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Synthesis and Photoisomerization of Highly Fluorescent Stilbene Ionic Liquids

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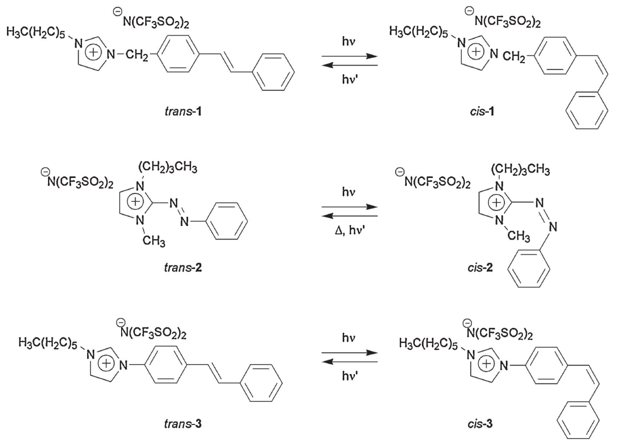
Photoresponsive stilbenes with imidazolium cation directly attached to the para-position of the phenyl ring were prepared and their properties were examined. Although the cis isomer was liquid at room temperature and practically gave no fluorescence, the trans isomer was solid and gave fluorescence emission with quantum yield as high as ca. 0.2. Furthermore photoisomerization from pure cis isomer in the liquid state to trans isomer in the solid state was observed.

Ionic liquids are salts which are liquid at low temperatures (<100 °C)[1,2] and consist of only cations and anions.[3,4] Ionic liquids have been recognized as useful reaction media[5,6] with characteristic features.[7,8] They are expected to be practical solvents because they have almost no vapor pressure and have interesting properties[9] such as high dielectric constant with considerably high viscosity compared with common organic solvents. In the study of photochemical reaction in ionic liquid as a solvent ultrafast photochemical reactions such as trans–cis isomerization in the excited singlet state have been studied. 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.[10] As to the photochemical reaction of ionic liquid compounds, only a few have been reported. One of them is the stilbene type ionic liquid **1**, where photochemical cis–trans isomerization could change the properties of ionic salts from room temperature ionic liquid of cis isomers to the ionic solid of the trans isomers (Scheme 1).[11] In this case one can change the fluorescence properties of these compounds between fluorescent trans isomers with quantum yield ca. 0.02 and the nonfluorescent cis isomers. Another example is the azobenzene type salts **2**,[12,13] where photochemical cis–trans isomerization also induces interconversion between ionic solid and ionic liquid; in this case both cis and trans isomers are nonfluorescent and the cis isomer thermally reverts to the trans isomer. We are interested in preparing photoreversible ionic salts, which can undergo photochemical change between ionic liquid and ionic solid with thermal stability and considerably high fluorescence efficiency. In this respect we have prepared stilbenes with imidazolium cation directly attached to the phenyl ring of stilbene **3**[20] and their photochemical properties are examined. We wish to report here the preparation and characteristic properties of ionic liquids **3** with photoresponsive stilbene group.[11–13]



Scheme 1. Structure of compounds **1**, **2**, and **3** and photochemical cis–trans isomerization.

Stilbene ionic salts **3** showed different properties depending on the conformation around the central C=C double bond. For example, the cis isomer is a room temperature ionic liquid with a melting point of −35.6 °C, but the trans isomer is ionic solid at room temperature with a melting point of 92.6 °C. These melting points are similar to those of **1** with 53.5 °C for *trans*-**1** and −39.4 °C for *cis*-**1**. The extinction coefficient of the absorption spectra of **3** is larger than that of **1** and the absorption maximum and fluorescence maximum of **3** shifted to a longer wavelength than that of **1**. In addition the quantum yield of fluorescence emission of **3** is more than 10 times larger than that of **1** and the quantum yield of trans-to-cis isomerization of **3** is lower than that of **1**. These values are summarized in Table 1, together with those of parent stilbene and phenylazo ionic liquid.

