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## Variable-Gap Conjugated Oligomers Grafted to CdSe Nanocrystals

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**Supporting Information** 

**ABSTRACT:** Three linear asymmetrically functionalized conjugated molecules composed of five or six aromatic rings were synthesized, bearing a terminal phosphonic acid group, with the objective of enabling their grafting onto inorganic CdSe nanocrystals. These chromophores—oligo(phenylene ethynylenes), oligothiophenes, or donor–acceptor–donor oligothiophenes with a benzothiadiazole acceptor—were designed with decreasing HOMO–LUMO energy gaps such that increasing amounts of light could be absorbed toward the longer wavelengths up to 600 nm. Electrochemical measurements show that the energy offsets between the HOMO and LUMO energies of the organic molecules and the energy bands of the CdSe nanocrystals are well-suited for charge transfer



between the organic and inorganic components. The characteristics of each component's excited state are studied by fluorescence spectroscopy and the interaction between the conjugated molecules and the CdSe nanocrystals in dilute solutions is monitored by photoluminescence quenching. In the latter experiments, where ester and acid derivatives are compared, the pronounced difference in luminescence quenching supports the ability of the phosphonic acid groups to strongly anchor onto the surface of the nanocrystals. Moreover, these results suggest that charge transfer likely occurs between the organic and the inorganic compounds, and appropriate ratios for the corresponding organic/inorganic hybrids preparation are identified. The preparation by direct ligand exchange and the photophysical properties of the hybrids are described, and spectroscopic analysis estimates that the nanocrystals are covered, on average, with 100–200 electroactive organic molecules. The incident photon-to-electron conversion efficiency reflects the solution absorption of the hybrids because it shows the response from both organic and inorganic components.

KEYWORDS: conjugated oligomers, nanocrystals, hybrid materials, donor-acceptor, phosphonic acid

## INTRODUCTION

The interest in organic/inorganic hybrid materials has flourished, in part, because of the evolution of the field in solar energy conversion, whether applied to photocatalysis,<sup>1,2</sup> solar fuels,<sup>3,4</sup> or photovoltaics.<sup>5–7</sup> Dye-sensitized solar cells (DSSCs) based on metal oxide/adsorbed dyes have been at the forefront of efficient solar cells combining organic and inorganic materials, with efficiencies reaching 10%.<sup>8</sup> Unlike the solid/liquid-based DSSCs, solid-state hybrid photovoltaics rely on blends of electroactive organic materials and inorganic semiconductors. Early reports by Alivisatos and co-workers of photovoltaic devices based on hybrid systems combining a conjugated polymer and cadmium selenide (CdSe) nanocrystals (NCs) in thin film blends have sparked considerable research efforts on organic semiconductor/chalcogenide NC hybrids.<sup>9</sup> Since NCs do not disperse well within the unfunctionalized polymer matrix and tend to aggregate,<sup>10,11</sup> a limiting factor to the efficiency of the latter type of hybrid solar cells is the unfavorable phase segregation in the active layers. By varying the shape of the inorganic NCs,<sup>12,13</sup> inorganic chemists have offered solutions to this morphology issue: blends of three-dimensional branched NCs with unfunctionalized polymers afforded power conversion efficiencies up to 2.2% with poly(3-hexylthiophene),<sup>9,14</sup> 2.1% with poly(phenylene vinylene),<sup>15,16</sup> and up to 3.2% with polymers taking advantage of the donor–acceptor approach.<sup>17,18</sup> Since NCs are often coated with trialkylphosphine oxide or alkylcarboxylate surfactants, depending on the colloidal NC synthesis method employed, they are inherently surrounded by an insulating layer of aliphatic molecules, which has been determined earlier to be

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Scheme 1. Synthesis of the OPE-A Electroactive Ligand from Hydroquinone and 1,4-Diiodobenzene



detrimental to the electronic interaction between the organic and inorganic components of the hybrids.<sup>19</sup> Subjecting the NCs to a solvent treatment aimed at replacing the original surfactants also contributed to increased efficiencies of hybrid solar cells.<sup>10,20–23</sup>

As a means of controlling both the morphology of the hybrid active layer and the NCs surfactant composition, conjugated polymers that feature functional groups such as amines,<sup>24,25</sup> phosphine oxides,<sup>26–28</sup> thiols,<sup>25,28,29</sup> and carbodithioic acids<sup>30</sup> were introduced. Although they provided better control of the dispersion of the NCs in the polymer matrix, little enhancement of the overall power conversion efficiency was observed. A related approach consists in using discrete conjugated oligomers in place of polymers, allowing for greater molecular control of the hybrids formation, because of the well-defined structure of the oligomers. In most previous studies, the oligomer's functional groups enable their grafting onto the inorganic NCs: carbazoles with phosphonate groups,<sup>3</sup> <sup>31</sup> perylene diimide with dicarboxylic acid groups,<sup>32</sup> oligoanilines with carbodithioic acid groups,<sup>33,34</sup> oligo(phenylene vinylene)s with phosphine oxide groups,<sup>35,36</sup> oligo(phenylene ethynylene)s with thiol groups<sup>37</sup> and oligothiophenes with thiol,<sup>38</sup> carbodithioic acid,<sup>30</sup> carboxylic acid,<sup>39–41</sup> phosphonate,<sup>42</sup> and phosphonic acid<sup>43–45</sup> anchoring groups have been reported. Some report the further electropolymerization of the attached ligands,<sup>31,39,40,46</sup> but most systems are treated as discrete inorganic core/organic-shell-type entities to be characterized and processed as such into optoelectronic devices.

