

# Phase-stable photochemical photon upconverters based on ionic liquids for efficient solar energy utilization

Yoichi Murakami

Global Edge Institute, Tokyo Institute of Technology  
2-12-1 Ookayama, Meguro, Tokyo 152-8550 Japan

## Introduction

In the conversion of solar energy to secondary energy such as electrical power (by photovoltaics) and hydrogen (by water-splitting photocatalysts), only a portion of the solar spectrum is utilized. Namely, photons with energies below a threshold energy, which is system dependent, are not utilized in secondary energy generation. To resolve this problem, one proposed strategy has been the use of photon upconversion (UC) [1], which is a process of converting two photons of lower energy into one photon of a higher energy.

One approach for this is to photochemically perform UC by utilizing triplet-triplet annihilation (TTA) of excited molecules. Recently, such triplet-triplet annihilation based photon upconversion (TTA-UC) has been studied using metallated organic molecules as efficient triplet sensitizers along with molecules possessing high fluorescence quantum yields as emitters [2–7]. This strategy has turned out to work with weak non-coherent light sources of intensities even close to terrestrial solar irradiance [3, 4]. Since the energy transfer between triplet states of molecules relies on the Dexter mechanism [8, 9], a fluidic media has been used to allow for sufficient diffusional motion and collisions in order to realize efficient energy transfers between molecules. Due to this reason, the majority of reported TTA-UCs have been performed with organic solvents such as toluene and benzene [2–7]. However, the use of such flammable and volatile solvents is a hurdle for their application.

This paper reports the development and characterizations of a new class of TTA-based photon upconverters fabricated with ionic liquids (ILs) as the fluidic host. Ionic liquids are room-temperature molten salts [10], which have recently drawn attention partly because of their negligible vapor pressures [11] and high thermal stabilities up to several hundred degrees Celsius [12]. As imagined by their ionic nature, ILs are known to have polarities similar to those of short chain alcohols [13–15], while the polycyclic aromatic molecules used in TTA-UC are non-polar or weakly polar. This leads to an intuitive prediction that ILs are an unsuitable media for the purpose of TTA-UC. In this study, however, the molecules have been found to be stable in ILs for a long time, contrary to this expectation. The solvation mechanism is proposed and the characterization of developed samples is presented along with the measured upconversion quantum yields (UC-QYs), regarding photon UC for the peak-to-peak anti-Stokes energy shift of  $\Delta E \sim 0.65$  eV corresponding to red-to-blue upconversion.

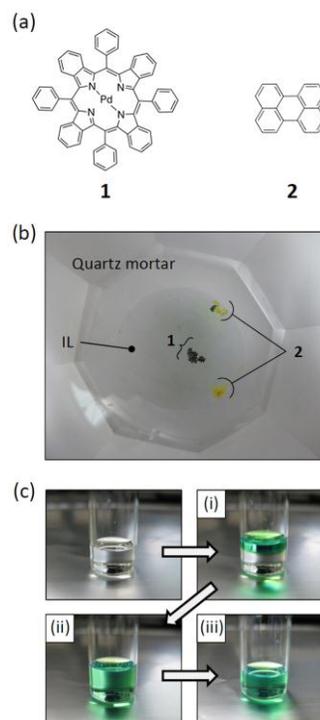
## Experimental

The ILs tested in this report are listed in Table 1. These were purchased from IoLiTec (#1 – #7, #10), Covalent Associates (#1, #2, #6, #9), Kanto Chemical (#8, #13), Merck (#11), and TCI (#12), and used without further purifications. They were stored under nitrogen until just before use. For the triplet sensitizer and photon emitter molecules, *meso*-Tetraphenyl-tetrabenzoporphine Palladium (PdPh<sub>4</sub>TBP) and perylene [4] (**1** and **2** in Figure 1a, from Sigma-Aldrich) were used, respectively.

