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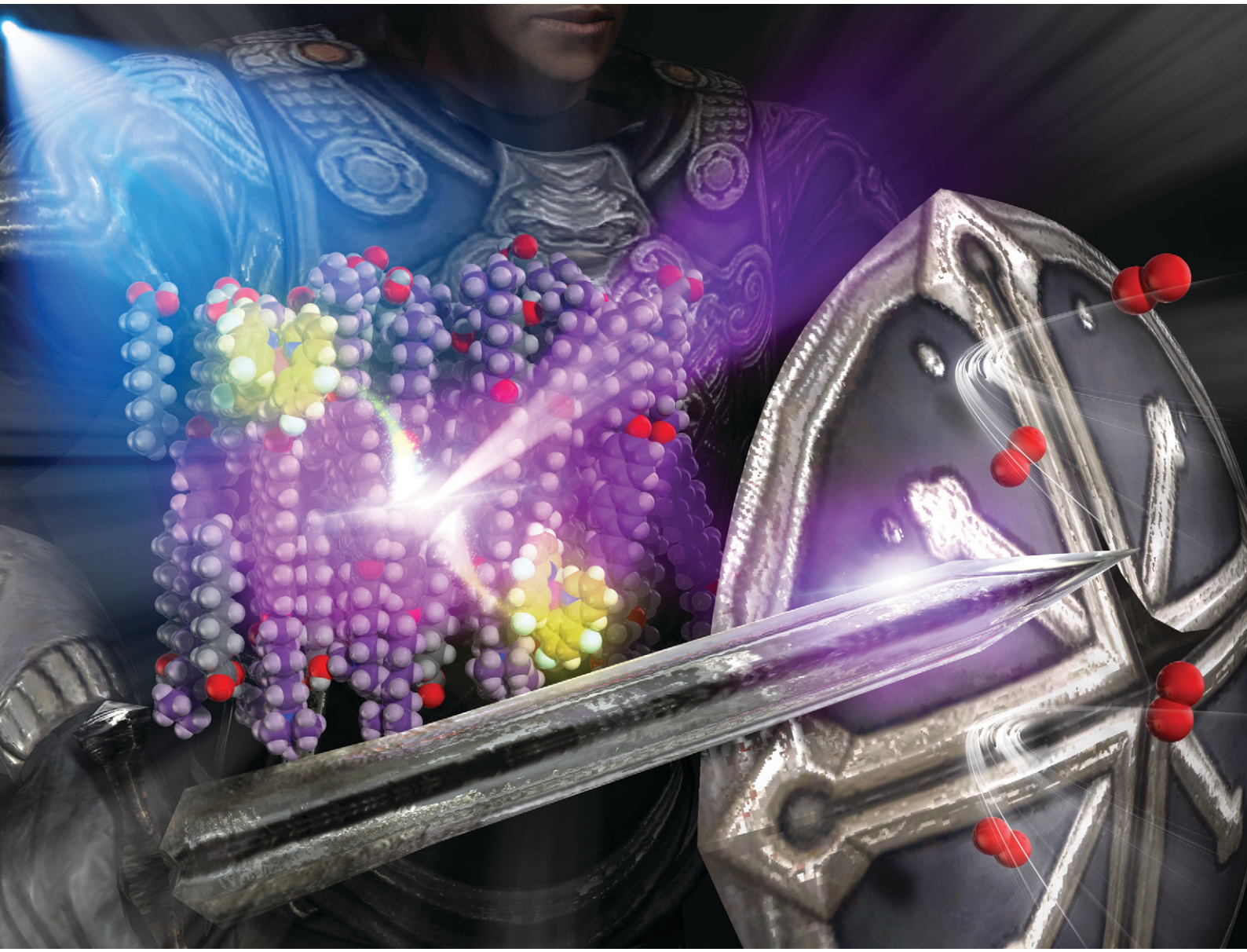

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Visible-to-UV photon upconversion in air-saturated water by multicomponent co-assembly†

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Air-stable, visible-to-UV photon upconversion based on triplet–triplet annihilation (TTA-UC) in water has been an outstanding issue despite its importance in a wide range of applications. This is achieved by giving oxygen barrier properties to cationic acceptor self-assemblies through ion complex formation with anionic fatty acids, *i.e.*, supramolecular crowding.