Here, we report the synthesis of three monofunctionalized conjugated molecules as electroactive ligands: a five-ring oligo(phenylene ethynylene) (OPE), a six-ring oligothiophene (T6), and a five-ring benzothiadiazole (BTD)-containing oligothiophene (T4BTD). Each was functionalized with one phosphonic acid anchoring group, which has been shown to bind strongly to CdSe NC surfaces from both experimental and theoretical standpoints.43,44,47,48 By varying the nature of the aromatic rings in the molecular structures, the position of their HOMO and LUMO energy levels is adjusted with respect to that of the CdSe NCs, as measured electrochemically, especially as the donor-acceptor approach is employed for the first time in this type of organic oligomer/CdSe NC hybrids. The interaction of the conjugated molecules and the NCs in solution was monitored by photoluminescence quenching experiments. The hybrids were then prepared and purified: we chose the direct ligand exchange method to replace the superficial aliphatic ligands inherent to the NC synthesis with the newly synthesized monofunctional electroactive ligands. This afforded oligomer-capped CdSe NC hybrids, for which the

photophysical properties were investigated. Thin films of the hybrids were also used as the active layer of hybrid organic inorganic solar cells, and the incident photon-to-electron conversion efficiency (IPCE) measurement clearly showed the photocurrent contribution from both bound oligomers and CdSe NCs for each hybrid.

#### RESULTS

Electroactive Ligand Synthesis. The oligomers that we employed were designed as electroactive and photoactive rods bearing a single phosphonic acid functional group at one end. Each oligomer backbone was functionalized with two linear alkyl chains for solubility purposes. In the case of the oligothiophenes, the terminal ring opposite to that bearing the phosphonic acid group was functionalized with a linear alkyl chain at the  $\alpha$  position, in order to prevent any side reaction upon photoexcitation of the electron-rich thiophenes. To achieve the well-defined monofunctionalized asymmetrical oligomers, the approach used in this study consists of building the unfunctionalized and the functionalized conjugated units separately, then coupling them in the last steps of the synthesis. As described in Scheme 1, the synthesis of the OPE oligomer bearing one phosphonic acid group (OPE-A) begins with the alkylation of hydroquinone to 1, followed by diiodination of the benzene ring to afford 2, which is the precursor to the central benzene ring in OPE-A.

The two other precursors to **OPE-A**, the extended phenylene ethynylene moieties 4 and 7, were synthesized from 1,4diiodobenzene: under Sonogashira cross-coupling conditions, phenyl acetylene and propargyl alcohol were added to yield 3, which was subsequently deprotected under basic conditions to afford di(phenylene ethynylene) 4 bearing one terminal alkyne. In a nickel-mediated Arbuzov-type reaction with one equivalent of triethylphosphite, 1,4-diiodobenzene was converted to diethyl (4-iodophenyl)phosphonate 5. Similar conditions as described for 3 were applied to transform 1,4-diiodobenzene into intermediate 6, which is then coupled with 5 to generate the di(phenylene ethynylene) 7, bearing a phosphonate group on one side and a terminal alkyne on the other end. Precursors 2, 4, and 7 were then reacted in a one-pot synthesis to yield the phosphonate-monofunctionalized oligo(phenylene ethynylene) **OPE-E**. The symmetrical side products (the non-functionalized and the difunctionalized OPEs) were readily removed by column chromatography, because of their substantial polarity difference. The phosphonate ester of OPE-E was finally treated with trimethylsilyl bromide (TMSBr) and hydrolyzed with methanol. Subsequent dissolution in a minimum of dichloromethane and reprecipitation in methanol afforded the pure Scheme 2. Synthesis of the T6-A and T4BTD-A Electroactive Ligands from Dibromo-bithiophene and Dibromo-2,1,3-benzothiadiazole, Respectively



phosphonic acid-functionalized **OPE-A**, in 8% overall yield from diiodobenzene.

In the synthesis of the first thiophene-based oligomer—a sexithiophene (T6) bearing one phosphonic acid group (T6-A), shown in Scheme 2—the oligothiophene core is extended from the 5,5'-dibromo-2,2'-bithiophene starting compound into a symmetrical dialkylated quaterthiophene 10 by reacting the dibromobithiophene with the Grignard derivative of 2-bromo-3-hexylthiophene under nickel-catalyzed Kumada cross-coupling conditions in high yields.

Dibromination of 10 at the 5,5'''-positions using Nbromosuccinimide (NBS) in dimethylformamide affords 11 with little purification as the insoluble product can be filtered and recrystallized from a hexanes/ethanol mixture. In the following step targeting a monocoupled product, 11 is reacted with 1.5 equiv of 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, in a Suzuki cross-coupling reaction in toluene. We selected Pd<sub>2</sub>dba<sub>3</sub> and tri(*ortho*-tolyl)phosphine as palladium source and phosphine ligand, respectively, and tetraethylammonium hydroxide as boron-activating base. Under such conditions and after purification by column chromatography, yields of 31% for the targeted monocoupled product 12 and 23% for the dicoupled symmetrical sexithiophene byproduct were obtained. Moderate yields are expected in this asymmetrical synthesis step, because of the necessary stoichiometry and the purification process. The phosphonate functionality was installed separately on a thiophene ring by the nickel-mediated Arbuzov-type conversion of 2-bromothiophene into diethyl thiophen-2-ylphosphonate 13, followed by stannylation at the 5-position of the thiophene ring to afford compound 14. Monobrominated pentathiophene 12 was reacted with the stannylation product 14 under Stille coupling conditions using the same palladium source and phosphine ligands as for the previous Suzuki coupling, which yielded the phosphonate-monofunctionalized sexithiophene T6-E. The increased polarity of the oligomer induced by the presence of the phosphonate group facilitated purification by column chromatography. Starting with 2.67 g of dibromobithiophene, 650 mg of T6-E were obtained. The last step to the phosphonic acid T6-A involved treatment of the phosphonate T6-E using TMSBr in DCM followed by hydrolysis with methanol. This afforded T6-A in 5% overall yield from the dibromo-bithiophene starting material.

