

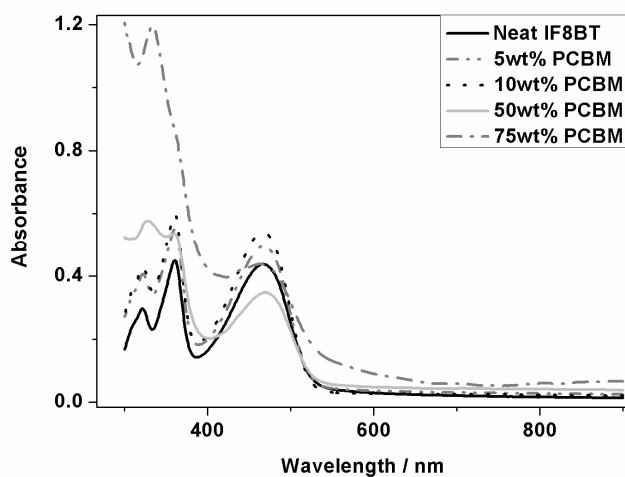
Energy versus electron transfer in organic solar cells: a comparison of the photophysics of two indenofluorene : fullerene blend films.

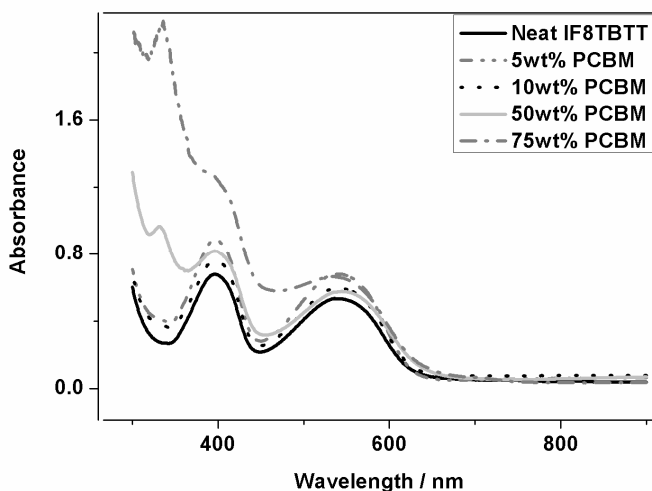
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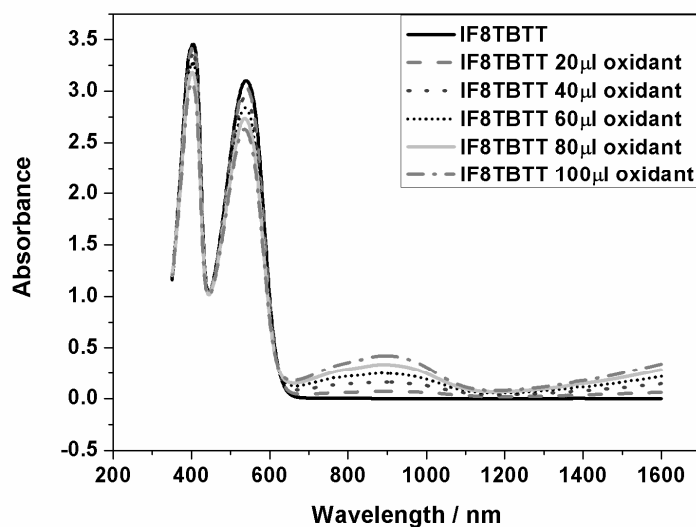
Supporting Information

S1: The ground state absorption spectra of IF8BT and IF8TBTT neat films and different PCBM composition blend films.





S2: Experimental details for radical cation absorption coefficient experiment.



100 μ l tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich) in acetonitrile (5×10^{-4} M) was added in 10 μ l aliquots to a solution of IF8TBTT in chlorobenzene (3×10^{-2} mg/ml, corresponding to a monomer concentration of 3×10^{-8} M). The absorption spectra of the products of the one-electron oxidation reaction were recorded using a Perkin-Elmer Lambda-950 spectrophotometer and the extinction coefficient calculated from the gradient of a linear fit to solution absorption as a function of polaron concentration (assumed equal to concentration of oxidant) using the Beer-Lambert law with a path length of 1 cm.⁷² The assumption that the oxidation reaction is complete (and that the polaron concentration is the same as the concentration of oxidant) indicates that the calculated value of 26400 ± 500 L mol⁻¹ cm⁻¹ is a lower bound on the extinction coefficient.

