

# Quantum dots coordinated with conjugated organic ligands: new nanomaterials with novel photophysics

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**Abstract** CdSe quantum dots functionalized with oligo-(phenylene vinylene) (OPV) ligands (CdSe-OPV nanostructures) represent a new class of composite nanomaterials with significantly modified photophysics relative to bulk blends or isolated components. Single-molecule spectroscopy on these species have revealed novel photophysics such as enhanced energy transfer, spectral stability, and strongly modified excited state lifetimes and blinking statistics. Here, we review the role of ligands in quantum dot applications and summarize some of our recent efforts probing energy and charge transfer in hybrid CdSe-OPV composite nanostructures.

**Keywords** Single molecule spectroscopy · Hybrid nanomaterial · Quantum dot · Blinking · Conjugated polymer · Energy transfer · Charge transfer · Photovoltaic · Atomic force microscope

## Introduction

Over the past several years, semiconductor nanocrystals (quantum dots) have attracted enormous interest in virtually all areas of the physical sciences. The tunable optical

and electronic properties of quantum dots make them ideal building blocks in nanoscale photonic, photovoltaic, and light-emitting diode (LED) device applications [1–19]. In addition, their robust photoluminescence makes them attractive for probing dynamics in biological systems at the single molecule level [20–23]. One of the keys to the successful use of quantum dots in any application is the ability to tailor their surface with ligands. The ligands bound to the surface of quantum dots largely dictate solution properties, and their miscibility in a particular medium including organic solvents, water, and polymer films. The ability to control this surface functionality has been the subject of considerable research in recent years, [21, 24–29] and promises to direct the feasibility of quantum dots in applications. Here, we summarize some of our recent efforts probing energy and charge transfer between quantum dots and their bound ligands and discuss new possibilities for their use as building blocks in next generation nanoscale devices.

## The role of ligands in quantum dot synthesis

The most widely utilized quantum dots to date are II–VI semiconductor nanocrystals such as cadmium selenide, cadmium sulfide, and cadmium telluride. Preparation methods for the synthesis of high quality and nearly monodisperse cadmium selenide quantum dots have typically utilized tri-*n*-octylphosphine oxide (TOPO) and tri-octylphosphine (TOP) as these compounds provide the most controlled growth conditions. Prior to the use of TOPO, CdSe nanocrystals were prepared by using organometallic reagents in inverse micellar solution [30]. Bawendi and co-workers showed that injection of the metal-organic precursors into a hot (~150–300 °C) reaction pot with TOPO

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and TOP as solvent resulted in a short burst of homogeneous nucleation and a narrow size distribution covered by TOPO ligands [31]. Size-control is primarily achieved by varying the reaction temperature and the initial precursor concentration. Since TOPO serves as the primary surface ligand, the nanoparticles obtained by this method are soluble in hydrophobic solvents such as toluene and hexanes.

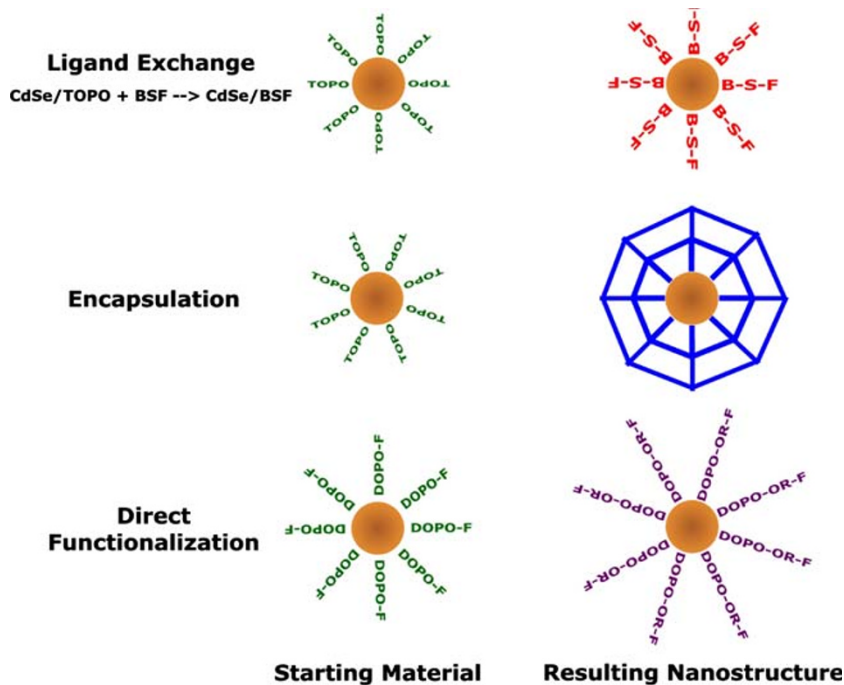
Nanocrystal surface defects such as dangling selenide bonds have been described as charge carrier trap sites, and have been associated with less than optimal optical (and device) performance [32]. The objective of increased brightness of photoluminescence (quantum yield) has led to efforts of passivating surface defects with organic or inorganic ligands, either during the synthesis or afterwards. For example, Talapin et al. showed that incorporation of alkylamines, particularly hexadecylamine (HDA), into the synthesis led to much improved quantum yields (as high as 50%) [33]. This dramatic improvement was attributed to the passivation of the cadmium selenide surface defects with the HDA ligands. However, Alivisatos pointed out that it is generally very difficult to simultaneously passivate both anionic and cationic surface sites by organic ligands because there would always remain some dangling bonds [34]. For this reason, inorganic passivation is generally more effective for creating very bright quantum dots. An additional layer (shell) of higher band gap material grown around the surface of the nanocrystal (core) serves to passivate both the anionic and cationic surface dangling bonds in these “core/shell” or “capped” systems. In the case of zinc sulfide (CdSe/ZnS) [33, 35, 36] or cadmium