It has been known that ILs, including those employed in this study, have polarities similar to those of short chain alcohols [13–15]. On the other hand, polycyclic aromatic molecules used for TTA-UC, including **1** and **2**, are non-polar or weakly polar and generally do not

dissolve in methanol. Figure 1b is a photograph taken 24 h after the powders of **1** and **2** were sprinkled over IL #1 held in a quartz mortar. The powders were still floating on the IL's surface, while only a part of the IL around the powders was faintly colored, showing that they hardly dissolve in the IL spontaneously.

The sample fabrication procedure developed is as follows. First, stock solutions of **1** and **2** in toluene (concentrations:  $4 \times 10^{-4}$  M and  $4 \times 10^{-3}$  M, respectively) were prepared and stored under nitrogen until just before use. The stock solutions were added with a mechanical pipette to an IL held in a glass vial, which resulted in a layer-separation (panel (i) of Figure 1c). Typically, the sensitizer stock solution (10 – 50  $\mu$ l) and the emitter stock solution (100 – 300  $\mu$ l) were added to an IL (400  $\mu$ l). The ILs with high hydrophobicity (#1 – #9) have been found to be miscible with toluene in finite amounts (e.g., up to  $\sim 240$   $\mu$ l toluene miscible with 400  $\mu$ l of IL #1 [16]). For this group of ILs, the solutions were made uniform looking using shear mixing done by gentle repeated suction-and-ejection with a glass Pasteur pipette (panel (ii) of Figure 1c). Immediately after this, the vial was capped and underwent moderate ultrasonication for 10 minutes. Subsequently, the vial was set in a vacuum chamber and pumped by an oil-free scroll pump for 4 – 10 h to remove the toluene (panel (iii) of Figure 1c). In the case of higher molecular densities that could not be achieved in one step due to miscibility limitations, the stock solution was further added at this point, followed by an additional cycle of shear mixing, ultrasonication, and vacuum evacuation. The vial was then set in a purpose-made high-vacuum chamber that was inside of a stainless steel (SUS) vacuum glovebox. The high-vacuum chamber was evacuated by a turbo-molecular pump for at least 12 h to reach  $10^{-4}$  –  $10^{-5}$  Pa, while the vapor pressure of ILs at room temperature are several orders of magnitude lower ( $10^{-10}$  –  $10^{-9}$  Pa [11]). Finally, the high-vacuum chamber was opened in the



**Figure 1.** (a) The sensitizer (PdPh<sub>4</sub>TBP, **1**) and the emitter (perylene, **2**) used in this study. (b) A photograph taken 24 h after **1** and **2** were sprinkled over ionic liquid (IL #1) held in the bottom of a quartz mortar. (c) Photographs taken at each step of the sample fabrication.

**Table 1. List of the Ionic Liquids Tested and Upconversion Quantum Yields Measured**

#	Ionic Liquid	Mixture Uniformity	UC-QY (%) <sup>†</sup>
1	[C <sub>2</sub> mim][NTf <sub>2</sub> ]	Yes	3.3
2	[C <sub>4</sub> mim][NTf <sub>2</sub> ]	Yes	4.4
3	[C <sub>6</sub> mim][NTf <sub>2</sub> ]	Yes	5.2
4	[C <sub>8</sub> mim][NTf <sub>2</sub> ]	Yes	4.2
5	[C <sub>2</sub> dmim][NTf <sub>2</sub> ]	Yes	< 1
6	[C <sub>3</sub> dmim][NTf <sub>2</sub> ]	Yes	< 1
7	[C <sub>4</sub> dmim][NTf <sub>2</sub> ]	Yes	10.6
8	[NR <sub>4</sub> ][NTf <sub>2</sub> ]	Yes	2.5
9	[C <sub>3</sub> dmim][CTf <sub>3</sub> ]	Yes	–
10	[C <sub>2</sub> mim][CH <sub>3</sub> CO <sub>2</sub> ]	No	–
11	[C <sub>2</sub> mim][CF <sub>3</sub> CO <sub>2</sub> ]	No	–
12	[C <sub>3</sub> mim][I]	No	–
13	[NR <sub>4</sub> ][BF <sub>4</sub> ]	No	–

