Singlet oxygen formation from photoexcited P3HT:PCBM films applied in oxidation reactions

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Poly(3-hexylthiophene) synthesis

3-Hexylthiophene (>98%) and iron(III) chloride (>97%, Fisher Chemical) were obtained from commercial sources and used without further purification. Reactions were conducted under dry nitrogen flow, in oven-dried glassware. Poly(3-hexylthiophene) (P3HT) was synthesized by means of oxidative polymerization with $FeCl_3$ based on procedure by Niemi et al.[1] as follows: A dry 500 ml flask was charged with iron(III) chloride(9.45 g) and chloroform (112 cm^3) and the solution was purged with nitrogen for 10 minutes. Next 3-hexylthiophene (2.5 cm^3) was added and the reaction mixture was stirred for 1.5 h under nitrogen flow. In order to terminate the reaction deionized water (50 cm^3) was added. The crude polymer was

[1] V.M. Niemi, P. Knuuttila, J.-E. Österholm, J. Korvola, Polymerization of 3-alkylthiophenes with $FeCl_3$, *Polymer* 33 (1992) 1559–1562. doi:10.1016/0032-3861(92)90138-M

precipitated with acidified ethanol. The black precipitate was filtered under vacuum, and then purified and fractionated by sequential Soxhlet extraction with ethanol, hexane, and chloroform. Polymer fraction (yield 65%) was isolated from the chloroform extract by evaporating solvent on a rotary evaporator, pouring concentrated solution over a Petri dish and drying in an oven at 35 °C to give a dark green opalescent film, slightly flexible and easily removable from the glass substrate. The polymer was then dried under vacuum (40 °C, 20 mbar).

^{1}H-NMR analysis of the polymer was performed on a Varian Unity Inova 300 MHz Spectrometer in $CDCl_3$ solution using TMS as an internal standard. P3HT: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ_H, ppm: 6.98 (1H), 2.81 (2H), 1.76-1.66 (2H), 1.47-1.34 (6H), 0.91 (3H). All peaks were broadened, with no distinct multiplet structure. The signal at 2.81 ppm was split into two: 2.81 and 2.57 ppm with relative integral ratios of 1.6 and 0.4, indicating regioregularity of 80%. The number average molecular weight (M_n) and dispersity (D) were determined using a size-exclusion (SEC) 1100 Agilent 1260 Infinity chromatograph, equipped with a differential refractometric MDS RI Detector. The molecular weight obtained by SEC was based on calibration with linear polystyrene standards (580- 300,000 g/mol). P3HT: M_n = 48,000 g/mol, D = 5.1.

Table S1. The average thickness of the photoactive layers deposited on borosilicate glass

	P3HT:PCBM	P3HT:C_{60}	P3HT:SWCNT
Mean layer thickness [nm]	35.0 ± 1.4	34.8 ± 2.2	35.5 ± 2.1

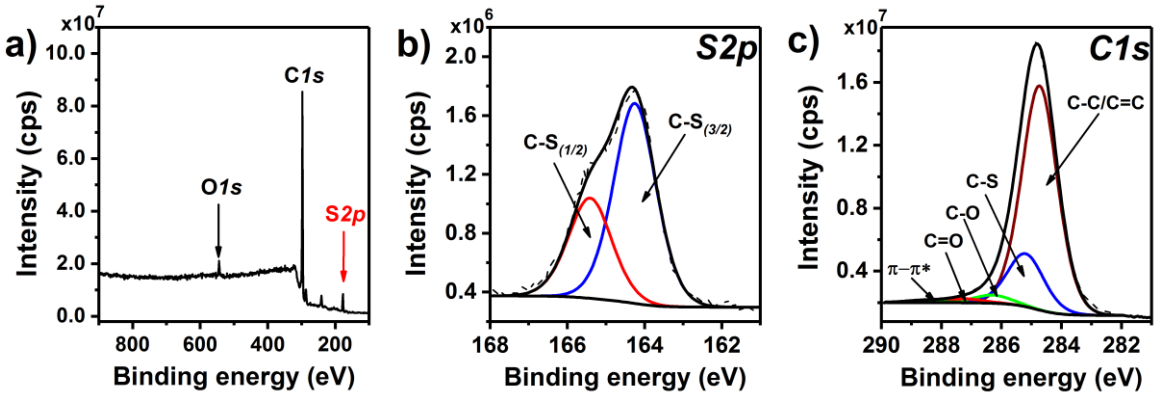

Figure S1. XPS of P3HT:PCBM (2:1) photoactive layers deposited on borosilicate glass. (a) Survey spectrum. (b) High-resolution S2*p* region. (c) High-resolution C1*s* region.

^{1}H-NMR of product of DHN oxidation in the presence of P3HT:PCBM (1:2) layer

^{1}H-NMR ($CDCl_3$, 300 MHz) δ_H, ppm: 11.92 (1H), 7.64-7.66 (2H), 7.26-7.31 (1H), 6.96 (2H)