sulfide (CdSe/CdS) [34, 37, 38] coated cadmium selenide quantum dots, much improved photoluminescence properties and photostability is observed with quantum yields of up to 85% in solution [38]. However, this inorganic surface modification creates a new nanocrystal system with properties which are dependent on both core and shell materials. In addition, the shell can serve as an insulating medium that limits electronic communication with surface ligands or the environment.

### Ligand functionalization of quantum dots

The hydrophobicity of TOPO and other ligands on the CdSe surface renders these quantum dots soluble in organic solvents only. Ligand exchange, in which the TOPO ligands are replaced with the ligand of choice can, for example, give quantum dots solubility in water or make them amenable to chemical reactions. Quantum dots can be also be encapsulated by a shell of material such as a polymer, micelle, or bead that makes them more soluble in particular media [39]. Such encapsulation, of course, significantly increases the volume of the quantum dot-based material, which may not be desirable in some applications, such as biosensors and live cell imaging. More recent efforts have concentrated on replacing TOPO as the solvent during the synthesis with a ligand that possesses functionality that allows for subsequent surface grafting without the need for ligand exchange [40]. Figure 1 depicts these different methods schematically.

**Fig. 1** Comparison of the different methods of modifying ligand coverage on CdSe quantum dots where **B**, **S**, **F**, and **OR** refer to binding, spacer, functional, and organic oligomer groups, respectively



Ligand exchange typically employs a functional moiety with a high affinity for binding to the surface of quantum dots (**B**), a spacer group (such as an alkyl or aryl chain, **S**), and a functional group or chain that possesses the chemical property of interest (**F**). Thiols have proven useful in ligand exchange due to their high affinity for the particle surface. For example, Chan and Nie used mercaptoacetic acid to render CdSe/ZnS quantum dots soluble in biological (aqueous) media by taking advantage of the fact that the mercapto group would easily bind to a zinc atom [21]. The value of  $\alpha,\omega$ -thioalkanoic acids is found in part in the chain-end carboxyl group that can be used in coupling to biomolecules. This method has its limitations, however, with inefficient loading of the desired ligands onto the quantum dots and poor long-term stability due to oxidation [24, 25]. Alternatives to thiols include carbodithioates, [26] dendrons, [27] peptides, [28], and oligomeric phosphines [29]. In the case of carbodithioates, nearly quantitatively exchange has been achieved with the initial TOPO surface ligands [26].

