

Semiconductor Anisotropic Nanocomposites Obtained by Directly Coupling Conjugated Polymers with Quantum Rods**

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Conjugated polymers (CPs) have received considerable attention as promising materials for use in organic photo-voltaics, light-emitting diodes (LEDs), thin film transistors, and biosensors.^[1] Among various types of CPs, poly(3-hexylthiophene) (P3HT) is one of the most widely studied organic semiconductors. P3HT possesses excellent solution processability, environmental stability, high charge-carrier mobility, and tailorable electrochemical properties.^[2] Owing to their quantum-confined nature, for quantum dots (QDs) such as cadmium selenide (CdSe),^[3] variation of the nanocrystal size provides continuous and predictable changes in fluorescence emission,^[4,5] thus rendering them useful for a wide range of applications in photovoltaic cells,^[6,7] LEDs,^[8] biosensors,^[9] and bio-imaging.^[9] CP-based organic/inorganic hybrid solar cells (e.g., CP/QD composites) are favorable alternatives to inorganic solar cells as they have many advantages peculiar to CPs, such as light weight, flexibility, processability, roll-to-roll production, low cost, and large area. However, the CP/QD composites are most often prepared by simply physically mixing the CPs and QDs. This procedure, however, suffers from several severe problems, including microscopic phase separation and the existence of insulating interfacial layers,^[10] thereby reducing the interfacial area between CPs and QDs and thus limiting the performance of the resulting devices. Recently, various methods have been utilized to overcome these problems, such as the use of cosolvent mixtures^[11] or binary solvent mixtures^[12] and surface modification of QDs.^[10,13,14] The most elegant approach is to chemically tether CPs on the QD surface (i.e., preparing CP–QD nanocomposites), hence enabling direct electronic coupling between CPs and QDs.^[10,15] Notably, this strategy has only recently been developed and has been primarily implemented by ligand exchange, which permits the derivatization of the composite with a broad range of functional groups.^[10] However, ligand-

exchange chemistry suffers from incomplete surface coverage.^[10]

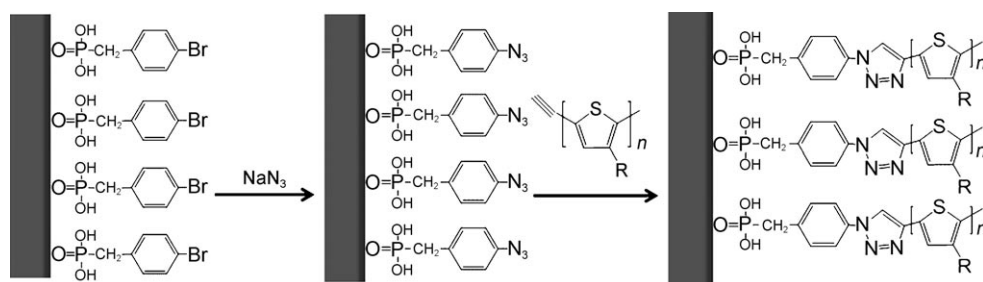
In this context, recently P3HT–CdSe–QD nanocomposites have been synthesized by directly grafting vinyl-terminated P3HT onto a [(4-bromophenyl)methyl]dioctylphosphine oxide(DOPO–Br)-functionalized CdSe QD surface by a mild palladium-catalyzed Heck coupling without the need for ligand exchange.^[16] The ability to manipulate the shape of nanocrystals has led to quantum rods (hereafter referred to as nanorods; NRs) with diameters that range from 2 to 10 nm and lengths ranging from 5 to 100 nm.^[3] Owing to their intrinsic structural anisotropy, NRs possess many unique properties that make them potentially better nanocrystals than QDs for photovoltaics and biomedical applications. Photovoltaic cells made of NRs and CPs show an improved optical absorption in the red and near-infrared ranges that originates from the NRs.^[6,7] Moreover, the long axis of the NRs provides continuous paths for the transport of electrons, an advantage over QDs, in which electron hopping between QDs is required.^[11] The performance of photovoltaic cells can be further improved if NRs are vertically aligned between two electrodes to minimize the carrier transport pathways.^[17] It is worth noting that although CP–NR nanocomposites were recently produced by ligand exchange of CPs with insulating ligands that were initially attached to the NR surface,^[18] direct grafting of CPs onto anisotropic nanocrystals has not yet been explored.

