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Photon Upconverting Liquids: Matrix-Free Molecular Upconversion Systems Functioning in Air

Pengfei Duan, Nobuhiro Yanai,* and Nobuo Kimizuka*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), JST CREST, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

Supporting Information

ABSTRACT: A nonvolatile, in-air functioning liquid photon upconverting system is developed. A rationally designed triplet sensitizer (branched alkyl chain-modified Pt(II) porphyrin) is homogeneously doped in energy-harvesting liquid acceptors with a 9,10-diphenylanthracene unit. A significantly high upconversion quantum yield of ~28% is achieved in the solvent-free liquid state, even under aerated conditions. The liquid upconversion system shows a sequence of efficient triplet energy transfer and migration of two itinerant excited states which eventually collide with each other to produce a singlet excited state of the acceptor. The observed insusceptibility of upconversion luminescence to oxygen indicates the sealing ability of molten alkyl chains introduced to liquefy chromophores. The involvement of the energy migration process in triplet−triplet annihilation (TTA) provides a new perspective in designing advanced photon upconversion systems.

Upconversion (UC), the population of luminescent higher-energy excited state with excitation at lower-energy light, has attracted much attention because of its potential to overcome the thermodynamic efficiency limits in solar energy conversion devices.[1] The most actively investigated UC systems are based on nonlinear phenomena such as multiple-photon absorption which, however, suffer from a fateful flaw in requiring high excitation intensities (~MW/cm^2) that detracts from its appeal.[2] Consequently, an alternative UC mechanism based on the triplet−triplet annihilation (TTA, Figure S1 in Supporting Information [SI]) has come under the spotlight since it offers numerous advantages over the aforementioned techniques.[3] For example, noncoherent light with low excitation power density can be used to achieve UC, with excitation/emission wavelengths tunable, depending on the independently selected donor and acceptor molecules. A triplet excited state of sensitizer (donor) is formed by intersystem crossing from the excited singlet state, which exerts triplet−triplet energy transfer (TTET) in the presence of suitable acceptors (Figure S1, SI). When two acceptor molecules in the triplet state diffuse and collide during their lifetimes, a higher singlet energy level is populated by TTA which consequently produces delayed fluorescence.

To date, efficient UC has been achieved in solution because diffusion of triplet molecules is essential for both of the TTET and TTA processes. However, the use of volatile organic solvents and deactivation of triplet states by molecular oxygen significantly limit their practical applications. Although recently the TTA-based UC has been investigated in solid polymer films,[4] such macromolecular matrices inevitably restrict the diffusion of triplet molecules that limit the efficiency of UC. To solve problems in the conventional dispersion systems, it is essential to develop an oxygen-impermeable TTA system which exerts migration of triplet excitons among densely clustered chromophores. Here we present a first example of solvent-free UC in liquid molecular networks; a set of organic donor and liquid acceptor chromophores displays a sequence of efficient triplet energy transfer, migration, and TTA in the matrix-free liquid state (Figure 1). It is known that the modification of aromatic chromophores with branched alkyl chains gives nonvolatile organic liquids.[5] Although luminescence characteristics of some liquid chromophores have been reported,[5] triplet energy transfer, migration, and consequent photon UC in such

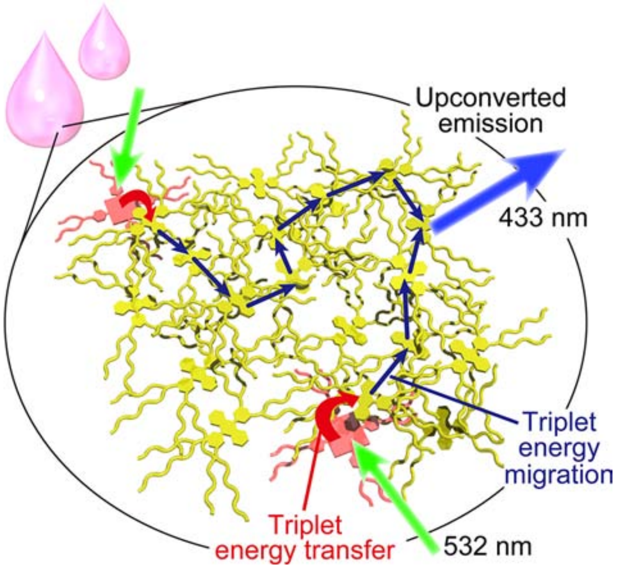

Figure 1. A schematic representation of the matrix-free liquid UC system. Donor molecules (red) in acceptor liquid (yellow) are excited by long-wavelength light. This is followed by a sequence of TTET from the donor to the acceptor, triplet energy migration, TTA, and delayed fluorescence from the upconverted singlet state of the acceptor.

