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Designing Transmitter Ligands That Mediate Energy Transfer between Semiconductor Nanocrystals and Molecules

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ABSTRACT: Molecular control of energy transfer is an attractive proposition because it allows chemists to synthetically tweak various kinetic and thermodynamic factors. In this Perspective, we examine energy transfer between semiconductor nanocrystals (NCs) and π -conjugated molecules, focusing on the transmitter ligand at the organic–inorganic interface. Efficient transfer of triplet excitons across this interface allows photons to be directed for effective use of the entire solar spectrum. For example, a photon upconversion system composed of semiconductor NCs as sensitizers, bound organic ligands as transmitters, and molecular annihilators has the advantage of large, tunable absorption cross sections across the visible and near-infrared wavelengths. This may allow the near-infrared photons to be harnessed for photovoltaics and photocatalysis. Here we summarize the progress in this recently reported hybrid upconversion platform and point out the challenges. Since triplet energy transfer (TET) from NC donors to molecular transmitters is one of the bottlenecks, emphasis is on the design of transmitters in terms of molecular energetics, photo-physics, binding affinity, stability, and energy offsets with respect to the NC donor. Increasing the efficiency of TET in this hybrid platform will increase both the up- and down-conversion quantum yields, potentially exceeding the Shockley–Queisser limit for photovoltaics and photocatalysis.

1. INTRODUCTION

In hybrid material systems, the goal is to retain the desirable properties associated with the original components while creating synergies between various elements for added value. For the purpose of this Perspective, a hybrid material comprises of semiconductor nanocrystals and organic semiconductors, i.e., conjugated small molecules or polymers. The key idea is to retain the mechanical strength and electronic properties of the inorganic portion and the processability and ease of functionalization of the organic constituents while directing energy at nanoscale dimensions by control of multiexcitonic processes. Hybrid materials can overcome the traditional limits associated with the individual building blocks, as seen in applications in optics,¹ electronics,² biosensors,³ and photovoltaics.⁴ For example, dye-sensitized solar cells (DSSCs)⁵ combine a stable titania photoanode that has excellent transport properties with synthetically tunable organometallic complexes. This combination addresses the relatively low electron mobility in molecular systems and the transparency of titania to visible light. Compared to titania, the high extinction coefficients of

the organometallic dyes in the visible and near-infrared (NIR) allow much more of the solar spectrum to be collected for a power conversion efficiency of up to 15%.⁶

In this Perspective, we discuss a hybrid platform consisting of semiconductor nanocrystals (NCs) and organic molecules for photon upconversion that can potentially improve the efficiencies of photovoltaics and photocatalysts under one-sun conditions. Photon upconversion occurs when low-energy photons are converted to high-energy photons. Like DSSCs, this hybrid platform makes use of the unique properties of each component. It exploits (1) the large absorption coefficients of the NCs,⁷ (2) their ability to extend into the NIR,^{8–10} and (3) triplet–triplet annihilation (TTA) in organics for photon upconversion.¹¹ These characteristics are unavailable simultaneously in existing lanthanide-based¹² and molecule-based¹¹ photon upconversion systems. Lanthanide-doped matrices, or rare-earth glasses, have been studied for decades but are generally excited with pulsed or high-power lasers because of their low photon upconversion efficiencies. The best reported quantum yields (QYs) are 3–12% in the bulk^{13,14} and 5% and 7.6%¹⁵ at the nanoscale. Typical QYs are between 10^{-2} to 10^{-4} % for nanosized lanthanide doped NCs.¹⁶ This low efficiency stems from the extremely small absorption cross section ($\sim 10^{-20}$ cm²)¹⁷ of the single absorbing ions (typically Yb³⁺) dispersed in the glassy matrix and the parity-forbidden nature of these 4f–4f transitions.¹⁸ Despite efforts in the field of organic photovoltaics to design conjugated polymers that harvest infrared photons,¹⁹ it remains difficult to find organic structures that absorb strongly at wavelengths to the red of 900 nm. In addition to lower photostability, organic chromophores that absorb strongly in the NIR undergo rapid internal conversion to the ground state.²⁰

