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Thiol-Anchored TIPS-Tetracene Ligands with Quantitative Triplet Energy Transfer to PbS Quantum Dots and Improved Thermal Stability

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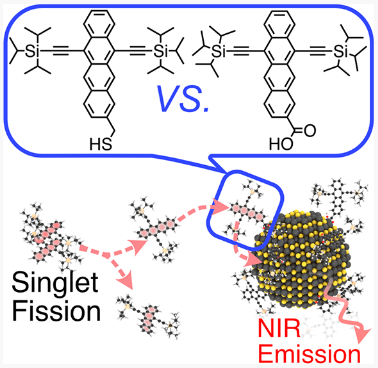
ABSTRACT: Triplet energy transfer between inorganic quantum dots (QDs) and organic materials plays a fundamental role in many optoelectronic applications based on these nanocomposites. Attaching organic molecules to the QD as transmitter ligands has been shown to facilitate transfer both to and from QDs. Here we show that the often disregarded thiol anchoring group can achieve quantitative triplet energy transfer yields in a PbS QD system with 6,11-bis[(triisopropylsilyl)ethynyl]tetracene-2-methylthiol (TET-SH) ligands. We demonstrate efficient triplet transfer in a singlet fission-based photon multiplication system with 5,12-bis[(triisopropylsilyl)ethynyl]tetracene generating triplets in solution that transfer to the PbS QDs via the thiol ligand TET-SH. Importantly, we demonstrate the increased thermal stability of the PbS/TET-SH system, compared to the traditional carboxylic acid counterpart, allowing for higher photoluminescence quantum yields.



Quantum dot−organic nanocomposites are optoelectronic materials with both organic semiconductor molecules and quantum dots (QDs) as counterparts. Ideally, these nanocomposites are able to harness the advantage of both classes of materials to tailor the material's properties for specific applications.[1] With almost unlimited possible combinations of materials, many fields have come to exploit these types of nanocomposites, including photocatalysis,[2,3] bioimaging and sensing,[4] solar energy harvesting and photon upconversion,[5,6] light-emitting diodes,[5] and, recently, singlet fission-based photon multiplication.[7−9] The choice of the organic and inorganic counterparts will depend on the desired use of the nanocomposite; i.e., charge transfer, energy transfer, or photon emission will require different QD−organic combinations.

Because organic molecules have relatively large singlet−triplet splitting and small spin−orbit coupling, the interconversion between singlets and triplet states is inefficient. In QDs, on the other hand, spin−orbit coupling is large and spin states can be separated by <10 meV.[1,10,11] QDs can therefore act as "spin mixers" in QD−organic nanocomposites.[12] These "spin-mixing" materials have attracted significant attention as triplet sensitizers for photon upconversion applications and, recently, as "triplet" emitters in singlet fission-based photon multiplication. In such systems, an organic molecule is attached to the QD as a ligand and serves either to transfer triplet energy into or to receive it from the QD. The choice of ligand is crucial in such QD−ligand systems and must fulfill two main requirements. First, triplet energy transfer from or to the QD must be efficient. Second, the ligand must be stably bound on the QD; otherwise, the composite system will fall apart in time.

Singlet fission is a spin- and energy-conserving exciton multiplication process in organic semiconductors that splits a singlet excited state into two triplet excited states.[7,13] As an exciton multiplication process, it has been proposed as a means to overcome thermalization losses in photovoltaic (PV) devices and surpass the Shockley−Queisser limit.[7,13] There are two main approaches to integrating singlet fission materials with PVs: either direct integration, where the singlet fission material transfers the electrons or excitons directly to the PV material,[14−16] or a photon multiplication integration, where the generated triplets are first transferred to an emitting material, e.g., QDs, which re-emits the exciton energy as photons for the PV to absorb, effectively converting the exciton process to a photon multiplication process.[7−9,17] The first approach might at first appear to be a simpler integration method; however, despite its suggestion 40 years ago,[14] many challenges remain. We have recently demonstrated the feasibility and limitations of the photon multiplication system.[8,9] Crucial for a singlet

