CHEMISTRY
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Accepted Article

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To be cited as: *Chem. Asian J.* 10.1002/asia.201801666

Link to VoR: http://dx.doi.org/10.1002/asia.201801666

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

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Oligo(ethylene glycol)/alkyl-modified chromophore assemblies for photon upconversion in water

Rena Haruki,[a] Hironori Kouno,[a] Masanori Hosoyamada,[a] Taku Ogawa,[a] Nobuhiro Yanai,*[a,b] and Nobuo Kimizuka*[a]

Abstract: Molecular self-assembly is a powerful means to construct nanoscale materials with advanced photophysical properties. Although the protection of the photo-excited states from oxygen quenching is a critical issue, it still has been in an early phase of development. In this work, we demonstrate that a simple and typical molecular design for aqueous supramolecular assembly, modification of chromophoric unit with hydrophilic oligo(ethylene glycol) chains and hydrophobic alkyl chains, is effective to avoid oxygen quenching of triplet-triplet annihilation-based photon upconversion (TTA-UC). While a TTA-UC emission is completely quenched when the donor and acceptor are molecularly dispersed in chloroform, their aqueous co-assemblies exhibit a clear upconverted emission in air-saturated water even under extremely low chromophore concentrations down to 40 μM. The generalization of this nano-encapsulation approach offers new functions and applications using oxygen-sensitive species for supramolecular chemistry.

Introduction

Inspired by the elegant natural photosynthetic systems, chemists have devoted much efforts to construct light-harvesting molecular systems by employing self-assembly of π-conjugated chromophores.[1] Sophisticated molecular designs have been developed for effective energy transfer and harvesting among chromophore arrays. On the other hand, less attention has been paid to the effect of oxygen molecules on the photophysical properties of self-assembled chromophores.[2] The quenching of photo-excited state by oxygen is particularly a serious issue for the triplet states. Since the photo-excited triplet is important for several functions such as phosphorescence, thermally-activated delayed fluorescence (TADF), and photon upconversion (UC), it is highly desired to enrich molecular design libraries for oxygen-tolerant supramolecular chromophoric systems.

The UC is a methodology to convert lower energy photons into higher energy photons.[3] It shows diverse applications in many disciplines with recent rising interest for biological applications such as bioimaging, photo-triggered drug delivery and photodynamic therapy.[4] Rare-earth metal doped nanomaterials have been extensively exploited for this purpose, however, they often require undesirably high excitation intensities.[5] On the other hand, it has been demonstrated that triplet-triplet annihilation-based photon upconversion (TTA-UC) holds the potential to significantly reduce the excitation intensity.[3] The TTA-UC process involves a sequence of photochemical events in which triplet donor and acceptor molecules are involved (Supporting Information, Figure S1). First, the triplet excited state of the donor (sensitizer) is generated via intersystem crossing (ISC) from its photoexcited singlet state. The triplet state energy is transferred to the acceptor (emitter) by triplet-triplet energy transfer (TTET). When two acceptor triplets diffuse and collide during their lifetime, TTA occurs and the resulting acceptor excited singlet state exhibits an upconverted fluorescence. TTET and TTA processes occur by electron-exchange Dexter mechanism, which requires the close contact of these molecules within the distance of 1 nm.

The application of TTA-UC for bio-related research fields requires efficient upconversion in aerated aqueous environments, however, it is confronted by limited solubility of hydrophobic TTA-UC dyes in water and quenching of triplet state by dissolved molecular oxygen. Accordingly, TTA-UC in aqueous systems has been studied for water-dispersible micro/nanoparticles coated with silica or polymer shell,[6] in which pairs of donor/acceptor were dissolved in viscous organic solvents with or without oxygen scavengers. The diffusion-controlled TTET and TTA are inevitably suppressed in such viscous media.[6a] Hydrophobic interiors of aqueous micelles[7] and lipid bilayers[8] have also been employed as matrixes to dissolve TTA-UC dyes. However, they require deaerated conditions or addition of a large amount of oxygen scavengers that limits their long-term operation. It remains challenging to develop rational strategies to achieve aqueous TTA-UC in the presence of dissolved oxygen that overcomes the drawbacks of previous approaches.[9] We have integrated the concept of molecular self-assembly with TTA-UC and developed various acceptor assemblies which proved the advantage of harnessing triplet energy migration compared with the conventional molecular diffusion-based mechanism.[10] The triplet energy migration-based UC in air-saturated aqueous media has been limited to a single-chained, bola-type cationic amphiphilic acceptor, where the hydrogen bonding networks among chromophores play a key role in exerting the oxygen blocking ability.[11] However, it required high acceptor concentration (1 mM) to observe the TTA-UC emission. The development of self-assembled systems that possess cellular nontoxic poly(ethylene glycol) (PEG) units and work at even much lower concentration is desired for the biological applications since the chromophores spread in the blood after injection to the body.

