



Study of energy transfer phenomenon between quantum dots and zinc porphyrin in solution

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ARTICLE INFO

Article history:

Received 17 July 2017

Received in revised form 16 August 2017

Accepted 23 August 2017

Available online 24 August 2017

Keywords:

Quantum dots

Zinc porphyrin

FRET

Surface passivation

Ultrafast quenching mechanism

ABSTRACT

The mechanism of energy transfer (ET) phenomenon from the excited $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ alloyed quantum dots (QDs) to 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine zinc(II) (**1**) molecule is investigated in solution through Förster resonance energy transfer (FRET) calculations, photoluminescence intensity measurements and lifetime quenching experiments. The process of ET from the excited QDs to **1** in toluene is established by FRET calculations. ET efficiency in QDs/**1** complex is regulated by surface passivation and ultrafast quenching mechanism. We propose that $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ alloyed quantum dots may be suitably employed as an efficient energy transfer donor for zinc-porphyrin for possible application in light harvesting devices.

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1. Introduction

Semiconductor quantum dots (QDs) have emerged as a novel class of fluorophore with unique photoluminescence properties and exhibit interesting phenomena such as solution processability, broad absorption spectra and narrow emission peak. For QDs, higher photochemical stability can be achieved by passivation of surface trap states using higher band gap semiconductor [1–6]. Associated with their engrossing optical features, QDs has been the focus of research in optoelectronics in recent past [7]. QDs find tremendous application in biology for its uses in imaging, labelling and sensing [8]. Apart from that, utilizing the concept of energy-transfer processes, QDs have been employed in various applications like imaging, luminescence tagging, sensors, and also as light harvesting devices [9]. When QDs are photoexcited, electron-hole pairs are generated and upon their recombination, fluorescence light is emitted due to the small size quantum effect [10,11]. For this reason, several researchers adopt colloidal QDs as an efficient donor which exhibits characteristic absorption spectral feature in the visible region of light; this particular property of QDs can be successfully utilized to undergo interaction with an organic dye molecule via Förster energy transfer (FRET) mechanism. It has a broad absorption spectrum in the visible light to enhance light capture from an organic dye (known as an acceptor) via a Förster resonance energy transfer (FRET) mechanism

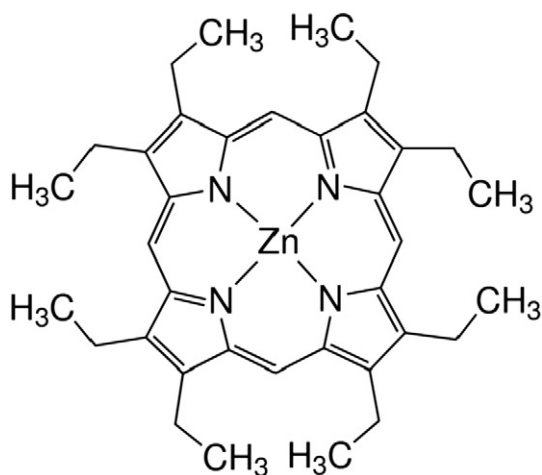
[12–14]. The study of successful use of QDs as donors in FRET has been reported in developing chemical and biosensors [15,16]. In recent past, the potential of the InP, InP/ZnS and InP/ZnSeS QDs as FRET donors were demonstrated by various researchers [17–26]. Very recently, Mutlugun et al. have successfully employed In(Zn)P/ZnS QDs as an efficient donor in FRET among different QD-QD pairs [27].

On the other hand, synthetic porphyrins have received considerable attention as an important candidate in light harvesting materials for the construction of photovoltaic cells [28,29]. The relatively higher molar extinction coefficient between Soret ($S_2 \leftarrow S_0$ transition) and Q absorption bands ($S_1 \leftarrow S_0$ transition) in metalloporphyrins exemplify another remonstrance for their application in making light-harvesting materials. In addition to high energy transfer efficiency from QDs to organic dye molecules [30,31], there are some reports which put forward the photo-induced charge transfer mechanism in the excited state for QDs/porphyrin complex [32,33].

Thus, taking into consideration the research on the development of QD based chemical sensors, we have focused our attention on the interaction between $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ alloyed QDs as donor and porphyrin molecule, namely, 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine zinc(II) (**1**, Scheme 1) as acceptor through FRET mechanism. Although, there are several studies done on Type I QDs like CdSe/ZnS and CdSe/CdS core-shell semiconductor nanocrystallites in recent past [34–37], the present work for the first time demonstrate $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ alloyed quantum dots as a potential self-assembled donor undergoing FRET with metallo-porphyrin. The present paper, therefore, aims at

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Scheme 1. Structure of 1.

understanding the chemical physics behind energy transfer in QDs/zinc-porphyrin system.

