Letter

Triplet−Triplet Annihilation-Based Photon Upconversion with a Macrocyclic Parallel Dimer

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ABSTRACT: The integration of multiple chromophore units into a single molecule is expected to improve the performance of photon upconversion based on triplet−triplet annihilation (TTA-UC) that can convert low energy photons to higher energy photons at low excitation intensity. In this study, a macrocyclic parallel dimer of 9,10-diphenylanthracene (DPA) with a precisely parallel orientation, named MPD-2, is synthesized, and its TTA-UC properties are investigated. MPD-2 shows a green-to-blue TTA-UC emission in the presence of a triplet sensitizer, platinum octaethylporphyrin (PtOEP). Compared to monomeric DPA, MPD-2 results in an enhancement of the spin statistical factor of TTA and a decrease in the excitation light intensity due to the intramolecular TTA process. The obtained structure−property relationship provides important information for the further improvement of TTA-UC properties.

Intramolecular TTA in Parallel Oriented Dimer

KEYWORDS: *photon upconversion, triplet−triplet annihilation, macrocyclic parallel dimer, spin statistical factor, anthracene*
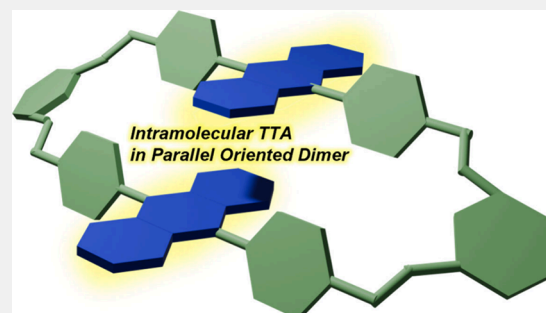
INTRODUCTION

Sunlight is one of the most crucial renewable energies in our environment and its effective use is demanded. Photon upconversion is a methodology for converting low energy photons to higher energy ones and has the potential to improve the efficiency of sunlight-powered devices.[1,2] Among several UC mechanisms, triplet−triplet annihilation-based photon upconversion (TTA-UC) is particularly attractive due to the possibility of utilizing low intensity, noncoherent light.[3−8] The general TTA-UC mechanism is shown in Figure 1. TTA-UC occurs in multichromophore systems: a triplet sensitizer and an emitter. First, the sensitizer molecule is photoexcited from the ground state ($S_{0,S}$) to the excited singlet

state ($S_{1,S}$), followed by intersystem crossing (ISC) to the excited triplet state ($T_{1,S}$). Triplet energy transfer (TET) from the sensitizer to emitter is followed by annihilation between two acceptor triplets ($T_{1,E}$) and generation of an emitter excited singlet state ($S_{1,E}$).

Since the TTA event proceeds based on the Dexter mechanism, it depends on the molecular diffusion of the excited triplet. Therefore, it is necessary to increase the emitter concentration to get the excited triplet closer for an efficient TTA-UC process. However, a high emitter concentration causes undesired phase separation and aggregation, leading to a decrease in the luminescence efficiency.[3,9,10] One promising way to mitigate this challenge is to introduce multiple emitter sites within a single molecule and allow intramolecular-TTA (*intra*-TTA) as well as intermolecular-TTA (*inter*-TTA) events.[11−26] The *intra*-TTA process is independent of molecular diffusion and thus avoids the diffusion limitations of Dexter-type TTA. So far, the *intra*-TTA process has been focused on emitter molecules with dimer,[11,15,16,18,23−26] dendrimer,[14,17,19] and polymer structures.[12,13,21,22] In several recent studies, various dimer molecules based on diphenylanthracene (DPA) have been studied to investigate the effect of
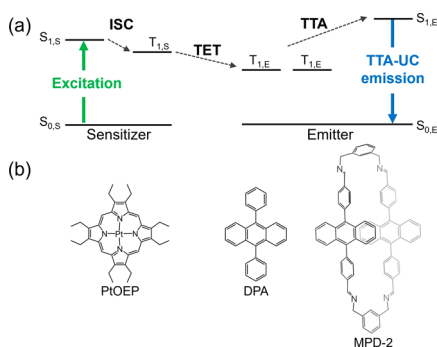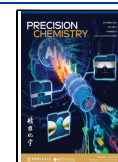

Figure 1. (a) Energy level diagram of TTA-UC. (b) Molecular structures of a sensitizer (PtOEP) and emitters (DPA, MPD-2).

chromophore structure on TTA-UC.[11,15,16,23,24] However, a decrease in the *f* value, the spin statistical factor for obtaining an excited singlet state after TTA, and an increase in the excitation light intensity required to obtain an efficient TTA-UC emission have been reported relative to those of the DPA monomer. Therefore, the fine-tuning of the dimer structure and deeper understanding of the structure−property relationship are highly desired.

