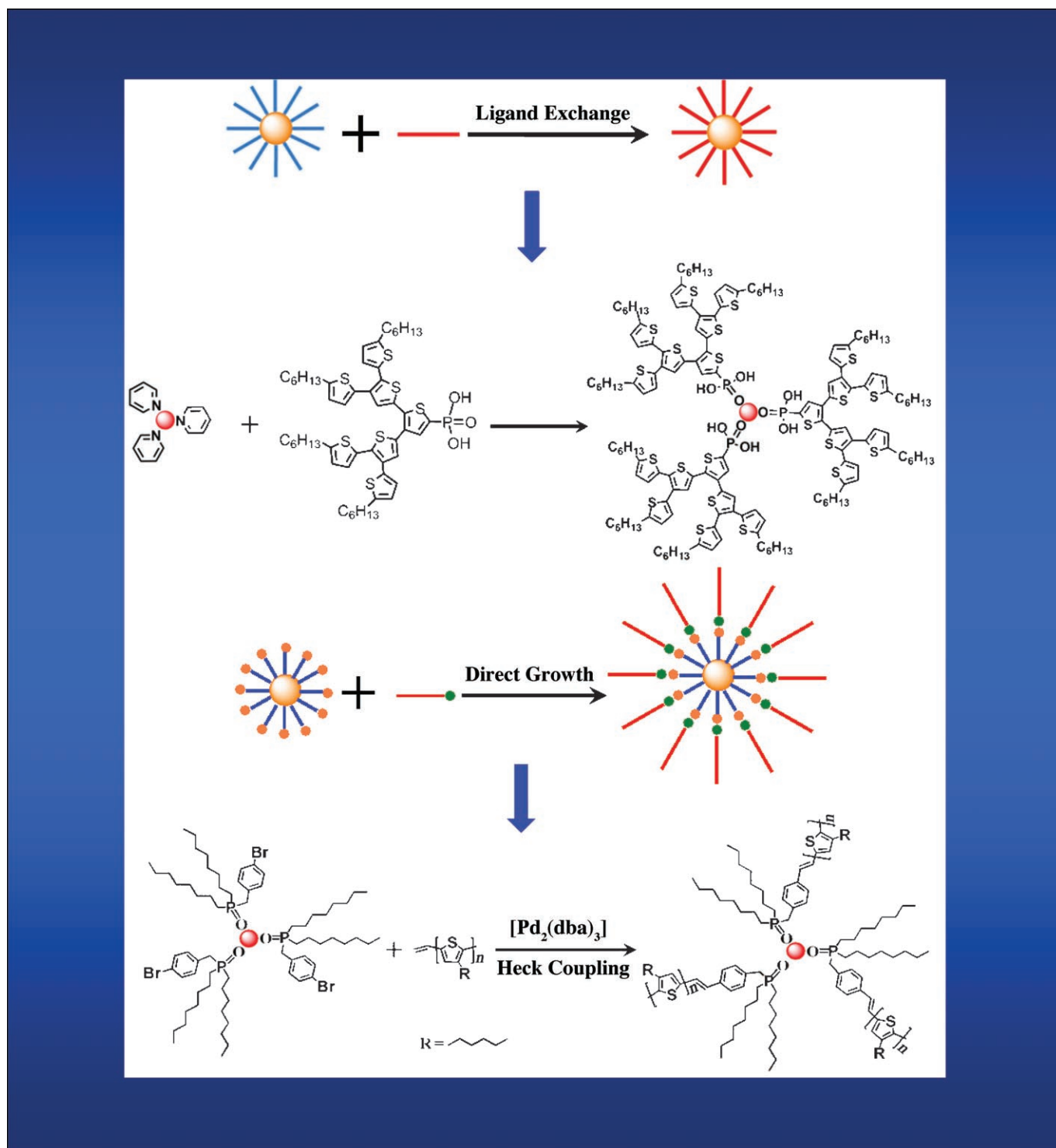


# Organic–Inorganic Nanohybrids through the Direct Tailoring of Semiconductor Nanocrystals with Conjugated Polymers

Zhiqun Lin\*<sup>[a]</sup>



**Abstract:** Two main synthetic strategies are used to prepare conjugated oligomer- or polymer-nanocrystal nanohybrids. In the first strategy ligand exchange is invoked to either replace with a bifunctional ligand, which contains a second functional group for coupling with conjugated oligomers or polymers (COs or CPs), or exchange for the functionalized COs or CPs in a “grafting-onto” process. Alternatively, in the second strategy the nanocrystal (NC) is passivated with functional ligands from which COs or CPs are directly grown in the absence of ligand exchange. The well-defined interface between the COs or CPs and NCs facilitates an efficient charge-transfer between them.

**Keywords:** charge transfer • direct grafting • ligand exchange • nanohybrids • organic–inorganic hybrid composites • semiconductors

## Introduction

Semiconductor nanocrystals (NCs) are promising building blocks for functional materials.<sup>[1–4]</sup> They are synthesized by a conventional, organometallic, high-temperature growth method. The optical bandgaps of widely studied NCs, for example, CdE (E = S, Se, Te), are typically in the visible and near-infrared range, making them intriguing nanomaterials for use in optoelectronic devices.<sup>[5]</sup> The variation of the NC size provides continuous and predictable changes in fluorescence emission associated with quantum confinement effects.<sup>[6,7]</sup> An appropriate surface coating with a monolayer of coordinating organic ligands is key to ensuring the solubility and miscibility of NCs within the host environment, and to retaining the spectroscopic properties of the materials by preventing quantum dots (QDs) from aggregation.<sup>[8,9]</sup> The most common and readily accessible ligands are phosphine oxides, phosphanes, alkyl thiols, amines, and carboxylic acids. They are insulate ligands with a large band gap, thereby sufficiently reducing the electron-transfer efficiency.<sup>[5]</sup> For use in photovoltaic cells, it is highly desirable to integrate electron-accepting NCs with electron-donating conjugated polymers (CPs; i.e., forming the CP/NC hybrids).

