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Enhancing triplet sensitization ability of donor-acceptor dyads *via* intramolecular triplet energy transfer⁺

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Two covalently linked porphyrin palladium (PdPor)-9,10-diphenylanthracene (DPA) donor-acceptor (D-A) systems, connected through 2-position (PdPor-2-DPA) or 9-position (PdPor-9-DPA) of DPA, are prepared as sensitizers of triplet-triplet annihilation upconversion (TTA-UC). The steady-state absorption spectra demonstrate that PdPor and DPA in these compounds are electronically independent in the ground state. Phosphorescence spectra and femtosecond transient absorption spectra reveal that ultrafast intramolecular triplet energy transfer (iTET) from PdPor unit to DPA unit can be conducted in PdPor-9-DPA instead of PdPor-2-DPA. This may be caused by the stronger electronic coupling between PdTPP and DPA in PdPor-9-DPA that is essential for Dexter type triplet energy transfer. In addition, these two dyads are used as triplet energy donor in TTA-UC for sensitizing DPA. The maximum upconversion efficiency for PdPor-9-DPA is about 23.59%, which is much larger than that of PdPor-2-DPA (10.48%). These results confirm that the iTET efficiency would affect the upconversion efficiency when the D-A system is adopted as triplet donor. This provides new insights into designing D-A systems with highly efficient iTET as candidates for triplet energy donor in TTA-UC.

Introduction

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Triplet–triplet annihilation upconversion (TTA-UC) is promising for application in photovoltaics, photocatalysis, and many other light-driven photophysical and photochemical processes due to its low excitation power density demand (solar light is sufficient), high upconversion quantum yield and readily tunable excitation/emission wavelength.^{1,2} TTA-UC is a bimolecular diffusion-controlled process, needs two molecules, a triplet sensitizer and a triplet acceptor.^{3,4} The sensitizer absorbs exciting light and is excited to triplet excited state. Then it transfers excitation energy to the acceptor via triplettriplet energy transfer (TET) and creates triplet excited state of acceptor. When two adjacent excited triplet acceptors annihilate (TTA) via collision and form one acceptor in singlet state and another one in the ground state.^{5,6}

An ideal triplet sensitizer should efficiently absorb visible and near-infrared light, have high triplet state quantum yields (efficient intersystem crossing (ISC)) and long-lived triplet excited states.^{7,8} At the beginning, some molecules, including heavy-metal complexes (Pt(II), Pd(II), Ru(II), Re(I), and Ir(III) substituted dyes and C_{60} derivatives), have been successfully developed as triplet sensitizers.⁴ Recently, bichromophoric triplet sensitizers, composed of covalently linked triplet donoracceptor (D-A) systems, have drawn lots of research interests.9-14 In these systems, triplet donor harvests the excitation energy to generate its singlet excited state, which subsequently converts into its triplet excited state through ISC. Followed by a rapid intramolecular TET (iTET) process, the triplet excited of acceptor is generated.^{9,10,11} Triplet lifetimes of these sensitizers could be prolonged by establishing a tripletstate equilibrium between the triplet states of donor and acceptor or replacing of the short-lived triplet state of donor with long-lived triplet state of acceptor. For example, Zhao's group attached the triplet acceptor pyrene or anthracene to ruthenium(II) polyimine complexes and got the extended triplet lifetime.^{12,13} When these systems were used as triplet sensitizers, the TTA-UC efficiency is promoted approximately 10 times compared with that of the corresponding ruthenium(II) polyimine complexe. Besides the extended triplet lifetime, Ma's group found out that iTET could also effectively out-compete the radiative and nonradiative decays of sensitizer and a dual-path intermolecular TET mechanism was developed.¹⁰ Both the extended triplet lifetime and the dual-path intermolecular mechanism will lead to the improved TTA-UC efficiency. Many other D-A systems have also been designed and showed enhanced sensitization ability.14 Nevertheless, all the TTA-UC systems with an intramolecular

complexes with porphyrin, phthalocyanine, polyimines, and

cyclometalated ligands) and organic dyes (iodo- or bromo-

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triplet sensitization step reported so far involve also intermolecular sensitization process, which normally involve collision of two molecules in solution and affected by the diffusion rate. Because diffusion rate of a molecule in solution depends on its molecular weight and size, therefore, to assess more exactly the advantage of intramolecular sensitization over intermolecular sensitization, two systems with similar molecular weight and dimensions, but different intramolecular sensitization efficiency should be more applicable.

