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Intramolecular versus Intermolecular Triplet Fusion in Multichromophoric Photochemical Upconversion

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ABSTRACT: Photon upconversion is a process that creates high energy photons under low photon-energy excitation. The effect of molecular geometry on the triplet fusion upconversion process has been investigated in this work through the design and synthesis of four new 9,10-diphenylanthracene (DPA) derivatives by employing platinum octaethylporphyrin (PtOEP) as the triplet sensitizer. These new emitter molecules containing multiple DPA subunits linked together via a central benzene core exhibit high fluorescence quantum yields. Interestingly, large differences in the triplet fusion upconversion performance were observed between the derivatives with the *meta*-substituted dimer showing the closest performance to the DPA reference. The differences are discussed in terms of the statistical probability for obtaining a high energy singlet excited state from triplet fusion, *f*, for both inter- and intra-molecular processes, and the effect of magnetic field on the upconversion efficiency. These results demonstrate the challenges to be overcome in improving triplet fusion upconversion efficiency based on multichromophoric emitter systems.

INTRODUCTION

Photon upconversion has the potential to improve current photovoltaic device efficiencies by harvesting sub-bandgap photons. Triplet fusion (TF) upconversion, also known as triplet-triplet annihilation (TTA) upconversion, is a particularly promising process as it requires lower photon flux for efficient conversion compared to two-photon absorption upconversion or annihilation of excited states of rare-earth materials.[1-7] The highest TF upconversion quantum yield reported to date in solution is 38%[8] (the theoretical maximum is 50% as two photons are needed to form one photon with higher energy), 6% in a gel matrix[9], and 0.26% in nanocrystals[10]. Even though there are many instances of high efficiencies being attained under monochromatic radiation, improvements in all aspects for TF upconversion are required to enable successful uptake of this approach in solar harvesting applications, particularly in terms of device integration with existing photovoltaic technology.[11-17]

Before discussing the parameters affecting TF upconversion performance, the mechanism of the TF upconversion process is summarized here. A triplet sensitizer molecule absorbs a low energy photon leading to the formation of its singlet excited state ($^1\text{S} \rightarrow {}^1\text{S}_n^*$), which is quickly converted to the triplet excited state ($^3\text{S}^*$) through intersystem crossing (ISC). The excited sensitizer transfers its energy to an emitter molecule through triplet-triplet energy transfer (TTET), forming a triplet state species ($^3\text{E}^*$) of the emitter molecule. With a sufficiently high triplet population of the emitter molecules, two $^3\text{E}^*$ states can interact to produce one emitter in its ground state (^1E) and one in the singlet excited state ($^1\text{E}^*$). Finally, the excited singlet state decays radiatively, producing a photon of higher energy than those initially absorbed by the sensitizer molecules (Fig. S1).

The TF upconversion quantum yield, Φ_{UC}, is an essential parameter to evaluate the efficiency of TF upconversion performance, which is related to the efficiency of the ISC, TTET, TF and fluorescence processes, as shown in Eqn 1,

$$\Phi_{\text{UC}} = \frac{1}{2} f \Phi_{\text{ISC}} \Phi_{\text{TTET}} \Phi_{\text{TF}} \Phi_{\text{FL}} \qquad (1)$$

where Φ_{ISC}, Φ_{TTET}, Φ_{TF}, Φ_{FL} are the quantum efficiencies of: ISC of the sensitizer, TTET from the sensitizer in its triplet excited state to the emitter, TF between two emitters in their triplet excited states, and the fluorescence of the emitter, respectively. The Φ_{TF} can be considered as the statistical likelihood of each triplet undergoing a triplet-triplet interaction before the triplet state decays. The factor of ½ originates from the stoichiometry of the TF upconversion process in which two excited triplets are required to generate one higher energy singlet excited state, thus the maximum achievable Φ_{UC} is 50%. Lastly, *f* represents the statistical probability of obtaining the emitter singlet state after fusion of two excited triplet states.[18]