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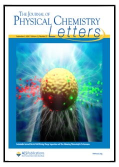

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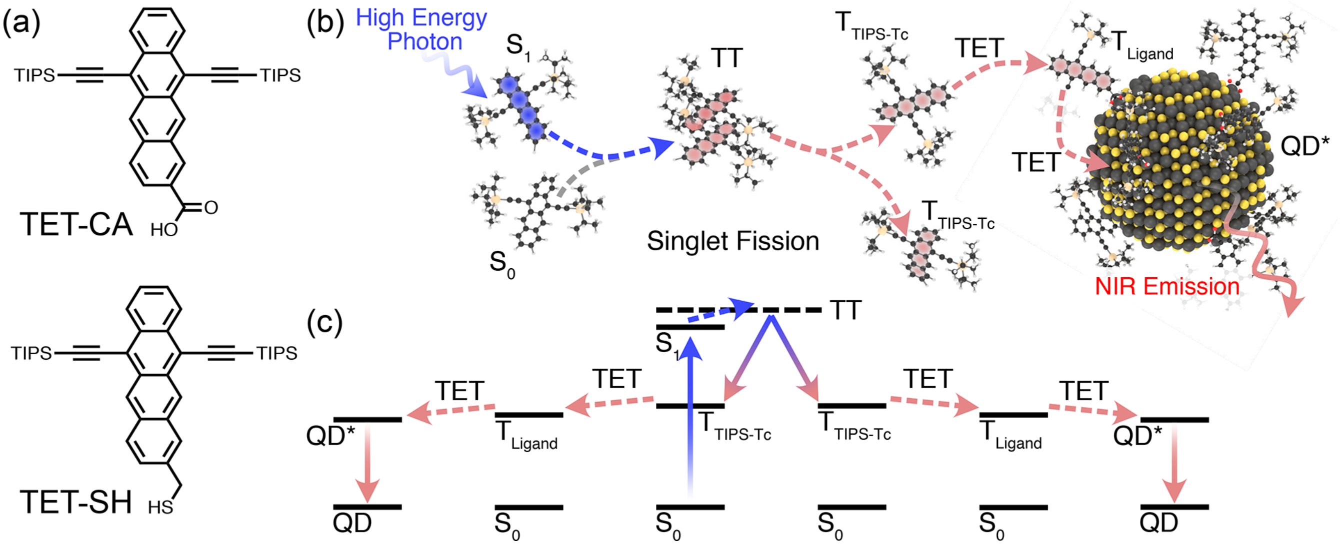

Figure 1. (a) Structures of the triplet transmitter ligands TET-CA and TET-SH. (b) Schematic illustration of the singlet fission-based photon multiplication process in solution. First, a high-energy photon is absorbed by TIPS-Tc to form its first singlet excited state, S_1. Together with a ground state molecule, singlet fission proceeds via an intermediate triplet pair state (TT) to form two independent triplets. Triplet energy transfer (TET) occurs from TIPS-Tc to a transmitter ligand followed by another TET step to populate the QD excited state (QD*) from which a NIR photon is emitted. (c) Photon multiplication process in panel b described in a Jablonski diagram.

