Ionic Liquids

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Photon-Upconverting Ionic Liquids: Effective Triplet Energy Migration in Contiguous Ionic Chromophore Arrays

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Abstract: *Inspired by the bicontinuous ionic-network structure of ionic liquids (ILs), we developed a new family of photofunctional ILs which show efficient triplet energy migration among contiguously arrayed ionic chromophores. A novel fluorescent IL, comprising an aromatic 9,10-diphenylanthracene 2-sulfonate anion and an alkylated phosphonium cation, showed pronounced interactions between chromophores, as revealed by its spectral properties. Upon dissolving a triplet sensitizer, the IL demonstrated photon upconversion based on triplet–triplet annihilation (TTA-UC). Interestingly, the TTA-UC process in the chromophoric IL was optimized at a much lower excitation intensity compared to the previous nonionic liquid TTA-UC system. The superior TTA-UC in this IL system is characterized by a relatively high triplet diffusion constant (1.63×10^{-6} cm^2 s^{-1}) which is ascribed to the presence of ionic chromophore networks in the IL.*

Photon upconversion (UC) is the process of converting lower-energy photons into higher-energy photons. Triplet–triplet-annihilation-based UC (TTA-UC) has particularly attracted attention for solar energy and biological applications as it works with low-power excitation light such as sunlight.[1–13] A TTA-UC system consists of triplet donors (sensitizers) and acceptors (emitters), as shown schematically in Figure S1 in the Supporting Information. The collision of two triplet acceptors, populated by triplet–triplet energy transfer (TTET) from photoexcited donors, leads to TTA within the lifetimes of the acceptor triplets. The annihilation generates a higher-energy excited singlet state, from which upconverted delayed fluorescence occurs. Because the TTET and TTA processes proceed via an electron-exchange Dexter mechanism, the excited triplet molecules need to be in close proximity to each other, within a distance of 1 nm, to allow the overlap of molecular orbitals.

Although efficient TTA-UC has been achieved by using fast molecular diffusion in solutions,[1,9,10] the use of such volatile organic solvents significantly hampers their real-world application. To develop nonvolatile TTA-UC systems, previous approaches introduced rubbery polymers[14–18] or involatile liquids[6,7,19,20] as matrices for the diffusion of molecules in the triplet excited state. However, molecular diffusion is inevitably limited in these viscous environments, which consequently required an undesirably high intensity of excitation light. An innovative solution for these issues is to change the strategy from molecular diffusion to energy migration among dye assemblies.[12,13,21–23] We have previously reported the first example of a matrix-free, efficient TTA-UC system based on a nonionic liquid acceptor having multiple branched alkyl chains.[12] This liquid-phase upconversion material has many advantages, such as nonvolatility and transparency, but it unfortunately required a relatively high excitation-light intensity to optimize the TTA-UC processes. This is due to the bulky alkyl chains introduced onto the acceptors which impeded effective triplet energy migration among them. It is therefore highly desirable to realize a much closer arrangement of acceptor molecules and the formation of continuous chromophore networks that facilitate the diffusion of excited triplet states.

In this work, we report the first example of TTA-UC using chromophoric ionic liquids (ILs) that contain ionic acceptors. Several reports on imidazolium-cation-based ILs showed that the polar charged moieties form interconnected three-dimensional ionic networks by segregation from the nonpolar alkyl chains.[24–28] Inspired by this bicontinuous ionic-molecular-network arrangement, we envisaged the formation of an interconnected array of aromatic chromophores in ILs that serve as effective pathways for triplet energy migration (Figure 1). A newly developed chromophoric IL **1** is composed of anions based on 9,10-diphenylanthracene (DPA) and alkylated phosphonium cations (Figure 1), where no alkyl chains were introduced onto the DPA chromophore. This IL showed salient interactions between chromophores which enabled fast triplet energy migration among acceptor molecules after quantitative TTET from the donor Pt^{II} octaethylporphyrin (PtOEP). These features allowed optimization of the TTA-UC processes at a relatively low excitation power.

The chromophoric IL **1**, synthesized from sodium 9,10-diphenylanthracene-2-sulfonate and trihexyl(tetradecyl) phosphonium chloride,[29] was fully characterized by various analytical methods (Figure S2–S4). The viscous liquid obtained emitted bright-blue fluorescence under UV excitation (Figure 2b,c). Differential scanning calorimetry (DSC) measurements of **1** showed a glass transition temperature at −30 °C (Figure S5). IL **1** exhibited a relatively high viscosity of 2760 Pa s at room temperature, as determined by rheological measurements (Figure S6).

