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Triplet-Fusion Upconversion Using a Rigid Tetracene Homodimer

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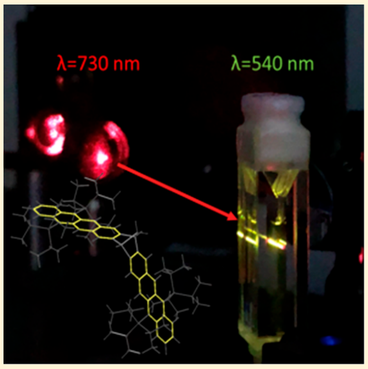
Supporting Information

ABSTRACT: We demonstrate that a structurally rigid, weakly coupled molecular dimer can replace traditional monomeric annihilators for triplet fusion upconversion (TUC) in solution by observing emitted photons (λ = 540 nm) from a norbornyl-bridged tetracene homodimer following excitation of a triplet sensitizer at λ = 730 nm. Intriguingly, steady-state spectroscopy, kinetic simulations, and Stern−Volmer quenching experiments show that the dimer exhibits qualitatively different photophysics than its parent monomer: it is less effective at diffusion-mediated triplet exciton transfer, but it fuses extracted triplets more efficiently. Our results support the development of composite triplet-fusion platforms that go beyond diffusion-mediated triplet extraction, ultimately circumventing the concentration dependence of solution-phase TUC.



Photon upconversion (UC) refers to a range of strategies that generate high-energy photons by combining the energies of multiple low-energy photons.[1−3] It is a form of spectral management that could enhance solar energy harvesting, infrared sensing,[4] and photocatalysis.[1,5] UC is particularly attractive as a bioimaging technique, because anti-Stokes wavelength conversion could enable in vivo imaging free from background endogenous fluorescence.[6,7] Triplet fusion (TF), also referred to as triplet−triplet annihilation (TTA), is a photophysical phenomenon employed to achieve excitonic photon upconversion.[4,8−10] Triplet fusion upconversion (TUC) uses long-lived, triplet (spin 1) excited states in molecular species to store photoexcitations until a beneficial energy outlet can be found, thus reducing the intensity of incident light required for efficient performance.[11] However, spin selection rules dictate that triplet excitons must be donated by a sensitizing species capable of efficiently converting directly photoexcited singlet (spin 0) excitons to triplets via intersystem crossing (ISC).[12] Sensitizing species presently include coordination complexes,[2,3,13−15] molecular oxygen,[16] and emerging colloidal semiconducting nanocrystals,[4,10,17−19] which can all have higher absorption cross sections than those of conventional lanthanide-doped upconversion nanoparticles.[1] Sensitizing species then transfer this triplet energy to an acceptor species through a Dexter mechanism.[20] TUC occurs once two triplet excitons meet and form a higher-energy spin-singlet excitation that can emit a photon, the probability of which is influenced by spin-statistical factors.[21,22] Thus, the overall result of excitonic upconversion is the emission of one high-energy photon from the input of two incident, low-energy, photons, which has even been achieved at subsolar irradiance thresholds.[23−26]

TUC using free-floating molecular acceptor/annihilator/emitters (hereafter annihilators) and sensitizers in solution is a leading strategy for incoherent photon upconversion, as molecular diffusion effectively achieves the long-range transport of photoexcitations that promotes triplet fusion.[13] However, it is challenging to directly apply this approach in vivo, due in part to the dependence on controlled molecular concentrations.[27] Consequently, researchers have begun to design TUC platforms that circumvent diffusive steps.[24,28,29] The recent syntheses of structurally rigid acene dimers with weak electronic coupling for the study of singlet exciton fission offers an attractive new class of candidate materials for this effort.[30−34] This molecular architecture avoids excimeric effects and strong interchromophore electronic coupling,[35] and so preserves the advantageous long triplet lifetimes and high emissive yields of proven monomeric annihilators. Though some degree of electronic coupling must exist (at least transiently) for TF to occur, the recent demonstrations of efficient singlet fission in many molecular dimers suggests that this is readily attained.[32,36−40]

