Article

Quantum Dots Tailored with Poly(*para*-phenylene vinylene)

Habib Skaff, Kevin Sill, and Todd Emrick

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 16 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Quantum Dots Tailored with Poly(*para*-phenylene vinylene)

Habib Skaff, Kevin Sill, and Todd Emrick*

Contribution from the Polymer Science & Engineering Department, Conte Center for Polymer Research, 120 Governors Drive, University of Massachusetts, Amherst, Massachusetts 01003

Abstract: In polymer–nanoparticle composites, uniform dispersion of the nanoparticles carries advantages over cases where nanoparticle aggregation dominates. Such dispersion has been particularly difficult to obtain in the case of composites prepared from nanoparticles and conjugated polymers. Here, we show that cadmium selenide nanocrystals, or quantum dots, can be integrated into thin films of poly(*para*-phenylene vinylene) (PPV) without aggregation. The two key departures from previous studies of quantum-dot/electronic polymer composites are (1) the synthesis of high-quality quantum dots directly in novel, functional ligands, thus eliminating the need for ligand exchange, and (2) polymerization chemistry that grafts PPV to the quantum dot surface. Solid-state photoluminescence spectra of composite materials prepared by these novel techniques reveal the critical importance of the quantum dot–polymer interface that will enable new investigations in nanoparticle-based light-emitting devices.

Introduction

Quantum dots provide a functional platform for novel materials and devices that benefit from the unique physical properties that arise from their quantum-confined nature, giving rise to properties between those of the molecular and the bulk.[1,2] For semiconductor quantum dots such as CdSe, variation of particle size provides continuous and predictable changes in fluorescence emission. Such quantum dots are under investigation as the basis for new materials and devices including photovoltaic cells,[3,4] light-emitting diodes,[5–7] bio-sensors,[8–11] and hybrid materials prepared by directed- and self-assembly techniques.[5,12–16] However, exploitation of quantum dots in device applications requires an appropriate manipulation of their solubility or miscibility within the host environment. This in turn requires a tailoring of the ligand periphery at the quantum dot surface.

Seminal efforts and subsequent studies centered on the preparation of cadmium selenide quantum dots have provided samples of extremely high quality, that are chemically passivated by tri-*n*-octylphosphine oxide (TOPO) ligands to give a hydrophobic and chemically inert ligand shell.[17–19] Subsequent conversion of TOPO-covered quantum dots to water-dispersible materials requires ligand exchange to give coverage, for example, with α,ω-thioalkanoic acids,[20] or related compounds with multivalent coordination sites.[21] Recent studies centered on tailored ligands to cover quantum dots include the use of synthetic polymers,[12,22,23] oligopeptides,[10] oligonucleotides,[9] and electronically active materials.[24] There remain significant challenges associated with the use of ligand-exchange techniques to give these tailored coverages, as surface oxidation, changes in quantum dot size and size distribution, and diminished photoluminescence often accompany ligand-exchange chemistries. Nevertheless, ligand exchange is standard practice for the introduction of new surface functionality to quantum dots, as the high-temperature nanocrystal growth methods are not compatible with most organic functional groups. Here, we present (1) the growth of highly photoluminescent CdSe