<sup>†</sup> Measured by 632.8 nm, 30 mW excitations for the samples fabricated with [PdPh<sub>4</sub>TBP] = 1 × 10<sup>-5</sup> M and [perylene] = 3 × 10<sup>-3</sup> M.  
[C<sub>n</sub>mim]: 1-Alkyl-3-methylimidazolium  
[C<sub>n</sub>dmim]: 1-Alkyl-2,3-dimethylimidazolium  
[NR<sub>4</sub>]: N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium  
[NTf<sub>2</sub>]: Bis(trifluoromethylsulfonyl)imide  
[CTf<sub>3</sub>]: Tris(trifluoromethylsulfonyl)methide

Ar-filled SUS glovebox, and the sample liquid was injected and sealed in an appropriate glass container depending on the purpose. As for the rest of the tested ILs shown in Table 1 (#10 – #13), which are moderately-to-highly miscible with water [10], they have been found to be unable to form uniform mixtures with the stock solutions and hence are not further investigated.

The UC-QYs were measured based on previously described methods [4]. Briefly, the sample was injected into a square cross-section quartz tube (outer: 2 × 2 mm, inner: 1 × 1 mm, length: 25 mm) and sealed with solder inside the Ar-filled glovebox. The spectrum of UC emission was measured by an electronically cooled CCD mounted after a 30 cm monochromator and compared with the photoluminescence from a solution of 9,10-bis(phenylethynyl)anthracene in toluene (reference, 10<sup>-5</sup> M) measured with the same optical alignment. The UC-QY in this study was defined so that it is 100 % when two absorbed photons lead to one upconverted photon.

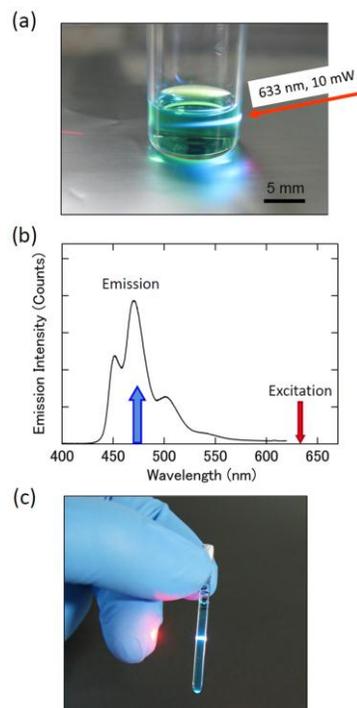
## Results and Discussion

**Stability of the samples.** The upconversion of a continuous wave (CW) laser light (632.8 nm, 10 mW, ~ 2 W/cm<sup>2</sup>) is shown in Figure 2a. Bright blue emission was clearly seen under room light illuminations. The typical emission spectrum is shown in Figure 2b. As was shown by Figure 1b, the powders of 1 and 2 (which prefer non-polar media) show poor spontaneous dissolution into the ILs (polar media). This causes concerns about the stability of these molecules in ILs after the removal of toluene by vacuum pumping. However, Figure 2c shows a photograph of a sample performing UC that was taken 7 months after fabrication, which had been left in air, to demonstrate its temporal stability. To further examine this result, an aging experiment (maintained at 80 °C for 100 h then at R. T. for 39 h) was performed. The optical absorption spectra after the aging process showed no change, indicating that the molecules were stably solvated in the ILs.

