Shell-dependent hole transport in highly luminescent CdSe-core CdS/ZnCdS/ZnS multi-shell nanocrystals

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ABSTRACT

The photoinduced hole transfer dynamics from CdSe quantum dots (QDs), shelled with ZnS or CdS/CdZnS/ZnS layers, to organic hole transporting materials (HTMs) is investigated by absorption, steady-state and time-resolved photoluminescence (PL) spectroscopy. The PL intensity and lifetime of the QDs are dramatically quenched when HTMs are added into the dilute QD solution. The quenching efficiency of the QDs significantly decreases with increasing the shell thickness and increases with decreasing the oxidation potential of the HTMs. These facts are correlated with the photoinduced hole transfer from the QDs to the HTMs. The above results are helpful in understanding the photoexcitation dynamics-related phenomena of organic molecule conjugated nano-object.

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1. Introduction

In the past two decades, colloidal quantum dots (QDs) have attracted a lot of interest owing to their unique size-dependent optical and electronic properties, based on quantum confinement effect of the electronic states. These unique properties make QDs highly desirable for various applications such as biological markers [1,2], solar cells [3] and light-emitting diodes (LEDs) [4–6], where a fundamental process often involved is charge/energy transfer between the QDs and organic molecules. A clear picture of the dynamics is essential for the further improvement of the performance of QD-based devices.

The optical properties of QDs can be modified by coating the particles with a protective shell of a semiconductor material of a wider band gap [7–9]. For example, CdSe QDs were covered either with ZnS [7] or with CdS [8] to construct a core–shell system, and the photoluminescence (PL) properties of the constructed core–shell QDs were successfully improved [10]. Further increase of the shell thickness, however, resulted in a decrease of PL quantum

yield which was ascribed to lattice imperfection [8,11]. In order to overcome these problems, CdSe QDs with stepwise adjustment of shell lattice parameters from CdS to ZnS have been reported, which have demonstrated higher PL quantum yield and superior photochemical and colloidal stability [12].

The hole transporting materials (HTMs) are usually used, as a hole transporting layer, in QD-LEDs [4–6]. It is natural to imagine that the electronic interaction between QDs and the HTMs will affect the electronic and optical performance of QD-LEDs. One simple and straight way to study the interaction would be to monitor the PL of QDs with the parameter variation of the HTM molecules. A number of reports have appeared on the interaction between organic molecules and the surface of core and core–shell QDs [13–17]. But to date, little is known about how the HTMs affects the PL properties of the multi-shell QDs.

In this work we have performed the study on the photoinduced charge transfer from CdSe QD to HTMs via steady-state and time-resolved PL spectroscopy. Employing the HTMs of different oxidation potentials, e.g. N,N′-bis-(1-naphthyl)-N,N′-diphenyl-1,1′-bi-phenyl-4,4′-diamine (NPB), N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-bi-phenyl-4,4′-diamine (TPD) and 4,4′,4″-tri(N-carbazolyl) triphenyl-amine (TcTa) and varying the shell thickness of the QDs, the role of the hole transfer in photodynamics has been unraveled.

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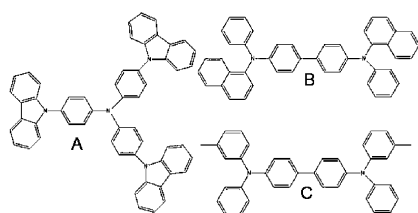
Scheme 1. The molecular structure of TcTa (A), NPB (B) and TPD (C).

2. Experimental section

The CdSe/(2ML) ZnS QDs and CdSe/(2ML) CdS/(2ML) CdZnS/(2ML) ZnS multi-shell QDs were prepared by using the successive ion layer adsorption reaction (SILAR) method as described in detail in the Ref. [6,12]. The average thicknesses [12] of one CdS-ML, one ZnS-ML and one alloyed shell $Cd_{0.5}Zn_{0.5}S$-ML are 0.35, 0.31 and 0.33 nm, respectively. So the shell thickness of CdSe/ZnS and CdSe/CdS/CdZnS/ZnS is 0.62 and 1.98 nm. Stock solutions of HTMs: NPB, TPD and TcTa were diluted with chloroform, and their molecular structures are shown in Scheme 1. Appropriate amounts were then added by a micropipette to 2 ml of QDs solution with optical density (OD) of about 0.02 at the first exciton absorption peak, 576 nm. The samples were mixed and measured immediately after preparation.

