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# Enhancing NIR-to-visible upconversion in a rigidly coupled tetracene dimer: approaching statistical limits for triplet–triplet annihilation using intramolecular multiexciton states†

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Important applications of photon upconversion through triplet–triplet annihilation require conversion of near-IR photons to visible light. Generally, however, efficiencies in this spectral region lag behind bluer analogues. Herein we consider potential benefits from a conformationally well-defined covalent dimer annihilator TIPS-BTX in studies that systematically compare function to a related monomer model TIPS-tetracene (TIPS-Tc). TIPS-BTX exhibits weak electronic coupling between chromophores juxtaposed about a polycyclic bridge. We report an upconversion yield  $\phi_{UC}$  for TIPS-BTX that is more than 20× larger than TIPS-Tc under comparable conditions (0.16%). While the dimer  $\phi_{UC}$  is low compared to bluer champion systems, this yield is amongst the largest so-far reported for a tetracenic dimer system and is achieved under unoptimized conditions suggesting a significantly higher ceiling. Further investigation shows the  $\phi_{UC}$  enhancement for the dimer is due exclusively to the TTA process with an effective yield more than 30× larger for TIPS-BTX compared to TIPS-Tc. The  $\phi_{TTA}$  enhancement for TIPS-BTX relative to TIPS-Tc is indicative of participation by intramolecular multiexciton states with evidence presented in spin statistical arguments that the  $^5TT$  is involved in productive channels. For TIPS-BTX we report a spin-statistical factor  $f = 0.42$  that matches or exceeds values found in champion annihilator systems such as DPA. At the same time, the poor relative efficiency of TIPS-Tc suggests involvement of non-productive bimolecular channels and excimeric states are suspected. Broadly these studies indicate that funneling of photogenerated electronic states into productive pathways, and avoiding parasitic ones, remains central to the development of champion upconversion systems.

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## Introduction

Generation of anti-stokes shifted electronic states relative to their excitation source and their application towards driving photophysical processes is an area of interest for both fundamental science and a blossoming scope of applications including solar energy conversion,<sup>1–7</sup> photoredox catalysis,<sup>8–11</sup> bioimaging and therapies,<sup>12–16</sup> and 3D printing<sup>17,18</sup> to name a few. One method of anti-stokes generation heralded for its promise in low excitation intensity scenarios is triplet–triplet annihilation upconversion (TTA-UC).<sup>2,19–24</sup> TTA-UC generally comprises a system of molecules where one species with a low energy singlet ( $S_1$ ) state, referred to as the sensitizer (Sen), is

first photoexcited and efficiently undergoes intersystem crossing into its triplet ( $T_1$ ) state. This is often driven by the heavy atom effect, for example in the palladium phthalocyanine species used here. Following collision in solution-phase diffusional systems that are common, the energy is transferred to the  $T_1$  of a harvesting molecule, referred to as the annihilator (An). Finally, collisions between two excited triplet annihilators (homofusion) or between a triplet sensitizer and a triplet annihilator (heterofusion) lead to the generation of an annihilator  $S_1$  that can fluoresce with photon energy greater than the excitation source (see Scheme 1). The conversion is mediated by an intermolecular multiexciton state and potentially other higher excited states within the collisional partners.

While upconversion has been studied with many molecular partners, a prototypical champion system in solution to be emulated consists of the annihilator 9,10-diphenylanthracene (DPA) and a metal porphyrin species (Zn, Pd or Pt octaethylporphyrin for example). Indeed, a growing body of literature on DPA has reported upconversion quantum yields  $\phi_{UC}$  of order ~25%.<sup>25,26</sup> However, usage of DPA restricts upconversion

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diethynyladamantyl bridge relative to monomer models with bridge-specific substituents.<sup>56</sup> They also found that the dimers are brighter TTA-UC emitters compared to the respective monomer models at comparable annihilator concentrations, with relative ratios of approximately 4 and 3 for the phenylene and adamantyl comparisons, respectively. They have also considered upconversion yields  $\phi_{UC}$ , as we do here, and at the highest annihilator concentrations they consider, found ratios of 3.7 and 2.8 favoring the dimers for the phenylene and adamantyl comparisons, respectively. In the current work, we consider the behavior of another rigid dimer system, this time utilizing a larger fused polycyclic bridge comprising both saturated and unsaturated fragments constructed using Pd-catalyzed annulation chemistry.<sup>58,59</sup> We measure upconversion yields and disentangle them into yields of contributing photo-physical processes with an eye towards enabling direct comparisons between dimer *versus* monomer. The results suggest significant advantages for the dimer including a  $\sim 20\times$  enhancement of  $\phi_{UC}$  and a  $\sim 35\times$  enhancement of  $\phi_{TTA}$  relative to TIPS-Tc at comparable concentrations. These studies provide evidence that intramolecular multiexciton states play decisive roles controlling upconversion yield in these NIR-visible TTA-UC systems.

## Results and discussion

### Annihilator properties

As described in the Introduction, this work seeks to compare TTA-UC properties of the monomer model TIPS-Tc relative to a new rigid dimer system TIPS-BTX that utilizes the same acene chromophore (see stick structures for both in Fig. 1). The synthesis of TIPS-BTX and the isolation of the syn-diastereomer were reported elsewhere,<sup>58,59</sup> but briefly, it is prepared through a palladium-catalyzed arene-norbornene annulation reaction (CANAL) that generates the two cyclobutene rings flanking the central xylene unit. The lowest energy electronic absorption spectrum and its mirrored emission (short-axis transition dipole moments) are vibronically structured in the expected way for delocalized acene units with low excited state nuclear reorganization, with the 0-0 features determining the band maxima. For example, in Fig. 1(b) it is seen that the absorption and emission features closely match those of TIPS-Tc. The average of the 0-0 absorption and emission features indicate an  $S_1$  energy of 2.32 eV in TIPS-BTX<sup>60</sup> and 2.30 eV for TIPS-Tc (Table 1). The similarity of absorption and emission features of TIPS-BTX relative to the monomer TIPS-Tc, particularly the lack of enhancement of the second vibronic component relative to the 0-0 band, is indicative of weak electronic coupling between the two chromophores of the dimer.<sup>61</sup> In support of this we also observe an approximate doubling of the lowest energy transition in the dimer *versus* the monomer (Fig. S1†). An absorption spectrum for TIPS-BTX was also collected in room-temperature chloroform (Fig. S2†) which has a higher energy UV cutoff than toluene. These data show the intense UV transition (peaked at 296 nm) derived from the long-axis transition dipole moment of the chromophore units. No Davydov splitting is observed, as is expected from the long bridge including two norbornyl spacers

