

Shell-Dependent Energy Transfer from 1,3,5-Tris(*N*-phenylbenzimidazol-2-yl) Benzene to CdSe Core/Shell Quantum Dots

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We studied the energy transfer between CdSe core/shell quantum dots (QDs) and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene (TPBI) in inorganic/organic blend films using steady-state and time-resolved photoluminescence (PL) spectroscopy. The shortening in PL lifetime of TPBI molecules and the resulting lengthening in PL lifetime of the QDs demonstrated an efficient energy transfer process from donor to acceptor. The slowest PL decays of CdSe core/shell QDs observed in the blend films with low QD concentration were considered to result from the maximum energy transfer process from the surrounding TPBI molecules of a QD to itself. The PL decay curves of the core/shell QDs with a CdS, ZnS, and CdS/ZnCdS/ZnS shells were simulated to obtain the excited state lifetimes of the surrounding TPBI molecules for understanding the effect of the shells on the energy transfer process. It was surprisingly found that the obtained energy transfer rate to a QD with a thick CdS/ZnCdS/ZnS multishell from the surrounding TPBI molecules with the maximum contribution of the energy transfer was almost the same as that to a QD with a thin ZnS monoshell and smaller than that to a QD with a CdS monoshell. The experimental results indicated the energy level alignment and the structure of shells in CdSe core/shell QDs determined the energy transfer efficiency from TPBI molecules to the core/shell QDs.

Introduction

Quantum dot (QD)/organic composite nanomaterials have recently attracted great attention due to their potential application in optoelectronic devices such as light-emitting diodes (LEDs)^{1–13} and photovoltaic cells.^{14,15} It is known that the high photoluminescence quantum yield (PL QY) and good photostability of CdSe QDs can be realized by growing a monoshell (CdS or ZnS) on a CdSe core.¹⁶ Recently, the PL QY up to 85% was reached by using a multishell (CdS/Zn_{0.5}Cd_{0.5}S/ZnS), which integrated advantages of a small lattice mismatch between a CdSe core and CdS shell and a high-energy barrier between the CdSe core and an outer ZnS shell.¹⁷ It was also noted that the blinking behavior of single QDs was suppressed by coating a thick CdS shell on a CdSe core¹⁸ or growing a thick ZnSe shell on a (Cd, Zn)Se ternary core.¹⁹ Growing a monoshell or multishell on a core QD is a reliable and effective method for passivating the surface states to improve the optical performances of the QDs. However, currently the most efficient QD-LEDs were fabricated by sandwiching an inorganic QD layer between organic hole and electron transporting layers, in which exciton in the QD layer was generated by energy transfer or direct charge injection from host organic materials.² The shell

structure of the QDs as an energy barrier and a spacer should significantly influence the energy/charge transfer efficiency from the organic molecules to the QDs, determining the performance of QD-LEDs.^{2,8,9} Therefore, it is necessary to explore the effect of the shells on the energy/charge transfer mechanism in the QD/organic composite nanomaterials to optimize the structures of core/shell QDs and their optoelectronic devices.

After the theoretical prediction of Förster resonant energy transfer (FRET) between inorganic nanostructures and organic molecules,^{20–24} and the first experimental demonstration of FRET from a blue-emitting polymer to colloidal CdSe/ZnS core/shell QDs, the interaction between QDs and organic molecules has been extensively studied.²⁵ The energy transfer efficiency is dependent not only on the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor but also on the spatial distance between the donor and acceptor, which is generally proportional to $1/R_{DA}^6$ based on the Förster's theory.^{26,27} Anikeeva et al. explained the energy transfer of triplet excitons from a phosphorescent dye, tris(2-phenylpyridine) iridium (Ir(ppy)₃), to a CdSe/ZnS core/shell QD layer in terms of exciton diffusion within the Ir(ppy)₃ film to the QD layer.²⁷ Recently, Stöferle et al. investigated the effect of temperature-dependent exciton diffusion in poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6) on the energy transfer efficiency from the polymer to CdSe/ZnS core/shell QDs and found that the exciton need to migrate very close to the QD surface to couple with the polymer, indicating that the coupling strength is much weaker than that anticipated by the Förster's theory.²⁸ More recently, the efficiency of energy transfer versus charge separation observed in type-II hybrid organic/inorganic

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nanocomposites (blend of thioglycolic acid capped CdTe QDs and poly[9,9-bis(3'-((*N,N*-dimethyl)-*N*-ethylammonium)-propyl)-2,7-fluorene-alt-1,4-phenylene] dibromide (PDFD) was found to be related to the alignment of energy levels and the physical geometry of the hybrid system.²⁹ Organic electron transporting materials, aluminum tris(8-hydroxyquinoline) (Alq₃) and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene (TPBI) have been widely used to prepare highly efficient QD-LEDs.^{2–13} However, the detailed energy transfer processes between these functional organic molecules and CdSe core/shell QDs have not been understood yet.

