

Photomodulation of Ionic Interaction and Reactivity: Reversible Photoconversion between Imidazolium and Imidazolinium

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Abstract: An interconversion system between imidazolium and imidazolinium has been proposed for the first time. Imidazolium and imidazolinium cations exhibit different reactivity due to the difference in the aromaticity and charge localization structure, which is successfully controlled by means of photoirradiation in the present system. A 4,5-dithiazolylimidazolium salt was prepared and studied as a new class of photochromic materials modulating electrostatic interactions and chemical reactivities. The photochromic 4,5-dithiazolylimidazolium showed reversible photoconversions between imidazolium open-form and imidazolinium closed-form upon successive irradiation with UV and visible light. The imidazolinium closed-form exhibited characteristic solvato- and ionochromisms in which the absorption maximum shifted by more than 80 nm depending on the solvent polarity and counteranions, whereas the imidazolium open-form showed no such solvent-dependent property. Because the corresponding nonionic 4,5-dithiazolylimidazole also did not exhibit the solvent-dependent absorption profile both in open- and closed-forms, the appearance of these chromisms in imidazolinium closed-form was attributed to the change in the extent of ionic interaction, which was brought about by the photoconversion of imidazolium to imidazolinium. The photoderived strong ionic interaction of imidazolinium with counteranion was further applied to the photocontrolled nucleophilic reaction system. Whereas the imidazolium open-form was inert to nucleophiles such as sodium methoxide, the imidazolinium closed-form was reactive to the nucleophilic reaction, demonstrating a photogated reaction system.

Introduction

Imidazoles are an important class of aromatic heterocycles because of their attractive chemical properties, such as acid–base reactions and metal complex forming reactivity.¹ Apart from their importance in biological systems as potential bridging ligands between metal ion centers in metalloenzymes, recent studies have focused on their use as building blocks for extended π -conjugation molecules.^{2–5} Imidazole is readily converted into cationic imidazolium by the protonation or disubstitution of two N-positions. The 1,3-disubstituted imidazolium ring (Figure 1a), a cationic N-heteroaromatic ring, is well-known as the most popular and investigated class of the cationic structure of room-temperature ionic liquids.^{6,7} The reaction of 1,3-disubstituted

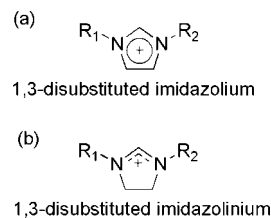


Figure 1. Chemical structures of 1,3-disubstituted imidazolium (a) and imidazolinium (b) cations.

imidazolium cations is restricted due to the chemical stability of the imidazolium ring derived from the delocalization or burying of cationic charge, the aromaticity, and the low reduction potential. The reactivity of imidazolium cations mainly stems from the relatively high acidity of the H(2) hydrogen of the imidazolium ring. 1,3-Disubstituted imidazolium groups have been used as subunits for several anion receptors that bind anions by forming a C(2)–H \cdots X[–] hydrogen bond.^{8–10} It is

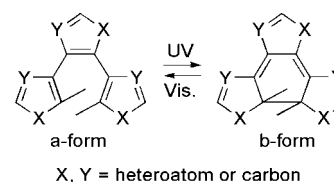
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also well-known that deprotonation at the C(2) position of imidazolium generates N-heterocyclic carbene ligands¹¹ to form the carbene-metal complexes being used in homogeneous catalysis.^{12–16} Except for the case of such reaction conditions as those described above, 1,3-disubstituted imidazolium ionic liquids are principally stable toward many organic and inorganic substances, which enables a number of organic chemical reactions,^{17,18} including nucleophilic reactions^{19–22} to be carried out in ionic liquids. Alternatively, the imidazolinium cations, having the structure of C(4)–C(5) saturated imidazolium (4,5-dihydroimidazolium, Figure 1b), show similar but different chemical reactivity from imidazolium cations due to their nonaromaticity and their partly localized cationic structure. Similar to imidazoliums, imidazoliniums are also famous precursors for free Arduengo-type carbenes.²³ The acidity of H(2) hydrogen of imidazolinium is higher than that of imidazolium, and the pK_a value is roughly estimated to be less than 20,²⁴ which is apparently smaller than that of a simple imidazolium cation ($pK_a = 21–23$).²⁵ Because of the high electrophilicity at the C(2) position, imidazolinium cations are potential substrates for some nucleophilic reactions,^{24,26} which makes the imidazolinium-based ionic liquids uncommon.^{27,28} Thus, imidazolium and imidazolinium exhibit different reactivities due to the difference in aromaticity and the localization state of cationic charge, while they are both N-heterocyclic cations. In this study, we propose the reversible photointerconversion system between imidazolium and imidazolinium by means of photochromic reactions.