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10.1002/asia.201801666

In this work, we show that the modification of chromophoric unit with a hydrophilic non-ionic oligo(ethylene glycol) chain and double-chained hydrophobic groups is effective to protect the resulting molecular nanoassemblies against oxygen quenching and for producing TTA-UC emission in air-saturated water. A newly-synthesized non-ionic amphiphilic acceptor **A1** self-assembles even at low concentrations down to 40 µM (Figure 1a). It is designed by introducing a hydrophilic octa(ethylene glycol) group and two hydrophobic alkyl chains to an acceptor chromophore, 9,10-diphenylanthracene (DPA). We employ the non-ionic hydrophilic moiety due to its high biocompatibility.[12] The introduction of both hydrophilic unit and two long alkyl chains follows the design of synthetic bilayer membranes, which secures intermolecular interactions and regular molecular orientation required for stable self-assembly in water.[13] It also provides hydrophobic interior to accommodate hydrophobic donor Pt(II) octaethylporphyrin (PtOEP).[13] As expected, the rationally designed amphiphilic acceptor **A1** self-assembled in water even at very low concentration. Significantly, the simple dense hydrophobic assemblies show enough resistance against oxygen quenching to exhibit a TTA-UC emission in air-saturated aqueous dispersions even at the low concentration (Figure 1b). This work indicates that the suitable molecular design of amphiphilic chromophore units is important in giving the oxygen-blocking ability to their self-assemblies, which permits sophisticated photofunctionalities and their applications.

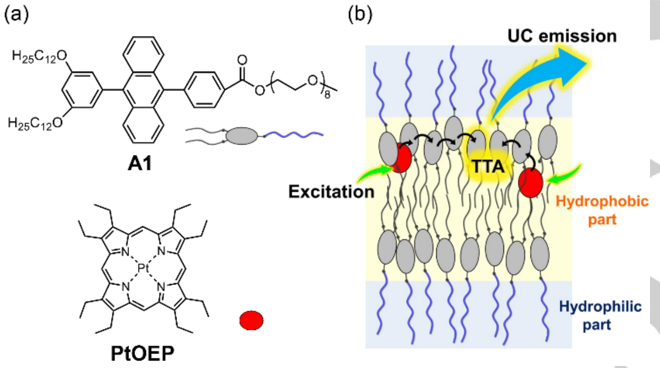

Figure 1. (a) Chemical structures of **A1** and PtOEP. (b) Schematic illustration of TTA-UC system using **A1** and PtOEP assembly in water.

Results and Discussion

The novel acceptor **A1** was synthesized and obtained as a pale yellow liquid (Scheme S1). The purity of **A1** was confirmed by ^{1}H- and ^{13}C-NMR measurements and elemental analysis. When **A1** was added to water and sonicated for several minutes, a turbid aqueous dispersion was obtained ([**A1**] = 400 µM, Figure 2a inset). Dynamic light scattering (DLS) measurements of this dispersion showed the formation of molecular assemblies with an average size of 160 ± 25 nm based on intensity distribution (Figure 2a) and 71 ± 6 nm based on number distribution (Figure S2), suggesting the co-existence of assemblies with different sizes. Transmission electron microscopy (TEM) was conducted for the aqueous dispersion of **A1** ([**A1**] = 400 µM, Figure 2b). The TEM images revealed that the presence of the round shape structures and the nanostructure diameters around 180 nm and 50 nm agrees well with the results of DLS measurement. While sharp ^{1}H-NMR peaks were observed for **A1** in $CDCl_3$, a significant broadening was observed for **A1** in D_2O, supporting the self-assembly of **A1** in water (Figure 2c).[14]

