Design and Synthesis of n-Type Organic−Inorganic Hybrid Material Incorporating CdSe Quantum Dots Nanocrystal Core and Diphenylquinoline Peripheral Group

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Many of today's devices such as photovoltaic (PV) cells, light-emitting diodes (LEDs), photodiodes, photoxerographic receptors, transistors, lasers, switches, memory devices, and sensors can be rendered substantially more efficient by utilizing novel materials.[1−4] The amalgamation of organic semiconducting materials with nanocrystalline quantum dots (QDs) as macromolecular architectures has the potential to deliver such a novelty.[5−8] While attempts have been made to combine the two as a hybrid in the past, results have been unsatisfactory.[6] The uniform miscibility of the quantum dots with organic−electronic materials is a challenging task that requires tailoring of the ligand periphery at the quantum dot surface and/or designing a new architecture to attain QD nanocrystals−organic hybrid material through synthetic manipulation.

The QDs−organic semiconducting hybrid materials were prepared by directed and self-assembly techniques.[9a,10] Despite numerous advances, technical difficulties relating to the fabrication of such devices from nanoparticle-based composites have been encountered. One key problem is centered at the organic material−QD interface. The insulating tri*n*-octylphosphine oxide (TOPO) coverage limits charge transport between the QDs and the surrounding matrix. In addition, the use of either TOPO-covered or TOPO-free ("stripped") QDs leads to nanoparticle aggregation within the organic matrix and diminished interfacial interactions. These effects reduce the overall device performance and efficiency. Recent studies on customized ligands to cover QDs include the use of synthetic polymers, oligonucleotides, oligopeptides, and electronically active materials.[10−13] However, there remain significant challenges associated with the use of ligand-exchange chemistry to give tailored coverage as surface oxidation, changes in QD size and size distribution, and diminished photoluminescence often accompanying ligand-exchange chemistry. Thus, a new design and synthetic approach are required to combine the QD nanocrystals and the organic electronic/semiconducting materials to overcome the existing limitations and enable the development and exploitation of a new generation of high-performance PVs, LEDs, and sensors.

In addition, functional macromolecules are useful in a variety of nano- and biotechnological, therapeutic, and drug delivery applications.[4−8,14,15] Compared to well-known conjugated linear chain polymers, the unusual electronic and photophysical properties of π-conjugated macromolecules, for example intramolecular energy transfer in multichromophoric systems,[5] exciton and charge localization phenomena,[15,16] and charge carrier mobility,[16] are also of broad fundamental interest. Regarding emissive materials for optoelectronic devices, the macromolecular topology is expected to reduce or eliminate strong intermolecular interactions and aggregation that often lead to excimer formation and reduced emission quantum yields in linear chain conjugated polymers.[6,8,15,17] However, while p-type (donor or hole transport) conjugated macromolecules have been extensively investigated to date,[1,6,8,15−17] n-type (electron acceptor) conjugated macromolecules capable of electron transport and light emission are required for applications in organic electronics and sensors.[5a,18,19]

In this communication, we report design, synthesis, and characterization of a novel n-type nanocrystalline organic−inorganic hybrid material by incorporating electron-accepting and light-emitting CdSe QD nanocrystals in the core and 4-hexylphenyl-4-phenylquinoline n-type emissive chromophore in the periphery. The monomers and key compounds were characterized by ^{1}H and ^{13}C NMR, FT-IR, elemental, thermogravimetric, X-ray diffraction (XRD: Rigaku X-ray diffractrometer), and transmission electron microscope (TEM: Joel JEM-1230 equipped with a Gatan UltraScan 4000SP 4K × 4K CCD camera) analyses. In addition, their optical (Shimadzu UV-2401PC UV−vis spectrophotometer) and photoluminescent (PL: PTI QuantaMaster Model QM-4/2005 spectrofluorometer) properties were investigated.

