Synthesis and Characterization of CdSe Nanorods Functionalized with Regioregular Poly(3-hexylthiophene)

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Nanorod−polymer composites consisting of intimately connected regioregular poly(3-hexylthiophene) (P3HT) and CdSe nanorods hold promise for applications in photoactive devices. As phase separation typifies nanorod−polymer or nanoparticle−polymer composites, synthetic routes to chemically attach P3HT to CdSe nanorods are needed. In this study, arylbromide-functionalized CdSe nanorods were prepared by ligand exchange from conventional alkane-covered CdSe nanorods. Vinyl-terminated P3HT was then attached to the nanorod surface by Heck coupling with the arylbromide ligands. Transmission electron microscopy (TEM) of the P3HT-functionalized CdSe nanorods showed excellent nanorod dispersion in the P3HT matrix, unlike that seen for alkane-covered nanorods in P3HT. Importantly, photoluminescence characterization performed on thin films of the P3HT-covered nanorods showed photoluminescence quenching of P3HT, making these hybrid materials good candidates for photovoltaic applications.

Introduction

Spherical semiconductor nanoparticles, such as CdSe quantum dots, have been the subject of extensive studies over the past decade because of their unique optical and electronic properties.[1−3] CdSe nanorods with narrow size distribution are also readily available because of recent synthetic advances.[4,5] Quantum dots are attractive for both electronic materials applications, for example, as light-emitting diodes (LEDs),[6−8] and for biotechnology, for example, as fluorescence tags in diagnostics.[9,10] Although spherical CdSe nanoparticles and organic conjugated polymers have been tested in photovoltaic applications,[11−17] CdSe nanorods may be advantageous, as the long axis of the nanorods provides a continuous pathway for electron transport, precluding the need for electron hopping in nanoparticle-based photovoltaics.

Inorganic nanorods have a strong tendency to aggregate in the solid state, and CdSe nanorods have been shown to exhibit liquid crystal phases in concentrated solutions, or when cast from solution onto a substrate.[17−20] CdSe nanorods also show gross phase separation when blended with most polymers as composite films.[12−14,21] However, appropriate surface modification of the nanorods enables their cleanly dispersed integration into a wider range of materials, and thus potentially into numerous applications. In prior work, we showed that CdSe nanorods can be integrated readily into diblock copolymer templates when the nanorod surface is functionalized with poly(ethylene oxide) ligands, such that the control over the lateral distribution of nanorods is possible.[22] Fréchet and Alivisatos showed that pyridine-functionalized CdSe nanorods can form dispersed composite films when spin-coated with amine-terminated regioregular P3HT, giving markedly improved photovoltaic efficiency in devices.[14] The amine-terminated P3HT is thought to coordinate to the nanorods, partially replacing the pyridine surfactant, and thereby enhancing the nanorod miscibility with P3HT. In that study, the amine-terminated P3HT-covered CdSe nanorods were not isolated, but rather used directly with pyridine-covered CdSe nanorods for casting

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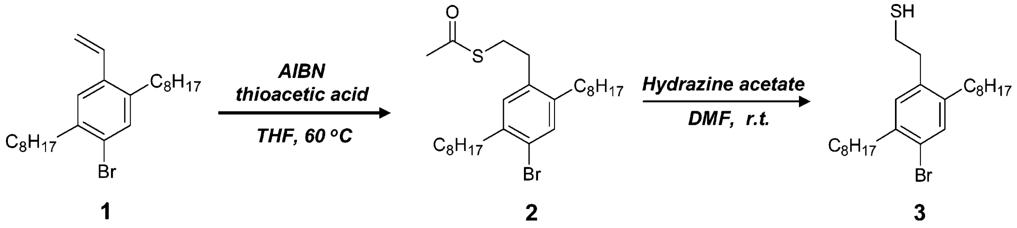
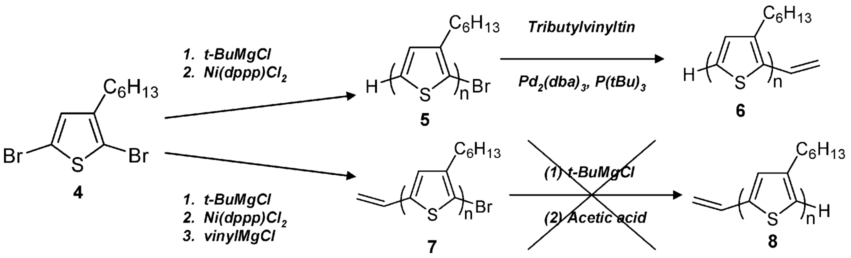
Scheme 1