Design, System, Application

Ion-paring-based multicomponent self-assembly is proposed as a means to realize visible (vis)-to-ultraviolet (UV) triplet–triplet annihilation-based photon upconversion (TTA-UC) in air-saturated water. Generally, the photoexcited triplet state is deactivated by molecular oxygen, and therefore TTA-UC emission is quenched in air-saturated water. The development of a methodology to achieve air-stable vis-to-UV TTA-UC is highly desired to boost sunlight-powered renewable energy production such as water-splitting photocatalysis. An amphiphilic cationic acceptor is designed by modifying a typical vis-to-UV TTA-UC acceptor *p*-terphenyl with alkyl chain spacers and quaternary ammonium groups. This cationic acceptor is co-assembled with an anionic fatty acid through ionic and hydrophobic interactions, and a hydrophobic triplet donor is incorporated in the co-assemblies. The dense packing of alkyl moieties prevents the intrusion of oxygen molecules, resulting in the air-stable vis-to-UV TTA-UC emission. The current work offers an important rational strategy not only for TTA-UC but also for other functions based on air-sensitive photoexcited triplet states.

The efficient utilization of solar energy is the key to solve current energy problems. Water-splitting photocatalysts can convert solar energy into molecular hydrogen, which is anticipated as a clean energy source. Highly efficient water-splitting reactions occur under the illumination of ultraviolet (UV) light, however, the portion of UV light is limited to only *ca.* 5% in the whole solar irradiance.[1] Therefore, the visible (vis)-to-UV photon energy conversion is expected to expand the available wavelength range for water-splitting photocatalysis.

Photon upconversion (UC) is a method to convert lower-energy photons to higher-energy photons by combining the energy of multiple photons. For solar energy applications, photon upconversion based on triplet–triplet annihilation (TTA-UC) is particularly promising since it can operate under low-intensity light comparable to sunlight.[2–23] As summarized in Fig. S1,† TTA-UC is composed of two kinds of chromophores, a donor (triplet sensitizer) and an acceptor (emitter). Donor triplets are generated *via* intersystem crossing (ISC) from photoexcited singlets. Triplet energy transfer (TET) from the donor to the acceptor generates acceptor triplets. Two acceptor triplets generate a higher-energy singlet state of the acceptor through TTA, which results in the upconverted delayed fluorescence. As noted, the vis-to-UV TTA-UC is expected to boost the efficiency of photocatalytic reactions.[24–39] However, TTA-UC has a fatal problem where the photoexcited triplets are easily quenched by molecular oxygen dissolved in water. A common strategy to avoid oxygen quenching is to employ viscous droplets or polymers,[5,40,41] which inevitably makes the diffusion of large TTA chromophores slow.

As an alternative strategy, we have reported that the self-assembly of amphiphilic chromophores enables TTA-UC even in air-saturated water.[15,42–44] In this mechanism, TTA-UC occurs *via* triplet energy migration in densely self-assembled chromophore arrays and is not dependent on the conventional molecular diffusion. High oxygen blocking ability was achieved by co-assembly of cationic amphiphilic acceptors with anionic fatty acids, which increased the molecular density around the chromophores, the so-called supramolecular crowding.[44] Meanwhile, the demonstration of this strategy has been limited to the model vis-to-vis (green-to-blue) TTA-UC.

Here, we report the first example of air-stable vis-to-UV TTA-UC in water by generalizing the supramolecular design concept. We designed a novel UV-emitting bola-type amphiphile **A1** in which a *p*-terphenyl chromophore was

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† Electronic supplementary information (ESI) available: Experimental details, TTA-based UC mechanism, absorption and emission spectra. See DOI: 10.1039/d0me00003e

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introduced as an acceptor to perform vis-to-UV TTA-UC (Fig. 1).[31] Alkyl chains and quaternary ammonium groups are attached to the *p*-terphenyl skeleton as hydrophobic spacers and hydrophilic groups, respectively. Following our successful design for air-stable green-to-blue TTA-UC,[44] cationic **A1** was co-assembled with anionic decanoate (Dec) whose alkyl chain length is close to the alkyl spacer of **A1**. By introducing a visible light absorbing triplet donor FIrpic,[45] the ternary co-assemblies showed stable vis-to-UV TTA-UC even in air-saturated water.

