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Mechanistic Understanding and Rational Design of Quantum Dot/Mediator Interfaces for Efficient Photon Upconversion

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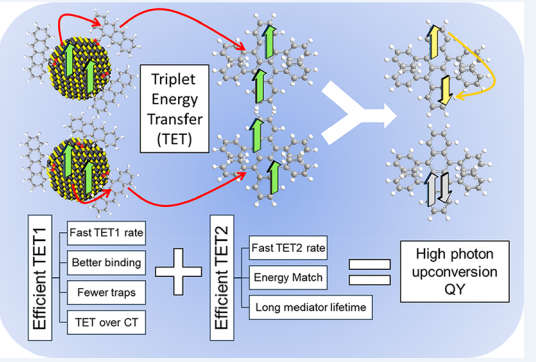
CONSPECTUS: The semiconductor-nanocrystal-sensitized, three-component upconversion system has made great strides over the past 5 years. The three components (i.e., triplet photosensitizer, mediator, and emitter) each play critical roles in determining the input and output photon energy and overall quantum efficiency (QE). The nanocrystal photosensitizer converts the absorbed photon into singlet excitons and then triplet excitons via intersystem crossing. The mediator accepts the triplet exciton via either direct Dexter-type triplet energy transfer (TET) or sequential charge transfer (CT) while extending the exciton lifetime. Through a second triplet energy-transfer step from the mediator to the emitter, the latter is populated in its lowest excited triplet state. Triplet−triplet annihilation (TTA) between two triplet emitters generates the emitter in its bright singlet state, which then emits the upconverted photon. Quantum dots (QD) have a tunable band gap, large extinction coefficient, and small singlet−triplet energy losses compared to metal−ligand charge-transfer complexes. This high triplet exciton yield makes QDs good candidates for photosensitizers. In terms of driving triplet energy transfer, the triplet energy of the mediator should be slightly lower than the triplet exciton energy of the QD sensitizer for a downhill energy landscape with minimal energy loss. The same energy cascade is also required for the transfer from the mediator to the emitter. Finally, the triplet energy of the emitter must be slightly larger than one-half of its singlet energy to ensure that TTA is exothermic. Optimization of the sensitizer, mediator, and emitter will lead to an increase in the anti-Stokes shift and the total quantum efficiency. Evaluating each individual step's efficiency and kinetics is necessary for the understanding of the limiting factors in existing systems.



This review summarizes chalcogenide QD-based photon upconversion systems with a focus on the mechanistic aspects of triplet energy transfer conducted by the Tang and Lian groups. Via time-resolved spectroscopy, the rates and major loss pathways associated with the two triplet energy-transfer steps were identified. The studies are focused on the near-infrared (NIR) to visible (VIS) PbS-tetracene-based systems as they allow systematic control of the QD, mediator, and emitter. Our results show that the mediator triplet state is mostly formed by direct TET from the QD and the transfer rate is influenced by the density of bound mediator molecules. Charge transfer, a loss pathway, does not produce triplet excitons and can be minimized by adding an inert shell to the QD. This transfer rate decreases exponentially with the distance between the QD and mediator molecule. The second TET rate was found to be much slower than the diffusion-limited collision rate, which results in the triplet lifetime of the mediator being the main factor limiting its efficiency. Finally, the total quantum efficiency can be calculated using these measured quantities including the TET1 and TET2 efficiencies. The agreement between calculated and measured quantum efficiencies suggests a firm understanding of QD-sensitized photon upconversion. We believe the above conclusions are general and should be widely applicable to similar systems, including singlet fission in hybrid organic−nanocrystal materials.

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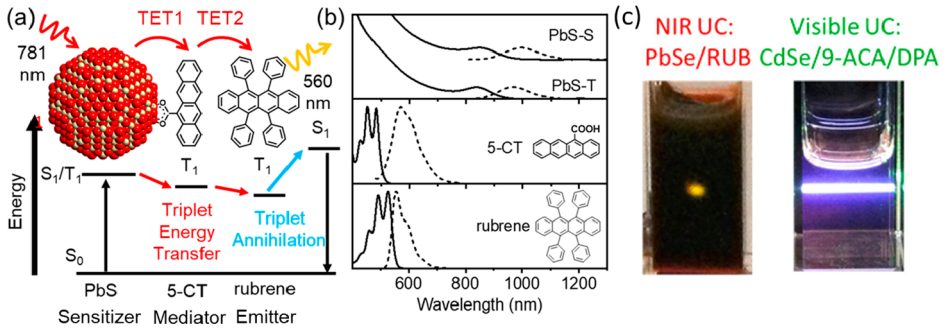

Figure 1. (a) Schematic of the QD (PbS)/mediator (5-CT)/emitter (rubrene) photon upconversion system. (b) Vis–NIR absorbance (solid lines) and photoluminescence (dashed lines) spectra of the sensitizer, mediator, and emitter. PbS-S and PbS-T are PbS QDs synthesized with bis(trimethylsilyl)sulfide and thiourea sulfur precursors, respectively. (c) Upconverted yellow photons from NIR photons in the PbSe/rubrene system. (a) Adapted and (b) reproduced with permission from ref 2. Copyright 2019 American Chemical Society. (c) Reproduced with permission from ref 21. Copyright 2015 American Chemical Society.