Experimental Section

Both the polymers, IF8BT and IF8TBTT used in this project were synthesized by Professor Iain McCulloch's group at Imperial College London while 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM) used was from HC Starck. Polymer and PCBM of the desired weight ratio were dissolved in dichlorobenzene solution with a concentration of ~20mg/ml. For film fabrication, spectroil glass slides were used as the substrate. The glass slides were cleaned by sonication in acetone and isopropanol for 15 minutes successively, followed by drying with nitrogen gas. About 50µl of the solutions were then spin-coated onto 1cm² glass substrates at 1500 – 3000 rpm for 1 minute. For device fabrication, 1cm² ITO glass was used as the substrate instead. ITO glass was also sonicated in acetone and iso-propanol. PEDOT:PSS from HC Starck (Baytron P) was spin coated onto the ITO glass at 3000rpm for 1 minute and annealed at 200°C for 30 minutes. The polymer/PCBM solutions were then spin coated at around 1500 – 3000 rpm for 1 minute on the ITO glass and PEDOT:PSS. Aluminium layer was then deposited by thermal evaporation *in vacuo*.

Ionisation potential (IP) of the polymer neat films was measured by Scott Watkins from CSIRO with photoelectron spectroscopy in air (PESA) using a Riken Kekei AC-2 spectrometer. Absorption and PL spectra were measured at room temperature with a UV-visible spectrophotometer (Shimadzu, UV-1601) and a spectrofluorimeter (Horiba Jobin Yvon), respectively, with the fluorescence spectrum being corrected for the fluorimeter's spectral response.

Transient absorption data were collected with a microsecond transient absorption system under N₂ or O₂ atmosphere. The pump pulse was produced by a LN1000 Megaplas nitrogen laser which pumps a PTI dye laser at 4kHz repetition frequency rate. This pump pulse was then focussed on the sample in a quartz cuvette using a light guide. The probe pulse was produced from a 150W tungsten lamp, which passes through two monochromators for the selection of probe wavelengths. The detection system consisted of a silicon photodetector and a Tektronix TDS 220 oscilloscope, connected to a computer.

J-V characteristic of IF8TBTT devices were measured using a solar simulator with light intensity of 100mW/cm², at 1 sun AM 1.5 under N₂ atmosphere. Current density as a

function of voltage (J-V) characteristics was measured with a computer controlled Keithley 237 source meter.

For the quantum mechanical calculations performed on dimer models of IF8BT and IF8TBTT: Ground state geometries and ionization potentials in the ground state are calculated using the hybrid density functional B3LYP and a double split basis set with add polarization basis sets (6-31g*). Calculations of the excited state absorption energies were carried out in the time dependent formalism (TDDFT). Computations were carried out in Gaussian 09.

Emission Quenching and Energy Transfer Calculation.

Our analysis of polymer to fullerene singlet energy transfer is based upon a simple analysis of emission quenching. The efficiency of energy transfer η_{entr} can be readily determined from the magnitude of the emission quenching:

$$\eta_{entr} = 1 - \frac{PL_B}{PL_{NP}} = PLQ \quad (1)$$

where PL_B and PL_{NP} are the photoluminescence intensities of the blend and neat polymer films respectively, and PLQ the relative emission quenching.

From simple kinetic considerations, η_{entr} is also given by

$$\eta_{entr} = \frac{k_{entr}}{k_{entr} + k_0} \quad (2)$$

where k_{entr} is the energy transfer rate constant and $\tau_0 = (k_0)^{-1}$ is the polymer exciton lifetime in the absence of PCBM.

Rearranging (1) and (2), we obtain

$$k_{entr} = \frac{k_0 PLQ}{1 - PLQ} \quad (3)$$

which allows us to determine estimated energy transfer rate constant directly from the observed emission quenching, and assuming a reasonable value for τ_0 .

In addition, from Förster theory, the energy transfer rate constant is proportional

$$\text{to } k_{entr} \propto \int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (4)$$

where f_D is the (unnormalised) emission spectrum of the donor and ϵ_A the absorption spectrum of the acceptor (we note in the literature, this integral often employs a normalised emission spectrum, with the integral multiplied by the donor emission quantum yield). From equation 4, we are able to calculate relative energy transfer rate constants for different donor emission spectra.