

# A ternary system of quantum dot – Porphyrin – Semiconducting organic nanoparticles for light harvesting



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## ABSTRACT

Inorganic–organic semiconductor hybrid nanostructures remain a frontier area of research to design optoelectronic, photovoltaic and light harvesting devices because of efficient energy or charge transfer process. Here, we have designed a system where inorganic semiconducting nanocrystals ( $\text{Cd}_{0.52}\text{Zn}_{0.48}\text{S}$ ) are encapsulated into semiconducting organic poly (9-vinylcarbazole) [PVK] nanoparticles with 5-(4-aminophenyl)-10,15,20-triphenyl-21,23H-porphyrin (APTPP) molecule. Steady state and time resolved spectroscopic study reveal the efficient energy transfer from host PVK nanoparticle to QD and porphyrin molecule which is found to be cascade energy transfer. The energy transfer enhances from 68% to 86% by incorporating porphyrin molecule into QD doped PVK nanoparticles. This high efficiency of cascade energy transfer opens further prospects to design new porphyrin and quantum dot based functional polymer nanoparticles for the application in efficient light harvesting system and other photodriven devices.

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## 1. Introduction

Nanoscale materials have recently emerged as a new class of functional materials for developing efficient light harvesting by using solar energy because of their tunable electronic structure, ability to generate multiple charge carriers. The fundamental understanding of photophysics of nanoscale systems remains at forefront of research area. It is now evident that inorganic nanocrystals are used as light absorbing antenna material for the light harvesting process as optical properties can be engineered over a wide spectral window with varying size, shape and composition of nanocrystal [1–3]. The development of organic semiconductor – inorganic hybrid nanostructures is found to be a frontier area of research for light harvesting where electronic energy level alignments, morphology, size and shape of inorganic nanocrystals control the performance of the inorganic nanocrystals/polymer hybrid nanocomposites devices. In conjugated polymer, the  $\pi$ -electrons of every monomeric unit are delocalized over a significant part of the chain and their properties depend on

both the chain length and exciton diffusion length [4].  $\pi$ -conjugated polymers and inorganic nanoparticles (NPs) hybrid nanostructures exhibit unprecedented electrical and optical properties [5–7], because of large absorption cross section of organic semiconductor due to delocalized  $\pi$ -electron transition from ground state ( $S_0$ ) to excited state ( $S_n$ ) and unique optical properties of inorganic semiconductor due to quantum confinement. Feldmann et al. [8] have demonstrated the efficient energy transfer occurs from blue emitting conducting polymer (PDFD) to CdTe nanocrystals where the valence band of CdTe QD is  $-6.3$  eV and the organic–inorganic hybrid structures of PDFD–CdTe QDs are formed by electrostatically attached with anionic CdTe QDs with positively charged PDFD molecules. In our previous work, we have demonstrated the energy transfer and hole transfer of inorganic–organic hybrid structure of hole transporting  $\alpha$ -sexithiophene ( $\alpha$ -STH) nanoparticles–CdTe QD [9].

Photoactive molecules encapsulated semiconducting organic molecules have given emphasis for light harvesting system because of better stability, functionality and aggregation free molecular arrangement [10,11]. Fundamental understanding photophysics of encapsulated photoactive molecules in polymer nanoparticles and their dependence on confined motions, matrix rigidity, and heterogeneous population have been reported very recently [12,13]. Near-infrared fluorescent dye-doped semiconducting polymer dots are found to have efficient light harvesting

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application [14]. We have also designed inorganic organic hybrid system where CdTe QDs acts as an antenna material, and transfer the exciton to an acceptor molecule (Nile red) which is confined in PMMA polymer nanoparticles [15]. Poly(9-vinylcarbazole) (PVK) is one of the important non-conjugated semiconducting molecule [16–18] which are being used to prepare stable nanoparticles in aqueous medium because it is capable to encapsulate the hydrophobic dyes, porphyrin molecules and other organic small molecules [13,19,20]. Porphyrin molecules are found to be used for efficient light harvesting and photodynamic therapeutic (PDT) applications because of their excellent photophysical, photochemical, electrochemical, structural properties and self-assembly [21–26]. Mcneill and his co-workers reported the use of platinum octaethylporphyrin doped polyfluorene nanoparticle for biological oxygen sensing [27]. Recently, the high efficiency of energy transfer from PVK to dye/porphyrin in dye/porphyrin doped PVK nanoparticles in aqueous medium is demonstrated [19,20,28]. It is evident that J-type aggregation of porphyrin molecules inside PVK nanoparticles plays an important for artificial light harvesting systems.

Less attention has been paid on incorporation of the quantum dots into polymer nano-nanoparticle to design inorganic-organic conjugate system where QDs will absorb the light as an antenna material, and then transfer the exciton to an acceptor molecule which is confined in polymer nanoparticles. The quantum dot doped polymer nanoparticles, nanofiber and nanowires have been used for optical sensing, biological sensing and photonic crystals [29–31]. Di Corato et al. [32] recently have synthesized magnetic nanoparticles and quantum dots encapsulated polymer nanobeads for the cancer cell targeting. Dye or small molecule doped polymer nanoparticles, dual dyes or small molecules doped polymer nanoparticles, quantum dot-polymer nanoparticles composites and quantum dot doped polymer nanoparticles system are being investigated to find out potential applications. It is reported that the co-doped polymer nanomaterials have potential applications in white light generation and light harvesting [33,34].

