Random Poly(3-hexylthiophene-*co*-3-cyanothiophene) Copolymers with High Open-Circuit Voltage in Organic Solar Cells

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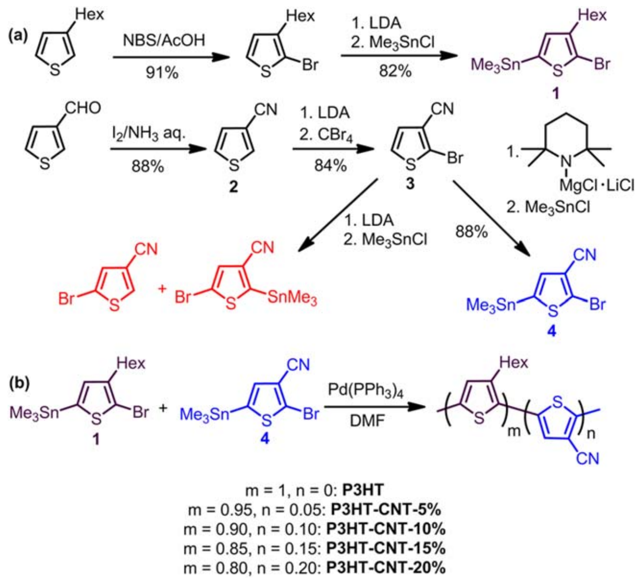
State-of-the-art organic photovoltaics (OPV) based on polymer donors and fullerene acceptors[1–3] have reached efficiencies exceeding 9% in bulk heterojunction (BHJ) solar cells.[4] However, further efficiency increase, where efficiency is defined as $\eta = (J_{sc} \times V_{oc} \times FF)/P_{in}$ (J_{sc} is short-circuit current density, V_{oc} is open-circuit voltage,[5] FF is fill factor,[6] and P_{in} is solar input power), is limited by the interplay of J_{sc} and V_{oc}, and the necessity to maintain high FF.[1,7] High J_{sc}, exceeding 18 mA cm^{-2}, is achieved for a number of polymer donors, while the V_{oc}, which is roughly proportional to the difference between donor HOMO level (HOMO^D) and acceptor LUMO level (LUMO^A), is still limited to around 0.75 V for the majority of state-of-the-art donors, but can approach 1 V in some cases.[1] Furthermore, the vast majority of the most efficient OPVs utilize polymers which require complicated, multistep syntheses.[1] As a result, polymers with a deep-lying HOMO level and simple synthetic route are in great demand. Here, we report four novel random poly(3-hexylthiophene) (P3HT)-based copolymers containing 5–20% of 3-cyanothiophene (CNT) with deep-lying HOMO levels. We have previously shown that random copolymers offer an effective route to tune polymer properties while maintaining simplicity in synthesis.[8] Polymers were synthesized in only a few steps, as opposed to the lengthy synthesis typical for polymers with high V_{oc}, and upon blending with PC$_{61}$BM, organic BHJ solar cells showed significant V_{oc} increase from 0.6 V for 0% of CNT to 0.81 V at only 15% of CNT in the polymer backbone. Furthermore, J_{sc} and FF were found to remain high and comparable to P3HT:PC$_{61}$BM at similar film thicknesses.

The synthesis of all poly(3-hexylthiophene-*co*-3-cyanothiophene) (P3HT-CNT) polymers was carried out using Stille polycondensation[9] of the stannylated monomers **1** and **4** [Scheme 1(a)], as illustrated in Scheme 1(b). Previously reported monomer **1** was prepared from 3-hexylthiophene (3HT)[10] in two steps, the first step being the electrophilic substitution in the second position of the thiophene ring with bromine using NBS and the second step, lithiation–stannylation at −78 °C in the fifth position. For the goal of preparing the regioregular random copolymers of 3HT and CNT, previously unknown monomer **4** was designed. Despite the structural similarity between monomers **1** and **4**, the strategy for obtaining **4** was very different from the synthesis of **1**. As a starting point, CNT **2** was prepared with a high yield using an established protocol for converting aromatic aldehydes into nitriles.[11] The selective bromination of **2** in the second position via an electrophilic substitution pathway is very difficult to accomplish due to the electron-deficient nature of CNT. Although there are no reports of direct conversion of CNT into 2-bromo-3-cyanothiophene (**3**) to the best of our knowledge, we employed a lithiation–bromination approach that has previously been used for the similar electron-deficient thiophene-3-carboxylic acid[12] to yield **3** selectively in high yield.