Scheme 2



films. As amines are not strong ligands for CdSe nanorods,[23] we decided to investigate methods to isolate P3HT-covered CdSe nanorods, and characterize their photoluminescence behavior relative to conventional alkane-covered CdSe nanorods. Optimized ligand chemistries for nanoparticles and nanorods can prevent their phase separation from the polymer during film formation, which in turn promotes the efficient use of the inorganic component within the polymer matrix.

Here, we report an effort to prepare arylbromide-functionalized phosphine oxides and thiols as ligands for CdSe nanorods, followed by coupling of the ligands to vinyl-terminated P3HT to provide the desired P3HT-hybrid nanocomposites. Through this method, P3HT-covered CdSe nanorods were prepared, isolated, and characterized. These p-type/n-type hybrid nanocomposites showed fluorescence quenching of P3HT, indicating a charge transfer between the two semiconductors that is characteristic of this type of photovoltaic material.

Results and Discussion

Arylbromide-functionalized ligand **3** was synthesized as shown in Scheme 1. 2,5-Di-*n*-octyl-4-bromostyrene was converted to thioacetate **2** by free radical addition of thioacetic acid to the double bond. Thioacetate **2** was hydrolyzed to give thiol **3**, and arylbromide-functionalized ligand **3** was attached to the CdSe nanorod surface by ligand-exchange chemistry, going through pyridine-covered CdSe nanorods as an intermediate step. The ligand-exchange procedure involved refluxing pyridine-covered nanorods with thiol **3** in anhydrous toluene; excess ligand was removed by repeated precipitation in anhydrous methanol. Successful ligand exchange using thiol **3** was verified by ^{1}H NMR spectroscopy, which showed the aromatic protons of the benzene ring. In a similar fashion, *p*-bromobenzyl-di-*n*-octylphosphine oxide (DOPO-Br) was used to modify the CdSe nanorod surface. In each case, the arylbromide group is available for further modification, whereas the thiol or phosphine oxide group fixes the ligands to the nanorod surface. Our prior study describing the growth of CdSe nanoparticles directly in these DOPO-Br ligands[24] was unfortunately not extendable to the CdSe nanorod synthesis. Nonetheless, ligand exchange proved suitable for obtaining the desired functionalized CdSe nanorods.

Vinyl-terminated P3HT **6** was prepared as shown in Scheme 2. First, bromide-terminated P3HT **5** was prepared by Grignard metathesis (GRIM) polymerization as described by McCullough and co-workers.[25] Then, Stille coupling of P3HT-bromide **5** with vinyl tri-*n*-butyltin gave the desired vinyl-terminated polythiophene **6**.[26] It is also known that vinyl-P3HT-Br **7** can be made by a modified one-pot GRIM polymer method, quenching the polymerization with vinyl magnesium bromide.[27] However, our attempts to reduce the chain-end bromide (by treatment of polymer **7** with *t*-butyl magnesium bromide in refluxing THF) failed, probably because of competing reactions at the terminal vinyl group. The presence of the bromide chain end in **7** precludes its use in subsequent Heck coupling with arylbromide-functionalized CdSe nanorods. Thus, Stille coupling between bromide-terminated P3HT and vinyl tri-*n*-butyltin proved most effective in preparing vinyl-terminated P3HT for this study. P3HT-functionalized CdSe nanorods were prepared by Heck coupling of vinyl-terminated P3HT (vinyl-P3HT **6**) and arylbromide-functionalized CdSe nanorods, as shown in Scheme 3. The coupling was carried out in THF at 55 °C using the tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and tri(*t*-butyl)phosphine ($P(tBu)_3$) catalyst system. These conditions, as described by Fu and co-workers,[28] proved effective even at room temperature. Following this grafting reaction, excess (unreacted) vinyl-P3HT **6** was separated from the functionalized nanorods by dialysis in a chloroform bath using a PVDF dialysis bag (molecular