We successfully synthesized an n-type nanocrystalline CdSe QDs core−4-hexylphenyl-4-phenylquinoline organic−inorganic hybrid material, including monomers, CdSe QD core precursor compound, and peripheral organic group. This was achieved utilizing a multistep convergent synthetic approach as shown in Figure 1. The diphenylphosphinic chloride-capped CdSe nanocrystal core material (**5**) was prepared by reacting diphenylphosphinic chloride, cadmium acetate, and selenium in tri-*n*-octylphosphine at 270 °C in a one-step reaction. Red powder of the core compound was obtained. The details of reaction procedure, characterization, and properties are described in the Supporting Information. The details of synthesis and characterization of 6-bromo-2-(4-hexylphenyl)-4-phenylquinoline (**4**) are also described in the Supporting Information. The 4-hexylphenyl-4-phenylquinoline chromophore has been chosen as peripheral group because of its excellent photoluminescence, electroluminescence, nonlinear optical, electron accepting, and electron transport properties and thermal stability.[5a]

Using the convergent Grignard reaction (last step in Figure 1), nanocrystalline CdSe QDs−4-hexylphenyl-4-phenylquinoline hybrid material was synthesized by reacting compound **4** with **5** (the reaction procedure is described in the Supporting Information). The hybrid material was separated and purified based on the solubility difference from its reacting components **4** and **5** in methanol and toluene, respectively. This hybrid material forms a red solution in chloroform and is soluble in other common organic solvents such as tetrahydrofuran, toluene,

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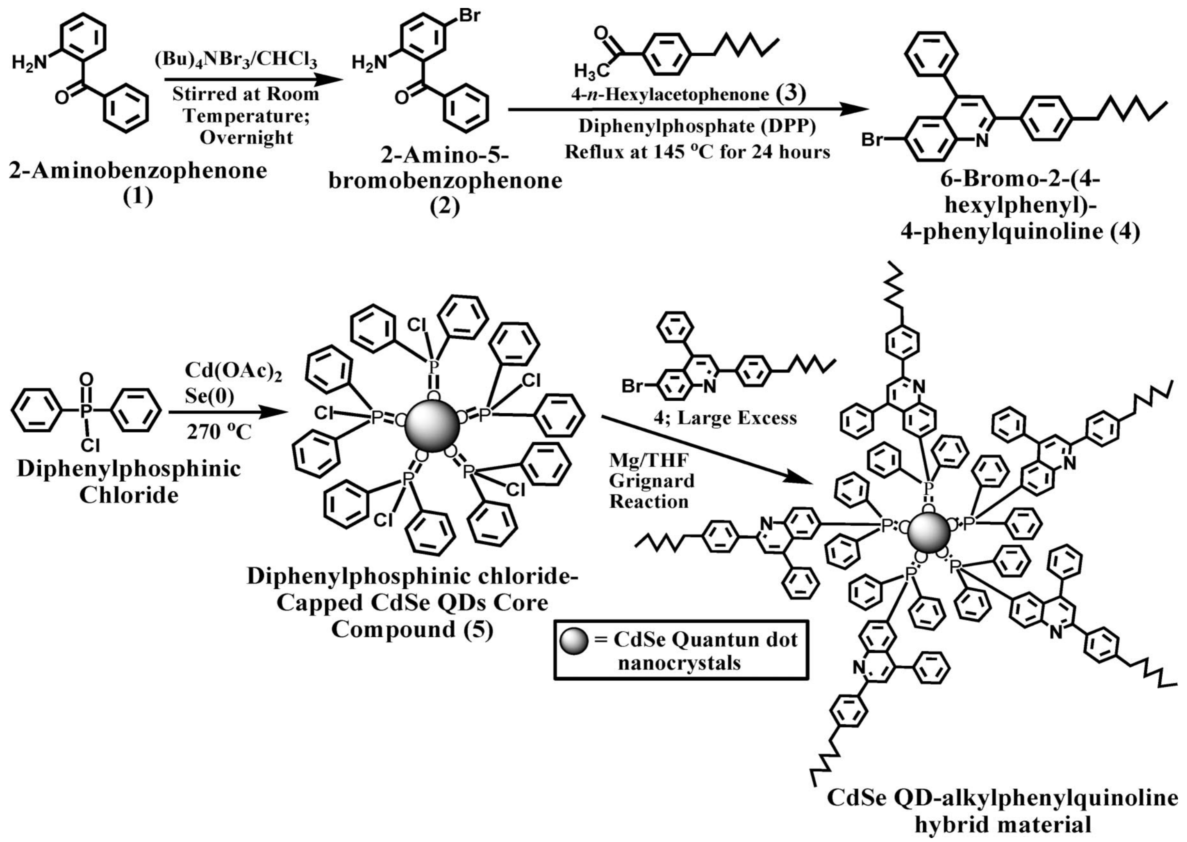

