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Molecular Engineering of Chromophores to Enable Triplet–Triplet Annihilation Upconversion

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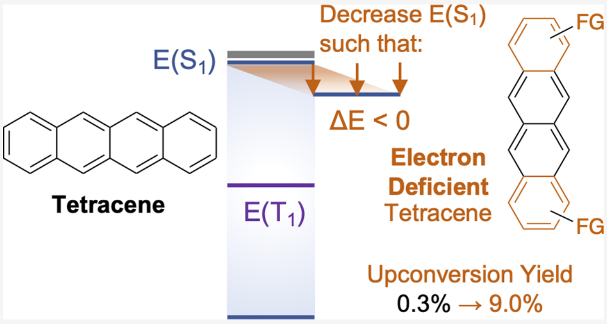
ABSTRACT: Triplet–triplet annihilation upconversion (TTA-UC) is an unconventional photophysical process that yields high-energy photons from low-energy incident light and offers pathways for innovation across many technologies, including solar energy harvesting, photochemistry, and optogenetics. Within aromatic organic chromophores, TTA-UC is achieved through several consecutive energy conversion events that ultimately fuse two triplet excitons into a singlet exciton. In chromophores where the singlet exciton is roughly isoergic with two triplet excitons, the limiting step is the triplet–triplet annihilation pathway, where the kinetics and yield depend sensitively on the energies of the lowest singlet and triplet excited states. Herein we report up to 40-fold improvements in upconversion quantum yields using molecular engineering to selectively tailor the relative energies of the lowest singlet and triplet excited states, enhancing the yield of triplet–triplet annihilation and promoting radiative decay of the resulting singlet exciton. Using this general and effective strategy, we obtain upconversion yields with red emission that are among the highest reported, with remarkable chemical stability under ambient conditions.



INTRODUCTION

Photons emitted from photoexcited organic materials are generally lower in energy than the incident radiation used for excitation, with the Stokes shift[1] between the absorption and fluorescence dictated by rapid relaxation of the excited state. Very few examples of anti-Stokes shifting systems are known, but the ability to upconvert long wavelength (low-energy) incident light to short wavelength (high-energy) light offers attractive avenues of innovation across several technologies,[2] notably those that rely on the penetration of light.[3–5] For example, photochemical reactions can be limited by light penetration, requiring engineering of reaction vessels to maximize surface area.[6–8] However, the use of localized apparent anti-Stokes photoluminescence can mitigate penetration, allowing for efficient large-scale photochemical reactions.[9,10] Moreover, the efficiency of photovoltaic devices could benefit from upconversion systems, harvesting transmitted low-energy photons that can be converted to wavelengths to be absorbed in active layers.[11,12]

Triplet–triplet annihilation upconversion (TTA-UC, Figure 1A,B) is a bimolecular process that enables apparent anti-Stokes emission. Low-energy incident light selectively excites a ground state sensitizer (^{1}[Sen]) molecule to its singlet excited state (S$_1$, ^{1}[Sen]*). This sensitizer then undergoes intersystem crossing (ISC) to form a triplet exciton (T$_1$, ^{3}[Sen]*). The second component—the annihilator ^{1}[An]—has a triplet state (^{3}[An]*) energy lower than $E(\mathrm{T}_1)$ of the sensitizer such that triplet energy transfer (TET) from the sensitizer to the annihilator is efficient. Finally, provided that the combined energy of two annihilator triplet excitons, $2E(\mathrm{T}_1)$, is larger than the energy of the annihilator's singlet excited state, triplet–triplet annihilation results in the generation of one singlet exciton (^{1}[An]*). This exciton can then emit a photon of energy higher than the incident photon used to excite the sensitizer. The exoergicity for triplet fusion can be described by the energy gap $\Delta E = E(\mathrm{S}_1) - 2E(\mathrm{T}_1)$, and the process of TTA-UC is favored when $\Delta E < 0$.

In the mechanism of TTA-UC, there are multiple events that can impact the yield of high-energy-output photons relative to the low-energy-input excitation. The total efficiency is a product of four quantum yields: (1) intersystem crossing of the sensitizer (Φ_{ISC}); (2) triplet energy transfer from the sensitizer to the annihilator (Φ_{TET}); (3) TTA of two annihilators in their triplet excited state (Φ_{TTA}); (4) photoluminescence of the annihilator singlet state (Φ_{PL}). Of these processes, Φ_{TTA} is the

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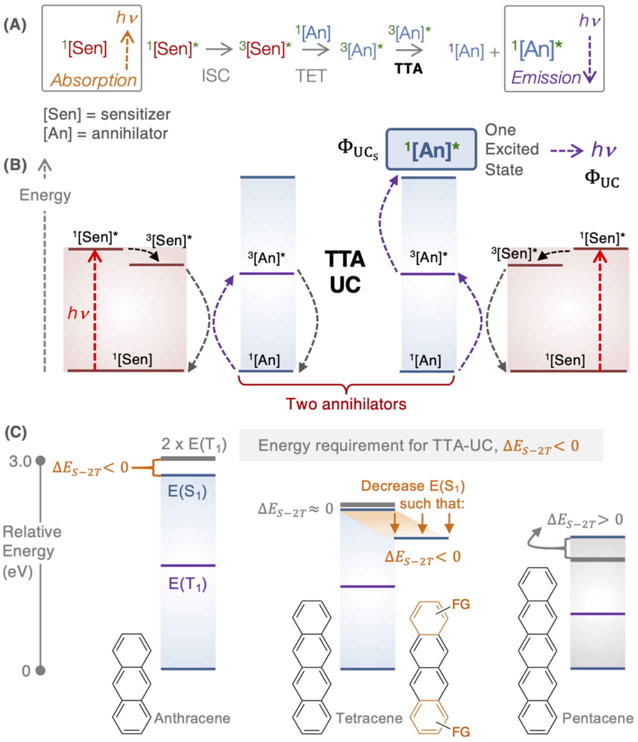