Considerable interest has been focused on organic photochromic molecules, which undergo reversible photoisomerizations between pairs of bistable isomers with different absorption spectra upon irradiation at appropriate wavelengths.^{29,30} Pho-

Scheme 1



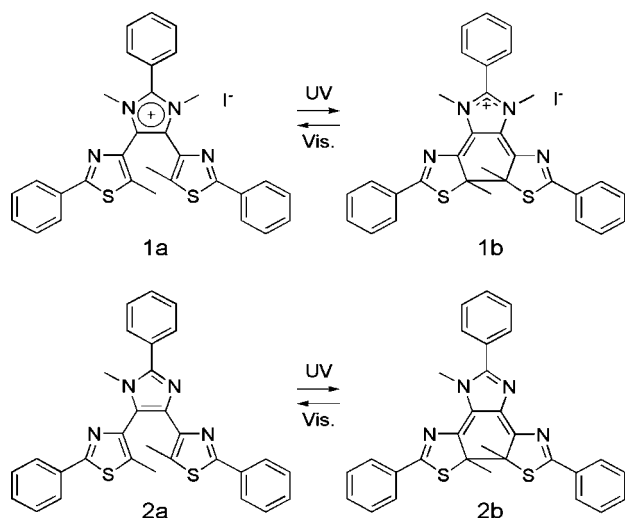
to-switching effects, especially in photochromic diarylethenes,³¹ have been extensively studied for controlling various chemical and physical properties.^{31–34} Some recent studies highlight the gated photochromic systems, in which the photochromic reactivity is controlled with other stimuli, such as chemicals, with an eye toward applications in display and memory technologies.^{35–39} However, there have been few reports on the photogated reactivity of diarylethenes.^{37b,40,41} In photogated reactivity, light triggers a structural change in the molecule and imparts chemical reactivity unique to the photogenerated isomer.

We describe herein a photomodulated electrostatic interaction and reactivity by taking advantage of the photochromic reaction of 4,5-diarylethene, which rearranges the π -conjugation system with light irradiation.^{42–44} As shown in Scheme 1, the open-ring isomer (a-form) consists of three heteroaromatic rings, so-called “triangle terarylene”, and includes a hexatriene component in their molecular structure, which undergoes reversible photoinduced cyclization reaction to form a closed-ring isomer (b-form) in a similar manner to diarylethenes³¹ and fulgides.⁴⁵ The three heteroaromatic rings collapse simultaneously with the rearrangement of the π -connection, and our strategy is to incorporate a cationic imidazolium ring into the terarylene structure as one of the heteroaromatics. The open-ring form contains the chemically stable imidazolium ring with delocalized cationic charge, while closed-ring photoisomer possesses the reactive imidazolinium structure. Thus, by controlling the

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Scheme 2



aromaticity and the localized state of the cationic charge of N-heterocyclic ring with the photochromic reaction, the electrostatic interaction with anions and the reactivity with nucleophiles are expected to be modulated. A guiding principal for designing future photoresponsive ionic assemblies and ionic liquids relating to photochromism is proposed for the first time.