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- Xu, Z.; Huang, Z.; Li, C.; Huang, T.; Evangelista, F. A.; Tang, M. L.; Lian, T. Tuning the Quantum Dot (QD)/Mediator Interface for Optimal Efficiency of QD-Sensitized Near-Infrared-to-Visible Photon Upconversion Systems. *ACS Appl. Mater. Interfaces* **2020**, *12*, 36558.[4] *By varying the distance between the PbS quantum dot and mediator, an exponentially distance-dependent rate of TET1- and QD-induced triplet lifetime quenching with similar β values is revealed. The experimentally measured upconversion quantum efficiency is reproduced by the product of TET1 and TET2 quantum efficiencies, with the additional limiting factor of the triplet–triplet annihilation process.*

1. INTRODUCTION

Photon upconversion, where two or more low-energy photons are converted into one high-energy photon, shows great potential in bioimaging, catalysis, and solar energy conversion.[5−7] Photon upconversion has traditionally been realized with lanthanide-doped nanoparticles[8−10] or organic-dye-sensitized triplet–triplet annihilation (TTA)-based upconversion platforms.[11] Each strategy has its unique advantages. Large anti-Stokes shifts and narrow line widths characterize lanthanide-doped upconversion nanoparticles, but these materials have low spectral coverage and need strong excitation, which limits their use in optoelectronic applications. Currently, the best internal quantum efficiencies (QEs) are >16% using Er^{3+}-doped $NaYF_4$[12,13] but with an excitation intensity much higher than the solar flux. In comparison, TTA-based upconversion with organic dyes can operate under the solar flux, with the highest efficiencies of 36–38%.[14−16] However, it is challenging to find a photostable organic chromophore in the NIR region, and semiconductor QDs address this limitation effectively.

Over the past 5 years, we have led a foray into photon upconversion using QDs as photosensitizers. QD-sensitized triplet–triplet annihilation-based upconversion systems combine the high photostability of lanthanide upconversion nanoparticles and the low excitation intensity of organic triplet–triplet annihilation-based upconversion systems, with high spectral coverage and tunability. In this 5-year period, the QD photosensitized upconversion quantum efficiency (UCQE) has increased to a high of 18.6% in solution (100% UCQE is defined as 1 output photon for every 2 input photons).[1,17−20] Compared to previously established lanthanide-based systems,[10] QD photosensitizers have several advantages, such as a better spectral tunability of photons absorbed and emitted[21−24] and a lower input photon flux required. Thus, QD-based upconversion systems are potentially useful for photovoltaic devices that can surpass the Shockley–Queisser limit.[25−27]

In this account, we provide an overview of QD-sensitized photon upconversion systems and summarize recent progress. Much of these efforts have focused on optimizing the QD/mediator interface. Focusing on upconversion systems based on a series of PbS-tetracene-rubrene derivatives, we summarize the main results of detailed mechanistic studies on the various factors affecting the rate of triplet energy transfer (TET), first from the QD to the mediator (TET1) and then from the mediator to the emitter (TET2), and their net effect on overall UCQE. Finally, we provide a summary and outlook on key unanswered questions in this field.

2. QUANTUM DOT UPCONVERSION SYSTEM DEVELOPMENT

2.1. QD Upconversion (UC) System Overview

QD-sensitized upconversion systems usually consist of three components: light-absorbing QD sensitizers, QD surface-bound mediators, and light-emitting dye molecules. Because QDs are capped by ligands with long aliphatic tails (such as oleic acid) to provide colloidal stability and to passivate defects, direct TET from the QD to emitters in solution is

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inhibited. Thus, mediators bound to the QD surface are used to increase the rate and efficiency of short-range triplet energy transfer in order to outcompete the self-recombination of QD excitons.[21,28] In the example shown in Figure 1a, the upconversion process starts with the absorption of a near-infrared photon to generate an exciton in the PbS QD, which at room temperature contains a mixture of spin singlet and triplet character.[29] The singlet and triplet states of the surface-bound 5-carboxylic acid tetracene (5-CT) mediator are energetically above and below the QD band edge exciton respectively, ensuring that downhill TET1 from the QD to the mediator selectively occurs (Figure 1b).[1,22] This mediator triplet excited state is then transferred to the rubrene emitter in a second TET step (TET2). Two rubrene molecules in their triplet excited state collide to form one in a bright singlet excited state and the other in the ground state.[11,30] Singlet rubrene emits yellow photons to complete photon upconversion (Figure 1c).

The size and composition of the QD photosensitizer determine the range of photons that can be upconverted, and the vast varieties of QDs (e.g., PbS and CdSe) allow photons from the near-infrared to the visible to be utilized.[1,2,18,20−22,28,31−39] Currently, mediators that are used commonly in photon upconversion are asymmetric acenes with an anchoring group (e.g., 1-NA, 9-ACA, 5-CT, and TIPS-pentacene).[1−3,18,20,21,23,24,28,33,34,38] Emitters usually involve 9,10-diphenylanthracene (DPA) and rubrene.