Figure 1. Energetic landscape of TTA-UC. (A) Net process of TTA-UC, where the notation ^{m}[Molecule]* represents the multiplicity, *m*, of the systems involved and the asterisk corresponds to excited states (no asterisk corresponds to a ground state molecule). (B) Jablonski diagram of the process of TTA-UC: the sensitizer ^{1}[Sen] is excited with low-energy light; the singlet exciton ^{1}[Sen]* undergoes intersystem crossing (ISC) to a triplet exciton ^{3}[Sen]*, which then undergoes triplet energy transfer (TET) to the annihilator ^{3}[An]*; and, finally, the interaction between two ^{3}[An]* yield one annihilator in the ground state ^{1}[An] and other in the singlet state ^{1}[An]* by triplet−triplet annihilation. (C) Relative energies[26] $E(S_1)$ and $E(T_1)$ of three molecules that undergo TTA, singlet fission (SF), and competing pathways. The strategy to access the TTA channel in tetracene derivatives by lowering $E(S_1)$ with functional groups (FG), while maintaining $E(T_1)$ fixed, is the focus of this paper.

value that typically deviates the most from unity, dominating the net efficiency of TTA-UC.[2,13] While a large variety of chemical annihilators have been examined, including acenes,[2] diketopyrrolopyrrole,[14] diphenylisobenzofuran,[15] BODIPY,[16] rylenedimides,[17,18] diphenyloxazole,[19] and polymeric systems,[20−23] overall upconversion yields consistently fall well short of the theoretical maximum. As such, we postulate that through molecular engineering it may be possible to tune Φ_{TTA} by altering the frontier energy levels by design, particularly in known red emitters where the singlet and triplet pair energy is nearly isoergic (e.g., Figure 1C, tetracene).[24,25]

In order to exploit TTA-UC in many applications, it is imperative to develop systems that are efficient, stable, and modular in terms of energy input and output. However, the rational design of TTA-UC annihilators is still in its infancy. Previous studies investigating the chemical functionalization of anthracene have revealed interesting insights into TTA-UC dynamics, although these reports focus solely on the functionalization of the acetylene component using a variety of functional groups in each study.[27−30] While complexation, self-assemblies, and dimerization have also been explored,[31−34] here we focus on the systematic functionalization using a single type of functional group on the core acene motif.

Interestingly, in tetracene—a well-known chromophore involved in multiexciton processes—the energy difference between the singlet energy and twice the energy of the triplet, $\Delta E[S_1{-}2T_1]$, is ∼0 eV and is thus isoergic to both singlet fission and triplet−triplet annihilation. While upconversion in tetracene can be altered using intermolecular assemblies[35,36] and chromophore connectivity,[37,38] the only tetracene derivative exhibiting high upconversion efficiency is rubrene.[39,40] While in rubrene TTA-UC quantum yields are high, reaching 8% (where the limit is 50%, *vide infra*), photochemical processes with rubrene are very sensitive to oxygen, leading to degradation within 30 min.[39]

While rubrene exhibits high upconversion efficiency, little is known about how chemical structure modifications to the tetracene core impact multiexciton dynamics of TTA-UC. Therefore, we sought to test how functional group substitutions in tetracene affect the energy of the singlet state, such that $\Delta E[S_1{-}2T_1] < 0$. We posit that the frontier energy levels of tetracene ($\Delta E[S_1{-}2T_1] \sim 0$) can be tuned through molecular engineering to meet the energetic requirement for TTA-UC,[41,42] specifically using electron withdrawing groups to lower the singlet state energy (Figure 1C). These changes are known to have large consequences for the optoelectronic properties of acenes. In anthracene, $\Delta E[S_1{-}2T_1]$ is negative and triplet−triplet annihilation is exoergic.[43] In pentacene, $\Delta E[S_1{-}2T_1]$ is positive, rendering it inefficient at TTA but highly efficient at the reverse process: singlet fission.[44−46] Working with derivatives of tetracene, we find that carbonitrile substitution (a strong electron withdrawing group) can effectively lower $E(S_1)$, such that $\Delta E[S_1{-}2T_1]$ becomes negative, thus leading to remarkable increases in TTA-UC efficiencies (by up to 40-fold). Moreover, the aerobic stability of these systems showed drastic improvements, which is important for a variety of applications outside of an inert atmosphere.[47,48]

■ RESULTS AND DISCUSSION

Synthesis and Optical Properties. Tetracene **1** (Figure 2A) has low solubility, poor stability, and a tendency to aggregate in solution. For these reasons triisopropylsilylacetylene tetracene (TIPS-tetracene, **2**)—along with TIPS-anthracene[43] and TIPS-pentacene[44−46]—have become ubiquitous in solution-based excitonic studies. The bulky isopropyl groups protect the acene core sterically from degradation reactions, while the acetylene groups stabilize the diradical nature of the acene in its triplet state.[49]

In the tetracene derivatives studied herein, **2**−**8**, we refer to the short edge of the acene nearest the TIPS groups as the "head" in tetracene, and the opposite edge we refer to as the "tail." To reduce the energy of the singlet state, the chromophore was functionalized with strong electron withdrawing carbonitrile functional groups. All carbonitrile groups were installed on the corresponding aryl bromides using microwave-assisted Pd-catalyzed cross-coupling with copper(I) cyanide; additional synthetic details are available in the Supporting Information.

