

Crafting Semiconductor Organic–Inorganic Nanocomposites via Placing Conjugated Polymers in Intimate Contact with Nanocrystals for Hybrid Solar Cells

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Semiconductor organic–inorganic hybrid solar cells incorporating conjugated polymers (CPs) and nanocrystals (NCs) offer the potential to deliver efficient energy conversion with low-cost fabrication. The CP-based photovoltaic devices are complimented by an extensive set of advantageous characteristics from CPs and NCs, such as lightweight, flexibility, and solution-processability of CPs, combined with high electron mobility and size-dependent optical properties of NCs. Recent research has witnessed rapid advances in an emerging field of directly tethering CPs on the NC surface to yield an intimately contacted CP–NC nanocomposite possessing a well-defined interface that markedly promotes the dispersion of NCs within the CP matrix, facilitates the photoinduced charge transfer between these two semiconductor components, and provides an effective platform for studying the interfacial charge separation and transport. In this Review, we aim to highlight the recent developments in CP–NC nanocomposite materials, critically examine the viable preparative strategies geared to craft intimate CP–NC nanocomposites and their photovoltaic performance in hybrid solar cells, and finally provide an outlook for future directions of this extraordinarily rich field.

1. Introduction

Semiconductor organic/inorganic hybrid solar cells have attracted considerable attention as a promising low-cost alternative to conventional inorganic solar cells that often require expensive processing.^[1,2] They capitalize on many advantageous attributes peculiar to conjugated polymers (CPs), such as light weight, flexibility, non-vacuum processability, roll-to-roll production, low cost, and large area,^[3–9] in conjunction with the high electron mobility necessary for charge injection from CP, tunable optical properties, and physical and chemical stability of inorganic nanocrystals (NCs). During the last decade significant progress have been made in colloidal synthesis^[10–14] and self-assembly^[15–20] of NCs with well controlled shapes (dots,^[21–30] rods,^[2,31–33] tetrapods,^[34–37] hyperbranched,^[38] wires,^[39–42] etc.) from a broad spectrum of semiconductor materials (e.g.,

metal sulfides,^[43–45] metal selenides,^[46–48] metal tellurides,^[49,50] and metal oxide^[51]), offering greatly reduced materials cost as a result of colloidal synthesis.^[10,52] The ability to precisely tuning optical band gap of NCs (e.g., CdSe, CdTe, PbS, etc.) from ultraviolet to near-infrared (NIR) range, together with their capacity for multiple exciton generation (i.e., multiple excitons per photon formed in PbSe, PbS, PbTe, CdSe, etc.),^[53–65] provides the prospect for expanded solar spectral coverage as active light absorbers. In addition, CPs possess complementary absorption and high light absorption efficiency.^[1] As such, the CP/NC composites composed of *p*-type donor CPs and *n*-type acceptor inorganic NCs are of great interest and technological importance for use in cost-effective, high-performance solar cells relative to the non-hybrid counterparts.

The basic operation of semiconductor organic/inorganic hybrid solar cells, fabricated from thin films comprising a solution-processed mixture of interpenetrating electron donor phase (i.e., CPs such as regioregular poly(3-hexylthiophene) (P3HT)) and electron acceptor phase (i.e., NCs; e.g., CdSe and CdTe) sandwiched between two charge-collecting electrodes is based on a photoinduced charge separation at the organic/inorganic interface. Upon the absorption of photons, the photogenerated electrons and holes, formed from dissociation of excitons at the CP/NC interface, transport through CP and NC, respectively, and are collected at the appropriate device electrodes.^[66] The photovoltaic performance is dictated by the optimization of the underlying processes, including the light absorption, exciton diffusion, photo-induced charge transfer at the donor/acceptor interface, and effective charge transport to the respective electrodes. Two key challenges that restrict the design of efficient hybrid solar cells are (a) the ability to achieve fast and high-yield charge separation at the CP/NC interface (i.e., charge separation process must be fast enough to compete with radiative and nonradiative decays of the singlet exciton at the CP/NC interface that occur on a time scale of 100–1000 picoseconds^[67]), and (b) interpenetrating network of NCs to promote charge carrier transport and collection at the electrodes.^[66] Clearly, interfacial behavior is a critical performance factor for hybrid solar cells.

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It is noteworthy that high quality NCs utilized in hybrid solar cells are primarily prepared by the colloidal synthesis that affords the capability of tailoring the growth process of NCs, leading to the formation of NCs with well controlled size and shape largely determined by small molecular ligands (e.g., alkyl thiols, amines, phosphines, and phosphine oxides).^[68,69] After reaction, these ligands are capped on the NC surface, ensuring the solubility and miscibility of NCs with the host environment, and retaining the spectroscopic properties of materials by preventing them from aggregation. Ever since the pioneer work of Greeham et al. in 1996,^[70] the CP/NC hybrid solar cells have been widely prepared by simply *physically mixing* CPs and NCs. Despite the simplicity of this approach, the presence of several central issues originating from incompatible CP/NC interface, including microscopic phase separation^[71,72] and the insulating nature of surface ligands,^[67,72] severely reduces the interfacial area and impedes the charge transfer between CPs and NCs as well as the electron transport between adjacent NCs. Moreover, the loosely connected NC network further scatters the electron current, resulting in limited amount of photogenerated electrons that can finally transport to the electrode. Finally, directly stripping originally passivated ligands from the NC surface makes it difficult to control the composite morphology due to low solubility of inorganic NCs in CPs, and strongly impact the device performance.^[70,73] The power conversion efficiency of the photovoltaic devices is much lower for devices to be practical.^[74–76] Recently, many approaches have been developed to achieve a favorable three-dimensional interpenetrating network in NC/CP composites, using for example co-solvent mixtures,^[2] binary solvent mixtures,^[72] direct polymerization of CPs (e.g., polypyrrole/CdTe composites prepared by the electrochemical polymerization of pyrrole in the presence of CdTe NCs^[77]), etc. In stark contrast to them, the most elegant strategy is to *chemically tether* CPs on the NC surface (i.e., preparing CP–NC nanocomposites), thereby providing a means of achieving a uniform dispersion of NCs, and more importantly substantially promoting the electronic interaction between the electron-donating CPs and electron-accepting NCs.^[78,79]

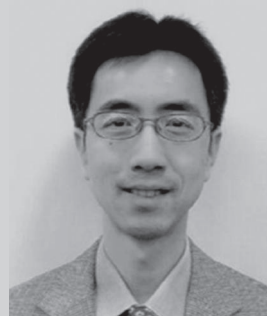
Over the past decade, three main synthetic strategies, namely, ligand exchange, direct grafting, and direct NC growth, have stood out as viable synthetic routes to imparting intimate contact between CPs and NCs, forming CP–NC nanocomposites. In the first strategy, ligand exchange is an essential step to either directly replace insulating small molecular ligands that originally passivate the NC surface with functionalized CPs in a *grafting-onto* process, or first exchange with bifunctional ligands and subsequently couple with functionalized CPs. The second strategy (i.e., direct grafting) utilizes direct grafting of CPs from/onto functionalized NCs in the absence of ligand-exchange chemistry, yielding CP–NC nanocomposites with improved grafting density. For the third strategy (i.e., direct NC growth), CPs closely contacted with semiconductor NCs can also be realized by direct growth of NCs in the CP matrix in a simple yet efficient manner without introducing any insulating capping ligands or groups and the need for the grafting process.

This Review seeks to summarize recent developments exclusively in intimate CP–NC nanocomposites for hybrid solar cells, focusing primarily on the current state-of-the-art synthetic



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strategies that render the crafting of CP–NC nanocomposites composed of intimately contacted CPs and NCs, and the resulting photovoltaic performance. A perspective on a further step to rationally design and produce advanced CP–NC nanocomposites for hybrid solar cells with improved efficiency is also presented.

2. Nanocomposites Prepared by Ligand Exchange Chemistry

Ligand exchange based on the adsorption-desorption dynamics of capping ligand^[80] permits derivatization with a broad range of functional groups on the NC surface, and is probably the most widely utilized method for surface functionalization of NCs.^[81,82] The bonding and dynamics of ligand on NCs have only recently been scrutinized through the adsorption-desorption process.^[80] When a small amount of colloidal nanocrystals with a given ligand coverage is rapidly injected into a large volume of pure solvent (i.e., any solvent that dissolves the ligand molecules), a certain amount of original capping ligands can immediately dissociate from the NC surface until a dynamic equilibrium is established between the ligand absorption ($M + L \rightarrow ML$) and

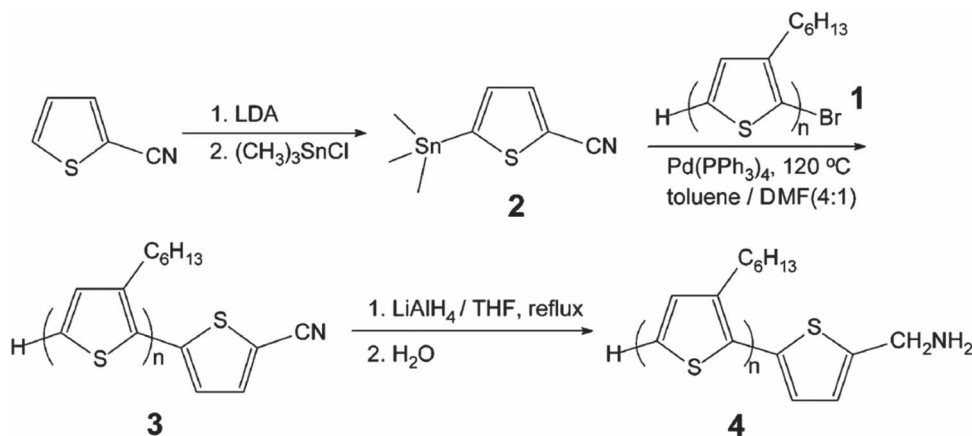


Figure 1. Synthesis of P3HT with amino end-functionality. Figure reproduced with permission.^[90] Copyright 2004, ACS.

