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New Meta Nanomaterials Extension II of Optical Enhancement and Photorefractive Two-Beam Coupling - Synthesis and Fabrication of Quantum Dot NLO Polymer Composites

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Composites of CdS quantum dots and a new conjugated polymer were prepared by reacting CdS capped with (3-mercaptopropyl)trimethoxysilane (MPS) and a new conjugated copolymer at different pH (5.5., 7 and 10) at 50 °C for 3 h, under magnetic stirring. Cadmium sulfide quantum dots with face centered cubic zinc blende structure and an average size of 3.02 ± 0.46 nm (Figure 1) were prepared in the presence of MPS following the procedure of Fang, et al. The conjugated polymer, a poly(phenyleneethynylene) copolymer hereafter called pPE (OC12-Co-BzC11OH), was synthesized by Sonogashira-Heck reaction. 13C and 29Si SSNMR spectroscopy of CdS(MPS), the copolymer and composite was studied in order to investigate the functionalization at different pH. The hydrolysis of the methoxy groups of the silane and their successive polymerization, induced by the presence of the OH groups of the phenyleneethynylene, gives rise to superstructures of 200-600 nm in diameter. STEM analysis shows the presence of CdS clusters inside the larger particles and TEM tomography suggests a bilayer vesicle assembly. We note further that the tomographic STEM data and analyses demonstrate that the 3D vesicles formed in the nanocomposites are stable in the solid state under high vacuum conditions.

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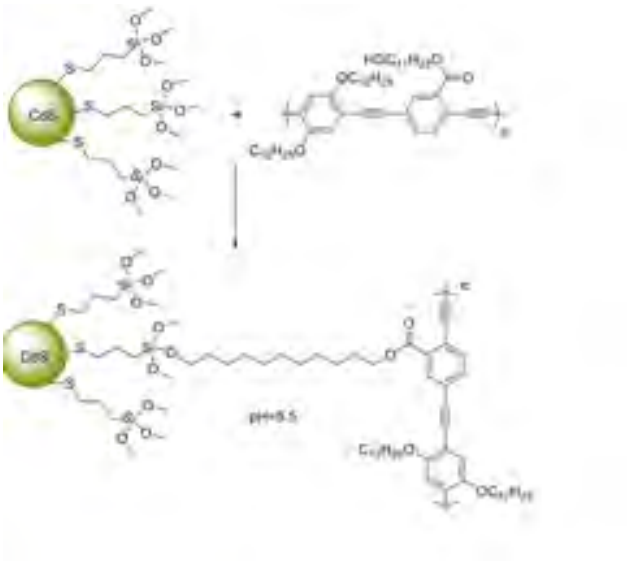
Micellar supramolecular organization of composites based on CdS Quantum Dots and a Phenyleneethynylene copolymer

In search of novel nanomaterials for optical applications, composites of CdS quantum dots and a new conjugated polymer were prepared by reacting CdS capped with (3-mercaptopropyl)trimethoxysilane (MPS) and a new conjugated copolymer at different pH (5.5. 7 and 10) at 50 °C for 3 h, under magnetic stirring, Scheme 1.



Scheme 1. Synthesis of CdS composites.

Cadmium sulfide quantum dots with face centered cubic zinc blende structure and an average size of 3.02 ± 0.46nm(Figure 1) were prepared in the presence of MPSfollowing the procedure of Fang, et al. [1].

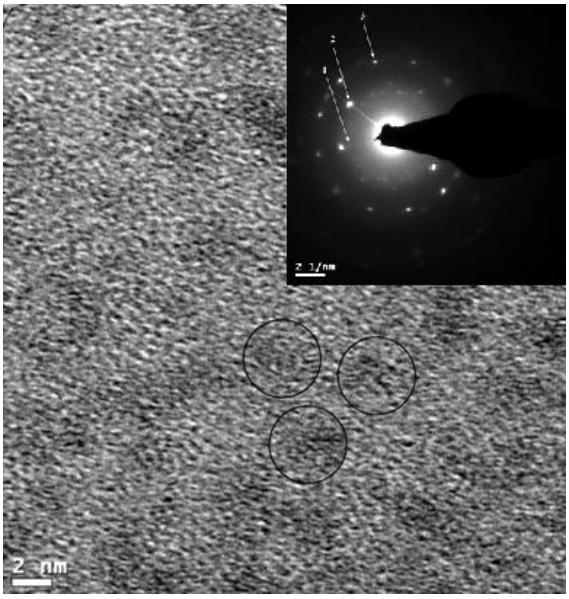


Figure 1. STEM image of CdS(MPS) with (inset) ED pattern.