The energy of the lowest singlet excited state was estimated from the crossing point of the absorption and emission spectra of each molecule in dilute toluene (Figures S1−S3). The normalized absorption spectra of compounds **2**−**8** are shown in Figure 2B. The functionalization of tetracene lowered $E(S_1)$

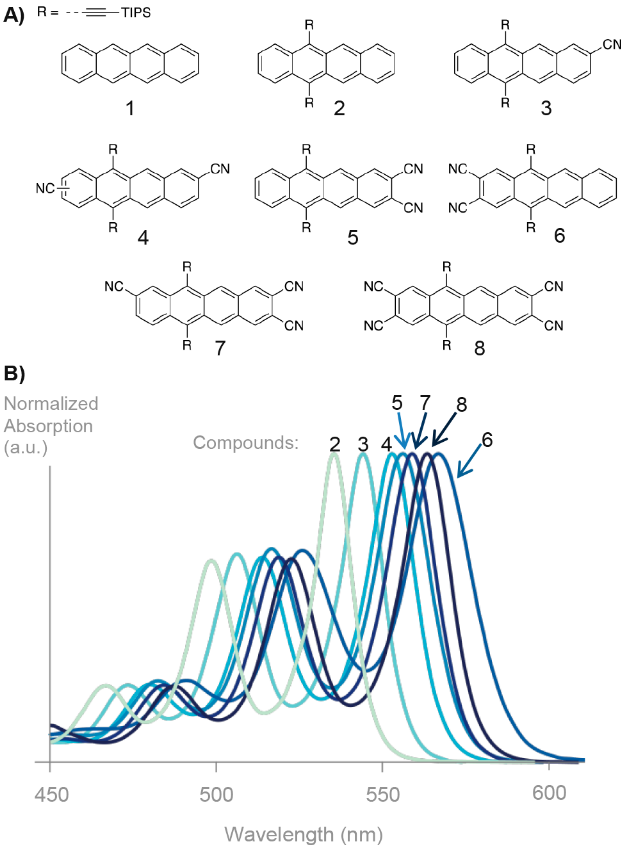

Figure 2. (A) Structures of tetracene and its derivatives, functionalized with TIPS-acetylene and carbonitrile groups. We refer to the edge of tetracene nearest the TIPS-acetylene groups as the "head" (e.g., **6**) and the furthest edge the "tail" (e.g., **5**). Compound **4** is a mixture of two inseparable regioisomers. (B) Normalized steady state absorption spectra of compounds **2**−**8**, taken in dilute solutions in toluene.

on average by ~30 meV per carbonitrile group. However, the reduction in the three dicarbonitrile stereoisomers was inequivalent: −70 meV for **4**, −90 meV for **5**, and −140 meV for **6**. Notably, the reduction in singlet state energy in **6** was greater than that of the tetracarbonitrile compound **8**. The effect of the degree of carbonitrile functionalization on the fluorescence lifetime of the functionalized tetracenes was investigated using time-correlated single photon counting (Figure S4). The lifetimes ranged between 14 and 18 ns (Table S4), comparable but slightly longer than those of both TIPS-tetracene (11 ns, Figure S5) and literature reports of rubrene (10 ns).[50]

Triplet−Triplet Annihilation Upconversion. The reduction in $E(S_1)$ in this family of chromophores allowed us to test how $\Delta E[S_1{-}2T_1]$ affects Φ_{TTA}. If the carbonitrile groups do not drastically change the energy of the triplet state, then $\Delta E[S_1{-}2T_1]$ should become negative, thus favoring TTA to the singlet state. The tetracene materials were paired with palladium(II) octabutoxyphthalocyanine (PdPc),[51] which when excited at 730 nm (1.7 eV) undergoes efficient intersystem crossing to generate a triplet exciton with $E(T_1)$ ~1.3 eV.[40] This energy is higher than $E(T_1)$ of tetracene (~1.15 eV), so the triplet exciton transfers to the annihilator via Dexter energy transfer. Photon upconversion characteristics were determined following the integrating sphere method from de Mello et al.,[52] and a brief overview is given in the Supporting Information. Excitation with a 730 nm laser furnished upconverted photoluminescence (Figure 3), while the photoluminescence quantum yield (Φ_{PL}) of each sample was determined for each sample by excitation at 365 nm. Intrinsic photoluminescence quantum yield (PLQY) measurements of the neat annihilators are also given in Tables S1−S3.

