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Putting the "P" Back in Delayed Fluorescence – Silylethynyl Substitution Generates Efficient Pyrene Annihilators for Red-to-Blue Photon Upconversion

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Triplet-triplet annihilation photon upconversion (TTA-UC) converts low-energy photons to higher-energy ones under low-intensity incoherent excitation, thus enabling applications in fields ranging from medicine to solar energy conversion. Silylethynyl mono- and di-substitution of acenes offers an attractive route to creating new annihilators that operate with minimal energy loss. Here, it is demonstrated that this approach can be extended to pyrene, yielding annihilators that display efficient red-to-blue upconversion. While pyrene is the namesake of P-type delayed fluorescence, the original name for triplet-triplet annihilation, it is known to be a poor annihilator due to its propensity for forming excimers. By tetra-substituting pyrene with silylethynyl groups, excimer formation is substantially hindered while simultaneously minimizing the energy gap between the singlet and triplet pair states that participate in TTA-UC, yielding outstanding annihilators for red-to-blue upconversion that operate with quantum yields of upward of 19% (29% when corrected for inner filter effects). Further, it is found that reducing the bulkiness of the silyl substituents is key to achieving high TTA-UC quantum yields, which highlights the importance of annihilator side group selection when optimizing photon upconversion.

1. Introduction

Pyrene (Py) is the namesake of P-type delayed fluorescence,[1,2] which is now called triplet fusion or triplet-triplet annihilation (TTA). TTA occurs when two annihilator (Ann) molecules in their excited spin-triplet states collide, promoting one to a high-energy, emissive spin-singlet state while the other reverts to its ground state. The triplet state of the Ann is typically populated via triplet energy transfer (TET) from a photoexcited triplet sensitizer (Sen). If the Ann emits photons of higher energy than the Sen absorbs, TTA can be used to drive photon upconversion (TTA-UC, **Figure 1A**), which has found numerous applications, from light-triggered drug release and photopharmacology[3] to additive manufacturing,[4,5] photovoltaics,[6] and photocatalysis.[7,8]

TTA-UC may occur if the annihilator meets the energy requirement of $2 \times E(T_1) \geq E(S_1)$, which Py satisfies ($E(T_1) \approx 2.1$ eV; $E(S_1) \approx 3.2$ eV).[13] Despite fulfilling this rudimentary requirement, Py is a poor TTA-UC annihilator as it displays a large energetic loss during TTA ($\Delta E_{loss} = 2 \times E(T_1) - E(S_1) = 0.9$ eV), shows a low fluorescence quantum yield ($\Phi_{fl} = 0.3$–0.4),[13] and exhibits a high propensity to form excited state dimers, or excimers (Ex),[14] that hamper light emission. Overall, this results in a low upconversion quantum yield of less than 1% in native pyrene,[15] whereas adding bulkier side groups to prevent excimer formation improves the quantum yield to only ≈3%.[16] Herein, through molecular design, we overcome these drawbacks of Py by installing electron-donating and π-conjugation-extending silylethynyl groups that lower Py's HOMO-LUMO gap, increase its transition dipole moment, and mitigate aggregation.[17–20]

While the electronic effects of silylethynyl addition have been investigated for a range of aromatic hydrocarbons, it has historically been in the context of modifying their spin-singlet manifold to yield new emitters, sensors, and organic electronics.[17,21–24] More recently, acenes ranging from benzene to tetracene that have been modified with triisopropylsilylethynyl (TIPS) groups have been demonstrated as TTA-UC annihilators.[11,25–27] These "TIPSified" annihilators exhibit efficient upconversion thanks to an enhanced Φ_{fl} compared to their parent acene and improved energy economics of the TTA process as silylethynyl substitution tends to lower both the singlet and triplet energies of the annihilator, reducing ΔE_{loss} (Figure 1B). Surprisingly, however,