(1) Brus, L. *J. Phys. Chem. Solids* **1998**, *59*, 459.
(2) Alivisatos, A. P. *Science* **1996**, *271*, 933.
(3) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.
(4) Leatherdale, C. A.; Kagan, C. R.; Morgan, N. Y.; Empedocles, S. A.; Kastner, M. A.; Bawendi, M. G. *Phys. Rev. B* **2000**, *62*, 2669.
(5) Lee, J.; Sundar, V. C.; Heine, J. R.; Bawendi, M. G.; Jensen, K. F. *Adv. Mater.* **2000**, *12*, 13.
(6) Schlamp, M. C.; Peng, X. G.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837.
(7) Gao, M. Y.; Richter, B.; Kirstein, S. *Adv. Mater.* **1997**, *9*, 802.
(8) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016.
(9) Pathak, S.; Choi, S. K.; Arnheim, N.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4103.
(10) Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Green, T. M.; Anderson, G. P.; Sundar, V. C.; Bawendi, M. G. *Phys. Status Solidi B* **2001**, *224*, 277.
(11) He, L.; Musick, M. D.; Nicewarner, S. R.; Salinas, F. G.; Benkovic, S. J.; Natan, M. J.; Keating, C. D. *J. Am. Chem. Soc.* **2000**, *122*, 9071.
(12) Fogg, D. E.; Radzilowski, L. H.; Dabbousi, B. O.; Schrock, R. R.; Thomas, E. L.; Bawendi, M. G. *Macromolecules* **1997**, *30*, 8433.
(13) Thompson, R. B.; Ginzburg, V. V.; Matsen, M. W.; Balazs, A. C. *Science* **2001**, *292*, 2469.
(14) Lin, Y.; Skaff, H.; Emrick, T.; Dinsmore, A. D.; Russell, T. P. *Science* **2003**, *299*, 226.
(15) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
(16) Sill, K.; Emrick, T. *Chem. Mater.* **2004**, *16*, 1240.

(17) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
(18) Peng, X. G.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019.
(19) Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 183.
(20) Aldana, J.; Wang, Y. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 8844.
(21) Clapp, A. R.; Medintz, I. L.; Manro, J. M.; Fisher, B. R.; Bawendi, M. G.; Mattoussi, H. *J. Am. Chem. Soc.* **2004**, *126*, 1240.
(22) Skaff, H.; Emrick, T. *Chem. Commun.* **2003**, 52.
(23) Skaff, H.; Ilker, M. F.; Coughlin, E. B.; Emrick, T. *J. Am. Chem. Soc.* **2002**, *124*, 5729.

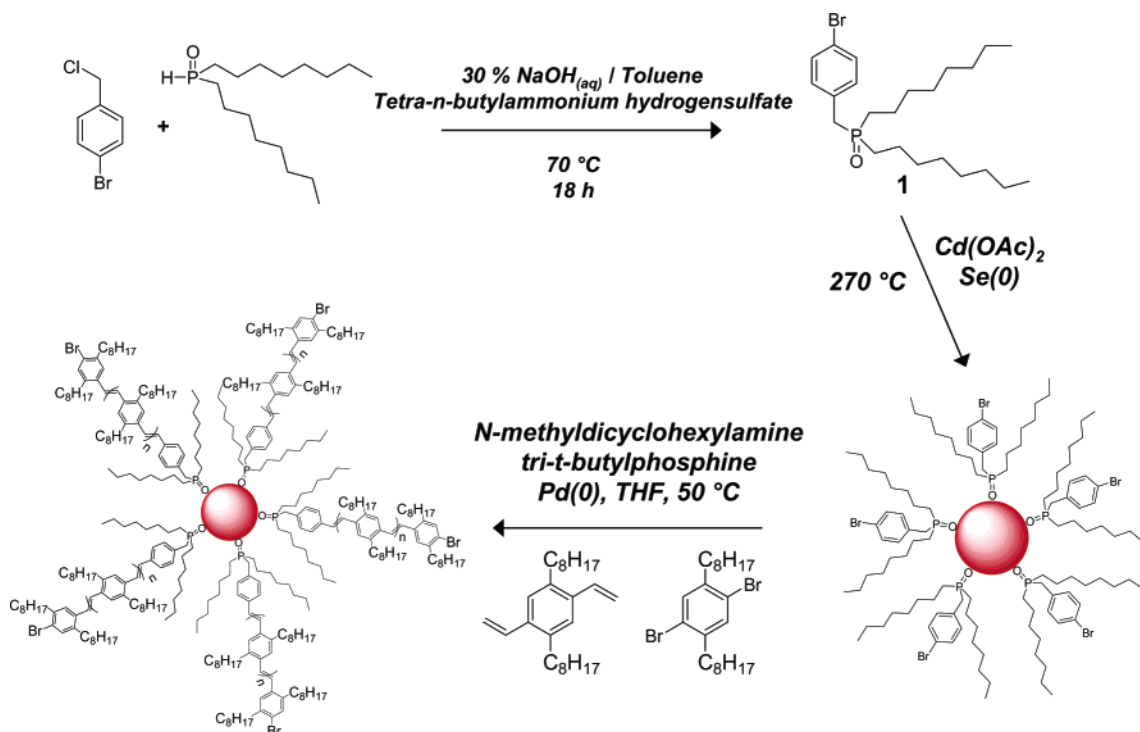**Figure 1.** Synthesis of ligand **1**, growth of **1**-covered CdSe nanocrystals, and tailoring of nanocrystals with PPV by polymerization from the crystal surface.