Despite the drawbacks, such as loss of fluorescence and incomplete ligand coverage, ligand exchange is necessary in most cases, as the high-temperature of nanocrystal growth is not compatible with most organic functional groups. Recently, as an alternative to TOPO, [40] phenyl bromide-functionalized dioctylphosphine oxide, DOPO-Br, (shown in Fig. 2) was used. DOPO-Br proved stable to the high temperature reaction conditions of quantum dot growth, giving DOPO-Br covered CdSe nanocrystals. Subsequently, Heck-type coupling was used to grow

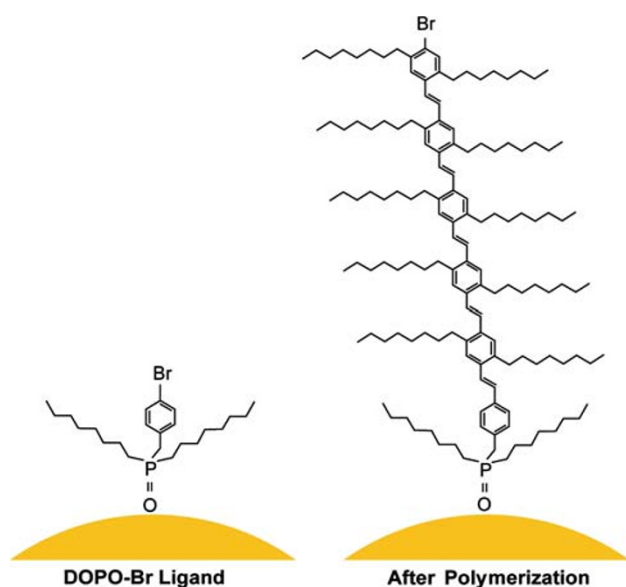
poly- or oligo-(phenylene vinylene) (PPV or OPV) ligands from the functional quantum dots.

## Photophysics of isolated QD-OPV nanostructures

### Biological applications of quantum dots

Applications involving quantum dot—ligand combinations are most numerous in the biological arena, especially for imaging and tracking of biological structures or single biomolecules of interest [20–22]. Conventional organic dyes possess broad emission spectra and narrow absorption profiles. This combination results in fluorescence signal overlap from the different dyes employed and also requires as many excitation sources as the number of dyes used. Quantum dots, on the other hand, possess narrow emission profiles and broad absorption bands. In addition, quantum dots allow for long-term observation of tagged molecules with less photobleaching than seen for conventional organic dyes. Weiss has recently reviewed biologically relevant applications of the many relevant quantum dot—ligand combinations [22]. For example, streptavidin coverage has proven attractive for its use in combination with biotinylated proteins and antibodies [41].

There has recently been a great deal of interest in energy transfer involving quantum dots and fluorescently-labeled biomolecules [42–55]. Fluorescence resonance energy transfer (FRET) from an excited state donor to a ground state acceptor occurs such that the overlap of the donor's emission and acceptor's excitation spectra, and the spatial distance between the two components, determine the efficiency of the energy transfer process [56]. Mattoussi recently reviewed many of the studies of FRET involving quantum dots and biological systems [55]. Bawendi and co-workers first demonstrated FRET energy transfer involving mixtures of different sizes of quantum dots [57]. Emission from smaller, higher energy, quantum dots decreased as emission from the larger, smaller energy level spacing, quantum dots increased. The first observation of FRET between quantum dots and biological molecules was made in 2001 by Van Orden and co-workers [42]. In that study quantum dots with biotinylated bovine serum albumin ligands interacted with streptavidin that was labeled with a rhodamine dye. Emission from the dye was observed to increase as emission from the quantum dot diminished. Kotov and co-workers reported energy transfer to quantum dots from native tryptophan molecules in an interacting protein [43]. Other interesting FRET applications include interactions with metalloproteins [51] and DNA, [49] a basis for photodynamic therapy, [54] and nanosensor design [52]. Ha recently demonstrated FRET between single quantum dots and their ligands, [46] and Mattoussi



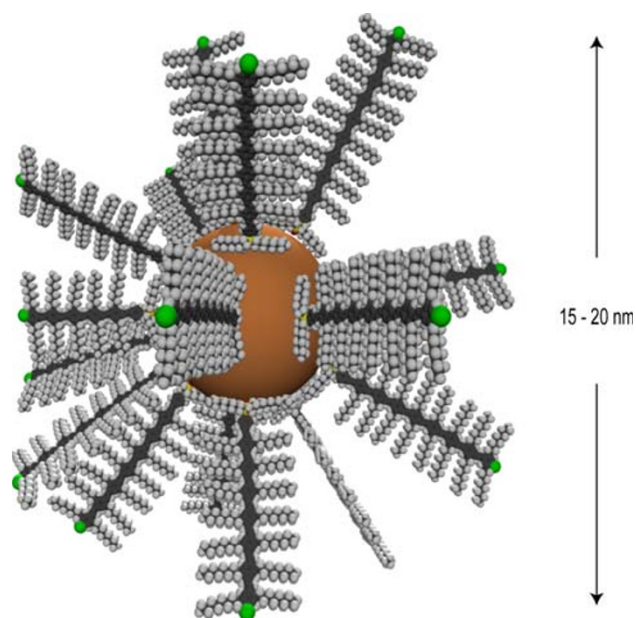
**Fig. 2** *Left*: Phenyl bromide-functionalized dioctylphosphine oxide, DOPO-Br ligand and *Right*: oligo-(phenylene vinylene) (OPV) ligand grown from the DOPO-Br precursor

