

Long-lived Triplet State Formation Caused by Intramolecular Energy Hopping in Diphenylanthracene Dyads Oriented to Undergo Efficient Triplet–Triplet Annihilation Upconversion

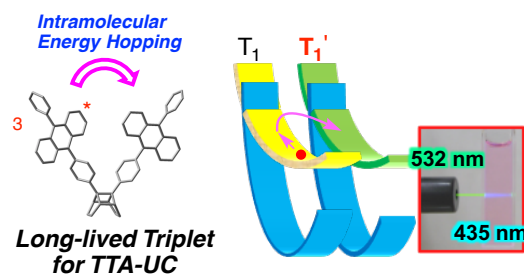
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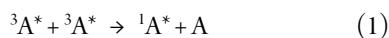
KEYWORDS: Upconversion, Intramolecular TTA, Transient Absorption Spectroscopy

ABSTRACT: Triplet–triplet annihilation (TTA)-assisted photon upconversion (TTA-UC) in three dyads (DPA–Cn–DPA), comprised of two diphenylanthracene (DPA) moieties connected by nonconjugated C1, C2, and C3 linkages (Cn), has been investigated. The performance of these dyads as energy acceptors in the presence of the energy donor platinum octaethylporphyrin are characterized by longer triplet lifetimes (τ_T) and different TTA rate constants than those of the parent DPA. The larger τ_T of the linked systems, caused by “intramolecular energy hopping” in the triplet dyad ³DPA*–Cn–DPA, results in a low threshold intensity, a key characteristic of efficient TTA-UC.



INTRODUCTION

Triplet–triplet annihilation (TTA)-upconversion (UC),^{1,2} a photophysical phenomenon in which long-wavelength light is converted to short-wavelength light of various wavelengths,^{3–7} is a promising approach to the efficient use of the sunlight.^{8,9} The system comprised of platinum 2,3,7,8,12,13,17,18-octaethylporphyrin (PtOEP) and 9,10-diphenylanthracene (DPA) as a respective energy donor (D) and energy acceptor (A), is a representative of those undergoing TTA-UC. In a conventional TTA-UC mechanism (Fig. 1), an excitation ($h\nu$) of D by using a low-energy photon followed by intersystem crossing (ISC) gives a triplet excited state of D (³D*). The succeeding energy transfer (ET) from ³D* to A affords ³A*. Bimolecular TTA of two ³A* forms a singlet state of A (¹A*) together with A (eqn 1), and ¹A* finally



shows a high-energy UC emission ($h\nu$). The least efficient step in the overall TTA-UC process is bimolecular TTA, which is typically slow because it requires collision of two short lived triplet excited states ³A*. Thus, new approaches that lead to improvement of the efficiencies of the TTA process are important because they are bound to serve as the basis of innovative strategies for the design of potentially important TTA-UC systems.

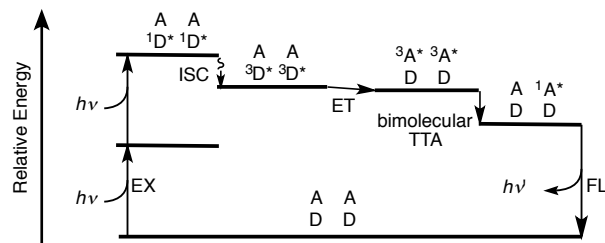
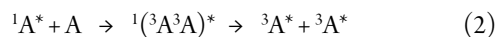


Fig. 1. Conventional mechanism for TTA-UC.

By using time-resolved spectroscopic studies, several factors that improve the efficiency of singlet fission (SF, eqn 2),^{10–16} the reverse of TTA, have been



elucidated recently. Importantly, the results of these investigations demonstrate that rapid intramolecular SF takes place in dyads composed of two acceptors and a linker, and that the rate of intramolecular SF and the lifetime (τ_T) of the resulting exciton, ³A*, is governed by the nature of the linker through control of through-space and through-bond electronic coupling between two As.^{17–20}

Similarly, many TTA-UC systems that operate through “intramolecular TTA” contain dyads of acceptors connected by conjugated^{21–23} or nonconjugated^{24–27} linkers. It is expected that the rate constant for energy transfer (k_{ET}) from ³D* to A in these types of dyads would be remarkably high due to the existence of two As in the sole molecule. However, the effects of linkers, especially on

controlling the distance between and orientation of the two As, on the efficiency of TTA-UC have not yet been fully explored.

In the investigation described below, we evaluated the photophysical properties and TTA-UC performances of systems composed of the energy donor PtOEP, and three dyads (DPA–C_n–DPA, Fig. 2) in which the DPA acceptors have different relative orientations and distances. In one of the three dyads, the two DPA acceptors are linked by a C1 unit of a dimethylmethylene moiety, in the other a C2 unit of a rigid cage structure containing dimethylene moiety serves as the linker,²⁸ and the last linker is comprised of a C3 unit of an adamantane containing trimethylene moiety.²⁴ The results of this effort show that systems containing these dyads have larger τ_T as compared to that of DPA monomer, owing to “intramolecular energy hopping”, which reduces the threshold intensity (I_{TH}) and leads to efficient TTA-UC.