Steady-state absorption measurements were done with a Cary 300 double beam spectrometer at a spectral resolution of 1 nm. Steady-state fluorescence spectra were measured with the emission spectrometer described before [18]. In these experiments, excitation was set at 480 nm. The picosecond fluorescence transients of all samples were measured with a calibrated fluorescence setup outfitted with a time-correlated single-photon-counting (TCSPC) detection system [18] with the instrumental response of ∼17 ps. In the femtosecond transient absorption experiments, the pump (at 480 nm) is generated by the laser system (Hurricane (Spectra-Physics), 800 nm pulse, 120 fs pulse duration, and OPA-800c), while the probe is a white light continuum pulse generated by focusing the 800 nm beam into a sapphire plate. The detector is 2048 pixels CCD camera (Ocean Optics, S2000) [19]. The instrumental response time, as characterized by the cross correlation, was approximately 300 fs.

3. Results and discussion

Fig. 1 displays the steady-state absorption spectra of the core–shell QDs and HTMs (TPD, NPB and TcTa) in chloroform solution. The absorption of the HTMs is in the spectral range of less than 400 nm. Therefore, the HTMs cannot be directly excited when the excitation is set at wavelength longer than 400 nm. Besides, the absorption energies of all three HTMs are significantly higher than that of the emission band of QDs, and the possibility of resonant energy transfer process from QDs to HTMs can thus be excluded. To study the charge transfer from QDs to HTMs, PL spectra and decay curves were collected under 480 and 450 nm excitation, respectively.

The steady-state UV–vis absorption and PL spectra of the QDs with various concentration of NPB are shown in Fig. 2. The PL of the QDs is significantly decreased in intensity when the NPB molecules are added into the solution. No obvious first exciton absorption change of the QD is observed after NPB is added into the QD solution, indicating the high stability of the QDs. No new PL peak is observed in the emission spectra when the concentration of NPB varies in the QD solution.
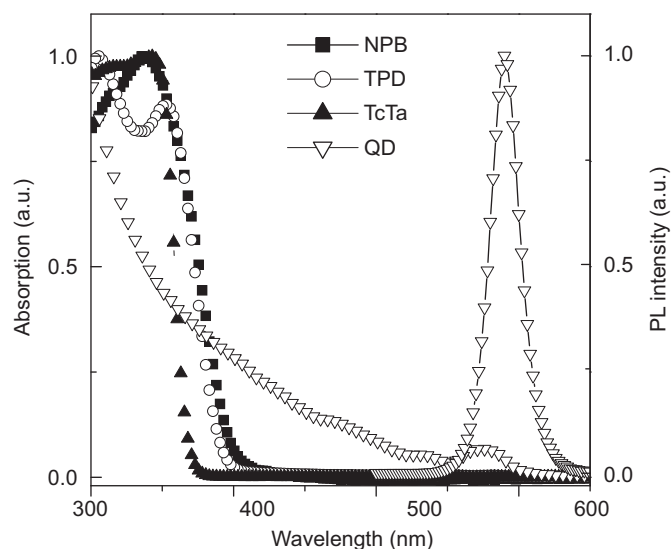

Fig. 1. Absorption spectra of CdSe/CdS/CdZnS/ZnS QDs and HTMs (TPD, NPB and TcTa) in chloroform solution. PL spectrum of the QDs is also shown in the figure.
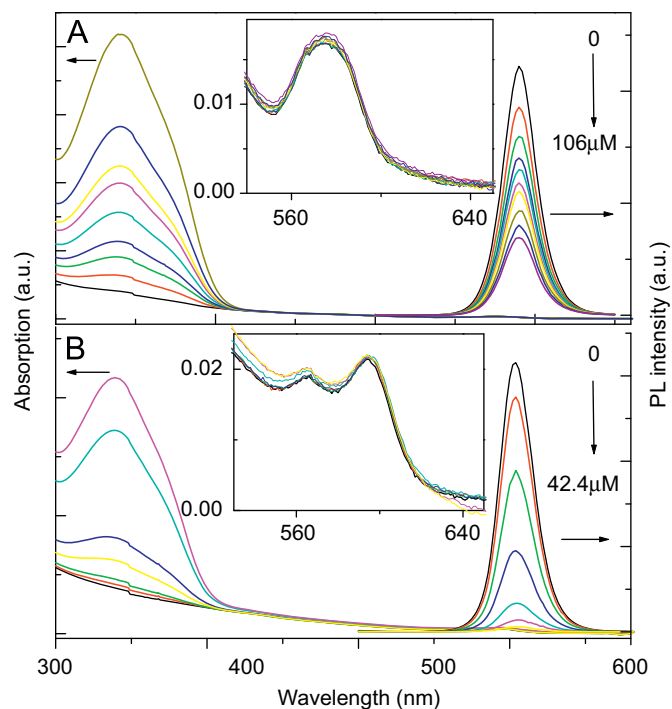