In donor-acceptor chemistry, an electron-rich unit and an electron-deficient unit are linked together in conjugation, typically via palladium-catalyzed cross-coupling.<sup>49,50</sup> Following the latter approach, we synthesized the second thienylene oligomer-a five-ring oligomer consisting of one central BTD unit flanked by two thiophene rings on each side and bearing one phosphonic acid (T4BTD-A), also shown in Scheme 2by reacting 4,7-dibromo-2,1,3-benzothiadiazole with 2 equiv of 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane under the same Suzuki cross-coupling conditions than that used for the synthesis of the pentathiophene 12, to afford compound 15 in high yields. Subsequent dibromination by NBS in chloroform yields the symmetrical precursor 16. As for the conversion of 11 into 12 during the synthesis of the T6-A oligomer, the stoichiometry of the reaction of 16 with 2-(5hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane needed to be adjusted in order to optimize the ratio of targeted monocoupled compound 17 to the unreacted and dicoupled byproduct. Unlike for the synthesis of the sexithiophene, for which 1.5 equiv of the thienyl borolane were used, in this case, we reacted 16 with 0.80 equiv of the borolane. We expected such a stoichiometry to still afford 17 in acceptable yields while being able to recover the valuable starting material 16 rather than the unreactive dicoupled byproduct. After purification of the reaction by flash chromatography, the monocoupled product 17 was obtained in 26% yield while the recovered starting compound 16 accounted for 53% of the material. Although slightly lower, the yield for the latter asymmetrical coupling was comparable to that when 1.5 equiv of the borolane were used. Therefore, the stoichiometry for this type of asymmetrical cross-coupling can be chosen, depending on the interest for a specific byproduct. Compound 17 was then coupled to tin compound 14 to install the phosphonate group onto the oligomer, affording T4BTD-E in 64% yield. Starting with 3 g of 4,7-dibromobenzothiadiazole, 1.34 g of T4BTD-E were obtained. The phosphonate was hydrolyzed as done previously, using TMSBr to yield the phosphonic acid monofunctionalized T4BTD-A in 14% overall yield.

The CdSe nanocrystals used in this study were synthesized according to a previously reported procedure<sup>51</sup> with some modification.<sup>52</sup> The as-synthesized CdSe nanocrystals were capped by a mixture of oleic acid (OA) and trioctylphosphine oxide (TOPO), given that the molar feed ratio during NC

synthesis was  $\sim 1:1$  in the two ligands. (See the Supporting Information for CdSe NC synthesis details.)

**Photophysics of the Free Oligomers.** With OPE-A, T6-A, and T4BTD-A on hand, the UV-visible absorption and fluorescence spectra were obtained, as shown in Figure 1. All



Figure 1. Normalized UV-visible absorption (a) and photoluminescence (b) of OPE-A (black line), T6-A (blue line), T4BTD-A (red line), and the CdSe NCs (dashed line) in chloroform solution.

the absorption spectra feature a strongly allowed long wavelength absorption band, which shifts systematically from 383 nm for **OPE-A** to 426 nm for **T6-A** to 508 nm for **T4BTD-A**. High molar absorptivities of 30 000–50 000 M<sup>-1</sup> cm<sup>-1</sup> were recorded in CHCl<sub>3</sub> solutions, as summarized in Table 1. From the absorption onset of **OPE-A** and **T6-A** in solution, a relatively large energy gap of 2.8 and 2.4 eV, respectively, is calculated, as expected of oligomers with homogeneous  $\pi$ electronic systems. The BTD-based oligomer, on the other hand, features a longer wavelength absorption onset corresponding to a smaller HOMO–LUMO gap of 2.0 eV. This is due to the D–A interaction attributable to the mixing of the BTD acceptor unit with the flanking bithiophene donors.<sup>53</sup> The molar absorptivity of **T4BTD-A** is also lower in comparison to the **OPE** and **T6** and is consistent with the D–A transition.

The CdSe NCs have a first excitonic absorption peak at 624 nm characteristic of the quantum confinement effect, and the absorption increases steadily toward the UV region of the spectrum. The peak position for the NC absorption is in accordance with their size (see Supporting Information, Figure S10, for NCs TEM images), and an optical energy gap of 1.9 eV is calculated. The fluorescence quantum yield is comparatively low for the CdSe NCs (Table 1), presumably due to the formation of defect states at the NCs surface during the removal of excess TOPO and oleic acids.<sup>52</sup>

The photoluminescence of each oligomer was measured in ester and acid form, in dilute chloroform solution, and the results are also summarized in Table 1. The oligomer solutions exhibit intense fluorescence with a quantum efficiency near or above 50%. The peak emission wavelengths red-shift in sequence from OPE to T4BTD: the peak fluorescence is at 434 nm for OPE-A, 565 nm for T6-A, and 676 nm for T4BTD-A, which is consistent with the absorption results. The emission band broadens for the T4BTD oligomer, reflecting the charge transfer nature of the excited state.

Fluorescence lifetimes were determined for both acids and esters; in each case, the decays followed first-order (single exponential) kinetics. There is little difference between the acid form and the ester form for each oligomer, as expected for the dilute solutions used where little aggregation is expected. While the OPE and T6 oligomers show short lifetimes of ca. 0.9-1.0 ns (with radiative rate,  $k_{\rm r} \approx 0.6-0.8~{\rm ns}^{-1}$ ), the T4BTD oligomers exhibit significantly longer lifetimes of ca. 5.6 ns. The longer lifetime for T4BTD results from a significantly lower radiative rate ( $k_r \approx 0.16 \text{ ns}^{-1}$ ); this is again consistent with the D-A nature of the fluorescent excited state, with a magnitude typical of bis(diaryl)benzothiadiazoles.<sup>55,56</sup> For applications such as hybrid photovoltaics, where the photogenerated exciton should be dissociated into separated charged species, a longer lifetime is beneficial, because it increases the probability for charge separation to occur.