In TTA-UC, two low-energy photons are required for the generation of one high-energy photon, meaning that Φ_{TTA}, and thus Φ_{UC}, have upper limits of 50%.[53] Importantly, we focus our discussion on two distinct upconversion quantum yields (following the convention of ref 53): Φ_{UC} denotes the TTA-UC quantum yield of observed upconverted emission from the experiment; Φ_{UC_S} denotes the derived quantum yield of singlet states produced in the experiment, removing optical losses from the photoluminescence event. While the observed emission Φ_{UC} is desirable for applications, Φ_{UC_S} better quantifies the chromophore's intrinsic protentional for TTA-UC, and maximizing both requires optimization of both the intrinsic photophysics and experimental conditions. We also note that we discuss the quantum yields in terms of percent, where the limit of both Φ_{UC} and Φ_{UC_S} is 50%, i.e.

$$\Phi_{UC} = \Phi_{ISC}\Phi_{TET}\Phi_{TTA}\Phi_{PL} \times 100\% \tag{1}$$

$$\Phi_{UC_S} = \Phi_{UC}/\Phi_{PL} \times 100\% \tag{2}$$

These two figures of merit are typically optimized under different conditions: Φ_{UC_S} is usually enhanced in concentrated solutions where intermolecular interactions are maximized; however, photon reabsorption and singlet energy transfer in such systems will result in low Φ_{PL} (and hence low Φ_{UC}). Likewise, in dilute solutions, photon/singlet state trapping is minimized, typically resulting in high Φ_{PL} (and hence high Φ_{UC}) but lower Φ_{UC_S} due to nonradiative losses of transient triplet excitons. As studying the upconversion characteristics for each compound across the entire concentration space would be very difficult, we analyzed each chromophore in two types of solutions, (a) dilute and (b) concentrated, where the annihilator/sensitizer quantities were (a) 1 mM/1 mol % and (b) 9 mM/9 mol %. The upconversion quantum yields are shown in Table 1.

The highest Φ_{UC_S}/Φ_{UC} of the benchmark TIPS-tetracene **2** was 0.3/0.12%, respectively. All the carbonitrile tetracene

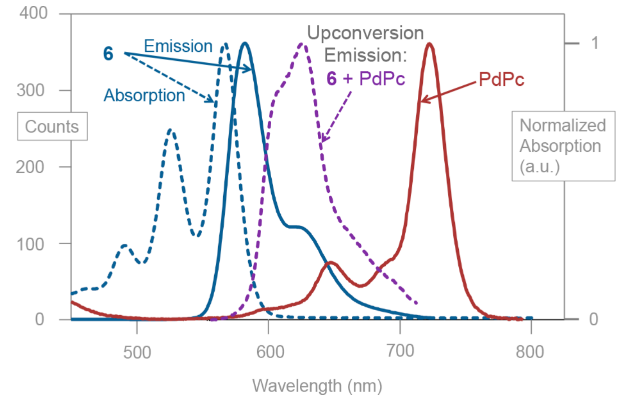

Figure 3. Absorption of PdPc (red); absorption (blue dashed) and PL (blue solid) of **6**. Upconversion experiment (purple dashed) showing UCPL of **6** between 600 and 700 nm and reabsorption losses between 550 and 600 nm.

Table 1. Triplet−Triplet Annihilation Upconversion Characteristics of Annihilator Compounds 2−8 (An)

	dilute[a]			concentrated[b]		
An	$\Phi_{\mathrm{UC_S}}$[c] (%)	Φ_{PL}[d] (%)	Φ_{UC}[c] (%)	$\Phi_{\mathrm{UC_S}}$ (%)	Φ_{PL} (%)	Φ_{UC} (%)
2	0.14	82.4	0.12	0.30	3.6	0.01
3	0.21	79.1	0.17	0.12	2.7	0.005
4	0.18	78.5	0.15	0.38	3.3	0.01
5	1.6	83.8	1.3	3.5	2.3	0.1
6	3.5	71.4	2.5	9.0	1.8	0.15
7	0.65	74.4	0.5	1.8	2.5	0.05
8	1.4	72.4	1.0	0.9	1.4	0.02
rubrene[e]	0.13	92.2	0.12	1.8	3.9	0.07

[a] Dilute: [An] = 1×10^{-3} M, [PdPc] = 1×10^{-5} M. [b] Concentrated: [An] = 9×10^{-3} M, [PdPc] = 8.1×10^{-4} M. Experiments were carried out on 1 mL samples at the aforementioned concentrations in 1 cm^2 cuvettes at RT. Samples were prepared in a degassed environment (N_2 glovebox) with the use of anhydrous degassed (N_2) toluene. Cuvettes were capped, sealed with Parafilm, and analyzed immediately on the optics table. The fluence of the incident excitation was such that the experiment was in the linear regime. [c] QY limit is 50%. [d] QY limit is unity. [e] Aldrich sublimed grade.

materials exhibited higher Φ_{UC}, and all with the exception of **3** exhibited higher $\Phi_{\mathrm{UC_S}}$. Focusing on the intrinsic ability of the compounds to undergo upconversion, $\Phi_{\mathrm{UC_S}}$ shows a strong correlation to the reduction in singlet state energy; interestingly, the dicarbonitrile derivative **6** has the largest $\Delta E[S_1{-}2T_1]$ and it yielded the highest $\Phi_{\mathrm{UC_S}}/\Phi_{\mathrm{UC}}$ of 9.0/2.5%, respectively.