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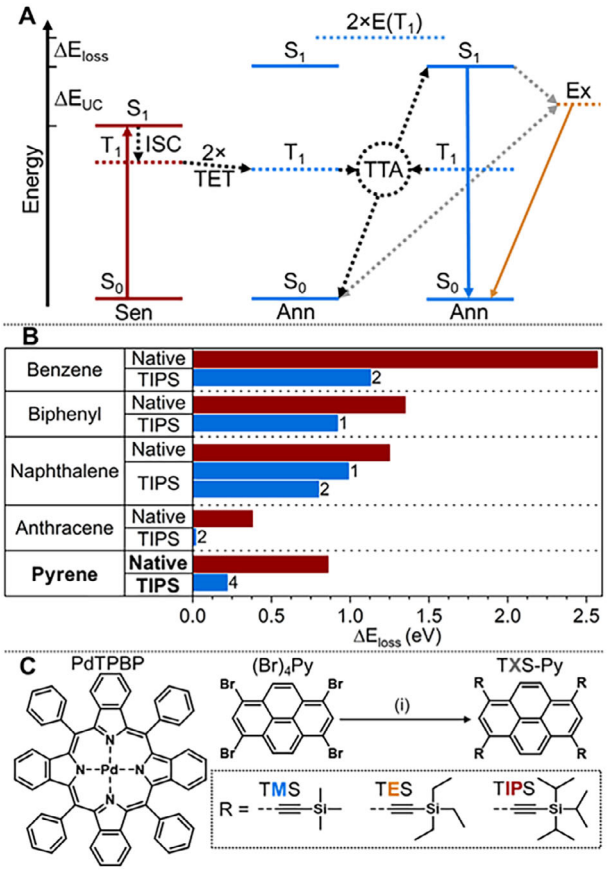

Figure 1. A) Energy cascade enabling TTA-UC. B) TTA energy loss, $\Delta E_{loss} = 2E(T_1) - E(S_1)$, for native and TIPS-substituted aromatic hydrocarbons. The number of silylethynyl substitutions for each TIPS derivative is indicated. See Figure S1 (Supporting Information) for $E(S_1)$ and $E(T_1)$ values.[9–12] C) Chemical structures of the sensitizer (PdTPBP) and annihilators (TXS-Py) used in this work. TES-Py and TIPS-Py were synthesized from tetrabromopyrene ($(Br)_4Py$). Reagents and yields: i) tetrakis(triphenylphosphine)palladium(0), copper (I) iodide, triphenylphosphine, diisopropylamine and triisopropylsilylacetylene (TIPS) or triethylsilylacetylene (TES) in THF, 53–55%.

"TIPSifying" has only been utilized on acene-based annihilators, with biphenyl[28] being the sole exception. Further, the effect of the size of the silylethynyl sidegroups (TXS, Figure 1C) on TTA-UC performance has only been investigated in naphthalenes.[29] Thus, by examining tetra-substituted Pys, we can elucidate how both electronic and steric effects impact TTA-UC beyond mono- and di-substitution motifs.

2. Results and Discussion

We began our evaluation of TXS-Pys as potential annihilators by calculating their singlet and triplet energies (see "Computational details" in Supporting Information). These calculations return values of $E(T_1) = 1.51$ eV and $E(S_1) = 2.59$ eV, which predict TXS-substitution will lower both $E(T_1)$ and $E(S_1)$ of the Py core by ≈0.6 eV and thereby reduce ΔE_{loss} by >2× relative to Py. Primed by these computational results, we obtained TXS-Pys bearing three different alkyl substituents with increasing steric bulk, namely methyl (TMS), ethyl (TES), and isopropyl (TIPS) groups. TES-Py and TIPS-Py were synthesized from commercially available tetrabromopyrene (Figure 1C), while TMS-Py was purchased and recrystallized. The side groups induce minimal changes in electronic structure as indicated by their common absorption and fluorescence spectra (**Figure 2**).

We experimentally determined $E(S_1) \approx 2.8$ eV for the TXS-Pys, which is ≈0.2 eV higher than their calculated $E(S_1)$ values. Using the calculated $E(T_1)$ and experimentally determined $E(S_1)$ values, we estimated $\Delta E_{loss} \approx 0.2$ eV, which is substantially lower than that of Py (0.9 eV). In addition to the aforementioned effects, TXS-substitution enhances the transition dipole moment of the lowest singlet transition of TXS-Pys compared to native pyrene by stabilizing the so-called L_a transition over the more symmetry forbidden L_b,[29–31] which manifests in TXS-Pys as Φ_{fl} of unity and a high molar extinction coefficient of ≈12 0000 M^{-1} cm^{-1} for their lowest-energy vibronic peak in toluene.

Based on the calculated $E(T_1)$ of 1.51 eV and experimentally determined $E(S_1)$ of 2.8 eV, we expected TXS-Pys to operate as annihilators for red-to-blue photon upconversion when paired with a Pd(II)-tetraphenyl-tetrabenzoporphyrin (PdTPBP) triplet sensitizer ($E(T_1) = 1.56$ eV, $\Phi_{ISC} = 97\%$).[32] Indeed, all TXS-Pys readily generate blue emission upon red (640 nm) laser excitation of PdTPBP (**Figure 3**A). We obtain maximum upconversion quantum yields (Φ_{UC}) of 19%, 16%, and 13% (out of a 50% theoretical maximum) for TMS-Py, TES-Py, and TIPS-Py, respectively (Figure 3A, inset). Due to the high molar extinction coefficients of the TXS-Pys, the upconverted PL spectra are distorted by a decrease of the 0-0 fluorescence peak relative to emission spectra measured at low concentration (Figure 2). By adjusting for this inner filter effect (see Figure S5, Supporting Information, for details) and assuming no other processes distort the PL spectra and change the internal upconversion quantum yield, we obtain "corrected" Φ_{UC}^{corr} values of 29%, 26%, and 21% for TMS-Py, TES-Py, and TIPS-Py, respectively. Overall, these Φ_{UC} values represent the

