



Energy transfer between lead sulfide quantum dots in the liquid phase



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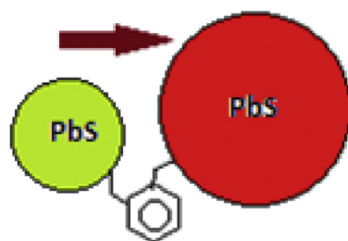
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HIGHLIGHTS

- Förster resonance energy transfer from 3.2 nm to 4.7 nm PbS QD in liquid phase.
- Particles brought closer than Förster radius by dithiol linkers.
- Intensity of fluorescence peak corresponding to smaller sized particles decreases.
- Intensity of fluorescence peak corresponding to larger sized particles increases.
- Ratio of absorption intensities remain same.

GRAPHICAL ABSTRACT

FRET in Tetrachloroethylene



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ABSTRACT

Förster resonant energy transfer (FRET) from smaller sized PbS Quantum Dots (QDs) to larger sized ones occurs in the liquid phase when adjacent QDs are brought in close proximity by the bridging action of the two SH groups in aromatic or aliphatic dithiols. Signatures of FRET were observed by the lowering of the fluorescence peak corresponding to the smaller particle group and intensification of the peak corresponding to the larger particle group in a mixture of the two in the liquid phase. The suspensions of the two QDs size distributions were mixed in a ratio such that total surface area of the smaller QDs was equal to that of the larger QDs. A 10–13% size deviation in each PbS QDs group also allows this phenomenon to be observed in these samples and is manifested by red-shift and broadening of the fluorescence peak. The ratio of the absorption peak intensity corresponding to the two groups of PbS QDs in the mixture remains the same.

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1. Introduction

Lead sulfide (PbS) and lead selenide semiconductor nanoparticles (NPs), due to their large exciton Bohr radii of 20 and 46 nm respectively permit greater quantum confinement than other II–VI and III–V NPs [1]. The calculated band gap for PbS in the bulk state

is 0.4 eV at 298 K [2]. If size for PbS NP is less than 10 nm, these particles are highly “quantum confined” and show size dependent tunable absorption and emission characteristics that can be modified in the near-infrared (NIR) region (~800–1700 nm) of the electromagnetic spectrum. This region is highly significant for a variety of applications. For example, a significant amount of the solar energy radiation reaching the earth (~40%) lies in this region [3]. In biological imaging applications, the biological fluids like water, hemoglobin and proteins absorb poorly in the NIR region [4]. In the field of telecommunications the region from 850 nm to 1580 nm is important as silica optical fibers use these wavelengths to transmit information [5]. Quantum confined semiconductor PbS

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NPs also known as quantum dots (QDs), by absorbing energy in the NIR region, can potentially act as “sensitizers” for QD sensitized solar cells [6]. Electron flow in PbS–TiO₂ nanotube composites have been demonstrated by catalyzing dye degradation reactions [7]. PbS QDs exhibit photoluminescence over the entire transmission window of silica optical fibers [5] and hence have potential application as optical amplifiers [8]. In the light of the above potential and demonstrated applications of lead chalcogenides and other semiconducting QDs include development of solar cell [9–13], biological sensors [14,15], telecommunications [16–18], optical amplification [19], and lasers [19].

One of the mechanisms by which sensors and energy harvesting work is FRET (Förster or fluorescence resonance energy transfer) [20]. In general, quantum dots based probes are deemed better than organic dyes for FRET since the former have better photostability and narrower emission spectra than the latter [21]. FRET from one group of semiconductor QDs to another group of QDs of a different size has been demonstrated for CdSe and PbS NP films [20,22,23]. For PbS QDs stabilized by oleic acid, signatures of energy transfer were observed in solid films by observing a red-shift in the NIR fluorescence spectra and changes in relative fluorescence intensities emitted by two groups of PbS QDs of different sizes [22,23]. This FRET phenomenon is not observed when the oleic acid stabilized PbS QDs are mixed in liquid suspension phase. Kempa et al. presented a theoretical treatment of energy transfer of PbS QDs by considering a quantum dots arranged 2D lattice [24]. Clark et al. have estimated a Förster radius of 8 nm for the PbS quantum dots FRET in solids [23].

For certain applications like biological sensors [15] and flow cytometry [25] that exploit FRET in NPs, films are unsuitable. Hence research conducted on FRET in solution phase NP systems is of significance. FRET has been demonstrated in the solution phase for CdTe [26], CdSe [27] and core shell CdSe–ZnS QDs [28]. For CdTe two adjacent QDs of a similar size distribution were brought close together by hexanedithiol [28]. By experiments and theoretical calculations it was shown that the two SH functional groups on the dithiol attach to adjacent QDs facilitating FRET. In this paper, we present evidence of energy transfer between PbS QDs of different sizes in a liquid suspension in presence of aromatic or aliphatic dithiols. The liquid phase FRET phenomenon is not observed in presence of the monothiols tested. This appears to be the first report of FRET between different sizes of PbS semiconductor quantum dots occurring in the liquid phase.