The conversion of **3** into monomer **4** could not be accomplished via lithiation–stannylation. The major components of the isolated mixture of products of the lithiation–stannylation reaction were 2-bromo-4-cyanothiophene and 2-trimethylstannyl-3-cyano-5-bromothiophene, which indicates isomerization of the lithiated species even at −78 °C. In order to overcome this challenge, the more stable magnesiated intermediate species was generated with the recently developed Knöchel–Hauser base,[13] which was subsequently quenched with Me$_3$SnCl to yield the target monomer **4** selectively in high yield. This new synthetic strategy is significant because it allows for the preparation of the individual

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Synthesis of (a) monomers and (b) polymers P3HT-CNT-5%, P3HT-CNT-10%, P3HT-CNT-15%, and P3HT-CNT-20%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

metallated cyanothiophene monomer which upon copolymerization with **1** yields regioregular random copolymers with a greater variety of linkage patterns between the monomers in contrast with previously reported conjugated polythiophenes containing the CNT unit[14] which were polymerized using a metallated 3-alkylthiophene-CNT dimer such that CNT-CNT linkages are forbidden.

All polymers showed similar molecular weights (M_n) between 10 and 18 kg mol^{-1}, as shown in Table 1, which is consistent with the molecular weight range previously found optimal for photovoltaic performance in reported random and semi-random polymers.[1] The resulting polymers are represented by the acronyms P3HT-CNT-X%, where the percentage of CNT monomer is indicated, giving P3HT-CNT-5%, P3HT-CNT-10%, P3HT-CNT-15%, and P3HT-CNT-20% [Scheme 1(b)]. The choice of CNT unit was influenced by the known effect of CNT to lower the position of the HOMO level of polymers.[14] The random incorporation[8] of different amounts of CNT monomer in the polymer backbone allowed study of a model system based on rr-P3HT and its effect on the polymer's HOMO level, UV–vis absorption and crystallinity, as well as the V_{oc} and device performance in organic solar cells.

The HOMO energy levels of polymers were measured by cyclic voltammetry (CV) with ferrocene as a reference (Fc/Fc$^+$ = 5.1 eV).[15] As shown in Table 1, the increase of the CNT content in the polymer backbone leads to a decrease in the position of the polymer HOMO from 5.2 eV for P3HT to 5.3 for all P3HT-CNT polymers. The saturation of the HOMO level suggests likely aggregation of the polymer chains with increasing CNT content, which is supported by UV–vis measurements (discussed below), thus preventing further HOMO level decrease.[16] Therefore, we can conclude that even a small amount of the CNT is enough to effectively lower the position of the HOMO level and as a result affect the V_{oc}.

The optical properties of the P3HT-CNT polymers in *o*-dichlorobenzene (*o*-DCB) solutions and thin films were studied using UV–vis spectroscopy as shown in Figure 1(a) and Supporting Information. Despite the pronounced effect on the HOMO levels, incorporation of CNT in the polymer backbone has a minor effect on the absorption profiles and optical band gaps of polymers in thin films. All polymers exhibit strong absorption in the visible with peaks in the range of 550–563 nm and absorption onsets of about 1.9 eV. The peak intensities decrease going from P3HT to P3HT-CNT-15% and then increase beyond that of P3HT in the case of P3HT-CNT-20%. The increase of the absorption strength for P3HT-CNT-20% in thin films can be attributed to the increase of aggregation at room temperature, which is illustrated by a strong vibronic shoulder in dilute solution (see Supporting Information). Another interesting feature in the thin film absorption spectra of all polymers is the presence

TABLE 1 Molecular Weights (PDIs), Electrochemical HOMO Values, Optical Band Gaps, SCLC Mobilities, and Photovoltaic Properties of P3HT, P3HT-CNT-5%, P3HT-CNT-10%, P3HT-CNT-15%, and P3HT-CNT-20%.

Polymer:PC$_{61}$BM (Ratio)[a]	M_n[b] (kg/mol) (PDI)	HOMO[c] (eV)	E_g[d] (nm/eV)	μ[e] (cm^{2}V^{-1}s^{-1})	J_{sc}[f] (mAcm^{-2})	V_{oc} (V)	FF	η (%)
P3HT (1:0.9)	18 (2.5)	5.20	646/1.92	2.31×10^{-4}	9.20	0.60	0.57	3.15
P3HT-CNT-5% (1:1)	11 (1.9)	5.30	653/1.90	1.51×10^{-4}	7.02	0.72	0.58	2.96
P3HT-CNT-10% (1:1.3)	12 (2.4)	5.31	658/1.88	1.03×10^{-4}	8.16	0.75	0.55	3.33
P3HT-CNT-15% (1:1.3)	10 (2.1)	5.34	653/1.90	8.54×10^{-5}	7.56	0.81	0.55	3.28
P3HT-CNT-20%	14 (2.1)	5.31	654/1.87	6.15×10^{-5}	–	–	–	–

[a] All devices were spin-coated from *o*-dichlorobenzene (*o*-DCB) and stored under N_2 before aluminum deposition for 30 min.

