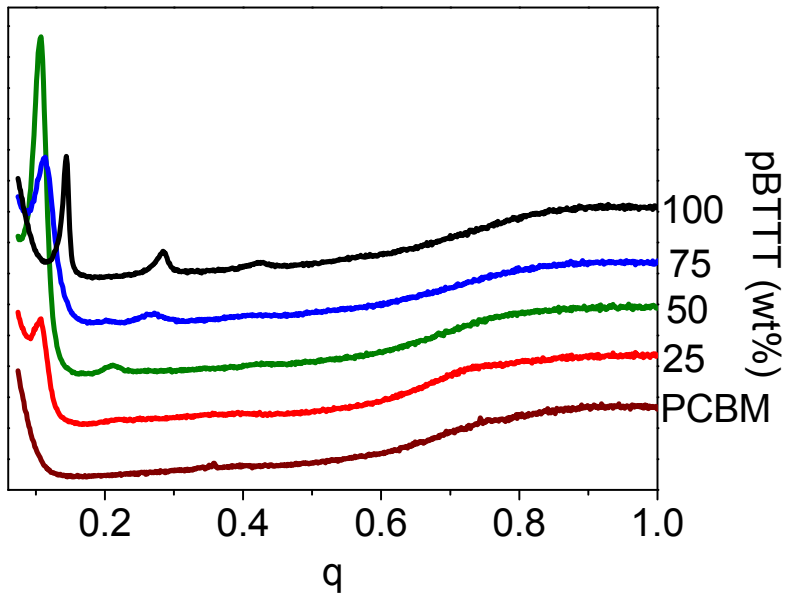
* j.durrant@imperial.ac.uk and n.stingelin-stutzmann@imperial.ac.uk



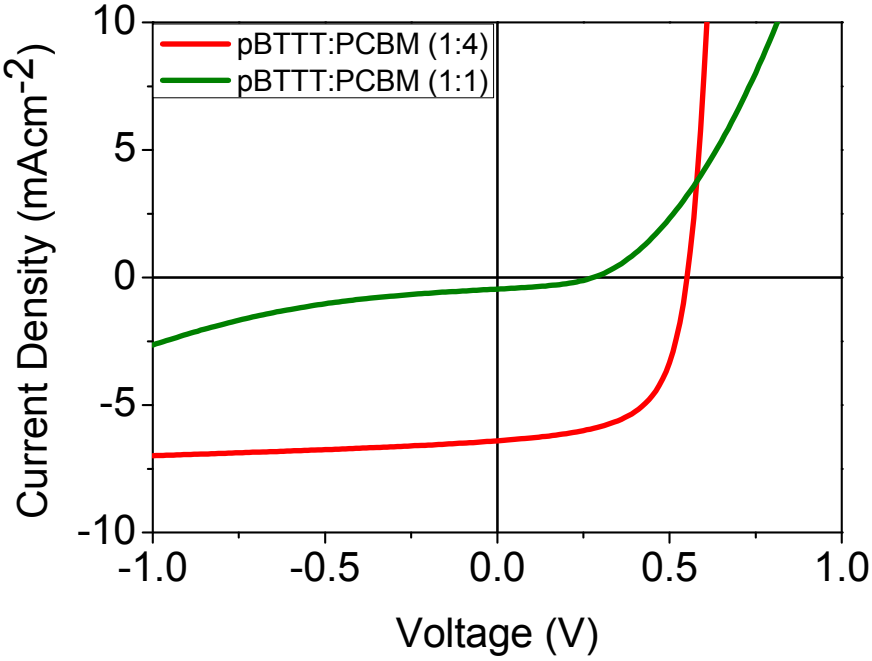
Supporting Information Figure 1: Chemical structure of polymers used for photoluminescence quenching studies in Figure 1 and excitation wavelengths used. Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT)650 nm ,[1] poly(3-hexylthiophene) (P3HT) 520 nm, poly(2,5-bis(3-tetradecyllthiophen-2-yl)thieno[3,2,-*b*]thiophene) (pBTTT), 520 nm,[2] Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) 560nm,[3] poly[2,8-(6,6,12,12-tetraoctylindenofluorene)-co-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiodiazole] (IF8TBTT) 540 nm[4] and poly(3,6-dialkylthieno[3,2-b]thiophene-co-bithiophene) (pATBT) 520 nm[5] and the alternative fullerene, indene-C 60 bisadduct (ICBA).[6]