reported spectrally resolved energy transfer between quantum dots and fluorescently tagged proteins [53].

### Solid state applications of quantum dots

The optoelectronic properties (broad absorption spectrum and narrow emission profile) of quantum dots make them very attractive building blocks for photovoltaics, [1–7] lasers, [8–11] and light emitting diodes (LED) [12–19]. Energy transfer between quantum dots and other building blocks (such as conjugated organic polymers) that compose such devices has been studied [58–62]. In addition, unique quantum dot—ligand combinations enable the preparation of novel nanostructure materials. For example, Raymo and co-workers introduced quantum dots with photochromic ligands that allow for a mechanism to activate and suppress energy transfer to the ligands [63]. The same authors also functionalized quantum dots with pH sensitive ligands that allow luminescence switching under chemical stimulation [64, 65].

One of the difficulties involved in constructing devices from quantum dots is creating electrical contacts to electrodes that allow charge transport while at the same time preventing quantum dot aggregation. Early photovoltaic devices incorporating quantum dots suffered from aggregation of the particles, which is far from optimal for facilitating charge separation and transport to the respective electrodes [1]. However, aggregation is greatly reduced or eliminated when the conjugated organic molecules are prepared as ligands for binding to the quantum dot surface [5, 40]. Figure 3 shows a structural schematic depicting a CdSe



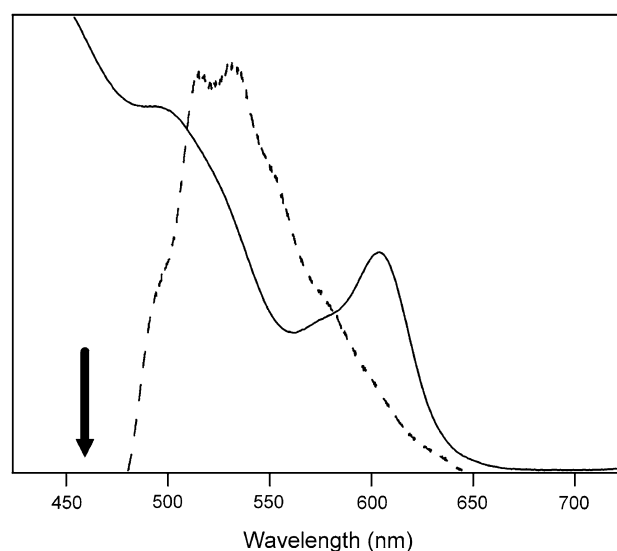
**Fig. 3** Schematic depiction of a 4 nm CdSe quantum dot with oligo-(phenylene vinylene) ligands attached to the particle surface

quantum dot with oligo-(phenylene vinylene) ligands (CdSe-OPV nanostructure).

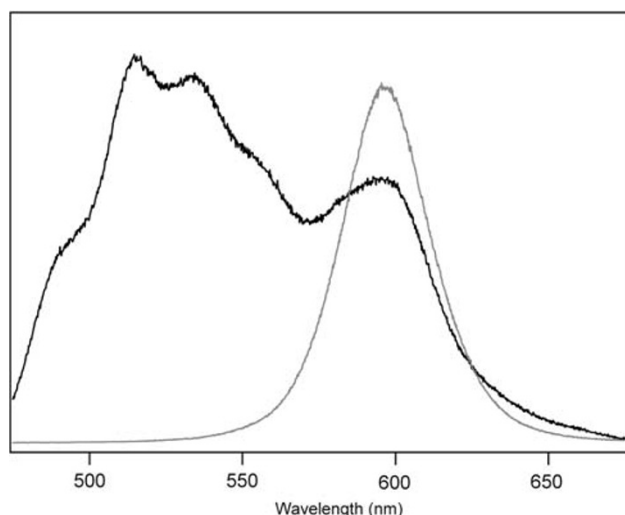
### Enhanced energy transfer in CdSe-OPV nanostructures