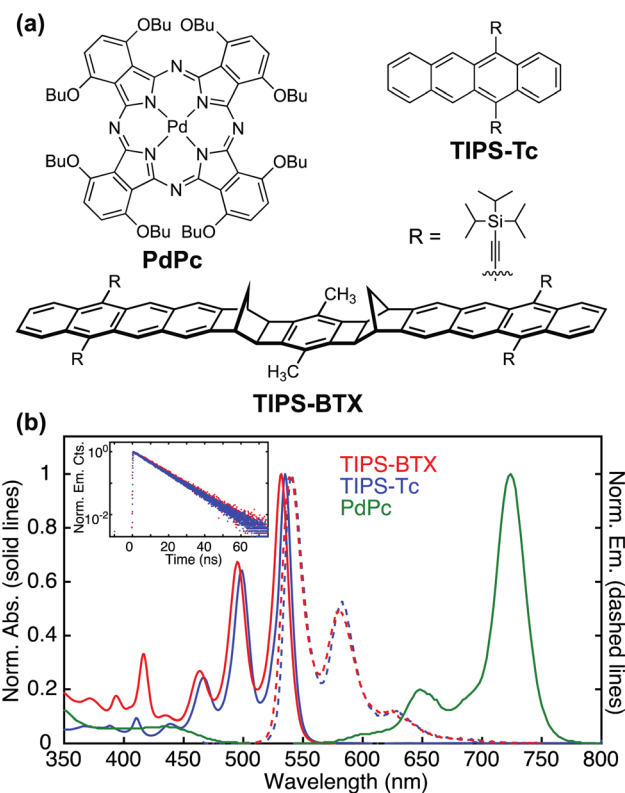


Fig. 1 (a) Chemical stick structures of annihilators TIPS-BTX & TIPS-Tc and sensitizer PdPc. (b) Room temperature absorption (solid lines) and emission (dashed lines) spectra of TIPS-BTX, TIPS-Tc and PdPc in toluene. Inset: TCSPC decay traces of TIPS-BTX & TIPS-Tc in deoxygenated 298 K toluene ( $\lambda_{ex} = 405$  nm;  $\lambda_{em} = 540$  nm).

as well as the near-collinear arrangement of the two chromophores of the dimer such that the higher energy transition of a split pair would be dark.

Further photophysical characterization confirms similarities between the dimer and the monomer model. The quantum yield of fluorescence for TIPS-BTX was measured to be  $\phi_{FL} = 72$

Table 1 Summary of relevant photophysical parameters for sensitizer and annihilators

	TIPS-Tc	TIPS-BTX	PdPc
$S_1$ (eV)	2.30	2.32	1.71
$T_1$ (eV)	1.21 <sup>a</sup>	$\sim 1.21^b$	1.13 <sup>c</sup>
TT (eV)	2.42 <sup>d</sup>	$< 2.41^e$	—
$\phi_{FL}$ (%)	74	$72 \pm 7$	—
$\tau_{0,S}$ (ns)	12.4	$12.7 \pm 0.5$	—
$\tau_{0,T}$ ( $\mu$ s)	290	410	3.42

<sup>a</sup> Reported from a phosphorescence measurement of TIPS-Tc in a polystyrene thin film.<sup>78</sup> <sup>b</sup> It is assumed that the dimer will have a  $T_1$  energy that is similar to TIPS-Tc (see (a)) given the nature of the chromophores. <sup>c</sup> Reported from a phosphorescence measurement of PdPc in toluene.<sup>33</sup> <sup>d</sup> The energy of the intermolecular multiexciton state for the monomer is approximated to be twice the  $T_1$  energy. <sup>e</sup> The upper bound in this TT energy estimation relates to the  $T_1$  yield measurement made by TA (Fig. 2) See equilibrium analysis in ESI (section S6) for details.

$\pm 7\%$ , comparable to that for TIPS-Tc at  $\phi_{\text{FL}} = 74\%$ . Regarding emissive singlet lifetimes, time-correlated single photon counting (TCSPC) measurements at 540 nm (coincident with the 0-0 transition) following excitation at 405 nm indicate mono-exponential decay for both molecules with lifetimes of  $\tau_{0,\text{S}} = 12.7 \pm 0.5$  ns and  $\tau_{0,\text{S}} = 12.4$  ns for TIPS-BTX and TIPS-Tc, respectively (see inset in Fig. 1(b)). Results collected at 578 nm, corresponding to the 0-1 emission transition, were consistent.

As photoluminescence measurements are insensitive to dark states that may be produced in the dynamical evolution away from the emissive state, a transient absorption (TA) experiment was performed over a time range spanning  $\sim 500$  ps to 100  $\mu\text{s}$ . The TA spectra obtained for TIPS-BTX (Fig. 2) are comparable to those previously reported for TIPS-Tc,<sup>62</sup> showing a strong ESA at  $\sim 420$  nm, negative features at  $\sim 540$  nm and  $\sim 580$  nm, and broad weak ESA  $\geq 600$  nm. Of the negative features, 580 nm corresponds to stimulated emission of the 0-1 band while 540 nm is a convolution of ground state bleach and stimulated emission of the 0-0 band. The ESA with peaks at 480 nm and 520 nm and valleys at 470 nm and 490 nm comes from contributions due to bleach of the vibronically structured ground-state absorption, a quality that is also observed in TIPS-Tc and other related dimers.<sup>62,63</sup> These spectral features begin decaying on the order of nanoseconds with no other significant spectral evolution observed. Single wavelength kinetics traces extracted from the overall dataset exhibit decay to baseline at most wavelengths with a time scale of order 10 ns, consistent with the TCSPC measurements. However, there is minor  $\Delta\text{Abs}$

persistence at long times at the 520 nm ESA maximum. The full wavelength/time dataset can be cleanly modeled using a biexponential decay function (Fig. 2), returning a major component with a lifetime of 12.9 ns (Fig. S4†) that matches well with the singlet lifetime observed *via* TCSPC (Fig. 1(b)). A long-lived component peaking at  $\sim 520$  nm is also observed, but it is significantly weaker (Fig. S4†). TIPS-Tc based dimers in singlet fission studies are known to have ESA intensity in this wavelength region heralding triplet character from either triplet multiexcitonic states ( $^{2\text{S}+1}\text{TT}$ ) or isolated triplets ( $\text{T}_1$ ).<sup>63-70</sup> Given the long lifetime that approximately matches sensitization experiments (Fig. S6†) this weak feature observed in TIPS-BTX is best explained as arising due to formation of a small amount of isolated  $\text{T}_1$ .

The observation of  $\text{T}_1$  population in such a dimer is an interesting one for fundamental reasons involving singlet fission, although we primarily address it here given its potential to complicate a comparative analysis (dimer *versus* monomer) of TTA-UC. First, we do not believe that  $\text{T}_1$  population arises due to intersystem crossing, on the basis that no  $\text{T}_1$  is observed in the monomer model TIPS-Tc.<sup>62</sup> This then raises the likelihood of an origin in singlet fission, although there is underlying complexity. In related rigid tetracenic dimers such as TIPS-BT1<sup>62</sup> and TIPS-BT1',<sup>63</sup> where the acene chromophores are separated by a single norbornyl bridge, we have observed formation of the multiexciton singlet  $^1\text{TT}$  in equilibrium with  $\text{S}_1$ , but this equilibrated set of states decays to the ground state without observation of isolated  $\text{T}_1$ . However, other non-rigid tetracenic dimer systems have shown long-lived  $\text{T}_1$  populations that may be presumed to originate from the multiexcitonic triplet ( $^{2\text{S}+1}\text{TT}$ ) manifold, likely following internal conversion *via* the  $^3\text{TT}$ ,<sup>56,67,69</sup> something that is more commonly seen in pentacene-based dimers (*e.g.* ref. 71-73). We suspect that TIPS-BTX is behaving in a similar way and that the difference in its photophysics relative to the other rigid dimers TIPS-BT1 and TIPS-BT1' has origins in its smaller isotropic spin-spin exchange interaction  $J$  due to the significantly larger bridge. Detailed studies, including time resolved EPR measurements, will be needed to fully disentangle the dynamics. A cursory estimate of  $\text{T}_1$  yield is made for TIPS-BTX using information that includes the focal volume of the pump laser in the sample as well as a  $\Delta\epsilon$  measurement that was made for the  $\text{T}_1$  in the related rigid dimer system TIPS-BT1' (see ESI for details†). We find an upper bound in  $\text{T}_1$  yield in TIPS-BTX of 6.5% and suggest that this yield is low enough to proceed with an analysis of TTA-UC that hinges upon comparisons between dimer and monomer.