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photofunctional liquids have not been achieved. With this in mind, we synthesized an organic liquid acceptor with a 9,10-diphenylanthracene moiety[6] and a branched alkyl chain-containing Pt(II) porphyrin derivative as a triplet sensitizer (donor) (Figure 2). This pair of chromophores was selected since 9,10-diphenylanthracene (acceptor and emitter) and Pt(II) octaethylporphyrin (PtOEP, sensitizer) have been popularly used as a benchmark in solution UC systems.[3c,f] Branched alkyl chains were introduced in the periphery of **2**, in order to ensure good miscibility with the liquid acceptor **1**.

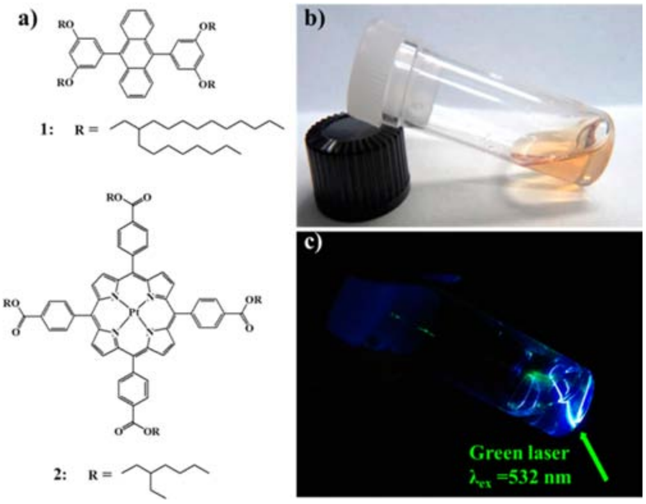

Figure 2. (a) Chemical structures of liquid acceptor **1** and sensitizer **2**. Photographs of the doped liquid (**2**/**1** = 0.01 mol %) upon being exposed to (b) white light and (c) 532 nm green laser (incident laser direction is indicated by a green arrow). Bright blue luminescence is due to UC emission, and green spots are scattered incident laser.

The nonvolatile liquid **1** showed strong blue emission under UV light (Figure S2, SI). Differential scanning calorimetry (DSC), rheology, X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS) experiments confirmed the fluid nature of **1** at ambient temperature (Figures S3−S5, SI). The DSC and rheology results indicated a glass transition temperature at −59 °C and a low-viscosity of 0.99 Pa·s, respectively. The diphenylanthracene chromophores in liquid **1** showed an averaged core-to-core distance of 2.1 nm by SAXS measurement. When PtOEP was used as donor, it was not molecularly dissolved in **1**, and irregular crystalline structures were observed under polarized optical microscopy (Figure S6, SI). Meanwhile, the sensitizer **2** modified with branched alkyl chains was homogeneously miscible with liquid **1** in the examined concentration range up to **2**/**1** = 1 mol %. To optimize the donor-to-acceptor ratio, we measured absolute emission quantum yields of **1** at various mixing ratios (**2**/**1** = 0.001−1 mol %, λ_{ex} = 365 nm; Table S1 in SI). **1** in the pure liquid form showed a high quantum yield of 0.68, while its fluorescence underwent quenching upon increasing the molar ratio of **2** notably above 0.1 mol %. It indicates the occurrence of singlet Förster resonance energy transfer from **1** to **2** at the higher doping ratio. Accordingly, **2** was added to **1** at the low molar ratio of 0.01 mol % in all of the following experiments.

