

Organic–Inorganic Nanocomposites by Placing Conjugated Polymers in Intimate Contact with Quantum Rods

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Recent advances in the synthesis^[1] and assembly^[2] of nanocrystals (NCs) provide unique opportunities to exploit NCs for the development of next generation organic/inorganic hybrid solar cells as one of the most promising alternatives to Si solar cells to deliver efficient energy conversion with inexpensive fabrication.^[1,2] These conjugated polymer-based photovoltaic devices capitalize on the advantages peculiar to conjugated polymers (CPs), such as light weight, flexibility, processability, roll-to-roll production, low cost, and large area, in conjunction with the high electron mobility and tunable optical properties of inorganic NCs. Of the organic/inorganic hybrids, poly(3-hexylthiophene) (P3HT) is one of the most extensively utilized CPs due to its excellent solution processability, environmental stability, high charge carrier mobility, and tailorable electrochemical properties.^[3,4] CdSe quantum dots (QDs) are the most commonly investigated NCs because of their quantum-confined nature and well-matched energy level with P3HT.^[5–11]

However, CP/NC hybrids are widely prepared by simply physically mixing CP and NC. As such, it remains challenging to control the detailed morphology and dispersion of NCs within CPs at the nanoscale. The NCs are often passivated with an insulating organic ligand that hinders the efficient electronic interaction (e.g., charge transfer) with the surrounding CPs.^[12] Moreover, due to the large difference in their solubilities, phase separation of CPs and NCs is inevitable, thereby reducing the interfacial area between them and limiting the performance of the resulting devices.^[13] To this end, the ability to chemically tether NCs with CPs (i.e., preparing CP–NC nanocomposites with well-controlled interfaces) provides a means of achieving a uniform dispersion of NCs and, most importantly, significantly promotes the electronic interaction between the electron-donating CPs and electron-accepting NCs.^[14,15] Notably,

this strategy has only recently been developed and primarily implemented via ligand exchange, which suffers from incomplete surface coverage.^[14,16]

The ability to manipulate the shape of semiconductor NCs has led to quantum rods (QRs) with diameters ranging from 2 to 10 nm and lengths ranging from 5 to 100 nm.^[17,18] QRs possess improved optical absorption in the visible and near-infrared ranges^[5] and enhanced electron mobility when aligned in the direction of transport, an advantage over QDs where electron hopping between QDs is required. These optical and electronic properties make QRs better NCs than QDs for use in solar cells.^[19] Herein, we report a simple yet robust route to directly placing conjugated polymer, P3HT, in intimate contact with anisotropic CdSe QRs (i.e., creating P3HT–CdSe QR nanocomposites), dispensing with the need for ligand exchange chemistry. Bromobenzylphosphonic acid (BBPA) was utilized as a novel bifunctional ligand with phosphonic acid and aryl bromide at each end. The phosphonic acid group coordinated with CdSe to induce elongated growth, yielding BBPA-functionalized CdSe QRs (i.e., BBPA–CdSe QRs) with the aryl bromide group on their surface. Subsequently, P3HT–CdSe QR nanocomposites were obtained by Heck coupling of vinyl-terminated P3HT with BBPA–CdSe QRs (i.e., the coupling reaction between the vinyl endgroup of P3HT with the aryl bromide of BBPA–CdSe). The success of direct coupling was confirmed by NMR spectroscopy and dynamic light scattering (DLS). The occurrence of charge transfer at the P3HT/CdSe interface was evident from UV-vis absorption, photoluminescence (PL), and time-resolved PL studies. As such, it stands out as a promising method to simplify the synthesis procedure and opens opportunities to increase the grafting density for large-scale synthesis for use in solar cells.