The hybrid TTA-based upconversion system discussed here is able to utilize both visible and NIR photons. As shown in Figure 1a, d, it is composed of inorganic semiconductor NCs as sensitizers (CdSe NCs in Figure 1a and PbS/PbSe NCs in Figure 1d), bound organic ligands on NCs as transmitters (9-anthracenecarboxylic acid (9-ACA) in Figure 1a and 4-(tetracen-5-yl)benzoic acid (CPT) in Figure 1d), and organic annihilators (9,10-diphenylanthracene (DPA) in Figure 1a and rubrene in Figure 1d) in solution. As the light absorbers, these photostable semiconductor NCs have size- and shape-dependent optical properties that are easily controlled via colloidal synthesis. Here, the NCs absorb the low-energy photons that are then transferred as triplets to the transmitter ligand covalently bound to the NC surface. Triplet energy transfer (TET) then occurs again down an energy cascade, this time

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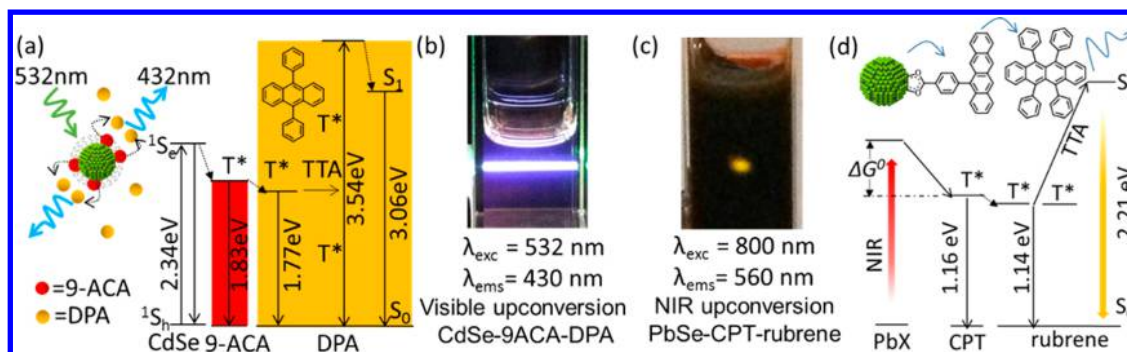


Figure 1. (a) Schematic illustration of the energy transfer for CdSe/9-ACA/DPA-based photon upconversion of green to violet light. The green arrow indicates the photoexcitation of sensitizer CdSe nanocrystals (NCs, green ball). Energy is transferred to the transmitter, i.e., the bound 9-ACA ligands (red balls) and then to the annihilator DPA (yellow balls), followed by the annihilation between two triplet DPA molecules and subsequent emission from the singlet state of DPA (blue arrows). The same process for the upconversion of near-infrared (NIR) light is shown in (d), with PbX (X = S, Se), CPT, and rubrene as the sensitizer, transmitter, and annihilator, respectively. (b) Photograph of visible upconversion in a cuvette containing CdSe/9-ACA/DPA, with excitation by a cw 532 nm green laser and 430 nm violet emission. (c) Photograph of NIR upconversion in a cuvette containing PbSe/rubrene. The sample is excited with a cw 800 nm laser, and the yellow emission at 560 nm can be seen. (a–c) Reproduced from ref 25. Copyright 2015 American Chemical Society. (d) Reproduced with permission from ref 32. Copyright 2016 Royal Society of Chemistry.

from the transmitter to the annihilator. Two annihilator molecules in their triplet excited states collide in a spin-allowed, energy-conserved manner known as TTA to emit a higher-energy photon. Figure 1b, c shows the upconverted photons that are emitted upon excitation by visible and NIR light, respectively.

In this Perspective, we summarize the current results in the subfield of triplet energy transfer specifically across this hybrid nanocrystal–molecule interface. We then examine the factors limiting the upconversion QYs, followed by strategies to improve the QY by improving TET. In particular, we focus on the molecular design of the transmitter ligands, including molecular energetics, photophysics, energy offsets relative to the NC donor, and groups binding to the NC donors, and finally conclude with suggestions for alternatives to the acene family.

2. CURRENT STATUS AND CHALLENGES

The first observations of triplet energy transfer between nanocrystals and molecules were reported in two joint publications in 2014. It was demonstrated that conjugated molecules in the form of linear fused acenes donated triplet excitons to lead chalcogenide NCs. These triplet excitons were created when a singlet excited state in the acene created by the absorption of light split or fissioned into two bound electron–hole pairs with unpaired spins. Singlet fission can be considered as downconversion of photons because the original high-energy singlet state is split into two triplet excitons.^{21,22} Baldo, Bawendi, and co-workers reported enhanced photoluminescence (PL) of PbS NCs due to the downconversion of singlets formed in tetracene and subsequent TET to PbS acceptors.²³ Using transient absorption spectroscopy, Rao and co-workers showed that triplets derived from singlet fission migrated from pentacene to PbSe NCs, followed by backward hole and then electron transfer from the NCs to the acene.²⁴ These studies hinted at the possibility of the reverse processes involving triplet energy transfer from NCs to molecules. After our first report of transfer of triplet excitons from inorganic semiconductor NCs to organic molecules,²⁵ Wu et al.²⁶ reported the same physical phenomenon. We employed CdSe and PbS/PbSe NCs as sensitizers of conjugated molecules, or triplet donors, to acenes for photon upconversion.²⁵ Wu et al.