In this work, we study the shell-dependent FRET processes between TPBI molecules and CdSe core/shell QDs in blend films by steady-state and time-resolved PL spectroscopy. The energy transfer process from TPBI molecules to the QDs has been demonstrated by the quenching of PL lifetime of the donors, TPBI, and the enhancement of PL lifetime of the acceptors, CdSe core/shell QDs, in blend films. Further, the average excited state lifetimes of the surrounding TPBI molecules with the maximum contribution of energy transfer to the QDs with CdS, ZnS, and CdS/ZnCdS/ZnS shells are estimated by stimulating the PL decay profiles of the QDs in the blend films with a low QD/TPBI molar ratio. On the basis of the obtained energy transfer rates to the QDs, we will discuss the influence of shells (i.e., energy level alignment, structure and thickness of shells, as well as surface/interface trap states) on the energy transfer processes.

Experimental Section

Synthesis of CdSe QDs with different shell structures were carried out following ref 17 as described in the Supporting Information. The shell thicknesses were determined via the comparison of the sizes of core and core/shell QDs measured by a Tecnai G2 transmission electron microscope (TEM) as seen in Figure S1 in Supporting Information, and the shell layers were estimated on the basis of one monolayer (ML) of 0.31, 0.32, and 0.33 nm with respect to ZnS, ZnCdS, and CdS shell materials. The TPBI and QD blend films were deposited on quartz substrates by a spin coater with a speed of 1000 rpm from the QD/TPBI solutions in chloroform with TPBI molecule and QD concentrations of 5–10 mg/mL and 2–20 μ M, respectively. The thickness of films was measured to be about 50–80 nm with a KLA-Tencor P-16+ surface profiler. The QD/TPBI molar ratio was changed from 1/100 to 1/2000. The QD/PMMA (poly(methyl methacrylate), molecular weight 15 000) films as reference samples were prepared by doping QDs into PMMA matrix to avoid the interaction between QDs with different sizes.

The absorption spectra were recorded on a UV-3101PC UV–vis-NIR scanning spectrophotometer (Shimadzu). Fluorescence and excitation spectra were recorded by an F-4500 spectrophotometer (Hitachi) equipped with a 150 W Xe arc lamp at room temperature. The time-resolved PL spectra were measured by FL920 fluorescence lifetime spectrometer (Edinburgh Instruments). The excitation source is a hydrogen flash lamp with a pulse width of 1.5 ns. All measurements were carried out at room temperature. The modeling of the PL decay kinetics was done by the symbolic language Wolfram Mathematica 4.2.

Results and Discussion

Figure 1 shows absorption spectrum of CdSe/CdS(2 ML) core/shell QDs and PL spectrum of TPBI molecules and in chloroform under excitation at 300 nm. The spectral overlap of

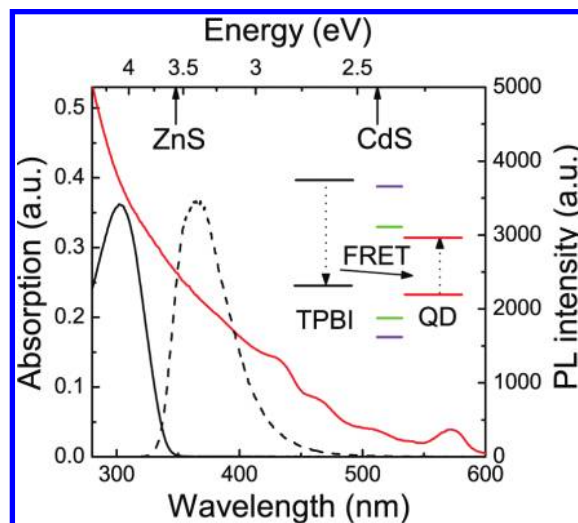


Figure 1. Absorption spectrum of CdSe/CdS(2 ML) core/shell QDs (red solid line) and PL spectrum of TPBI molecules (black dashed line) in chloroform under excitation at 300 nm. The black solid line represents absorption spectrum of TPBI molecules. Arrowheads represent the band gap of bulk CdS and ZnS with wurtzite structure. The inset shows the schematic of energy level alignment of donor TPBI (black lines) and acceptor CdSe core QDs (red lines) with a CdS (green lines) or ZnS (blue lines) shell. The arrow represents the FRET process from the TPBI molecule to the QD.