nanocrystals in a functional ligand that is stable at high temperatures, and (2) the subsequent use of these functionalized quantum dots for the preparation of PPV−CdSe composite materials.

The interest in quantum dot−electronic polymer composites is based on the use of these composites for a new generation of devices such as photovoltaic cells[3,24] and light-emitting diodes.[7,25,26] Numerous advances, as well as difficulties, related to the fabrication of such devices from nanoparticle-based composites have been encountered. One key problem is centered at the polymer−quantum dot interface. The insulating TOPO-coverage limits charge transport between the quantum dots and the surrounding matrix. Furthermore, the use of either TOPO-covered or TOPO-free ("stripped") quantum dots leads to nanoparticle aggregation within the polymer matrix and diminished interfacial interactions. Recent elegant approaches have targeted a tuning of the ligand environment to match the polymer of interest, for example, polythiophene-covered nanocrystals in a polythiophene matrix.[24] Here, we show that for poly(*para*-phenylene vinylene)−quantum dot composites, an intimate connection of the polymer to the quantum dot surface profoundly impacts the photophysics of the resulting composites.

Results and Discussion

Two novel methods, depicted in Figure 1, enable the effective dispersion of CdSe quantum dots into thin films of PPV: (1) growth of the quantum dots in a phenyl bromide-functionalized phosphine oxide ligand, shown as compound **1**, and (2) copolymerization of 1,4-divinylbenzene and 1,4-dibromobenzene derivatives in the presence of **1**-covered quantum dots for the surface-grafting of PPV. The nanoparticle growth method

gives quantum dots with high quantum yield, and the absence of ligand-exchange chemistry allows for the inherent photoluminescence properties of the as-grown particles to be maintained. Furthermore, the polymerization method eliminates the difficulties associated with attempted blending of quantum dots into polymer materials such as PPV.

Compound **1** contains a phosphine oxide group similar to that of TOPO, as well as a phenyl bromide substituent to be used in subsequent polymerization chemistry. This novel phosphine oxide was prepared in 85% yield by nucleophilic substitution of di-*n*-octylphosphine oxide[27] on 4-bromobenzyl chloride under phase transfer conditions, using tetra-*n*-butyl-ammonium hydrogen sulfate (Bu$_4$NHSO$_4$) in a mixture of toluene and NaOH$_{(aq)}$. Compound **1** showed good stability at high temperatures (250−275 °C), a critical feature for growth of high-quality nanocrystals with narrow size dispersion. When **1** was used in place of TOPO in the quantum dot synthesis, high-quality, spherical nanocrystals were obtained. Figure 2a shows a high-resolution transmission electron microscope (TEM) image taken on a typical sample of **1**-covered quantum dots. Electron diffraction revealed the crystalline nature of these functionalized quantum dots, and UV−vis and photoluminescence measurements on hexane solutions of **1**-covered nanocrystals confirmed their quantum-confined nature and considerable quantum yield (65%) (Figure 2b). Taken together, these data confirm the successful preparation of high-quality, functionalized quantum dots, where ligand-exchange chemistry is not necessary to achieve the functionalized nanocrystal periphery.