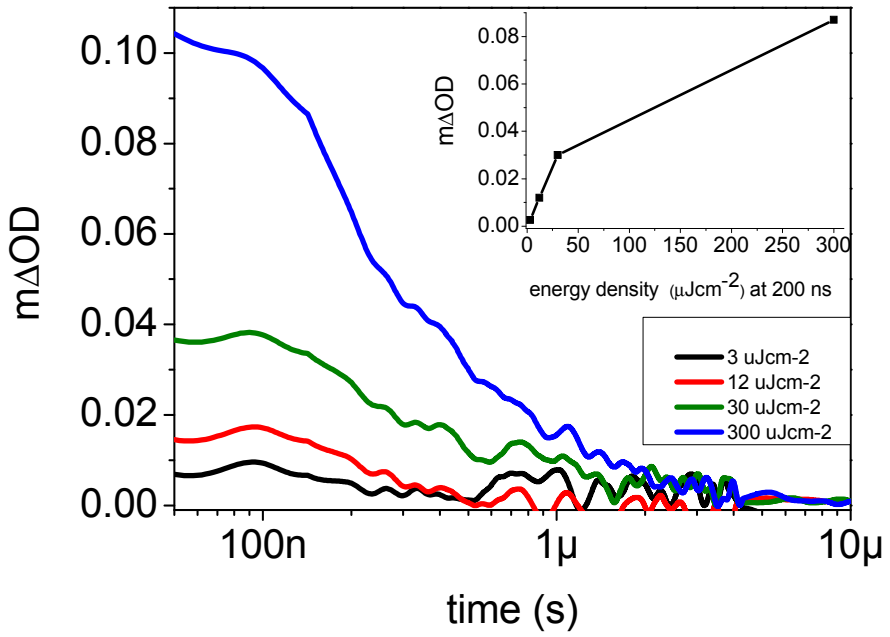
Supporting Information Figure 2: Photoluminecence quenching (PL) of neat pBTTT, pBTTT:PCBM (4:1), pBTTT:PCBM (1:1) and pBTTT:PCBM (1:4) showing nearly complete photoluminescence quenching with the addition of 25 wt% PCBM, increasing to >99% quenching with 50 wt% and 80 wt% PCBM.



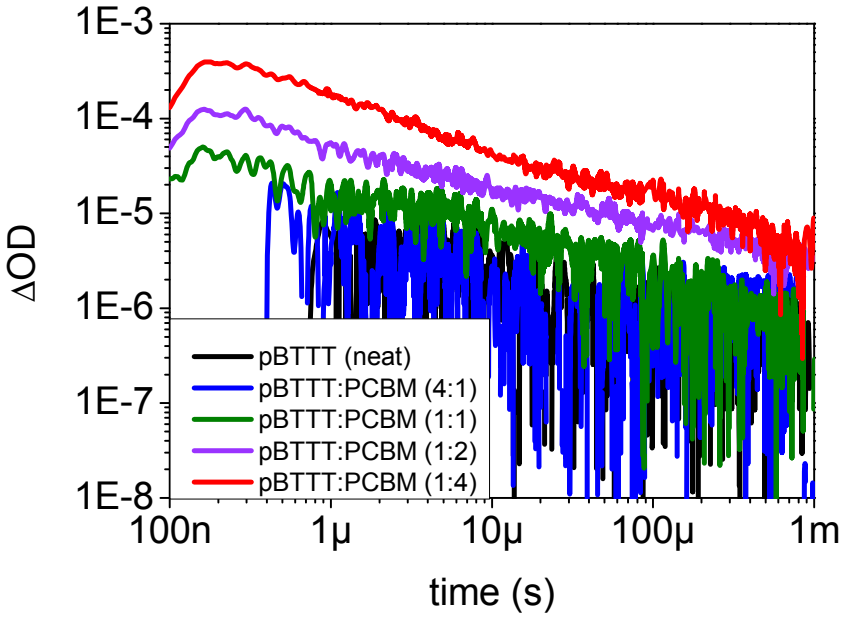
Supporting Information Figure 3:) XRD patterns showing how the lamellar packing distance of the pBTTT changes upon the addition of PCBM, showing in particular the formation of pBTTT/PCBM co-crystals. Wide-angle X-ray scattering (WAXS) were carried out with a PANALYTICAL X' PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu-$K_{\alpha 1}$ beam and X' CELERATOR detector, using current I = 40 mA and accelerating voltage U = 40kv.



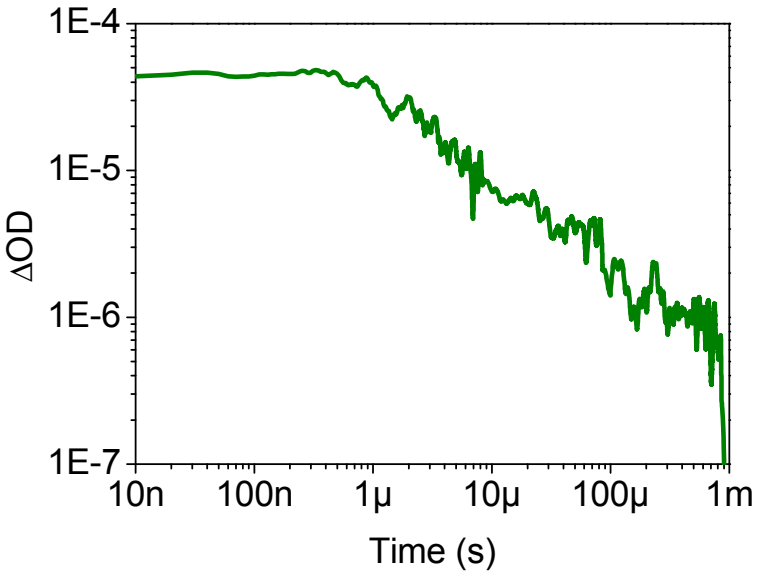
Supporting Information Figure 4: Current / Voltage (J/V) data for pBTTT:PCBM 1:1 and 1:4 devices. Power conversion efficiencies are 0.05% and 2.12% respectively. J/V data was measured using a Keithley 238 Source Measure Unit and illumination at 1sun was provided using a 300W xenon arc lamp solar simulator (Oriel Instruments) and calibrated with a silicon photodiode.