[b] Determined by GPC with polystyrene as standard and *o*-DCB as eluent.

[c] Cyclic voltammetry (vs. Fc/Fc$^+$) in acetonitrile containing 0.1 M TBAPF$_6$.

[d] Calculated from the absorption band edge in thin films, $E_g = 1{,}240/\lambda_{edge}$.

[e] Measured for neat polymer films.

[f] Mismatch corrected.

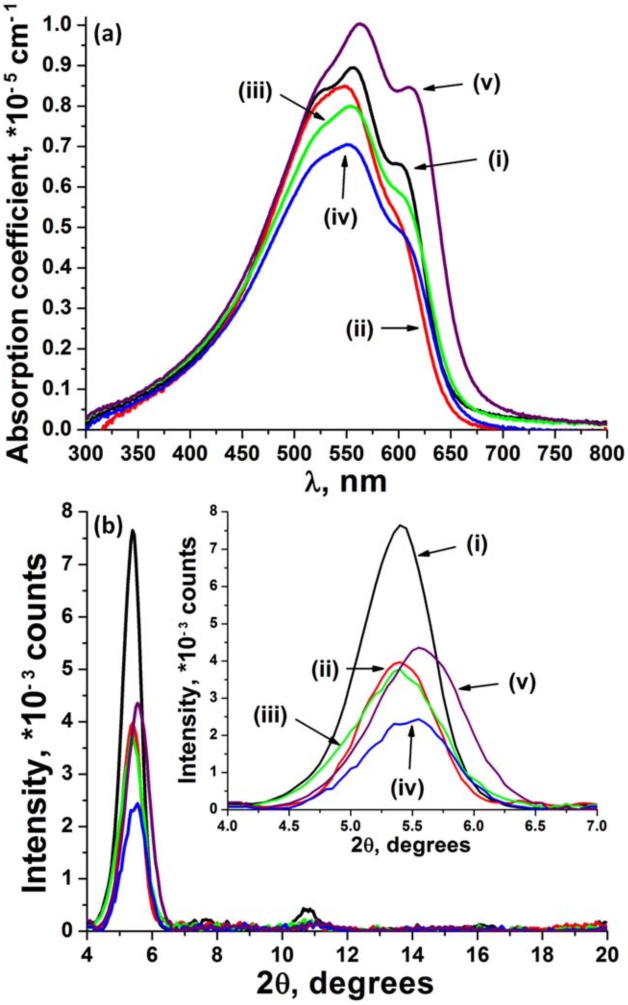


FIGURE 1 (a) UV–vis absorption spectra of polymers in thin films and (b) GIXRD patterns of thin films, where (i) is P3HT (black line), (ii) is P3HT-CNT-5% (red line), (iii) is P3HT-CNT-10% (green line), (iv) is P3HT-CNT-15% (blue line), and (v) is P3HT-CNT-20% (purple line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the vibronic features. The presence of the vibronic shoulder in the UV–vis of the polymer thin films is attributed to the interchain vibrational absorption induced by a high degree of ordering and strong interchain interaction.[17] The ordering in the solid state is further supported by the strong red-shift going from solution to thin films observed for all polymers.

Grazing-incidence X-ray diffraction (GIXRD) was used to further study the semicrystalline nature of the CNT-containing polymers. All polymer films prepared under identical conditions were found to be semicrystalline, as can be seen in Figure 1(b), with an interchain distance (100) of 16.4 Å for P3HT, P3HT-CNT-5%, and P3HT-CNT-10% and slightly smaller interchain distance of 15.9 Å for P3HT-CNT-15% and P3HT-CNT-20%. The peak intensities for P3HT-CNT-5%, P3HT-CNT-10%, P3HT-CNT-15%, and P3HT-CNT-20% were observed to follow the same trend as in case of UV–vis intensities; however, the P3HT peak was found to be about two times higher than that of CNT-containing polymers. Overall, CNT-containing polymers retain optical and semicrystalline properties of rr-P3HT, while HOMO energy levels are affected by the presence of the CNT.

