

Diffusion-Free Intramolecular Triplet–Triplet Annihilation in Engineered Conjugated Chromophores for Sensitized Photon Upconversion

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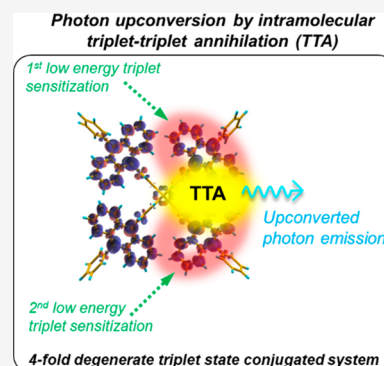


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Supporting Information

ABSTRACT: The photon upconversion based on sensitized triplet–triplet annihilation (s TTA-UC) is a spin-flip mechanism exploited to recover the energy stored on dark triplet states in conjugated systems. In this process, a high-energy fluorescent singlet is created through the collision and fusion of two low-energy triplets belonging to different diffusing molecules. Its high yield in solution under low excitation intensity and noncoherent light highlighted the huge potential of s TTA-UC to provide a breakthrough in solar technologies. However, its diffusion-limited nature restrains its efficiency in the solid state. To overcome this issue, we propose a single-molecule system that is able to host simultaneously more than one triplet, thus enabling a diffusion-free intramolecular TTA. We obtain the first direct demonstration of intramolecular triplet fusion by tailored photoluminescence spectroscopy experiments, thus opening the way to realize a new family of single-molecule upconverters with huge potential in solar and lighting technologies by accessing the natural triplets' energy reservoir.



Organic conjugated materials feature unique interactions with near-ultraviolet, visible, and near-infrared photons, thus enabling discovery of new fundamental physics as well as sustainable technological applications. Very recent literature demonstrates their huge potential to manage the energy of the absorbed photons by exploiting spin-flip mechanisms involving triplet states like singlet fission, thermally activated delayed fluorescence, and intersystem crossing (ISC) enhanced phosphorescence. Indeed, the most recent advancements in both molecular materials and organic devices are related to triplet mediated processes capable of boosting the efficiency of silicon solar cells,¹ enabling the fabrication of vivid and low-consuming OLEDs^{2–4} as well as cheap, light, and easy-to-handle screens for broad use in daily noninvasive diagnostics.^{5,6} Innovative photochemistry was also reported.⁷

Among spin-flip photophysical processes, the mechanism of photon upconversion based on sensitized triplet–triplet annihilation (s TTA-UC) has been extensively investigated in multicomponent solution systems in the past decade. As shown in Figure 1A, generally in this case, the photon upconversion is the result of the fusion of the metastable triplet state of two different annihilator/emitter molecules upon diffusion-medi-

ated collision (i.e., an intermolecular TTA), which results in the formation of a high-energy singlet excited state that decays radiatively. The emitter triplets are populated via energy transfer (ET) from the triplets of a low-energy absorbing molecule (or functionalized nanocrystal), that is, a light-harvester/sensitizer.^{8–12} Due to its excellent yield in optimized systems surpassing 30%—close to the thermodynamic limit of 50%—under low excitation intensity comparable to the solar irradiance,^{13,14} and considering its efficiency also under noncoherent light, the s TTA-UC surpasses the limitations of traditional photon upconversion mechanisms, such as two-photon absorption or sequential excited-state absorption, that requires coherent and/or high-intensity radiation to be efficient.^{15,16} For such reasons, the s TTA-UC is intensively investigated to provide a breakthrough in solar technolo-