We recently studied the optical properties of hybrid CdSe-OPV nanostructures. The length of the OPV ligands on the quantum dots was designed such that the OPV's fluorescence emission spectrum would overlap the absorption profile of the quantum dots, and thus promote energy transfer. Compared in Fig. 4 are emission and absorption spectra of OPV and quantum dots, respectively, that are representative in the CdSe-OPV nanostructures. Figure 5 compares the emission spectrum of a blended mixture of OPV and CdSe quantum dots with that of a thin film of CdSe-OPV nanostructures. The fluorescence emission spectra of bulk mixtures or blends of OPV and CdSe quantum dots revealed emission from both components. In the case of the CdSe-OPV nanostructures, however, virtually no OPV emission was observed, [66] implying quenching of the OPV emission when coupled to the quantum dot. Possible mechanisms for this observation include energy transfer from the OPV to the CdSe, which is afforded by the close coupling of the quantum dot and its ligands, and charge transfer, which is energetically favorable from OPV to the CdSe.

In an effort to determine the effects of the bound conjugated organic ligands on individual quantum dot photo-physics, single molecule spectroscopic measurements were performed on the CdSe-OPV nanostructures deposited on



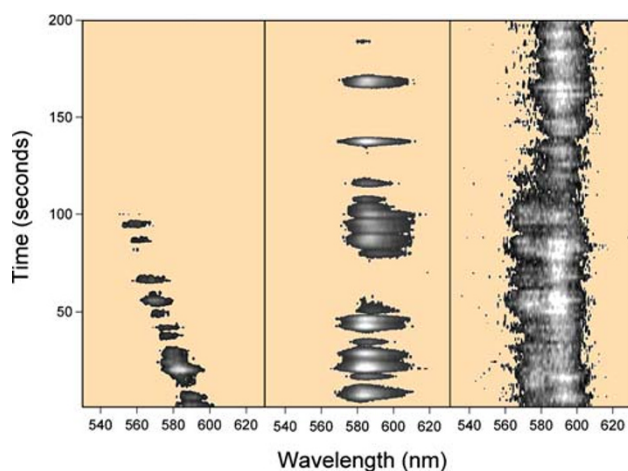
**Fig. 4** Absorption curve for ~4.5 nm CdSe quantum dots (*solid curve*) and oligo-(phenylene vinylene) (OPV) photoluminescence spectrum (*dashed curve*). The arrow denotes the wavelength location of the excitation laser (457 nm). The cutoff below 500 nm in the OPV photoluminescence is due to the choice of filters



**Fig. 5** Fluorescence emission spectra of a CdSe/OPV bulk blend (*black*) and CdSe-OPV nanostructures (*gray*). The weight percentage of quantum dots and OPV in the samples is approximately the same (~50:50)

clean glass coverslips from extremely dilute solutions [66]. A Nikon TE300 inverted microscope with a 1.4NA oil objective was used to obtain single nanostructure fluorescence emission spectra. Spectra were acquired by focusing the CdSe-OPV emission from the side-port of the microscope onto an Acton SP2150i dual-grating spectrograph, and detected with a PI/Acton Pixis 400B back-illuminated CCD camera, with a typical exposure time of 2 s.

Significant differences are apparent when comparing the photoluminescence emission spectra of the CdSe-OPV nanostructures and the DOPO-Br covered or TOPO covered ZnS capped CdSe quantum dots. Figure 6 compares the emission spectra of single DOPO-Br covered (*left*),



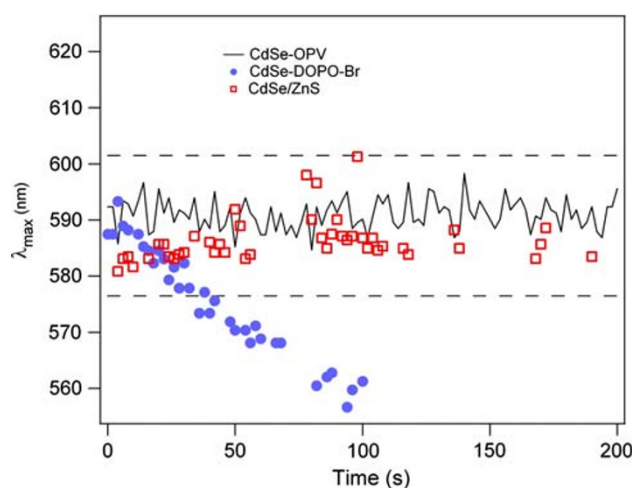
**Fig. 6** Time resolved fluorescence emission spectra of DOPO-Br covered (*left*), ZnS-capped (*middle*), and OPV covered (*right*) CdSe quantum dots. The integration time of the experiment was 2 s