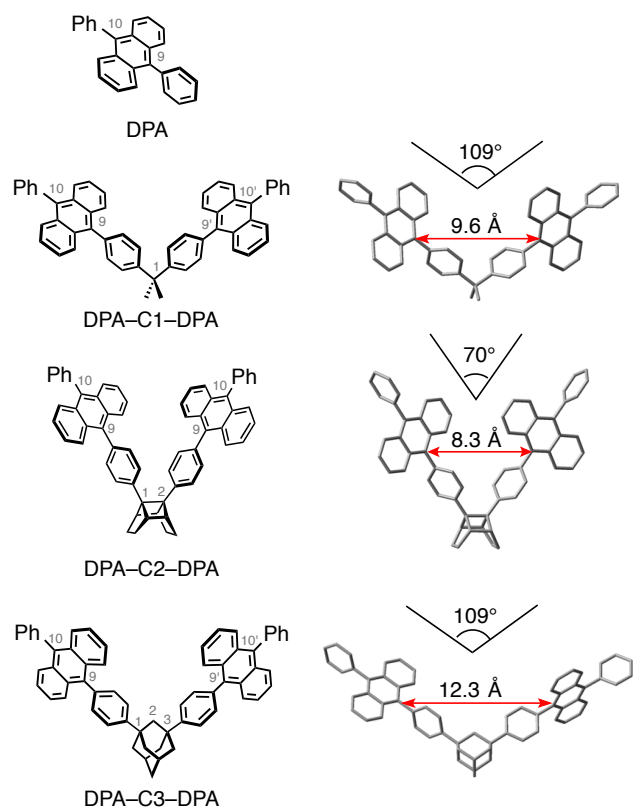
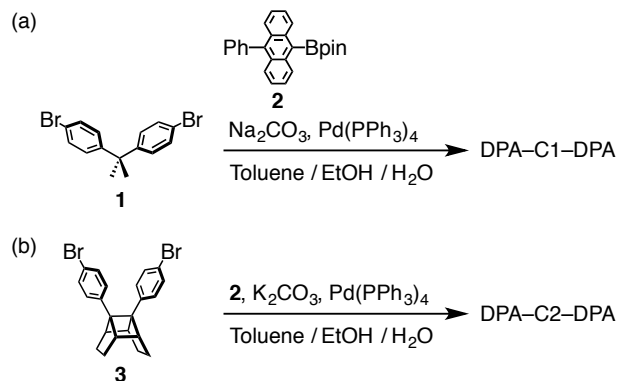


Fig. 2. Structures and DFT (B3LYP/6-311G*)-optimized geometries of DPA and DPA–C_n–DPA (n = 1–3).

Experimental Section

Preparation of Substrates. Dyads, DPA–C1–DPA and DPA–C2–DPA, were synthesized by using Suzuki–Miyaura cross-coupling reaction of the corresponding bis-bromoarenes **1** and **3**,²⁸ with 4,4,5,5-tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane (**2**, Scheme 1). Synthesis of DPA–C3–DPA and PtOEP have been reported previously.²⁴



Scheme 1. Routes for synthesis of (a) DPA–C1–DPA and (b) DPA–C2–DPA.

Steady-state Spectroscopy. UV–Vis absorption and photoluminescence spectra were recorded using JASCO V-570 and FP-8500 spectrophotometers, respectively. Absolute fluorescence quantum yields were determined by utilizing the integrating sphere method with a Hamamatsu Photonics C9920-02 under argon. Fluorescence decay profiles were determined under argon by using a HORIBA Jobin Yvon FluoroCube time-correlated single photon counting photometer.

UC Luminescence. UC luminescence measurements were made using an Ocean Optics USB4000 multichannel detector upon CW-laser (RGB Photonics, Minilas Fiber, 520 nm) excitation. Laser power was controlled by using Ltune software and neutral density filters. The sample solutions in J. Young valve-fused quartz vessels were degassed using three freeze (77 K)–pump (0.1 mmHg)–thaw (room temperature) cycles and then sealed before measurements were made.

Time-resolved Absorption Spectroscopy. Measurements were conducted by using a sample solution with an optical density (OD) = 0.6 at excitation wavelength in a vessel of 1 cm thickness. The sample solution was degassed by three freeze (77 K)–pump (0.1 mmHg)–thaw (room temperature) cycles. Nanosecond transient absorption was measured on a UNISOKU TSP-1000 setup with THG of YAG laser (355 nm, Spectra Physics Quanta-Ray GC-100, 10 Hz, fwhm = 8 ns, 15 mJ pulse⁻¹) or OPA-equipped YAG laser (410–700 nm, Continuum Surelite-3, fwhm = 4 ns, ~10 mJ pulse⁻¹) excitation and Xe arc monitoring lamp (150 W).

Theoretical Calculations. Density functional theory (DFT) calculations were carried out using Gaussian 09W program²⁹ using B3LYP functional and 6-311G(d) basis set. Scan calculations were carried out using semiempirical PM5 level of theory. Geometries and orbitals were plotted by using an Avogadro³⁰ or Gaussview³¹ program.