the TPBI molecule (donor) PL emission and CdSe/CdS(2 ML) core/shell QD (acceptor) absorption is a prerequisite for the Förster type energy transfer.^{29,30} The PL intensity of CdSe core/shell QDs in chloroform keeps constant under excitation wavelength of 450 nm below TPBI absorption edge when TPBI molecules are added into the QD solution as shown in Figure S2 in Supporting Information. However, significant PL quenching of CdSe core/shell QDs in chloroform is observed when Alq₃ molecules are added.^{30,31} The quenching was explained in terms of the field induced exciton dissociation³⁰ or charge and energy transfer processes.³¹ Unlike the QDs in the organic hole transporting materials,³² no hole transfer or static PL quenching is observed in the QD/TPBI hybrid system under excitation below the TPBI absorption edge when TPBI molecules attach to the QD surface, which is attributed to the energy level alignment of TPBI and CdSe QDs as seen in the inset of Figure 1 and the weak interaction between them.³² The energy offset between the highest occupied molecular orbital (HOMO) level of TPBI (−6.3 eV) and the valence band of CdSe QDs (−6.4 eV) is about 0.1 eV, which is much smaller than that (0.9 eV) between the HOMO of Alq₃ (−5.5 eV) and the valence band of CdSe QDs.^{3–5} This indicates that the CdSe QD/TPBI hybrid system is a good candidate for exploring the energy transfer mechanism between inorganic/organic nanomaterials.

PL excitation (PLE) spectra of CdSe/CdS(2 ML) core/shell QDs in QD/TPBI blend films with different QD/TPBI molar ratio are shown in Figure 2. The PLE spectra detecting PL at the wavelength of QD emission²⁹ are normalized at wavelength 450 nm without TPBI absorption. The relative enhancement in PLE intensity of the QDs in the blend films is clearly observed at the donor TPBI absorption peak of 300 nm in the PLE spectra of the QDs compared with that of the QDs with low concentration in PMMA film (without absorption at 300 nm), indicating an energy transfer process from TPBI molecules to CdSe/CdS(2 ML) core/shell QDs. Further, the PLE intensity at 300 nm of the QDs in the blend films is found to significantly enhance from 1.2 to 12.2 times when the QD/TPBI molar ratio decreases from 1/100 to 1/2000. This indicates that the surrounding TPBI

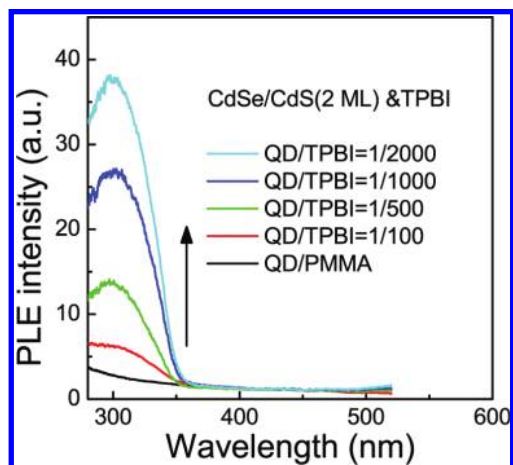


Figure 2. Normalized PL excitation spectra of CdSe/CdS(2 ML) core/shell QDs in QD/TPBI blend films with different QD/TPBI molar ratio detected at an emission wavelength of 580 nm.

molecules can more efficiently transfer their energy to the QDs in the blend film with decreasing the QD concentration.

From the steady-state absorption and PLE measurements of QD/PMMA and QD/TPBI blend films as well as the QD/TPBI solutions, we can quantify the energy transfer efficiency from TPBI molecules to CdSe core/shell QDs. The energy transfer efficiency can be estimated by using the following relation:^{26,29}

$$\eta_{ET} = \frac{A_{QD}(\lambda_{exc})}{A_{TPBI-QD}(\lambda_{exc}) - A_{QD}(\lambda_{exc})} \left(\frac{I_{QD}}{I_{QD}^0} - 1 \right) \quad (1)$$

where A_{QD} and $A_{TPBI-QD}$ are the absorption of QD and QD/TPBI solution for preparation of blend film at wavelength of 300 nm, respectively. $(I_{QD}/I_{QD}^0 - 1)$ is the relative enhancement of the PL intensity (I_{QD}) of QD/TPBI blend films compared with that (I_{QD}^0) of QD/PMMA films as shown in the normalized PLE spectra, resulting from energy transfer from TPBI molecules to QDs under excitation wavelength of 300 nm. Applying eq 1, energy transfer efficiencies for the blend films with QD/TPBI molar ratios of 1/100, 1/500, 1/1000, and 1/2000 were obtained to be 36%, 25%, 25%, and 18%, respectively. Figure 3 shows energy transfer efficiency from TPBI molecules to CdSe/CdS(2 ML) QDs in QD/TPBI blend films as a function of QD/TPBI molar ratio. As seen in Figure 3, in contrast to the energy transfer induced PL enhancement of the QDs in the blend films, the energy transfer efficiency is found to decrease with decreasing with QD/TPBI molar ratio, resulting from the increase of donor–acceptor distance based on the Förster theory²⁶ because most of TPBI molecules are far away from the QD surface and the decrease of the number of the QDs in the blend film with low QD concentration.