desorption ($\text{ML} \rightarrow \text{M} + \text{L}$) process, where M and L refer to the surface bonding sites on NCs, and the ligand concentration in free state (L) and bonded state (ML), respectively. The reaction processes can be described as follows.^[80]

$$\text{Adsorption: } (d[\text{ML}]/dt)_a = k_a[\text{M}][\text{L}] \quad (1)$$

$$\text{Desorption: } (d[\text{ML}]/dt)_d = k_d[\text{ML}] \quad (2)$$

where k_a and k_d are the absorption and desorption reaction rate constant, respectively. The average surface ligand coverage can be given as

$$\theta = [\text{ML}]/([\text{M}] + [\text{ML}]) \quad (3)$$

As the number of bonding sites ($[\text{M}] + [\text{ML}]$) are constant for a given system, Equations 1 and 2 can therefore be written as:^[80]

$$\text{Adsorption: } (d\theta/dt)_a = k_a(1 - \theta)[\text{L}] \quad (4)$$

$$\text{Desorption: } (d\theta/dt)_d = k_d\theta \quad (5)$$

Clearly, the average surface ligand coverage is directly related to the ligand absorption reaction rate constant, k_a and desorption reaction rate constant, k_d ; it is also governed by the binding ability of functional groups on the capping ligand and steric effect originating from adjacent chain repulsion.^[34,80,83] Especially, ligands of strong binding ability coordinate more stably on the NC surface, resulting in higher surface coverage due to reduced k_d and increased k_a ,^[80] and thus are largely utilized to replace weaker ligands that originally passivate NCs in the solution state. The binding ability of the most common and readily accessible groups can be arranged in the following order: phosphoric acid > carboxyl acid > alkyl thiols > phosphine oxide > amines > hydroxyl. Therefore, ligands with terminal phosphoric acid and carboxyl acid groups have been commonly employed to ligand exchange with tri-*n*-octylphosphine oxide (TOPO; phosphine oxide as the capping group).^[80,84,85] On the other hand, due to steric effect caused by previously anchored ligands on the subsequent ligands to be attached,^[86] short ligands carry advantage over long ones to be tethered on the NCs surface, thereby leading to higher surface coverage; for CPs, this effect

imposes a severe issue as the targeted CPs are always much longer than the small molecular ligands originally present on the NC surface. To this end, pyridine, a volatile small molecule with weak binding ability, is often used as an intermediate agent to enable the exchange process.^[80] For example, in the case of TOPO-coated CdSe NCs, TOPO capps the CdSe surface much stronger than pyridine. However, pyridine still effectively replaces TOPO when a small amount of TOPO-capped CdSe dissolved into a large amount of pyridine due to its high concentration according to Equations 4 and Equations 5.^[2] After ligand exchange for several times, a thin layer of pyridine is coated on CdSe. The resulting CdSe NCs can be considered as almost “naked” to be replaced by relatively strong ligands, such as fatty amines and thiols.^[80] It is interesting to note that this strategy has also been largely applied to exchange strong ligands (e.g., phosphoric acid and carboxyl acid) with weaker ones (e.g., amines and thiol-functionalized polymers).^[87] Two approaches involving the use of ligand exchange as an intermediate step have been introduced to prepare the CP–NC nanocomposites, namely, one-step ligand exchange of insulating ligand-capped NCs with functionalized conjugated polymers or conjugated oligomers and ligand exchange followed by direct coupling.

2.1. One-Step Ligand Exchange of Insulating Ligand-Capped NCs with Functionalized Conjugated Polymers or Conjugated Oligomers

Ligand exchange allows for the introduction of a wide diversity of functional groups to NCs. The CP–NC nanocomposites can be prepared by a one-step ligand-exchange of original insulating capping ligand on the NC surface with functionalized CPs. In this strategy, strong coordinating group (e.g., phosphoric acid^[84] and carbodithioic acid^[85])-functionalized CPs is first synthesized, and then *directly* anchored onto NCs by substituting original ligands on the NC surface.^[88,89] In a seminal work by Frechet et al., poly(3-hexylthiophene) (P3HT) with amino end-functionality was synthesized to improve the dispersion of CdSe nanorods (NRs) in P3HT matrix in the P3HT–CdSe NR hybrid solar cells (**Figure 1**).^[90] Specifically, the original ligands, TOPO and tetradecylphosphonic acid (TDPA) on the

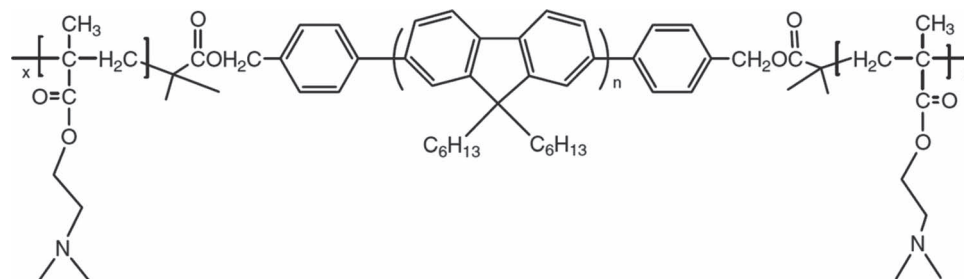


Figure 2. Chemical structure of PDMAEMA-PF-PDMAEMA. Figure reproduced with permission.^[93] Copyright 2007, IOP.

surface of CdSe NRs were first replaced by refluxing the NRs in pyridine. Subsequently, the CdSe NRs were mixed with either non-end-functionalized P3HT (polymer 1 in Figure 1) or amino end-functionalized P3HT (polymer 4 in Figure 1). Interestingly, non-functionalized P3HT/CdSe NR blends showed significant phase segregation. By contrast, CdSe NRs possessed a high degree of homogeneity in the hybrid of P3HT–CdSe NR composed of amino end-functionalized P3HT as evidenced by the TEM measurement. The resulting photovoltaic device exhibited largely enhanced power conversion efficiency, *PCE* of 1.4% as compared to *PCE* of 0.5% from the device fabricated using non-functionalized P3HT.^[90] The polymer 4 was believed to partially replace the pyridine surfactant on the CdSe NR surface through the coordination of its amino end group with CdSe NRs (i.e., forming P3HT–CdSe nanocomposites), thus improving the miscibility of CdSe with P3HT. Moreover, larger interfacial area for charge separation due to the good dispersion of CdSe in polymer 4 favored the improvement of device performance.^[90] This early work clearly showed that the feasibility of dramatically enhancing the performance of organic–inorganic hybrid solar cells via chemically linking CPs to NCs,

Notably, in the above study pyridine was utilized as an intermediate ligand to facilitate the ligand exchange process. The amine-terminated P3HT only replaced pyridine in part as amine are not a strong functional group to passivate the CdSe surface. To this end, phosphoric acid was recently introduced as end groups to functionalize P3HT.^[84] Among the various capping groups, phosphoric acid is the strongest type to passivate CdSe NCs,^[83,91] thereby dispensing with the need for involving pyridine as the intermediate ligand. Briefly, TOPO-capped CdSe quantum dots (QDs) and phosphonic acid-terminated P3HT were simply co-dissolved in chloroform and allowed to react overnight.^[84] The success of bonding P3HT to CdSe was confirmed by ¹H NMR, from which both the shift and the broadening of signal peaks were observed.^[84] Approximately 50 P3HT chains were estimated to graft onto one CdSe QD according to the absorption spectra analysis. The quenching of grafted P3HT and CdSe QDs clearly indicated the photoinduced charge transfer, suggesting that the electronic interaction between functional components can be facilitated by end-functionalizing CP with strong binding groups.^[84] Similarly, a family of carbodithioic acid-terminated polythiophene were grafted onto the CdSe QD surface.^[85] Due to the strong binding affinity, carbodithioic acid-functionalized polythiophene can directly ligand-exchange TOPO and carboxylic acids that were originally situated on CdSe QDs without the need of introducing pyridine

as the intermediate ligand. In this study, an efficient quenching of photoluminescence (PL) was also observed in the polythiophene–CdSe nanocomposite, revealing the charge transfer at the polythiophene/CdSe interface.^[85]

It is worth noting that the stability of nanocomposites relies primarily on the strength of single coordination bond between the end functional group of CPs and NCs. In light of the ligand exchange dynamics,^[80] such monodentate CPs are labile and in dynamic equilibrium with their surrounding media.^[92] When this anchoring bond between CPs and NCs breaks, the nanocomposites would dissociate, leading to low stability, phase segregation, high impurity, etc.^[93] In this context, an intriguing multidentate electroactive CP, amine-containing rod-coil triblock copolymer poly(2-(dimethylamino)ethylmethacrylate)–poly(fluorene)–poly(2-(dimethylamino)ethylmethacrylate) (PDMAEMA-PF-PDMAEMA) has been utilized to bind intimately to CdSe QDs (i.e., forming PDMAEMA-PF-PDMAEMA–CdSe nanocomposites) through a simple ligand exchange approach without the use of pyridine as an intermediate ligand (Figure 2).^[93] The nanocomposites were formed through the nitrogen atoms in PDMAEMA-PF-PDMAEMA covalently attaching the surface of CdSe QDs. The partial replacement of original ligand TOPO with PDMAEMA-PF-PDMAEMA was proven by ³¹P NMR. A good dispersion of CdSe QDs in the CP was confirmed by TEM and UV-vis absorption. The PL spectra of the resulting nanocomposites exhibited a photoinduced charge transfer facilitated by the direct contact of PDMAEMA-PF-PDMAEMA and CdSe. This study offers a new prospective in improving the stability of CP–NC nanocomposites via a rational design of CPs with multidentate linkers (i.e., CPs with lower bandgap and higher charge mobility incorporating stronger multidentate ligands as the binding strength of amine groups was much weaker than that of TOPO in this work),

In addition to CdSe NCs, functionalized conjugated oligomers (COs) have also been grafted onto metal oxide semiconductors (e.g., TiO₂) by direct ligand exchange process. Recently, a new carboxylic acid and bromine-terminated 3-hexyl thiophene oligomer (oligo-3HT-(Br)COOH) was synthesized by the Heck reaction of vinyl-terminated 3-hexylthiophene oligomer and 1,4-dibromo-3-carboxylic thiophene, and grafted onto pyridine-capped environmentally friendly TiO₂ NR surface by ligand exchange process (Figure 3).^[94] The replacement of pyridine with oligo-3HT-(Br)COOH was supported by X-ray photoelectron spectroscopy (XPS), which showed only the signal of sulfur atom of thiophene ring in oligo-3HT-(Br)COOH. The