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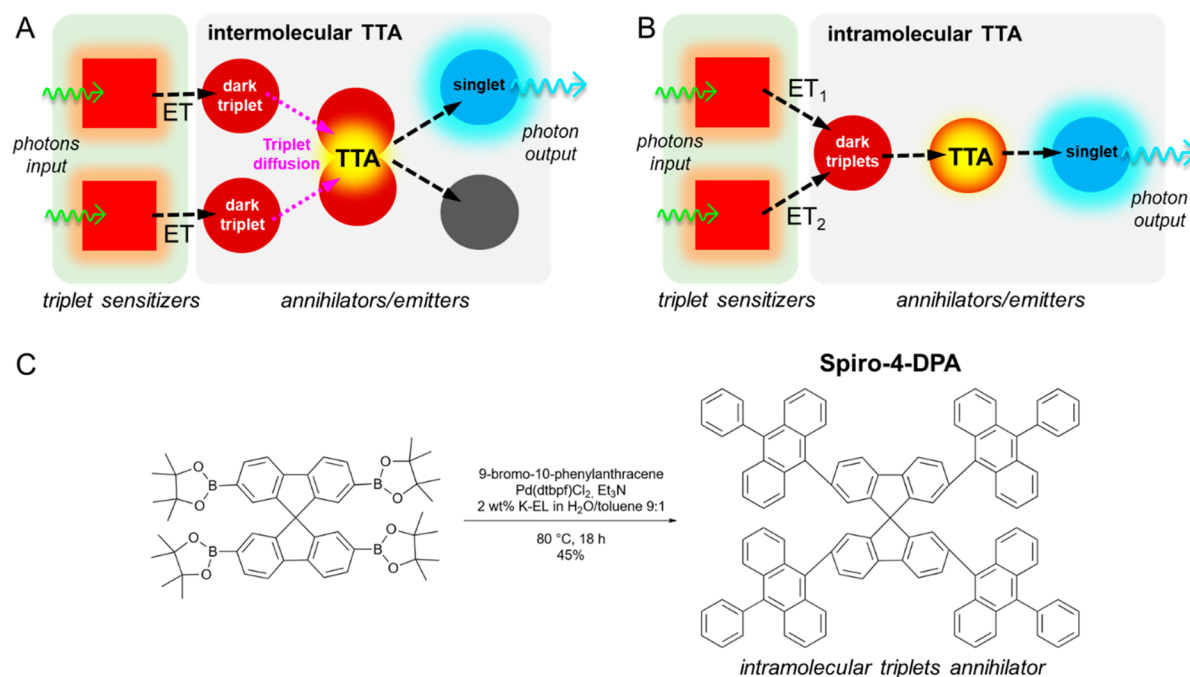


Figure 1. Principles of photon upconversion based on sensitized triplet–triplet annihilation (sTTA-UC). (A) In the standard intermolecular upconversion mechanism, the dark triplets of two emitter moieties are excited independently by energy transfer (ET) from excited triplet sensitizers that absorb low energy photons (green arrows). During their random diffusion, the two emitters can collide and experience intermolecular TTA, generating an emitting singlet state from which upconverted emission is produced (blue arrow). (B) If two triplets can be generated on the same emitter by a subsequent two-step energy transfer (ET_1 and ET_2), the intramolecular TTA process can occur without the need of any diffusion of the annihilating triplets. (C) Synthetic route and molecular structure of the conjugated Spiro-4-DPA system designed for intramolecular TTA.

gies,^{12,17–19} low power bioimaging,^{20,21} optogenetics,²² anti-counterfeiting,²³ and oxygen sensing applications.²⁴ Nevertheless, achieving sTTA-UC in the solid state—which is more technologically manageable to make devices—is still an open challenge. Indeed, the sensitized TTA mechanism is a diffusion-limited bimolecular process; thus, its effectiveness in solids is hindered by several factors such as poor excitons' mobility, aggregation and phase segregation effects, and excited-state quenching²⁵ that can heavily affect both the energy transfer from sensitizers and the TTA steps. Many efforts have been concentrated in developing solid upconverters, with encouraging results obtained with nanoparticles,^{26,27} nanocrystals,^{28,29} polymeric films,^{30,31} cocrystals³² and multi-layer devices,³³ all of them able to partially overcome the triplets' diffusion limits.^{34–36} In several cases, different sensitizer systems have also been introduced to realize better solid-state upconverters such as semiconductor quantum dots^{37,38} and more recently perovskites nanocrystals.^{10,12,39}

From a general perspective, regardless of the nature of the sensitizer and annihilator moieties employed, the confinement in colloidal nanostructures of both the optically active components is a winning approach in mitigating at least the diffusion dependency of the TTA yield (i.e., half of the problem) by exploiting the confined-TTA process.⁴⁰ This mechanism can be observed when triplets are sensitized and physically confined in discrete volumes that are smaller than the space potentially explored by their random diffusion. When two emitter triplets are simultaneously created in such a confined space, they can decay only by annihilation, with a resulting TTA efficiency of 100% and potentially reaching the maximum conversion efficiency at excitation intensities lower than in the classical bulk counterpart, because their confined

diffusion does not allow to avoid collision with the other triplet.^{28,29,41,42} Notably, the confined-TTA can also occur in large molecular structures or polymeric systems where triplet hopping is still permitted between the annihilator units included,^{43–46} but it is still a diffusion-mediated process.

An intramolecular TTA mechanism pushes the limits of this approach. In this case, two triplet excitons are simultaneously created on the same annihilator and can experience TTA without diffusing, thus overcoming straightforwardly any related issues (Figure 1B). Some recently obtained evidence hint the existence of this process,^{43,47–50} but a clear-cut demonstration is missing, especially of the existence of molecular systems showing the intrinsic ability to host multiple triplets that enables their instantaneous annihilation and the creation of upconverted high energy states by an intrinsic diffusion-free intramolecular TTA process.