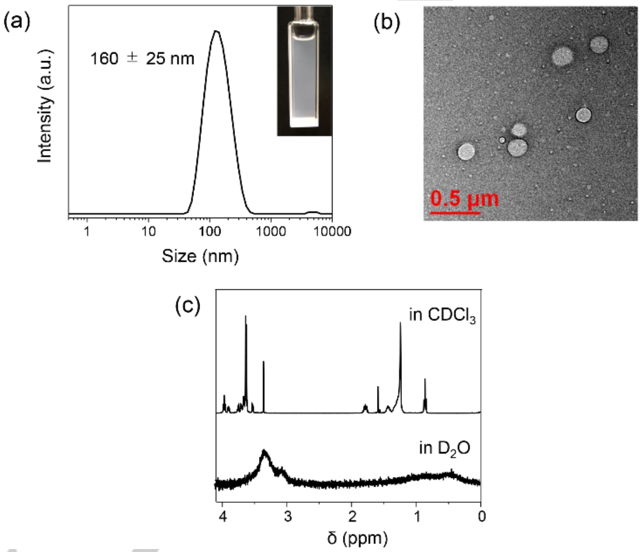

Figure 2. (a) DLS profile of **A1** in water based on intensity distribution ([**A1**] = 400 µM, 298 K). The inset shows a picture of the aqueous dispersion of **A1**. (b) TEM image of **A1** aqueous dispersion ([**A1**] = 400 µM). (c) ^{1}H-NMR spectra of **A1** in $CDCl_3$ and in D_2O ([**A1**] = 400 µM, 298 K).

The assembly formation of **A1** in water was further supported by absorption measurements. The UV-vis absorption spectrum of **A1** in $CHCl_3$ ([**A1**] = 400 µM) exhibited π-π^* absorption bands at 261.5 nm, 357.5 nm, 376 nm, 396.5 nm (Figure 3a). The former 261.5 nm-band corresponds to the transition moment polarized along the long axis of the anthracene chromophore, and the latter three vibronic absorption peaks are polarized along the short axis.[15] Similar absorption spectra were also observed in other organic solvents with varied dielectric constants from hexane (1.9) to MeOH (32.6).[16] On the other hand, the absorption bands of **A1** dispersed in water ([**A1**] = 400 µM) showed a large red-shifted to 265.5 nm with considerable hypochromism, and small red-shifts to 358.5 nm, 377.5 nm and 398 nm. The observed spectral red-shifts are explainable in terms of exciton coupling between transition dipoles of the anthracene chromophores in self-assembled **A1**.[15] Such closely aligned chromophores would be beneficial for the triplet energy migration. Under UV excitation, the aqueous dispersion of **A1** showed a blue fluorescence with a high absolute quantum yield of 53% (Figure 3b).

To achieve an efficient donor-to-acceptor TTET, it is of key importance to molecularly disperse the donor in acceptor assemblies, which was confirmed by absorption measurements. The donor PtOEP molecules were dispersed in the aqueous **A1** assemblies by the following procedure. First, **A1** and PtOEP were homogeneously dissolved in $CHCl_3$, followed by evaporation of the solvent. Milli-Q water was added to the residue and the mixture was then sonicated for several minutes, giving a homogeneous aqueous dispersion of **A1**-PtOEP ([**A1**] = 400 µM, [PtOEP] = 1 µM). Figure 3c compares absorption spectra of

