10-3-2007

Organic–Inorganic Nanocomposites via Directly Grafting Conjugated Polymers onto Quantum Dots

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Received June 6, 2007; E-mail: zqlin@iastate.edu

Abstract: Nanocomposites of poly(3-hexylthiophene)−cadmium selenide (P3HT−CdSe) were synthesized by directly grafting vinyl-terminated P3HT onto [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br)-functionalized CdSe quantum dot (QD) surfaces via a mild palladium-catalyzed Heck coupling, thereby dispensing with the need for ligand exchange chemistry. The resulting P3HT−CdSe nanocomposites possess a well-defined interface, thus significantly promoting the dispersion of CdSe within the P3HT matrix and facilitating the electronic interaction between these two components. The photophysical properties of nanocomposites were found to differ from the conventional composites in which P3HT and CdSe QDs were physically mixed. Solid-state emission spectra of nanocomposites suggested the charge transfer from P3HT to CdSe QDs, while the energy transfer from 3.5 nm CdSe QD to P3HT was implicated in the P3HT/CdSe composites. A faster decay in lifetime further confirmed the occurrence of charge transfer in P3HT−CdSe nanocomposites.

Introduction

Because of their semiconductor-like optical and electronic properties, conjugated polymers (CPs) have been extensively researched for two decades. The optoelectronic properties of CPs depend heavily on the physical conformation of polymer chains.[1−3] The most widely studied CP is regioregular poly(3-hexylthiophene) (*rr* P3HT), consisting of a rather rigid backbone with pendant hexyl side chains that allow solubilization.[4−7] Quantum dots (QDs) are highly emissive, spherical nanoparticles with a few nanometers in diameter.[8−11] For QDs such as cadmium selenide (CdSe),[8,12] the variation of particle size provides continuous and predictable changes in fluorescence emission due to their quantum-confined nature. An appropriate surface passivation with a monolayer of coordinating organic ligands is crucial to ensure the solubility and miscibility of QDs with the host environment, and to retain the spectroscopic properties of materials by preventing QDs from aggregation.[13,14] Ligand exchange permits derivatization with a broad range of functional groups. However, it suffers from incomplete surface coverage, although a study on nearly quantitatively exchange has been reported recently.[15] As a consequence, the fluorescence emission is quenched due to aggregations of QDs,[16] or oscillates due to adsorption and desorption of surface ligand.[17]

Composites of conjugated polymers/quantum dots (CP/QD) are of interest from the standpoint of increased performance relative to either of the non-hybrid counterparts with many applications envisioned in the areas of photovoltaic cells[18−21] and LEDs.[14,22−24] They inherit decent mechanical strength from CPs and good photostability and high conductivity from QDs. The CP/QD composites are widely prepared by mixing these two components or by constructing a CP/QD bilayer (only a small fraction of excitons, i.e., the bound electron−hole pairs, are able to diffuse to the interface where they are ionized) or CP/QD alternating multilayer either physically or chemically. Thus, it is difficult to control the detailed morphology and