As a final photophysical characterization of the annihilators, triplet lifetimes of TIPS-BTX and TIPS-Tc have been measured, as the rate constant for triplet decay is intimately tied to the probability/yield of TTA mediated by collisional interactions between excited state annihilator species. Using triplet sensitization experiments initiated by photoexcited anthracene ( $\phi_{\text{ISC}} = 0.71$ ;<sup>74</sup> see ESI for details†), modest differences are uncovered between dimer and the monomer model where TIPS-BTX exhibits a triplet lifetime of  $\tau_{0,\text{T}} = 410$   $\mu\text{s}$  ( $k_{0,\text{T}} = 2.4 \times 10^3$   $\text{s}^{-1}$ ) and where TIPS-Tc is slightly shorter at  $\tau_{0,\text{T}} = 290$   $\mu\text{s}$  ( $k_{0,\text{T}} = 3.4$

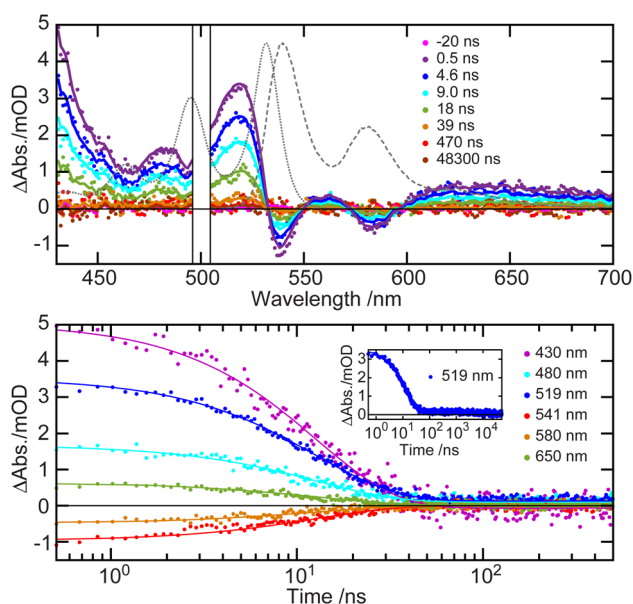


Fig. 2 (Top) Selected transient absorption spectra for TIPS-BTX in deaerated room temperature toluene as a function of time (dots are raw data; lines are from a global biexponential decay model). The region surrounding the excitation wavelength of 500 nm is removed due to pump scatter. Absorption (dotted line) and emission (dashed line) are included for reference. (Bottom) Single wavelength kinetic traces (dots) with inclusion of the biexponential model (lines). The insert is a selected kinetic trace at 519 nm to highlight the minor long-lived ESA feature.

$\times 10^3 \text{ s}^{-1}$ ) (Fig. S6†). We anticipate these lifetime differences are tied to the energy gap law where the cyclobutene/norbornyl bridge slightly raises the  $T_1$  energy in TIPS-BTX relative to TIPS-Tc as was seen for the  $S_1$  energies in Table 1. To put these triplet lifetime values in some context, they are long enough to expect opportunities for collision-mediated TTA, with some modest advantage expected for the dimer. However, both lifetimes remain more than an order of magnitude shorter than champion annihilator systems like DPA,<sup>75</sup> and several times shorter than TIPS-anthracene.<sup>76</sup> This general trend is understood as being due to the smaller amount of triplet energy stored in tetracenic *versus* anthracenic annihilator systems, with consequences in non-radiative excited state decay as predicted using the energy gap law. This highlights a need to identify strategies for improving TTA-UC in systems designed to process lower energy photons.

### Sensitizer properties

Sensitization of TIPS-BTX and TIPS-Tc utilized the *n*-butoxide-substituted palladium phthalocyanine species shown in Fig. 1a abbreviated as PdPc, that was also previously used with another TIPS-tetracene derived rigid dimer system as mentioned in the Introduction.<sup>33</sup> The intersystem crossing yield  $\phi_{ISC}$  has been reported to be 0.75 in room temperature deoxygenated benzene;<sup>77</sup> *i.e.* a solvent similar to the toluene used herein. Phosphorescence measurements<sup>33</sup> indicate the triplet stores 1.13 eV and we measure a lifetime of 3.42  $\mu\text{s}$  in room temperature deoxygenated toluene (Fig. S5†). Although a unity  $\phi_{ISC}$  is desirable, these sensitizer properties are adequate for exploration of dimer *versus* monomer trends. The electronic spectrum of PdPc is characterized by a strongly absorbing Q band observed from  $\sim 600$ –750 nm (see Fig. 1(b)) with minimal absorption overlap with the  $S_1$  emission of the annihilators.

### Annihilator and sensitizer together in UC systems

To explore TTA-UC property differences between dimer and monomer, a focus is placed on upconversion quantum yields ( $\phi_{UC}$ ). The expression shown in Eq. 1a is fundamentally bound at 1/2, because two absorption events are minimally required for the emission of one photon. This bounding occurs within  $\phi_{TTA}$  (see Eq. S10†) a quantity that refers to annihilation exclusively through the singlet channel. The term  $f$  is a spin statistical factor used to account for different reactive pathways associated with singlet, triplet, and quintet character in encounter complexes between two triplets ( $S = 1$  particles). It is simplified under conditions of strong exchange coupling between the two triplets such that overall spin in the encounter complex is a good quantum number (*i.e.*,  $^{2S+1}(T\cdots T)$ ).<sup>79</sup> The factor  $f$  is bound at 1, a rare situation where all spin channels are without loss, for example because both  $^5(T\cdots T)$  and  $^3(T\cdots T)$  are unreactive and simply re-dissociate to form isolated  $T_1$ 's, while the singlet encounter complex  $^1(T\cdots T)$  engages in annihilation to  $S_1 + S_0$ .<sup>80</sup> If, on the other hand,  $^5(T\cdots T)$  and  $^3(T\cdots T)$  are fully unproductive, leading to  $S_0$  for all species  $f = \frac{1}{9}$ , reflecting only the statistical weight of the singlet channel. If the  $^5(T\cdots T)$  is