Hybrids of electroactive CPs with NCs inherit decent solution processability, flexibility, mechanical strength, and light-weight characteristic from CPs<sup>[10–13]</sup> and broad spectral absorption, good photostability, and high carrier mobility from NCs. The light-absorbing CPs possess strong absorp-

tion bands that coincide with part of the solar spectrum. The achievable hole mobilities in CPs far exceed electron mobilities.<sup>[14]</sup> Inorganic NCs have greater electron affinities than organic CPs, so charge transfer at the CP/NC interface occurs rapidly.<sup>[5]</sup> The CP/NC hybrids are often prepared by blending these two components or by constructing a CP/NC bilayer or CP/NC alternating multilayer, both physically or chemically,<sup>[15]</sup> in which only a small fraction of excitons, that is, the bound electron-hole pairs, are able to diffuse to the interface at which they are dissociated.<sup>[16]</sup> The two components are always in physical contact and generally consist of NC aggregates, thus it is difficult to control the detailed morphology and dispersion of NCs within CPs. The interface between the CP and the NC, accomplished by stripping original insulate ligands from NCs during film processing, is not well controlled, thereby reducing the efficient electronic interfacial interactions between them.<sup>[14,16]</sup> The effective charge transfer, which depends on the quality of the interface, is key for the CP/NC hybrids for use in photovoltaic cells.<sup>[17–19]</sup> This indicates that an interpenetrated network of CP/NC on the scale of the exciton diffusion length is highly favorable for charge generation and transport, which is extremely difficult to realize by using a conventional blending approach.<sup>[15,20,21]</sup>

To this end, better control over the hybrid morphology can be accomplished by direct tethering the NC with the CP; that is, preparing the CP–NC nanohybrids with well-controlled interfaces as opposed to the CP/NC hybrids. As a result, efficient light-induced electronic interactions between the CP and the NC are facilitated. The ability to chemically anchor the NC to the CP offers a means of achieving uniform dispersion of NCs and maximizing the interfacial area. To date a few elegant studies have concentrated on the direct integration of NCs into electroactive conjugated oligomers (COs) and/or CPs by means of ligand exchange with insulate surfactants,<sup>[5,14,22–28]</sup> direct growth from/onto the NCs’ surface,<sup>[8,16]</sup> electrostatic interaction,<sup>[29,30]</sup> or molecular recognition process by forming hydrogen bonds (i.e., using supramolecular chemistry)<sup>[31]</sup> to achieve a more controlled interface on a molecular scale and morphology. By changing the conjugation length of the CP backbone, the energy level of nanohybrids can be optimized in order to enhance charge transfer and minimize recombination processes.<sup>[22]</sup>

In the following we will discuss recent advances in design and characterization of CO–NC and CP–NC nanohybrids. It is important that the synthetic conditions used retain the inherent fluorescence of the NCs.<sup>[32]</sup> Two main synthetic strategies have been successfully applied to yield CO–NC and CP–NC nanohybrids. In the first strategy, ligand exchange is an essential step to either replace original, insulate, small-molecule-capped NCs with bifunctional ligands or directly exchange for functionalized COs and CPs in a “grafting-onto” process. The second strategy utilizes direct grafting of CO or CP from/onto functionalized NCs in the absence of ligand-exchange chemistry.

[a] Prof. Z. Lin  
Department of Materials Science and Engineering  
Iowa State University, Ames, IA 50011 (USA)  
Fax: (+1) 515-294-7202  
E-mail: zqlin@iastate.edu

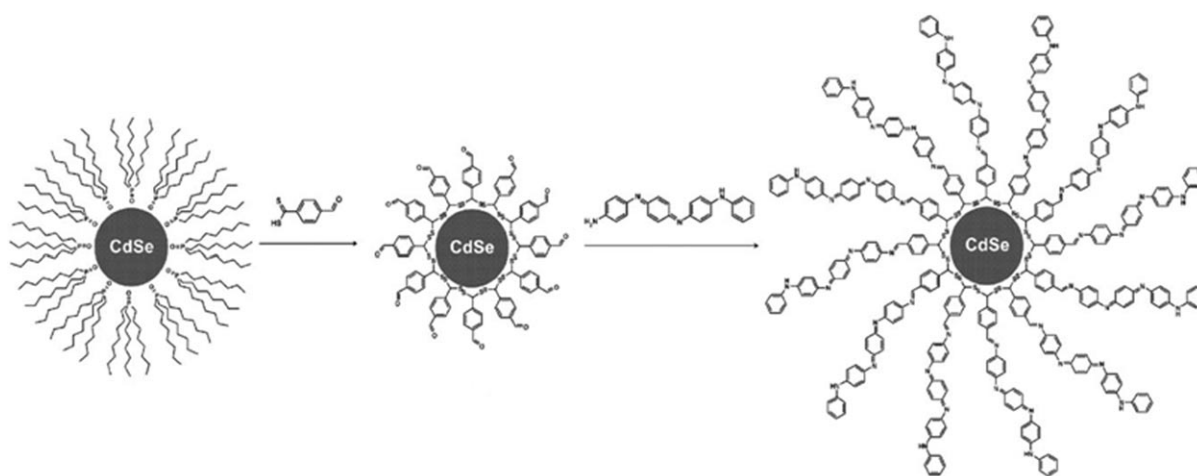
## Nanohybrids Prepared by Ligand-Exchange Chemistry

