NANO LETTERS
Letter
pubs.acs.org/NanoLett

Hybrid Molecule–Nanocrystal Photon Upconversion Across the Visible and Near-Infrared

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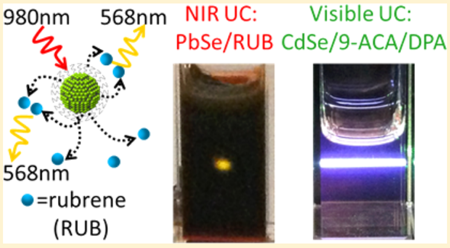
Supporting Information

ABSTRACT: The ability to upconvert two low energy photons into one high energy photon has potential applications in solar energy, biological imaging, and data storage. In this Letter, CdSe and PbSe semiconductor nanocrystals are combined with molecular emitters (diphenylanthracene and rubrene) to upconvert photons in both the visible and the near-infrared spectral regions. Absorption of low energy photons by the nanocrystals is followed by energy transfer to the molecular triplet states, which then undergo triplet–triplet annihilation to create high energy singlet states that emit upconverted light. By using conjugated organic ligands on the CdSe nanocrystals to form an energy cascade, the upconversion process could be enhanced by up to 3 orders of magnitude. The use of different combinations of nanocrystals and emitters shows that this platform has great flexibility in the choice of both excitation and emission wavelengths.



KEYWORDS: *Triplet, upconversion, solar, hybrid, nanocrystals, acenes*

The sequential absorption of two low energy photons, followed by emission of one higher energy photon, is known as photon upconversion. This incoherent two-photon process has potential applications in biological imaging[1] and shown promise for high density data storage.[2] In solar energy conversion, photon upconversion has the potential to generate substantial gains in overall solar conversion efficiency, e.g., from 32% under the Shockley–Queisser limit to 43% under one sun for photovoltaic cells with a bandgap of 1.76 eV.[3,4] Two key challenges in the field are to find new upconversion materials that can (1) operate at with high conversion efficiencies and (2) can operate in the near-infrared (NIR) spectral region.

A successful approach to achieve efficient upconversion at low light intensities has been to use mixed conjugated organic systems in which triplet–triplet annihilation (TTA) can occur.[5−7] A sensitizer molecule absorbs a long wavelength photon, creating a singlet state that undergoes intersystem crossing to its triplet state, which then transfers its energy to the triplet state of a second molecule that acts as an emitter. When two sensitizers transfer their triplet states to the emitter, the two triplets can fuse into a higher energy singlet state on the emitter. Organic upconversion systems based on TTA can operate under low light conditions (equivalent to sunlight), have demonstrated upconversion efficiencies of up to 28%,[8] and have been used to upconvert photons at wavelengths as long as 790 nm.[9]

Unfortunately, it has proved challenging to find photostable, long-lived organic chromophores that allow organic upconversion systems to operate beyond 800 nm. This NIR spectral region is of interest because commonly used photovoltaic materials like silicon (bandgap, E_g = 1.1 eV) and cadmium telluride (E_g = 1.5 eV), are unable to collect photons that have wavelengths exceeding 1100 and 800 nm, respectively. Furthermore, NIR photons are only weakly absorbed in aqueous environments, making them useful for probing biological systems. The rational design of lanthanide doped crystals[10] has yielded high (5% or more) upconversion quantum yields,[4,8] but these materials have limited spectral coverage and require large optical thicknesses due to the forbidden nature of the optical transitions employed for upconversion.[8,11] Lanthanide-doped nanoparticles have shown promise as biological imaging agents,[12] but their efficiency tends to be lower than that in single crystals, with maximum quantum yields below 1% when irradiated at 980 nm at intensities of 50 W/cm^2 or more.[13,14]

