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Toward High-Performance Organic−Inorganic Hybrid Solar Cells: Bringing Conjugated Polymers and Inorganic Nanocrystals in Close Contact

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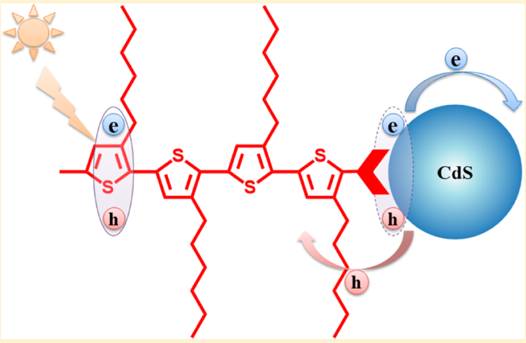
ABSTRACT: Organic−inorganic hybrid solar cells composed of conjugated polymers (CPs) and inorganic nanocrystal (NC) semiconductors have garnered considerable attention as a potential alternative to traditional silicon solar cells due to the capacity of producing high-efficiency solar energy in a cost-effective manner. The combination of advantageous characteristics of CPs and NCs enables the construction of nanostructured high-performance, lightweight, flexible, large-area, and low-cost hybrid solar cells. However, it remains a grand challenge to control the film morphology and interfacial structure of such organic/inorganic semiconductor blends on the nanoscale. In this Perspective, we highlight the strategies of implementing close contact between CPs and NCs by tailoring the colloidal synthesis, the coordination reaction, and the chemical modification of CPs. As such, they offer promising opportunities for rationally controlling the phase separation between electron-donating CPs and electron-accepting NCs, increasing the interfacial areas between them, enhancing their electronic interaction, and thus substantially promoting the photovoltaic performance of the resulting organic−inorganic hybrid solar cells.



Organic−inorganic hybrid solar cells that are widely prepared by simply blending conjugated polymer (CP) and inorganic nanocrystal (NC) semiconductors have received much attention as a promising route to low-cost, high-performance, and long-term stable photovoltaic power generation.[1−3] These nanostructured hybrids integrate the advantageous attributes of CPs, such as lightweight, large area, flexibility, solution processability, and roll-to-roll production,[4−7] with the size-dependent electronic structure, a broad absorption extending to near-infrared region, excellent charge carrier mobility, and good environmental stability of inorganic NCs.[8] Since the pioneering work on organic−inorganic hybrid nanocomposites consisting of the CP poly(2-methoxy-5-(2′-ethyl)-hexyloxy-*p*-phenylenevinylene) (MEH-PPV) and CdSe NCs with a power conversion efficiency (PCE) of 0.2%,[9] the performance of organic−inorganic hybrid solar cells has been greatly improved with recent advances in chemical synthesis of CPs and NCs as well as device engineering. These advances include (1) the colloidal synthesis of NCs (e.g., CdTe, PbS, ZnO, TiO_2, $CuInSe_2$, and Cu_2ZnSnS_4),[10−12] (2) the self-assembly of NCs (e.g., nanowires (NWs), nanorods, tetrapods, and hyperbranched nanorods) into large-scale aligned structures,[13] (3) the design of new CP donors, especially low-bandgap CPs (e.g., poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]-dithiophene-2,6-diyl]] (PCPDTBT), and poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7)),[14,15] and (4) the optimization of photoactive architectures (e.g., bulk-heterojunction solar cells, inverted solar cells, and tandem solar cells).[16−18] Despite all these advantages and progress, organic−inorganic hybrid solar cells still exhibit much lower PCEs (i.e., the highest PCE of ∼3.6% as in PCPDTBT/CdSe solar cells)[15] than either all-organic solar cells (i.e., ∼9.2% in PTB7/$PC_{71}BM$ solar cells),[19] or all-inorganic solar cells (i.e., ∼19.9% in $CuIn_{1-x}Ga_xSe_2$ solar cells).[20]

Due to the low relative dielectric constant ($\varepsilon_r \approx 3$) of CPs, photogenerated excitons (i.e., electron and hole pairs) in polymer solar cells are strongly bound by Coulomb force (Figure 1).[18] As the binding energy is typically larger than the thermal energy, the excitons cannot be dissociated within polymer donors. Thus the excitons need to diffuse to the donor−acceptor interface, where the interface potential arising from the energy offset between the LUMO of CP donor and the electron affinity (i.e., the conduction band edge) of inorganic NC acceptor is able to dissociate excitons into free charge carriers by charge transfer.[21] The resulting free charge

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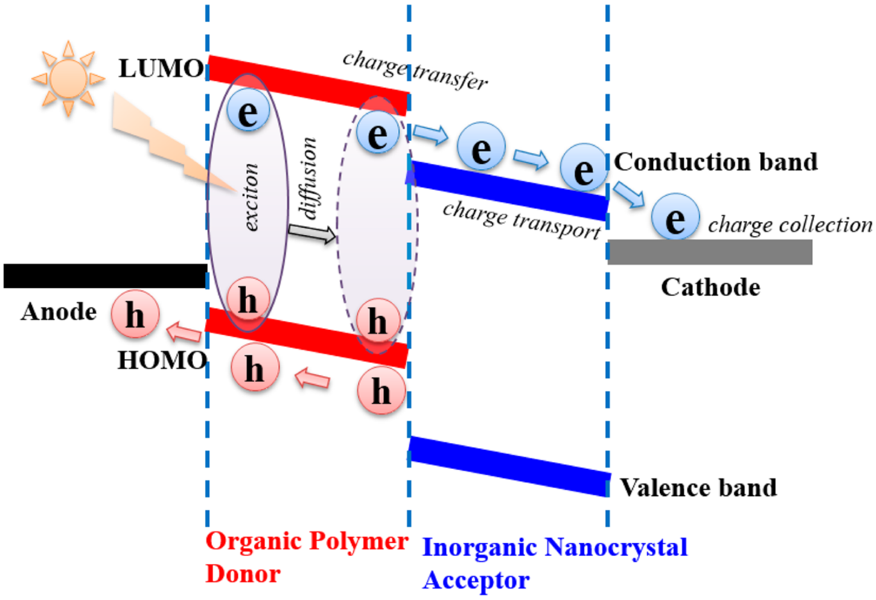

Figure 1. Schematic illustration of the working principle of organic–inorganic hybrid solar cells.

carriers (i.e., holes and electrons) are then transported to and collected on their respective electrodes.[22] It is noteworthy that the excitons may also be partially generated in the NC acceptor. For inorganic bulk materials, in which the Bohr radius is larger than the lattice spacing, Wannier–Mott excitons with a weak binding energy are generated. For inorganic NCs, however, the exciton Bohr radius is comparable to the NC size, and the photogenerated electron–hole pairs are bound by Coulomb force, leading to the formation of Frenkel excitons.[23,24] These Frenkel excitons need to be dissociated by the energy offset between the highest occupied molecular orbital (HOMO) of the CP donor and the ionization potential (i.e., the valence band edge) of the NC acceptor at the donor/acceptor interface.[25] Therefore, the PCE of organic–inorganic hybrid solar cells relies largely on the electronic band structures of both donor and acceptor materials, as well as the energy-level alignment at the donor/acceptor interface.