Herein, we report one simple yet robust route to CP–NR nanocomposites that displaces the need for ligand-exchange chemistry. In this strategy, the catalyst-free alkyne–azide cycloaddition, which belongs to the emerging field of click chemistry,^[19] was utilized in the preparation of P3HT–CdSe–NR nanocomposites. As shown in Scheme 1, CdSe NRs were passivated with bromobenzylphosphonic acid (BBPA), which not only induced elongated growth but also functionalized the CdSe NR surface and led to the formation of BBPA–CdSe–NRs. Subsequently, the aryl bromide groups of BBPA were converted into azide groups, thus forming N₃–BPA–CdSe NRs. Finally, catalyst-free Huisgen 1,3-dipolar cycloaddition between ethynyl-terminated P3HT and N₃–BPA–CdSe NRs successfully gave P3HT–CdSe NR nanocomposites without the introduction of any deleterious metallic impurity. Click reactions possess several attractive features, including an extremely versatile bond-formation process, no need for protecting groups, good selectivity, nearly complete conversion, and generally no need for purification.^[20] As such, it stands out as a promising method to simplify the synthetic procedure and opens opportunities to increase the grafting density for large-scale synthesis. The charge transfer occurred at the P3HT/CdSe NR interface and was confirmed by

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Scheme 1. Grafting P3HT onto bromobenzylphosphonic acid functionalized CdSe NRs by catalyst-free click reaction.

systematic UV/Vis absorption, photoluminescence (PL), and time-resolved PL studies.

It has been demonstrated that end-functionalized P3HT can be successfully grafted onto [(4-bromophenyl)methyl]-dioctylphosphine oxide (DOPO-Br)-functionalized CdSe QD surfaces by Heck coupling of the aryl bromide of DOPO-Br with a vinyl end group of P3HT.^[16] Quite intriguingly, however, the strategy of preparing DOPO-Br-capped CdSe QDs could not be applied to the synthesis of DOPO-Br-capped CdSe NRs,^[18] because phosphine oxide, the capping group on DOPO-Br, was not a suitable ligand to induce elongated growth of CdSe nanocrystals.^[3] Growth in phosphine oxide occurred too rapidly at the high monomer concentration desired for the elongated growth, thus the resulting nanocrystals are primarily isotropic dotlike.^[3] By contrast, phosphoric acid coordinates more strongly than phosphine oxide and is very effective at adjusting the growth rate of nanocrystals and raising the energy of (001) faces of the CdSe wurtzite structure, which leads to the formation of elongated architectures.^[3,21] Moreover, a recent NMR-spectroscopic study showed that phosphoric acid is the only capping ligand on the elongated CdSe structure, even though an excess amount of phosphine oxide was used as the solvent.^[22] Taken together, in order to enable the ligands not only to bear functional groups, that is, aryl bromide groups (later converted into azide groups) that can react with end-functionalized P3HT by click reactions, but that also can strongly anchor on the NR surface, new bifunctional ligands with phosphonic and aryl bromide groups at each end are needed.

To this end, CdSe NRs functionalized with bromobenzylphosphonic acid (BBPA) were synthesized based on a ligand-exchange-free procedure (see the Experimental Section). TEM measurements revealed a high-quality one-dimensional CdSe NR morphology with wurtzite structure (Figure S1 a in the Supporting Information) and dimensions of 40 ± 6 nm in length and 5 ± 1 nm in diameter (Figure S1 b). The local weak aggregation was due to the self-assembly of BBPA-CdSe NRs on the TEM grid after solvent evaporation.^[3,23] The NRs possessed a monodisperse size distribution as evidenced by the dynamic light scattering (DLS) measurements in which a relatively narrow single peak was observed (Figure S2 a). Anchoring of BBPA on CdSe was detected by solution-based ³¹P NMR spectroscopy after the ligand-recovery process (see the Supporting Information); this observation is due to the confinement of ligand vibration by the solid surface.^[24] The

³¹P NMR spectrum of octadecylphosphonic acid (ODPA; $\delta = 27.66$ ppm) and BBPA ($\delta = 21.29$ ppm) showed similar intensity despite the initial molar ratio of ODPA/BBPA 5:1 (Figure S3). Compared with ODPA, BBPA has much shorter chains and thus has a much higher reactivity because of less steric hindrance during the monomer diffusion and crystal growth process.^[21,22] This result was consistent with a previous study using hexylphosphonic acid (HPA) and tetradecane phosphoric acid (TDPA) mixtures to grow CdSe NRs, where more active HPA predominately covered the NR surface.^[25] Additionally, in the present study, no peak of tri-*n*-octylphosphine oxide (TOPO, solvent) was observed (data not shown), which is due to its much weaker capping ability as compared to phosphoric acid; this observation is consistent with previously reported results.^[24,25]

