

Photon upconversion — A technology for utilizing sub-bandgap wasted energies

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1. Background and aim of this research

Background

- Reserves-to-production (R/P) ratio (as of the end of 2011^[1])

Oil: 54 years, Natural gas: 64 years, Coal: 112 years

⇒ Although the R/P ratios change year by year, *in the long term*, the finite nature of fossil-based resources would be a problem

- Solar energy

~ 2.7×10^{24} J/year (on earth surface)

World's primary energy consumption^[1]

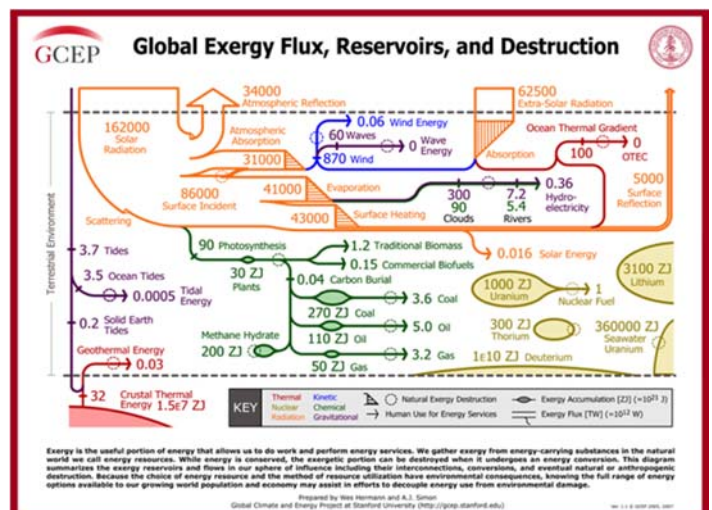
~ 5×10^{20} J/year

World's electricity generation^[1]

~ 8×10^{19} J/year

However, dilute (≈ 0.1 W/cm²)

⇒ Efficient conversion is essentially required for large-scale utilizations



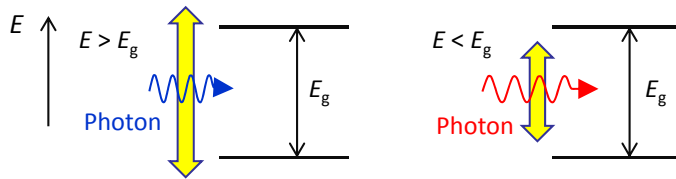
<http://gcep.stanford.edu/research/exergy/resourcechart.html>

[1] BP Statistical Review of World Energy June 2012, <http://www.bp.com/statisticalreview>

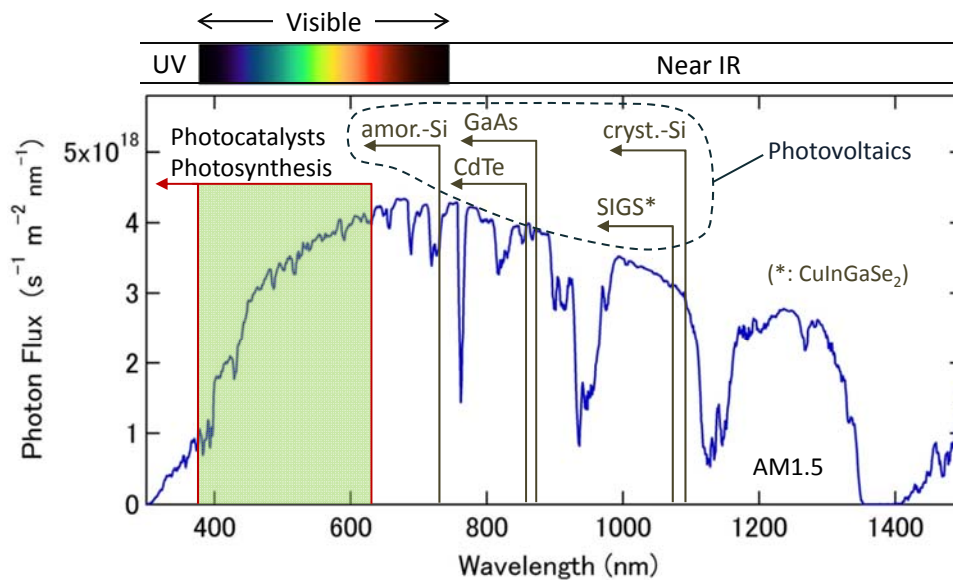
Limitation imposed on the solar-energy utility

In the present energy conversions by photovoltaics, photocatalysts, and photosynthesis:

Only a portion of the spectrum whose photon energy is higher than threshold energy (E_g) is used.



E_g : Bandgap energy (semiconductors)
or
HOMO-LUMO gap energy (molecules)



Threshold wavelength λ_g
is related to E_g by

$$\lambda_g \text{ (nm)} = 1240 / E_g \text{ (eV)}$$

Vertical lines in the left panel:
Positions of λ_g

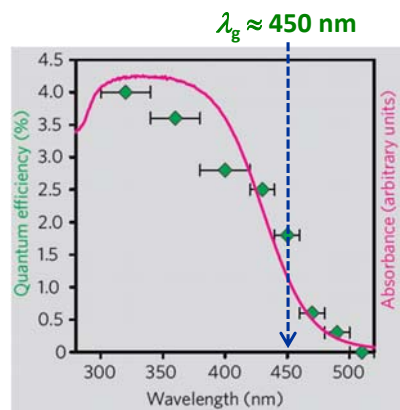
⇒ No matter how much power is input, lights with $\lambda > \lambda_g$ are wasted.

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Adverse effect of increasing λ_g

- An increase of λ_g induces a negative side-effect of *decreasing* the free-energy of generated electrons (e.g. output voltage, chemical reactivity) and hence there is a trade-off dilemma.[†]
- Originally, UV water-splitting photocatalysts have the quantum efficiency (Q. E.) of > 50 %^[1]

A typical outcome of
visible-light-responsive
photocatalyst:



K. Domen et al., *Nature* **440**, 295 (2006)

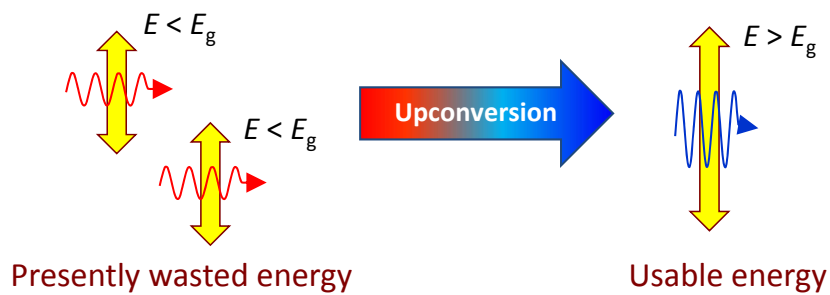
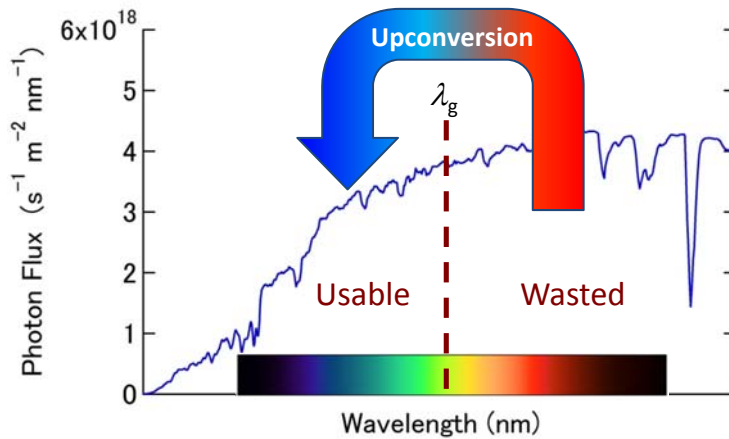
Q. E. \cong 2.5% for 420 – 440 nm

⇒ We want to utilize the presently wasted sub-bandgap portion of the spectrum ($\lambda > \lambda_g$)
without suffering from the side-effects associated with the increase of λ_g .