In order to understand the energy transfer dynamics in QD/TPBI blend films, their PL decays were measured to monitor the change in PL lifetime of donor TPBI molecules and acceptor CdSe/CdS(2 ML) core/shell QDs at 380 and 580 nm, respectively. The evolution of the time-resolved PL spectra for the donor and acceptor in the blend films with different QD/TPBI molar ratios is shown in Figure 4. The shortening in PL lifetime of TPBI molecules is significantly observed in the blend films with increasing QD/TPBI molar ratio, as seen in Figure 4(a). We simply analyzed the PL decays of TPBI molecules in pure TPBI and QD/TPBI blend films by a monoexponential decay function. From the deconvolution fitting of the decay curves,

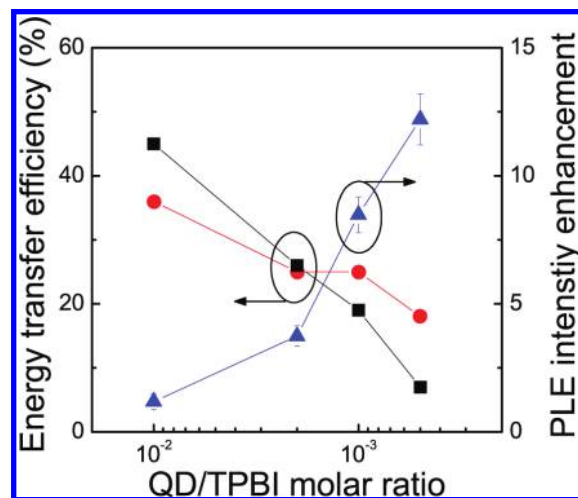


Figure 3. Energy transfer efficiency from TPBI molecules to CdSe/CdS(2 ML) QDs in QD/TPBI blend films as a function of QD/TPBI molar ratio. The red cycles and black squares represent energy transfer efficiencies calculated from the PLE intensity enhancement of QDs and the lifetime shortening of TPBI molecules, respectively. The PLE intensity enhancement of the QDs at 300 nm as a function of QD/TPBI molar ratio is also plotted in this figure by blue triangles.

the PL lifetimes of the TPBI molecules are obtained as 1.5, 2.0, 2.2, 2.5, and 2.7 ns, respectively for QD/TPBI blend films with molar ratios of 1/100, 1/500, 1/1000, and 1/2000 and the pure TPBI film, indicating that the energy transfer process is an additional nonradiative de-excitation path for donors, causing their PL lifetime shortening.^{20–29} The corresponding energy transfer efficiencies and rates are obtained to be 45%, 26%, 19%, 7% and 0.30, 0.13, 0.08, 0.03 ns⁻¹ by relations $1 - \tau_{TPBI-QD}/\tau_{TPBI}$ and $1/\tau_{TPBI-QD} - 1/\tau_{TPBI}$, respectively, where $\tau_{TPBI-QD}$ and τ_{TPBI} are the PL lifetimes of TPBI molecules in blend and pure TPBI films.²⁶ The energy transfer efficiencies from TPBI molecules to the QDs as a function of QD/TPBI molar ratio are also plotted in Figure 3 by solid squares, similar to that estimated from the PLE measurements. Therefore, the large energy transfer efficiency demonstrates the strong dipole–dipole coupling between TPBI molecules and CdSe core/shell QDs in these blend films.

From the Förster theory, the energy transfer rate for an isolated single donor–acceptor pair separated by a distance R_{DA} can be expressed by the Förster formalism as follows:^{22,26}

$$k_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{R_{DA}} \right)^6 \quad (2)$$

where τ_D is excited-state lifetime of donor and R_0 is the Förster radius. The Förster radius (R_0) is a function of the refractive index of the medium n_D , Avogadro's number N_A , a parameter κ , that depends on the relative orientation of the donor and acceptor dipoles, and the overlap integral, $J(\lambda)$:²⁶

$$R_0 = \left(\frac{9000(\ln 10) Q_D \kappa^2}{128 \pi^5 N_A n_D^4} J(\lambda) \right)^{1/6} \quad (3)$$

where $\kappa^2 = 2/3$ for randomly oriented dipoles and varies between 0 and 4 for the cases of orthogonal and parallel dipoles, respectively. The overlap integral, $J(\lambda)$, is defined as follows:²⁶