ZnS-capped (*middle*), and OPV- covered (*right*) CdSe quantum dots. Whereas the emission intensity from both the DOPO-Br covered and ZnS capped quantum dots is intermittent, the emission from the single CdSe-OPV nanostructure is continuous on the time scale of the experiment. As expected, the spectrum of the single DOPO-Br covered quantum dot quickly blue-shifts and disappears, due to photodegradation of the nanocrystal.

Interestingly, the emission spectra from some of the CdSe-OPV nanostructures revealed a shoulder to the high energy side. This higher energy shoulder is not discernable in the bulk emission spectra and only recovered in the single nanocrystal emission studies. Further, the magnitude of the intensity of this shoulder varied with time and also from nanostructure to nanostructure. We attribute this peak to incomplete energy transfer from the OPV ligands to the quantum dot. Figure 7 compares the peak emission wavelengths of the three nanocrystals from Fig. 6 and reveals that the CdSe-OPV nanostructures exhibit very little spectra drift.

#### Charge transfer in quantum dot applications

Charge transfer between quantum dots and the surrounding environment is the basis for many of the solid state applications involving semiconductor nanocrystals [1–19]. The transfer of electrons (or holes) between a conjugated organic polymer matrix and a quantum dot, for example, enables the flow of charge throughout a device [67]. Lian has written a comprehensive review of this process with respect to these applications [68]. Recently, the transfer of charge carriers between quantum dots and their ligands has led to the development of new analyte sensing protocols



**Fig. 7** Spectral fluctuations of a CdSe-OPV nanostructure compared with that of representative DOPO-Br covered and ZnS-capped CdSe quantum dots. The dotted lines indicate the full-width at half maximum (FWHM) of the quantum dot emission peak

[69–72]. A most exciting area of quantum dot research is related to the use of electron donating organic ligands for blinking suppression [66, 73–79].

Brus and co-workers first demonstrated that single quantum dots exhibit fluorescence intermittency, or the tendency to blink [80]. Since that time, researchers have studied this phenomenon intensely using various experimental parameters and theoretical models [81–87]. The most common explanation for blinking in quantum dots revolves around the trapping of exciton charge carriers in surface defects. When a quantum dot is excited, the resulting exciton delocalizes over the volume of the nanocrystal. If the electron or hole becomes “trapped” in a surface defect, photoluminescence ceases.

Recently, Hohng and Ha reported a blinking suppression in solutions of quantum dots [73]. When the individual streptavidin-coated CdSe/ZnS quantum dots were exposed in solution to  $\beta$ -mercaptoethanol, their blinking essentially disappeared and constant radiative emission was observed. The authors determined that only thiol-containing species with short chain lengths were able to suppress the quantum dot blinking. Since thiols are effective electron donors, the authors argued that these ligands donate electrons to fill surface traps. This deactivates the blinking mechanism, and leads to a more constant emission. Tinnefeld and co-workers soon after reported similar blinking suppression using mercaptoethylamine but interpreted their observations as a dramatic increase in the blinking kinetics [77]. In other words, the presence of the ligands perturbed the dynamics of the exciton. Recently, Mulvaney and co-workers were also able to modify the blinking dynamics in quantum dots through the variation in the choice of ligands [76].

