

Photochromic Reaction of a Novel Room Temperature Ionic Liquid: 2-Phenylazo-1-hexyl-3-methylimidazolium Bis(pentafluoroethylsulfonyl)amide

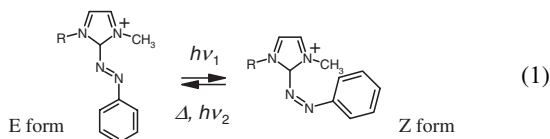
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We synthesized a new room temperature ionic liquid, [2PA-Hmim][Pf₂N], and characterized the photochromic behavior by absorption spectroscopy. [2PA-Hmim][Pf₂N] was found to be a photochromic liquid where solvent itself undergoes photochromic reaction.

Since the discovery of air- and water- stable room temperature ionic liquids (RTILs), various solvent properties have been created by combinations of anion and cation.¹ This variety of RTIL attracts much interest from researchers who aim to discover a novel solvent with some unique properties that have never been created.^{2–8} In this study, we show recent results through our challenging intention to introduce photochromic character into RTIL and to obtain new photochromic solvent which shows photochromism as solvent itself. For this purpose, a series of phenylazo-substituted imidazolium-based ionic compounds, [2PA-Rmim][anion] (2PA-Rmim: 2-phenylazo-1-R-3-methylimidazolium, R= methyl, *n*-butyl, or *n*-hexyl) were newly synthesized according to a similar preparation procedure described for [2PA-Bmim][Tf₂N] {B: *n*-butyl, [Tf₂N][−]: bis(trifluoromethylsulfonyl)amide}.^{8,9} Table 1 lists the melting point (mp) of these compounds measured by differential scanning calorimetry (Shimadzu DSC-60). It is noteworthy that the mp of [2PA-Hmim][Pf₂N] {H: *n*-hexyl, [Pf₂N][−]: bis(pentafluoroethylsulfonyl)amide} is 306 K being close to room temperature and more interestingly, [2PA-Hmim][Pf₂N] was found to be quite stable supercooled liquid. Since our interest lies in photochromic reaction of the liquid, we measured photoisomerization and thermal isomerization of [2PA-Hmim][Pf₂N] in the liquid phase at around 298 K.

Photochromic reaction of cation components, [2PA-Rmim]⁺ may be described by the following scheme,



according to our previous study for photochromism of [2PA-Bmim]⁺ dissolved in various solvents.⁸ DFT calculation (B3LYP/6-31G*) suggested the E form of this cation is ca.

Table 1. Melting points of a series of [2PA-Rmim][anion]

Cations	mp/K			
	Anions:	I [−]	[Tf ₂ N] [−]	[Pf ₂ N] [−]
Methyl		>523	362	393
<i>n</i> -Butyl		441	329	313
<i>n</i> -Hexyl		397	321	306

80 kJ mol^{−1} more stable than the Z form. Phenylazo moiety absorbs light in the UV and vis region and the E to Z photoisomerization occurs. The Z form undergoes backward thermal isomerization and [2PA-Bmim]⁺ has thus been classified as a T-type photochromic ion. We expect similar photochromic reaction for the newly-synthesized liquid, [2PA-Hmim][Pf₂N].

Generally speaking, absorption spectroscopy has been applied as a powerful method for the study of isomerization. However, neat [2PA-Hmim][Pf₂N] has extremely strong absorption and therefore the conventional absorption method using a cubic cell with 1 cm optical path length was no longer applicable. We prepared a thin layer sample of about 1 μm thickness by utilizing two quartz plates, which was a similar set up employed for thin layer absorption spectroscopy of RTILs.¹⁰ Figure 1a shows the absorption spectra of [2PA-Hmim][Pf₂N] thin layer at 298 K. We observed absorption spectral changes during 436 nm light irradiation of a mercury high-pressure lamp (USHIO USH-500SC) with appropriate filters. Although the spectral change is rather small, we could recognize the isosbestic points at 265 and 428 nm. The transition bands to S₂(ππ*) and S₁(nπ*) appear around 350 and 460 nm, respectively. The absorbance due to the S₂(ππ*) band was much larger than unity even though we used a thin layer sample. Meanwhile, the S₁(nπ*) forbidden band shows absorbance less than unity, which allows us to make quantitative absorption measurements.

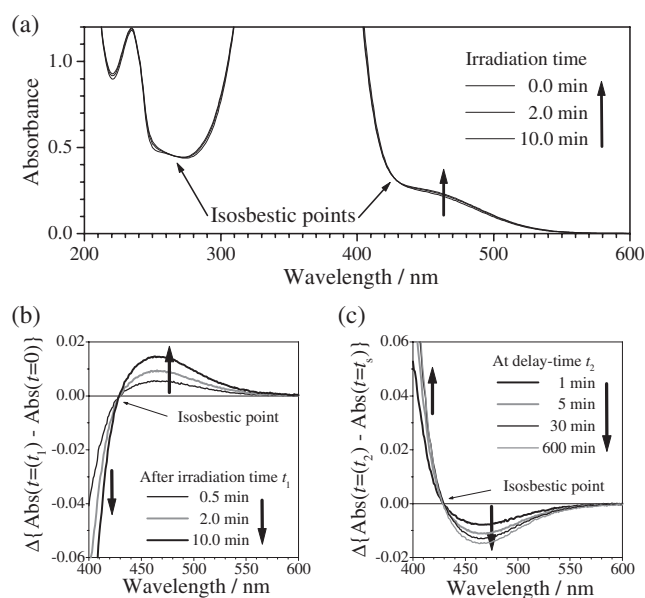


Figure 1. Absorption spectra of [2PA-Hmim][Pf₂N] liquid (a), and difference spectra for photoinduced E to Z reaction time *t*₁ (b) and for dark Z to E reaction time *t*₂ (c).

