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Poly(3-hexylthiophene)−CdSe Quantum Dot Bulk Heterojunction Solar Cells: Influence of the Functional End-Group of the Polymer

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The pending global energy crisis requires the development of new technologies that exploit the potential of renewable sources of energy, such as solar power. For example, inorganic semiconductor-based photovoltaic technology has reached the performance level of converting 30% solar energy into electric power.[1,2] Despite the high performance, inorganic photovoltaics based on crystalline silicon are still too expensive to compete with the conventional sources of electricity. While extensive research in the field of inorganic photovoltaics is expected to result in a decrease in their fabrication cost, polymer-based photovoltaics represent a very attractive alternative for low-cost, lightweight, large-area, and flexible solar panels.[3−5] The most used conjugated polymers in photovoltaic structures are regioregular poly(3-alkylthiophenes) and alkoxy-substituted poly(phenylenevinylenes), such as poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylenevinylene].[4] Because of their solubility in organic solvents, these polymers are suitable for casting from solution using wet-processing techniques, such as spin-casting, dip-coating, ink jet printing, screen printing, and micromolding.[4] Blending of two materials having donor and acceptor properties results in the formation of a bulk heterojunction.[4] Research has been directed toward four important types of bulk heterojunctions. The first type consists of a polymer−polymer heterojunction obtained by mixing of two conjugated polymers with offset energy levels. The second type is obtained by blending a conjugated polymer with (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) as a soluble electron acceptor, which currently shows the best performance.[2,6] Polymer/titania (TiO_2) photovoltaic cell represents the third type of bulk heterojunction, which has received attention due to the possibility of TiO_2 patterning into a continuous network for electron transport.[7,8] Conjugated polymer quantum dots can be considered the fourth type of bulk heterojunction solar cells. For example, CdSe nanocrystals with an electron affinity in the range 3.8−4.5 eV are suitable materials to act as electron acceptors when combined with conjugated polymers.[9−12] The band gap for quantum dots is controlled simply by adjusting the size of the dots.[13]

Semiconductor quantum dots (QDs) have attracted enormous interest in the past two decades due to their tunable optical and electronic properties. Remarkable efforts have been devoted to the synthesis of high-quality, defect-free QDs with narrow size distribution ($<5\%$).[13] These interesting properties of QDs have been employed for various applications including biosensing, light-emitting diodes, and photovoltaics.[14−17]

Poly(3-alkylthiophenes) are one the most attractive candidates for photovoltaic applications due to their opto-electronic properties, stability, and solution processability.[18] Poly(3-hexylthiophene) (P3HT) has shown hole mobilities as high as 0.1 $cm^2\ V^{-1}\ s^{-1}$ and crystallinities as a function of the processing conditions.[19,20] These are important parameters when considering photovoltaic applications where the effect of charge recombination should be minimized.

Solar cells incorporating inorganic nanocrystals and organic semiconducting polymers have some potential advantages over silicon-based cells, such as low cost, solution processability, and the possibility of obtaining flexible thin-film solar cells.[9,10,21−24] The ability to tune the band gap of QDs by simply controlling their size makes them promising candidates for photovoltaic applications.[25,26] Power efficiency as high as 2.8% have been reported using tetrapod-shaped CdSe with a poly(phenylenevinylene) derivative. [27] The dispersion of QDs in the polymer matrix, however, has been a major issue for an efficient charge transfer. The presence of functional groups such as amines can provide intimate contact between the polymer and the CdSe through covalent interactions. Such amine-functionalized P3HT have been blended with CdSe nanorods and showed a maximum efficiency of 1.4%.[11]

Here for the first time we report the synthesis of H/thiol-terminated P3HT from Br/allyl-terminated P3HT precursor (Scheme 1). Br/allyl-terminated regioregular poly(3-hexylthiophene) was synthesized by in situ end-functionalization of the *living* nickel-terminated polymer, as previously reported.[28−30] Br/hydroxypropyl-terminated regioregular poly(3-hexylthiophene) was synthesized by hydroboration/oxidation of the corresponding Br/allyl-terminated polymer.[31−34] Br/hydoxypropyl-terminated P3HT was converted to an acetyl-protected thiolpropyl-terminated P3HT by a Mitsunobu reaction, which subsequently was reduced with $LiAlH_4$.[35] ^1H NMR (Figure 1) and MALDI-TOF MS (Supporting Information) confirmed the successful end-group transformation. Thiols are known to have strong interactions with metals such as Au, Ag, and Cd.[36] Thiol end-groups were expected to interact with the CdSe surface, providing a better contact with the semiconducting polymer.