The addition of ODPA as a coligand was found to play an important role for the production of high-quality, well-dispersed elongated nanocrystals. Growth with BBPA solely led to the formation of highly aggregated elongated nanostructures (Figure S4 a) because of the poor stabilization of BBPA in organic solvents with relatively low polarities (i.e., THF and toluene used in the study), in which P3HT, however, was fully dissolved during the grafting process. Furthermore, a lower molar ratio of ODPA in the ligand mixture (i.e., ODPA/BBPA 1:1 and 3:1) generally led to less well-defined nanostructures that possess more branches, kinks, and nonuniform cross-sections along the diameter of the NRs (Figure S4 b and S4 c). The sufficiently present ODPA acted as the monomer buffer (i.e., metal-organic precursors) in conjunction with BBPA, thus effectively regulating the monomer concentration during the nanocrystal growth.^[25] Otherwise, the highly active BBPA-Cd precursor would greatly accelerate the growth process and would result in structures more susceptible to lattice defects (e.g., stacking faults, twinning defects, etc.^[26]).

The click reaction has been widely recognized as an attractive route for the functionalization of a variety of nanomaterials with high yield, including Au nanoparticles,^[27] carbon nanotubes,^[28] and QDs.^[29] To the best of our knowledge, no study has been performed on direct grafting of conjugated polymers onto nanocrystals by using click reactions. In the present study, the synthesis of P3HT-CdSe NR nanocomposites was accomplished as follows (Scheme 1). Firstly, the aryl bromide of BBPA was converted into an azide group by adding NaN₃ to the BBPA-CdSe solution. As NaN₃ is not readily dissolved in organic solvents (i.e., THF), a reaction period of three days was necessary to ensure complete conversion into azide-benzylphosphonic acid-capped CdSe (i.e., N₃-BPA-CdSe). Subsequently, the azide groups of N₃-BPA-CdSe reacted with the ethynyl-terminated P3HT under the formation of 1,2,3-triazoles, thus grafting P3HT onto the CdSe NR surface (see the Experimental

Section). Notably, the use of catalysts (e.g., copper) was avoided in this process, as metallic impurities can be easily bonded to the nanocrystal surface and can hardly be removed from the product, which is deleterious to the performance of nanocomposite solar cells.

The color of the solution changed from brown (CdSe) to light purple (P3HT) after the reaction and subsequent purification, thereby indicating that P3HT was grafted onto CdSe NRs. TEM images of P3HT/CdSe NR composites prepared by physically blending ethynyl-terminated P3HT

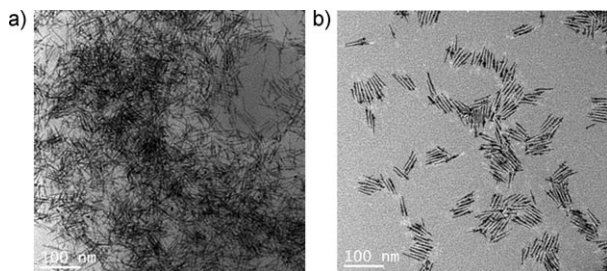


Figure 1. TEM images of P3HT/CdSe NR composites prepared by a) physically mixing ethynyl-terminated P3HT and azide benzylphosphonic acid functionalized CdSe NRs, and b) P3HT-CdSe NR nanocomposites synthesized by click reaction.

and BBPA-CdSe, and P3HT-CdSe NR nanocomposites are shown in Figure 1 a and b, respectively. Compared to the physical mixture counterpart, which showed significant phase segregation (Figure 1 a) and thus reduced the interfacial area needed for charge separation, CdSe NRs were well dispersed within the P3HT-CdSe NR nanocomposites as evidenced in Figure 1 b. The self-assembly of nanocomposites was clearly evident, which can be attributed to strong dipole-dipole interactions of CdSe NRs observed in the elongated nanostructures (Figure 1 b).^[3] The P3HT/CdSe weight ratio in the composites (approximately 1: 3.358) was matched to that of the nanocomposites; the ratio in the latter was determined by TGA measurements (Figure S5). Notably, the P3HT-CdSe NR nanocomposites can also be readily dispersed in the P3HT homopolymer matrix (Figure S6) in comparison to phase segregation seen in the P3HT/CdSe composites (Figure 1 a).^[10] It is worth noting that no clearly grafted P3HT at the periphery of CdSe NRs was imaged by TEM (Figure S6 a) because of the low electron density of P3HT compared to inorganic NRs.^[16] However, the existence of grafted P3HT can be indirectly verified by DLS measurements, which had been proven previously to be an effective method to confirm the coating at the surface of NRs (e.g., Au).^[30] After P3HT grafting, the average size of NRs increased from 17.37 to 19.56 nm (Figure S2).

