ChemPubSoc Europe
DOI: 10.1002/chem.201504498
CHEMISTRY
A European Journal
Full Paper

Photosensitizers

Pd–Porphyrin Oligomers Sensitized for Green-to-Blue Photon Upconversion: The More the Better?

Zhiqing Xun,[a] Yi Zeng,*[a] Jinping Chen,[a] Tianjun Yu,[a] Xiaohui Zhang,[a] Guoqiang Yang,[b] and Yi Li*[a]

Abstract: A series of directly *meso-meso*-linked Pd–porphyrin oligomers (PdDTP-M, PdDTP-D, and PdDTP-T) have been prepared. The absorption region and the light-harvesting ability of the Pd–porphyrin oligomers are broadened and enhanced by increasing the number of Pd–porphyrin units. Triplet–triplet annihilation upconversion (TTA-UC) systems were constructed by utilizing the Pd–porphyrin oligomers as the sensitizer and 9,10-diphenylanthracene (DPA) as the acceptor in deaerated toluene and green-to-blue photon upconversion was observed upon excitation with a 532 nm laser. The triplet–triplet annihilation upconversion quantum efficiencies were found to be 6.2 %, 10.5 %, and 1.6 % for the [PdDTP-M]/DPA, [PdDTP-D]/DPA, and [PdDTP-T]/DPA systems, respectively, under an excitation power density of 500 $mW\,cm^{-2}$. The photophysical processes of the TTA-UC systems have been investigated in detail. The higher triplet–triplet annihilation upconversion quantum efficiency observed in the [PdDTP-D]/DPA system can be rationalized by the enhanced light-harvesting ability of PdDTP-D at 532 nm. Under the same experimental conditions, the [PdDTP-D]/DPA system produces more ^{3}DPA* than the other two TTA-UC systems, benefiting the triplet–triplet annihilation process. This work provides a useful way to develop efficient TTA-UC systems with broad spectral response by using Pd–porphyrin oligomers as sensitizers.

Introduction

Photon upconversion, which refers to converting photons of lower energy to those of higher energy, has attracted much attention because of its potential applications in photovoltaics,[1,2] bioimaging,[3,4] displays,[5,6] and photodynamic therapy (PDT).[7,8] Triplet–triplet annihilation upconversion (TTA-UC) has been at the forefront of upconversion in recent years,[9,10] because TTA-UC can take place upon excitation with low-intensity, noncoherent light sources and the upconversion emission wavelengths can be simply tuned by molecular tailoring. TTA-UC involves a bimolecular system consisting of sensitizers and acceptors. Acceptors, also known as emitters, give upconverted and delayed fluorescence through triplet–triplet annihilation, in which two triplet acceptors diffuse and meet within their lifetime, and this effective encounter produces a ground-state singlet and an excited singlet. The radiative transition from the excited singlet acceptor gives delayed fluorescence, achieving photon upconversion. However, given that the transition from ground state to triplet state is spin forbidden, absorption coefficients are too small to generate the triplet state of the acceptor by direct excitation. The triplet state of acceptor is obtained through photosensitization, an indirect method of excitation, by electronic energy transfer from triplet sensitizers, which absorb low energy photons. Therefore, the TTA-UC efficiency is affected not only by the TTA processes and fluorescence quantum yield of acceptors, but also by the triplet production and the triplet–triplet energy transfer, which are deeply dependent on the properties of the triplet sensitizers, such as the light-harvesting ability, the efficiency of intersystem crossing, and the lifetime of the triplet states.

Many contributions to TTA-UC systems are made through the modification of the sensitizers,[11,12] including increasing the light-harvesting ability, the intersystem crossing efficiency, and the lifetime of the triplet states. Pt^{II}, Ir^{III}, Ru^{II}, and Re^{II} complexes are commonly used triplet sensitizers because the intersystem crossing efficiencies of these complexes are nearly 1. However, their absorptions are in the relatively short wavelength region with low molar absorption coefficients (ε) and the lifetimes of their triplet excited states are not very long (usually a few microseconds or shorter), which limit the application of these sensitizers in TTA-UC systems. A strategy for improving the photophysical characteristics of these metal complex sensitizers has been reported that introduces conjugated chromophores such as BODIPY, perylenediimide, and coumarin to the complexation ligands. The triplet states of these sensitizers

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[a] Dr. Z. Xun, Dr. Y. Zeng, Dr. J. Chen, Dr. T. Yu, Dr. X. Zhang, Prof. Dr. Y. Li
Key Laboratory of Photochemical Conversion and Optoelectronic Materials
Technical Institute of Physics and Chemistry, Chinese Academy of Sciences
University of Chinese Academy of Sciences, Beijing 100190 (P.R. China)
E-mail: zengyi@mail.ipc.ac.cn
yili@mail.ipc.ac.cn

[b] Prof. Dr. G. Yang
Beijing National Laboratory for Molecular Sciences (BNLMS)
Key Laboratory of Photochemistry
Institute of Chemistry, Chinese Academy of Sciences
University of Chinese Academy of Sciences, Beijing 100190 (P.R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504498.

thus change from the metal-to-ligand charge-transfer (^{3}MLCT) excited states to the ligand-localized/intraligand (^{3}IL) excited states, resulting in prolonged lifetimes of the triplet state. Furthermore, the absorptions of these complexes were extended into the visible region with high molar extinction coefficients. Modification of these complexes used in TTA-UC systems as sensitizers effectively enhances the upconversion efficiencies.[13–16]

Porphyrin complexes with heavy metal complexation or heavy atom substitution are another popular type of triplet sensitizer used in TTA-UC systems.[17–22] The Q band absorptions of porphyrin complexes locate in the green region and the lifetimes of their triplet states can last tens to hundreds of microseconds, which benefit the TTA-UC process. Furthermore, porphyrinoids with strong and broad absorption have also been applied to improve the TTA-UC performance.[23–26] Developing and improving TTA-UC systems based on porphyrin complexes with broad absorption bands of long wavelength and intense absorption coefficients is an attractive focus. Researchers have developed a series of *meso-meso*-linked porphyrin complexes, which exhibit broad and enhanced absorption bands arising from the excitonic interactions between constituent porphyrin units.[27–33] It is anticipated that promising triplet–triplet annihilation upconversion systems can be developed by utilizing *meso-meso*-linked porphyrin complexes as sensitizers.