Throughout the report, we use the notation of CdS(MPS) to designate CdS nanoparticles surrounded by MPS molecules but imply no stoichiometric relationship between the CdS and MPS capping molecules. Figure 2 reports the ^{13}C and ^{29}Si solid state nuclear magnetic resonance (SSNMR)[1] results for CdS(MPS).

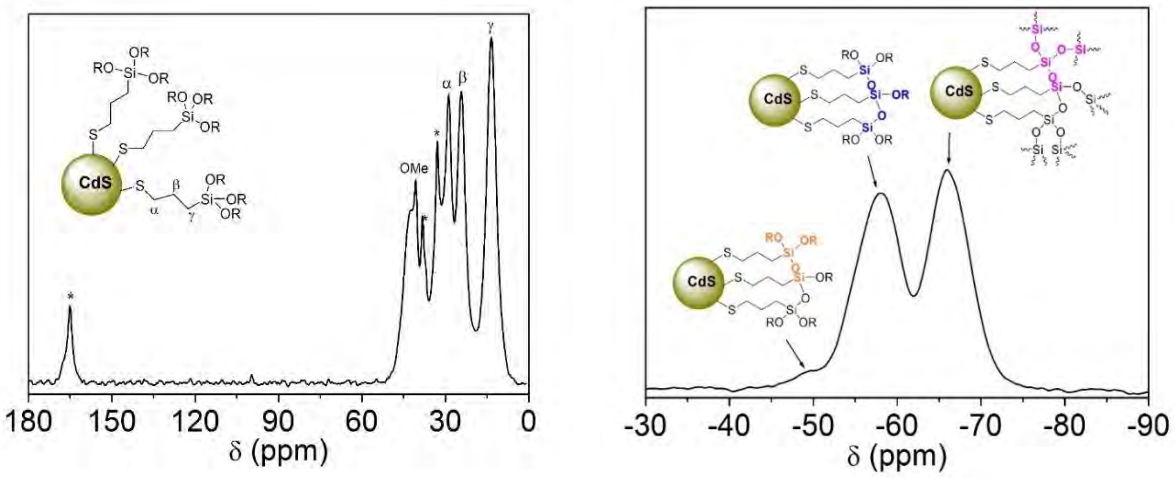


Figure 2.^{13}C (left) and ^{29}Si (right) SSNMR spectra of CdS(MPS)[1]. Inserted figures: sketch of proposed structures that are consistent with the signals.

[1] Studies carried out by Prof. Matthew Espe and his group at the Department of Chemistry, University of Akron.

The ^{13}C peaks at 13, 24 and 28 ppm are assigned to the methylene carbons in Si-CH_2-CH_2-CH_2-S(CdS) with the 42 ppm peak assigned to the O-CH_3 groups. The peaks at 32, 38, and 165 ppm are associated with DMF (b.p. 153° C) trapped in the solid. The ^{29}Si spectrum shows an intense peaks at -65, which is assigned to Si(-OSi)$_3$. All of these signals are consistent with the functionalization of CdS with MPS. However, another intense peak at -57 ppm and a weak signal at -50 ppm are observed in the ^{29}Si spectrum. MPS is a organofunctionalizedalkoxysilane molecule and as such is susceptibleto hydrolysis and successive polymerization and condensation [2,3].Accordingly, alternative nanostructures can be obtained during the CdS(MPS) synthesis; some of the most representative and ones that can explain the additional NMR signalsare shown in Figure 3.