Herein, we designed two porphyrin-anthracene dyads with tetraphenylporphyrin palladium (PdTPP) as the triplet energy donor and 9,10-diphenylanthracene (DPA) as acceptor. According to the literature,¹⁵ the connected position of triplet donor to acceptor has a significant influence on the iTET efficiency between donor and acceptor. So, the PdTPP was introduced onto the 2-position (PdPor-2-DPA) and 9-position (PdPor-9-DPA) of DPA, respectively (Fig. 1). By changing connecting position, the torsion angle, orbital overlap, electronic coupling, and triplet energy transfer between the donor and acceptor can be changed. We found that ultrafast iTET from PdTPP to DPA is conducted in PdPor-9-DPA instead of PdPor-2-DPA. When these two dyads are used as triplet energy donor in TTA-UC for sensitizing DPA, the maximum upconversion efficiency for PdPor-9-DPA is about 23.59%, which is much larger than that for PdPor-2-DPA (10.48%). Because PdPor-9-DPA and PdPor-2-DPA are very similar in molecular weight and molecular dimensions, this difference on upconversion efficiency can be attributed exclusively to the intramolecular sensitization in PdPor-9-DPA. This information should be useful in the design of new TTA-UC systems.

Experimental section

General methods

¹H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with chemical shifts reported in ppm (TMS as an internal standard). MALDI-TOF mass spectra were recorded with a Bruker/ultra flex instrument. Absorption spectra were measured on a Hitachi U-3900 spectrophotometer. Steadystate luminescence spectra were recorded on an Edinburgh FLS980 Instruments with three-monochromator spectrophotometers and three photomultiplier detectors. The emission spectra were corrected for the wavelength dependence of the sensitivity of the detection system. The phosphorescence lifetimes of porphyrins were measured on FLS980 with a microsecond lamp (50 Hz, 100W), and 532 nm (0.46 mJ) was chosen as the excitation wavelength. The phosphorescence quantum yields were measured with an integrating sphere (by using a system for the measurement of absolute fluorescence yield). quantum

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The solvents used for preparing solutions for photophysical measurement were degassed by the Freeze-Pump-Thaw method prior to use. All samples for the photophysical measurements were prepared in a glovebox.

Femtosecond transient absorption spectroscopy

The pump beam was generated from a regenerative amplified Ti:sapphire laser system from Coherent (800 nm, 100 fs, 6 Mj per pulse, and 1 kHz repetition rate). The 800 nm output pulse from the regenerative amplifier was split into two parts with a beam splitter. The reflected part was used to pump a TOPAS Optical Parametric Amplifier (OPA) which generates a wavelength-tunable laser pulse from 250 nm to 2.5 mm as the pump beam. The transmitted 800 nm beam was attenuated with a neutral density filter and focused into a rotating CaF₂ disk to generate a white light continuum (WLC) from 350 nm to 800 nm used for the probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. After the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer and detected at a frequency of 1 kHz. The intensity of the pump pulse used in the experiment was controlled by a variable neutral-density filter wheel. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz. The global analysis of the femtosecond resolved transient absorption (fs-TA) data was conducted in glotaran software.

TTA-UC experiment

The TTA-UC emission spectra were also measured on an Edinburgh Instrument FLS980 with a continuous diode laser (532 nm) as the excitation resource. The diameter of the laser beam was about 3 mm. The solvent used for preparing solutions for the TTA-UC experiment was degassed by the Freeze–Pump–Thaw method prior to use. The sample was prepared in a glovebox. The upconversion quantum yields were determined with rhodamine B as the quantum-yield standard. The absolute fluorescence quantum yield of rhodamine B was determined to be 67.94% by using the integrating sphere. The quantum yields were calculated with eqn (1), $^{\rm 4}$ where ${\cal D}_{\rm UC}$ ${\it A}_{\rm sam}$, ${\it I}_{\rm sam}$ and $\eta_{\rm sam}$ represent the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples and the solvents. The equation is multiplied by a factor of two in order to make the maximum quantum yield be unity.

$$\mathcal{D}_{UC} = 2\mathcal{D}_{std} \left(\frac{A_{std}}{A_{sam}}\right) \left(\frac{I_{sam}}{I_{std}}\right) \left(\frac{\eta_{sam}}{\eta_{std}}\right)^2$$
(1)

The Stern–Volmer curves were obtained based on eqn (2),12 where I_0 , I and [emitter] represent the integrated phosphorescence intensity of pure sensitizer, the integrated phosphorescence intensity of sensitizer in the mixture and the concentration of DPA.

$$I_0/I = 1 + K_{SV}[\text{emitter}]$$
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All commercially obtained reagents/solvents were used as received without further purification unless otherwise noted. Synthetic procedures of PdPor-2-DPA and PdPor-9-DPA are shown in Scheme 1. Both of them were fully characterized by MALDI-TOF mass spectra and ¹H NMR (Fig. S1 and S2, ESI†).^{16,17,18,19}

5-(4-bromophenyl)-10,15,20-triphenylporphrinato palladium(II):

