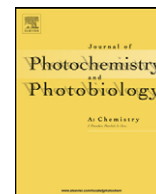




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## Photochromism of 3-butyl-1-methyl-2-phenylazoimidazolium in room temperature ionic liquids

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### ABSTRACT

We studied the photochromism of a newly synthesized ionic liquid, [2PA-Bmim]Tf<sub>2</sub>N ([2PA-Bmim]<sup>+</sup>: 3-butyl-1-methyl-2-phenylazoimidazolium, Tf<sub>2</sub>N<sup>-</sup>: bis(trifluoromethanesulfonyl)-amide) which is characterized by a phenylazo group substituted on the imidazolium ring. The melting point of [2PA-Bmim]Tf<sub>2</sub>N is 329 K. The absorption spectrum of [2PA-Bmim]<sup>+</sup> dissolved in conventional organic solvents or in ionic liquids changes drastically upon UV-light irradiation, which is attributed to the photoisomerization of the phenylazo group from E- to Z-forms during irradiation and the backward thermal isomerization from Z- to E-forms in the dark. The E–Z photoisomerization quantum yield,  $\Phi_{\text{iso}}$ , was determined by 355 nm laser photolysis. The  $\Phi_{\text{iso}}$  value slightly depends on solvent viscosity, from 0.12 in 3-butyl-1-methylimidazolium PF<sub>6</sub><sup>-</sup> ( $\eta = 241$  cP) to 0.19 in toluene ( $\eta < 1$  cP). On the other hand, no solvent dependence was observed for Arrhenius parameters of the backward Z–E thermal isomerization. We discuss the isomerization mechanism and the reason why the E–Z photoisomerization yield depends on solvent viscosity.

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### 1. Introduction

Ionic liquids which are salts having low melting points have been studied in various fields to understand their interesting properties such as high viscosity, non-volatility, high ion conductivity and so on [1]. These properties are controlled by a choice of anion and/or cation components, which enables us to create novel properties of solvent by introducing a functional group into an ionic liquid. In this view point, we are interested in creating photofunctional ionic liquids, and planning to synthesize imidazolium based ionic liquids with a phenylazo group which is known to show photochromism [2]. As the first step to create photochromic ionic liquids, we synthesized 3-butyl-1-methyl-2-phenylazoimidazolium ([2PA-Bmim]<sup>+</sup>) bis(trifluoromethanesulfonyl)amide ([Tf<sub>2</sub>N<sup>-</sup>]) (see Scheme 1) and studied photochromic reaction of [2PA-Bmim]<sup>+</sup> both in organic solvents and in ionic liquids. Unfortunately, the melting point of [2PA-Bmim]Tf<sub>2</sub>N was found to be 329 K which is above room temperature, but some modification such as replacements of alkyl group and/or anion may lower the melting point and give us phenylazoimidazolium-based room temperature ionic liquids. The photochromism of phenylazo compounds is owing to isomeriza-

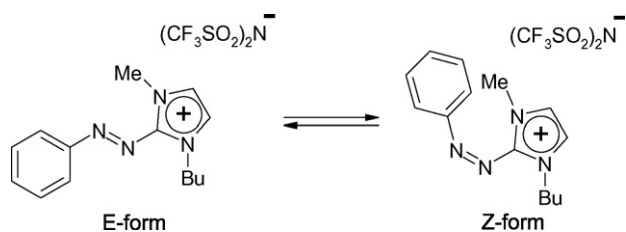
tion around NN bond of E and Z conformers accompanying a large conformational change and there should be solvent effects on the reaction. Since viscosity of ionic liquids is remarkably high, rotational [3–9] and translational [10–16] diffusion motions of solutes are different from those in conventional solvents. Solvation [3,4,6,17–23] in ionic liquids is another interesting subject and it has been reported that polarity of ionic liquids is close to those of alcohols [17–19]. To develop phenylazo-substituted ionic liquids with excellent photochromic character, we should evaluate how viscous and polar ionic liquids inhibit isomerization. Although there are a few studies [24–26] about photoisomerization of E- and Z-forms in ionic liquids, we intend to understand photo- and thermal-isomerization of a phenylazo group attached to the imidazolium ring, which should be important when we develop photochromic ionic liquids. As the first step, we examined the photochromism of [2PA-Bmim]<sup>+</sup> as a solute. This knowledge will be useful when we study phenylazoimidazolium-based room temperature ionic liquids whose developments are under progress.

Photo- and thermal-isomerization of azocompounds are rather complicated and the isomerization mechanism has been argued for long time. Here we briefly review isomerization of azobenzene and its derivatives [2,27–43], which is important to understand photochromism of [2PA-Bmim]<sup>+</sup>. Both E- and Z-forms undergo photoisomerization and Z-form thermally isomerizes to E-form [2]. Photoisomerization mechanism [27,28] has not been fully understood yet and there remains unknown whether photoisomerization proceeds through in-plane bending of CNN moiety (*inversion* mechanism) or an out-of-plane torsion of CNNC moi-

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**Scheme 1.** Two structural forms of [2PA-Bmim]Tf<sub>2</sub>N.

ety (*rotation* mechanism). In these arguments, solvent viscosity is certainly important and ethylene glycol which has lower viscosity than ionic liquids gives remarkable viscosity effects on the photoisomerization. As for the thermal process, isomerization proceeds through the *inversion* but, some azobenzene derivatives such as 4-dimethylamino-4'-nitroazobenzene (=DNAB), the *rotation* is major channel. This feature is schematically shown in Fig. 1. The activated state of DNAB in *rotation* mechanism has charge transfer (CT) character and *rotation* is dominant in polar solvents [39–42] and in ionic liquids [43]. Since our sample is an azobenzene derivative, we should consider solvent polarity effects on its isomerization in ionic liquids.

