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Observation of Enhanced Energy Transfer in Individual Quantum Dot−Oligophenylene Vinylene Nanostructures

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Blends of conjugated organic polymers with inorganic quantum dots have received a great deal of recent attention for their potential in advanced optoelectronic devices and photovoltaic energy-harvesting applications.[1−6] Among the interesting features of these composite systems is the electronic communication between conjugated organic and quantum dot[7,8] or quantum rod[9] components, which results in enhanced fluorescence quantum yields,[10] energy transfer, and charge transport in bulk thin films.[11] However, as noted by several authors, phase segregation of the organic and inorganic components becomes problematic when constructing efficient thin-film optoelectronic devices. Some recent efforts have centered on preparing a new class of quantum dot−organic composite nanostructures with conjugated organic ligands directly connected to the quantum dot surface.[7,12] This approach results in efficient suppression of phase separation in bulk films, as well as significant differences in bulk photoluminescence relative to blended samples. In this paper, we report single-molecule fluorescence studies from single quantum dot-conjugated organic nanostructures that show a significant modification in the spectral distribution of fluorescence relative to blended films of the inorganic and organic components, as well as enhanced temporal stability. These effects are attributed to enhanced energy transfer between the conjugated ligand and the quantum dot facilitated by the molecular composite architecture.

The quantum dot−OPV composite materials used in this study were prepared by growing the OPV ligands of three to six phenylene vinylene repeat units directly from phenylbromide-functionalized ∼4.3 nm diameter CdSe quantum dots, where the OPV coordination to the CdSe surface is through chain-end phosphine oxides. This procedure was used to generate the desired composite materials without the need for ligand exchange on tri-*n*-octylphosphine oxide (TOPO)-covered CdSe nanoparticles, which can compromise the photophysical properties of the quantum dots.[13] While inorganic protective layers of ZnS and other larger band gap materials are commonly applied to CdSe quantum dots to prevent surface oxidation and enhance the photoluminescence quantum yield of the CdSe core, this insulating shell also increases the distance between the CdSe core and the surrounding environment, which can decrease energy transfer efficiency in composite blend films. In addition, synthetic constraints limit the ligand chemistries associated with core−shell materials relative to the CdSe core itself.

Individual CdSe−OPV nanostructures were isolated from dilute solution ($\sim 10^{-10}$ M) on clean glass coverslips. All measurements were performed under ambient conditions using a Nikon TE300 inverted microscope with 1.4NA oil objective. Spectra were acquired by focusing the QD−OPV emission from the side-port of the microscope onto an Acton SP2150i dual-grating spectrograph and detected with a Roper Scientific Pixis 400B back-illuminated CCD, with an exposure time of 2 s.

Figure 1A shows typical photoluminescence emission spectra from a blended bulk film of OPV and dioctyl-*para*-bromobenzylphosphine oxide (DOPO−Br)-covered CdSe quantum dots compared with the bulk emission spectrum from a film CdSe−OPV nanostructures—both excited with the 457 nm line of an Ar^+ laser. The spectrum from the blend film was obtained with a CdSe mass fraction of about 50% and is similar to previous reports.[12,14] The fluorescence emission of a bulk film of the CdSe−OPV composite, made by growth of the OPV from the QD surface, is dominated by quantum dot emission, in contrast to the blended case. Figure 1B shows a comparison of the emission spectrum of a single CdSe−OPV nanostructure with that of a single DOPO−Br-covered QD. Interestingly, we observe nearly *complete* extinction of the OPV luminescence in the emission from the single CdSe−OPV nanostructure in the spectral region associated with bulk OPV (500−540 nm). However, a small fraction of spectral measurements show a weak shoulder present immediately to the blue of the quantum dot peak. This additional feature varies considerably in intensity and peak position with time; in fact, most of the spectral measurements are indistinguishable from a DOPO−Br-covered quantum dot. Due to the intermittency of this feature, it is not surprising that it is not observed in the ensemble measurement.

This interesting spectral feature associated with single QD−OPV nanostructure luminescence is seen more clearly by time-resolved fluorescence spectral imaging. Figure 2 compares the emission spectra as a function of time for a single DOPO−Br-covered CdSe QD (2A), a ZnS-capped CdSe dot (2B), and a single CdSe−OPV nanostructure (2C), all for similar sized quantum dot cores. Both the DOPO−Br-covered and ZnS-capped quantum dots exhibit on−off blinking[15,16] (evidenced by the vertical gaps in emission intensity), with the DOPO−Br-covered sample showing a progressive blue shift with time, associated with photodegradation of the dot. The single-molecule CdSe−OPV fluorescence shows similar intensity fluctuations, but interestingly, the quantum dot component of the composite nanostructure does not show evidence of a fully off dark state.