Ligand exchange permits derivatization with a broad range of functional groups on the NC surface. Two approaches involving the use of ligand exchange as an intermediate step have been introduced to prepare the nanohybrids.<sup>[5,14,22–28,33]</sup> The commonly used, insulate, small-molecule-capped NCs are exchanged with a bifunctional ligand (e.g., aldehyde-terminated dithiol<sup>[26–28]</sup> or arylbromide-functionalized phosphine oxide and thiol<sup>[25]</sup>), followed by direct coupling with COs or CPs of interest on the NC surface by a condensation reaction (e.g., tetraaniline)<sup>[26,27]</sup> or by Heck coupling with a vinyl-terminated CP.<sup>[25]</sup> Alternatively, the nanohybrids can be made by a one-step ligand-exchange reaction with functionalized COs and CPs that were prepared from a multi-step synthesis.<sup>[5,14,22–24]</sup>

**Ligand exchange followed by direct coupling:** Organic ligands containing the chelating carbodithioate group are excellent binding ligand for the surface passivation of various NCs. The new ligand possesses a high chemical affinity for the NC's surface by forming strong chelate-type bonds with metal atoms, thereby allowing for the nearly quantitative exchange with the original trioctylphosphine oxide (TOPO) ligand in very mild conditions and thus improving the resistance of NCs against photooxidation as compared to corresponding thiol ligands.<sup>[26]</sup> By using carbodithiate derivatives, an electroactive aniline tetramer was successfully grafted on CdSe QDs, resulting in the tetraaniline–CdSe nanohybrids.<sup>[26]</sup> The nanohybrids were synthesized in two steps as depicted in Scheme 1.<sup>[27]</sup> The initial TOPO ligands on the CdSe surface were quantitatively exchanged with 4-formyldithiobenzoic acid. Subsequently, the aniline tetramer was grafted onto CdSe surface by a condensation reaction between the terminal primary amine group of the tetramer and the aldehyde group of 4-formyldithiobenzoic acid. The key to chemically attaching end-functionalized COs or CPs

onto functionalized NCs is to first synthesize both COs or CPs and NCs with compatible functional groups that allow them to react with each other under relatively mild condition without sacrificing the stability and photophysical properties of each component. The success of grafting reaction was demonstrated by <sup>1</sup>H NMR, FTIR, and XPS measurements.<sup>[28]</sup> The nanohybrids exhibited complete quenching of the constituents. The electrochemical studies of the nanohybrids with complementary spectroscopic and spectroelectrochemical techniques revealed that ligand exchange with oligoaniline dramatically affected the voltammetric peaks associated with the HOMO oxidation and LUMO reduction of CdSe QDs, which were shifted to higher and lower potential, respectively.<sup>[27]</sup> The grafted oligothiophene ligand can be switched between the semiconducting and the conducting states through an electrochemically imposed change in its oxidation state.<sup>[27]</sup>

The ability to manipulate the shape of NCs has led to quantum rods (QRs) with diameters ranging from 2 to 10 nm and lengths ranging from 5 to 100 nm.<sup>[34,35]</sup> Due to their intrinsic structural anisotropy, QRs possess many unique properties that make them potentially better NCs for photovoltaic cells and biomedical applications than QDs. The photovoltaic cells made of QRs and CPs show an improved optical absorption in the red and near-infrared range originating from the QRs.<sup>[36]</sup> Moreover, the long axis of the QRs provides continuous paths for transporting electrons. High aspect ratio of the length/diameter renders a lower percolation ratio of QR to CP, thereby producing more electrical conduction routes through the film. The performance of the photovoltaic cells could further be improved if the QRs were vertically aligned between two electrodes to minimize the carrier transport pathways.<sup>[36]</sup> Recently, a CdSe QR (8 nm in diameter and 40 nm in length) has been connected to regioregular poly(3-hexylthiophene) (P3HT; molecular weight, MW = 8600 g mol<sup>-1</sup>), that is, forming P3HT–CdSe QR nanohybrids.<sup>[25]</sup> The nanohybrids were synthesized as follows. First, arylbromide-functionalized CdSe QRs were



Scheme 1. Synthetic route to the tetraaniline–CdSe nanohybrids. Reproduced with permission from *Phys. Chem. Chem. Phys.* **2005**, *7*, 3204. Copyright 2006 The Royal Society of Chemistry.

synthesized by ligand exchange of pyridine-capped CdSe QRs with *p*-bromobenzyl-di-*n*-octylphosphine oxide (DOPO-Br). The vinyl-terminated P3HT was then chemically tethered to the CdSe QR surface by a Heck coupling with arylbromide moieties. With respect to the hybrid of P3HT/pyridine-capped CdSe QRs, the P3HT–CdSe QR nanohybrids exhibited an excellent dispersion of QRs in P3HT matrix as revealed by TEM (Figure 1).<sup>[25]</sup> The solid-state photoluminescence (PL) measurement on the thin film of the nanohybrids showed quenching of the emission of