In the present work, a series of *meso-meso* directly linked Pd–porphyrin oligomers with broadened and enhanced absorption bands, that is, the Pd–porphyrin monomer, dimer, and trimer complexes (PdDTP-M, PdDTP-D, and PdDTP-T), were synthesized. TTA-UC systems were successfully constructed by using the Pd–porphyrin oligomers and 9,10-diphenylanthracene (DPA) as the sensitizer and the acceptor, respectively, and the best TTA-UC efficiency was observed in the [PdDTP-D]/DPA system. Thorough photophysical studies indicate that the enhance absorption at the excitation wavelength can evidently improve the TTA-UC efficiencies.

Results and Discussion

Synthesis and characterization of the Pd–porphyrin oligomers

The *meso-meso*-linked Pd–porphyrin oligomers PdDTP-M, PdDTP-D, and PdDTP-T were synthesized by replacing the metal of zinc(II) 5,15-di(3,5-di-*tert*-butylphenyl)porphyrin oligomers with palladium(II) acetate. The precursor zinc(II) 5,15-di(3,5-di-*tert*-butylphenyl)porphyrin oligomers were synthesized according to literature reports.[29,34] The details of the synthesis and the characterization of the Pd–porphyrin oligomers are described in the Supporting Information. The structures of the Pd–porphyrin oligomers are depicted in Figure 1, which were characterized by ^{1}H NMR and IR spectroscopy as well as MALDI-TOF mass spectrometry (Figures S1–S3 in the Supporting Information).

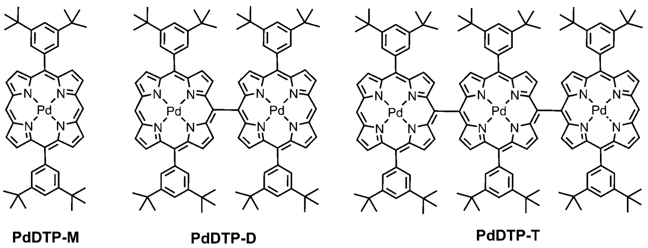

Figure 1. Structures of the Pd–porphyrin oligomers.

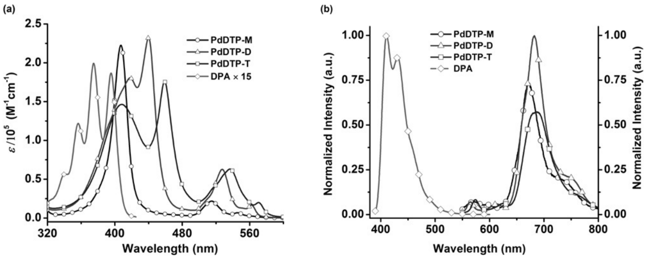

Figure 2. (a) Absorption and (b) emission spectra of the Pd–porphyrin oligomers and DPA in deaerated toluene. The emission spectra of the Pd–porphyrin oligomers are normalized to the specific absorbance of the sample at the excitation wavelength (532 nm).

The absorption spectra of the Pd–porphyrin oligomers and DPA were measured in deaerated toluene (Figure 2a). PdDTP-M exhibits a strong absorption band at 406 nm and two weak ones at 515 and 546 nm, which are assigned to the Soret band and the Q bands, respectively. With increasing the number of porphyrin units, the Soret bands of PdDTP-D and PdDTP-T exhibit splitting as a result of exciton coupling between the adjacent porphyrin units,[27] and the Q bands are enhanced and broadened along with a slight bathochromic shift. Consequently, the light-harvesting ability and the excitation region of the TTA-UC systems using PdDTP-D or PdDTP-T as photosensitizers will be enhanced and broadened in comparison to that using PdDTP-M. The molar extinction coefficients at 532 nm are determined to be 6.62×10^3, 5.26×10^4, and $5.91\times10^4\,\text{M}^{-1}\,\text{cm}^{-1}$ for PdDTP-M, PdDTP-D, and PdDTP-T, respectively. All the absorption bands of DPA lie below 420 nm, indicating that the Pd–porphyrin oligomers can be selectively excited by their Q band in the TTA-UC systems.

The emission spectra of the Pd–porphyrin oligomers and DPA in deaerated toluene are shown in Figure 2b (non-normalized emission spectra shown in Figure S10 in the Supporting Information for comparison). Dual weak fluorescence bands with maxima at approximately 570 and 620 nm and dual intense phosphorescence bands with maximum at approximately 680 nm and a shoulder at approximately 740 nm were detected for all three Pd–porphyrin oligomers upon excitation of the Q band with 532 nm light. The phosphorescence quantum yields of PdDTP-M, PdDTP-D, and PdDTP-T were measured to be 1.1 %, 1.4 %, and 0.98 %, respectively, by using Pd$^{\text{II}}$ octaethylporphyrin ($\Phi_{\text{P}}=0.022$ in acetone) as the standard. The parameters of the absorption spectra and the emission spectra are summarized in Table 1. The fluorescence of DPA is located at a higher energy region in comparison to the emission of the Pd–porphyrin oligomers and the fluorescence quantum yield

Table 1. Absorption and emission properties of the Pd–porphyrin oligomers in deaerated toluene.

Compound	Absorption (λ_{abs}) [nm]	ε_{max} [10^5 M^{-1} cm^{-1}]	Emission (λ_{max}) [nm]	Φ_P [%]
PdDTP-M	407, 515, 546	2.2, 0.24, 0.08	570, 598, 672, 734	1.1
PdDTP-D	417, 440, 527, 563	1.8, 2.3, 0.63, 0.18	565, 613, 682, 747	1.4
PdDTP-T	408, 459, 537, 570	1.5, 1.8, 0.64, 0.22	574, 625, 686, 759	0.98

of DPA in toluene was determined to be 0.85 by reference to that in cyclohexane ($\Phi_F = 0.95$).