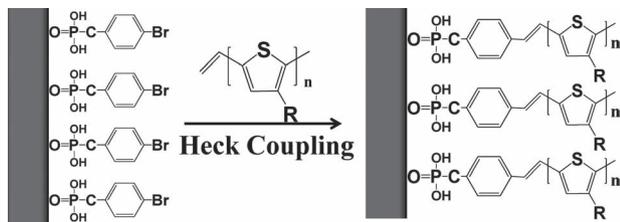
Bromobenzylphosphonic acid (BBPA; bearing aryl bromide end group) functionalized CdSe QRs (i.e., BBPA–CdSe QRs) were synthesized based on a ligand-exchange free procedure (**Scheme 1**; also see Experimental Section). Notably, phosphonic acids are the most widely utilized ligands to induce the anisotropic growth of NCs as they coordinate more strongly on the NC surface than other ligands, thereby effectively regulating the growth rate of NCs and raising the energy of (001) faces of the CdSe wurtzite structure. Moreover, a recent NMR study showed that phosphonic acid was the only capping ligand on the elongated CdSe nanostructures, even though an excess amount of phosphate oxide was used as the solvent.^[20] Transmission electron microscopy (TEM) measurements revealed a high-quality, 1D CdSe QR morphology with a wurtzite structure and dimensions of 40 ± 6 nm in length and 5 ± 1 nm in

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DOI: 10.1002/adma.201100923



Scheme 1. Direct grafting of vinyl-terminated P3HT onto bromobenzylphosphonic acid-functionalized CdSe QRs (i.e., BBPA–CdSe QRs) by Heck coupling, yielding P3HT–CdSe QR nanocomposites.

diameter (Figure 1). The local weak aggregation was due to the self-assembly of BBPA–CdSe QRs on the TEM grid after solvent evaporation.^[21,22] The QRs possessed a monodispersed size distribution as evident in the DLS measurement in which a relatively narrow single peak was observed (Figure S1a, Supporting Information). BBPA acted as a bifunctional ligand, in which the aryl bromide on one end readily reacted with vinyl-terminated P3HT via Heck coupling and the phosphonic acid group on the other end promoted the strong anchoring of BBPA to the CdSe QR surface.

The ³¹P NMR of BBPA–CdSe QRs clearly showed the existence of BBPA. No signal of tri-*n*-octylphosphine oxide (TOPO), which was used as the solvent (see Experimental Section) was observed due to the much weaker capping ability of TOPO compared to phosphonic acid (Figure S2a, Supporting Information); this is in good agreement with previously reported work.^[23,24] The addition of octadecyl phosphonic acid (ODPA; an 18-carbon chain) as a co-ligand was found to play an important role in producing high-quality, well-dispersed elongated NCs. Growth of QRs solely with BBPA led to the formation of highly aggregated elongated nanostructures (Figure S3a, Supporting Information) due to poor stabilization of BBPA in the relatively low polar organic solvent (i.e., tetrahydrofuran (THF) and toluene used in the study), in which P3HT was fully dissolved during the grafting process.^[25] Moreover, the CdSe QRs synthesized with solely BBPA also suffered from low quality and possessed branches, kinks, and non-uniform cross sections along the diameter of the QRs (Figure S3a, Supporting Information). Therefore, phosphonic acids with long alkyl chains (e.g., tetradecyl phosphonic acid (TDPA; an 18-carbon chain) or ODPA) were needed to stabilize the hydrophobic QRs in

THF. We note that compared to ODPA or TDPA, which are widely used ligands in the synthesis of CdSe QRs, BBPA had much shorter chain length, and thus much higher reactivity due to less steric hindrance during the monomer diffusion and crystal growth process.^[20,26] The QRs synthesized with BBPA are more susceptible to having certain defects,^[27] including stacking faults and twinning defects, which lead to extensive branching.^[24] As such, in order to reduce the overall growth rate, phosphonic acid with longer length was added. The presence of these ligands (ODPA or TDPA) acted as the monomer buffer in conjunction with BBPA, thereby effectively regulating the monomer concentration during the anisotropic growth of QRs.^[22,28]

Both TDPA and ODPA were explored in order to improve the quality and dispersion of QRs. Ligand mixtures at different molar ratios (i.e., ODPA (or TDPA):BBPA = 3:1, and ODPA (or TDPA):BBPA = 5:1) were systematically investigated. The QR quality can be greatly improved with an increase of the ODPA (or TDPA) ratio in the ligand mixture (Figure S3, Supporting Information), with ODPA being more effective than TDPA (i.e., ODPA:BBPA = 3:1 in Figure S3d (Supporting Information) and ODPA:BBPA = 5:1 in Figure 1a). The best quality CdSe QRs were obtained at an ODPA:BBPA ratio of 5:1 (Figure 1a), which was comparable to those reported using an HPA:TDPA ligand mixture.^[23,28] Compared to TDPA, ODPA had longer alkyl chain and thus lower reactivity, leading to shorter and less branched structures.^[24] The TEM observations suggested that larger activity difference in the ligand mixture (e.g., ODPA:BBPA) tended to yield better quality QRs by serving as the precursor concentration buffer and regulating the anisotropic growth of QRs.