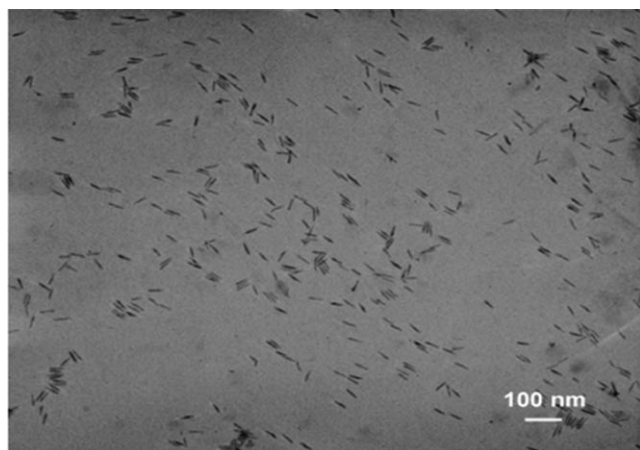
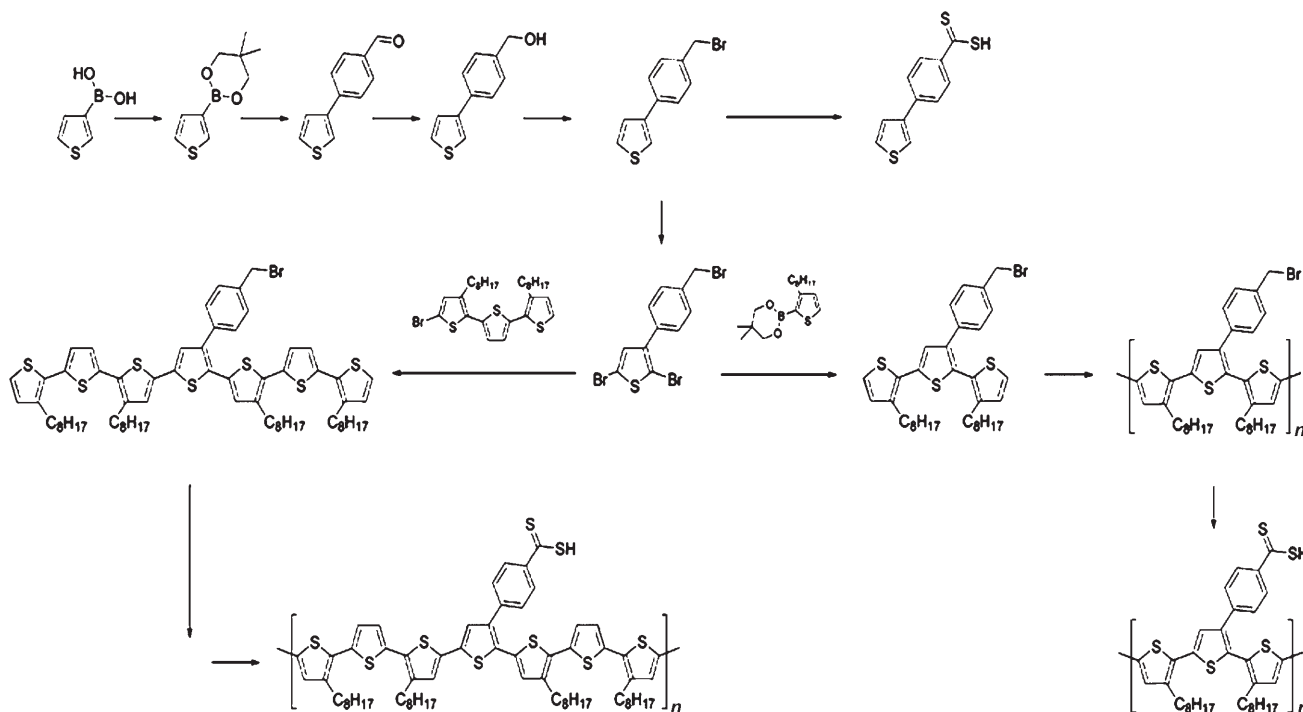


Figure 1. TEM image of 20 wt% P3HT–CdSe QR nanohybrids in P3HT homopolymer. Reproduced with permission from *Chem. Mater.* **2007**, *19*, 3712. Copyright 2007 The American Chemical Society.

P3HT, indicating charge transfer between P3HT and CdSe QRs. The success of grafting P3HT to the CdSe QR surface was confirmed by spectroscopic and microscopic characterization.<sup>[25]</sup>

#### One-step ligand exchange of insulate surfactant-capped NCs with functional conjugated oligomers or polymers:

A family of carbodithioic acid functionalized regioregular oligo- and polythiophene were synthesized as follows. The functionalized thiophene monomer was coupled with oligothiophenes, followed by the oxidative polymerization of the resulting symmetric oligomers. Finally, the carbodithioate moiety was introduced through a post-functionalization reaction as illustrated in Scheme 2.<sup>[22]</sup> These carbodithioate-containing oligo- and polythiophenes were subsequently grafted on the CdSe surface by ligand exchange with TOPO-capped CdSe QDs (diameter,  $D=3.2$  nm) under mild conditions to form the nanohybrids. The success of grafting reaction was confirmed by the absorption spectra studies and by <sup>1</sup>H NMR spectroscopy. The peak of the carbodithioic acid proton disappeared after formation of nanohybrid. All peak positions were down-shifted upon grafting on the CdSe surface, as electron density was delocalized over the chelating bond formed between a surface Cd atom and the sulfur atoms.<sup>[22]</sup> Furthermore, peak broadening was also seen due to the restricted motion of the grafted ligands. Photoluminescence (PL) studies of the nanohybrids revealed a photoinduced charge-transfer process at the polythiophene–CdSe interface, leading to an efficient quenching of the emission,



Scheme 2. Synthetic pathway for the preparation of carbodithioate-functionalized oligo- and polythiophene. Reproduced with permission from *Chem. Mater.* **2006**, *18*, 4817. Copyright 2006 The American Chemical Society.