Results and Discussion

Reversible Photochromism in Solution. 4,5-Dithiazolylimidazolium iodide **1a** was prepared and investigated in this study. Thiazole units bridged by the central imidazolium ring were introduced to improve the photochromic reactivity of terarylene.^{42b} Corresponding 4,5-dithiazolylimidazole **2a** was a synthetic intermediate of **1a** and used as a reference compound. Compound **2a** was synthesized by conventional cross-coupling reactions of corresponding thiazolyl pinacol borate and 4,5-diiodimidazole unit and then the N(3) position of **2a** was methylated with iodomethane to afford the cationic compound **1a**. Their chemical structures were confirmed by high-resolution mass spectroscopy, ¹H NMR and ¹³C NMR. Both terarylenes **1a** and **2a** showed thermally irreversible,^{42b,46} but photochemically reversible, photochromism in various organic media, as shown in Scheme 2. The closed-ring isomer **2b** formed by the UV light irradiation was isolated from the colored solution by reversed-phase HPLC using methanol as an eluent, whereas the closed-ring **1b** could not be isolated by the chromatographic methods because of its ionic nature. Formation of both closed-ring isomers, **1b** and **2b**, was confirmed by ¹H NMR spectroscopic study in CDCl₃ solution.

As shown in Figure 2, **1a** had no absorption band in the visible range in acetonitrile. Upon irradiation with UV light ($\lambda = 313$ nm), the colorless solution of **1a** turned blue, and a new absorption band appeared at around 640 nm. The colored solution can be completely bleached upon irradiation with visible light, giving an absorption spectrum identical to that of the initial solution of **1a**.⁴⁶ An isosbestic point appeared at 306 nm and supported the two-component photochromic reaction. The coloration and bleaching cycles can be repeated at least 20× without any photodegradation. That is, 4,5-dithiazolylimidazolium **1a** underwent reversible photochromic reactions, even though positively charged imidazolium rings participate in the

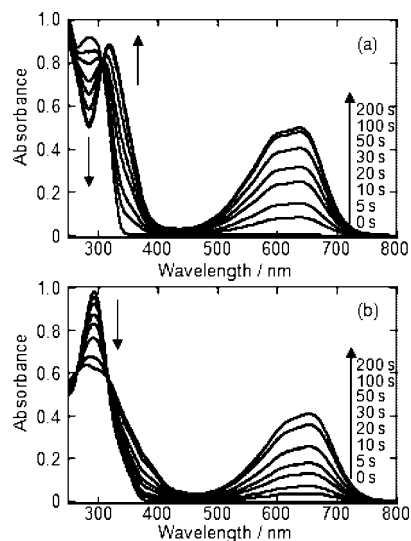


Figure 2. Absorption spectral change of **1a** and **2b** in acetonitrile and hexane, respectively, upon UV irradiation ($\lambda = 313$ nm). Each trace was measured after the irradiation for 0, 5, 10, 20, 30, 50, 100, and 200 s. The concentrations were 2.4×10^{-5} M for **1** and 2.1×10^{-5} M for **2**.

Table 1. Absorption Maxima and Coefficients of the Open- and Closed-Ring Isomers of **1** and **2**, together with the Quantum Yields

$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1}\text{cm}^{-1}$)	$\phi_{\text{a-b}}^d$	$\phi_{\text{b-a}}^e$
1a ^a	293 (3.7)	0.56
1b ^a	639 ^c (2.2)	5.7×10^{-2}
2a ^b	293 (4.6)	0.65
2b ^b	654 ^c (2.3)	6.3×10^{-2}

^a In acetonitrile. ^b In hexane. ^c Absorption maximum in the visible region. ^d $\lambda_{\text{irrad}} = 313$ nm. ^e $\lambda_{\text{irrad}} = 517$ nm.

Table 2. Solvent Effects on the Absorption Maxima (λ_{max}) of **1a**

	acetonitrile	acetone	dichloromethane	2-methylTHF	toluene
1a	293		294	296	
1b ^b	639	642	654	566	565
1b-ClO₄				645	

^a Solvent dielectric constants are as follows: acetonitrile = 37; acetone = 21; dichloromethane = 9.1; 2-methylTHF = 7.0; toluene = 2.4. ^b Absorption maximum in the visible region.