Fig. 2. UV–vis absorption and PL spectra of CdSe/CdS/CdZnS/ZnS (A) and CdSe/ZnS (B) QDs with various concentration of NPB in chloroform solution. Inset: enlarged absorption spectra near the first exciton absorption peak.

Photodynamics of the QD and HTM system was studied under 450 nm excitation. Fig. 3 shows the PL decay curves of the QDs with different concentration of NPB, where the decay is distinctly accelerated with increasing NPB concentration. The PL decay curves in this work exhibit a non-exponential decay and can be well fitted with a triexponential function: $I(t) = A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2) + A_3 exp(-t/\tau_3)$ for different concentration of NPB. The multiexponential decay of the QDs was attributed to the recombination of bright-dark exciton states, surface states or the fluctuation in the decay lifetime of individual QDs [20]. In order to grasp the physical picture of the phenomena we employ the
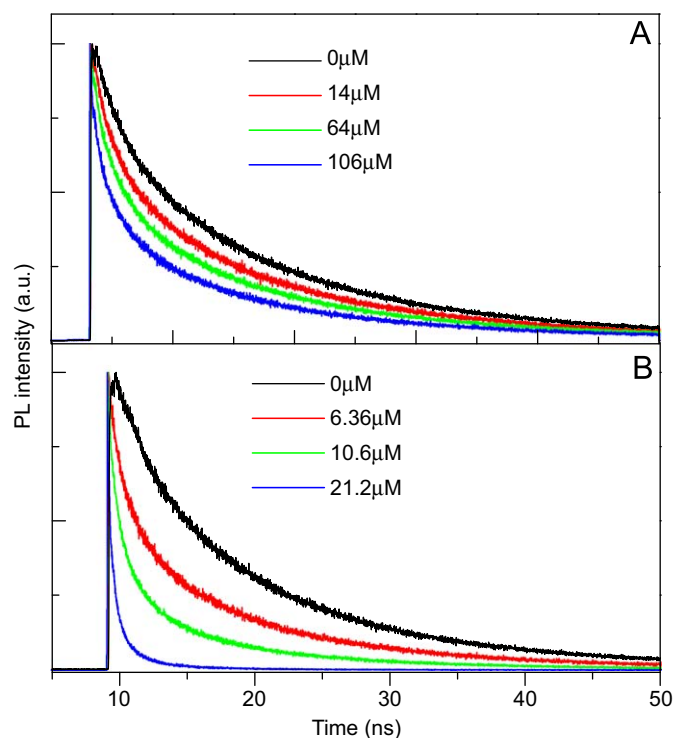
Fig. 3. The PL decay of the QDs CdSe/CdS/CdZnS/ZnS (A) and CdSe/ZnS (B) with different concentration of NPB. Excitation wavelength is at 450 nm.
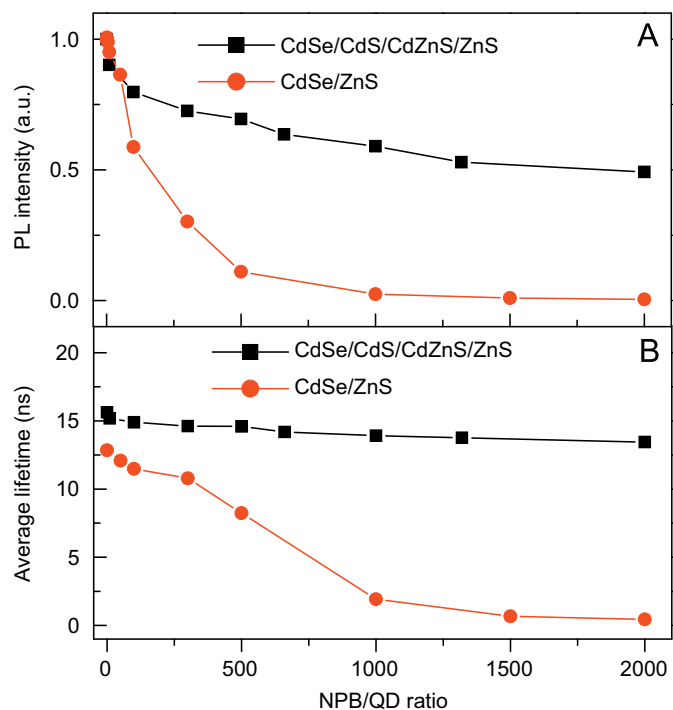

Fig. 4. Normalized PL intensity (A) and average lifetime (B) of QDs with different shell structure as a function of NPB concentration.

concept of average lifetime of the QDs defined as: $\tau_{AV} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$.