It is noteworthy that similar amounts of BBPA and ODPA passivated the CdSe QR surface, as revealed by ³¹P NMR, regardless of the initial molar ratio of ODPA:BBPA = 5:1 (Figure S2b, Supporting Information).^[29] The higher coordination efficiency of short-chain molecules compared to the long-chain counterparts has been widely observed in the synthesis of CdSe QRs. For example, hexylphosphonic acid (HPA) was found to predominately cover the QR surface when the ligand mixture of HPA:TDPA was utilized.^[23,24] This phenomenon can be explained by the change in free energy after the attachment of free molecules on the solid surface. It was less energetically favorable for the longer-chain ligand to coordinate with CdSe because of the larger repulsive osmotic force experienced by long chains that were packed on the surface.^[30] As a result, due to its long alkyl chain, the ODPA ligand was much less competitive than BBPA in functionalizing the QR surface. This led to CdSe QRs possessing a high density of BBPA despite the fact that the initial molar ratio of ODPA:BBPA was 5:1. By contrast, TDPA (a shorter chain than ODPA) may be comparable to BBPA for QR surface passivation. As a result, the QR surface was primarily capped with TDPA due to the large initial molar ratio of TDPA:BBPA, and the extremely weak ³¹P NMR signal of BBPA was detected from the CdSe QRs at the TDPA:BBPA = 5:1 (data not shown). Taken together, among the various mixed ligands investigated, CdSe QRs synthesized with an ODPA:BBPA ratio of 5:1 possessed the best quality and BBPA grafting density, making them the most suitable for grafting vinyl-terminated P3HT (a “grafting-onto” approach; Scheme 1).

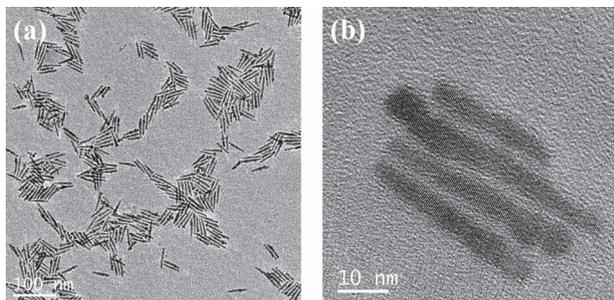


Figure 1. TEM images of a) BBPA-functionalized CdSe QRs (i.e., BBPA–CdSe QRs) prepared using the ODPA:BBPA mixture in a 5:1 molar ratio, and b) close-up of individual BBPA–CdSe QRs in which the crystalline lattice is clearly evident.

We note that in our previous work, P3HT–CdSe QDs nanocomposites were synthesized by directly grafting vinyl-terminated P3HT onto [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO–Br) functionalized CdSe QD surface.^[25] The strategy of capitalizing on the DOPO–Br ligand to produce DOPO–Br-functionalized CdSe QDs to render the chemical tethering of vinyl-terminated P3HT, however, cannot be extended to the CdSe QR synthesis. This is because phosphate oxide, the capping group in DOPO–Br, was not a suitable ligand to induce elongated growth of CdSe NCs.^[22] The growth in phosphate oxide occurred too rapidly at the high monomer concentration desired for the elongated growth, thereby resulting in primarily isotropic, dot-like NCs.^[22] Thus, prior to the coupling with vinyl-terminated P3HT, ligand exchange was utilized to functionalize QR with DOPO–Br.^[31] However, the ligand exchange process is often plagued by incomplete surface coverage.^[14]