Redox Properties. The redox properties of each oligomer were investigated using cyclic and differential pulse voltammetry (CV and DPV) in solution. For each oligomer, a small amount of material was dissolved in a dry and degassed dichloromethane electrolyte solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), to achieve a concentration of 1 mM in oligomer. All measurements were performed in an argon-filled glovebox, and the background current for an oligomer-free electrolyte is shown in Figure S1 in the Supporting Information. All potentials are reported against the Fc/Fc<sup>+</sup> standard. For the OPE-A oligomer in solution, the oxidative CV (see Figure S1-b in the Supporting Information) shows one irreversible oxidation process with an onset at 0.78 V, and no further oxidation wave at higher potentials was observed. In the cathodic CV scans, no electrochemical process was observed other than the beginning of electrolyte breakdown at a potentials negative of -2.0 V, as evident from the background CV shown in Figure S1-a in the Supporting Information. We conducted similar CV experiments with T6-A, for which the oxidative CV shows two quasireversible processes centered at half-wave potentials of 0.33 and 0.56 V (see Figure S1-c in the Supporting Information). Similar

|  | Гable 1. | . Optical D | ata of the Olig | omer Esters a | ind Acids and | CdSe NC in | CHCl <sub>2</sub> Soluti |
|--|----------|-------------|-----------------|---------------|---------------|------------|--------------------------|
|--|----------|-------------|-----------------|---------------|---------------|------------|--------------------------|

|         | $\lambda_{\max}$ abs (nm) | optical $\Delta E^a$ (eV) | $\varepsilon_{\rm abs}~({ m M}^{-1}~{ m cm}^{-1})$ | $\lambda_{\max}$ Fl (nm) | Stokes shift (cm <sup>-1</sup> ) | $\Phi_{ m Fl}{}^c$ | $	au_{ m Fl}{}^{c}( m ns)$ |
|---------|---------------------------|---------------------------|--|--------------------------|----------------------------------|--------------------|----------------------------|
| OPE-E   | 381                       | 2.8                       | 42 700   | 436                      | 3100                             | $0.79^{d}$         | 0.91                       |
| OPE-A   | 383                       | 2.8                       | 33 800   | 434                      | 3068                             | 0.53 <sup>d</sup>  | 0.89                       |
| Т6-Е    | 424                       | 2.4                       | 55 600   | 537/564                  | 5854                             | $0.54^{d}$         | 0.86                       |
| T6-A    | 426                       | 2.4                       | 48 700   | 539/565                  | 5775                             | $0.49^{d}$         | 0.85                       |
| T4BTD-E | 504                       | 2.1                       | 30 000   | 675                      | 5026                             | 0.71 <sup>e</sup>  | 5.60                       |
| T4BTD-A | 508                       | 2.0                       | 21 000   | 676                      | 4892                             | 0.71 <sup>e</sup>  | 5.55                       |
| CdSe NC | 624                       | 1.9                       | 632 000 <sup>b</sup>                               | 650                      | 641                              | 0.001 <sup>e</sup> | 1.26 <sup>f</sup>          |

<sup>*a*</sup>From low-energy onset of absorption in the solution UV–vis spectra. <sup>*b*</sup>Calculated by the method described in ref 54. <sup>*c*</sup> $\Phi_{Fl}$  and  $\tau_{Fl}$  are fluorescence quantum efficiency and lifetime, respectively. <sup>*d*</sup>Quinine sulfate in 0.1 M sulfuric acid ( $\Phi_F = 0.54$ ) as standard. <sup>*c*</sup>Ru(bpy)<sub>3</sub>Cl<sub>2</sub> in H<sub>2</sub>O ( $\Phi_F = 0.056$ , degassed) as standard. <sup>*f*</sup>Average lifetime from a multiexponential decay.

to OPE-A, no reduction was observed when the potentials were scanned cathodically of 0 V up to -2.0 V, after which the electrolyte breakdown started. The absence of reduction processes for OPE-A and T6-A is not surprising, since both oligomers are electron-rich chromophores that would require even more negative potentials to accommodate the addition of an electron. For T4BTD-A, the oxidative CV shows one reversible oxidation process centered at a half-wave potential of 0.50 V (see Figure S1-d in the Supporting Information). In contrast to the latter two oligomers, the reductive CV of T4BTD-A features a single reversible reduction centered at a half-wave potential of -1.66 V. This is consistent with the D–A nature of the chromophore, which results in a deeper LUMO energy level.

The input signal of a DPV experiment involves short pulses with a stepwise increase of the base potential, and since the recorded current in this experiment is the difference between currents measured before and after each pulse, the overall output signal in a DPV is free of the capacitive current, which is otherwise part of the output in a CV experiment. Therefore, the differential current recorded in a DPV is mostly Faradaic, involving the actual redox process of adding or removing an electron at the electrode surface. This results in well-defined oxidation (reduction) onsets during the oxidative (reductive) DPV, which is why we employed the latter electrochemical technique to measure the energies of the frontier molecular orbitals of all three oligomers, using the same solutions as for the CV experiments. From the oxidative DPV, oxidation onsets for OPE-A, T6-A, and T4BTD-A were measured at 0.78, 0.22, and 0.40 V, respectively. As previously described, only T4BTD-A exhibits a reduction process in reductive DPV experiments, with an onset of reduction at -1.55 V (see Figure S1 in the Supporting Information). In order to convert the voltage values calibrated against the Fc/Fc<sup>+</sup> standard into energy values against vacuum, the value for  $Fc/Fc^+$  against vacuum must be known. Since Fc/Fc<sup>+</sup> is +0.380 V vs SCE,<sup>57</sup> and the energy of SCE is 4.7 eV vs vacuum,<sup>58</sup> we used a Fc/Fc<sup>+</sup> redox standard set at -5.1 eV versus vacuum, a value recently discussed by Bazan and co-workers.<sup>59</sup> Figure 2 depicts the position of the



Figure 2. Band structure diagram comparing the HOMO and LUMO levels of OPE-A, T6-A, and T4BTD-A, and their offsets relative to the CdSe NCs valence- and conduction-band energy ranges.

HOMO and LUMO energy levels for the three oligomers: from the DPV oxidation onsets, **OPE-A** has a HOMO energy level at -5.84 eV, **T6-A** at -5.32 eV, and **T4BTD-A** at -5.50 eV, all vs vacuum.