It has been reported that the chromophore structure and orientation of the dimer molecules are crucial for controlling the dynamics of multiexcitonic triplet dimer states in the singlet fission, which is the inverse process of TTA.[27−30] Recent simulations have also indicated that parallel orientation in the triplet dimer state could be the key for improving the *f* value of the TTA-UC process.[31] To experimentally address the effect of chromophore orientation on the *f* value, it is crucial to create an emitter dimer with a parallel orientation.

In this study, a macrocyclic parallel dimer (MPD-2) with two DPA units precisely parallel-oriented has been synthesized, and its TTA-UC properties were investigated. The synthetic procedure follows our previous work, where we synthesized a macrocyclic parallel dimer with pentacene chromophores (MPD-1).[32] The TTA-UC properties of MPD-2 were compared to those of a DPA monomer by utilizing platinum octaethylporphyrin (PtOEP) as a triplet sensitizer (Figure 1b). MPD-2 showed an increase in the *f* value and a decrease in excitation light intensity compared with DPA were observed, demonstrating the positive effect of the precisely parallel-oriented chromophore dimer.

■ RESULT AND DISCUSSION

The synthesis of MPD-2 was performed in two steps (Figure S1). 4,4′-(Anthracene-9,10-diyl)dibenzaldehyde (DPA-2CHO) was synthesized by a Suzuki Miyaura cross-coupling reaction as previously reported.[33] DPA-2CHO and *m*-xylylenediamine were then mixed, and acetic acid was added dropwise as a catalyst. The formation of the Schiff base gave MPD-2 with a yield of 56% (Figure 2a, see the Supporting Information for details). The purity of MPD-2 was fully confirmed by ^{1}H NMR, high-resolution mass spectroscopy (HR-MS), and elemental analysis (Figures S2 and S3).

Single crystal X-ray diffraction (SCXRD) measurements revealed that the distance between the proximate aromatic rings of two anthracene units is 3.7 Å, indicating the presence of π−π interactions (Figure 2b, see the Supporting Information for details). The interplanar angle between the two anthracene units was found to be 0°, indicating a precisely parallel orientation.

