Quantum dot photosensitizers as a new paradigm for photochemical activation

Cédric Mongin, Sofia Garakyaraghi, and Felix N. Castellano

Interfacial triplet-triplet energy transfer is used to significantly extend the exciton lifetime of cadmium selenide nanocrystals in an experimental demonstration of their molecular-like photochemistry.

Photosensitizers are an essential component of solar energy conversion processes, in which they are used to generate the highly reactive excited states that enable energy conversion (e.g., photochemical upconversion).\(^1\)\(^,\)\(^2\) Typically, molecular triplet photosensitizers are used for such applications, but to improve the solar energy conversion process, the identification and preparation of next-generation triplet photosensitizers is required. However, the design of such photosensitizers—suitable for solar energy conversion and photocatalytic applications—remains a challenge.\(^3\)

Semiconductor nanocrystals are stable light-emitting materials that can be systematically tuned to produce intense absorptions and photoluminescence. Furthermore, semiconductor nanocrystals offer several advantages over molecular photosensitizers, e.g., simple preparative synthesis, photochemical stability, size-tunable electronic and photophysical properties, high molar extinction coefficients, and trivial post-synthetic functionalization. Moreover, the inherently large, energy-consuming singlet-triplet gaps that are characteristic of molecular sensitizers can be avoided with the use of semiconductor nanocrystals that feature closely spaced excited-state energy levels.\(^4\) The characteristic broadband light absorption properties of these materials can be extended into the near-IR and can thus potentially be exploited for numerous triplet excited-state reactions, such as photoredox catalysis, singlet oxygen generation, photochemical upconversion, and excited state electron transfer.

In this work,\(^5\) we have investigated the possibility of using quantum dots as effective alternatives to molecular triplet photosensitizers. With our experiments, we show definitively that triplet energy transfer proceeds rapidly and efficiently from energized semiconductor nanocrystals to surface-anchored molecular acceptors. In particular, we find that cadmium selenide (CdSe) quantum dots can serve as effective surrogates for molecular triplet sensitizers and can easily transfer their triplet excitons to organic acceptors (see Figure 1). These semiconductor nanomaterials are thus highly suited to energy-conversion applications.

The nanoparticle-to-solution triplet exciton transfer methodology we used in our experiments is shown in Figure 2. Quantum dots are typically capped with a ligand shell, and in our experiments we used oleic acid (OA) to ensure solubility of the dots (while also preventing inter-particle aggregation). This ligand periphery also serves as an insulating layer that prevents collisional quenching with the freely diffusing molecules.
Schematic representation of the quantum dot-to-solution triplet energy transfer process. The associated energy (E) levels, as well as the various triplet-triplet energy transfer (TTET) and decay pathways investigated in this study are also depicted. Cadmium selenide (CdSe) nanocrystals—capped with oleic acid (OA)—are used as the light-absorbing triplet sensitizer, in conjunction with 9-anthracenecarboxylic acid (ACA) as the triplet acceptor. The long-lived ACA triplets enable exothermic triplet energy transfer to freely diffusing 2-chlorobisphenylethynylanthracene (CBPEA) and dioxygen ($\text{O}_2$).

Since the energy transfer process in our experiments takes place at the molecule–nanoparticle interface (i.e., resembling an intramolecular process), the dynamics occur on ultrafast timescales. To monitor the photoinduced processes in these materials, we used femtosecond transient absorption spectroscopy to observe the excited-state dynamics following a 500nm laser pulse (100fs full width at half-maximum, 0.2µJ). We find—that direct triplet-triplet energy transfer (TTET) between the CdSe excited states and the surface-anchored molecular acceptors occurs within hundreds of picoseconds after the laser pulse (with an average rate constant of $2.0 \times 10^9 \text{s}^{-1}$) and with a nearly quantitative yield. Consequently, the CdSe photoluminescence was completely quenched, and the CdSe exciton ground-state recovery correlated with the molecular ACA triplet excited-state ($^3\text{ACA}^*$) signal growth (which occurred at a rate of $2.2 \times 10^9 \text{s}^{-1}$).

The $^3\text{ACA}^*$ has an extremely long lifetime because of the strongly spin-forbidden nature of the $\text{T}_1 \rightarrow \text{S}_0$ transition (i.e., between the lowest energy triplet excited state and the singlet ground state). Our results also show the decay of the $^3\text{ACA}^*$ excited states that formed on the CdSe surfaces had lifetimes on the order of milliseconds. This result represents a remarkable six-order-of-magnitude increase from the initial CdSe excited-state lifetime. Such a long excited-state lifetime is promising for numerous applications because it provides the opportunity for additional chemical reactivity within the bulk solution.

As a proof of concept, we used a secondary freely diffusing molecular triplet acceptor—2-chlorobisphenylethynylanthracene (CBPEA)—in solution (toluene), to demonstrate the extraction of triplet energy from the CdSe surface. We observed—that near-quantitative TTET between the $^3\text{ACA}^*$ and the triplet excited CPBEA ($^3\text{CPBEA}^*$) states, which can thus enable highly efficient triplet energy extraction from the initially in the solution. As a consequence, bimolecular energy transfer cannot proceed in the solution within the approximately 30ns-lifetime of CdSe excitons. To circumvent this limitation, we modified the CdSe surfaces by replacing some of the native OA ligands with molecular triplet acceptors that bear a carboxylic acid moiety, e.g., 9-anthracene carboxylic acid (ACA). We then purified the resultant nanocrystals by successive precipitation/centrifugation washing cycles that provided the desired donor/acceptors (termed CdSe/ACA).

