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Quantum Dots

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Fluorescent Quantum Dots as Artificial Antennas for Enhanced Light Harvesting and Energy Transfer to Photosynthetic Reaction Centers**

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The development of artificial photosynthetic systems that utilize solar energy is one of the most challenging goals of chemistry and material sciences.[1] The straightforward way to construct an artificial photosynthetic device for practical solar fuel production for the practical use of solar energy is to mimic the structural and functional organization of the natural photosynthetic machinery. In photosynthetic organisms, light is initially absorbed by antenna protein–pigment complexes in which it induces an excited electronic state (exciton), and then excitons (or electron–hole pairs) are transferred by means of Förster resonance energy transfer (FRET) to specialist chlorophyll cofactors in specialized reaction centers (RCs); here, excitons dissociate into their constituent carriers which are used in chemical transformations for the synthesis of high-energy molecules that fuel the organism.[2] An artificial device that mimics this process for solar energy conversion should include, among other components, an efficient light-harvesting antenna capable of transferring the excitation energy to the RC.

Based on the principle of photosynthesis, a variety of artificial antenna systems have been developed using supramolecular chemistry in which dendrimers incorporate porphyrins or other organic fluorophores or organometallic complexes.[3,4] Although efficient excitation-energy transfer was obtained in such systems, the use of organic fluorophores in light-harvesting systems is rather limited because of their narrow spectral windows for light-collecting and lack of photostability.[3,5]

Recently it was suggested that inorganic nanocrystals, which are able to collect light over a wide spectral window, may achieve significantly greater absorption than natural photosystems, thus enhancing and could thus be used to enhance the light-harvesting process.[6,7] Simultaneously, these nanocrystals may also be very efficient in excitation-energy transfer.[8,9] This has led us to contemplate the development of hybrid materials in which light energy harvested by the nanocrystals in the optical region may be transferred to the RC in order to enhance the efficiency of the photosynthetic process. The simplest and best understood photosynthetic RC is that found in purple bacteria (*Rhodobacter sphaeroides*, for example). Although RCs from different photosynthetic organisms vary in their structure and composition, they are always composed of complexes of pigments and proteins, and RC from *Rb. sphaeroides* is known to be a good model of all the photosynthetic RCs.[10,11] Here, we demonstrate that photoluminescent quantum dots (QDs) of these selected photoluminescence (PL) wavelengths may be tagged with the RC of *Rh. sphaeroides* in such a way that FRET from the QD to the RC is realized (Figure 1). A nearly threefold increase in the rate of generation of excitons in the RC is demonstrated, and theoretical estimates predict even stronger enhancements, thus indicating that further optimization is possible.

Advances in inorganic synthesis have resulted in the production of monodispersed QDs such as highly photoluminescent CdSe/ZnS core/shell[12] and CdTe[13] nanocrystals. The light absorption by these QDs appears as a quasi-continuous superposition of peaks with extinction coefficients orders of magnitude higher than those of organic molecules. QDs are ultrastable against photobleaching, and the quantum

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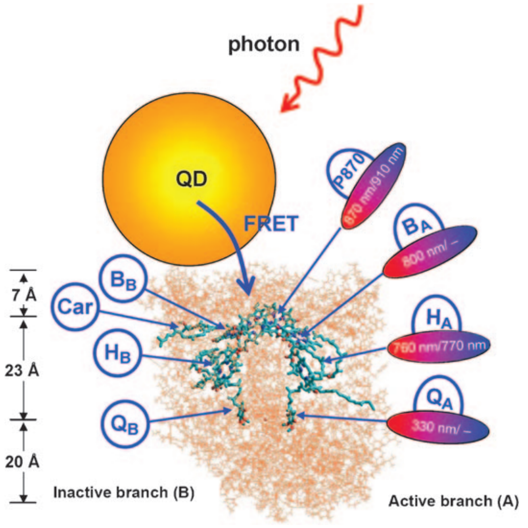

Figure 1. Organization and functionality of a complex composed of the reaction center (from *Rb. sphaeroides*) and a QD; the diagram is given to scale. Active (A) and inactive (B) branches in the electron-transfer cofactor are shown. The positions of the absorption/photoluminscence maxima for the BChl special pair (P870), BChl monomer (B), bacteriopheophytine (H), and quinone (Q) are indicated for the active branch (A) only. Photons are absorbed by both the RC and the QD. An exciton from the QD is transferred to the RC by FRET. Car = carotenoid.