Clearly, it is essential to choose triplet sensitizer and emitter molecules that enable the processes described above from an energy cascade perspective. Much work has been reported on developing molecular self-assemblies and supramolecular systems to facilitate the triplet energy transfer and oxygen barrier properties.[19-23] However, fewer studies report new emitter molecules for efficient TF upconversion.[24-28] Two previous studies on DPA dendrimers, oligomers and polymers focused on the demonstration of intramolecular TF upconversion[24-25] while another study investigated tetracene dimers with increasing distance between the tetracenes on TF upconversion performance.[27] In our study, the focus is on examining the influence of molecular geometries on TF upconversion efficiency in multichromophoric emitter molecules. In contrast to the polymeric TF upconversion systems, we aim to investigate the effect of the interaction between two or three individual chromophores on the efficiency of TF upconversion.

There are four main design requirements for the emitter: 1) a triplet excited state lower in energy than the triplet of the sensitizer; 2) a singlet state at just below double the energy of its triplet to make TF energetically favorable; 3) a high Φ_{FL}; and 4) the T_2 state should not be energetically accessible from the triplet fusion event.[1] These requirements can be readily achieved in many emitter molecules. For example, 9,10-diphenylanthracene (DPA) is widely used as the emitter in TF upconversion due to its suitable energy levels and high Φ_{FL}.[29-31] However, the overall efficiency of the TF upconversion process also depends on the TTET, TF efficiencies and *f* value (see Eqn 1).

With this in mind, three dimeric and one trimeric DPA-based molecules were synthesized to probe the effect of chromophore geometry on TF upconversion (Fig. 1). The performance of these multi-chromophore molecules was compared to DPA with platinum octaethylporphyrin (PtOEP) as the triplet sensitizer (Fig. 1). As will be shown, covalently-linked multichromophoric molecules do not always enhance triplet fusion upconversion.[27]

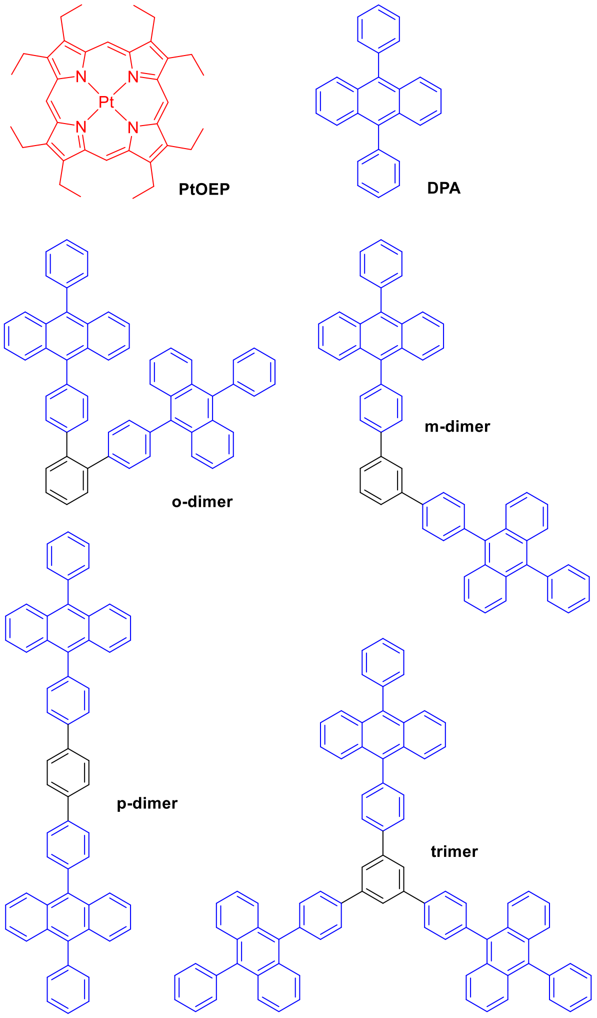

Fig. 1. Chemical structures of PtOEP and DPA derivatives.