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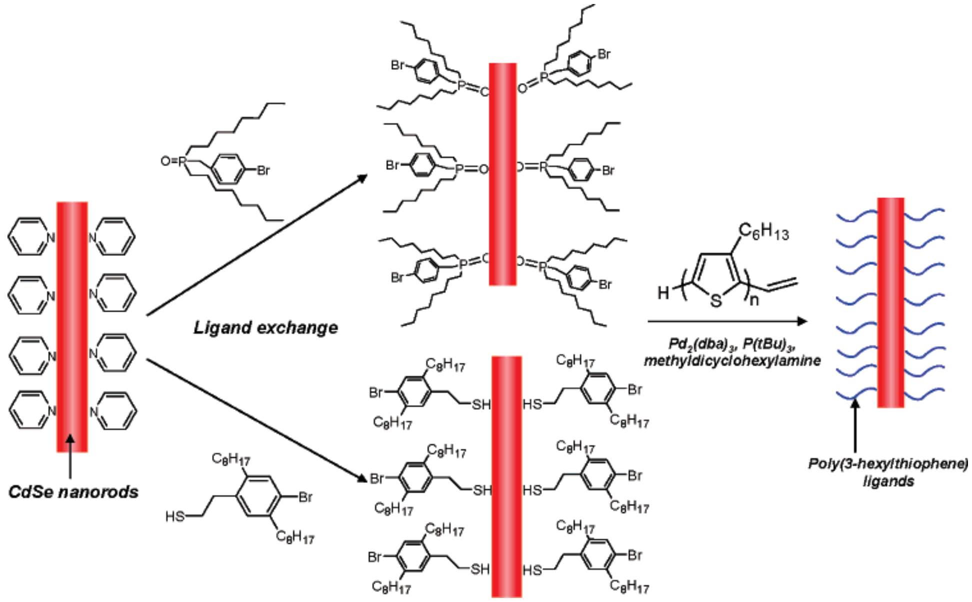
Scheme 3



weight cutoff 250 kDa, from Spectrum Laboratories, Inc.). The solubility of the CdSe nanorods changed markedly following the coupling, from the hexane-soluble arylbromide-covered nanorods to the hexane-insoluble but THF-, toluene-, and chloroform-soluble nanorods. This solubility is typical of P3HT and is expected for nanorod samples covered with P3HT. After removing excess and unreacted vinyl-terminated P3HT by dialysis, the ^{1}H NMR spectrum of the pure P3HT covered CdSe nanorods showed the characteristic aromatic protons at 6.9 ppm, and methylene protons directly connected to the thiophene at 2.5 ppm. When these P3HT-covered CdSe nanorods were mixed with P3HT homopolymer (molecular weight 17 500 g/mol, and 20 wt % (~5 vol %) nanorods), a homogeneous distribution of nanorods in the polymer matrix was observed by transmission electron microscopy (TEM), as shown in Figure 1. Removing unfavorable enthalpic interactions between the nanorods and polymer matrix enables this dispersion. Taken together, these spectroscopic and microscopic observations indicate the successful grafting of P3HT to the CdSe nanorod surface.

Thermogravimetric analysis (TGA) was conducted to quantify the P3HT coverage on the CdSe nanorods. As shown in Figure 2, TGA analysis of P3HT homopolymer (molecular weight 8600 g/mol) indicated an onset of degradation at 400−450 °C, and a char yield of about 20%. The P3HT-covered CdSe nanorod sample showed significant mass loss in the 400−450 °C range, similar to that of P3HT homopolymer. The mass loss in this temperature range is due to the grafted P3HT. The P3HT-covered nanorods with the phosphine oxide (DOPO-Br) ligand had ~13 wt % P3HT, whereas P3HT covered nanorods with thiol ligand **3** had ~18 wt % P3HT. Assuming a CdSe nanorod density of 5.8 g/cm^3 (as for the bulk), the volume percentage of P3HT in the P3HT-covered CdSe nanorods is 46% and 56% for the phosphine oxide and thiol-linked coverages, respectively. For a CdSe nanorod of 8 nm diameter and 40 nm length covered with P3HT ligands, this leads to roughly 250 P3HT chains per nanorod for P3HT-covered nanorods with phosphine oxide linkage to the surface, and 400 P3HT chains per nanorod for P3HT-covered nanorods with thiol linkage to the surface.

