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Photoisomerization and Fluorescence Characteristics of Tetramethoxystilbene in Ionic Liquid

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Photochemical behavior of 3,3′,5,5′-tetramethoxystilbene (TMST) has been explored in ionic liquid. Two fluorescence components with the lifetime of 4.3 and 23.0 ns were observed for *trans*-TMST in ionic liquid solution. From this experimental evidence one could propose that ionic liquid may provide two different environments with highly different polarity, nonpolar and highly polar environments.

We have been studying photoresponsive materials having C=C double bonds as a basic chromophore of photochemical reactions.[1] As to the usual aromatic compounds we have revealed that the photoisomerization properties such as quantum yield of isomerization and isomerization selectivity are controlled by the excited state energy of the substituent of the aromatic groups substituted at the C=C double bond. In order to develop different photoresponsive compounds we are interested in exploring more complex molecules such as high-molecular-weight compounds as well as functionalized molecules by intermolecular[2] or intramolecular[3–5] hydrogen bonding. In the study of high-molecular-weight dendritic compounds, we have prepared water-soluble compounds related to unimolecular micelles as well as compounds soluble in organic solvent. Particularly, for water-soluble stilbene dendrimers we could afford nanoscale unimolecular compounds which have hydrophobic interior and hydrophilic exterior and found several unprecedented photochemical reactions such as highly selective almost one-way *trans*-to-*cis* photoisomerization in water.[6]

Aromatic C=C compound with hydrogen bonding also exerted interesting photochemical properties showing one-way *trans*-to-*cis* isomerization induced by ultrafast intramolecular hydrogen atom transfer in the excited state.[7]

As another approach to functionalizing molecules with C=C double bonds we are interested in introducing potentially ionic salts in photoresponsive compounds such as stilbene. Some of the work concerning photoresponsive ionic liquid has been published by us[8,9] for stilbene and by Kawai et al.[10,11] for azobenzene as chromophore. We should briefly mention that ionic liquid is fluid despite being composed of anions and cations and is very much different from inorganic salts which have considerably high melting point.

In a previous paper, stilbene ionic liquids with imidazolium cation directly or indirectly attached to the benzene ring at the C=C double bond (Figure 1) have been prepared and it has been found that most of these ionic compounds are ionic liquids either at room temperature or below 100 °C.[8,9] Furthermore, *cis* ionic liquids are all nonfluorescent and *trans* ionic liquids are all fluorescent and therefore, one can photochemically switch the fluorescence properties as well as morphology of either liquid or solid. Moreover, the stilbene-like compounds are easily isolated as pure *cis*- and *trans*-isomers and are stable at room temperature, and therefore we have proposed that the previously reported studies may help to understand the basic properties of stilbene ionic liquids and give some directions for preparing functionalized ionic liquids.

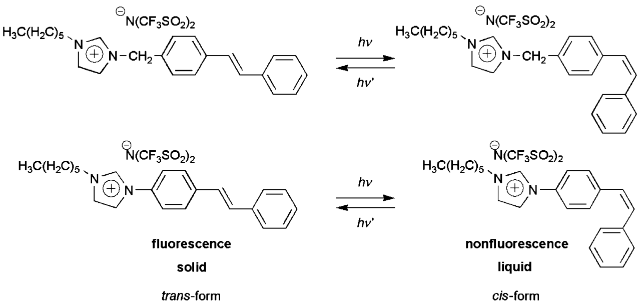

Figure 1. Structure of stilbene ionic liquids and photochemical *cis*–*trans* isomerization.

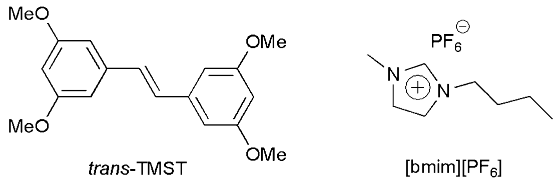

Figure 2. Structure of 3,3′,5,5′-tetramethoxystilbene (TMST) and ionic liquid solvent, [bmim][PF$_6$].

In this study we are interested in the effect of ionic liquid[12,13] as a solvent on photochemical properties of *trans*-3,3′,5,5′-tetramethoxystilbene (TMST) by comparing the behavior in usual solvents with that in ionic liquid solvent, [bmim][PF$_6$] (Figure 2). In brief, we have observed the fluorescence lifetime of *trans*-TMST with two components in ionic liquid, while the fluorescence decay fits single components in other organic solvents. Thus, the studies on fluorescence lifetime of stilbene derivatives may help to understand the microenvironment of ionic liquids which could be used as special solvents with potentially high viscosity but seemingly not very high viscosity compared to the viscosity suggested by the η values.