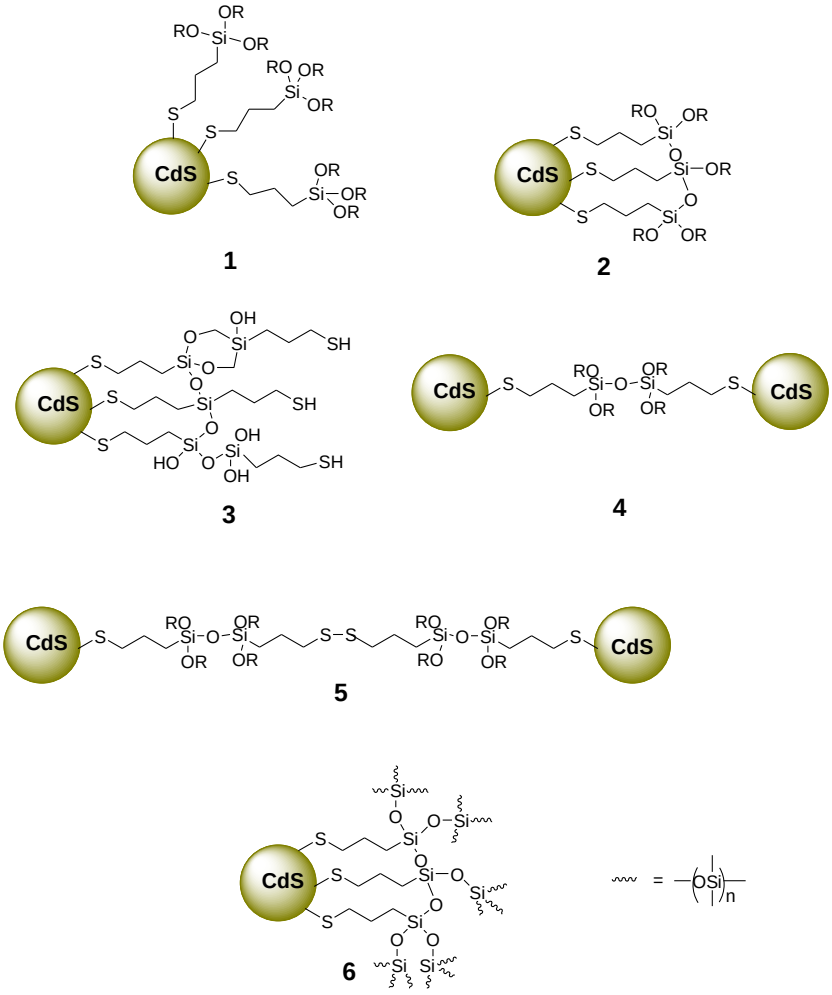
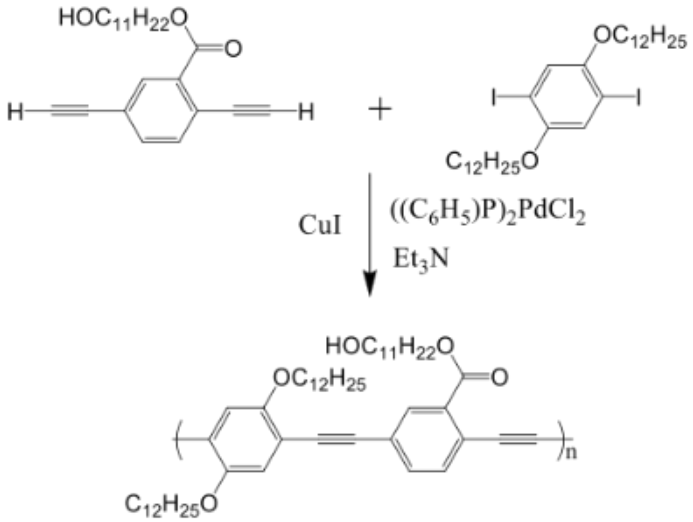


Figure 3. Possible alternative interactions and nanostructures that can be obtained in the CdS(MPS) synthesis.

Based on this assumption, we attribute the peak in the ^{29}Si SSNMR spectrum at-57 ppm to Si(-OSi)$_2$O(R/H) groups, respectively, where R = CH_3 and the weak signal at -50 ppm to the presence of a small amount of Si(-OSi)O(R/H)$_2$ groups as marked in the inserted sketches of Figure 2. It is noteworthy that in the case of the CdS(MPS) there appears to be no interaction that prevents the conversion of groups - Si(-OCH3)3 to Si(OSi-)2O(R/H) or (-OSi)3; the system can continue to form these species depending on time and exposure to a humid environment.The CdS(MPS) nanoparticles were also characterized by ^{113}Cd SSNMR[1]. The unique peak for bulk CdS particles is observed at ~700ppm. The exact chemical shift depends on nanoparticles size; the particles with diameter of 2-5nm have a peak in the ^{113}Cd NMR in the range of 670ppm to 725ppm. The position of the signal in the CdS(MPS) spectrum is consistent with the average mean size. However, due to the different size of the nanoparticles, the CdS peak becomes very broad which is very difficult to observe in the spectrum.