Here, we explore a recently synthesized, rigid triisopropylsilylethynyl-functionalized norbornyl-bridged bistetracene (TIPS-BTc) dimer as a novel annihilator for excitonic upconversion (Scheme 1).[41] Weak electronic coupling of this molecule was established in prior studies,[30−33] and it is supported by both the lack of splitting in the dimer emission spectra (Figures 1A and S1)[31,35] as well as the minimal modification of the relative heights of the 0 → 0 to 0 → 1

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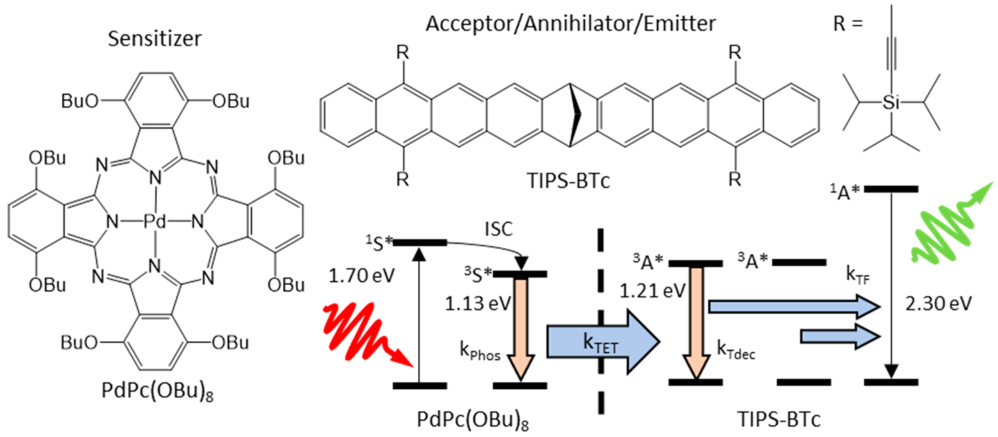
Scheme 1. Molecular Diagrams of Triplet Sensitizer ($PdPc(OBu)_8$) and Dimeric Acceptor/Annihilator/Emitter (TIPS-BTc)[a]



[a] Energetic diagram of triplet fusion mechanism, including states, energies, and rate constants of interest. Orange arrows indicate parasitic processes, whereas blue arrows indicate beneficial energy transfer steps.

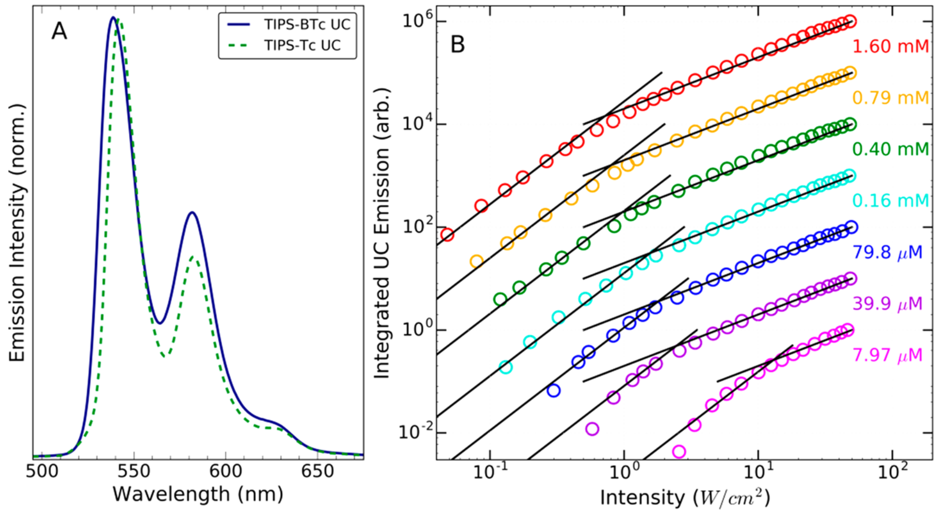


Figure 1. (A) Upconverted emission spectrum from TIPS-BTc and TIPS-Tc annihilators. (B) Intensity dependence of upconverted emission (spectrally integrated) from TIPS-BTc solutions with a range of annihilator concentrations while maintaining a constant concentration (7.25×10^{-5} M) of the $PdPc(OBu)_8$ sensitizer.

vibronic features in the dimer relative to the monomer.[42] We observe upconverted emission from TIPS-BTc following triplet sensitization from a well-established[2] coordination complex ($PdPc(OBu)_8$) (Figure 1A; see the Supporting Information for Methods). The UC emission spectrum from TIPS-BTc is identical to directly excited fluorescence, and closely resembles emission from TIPS-Tc monomers (Figure S1) while having a comparably high PLQY (Table S1).[30,32] These results validate the concept of rigid, weakly coupled dimeric annihilators for upconversion.