Over the past decade, many efforts have been concentrated on the solution-phase colloidal synthesis of inorganic NCs stabilized by a layer of organic alkyl ligands (e.g., alkyl thiols, acids, amines, phosphines, and phosphine oxides).[26] The ligands have been demonstrated to play a crucial role in determining the size, shape, chemical composition, and thus electronic property of synthesized colloidal NCs.[27−30] In particular, the electronic density of states (DOS) of semiconducting NCs deviates from the continuous energy spectrum of bulk materials, and forms the discrete atomic-like states when the NC size becomes comparable to or smaller than the bulk exciton Bohr radius (i.e., $\leq$ 10 nm), which is attributed to the spatial confinement of electronic excitons to the physical dimension of NCs (i.e., quantum confinement effect).[31] The quantum confinement effect not only allows the tailoring of the optical band gap of NCs to achieve a strong light absorption from the UV to near-IR spectral region, but also promotes the interfacial charge transfer between inorganic and organic semiconductors with less recombination.[32] As such, the tunable nanostructure and electronic activity of semiconducting NCs offer expanded flexibility for realizing high-performance photovoltaic architectures in organic–inorganic hybrids.

However, the control over the film morphology and interfacial structure of NCs within the CP matrix on the nanoscale when blending them together as an active layer constitutes a major challenge. This is due primarily to the exclusion of alkyl ligands capped on the NC surface from the crystalline domain of CPs, leading to microscopic phase separation between CPs and NCs.[33] The thoroughly mixed CP and NC domains in the dimension close to the exciton diffusion length of CPs (i.e., typically $\leq$10 nm) is necessary to impart the maximum exciton diffusion to the donor/acceptor interface for subsequent dissociation. Moreover, the insulating nature of organic ligands severely impedes the exciton dissociation at the donor/acceptor interface as well as the charge transport in the active layer owing to the formation of spatial barrier outside semiconducting NCs (e.g., the thickness of insulating trioctylphosphine oxide (TOPO) on the CdSe NC surface was approximately 11 Å).[9] In this Perspective, we highlight the strategies of implementing close contact between CPs and NCs, thereby facilitating their electronic interaction and in turn promoting the photovoltaic performance of organic–inorganic hybrid solar cells.

Control over the film morphology and interfacial structure of NCs within the CP matrix on the nanoscale when blending them together as an active layer constitutes a major challenge.

Ligand Exchange with Organic Molecules. Although alkyl ligands play an important role in controlling the size, shape, and stability of NCs during the solution-phase colloidal synthesis, the insulating nature of alkyl ligands unfavorably suppresses the electronic properties of NCs within the CP matrix. Direct removal of alkyl ligands via thermal degradation or physical sonication often produces the energy trap states within the NC bandgap due to the uneven passivation of organic residual ligands, which subsequently act to localize charge carriers and lead to an increased carrier recombination of NCs.[34] Moreover, the naked NCs tend to precipitate from the colloidal dispersion very quickly, preventing them from being mixed with CPs.[35] In this context, ligand exchange is widely regarded as a simple yet effective strategy to minimize the interparticle spacing by redecorating the NC surface with small molecules such as pyridine, butylamine, and hexanoic acid, followed by the removal of these small ligands under vacuum.[36−39] The ligand exchange process can be described by the adsorption−desorption dynamics of capping ligands on NCs, which depends largely on the dynamic equilibrium of the adsorption reaction kinetic constant, desorption reaction kinetic constant, and steric repulsion of ligand molecules.[40] In general, due to the stronger binding ability of acids, the long-alkyl ligands with phosphoric acid groups are more favorable in capping NCs than that terminated with phosphine oxide groups. However, the short-alkyl ligands terminated with the weak hydroxyl bonding groups still tend to achieve a higher surface coverage on NCs than the long-alkyl ligand with acid groups due to the steric effect.

Notably, pyridine, a volatile small molecule with weak binding ability,[33] has been commonly employed as a compelling small molecular ligand to achieve an effective ligand passivation and enable the solution processability, followed by its removal under vacuum.[41] Compared with alkyl ligand-capped NCs, pyridine-capped NCs can be considered as almost "naked" to be mixed with CPs, resulting in close contact between CPs and NCs that decreases the contact resistance, promotes the charge carrier transport, reduces the recombination loss, and thus improves the short circuit current (J_{sc}) of the resulting solar cells.[36] In addition to the improvement in charge transport, ligand exchange may also alter the energy alignment of organic−inorganic semiconductor interfaces, providing a potential route to increasing the open voltage (V_{oc}), which is directly proportional to the energy offset between the HOMO of CP donor and the electron affinity (i.e., the conduction band edge) of the NC acceptor. It was found that thiol ligand possessed a higher efficiency than pyridine in exchanging the negatively charged stearate and alkyl phosphonate ligands. The electron affinity of CdSe NCs was slightly lifted from −3.92 eV to −3.73 eV when exchanging the pyridine ligand with the *tert*-butylthiol ligand, leading to the increase of V_{oc} from 0.57 to 0.80 V, and correspondingly, the increase of PCE from 1.0% to 1.9%.[42]

Ligand Exchange with Inorganic Compounds. It is noteworthy that the NCs capped with small organic molecules such as short alkylthiols, alkylamines, and pyridine, are very sensitive to oxidation and thermal degradation attributed to the relatively weak binding strength of small molecules,[36] which leads to the reduced NC size and charge transfer, and the increased carrier recombination. To address this shortcoming of organic ligands, inorganic ligands, especially the metal chalcogenide (e.g., $Sn_2S_6^{4-}$, $In_2Se_4^{2-}$, and MoS_4^{2-}) and the metal-free hydrochalcogenide (e.g., S^{2-}, HS^-, Se^{2-}, HTe^-, and TeS_3^{2-}) ligands, have been developed,[43,44] based on the concept of a Lewis base that donates one or more electron pairs to form the coordination complex with inorganic NCs (e.g., $Sn_2S_6^{4-}$ ion-capped CdSe NCs).[43] The surface of the resulting NCs is negatively charged by the multivalent inorganic ligands. Consequently, the electrostatic repulsion between NCs facilitates the retention of stable dispersion of NCs in various polar solvents (e.g., dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile (MeCN)).[45] Furthermore, in comparison to the NCs passivated with long alkyl ligands, the reduced interparticle spacing enables strong electronic coupling between neighboring NCs for an enhanced charger carrier transport.[46] Obviously, inorganic ligands may constitute a significant step forward in facilitating the mixing of NCs within the CP matrix to form close contact between them.[47]

Recently, a new surface modification approach using inorganic nitrosonium tetrafluoroborate ($NOBF_4$) ligands to replace the original organic ligands attached to the NC surface has been reported.[48,49] Such surface modification rendered the phase transfer of NCs from hydrophobic to hydrophilic media without affecting the NC size and shape. The NO^+ cation was a good leaving group, as it was readily reduced to NO followed by reacting with oxygen to yield NO_2, and it can also react with the solvated water molecules to form nitrous acid.[48,49] The formation of an acidic environment facilitated the coordination of BF_4^- anions with the positively charged NC surface (i.e., metal cations or oxidized metal atoms formed by the oxidation of NC surfaces) by removing the original oleyl acid or oleylamine ligands via the protonation reaction (Figure 2a).[48,49] It is noteworthy that DMF can not only act as a solvent but also a stabilizer for NCs, and thus the tetrafluoroborate-capped NCs were highly soluble in DMF due to the stabilization from BF_4^- anions and DMF molecules, which can even exceed the solubility of oleylamine-capped NCs, especially for large-sized

