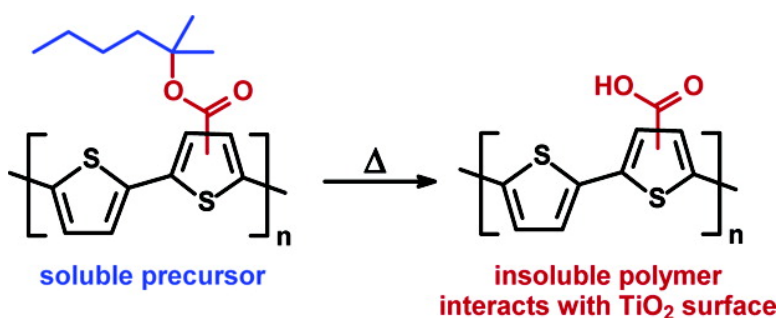


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## Polythiophene Containing Thermally Removable Solubilizing Groups Enhances the Interface and the Performance of Polymer–Titania Hybrid Solar Cells

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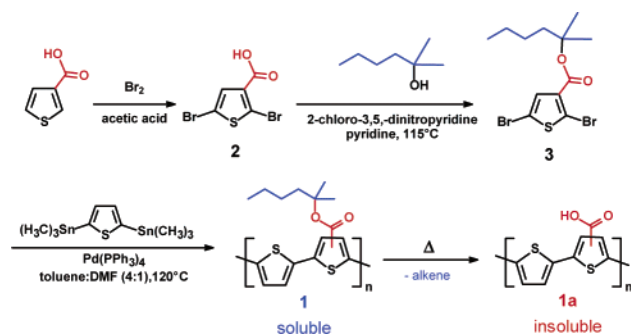
Solution-processable p-conjugated polymers are likely to play an important role in low-cost solar cells.<sup>1</sup> However, since  $\pi$ -conjugated polymers have a relatively low charge mobility when compared to inorganic semiconductors, it is important to ensure that both charge separation and transport are efficient in order to achieve good performance of the cell. To achieve these goals, while ensuring adequate light absorption, a relatively thin active polymer layer with a large absorption coefficient is required.

To make the highly conjugated organic materials solution-processable, introduction of solubilizing groups is necessary. However, typical nonconjugated solubilizing groups reduce the density of chromophores in the polymer. Therefore, it is advantageous to be able to remove these groups in a postprocessing step. The thermal removal of solubilizing groups, key to our design of chemically amplified photoresists,<sup>2</sup> was also used in the Durham polyacetylene,<sup>3</sup> in polyphenylene vinylene (PPV),<sup>4</sup> and for solution-processable pentacene.<sup>5</sup> We recently applied this approach to increase the solubility of sexithiophene and to allow solution processing of organic thin-film transistors (OTFTs), resulting in mobilities and on/off ratios that were the highest ever reported for the for solution-processed thiophene oligomers.<sup>6</sup> Herein, we report the synthesis of functionalized polythiophene with high chromophore density, which can improve the performance of polymer/TiO<sub>2</sub> photovoltaic cells.

The structure of **1** was selected on the basis of several considerations: (i) The tertiary nature of the ester group enables its removal at a relatively low temperature. (ii) The branched character of the ester group contributes to higher solubility, facilitating synthesis, purification, and processing. (iii) Following thermal cleavage of the ester group, a carboxylic acid  $\pi$ -conjugated to the polymer backbone remains. This is important, as such an electron-withdrawing moiety in direct conjugation with the polythiophene backbone not only allows tuning of the energy levels but also enables the interface interaction between the polymer and TiO<sub>2</sub>, which can potentially enhance the interfacial charge-transfer efficiency.<sup>7</sup> Finally, (iv) the ability to change the solubility of **1** through its thermal solubility switch enables the preparation of multilayer devices.

Polymer **1** was synthesized by Stille-type cross-coupling reaction between bis-stannylated and bis-brominated monomers (Scheme 1). Bromination of thiophene-3-carboxylic acid afforded acid **2**, esterification of which with 2-methyl-2-hexanol yielded compound **3**. Pd-catalyzed coupling of **3** with 2,5-di(trimethylstannyl)thiophene gave rise to polymer **1**. According to size-exclusion chromatography

**Scheme 1.** Synthesis of Ester-Functionalized Polythiophene **1** and Its Thermal Conversion into Insoluble Acid-Functionalized Polymer **1a**



(polystyrene standards), unfractionated polymer **1** has a  $M_n = 16\,600$  g/mol and a polydispersity index = 2.2.

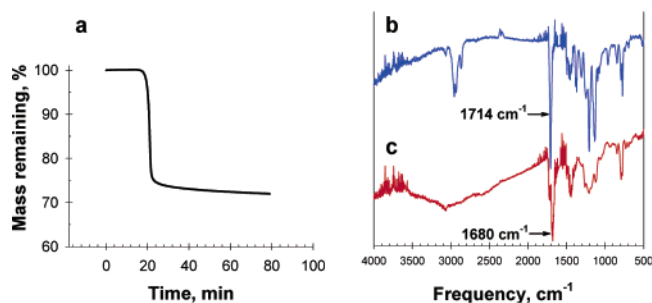
Thermogravimetric analysis (TGA) of **1** confirmed the occurrence of the thermolysis reaction (Figure 1a and Supporting Information). Infrared spectroscopy (IR) of polymer **1** before and of **1a** after thermal treatment confirms the loss of ester protecting groups with appearance of carboxylic acid groups (Figures 1b and 1c). The increase in the polymer film density from 1.20 g/cm<sup>3</sup> for **1** to 1.45 g/cm<sup>3</sup> for **1a** suggests that the thermal deprotection does not create voids in the film but may instead contribute to an improved  $\pi$ - $\pi$  stacking among the polymer chains. At the same time, the larger absorption coefficient of **1a** compared to that of P3HT indicates that the chromophore density is larger in polymer **1a** than in P3HT (see Supporting Information for X-ray reflectometry and absorbance data).