without loss but the  $^3(T\cdots T)$  decays to a single  $T_1$  (for example due to annihilation to  $T_2 + S_0$  followed by rapid internal conversion  $T_2 \rightarrow T_1$ ) then  $f = \frac{2}{5}$  (*i.e.*, 0.4) and  $\phi_{UC}$  is bound at 20% (*i.e.*,  $\frac{2}{5} \times \frac{1}{2}$ ). For now, we fold the  $f$  into  $\phi'_{TTA}$  and organize initial discussions around the simpler Eq. 1b.<sup>81</sup> Further discussions about Eq. 1a will follow later. It is noted that when systems experience losses that are otherwise unaccounted for, the statistical factor  $f$  is the repository manifesting as a low value. This limitation of the framework is taken into account and guides the discussion later.<sup>82</sup>

$$\phi_{UC} = f\phi_{ISC}\phi_{TET}\phi_{TTA}\phi_{FL} \quad (\text{Eq. 1a})$$

$$\phi_{UC} = \phi_{ISC}\phi_{TET}\phi'_{TTA}\phi_{FL} \quad (\text{Eq. 1b})$$

$$\phi_{TET} = \frac{k_{TET}[\text{An}]}{k_{TET}[\text{An}] + k_{0;T(\text{Sen})}} \quad (\text{Eq. 1c})$$

$$\begin{aligned} \phi_{TTA}(\text{homofusion}) &= \frac{\phi'_{TTA}}{f} = \frac{1}{2} \times \frac{2k_{TTA}[^3\text{An}^*]}{2k_{TTA}[^3\text{An}^*] + k_{0;T(\text{An})}} \\ &= \frac{k_{TTA}[^3\text{An}^*]}{2k_{TTA}[^3\text{An}^*] + k_{0;T(\text{An})}} \end{aligned} \quad (\text{Eq. 1d})$$

The outer quantities of Eq. 1b are unimolecular and depend on the yield of ISC in the sensitizer and the yield of fluorescence in the annihilator ( $\phi_{ISC}$  and  $\phi_{FL}$ , *vide supra*). The inner quantities on the other hand are bimolecular in nature (see typical UC schematic in Scheme 1). For the first, the yield of triplet-triplet energy transfer ( $\phi_{TET}$ ; Eq. 1c) involves photoexcited sensitizer and ground state annihilator, with dependence on the rate constant for TET ( $k_{TET}$ ), on the rate constant for triplet loss in the absence of interactions with annihilator ( $k_{0;T(\text{Sen})} = 1/\tau_{0;T(\text{Sen})}$ ), and on the ground state concentration of the annihilator ( $[\text{An}]$ ). The second term derives from collisional interaction between a triplet excited state annihilator and another triplet. In principle this can occur either from the excited sensitizer (heterofusion) or from an excited-state annihilator species (homofusion). However, in the low relative sensitizer concentration regime that was investigated, homofusion is expected to be the dominant pathway. The simplest expression for  $\phi_{TTA}$  under these conditions is Eq. 1d, which assumes the only loss pathways for  $[^3\text{An}^*]$  population is *via* unimolecular decay of the triplet (governed by the rate constant  $k_{0;T(\text{An})}$ ) and bimolecular loss *via* annihilation of two  $[^3\text{An}^*]$  species producing one  $S_1$  and one  $S_0$ , governed by the rate constant  $k_{TTA}$  as well as  $[^3\text{An}^*]$ . As described more below, this expression can enable preliminary estimates of  $k_{TTA}$ , but there are limits to its utility under conditions where other bimolecular channels contributing to triplet loss are active.

### Determination of $\phi_{TET}$

Stern-Volmer studies using nanosecond TA were performed to determine  $\phi_{TET}$  between PdPc and each of the two annihilators.



PdPc was photoexcited at 650 nm and monitored with a probe wavelength of 600 nm where the PdPc  $T_1$  exhibits a broad excited-state absorption. Unquenched  $T_1$  in PdPc decays to baseline monoexponentially with a fitted lifetime of  $\tau_{0,T(\text{Sen})} = 3.42 \mu\text{s}$  (Fig. S5†), matching well with previous literature.<sup>33,77</sup> On the other hand, samples prepared with either TIPS-BTX or TIPS-Tc show a reduction of the PdPc  $T_1$  lifetime that is proportional to annihilator concentration, *i.e.*, a hallmark of dynamic quenching (Fig. 3 (top)). Fitting the plotted data to the classic Stern–Volmer equation (Eq. 2) allows for the determination of the constant  $K_{\text{SV}}$ , and from this and the triplet lifetime of the sensitizer, the determination of a quenching rate constant  $k_q$ .

$$\frac{\tau_{0,T(\text{Sen})}}{\tau_{T(\text{Sen})}} = 1 + K_{\text{SV}}[\text{An}]$$

$$= 1 + \tau_{0,T(\text{Sen})}k_q[\text{An}] \approx 1 + \tau_{0,T(\text{Sen})}k_{\text{TET}}[\text{An}] \quad (\text{Eq. 2})$$

An assumption follows that Dexter energy transfer is the only operative pathway for quenching and  $k_q$  is equated with  $k_{\text{TET}}$ . From the data shown in Fig. 3 (top), a slope  $K_{\text{SV}}$  of  $1026 \text{ M}^{-1}$  and  $2019 \text{ M}^{-1}$  are determined for TIPS-BTX and TIPS-Tc, respectively, demonstrating that the monomer engages in energy transfer with the sensitizer triplet excited state more readily than the dimer, consistent with its smaller size. These slopes

along with  $\tau_{0,T(\text{Sen})} = 3.42 \mu\text{s}$  indicate  $k_{\text{TET}} = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for TIPS-BTX and  $k_{\text{TET}} = 5.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for TIPS-Tc.

With these  $k_{\text{TET}}$  values in hand, the quantum yield  $\phi_{\text{TET}}$  was calculated for all upconversion samples as  $[\text{An}]$  is varied for both monomer and dimer according to Eq. 1c. As expected from the quenching constants, TIPS-BTX at equimolar concentrations shows less efficient transfer of the triplet from the sensitizer to the annihilator as compared to TIPS-Tc (Fig. 3 (bottom)). This behavior has been seen in several previous dimeric systems<sup>26,33,47,51</sup> and again is explained by the larger molecular volume of dimers slowing diffusion in the solvent medium.

### Exploration of $\phi_{\text{UC}}$ and elucidation of $\phi'_{\text{TTA}}$ and $k_{\text{TTA}}$

From the yield quantities discussed so far that depend in some way on annihilator properties ( $\phi_{\text{FL}}$  and  $\phi_{\text{TET}}$ ), one can assume a modest advantage for the monomer TIPS-Tc over the dimer TIPS-BTX. From this perspective  $\phi_{\text{UC}}$  is particularly interesting. Unlike for  $\phi'_{\text{TTA}}$ , the quantification of  $\phi_{\text{UC}}$  is experimentally straightforward using actinometry, and the value can then be used to determine  $\phi'_{\text{TTA}}$  via Eq. 1b (*vide infra*). As has been discussed elsewhere,<sup>21</sup> there is complexity in reporting  $\phi_{\text{UC}}$  because it is not simply dependent on the nature of the annihilator and sensitizer being used, but also on the experimental conditions of annihilator concentration  $[\text{An}]$  and photoexcitation fluence. The variable  $[\text{An}]$  influences  $\phi_{\text{TET}}$  (Eq. 1c and Fig. 3 (bottom)) but it also impacts  $\phi'_{\text{TTA}}$  by altering the concentration of triplets [ $^3\text{An}^*$ ] that are formed following collision with photoexcited sensitizer molecules. In a related way, photoexcitation fluence also controls [ $^3\text{An}^*$ ]. In experiments described below, both variables are explored independently in dimer *versus* monomer comparisons.