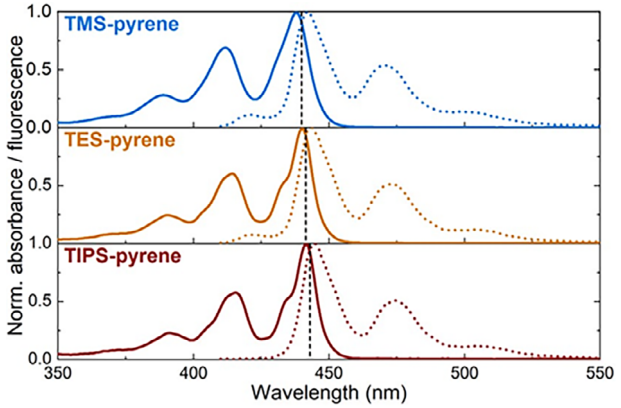

Figure 2. Normalized absorption (solid) and fluorescence (dotted, excited at 380 nm) spectra of TXS-Pys (0.8 μM) in toluene. The dashed vertical lines depict the absorption and fluorescence crossover points ($E(S_1)$) of TMS-Py at 440 nm (2.82 eV), TES-Py 442 nm (2.81 eV), and TIPS-Py 443 nm (2.80 eV). The small peak present ≈420 nm in TMS and TES-Py fluorescence spectra may originate from an emissive impurity (see Figure S3, Supporting Information).

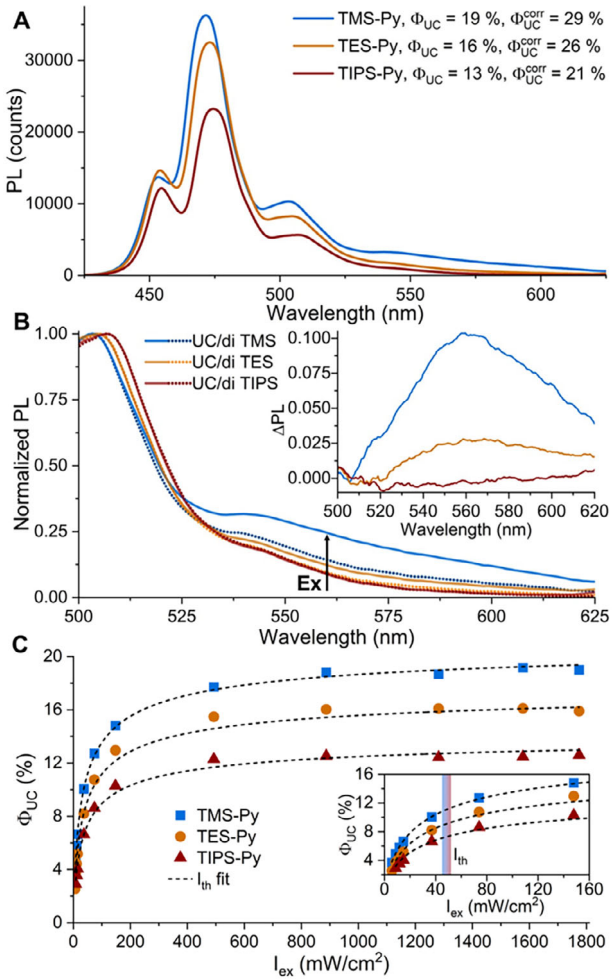

Figure 3. A) Upconverted photoluminescence spectra of TXS-Pys (1 mM) under 640 nm (1770 mW cm^{-2}) excitation of PdTPBP (20 μM) in toluene. B) Photoluminescence of the upconversion systems under 640 nm (UC; solid) and 365 nm (direct, di; dotted) excitation. The spectra are normalized to the vibronic peak between 503 and 507 nm (full spectra are shown in Figure S4, Supporting Information). The inset shows the differential spectrum between upconversion and direct excitation, which we attribute to excimers. C) Upconversion quantum yields (Φ_{UC}) under varied excitation intensities (I_{ex}) and fits used to determine the intensity threshold (I_{th}) for each system. The inset shows a zoom in of the data, highlighting I_{th}, which is similar for each TXS-Py.

top end for red-to-blue TTA-UC systems (see Table S5, Supporting Information)[33–36].