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Scheme 1. Grafting Vinyl-Terminated P3HT onto [(4-Bromophenyl)methyl]dioctylphosphine Oxide (DOPO-Br)-Functionalized CdSe QDs
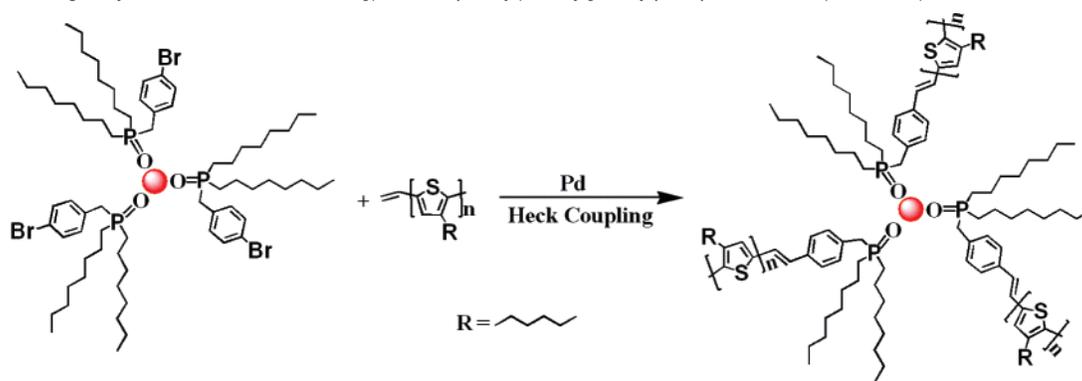
dispersion of QDs within CPs. The interface between CP and QD, accomplished by stripping ligand from QDs during film processing, is not well controlled, thereby reducing the efficient electronic interactions between them. The effective charge transfer, profoundly influenced by the quality of the interface, is crucial for CP/QD composite for use in photovoltaic cells.[25−27] This implies that a bicontinuous and nanoscopic phase-separated mixture of CP/QD is favorable for charge generation and transport, which is currently difficult to realize by using a conventional blending approach.[28−30] On the other hand, for use in LED, it is important to stabilize QDs in an appropriate host with retention of the fluorescence emission. However, possible nanoparticle aggregation in composites often limits the energy-transfer pathway and leads to self-quenching of the fluorescence of QDs.

In this context, the ability to chemically tether QD with CP (i.e., preparing CP−QD nanocomposites with well-controlled interfaces) provides a means of achieving uniform dispersion of nanoparticles and maximizing the interfacial area, which carries advantages over cases where nanoparticle aggregation dominates. To date, only a few elegant studies have centered on the direct integration of QDs into oligomeric CPs (including branched conjugated oligomeric dendrons[31]) via ligand exchange with insulated surfactants,[15,20,21,31,32] electrostatic interaction, or direct growth from the QDs' surface[13,14] to achieve a more controlled interface on a molecular scale and morphology. The length of the conjugated oligomers (trimer, tetramer, or pentamer) was shorter than the conjugation length of the corresponding CPs. To further manipulate the photophysics of nanocomposites by controlling the chain conformation of CPs in the surrounding environment, it is of importance to graft longer chain CPs on the QD surface.

To this end, here we report the preparation of CP−QD nanocomposites based on a rational design in which QDs were tailored with relatively long chain CPs (i.e., the chain length

was longer than the conjugation length of CP). Nanocomposites of poly(3-hexylthiophene)−cadmium selenide (P3HT−CdSe) were synthesized by directly grafting relatively long chain, vinyl-terminated P3HT onto [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br)-functionalized CdSe QD surfaces via a mild palladium-catalyzed Heck coupling (i.e., a "grafting onto" method) as outlined in Scheme 1, thereby dispensing with the need for ligand exchange chemistry. The resulting P3HT−CdSe nanocomposites possess a well-defined interface, thus significantly promoting the dispersion of CdSe within the P3HT matrix and facilitating the electronic interaction between these two components. The photophysical properties of nanocomposites were found to differ from the conventional composites in which P3HT and CdSe QDs were physically mixed. Solid-state emission spectra of nanocomposites suggested the charge transfer from P3HT to CdSe QDs, while the energy transfer from CdSe QD to P3HT was implicated in the P3HT/CdSe composites. A faster decay in lifetime further confirmed the occurrence of charge transfer in P3HT−CdSe nanocomposites.

Experimental Methods

All chemicals, including hexadecylamine (HDA), hexylphosphoric acid (HPA), cadmium acetate (Cd(OAc)₂), trioctylphosphine (TOP), tri-*t*-butylphosphine, tris(dibenzylideneacetone)dipalladium(0) (Pd₂-(dba)₃), and *N*-methyldicyclohexylamine, were purchased from Aldrich and used as received. THF was used freshly from distillation.

Synthesis of (DOPO-Br)-Functionalized CdSe. The [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br)-functionalized CdSe was synthesized on the basis of a ligand-exchange-free procedure.[13,14] Briefly, 50 mg of Cd(OAc)₂, 160 mg of HPA, 0.93 g of HDA, and 1.5 g of [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br) were degassed at 120 °C and heated to 270 °C under Ar. Next, 1.2 mL of Se−TOP stock solution, made by dissolving 0.4 g of Se in 8 g of TOP, was injected swiftly. The size of CdSe QDs was readily controlled by altering the growth time. The final product was dissolved in chloroform and precipitated twice by adding a minimum amount of methanol.