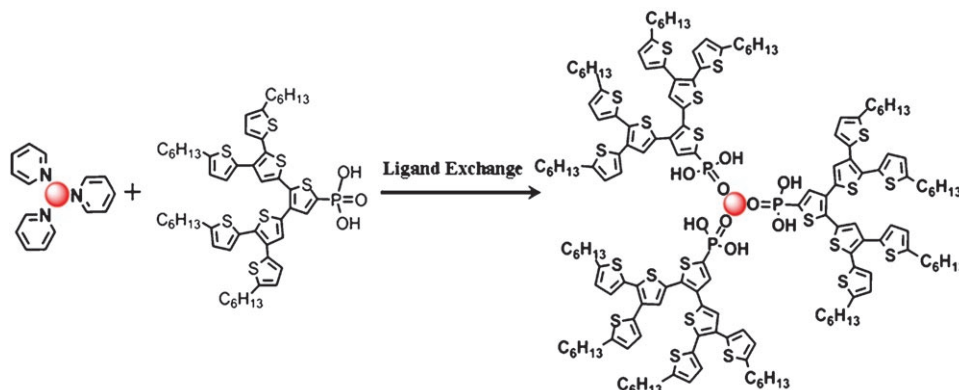
which suggested potential application in thin film solar cells. Similar to the side-chain-mediated electronic contact discussed above, a polythiophene–CdTe QD nanohybrid has recently been made through a ligand-exchange process. Polythiophenes with tetrahydro-4H-thiopyran-4-ylidene side chains induce substantial electronic contact between polythiophene and CdTe QDs, and thus mediate charge transport between CdTe and polythiophene backbone.<sup>[37]</sup>

Another example with a multidentate electroactive polymer, that is, amine-functionalized rod-coil triblock copolymer [poly(2-(dimethylamino)-ethylmethacrylate)-poly(fluorene)-poly(2-(dimethylamino)-ethylmethacrylate), denoted PDMAEMA-PF-PDMAEMA] as the surface ligand to prepare the PF–CdSe nanohybrids by replacing initial insulate TOPO ligand on the 5 nm CdSe QD surface was reported.<sup>[38]</sup> PDMAEMA-PF-PDMAEMA with the MW of 16000 was synthesized by atom-transfer radical polymerization (ATRP). Owing to the steric hindrance imposed by non-conjugated PDMAEMA chains, which acted as a barrier for the charge transfer, the PL was not completely quenched.<sup>[38]</sup>

Recently, phosphonic acid substituted pentathiophene (PA-5T) was prepared by a multistep synthesis.<sup>[5]</sup> The phosphonic acid ligand coordinates more strongly with CdSe QDs than thiols, amines, phosphines, and phosphine oxides,<sup>[5]</sup> although the amine-terminated P3HT partially replacing the pyridine ligand to yield P3HT–CdSe QR was demonstrated.<sup>[33]</sup> Ligand exchange of PA-5T with TOPO-capped CdSe QDs yielded the 5T–CdSe nanohybrids.<sup>[39]</sup> The number of PA-5T molecules chemically bound to the CdSe surface was estimated by deconvoluting the absorption spectra of the nanohybrids. PL measurements showed the charge transfer from 5T to CdSe.

In addition to linear oligothiophene and polythiophene, conjugated oligothiophene dendrons were also rationally designed and utilized as electroactive surfactants for the capping of CdSe QDs by a ligand-exchange process to mediate the charge transfer between CdSe and organic semiconductors.<sup>[23,24]</sup> The variation of the number of thiophene units produced oligothiophene dendrons with tunable absorbance and emission. The steric crowding of the dendrons allowed the close packing of dendron ligands in a cone shape on the CdSe surface. To completely exchange the TOPO ligand for the dendron, it was found necessary to first displace the TOPO with pyridine. Subsequently, the pyridine-capped CdSe QDs (diameter,  $D = 2.79$  nm) was substituted for oligothiophene dendrons, either 5,5''-dihexyl-[2,2';3',2'']terthiophene-ylphosphonic acid (P3T), or 2,3-Di(5,5''-dihexyl-

[2,2';3',2'']terthiophene-5'-yl)thiophene-ylphosphonic acid (P7T), resulting in the P3T–CdSe and P7T–CdSe nanohybrids (Scheme 3). The absorption and PL spectra of P7T and the P7T–CdSe nanohybrid are depicted in Figure 2. An average of 34 P7T dendrons per CdSe QD was found in the P7T–CdSe nanohybrid by deconvolution of the absorption spectra. The PL of both P7T and CdSe QD was completely quenched, suggesting the charge transfer between them. One-layer photovoltaic cells fabricated by spin-coating the



Scheme 3. Synthesis of the P7T–CdSe nanohybrid via ligand exchange of pyridine-capped CdSe QDs for P7T.<sup>[23]</sup>

