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Enhancing photon upconversion properties in anthracene derivatives through meticulous control of excluded volume around π-systems

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Photon upconversion, which converts low-energy photons into high-energy photons, provides a strategy for overcoming the limitations imposed by excitation wavelengths in energy and biology applications. Recent advancement in triplet–triplet annihilation-based photon upconversion (TTA-UC) witnesses the importance of the bulkiness of the substituents in chromophores to avoid quenching of the singlet and triplet. One of the simplest bulky substituents, the *tert*-butyl (*t*Bu) group, has been introduced into acene derivatives and shown both positive and negative effects on UC performance, underscoring the importance of further structure–property investigations. Here, we systematically synthesized anthracene derivatives of 9,10-bis(phenylethynyl)anthracene (BPEA) and 9,10-bis[(triisopropylsilyl)ethynyl]anthracene (TIPS-Ac), each bearing bulky *t*Bu substituents. The relationship between the excluded volume imparted by these substituents and UC performance in both solution and the solid state was investigated. A moderate intermolecular distance effectively suppressed singlet and triplet quenching, yielding high UC quantum yields of approximately 15% in the solution state with both chromophores. A significant extension of the triplet lifetime was also observed in a donor–acceptor bilayer solid film, demonstrating the simple yet positive effects of *t*Bu on the anthracene backbone, thereby boosting the UC performances in versatile material forms.

Introduction

Photon upconversion (UC) is a molecular-based photophysical process that converts low-energy photons into high-energy photons. This process has advanced to overcome limitations in excitation wavelength in fields such as energy, biology, materials chemistry, and more. In particular, triplet–triplet annihilation-based UC (TTA-UC), which exploits energy transfer processes involving long-lived excited triplets in molecules, can be driven even under non-coherent, low-excitation-intensity conditions, such as sunlight.[1–14] The ability to utilize a broad spectrum of light by applying appropriate molecular systems enables applications in solar energy harvesting,[15,16] biosensing,[17–19] and photocatalytic reactions.[20,21]

As the TTA-UC process requires the collision of two triplets that are not populated by direct transitions from ground singlet states, triplet sensitizers (donors) showing highly efficient singlet-to-triplet intersystem crossing (ISC) are primarily combined with the UC chromophores (acceptors, Fig. 1). After the Dexter-type triplet energy transfer (TET) from the donor to the acceptor, two triplet-excited acceptors undergo TTA and generate one singlet-excited acceptor that emits upconverted photons. The key indices for TTA-UC materials are a high UC quantum yield (Φ_{UC}, theoretical maximum: 50%), a low threshold excitation intensity (I_{th}) above which the TTA process becomes efficient, and the wavelength shift from excitation to emission. The Φ_{UC} relies on each process of ISC, TET, TTA, fluorescence, and probability to obtain a singlet in TTA (f) as shown in eqn (1),[5,22]

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

where Φ_{ISC}, Φ_{TTA}, and Φ_F represent the quantum yields of ISC, TTA, and acceptor fluorescence, respectively.

While studies over the past two decades have optimized each process, the molecular design for achieving high f values has been unclear. The f values are affected not only by the