The new amphiphilic acceptor **A1** was synthesized and characterized by ^{1}H NMR and elemental analysis (Scheme S1†). **A1** was molecularly dispersed in methanol, as confirmed by its concentration dependence of absorption spectra (Fig. S2†). The molecularly-dispersed **A1** in methanol ([**A1**] = 0.25 mM) showed a fluorescence peak at 358 nm (Fig. S3†) and a fluorescence quantum yield of 86%.

To form the vis-to-UV upconverting ternary molecular system, **A1** was co-assembled with FIrpic and Dec. The three components, **A1**, FIrpic and Dec, were mixed by dissolving in methanol and the ternary mixture was obtained by removing the solvent under reduced pressure. After adding water, ultrasonication and heating treatment of the mixture gave a pale-yellow translucent dispersion (Fig. 2a, [**A1**] = 10 mM, [FIrpic] = 100 μM and [Dec] = 80 mM). The appearance of this **A1**–FIrpic–Dec ternary dispersion is totally different from aqueous Dec and **A1** (Fig. 2a). Since the concentration of Dec is below its critical micellar concentration (cmc) of 86 mM, Dec provided a transparent solution.[46] **A1** was poorly soluble in water, and some precipitates were observed. However, a stable dispersion was obtained when Dec (80 mM) was added in excess as compared to the concentration of **A1** (10 mM). Apparently, the co-assembly of **A1** with Dec through electrostatic and hydrophobic interactions improved the dispersibility of **A1** in water.

Dynamic light scattering (DLS), zeta potential, UV-vis absorption, fluorescence, and scanning electron microscopy (SEM) measurements were performed to obtain further information about the ternary assembly. The DLS profile of the ternary dispersion of **A1**–FIrpic–Dec showed a particle size of

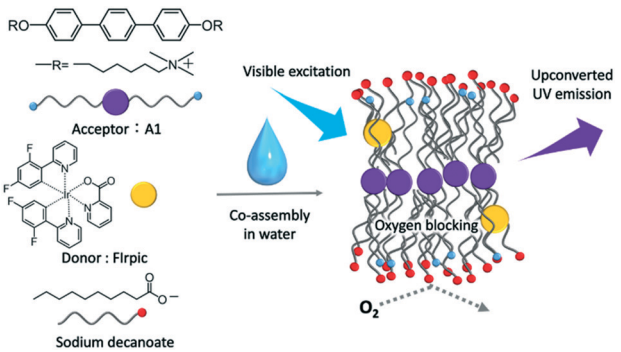

Fig. 1 Schematic illustration of the supramolecular system for air-stable aqueous vis-to-UV TTA-UC. Cationic acceptor **A1**, donor FIrpic, and anionic sodium decanoate (Dec) form aqueous co-assemblies with oxygen blocking ability.