confinement effect yields PL emission energy that varies as a function of the size of the QD. The spectral width and position of the optical bands of the QD can be tailored by controlling its size and surface functionality.[12,14,15]

Herein, we utilize photoluminscent QDs as artificial antennae that absorb light very efficiently in a wide range of photon energies (within the solar spectrum); these QDs are then able to transfer the harvested energy to optical enhancement of RC. In our experiments we used the RC complex of *Rb. sphaeroides* purified from natural light-harvesting complexes. QDs that strongly absorb light and strongly photoluminesce were then assembled with the RC (Figure 1). In order to develop an efficient hybrid material operating in the FRET regime, we carefully selected the PL colors (diameters) of the QDs (donors of energy) to be optically coupled with the RC pigment chromophores (acceptors). The data show that although the RC has its own light-harvesting system with a significant absorption cross section, properly designed QDs can easily dominate over the intrinsic absorption of the RC.

Figure 1 shows a model of the system under study: the purified RC from purple bacteria *Rb. sphaeroides* assembled with photoluminscent QDs (for a full description of the methods, see the Supporting Information). The RC is composed of cofactors (building blocks) arranged into two (active and inactive) membrane-spanning branches.[16] The active branch is responsible for electron–hole separation and sequential transmembrane electron transfer. Each branch (A or B in Figure 1) consists of one molecule of bacteriochlorophyll (BChl; B_A or B_B), one bacteriopheophytin (H_A or H_B), and one quinone (Q_A or Q_B). Only one of the branches (branch A) is active in catalyzing electron transfer across the RC. Both branches are connected to a key element of the RC which is a dimer of BChl molecules, the so-called "special pair" (P or P870). In nature, a solar photon first creates an excitation in the RC and then this excitation moves towards P870, where the electron separates from the hole within 2–3 ps.[17,18] In the next step, this electron moves along the electron-transfer chain towards Q_A. Afterwards, this electron takes part in chemical transformations eventually leading to synthesis of high-energy molecules such as ATP, which fill the majority of the energy needs of the bacterium.[4] However, the environmental conditions in our experiments, with isolated RC in water, are different from those in nature, where RCs are built into a membrane inside a bacterium. In water, an isolated RC is a delicate object and can be easily photo-oxidized even under very weak illumination on the order of $0.02\ \mathrm{mW\,cm^{-2}}$.[19] To avoid photo-oxidation and to keep P870 in the reduced form in the dark and under light illumination, we used sodium ascorbate molecules as a source of electrons (see the Supporting Information).

When added to the RC, sodium ascorbate supplies electrons to the photo-ionized $P870^+$ species, thus leading to the reduction reaction $P870^+ \rightarrow P870$. By adding sodium ascorbate, we create the so-called "closed state" of the RC, $P870/Q_A^-Q_B^-$, in which the quinones are fully reduced. When the closed-state RC absorbs a photon, the electron and hole are not separated; instead, they recombine in the P870 unit, resulting in the photoluminscent band at 910 nm (Figure 2a).[19] Importantly, the closed-state RC ($P870/Q_A^-Q_B^-$) is stable against photo-oxidation at experimental light fluxes ($12.5\ \mathrm{mW\,cm^{-2}}$), and its energy structure is similar to that of the natural-state $P870/Q_AQ_B$ in operational photosynthetic systems.

The diagram of energy relaxation inside the RC is of crucial importance for understanding the photo-electronic response of our QD–RC system (Figure 2a). This energy structure reflects and explains the RC absorption spectrum (Figure 2b). Figure 2b also shows, as an example, the experimental extinction coefficient for the CdTe QDs emitting at 570 nm (QD570) used in this work. In particular, we see that at the comparable molar concentrations, the QD570 absorption at wavelengths from 400 nm to 570 nm is stronger than that of the RC and, therefore, optical enhancement of the RC absorption is possible. We calculated the QD diameter from the PL wavelength using the convenient empirical fitting functions[20] (see the Supporting Information for the calculation and complete parameters of the QDs used in our study).