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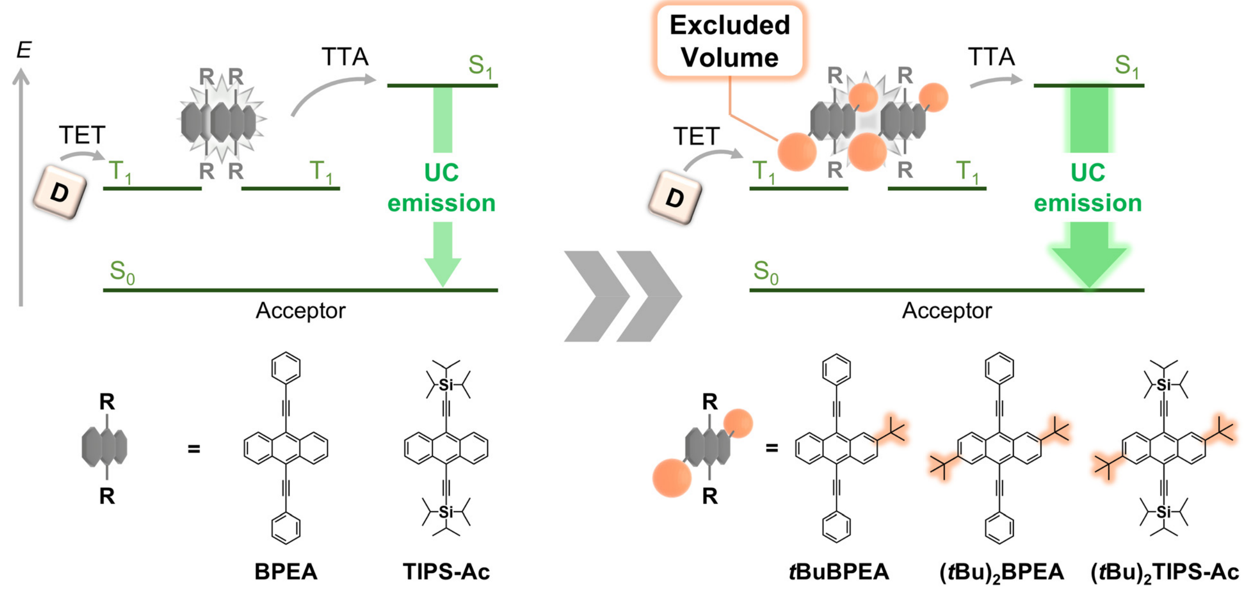

Fig. 1 Scheme of TTA-UC mechanism and excluded volume design on acceptor anthracene derivatives. D: donor.

spin-statistically predicted singlet generation efficiency from two excited triplets, but also by reverse intersystem crossing from higher-lying excited states[23–25] and the effect of excimer formation from singlet and triplet pair states.[26] Based on conventional spin-statistical probability, assuming that only singlet and triplet states are formed in a 1 : 3 ratio and that the triplets will be recycled to undergo TTA, the *f* value reaches 40%, as reported for several UC chromophores.[27] The effect of substituents has been investigated since the 2010s,[28,29] but with growing interest after the successful demonstration of efficient UC quantum yields by (triisopropylsilyl)ethynyl (TIPS)-substituted anthracene and naphthalene derivatives.[30,31]

The attempts to reduce I_{th} are categorized into optimizations of sensitization and TTA processes. Based on the widely used TTA model in an isotropic system with almost unity ISC efficiency, I_{th} is expressed as follows,[32]

$$I_{th} = \frac{1}{8\pi \alpha \Phi_{TET} D_T a_0 \tau_T{}^2} \tag{2}$$

where α is the donor absorption coefficient at the excitation wavelength, and D_T denotes the diffusion constant of acceptor triplets, a_0 denotes the interaction distance between acceptor triplets, and τ_T denotes the acceptor triplet lifetime.

To achieve unity TET and TTA efficiency, it is ideal to use donors with high molar absorption coefficients, high ISC efficiency, and donors and acceptors with long excited-state lifetimes. In the solution state, the triplet diffusion constant depends on the molecular diffusion rate; thus, the use of acceptor molecules with a long triplet lifetimes is particularly important to reduce the I_{th} value. Albinsson *et al.* focused on substituted naphthalene derivatives to clarify the effect of bulkiness. They found a significant reduction in triplet lifetime at high acceptor concentrations, assigning the additional quenching pathway as triplet excimer formation.[31,33] With these works, control of intermolecular interaction with bulky substituents significantly suppresses the quenching of both singlets and triplets. However, bulkiness can reduce the triplet diffusion constant and TTA rates by increasing the net intermolecular distance[28,34–36]. To elucidate optimal intermolecular distance and relative geometry that simultaneously affect UC properties, further systematic studies on the effect of steric bulkiness on UC chromophores are necessary.

