Controlling the Hydrophobic Properties of Water-soluble Stilbene Dendrimers

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(Received August 5, 2003; CL-030727)

The Intramolecular energy transfer from the dendron subunit to the stilbene core in water-soluble stilbene dendrimer **2** increased from 49% to ca. 100% by added salt.

Dendrimers are structurally regular macromolecules with high concentration of peripheral chain ends which decrease the interaction between the inside of the molecules and the solvents.[1–5] We have studied the dendrimer effects on the photochemistry of stilbenoid compounds so far.[6–10] Our next goal in this field is to create an artificial nano-scale hydrophobic space in a water-soluble dendrimer, which works like micelles but is chemically, physically, and biologically stable. It is important to study the fluorescence properties of the dendrimer core because the fluorescence emission from the core may reflect the interaction between the dendrimer core and the solvent water. In this report, we explore the effect of added salt on the fluorescence properties of water-soluble stilbene dendrimers (WSDs) (Figure 1).[10] We wish to report a novel salt effect on the molecular structure of the hydrophobic environment of water-soluble stilbene dendrimers as photoresponsive unimolecular micelles.

Figure 2 shows a change in the fluorescence spectra of **2** (4.7 μM) in 2.0 mM KOH aqueous solution at room temperature, where the spectra blue-shifted from 411 to 390 nm with increasing the concentration of KCl from 0 to 40 mM. Comparison of the fluorescence λ_{max} among **1**–**3** versus increasing the concentration of KCl is shown in the inset in Figure 2. In general, the excited states of stilbenoid compounds are stabilized by interaction with polar solvents to be red-shifted. Therefore, the excited state of the core of **1** without KCl (λ_{max}: 424 nm) is stabilized more efficiently by the interaction with water than that of **2** (λ_{max}: 411 nm) and **3** (λ_{max}: 389 nm). The core moiety of **2** and **3** should be partially isolated from water by peripheral dendron groups. When KCl was added to the solution of **1**–**3**, only the fluorescence λ_{max} of **2** shifted to shorter wavelength with increasing the KCl concentration (Figure 2, inset), while almost no salt effects were observed on the fluorescence spectra of **1** or **3**. The addition of KCl to the dendrimer solution may cause the conformational change, or folding-up of the peripheral dendron. The spectral shift in the fluorescence spectra in **2** indicates the dendron subunit was folded up by addition of KCl, which resulted in the decrease of core-water interaction to destabilize the excited state of the core. The fluorescence λ_{max} of **3** was not changed by added KCl probably because core-water interaction in **3** was already inhibited by the peripheral dendron even in the absence of KCl, and KCl could not affect the singlet excited state of stilbene core of **3** in aqueous solution.

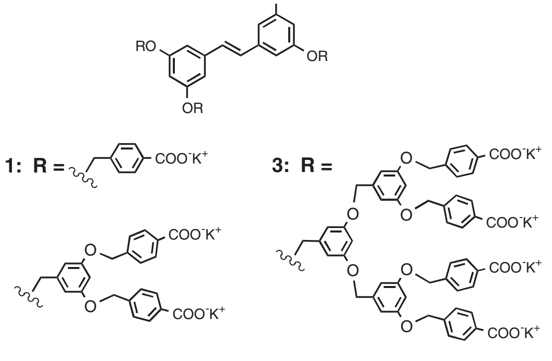

Figure 1. Structure of water-soluble stilbene dendrimers **1**–**3**.

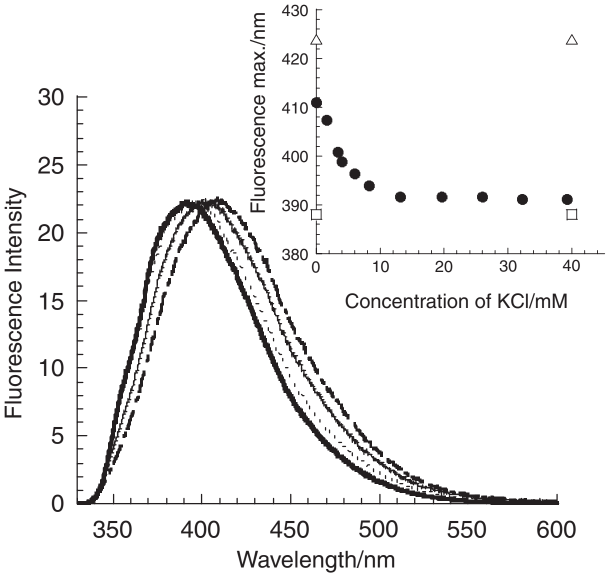

Figure 2. Fluorescence spectral change of **2** (4.7 μM) in 2.0 mM aqueous KOH solution upon the addition of KCl: 0 mM (dash-dot line), 9 mM (thin line), 20 mM (dotted line) and 40 mM (solid line). The spectra were measured with the absorbance of absorption maximum to be <0.1 and were normalized. Inset shows the change in the fluorescence maxima of **1**(△), **2**(●), and **3**(□) with increasing the concentration of KCl.