Upconversion samples of  $\sim 1.3 \mu\text{M}$  PdPc sensitizer and annihilators of varying higher concentrations were prepared in deaerated toluene (Fig. S3†) and excited with a 730 nm diode laser with fluences ranging from  $\sim 500$ – $250\,000 \text{ mW cm}^{-2}$ . For all dimer and monomer annihilator concentrations explored, we observe the expected crossover in the upconversion emission intensity from quadratic dependence on laser fluence to linear dependence (Fig. S7–S10†). At the highest concentrations explored for TIPS-Tc, this crossover occurs at  $52 \text{ W cm}^{-2}$  (see ESI, Fig. S8 and S9† for TIPS-Tc/TIPS-BTX fluence crossover points), comparable to the crossover observed by Pun *et al.* ( $44.5 \text{ W cm}^{-2}$ ).<sup>47</sup> The crossover for TIPS-BTX is observed to be  $37 \text{ W cm}^{-2}$  at the highest concentration investigated. While still lower than the crossover observed for TIPS-Tc, we expect this would be further reduced at higher annihilator concentration where we could expect increased triplet energy transfer efficiency.<sup>83</sup> The crossover could be further reduced under optimal sample conditions, such as greater absorption at the excitation wavelength or when paired with an alternative sensitizer. We acknowledge that these crossing values are not insignificant, particularly when compared with those observed in anthracene system, nor expected solar fluxes. Still, this higher fluence region signals the strong annihilation regime where measurement of upconversion yield should be constant as laser fluence

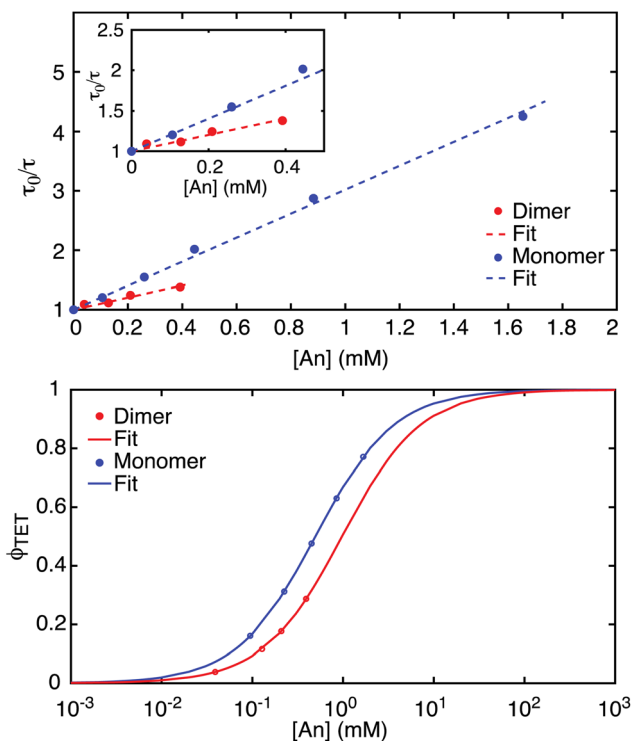


Fig. 3 (Top) Stern–Volmer plot for TIPS-BTX and TIPS-Tc in room-temperature toluene. Slopes reflecting  $K_{\text{SV}}$  along with sensitizer lifetime leads to values of  $k_{\text{TET}} = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for TIPS-BTX and  $k_{\text{TET}} = 5.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for TIPS-Tc. The inset focuses on the lower annihilator concentration regime. (Bottom) Concentration dependent triplet energy transfer (TET) yields from Eq. 1c for TIPS-BTX and TIPS-Tc in room-temperature toluene.

increases,<sup>84</sup> thus allowing for independent interrogation of annihilator concentration effects (*vide infra*).

Fig. 4 (top) shows upconversion quantum yields measured *versus* laser fluence for TIPS-BTX at 0.39 mM and TIPS-Tc at 0.45 mM and at 1.67 mM. Upconversion emission spectra were corrected for self-absorption prior to integration and yields determined actinometrically against a directly excited TIPS-Tc reference in room temperature toluene (see ESI for details†). In the three cases,  $\phi_{UC}$  saturates at higher fluences consistent with measurement in the strong annihilation regime. Critically, the dimer consistently outperforms the monomer. At comparable concentrations (0.39 mM for TIPS-BTX and 0.45 mM for TIPS-Tc) the dimer shows a maximum  $\phi_{UC}$  (3.3%) that is more than 20 times that observed for the monomer (0.16%). But even when the monomer concentration is increased by more than a factor of three to 1.67 mM in order to affect an increase in  $[^3An^*]$ , the dimer outperforms the monomer (3.3% *versus* 0.52%; *i.e.*, a factor of 6.3 improvement).

Having established boundaries for the strong annihilation regime, a concentration-dependent study of  $\phi_{UC}$  for dimer *versus* monomer was also made using a fixed laser fluence well into this regime at  $2.3 \times 10^5 \text{ mW cm}^{-2}$  for TIPS-BTX and at  $2.4 \times 10^5 \text{ mW cm}^{-2}$  for TIPS-Tc. Neither sample reaches saturation of  $\phi_{UC}$  as a function of annihilator concentration in the range

employed here, but both appear on their way, particularly in the case of the monomer where we had access to larger amounts of compound during these studies (Fig. 4 (bottom)). As was seen for excitation fluence, this plot highlights significant advantages held by the dimer *versus* the monomer. For example, at common concentrations (see the vertical dashed arrows to guide the eye), the dimer outperforms the monomer by well over an order of magnitude, even though it is worse at TET (seen in Fig. 3 (bottom)). As another example, the same UC brightness measured as  $\phi_{UC}$  for TIPS-Tc at 1.67 mM can be achieved for TIPS-BTX at approximately an order of magnitude lower concentration (see the horizontal dashed arrow to guide the eye). At the highest fluence and concentration investigated for the dimer, a steady-state triplet concentration is calculated to be  $14 \mu\text{M}$ , a factor of  $27\times$  less than the ground state concentration. This argues strongly against advantage being gained by the dimer in this diffusional setting due to a double sensitization mechanism.<sup>26</sup> While the maximum upconversion yield of 3.3% achieved at 0.39 mM TIPS-BTX is encouraging relative to monomer results, it does remain significantly below bluer upconverting champion systems like DPA that achieve yields  $\sim 25\%$ .<sup>25,26</sup> But it is emphasized that our UC system as a whole is unoptimized, for example from the perspective of the sensitizer whose  $\phi_{ISC}$  is 75% and whose triplet lifetime limits  $\phi_{TET}$  at 29% at the highest annihilator concentration that was used (Fig. 3 (bottom)).