We report here the direct observation of intramolecular triplet fusion by TTA (*intra*-TTA) in the single-molecule conjugated acceptor 2,2',7,7'-tetrakis(10-phenyl-anthracen-9-yl)-9,9'-spirobifluorene (Spiro-4-DPA). The system has been designed to allow the simultaneous coexistence of more than one independent triplet molecular exciton. As shown in Figure 1B, upon a first energy transfer event (ET_1) from a sensitizer, one of the equivalent triplets is populated while the remaining triplet orbitals can host a second energy transfer event (ET_2), thus creating simultaneously two triplet excitons on the same molecule and enabling their localized interaction and annihilation, in agreement with the analysis of its quantum mechanical properties. The demonstration of this intramolecular TTA mechanism is obtained by steady-state and time-resolved photoluminescence spectroscopy experiments on the upconverted emission, finely tailored to clearly distinguish

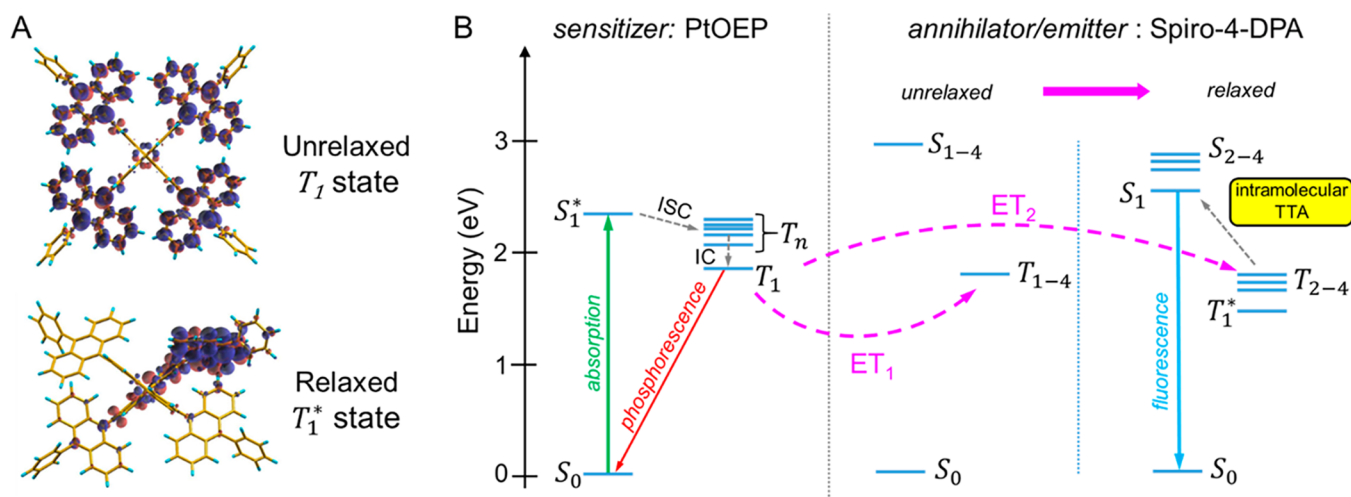


Figure 2. Photophysics of photon upconversion based on intramolecular triplet–triplet annihilation (TTA). (A) Transition densities for the unrelaxed (T_1 , ground state geometry) and relaxed (T_1 , excited molecule) triplet state of the conjugated Spiro-4-DPA molecule proposed as annihilator/emitter. (B) Energy-level diagram and sketch of the energy flux for the intramolecular TTA upconversion process. Dashed arrows mark radiationless transitions. The sensitizer molecule PtOEP is excited into a singlet state S_1 that undergoes intersystem crossing (ISC) into its triplet state manifold T_2 – T_6 . The system then relaxes by nonradiative internal conversion (IC) to the lower triplet state T_1 . Energy transfer (ET_1) then occurs to the annihilator/emitter triplet T_1 , which is 4-fold degenerate in the ground state. For clarity, the competitive back-ET to sensitizers triplets is omitted here due to its negligible efficiency. The emitter molecule then relaxes to a distorted excited state configuration where three triplet states (T_2 , T_3 , T_4) are still available to harvest a second excitation from sensitizers by ET_2 . If the two triplets are simultaneously present on a single emitter molecule, they fuse by TTA and generate a high-energy singlet-state S_1 , whose spontaneous recombination to the ground state produces the upconverted fluorescence.

intra- from intermolecular TTA thanks to the inherently different dynamics of the two phenomena. Our results unequivocally demonstrate the possibility of achieving multiple triplet excitations injected in the same molecule within a time span compatible with the triplet spontaneous lifetime, therefore allowing a diffusion-free instantaneous TTA. This is a crucial step toward the realization of single-molecule upconverters that could have disrupting applications in solar and lighting technologies profiting from the energy naturally stored in the omnipresent metastable triplets of conjugated systems.