Figure 3a presents normalized absorption and emission spectra of **1** and **2** in $CHCl_3$ (concentration, 0.1 mM). **1** showed a typical vibrational structure of the L_a absorption band (320−390 nm), with its fluorescence observed with a maximum at 433 nm. On the other hand, **2** exhibited Soret- and Q-bands at 403 and 510 nm, respectively. When **2** dissolved in deaerated $CHCl_3$ was photoexcited at 520 nm, phosphorescence was observed at 660 nm. Absorption and fluorescence spectra of **1** without solvent are shown in Figure 3b. The liquid **1** showed a less-structured absorption band, reflecting molecular crowding in the liquid. Meanwhile, the fluorescence spectrum of **1** in its pure liquid form is almost identical to that observed in $CHCl_3$ solution.

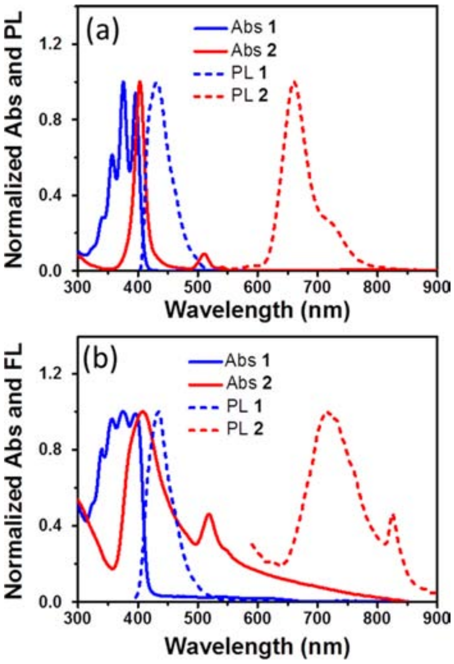

Figure 3. (a) Normalized absorption and emission spectra of $CHCl_3$ solution of **1** (λ_{ex} = 375 nm, 0.1 mM) and **2** in deaerated $CHCl_3$ (λ_{ex} = 510 nm, 0.1 mM). (b) Normalized absorption and emission spectra of liquid **1** (λ_{ex} = 375 nm) and cast film of **2** (λ_{ex} = 520 nm).

Consistently, the fluorescence lifetimes and quantum yields for **1** in pure liquid were comparable to those observed for dilute $CHCl_3$ solution (Figure S7, Table S1 in SI). These observations indicate the absence of strong electronic interactions among chromophores in the ground or excited states in liquid **1** (Figure 3b). On the other hand, the sensitizer **2** doped in liquid acceptor **1** (**2**/**1** = 0.01 mol %) showed a Q-band at 511 nm (Figure S8, SI), which is almost identical to that of **2** dissolved in $CHCl_3$. Note that aggregates of **2** in cast films showed spectral shift in λ_{max} to 518 nm (Figure 3b). Together with the polarized optical microscope observation, we conclude that **2** is molecularly dispersed in liquid **1**.

Figure 4a shows steady-state luminescence spectra of **2**-doped liquid **1** obtained at varied incident laser power (**2**/**1** = 0.01 mol %). Very interestingly, blue UC emission peaks were clearly observed upon excitation of **2** by a 532 nm green laser. The spectral shape of UC emission (λ_{ex} = 532 nm) is similar to that of the normal fluorescence (λ_{ex} = 375 nm; Figure 3b). It is noteworthy that the phosphorescence of sensitizer **2** was completely quenched regardless of the excitation power, indicating the efficient triplet−triplet energy transfer from **2** to the acceptor liquid **1**. To prove the TTA-based UC mechanism, dependence on the power density of incident light was investigated. In general, TTA-assisted UC shows a quadratic incident light power dependence of emission intensity in the weak-annihilation limit, which consequently