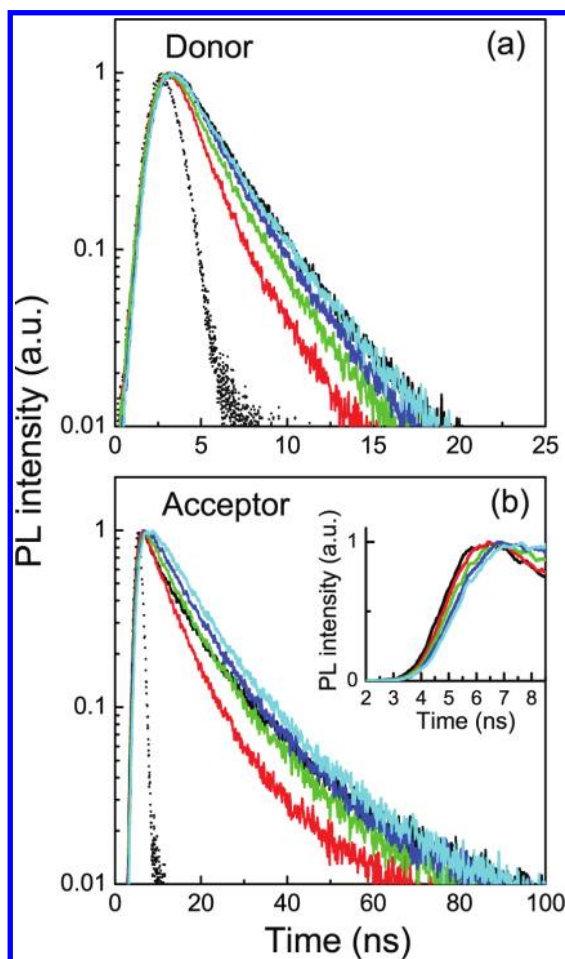


Figure 4. Time-resolved PL spectra of QD/TPBI blend films with different QD/TPBI ratios monitored at wavelength of 380 nm (a) and 580 nm (b). The red, green, blue, and cyan lines represent QD/TPBI blend films with QD/TPBI molar ratios of 1/100, 1/500, 1/1000, and 1/2000, respectively. The inset in (b) shows enlarged initial rise processes of QDs in these films. The black solid lines represent pure TPBI (a) and QD/PMMA films (b). The excitation wavelength is 300 nm. The black dotted lines represent instrument response function (IRF).

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

where $J(\lambda)$ is a quantitative measure of the donor–acceptor spectral overlap over all wavelengths λ , which is a function of the normalized donor emission spectrum (dimensionless property), $F_D(\lambda)$, and the acceptor absorption spectrum (expressed as an extinction coefficient), ε_A . From eqs 2–4, the decrease of the energy transfer efficiency and rate for QD/TPBI films as shown in Figure 3 with decreasing the QD/TPBI molar ratio can be explained by the decreased QD number in the blend film and no contribution of energy transfer to the QDs from most of the TPBI molecules in the blend films, which are far away from the QD surface due to the long donor–acceptor distance. However, the energy transfer induced PL enhancement of the QDs was found to reach 12.2 times in the blend film with low QD concentration. This is because that many TPBI molecules replacing the QDs that were originally on or near the surface of a QD efficiently contribute their energy to the QD. Therefore, this also means that the CdSe core/shell QDs in QD/TPBI blend films with the low QD concentration can be considered to be absolutely isolated, and no interaction occurs between the QDs because they are surrounded by a large amount of TPBI molecules.

The information about energy transfer dynamics from TPBI molecules to QDs is also provided in the time-resolved PL spectra of acceptor QDs. The initial rise and final decay processes in time-resolved PL spectra of QDs in blend films become slower than those of a QD/PMMA film due to the filling of excited states of the QDs via an energy transfer process as seen in Figure 4(b) for QD/TPBI blend films with QD/TPBI molar ratios of 1/2000, 1/1000, and 1/500.²⁹ Although the PL decay lifetime of QDs in the QD/TPBI film (1/100) is shorter than that in QD/PMMA film, perhaps resulting from the aggregation of QDs in the blend film with high QD concentration,^{23,33} as seen in Figure S3 of the Supporting Information, the energy transfer induced delay of the initial rise is clearly observed in the inset of Figure 4(b). From the experimental results, two paths can be considered to be excitation sources of the QDs: (i) direct excitation of light (300 nm); and (ii) energy transfer from the surrounding TPBI molecules. The contribution of these excitation sources to QD PL can be seen clearly in PLE spectra as seen in Figure 2. Further it is needed to consider that the PL origins and excited state lifetime of core/shell QDs are not changed after excitation energy transfer from the surrounding TPBI molecules. It is also noted that the time-resolved PL decay curves of QDs in QD/PMMA and QD/TPBI films under excitation at 450 nm are almost the same, as seen in Figure S4 of the Supporting Information, indicating the environmental effect on the PL lifetime of QDs can be ignored. Under the excitation condition of low pump power and ultrafast pulse, the PL decay curve of the acceptor QD in a blend film can be phenomenologically described as follows:^{21,22,26,29}

$$n_{\text{QD}}(t) = n_{\text{QD}}^0(t) + I_D \int_0^t n_{\text{QD}}^0(t-s)n_{\text{TPBI-QD}}(s)ds \quad (5)$$