2. Materials and methods

2.1. Chemicals and expendables

PbS QD samples stabilized by oleic acid (PbS-AE, 3.2 nm and PbS-BE, 4.7 nm in diameter) in toluene were obtained from Evident Technologies, NY. Tetrachloroethylene (TCE) and Benzyl mercaptan (BM) (99%) were obtained from Alfa Aesar. Pentanethiol (98%), 1,2-benzenedimethanethiol (1,2-BDMT) (95%) and Dodecanethiol (98%) were obtained from Sigma–Aldrich. 1,6-hexanedithiol (97%) was obtained from Acros Organics.

Depression slides used were Sail Brand, Cat. No. 7104. All chemicals were used as obtained without any further purification. Table S1 in the supporting information lists out the various abbreviations used for the PbS QD.

2.2. Instrumentation and software

NIR emission spectra were measured in a 1 cm optical path length quartz cuvette at room temperature with a Horiba Jobin-Yvon Nanolog 916B fluorescence spectrophotometer equipped

with an IGA 512 InGaAs detector cooled to 77 K using liquid N₂. Five nm slit-width for both excitation and emission slits were used. Excitation wavelength was 450 nm. Absorption spectra were obtained using a Guided Wave (Rancho Cordova, CA) model LS–E–VIS–NIR spectrometer and a HP 8453 UV–Vis scanning spectrophotometer. Fluorescence and absorbance spectra were processed using GRAMS 32 software version 5.21 obtained from Galactic Industries Corporation.

3. Experimental

3.1. FRET studies in solution phase

PbS-A, suspension of the smaller sized QD, was prepared by diluting 20 μ L of the commercially obtained PbS-AE (5 mg mL⁻¹) to 1 mL using TCE. PbS-B, suspension of the larger sized QD, was prepared by diluting 43.1 μ L of the commercially obtained PbS-BE (5 mg mL⁻¹) to 1 mL using TCE. The significance of these particular quantities is discussed in result and discussion section. For FRET studies on individual QD suspensions 1 mL of PbS-A or PbS-B was used and for FRET studies on mixture of two QD suspensions 0.5 mL of each PbS-A and PbS-B was used. NIR absorption and fluorescence spectra of a sample were measured in a cuvette. A thiol solution in TCE was then added to the cuvette and the contents were stirred by means of a micro stir bar at approximately 600 rpm for 1 min. Optical spectra were measured again. The dithiols tested were 1,2-BDMT, and 1,6-hexanedithiol. The monothiols tested were pentanethiol, dodecanethiol, and BM. Typically, 0.9 μ mol of a dithiol (10 μ L of 0.09 M solution in TCE) or 0.18 μ mol of the mono-thiol (10 μ L of 0.18 M solution in TCE) was added to the PbS suspension. Throughout this paper, for simplicity, results would be reported for 1,2-BDMT as an example for dithiols. For individual suspensions (PbS-A or PbS-B) to which 1,2-BDMT was added, the suspension is referred to as PbS-X-LEx, where X = A or B and LEx means ligand exchange. For mixtures of PbS-A and PbS-B to which 1,2-BDMT had been added is referred to as PbS-A-B-LEx. If the identity of the di- or mono-thiol is different than 1,2-BDMT, the corresponding suspensions would be referred to as PbS-A-N, PbS-B-N or PbS-A-B-N in lieu PbS-A-LEx, PbS-B-LEx or PbS-A-B-LEx respectively, where N is the thiol. The thiol (solution in TCE) was added to the cuvette itself to discount the possibility of loss during transfer. For FRET experiments with mixtures of PbS-A-LEx and PbS-B-LEx, 0.5 mL of each were mixed in an 8 mL vial and the reaction mixture was stirred at 300 rpm with the aid of a Teflon coated stir bar. Periodically, the mixture was transferred to a cuvette for optical spectra measurements. Simultaneously as a blank experiment, 0.5 mL of PbS-A-LEx diluted to 1 mL with TCE

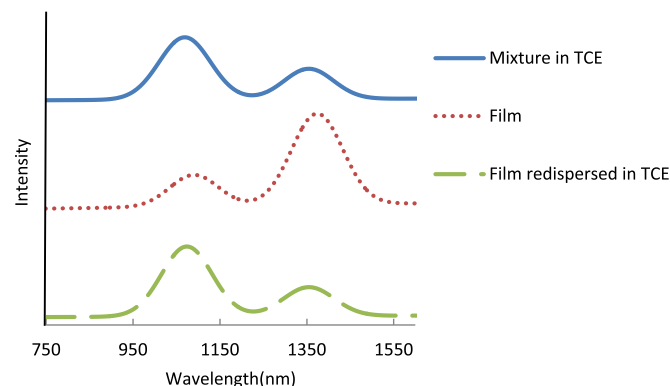


Fig. 1. Fluorescence spectra of mixture of oleic acid stabilized QD in TCE, in solid film on depression slide, and in TCE after re-dissolution of the film.

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