Recently, a notable study was reported on 1-methyl-2-phenylazoimidazole (=Pai-Me) [44], which has similar structure to [2PA-Bmim]<sup>+</sup>. Photoisomerization quantum yield ( $\Phi_{\text{iso}}$ ) of Pai-Me is 0.25 in toluene, which seems promising that our synthetic sample will have photochromic activity. In this study, we measured  $\Phi_{\text{iso}}$  value to evaluate if [2PA-Bmim]<sup>+</sup> shows photochromism. Arrhenius parameters of the thermal isomerization were also measured. We discuss how the viscosity and polarity of ionic liquids influences the isomerization of [2PA-Bmim]<sup>+</sup>.

## 2. Experimental

### 2.1. Synthesis and sample characterization

#### 2.1.1. 1-Methyl-2-phenylazoimidazole (=Pai-Me)

2-Phenylazoimidazole (=Pai-H) was synthesized by a previously reported method [45]. Pai-H, methyl iodide, and 1,8-diazabicyclo[5.4.0]undec-7-ene (=DBU) were dissolved in methanol. The solution was heated to 338 K, refluxed for 6 h, and then evaporated. The separated crystal was washed with water.

#### 2.1.2. 3-Butyl-1-methyl-2-phenylazoimidazolium iodide (= [2PA-Bmim]I)

[2PA-Bmim]I was synthesized by the similar synthetic procedure of 3-butyl-1-methylimidazolium chloride (BmimCl) [46]. Pai-Me and butyl iodide were dissolved in toluene. The solution was heated to 383 K and refluxed for 5 h. The orange precipitation was washed with ethyl acetate and toluene.

#### 2.1.3. 3-Butyl-1-methyl-2-phenylazoimidazolium Tf<sub>2</sub>N (= [2PA-Bmim][Tf<sub>2</sub>N])

The synthesis of [2PA-Bmim]Tf<sub>2</sub>N followed the synthetic procedure of 3-butyl-1-methylimidazolium Tf<sub>2</sub>N (Bmim Tf<sub>2</sub>N) [46]. [2PA-Bmim]I and lithium bis(trifluoromethanesulfonyl)amide were dissolved in water. After the solution was stirred for 24 h at room temperature, orange precipitation was corrected and washed with water.

Melting points of synthetic products were measured using a differential scanning calorimeter (Shimadzu, DSC-60) and the identification was done by <sup>1</sup>H NMR (JEOL, JNM-AL300) in CDCl<sub>3</sub>. Viscosity of ionic liquid solvents were measured by a viscometer (BROOKFIELD, DV-II+ Pro).

#### 2.1.4. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

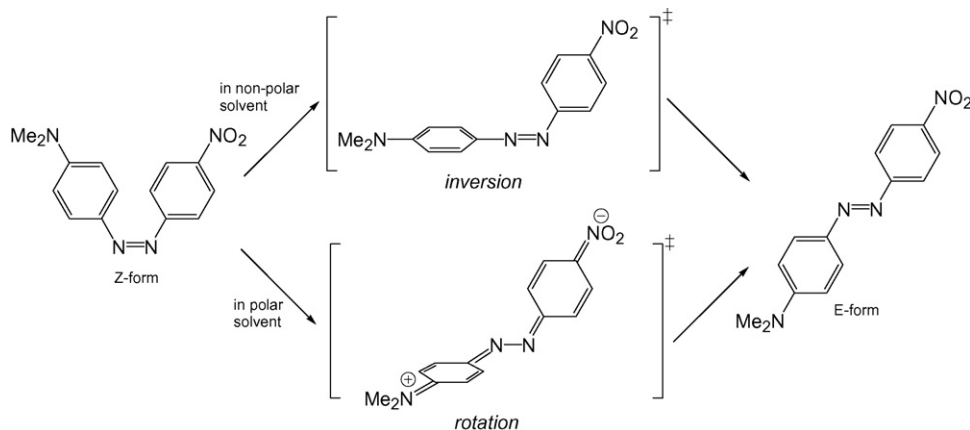
Pai-Me (m.p. = 393 K): 4.17 (s, 3H, NCH<sub>3</sub>), 7.26 (s, 1H, CH), 7.39 (s, 1H, CH), 7.60 (m, 3H, phenyl), 8.11 (d, 2H, phenyl).

[2PA-Bmim]I (m.p. = 441 K): 1.00 (t, 3H, CH<sub>3</sub>), 1.46 (m, 2H, CH<sub>2</sub>), 1.95 (m, 2H, CH<sub>2</sub>), 4.34 (s, 3H, NCH<sub>3</sub>), 4.66 (t, 2H, NCH<sub>2</sub>), 7.60–7.75 (m, 3H, phenyl), 8.00 (d, 2H, phenyl), 8.12 (d, 1H, CH), 8.33 (d, 1H, CH).