The QD–RC complex was prepared by electrostatic assembly. The complex displayed efficient quenching of QD′ exciton emission (Figure 3 and Figures S3 and S5 in the Supporting Information), suggesting efficient FRET from the QD to the RC. The efficiency of FRET is conveniently described by the parameter E: $E = 1 - PL_{\text{QD-RC}}/PL_{\text{QD}}$, where $PL_{\text{QD-RC}}$ and PL_{QD} are the peak intensities of QD exciton emission for QD–RC complexes and individual QD, respectively. It was found that FRET was more efficient for CdTe QDs than for CdSe QDs; this can be explained by the smaller

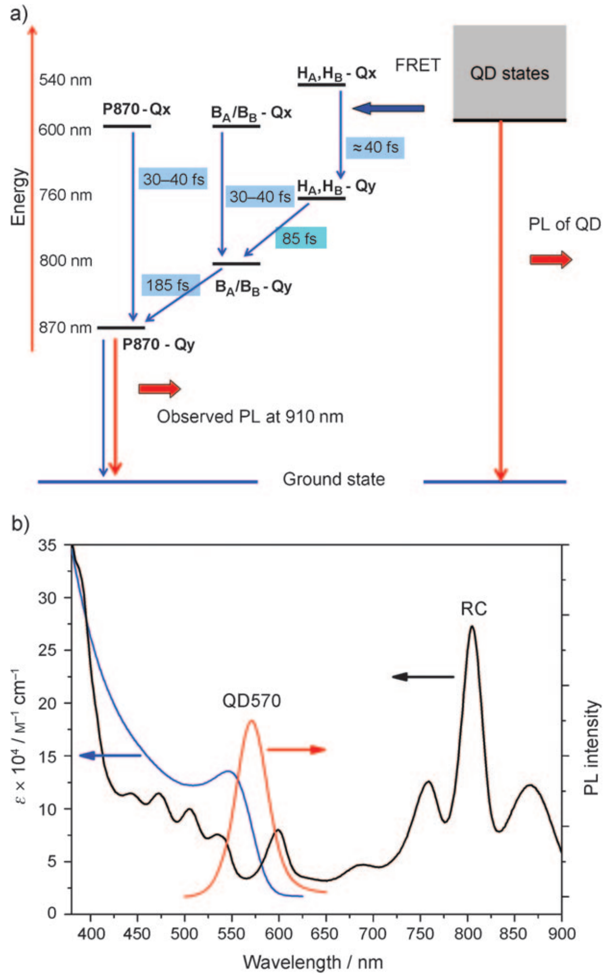

Figure 2. a) The energy-level diagram for the states of the reaction center. QD supplies excitation to the RC by means of FRET. Excitation quickly relaxes to the P870–Qy level. The relaxation times are taken from Ref. [11]. b) Plot of the molar extinction coefficients of RC and QD570 along with the PL spectrum of QD.

radii and thinner ligand shells in the CdTe QDs, and the resulting smaller QD–RC separations. Within the standard theory, the FRET efficiency for the complex involving one QD and one RC (complex "QD_1–RC_1") can be expressed as: $E_0 = 1/(1+(R/R_F)^6)$, where R is the QD–RC spatial separation (see the Supporting Information).

Changes in the CdTe QD lifetime as a result of the FRET process were monitored by time-resolved photoluminscence measurements recorded in the spectral region of the QD′ emission. This data, presented in Figure 3 a,b clearly shows the key signature of FRET: the lifetime of the donor (QD) shortens when QDs are assembled with RC. Significantly, very good correlation was observed between quenching of QD′ photoluminscence and shortening of their lifetimes (Figure 3 c,d), suggesting that FRET is the dominant mechanism of quenching of QD′ photoluminscence (see the Supporting Information); this validates the assumption made above in the definition of parameter E.