We calculate the LUMO energy of **T4BTD-A** from the reductive DPV onset to be at -3.55 eV, giving an electrochemical energy gap of 1.95 eV, which is close to the optical energy gap value of 2.0 eV measured spectroscopically. The absence of a voltammogram wave attributable to the reduction of the oligomer for **OPE-A** or **T6-A** prevented the electrochemical estimation of LUMO energies for the latter two compounds. Since the optical energy gap of the BTD-based oligomer is within 0.05 eV of its electrochemical energy gap, we therefore used the corresponding optical energy gaps listed in Table 1 to estimate the energies of the LUMOs for **OPE-A** and **T6-A**, which are at -3.04 and -2.92 eV, respectively, vs vacuum.

The energy diagram in Figure 2 also shows the range of energies that one can estimate for the conduction and valence bands (CB and VB, respectively) of the CdSe NCs used in this study. For bulk CdSe, the CB energies are set between -4.3 eV and -4.5 eV, and between -6.2 eV and -6.3 eV for the VB.<sup>52</sup> Energy band measurements have been reported for CdSe nanoparticles in the 3-4-nm-diameter range, setting the CB around -3.5 eV and the VB around -5.5 eV.<sup>60</sup> For the 6-nmdiameter CdSe NCs used in this study, it is thus safe to estimate that the CB is found between -3.8 eV and -4.3 eV, and with an optical bandgap of 1.9 eV, the VB is found between -5.7 eV and -6.2 eV. For the three oligomers, the LUMO levels are thus likely higher than the VB the NCs. Although the HOMO level of **OPE-A** is rather deep (-5.84 eV), likewise the HOMO levels of the organic molecules are likely higher than the VB of the NCs. Such energetic offsets would result in staggered energy gaps for each organic oligomer/CdSe NCs complex, which is analogous to that described as type II heterojunctions in solid-state semiconductor physics. In terms of the expected photoelectrochemical behavior, this type of heterojunction suggests that photoexcitation of either the oligomers or the NCs will lead to electron transfer from the oligomer (as an electron donor) to the CdSe NCs (as an electron acceptor).

Photoluminescence Quenching. Photoluminescence (PL) quenching is a powerful tool to probe the electronic interactions between and among chromophores and electroactive species. This technique was used in particular by Frechet and co-workers to decipher between charge- and energytransfer processes in a system composed of 4 nm CdSe NCs and phosphonic acid functionalized pentathiophenes.<sup>45</sup> They observed significant photoluminescence quenching of the pentamer's fluorescence in solution upon the addition of CdSe NCs, and, likewise, significant quenching of the NCs' emission upon addition of the pentamer. The luminescence of shorter thiophene trimers was also quenched by CdSe NCs, but the emission of the NCs increased with the trimer concentration. This was accounted for by the difference in staggered energy gaps between the NCs and the pentamer (type II heterojunction), compared to straddling energy gaps (type I heterojunctions) between the NCs and the widerenergy gap trimer. Ruling out the possibility of energetic surface defect passivation by the phosphonic acid anchoring group itself, the dual luminescence quenching was explained by an electron-transfer mechanism from the thiophene pentamers to the NCs. Similar observations were reported by Advincula and co-workers for phosphonic acid-functionalized thiophene dendrons, and this type of experiment was used by others as well.<sup>11</sup> In the dilute solutions typically used for fluorescence experiments, fluorescence quenching upon the interaction of two different species requires them to be in close proximity, regardless of the quenching mechanism. The synthesis of CdSe NCs involves the use of surfactants usually composed of long alkyl chains and a polar functional group, with which the NC surface is coated after the reaction is over. The surfactants used



Figure 3. (a) Evolution of the fluorescence in chloroform of OPE-E (left) and OPE-A (right) upon the addition of CdSe NCs into the solution, and (b) evolution of the peak fluorescence intensities for the ester (solid lines) and acid (dashed lines) forms of OPE (black line), T6 (blue line), and T4BTD (red line) upon the incremental addition of CdSe NCs.

in the synthesis of the CdSe NCs for this study are oleic acid (OA) and trioctylphosphine oxide (TOPO), in a feed ratio close to one. There is thus an inherent insulating layer of aliphatic surfactants (OA and TOPO) coating each NC, which has been shown to be detrimental to their electronic interaction with conjugated polymers.<sup>19</sup> The exact nature and distribution of the aliphatic surfactants at the surface of the NCs is not straightforward, because it depends on the nature and purity of that used during NC synthesis, and the purification process that followed. Nevertheless, the use of functional groups such as phosphonic acids or carboxylates, which bind strongly to the NCs surface, have been shown to displace the aliphatic native surfactants, during a ligand exchange process, which results in new molecules anchored to the NC surface.<sup>61</sup>

With this in mind, the three phosphonic acid-functionalized oligomers in this study were designed to undergo efficient ligand exchange with native surfactants on the surface of CdSe NCs. For each chromophore solution, we monitored the evolution of the PL intensity upon addition of aliquots of CdSe NCs in solution, and compared the evolution for the phosphonate ester derivative, with respect to the corresponding phosphonic acid. Figure 3a shows the PL evolution for the OPE phosphonate ester (OPE-E, left) and the OPE phosphonic acid (OPE-A, right) in dilute chloroform solution (5  $\mu$ M) as 20  $\mu$ M CdSe in chloroform was added, in increments. The increments were chosen so that each addition doubled the concentration of CdSe NCs in the oligomer solution up to an oligomer:CdSe ratio of 50:1. The concentrations of the starting solutions (pure oligomer, 5  $\mu$ M and pure CdSe NCs, 20  $\mu$ M) were such that only microliters of CdSe solution were added to the fixed volume of 2 mL of oligomer solution, thereby negating the effect of dilution on the PL intensity. For the phosphonate OPE-E, the addition of the CdSe reduced the oligomer fluorescence by 20% at the 50:1 ratio. When the acid form OPE-A was subjected to the same procedure, very strong luminescence quenching was observed: the fluorescence is essentially fully quenched when the molar ratio of OPE-A:CdSe equals 50:1 in solution.