In this context, as illustrated in Scheme 1, vinyl-terminated P3HT was grafted onto BBPA-functionalized CdSe QRs via a mild palladium-catalyzed Heck coupling of the aryl bromide of BBPA with the vinyl group of P3HT, yielding P3HT–CdSe QR nanocomposites in the absence of ligand exchange chemistry. The color of the solution changed from brown (CdSe) to light purple (P3HT) after the reaction and subsequent purification, indicating P3HT was grafted onto CdSe QRs. TEM images of P3HT/CdSe QR composites prepared by physically blending vinyl-terminated P3HT and BBPA–CdSe with P3HT–CdSe QR nanocomposites are shown in Figure 2a,b, respectively. Compared to the physical mixture counterpart that showed significant phase segregation (Figure 2a) and thus reduced interfacial area needed for charge separation, CdSe QRs were well dispersed within the P3HT–CdSe QR nanocomposites, as evident in Figure 2b. The self-assembly of nanocomposites was clearly evident, which can be attributed to the strong dipole–dipole interaction of CdSe QRs typically observed in elongated nanostructures (Figure 2b).^[32,33] The P3HT/CdSe weight ratio in composites ($\approx 1:3.135$) was made to be the same as that of nanocomposites; the ratio in the latter was determined by thermogravimetric analysis (TGA) measurements (Figure S4, Supporting Information). Quite intriguingly, the P3HT–CdSe QR nanocomposites can also be readily dispersed in the P3HT homopolymer matrix (Figure 2c); this is in sharp contrast to the phase segregation observed in the P3HT/CdSe composites (Figure 2a).^[13] It is interesting to note that no clear grafted P3HT at the periphery of the CdSe QRs was imaged by TEM (Figure S5, Supporting Information) due to the low electron density of

P3HT compared to inorganic QRs.^[25] However, the existence of P3HT grafting can be indirectly verified by the DLS measurement, which has been proven to be an effective method to confirm the coating at the surface of QRs (e.g., Au).^[34] After P3HT grafting, the average size of the QRs actually increased from 17.37 nm to 20.03 nm (Figure S1, Supporting Information).

The success of coupling of vinyl-terminated P3HT with BBPA–CdSe QRs was confirmed by solution ¹H NMR. Compared with the molecules and QDs,^[35] QRs are large in volume, and the vibration of bonded P3HT was strongly confined by the magnetic wave, resulting in a low-resolution NMR signal of the vinyl coupling group (i.e., double bond) near the QR surface.^[24] Therefore, a dissociation procedure was employed to detach grafted P3HT chains from the QR surface, and thus, P3HT coupled with BBPA ligand can be characterized in a free, unbonded state (see Experimental Section). After Heck coupling, the proton signal from the thiophene ring at 6.93 ppm was observed,^[25] and it was shifted to 6.97 ppm after dissociation of P3HT, indicating that P3HT was originally bonded to CdSe (Figure S6a, Supporting Information).^[29] Furthermore, two proton signals from the vinyl end group on P3HT at 5.1 and 5.5 ppm disappeared after coupling with BBPA–CdSe QRs, suggesting that P3HT was grafted onto the CdSe QRs (Figure S6b, Supporting Information).^[25] The grafting density of the P3HT chains was determined by TGA (Figure S4, Supporting Information). The molecular weight of CdSe QRs was estimated to be $9.81 \times 10^6 \text{ g mol}^{-1}$ based on the TEM images shown in Figure 1, and the P3HT/CdSe weight ratio was 1:3.135 from TGA. Thus the P3HT/CdSe molar ratio was approximately 600:1, much higher than that obtained from ligand exchange approach, which was 250:1.^[31]

The photophysical properties of the resulting P3HT–CdSe QR nanocomposites were explored by absorption and solid state photoluminescence (PL) studies. Figure 3a shows the absorption spectra of BBPA–CdSe QR, vinyl-terminated P3HT, and P3HT–CdSe QR nanocomposites in THF. The absorption maxima for P3HT and CdSe QRs were at 448 nm and 614 nm, respectively. It is clear that the absorption spectrum of the nanocomposites was simply the sum of the absorption spectra of its constituents, which served as additional evidence of successful coupling of nanocomposites. The dry nanocomposite film was characterized by PL measurement, which was acquired from a sample sealed in an Ar-filled vial to prevent possible photodegradation (Figure 3b).^[36] The vibronic structures of vinyl-terminated P3HT were clearly evident.^[25] In contrast, a nearly complete quenching of P3HT fluorescence was seen, implying efficient charge transfer from P3HT to CdSe QRs. This observation further confirmed intimate chemical contact between P3HT and CdSe.^[31]