To evaluate TIPS-BTc, we compare its performance to two established annihilator molecules, a TIPS-functionalized tetracene (TIPS-Tc) monomer and the ubiquitous rubrene (Scheme S1). We observe upconverted emission from all three species following sensitization from $PdPc(OBu)_8$ (Figures 1A and S1). This occurs despite the expectation that triplet transfer from $PdPc(OBu)_8$ (T_1 = 1.13 eV from phosphorescence, Figure S1) to the three annihilator species (TIPS-BTc, TIPS-Tc, and rubrene, T_1 = 1.21, 1.21, and 1.14, respectively[8,43]) is slightly endothermic. Though the emission spectra of all three annihilators show spectral shifts that indicate reabsorption at the highest concentrations (Figure S2A,C,E), the time-resolved emission dynamics are unchanged (Figure S2B,D,F), which is consistent with minimal aggregation.

The UC emission power dependence is also qualitatively consistent with diffusion-limited TUC for TIPS-BTc (Figure 1B) and the two established annihilators (Figure S4). Typically, at low incident power densities, a portion of triplet excitations decay through nonradiative, monomolecular pathways before an annihilation partner can be found, resulting in a quadratic dependence of the UC emission on the excitation fluence.[11] Maximum UC efficiency occurs above a threshold excitation intensity where nearly all sensitized triplets find an annihilation partner, and UC emission varies linearly with the excitation fluence.[11,13] TIPS-BTc clearly shows this threshold behavior at a range of incident intensities that depend on the annihilator concentration (Figure 1B). For any fixed sensitizer concentration (here, [$PdPc(OBu)_8$] = 72.5 μM), lower annihilator concentrations require greater incident power to achieve max-efficiency UC. However, elevated annihilator concentrations eventually achieve diminishing returns and

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improvements to the threshold for max-efficiency performance approach an asymptote for all three annihilators (Figure 2A). Specifically, we observe that the threshold for TIPS-BTc asymptotes at an incident irradiance of 1.9 ± 0.7 W/cm^2 (standard error of nine trials in the asymptotic regime), which is comparable to other annihilators studied using the same sensitizer at similar concentrations.[8,28,44] These results provide proof-of-concept evidence that a rigid, weakly coupled dimeric annihilator can achieve TUC on par with established systems.

However, Figure 2A highlights that the threshold for TIPS-BTc sharply asymptotes for annihilator concentrations above 0.3 mM, while the thresholds for monomeric controls continue to decrease gradually at our highest experimental concentrations. This asymptotic behavior of the *threshold* is expected to occur when there are enough ground-state annihilators to extract substantially all triplet excitations from the sensitizer, beyond which additional ground-state annihilators have little effect. This is because if the rate constant for triplet fusion does not have explicit concentration dependence, the absolute concentration of triplet-excited annihilators ([$^3A^*$]) required to achieve max-efficiency upconversion is constant for a given molecule (Figure S7A). Then, because diffusion-mediated TET from the sensitizer is first-order in [A], the necessary [$^3A^*$] is achieved at lower light intensities for higher annihilator concentrations (see Figures S9−S13). This behavior is distinct from that in previous studies of saturable UC brightness[45,46] arising when the triplet supply (due to excitation intensity and/or sensitizer concentration) exceeds the capacity of the ground-state annihilator population. Indeed, the overall UC brightness does not saturate at our experimental concentrations (Figure S5).

