



Tailoring properties of the photoactive layer through blending polymers with different functional groups



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ABSTRACT

Opportunities for fine-tuning conjugated polymer properties are needed to continue enhancing photovoltaic performance. Herein an amide- or ester-functionalized 3-fluorothiopheno[3,4-*b*]thiophene (FTT(N) or FTT(E)) were used in alternating copolymers with benzo(1,2-*b*:4,5-*b'*)dithiophene (BDT). The amide-functionalized polymer had a blue-shifted absorption spectrum and was blended with the ester-functionalized polymer in photovoltaic devices in an effort to increase light absorption of the photoactive layer. A 50:50 blend of the two polymers resulted in unfavorable morphology, leading to decreased power conversion efficiency (PCE), however, the blended mixture had a slightly enhanced stability relative to devices containing a single PBBDT-FTT(E) polymer. Reducing the loading of the amide-functionalized polymer, PBBDT-FTT(N), to 3 wt.% led to a certified PCE of 10.1%. To allow a higher loading of the FTT(N) monomer in the photoactive layer, a random copolymer containing both FTT(N) and FTT(E) was also prepared, which exhibited broader absorption and reached a PCE of 7.9%.

1. Introduction

The potential for low-cost, solution-processable photovoltaics on organic plastic substrates has spurred wide interest in the development of light harvesting conducting polymers [1–5]. Generating sufficient conversion of light to electrical energy is a critical challenge for the organic photovoltaic (OPV) charge generation mechanism. This energy transfer first requires the absorption of light by the photoactive layer materials, primarily driven by the donor polymer. In general, the more light absorbed (i.e. layer extinction coefficient) and the greater the spectral overlap of the absorbing polymer with the solar spectrum, the higher the short-circuit current density (J_{sc}) in devices.

Decreasing the bandgap is a common method for improving the number of photons absorbed by the photoactive layer. This can be achieved through polymer design by using alternating electron-donating (D) and electron-accepting (A) units in the polymer backbone [6]. Only a few D-A polymers have been used in single junction organic photovoltaics exceeding 10% power conversion efficiency (PCE) [7–9]. Broadening the absorption range allows for additional photon absorption, which may provide an avenue for further improvements to device performance. Approaches used for increasing light absorption in OPVs include the addition of plasmonic particles [10], using an inverted structure [11], absorption of the acceptor material [12], photoactive layer post-processing techniques [1], semiconducting random

copolymers [13–20] and ternary blends [21–26].

Using the design of the copolymer to influence the absorption properties is advantageous because the monomer composition can also be used to simultaneously influence the film morphology and molecular packing [27–29]. A random copolymer approach allows for the tailoring of the polymer properties, but can be disruptive to the electron delocalization across the polymer backbone [14,19]. In contrast, mixing multiple well-defined polymers with complementary absorption together in a blend system can be used to widen the absorbance bandwidth, and under ideal energy alignment and absorption conditions has been predicted to increase the PCE by up to 40% [30]. Experimentally, this approach has been accomplished by blending two donor polymers [21–24], two acceptor materials [25,26], and by combining semi-crystalline and crystalline materials [23,31]. These approaches have been used to demonstrate 20–30% improvement in blended device performance compared to single polymer systems [21].

Another approach to enhance the absorption bandwidth is to modify the sidechains while maintaining the polymer backbone. Changing the functionality of the side chains from linear or branched alkyl chains, to containing electron donating or accepting moieties can change the absorption properties of the polymer [32]. This approach has been successfully applied to the terminal groups of small molecules, where changing from an ester to amide functionality resulted in a 26–70 nm hypsochromic shift in the solid state absorbance spectrum depending on

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the alkyl chain used [33]. The origin of the shift was due to the weaker electron withdrawing effect of the polar amide terminal group.

Copolymers containing benzo(1,2-*b*:4,5-*b'*)dithiophene (BDT) and 3-fluorothiopheno[3,4-*b*]thiophene (FTT) have been widely studied for use in organic photovoltaics, achieving high PCE [4,34–37]. In this study, polymers containing an amide-functionalized FTT monomer are prepared and characterized for the first time. In an effort to broaden the absorption spectrum, a random copolymer containing both the amide- and ester-functionalized FTT is prepared and compared to that of polymer blends of the respective homopolymers. A high, externally-certified PCE of 10.1% is obtained for a device containing a 3 wt.% loading of the amide-functionalized polymer.

2. Experimental details

2.1. Reagents and instrumentation

The acceptor, [6,6]-phenyl-C70-butyric acid methyl ester (PCBM), was purchased from SES Research. The transparent cathode, indium tin oxide (ITO) was purchased from Thin Film Devices, Inc. The monomer and polymer synthesis is described in the Supplementary material. All other solvents (anhydrous where possible) and materials were acquired from Sigma-Aldrich unless otherwise specified. Absorption spectroscopy was performed with an Agilent 8453 spectrophotometer. A blank glass slide background was subtracted from all spectra. Gel permeation chromatography (GPC) measurements were obtained on an Agilent high temperature PL-GPC 220 system with three 300 × 7.5 mm PL gel 10 μm Mixed-B LS column set. In order to avoid strong aggregation, the polymer samples were first dissolved in the mobile phase trichlorobenzene at 130 °C for 90 min to prepare a 3 mg/mL solution concentration. Occasionally, agitation was used to help the dissolution. The instrument was run at 160 °C with trichlorobenzene (125 ppm, BHT) as the mobile phase, at the flow rate of 1.0 mL/min. The injection volume was 100 μL and the run time was 65 min. Refractive index, light scattering 15°/90° and viscometer were used for detection.

