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Electrostatically regulated photoinduced electron transfer in "cationic" eco-friendly CuInS₂/ZnS quantum dots in water†

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The potency of eco-friendly copper indium sulfide/zinc sulfide core/shell quantum dots (CIS/ZnS QDs) as efficient light harvesters in water is presented. A place exchange protocol is developed to prepare the much demanded cationic ([+]) CIS/ZnS QDs carrying a permanent positive charge, with ~60% retention of the QD photoluminescence (PL) in water. Both steady-state and time-resolved photophysical studies confirm efficient electron transfer from the photoexcited CIS/ZnS QDs to indocyanine green (ICG) dye. The electrostatic attraction between the oppositely charged [+] CIS/ZnS QDs and [–] ICG dye is responsible for the formation of a strong ground state complex, which is vital for achieving an efficient electron transfer process in water. The successful demonstration of the efficient light harvesting properties using [+] CIS/ZnS QDs will be decisive in the development of artificial photosynthetic systems based on eco-friendly quantum dots.

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Introduction

Mimicking and understanding of various processes in photosynthesis is the basis for modern solar energy research.¹⁻⁶ From a photophysical perspective, light harvesting phenomena such as electron and energy transfer processes form the integral part of all energy sciences including artificial photosynthesis.7-10 Various artificial molecules and materials with varying dimensions have been proposed and used extensively for light harvesting studies.11-17 Among them, semiconductor nanoparticles or quantum dots (QDs) have achieved a unique feat due to their quantum confinement effect and size-dependent optoelectronic properties.¹⁸⁻²⁴ Oftentimes, the light harvesting properties of QDs are comparable or even superior to the best-known materials in energy research. However, most of the exciting studies and applications have emerged from QDs containing toxic metal ions like Cd, Pb, Se, Te and so on. The growing restriction and regulation on the use of toxic ions have led to the development of eco-friendly QDs.25 Thus, the first generation research on QDs was focused on exploring the intriguing properties that scale with size, shape and composition.²⁶⁻³² The current and future studies have aimed to identify and replicate such exciting properties in eco-friendly QDs, along with

improving the existing knowledge.³³⁻⁵⁵ Consequently, QDs based on less toxic metal ions like InP,³³⁻³⁹ $CuInS_2$,⁴⁰⁻⁴⁹ AgInS₂,⁵⁰⁻⁵³ *etc.* are emerging as alternatives to the traditional toxic metal ion based QDs. Studies on their fundamental properties (like surface engineering, photophysics and light harvesting) are gaining scientific attention;³³⁻⁵⁵ however the corresponding studies in water still remain in their early stages.^{38,39,41a,54-58} On top of this, there is a high demand for cationic QDs due to their improved biomedical properties compared to the anionic counter parts.^{39,59} In general, it is extremely challenging to prepare stable QDs with permanent positive surface charge,^{39,59,60} with no reports on the synthesis of cationic CuInS₂ QDs to date. In this regard, the present study provides deeper insights into the fundamental light harvesting properties of stable cationic CuInS₂/ZnS QDs in water.

Generally in artificial photosynthesis, one of the fundamental challenges is to design a donor–acceptor system capable of participating in an efficient electron transfer process in an aqueous medium. The high solvent reorganization energy of water often destabilizes the charge separated state, thereby resulting in an inefficient electron transfer process.^{61–64} We have overcome this challenge by creating a favourable environment around CIS/ZnS QDs to facilitate a strong interaction between the QD donor and a biologically relevant organic dye acceptor, indocyanine green (ICG). For this, cationic ([+]) CIS/ZnS QDs were developed through proper surface modification using positively charged ligands, while retaining ~60% of the QD photoluminescence (PL; Fig. 1). Further, the ability of these [+] CIS/ZnS QDs to participate in light harvesting processes in water, as efficient electron donors, was systematically