EXPERIMENTAL SECTION

Synthesis and sample preparation

The initial synthesis plan for the new DPA derivatives involved Suzuki coupling of 1,2-, 1,3-, 1,4- dibromobenzene and 1,3,5-tribromobenzene with 4,4,5,5- tetramethyl-2-(4-(10-phenyl-anthracen-9-yl))-phenyl-1,3,2-dioxaborolane. However, the boronic acid compound deborylated quickly to 9,10-diphenylanthracene during the reaction leading to very low yields. As a result, the DPA derivatives were synthesized as shown in Fig. 2. First, the di(trimethylsilylphenyl)benzenes (2) were synthesized from dibromobenzenes (1) via Suzuki coupling reaction. These were converted to boronic acid derivatives (3) using BBr_3 followed by Suzuki coupling with 9-bromo-10phenylanthrancene to give the o-, m- and p-dimer target compounds. For the synthesis of the trimer, 1,3,5-tribromobenzene was borylated using palladium-catalyzed Miyaura borylation followed by Suzuki coupling with 9-(4-bromophenyl)-10-phenylanthracene. The synthesis details and general procedures are described in the Supporting Information.

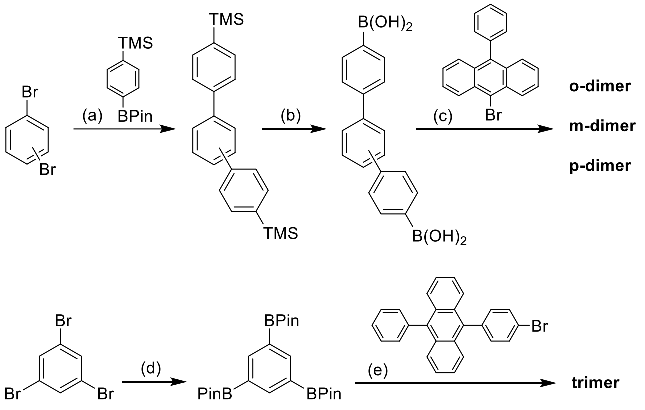

Fig. 2 Synthetic routes for the new DPA derivatives. a, c) 2% Aliquot 336 in toluene, $Pd_2(dba)_3$, P(o-tolyl)$_3$, 2 M K_2CO_3, 90 ˚C, 18 h. b) BB_3, dry DCM, H_2O, rt, 3 h. d) 1,4-dioxane, Pd(dppf)Cl_2, KOAc, 100 ˚C, 20 h. e) 2% Aliquot 336 in toluene, Pd(PPh$_3$)$_4$, 2 M K_2CO_3, 70 ˚C, 32 h.

De-aerated samples in toluene were prepared using three freeze-pump-thaw cycles. The samples of DPA and the new DPA derivatives for TF upconversion measurements contained the same PtOEP (0.01 mM) and DPA subunit (0.6 mM) concentrations. The samples containing PtOEP (0.1 mM) and DPA subunit (0 ~ 2.25 mM) were used for a Stern-Volmer quenching measurement.

Optical measurements

Steady-state absorption and photoluminescence (PL) spectra were recorded on a Cary 50 UV-vis spectrophotometer and Varian Cary Eclipse fluorimeter, respectively. Relative Φ_{FL} values were determined by using DPA as a standard in dilute toluene solution. Stern-Volmer quenching dynamics were investigated in different concentrations of sensitizer and emitter in toluene solution.[26] Fluorescence decay measurements of the emitters were acquired in toluene solutions on a time correlated single photon counting (TCSPC) setup using the frequency doubled output of a mode-locked and cavity dumped Ti:Sapphire laser (Coherent Mira 900F/APE PulseSwitch) with excitation at 390 nm. Triplet decay measurements of the emitters were determined on a nanosecond flash photolysis setup by exciting at 532 nm (Ekspla NT340, operating at 10 Hz) and monitoring at 452 nm. The probe light source was MCWHLP1 Thorlabs broadband LED with DC2200 controller to generate 10ms pulses at 10 Hz, synchronized with the pump laser. The intensity of the transmitted light as a function of time was recorded on a R928 Hamamatsu PMT detector and Tektronix (TDS520) digital storage oscilloscope over 500 averages. TF upconversion performances were measured by exciting with a 532 nm CW laser and spectrally detecting the emission using an Ocean Optics (HR2000) optical fiber-based spectrometer.