4-Bromobenzaldehyde (1.85 g, 10 mmol) and benzaldehyde (3.20 g, 30 mmol) were dissolved in propanoic acid (20 mL) in a 250 mL flask. After stirring at 138 °C for 10 min, 15 ml propanoic acid including pyrrole (3.35 g, 50 mmol) were added to the solution by dripping slowly within 20 min-30 min. The reaction mixture was continually stirred at 138 °C for 30 min. After cooling, added 200 ml methanol and refrigerate at least 12 hours for recrystallization. The resulting mixture was washed with methanol after filtration. Then purified by column chromatography on silica gel (dichloromethane/hexane =1/1.5) to give the metal free porphyrin (140 mg, 2.2%). A mix of metal free porphyrin and palladium(II) acetate (90 mg, 0.40 mmol) were dissolved in toluene (50 mL) in a 250 mL flask. After reflux for 4 hours, The combined organic extracts were evaporated by rotavapor and purified by column chromatography on silica gel (dichloromethane/hexane =1/2) to give the target compound (145 mg, 82.5%). ¹H NMR (400 MHz, CDCl₃): δ 8.83-8.77 (m, 8H), 8.17-8.15 (d, 6H), 8.05-8.03 (d, 2H), 7.88-7.86 (d, 2H), 7.78-7.71 (m, 9H). MALDI-TOF: m/z: calcd: 798.05 [M]+; found: 798.13 [M]+.

5-(4-boronic acid pinacol ester phenyl)-10,15,20triphenylporphrinato palladium(II):

mixture of 5-(4-bromophenyl)-10,15,20-Α triphenylporphrinato palladium(II) (159.61 mg, 0.2 mmol), bis(pinacolato)diboron (254 mg, 1.0 mmol), PdCl₂(dppf) (14.62 mg, 0.02 mmol) and CH₃COOK (58.8 mg, 0.6 mmol) were dissolved in DMF (15 mL) heated at 80 °C for 5 h under N_2 and then cooled to room temperature, after which 50 mL of distilled water was added to the flask. The product was extracted with dichloromethane, and a solid was obtained upon drying under vacuum. The product was purified by column chromatography on silica gel (dichloromethane/hexane =2/1) to deliver a red solid (75 mg, 44.3%). ¹H NMR (400 MHz, CDCl₃): δ 8.72 (s, 8H), 8.11 (s, 8H), 7.65 (m, 11H), 1.47 (s, 12H). MALDI-TOF: m/z: calcd: 845.12 [M]⁺; found: 845.32 [M]⁺.

PdPor-2-DPA:

A mixture of 5-(4-boronic acid pinacol ester phenyl)-10,15,20triphenylporphrinato palladium(II) (42.2 mg, 0.05 mmol), 2bromo-9,10-diphenyl-anthracene (24.56 mg, 0.06 mmol), Pd(PPh₃)₄ (5.78 mg, 5 μ mol), K₂CO₃ (0.5 mL, 138 mg, 1.0 mmol), and nitrogen-saturated toluene/ethanol (15 mL/7.5 mL) were mixed in a flask. The reaction mixture was heated at 80 °C for 4 h under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with distilled water. The



Scheme 1. The synthesis of PdPor-2-DPA and PdPor-9-DPA

product was extracted with dichloromethane, and a solid was obtained upon drying under vacuum, and successfully purified by column chromatography using (dichloromethane/hexane =4/5) as the eluent, and the isolate was recrystallized from hexane to give PdPor-2-DPA as a orange powder (20 mg, 38.0%). ¹H NMR (400 MHz, CDCl₃): δ 8.89-8.87 (d, 2H), 8.81 (s, 6H), 8.24 (s, 1H), 8.21 (s, 1H), 8.18-8.16 (d, 6H), 7.94-7.92 (d, 4H), 7.77-7.71 (m, 11H), 7.70-7.66 (m, 5H), 7.64-7.59 (m, 5H), 7.40-7.37 (m, 3H). C₇₀H₄₄N₄Pd, MALDI-TOF: m/z:, calcd: 1046.26 [M]⁺; found: 1045.29 [M]⁺.

PdPor-9-DPA:

A mixture of 5-(4-boronic acid pinacol ester phenyl)-10,15,20triphenylporphrinato palladium(II) (42.2 mg, 0.05 mmol), 9bromo-10-phenyl-anthracene (19.92 mg, 0.06 mmol), Pd(PPh₃)₄ (5.78 mg, 5 µmol), K₂CO₃ (0.5 mL, 138 mg, 1.0 mmol), and nitrogen-saturated toluene/ethanol (15 mL/7.5 mL) were mixed in a flask. The reaction mixture was heated at 80 °C for 4 h under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with distilled water and extracted with dichloromethane. The product was extracted with dichloromethane, and a solid was obtained upon drying under vacuum, and successfully purified by column chromatography using (dichloromethane/hexane =4/5) as the eluent, and the isolate was recrystallized from hexane to give PdPor-2-DPA as a orange powder (9 mg, 18.5%). ¹H NMR (400 MHz, CDCl₃): δ 9.11-9.09 (d, 2H), 8.94-8.93 (d, 2H), 8.85-8.83 (m, 4H), 8.44-8.42 (d, 2H), 8.23-8.18(m, 6H), 8.16-8.14(d, 2H), 7.87-7.82(d, 2H), 7.80-7.75 (m, 9H), 7.68-7.65(m, 3H), 7.62-7.55(m, 5H), 7.44-8.48(m, 3H). C₆₄H₄₀N₄Pd, MALDI-TOF: m/z: calcd: 970.23 [M]+; found: 969.62 [M]+.