2.2. Advances in UCQE in QD-Sensitized Photon Upconversion Systems

In the QD-sensitized upconversion systems, one of the most important metrics is the total UCQE. UCQEs have increased from less than 1% up to ∼20% since the first report in 2015.[21] This fast growth in efficiencies benefits from an understanding of the mechanisms and factors that affect TET at the QD/mediator interface, such as the QD size[18,38] and surface traps[1,20,34,43,44] as well as the surface density[28] and spatial proximity to QD[37] of bound mediators. These improvements in UCQEs within the past 5 years are summarized in Figure 2, classified by the energy of the upconverted photon. For lead chalcogenide QD-sensitized NIR-to-visible upconversion, 0.01% QE was first reported by Huang et al. in 2015,[21] with PbSe QDs as the sensitizer and rubrene as the emitter. The low QE is mainly due to the native oleic acid ligand which works as a barrier that blocks efficient TET from the QD to rubrene. This problem is later overcome by loading tetracene mediators on the QD surface, which yields a UCQE of 2.1%.[28] Further improvement was realized by the investigation into the role of surface traps by transient absorption (TA) spectroscopy,[1] revealing that surface passivation by inorganic shells suppresses undesired charge transfer from the QD to the mediator. For example, coating the PbS QD core with a CdS shell improves the UCQE by up to 8.4%.[34] In addition to surface passivation, the precursors used for the synthesis of QDs were discovered to greatly impact the lifetime of the QD exciton and the surface-anchored mediator, both of which affect the TET efficiencies from the QD to the mediator and from the mediator to the emitter. With highly purified lead oleate and thiourea precursors, 11.8%, the highest NIR-to-visible UCQE so far, is obtained.[2] Green to blue photon upconversion follows a similar pathway. By optimizing the QD size, surface passivation, and ligand selection, the UCQE quantity is increased from 0.01 to 18.6%,[20,21,37,40] with the current record reported by Han et al. using $CuInS_2$ QDs.[20] For Vis to NUV upconversion, the initially reported 5.2% QE with CdS/ZnS core−shell QDs by Gray et al.[33] has been improved to 10.2% with $CsPbBr_3$ perovskite QDs by He et al.[31]

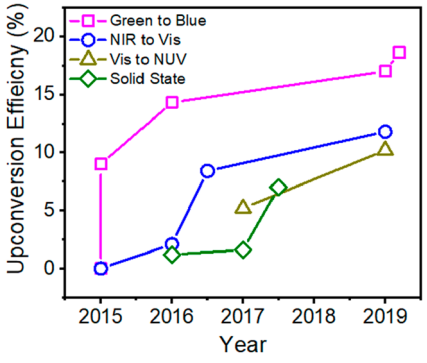

Figure 2. Champion quantum efficiencies of QD-sensitized triplet−triplet annihilation-based photon upconversion. Values of upconversion efficiencies in the plot are from refs 20, 21, 37, and 40. (Green to blue) refs 2, 21, 28, and 34. (NIR to vis) refs 31 and 33. (Vis to NUV) refs 23, 41, and 42 (solid state).

Several optoelectronic applications require upconversion in the solid state.[45] Despite the relatively high efficiencies in solution-based TTA platforms, solid-state upconversion systems are substantially less efficient because the slow diffusion of mediators and emitters limits TET efficiencies and enhances back transfer from the emitter to sensitizer. In 2016, Wu et al.[23] first reported upconversion thin films with PbS QD as a sensitizer, rubrene as an annihilator, and dibenzotetraphenylperiflanthene as the emitter with 1.2% UCQE obtained with 808 nm excitation. Later, with an optical spacer layer and a silver-film back reflector in a QD-emitter bilayer device, an internal QE of 1.6% was reported.[41] By replacing oleic acid with shorter aliphatic capping ligands on PbS QD, the UCQE was further boosted to 7% in solid thin films.[42]

The total UCQE is the product of the QEs of multiple elementary steps:[11]

$$\Phi_{UCQE} = \Phi_{ex}\Phi_{TET1}\Phi_{TET2}\Phi_{TTA}\Phi_{FL} \quad (1)$$

Here, Φ_{ex} is the QE for generating a triplet exciton in the QD per absorbed photon; Φ_{TET1} and Φ_{TET2} are the QEs of TET1 from the QD to mediator and TET2 from the mediator to emitter, respectively; Φ_{TTA} is the QE of triplet−triplet annihilation to generate an emitter singlet state; and Φ_{FL} is the fluorescence QE of the emitter. Φ_{ex} can be considered to be unity due to strong spin−orbit coupling in QDs. Φ_{TTA} and Φ_{FL} depend on the intrinsic properties of the emitter and its concentration.[29,46,47] Much of the recent work in QD-sensitized upconversion systems has focused on the design and optimization of the QD/mediator interface, which affects both Φ_{TET1} and Φ_{TET2}. Below, we provide an overview of recent progress in understanding the mechanisms of these processes and key factors affecting their efficiencies with a focus on the PbS-tetracene system.

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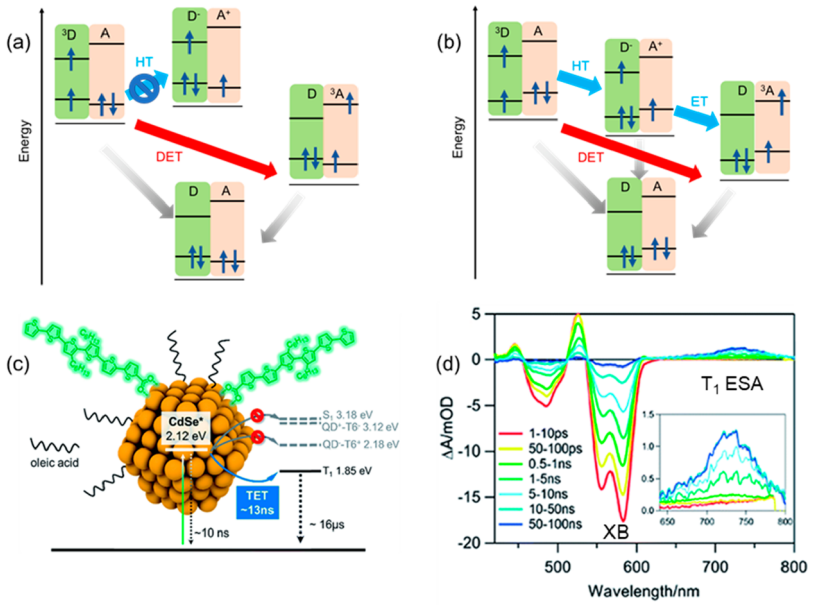