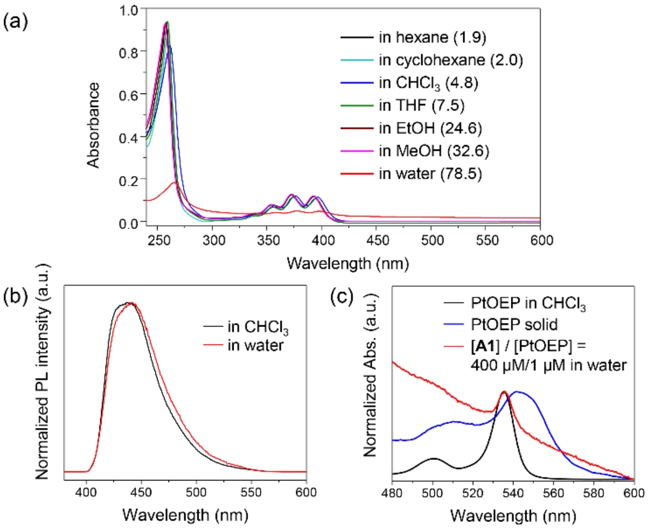

Figure 3. (a) UV-vis absorption spectra of **A1** in water and common organic solvents ([**A1**] = 400 μM, 298 K). Dielectric constants of each solvent are shown in blackets. (b) Fluorescence spectra of **A1** in $CHCl_3$ and water ([**A1**] = 400 μM, 298 K, λ_{ex} = 370 nm). (c) Normalized UV-vis absorption spectra of PtOEP $CHCl_3$ solution ([PtOEP] = 100 μM), bulk PtOEP solid, **A1**-PtOEP aqueous dispersion ([**A1**] = 400 μM, [PtOEP] = 1 μM).

PtOEP in $CHCl_3$, bulk PtOEP solid and **A1**-PtOEP aqueous dispersion. The absorption peak of bulk PtOEP at 542 nm showed a redshift as compared to that in $CHCl_3$ solution (536 nm), reflecting the electronic interactions in PtOEP crystals. Interestingly, an aqueous dispersion of **A1**-PtOEP showed a peak of PtOEP at 536 nm, which is identical to that observed for PtOEP in $CHCl_3$. This result indicates that the majority of the donor PtOEP is molecularly dispersed in the hydrophobic interior of the acceptor assemblies through hydrophobic interactions.

The aqueous dispersion **A1**-PtOEP was deaerated by repeated freeze-pump-thaw cycles, and the obtained specimen showed UC emission at 435 nm under excitation at 532 nm (Figure 4a, [**A1**] = 400 μM, [PtOEP] = 1 μM). A weak luminescence at 645 nm is ascribed to residual phosphorescence of PtOEP, and a peak at 784 nm is assignable to the emission from minorly-present aggregated PtOEP species.[17] The excitation intensity dependence and lifetime of UC emission were measured to confirm the TTA-based UC mechanism. Generally, the excitation intensity dependence of TTA-UC emission intensity shows quadratic and linear dependences in low- and high-power regimes, respectively.[18] A double logarithmic plot of UC emission intensity against excitation intensity showed a transition from the slope of ca. 2 to 1 (Figure 4b) at a threshold intensity I_{th} of 0.97 W cm^{-2}. It is also to note that a millisecond-scale fluorescence decay was observed at 430 nm, which is characteristic of the TTA-based UC emission via long-lived excited triplet states (Figure 4c). The triplet lifetime τ_T was estimated as 0.53 ms according to the known relationship of $I_{UC}(t) \propto \exp(-2t/\tau_T)$.[19] These results clearly demonstrate that the UC emission observed for aqueous **A1**-PtOEP is based on the TTA mechanism. A modest UC efficiency of 0.7% was observed at an excitation intensity of 18 W cm^{-2}. This UC efficiency is inferior to our previous work using the cationic amphiphilic acceptor probably due to the partial aggregation of the donor and the formation of quenching sites for triplet excitons.[11,20] We note that we employ an absolute method to estimate the TTA-UC efficiency of the turbid **A1**-PtOEP aqueous dispersion in an integrating sphere for the reliable estimation of absorbance. This method, however, underestimates the TTA-UC quantum yield due to the re-absorption of upconverted emission by the donor in the integrating sphere. We will separately report this technical issue more in detail. The UC emission was observed even from the frozen **A1**-PtOEP aqueous dispersion at 77 K, demonstrating the triplet energy migration mechanism among the aligned acceptor chromophores (Figure 4d).