pericyclic reaction, indicating a certain degree of localization of the double bond on the C(4)–C(5) position. Similar reversible photochromic behavior was also observed for neutral compound **2a** (Figure 2 b). The conversion ratios from **1a** to **1b** and **2a** to **2b** at the photostationary state, which was achieved by irradiation with UV light ($\lambda = 313$ nm) were estimated to be 93% and 86%, respectively. The values of λ_{max} and ϵ of **1** and **2** are summarized in Table 1 with photochromic reaction quantum yields ($\phi_{\text{a-b}}$ and $\phi_{\text{b-a}}$) evaluated with the standard procedure using 1,2-bis(5-(2,4-diphenylphenyl)-2,4-dimethyl-3-thienyl)perfluorocyclopentene in hexane⁴⁷ as a standard. Both **1a** and **2a** demonstrated quite high quantum yields in cyclization reaction due to the reduced steric hindrance with the introduction of thiazole units.^{42b}

Photomodulation of Ionic Interaction. Interestingly, 4,5-dithiazolylimidazolium **1** showed characteristic solvent-dependent absorption spectra in the closed-ring imidazolinium state. Table 2 summarizes the values of λ_{max} of open- and closed-ring isomers of **1** in various solvents. In polar solvents such as

(46) See Supporting Information.

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acetonitrile, acetone, and dichloromethane, the λ_{max} of closed-ring isomer **1b** appeared at around 640 nm, which shifted to a shorter wavelength with increasing dielectric constants of solvents, indicating the stronger stabilization of the ground-state of **1b** than that of the excited-state in polar media. However, that is not the case with the λ_{max} in low polar media such as 2-methyltetrahydrofuran (2-MeTHF) and toluene. The absorption peak shifted to a shorter wavelength by more than 80 nm, and the color of solution changed from blue to red. Such a large blue-shift cannot be explained with ordinary solvatochromism, in which the absorption maximum responds to the solvent dielectric constants in a manner consistent with changes in the polarity of the chromophore upon the transition from the ground-state to the excited state.⁴⁸

The nonionic 4,5-dithiazolylimidazole **2** never showed such a solvent-dependent absorption behavior in both open- and closed-ring states. The optical response observed for the closed-ring isomer **1b**, therefore, should be attributed to the solvent-modulated ionic interaction specifically between the imidazolinium unit in **1b** and the iodide anion. In polar media, each imidazolinium cation **1b** and iodide anion would be well solvated with solvent molecules to result in weak electrostatic interaction, while the insufficient solvation of ionic species in low polar media may give rise to the formation of a certain kind of contact ion pair in which the iodide anion strongly binds to the imidazolinium cation at ground state. This explanation was also supported by the anion-exchange measurement. The counteranion I^- was readily exchanged with perchlorate anion (ClO_4^-) by the addition of silver perchlorate to capture the iodide anion as silver iodide. By changing the anion from iodide to perchlorate, the absorption peak of **1b-ClO₄** in 2-MeTHF appeared at around 650 nm corresponding to those of **1b** in polar solvents. Once the anion was replaced with bulky and soft perchlorate anion, the electrostatic interaction between imidazolinium cation and anion should be weakened even in less polar media to give the absorption profile identical with those of **1b(I⁻)** in well solvating polar media.

Alternatively, the λ_{max} of 4,5-dithiazolylimidazolium **1a**, opening isomer remained almost constant against the solvent polarity (Table 2), which clearly demonstrates the difference in the electrostatic interaction of imidazolium and imidazolinium rings with iodide anion. As described above, the cationic charge is more localized in the nonaromatic imidazolinium ring than in the aromatic imidazolium ring, leading to the stronger electrophilicity for imidazolinium **1b** than **1a**. Thus, the enhancement of electrophilic nature seems to be indispensable for the observation of solvatochromism, which was achieved by the photoconversion of imidazolium to imidazolinium. The similar effect of electrophilicity of C(2)-carbon on the electronic transition has been recently reported by Bielawski⁴⁹ as the solvatofluorochromism of benzobis(imidazolium) salts with electron-withdrawing substituents. However, in that case, the nucleophiles bond to benzobis(imidazolium) cation only at the electronic excited state.⁴⁹

Photomodulation of Reactivity. To demonstrate the different reactivity of imidazolium and imidazolinium, especially the strong electrophilicity of imidazolinium, we then investigated the reaction of imidazolinium **1b** with a strong nucleophile such