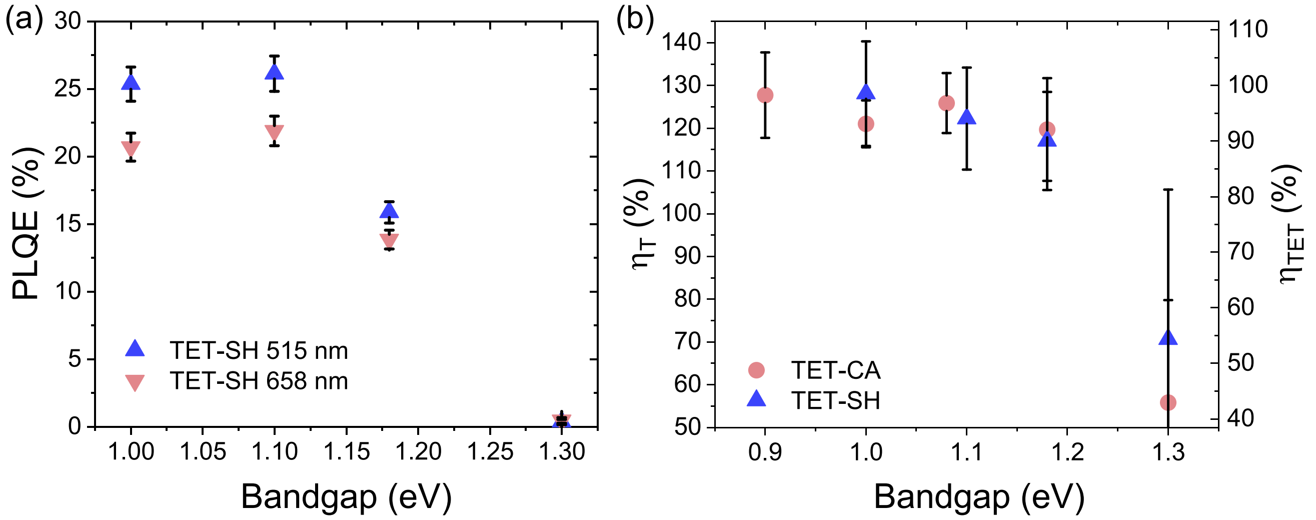

Figure 2. (a) Photoluminescence quantum efficiency (PLQE) of PbS quantum dots of different bandgaps after ligand exchange to TET-SH in a toluene solution with 200 mg/mL TIPS-Tc, exciting the QDs directly (658 nm) or the singlet fission material TIPS-Tc (515 nm). QD concentrations are 0.2 mM. (b) Triplet transfer efficiency per absorbed photon (η_T, left axis) and internal triplet transfer efficiency (η_{TET}, right axis), calculated from the PLQE enhancement in panel a compared to the triplet transfer efficiency of TET-CA-ligated dots.

fission-based photon multiplication system is efficient triplet transfer from the organic singlet fission material to the inorganic QDs. To achieve efficient triplet transfer, the QD is covered by a triplet transmitter ligand.[8] The transmitter ligand should enable efficient coupling between the QD and the ligand without introducing parasitic excited state deactivation pathways and traps. In this way, the QD−organic ligand system for photon multiplication is very similar to that used for triplet-sensitized triplet−triplet annihilation (TTA) photon upconversion and much can be learned from these well-studied systems.[18−22] On the basis of the many studies of CdSe QD−ligand systems, it has been concluded that ligands anchored with thiols, even though more strongly bound, are undesirable as they result in intramolecular or interfacial charge transfer events competing with the desired triplet energy transfer and photon emission events.[21,23−27] This assumption, that thiols introduce charge transfer pathways, could explain the lack of reports of thiol-anchored ligands used for QD−organic nanocomposites designed for triplet energy transfer. However, we note that for other QD materials, such as CdTe and PbS, there are reports of thiol-anchored ligands that do not quench the QD photoluminescence (PL).[23,28−30]

We therefore chose to investigate a thiol-anchored TIPS-tetracene ligand as a triplet transmitter ligand for PbS QDs. We establish that the *a priori* disregarding of thiol-anchored ligands for triplet energy transfer reactions should be reconsidered. By comparing the 6,11-bis[(triisopropylsilyl)ethynyl]tetracene-2-carboxylic acid (TET-CA) ligand with a thiol counterpart 6,11-{bis[(triisopropylsilyl)ethynyl]tetracen-2-yl}methanethiol (TET-SH) in a solution-based photon multiplication system,[8,9] we demonstrate that the thiol-anchored ligand allows for equally efficient triplet energy transfer to the PbS QD. Triplet energy transfer from the singlet fission materials in solution to the ligand and subsequent transfer from the ligand to PbS QDs approaches 100% efficiency with both carboxylic acid and thiol ligands. Furthermore, we demonstrate the advantage of using a stronger-binding thiol anchor as the thermal stability of the QD−organic nanocomposite distinctly improves.

