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Fluorescence Energy Transfer from Doped to Undoped Quantum Dots

Suresh Sarkar, Amit Ranjan Maity, Niladri S. Karan, and Narayan Pradhan*

Department of Materials Science and Centre for Advanced Materials, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

S *Supporting Information*

ABSTRACT: We report here the fluorescence energy transfer between two types of inorganic semiconductor nanocrystals: one is doped (d-dots) with optically active transition metal ion and other one is the undoped quantum dots (q-dots). While the two types of undoped quantum dots do not show significant energy transfer, the doped quantum dots under similar conditions show efficient energy transfer to the undoped one. The difference in the lifetime makes the doped quantum dots as donor for quantum dots. Exploring Cu-doped and Mn-doped d-dots as donor with the suitable size of CdSe q-dots as acceptor, we report here a detailed study of d-dot to q-dot energy transfer and investigate the possible mechanism.
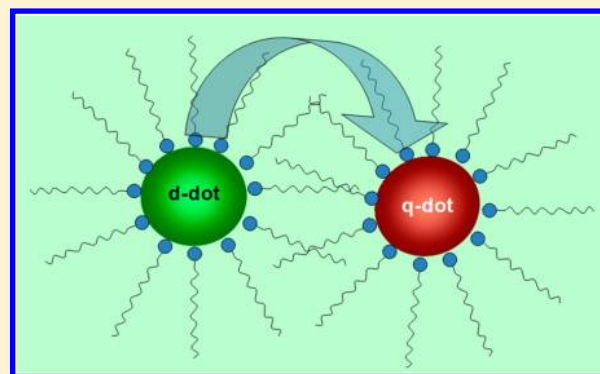
INTRODUCTION

Light-emitting colloidal semiconductor nanocrystals (quantum dots) have widely been studied as fluorescence energy donor in the conjugation of wide varieties of organic dyes[1−4] as well as with different types of nanocrystals.[5−8] Quantum dots (q-dots) have unique optical properties that offer a compelling alternative to that of the traditional dye fluorophore. The advantages associated with q-dots are the size-dependent tunable emission,[9] high quantum yield,[10] emission color purity,[9,10] and possible dispersion in both aqueous and nonaqueous medium,[11] which have led these q-dots to be the workhorse to study fluorescence energy transfer in conjugation with different fluorophore acceptors. Thus, using q-dots as donor, wide varieties of applications especially in biological systems such as DNA hybridization, protein conformation analysis, and intercellular receptor−ligand binding dynamics have been accomplished.[2,12−15]

In fluorescence resonance energy transfer (FRET), the donor nanocrystals transfer their emitted photon energy to the ground state of the acceptor fluorophore nonradiatively through dipole−dipole interaction when they are in close proximal distance within 1−10 nm.[1,8,16,17] For the ideal case, the donor must have a wide range of emission tunability for the better control of the spectral overlap with the absorption spectra of a particular acceptor, the ability to get excited at a wavelength far away from the respective emission to allow selective excitation of the donor only, and higher excited-state lifetime than the acceptor.[1,8,16,17] The efficiency of FRET essentially depends on the extent of spectral overlap, separation between the donor and acceptor, and relative orientation of the transition dipole moment as well as on the excited-state lifetime of the donor and acceptor.[8] Despite q-dots having several advantages

compared to dye fluorophore, two q-dots cannot be an efficient FRET pair because of the similarity in their excited-state lifetimes. However, there are still few reports on such kind of energy transfer with low efficiency.[7,18−20]