The coverage of P3HT on the nanorod surface will be dictated by the initial coverage density of arylbromide ligands and the efficiency of Heck coupling between vinyl-terminated P3HT and arylbromide-covered nanorods. The Heck coupling between vinyl and bromide with $Pd_2(dba)_3/P(t\text{-bu})_3$ appears to be effective and not a limiting factor in determining P3HT coverage. Thiol ligands are known to be more effective than phosphine oxides for cadmium sites on CdSe nanoparticles.[23] Thus, the greater P3HT coverage found in the thiol case is attributed to a higher initial coverage of thiol ligand **3** relative to that of the DOPO-Br ligand.

The direct attachment of P3HT onto the CdSe nanorod surface was found to impact the photophysics of the composite material. P3HT homopolymer (molecular weight 8600 g/mol, prepared using the GRIM method) showed the expected broad photoluminescence emission from ~620−750 nm (excitation wavelength 450 nm), when measured in solid state using films cast from chloroform, as shown in Figure 3. The solid-state photoluminescence emission of alkane-covered CdSe nanorods (8 nm in diameter and 40 nm in length) was centered at ~660 nm, with peak width at half-height of ~35 nm (inset of Figure 3). It should be noted that the photoluminescence from the CdSe nanorods is relatively weak compared to that from P3HT, and that the photoluminescence spectra of the nanorods and P3HT overlap. Therefore, in the composite films we focused mainly on the photoluminescence changes seen in P3HT. Films consisting of mixtures of the alkane-covered CdSe nanorods and P3HT showed a slight decrease in P3HT photoluminescence relative to P3HT homopolymer. However, the P3HT-covered CdSe nanorods in the solid state showed a nearly complete quenching of P3HT photoluminescence. This photoluminescence quenching is indicative of charge transfer between P3HT and CdSe nanorods and is consistent with an intimate mixture of the two semiconductors both in terms

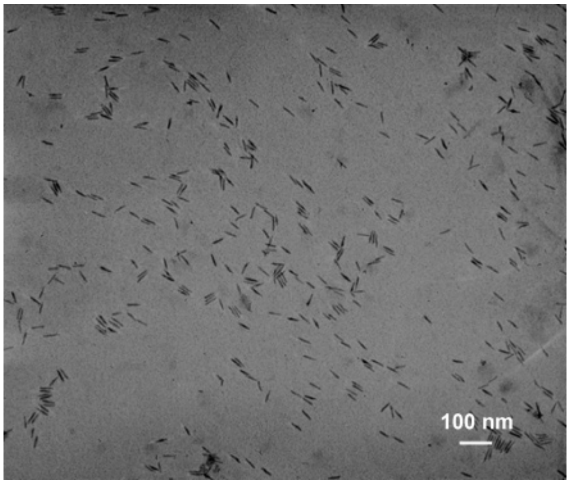


Figure 1. TEM image of 20 wt % P3HT-functionalized CdSe nanorods in P3HT homopolymer.

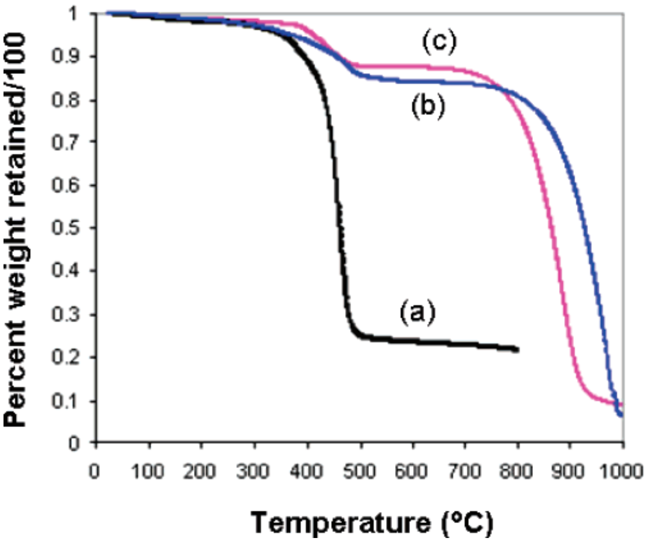


Figure 2. Thermogravimetric analysis of (a) P3HT homopolymer, (b) P3HT-functionalized CdSe nanorods with thiol ligands, and (c) P3HT-functionalized CdSe nanorods with phosphine oxide ligands.