described the emission of yellow light by rubrene, created when triplets donated from PbS NCs annihilated each other to create a singlet exciton. They showed the photon upconversion of NIR light absorbed by PbS NCs in thin films. In terms of mechanistic studies, Mongin et al.²⁷ observed the formation of triplet excitons on anthracene ligands bound to CdSe NCs that occurred after the NCs were photoexcited. These transient absorption experiments directly showed triplet energy transfer from inorganic NCs to bound organic ligands.

Analysis of the kinetics of the energy transfer from CdSe NCs to 9-ACA suggests that the overall efficiency is limited by the fast nonradiative decay channels in NCs and the low coverage of 9-ACA ligands.²⁸ In line with this, CdSe–ZnS core–shell NCs as sensitizers have been reported to enhance the upconversion QYs by a factor of 50 (to 1.4%) compared with core-only CdSe NCs,²⁹ as the trap states for nonradiative recombination on the CdSe core are passivated by the ZnS shell. Similarly, CdS–ZnS and PbS–CdS core–shell NCs were essential in achieving photon upconversion QYs of 5.2% and 8.4% for the production of UV and visible light, respectively.³⁰ With NC light absorbers, visible-to-UV upconversion is 5 times more efficient than with organic sensitizers,^{30–32} while a relatively high NIR-to-visible upconversion QY of 8.4% was realized with an excitation intensity of 3.2 mW/cm², approximately 3 times lower than the available solar flux.³³ We have also found that CdSe NCs with higher PL QYs result in higher upconversion QYs because of reduced midgap and surface trap states.³⁴ For example, for CdSe NCs of the same size, NC donors with PL QYs of 8.9% and 3.5% have photon upconversion QYs of 4.4% and 1.4%, respectively.³⁴

In contrast to triplet energy transfer from pentacene to PbSe NCs, triplet exciton migration in the opposite direction, i.e., from NCs to acenes, does not show the same dependence on the energy offset between the donor and acceptor. The Cambridge group reported that resonant energy transfer occurs from the acene to the NC, where the highest rate of TET occurs when the band gaps of the PbSe NCs are resonant with the T₁ state of pentacene (0.86 eV).²⁴ However, in our hands, smaller NCs gave higher upconversion QYs because of the larger driving force for TET (ΔG^0 in Figure 1d). The same trend was observed in two different NC–acene combinations, i.e., PbX (X = S, Se)-sensitized NIR upconversion³⁵ and CdSe-

sensitized conversion of green to violet light.³⁴ This discrepancy may be due to the higher density of states in the NCs that can accept triplets from acenes, compared with the reverse process where the T_1 acceptor state on the acene is a discrete state that can accept only one exciton. More work has to be done to increase our understanding of the fundamental aspects of TET across this hybrid interface.

A transmitter ligand can greatly enhance photon upconversion QYs in this hybrid platform by creating an energy cascade between the sensitizer and annihilator and facilitating the orbital overlap required for efficient Dexter transfer. For example, we have shown that the use of 9-ACA as a transmitter enhances CdSe-sensitized photon upconversion by 3 orders of magnitude²⁵ and that the tetracene derivative CPT enhances photon upconversion QY by factors of 81 and 11 for PbS and PbSe NCs, respectively.³⁶ The upconversion QYs were found to be exponentially dependent on the distance between the NC and the transmitter when this distance was varied as a function of the number of *p*-phenylene units bridging the CdSe donor and anthracene acceptor. Thus, the anthracene transmitter with the shortest bridge had the highest upconversion QY reported to date for the conversion of green to violet light for this hybrid platform (14.3%).³⁷

In order to improve the upconversion QY, Φ_{UC} , the efficiency of each elementary step in Figure 2 should be