Result and discussion

Design and Synthesis of Compounds

TET process includes a triplet state energy donor and a triplet state energy acceptor.²⁰ In this work, we choose 9,10diphenylanthracene (DPA) as the triplet state energy acceptor because of its high fluorescence quantum yield.⁴ Furthermore, 5,10,15,20-tetraphenylporphyrin (PdTPP) is used as the triplet energy donor due to its easy synthesis and molecular modification, near unity intersystem crossing efficiency (ISC) and proper triplet state energy (1.78 *eV*) with respect to that of DPA (1.77 *eV*).^{21,22} PdTPP was attached to the 2- or 9position of DPA (Fig. 1, PdPor-2-DPA and PdPor-9-DPA). By

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changing connecting position and the torsion angle, orbital overlap and electronic coupling between the donor and acceptor are changed. As a result, the iTET rate and efficiency will be altered.

The synthetic route is shown in Scheme 1. 5-(4-bromophenyl)-10,15,20-triphenylporphrinato palladium(II) was synthesized following the standard method of Alder and Longoby.¹⁶ Then 5-(4-boronic acid pinacol ester phenyl)-10,15,20triphenylporphrinato palladium(II) was prepared according to the previous report.^{17,18} At last, under the Suzuki coupling protocol,²³ 5-(4-boronic acid pinacol ester phenyl)-10,15,20triphenylporphrinato palladium(II) reacted with 2-bromo-9,10diphenyl-anthracene or 9-bromo-10-phenyl-anthracene to get PdPor-2-DPA or PdPor-9-DPA. These two compounds are highly soluble in conventional organic solvents, which can effectively avoid molecular aggregation in solution and allow us to study the single molecule photophysical properties of them.

Minimized molecular structure

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The minimized molecular structures of PdPor-2-DPA and PdPor-9-DPA are calculated at the B3LYP/GENECP/LANL2DZ level using Gaussian 09W and shown in Fig. 2.24,25 As shown in Fig. 2, the center-to-center distances between DPA and PdPor in PdPor-2-DPA and PdPor-9-DPA are 12.92 Å and 10.72 Å, respectively. The different connection position did not significantly change the center-to-center distance between DPA and PdPor unit in these two compounds. However, the dihedral angle between the DPA ring and porphyrin ring in these two compounds is obviously different. The DPA ring is nearly perpendicular to the porphyrin ring with a dihedral angle of 74.47° in PdPor-2-DPA. Instead, the dihedral angle in PdPor-9-DPA is only 29.66° (side view). It has been widely recognized that a small interplanar dihedral angle between adjacent units will bring a large molecular orbital overlap and electronic coupling.^{26,27} In other words, the molecular orbital overlap between DPA and PdPor unit in PdPor-9-DPA is larger than that in PdPor-2-DPA.

UV-vis absorption and luminescence emission spectra

The UV–vis absorption spectra of PdPor-2-DPA, PdPor-9-DPA and their monomeric model compounds (PdTPP and DPA) were measured and shown in Fig. 3A. As shown in Fig. 3A, two main absorption bands centered at 417 and 524 nm are observed in the absorption spectra of PdPor-2-DPA and PdPor-9-DPA, which match well with that of PdTPP and can be assigned to the Soret band and B band of palladium porphyrin, respectively.²⁸ Besides those bands, three weak absorption bands located at 338, 356 and 374 nm can be identified in the enlarged spectra (the inset of Fig. 3A), which can be attributed to the absorption of DPA.²² More importantly, the absorption spectrum of PdPor-2-DPA or PdPor-9-DPA is nearly identical to the sum of the absorption spectra of PdTPP and DPA (Fig. S3, ESI†), suggesting no electronic coupling between PdTPP and DPA at the ground state.



Fig. 2 The minimized molecular structures of PdPor-2-DPA (A) and PdPor-9-DPA (B). α_1 and α_2 are the dihedral angle between the porphyrin unit and DPA unit