RESULTS AND DISCUSSION

Dyad Geometries. In contrast to those in DPA–C1–DPA, the two DPA moieties in dyads DPA–C2–DPA and DPA–C3–DPA have fixed, framework-mandated cisoid geometries. In addition, the distances between and relative orientations of the DPA acceptors in

the latter two dyads differ. The results of DFT calculations show that the respective distances between the C₉–C₉' positions of the DPA moieties in DPA–C1–DPA, DPA–C2–DPA, and DPA–C3–DPA (Fig. 2) are 9.6, 8.3, and 12.3 Å. The short C₉–C₉' distance in DPA–C2–DPA is a consequence of the narrow angle (ca. 70°) that exist between C₉–C₁₀ and C₉'–C₁₀'. These distances suggest that relatively strong through-space interaction should take place between the DPA groups in DPA–C2–DPA. It is known that TTA requiring electron exchange is efficient when the distance between the two triplet species ³A* is shorter than 10 Å.^{32,33} Thus, it was expected that efficient intramolecular TTAs would occur in DPA–C1–DPA and DPA–C2–DPA despite the fact that free rotation of the DPA moieties should take place in these dyads (all PM5 level of theory calculated DPA–C_n single bond rotational barriers are <2 kcal mol⁻¹, Fig. S11).

Photophysical Properties. DPA in CH₂Cl₂ has respective absorption and fluorescence maxima at 395 and 413 nm (Fig. 3, black, Table 1), an fluorescence lifetime (τ_{FL}) of 7.7 ns, and a quantum yield (Φ_{FL}) of 0.91. Solutions of DPA–C_n–DPA in CH₂Cl₂ display absorption bands at 396 nm (Fig. 3, red, blue, and green). Excitation of solutions of DPA–C1–DPA, DPA–C2–DPA and DPA–C3–DPA at 376 nm leads to intense fluorescence with wavelength maxima at 415, 419, and 415 nm, respectively (Fig. 3, red, blue, and green). Although the dyads do not form remarkable intramolecular excimers, DPA–C2–DPA displays a slightly redshifted and broadened fluorescence band, probably as a result of weak through-space excitonic coupling. The values of Φ_{FL} and τ_{FL} of the three dyads along with those of DPA are listed in Table 1. Also included in this table are rate constants for fluorescence emission (k_{FL}) and nonradiative deactivation (k_{NR}) calculated using eqns 3 and 4. The

$$k_{\text{FL}} = \Phi_{\text{FL}} / \tau_{\text{FL}} \quad (3)$$

$$k_{\text{NR}} = (1 - \Phi_{\text{FL}}) / \tau_{\text{FL}} \quad (4)$$

results show that the Φ_{FL} of DPA–C2–DPA (0.72) is slightly lower than those of DPA and the other dyads as a result of having a larger rate constant of nonradiative deactivation (k_{NR}). The nearly identical k_{FL} values of DPA and the three dyads suggest that through-space and through-bond interactions between two DPA moieties in the S₁ states of DPA–C_n–DPA are not remarkable.

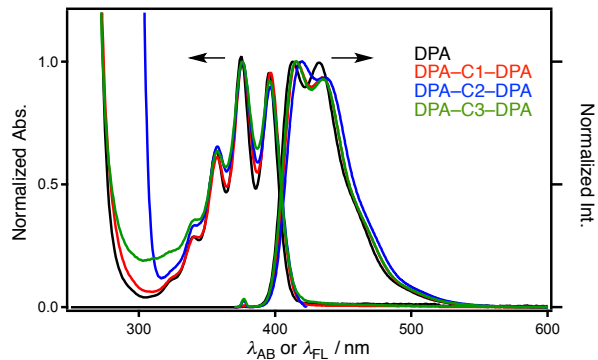


Fig. 3. UV-Vis absorption and fluorescence spectra of (black) DPA, (red) DPA–C1–DPA, (blue) DPA–C2–DPA, and (green) DPA–C3–DPA in CH₂Cl₂ ($\lambda_{\text{EX}} = 375$ nm).

Table 1. Photophysical Properties of DPA and DPA–C_n–DPA [a]

Compound	$\lambda_{\text{AB}} / \text{nm}$	$\lambda_{\text{FL}} / \text{nm}$	Φ_{FL}	$\tau_{\text{FL}} / \text{ns}$	$k_{\text{FL}} / 10^6 \text{ s}^{-1}$	$k_{\text{NR}} / 10^6 \text{ s}^{-1}$
DPA	375, 395	413	0.91	7.7	11.8	1.17
DPA–C1–DPA	376, 396	415	0.87	6.7	13.0	1.94
DPA–C2–DPA	376, 396	419	0.72	5.5	13.1	5.10
DPA–C3–DPA	376, 396	415	0.87	6.7	13.0	1.94

[a] Measured in CH₂Cl₂.