Figure 3. Direct and sequential triplet energy transfer in QD-acceptor complexes. (a) Scheme of the direct Dexter energy transfer (DET) pathway (red arrow) and energetically unfavorable charge-transfer pathway (blue arrow). (b) Scheme of competition between DET (red arrow) and indirect energy transfer from donor to acceptor through a charge-transfer intermediate (blue arrows). Also shown in A and B are deactivation pathways (gray arrow). (c) Scheme of direct DET from a CdSe QD donor to an oligothiophene (T6) acceptor, the energetics of the relevant states, and competing deactivation processes. (d) TA spectra of QD-T6 complexes at indicated delay times after 520 nm excitation of the QD. (Inset) Expanded view of the T6 triplet TA absorption spectra at 540−800 nm. (c, d) Reproduced with permission from ref 3. Copyright 2019 Royal Society of Chemistry.

3. TRIPLET ENERGY TRANSFER FROM QDS TO MEDIATORS

3.1. Direct vs Sequential TET

In addition to TET, excitons in QD-mediator complexes can also undergo Förster resonance energy transfer (FRET), electron or hole transfer, and nonradiative/radiative recombination depending on the energetics of relevant states and the relative rates of these processes. TET can proceed by direct Dexter energy transfer (DET) as well as indirect sequential charge-transfer pathways.[3,36,48−52] DET from QD donors (D) to mediator acceptors (A) is a concerted electron- and hole-transfer process without involving a charge-transfer (CT) intermediate state (Figure 3a).[53−58] The rate of this process is determined by the two-electron exchange integral between the donor and acceptor and can be enhanced by virtual charge-transfer states.[53−58] In the QD-acceptor complex, this pathway is manifested by the simultaneous depletion of the QD exciton and growth of the triplet excited state of the acceptor, which can be directly probed by transient absorption (TA) spectroscopy following the exciton bleach (XB) recovery and the growth of the ground state bleach (GSB) and triplet excited state absorption ($T_1 \rightarrow T_n$) signals of the acceptor, respectively.[3,48] Using CdSe-oligothiophene complexes (Figure 3c) as an example, their TA spectra (Figure 3d) and kinetics show that the decay of the QD XB at 580 nm agrees well with the growth of oligothiophene GSB at 415 nm and $T_1 \rightarrow T_n$ absorption at 715 nm, with no involvement of intermediate states, suggesting direct DET.[3] The intrinsic TET1 rate CdSe-oligothiophene complexes were determined to be 0.077 ± 0.002 ns^{-1} with a maximum TET1 efficiency of 31.8 ± 1.2%.[3] Similarly, we demonstrated direct DET from CdSe QD to the bidentate anthracene diphosphate ligand with a TET1 efficiency close to unity.[59]

When the energy of a CT state is in between those of the triplet excited state of the acceptor and of the QD exciton, as shown in Figure 3b, TET from the QD to acceptor can also proceed through a sequential charge-transfer pathway: a hole/electron transfer followed by an electron/hole transfer.[60−62] Evolution from the CT state, which is a radical pair state, to the triplet excited state has been well studied in molecular donor−acceptor systems, and two mechanisms—radical pair intersystem crossing (RP-ISC) and spin−orbit charge-transfer intersystem crossing (SOCT-ISC)—have been proposed.[63−66] Charge recombination in the CT state also generates the singlet ground state in a spin-allowed process, and the branching ratio of these pathways is the key factor determining the triplet generation yield in the sequential pathway (Figure 3b).[67] The sequential charge-transfer mechanism can be identified by the formation of a CT state intermediate and the delayed generation of mediator triplet state signals accompanied by the decay of the CT state.[62] We demonstrated recently in CdSe QD-boron dipyrromethene (BODIPY) complexes that triplet energy transfer occurs through sequential charge transfer, outcompeting the direct DET pathway.[62,68] Similar indirect triplet state sensitization has also been reported in other QD-molecule complexes, including the CdS-thiol-modified bis(diarylamino)4,4′-biphenyl (TPD) complex,[60] $CsPbBr_3$-tetracene,[61] $CsPbBr_3$-rhodamine B,[69] and CdS-alizarin.[67] The CT intermediate state is a radical pair state, and it is unclear in these QD/mediator complexes whether the spins of the radical pairs are correlated and what controls the branching of the singlet vs triplet product states.

3.2. Competition between Charge and Dexter Energy Transfer

Charge transfer from the QD to mediator may be detrimental to TET1 in some systems, when the CT state decays to form mostly the singlet ground state instead of the triplet excited

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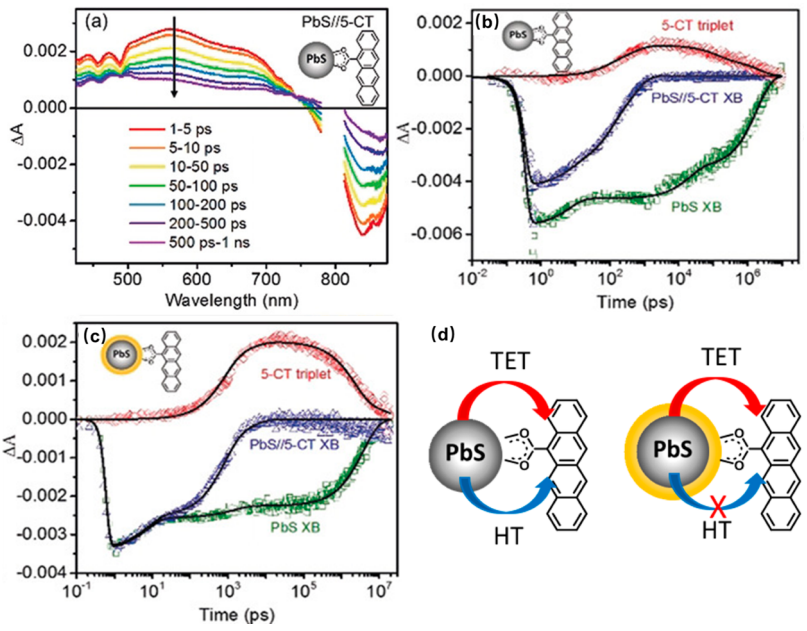