The Spiro-4-DPA system has been synthesized by a micellar catalyzed Suzuki–Miyaura coupling between 2,2',7,7'-tetrakis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobifluorene and 9-bromo-10-phenylanthracene performed in water solution of the industrial surfactant Kolliphor EL (K-EL) in the presence of a small amount of toluene. The product can be isolated by filtration and further purified by crystallization from toluene. Overall, the process is simple, efficient, and requires minimal amounts of organic solvents. Figure 1C summarizes the synthetic route exploited and the molecular structure of the conjugated annihilator Spiro-4-DPA. Synthesis details and structural characterization are reported in the Supporting Information file (Supplementary Figures S1–S5). In optimized geometry, the use of the *spiro* linking center that exploits a compact sp^3 hybridized carbon atom makes the center-to-center distance between DPA lobes as short as 1.1 nm, thus fully enabling a localized TTA process.

Figure 2A shows the calculated transition densities to unravel the spatial distribution of excited states.^{51,52} In particular, we focus on changes on the T_1 triplet state of Spiro-4-DPA by comparing the transition density just after the first ET (top), when the unrelaxed molecule retains the symmetrical structure of its ground state, to that calculated after the structural relaxation of the same excited state

(bottom). Accordingly, panel B reports the calculated energy level diagram for the upconversion system investigated, where the Pt(II)-octaethyl porphyrin (PtOEP) is employed as triplet sensitizer.²⁷ Transition densities and electronic energies are calculated in the framework of time-dependent density functional theory (TD-DFT), as detailed in the Supporting Information file.⁵³ Computational results are in excellent agreement with experiments, yielding a ground-state absorption maximum at 3.16 eV (393 nm) with respect to the measured 3.11 eV (398 nm), as well as a fluorescence peak predicted at 2.95 eV (421 nm) vs the 2.92 eV (424 nm) observed (Figure S6). Control calculations performed on the reference 9,10-diphenylanthracene (DPA) molecule further confirm the reliability of the quantum mechanical modeling employed also for the estimation of the triplet-state energies (Figures S6, S7). The obtained results point out a crucial feature of the system, a particularly weak coupling between the four equivalent DPA units in the ground state. As a result, the triplet-state T_1 is delocalized over the entire molecule (Figure 2A, top), but its energy of 1.75 eV is only marginally different from that of 1.77 eV of an isolated DPA (Supplementary Table S1). The excitation energy transfer (ET_1) from the PtOEP triplet at 1.94 eV to T_1 is thus energetically favorable in both cases. Now, it is worth noting that the Spiro-4-DPA system belongs to the S_4 symmetry group (Supplementary Table S2), which does not imply any intrinsic 4-fold degeneracy of orbitals.⁵⁴ However, in the symmetrical ground state, the frontier orbitals display a close accidental 4-fold degeneracy, which is reflected on excited singlet (S_1 – S_4) and triplet (T_1 – T_4) states, because of the presence of four weakly coupled identical lobes. The key feature of the excited-state manifold of the Spiro-4-DPA with respect to DPA is that, after the first excitation transfer (ET_1), the populated T_1 localizes in one of the four lobes and its energy relaxes from 1.75 to 1.38 eV (Figure 2A, bottom). This process also lifts the degeneracy of

the T_2 – T_4 states, yet their energies remain in a limited 1.74–1.76 eV range (Figure 2B). Such a rearrangement makes energetically feasible the transfer of a second excitation (ET_2) from sensitizers to any one of the T_2 – T_4 states during the T_1 lifetime, while preserving the energetic constraint $T_1 + T_{2(3,4)} > S_1$ pivotal to enable the formation of a singlet upon TTA. Moreover, given that the Spiro-4-DPA van der Waals diameter is 2.82 nm (Figure S6), two neighboring DPA lobes simultaneously hosting triplet excitons are within the ~ 1 nm distance typically required for the short-range TTA mechanism.⁵⁵ Therefore, the proposed system presents all the requirements to observe a spontaneous intramolecular TTA process without the need of triplet excitons diffusion, thus overcoming the process limitations in the solid state discussed above.