Figure 1. Multistep convergent synthesis of nanocrystalline CdSe QDs−4-hexylphenyl-4-phenylquinoline n-type organic−inorganic hybrid material.

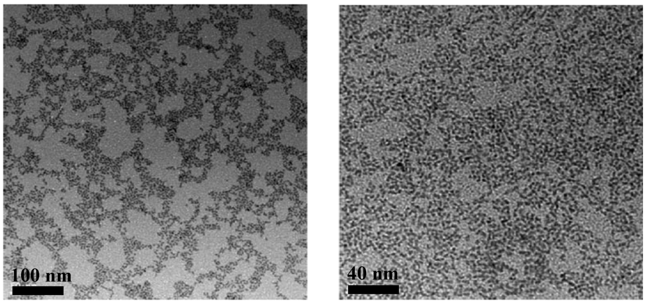

Figure 2. TEM images of CdSe nanocrystal−4-hexylphenyl-4-phenylquinoline hybrid material.

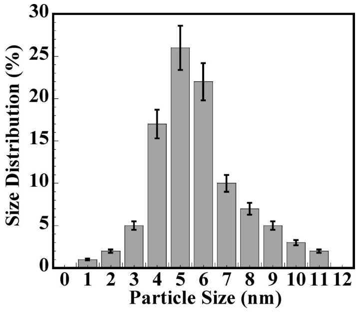

Figure 3. A histogram summarizing the particle size distribution of CdSe nanocrystal−4-hexylphenyl-4-phenylquinoline hybrid material.

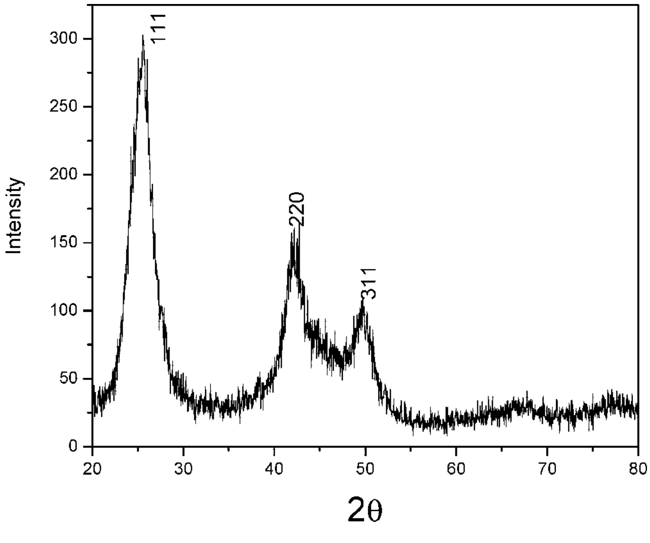

Figure 4. XRD pattern of organic−inorganic hybrid material.

dichloromethane, and dichloroethane. We estimated that 65% of the grafting reaction was completed by analyzing the recovered unreacted 6-bromo-2-(4-hexylphenyl)-4-phenylquinoline group and CdSe QDs core compound and based on the TEM analysis, optical absorption, and photoluminescence measurements described below.