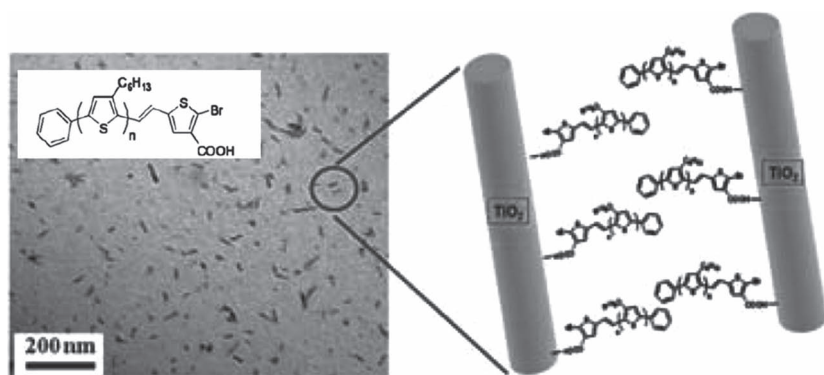


Figure 3. TEM image of bromine-terminated 3-hexyl thiophene oligomer (i.e., oligo-3HT-(Br)COOH) grafted TiO₂ NRs (i.e., oligo-3HT-TiO₂). The chemical structure of end-functionalized oligo-3HT-(Br)COOH is shown in the insert. Figure reproduced with permission.^[94] Copyright 2011, RSC.

oligo-3HT-(Br)COOH was tethered to the TiO₂ surface through a chelating bond between -COOH and Ti atoms.^[94] The grafting rendered TiO₂ NRs with good hydrophobicity, improved compatibility with P3HT and thus increased dispersion (Figure 3).^[94] The efficient charge transport and reduced charge recombination in the P3HT-oligo-3HT-(Br)COOH-TiO₂ nano-hybrids were observed, resulting in increased power conversion efficiency, *PCE* of the resulting solar cells (*PCE* $\approx$ 1.19%), which was more than 2 times higher than that of the device made from the physical mixture of P3HT/pyridine-capped TiO₂ NRs (*PCE* $\approx$ 0.54%).

In addition to introducing ligands with strong binding functional groups, the increase in the number of functional groups on each ligand will result in higher grafting density of CPs on metal oxide NCs. Recently, a new regioregular poly(3-hexylthiophene) with both ends functionalized with carboxyl group (i.e., HOOC-P3HT-COOH) was shown to anchor strongly onto the mesoporous TiO₂ and use as a polymer sensitizer to allow for a better surface coverage of TiO₂ and thus avoiding any recombination between TiO₂ and hole conductor (i.e., spiro-OMeTAD) in a solid-state dye-sensitized solar cell.^[95] Additionally, HOOC-P3HT-COOH also acted as a hole conductor for charge transport. The *PCE* of 0.9% was achieved.

Obviously, direct ligand exchange is likely the simplest but not an efficient approach to link CPs to NCs. As the targeted CP chains are always much longer than those of small ligands to be replaced, the ligand exchange efficiency is usually low, especially when NCs are originally passivated with strong ligands.^[86] As a result, this approach is restricted mainly to the grafting of COs^[96,97] or CPs with limited molecular weight.^[84] In this regard, an alternative strategy, ligand exchange followed by direct coupling, was developed to graft large molecular weight CPs through the utilization of small molecular bifunctional ligands.

2.2. Ligand Exchange Followed by Direct Coupling of Conjugated Polymers with Nanocrystals

In this strategy, CP-NC nanocomposites are produced by a two-step process. First, the original insulating ligand coated at the NC surface is exchanged with a bifunctional ligand, X-Y-Z, where X, Y, and Z are the capping group that passivates NCs, the spacer, and the functional group capable of coupling with CPs, respectively. Subsequently, end-functionalized CPs of interest are tethered to NCs through the coupling reaction between functional group in CPs and Z in NCs. In comparison with end-functionalized CPs, the bifunctional ligand has much shorter length and thus improved ligand exchange efficiency.

A representative example is the recently reported grafting P3HT onto CdSe NRs.^[87] The CdSe NR with 8 nm in diameter and 40 nm in length was connected to relatively high molecular weight regioregular P3HT (molecular weight, *MW* = 8,600 g mol⁻¹), forming P3HT-CdSe NR nanocomposites as depicted in **Figure 4**. Specifically, arylbromide-functionalized CdSe NRs were first synthesized by ligand exchange of pyridine-capped CdSe NRs with arylbromide-functionalized phosphine oxides and thiols. The vinyl-terminated P3HT was then chemically grafted onto the CdSe NR surface by Heck coupling of arylbromide moieties in CdSe and vinyl end groups in P3HT. The ¹H NMR analysis confirmed the existence of P3HT chain on the CdSe surface; the homogeneous dispersion of NRs in the polymer matrix was observed by TEM. As thiol ligands are known to coordinate more effectively than phosphine oxides for cadmium sites on CdSe NCs, a higher initial coverage of thiol ligands relative to that of the [(4-bromophenyl)methyl]diocetylphosphine

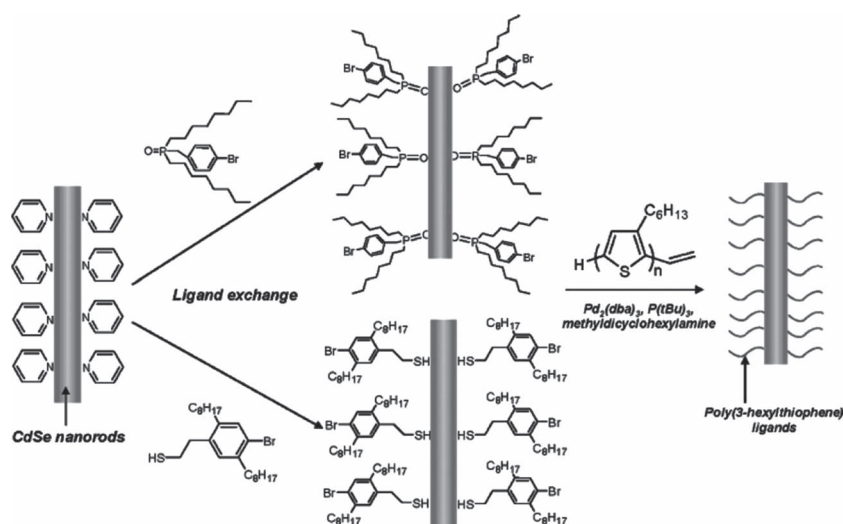


Figure 4. Synthesis of P3HT-CdSe NR nanocomposites by ligand exchange with bifunctional ligands (i.e., thiol or phosphine oxide at each end), followed by coupling vinyl-terminated P3HT with arylbromide-functionalized CdSe NRs. Figure reproduced with permission.^[87] Copyright 2007, ACS.

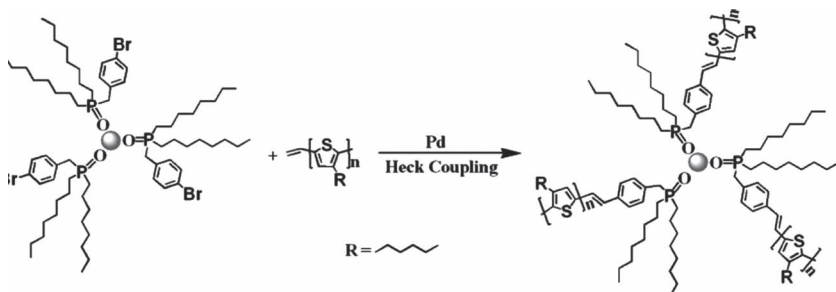


Figure 5. Grafting vinyl-terminated P3HT onto [(4-Bromophenyl)methyl]diethylphosphine oxide (DOPO-Br)-functionalized CdSe QDs by Heck coupling. Figure reproduced with permission.^[79] Copyright 2007, ACS.

oxide (DOPO-Br) ligand was produced.^[87] The thermogravimetric analysis (TGA) revealed that roughly 250 P3HT chains per NR and 400 P3HT chains per NR for P3HT-covered NRs with phosphine oxide linkage and thiol linkage, respectively, to the NR surface. Importantly, the solid-state PL measurement on thin films of nanocomposites showed PL quenching of P3HT, which was indicative of charge transfer between P3HT and CdSe NRs.^[87]

3. Nanocomposites Elaborated by Direct Grafting

Although ligand exchange provides derivatization of NCs with functional ligands, it suffers from incomplete surface coverage.^[98] As a consequence, the fluorescence emission is quenched due to aggregations of NCs,^[99] or oscillates due to adsorption and desorption of surface ligand.^[100] In this context, an attractive strategy, referred to as direct grafting, was recently developed, which relies on the design of novel bifunctional ligand that not only act as the coordinating ligand to tune the crystal growth with one end-functional group, forming high quality NCs with defined size and shape, but also is capable of coupling with functionalized CPs afterward with the other end-functional group. It is well known that the NC growth depends sensitively on the characteristic of ligands (e.g., coordinating ability,^[68,83] chain length and configuration,^[34,91,101,102] etc.), imposing a challenge on the design of bifunctional ligands. However, the use of bifunctional ligand enables much higher surface coverage of CPs than that by ligand exchange which is restricted by the ligand adsorption-desorption dynamics.^[80]

Recently, an intriguing approach was exploited to synthesize P3HT–CdSe QD nanocomposites by directly grafting vinyl-terminated P3HT onto the [(4-bromophenyl)methyl]diethylphosphine oxide (DOPO-Br)-functionalized CdSe QD surface via mild Pd-catalyzed Heck coupling, as outlined in **Figure 5**.^[79] The bifunctional ligand (i.e., DOPO-Br) bears a phosphine oxide group at one end similar to that of TOPO to anchor on the QD surface, and an arylbromide at the other end to allow for subsequent surface grafting process.^[79] Monodispersed CdSe QDs were grown in DOPO-Br, directly yielding the DOPO-Br capped CdSe QDs, eliminating the need for the complex and often incomplete ligand exchange process. Regioregular P3HT was synthesized through a quasi-living polymerization, and one of its ends was terminated with the vinyl group by using

a modified Grignard metathesis reaction.^[103] The success of coupling of vinyl-terminated P3HT and DOPO-Br functionalized CdSe QD was confirmed by ¹H and ³¹P NMR spectroscopy. The grafting density of P3HT chains was determined by TGA, showing an average of 22 P3HT chains bound to one CdSe QD surface. The effective charge transfer from P3HT to CdSe in P3HT–CdSe nanocomposites was confirmed by the static PL and the PL decay measurements.^[79] The quenching of the PL emission of P3HT suggested the charge transfer from P3HT to CdSe. 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, thereby enhancing the radiative recombination probability within CdSe QDs. A faster decay in fluorescence lifetime of P3HT–CdSe nanocomposites than that of P3HT and physically mixed P3HT/CdSe composites measured by using time-correlated single-photon counting (TCSPC) methodology further confirmed the occurrence of rapid charge transfer in P3HT–CdSe nanocomposites; this can be attributed to the improved interfacial contact between P3HT and CdSe in the nanocomposites due to direct grafting, where it is easy for the exciton to find the interface and dissociate.