Rubrene performed poorly in dilute solution but achieved high $\Phi_{\mathrm{UC_S}}$ in concentrated solution. We explored the concentration dependence (Figure S7) of this system and optimized the [rubrene]/[PdPc] pair at 9×10^{-3} M/9×10^{-5} M, respectively, where we observed the highest $\Phi_{\mathrm{UC_S}}$ of 5.5%, in line with concentrations used in other literature reports.[54] At the same concentration, **6** exhibits $\Phi_{\mathrm{UC_S}}$ of 7.9%, showcasing the impact of functional group substitution to favor the TTA channel.

Combining eqs 1 and 2, it is clear that Φ_{UC} is affected by three quantum yields, but intersystem crossing (Φ_{ISC}) can be ignored as the sensitizer species is constant. It is therefore important to deduce whether the observed improvements in $\Phi_{\mathrm{UC_S}}$ result from improved (a) triplet energy transfer (Φ_{TET}) and/or (b) triplet−triplet annihilation (Φ_{TTA}). To distinguish between these two quantum yields, we used transient absorption spectroscopy to calculate the quantum yield of triplet energy transfer from the sensitizer to the annihilator as

$$\Phi_{\mathrm{TET}} = (1 - [\tau_{(\mathrm{S+A})}/\tau_{\mathrm{S}}]) \times 100\% \tag{3}$$

Here, τ_{S} is the lifetime of the triplet exciton of the sensitizer and $\tau_{(\mathrm{S+A})}$ is the same lifetime but in the presence of an annihilator. To measure τ_{S}, a 10^{-5} M solution of the sensitizer in degassed toluene was excited with a 730 nm laser pulse. After a delay, a broadband probe pulse examined photoinduced absorption of the excited states in the nanosecond to microsecond range, which can be attributed to triplet excitons (singlet states decay before this time scale). The triplet state photoinduced absorbance in PdPc is broad over 570−635 nm, peaking at ∼615 nm, and decays with a time constant (τ_{S}) of 3.0 μs (Figure S9), in good agreement with the literature.[55] The lifetime of the triplet exciton in the presence of each annihilator ($\tau_{(\mathrm{S+A})}$) ([An] = 1×10^{-3} M) was probed similarly, and eq 3 was used to deduce Φ_{TET} (Table 2).

Triplet energy transfer in TIPS-tetracene **2** is reasonably efficient (Φ_{TET} = 64%), and functionalized tetracenes show comparable quantum yields with slightly higher values but within range of experimental error. With the similarities in Φ_{TET}, it may be inferred that the TTA-UC efficiency improves as a result of increased exoergic triplet−triplet annihilation: Φ_{TTA} is improved 24-fold in **6** (5.0%) versus **2** (0.21%).

Stability of Tetracene Upconversion Chromophores. To date, rubrene is by far the most widely employed NIR to orange TTA-UC annihilator. However, it is unstable under irradiation in aerobic conditions, degrading within 30 min. Electron-deficient aromatic systems in general tend to exhibit higher ambient stability due to a deepening of the energetic states away from the oxidation potential, resulting in an excited state less prone to oxidation or photodimerization.[56−58] Furthermore, the addition of strongly electron withdrawing groups to tetracene may lower its reactivity toward endoperoxide formation with molecular oxygen. To assess the stability of the family of tetracene materials, the steady state absorption spectra of dilute solutions in untreated (i.e., not degassed) toluene were taken over a period of 14 days (Figure 4). The samples were stored aerobically in a well-lit area but out of direct sunlight. The absorption maximum of TIPS-tetracene **2** after 14 days was reduced to 20% of its initial absorbance. As hypothesized, the addition of each carbonitrile group increases the stability of the materials, with the highest stability seen in **8**, which exhibited 85% of its original absorbance after 14 days.

Computational Studies. Triplet−triplet annihilation can only be more exoergic in tetracenes with lower $E(S_1)$ if $E(T_1)$ is relatively unchanged or increased, such that $\Delta E[S_1{-}2T_1]$ becomes more negative. Our results strongly suggest this is the case, but they also reveal unusual characteristics, particularly in that **6** shows the largest $\Delta E(S_1)$, 30 meV larger than **8**. To understand our observations with more clarity, we investigated the excited state energetic landscape using quantum chemical calculations. Time-dependent density functional theory (TD-DFT) with range-separated functionals has been shown to provide accurate descriptions of singlet excited states of polyacenes.[59] With the use of optimized ground state geometries (B3LYP/cc-pVTZ), vertical S_1 energies were first

Table 2. Quantum Yields of Triplet Energy Transfer (Φ_{TET}) and Triplet−Triplet Annihilation (Φ_{TTA}) of Annihilator Compounds 2−8 (An)

An	Φ_{TET}[a] (%)	Φ_{TTA}[b] (%)
2	64	0.21
3	68	0.30
4	68	0.26
5	70	2.2
6	69	5.0
7	62	1.1
8	82	1.7

[a] QY limit is 100%. [b] QY limit is 50%. Experiments were performed in degassed (bubbling with argon) toluene on samples where [PdPc] = 1 × 10^{-5} M and [An] = 1×10^{-3} M at RT with a cuvette having a 2 mm path length.