TTA-UC Characteristics. As expected, degassed CH₂Cl₂ solutions of dyads DPA–C_n–DPA and PtOEP display TTA-UC luminescence at 435 nm upon excitation at 520 nm (Fig. S2). The I_{TH} value is an important index for evaluating how the system works with the low excitation intensity.^{34,35} Consequently, double-logarithmic plot analyses of UC emission intensities (I_{UC}) against various excitation intensities (I_{EX}) were carried out on degassed CH₂Cl₂ solutions containing PtOEP along with DPA or the DPA–C_n–DPA dyads (Fig. 4). In these measurements, the quantum yields for triplet ET process (Φ_{ET}) were adjusted to be 0.98, based on a consideration of ET rate constants (k_{ET} , Table S1) and by controlling DPA–C_n–DPA concentrations. The I_{UC} of TTA-UC for DPA–C1–DPA and DPA–C3–DPA are nearly the same as that of the parent DPA. These results clearly show that I_{UC} is governed by concentration of the triplet state ³DPA*, not by the prepared concentration of the ground state DPA. Employment of Kamada fitting function shown in eqn 5,^{36–38} where K is a proportionality constant,

$$I_{\text{UC}} = KI_{\text{EX}} \left[1 + \frac{1 - \sqrt{1 + 4I_{\text{EX}}/I_{\text{TH}}}}{2I_{\text{EX}}/I_{\text{TH}}} \right] \quad (5)$$

provided the respective I_{TH} values of 13, 27, 10, and 28 mW cm⁻² for DPA, DPA–C1–DPA, DPA–C2–DPA, and DPA–C3–DPA.

Importantly, the results demonstrate that dyad DPA-C2-DPA has a low I_{TH} value that is comparable to that of DPA.

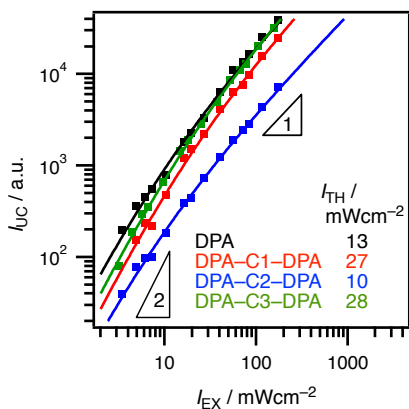


Fig. 4. Double-logarithmic plots and fitted curves of I_{UC} at 435nm against I_{EX} upon the 520-nm excitation of a degassed CH_2Cl_2 solution of DPA (black, 0.7 mM), DPA-C1-DPA (red, 0.4 mM), DPA-C2-DPA (blue, 0.5 mM), or DPA-C3-DPA (green, 0.5 mM) containing PtOEP (0.05 mM). Kamada fitting function (eqn 5)³⁶⁻³⁸ was employed.

Triplet Lifetime Analysis. The I_{TH} value can be related to the rate constant for triplet-triplet annihilation (k_{TTA}), the quantum yield for triplet energy transfer (Φ_{ET}), and the triplet lifetime (τ_T) by the relationship shown in eqn 6.^{6,34} Thus, τ_T is an

$$I_{TH} \propto 1 / k_{TTA} \Phi_{ET} \tau_T^2 \quad (6)$$

essential factor controlling I_{TH} . Recently, it was reported that covalently-linked dyads of π -conjugated systems have remarkably large τ_T .^{12,14,22} To gain further insights into the TTA-UC of the three dyads, τ_T values of DPA-C1-DPA, DPA-C2-DPA, and DPA-C3-DPA in degassed CH_2Cl_2 were determined using PtOEP-sensitized transient absorption analysis. The τ_T value for $^3DPA^*$ was determined to be 190 μs by analysis of the 450-nm decay profile (Fig. 5, black).³⁹ Similar measurements gave τ_T values for DPA-C1-DPA, DPA-C2-DPA, and DPA-C3-DPA of 318, 226, and 261 μs , respectively (Fig. 5, red, blue, and green). Thus, the τ_T values of all dyads are larger than that of DPA.¹² If the parent DPA and the three dyads were to have the same k_{TTA} values, the expected I_{TH} values obtained by using τ_T and eqn 6 for DPA-C1-DPA, DPA-C2-DPA, and DPA-C3-DPA would be 0.36, 0.71, and 0.53 times the I_{TH} value of DPA, respectively. However, the actual I_{TH} values for the corresponding dyads are 2.1, 0.77, and 2.2 times the I_{TH} value of DPA. This finding indicates that the k_{TTA} values of the dyads are different and uniquely dependent on their molecular structure. Because Φ_{ET} was adjusted to 0.98 in all systems, relative k_{TTA} values can be obtained using eqn 6 (Table 2). Note that the “TTA” discussed here is not an elementary process, but an overall process that includes association of two $^3DPA^*-Cn-DPA$.