The same set of experiments was carried out for the ester and acid forms of T6 and T4BTD, respectively, for which the evolution in the fluorescence intensities is displayed in the Supporting Information (Figures S3 and S4, respectively). The results for T6-A versus T6-E and T4BTD-A versus T4BTD-E follow the same trend as that shown in Figure 3a for OPE. Figure 3b shows the evolution of the peak fluorescence

intensities for all six experiments: for all three chromophores, the fluorescence of the ester form decreases by 5%–20% upon addition of the CdSe NCs, whereas the fluorescence of the acid form is quenched by more than 95% under the same conditions. In these experiments, diffusional quenching can be ruled out, because of the low concentrations employed; therefore, any evolution in the PL intensity would be due to oligomer/NC complex formation. The PL quenching results suggest that the phosphonate ester forms have, at best, a weak interaction and, thus, there is little binding of the oligomers to the NCs, while the acid forms bind to the NCs, likely via surface binding of the phosphonic acid moiety.

In the experiments described above, no luminescence increase was observed when carefully monitoring the 610-630 nm range for any enhancement of the emission from the CdSe in the oligomer/CdSe mixture. This was not surprising, considering the low concentration of CdSe NCs in solution (up to 100 nM, after the final increment), and was not sufficient to decipher between either electron- or energy-transfer mechanisms. This point was further addressed by performing the reverse experiment, i.e., studying the PL quenching of CdSe emission by the oligomers. Thus, when solutions of CdSe NCs were selectively excited at 630 nm, the emission intensity was recorded as aliquots of oligomer solution were added. This was only possible for the OPE and T6 oligomers, since, for T4BTD, the absorption of the oligomer and CdSe overlap significantly. For OPE and T6, the procedure is described in detail in the Supporting Information. After mixing the oligomer and CdSe NCs, the solutions were stirred and excited at the CdSe peak absorption wavelength (which does not overlap with the absorption of OPE or T6). The resulting emission was recorded and plotted against that of oligomer:CdSe ratio mixtures. The photoluminescence of CdSe decreased upon addition of OPE-A, whereas the same amount of OPE-E had no influence on the CdSe emission, as displayed in Figure S5 in the Supporting Information. Similar results were observed for the T6 derivatives (see Figure S6 in the Supporting Information).

In summary, the intensity of the PL quenching in all cases suggests that the phosphonic acid group anchors the oligomers onto the CdSe NCs, to an extent where a 50:1 oligomer:NC ratio is sufficient to achieve complete quenching of the excited state of the oligomer by the NC. The quenching likely occurs via a charge-transfer process rather than energy transfer as the emission of both species is quenched for **OPE-A**:CdSe and **T6**-A:CdSe.

Preparation and Characterization of Hybrids. In order to prepare and isolate CdSe NCs that are coated with the oligomers (oligomer/NC hybrids), solutions of the two components were mixed and the resulting NCs isolated by precipitation/centrifugation. From the PL quenching experiments, a 50:1 ratio of oligomer:NC was found to be sufficient to completely quench the luminescence of the organic chromophore. Thus, we rationalized that such a ratio or higher would be suitable for the synthesis of the NC hybrids. The preparation consists in the exchange of the OA and TOPO ligands of the as-synthesized NCs with OPE-A, T6-A, or T4BTD-A by mixing in chloroform, followed by precipitation of the oligomer/NC hybrid in an appropriate solvent and centrifugation to remove the supernatant containing any unbound species. Experimentally, 10 mg of the oligomer was dissolved in 5 mL of degassed chloroform, to which was added a solution of the NCs in chloroform at the appropriate concentration for an oligomer:NCs ratio in excess of 200:1. The mixture was stirred vigorously in the absence of light at room temperature for 30 min, after which it was precipitated in a poor solvent for the oligomer/NC hybrid, but a good solvent for the unbound surfactants and excess oligomer. For the T6-A/CdSe NC system, ethyl acetate was used to precipitate the hybrids, while methanol was suitable to precipitate the OPE-A/ CdSe NC and T4BTD-A/CdSe NC systems. After centrifugation of the suspension and removal of the supernatant containing unbound species, the precipitates were redissolved in chloroform and precipitated once again in the proper solvent. This was repeated several times, while recording the UV-visible absorption spectrum of the chloroform solutions in each step. Since unbound oligomers remained in the supernatant, which was removed after each precipitation, the overall absorption profile of the redissolved precipitates featured less absorption contribution from the oligomers. Once the relative absorption intensities of the NCs versus that of the oligomer stabilized, the chloroform solution containing the redissolved oligomer/NC hybrid was considered free of unbound oligomers. The UV-visible absorption spectra of the resulting washed hybrids are shown in Figure 4.

Compared to the pure CdSe NC solution absorption which is displayed as a dashed line, the absorption profile of the **OPE** hybrid (black line) has an absorption band emerging out at 410



Figure 4. Absorption spectra of the OPE-based hybrid (black line), the T6-based hybrid (blue line) and the T4BTD-based hybrid (red line) along with the spectrum of free CdSe NCs (dashed line) in chloroform solution (spectra were normalized at the CdSe band maximum (625 nm)).

nm toward shorter wavelengths, and peaking at 325 nm with a shoulder at 370 nm, which shows the contribution of the bound **OPE-A**. The **T6** hybrid (blue line) has a broad absorption band centered at 426 nm from the contribution of the bound **T6-A** oligomers. Similarly, the absorption profile of the **T4BTD** hybrid shows the contribution of the NCs-bound **T4BTD-A** peaking at 360 and 508 nm. In all three spectra, the contribution of the NCs to the overall absorption is observed as a peak or shoulder around 625 nm. The optical properties of the hybrids are summarized in Table 2. Extremely weak fluorescence was observed in dilute solutions of the hybrids in chloroform, with quantum yields below 0.1% at 433 nm for the **OPE** hybrid solution, 564 nm for the **T6** hybrid solution, and 676 nm for the **T4BTD** hybrid solution.