We recently developed a singlet fission-based photon multiplication system in solution.[8] The photon multiplication process is schematically described in Figure 1. It consists of a highly soluble singlet fission material, 5,12-bis-[(triisopropylsilyl)ethynyl]tetracene (TIPS-Tc), and PbS QDs with triplet transmitter ligands attached. TIPS-Tc undergoes singlet fission in a concentrated solution generating triplet excitons in approximately 130% yield.[8,9,31] The triplets are transferred via the transmitter ligand to the PbS QDs, which subsequently emit an NIR photon when returning to the ground state. If triplet transfer is inefficient or does not occur, as is the case without transmitter ligands,[8] no or inefficient NIR emission from the QDs is observed. Therefore, by measuring the photoluminescence quantum efficiency (PLQE) of the QDs when exciting the QDs directly (658 nm) and comparing to when exciting the singlet fission material TIPS-Tc (515 nm), we can obtain a direct measure of the triplet transfer efficiency. We therefore choose this system as a straightforward way to evaluate a new triplet transmitter ligand, {6,11-bis[(triisopropylsilyl)ethynyl]tetracen-2-yl}methanethiol (TET-SH), containing a thiol anchoring group and compare it to the carboxylic acid counterpart (TET-CA) (Figure 1a).

Ligand exchange of PbS QDs with bandgaps ranging from 1.0 to 1.3 eV was performed following a procedure similar to that we have reported previously for TET-CA,[9] resulting in similar ligand coverage for both TET-CA and TET-SH ligands on the PbS QDs (see the Supporting Information and Figure S1 for more details).

After ligand exchange, the QD intrinsic PLQE slightly drops for QDs with bandgaps of <1.1 eV (Figure 2). This minor drop was observed previously for TET-CA-ligated PbS QDs with similar bandgaps and was ascribed to trap quenching from traps introduced during the ligand exchange.[9] For QDs with bandgaps close to or higher than the triplet energy of the ligand ($T_{\text{Ligand}} \sim 1.2$ eV), the PL is quenched more substantially, as triplet transfer from the QD to the ligand becomes possible. A blue shift of the QD peak absorption and a minor red shift of the ligand absorption are also observed after ligand exchange. Similar spectral shifts are commonly observed in QD−ligand nanocomposites and can arise due to the electronic interactions between the ligand and QD.[32−34]

Dissolving the TET-SH-ligated QDs in concentrated TIPS-Tc/toluene solutions produces a photon multiplication system in which the TIPS-Tc singlet fission material functions as the excition multiplication material and the ligand-covered QDs are the emitters. Figure 2a compares the QD PL response when either exciting the QD directly (658 nm) or exciting mainly the TIPS-Tc singlet fission material (515 nm). We note that approximately 95% of incoming photons are absorbed by TIPS-Tc.[8] It is clear that there is an enhancement of the QD PLQE when TIPS-Tc is excited. Assuming that the enhancement is due to singlet fission followed by triplet transfer to the QD, as we have shown previously for TET-CA-ligated QDs,[8,9] the number of transferred triplets per absorbed photon (η_T) can be calculated from eq 1.[8,9,35]

$$\eta_T = \left(\frac{\Phi_{\text{PM}}}{\Phi_{\text{QD}}} - \frac{\text{Abs}_{\text{QD}}^{515\text{nm}}}{\text{Abs}_{\text{Tot}}^{515\text{nm}}}\right)\left(\frac{\text{Abs}_{\text{TIPS-Tc}}^{515\text{nm}}}{\text{Abs}_{\text{Tot}}^{515\text{nm}}}\right)^{-1} = \eta_{\text{SF}}\eta_{\text{TET}} \tag{1}$$

where Φ_{PM} and Φ_{QD} are the measured PLQE values when exciting the singlet fission material TIPS-Tc and the QD, respectively. $\text{Abs}_{\text{Tot}}^{515\text{nm}}$ is the total absorption at the excitation wavelength affording photon multiplication, here 515 nm. The total absorption is the sum of the absorption of the two components, TIPS-Tc ($\text{Abs}_{\text{TIPS-Tc}}^{515\text{nm}}$) and the QDs ($\text{Abs}_{\text{QD}}^{515\text{nm}}$). η_{SF} and η_{TET} are the singlet fission quantum yield and the internal triplet transfer efficiency, respectively.

