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Synthesis and Photochemistry of Stilbene Ionic Liquids

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Ionic liquids having a photoresponsive stilbene chromophore were prepared and their properties were examined. While the trans isomers were all solid, most of the cis isomers were liquid at room temperature. The trans isomers give fluorescence emission with a quantum yield of ca. 0.02, while the cis isomers practically give no fluorescence. Thus, we could photochemically switch the properties of ionic liquid as well as emission properties by photochemical processes.

Although ionic liquids consist of cations and anions,[1,2] they melt at or below 100 °C[3,4] and have been recognized as useful reaction media[5,6] with characteristic structure and features.[7,8] Because ionic liquids have almost no vapor pressure they can be used as solvent for practical processes as well as for spectroscopic measurement. For example, they have potential properties for use as electrolytes and reaction solvent.[9] As for reaction media, ionic liquids may show interesting properties[10] of high dielectric constant with considerably high viscosity compared with common organic solvents. Therefore, ionic liquid have been used as reaction media for the study of different types of fundamental reactions. Among reactions ultrafast photochemical reactions such as trans–cis isomerization in the excited singlet state have been studied in ionic liquid. In this case, photoisomerization of *trans*-stilbene took place efficiently with faster rate constant than that expected from the relatively high viscosity of an ionic liquid.[11] And functional ionic liquids have been expected to be new materials.[12,13] However, ionic liquids with photoresponsive groups have scarcely been reported. We are interested in preparing molecules exhibiting properties of ionic liquid with photoreversibility and emissive properties. In this respect, we have prepared compounds having stilbene chromophore with an imidazolium group as pure cis and trans isomers and then prepared ionic liquids (Figure 1). Imidazolium cation[14] has been used to prepare various ionic liquids with low melting point.[15] Thus, we prepared ionic liquid with a photoresponsive group by introducing imidazolium cation unit such as 1-{[4-(2-phenylethenyl)-phenyl]methyl}-3-methylimidazolium trifluoromethanesulfonate (**a**) as shown in Figure 1. Pure compounds **a**–**e** underwent mutual cis–trans isomerization in acetonitrile (Figure 1).

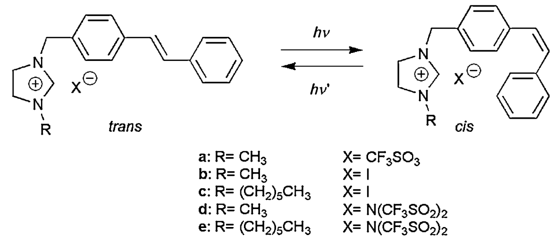

Figure 1. Structure of compounds **a**–**e** and photochemical cis–trans isomerization.

Table 1. Experimental values of compounds **a**–**e**

Compound	Mp /°C	λ_{max} (abs) /nm	λ_{max} (fl) /nm	Φ_f
trans-**a**	144.2	297, 309	357	0.018
cis-**a**	−22.2	279	—	—
trans-**b**	216.9	298, 311	357	0.019
cis-**b**	150.6	282	—	—
trans-**c**	124.2	298, 311	356	0.017
cis-**c**	−29.1	282	—	—
trans-**d**	47.6	299, 311	358	0.018
cis-**d**	−30.9	282	—	—
trans-**e**	53.5	299, 311	357	0.016
cis-**e**	−39.4	282	—	—

Among the compounds **a**–**e**, cis isomers have lower melting point than trans isomers (Table 1). Thus, most of the cis isomers are liquid at room temperature except **b** with R = Me and X = I and we have succeeded to prepare room temperature ionic liquids. Among the trans isomers, with R = CH$_3$ or (CH$_2$)$_5$CH$_3$, X = (CF$_3$SO$_2$)$_2$N, **d** and **e** are ionic liquid, but the other three compounds are ionic solid. These melting points were determined by differential scanning calorimetry and as shown in Supporting Information[22] for typical example *cis*-**b**. Not only the heat release for the melting point at 150.6 °C but also the heat release by cis-to-trans isomerization was observed at 220–270 °C. From the DSC curve at 220–270 °C, one can calculate the energy difference between cis and trans isomers to be 5.45 kcal mol^{-1}, which is quite similar to the usually accepted value of the energy difference between cis and trans isomers of the parent stilbene, 5.66 kcal mol^{-1}.[16]

The absorption, fluorescence, and fluorescence excitation spectra of trans isomers in acetonitrile solution are shown in Figure 2 and Supporting Information.[22] All the spectra showed similar absorption spectra and fluorescence excitation spectra indicating that the fluorescence is really observed from the ionic compounds. The cis isomers did not give detectable fluorescence and therefore only the absorption spectra of the cis isomers are included in these figures. The spectral profiles are similar to those of stilbene, but the spectral peaks are slightly shifted to longer wavelength.