[2PA-Bmim]Tf<sub>2</sub>N (m.p. = 329 K): 0.98 (t, 3H, CH<sub>3</sub>), 1.43 (m, 2H, CH<sub>2</sub>), 1.90 (m, 2H, CH<sub>2</sub>), 4.19 (s, 3H, NCH<sub>3</sub>), 4.54 (t, 2H, NCH<sub>2</sub>), 7.59–7.74 (m, 5H, phenyl, CH), 7.95 (d, 2H, phenyl).

### 2.2. Optical measurements

The absorption spectra of [2PA-Bmim]Tf<sub>2</sub>N were measured by a UV-vis spectrometer (Shimadzu, UV-2450). A light at 365 nm from an ultrahigh pressure mercury lamp (USHIO, USH-500SC) was used for the photoisomerization from the E-form to the Z-form. The thermal isomerization of the samples was monitored by a UV-vis absorption method at various temperatures using a temperature controller (Shimadzu TCC-240A). The  $\Phi_{\text{iso}}$  values of E–Z photoisomerization were determined by a transient absorption method [47]. A Xe-flash lamp was used for a monitor light and the third harmonics of a Nd<sup>3+</sup>-YAG laser (Continuum, Surelight) was used for an excitation light source. A laser energy meter (Gentec, QE-25-SP-S) was used to measure relative laser power.



**Fig. 1.** Mechanisms proposed for the thermal isomerization of an azobenzene derivative, 4-dimethylamino-4'-nitroazobenzene (=DNAB) [40–43].

Degassed acetonitrile solution of benzophenone was used as a standard sample to determine  $\Phi_{\text{iso}}$  values. The transient absorption was measured at 516.5 nm for the standard sample triplet–triplet absorption and 376.5 nm for the photoisomerization of the present interest. For the determination of quantum yield, the transient absorbance change by only a single laser shot was accumulated for the data acquisition and the sample was replaced after every laser shot to avoid the photodegradation of solvents, i.e. ionic liquids.

The spectroscopic grade toluene and methanol, the fluorometry grade acetonitrile, and ionic liquids were purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan) and used as received for measurements. All spectroscopic experiments were performed at room temperature, except for the measurements of the thermal isomerization (293–308 K).

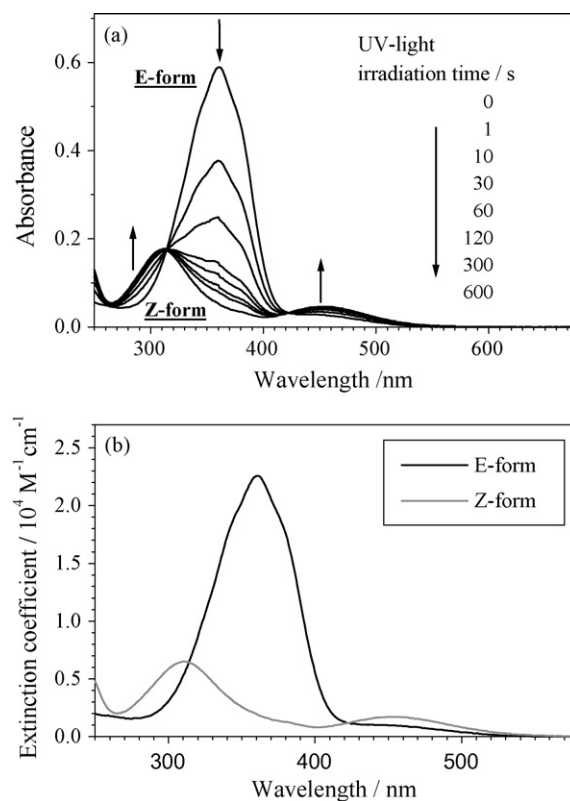
### 2.3. Quantum chemical calculations

The energies of the E- and Z-forms of [2PA-Bmim]<sup>+</sup> in the ground state were obtained by a DFT calculation. The molecular geometry optimizations and frequency calculations were performed at the B3LYP/6-31G\* level using the Gaussian 03 program [48].

