Observation of Non-Förster-Type Energy-Transfer Behavior in Quantum Dot−Phthalocyanine Conjugates

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Quantum dots (QDs) and their molecular conjugates are becoming increasingly important for a wide range of applications in biomedicine.[1] Besides their more common application of QDs in imaging, several groups have recently addressed their potential as photosensitizers and phototherapeutic agents.[2] The photophysics of QD sensitization is complex, whereby surface and defect states can have profound effects on the involved radiative and nonradiative processes.[3] Thus, understanding and controlling the relaxation dynamics of photoexcited QD conjugates is crucial for an optimization of QD-based properties.

Over the past years, the study of energy transfer (ET) between energy donor−acceptor (DA) pairs has proven to be a very useful tool in many photobiological studies. This process has been very well studied for molecular systems.[4] However, such systematic investigations are still needed for QD-based energy DA systems. Compared to traditional molecular ET DA pairs, QD-based systems offer potentially exceptional photophysical properties, which can be attributed to the excellent photostability, broad excitation profile, and tunable emission band of QD donors.[1−3]

In bridged DA pairs, the ET may occur through-space or through-bond.[4,5] While the classical Förster theory predicts a negative sixth-order power dependence of the transfer efficiency on the separation distance, recent experimental and theoretical studies reveal that, depending on the nature of the constituents, the distance dependence may also vary between zeroth and negative fourth power.[4] Moreover, in studying QD-based DA systems, since the size of QDs lies in between those of a molecule and a bulk crystal, the actual dependence of ET on separation distance is not readily predicted from any existing theory alone, and therefore additional experiments are required to gain a better understanding of the actual mechanisms involved. In addition, QDs may also show deviation from Förster dependence because optically dark states and surface states may contribute to the measured ET dynamics.[4]

To date, several excellent studies on QD-based ET processes have demonstrated the Förster resonance ET (FRET)-type mechanism in effect in the different QD−bioconjugate systems investigated.[6] In many DA systems, FRET accounts very accurately for the observed processes; however, other systems may have other processes at work which are not as well understood or explained.

In this Communication, we report on an additional non-Förster-type ET behavior of a series of QD conjugates. We present herein the measurements of the ET from 3.8 nm diameter CdSe QDs, synthesized on the basis of the Peng method,[7] to a homologous series of conjugated silicon phthalocyanines (Pc's) with an axial ligand of variable chain length (i.e., Pc−O−Si(CH$_3$)$_2$−(CH$_2$)$_n$−N(Me)$_2$, with $n = 1-6$, providing linker chain lengths with 4−9 bonds; see Supporting Information for details).[8] The utilized Pc's have shown potential for photodynamic therapy.[8] Particularly, the conjugate with $n = 3$, known as Pc 4, is in two Phase I clinical
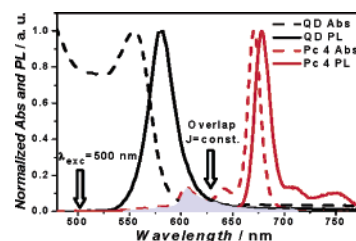

Figure 1. Steady-state absorption and PL spectra of CdSe QDs (black) and Pc's (red). While here the specific spectrum of conjugate $n = 3$ is shown, the Pc absorption did not vary with a change in linker chain length, and therefore the overlap integral between QD emission and Pc absorption is kept constant throughout the study. The dashed lines show the corresponding absorption and emission spectra of the QD and Pc, respectively.

trials. In this study, two sets of CdSe QDs with 3.8 nm mean diameter and (a) trioctylphosphine oxide (TOPO) or (b) tributylphosphine oxide (TBPO) as capping material were synthesized. The different Pc's were linked to the QDs through interdigitization of the axial alkylamino chain on the Pc's into the alkyl-capping layer on the QDs.[2a,b,8a] In these QD−Pc conjugates (conjugates with $n = 1-6$), the linker chain lengths are in the range of 4−9 bonds, respectively. An optimum conjugation time was determined via steady-state PL measurements (see Supporting Information) by mixing the QD and Pc solutions with known concentrations and monitoring when the increase in ET efficiency levels off. Selective excitation at 500 nm was chosen so that only QDs are excited but not the Pc's.

Figure 1 illustrates the absorption and emission spectra for the QDs used along with the spectrum of the Pc's used. The absorption properties of the Pc's were not affected by the variation in linker chain length. It is important to note that the overlap integral between the QD emission and the Pc absorption was therefore kept accurately constant during all measurements in this report.