The nearly complete extinction of OPV luminescence from the CdSe−OPV nanocomposite structures can be understood as highly efficient quenching by energy transfer from the OPV moieties to the quantum dot core, as well as from dissociation of excitons in the OPV followed by electron transfer to the quantum dot surface.[11] With the OPV ligands directly attached to the quantum dot surface, we estimate a Förster radius of ∼3 nm (the center-to-center spacing between the dot and OPV ligand) which would correspond to energy transfer rates at least 40 times larger than those of bulk blends of a blue-emitting polyfluorene and ZnS-capped CdSe quantum dots reported previously.[14] The modification of the OPV spectral signature in the composite nanostructure can be understood qualitatively as a “filtering” of the OPV emission by absorption into the quantum dot. The intermittent spectral component associ-

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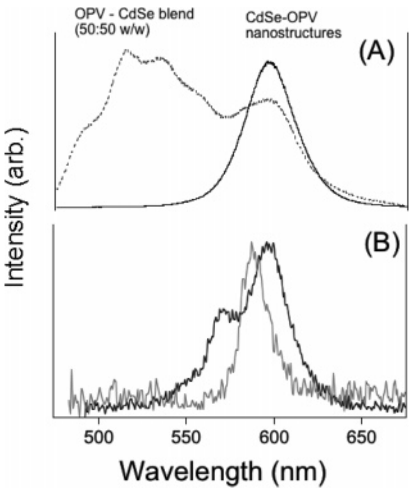

Figure 1. (A) Comparison of bulk-film photoluminescence from a blend of oligophenylene vinylene (OPV) and CdSe quantum dots (dashed curve) and CdSe−OPV nanostructures. (B) Photoluminescence spectrum (2 s integration) from a single CdSe−OPV nanostructure (dark curve) compared with a DOPO−Br-covered CdSe quantum dot of similar size.

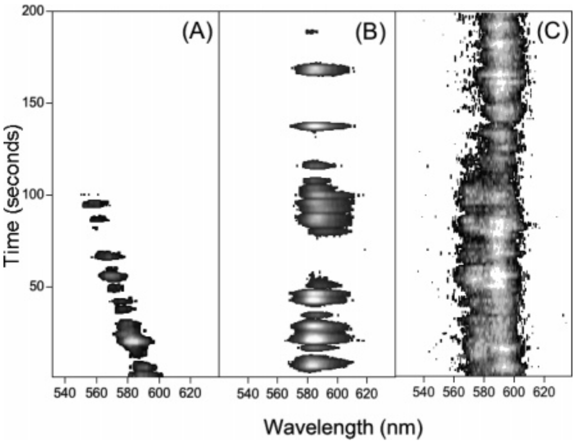

Figure 2. Time-resolved fluorescence spectra from (A) a single DOPO−Br-covered CdSe quantum dot; (B) ZnS-capped CdSe quantum dot; and (C) a single CdSe−OPV nanostructure. Each individual spectral measurement was made with a 2 s exposure time. The quantum dot diameter (∼4 nm) was similar for each example.

ated with OPV emission shown in Figures 1B and 2C is in a wavelength region (∼575 nm) that does not overlap substantially with the quantum dot absorption spectrum due to a characteristic dip in the absorption spectra of CdSe nanocrystals (see Supporting Information), making energy transfer in that particular spectral range less efficient.

The suppression of blinking in the nanocomposite system may be attributed to a diminished vacancy of surface trap states resulting from fast electron transfer (followed by slow nonradiative recombination) from the excited OPV to surface trap states on the quantum dot. Dissociation of excitons within the dot, and subsequent trapping of carriers leading to dark state formation, is thus inhibited because of a competition for a limited number of trap sites. Such suppression was recently observed by Ha and co-workers for CdSe/ZnS quantum dots in solution containing β-mercaptoethanol (BME).[17] They proposed that blinking suppression derived from electron donation from the thiol moiety of the BME to vacant trap sites on the quantum dot. In this composite system, such a mechanism could be facilitated by charge transfer from excited OPV to vacant surface traps on the quantum dot surface.[11] The extent to which the observed blue shift and degradation is suppressed in OPV-coordinated quantum dots varies among individual quantum dots chosen for analysis. However, the effect of the OPV ligands is clear and consistent from batch-to-batch, and the DOPO−Br-covered quantum dots never exhibit this behavior. Further detailed investigations on spectrally resolved fluorescence intensity statistics and correlation of blinking statistics with particle size (see Supporting Information) using an atomic force microscope (AFM) will provide further insight into this interesting new observation.

In summary, single-molecule spectral studies on quantum dot-conjugated organic composite nanostructures have provided evidence of enhanced energy transfer between the OPV and quantum dot components, resulting in dramatically different photoluminescence spectra relative to blended films. A suppression of blinking is also observed in the CdSe−OPV nanostructures that is attributed to efficient charge transport from the excited OPV ligands to trap sites on the quantum dot surface. These results suggest new possibilities in nanostructured organic/inorganic composite nanomaterials for use in optoelectronic and photovoltaic applications.

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Supporting Information Available: Nanostructure preparation, AFM measurements, and additional figures are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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