Inorganic nanocrystals (NCs) are relatively photostable chromophores whose bandgap absorption spectra can be tuned from the near-ultraviolet to the infrared. Previous reports of triplet energy transfer from organics to semiconductors suggest that it is possible for NC excitons to exchange energy with molecular triplet states.[15] A good example is the recent demonstration that triplet excitons produced by singlet fission in pentacene and tetracene layers can efficiently transfer their energy to adjacent semiconductor NC layers.[16,17] Evidence for the reverse process, i.e., energy transfer from the NC to the triplet state of an organic molecule, can be found in earlier experiments showing that CdSe NCs could sensitize singlet oxygen formation[18] and that the triplet state of a naphthyl ligand could act as an energy acceptor for NC excitons.[19] Although NCs were recently used as luminescence recyclers for

Received: May 29, 2015
Revised: July 2, 2015
Published: July 10, 2015

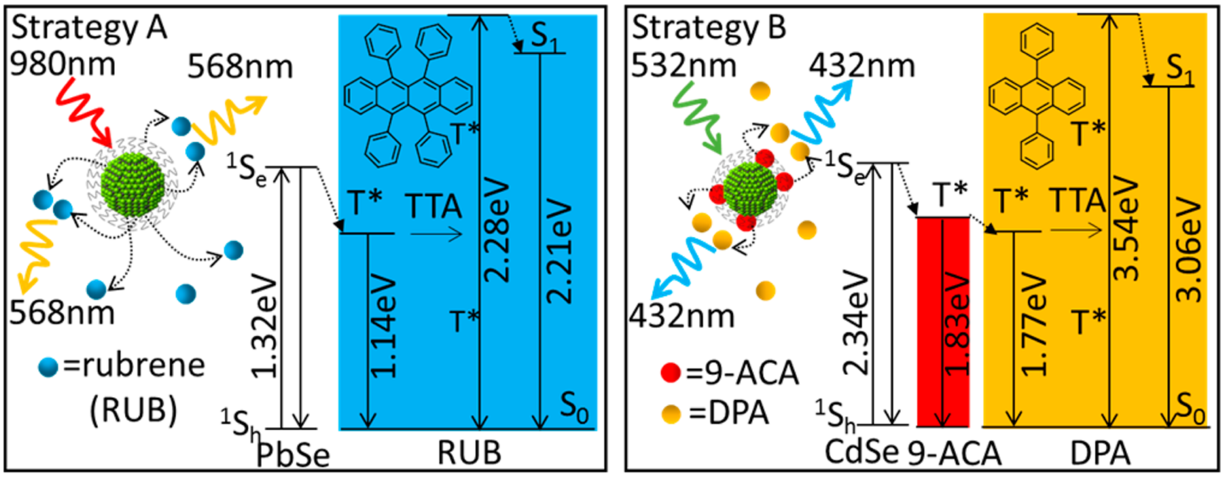


Figure 1. Schematic illustration of NC-organic upconversion strategies. In Strategy A, the organic ligands of the PbSe NC are electronically inert, and energy must be transferred directly to the triplet state of the organic emitter RUB. In Strategy B, the energy is first transferred to the triplet state of an anthracene-based ligand, 9-ACA, which then transfers it to the DPA emitter.

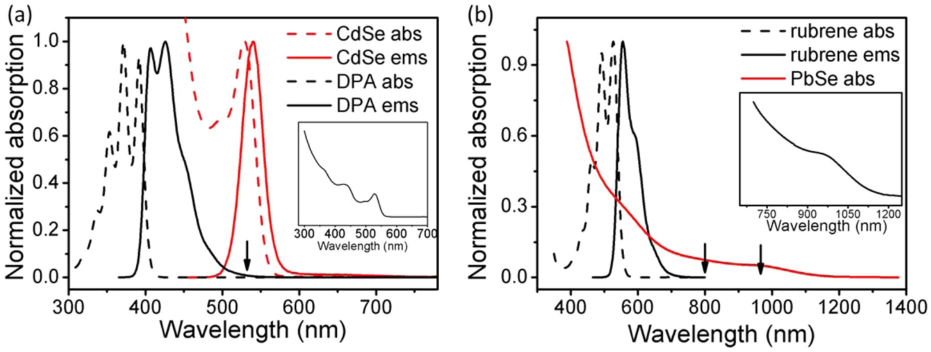


Figure 2. (a) Absorption and emission spectra of 2.7 nm CdSe/DPA sensitizer/emitter pair in hexane at room temperature. Inset is the full absorption spectrum of CdSe. (b) Absorption and emission spectra of 2.1 nm PbSe/RUB sensitizer/emitter pair taken in toluene at room temperature. Inset is the absorption of PbSe's first exciton. Arrows indicate excitation wavelengths for photon upconversion.