[†]: In the case of photovoltaics, an increase of λ_g up to the wavelength corresponding to Shockley-Queisser limit ($\lambda \sim 850$ nm) may improve the overall solar-energy conversion efficiency, but further increase causes a decrease of the efficiency.

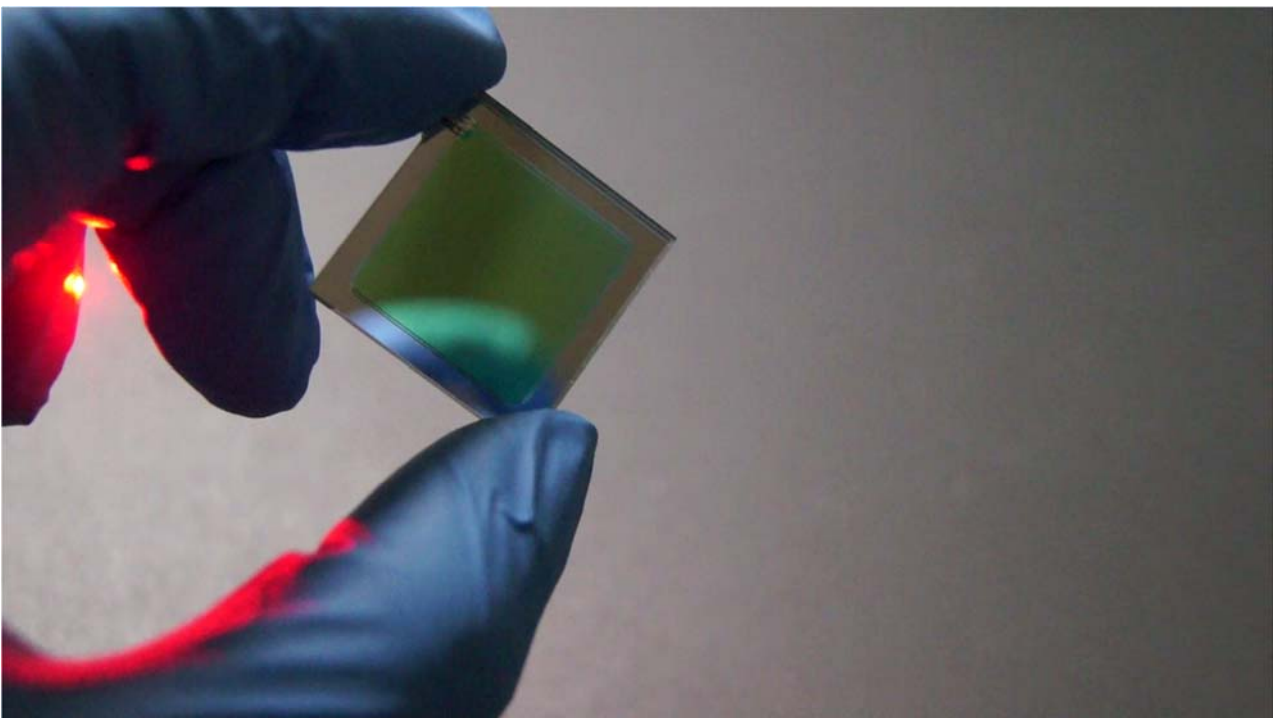
Benefit of performing upconversion

Photon upconversion (UC) is a technology that makes presently wasted part of the solar spectrum usable for generating secondary energies *without necessitating an increase of λ_g in the solar-conversion systems.*



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The devices fabricated in this study



YouTube <http://youtu.be/TrvGDZWas-Y>

Nikkei Electronics, vol. 2012-8-20, pp. 14–15.

- Excitation: 633 nm (red), 10 mW (about 10 laser-pointers)
- An aluminum mirror has been deposited on the backside and is reflecting unabsorbed incident light

Such devices have become possible due to the use of “non-volatile” medium, as described later.

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2. Some basis and previous problems

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Previous methods of performing UC

• Previous UC methods

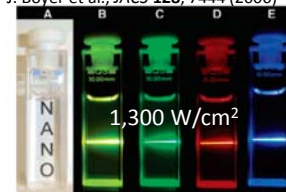
- ◆ Two photon absorption (TPA)
- ◆ Second harmonic generation (SHG)
- ◆ Ceramics doped with rare-earth ions (Er^{3+} , Yb^{3+} , Tm^{3+} , etc.) example →
(The UC quantum efficiencies reported are much less than 1 %.)

⇒ These methods essentially necessitates high-intensity laser lights.
(Either “coherence” or “liner polarization”, or both, is required.)

S. Heer et al., *Adv. Mater* **16**, 2102 (2004)



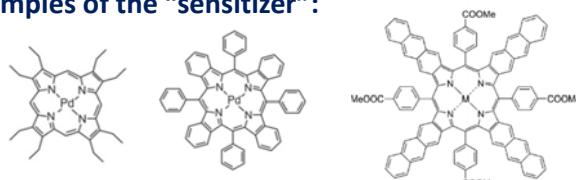
J. Boyer et al., *JACS* **128**, 7444 (2006)



• The method used in this study

- ◆ Proposed recently (around 2005)^[1,2]
- ◆ Applicable to weak *non-coherent and randomly polarized lights*, such as sunlight
- ◆ Higher efficiencies (~ several % or more) are achievable with much lower intensities (0.1–10 W/cm²)
- ◆ Utilizes spin-triplet energy states of *organic molecules*, and hence the system-design is highly flexible

Examples of the “sensitizer”:



Examples of the “emitter”:



[1] R. R. Islangulov et al., *Chem. Comm.*, 3776 (2005)

[2] S. Balushev et al., *Phys. Rev. Lett.* **97**, 143903 (2006)

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Terminologies used in this presentation

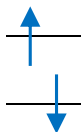
• The ways how two electrons are correlated

- ◆ When the spins of two electrons are anti-parallel, this is called “singlet”

Ground state singlet, S_0



Lowest excited singlet, S_1^*



Allowed

Ground state (= unexcited state) is always singlet state.

- ◆ When the spins of two electrons are parallel, this is called “triplet”



Basically forbidden

Lowest excited triplet, T_1^*



• Characteristics of S_1^* and T_1^*

S_1^* ... Decay into S_0 is **allowed** (\Rightarrow lifetime is very short: $\sim 10^{-9}$ s)

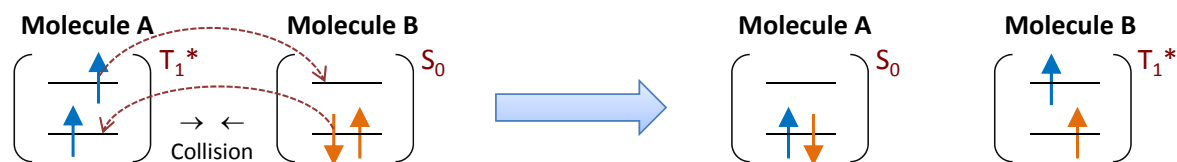
T_1^* ... Decay into S_0 is **basically forbidden** (\Rightarrow lifetime is long: $\sim 10^{-5} - 10^0$ s)

\Rightarrow Triplet states can be regarded as a “robust container of energy.”