where the first term, $n_{\text{QD}}^0(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$,^{34,35} describes the PL decay with biexponential decay function for QDs in the QD/TPBI blend film with high QD concentration under excitation of light at 450 nm without energy transfer from TPBI to QD or for QDs in QD/PMMA films with low QD concentration under excitation at 300 nm. The second term describes the PL decay of the QDs under excitation from energy transfer. I_D is an enhancement factor of the PLE intensity at 300 nm in the blend film with respect to a QD/PMMA film as plotted in Figure 3. The $n_{\text{TPBI}}(s) = \exp(-s/\tau_{\text{TPBI-QD}})/\tau_{\text{TPBI-QD}}$ represents the time-dependent excited state population of the TPBI molecules with the contribution of energy transfer to QDs in the blend film, normalized by the total area of the decay profile.^{22,29} Figure 4 shows the PL decay curves of CdSe/CdS(2 ML) core/shell QDs and TPBI molecules in QD/TPBI blend film under excitation at 300 nm. Combining the obtained parameters and instrument response function (IRF), the calculated time-resolved PL curve for acceptor CdSe/CdS(2 ML) core/shell QDs in the blend film (QD/TPBI ratio of 1/100) is well consistent with the experimental result, as shown in Figure 5. This means that the fitting result is self-consistent with the lifetime change of the donor and the acceptor in the experiment, indicating that the energy transfer process is an additional de-excitation path for TPBI and also an additional excitation source for QDs.

As known, the PL QY of the CdSe core QDs are significantly improved by the growth of CdS and ZnS monoshells or CdS/ZnCdS/ZnS multishell.^{16,17} Therefore, we investigated the time-resolved PL spectra of these core/shell QD/TPBI blend films to understand the effect of the shells on the energy transfer process from TPBI molecules to CdSe core/shell QDs. In our

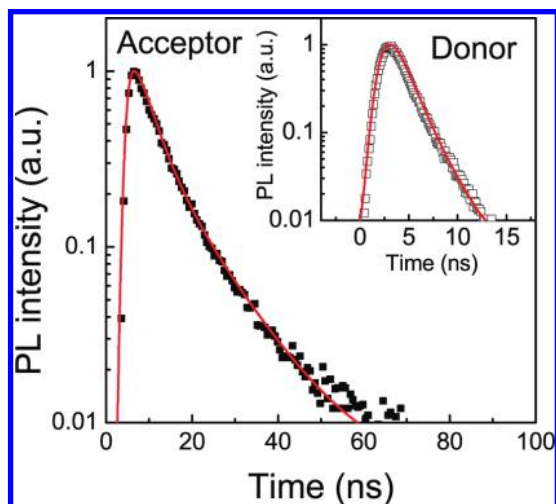


Figure 5. The PL decay curve of CdSe/CdS(2 ML) core/shell QDs in QD/TPBI blend film with QD/TPBI ratio of 1/100 under excitation at 300 nm (black solid squares). The inset shows a PL decay curve of TPBI molecules in the (black empty squares). The solid red lines represent calculated PL decay curves including the excitation pulse and the system response.

experiments, the shell structures, the PL peak wavelengths, and dot diameters of the CdSe core/shell QDs are described as follows: (A) CdSe/CdS(2 ML) (580 nm) (4.5 nm), (B) CdSe/ZnS(3 ML) (565 nm) (5.0 nm), (C) CdSe/CdS(6 ML) (605 nm) (7.0 nm), (D) CdSe/CdS(2 ML)/ZnCdS(3 ML)/ZnS(2 ML) (615 nm) (8.0 nm), respectively. The size of the CdSe core was estimated to be about 3.0 nm. The transmission electron microscope (TEM) images of the CdSe core and core/shell QDs as well as a high resolution (HR) TEM image of CdSe/CdS(2 ML)/ZnCdS(3 ML)/ZnS(2 ML) core/multishell QDs are shown in Figure S1 of the Supporting Information. The steady-state absorption and PL spectra of CdSe core/shell QDs with different shell structures are shown in Figure S5 of the Supporting Information. The PL QY of these QD samples were determined to be about 44%, 40%, 47%, and 70%, respectively. When QD/TPBI molar ratio is roughly 1/100, the PL lifetimes of the TPBI molecules are obtained to be 1.2, 1.0, and 1.7 ns, respectively for CdSe/ZnS(3 ML), CdSe/CdS(6 ML) and CdSe/CdS/ZnCdS/ZnS(7 ML) core/shell QDs by fitting the time-resolved PL decay curves of these TPBI molecules. The energy transfer efficiencies are estimated to be 56%, 63%, and 37%, respectively, implying the efficient energy transfer from TPBI molecules to QDs with different shell structures. However, the analysis of the shell effect on the energy transfer efficiency is disturbed by the unprecise QD/TPBI molar ratio. The absorption of the first exciton absorption peak for CdSe QDs is significantly decreased with coating a CdS shell due to the lower energy barrier for the conduction band because the oscillator strength of QDs was found to dependent on the energy barrier height of shell materials.^{16,17,36} Therefore, it is difficult to accurately determine the QD concentration from absorbance of the first exciton absorption peak for core/shell QDs, especially for the CdS thick shell coated QDs.³⁷ From eq 3, the Förster radii (R_0) of the energy transfer between TPBI and CdSe core/shell QDs were estimated to be about 5.7, 6.1, 7.1, and 7.3 nm, respectively for CdSe/CdS(2 ML), CdSe/ZnS(3 ML), CdSe/CdS(6 ML), and CdSe/CdS/ZnCdS/ZnS(7 ML) core/shell QDs. This means that the surrounding TPBI molecules only distributed in the spherical space with a Förster radius R_0 (about 5–7 nm) around a QD can efficiently transfer their excitation energy to the QDs. This suggests that the excitation sources for the acceptor QDs