If we discuss details of the physicochemical and photochemical properties between **1** and **3**, the melting points of *trans*- and *cis*-**3** were higher than that of *trans*- and *cis*-**1** with methylene chain, respectively (Table 1). Direct attachment of imidazolium cation to the phenyl ring caused the melting point to rise due to a more rigid structure. The absorption, fluorescence, and fluorescence excitation spectra of *trans*-**3** in acetonitrile are shown in Figure 1. *cis*-**3** did not give detectable fluorescence, and, therefore, only the absorption spectrum is included in the figure. Similarity in absorption and fluorescence excitation spectra for *trans*-**3** indicated that the fluorescence is really observed from the ionic compounds. Compared with the absorption spectrum of *trans*-**1** in acetonitrile, the absorption maximum shifted slightly to longer wavelength, and the molar extinction coefficient increased. The fluorescence maximum of *trans*-**3** shifted considerably to longer wavelength than that of *trans*-**1**, and the fluorescence quantum yield increased by more than 10 times from 0.016 to 0.19 under Ar (Table 1). *trans*-**3** showed quite a high fluorescence quantum yield in comparison with *trans*-4-cyanostilbene ($\Phi_f = 0.005$),[17] and even donor-substituted stilbenes such as *trans*-4-aminostilbene ($\Phi_f = 0.03$)[18] and *trans*-4-dimethylaminostilbene ($\Phi_f = 0.037$).[19]

Figure 2 shows absorption spectra of *cis*-**3** and *trans*-**3** in acetonitrile and the spectral change on photoirradiation. On irradiation with 275-nm light from a xenon lamp, the absorption spectrum of *trans*-**3** changed to approach a spectral profile of a mixture of cis and trans isomers, and the spectrum of *cis*-**3**

Table 1. Experimental values of compound **3** compared with the related imidazolium salts and stilbene in acetonitrile at 298 K

Compound	Mp /°C	λ_{max} (abs) /nm	ε_{max} /$cm^{-1}\,mol^{-1}\,dm^{3}$	λ_{max} (fl) /nm	Φ_f	Φ_{tc}
trans-**1**[a]	53.5	299, 311	33000, 33200	357	0.016	0.41
cis-**1**[a]	−39.4	282	12300	—	—	—
trans-**2**[b]	56	360	25000	—	—	0.16
cis-**2**[b]	—	311	7500	—	—	—
trans-**3**	92.6	315	37500	392	0.19	0.32
cis-**3**	−35.6	288	13700	—	—	—
trans-stilbene	123.9[c]	295, 307	28400, 27800	352	0.026	0.45[e]
cis-stilbene	6[d]	275	12500	—	—	—

[a]ref 11. [b]ref 12. [c]ref 14. [d]ref 15. [e]ref 16.

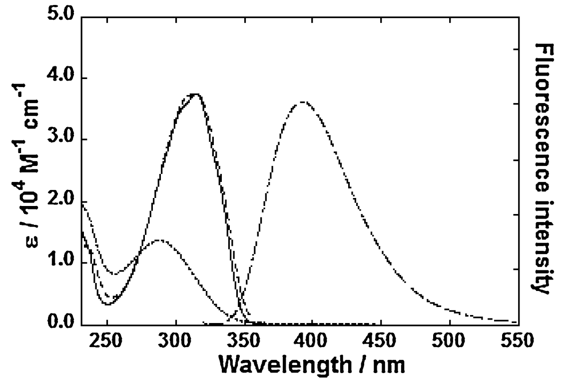


Figure 1. The absorption (solid line), fluorescence (dot–dash line), and fluorescence excitation spectra (dash line) of *trans*-**3** and the absorption spectra of *cis*-**3** (dotted line) in acetonitrile under Ar.