The stability of molecules in ILs opposes the intuitive expectation because ILs are polar solvent [13–15] while the aromatic molecules prefer non-polar environments. However, this viewpoint relies only on the consideration of polarity and neglects cation- $\pi$  interaction. Cation- $\pi$  interaction has been proposed to be an

important stabilization mechanism based on an electrostatic attraction between a positive charge and a  $\pi$  face of an aromatic system [17]. I propose cation- $\pi$  interaction is the mechanism for the observed stabilization of the molecules in the ILs. The emitter and sensitizer molecules are abundant in  $\pi$  electrons. To examine its role in the present study, the miscibility of ILs with benzene (C<sub>6</sub>H<sub>6</sub>) and cyclohexane (C<sub>6</sub>H<sub>12</sub>), both typical non-polar solvents, were compared. The result (not presented in this preprint) shows that benzene was moderately miscible but cyclohexane, which is similar but lacking  $\pi$  electrons, is completely immiscible with the same ILs. This result implies that an existence of  $\pi$  electrons in the molecules, not the extent of polarity, dominates the solvation in this study.

**Upconversion quantum yields.** The UC-QYs measured for samples made with ILs #1 – #8 are shown in Table 1. The excitation light was a 632.8 nm CW laser (30 mW with a spot diameter of 0.8 mm, ~ 6 W/cm<sup>2</sup>). The UC-QYs in Table 1 are typical values, acquired in one carefully performed experiment. The reproducibility of the UC-QYs in Table 1 has been confirmed by additional experiments. The variance of the UC-QY for a specific IL was found to be up to 20 % which may have been caused by untraced impurities or residual O<sub>2</sub>. Within the measurement of one identical sample, the uncertainty of the photoemission intensity or UC-QY has been found to vary by up to 5 %. As for sample #6 the UC-QY of 1 % or less has been repeatedly confirmed with ILs purchased from different suppliers (IoLiTec and Covalent Associates). Along the series of [C<sub>n</sub>mim][NTf<sub>2</sub>] (#1 – #4 for n = 2, 4, 6, and 8), the UC-QY takes a maximum at n = 6. Especially among ILs #1 – #3, the result is



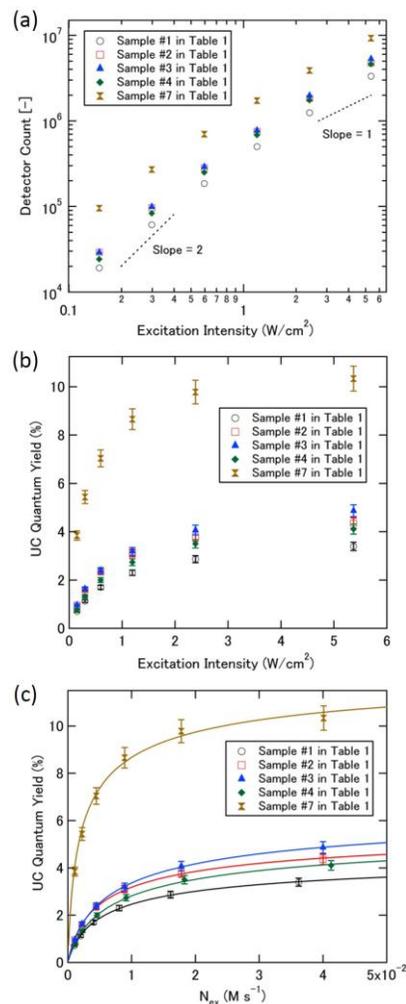
**Figure 2.** (a) A typical looking photograph of an upconversion of 632.8 nm incident CW light to blue emission under room light illuminations by the sample made with IL #1. (b) Photoluminescence spectrum. (c) A photograph of an upconversion of 632.8 nm CW laser light (10 mW, ~ 2 W/cm<sup>2</sup>) taken 7 months after its fabrication. The sample was prepared with IL #1 and had been firmly sealed with low melting point solder in a square cross-section quartz tube. This sample was left in ambient air under room light illumination for 7 months.

noteworthy because the ILs with longer alkyl chain, which have higher viscosities [18, 19], resulted in higher UC-QYs. This is different from previous findings for TTA-UC, where an increase in the media's viscosity led to a significant lowering of UC-QYs [20].