Magnetic measurements

The cw upconversion intensity of compositions was measured as a function of magnetic field strength. A sealed cuvette containing the sample was placed in the field of an electromagnet (Magnetech MFG-6-24), and irradiated with a 532 nm diode laser (Thorlabs). The field was calibrated using a gaussmeter (Lakeshore 475 DSP), with the applied current controlled by a Keithley 2230G-30-A power supply. The upconverted photoluminescence was detected using an iCCD spectrograph (Princeton Instruments Pi-Max4/SP-2150). To eliminate systematic errors such as sample-heating effects, the electromagnet current was chosen in a randomized order from a set linearly interpolated between 0 - 1.5A. All measurements were referenced to a recording at 0 A, between each randomly applied current.

RESULTS AND DISCUSSION

Photophysical characterization

The phenylene linker was used to minimize the electronic interaction between the DPA subunits at least in ground state. This was evident in the very similar UV-Vis absorption spectra obtained in toluene solution (6 μM with respect to DPA subunits, Fig. 3). Density functional theory calculations showed expected dihedral angles (between 38° and 85°) between the phenyl and anthracene moieties in the optimized geometry of the molecules (Fig. S13, see SI for calculation details). As a result, the frontier molecular orbitals of the DPA derivatives were localized on the anthracene moieties indicating no intramolecular through-bond electronic interaction between anthracenes. The photoluminescence (PL) spectrum of the dimers and trimer were slightly broadened compared to DPA (Fig. 3). The Φ_{FL} values of the DPA derivatives were determined with DPA as a standard (Φ_{FL} = 1.0).[26] The DPA derivatives all showed slightly lower Φ_{FL} (above 0.9, Table 1) in toluene solution and their fluorescence lifetime were also shorter indicating non-radiative decay pathways from the singlet excited state (Table 1, see Fig. S11 for fluorescence decay curves). The data suggested the DPA subunits in the dimers and trimer were behaving as individual chromophores but the phenylene linker had some effects on excited state dynamics.

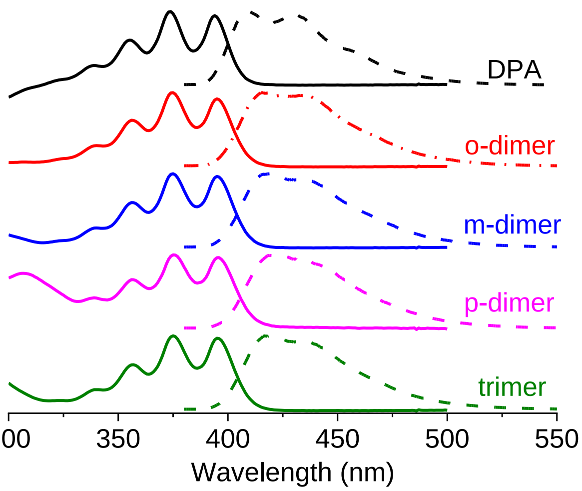

Fig. 3 Normalized absorption (solid traces) and emission (dashed traces) spectra of DPA, o-dimer, m-dimer, p-dimer and trimer in dilute toluene solution.

Table 1 Photophysical properties of **DPA** and **DPA** derivatives

	λ_{abs} [a]	λ_{em} [b]	Φ_{FL} [c]	τ_{FL} [d]	k_{sv} [e]	τ_t [f]	Φ_{UC} [g]	Φ_{TTET} [h]	f_{all} [i]	f_{int} [j]
DPA	373 (13.2)	413	1.0[26]	9.25	2.6	1.14	0.26[32]	0.99	0.52	--
o-dimer	375 (23.6)	420	0.96	5.04	2.7	0.97	0.15	0.99	0.31	0.21
m-dimer	375 (29.8)	420	0.96	6.48	1.1	0.91	0.21	0.98	0.44	0.41
p-dimer	375 (17.7)	420	0.92	4.02	0.2	0.99	0.11	0.91	0.26	0.13
trimer	375 (50.5)	420	0.95	4.75	0.6	1.17	0.09	0.97	0.20	0.11