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Fig. 1 (a) Schematic representation of the place exchange of OAm ligands with TMA ligands to generate stable [+] CIS/ZnS QDs in water. Optical photographs, under normal and UV light, clearly show the transfer of CIS/ZnS QD PL from the organic to aqueous phase. (b) Normalized steady-state absorption and PL spectra showing negligible changes in the position of the first excitonic peak and PL emission of CIS/ZnS QDs as a function of place exchange. The inset shows the unnormalized PL spectra, confirming that ~60% of the PL is retained in [+] CIS/ZnS QDs. (c) PL lifetime decay profiles of CIS/ZnS QDs before and after the place exchange reaction. (d) A representative TEM image of the 3.3 \pm 1.3 nm sized [+] CIS/ZnS QD.

investigated. Both steady-state and time-resolved spectroscopic studies confirmed an efficient PL quenching of [+] CIS/ZnS QDs in the presence of ICG dyes. A PL quenching efficiency of as high as \sim 80% was observed in water with [+] CIS/ZnS QDs as the donor and the [-] ICG dye as the acceptor. The [+] CIS/ZnS QD-[-] ICG dye pair satisfies the requisites for both resonance energy transfer and electron transfer processes. However, the solvent polarity and temperature dependent studies revealed the electron transfer process as the main pathway for the PL quenching in the [+] CIS/ZnS QD:::[-] ICG dye nanohybrid system. The electrostatic attraction between the oppositely charged [+] CIS/ZnS QDs and [-] ICG dye was responsible for the formation of a strong ground state complex, which was decisive in achieving an efficient electron transfer in water. The ability of [+] CIS/ZnS QDs to participate in an efficient electron transfer process will be decisive in the development of artificial photosynthetic systems based on eco-friendly quantum dots.

Results and discussion

Preparation and characterization of cationic CIS/ZnS QDs

The present work focuses on the light harvesting properties of eco-friendly [+] CIS/ZnS QDs in an aqueous medium. The first step towards this was to prepare stable [+] CIS/ZnS QDs in water, which was achieved by developing a place exchange protocol (Fig. 1a). The CIS/ZnS QDs stabilized with the oleyl amine (OAm) ligand were prepared using a reported protocol,⁴⁷ and further place exchanged with a positively charged thiolated ligand. In a typical place exchange protocol, 5 mL of a chloroform solution of OAm capped CIS/ZnS QDs (1 μ M) was mixed

with 2 mL aqueous solution of N,N,N-trimethyl(11-mercaptoundecyl)ammonium chloride (TMA, [+]) ligands (~0.2 mmol) and stirred for 4 h. The close to soft acid nature of Zn^{2+} ions present in the shell of the CIS/ZnS ODs will lead to a stronger bond formation with soft thiolates when compared to hard amines.65 Thus, the thiol group in the TMA ligand replaced the OAm ligand, and the quaternary ammonium group imparted the permanent positive charge and stability to CIS/ZnS QDs in water. The success of the place exchange reaction was visualized by the transfer of red colour of CIS/ZnS QDs from the organic to aqueous phase (Fig. 1a). The presence of OAm and TMA on CIS/ ZnS QDs was confirmed using Fourier transform infrared (FTIR) experiments (Fig. S1, Tables S1 and S2[†]). Detailed thermogravimetric analysis (TGA) revealed the surface coverage of OAm and TMA ligands to be 11.2 and 7.5 nm^{-2} on the surface of OAm capped CIS/ZnS and [+] CIS/ZnS QDs, respectively (Fig. S2⁺). Further, the nuclear magnetic resonance (NMR) studies confirmed the quantitative replacement of OAm with TMA ligands during the place exchange reaction (Fig. S3[†]). The details on the surface coverage and characterization are provided in the Section 2 of the ESI.†