Triplet–triplet annihilation upconversion

The quenching experiments of the triplet excited state of the Pd–porphyrin oligomers by DPA were carried out in deaerated toluene; these were performed to ensure that the TTA-UC system can be constructed from the Pd–porphyrin oligomers and DPA. As shown in Figure 3 a and Figure S4 (in the Supporting Information), the phosphorescence of the Pd–porphyrin oligomers was clearly quenched by DPA. To classify the reason for the phosphorescence quenching of the Pd–porphyrin oligomers by DPA, the feasibility of the electron transfer process from the triplet state of the Pd–porphyrin oligomers to DPA as well as the triplet energy transfer from the Pd–porphyrin oligomers to DPA was evaluated. The free-energy change involved in an electron transfer process from the triplet state of the Pd–porphyrin oligomers to DPA were determined to be positive (~ 1.36 eV, see the Supporting Information) by calculation with the Rehm–Weller equation, suggesting that the electron transfer is endothermic and thermodynamically unfavorable. The triplet energy levels of the Pd–porphyrin oligomers are estimated from their phosphorescence spectra to be 1.82, 1.81, and 1.79 eV for PdDTP-M, PdDTP-D, and PdDTP-T, respectively, which are higher than that of DPA (1.77 eV).[35] Thus, the thermodynamic triplet–triplet energy transfer from the triplet state of the Pd–porphyrin oligomers to DPA accounts for the quenching of phosphorescence of the Pd–porphyrin oligomers, which is also confirmed by the transient absorption experiments. The phosphorescence Stern–Volmer plots of the Pd–porphyrin oligomers with DPA are shown in Figure 3 b. When the concentration of DPA is less than 50 μM, the plots are nearly linear, which is in accordance with the Stern–Volmer plots measured with the phosphorescence lifetimes of the Pd–porphyrin oligomers in the presence of different concentrations of DPA. The linear plots below 50 μM DPA indicate that the dynamic quenching is responsible for the decrease in the phosphorescence intensity. Upon further increasing the concentration of DPA, the phosphorescence intensity continues to be quenched, but the quenching efficiency decreases. When the concentration of DPA reaches 100 μM, over 90 % of the phosphorescence of the Pd–porphyrin oligomers have been quenched by DPA, giving the quenching efficiencies of 0.96, 0.93, and 0.91 for PdDTP-M, PdDTP-D, and PdDTP-T, respectively.

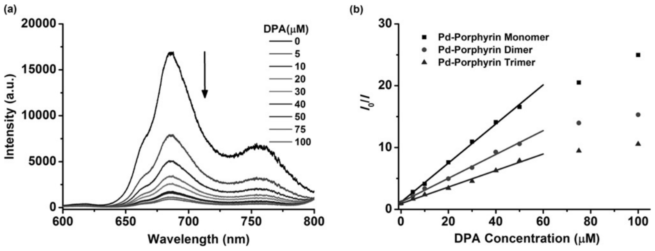

Figure 3. (a) The phosphorescence spectra of the PdDTP-D evaluated with DPA in different concentrations in deaerated toluene; (b) Stern–Volmer plots of Pd–porphyrin oligomers and DPA in deaerated toluene; [PdDTP-D] = 5 μM, λ_{ex} = 532 nm.

The TTA-UC systems were constructed in deaerated toluene by using the Pd–porphyrin oligomers and DPA as the triplet photosensitizer and the acceptor, respectively. Selective excitation of the Pd–porphyrin oligomers in the TTA-UC systems ([Pd–porphyrin oligomer] = 5 μM, [DPA] = 50 μM) by using a green laser (λ = 532 nm) results in blue emission (inset of Figure 4 a), indicative of the occurrence of the TTA-UC process. The emission spectra of the TTA-UC systems upon different ex-

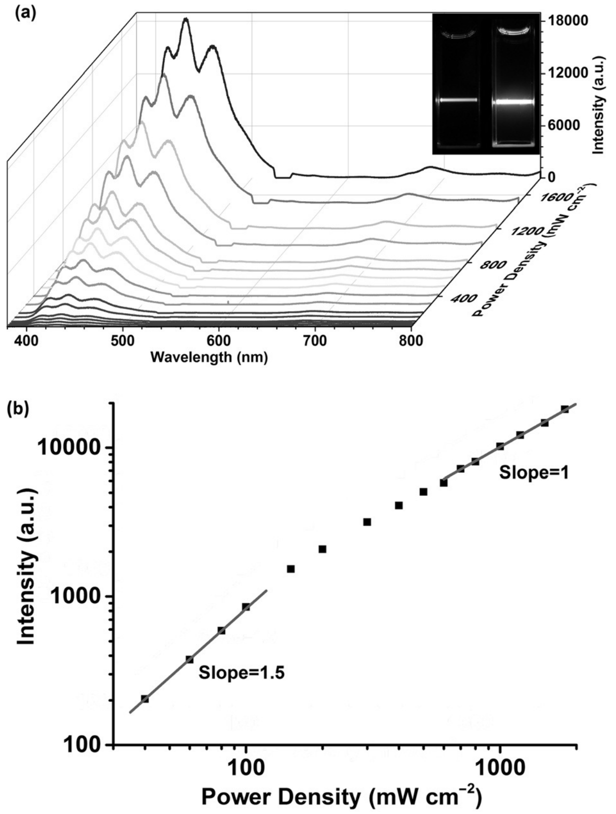

Figure 4. (a) Photoluminescence spectra at different excitation power. Inset is the photo obtained from PdDTP-D (left, red emission) and PdDTP-D/DPA (right, blue emission) upon excitation with a 532 nm laser. (b) Double logarithmic plots of upconversion intensity at 430 nm measured as a function of power density of a 532 nm incident laser for [PdDTP-D]/DPA in deaerated toluene. [PdDTP-D] = 5 μM, [DPA] = 50 μM.

citation power are presented in Figure 4 a and Figure S5 (in the Supporting Information). With increasing the excitation power density from 60 to 1800 mW cm^{-2}, a rapid enhancement of the blue upconversion emission with maximum at 430 nm was observed, accompanied by weak phosphorescence with maximum at 680 nm emitted from the Pd–porphyrin oligomers. The maxima of the upconversion emission spectra obtained in the [PdDTP-M]/DPA, [PdDTP-D]/DPA, and [PdDTP-T]/DPA systems are the same, but the detailed structures of the spectra show slight difference, which can be ascribed to reabsorption by the Pd–porphyrin oligomers.

