Solid state photon upconversion utilizing thermally activated delayed fluorescence molecules as triplet sensitizer

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The ability to upconvert light is useful for a range of applications, from biological imaging to solar cells. But modern technologies have struggled to upconvert incoherent incident light at low intensities. Here, we report solid state photon upconversion employing triplet-triplet exciton annihilation in an organic semiconductor, sensitized by a thermally activated-delayed fluorescence (TADF) dye. Compared to conventional phosphorescent sensitizers, the TADF dye maximizes the wavelength shift in upconversion due to its small singlet-triplet splitting. The efficiency of energy transfer from the TADF dye is 9.1%, and the conversion yield of sensitizer exciton pairs to singlet excitons in the annihilator is 1.1%. Our results demonstrate upconversion in solid state geometries and with non-heavy metal-based sensitizer materials. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4926914]

Optical upconversion is a process that captures multiple incident photons, combines their energy, and then re-emits a photon at a shorter wavelength than the incident photons. The process can be very efficient in phase-matched nonlinear materials, pumped by high intensity coherent beams. But many applications, such as enhancing the infrared response of a solar cell, call for upconversion of low intensity, incoherent light. To achieve operation at low intensities, it is necessary to localize the energy contained in the incident light. The most common solution is to store the optical energy in the excited states of rare earth materials, but these materials suffer from narrow absorption lines and relatively weak optical cross sections.

Molecular excitons offer another approach to optical upconversion. The triplet exciton typically has a long lifetime since transitions between triplet states (total spin $S=1$) and singlet ground states ($S=0$) are spin disallowed. Two separate triplet excitons can also combine with each other, forming a higher energy singlet or triplet exciton in a process known as triplet-triplet annihilation (TTA). It can form a radiative singlet state, because the two triplet excitons can combine with fractional $S=0$ character, and if the molecule’s singlet energy is slightly lower than twice the triplet state energy, TTA can provide an energy efficient upconversion process.

TTA requires two molecules, a sensitizer that absorbs low energy photons and generates triplet excitons that can then Dexter transfer to the annihilator, where the TTA process occurs. In most optical TTA upconversion systems, a heavy metal atom is used to promote spin orbit coupling in the sensitizer, enhancing intersystem crossing and the generation of triplet excitons. Here, in contrast, we utilize thermally activated-delayed-fluorescence (TADF) molecules to generate triplets for TTA. In TADF molecules, the splitting between singlet and triplet energy is small ($\Delta E_{ST} < 100$ meV), promoting intersystem crossing without the inclusion of a heavy metal. For example, Adachi and co-workers have shown that optically pumped TADF molecules can efficiently generate triplet excitons at efficiencies up to 70%, making them suitable substitutes for traditional phosphorescent sensitizers. More importantly, the smaller exchange splitting, $\Delta E_{ST}$, characteristic of TADF materials, yields a smaller Stokes shift, and therefore, wastes less energy than a phosphorescent sensitizer (Fig. 1).

![FIG. 1. Schematic graph for the exciton transitions in the upconversion device. The low energy excitation light is first absorbed by the TADF molecule 4CzTPN-Ph, creating singlet excitons. Due to strong intersystem crossing in TADF, the singlet excitons form triplet excitons, which then Dexter transfer to the triplet states in DPA. For a sufficient density of triplet excitons in DPA, triplet collisions generate singlet excitons through the process of triplet-triplet annihilation. Finally, DPA singlet exciton fluorescence yields high energy output photons.](http://dx.doi.org/10.1063/1.4926914)
layer structures, but the bilayer DPA/4CzTPN-Ph thin film shows strong upconversion emission from $\lambda = 400$ nm to 500 nm. The emission peaks from $\lambda = 400$ nm to 475 nm are characteristic of DPA fluorescence. The prominent peak at $\lambda = 490$ nm is not observed in the fluorescent spectrum of neat DPA and is attributed to an exciplex of DPA and 4CzTPN-Ph. Indeed, we note the HOMO-LUMO offset at the DPA/4CzTPN-Ph interface suggests electron transfer from DPA to 4CzTPN-Ph and hole transfer from 4CzTPN-Ph to DPA; see Fig. 2(a). The absorption of 4CzTPN-Ph is observed to be broad and red-shifted as compared to DPA. The strong donor-acceptor character of the excited state in 4CzTPN-Ph, however, is associated with both weak exchange splitting and weak oscillator strength. As a consequence, the 20-nm-thick film of 4CzTPN-Ph absorbs just 6.8% of the incident pump light at $\lambda = 532$ nm. Thicker films suffer from excessive losses due to poor exciton diffusion.

In Fig. 3(a), we confirm the presence of TTA upconversion by measuring the modulation of the DPA fluorescence under magnetic field. The magnetic field redistributes the singlet character of the nine possible triplet-triplet pairs in the TTA process, modifying the effective conversion rate of triplet-triplet pairs into singlet states. As expected from the magnetic field model of Johnson and Merrifield, the upconverted photoluminescence increases under small magnetic field ($\sim 0.1$ T) and decreases under strong magnetic field ($>0.3$ T). No magnetic field effect is observed for 4CzTPN-Ph alone. In Fig. 3(b), we measured the excitation intensity dependence of the upconversion photoluminescence. We model the trend as $PL \propto AI^2$. The data show $x = 1.28$ under regression.