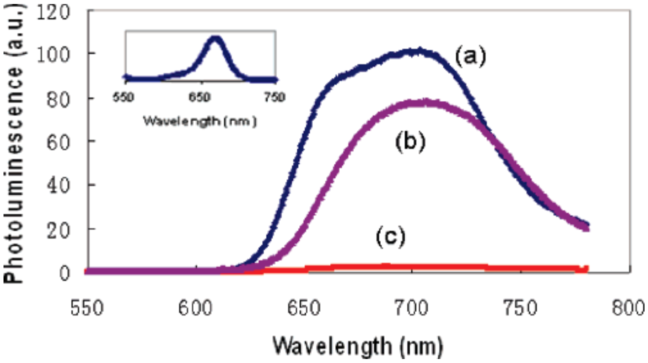


Figure 3. Solid-state photoluminescence of thin film cast from (a) P3HT homopolymer, (b) alkane-covered nanorods in P3HT (90 wt % nanorods), and (c) P3HT-functionalized CdSe nanorods (90 wt % nanorods). Inset: solid-state photoluminescence of CdSe nanorods.

of the nanorod dispersion and the electronic structures (LOMO/HOMO levels) of the two materials.[12] An efficient charge transfer between P3HT and CdSe nanorods in P3HT-functionalized nanorods, in conjunction with orientation of nanorods under external fields (i.e., electric fields),[21] is promising for the enhancement of the power efficiency of photovoltaic devices based on these materials. Efforts along these lines are in progress.

Experimental Section

n-Tetradecylphosphonic acid (97%) was purchased from Alfa Aesar, 3-bromothiophene from TCI America, and all other reagents from Aldrich. *p*-Bromobenzyl-di-*n*-octylphosphine oxide (DOPO-Br) was prepared as described previously.[24] Tetrahydrofuran (THF) was dried and distilled over sodium/benzophenone. All reactions were run under an inert atmosphere of nitrogen or argon. Infrared spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with an ATR accessory. HRMS data were acquired on a JEOL JMS 700 spectrometer. NMR spectra were obtained on a Brüker DPX 300 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard. $CHCl_3$ (δ 7.26 for ^1H spectra) was used as an internal standard for $CDCl_3$. Gel permeation chromatography (GPC) was performed in THF (35 °C, 1.0 mL/min) using a Knauer K-501 Pump with a K-2301 refractive index detector and K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns, and one PLGel 50 Å column (1.5 × 30 cm). Molecular weights are reported relative to polystyrene standards. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Brüker Reflex III spectrometer. MALDI-TOF samples were prepared by drop-casting a THF solution of polymer with terthiophene as matrix. Fluorescence measurements were recorded on a Perkin-Elmer LS-55 fluorimeter. Transmission electron microscopy was performed on a JEOL 100CX microscope with an accelerating voltage of 100 kV. Thermogravimetric analysis was performed under a nitrogen atmosphere on a DuPont TGA 2950 using a heating rate of 10 °C per minute.

Preparation of Thioester 2. 2,5-Di-*n*-octyl-4-bromostyrene **1**[24,29] (1.00 g, 2.54 mmol), α,α'-azoisobutyronitrile (AIBN) (41.7 mg, 0.254 mmol), and thioacetic acid (773 mg, 10.2 mmol) were dissolved in anhydrous THF (4 mL) in a reaction tube equipped with a stir bar. The solution was subjected to three freeze−pump−thaw cycles; the tube was then sealed and the solution stirred at 60 °C for 24 h. The solvent was removed by rotary evaporation, and the product residue dissolved in dichloromethane. The dichloromethane solution was extracted twice with water. The organic layer was dried over $MgSO_4$ and concentrated under a vacuum to give a yellow liquid (1.10 g, 90% yield). ^1H NMR (ppm) in $CDCl_3$: δ 7.30 (s, 1H), 7.00 (s, 1H), 3.02 (t, 2H), 2.80 (t, 2H), 2.55 (m, 4H), 2.35 (s, 3H), 1.55 (m, 4H), 1.32 (m, 20H), 0.88 (t, 6H). ^{13}C NMR (ppm) in CDCl3: δ 195.6, 140.4, 139.4, 136.9, 133.1, 131.2, 122.3, 35.7, 32.3, 31.9, 31.9, 31.9, 31.2, 30.6, 30.1, 29.9, 29.6, 29.4, 29.4, 29.3, 29.2, 22.7, 14.1. FT-IR (cm^{-1}): 2923, 2854, 1693, 1483, 1465, 1378, 1352, 1241, 1132, 947, 890, 722. HRMS (ES^+): Calcd, 484.220; found, 484.218.