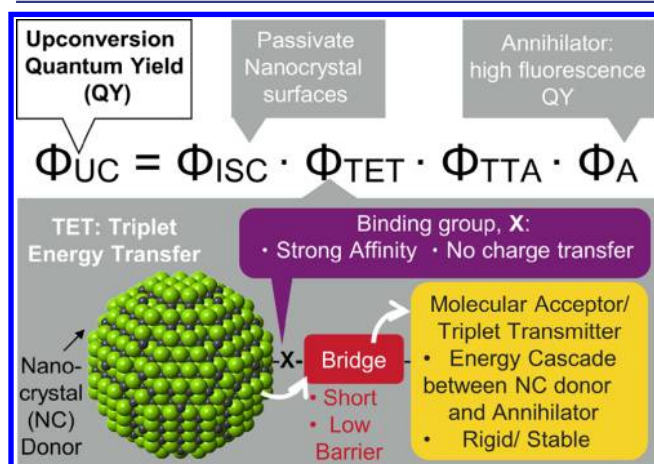


Figure 2. Upconversion QY, Φ_{UC} , is a convolution of four factors: (1) the efficiency of intersystem crossing (ISC) within the NC, Φ_{ISC} ; (2) the efficiency of triplet energy transfer (TET) from the NC to the transmitter, Φ_{TET} ; (3) the efficiency of triplet–triplet annihilation (TTA) between two annihilators, Φ_{TTA} ; and (4) the fluorescence quantum yield of the annihilators, Φ_A . Strategies to enhance Φ_{TET} from NC donors to molecular acceptors by synthetic control of the binding group, X, the bridge between the donor and acceptor, and the functionalized conjugated core of the transmitter are discussed in this Perspective.

considered: (1) Φ_{ISC} , the efficiency of intersystem crossing (ISC) within the NC; (2) Φ_{TET} , the efficiency of TET from the NC to the transmitter, (3) Φ_{TTA} , the efficiency of TTA between two annihilators, and finally (4) Φ_A , the fluorescence quantum yield of the annihilators. The efficiency of TET from transmitters to annihilators is not a factor in solution because it is close to unity when the concentration of the annihilator is high, as shown by Schmidt and Castellano.³⁸ For example, for transmitters with triplet lifetimes exceeding 10 μ s, an annihilator concentration of 10 mM leads to a near-unity efficiency for TET from transmitters to annihilators.³⁹ As

discussed above, first trap states on the NC need to be passivated in order to maximize Φ_{ISC} . Second, Φ_{TTA} can be increased if the higher-order excited states of the annihilators are energetically inaccessible at room temperature. Standard spin statistics predict an efficiency of 1/9 for TTA, but usually the efficiency of TTA is higher because the high-energy quintet states are not accessible. Φ_{TTA} is 0.52 for DPA^{40,41} and 0.33 for rubrene.⁴² Third, molecules with high PL QYs meet the requirements for sensitizers, such as the PL QYs of 0.90 for DPA^{43,44} and 0.98 for rubrene.⁴⁵ Therefore, Φ_{TET} is the bottleneck currently limiting the upconversion QY, since the other factors in the equation shown in Figure 2 more or less stem from the intrinsic properties of the NCs and annihilators. To maximize Φ_{TET} , we can synthetically tune the properties of the transmitter to control the rate of TET from the NC to the transmitter in terms of the binding group, the bridge, and the transmitter core, as shown in Figure 2. This is discussed in section 3.

3. MOLECULAR DESIGN OF TRANSMITTERS

a. Molecular Energetics: Balancing the Trade-off between Upconversion QY and Energy Conservation.

To date, triplet energy transfer from a semiconductor NC to a transmitter has been adequately modeled by the Dexter mechanism. It can be explained by Marcus theory.⁴⁶ In eq 1, the rate of TET, W_{ij} , is related to the energy offset between the triplet states of the NC donor and molecular transmitter, ΔG^0 (Figure 1d), the reorganization energy, λ , and the electronic coupling between the NC and the transmitter, J_{ij} .

$$W_{ij} = \frac{|J_{ij}|^2}{h} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left[-\frac{\lambda}{4k_B T} \left(1 + \frac{\Delta G^0}{\lambda}\right)^2\right] \quad (1)$$

With increasing ΔG^0 , W_{ij} increases to a maximum in the Marcus normal region and then decreases in the Marcus inverted region. For TET from an NC to a bound transmitter, ΔG^0 can be tuned by varying the size of the NC, and experimentally, higher upconversion QYs are obtained from smaller NCs.^{34,35} This suggests that TET is in the Marcus normal region. Along these lines, within the Marcus normal region, the triplet energy levels of the transmitter should be lower than the dark excitonic state of the NC, thus providing a driving force for higher Φ_{TET} . The energy levels of the molecular transmitter used in photon upconversion can be tuned by varying the degree of conjugation^{47,48} and the position and number of electron-donating and -withdrawing functional groups.^{47,49,50}