As was suggested at the beginning of this section, the quantification of  $\phi_{UC}$  as a function of annihilator concentration while in the strong annihilation regime enables determination of  $\phi'_{TTA}$  using the other known quantities in Eq. 1b. These  $\phi'_{TTA}$  are shown in Fig. 5 and like  $\phi_{UC}$  highlight the advantage held by the dimer but now with considerations of poorer TET from the sensitizer due to the larger dimer size removed. These data also expose the overall quality of the dimers at negotiating productive TTA. As described earlier, the theoretical limit for  $\phi'_{TTA}$  is  $\frac{1}{2}$ , corresponding to a case where the spin statistical factor  $f=1$ . At the larger annihilator concentrations considered here, Fig. 5

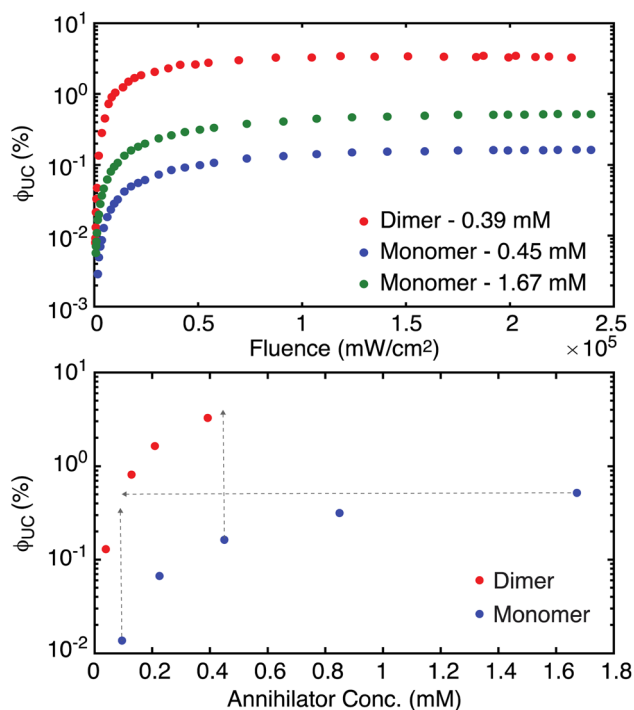


Fig. 4 (Top) Fluence dependent upconversion QY for the highest concentration dimer sample (red; 0.39 mM TIPS-BTX), a comparable concentration monomer sample (blue; 0.45 mM TIPS-Tc), and for a higher concentration monomer sample (green; 1.67 mM TIPS-Tc). Upconversion QYs asymptotically approach an upper limit as fluence increases, corresponding the transition from quadratic to linear fluence behavior. (Bottom) Upconversion QY as a function of varied annihilator concentration, measured with excitation fluence at  $2.3 \times 10^5 \text{ mW cm}^{-2}$  for TIPS-BTX and  $2.4 \times 10^5 \text{ mW cm}^{-2}$  for TIPS-Tc.

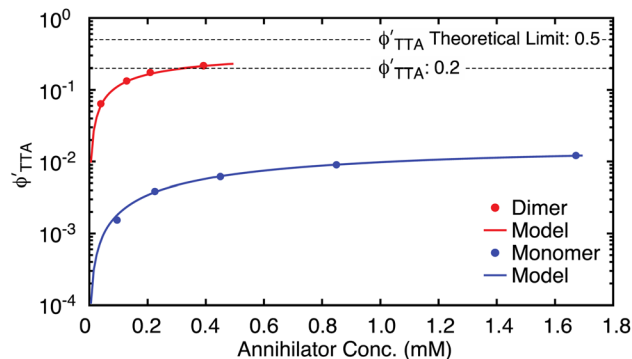


Fig. 5  $\phi'_{TTA}$  plotted against annihilator concentration for TIPS-Tc (blue) and TIPS-BTX (red). The results of a simplistic fitting model are included which assumes that annihilator triplet loss is only due to unimolecular decay and TTA *via* the singlet channel. See text and ESI† for discussion.

indicates that TIPS-BTX is asymptotically approaching its maximal value of  $\phi'_{\text{TTA}}$  at the highest concentration considered (0.39 mM). The largest value that we measure is  $\phi'_{\text{TTA}} = 0.21$ , corresponding to  $f = 0.42$  if annihilation from the singlet channel is unity. This value reflects 42% of the theoretical maximum of  $\phi'_{\text{TTA}} = \frac{1}{2}$  (a case that demands  $f = 1$ ). While smaller than what is seen in perylene-based upconversion,<sup>80</sup> this is on par with champion DPA systems.<sup>25,76,85</sup> Juxtaposed relative to the monomer at a similar concentration of 0.45 mM where  $\phi'_{\text{TTA}} = 0.0062$  (corresponding to 1.2% of the theoretical maximum), this is a compelling finding. Importantly, in the limit that the other efficiencies invoked by Eq. 1b are well characterized, any additional loss pathways that detract from productive TTA would be attributed to the spin statistical factor by this analysis,<sup>82</sup> even when such parasitic pathways do not necessarily relate to spin statistics. In the case of TIPS-Tc presented here, we suspect a parasitic excimer state<sup>86</sup> (discussed in more detail later) to form from the multiexciton collision complex, leading to the low observed yield.

These  $\phi'_{\text{TTA}}$  data can be subjected to a simple model, albeit with significant caveats alluded to below. The impetus for modeling flows from Eq. 1d which suggests that while annihilation yields are influenced by annihilator triplet lifetimes (where the dimer holds a modest advantage over the monomer (Table 1)), the rate constant  $k_{\text{TTA}}$  might in principle serve as a fundamental measure of the probability of these photophysics for a given triplet concentration. If we make the likely too-simplistic (*vide infra*) assumptions that the dimer and monomer react similarly and that the only loss pathways for annihilator triplets is from unimolecular decay and TTA *via* the singlet channel, it is possible to obtain an expression for  $[^3\text{An}^*]$  as a function of annihilator concentration, with  $k_{\text{TTA}}$  as a single unknown (see Eq. S12<sup>†</sup>). This expression is then placed into Eq. 1d (or Eq. S10<sup>†</sup>), providing a fitting model for  $\phi_{\text{TTA}}$  *versus*  $[\text{An}]$  that reveals  $k_{\text{TTA}}$ . Fig. 5 shows this modeling with the result that  $k_{\text{TTA}} = 6.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for the dimer TIPS-BTX, nearly two orders of magnitude larger than  $k_{\text{TTA}} = 6.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  obtained for the monomer TIPS-Tc. It is expected that  $k_{\text{TTA}}$  is higher than stated here for the monomer, and instead TTA is in competition with parasitic second-order pathways. However, this is a behavior that is unaccounted for by a simple model, and further discussion will be focused on the apparent gains in efficiency made by the dimer TIPS-BTX.