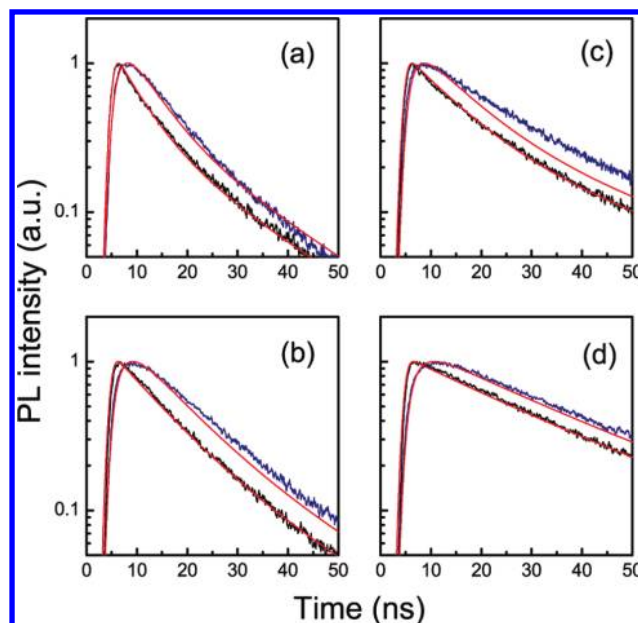


Figure 6. PL decay curves of CdSe core/shell QDs in QD/PMMA (black lines) and QD/TPBI films with QD/TPBI molar ratio of 1/2000 (blue lines) under excitation at 300 nm. The red solid lines represent the calculated PL decay curves including the excitation pulse and the system response. (a) CdSe/CdS(2 ML) QDs, (b) CdSe/ZnS(3 ML) QDs, (c) CdSe/CdS(6 ML) QDs, and (d) CdSe/multishell (7 ML) QDs.

dominantly come from the energy transfer of the surrounding TPBI molecules while the most of TPBI molecules far away from the QD surface do not efficiently transfer energy to the QDs due to long donor–acceptor distance in the blend film with low QD concentration. As a result, the PL decay of the TPBI molecules in the blend film with very low QD concentration is almost same as that of the pure TPBI film as shown in Figure S6 of the Supporting Information. This means that the time-dependent excited state population of the surrounding TPBI molecules with the maximum contribution of the transfer energy to one QD cannot be directly known from the time-resolved PL measurements. In order to safely compare the shell effect on the energy transfer process from TPBI molecules to the QDs with different shell structures in blend films with very low QD concentration, we need to know the excited state lifetime of the surrounding TPBI molecules without the puzzle of unprecise QD/TPBI molar ratio. Therefore, this is the only way that we can extract the excited state lifetime of the surrounding TPBI molecules by fitting the PL decay curve of the QDs in the blend film with low QD concentration based on eq 5.

Figure 6 shows PL decay curves of CdSe core/shell QDs in QD/PMMA and QD/TPBI films with a QD/TPBI molar ratio of 1/2000 under excitation at 300 nm. When the QD/TPBI molar ratio is about 1/2000, the PLE intensities of the QDs with CdS(2 ML), ZnS(3 ML), CdS(6 ML), and CdS/ZnCdS/ZnS(7 ML) shells at 300 nm are significantly enhanced about 12.2, 12.4, 6.9, and 9.9 times, respectively, indicating that the excitation for QDs in low QD concentration blend films mainly comes from the energy transfer process. The deconvolution fitting results of the PL decay curves for QD/PMMA films are summarized in Table 1. Knowing above parameters, we obtained the excited state lifetime (τ_{TPBI}) of the surrounding TPBI molecules of one QD with different shell structure by fitting the time-resolved PL decay curves of QDs as shown in Figure 6. The excited state lifetimes of the surrounding TPBI molecules are determined to be 1.9, 2.3, 2.0, 2.3 ns, and the resulting energy transfer rates from the surrounding molecules to one

TABLE 1: PL Lifetimes of CdSe Core-Shell QDs with Different Shell Structures in the QD/PMMA Films

samples (QD)	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{ave} (ns)
CdSe/CdS(2 ML)	70	5.5	30	18.5	13.2
CdSe/ZnS(3 ML)	78	9.9	22	23.5	15.4
CdSe/CdS(6 ML)	76	10.3	24	39.7	26.4
CdSe/multishell(7 ML)	64	21.5	46	45.0	35.6

QD are estimated to be 0.16, 0.06, 0.13, 0.06 ns⁻¹, respectively, for CdS(2 ML), ZnS(3 ML), CdS(6 ML), and CdS/ZnCdS/ZnS(7 ML) shell coated CdSe QD doped in blend films with low QD concentration. It is clearly noted that the energy transfer rate to one QD with a CdS monoshell from the surrounding TPBI molecules with the maximum contribution of the energy transfer is larger than that to one QD with a ZnS monoshell. Further, it is surprisingly found that the energy transfer rate to a thick multishell(7 ML) coated QD is almost the same as that to a ZnS(3 ML) thin monoshell coated QDs despite a thick multishell between the CdSe core and TPBI molecules.