There is a trade-off between the conservation of energy and the upconversion QY. A low-lying T_1 state in the transmitter leads to a high Φ_{TET} , but this energy offset means that not all of the energy in the photons absorbed by the NC is utilized. Similarly, in DSSCs the energy levels of the dye molecule relative to the TiO_2 conduction band are crucial for high performance.⁵¹ An efficient dye molecule should have molecular excited states with potentials sufficiently low for dye regeneration³⁹ and sufficiently high for electron injection into the conduction band of titania.⁴⁷ However, the increased band gap leads to a lower spectral coverage. The trade-off between open-circuit voltage and short-circuit current in DSSCs parallels the trade-off between photon upconversion QY and efficiency in this hybrid upconversion platform.

To minimize energy loss during upconversion, the triplet energy of the annihilator should be close to that of the

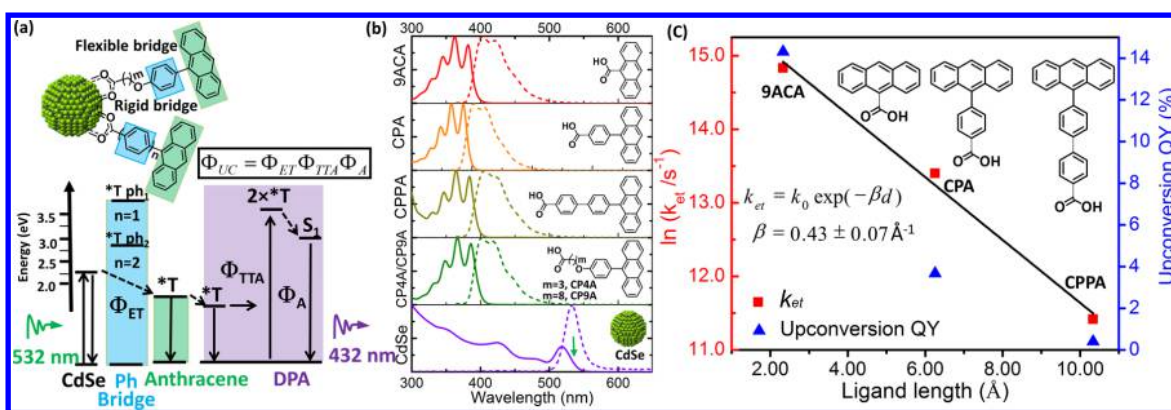


Figure 3. (a) Schematic of the energy transfer in the CdSe–anthracene hybrid photon upconversion platform. The energy diagram depicts the triplet exciton states of the CdSe NC donor, the *p*-phenylene bridges with $n = 1$ and 2 , and the anthracene acceptor, which also serves as the transmitter ligand. (b) Absorption spectra (solid lines) and fluorescence spectra (dashed lines) for different transmitters and CdSe NCs. (c) Plots of the rate of triplet energy transfer (k_{et} , red squares) and the maximum upconversion QY (blue triangles) vs the length of the phenylene bridge in the covalently bound anthracene transmitter ligands on CdSe nanocrystals. Reproduced from ref 33. Copyright 2016 American Chemical Society.

transmitter and the energy of the S_1 state of the annihilator should be lower than but close to twice the T_1 energy for energy conservation. For example, pentacene cannot be used as an upconversion annihilator because the energy of 2.15 eV for the S_1 state⁵² is more than twice the energy of 0.86 eV for the T_1 state,⁵³ and thus, three pentacene triplets would be required for TTA to be observed.

b. Bulky or Rigid Transmitters with High Fluorescence QYs. The addition of phenyl or other rigid side groups to the conjugated core of the transmitter is proposed to enhance triplet energy transfer by decreasing vibrational relaxation. A good transmitter should have minimal pathways for excited electronic states to decay by vibrational relaxation. This is usually reflected in a high fluorescence QY. The idea is to minimize access to nonradiative decay pathways in TET from the NC to the transmitter and then to the annihilators, thus increasing the upconversion QY. Bulky groups should also prevent excimer formation or triplet exciton quenching/TTA between two neighboring transmitters bound to the surface of the NC. We have seen that the upconversion QY increases and then decreases with the surface density of transmitter ligands.^{36,37} The initial increase is associated with the increasing number of transmitter ligands, which facilitates energy transfer, while the drop is linked to excimer formation or intermolecular TTA, both of which can be avoided by installing rigid, bulky transmitter ligands. Finally, by group theory arguments, molecular symmetry is directly related to the number of allowed vibrational modes that can couple to electronic states,⁵⁴ and thus, transmitters with higher symmetry may minimize coupling to vibrational states and increase the overall TET efficiency.