The photophysical characterization of the as synthesized [+] and [-] CIS/ZnS QDs showed negligible changes in the absorption (first excitonic peak), PL emission and lifetime decay profiles (Fig. 1b and c and S4†). Approximately 60% of the PL was retained after the dispersion of CIS/ZnS QDs in water (inset of Fig. 1b and S5†). This decrease in the PL is commonly observed during the surface functionalization of QDs with thiolates, which is attributed to the increase in surface defects during the oxidation of thiols by the QDs.^{66,67} Also, the

tri-exponential PL lifetime decay of [+] CIS/ZnS QDs was well retained after the place exchange reaction ($\tau_{av} \sim 121$ ns; Fig. 1c and Table S3†). The representative transmission electron microscope (TEM) image of [+] CIS/ZnS QDs shown in Fig. 1d proves that the size (3.3 \pm 1.3 nm) and shape uniformity was well preserved after the place exchange reaction. The powder X-ray diffraction study confirms that the surface engineered [+] CIS/ZnS QDs retain their chalcopyrite⁶⁸ crystal structure after dispersion in water (Fig. S6†). Finally, the presence of cationic and anionic groups on CIS/ZnS QDs was confirmed using zeta potential (ζ) measurements ($\zeta_{[+]CIS/ZnS QD} = +28.3 \pm 0.4$ mV and $\zeta_{[-]CIS/ZnS QD} = -32.6 \pm 1.3$ mV; Fig. S7†).

Steady-state and time-resolved PL quenching studies in the [+] CIS/ZnS QD:::[-] ICG dye complex

Having accomplished success in preparing water stable [+] CIS/ ZnS QDs, our next objective was to test its ability to participate in light harvesting studies as an efficient electron/energy donor. The cationic charge on water soluble CIS/ZnS QDs allowed us to use oppositely charged organic dye molecules as the counterpart in light harvesting studies. Accordingly, the NIR emitting indocyanine green (ICG) dye was selected as the acceptor moiety for our studies ($\lambda_{max/abs} = 780$ nm and $\lambda_{max/em} = 813$ nm, Fig. S8[†]).^{69a} The presence of two sulfonate groups provided a net anionic charge to the ICG dye. Also, the fluorescence properties of the ICG dye have been extensively used in various clinical applications including medical diagnostics and laparoscopic surgery,^{69b-d} which further justifies the selection of the ICG dye in the present study. The suitability of [+] CIS/ZnS QDs and the [-] ICG dye to participate in light harvesting processes was checked by analysing the photophysics and energetics of the QD-dye pair (Fig. 2a). A strong spectral overlap integral (J) of \sim 6.78 \times 10¹⁵ M⁻¹ cm⁻¹ nm⁴, between the PL of [+] CIS/ZnS QDs



Fig. 2 Photophysical and energy level analysis for plausible energy and electron transfer processes. (a) A schematic representation of the plausible PL quenching process occurring between the [+] CIS/ZnS QDs and [–] ICG dye. (b) A spectral overlap between the PL of [+] CIS/ZnS QDs and the absorption of the [–] ICG dye. (c) Energy levels of the [+] CIS/ZnS QDs and [–] ICG dye against vacuum, estimated from a combination of absorption and cyclic voltammetry studies.

and the absorption of the [-] ICG dye, indicated that CIS/ZnS QDs and the ICG dye form an effective donor-acceptor pair for resonance energy transfer process (Fig. 2b).⁷⁰⁻⁷⁴ Additionally, the energy level calculations (from absorption & cyclic voltammetry studies, Fig. S9 Section 3 in the ESI†) showed that an electron transfer is thermodynamically feasible from the photoexcited [+] CIS/ZnS QDs to the ICG dye ($\Delta G = -38.6$ kJ mol⁻¹) (Fig. 2c). Hence, it can be concluded that the CIS/ZnS QD-ICG dye pair, in principle, can participate in both resonance energy transfer and electron transfer processes, under photoirradiation.⁷⁵ Accordingly, detailed photophysical studies based on both steady-state and time-resolved spectroscopic techniques were performed to understand the mode of photophysical interaction between [+] CIS/ZnS QDs and the [-] ICG dye.