We tested polymer **1** as an interface material in a very simple trilayer cell designed to enable the careful comparison of the performance of the new functional poly(thiophene) with standard, unfunctionalized poly(3-hexylthiophene) (P3HT) (Figure 2a). A 50 nm-thick solid titania film was deposited onto glass substrates coated with fluorine-doped tin oxide (FTO). A 5 nm layer of **1** was spin-coated onto the titania film and heated at 210 °C for 45 min to eliminate the protecting groups. As the resulting polymer **1a** film was insoluble in common organic solvents, a 50 nm layer of P3HT could then be spin-coated on top, followed by evaporation of an 80 nm silver top electrode. The trilayer device (FTO/TiO<sub>2</sub>/polymer **1a**/P3HT/Ag) was then annealed at 150 °C for 4 h to improve the contact between P3HT and the silver electrode. For comparison, we also made devices without polymer **1a** (FTO/TiO<sub>2</sub>/P3HT/Ag).

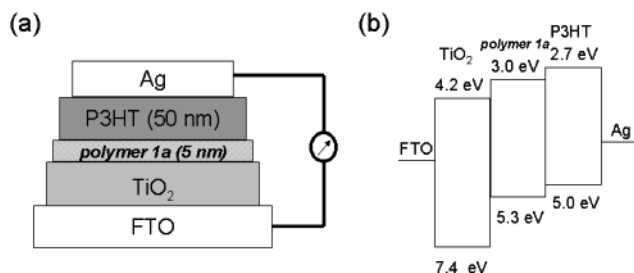
As Figure 3 shows, the device containing a layer of polymer **1a** shows a 3-fold increase in photocurrent, compared to the control without **1a**. Under 39 mW/cm<sup>2</sup> 514 nm illumination, the FTO/TiO<sub>2</sub>/

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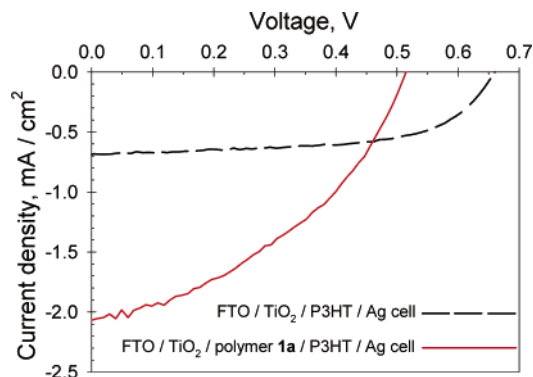
<sup>‡</sup> Stanford University.



**Figure 1.** Thermolysis of polymer **1**. (a) Thermogravimetric analysis of **1** heating from 25 to 200 °C at 10°/min and holding at 200 °C for 60 min. A mass loss of 28% vs 32% calcd was observed. Infrared spectra of **1** before (b) and after (c) heating at 200 °C for 20 min. Ester is converted to carboxylic acid during the course of thermolysis.



**Figure 2.** Device architecture (a) and energy diagram (b) of the FTO/TiO<sub>2</sub>/polymer **1a**/P3HT/Ag cell.



**Figure 3.**  $I$ - $V$  curves of FTO/TiO<sub>2</sub>/polymer **1a**/P3HT/Ag cell (solid line) and FTO/TiO<sub>2</sub>/P3HT/Ag cell (dashed line) under 39 mW/cm<sup>2</sup> 514 nm illumination.

**1a**/P3HT/Ag cell has an external quantum efficiency (EQE) of 12.6%,  $V_{oc}$  of 0.52 V,  $I_{sc}$  of 2.06 mA/cm<sup>2</sup>, ff of 0.40, and power efficiency of 1.10%, while the control cell (FTO/TiO<sub>2</sub>/P3HT/Ag) has an EQE of 4.2%,  $V_{oc}$  of 0.66 V,  $I_{sc}$  of 0.68 mA/cm<sup>2</sup>, ff of 0.60, and power efficiency of 0.69%.

The enhancement in photocurrent upon introduction of polymer **1a** may be attributed to several factors. The removal of solubilizing groups results in the higher chromophore density, manifesting itself

in the higher light absorption coefficient of **1a** compared to that of P3HT (see absorbance spectra in Supporting Information). Moreover, **1a** is likely to have a larger exciton diffusion length than P3HT, since the shorter average interchain distance in **1a** can contribute to a faster energy transfer from the excited polymer chain onto the next one.<sup>8</sup> In addition, we cannot rule out the possibility that the chelation of -COOH groups of polymer **1a** to the TiO<sub>2</sub> contributes to this enhancement by promoting forward interfacial electron transfer and eliminating the subconducting band trap sites, much in the same manner as in the Grätzel-type solar cells.<sup>9</sup> In addition, it is possible that the enhancement in photocurrent is partially due to the cascade charge transfer along the LUMOs of P3HT, **1a**, and TiO<sub>2</sub> (Figure 2b). We are currently studying substituted polythiophenes, in which energy effects and interaction effects can be separated, to help us better understand our observations.

The synthesis of polythiophenes with removable solubilizing groups allows access to processable polymers with tunable electronic and chemical properties. These polymers show promise as interface materials in solution-processed multilayer solar cells.

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**Supporting Information Available:** Complete experimental procedures and characterization of **1–3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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