c. Decreasing the Tunneling Barrier during TET. The upconversion QY is exponentially dependent on the distance between the NC donor and the transmitter. Li et al.³⁷ used oligo(*p*-phenylene) bridges to covalently link anthracene acceptors to CdSe NCs. As shown in Figure 3a, TET from the CdSe NC to the anthracene ligand is based on a mechanism involving tunneling through the phenylene bridge. By variation of the length of this rigid phenylene spacer (Figure 3b), the rate of TET from the CdSe NC to the anthracene core was found to be exponentially dependent on the length of the bridge, as described by the Dexter equation (shown in Figure 3c). Though the rates of triplet energy transfer showed this

exponential dependence, the photon upconversion QYs did not show the same trend. This is due to the different numbers of bound transmitters. The upconversion QYs were lower than expected for the transmitters with the phenyl bridges, CPA and CPPA, because these transmitters were less soluble than 9-ACA and fewer transmitters were bound to the CdSe donor surface, resulting in a lower overall rate of triplet energy transfer to the DPA annihilator. Therefore, because the Dexter transfer should be optimized, a good transmitter should be designed to have a short distance between the transmitter core and the NC. Dexter-type transfer is a short-range interaction based on the wave function overlap between the donor and acceptor, usually occurring within 1 nm,^{37,55} parametrized by the damping coefficient, β , which describes the extent of coupling of the donor and acceptor through the barrier material. A higher β value means weaker coupling, which leads to a lower rate of energy transfer. The β value is dependent on the energy offset between the energy donor and acceptor as well as the tunneling barrier and the length of the bridging units.⁵⁶ The β value for the rigid, aromatic phenyl groups is 0.43 \AA^{-1} for Dexter energy transfer for the thermodynamically downhill (0.5 eV) TET between the CdSe donor and anthracene acceptor in Figure 3.³⁷ Interestingly, this attenuation factor is very close to the β value obtained for dinuclear heterometallic complexes with poly(*p*-phenylene) spacers. De Cola and co-workers⁵⁷ reported $\beta = 0.50 \text{ \AA}^{-1}$ for triplet transfer from Ru(bipyridine)₃²⁺ to Os(bipyridine)₃²⁺ for $\Delta G = -0.37 \text{ eV}$, and Barigelletti et al.⁵⁸ reported $\beta = 0.33 \text{ \AA}^{-1}$ for a structurally related Ru(II)/Os(II) complex. Acetylene, alkene, thiophene, *p*-phenylene ethynylene, and *p*-phenylenevinylene bridges present lower tunneling barriers than the *p*-phenylene bridges explored in Figure 3 and may result in lower β values.

The length of the bridge and its tunneling barrier are anticipated to dictate the pathway for Dexter energy transfer. Skourtis, Beratan, and co-workers⁵⁹ predicted that in the presence of long bridges that have energy levels resonant with a donor and acceptor, triplet energy transfer can occur via a bridge excitonic state that accommodates both the hole and electron simultaneously (Figure 4a). Mechanistically, this is a departure from the Closs–McConnell model,⁶⁰ where TET consists of two individual charge transfer events, with either the hole or the electron sequentially traversing virtual excitonic states in the bridge (Figure 4b). It should be noted that

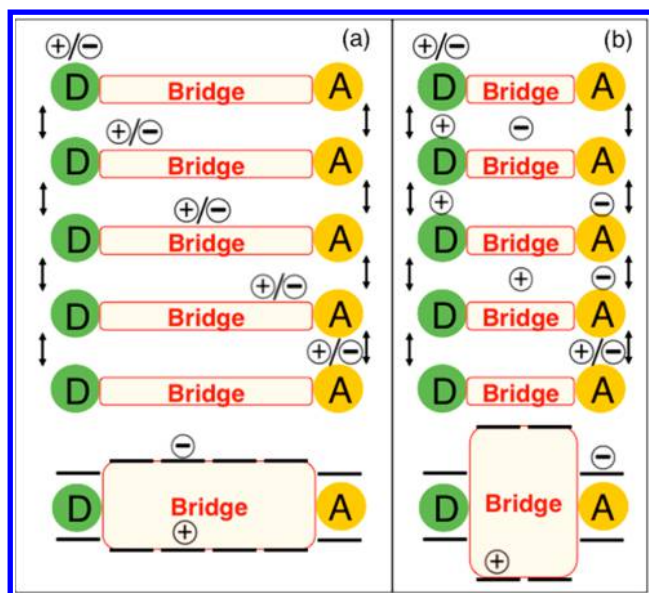


Figure 4. Dexter energy transfer across the bridge between the donor (D) and acceptor (A) can occur via two different pathways. (a) For long bridges or bridges with energy levels that may be resonant with the donor or acceptor, the triplet exciton moves across the bridge as an unseparated hole and electron.⁵² (b) In the Closs model, the triplet energy transfer consists of individual charge transfer events, typically through short bridges with high tunneling barriers.⁵³

