

## Unusual Solvatochromism Based on Intramolecular Hydrophobic Interaction in Water-soluble Azobenzene Dendrimers

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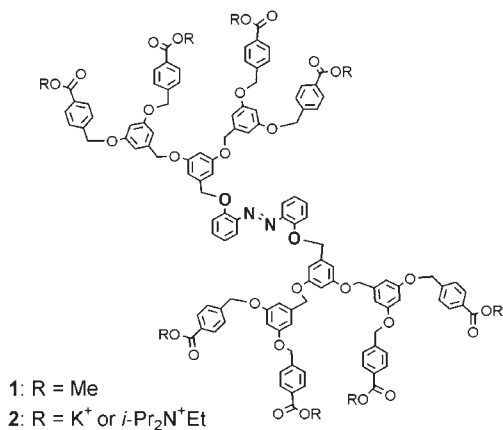
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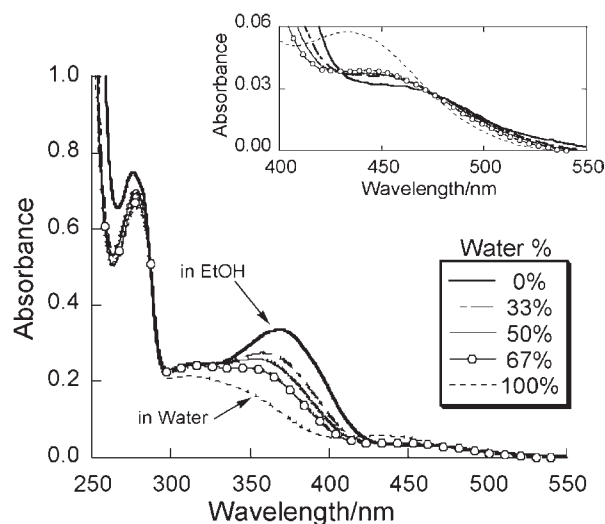
Azobenzene dendrimer **E-2**, having water-soluble dendrons at the *ortho*-position in azobenzene, showed novel solvatochromism with changing the solvent ratio of water/EtOH which is based on the intramolecular hydrophobic interaction due to poly-aryl(ether) dendrons. The thermodynamic parameters for Z-to-E thermal isomerization of **2** also greatly depended on the water/EtOH ratio.

In our previous paper, we reported the synthesis and the Z-E photochemical- and Z-to-E thermal isomerization of azobenzene-cored dendrimers.<sup>1,2</sup> In organic solvents, the absorption spectra of the azobenzene unit and the activation parameters for thermal isomerization were not very different as regards their dendrimer generation. In addition, the absorption spectra of the azobenzene unit in dendrimers synthesized in other groups exhibit similar spectra to those of the original azobenzene unit, or are independent of dendrimer generation.<sup>3-8</sup> Meanwhile, both the absorption spectra and the activation parameters for the thermal isomerization of our water-soluble azobenzene dendrimers (Figure 1) in aqueous solution were considerably influenced by dendrimer generation. In this paper, we report the solvatochromism of water-soluble azobenzene dendrimer **E-2** in the solvent of the water-EtOH system. The mechanism of the solvatochromism of **E-2** is totally different from the 'typical' solvatochromism, and is based on the intramolecular hydrophobic interaction due to the poly-aryl(ether) branching units in the dendrimer. The activation parameters for Z-to-E thermal isomerization of **2** will be discussed which could be correlated with the mechanism of the solvatochromism.

Figure 2 provides the UV-vis absorption spectra of **E-2** in water, EtOH, and the water-EtOH mixed solvents: water/EtOH



**Figure 1.** Structures of azobenzene dendrimers **E-1** and water-soluble azobenzene dendrimers **E-2**.

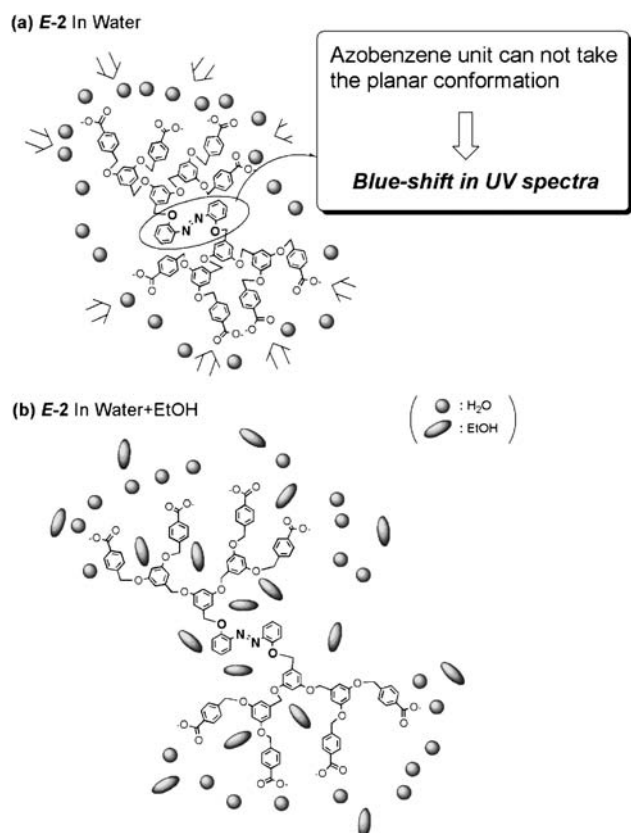


**Figure 2.** Change in the UV absorption spectra of **E-2** ( $3.65 \times 10^{-5}$  M) in water, EtOH, and the water-EtOH mixed solvents: water/EtOH 67/33, 50/50, and 33/67, respectively. Counter cation for the dendrimer is K<sup>+</sup> in H<sub>2</sub>O and in EtOH/H<sub>2</sub>O mixed solvents, while *i*-Pr<sub>2</sub>N<sup>+</sup>Et is used in EtOH to avoid precipitation. Inset shows the expanded spectra.