1-Covered quantum dots were then used as starting materials in the synthesis of PPV−quantum dot composite materials, using the mild, palladium-catalyzed Heck-type coupling conditions

(24) Milliron, D. J.; Alivisatos, A. P.; Pitois, C.; Edder, C.; Fréchet, J. M. J. *Adv. Mater.* **2003**, *15*, 58.
(25) Gao, M. Y.; Richter, B.; Kirstein, S. *Synth. Met.* **1999**, *102*, 1213.
(26) Coe, S.; Woo, W. K.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800.

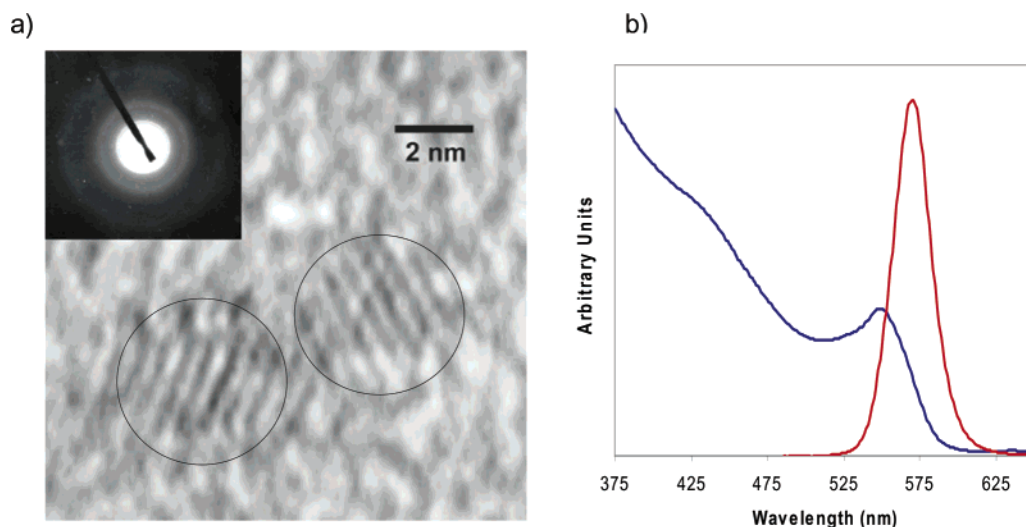(27) Williams, R. H.; Hamilton, L. A. *J. Am. Chem. Soc.* **1952**, *74*, 5418.

Figure 2. (a) Transmission electron micrograph of two functional CdSe nanocrystals (circled for clarity) at 650 K magnification. The lattice structure observed, as well as the electron diffraction pattern (inset), shows the crystalline nature of the functionalized quantum dots. (b) UV−vis spectrum (blue curve, band-edge absorption at 550 nm) and photoluminescence spectrum (red curve, emission maximum at 570 nm; fwhm 30 nm) of **1**-covered quantum dots in chloroform.

reported recently by Fu and co-workers.[28] A tetrahydrofuran solution of **1**-covered quantum dots was stirred at 50 °C for 24 h in the presence of the monomers 1,4-di-*n*-octyl-2,5-divinyl-benzene and 1,4-dibromo-2,5-di-*n*-octylbenzene[29] using Pd(0) catalysis. The PPV−quantum dot product was isolated by precipitation into methanol, which effectively separated the palladium catalyst and short-chain PPV not bound to the quantum dot surface. The quantum dot−PPV composite material was isolated as the precipitate and was subsequently redissolved in common organic solvents (e.g., hexanes, CH_2Cl_2, THF, etc.). Evidence to support successful polymerization was given by nuclear magnetic resonance (NMR) spectroscopy on $CDCl_3$ solutions of the composite material, where singlet resonances at δ 7.33 and 7.23 ppm were observed, corresponding to aromatic and vinylic resonances, respectively, in the polymer backbone. Matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry measurements performed on this quantum dot−PPV composite material confirmed the formation of PPV oligomers, primarily trimers and tetramers. The polycondensation method used in this study is designed to give a mixture of PPV connected to the quantum dots and "free" or unconnected PPV that acts as the host matrix. It should be emphasized that the observed compatibility of the quantum dots with the polymerization conditions was key, as quantum dot degradation was not observed by any of the analytical methods used (TEM, UV−vis, and fluorescence).