The double logarithmic plots of the upconversion fluorescence emanating from DPA at 430 nm as a function of the incident light power density are shown in Figure 4 b and Figure S6 (in the Supporting Information). A slope of near 2.0 is obtained in the low power density region for all three TTA-UC systems, which means that the triplet–triplet annihilation process is much less than the spontaneous decay of the triplet state of DPA. With increasing the power density on the samples, the plots incline towards the *x*-axis and approach a slope of 1 in the high power density region, indicating that the triplet–triplet annihilation reaches a saturated region and is the main decay process of the triplet of DPA.[36,37] The slope decrease in the TTA-UC system containing PdDTP-D or PdDTP-T caused by the possibly intramolecular TTA of the sensitizers is excluded by the phosphorescence measurements at different laser power. The dependence of phosphorescence of the porphyrin dimer or trimer on laser power demonstrates that the power threshold of TTA within the porphyrin dimer or trimer is about 500 mW cm^{-2} in the absence of DPA. By taking account of the effective quenching of the sensitizers by large amounts of DPA, the power threshold will be much higher and the TTA within the porphyrin dimer and trimer is not likely evident in the TTA-UC systems.

The dependence of the upconversion efficiency on the DPA concentration was investigated by measuring the emission spectra of the TTA-UC systems at different concentrations of DPA upon excitation of the Pd–porphyrin oligomers with a 532 nm laser of 500 mW cm^{-2}. As shown in Figure 5 a and Figure S7 (in the Supporting Information), when the concentration of DPA increases from 5 to 50 μM, the upconversion fluorescence of DPA is significantly enhanced, and is accompanied by a decrease in the phosphorescence of the Pd–porphyrin oligomers. This can be ascribed to the increased chance of the collision between the Pd–porphyrin oligomers and DPA, which promotes the triplet–triplet energy transfer from the photosensitizer to the acceptor and produces more triplet states of the acceptor, favoring the triplet–triplet annihilation process and then the upconversion fluorescence. When the concentration of DPA increases from 50 to 100 μM, the increment of the upconversion intensity diminishes distinctly and the variation of the phosphorescence intensity of the Pd–porphyrin oligomers is small. This indicates that the redundant DPA makes little contribution to the triplet–triplet energy transfer from the Pd–porphyrin oligomers to DPA, which is consistent with the results of the phosphorescence quenching experiment. The changes in the upconversion quantum yields of the [Pd–porphyrin oligomer]/DPA systems with the concentration of DPA are depicted in Figure 5 b. Under the same experimental conditions, the upconversion quantum yield of [PdDTP-D]/DPA is higher than those of [PdDTP-M]/DPA and [PdDTP-T]/DPA. Upon excitation with 532 nm light of 500 mW cm^{-2}, the upconversion quantum yields of the [Pd–porphyrin oligomer]/DPA systems ([Pd–porphyrin oligomer] = 5 μM, [DPA] = 100 μM) were determined to be 6.2 %, 10.5 %, and 1.6 % for [PdDTP-M]/DPA, [PdDTP-D]/DPA, and [PdDTP-T]/DPA, respectively. Considering solar irradiation intensity (ca. 100 mW cm^{-2}) and to allow comparisons with other TTA-UC systems, the upconversion quantum yields at a power density of 100 mW cm^{-2} have also been examined and were found to be 3.4 %, 8.3 %, and 0.47 % for [PdDTP-M]/DPA, [PdDTP-D]/DPA, and [PdDTP-T]/DPA, respectively. The combination of palladium octaethylporphyrin (PdOEP) and DPA was used as a TTA performance reference. The upconversion quantum yields of PdOEP/DPA under the same conditions were found to be 6.8 % and 9.2 % upon the excitation power densities of 100 and 500 mW cm^{-2}, respectively. The stability of the TTA-UC systems under irradiation was also carried out and the results are shown in Figure S11 (in the Supporting Information). The upconversion emission is stable for more than 2 h under 100 mW cm^{-2} irradiation, and a negligible change in the upconversion emission can be observed, indicative of good stability of the TTA-UC systems.

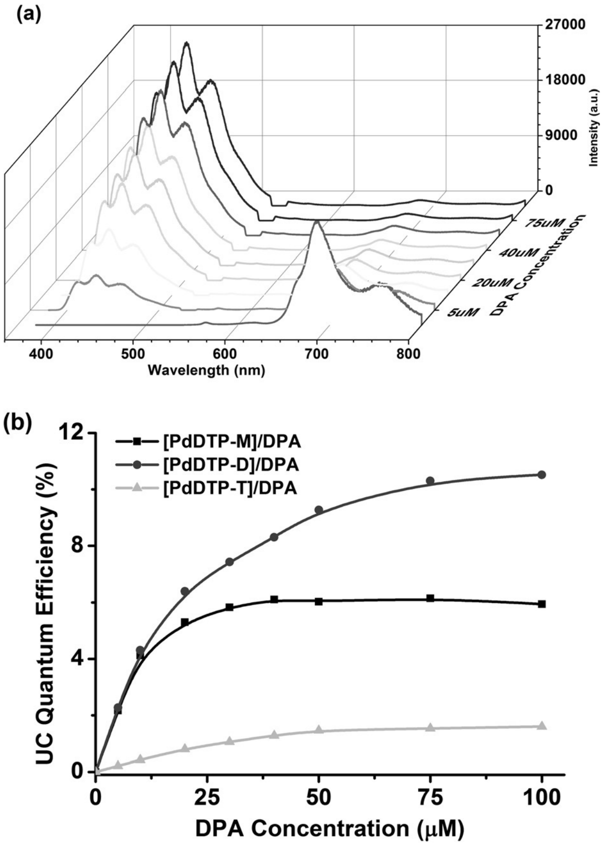

Figure 5. (a) The concentration-dependent upconversion spectra of DPA combined with PdDTP-D. (b) Upconversion efficiencies (Φ_{UC}) as a function of DPA concentration with the sensitizer at fixed concentration (5 μM) in deaerated toluene (532 nm, 500 mW cm^{-2}).