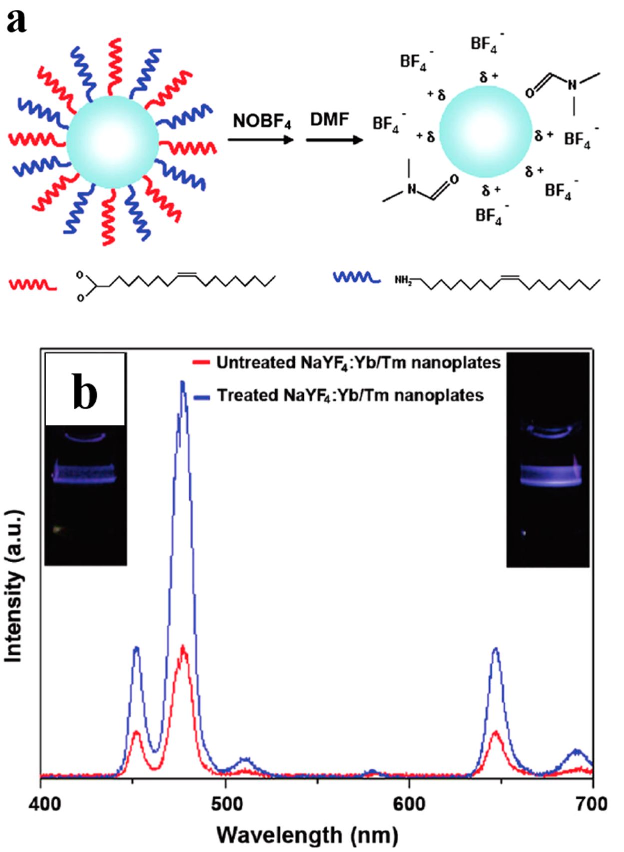

Figure 2. (a) Schematic illustration of the ligand-exchange process by using inorganic $NOBF_4$ ligands to replace the original oleic acid and oleylamine ligands in DMF. (b) Comparison of upconversion emission spectra of NaYF$_4$:Yb/Tm nanoplates before and after $NOBF_4$ treatment. The corresponding visible upconversion luminescence are shown in the upper left and right insets, respectively. Adapted with permission from ref 48. Copyright 2010 American Chemical Society.

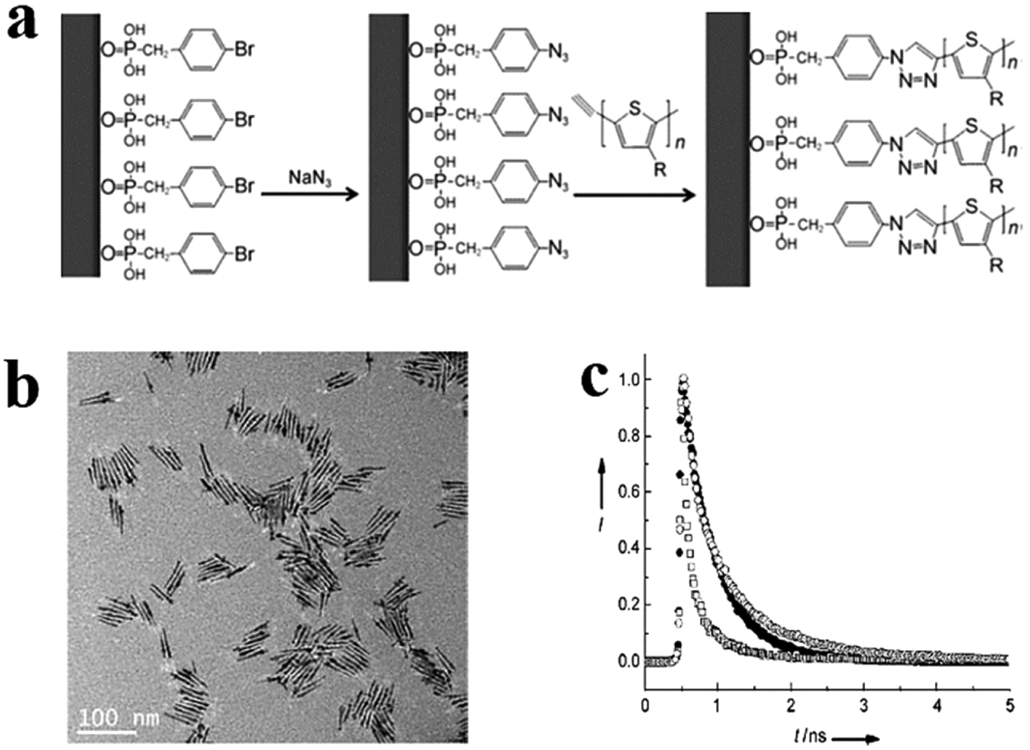

Figure 3. (a) Schematic illustration of grafting P3HT onto BBPA-functionalized CdSe (BBPA-CdSe) QRs by the click reaction. (b) Transmission electron microscopy (TEM) image of P3HT/CdSe QR nanocomposites synthesized by the click reaction. (c) Normalized time-resolved photoluminescence decays of P3HT (solid circles), physical mixture of P3HT/CdSe QR (open circles), and P3HT-CdSe QR nanocomposites prepared by click coupling (open squares), respectively, monitored at λ_{exc} = 407 nm and $\lambda_{em} \geq 500$ nm. The curve fitting yielded average lifetimes of 370 ps for P3HT, 320 ps for P3HT/CdSe QR composite, and 105 ps for P3HT-CdSe QR nanocomposites by click reaction, respectively. Adapted with permission from ref 56. Copyright 2011 Wiley-VCH.

NCs, in nonpolar solvents (i.e., hexane).[48] For example, the upconversion $NaYF_4$:Yb nanoplates in the size of several-hundred nanometers quickly precipitated from their colloidal dispersion in hexane when they were capped with oleylamine, but their solubility was largely increased to 5 mg/mL in DMF without precipitation for several months when BF_4^- anions were used as the ligands.[48] The improved solubility of $NaYF_4$:Yb nanoplates not only significantly promoted the emission intensity of $NaYF_4$:Yb-nanoplate solution (Figure 2b),[48] but also provided a facile solution-processable route to fabricating upconversion nanoparticle-based organic−inorganic hybrid solar cells to decrease the energy transfer loss by producing high-energy photons from the combination of multiple low-energy photons.[50]

Grafting of CPs on NCs with Bifunctional Ligands. Another intriguing strategy to promote the charge transfer between CPs and the organic ligand-capped NCs is to directly graft CPs onto NCs using a bifunctional ligand.[38] To this end, one end functional group of bifunctional ligand should possess a high chemical affinity to the NC surface, serving as the coordination ligand to prevent the unfavorable aggregation of NCs, while its other end should be able to chemically couple with the end-functionalized CPs, thus tethering CPs onto the NC surface.[51] The end-group functionalization of CP chains is commonly used in preparing tailored hybrid materials,[52,53] enabling the formation of close polymer-to-NC interaction via specifically chosen ligating moieties.[54] The implement of bifunctional ligand is expected to yield an improved chemical and electronic stability of the resulting inorganic NCs. The bifunctional ligand favors a high surface coverage due to the strong anchoring ability, imparts a direct electronic coupling of NC with CP, and enables a well-defined CP donor/NC acceptor interface for an effective charge transfer in organic−inorganic hybrid solar cells.