We recently showed that η_T is 120 ± 10% for TET-CA-ligated QDs for bandgaps of <1.25 eV.[8,9] In Figure 2b, we compare η_T for QDs with TET-SH ligands to the case with TET-CA ligands. It is evident that both the carboxylic acid- and thiol-anchored ligands allow for equally efficient triplet transfer. Considering that the singlet fission triplet yield (η_{SF}) in concentrated TIPS-Tc solutions is 130 ± 10%, the internal triplet transfer efficiency (η_{TET}) is close to unity for QDs with bandgaps of <1.2 eV (Figure 2b).

We also investigate the possibility for charge transfer pathways by comparing the energetic alignment of the ligand HOMOs and the PbS QD valence band (Figure 3). From UPS and cyclic voltammetry (CV) measurements, the conduction bands of PbS QDs of bandgaps similar to those studied here have been reported to be in the interval of −4.9 to −5.1 eV versus vacuum.[36−40] From CV measurements, we determine the HOMO level of TIPS-Tc to be −5.5 eV. The relative change in the ligand ionization potential is estimated from density functional theory (DFT) calculations. The orbital energies of the three molecules were calculated on the basis of DFT, at the B3LYP/cc-pVDZ level of theory, using the NWChem software.[41] Relative to that for TIPS-Tc, the HOMO for TET-SH is practically unchanged (+0.01 eV). The ligand TET-CA shifts to more negative potentials by <0.2 eV. The triplet energy of these tetracene derivatives is ∼1.25 eV.[9] On the basis of these calculations, hole transfer is more likely for the TET-CA ligand. However, in our previous work, we did not find any indication of hole transfer or hole transfer-

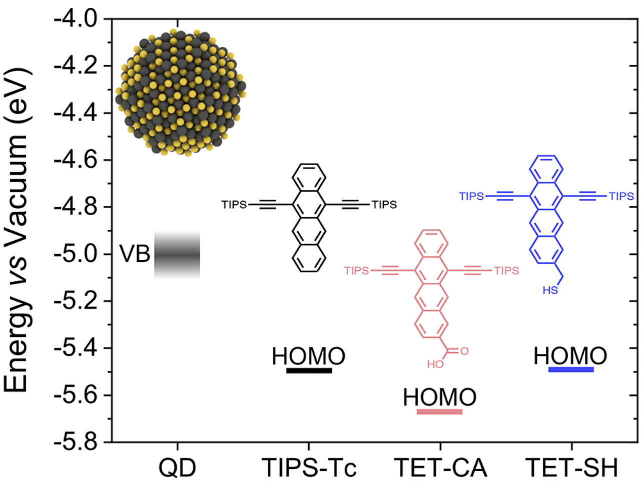

Figure 3. Band alignment vs vacuum of the PbS QD valence band edge (range of −5.1 to −4.9 eV from the literature) compared to the HOMO of TIPS-Tc (from cyclic voltammetry) and the HOMO of ligands TET-CA and TET-SH (relative difference vs TIPS-Tc from DFT calculations).

mediated triplet transfer for the PbS/TET-CA system, suggesting that hole transfer is not an issue for the PbS/TET-SH system either.[8,9] We note that the band alignment also indicates that triplet energy transfer from a higher-energy (>1.25 eV) QD to ligand TET-SH or TET-CA is not mediated by charge transfer.[22] Hole trapping due to surface states introduced by the ligand cannot be ruled out by this simple band alignment argument. With close to quantitative triplet transfer, however, hole trapping is not likely to be an issue for the TET-SH ligand.

