Observation of enhanced energy transfer in individual quantum dot-oligophenylene vinylene nanostructures

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Preparation of CdSe-oligo(phenylene vinylene) composite nanostructures.
In an inert atmosphere glovebox, a THF solution of phenylbromide-functionalized CdSe nanoparticles (10 mg/mL) was combined in a glass tube with N-methyldicyclohexylamine (0.10 g), tetrakis(triphenylphosphine) palladium (2 mg), and 1-bromo-2,5-di-n-octyl-4-vinylbenzene (0.15 g). The tube was sealed with a Teflon valve, removed from the glovebox, and heated to 90 °C for 16 h. The solution was allowed to cool to room temperature, then centrifuged for 30 minutes. The supernatant was decanted, and the CdSe-oligo(phenylene vinylene) composite material was precipitated using methanol, isolated by centrifugation, dried under a stream of nitrogen, and stored as a solution in THF. 1H NMR spectroscopy on the composite material was used to confirm the successful preparation of oligo(phenylene vinylene): 1H NMR (300 MHz, CD2Cl2, δ) 7.37 (Ar-H), 7.27 (Ar-C=CH-Ar), 2.58 (Ar-CH2), 1.68 (Ar-CH2CH2), 1.21 (alkyl CH2), 0.88 (CH2-CH3) ppm. Photophysical characterization of the composite is described in the text.

Atomic Force Microscope (AFM) Measurements
The fluorescence spectra and intensity profiles of individual CdSe-OPV nanostructures were correlated directly with particle size, using a Digital Instruments Bioscope Atomic Force Microscope in tapping mode. The measured size distribution (9 – 14 nm) agrees well with a 4 nm dot fully decorated with oligo-phenylene vinylene with an average ligand length of 6 monomer units. Figure 1 shows a representative fluorescence image (left), along with a surface height scan of the same area using AFM (right). A z-scan of the particle indicated by the circle is shown in the lower panel.

Figure 1  Fluorescence image (left) correlated with atomic force microscope image (right) of the same individual CdSe-OPV nanostructures. The height trace of the circled nanostructure is also included (bottom). The real-space dimensions of the two images are 2.5 x 2.5 μm.
Absorption and Photoluminescence Emission Curves

Figure 2 shows the absorption curve for a 4.5 nm CdSe quantum dot sample along with a photoluminescence spectrum typical of the oligo-phenylene vinylene (OPV) ligands used in quantum dot-OPV nanostructure single-molecule experiments. The blue edge of the OPV photoluminescence spectrum of OPV is truncated by reflection of wavelengths < 500 nm from the dichroic filter used for 457-nm excitation (arrow).

**Figure 2** Absorption curve for ~4.5 nm CdSe quantum dots (solid curve) and OPV photoluminescence spectrum (dashed curve). The arrow denotes the wavelength location of the excitation laser (457 nm).