To investigate the arrangement of chromophores in IL **1**, the UV/Vis absorption spectra of **1** were measured for the

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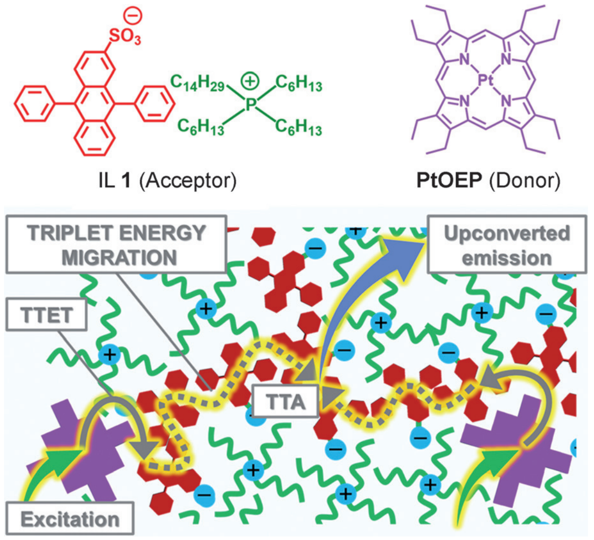

Figure 1. Chemical structures of IL **1** and Pt^{II} octaethylporphyrin (PtOEP) and schematic representation of nonvolatile TTA-UC systems using triplet energy migration in acceptor ILs.

neat IL and solutions of **1** in different solvents ([**1**] = 0.01 mM; Figure 2d). By changing the solvent polarity from methanol to cyclohexane, the ^1B_b absorption band of the anthracene unit exhibited small band shifts from $\lambda = 264$ to 267 nm, demonstrating that it was not particularly susceptible to solvent polarity. Meanwhile, the solvent-free IL **1** showed a significantly red-shifted and broadened absorption spectrum with a maximum absorption band at $\lambda = 272$ nm. Spectral red-shifts were also detected for the ^1L_a absorption band (Figure S7). These results clearly indicate the presence of intermolecular interactions among DPA chromophores in the neat IL state.[30] This is in contrast with the highly emissive nonionic liquids reported by Nakanishi et al. in which the DPA chromophore is covalently modified with multiple branched alkyl chains.[31,32] These nonionic liquids showed almost no spectral shifts from their solutions, reflecting the isolation of the DPA cores. Considering these differences, it is apparent that the absence of covalently attached alkyl chains to the DPA unit facilitated interactions between chromophores in IL **1**.

The presence of specific interactions between chromophores in IL **1** was further manifested by a red-shift in the fluorescence band detected for the solvent-free IL state ($\lambda =$ 454 nm) as compared to that recorded for the solution of **1** in methanol ($\lambda = 423$ nm; Figure 2c). Although the time-resolved fluorescence measurement of **1** in methanol solution showed a single-exponential decay with a lifetime of 7.3 ns, the neat IL **1** showed a biexponential decay with lifetimes of 3.7 ns (12.7 %) and 12.6 ns (87.3 %; Figure S8). Interestingly, the fluorescence quantum yield of **1** was slightly higher in the neat IL state (70 %) than in methanol (67 %; [**1**] = 0.01 mM) probably because of less overlap between the absorption and emission bands, that is, less self-absorption in the neat IL state. Hence, given the interactions of chromophores within **1** and the high quantum yield, IL **1** satisfies both criteria that would render it suitable for energy-migration-based TTA-UC.