We propose a qualitative framework towards understanding the strong variation in  $\phi'_{\text{TTA}}$  that favors the dimer TIPS-BTX over the monomer model TIPS-Tc. This is presented in Scheme 2 which aims to highlight differences in reactive pathways available to the two systems. Both monomer and dimer start from the perspective of a collisional encounter between two triplet ( $T_1$ ) excited state annihilator species (*i.e.*, relevant for homo-fusion). These collisional encounters are ongoing in competition with nonradiative triplet decay to ground state. The schemes for both dimer and monomer also acknowledge the underlying spin statistics where, for example, there is a  $5\times$

higher probability that the encounter complex gains quintet character compared to that of a singlet.

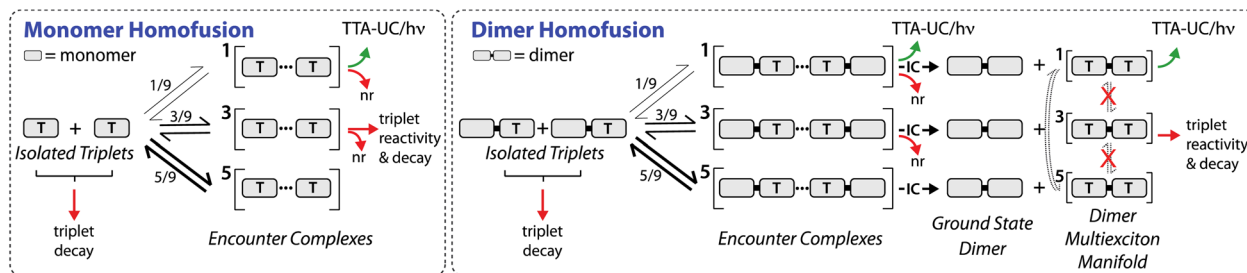
In the monomer system, the set of available pathways largely reflects expectations in place from studies of diffusional TTA-UC cases in the literature.<sup>84,87</sup> For example, the route towards  $S_1$  emission ( $h\nu$ ) is *via* TTA originating from a spin singlet encounter complex (summarized with the upward curved green arrow in Scheme 2 towards TTA-UC/ $h\nu$ ). Encounter complexes with quintet character are not expected to confront loss pathways. Rather, the absence of an energetically accessible monomer-based quintet state means that re-dissociation is the most relevant outcome, forming isolated triplets that are again subjected to their own non-radiative losses.

The triplet encounter complex pathway could either dissociate in the same way just described for the quintet, or it could engage in its own reactivity such as annihilation to an energetically accessible triplet excited state followed by conversion to a single  $T_1$  plus heat. Although general, the diagram can address why monomers such as TIPS-Tc compete poorly relative to champion systems such as DPA. The pathway 'triplet decay' is important, with the Energy Gap Law driving shorter lifetimes for the lower energy  $T_1$  in TIPS-Tc compared to DPA. Also important and related are processes relevant to singlet fission (SF), the microscopic reverse of TTA ( $S_1 \rightarrow$  multiexciton singlet  $\rightarrow T_1 + T_1$ ). In TIPS-Tc the energy of two isolated triplets is expected to be comparable to the singlet multiexciton encounter complex or to a monomeric  $S_1$ . In other words, while singlet fission is energetically relevant in TIPS-Tc, in DPA it is uphill. As SF transiently occurs in TIPS-Tc – in particular the final step where the multiexciton singlet encounter complex dissociates (the reverse equilibrium arrow in the singlet channel) – a pair of isolated  $T_1$  species are formed and again these are subject to their own nonradiative decay.

The reactive weight of triplet decay in this TIPS-Tc system compared to DPA means that one must work harder, in terms of excitation fluence, annihilator concentration, or both, to drive into the strong annihilation limit. However, once there,  $\phi_{\text{TTA}}$  should not inherently be limited by smaller triplet lifetimes.<sup>83</sup> This then suggests other effects driven by second order interactions between excited-state annihilators. These are symbolized by the downward curved red arrows in the Scheme 2 diagram signaling non-radiative decay from the singlet or triplet encounter complexes. Here we invoke observations made by Schmidt and coworkers studying excited-state dynamics of TIPS-Tc photoexcited in high-concentration solutions.<sup>86</sup> These workers see evidence for singlet fission, but they also see evidence for a loss pathway *via* a spin-singlet excimer state.<sup>87</sup> In the context of Scheme 2 we are implying that spin-singlet or spin-triplet encounter complexes could, for certain collision geometries, encounter non-radiative loss *via* excimer channels.

For the dimer system, the key distinction relative to the TIPS-Tc monomer lies in the fact that each spin-state encounter complex ( $^{1,3,5}(\text{T}\cdots\text{T})$ ) has an energetically accessible internal conversion (IC) pathway where energy reapporitions, leading to formation of an *intramolecular* multiexciton state ( $^{1,3,5}\text{TT}$ ) along with one ground state dimer. In all cases this is competing against triplet dissociation. Thus, to the extent that the  $^{1,3,5}\text{TT}$





**Scheme 2** Framework highlighting pathway differences available to the dimer TIPS-BTX compared to the monomer TIPS-Tc. Both systems start with an encounter complex between isolated triplets on either monomers (left) or dimers (right) and therefore the diagrams correspond to homofusion. For simplicity spin is shown as a good quantum number with spin statistics of the singlet versus triplet versus quintet channels reflected in the thickness of the equilibrium arrows. The key difference for dimers follows from internal conversion (IC) pathways. See text for further discussion.

might then access productive outcomes, IC can provide a valuable alternative to annihilator triplet decay or non-radiative loss from encounter complexes. To this last point, while TIPS-BTX has additional steric bulk relative to the monomer TIPS-Tc, its two chromophores that are juxtaposed outward remain exposed to the environment and intermolecular excimeric geometries that would be loss-inducing should remain possible. Thus, the marked improvement in  $\phi_{\text{TTA}}$  for TIPS-BTX relative to TIPS-Tc points to the relevance of intramolecular multiexciton states.

We reason that the singlet channel is likely to be productive although we have not observed the  $^1\text{TT}$  in TIPS-BTX directly (*vide supra*) and only know that the  $\text{S}_1$  radiates efficiently ( $\phi_{\text{FL}} = 0.72$ ) with observed decay in 12.7 ns when formed directly (Table 1). However, we can infer from a related norbornyl-bridged TIPS-pentacene dimer (TIPS-BP1') where the  $^1\text{TT}$  (storing  $\sim 1.7$  eV) is formed quantitatively following visible photoexcitation. Its primary decay pathway involves non-radiative ground-state recovery in 102 ns in room temperature toluene.<sup>63</sup> For a system like TIPS-BTX studied here that is similarly rigid compared to TIPS-BP1' but that stores significantly more energy in its  $^1\text{TT}$  ( $\sim 2.41$  eV; Table 1), our expectation is that direct  $^1\text{TT} \rightarrow \text{GS}$  non-radiative decay will be slowed due to the energy gap law, thus affording ample time ( $>100$  ns) for conversion to the  $\text{S}_1$  with access to its dominant ( $\phi_{\text{FL}} = 0.72$ ) radiative decay channel.

