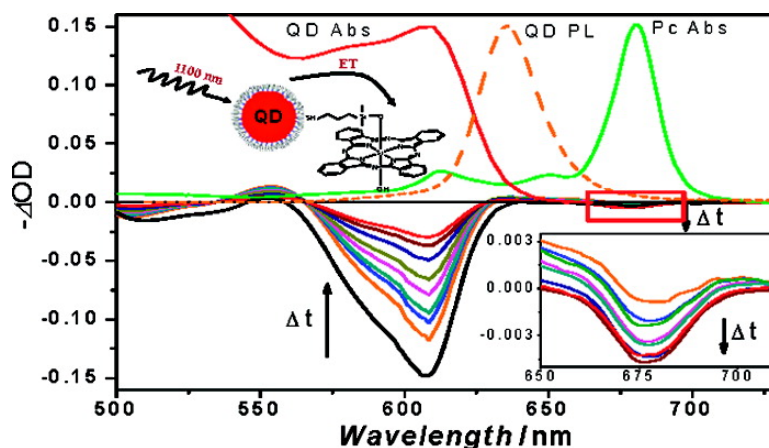


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Semiconductor Quantum Dots as Two-Photon Sensitizers

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Near-infrared (NIR) bioapplications of quantum dots (QDs) have been a research focus since it became evident that deeper penetration of tissues for imaging and sensitization applications is only accessible within the spectral therapeutic window of 700–1200 nm.¹ At shorter wavelengths cell chromophores and organelles absorb and scatter visible light, respectively. Contrary, at longer wavelengths the overtone vibrational absorption from water and melanin prevent penetration as well.¹

In addition to captivating properties such as high fluorescence quantum yields, photostability, and narrow and symmetric photoluminescence spectra independent of excitation wavelengths, QDs are extremely attractive sensitizers for near-infrared (NIR) two-photon (2P) absorption for various reasons. First, they have a large 2P absorption cross section;² second, the wavelength of the maximum 2P absorption can be adjusted via the size of the QDs, and appropriate QDs fall in a useful size regime of 2–5 nm.² In addition, the benefit of the large surface-to-volume ratio can aid in attaching the actual targeting moieties.³ QDs have shown extremely efficient renal clearance within hours of application if the QD size is kept small enough.⁴ We have quite extensively studied the possibilities to sensitize silicon-phthalocyanine derivatives via energy transfer from QDs with visible light.⁵ The silicon phthalocyanine Pc 4 has an absorption maximum at 680 nm and is approved for phase II clinical trials. These QD–Pc conjugates provide a clean window where the conjugates can be excited with one- or two-photon excitation of QDs without having any significant direct excitation of the acceptor molecules. The 2P excitation of Pc's is under study, but it is faced with practical problems such as the need of longer wavelengths (1300–1400 nm) for 2P excitation that fall in the vibrational overtone regime of water and a host of other biomolecules. Second, the relatively small 2P absorption cross-section area of 700 Goepfert–Mayer (GM) units limits the efficiency of 2P absorption by Pc's. A completely wavelength-targeted excitation of QD–Pc conjugates can be realized by utilizing the outstanding 2P absorption properties of QDs for the Pc sensitization. In this communication we show that QD–Pc conjugates provide an excellent opportunity to perform NIR excitation of Pc molecules via 2P sensitization of the QD followed by energy transfer (ET) to the Pc.

CdSe QDs with a 5 nm average diameter and narrow size distribution were synthesized⁶ and conjugated⁵ to Pc 4 by using previously reported methods.^{5,6} Time-resolved transient absorption measurements with 120-fs resolution were recorded on a femtosecond laser system, as previously described.⁷ The 1100 nm wavelength light was obtained from the signal of the optical parametric amplifier (TOPAS, Light Conversion). A long pass filter for wavelengths > 900 nm was used to avoid any 1P excitation at shorter wavelengths. An additional lens with 25 cm focal length was used to focus the excitation wavelength on the sample. The steady-state photoluminescence spectrum of the QDs and conjugates