Continued on next page
Figure 3. (a) Ultrafast differential transient absorption (TA) spectra of CdSe-OA quantum dots suspended in toluene. These spectra were obtained upon selective excitation of CdSe, with the use of a 500nm laser pulse. The inset shows the TA kinetics for the growth of the molecular ACA triplet excited state \( (^3ACA^*) \) at 441nm. \( \Delta A \): Change in absorbance. \( \langle k \rangle_{\text{TTET}} \): Average TTET rate constant. (b) TA difference spectra (from a 1mJ laser pulse with 505nm excitation wavelength, 5–7ns full width at half-maximum) measured at selected delay times after the laser pulse for CdSe/ACA CBPEA in deaerated toluene (at concentrations of 5 and 6 \( \mu \)M, respectively) at room temperature. The inset illustrates the triplet energy transfer reaction between \( ^3ACA^* \) and CBPEA. It shows TA decay kinetics at 430nm (red), as well as the rise and decay at 490nm (blue) along with their biexponential fits (solid and dashed lines, respectively).  

Figure 4. (a) Delayed fluorescence (DF) spectra of triplet-sensitized upconversion emission that occurred as a result of TTET from CdSe/\(^3\)ACA* to CBPEA, followed by triplet-triplet annihilation. The inset shows the emission decay kinetics of the integrated delayed emission. (b) Near-IR singlet oxygen phosphorescence emission from CdSe-OA and CdSE-OA/ACA in aerated toluene (both at a concentration of 4\( \mu \)M), under 505nm excitation at room temperature. Prepared CdSe excitons. Our results also show that once the triplet exciton energy is transferred to the freely diffusing acceptors in a deoxygenated solution, they eventually undergo triplet-triplet annihilation. This leads to upconverted emission from the \(^1\)CBPEA* (at 490nm), with a lifetime of hundreds of microseconds, as shown in Figure 4(a). Moreover, in an aerated solution

Continued on next page
of CdSe/ACA we detected the characteristic photoluminescence (centered at 1277nm) of singlet oxygen ($^1$O$_2$), which results from the quenching of $^3$ACA* by freely diffusing ground-state oxygen. In contrast—see Figure 4(b)—we observed no such signal when we used CdSe nanoparticles that were devoid of ACA ligands. This work therefore represents the first example of $^1$O$_2$ sensitization by semiconductor nanocrystals via a mechanism other than Förster energy transfer.

In summary, we have conducted proof-of-concept experiments in which we show that CdSe quantum dots are effective surrogates for more-ubiquitous molecular triplet photosensitizers in energy conversion processes. The high photostability, broad absorption spectra, and tunable optical properties of such quantum dots give rise to their superior properties. We have also demonstrated that the behavior of semiconductor quantum dots mimics the classical behavior of molecular triplets, and that triplet excitons in nanocrystals can be efficiently transferred to a bulk solution through successive (and nearly quantitative) triplet energy transfer steps. This photofunctionality may be exploited for numerous triplet excited-state reactions, including photoredox catalysis, singlet oxygen generation, photochemical upconversion, and excited-state electron transfer. Our current research activities include generalizing this approach across a range of semiconductor nanocrystalline materials, probing the ‘molecular’ nature of these materials, and applying these long-lived excited states in a range of photoactivated chemistry.

This work was supported by the US Air Force Office of Scientific Research (FA9550-13-1-0106) and the Ultrafast Initiative of the US Department of Energy, Office of Science, Office of Basic Energy Sciences, through Argonne National Laboratory (under contract DE-AC02-06CH11357).

Author Information

Cédric Mongin, Sofia Garakyaraghi, and Felix N. Castellano
Department of Chemistry
North Carolina State University (NCSU)
Raleigh, NC

Cédric Mongin received his PhD in organic chemistry (on photoswitchable molecular cages) from the University of Bordeaux, France, in 2013. Since 2014 he has been a postdoctoral researcher in the Castellano research group at NCSU, where his research focuses on the exploitation of semiconductor quantum dots as promising triplet sensitizers. He will begin his independent career later this year, as a faculty member in chemistry at the École Normale Supérieure de Cachan, France.

Sofia Garakyaraghi received her BS in chemistry (with a minor in mathematics) from the College of William and Mary in 2013. She is currently a PhD candidate under the guidance of Felix Castellano. She is studying the excited-state dynamics of various molecular- and nanocrystal-based systems with the use of ultrafast spectroscopy.

Felix (Phil) Castellano earned a BA from Clark University in 1991 and a PhD from Johns Hopkins University in 1996 (both in chemistry). Following a National Institutes of Health postdoctoral fellowship at the University of Maryland’s School of Medicine, he accepted a position as assistant professor at Bowling Green State University in 1998. He was promoted to associate professor in 2004, to professor in 2006, and was appointed director of the Center for Photochemical Sciences in 2011. In 2013 he moved his research program to NCSU, where he is currently a professor. He was appointed as a fellow of the Royal Society of Chemistry in 2015. His current research focuses on metal-organic chromophore photophysics and energy transfer, photochemical upconversion phenomena, solar fuel photocatalysis, energy transduction at semiconductor/molecular interfaces, and excited-state electron transfer processes.

References