2-(4-Bromo-2,5-di-*n*-octyl-phenyl)-ethanethiol 3. To a solution of compound **2** (1.00 g, 2.07 mmol) in anhydrous DMF (10 mL) was added hydrazine acetate (0.560 g, 6.21 mmol). The mixture was stirred overnight. Ether (100 mL) was then added, and the organic solution was extracted with water (3 × 20 mL). The organic layer was dried over $MgSO_4$ and concentrated to give a colorless liquid (0.84 g, 92% yield). ^1H NMR (ppm) in $CDCl_3$: δ 7.31 (s, 1H), 6.98 (s, 1H), 2.83 (t, 2H), 2.64 (m, 4H), 2.53 (t, 2H), 1.57 (m, 4H), 1.31 (m, 20H), 0.89 (t. 6H). ^{13}C NMR (ppm) in $CDCl_3$: δ 140.3, 139.4, 136.7, 133.1, 131.2, 122.3, 36.7, 35.7, 32.0, 31.9, 30.1, 29.7, 29.5, 29.47, 29.45, 29.3, 29.2, 25.4, 22.7, 14.1. FT-IR

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(29) Sill, K.; Emrick, T. unpublished results.

(cm^{-1}): 2922, 2853, 1483, 1465, 1378, 1122, 964, 889, 806, 721. HRMS (ES$^+$): Calcd, 442.209; found, 442.210.

Preparation of CdSe Nanorods. CdSe nanorods were prepared according to known methods.[5] Briefly, CdO (0.200 g), *n*-tetradecylphosphonic acid (TDPA, 0.89 g), and tri-*n*-octylphosphine oxide (TOPO, 2.9 g) were combined and heated under argon at 300 °C to give a colorless solution. The heat was removed, and the mixture was left to stand at room temperature for 3 days. The mixture was heated under argon to 320 °C, and a solution of selenium (0.025 g), tri-*n*-butylphosphine (0.23 g), tri-*n*-octyphosphine (1.45 g), and toluene (0.30 g) was injected. Following the injection, a reduction in temperature to 250 °C was observed, and the nanorods were allowed to grow at this temperature for 30 min. The heating mantle was then removed, and when the temperature reached 60 °C, anhydrous methanol (10 mL) was added. The CdSe nanorods were isolated by repeated dissolution in chloroform and precipitation in methanol.

Preparation of DOPO-Br-covered CdSe nanorods. CdSe nanorods (20 mg) synthesized as described above were stirred in refluxing anhydrous pyridine (2 mL) for 24 h under nitrogen. Most of the pyridine was removed by a vacuum, and the pyridine-covered nanorods were precipitated in hexane. The pyridine-covered nanorods were washed twice with hexane to remove residual pyridine and then transferred to a reaction tube. Anhydrous toluene (2 mL) and DOPO-Br (200 mg) were introduced, and the mixture was refluxed under nitrogen for 12 h. The solution became homogeneous during this period, indicating successful functionalization of the nanorods with DOPO-Br. The DOPO-Br-covered nanorods were purified by dissolution in chloroform and precipitation in methanol. ^{1}H NMR (ppm): δ 7.39 (2H), 7.04 (2H), 3.00 (2H), 1.2−1.6 (28H), 0.8 (6H). ^{31}P NMR (ppm): δ 48.0.

3-Covered CdSe Nanorods. **3**-covered CdSe nanorods were prepared in a fashion similar to that of the DOPO-Br-covered CdSe nanorods, using thiol **3** instead of DOPO−Br.