To study iTET process from PdTPP to DPA unit in these two dyads, we selectively excite the PdTPP part of PdPor-2-DPA or PdPor-9-DPA with a 532 nm excitation light. As shown in Fig. 3B, two main emission bands located at 697 and 772 nm are observed for both PdPor-2-DPA and PdPor-9-DPA in deaerated toluene, which can be ascribed to the phosphorescence of PdTPP unit following the literature.²¹ This assignment is also supported by the significant quenching of these two bands in aerated toluene (Fig. S4, ESI⁺). Moreover, a weak luminescence band centered at 610 nm is also detected for PdTPP, PdPor-2-DPA and PdPor-9-DPA in deaerated toluene. This band remains unchanged in aerated toluene, which indicates that this band is the fluorescence of PdTPP.²¹ Notably, the phosphorescence quantum yields of PdTPP (0.41±0.05%), PdPor-2-DPA (0.26±0.03%) and PdPor-9-DPA (0.23±0.03%) are extremely low (Table S1, ESI⁺), which indicates that the decay of the triplet excited state of these three compounds is mainly caused by the nonradiative transition, but not the radiative phosphorescence emission. Interestingly, the intensities of phosphorescence bands centered at 697 and 772 nm of PdPor-2-DPA and PdPor-9-DPA are obviously decreased compared to the intensity of phosphorescence band of PdTPP in the same (1.0×10⁻⁵ M). concentration Furthermore. the phosphorescence quantum yields of PdPor-2-DPA and PdPor-9-DPA decrease a lot in comparison with that of PdTPP. This may be attributed to the increased nonradiative transition caused by the more flexible molecular structure after linking of DPA.^{31,32,33} In addition, the phosphorescence intensity of PdPor-9-DPA decreases slightly compared to that of PdPor-2-DPA, as well as the decreased phosphorescence quantum yield of PdPor-9-DPA, which may be caused by the extra iTET process from PdTPP unit to DPA unit in PdPor-9-DPA.^{29,30} In addition, the phosphorescence quantum yield of PdTPP measured by us is identical to the previous report,²¹ which suggests that our measurement is reliable.

Furthermore, the phosphorescence dynamics of PdPor-2-DPA and PdPor-9-DPA at 293 K (Fig. 3C) were also determined and the fitting results were shown in Table S1 (ESI⁺). We can see that the phosphorescence of PdPor-2-DPA and PdPor-9-

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Fig. 3 (A) Absorption spectra of PdPor-2-DPA, PdPor-9-DPA, PdTPP and DPA in toluene. (B, C) Phosphorescence spectra (B) and dynamics (C) of PdPor-2-DPA, PdPor-9-DPA and PdTPP in deaerated toluene (λ_{ex} = 532 nm, c = 1.0×10⁻⁵ M, 293K).

DPA decay faster than that of PdTPP, which agrees with the decrease on phosphorescence intensity as shown in Fig. 3B.

Femtosecond transient absorption spectra

In order to reveal the iTET process within PdPor-2-DPA and PdPor-9-DPA, femtosecond transient absorption (fs-TA) spectra of these two compounds were measured in deaerated toluene with the excitation at 532 nm (150 nJ) (Fig. 4). Only PdTPP unit in these two dyads can be excited with the 532 nm excitation. The photo-induced bleach (PIB) bands were observed at 417 and 525 nm in the fs-TA spectra of both PdPor-2-DPA and PdPor-9-DPA immediately after photoexcitation, which is close to the ground-state absorption peaks of PdTPP unit (Fig. 3A). So these two PIB bands can be assigned to the ground state bleach (GSB) of PdTPP unit. Moreover, a broad photoinduced absorption (PIA) band ranged from 430 nm to 520 nm was found and can be attributed to the excited-state absorption (ESA) of singlet state of PdTPP derivatives.³⁴ With the delay of the time, the intensity of the ESA band centered at 450 nm decreased slightly, meanwhile the intensity of the ESA band located at 480 nm increased in the fs-TA spectra of these two dyads. From the single-wavelength dynamics of 450 and 480 nm (Fig. 4C-D), we can see that this process is completed in 10 ps. Moreover, this conversion can also be seen in PdTPP (Fig. S5, ESI⁺)) and the lifetime of the ESA band centered at 480 nm can reach to microsecond range (Fig. S6, ESI⁺). This ESA band with long lifetime should be assigned to the triplet state of PdTPP according to the previous report.34,35 So this fast process should be intersystem crossing (ISC).

After ISC, a significant difference can be seen in the *fs*-TA spectra of these two dyads. The intensity of the GSB band at 417 nm and the ESA band at 480 nm in PdPor-9-DPA have a huge decrease after 10 ps (Fig. 4B). However, the TA spectrum of PdPor-2-DPA keeps almost unchanged and no obvious decay is observed after 10 ps (Fig. 4A), which is similar to that of PdTPP (Fig. S5A, ESI⁺). This huge discrepancy can also be clearly seen from the single-wavelength dynamics probed at 417 and 480 nm of PdPor-9-DPA, PdPor-2-DPA and PdTPP (Fig. 4E and 4F). The dynamics of PdPor-9-DPA probed at 417 and

480 nm shows a fast decay (<100 ps). Nevertheless, no distinct decay is detected in the dynamics of PdPor-2-DPA and PdTPP probed at 417 and 480 nm. This suggests the presence of extra process that quenches the triplet state of PdTPP unit in PdPor-9-DPA, but not in PdPor-2-DPA. Based on the previous report,^{29,30,36} TET process can be proceeded from PdTPP to DPA. So the extra process in PdPor-9-DPA should be iTET from PdTPP unit to DPA unit. Unfortunately, we cannot distinguish the signal of the triplet state of DPA unit due to the spectral overlap between the triplet state of PdTPP and DPA.^{35,37} Furthermore, due to the molar extinction coefficient of GSB and ESA bands of PdTPP are much larger than those of the