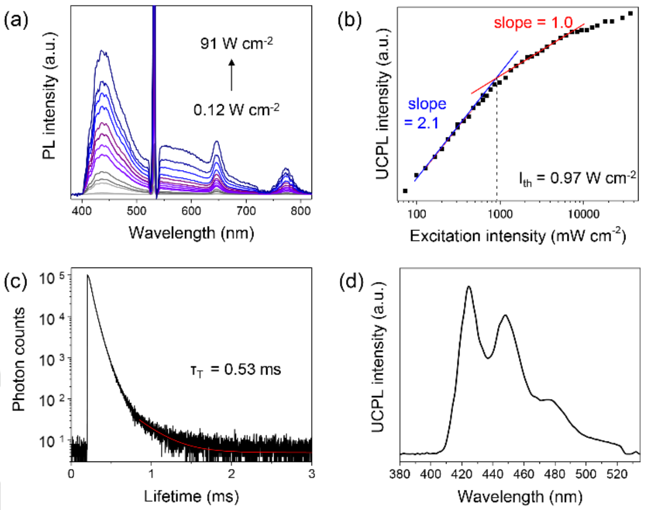

Figure 4. (a) Photoluminescence (PL) spectra of the **A1**-PtOEP deaerated aqueous dispersion at different excitation intensity of 532 nm laser ([**A1**] = 400 μM, [PtOEP] = 1 μM, 532 nm notch filter). (b) Excitation intensity dependance of UC emission intensity of **A1**-PtOEP deaerated aqueous dispersion. (c) UC emission decay of **A1**-PtOEP deaerated aqueous dispersion at 430 nm ([**A1**] = 400 μM, [PtOEP] = 1 μM, λ_{ex} = 531 nm). (d) Photoluminescence (PL) spectrum of frozen **A1**-PtOEP aqueous dispersion at 77 K ([**A1**] = 400 μM, [PtOEP] = 1 μM, λ_{ex} = 532 nm, excitation intensity = 7.2 W cm^{-2}, 532 nm notch filter).

Remarkably, the aqueous dispersion of **A1**-PtOEP ([**A1**] = 400 μM, [PtOEP] = 1 μM) showed an UC emission even under the aerated conditions (Figure 5a). In stark contrast, no UC emission was observed from an air-saturated $CHCl_3$ solution of **A1** and PtOEP at the same concentrations (Figure 5a). In addition, we did not observe any UC emission from the $CHCl_3$ solution even by increasing the excitation intensity from 6.7 W cm^{-2} to 34 W cm^{-2}. In $CHCl_3$, **A1** is molecularly dissolved as shown by the ^{1}H-NMR spectrum (Figure 2c) and the absence of detectable signals in DLS measurements ([**A1**] = 400 μM). The difference between oxygen concentrations in $CHCl_3$ (1.9 mM) and water (0.26 mM) would not be large enough to explain the observed difference in the UC emission intensity.[21] While the oxygen concentration is lower in water, it is usually necessary to remove oxygen from water to enable TTA-UC in the case of non-assembled, molecularly dissolved chromophores.[22] These results indicate that the observed air-stable TTA-UC is achieved by virtue of the simple hydrophobic assembly in water.

The stability of the UC emission under the stationary excitation with the 532 nm laser was further examined for the period of 1000 s with continuous stirring. The UC emission of the deaerated **A1**-PtOEP aqueous dispersion showed a slight continuous increase (Figure 5b). The reason for this behavior is currently unclear, but it could be related to the rearrangement of assembly structure upon the laser exposure. In air-saturated water, the UC emission of **A1**-PtOEP showed a gradual decrease but it remained observable for more than the period of 10 min. By considering the rather strong laser irradiance employed, the observed durability of UC emission in the aerated aqueous dispersion indicates the ability of amphiphilic self-assembly **A1** to reduce dissolution of molecular oxygen into the hydrophobic interior of the nanoassemblies. This is remarkable since **A1** does not have strong hydrogen bonding networks which have been shown to effectively prevent the incorporation of dissolved oxygen into self-assemblies.[2b, 11, 13b, 23] We note that our previous aqueous assemblies showed better stability under continuous excitation probably due to the strong hydrogen bonding networks. The optimization of the present simple hydrophobic self-assembly structure would further enhance the oxygen blocking ability.

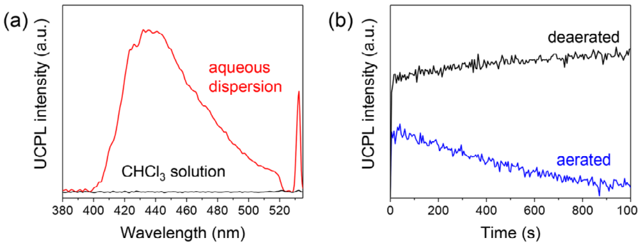

Figure 5. (a) UC emission spectra of **A1** and PtOEP in air-saturated water (red) and $CHCl_3$ (black) ([**A1**] = 400 μM, [PtOEP] = 1 μM, λ_{ex} = 532 nm, excitation intensity = 6.7 W cm^{-2}, 532 nm notch filter). (b) Time-dependence of the UC emission intensity of **A1**-PtOEP aqueous dispersion at 440 nm under continuous excitation at 532 nm in aerated (blue) and deaerated (black) condition (excitation intensity = 2.5 W cm^{-2}).