Subsequently, the behavior of P3HT–CdSe QD nanocomposites at the air/water interface was investigated.^[104] The photovoltaic device fabricated from five Langmuir–Blodgett (LB) deposition cycles of nanocomposites, approximately 30 nm thick, exhibited a relatively high short circuit current, I_{SC} , while maintaining an ultrathin film profile, yielding a *PCE* of 0.08%.^[104] The 30-nm thick active layer may result in low light absorption and thus low *PCE*. On the basis of these results, improved photovoltaic performance may be achieved by capitalizing on conjugated polymer–quantum rod (CP–QR) nanocomposites.

Due to their intrinsic structural anisotropy, QRs possess many unique properties that make them potentially better NCs than QDs for photovoltaics. Solar cells made of CPs and QRs exhibit an improved optical absorption in the red and near-infrared ranges originating from QRs.^[105] Additionally, the long axis of QRs provides continuous pathway for charge transport, carrying an advantage over QDs where electron hopping between QDs is required.^[106] However, the strategy that produced DOPO-Br-capped CdSe QDs noted above cannot be extended to the synthesis of DOPO-Br-capped CdSe QRs,^[87] as phosphine oxide, the capping group on DOPO-Br, was not a suitable ligand to induce elongated growth of CdSe NCs.^[83]

To this end, a new bifunctional ligand, bromobenzylphosphonic acid (BBPA), was synthesized with phosphonic and aryl bromide groups at each end (**Figure 6**).^[107,108] The phosphonic acid group coordinates more strongly with CdSe than phosphonic oxide group to induce the elongated growth, yielding BBPA-functionalized CdSe QRs (i.e., BBPA–CdSe QRs) with aryl bromide group on the surface. Subsequently, the direct grafting of end-functionalized P3HT onto CdSe QRs was accomplished by two coupling reactions (i.e., Heck coupling and click reaction),^[107,108] dispensing with the need for ligand exchange

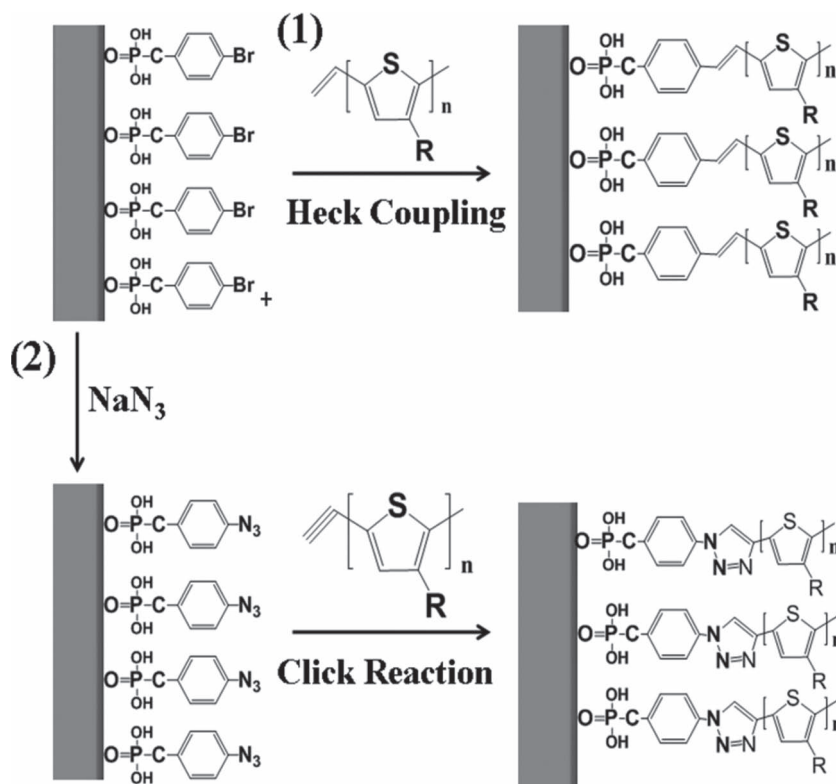


Figure 6. Grafting P3HT onto bromobenzylphosphonic acid (BBPA)-functionalized CdSe QRs by (1) Heck coupling, and (2) catalyst-free click reaction, respectively. Figure reproduced with permission.^[107,108]

chemistry. In the first strategy (Figure 6), CdSe QRs were passivated with BBPA which functionalized the CdSe QR surface with active aryl bromide group. Subsequently, P3HT–CdSe QRs were yielded by Heck coupling of vinyl-terminated P3HT with BBPA–CdSe QRs. The reduced insulating length of BBPA facilitated improved electron interaction between CPs and QRs, greatly promoting the potential of P3HT–CdSe QR nanocomposites for use in solar cells with enhanced performance. In the second strategy, the alkyne–azide cycloaddition, which belongs to an emerging field of click chemistry,^[109–113] was utilized in the preparation of P3HT–CdSe QR nanocomposites (Figure 6). The aryl bromide of BBPA was converted into azide functional group, forming $\text{N}_3\text{-BPA-CdSe}$ QRs. Subsequent catalyst-free Huisgen 1,3-dipolar cycloaddition between ethynyl-terminated P3HT and $\text{N}_3\text{-BPA-CdSe}$ QRs successfully yielded intimate P3HT–CdSe QR nanocomposites without introducing any deleterious metallic impurity. The click reaction possessed several attractive features, including extremely versatile bond formation process, no requirement of protecting groups, good selectivity, nearly complete conversion, and generally no need for purification.^[114] The success of two coupling reactions (i.e., forming P3HT–CdSe QR nanocomposites) was confirmed by ^1H and ^{31}P NMR spectroscopy, displaying the signals of P3HT on the QR surface, and DLS measurements, showing the increase in CdSe QR size after the grafting of P3HT. The grafting density of P3HT was greatly increased as compared to that obtained by using conventional ligand-exchange approach.

Figure 7 shows the TEM images of P3HT/CdSe QR composites prepared by physically blending end-functionalized P3HT and CdSe QRs (Figures 7a and 7b), and P3HT–CdSe QR nanocomposites (Figures 7c and 7d). In comparison to the physical mixtures, which displayed significant phase segregation (Figures 7a and 7b) and thus reduced the interfacial area needed for efficient charge separation, CdSe QRs were well dispersed within the P3HT–CdSe QR nanocomposites as evidenced in Figure 7c and 7d.

The charge transfer occurred at the P3HT/CdSe QR was substantiated by UV-Vis absorption, PL, and time-resolved PL studies. The solid-state PL measurement showed a dramatic quenching of the emission of P3HT, revealing a photoinduced charge transfer from P3HT to CdSe. A much faster lifetime (i.e., fast exciton dissociation at the P3HT/CdSe interface) for the nanocomposites was observed after chemical binding P3HT onto the QR surface. Quite intriguingly, the nanocomposites made by the catalyst-free click reaction exhibited a faster charge transfer from P3HT to CdSe than those produced by Heck coupling. It may be attributed to more rigid morphology of cycloaddition in click reaction, which brought the neighboring

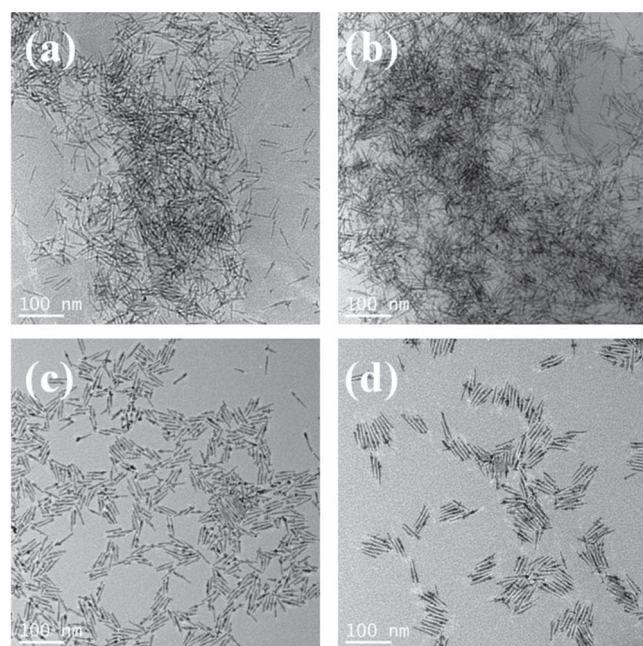


Figure 7. TEM images of P3HT/CdSe QR composites prepared by physically mixing (a) vinyl-terminated P3HT and BBPA-functionalized CdSe QRs, and (b) ethynyl-terminated P3HT and azide-BBPA-functionalized CdSe QRs, respectively. TEM images of P3HT–CdSe QR nanocomposites synthesized by (c) Heck coupling and (d) click reaction, respectively. Figure reproduced with permission.^[107,108]