The conjugated polymer, a poly(phenyleneethynylene) copolymer hereafter called pPE (OC12-Co-BzC11OH), was synthesized by Sonogashira-Heck reactionaccording to Scheme 2.



Scheme 2. Synthetic route for the conjugated polymer pPE(OC12-Co-BzC11OH).

The conjugated moiety is responsible for absorption in the blue region (423 nm) and the good fluorescence quantum yield (37%) while the long lateral chains are introduced in order to give solubility in common organic solvents. Note that the alternation of polar benzoate and nonpolar dodecanoxy lateral chains imparts a light amphiphilic character to the copolymer, which can be

dissolved in solvents of different dielectric constants (toluene, chloroform, THF, DMF). However, is not soluble in methanol and acetone. The terminal hydroxyl group of the benzoate unit allows the reaction with CdS(MPS) through condensation with the methoxy groups of the silane capping agent of the nanoparticles. ^{13}Cand ^{29}SiSSNMR spectroscopy of the copolymer (Figures 4 and 5) was studied[1] in order to investigate the functionalization at different pH.For sake of discussion, the spectra of the CdS(MPS) nanoparticles and of the copolymer are included in the Figures 4 and 5. The ^{13}C NMR spectrum of the composite at acid conditions (c line) shows all the peaks from polymer (b) where the peaks at 30ppm and 15 ppm are broadened due to the overlapping of peaks from MPS. A small shoulder can also be seen at 45ppm due to the presence of O-CH_3 carbon from MPS as in the corresponding spectrum (a). The intensity of the peak at 63ppm from –CH_2OH groups is reduced in comparison to the same peak of the pure polymer as a consequence of the reaction and a small shoulder at 58 ppm is observed due to the condensation reaction (SiOCH_2 formation). However, the change in peak intensity is small indicating that only small fraction of the alcohol sites reacts with the nanoparticles. Notice that in the spectrum of the product of the reaction in basic conditions (d line) the peak at 58 ppm is not observed indicating the no reaction occurs. The same result was found for the reaction at pH 7 (spectrum not shown). On the basis of these results, the following the term,CdS(pPE), will be used for the composite at pH 5.5, where the covalent functionalization was corroborated.

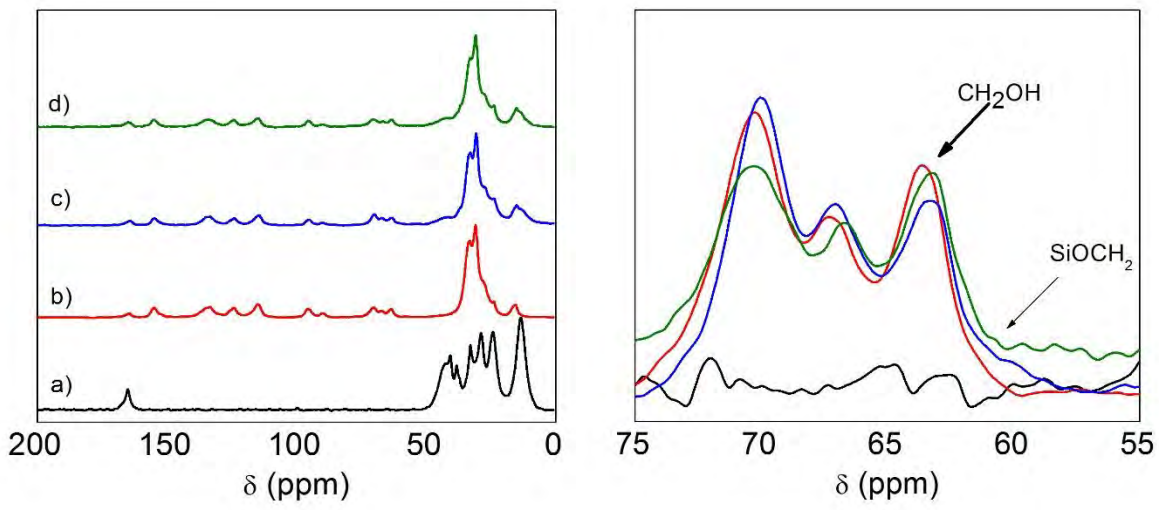


Figure 4. Left: ^{13}C SSNMR spectra of (a) CdS(MPS), (b) pPE(OC12-Co-BzC11OH), (c) composite, pH 5.5 and (d)composite at pH 10. Right: magnification of the region between 75 and 55 ppm.