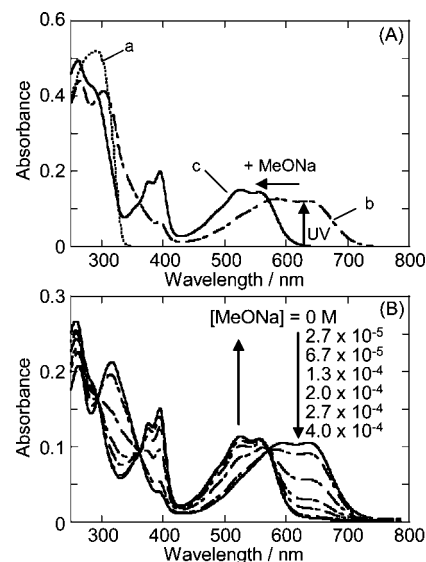
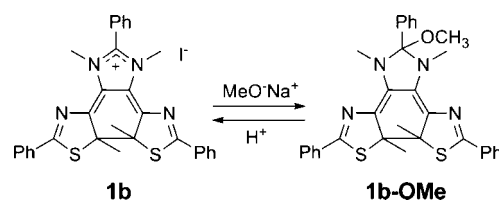


Figure 3. A: Absorption spectral change of **1** with photochemical and chemical reactions in methanol. (a) dotted line: **1a**, (b) broken line: after UV irradiation to spectrum a, (c) solid line: after the addition of MeONa to spectrum b. ($[\mathbf{1}] = 1.6 \times 10^{-5} \text{ M}$). B: Absorption spectra of **1b** ($7.7 \times 10^{-6} \text{ M}$) in the presence of MeONa (0 M to $4.0 \times 10^{-4} \text{ M}$).

Scheme 3



as alkoxide anions, and the reaction was studied with absorption spectra and ^1H NMR measurements. Figure 3A shows the absorption spectral change of **1** in anhydrous methanol with UV irradiation, followed by addition of an excess amount of sodium methoxide (MeONa) as a nucleophile. The photo-generated product in methanol was also colored in blue, reflecting the high polarity of methanol and showed absorption band at around 640 nm as shown in Figure 3A(b). The blue-colored solution of **1b** turned red with the addition of MeONa/methanol, giving an absorption peak at around 560 nm (Figure 3A(c)). These two absorption bands coincided with those observed in the solvatochromic behavior as summarized in Table 2. The titration measurement gave the continuous progress and suppression of the absorption bands at 560 and 640 nm, respectively, accompanied by an isosbestic point at 571 nm, supporting two-component chromic reaction of the colored isomer (Figure 3B). The red-colored substance was easily transferred to nonpolar hexane by the simple biphasic extraction process with methanol. However, the blue color remained in the methanol phase, indicating the different polarity between the red- and blue-colored species. Because the ionic **1a** was never soluble in hexane, the nonionic **1b-OMe** depicted in Scheme 3 seems to be the most plausible structure as the red-colored photoproduct in the presence of MeONa.

We then confirmed the structure at each state with ^1H NMR measurements. Figure 4 shows ^1H NMR spectra of the aliphatic region, where a, b, and c correspond to each absorption spectrum a, b, and c in Figure 3A, respectively. Because the methyl protons of **1** are of note here, chloroform-*d* for a, b and hexane-*d*₁₄ for c were used as the solvents of ^1H NMR measurements.

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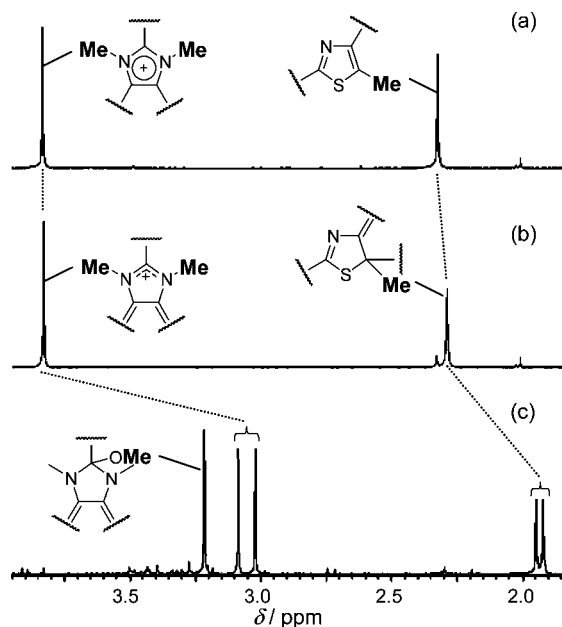