Photophysical studies were performed by titrating small aliquots of the [-] ICG dye (3 µL of 0.17 mM) with a 3 mL aqueous solution of ~0.7 µM [+] CIS/ZnS QDs, under inert conditions (details are provided in the ESI†). A bathochromic shift of ~27 nm in the absorption of the [-] ICG dye was observed in the presence of [+] CIS/ZnS QDs, indicating a strong ground state interaction (Fig. 3a and S10†).⁷⁰⁻⁷⁴ The steady state PL studies were done by selectively exciting the [+] CIS/ZnS QDs at 450 nm, wherein the absorption for the ICG dye was minimal (Fig. S8†). A steady and gradual decrease in the PL of [+] CIS/ZnS QDs was observed upon the addition of the ICG dye, without the emergence of any new PL peak (Fig. 3b). The linear nature of the Stern–Volmer plot (slope $K_{SV} = ~2.46 \times 10^6 \text{ M}^{-1}$) and the high bimolecular quenching constant ($k_q = ~2.18 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$) confirm that the nature of binding in the [+] CIS/ZnS QD::::[-]



Fig. 3 PL quenching studies of the [+] CIS/ZnS QD:::[-] ICG dye nanohybrid. (a) Absorption spectra of the [-] ICG dye in the absence and presence of [+] CIS/ZnS QDs. (b) Spectral changes in the PL of [+] CIS/ZnS QDs, excited at 450 nm, upon sequential addition of the [-] ICG dye. The corresponding Stern–Volmer plot is shown in the inset. (c) A graph showing the saturation of relative PL of [+] CIS/ZnS QDs (// $_0$) and PL quenching efficiency vs. the concentration of ICG dye. (d) PL lifetime decay profiles of [+] CIS/ZnS QDs collected at the QD emission of 655 nm in the absence and presence of the [-] ICG dye (~1.4 μ M).

ICG dye complex is predominantly static in nature (inset of Fig. 3b).⁷⁰⁻⁷⁴ The steady-state PL quenching efficiency was estimated to be ~80% ($E = 1 - I/I_0$; where I and I_0 are donor PL intensities in the presence and absence of the acceptor). The quenching in the PL of [+] CIS/ZnS QDs as well as the steadystate quenching efficiency got saturated after the addition of ${\sim}1.4~\mu M$ [–] ICG dye (Fig. 3c). Time-resolved PL studies were performed to overrule the role of lack of selective excitation as well as to confirm the PL quenching in the [+] CIS/ZnS QD:::[-]ICG dye complex. Time-correlated single photon counting (TCSPC) studies revealed that the average lifetime of [+] CIS/ZnS QDs quenched from \sim 121 ns to \sim 35 ns in the presence of \sim 1.4 μ M [-] ICG dye (Fig. 3d, S11 and Table S4[†]). A PL quenching efficiency of ~70% was estimated from lifetime experiments $(E = 1 - \tau/\tau_0; \tau \text{ and } \tau_0 \text{ are donor PL average lifetimes in the})$ presence and absence of the acceptor), which is in good agreement with the steady-state values.

Proof for photoinduced electron transfer in the [+] CIS/ZnS QD:::[-] ICG dye complex

In general, quenching of the donor PL in the presence of an acceptor can be due to two main photophysical processes, namely resonance energy transfer and electron/charge transfer.⁷¹ Typically, a resonance energy transfer process is characterized by a gradual decrease in the PL of the donor along with a concomitant increase of the acceptor peak, through an isosbestic point.^{38,39,71,72} The absence of any PL peak corresponding to the ICG dye rules out the possibility of resonance energy transfer as the main pathway for the PL quenching of [+] CIS/ ZnS QDs, despite having a strong spectral overlap integral value. This leaves the electron transfer as the main mechanism for the PL quenching in the [+] CIS/ZnS QD donor:::[-] ICG dye acceptor complex.75,76 A photoinduced electron transfer (PET) process involves the transfer of an electron from the photoexcited donor to the ground state acceptor, resulting in the formation of a transient charge separated complex.⁷¹ Solvent polarity and reaction temperature are well known to influence the electron transfer processes.^{61–64,77,78} The charge separated complex formed due to the electron transfer process is more stabilized in a polar medium compared to a less-polar medium, resulting in higher efficiency of the electron transfer in polar solvents.61-64 Similarly, an increase in the temperature of the system will help in crossing the activation barrier, thereby increasing the rate and efficiency of the electron transfer process.^{77,78} Thus, performing PL quenching studies by varying the above mentioned parameters have been extensively used as a standard tool to ascertain the PET process in donor-acceptor systems.79-81 Accordingly, systematic PL quenching experiments were performed in the [+] CIS/ZnS QD donor:::[-] ICG dye acceptor complex, by varying the solvent polarity and temperature, to validate the process of electron transfer.

