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All-Polymer Photovoltaic Devices of Poly(3-(4-*n*-octyl)-phenylthiophene) from Grignard Metathesis (GRIM) Polymerization

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The demand for cheap, shape-conforming and lightweight solar energy harvesting materials has motivated the development of organic polymer photovoltaics (OPVs). A well studied system is the solution processable poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:$PC_{61}BM$) bulk heterojunction (BHJ) OPV. With efficiencies of 4−5%, P3HT has demonstrated exceptional optoelectronic properties.[1a] However, for OPVs to compete with commercial inorganic PVs, more of the solar spectrum will have to be harvested while achieving larger open-circuit voltages (V_{oc}).[1b] For these reasons, poly[3-(4-*n*-octyl)-phenylthiophene] (POPT)[2] is an attractive alternative to P3HT. POPT has increased spectral breadth compared to P3HT (Figure 1); exhibits a lower-lying HOMO,[3] correlated to increased V_{oc}[4] and air stability;[5] and has a phenyl ring useful for tuning polythiophene optoelectronic properties.[6] In fact, POPT has been investigated for use in OPVs by Friend *et al.* in 1998 using a laminate bilayer POPT:poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CN-PPV) device, which yielded the highest photocurrent of its time with peak EQE of 28%.[7] However, more thorough studies of POPT and derivatives have yielded only modest OPV performance ($\eta <$ 0.5%).[8]

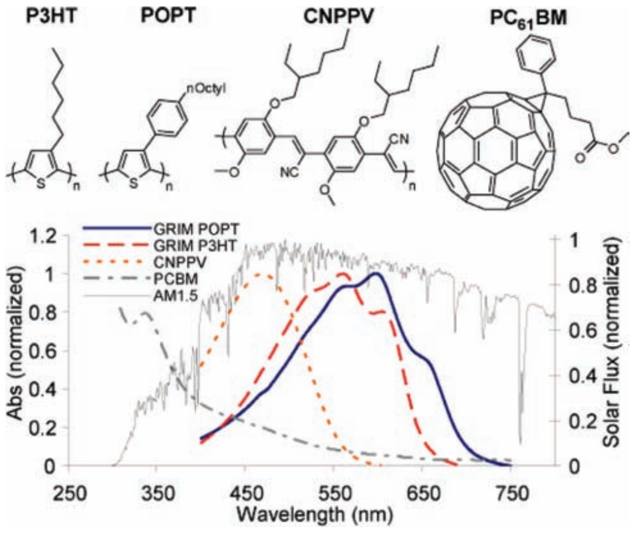

Figure 1. Material structures and absorption spectra with overlaid AM1.5 photon flux.

One barrier to high efficiency may have been the oxidative method used to synthesize poly(3-phenylthiophene) semiconductors. It is known that polythiophene polymerization method[9a,c] and regioregularity[9b,c] critically impact the optical and electronic properties of the resulting material, which in turn affects OPV performance. Grignard metathesis (GRIM), which is a redox neutral organomagnesium/aryl-halide cross-coupling polymerization, has been a particularly successful method for P3HT synthesis.[10] GRIM yields high number average molecular weight (M_n), low polydispersity index (PDI), and regioregular (RR) P3HT.

For this study, POPT was polymerized from the 2-bromo-5-iodo-3-(4-*n*-octyl)thiophene monomer in ∼50% final yield with a modified GRIM procedure. Due to the steric and electronic effects of the 3-phenyl ring, elevated metal−halogen exchange and polymerization temperatures were required to achieve a suitable polymer yield and molecular weight. POPT with M_n up to 75 kDa and PDI < 1.2 was obtained after Soxhlet purification. The purified polymer was >99% RR as determined by NMR. All subsequent electronic and device characterization was performed with 35 kDa POPT (see Supporting Information, SI).

As spun-cast from high boiling point solvents, thin films of GRIM POPT display UV−Vis vibronic structure unlike oxidatively synthesized POPT, which does not show such structured absorption without additional processing steps.[2a] This difference in processing properties qualitatively illustrates the distinctive improvement to POPT afforded by the GRIM synthetic approach. We have also determined, for the first time, hole mobility values of 1×10^{-4} and 0.05 $cm^2/(V \cdot s)$ for POPT using space-charge limited current and field effect transistor measurements, respectively. No change in mobility was observed upon thermal annealing. These mobility values are similar to those obtained for P3HT and suggest that hole extraction in OPV devices is not likely to differ much between these polythiophenes.

As a standard test for OPV material quality, we fabricated POPT:$PC_{61}BM$ (1:1) BHJ devices. A peak efficiency of 3.1% under AM 1.5 illumination with an intensity of 100 mW cm^{-2} and an average efficiency of 2% was achieved after 1 min of thermal annealing at 180 °C. These devices are ostensibly limited by the blend morphology: efficiencies decrease after longer annealing times (5−30 min), and TEM characterization of the optimized film morphology showed gross phase segregation (SI).

