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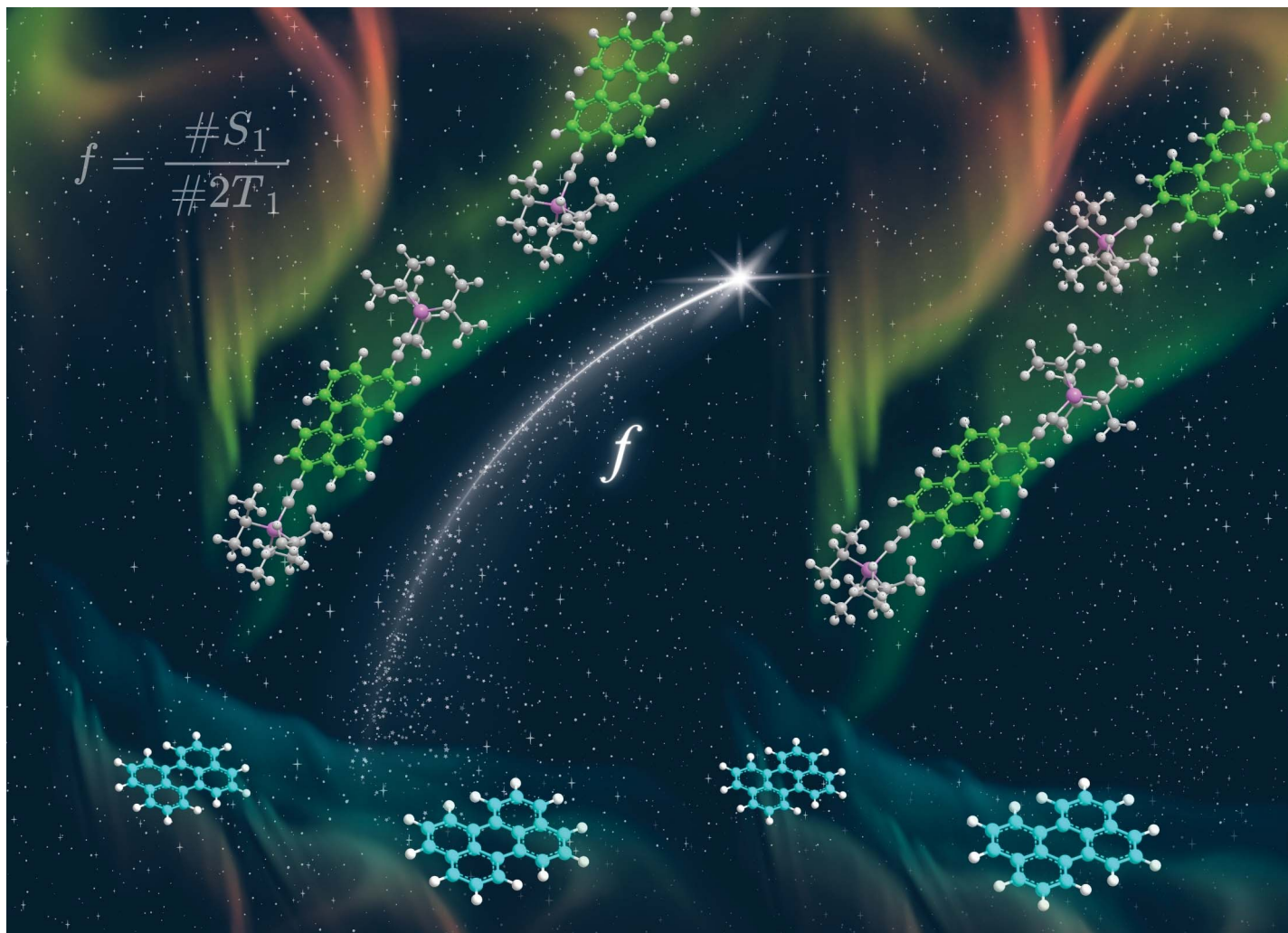
## **Enhancing the statistical probability factor in triplet-triplet annihilation photon upconversion via TIPS functionalization**

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Naimovicus, L., Dapkevicius, M., Radiunas, E. et al (2025). Enhancing the statistical probability factor in triplet-triplet annihilation photon upconversion via TIPS functionalization. *Chemical Science*, 16(43): 20255-20264.  
<http://dx.doi.org/10.1039/d5sc05248c>

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Enhancing the statistical probability factor in triplet-triplet annihilation photon upconversion *via* TIPS functionalization

This work shows the influence of triisopropylsilyl functionalization on annihilators in triplet-triplet annihilation photon upconversion, specifically focusing on their spin statistical probability factor ( $f$ ). The  $f$  determines the probability of singlet generation after triplet coupling. A new green-emitting annihilator 3,9-bis((triisopropylsilyl)ethynyl)perylene (**TIPS-PY**) was synthesized, which shows a high red-to-green TTA-UC quantum yield,  $\Phi_{uc} = 13.7\%$  due to high  $f = 39.25\%$ . Computation analysis revealed that high  $f$  of **TIPS-PY**, resulted from enhanced coupling of the triplet-pair state with the singlet state due to high singlet character of the triplet state.

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See Pankaj Bharmoria, Kasper Moth-Poulsen *et al.*, *Chem. Sci.*, 2025, **16**, 20255.

Cite this: *Chem. Sci.*, 2025, 16, 20255

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# Enhancing the statistical probability factor in triplet–triplet annihilation photon upconversion via TIPS functionalization

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We investigated the influence of triisopropylsilyl (TIPS) functionalization on annihilators in triplet–triplet annihilation photon upconversion, specifically focusing on their spin statistical probability factor. A new green-emitting annihilator 3,9-bis((triisopropylsilyl)ethynyl)perylene (TIPS-PY) displaying a record red-to-green TTA-UC quantum yield of 13.7% (50% theoretical maximum) was synthesized. This remarkable efficiency was achieved due to the following features of the TIPS functionalization of PY: (1) retaining a high fluorescence quantum yield of 95%, (2) reduced triplet energy to 1.29 eV enabling efficient triplet energy transfer (~100%) from the sensitizer PdTPBP ( $T_1 = 1.55$  eV), and (3) a high efficiency of singlet generation after triplet coupling, indicated by the statistical probability factor,  $f = 39.2\% \pm 2.4\%$ . Notably, the  $f$  value of TIPS-PY surpasses other annihilators in the 470–570 nm emission range. Excited state computational analysis using TheoDORE revealed a higher percentage of charge transfer character in  $S_0S_1$  in TIPS-PY compared to PY, indicative of higher singlet-like character in their triplet-pair state ( $^1(T_1T_1)$ ), which can enhance the coupling of the triplet-pair state with the excited singlet-state, thereby increasing the efficiency of singlet generation, a phenomenon undisclosed before. Furthermore, the suitable  $T_1$  of TIPS-PY enables upconversion of 730 nm light when sensitized with  $Os(m-peptpy)_2(TFSI)_2$  ( $T_1 = 1.63$  eV), demonstrating the broad upconversion range of TIPS-PY in the phototherapeutic window desired for biological applications.