evidence for the Closs model mainly arises from aliphatic bridges with high tunneling barriers. It will be exciting to find experimental evidence of holes and electrons arising from triplets concurrently within the bridging aromatic ligands.

d. Increasing the Binding Affinity of Transmitters to NCs. The binding affinity of the transmitter ligand for the NC surface is an important consideration because at low ligand loadings Φ_{TET} is proportional to the number of bound transmitters per NC. The upconversion QY decreases if the NC–transmitter complexes are cleaned more than once or if good solvents for the transmitter ligands are used to dissolve the isolated hybrid complex.³⁴ This is the case because the transmitter ligands can detach from the surface of the NCs when exposed to good solvents. The higher the binding affinity of the transmitter ligand (i.e., the semiconductor NC–transmitter bond strength), the more stable is the NC–transmitter complex and the more easily the native ligands can be displaced. Generally, commonly used organic ligands on NCs can be classified as neutral L-type ligands that can datively bind to NCs (i.e., amines, pyridines, and phosphine oxides) and anionic X-type ligands that covalently bind to NCs (e.g., carboxylates, thiolates, and phosphonates). While carboxylic acids, thiols, and phosphonic acids can be introduced as neutral molecules dissolved in organic solvent during ligand exchange, it is thought that these ligands bind as X-type ligands in their deprotonated form.⁶¹ Different functional groups present different binding affinities for NC surfaces. Several studies^{62–64}

have measured the binding constants of ligands to CdSe NCs by NMR or NC PL quenching methods. However, these equilibrium constants are not comparable because these values are dependent on the solvent, concentration, native ligands, etc. Various computational methods^{65,66} have been used to calculate the binding energies of a series of ligands to NCs. Generally, for CdSe NCs, the anionic X-type ligands bind more strongly than neutral ligands, while L-type ligands bind weakly

and reversibly because of the weaker dative bond to the NC surface. The relative binding affinity can also be indicated by the ease of displacement of one ligand compared with another. In ligand exchange reactions, carboxylic acid ligands can be displaced by thiols and phosphonic acids, but the reverse process is not efficient.^{67,68} Thiols can easily displace amines, trioctylphosphine oxide (TOPO), and trioctylphosphine (TOP) from NCs.⁶⁹ Pyridine binds weakly and can be easily displaced by aliphatic amines.

Instead of weakly bound monodentate ligands, multidentate ligands can be used to strengthen the bonding to NCs. For example, in biological applications of thiol-capped CdSe–ZnS core–shell NCs, monodentate thiols bound on the ZnS shell are stable for a week.⁷⁰ The use of bidentate thiol-based ligands enhances the shelf lives of functionalized NCs from a few days to a year.^{71,72} In a series of bidentate anthracene transmitters with pyridine binding groups, only one of the three isomers gave a high photon upconversion QY exceeding 12% when paired with a CdSe NC sensitizer. The lower upconversion QYs of the other two isomers (8% and 2.5%) show that transmitter ligands can be designed to bind in a complementary “lock and key” manner to NC surfaces. The bidentate binding geometry here increases the orbital overlap and the efficiency of energy transfer.⁷³