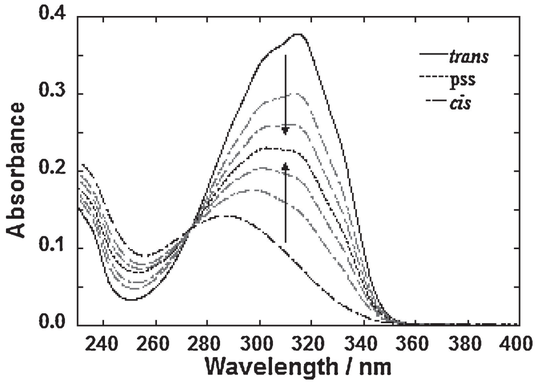


Figure 2. Change of absorption spectra of *trans*-**3** and *cis*-**3** in acetonitrile on irradiation at 275 nm under Ar.

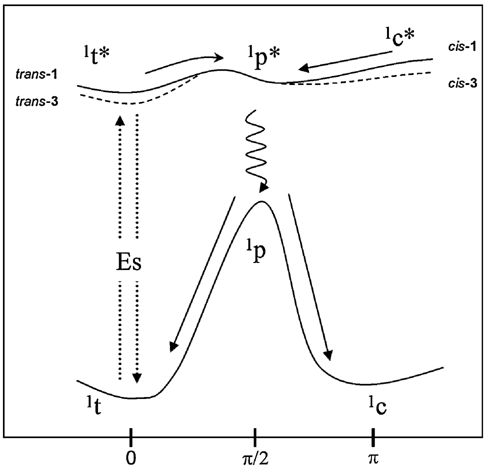


Figure 3. Proposed potential energy curves for twisting about the central bond of stilbene unit of compound **1** and compound **3** in S_0 and S_1.

changed to approach the same spectral profile of the mixture, which indicates the occurrence of trans–cis photochemical isomerization. The photostationary state (pss) isomer ratio is determined to be trans:cis = 48.0:52.0 on irradiation with 275 nm light under Ar. The quantum yields of isomerization from the trans-to-cis direction was estimated using 0.45[16] of the *trans*-stilbene as a reference. The trans-to-cis isomerization quantum yield of *trans*-**1** was determined to be 0.41, and that of *trans*-**3** was determined to be 0.32 (Table 1). So *trans*-**1** with spacer underwent more efficient photoisomerization than *trans*-**3** without spacer. Thus photochemical properties of *trans*-**3** were different from *trans*-**1** in fluorescence emission and the photoisomerization. *trans*-**1** showed a low fluorescence quantum yield but showed a high isomerization quantum yield. In contrast, *trans*-**3** showed a low isomerization quantum yield but showed high fluorescence quantum yield. It can be proposed that there is a potential energy difference for twisting about the central bond of the stilbene unit of *trans*-**1** and *trans*-**3** in S_1 (Figure 3). The singlet excitation energy (E_s) of *trans*-**1** was estimated to be 85.3 kcal mol^{-1} and that of *trans*-**3** was estimated to be 82.1 kcal mol^{-1} from the point of intersection of each absorption and fluorescence spectra. The photoexcited $^1t^*$ state slides along the S_1 potential energy surface to $^1p^*$, and photoisomerization occurs through this process. *trans*-**3** should have a higher barrier for the torsional isomerization from $^1t^*$ to $^1p^*$ compared with that of *trans*-**1**. A methylene chain spacer made a difference in the barrier for torsional isomerization in the singlet excited state and led to the success in controlling photochemical properties of fluorescence emission and photoisomerization.