Figure 4. ^1H NMR spectra of methyl group protons. (a) **1a** in chloroform- d , (b) after UV irradiation to a, (c) the extract in hexane- d_{14} from the mixture of photoproduct of **1** in the presence of MeONa in methanol. For the clarity of assignment, the parts of the structure were depicted at the corresponding peaks.

For the measurement of spectrum b, methanol was evaporated and replaced with chloroform- d after the photoconversion to **1b**, while spectrum c was measured in hexane- d_{14} after the extraction of the product from the methanol solution of **1b** with MeONa. Two characteristic singlet methyl signals at 3.83 and 2.32 ppm were observed for the open-ring isomer **1a** (Figure 4a), and each signal was assigned as described in Figure 4a. These methyl signals slightly shifted to the high magnetic field after the photoconversion to **1b** (Figure 4b). The shift was significant for the methyl groups attached to the thiazole groups because the hybrid orbital of the α -carbon (C(5) in thiazole ring) was converted from sp^2 to sp^3 with the rearrangement of the π -connection. A further shift of these signals to the high magnetic field and peak splitting was observed, together with the appearance of a new singlet signal at 3.24 ppm for the extract in hexane- d_{14} (Figure 4c) after the addition of MeONa to **1b**. All of these signals were assigned as depicted in Figure 4c for the following reasons. The new signal at 3.24 ppm was assigned as the methoxy group bound to the C(2) position of the imidazolinium ring because the MeO^- ion was insoluble in hexane and the measurement of the differential nuclear Overhauser effect (1D-NOE) exhibited the strong correlation of this peak with the splitting of two peaks of N-Me groups at 3.02 and 3.08 ppm.⁴⁶ The significant upfield shift of methyl peaks should be explained by the absence of positive charge and accompanying increase in electron density on the fused heterocycle. The closed-ring isomer **1b** has a planar structure of C_2 symmetry, and the nucleophilic addition of MeO^- to the C(2) position of the imidazolinium ring breaks it, giving the split of signals of the methyl groups on the fused heterocycle. All of these findings described above clearly indicate that the red-colored product that gave the absorbance peak at around 560 nm is **1b-OMe**, as depicted in Scheme 3. The results of time-

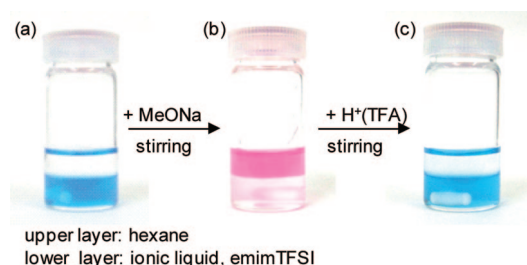


Figure 5. Reversible color change and phase transfer of **1b** by the successive addition of MeONa and TFA in the hexane/ionic liquid biphasic system. (a) **1b** in emimTFSI after UV irradiation, $[1] = 0.30$ mM; (b) **1b-OMe** in hexane by the addition of excess amount of MeONa to (a); and (c) **1b** in emimTFSI by the addition of excess amount of TFA to (b).

dependent density functional theory (TDDFT)⁵⁰ calculation at the B3LYP/6-31G*⁵¹ level for **1b**⁺ (without I^-) and **1b-OMe** were in good agreement with the experimentally observed wavelength of the absorption maxima for **1b**⁺ and **1b-OMe**.⁴⁶

Because the nucleophile adducts have unstable, distorted structures with a quarternary imidazolidine C(2) atom, the neutral products reversibly converted to a blue-colored ionic compound **1b** by the addition of acids such as hydrochloric acid and trifluoroacetic acid (TFA) to eliminate the methoxy group as methanol (Scheme 3). The red-colored product **1b-OMe** still showed reversible photochromism in hexane between the red and colorless states, whereas the reversibility of photoconversion gradually diminished with repetitive UV-vis irradiations.