We explore here the energy transfer between two types of inorganic semiconductor nanocrystals; one is the doped nanocrystals (d-dots) in which specific optically active dopants such as Cu^+ or Mn^{2+} ions are doped in a specific nanocrystal and another one is the quantum dots (q-dots). The d-dots, which have significantly higher excited-state lifetime (a few microseconds to milliseconds)[21−24] than the q-dots (a few nanoseconds), can act as donor for the particular size of q-dots in their mixture in solution. Although there are a few reports on the fact that the doped nanocrystals can act as an efficient donor in conjugation with dye fluorophore,[25,26] the energy transfer between doped and undoped nanocrystals has not yet been studied. The efficient energy transfer between these two types of dots has been studied here by simply titrating one with other dots in solution. With the progress of the mixing, switching of emission energy from d-dots to q-dots is observed with almost complete quenching of dopant emission with concomitant enhancement of q-dots excitonic emission. Using Cu-doped ZnSe/S, Cu-doped ZnInSe, and Mn-doped ZnS as d-dots with different sizes of CdSe q-dots, we have studied the energy transfer here in detail. From different observations, this energy transfer is understood as FRET and finally a possible mechanism is proposed.
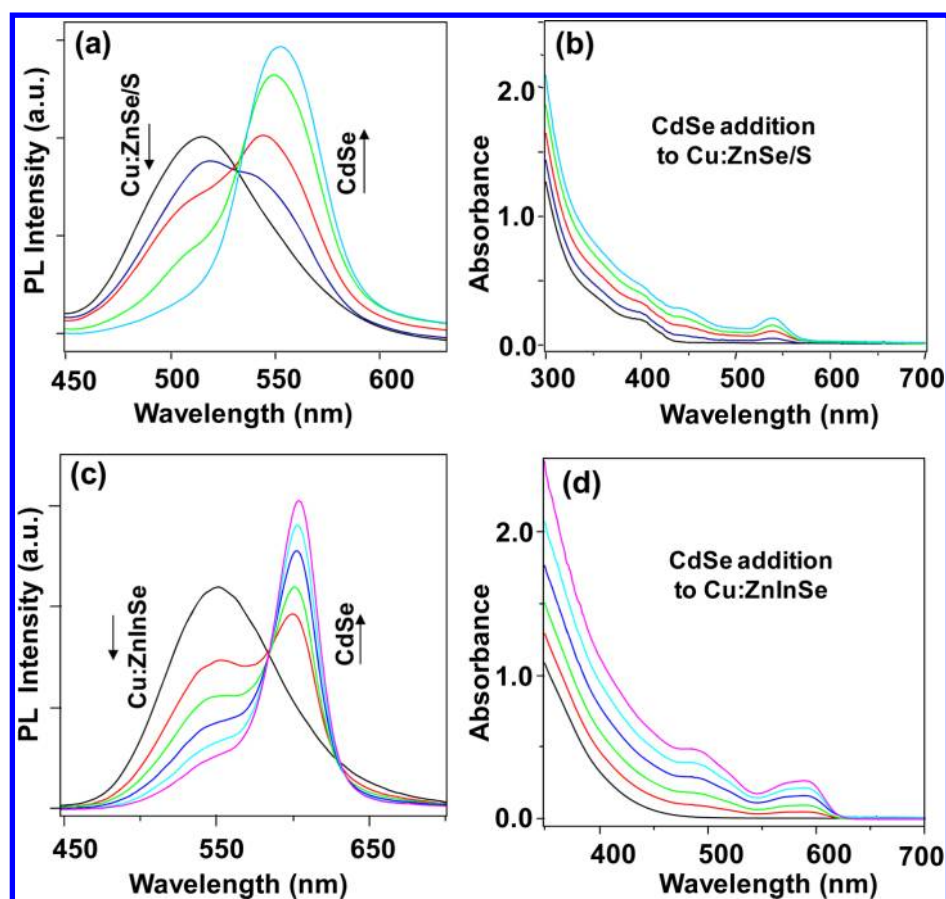
Figure 1. (a,c) Changes of photoluminescence (PL) spectra of Cu-doped ZnSe/S and Cu-doped ZnInSe on successive addition of CdSe, respectively. (b,d) Corresponding absorption (UV−vis) spectra of the titration of d-dots with CdSe q-dots as presented in (a) and (c), respectively.

■ EXPERIMENTAL SECTION

Synthesis of d-Dots and q-Dots. Cu-doped ZnSe/S,[22] Cu-doped ZnInSe,[27] and Mn-doped ZnS[28] nanocrystals (d-dots) were synthesized following literature-reported synthetic protocol. Similarly, the CdSe[29] and CdS[30] q-dots were also prepared using reported methods. Details of the synthetic methods are provided in the Supporting Information File (SI).