To explore the potential of the current nonionic assembly system, the UC emission measurement was carried out at even lower chromophore concentration, [**A1**] = 40 μM and [PtOEP] = 0.1 μM. DLS measurements confirmed the formation of assembly structure with a size of 141 ± 41 nm even under such an extremely diluted condition (Figure 6a). Significantly, even at this lower-concentration, UC emission efficiency (0.7% at an excitation intensity of 18 W cm^{-2}), threshold intensity I_{th} (2.9 W cm^{-2}, Figure 6b), and triplet lifetime (0.27 ms, Figure 6c) were maintained compared with the higher concentration dispersion. These results indicate the remarkable tolerance of basic UC properties against dilution, emphasizing the diversity and broadened utility of the current aqueous nanoassembly system. It was difficult to obtain UC emission spectra with a good signal-to-noise ratio below this concentration due to the sensitivity limit of the measurement setup. Significantly, the UC emission was observed from the aerated aqueous dispersion of 40 μM **A1** and 0.1 μM PtOEP (Figure 6d). From these results, the non-ionic amphiphilic molecular design is found to be powerful to achieve TTA-UC emission in air-saturated water even at very low chromophore concentration.

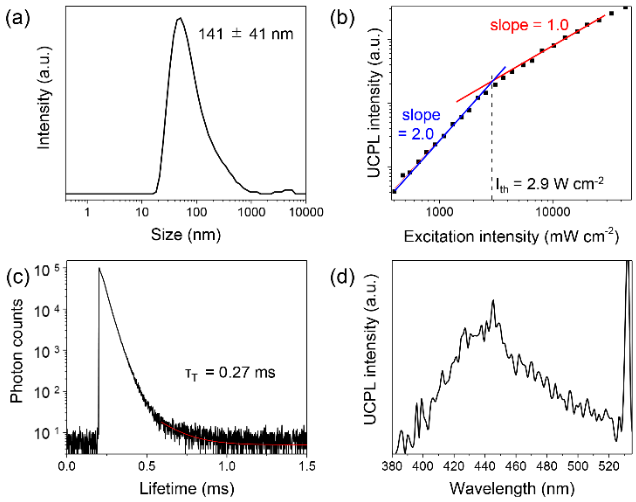

Figure 6. (a) DLS profile based on intensity distribution of diluted **A1**-PtOEP aqueous dispersion ([**A1**] = 40 μM, [PtOEP] = 0.1 μM). (b) Excitation intensity dependance of UC emission intensity of diluted **A1**-PtOEP deaerated aqueous dispersion ([**A1**] = 40 μM, [PtOEP] = 0.1 μM). (c) UC emission decay of diluted **A1**-PtOEP deaerated aqueous dispersion at 430 nm ([**A1**] = 40 μM, [PtOEP] = 0.1 μM, λ_{ex} = 531 nm). (d) Photoluminescence spectrum of diluted **A1**-PtOEP aerated aqueous dispersion ([**A1**] = 40 μM, [PtOEP] = 0.1 μM, excitation intensity = 8.2 W cm^{-2}, 532 nm notch filter)

Conclusions

In this work, we unveiled the unexplored oxygen-blocking ability of chromophoric assemblies based on the mastery amphiphilic molecular design with a nonionic oligo(ethylene glycol) head group and double-chained hydrophobic groups directly connected to the acceptor. TTA-UC emission in air-saturated water was achieved by the assembly of the novel non-ionic acceptor **A1** and the donor PtOEP at extremely low chromophore concentrations. The suitably designed amphiphilic acceptor **A1** enabled the stable self-assembly even at the low concentration down to 40 μM. The donor PtOEP was accommodated in acceptor assemblies with good dispersibility. Although the total chromophore concentration was low, the triplet energy migration in chromophoric self-assemblies resulted in the stable upconverted emission. The comparison between molecularly-dispersed and self-assembled conditions clearly demonstrated the essential role of the simple hydrophobic assembly to suppress the oxygen quenching of UC emission. The future generalization of the current nano-encapsulation strategy against oxygen quenching with different assembly structures would open new aspects and applications of supramolecular chemistry.