Synthesis of P3HT−CdSe Nanocomposites. The regioregular vinyl terminated P3HT (*rr* P3HT) was synthesized via a quasi-living polymerization.[5,33−35] 1 mg of Pd₂(dba)₃, 10 mg of vinyl-terminated P3HT, and 20 mg of (DOPO-Br)-functionalized CdSe QDs were loaded in a reaction vial. The vial was vacuumed and refilled with Ar. Next, 0.08 mL of *N*-methyldicyclohexylamine, 0.06 mL of tri-*t*-butylphos-phine THF solution at a concentration of 100 mg/mL, and 0.5 mL of THF were loaded in sequence. The reaction mixture was kept stirring

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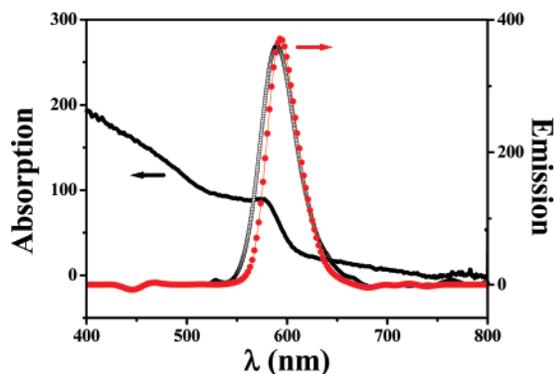
Figure 1. Absorption and emission spectra of (DOPO-Br)-functionalized CdSe QD (diameter, $D = 3.5$ nm). The absorption spectrum was obtained from the CdSe chloroform solution. The emission spectrum of QDs red-shifted upon drying (red ●) from the chloroform solution (○).

under Ar environment in a 50 °C oil bath for 20 h. The final product, that is, P3HT−CdSe nanocomposites, was diluted 20 times and precipitated with a minimal amount of methanol.

Characterizations. The diameter of CdSe QD was determined by TEM measurements (JEOL 1200EX scanning/transmission electron microscope (STEM); operated at 80 kV). The absorption spectra were recorded with a homemade UV−vis spectrometer. The emission spectra were taken with a Nikon Eclipse TE2000-E microscope coupled with an optical insights hyperspectral unit and a Cascade 512B camera (Roger Scientific). The regioregularity of P3HT was determined by ^{1}H NMR (Varian VXR-300). The absolute molecular weight and polydispersity index of *rr* P3HT were measured by MALDI-TOF (Thermo Bioanalysis Dynamo Mass Analyzer). The coupling of vinyl-terminated P3HT with DOPO-Br capped CdSe QDs was verified by ^{1}H NMR and ^{31}P NMR (Varian VXR-400) spectroscopies. The grafting density of P3HT chains on the CdSe surface was determined by thermogravimetry analysis (TGA; TA Instrument TGA Q 50). The fluorescence lifetimes were measured using time-correlated single-photon counting (TCSPC) methodology.[1] The full-width at half-maximum (fwhm) of the instrument response function was ≤100 ps. All decays were collected by exciting the sample with vertical polarization. The fluorescence emission was collected with a perpendicular orientation of the emission polarizer with respect to the excitation polarization. This arrangement eliminated possible interference from scattered light in solid-state fluorescence measurements.

Results and Discussion

The [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br)-functionalized CdSe was synthesized on the basis of a ligand-exchange-free procedure (see Experimental Methods).[13,14] The diameter of CdSe QD (orange-emitting) was 3.5 ± 0.3 nm, as estimated from TEM imaging. Figure 1 shows the absorption and emission spectra of (DOPO-Br)-functionalized CdSe. The emission of CdSe QD in dry state was slightly red-shifted by 3 nm ($\lambda_{em,CdSe} = 593$ nm) as compared to that in chloroform solution. This probably resulted from a slight aggregation of QDs in dry state.

