Binary Organic Photovoltaic Blends: A Simple Rationale for Optimum Compositions

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Fig. S1. Glass formation of P3HT:PC_{61}BM. (Left) Differential scanning calorimetry thermograms recorded during cooling at a rate of 10 °C min\(^{-1}\) and (right) temperature/composition diagram constructed therewith.
Fig. S2. Wide-angle X-ray scattering (WAXS) and UV-vis spectroscopy of P3HT:PC₆₁BM blends. a) WAXS, and b) corresponding UV-vis spectra for blends: (i) cast from solution; (ii) treated at 140 °C for 45 min; (iii) solidified from the melt; (iv) treated at 140 °C for 45 min after solidification from the melt.
Fig. S3. Dark current density – voltage characteristics of P3HT:PC$_61$BM devices. Dark current density – voltage curves for photovoltaic cells made from blends containing 50 wt% P3HT, according to the following processing routes: a) quenched from the melt, b), c) spin coated, not annealed (both devices were prepared according to identical procedures with materials of similar molecular weight and regio-regularity – data for c) taken from [1]), and d) spin coated and thermally annealed at 140 °C. Blend films of type a) and b) showed glassy behaviour when studied with WAXS, while films of type c) and d) showed a good degree of polymer crystallinity. High crystallinity is therefore correlated to rectifying current-voltage characteristics with a high forward current. The comparison shows, first, that spin coating leads to a variable degree of crystallinity, and hence to variable device behaviour. For this reason we choose quenching from the melt (a)) as a reliable protocol to obtain glassy film structure. Secondly, the glassy films show low forward current and pronounced series resistance effects (compare the glassy films a) and b) and the more crystalline films c) and d)). This observation can be explained by the disruptive effect of PC$_61$BM addition on P3HT chain packing and hence on hole mobility, in agreement with previous reports (e.g. [2]).
Fig. S4. Effect of blend composition on solar photon harvesting. a) Effective extinction coefficients for P3HT:PC$_{61}$BM blends as a function of blend composition, deduced by combining the extinction coefficients of the pristine materials [3] via the effective medium approximation (Bruggeman model). This procedure does account for variations in the degree of crystallinity with varying polymer content. b) Calculated solar photon flux density absorbed by a P3HT:PC$_{61}$BM blend film as a function of blend composition, obtained by calculating the overlap integral between the Air Mass 1.5 solar photon flux spectrum and the absorbance of 200 nm thick blend films of different composition. Film absorbances were calculated using the extinction coefficient data in a) and neglecting internal reflections. The data are presented as a percentage change with respect to the absorption for P3HT:PC$_{61}$BM blends containing 50 wt% P3HT.
Fig. S5. Effect of blend composition on the polaron pair binding energy. Previous reports have argued that the Coulombic binding energy for a charge pair, $E_B = e^2 / (4\pi \varepsilon_r \varepsilon_0 a)$, varies by up to a factor of two as the composition of a polymer:PCBM blend is varied [4]. Here, $E_B$ is calculated using the measured dielectric function in the near infrared [5], $\varepsilon_r = \varepsilon_{IR}$ (deduced using an effective medium approximation from the dielectric function of the pristine materials), and presented as percentage change with respect to the binding energy for P3HT:PC$_{61}$BM blends containing 50 wt% P3HT. The plot shows that variations with composition in the macroscopic dielectric function are unlikely to lead to large changes in Coulombic interactions or, therefore, in charge separation efficiency. A microscopic analysis of Coulombic interactions would be required to explore this further.
Fig. S6. Simulated composition dependence of electron and hole mobility in a blend film. a) Simulated morphology of a blend film containing equal concentrations of P3HT (purple) and PCBM (grey) after simulated thermal annealing. Such morphologies were produced using a Metropolis Monte Carlo technique whereby fullerene molecules diffuse and polymer chains reptate at random [6]. Attractive interaction energies within each phase encourage aggregation of small molecules and of polymers as annealing progresses. Molecules are constrained to a cubic lattice, with each molecule of fullerene and each tetramer of polymer occupying exactly one site. The ratio of fullerene to polymer volume is varied to simulate different blend compositions while the total solid content is constrained to 60% of the volume. b) Simulated electron mobility within the fullerene phase (black) and hole mobility within the polymer phase (red) as a function of blend film composition, after a limited degree of thermal annealing. Mobility is calculated by simulation of a steady state drift current within typical simulation volumes for a given composition and degree of annealing. The coefficients for hopping between unconnected monomers of the same materials were chosen to be equal in the two materials, while the hopping rate between connected neighbours in polymer chains was larger by a factor of 10 (leading to the higher mobility for holes when normalised in this way). The results show that electron mobility varies rapidly at the eutectic composition for P3HT:PC$_{61}$BM (indicated approximately by the vertical dotted line) while the hole mobility has already saturated near its limiting value.
Fig. S7. Complex refractive indices of poly(3-alkylthiophenes). Refractive indices, \( n \), (triangles) and extinction coefficients, \( \kappa \), (circles) of P3BT (filled black), P3HT (filled grey) and P3DDT (open symbols) films. The optical constants for pristine polymer films spin-coated on quartz were deduced from variable angle spectroscopic ellipsometry data analysed via the critical point model of the dielectric function [3].

References