[a] Wavelength (nm) of maximum absorption in dilute toluene solution (6 μM with respect to the DPA subunit) with molar absorption coefficients, ε ($\times 10^3$ $M^{-1}cm^{-1}$), in brackets. [b] Wavelength (nm) of maximum emission. [c] Fluorescence quantum yield (Φ_{FL}). [d] Fluorescence lifetime (ns). [e] Stern-Volmer quenching constant ($\times 10^9$ $M^{-1}s^{-1}$). [f] Triplet lifetime (ms). [g] TF upconversion quantum yield. [h] TTET quantum yield. [i] Statistical probability for obtaining singlet excited state from both intermolecular and intramolecular triplet fusion (f_{all}). [j] Statistical probability for obtaining singlet excited state from intramolecular triplet fusion (f_{int}).

Triplet fusion upconversion study

To analyze the TTET rate from the sensitizer to the emitter, the phosphorescence of the PtOEP sensitizer was measured with various concentrations of the DPA emitters. Plotting the phosphorescence intensity data in the form of the Stern-Volmer relationship gave the rate of TTET as described in Eqn 2:

$$I_0/I \; = \; 1 \; + \; k_{\mathrm{TTET}} \, \tau_0 \, [\mathrm{E}] = 1 + \; k_{\mathrm{sv}} \, [\mathrm{E}] \tag{2}$$

where I_0 and I are the unquenched and quenched phosphorescence intensities from PtOEP, respectively, k_{TTET} is the triplet energy transfer rate, τ_0 is the lifetime of the unquenched state and [E] is the concentration of the emitter.

The relative TF upconversion quantum yield, Φ_{UC}, was determined by measuring the UC emission intensity compared to the quantum yield of a standard sample, Φ_{std}, using the relation given in the Eqn 3:

$$\Phi_{\mathrm{UC}} \; = \; \Phi_{\mathrm{std}} \frac{A_{\mathrm{std}}}{A_{\mathrm{UC}}} \frac{P_{\mathrm{std}}}{P_{\mathrm{UC}}} \frac{I_{\mathrm{UC}}}{I_{\mathrm{std}}} \frac{\eta_{\mathrm{UC}}^2}{\eta_{\mathrm{std}}^2} \tag{3}$$

where A is the absorbance at the excitation wavelength (532 nm); P is the excitation intensity; I is the integrated intensity of the emission spectrum and η is the refractive index of the medium. "UC" and "std" represent the UC samples and the standard.

The TF upconversion excitation intensity threshold, I_{th}, is another important parameter that is used to judge the TF upconversion performance.[33] The maximum TF upconversion efficiency is achieved above this excitation intensity and generally shows quadratic and linear dependences on the incident intensity in the low- and high- excitation intensity ranges, respectively, and the I_{th} value is experimentally determined as the crossover point of the weak annihilation region and strong annihilation regions, respectively. Materials that show low thresholds are particularly promising for low power TF upconversion applications.[33]

Solutions containing PtOEP (0.01 mM in toluene) as the sensitizer and increasing emitter concentrations were prepared for the Stern-Volmer quenching studies. As shown in Fig. 4a and Table 1, the o-dimer exhibits a similar Stern-Volmer constant (2.7×10^9 M^{-1} s^{-1}) to that of DPA (2.6×10^9 M^{-1} s^{-1}), which is higher than that of the m-dimer and trimer (1.1×10^9 M^{-1} s^{-1} and 0.6×10^9 M^{-1} s^{-1}, respectively). The smallest Stern-Volmer constant was observed for the p-dimer at 0.2×10^9 M^{-1} s^{-1}, indicating reduced triplet energy transfer between PtOEP and the p-dimer. It is important to note that the solubility of the p-dimer was substantially poorer than the other DPA derivatives in toluene and aggregate formation was possible, leading to inhibited diffusion.