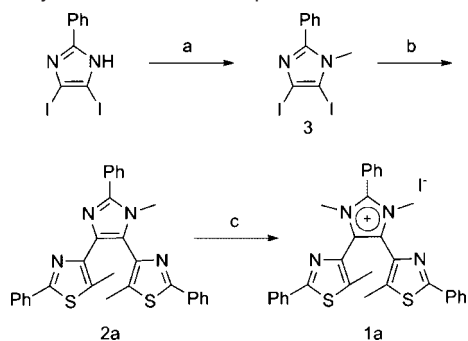
Similar to the case of solvatochromism, the nucleophilic addition was not observed for open-ring isomer **1a** and 4,5-dithiazolylimidazole **2a** and **2b**, demonstrating the specific reactivity of imidazolinium cation against nucleophiles. Furthermore, the nucleophilic reaction of imidazolinium **1b** with MeO^- was also observed in an imidazolium-based ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (emimTFSI), which directly represents the higher reactivity of imidazolinium than imidazolium. The 4,5-dithiazolylimidazolium **1** showed reversible photochromic reaction even in emimTFSI and was a blue color, forming closed-ring isomer **1b** by UV irradiation (Figure 5a). Upon addition of MeONa into the blue-colored ionic liquid phase, the color turned to red and transferred into an upper hexane layer by vigorous stirring (Figure 5b). The color reversibly changed to blue and transferred into the lower ionic liquid phase through the addition of acid (TFA) to again form ionic **1b** (Figure 5c).

Thus, the reactivity of the imidazolium cation has been readily controlled by combination with the photochromic reaction, which reversibly converts the stable imidazolium to the reactive imidazolinium. Such a compound could be demonstrated as one of the few examples of a photogated reaction system,⁴¹ in which light triggers a structural change in the molecule and imparts chemical reactivity unique to the photogenerated isomer.

Conclusions

We have designed a reversible transformation system between chemically stable imidazolium and reactive imidazolinium on the basis of the design of a photochromic terarylene that undergoes reversible aromatic/nonaromatic conversions with the

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Scheme 4. Synthetic Route to Compounds **1a** and **2b**^a

^a Reagents and conditions: (a) NaH, iodomethane, dry THF; (b) 5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole, Pd(OAc)₂, 2'-(dicyclohexylphosphino)-N,N-dimethylbiphenyl-2-amine, CsF, DMF/1,4-dioxane; (c) iodomethane, acetonitrile.

rearrangement of the π -conjugation structure. The 4,5-dithiazolylimidazolium terarylene showed reversible photochromism with good performance in organic media and exhibited the characteristic solvato- and ionochromisms responding to the extent of ionic interaction between the photogenerated imidazolinium cation and counteranions. In less polar solvents, the iodide anion strongly bonds to the electrophilic imidazolinium closed-form at the ground state. The mechanism of solvato- and ionochromisms was clearly demonstrated by the nucleophilic addition of methoxide to the electrophilic C(2) position of imidazolinium cation. Because the imidazolium open-ring isomer was stable to strong nucleophiles, such as sodium methoxide, the reaction only occurred for the imidazolinium closed-ring isomer, demonstrating the photogated reactivity. The present concept of the photoswitching of charge delocalization—localization states would give us a new strategy for the design of photoresponsive ionically self-assembling dye systems,⁵² as well as for the photomodulation of chemical reactivity.

Experimental Section

General. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL AL-300 spectrometer. Separative HPLC was performed on a HITACHI LaChrom ELITE HPLC system and a JASCO LC-2000 Plus Series. Mass spectra were measured with a mass spectrometer JEOL JMS-T100LC AccuTOF. Absorption spectra in solution were studied with a JASCO V-670 spectrophotometer. Photoirradiation was carried out using an USHIO 500 W ultrahigh-pressure mercury lamp as an exciting light source. Monochromatic light was obtained by passing the light through a monochromator (Shimadzu SPG-120S, 120 mm, $f = 3.5$). The intensity of incident light after passing the monochromator was found to be 10 mW cm⁻².