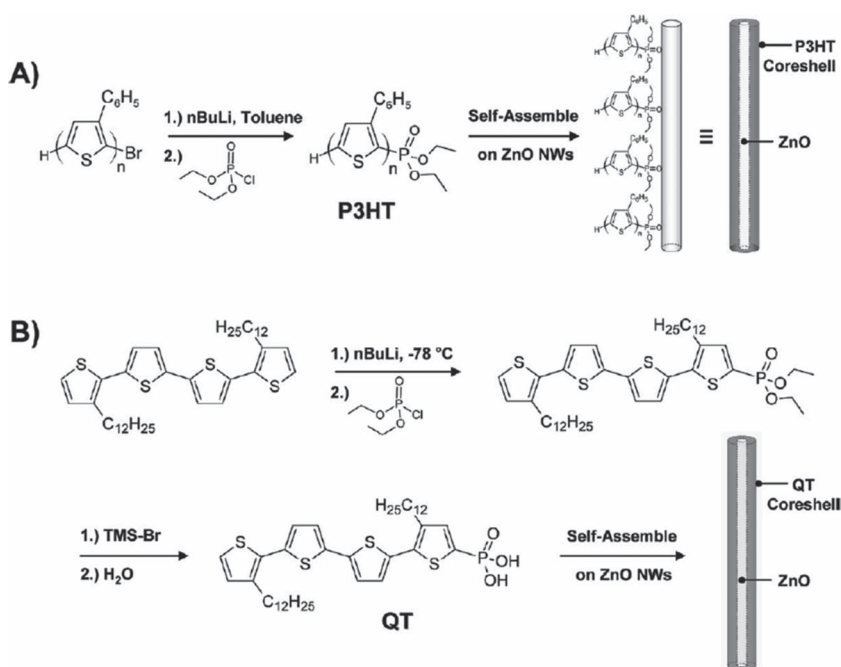


Figure 8. Synthesis of end-functionalized (A) P3HT and (B) didodecylquaterthiophene (QT) with a phosphonic ester and acid, respectively. They were subsequently self-assembled onto ZnO nanowires. Figure reproduced with permission.^[115] Copyright 2010, ACS.

thiophene and benzene ring in the same plane, forming a new kind of conjugated system to transfer the electron from P3HT to CdSe. This work provides a promising method to simplify the synthesis procedure and opens opportunities to increase the grafting density for large-scale synthesis.

It is clear that the two strategies (i.e., ligand exchange and direct grafting) discussed above involved the colloidal synthesis and coupling reactions that are relatively complex (e.g., a multi-step process, the need of rational design of ligands and CPs, etc.). In this context, it may be convenient if NCs with bare surface can be utilized, and end-functionalized CPs can directly attach to the NC surface, with no need for ligand exchange and/or direct bifunctional ligand growth processes. Recently, end-functionalized *p*-type oligo- and polythiophene was chemically grafted onto an *n*-type non-colloidal ZnO nanowire (i.e., nanowire with no capping ligands; it was several micrometers in length and 30–100 nm in diameter), producing a *p*-*n* core/shell nanowire from which a single nanowire solar cell was successfully fabricated (Figure 8).^[115] In this study, ZnO nanowires were prepared via both vapor phase and hydrothermal solution phase synthesis, forming one-dimensional nanostructures with no surface ligands. P3HT and didodecylquaterthiophene (QT), terminated with phosphonic ester and acid, respectively (Figure 8), can directly coordinate and self-assemble onto the ZnO surface to yield organic shells of P3HT or QT by stirring a suspension of ZnO nanowires in a chlorobenzene solution of the respective functionalized P3HT or QT. Notably, this is the only research on the organic–inorganic hybrid single nanowire solar cells. Despite its low efficiency of 0.036%, the nanowire devices offered an effective way of isolating and studying many phenomena that affect the performance of bulk hybrid

solar cells.^[115] As a number of parameters, including the nanostructure size, uniformity, phase segregation of NCs, crystallinity, interfacial interactions between CPs and NCs, carrier mobilities, trap density, among many other factors, can vary significantly over the active area, it is difficult to attribute any change in performance to a particular phenomenon.^[67,74] By contrast, single nanowire devices impart more precise control over and characterization of the parameters noted above, thereby substantially reducing the uncertainty in data interpretation.^[115] In other words, the influence of certain parameter can be readily identified and evaluated in a much simplified system, in comparison to the bulk hybrid solar cells where several parameters may most likely affect the performance simultaneously. For example, increasing the P3HT thickness layer on ZnO surface was found to not greatly improve the performance of the nanowire device; however, the open circuit voltages, V_{OC} in single-wire devices ($V_{\text{OC}} \approx 0.40$ V) was larger than the literature value of $V_{\text{OC}} \approx 0.17$ V for P3HT/ZnO bulk nanowire array devices, suggesting that the P3HT/ZnO interface for the grafted polymer was superior to the bulk spin-coated

counterpart.^[115]

To date, due primarily to its simplicity and controllability, the *grafting-onto* approach has been the widely used to connect CPs with a great diversity of NCs despite its intrinsic limitation (e.g., the steric hindrance caused by previously anchored polymers on the subsequent grafting,^[86] and the entropy penalty due to constraining polymer chains on the NC surface^[116]). By contrast, the *grafting-from* approach, on the basis of direct synthesis of CPs from monomer through polymerization from the NC surface,^[98,117–119] can enable higher grafting density of CPs, but be explored in much less intensity, owing largely to great challenges in controlling the complicate surface polymerization process.

Nonetheless, similar to the *grafting-onto* strategy of synthesizing P3HT–CdSe QD nanocomposites, the DOPO-Br functionalized CdSe QDs were also employed to form poly(*para*-phenylenevinylene) (PPV)–CdSe nanocomposites via a surface-initiated polymerization (i.e., a grafting-from approach by polymerizing of conjugated monomers in the presence of semiconductor NCs).^[120] As illustrated in Figure 9, PPV was grown radially outward from the surface of DOPO-Br functionalized CdSe QD by copolymerization of 1,4-divinylbenzene and 1,4-dibromobenzene derivatives. The grown PPV was primarily trimers and tetramers according to the matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry measurement. The unattached PPV was served as a host matrix for dispersing CdSe QDs. The improved dispersion of QDs within PPV matrix was confirmed by the TEM study. It is worth noting that, by combining single-molecule fluorescence and scanning probe microscopy studies, a suppression of CdSe QD blinking in PPV–CdSe nanohybrids was observed

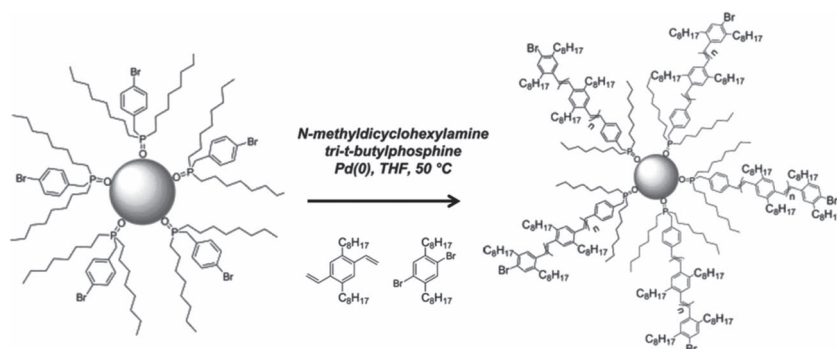


Figure 9. Synthesis of PPV–CdSe nanocomposites by tailoring CdSe QDs with PPV via a grafting-from approach. Figure reproduced with permission.^[120] Copyright 2004, ACS.

that can be attributed to efficient charge transfer from photo-excited PPV to vacant trap sites on the QD surface.^[120–122]

Additionally, a facile *grafting-from* strategy towards the synthesis of organic–inorganic nanocomposites consisting of semiconductor NCs and wide-bandgap CPs was also recently reported.^[123] In this study, amino-functional fluorene (6,6'-(2,7-dibromo-9H-fluorene-9,9-diyl)dihexan-1-amine) was used as a co-ligand in the synthesis of CdSe QDs (NC 1 in Figure 10), enabling a direct design of CdSe surface during the synthesis. Subsequently, CdSe QDs modified with oligo(fluorene) (nanocomposite 2 in Figure 10) was obtained via a straightforward Yamamoto C–C coupling protocol using NC 1 as a starting material, Ni(0)(COD)₂ as a C–C coupling mediator, and THF/toluene as a mixed solvent.^[123] Similarly, nanocomposite 3 (Figure 10) was also prepared with the Yamamoto procedure with the addition of 2,7-dibromo-9,9-dioctyl-9H-fluorene as a comonomer to induce chain growth on the surface of CdSe QDs. The PL quenching and faster PL decays of the resulting nanocomposites supported efficient charge transfer between CdSe QDs and fluorene moieties due to their close contact facilitated by chelating amine groups with CdSe.

4. Nanocomposites Crafted by Direct Growth of NCs within CP Matrix

The two strategies discussed above have concentrated on synthesizing CPs and NCs separately, and then intimately connecting

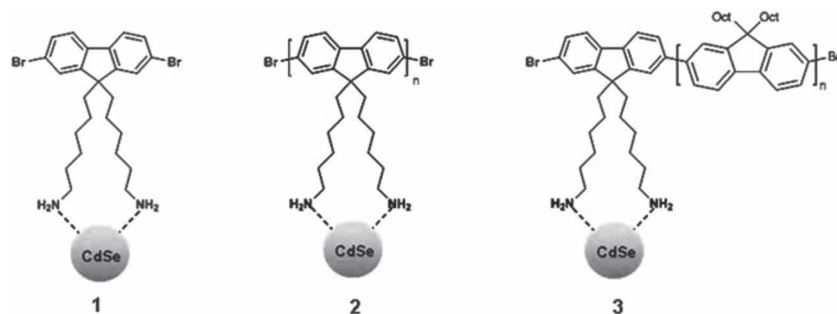


Figure 10. Amino-fluorene modified CdSe NC 1 utilized to produce NC–oligo(fluorene) nanocomposite 2 and NC–poly(fluorene) nanocomposite 3. Figure reproduced with permission.^[123] Copyright 2011, RSC.

them through rather complex chemical coupling to yield a multitude of CP–NC nanocomposite materials with various shapes and chemical compositions. However, these techniques have a few limitations. Firstly, bifunctional ligands and functionalized CPs must be judiciously designed for the control growth of NCs and efficient grafting of NCs, respectively; and subsequent surface grafting or polymerization of CPs are usually complicated. All these represent grand challenges and may potentially make it costly in the synthesis of CP–NC nanocomposites. Secondly, despite short and often negligible, the functional moieties in CPs that attach to the NC surface, such as phosphonic acid, carboxylic

acid, and alkyl thiols, are intrinsically insulating and become a spacer bridging CPs and NCs, and thus may affect the charge transfer process.

