Charge photogeneration in polythiophene/ perlyne diimide films

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Supporting Information

Experimental Section. Six polythiophenes were synthesized as reported elsewhere.[1,2] 1-(3-Methoxycarbonyl)propyl-1-phenyl-[6,6]-C61 (PCBM) was purchased from Solenne and N,N'-bis[3,4,5-tri(dodecyloxy)benzyl]-3,4,9,10-tetracarboxylic perylene diimide (**1**) was prepared essentially as described in the literature.[3,4] Chloroform purchased from Aldrich, was used as the solvent. All materials were used as received. To the polythiophene solutions (~20 mg mL^{-1}), solutions of PCBM or **1** were added at a concentration of ~20 mg mL^{-1}. Pristine polymer films were spun from solution onto glass substrates at a spin rate of 3000 rpm for 90 s under N_2 atmosphere. The weight concentration of **1** and PCBM in the final polymer blend solutions was fixed at 50 wt %. Solid blend films of polythiophene/ **1** and polythiophene/PCBM were prepared by spin-coating blend solutions at 500 rpm and 1100 rpm for 60s respectively. Before spin-coating, the substrates were pre-cleaned by sonication in acetone and isopropanol for 15 minutes successively. The resultant blend films were approximately 100 nm thick as measured Atomic Force Microscopy (Pacific Nanotechnology). Absorption and PL spectra were measured at room temperature with a UV-visible spectrophotometer (Shimadzu, UV-1601) and a spectrofluorimeter (Horiba Jobin Yvon, Spex Fluoromax1), respectively. Transient absorption data were collected with a highly sensitive microsecond transient absorption system under N_2 or O_2 atmosphere as described elsewhere.[5] For all the blend films, the excitation wavelengths were chosen to correspond to the maximum absorption peak.

Electron Acceptor Strength. Estimates of the solid-state EAs of PCBM and **1** have been previously reported as 3.7 eV and 3.3 eV, respectively, using different cyclic-voltammetry-based approaches.[6,7] The estimate for PCBM is supported by a recent inverse photoelectron study giving a value of 3.9±0.1 eV;[8] however, direct measurements of the EAs of PDIs have not been published. In fact, solution electrochemical data[9,10] indicate similar reduction potentials (ca. −1.0 to −1.1 V vs. FeCp2$^{+/0}$) for **1** and

PCBM. However, due to different solvents used for each study, and due to the possibility of differing effects of intermolecular interactions in the two solids, the relative EAs of the two materials in the solid state remains unclear. In order to address this issue directly, we studied the photophysics of **1**/PCBM blend films. As shown by TAS in Fig. S1, photoexcitation of a blend of the two molecular n-type materials, PCBM and **1**, resulted in electron transfer from **1** to PCBM. Consistent with previous reports, the transient spectrum exhibited an absorption maximum at ~850 and ~1040 nm indicative of the formation of PDI cations[11] and PCBM anions[12] respectively, distinguishable from PDI triplet absorption at 480 nm and PDI radical anions that have been reported to show structured absorption with a sharp absorption maximum at shorter wavelengths of 700 nm.[13] The ΔOD of the transient peak at ~850 nm correspond to the formation of $\mathbf{1}^{+}$ whilst the ΔOD at ~1040 nm is assigned to PCBM^{-}. These TAS data are consistent with PCBM exhibiting a higher electron affinity than **1**.
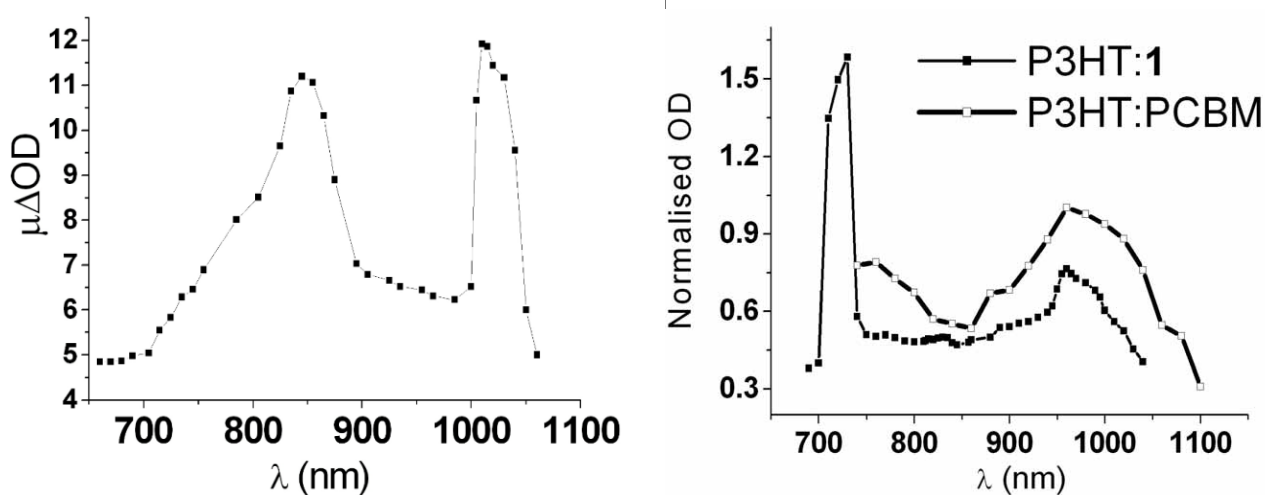