a TTA upconversion scheme,[20] the use of semiconductor NCs as sensitizers for photon upconversion has not been explored. In this Letter, we show that NC-organic triplet sensitization is a robust phenomenon that can be optimized through ligand chemistry. It has the potential to extend TTA upconversion into the infrared spectral region, where it could be used to enhance the efficiency of commercially viable photovoltaic materials like CdTe and Si.

The general idea of upconversion using NC sensitizers is outlined in Figure 1. We illustrate two potential strategies. In Strategy A, the as-synthesized NC is surrounded by the native alkyl-terminated carboxylic acid or phosphonic acid ligands. Since these ligands do not have low-lying triplet states, energy transfer must occur directly from the NC to the emitter in solution. Given that triplet−triplet energy transfer is generally believed to require wave function overlap between acceptor and donor and operates on short (∼1 Å) length scales, it is not clear that Strategy A could be successful with ligands that typically have alkyl chain lengths on the order of 10 Å or more. In Strategy B, the ligand itself has a triplet state that can accept the energy from the NC exciton. The triplet state on the ligand acts as a transmitter that mediates triplet energy transfer from the NC sensitizer to an emitter in solution.[21] This strategy relies on an energy transfer cascade to move energy from the NC to the emitter. In this paper, we show both strategies work, but Strategy B with the energy cascade shows superior upconversion efficiencies.

As emitter molecules, we use diphenylanthracene (DPA) and rubrene (RUB). Both are commonly used in organic−organic upconversion schemes due to their long-lived, low-lying triplet states and high (>97%) singlet state fluorescence quantum yields.[22] As sensitizers, we use CdSe in combination with DPA to upconvert visible (532 nm) light to the blue region (DPA's emission peaks at ∼420 nm) and PbSe in combination with RUB to upconvert the NIR (800−980 nm) to the visible (RUB's emission peaks at ∼550 nm). The absorption and fluorescence spectra of both the NC sensitizers and the organic emitters are shown in Figure 2, along with the laser wavelengths used in the upconversion experiments described below. Details regarding NC synthesis,[23−25] ligand exchange and characterization by NMR, quantum efficiency measurements, etc. can be found in the Supporting Information.

Since one of our goals is to extend the spectral response of upconversion systems into the NIR, we first used 2.1 nm PbSe NCs capped with oleic acid ligands with RUB as the emitter. These samples gave visible upconversion, as shown in Figure 3a. A bright yellow fluorescence originates from the spot where a 3 mm diameter, 100 mW 800 nm cw laser beam hits the sample. The black color of the cuvette is due to the PbSe NCs, whose absorption extends across the entire visible spectrum. The intensity dependence of the upconverted signal, shown in

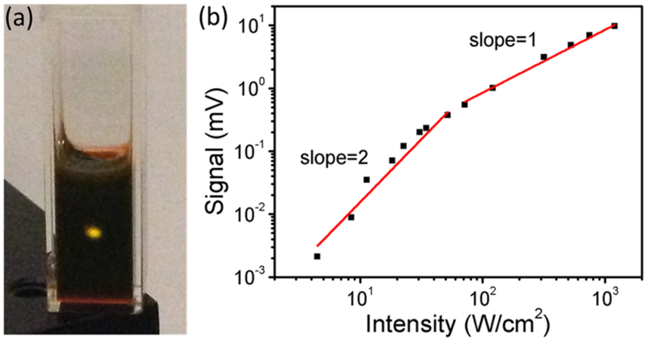


Figure 3. (a) Photograph of upconversion in a cuvette containing the 2.1 nm PbSe/RUB mixture. The yellow spot is emission from the RUB originating from an unfocused cw 800 nm laser with an intensity of 1 W/cm^2. (b) Log–log plot of upconversion signal versus laser intensity (W/cm^2) for the PbSe/RUB mixture, showing the transition from quadratic (slope = 2) to linear (slope = 1) regimes. (a) and (b) were conducted in dry and degassed toluene with 3.84 mM rubrene and 58.1 μM PbSe NCs at room temperature.