Transient absorption kinetics of the DPA derivatives were monitored to determine the triplet lifetimes of the various emitters in toluene by using PtOEP as the sensitizer. (Fig. S10 and Table 1). A long triplet lifetime and a high triplet fusion rate constant are key features of an upconverting system. The samples were excited at 532 nm and the triplet-triplet absorption signal was monitored at 452 nm. The transient decays are shown in Fig. S10 and the lifetimes are summarized in Table 1. In toluene, all the new DPA derivatives show very similar triplet lifetimes with DPA at around 1 ms, which is appropriate for the triplet fusion upconversion process.

The threshold intensity, I_{th}, values for the DPA derivatives were obtained by measuring the TF upconversion emission intensity against varying excitation power density (Fig. S12). The I_{th} values were all in the range of 40 to 100 mW cm^{-2}, which were comparable to reported PtOEP/DPA upconversion systems in solution.[26] These results indicate that all the materials showed triplet fusion upconversion at acceptably low excitation power levels, which is an important consideration for light harvesting applications under terrestrial solar irradiation conditions.

The TF upconversion quantum yield was determined by using the DPA-PtOEP upconversion pair as the standard (Φ_{UC} = 0.26).[32] To compare the TF upconversion performance of the new DPA derivatives, the upconverted emission of samples containing PtOEP (0.01 mM) and the same DPA subunit concentration (0.6 mM) were recorded over a range of excitation intensities (Fig. 4b). The DPA derivatives showed large differences in TF upconversion performance with Φ_{UC} values ranging from 0.09 to 0.21 (as summarized in Table 1). The m-dimer performs the best among the DPA derivatives with a maximum Φ_{UC} of 0.21, which is close to that of DPA (Φ_{UC} = 0.26). The maximum Φ_{UC} of the sample containing the o-dimer and the trimer was close to a half (0.15) and a third (0.09) of the DPA reference (0.26), respectively.

Eqn 1 can be used to interpret the TF upconversion performance in greater detail. The intersystem crossing efficiency Φ_{ISC} was the same for all samples in this study as only PtOEP was used as the sensitizer. The fluorescence quantum yield Φ_{FL} of all DPA derivatives in solution was > 0.9 (Table 1). The triplet-triplet energy transfer efficiency Φ_{TTET} was calculated as shown in Table 1 according to the Stern-Volmer quenching constant. All the values of the Φ_{TTET} for DPA and derivatives are above 0.9, which results in a small impact on the differences of Φ_{UC}. As the excitation power for the maximum TF upconversion efficiency measurement is much higher than the I_{th}, the statistical likelihood of each triplet undergoing a triplet-triplet interaction before the triplet state decays was assumed to be unity. Thus, the variation in the Φ_{UC} value can be mainly attributed to the triplet fusion statistical probability factor, f. This is strongly related to the interactions between the excited-state chromophores. The overall statistical probability f_{all} from both intermolecular and intramolecular TF for DPA and derivatives is shown in Table 1.

When two triplet-excitesd n-mers collide, providing that the exciton is located on one chromophore, there are n^2 possible interchromophore interactions. If the chromophores collide statistically, only one of these collosions results in a possible intermolecular TF event. 2(n-1) collisions can lead to a biexcitonic state via TTET, which then undergoes intramolecular TF, and the remainder of the events are (potentially) excitonically benign. Assuming that the intermolecular TF events have a similar f-value to DPA, we can estimate f_{int} from Eqn 4.

$$f_{all} \; = \frac{1}{2n-1} f_{DPA} + \frac{2n-2}{2n-1} f_{int} \tag{4}$$

The modelled internal statistical probabilities, f_{int}, for intramolecualr TF for the DPA derivatives are listed in Table 1. A clear observation is that all of the f_{int} values are far below f_{DPA}.