In addition to optimizing solution-based TTA-UC systems, the development of efficient matrix-free solid-state UC systems has been pursued for practical applications. Developing efficient solid-state UC materials has been more challenging due to the tendency for strong chromophore interactions in

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the condensed state, which quench UC fluorescence.[37] In addition, such systems are sensitive to the compatibility within the mixed solid. Phase separation of the donor and acceptor significantly reduces the triplet energy transfer efficiency.[5] To control the donor-dispersibility and triplet diffusion processes in the solid state, several side groups and molecular backbones have been proposed to manage molecular assembly.[28,37–44] One of the simplest substituents is the *tert*-butyl (*t*Bu) group, composed of saturated sp^3 carbons, which provides only a slight difference in π-conjugation. Several UC acceptors incorporating the *t*Bu group have been proposed to date[26,42,43,45]. The introduction of a *t*Bu group into rubrene successfully reduced intermolecular interactions, thereby slowing detrimental singlet fission.[42] Börjesson *et al.* successfully suppressed excimer formation in perylene with alkyl groups and improved the UC quantum yield from 5% to 10%.[28] Pun *et al.* investigated a diketopyrrolopyrrole derivative with *t*Bu groups and found a decrease in the *f* value due to a reduction in the effective annihilation radius.[43] These works show that the effect of the bulky substituent is structure-dependent. Despite extensive research over the past two decades, the impact of the *t*Bu group on the UC performance of anthracene derivatives, which are essential benchmarks, remains unclear.

In this work, to control intermolecular interactions in anthracene derivatives, *t*Bu groups were introduced, and their TTA-UC properties were investigated in solution and in the solid state. Ethynylphenyl or triisopropylsilylethynyl (TIPS) groups were introduced to the anthracene skeleton, having one or two *t*Bu groups,[46] and a series of 9,10-bis(phenylethynyl)anthracene (BPEA) or 9,10-bis[(triisopropylsilyl)ethynyl]anthracene (TIPS-Ac) derivatives with *t*Bu groups were synthesized (Fig. 1, *t*BuBPEA,[47] (tBu)$_2$BPEA, and (tBu)$_2$TIPS-Ac). To clarify structure–UC profile relationships, TTA-UC properties of systems composed of palladium(II) tetraphenyl-tetrabenzoporphyrin (PdTPTBP) as a donor and the anthracene derivatives as an acceptor, were compared in the solution state. Furthermore, matrix-free donor–acceptor solid bilayer films were fabricated by vacuum deposition. In both systems, molecules bearing bulky substituents exhibited higher or comparable UC quantum yields and lower threshold excitation intensities than unsubstituted structures. The effects of *t*Bu groups on the singlet and triplet dynamics were systematically investigated, and the potential quenching processes are discussed.

Results and discussion

The effect of *t*Bu groups on solution-state photophysical properties was investigated for BPEA and TIPS-Ac. The absorption and emission peaks of both compounds showed slight shifts, indicating hyperconjugation with the *t*Bu group (Fig. 2).[48] This result is supported by the time-dependent density functional theory (TD-DFT) calculations (Fig. S6 and S7). All these molecules were found to satisfy the energetic conditions $E(S_1) < E(2T_1) < E(T_2)$, which are ideal to maximize singlet formation *via* TTA. High fluorescence quantum yields ($\Phi_F > 90\%$) are retained after substitution, showing the *t*Bu groups introduced in anthracene chromophores do not promote nonradiative deactivation (Table 1).[49]