## 3. Results and discussion

### 3.1. Observation of spectral changes upon UV-light irradiation

Fig. 2 shows changes in the absorption spectra of [2PA-Bmim]Tf<sub>2</sub>N in BmimTf<sub>2</sub>N upon the UV-light irradiation. The spectral carrier is surely [2PA-Bmim]<sup>+</sup> without doubt since neither Bmim<sup>+</sup> nor Tf<sub>2</sub>N<sup>-</sup> have absorption in this spectral region. Before the UV-light irradiation, the strong  $\pi$ - $\pi^*$  band ( $\epsilon \sim 23,000 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $M = \text{mol dm}^{-3}$ ) at 361 nm and the weak  $n$ - $\pi^*$  band around 455 nm ( $\epsilon \sim 1800 \text{ M}^{-1} \text{ cm}^{-1}$ ) were observed. The spectral feature is quite similar to that of E-form Pai-Me [44]. After the UV-light irradiation, the 361 nm band decreased in intensity and the maximum wavelength shifted from 361 to 311 nm ( $\epsilon \sim 7000 \text{ M}^{-1} \text{ cm}^{-1}$ ). Besides, the  $n$ - $\pi^*$  band at 455 nm increased in intensity. The spectral carrier generated after the UV irradiation is attributed to the Z-form based on the spectrum of Z-form Pai-Me [44]. It is notable the  $S_1(n-\pi^*)$  band intensity of Z-form is higher than that of E-form. This may be due to more twisted structure of CNNC moiety in Z-form which results in partially allowed optical transition for  $n-\pi^*$  excitation. Optical properties of E- and Z-form [2PA-Bmim]<sup>+</sup> are summarized in Table 1. Three isosbestic points were observed at 265, 314, and 423 nm. The similar results were obtained in other solvents. Z-form produced by the UV irradiation of E-form undergoes thermal Z-E isomerization. The absorption spectrum recorded at 60 min after the UV-light irradiation finished is exactly the same as the initial



**Fig. 2.** Absorption spectral change of [2PA-Bmim]Tf<sub>2</sub>N in BmimTf<sub>2</sub>N ( $2.6 \times 10^{-5} \text{ M}$ ). (a) Spectral changes upon the UV-light (365 nm) irradiation at room temperature. The spectral carrier is [2PA-Bmim]<sup>+</sup>. Three isosbestic points are recognized at 265, 312 and 423 nm. (b) Reproduced absorption spectra of E-form and Z-form [2PA-Bmim]<sup>+</sup>. See the text for details.

one of E-form. From these results, [2PA-Bmim]<sup>+</sup> is concluded as a T-type photochromic compound [49].

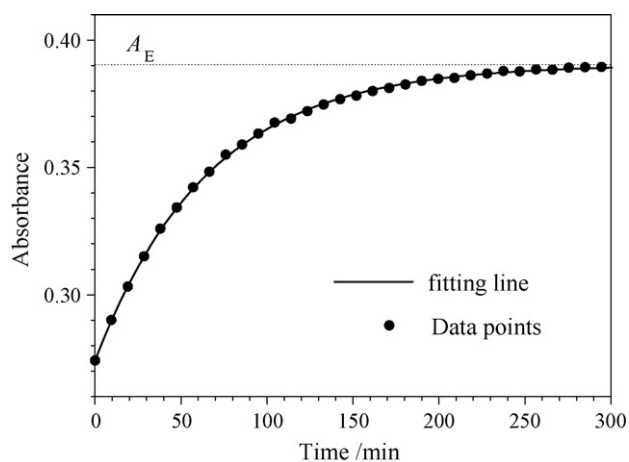
It is worthwhile to evaluate purity of Z-form spectrum in Fig. 2a to compare pure spectra of E- and Z-forms. As explained later, E-form energy of [2PA-Bmim]<sup>+</sup> is much lower than Z-form and we safely attributed the absorption spectrum before UV-light irradiation to pure E-form. On the other hand, pure Z-form spectrum was hardly obtained under steady state condition of the mixture solution of E- and Z-forms during 365 nm irradiation. Here we assume that photoisomerization quantum yield from E-form to Z-form at 365 nm excitation equals to that from Z-form to E-form, which means that a half of absorbance at 365 nm of absorption spectrum at 600 s after UV-light irradiation is due to pure E-form. Under this assumption, we reproduced pure Z-form spectrum by subtracting E-form spectrum from the absorption spectrum at 600 s after UV-

**Table 1**  
Optical properties of E- and Z-form [2PA-Bmim]<sup>+</sup>.

Solvent	E-form		Z-form			$\lambda_{\text{iso}}^{\text{a}}$ /nm	
	$\pi$ - $\pi^*$		$\pi$ - $\pi^*$		$n$ - $\pi^*$		
	$\lambda_{\text{max}}^{\text{b}}$ /nm	$\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{max}}^{\text{b}}$ /nm	$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{max}}^{\text{b}}$ /nm		
Toluene	367	1.9	–	–	459	1.8	–, 321, 442
Methanol	360	2.4	310	8.2	450	2.1	266, 314, 426
Acetonitrile	360	2.5	311	7.5	455	2.0	263, 313, 421
Ethylene glycol	365	2.2	315	7.1	455	2.0	266, 319, 429
EmimBF <sub>4</sub>	360	2.1	311	6.5	450	1.7	265, 313, 421
BmimTf <sub>2</sub> N	361	2.3	311	7.0	455	1.8	265, 314, 423
BmimBF <sub>4</sub>	358	2.3	311	6.9	453	1.9	265, 315, 423
BmimPF <sub>6</sub>	359	2.2	310	6.8	452	1.8	265, 314, 420

<sup>a</sup> Wavelength of isosbestic point.  $\lambda_{\text{iso}}$  around 265 nm in toluene were not observed because of electronic absorption of solvent toluene.

<sup>b</sup> Wavelength of band peak.