Most of these limitations can be circumvented by capitalizing on a new approach that involves direct growth of NCs in CPs without ligands (i.e., *direct NC growth*) to craft nanocomposites in a much simpler manner. Although the quality of the resulting nanocomposites is not comparable to (i.e., less controlled than) those synthesized by *ligand exchange* and *direct grafting* in the aspects of the quality of NCs (i.e., size and shape distribution), the well-defined CP/NC interface, etc., the dynamics of NC growth is rather complex, and the details of the interaction between CPs and NCs are not completely understood, the strategy of *direct NC growth* has received much attention due to its simplicity and the potential of producing high-efficiency hybrid solar cells.

In an early work, lead sulfide (PbS) NCs were directly grown in the CP, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV), without the need for additional ligands using a simple one pot process.^[124] The PbS was chosen as inorganic material due to its broad band absorption. In a typical synthesis, a sulfur precursor solution was injected into MEH-PPV and lead acetate mixture solution, and allowed to react at high temperature. The nanocomposites were obtained after centrifugation and redispersion in desired organic solvent. Based on the TEM analysis, the prepared PbS NCs were highly crystalline with an average size of 4 ± 2 nm. On one hand, due to the lack of growth tailoring assisted by the capping ligand, the size and shape of PbS NCs were hardly controlled, producing low quality NCs in comparison with those made from colloidal synthesis. On the other hand, compared to two strategies (i.e., *ligand exchange* and *direct grafting*) reviewed above, it is a markedly less complicated synthetic route as it eliminates the need for not only an initial surfactant to terminate NC growth, but also the subsequent coupling to CPs.^[124] It affords intimate contact between CPs and NCs, largely improving their electronic coupling and thus effective charge transfer in the system. A direct evidence of electronic coupling was manifested in the diminishing of

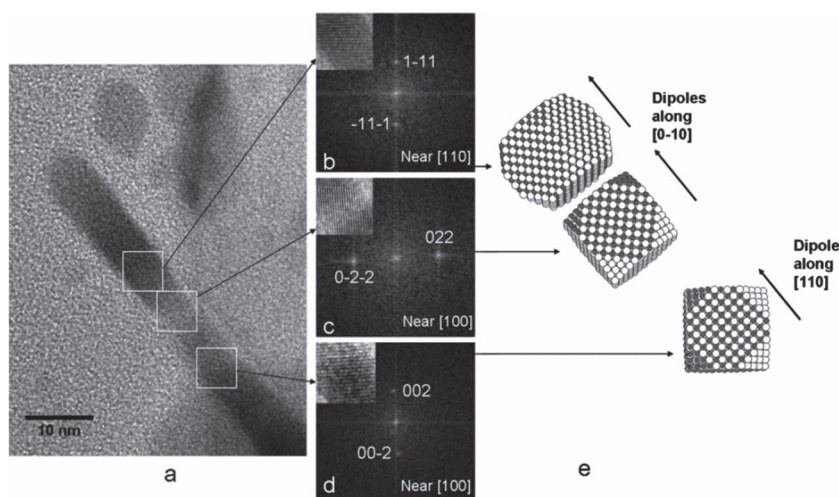


Figure 11. (a) High-resolution TEM image of a PbS NR in the nanocomposite. (b–d) Fast Fourier transformed images of three square regions marked in (a) with indexed reflections and zone axes. (e) Schematic illustration of three corresponding nanocrystals in the analyzed regions, as projected in the image plane. Figure reproduced with permission.^[125]

PL emission from CP as the growth of PbS NCs progressed. In the synthesis of colloidal NCs, growth control is derived from a combination of electrostatic effects from the capping group of ligands (e.g., phosphoric acid, phosphine, etc.), and the steric effects of the long ligand chains.^[124] As no ligand was involved in the NC growth process in the *direct NC growth* strategy, the CP acted as not only the continuous conductive matrix, but also a colloidal template as bulk PbS was formed if there was no polymer present in the reaction mixture.^[124] The growth of PbS NCs was likely affected by steric effects of the long chain MEH-PPV since MEH-PPV possessed no charged functional groups to allow for electrostatically control the NC growth.^[124] However, the exact interaction that enables intimate contact between the two components has yet to be explored.

As discussed previously, it is favorable to form elongated nanostructures in nanocomposites to act as large-surface-area electron acceptors and offer continuous pathway for electron transport in photovoltaic devices.^[125,126] Recently, controlled assembly of PbS NRs through oriented attachment of PbS NCs was demonstrated utilizing a post-synthesis treatment of PbS NC/MEH-PPV composites prepped by a low temperature and surfactant-free approach.^[124,125] Prior to the treatment, PbS NCs with a broad size distribution (~2–10 nm) were well-dispersed in MEH-PPV. Upon precipitation with alcohols (e.g., ethanol, propanol, or hexanol), the NCs aggregated linearly into elongated NRs.^[125] The intimate contact between PbS and MEH-PPV was represented by the quenching of intrinsic PL signature of MEH-PPV in the composites sample compared to the MEH-PPV homopolymer. The aggregation of NCs into NRs was proposed to be caused by the dipole-induced oriented attraction, which was widely observed in various elongated nanostructure synthesis.^[41,68,127] **Figure 11** shows TEM images from an individual NR, depicting the mechanism of orientated attachment. Three distinct crystallographic orientations from three regions of close vicinity marked by squares on the rod in Figure 11a were observed as shown in the insets of Figure 11b–d. The

relative orientation of NCs was illustrated in the schematic as projected in the image plane (Figure 11e). Obviously, compared to NCs made by colloidal chemistry, the quality of the resulting PbS NRs was low.

Unfortunately, the success in synthesizing PbS NCs and NRs in the presence of MEH-PPV cannot be extended to the synthesis of CdSe QDs due to the poor precursor solubility and inferior crystal structure obtained at low reaction temperature.^[128] Recently, a high boiling point solvent, 1-octadecene (ODE), was employed to synthesize good quality CdSe QDs in a P3HT solution.^[128] Briefly, P3HT was dissolved in trichlorobenzene and ODE under argon protection, and the Se precursor was made by dissolving Se powder in ODE. Subsequently, Cd and Se precursors in ODE were injected into the P3HT solution at high temperature to yield CdSe QDs (Figure 12). Dimethylcadmium was used as Cd precursor due to the insolubility of other cadmium salts in ODE.^[128] Notably, this syn-

thetic strategy (i.e., direct NC growth) produced dispersed CdSe QDs. However, the control over the size and shape distribution was still low in comparison to QDs synthesized with the other two strategies (i.e., ligand exchange and direct growth) mentioned above (Figure 12). These P3HT–CdSe nanocomposites can be dissolved in common solvents for the polymer, from which thin films can be readily formed for device fabrication.^[128]

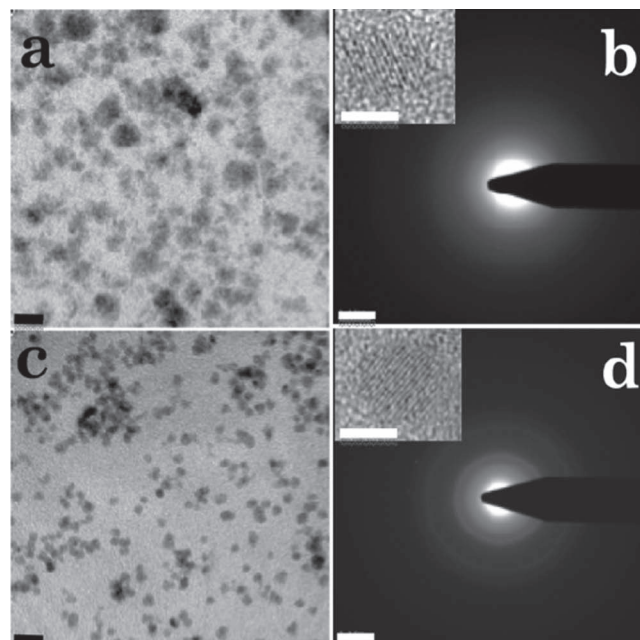


Figure 12. (a,c) TEM images of CdSe QDs synthesized at 200 and 260 °C, respectively (scale bar = 20 nm). (b,d) Corresponding selected area electron diffraction patterns; the high-resolution TEM images are shown in insets (scale bar = 5 nm). Figure reproduced with permission.^[128] Copyright 2010, ACS.

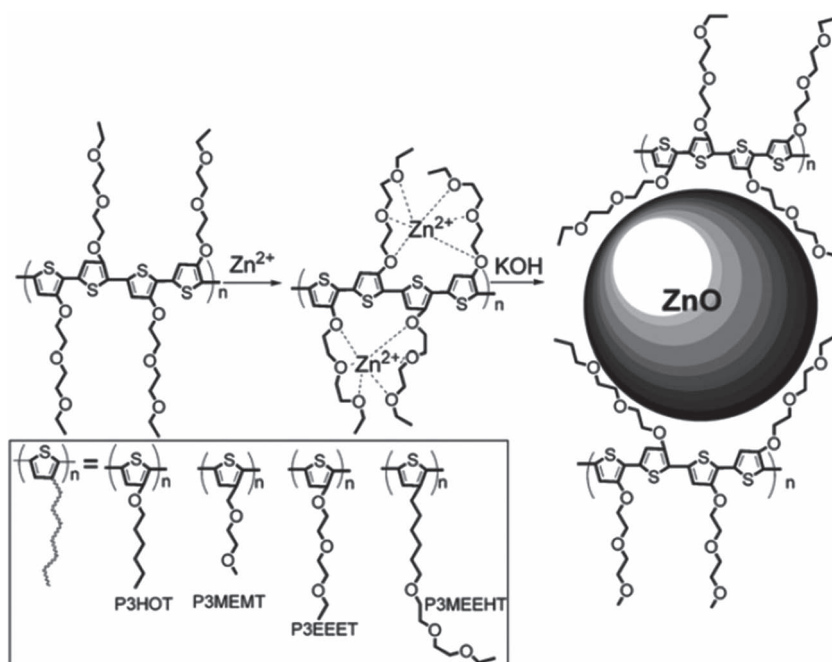


Figure 13. Schematic illustration of conjugated polymer conformation with Zn(II) ion complexation and conjugated polymer–ZnO nanocomposite utilizing P3EEET as template. The chemical structures of P3HOT, P3MEMT, P3EEET, and P3MEEHT are shown in the lower left panel. Figure reproduced with permission.^[129] Copyright 2010, ACS.