Energy transfer from the QD to the RC was also monitored by measuring the enhancement of the photoluminescence emission of the BChl special pair in the RC (at 910 nm) defined as Equation (1),

$$A_{910\mathrm{nm}}(\lambda_{\mathrm{exc}}) = \frac{\mathrm{PL}^{910\mathrm{nm}}_{\mathrm{QD-RC}}}{\mathrm{PL}^{910\mathrm{nm}}_{\mathrm{RC}}} = \frac{n_{\mathrm{QD-RC}}}{n_{\mathrm{RC}}} \qquad (1)$$

where λ_{exc} is the excitation wavelength, $\mathrm{PL}_{\mathrm{QD\text{-}RC}}$ and $\mathrm{PL}_{\mathrm{RC}}$ are the photoluminescence peak intensities at 910 nm for the QD–RC complex and for the individual RC, respectively, and n_{RC} and $n_{\mathrm{QD\text{-}RC}}$ are the numbers of electron–hole pairs generated at the special pair in RC and in the QD–RC hybrid complexes, respectively.

The experimentally determined factors A (λ_{exc}) are found to be larger than unity for $\lambda_{\mathrm{exc}} < \lambda_{\mathrm{QD,exciton}}$, where $\lambda_{\mathrm{QD,exciton}}$ is the exciton wavelength of QD. Therefore, our hybrid structures demonstrate optical enhancement; that is, the number of electron–hole pairs arriving at the special pair of RC is increased. The physical reason for the optical enhancement of RC is that additional electron–hole pairs are arriving at the RC from QD by means of FRET coupling. The complex QD570–RC shows stronger enhancement (up to threefold at $\lambda_{\mathrm{exc}} = 550$ nm) than QD530–RC (Figure 4) which may be explained by the stronger absorption of QD570. Another important parameter contributing to the enhancement effect is the FRET efficiency, E_0, of the RC–QD complexes. Also, we see that at smaller RC/QD molar ratios, the enhancement effect increases because more QDs interact with a single RC and, therefore, more energy can be transferred.

To support the above explanations and as a consistency check, we calculated the enhancement factor using experimental extinction coefficients and FRET efficiencies. From a simple rate model (see the Supporting Information) we obtained Equation (2),

$$A_{910\mathrm{nm}}(\lambda_{\mathrm{exc}}) = 1 + E\frac{I_{\mathrm{QD}}(\lambda_{\mathrm{exc}})}{I_{\mathrm{RC}}(\lambda_{\mathrm{exc}})} = 1 + Ex\frac{\varepsilon_{\mathrm{QD}}(\lambda_{\mathrm{exc}})}{\varepsilon_{\mathrm{RC}}(\lambda_{\mathrm{exc}})} \qquad (2)$$

where $I_{\mathrm{QD(RC)}}$ is the absorbance of QD and RC, respectively, $\varepsilon_{\mathrm{QD(RC)}}$ is the extinction coefficients, and x is the QD/RC molar ratio. Figure 4 c,d shows overall good correspondence between the measured and calculated results. The calculation reproduces both trends well: enhancement of emission at $\lambda_{\mathrm{exc}} < \lambda_{\mathrm{QD,exciton}}$ and increase of $A(\lambda_{\mathrm{exc}})$ for small RC/QD ratios. The enhancement occurs at the wavelengths at which the QD strongly absorb.

Figure 4 also shows that the enhancement arising from FRET from QD530 and QD570 to the RC occurs at excitation wavelengths present in the solar spectrum. Stronger overlap between the absorptions of QD and the solar spectrum can be tailored by choosing nanocrystals with suitable optical spectra. In addition, the CdTe QDs used in our study have relatively small radii and consequently moderate absorptions. The light-harvesting complexes can be optimized further by using larger QDs having much stronger absorptions[6] or by forming hybrid complexes from RC and nanowires or nanorods, which typically have very strong absorptions.