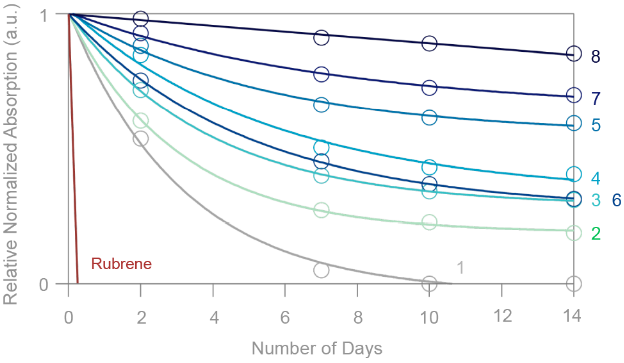

Figure 4. Stability of tetracene materials over a 2 week period when stored in a well-lit (conventional fluorescent tube lighting) aerobic environment. Plot shows λ_{max} intensity relative to intensity on day 0.

calculated with TD-DFT (CAM-B3LYP/cc-pVTZ). To obtain the adiabatic $E(S_1)$ values reported, geometries corresponding to the minima of the S_1 surfaces were optimized within the Tamm–Dancoff approximation (TDA). Finally, the differences of the total energies (computed via TD-DFT without the TDA, using CAM-B3LYP/cc-pVTZ) between the Franck–Condon regions and the S_1 minima were added to the vertical excitation energies in the ground state geometry.

The calculated $E(S_1)$ values (Figure 5) are consistent with experimental observations, crucially in that the lowest energy singlet state is expected for **6**. In order to better understand the electronic effects of the carbonitriles, we calculated difference density plots (Figure S11) in which the electron density of the ground state is subtracted from that of the singlet excited state. In essence, the results reveal the character of intramolecular charge transfer upon excitation. Figure 5A shows the difference density plots for four of the studied tetracenes.

For the singlet excited states in **2**, there is an increase of electron density on the acene core carbons where the acetylene groups are installed, while the π-system at the tail of the tetracene is depleted. Compounds **3**, **4**, and **8** show relatively balanced redistributions of electron density in the excited states, and we attribute the stabilization of $E(S_1)$ in these materials predominately to the effect of the addition of the electron withdrawing and π-system extending carbonitriles on the chromophore. However, both **5** and **6** exhibit considerable increases in electron density localized at the end of the molecule where the two carbonitrile functional groups are installed. We postulate that the directional charge transfer is more stabilizing in **6** than in **5**, as in the former the increased density in the adjacent acetylene units serves to extend the conjugated π-system occupancy to a larger area.

The difference density plots of the triplet excited states show a contrasting picture to the singlet states (Figure S11), where all tetracenes exhibit relatively similar charge transfer characteristics. This suggests that the chemical functionalization affects the character of the triplet state to a much smaller degree than the singlet states. As measuring the energy of the triplet states in organic materials is particularly challenging, we employed a high-level *ab initio* method to probe the effects of these functionalizations on the triplet state energies. Coupled cluster theory with single, double, and perturbative triple excitations (CCSD(T)) is a robust and size-extensive wave function method that has been previously employed to investigate the electronic properties of polycyclic aromatic hydrocarbons with high accuracy.[60−62] The high computational cost of canonical CCSD(T) calculations has been substantially reduced via the DLPNO approximation, which exploits the locality of electronic correlations.[63] As such, we employed DLPNO-CCSD(T) to calculate the triplet state energies using the optimized geometries of the singlet and triplet states (B3LYP/cc-pVTZ). The $E(T_1)$ of **2** was calculated to be 1.23 eV, in good agreement with reported phosphorescence of ∼1.25 eV of TIPS-tetracene in a polystyrene matrix;[64] however, we emphasize that we focus our investigation and discussion on trends in the calculated energies and not on the absolute values of the energies themselves. Remarkably, at this level of theory, the energies of the triplet states of the family of tetracenes are relatively comparable: the largest difference in triplet energy across the series is 14 meV, an order of magnitude less than the largest experimental $\Delta E(S_1)$ (140 meV) within the series. These results correlate strongly with the difference density plots in that the energy of T_1 in tetracene is largely unaffected by the addition of carbonitrile functionality.