Titration of d-Dots with CdSe. To study the energy transfer between d-dots and q-dots, purified fatty amine-capped respective nanocrystals are dissolved in chloroform and stored in inert atmosphere. For the titration, d-dots are taken in a cuvette and q-dots are added dropwise with stirring. The optimum concentration of the q-dots is chosen to avoid self-quenching and the optical changes are measured by both UV−visible and fluorescence spectroscopy. In a typical case, 2 mL of Cu-doped ZnSe/S d-dots solution in chloroform was taken in a standard fluorometer cuvette having optical density (OD) ∼0.4 at 365 nm. To this solution, CdSe q-dots in chloroform were added dropwise (each addition of CdSe contributes ∼0.2 OD at 365 nm to the mixture solution) and the optical changes were measured spectrophotometrically. Details of the experimental setup are shown in Figure S1 in the SI.

The titration for Cu-doped ZnInSe and Mn-doped ZnS with q-dots was carried out in similar procedure to that of Cu-doped ZnSe/S-CdSe system.

■ RESULTS AND DISCUSSION

To study the energy transfer between two kinds of dots, CdSe q-dots are preferred as acceptor that show size-dependent wide window tunable emission and Cu-doped ZnSe/S, Cu-doped ZnInSe, and Mn-doped ZnS d-dots are chosen as donor which possess longer excited-state lifetime and tunable emission spectrum. Literature reports reveal that the charge recombination for Cu-doped nanocrystals occurs involving the conduction band of the host and the Cu state. Hence, Cu-doped nanocrystals exhibit band-gap-dependent tunable dopant emission.[31,32] Consequently, Cu-doped ZnSe exhibits tunable dopant emission in blue-green window[22,24] and Cu-doped ZnInSe shows tunable dopant emission from green to red window of the visible spectrum.[27] The dopant emission of Mn-doped ZnS originates due to the d−d $^4T_1-^6A_1$ transition of Mn^{2+} states, exhibiting at ∼580−590 nm.[33] The excited-state lifetime of the Cu dopant emission remains in the microsecond range, but for Mn dopant it is in millisecond.

As Cu-doped nanocrystals show wide window tunable emission, we have first investigated the fluorescence energy transfer using these d-dots with desired size of CdSe. Figure 1a,b shows the successive photoluminescence and absorption spectra obtained during titration of CdSe q-dots having emission center ∼550 nm with Cu-doped ZnSe/S emitting at ∼515 nm. Initially, Cu-doped ZnSe/S nanocrystals are synthesized and purified, and the required concentrations of these d-dots are taken in a cuvette. Similarly, CdSe nanocrystals are synthesized and, after purification, appropriate concentrated solution of these q-dots is added dropwise to the d-dots taken in the cuvette. On addition of q-dots, the emission intensity of d-dots reduces and that of q-dots enhances. It has been observed that the final intensity of q-dots remains less in the
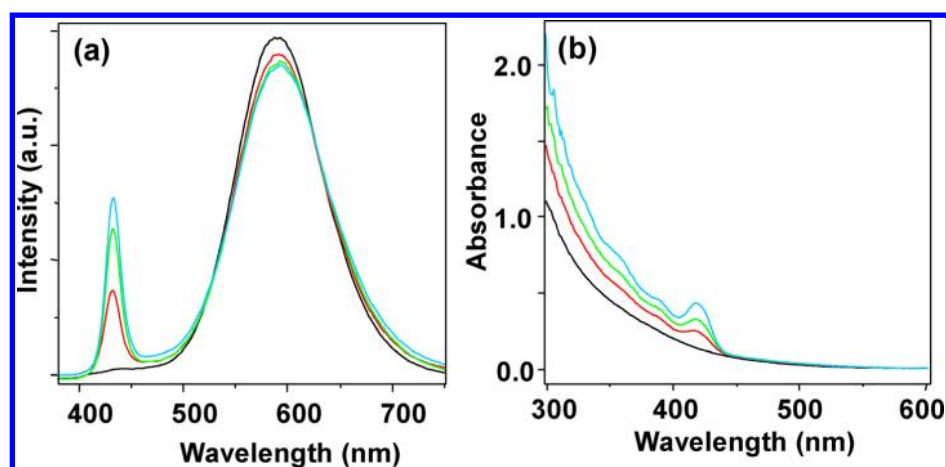
Figure 2. (a,b) Changes of photoluminescence and the corresponding absorption spectra of Cu-doped ZnInSe on successive addition of CdS, respectively.
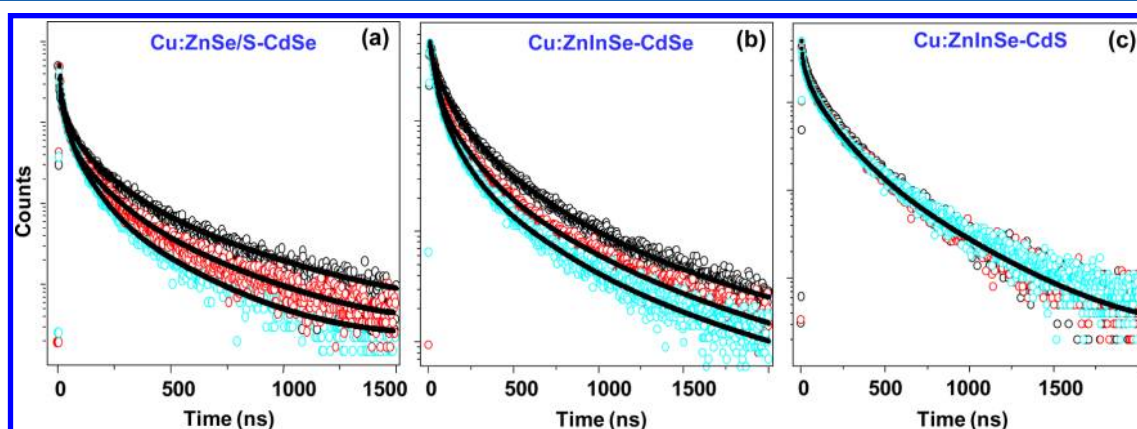

