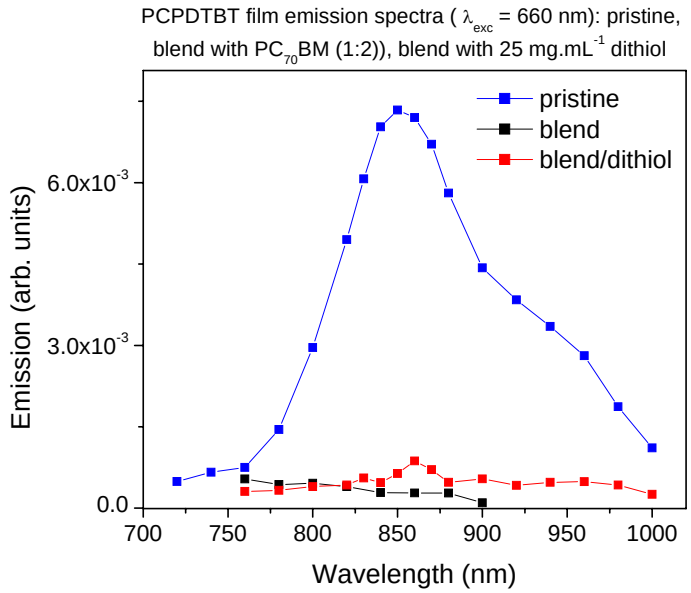
Supplementary Material (ESI) for Chemical Communications

Transient absorption spectroscopy of charge photogeneration yields and lifetimes in a low bandgap polymer/ fullerene film.

Tracey Clarke,*[a] Amy Ballantyne,[b] Fiona Jamieson,[a] Christoph Brabec,[c] Jenny Nelson[b] and James Durrant*[a]

Supporting Information



Supporting Figure 1. Emission spectra (uncorrected for detector response) for PCPDTBT / $PC_{70}BM$ blend films with/without dithiol and pristine PCPDTBT film .

Estimation of ΔG_{CS}^{rel}

The estimation of ΔG_{CS}^{rel} relies upon establishing both S_1 and the ionisation potential of the polymer. PCPDTBT is reported to have an ionisation potential (IP) of 5.3 eV. However, given the difficulties in accurately determining polymer ionisation potentials due to their inherently ill-defined band edges, the methods utilised for establishing IPs, such as cyclic voltammetry (which was used for PCPDTBT) and ultraviolet photoelectron spectroscopy, often provide subjective estimations that are difficult to compare between laboratories. Similarly we note electron affinities for PCBM have been reported in the range 3.7 to 4.2 eV. For this reason, our determination of ΔG_{CS}^{rel} is only employed herein for consideration of the relative energetics of different polymer / fullerene films, rather than an absolute determination of these energetics The method that provided 5.3 eV for the IP of PCPDTBT also gave 5.1 eV for P3HT.[1] For the polythiophenes studied by Ohkita et al, a different methodology determined the IP of P3HT as 4.8 eV.[2] Using P3HT as a reference, we can estimate the effective ionisation

potential of PCPDTBT as 5.0 eV such that it is directly comparable to Ohkita's polythiophene series. The S1 state of the PCPDTBT in the blend film is ~ 1.5 eV (estimated from the absorption spectra for the pristine and blend film with dithiol). The electron affinity of $PC_{70}BM$ is very similar to that of $PC_{60}BM$[3] (taken to be 3.7 eV). Thus ΔG_{CS}^{rel} can be estimated for as 0.2 eV for the blend film with dithiol. For the blend film, the shifts in S_1 and IP energies detailed in the text result in a value for ΔG_{CS}^{rel} of 0.1 eV.

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