67/33, 50/50, and 33/67, respectively. The absorption band for **E-2** largely changed with changing the ratio of EtOH/H<sub>2</sub>O. The band at 300–420 nm, attributed to the  $\pi$ - $\pi^*$  transition band, exhibited increased intensity and the red-shift of the wavelength when the ratio of EtOH was increased, while the band for  $n$ - $\pi^*$  transition at 420–530 nm decreased. In general, the  $\pi$ - $\pi^*$  transition state is stabilized by the interaction with polar solvents, which results in the red-shift of the absorption spectra. For example, donor-acceptor-substituted (push-pull) azobenzenes show typical solvatochromism and their absorption spectra red-shift with quantitative sensitivity to increasing the solvent polarity scale  $\pi^*$ .<sup>9,10</sup> In the case of this azobenzene dendrimer, however, the absorption peak due to  $\pi$ - $\pi^*$  transition in water was at much shorter wavelength (312 nm) than that in EtOH (369 nm) and the peaks in the mixed solvents were at 317, 353, and 359 nm in water-EtOH 67/33, 50/50, and 33/67, respectively. This unusual solvatochromic behavior probably comes from a different mechanism correlated with the molecular structure and its environment. It should be noted that the introduction of the water-soluble dendron should be at the *ortho*-position in the azobenzene ring to give this unusual solvatochromism. Unlike **E-2**, the water-soluble azobenzene dendrimers having the same dendrons at *para*-positions in the azobenzene ring did not show the large blue-shift in water (data not shown). In addition, the water-soluble azobenzene derivative without den-

**Table 1.** Activation energy, frequency factor, activation enthalpy, and activation entropy of thermal *Z*-to-*E* isomerization of **1** and **2** under various conditions

Compounds	Counter cations	Solvents	Ea/kcal mol <sup>-1</sup>	A/10 <sup>12</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ /cal mol <sup>-1</sup> K <sup>-1</sup>
<b>1</b> <sup>a</sup>	none	CHCl <sub>3</sub>	21.8	1.18	21.1	-12.6
<b>2</b> <sup>a</sup>	K <sup>+</sup>	H <sub>2</sub> O	29.7	86000	29.0	9.6
<b>2</b>	K <sup>+</sup>	EtOH/H <sub>2</sub> O = 50/50	28.1	21600	27.4	6.9
<b>2</b>	<i>i</i> -Pr <sub>2</sub> N <sup>+</sup> Et	EtOH	23.9	32.7	22.8	-6.0

<sup>a</sup>Data in Ref. 2.**Figure 3.** Schematic drawing for solvatochromism of dendrimer *E-2*. (a) *E-2* dissolved in H<sub>2</sub>O. Intermolecular hydrophobic interaction of aryl(ether) dendrons in *E-2* causes the conformational change of the azobenzene moiety to give blue-shift in UV spectra. (b) *E-2* in EtOH/H<sub>2</sub>O mixed solvent. Existence of EtOH reduces the intermolecular hydrophobic interaction in *E-2*, and results in similar spectra of *E-1* in CHCl<sub>3</sub>.

dron, reported in the previous paper, also did not show this unusual solvatochromism observed in dendrimer *E-2*.

Figure 3 shows a schematic drawing for the mechanism of the solvatochromic behaviors. When the dendrimer dissolved in water, intramolecular hydrophobic interaction should be operative, which results in shrinkage of the dendrimer (Figure 3a). The molecular shrinkage is supported by decrease of the molar extinction coefficients at 280 nm compared to those in organic solvents, and this phenomenon is generally observed in other poly-aryl(ether) dendrimers in aqueous solution and in organic solvents. (Figure 2 and Refs. 11, 12). The hydrophobic interaction in *E-2* is strong enough to change the conformation of the central azobenzene unit to give a considerable blue-shift of the absorption. When EtOH is added to the aqueous solution of

*E-2*, the EtOH molecules should be preferably inside the dendrimer (Figure 3b), which would induce the 'expanded' form and the azobenzene unit would take the conformation as in other organic solvents.

Interestingly, this unusual solvatochromic behavior reflects *Z*-to-*E* thermal isomerization of **2**, or the activation parameters for the thermal isomerization largely depended on the water–EtOH solvent ratio. In water, **2** showed a considerably large value of the frequency factor (second line in Table 1), obtained by Arrhenius plots, and the other parameters, activation energy, activation enthalpy, and the activation entropy were also significantly larger than those in azobenzene dendrimer **1** in organic solvents. However, in water/EtOH = 1/1, these values of the parameters were decreased, and were further decreased in EtOH to become similar to those for compound **1** in CHCl<sub>3</sub>. The results also suggest that the hydrophobic interaction due to dendron groups in dendrimer **2** is strong enough to give the azobenzene unit unusual conformation to change the activation parameter in water.

To the best of our knowledge, this is the first clear evidence that the absorption maximum of azobenzene chromophore is considerably influenced by environmental solvent composition in aqueous solutions.

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