Received 15th July 2025

Accepted 6th October 2025

DOI: 10.1039/d5sc05248c

rsc.li/chemical-science

## Introduction

Triplet–triplet annihilation photon upconversion (TTA-UC) is a molecular nonlinear optical process that converts two photons with low-energy into one photon with high energy (Scheme 1a).<sup>1</sup>

This phenomenon is attractive compared to other UC processes<sup>2</sup> due to its operation under incoherent low energy density excitations<sup>3</sup> which opens many potential applications such as photocatalysis, biological photoactivation, 3D printing, and photovoltaics.<sup>4–11</sup> A typical TTA-UC system consists of a sensitizer and an annihilator ensemble. The sensitizer absorbs low-energy photons and generates triplet states via intersystem crossing (ISC). The annihilator accumulates the triplets through Dexter triplet energy transfer (TET) from the sensitizer and undergoes TTA-UC, generating a photon-emitting high-energy singlet state (Scheme 1a). The efficiency of singlet generation is evaluated by TTA-UC quantum yield ( $\phi_{UC}$ ), which is the product of all operational processes within the TTA-UC system (eqn (1)) and the spin-statistical probability factor ( $f$ ). The  $f$  determines the probability of singlet generation after triplet coupling (Scheme 1b).

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

In the eqn (1),  $\phi_{UC}$ ,  $\phi_{ISC}$ ,  $\phi_{TET}$ ,  $\phi_{TTA}$ ,  $\phi_{FL}$  represent the quantum yields of upconversion (UC), intersystem crossing (ISC), triplet

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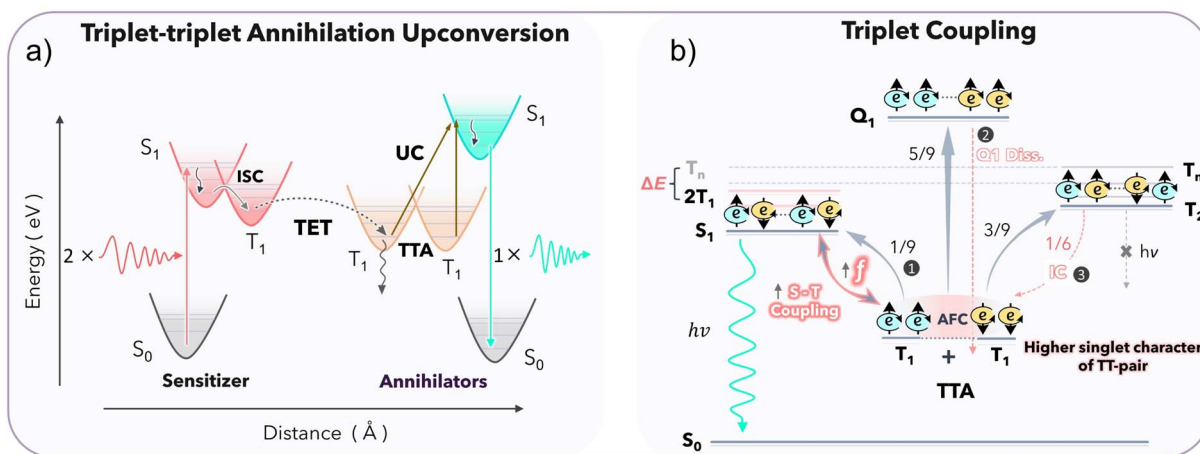
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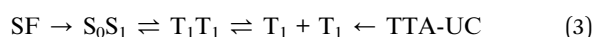
**Scheme 1** (a) Scheme of TTA-UC indicating conversion of two low-energy photons into one high-energy photon through a series of energy transfer processes. ISC – intersystem crossing, TET – triplet energy transfer, TTA – triplet-triplet annihilation and UC – upconversion (b) schematic illustration of the post-TTA events resulting in the formation of the TT pair with singlet ( $S_1$ ,  $f = 1/9$ ), triplet ( $T_2$ ,  $3/9$ ) and quintet ( $Q_1$ ,  $5/9$ ) states due to the anti-ferromagnetic coupling (AFC) between triplet-pairs. Further recycling *via* quintet dissociation (Q1 diss.) or internal conversion (IC) can increase the  $f$  of  $S_1$  formation to  $1/2$ . A higher singlet character of the TT pair increases the coupling between the TT pair and the singlet state, which further increases the  $f$ .

energy transfer (TET), triplet-triplet annihilation (TTA), and annihilator fluorescence (FL), respectively.

The  $f$  plays an essential role in TTA-UC by defining the maximum achievable  $\phi_{UC}^\infty$  as  $f/2$  when all other processes approach unity. As follows, the  $f$  allows us to assess the intrinsic potential of the annihilator triplets to generate an emissive singlet state (Scheme 1b). It can be altered by suitable molecular engineering of annihilator chromophores to control the triplet coupling strength, which has been investigated in this work. The TTA results in the formation of a triplet-pair ( $T_1 \cdots T_1$ ) whose net spin can be  $S = 0, 1$ , or  $2$ , hence possessing singlet, triplet, or quintet character. According to the adapted Merrifield model including exchange interactions ( $J$ ), under zero-field splitting, coupling results in the formation of 9 spin eigenstates of  $T_1T_1$  pairs with an overall fraction of  $1/9$ ,  $3/9$ , and  $5/9$  of singlet, triplet, and quintet pair states (Scheme 1b). Triplet coupling can be expressed simply by Heisenberg's spin-only Hamiltonian ( $\hat{H}$ ) using eqn 2

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad (2)$$

where  $\hat{S}_1$  and  $\hat{S}_2$  are individual spin operators of the two individual interacting triplets, and  $J$  is the magnetic exchange parameter that also defines the strength of inter-triplet exchange interactions.<sup>1,5</sup> In the case of strong electronic coupling, the quintet state ( $Q_1$ ) is energetically inaccessible and cannot form the excited singlet state. This limits the  $f$  of singlet formation to  $1/4$ , leading to low UC efficiencies. However, the quintet and triplet ( $T_2$ ) states may re-participate in singlet formation *via* other channels like  $Q_1$  to  $T_1$  dissociation, and  $T_2$  to  $T_1$  internal conversion (IC).<sup>12,13</sup> This recycling can increase the experimentally obtained  $f$  value even up to  $\sim 1/2$ .<sup>5,14,15</sup> The TTA-UC ( $^1(T_1T_1) > S_1S_0$ ) is the reverse process of singlet fission ( $S_1S_0 > ^1(T_1T_1)$ ) with an intermediate correlated triplet-pair state,  $^1(T_1T_1)$  as per the Johnson-Merrifield model eqn (3).<sup>16,17</sup>



It is according to the Merrifield model that the singlet character of the  $T_1T_1$  pair determines its coupling to the singlet state.<sup>18</sup> Hence, annihilators with a triplet-pair state exhibiting a significant singlet character can have a high probability of singlet formation and consequently, a higher  $f$  factor<sup>19</sup> which has been investigated in this work by calculating the percentage of charge resonance/transfer character in the  $S_0S_1$  dimer.

