Monodisperse Oligo(phenylene vinylene) Ligands on CdSe Quantum Dots: Synthesis and Polarization Anisotropy Measurements

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Nanocomposites composed of π-conjugated polymers and semiconductor nanoparticles have attracted enormous recent interest in the context of optoelectronic and photovoltaic devices because of their combined optoelectronic properties and facile solution processability.[1−4] Electroluminescent materials fabricated by casting films from solutions of blended poly(phenylene vinylene) (PPV) and CdSe quantum dots are promising examples of such nanocomposites, exhibiting low operating voltage and voltage-dependent emission.[1] However, nanoparticle−polymer blends typically suffer from phase separation and nanoparticle aggregation, as well as the presence of insulating surfactant ligands on the particle surface. Both issues can be addressed effectively and simultaneously by surface functionalizing the nanoparticles with the polymer of interest, as seen in films of quantum dots functionalized with polythiophene or PPV ligands.[5−8] The improved and interesting properties of CdSe−polymer nanocomposite materials prepared through this surface functionalization design, relative to simply blended materials, warrant further exploration of this concept.

In prior work, we prepared oligo(phenylene vinylene) (OPV)−CdSe hybrid nanocomposites by polymerization of suitable OPV precursors from arylbromide-functionalized quantum dots. This "grafting-from" polymerization leads to a polydispersity of chain lengths emanating from the nanoparticles. Thus, we undertook a synthesis of well-defined OPV ligands for quantum dot surface functionalization by "grafting-to" (i.e., ligand exchange). In principle, this approach enables better tuning of OPV absorption and emission properties to those of the quantum dots. Moreover, this method refines the size distribution of a given nanostructure sample, precluding size variation due to ligand length heterogeneity, to more closely mirror the size distribution of the core nanoparticles. Here we describe the synthesis and single nanoparticle spectroscopy of such nanostructures, revealing a surprising correlated directionality in absorption and emission moments from the quantum dot core, suggesting new ways for these species to be used in optoelectronic devices.

The OPV ligands for this study were prepared by the stepwise process shown in Scheme 1, utilizing conditions reported by Jorgensen and co-workers,[9] but installing a di-n-octylphosphine oxide group onto the OPV chain-end for coordination to the nanoparticle surface. Diethylphosphonate ester-functionalized benzaldehyde **3** was prepared by palladium-catalyzed Heck coupling of phenylbromide **1** and vinylbenzene **2**. Acetal protection of **3** gave **4**, which was converted to **6** (denoted **OPV-1**) by Horner−Wadsworth−Emmons (HWE) coupling with phosphine oxide-functionalized benzaldehyde **5**. The longer oligomer **7** (**OPV-2**) was generated by coupling the deprotected version of **6** with phosphonate **4**. Both **OPV-1** and **OPV-2** were purified by column chromatography, eluting with dichloromethane/methanol mixtures.

Scheme 1
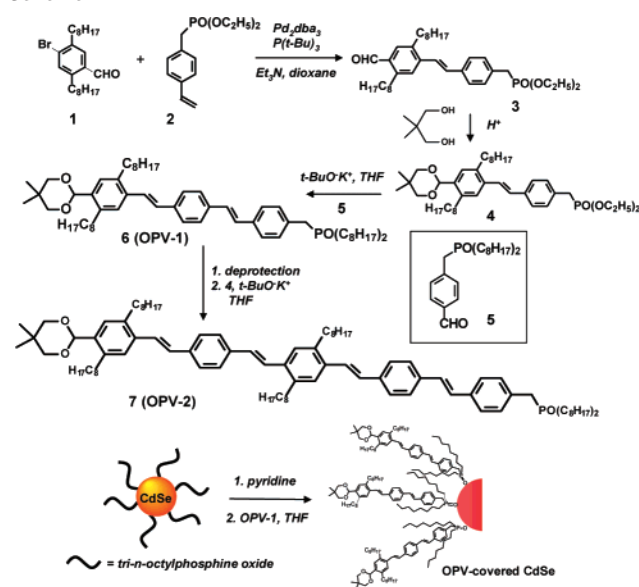
The HWE couplings to give **OPV-1** and **OPV-2** were achieved in 70 and 50% yields, respectively. Detailed syntheses and characterization are given in the Supporting Information. Characterization of **OPV-1** and **OPV-2** by ^{1}H NMR spectroscopy revealed the characteristic trans-vinylic signal at 6.97 ppm ($J = 16.2$ Hz) and a doublet from the methylene group attached to the phosphorus at 3.15 ppm. ^{31}P NMR spectroscopy showed a single peak at 47 ppm.