Solvent polarity dependent PL quenching experiments were performed by varying the dielectric constant of the medium from ~78 (H₂O) to ~47 (1 : 1 v/v H₂O : CH₃CN) at 298 K.⁶² Lower quenching of the steady-state PL of [+] CIS/ZnS QDs by the [-] ICG dye was observed in 1 : 1 H₂O : CH₃CN compared to water

(Fig. 4a and c). Consequently, the slope of the Stern–Volmer plot constructed from the steady-state PL quenching studies in water was higher than that in the 1 : 1 H₂O : CH₃CN mixture (Fig. 4d and S12†). A similar effect of solvent polarity was observed in the time-resolved PL quenching studies as well (Fig. 4b; $E_{H_2O} \sim$ 70% *vs.* $E_{1:1 \ H_2O: CH_3CN} \sim 60\%$). Also, the rate of electron transfer (k_{ET}) was observed to be higher in H₂O compared to the 1 : 1 H₂O : CH₃CN mixture (k_{ET} in H₂O = 2.0 × 10⁷ s⁻¹ and k_{ET} in 1 : 1 H₂O : CH₃CN = 1.44 × 10⁷ s⁻¹).

Analogous to the solvent polarity experiments, temperature dependent experiments too revealed an increase in the efficiency of PL quenching in the [+] CIS/ZnS QD:::[-] ICG dye complex with an increase in the temperature (Fig. 5 and S13[†]). For instance, the extent of quenching in the steady-state PL of [+] CIS/ZnS ODs by the [-] ICG dye was higher at 308 K followed by 298 K and 288 K (Fig. 5a-c and S13[†]). A similar temperature effect was observed in the lifetime quenching of [+] CIS/ZnS QDs in the presence of the [-] ICG dye (inset of Fig. 5a and b and S13[†]). The slopes of Stern-Volmer plots, constructed from the steady-state PL quenching studies, also increased as a function of temperature (Fig. 5d). The $k_{\rm ET}$ increased from 6.78 \times 10⁶ s⁻¹ to $3.28 \times 10^7 \text{ s}^{-1}$ as the temperature was increased from 288 K to 308 K. The linear nature of the plot of $\ln k_{\rm ET}$ vs. temperature confirms the Arrhenius dependence of $k_{\rm ET}$ on temperature, which is in agreement with the Marcus theory of electron transfer.82,83 Thus, both solvent polarity and temperature dependent PL quenching studies, along with energy level calculations, confirm the efficient light induced electron transfer from the [+] CIS/ZnS QD donor to the [-] ICG dye acceptor. Various electron transfer parameters in the [+] CIS/ZnS QD:::[-] ICG dye complex are summarized in Table 1 and S5.†



Fig. 4 Effect of solvent polarity on the PL quenching in the [+] CIS/ZnS QD donor:::[-] ICG dye acceptor complex. (a) PL spectral changes and (b) lifetime profiles of [+] CIS/ZnS QDs in the presence of ~1.4 μ M [-] ICG dye in the 1 : 1 H₂O : CH₃CN solution. (c) Comparison between the steady-state PL quenching in H₂O and 1 : 1 H₂O : CH₃CN solution in the presence of ~1.4 μ M [-] ICG dye and (d) the corresponding Stern–Volmer plots.