Figure 3. Excited-state lifetime decay of d-dots at the different stages during titration with q-dots. (a,b) Lifetime decay plots of Cu-doped ZnSe/S (emission position 515 nm) and Cu-doped ZnInSe (emission position 550 nm) with successive addition of CdSe, respectively. (c) Lifetime decay plot of Cu-doped ZnInSe (emission position 591 nm) with successive addition of CdS. Details of the lifetime fitting parameters and average lifetimes are provided in Tables 1, 2, and 3.

control reaction without d-dots than that obtained in the titration with d-dots. This suggests that the excess intensity of q-dots is gained from d-dots. The concentrations of both d-dots and q-dots are maintained relatively low to avoid the self-absorption.

Further, to understand more about this energy transfer, Cu-doped ZnInSe nanocrystals are considered as donor instead of Cu-doped ZnSe/S d-dots. Figure 1c,d shows the successive photoluminescence (PL) and absorption spectra obtained during the titration of this d-dots (emission center 550 nm) with CdSe emitting at 603 nm. Interestingly, similar observation has also been obtained here in this case as observed for Cu-doped ZnSe/S−CdSe pair case.

To understand more about the fluorescence energy transfer with our selected d-dots and q-dots pairs, we have further analyzed the importance of the spectral overlap. It has been observed that in both cases (Cu-doped ZnSe/S-CdSe or Cu-doped ZnInSe−CdSe pair, Figure 1) there is an overlap of the absorption spectra of the q-dots with the emission spectra of the d-dots (Figure S2a,b in the SI). To understand this as a precondition for the energy transfer, we have carried out the titration with a different set of q-dots whose absorption spectra do not have such overlap with the emission spectra of the d-dots (Figure S2c in the SI). However, it remains practically

difficult to obtain CdSe dots with absorption energy higher than the emission of Cu-doped d-dots. Hence, we have considered CdS nanocrystals to perform this study. The CdS q-dots are also synthesized following the literature-reported protocol[30] and, after purification, they are dissolved in chloroform. These nanocrystals (emission maxima at 433 nm) are used for the titration with Cu-doped ZnInSe d-dots (emission maxima at 591 nm).

Figure 2a,b shows the changes in the photoluminescence and absorption spectra on successive addition of CdS q-dots to Cu-doped ZnInSe d-dots. Interestingly, herein, the dopant emission intensity is not observed to be affected much during the titration and only the CdS q-dots intensity increases on its successive addition. This suggests that there is no fluorescence energy transfer in this d-dots and q-dots pair.