The advantage of using thiol-anchored ligands is arguably the stronger binding affinity for chalcogenide QDs.[21,42] Binding affinity can be particularly important when considering future processing and commercialization of applications as it may limit process parameters such as temperature and solvent. To illustrate the advantage of using a thiol linker, we measured the PbS QD intrinsic PL of 1.1 eV QDs with oleic acid, TET-CA, and TET-SH before and after heating the liquid samples to 100 °C for 1 and 32 h. As shown in Figure 4 the TET-SH-capped PbS QDs retain their PL even after being heated for 32 h, whereas the TET-CA-capped QDs lose >30% of their PL intensity. We hypothesize that the PL drop is due to ligand loss, because it is accompanied by an increase in emission from the ligand upon excitation at 515 nm, indicative of more unbound ligand. We also note that there is only a minor red shift in the peak position (<25 nm) of the QD PL after heating (Figure S4), indicating any change in QD size due to surface etching or QD fusion was minimal, <0.1 nm.

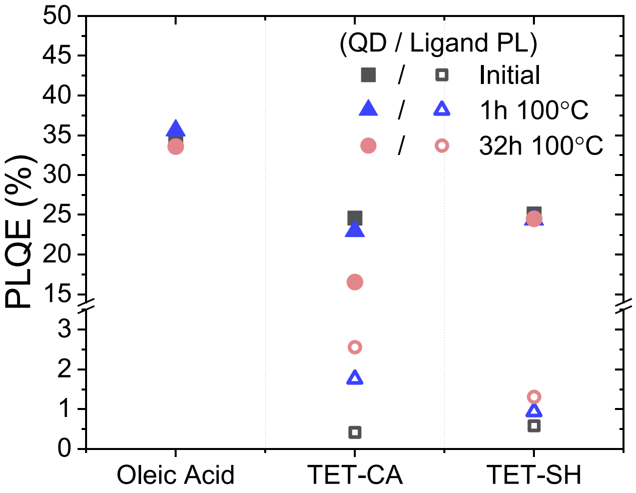

Figure 4. Photoluminescence quantum efficiency (PLQE) of PbS QDs capped with oleic acid, TET-CA, or TET-SH ligands in toluene, before and after the samples had been heated to 100 °C. Also shown is the PLQE for the ligand emission. Excitation at 515 nm, 0.8 mW/cm^2, excites the QD and ligand simultaneously.

To conclude, we have shown that a thiol-anchored TIPS-tetracene ligand attached on PbS QDs functions as an efficient triplet transfer ligand. We also show that the stronger binding afforded by the thiol group leads to an improved thermal stability compared to that of the traditional carboxylic acid-anchored ligand and therefore to higher photoluminescence quantum yields in photon multiplication-based applications. Thiol-anchored active ligands have previously been disregarded for applications requiring triplet energy transfer due to possible hole trapping.[21,23] However, our results unambiguously demonstrate that hole trapping is not necessarily an issue and that there are benefits when using a stronger-binding ligand. Recent work has shown that the relative band alignment of the ligand and QD governs the possibility of charge transfer and triplet energy transfer in this type of nanocomposite.[22] It has also been shown that the band alignment of PbS QDs can be tuned by varying the thiol ligand composition,[37] which might complicate the choice of thiol ligands. However, we argue that thiol ligands can be good candidates for mediating triplet energy transfer as long as the band alignment is kept to favor triplet transfer. Our findings are relevant for both photon upconversion and photon multiplication materials as well as general QD−organic nanocomposite materials for other optoelectronic applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02031.

Additional experimental details and data for the synthesis and ligand exchange of the QDs, calculation of QD ligand coverage, and size distribution (PDF)

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Notes

The authors declare no competing financial interest.
Data underlying the figures and conclusions in this publication is available at the University of Cambridge data repository at: https://doi.org/10.17863/CAM.56227.

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