Sample #7 showed the highest UC-QY of approximately 10 % among the samples fabricated. The peak-to-peak anti-Stokes energy shift,  $\Delta E$ , is approximately 0.65 eV in this study. Castellano et al. employed boron dipyrromethene chromophores as emitter in benzene and reported the UC-QYs of  $\sim 6\%$  (for  $\Delta E \sim 0.4$  eV) and  $\sim 15\%$  (for  $\Delta E \sim 0.2$  eV) [6, 7]. Apart from CW excitation, the UC-QY of 16 % for  $\Delta E \sim 0.4$  eV has been reported for 1 kHz femto-second laser pulse excitations (the intensity during pulse was as high as 13 GW/cm<sup>2</sup>, corresponding to a steady-state triplet concentration achieved with 60 W/cm<sup>2</sup> CW excitation) of toluene solutions [21].

The UC-QYs in Table 1 are dependent on IL employed. This variance is considered to be caused by the differences in the microscopic electronic environment (electrostatic interaction, hydrogen bonding, dipole-dipole interaction, etc.) in an IL. This essentially arises from the molecular structures of ions and the spatial coordination of anions around a cation (or vice versa). So far, it has been well established that different molecular structures, or *conformational isomers*, coexist in the liquid phase of an IL [22–26]. The number of possible conformers rapidly increases as the length of an alkyl chain in an imidazolium cation increases [27]. As for a butyl imidazolium cation ([C<sub>4</sub>mim]<sup>+</sup>), the number of possible structures reported by DFT calculations has been between 9 to 12 [24–27]. Among these predicted structures, 4 conformers of [C<sub>4</sub>mim]<sup>+</sup> have been experimentally observed for the liquid phase of [C<sub>4</sub>mim][BF<sub>4</sub>] [23]. However, quantitative determination of their relative population is still of significant experimental difficulty [25]. Recent DFT calculations have shown that the conformational isomerism of an imidazolium cation significantly changes the charge distribution on the imidazolium ring [26]. Namely, the actual number of molecular structures existing in the liquid phase of ILs, their population ratios, and the resultant effects on the microscopic electronic environment within ILs remain open questions. The difference in the observed UC-QYs between #1 and #5, or #2 and #7, may originate from such complex influences at the microscopic level.

**Excitation intensity dependence.** To further investigate the character, the excitation intensity dependence was examined. Figure 3a shows the dependence of measured UC emission intensity on the excitation intensity plotted on a double-logarithmic scale. At lower excitation intensities, the slopes of the plots are close to (but less than) two, and as the intensity increases, the slopes monotonically decrease and approach unity. Accordingly, the UC-QYs start to saturate toward their respective values (Figure 3b). In previous TTA-UC studies measured with CW excitation (where volatile organic solvents were employed), the emission intensities were reported to vary quadratically with excitation powers [6, 7]. This quadratic dependence was explained in terms of the fact that the TTA-UC is a two-body process and hence the chance for a triplet molecule to find an annihilation partner within its lifetime is proportional to the square of the created triplet concentration. Under such circumstances, the UC-QY increases linearly with the excitation power. Recently, Cheng et al. have reported a quadric-to-linear transition in UC emission intensity by exciting their toluene-based samples with intense femtosecond laser pulses [21]. The authors have suggested two possibilities for the observed quadric-to-linear transition: (i) photo-saturation (or transient bleaching) caused in the sensitizing molecules by the intense pulse excitations and (ii) achievement of sufficiently high triplet densities so that virtually all of the created triplets could find their annihilation partners within their lifetimes and hence the



**Figure 3.** (a) Dependence of the UC emission intensities on the excitation intensity of a 632.8 nm CW laser light for the samples fabricated with ILs #1 – #4, and #7, plotted in double logarithmic scale. Dashed lines represent linear and quadric increments shown for eye-guides. (b) Dependence of the UC-QY on the excitation intensity for the same samples. The error bars account for the  $\pm 5\%$  certainty in the photoemission measurement. (c) Plot of the UC-QY vs.  $N_{ex}$  relations for the same experimental data. The solid curves are from Eq. (3).

emission intensities linearly correlated with the excitation powers. They stated that both mechanisms were considered to coexist in the results [21].