Successful coupling of ethynyl-terminated P3HT with N_3 -BPA-CdSe NRs was confirmed by solution ^1H NMR spectroscopy. Compared with molecules and QDs, NRs are large in volume; the vibration of bonded P3HT was strongly confined under the magnetic wave, thus resulting in low-resolution NMR signals of the coupling groups nearby the NR surface.^[24] Therefore, a dissociation procedure was employed to detach grafted P3HT chains from the NR surface and

P3HT coupled with BBPA ligand could be characterized in a free unbonded state (see the Supporting Information). After click reaction, the proton signal from the thiophene ring at $\delta = 6.98$ ppm was observed,^[10,16] and it was shifted to $\delta = 6.88$ ppm after dissociation of P3HT, thus indicating that P3HT was originally bonded to CdSe (Figure S7). Furthermore, the proton signal at $\delta = 3.5$ ppm (i.e., peak i in Figure S8 a) from the ethynyl group on P3HT disappeared after the click reaction (Figure S8 b) and indicated that P3HT was successfully grafted onto CdSe. Additionally, the signal of the proton from the thiophene ring connected with the ethynyl group (i.e., peak h in Figure S8 a) also disappeared because of lack of influence of the ethynyl group after cycloaddition formation. The grafting density of P3HT chains was determined by thermogravimetry analysis (TGA; Figure S5). The molecular weight of CdSe NRs was estimated to be $9.81 \times 10^6 \text{ g mol}^{-1}$ based on TEM images shown in Figure S1, and the P3HT/CdSe weight ratio was 1:3.358 from TGA. Thus the P3HT/CdSe molar ratio was approximately 560:1, which is much higher than that obtained from the ligand exchange approach, which was 250:1.^[18]

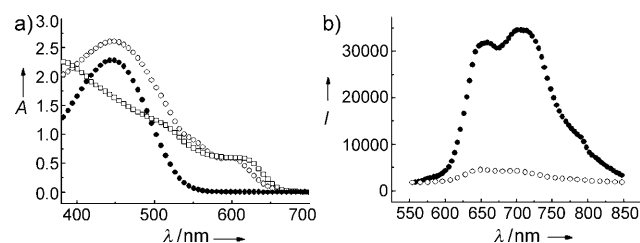


Figure 2. a) Absorption spectra of azide benzylphosphonic acid functionalized CdSe NRs (open squares), ethynyl-terminated P3HT (solid circles), and P3HT-CdSe nanocomposites prepared by click reaction (open circles). b) Emission spectra of ethynyl-terminated P3HT (solid circles) and nanocomposites (open circles) in dry state.

The photophysical properties of the resulting P3HT-CdSe NR nanocomposites were explored by absorption and solid-state photoluminescence (PL) studies. Figure 2 a shows the absorption spectra of N_3 -BPA-CdSe NRs, ethynyl-terminated P3HT, and P3HT-CdSe NR nanocomposites in THF. The absorption maxima for P3HT and CdSe NRs were located at 448 nm and 615 nm, respectively. It is clear that the absorption spectrum of the nanocomposites was the sum of the absorption spectra of its constituents, which served as additional evidence of successful coupling of the nanocomposites. Moreover, the absorption spectrum also revealed the effect of P3HT coating on the band structure of CdSe NRs (Figure 2). The absorption maximum was blue-shifted from 615 nm in N_3 -BPA-CdSe to 601 nm in P3HT-CdSe nanocomposites, which can be attributed to 1) the changes in the dielectric environment (i.e., grafting a layer of P3HT) that perturb the energy of quantum-confined excitation,^[31] or 2) enhanced confinement of the electron wave function because of an increased exciton-free dead layer thickness on the CdSe NR surface.^[32] The dry nanocomposite film was characterized by PL measurements, which were acquired