Recent advances on the organic synthetic methodology render the design and synthesis of a broad range of bifunctional ligands,[55] which can simultaneously meet the requirements in manipulating the growth of NCs into the specific size and shape as well as grafting the end-functionalized CPs onto the ligand-capped NCs. Recently, bromobenzylphosphonic acid (BBPA) with phosphonic and aryl bromide groups at the respective ends has been synthesized as an effective ligand for chemically tethering poly(3-hexylthiophene-2,5-diyl) (P3HT) chains on CdSe quantum rods (QRs) (Figure 3a).[56] Owing to the strong coordination reaction, the phosphonic acid passivated on CdSe induced the elongated growth of CdSe QRs, and the aryl bromide groups were situated on the QR surface.[57] Subsequently, these aryl bromide groups were converted into azide groups. Finally, the grafting of ethynyl-terminated P3HT onto azide-functionalized CdSe QRs was accomplished via the click reaction between the azide and ethynyl groups (i.e., forming P3HT-CdSe QR nanocompsoites), thereby dispensing with the need for ligand change or the introduction of any deleterious metallic impurity.[56,58] It is noteworthy that the click reaction possesses several attractive features, including an extremely versatile bond-formation process, no need for protecting groups, good selectivity, nearly complete conversion, and generally no need for purification.[59] The CdSe QRs were readily dispersed within the P3HT-CdSe QR nanocomposites (Figures 3b). The enhanced charge transfer from P3HT to CdSe QR was evidenced by the much faster photoluminescence lifetime of ~105 ps in the P3HT-CdSe QR nanocomposites as compared to that of ~320 ps in the physically mixed P3HT/CdSe QR composites (Figure 3c). Clearly, the combination of coordination chemistry and click chemistry opens opportunities to potentially improve the performance of organic−inorganic hybrid solar cells by crafting well-defined interfacial contact between these two semiconducting constituents.

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The close contact of P3HT chains with TiO_2 NCs has also been realized by the difunctionalization of cyanoacetic groups on both the ends of P3HT backbones, resulting in an improved charge injection and thus an enhanced PCE of 2.2%, as compared to that of 0.1% in the unfunctionalized-P3HT/TiO_2 solar cells and that of 0.2% in the monocyanoacetic-P3HT/TiO_2 solar cells.[60]

We note that the property of the donor/electrode interface partially determines the charge transfer and transport of organic−inorganic hybrid solar cells, especially in the case that the NC layer serves as the electrode,[61] through the following four aspects: (1) adjusting the energy barrier between the active layer and the electrodes, (2) improving the charge selectivity at the active layer/anode interface for holes as well as at the active layer/cathode interface for electrons, (3) prohibiting chemical reaction between the active layer and the electrodes, and (4) modulating the light interference effect at the active layer/electrode interface to maximize light absorption in the active layer.[62−65] In this context, the formation of an interfacial dipolar layer has been demonstrated to alter the work function of electrodes, which can be ascribed to the electron redistribution by charge transfer and the hybridization of the wave functions of donor/electrode materials.[66,67] Recently, the molecular modification of cyanoacrylic acids by incorporating a variety of thienyl and benzothiadiazole units has been shown to endow the resulting cyanoacrylic-acid ligands with different LUMO levels (Figure 4), which increased the electron affinity in the regions close to the TiO_2 surface and facilitated a cascade of electron transport from P3HT to TiO_2.[68] The interaction between the −COOH group on cyanoacrylic acid and the −OH group on TiO_2 connected cyanoacrylic acid to TiO_2, while the π−π interaction between thienyl units on cyanoacrylic acid and P3HT chains improved the compatibility between P3HT and cyanoacrylic acid-capped TiO_2.[68] Moreover, the tethering of cyanoacrylic acid ligands on the TiO_2 surface formed a molecular dipole that was orientated away from the TiO_2 surface. This induced a step

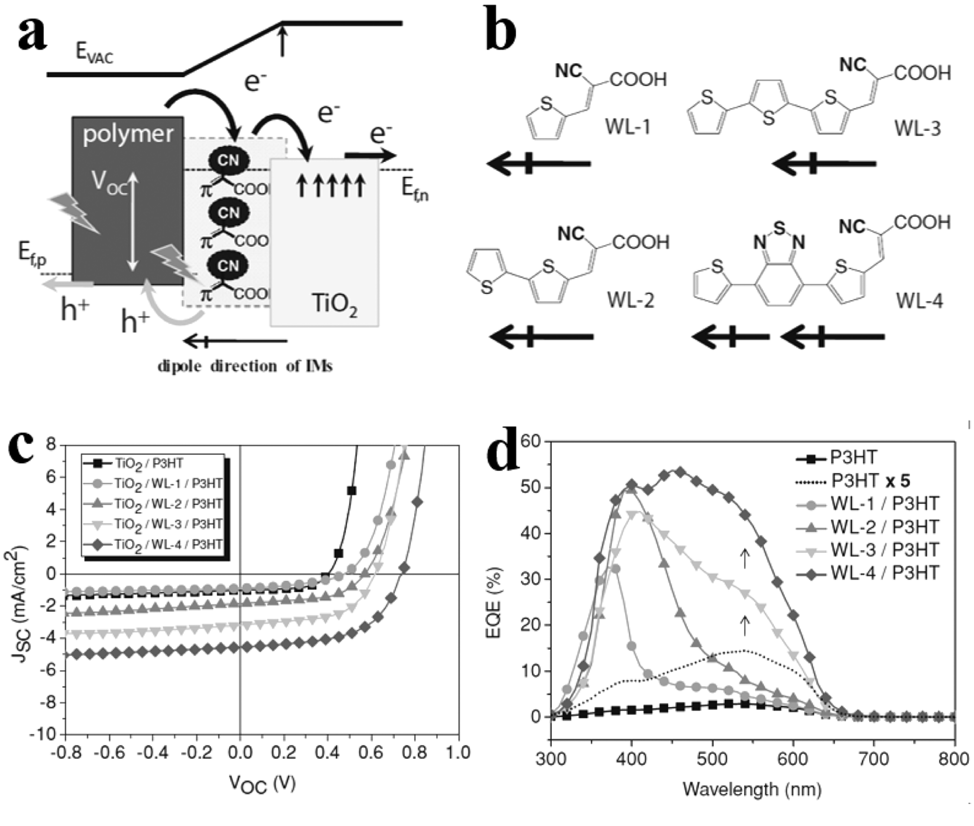

Figure 4. (a) Energy level diagram of the interface of polymer/interfacial modifier/TiO_2 in a hybrid solar cell. (E_{VAC}: vacuum level, $E_{f,p}$: quasi-Fermi level of holes, $E_{f,n}$: quasi-Fermi level of electrons, and V_{OC}: open-circuit voltage). (b) Chemical structures of interfacial modifiers (WL-1 to WL-4). (c) Current−voltage curves of solar devices fabricated from P3HT/interfacial modifiers (WL-1 to WL-4)/TiO_2. (d) EQE spectra of P3HT/TiO_2 hybrid solar cells with bare or various interfacial modifiers, WL-1 to WL-4, treated TiO_2. Adapted with permission from ref 68. Copyright 2012 Wiley-VCH.