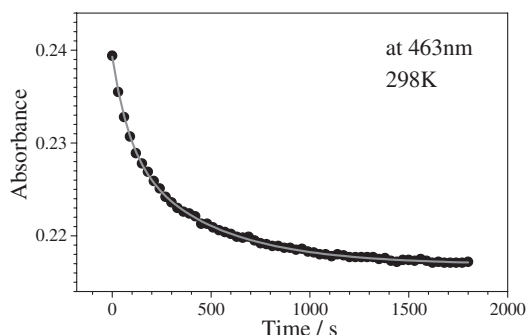


Figure 2. Time profile of dark Z to E isomerization reaction of [2PA-Hmim][Pf₂N] liquid.

Figure 1b shows the difference absorption spectra of the S₁ observed before and after 436 nm light irradiation. The clear isosbestic point at 428 nm is recognized, which indicates that photoisomerization from E to Z forms occurs in the neat liquid of [2PA-Hmim][Pf₂N]. After the light irradiation, the backward isomerization from Z to E forms took place under dark conditions. Figure 1c shows difference spectra observed with different delay times in the dark. The isosbestic points again appear, which suggests that the Z form produced by the 436 nm light irradiation undergoes thermal isomerization to the E form without yielding any by-product. Therefore, we conclude that [2PA-Hmim][Pf₂N] neat liquid shows T-type photochromism around room temperature.

Second, we evaluated a steady-state molar fraction of Z form, f_Z , under the 436 nm light irradiation. For determination of f_Z , we observed absorbances, $Abs_1 = \epsilon_E C d$ before irradiation and $Abs_2 = \{\epsilon_E(1 - f_Z) + \epsilon_Z f_Z\} C d$ under photostationary conditions with photon flux of $2.4 \times 10^{-2} \text{ W cm}^{-2}$. The C and d are the concentration of [2PA-Hmim]⁺ in the neat liquid and thickness of the thin layer. For extinction coefficients, ϵ_E and ϵ_Z , of E and Z forms [2PA-Hmim]⁺, we adopt the corresponding values of [2PA-Hmim]⁺ in solution since there are no remarkable spectral difference in absorption between [2PA-Hmim][Pf₂N] liquid and [2PA-Hmim]⁺ dissolved in organic solvents. We obtained $C \times d$ from Abs_1 , and then, f_Z of about 5% from Abs_2 . The f_Z value seems rather low for practical photochromic materials, but this value is large enough to lead us to the conclusion that [2PA-Hmim][Pf₂N] is *photochromic liquid*, where solvent itself undergoes photochromic reaction. The low f_Z is due to a relation of $\epsilon_E < \epsilon_Z$ at 436 nm. The reverse relation of $\epsilon_E \gg \epsilon_Z$ holds at 360 nm and therefore the f_Z value under the 360 nm irradiation is expected to be larger. However, the UV light irradiation might destroy the imidazolium ring,¹¹ and the UV photochemistry must be examined before we report the UV photochromic properties.

Third, we report the fast thermal isomerization of [2PA-Hmim][Pf₂N] liquid. Figure 2 shows the time profile of the dark isomerization monitored at 298 K after the 436 nm light irradiation. The Z to E thermal isomerization took place in the dark and the decay is characterized by double exponential functions with the first-order reaction rate constants of

1.1×10^{-2} and $2.2 \times 10^{-3} \text{ s}^{-1}$. It is noteworthy that even the slower component rate is about 10 times faster than the corresponding dark reaction rate of [2PA-Bmim]⁺ in solution.⁸ As neat [2PA-Hmim][Pf₂N] is a viscous RTIL and internal motions are restricted,^{6,12-14} it is not straightforward to explain such a fast rate. Since [2PA-Hmim]⁺ concentration in neat liquid is very much higher than those in solution, we speculate that certain intermolecular interaction among [2PA-Hmim]⁺ may contribute to fast and nonexponential isomerization. To evaluate the mechanism, we need detailed experiments such as Arrhenius parameter measurements which are now under progress. One important revelation from the results is that this fast recovery from Z to E forms is perhaps one of the reasons why f_Z is low. Another realization is that the fast thermal isomerization gives one advantage to [2PA-Hmim][Pf₂N] liquid; this *photochromic liquid* recovers to the initial form quickly after the light irradiation ceases. This characteristic will be useful when building *photochromic liquid* that shows fast recovery in the dark.

In this letter, we reported on *photochromic liquid*, [2PA-Hmim][Pf₂N] with a mp of nearly room temperature. This liquid undergoes E to Z photoisomerization with vis light irradiation and Z to E thermal isomerization in the dark, which indicates that the liquid is a T-type photochromic compound.

We thank Prof. Tomoya Kitazume (Tokyo Institute of Technology) for his unfailing advice. This work was supported in part by a Grant-in-Aid for Scientific Researches (Nos. 17073006 and 19350008) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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