From eqs 2–4, the determined factor for the energy transfer rate from TPBI molecules to QDs with different shell structures is the spectral overlap integral of donor emission and acceptor absorbance. The absorption spectrum of the core/shell QDs at the high energy side generally includes the absorption of the shell material.^{16–18,38} Furthermore, the photon energy of TPBI PL emission peaked at 380 nm is about 3.26 eV, which is above the band gap of CdS (2.42 eV) but under the band gap of ZnS (3.67 eV)^{16,17} as shown in Figure 1. This implies that the energy transfer process from TPBI molecules to the QDs is also dependent on the band gap of the shell. The dipole–dipole interaction occurs not only between TPBI molecules and the CdSe core but also between TPBI molecules and the CdS shell. Therefore, we can explain that the larger energy transfer rate from TPBI molecules to the QDs with a CdS shell by the energy transfer from TPBI molecules to the CdS shell. There is no spectral overlap between TPBI emission and ZnS shell absorption because the band gap energy of ZnS is larger than TPBI emission peak energy. In this situation, for CdSe/ZnS(3 ML) core/shell QDs the dipole–dipole interaction only occurs between TPBI molecules and the CdSe core with a spacer of the ZnS shell (about 1 nm).²⁶ Therefore, the decreased spectral overlap and increased distance between TPBI molecules and the QDs with a ZnS shell results in a relative lower energy transfer rate (0.06 ns⁻¹) than those (0.16 and 0.13 ns⁻¹) of the QDs with a 2 and 6 ML CdS shell. In particular, the increased spectral overlap of CdS and ZnCdS shells significantly causes a large transfer rate to multishell coated QDs despite the long distance between TPBI molecules and the CdSe cores. In addition, the energy transfer rate from TPBI to QDs with a thick CdS shell is slightly smaller than that of the QDs with the thin shell perhaps due the contribution of the thick shell to the energy transfer process. As shown in Figure 6(c), it is also noted that the PL decay tails are significantly slower than that of the calculated ones in CdSe QDs with a thick CdS shell, perhaps indicating the existence of emission centers with different PL lifetimes. Previous studies have shown that some surface and interface trap states do exist in epitaxial layers in core–shell structures or at the interface between the CdSe core and its shells, causing low PL QY of QDs under high energy photon excitation.^{39–41} The observation of the PL lifetime enhancement in CdSe/CdS/ZnS core/multishell QDs with increasing temperature indirectly confirmed that the localized state constitutes the dominant perturbative effect on the exciton dynamics in core/shell CdSe QDs.³⁹ In our previous work, we found the PL

intensity enhancement in CdSe QDs only with a thick multishell or thick CdS shell when the temperature increases.⁴⁰ Therefore, this indicates that the efficiency of energy transfer from TPBI molecules to the core/multishell QD can be further improved by effectively passivating surface/interface trap states in QDs.

Conclusions

In summary, we have studied the energy transfer from TPBI molecules to CdSe core/shell QDs in the hybrid systems using steady-state and time-resolved PL spectroscopy. We successfully demonstrated the efficient energy transfer process between TPBI molecules and CdSe core/shell QD via the shortening in PL lifetime of the donors, electron transporting materials, and the lengthening in PL lifetime of the acceptors, the CdSe core/shell QDs, in the inorganic/organic blend films. In the blend films with low QD concentration, we found that the obtained energy transfer rate to one QD with a thick CdS/ZnCdS/ZnS multishell from the surrounding TPBI molecules with the maximum contribution of the energy transfer is almost the same as that to one QD with a thin ZnS monoshell and smaller than that to one QD with a CdS monoshell due to the matching of TPBI PL emission energy and the band gap of CdS or ZnCdS shell material. Therefore, the energy transfer rate (efficiency) between organic electron transporting materials and core–shell QDs can be maximized to improve the performance of QD-based optoelectronic devices by using a multishell coated QDs with optimized energy level alignment and structure of the core/shell QDs.

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Supporting Information Available: Detailed synthetic methods of CdSe core/shell QDs; TEM images of CdSe core/shell QDs with different shell structures; PL and absorption spectra of CdSe core/shell QDs in solution with addition of TPBI molecules; Time-resolved PL decay curves of QDs in blend film excited at different wavelength; Steady-state absorption and PL spectra of CdSe core/shell QDs with different shell structures; Time-resolved PL decay curves of TPBI in QD/TPBI blend films with low QD concentration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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