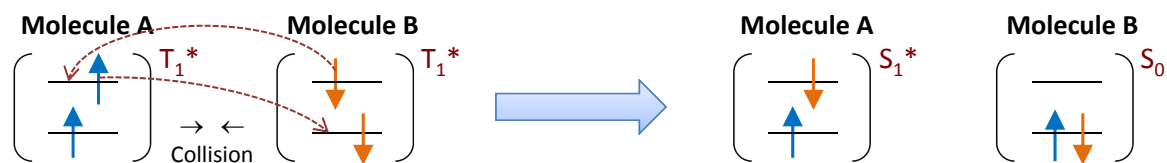
10

Inter-molecular spin-energy transfer mechanisms

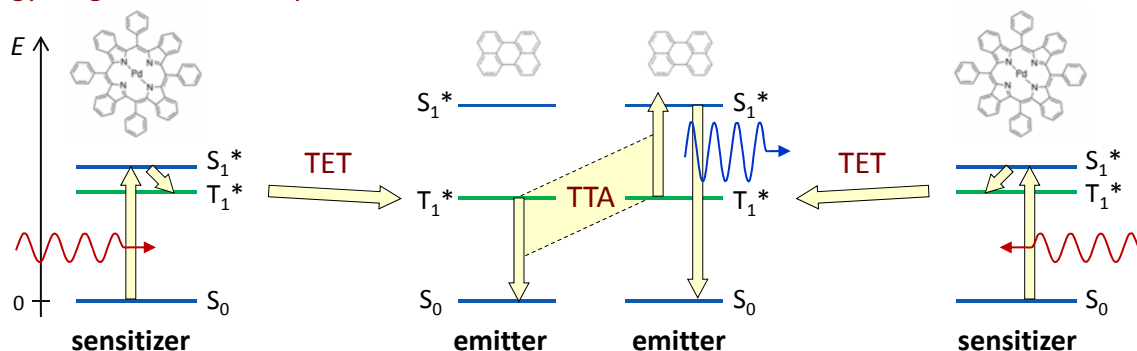
• Triplet energy transfer (TET) †



• Triplet-triplet annihilation (TTA)



• Energy diagram of the UC process



†: Often termed “Dexter mechanism” or “electron-exchange mechanism”.

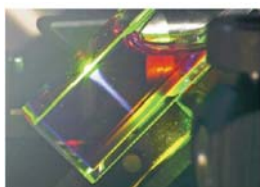
11

Problem of the previous TTA-UC studies

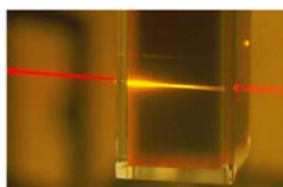
Since both the TET and TTA require intermolecular collision, the host medium must be fluidic in order to sufficiently allow for diffusion of the energy-carrying molecules.

Due to this reason, all the previous studies that observed meaningful UC efficiency were carried out in organic solvents, such as toluene and benzene.^[1-12]

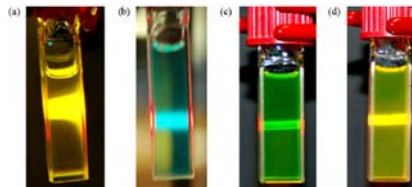
Phys. Rev. Lett. **97**, 143903 (2006)



J. Phys. Chem. Lett. **1**, 1795 (2010)



Coord. Chem. Rev. **254**, 2560 (2010)



However, the use of such solvents, which have high volatility, flammability, vapor toxicity and incompatibility with many plastic materials, had been hurdles for the application.

⇒ Upon making practical samples, both deoxygenation and sealing are difficult for such volatile liquids.

└─ necessary because this is an organic-molecule-based system

[1] R. R. Islangulov et al., *Chem. Comm.*, 3776 (2005)

[3] S. Balushev et al., *New J. Phys.* **10**, 013007 (2008)

[5] T. N. Singh-Rachford et al., *J. Am. Chem. Soc.* **130**, 16164 (2008)

[7] Y. Y. Cheng et al., *Phys. Chem. Chem. Phys.* **12**, 66 (2010)

[9] W. Wu et al., *J. Org. Chem.* **76**, 7056 (2011)

[11] Y. Y. Cheng et al., *Energy Environ. Sci.* **5**, 6953 (2012)

[2] S. Balushev et al., *Phys. Rev. Lett.* **97**, 143903 (2006)

[4] V. Yakutkin et al., *Chem. Eur. J.* **14**, 9846 (2008)

[6] T. N. Singh-Rachford et al., *J. Phys. Chem. A* **113**, 5912 (2009)

[8] T. N. Singh-Rachford et al., *J. Phys. Chem. Lett.* **1**, 195 (2010)

[10] Q. Li et al., *J. Mater. Chem.* **22**, 5319 (2012)

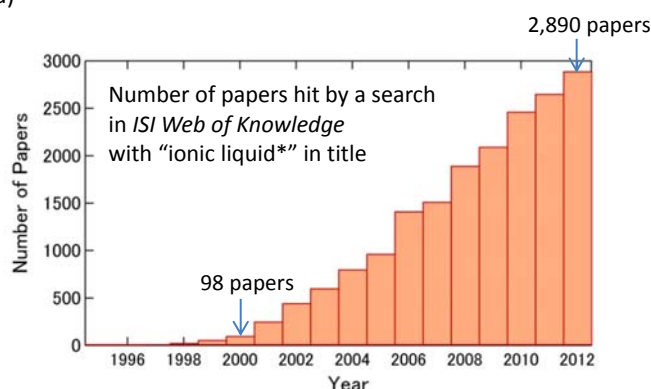
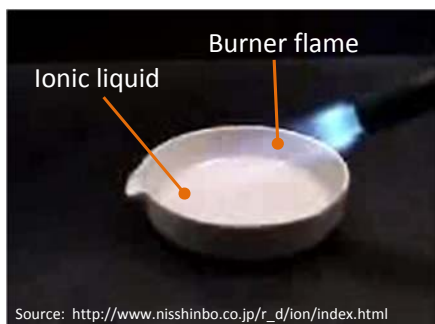
[12] A. Turshatov et al., *Chem. Phys. Chem.* **13**, 3112 (2012)

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3. How the previous problems have been resolved

An idea of using "ionic liquids"

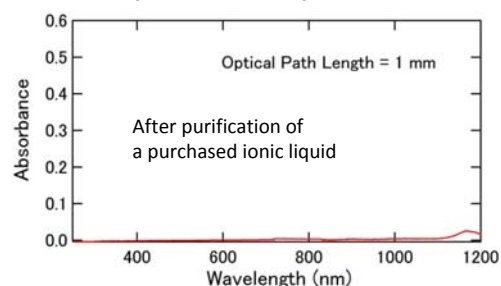
Ionic liquids — Novel room-temperature molten salts *composed solely of ions*, having negligible vapor pressures and non-flammability ($\sim 10^{-10} - 10^{-9}$ Pa)^[1]



Many engineeringly-important unique properties:

- ◆ Practical non-volatility and non-flammability
- ◆ High ionic conductance
- ◆ Wide electrochemical window (≈ 6 V or wider)
- ◆ Liquidity over wide temperature range (300–500 °C wide)
- ◆ No intrinsic optical absorption from ~ 250 nm to ~ 1100 nm
 \Rightarrow Good also for optical applications

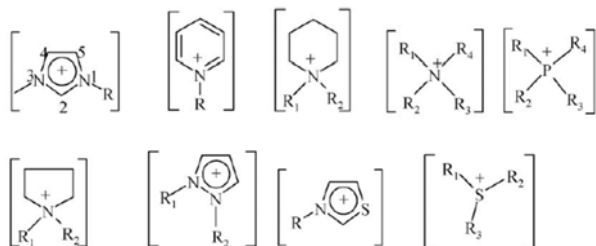
An example of UV-vis spectrum:



[1] D. H. Zaitsau et al., *J. Phys. Chem. A*, **110**, 7303 (2006)

Characteristics of ionic liquids

Typical cations (+):



"R" above: alkyl chain ($-C_nH_{2n+1}$)

Typical anions (-):

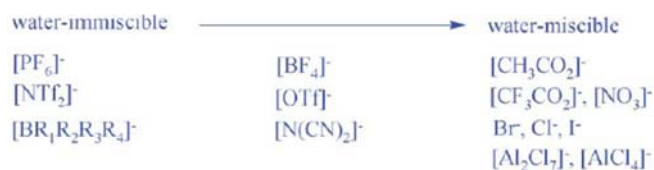


Table 4 Comparison of organic solvents with ionic liquids^a

N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.* **37**, 123 (2008)

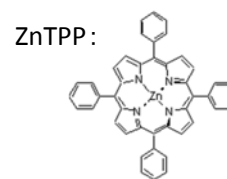
Property	Organic solvents	Ionic liquids
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tuneable
Chirality	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius–Clapeyron equation	Negligible vapour pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Polarity	Conventional polarity concepts apply	Polarity concept questionable
Tuneability	Limited range of solvents available	Virtually unlimited range means "designer solvents"
Cost	Normally cheap	Typically between 2 and 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cP	0.2–100	22–40,000
Density/g cm ⁻³	0.6–1.7	0.8–3.3
Refractive index	1.3–1.6	1.5–2.2

The difficulty expected: Solubility problem

Previous experimental observation about this very low solubility:

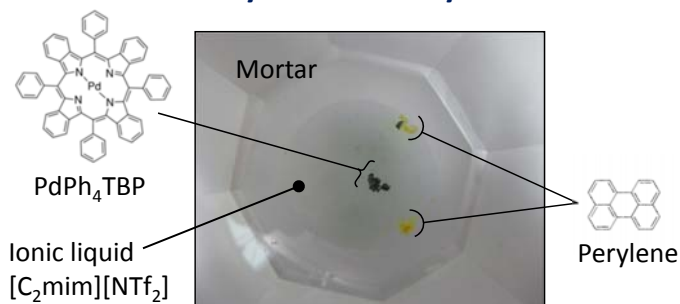
A. Kawai et al., *Mol. Phys.* **104**, 1573 (2006)

which is important in more quantitative discussion. The weak signal is due to very low concentration of ZnTPP because of its low solubility in RTILs. The polarity of RTILs are similar to acetonitrile and alcohols such as methanol and 2-propanol according to the previous studies [10–13], and we assume that typical aromatic compounds are not soluble in RTILs.



(RTIL = room-temperature ionic liquid)

Confirmation of the very low solubility:



Left photograph: A looking 24 hours after the powders of those molecules were sprinkled over an ionic liquid.

→ Charge-neutral flat aromatic molecules, such as porphyrins, are empirically been known to be hardly soluble in ionic liquids (which have been reported to be polar liquids^[1,2])

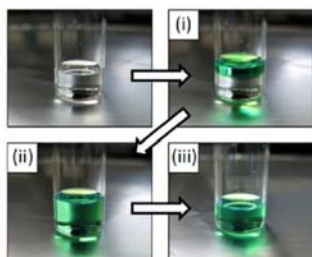
[1] A. J. Carmichael et al., *J. Phys. Org. Chem.* **13**, 591 (2000)

[2] L. Crowhurst et al., *Phys. Chem. Chem. Phys.* **5**, 2790 (2003)

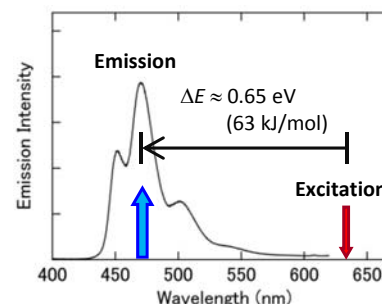
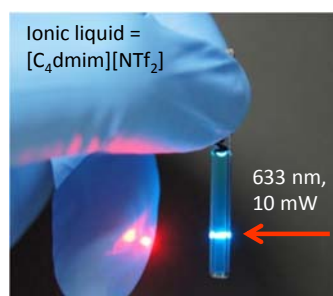
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Invented sample prep. method and the discovered stability

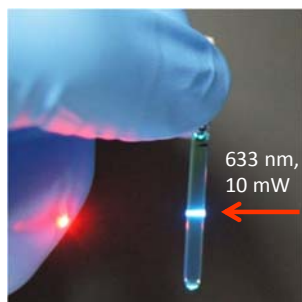
Development of the “toluene-mediated shear mixing method”:



Confirmation of upconversion by the samples made:



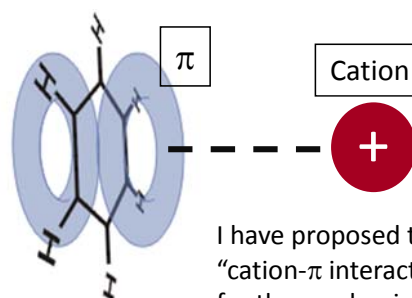
Discovery of an unexpected sample stability:



A photograph taken > 2 years after the sample was fabricated.

The sample was made and sealed on Sep. 8, 2010, and had been left in the air and under room light illumination since then. This photo was taken on Nov. 26, 2012.

Proposition/Demonstration of the mechanism regarding this unexpected solvation stability:



⇒ Non-volatile, non-flammable, and long-term stable photon upconverters have been invented.

References: Y. Murakami, *Chem. Phys. Lett.* **56**, 516 (2011)
村上, *ケミカルエンジニアリング* **57**, 1 (2012)

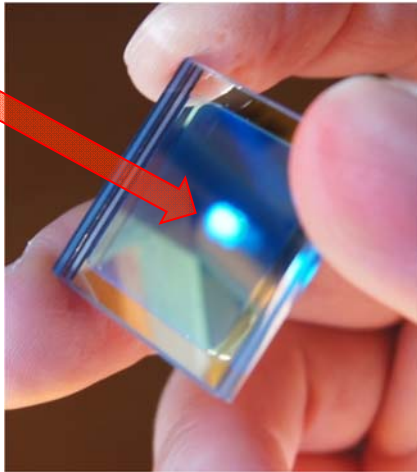
Y. Murakami, *Thermal. Sci. Eng.* **20**, 15 (2012)
International Patent Application, PCT/JP2011/073443

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Confirmation of the applicability to sunlight

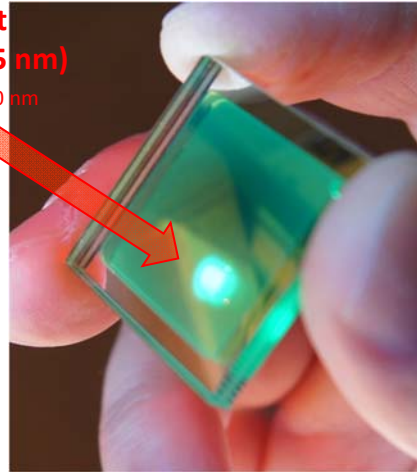
Experimental date: Dec 30, 2011

Sunlight
($\lambda \sim 625 \text{ nm}$)
FWHM = 10 nm

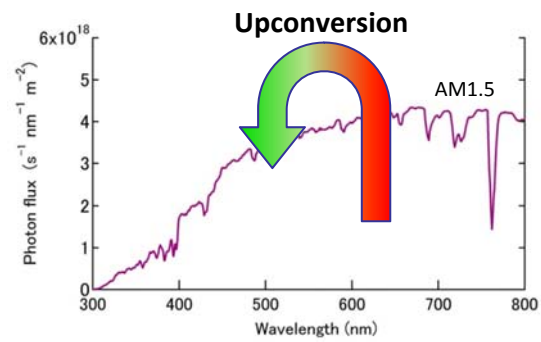
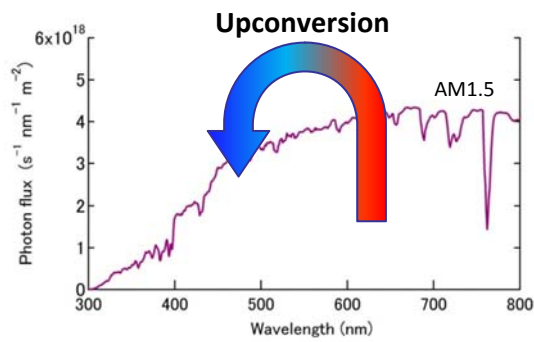