As illustrated in Figure 3, striking differences were observed in the transmission electron micrographs and photoluminescence spectra of the composite material relative to PPV−CdSe blends prepared by simply mixing the two components. By TEM, blends of **1**- and pyridine-functionalized quantum dots (Figure 3a and b, respectively) are seen to aggregate in PPV, while the quantum dots are observed to be well-dispersed throughout the PPV matrix in the case of the composite material (Figure 3c). The PPV−quantum dot composites were found to possess unique optical properties not found in the blends, also illustrated in Figure 3. In dilute solution of both blends and composites

(blue curves of Figure 3), PPV oligomers dominate the photoluminescence emission spectra (emission maxima approximately 440 nm), and only a small fluorescence contribution from the quantum dots is seen. In the solid state, PPV also dominates the photoluminescence of the blends (red curves of Figure 3a and b). However, in the solid-state photoluminescence spectrum of the composite, the quantum dot emission dominates (red curve, Figure 3c, emission maximum approximately 570 nm), with almost complete quenching of the PPV emission. Loss of PPV fluorescence in the solid state, and emergence of a strong quantum dot emission, is observed even in cases of very low quantum dot loading (2−5 wt %). This stands in marked contrast to the high loadings (50% or greater) typically needed to observe quantum dot emission in quantum dot−conducting polymer blends.

The spectra and micrographs of Figure 3 demonstrate the importance of nanocrystal dispersion and effective surface tailoring. While the quantum yield of PPV is expected to diminish when going from solution to the solid state, due to self-quenching, this in itself does not explain the spectroscopic observations of Figure 3c. These observations can be rationalized by the increased PPV−quantum dot contact in the solid state relative to the more extended conformation of PPV around the quantum dots in solution. Such contact facilitates energy transfer, such that holes generated in the PPV are transferred to the quantum dots, where they subsequently recombine with electrons in the quantum dot core, resulting in emission. Photoluminescence emission from the quantum dots in the solid state is by far more intense in the composite materials prepared by the novel polymerization reported here. Figure 4 reveals the high quantum dot loadings required to observe emission in PPV−quantum dot blends, for the examples of 10, 30, and 50 wt % quantum dots in PPV. In these blends, the presence of substantial nanoparticle aggregation, as demonstrated by TEM measurements, limits interfacial contact between the polymers and quantum dots, thus limiting energy transfer pathways, and furthermore leading to self-quenching of nanoparticle fluorescence. Even at quantum dot loadings of 50 wt %, emission from PPV dominates the photoluminescence profile. The low weight