We have also tried to change the state of the compounds by irradiation with UV light on pure liquid of *cis*-**3** and pure solid of *trans*-**3**. The change of ^{1}H NMR spectra and pictures of morphology change on irradiation of *cis*-**3** with UV light from the UV-lamp are shown in Figure 4. After irradiation, the spectrum shows a cis–trans mixture, and we were able to

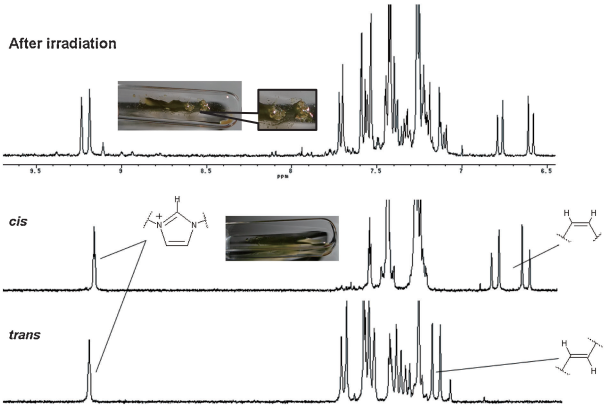


Figure 4. ^{1}H NMR spectrum and pictures on irradiation 365-nm light from the mercury lamp to *cis*-**2** for 5 h, ^{1}H NMR spectrum and picture of pure *cis*-**2** and pure *trans*-**2**.

visually see the liquid state of *cis*-**3** changing into the solid state of *trans*-**3**. However, irradiation of *trans*-**3** did not give *cis*-**3**. The reason for the lack of isomerization from trans-to-cis direction in this experiment may be the following. Because the cis isomer is a liquid and has more space freedom, the stilbene part is capable of undergoing isomerization. On the other hand the trans isomer is a solid, and the twisting of the double bond is restrained by tight molecular packing. Therefore, in acetonitrile, photoisomerization occurs reversibly between trans and cis isomers, but in neat conditions, only cis-to-trans photoisomerization occurs.

In conclusion we have prepared highly fluorescent stilbene ionic liquid with imidazolium cation directly attached to the para-position of the phenyl ring and revealed that the key factor controlling the fluorescence emission and photoisomerization between *trans*-**1** and *trans*-**3** was the methylene chain as the spacer. Furthermore we have succeeded in changing liquid state of cis isomer into the solid state of trans isomer with photoswitchable fluorescence properties by photoirradiation. These findings can greatly contribute to the preparation and development of fluorescent and photoreversible ionic liquids.

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References and Notes

1 T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
2 J. S. Wilkes, *Green Chem.* **2002**, *4*, 73.
3 M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391.
4 R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792.
5 P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.
6 R. Sheldon, *Chem. Commun.* **2001**, 2399.
7 N. Akai, A. Kawai, K. Shibuya, *Chem. Lett.* **2008**, *37*, 256.
8 Y. Miyake, T. Hidemori, N. Akai, A. Kawai, K. Shibuya, S. Koguchi, T. Kitazume, *Chem. Lett.* **2009**, *38*, 124.
9 P. Bonhôte, A. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.
10 R. Ozawa, H. Hamaguchi, *Chem. Lett.* **2001**, 736.
11 H. Tamura, Y. Shinohara, T. Arai, *Chem. Lett.* **2010**, *39*, 240.
12 T. Asaka, N. Akai, A. Kawai, K. Shibuya, *J. Photochem. Photobiol., A* **2010**, *209*, 12.
13 A. Kawai, D. Kawamori, T. Monji, T. Asaka, N. Akai, K. Shibuya, *Chem. Lett.* **2010**, *39*, 230.
14 R. H. Smith, D. H. Andrews, *J. Am. Chem. Soc.* **1931**, *53*, 3644.
15 L. F. Fieser, *J. Chem. Educ.* **1961**, *38*, A501.
16 U. Muzzucato, *Pure Appl. Chem.* **1982**, *54*, 1705.
17 A. K. Singh, S. Kanvah, *J. Chem. Soc., Perkin Trans. 2* **2001**, 395.
18 F. D. Lewis, R. S. Kalgutkar, J.-S. Yang, *J. Am. Chem. Soc.* **1999**, *121*, 12045.
19 F. D. Lewis, W. Weigel, *J. Phys. Chem. A* **2000**, *104*, 8146.
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