Another way to increase the  $f$  factor is to avoid secondary loss channels such as  $2T_1$  to  $T_n$  non-radiative decay (Scheme 1b). This can be achieved *via* the molecular engineering of an annihilator with  $2T_1 \approx S_1$  and  $Q_n$  and  $T_n$  states higher in energy than the  $2T_1$  state. This prevents  $2T_1$  decay to  $Q_n$  or  $T_n$  states due to the energy gap law relation<sup>5</sup> (eqn (3)). This results in preferential decay of  $2T_1$  to the  $S_1$  state, leading to more efficient singlet generation.

$$k_{nr} \sim \exp\left(\frac{-\gamma|\Delta E|}{\hbar\omega_M}\right) \quad (4)$$

where  $k_{nr}$  is the rate of non-radiative decay and  $\Delta E$  is the energy gap between electronic states.

Several derivatives of naphthalene,<sup>14,20</sup> anthracene,<sup>21–23</sup> perylene,<sup>24,25</sup> rubrene,<sup>26–30</sup> and diketopyrrolopyrrole<sup>31,32</sup> based compounds have been investigated to achieve high  $f$  values to boost the overall  $\phi_{UC}$ .<sup>5</sup> The UC emission of these compounds spans across the majority of the UV-visible spectrum. However, the lack of an efficient annihilator emitting within the 470–540 nm range impedes important biological applications which can be photoactivated with upconverted green light upon excitation within or close to the phototherapeutic window (650–850 nm).<sup>33</sup> These applications include targeted drug delivery,<sup>34</sup> light-gated ion channel control,<sup>35</sup> light-activated CRISPR,<sup>36</sup> photo-pharmacology,<sup>37</sup> and photosynthesis.<sup>38</sup> While 9,10-



bis(phenylethynyl)anthracene (**BPEA**) is a well-known commercially available green annihilator, its low UC quantum yield due to the small  $f = 5.6$  to  $6.3\%$  is an issue.<sup>21</sup> Therefore, an efficient annihilator within the 470–540 emission range could serve as a powerful photoactivation tool in biological applications upon low-density red or NIR excitation *via* TTA-UC for embracing higher penetration into biological tissue.

Herein, we report the synthesis of a new perylene (**PY**) based annihilator functionalized with triisopropylsilyl (TIPS) groups, **TIPS-PY** (Fig. 1a). **TIPS-PY** demonstrates highly efficient TTA-UC, with experimental  $\phi_{UC}$  of  $13.7\%$  (out of  $50\%$ ), with  $f = 39.2\%$  upon combining with Pd(II) *meso*-tetraphenyl tetra-benzoporphine (PdTPBP) as sensitizer ( $\lambda_{ex} = 640$  nm CW laser). The  $\phi_{UC}$  is shown to be greater compared to unfunctionalized **PY** due to the increase in  $f$  value implying enhanced triplet-pair-singlet coupling, which may be governed by the singlet-like character of the triplet-pair state of **TIPS-PY**, revealed from the higher percentage charge resonance or charge transfer character of the  $S_0S_1$  excitations of the **TIPS-PY** compared to **PY**

using TheoDORÉ program.<sup>19,39</sup> To our knowledge, an efficient annihilator in 470–540 nm emission range with a high  $f$  value of  $39.2\% \pm 2.4\%$  and  $\phi_{UC}^\infty$  up to  $19.6\%$  (theoretical limit) has not been reported before.<sup>40</sup> This study demonstrates the value of TIPS-functionalization in engineering the triplet energy, singlet-triplet character, and  $T_1T_1$  coupling of annihilator triplets to yield a high statistical probability factor for upconverted singlet-state generation, which is a key limiting factor in TTA-UC. When combined with Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub> as a sensitizer, **TIPS-PY** upconverted the 730 nm light into yellow-green light, thus reaching deep into the phototherapeutic window<sup>33</sup> that is highly sought after for various biological applications.<sup>34–38</sup>

## Results and discussion

### Synthesis of 3,9-bis((triisopropylsilyl)ethynyl)perylene (**TIPS-PY**)

The annihilator **TIPS-PY** was synthesized in a two-step reaction as depicted in Scheme 2. A mixture of 3,9- and 3,10-dibromoperylene was obtained *via* an electrophilic aromatic bromination reaction between **PY**, and *n*-bromosuccinimide (**NBS**).<sup>41</sup> The final compound, **TIPS-PY**, was obtained *via* a Sonogashira coupling between the mixture of 3,9- and 3,10-dibromoperylene and TIPS-acetylene. The purified-orange colored compound was characterized by <sup>1</sup>H NMR, <sup>13</sup>C {<sup>1</sup>H} NMR, MALDI-TOF, and single-crystal X-ray diffraction analysis (for detailed synthesis procedure and characterization see Annexure 1, Fig. S1–S5) and found to be 3,9-bis(TIPS)perylene.

### Photophysical properties

The photophysical properties of **TIPS-PY** were studied in comparison to other competitive annihilators, **PY** and **BPEA** in the 470 to 540 nm emission range. The molecular structures of **TIPS-PY**, **PY**,<sup>42</sup> and **BPEA** (ref. 21) are shown in Fig. 1a along with PdTPBP, the sensitizer used in this study for red-to-green upconversion.<sup>43</sup>

**TIPS-PY** demonstrated absorption and emission peaks at 483 nm ( $\epsilon \sim 73\,000\text{ M}^{-1}\text{ cm}^{-1}$ , Fig. S6) and 489 nm ( $\phi_{FL} = 95\%$  and  $\tau_{FL} = 5.5$  ns), respectively (Fig. 1b, S7, and S8). Compared to **PY**, the emission spectrum of **TIPS-PY** is red-shifted by 0.29 eV due to the extension of conjugation upon introduction of TIPS-acetylene moieties (Fig. 1b). However, the  $\Phi_{FL}$  remained almost the same (96% and 95%). This red shift in the emission spectrum of **TIPS-PY** overcame the secondary inner filter issue caused by reabsorption of UC light by the PdTPBP Soret band to