Figure 3b, exhibits the signature linear-to-quadratic behavior that is a general feature of upconversion systems that rely on sequential photon absorption.[26,27] The photophysical quantum yield of the upconversion process Φ_{UC} is given by

$$\Phi_{UC} = 2\Phi_{ref} \times \frac{(\text{photons absorbed by reference})}{(\text{photons absorbed by UC sample})} \times \frac{\text{PL signal (UC sample)}}{\text{PL signal (reference)}} \tag{1}$$

where Φ_{ref} is the one photon quantum yield of a reference compound. Note that we follow previous literature by including a factor of 2 so that if 100 incident photons produce 50 upconverted photons, eq 1 predicts a 100% yield.[5] The Supporting Information contains detailed descriptions of how we measured the photons absorbed and the PL signal for reference and sample. For the PbSe samples, Φ_{UC} was determined by comparing the RUB output from the upconversion to that from direct excitation of the RUB by 400 nm light. The upconversion quantum yield was measured to be $1.0 \pm 0.5 \times 10^{-4}$ (or 0.01%) in the linear intensity regime where the efficiency is maximized. When a 980 nm laser diode was used to excite the sample, yellow upconverted light was also observed. The 980 nm source was not sufficiently intense to reach the linear regime, but the efficiency at this wavelength was estimated to be within a factor of 3 of that at 800 nm (Supporting Information). To our knowledge, 980 nm is the longest wavelength that has been upconverted using the TTA strategy. While this efficiency is lower than that of lanthanide-doped crystals that have been used in conjunction with photovoltaic cells,[28] we emphasize that there are still many parameters that can be optimized in this system, including the implementation of Strategy B.

The TTA mechanism of upconversion was confirmed by time-resolved fluorescence measurements on the upconversion sample. Pulsed excitation at 800 nm leads to two RUB emission components, widely separated in time. Direct two-photon excitation of the RUB by itself leads to a prompt fluorescence decay on the nanosecond time scale. This fluorescence decay in the PbSe/RUB mixture is 14.3 ns, as compared to 16.2 ns measured for RUB by itself in toluene (Figure 4a). Despite the high concentration of PbSe NCs, there is only a slight decrease in fluorescence lifetime that corresponds to a decrease in fluorescence yield from 98% (RUB by itself) to 86% in the mixed solution. On longer time scales, there is a delayed fluorescence component that decays with a 41 μs time constant (Figure 4b) that is entirely absent in the RUB-only sample. The delayed fluorescence arises from the fusion of pairs of RUB triplets formed by energy transfer from the excited PbSe NCs. If we assume that most of the PbSe → RUB energy transfer occurs within the ~1 μs lifetime of the luminescent exciton in PbSe,[29] then the delayed fluorescence reflects the RUB triplet lifetime. In the limit of bimolecular triplet encounters, the delayed fluorescence lifetime is half the triplet lifetime, allowing us to estimate a RUB triplet lifetime of 82 μs in the mixed solution. This lifetime is close to the 120 μs lifetime reported for RUB in nonpolar liquids,[30] indicating that quenching of the RUB triplet state is not pronounced in the mixed solution. Note that there is a small (5%) component of the delayed fluorescence that persists for longer times, as can be seen from the fact that some upconversion signal is detectable even at 300 μs. This long-lived component could arise from the photon recycling seen in other upconversion systems,[31] or it could reflect the contribution from a separate state in the NCs,