The ^{29}Si SSNMR spectrum (Figure 5) confirms the functionalization as the intensity of the peak at -65ppm relative to that at -57 ppm (previously assigned to R-Si(-OSi)$_3$ and R-Si(-OSi)$_2$O(R/H), respectively) decreases for the composite with respect to the CdS(MPS), indicating that the interaction of the MPS molecule with the copolymer prevents the conversion of some of the R-Si(-OSi)$_2$O(R/H)species to R-Si(-OSi)$_3$ by converting the Si-O-CH$_3$ group to an Si-OCH$_2$-R group. On the contrary, the spectrum of the composite obtained at pH 10 presents a stronger intensity for the signal associated with the complete hydrolysis in agreement with the ^{13}C SSNMR spectrum. It is important to remark that there is no evidence of unreacted MPS molecules since there is no peak at ~-40 to -45ppm in both the CdS(MPS) nanoparticles and composite.

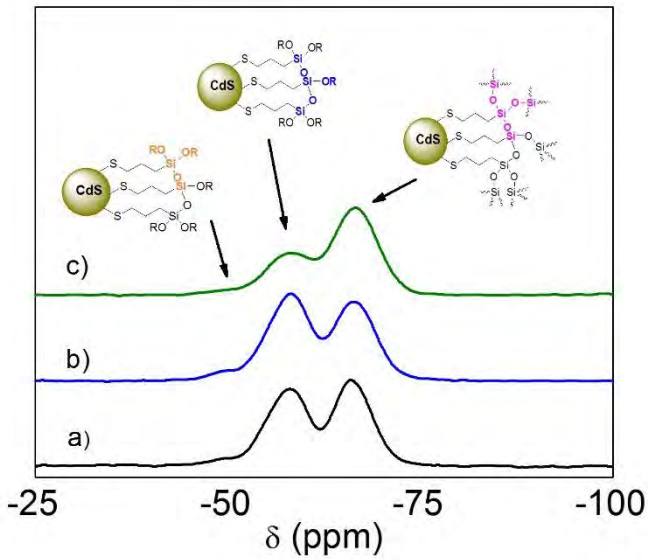


Figure 5. ^{29}Si SSNMR spectra of (a) CdS(MPS), (b) composite, pH 5.5 and (c) composite at pH 10.

The hydrolysis of the methoxy groups of the silane and their successive polymerization, induced by the presence of the OH groups of the phenyleneethynylene, gives rise to peculiar superstructures of 200-600 nm in diameter. The diameter of these structures appears to depend on the pH of the medium with the diameters being larger at basic pH. STEM analysis (Figure 6) shows the presence of CdS clusters inside the larger particles and TEM tomography reveals that these superstructures are transparent and look 'hollow' as one might expect for a bilayer vesicle assembly. We note further that the tomographic STEM data and analyses demonstrate that the

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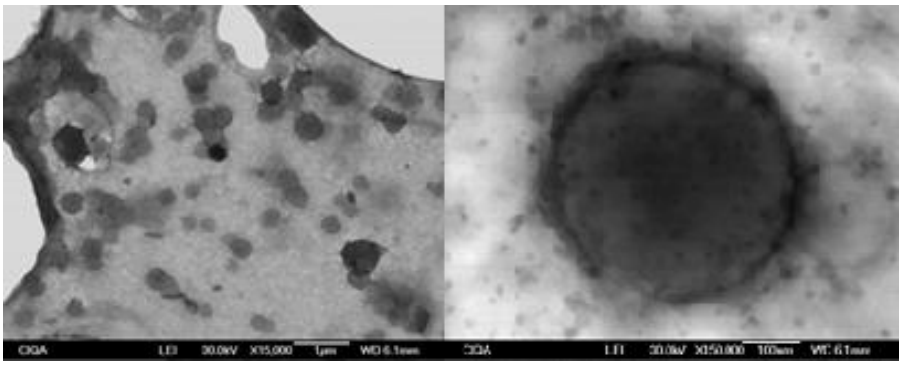

Figure 6. Left: STEM images of the composite. Right: magnification of a superstructure