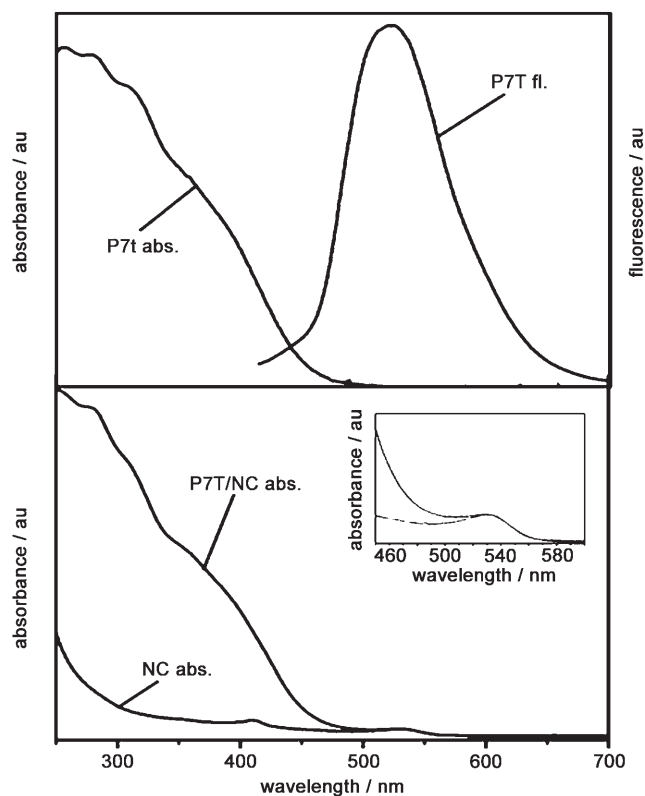


Figure 2. Absorption and PL spectra of P7T in chloroform solution (upper panel) and of the P7T–CdSe nanohybrids (lower panel). The emission of both P7T and CdSe QD was completely quenched (lower panel). Reproduced with permission from *Chem. Mater.* **2004**, *16*, 5187. Copyright 2004 The American Chemical Society.



nanohybrids on ITO exhibited initial power conversion efficiency of 0.29%. The efficiency may be further improved by manipulating the size and shape of CdSe NC.

### Nanohybrids via Direct Grafting

Nanohybrids can also be prepared by directly grafting COs or CPs from/onto functionalized NCs, dispensing with the need for ligand exchange chemistry.

**Growing COs on the NC surface in a “grafting from” process:** An elegant synthetic approach has recently been reported by which NCs were directly tailored with COs in the absence of ligand-exchange process. A novel bifunctional ligand, which contains a phosphine oxide function similar to that of TOPO serving as the anchoring group for the NC surface and an arylbromide functionality allowing subsequent surface-initiated polymerization chemistry, was rationally designed.<sup>[8]</sup> This tailor-made ligand, *p*-bromobenzyl-di-*n*-octylphosphine oxide (DOPO-Br) possesses high affinity for metal atoms (i.e., compound **1** in Scheme 4), and was prepared by nucleophilic substitution of di-*n*-octylphosphine oxide on 4-bromobenzyl chloride under phase-transfer conditions.<sup>[8]</sup> Monodispersed CdSe QDs were grown in DOPO-Br, which was remarkably stable at high temperature (250–275 °C), yielding the DOPO-Br-capped CdSe QDs. Then it was used to grow oligo(*para*-phenylene vinylene) (OPV) radially outward from its surface by copolymerization of 1,4-divinylbenzene and 1,4-dibromobenzene derivatives (i.e., a “grafting-from” approach), by using a mild palladium-cata-

lyzed Heck coupling (i.e., forming the OPV–CdSe nanohybrids).<sup>[8]</sup>

The OPV was primarily trimers and tetramers as confirmed by the matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry measurement.<sup>[8]</sup> The unattached OPV were acted as a host matrix for dispersing CdSe QDs. TEM studies showed marked morphological difference of the OPV–CdSe nanohybrids with respect to the blend of CdSe and OPV (i.e., the OPV/CdSe hybrids; Figure 3). The DOPO-Br-capped CdSe QDs were observed to aggregate in OPV in the hybrid (Figure 3a), while they were well-dispersed in the OPV matrix in the nanohybrids (Figure 3b).<sup>[8]</sup> It is worth noting that the efficient suppression of CdSe QD blinking in the OPV–CdSe nanohybrid was demonstrated for the first time by combin-