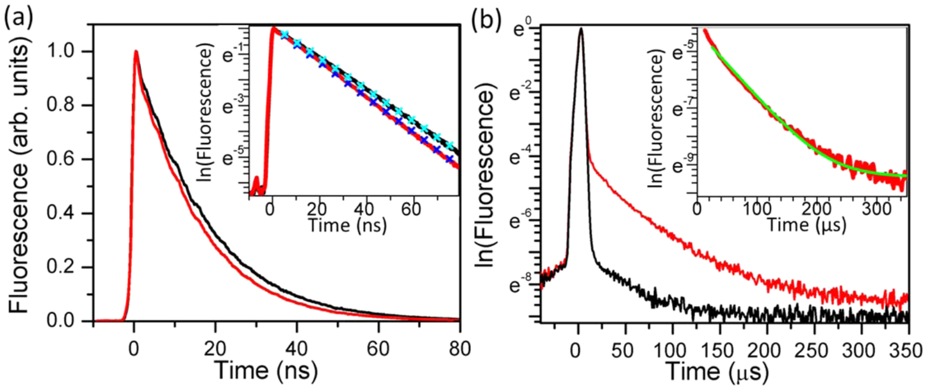


Figure 4. (a) Prompt fluorescence decay of PbSe/RUB (red line) and RUB (black line) samples in a 100 ns time window. Inset: logarithmic plot of decay along with exponential fits (crosses). The singlet decay time decreases from 16.2 ns for RUB alone to 14.3 ns in the PbSe mixture. (b) Logarithmic plot of the delayed fluorescence decay of PbSe/RUB (red) and RUB (black) samples on the μs time scale. The spike at time = 0 is due to prompt fluorescence due to direct two-photon excitation of the RUB. Inset: logarithmic plot of delayed fluorescence component overlaid with fit with 41 μs decay time and a 5% offset.

DOI: 10.1021/acs.nanolett.5b02130
Nano Lett. 2015, 15, 5552–5557

possibly a surface or defect state. In any case, the long lifetime of the upconverted luminescence confirms that energy transfer from the PbSe NCs to the RUB is the dominant process in these mixed solutions, despite the fact that the PbSe has low energy states that can accept energy from both RUB's singlet and triplet states.

We can make some general observations about the physical mechanism of the NC sensitization of the molecular triplet states. Both experiment and theory have shown that quantum confinement enhances the exchange interaction in semiconductor NCs, leading to dark states with triplet character just below the optically allowed state.[32−34] Energy transfer from these states to the molecular triplet state would be spin-allowed. Triplet−triplet energy transfer typically occurs via a Dexter mechanism that relies on wave function overlap. One way to enhance wave function overlap is to increase the extent of the excitonic wave function beyond the NC surface. Previous work on charge transport in NC arrays has shown that electronic wave functions can extend well beyond the NC surface.[35−37] We suspect that semiconductors with smaller carrier effective masses and larger Böhr radii will also have a larger evanescent component of the exciton wave function, leading to more efficient Dexter energy transfer. As a preliminary test of this idea, we compared PbSe (Böhr radius = 46 nm) to PbS (Böhr radius = 18−20 nm). We found that under identical conditions (absorption at 800 nm, laser power, RUB concentration), the PbS upconversion output was consistently a factor of 3.5−3.8 times less than that of the PbSe sample. This observation lends qualitative support to the hypothesis that the Böhr radius is important, but more work needs to be done to assess factors like ligand binding and exciton relaxation in the different semiconductors.

The low upconversion efficiency of the PbSe/RUB system provided motivation to identify strategies that can increase its efficiency. Strategy B provides a promising way forward, but the design and synthesis of organic ligands with triplet energy levels appropriate for PbSe is a challenging problem. This synthesis is currently underway. In the meantime, we have used the CdSe/DPA combination as a model system to demonstrate that Strategy B is a viable way to enhance upconversion yields by the required amount.

When octadecyl phosphonic acid (ODPA) is used as the ligand for 3.3 nm diameter CdSe NCs, there was no detectable emission from DPA under 532 nm laser excitation (Figure S8). This experiment corresponds to Strategy A in Figure 1, and it appears that energy transfer across the ligand shell is even less efficient than in PbSe/RUB, placing an upper bound on the quantum yield of 1 × 10^{-4}. The arguments used above to explain the difference between PbSe and PbS also predict that CdSe (Böhr radius = 4−5 nm) would show very little upconversion, as observed.