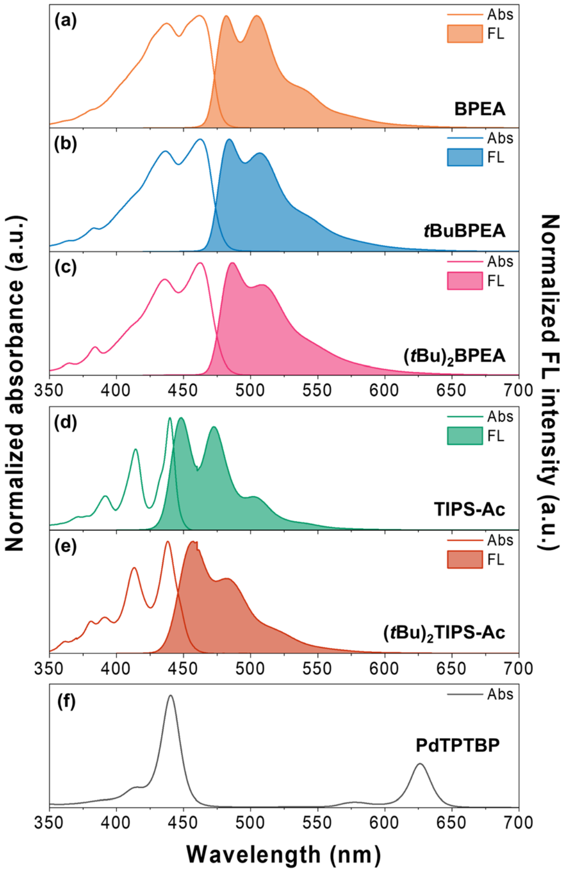

Fig. 2 (a–e) Normalized absorption (solid line) and fluorescence (filled in) spectra of BPEA and TIPS-Ac derivatives. (a) BPEA, (b) *t*BuBPEA, and (c) (tBu)$_2$BPEA in deaerated 100 μM THF. (d) TIPS-Ac and (e) (tBu)$_2$TIPS-Ac in deaerated 10 μM THF. (f) Normalized absorption spectrum of PdTPTBP in dearated 50 μM THF.

Upon irradiation with a 635 nm laser under Ar, THF solutions containing PdTPTBP and anthracene derivatives yielded blue-to-green upconverted emissions (Fig. 3a and 4a). The double logarithmic plots of the UC emission intensity as a function of the excitation intensity showed a transition from quadratic to linear dependence as the excitation intensity increased, confirming the TTA-UC-based mechanism (Fig. 3b and 4b). The excitation intensity at the intersection of the fitting lines of the quadratic and linear regimes is defined as I_{th} (eqn (2)). The impact of *t*Bu substitution on the I_{th} was dependent on the core acceptor structure. For the TIPS-Ac derivatives, the introduction of the *tert*-butyl group led to a decrease in I_{th} from 45 mW cm^{-2} to 24 mW cm^{-2}, while the BPEA derivatives showed the opposite trend from 6.9 mW cm^{-2} to 19 mW cm^{-2}. The observed difference is likely due to a trade-off between the reduction in the TTA rate and the extension of the excited-state lifetime conferred by the *t*Bu

Table 1 Fluorescence peak wavelength (0–0 transition), quantum yield (BPEA derivatives: λ_{ex} = 425 nm, TIPS-Ac derivatives: λ_{ex} = 440 nm) and fluorescence lifetime (λ_{ex} = 405 nm) of anthracene derivatives in deaerated THF at a concentration of 100 µM. Calculated radiative and non-radiative rate constant are also shown

	λ_F (nm)	Φ_F (%)	τ_F (ns)	k_r (10^8 s^{-1})	k_{nr} (10^6 s^{-1})
BPEA	482	91	3.7	2.5	24
*t*BuBPEA	484	93	3.9	2.4	18
(*t*Bu)$_2$BPEA	486	93	3.9	2.4	17
TIPS-Ac	448	93	6.0	1.5	12
(*t*Bu)$_2$TIPS-Ac	457	94	6.4	1.5	8.5

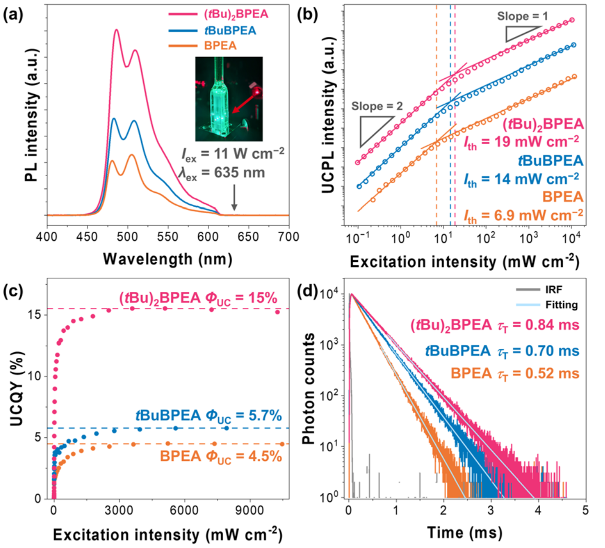

Fig. 3 UC properties of BPEA derivatives in deaerated THF solution ([BPEA derivatives] : [PdTPTBP] = 1 mM : 50 µM, λ_{ex} = 635 nm). (a) UC emission spectra and (b) excitation intensity dependence of the upconverted emission intensity around emission peak wavelength (BPEA: 479.5 nm, *t*BuBPEA: 483 nm, (*t*Bu)$_2$BPEA: 486 nm). The UCPL intensity is plotted in arbitrary units for clarity. (c) UC quantum yield (Φ_{UC}) at various excitation intensities. (d) UC emission decay curves of BPEA derivatives. Excitation light was removed with a 610 nm short-pass filter.