Samples for TEM analysis were prepared by placing a droplet of chloroform solution of the hybrid material on a Formvar lacey carbon-coated 300-mesh copper grid and allowed to evaporate in air at room temperature. The TEM micrographs (Figure 2) show a uniform size distribution of the hybrid nanoparticles (diameter ~ 5 nm), whereas a cluster-like TEM image (Figure S3 in Supporting Information) was obtained for CdSe QDs core compound. These results clearly

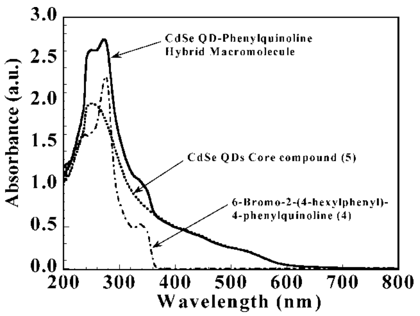

Figure 5. UV−vis optical absorption spectra of CdSe QD nanocrystal−4-hexylphenyl-4-phenylquinoline hybrid compound, CdSe QD core compound, and 6-bromo-2-(4-hexylphenyl)-4-phenylquinoline in chloroform solution.

indicate the successful grafting of 4-hexylphenyl-4-phenylquinoline peripheral group to the CdSe QD nanocrystal core because the grafted 4-hexylphenyl-4-phenylquinoline peripheral group prevents the formation of clusters (or aggregates) of the CdSe QD nanocrystal core of the hybrid material, whereas nongrafted CdSe QDs core compound tend to aggregate. We summarize the hybrid nanoparticles' size and distribution, by analyzing the TEM micrographs, as a histogram which is shown in Figure 3. The hybrid nanoparticles' size and distribution is as follows: 26%, 5 nm; 22%, 6 nm; 17%, 4 nm; 7%, 8 nm; 5%, 9 nm; 5%, 10−11 nm; 5%, 3 nm; 3%, 1−2 nm. The XRD scan, ranging from 20° to 80° (2θ), was carried out using a Cu Kα radiation (λ = 1.545 Å) operating at 30 kV and 25 mA. The sample was run with a continuous scan at a rate of 0.100 deg/min. The crystalline structure of the hybrid dendrimer was confirmed by its XRD patterns (Figure 4), and all the peaks match well with the Bragg reflections of the standard wurtzite structure ($P6_3mc$, a (Å) 4.2990 and c (Å) 7.0100).[20,21] These results demonstrate the development of a monodispersed, nanocrystalline organic−inorganic hybrid material.

Figure 5 shows the UV−vis absorption spectra of the hybrid material along with 6-bromo-2-(4-hexylphenyl)-4-phenylquinoline and CdSe core compound in chloroform solution. The hybrid material exhibits broad optical absorption in the range of 200 − 620 nm with a shoulder band at 340 nm. Its absorption spectrum is slightly different than those of the isolated CdSe core compound and peripheral 6-bromo-2-(4-hexylphenyl)-4-phenylquinoline group, which absorbs in the range of 200−365 nm with the lowest energy absorption band at 340 nm. This observation suggests that both organic and inorganic components, 4-hexylphenyl-4-phenylquinoline peripheral group and CdSe core, contribute to the broad absorption of the hybrid material. The PL spectrum of the hybrid material shows two emission bands at 380 and 560 nm (Figure 6) with an excitation wavelength (λ_{ex}) of 335 nm. In contrast, only the 560 nm emission band with low intensity was observed for the CdSe QD core compound (Figure 6a) by exciting with the same excitation wavelength of 335 nm. The longer wavelength emission band, with a peak at 560 nm, is the characteristic emission band of the CdSe QD core. The shorter wavelength emission band, with a peak at 380 nm, is from the peripheral 4-hexylphenyl-4-phenylquinoline moiety. The intensity of the 380 nm emission band in the hybrid material is significantly reduced compared to that of the isolated peripheral 4-hexylphenyl-4-phenylquinoline compound **4** (Figure 6b), indicating the intramolecular charge transfer (IMCT) from the peripheral 4-hexylphenyl-4-phenylquinoline ligand to the CdSe core. The enhanced intensity of the 560 nm band in the hybrid material compared to that of the isolated CdSe QD compound **5** (Figure 6a) can be attributed to the charge and/or energy transfer from the peripheral 4-hexylphenyl-4-phenylquinoline ligand to the CdSe QD core. Our observations agree with the literature reported charge and/or energy transfer processes observed for macromolecular materials with CdSe nanocrystal core.[22] This charge transfer process can also be rationalized by a simple energy diagram (Figure 7) based on the literature reported energy values of the component moieties.[5a,23] In the present CdSe QD−phenylquinoline hybrid material system, photoinduced electron transfer from the excited 4-hexylphenyl-4-phenylquinoline peripheral group to the CdSe QD nanocrystal core (or from the 4-hexylphenyl-4-phenylquinoline peripheral group to the excited CdSe QD nanocrystal core) is highly favored energetically, based on the known electron affinities (EA) and ionization potentials (IP) of the 4-hexylphenyl-4-phenylquinoline group (EA = 2.85 eV and IP = 5.4 eV)[5a] and CdSe QD core (EA = 3.5 eV and IP = 5.5 eV).[23]