Fig. 5 Effect of temperature on the PL quenching in the [+] CIS/ZnS QD donor:::[–] ICG dye acceptor complex. PL spectral changes of [+] CIS/ZnS QDs in the presence of ~1.4 μ M [–] ICG dye at (a) 288 K and (b) 308 K. The corresponding quenching in the PL lifetime is shown in the insets. (c) Comparison between the steady-state PL quenching of [+] CIS/ZnS QDs by ~1.4 μ M [–] ICG dye at different temperatures, and (d) the corresponding Stern–Volmer plots. Inset shows the plot of ln $k_{\rm ET}$ vs. 1/T, confirming the Arrhenius dependence of $k_{\rm ET}$ on temperature.

Proof for electrostatically assisted photoinduced electron transfer

Next we discuss about the mode of interaction in the [+] CIS/ZnS QD donor:::[-] ICG dye acceptor complex that is responsible for achieving a highly efficient electron transfer process in water. The addition of excess salts to the [+] CIS/ZnS QD:::[-] ICG dye complex resulted in the recovery of the QD PL, revealing the screening of the charges and breaking of the complex by the salts^{84,85} (Fig. S14[†]). This preliminary study along with the presence of opposite surface charges, on the [+] CIS/ZnS QD donor and [-] ICG acceptor, points towards electrostatics as the main mode of interaction. Accordingly, a series of control experiments were performed to ascertain the potency of electrostatic forces (Fig. 6). The logical plan of replacing [+] CIS/ZnS QDs with [-] CIS/ZnS QDs, to impart electrostatic repulsion, cannot be adopted here due to the presence of both negative (due to two sulfonate groups) and positive charges (due to quaternary ammonium) on the [-] ICG dye. The positive charge



Fig. 6 Proof of electrostatically driven electron transfer process. (a) Variation in the absorption of the [+] MB dye in the presence of [+] and [-] CIS/ZnS QDs. (b) Spectral changes in the PL of [+] CIS/ZnS QDs upon sequential addition of the [+] MB dye. The corresponding lifetime profiles are shown in the inset. (c) Spectral changes in the PL of the [-] CIS/ZnS QD upon sequential addition of the [+] MB dye. The corresponding lifetime profiles are shown in the inset. (d) Stern–Volmer plot comparing the PL quenching between the similarly charged [+] CIS/ZnS QD:::[+] MB dye complex and the oppositely charged [-] CIS/ZnS QD:::[+] MB dye complex.

on the [-] ICG dye can still participate in electrostatic attraction with [-] CIS/ZnS QDs, leading to the complex formation and PL quenching. In order to get a conclusive proof for the role of electrostatics, PL quenching experiments were carried out by changing the acceptor moiety to a positively charged methylene blue dye ([+] MB), while retaining [+] CIS/ZnS QDs as the donor (Fig. S15[†]). CIS/ZnS QDs having a $\lambda_{max/em} = 620$ nm were synthesized to study the interaction with the MB dye, in order to have a clear differentiation between the donor and acceptor emission (MB, $\lambda_{max/em} = 682$ nm). The photophysical analysis and energy level calculations prove that the CIS/ZnS QDs and MB dye can, in principle, form an efficient donor-acceptor pair for both resonance energy transfer and electron transfer processes (Fig. S16[†]). No noticeable changes were observed in the absorption of the [+] MB dye in the presence of [+] CIS/ZnS QDs, indicating negligible ground state interaction between the similarly charged QD-dye pair (Fig. 6a). The lack of formation of

 Table 1
 Table summarizing various electron transfer parameters in the [+] CIS/ZnS QD donor:::[-] ICG dye acceptor complex under different experimental conditions