Photophysical processes in triplet–triplet annihilation upconversion

The upconversion quantum efficiency (Φ_{UC}) is related to the intersystem crossing efficiency of the sensitizer (Φ_{ISC}), the triplet–triplet energy transfer efficiency from the sensitizer to acceptor (Φ_{TTET}), the triplet–triplet annihilation efficiency of the acceptor (Φ_{TTA}), as well as the fluorescence quantum yield (Φ_F) of the acceptor. To understand the effect of each parameter on Φ_{UC} in the [Pd–porphyrin oligomer]/DPA systems, the photophysical processes between the Pd–porphyrin oligomers and DPA were studied by means of transient absorption spectra. The transient absorption spectra of Pd–porphyrin oligomers were carried out in deaerated toluene (5 μM) by using 532 nm excitation light and are given in Figure 6a and Figure S8 (in the Supporting Information). Three absorption bands with maxima at 336, 453, and 535 nm are observed in the transient absorption spectrum of PdDTP-M. The transient absorption spectra of PdDTP-D and PdDTP-T are similar to that of PdDTP-M and the maxima of the transient absorption bands of PdDTP-D and PdDTP-T are 338, 466, 549 nm and 337, 483, 559 nm, respectively. The transient absorption spectra of the Pd–porphyrin oligomers are similar to those of Pd–porphyrin sensitizers reported before[36] and can be quenched by oxygen and triplet acceptors. Thus, these absorption bands are assigned to the transient absorption of the Pd–porphyrin oligomer triplet states. The negative band that appears in the transient absorption spectra is assigned to ground-state bleaching according to the ground-state absorption spectra. The transient absorption spectra of the Pd–porphyrin oligomers (5 μM) in the presence of 100 μM DPA were further investigated under the same conditions (Figure 6b and Figure S8). The transient absorption of the triplet Pd–porphyrin oligomers in the presence of DPA decays much faster than that in the absence of DPA and nearly disappear within 20 μs. A new transient absorption band located at 400–500 nm arises simultaneously, which is assigned to the transient absorption from the lowest triplet state of DPA to its higher triplets.[35,38] Only the Pd–porphyrin oligomers in the [Pd–porphyrin oligomer]/DPA systems absorb the light under the experimental conditions, therefore, the formation of triplet DPA must be attributed to the triplet–triplet energy transfer from the Pd–porphyrin oligomers to DPA.

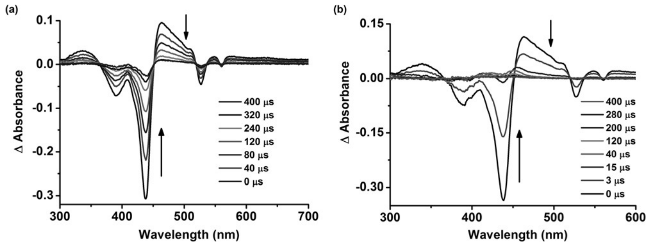

Figure 6. Transient absorption spectra of PdDTP-D (5 μM) in the absence (a) and presence (b) of DPA (100 μM) upon excitation with 532 nm light in deaerated toluene.

The kinetic traces of the triplet of the Pd–porphyrin oligomers in the absence and presence of DPA were obtained by taking the transient absorption of the Pd–porphyrin oligomers at the maxima (455, 470, and 485 nm for PdDTP-M, PdDTP-D, and PdDTP-T, respectively) as a function of time, as shown in Figure 7 and Figure S9 (in the Supporting Information). In the absence of DPA, the kinetic traces can be fitted mono-exponentially, giving the triplet lifetimes of 99.6, 107.3, and 62.8 μs for PdDTP-M, PdDTP-D, and PdDTP-T, respectively. In the presence of DPA (100 μM), the kinetic traces can be visually divided into two parts, a fast decay and a slower one, which can be rationalized by the overlap of the transient absorption of the Pd–porphyrin oligomers and DPA. The fast and the slow decay can be assigned to the triplet state of the Pd–porphyrin oligomers and ^{3}DPA*, respectively.[38] The triplet lifetimes of PdDTP-M, PdDTP-D, and PdDTP-T in the presence of DPA are determined to be 5.1, 5.9, and 6.4 μs, respectively, by double-exponential fitting of the decay traces. The triplet lifetimes in the present of DPA are much shorter than those without DPA because of the triplet–triplet energy transfer from the Pd–porphyrin oligomers to DPA. The rate constants and the efficiencies of the triplet–triplet energy transfer from the sensitizer to the acceptor are calculated to be 1.8×10^5, 1.5×10^5, 0.9×10^5 s^{-1} and 0.95, 0.94, 0.90 for the [PdDTP-M]/DPA, [PdDTP-M]/DPA, and [PdDTP-T]/DPA systems, respectively. The triplet–triplet energy transfer efficiencies obtained from the transient absorption data are consistent with those estimated from the phosphorescence quenching. The triplet lifetimes of the Pd–porphyrin oligomers in the absence and presence of DPA and the rate constants and efficiencies of the triplet–triplet energy transfer are summarized in Table 2.

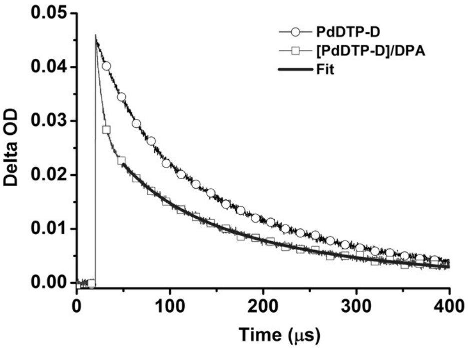

Figure 7. The kinetic traces of PdDTP-D (5 μM) in the absence or presence of DPA (100 μM); the intensity of the signal in the absence of DPA is normalized to that in the presence of DPA, $\lambda_{ex}=532$ nm.