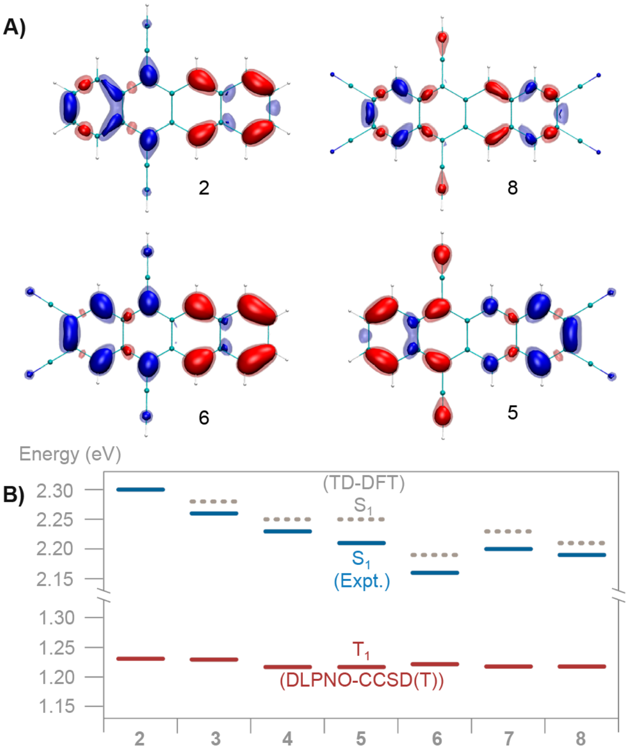

Figure 5. (A) Plots of the difference in electron density in the excited singlet states of four tetracenes. Red regions indicate locations of lower electron density in the excited state compared to the ground state, while blue regions indicate higher electron density in the excited state. (B) Experimental (blue) singlet state energies estimated from the crossing point of absorbance and PL. The trend in the theoretical singlet state energies (gray dash, TD-DFT) is in excellent agreement with experimental observations. Calculated energies (DLPNO-CCSD(T)) of the T_1 states are shown with red bars. Both axis segments show a 200 meV window to allow energy differences between all states to be directly visually comparable.

Functionalization of Other Polyaromatic Hydrocarbons. In order to test the model, we turn to tuning the value of $E(S_1)$ via carbonitrile substituents with two other common upconverting chromophores: perylene and anthracene derivatives (Figure 6).

The carbonitrile derivatives of 2,5,8,9-tetra-*tert*-butylperylene **9** exhibited the largest changes in singlet energies, with a lowering by 180 meV for the monocarbonitirile compound **10**

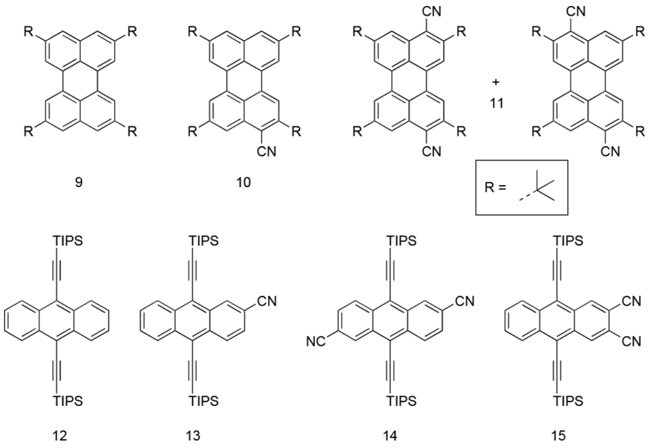

Figure 6. Functionalization of perylene and anthracene with carbonitrile groups. Compound **11** is a mixture of two inseparable regioisomers.

and an additional 70 meV for the dicyano **11**. For derivatives of TIPS-anthracene **12**, the singlet state was lowered by 90 meV in **13** and a further 50 meV for both **14** and **15** (Tables S2 and S3). In order to characterize TTA-UC, the perylene and anthracene chromophores were paired with the sensitizer palladium(II) *meso*-tetraphenyl-tetrabenzoporphyrin (PdTPTBP),[2,35,65] which was excited at 635 nm. The resulting upconversion characteristics are shown in Table 3.

Considering the perylene annihilators, the benchmark tetra-*tert*-butylperylene **9** is an efficient TTA-UC chromophore in dilute solution (Φ_{UC_S} = 5.6%, Φ_{UC} = 3.9%) but less so in concentrated media (Φ_{UC_S}= 2.0%, Φ_{UC} = 0.05%); it was found that the addition of carbonitrile groups to perylene increased the photoluminescence quantum yield (Φ_{PL}) from 70% in **9** to near unity (97%) in **11**. The functionalized perylenes exhibited improved Φ_{UC_S} and Φ_{UC}, with the most notable result being that the Φ_{UC} starkly improved in concentrated systems: the Φ_{UC} of **11** is 13 times higher than that of **9**, originating from higher Φ_{PL}, but with notably an almost 4-fold improvement in Φ_{UC_S} (7.7%). While the higher Φ_{UC_S} in functionalized perylenes is more likely due to enhancements of the rate of triplet−triplet annihilation, we also suggest that the higher solubility of the functionalized perylene derivatives contributes to increased yields in concentrated solutions.

Table 3. Photon Upconversion Characteristics of the Carbonitrile Functionalized Perylenes (Annihilators [An] 9−11) and Anthracenes (Annihilators [An] 12−15)

	dilute[a]			concentrated[b]		
An	Φ_{UC_S}[c] (%)	Φ_{PL}[d] (%)	Φ_{UC}[c] (%)	Φ_{UC_S} (%)	Φ_{PL} (%)	Φ_{UC} (%)
9	5.6	69.9	3.9	2.0	4.9	0.05
10	7.5	82.8	6.2	7.5	6.8	0.51
11	8.4	97.1	8.2	7.7	8.4	0.65
12	12.8	65.4	8.4	9.6	1.7	0.15
13	11.6	75.8	8.8	8.0	3.8	0.30
14	13.9	87.5	12.1	11.3	5.4	0.61
15	9.7	83.0	8.0	11.4	4.7	0.55

[a]Dilute: [An] = 1×10^{-3} M, [PdTPTBP] = 1×10^{-5} M. [b]Concentrated: [An] = 9×10^{-3} M, [PdTPTBP] = 8.1×10^{-4} M. Experiments were carried out on 1 mL samples at the aforementioned concentrations in 1 cm^2 cuvettes at RT. Samples were prepared in a degassed environment (N_2 glovebox) with the use of anhydrous degassed (N_2) toluene. Cuvettes were capped, sealed with Parafilm, and analyzed immediately on the optics table. The fluence of the incident excitation was such that the experiment was in the linear regime. [c]QY limit is 50%. [d]QY limit is unity.