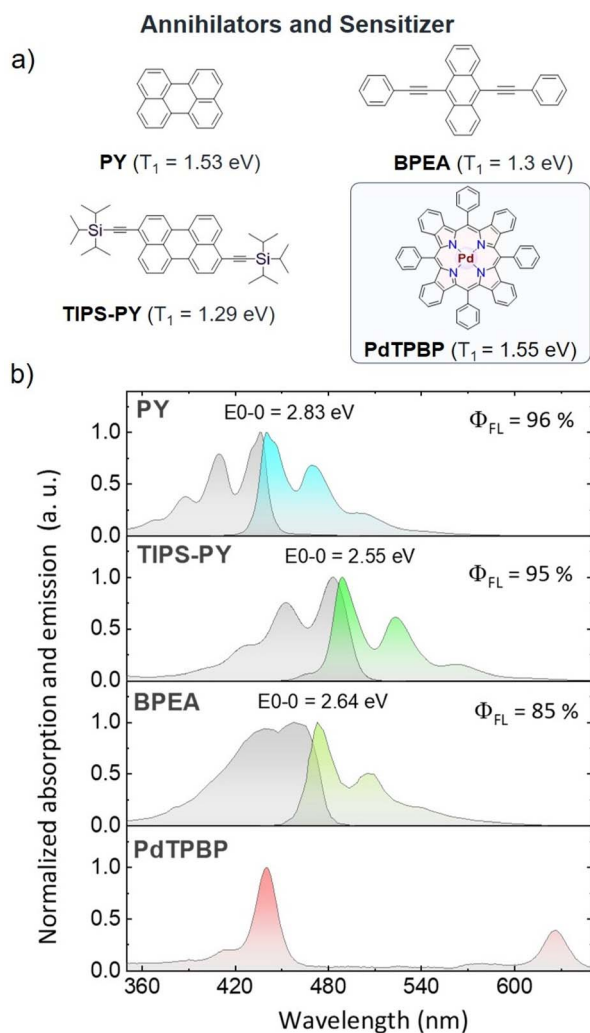
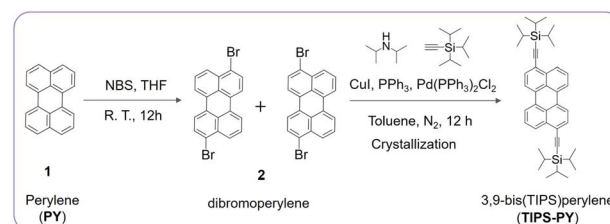


Fig. 1 Molecular structures and  $T_1$  energies (a), and absorption and emission spectra (b) of annihilators (**PY**, **TIPS-PY**, **BPEA**), and sensitizer (**PdTPBP**) at concentrations of  $20\ \mu\text{M}$  and  $1\ \mu\text{M}$  in THF, respectively.



Scheme 2 Synthesis of 3,9-bis(TIPS)perylene (**TIPS-PY**).



boost the  $\phi_{UC}$  (Fig. S9). When compared to **BPEA**, the emission spectrum of **TIPS-PY** is red-shifted by just 0.1 eV (Fig. 1b). However, the lower  $\phi_{FL} = 85\%^{21}$  of **BPEA** implies a negative effect on the overall  $\phi_{UC}$  according to eqn (1). Besides  $\phi_{FL}$ , our previous time-dependent density functional theory (TD-DFT) investigations (Gray *et al.*<sup>21</sup>) found that the difference in geometry of singlet and triplet surfaces of **BPEA** makes the triplet-state energetically inefficient to generate the first excited singlet-state to yield low  $\phi_{UC}$ .<sup>21</sup> Hence, prior to TTA-UC experiments, molecular geometry optimization, and excited state modeling studies of **TIPS-PY** in comparison to **PY** were conducted (Fig. 1 and S10).

### Excited-state modeling studies

The DFT and TD-DFT calculations carried out at the (U)PBE0-D3(BJ)/6-311G(d,p) level of theory have shown the  $T_1$  states of **PY** and **TIPS-PY** at 1.49 eV and 1.29 eV, respectively (see SI for a more detailed description of the computational method). The calculated  $T_1$  of **PY** is almost similar to the reported experimental<sup>8</sup> and theoretical values  $\sim 1.5$  eV.<sup>42</sup> The calculated singlet-state ( $S_1$ ) energies of **PY** and **TIPS-PY** (Fig. S10) are also in agreement with the experimental  $S_1$  values. Due to the  $T_1$  of **TIPS-PY** at 1.29 eV, **PdTPBP** having  $T_1$  at 1.55 eV<sup>42</sup> (Fig. 1a) was selected as a sensitizer to ensure the feasible sensitization of **TIPS-PY** *via* an exothermic triplet energy transfer pathway. Moreover, the non-overlapping of the emission spectrum of **TIPS-PY** with the absorption spectrum of **PdTPBP** (Fig. 1b and S9), and a high  $\phi_{ISC}$  of **PdTPBP** approaching unity<sup>44</sup> were other key factors for **PdTPBP** selection as a sensitizer.

The calculated energy level distributions (Fig. S10) demonstrate that **TIPS-PY** complies with the  $2T_1 > S_1$  energetic condition for TTA-UC to occur.<sup>5</sup> However, the proximity of  $2T_1$  to higher energy triplet-states ( $T_n = T_2, T_3$ ) plays a crucial role in the probability of singlet generation due to the energy gap law relation (eqn (4)), imposing a non-radiative decay channel if  $2T_1$  is in the vicinity of  $T_2$  and further from  $S_1$ .<sup>45,46</sup> We investigated the implication of the energy gap law in affecting the  $f$  factor of **TIPS-PY** and found a  $2E_{T_1} - E_{T_2}$  energy gap of +70 meV. The gap is significant enough to substantially reduce the non-radiative decay.<sup>45-47</sup> Hence, it could be one of the key contributors to the high  $f$  factor of **TIPS-PY**. However, when compared with the  $2E_{T_1} - E_{T_2} = -140$  meV of **PY** having  $f$  value of 17.9%<sup>42</sup> this parameter does not seem enough to explain the high  $f$  factor observed of **TIPS-PY**. Hence, we explored another possible channel to understand the high  $f$  factor of **TIPS-PY**. One key argument of the Merrifield model of triplet-triplet coupling is that the efficiency of singlet generation depends on the triplet pair-singlet coupling.<sup>18,29,48</sup> Hence, a higher singlet character of the triplet-state can increase the singlet-triplet coupling post triplet-triplet annihilation to generate a high singlet population.<sup>18</sup> Therefore, we calculated the charge resonance or charge transfer character of  $S_1S_0$ , commonly shared by  $^1(T_1T_1)$ , of **TIPS-PY** compared to that of **PY** to assess the singlet character using TheoDOR program (Fig. 2).<sup>39</sup> Fig. 2a shows the change in electron density from the ground state to the excited state, resulting from a linear combination of orbital replacement

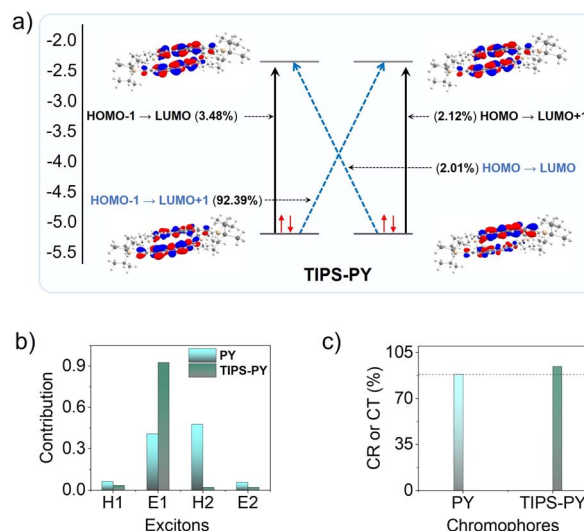


Fig. 2 (a) Illustration of the contribution of the linear combination of orbital replacement in **TIPS-PY**. (b) Plot showing comparative electron (E), and hole (H) contributions during orbital replacement in **PY** and **TIPS-PY**. (c) Percentage of charge resonance (CR) or charge transfer (CT) calculated from E and H contributions during orbital replacement in **PY** and **TIPS-PY**.

involving charge transfer (blue arrows) and local excitations (black arrows). The HOMO-1 to LUMO+1 transition in **TIPS-PY**, which contributes the strongest (92.39%), has charge transfer (CT) character, moving one electron each from left to right and from right to left. Contrary to this, the HOMO-1 to LUMO+1 transition in **PY**, which contributes the strongest (88.24%), has a charge resonance (CR) character. The percentage of CT or CR character is indicative of the singlet character of the dimer.<sup>39</sup> These results indicate that **TIPS**-functionalization increases the singlet character of the **TIPS-PY** dimer, which is likely to have a positive effect on  $f$  value (Scheme 1b)<sup>16,49-51</sup> and UC quantum yield.