#### Blinking suppression in CdSe-OPV nanostructures

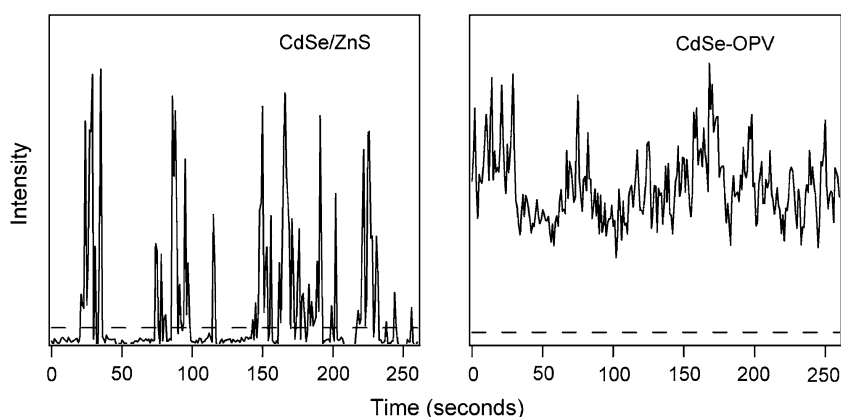
Charge transfer in the form of electrons from phenylene vinylene to CdSe quantum dots has been shown to be

energetically favorable because of the relative electron affinities of the two species [1]. Oligo-(phenylene vinylene), or OPV, ligands would therefore be expected to serve as good electron donating ligands for quantum dots and in principle suppress quantum dot blinking. Figure 8 compares the solid state emission from ZnS-capped quantum dots with that from OPV-covered CdSe quantum dots recorded using an electron multiplying CCD camera (PI/Acton PhotonMax) with an integration time of 2 s. Whereas significant intensity fluctuations and dark periods lasting tens of seconds are commonly observed in either TOPO-covered or ZnS-capped quantum dots, CdSe quantum dots with OPV ligands (see Fig. 3 for a structural schematic), on the other hand, reveal continuous emission.

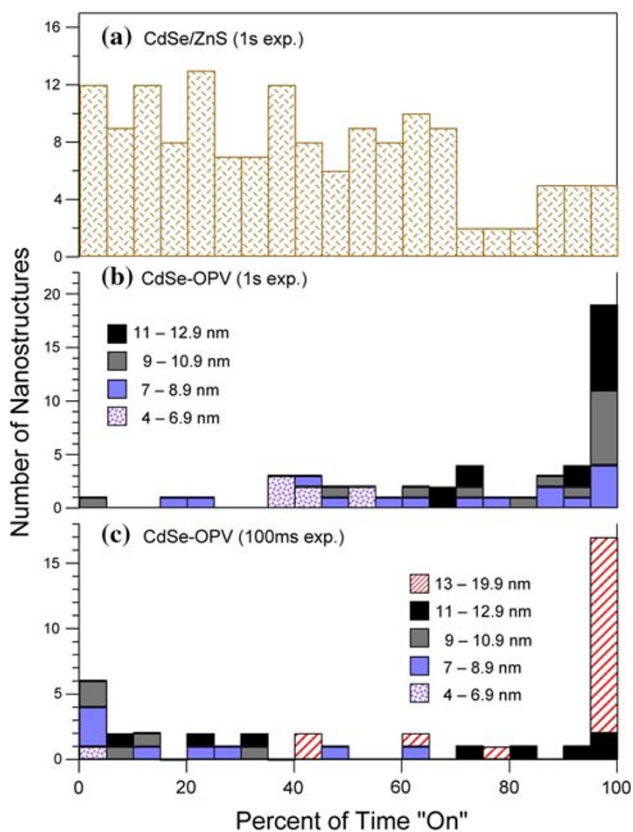
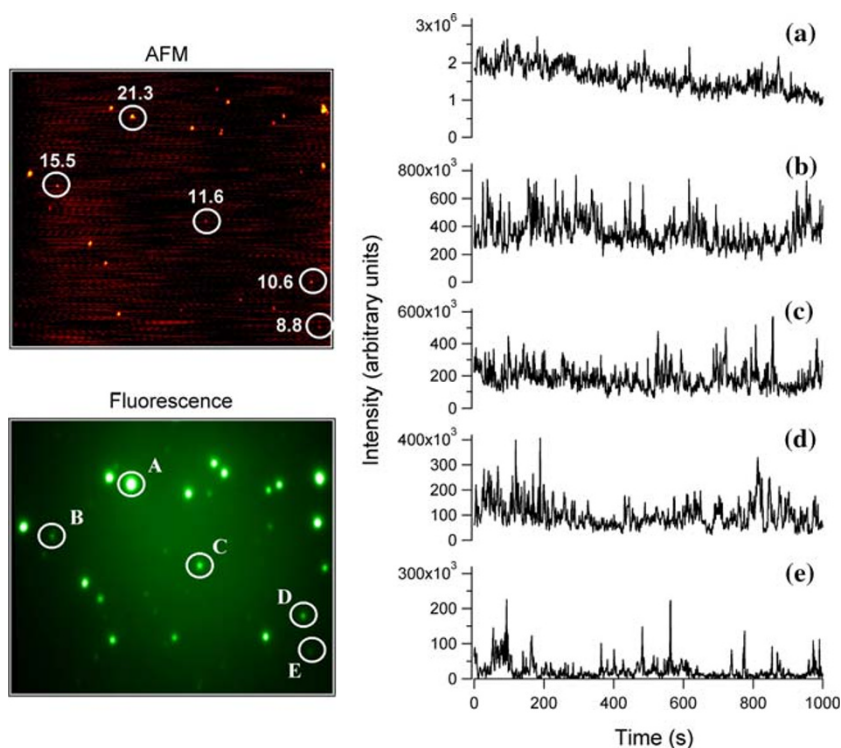
Although blinking suppression was observed in many of the individual CdSe-OPV nanostructures studied, the total intensity from each nanostructure and time spent in an “off” or “dark” state varied. For this reason we decided to correlate OPV ligand coverage to the fluorescence properties for each nanostructure using atomic force microscopy (AFM) as a measure of ligand coverage [74]. Figure 9 shows typical correlated AFM and fluorescence images, as well as emission timetraces for the indicated CdSe-OPV nanostructures. Of the nanostructures shown, only the one with the smallest (8.8 nm) height measurement revealed true blinking behavior (i.e., with dark periods), indicating that ligand coverage was playing a significant role in the blinking mechanism.