Our results show that side group size modulates Φ_{UC}, which can be expressed as the individual efficiencies (Φ) of the photophysical processes involved in TTA-UC:

$$\Phi_{UC} = \frac{1}{2} f \Phi_{ISC} \Phi_{TET} \Phi_{TTA} \Phi_{fluo} \quad (1)$$

where f is the spin-statistical factor[37] for forming a singlet upon TTA. As the same sensitizer is used with all TXS-Pys, Φ_{ISC} is equal for all systems. Therefore, we postulate the increased steric hindrance and slowed molecular diffusion due to the higher weight of TES-Py and TIPS-Py relative to TMS-Py (589, 757, and 926 g mol^{-1} for TMS-Py, TES-Py, and TIPS-Py, respectively) act to lower Φ_{UC}.

To evaluate this hypothesis, we determined Φ_{TET} for energy transfer from PdTPBP to TXS-Pys by performing a Stern-Volmer analysis (see Figure S9, Supporting Information) for how efficiently the TXS-Pys quench the triplet state of PdTPBP. At [TXS-Py] = 1 mM, the concentration used in the upconversion characterization, we estimate similar Φ_{TET} values of 93% and 92% for TMS-Py and TES-Py while TIPS-Py, manifests a lower Φ_{TET} value of 89%. These results reinforce our hypothesis that steric bulk impedes TET. However, these variations in Φ_{TET} are not large enough to solely account for the differences in Φ_{UC} between TMS-Py, TES-Py, and TIPS-Py.

Thus, we turn our attention to singlet excimer formation, which can decrease Φ_{fl} and consequently Φ_{UC}. Notably, the upconverted PL of TMS-Py at longer wavelengths is more intense relative to TES-Py and TIPS-Py. To probe this effect, we used a low-intensity 365 nm LED to directly excite each TXS-Py, which yielded emission spectra with lower intensity at their red edge relative to those measured during TTA-UC (Figure 3B). Subtraction of the normalized PL spectrum of TMS-Py obtained via direct excitation from its upconversion PL spectrum yields a broad and featureless band that is redshifted from the PL spectrum of dilute TMS-Py, which we assign to TMS-Py excimers. The same excimer feature is present to a lesser extent in TES-Py, while no excimer is observed for TIPS-Py. These steady–state results were corroborated with time-resolved PL measurements that show the existence of a long-lived decay component at an emission wavelength of 560 nm whose amplitude increases with decreasing TXS-Py steric bulk (see Figure S10, Supporting Information). This indicates under the conditions used for upconversion, Φ_{fl} must be lowest in TMS-Py and highest in TIPS-Py, which contrasts with the measured Φ_{UC} values. This reveals that excimer formation is not a significant enough effect to account for the variation in Φ_{UC} among TXS-Pys.

Thus, the different Φ_{UC} values for TXS-Pys must result from varying f (Equation 1) and Φ_{TTA}. The distinct tendency to form excimers indicates subtle differences in the intermolecular couplings upon encounter, which may modulate f.[37] Using Equation 1, we can estimate f by assuming that Φ_{TTA} is unity when the upconversion system is operating at its maximum quantum yield.[38,39] This estimation yields f values of 64%, 58%, and 49% for TMS-Py, TES-Py, and TIPS-Py, respectively, which is consistent with the recent results of Naimovičius et al. that suggested reducing steric bulk can enhance the probability of forming an excited singlet state upon TTA.[38]

Another handle for examining the efficiency of TTA is the intensity threshold (I_{th}) for TTA-UC. I_{th} indicates the excitation intensity required for TTA to become the predominant triplet decay pathway in a TTA-UC system and its dependencies can be expressed as[40,41]

$$I_{th} \propto \frac{k_{Ann}^2}{\alpha \Phi_{TET} k_{TTA}} \quad (2)$$

where α is the absorption coefficient of the sensitizer (equal for all systems), k_{Ann} is the unimolecular triplet decay rate of the annihilator, and k_{TTA} is the second-order rate constant for TTA. Using the Murakami–Kamada model[41] (Figure 3C; Figures S11–S13,