[+] CIS/ZnS QD:::[-] ICG dye complex	Solvent polarity		Temperature (K)		
	$H_2 O\left(\epsilon \sim 78\right)$	$1:1 \text{ H}_2\text{O}: \text{CH}_3\text{CN} (\varepsilon \sim 47)$	283	298	308
PL quenching efficiency (steady state) ^{<i>a</i>} PL quenching efficiency (lifetime) ^{<i>b</i>} Rate of electron transfer $(k_{ET})^c$	$\begin{array}{l} 80\% \\ 70\% \\ 2.0 \times 10^{7} \ \mathrm{s^{-1}} \end{array}$	$63\% \\ 60\% \\ 1.44 \times 10^7 \text{ s}^{-1}$	$\begin{array}{l} 60\% \\ 48\% \\ 6.78\times 10^6 \ {\rm s}^{-1} \end{array}$	$\begin{array}{l} 80\% \\ 70\% \\ 1.89 \times 10^7 \ \mathrm{s}^{-1} \end{array}$	$\begin{array}{l} 89\% \\ 78\% \\ 3.28\times 10^{7}~{\rm s}^{-1} \end{array}$

^a $E = 1 - I/I_0$. ^b $E = 1 - \tau/\tau_0$. ^c $k_{\rm ET} = 1/\tau - 1/\tau_0$.

the ground state complex resulted in negligible PL changes of [+] CIS/ZnS QDs in the presence of the [+] MB dye (Fig. 6b, S17 and Scheme S1[†]). A similar trend was observed in the lifetime quenching studies as well (inset of Fig. 6b and Table S6[†]). However, a strong ground state interaction was present between the oppositely charged [-] CIS/ZnS QDs and [+] MB dye (Fig. 6a). This was also reflected in the quenching of the steady-state PL and lifetime of [-] CIS/ZnS QDs by the [+] MB dye (Fig. 6c). Both steady-state and time-resolved PL quenching studies confirm that the [-] CIS/ZnS QDs was able to participate in an efficient electron transfer process with the [+] MB dye (Fig. 6, S18 and Table S7[†]). The Stern–Volmer plots shown in Fig. 6d compare the PL quenching between the similarly charged [+] CIS/ZnS QD:::[+] MB dye complex and oppositely charged [-] CIS/ZnS QD:::[+] MB dye complex. Thus, the dependence of the PL quenching on the surface charges of the CIS/ZnS QD donor and the dye acceptor confirms the necessity of electrostatic attraction in achieving an efficient electron transfer process in the [+] CIS/ZnS QD:::[-] ICG dye complex in water. It is worth mentioning that the electron transfer is predominantly observed in both CIS/ZnS QD-ICG dye and CIS/ZnS QD-MB dye nanohybrid systems; even though they satisfy the requisite for resonance energy transfer process as well. Similar observations have been previously reported in the CdTe QD-cresyl violet dye donor-acceptor system.75 Thus, further experiments with more donor-acceptor systems should be carried out to generalize whether the electron transfer will always dominate over the energy transfer, when a donor-acceptor system satisfies the requisite for both these processes.

Conclusions

The light harvesting properties of eco-friendly cationic CIS/ZnS QDs in water is summarized in the present study. The surface of CIS/ZnS QDs was functionalized with both cationic and anionic thiolated ligands to impart stable dispersion in water, with \sim 60% retention of their photoluminescence. Both the steadystate and time-resolved photophysical studies confirmed an efficient PL quenching of the [+] CIS/ZnS QD donor by the [-] ICG dye acceptor, in water. Solvent polarity and temperature dependent PL quenching studies revealed an electron transfer process as the main pathway for the PL quenching in the [+] CIS/ ZnS QD:::[-] ICG dye nanohybrid system. The strong electrostatic attraction between the oppositely charged [+] CIS/ZnS QDs and [-] ICG dye was responsible for the formation of a strong ground state complex, which was vital in achieving an efficient electron transfer process in an aqueous medium. Successful demonstration of an efficient electron transfer process with [+] CIS/ZnS QDs can serve as a model system for future light harvesting studies using eco-friendly CIS/ZnS QDs, especially for applications in an aqueous medium like photocatalysis, sensing, bioimaging etc.

Conflicts of interest

There are no conflicts to declare.

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