The semicrystalline nature of P3HT-CNT polymers translated into high hole mobilities for neat polymers as measured using the space-charge limited current (SCLC) method.[18] As expected from the GIXRD data, the increase of the CNT monomer amount in the polymer backbone leads to a steady decrease of the hole mobility, as shown in Table 1. However, P3HT, P3HT-CNT-5%, P3HT-CNT-10%, and P3HT-CNT-15% still have hole mobilities in the range of $0.8–2.3 \times 10^{-4}$ $cm^2/(V*s)$. At the same time, the most crystalline among CNT-containing polymers, P3HT-CNT-20%, exhibits the smallest hole mobility of 6.15×10^{-5} $cm^2/(V*s)$. This decrease can be explained based on the crystallite sizes estimated using Scherrer's equation (see Supporting Information).[19] The smallest size of the crystallites in case of P3HT-CNT-20% leads to the increase of the lattice disorder and requires more frequent charge hopping from one crystalline domain to another, thus possibly increasing the loss mechanisms associated with charge trapping.[20]

The observed electro-optical, semicrystalline and charge transport characteristics of the P3HT-CNT polymers make them promising candidates for BHJ solar cells. Photovoltaic devices in a conventional device configuration ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Al were fabricated in air. Optimal processing conditions include slow solvent evaporation (solvent annealing) from the polymer:$PC_{61}BM$ blends after spin-coating and before aluminum deposition. The optimized polymer:$PC_{61}BM$ weight ratios for P3HT-CNT-5%, P3HT-CNT-10%, and P3HT-CNT-15% were found to be 1:1, 1:1.3, and 1:1.3, respectively, which is similar to the one of P3HT:$PC_{61}BM$ and is beneficial for achieving high currents.[1] P3HT-CNT-20% was found to be insoluble at the concentrations necessary for solar cell fabrication. Consistent with previous reports on random copolymers,[1] several batches of each polymer were used in solar cells and photovoltaic properties were found to be reproducible in all cases. Table 1 lists the average values of J_{sc}, V_{oc}, FF, and η obtained under simulated AM 1.5G illumination (100 mW cm^{-2}).

As expected from the deep-lying HOMO levels of the CNT polymers, the V_{oc} of the solar cells increases from 0.60 V for P3HT to 0.72 V for P3HT-CNT-5%, 0.75 V for P3HT-CNT-10%, and 0.81 V for P3HT-CNT-15%, as shown in Table 1. The difference between the HOMO level saturation and the constant V_{oc} increase for P3HT-CNT:$PC_{61}BM$ solar cells indicates a likely decrease in polymer aggregation in the polymer:$PC_{61}BM$ blends upon fullerene introduction, thus likely lowering the HOMO level of the P3HT-CNT polymers with the CNT amount increase.

Strong absorption in the visible and the semicrystalline nature of CNT-containing polymers translates into strong photoresponses (see Supporting Information) and consequently high J_{sc}, (Table 1) which are comparable to that for P3HT:PC$_{61}$BM. Small decreases of the J_{sc} for CNT-containing polymers can be attributed to different optimal polymer:fullerene ratios and similar, but unoptimized active layer thicknesses (80–90 nm) that do not account for the different fullerene loadings or polymer absorption coefficients. High FF, above 0.55, were obtained for all polymer:PC$_{61}$BM solar cells. High J_{sc} and FF are attributed to balanced and trap free charge transport through the bulk[6,21,22] and favorable morphology.[23,24] Further morphological studies, performed using transmission electron microscopy (TEM), confirmed the formation of similar bicontinuous blends with nanometer scale phase separation for all polymer:PC$_{61}$BM blends (see Supporting Information). As a result of high J_{sc} and FF, as well as enhanced V_{oc}, the efficiencies of P3HT-CNT:PC$_{61}$BM solar cells exceeded 3%, comparable to that for P3HT:PC$_{61}$BM while using the same thicknesses for the active layers.

In summary, we developed a new synthetic route and synthesized an easily attainable family of P3HT-CNT polymers with deep-lying HOMO levels, where the amount of CNT was varied from 5 to 20%. P3HT-CNT polymers preserved important properties of rr-P3HT, such as strong absorption in the visible, semicrystallinity and high hole mobility. In polymer:PC$_{61}$BM BHJ solar cells, high V_{oc} in the range 0.72–0.81 V was achieved, which together with high J_{sc} and FF showed promising efficiency.

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