Following Kondakov, the near-linear intensity dependence can be understood from a simple model of the TTA kinetics. Assuming a triplet generation rate, $G$, in the DPA film, we can identify linear and quadratic processes $k_{\text{decay}}[T] + k_{\text{up}}[T]^2 = G$. The linear process $k_{\text{decay}}$ represents geminate triplet losses in DPA, including nonradiative recombination to the ground state. The bimolecular process $k_{\text{up}}$ represents the TTA process. If geminate triplet losses dominate the triplet dynamics, then we observe that the TTA process depends quadratically on $G$. But if TTA dominates, then upconversion exhibits a linear dependence on optical pump power. The transition from quadratic to linear intensity dependence is, therefore,

\[ k_{\text{decay}}[T] + k_{\text{up}}[T]^2 = G. \] (1)

As an optical pump, we use a $\lambda = 532$ nm green laser with a maximum power of 400 mW. The TTA upconverted emission is filtered through a $\lambda = 500$ nm short pass filter and measured in a spectrometer, yielding the emission spectrum shown in Fig. 2(b). Upconverted light is absent in both single
an indication of the minimum pump power required to realize efficient TTA.\textsuperscript{11,12}

We cannot identify the quadratic-linear transition at low intensities in this system due to weak absorption in the thin sensitizer film and the low overall yield of upconversion. The power law exponent of 1.28 suggests, however, that some important non-geminate loss mechanism not considered in Eq. (1) remains even at high intensities. Possible candidates for this loss include triplet-singlet or triplet-triplet annihilation in the sensitizer, where delayed fluorescence is quenched by Förster transfer to neighboring singlet or triplet excited states.\textsuperscript{14} Trap filling during diffusion could also affect the intensity dependence. Nevertheless, the minimum incident intensity of 0.5 W/cm\textsuperscript{2} corresponds to approximately 30 mW/cm\textsuperscript{2} of absorbed power. This is consistent with prior work of Kondakov et al. showing that the high density of triplet excitons created in solid-state devices can exhibit high yields of upconversion at low excitation densities.\textsuperscript{12}

The quantum yield of upconversion (\(\eta_{UP}\)) of a system is the ratio of emitted short wavelength photons to absorbed long wavelength photons. Typically, the ratio is normalized to a maximum efficiency of 100%,\textsuperscript{15} corresponding to two long wavelength photons combining to form a single short wavelength photon. We decompose the overall upconversion yield into: (i) efficiency of intersystem crossing, \(\eta_{ISC}\), from singlet to triplet on the sensitizer; (ii) the Dexter transfer efficiency, \(\eta_{DEX}\), of triplets coupled from the sensitizer to the emitter; (iii) the TTA efficiency, \(\eta_{TTA}\), for triplets upconverting into singlets; (iv) “back transfer” losses, \(\eta_{BL}\), caused by Förster energy transfer from the emitter back to the sensitizer, and (v) the fluorescent quantum yield of the emitter, \(\eta_{PL}\).

\[
\eta_{UP} = \eta_{ISC}\eta_{DEX}\eta_{TTA}\eta_{BL}\eta_{PL} \tag{2}
\]

The upconversion process is quantified by comparing the photoluminescent quantum yield of DPA and 4CzTPN-Ph excitation using a \(\lambda = 365\) nm light-emitting diode (LED) and the green laser, respectively. The comparison yields \(\eta_{UP}/\eta_{PL} = 1.1\%\). The efficiency is understood as the conversion yield of exciton pairs in the sensitizer into singlet excitons in the annihilator. The photoluminescent quantum yield of DPA in this structure is \(\eta_{PL} = 25\%\), resulting in an upconversion efficiency of \(\eta_{up} = 0.28\%\). Scaling by the absorption yields an external quantum efficiency at \(\lambda = 532\) nm of \(\eta_{EQE} = 0.1\%\), demonstrating that substantial improvements in the device structure are still required. For example, future solid-state device structures should improve absorption using multilayers, rough interfaces with large surface areas, or exothermic gradients to guide excitons to the sensitizer/annihilator interface.

The losses in the upconversion process are probed further in Fig. 4, where we compare the transient delayed fluorescence of neat 4CzTPN-Ph to the transient delayed fluorescence of 4CzTPN-Ph in the bilayer DPA structure. The delayed fluorescence reports the triplet exciton lifetime in the 4CzTPN-Ph TADF dye, and hence allows us to extract \(\eta_{DEX}\) in this system. Based on delayed fluorescence lifetimes of 1.72 \(\mu\)s and 1.56 \(\mu\)s in the neat film and bilayer structures, respectively, we obtain \(\eta_{DEX} = 9.1\%\). The result is presumably limited by poor excited state diffusion in the 20-nm-thick 4CzTPN-Ph film. Improving triplet energy transfer is, consequently, a second attractive target after increasing the absorption for future generations of upconversion devices.

In conclusion, we demonstrate optical upconversion utilizing TADF molecules in a double layer film. Although the overall quantum yield of upconversion remains lower than prior work in solution using conventional sensitizers with high spin-orbit coupling, TADF materials are promising because their very small splitting is closer to the ideal case of halving the wavelength during upconversion, and the absence of heavy metals such as Pd or Pt could lower the cost if this technology becomes widespread. Thus, these results open the door to the non-heavy metal sensitizer materials that show upconversion in solid state structures.

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