In order to understand the effect of shell structure on the quenching efficiency of PL of QDs, the HTM concentration dependence of the PL intensity and average lifetime of QDs are
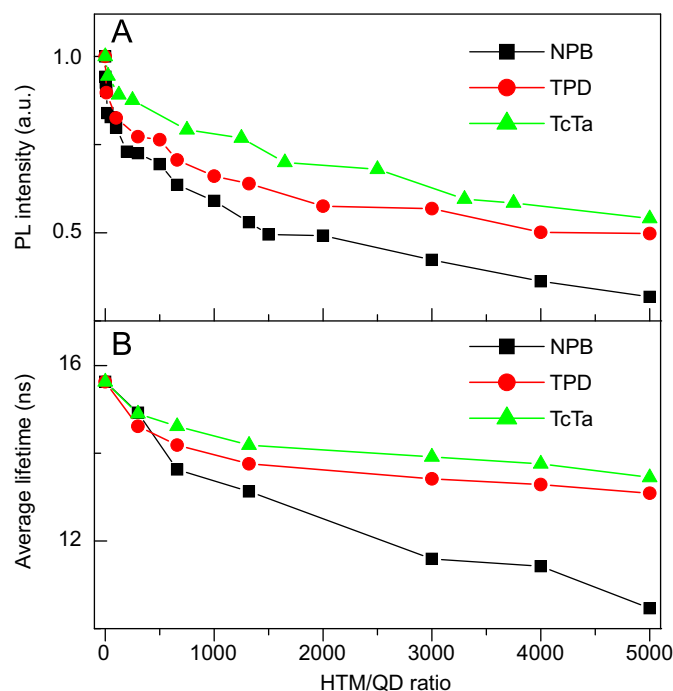

Fig. 5. Normalized PL intensity (A) and average lifetime (B) of CdSe/CdS/CdZnS/ZnS QDs as a function of various HTM concentration.

plotted for the QDs of different shell thicknesses, as is shown in Fig. 4. The decrease of the average lifetime with increasing NPB concentration is different from the decrease in emission yield. The quenching efficiency of CdSe/ZnS QDs is much larger than that of CdSe/CdS/CdZnS/ZnS QDs.

To illustrate the effect of the oxidation potential of HTM on the PL intensity and lifetime of CdSe/CdS/CdZnS/ZnS QDs, we have also studied the PL quenching of the QDs using the other two HTMs: TPD and TcTa to replace NPB. The dependence of the PL intensity and average lifetime of QDs on the concentration of NPB, TPD and TcTa is shown in Fig. 5. For all of the three HTMs, concentration lifting causes a reduction in the PL of multi-shell QDs. The quenching effect was strongest for NPB and weakest for TcTa. Since the oxidation potential of NPB, TPD and TcTa is about 0.27, 0.48 and 0.69 V vs. NHE [21], respectively, we can conclude that the quenching efficiency increases with decreasing the oxidation potential of HTMs.