The absorption and emission spectra of DPA, MPD-2, and PtOEP in chloroform are shown in Figure 3. The molar absorption coefficient of MPD-2 is about 1.6 times that of DPA, consistent with the property of DPA dimers as previously reported.[23,24] The absorption peaks of MPD-2 at 358, 377, and 397 nm showed a slight red shift compared to those of DPA at 357, 375, and 396 nm. The emission spectrum of MPD-2 was observed to be red-shifted compared to that of DPA, resulting in the disappearance of the vibrational structure. The fluorescence quantum yield (Φ_{FL}) and fluorescence lifetime (τ_{FL}) of MPD-2 were 61.1% and 4.7 ns, both of which were decreased compared to the monomer (Φ_{FL} = 98.0%, τ_{FL} = 7.7 ns, Figure S4). These results indicate an increased nonradiative rate constant from the excited singlet state due to electronic interactions between DPA chromophores (Table S2). The
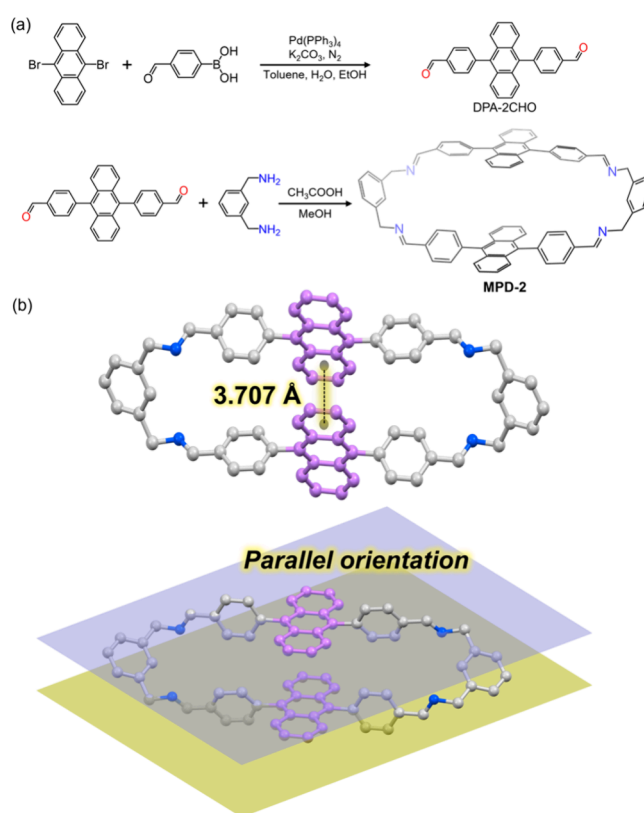
Figure 2. (a) Synthetic scheme and (b) single crystal structure of MPD-2.
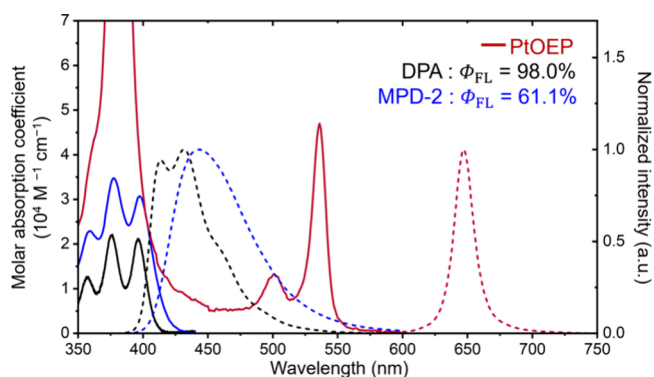
Figure 3. Absorption (solid) and photoluminescence (dashed) spectra of DPA (black), MPD-2 (blue), and PtOEP (red) in chloroform ([DPA] = 20 μM, [MPD-2] = 10 μM, [PtOEP] = 10 μM).

excited triplet energy level of DPA is reported to be 1.77 eV.[34] The sensitizer PtOEP has been used in various green-to-blue TTA-UC systems in combination with DPA due to its strong absorption properties above 500 nm and high intersystem crossing efficiency ($\Phi_{ISC} \sim$ 100%).[5,35−37] The reabsorption of the TTA-UC emission can be suppressed due to the weak absorption of PtOEP at 400−500 nm, where DPA exhibits emission. The T_1 energy level of PtOEP is estimated from the 0−0 emission peak in the phosphorescence spectrum to be 1.92 eV, which is high enough to efficiently sensitize a DPA unit.

There are two TTA pathways, intermolecular- and intramolecular-TTA (*inter*-TTA and *intra*-TTA). The *intra*-TTA pathway has been reported to predominate when an emitter's

concentration is low relative to a sensitizer.[24] Therefore, the TTA-UC characterization were performed on samples with different emitter concentrations. The concentration of PtOEP was fixed at 10 μM, and the concentration ratios of the emitter/sensitizer unit ([E]/[S]) were determined to be 25 and 2, respectively. The further increase of the emitter concentration was difficult due to the solubility limitation of MPD-2. The molecular dispersion of MPD-2 up to 125 μM was confirmed from a Beer−Lambert plot (Figure S5).

Under the irradiation of a 532 nm laser to PtOEP/DPA or PtOEP/MPD-2 mixed solution in deaerated chloroform, blue upconverted emissions were observed (Figure 4a and Figure S6). The millisecond-scale delayed emission supports the triplet-mediated mechanism (Figure S7). The TTA-UC efficiency (η_{UC}, theoretical maximum: 100%) was determined by the relative method (see Supporting Information for details) to be 17.5% for DPA and 11.9% for MPD-2 when

[E]/[S] was 25, and 4.6% for DPA and 3.7% for MPD-2 when [E]/[S] was 2, respectively (Figure 4b). The η_{UC} can be expressed as the product of the efficiency of each process and is given by the following equation,[5,38]

$$\eta_{UC} = f\Phi_{ISC}\Phi_{TET}\Phi_{TTA}\Phi_{FL}$$

where f is the spin statistical factor of obtaining an excited singlet state ($S_{1,E}$) after TTA, Φ_{ISC}, Φ_{TET}, Φ_{TTA}, and Φ_{FL} are the quantum yields of ISC, TET, TTA, and emitter fluorescence, respectively. Each of the parameters determining η_{UC} is summarized in Table 1. The TET efficiency (Φ_{TET}) from PtOEP to DPA or MPD-2 was obtained by phosphorescence quenching experiments according to the following equation,