Chemically attaching end-functionalized polymers onto functionalized nanoparticles has been a common approach to modify nanoparticles (NPs), such as Au NP.[36,37] The key is to first synthesize both NPs and polymers with compatible functional groups, which allow them to react with each other under relatively mild condition without sacrificing the stability and
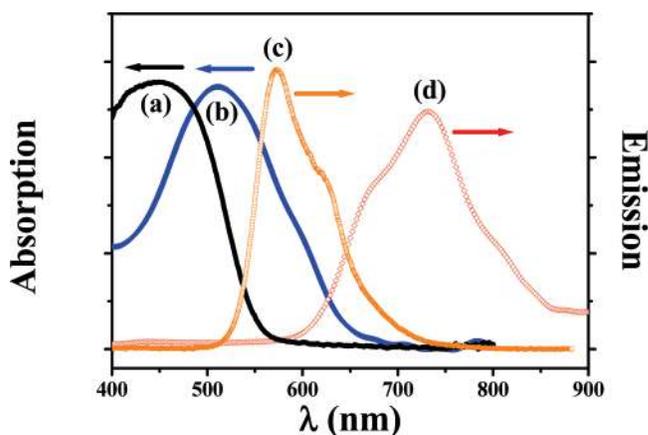

Figure 2. Absorption and emission spectra of vinyl-terminated P3HT in THF solution in (a) and (c), respectively, and in dry film in (b) and (d), respectively.

photophysical properties of each component. In the present study, the regioregular P3HT (*rr* P3HT) was synthesized via a quasi-living polymerization.[5,33−35] One of its ends was functionalized with the vinyl group using a modified Grignard metathasis reaction.[4] The regioregularity was greater than 94% as determined by ^{1}H NMR.[4,5] The absolute molecular weight and polydispersity index of *rr* P3HT were 2404 and 1.12, respectively, as measured by MALDI-TOF. This corresponds to 14 repeat units (i.e., 10.4 nm long given that the length of a thiophene unit is 0.74 nm). It is relatively longer than the effective conjugation length, which is approximately 9−10 thiophene units.[38,39]

The absorption and emission spectra of *rr* P3HT are shown in Figure 2. For the P3HT THF solution, the absorption and emission maxima were at 450 and 572 nm, respectively. A red-shift to 510 and 730 nm ($\lambda_{em,P3HT} = 730$ nm), respectively, was observed upon drying.[39] The emission spectrum of the dried film was acquired from a sample sealed in an Ar-filled vial to prevent photo degradation.[39] The vibronic structures of P3HT are clearly evident (i.e., 0−0 emission peak at 670 nm and 0−1 emission peak at 730 nm).[40] Subsequently, P3HT−CdSe nanocomposites were obtained by a mild palladium-catalyzed Heck coupling of vinyl-terminated *rr* P3HT chains with DOPO-Br-functionalized CdSe QDs (i.e., a "graft onto" method; Scheme 1) (see Experimental Methods).

We note that coating CdSe surface with higher band gap materials, such as zinc sulfide (ZnS), prevents the surface quenching of excitons in the emissive CdSe core by passivating most of the vacancies and trap sites on the CdSe surface, and thus increases the quantum yield and photostability of the QDs. However, the ZnS shell also increases the distance between the CdSe core and the ligand attached onto it, thereby decreasing energy- or charge-transfer efficiency in the CP−QD nanocomposites. On the other hand, the performance of photovoltaic cells based on the CP/QD composites is limited by the hole mobility in the CP.[41] As compared to other CPs, the regioregular (*rr*)

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P3HT possesses excellent environmental stability, fast hole mobility (0.1 cm^2/V·s in field-effect transistors), and tailorable electrochemical properties.[7,42] Taken together, CdSe and *rr* P3HT were chosen as model QD and CP to prepare P3HT–CdSe nanocomposites.