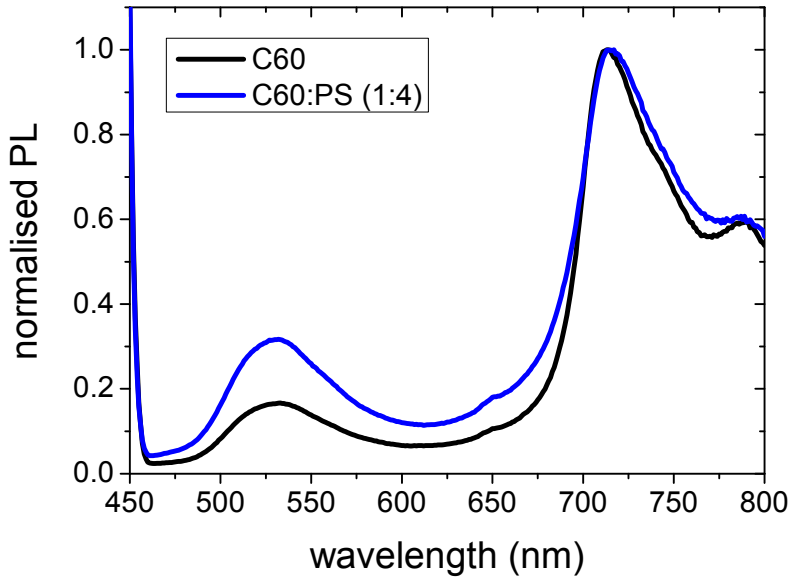
Supporting Information Figure 5: Transient absorption (TA) decay kinetics from 50 ns to 10 μs for a 1:4 pBTTT:PCBM blend as a function of excitation density. Inset the optical density at 200 ns as a function of excitation density. The optical density increases linearly with excitation density up to 30 μJcm^{-2} however, above this there is a sub-linear dependence of the absorbance with excitation density. The data in Figure 3 was recorded at 8 μJcm^{-2} which is in linear regime.



Supporting Information Figure 6: TA decay kinetics from 100 ns to 1 ms for neat pBTTT, pBTTT:PCBM (4:1), pBTTT:PCBM (1:1), pBTTT:PCBM (1:2) and pBTTT:PCBM (1:4) from Figure 3. Excitation at 520nm (8 μJcm^{-2}) and probed at 980nm. This shows the non geminate recombination rates, as determined from the α value,[7] are similar for all compositions, varying between α = 0.3 - 0.4. However, the charge generation yield increases with increasing PCBM concentration.



Supporting Information Figure 7: Transient absorption decay kinetics of a pBTTT:PCBM (1:1) blend, from 10ns to 1ms. This shows that geminate recombination occurs faster than 10ns, as observed in the signal plateau at early timescales.[8] Collected as described previously[8] using a 50mW, 980nm laser diode.



Supporting Information Figure 8: Photoluminescence of pyrazolinofullerene following fullerene excitation at 430 nm for a neat fullerene film and a 1:4 (by weight) blend of pyrazolinofullerene:polystyrene.

Supporting Information: Derivation of Equation 1: The diffusion length L_{ex} of a polymer excition in the absence of quencher (PCBM) is related to its lifetime τ_0 by $L_{ex} = (D*\tau_0)^{1/2}$. In the presence of PCBM, both the exciton lifetime τ and the diffusion length L are reduced such that $L = (D*\tau)^{1/2}$. Assuming that the addition of PCBM only introduces an a new exciton quenching pathway, and does not otherwise change the properties of the polymer excitons, the fractional residual photoluminescence emission intensity, $PL/PL_0 = 1-PLQ$, where PL and PL_0 are the emission intensities in the presence and absence of PCBM, is related to the exciton lifetime by $1-PLQ = \tau / \tau_0$ Combining these equations gives the equation (1) stated in the manuscript. We note that L_{ex} is measured typically measured for diffusion to flat (2-Dimensional) quenching interfaces, whilst the quenching site distribution we are describing is most probably 3-dimensional. This difference is likely

to result in a small underestimation in our determination of exciton diffusion lengths in the presence of PCBM. We also note that our analysis assumes that diffusion of a polymer exciton to adjacent to a PCBM results in ultrafast, irreversible quenching (and so in this regard is an upper limit for the diffusion length).

References

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