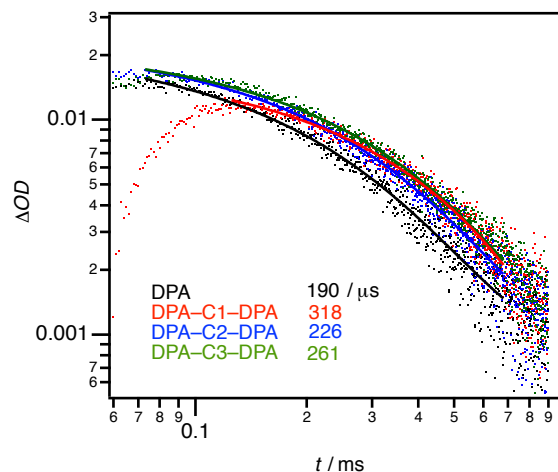


Fig. 5. Decay profiles of the absorption of the $^3DPA^*$ moiety at 450 nm in degassed CH_2Cl_2 solution of the parent DPA (black, 0.05 mM) or DPA-C1-DPA (red, 0.05 mM), DPA-C2-DPA (blue, 0.05 mM), or DPA-C3-DPA (green, 0.05 mM) containing PtOEP (0.05 mM).

Table 2. Parameters Related to TTA-UC of DPA and DPA-Cn-DPA

Compound	$\theta / ^\circ$ ^[a]	$d / \text{\AA}$ ^[a]	$\tau_T / \mu s$ ^[b]	$I_{TH} / mW cm^{-2}$	Relative k_{TTA} ^[c]
DPA	—	—	190	13	1
DPA-C1-DPA	109	9.6	318	27	0.17
DPA-C2-DPA	70	8.3	226	10	0.92
DPA-C3-DPA	109	12.1	261	28	0.23

[a] Obtained by using DFT-optimized geometries. [b] Obtained using degassed CH_2Cl_2 solutions containing PtOEP. [c] Determined by using τ_T , I_{TH} , and eqn 6 relative to k_{TTA} of DPA.

The large τ_T values of triplet DPA containing dyads can be explained by invoking “intramolecular energy hopping” from $^3DPA^*$ to the other DPA moiety. Using the generally-accepted explanation,^{40,41} nonradiative deactivation of excited triplet species of monomeric systems takes place at the conical intersection (CI) of T_1 and S_0 surfaces (Fig. 6a), and is associated with a motion along with the potential surface (e.g., molecular distortion). If, as is the case in DPA-Cn-DPA, another DPA moiety exists within close distance, “intramolecular energy hopping” to another triplet energy surface T_1' (Fig. 6b) before reaching CI is possible. Thus, nonradiative deactivation of $^3DPA^*-Cn-DPA$ is suppressed, as compared with that of the parent $^3DPA^*$. This type of phenomenon has been frequently observed for dyads linked by conjugated or nonconjugated tethers.^{12,14,22,42} Actually, the longer τ_T of $^3DPA^*-Cn-DPA$ were obtained under the heavy-atom free benzophenone-sensitized conditions (e.g. 623 μs for DPA-C1-DPA, Fig. S4).⁴³ Thus, the magnitude of elongation of τ_T is strongly depending on the environment, such as solvent, heavy atom, temperature, and etc.

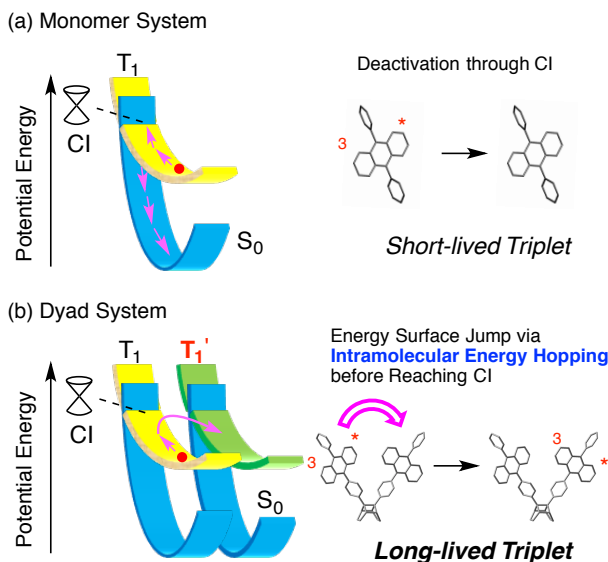


Fig. 6. Schematic representations of mechanism for deactivation of triplet excited species of (a) monomer and (b) dyads system through CI. The elongation of τ_T of dyad system caused by “intramolecular energy hopping”.

CONCLUSIONS

In the investigation described above, we examined the TTA-UC behavior of three dyads DPA–C_n–DPA ($n = 1\sim 3$), in which the DPA moieties are linked by nonconjugated units. Although the fluorescence properties of the dyads are almost identical, their TTA-UC characteristics reflected in I_{TH} values differ greatly. The results of spectroscopic analysis demonstrate that the structures of the dyads affect their triplet lifetimes (τ_T) and TTA rate constants (k_{TTA}). The nonconjugated linkers in these systems effectively elongate τ_T by suppressing nonradiative deactivation, through “intramolecular energy hopping”. It is anticipated that a better dyad orientation would also enable a faster TTA through an intramolecular process, though the analysis of TTA process have not reached to the level that reveals an acceleration of k_{TTA} . The original strategy of elongation of τ_T described in this effort will play an important role in improving the characteristics of not only TTA-UC systems⁴⁴ but also other devices that operate through formation and decay of triplet-excited species⁴⁵ such as organic light-emitting diodes^{46,47} and organic solar cells.^{8,9,48,49}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the Publications website at DOI: XXXX.