The Φ_{UC} of the [Pd–porphyrin oligomer]/DPA systems is also affected by the triplet–triplet annihilation process of ^{3}DPA*. The triplet–triplet annihilation process of the [Pd–porphyrin oligomer]/DPA system was also analyzed by using the transient absorption spectra. In the TTA-UC systems, ^{3}DPA* undergoes decay through two pathways: one is a first-order decay process, including a combination of the intrinsic phosphorescence and the intersystem crossing to the singlet ground state; the other is the triplet–triplet annihilation decay process. The time

Table 2. The triplet lifetimes of the Pd–porphyrin oligomers in the absence and presence of DPA and the energy transfer efficiencies and rate constants for the [Pd–porphyrin oligomer]/DPA systems.

Compound	τ [μs] Without DPA	With DPA	k_{TTET} [10^5 s^{-1}]	Φ_{TTET}[a]	Φ_{TTET}[b]
PdDTP-M	99.6	5.1	1.8	0.96	0.95
PdDTP-D	107.3	5.9	1.5	0.93	0.94
PdDTP-T	62.8	6.4	0.9	0.91	0.90

[a] From the phosphorescence quenching spectra. [b] From the transient absorption spectra.

Table 3. Photophysical data in the [Pd–porphyrin oligomer]/DPA upconversion systems.

	[PdDTP-M]/DPA	[PdDTP-D]/DPA	[PdDTP-T]/DPA
$\Delta A(^3\mathrm{DPA}^*)_0$	0.007	0.028	0.003
[^{3}DPA*]$_0$ [10^{-6} M]	0.45	1.8	0.96
k_T [10^3 s^{-1}]	4.3	3.9	5.4
k'_{TT} [10^5 s^{-1}]	0.9	1.7	1.1
k_{TT} [10^9 M^{-1} s^{-1}]	1.4	2.6	1.7
f_{TT}	0.08	0.26	0.11
Φ_{ISC}	1.0[a]	0.89	0.81
Φ_{TTET}	0.95	0.94	0.90
Φ_{TTA} [%]	7.7	14.7	2.4
Φ_{UC} [%]	6.2	10.5	1.6

[a] From ref. [42].

dependence of the transient absorption of ^{3}DPA* ($\Delta A(^3\mathrm{DPA}^*)_t$) and the fraction ($f_{TT}$) of ^{3}DPA* decaying through the triplet–triplet annihilation pathway can be described by equations (1) and (2)[39–41]:

$$\Delta \mathrm{A}(^3\mathrm{DPA}^*)_1 = \frac{1}{(\frac{1}{\Delta \mathrm{A}(^3\mathrm{DPA}^*)_0} + \frac{k'_{TT}}{k_T})\exp(k_T t) - \frac{k'_{TT}}{k_T}} \qquad (1)$$

$$f_{TT} = 1 - \frac{k_T}{\Delta \mathrm{A}(^3\mathrm{DPA}^*)_0 \times k'_{TT}} \ln(1 + \frac{\Delta \mathrm{A}(^3\mathrm{DPA}^*)_0 \times k^*_{TT}}{k_T}) \qquad (2)$$

in which k_T is the first-order triplet decay rate constant, $k'_{TT} = k_{TT}/\varepsilon_T l$ is the apparent rate constant of triplet–triplet annihilation, k_{TT} is the triplet–triplet annihilation rate constant, the ε_T is the molar extinction coefficient of ^{3}DPA*, and l is the path length of the laser passed through the sample, $\Delta A(^3\mathrm{DPA}^*)_0$ and $\Delta A(^3\mathrm{DPA}^*)_t$ are the initial and time-dependent transient absorption intensities. Nonlinear fitting of the transient absorption kinetic traces of ^{3}DPA* with equation (1) yields the three parameters $\Delta A(^3\mathrm{DPA}^*)_0$, k_T, and k'_{TT}, and then f_{TT} can be calculated with equation (2).

Although the transient absorption of the Pd–porphyrin oligomer triplet state (^{3}PS*) overlaps that of ^{3}DPA* in the range 400–500 nm, ^{3}PS* decays much faster than ^{3}DPA*. The transient absorption of ^{3}PS* faded away within 30 μs after the excitation pulse. Therefore, the kinetic traces at the maximum of the transient absorptions (455, 455, and 485 nm for the [PdDTP-M]/DPA, [PdDTP-M]/DPA, and [PdDTP-T]/DPA systems, respectively) after 30 μs belong to ^{3}DPA*, which can be fitted nonlinearly with equation (1) and $\Delta A(^3\mathrm{DPA}^*)_0$, k_T, and k'_{TT} of the TTA-UC systems can be obtained. The data for f_{TT} of the TTA-UC systems are calculated by using equation (2). The molar extinction coefficient of ^{3}DPA* at 485 nm is estimated to be 3370 M^{-1} cm^{-1} by using its transient absorption spectrum and its molar extinction coefficient at 455 nm (1.55×10^4 M^{-1} cm^{-1}) reported in the literature.[35,38] With ε_T of ^{3}DPA*, the initial concentration of ^{3}DPA* ([^{3}DPA*]$_0$) and k_{TT} in the [Pd–porphyrin oligomer]/DPA systems can be calculated from $\Delta A(^3\mathrm{DPA}^*)_0$ and $k'_{TT} = k_{TT}/\varepsilon_T l$, respectively. All the fitted and calculated data, $\Delta A(^3\mathrm{DPA}^*)_0$, [^{3}DPA*]$_0$, k_T, k'_{TT}, k_{TT}, and f_{TT} are summarized in Table 3. Under the same experimental conditions, the [PdDTP-D]/DPA system exhibits the highest [^{3}DPA*]$_0$, f_{TT}, and k_{TT} in these three TTA-UC systems.