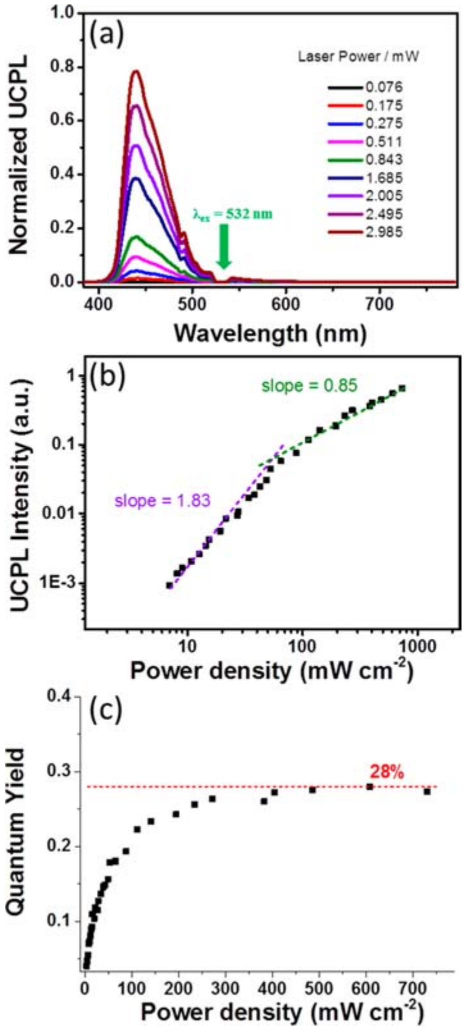

Figure 4. (a) Photoluminescence spectra of the doped liquid (**2**/**1** = 0.01 mol %) with different incident power density of 532 nm laser in air. (b) Dependence of UC emission intensity at 433 nm on the incident power density (**2**/**1** = 0.01 mol %). The dashed lines are fitting results with slopes of 1.83 (purple) and 0.85 (green) in the low- and high-power regimes, respectively. (c) Quantum yield of the doped liquid (**2**/**1** = 0.01 mol %) measured as a function of 532 nm incident power density.

turns into first-order dependence in the saturated annihilation regime.[7] Figure 4b presents a double logarithm plot for the UC emission intensity of the **2**-doped liquid **1** (**2**/**1** = 0.01 mol %) as a function of incident light power density (λ_{ex} = 532 nm). At the lower-power regime of <50 mW cm^{-2}, a slope close to 2 was observed, whereas it changed to ~1 at higher-power density (>50 mW cm^{-2}). It provides decisive experimental evidence for TTA-based photon UC in this solvent-free liquid system. It is noteworthy that the crossover threshold was observed at a relatively low power density around 50 mW cm^{-2}, which is comparable to those reported for the solvent-free polymer systems.[4f,8] The TTA-based UC in the present liquid system was further characterized by the luminescence decay measurements. The UC emission of the doped liquid (**2**/**1** = 0.01 mol %) showed a decay in the millisecond time scale under excitation at 531 nm, which is significantly longer than the fluorescence lifetime of pure liquid **1** (τ = 7.6 ns; λ_{ex} = 365 nm; Figure S7 in SI). Such prolonged luminescence decay is characteristics of the TTA-based UC processes which occurred via long-lived triplet states.

We then quantified the UC efficiency of the **2**-doped liquid (**2**/**1** = 0.01 mol %) by using Nile red-dissolved liquid **1** (concentration, 0.01 mol %) as a reference (see SI for details).[3a,9] Figure 4c shows a dependence of quantum yield on the excitation power density, in which each represents an average of at least three independent measurements using different batches. With increase in the power density, the quantum efficiency increased and reached saturation at 28%. Another set of experiments conducted by using rhodamine B in liquid **1** as a reference also reproducibly gave similar quantum yields. The observed remarkably high quantum yield is close to the highest records reported for solvent-free UC systems,[4f,8] showing a great potential of the present liquid upconverting system. Although higher concentration of the sensitizer is desirable to generate excited triplet states in higher density, the donor/acceptor molecular ratio (**2**/**1** = 0.01 mol %) employed was optimal in terms of UC quantum yield. At the higher donor/acceptor ratio of **2**/**1** = 0.1 mol %, the obtained quantum yield showed a decrease to 13% because of the lower fluorescence efficiency of **1** caused by the quenching via singlet energy transfer to **2** (Table S1, SI).