In this study, the excitation was moderate CW light (0.15 – 6 W/cm<sup>2</sup>) and hence the first possibility (photo-saturation) is excluded. The results in Figure 3b are explained as follows based on the second possibility. When the excitation intensity (hence the triplet concentration) is low, the TTA rate is determined by the probability of triplet species to find annihilation partners. This is a competing process with their decay to the ground state, which may be caused by spontaneous intersystem crossing or by the residual oxygen molecules that efficiently quench excited triplet states at nearly diffusion-controlled rate. However, when the excitation intensity is high enough to create a sufficient spatial density of the triplets *and when the oxygen concentrations in the media is sufficiently low*,

virtually all of the created triplets find annihilation partners before they decay into the ground state even under weak excitation, leading to the saturation of the UC-QY values. In general, the viscosities of the ILs are about two-orders of magnitude higher than the common volatile solvents. In the previous TTA-UC study [21], however, the authors also mentioned the possibility of the incomplete removal of oxygen molecules from the samples. One distinct difference of the present study is that IL-based samples can be thoroughly degassed. Unlike organic solvents, ILs have negligible vapor pressures that allows for degassing with ultra-high vacuum turbo-molecular pumps.

**Analysis.** To investigate whether efficient collisional energy transfer between molecules is possible in ILs and to explain the observed saturation behaviors in Figure 3b, an analytical study is performed. In this preprint, only the basics are described. First, the condition of highly efficient triplet energy transfer between donor-acceptor molecules is given by [28]:

$$k_{\text{TET}}[{}^1\text{E}^{\text{G}}] \gg k_{\text{T(S)}}. \quad (1)$$

Here,  $k_{\text{TET}}$  is the triplet energy transfer rate from sensitizer to emitter ( $\text{M}^{-1} \text{s}^{-1}$ ),  $k_{\text{T(S)}}$  is the triplet decay rate of the sensitizer ( $\text{s}^{-1}$ ), and  $[{}^1\text{E}^{\text{G}}]$  is the molar concentration of the emitter in the ground singlet state. This condition has been found to hold from an order-of-magnitude analysis (details not shown in this preprint) based on the Debye equation [28]

$$k_{\text{TET}} \approx \frac{8RT}{3000\eta}, \quad (2)$$

calculated with the reported viscosities of the ILs. In Eq. (2),  $R$ : the gas constant ( $8.31 \times 10^7 \text{ erg mol}^{-1}$ ),  $T$ : temperature (300 K), and  $\eta$ : viscosity of the ILs expressed in unit of poise (0.4 – 1 P [18, 19]). Then, adopting the assumption of Eq. (1), the relationship between the molar rate of photons absorbed by the sensitizer,  $N_{\text{ex}}$  ( $\text{M s}^{-1}$ ), and the UC-QY,  $\theta$  ( $0 \leq \theta \leq 1$ ), is represented by the following dimensionless equation in terms of two dimensionless variables  $\Theta$  and  $\Lambda$  ( $0 \leq \Theta \leq 1, 0 \leq \Lambda$ ):

$$\Theta = 1 + \frac{1 - \sqrt{1 + 2\Lambda}}{\Lambda} \left( \Theta \equiv \frac{\theta}{\varepsilon\varphi}, \quad \Lambda \equiv \frac{4k_{\text{TTA}}}{k_{\text{T(E)}}^2} N_{\text{ex}} \right). \quad (3)$$