In order to provide additional information on the charge transfer dynamics in P3HT–CdSe nanocomposites, time-resolved PL measurements (i.e., ultrafast emission dynamics) monitoring the wavelengths above 550 nm were performed by measuring the fluorescence lifetime using a time-correlated single-photon counting (TCSPC) methodology.^[25] The solid-state dynamics took place

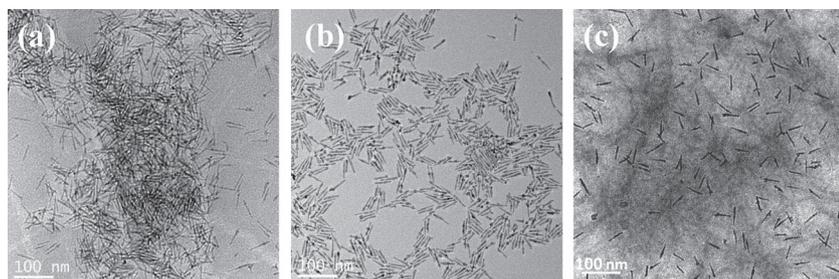


Figure 2. TEM images of a) physical mixture of vinyl-terminated P3HT and BBPA–CdSe QRs, b) P3HT–CdSe QR nanocomposites synthesized by Heck coupling, and c) P3HT–CdSe QR nanocomposites in the P3HT homopolymer matrix.

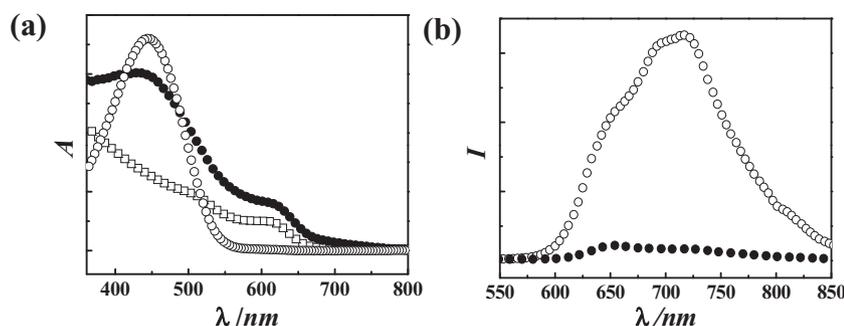


Figure 3. a) Absorption spectra of the P3HT–CdSe nanocomposites prepared by Heck coupling (solid circles), BBPA–CdSe QRs (open squares), and vinyl-terminated P3HT (open circles). b) Emission spectra of vinyl-terminated P3HT (solid circles) and the P3HT–CdSe nanocomposites (open circles) in the dry state.

on the picosecond time scale and involved the diffusion of electronic excitations from P3HT to CdSe.^[25,37] The measurements revealed that P3HT/CdSe composites (i.e., mixture of P3HT and BBPA–CdSe) had a fluorescence lifetime of 320 ps, close to the 375 ps lifetime for P3HT homopolymer;^[30] this is because the charge transfer between P3HT and CdSe was hindered by the insulating ligands (i.e., BBPA and ODPa) as well as the strong phase segregation in the composites (Figure 2a).^[25] The P3HT–CdSe nanocomposites formed by Heck coupling, however, exhibited a much faster lifetime of 170 ps, an important signature of an improved interfacial contact between P3HT and CdSe. The direct chemical anchoring of P3HT on CdSe made it easy for excitons to find the interface and dissociate, representing as a rapid charge transfer from P3HT to CdSe.^[5,25] This result was well correlated with the static PL study (Figure 3b). The charge transfer led to the PL quenching since the photogenerated exciton was dissociated before luminescence occurred.

In summary, a simple yet robust “grafting-onto” strategy was exploited to successfully produce semiconductor organic–inorganic nanocomposite by anchoring end-functionalized CPs (i.e., vinyl-terminated P3HT) onto anisotropic NCs that possessed a complementary functional group (i.e., BBPA–CdSe QRs) via a mild palladium-catalyzed Heck coupling, thereby affording direct contact between P3HT and CdSe QRs and dispensing with the need for ligand exchange chemistry as in copious previous work. The success of grafting was confirmed by NMR and DLS measurements. The CdSe QRs were well dispersed within the resulting P3HT–CdSe QR nanocomposites, and the nanocomposites can also be well distributed in the P3HT homopolymer matrix. The grafting density of P3HT was greatly increased as compared to that using conventional ligand exchange approach. Solid-state emission spectra of nanocomposites suggested charge transfer from P3HT to CdSe. While only CdSe QRs were studied here, this synthetic strategy is not restricted to them alone, but can be easily extended to other various elongated nanostructures (e.g., nanowire, tetrapods, etc.) as well as other types of semiconductors (e.g., CdS, CdTe, PbS, PbSe, etc.). Such nanocomposites, in which CPs and anisotropic NCs are intimately contacted, may be very promising for use in organic–inorganic hybrid solar cells with improved power conversion efficiency due to