Figure S1. a) Transient absorption data collected for a 1:1 **1**:PCBM blend film spun coated from CHCl$_3$ at 1100 rpm for 40s. Excited at 447 nm and measured at 1μs, using an excitation density of 50 μJ cm^{-2}. b) . (right): P3HT:1 (filled square) and P3HT:PCBM (open squares) spun from CHCl$_3$ at 1100 rpm for 40s and chlorobenzene at 1500 rpm for 90s respectively. Both were excited at 520 nm and measured at 1 μs using an excitation density of 50 μJ cm^{-2}.

Photophysics. Table S1 tabulates the transient absorption decay of as-prepared polythiophene: **1** and polythiophene:PCBM blend films spun from a 1:1 solution ratio in chloroform. The amplitudes have been normalized for variation in thickness and optical densities between blend films. With the exception of P3HT:**1** blend, in all cases, it is observed that the polymer:**1** blends give a higher yield than the $PC_{60}BM$ counterpart blends. Due to the higher extinction coefficient of **1** anions, the transient decay of the **1** blends are probed at 830 nm, a wavelength with partial contribution both from polymer cations and **1** anions. Furthermore, this probing wavelength is chosen such that it corresponds to the lowest ΔOD on the spectra of P3HT: **1** and hence emphasizing the higher yield of **1** blends.

Table S1: Photophysical Properties of 1:1 Polythiophene:**1** and Polythiophene:PCBM blend Films:

	Assignement	$\Delta G_{rel}^{CS\ a}$	$m\Delta OD^b$	Qe^c %
P3HT				
1	$P^+/\mathbf{1}^-$	0.5	0.2	65
PCBM	$P^+/PCBM^-$	0.9	0.18	>95
$P(T_{10}T_{10}TT_0)$				
1	$P^+/\mathbf{1}^-$	0.2	0.25	95
PCBM	$P^+/PCBM^-$	0.6	0.06	>95
$P(T_{16}T_{16}TT_0)$				
1	$P^+/\mathbf{1}^-$	0.2	0.2	85
PCBM	$P^+/PCBM^-$	0.6	0.04	90
$P(T_0TT_{16})$				
1	$P+/\mathbf{1}-$	0.35	0.13	80
PCBM	$P+/PCBM-$	0.75	0.08	95
$P(T_{12}SeT_{12})$				
1	$P^+/\mathbf{1}^-$	0.18	0.15	80
PCBM	-	0.58	0.04	95
$P(T_{12}NpT_{12})$:				
1	$P^+/\mathbf{1}^-$	0.56	0.1	70
PCBM	^3PCBM	0.96	0.006	95

a -ΔG_{CS} estimated as E_S - (IP - EA) where E_S is the energy level of polymer singlet excitons. IP is the Ionisation potential of the polymer and EA is the electron affinity of the electron acceptor . b Evaluated from the amplitude of the transient absorbance power-law decay phase at 1 μs normalized by the ground state absorbance at the excitation wavelength. c Steady-state PL quenching of the blend film relative to the corresponding pristine polymer film.

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