in the local vacuum level due to the electric field across the dipolar layer,[69] and shifted the band edge of TiO_2 closer to the vacuum level of P3HT, thus enabling the simultaneous increase in both V_{oc} and J_{sc}.[68]

Direct Grafting of CPs on NCs without Ligands. In addition to tuning the molecular structure of the semiconductor organic/inorganic interface by elaborately designing various functional ligands, the ability to control the film morphology and interfacial structure of organic−inorganic hybrid nanocomposites via their direct coordination interaction on the nanoscale represents a much facile route to intimate CP−NC nanocomposites.[70,71] For example, owing to the existence of the intermediate bonding energy between P3HT and CdS, which was referred to as the C−S−Cd bond,[72] CdS NCs can be directly bound onto crystalline P3HT NWs through the solvent-assisted chemical grafting and ligand exchange.[73] The strong electronic interaction between P3HT and CdS led to an improved PCE of 4% in the CdS-grafted-P3HT device (Figure 5), as compared to that of 0.6% for the nongrafted device.[73−75]

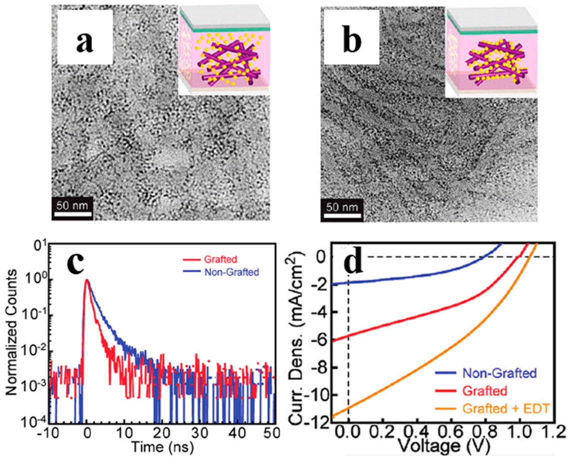

Figure 5. TEM images of P3HT NW/CdS quantum dot (QD) hybrid films synthesized (a) without grafting and (b) using grafting process by dissolving both P3HT NWs and CdS QDs in compatible solvents to allow them to interact with each other while preserving their respective chemical stabilities. The insets show schematic representations of the corresponding films in (a) and (b), respectively; the nongrafting and grafting methods were used to control the interface between CdS QDs (yellow spheres) and P3HT NWs (purple lines). (c) Time-resolved photoluminescence spectra of the nongrafted and grafted films. (d) Current−voltage characteristics of P3HT NW/CdS QD hybrid solar cells from nongrafted, grafted, and grafted followed by subsequent ligand exchange. Adapted with permission from ref 73. Copyright 2011 American Chemical Society.

The formation of C−S−Cd bonding may be feasible to control the in situ growth of CdS NCs in the P3HT matrix through the dipole−dipole or ion-dipole interaction between the inorganic ions (i.e., Cd^{2+}) and the coordination atom (i.e., S in thienyl) in P3HT.[76,77] Such intrinsic molecular interaction between CP and NC offered a unique yet practical way of optimizing the molecular structure, film morphology, and electronic interaction in organic−inorganic hybrid solar cells.

In summary, the efforts toward better controlled interfacial contact between CP and inorganic NC semiconductors by imparting chemically compatible, electronically favorable, and spatially close interactions are expected to further improve the performance of organic−inorganic hybrid solar cells, which could probably be realized by the following three approaches: (1) ligand-exchanging the long alkyl ligands with the short organic or inorganic small molecules (i.e., pyridine) to reduce the electron-hopping distance without significantly disturbing the solution processability of NCs; (2) grafting CPs onto the NC surface using a bifunctional ligand to improve the dispersion and connection of NCs in the CP matrix with an enhanced grafting density; and (3) direct grafting of CPs onto NCs via the coordination interaction between them on the nanoscale to facilitate the charge transfer and transport in the organic−inorganic hybrids without the electron trap states caused by the insulating capping ligands.

Efforts toward better controlled interfacial contact between CP and inorganic NC semiconductors by imparting chemically compatible, electronically favorable, and spatially close interactions are expected to further improve the performance of organic−inorganic hybrid solar cells.

The success of establishing close contact between CP and NC semiconductors exerted crucial influences on improving photovoltaic performance of organic−inorganic hybrid solar cells by controlling the phase separation of CP and NC, increasing the CP donor/NC acceptor interface, and promoting the charge transfer.[70,73,78] All the recent progress has shown certain promise but is not significant enough for practical applications. To date, the PCEs of all-organic solar cells (e.g., low bandgap CP-based) and all-inorganic solar cells (e.g., multinary chalcogenide NC-based) have exceeded 10%, attributing largely to the success in designing new donor/acceptor materials.[79−83] Clearly, the strategies discussed above to yield CP−NC nanocomposites can be readily and appropriately extended to these new donor and acceptor materials rather than being limited to commonly used MEH-PPV and P3HT, and II−VI and IV−VI NCs. Nonetheless, with the rapid development being made in chemical synthesis, polymer engineering, and device fabrication, the close mixing of organic and inorganic semiconductors will probably evolve into a general yet robust strategy to enhance the device performance of organic−inorganic hybrid solar cells via rational control of the donor/acceptor electronic interactions.

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Notes

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■ REFERENCES

(1) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Hybrid Nanorod−Polymer Solar Cells. *Science* **2002**, *295*, 2425−2427.

(2) McGehee, M. D. Nanostructured Organic-Inorganic Hybrid Solar Cells. *MRS Bull.* **2009**, *34*, 95−100.

(3) Talapin, D. V.; Lee, J. S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem. Rev.* **2010**, *110*, 389−458.

(4) He, M.; Han, W.; Ge, J.; Yang, Y. L.; Qiu, F.; Lin, Z. Q. All-Conjugated Poly(3-alkylthiophene) Diblock Copolymer-Based Bulk Heterojunction Solar Cells with Controlled Molecular Organization and Nanoscale Morphology. *Energy Environ. Sci.* **2011**, *4*, 2894−2902.

(5) He, M.; Ge, J.; Lin, Z. Q.; Feng, X. H.; Wang, X. W.; Lu, H. B.; Yang, Y. L.; Qiu, F. Thermopower Enhancement in Conducting Polymer Nanocomposites via Carrier Energy Scattering at the Organic−Inorganic Semiconductor Interface. *Energy Environ. Sci.* **2012**, *5*, 8351−8358.

(6) He, M.; Han, W.; Ge, J.; Yu, W. J.; Yang, Y. L.; Qiu, F.; Lin, Z. Q. Annealing Effects on the Photovoltaic Performance of All-Conjugated Poly(3-alkylthiophene) Diblock Copolymer-Based Bulk Heterojunction Solar Cells. *Nanoscale* **2011**, *3*, 3159−3163.