i) an increased interfacial contact between these two constituents and ii) continuous pathways provided by the long axis of anisotropic NCs.

Experimental Section

All chemicals, including 4-bromobenzyl bromide, triethyl phosphate, cadmium oxide (CdO), tri-n-octylphosphine oxide (TOPO), *N*-methyl-dicyclohexylamine, 2,5-dibromo-3-hexylthiophene, Ni(dppp)Cl₂, tert-Butylmagnesium chloride (2 mol L⁻¹ in diethyl ether), and vinylmagnesium bromide (0.5 mol L⁻¹ in THF) purchased from Sigma Aldrich and tetra decyl phosphonic acid (TDPA) and octadecyl phosphonic acid (ODPA) purchased from PCI Synthesis, were used as received. THF (Fisher, 99%) was refluxed over sodium wire and distilled from sodium naphthalenide solution.

Synthesis of Bromobenzylphosphonic Acid (BBPA): Bromobenzylphosphonic acid (BBPA) was synthesized by modifying a reported procedure.^[38] In general, a mixture of 4-bromobenzyl bromide and triethyl phosphate (molar ratio = 1:2) was heated and stirred under Ar at 150 °C for 5 h to yield diethylphosphonate ester. The excess triethyl phosphate and byproducts were then removed by heating to 100 °C under vacuum for several hours. Then, diethylphosphonate ester was hydrolyzed to yield BBPA by adding excess concentrated aqueous HCl and heated to 100 °C overnight. After cooling down to room temperature, the BBPA was filtered out, and then redissolved in CH₃CN. The addition of CH₃CN and its evaporation using rotary evaporator were repeated three times to remove trace amounts of water and HCl. Finally BBPA was recrystallized using ethyl acetate to obtain a pure product. Yield: 56%. ¹H NMR: 7.46 and 7.19 (AA'XX', 4H), 2.94 (d, 2H, J = 21 Hz)

Synthesis of BBPA-Capped CdSe QRs: A mixture of BBPA (67 mg), ODPa (333 mg), TOPO (1.5g), and CdO (0.1 g) was first degassed in a 25 mL three-neck flask connected to a Liebig condenser at room temperature in vacuum and subsequently at 120 °C for 60 min. It was then slowly heated under Ar until CdO decomposed and the solution turned clear and colorless. Next, TOP (0.7 mL) was added and the temperature was further raised to 320 °C. Selenium (36 mg) dissolved in TOP (0.5 mL) was rapidly injected to the vigorously stirred Cd precursor. The CdSe QRs were allowed to grow for 5 min. The heating mantle was then removed to stop the reaction. After the solution was cooled to 60 °C, THF (2 mL) was added to the flask. The BBPA-functionalized CdSe was isolated by repeated dissolution in THF and precipitation in methanol three times.

Synthesis of Vinyl-Terminated P3HT: Vinyl-terminated P3HT was synthesized by a quasiliving Grignard metathesis (GRIM) method.^[39] Briefly, 2,5-dibromo-3-hexylthiophene (0.815 g, 2.5 mmol) was dissolved in THF (5 mL) in a three-neck flask and stirred under Ar. Tert-butylmagnesium chloride (1.25 mL, 2.5 mmol) was added via a syringe. The mixture was stirred for 2 h at room temperature. Subsequently, it was diluted to 25 mL with THF, and Ni(dppp)Cl₂ (22.5 mg, 0.041 mmol) was added. The resulting mixture was first stirred for 10 min at room temperature, producing the intermediate P3HT, followed by a reaction with vinylmagnesium bromide (2 mL, 1 mmol) in THF for 30 min. The product, vinyl-terminated P3HT, was obtained by precipitating the reaction mixture in methanol, filtering in an extraction thimble, and washing by Soxhlet extraction with methanol, hexanes, and chloroform sequentially. The final pure vinyl-terminated P3HT was recovered after the chloroform evaporated. The regioregularity of P3HT was greater than 98%, as determined by ¹H NMR. The number average molecular weight and polydispersity index (PDI) of P3HT were 4900 g mol⁻¹ and 1.2, respectively, as measured by gel permeation chromatography (GPC). Yield: 46.6%. ¹H NMR (300 MHz, CDCl₃, δ (ppm)): 6.98 (s, 1H), 6.0 (m, 1H), 5.19 (dd, J = 8 Hz and 3 Hz, 1H), 5.10 (dd, J = 8 Hz and 3 Hz, 1H),