We studied the photovoltaic response of blends of H/thiol-terminated P3HT with spherical CdSe QDs and compared the experimental results with regioregular H/Br and Br/allyl-terminated P3HT. All the P3HT polymers used in this study have similar molecular weights ($DP_n = 60$). Prior to our work, several attempts have been made to directly modify QDs with functionalized P3HT.[37,38] Even though these reports have shown the successful modification of the QDs, the photovoltaic response of these materials have not been studied in detail.[37,38] Nearly monodispersed CdSe quantum dots have been synthesized using a reported procedure with slight modifications (experimental procedure given in the Supporting Information).[39] The CdSe QDs were treated with pyridine to replace trioctylphosphine oxide (TOPO) ligand and stored in pyridine for blend preparation. Solution UV−vis data showed no shift in absorption of the CdSe QDs, indicating that there is no oxidation or aggregation after the pyridine ligand exchange treatment (see Supporting Information for experimental details). The particle size of CdSe QDs was estimated to be ∼4 nm from

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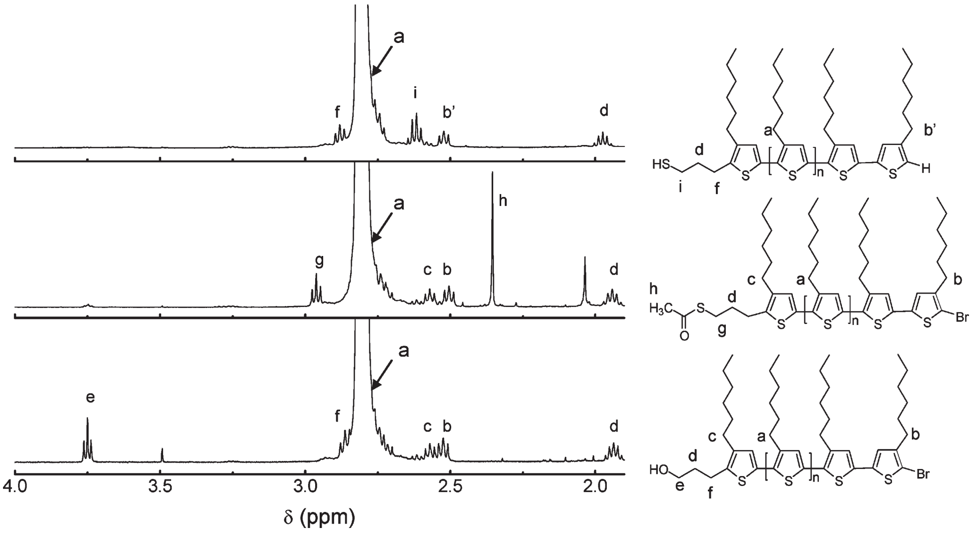
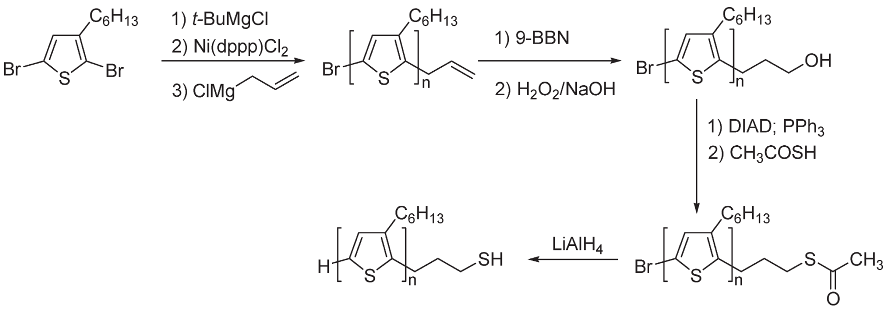


Figure 1. ^{1}H NMR spectra (500 MHz, $CDCl_3$) (expansion in the 1.9−4 ppm region) of Br/hydroxypropyl-terminated (bottom), Br/propylthiolacetyl-terminated P3HT (middle), and H/propylthiol-terminated P3HT (top).