$$\Phi_{TET} = 1 - \frac{\Phi_{PL}}{\Phi_{PL,0}}$$

where Φ_{PL} and $\Phi_{PL,0}$ are the phosphorescence quantum yields of sensitizer in the presence or absence of an emitter, respectively. The Φ_{TET} values from PtOEP to DPA and MPD-2 were over 90% at the [E]/[S] ratio of 25 and decreased at the [E]/[S] ratio of 2 (Table 1). The Φ_{TET} was slightly reduced for MPD-2 compared to that for DPA. This is due to the larger molecular size of MPD-2 compared to that of the DPA monomer, which results in slower diffusion dynamics. By increasing the MPD-2 concentration from 10 to 125 μM, the Φ_{FL} value slightly decreased due to the self-absorption. While the Φ_{TTA} value is assumed to be unity in the region well above the threshold excitation intensity (I_{th}),[39] the triplet back energy transfer may take place at low emitter concentration conditions. In addition, under low emitter concentration conditions, the number of emitters available for triplet energy transfer may decrease due to saturation of the emitter triplet as the excitation light intensity increases.[5] Therefore, it should be noted that, under low emitter concentration conditions, the f value may be underestimated for both DPA and MPD-2 due to the triplet back energy transfer and decrease in the Φ_{TET} caused by the saturation effect.

According to the model reported by Gao and co-workers, the f values for *inter-* and *intra-*TTA processes can be estimated as shown in the following equation, assuming that the f value derived from the *inter-*TTA of MPD-2 is similar to that of the DPA monomer,[16]

$$f_{all} = \frac{1}{2n-1}f_{DPA} + \frac{2n-2}{2n-1}f_{intra}$$

where n represents the number of chromophore units that exist in one molecule. Interestingly, a higher f value was observed in MPD-2 than in the DPA monomer, suggesting that the parallel orientation between chromophores contributes to improving the f value. This might be due to the enhanced mixing between the singlet and quintet states of TT dimer, resulting in the effective use of quintet TT dimer in the formation of the emitter singlet excited state $S_{1,E}$.[31,40] Furthermore, the difference in the f value between DPA and MPD-2 under low emitter concentration conditions ([E]/[S] ratio of 2) was larger than that under high emitter concentration conditions ([E]/[S] ratio of 25). This may be due to the *intra-*TTA process becoming predominant, as the emitter triplet is more easily saturated.[5]

In addition to the η_{UC}, the threshold excitation intensity (I_{th}) is also one of the key parameters for evaluating the TTA-UC
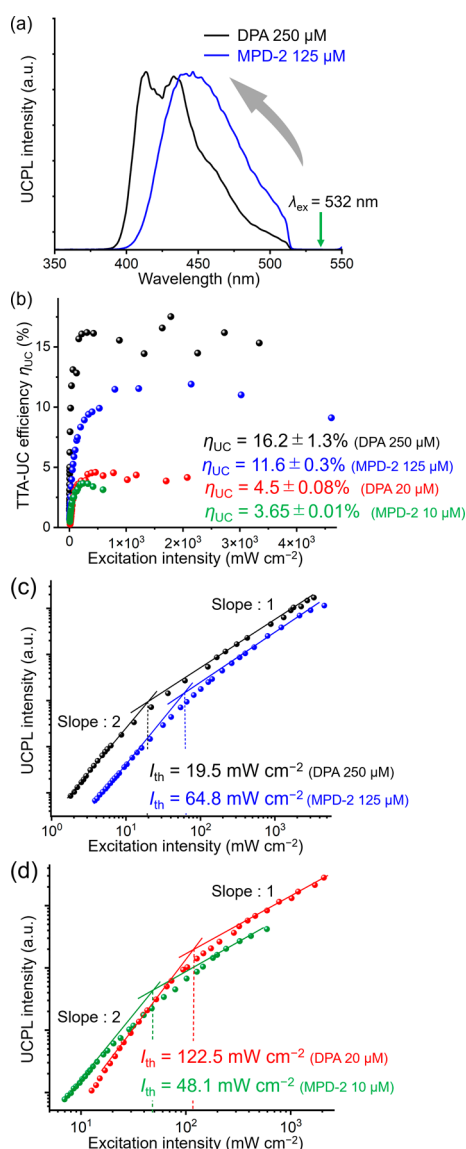
Figure 4. (a) TTA-UC emission spectra, (b) TTA-UC efficiency (η_{UC}), (c, d) excitation intensity dependence of UC emission intensity of PtOEP/DPA and PtOEP/MPD-2 in deaerated chloroform ([PtOEP] = 10 μM, [DPA] = 250 or 20 μM, [MPD-2] = 125 or 10 μM, λ_{ex} = 532 nm, 532 nm notch filter, under Ar).