However, to understand the details of this energy transfer, lifetime decay measurements were carried out for the different sets of d-dots-q-dots pairs. Figure 3a−c shows the change in the lifetime decay plots for Cu-doped ZnSe/S with CdSe, Cu-doped ZnInSe with CdSe and Cu-doped ZnInSe d-dots with CdS q-dots, respectively. For the first two cases (Figure 3a,b), where d-dots are titrated with CdSe q-dots, the lifetime of d-dots is found to be reduced gradually with successive addition of CdSe. Interestingly, for the third case (Figure 3c), the

Table 1. Lifetime Fitting Parameters for Cu-Doped ZnSe/S−CdSe

spectra	[QD] (M)	$\tau_1{}^a$ (ns)	A_1	$\tau_2{}^a$ (ns)	A_2	τ_3 (ns)	A_3	$\chi_R{}^2$	$\tau_{av}{}^a$ (ns)
black	0.0	4.201	0.022	36.98	0.681	318.6	0.431	1.10	143.2
red	1.07×10^{-6}	3.138	0.039	32.48	0.890	285.3	0.340	1.04	108.1
sky blue	2.68×10^{-6}	2.872	0.030	30.42	0.735	227.1	0.318	0.99	87.25

$^a\pm10\%$ (error).

Table 2. Lifetime Fitting Parameters for Cu-Doped ZnInSe−CdSe

spectra	[QD] (M)	$\tau_1{}^a$ (ns)	A_1	$\tau_2{}^a$ (ns)	A_2	τ_3 (ns)	A_3	$\chi_R{}^2$	$\tau_{av}{}^a$ (ns)
black	0.0	5.130	0.049	38.98	0.427	392.9	0.431	1.11	205.2
red	3.58×10^{-7}	4.932	0.034	35.19	0.361	357.4	0.296	1.08	171.5
sky blue	8.23×10^{-7}	4.216	0.028	30.7 2	0.313	306.5	0.210	1.13	134.4

$^a\pm10\%$ (error).

Table 3. Lifetime Fitting Parameters for Cu-Doped ZnInSe−CdS

| spectra	[QD] (M)	$\tau_1{}^a$ (ns)	A_1	$\tau_2{}^a$ (ns)	A_2	τ_3 (ns)	A_3	$\chi_R{}^2$	$\langle \tau \rangle^a$ (ns)
black	0.0	5.467	0.036	44.19	0.453	369.2	0.615	1.01	223.9
red	4.68×10^{-7}	5.686	0.068	45.10	0.499	375.7	0.681	1.05	223.0
sky blue	8.43×10^{-7}	5.580	0.049	45.2	0.479	373.9	0.598	1.09	217.9

$^a\pm10\%$ (error).

lifetime of the d-dots remains the same. These results suggest the fluorescence energy transfer from d-dots to q-dots is observed only when there is a spectral overlap between the absorption spectra of the q-dots with the emission spectra of the d-dots.

However, to understand this energy transfer as FRET we correlate our results with the effective requirements for FRET. The spectral overlap, higher excited-state lifetime of donor, and close proximity of donor and acceptor are the essential conditions to exhibit FRET. While the first two conditions are already verified with our chosen donor−acceptor pair, the third one is the proximal distance between these two types of dots which must be within FRET distance in solution and needs to be debated further.

These nanocrystals being capped with long-chain hydrophobic ligands, it is expected that they would come within the optimal FRET distance via weak hydrophobic−hydrophobic interaction of the surface ligands in solution and would exhibit FRET. Literature reports reveal that the FRET can be observed in nonaqueous solution between q-dots and dye fluorophore through hydrophobic interaction.[34,35] Even this hydrophobic interaction can lead to conjugate formation of spherical nanocrystals in solution[36] as well as the self-assembly formation of nonspherical nanocrystals (rods) due to the interdigitation of the surface hydrophobic ligands.[37] Moreover, this interaction has intensively been exploited in coating chemistry for the water solubilization where the hydrophobic ligands on the surface of the nanocrystals and the hydrophobic tails of the amphiphilic ligands interact, making the hydrophobic nanocrystals water solubilized.[38,39] All these reports suggest that the hydrophobic ligand capped nanocrystals effectively interact through hydrophobic−hydrophobic interaction of the surface ligands of the nanocrystals in their dynamic motion in solution.