$\sim 625 \text{ nm} \rightarrow \sim 475 \text{ nm}$

Sunlight
($\lambda \sim 625 \text{ nm}$)
FWHM = 10 nm



$\sim 625 \text{ nm} \rightarrow \sim 510 \text{ nm}$



村上, ケミカルエンジニアリング57, 1 (2012)

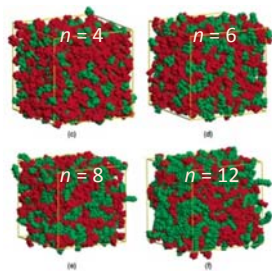
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4. Mass-transport characteristics

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Microscopic structures in ionic liquids

• Unique “microstructured” fluid

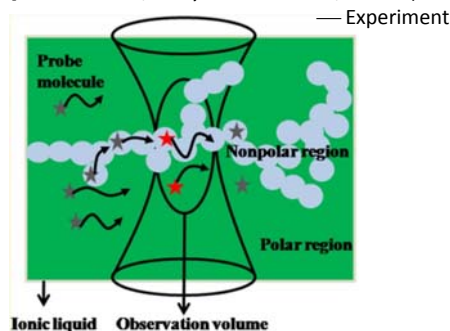


[1] J. N. C. Lopes et al., *J. Phys. Chem. B* **110**, 3330 (2006) — MD simulation

Red: Polar region
Green: Non-polar region

Figure 5. Snapshots of simulation boxes containing 700 ions of $[C_nmim][PF_6]$. The application of a coloring code enables clear identification of the charged and nonpolar domains that form in ionic liquids. The lengths of the box sides are given: (a) $[C_2mim][PF_6]$ CPK coloring; (b) $[C_2mim][PF_6]$ same configuration as in a with red/green (charged/nonpolar) coloring; (c) $[C_4mim][PF_6]$ $l = 49.8 \text{ \AA}$; (d) $[C_6mim][PF_6]$ $l = 52.8 \text{ \AA}$; (e) $[C_8mim][PF_6]$ $l = 54.8 \text{ \AA}$; (f) $[C_{12}mim][PF_6]$ $l = 59.1 \text{ \AA}$.

[2] S. Patra et al., *J. Phys. Chem. B* **116**, 12275 (2012)



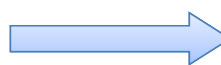
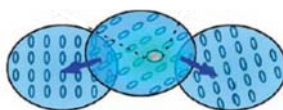
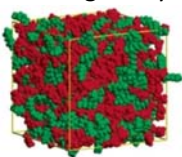
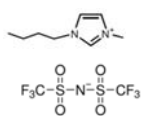
Scales relevant to ionic liquids:

Size of constituent molecules

Size of microscopic heterogeneity^[1,2]

Size of local structure^[3,4]

Applications



⇒ In order to contribute to the proposed applications, elucidation of the mass-transport properties inside ionic liquids are essentially needed.

[3] K. Iwata et al., *Acc. Chem. Res.* **40**, 1174 (2007)

[4] K. Yoshida et al., *J. Chem. Phys.* **136**, 104504 (2012)

([3,4]: Experiment)

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Diffusion-controlled rate constant by Debye equation

Suppose molecule species α and β are colliding with each other in a fluid.

• Smoluchowski theory

$$k_{\text{diff}} = 4000\pi N\rho_{\alpha\beta}D \quad [M^{-1} s^{-1}]$$

where N : Avogadro number, $\rho_{\alpha\beta}$: reaction radius between α and β , and D : relative diffusion constant between α and β .

• Stokes relation of friction coefficient for the species α

$$\zeta_{\alpha} = 6\pi\eta r_{\alpha}$$

where r_{α} is the radius of the molecule α . In this, a stick (non-slippage) condition is assumed.

• Einstein relation of diffusion constant for the species α

$$D_{\alpha} = \frac{k_B T}{\zeta_{\alpha}}$$

where ζ_{α} is the coefficient of friction between the molecule α and the solvent.

Assuming $\rho_{\alpha\beta} = 2r_{\alpha} = 2r_{\beta}$, and hence $D = 2D_{\alpha} = 2D_{\beta}$ in the above equations, together with $R = k_B N$, the so-called Debye equation is obtained as below:

$$k_{\text{diff}} = \frac{8RT}{3000\eta} \quad [M^{-1} s^{-1}]$$

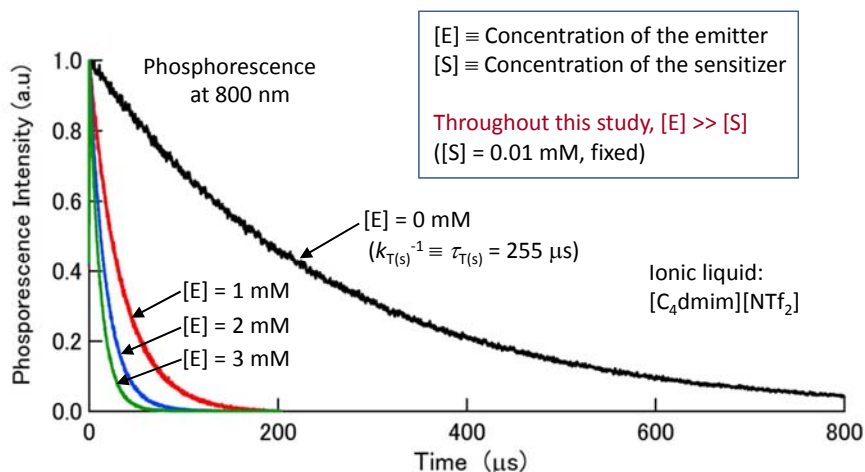
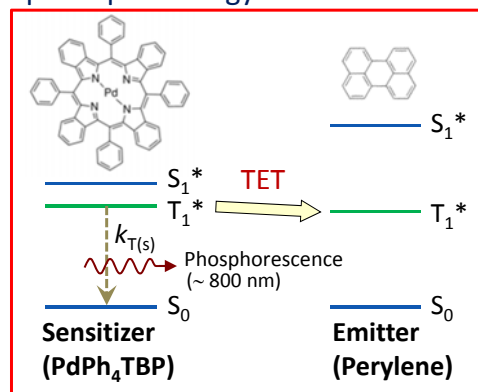
R : Gas constant ($= 8.31 \times 10^7 \text{ erg mol}^{-1}$)
 T : Temperature ($= 300 \text{ K}$)
 η : Bulk viscosity of solvent [P]

↑ In spite of the assumptions, this equation is known to provide good estimates for conventional liquids.

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Quenching of the phosphorescence by collision

Spin-triplet energy transfer:



[E] ≡ Concentration of the emitter
[S] ≡ Concentration of the sensitizer

Throughout this study, [E] >> [S]
([S] = 0.01 mM, fixed)

While the decay from T_1^* to S_0 is basically forbidden, there actually is a slow decay from the T_1^* level accompanying phosphorescence, due to a heavy-atom effect induced by a Pd-atom in the sensitizer.