Scheme 1. Synthesis of H/Thiol-Terminated Regioregular Poly(3-hexylthiophene)



TEM images (see Supporting Information). When CdSe QDs were mixed with P3HT with various end-groups (H/Br, Br/allyl, and H/thiol) in a weight ratio of 5:1, the formation of close-packed clusters was observed in the AFM images of the blends. These clusters were observed for both H/thiol- and Br/allyl-terminated P3HT. Phase segregation was driven by mixing relatively polar pyridine-treated CdSe QDs with nonpolar P3HT. Cluster formation was also observed for P3HT/polymer blends but at high CdSe QDs concentrations.[24] Solid-state UV−vis of H/Br, Br/allyl-P3HT, and H/thiol-P3HT shows three vibronic shoulder peaks between 500 and 650 nm. The UV−vis spectra of both pristine Br/allyl-P3HT and Br/allyl-P3HT-CdSe blend (Supporting Information) show the presence of the vibronic structures, indicating the conservation of the π stacking of the polymer after blending.

Six device coupons were fabricated for this study, with four devices per coupon. The blends of P3HT-CdSe (active layer) were spin-coated such that the film would be wet (orange) when the spin cycle was completed. This allowed the comparison between samples that were directly annealed (DA) after spinning versus coupons that were placed in a covered Petri dish to allow "slow evaporation" (SE) of the solvent (Supporting Information). This solvent annealing effect has been reported to increase the device efficiency for the P3HT/PCBM system.[40]

Table 1 and Supporting Information show a comparison of the averaged $I-V$ data obtained from the devices, where power conversion efficiencies (PCE) as high as 0.9% and 0.6% were measured for the Br/allyl- and H/thiol-terminated P3HT, respectively. The Br/allyl-P3HT devices showed the highest PCE for both the SE and the DA sample sets. The open-circuit voltage (V_{oc}) and fill factor (FF) of the devices were fairly similar between the SE and DA coupons and between the different polymers. However, some variation in the average V_{oc} has been observed, though all coupons had at least one device with a V_{oc} less than 700 mV, but the short-circuit current/series resistance were markedly different. The coupons that were allowed to "solvent-anneal" in the Petri dish showed efficiencies approximately 2−10 times greater than corresponding DA coupons. The H/thiol-P3HT and H/Br−P3HT devices both exhibited a 5−10 times increase in short-circuit current (J_{sc}) with a corresponding drop in series resistance (R_s) with the SE process compared to the DA. However, the H/allyl-P3HT devices did not show such a dramatic increase in performance with the SE step, but the short-circuit current increased by ~50% and the PCE nearly doubled. This experimental result requires further investigation to understand if there is any correlation between the film uniformity of the blend layer from DA and SE experiments.

The film thickness for SE coupons ranged between 135 and 160 nm, while the thickness for the DA samples ranged from 85 to 125 nm, as measured by profilometry. The higher thickness of SE samples could indicate a larger aggregation of CdSe-P3HT blends during the slow evaporation process.

AFM images shown in Figure 2 and Supporting Information indicate that CdSe-H/allyl-P3HT blend possessed a significantly rougher surface morphology as compared with CdSe-H/thiol-P3HT blend. Increased roughness has been shown to be a desirable attribute in P3HT/PCBM systems, which is usually achieved through particle loading, spin conditions, "slow evaporation", and annealing processes. The rougher surface morphology of CdSe-H/allyl-P3HT could be indicative of a higher degree of nanoscale phase separation, allowing for improved charge transport.[41]

Table 1. Comparison of Device Performances for Different P3HT−CdSe Blends (Slow Evaporation, SE; Direct Annealing, DA); [CdSe]:[P3HT] = 5:1 (w/w); Samples Prepared by Slow Evaporation from Dichlorobenzene/Pyridine Mixture