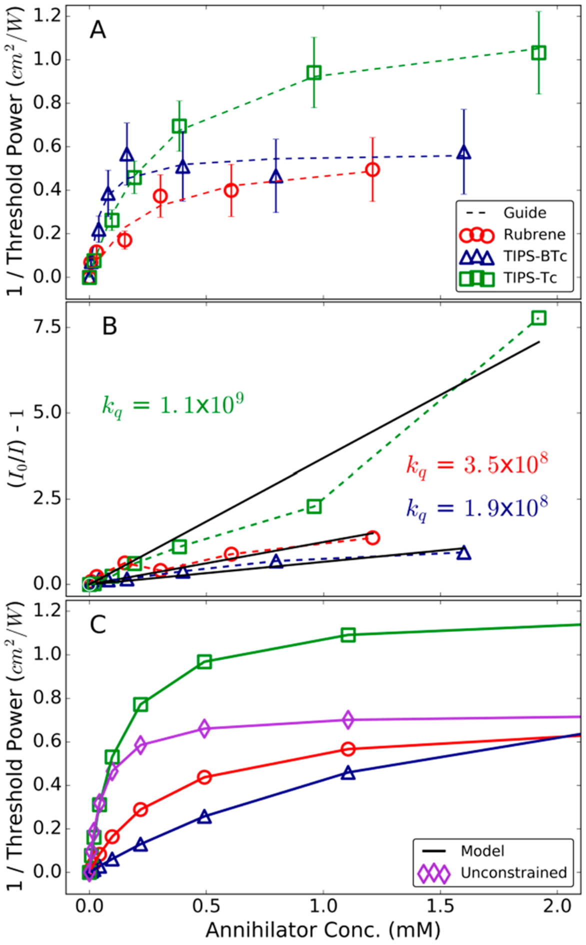

Figure 2. (A) Concentration dependence of the max-efficiency UC threshold. The dependent variable is presented as the reciprocal of threshold power for clarity. Error bars represent the standard error across repeated measurements (n = 3), and dashed curves are guides to the eye. (B) Stern−Volmer phosphorescence quenching of the PdPc(OBu)$_8$ sensitizer by three annihilators. The fitted slope is equal to $k_q\tau$, where τ is the phosphorescent lifetime of the PdPc(OBu)$_8$ sensitizer (3.5 μs).[58] (C) Simulated concentration dependence of the max-efficiency UC threshold, where k_{TET} are extracted from our Stern−Volmer phosphorescence quenching measurements and k_{TF} is fitted. The unconstrained (violet) curve uses free-fit k_{TET} and k_{TF} to best reproduce the experimental TIPS-BTc curve (see the Supporting Information).

To clarify the contributions of triplet supply to overall TUC dynamics, we performed Stern−Volmer experiments to explore the triplet transfer from PdPc(OBu)$_8$ to each of the annihilators. We extracted quenching rate constants for each system by monitoring the sensitizer phosphorescence as a function of the annihilator concentration (Figure 2B). The quenching rate constant is the upper bound on the rate constant of triplet transfer, and, as discussed further below, for the purposes of our analysis we assert that $k_q = k_{\mathrm{TET}}$, i.e., all phosphorescence quenching arises from TET. We observe that $k_{\mathrm{TET}} = 1.9 \times 10^8$ M^{-1} s^{-1} for TIPS-BTc, which is 2−5 times lower than that for the monomeric annihilators (rubrene: $k_{\mathrm{TET}} = 3.5 \times 10^8$ M^{-1} s^{-1}, TIPS-Tc: $k_{\mathrm{TET}} = 1.1 \times 10^9$ M^{-1} s^{-1}). This is distinct from the slight enhancements previously observed in two flexible, multichromophoric annihilators,[28,47] but it may reflect slight additional endothermicity of TET to the dimer relative to the monomer (Figure 1A) as well as the slow diffusion dynamics expected due to the increased molecular size of the dimer (MW = 1213 g/mol) compared to the monomers (MW rubrene = 533 g/mol, MW TIPS-Tc 589 g/mol),[48] in addition to the possible steric hindrance of TET given the nonplanar molecular structure of the rigid dimer. However, our finding that the dimer is a weaker triplet extractor than the two monomers runs contrary to the intuitive explanation of the unusually low concentrations at which the threshold of the dimeric annihilator asymptotes, which would instead be consistent with very efficient TET.