In this study, semiconducting quantum dot and porphyrin encapsulated semiconducting organic nanoparticles system has been designed for potential light harvesting system. Herein, we have demonstrated the design of alloy quantum dot and porphyrin co-doped PVK nanoparticles system and we have tried to understand the multistep cascade energy transfer processes from the host semiconducting organic nanoparticle to quantum dot and porphyrin molecules by steady-state and time resolved spectroscopy. The fundamental understanding on photophysical properties in this inorganic-organic hybrid system will enable us to construct efficient light harvesting system and other photodriven devices.

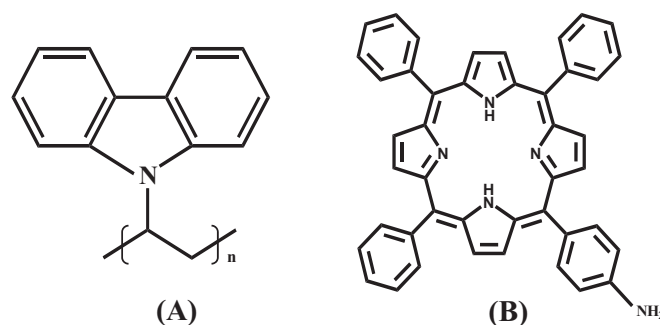
## 2. Experimental procedure and characterization

### 2.1. Materials

Oleylamine (Aldrich), cadmium acetate (Merck), zinc acetate (Merck), sulphur powder (Merck), PVK [Poly (9-vinylcarbazole)] (Aldrich), distilled tetrahydrofuran (THF) (MERCK), de-ionized water (MERCK), dichloromethane (MERCK) were used as received for our synthesis. Scheme 1 shows the molecular structures of PVK and 5-(4-aminophenyl)-10,15,20-triphenyl-21,23H-porphyrin (APTTP). Synthesis of APTTP has been given in Supporting information. All solvents (toluene, ethanol) were of GR grade and were used without further purification.

### 2.2. Synthesis of Cd<sub>0.52</sub>Zn<sub>0.48</sub>S

Cd<sub>0.52</sub>Zn<sub>0.48</sub>S alloy were synthesized by our previously reported method [35,36]. In brief, 0.067 g (0.25 mmol) cadmium acetate,



**Scheme 1.** Molecular structures of (A) Poly(9-vinylcarbazole) [PVK] and (B) 5-(4-aminophenyl)-10,15,20-triphenyl-21,23H-porphyrin (APTTP).

0.051 g (0.25 mmol) zinc acetate and 5 ml of oleylamine were firstly taken in a two necked round bottom flask. Then the mixture was heated to 150 °C under continuous Ar gas flow for 20 min to make a clear solution. At this condition, an excess amount of sulfur solution containing 0.096 g (3.0 mmol) sulfur dissolved in 2.5 ml of oleylamine was swiftly injected into the hot reaction mixture with mild stirring and the temperature was kept constant at 150 °C for desired growth of QD. After 3 h, the reaction was quenched by adding the excess amount of toluene at a once. Then, the QD was washed with ethanol followed by centrifugation at 10,000 rpm and it was repeated twice. Then the precipitated part was dried in room temperature and required amount of this QDs were used for further experiment. Atomic absorption, X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDAX) studies confirm the stoichiometric constituent of the different compositions of nanocrystals which is reported in our previous publications [35,36].

### 2.3. Synthesis of PVK nanoparticles, QDs encapsulated PVK nanoparticles and QDs, porphyrin co-doped PVK nanoparticles

PVK nanoparticles were prepared by the previously reported re-precipitation method [19,37] PVK was properly dissolved in dried THF to maintain the 1.0 mg/ml concentration of PVK. A 500  $\mu$ l aliquot of this THF solution was rapidly injected into 10 ml double distilled water under vigorous stirring for 10–15 min followed by ultrasonication for 15 min. As a result, an aqueous solution of PVK nanoparticles was obtained. Then to avoid aging of the PVK nanoparticles THF was evaporated from aqueous solution by partial vacuum evaporation for 1 h followed by filtration through a 0.2  $\mu$ m filter paper. Finally, we obtained a stable aqueous solution of PVK nanoparticles, which was stable for 3–4 days.

The QDs doped PVK nanoparticles were prepared by similar re-precipitation method as described above. In this particular case, the THF solutions of QDs and PVK were mixed thoroughly to maintain the 3.5  $\mu$ M concentration of QDs and 1.0 mg/ml concentration of PVK, followed by ultrasonication for 5 min to obtain a clear mixed solution. Then 500  $\mu$ l of this THF solution was rapidly injected into double distilled water under vigorous stirring for 10–15 min followed by the standard procedures of ultrasonication, vacuum evaporation and filtration through a 0.2  $\mu$ m filter paper. Finally a solution of QDs doped PVK NP was obtained.

The QD, APTTP co-doped PVK nanoparticles were also prepared by re-precipitation method. In this case, the THF solutions of QDs, APTTP and PVK were mixed thoroughly to maintain the 3.5  $\mu$ M concentrations of QDs, 10  $\mu$ M concentration of APTTP and 1.0 mg/ml concentration of PVK, followed by ultrasonication for 5 min to obtain a clear mixed solution. Then same procedure was followed to obtain a solution of QDs, APTTP co-doped PVK nanoparticles.

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