Figure 4. Competition between charge transfer and triplet energy transfer in PbS-5-CT complexes. (a) TA spectra of PbS-5-CT complexes at the indicated delay times after 800 nm excitation. Kinetics of XB of QD-5-CT, pure QDs at 820 nm, and the 5-CT triplet signal at 489 nm for (b) PbS and (c) PbS/CdS. (d) Competition of hole transfer (HT) and TET processes in PbS-5-CT and PbS/CdS-5-CT complexes. Reproduced with permission from ref 1. Copyright 2017 John Wiley and Sons.

state. Such detrimental effects of the CT state are observed in PbS-tetracene complexes.[1,2] As shown in Figure 4a, in PbS-5-CT complexes, after excitation of the PbS QD, the GSB of 5-CT at 475 and 489 nm is formed within 1 ps along with ultrafast loss of the PbS XB signal. These spectral features are attributed to ultrafast fast hole transfer from QD to 5-CT to generate the CT state ($QD^-/5\text{-}CT^+$), because no triplet of 5-CT was observed at this early delay time. Detailed analysis shows that the decay of this CT state population does not agree with the growth of the triplet 5-CT population, suggesting the charge recombination of this CT state leads to the formation of the ground state, with a negligible contribution to the formation of the 5-CT triplet state.[1] As shown in Figure 4b, the kinetics of 5-CT triplet excited state growth agrees well with the consumption of the PbS exciton from 10 ps to 1 ns, suggesting that the 5-CT triplet is formed by direct DET from the PbS exciton to 5-CT. The efficiency of TET1 from PbS to 5-CT is calculated to be 60.3 ± 6.1%.[1] The energetics of the charge-transfer state and the QD band edges suggest that the fast hole transfer is likely from hot hole states. This pathway can be suppressed by the growth of a CdS shell on PbS, which slows down hole transfer to 5-CT (see the energetics of the PbS core and CdS shell relative to 5-CT[1]), removing competition with hot hole relaxation in the QD (Figure 4d). Indeed, transient kinetics of the PbS/CdS-5CT complexes shows the suppression of the initial ultrafast loss of PbS XB (Figure 4c), and the TET1 efficiency is improved to 71.8 ± 6.2%.[1]

When PbS QDs are functionalized with TIPS-pentacene instead of 5-CT, an intermediate in triplet energy transfer is observed. In PbS-TIPS-pentacene complexes, the PbS XB bleach and the delayed formation of the pentacene triplet is bridged in time by an intermediate with nanosecond lifetimes.[39,43] The physical origin of this intermediate has not been concretely assigned and is currently attributed to surface localized states that partially mediate TET.[43,70]

3.3. DET Rate/Efficiency from QDs to Mediators

The rate and efficiency of TET1 from QDs can be tuned through QD or molecular mediator engineering.[2,18,49−51] The intrinsic direct DET rate constant from one QD donor to one adsorbed mediator can be expressed as[53−55]

$$k_{\text{det}}^0 = \frac{2\pi}{\hbar}|V(r)|^2\,\text{FCWD} = \frac{2\pi}{\hbar}|V(0)|^2\,e^{-\beta r}\frac{1}{\sqrt{4\pi\lambda k_B T}}e^{-\left[\frac{(\Delta G+\lambda)^2}{4\lambda k_B T}\right]} \quad (2)$$

Here, $|V(r)|^2$ and $|V(0)|^2$ are the electronic coupling strength between the QD and mediator at distances of r and 0, respectively, β is the exponential decay constant of $|V(r)|^2$ with distance, FCWD is the Franck−Condon overlap weighted density of states, and ΔG and λ are the driving force and reorganization energy for the DET process, respectively.

It is important to note that in QD-acceptor (A) complexes the number of acceptors on QDs (n) follows a Poisson distribution and the DET rate in QD/acceptor complexes with n acceptor molecules is nk_{DET}^0.[71] Thus, to obtain k_{DET}^0 from the experimentally measured kinetics, a model that accounts for the Poisson distribution has been developed and successfully applied.[3,71]

Equation 2 suggests that the intrinsic DET rate in QD-mediator complexes can be tuned by changing the coupling strength, the spectral overlap between the QD emission and mediator triplet absorption, and the driving force. Furthermore, the apparent DET rate is also determined by the number of mediators per QD. To examine the effect of coupling strength on the TET rate, TET from PbS QDs to a series of modified 5-CT mediator molecules with 0−2 phenyl spacers between the carboxylic acid anchoring group and the tetracene conjugated core (Figure 5) was studied. As shown in Figure 5, k^0_{DET} decreases exponentially with the increasing donor−acceptor distance with an exponential decay constant β of 0.32