To substantiate these results, we also investigated biphenyl (**BP**) and bis-**TIPS**-biphenyl (**TIPS-BP**), having a similar transition dipole axis as that of **PY** (Fig. S11a and b)<sup>52,53</sup> using the TheoDOR program (Fig. S12). Similar to **PY**, the CT character of **BP** increased upon **TIPS**-functionalization (Fig. S12d), thus supporting the proposed argument. Recently, **TIPS-BP** was shown to demonstrate superior UC performance compared to **BP**, confirming our prediction experimentally.<sup>54</sup> Seeking further generalization of this argument, we also calculated the CT or CR character for highly efficient **TIPS**-functionalized annihilators such as **TIPS**-anthracene (**TIPS-An**) (ref. 23) and **TIPS**-naphthalene (**TIPS-Naph**).<sup>55</sup> However, the CT or CR character decreased for these molecules upon **TIPS**-functionalization (Fig. S13a-d). This could be due to the difference in the main transition dipole axis of **Naph** and **An** ( $^1L_a$ ), which unlike **BP** and **PY** is along the horizontal axis (Fig. S11b). It is to mention that the transition dipole axis plays a key role in the electronic interactions of the molecules in the excited state.<sup>56</sup> Nevertheless, it shows that the singlet character of the triplet pair may not be the sole criterion to evaluate the high TTA-UC quantum



yields in molecules with different transition dipole axes. Therefore, we also investigated the role of energy gap law<sup>5</sup> in **TIPS-An** and **TIPS-Naph** and found  $2E_{T_1} - E_{T_2}$  of  $-103$  meV, and  $+186$  meV, respectively (Table S2), which is in synergy with results obtained upon application of the energy gap law in the case of **PY** and **TIPS-PY**. Therefore, the energy gap law could be the common factor contributing to high  $\phi_{UC}$  (27%)<sup>23</sup> of **TIPS-An** and high  $f$  value (54%)<sup>55</sup> of **TIPS-Naph** chromophores, as well as **TIPS-PY**. Seeking further insights, we also computed the  $S_0S_0$  and  $T_1T_1$  states for **PY** and **TIPS-PY** and found a smaller dimerization energy for **TIPS-PY** ( $-31.6$  kcal mol<sup>-1</sup>) compared to that of **PY** ( $-20.43$  kcal mol<sup>-1</sup>) (see Fig. S14).<sup>57</sup> In both cases, the potential energy surface is relatively flat, allowing for easy rotation and translation of the dimers. In the particular case of **PY**, we have also computed the  $S_0S_1$ ,  $S_0T_1$ ,  $S_0T_2$ , and  $T_1T_2$  states (Fig. S15). As the emission of **TIPS-PY** is red-shifted due to the presence of TIPS moieties, the extended conjugation leads to a decrease of excited state energies (Fig. 1a) as well as the polarization of the  $C\equiv C$  bond in the opposite direction by the triplet spin compared to **PY** (Fig. S16). The higher stability of the  $T_1$  state in **TIPS-PY** can be attributed to the reduction of the HOMO-LUMO gap by  $0.37$  eV in **TIPS-PY** compared to **PY**.<sup>57</sup> Given the extension of conjugation, the  $T_1$  energy of **TIPS-PY** ( $1.29$  eV) decreased by  $0.24$  eV compared to **PY** ( $1.53$  eV) making it suitable for exothermic triplet-energy transfer.

### Triplet-triplet annihilation photon upconversion

Following photophysical characterization and excited-state modeling studies, the **TIPS-PY** annihilator was applied in TTA-UC in combination with **PdTPBP** as a sensitizer in deaerated THF. The investigated **TIPS-PY: PdTPBP** UC system demonstrated UC emission upon  $640$  nm laser excitation (Fig. 3a, b and S17), confirming the DFT prediction of the most favourable energetic condition ( $2T_1 \geq S_1$ ) for TTA-UC.<sup>5</sup> To demonstrate the full potential of **TIPS-PY**, the annihilator concentration was varied from  $0.1$  mM to  $100$  mM while the **PdTPBP** concentration was maintained at  $0.01$  mM (Fig. 3a and c). The **TIPS-PY: PdTPBP** system demonstrated a high experimental  $\phi_{UC}$  varying from  $7.0\%$  to  $13.7\%$  (Fig. 3c and Table 1) at  $100$  mM and  $1$  mM annihilator concentrations, respectively. The  $\phi_{UC}^\infty$  and UC threshold ( $I_{th}$ ) were estimated from  $\phi_{UC}$  vs. excitation power density ( $I_{ex}$ ) profile according to previously reported procedures<sup>58</sup> (Fig. S18 and Table 1).

The  $I_{th}$  values for **TIPS-PY: PdTPBP** vary from  $0.19$  W cm<sup>-2</sup> to  $0.43$  W cm<sup>-2</sup>, a low threshold barrier desired for most applications. The difference in  $\phi_{UC}^\infty$  at varying **TIPS-PY** concentrations can be explained by concentration effects on  $\phi_{FL}$  and  $\phi_{TET}$  according to eqn (1). While the  $\phi_{FL}$  ( $75.5$ – $73.5\%$ ) for  $0.1$  mM to  $10$  mM concentrations are similar, the  $100$  mM concentration sample demonstrates a decrease in  $\phi_{FL}$  to  $65.5\%$  owing to the aggregation of the annihilator species (Fig. 3a and S19). This suggests an enhanced non-radiative decay channel, potentially due to the aggregation. It was also reflected in the anti-Stokes shifts, which varied from  $0.56$  to  $0.21$  eV between  $0.1$  to  $100$  mM **TIPS-PY** (Table S3).<sup>59</sup> No significant aggregation is observed up to a concentration of  $10$  mM, as evidenced by the