(7) He, M.; Jung, J. H.; Qiu, F.; Lin, Z. Q. Graphene-Based Transparent Flexible Electrodes for Polymer Solar Cells. *J. Mater. Chem.* **2012**, *22*, 24254−24264.

(8) Kamat, P. V. Meeting the Clean Energy Demand: Nanostructure Architectures for Solar Energy Conversion. *J. Phys. Chem. C* **2007**, *111*, 2834−2860.

(9) Greenham, N. C.; Peng, X. G.; Alivisatos, A. P. Charge Separation and Transport in Conjugated-Polymer/Semiconductor-Nanocrystal Composites Studied by Photoluminescence Quenching and Photoconductivity. *Phys. Rev. B* **1996**, *54*, 17628−17637.

(10) Wang, J. J.; Wang, Y. Q.; Cao, F. F.; Guo, Y. G.; Wan, L. J. Synthesis of Monodispersed Wurtzite Structure $CuInSe_2$ Nanocrystals and Their Application in High-Performance Organic−Inorganic Hybrid Photodetectors. *J. Am. Chem. Soc.* **2010**, *132*, 12218−12221.

(11) Xin, X. K.; He, M.; Han, W.; Jung, J. H.; Lin, Z. Q. Low-Cost Copper Zinc Tin Sulfide Counter Electrodes for High-Efficiency Dye-Sensitized Solar Cells. *Angew. Chem., Int. Ed.* **2011**, *50*, 11739−11742.

(12) Cozzoli, P. D.; Pellegrino, T.; Manna, L. Synthesis, Properties and Perspectives of Hybrid Nanocrystal Structures. *Chem. Soc. Rev.* **2006**, *35*, 1195−1208.

(13) Gur, I.; Fromer, N. A.; Chen, C. P.; Kanaras, A. G.; Alivisatos, A. P. Hybrid Solar Cells with Prescribed Nanoscale Morphologies Based on Hyperbranched Semiconductor Nanocrystals. *Nano Lett.* **2007**, *7*, 409−414.

(14) Lek, J. Y.; Lam, Y. M.; Niziol, J.; Marzec, M. Understanding Polycarbazole-Based Polymer: CdSe Hybrid Solar Cells. *Nanotechnology* **2012**, *23*, 315401.

(15) Jeltsch, K. F.; Schadel, M.; Bonekamp, J. B.; Niyamakom, P.; Rauscher, F.; Lademann, H. W. A.; Dumsch, I.; Allard, S.; Scherf, U.; Meerholz, K. Efficiency Enhanced Hybrid Solar Cells Using a Blend of Quantum Dots and Nanorods. *Adv. Funct. Mater.* **2012**, *22*, 397−404.

(16) Beiley, Z. M.; McGehee, M. D. Modeling Low Cost Hybrid Tandem Photovoltaics with the Potential for Efficiencies Exceeding 20%. *Energy Environ. Sci.* **2012**, *5*, 9173−9179.

(17) Seo, J. H.; Kim, D. H.; Kwon, S. H.; Song, M.; Choi, M. S.; Ryu, S. Y.; Lee, H. W.; Park, Y. C.; Kwon, J. D.; Nam, K. S.; et al. High Efficiency Inorganic/Organic Hybrid Tandem Solar Cells. *Adv. Mater.* **2012**, *24*, 4523−4527.

(18) He, M.; Qiu, F.; Lin, Z. Q. Conjugated Rod−Coil and Rod−Rod Block Copolymers for Photovoltaic Applications. *J. Mater. Chem.* **2011**, *21*, 17039−17048.

(19) He, Z. C.; Zhong, C. M.; Su, S. J.; Xu, M.; Wu, H. B.; Cao, Y. Enhanced Power-Conversion Efficiency in Polymer Solar Cells Using an Inverted Device Structure. *Nat. Photonics* **2012**, *6*, 591−595.

(20) Hagfeldt, A.; Boschloo, G.; Sun, L. C.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110*, 6595−6663.

(21) Moule, A. J.; Chang, L. L.; Thambidurai, C.; Vidu, R.; Stroeve, P. Hybrid Solar Cells: Basic Principles and the Role of Ligands. *J. Mater. Chem.* **2012**, *22*, 2351−2368.

(22) Zhou, Y. F.; Eck, M.; Kruger, M. Bulk-Heterojunction Hybrid Solar Cells Based on Colloidal Nanocrystals and Conjugated Polymers. *Energy Environ. Sci.* **2010**, *3*, 1851−1864.

(23) Nizamoglu, S.; Sun, X. W.; Demir, H. V. Observation of Efficient Transfer from Mott−Wannier to Frenkel Excitons in a Hybrid Semiconductor Quantum Dot/Polymer Composite at Room Temperature. *Appl. Phys. Lett.* **2010**, *97*, 263106.

(24) Birman, J. L.; Huong, N. Q. Wannier-Frenkel Hybrid Exciton in Organic-Semiconductor Quantum Dot Hetero Structures. *J. Lumin.* **2007**, *125*, 196−200.

(25) Reiss, P.; Couderc, E.; De Girolamo, J.; Pron, A. Conjugated Polymers/Semiconductor Nanocrystals Hybrid Materials-Preparation, Electrical Transport Properties and Applications. *Nanoscale* **2011**, *3*, 446−489.

(26) Zhuang, Z. B.; Peng, Q.; Li, Y. D. Controlled Synthesis of Semiconductor Nanostructures in the Liquid Phase. *Chem. Soc. Rev.* **2011**, *40*, 5492−5513.

(27) Yin, Y.; Alivisatos, A. P. Colloidal Nanocrystal Synthesis and the Organic−Inorganic Interface. *Nature* **2005**, *437*, 664−670.

(28) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of Monodisperse Spherical Nanocrystals. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630−4660.

(29) Sone, E. D.; Zubarev, E. R.; Stupp, S. I. Supramolecular Templating of Single and Double Nanohelices of Cadmium Sulfide. *Small* **2005**, *1*, 694−697.

(30) Khanal, B. P.; Zubarev, E. R. Polymer-Functionalized Platinum-on-Gold Bimetallic Nanorods. *Angew. Chem., Int. Ed.* **2009**, *48*, 6888−6891.

(31) Brus, L. E. Electron−Electron and Electron−Hole Interactions in Small Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984**, *80*, 4403−4409.

(32) Huang, J.; Huang, Z. Q.; Yang, Y.; Zhu, H. M.; Lian, T. Q. Multiple Exciton Dissociation in CdSe Quantum Dots by Ultrafast Electron Transfer to Adsorbed Methylene Blue. *J. Am. Chem. Soc.* **2010**, *132*, 4858−4864.

(33) Zhao, L.; Lin, Z. Q. Crafting Semiconductor Organic−Inorganic Nanocomposites via Placing Conjugated Polymers in Intimate Contact with Nanocrystals for Hybrid Solar Cells. *Adv. Mater.* **2012**, *24*, 4353−4368.