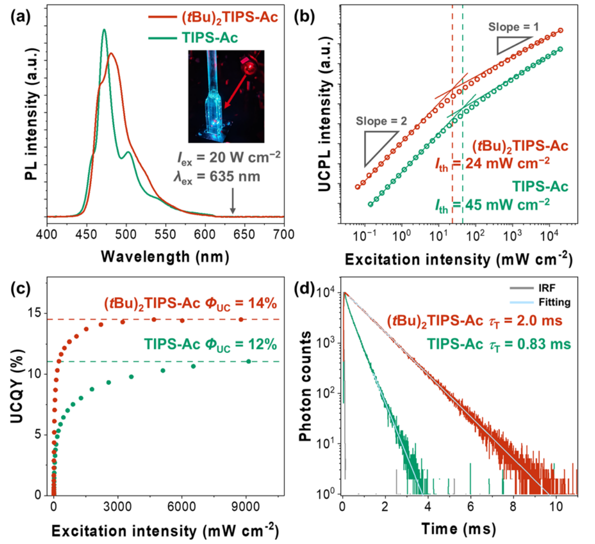

Fig. 4 UC properties of TIPS-Ac derivatives in deaerataed THF solution ([TIPS-Ac derivatives] : [PdTPTBP] = 10 mM : 50 µM, λ_{ex} = 635 nm). (a) UC emission spectra and (b) excitation intensity dependence of the upconverted emission intensity around emission peak wavelength (TIPS-Ac: 472 nm, (*t*Bu)$_2$TIPS-Ac: 481 nm). The UCPL intensity is plotted in arbitrary units for clarity. (c) UC quantum yield (Φ_{UC}) at various excitation intensities. (d) UC emission decay curves of TIPS-Ac and (*t*Bu)$_2$TIPS-Ac. Excitation light was removed with a 610 nm short-pass filter.

groups that reduce intermolecular interactions. The introduction of bulky substituents extended the triplet lifetimes τ_T of both chromophores ($\tau_T = 2\tau_{UC}$,[50,51] Fig. 3d and 4d), indicating the suppressed triplet quenching at high acceptor concentrations.[33] (*t*Bu)$_2$TIPS-Ac showed longer τ_T than (*t*Bu)$_2$BPEA, which is probably due to the rotation of phenyl rings in BEPA that can fluctuate energy levels and facilitate nonradiative decay.[52] It is also considered that the bulkier TIPS group suppressed quenching in (*t*Bu)$_2$TIPS-Ac.

The UC parameters obtained from the experiments are summarized in Table 2. The introduction of bulky substituents was found to boost the maximum upconversion (UC) quantum yield (Φ_{UC}, max 50%). The ISC efficiency was taken as 97%, following previously reported values.[53] The donor phosphorescence decays within several microseconds in the presence of the acceptor, suggesting high TET efficiency ($\Phi_{TET} \approx 100\%$, Table 2 and Fig. S9). The donor's phosphorescence quantum yield also confirms high TET efficiency (Table S2). Although the Stern–Volmer plot indicated a reduction in the donor–acceptor energy transfer rate due to the excluded volume of bulky substituents in acceptors (Fig. S10 and Table S3), the estimated TET efficiencies were unaffected, thanks to the long excited-state lifetime of PdTPTBP (τ_T = 139 µs, Fig. S8).