Atomic force microscopy (AFM) was performed with a Veeco Multimode Scanning Probe Microscope using Digital Instruments Nanoscope V electronics. The backside of each sample was mounted to a stainless steel specimen disc (430 SS, 15 mm dia.) by a nonconductive adhesive. Measurements were performed in tapping mode with a MikroMasch HQ:NSC14/AL BS aluminum coated AFM tip, with a resonance frequency of 160 kHz and a force constant of 5 N/m.

OPV devices with an active area of 0.088 cm² were tested under AM 1.5G 100 mW/cm² conditions with a Newport Thermal Oriel 91192 1000 W solar simulator (4" × 4" illumination size). The current density – voltage curves were measured using a Keithley 2400 source meter. The light intensity was calibrated with a crystalline silicon reference photovoltaic (area = 0.4957 cm²) fitted with a KG-5 filter (calibrated by the Newport to minimize spectral mismatch). The average and standard deviation of devices are reported in tables.

External quantum efficiency measurements were made using an Oriel quantum efficiency measurement kit. A 300 W xenon lamp was used as the illumination source. A 74125 Cornerstone monochromator was used to separate the light into different wavelengths. A silicon diode reference detector was used to calibrate the lamp emission. A Merlin lock-in amplifier was used to detect the power from the reference and OPV sample cells.

2.2. Solar cell device fabrication

Zinc oxide sol-gel solutions were prepared by dissolving zinc acetate dihydrate (1 g) in 2-methoxyethanol (10 mL) with ethanolamine (276 μL). Solutions were stirred for a minimum of 8 h before use. The photoactive layer consisted of the polymer, or a blend of two polymers, and acceptor PCBM at a ratio of 1:1.6 (polymer(s):PCBM) in *o*-xylene. Polymer blend solutions were prepared as described in the

Supplementary material.

ITO patterned glass substrates were cleaned by successive 10 min cycles using ultra-sonication, using detergent, deionized water, acetone, and isopropanol. The freshly cleaned substrates were left to dry overnight at 80 °C. Preceding fabrication, the substrates were further cleaned for 1 min in a UV-ozone chamber and the electron transport layer was immediately spin coated on top. The zinc oxide sol-gel solution was filtered directly onto ITO with a 0.25 μm poly(tetrafluoroethylene) filter and spin cast at 5000 rpm for 40 s. Films were then annealed at 170 °C for 15 min and directly transferred into a nitrogen-filled glove box. The photoactive layer was deposited on the electron transport layer via spin coating at 1200 rpm for 40 s and directly transferred into a closed glass petri dish to solvent anneal for 1 + h. After solvent annealing, the substrates were loaded into the vacuum evaporator where MoO_x (hole transport layer) and Ag (anode) were sequentially deposited by thermal evaporation. Deposition occurred at a pressure of 1 × 10⁻⁶ Torr. MoO_x and Ag had thicknesses of 3.5 nm and 120 nm, respectively. The deposition rate for the MoO_x was 0.8–1.0 Å/s and Ag was 1.5–2 Å/s. Samples were encapsulated with glass using an epoxy binder and treated with UV light for 3 min.

2.3. Lifetime measurements

The stability of OPV devices was measured under constant illumination using a temperature-controlled lifetime setup. A CP-200TT cold plate cooler from TE Technology maintained the substrate temperature at a maximum of 25 °C. Illumination of devices was performed under an OAI TriSol Continuous Steady State TSS-208, class AAA, 1000 W/m² solar simulator with illumination area of 208 mm × 208 mm. The light intensity was calibrated with a crystalline silicon photovoltaic cell (with KG-5 visible color filter) certified by Newport to minimize spectral mismatch. Devices were placed under illumination with a 455 nm longpass filter from Edmund Optics for 7 h followed by a 1 h dark rest period. The photovoltaic performance of devices was measured using the same method above.

3. Results and discussion

3.1. Polymer synthesis and characterization

The structures of the polymers in this study are presented in Fig. 1. The synthesis of monomers and polymers is described in the Supplementary material. Alternating copolymers PBBDT-FTT(E) and PBBDT-FTT(N), and random copolymer PBBDT-FTT(R), were prepared with palladium-catalyzed Stille polymerization conditions. The molecular weights of the polymers ranged from 15 to 30 kDa. Equal proportions of both the FTT(E) and FTT(N) monomers were used in the random copolymer to increase the absorption contribution from both moieties.

The optical properties of the polymer thin films were measured by solid-state UV–vis absorption spectroscopy as shown in Fig. 2. Both polymers have two characteristic absorption peaks, with the lower energy peak having higher intensity. The λ_{max} of PBBDT-FTT(E) and PBBDT-FTT(N) are 705 nm and 668 nm, respectively. The blue shift in absorption for PBBDT-FTT(N) can be attributed to the polar electron withdrawing amide functional group, as observed in other materials [33]. Other electron withdrawing groups on the side chains have been shown to lower the lowest unoccupied molecular orbital level and decrease the bandgap [38]. When the amide- and ester-functionalized FTT monomers are combined with BDT to form the random copolymer PBBDT-FTT(R), the bandwidth of the polymer is slightly broadened, with a maximum absorbance of 684 nm. Blending 10% and 20% of PBBDT-FTT(N) with PBBDT-FTT(E) increases the absorption in the 550–675 nm range concomitant with the amide homopolymer absorption as shown in Fig. S11.

To explore broadening the absorption range of the polymer active layer by physically mixing the differently substituted polymers, the

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