⇒ Regarding the decay of T_1^* sensitizer, there is a competition between the quenching induced by collision with the emitter molecules and the slow spontaneous decay

at $k_{T(s)} [s^{-1}]$

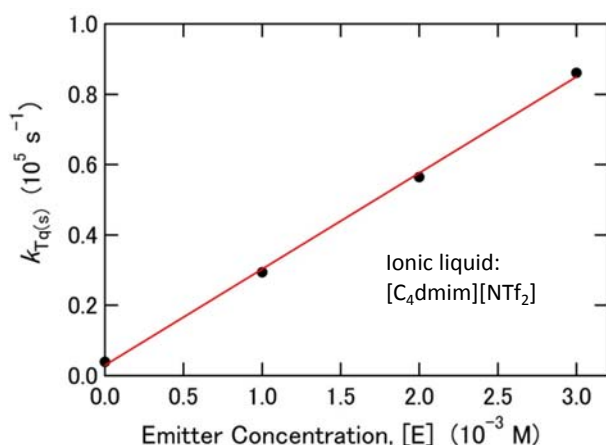
Y. Murakami et al., *J. Phys. Chem. B* **117**, 2487 (2013)

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Determination of the quenching rate constant

Stern-Volmer plot:

= A plot of the phosphorescence quenching rate, $k_{Tq(s)}$, as a function of the emitter concentration, [E].



The linearity of the plot means that:

- 1) This process follows pseudo-first-order kinetics
- 2) No molecular aggregates formed in the samples †

The quenching rate constant, $k_q [M^{-1} s^{-1}]$, is determined from the slope of the plot, based on:

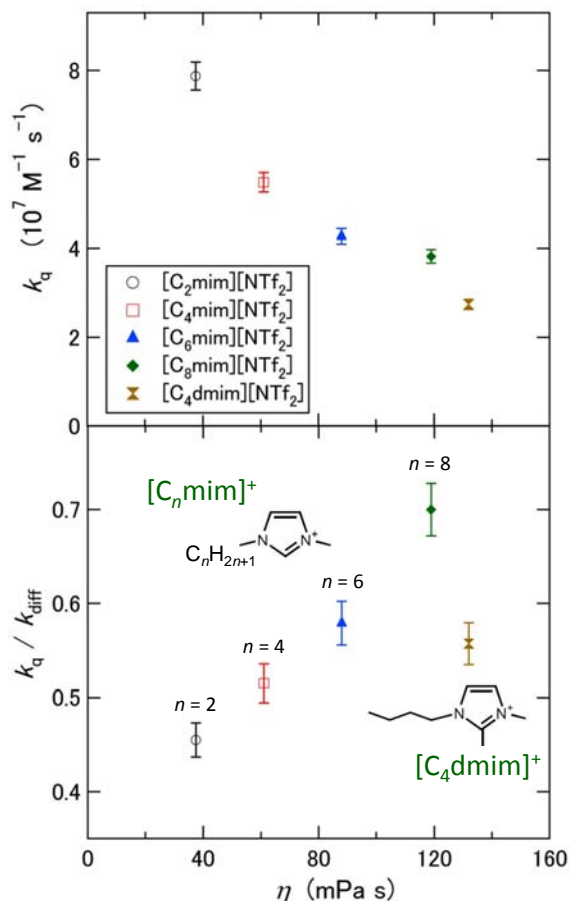
$$k_{Tq(s)} = k_{T(s)} + \underset{\substack{\uparrow \\ \text{slope}}}{k_q [E]}$$

† If molecular aggregate (such as J-aggregate) was formed, the slope should have decreased with increasing [E]; see, e.g., *Phys. Rev. E* **72**, 041710 (2005).

Y. Murakami et al., *J. Phys. Chem. B* **117**, 2487 (2013)

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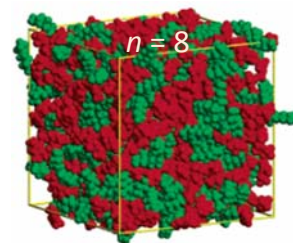
Ionic liquid dependence of molecular diffusion



On the other hand, a diffusion-controlled rate constant, $k_{\text{diff}} [\text{M}^{-1} \text{ s}^{-1}]$, is predicted by the Debye equation:

$$k_{\text{diff}} = \frac{8RT}{3000\eta}$$

R : Gas constant ($= 8.31 \times 10^7 \text{ erg mol}^{-1}$)
 T : Temperature ($= 300 \text{ K}$)
 η : Bulk viscosity of solvent [P]



Translational motion of aromatic molecules in ionic liquid is more favored against the bulk viscosity with increasing volumetric fraction of the microscopic non-polar domain formed by aggregation of the alkyl chains. (Note that $k_q/k_{\text{diff}} < 1$ in this result.)

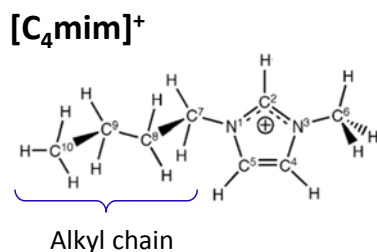
Y. Murakami et al., *J. Phys. Chem. B* **117**, 2487 (2013)

See also a recent mass-transport paper: S. Patra and A. Samanta, *J. Phys. Chem. B* **116**, 12275 (2012)

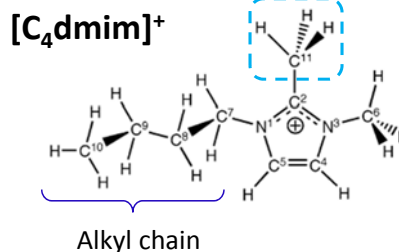
24

Why $[\text{C}_4\text{dmim}]^+$ deviates from the tendency?

Based on theoretical calculations, Hunt^[1] pointed out that, in $[\text{C}_4\text{dmim}]^+$, the methyl group serves as a steric hindrance to the conformation of the adjacent alkyl chain, giving rise to a significant lowering of the entropy or increased microscopic ordering, compared to the case of $[\text{C}_4\text{mim}]^+$.



vs.



⇒ It is no longer appropriate to quantitatively estimate the mass-transport by the Debye equation that solely relies on the bulk viscosity η , different from the cases of conventional solvents. This aspect requires us to take into account the detailed structures of the constituent molecules as well as the microscopic heterogeneity of ionic liquids.

[1] P. A. Hunt, *J. Phys. Chem. B* **111**, 4844 (2007)

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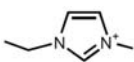
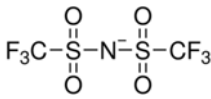
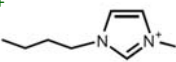
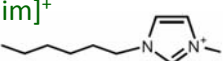
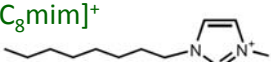
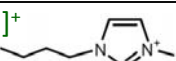
5. Photon upconversion kinetics

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Further objective: Study of the mechanism

It has been found that the UC efficiency (Φ_{UC}) is dependent on the type of ionic liquid:

Y. Murakami, *Chem. Phys. Lett.* **56**, 516 (2011)

Ionic liquid [†]	Cation (+)	Anion (-)	Viscosity, η^{\ddagger} [mPa·s]	Φ_{UC}^{\S} [%]
[C ₂ mim][NTf ₂]	[C ₂ mim] ⁺ 		38	3.3 ±0.5
[C ₄ mim][NTf ₂]	[C ₄ mim] ⁺ 		61	4.4 ±0.7
[C ₆ mim][NTf ₂]	[C ₆ mim] ⁺ 		88	5.2 ±0.8
[C ₈ mim][NTf ₂]	[C ₈ mim] ⁺ 		119	4.2 ±0.6
[C ₄ dmim][NTf ₂]	[C ₄ dmim] ⁺ 		132	10.6 ±1.5

[†]: Those five ionic liquids are to be investigated in the present study below.