Time-resolved microwave conductivity (TRMC) measurements on these films suggested the occurrence of photoinduced charge separation at the P3HT/CdSe interface, which was desired for efficient hybrid solar cells. Similarly, the force that affords direct contact of CdSe QDs with P3HT in this approach was also unclear and may merit a detailed study.

As noted above, the growth of PbS NCs in the MEH-PPV matrix was influenced by the steric effect of long MEH-PPV chain as there was no charged functional groups on MEH-PPV to tailor the NC growth.^[124] Interestingly, polyalkoxythiophene–ZnO nanocomposites containing highly luminescent, homogeneous ZnO nanoparticles without the addition of capping agents were recently prepared by judiciously modifying polythiophene with alkoxy groups as side chains (i.e., alkoxy-modified polythiophene) to facilitate the electronic affinity with Zn(OAc)₂.^[129] This new approach offered several advantages in terms of homogeneous size distribution, good dispersion, and distinctive band-gap emission free from defect trapping.^[129] Specifically, various alkoxy-modified polythiophene analogues, poly(3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene) (P3MEEHT), poly((3-hexyloxy)thiophene) (P3HOT), poly(3-((2-methoxyethoxy) methyl)thiophene) (P3MEMT), and poly(3-(2-(2-ethoxyethoxy)ethoxy)thiophene) (P3EEET) were firstly synthesized (Figure 13). Subsequently, synthesis of ZnO was performed by adding Zn(OAc)₂ to a solution containing as-prepared polythiophene analogues as templates (for example, P3EEET as shown in Figure 13) to allow the Zn²⁺ ion chelation to proceed. The Zn²⁺ ion was presumably encapsulated by P3EEET under basic (KOH) conditions and then aged to grow the P3EEET-encapsulated ZnO nanoparticles in which alkoxy groups within the alkyl chain played

a key role in encapsulation by forming the chelation with Zn²⁺ ion (Figure 13). The P3EEET-coated ZnO nanoparticles were well dispersed in the polymer matrix as revealed by TEM. These high quality NCs with an average diameter of 3.5 ± 0.5 nm possessed a wurtzite (hexagonal) structure. As the length of alkoxy side chains can be readily regulated, this approach can, in principle, be extended to prepare other CP–NC nanocomposites, in which NCs are derived from the corresponding semiconducting metal cation precursor.^[129]

In the *direct NC growth* strategy, the quality of obtained NCs depends heavily on the electrostatic and steric effects imposed by CPs that act as template for the NC growth.^[124] It is thus feasible to control the growth of NCs into different shapes through modifying the architecture of CP templates. A new method was recently demonstrated to synthesize CdS single-crystal NRs directly in the P3HT template that provided geometrical manipulation of CdS nanocrystals.^[130] The CdS NRs with different aspect ratios can be easily obtained via a controlled solvency of a cosolvent mixture, under which the conformation of the P3HT chain can be manipulated.^[130]

In a typical synthesis, cadmium acetate dihydrate and P3HT were dissolved in the mixed solvents of 1,4-dichlorobenzene (DCB) and dimethyl sulfoxide (DMSO), followed by the injection of the sulfur DCB solution at elevated temperature, forming CdS NCs in the P3HT matrix. TEM images revealed that CdS NCs possessed high crystallinity, and the size of NCs was increased with the reaction temperature. The NRs with various aspect ratios from 4 to 16 were obtained by varying the DCB to DMSO ratio of the mixed solvents. The improved PL quenching was observed, suggesting the electronic coupling between P3HT and the high-aspect-ratio CdS NRs. The photovoltaic device composed of P3HT and CdS NR with the aspect ratio of 16 showed a *PCE* of as high as 2.9%.^[130] The growth mechanism was proposed based on the FTIR and TEM measurements (Figure 14). The planar conformation of P3HT can provide stacking molecular architecture (Figure 14a). As a result, the Cd²⁺ ions may be confined within the network-like structure of P3HT through dipole-dipole or ion-dipole interaction between the Cd²⁺ ions and S atoms and subsequently experienced the nucleation-and-growth process with the adding sulfur ions,^[130] leading to the formation of uniformly and randomly distributed CdS NCs and NRs within P3HT.^[130] Furthermore, as the conformation of P3HT was determined by the ratio of DCB (good solvent for P3HT)/DMSO (poor solvent for P3HT), the shape of CdS NRs can be tuned by modifying the solvent ratio.^[130] The NC morphology was dominated when the concentration of was lower than 2.5 mg/mL, above which the NR morphology started to form. The lower concentration of Cd²⁺ ions cannot afford sufficient growth to yield a rod-like structure, thereby leading to the formation of equiaxial NCs (Figure 14b),

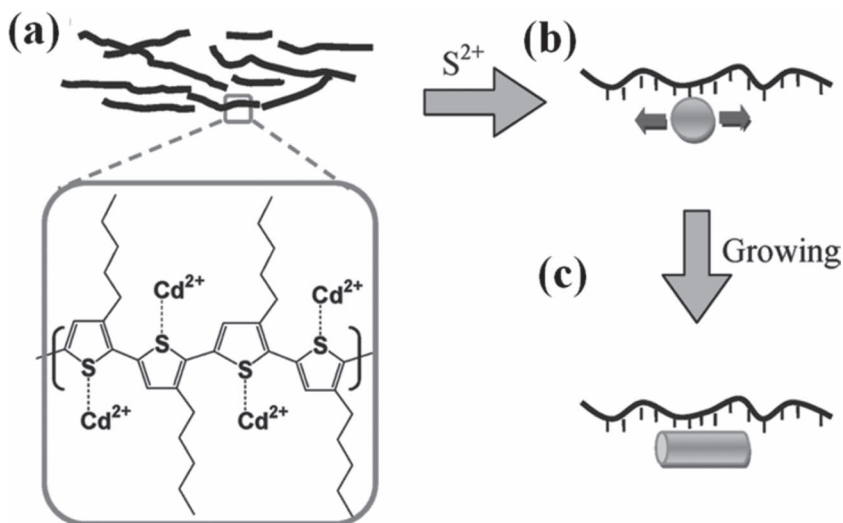


Figure 14. (a) Schematic representation of the synthesis scheme of P3HT–CdS nanocomposites. The Cd^{2+} ions were assumed to be coupled with the unpaired S along the planar P3HT chain network. Proposed mechanism for the growth of (b) CdS NPs and (c) CdS NRs. Figure reproduced with permission.^[130] Copyright 2009, ACS.

It is worth noting that an intriguing alternative strategy was developed recently to directly grow NCs in solid-state CP films (i.e., controlled *in situ* thermal decomposition of a single-source precursor, namely, metal xanthate, in the CP film) for hybrid solar cells.^[66,131] Specifically, a solid-state thin film was first obtained by spin-coating a chlorobenzene solution (Figure 15a) containing the single-source cadmium ethylxanthate pyridine ($\text{Cd}(\text{S}_2\text{COEt})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$) (Figure 15c) and P3HT (Figure 15b), followed by thermal annealing to yield P3HT–CdS nanocomposites (Figure 15e). Metal xanthates were utilized as precursors as they decompose cleanly at low temperatures into metal sulfide and generate only volatile side products (e.g., H_2S , COS, etc.), thereby rendering the *in situ* growth of inorganic NCs in relatively fragile polymer hosts.^[66,131] TEM studies showed phase segregation morphology composed of dark regions of CdS and lighter regions of P3HT. The length scale of phase segregation

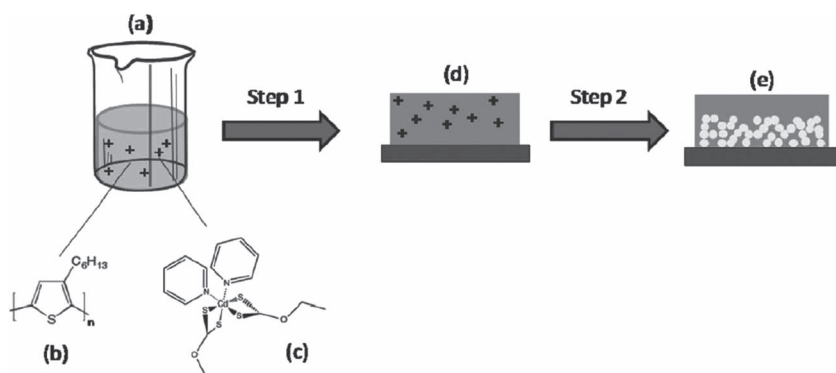


Figure 15. Schematic illustration of directly growing CdS NPs within P3HT solid films. (a) solution of (b) P3HT and (c) cadmium ethylxanthate pyridine, (d) deposition of the mixture solution (i.e., (a)) through spin coating (step 1) led to the formation of a thin film composed of the metal xanthate precursor and P3HT. Upon annealing (step 2) a hybrid polymer–CdS NP film (e) was formed. Figure reproduced with permission.^[66]

depended strongly on the annealing temperature. An increase in the annealing temperature from 105 to 160 °C led to a reduction in the domain size of CdS embedded in the P3HT matrix from approximately 100 nm (Figure 16a) to below 40 nm (Figure 16b). An interconnected network of CdS nanoparticles was formed when annealing at 160 °C (Figure 16b); after the selective removal of P3HT in P3HT–CdS film with chlorobenzene, a highly mesoporous structure was clearly emerged with interconnected CdS nanoparticle aggregates of approximately 30–50 nm in diameter (Figure 16c).^[66] Such mesoporous structures are strongly desirable for use as photoactive layers in organic–inorganic hybrid solar cells because of (1) large interfacial area at the nanoscale for efficient charge generation, and (2) a nanoscale interpenetrating network of inorganic NCs to facilitate efficient charge transport and collection at the device electrodes.^[66,131] Transient absorption spectroscopy measurement suggested a remarkably efficient charge generation

at the CdS/P3HT heterojunction. The resulting photovoltaic devices exhibited a PCE of 2.17%. Clearly, the *in situ* thermal decomposition of single-source precursors in solid-state polymers remains an promising route to hybrid solar cells,