The success of coupling of vinyl-terminated P3HT with DOPO-Br capped CdSe QDs was confirmed by ^{1}H NMR and ^{31}P NMR spectroscopies. The two proton signals from the free vinyl end group on P3HT at 5.1 and 5.5 ppm disappeared after coupling (see Supporting Information, Figure S1). Furthermore, the ^{31}P signal from DOPO-Br shifted from 47 to 50 ppm after it was bonded to the CdSe surface (i.e., forming (DOPO-Br)–CdSe). It further shifted by 17 to 67 ppm after (DOPO-Br)–CdSe was coupled with vinyl-terminated P3HT, suggesting that P3HT was grafted onto the DOPO-Br capped CdSe surface (see Supporting Information, Figure S2). The "grafting onto" method was simple to perform. Thus, rather than oligomer or oligomeric dendron, relatively high molecular weight CP was chemically anchored to QDs. More importantly, the absence of ligand-exchange chemistry in the present synthesis allowed the inherent fluorescence of the P3HT-tailored CdSe QDs to be maintained.

The grafting density of P3HT chains on the CdSe surface was determined by thermogravimetry analysis (TGA) (see Supporting Information, Figure S3). The molecular weight of the 3.5 nm CdSe QDs was estimated to be 113 000 g/mol.[43] The mass loss between 400 and 600 °C was attributed exclusively to the decomposition of P3HT, while the combined mass loss due to partial decomposition of P3HT and the decomposition of unreacted DOPO-Br was found at temperature below 400 °C. Thus, the CdSe QD was grafted with 22 P3HT chains (i.e., 22 P3HT molecules per CdSe QD).

Figure 3 shows the TEM images of P3HT/CdSe composites and P3HT–CdSe nanocomposites prepared by physically mixing vinyl-terminated P3HT and DOPO-Br functionalized CdSe (i.e., without adding catalyst, Pd$_2$(dba)$_3$) and by Heck coupling of these two functionalized components (Scheme 1), respectively. The P3HT/CdSe composites exhibited a significant phase separation as evidenced in Figure 3a. In sharp contrast, the CdSe QDs were well dispersed in P3HT–CdSe nanocomposites (Figure 3b). It is noteworthy that, as compared to other polymer-coated nanoparticles (e.g., nanocomposite of polystyrene-*b*-poly-(ethylene oxide) and Au nanoparticles[37]), no clear P3HT coating at the periphery of the QDs can be imaged. This may be due to that the electron density of CdSe is relatively low as compared to other noble metals, for example, Au, and P3HT had high regioregularity (i.e., behaves like a rigid rod), which makes it difficult for the P3HT chains to collapse at the surface of CdSe core into a dense shell layer, as in the case of flexible homopolymer.[44]

To explore the difference in photophysical properties between nanocomposites (chemically anchoring) and composite (physical mixing), a composite of P3HT/CdSe was prepared to serve as a control. Figure 4a shows the absorption spectra of the P3HT/CdSe composite and the P3HT–CdSe nanocomposites in THF. The absorbance resembled a superposition of the two compo-
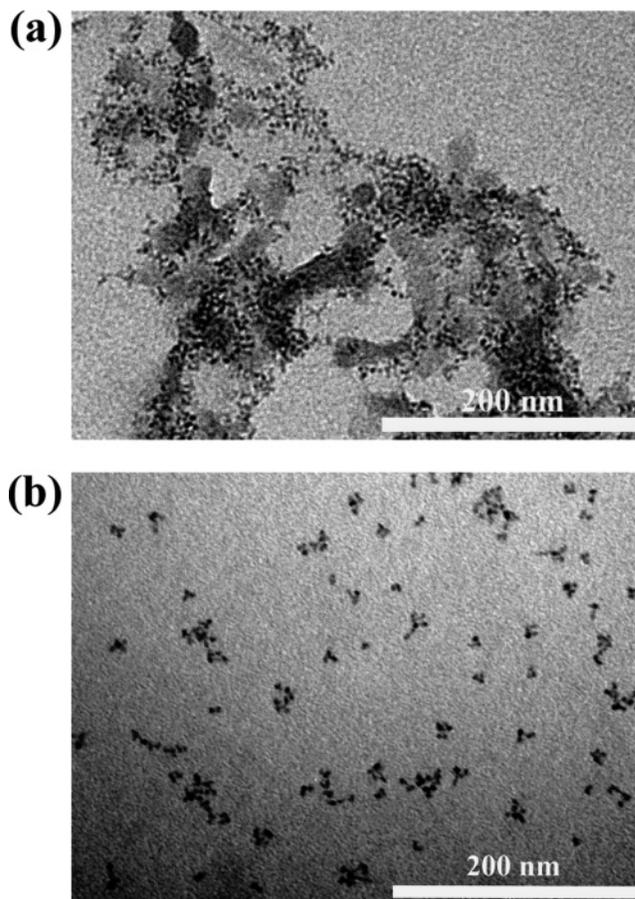