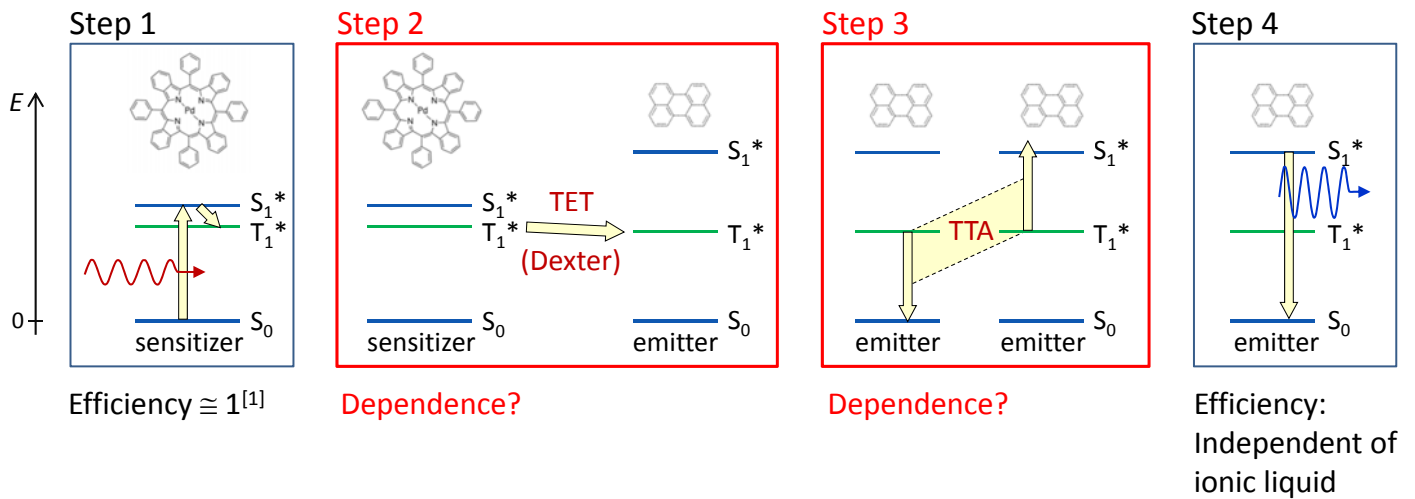
[‡]: Measured at 20 ± 0.2 °C.

[§]: Measured with 633 nm cw excitation with $\cong 6$ W/cm².

⇒ Since more than 1,000,000 ionic liquids are known, an elucidation of the mechanism that controls Φ_{UC} is necessary for establishing a guideline for further increasing Φ_{UC} .

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From where the dependence arises?

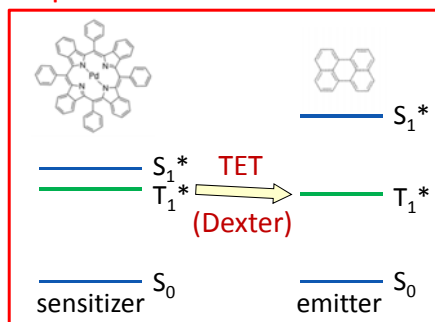


⇒ The Ionic liquid dependence of Φ_{UC} should originate from either Step 2 or Step 3.

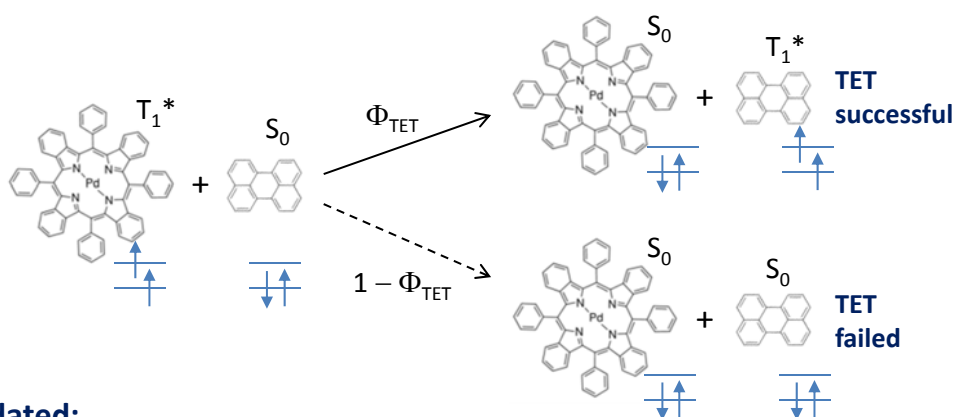
[1] D. Eastwood et al., *J. Mol. Spectroscopy* **35**, 359 (1970)

Issues needed to be elucidated regarding the Step 2

Step 2



Φ_{TET} : Triplet energy transfer efficiency ($0 \leq \Phi_{TET} \leq 1$)



Issues that need to be elucidated:

- Whether or not there is a dependence of Φ_{TET} on ionic liquid type
- Whether this step is a bottleneck for the entire UC efficiency (i.e., the magnitudes of Φ_{TET})
 - ◆ In the previous kinetics studies^[1,2], Φ_{TET} was assumed to be unity for simplicity.
 - ◆ However, a recent paper^[3] suggested the importance of quantifying Φ_{TET} .

[1] Y. Y. Cheng et al., *Phys. Chem. Chem. Phys.* **12**, 66 (2010)

[2] Y. Y. Cheng et al., *J. Phys. Chem. Lett.* **1**, 1795 (2010)

[3] A. Turshatov et al., *ChemPhysChem* **13**, 3112 (2012)

Results for the Step 2

Kinetics of Photon Upconversion in Ionic Liquids: Energy Transfer between Sensitizer and Emitter Molecules

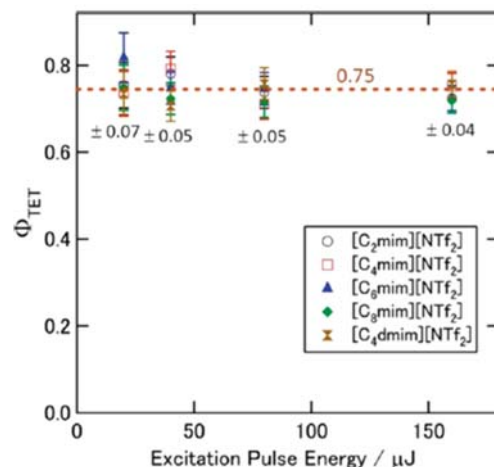
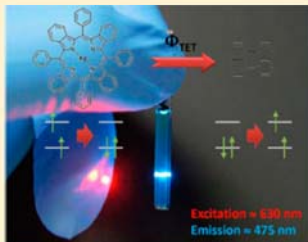
Yoichi Murakami,^{*,†} Hitomi Kikuchi,[‡] and Akio Kawai[‡]

[†]Global Edge Institute, Tokyo Institute of Technology, 2-12-1-II-15 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

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Supporting Information

ABSTRACT: The efficiency of triplet-sensitized photon upconversion in ionic liquids was previously found to be dependent on the type of ionic liquid employed. The properties of the intermolecular energy transfer need to be understood in order to improve the upconversion efficiency. Here, we investigate the kinetics of the triplet energy transfer from the triplet sensitizing molecule to the emitter molecule where the latter is responsible for delayed upconversion fluorescence emission. The collision kinetics between the sensitizer and emitter molecules in imidazolium ionic liquids are investigated by systematically changing the alkyl chain length of the ionic liquid cation. Stern–Volmer analysis reveals unique diffusion behavior of the solute molecules in ionic liquids, and this observation is attributed to the microheterogeneity of the ionic liquids. Through time-resolved transient absorption measurements and determination of the triplet–triplet absorption coefficient of the sensitizer molecule used, we find that the quantum efficiency of the triplet energy transfer in the present system is sufficiently high (ca. 0.75) and independent of the type of ionic liquid. These findings show that the ionic liquid dependence of the upconversion efficiency arises from the later processes pertaining to the emitter molecule rather than the triplet energy transfer process.