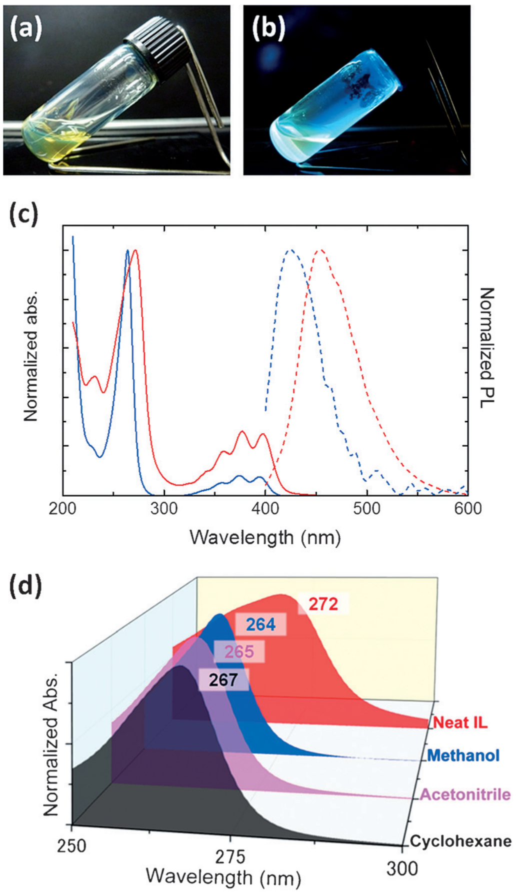

Figure 2. Photographs of IL **1** under a) white light and b) UV light ($\lambda_{ex} = 365$ nm). c) UV/Vis absorption (solid lines) and photoluminescence (PL; dashed lines) spectra of **1** in methanol (blue trace; [**1**] = 0.01 mM) and in the neat IL state (red trace). d) UV/Vis absorption spectra of **1** in various solvents ([**1**] = 0.01 mM) and in the neat IL state.

As a triplet sensitizer, PtOEP was employed because DPA and PtOEP have been popularly used as a benchmark acceptor/donor pair in solution-based TTA-UC systems.[2–5,8,10,11] The donor PtOEP was doped in the acceptor **1** by simply drying a dichloromethane solution containing **1** and PtOEP (0.01 mol % of PtOEP in **1**). The obtained liquid **1**–PtOEP was then sealed in a quartz cell (optical path length = 0.05 mm) in an Ar-filled glove box ($[O_2] < 0.1$ ppm). PtOEP was found to be homogeneously dissolved in IL **1**, as evidenced by the absence of crystalline aggregates when the liquid was examined under a polarizing microscope (Figure S9). Under excitation with a green-light-emitting laser at $\lambda_{ex} = 532$ nm, an upconverted blue emission was clearly detected around at $\lambda = 450$ nm (Figure 3a). The spectral shape of upconverted emission matches well with the normal fluorescence of the IL **1** (Figure 2c). Additionally, this UC emission showed a decay process on the millisecond timescale characteristics of TTA-UC through long-lived triplet states, giving a reasonably long acceptor triplet lifetime $\tau_{A,T}$ of 2.5 ms (Figure S10). The phosphorescence of donor PtOEP at around $\lambda = 650$ nm was not detected regardless of the excitation power, indicating complete quenching by