The suppressed intermolecular interaction improved Φ_F of TIPS-Ac from 81% to 93% in 10 mM THF solution (Table S1), which resulted in the higher Φ_{UC} of 14% in the (*t*Bu)$_2$TIPS-Ac/PdTPTBP system (Fig. 4c). By assuming that the TTA efficiency Φ_{TTA} approaches 100% at higher excitation intensity, the *f* value of TIPS-Ac and (*t*Bu)$_2$TIPS-Ac were calculated as 0.31 and 0.32, respectively. The negligible change in the *f* value indicates that the bulkier TIPS group dominantly contributes to the net intermolecular interactions. In contrast, the *f* value for BPEA derivatives increased from 0.10 to 0.34 as the number of *t*Bu groups increased. A previous report explained the low *f* value of BPEA as due to rotation of the phenyl groups, which fluctuate the T_1 energy,[52] and discussed the contributions of the T_1 and T_2 energy gaps to the *f* value.[23,25] The small differences in the calculated T_1 and T_2 energy levels for the current BPEA derivatives indicate that the improvement in the *f* value is ascribable to moderate intermolecular interactions and reduced nonradiative deactivation channels by the bulky *t*Bu groups. The similar *f* value of (*t*Bu)$_2$BPEA as TIPS-Ac, together with the reported improvements in Φ_{UC} with TIPS substituents,[30,31,33,35,36,45,54–58] indicates that the steric effect is crucial for achieving high *f* values regardless of the skeleton.[42,43] Therefore, the effect of bulky substituents

Table 2 Summary of UC properties in deoxidized THF ([BPEA derivatives] : [PdTPTBP] = 1 mM : 50 μM, [TIPS-Ac derivatives] : [PdTPTBP] = 10 mM : 50 μM)

	Φ_{UC} (%)	f	Φ_{TET} (%)	Φ_F (%)	I_{th} (mW cm^{-2})	τ_T (ms)
BPEA	4.5	0.10	≈100	87	6.9	0.52
*t*BuBPEA	5.7	0.13	≈100	88	14	0.70
(tBu)$_2$BPEA	15	0.34	≈100	91	19	0.84
TIPS-Ac	12	0.31	≈100	81	45	0.83
(tBu)$_2$TIPS-Ac	14	0.32	≈100	93	24	2.0

improves the UC performance of anthracene derivatives in solution through multiple benefits from the moderately reduced intermolecular interactions: an enhancement of key photophysical parameters, such as the fluorescence quantum yield and *f* value, and an extension of the triplet lifetime.

Furthermore, we observed UC emission from bilayer solid UC films fabricated by sequential thermal deposition of the donor and the acceptors TIPS-Ac or (tBu)$_2$TIPS-Ac onto a quartz substrate (Fig. 5, S12, S13 and Table S4). In the solid bilayer architecture, which separates the donor and acceptor layers, potentially suppresses back energy transfer from the acceptor to the donor when triplet diffusion in acceptors is fast.[60] In both films, blue UC emission was observed under the excitation at 635 nm (Fig. 5a). The (tBu)$_2$TIPS-Ac showed one order of magnitude longer triplet lifetime of 1.1 ms (Fig. 5c), resulting in a low threshold excitation light intensity of 12 mW cm^{-2}. This significant improvement underscores the importance of a controlled excluded-volume concept that reduces radiationless quenching by introducing bulky substituents around the π-electron systems to moderately isolate them, while maintaining the appropriate intermolecular distance (<1.0 nm) for triplet energy migration within solid acceptor assemblies. To estimate TET efficiency, we compared phosphorescence quantum yield (Φ_P). However, we did not observe clear difference between the PdTPTBP film (1.9%) and PdTPTBP/TIPS-Ac (1.6%) and PdTPTBP/(tBu)$_2$TIPS-Ac (2.2%), which indicates the TET is not efficient in the bilayer systems. The double-logarithmic plots of phosphorescence intensity *versus* excitation intensity yielded slopes of 0.93 for PdTPTBP/TIPS-Ac and 0.80 for PdTPTBP/(tBu)$_2$ TIPS-Ac (Fig. S1). These sub-linear slopes indicate the presence of additional quenching pathways or exciton saturation within the sensitizer thin films. By accounting for this excitation intensity dependence of the reference sensitizer's phosphorescence quantum yield, the relative Φ_{UC} values were determined to be 0.41% and 0.20%, respectively (Fig. 5d). In addition to the low TET efficiency, singlet back energy transfer (BET) from acceptor to donor potentially reduces Φ_{UC}. Based on the fluorescence decay profile, the singlet BET efficiency ($\Phi_{BET} = 1 - \tau_F/\tau_{F,0}$) of TIPS-Ac/PdTPTBP and (tBu)$_2$TIPS-Ac/PdTPTBP were estimated to be 49% and 58%, respectively (Fig. S16 and Table S5). Therefore, suppression of the BET using singlet energy collectors with properly designed molecular assemblies is necessary for further improvement.[61,62] The reduction of the Φ_{UC} under high excitation light intensity is attributed to the triplet back energy transfer from the acceptor to the donor.[5] A remaining challenge in the bilayer system is that TET is limited to the donor–acceptor interface, which can lead to the loss of a fraction of absorbed photons *via* competing decay pathways such as phosphorescence. The need remains to resolve challenges through integrated structure design and energy collectors.