⇒ Φ_{TET} was found to be independent of the type of ionic liquid

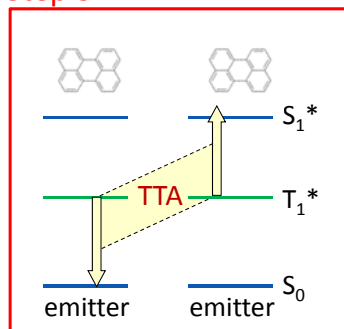
⇒ Φ_{TET} was found to be large enough ($\approx 75\%$ in this system), and hence this process is not a bottleneck of the entire UC efficiency

⇒ The first determination of Φ_{TET} in this research field

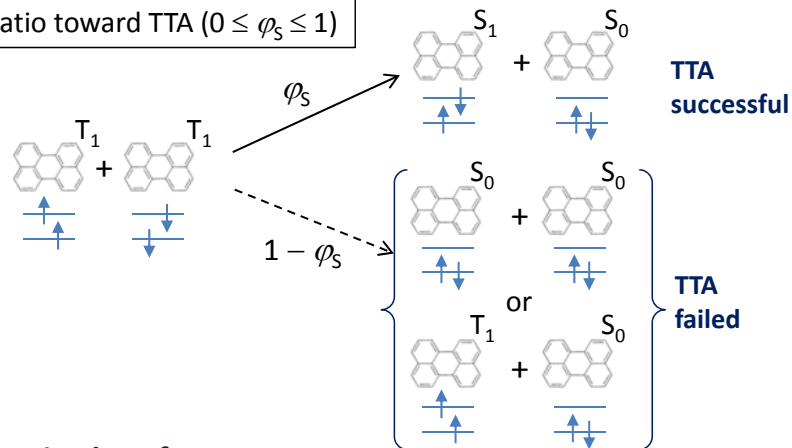
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Issues needed to be elucidated regarding the Step 3

Step 3



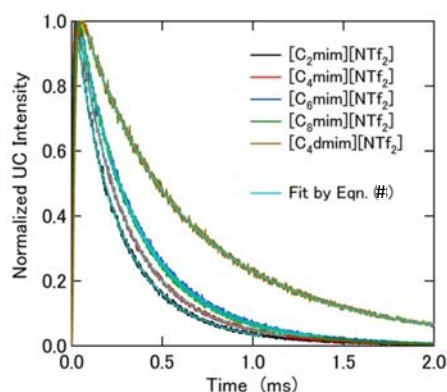
φ_S : Branching ratio toward TTA ($0 \leq \varphi_S \leq 1$)



An invented way of obtaining relative magnitudes of φ_S :

⇒ “Time-resolved UC measurement” + “fitting by an analytical model (* below)”

+ “substitution of Φ_{UC} determined with cw excitation”



$$\Psi = \left\{ (1 + \Omega) \exp(k_{T(e)} t) - \Omega \right\}^{-2} \quad (*)$$

Ψ : dimensionless UC emission intensity ($0 \leq \Psi \leq 1$)

Ω : degree of 2nd order decay over 1st order decay

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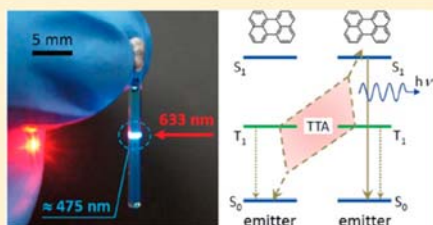
Kinetics of Photon Upconversion in Ionic Liquids: Time-Resolved Analysis of Delayed Fluorescence

Yoichi Murakami,^{*,†} Hitomi Kikuchi,^{‡,§} and Akio Kawai[‡]

[†]Global Edge Institute and [‡]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, Japan

Supporting Information

ABSTRACT: Photon upconversion (UC) based on triplet–triplet annihilation (TTA) is an emerging wavelength shifting technology, which is applicable to sunlight. Previously we found that the quantum efficiency of TTA-UC (Φ_{UC}) carried out in ionic liquids (ILs) is dependent on the type of IL employed. In this article we investigate the kinetics of the triplet emitter molecules (perylene) that implement TTA to determine the origin of the IL dependence of Φ_{UC} . We measure the time-resolved delayed UC fluorescence intensities from samples made with five imidazolium-based ILs, and their intensity decay curves are analyzed with an analytical model. Consequently, several important aspects regarding both the first-order and second-order decays are elucidated. It is revealed that the IL dependence of Φ_{UC} primarily originates from the IL dependence of the branching ratio toward TTA upon an encounter of two triplet emitter molecules. Additionally, a strong correlation between the viscosity of the ILs and the branching ratios toward TTA is found. This finding is supported by temperature-dependent measurements, from which Φ_{UC} is found to be significantly affected by the viscosity of the IL. The results of this study should provide a clue for further improving Φ_{UC} .



Ionic Liquid	η [†] [mPa·s]	ϕ_S , relative [‡]
[C ₂ mim][NTf ₂]	38	0.29
[C ₄ mim][NTf ₂]	61	0.50
[C ₆ mim][NTf ₂]	88	0.66
[C ₈ mim][NTf ₂]	119	0.68
[C ₄ dmim][NTf ₂]	132	1*

[†]: Measured at 20 ± 0.2 °C [‡]: Normalized relative to *

⇒ It was discovered that the branching ratio ϕ_S , which is proportional to the UC efficiency Φ_{UC} , has a strong correlation with the viscosity η and hence that the higher η gives rise to higher Φ_{UC} , contrary to our intuitive expectation.

6. Summary

Talk Summary

From engineering viewpoint:

Y. Murakami, *Chem. Phys. Lett.* **56**, 516 (2011)

Y. Murakami, *Thermal. Sci. Eng.* **20**, 15 (2012)

- invented a method to dissolve charge-neutral aromatic molecules such as porphyrins into ionic liquids, and discovered that, contrary to the conventional knowledge of solvation, these molecules are stably solvated by the proposed “cation- π ” mechanism. This discovery has broadened the usage of ionic liquids.
- developed non-flammable, non-volatile, long-term (= for years) stable, and sunlight-applicable TTA photon upconverters. This has not only resolved the problems of previous TTA photon upconverters, but also allowed for the fabrication of the prototype upconversion devices owing to the improved sealability.

From scientific viewpoint:

Y. Murakami, H. Kikuchi, A. Kawai, *J. Phys. Chem. B* **117**, 2487 (2013)

Y. Murakami, H. Kikuchi, A. Kawai, *J. Phys. Chem. B* **117**, 5180 (2013)

- found that the molecular structure of ionic liquid cation strongly affect the mass-transport characteristics, rendering one major cause of the deviation from the prediction by the classical Debye equation.
- quantitatively determined the inter-molecular triplet energy transfer efficiency (Φ_{TET}) and found that this efficiency is independent of the ionic liquid type.
- elucidated that the ionic-liquid-dependence of the UC efficiency (Φ_{UC}) predominantly originates from the ionic-liquid-dependence of the branching ratio toward TTA (φ_{S}).

Overall, it has turned out that the high viscosities of ionic liquids are actually an *advantage*, and a guiding principle for increasing Φ_{UC} has been acquired. Now I have a hypothesis that could explain the above observation, whose confirmation is to be undertaken.

Thank you for your attentions.