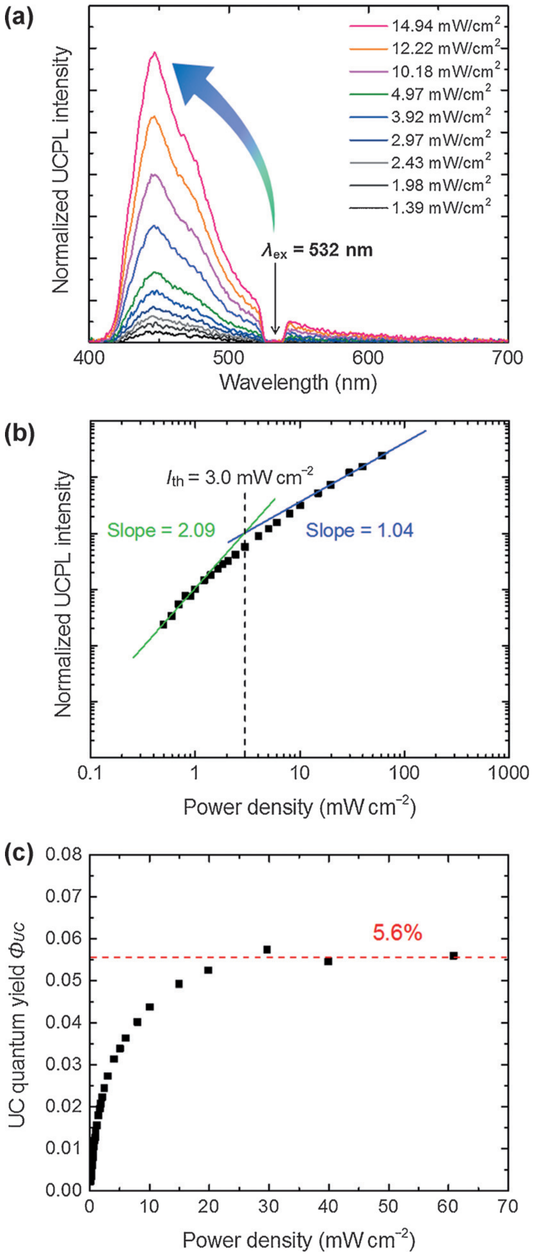

Figure 3. a) Photoluminescence spectra of the IL **1**–PtOEP sealed under Ar (0.01 mol% PtOEP in **1**) measured at different incident power densities using a laser with excitation wavelength $\lambda_{ex} = 532$ nm. A notch filter ($\lambda = 532$ nm) was used to remove the scattered excitation laser light. b) Dependence of UC photoluminescence (UCPL) intensity at $\lambda = 450$ nm on the incident power density (0.01 mol% PtOEP in **1**). The lines are fitting results with slopes of 2.09 (green, below 1.0 mW cm^{2}) and 1.04 (purple, above 15 mW cm^{-2}) in the low- and high-power regimes, respectively. c) TTA-UC quantum yield Φ_{UC} of **1**–PtOEP (0.01 mol% PtOEP in **1**) measured as a function of incident power density at excitation wavelength $\lambda_{ex} = 532$ nm.

donor-to-acceptor TTET. Notably, the UC emission was clearly detected even after being exposed to air for many days, similar to the previous nonionic liquid UC system (Figure S11).[12] However, to properly evaluate the effect of chromophore arrangement on TTA-UC, all the following measurements were carried out under deaerated conditions.

In general, TTA-UC emission intensity shows a quadratic dependence on the incident light power under low excitation power, which turns into linear dependence by increasing the excitation power.[33–35] A useful figure-of-merit of TTA-UC, threshold excitation intensity I_{th}, can be determined as occurring at the intersection of these two regimes. The efficiency of TTA (Φ_{TTA}) becomes 50% at I_{th}.[33–35] Figure 3b shows a double logarithmic plot for the UC emission intensity of solvent-free **1**–PtOEP as a function of incident-light power density. The plot clearly showed a transition from a quadratic to a linear dependence, providing evidence for TTA-UC in the IL. Remarkably, the obtained I_{th} value of 3.0 mW cm^{-2} is much lower than our previous result obtained for the neutral solvent-free liquid system (50 mW cm^{-2}),[12] and it is comparable to the solar irradiance of 1.6 mW cm^{-2} at $\lambda = 532 \pm 5$ nm.[13] The TTA-UC quantum yield (Φ_{UC}) was determined by the relative method using Nile red in the IL **1** as a standard (see the Supporting Information for details). Note that the theoretical maximum of Φ_{UC} is defined as 50% since two incident photons are used to produce one upconverted photon.[4,8] In agreement with the low I_{th} value, the Φ_{UC} value also saturated at low excitation power density around 20 mW cm^{-2} (Figure 3c). The saturated Φ_{UC} value of 5.6% is relatively high for solvent-free upconversion materials.[1–5,8–13] In the present system, there is a partial overlap between the donor absorption and acceptor IL emission, which may have decreased the Φ_{UC} value by a Förster energy-transfer mechanism. However it should be possible to further improve the UC efficiency by properly tuning the spectral properties of the donor and acceptor based on their chemical structures.

To understand the origin of the low I_{th} value in the liquid **1**–PtOEP system, the triplet diffusion constant D_T was estimated using Equation (1):

$$D_T = (8\pi a_0 \alpha \Phi_{ET} I_{th})^{-1} \tau_{A,T}^{-2} \qquad (1)$$

where a_0 is the effective triplet–triplet interaction distance (9.1 Å between two DPA molecules in the triplet excited state),[33] α is the absorption coefficient at excitation wavelength $\lambda_{ex} = 532$ nm, Φ_{ET} is the donor-to-acceptor TTET efficiency, and $\tau_{A,T}$ is the acceptor triplet lifetime.[33] It turns out that the D_T value of 1.6×10^{-6} cm^2 s^{-1} in IL **1** is significantly high as an amorphous material.[36,37] A triplet diffusion length in IL **1** was estimated as $L_T = (D_T \tau_{A,T})^{0.5} = 0.63$ μm. This is relatively large for amorphous materials, confirming the superior potential of chromophoric ILs as exciton diffusion media.