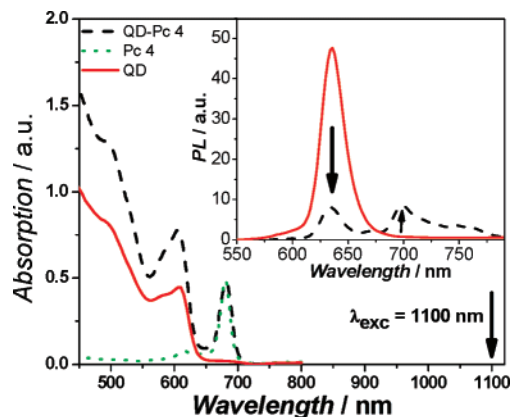


Figure 1. Steady-state absorption spectrum of QDs (solid line), Pc 4 (dotted line), and QD–Pc conjugates (dashed line) in toluene. The inset shows the fluorescence of QDs (solid line) and QD–Pc conjugates (dashed line). A 1100 nm wavelength light was used for the exclusive 2P excitation of the QDs in the conjugates, and the observed peak at 700 nm corresponding to the Pc emission occurs as a result of energy transfer.

were monitored in a Varian Eclipse fluorescence spectrophotometer upon excitation with 1100 nm laser light.

Figure 1 shows the steady-state absorption spectra of QDs, Pc 4, and conjugates of QD–Pc. The 5 nm QDs with an absorption band edge at 608 nm and with a photoluminescence (PL) maximum at 635 nm were chosen in order to establish a good spectral overlap with the absorption spectrum of the energy acceptor Pc molecules and also to make use of the extra large 2P absorption cross section at an energy equivalent to 550 nm.^{2c} It should be noted that the maximum 2P absorption of these QDs occurs just where the 1P absorption (black curve) is at a minimum. Indeed, the 1- and 2P absorptions are mutually exclusive for centrosymmetric systems,^{2a} a quantum mechanical selection rule, that can experimentally be observed in these experiments. The inset shows the 2P PL spectra before and after conjugation with the phthalocyanines. An energy efficiency of ~70% was calculated based on the decrease in the QD PL upon conjugation with the energy acceptor Pc 4. The arrow indicates the excitation wavelength used. A 1100 nm excitation wavelength was also used in order to avoid the direct 2P excitation of the Pc molecules. Phthalocyanines exhibit a large 2P absorption cross section of about 700 GM compared to other organic molecules (10–100 GM). Nanoparticles are to our knowledge the best sensitizers for which the 2P absorption cross sections are orders of magnitudes larger with 10³–10⁵ GM, depending on their size.^{2b–d} This renders QDs truly outstanding 2P sensitizers for many photoinduced processes.

To follow the 2P induced sensitization of the Pc, real time spectra of the QD–Pc conjugates were measured in a femtosecond pump–probe experiment. The results are shown in Figure 2. For the conjugates, in addition to the 608 nm bleach, which indicates

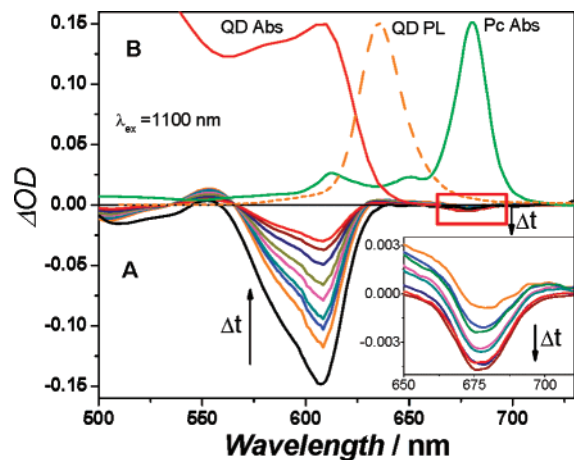


Figure 2. (A) Transient differential absorption spectra of QD–Pc conjugates upon excitation with 1100 nm wavelength light. In addition to the 608 nm signal corresponding to the QD bleach, a signal at 676 nm was observed corresponding to the Pc bleach, which is due to energy transfer upon 2P excitation of the QDs. The inset shows an expanded view of the Pc bleach signal at 676 nm. (B) For comparison, the steady-state absorption and PL spectra of QDs and the absorption spectrum of Pc 4 are added in arbitrary units.