To construct a more rigorous understanding of the unusual behavior of the dimer, we extend a kinetic model for diffusion-mediated upconversion from the work of Haefele and co-workers, incorporating literature parameters and values from our own measurements.[11,21] The full derivation is included in the Supporting Information. In brief, we consider that the UC emission intensity (brightness, N_{f}) under steady-state excitation is given by

$$N_{\mathrm{f}} = \eta_{\mathrm{f}}(k_{\mathrm{TF}}[^3A^*]^2 + k_{\mathrm{HF}}[^3A^*][^3S^*]) \qquad (1)$$

Here, η_{f} is a proportionality constant that includes the direct excitation photoluminescence quantum yield (PLQY) of the annihilator and spin statistical factors[11,49,50] and k_{TF} is the TF bimolecular rate constant. In light of the unexpected behavior of the dimer, we extended the model by explicitly including a channel for heterogeneous fusion from the collision of excited-state annihilators [$^3A^*$] with excited-state sensitizers [$^3S^*$]. The rate constant for this heterofusion is k_{HF}, and we implicitly assume that heterofusion and homofusion generate annihilator emission with equal efficiency to capture the greatest plausible effect that heterofusion would have on our observables (see the

Supporting Information for further discussion). In the interests of a parsimonious model, and motivated by the rapid time scales of energy transfer, thermalization, and triplet fusion, we made the assumption that each bimolecular interaction is diffusion-limited, i.e., where any molecules that come into close proximity reach their photophysical end points.[51] In this limit, the processes of (1) energy transfer from an excited sensitizer to a ground-state annihilator and (2) heterofusion between an excited sensitizer and an excited annihilator are viewed similarly because they involve similar molecular diffusivities/sterics. Under these assumptions, $k_{\mathrm{HF}} = \frac{1}{4}k_{\mathrm{TET}}$, where k_{TET} can be measured via Stern−Volmer experiments. The factor of a quarter arises in the following way. First, the overall-quintet triplet pair states (^5TT) are neglected under the now-common assumption that they are energetically inaccessible[49] (though this is called into question below). Of the four remaining pathways that will deplete the sensitizer, only the one generating the overall-singlet triplet pair (^1TT) will ultimately leave the triplet-excited annihilator in the ground state following photon emission. By contrast, interactions generating multiexcitonic states in the triplet manifold (^3TT) would then undergo rapid internal conversion and leave the concentration of triplet-excited annihilators unchanged following thermalization.[21,49,52]

In turn, we obtain $[^3A^*]$ from the steady-state limit of the following rate equation:

$$\frac{\mathrm{d}[^3A^*]_{\mathrm{t}}}{\mathrm{d}t} = -k_{\mathrm{TF}}[^3A^*]_{\mathrm{t}}^{\,2} - \frac{1}{4}k_{\mathrm{TET}}[^3A^*]_{\mathrm{t}}[^3S^*]_{\mathrm{t}} - k_{T\mathrm{dec}}[^3A^*]_{\mathrm{t}} + k_{\mathrm{TET}}[A]_t[^3S^*]_{\mathrm{t}} \qquad (2)$$

Here, $k_{T\mathrm{dec}}$ is the rate constant encompassing all monomolecular decay processes for triplet-excited annihilators, k_{TET} is the rate constant for TET from sensitizer to the annihilator species in either the ground state, $[A]_t$, or excited state, $[^3A^*]_t$, and $[^3S^*]$ is the concentration of triplet-excited sensitizers. Importantly, $[^3S^*]$ is related to experimental parameters by a final rate equation (see the Supporting Information), varies linearly with the incident laser intensity in the low occupation limit, and is fractionally suppressed by bleaching/state-filling as $[^3S^*] \to [S_0]$.[50] We again include a heterogeneous fusion term ($\propto[^3A^*]_{\mathrm{t}}[^3S^*]_{\mathrm{t}}$) with a spin-statistical factor. Notably, our model implicitly captures any transient two-triplet occupation of dimers if our basic assumptions holds: that intramolecular TF (whether yielding a singlet, or higher-lying triplet excitation) is fast compared to any diffusional interactions. (See the Supporting Information for additional discussion.)