Seeking evidence for the dynamics of the hybrids fluorescence, we measured the fluorescence lifetime of each hybrid in solution. As recorded in Table 2, two components contribute to the average lifetime of the hybrids fluorescence: one from the ligands emission and the other from the CdSe emission. Compared with the fluorescence lifetime of the free ligands or CdSe NCs (Table 1), we observed that the fluorescence of each hybrid solution has almost identical lifetime with their corresponding free oligomer and CdSe NCs. This observation suggests that the fluorescence of the hybrids results from trace amounts of free ligands and CdSe NCs, while the hybrids themselves are nonemissive, presumably because of the charge transfer between the components as described earlier. This finding also points to the fact that the quenching process is very rapid, occurring on a time scale of  $<100 \text{ ps.}^{62,63}$ The efficient quenching, along with the absorption profiles of the hybrids, supports the strong surface binding and interaction between the oligomers and the NCs.

Transmission electron microscopy (TEM) images of the hybrids displayed in the Supporting Information (Figure S10) show that the hybrids are prone to aggregation, compared to the TOPO/OA-coated NCs, which unfortunately makes dispersity analysis of the hybrids complicated. But, with the hybrids synthesized, and the presence of surface-bound oligomers established, a semiquantitative estimation of the average number of oligomers at the NCs surface was carried out. First, thermogravimetric analysis (TGA) was employed to determine a total weight loss difference between the pristine NCs (TOPO and OA-coated) and those functionalized with the electroactive oligomers. In principle, during the ligand exchange process, if a native surfactant such as TOPO (MW = 415 g/mol) or OA (MW = 282 g/mol) is replaced by OPE-A (MW = 815 g/mol), T6-A (MW = 827 g/mol), or T4BTD-A (MW = 797 g/mol), then an oligomer/NC hybrid should have a higher organic content by weight than the pristine NC. Displayed in the Supporting Information (Figure S7), the TGA thermograms for a CdSe sample before ligand exchange (dashed line) and after ligand exchange with OPE-A (black line), T6-A (blue line), or T4BTD-A (red line) are plotted. Weight loss differences for the hybrids were 4%-8% greater, compared to the pristine CdSe sample ( $T \approx 500$  °C). This result implies that the ligand exchange process increases the organic content in the hybrid, supporting the presence of a higher-molecular-weight species bound to the surface of the NCs. One obvious limitation to this method is that it is, in fact, very difficult to determine the exact number of native surfactants before ligand exchange. Thus, the results from the TGA experiments are, at best, qualitative.

| Table 2. Optical | Data of the Three | Oligomer/CdSe NC | Hybrids in | CHCl <sub>3</sub> Solution |
|------------------|-------------------|------------------|------------|----------------------------|
|------------------|-------------------|------------------|------------|----------------------------|

|   | $\lambda_{\max}$ abs (nm) | $\lambda_{\max}$ Fl (nm) | fluorescence quantum efficiency, $\Phi_{\mathrm{Fl}}^{}a}$ (%) | fluorescence lifetime, $\tau_{\rm Fl}^{\ a}$ (ns) |  |  |  |
|---|---------------------------|--------------------------|--|---|--|--|--|
| <b>OPE</b> hybrid   | 325/370/625               | 433                      | <0.1   | 0.88(450 nm)/1.24(650 nm)                         |  |  |  |
| T6 hybrid   | 426/625                   | 564                      | <0.1   | 0.83(560 nm)/1.23(650 nm)                         |  |  |  |
| T4BTD hybrid  | 360/508/625               | 676                      | <0.1   | 5.2(680 nm)/1.48(650 nm)                          |  |  |  |
| $a\Phi$ , and $\tau$ , are fluorescence quantum efficiency and lifetime, respectively |                           |                          |  |   |  |  |  |

A second approach to estimate the number of surface-bound oligomers consists in a careful comparison of the hybrids' absorption with that of the pristine NCs and the free oligomer.<sup>11</sup> The absorption spectra of the latter three species in the case of **T6** is shown in Figure 5. The relative absorption



Figure 5. Absorption profiles of the T6-A:CdSe hybrid (solid line), the free T6-A (dotted line), the free CdSe (dashed line), and the sum of the latter two (dash-dotted line).

intensity of the free oligomer (dotted line) and the free NCs (dashed line) was adjusted such that the sum of their absorption spectra (dash-dotted line) resulted in a profile for which the intensities at the respective absorption maxima (at 426 and 624 nm) matched that of the hybrid (solid line).

This was achieved for an absorbance of 0.912 at 426 nm for T6-A and 0.087 at 624 nm for the NCs. From Beer's law, concentrations of 18.7  $\mu$ M and 136 nM, respectively, were calculated, using the extinction coefficients listed in Table 1, resulting in an oligomer:NC ratio of 137. The same spectral analysis and calculations were applied to the OPE and T4BTD hybrids (see Supporting Information, Figures S8 and S9, respectively), yielding ratios of 200 OPE-A and 140 T4BTD-A per NC, respectively. These ratios are, of course, average values and remain an approximation of the number of oligomers bound to the NCs, but they suggest that a significant coverage of the NCs was achieved using each phosphonic acid derivative. For 6-nm-diameter NCs, this corresponds to one oligomer bound onto every 1 nm<sup>2</sup> of NC surface, on average.

With varied HOMO–LUMO gaps, the three oligomers were designed such that an increasing amount of light toward the higher wavelengths could be absorbed by the photoactive and electroactive ligands, in going from **OPE** to **T6** to **T4BTD**. In order to study the possibility of these oligomers/NCs hybrids for photovoltaic (PV) application, we then fabricated hybrid PV devices with a device structure of ITO/PEDOT:PSS/ oligomer:CdSe/ZnO/Al. Here, the oligomer:CdSe is the active layer, and ZnO NCs serve as an optical spacer and hole-blocking layer.<sup>64</sup> The incident photon-to-electron conversion efficiency (IPCE) was recorded for each hybrid as displayed in Figure 6.