Although the interaction of the copolymer and CdS(MPS) moieties in the nanocomposite was shown to be through direct chemical bonding, the nature of how or where the CdS(MPS) moieties are placed or located in the polymer composite cannot be ascertained presently, particularly because of the associated structural complexities introduced by the MPS and its hydrolysis products as previously mentioned. It is noted that the composite films may be planar as well as vesicular in nature as seen in the STEM images. In this context, it is well known that amphiphilic molecules self-assemble into a variety of structures such as globular micelles, ellipsoids, discs, cylinders, vesicles and lamella, depending on their specific molecular architecture, concentration and solvent environment. The formation of self-assembled vesicles from an amphiphilic o-phenyleneethynylene macrocycle from aqueous chloroform, for example, was demonstrated by Seo, et al., to give vesicles with an average diameter of about 500 nm [4]. Nevertheless, neither pPE(OC12-Co-BzC11OH)nor CdS(MPS)samples prepared in the same condition as those of the composite (i.e. the THF:DMF mixture) present vesicle formation. A molecular dynamics study carried out by Dr. Heinz group on CdS composites with oligomeric model systems [5] supports the evidence that the hydroxyl group of the phenyleneethynylenes tends to react with the trimethoxysilyl shell of the nanoparticle surface and this causes bending of the conjugated backbone.

The electrochemical analysis (Table 1) carried out with cyclic voltammetry suggests that the particles of cadmium sulfide can be easily oxidized (Eox=1.1934) and has the ability to inject more holes (HOMO=-5.9934) with respect to the copolymer pPE(OC12-Co-BzC11OH), which,

by having the lowest LUMO level, has the ability to rather deliver electrons; i.e. the CdS(MPS) can act as electron acceptor and pPE(OC12-Co-BzC11) as electron donor.

Table 1. Electrochemical properties obtained by cyclicvoltammetry of CdS(MPS) particles in DMF, pPE(OC12-Co-BzC11OH) in THF and the composite in DMF:THF.

Material	E_{ox}(V)	E_{red}(V)	HOMO (eV)	LUMO (eV)	Eg_{elect}(eV)
pPE(OC12-Co-BzC11OH)	1.64	-1.21	-6.44	-3.59	2.85
CdS(MPS)	1.19	-0.62	-5.99	-4.18	1.81
composite	1.41	-1.15	-6.21	-3.65	2.56

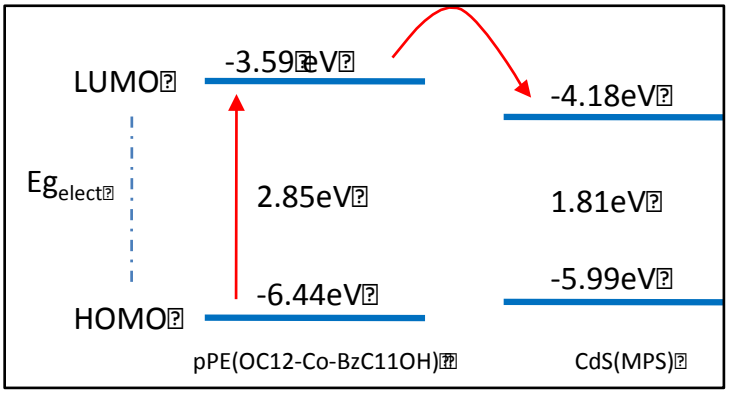

Figure 7. Comparison of the HOMO-LUMO energy levels of pPE(OC12-Co-BzC11OH) and CdS(MPS).

The energy diagram related to the HOMO-LUMO levels (Figure 7) meets the required energy level relationshipsfor photoinduced electron transfer as the LUMO level of the electron-donor is at higher energy than that of the LUMO of the electron-acceptor.

Despite this, the photophysical properties (Table 2) of the composite are practically identical to those of the polymer. The optical properties of CdS(MPS) are not affecting the spectrum of the composite. Both polymer and composite absorb at 423 nm(Figure 8);only a slight baseline is observed in the composite spectrum at wavelength larger than 500 nm due to light scattering produced by the superstructures.