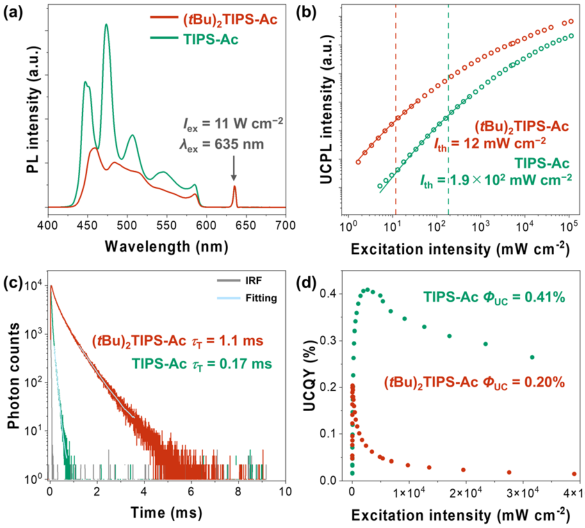

Fig. 5 UC properties of TIPS-Ac derivatives in the solid-state (λ_{ex} = 635 nm). (a) UC emission spectra and (b) excitation intensity dependence of the upconverted emission intensity around emission peak wavelength (TIPS-Ac: 473.5 nm, (tBu)$_2$TIPS-Ac: 459.5 nm). I_{th} values were estimated by theoretical fitting equation reported by Murakami *et al.* (SI, section S10).[59] (c) UC emission decay curves of TIPS-Ac (green) and (tBu)$_2$TIPS-Ac (red). Excitation light was removed with a 590 nm short-pass filter. (d) UC quantum yield (Φ_{UC}) at various excitation intensities calculated with relative method (standard: PdTPTBP phosphorescence).

Conclusions

In conclusion, the introduction of a bulky *t*Bu group to the anthracene backbone enhances TTA-UC performance in solution and the solid state with minimal change in energy levels. Both (tBu)$_2$BPEA and (tBu)$_2$TIPS-Ac showed longer triplet lifetimes, consistent with previous studies with naphthalene derivatives.[33] The threshold excitation intensities decrease or increase with substitution, indicating the trade-off between the reduction in the TTA rate and the extension of the excited-state lifetime. Furthermore, controlled steric hindrance enhances the UC quantum yield, with a maximum of around 15%. The increase in triplet lifetime after *t*Bu substitution was more apparent in the solid state, where a significant decrease in the threshold intensity was observed in (tBu)$_2$TIPS-Ac. These results demonstrate that control of intermolecular interactions with sp^3 carbon-based excluded-volume engineering provides an effective molecular design strategy for extending triplet lifetimes, particularly in the solid state, thereby achieving low threshold intensities.

Author contributions

Y. S. conceived the project using sp^3 carbon-based bulky substituents. M. M. synthesized and characterized the compound. M. M. conducted the UC measurements with K. Mizukami and K. Matsumoto. M. M., Y. S., and N. K. wrote the manuscript with input from the other authors. Y. S. and N. K. supervised the project. All authors contributed to and have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article are included in the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5nr05481h.

The data underlying the figures and conclusions in this publication will be made available in the Zenodo data repository after publication of the manuscript.

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