Photoisomerization of *trans*-stilbene proceeds in a potential energy surface as shown in Figure 3. On excitation of *trans*-stilbene to the excited singlet state it will either undergo fluorescence emission or twisting around the C=C double bond overcoming an activation barrier of ca. 3.6 kcal mol^{-1} in acetonitrile.[14] The resulting perpendicular excited singlet state undergoes deactivation to the ground state perpendicular geometry finally giving stable *cis*- and *trans*-stilbene in nearly equal ratio. If the viscosity of ionic liquids may increase the activation barrier for isomerization in the excited state, we thought that an intrinsically higher rotation barrier may suffer

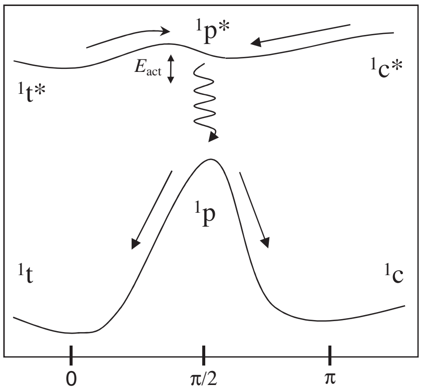

Figure 3. Potential energy surface for twisting about the central bond of stilbene in S_0 and S_1.

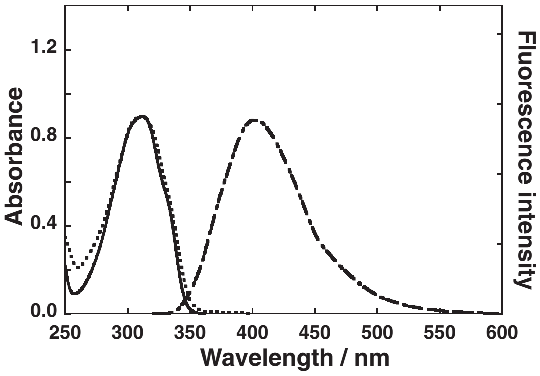

Figure 4. The absorption (solid line), fluorescence (dot-and-dash line), and fluorescence excitation spectra (dotted line) of *trans*-TMST in [bmim][PF_6] under Ar.

more than a system with low activation barrier. We have found that *trans*-TMST has considerably long fluorescence lifetime of more than 10 ns in polar solvent such as acetonitrile and decreases with decreasing polarity of the solvent.[15] Thus, TMST was thought to be an appropriate compound to study the real viscosity of ionic liquid and the polarity of ionic liquid from the point of view of microviscosity and bulk viscosity. The measured viscosity of ionic liquid [bmim][PF_6] (260 cP)[16] used in these experiments as a solvent is much higher than that of acetonitrile (0.34 cP),[16] while the polarity of [bmim][PF_6] ionic solvents in $E_T(30)$ is 52.3 kcal mol^{-1}[17] and slightly higher than that of acetonitrile (45.3)[18] but is almost equivalent with the value of methanol (55.0).[18] In other words the viscosity of this ionic liquid is much higher than that of acetonitrile, but the polarity in $E_T(30)$ value is almost the same with that of alcohol and acetonitrile.

Figure 4 shows absorption, fluorescence, and fluorescence excitation spectra of *trans*-TMST in ionic liquid, [bmim][PF_6]. The absorption maximum and fluorescence maximum in [bmim][PF_6] shifted slightly to longer wavelength compared to the spectra in acetonitrile, while the absorption profile and the fluorescence quantum yield were almost the same. On irradiation of *trans*-TMST at 313 nm, one can observe spectral change to give the photostationary state isomer ratio of $([t]/[c])_{pss} = 31.4/61.8$ (Figure 5). Thus, TMST in [bmim][PF_6] underwent *trans*–*cis* photoisomerization mutually. A similar photoisomerization of stilbene has already been reported.[19]

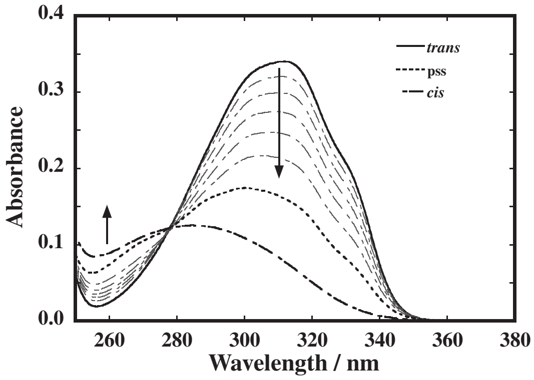

Figure 5. Change of absorption spectra of *trans*-TMST in[bmim][PF_6] on irradiation at 313 nm under Ar.