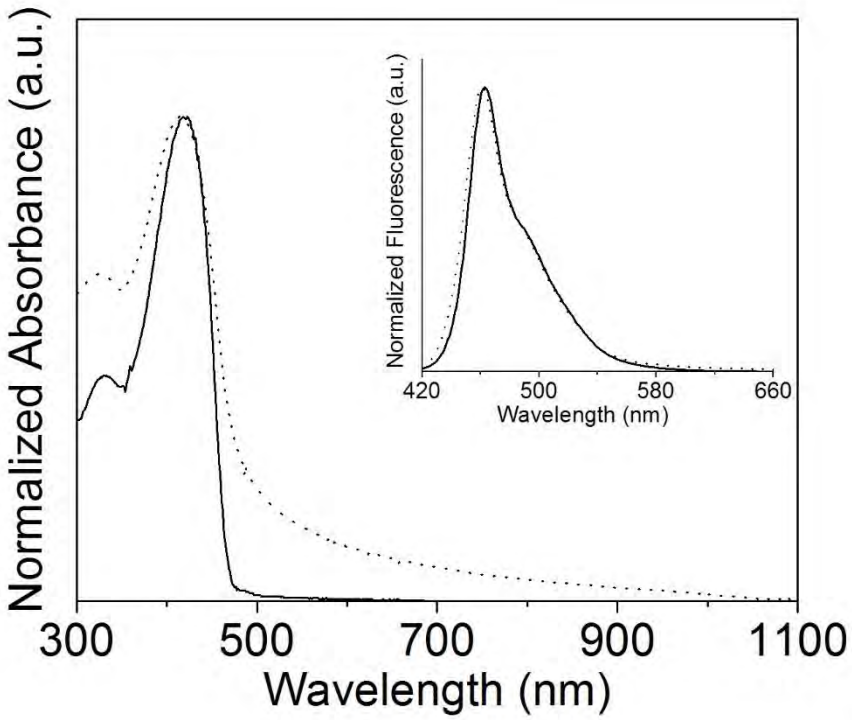

Figure 8. UV-Vis-NIR and fluorescence (inset) of pPE(OC12-Co-BzC11OH) (solid lines) and composite (dotted lines).

Both materials emit at 466 nm (Figure 8, inset), with identical fluorescence lifetime,τ. The fluorescence quantum yield (ϕ) is slightly higher for the composite, contrary to photoinduced electron transfer that could be expected on the basis of the electrochemical characterization. This result can be explained on the basis of the large distance between the CdS nanocore and the copolymer, because of both the long lateral chains and the micellar superstructures. This is also confirmed by the molecular dynamics study. A further experimental result that reveals no photoinduced electron transfer is the absence of photogeneration in solar cells made of just the composite.

Table 2. Photophysical properties of the composite and its precursors: CdS(MPS) and copolymer PE(OC12-Co-BzC11OH)

Material	Solvent	λabs (nm)	λemis (nm)	ϕ (%)	τ (ns)
pPE(OC12-Co-BzC11OH)	THF	423	466	37	0.67
CdS(MPS)	DMF	360	506	0.18	n.d.
composite	THF:DMF	423	465	45	0.62

The formation of the superstructure is an interesting and unexpected result for materials science, which is part of a manuscript in preparation.

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Abstract

Composites of CdS quantum dots and a new conjugated polymer were prepared by reacting CdS capped with (3-mercaptopropyl)trimethoxysilane (MPS) and a new conjugated copolymer at different pH (5.5., 7 and 10) at 50 °C for 3 h, under magnetic stirring. Cadmium sulfide quantum dots with face centered cubic zinc blende structure and an average size of 3.02 ± 0.46 nm (Figure 1) were prepared in the presence of MPS following the procedure of Fang, et al. The conjugated polymer, a poly(phenyleneethynylene) copolymer hereafter called pPE (OC12-Co-BzC11OH), was synthesized by Sonogashira-Heck reaction. 13C and 29Si SSNMR spectroscopy of CdS(MPS), the copolymer and composite was studied in order to investigate the functionalization at different pH. The hydrolysis of the methoxy groups of the silane and their successive polymerization, induced by the presence of the OH groups of the phenyleneethynylene, gives rise to peculiar superstructures of 200-600 nm in diameter. The diameter of these structures appears to depend on the pH of the medium with the diameters being larger at basic pH. STEM analysis (Figure 6) shows the presence of CdS clusters inside the larger particles and TEM tomography reveals that these superstructures are transparent and look ‘hollow’ as one might expect for a bilayer vesicle assembly. Tomographic STEM data and analyses demonstrate that the 3D vesicles formed in the nanocomposites are stable in the solid state under high vacuum conditions. Comparative cyclic voltametry data and

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