The relatively high solvent resistance of GRIM POPT resulting from its high M_n and regioregularity enables a better examination of the all-polymer system first explored by Friend.[7] Therefore, CNPPV can be spin-coated directly on top of a POPT film using solvents such as tetrahydrofuran or ethyl acetate which are too weak to dissolve POPT, leading to bilayer devices as opposed to the previously explored laminate design. A peak efficiency of 2.0% was achieved with this system after 2 hrs of thermal annealing at 110 °C after electrode deposition (average η = 1.5%). This

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constitutes the highest reported efficiency to date for a solution processed all-polymer OPV.[11]

Significantly, similar all-polymer devices optimized from GRIM P3HT yielded a max efficiency of 0.93% (Figure 2A) with an average of 0.75%. This lower efficiency in P3HT devices is due to a reduction in the short circuit current (J_{sc}). The increased J_{sc} exhibited by the POPT/CNPPV devices does not derive from increased absorption, as illustrated by the absorption spectra in Figure 2C. Under optimized conditions, the POPT/CNPPV bilayer absorbs ~75% of the light but exhibits approximately twice the photocurrent of the P3HT/CNPPV bilayers with improved photocurrent across the entire absorption spectrum of the device (Figure 2D). Additionally, all-polymer POPT:CNPPV blend devices were fabricated but did not perform as well as the bilayer devices, making a POPT/P3HT comparison hard to evaluate in that architecture. As neither light absorption nor hole mobility can explain this striking difference in photocurrent, we examined the electronic driving forces behind charge separation.

Considering that OPVs require a donor/acceptor interface to separate excitons and generate free charges, understanding charge separation is critical for advancing the field of OPVs.[12] Recent literature has attempted to relate ΔG_{CS}^{rel} (the relative free energy of charge separation) to the excited state energy (E_s) and the relative band offsets in the abbreviated Weller equation $\Delta G_{CS}^{rel} = E_S - (\mathrm{HOMO_{donor}} - \mathrm{LUMO_{acceptor}})$.[12a] Values for ΔG_{CS}^{rel} calculated from this equation correlate well with the observed short circuit currents for several polymer:PCBM devices.[12a] However, in our case this equation predicts a larger driving force for charge separation in the P3HT/CNPPV device, as ΔG^{rel} is 0 eV for POPT/CNPPV but is 0.3 eV for P3HT/CNPPV (Figure 2B). The large difference in J_{sc} between these polythiophene devices indicates that charges are either extracted or generated more efficiently from the POPT device, contrary to measured hole mobilities, light absorption, and predicted ΔG^{rel}. Notably, the abbreviated Weller equation does not include the lattice polarization energy or Coulombic attraction between bound electron−hole pairs. We believe these neglected terms are important in explaining the increased J_{sc} in POPT/CNPPV devices.

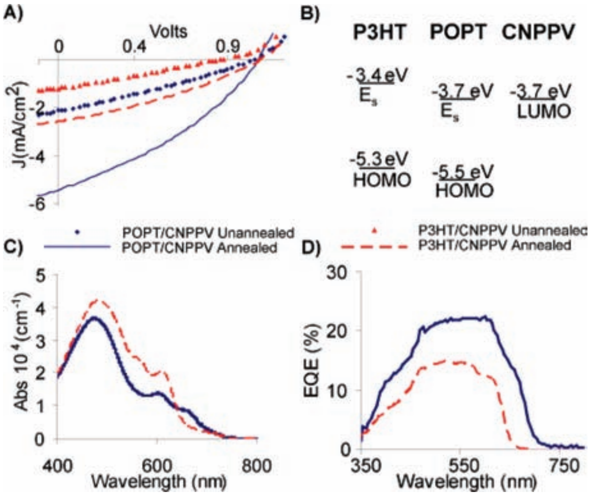

Figure 2. (A) $J-V$ curves for POPT and P3HT devices under AM 1.5 100 mW/cm^2 illumination. (B) Material energy band levels. (C) Absorption spectra of bilayers at optimized thicknesses for devices. (D) EQE plots of optimized devices.

In conclusion, it is clear that the more controlled GRIM method we have used to prepare POPT affords a polymer with desirable electronic and structural properties for application to OPVs. The AM 1.5 efficiency of 2% achieved with POPT/CNPPV is the highest reported to date for an all-polymer based device. POPT outperformed P3HT in all-polymer devices due to a doubling of the J_{sc}. At individually optimized bilayer thicknesses, the superior performance of POPT vs P3HT in the devices with CNPPV is counter to expectations based on absorption, charge mobility, and energy level comparisons. This emphasizes the importance of understanding charge separation processes in OPV devices, particularly the effects of Coulombic attraction and lattice polarization energy. Additionally, the synthetic simplicity and tunability of the phenylthiophene class of polymers makes POPT and other 3-phenyl derivatives attractive materials for further exploration of structure−property relationships in the field of polymer-based solar cells.

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Supporting Information Available: Synthetic and device fabrication procedures, NMR, SEC, CV, mobility, and TEM data. This material is available free of charge via the Internet at http://pubs.acs.org.

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