Fig. 4 (A, B) *fs*-TA spectra of PdPor-2-DPA (A) and PdPor-9-DPA (B). (C, D) Single-wavelength dynamics probed at 450 and 480 nm of PdPor-2-DPA (C) and PdPor-9-DPA (D). (E, F) Normalized single-wavelength dynamics of PdPor-2-DPA and PdPor-9-DPA probed at 417 nm (E) and 480 nm (F). λ_{ex} = 532 nm, c = 2.0×10⁻⁵ M in deaerated toluene, 293K.

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Fig. 5 Species-associated spectra and population dynamics of PdPor-2-DPA (A, D), PdPor-9-DPA (B, E) and PdTPP (C, F) obtained from global analysis.

signals of DPA unit, the GSB and ESA peaks of DPA cannot be identfied.35,37 This fast iTET process would quench the phosphorescence of PdTPP unit in PdPor-9-DPA, which is consistent with the reduced lifetimes and quantum yield compared to those of PdTPP (Fig. 3B). However, due to the absence of iTET process in PdPor-2-DPA, the quenching of the phosphorescence of PdTPP unit in PdPor-2-DPA should be mainly caused by the flexible molecular structure after linking DPA, which results in the increasing on non-radiation transitions.³¹⁻³³ Notably, the GSB band of PdTPP unit centered at 417 nm show certain intensity after a very long time delay (5 ns), even after the end of iTET process in PdPor-9-DPA (Fig. 4B), suggesting that a triplet-state equilibrium between PdTPP unit and DPA unit may be established. This is reasonable because of the similar triplet energy between PdTPP and DPA (1.78 eV for PdTPP and 1.77 eV for DPA).^{21,22} As revealed by the minimized molecular structure, the orbital overlap in PdPor-9-DPA is larger than that in PdPor-2-DPA. In addition, the 9-position of anthracene is more active to exchange charge compared to 2-position anthracene. Both these two factors lead to a stronger electronic coupling in PdPor-9-DPA, which is necessary for efficient Dexter-based TET process.^{38,39,40} As a result, PdPor-9-DPA shows an efficient iTET process instead of PdPor-2-DPA.^{41,42,40} This is similar with the observation by Tang group in which TET process between CdSe nanocrystal and 9position substituted anthracene is more efficient in comparison with those in 1-position and 2-position anthracene.15

Next, we used global analysis to decompose the *fs*-TA data of PdPor-2-DPA, PdPor-9-DPA and PdTPP with the help of Glotaran software.⁴³ Based on the above discussion, a sequential three-species model ($S_1(PdPor^{1*}-DPA) \rightarrow T_1(PdPor^{3*}-DPA) \rightarrow T_1(PdPor^{3*})$) was adopted in the deconvolution of

the fs-TA spectra of PdPor-9-DPA. As for PdPor-2-DPA and model PdTPP, sequential two-species (S₁(PdPor^{1*}-DPA) \rightarrow T₁(PdPor^{3*}-DPA) and S₁(PdTPP^{1*}) \rightarrow T₁(PdTPP^{3*})) was employed. The obtained spectra and dynamics of each population were shown in Fig. 5. The fitting result agrees very well with the raw data (Fig. S7-S9, ESI+), which confirms our deconvolution method is reliable. As shown in Fig. 5, the spectral signature of the first state in these three compounds resembles the typical singlet (S1) state absorption of PdPor, with a board absorption band at 430 nm to 520 nm.^{35,37} So we ascribed the first state to the S1 state of PdPor unit. The second state in these three compounds shows an enhanced absorption band at 480 nm compared with that of the S_1 state. This change is ascribed to the formation of the triplet state (T_1) of PdPor.³⁷ The spectrum of the third component in PdPor-9-DPA has an enhanced absorption at 450 nm with respect to that of the second state (Fig. 5B), which may be caused by the T_1 state of DPA with a main absorption band at about 450 nm.³⁵ But the GSB of the PdPor unit is also resolved and so we ascribe the third state to the triplet equilibrium state between PdPor unit and DPA unit.^{10,11}

In addition, from the population dynamics of these three compounds, we can see that the S₁ state decays rapidly with a time constant of about ~ 10 ps (Fig. 5D-5F), accompanied by a rise of the T₁ state of PdPor unit. This is consistent with the ISC rate of PdTPP in the previous report,³⁷ suggesting the reliability of our deconvolution method. As for PdPor-9-DPA, the T₁ state of DPA unit is generated within 36.05±0.11 ps from the T₁ state of PdPor unit (Fig. 5E).