from samples sealed in an Ar-filled vial to prevent possible photodegradation (Figure 2b).^[33] The vibronic structures of ethynyl-terminated P3HT were clearly evident.^[16] By contrast, a nearly complete quenching of P3HT fluorescence was seen, hence implying efficient charge transfer from P3HT to the CdSe NRs. This observation further confirmed close chemical contact between P3HT and CdSe.^[18] Furthermore, the emission of P3HT at 710 nm after bonding to the CdSe surface was also blue-shifted to 697 nm (Figure S9). As the electronic structure of conjugated polymers strongly relates to their configuration,^[34] the blue-shift may be associated with a different configuration of the P3HT backbone on the CdSe surface than in the crystalline bulk.

In order to provide additional information on the charge-transfer dynamics in P3HT–CdSe nanocomposites, time-resolved PL measurements (i.e., ultrafast emission dynamics)

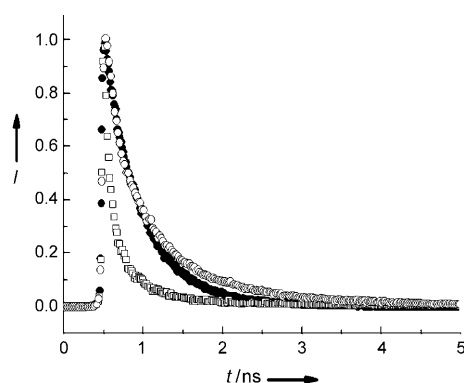


Figure 3. Normalized time-resolved photoluminescence decays of P3HT (solid circles), physical mixture of P3HT/BBPA–CdSe NR (open circles), P3HT–CdSe nanocomposites prepared by click coupling (open squares), respectively, monitored at $\lambda_{\text{exc}} = 407$ nm and $\lambda_{\text{em}} \geq 500$ nm. The curve fitting gave average lifetimes of 370 ps for P3HT, 320 ps for P3HT/CdSe NR composite, and 105 ps for P3HT–CdSe nanocomposites by click reaction, respectively.

monitored at wavelengths above 500 nm were performed by measuring the fluorescence lifetime using a time-correlated single-photon-counting (TCSPC) methodology (Figure 3). The solid state dynamics took place on the picosecond time scale and involved the diffusion of electronic excitations from P3HT to CdSe.^[16] The measurements revealed that P3HT/CdSe composites (i.e., mixtures of ethynyl-terminated P3HT and BBPA–CdSe) had a fluorescence lifetime of 320 ps, which is close to a 370 ps lifetime for the P3HT homopolymer; this result is due to the charge transfer between P3HT and CdSe being hindered by the insulating ligands (i.e., BBPA and ODPA) as well as the strong phase segregation in composites (Figure 1a).^[16] The P3HT–CdSe nanocomposites formed by click coupling, however, exhibited a much faster lifetime of 105 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, thus representing a rapid charge transfer from P3HT to CdSe.^[16,17] This result was consistent with the static PL study (Figure 2b). Charge

transfer led to the PL quenching because the photogenerated exciton was dissociated before luminescence occurred.

In summary, semiconductor organic–inorganic nanocomposites were successfully synthesized by directly grafting end-functionalized conjugated polymers onto anisotropic nanocrystals that possessed complementary functional groups for coupling reactions. A simple, yet robust “grafting-onto” strategy was exploited to create P3HT–CdSe NR nanocomposites, namely, catalyst-free click reaction of ethynyl-terminated P3HT with azide benzylphosphonic acid functionalized CdSe NRs, thereby affording direct contact between P3HT and CdSe and avoiding the need for ligand-exchange chemistry as in copious previous work. The success of the formation of nanocomposites was confirmed by NMR spectroscopy and DLS measurements. The CdSe NRs can be well dispersed within the resulting nanocomposites. The grafting density of P3HT was greatly increased as compared to that obtained by using conventional ligand-exchange approach. The solid-state emission spectra of the nanocomposites suggested the charge transfer from P3HT to CdSe. A much faster lifetime (i.e., fast exciton dissociation at the P3HT/CdSe interface) for the nanocomposites prepared by click reaction was observed. Such nanocomposites, in which P3HT and CdSe NRs are in intimate contact, may be very promising for use in organic–inorganic hybrid solar cells with improved power-conversion efficiency because of 1) an increased interfacial contact between conjugated polymers and one-dimensional nanocrystals, and 2) vectorial pathways provided by the long axis of NRs when they are aligned perpendicularly between two electrodes for effective exciton dissociation and transport; further studies are currently underway.