Figure 3. TEM images of (a) the composites of (DOPO-Br)-functionalized CdSe and vinyl-terminated P3HT prepared by physically mixing these two components, and (b) the nanocomposites of P3HT–CdSe prepared by grafting vinyl-terminated P3HT onto (DOPO-Br)-functionalized CdSe.

nents with no other apparent features present. The P3HT/CdSe composite was prepared in such a way that its absorption spectrum was delicately tuned to match that of the P3HT–CdSe nanocomposites. Thus, the number of P3HT chains per CdSe QD in the P3HT/CdSe composites can be roughly estimated on the basis of the TGA results of the P3HT–CdSe nanocomposites (Figure S3): the approximate ratio of P3HT to CdSe is 22:1. It is worth noting that the TEM image of the P3HT/CdSe composites in Figure 3a was actually taken from the sample prepared by casting the above-mentioned P3HT/CdSe THF solution onto carbon-coated TEM copper grids. For the P3HT/CdSe composite in THF solution, two peaks at 432 and 550 nm were seen, corresponding to the P3HT and CdSe absorption, respectively (Figure 4a). The absorption of P3HT in the composite blue-shifted to 432 nm from 450 nm in the vinyl-terminated P3HT THF solution (Figure 2). This may be due to the overlap of the absorption spectrum of P3HT (Figure 2) with the broad absorption band of CdSe below 550 nm (Figure 1). Relative to the spectrum of the P3HT/CdSe composites in which the absorption maximum of CdSe was at 550 nm, the absorption of CdSe upon grafting with P3HT (i.e., P3HT–CdSe nano-composites) was red-shifted (Figure 4a). This can be attributed to the changes in the dielectric environment (i.e., placing CdSe QDs in intimate contact with P3HT) that perturb the energy of the quantum-confined exciton of CdSe.[45]

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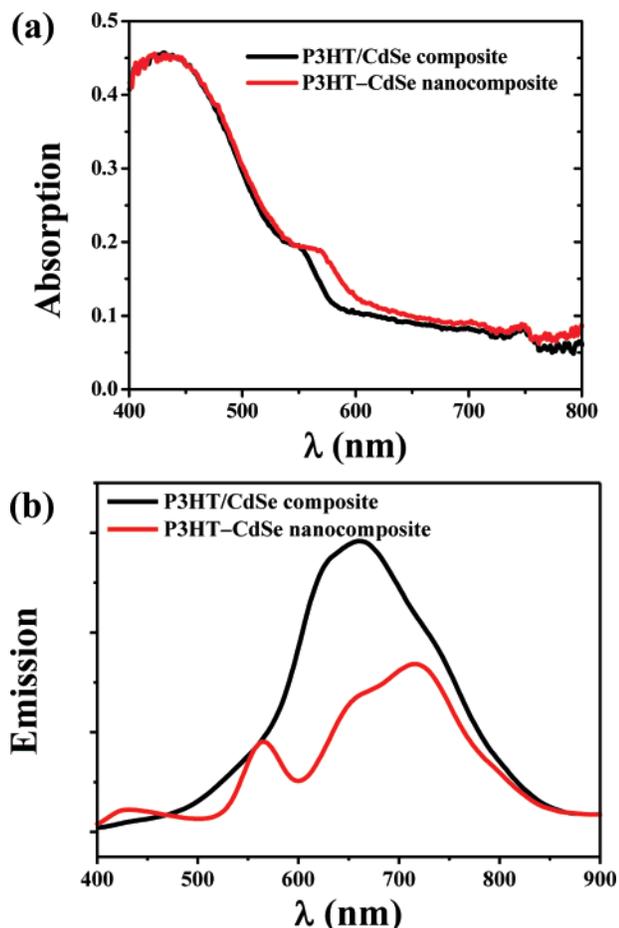
(a)