Experimental Section

Materials. All reagents and solvents for synthesis were used as received without further purification. Pt (II) octaethylporphyrin (PtOEP) was purchased from Aldrich and used as received. A synthetic scheme of the new acceptor **A1** is shown in the Supporting Information.

Characterizations. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (101 MHz) spectra were measured on a JNM-ECZ400S using TMS for $CDCl_3$ and DSS for

D_2O as the internal standard. The elemental analysis was carried out by using Yanaco CHN Corder MT-5 at the Elemental Analysis Center, Kyushu University. Dynamic light scattering measurements were carried out by using Malvern Nano-ZS ZEN3600. Absorption spectra were recorded on a JASCO V-770 spectrophotometer. Fluorescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. The absolute fluorescence quantum yield was measured in an integrating sphere using a HAMAMATSU multichannel analyzer C10027-01. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11367-02 (for fluorescence lifetime) and C11567-01 (for delayed luminescence lifetime).

For TTA-UC emission spectra, a diode laser (532 nm, 200 mW, RGB Photonics) was used as an excitation source. The laser power was controlled by combining a software (Ltune) and a variable neutral density filter and measured using a PD300-UV photodiode sensor (OPHIR Photonics). The laser beam was focused on a sample using a lens. The diameter of the laser beam ($1/e^2$) was measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics). A typical area of laser irradiation spot estimated from the diameter was 2.6×10^{-4} cm^2. The emitted light was collimated by an achromatic lens, the excitation light was removed using a notch filter (532 nm), and the emitted light was again focused by an achromatic lens to an optical fiber connected to a multichannel detector MCPD-9800 which was supplied and calibrated by Otsuka Electronics and equipped with a CCD sensor for the detection of whole visible range with high sensitivity.

TTA-UC efficiency was measured by using an absolute quantum yield measurement system C13534-01 (Hamamatsu Photonics).[2b] The sample was held in an integrating sphere and excited by the laser excitation source (532 nm, 200 mW, RGB Photonics). The scattered excitation light was removed using a 532 nm notch filter and emitted light was monitored with a multichannel detector. The spectrometer was calibrated including the integration sphere and notch filter by Hamamatsu Photonics. The absorbance of the lower concentration **A1**-PtOEP dispersion ([**A1**] = 40 μM, [PtOEP] = 0.1 μM) was difficult to be determined, and thus it was estimated as 10% of the absorbance of the higher concentration **A1**-PtOEP dispersion ([**A1**] = 400 μM, [PtOEP] = 1 μM). Note that the theoretical maximum of TTA-UC efficiency is standardized to be 1 (100%).

Acknowledgments

This work was partly supported by JSPS KAKENHI Grant Numbers JP25220805, JP17H04799, JP16H06513, JP16H00844, PRESTO program on “Molecular Technology and Creation of New Functions” from JST (JPMJPR14KE), and The Murata Science Foundation. We are grateful to Prof. D. Kohda, Prof. K. Mayanagi, and Dr. R. Ugawa at Medical Institute of Bioregulation, Kyushu University for the TEM observation and helpful discussions about the assembly structure.

Keywords: photochemistry • photon upconversion • self-assembly • oxygen quenching • triplet-triplet annihilation

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10.1002/asia.201801666

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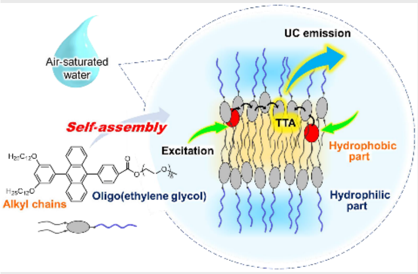
FULL PAPER

Simple molecular design for supramolecular assembly in water, oligo(ethylene glycol) and alkyl chain modification of chromophoric unit, is found to be effective to avoid oxygen quenching of photo-excited triplet state. Triplet-triplet annihilation (TTA)-based upconversion emission is obtained in air-saturated water even at low chromophore concentrations.



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Oligo(ethylene glycol)/alkyl-modified chromophore assemblies for photon upconversion in water