

Efficient Energy Transfer from 1,3,5-Tris(N-phenylbenzimidazol-2,yl) Benzene to Mn:CdS Quantum Dots

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Abstract

We report the energy transfer between Mn doped CdS quantum dots (Mn:CdS QDs, with the structure of MnS/ZnS/CdS) and 1,3,5-tris(N-phenylbenz-imidazol-2,yl) benzene (TPBI) in inorganic/organic blend films using steady-state and time-resolved photoluminescence (PL) spectroscopy. The change in the PL excitation intensity of the Mn:CdS QDs and the PL lifetime of the TPBI clearly demonstrates an efficient energy transfer process in the QDs/TPBI blend films. Further, it is found that the efficiency of Förster resonance energy transfer increases with increasing the CdS shell thicknesses and reaches as high as 50%. These results highlight the potential of Mn doped QDs for fabricating high-performance QD light-emitting diodes.

1. Introduction

The inorganic/organic composites with quantum dots (QDs) and organic functional molecules have been explored for their applications in light emitting diodes (LEDs) due to their size-tunable optoelectronic properties and flexible fabrication conditions.¹⁻⁴ Up to now, the CdSe pristine QDs are the most studied ones due to their excellent optical properties. As compared to pristine QDs, recent studies indicated that transition-metal Mn ions doped QDs have many advantages, such as minimum self-quenching due to the large Stokes shift, and very high thermal, chemical, and photochemical stability. They are considered to be the especially ideal emissive material for applications requiring significant power and high density of QDs, such as QD-LEDs.⁵⁻⁷

Benefit from the quick improvement in the optical properties of Mn ions doped QDs in recently years, applying them in QD-LEDs become possible. It is known that the highly efficient archetypical QD-LEDs are fabricated by sandwiching an inorganic QD layer between two layers of organic charge transporting materials (CTMs), in which excitons in the QD layer can be generated by exciton energy transfer and charge injection from the organic molecules.^{4,8-9} The key to optimize the performance of QD-LEDs seems to be a detailed understanding of the energy transfer process, which is dependent not only on the donor-acceptor separation distance, but also the energy level alignments between the QDs and CTMs. However, to date, no report about them for Mn ions doped QDs and CTMs has been given yet.

Here, we report a study on the energy transfer process

from 1,3,5-tris(N-phenylbenz-imidazol-2,yl) benzene (TPBI, commonly used CTM) to Mn:CdS QDs in inorganic/organic blend films. The PL intensities and lifetimes of the QDs and TPBI in the films were measured by steady-state and time-resolved PL spectroscopy to demonstrate the energy transfer process. On the basis of obtained energy transfer rates to the QDs, we discussed the effect of the CdS shell thickness on the energy transfer rate and efficiency.

2. General Instructions

Mn:CdS QDs with different CdS shell thicknesses were synthesized following Ref.6. The CdS shell layer thicknesses of the QDs are 1.5, 2.2, and 2.5 MLs, for Samples A, B, and C, respectively. The QD/TPBI blend films were deposited on quartz substrates from QD and TPBI mixed solutions with a mole ratio of 1/200-1/3200 by a spin coater with a speed of 1000 rpm. The QD/PMMA (poly(methyl methacrylate)) films were prepared as reference samples. PL spectra, and PL decays were recorded using a Horiba Jobin Yvon Fluoromax-4P with a time-correlated single-photon-counting (TCSPC) spectrometer.

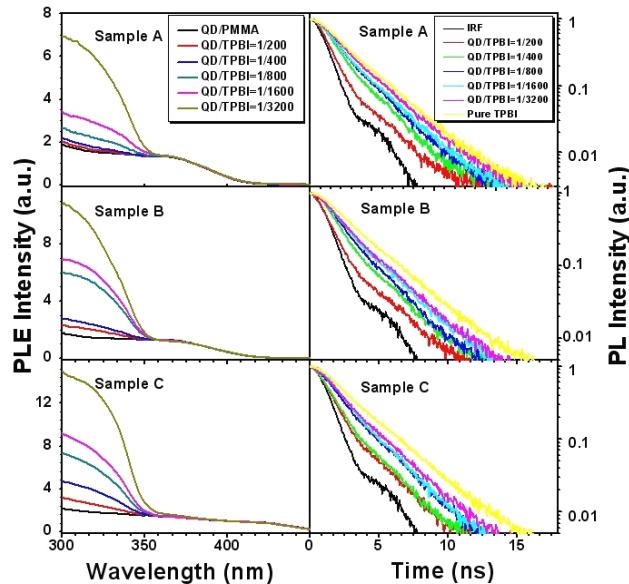


Fig. 1 Normalized PL excitation spectra of QDs (left) and PL decay curves of TPBI (right) in QD/TPBI blend films with different QD/TPBI molar ratio.