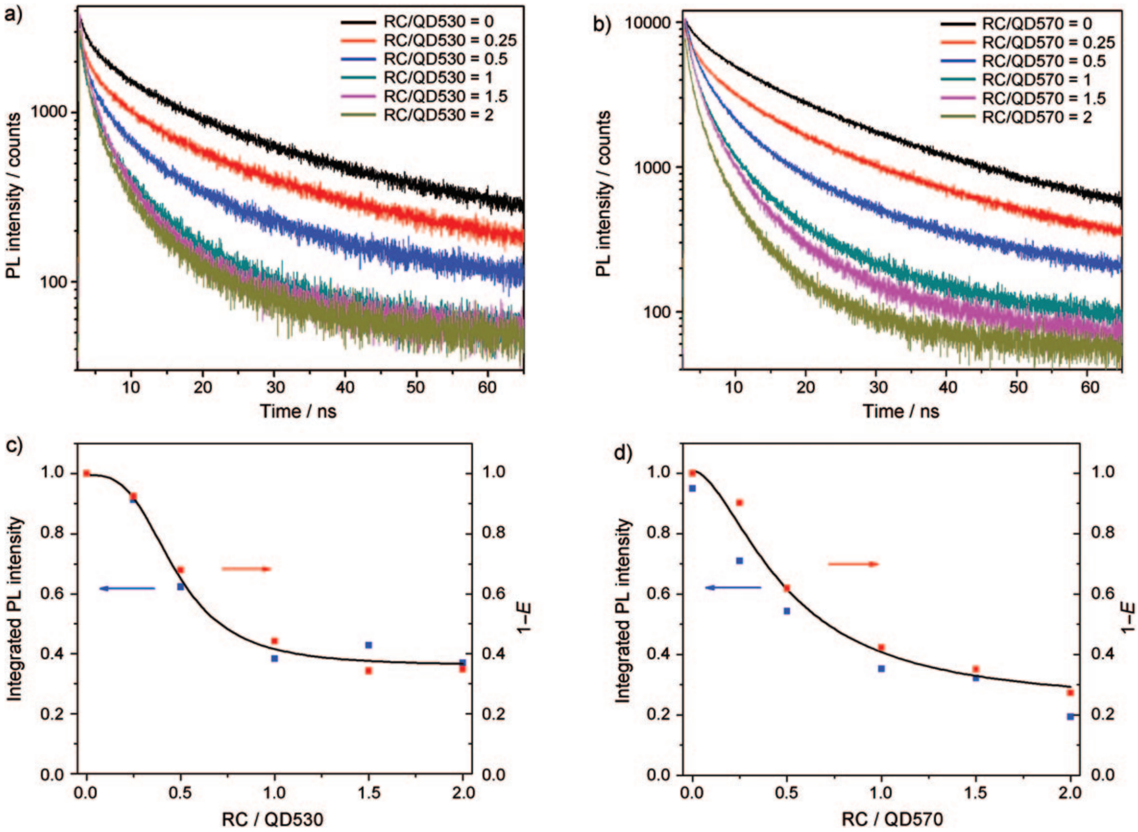

Figure 3. Time-resolved fluorescence measurements on CdTe QD–RC complexes. a,b) Fluorescence decay curves for CdTe QD530–RC and QD570–RC complexes measured in the spectral region of QD emission at different RC/QD molar ratios. c,d) Comparison of the normalized integrated intensity of the steady-state fluorescence and the modification of fluorescence lifetime as a function of RC/QD molar ratios. $E = 1-\tau_{DA}/\tau_{D}$, where τ_{DA} is averaged fluorescence lifetime of donor (QD) in the presence of acceptor (RC); τ_{D} is the average lifetime of donor (QD) alone. The arrows in c,d are a guide to the eye.

It was mentioned above that the RC system is in the "closed" state P870/$Q_a^{-}Q_b^{-}$. To keep this state non-oxidized, an efficient supply of electrons from sodium ascorbate is needed. One can imagine that attached QD can block the delivery of electrons to the special pair. However, time-resolved PL kinetic studies show that this is not the case (see Figure S4 in the Supporting Information). Delivery of electrons to the special pair remains fast in the QD–RC complexes since the observed recovery times in the absorption spectra of RC–QD complexes in Figure S4 remain similar to those of RC.

Potential applications of hybrid materials assembled from nanocrystals and biological molecules include such emerging fields as sensing[21,22] and light harvesting.[23,24] In sensor structures,[21,22] nanocrystals conjugated with a biomolecule have optical emission sensitive to environmental parameters. In light-harvesting nanocrystal complexes coupled by FRET,[23,24] the absorbed optical energy flows from the absorbing elements to the acceptor region and, in this way, becomes concentrated. In contrast to the light-harvesting structures previously reported,[23,24] our complexes incorporate biological photosynthetic reaction centers with an important photochemical functionality (charge separation).