(b)

Figure 4. (a) Absorption spectra of the composites of (DOPO-Br)-functionalized CdSe and vinyl-terminated P3HT (black curve) and the nanocomposites of P3HT−CdSe (red curve) in THF. (b) Corresponding emission spectra in dry state. Emission spectra were rescaled to show the emission peak positions. The small shoulder between 400 and 500 nm in the nanocomposite emission spectrum came from the UV excitation. Such tail was only observed when the emission of nanocomposites was relatively weak. The absence of this tail in the composite emission spectrum suggested that the emission P3HT/CdSe composites was much stronger.

In the solid state, the emission spectrum of CdSe QD ($\lambda_{em,CdSe}$ = 593 nm) overlapped the absorption spectrum of P3HT (Figures 1 and 2b); thus, upon excitation, the energy transfer from excited CdSe QD to P3HT may be expected in which the quenching of CdSe emission would be accompanied by a complementary growth of emission of P3HT at longer wavelength.[46] The P3HT/CdSe composites exhibited emission maximum at 670 nm, and the emission of CdSe QDs was completely suppressed, indicating the energy transfer from excited CdSe QDs to P3HT. The emission maximum of P3HT in the composite blue-shifted to 670 nm (Figure 4b) as compared to the vinyl-terminated P3HT in dry state in which $\lambda_{em,P3HT}$ = 730 nm (Figure 2d). This may be attributed to the presence of CdSe QDs in the composite that disrupted P3HT crystalline order and, thus, suppressed the P3HT interchain excitation.[47] The formation of exciplex between holes on P3HT and electrons on CdSe QDs[47] may also account for the blue-shift of emission peak to 670 nm.

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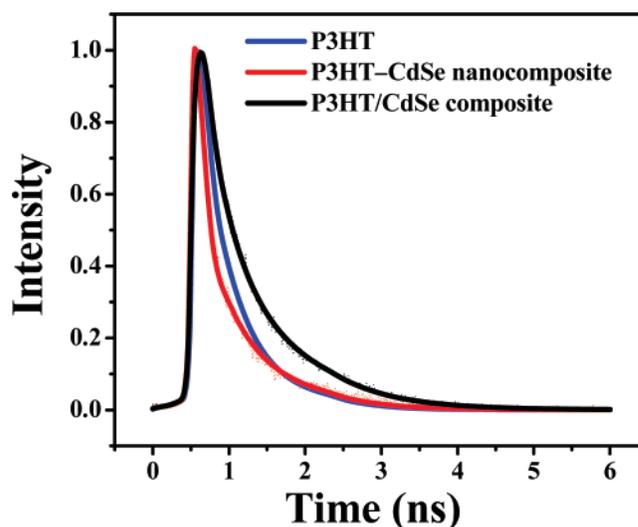
Figure 5. Normalized time-resolved photoluminescence decays of P3HT (blue), the P3HT/CdSe composites (black), and the P3HT−CdSe nanocomposites (red), respectively, monitored at λ_{exc} = 410 nm and $\lambda_{em} \geq 550$ nm. The curve fitting yielded the average lifetimes of P3HT, P3HT/CdSe, and P3HT−CdSe of 240, 490, and 160 ps, respectively.