The PL excitation spectra of the QDs in QD/TPBI

blend films with different molar ratio are shown in Fig. 1a, b, and c. The PLE spectra detected at an emission wavelength of QD (580 nm) were normalized at a wavelength of 380 nm without the absorption from TPBI. The relative enhancement in the PL excitation intensity of the QDs in the blend films is clearly observed at the absorption wavelength of the TBPI, compared with that in PMMA films, indicating an obvious energy transfer process from the TPBI to QDs.^{10, 11}

In order to clarify the energy transfer dynamics in the blend films, the PL decays are studied. Fig. 1d, e, and f shows the time-resolved PL decay profiles of TPBI (probed at 370 nm) in QD/TPBI blend films with different molar ratio. It is evident that the PL decays of TPBI molecules significantly became faster in the blend films. This suggests that the energy transfer adds another decay channel to the excited states of the TPBI.

To quantify the energy transfer progress, the PL lifetime, energy transfer efficiencies (η) and rates (K_{ET}) are summarized in Table I, in which the lifetimes were obtained by fitting the PL decay curves of the TPBI with a monoexponential function. The η and K_{ET} were determined by expressions:

$$\eta = 1 - \tau_{\text{donor-acceptor}} / \tau_{\text{donor}} \quad (1)$$

$$K_{ET} = 1 / \tau_{\text{donor-acceptor}} - 1 / \tau_{\text{donor}} \quad (2)$$

where $\tau_{\text{donor-acceptor}}$ and τ_{donor} are the PL lifetimes of TPBI in blend and neat films, respectively.¹⁰

Table I Summary of time-resolved TPBI PL decay fitting parameters for blend films with various molar ratios.

	QD/TPBI					Pure
	1/200	1/400	1/800	1/1600	1/3200	TPBI
Sample A	τ (ns)	1.25	1.77	2.04	2.20	2.43
	η (%)	52.5	32.7	22.4	16.3	7.6
Sample B	K_{ET} (ns ⁻¹)	0.42	0.18	0.11	0.07	0.03
	τ (ns)	1.26	1.66	1.88	2.13	2.28
Sample C	η (%)	52.1	36.9	28.5	19.0	13.3
	K_{ET} (ns ⁻¹)	0.41	0.22	0.15	0.09	0.06
	τ (ns)	1.40	1.53	1.8	2.01	2.25
	η (%)	46.8	38.0	31.6	23.6	14.4
	K_{ET} (ns ⁻¹)	0.33	0.27	0.18	0.12	0.06

It is noted that the energy transfer efficiency decreases as increasing the concentration of the TPBI. This result confirms that the FRET process in the blend films of TPBI and QDs is dependent on the donor/acceptor molar ratio due to the change of the average distance between TPBI donor molecules and the QD acceptors.¹⁰⁻¹¹

It is also clearly shown that the energy transfer efficiency has been improved with the increase of the shell thicknesses. According to the Förster theory¹⁰, the energy transfer efficiency depends on the overlap integral (J) between donor TPBI and Mn:CdS QDs, which can be calculated by the eq. (3):

$$J(\lambda) = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (3)$$

where $F_D(\lambda)$ is normalized donor emission spectrum, and $\varepsilon_A(\lambda)$ is the acceptor molar extinction coefficient. The calculated values of J are 1.01×10^{-14} , 1.27×10^{-14} , and $1.29 \times 10^{-14} \text{ M}^{-1}\text{cm}^3$ for samples A, B, and C, respectively. This result suggests that the energy transfer efficiency can be improved by controlling the CdS shell thickness of acceptor Mn:CdS QDs because of the increase of the spectral overlap between CTMs and QDs, which could strongly recommend tailored shell thicknesses for fabricating QD-based LEDs devices.

3. Conclusions

In summary, we have investigated the energy transfer process from electron-transporting materials, TPBI, to Mn:CdS QDs in inorganic/organic blend films. The change in the PL excitation intensity of the Mn:CdS QDs and the PL decay time of the TPBI clearly demonstrated an efficient energy transfer process in the QDs/TPBI blend films. Meanwhile, the energy transfer efficiency was improved with the increase of the CdS shell thicknesses. These results show the possible ways of optimizing the energy transfer efficiency by controlling the shell thickness in QD-based LEDs.

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