Table 1. Decay Times Obtained upon a Biexponential Curve Fitting at the QD Bleach Maximum at 608 nm for QDs and QD–Pc Conjugates and at 676 nm for the Sensitized Pc's in QD–Pc Conjugates^a

$\lambda_{\text{kinetics}}$	A_1	τ_1/ps	A_2	τ_2/ps
pure QD ($\lambda_{608\text{nm}}$)	-0.1467	1042.65	-0.0620	59.63
QD–Pc ($\lambda_{608\text{nm}}$)	-0.1183	699.80	-0.0676	59.08
QD–Pc ($\lambda_{676\text{nm}}$)	0.0008	218.91		

^a Excitation wavelength was 1100 nm.

photoexcited QDs, one observes a second subsequent bleach signal at 676 nm corresponding to the Pc excitation. The spectra in the inset of Figure 2 clarifies that the Pc signal appears simultaneously to the decay process of the QD bleach, as a result of the 2P sensitization via QD-based ET. Furthermore, it is found that, at the delay times at which the spectra are measured, the 2P-induced transient absorption spectra are very similar to the 1P transient absorption spectra that were obtained before for photoexcited QDs and conjugates.⁵ This indicates that the excited electronic states populated at these delay times are not different from those populated after 1P excitation.

Kinetic analysis of the observed spectral changes at 608 nm for the QD bleach in the presence and the absence of the Pc allows quantification of the ET rates (Table 1) and direct monitoring of the sensitization process (Figure 3). The obtained kinetic traces were fitted with biexponential decay curves. The resulting relaxation times are summarized in Table 1. Acceleration in the slower decay component was observed upon conjugation with the Pc, which indicates the ET to the Pc. The kinetics for Pc bleach formation is presented in the inset of Figure 3, and a time constant of 218 ps was obtained with a monoexponential fit. An energy transfer efficiency of 38% was calculated based on the acceleration of the observed decay times for QDs upon conjugation with Pc molecules.

The singlet oxygen production efficiency of these conjugates has not yet been explored and may be less efficient than the unconjugated photosensitizers as recently studied by Weiss et al.⁸ Although

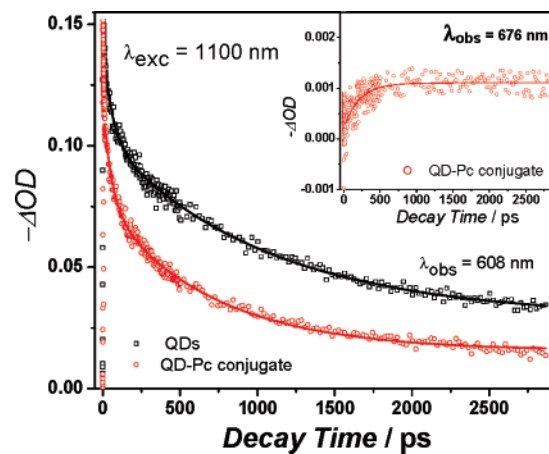


Figure 3. Kinetic traces for QDs (black squares) and QD–Pc conjugates (red circles) observed at 608 nm upon 2P excitation of the QDs with the corresponding biexponential fits (solid lines). The inset shows the kinetic trace observed at 676 nm (red circles) with a monoexponential fit (solid line) corresponding to the Pc bleach formation in the QD–Pc conjugates.

the issue of QD toxicity is much discussed and is currently being studied in many labs, the recent work by Bawendi et al.^{4a} once more emphasizes the importance of size and surface control at the nanoscale. One might find in the future that nanomolar concentrations of QDs could be acceptable not only for in vivo imaging but also for sensing and medicinal applications. In summary, we have identified the two-photon sensitization of Pc 4 molecules via the excitation of 5 nm QDs with 1100 nm light. This study underlines the excellent potential of QDs for applications that require NIR sensitization.

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