To facilitate energy transfer, we replaced the ODPA ligands with anthracene derivatives functionalized with carboxylic acid groups. The use of the anthracene ligands enhances the DPA emission by roughly a factor of $\sim 10^3$, resulting in a blue fluorescence output that is easily visible by eye using a 532 nm laser (Figure 5a). The dependence of the DPA emission on laser intensity (Figure 5b) again shows the quadratic-to-linear transition that is a signature of two-photon upconversion systems. At the lowest intensities, our experimental data points fall slightly below the slope = 2 line, but this likely reflects uncertainty at these low signal levels, rather than a systematic deviation from the expected quadratic intensity dependence.

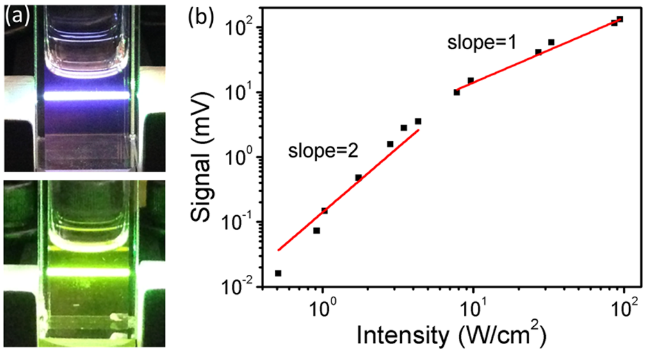


Figure 5. (a) Photographs of upconversion in a cuvette containing an optimized CdSe/9-ACA sample (top) and a CdSe/ODPA sample (bottom). The spectra of these samples are shown in the Supporting Information, Figure S7. The violet DPA output in the 9-ACA sample (top) swamps the green CdSe emission and laser scatter that is clearly seen in the ODPA sample (bottom). (b) Log−log plot of upconversion versus laser intensity for the 3.3 nm CdSe/9-ACA/DPA sensitizer/ligand/emitter system, showing the transition from quadratic (slope = 2) to linear (slope = 1) regimes. All experiments were conducted in dry and degassed hexanes respectively with 1 mM DPA and 5 μM CdSe NCs at room temperature.

The best performance was obtained for 9-anthracene carboxylic acid (9-ACA). Shown in Figure 6a is a comparison of the relative output levels for the five ligands tested at high laser power. Using Rhodamine 6G as fluorescence standard, we calculated an overall conversion efficiency of 9 ± 2% for the 2.7 nm CdSe/9-ACA/DPA system (Supporting Information). Time-resolved fluorescence measurements on the CdSe/DPA mixtures confirmed that the DPA singlet lifetime is unaffected by the presence of the NCs. We note that this system still has room for further efficiency gains by modifying the NC size or geometry, ligand structure, and emitter molecule.

To explain the enhanced upconversion, our hypothesis is that the anthracene-COOH ligands form an energy cascade outlined in Strategy B in Figure 1. Given the CdSe bandgap of 18870 cm^{-1} (or 2.34 eV), as estimated from the PL peak, the triplet energy of 9-ACA (14760 cm^{-1} or 1.83 eV) and the triplet energy of DPA (14290 cm^{-1} or 1.77 eV),[38] there is a downhill path for the energy from the CdSe to the 9-ACA to the DPA. To confirm that the anthracene ligands act as intermediate energy acceptors, we measured the PL lifetimes of CdSe NCs with and without the 9-ACA ligand. The results (Figure 6b) show that this ligand generates substantial quenching of the NC PL on time scales >10 ns. This quenching is consistent with downhill energy transfer from the NC to the 9-ACA triplet state. The observed shortening of the CdSe lifetime, combined with the large enhancement in upconversion efficiency, suggest that Strategy B is an effective way to enhance energy transfer from the semiconductor NC to the emitter triplet state.