Tri-n-octylphosphine oxide (TOPO)-covered CdSe quantum dots were prepared according to literature methods,[10] then subjected to ligand exchange with **OPV-1**, going through pyridine-covered particles (Scheme 1, bottom). Pyridine-covered quantum dots were dispersed in a THF solution of **OPV-1** and heated to 55 °C for 24 h under argon atmosphere. The **OPV-1**-covered quantum dots obtained were precipitated repeatedly in chloroform/methanol mixtures to remove unbound ligands. The solid-state emission spectrum of thin films of **OPV-1**-covered CdSe (350 nm excitation) showed emission primarily from the quantum dots, reflecting an energy transfer from the OPV to the quantum dots, in accord with our prior studies on CdSe nanoparticles covered with polydisperse phenylene vinylenes.[7] The excitation spectrum of **OPV-1**−CdSe, recorded by collecting the emission of quantum dots (at 560 nm), resembles the OPV absorption spectrum, further supporting the proposed energy transfer process. Longer oligomers such as **OPV-2** are desired for ligand coverage but, so far, give particles with low solubility, possibly due to unfavorable sterics associated with using these longer oligomers in the grafting-to approach.
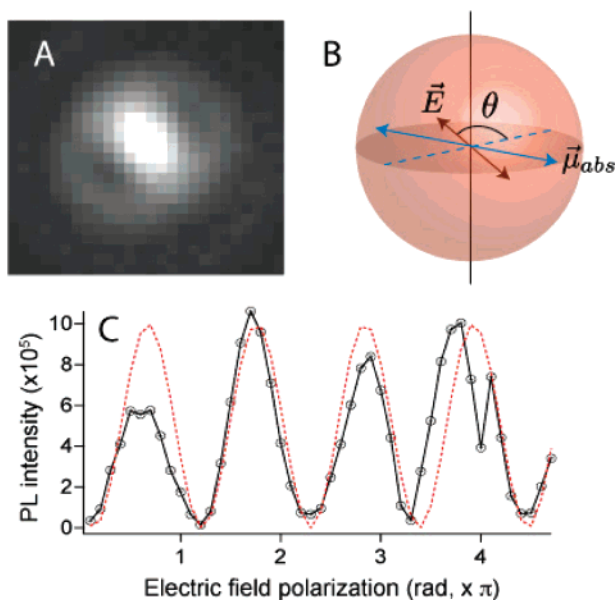
Figure 1. (A) Defocused fluorescence image of OPV−CdSe nanostructure, showing a spatial intensity pattern characteristic of a linear dipole oriented in the x−y plane. (B) Schematic showing a polarized excitation geometry of absorption moment (μ_{abs}), laser electric field (E), and separation angle (θ). (C) PL intensity of a single CdSe−OPV nanostructure during 4π full rotations of E (lines and markers), showing nearly 100% extinction for perpendicular excitation, along with a $\sin^2\theta$ fit (dashed line).

Interestingly, **OPV-1**-covered CdSe nanostructures exhibit absorption and emission properties characteristic of linear dipoles, similar to those found in organic dyes[11] and collapsed polymer chains.[12] Figure 1A shows the spatial photon distribution from a single **OPV-1**−CdSe nanostructure under slight defocusing in a high numerical aperture (NA) optical system (Inverted Nikon TE300 microscope, 1.4NA) excited in epi-illumination geometry using a 405 nm GaN diode laser. These images, along with aberration-corrected numerical simulations (Supporting Information), provide evidence of a highly linear electric dipole radiator.[13] The dipole images are filtered spectrally to exclude any photoluminescence emission from the OPV ligands, such that the dipole emission distribution originates only from the pseudo-spherical CdSe core. A typical dipole image is shown in Figure 1A. Thus, it appears that the presence of OPV ligands on the quantum dot surface results in a one-dimensional emission dipole moment, in contrast with the ordinarily observed 2-D degenerate emission moments.[14,15] To rule out a potential contributing dipole emission from high aspect ratio particles (nanorods), which are known to exhibit such linear emission geometries,[16] transmission electron microscopy (TEM) was performed, confirming the spherical nature of the particles following ligand exchange with **OPV-1**.

To further probe the one-dimensional nature of this transition, polarization anisotropy measurements were performed on single OPV-covered nanostructures, similar to studies by Chung et al.[14c] on quantum dots and Hu et al. on flexible MEH-PPV chains.[17] Figure 1B depicts the experimental excitation geometry; the linearly polarized electric field of the excitation laser E is rotated at a constant rate in the x−y plane, thereby sweeping angles θ between the absorption transition moment and E. For a linear absorber, this results in a $\sin^2\theta$ intensity variation during constant rotation. Figure

1C shows the transient for a single **OPV-1**−CdSe nanostructure undergoing 4π rotations of E (lines and markers), along with a $\sin^2\theta$ fit (dashed line) taken over 50 s (angular integration ∼14°). This transient shows a remarkable reproducibility in phase of the polarization response, and >90% extinction of emission for μ_{abs} orthogonal to E, making these nanoparticles attractive as potential robust polarization-sensitive optical switches. We note that all the CdSe−**OPV-1** particles observed gave very deep modulation depth, a result inconsistent with a random distribution of 2-D degenerate dipole emitters, in which an appreciable fraction of dots would give near zero modulation depth.

In summary, OPV-covered quantum dots were prepared and characterized as single nanostructures. Defocused optical imaging and excitation polarization anisotropy measurements separately reveal a l-D character to both the absorption and emission dipole moments, a novel effect in functionalized quantum dot systems. While the origin of this effect is not clearly understood, we speculate that the appearance of linear polarization in the QD emission is associated with photoinduced charge transfer from the ligand to the QD surface.[18,19] The pinned excess surface charges act to break the spherical symmetry and thus the 2-D degeneracy. While further experiments are necessary to confirm this, we note that this effect might be exploited to produce novel polarization modulation devices.

Supporting Information Available: Experimental procedures and characterization of compounds in Scheme 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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