To further investigate the mechanism of PL quenching, time-resolved transient absorption measurements were performed. The excitation selected at 480 nm ensures that only QDs are exclusively excited. The transient absorption spectra representing the bleaching recovery of QDs were recorded in the absence (Fig. 6B) and presence of NPB (Fig. 6C). In the absence of NPB, the recovery of the 580 nm band occurs slowly, and only about 66% of the bleaching within the first 0.85 ns. On the other hand, the presence of NPB in the solution accelerates the recovery and nearly 81% of the recovery is seen in the same time period. The enhanced recovery of the 580 nm band reflects the influence of NPB. The bleach dynamics of 580 nm peak in QDs alone and in the presence of NPB are shown in Fig. 7. The bleaching transient is fitted with a bi-exponential function with the long component taken as background, and the parameters are summarized in Table 1. The recovery of the transient bleaching represents the disappearance of the photogenerated electrons and holes via charge recombination and charge trapping processes [22–24]. The bleaching is dominated by the presence of the electrons in the conduction band [25], while holes have negligible contribution.
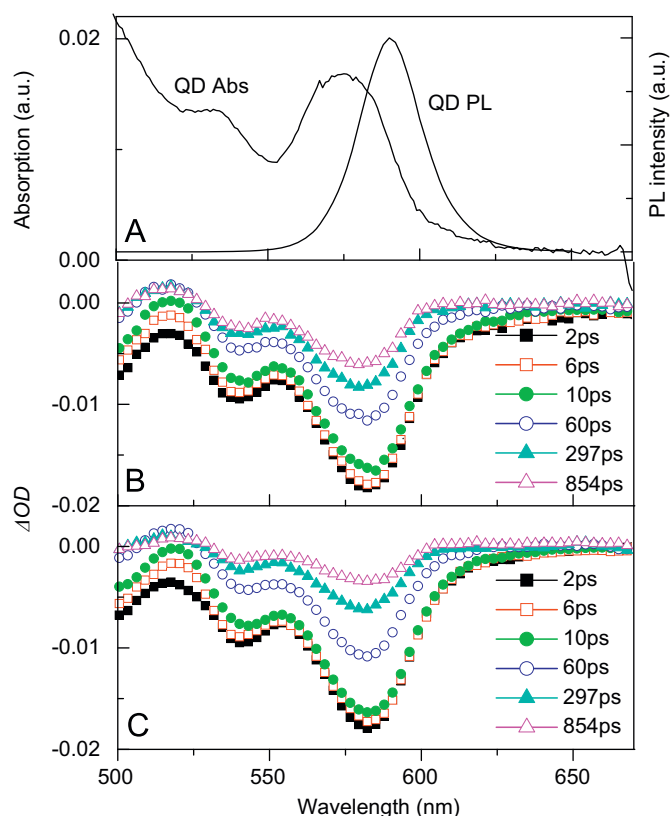
Fig. 6. (A) Absorption and emission spectra of CdSe/CdS/CdZnS/ZnS QDs. (B) and (C) represent bleaching recovery spectra of QDs in the femtosecond transient absorption spectra without and with NPB, respectively. Excitation wavelength is 480 nm.
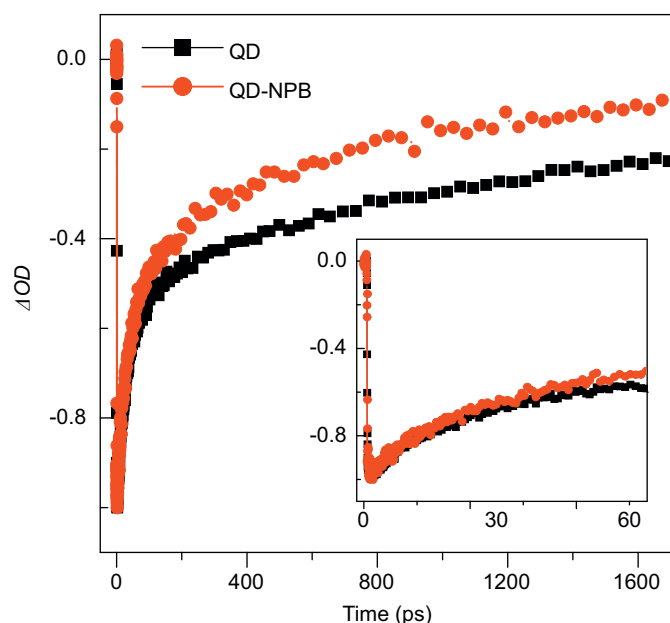
Table 1
Kinetic parameters of the transient bleaching for QD and QD–NPB system.