Preliminarily to the upconversion experiments, we investigated the electronic and emission properties of Spiro-4-DPA in tetrahydrofuran (THF) diluted solution (10^{-6} M) by means of steady-state and time-resolved photoluminescence spectroscopy. As reported in Figure 3A, with respect to the reference DPA standard, the Spiro-4-DPA shows a slightly red-shifted absorption spectrum in the blue-near UV spectral region peaked at 389 nm, accompanied by a clearly resolved vibronic replica series at 378, 360, and 342 nm. Under UV excitation,

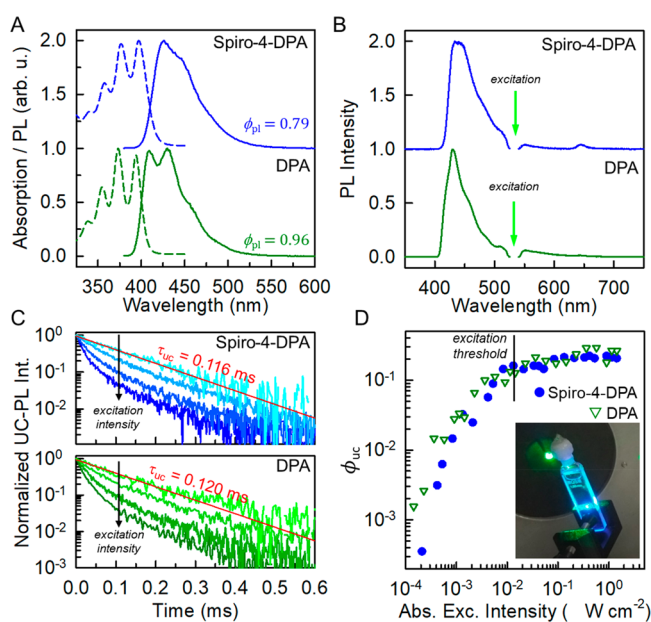


Figure 3. Fluorescence and upconversion properties of Spiro-4-DPA. (A) Normalized absorption and photoluminescence spectra under cw excitation at 350 nm of Spiro-4-DPA and reference DPA solutions (10^{-6} M) in tetrahydrofuran (THF). (B) Photoluminescence spectra of Spiro-4-DPA and DPA 10^{-2} M solutions in THF with the PtOEP (10^{-4} M) triplet sensitizers under continuous wave 532 nm laser excitation (1 W cm $^{-2}$). The weak residual laser stray light has been removed for clarity. (C) For the same solutions, upconverted photoluminescence (UC-PL) intensity decays with time at 435 nm under modulated laser excitation at 532 nm (500 Hz, duty cycle 50%) as a function of the excitation intensity from 10^{-3} W cm $^{-2}$ to 5 W cm $^{-2}$. Solid lines are the fit with a single exponential decay function with a characteristic decay time of τ_{uc} . (D) For the same solutions, upconversion quantum efficiency (ϕ_{uc}) as a function of the absorbed excitation intensity under cw laser excitation at 532 nm. The vertical line marks the excitation intensity threshold at which ϕ_{uc} is half of its maximum.

the system shows a bright blue photoluminescence, peaked at 424 nm, with an excellent quantum efficiency ϕ_{pl} of 0.79 ± 0.08 and a characteristic emission lifetime of 3.2 ns (Figure S8). These findings confirm the absence of strong coupling between the anthracene-like lobes of the Spiro-4-DPA, thus avoiding significant modification of their conjugation length and allowing to retain the excellent emission properties of the parent molecule DPA ($\phi_{pl} = 0.96$). The partial reduction of the ϕ_{pl} can be ascribed to a different efficiency of vibrational quenching pathways in the Spiro-4-DPA, thus hinting a less rigid structure with respect to DPA. We tested the Spiro-4-DPA performances as annihilator/emitter for sTTA-UC in a 10^{-2} M THF solution with PtOEP (10^{-4} M) as triplet sensitizer (Figure S10). Upon continuous wave excitation with a 532 nm laser, the bicomponent solution shows a bright blue upconverted photoluminescence (Figure 3B, inset of panel 3D, Figure S11). A minimal residual phosphorescence from PtOEP can be still observed at 645 nm, in agreement with the measured energy transfer yield ϕ_{ET} of 95% (Figure S12). The occurrence of upconversion by intermolecular TTA is demonstrated by the time-resolved photoluminescence experiments shown in Figure 3C. Under modulated excitation at 532 nm, the photoluminescence intensity at 430 nm shows a slow decay in the hundreds of microseconds time scale, with a characteristic lifetime that increases by reducing the excitation intensity. This behavior mirrors the generation of fluorescent singlets by intermolecular TTA.⁵⁶ Specifically, at the lowest excitation intensity employed of 0.1 W cm $^{-2}$, the emission intensity decays as a single exponential function with a characteristic lifetime of τ_{uc} . This means that in this excitation regime, the TTA is a negligible deactivation channel for the Spiro-4-DPA triplets; thus, the spontaneous decay time of the T_1 state can be directly calculated as twice that of τ_{uc} . This analysis gives a T_1 lifetime of 232 μ s for the Spiro-4-DPA system, very similar to the 240 μ s estimated for DPA by analyzing the upconverted emission decay of a reference DPA/PtOEP solution (Figure 3C, bottom). The suitability of Spiro-4-DPA as a triplets' annihilator is further confirmed by the measurement of the solution upconversion quantum efficiency, ϕ_{uc} , defined as the ratio between the number of upconverted photons emitted and the number of the absorbed ones.^{13,14} Figure 3D reports the observed ϕ_{uc} as a function of the absorbed excitation intensity for the Spiro-4-DPA:PtOEP solution, in direct comparison with the reference DPA:PtOEP (Figures S10, S11). Due to the bimolecular nature of the intermolecular TTA process, in both samples the ϕ_{uc} increases with the excitation intensity until it saturates to a plateau at high powers.⁵⁷ With the Spiro-4-DPA as annihilator/emitter the conversion efficiency reaches its maximum value at $\phi_{uc}^{\max} = 0.21$. Notably, this value is only barely lower than the one of the DPA:PtOEP reference solution of 0.25, in agreement with its ϕ_{pl} .