**Fig. 3.** Time profile of absorbance of [2PA-Bmim]<sup>+</sup> in BmimTf<sub>2</sub>N in the dark measured at 360 nm. Temperature was kept at 307 K. The fitting line reproduces the data points measured at 360 nm. The  $A_E$  value (0.39) corresponds to the absorbance of [2PA-Bmim]<sup>+</sup> for this sample solution when all the Z-form returns to the E-form. See the text for details.

light irradiation. These E- and Z-form spectra are shown in Fig. 2b. It is clearly shown that pure Z-form spectrum is essentially the same with the absorption spectrum at 600 s after UV-light irradiation as given in Fig. 2a. Therefore, we consider that extinction coefficients given in Table 1 are reasonable values.

### 3.2. Thermal backward isomerization

After the long-time UV-light irradiation to prepare Z-form, absorbance around 360 nm was dominantly due to Z-form of [2PA-Bmim]<sup>+</sup>. Fig. 3 shows a time profile of 360 nm absorbance in the dark. The thermal isomerization in BmimTf<sub>2</sub>N takes place slowly, and the reaction rate is characterized by a single exponential function. The unimolecular rate constant of the thermal backward isomerization ( $k$ ) was obtained by the analysis of the measured absorbance,  $Abs(t)$ , using Eq. (1).

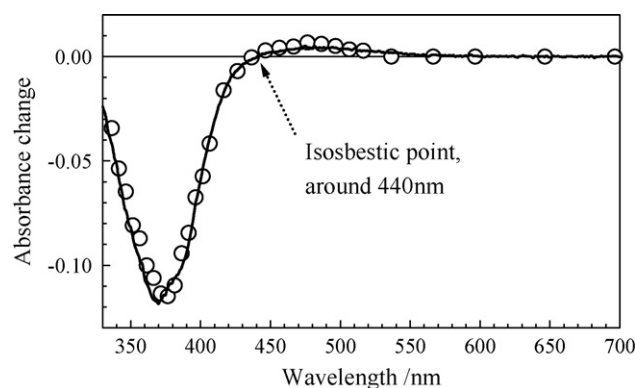
$$Abs(t) = (Abs_Z - Abs_E)e^{-kt} + Abs_E \quad (1)$$

where  $Abs_E$  and  $Abs_Z$  are absorbances corresponding to pure samples of E- and Z-forms, respectively. The experimental data were fitted by a nonlinear algorithm with Eq. (1). The activation energy,  $E_a$ , of thermal backward isomerization, and the frequency factor,  $A$ , were determined by fitting the temperature dependent  $k$  values and the results are listed in Table 2. We measured viscosities of the solvents at 298 K and the values were also tabulated. Both the  $E_a$  and the  $A$  values are essentially identical within experimental error for seven solvents of largely different viscosity. This result is consistent with the observation in the thermal isomerization of azobenzene whose Arrhenius parameters show no clear correlation with solvent viscosity [43]. We addressed here that thermal back-

**Table 2**

Arrhenius parameters for backward Z–E thermal isomerization in various solvents and measured viscosities,  $\eta$  of solvents at 298 K.

Solvent	$E_a$ /kJ mol <sup>-1</sup>	$A$ /s <sup>-1</sup>	$\eta$ /cP
Toluene	77 ± 2	(1.4 ± 1.0) × 10 <sup>10</sup>	<1
Acetonitrile	80 ± 4	(3.4 ± 3.2) × 10 <sup>10</sup>	<1
Ethylene glycol	79 ± 5	(2.5 ± 2.4) × 10 <sup>10</sup>	17
EmimBF <sub>4</sub>	90 ± 5	(1.3 ± 1.2) × 10 <sup>11</sup>	34
BmimTf <sub>2</sub> N	85 ± 3	(1.3 ± 1.0) × 10 <sup>11</sup>	50
BmimBF <sub>4</sub>	90 ± 4	(1.3 ± 1.2) × 10 <sup>12</sup>	93
BmimPF <sub>6</sub>	85 ± 4	(1.8 ± 1.7) × 10 <sup>11</sup>	241



**Fig. 4.** Difference spectra of [2PA-Bmim]<sup>+</sup> upon the UV irradiation. Black circles represent the absorbance change spectrum of [2PA-Bmim]<sup>+</sup> in toluene measured at 2 μs after 355 nm laser excitation obtained by a transient absorption method. The solid line shows the difference spectrum of [2PA-Bmim]<sup>+</sup> in toluene before and after UV irradiation for 1 h obtained by a UV–vis spectrometer and the spectrum was scaled to fit the black circles. The sample solution was prepared by dissolving [2PA-Bmim]Tf<sub>2</sub>N in toluene (2.8 × 10<sup>-5</sup> M).

ward isomerization of [2PA-Bmim]<sup>+</sup> certainly occurs within several hours even in highly viscous solvent.