General, Preparation of Substrates, Phosphorescence Quenching Experiments, Raw Data of UC Luminescence Spectrum, Determination of Triplet Lifetime under the Benzophenone-sensitization Conditions, NMR Spectra, and Theoretical Calculations

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Dedication

This paper is dedicated to the memory of Emer. Prof. Toshio Mukai and Emer. Prof. Tsutomu Miyashi at Tohoku University.

Notes

The authors declare no competing financial interests.

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REFERENCES and NOTES

- (1) Singh-Rachford, T. N.; Castellano, F. N. Photon Upconversion Based on Sensitized Triplet-Triplet Annihilation. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.

- (2) Zhou, J.; Liu, Q.; Feng, W.; Sun, Y.; Li, F. Upconversion Luminescent Materials: Advances and Applications. *Chem. Rev.* **2015**, *115*, 395–465.
- (3) Zhou, J.; Liu, Q.; Feng, W.; Sun, Y.; Li, F. Upconversion Luminescent Materials: Advances and Applications. *Chem. Rev.* **2015**, *115*, 395–465.
- (4) Haruki, R.; Sasaki, Y.; Masutani, K.; Yanai, N.; Kimizuka, N. Leaping across the Visible Range: Near-Infrared-to-Violet Photon Upconversion Employing a Silyl-Substituted Anthracene. *Chem. Commun.* **2020**, *56*, 7017–7020.
- (5) Pristash, S. R.; Corp, K. L.; Rabe, E. J.; Schlenker, C. W. Heavy-Atom-Free Red-to-Yellow Photon Upconversion in a Thiosquaraine Composite. *ACS Appl. Energy Mater.* **2020**, *3*, 19–28.
- (6) Monguzzi, A.; Tubino, R.; Hoseinkhani, S.; Campione, M.; Meinardi, F. Low Power, Non-Coherent Sensitized Photon up-Conversion: Modelling and Perspectives. *Phys. Chem. Chem. Phys.* **2012**, *14*, 4322–4332.
- (7) Sasaki, Y.; Amemori, S.; Kouno, H.; Yanai, N.; Kimizuka, N. Near Infrared-to-Blue Photon Upconversion by Exploiting Direct S-T Absorption of a Molecular Sensitizer. *J. Mater. Chem. C* **2017**, *5*, 5063–5067.
- (8) Dilbeck, T.; Hanson, K. Molecular Photon Upconversion Solar Cells Using Multilayer Assemblies: Progress and Prospects. *J. Phys. Chem. Lett.* **2018**, *9*, 5810–5821.
- (9) Shang, Y.; Hao, S.; Yang, C.; Chen, G. Enhancing Solar Cell Efficiency Using Photon Upconversion Materials. *Nanomaterials* **2015**, *5*, 1782–1809.
- (10) Smith, M. B.; Michl, J. Singlet Fission. *Chem. Rev.* **2010**, *110*, 6891–6936.
- (11) Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M. Intramolecular Singlet Fission in Oligoacene Heterodimers. *Angew. Chem. Int. Ed.* **2016**, *55*, 3373–3377.
- (12) Nakamura, S.; Sakai, H.; Nagashima, H.; Kobori, Y.; Tkachenko, N. V.; Hasobe, T. Quantitative Sequential Photoenergy Conversion Process from Singlet Fission to Intermolecular Two-Electron Transfers Utilizing Tetracene Dimer. *ACS Energy Lett.* **2019**, *4*, 26–31.
- (13) Bhattacharyya, K.; Dey, D.; Datta, A. Intramolecular Singlet Fission in Quinoidal Dihydrothiophene. *J. Phys. Chem. C* **2019**, *123*, 4749–4754.
- (14) Matsui, Y.; Kawaoka, S.; Nagashima, H.; Nakagawa, T.; Okamura, N.; Ogaki, T.; Ohta, E.; Akimoto, S.; Sato-Tomita, A.; Yagi, S.; Kobori, Y.; Ikeda, H. Exergonic Intramolecular Singlet Fission of an Adamantane-Linked Tetracene Dyad via Twin Quintet Multiexcitons. *J. Phys. Chem. C* **2019**, *123*, 18813–18823.