Our kinetic simulations (see Figures S6−S14 and Tables S2−S7) validate the intuitive understanding that larger values of k_{TET} accelerate the asymptotic behavior of the threshold for max-efficiency upconversion with annihilator concentration (Figure S13). Indeed, we find that this is the only TUC parameter that affects the functional form of this dependence, so plots of this particular relationship are incisive. Further, this approach is experimentally advantageous, as this relative measurement of the concentration-dependent threshold is insensitive to an overall scaling of the brightness or excitation/detection efficiency, and thus permits the convenient comparison of material properties.

As shown in Figure 2C and Table S8, the kinetic model accurately reproduces the concentration-dependence of the threshold for monomeric annihilators using k_{TET} extracted directly from our Stern−Volmer experiments, literature values for $k_{T\mathrm{dec}}$, and best-fit k_{TF} values that are consistent with previous reports.[13] However, it is important to note that the sharply asymptoting experimental data from TIPS-BTc (Figure 2A) can only be reproduced (Figure 2C, violet curve) with a rate constant for TET ($k_{\mathrm{TET}} = 1.00 \times 10^{10}$ M^{-1} s^{-1}) that is 2 orders of magnitude higher than what was extracted from our Stern−Volmer experiments. Qualitatively, the rapid rise and asymptoting of the threshold with dimer concentration would suggest an efficient triplet extractor (high k_{TET}) but inefficient triplet fuser (low k_{TF}). However, this is counterintuitive for a dimer, given the expected slower diffusion and the lower observed k_{TET}. Further, this shows that our assertion that $k_{\mathrm{TET}} = k_{\mathrm{q}}$ is conservative for evaluating the performance of the dimeric species. k_{TET} cannot be greater than k_{q}, and any other triplet quenching processes (not contributing to UC) influencing the Stern−Volmer measurement would lower our estimate for k_{TET}. This would lead to a more slowly rising curve, all things equal, and hence is not able to explain the sharp rise/hard saturation of the TIPS-BTc curve. Thus, we consider that the UC dynamics of the dimeric system involve factors beyond our model.

We specifically considered two possible additional extensions to our model. First, we examined the dependence on our assumptions around heterofusion, given that our model estimated that heterofusion interactions could be up to 80% of sensitizer-annihilator interactions. However, this only occurred at the limit of lowest-annihilator-concentrations/highest-excitation-intensities where UC efficiency is low (Figures S6−S8 and discussion). Further, though the heterofusion channel increased the simulated UC brightness under these conditions, it did not significantly alter the functional dependence of the threshold on the annihilator concentration, compared to a model where heterofusion was neglected (Figure S10). As a result, though we cannot rule out this possibility, we do not expect that heterofusion accounts for the anomalous behavior of the dimer. Then, intriguingly, we noted that our model would break down in a specific case involving triplet-pair states in the quintet manifold (i.e., ^5TT), which may be thermally accessible in TIPS-BTc.[32] If so, and if the coupling between ^5TT and ^1TT is preferred to the coupling between ^5TT and ^3TT (suggested by wave function symmetry),[53,54] we hypothesize that additional upconversion emission could be indirectly generated via ^5TT states at low concentrations, where the average time between annihilator collisions is longer than the spin-dephasing time of a triplet-pair on a single dimer.[53−55] However, our present experiments do not robustly test this hypothesis. (See Supporting Information for additional discussion.)

Despite the dimer being the weakest triplet extractor (Figure 2B) and the ambiguity in the fusion mechanism, we observe that the TIPS-BTc annihilator yields brighter UC emission than either monomer when at comparable concentrations <0.5 mM (Figures 3A and S5). This occurs even though the photoluminescence quantum yield of the dimer is lower than rubrene (Table S1). The advantage is even more apparent when controlling for the flux of extracted triplets (Figure 3B) and persists when excited in the max-efficiency regime (>10 W/cm^2). When considering the overall concentration-dependent UC brightness as a function of extracted triplets (Figure 3C), it is clear that TIPS-BTc fuses extracted triplet excitons more efficiently than either monomer, especially at low concentrations. Instead, a present limit to its overall brightness