Here,  $k_{\text{TTA}}$  is the TTA rate between molecules in triplet states ( $\text{M}^{-1} \text{s}^{-1}$ ) and  $k_{\text{T(E)}}$  is the triplet decay rate of the emitter ( $\text{s}^{-1}$ ).  $\varepsilon$  and  $\varphi$  denote the photoemission quantum efficiency from the  ${}^1\text{E}^{\text{G}}$  level and the statistical branching ratio of the  ${}^3\text{E}^* + {}^3\text{E}^* \rightarrow {}^1\text{E}^* + {}^1\text{E}^{\text{G}}$  in the TTA process, respectively ( $0 \leq \varepsilon \leq 1; 0 \leq \varphi \leq 1$ ). Namely, Eq. (3) provides a universal curve that describes the relationship between the excitation intensity ( $N_{\text{ex}}$ ) and the UC-QY ( $\theta$ ) in case the assumption of Eq. (1) holds. The markers in Figure 3c are the experimental points of  $N_{\text{ex}}$  vs.  $\theta$  derived from the results of Figure 3b. The values of  $N_{\text{ex}}$  were calculated based on the laser beam spot (0.8 mm), the optical path length (1 mm), the molar concentration of the sensitizer, and the sample's absorbance at the excitation wavelength. The solid curves shown in Figure 3c are the fitting by Eq. (3) to the experimental data. The agreement between the predicted curves and the experimental data corroborates the idea that inter-molecular energy transfer between molecules in the ILs occurs efficiently, in agreement with the outcome of the aforementioned order-of-magnitude analysis for Eq. (1). Detailed kinetics investigations including Stern-Volmer experiments are currently under preparation.

## Conclusions

Stable photochemical photon upconverters with negligible volatility/flammability have been fabricated using ionic liquids as the media for triplet energy transfer. It has been found that the polycyclic aromatic molecules used for the triplet sensitization and triplet-triplet

annihilation are stably solvated in the ionic liquids. The cation- $\pi$  interaction has been proposed as the mechanism for the observed stable solvation.

The dependence of the emission intensities on the excitation intensity was measured, and the upconversion quantum yield saturates to a certain limit depending on the ionic liquid under moderate excitation condition. The saturation behavior has been explained in terms of efficient energy transfer between triplet states. The direct reason for the efficient energy transfer has been attributed to the suppressed oxygen concentrations in the samples, which was made possible with the direct pumping of the samples with an ultra-high vacuum turbo-molecular pump which exploits the negligible vapor pressures of ionic liquids. From the analysis, it has been found that the triplet energy transfer between the molecules is efficient against decay of the triplet state to the ground state, showing that viscosities of the ionic liquids are not a practical problem for the purpose of triplet-triplet annihilation based upconversions.

In essence, ionic liquids have been found to be useful for triplet-triplet annihilation based photon upconverters. The core advantage of using ionic liquids lies in the non-volatility and non-flammability. Although the quantum yields of the developed upconverters are maximized at relatively low incident light intensities ( $\sim 1 - 2 \text{ W/cm}^2$ , Figure 3b), for applications to non-concentrated solar irradiances ( $\sim 0.1 \text{ W/cm}^2$ ), upconverters whose quantum yields can reach the maximum at even lower light intensities are desired. This might be achieved by prolonging the triplet lifetime of emitter molecules, if the lifetime is dependent on ionic liquid in which the molecules are solvated. The mechanism responsible for the differences in upconversion quantum yield for different types of ionic liquids is currently under investigation. As the number of ionic liquids known thus far exceeds 1,000,000 [10], further exploration for optimal ionic liquids is expected to give rise to enhancement of the quantum yield.