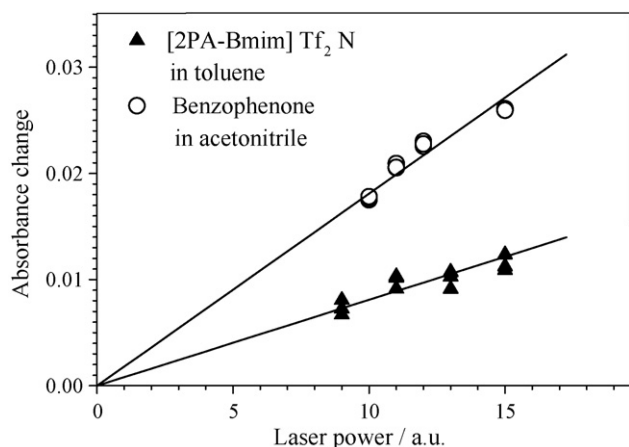
As described before, the thermal isomerization process of DNAB depends on polarity of solvents: The  $E_a$  for DNAB in polar solvents (ca. 40 kJ mol<sup>-1</sup>) are smaller than those in non-polar solvents (ca. 80 kJ mol<sup>-1</sup>) [43]. The difference of the  $E_a$  value is very large of about 40 kJ mol<sup>-1</sup>. This is because the activated state of DNAB has strong CT character and is stabilized in polar solvents. On the other hand, the  $E_a$  for [2PA-Bmim]<sup>+</sup> are almost the same in non-polar toluene, polar acetonitrile, ethylene glycol and four ionic liquids. This may mean that the activated state of [2PA-Bmim]<sup>+</sup> does not have CT character. According to the previous studies on the thermal isomerization of azobenzene, the reaction takes place through *inversion* mechanism and there are few differences in the activation energy ( $E_a$  = 80–100 kJ mol<sup>-1</sup>) among non-polar and polar solvents. Although the  $E_a$  of about 80 kJ mol<sup>-1</sup> for [2PA-Bmim]<sup>+</sup> is slightly lower than that of azobenzene, a characteristic point of [2PA-Bmim]<sup>+</sup> isomerization, namely no dependence on solvent polarity, is quite similar to that of azobenzene. From these reasons, we concluded that Z-form [2PA-Bmim]<sup>+</sup> thermally isomerizes by *inversion* mechanism.

### 3.3. Photoisomerization from E-form to Z-form

The photoisomerization of azobenzene takes place by both S<sub>1</sub> and S<sub>2</sub> excitation [2]. Here, we determined the quantum yields of the photoisomerization of [2PA-Bmim]<sup>+</sup> by a transient absorption method after S<sub>2</sub>( $\pi$ – $\pi^*$ ) excitation. Fig. 4 shows the difference spectrum of [2PA-Bmim]<sup>+</sup> in toluene obtained by the spectra before and 2 μs after laser excitation. The spectral shape is quite similar to the spectrum obtained by subtracting the initial E-form spectrum from the product of Z-form spectrum measured by the UV–vis spectrometer. The isosbestic point around 440 nm is consistent with the result (442 nm, see Table 2) in absorption spectral change in toluene under the continuous-wave lamp irradiation. The depletion around 375 nm and the increase around 450 nm are thus attributed to the photoisomerization from E-form to Z-form within [2PA-Bmim]<sup>+</sup>. The spectral change occurs promptly within a laser pulse (ca. 10 ns). A previous femtosecond spectroscopic study [29–33] reported the lifetime of excited E-azobenzene is around 10 ps or much shorter. Thus, we consider that the initial spectral change of [2PA-Bmim]<sup>+</sup> certainly reflects the photoisomerization.

Fig. 5 shows absolute value of absorbance change,  $|\Delta Abs|$  of [2PA-Bmim]<sup>+</sup> monitored at 376.5 nm as a function of the laser





**Fig. 5.** Laser power dependence of absolute values of absorbance changes. Black triangles are data for [2PA-Bmim]Tf<sub>2</sub>N in toluene, while white circles are for the standard sample, benzophenone in acetonitrile. Each fitting line was obtained by the least square fitting method.

power. E–Z photoisomerization is a one-photon process and the linear dependence of absorbance change was observed. We also examined the laser power dependence of triplet–triplet absorbance change of benzophenone at 516.5 nm in acetonitrile,  $|\Delta Abs_{bp}|$ , to evaluate an apparatus factor. The relation between absorbance changes and laser power are described by the following equations,

$$|\Delta Abs| = \Phi_{iso} \alpha l \Delta \varepsilon (1 - 10^{-Abs^{355}}) x \quad (2)$$

$$|\Delta Abs_{bp}| = \Phi_{ISC} \alpha l \varepsilon_{T-T} (1 - 10^{-Abs^{355}}) x_{bp} \quad (3)$$

for [2PA-Bmim]<sup>+</sup> and benzophenone, respectively. In these equations,  $\alpha$  means an apparatus factor,  $l$  a monitoring light pass length,  $x$  and  $x_{bp}$  relative values of the laser power for [2PA-Bmim]<sup>+</sup> and benzophenone samples, respectively, and  $\Phi_{ISC}$  (=1) is an S<sub>1</sub>–T<sub>1</sub> ISC yield. The  $\Delta \varepsilon$  of 15,000 M<sup>-1</sup> cm<sup>-1</sup> is the difference of extinction coefficients between E- and Z-forms at 376.5 nm. This value was determined from the absorption spectra of E- and Z-forms in toluene. The  $\varepsilon_{T-T}$  of 6200 M<sup>-1</sup> cm<sup>-1</sup> is an extinction coefficient of triplet benzophenone at 516.5 nm [50]. The  $Abs^{355}$  is an absorbance at 355 nm before the laser irradiation for both samples, and they were equalized ( $Abs^{355} < 0.5$ ) for [2PA-Bmim]<sup>+</sup> and benzophenone when we prepared the samples. Hence we combined Eqs. (2) and (3) as

$$\Phi_{iso} = \frac{\varepsilon_{T-T} (|\Delta Abs|/x)}{\Delta \varepsilon (|\Delta Abs_{bp}|/x_{bp})} \quad (4)$$

where  $(|\Delta Abs|/x)$  and  $(|\Delta Abs_{bp}|/x_{bp})$  are the slopes for [2PA-Bmim]<sup>+</sup> and benzophenone in Fig. 5, respectively. From Eq. (4),  $\Phi_{iso}$  value in toluene was determined as  $0.19 \pm 0.02$ .  $\Phi_{iso}$  values in other solvents were also determined and the results were summarized in Table 3.