(34) Kuno, M.; Lee, J. K.; Dabbousi, B. O.; Mikulec, F. V.; Bawendi, M. G. The Band Edge Luminescence of Surface Modified CdSe Nanocrystallites: Probing the Luminescing State. *J. Chem. Phys.* **1997**, *106*, 9869−9882.

(35) Sun, B. Q.; Marx, E.; Greenham, N. C. Photovoltaic Devices Using Blends of Branched CdSe Nanoparticles and Conjugated Polymers. *Nano Lett.* **2003**, *3*, 961−963.

(36) Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X. H.; Debnath, R.; Cha, D. K.; et al. Colloidal-Quantum-Dot Photovoltaics Using Atomic-Ligand Passivation. *Nat. Mater.* **2011**, *10*, 765−771.

(37) Li, M.; Johnson, S.; Guo, H. T.; Dujardin, E.; Mann, S. A Generalized Mechanism for Ligand-Induced Dipolar Assembly of Plasmonic Gold Nanoparticle Chain Networks. *Adv. Funct. Mater.* **2011**, *21*, 851−859.

(38) Lin, Z. Q. Organic−Inorganic Nanohybrids through the Direct Tailoring of Semiconductor Nanocrystals with Conjugated Polymers. *Chem.—Eur. J.* **2008**, *14*, 6294−6301.

(39) Ingrosso, C.; Panniello, A.; Comparelli, R.; Curri, M. L.; Striccoli, M. Colloidal Inorganic Nanocrystal Based Nanocomposites: Functional Materials for Micro and Nanofabrication. *Materials* **2010**, *3*, 1316−1352.

(40) Ji, X. H.; Copenhaver, D.; Sichmeller, C.; Peng, X. G. Ligand Bonding and Dynamics on Colloidal Nanocrystals at Room Temperature: The Case of Alkylamines on CdSe Nanocrystals. *J. Am. Chem. Soc.* **2008**, *130*, 5726−5735.

(41) Liu, I. S.; Lo, H. H.; Chien, C. T.; Lin, Y. Y.; Chen, C. W.; Chen, Y. F.; Su, W. F.; Liou, S. C. Enhancing Photoluminescence Quenching and Photoelectric Properties of CdSe Quantum Dots with Hole Accepting Ligands. *J. Mater. Chem.* **2008**, *18*, 675−682.

(42) Greaney, M. J.; Das, S.; Webber, D. H.; Bradforth, S. E.; Brutchey, R. L. Improving Open Circuit Potential in Hybrid P3HT:CdSe Bulk Heterojunction Solar Cells via Colloidal *tert*-Butylthiol Ligand Exchange. *ACS Nano* **2012**, *6*, 4222−4230.

(43) Kovalenko, M. V.; Scheele, M.; Talapin, D. V. Colloidal Nanocrystals with Molecular Metal Chalcogenide Surface Ligands. *Science* **2009**, *324*, 1417−1420.

(44) Nag, A.; Kovalenko, M. V.; Lee, J. S.; Liu, W. Y.; Spokoyny, B.; Talapin, D. V. Metal-Free Inorganic Ligands for Colloidal Nanocrystals: S^{2-}, HS^{-}, Se^{2-}, HSe^{-}, Te^{2-}, HTe^{-}, TeS_3^{2-}, OH^{-}, and NH^{2-} as Surface Ligands. *J. Am. Chem. Soc.* **2011**, *133*, 10612−10620.

(45) Kovalenko, M. V.; Bodnarchuk, M. I.; Zaumseil, J.; Lee, J. S.; Talapin, D. V. Expanding the Chemical Versatility of Colloidal Nanocrystals Capped with Molecular Metal Chalcogenide Ligands. *J. Am. Chem. Soc.* **2010**, *132*, 10085−10092.

(46) Lee, J. S.; Kovalenko, M. V.; Huang, J.; Chung, D. S.; Talapin, D. V. Band-like Transport, High Electron Mobility and High Photoconductivity in All-Inorganic Nanocrystal Arrays. *Nat. Nanotechnol.* **2011**, *6*, 348−352.

(47) Liu, W.; Lee, J. S.; Talapin, D. V. III−V Nanocrystals Capped with Molecular Metal Chalcogenide Ligands: High Electron Mobility and Ambipolar Photoresponse. *J. Am. Chem. Soc.* **2013**, *135*, 1349−1357.

(48) Dong, A. G.; Ye, X. C.; Chen, J.; Kang, Y. J.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. A Generalized Ligand-Exchange Strategy Enabling Sequential Surface Functionalization of Colloidal Nanocrystals. *J. Am. Chem. Soc.* **2011**, *133*, 998−1006.

(49) Kim, S. B.; Cai, C.; Kim, J. M.; Sun, S. H.; Sweigart, D. A. Surface Modification of Fe_3O_4 and FePt Magnetic Nanoparticles with Organometallic Complexes. *Organometallics* **2009**, *28*, 5341−5348.

(50) Haase, M.; Schafer, H. Upconverting Nanoparticles. *Angew. Chem., Int. Ed.* **2011**, *50*, 5808−5829.

(51) Querner, C.; Reiss, P.; Bleuse, J.; Pron, A. Chelating Ligands for Nanocrystals' Surface Functionalization. *J. Am. Chem. Soc.* **2004**, *126*, 11574−11582.

(52) Osaka, I.; McCullough, R. D. Advances in Molecular Design and Synthesis of Regioregular Polythiophenes. *Acc. Chem. Res.* **2008**, *41*, 1202−1214.

(53) Jeffries-El, M.; Sauve, G.; McCullough, R. D. In-Situ End-Group Functionalization of Regioregular Poly(3-alkylthiophene) Using the Grignard Metathesis Polymerization Method. *Adv. Mater.* **2004**, *16*, 1017−1019.

(54) Pentzer, E. B.; Bokel, F. A.; Hayward, R. C.; Emrick, T. Nanocomposite "Superhighways" by Solution Assembly of Semiconductor Nanostructures with Ligand-Functionalized Conjugated Polymers. *Adv. Mater.* **2012**, *24*, 2254−2258.

(55) Xu, J.; Wang, J.; Mitchell, M.; Mukherjee, P.; Jeffries-El, M.; Petrich, J. W.; Lin, Z. Q. Organic−Inorganic Nanocomposites via Directly Grafting Conjugated Polymers onto Quantum Dots. *J. Am. Chem. Soc.* **2007**, *129*, 12828−12833.

(56) Zhao, L.; Pang, X. C.; Adhikary, R.; Petrich, J. W.; Lin, Z. Q. Semiconductor Anisotropic Nanocomposites Obtained by Directly Coupling Conjugated Polymers with Quantum Rods. *Angew. Chem., Int. Ed.* **2011**, *50*, 3958−3962.

(57) Zhao, L.; Pang, X. C.; Adhikary, R.; Petrich, J. W.; Jeffries-El, M.; Lin, Z. Q. Organic−Inorganic Nanocomposites by Placing Conjugated Polymers in Intimate Contact with Quantum Rods. *Adv. Mater.* **2011**, *23*, 2844−2849.

(58) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.

(59) Moses, J. E.; Moorhouse, A. D. The Growing Applications of Click Chemistry. *Chem. Soc. Rev.* **2007**, *36*, 1249−1262.