Triplet-triplet annihilation upconversion (TTA-UC)

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We first measured the emission spectra of PdPor-2-DPA or PdPor-9-DPA without adding free DPA molecules (Fig. S10, ESI†), but no DPA fluorescence was observed no matter what concentration of PdPor-2-DPA or PdPor-9-DPA was used. This phenomenon is also observed in other covalently linked photosensitizer-acceptor systems in which the ultrafast intramolecular re-absorption of photosensitizer to the acceptor emission.^{9,11} As for PdPor-2-DPA or PdPor-9-DPA, we can see that the fluorescence spectrum of DPA overlaps significantly with the absorption spectrum of PdTPP (Fig. S11, ESI†). So the reason for no DPA emission in PdPor-2-DPA and PdPor-9-DPA may be also the intramolecular re-absorption of PdTPP to the DPA emission.

According to the previous report,^{9,44,45} this re-absorption effect can be suppressed effectively by changing intramolecular process into intermolecular process. So we added extra free DPA molecules into PdPor-2-DPA or PdPor-9-DPA solution and observed an emission band ranged from 400 nm to 500 nm when a 532 nm laser was used as excitation light (Fig. 6). However, this emission was not detected when only DPA was presented in the solution with the same excitation wavelength (Fig. S11, ESI⁺). Furthermore, the shape of the emission spectrum is consistent with that of DPA after subtracting the strong absorption of Soret band (417 nm) of PdTPP (Fig. S11, ESI⁺).²² These results indicate that the emission from 400 nm to 500 nm is originated from TTA-UC.

As shown in Fig. 6, the intensity of the UC fluorescence is enhanced as the concentration of DPA increases, meanwhile the phosphorescence of PdTPP unit decreases. This suggests the existence of an efficient intermolecular TET from PdPor-2-DPA or PdPor-9-DPA or PdTPP to DPA. In order to quantitatively study the TET process, the phosphorescence intensity of PdPor-2-DPA or PdPor-9-DPA or PdTPP was measured as a function of the concentration of DPA at a constant PdPor-2-DPA or PdPor-9-DPA or PdTPP concentration and then the Stern-Volmer curves were obtained (Fig. 7A).¹² The Stern–Volmer quenching constant of PdTPP (K_{SV}= 1.26×10^{5} M⁻¹) is 1.5 times that of PdPor-2-DPA (K_{SV}= 8.26×10^{4} M⁻¹) and nearly three times that of PdPor-9-DPA (K_{SV}= 4.67×10^{4} M⁻¹), which indicates that the TET process from PdTPP to DPA is more efficient compared to those from the PdPor unit in PdPor-2-DPA or PdPor-9-DPA to DPA. As we known, the Dexter-based intermolecular TET is diffusion controlled process^{46,47} and the full process can be formally described as a direct collision between a triplet donor and an acceptor. In such a case, the TET rate (K_{TET}) is proportional to diffusion coefficient (D) according to the previous report⁴⁷ (K_{TET} = $4DR_0C_A$). Furthermore, diffusion coefficient (D) is inversely proportional to the molecular radii (R_m) ($D=3kT/6\pi\eta R_m$).⁴⁷ Thus, PdTPP with smaller radii should have a faster and more efficient TET with respect to those of PdPor-2-DPA and PdPor-9-DPA. However, the TET efficiency in PdPor-2-DPA and PdPor-9-DPA should be the same if only above factors are considered. Surprisingly, the Stern–Volmer quenching constant of PdPor-2-DPA is much larger than that of PdPor-9-DPA. This is because that the diffusion controlled intermolecular TET from the PdPor unit in PdPor-9-DPA to free DPA cannot compete with the fast iTET process (36.05±0.11 ps) in PdPor-9-DPA. So the phosphorescence quenching of PdPor unit in PdPor-9-DPA is mainly due to the iTET process. Instead, the intermolecular TET process is the main quenching pathway for the phosphorescence of PdPor unit in PdPor-2-DPA due to the absence of iTET process. This leads to a smaller Stern–Volmer quenching constant for PdPor-9-DPA with respect to PdPor-2-DPA.



Fig. 7 (A) Stern-Volmer plots for phosphorescence quenching of the PdPor unit in the mixture of PdPor-2-DPA, PdPor-9-DPA or PdTPP and DPA. (B) Dependence of the upconversion quantum yield (Φ_{uc}) on the concentration of DPA at a constant PdPor-2-DPA, PdPor-9-DPA or PdTPP concentration (10⁻⁵ M) in toluene with 532 nm laser excitation (25 mW).