Finally, we consider why the emissive singlet states of RUB and DPA are not quenched by the NC sensitizers. The Förster radii for RUB → PbSe and DPA → CdSe energy transfer lie in the 5−6 nm range (Supporting Information). If the RUB singlet state is excited while in close proximity to the NC, we would expect substantial fluorescence quenching. But given a diffusion coefficient of 10^{-5} cm^2/s[39] and a triplet lifetime of 80 μs, the RUB can diffuse more than 100 nm after its triplet state is populated by the PbSe exciton. The long triplet lifetime allows it to escape the critical Förster radius around the PbSe NC. Similar considerations apply to the CdSe/DPA system.

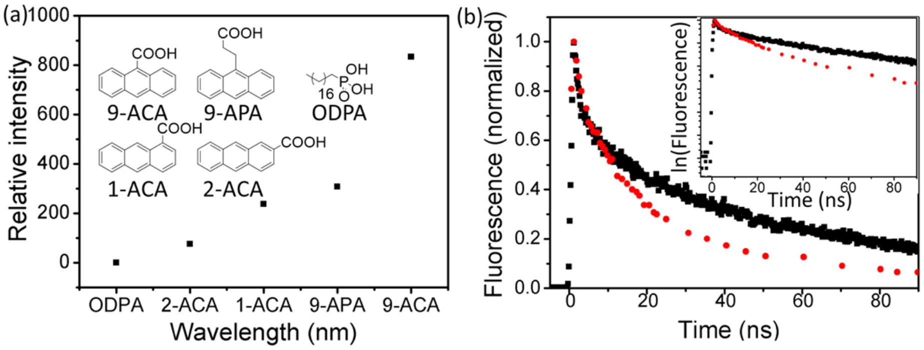


Figure 6. (a) The relative upconversion efficiency with different transmitter anthracene ligands and the ODPA ligand attached to the CdSe NCs in toluene. (b) Decay of CdSe/ODPA sample (black) and extracted CdSe component from CdSe/9-ACA sample (red). Details of the data analysis can be found in the Supporting Information. Inset: Logarithmic comparison of the decays.

The weak nonradiative quenching of the emitters means that there is no fundamental limit on the ability of the emitter molecules to emit upconverted photons.

The results of this Letter show that the use of inorganic NCs can be used as sensitizers for upconversion based on TTA. The ability of the PbSe/RUB system to upconvert 980 nm light to 550 nm opens up the possibility that these materials could be used to enhance the efficiency of photovoltaic materials like GaAs and CdTe. However, there are several issues that need to be addressed before NCs can be used in such an application. One obvious problem is that the NC sensitizers absorb strongly at the upconversion wavelengths, unlike many organic and inorganic sensitizers where narrow absorption features lead to "holes" in the high energy absorption. Since optically dense samples are needed to absorb solar radiation at the sensitizer wavelength, extraction of the upconversion output may require novel optical architectures. A second issue concerns the intensity dependence of the upconversion efficiency. For the NC samples in this Letter, the linear conversion regime (corresponding to maximum quantum yield) was achieved at intensities in the 10−100 W/cm^2 range. While comparable to the intensities used for lanthanide nanoparticle upconversion, these are still ~10^5× higher than single wavelength solar intensities at 532 and 980 nm, as given by the ASTM G-173 (AM 1.5) solar irradiance reference. If we integrate over a 100 nm wavelength interval, the total solar flux will still generate ~10^3× less excited sensitizers than our lasers. But it should be noted that recent advances in all-organic TTA systems suggest that efficient operation under single sun conditions is possible using this approach.[7,40]

One key to making NC-sensitized upconversion viable for solar energy conversion will be to increase its overall efficiency. There are multiple strategies for improving the NC sensitizer system. In this Letter we have shown that using conjugated organic ligands can lead to an energy cascade process that enhances the overall upconversion efficiency by up to 3 orders of magnitude in the CdSe/DPA system, providing one route to higher efficiencies. But we should also emphasize that there exist other applications of upconversion materials, like biological imaging, where the absolute efficiency of the upconversion is less of a concern. NC-sensitized upconversion will likely have applications beyond the field of solar energy conversion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Information on NC synthesis and characterizion, photophysical measurements, and Förster radius calcuations are available in the Supporting Information online. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b02130.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Science Foundation grant CHE-1152677 (C.J.B.) and from the US Army W911NF-14-1-0260 (M.L.T.).

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