Φ_{TTA} can be calculated according to equation (4) (see below) with the known values of Φ_{UC}, Φ_{ISC}, Φ_{TTET}, and Φ_F of DPA. Φ_{UC} and Φ_{TTET} have already been determined and Φ_F of DPA is 0.85 in toluene. The intersystem crossing efficiencies (Φ_{ISC}) of the Pd–porphyrin oligomers are required to calculate the triplet–triplet annihilation efficiency (Φ_{TTA}). Assuming the intersystem crossing efficiency of PdDTP-M to be unity,[42] the Φ_{ISC} of PdDTP-D and PdDTP-T are estimated to be 0.89 and 0.81, respectively, by comparing [^{3}DPA*]$_0$ in the [PdDTP-D]/DPA and [PdDTP-T]/DPA systems with that of the [PdDTP-M]/DPA system under the same experimental conditions. Thus, Φ_{TTA} is estimated to be 7.7%, 14.7%, and 2.4% for the [PdDTP-M]/DPA, [PdDTP-D]/DPA, and [PdDTP-T]/DPA systems, respectively.

Determinant of the difference of Φ_{UC} in the [Pd–porphyrin oligomer]/DPA systems

Φ_{UC} is the product of the Φ_{ISC} of the sensitizer, Φ_{TTET} from the triplet sensitizer to the acceptor, and Φ_{TTA} and Φ_F of the acceptor. Because the same acceptor, DPA, is used in the three [Pd–porphyrin oligomer]/DPA systems, their Φ_{UC} values are only affected by Φ_{ISC}, Φ_{TTET}, and Φ_{TTA}. Φ_{ISC} and Φ_{TTET} in the [Pd–porphyrin oligomer]/DPA systems show a downward trend with the increasing number of linked porphyrin units, whereas the order of Φ_{UC} is [PdDTP-D]/DPA (10.5%) > [PdDTP-M]/DPA (6.2%) > [PdDTP-T]/DPA (1.6%). Evidently, the intersystem crossing and the triplet–triplet energy transfer processes should not be the main causes for the difference of Φ_{UC}. Φ_{TTA} was found to be 7.7%, 14.7%, and 2.4% for the [PdDTP-M]/DPA, [PdDTP-D]/DPA, and [PdDTP-T]/DPA systems, respectively. The same tendency for Φ_{TTA} and Φ_{UC} to vary with the number of linked porphyrin units is observed, therefore, it can be inferred that Φ_{TTA} is the main determinant for the difference in Φ_{UC} in the [Pd–porphyrin oligomer]/DPA systems. Φ_{TTA} in the [PdDTP-D]/DPA system is higher than those in the other two systems, resulting in higher upconversion quantum efficiency.

We further looked into the factors affecting the triplet–triplet annihilation process. The triplet–triplet annihilation process involves two ^{3}DPA* molecules and is concentration-dependent, thus, it is advanced by higher concentrations of ^{3}DPA*. ^{3}DPA* is generated from the sensitization by the Pd–porphyrin oligomers, which begins with the formation of the singlet excited state of the Pd–porphyrin oligomers upon excitation and then an intersystem crossing process to the triplet sensitizer, followed by a triplet–triplet energy transfer from the Pd–porphyrin oligomer to DPA. Under the same experimental conditions, the concentration of the generated ^{3}DPA* relates to the molar extinction coefficient, the intersystem crossing efficiency of the sensitizers, and the triplet–triplet energy transfer efficiency from the sensitizer to DPA. Usually, the longer the triplet lifetime of the sensitizer is, the more chance it has of colliding with DPA within its lifetime, resulting in higher sensitization efficiency. In the present work, the concentration of the acceptor is high enough to quench the triplet sensitizer ($\Phi_{TTET} > 0.9$), so the effect of the triplet lifetime of the sensitizer can be ignored. Although Φ_{ISC} of PdDTP-M is near unity, its molar extinction coefficient at 532 nm is low (~1/8 of those of PdDTP-D or PdDTP-T), which limits the photons absorbed by the sensitizer at certain excitation intensities, resulting in low concentrations of ^{3}DPA*. The absorbance of PdDTP-D is similar to PdDTP-T and is about seven times higher than PdDTP-M, which means the excited dimer is seven times that of the monomer under the same experimental conditions. The TTA-UC quantum yields were found to be 8.3% and 10.5% for [PdDTP-D]/DPA, and 3.4% and 6.2% for [PdDTP-M]/DPA under 100 and 500 mW cm^{-2} irradiation, respectively. The TTA-UC quantum yield of PdDTP-D/DPA increases by factors of 2.4 and 1.7 compared with PdDTP-M/DPA under weak and strong irradiation, respectively, which can be mainly ascribed to the enhanced absorption of the sensitizer. The molar extinction coefficients at 532 nm, the efficiency of intersystem crossing, and the spectral overlap integral with DPA emission for PdDTP-D and PdDTP-T are comparable, but the TTA-UC quantum yields of PdDTP-D/DPA are 17.7 and 6.6 times higher than those of PdDTP-T/DPA under 100 and 500 mW cm^{-2} irradiation, respectively. The higher quantum yields of PdDTP-D/DPA can be accounted for by the higher k_{TTET}, which produces more ^{3}DPA* per unit time, thus giving higher [^{3}DPA*]$_0$ in the [PdDTP-D]/DPA system. The higher [^{3}DPA*]$_0$ favors the two-molecule process, resulting in higher fraction of ^{3}DPA* being involved in the TTA decay pathway and consequently much better k_{TTA} and Φ_{TTA}. The dynamic difference in ^{3}DPA* generation and f_{TT} amplifies the discrepancy in the TTA-UC performance for PdDTP-D and PdDTP-T, which is more pronounced under weak excitation. [^{3}DPA*]$_0$ in the [PdDTP-T]/DPA system is higher than that in the [PdDTP-M]/DPA system, but the magnitudes of Φ_{UC} in these two systems are opposite, which can be rationalized by the more efficient energy transfer from the singlet state of DPA to PdDTP-T than to PdDTP-M owing to the larger spectral overlap in the PdDTP-T/DPA system. The overlap between the absorption of the sensitizers and the fluorescence of the acceptor exists in all three [Pd–porphyrin oligomer]/DPA systems, which leads to energy transfer from the singlet state of DPA to the ground state of the Pd–porphyrin oligomers, decreasing the measured Φ_{UC} and the calculated Φ_{TTA}. For potential applications, TTA-UC systems should be further improved by avoiding the severe spectral overlap between the absorption of sensitizers and the emission of acceptors through molecular design and selection of sensitizer and acceptor. Another issue for application of TTA-UC systems is the aging caused by molecular oxygen and chromophore photobleaching, which may be overcome by adopting oxygen scavenger compounds, oxygen shielding components, as well as robust molecular design.[6,43–45]