- (15) Kumarasamy, E.; Sanders, S. N.; Tayebjee, M. J. Y.; Asadpoordarvish, A.; Hele, T. J. H.; Fuemmeler, E. G.; Pun, A. B.; Yablou, L. M.; Low, J. Z.; Paley, D. W.; Dean, J. C.; Choi, B.; Scholes, G. D.; Steigerwald, M. L.; Ananth, N.; McCamey, D. R.; Sfeir, M. Y.; Campos, L. M. Tuning Singlet Fission in π -Bridge- π Chromophores. *J. Am. Chem. Soc.* **2017**, *139*, 12488–12494.
- (16) Smith, M. B.; Michl, J. Recent Advances in Singlet Fission. *Annu. Rev. Phys. Chem.* **2013**, *64*, 361–386.
- (17) Korovina, N. V.; Pompetti, N. F.; Johnson, J. C. Lessons from Intramolecular Singlet Fission with Covalently Bound Chromophores. *J. Chem. Phys.* **2020**, *152*, 40904.
- (18) Basel, B. S.; Zirzmeier, J.; Hetzer, C.; Reddy, S. R.; Phelan, B. T.; Krzyaniak, M. D.; Volland, M. K.; Coto, P. B.; Young, R. M.; Clark, T.; Thoss, M.; Tykwinski, R. R.; Wasielewski, M. R.; Guldi, D. M. Evidence for Charge-Transfer Mediation in the Primary Events of Singlet Fission in a Weakly Coupled Pentacene Dimer. *Chem* **2018**, *4*, 1092–1111.
- (19) Korovina, N. V.; Joy, J.; Feng, X.; Feltenberger, C.; Krylov, A. I.; Bradforth, S. E.; Thompson, M. E. Linker-Dependent Singlet Fission in Tetracene Dimers. *J. Am. Chem. Soc.* **2018**, *140*, 10179–10190.
- (20) Hetzer, C.; Guldi, D. M.; Tykwinski, R. R. Pentacene Dimers as a Critical Tool for the Investigation of Intramolecular Singlet Fission. *Chem. Eur. J.* **2018**, *24*, 8245–8257.
- (21) Dzebo, D.; Börjesson, K.; Gray, V.; Moth-Poulsen, K.; Albinsson, B. Intramolecular Triplet-Triplet Annihilation Upconversion in 9,10-Diphenylanthracene Oligomers and Dendrimers. *J. Phys. Chem. C* **2016**, *120*, 23397–23406.
- (22) Pun, A. B.; Sanders, S. N.; Sfeir, M. Y.; Campos, L. M.; Congreve, D. N. Annihilator Dimers Enhance Triplet Fusion Upconversion. *Chem. Sci.* **2019**, *10*, 3969–3975.
- (23) Gao, C.; Prasad, S. K. K.; Zhang, B.; Dvořák, M.; Tayebjee, M. J. Y.; McCamey, D. R.; Schmidt, T. W.; Smith, T. A.; Wong, W. W. H. Intramolecular Versus Intermolecular Triplet Fusion in Multichromophoric Photochemical Upconversion. *J. Phys. Chem. C* **2019**, *123*, 20181–20187.
- (24) Matsui, Y.; Kanoh, M.; Ohta, E.; Ogaki, T.; Ikeda, H. Triplet-Triplet Annihilation-Photon Upconversion Employing an Adamantane-Linked Diphenylanthracene Dyad Strategy. *J. Photochem. Photobiol. A Chem.* **2020**, *387*, 112107.
- (25) Tilley, A. J.; Robotham, B. E.; Steer, R. P.; Ghiggino, K. P. Sensitized Non-Coherent Photon Upconversion by Intramolecular Triplet-Triplet Annihilation in a Diphenylanthracene Pendant Polymer. *Chem. Phys. Lett.* **2015**, *618*, 198–202.
- (26) Ribas, M. R.; Steer, R. P.; Rüther, R. Photophysical Properties of New Bis-Perylene Dyads for Potential Upconversion Use. *Chem. Phys. Lett.* **2014**, *605–606*, 126–130.
- (27) Yu, S.; Zeng, Y.; Chen, J.; Yu, T.; Zhang, X.; Yang, G.; Li, Y. Intramolecular Triplet-Triplet Energy Transfer Enhanced Triplet-Triplet Annihilation Upconversion with a Short-Lived Triplet State Platinum(II) Terpyridyl Acetylide Photosensitizer. *RSC Adv.* **2015**, *5*, 70640–70648.
- (28) Kuramoto, Y.; Matsui, Y.; Ohta, E.; Sato, H.; Ikeda, H. Unexpected Formation of a Phenonium Ion-Containing Salt by Single Electron-Transfer Oxidation of a Cage Compound Possessing Triphenylamine Moieties. *Tetrahedron Lett.* **2014**, *55*, 4366–4369.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.

- Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, 2009.
- (30) Hanwell, M. D.; Curtis, D. E.; Loni, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *J. Cheminform.* **2012**, *4*, 17.
- (31) Dennington, R.; Keith, T.; Millam, J. Gaussview, Version 5. *Semichem Inc., Shawnee Mission, KS*. 2016, p Semichem Inc.
- (32) Sato, R.; Kitoh-Nishioka, H.; Kamada, K.; Mizokuro, T.; Kobayashi, K.; Shigeta, Y. Does Inactive Alkyl Chain Enhance Triplet-Triplet Annihilation of 9,10-Diphenylanthracene Derivatives? *J. Phys. Chem. C* **2018**, *122*, 5334–5340.
- (33) Sato, R.; Kitoh-Nishioka, H.; Kamada, K.; Mizokuro, T.; Kobayashi, K.; Shigeta, Y. Synergetic Effects of Triplet-Triplet Annihilation and Directional Triplet Exciton Migration in Organic Crystals for Photon Upconversion. *J. Phys. Chem. Lett.* **2018**, *9*, 6638–6643.
- (34) Monguzzi, A.; Mezyk, J.; Scotognella, F.; Tubino, R.; Meinardi, F. Upconversion-Induced Fluorescence in Multicomponent Systems: Steady-State Excitation Power Threshold. *Phys. Rev. B* **2008**, *78*, 195112.
- (35) Schmidt, T. W.; Castellano, F. N. Photochemical Upconversion: The Primacy of Kinetics. *J. Phys. Chem. Lett.* **2014**, *5*, 4062–4072.
- (36) Kamada, K.; Sakagami, Y.; Mizokuro, T.; Fujiwara, Y.; Kobayashi, K.; Narushima, K.; Hirata, S.; Vacha, M. Efficient Triplet-Triplet Annihilation Upconversion in Binary Crystalline Solids Fabricated: Via Solution Casting and Operated in Air. *Mater. Horizons* **2017**, *4*, 83–87.
- (37) Abulikemu, A.; Sakagami, Y.; Heck, C.; Kamada, K.; Sotome, H.; Miyasaka, H.; Kuzuhara, D.; Yamada, H. Solid-State, Near-Infrared to Visible Photon Upconversion via Triplet-Triplet Annihilation of a Binary System Fabricated by Solution Casting. *ACS Appl. Mater. Interfaces* **2019**, *11*, 20812–20819.
- (38) Mori, T.; Mori, T.; Fujii, A.; Saito, A.; Saomoto, H.; Kamada, K. Effect of Crystallinity in Stretched PVA Films on Triplet-Triplet Annihilation Photon Upconversion. *ACS Appl. Polym. Mater.* **2020**, *2*, 1422–1428.
- (39) Aulin, Y. V.; van Seville, M.; Moes, M.; Grozema, F. C. Photochemical Upconversion in Metal-Based Octaethyl Porphyrin–Diphenylanthracene Systems. *RSC Adv.* **2015**, *5*, 107896–107903.
- (40) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*; University Science Books, 2009.
- (41) Suzuki, S.; Sasaki, S.; Sairi, A. S.; Iwai, R.; Tang, B. Z.; Konishi, G. Principles of Aggregation-Induced Emission: Design of Deactivation Pathways for Advanced AIEgens and Applications. *Angew. Chem. Int. Ed.* **2020**, *59*, 9856–9867.
- (42) Sakuma, T.; Sakai, H.; Araki, Y.; Mori, T.; Wada, T.; Tkachenko, N. V.; Hasobe, T. Long-Lived Triplet Excited States of Bent-Shaped Pentacene Dimers by Intramolecular Singlet Fission. *J. Phys. Chem. A* **2016**, *120*, 1867–1875.
- (43) This result indicates that the development of heavy-atom free donors is effective to reduce the threshold intensity.
- (44) Tokunaga, A.; Uriarte, L. M.; Mutoh, K.; Fron, E.; Hofkens, J.; Sliwa, M.; Abe, J. Photochromic Reaction by Red Light via Triplet Fusion Upconversion. *J. Am. Chem. Soc.* **2019**, *141*, 17744–17753.
- (45) Sasikumar, D.; John, A. T.; Sunny, J.; Hariharan, M. Access to the Triplet Excited States of Organic Chromophores. *Chem. Soc. Rev.* **2020**, *49*, 6122–6140.
- (46) Graf von Reventlow, L.; Matthias Bremer, A.; Ebenhoch, B.; Martina Gerken, A.; Schmidt, T. W.; Colsmann, A. An Add-on Organic Green-to-Blue Photon-Upconversion Layer for Organic Light Emitting Diodes. *J. Mater. Chem. C* **2018**, *6*, 3845–3848.
- (47) Ieuji, R.; Goushi, K.; Adachi, C. Triplet-Triplet Upconversion Enhanced by Spin-Orbit Coupling in Organic Light-Emitting Diodes. *Nat. Commun.* **2019**, *10*, 5283.
- (48) Paci, I.; Johnson, J. C.; Chen, X.; Rana, G.; Popović, D.; David, D. E.; Nozik, A. J.; Ratner, M. A.; Michl, J. Singlet Fission for Dye-Sensitized Solar Cells: Can a Suitable Sensitizer Be Found? *J. Am. Chem. Soc.* **2006**, *128*, 16546–16553.
- (49) Kinoshita, M.; Sasaki, Y.; Amemori, S.; Harada, N.; Hu, Z.; Liu, Z.; Ono, L. K.; Qi, Y.; Yanai, N.; Kimizuka, N. Photon Upconverting Solid Films with Improved Efficiency for Endowing Perovskite Solar Cells with Near-Infrared Sensitivity. *ChemPhotoChem* **2020**, in press. DOI: 10.1002/cptc.202000143