2.8 (t, $J = 3$ Hz, 2H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), and 0.92 (t, 3H).

Synthesis of P3HT–CdSe Nanocomposites by Heck Coupling: In a glove box, Pd₂(dba)₃ (1 mg), vinyl-terminated P3HT (10 mg), and BBPA-functionalized CdSe QRs (i.e., BBPA–CdSe) (10 mg) were loaded in a reaction vial. *N*-methylcyclohexylamine (0.08 mL), tri-*t*-butylphosphine THF solution (0.06 mL) at a concentration of 100 mg mL⁻¹, and THF (0.5 mL) were added sequentially. The reaction mixture was continuously stirred under Ar in a 50 °C oil bath for 20 h. The final product, P3HT–CdSe nanocomposites, was cooled to room temperature, transferred to new vial, and centrifuged at 2000 rpm for 0.5 h to remove the catalyst. The supernatant (i.e., P3HT–CdSe nanocomposites) was diluted 10 times with THF and precipitated with methanol twice to remove free P3HT chains that were coupled with CdSe.

P3HT Dissociation from Nanocomposites for NMR Analysis: The grafted P3HT could not be stripped from the CdSe QR surface using the recovery method for BBPA because of the degradation of P3HT caused by aqua regia.^[40] Despite the fact that pyridine is a weak ligand, grafted P3HT can still be partially exchanged in a thermodynamically controlled process.^[41] Briefly, the purified P3HT–CdSe QR nanocomposites were first dissolved in pyridine. The mixture was then heated at 80 °C and intensely stirred for 3 d under Ar in a 25 mL three-neck flask connected to a Liebig condenser. Excess pyridine was then vacuumed at 80 °C overnight, and the resulting solid was characterized by ¹H NMR in chloroform-*d*.

BBPA Ligand Recovery for NMR Analysis: To recover the capping ligand of CdSe QRs for NMR analysis, the QR solution was precipitated three times by adding methanol. The precipitate was isolated by centrifugation and decantation and dried under vacuum at 80 °C overnight. The QR powder was then dissolved in aqua regia (concentrated HNO₃:concentrated HCl = 1:3). The resulting solution was extracted with ethyl ether. After the ethyl ether evaporated under vacuum, the white solid was characterized by ³¹P NMR in dimethyl sulfoxide-*d*.

Characterizations: The morphology of CdSe QRs and nanocomposites were imaged by TEM (JEOL 1200EX scanning/transmission electron microscope (STEM); operated at 80 kV). The absorption spectra were recorded with a UV-vis spectrometer (UV-1600, SHIMADAZU). 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 ¹H NMR and ³¹P NMR were performed using a Varian VXR-400 spectrometer. The grafting density of P3HT chains on the CdSe surface was determined by TGA (TA Instrument TGA Q 50). The molecular weight of polymers was measured by GPC, equipped with an Agilent 1100 with a G1310A pump, a G1362A refractive detector, and a G1314A variable wavelength detector. Fluorescence lifetime measurements were performed using a TCSPC technique. The apparatus for TCSPC is described in detail elsewhere.^[42] The full width at half-maximum (FWHM) of the instrument response function was ≈40–45 ps. All samples were excited at λ_{ex} = 407 nm and the fluorescence emission was collected at λ_{em} ≥ 500 nm at perpendicular polarization orientation of the emission polarizer with respect to the vertical excitation polarization in order to eliminate possible interferences of scattered excitation light from solid surfaces.^[43]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge the support from the National Science Foundation (NSF-CBET 0824361).

Received: March 11, 2011
Published online: May 17, 2011

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