Table 1. Parameters Relevant to the η_{UC} and I_{th} of PtOEP/DPA and PtOEP/MPD-2 ([PtOEP] = 10 μM)

Sample	η_{UC}(%)	Φ_{TET}(%)	Φ_{FL}(%)	f_{all}(%)	f_{inter}(%)	f_{intra}(%)	I_{th} (mW cm^{-2})	Φ_{ISC}(%)	γ_{TT}(10^{-12} cm^3 s^{-1})	τ_T(ms)
PtOEP/DPA ([DPA] = 250 μM)	16.2 ± 1.3	97.0	97.4	17.1 ± 1.4	17.1 ± 1.4	-	19.5	~100	5.7	3.1
PtOEP/MPD-2 ([MPD-2] = 125 μM)	11.6 ± 0.3	94.2	57.2	21.5 ± 0.6	17.1[a]	23.7 ± 0.9	64.6	~100	10.1	1.3
PtOEP/DPA ([DPA] = 20 μM)	4.5 ± 0.08	71.6	98.0	6.4 ± 0.1	6.4 ± 0.1	-	122.5	~100	1.5	2.8
PtOEP/MPD-2 ([MPD-2] = 10 μM)	3.65 ± 0.01	52.6	61.1	11.3 ± 0.1	6.4[a]	13.8 ± 0.05	48.1	~100	16.2	1.6

[a]Assuming that the f value derived from the *inter*-TTA of MPD-2 is similar to that of the DPA monomer.

performance and can be expressed by the following equation,[39,41,42]

$$I_{th} = \frac{1}{\alpha \Phi_{ISC} \Phi_{TET} \gamma_{TT} (\tau_T)^2}$$

where α is a sensitizer absorption coefficient, γ_{TT} is the rate constant for TTA, and τ_T is the excited triplet lifetime of an emitter, respectively. In the TTA-UC system, the double log plot of the TTA-UC emission intensity versus excitation intensity changes from quadratic to linear. The I_{th} is defined as the intersection in the quadratic and linear fitting lines. With an [E]/[S] ratio of 25, the I_{th} in MPD-2 was 64.8 mW cm^{-2}, higher than the one in the DPA monomer (19.5 mW cm^{-2}), mainly due to the shorter τ_T (Figure 4c and Figure S7). On the other hand, the I_{th} in MPD-2 was 48.1 mW cm^{-2} when the [E]/[S] ratio was 2, which was notably lower than the I_{th} of 122.5 mW cm^{-2} in DPA (Figure 4d). Considering the values of Φ_{TET}, γ_{TT}, and τ_T that determine the I_{th}, the decrease in I_{th} in MPD-2 is due to the increase in γ_{TT}, highlighting the significance of the *intra*-TTA process (Table 1). The results indicate that the *intra*-TTA process within a precisely parallel oriented dimer is beneficial not only in improving the f value but also in lowering the I_{th}. The *intra*-TTA process is particularly promising for solid-state systems with limited molecular diffusion. However, the low photostability of MPD-2 in the solid state is a challenge. The development of high-performance solid-state UC materials based on the *intra*-TTA process remains as an important future task.

In conclusion, a macrocyclic parallel dimer with two DPA units was synthesized, and its optical and TTA-UC properties were evaluated. Single crystal X-ray structure analysis of MPD-2 confirmed the parallel interplanar orientation. MPD-2 showed a higher spin statistical factor (f) and lower threshold excitation light intensity (I_{th}) than the DPA monomer, indicating that the intramolecular TTA process between parallel oriented chromophores could be beneficial for improving the TTA-UC performance. Our results indicate the importance of controlling the orientation between excitons in the TTA process and could provide an improved molecular design for emitters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/prechem.4c00050.

> Experimental procedures and characterization for all compounds; synthetic, spectroscopic, and general methods (PDF)
>
> Crystallographic data for MPD-2 (CIF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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