Table 1. Experimental values of *trans*-TMST in benzene, acetonitrile, and [bmim][PF_6] under Ar

Solvent	λ_{max}(abs) /nm	λ_{max}(fl) /nm	Φ_f	$\Phi_{t\text{–}c}$	τ_s /ns
Benzene[a]	310	373	0.24	0.31	4.1
Acetonitrile[a]	307	395	0.29	0.32	16.6
[bmim][PF_6]	312	403	0.30	0.25	4.3 (0.16) 23.0 (0.84)

[a] Ref. 15.

The quantum yield of *trans*-to-*cis* isomerization of TMST slightly decreased from 0.32 in acetonitrile to 0.25 in [bmim][PF_6]. The decrease in quantum yield of *trans*-to-*cis* isomerization may have some relation to the polarity and microviscosity. However, despite the high viscosity of 260 cP for [bmim][PF_6] compared to that of acetonitrile (0.34 cP), the quantum yield of photoisomerization of *trans*-TMST seems to be considerably high indicating a nonuniform structure of ionic liquid [bmim][PF_6]. In other word, there is a possibility that viscosity at microlevel seems to be lower than that of bulk state and the ionic liquid [bmim][PF_6] molecules should make several different environments.

Actually, one can observe fluorescence properties of *trans*-TMST in ionic liquid. Thus, the fluorescence lifetime fits two exponential functions to give 4.3 and 23.0 ns indicating the existence of two different solvation environments. These results are summarized in Table 1 together with the results observed in benzene and in acetonitrile.

As already reported, fluorescence behavior of *trans*-TMST suffered the solvent effect and especially, the fluorescence lifetime increased with increasing solvent polarity from 2.3 ns in cyclohexane and 4.1 ns in benzene to 16.6 ns in acetonitrile. Furthermore, the dipole moment in the excited state ($\mu_e = 9.5$ D) is larger than that in the ground state ($\mu_g = 2.5$ D).[15] It should be noted here that the observed lifetime of 23 ns is the longest one in simply substituted stilbenes.

The observation of two components in fluorescence lifetime of *trans*-TMST in [bmim][PF_6] indicates that there are two microenvironments in [bmim][PF_6]. Otherwise, dynamic Stokes shift may influence the fluorescence dynamics to give two

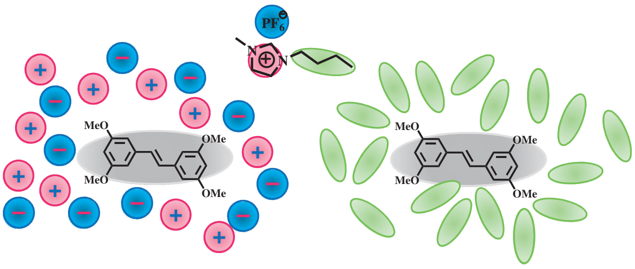

Figure 6. Proposed two microenvironments in [bmim][PF_6], highly polar and nonpolar.

exponential decays. However, it has been reported that the necessary time for the dynamic Stokes shift of dipolar molecules in [bmim][PF_6] is ca. 1 ns.[12] The observed lifetimes of TMST in [bmim][PF_6] are 4.3 and 23.0 ns and are far longer than the usual time for dynamic Stokes shift. Therefore, we can propose that the two components of fluorescence lifetime observed for TMST in [bmim][PF_6] are ascribable to the existence of two different solvation environments as shown in Figure 6. One of the possible environments is a nonpolar environment like benzene by agglomerating some alkyl chains and the other should be highly polar environments like ion pairs of [bmim][PF_6] (Figure 6). This observation is in accordance with the theoretical calculation that there are two environments in ionic liquid.[20]

In conclusion photochemical behavior of *trans*-TMST has been explored in ionic liquid. As a result, two fluorescence components with the lifetimes of 4.3 and 23.0 ns were observed. From this experimental evidence one could propose that ionic liquid may provide two different environments with highly different polarity, nonpolar and highly polar environments. The organic compounds may be dissolved in these two different environments existed in ionic liquid. In other words, if we consider the microenvironments of ionic liquids one may expect mostly two environments of different polarity of nonpolar and polar environment composed of cation and anion in close contact.

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