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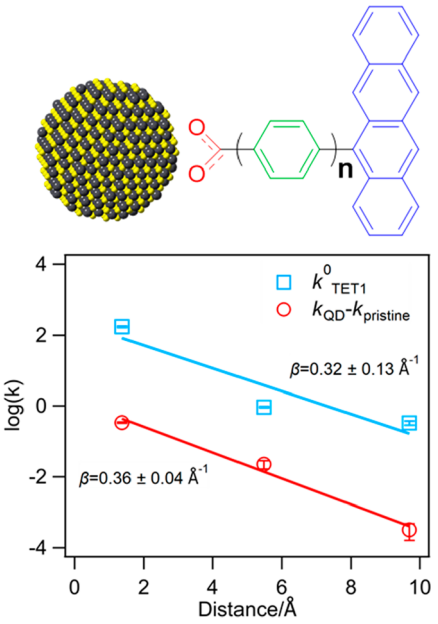

Figure 5. Distance dependence of TET and the mediator triplet lifetime of the PbS-tetracene complexes. (Top) Schematic of PbS-(phenyl)$_n$-5CT complexes with n = 0 (5-CT), 1 (5-CPT), and 2 (5-CPPT) phenyl units between carboxylic acid and tetracene. (Bottom) Logarithm of the intrinsic triplet energy transfer rate constant from the QD to acceptor (k^0_{TET1}, blue □) and QD-induced quenching of the mediator triplet lifetime ($k_{QD} - k_{pristine}$, red ○) as a function of the QD−mediator distance. $k_{QD} - k_{pristine}$ is the difference in the mediator's triplet decay rate constant on QD (k_{QD}) and in solution, which will be discussed in section 4. Reproduced with permission from ref 4. Copyright 2020 American Chemical Society.

± 0.13 Å^{-1}, consistent with the theoretical expectation shown in eq 2. Another study of CdSe-phenyl bridge-anthracene shows a similar trend with β = 0.43 ± 0.07 Å^{-1}.[72] The DET coupling strength in QD-mediator complexes can also be tuned with an inorganic shell on the QD. The coupling strength decreases at larger shell thickness, leading to a decrease in the DET rate/upconversion efficiency. Other factors influencing the coupling strength include the QD surface ligand length, QD size, and molecular geometry of the mediator, as shown in PbS-rubrene,[42] $CsPbBr_3$-pyrene,[50] and CdSe-anthracene,[73] respectively. The driving force for DET from the QD to mediator has been optimized mainly by changing the QD size, with smaller QDs having larger upconversion yields.[18,38] This may suggest that DET from the QD falls in the Marcus normal region (eq 2), with rate increasing at larger driving forces. However, it should be noted that for QDs, tuning its size or shell thickness affects both the driving force and coupling strength, as both are determined by the degree of quantum confinement.[37,74] Varying mediator energy levels by changing the degree of conjugation and electronegativity could also impact the driving force and the DET rate/efficiency.[49,75] For example, triplet energy transfer can vary between tunneling and incoherent hopping mechanisms with appropriate ligand design.[76]

4. REDUCED TRIPLET LIFETIMES OF QD-BOUND MEDIATORS DUE TO THE EXTERNAL HEAVY ATOM EFFECT

Interestingly, for the PbS-mediator complexes of 5-CT, 5-CPT, and 5-CPPT shown in Figure 5, the QD-bound mediator triplet state lifetime shows a similar distance dependence on the DET rate. Typically, the triplet state decays through slow intersystem crossing to the ground singlet state, with lifetimes ranging from 50 to 200 μs for these tetracene mediators in solution. However, when bound on the PbS QD surface, the triplet lifetime is significantly shortened. As shown in Figure 5, compared to the free molecule, the 5-CT triplet lifetime is shortened by nearly 50 times on the QD surface. The effective quenching rate of triplet tetracene by PbS QD, defined as the difference in the triplet decay rates on QDs and in solution ($k_{QD} - k_{pristine}$), shows a similar exponential distance dependence as for the DET rate from the QD to acceptor, with a decay constant, β, of 0.36 ± 0.04 Å^{-1}. This is attributed to enhanced spin−orbit coupling by the heavy Pb ions on the QD surface.[77] This external heavy atom (EHA) effect has been studied in molecular systems and occurs through exchange interaction or charge-transfer interaction between the molecule and the heavy atom.[78−80] It depends on the orbital overlap between the QD and tetracene core, similar to that for DET, thus giving rise to similar distance dependence (Figure 5). The EHA effect is sensitive to the QD surface composition. We showed that PbS QDs prepared with bis(trimethylsilyl)sulfide (referred to as PbS-S) and thiourea (referred to as PbS-T) with similar absorption, emission peak positions and photoluminescence QEs, show different exciton trapping times, presumably due to different surface composition.[2] Indeed, 5-CT molecules adsorbed on these QDs also have different

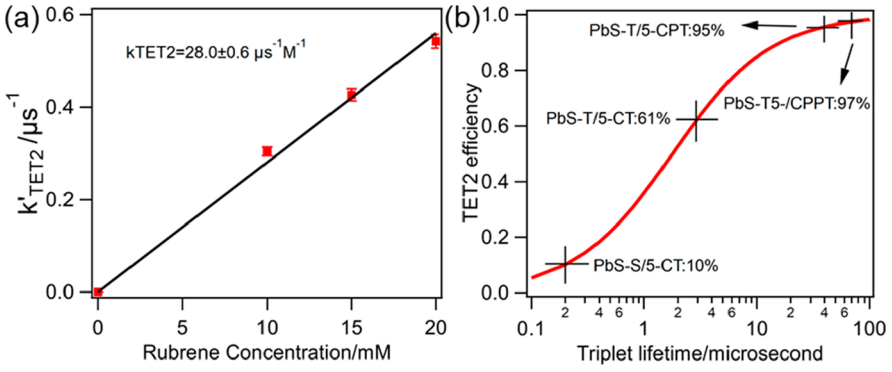

Figure 6. TET2 rate and efficiencies from QD-bound mediators to emitters. (a) Pseudo-first-order TET2 rate constant from PbS-T-bound 5-CT to rubrene as a function of rubrene concentration. (b) Calculated TET2 efficiency between PbS-bound mediators and rubrene (20 mM) for PbS-S-5CT, PbS-T-5-CT, PbS-T-5-CPT, and PbS-T-5-CPPT. Reproduced with permission from ref 4. Copyright 2020 American Chemistry Society.