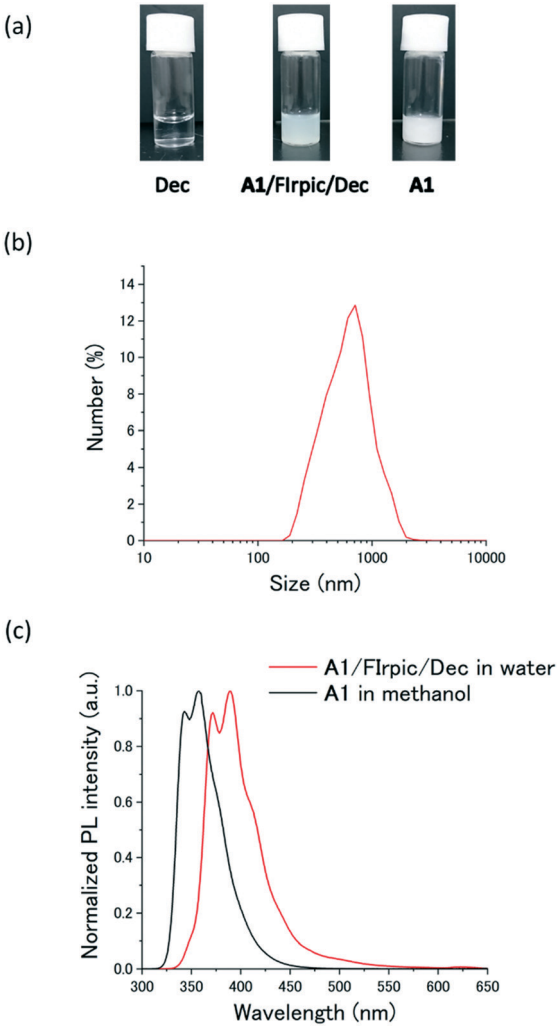

Fig. 2 (a) Photographs of Dec ([Dec] = 80 mM), **A1**–FIrpic–Dec ([**A1**] = 10 mM, [FIrpic] = 100 μM, [Dec] = 80 mM), and **A1** ([**A1**] = 10 mM) in water. (b) DLS profile of **A1**–FIrpic–Dec in water ([**A1**] = 10 mM, [FIrpic] = 100 μM, [Dec] = 80 mM). (c) Fluorescence spectra of **A1** in methanol (black, [**A1**] = 0.25 mM, λ_{ex} = 241 nm) and **A1**–FIrpic–Dec in water (red, [**A1**] = 10 mM, [FIrpic] = 100 μM, [Dec] = 80 mM, λ_{ex} = 280 nm).

871 ± 28 nm (Fig. 2b) that was close to that of the binary system **A1**–Dec (Fig. S4†). The SEM images of **A1**–FIrpic–Dec also showed a particle size of around 1 μm and a featureless morphology (Fig. S5†). The co-assembly of **A1** with excess Dec anions was further supported by the negative zeta potential of −24.7 mV observed for **A1**–FIrpic–Dec. Compared with the fluorescence peak at 358 nm of the molecularly-dispersed **A1** in methanol, a fluorescence spectrum of the **A1**–FIrpic–Dec ternary dispersion showed a redshift to 391 nm, which is still in the UV range (Fig. 2c). We also observed red-shifts in the excitation spectrum of aqueous **A1**–FIrpic–Dec as compared to that of **A1** in methanol (Fig. S6†). These results suggest the presence of excitonic interactions among the terphenyl chromophores in the aqueous co-assemblies.

The TTA-UC properties of the **A1**–FIrpic–Dec ternary co-assemblies were then characterized in deaerated water. The aqueous dispersion of **A1**–FIrpic–Dec ([**A1**] = 10 mM, [FIrpic]

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= 100 μM and [Dec] = 80 mM) was deaerated by repeated freeze–pump–thaw cycles. Under the irradiation of a visible laser at 445 nm, the aqueous dispersion showed upconverted UV emission at around 390 nm (Fig. 3a). The double logarithmic plots of the UC emission intensity at 390 nm against the excitation intensity showed a slope change from 2 to 1, which is a typical characteristic of TTA-UC (Fig. 3b).[47–49] Furthermore, the upconverted emission was observed for the microsecond scale, supporting the delayed fluorescence mechanism *via* the long-lived triplet state (Fig. S7†). Although the TTA-UC efficiency was not high (0.1% at 10 W cm^{-2}) compared with previous vis-to-UV TTA-UC systems,[24–39] this is partly due to a reduced fluorescence quantum yield (~26%) in the aqueous co-assemblies. It is also possible that the deactivation of triplets occurred at strongly interacting sites.[50] The optimization of the chemical structure of amphiphilic acceptors and the co-assembly conditions to improve the TTA-UC efficiency is an important future task. It is necessary to satisfy the balance between the optimized interchromophore interactions for the high TTA-UC efficiency and the high molecular packing density for oxygen blocking as mentioned below.

Significantly, the ternary **A1**–FIrpic–Dec co-assemblies showed a stable vis-to-UV TTA-UC emission even in air-saturated water (Fig. 4a). The oxygen-barrier efficiency (Φ_{OB}) was estimated by the time dependence of the UC emission