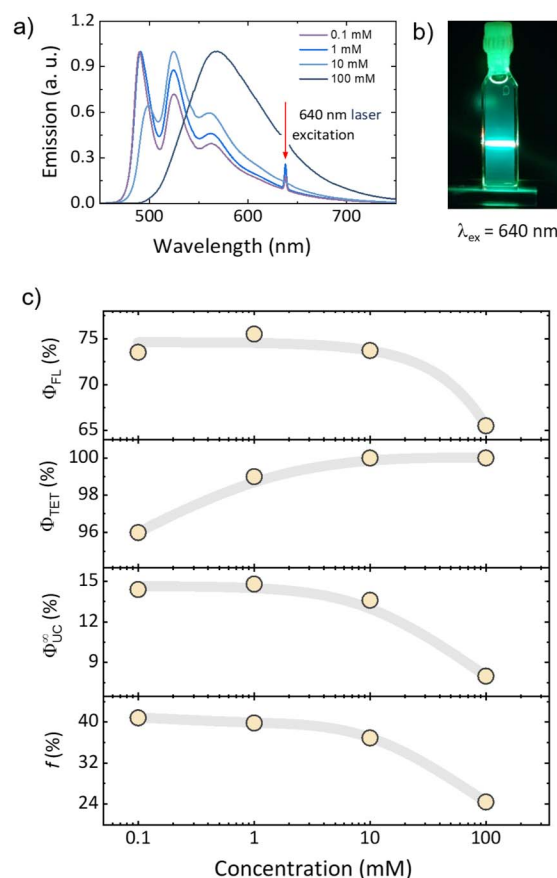


Fig. 3 (a) **TIPS-PY: PdTPBP** upconversion spectra at  $0.1$  mM,  $1$  mM,  $10$  mM, and  $100$  mM annihilator concentrations.  $640$  nm laser excitation indicated. (b) Digital image of TTA-UC emission, and (c)  $\phi_{FL}$ ,  $\phi_{TET}$ ,  $\phi_{UC}^\infty$ , and  $f$  dependence on **TIPS-PY** concentration. All solutions were prepared in deaerated THF. **PdTPBP** concentration in all UC solutions was maintained at  $0.01$  mM. The grey lines serve as a guide to the eyes.

absence of changes in the low-energy shoulder of the absorption spectra (Fig. S20). The growth of  $\phi_{TET}$  from  $96\%$  to  $100\%$  is explained by the higher concentration of acceptor chromophores surrounding sensitizer molecules. The longest triplet-lifetime,  $\tau_T = 1250$   $\mu$ s was observed at the lowest **TIPS-PY** concentration ( $0.1$  mM), and decreased further upon increasing the concentration (Table 1 and Fig. S21).

This decreases the average distance between **PdTPBP** and **TIPS-PY**, inferring higher TET probability.  $\phi_{TET}$  was evaluated *via* rise time ( $\tau_r$ ) of TTA-UC transients (Fig. S22 and Table S4) according to the following relation:

$$\phi_{TET} = 1 - \frac{2\tau_r}{\tau_0} \quad (5)$$

where  $\tau_0$  – intrinsic (unquenched) triplet lifetime of the sensitizer that, in the case of **PdTPBP**, is  $175.5$   $\mu$ s.<sup>42</sup> A high  $\phi_{TET} = 96\%$  was also confirmed from the quenching of the phosphorescence spectrum of **PdTPBP** by **TIPS-PY** (Fig. S22).

To further understand the higher TTA-UC quantum yields obtained with **TIPS-PY**, the  $f$  value of  $39.2\% \pm 2.4\%$  was evaluated according to eqn (1) as the average of 3 measurements at



**Table 1** UC parameters of TIPS-PY-PdTPBP UC solutions in deaerated THF at 0.1 mM, 1 mM, 10 mM, 100 mM, and 0.01 mM concentrations of TIPS-PY and PdTPBP

TIPS-PY	$\phi_{\text{FL}}^a$ , %	$\phi_{\text{UC}}^b$ , %	$\phi_{\text{UC}}^{\infty c}$ , %	$\phi_{\text{TET}}^d$ , %	$I_{\text{th}}^e$ , W cm <sup>-2</sup>	$\tau_T^f$ , $\mu\text{s}$	$f^g$ , %
0.1 mM	73.5	11.1	14.4	96	0.19	1250	40.8
1 mM	75.5	13.7	14.9	99	0.29	914	39.8
10 mM	73.7	13.0	13.6	100	0.43	741	36.9
100 mM	65.5	7.0	8.0	100	4.94	30–80	24.4

<sup>a</sup> FL quantum yield of annihilator in UC solution. <sup>b</sup> Reabsorption corrected maximum measured UC quantum yield values. <sup>c</sup> Maximum attainable UC quantum yield values. <sup>d</sup> TET quantum yield. <sup>e</sup> UC threshold at 38.2% of  $\phi_{\text{UC}}^{\infty}$ . <sup>f</sup> Triplet lifetime ( $=2 \times \tau_{\text{UC}}$ ). <sup>g</sup> Statistical probability of singlet generation from two triplets *via* TTA, calculated according to eqn (1).  $\tau_{\text{UC}}$  values in Table 1 were determined from the tail fit of the UC emission decay profiles in Fig. S21.

0.1 mM, 1 mM, and 10 mM annihilator concentrations (Fig. 3b and Table 1). The results obtained at 0.1 mM, 1 mM, and 10 mM support that  $f$  value is an intrinsic property of a molecule that does not experience a change due to the change in concentration. The  $f$  value of 24.4% recorded at 100 mM was omitted from the calculation due to the presence of **TIPS-PY** aggregates (Fig. 3a and S19) in the UC solution enabling non-radiative decay channels.

For a reliable comparison of  $f$  values between studied **PY**,<sup>42</sup> **TIPS-PY**, and **BPEA**, we conducted additional measurements at identical conditions with **BPEA-PdTPBP** UC system to determine the  $f$  value resulting in 6.3% (Fig. S23, S24, and Table S6). The reported  $f$  value of  $39.2\% \pm 2.4\%$  for **TIPS-PY** outperforms all previously studied annihilators within the 470–570 nm emission region and is among the top values in the entire spectrum (Fig. 4).<sup>5,40,54,60–62</sup> This leads to a high experimental  $\phi_{\text{UC}}$  of 13.7% with a possibility to approach the intrinsic limit  $\phi_{\text{UC}}^{\infty} \sim 19.6\%$  if all energy transfer processes approach unity. The main reason for the high  $f$  value of **TIPS-PY** is the TIPS functional groups, which increase the stability of the triplet state as well as form a singlet-like character of the triplet dimer ( $T_1T_1$ ) species, as revealed from the charge resonance or charge

transfer studies. This may exhibit a positive impact on  $T_1 \cdots T_1$  pair state and  $S_1$  coupling to generate the singlet-state with high efficiency according to the Merrifield model.<sup>18,29,48</sup> Additionally, the favourable energy distribution prevents  $2T_1$ -to- $T_2$  non-radiative decay from favouring the  $S_1$  formation.