For the P3HT−CdSe nanocomposites, however, the charge transfer from P3HT to CdSe dominated (Figure 4b). Placing P3HT in intimate contact with CdSe provided a direct electronic interaction between them. The electrons formed upon excitation of P3HT can be directly injected onto the CdSe surface to passivate the surface trap sites.[48] Because of a good quality surface passivation of the CdSe QD, represented as the high emission intensity, there was a limited amount of trap sites on the CdSe surface. Thus, the vacant trap sites could easily be passivated by electrons from P3HT, thereby enhancing the radiative recombination probability within CdSe QDs.[18,48] It is interesting to note that the emission maximum of CdSe in the nanocomposites was at 565 nm (Figure 4b) as opposed to 590 nm in CdSe chloroform solution (Figure 1). This may be due to uneven passivation of QD surface via the charge transfer from P3HT. The 3.5 nm CdSe QDs had a size distribution of ±0.3 nm. The smaller QDs had less surface/volume ratio; they possessed less vacant surface trap sites, which in turn were easily filled by electrons injected from excited P3HT. As a consequence, the emission of smaller QDs was enhanced the most, which caused the emission peak to blue-shift to 565 nm.

Time-resolved photoluminescence (PL) measurements (i.e., ultrafast emission dynamics), monitored at the wavelength above 550 nm, were performed to give additional information on the charge-transfer dynamics in the P3HT−CdSe nanocomposites by measuring the fluorescence lifetimes using time-correlated single-photon counting (TCSPC) methodology (Figure 5). The apparatus for the TCSPC measurements was described in detail elsewhere.[49,50] The solid-state dynamic process took place on the picosecond time scale and involved diffusion of the

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electronic excitations from P3HT to CdSe.[51] The measurements revealed that the luminescence of the P3HT−CdSe nanocomposites had a lifetime of 160 ps, while it was 240 ps in the pure homopolymer, *rr* P3HT (Figure 5). The faster PL decay of the P3HT−CdSe nanocomposites than that of P3HT can be attributed to the improved interfacial contact between P3HT and CdSe in the nanocomposites, where it is easy for the exciton to find the interface and dissociate, representing as a rapid charge transfer from P3HT to CdSe.[52,53] This is consistent with the static PL measurement (red curve in Figure 4). It is important to note that the lifetime of the P3HT/CdSe composites in solid state was 490 ps, which is longer than that of P3HT (i.e., 240 ps). This supported the energy-transfer mechanism hypothesized in the static PL measurement of the P3HT/CdSe composites (black curve in Figure 4). The insulating ligand (i.e., DOPO-Br) on the CdSe surface hindered the charge transfer between P3HT and CdSe, leading to the energy transfer dominant in the P3HT/CdSe composites.

Conclusion

In summary, placing CPs in intimate contact with QDs (i.e., preparing CP−QD nanocomposites) provided a means of achieving uniform dispersion of QDs and maximizing the interfacial area of P3HT and CdSe, thereby facilitating efficient electronic interaction between them. Rather than oligomeric CP, a relatively long chain CP, vinyl-terminated regioregular P3HT (14 thiophene units) was chemically tethered to the [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br)-func-

tionalized CdSe QD surface via a mild palladium-catalyzed Heck coupling (i.e., a "grafting onto" route to P3HT−CdSe nanocomposites; there is no need for ligand exchange chemistry). The "grafting onto" method was simple to perform. The success of the coupling was confirmed by the ^{1}H NMR and ^{31}P NMR spectroscopies. The number of P3HT bound to each CdSe QD was estimated by TGA. The photophysical properties of nanocomposites were found to differ from the conventional composites in which P3HT and CdSe QDs were physically mixed. Solid-state emission spectra of nanocomposites suggested the charge transfer from P3HT to 3.5 nm CdSe QDs, while the energy transfer from 3.5 nm CdSe QD to P3HT was implicated in the P3HT/CdSe composites. A faster decay in lifetime further confirmed the occurrence of charge transfer in the nanocomposites. We envision that the P3HT−CdSe nanocomposites can be utilized for constructing one layer of solar cell to explore the possible optoelectronic device application. This work is currently under investigation.

Supporting Information Available: ^{1}H NMR spectra of P3HT homopolymer and P3HT−CdSe nanocomposites; ^{31}P NMR spectra of DOPO-Br, DOPO-Br-functionalized CdSe QDs, and P3HT−CdSe nanocomposites; and TGA of vinyl-terminated P3HT, DOPO-Br, and CdSe−P3HT nanocomposites. This material is available free of charge via the Internet at http://pubs.acs.org.

JA074133X

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