Experimental Section

All chemicals, including 4-bromobenzyl bromide, triethyl phosphate, cadmium oxide (CdO), tri-*n*-octylphosphine oxide (TOPO), sodium azide (NaN_3), *tert*-butylmagnesium chloride, and ethynylmagnesium bromide purchased from Sigma Aldrich, and tetradecylphosphonic acid (TDPA) and octadecyl phosphonic acid (ODPA) purchased from PCI synthesis were used without further purification. Trioctylphosphine (TOP) was purchased from Strem Chemicals.

Synthesis of bromobenzylphosphonic acid (BBPA): A mixture of 4-bromobenzyl bromide and triethyl phosphite 1:2 was heated and stirred under Ar at 150°C for 5 h to give the diethylphosphonate ester. The excess triethyl phosphite and byproducts were then removed by heating at 100°C under vacuum for several hours. After that, the diethylphosphonate ester was hydrolyzed to give BBPA by addition of excess concentrated aqueous HCl and was heated at 100°C overnight. After cooling to room temperature, the BBPA was filtered out, and was then redissolved in CH_3CN . Finally BBPA was recrystallized using ethyl acetate to obtain the pure product. Yield: 56%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 7.46$ (d, 2H, $J = 7.6$ Hz) and 7.19 (d, 2H, $J = 7.4$ Hz; AA'XX', 4H), 2.94 ppm (d, 2H, $J = 21$ Hz).

Synthesis of BBPA-capped CdSe NRs: A mixture of BBPA (67 mg), ODPA (333 mg), TOPO (1.5 g), and CdO (0.1 g) was first degassed in a 25 mL three-neck flask 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. 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 into the vigorously stirred Cd precursor; the CdSe NRs were

allowed to grow for 5 min. The BBPA-functionalized CdSe was isolated by repeated dissolution in THF and precipitation in methanol (three times).

Synthesis of ethynyl-terminated P3HT: The ethynyl-terminated P3HT was synthesized by a quasi-living Grignard metathesis (GRIM) method.^[35] 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 through a syringe. The mixture was stirred for 2 h at room temperature; subsequently, it was diluted with THF (to 25 mL) 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 intermediate P3HT, followed by reaction with ethynylmagnesium bromide (2 mL, 1 mmol) in THF for 30 min at room temperature. The final product, ethynyl-terminated P3HT was obtained after precipitation in methanol and washing by Soxhlet extraction with methanol, hexane, and chloroform sequentially. The regioregularity of ethynyl-terminated P3HT was greater than 98%. The number average molecular weight and polydispersity index of ethynyl-terminated P3HT were 5100 g mol⁻¹ and 1.18, respectively. Yield: 40.8%. ¹H NMR (300 MHz, CDCl₃): δ = 6.98 (s, 1H), 6.0 (m, 1H), 3.05 (s, 1H), 2.8 (t, J = 3 Hz, 2H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), and 0.92 ppm (t, 3H).

Synthesis of P3HT–CdSe nanocomposites by click reaction: NaN₃ was added to a solution of BBPA–CdSe NRs in THF. The mixture was sealed and stirred at room temperature for three days. The excess amount of NaN₃ was removed by centrifugation and the resulting azide benzylphosphonic acid capped CdSe NRs (i.e., N₃–BPA–CdSe) were then precipitated with methanol. Subsequently, N₃–BPA–CdSe NRs (50 mg), ethynyl-terminated P3HT (50 mg), and THF (10 mL) were loaded in a flask and kept at 60 °C under Ar for two days. The reaction mixture was cooled, transferred, and centrifuged; the free P3HT molecules in the solution were removed by precipitation.

Characterization: The morphologies of CdSe NRs and nanocomposites were imaged by TEM (JEOL 1200EX scanning/transmission electron microscope (STEM)). 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). ¹H NMR and ³¹P NMR spectroscopy were performed using a Varian VXR-400 instrument. The grafting density of P3HT chains on the CdSe surface was determined by thermogravimetry analysis (TGA; TA Instrument). Fluorescence lifetime measurements were performed using time-correlated single-photon-counting (TCSPC) technique. The full width at half-maximum (FWHM) of the instrument response function was approximately 40–45 ps. All samples were excited at λ_{ex} = 407 nm, and the fluorescence emission was collected at λ_{ex} ≥ 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.

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