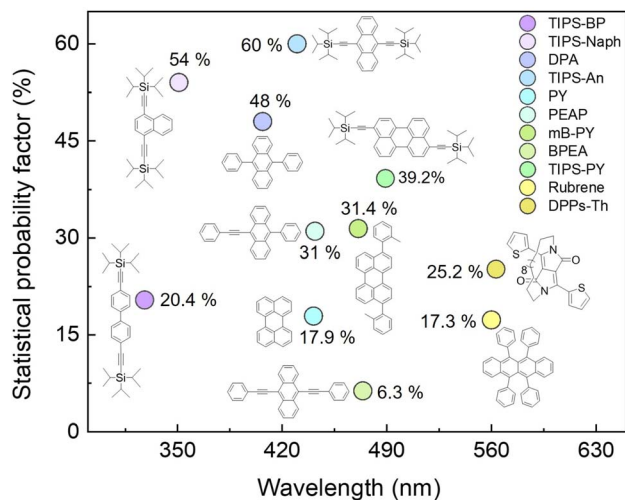
We also investigated the rate of TTA ( $k_{\text{TTA}}$ ) as a possible reason for higher UC performance in **TIPS-PY** compared to **PY** in THF. To determine  $k_{\text{TTA}}$  of **TIPS-PY**, UC intensity decay profiles of **TIPS-PY: PdTPBP** and **PY: PdTPBP** solutions containing 0.1 mM of annihilator were measured at increasing excitation power densities (Fig. 5) and fitted using the following relation.<sup>63</sup>

$$I(t) [\text{}^3A^*(t)]^2 = \left( [\text{}^3A^*]_0 \frac{1 - \beta}{\exp(t/\tau_T) - \beta} \right)^2 \quad (6)$$

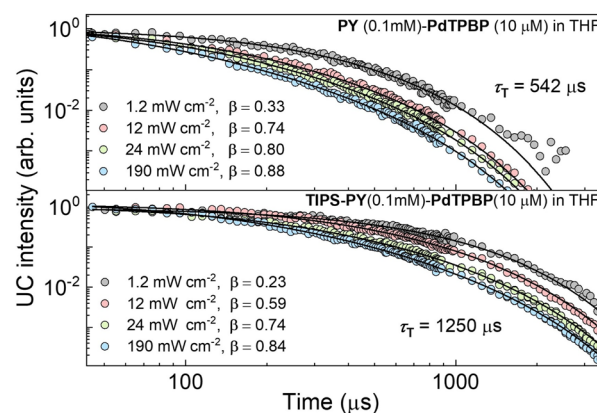
$$\beta = \frac{2k_{\text{TTA}}[\text{}^3A^*]_0}{2k_{\text{TTA}}[\text{}^3A^*]_0 + k_T} \quad (7)$$

Here,  $[\text{}^3A^*]_0$  denotes the initial triplet exciton concentration within the annihilator, and  $\tau_T (=1/k_T)$  is the spontaneous triplet decay lifetime.  $\tau_T$  was obtained from the tails of the transients, assuming that the condition  $k_T \gg k_{\text{TTA}}[\text{}^3A^*]_0$  is met at low triplet exciton concentration, where TTA is negligible.

The obtained  $\beta$  values, which describe TTA efficiency at particular excitation densities, are listed in Table S5, along with



**Fig. 4** Plot showing variation in statistical probability factor of various annihilators emitting across the visible spectral range. **TIPS-PY** synthesized in this work tops the list in the 470–570 nm range.



**Fig. 5** Normalized UC transients of **PY** and **TIPS-PY** on a log–log scale at different excitation densities (indicated) upon sensitization with PdTPBP at 640 nm. Circles present experimental data, while solid lines show global fits with a shared  $\tau_T$ .



$\tau_T$  values. Since pulsed nanosecond excitation with a pulse duration much shorter than triplet lifetime was used, quasi-steady-state conditions could not be achieved, preventing direct determination of  $[^3A^*]_0$  from these measurements. However, given that the  $\tau_T$  is known and remains invariant with excitation density,  $[^3A^*]_0$  at each pump level was estimated utilizing the reported  $k_{TTA}$  value for **PY** ( $19 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (ref. 64) according to the eqn (7). Considering the similar TET efficiencies for **PY**: **PdTPBP** ( $\phi_{TET} = 92\%$ )<sup>42</sup> and **TIPS-PY**: **PdTPBP** ( $\phi_{TET} = 96\%$ ; this work) at equivalent annihilator and sensitizer concentrations, the  $[^3A^*]_0$  values derived for **PY**: **PdTPBP** were also employed to estimate  $k_{TTA}$  in **TIPS-PY**. The estimated  $k_{TTA}$  for **TIPS-PY** is approximately  $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is 4-fold lower than that of **PY**. Hence,  $k_{TTA}$  may not be the reason for higher UC performance in **TIPS-PY** compared to **PY**. This observation is different from what has been reported by Han *et al.*<sup>40</sup> where the higher normalized triplet–triplet annihilation efficiency of 3,10-di-*o*-tolylperylene (**mB-PY**) triplets, due to the restricted motion of *o*-tolyl rings was cited as the key reason for enhanced UC quantum yield.<sup>40</sup> Nevertheless, the enhancement of UC performance by TIPS groups provides a novel strategy for molecular design for future annihilators as well as demonstrates the potential of **TIPS-PY** as another suitable compound to be implemented in numerous applications, especially in biology requiring 470–540 nm emission upon excitation with deep tissue penetrative red/far-red light.

To further demonstrate the potential of the **TIPS-PY** for long-wavelength far-red light upconversion, we performed TTA-UC study by combining **TIPS-PY** with **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** as sensitizer in deaerated DMF (Fig. 6a). The absorption spectrum of **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** shows vibronic peaks at 291, 318, 422, 447 nm due to ligand centred, at 494 nm due to singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT), and at 648 nm and 673 nm due to triplet MLCT (<sup>3</sup>MLCT) (Fig. 6b).<sup>65</sup> Furthermore, **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** shows <sup>3</sup>MLCT emission at 759 nm (1.63 eV) and phosphorescence emission due to meta-substituted perylene units at 827 nm (1.5 eV), respectively.<sup>65</sup> Unlike other Os-complexes, it shows a long phosphorescence lifetime ( $\tau_{Po}$ ) of 98  $\mu\text{s}$  (Fig. S25), which is among the key requirements for an efficient sensitizer in TTA-UC.<sup>5</sup> Upon excitation with a 730 nm CW laser, the **TIPS-PY**:**Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** (1 mM:0.01 mM) system demonstrated bright yellow-green UC emission (Fig. 6c and d), thus expanding the upconversion range into the phototherapeutic window to the far-red region.<sup>33</sup> The phosphorescence transients (Fig. S25) were used to determine the  $\phi_{TET} = 99.7\%$ , indicating almost complete quenching of **TIPS-PY**:**Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** phosphorescence by **TIPS-PY**. Despite the high  $\phi_{TET}$ , long triplet lifetime,  $\tau_T = 846 \mu\text{s}$  (Fig. S26) and high  $\phi_{FL} = 71\%$  of **TIPS-PY** in this system, a low absolute  $\phi_{UC} = 0.62\%$  was observed. This could be due to 1) the secondary inner filter effect caused by fast reabsorption of the upconverted light by **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** due to the high spectral overlap of its absorption spectrum with the emission spectrum of **TIPS-PY** (Fig. 6b and Fig. S27), or 2) aggregated UC emission due to complexation of **TIPS-PY** with **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** confirmed from the distorted UC emission spectrum showing shift in emission maxima to 572 nm in the yellow emission range