Figure 10 compares the fluorescence duty factors, or the time period of emission, for nearly 200 CdSe-OPV nanostructures and 150 ZnS-capped quantum dots. Whereas there is significant spread in the data, and the average emitting time is near 40% for the ZnS-capped quantum dots, most of the CdSe-OPV nanostructures were observed to emit light nearly 100% of the time [74]. Most interesting, however, is the fact that the larger the height signature (more OPV ligands), the longer the period of light emission. A quantum dot which has many OPV

**Fig. 8** Fluorescence emission from representative individual ZnS-capped and OPV-covered CdSe quantum dots. The size of the quantum dot was 4.3 nm in both cases and the integration time of the experiment was 2 s. The dotted lines indicate the  $2\sigma$  noise threshold of the experiment. When emission was below this cutoff the quantum dot was defined as residing in a “dark” or “off” state



**Fig. 9** Correlated AFM and fluorescence scenes for the same CdSe-OPV nanostructures. The intensity profiles for the labeled nanostructures are included at the right and the height signatures (in nm) of each are indicated



**Fig. 10** Histogram of fluorescence duty factors from (a) 4.3 nm ZnS-capped CdSe quantum dots; (b and c) CdSe-OPV nanostructures sorted using size-correlated measurements. The exposure time in (a) and (b) was 1 s and in (c) 100 ms

ligands is expected to have a higher height measurement than one which has few or none and those that are fully covered with OPV ligands are expected to exhibit a height of approximately 15 nm. In fact, an AFM height distribution of nanostructure sizes was obtained that agrees very well with the schematic shown in Fig. 3, and this distribution was confirmed through MALDI and dynamic light scattering experiments. For CdSe-OPV nanostructures greater than 13 nm in diameter, light was emitted all of the time, using a 1 s integration, and most of the time using 100 ms. At 100 ms integration times, however, blinking was observed in the smaller nanostructures. This observation indicates that blinking is not completely suppressed, but rather the blinking statistics are modified by the presence of the ligands.

## Summary and outlook

Quantum dots have received much attention in recent years due to their unique photophysical properties. Research into their surface chemistry is driven by the desire to optimize such structures for many applications that seek to take advantage of these photophysical properties. The surface-bound ligands of quantum dots in many ways dictate their success or failure in applications, as the ligands determine the solubility or miscibility in a particular medium, and also mediate energy and charge transfer with the surrounding environment. Interest in both energy and charge

transfer between quantum dots and their ligands has grown steadily over the years, and includes the design of novel architectures and hybrid structures that have led to some very exciting phenomena, such as blinking suppression. With the application of a growing list of synthetic methods for the functionalizing of quantum dots, the outlets for such engineered nanostructural components are growing rapidly.

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