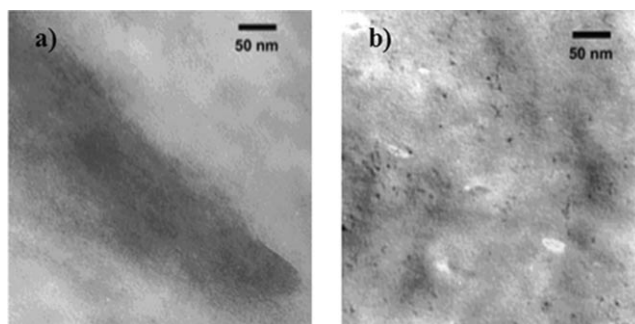
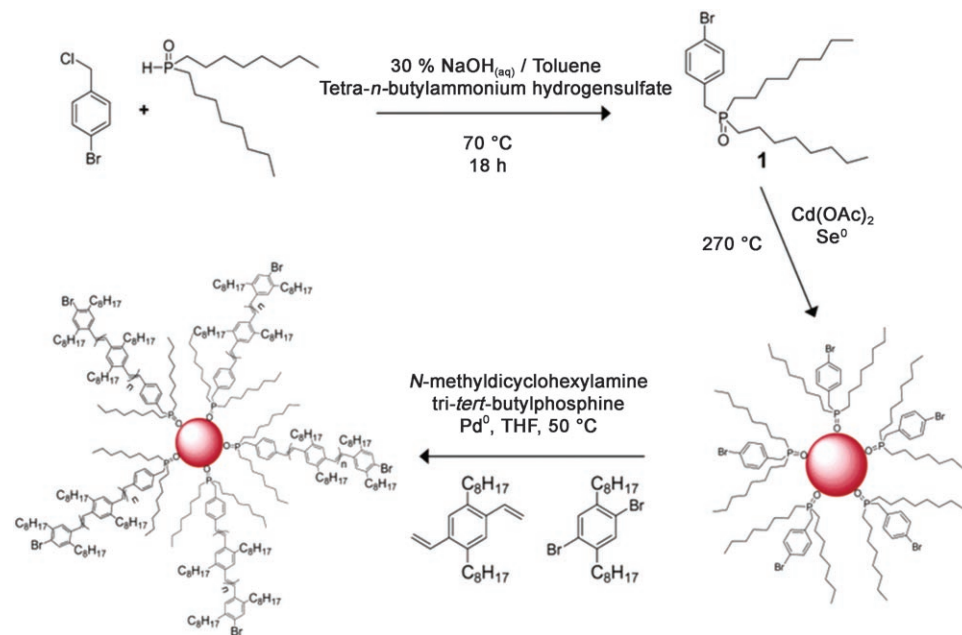


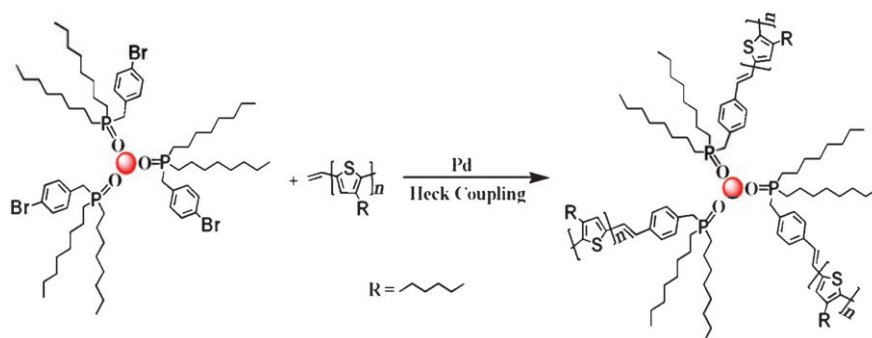
Figure 3. TEM images of a) the DOPO-Br-capped CdSe QDs mixed with OPV (i.e., the CdSe/OPV hybrids), and the b) the OPV–CdSe nanohybrids. Reproduced with permission from *J. Am. Chem. Soc.* **2004**, *126*, 11322. Copyright 2004 The American Chemical Society.



Scheme 4. Synthetic of MEH-PPV–CdSe nanohybrids. Reproduced with permission from *J. Am. Chem. Soc.* **2004**, *126*, 11322. Copyright 2004 The American Chemical Society.

ing single-molecule fluorescence and scanning probe microscopy studies.<sup>[40]</sup> This effect was attributed to charge transfer from photoexcited OPV into vacant trap sites on the CdSe QD surface.

**Growing CPs on the NC surface in a “grafting-onto” process:** In order to manipulate the photophysics of nanohybrids by controlling the chain conformation of CPs in the surrounding environment, it is of importance to graft longer chain CPs on the QD surface.<sup>[16]</sup> To this end, nanohybrids of P3HT–CdSe were prepared by directly grafting relatively long chain, vinyl-terminated P3HT onto DOPO-Br-functionalized CdSe QD surfaces by Heck coupling (i.e., a “grafting-onto” approach that



Scheme 5. Grafting vinyl terminated P3HT onto DOPO-Br-functionalized CdSe QDs via Heck coupling. Reproduced with permission from *J. Am. Chem. Soc.* **2007**, *129*, 12828. Copyright 2007 The American Chemical Society.

was simpler to perform) as outlined in Scheme 5.<sup>[16]</sup> The DOPO-Br ligand was used as the surface-binding group to prepare DOPO-Br-functionalized CdSe QD ( $D=3.5$  nm).<sup>[8]</sup> Regioregular P3HT was synthesized through a quasi-living polymerization.<sup>[41–44]</sup> One of its ends was terminated with the vinyl group by using a modified Grignard metathesis reaction.<sup>[45]</sup> The MW of P3HT measured by MALDI-TOF was 2404, which corresponds to 14 repeat units (i.e., 10.4 nm provided that the length of a thiophene unit is 0.74 nm). This is longer than the effective conjugation length, which is roughly 9–10 thiophene units.<sup>[16]</sup> The success of coupling of vinyl-terminated P3HT and DOPO-Br-functionalized CdSe QD was confirmed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. The grafting density of P3HT chains was determined by thermogravimetry analysis (TGA). An average of 22 P3HT chains was bound to a CdSe QD surface.<sup>[16]</sup> We note that the “grafting-onto” approach is often hindered by the chain-length effect of end-functionalized P3HT, therefore only relatively long-chain P3HT was grafted onto CdSe QD surface. The absence of ligand-exchange chemistry in the synthesis allowed the retention of inherent fluorescence of the P3HT-tailored CdSe QDs.<sup>[16]</sup>