The absorption maximum and the extinction coefficient as well as the fluorescence quantum yields are summarized in Table 1. The fluorescence as well as absorption spectra of **a**–**e** are almost the same with those of stilbene (Supporting Information[22] and Ref. 17). The fluorescence quantum yields are all ca. 0.02 and seem to be similar to that of stilbene (Φ_f = 0.025) as a reference compound. Thus the introduction of the ionic liquid part[18] in the molecules scarcely affect the excited state properties of stilbene, although the substituent is connected by only one methylene bond and may influence each other the

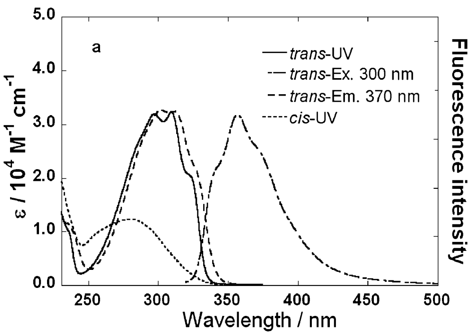

Figure 2. The absorption, fluorescence and fluorescence excitation spectra of *trans*-**a** and the absorption spectra of *cis*-**a** in acetonitrile under Ar.

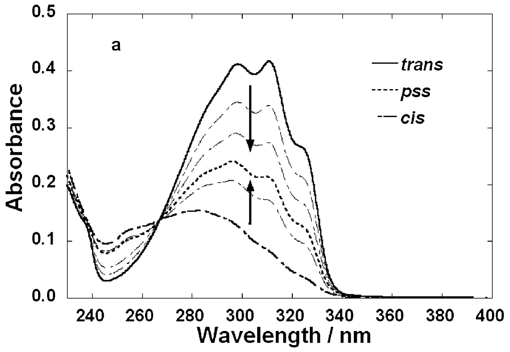

Figure 3. Change of absorption spectra of *trans*-**a** and *cis*-**a** in acetonitrile on irradiation at 267 nm under Ar.

electronic properties as is the case of β,γ-unsaturated compounds undergoing photochemical di-π-methane[19,20] or oxa-di-π-methane rearrangement.[21]

Figure 3 shows absorption spectra of *trans*- and *cis*-**a** in acetonitrile and the spectra change on photoirradiation. On irradiation with 267 nm light from a xenon lamp, the absorption spectrum of *trans*-**a** changed to approach the spectral profile of a mixture of cis and trans isomers, and the spectrum of *cis*-**a** changed in reverse too, which indicates the occurrence of trans–cis photochemical isomerization. The photostationary state isomer ratio is ca. 38:62 and the ratio of the quantum yield of isomerization from cis-to-trans and trans-to-cis processes ($\Phi_{\text{c-t}}/\Phi_{\text{t-c}}$) is 0.62. The ratio of the quantum yield of isomerizatin were calculated from the following equation. $([\text{t}]/[\text{c}])_{\text{pss}} = (\varepsilon_{\text{c}}/\varepsilon_{\text{t}})(\Phi_{\text{c-t}}/\Phi_{\text{t-c}})$ The irradiation at 267 nm where the extinction coefficient (ε_{t}) of the trans isomers are ca. 3 times higher than those of the cis isomers (ε_{c}). From the calculated ratio of the quantum yield, trans-to-cis process is 1.5–2.0 times more efficient than that of the reverse photochemical reaction.

We have also tried to change the state or the liquid-solid properties by irradiation of UV light on the oily *cis*- and powder *trans*-**a**. Thus, on irradiation of the 334 nm light from a mercury lamp one can change the state from the liquid of the cis isomer to the solid of the trans-rich compounds. These are only preliminary experiments, and we are continuing to make sure to detect the photoreversibility between ionic liquid and solid exhibiting and changing the fluorescence properties.

In conclusion one can successfully prepare ionic liquid and even room temperature ionic liquid with photoswitchable and fluorescent properties in a stilbene unit and can control its characteristics by irradiating photon and photoreversible reactions. It should be noted that as far as we are aware this is the first clear report to prepare ionic liquid having photoreversible stilbene chromophores to swich the ionic liquid and solid properties and fluorescence properties. Furthermore, these findings can greatly contribute to prepare and to develop fluorescent and photoreversible ionic liquid.

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22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.