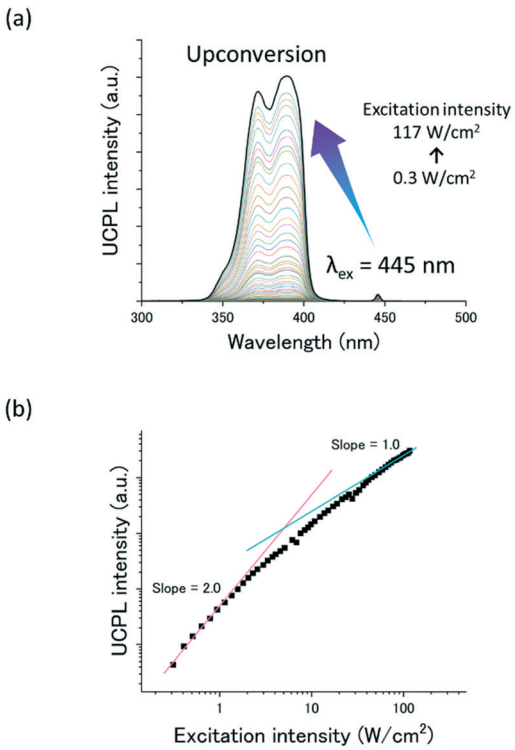

Fig. 3 (a) Photoluminescence (PL) spectra of **A1**–FIrpic–Dec in deaerated water ([**A1**] = 10 mM, [FIrpic] = 100 μM, [Dec] = 80 mM, λ_{ex} = 445 nm). Scattered excitation laser light was removed using 400 and 425 nm short-pass filters. (b) Excitation intensity dependence of the UCPL intensity of **A1**–FIrpic–Dec in deaerated water at 390 nm. The red and blue lines are the fitting results with slopes 2.0 and 1.0, respectively.

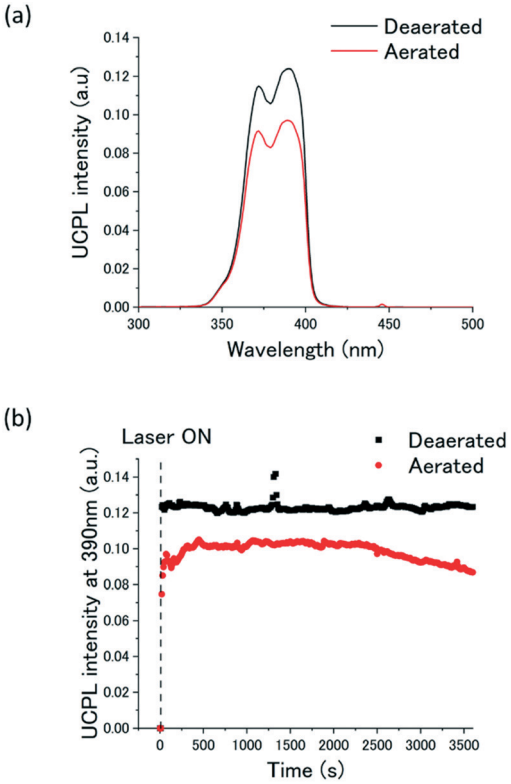

Fig. 4 (a) PL spectra of **A1**–FIrpic–Dec in deaerated (black) and aerated (red) water under 445 nm excitation ([**A1**] = 10 mM, [FIrpic] = 100 μM, [Dec] = 80 mM). Scattered excitation laser light was removed using 400 and 425 nm short-pass filters. (b) Time dependence of the UCPL intensity of **A1**–FIrpic–Dec in deaerated (black) and aerated (red) water at 390 nm.

intensity at 390 nm. It was found that the UC emission was maintained for more than one hour even in aerated water (Fig. 4b). By comparing the time-averaged UC emission intensity of the degassed and aerated samples, the Φ_{OB} was calculated as $\Phi_{OB} = I_{UC,aerated}/I_{UC,deaerated}$ = 80%, which is comparable to our previous aqueous co-assembled system showing air-stable green-to-blue TTA-UC.[44] In our previous work, we have shown that the oxygen blocking ability can be provided by enhancing the packing density of chromophores and alkyl chains in the aqueous co-assemblies. While it is difficult to study the effect of alkyl chain length in the current study due to the poor dispersibility of the co-assemblies with longer alkyl chains, our previous work also showed that the longer alkyl chain of the counter anions leads to a higher oxygen-barrier efficiency. It is notable that such a supramolecular crowding strategy which takes advantage of ion-paring-based co-assembly is generalized for single-chained, bola-type acceptor amphiphiles that lead to the aqueous vis-to-UV TTA-UC even under the aerated conditions.

Conclusions

In this work, we showed the first example of air-stable vis-to-UV TTA-UC in water. The novel anionic amphiphilic acceptor **A1** was co-assembled with the donor FIrpic and the cationic lipid Dec in water. The ternary aqueous co-assemblies showed a high

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oxygen barrier efficiency Φ_{OB} of 80%. The current system clarified the generality of our previous supramolecular crowding strategy in which the enhancement in molecular packing density in aqueous co-assemblies provided the remarkable oxygen blocking ability.[44] This work provides important design guidelines to protect air-sensitive species in water for various applications, including visible-light-driven water splitting.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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