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Next, the upconversion quantum yields (Φ_{UC}) were calculated and shown in Fig. 7B. The highest ${\cal P}_{\rm UC}$ values of PdPor-2-DPA, PdPor-9-DPA and PdTPP are 10.48%, 23.59% and 23.56%, respectively. The highest Φ_{UC} value of PdTPP is more than two times larger than that of PdPor-2-DPA, which is consistent with the larger K_{SV} value of PdTPP compared with that of PdPor-2-DPA. However, the highest ϕ_{UC} value of PdPor-9-DPA is much larger than that of PdPor-2-DPA even though PdPor-9-DPA has a smaller $K_{\mbox{\scriptsize SV}}.$ When PdPor-2-DPA was used as donor, the upconversion fluorescence can only be generated by the collision between two free DPA triplets (DPA^{3*}) intermolecularly sensitized by PdPor unit (PdPor^{3*}-2-DPA) of PdPor-2-DPA. However, in PdPor-9-DPA, the upconversion fluorescence can be produced not only by the collision between two free DPA3* intermolecularly sensitized by PdPor unit (PdPor^{3*}-9-DPA) of PdPor-9-DPA, but also by the collision between the DPA triplet (PdPor-9-DPA^{3*}) of PdPor-9-DPA and the free DPA^{3*} intermolecularly sensitized by PdPor^{3*}-9-DPA.¹⁰ Therefore, the upconversion efficiency of PdPor-9-DPA is higher than that of PdPor-2-DPA. If the collision between PdPor-9-DPA^{3*} and the free DPA^{3*} is not efficient, TTA-UC efficiency of PdPor-2-DPA should be close to that of PdPor-9-DPA due to the same diffusion rate induced by their same dimension and weight. In addition, it is notable that the TTA-UC efficiency of PdPor-9-DPA is lower than that of PdTPP in low concentration of DPA (10⁻⁵ M-10⁻⁴ M) while close to that of PdTPP at high DPA concentration (> 2×10^{-4} M). Due to the presence of the triplet state equilibrium between the PdPor unit and the DPA unit, PdPor^{3*}-9-DPA and PdPor-9-DPA^{3*} can both be formed in PdPor-9-DPA after photoexcitation. At low DPA concentration, the TTA-UC efficiency is determined by the diffusion controlled TET from PdPor3*-9-DPA to free DPA and/or the collision between PdPor-9-DPA^{3*} and free DPA^{3*}. However, no matter PdPor^{3*}-9-DPA or PdPor-9-DPA^{3*}, its diffusion rate is slower significantly than that of PdTPP due to the larger molecular dimension and weight of PdPor-9-DPA. Therefore, PdPor-9-DPA shows a lower TTA-UC efficiency with respect to that of PdTPP at low DPA concentration. When the DPA concentration increases significantly, the surrounding of the sensitizer (PdPor^{3*}-9-DPA or PdTPP^{3*}) is filled with many DPA molecules, the diffusion controlled TET is no longer the rate-limiting step for the TTA-UC process. So PdPor-9-DPA and PdTPP exhibit a similar TTA-UC efficiency. In other words, the diffusion controlled intermolecular TET plays an important role in TTA-UC process at low acceptor concentration. However, this diffusion limiting effect can be abated at the region of high acceptor concentration. Similar phenomenon was also found in the previous reports.^{14, 48}

Conclusions

In summary, two covalently linked PdPor-DPA systems, connected through 2-position (PdPor-2-DPA) or 9-position (PdPor-9-DPA) of DPA unit, have been prepared as triplet sensitizers of TTA-UC. A fast intramolecular triplet energy transfer from PdTPP unit to DPA unit can be conducted in PdPor-9-DPA instead of PdPor-2-DPA, which may be attributed

to the stronger electronic coupling between DPAevanderPelPer units within PdPor-9-DPA. When these two ଶ୍ୱିଏଥିଡ଼ି କଳି ଘରିହେଁ ଶିର୍ triplet energy donor in TTA-UC for sensitizing free DPA, the maximum upconversion efficiency of PdPor-9-DPA (23.59%) is about two times larger than that of PdPor-2-DPA (10.48%). This is most likely due to the extra triplet-triplet annihilation pathway existing in PdPor-9-DPA by the collision between the PdPor-9-DPA^{3*} and the free DPA^{3*} except for the collision between the two free DPA^{3*} as like in PdPor-2-DPA. These results confirm that the iTET process in covalently linked D-A systems can be controlled by changing the relative orientation and linked position between the donor and acceptor. This provides new insights into designing D-A systems with highly efficient iTET as candidates for triplet donor in TTA-UC. In addition, intramolecular TET in D-A dyads is more rapid and more efficient in comparison with intermolecular TET so that it can effectively compete and inhibit the radiative and nonradiative decays of the triplet excited states of donor moiety. However, due to the increased molecular dimension when connecting the donor to the acceptor, the diffusion rate of the D-A dyad will be inevitably reduced in solution. Therefore, the advantage of intramolecular TET in TTA-UC might be demonstrated more clearly in energy migration mechanism in solid state instead of the molecular diffusion mechanism in solution.

Conflicts of interest

There are no conflicts to declare.

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Enhancing triplet sensitization ability of donor-acceptor dyads via intramolecular triplet energy transfer

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Efficient intramolecular triplet-triplet energy transfer is beneficial for improving upconversion efficiency when the donoracceptor system is adopted as triplet donor. Journal of Materials Chemistry C Accepted Manuscript