(60) Kruger, R. A.; Gordon, T. J.; Baumgartner, T.; Sutherland, T. C. End-Group Functionalization of Poly(3-hexylthiophene) as an Efficient Route to Photosensitize Nanocrystalline TiO_2 Films for Photovoltaic Applications. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2031−2041.

(61) Tagliazucchi, M.; Tice, D. B.; Sweeney, C. M.; Morris-Cohen, A. J.; Weiss, E. A. Ligand-Controlled Rates of Photoinduced Electron Transfer in Hybrid CdSe Nanocrystal/Poly(viologen) Films. *ACS Nano* **2011**, *5*, 9907−9917.

(62) Steim, R.; Kogler, F. R.; Brabec, C. J. Interface Materials for Organic Solar Cells. *J. Mater. Chem.* **2010**, *20*, 2499−2512.

(63) Martinez-Ferrero, E.; Albero, J.; Palomares, E. Materials, Nanomorphology, and Interfacial Charge Transfer Reactions in Quantum Dot/Polymer Solar Cell Devices. *J. Phys. Chem. Lett.* **2010**, *1*, 3039−3045.

(64) Hains, A. W.; Liu, J.; Martinson, A. B. F.; Irwin, M. D.; Marks, T. J. Anode Interfacial Tuning via Electron-Blocking/Hole-Transport Layers and Indium Tin Oxide Surface Treatment in Bulk-Heterojunction Organic Photovoltaic Cells. *Adv. Funct. Mater.* **2010**, *20*, 595−606.

(65) Zhu, R.; Jiang, C. Y.; Liu, B.; Ramakrishna, S. Highly Efficient Nanoporous TiO_2-Polythiophene Hybrid Solar Cells Based on Interfacial Modification Using a Metal-Free Organic Dye. *Adv. Mater.* **2009**, *21*, 994−1000.

(66) Braun, S.; Salaneck, W. R.; Fahlman, M. Energy-Level Alignment at Organic/Metal and Organic/Organic Interfaces. *Adv. Mater.* **2009**, *21*, 1450−1472.

(67) Yip, H. L.; Jen, A. K. Y. Recent Advances in Solution-Processed Interfacial Materials for Efficient and Stable Polymer Solar Cells. *Energy Environ. Sci.* **2012**, *5*, 5994−6011.

(68) Yu, J.; Shen, T. L.; Weng, W. H.; Huang, Y. C.; Huang, C. I.; Su, W. F.; Rwei, S. P.; Ho, K. C.; Wang, L. Molecular Design of Interfacial Modifiers for Polymer−Inorganic Hybrid Solar Cells. *Adv. Energy Mater.* **2012**, *2*, 245−252.

(69) Goh, C.; Scully, S. R.; McGehee, M. D. Effects of Molecular Interface Modification in Hybrid Organic−Inorganic Photovoltaic Cells. *J. Appl. Phys.* **2007**, *101*, 114503.

(70) Briseno, A. L.; Holcombe, T. W.; Boukai, A. I.; Garnett, E. C.; Shelton, S. W.; Frechet, J. J. M.; Yang, P. D. Oligo- and Polythiophene/ZnO Hybrid Nanowire Solar Cells. *Nano Lett.* **2010**, *10*, 334−340.

(71) Lai, C. H.; Lee, W. F.; Wu, I. C.; Kang, C. C.; Chen, D. Y.; Chen, L. J.; Chou, P. T. Highly Luminescent, Homogeneous ZnO Nanoparticles Synthesized via Semiconductive Polyalkyloxylthiophene Template. *J. Mater. Chem.* **2009**, *19*, 7284−7289.

(72) Leventis, H. C.; King, S. P.; Sudlow, A.; Hill, M. S.; Molloy, K. C.; Haque, S. A. Nanostructured Hybrid Polymer−Inorganic Solar Cell Active Layers Formed by Controllable in Situ Growth of Semiconducting Sulfide Networks. *Nano Lett.* **2010**, *10*, 1253−1258.

(73) Ren, S. Q.; Chang, L. Y.; Lim, S. K.; Zhao, J.; Smith, M.; Zhao, N.; Bulovic, V.; Bawendi, M.; Gradecak, S. Inorganic−Organic Hybrid

Solar Cell: Bridging Quantum Dots to Conjugated Polymer Nanowires. *Nano Lett.* **2011**, *11*, 3998−4002.

(74) Palaniappan, K.; Murphy, J. W.; Khanam, N.; Horvath, J.; Alshareef, H.; Quevedo-Lopez, M.; Biewer, M. C.; Park, S. Y.; Kim, M. J.; Gnade, B. E.; et al. Poly(3-hexylthiophene)−CdSe Quantum Dot Bulk Heterojunction Solar Cells: Influence of the Functional End-Group of the Polymer. *Macromolecules* **2009**, *42*, 3845−3848.

(75) Palaniappan, K.; Hundt, N.; Sista, P.; Nguyen, H.; Hao, J.; Bhatt, M. P.; Han, Y. Y.; Schmiedel, E. A.; Sheina, E. E.; Biewer, M. C.; et al. Block Copolymer Containing Poly(3-hexylthiophene) and Poly(4-vinylpyridine): Synthesis and Its Interaction with CdSe Quantum Dots for Hybrid Organic Applications. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1802−1808.

(76) Reynolds, L. X.; Lutz, T.; Dowland, S.; MacLachlan, A.; King, S.; Haque, S. A. Charge Photogeneration in Hybrid Solar Cells: A Comparison between Quantum Dots and in Situ Grown CdS. *Nanoscale* **2012**, *4*, 1561−1564.

(77) Liao, H. C.; Chen, S. Y.; Liu, D. M. In-Situ Growing CdS Single-Crystal Nanorods via P3HT Polymer as a Soft Template, for Enhancing Photovoltaic Performance. *Macromolecules* **2009**, *42*, 6558−6563.

(78) Chang, J. A.; Rhee, J. H.; Im, S. H.; Lee, Y. H.; Kim, H. J.; Seok, S. I.; Nazeeruddin, M. K.; Gratzel, M. High-Performance Nanostructured Inorganic−Organic Heterojunction Solar Cells. *Nano Lett.* **2010**, *10*, 2609−2612.

(79) Li, G.; Zhu, R.; Yang, Y. Polymer Solar Cells. *Nat. Photonics* **2012**, *6*, 153−161.

(80) Li, Y. F. Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption. *Acc. Chem. Res.* **2012**, *45*, 723−733.

(81) Rampino, S.; Armani, N.; Bissoli, F.; Bronzoni, M.; Calestani, D.; Calicchio, M.; Delmonte, N.; Gilioli, E.; Gombia, E.; Mosca, R.; et al. 15% Efficient Cu(In,Ga)Se_2 Solar Cells Obtained by Low-Temperature Pulsed Electron Deposition. *Appl. Phys. Lett.* **2012**, *101*, 132107.

(82) Guo, Q. J.; Hillhouse, H. W.; Agrawal, R. Synthesis of Cu_2ZnSnS_4 Nanocrystal Ink and Its Use for Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 11672−11673.

(83) You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C. C.; Gao, J.; Li, G.; et al. A Polymer Tandem Solar Cell with 10.6% Power Conversion Efficiency. *Nat. Commun.* **2013**, *4*, 1446.