The obtained results demonstrate the possibility of using the Spiro-4-DPA as an annihilator/emitter system for sTTA-UC. When the annihilator concentration is kept very high (10^{-4} to 10^{-2} M) in order to maximize the energy transfer rate and yield, the same dependence of ϕ_{uc} vs the excitation intensity is observed using both Spiro-4-DPA and DPA because in such a condition the kinetics of the TTA is dominated by the intermolecular process, as usual in bicomponent solutions. To directly observe the possible occurrence of the intramolecular TTA mechanism, we therefore designed a dedicated experiment. The key point is the ability to create simultaneously two

triplets on the same emitter molecule. The quantum-mechanical model indicates that this is possible thanks to the Spiro-4-DPA electronic structure, but such result can be evidenced experimentally only in particular conditions. Basically, we must use a concentration of annihilators low enough to make the intermolecular TTA yield negligible. Considering the consequently low energy transfer yield from sensitizers, we must use an excitation intensity high enough to enable the efficient generation of two excitons in the same molecule within their lifetime, thus activating the intramolecular TTA and therefore having chances to detect the resulting upconverted emission. To point out the best sample composition to investigate the intramolecular phenomenon, we calculated the upconversion efficiency of the inter- and intramolecular TTA, taken as two independent processes, as a function of the excitation intensity for a series of solutions with different annihilator concentrations (Supporting Information). It is worth remembering that the intramolecular TTA obeys the kinetics of the confined-TTA,^{28,58} where the upconversion yield is determined by the binomial distribution of energy among annihilators. On the contrary, the intermolecular upconversion is classically controlled by the molecular diffusion with an efficiency which grows linearly with the excitation intensity up to its saturation value. This means that the global upconversion yield dependency on the excitation intensity is completely different in the two cases, thus enabling us to experimentally distinguish the two processes. Figure 4A shows the theoretical ϕ_{uc} values calculated for a series of upconverting solutions with annihilator concentrations ranging from 10^{-9} M up to 10^{-6} M. The efficiency curves have been plotted as a function of the excitation intensity ranging from 10^{-2} to 10^4 W cm⁻². The triplet sensitizer concentration is set at 10^{-4} M. In agreement with the confined-TTA kinetics,²⁸ the intramolecular TTA efficiency approaches very quickly the saturation to the maximum value. This is reached at approximately 1 W cm⁻², independently of the annihilator concentration because of its independence on the average distance between the annihilator molecules. Only the maximum yield increases with the Spiro-4-DPA amount following the enhancement of the energy transfer efficiency at higher annihilator concentrations (Supporting Table S3). On the other side, the curves calculated for the intermolecular TTA efficiency in the corresponding samples grow linearly with the excitation intensity, and the power required to reach the maximum efficiency plateau increases by lowering the annihilator concentration which is a direct consequence of the large average distance between two excited molecules.⁵⁷ The intra- and intermolecular mechanism behaviors can be therefore distinguished. The calculated curves indeed clearly show that for annihilator concentrations below 10^{-7} M and excitation intensities lower than the intensity threshold the probability to create two triplets on the same molecule is larger than that of bimolecular collision between two distinct excited annihilators. Thus, in this condition the intramolecular process is the dominating annihilation mechanism that could be directly observed. However, at concentrations of Spiro-4-DPA as low as 10^{-9} M the output upconverted emission signal is expected to be too weak to have reliable measurements. Accordingly, we chose as the model system a solution with 10^{-8} M of Spiro-4-DPA, where the intramolecular TTA is the dominant mechanism in the excitation range between 10^{-2} and 10^2 W cm⁻² and the energy transfer efficiency is $\sim 1\%$ (Supporting