**Acknowledgement.** The author thanks Professors I. Sato, O. Ishitani, A. Kawai, and T. Iyoda at Tokyo Inst. Tech. for valuable comments, and Mr. R. Gresback at Tokyo Inst. Tech. for improving English expressions. This work was financially supported by MEXT-JST program "Promotion of Environmental Improvement for Independence of Young Researchers" and by KAKENHI (#23686035, Grant-in-Aid for Young Scientists (A)). All the findings in this preprint have been filed as patent 2010-230938JP, 2011-021136JP, and PCT(JP2011/73443).

## References

- (1) Trupke, T.; Green, M. A.; Würfel, P. *J. Appl. Phys.* **2002**, *92*, 4117.
- (2) Islangulov, R. R.; Kozlov, D. V.; Castellano, F. N. *Chem. Comm.* **2005**, 3776.
- (3) Balushev, S.; Miteva, T.; Yakutkin, V.; Nelles, G.; Yasuda, A.; Wegner, G. *Phys. Rev. Lett.* **2006**, *97*, 143903.
- (4) Balushev, S.; Yakutkin, V.; Miteva, T.; Wegner, G.; Roberts, T.; Nelles, G.; Yasuda, A.; Chernov, S.; Aleshchenkov, S.; Cheprakov, A. *New J. Phys.* **2008**, *10*, 013007.
- (5) Singh-Rachford, T. N.; Castellano, F. N. *J. Phys. Chem. A* **2008**, *112*, 3550.
- (6) Singh-Rachford, T. N.; Haefele, A.; Ziessel, R.; Castellano, F. N. *J. Am. Chem. Soc.* **2008**, *130*, 16164.
- (7) Singh-Rachford, T. N.; Castellano, F. N.; *Coord. Chem. Rev.* **2010**, *254*, 2560.
- (8) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
- (9) Monguzzi, A.; Tubino, R.; Meinardi, F. *Phys. Rev. B* **2008**, *77*, 155122.
- (10) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*, 123.
- (11) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. *J. Phys. Chem. A* **2006**, *110*, 7303.

- (12) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochem. Acta* **2000**, *357*, 97.
- (13) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591.
- (14) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790.
- (15) Kawai, A.; Hidemori, T.; Shibuya, K. *Chem. Lett.* **2004**, *33*, 1464.
- (16) Shiflett, M. B.; Niehaus, A. M. S. *J. Chem. Eng. Data* **2010**, *55*, 346.
- (17) Dougherty, D. A. *Science* **1996**, *271*, 163.
- (18) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103.
- (19) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. *Green Chem.* **2006**, *8*, 172.
- (20) Singh-Rachford, T. N.; Lott, J.; Weder, C.; Castellano, F. N. *J. Am. Chem. Soc.* **2009**, *131*, 12007.
- (21) Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. *Phys. Chem. Chem. Phys.* **2010**, *12*, 66.
- (22) Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 948.
- (23) Holomb, R.; Martinelli, A.; Albinsson, I.; Lassègues, J. C.; Johansson, P.; Jacobsson, P. *J. Raman Spectrosc.* **2008**, *39*, 793.
- (24) Tsuzuki, S.; Arai, A. A.; Nishikawa, K. *J. Phys. Chem. B* **2008**, *112*, 7739.
- (25) Endo, T.; Kato, T.; Nishikawa, K. *J. Phys. Chem. B* **2010**, *114*, 9201.
- (26) Umebayashi, Y.; Hamano, H.; Tsuzuki, S.; Lopes, J. N. C.; Padua, A. A. H.; Kameda, Y.; Kohara, S.; Yamaguchi, T.; Fujii, K.; Kanzaki, R.; Ishiguro, S. *J. Phys. Chem. B* **2010**, *114*, 11715.
- (27) Turner, E. A.; Pye, C. C.; Singer, R. D. *J. Phys. Chem. A* **2003**, *107*, 2277.
- (28) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. In Chapter 7 of *Principles of Molecular Photochemistry: An Introduction*; University Science Books: Sausalito, USA, 2009.