2,5-Dibromo-3-hexylthiophene 4. 3-Hexylthiophene (19.4 g, 77.1 mmol) was dissolved in anhydrous THF (100 mL) in a round-bottom flask equipped with a magnetic stir bar. *N*-Bromosuccinimide (27.4 g, 154 mmol) was added to the solution over a 10 min period. The solution was stirred at room temperature for 4 h. THF was then removed under a vacuum and hexane (300 mL) was added. The mixture was filtered through a plug of silica, and hexane was removed under a vacuum. Purification by vacuum distillation gave a clear, colorless oil (21.4 g, 85% yield). Spectroscopic characterization was in accord with that found in the literature.[25]

P3HT 5.[25] A solution of 2,5-Dibromo-3-hexylthiophene **4** (4.89 g, 15.0 mmol) in anhydrous THF (150 mL) was stirred under nitrogen atmosphere. A diethylether solution of *tert*-butylmagnesium chloride (7.5 mL, 15 mmol) was added by syringe, and the mixture was heated to reflux for 2 h. The mixture was cooled to room temperature, and 1,3-bis(diphenylphosphino) propane nickel(II) chloride (Ni(dppp)Cl$_2$) (135 mg, 0.250 mmol) was added. The mixture was stirred at room temperature for 12 min, and then quenched by addition of methanol. The polymer was precipitated into methanol, and then filtered into an extraction thimble and purified by Soxhlet extraction, sequentially with methanol, hexanes, and chloroform. The chloroform fraction was collected and concentrated under a vacuum to give the desired product **5** (1.3 g, 52% yield). MALDI-TOF: m/z (M_p) 3901.91 (calcd, 3905.33; DP = 23, H/Br chain ends). GPC: $M_n = 8600$, PDI = 1.20, $M_p = 11360$.

Vinyl-P3HT 6. In a dry box, P3HT **5** (0.500 g, 0.150 mmol) was dissolved in anhydrous THF (5 mL) in a tube equipped with a stir bar. Tris(dibenzylideneacetone) dipalladium(0) (Pd$_2$(dba)$_3$) (20 mg, 0.023 mmol) and tri(*t*-butyl)phosphine (18 mg, 0.090 mmol) were introduced. Finally, tri-*n*-butylvinyl tin (0.475 g, 1.50 mmol) was added, and the tube was sealed and removed from the dry box. The mixture was stirred at 55 °C for 24 h, and then transferred into a vial and centrifuged at 3000 rpm for 3 h to remove palladium black. The supernatant was decanted and precipitated into methanol. The precipitated polymer was filtered and dried under a vacuum to give 0.470 g (95% yield) of desired product. GPC: $M_n = 8650$, PDI = 1.21. ^{1}H NMR (ppm) in CDCl3: δ 6.98 (s, 20H), 6.90 (m, 2H), 5.50 (d, 1H), 5.14 (d, 1H), 2.80 (t, 40H), 2.63 (m, 4H), 1.69 (t, 40H), 1.40 (m, 120H), 0.91 (t, 66H).^{13}C NMR (ppm) in CDCl3: δ 139.93, 133.74, 130.52, 128.63, 31.73, 30.54, 29.50, 29.29, 22.68, 14.15. FT-IR (cm^{-1}): 2954, 2922, 2853, 1562, 1509, 1453, 1376, 1260, 1205, 1018, 818, 724.

General Procedure for Obtaining P3HT-Covered CdSe Nanorods. In a dry box, DOPO-Br- or **3**-covered CdSe nanorods (~10 mg) and vinyl-terminated P3HT (~30 mg) were combined in a glass reaction tube equipped with a stir bar. Added to this were Pd$_2$(dba)$_3$ (~2 mg), tri(*t*-butyl)phosphine (~1.4 mg), methyldicyclohexylamine (~120 mg), and anhydrous THF (~2 mL). The tube was sealed and removed from the dry box. The mixture was stirred at 55 °C for 24 h. The reaction mixture solution was cooled to room temperature, transferred to a vial, and centrifuged at 3000 rpm for 3 h. The supernatant was decanted and transferred to a PVDF dialysis bag (molecular weight cutoff 250 kDa, Spectrum Laboratories, Inc.) and dialyzed in chloroform until the dialysis bath solution appeared colorless. ^{1}H NMR spectroscopy in CDCl$_3$ showed characteristic signals for P3HT (7.31, 6.98, 2.80, 1.69, 1.40, and 0.91 ppm). Thermal and photophysical data are reported in the Results and Discussion section.

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Supporting Information Available: Solution and solid-state characterization of P3HT-covered CdSe nanorods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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