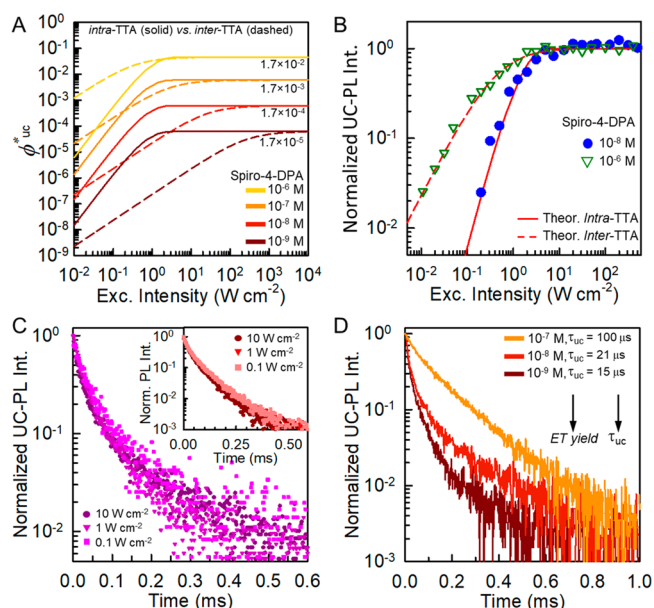


Figure 4. Modeling and observation of intramolecular triplet–triplet annihilation (TTA). (A) Calculated relative efficiencies of intermolecular (*inter*-, dashed line) and intramolecular (*intra*-, solid line) TTA in a series of THF solutions with the triplet sensitizer PtOEP (10^{-4} M, absorbance 0.45 with 0.1 cm optical path) and different concentrations of the annihilator Spiro-4-DPA as a function of the *cw* excitation intensity at 532 nm. (B) Normalized upconverted photoluminescence intensity (UC-PL) under 532 nm *cw* laser excitation for two upconverting THF solutions containing 10^{-8} M (dots) and 10^{-6} M (triangles) Spiro-4-DPA. The PtOEP concentration is fixed at 10^{-4} M. The lines are the fit of data with *intra*-TTA (solid line) and *inter*-TTA (dashed line) model functions. (C) UC-PL intensity at 435 nm as a function of time and excitation intensity with 10^{-8} M Spiro-4-DPA under modulated laser excitation at 532 nm (500 Hz, duty cycle 50%). Inset: residual phosphorescence intensity from PtOEP at 645 nm as a function of time and excitation for the same sample. (D) UC-PL intensity at 435 nm as a function of time and Spiro-4-DPA concentration under modulated laser excitation at 532 nm (5 W cm⁻², 250 Hz, duty cycle 50%).

Table S3), and a solution with 10^{-6} M of Spiro-4-DPA as the model system for the intermolecular TTA.

We investigated such upconverting solutions by steady-state photoluminescence spectroscopy. Figure 4B shows the normalized upconversion emission intensity of 10^{-8} M vs 10^{-6} M Spiro-4-DPA solutions in THF with 10^{-4} M PtOEP under *cw* laser excitation. In excellent agreement with the calculations (solid line), the efficiency of the 10^{-8} M solution increases according to the intramolecular-TTA dynamics. Conversely, the 10^{-6} M sample follows the standard behavior of the intermolecular process (dashed line) similar to the 10^{-8} M DPA upconverting solution (Figure S13). These findings strongly hint the occurrence of the intramolecular mechanism in the 10^{-8} M solution, which is then directly demonstrated with time-resolved experiments. Figure 4C shows the temporal evolution of the upconverted emission intensity under modulated laser excitation for the 10^{-8} M Spiro-4-DPA solution (see Supporting Information, section 3, Experimental Methods). In this experiment, the excitation intensity ranges from 0.1 W cm⁻² to 10 W cm⁻², thus below the excitation intensity threshold. In all the measurements, the observed upconversion lifetime is almost constant around 20 – 30 μ s, which