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triplet state lifetimes (~270 ns on PbS-S and ~2.9 μs on PbS-T). Furthermore, growing a CdS monolayer on the PbS-S QDs increases triplet lifetimes of 5-CT from ~0.27 to ~2.7 μs. Mediator triplet state quenching by QDs can be avoided by extending their distance and utilizing QDs with weaker EHA effects.[81,82] For example, the triplet lifetime of anthracene is not significantly quenched by CdSe (~100 μs).[40] In CdSe-oligothiophene complexes (Figure 3c), the T6 triplet lifetimes in solution and on CdSe QD are similar, indicating negligible EHA effects in the CdSe-T6 complexes.

5. TRIPLET ENERGY TRANSFER FROM ADSORBED MEDIATORS TO EMITTERS

The second triplet energy transfer (TET2) step from QD-bound mediators to emitters also determines the overall QE. Despite its importance, it has only been reported recently for the PbS-T QD-bound 5-CT with rubrene.[4] Because the 5-CT triplet concentration (<10 μM) is much smaller than the total rubrene concentration (10−20 mM), the reaction is pseudo-first-order with a rate constant of $k'_{TET2} = k_{TET2}[\text{rubrene}]$. Under this condition, the decay of the 5-CT triplet state concentration can be written as

$$\frac{d[^3CT]}{dt} = -k_{TET2}[\text{rub}][^3CT] - k_T[^3CT] = -(k_T + k'_{TET2})[^3CT] \quad (3)$$

The PbS-T-bound 5-CT triplet decay rate (k_T) was directly measured by TAS (0.35 ± 0.01 μs^{-1}). As shown in Figure 6a, the 5-CT triplet decay rate constant k'_{TET2} increases linearly with rubrene concentration. The slope is the bimoleuclar triplet energy transfer rate constant k_{TET2} and is determined to be (2.80 ± 0.06) × 10^7 s^{-1} M^{-1}, which is 3 orders of magnitude slower than the estimated diffusion-limited bimolecular rate (~2 × 10^{10} s^{-1} M^{-1}).[4] A similarly slow TET2 rate constant of 8.7 × 10^8 s^{-1} M^{-1} is also reported between [4CzPN-^{3}DBP]* and DBP in solution, in the absence of QDs.[83] These slow TET2 rate constants might be a result of strict geometric requirements of the TET2 process.

The mediator triplet state in these hybrid upconversion assemblies has two decay pathways: transfer to the emitter for photon upconversion or an undesired decay back to the ground state. Using the obtained k_{TET2} rate and mediator triplet lifetime (k_T), the TET2 efficiency with different triplet lifetime is calculated on the basis of

$$\Phi_{TET2} = \frac{k_{TET2}[\text{Rub}]}{k_{TET2}[\text{Rub}] + k_T} \quad (4)$$

The TET2 efficiency increases with the triplet lifetime ($1/k_T$) as shown in Figure 6b. The TET2 efficiency increases quickly from 5% to >80% when the triplet lifetime is extended from 100 ns to 10 μs. Under the assumption that the mediators with the same tetracene core share the same k_{TET2}, the TET2 efficiency of various systems studied is calculated and shown in Figure 6b. The extended triplet lifetime from PbS-S to PbS-T QD is shown to be the dominating factor in the total UCQE difference in upconversion systems using these QD sensitizers.[2] This analysis is applicable to studying general TET2 processes in hybrid QD photosensitized upconversion.

6. FACTORS AFFECTING THE OVERALL UPCONVERSION EFFICIENCY

When comparing the total UCQE of systems with the same emitter but different QD/mediator combinations, eq 1 can be rewritten as $\Phi_{UCQE} = A\Phi_{TET1}\Phi_{TET2}$, where $A = \Phi_{ex}\Phi_{TTA}\Phi_{FL}$ can be considered to be a constant. This equation provides a useful way to examine how the QD/mediator interface can be tuned to optimize UCQE. This idea was demonstrated in a study that compares the UCQE of upconversion systems consisting of 20 mM rubrene and different combinations of QD/mediator: PbS-S/5-CT, PbS-T/5-CT, PbS-T/5-CPT, and PbS-T/5-CPPT. The measured Φ_{UCQE}, measured Φ_{TET1}, and estimated Φ_{TET2} (from Figure 6b) of these systems are compared in Figure 7. By comparing the experimentally

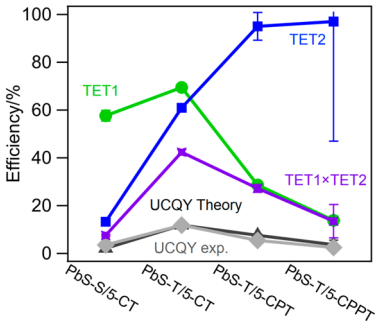

Figure 7. Comparison of measured (gray ♦) and calculated (black ▲) values for upconversion systems with the same emitter (20 mM rubrene) and different QD/mediator combinations as shown. Also compared are Φ_{TET1} (green ●) and Φ_{TET2} (blue ■) measured with TA spectroscopy, which are used to predict the UCQE. The product of Φ_{TET1} and Φ_{TET2} is the purple square. Reproduced with permission from ref 4. Copyright 2020 American Chemistry Society.