Considering the viscosity of IL **1** (2760 Pa s) and the molecular size of the DPA (0.45 nm),[33] the diffusion constant of the anion is estimated to be 1.76×10^{-12} cm^2 s^{-1} from the Stokes–Einstein equation. This value is circa six orders of magnitude smaller than that obtained from the upconversion data, indicating that the triplet excitons generated in IL **1** diffuse predominantly by energy migration rather than by molecular diffusion. This was further confirmed by measuring the temperature dependence of the triplet diffusion constant in IL **1** (Figure S12, Table S1). The TTA-UC emission was clearly detected below the glass transition temperature of

1 (−30 °C), demonstrating that triplet energy migration occurs among frozen acceptor molecules. As generally found, the triplet diffusivity gradually increased with the increase of temperature. It is notable that there is no drastic difference in the rate of increase of the triplet diffusivity between the glassy and liquid states. Although some contributions of local molecular reorientation would be involved in the liquid state, these results are reasonably explained by assuming the formation of developed chromophore networks in the IL, which is consistent with the spectroscopic properties of the system (Figure 2). Therefore, we draw the conclusion that contiguous ionic chromophore arrays provide efficient triplet energy migration pathways in IL **1**.[24,25]

To further support the presence of chromophore networks in IL **1**, we carried out control experiments by preparing a new IL, denoted **2**, composed of 9,10-dimethoxyanthracene-2-sulfonate anions (Figure S13a). This anion has two methoxy groups instead of two phenyl groups in the anion of **1**, giving rise to less steric hindrance around the anthracene moiety. The methoxylated anion should lead to better intermolecular orbital overlaps, whereas the decrease in the size of the aromatic units may also decrease the cohesive energy between chromophores and thus enhance the miscibility with aliphatic cations.[38] The absorption spectrum of **2** in the solvent-free state showed a red-shift compared with that in methanol (Figure S13c), but the energy difference associated with the red-shift (2.5 nm, 0.043 eV) was much smaller than in the case of **1** (7.5 nm, 0.13 eV; Figure 2 d). The larger red-shift indicates the presence of stronger interactions between chromophores in IL **1**. The TTA-UC properties of IL **2** were investigated after doping with PtOEP (0.01 mol % of PtOEP in **2**; Figure S13d–f). The triplet excited-state lifetime ($\tau_{A,T}$) of **2** (2.9 ms) was similar to that of **1** (2.5 ms). On the other hand, **2** had a higher I_{th} value of 18 mW cm^{-2} in **2** compared to that in **1** (3.0 mW cm^{-2}). The triplet diffusion constant D_T in **2** was found to be 19 times smaller (8.6×10^{-8} cm^2 s^{-1}) than that in **1** (1.6×10^{-6} cm^2 s^{-1}). These observations indicate that interactions between chromophores and the range of triplet energy migration in IL **2** are inferior to those for IL **1**. In general, anions and cations in ILs assume collective electrostatic interactions that ensure their molecular miscibility and proximity. As the miscibility of molecular components in liquids is determined by the difference in cohesive energy,[24–28,38] it is plausible that the anions with rich aromatic moieties show a preference for close contact with each other, giving contiguous molecular networks in coexistence with aliphatic counterions. Although bicontinuous IL structures based on polar and nonpolar domains has been reported,[24–28] spontaneous formation of such contiguous molecular network structures based on the difference in cohesive energy of aromatic and aliphatic ionic constituents is proposed herein. These systems have intriguing spectral and TTA-UC properties.

In conclusion, energy-migration-based TTA-UC using fluorescent ILs was achieved for the first time. The UC efficiency of the sensitizer-doped IL was maximized at low excitation intensity, by virtue of the high triplet diffusion constant (1.6×10^{-6} cm^2 s^{-1}) and long triplet lifetime (2.5 ms) of the IL. This high triplet diffusivity was rationally explained by the nanoscopic structuring of aromatic moieties and the interactions between the chromophores in the ILs. The further visualization of such extended aromatic cluster networks would require the help of molecular modeling techniques,[24] which will be implemented in due course. The current work offers an important conceptual bridge between ILs and exciton-based sciences, which would provide new platforms for the development of optically and electrically active IL materials.[30,39]

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