In summary, the method we describe in this communication opens up new possibilities of developing functionally important n-type, nanocrystalline organic−inorganic hybrid materials. Broad optical absorption, high PL emission, and uniformly size-distributed crystalline nanoparticles (diameter ∼ 5 nm) of the hybrid material show high potential of its use as efficient electronic and optoelectronic materials for the development of next generation, energy efficient, and highly durable LEDs, PV (solar) cells, photodiodes, photoxerographic receptors, transistors, lasers, switches, memory devices, and sensors. The hybrid material is soluble in common organic solvents, which makes process control step simpler. By utilizing this convergent synthetic approach, other analogous hybrid materials with proper peripheral groups can be synthesized.

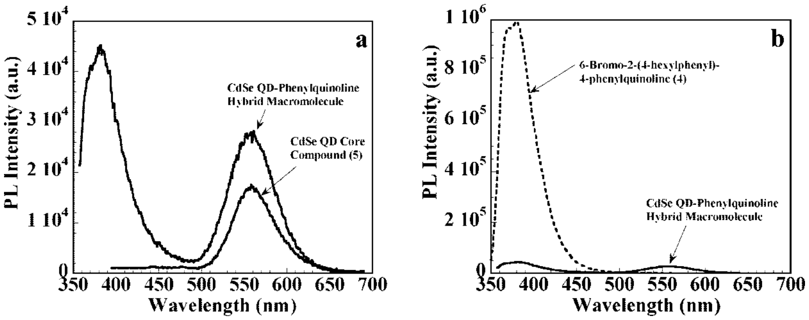

Figure 6. Photoluminescence spectra of CdSe nanocrystal−4-hexylphenyl-4-phenylquinoline hybrid material, CdSe QD core compound, and 6-bromo-2-(4-hexylphenyl)-4-phenylquinoline in chloroform solution.

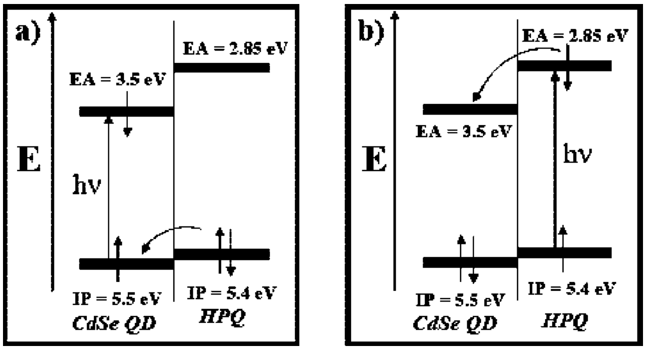

Figure 7. A simple schematic energy diagram based on the known literature energy values of the component moieties. HPQ represents the peripheral 4-hexylphenyl-4-phenylquinoline group.

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Supporting Information Available: Detailed synthetic procedures and characterizations of CdSe QDs core−4-hexylphenyl-4-phenylquinoline organic−inorganic hybrid material, CdSe QD core, key monomers, and phenylquinoline peripheral group. This material is available free of charge via the Internet at http://pubs.acs.org.

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