It is noteworthy that  $\Phi_{iso}$  value in ionic liquids are 0.12–0.14 and are slightly smaller than those in organic solvents. We exam-

ined  $\Phi_{iso}$  value for wide range of solvent viscosity, ca. 1–241 cP as listed in Table 3 and found two prominent features. One is that  $\Phi_{iso}$  value does not become zero even though we have used remarkably viscous solvents. This feature is very important for development of photofunctional ionic liquids. In general, the viscosity of ionic liquids is high, and one might be afraid that isomerization rate with large amplitude motion like phenyl torsion is slow. However, the present results indicate that isomerization certainly occurs in viscous ionic liquids. The other feature is that  $\Phi_{iso}$  value gradually decreases as viscosity increases. This may be related to the isomerization mechanism and we discuss this feature on the basis of photoisomerization mechanism of azobenzene in the following.

Although a large number of studies have been reported for photoisomerization of azobenzene, its mechanism seems still under debates. Here, we consider the photoisomerization mechanism after S<sub>2</sub>( $\pi$ – $\pi^*$ ) excitation proposed by recent ultra-fast time-resolved measurements and theoretical calculations. Fujino et al. determined the quantum yield of S<sub>2</sub> → S<sub>1</sub> relaxation as a unity by a femtosecond fluorescence spectroscopy, and suggested that both S<sub>1</sub> and S<sub>2</sub> excitations result in isomerization with the same mechanism along S<sub>1</sub> surface [31]. The  $\Phi_{iso}$  value is smaller for S<sub>2</sub> excitation because vibrationally hot S<sub>1</sub> produced after internal conversion undergoes fast relaxation to S<sub>0</sub> without isomerization. According to theoretical calculations, this relaxation occurs through conical intersection between S<sub>1</sub> and S<sub>0</sub> states along concerted CNN-bending coordinate (*concerted inversion* mechanism) [35]. To find direct evidence which well explains isomerization mechanism clearly, Chang et al. measured femtosecond fluorescence anisotropy relaxation times of the excited state in hexane and in ethylene glycol under S<sub>1</sub> excitation [33]. They evaluated contribution of *rotation* and *concerted inversion* processes for S<sub>1</sub> relaxation from the time dependence of the direction of transition moment. They suggested that isomerization due to *rotation* occurs in non-viscous hexane, while the *rotation* process is suppressed in ethylene glycol of viscous solvent and  $\Phi_{iso}$  drops due to relaxation through *concerted inversion* mechanism.

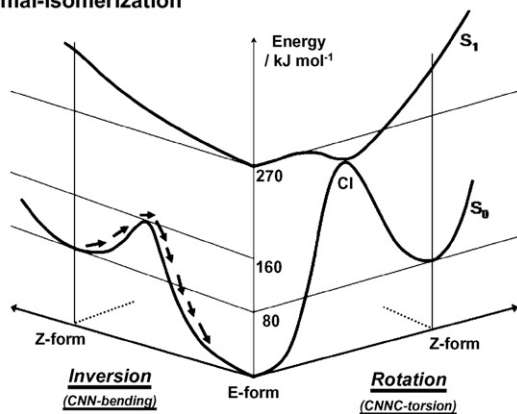
We discuss the photoisomerization mechanism of [2PA-Bmim]<sup>+</sup> according to these previous studies for azobenzene to rationalize the dependence of the quantum yields on solvent viscosity. Fig. 6 shows schematic potential surfaces along E–Z isomerization coordinate for *rotation*, *inversion* and *concerted inversion* mechanisms. Since both phenyl and imidazolium groups are included in bending motion of [2PA-Bmim]<sup>+</sup>, concerted inversion as discussed in azobenzene dynamics does not exist. Here, we consider pseudo concerted inversion for [2PA-Bmim]<sup>+</sup> where phenyl and imidazolium groups undergoes bending with having the same CNN angle. The result obtained by a DFT calculation is used for the energy difference of ca. 80 kJ mol<sup>-1</sup> between E- and Z-forms at S<sub>0</sub> state. The S<sub>1</sub> energy is roughly estimated from absorption spectrum. The activated state energy along the S<sub>0</sub> surface is 160 kJ mol<sup>-1</sup> which is estimated from the  $E_a$  value of ca. 80 kJ mol<sup>-1</sup>. The thermal backward isomerization may proceed through *inversion* mechanism as shown in Fig. 6a. This is because no solvent polarity dependence was found on  $E_a$  values as discussed before and theoretical calculation predicted much lower barrier height for *inversion* in case of azobenzene [37]. On the other hand, photoisomerization mechanism is rather complicated. After S<sub>2</sub> excitation, the E-form of [2PA-Bmim]<sup>+</sup> relaxes to S<sub>1</sub> state very rapidly. Radiation process is reasonably ignored because the natural radiation lifetimes estimated by absorption spectra are 8–9 ns and 200–300 ns for S<sub>2</sub>–S<sub>0</sub> and S<sub>1</sub>–S<sub>0</sub> transitions, respectively, which are too long for relaxation. According to the studies on azobenzene, S<sub>1</sub> surface along *rotation* coordinate has no barrier and S<sub>1</sub>/S<sub>0</sub> conical intersection exists. Therefore, [2PA-Bmim]<sup>+</sup> at S<sub>1</sub> also undergoes conformational change along *rotation* coordinate and isomerization occurs at the conical intersection. However, this process is suppressed