As described before, strict deoxygenation treatment is generally inevitable in solution to achieve UC phenomena since oxygen molecules quench triplet excited states[7] and it severely hampers their real-life applications. Upconverted emission has been exceptionally observed under aerated conditions by using rubber polymers,[4f,8] soybean oil,[3e] and a hexadecane/polyisobutylene mixture[3g] as matrices, in which the diffusion or concentration of oxygen was suppressed by these matrices. We therefore investigated sensitivity of the present liquid TTA-UC system to molecular oxygen. Remarkably, the current liquid UC system is unperturbed by the presence of oxygen molecules. The UC data obtained in vacuo—UC emission spectra, incident light power dependence of UC emission, and UC luminescence decay for **2**-doped liquid **1** (**2**/**1** = 0.01 mol %)—were almost identical to those obtained in air (Figures S7 and S9, SI). There was no obvious loss in the quantum efficiency within 20 days of air exposure, and a good quantum yield as high as 15% was still observed even after the longer period of 80 days (Figure S10, SI). These results are explicable by suppressed diffusion of oxygen molecules into liquid chromophores, indicating an air-sealing effect of molten alkyl chains introduced around the chromophores.

To prove the presence of triplet energy migration in the liquid acceptor UC system, UC experiments were conducted in the low-temperature glassy state. As shown in Figure S11 (SI), the relative UC emission intensity at 433 nm decreased with the decrease in temperature (**2**/**1** = 0.01 mol %; λ_{ex} = 532 nm).[4b] It is noteworthy that the UC emission is observed even below the glass transition temperature (−59 °C), with ~20% of the intensity preserved compared to those observed at ambient temperatures. This result clearly demonstrates that the triplet energy migration occurs among frozen acceptor molecules, without the help of molecular diffusion. This is a remarkable feature contrasting strongly with the previous solution/polymer dispersion systems in which UC emissions were completely suppressed below the frozen temperature of matrices.[4b] The involvement of triplet energy migration is a unique characteristic of the photon UC in condensed chromophores. It is understood that triplet energy transfer and energy migration occur via the electron exchange mechanism (Dexter excitation transfer).[10] It requires overlap of wave functions between donors and acceptors, and consequently, it has a much steeper exponential dependence on distance compared to that displayed by the dipole−dipole coupling mechanism (Förster resonance transfer), which occurs over distances considerably exceeding the sum of their van der Waals radii. Although the acceptor molecules **1** in the liquid state exhibited very short-ranged structural order as indicated by XRD data (Figure S5, SI), they lack long-range molecular ordering. Nevertheless, the observed efficient UC indicates the occurrence of facile triplet energy transfer between the donor−acceptor pairs (**2**−**1**) and triplet energy migration among the adjoining liquid acceptor molecules **1**. To achieve these performances, it is expected that the reorientation of excited triplet molecules in between the neighboring molecules is required to maximize the overlap of wave functions. The temperature dependence observed in Figure S11 (SI) therefore demonstrates the involvement of triplet energy migration processes which are thermally facilitated. It appears natural that such chained electron-exchange processes assume diffusion and efficient collision of triplet excitons in the condensed liquid chromophores.

The significance of the present study is three-fold. First, it demonstrates the first example of solvent-free liquid photon UC systems. Introduction of branched alkyl chains to both of the donor and acceptor molecules ensured their good miscibility, leading to a high quantum efficiency of ∼28%. Second, migration of triplet excited states occurs among liquid acceptor molecules. This is the first liquid TTA-UC system in which energy migration entered into the picture. Third, the liquid UC system keeps function even in air, due to the impermeable nature of molten alkyl chains introduced to acceptor molecules. This is in stark contrast with conventional solution UC systems which require the strict deaeration procedures. Integration of the air-stable, long-lived triplets in the photon upconverting liquids with the concepts of molecular self-assembly[11] would allow us to molecularly control energy landscapes of the collective excited states.[11] It should offer a new avenue for supramolecular photon UC systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization of liquid **1** (DSC, rheology, XRD, SAXS), luminescence decays, absolute quantum yield, temperature-dependent UC emission. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

yanai@mail.cstm.kyushu-u.ac.jp
n-kimi@mail.cstm.kyushu-u.ac.jp

Notes

The authors declare no competing financial interest.

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