measured Φ_{TET1} and Φ_{TET2} of PbS-T/5-CT to the experimentally measured Φ_{UCQE}, A is determined to be 0.28. Using the same A value, Φ_{UCQE} of the three systems can also be calculated from their $\Phi_{TET1}\Phi_{TET2}$ values. As shown in Figure 7, the calculated Φ_{UCQE} values agree well with the measured ones, suggesting that the above model provides a useful way to examine how the QD/mediator interface affects the UCQE. For example, PbS-S/5-CT and PbS-T/5-CT show similar Φ_{TET1} values but different Φ_{TET2} values, giving rise to the higher Φ_{UCQE} in PbS-T/5-CT. As discussed earlier, shorter triplet lifetimes on PbS-S reduce Φ_{TET2}. Increasing the QD−mediator distance has opposing effects on Φ_{TET1} and Φ_{TET2}. Therefore, a distance where $\Phi_{TET1}\Phi_{TET2}$ reaches its maximum value is optimal for achieving the largest Φ_{UCQE}. Since Φ_{TET1} depends more sensitively on distance than does Φ_{TET2}, the optimal distance is achieved with 5-CT.

7. CONCLUSIONS AND OUTLOOK

In this account, we review recent progress in the development of QD-sensitized triplet−triplet annihilation-based photon upconversion systems. The UCQE of these systems has shown impressive improvement from less than 1% to up to ~20% since the first report in 2015.[21] Much of the effort has focused on the rational design of the QD/mediator interface guided by a mechanistic understanding of the rates and efficiencies of the elementary steps. The QD/mediator interface affects the TET1 process from the QD to the mediator, the lifetime of the mediator triplet state, and the

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TET2 process from the mediator to emitter. The rates and efficiencies of these processes can be directly measured by transient spectroscopy to provide important insight into the factors affecting the overall UCQE. The TET1 process can proceed by direct Dexter energy transfer. However, when a CT state with energy in between the QD exciton and the mediator triplet state is present, it can function as an intermediate state to facilitate sequential TET from the QD to the mediator. The bimolecular rate constant of TET2 from the QD-bound 5-CT mediator to the rubrene emitter in solution is shown to be 3 orders of magnitude slower than the diffusion-limited value. Thus, even in the presence of a large emitter concentration, the TET2 efficiency can depend sensitively on the mediator triplet lifetime. Comparing PbS QDs with three mediators at different distances from the surface, the mediator triplet excited state decay can be accelerated by the QD through the EHA effect, which, interestingly, has the same exponential dependence on the distance as the TET1 process. As a result, for these complexes, increasing the QD/mediator distance has opposing effects on the efficiencies of these two TET processes, giving rise to nonintuitive changes in the overall UCQE.

The product of TET1 and TET2 efficiency in the PbS-T/5-CT system has reached nearly 50%. For QDs consisting of lighter atoms that have passivated surface traps, mediators with high binding affinities, and long triplet lifetimes, the combined efficiency could be further improved. However, as discussed in section 6, the total UCQE is limited by the product of other factors with $A = \Phi_{ex}\Phi_{TTA}\Phi_{FL} = 28\%$. Φ_{ex} is close to unity for PbS,[29] and Φ_{FL} is ∼95% for rubrene.[46] Therefore, the TTA process ($\Phi_{TTA} = 30\%$) appears to be the main step that limits the total UCQE. The low Φ_{TTA} of rubrene is not fully understood because theoretically it can be >80%.[30,47] Thus, while better PbS QD/mediator design may improve the value of $\Phi_{TET1}\Phi_{TET2}$ to unity (by 2-fold), a better understanding of the TTA step can potentially improve the total UCQE by 3-fold.

Taking into account both the CdSe and PbS QD upconversion systems, we now have the QEs of the TET1 and TET2 steps near unity. However, many improvements are needed for this QD-sensitized photon upconversion system for practical applications. The TET1 rate per molecule is on the order of 10 ns with mediators closest to the QD (∼2 Å apart) and is thus competitive with the intrinsic QD decay pathways. However, this fast TET1 comes at the expense of energy losses (0.4 eV for PbS QDs and 0.6 eV for CdSe QDs) and is observed only for small QDs with a large band gap.[84] Reducing this energy loss to ∼0.2 eV while maintaining high TET rates, perhaps by promoting Franck−Condon overlap, would increase the upconversion margin.[47] The PbS QD-based system discussed here with a high QE of 12% still requires NIR excitation densities that are at least 2 to 3 times greater than the solar flux. Since this threshold intensity is inversely proportional to the concentration of emitters in their triplet excited state, it can be lowered by a faster TET2 rate that significantly increases the TET2 efficiency, perhaps by promoting orbital overlap between the mediator and emitter, which is currently inhibited by the bulky phenyl groups on rubrene. Moving from rubrene to another emissive emitter which retains the same high fluorescence QY but a higher TTA QE (>30%) would greatly boost the UCQE for NIR to vis conversion. In terms of practical applications in thin film, reabsorption of the upconverted emission by QDs may be mitigated by employing 2D materials that have their transition dipoles for absorbing light aligned with incident NIR photons but orthogonal to out-coupled visible light. In addition, energy cascades directing triplet excitons from QDs to emitter molecules, perhaps via strong coupling between mediators and emitters, or two emitters, may overcome the low TET efficiencies in thin films attributed to the slow diffusion of mediators and emitters. The rational design of this organic−QD interface to optimize and control TET1 and TET2 was enabled by insight from time-resolved spectroscopy. Future improvements to this hybrid system will surely rely on similar interdisciplinary collaborations.

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