Synthesis. Compounds **1a** and **2b** were synthesized according to the reaction scheme depicted in Scheme 4.

4,5-Diiodo-1-methyl-2-phenyl-1H-imidazole (3). To a solution of 4,5-diiodo-2-phenyl-1H-imidazole (10 g, 25 mmol) in dry THF was added NaH (0.60 g, 25 mmol) at 0 °C under N₂, which was

stirred for 30 min. After the addition of iodomethane (1.6 mL, 26 mmol), the solution was further stirred for 10 h. The reaction mixture was extracted with ethylacetate and washed with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was dissolved in chloroform, and the insoluble part was removed by filtration. The filtrate was concentrated to give **3** (7.6 g, 74%) as a colorless powder. ¹H NMR (CDCl₃, TMS, 300 MHz) δ 3.75 (s, 3H), 7.44–7.50 (m, 3H), 7.54–7.57 (m, 2H).

4,4'-(1-Methyl-2-phenyl-1H-imidazole-4,5-diyl)bis(5-methyl-2-phenylthiazole) (2a). A 100-mL four-necked flask was charged with 5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole^{42b} (0.82 g, 2.7 mmol), **3** (0.43 g, 1.0 mmol), 2'-(dicyclohexylphosphino)-N,N-dimethylbiphenyl-2-amine (10 mg, 0.030 mmol), Pd(OAc)₂ (0.020 g, 0.11 mmol), and CsF (0.43 g, 2.8 mmol) in DMF/1,4-dioxane (1.5 mL/10 mL) solution. The mixture was then stirred at 80 °C under N₂. After having been stirred for a day, the reaction mixture was extracted with diethylether, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Alumina gel column chromatography (hexane/ethylacetate 8:1) and reversed phase HPLC (methanol) afforded **2a** (0.044 g, 9.0%) as a colorless solid. ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.13 (s, 3H), 2.45 (s, 6H), 3.76 (s, 3H), 7.30–7.35 (m, 3H), 7.40–7.57 (m, 6H), 7.78–7.84 (m, 4H), 7.96–8.00 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 12.2, 29.1, 33.6, 125.7, 126.2, 128.4, 128.6, 128.7, 128.9, 129.1, 129.3, 129.9, 130.2, 130.8, 133.7, 133.9, 134.4, 135.7, 142.8, 146.4, 148.6, 163.5, 164.3; ESI–HRMS (m/z) [M+H]⁺ Calcd. for C₃₀H₂₅N₄S₂, 505.1521; Found, 505.1527. Anal. Calcd. for C₃₀H₂₄N₄S₂: C, 71.39; H, 4.79; N, 11.10. Found: C, 71.44; H, 4.53; N, 11.17.

1,3-Dimethyl-4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenyl-1H-imidazolium iodide (1a). To a solution of **2a** (13 mg, 0.030 mmol) in 100 mL of acetonitrile, an excess amount of iodomethane was added and stirred for a day. The solution was concentrated, and the residue was purified with reversed-phase HPLC (methanol) to give **1a** (14 mg, 73%) as colorless solid. ¹H NMR (300 MHz, TMS, CDCl₃) δ 2.32 (s, 6H), 3.83 (s, 6H), 7.27–7.46 (m, 6H), 7.70–7.72 (m, 3H), 7.87–7.92 (m, 4H), 8.14–8.17 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 13.0, 35.4, 126.3, 127.6, 129.1, 129.8, 130.5, 131.6, 132.7, 137.3, 138.3, 146.5, 166.4; ESI–HRMS (m/z) [M]⁺ Calcd. for C₃₁H₂₇N₄S₂, 519.1677; Found, 519.1673.

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Supporting Information Available: Complete ref 51; ¹H NMR spectra of **1a**, **1b**, **2a**, and **2b**, ¹³C NMR spectra of **1a** and **2a**, photocycloreversion and thermalcycloreversion study of **1b** and **2b**, ¹H NMR and 1D NOE difference spectra of **1b-OMe**, and DFT/TDDFT calculations for **1b**⁺ and **1b-OMe** at B3LYP/6-31G*. This material is free of charge via the Internet at <http://pubs.acs.org>.

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