**Figure 6.** Incident photon-to-electron conversion efficiency of **OPE-A**/CdSe (black line), **T6-A**/CdSe (blue line), and **T4BTD-A**/CdSe (red line) hybrids films in a ITO/PEDOT:PSS/oligomer:CdSe/ZnO/ Al device architecture under AM1.5 illumination.

The IPCE for the **OPE** hybrid peaks at 350 nm to 10% with little response below 3% at wavelengths higher than 500 nm, except for a small shoulder at 620 nm, which is likely due to the contribution of CdSe NC absorption. For the **T6** hybrid, a broad band with a maximum IPCE of  $\sim$ 12% appears in the IPCE from 400 nm to 550 nm likely corresponding to light absorbed by the **T6** ligands bound on the CdSe NC surface. A shoulder at 620 nm is observed, signifying contribution of the CdSe NC absorption to the overall photocurrent.

The IPCE for the **T4BTD** hybrid is broadened further to 650 nm, with two bands centered at 371 and 505 nm, and the IPCE maximum is ~13%. This parallels the absorption of the **T4BTD** electroactive ligands which are bound onto the NCs. A slight shoulder at ~650 nm can be distinguished, likely corresponding to the NC contribution to the photocurrent. In summary, the IPCE spectra for three categories of hybrids indeed indicated the photocurrent contribution both from oligomers and CdSe NCs.

#### DISCUSSION

Hybrid photovoltaics bring together materials that are synthesized and characterized with very different methods, although both organic and inorganic parts present energetic similarities that justify their interaction as hybrid materials. The field has benefitted from research efforts in the design of each part of the hybrid, for instance with tailored NC sizes, shapes, composition, and surface treatments for improved optoelectronic performance.<sup>65</sup> On the organic materials side, one improvement came from functionalizing an electroactive molecule or polymer to improve their interaction with the NCs.<sup>11</sup>

Following this, the molecules in this study were functionalized with phosphonic acid groups, for which the binding strength to CdSe NCs had been previously reported with oligothiophenes.<sup>43–45</sup> Each molecule in this study was made asymmetrical so that grafting onto the CdSe surface can achieve a hybrid complex of CdSe NC "core" and electroactive ligand

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"shell". The synthesis of such asymmetrical oligomers can be tedious and low-yielding (see below), which is a major disadvantage when put in the perspective of the sought-after application. In this study, we investigated three variations of a synthetic route to afford asymmetrical molecules. First, the OPE oligomer was built by synthesizing three separate segments of the target molecule, and combining them in a final one-pot synthesis. Second, the T6 oligomer was synthesized starting from a symmetrical core then converted to an asymmetrical precursor (compound 12) using 1.5 equiv of an end-capping thienyl-borolane. Third, the T4BTD oligomer was synthesized also from a symmetrical core but reacted with only 0.8 equiv of the end-capping thienyl-borolane in the asymmetrical step to give compound 17. The remaining aryl bromide sites in both cases could finally be used to install the phosphonate functionality. Importantly, the overall yields for the synthesis of each oligomer remains  $\sim 10\%$ , regardless of the route employed, and the choice of the synthetic route can be done based on considerations for valuable side products.

Another improvement from the field of conjugated organic materials came with the advent of the donor-acceptor approach to the smaller HOMO-LUMO energy gap of the organic semiconductors. D-A systems were used also in hybrids, where fully conjugated D-A polymers were introduced in conjunction with CdSe NC to achieve 3% power conversion efficiency.<sup>17</sup> It is understood that adjusting the position of the HOMO and LUMO energy levels of the organic part, with respect to the CB and VB of the inorganic part, can help increase the efficiency of charge separation the organic/ inorganic interface. The D-A approach also allows the organic material to absorb more light toward the longer wavelengths. The molecules in this study were designed with varying HOMO-LUMO gaps from 2.8 eV for the OPE oligomer to 2.0 eV for the T4BTD oligomer, absorbing light up to 600 nm. With the latter molecule, the D-A-D structure is used for the first time in designing deep-LUMO, small-energy-gap (extended absorption) electroactive ligands for grafting onto inorganic structures.

We carefully studied the interactions between the electroactive ligands and CdSe NCs. The communication between the components characterizing photoinduced charge transfer is clearly facilitated by the anchoring groups on the organic ligands. Transient absorption was measured for the hybrid materials in an attempt to monitor charge-separated states; however, we were unable to observe any transients on the nanosecond time scale. Previous reports of the transient absorption of CdSe NCs revealed that the relative photophysical process is under a picosecond time scale.<sup>62,63</sup> As far as the mechanism of photoinduced charge transfer process is concerned, either (or both) of the following mechanisms can be considered: (1) Electron injection from the oligomer ligands to CdSe NCs by exciting the organic ligand, or hole migration from the NCs to the ligands by exciting the NCs. (2) Energy transfer occurs from the excited state of the ligands to the CdSe NCs generating excitons in the NCs, followed by hole migration from the NCs back to the ligands. In any of these mechanisms, charge separation between the components of the hybrid materials is involved, and the IPCE measurements clearly demonstrate the fact that carriers are generated via light absorption of either the oligomer-ligands or the NCs.

### CONCLUSION

Through synthetic tailoring of the conjugated chromophore, the absorption of the organic components of the hybrids described here was extended to 600 nm, and the presence of one phosphonic acid group on the chromophore allows for strong anchoring of the electroactive ligands onto the CdSe NCs surface. Under the conditions identified during the photoluminescence quenching experiments, hybrids were prepared and purified, leading to composites with significant coverage of the NCs by more than 100 electroactive ligands. This effectively increased the absorption of the hybrids in the visible region of the spectrum especially as the donoracceptor-donor (D-A-D) molecule was used, and the photocurrent response of hybrids thin films reflects the increased absorption at wavelengths longer than 400 nm. We anticipate that the type of phosphonic acid-functionalized conjugated molecules described here are good candidates as active layer components for efficient hybrid organic-inorganic solar cells, especially as the absorption is further increased by taking advantage of the donor-acceptor (D-A) approach.

#### ASSOCIATED CONTENT

#### **Supporting Information**

This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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