Spectroscopic studies revealed that the photophysical properties of the nanohybrid were quite different from the hybrid counterpart in which P3HT and CdSe QDs were physically blended. Solid-state PL spectra of nanohybrids suggested the charge transfer from P3HT to CdSe QDs, while the energy transfer from CdSe QD to P3HT was implicated in the P3HT/CdSe hybrids (Figure 4).<sup>[16]</sup> Since the emission spectrum of CdSe QD overlapped the absorption spectrum of P3HT, the energy transfer from excited CdSe QD to P3HT occurred in the P3HT/CdSe hybrids. The complete suppression of CdSe emission was accompanied by a complementary growth of emission of P3HT at longer wavelength.<sup>[16]</sup> For the P3HT–CdSe nanohybrids, the charge transfer from P3HT to CdSe dominated instead (Figure 4). The electrons can be directly injected from photoexcited P3HT into the surface trap sites on the CdSe surface,<sup>[40]</sup> thereby enhancing the radiative recombination probability within CdSe QDs.<sup>[16,40,46]</sup>

A faster decay in fluorescence lifetime measured by using time-correlated single-photon counting (TCSPC) methodology further confirmed the occurrence of rapid charge transfer in the P3HT–CdSe nanohybrids.<sup>[16]</sup> The fluorescence of nanohybrids had a lifetime of 160 ps, which is faster than 240 ps in the P3HT homopolymer (Figure 5). This can be attributed to direct attachment of P3HT onto CdSe QD surface in the nanohybrids. Thus the

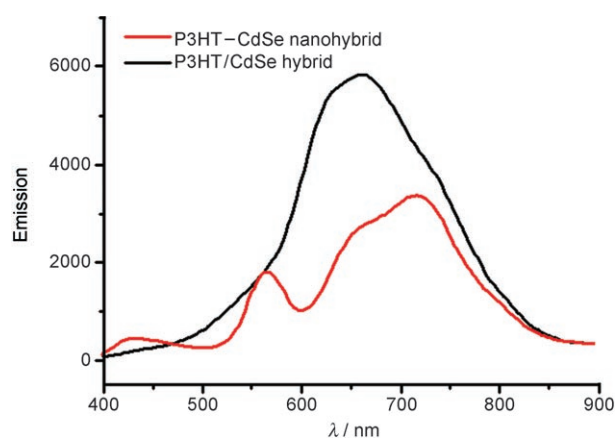


Figure 4. PL spectra of the hybrids of (DOPO-Br)-functionalized CdSe and vinyl terminated P3HT (black curve) and the P3HT–CdSe nanohybrids (red curve) in dry state. Reproduced with permission from *J. Am. Chem. Soc.* **2007**, *129*, 12828. Copyright 2007 The American Chemical Society.

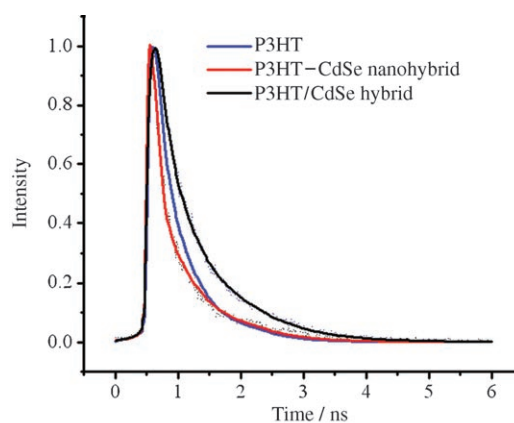


Figure 5. Time-resolved PL decays of the P3HT/CdSe hybrids (black), the P3HT homopolymer (blue), and the P3HT–CdSe nanohybrids (red) in solid state. The average lifetimes of P3HT/CdSe, P3HT, and P3HT–CdSe were 490, 240, and 160 ps, respectively, obtained by the curve fitting. Reproduced with permission from *J. Am. Chem. Soc.* **2007**, *129*, 12828. Copyright 2007 The American Chemical Society.

exciton can easily find the interface and dissociate. This correlates well with the static PL measurement (red curve in Figure 4). The lifetime of the P3HT/CdSe hybrids was 490 ps, longer than that 240 ps in P3HT, supporting the energy-transfer mechanism hypothesized from the static PL measurement of the P3HT/CdSe hybrids (black curve in Figure 4).<sup>[16]</sup>

## Conclusion

A series of new organic–inorganic nanohybrids consisting of electroactive COs or CPs tethered on the surface of semiconductor NC on a molecular scale have been synthesized by using two main synthetic strategies. In the first strategy, ligand exchange is an essential step to either replace initial insulate small-molecule-capped NCs with a bifunctional ligand or directly exchange for functional COs and CPs in a “grafting-onto” process. The second strategy utilizes direct grafting of COs or CPs from/onto functionalized NCs in the absence of ligand-exchange chemistry. While a few types of COs, CPs, QDs, and QRs are introduced here, the synthetic strategies reviewed above are not restricted to them, but can be easily extended to other types of electroactive organic polymers and inorganic NCs. Such direct connection of COs and CPs with NCs affords a well-defined interface between these two constituents, thereby promoting the electronic interfacial interaction between them. These nanohybrids are novel building blocks and hold promise for use in photovoltaic devices.

## Acknowledgement

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