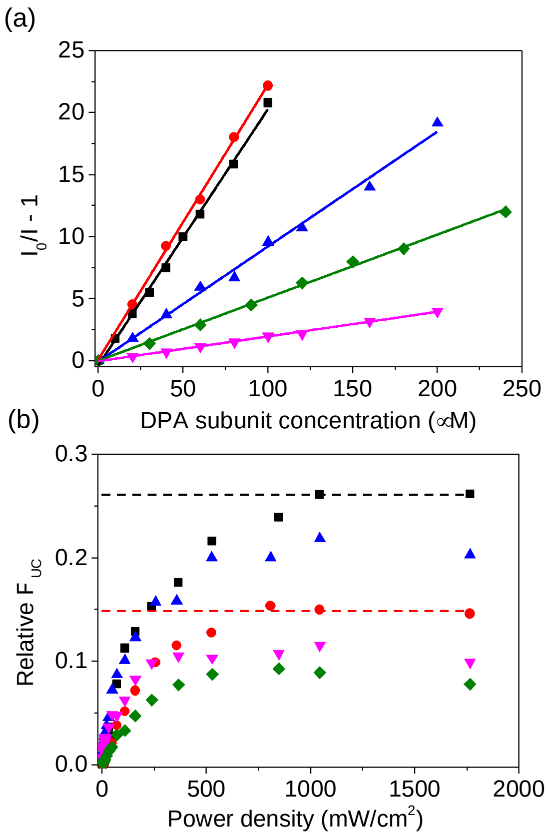

Fig. 4 Stern-Volmer quenching of PtOEP (0.01 mM) in toluene solution (a) and TF upconversion quantum yield as a function of excitation power density at 532 nm in solution ([PtOEP]: 0.01 mM, [DPA]: 0.6 mM, [dimer]: 0.3 mM, [trimer]: 0.2 mM) (b). DPA (■), o-dimer (●), m-dimer (▲), p-dimer (▼), trimer (◆).

In TF upconversion systems, the f value is dependent on the magnetic field which has been confirmed in PtOEP/DPA system.[34-37] The TF rate depends on the distribution of singlet character over the nine spin-states of the interacting triplet-triplet pair. Based on the theory developed by Merrifield[38], a more uniform singlet-character distribution leads to a higher TF rate. In the low-field, weak-exchange-coupling limit, the singlet distributes more uniformly over the pair states, resulting in a faster triplet fusion and thus higher upconverted emission intensity. In the high-field limit, the singlet is only distributed on two triplet pair states ($|00\rangle$ and $[|+-\rangle + |-+\rangle]/\sqrt{2}$), and the upconverted emission intensity decreases.

Fig. 5 shows the effect of magnetic field on upconversion. The magnetic field effect (MFE%) is defined as $\mathrm{MFE\%} = ((I - I_0)/I_0) \times 100\%$, where I and I_0 are the integrated upconverted emission intensities in the presence and absence of the magnetic field, respectively. The MFE% for DPA reaches about −2.0% at 326 mT, which is similar to previous reports.[35, 39] For the dimers, the MFE% reaches approximately −2.8%, −3.2% and −2.6% for o-, m- and p-dimer, respectively.

Of the dimers, the MFE% closest to DPA is that of the p-dimer, which is also the dimer with the highest proportion of upconversion resulting from intermolecular TF events. Likewise, the dimer with the largest proportion of successful intramolecular TF-events is the m-dimer, which shows the largest MFE% of the dimers. This indicates that the intramolecular TF events are more sensitive to the magnetic field. Furthermore, it is expected that the linkage at the *meta* position will result in the weakest exchange-coupling between the triplet states, leading to a larger MFE%. This is because, in the weak-exchange-coupling limit, the intramolecular singlet and quintet states are mixed and the application of a magnetic field has a significant effect on the distribution of singlet character. Conversely, in the strong-exchange-coupling limit the intramolecular singlet character is independent of the magnetic field.

Where the Merrifield model includes a triplet-pair dissociation rate, this should be replaced for intramolecular TF with a competing decay channel to accessible non-S_1 states (e.g. T_2). In the absence of competing channels, the intramolecular TF upconversion should be insensitive to the magnetic fields.