**Table 3**

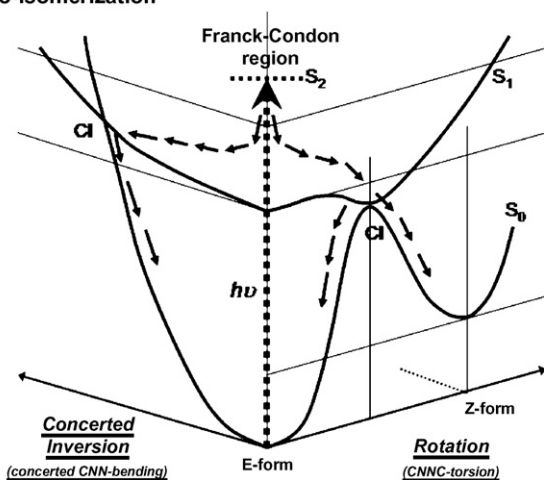
Quantum yields,  $\Phi_{iso}$  of E–Z photoisomerization of [2PA-Bmim]<sup>+</sup> under 355 nm excitation in several solvents and measured viscosities,  $\eta$  of solvents at 298 K.

Solvent	$\Phi_{iso}$	$\eta$ /cP
Toluene	0.19 ± 0.02	<1
Acetonitrile	0.16 ± 0.02	<1
Methanol	0.16 ± 0.02	<1
Ethylene glycol	0.15 ± 0.02	17
EmimBF <sub>4</sub>	0.14 ± 0.02	34
BmimTf <sub>2</sub> N	0.13 ± 0.02	50
BmimBF <sub>4</sub>	0.13 ± 0.02	93
BmimPF <sub>6</sub>	0.12 ± 0.02	241

## (a) Thermal-isomerization



## (b) Photo-isomerization



**Fig. 6.** Schematic drawings of the potential surfaces of [2PA-Bmim]<sup>+</sup> along *inversion*, *rotation* and *concerted inversion* coordinates. Potential surfaces for (a) thermal isomerization and (b) photoisomerization are described and solid arrows represent relaxation pathways. CI means conical intersection.

in viscous ionic liquids ( $\eta > 30$  cP) and  $S_1$ – $S_0$  relaxation through *concerted inversion* may occur. Perhaps, this is the reason why  $\Phi_{\text{iso}}$  value is smaller in viscous ionic liquids. It is unlikely that photoisomerization through *inversion* mechanism dominates the relaxation, because (1) no conical intersection has been found along *inversion* coordinate for azobenzene according to the recent theoretical calculations and (2) isomerization through *inversion* mechanism may not depend on solvent viscosity as compared to *rotation* mechanism. For the complete understanding of photoisomerization mechanism of [2PA-Bmim]<sup>+</sup>, photochemical process after  $S_1(n-\pi^*)$ – $S_0$  excitation should be examined by an ultra-fast time-resolved spectroscopy. The continuing work along this line is now in progress.

#### 4. Conclusion

A novel ionic liquid, [2PA-Bmim]Tf<sub>2</sub>N having azo-photochromophoric group was synthesized for the first time and was confirmed as a T-type photochromic compound by the present spectroscopic studies. Although the conformational change of the thermal isomerization is very large, Arrhenius parameters do not depend on the solvent properties such as viscosity and polarity. We concluded that the thermal isomerization from Z to E-form of [2PA-Bmim]<sup>+</sup> proceeds through *inversion* mechanism. The quantum yield of E–Z photoisomerization of [2PA-Bmim]<sup>+</sup>,  $\Phi_{\text{iso}}$ , was determined in various solvents. The  $\Phi_{\text{iso}}$  value is 0.15–0.19

in conventional organic solvents, and is smaller in ionic liquids, BmimX (X = Tf<sub>2</sub>N, BF<sub>4</sub>, PF<sub>6</sub>). These non-zero  $\Phi_{\text{iso}}$  values in viscous solutions promise that [2PA-Bmim]<sup>+</sup> can be used as photochromic material. The  $\Phi_{\text{iso}}$  value decreases as solvent viscosity increases, which suggests that isomerization at  $S_1$ – $S_0$  internal conversion along *rotation* coordinate becomes slow in viscous solvent like ionic liquids. We discussed *concerted inversion* mechanism as  $S_1$  relaxation channel in these viscous solvents.

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