is a lifetime much shorter than the natural lifetime of the Spiro-4-DPA triplet (Supplementary Table S3). Therefore, despite that we are well below the excitation power threshold, the emission lifetime does not change, and it does not reflect the long natural lifetime of the triplet states involved in the upconversion process as in the classical intermolecular TTA systems. On the contrary, the observed lifetime perfectly matches the lifetime of the sensitizer PtOEP excited states, the energy reservoir from which the energy transfer takes place to populate the annihilating triplets (inset of Figure 4C and Supplementary Table S4). Conversely, the lifetime of the upconverted emission in the 10^{-8} M DPA counterpart solution changes as a function of the excitation intensity, as expected for an inter-TTA based upconversion process (Figure S13). The peculiar behavior for the Spiro-4-DPA system can be explained only by supposing an intramolecular process in which the upconversion is due to a double excitation of a single molecule by two sensitizers that transfer their energy within their excited-state lifetime. Once the two quanta of energy have been transferred, the annihilation is an instantaneous process (at least in this time range),⁵⁹ and it does not require any additional migration step as in the intermolecular TTA. Further support to this picture comes from measurements of the upconversion lifetime above the excitation intensity threshold at different Spiro-4-DPA concentrations which span from the inter- to the intramolecular regime (Figure 4D). The data show that the upconverted emission lifetime, calculated as the time at which the emission intensity is reduced by a factor $1/e$, shortens by almost 1 order of magnitude from 100 to 15 μ s decreasing the emitter amount from 10^{-7} M (intermolecular regime) down to 10^{-9} M (intramolecular regime). This means that while the rate and yield of the energy transfer from sensitizers are decreasing, the TTA rate is increasing, thus accelerating the upconverted emission intensity decay. This behavior can be ascribed only to the occurrence of intramolecular TTA. Indeed, by reducing the energy transfer yield, we also increase the mean distance between excited emitters, thus progressively switching off the intermolecular process. This usually implies an increment of the upconverted emission lifetime, because of the reduction of the intermolecular TTA rate.⁵⁶ Conversely, in our sample the emission lifetime is shortened, in agreement with the fact that, by eliminating the intermolecular pathway, we can only detect the upconverted photons generated by confined intramolecular TTA, whose effective rate is faster than the intermolecular mechanism and usually hindered by the slower processes involved.²⁸ Considering these latest findings, the full set of time-resolved photoluminescence data presented and discussed supports unambiguously the fact that, at the selected low annihilator concentrations, the sTTA-UC mechanism is dominated by the intramolecular TTA processes on single Spiro-4-DPA molecules, from which the detected upconverted photons are generated.

In summary, we designed and synthesized a new conjugated annihilator/emitter for photon upconversion based on triplet fusion capable of hosting simultaneously more than one triplet exciton, thanks to its finely tuned electronic properties. This allows us to achieve and directly observe for the first time a photon upconversion entirely ascribed to an intramolecular TTA process, thus demonstrating the possibility to realize single-molecule upconverters for diffusion-free photon managing applications. This observation is a crucial milestone toward the fabrication of new materials for applications in solid-state

devices. Indeed, the possibility to exploit an intramolecular mechanism can completely change the classical layout of sTTA-UC materials, where annihilators are usually taken in large excess with respect to sensitizers, by guiding the development of supramolecular structures including multiple sensitizers (Figure 5) to be coupled with a single intra-

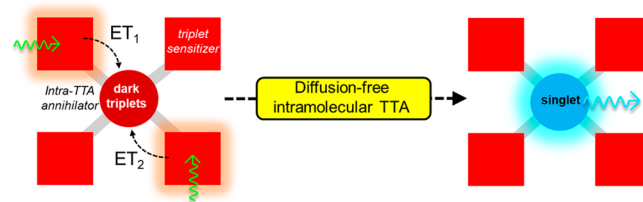


Figure 5. Photon upconversion in supramolecular systems based on intramolecular TTA mechanism. Diffusion-free photon upconversion can be achieved by coupling multiple sensitizers to a single annihilator/emitter moiety that shows intramolecular TTA. Sensitizers and emitter are therefore close packed, maximizing the energy transfer rate and enabling the creation of multiple sequential absorption of green photons.

molecular upconverter. This architecture will allow to exploit the energy of the triplets stored on a single annihilator directly sensitized by bonded light-harvesters, without any need of molecular/excitation diffusion, thus completely surpassing the actual limit of sTTA-UC application in the solid state and opening the way to alternative energetic pathways to exploit the energy naturally stored in triplet state of conjugated systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnenergylett.2c01224>.

Synthesis and characterization of Spiro-4-DPA, theoretical methods for quantum mechanical modeling, photoluminescence spectroscopy methods, modeling and additional data. Supplementary Figures S1–S12, Supplementary Tables S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

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