This study represents the first example of the efficient transfer of excitation energy harvested by nanoparticles (QDs) to a complex biological photosynthetic system (RC). The results are important because they pave the way for the use of nanocrystals as light-harvesting built-in antennae for artificial photosynthesis. In green plants the reaction center of Photosystem II has a charge-separation site very similar to that of the bacterial reaction center.[4] So, from a fundamental point of view, our results of efficient energy transfer from QDs to the bacterial RC offer one interesting possibility for the utilization of nanocrystals to enhance the efficiency of the photosynthetic biological function. Moreover, theory predicts much stronger enhancements (upon further optimizations of the hybrid complexes).[7] The predicted enhancement of light-harvesting from solar radiation with properly optimized hybrids can be as large as five times. It is worth mentioning that the enhancement of biological functions of natural photosynthetic systems, if realized, should have a strong impact on energy-related technologies.

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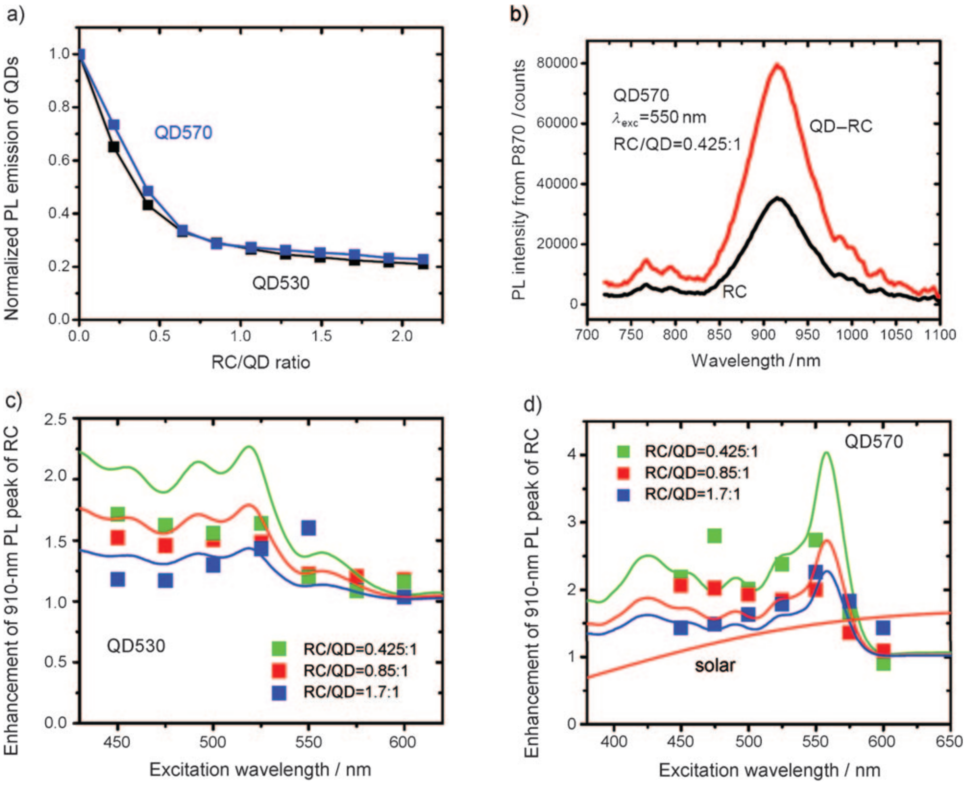

Figure 4. FRET and optical enhancement in complexes of CdTe QDs and reaction centers. a) Quenching of the QD photoluminescence as a function of the RC/QD molar ratio. Excitation wavelength: 450 nm; QD530 concentration: 0.5 μM; QD570 concentration: 0.25 μM. The volume of the RC solution added in each step was 4.8 μL and 2.4 μL, respectively. Dilution factors as well as inner-filter and re-absorption effects were taken into account (see the Supporting Information). b) Increase of the PL peak at 910 nm associated with the PL emission from the BChl special pair (P870) of RC. c,d) Summary of the data for enhancement of PL emission from RC. Enhancement coefficients (colored squares) as a function of the excitation wavelength are given for the 910 nm PL band of P870 for complexes based on CdTe QD530 and QD570; sodium ascorbate (10 mM) was added to prevent RC from photo-oxidizing. Solid curves are calculated from Equation (2) for the corresponding complexes. The solar spectrum is included in (d).

Keywords: energy transfer · hybrid materials · photosynthesis · quantum dots

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