In addition to metal sulfide, similar approach has been previously successfully applied to prepare other semiconductor nanocomposites for use in hybrid solar cells.^[132–135] The photoactive layer composed of P3HT–ZnO nanocomposites was made by spin-coating a mixed solution of diethylzinc and P3HT.^[134,135] During spin-coating, diethylzinc was exposed to humidity, forming $\text{Zn}(\text{OH})_2$ due to hydrolysis. Subsequently, the thin film was annealed at 100 °C to yield an interpenetrating network of ZnO inside P3HT.^[134,135] Despite the simplicity, NCs prepared by the method of *in situ* generation of semiconductor NCs inside the dry-state CP film were appeared as the aggregates that may reduce the effective CP/NC interfacial area. Compared to the nanocomposites crafted by *ligand exchange* and *direct grafting*, the bonding between CPs and NCs is rather weak as CPs can be removed from the resulting nanocomposite film, for example, P3HT in the P3HT–CdS film was eliminated by chlorobenzene,^[66] which may cause large-scale phase segregation during the post-treatment of photovoltaic devices (e.g., thermal annealing and solvent vapor annealing). Therefore, more work may be required to optimize this *in situ* growth approach.

5. Summary and Outlook

The intimacy of mixing of donor and acceptor semiconductors in organic/inorganic hybrid solar cells exerts profound influence on the

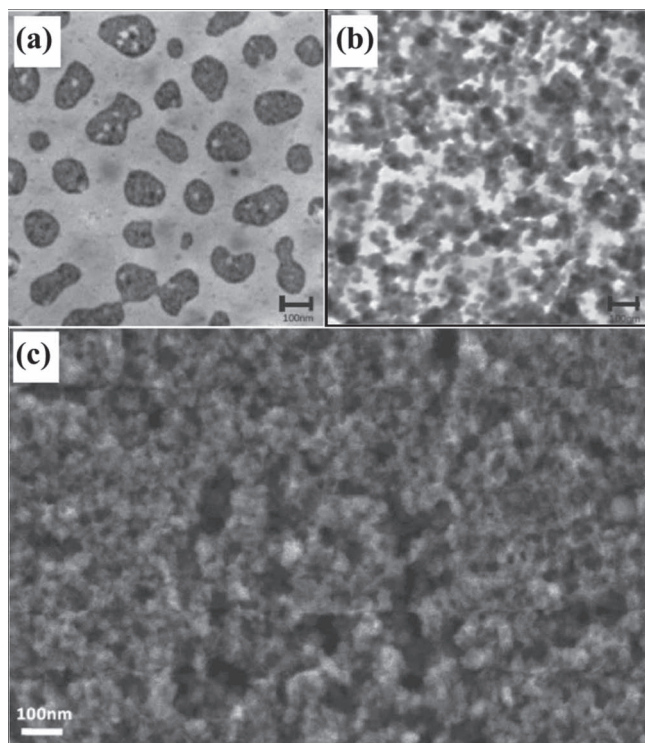


Figure 16. (a) and (b) TEM images P3HT–CdS films after annealing at 105 °C and 160 °C, respectively. (c) SEM image of a mesoporous CdS film after the removal of P3HT (annealed at 160 °C), showing a continuous CdS NP network. Figure reproduced with permission.^[66]

efficiency of the devices by providing efficient charge separation at the donor/acceptor interface. This Review highlights three robust strategies (i.e., ligand exchange direct grafting and direct NC growth) that are widely utilized to craft a large number of semiconductor organic–inorganic nanocomposites composed of intimately contacted CPs and inorganic NCs of different types and dimensions with the promising photovoltaic performance in hybrid solar cells.

Despite the significant advantages of these strategies to yield CP–NC nanocomposites over the conventional physical blending in order to provide unique practical opportunities by capitalizing on these intimate nanocomposites for use in next-generation high-efficiency photovoltaic devices, intense research efforts are still required. *Ligand exchange* is currently the most versatile approach to coat functional groups on the NC surface. However, due to the ligand exchange dynamics,^[80] the grafting density of functional ligands is often low, especially in the case of grafting CPs of high molecular weight. Thus, much work can be done to optimize this approach. For example, recent progress in side-chain functionalization of CPs enables the integration of strong capping groups into each repeat units,^[136,137] leading to a diversity of new multidentate CP ligands to promote their coordination ability and stability on the NC surface. In addition, although it requires replacing the alkane ligand with functionality that supports surface-initiated polymerization. Moreover, it is often challenging to control the complicated surface polymerization process, elaborate *grafting-from* approach allowing for the direct synthesis of long CPs from monomer via the

surface polymerization on NCs should be explored extensively to enable higher grafting density as it eliminates several limitations in the *grafting-onto* approach (e.g., only low molecular weight CP can be grafted onto due to the steric hindrance on the subsequent grafting, and the entropy loss associated with confining polymers chains on the NC surface).^[116]

The *direct grafting* strategy, which depends largely on the successful design of appropriate bifunctional ligand, usually offers severalfold high grafting density, thereby substantially increasing the effective semiconductor organic/inorganic interface for fast charge separation. However, if overly grafted (i.e., NCs heavily encapsulated by CPs), the efficient electron transport between adjacent NCs may be retarded. As a result, new rational designs may be necessary to impart a controlled surface grafting process (e.g., grafting density and location). For example, colloidal Janus NCs^[138–140] could be exploited to graft CPs partially on NCs, leaving certain area of NCs naked so the adjacent NCs may interconnect one another to form the NC network for efficient electron transport. Furthermore, two-dimensional electron conductors (e.g., graphene; an atomically thin and nearly transparent semimetal^[141,142]), capable of providing continuous electron pathway with high mobility, could also be utilized to enhance the electron collection at the electrode in hybrid solar cells. The use of CP–NC nanocomposites blended with graphene as photoactive layer promotes the photogenerated charge to transport directly from NCs to the electrode via graphene instead of inefficient hopping along the NC (e.g., nanoparticle) network. For an optimized design, CP–NC nanocomposites can be decorated on the graphene surface via selective chemical bonding between NC and graphene^[143–146] to ensure improved electronic connectivity between them. For example, the graphene surface can be functionalized with ethynyl groups, on which azide-functionalized NCs are tethered through click reaction, and finally the ethynyl-terminated CPs will selectively couple with NCs rather than graphene.

The *direct NC growth* strategy is a rapidly growing area of research due to its simplicity and recent advances in the NC synthesis. However, the quality of formed NCs in terms of the size and shape distribution is rather low, uncompetitive with those produced from colloidal synthesis.^[68,69,147,148] In some cases, for example direct NC growth from the dry CP film,^[66,131] the resulting NCs still form aggregates. As optical properties of NCs are strongly related to their size, shape, and dielectric environment,^[149] controlled growth of NCs within the CP matrix may be necessary for advanced photovoltaics. Additionally, the interaction enabling intimate contact between CPs and NCs in nanocomposites is usually weak, and large-scale phase segregation may occur in the post-treatment process of photovoltaic devices. To this end, the template approach by employing amphiphilic block copolymers may be introduced to guide the growth of NCs. We envision that microphase-separated structures and/or micelles of amphiphilic diblock copolymers composed hydrophilic block and hydrophobic CP block (e.g., poly(acrylic acid)-*b*-poly(3-hexylthiophene) (PAA-*b*-P3HT)) may be exploited as template to synthesize NCs that would be intimately and permanently connected with CPs (e.g., P3HT) due to strong affinity of inorganic precursors to the hydrophilic block (e.g., PAA), forming NCs with controlled size and shape. Importantly, as two blocks in amphiphilic block copolymer template

are covalently linked, the resulting CP–NC nanocomposites are expected to be much more stable than those prepared by *ligand exchange* and *direct grafting* strategies that rely on the coordination interaction between NCs and functional group of ligands.

In addition to isotropic nanoparticles and anisotropic NRs as discussed above, the use of other elongated single-crystalline nanostructures may enhance light absorption, extending into the often difficult to achieve near-infrared (NIR) range, and enable more effective charge transport by providing continuous pathway and reducing carrier traps. The utilization of anisotropic NCs, such as NRs,^[150–152] tetrapods,^[153,154] nanopillar arrays,^[105,155] in hybrid solar cells consisting of physical blend of NCs with CPs have yielded improved *PCE*. To date, only rod-like NCs has been reported in the synthesis of CP–NC nanocomposites for solar cells. In principle, tetrapods and hyperbranched NCs, capable of forming percolation network spanning the thickness of the device,^[153,156] can be grafted with CPs to effectively disperse these larger NCs, and provide even more efficient charge separation and collection at the electrodes due to their intrinsically percolated structures. Obviously, the recently developed two-dimensional semiconductor nanostructures, such as nanosheets^[157] and nanoribbons,^[158] are also expected to greatly improve the device performance when chemically tethered with CPs of high density, as they provide in-plane uninterrupted pathway for charge transport compared to that of one-dimensional elongated structures. Besides the nanostructures of individual NCs, their spatial arrangement within the photoactive layer is also of great technological importance. The photovoltaic performance can be further improved if some anisotropic NCs (e.g., NRs) are vertically aligned, instead of randomly distributed, between two electrodes to minimize the carrier transport pathways.^[105] Such ordering of NCs may be achieved by self-assembly^[159–161] or externally applied fields (e.g., electric and magnetic fields).^[20,162,163] Nonetheless, with the progress being made in colloidal synthesis, low-bandgap CPs, self-assembly, and device engineering and optimization, crafting semiconductor CP–NC nanocomposites will remain as an active field of exploration for low-cost, high-efficiency hybrid solar cells.

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