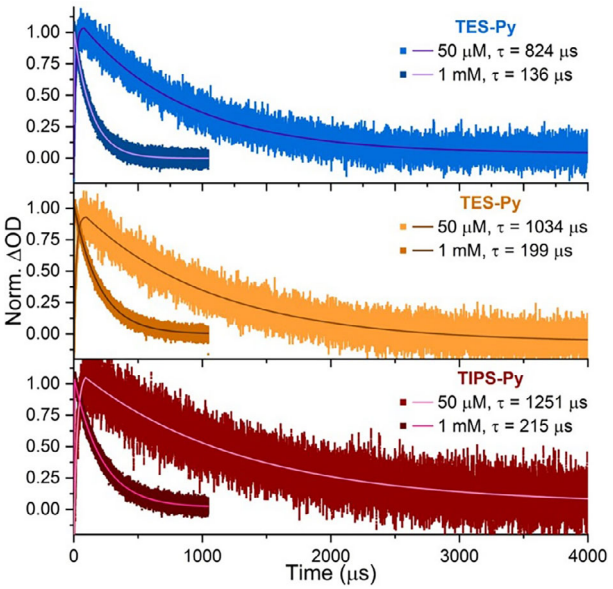

Figure 4. 50 μM and 1 mM TXS-Py triplet decays monitored at 500 nm in toluene. Transient absorption spectral profiles are shown in Figures S9–S11 (Supporting Information). The decays are fit to a sum of a rising and decaying exponential.

Supporting Information), we determine I_{th} values of 45, 52, and 49 mW cm^{-2} for TMS-Py, TES-Py, and TIPS-Py, respectively, which are equivalent within fitting error. Overall, these values represent the lower end of I_{th} values reported for red-to-blue TTA-UC systems (see Table S5, Supporting Information([33–36].

To further evaluate the I_{th} values, we determined the triplet lifetimes of each TXS-Py as k_{Ann} is squared in Equation 2 and is therefore critical in comparing annihilator performance. Using low TXS-Py concentrations (50 μM), we obtained triplet lifetimes of 824, 1034, and 1251 μs for TMS-Py, TES-Py, and TIPS-Py, respectively (**Figure 4**). To account for possible triplet excimer formation that Olesund et al. observed for TMS-naphthalene[29] at higher Ann concentrations, we measured triplet lifetimes using [TXS-Py] = 1 mM that matched conditions we employed for TTA-UC characterization (Figure 4). The triplet lifetimes are significantly shorter, i.e., 136, 199, and 215 μs at this higher concentration for TMS-Py, TES-Py, and TIPS-Py, but retain essentially the same ratios measured at lower concentration (1.52 at 50 μM and 1.58 at 1 mM between TIPS-Py and TMS-Py). If TMS-Py formed triplet excimers, its triplet lifetime would shorten drastically compared to TIPS-Py when their concentrations are increased 20-fold from 50 μM to 1 mM. Furthermore, although native Py is known for its bias toward excimer formation in its singlet manifold, triplet excimer formation has not been observed,[42] in contrast to naphthalene.[43]

Thus, based on the unimolecular triplet decay rates, TMS-Py should manifest an I_{th} more than 2.3× higher than TIPS-Py and almost 1.5× higher than TES-Py. As I_{th} appears equivalent in the TTA-UC systems studied here, the rate of TTA must "compensate" for the faster triplet decay rates of TMS-Py and TES-Py compared to TIPS-Py. To evaluate the efficiency of TTA, we measured the sensitized triplet decays of the TXS-Pys under varied excitation fluences (see Figures S17–S19, Supporting Information) and determined the fraction of triplets that decay via TTA (β):[44–46]

$$\beta = \frac{k_{TTA}\left[^3Ann\right]_0}{k_{Ann} + k_{TTA}\left[^3Ann\right]_0} \quad (3)$$

where $[Ann^3]_0$ is the initial concentration of annihilators placed into their triplet excited state. All TXS-Pys display comparable values of β (see Figure S20, Supporting Information) throughout the excitation fluence range, which indicates that the faster rates of TTA indeed compensate for the shorter triplet lifetimes of TMS and TES-Py compared to TIPS-Py. This verifies the similar I_{th} values observed above (Figure 3C).[46]

3. Conclusion

We have shown silylethynyl substitution of pyrene provides highly efficient annihilators for red-to-blue TTA-UC. The pyrene derivative decorated with the least bulky side groups, i.e., trimethylsilyls, exhibits the highest upconversion quantum yield of the compounds we report, 19% (29% after reabsorption correction). Despite showing some excimer formation, TMS-Py undergoes more efficient TTA relative to TES-Py and TIPS-Py that overcomes this loss channel. In addition to demonstrating new efficient annihilators by silylethynyl substitution, we show side group bulkiness is an underappreciated attribute that can be optimized to achieve efficient upconversion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict Of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

photochemistry, time-resolved spectroscopy, triplet-triplet Annihilation, upconversion

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