The specific variations are only in the capping layer thickness: (a) TOPO and (b) TBPO. In addition, on each type of QD, a series of six different Pc's were conjugated (conjugates 1−6). The concentrations used in this study were 5×10^{-6} M QDs and 8×10^{-6} M Pc for each measured solution. These concentrations provide the best possible ET efficiency while minimizing Pc self-quenching (for details, see Supporting Information). Shown in Figure 2 are the emission spectra obtained from the QD and the QD conjugates at 576 nm as well as the emission from the Pc's around 673 nm caused by the ET. The insets depict the trend for the ET efficiency as a function of the ET efficiency as a function of linker chain length (i.e., number of bonds), which reflects that the efficiency of the ET varies strongly for conjugates 1−6 for both capping types. For TOPO-capped QDs, the maximum transfer efficiency was observed for conjugate 6 (number of bonds = 9), which has the longest linker chain, while for TBPO-capped QDs, the ET efficiency
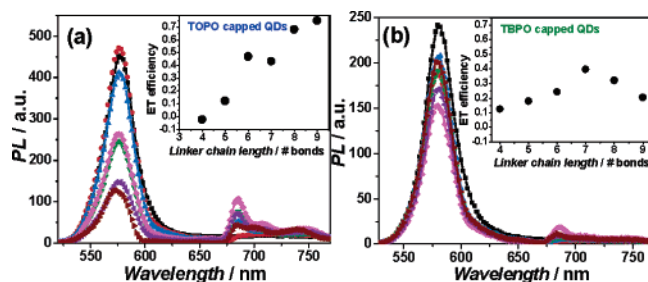
Figure 2. Steady-state PL spectra of pure QDs (black) and QD−Pc conjugates 1−6 with different linker chain lengths for (a) TOPO-capped QDs and (b) TBPO-capped QDs. The QDs in the conjugates were excited exclusively at 500 nm, where the Pc's do not absorb. The corresponding insets show the relation of the calculated ET efficiency (i.e., $\Phi_{ET} = 1 - I_{QD\,conj}/I_{QD}$) as a function of linker chain length between QDs and Pc molecules in terms of number of bonds.
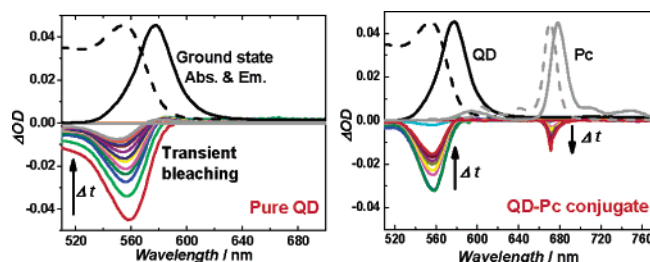
Figure 3. Transient differential absorption spectra of TOPO-capped CdSe QDs (left) and conjugate 3 (right) after 500 nm excitation. In addition to the 556 nm transient QD bleach, a signal at 673 nm was observed for conjugate 3, indicating excitation of the Pc by ET. Spectrally similar results were obtained for all other conjugates in both capping types.[8a] For comparison, the ground-state absorption and emission spectra of the QD and Pc are also added in arbitrary units to fit the scale.

increases to a maximum for number of bonds = 7 and then decreases for each additional methylene group added.

To further investigate the observed trend above, time-resolved transient absorption measurements with 120 fs resolution were performed using a femtosecond laser system, as previously described.[8a] The selective excitation at 500 nm (TOPAS, Light Conversion Ltd.) ensures that only QDs are excited but not the Pc's. In addition to the transient QD bleach signal at 556 nm, we observed in the QD conjugates a bleach signal at 673 nm, indicating the successful excitation of the Pc through ET (Figure 3, right). At both wavelengths, the transient bleach is due to a combination of excited-state filling and laser-stimulated emission, while the bleach intensity is a measure of the excited-state population. As shown in Figure 4, QDs (τ_{QD}) and their Pc conjugates 1−6 ($\tau_{QD\,conj}$) show a similar trend in ET efficiency when derived from lifetime measurements at 556 nm (the transient QD bleach wavelength). An increased efficiency for longer linker chain lengths was observed for TOPO-capped QDs, and a curve with maximum efficiency at number of bonds = 7 was obtained for TBPO-capped QDs. For both the steady-state and time-resolved measurements, the observed trend is not commensurate with a pure Förster-type ET mechanism. The observed linker chain dependence can, however, be explained with an additional surface-related process, whereby interdigitization of the Pc linker chain into the alkylphosphine oxide capping layer on the QDs occurs (Figure 4). Previous fluorescence depolarization experiments[8a] on conjugate 3 have shown that interdigitization takes place and the Pc ring locates parallel to the QD surface on the capping layer. In these studies, the interdigitization seems to be
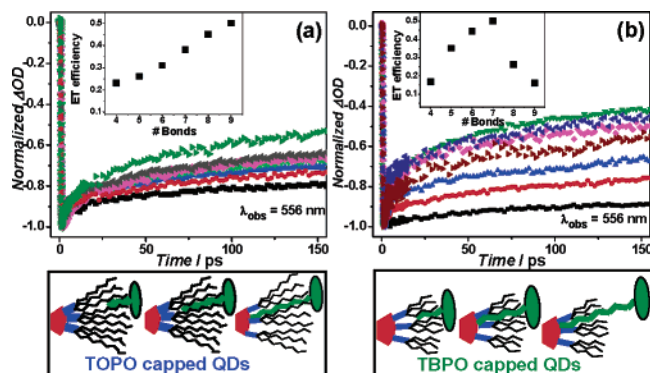
Figure 4. ET efficiencies obtained from lifetime measurements (i.e., $\Phi_{ET,kin} = 1 - \tau_{QD\,conj}/\tau_{QD}$) of QDs capped with TOPO and their conjugates (a) and for QDs capped with TBPO and their conjugates (b). The schematic diagrams at the bottom illustrate the proposed interaction of Pc linker chains with the TOPO- and TBPO-capping layers of the QDs, respectively, whereby interdigitization of different Pc linker chains occurs. For more details on the analysis, see the Supporting Information.

more efficient as the linker chains length approaches the thickness of the capping layer. This becomes evident with the increase in efficiency of the ET process. This trend is consistent with measurements on TBPO QD conjugates, wherein the ET efficiency increases until the chain length matches the capping layer thickness, and thereafter the Förster-type distance dependence becomes apparent for linker chain lengths >7 bonds.

In summary, we have studied the effect of the DA linker chain length on the ET efficiency between CdSe QDs and a series of Si phthalocyanines with steady-state and femtosecond time-resolved spectroscopy. From both sets of measurements, a non-Förster-type ET behavior was observed, which could be related to a surface DA interdigitization effect that can occur for QD-based donor−acceptor systems. We are currently evaluating the ET dependence on the overlap integral J and other ET parameters in order to provide additional insights into QD-based ET processes and their applicability to existing descriptions of ET mechanisms.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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