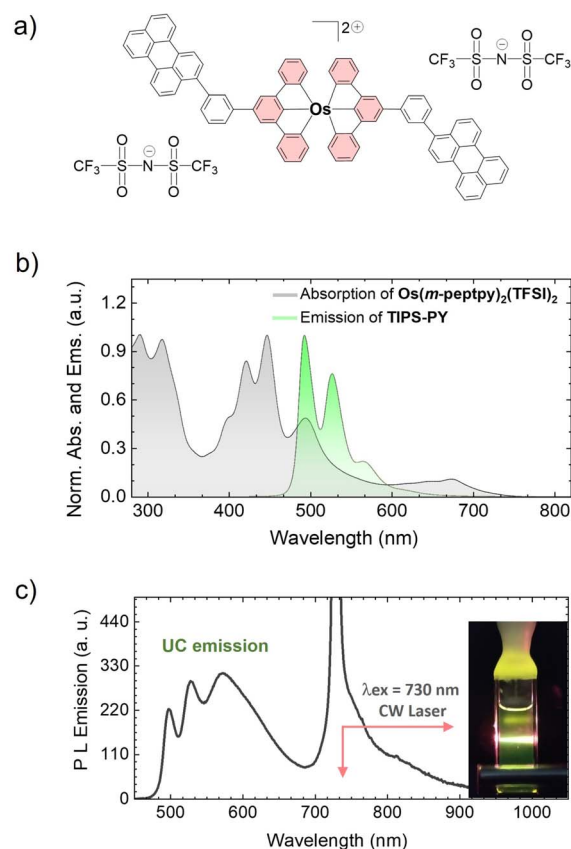


Fig. 6 (a) Molecular structure of **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>**. (b) Absorption spectrum of **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** and fluorescence emission spectrum of **TIPS-PY** (1 mM) in the presence of **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** (0.01 mM) in DMF ( $\lambda_{ex} = 420 \text{ nm}$ ). (c) Upconversion emission spectrum of **TIPS-PY**: **Os(m-peptpy)<sub>2</sub>(TFSI)<sub>2</sub>** (1 mM:0.01 mM) system ( $\lambda_{ex} = 730 \text{ nm}$  CW laser). (d) Digital image of the yellow-green UC emission upon 730 nm CW laser excitation.

(Fig. 6c). Comparatively low solubility of **TIPS-PY** in DMF also support the possible aggregated UC emission. A better far-red absorbing sensitizer with higher transparency window in the **TIPS-PY** emission range may yield higher  $\phi_{UC}$ .

## Conclusions

We synthesized a new green-emitting annihilator **TIPS-PY**, which exhibits the highest absolute TTA-UC quantum yield of 13.7% (50% theoretical maximum) for red-to-green (640 nm to 489 nm) TTA-UC upon combining with **PdTPBP** as a sensitizer. Such a high UC quantum yield is enabled by the combined effects of: (1) a high  $\phi_{FL} = 95\%$  of **TIPS-PY**, (2)  $\phi_{TET} \sim 100\%$  due to exothermic triplet energy transfer from **PdTPBP** to **TIPS-PY**, (3) minuscule secondary inner filter effects due to minimum spectral overlap of **PdTPBP** absorption and **TIPS-PY** emission, and (4) a high  $f$  value of  $39.2\% \pm 2.4\%$  of **TIPS-PY**, which generated a high singlet population after triplet-coupling. Further investigations of the  $f$  factor from the TheoDOR program revealed a singlet-like character of the triplet-pair state of **TIPS-PY** induced by the higher charge transfer character of



the  $S_0S_1$  excitations of **TIPS-PY** compared to **PY**. This may increase the coupling of the triplet-pair state with the excited singlet state of **TIPS-PY** to generate a high singlet population after triplet-triplet annihilation according to the Merrifield model. Interestingly, this behaviour was also observed for other TIPS-functionalized annihilators like **TIPS-BP**, having a similar transition dipole axis to that of **PY**, which was not previously explored. The obtained  $\phi_{UC}$  and  $f$  values for **TIPS-PY** are among the highest for annihilators in the green-to-red spectral range and outperform well-known annihilators such as **PY**, **BPEA**, **mB-PY**, rubrene, or DPPs.

## Author contributions

P. B., L. N., and K. M. P. conceptualized the idea of this work. M.M. synthesized the TIPS-Perylene. P. B. and M. M. carried out primary photophysical characterization. L. N., M. D., E. R, G. K., P. B., and K. K. carried out UC and time resolved measurements. C. A. and M. S. carried out computational calculations. Y. S., N. Y., and N. K. synthesized Os-complex. P.B., L. N., and K. M. P. wrote the first draft of the manuscript. All authors contributed to the analysis of results in their respective parts and editing of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The original datasets generated and analyzed during the current study are available from the corresponding authors on reasonable request and also available via open access on Zenodo at <https://doi.org/10.5281/zenodo.3755810>.

Supplementary information: synthesis, NMR, MALDI-TOF, and X-Ray diffraction analysis of TIPS-PY together with photophysical and upconversion measurements and DFT calculations. The authors have cited additional references within the SI.<sup>66–84</sup> Cartesian coordinates of the species studied for computational calculations. See DOI: <https://doi.org/10.1039/d5sc05248c>.

## Acknowledgements

L. N. acknowledges the Erasmus + Traineeship Program, P. B. and M. M. acknowledge financial support from the La-Caixa junior research leadership-post doctoral program (ID: 100010434, fellowship code: LCF/BQ/P122/11910023) the State Investigation Agency, through the Severo Ochoa Programme for Centres of Excellence in R&D (CEX2023-001263-S) and project PID2021-123873NB-I00 for financial support. L. N. and A. B. P. acknowledge the start-up funds provided by the University of California San Diego and the use of facilities and instrumentation supported by NSF through the UC San Diego Materials Research Science and Engineering Center (UCSD MRSEC), grant # DMR-2011924. K. M. P. acknowledges funding from the European Research Council (No. 101002131), the Swedish Energy Agency, the Göran Gustafsson Foundation, the Swedish

Research Council, Swedish Research Council Formas, the European Research Council (ERC) under grant agreement CoG, PHOTHERM – 101002131, the Catalan Institute of Advanced Studies (ICREA), and the European Union's Horizon 2020 Framework Programme under grant agreement no. 951801. M. D., G. K., K. K., acknowledge the “Universities” Excellence Initiative” programme by the Ministry of Education, Science and Sports of the Republic of Lithuania under the agreement with the Research Council of Lithuania (project No. S-A-UEI-23-6). M. S. is grateful for financial support from the Agencia Española de Investigación (MCIN/AEI/10.13039/501100011033) for projects RED2024-154178-T and PID2023-147424NB-I00 and from the Generalitat de Catalunya for Project 2021SGR623 and ICREA Academia 2025 prize to M. S. N. Y. acknowledges the support by JSPS KAKENHI (JP23H00304). N. K. acknowledges the support by JSPS KAKENHI (JP20H05676).

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