We also anticipate opportunities in the higher statistical weight quintet channel. Again, regarding the related TIPS-BP1', we have recently shown using time-resolved EPR (trEPR) measurements that  $^5\text{TT}$  signatures are observable,<sup>88</sup> a characteristic that has also been seen in other singlet fission systems including molecular dimers. This point is important because it means that the  $^1\text{TT}$  (formed first from the  $\text{S}_1$ ) is evolving in the multiexciton manifold to generate the  $^5\text{TT}$ . By converse, and therefore relevant to this current work, an intramolecular quintet ( $^5\text{TT}$ ) formed by IC in an upconversion system is coupled to the  $^1\text{TT}$  and through it to productive photoluminescence channels (see dotted equilibrium arrows in Scheme 2). Importantly and related, the trEPR studies of TIPS-BP1' also reveal a valuable null result: they show no evidence for evolution of the  $^5\text{TT}$  into the triplet manifold, an observation that is highly unusual in the scope of SF systems that have been

explored using trEPR (*e.g.* ref. 72, 73, 89 and 90). This avoidance is significant because the  $^3\text{TT}$  has access to spin-allowed loss pathways ( $^3\text{TT} \rightarrow \text{T}_1 + \text{heat}$ ). Thus, if avoidance of  $^5\text{TT} \rightarrow ^3\text{TT}$  on relevant time scales is a property built into these types of rigid dimer systems, of which TIPS-BTX is a member, it would afford an opportunity to harness the higher statistical weight quintet channel towards TTA while limiting exposure to non-radiative triplet biexciton loss followed by  $\text{T}_1$  decay. As noted in the introduction, non-rigid tetracenic dimers have been studied relative to TIPS-Tc with observation of an upconversion photoluminescence improvement of  $6 \times 10^{47}$  to  $10 \times 10^{56}$  at the highest annihilator concentrations used compared to the  $\sim 20 \times$  increase seen here (Fig. 4). It is possible that rigid tetracenic dimers are able to exploit the  $^5\text{TT}$  in addition to the  $^1\text{TT}$  while non-rigid systems utilize only the latter.

The last point was about protecting the  $^5\text{TT}$  against loss pathways that would manifest through the triplet manifold. But this also implies that it is challenging to expect upconversion benefits in TIPS-BTX when triplet encounter complexes are initially formed, even if internal conversion to an intramolecular  $^3\text{TT}$  outcompetes re-dissociation of the  $^3(\text{T} \cdots \text{T})$  or direct non-radiative losses to  $\text{T}_1$  via a triplet excimer state (*vide supra*). In TIPS-BTX,  $^3\text{TT} \rightarrow \text{T}_1$  would release  $\sim 1.2$  eV of heat (Table 1). While this conversion is likely slowed by Marcus inverted-region reactivity owing to expected small reorganization energy in the process (of order 200 meV),<sup>63</sup> it is unlikely slower than spin conversion to  $^5\text{TT}$  (where it might then access the singlet manifold), a process which is governed by minor terms in the already subtle spin Hamiltonian.<sup>88</sup> Note that  $^1\text{TT} \rightarrow \text{S}_0$  in TIPS-BP1' is also spin allowed while releasing an even larger  $\sim 1.7$  eV of heat within the Marcus inverted region. Such decay takes  $\sim 100$  ns in room temperature toluene solutions.<sup>63</sup>

As noted earlier, Fig. 5 indicates that TIPS-BTX reaches a value of  $\phi'_{\text{TTA}}$  that would correspond  $f = 0.42$  (a lower limit achieved when  $\phi_{\text{TTA}}$  is at its maximum of  $\frac{1}{2}$ ), with a modest increase in  $f$  expected had higher TIPS-BTX concentrations been available. In other words, these data suggest that  $f$  is not bound at  $\frac{2}{5}$  for this dimer, the scenario that would manifest if quintet encounter complexes simply dissociated while triplet encounter



complexes each decayed to a single  $T_1$ . This finding is consistent with participation by the intramolecular  $^5\text{TT}$  in a productive manner for upconversion as was suggested above in the context of Scheme 2. A statistical analysis that considers the singlet and quintet channels to be entirely productive while triplet encounter complexes decay to  $T_1$  would have  $f = \frac{12}{15} = 0.8$  (see ESI for discussion†) and we anticipate this is the limit achievable by dimer systems.

## Conclusion

In this work we have compared the NIR-to-visible upconversion efficacy of a new rigid dimer system TIPS-BTX relative to the monomer model TIPS-Tc, seeking to quantify differences in terms of fundamental parameters underlying upconversion yields. A key observation is that the dimer consistently and markedly outperforms the monomer. For example, at comparable concentrations (0.39 mM TIPS-BTX *versus* 0.45 mM TIPS-Tc), the dimer reaches an upconversion yield that is more than  $20\times$  larger than the monomer. When we disentangle the contribution to the yield due specifically to TTA, the dimer is found to be more than  $30\times$  more effective. To understand this, we need to look from the perspective of both types of annihilators. On one hand the monomer TIPS-Tc is highly ineffective. But the similarity of its unimolecular photophysics and single-exciton state structure compared to the dimer TIPS-BTX suggests that TIPS-Tc triplets engage in deleterious second order processes, likely from both singlet and triplet collision-complex channels. We anticipate that these involve lower-energy excimer states that steal excited state population against TTA. In the nearly co-planar dimer TIPS-BTX, the two opposing chromophores remain exposed to the environment (they are not significantly sterically crowded by the bridge), and it is difficult to imagine that excimer channels would be so significantly undermined. From this lens, the marked improvement in  $\phi'_{\text{TTA}}$  for TIPS-BTX, to the point that it matches or exceeds what is seen in champion annihilator systems such as DPA, heralds internal conversion and subsequent participation by intramolecular multiexciton states in productive TTA. This is important, particularly under conditions where non-diffusive constructs are implemented, for example with upconversion dimers covalently decorating nanomaterial triplet sensitizers such as quantum dots. In this same context, we see the emergence of evidence that the quintet channel is productive in this rigid dimer class. First, the greater than  $20\times$  improvement in  $\phi_{\text{UC}}$  compared to TIPS-Tc is more than  $2\times$  larger than the advantage reported for a non-rigid dimer compared to the same monomer.<sup>47,56</sup> This could reflect a situation where dimer rigidity prevents intramolecular  $^5\text{TT} \rightarrow ^3\text{TT} \rightarrow T_1$  loss channels while allowing for  $^5\text{TT} \rightarrow ^1\text{TT} \rightarrow S_1$  productive channels. Second, we calculate a spin-statistical value of  $f = 0.42$  for TIPS-BTX with evidence that  $f$  would increase in studies with higher concentrations of the dimer. A definitive demonstration of  $f > 0.4$  (*i.e.*,  $\frac{2}{5}$ ) would be strong evidence for productive participation by  $^5\text{TT}$  and this issue

should continue to be explored in rigid systems. Ultimately, we posit that rigid dimers could approach  $f = \frac{4}{5}$  indicating productive use of both  $^1\text{TT}$  and the higher statistical weight  $^5\text{TT}$ .

## Data availability

Data are available upon reasonable request.

## Author contributions

NHD, ATG, and RO conceived of the studies and wrote the manuscript. ATG and RO made most of the measurements. NFP collected longer-time TA data for the dimer. EGM synthesized the dimer TIPS-BTX and oversaw analyses checking against sample degradation.

## Conflicts of interest

There are no conflicts to declare.

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