The slight increase in TF upconversion seen in the dimers at very low fields is also observed in molecular crystals. This is a signature of chromophore alignment.[37] That the m-dimer does not exhibit this feature is consistent with the lack of conjugation at the *meta* position. The trimer exhibits a more complex MFE with a minimum of ~–3.0% at approximately 250 mT, rising –2.6% at the highest fields accessible to the present experiments.

One would naïvely expect the trimer to behave in a similar fashion to the m-dimer, but this is not so. Its f_{int} value is the lowest of the oligomers studied, and yet it exhibits the most dramatic MFE. This behavior cannot be accounted for by the Merrifield model and demands detailed study beyond the scope of the present paper.

The present results show that multichromophric emitters are not necessarily better than single chromophores. In a chromophore such as DPA, with $f = 0.52$, a substantial proportion of the TF events do not result in the emissive singlet. However, it is likely that many collisions do not have the required singlet character to generate the S_1 state, and simply dissociate back into free triplets which may then undergo successful triplet fusion. This is the mechanism by which triplet fusion surpasses the spin statistical limit.[40-41] However, in forming a multiexcitonic state on a dimer or trimer, dissociation requires a further collision, which may not occur until many times longer than it takes the prepared state to access a non-emissive channel. This would result in very low f_{int} values, as observed.

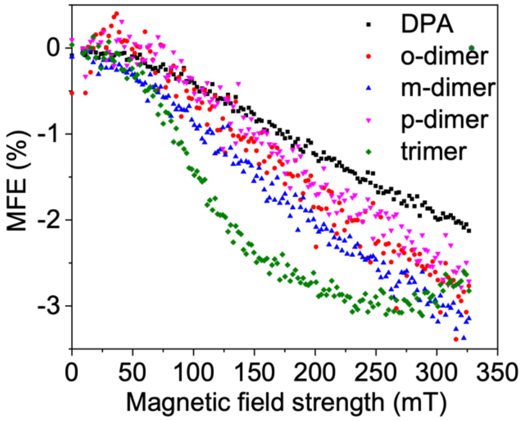

Fig. 5 The variation of the integrated upconverted emission intensity as a function of the magnetic field strength. Excited at 532 nm, [PtOEP]: 0.01 mM, [DPA]: 0.6 mM, [dimer]: 0.3 mM, [trimer]: 0.2 mM.

CONCLUSION

Four new DPA derivatives were synthesized and photophysically characterized. All four were found to exhibit high fluorescence quantum yields and demonstrated triplet fusion upconversion employing PtOEP as the sensitizer. Among the new multichromophore emitters, the m-dimer exhibited the highest Φ_{UC} (0.21), but all were inferior to the benchmark DPA-PtOEP couple. Magnetic field experiments yielded results consistent with intramolecular triplet fusion being less efficient and exhibitng a larger magnetic field effect than intermolecular triplet fusion. These results demonstrate the challenges associated with engineering improved emitter systems for triplet fusion upconversion based on multichromophore arrays.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The Supporting Information file contains detailed synthesis procedures and compound characterization data as well as additional spectroscopic data (docx).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

UC, upconversion; TF, triplet fusion; TTA, triplet-triplet annihilation; ISC, intersystem crossing; TTET, triplet-triplet energy transfer; PL, photoluminescence; DPA, 9,10-diphenylanthracene; PtOEP, platinum octaethylporphyrin; MFE, magnetic field effects.

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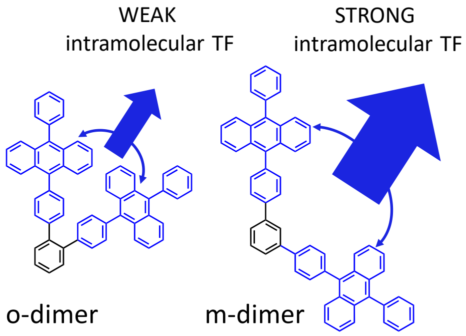
TOC Graphic


WEAK
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