Assuming FRET from the above results, we further propose here a probable mechanistic path of this kind of energy transfer from dopant states of d-dots to q-dots (Figure 4). While these nanocrystals are dispersed in nonaqueous solution (chloroform), there is always a chance of getting the average number of particles within the FRET distance.
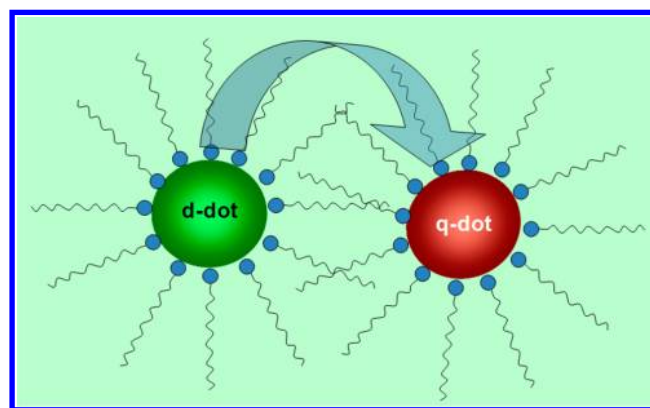
Figure 4. Schematic presentation of energy transfer from d-dots to q-dots.

Thus, on excitation of the d-dots, the generated exciton involves the dopant state for its recombination and this helps the dopant emission to have longer excited-state lifetime. This efficiently helps to excite the ground state of CdSe nanocrystals via FRET.

Further, all these facts that the decrease of d-dots' emission intensity with the concomitant increase of q-dots' emission intensity and the decrease of the excited-state lifetime of the d-dots on succesive addition of q-dots support the possible FRET between these two types of dots. The other possibility which may arise here is the reabsorption. But, this is less expected as we have used relatively low concentration of both the dots. Second, this energy transfer is not efficiently observed within q-dots and q-dots emitting at different wavelength positions. Hence, the fluorescence energy transfer observed here from d-dots to q-dots may not be due to reabsorption. But, the important issue to be concerned here is the common excitation window for both the donor and acceptor dots. In the case of the ideal FRET pair, there should be minimum excitation cross talk between the donors and acceptors. Hence, herein, with our chosen donor−acceptor pair the decrease of the emission intensity of the d-dots in the presence of q-dots might not be
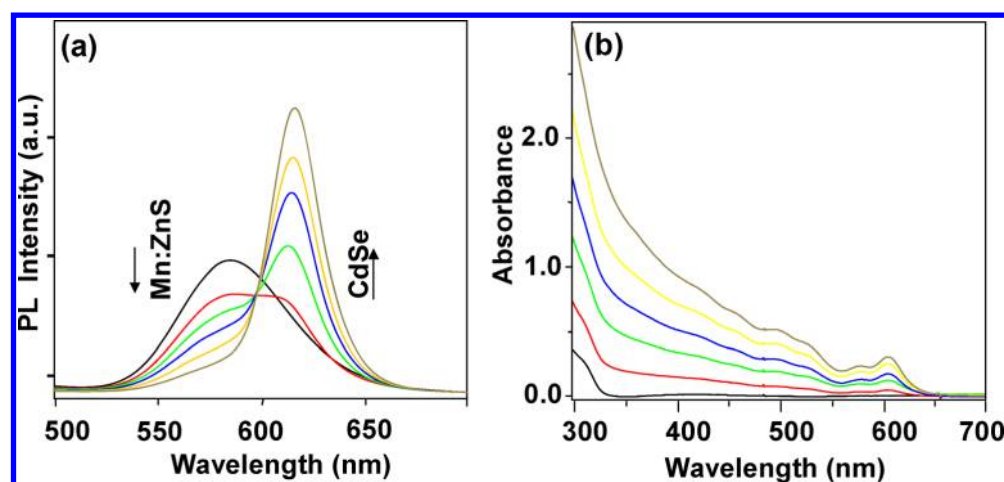
Figure 5. (a) Successive PL spectra obtained during addition of CdSe (emission at 618 nm) nanocrystals to Mn-doped ZnS (emission at 585 nm) nanocrystals. The nanocrystals solution has been excited at the best excitation of ZnS (320 nm). (b) Corresponding UV−vis spectra of the same titration as presented in (a).

due to FRET only. But, a certain extent of donor emission quenching is contributed due to their excitation energy distribution.