Conclusion

A series of directly *meso-meso*-linked Pd–porphyrin oligomers have been prepared by utilizing zinc(II) 5,15-di(3,5-di-*tert*-butylphenyl)porphyrin oligomers and palladium(II) acetate. The absorption region and the light-harvesting ability of the Pd–porphyrin oligomers are broadened and enhanced by increasing the number of porphyrin units. The TTA-UC systems were constructed by using the Pd–porphyrin oligomers and 9,10-diphenylanthracene as the sensitizer and the acceptor, respectively, and their photophysical processes were investigated thoroughly. The triplet–triplet annihilation upconversion quantum efficiencies of the TTA-UC systems under our experimental setup were measured to be 6.2%, 10.5%, and 1.6% when using PdDTP-M, PdDTP-D, and PdDTP-T as the sensitizer, respectively. The higher TTA-UC quantum efficiency observed in the [PdDTP-D]/DPA system can be attributed to the enhanced light-harvesting ability of PdDTP-D, which produces more ^{3}DPA*, consequently promoting the triplet–triplet annihilation process. Furthermore, reabsorption of the upconversion fluorescence by the sensitizer decreases the measured TTA-UC quantum efficiency, which must be taken into consideration when designing TTA-UC systems. These findings provide a new perspective on the construction of effective triplet–triplet annihilation upconversion systems.

Experimental Section

Materials

Reagents were purchased from Aldrich or Acros or J&K chemical and were used without further purification, unless otherwise noted. Palladium(II) acetate was purchased from Beijing Ouhe Technology Co. Ltd. Toluene was distilled over Na/benzophenone under a nitrogen atmosphere.

Instrumentation

^{1}H NMR spectra were recorded with a Bruker Avance Π-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. IR spectra were performed with an Excalibur 3100 IR spectrometer. MALDI-TOF-MS spectra were recorded with a Bruker BIFLEX III spectrometer. Steady-state absorption and emission spectra were measured by using a Shimadzu UV-2550PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Luminescence decay processes were recorded with a single photon counting technique with an Edinburgh FLS920 lifetime system. The transient absorption spectra were performed with an Edinburgh LP 920 pump-probe spectroscopic setup.

Absorption and emission measurements

All the absorption and emission spectra were measured in deaerated toluene by using a 1 cm quartz cuvette at room temperature (RT). The excitation wavelength was 532 nm for the emission measurements unless otherwise noted, and the spectra were normalized to a constant absorbance at the excitation wavelength.

TTA upconversion

A diode-pumped solid-state laser (MGL-III-532 nm, Changchun New Industries Optoelectronics Tech. Co. Ltd.) was used as the excitation light source in the TTA-UC measurements. The laser power was measured with an Ophir Nova II power meter with a PD300–3W photodetector. The sample solutions for the upconversion experiments were deaerated by purging with argon for 30 min prior to measurement. The upconverted fluorescence was recorded by a Princeton Instrument SPEC-10:400B/LN CCD coupled to an Acton SP2500 spectrometer. The oxygen contamination was examined by using the reaction of DPA with singlet oxygen and monitoring the DPA absorbance change.[44] After irradiation, singlet oxygen formed by sensitization reacts with DPA to form endoperoxide, subsequently the DPA absorption decreases. By monitoring the decrease amount of DPA, the oxygen quantity in deaerated samples was estimated to be $2–4\times10^{-7}$ M.

The upconversion quantum yields (Φ_{UC}) were determined with the prompt phosphorescence of tris(4,4′-dimethyl-2,2′-bipyridine)ruthenium bis(hexafluorophosphate) ($\Phi_{\mathrm{P}}=7.4\%$ in acetonitrile) as the standard. The upconversion quantum yields were calculated by equation (3), where Φ_{UC} stands for the upconversion quantum yield, and Φ_{std} is the phosphorescence quantum yield of the standard. A, I, and η represent the absorbance, the integrated photoluminescence intensity, and the refractive index of the solvent, sam and std refer to the sample and the standard, respectively. The equation is multiplied by a factor of 2 to make the maximum quantum yield be unity.

$$\Phi_{\mathrm{UC}} = 2\Phi_{\mathrm{std}}\left(\frac{A_{\mathrm{std}}}{A_{\mathrm{sam}}}\right)\left(\frac{I_{\mathrm{sam}}}{I_{\mathrm{std}}}\right)\left(\frac{\eta_{\mathrm{sam}}}{\eta_{\mathrm{std}}}\right)^2 \tag{3}$$

$$\Phi_{\mathrm{UC}} = \Phi_{\mathrm{ISC}}\Phi_{\mathrm{TIET}}\Phi_{\mathrm{TTA}}\Phi_{\mathrm{F}} \tag{4}$$

The upconversion efficiency can also be obtained by the product of the sensitizer intersystem crossing efficiency (Φ_{ISC}), the triplet–triplet energy transfer efficiency (Φ_{TTET}), and the triplet–triplet annihilation efficiency (Φ_{TTA}), as well as the fluorescence quantum yield (Φ_{F}) of DPA, as shown in equation (4).

Acknowledgments

Financial support from the 973 Program (Nos. 2013CB834703, 2013CB834505), the National Natural Science Foundation of China (Nos. 21573266, 21172229, 21233011, and 21273258), and the Chinese Academy of Sciences (KGZD-EW-T05) are gratefully acknowledged.

Keywords: energy transfer · light harvesting · sensitizers · triplet–triplet annihilation · upconversion

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Received: November 10, 2015