(28) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989.
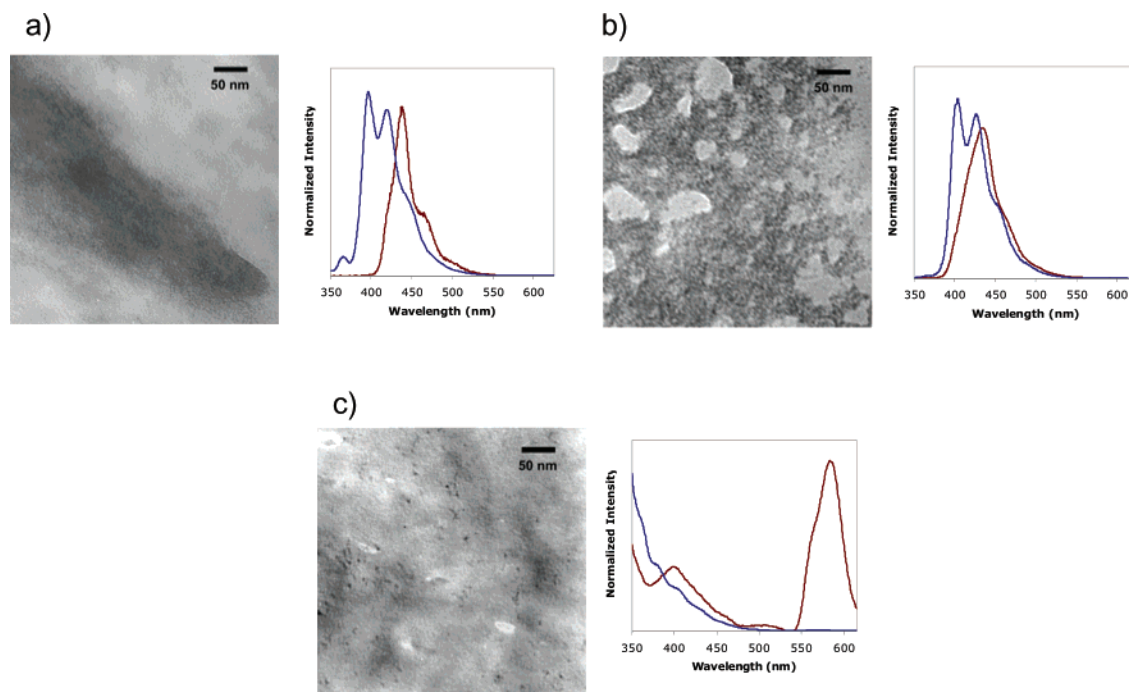(29) Rehahn, M.; Schlüter, A. D.; Feast, W. J. *Synthesis* **1988**, 386.

Figure 3. TEM micrographs and photoluminescence spectra of PPV−quantum dot composites. In each of the three photoluminescence profiles, the blue curve is solution photoluminescence and the red curve is solid-state photoluminescence. (a) **1**-Functionalized CdSe nanocrystals blended with PPV; (b) pyridine-covered CdSe nanocrystals blended with PPV; and (c) composite CdSe nanocrystal−PPV, where PPV was grown from the nanocrystal surface. Each sample contained about 5 wt % nanocrystal. In the dispersed example of case c, the solid-state photoluminescence emission profile is dominated by the quantum dots.
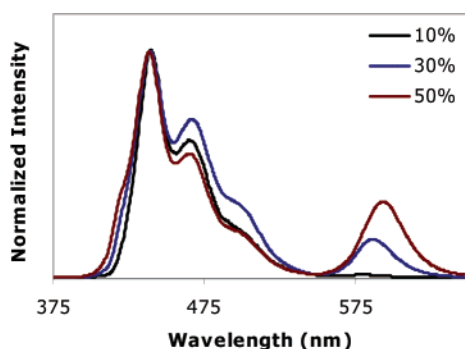

Figure 4. The effect of **1**-functionalized CdSe nanoparticle loading (10, 30, and 50 wt %) on the solid-state fluorescence emission spectra of CdSe−PPV oligomer blends.

percent of quantum dots that can be utilized effectively in the composite materials described here carries important fundamental and practical implications for future advances in quantum dot-based materials, assemblies, and devices. This will also open opportunities for the use of quantum dots in conjunction with a range of polymer materials, where the intrinsic structural, morphological, and self-assembly properties of the polymers can be exploited, rather than precluded by an overwhelming presence of the quantum dots.

In summary, we have demonstrated a preparation of "PPV-tailored quantum dots" by methods that allow for their direct connection to electronically active polymers. The ability to tailor and disperse quantum dots in PPV thin films in this fashion dramatically impacts the photophysical properties of these materials relative to conventional blends. While PPV coverage is emphasized here, the novel quantum dot growth methods, and the general polymerization methodology, carry the potential for broad applicability that will enable new physical studies and device fabrication using polymer−quantum dot composite materials.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

JA047260R