Hence, calculation of FRET efficiency from quenching of donor emission on successive additions of CdSe q-dots to a fixed amount of d-dots solution is complicated for this FRET pair, and the quantitative FRET efficiency estimation from the calculation of the decrease in the PL intensity of the donor in the presence of acceptor is expected to be associated with error. Alternatively, we have calculated the FRET efficiency considering the decrease of lifetime of the d-dots in the presence of q-dots. Here, we have considered the Cu-doped ZnSe/S for the calculation of the FRET efficiency. It is to be mentioned here that the Cu dopant emissions undergo quenching on air exposure and hence the entire titration has been carried out in inert atmosphere to avoid the decrease of Cu dopant emission due to surface oxidation.

For a typical case, amine-capped d-dots (Cu-doped ZnSe/S, QY = 0.19) and CdSe nanocrystals in chloroform (n_d = 1.446) are mixed, varying the q-dots to d-dots ratio. As we have synthesized two types of dots following the literature method, we have considered the size of these dots as reported in the respective literature. The molar extinction coefficient of CdSe has been calculated following the equation as reported by Peng et al.[40] and for our case of CdSe (2.84 nm) it is found to be 9.31×10^4 cm^{-1} M^{-1}. We have also calculated the overlap integral (I) following the equation as reported in the literature.[17] We have calculated the integrated area of the spectral overlap (Figure S2a in the SI) and the molar extinction coefficient of CdSe acceptor (CdSe in Figure 1a) from the literature method[40] to calculate the overlap integral. The calculated overlap integral (I) is found to be 5.10×10^{-13} cm^3 M^{-1}. We have also calculated the Förster distance to be R_o = 4.52 nm following the literature method (detailed equation is presented in the SI). We have observed 39% of FRET efficiency at a number ratio of ∼6. Here, we mention that due to prolonged time of annealing, the donor Cu-doped ZnSe/S nanocrystals get faceted but we have considered the average size of 4 nm for the calculation of the number of particles.

Further, in addition to Cu-doped d-dots, we have also studied the energy transfer from Mn-doped ZnS d-dots to CdSe q-dots. Figure 5a,b shows the change in the PL and

absorption spectra of a typical titration of Mn-doped ZnS d-dots having emission peak at 585 nm with CdSe q-dots having emission center at 618 nm. It is observed that the Mn dopant emission intensity reduces with a concomitant increase of CdSe emission intensity during the titration of Mn-doped d-dots with CdSe q-dots.

Further, to ascertain this phenomenon as energy transfer, we have carried out the experiments with different sizes of CdSe q-dots. Similar to the case of Cu-doped d-dots, we have observed the energy transfer only when there is spectral overlap of the emission spectra of Mn-doped ZnS with the absorption spectra of CdSe (details in Figure S3 in the SI). However, when we carried out the lifetime measurement of Mn-doped ZnS in the absence and presence of CdSe q-dots, with our several efforts, we have found little extent of decrease of excited-state lifetime of Mn-doped ZnS d-dots on addition of CdSe q-dots (Figure S4 in the SI). Nevertheless, the change in lifetime for this case is not significant as observed in Cu-doped CdSe pair. This may be due to the lesser extent of spectral overlap of Mn-doped d-dots in comparison to Cu-doped d-dots with CdSe. On the other hand, this might be due to the effect of common excitation. However, we believe there is also certain extent of energy transfer from Mn-doped ZnS to the suitable size of CdSe q-dots in solution but, to understand this, additional experimental support is required.

■ CONCLUSION

In conclusion, we report here efficient energy transfer between two types of inorganic semiconductor nanocrystals, doped and undoped quantum dots without any additional linker. The observed significant energy transfer between the d-dots and q-dots is possibly due to the difference of their excited-state lifetime and it is worth mentioning that the spectral overlap plays one of the most crucial roles here in this case. From different observations, it is assumed here that such energy transfer is the FRET between two different types of dots. Unlike organic dyes, both these nanocrystals resist photobleaching and, hence, these FRET pairs can be future alternatives for different biological applications.

■ ASSOCIATED CONTENT

S **Supporting Information**

Supporting results and figures are avaliable. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: camnp@iacs.res.in. Tel.: +91 33 2473 4971. Fax: +91 33 2473 2805.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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