	CdSe-H/Br-P3HT		CdSe-H/thiol-P3HT		CdSe-Br/allyl-P3HT	
drying conditions	SE	DA	SE	DA	SE	DA
efficiency (%)	0.45	0.11	0.60	0.04	0.90	0.52
V_{oc} (mV)	753	750	758	556	752	634
J_{sc} (mA cm^{-2})	1.681	0.441	2.165	0.228	3.009	2.094
FF (%)	35.62	34.06	34.37	34.91	39.7	39.11
R_s (Ohms)	1849	9107	1424	13 542	801	1168

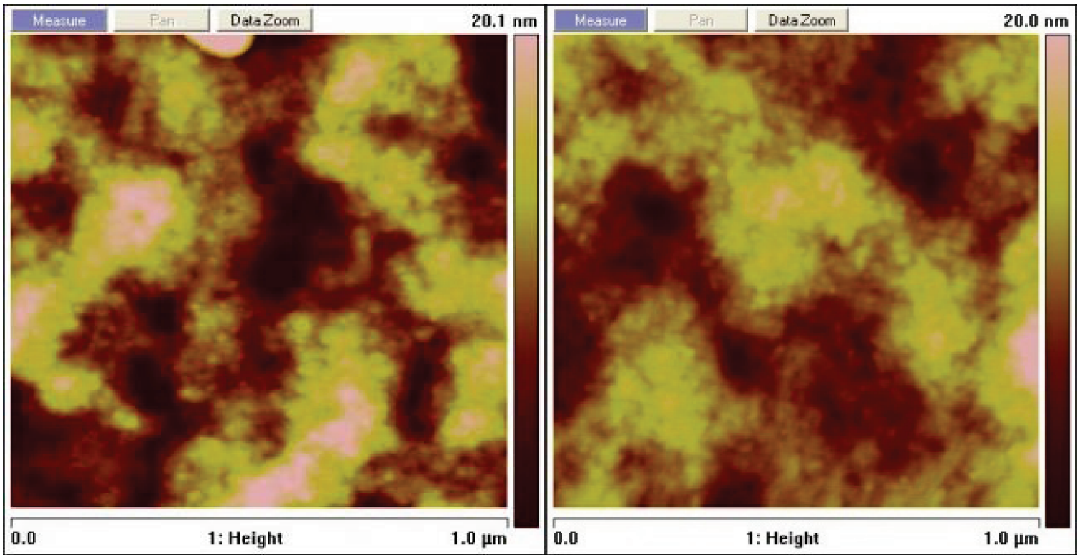


Figure 2. AFM height images of CdSe-H/allyl-P3HT blend (left) and CdSe-H/thiol-P3HT blend (right); [CdSe]:[P3HT] = 5:1 (w/w); samples prepared by slow evaporation from dichlorobenzene/pyridine mixture.

Because of a stronger interaction between the thiol groups and CdSe QDs, one would expect a better performance when compared to Br/allyl-P3HT blends. However, we have measured consistently larger PCE values for all our devices containing CdSe-Br/allyl-P3HT blends as the active layer. We speculate that the better performance of the CdSe-Br/allyl-P3HT is the result of a better phase separation of CdSe at the nanoscale rather than increased interaction with the CdSe QDs. The hypothesis that a stronger interaction between CdSe and thiol functional groups might require a lower load of QDs in the blend for an efficient charge transfer through the interface was tested. Blends of CdSe-H/thiol-P3HT have been prepared at weight ratios of 5:1 and 1.8:1. Power conversion efficiencies of 0.60% have been measured for the blend with weight ratio of 5:1, while a value of 0.25% was measured for the blend with weight ratio of 1.8:1 (see Supporting Information). These preliminary experiments indicate that a high loading of CdSe is necessary for an efficient charge transport. Different loading ratios of CdSe are currently investigated to correlate the photovoltaic response as a function of the ratio between donor H/thiol-P3HT polymer and acceptor CdSe quantum dots.

In conclusion, we have synthesized H/thiol-terminated P3HT and compared the photovoltaic response with H/Br and Br/allyl-terminated P3HT. Compared to H/Br-P3HT, H/thiol- and Br/allyl-terminated P3HT show better performance. All of our results were obtained with spherical CdSe QDs.

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Supporting Information Available: Experimental procedures and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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