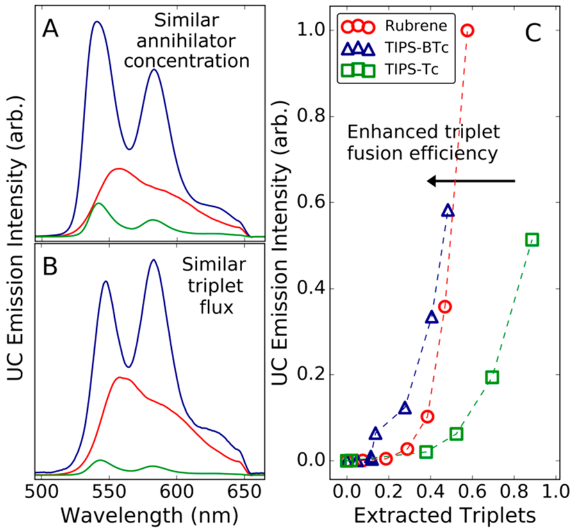

Figure 3. (A) Upconversion emission intensity using similarly low concentrations of each annihilator in solution ([TIPS-BTc] = 0.16 mM, [rubrene] = 0.15 mM, [TIPS-Tc] = 0.19 mM). All spectra are normalized to the peak of the strongest absolute emission spectrum (TIPS-BTc). (B) Upconversion emission intensity similar sensitizer quenching efficiencies for each annihilator (TIPS-BTc, 48%; rubrene, 47%; TIPS-Tc, 52%), indicating a comparable triplet flux. All spectra are normalized to the best performer (TIPS-BTc). (C) Upconversion brightness as a function of triplet excitations extracted from the sensitizer population estimated from phosphorescence quenching. The TIPS-BTc dimer generates upconverted emission more efficiently from a given triplet flux but is a less effective triplet extractor.

is its poor ability to quantitatively extract triplets from the sensitizer at our highest experimental concentrations. The striking advantage in the fusion efficiency of the dimeric TIPS-BTc over the monomeric TIPS-Tc is consistent with a distinct fusion mechanism.

In this work, we have shown that a rigid, weakly coupled TIPS-BTc dimeric annihilator can achieve triplet fusion upconversion. We observe that TIPS-BTc results in greater UC brightness than either monomeric control for a given triplet flux from a coordination complex sensitizer. This indicates that the dimer is an efficient triplet fuser (most notably compared to its parent monomer) and the improved triplet usage efficiency is consistent with a dissimilar TUC pathway. Further, introducing a convenient experimental paradigm for comparing conventional annihilators, we find that the max-efficiency threshold for this material asymptotes at lower concentrations than those of conventional monomeric annihilators. We built a kinetic model that successfully reproduces the experimental intensity- and annihilator-concentration-dependences of TUC in two monomeric controls with few assumptions and parameters that are consistent with literature.[11,13] However, for dimeric TIPS-BTc, we were unable to reconcile the experimentally observed concentration-dependent threshold for max-efficiency TUC and Stern−Volmer measurements of triplet transfer. This indicates that the mechanism of TUC in the dimer is more complex, and we speculate that the overall-quintet triplet-pair state may play a beneficial role. Our findings establish TIPS-BTc as an attractive triplet-fusion platform, and will motivate further photophysical experiments and extensions of the conventional kinetic treatment. Further, since TIPS-BTc fuses triplet excitons more efficiently than both TIPS-Tc and rubrene do, developing a composite system that circumvents its less-efficient diffusion-mediated triplet extraction would maximize this advantage. Recent experiments in TUC have explored the use of colloidal quantum dots as triplet sensitizing species, due to their high absorption cross section, synthetic tunability, and modifiable surface chemistry.[4,10,56,57] As a result, we encourage the development of "all-in-one" TUC systems, wherein a quantum dot sensitizer with a dimer-functionalized surface could provide a path to diffusionless UC by bringing the sensitizer and annihilator within close proximity and provide the opportunity to study unconventional intramolecular TF pathways.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.9b03115.

> Materials and methods; concentration- and excitation-intensity-dependent linear absorption and emission spectra; concentration-dependent photoluminescence dynamics of annihilators; intensity- and concentration-dependent upconversion data for monomeric annihilators; derivation and supplemental results of kinetic model for upconversion (PDF)

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Notes

The authors declare no competing financial interest.

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