2. Materials and methods

The QDs having diameter of 6 nm, is collected from Aldrich, USA (Catalogue no. 753750). **1** is purchased from Aldrich, USA. UV–Vis spectroscopic grade toluene (Spectrochem, India) is used as solvent to favour molecular interaction between QDs and porphyrins, at the same time, to ensure good solubility and photo-stability of the samples. UV–Vis spectral measurements are performed on a Shimadzu UV-2450 model spectrophotometer using quartz cell with 1 cm optical path length. Emission spectra have been recorded with a Hitachi F-7000 model spectrofluorimeter. For the time correlated single photon counting (TCSPC) measurements, the samples are excited at 463 nm using a nanosecond diode laser (IBH Nanoled) in an HORIBA Jobin Yvon Single Photon Counting Setup. The typical fwhm of the system response using a liquid scatter is about 1.3 ns. The repetition rate is 1 MHz. The fluorescence decay curves are analyzed using IBH DAS6 software. Photoluminescence quantum yield (ϕ) of QDs has been obtained by comparison with a reference dye, namely, quinine sulphate dihydrate in 0.5 (M) H_2SO_4 solution. The following equation is used for the determination of ϕ of QDs in toluene [38].

$$\phi_s = (F_s \times A_r \times \eta_s^2 \times \phi_r) / (F_r \times A_s \times \eta_r^2) \quad (1)$$

In Eq. (1), F_s and F_r are the integrated fluorescence emission of the sample (here QDs) and the reference (here quinine sulphate dihydrate), respectively. A_s and A_r are the absorbance at the excitation wavelength of the sample and the reference, respectively. ϕ_s and ϕ_r are the quantum yields of the sample and the reference [39]. The refractive indices of the solvents used for the preparation of the sample and reference are given by η_s (1.496) and η_r (1.35), respectively. The values of F_s and F_r are determined from the photoluminescence spectra corrected for the instrumental response, by integrating the emission intensity over the desired spectral range. Only the band edge luminescence peak is integrated for this purpose. The calculated quantum yield value of QDs is estimated to be 0.88.

3. Results and discussions

3.1. UV–vis absorption studies

In QD, electron is excited from the valence to the conduction band due to absorption of light; this process is known to form a hole. This hole when combines with an electron, an exciton is formed. However,

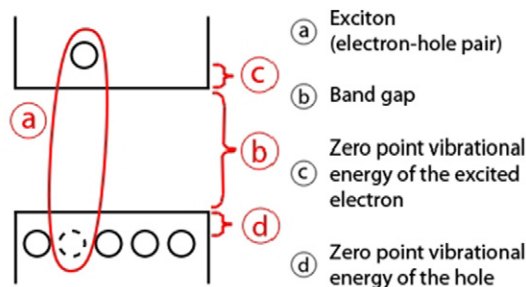
when exciton undergoes recombination assuming that the electron is in ground state, the exciton can also emit its energy as light. The bound energy of the exciton may be defined as electron-hole pair and the energy between the highest occupied energy level and the lowest unoccupied energy level corresponds to band gap energy of a QD. Together with the above mentioned energies, the hole and excited electron also known to contribute some amount of confinement energies towards the total energy of the emitted photon. This process is shown in Scheme 2. The first excitonic maximum of QDs appears at 470 nm (inset of Fig. 1). Fig. 1 also shows the UV–vis absorption spectrum of zinc porphyrin (here **1**) in absence and presence of QDs. It is observed that the absorption intensity of the Soret absorption band of **1** suffers little enhancement in presence of QDs, viz., 1.545 to 1.589. However, the absorption intensity at Q absorption band of **1** remains unchanged. It should be noted at this point that in the visible region between 400 and 600 nm, **1** shows very weak absorption coefficient; this particular absorption spectral region plays very important role for possible light-harvesting. As a result of this, QDs can be utilized as a promising energy donor in light-harvesting. As shown in Fig. 1, when QDs is added into the porphyrin solution, the visible absorption at the Soret absorption band increases. In addition, there is no significant shift or appearance of new absorption band upon mixing of QDs and **1**, suggesting no ground state interaction or complex formation between porphyrins and QDs [30].

3.2. Steady state fluorescence studies

In steady-state fluorescence measurements, it is expected that QDs can be excited at a particular wavelength at which **1** shows negligible absorbance. In our present study, we have excited the QDs at 450 nm where **1** does not absorb. Fluorescence measurements would also reveal the photoluminescence (PL) characteristic of QDs during QDs/**1** interaction (Fig. 2(a)). For efficient FRET phenomenon, it is an essential criterion to have a good spectral overlap between the absorption spectrum of an acceptor (here **1**) and emission spectrum of a donor (here QDs). The normalized overlap region of QDs/**1** system is demonstrated in Fig. 3. The degree of spectral overlap between the donor fluorescence spectrum and acceptor absorption spectrum is expressed by the factor $J(\lambda)$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^3$) in wavelength scale as follows:

$$J(\lambda) = \int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (2)$$

In Eq. (2), $F_D(\lambda)$ and $\epsilon_A(\lambda)$ are defined as the normalized emission spectrum of the donor (here QDs) and the molar extinction co-efficient of the acceptor (here **1**), respectively, at wavelength of measurement, i.e., λ [40]. Estimation of J values with the help of Eq. (2) confirms moderate extent of spectral overlap for QDs/**1** system (Table 1). We admit that the overlap between the donor emission spectrum and the acceptor absorption spectrum is minimal to consider the QDs/**1** system as an effective FRET pair. However, QDs like $\text{CdS}_x\text{Se}_{1-x}$ was shown to form an effective FRET pair with molecule like porphyrin in recent past [41]. In



Scheme 2. Schematic representation of (a) exciton, (b) band gap, (c) zero point vibrational energy of the excited electron, and (d) zero point vibration energy of the hole in QDs.

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