	A_1	τ_1 (ps)	A_2	τ_2 (ps)
QD	0.44 ± 0.003	30 ± 0.5	0.37 ± 0.004	735 ± 33
QD–NPB	0.45 ± 0.005	32 ± 0.8	0.43 ± 0.005	489 ± 19
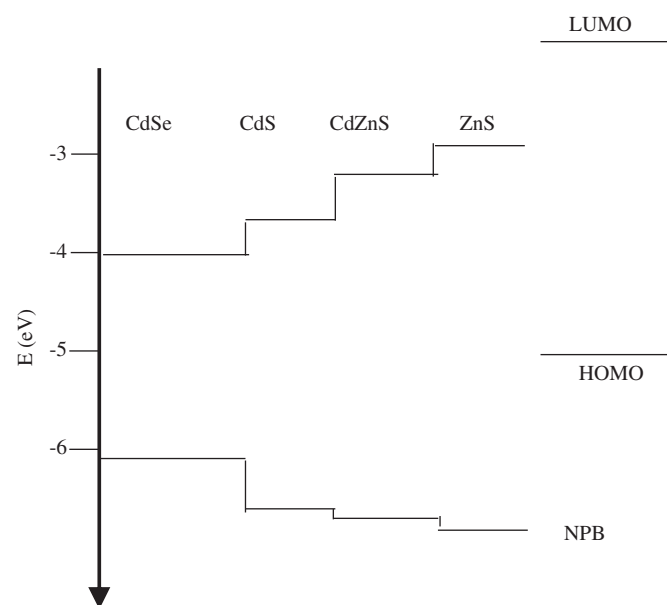
Fig. 8. The energy structures of QDs and NPB molecules.

Fig. 7. Long time-scale absorption recovery profiles of the QDs without and with NPB at 580 nm under excitation of 480 nm. Short time-scale absorption recovery profiles are shown in the inset.

The multiexponential nature of the recovery arises from the combination of the radiative and nonradiative (trapping) processes. It was reported before that the bleaching recovery is sensitive to the surface passivation [26]. The shorter bleaching time does not change as seen in Table 1. This indicates no apparent change in electron dynamics of QD and the surface anchored HTM molecules do not bring more traps.

In general, the PL quenching of QDs comes from four possible pathways [27–29]: (1) energy transfer from QD to NPB molecules; (2) existence of quenching centers due to the surface damage of QD; (3) electron transfer from QD to NPB molecules; (4) hole transfer from QD to NPB molecules. Based on the above results, hole transfer from QDs to HTM should be the mainly responsible for the PL quenching effect of QDs.

The photodynamics of QDs can also be discussed based on an electronic level structure [4–6,30], as shown in Fig. 8. By comparing the molecular levels of the NPB with the quantized electronic levels of the QDs, one might expect electron transfer from the NPB to the QD or hole transfer from the QD to the NPB. Interfacial electron transfer from NPB to the particle might occur in this model if the NPB molecules are photoexcited. But in our experiments, the excitation wavelength was selected at such that only QDs were excited. In this instance, only hole transfer from the QDs to the NPB would be favorable. The change of PL intensity and lifetime can be explained by the occurrence of an effective hole transfer from the QD to the occupied NPB level (HOMO). The oxidation potential dependence of quenching efficiency further proves the conclusion because the driving force decreases with increasing the oxidation potential.

The scavenging of holes at the QD surface by HTMs is the process responsible for the observed decrease in emission lifetime, we can estimate the rate constant of the hole transfer from expression: $k_{ht} = 1/\tau_{HTM} - 1/\tau$, where τ_{HTM} and τ are the average PL lifetime with and without HTM. The hole transfer rate

constants are calculated to be $1.03 \times 10^7 \, \text{s}^{-1}$ and $2.17 \times 10^9 \, \text{s}^{-1}$ for CdSe/CdS/CdZnS/ZnS and CdSe/ZnS QD solution with a NPB concentration of $42.4 \, \mu\text{M}$, respectively. The hole transfer rate constants from CdSe/CdS/CdZnS/ZnS to HTM are $3.16 \times 10^7 \, \text{s}^{-1}$, $1.13 \times 10^7 \, \text{s}^{-1}$ and $1.04 \times 10^7 \, \text{s}^{-1}$ for NPB, TPD and TcTa with a concentration of $106 \, \mu\text{M}$, respectively. As it is known from the charge transporting theory [31], the shell dependence of quenching efficiency comes from the difference in the distance between the core and HTM molecules.

4. Conclusion

We have studied the effect of HTMs on the PL properties of CdSe core QDs with a ZnS-shell and CdS/CdZnS/ZnS-multi-shell. PL emission intensity and lifetime of the QDs are significantly quenched by the HTMs (NPB, TPD and TcTa). The quenching efficiency of QDs follows the order NPB > TPD > TcTa, in relation with the difference of their HOMO levels. The quenching mechanism is discussed based on hole transfer from the VB of the QDs to the HOMO energy level of HTMs. The shell structure dependence of the quenching efficiency reflects the distance dependence of the hole transfer between the QDs core and HTMs.

Acknowledgements

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