It is well-known that the electro-optic properties of II–VI and III–V semiconductors are very sensitive to chemical perturbations of their surfaces.⁷⁴ In other words, energy transfer from NCs to transmitters may compete with charge transfer. Both result in the enhancement or quenching of NC PL, and time-resolved transient absorption or PL experiments are indispensable in identifying the loss mechanisms. For example, ligands that are initially added may bind preferentially to dangling bonds,⁷⁵ thus enhancing the PL of NCs at low loadings. Kalyuzhny and Murray⁷⁵ found that thiols quenched CdSe NCs, while hexadecylamine, pyridine, TOP, and TOPO enhanced the PL of CdSe NCs. Similarly, previous work indicated that thiol^{63,76} and dithiocarbamate⁷⁷ ligands serve as hole-trapping agents for CdSe NCs, as they quench the PL of NCs dramatically. However, thiol ligands enhance the PL of CdTe NCs because of the higher energy of the CdTe valence band.⁷⁶ Aliphatic amines are observed to enhance the PL of NCs, with primary amines enhancing the PL more than secondary and tertiary amines,⁶³ while aromatic amines quench NC PL by photoinduced hole transfer.⁷⁸ In a study of resonance energy transfer from CdS NCs to bound boron dipyrromethene (BODIPY) dye molecules,⁷⁹ both charge transfer and energy transfer were observed for the amino-functionalized BODIPY. The specific location of the binding group on the conjugated core of the transmitter ligand affects the photon upconversion QY, as 1-, 2-, and 9-carboxylic acid- or -dithiocarbamate-functionalized anthracene isomers lead to different rates of TET from CdSe NCs to bound anthracene ligands. This is the case because the isomeric substitutions either alter the relative energies of the higher-order excitonic states in anthracene or vary the orbital overlap between CdSe and anthracene, thus critically affecting the Dexter-based transfer.⁸⁰

In the same way, in DSSCs the anchoring group has a pronounced effect on the optical properties and energy levels of the dye molecules. For example, electron-withdrawing cyanoacrylic acid and carboxylic acid anchoring groups stabilize the complexes.⁸¹ In addition, polar functional groups may affect the band structure of the inorganic photoanode. For example,

some acidic anchoring groups can protonate the TiO₂ surface, which leads to an accumulation of positive charge and a lowering of the TiO₂ conduction bands.⁸¹ Though the phosphonic acid group can bind on oxides more strongly, the rate of charge transfer is low compared with that for the carboxylic anchor because of the tetrahedral geometry of the phosphorus center.⁸²

To sum up, anchoring groups that can strongly bind to NCs while preserving their photoinduced excitonic states are preferred, such as the carboxylic acid or phosphonic acid groups. Binding groups that result in intramolecular charge transfer or interfacial charge transfer between NCs should be avoided, e.g., thiols are undesirable even though they bind strongly to chalcogenide NCs. Multidentate transmitters are an unexplored class of ligands that should display higher binding affinities and more well-defined donor–acceptor geometries, which will shed light on the factors affecting TET at this organic–inorganic interface.

e. Stability of the Transmitter. The stability of the transmitter is important in TET. Currently, acene transmitters functionalized with anchoring groups are used.^{25,29,34,36,37} As triplet transmitters, acenes have low-lying triplet states⁸³ and long triplet lifetimes²⁸ to allow energy to be efficiently transferred to the annihilator. It is well-known that linear acenes with five or more fused rings, e.g., pentacene and hexacene, are unstable because of Diels–Alder reactions with ambient oxygen.⁸⁴ However, slightly electron-withdrawing alkynyl substitutions⁸⁵ stabilize the electron density in these linear fused acenes, making substituted hexacenes and higher-order analogues isolable. Therefore, as transmitter ligands, substituted linear acenes are superior to their parent molecules in terms of stability and solubility.

Other stable, nonlinear polycyclic aromatic hydrocarbons such as pyrene⁸⁶ and perylene⁸⁷ may also be used as transmitters, while nitrogen-containing chromophores such as perylenediimides or the BODIPY class of molecules are possible alternatives. Some of these molecules have been used in molecular TTA upconversion as sensitizers or annihilators.⁸⁸

4. CONCLUSION

This Perspective has described a novel hybrid photon upconversion platform that uses semiconductor NCs as sensitizers and acenes as the transmitters and the annihilators. The focus has been on enhancing the electronic communication between the NC donors and the molecular acceptor/transmitter ligands, or increasing the efficiency of triplet energy transfer across this hybrid interface. Currently, the upconversion QYs are factors of 3–4 below the limit imposed by the finite value of Φ_{TTA} . As we have discussed, transmitter ligands can be designed to minimize vibrational losses and maximize both the driving force for TET and orbital overlap with the NC donor, for example by tuning the functional groups and side chains on the conjugated core. Other improvements in the upconversion QYs could arise from alternative nanocrystal sensitizers or annihilators. Some of the principles discussed here can be applied to molecular engineering of efficient singlet fission or photon downconversion. As can be seen, more work is needed to establish the fundamental structure–property relationships governing energy transfer between semiconductor nanocrystals and organic semiconductors. Ultimately, this understanding will allow sunlight to be utilized efficiently in photocatalysis and photovoltaics.

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Notes

The authors declare no competing financial interest.

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