In contrast, TIPS-anthracene **12** is known to exhibit highly exoergic photon upconversion, reflected in its markedly high Φ_{UC} of 8.4% in dilute solutions. Therefore, upon the addition of carbonitriles, the reduction of $E(S_1)$ does not have a strong effect on its photon upconversion characteristics, as expected. Compound **14** showed an improved Φ_{UC}; however, it is particularly noteworthy that the cyanated anthracenes are considerably brighter compounds—the Φ_{PL} in **15** (88%) is 23% brighter than that in **12**. Interestingly, it was also found that the dilute solutions exhibit higher Φ_{UC_S} than concentrated solutions. Despite the concentration dependence, the observed trend in concentrated solutions resulted in higher Φ_{UC} yields from the cyanated compounds, in comparison to the benchmark compound **12**. We note the higher Φ_{PL} essentially raised the Φ_{UC}; e.g., in concentrated solution, compound **14** is 4 times more efficient than **12** due to both improved Φ_{UC_S} and a 3-fold increase in Φ_{PL}. This result is of particular importance for TTA-UC applications where the systems are constrained to local concentration environments, such as in nanoparticles or micelles.[47]

In order to test the contributions of triplet energy transfer to the upconversion quantum yields, we turn to transient absorption spectroscopy. For the perylene and anthracene derivatives, we determined the decay constant of T_1 of PdTPTBP (τ_S) to be ∼100 μs (Figure S10), in agreement with the literature.[66] In the presence of all compounds **9**−**15**, the sensitizer triplet decays ($\tau_{(S+A)}$) before 2 μs, showcasing the exceptional near-unity triplet energy transfer ($\Phi_{TET} > 96\%$) between PdTPTBP and these materials (Table 4). From these results, it can be inferred that changes in TTA-UC characteristics in these systems result almost exclusively from changes in the quantum yield of triplet−triplet annihilation and photoluminescence, not from changes in triplet energy transfer efficiency.

CONCLUSIONS

Since singlet fission is a deactivating channel for triplet−triplet annihilation upconversion chromophores that have relatively similar energies, $E(S_1)$ and $2E(T_1)$, such that $\Delta E[S_1 - 2T_1] \approx 0$, such systems generally exhibit low efficiencies for each

Table 4. Quantum Yields of Triplet Energy Transfer (Φ_{TET}) and Triplet−Triplet Annihilation (Φ_{TTA})

An	Φ_{TET}[a] (%)	Φ_{TTA}[b] (%)
9	96	5.8
10	98	7.7
11	97	8.6
12	99	12.9
13	99	11.8
14	99	13.9
15	99	9.8

[a]QY limit is 100%. [b]QY limit is 50%. Experiments were performed in degassed (Ar) toluene on samples where [PdTPTBP] = 1×10^{-5} M and [An] = 1×10^{-3} M at RT with a cuvette having a 2 mM path length.

process. In order to favor the TTA channel, it was hypothesized that with tuning the energy of the singlet state without changing the triplet state energy, such that $\Delta E[S_1-2T_1] < 0$, the TTA channel would be favored. Functionalization of the reported polyacenes with carbonitrile functional groups leads to a greater lowering of $E(S_1)$ relative to $E(T_1)$, which correlated strongly to increased quantum yields of triplet−triplet annihilation, impacting the TTA-UC process of three families of annihilators. For example, efficiencies of TTA-UC showed a drastic increase in a tetracene functionalized derivative (compound **6**), relative to the parent TIPS-tetracene (compound **2**), from 0.3 to 9.0%. Moreover, such a functionalized tetracene derivative exhibited orders of magnitude higher aerobic stability than rubrene, the current widely employed TTA-UC annihilator for NIR to orange light. In dilute solution, the half-life of **8** (~52 days) is up to 5 orders of magnitude greater than that of rubrene (<30 min). Of particular importance, the hypothesis was also tested with perylene and carbonitrile-functionalized derivatives, where upconversion efficiencies increased from 2.0% (**9**) up to 7.7% (**11**) and exhibited enhanced stability. We note that for applications it is necessary to maximize both Φ_{UC_S} and Φ_{UC} for any given system. The tuning of the latter can be achieved through careful optimization of the local environment (concentration, solvent, viscosity, etc.). As we analyzed only two environments for each annihilator, it is highly likely that higher and/or more balanced values of Φ_{UC_S} and Φ_{UC} can be achieved for these systems. Notably, it was also found that the molecular engineering approach led to high efficiencies in concentrated solutions. Chemical modifications that alter the energy levels of common chromophores can result in materials to be exploited in applications that require TTA-UC, such as biomaterials, imaging, and solar energy harvesting systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c06386.

> Synthesis and materials characterization, absorption and emission spectroscopies, detailed information on nanosecond transient absorption measurements and analysis, complete computational analysis images (PDF)

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Notes

The authors declare the following competing financial interest(s): DNC has an ownership stake in, and is Chief Scientific Advisor to, Quadratic 3D, Inc. SNS has an ownership stake in, and is Chief Technology Officer of, Quadratic 3D, Inc.

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