The relative intensity at certain wavelengths of the fluorescence excitation spectra was changed by added KCl to the solution of **2** and **3** (Figure 3). The ratio of the intensity of two peaks due to the dendron subunit (285 nm) and the stilbene core (310–320 nm) changed with increasing the concentration of KCl (inset in Figure 3). When the excitation spectrum and the absorption spectrum are normalized at the λ_{max} of the stilbene core, the value of the singlet energy transfer efficiency from the dendron groups to the stilbene core can be estimated.[7,11] Thus, relative intensity of the fluorescence excitation spectra at 280 and 320 nm

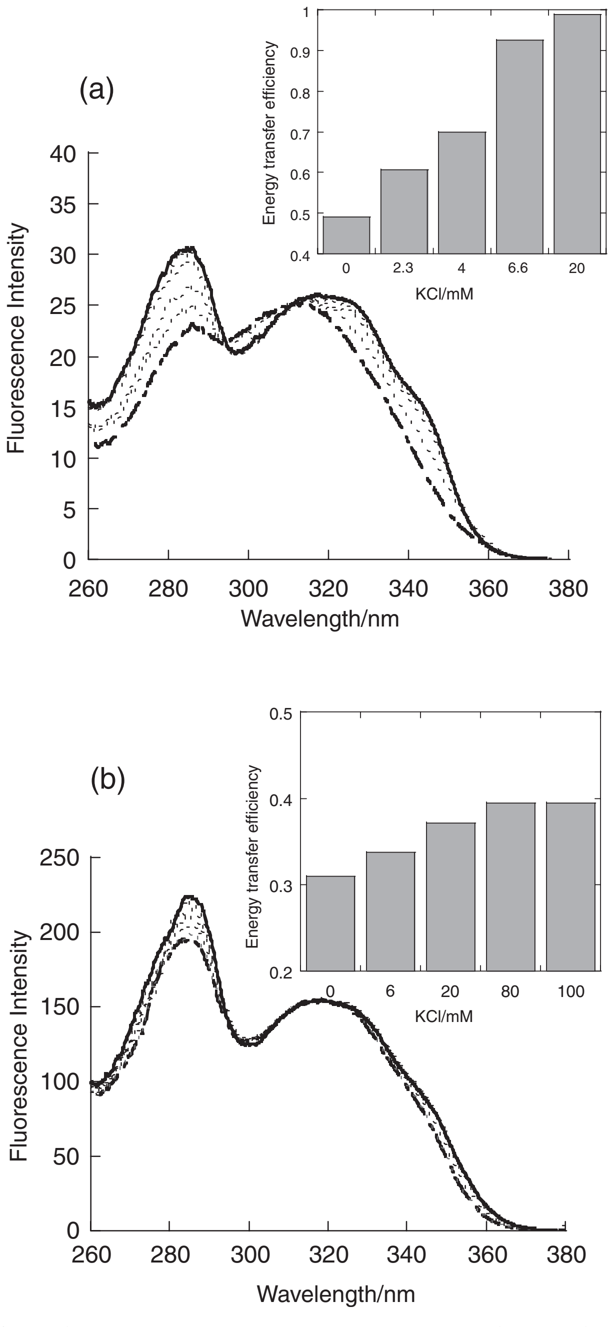

Figure 3. Change in fluorescence excitation spectra of **2** (a) and **3** (b) upon the addition of KCl: 0 mM (dash-dotted line), 20 mM (solid line in (a)), 100 mM (solid line in(b)). Insets in (a) and (b) show the corresponding increase of intramolecular singlet energy transfer vs concentration of KCl.

was compared to that of the absorption spectra and the energy transfer efficiency was determined.

Before addition of KCl, the energy transfer efficiencies were 49% for **2** and 31% for **3**, respectively. By addition of 20 mM of KCl, the energy transfer efficiency increased to ca. 100% for **2** and 37% for **3**. The energy transfer in **2** took place quite efficiently by added KCl probably because the outermost husks of dendron in **2** may approach within sufficient distance to carry out energy transfer. Increase of the energy transfer efficiency for **3** by added KCl was less sensible and less efficient as compared with **2**. Even after addition of 100 mM of KCl, the energy transfer efficiency for **3** was 40%. Increase of the energy transfer efficiency in the dendrimers by added salt indicates that the dendron moiety, which can move somewhat freely, is folded up and the distance between the aryl group of the dendron and the stilbene core is narrowed. These results indicate that the efficiency of the intramolecular energy transfer is dependent on the generation of the dendrimer. This type of dendrimers up to the 2nd generation could transfer excitation energy of the dendron to the core most efficiently. With the 3rd generation, however, the energy transfer takes place less efficiently than that of **2** because of the longer distance between the core and the outermost aryl groups. The present results in WSDs **2** and **3** are in accord with the usual Förster type energy transfer mechanism.

It should be noted that the added KCl affect the fluorescence excitation spectrum of **3** despite there being almost no effect on the fluorescence spectrum. The intensity of the fluorescence excitation spectra changed mainly around 285 nm. Since the fluorescence emits from the core moiety, the change in the fluorescence excitation spectra of **3** indicates that the added KCl does not affect the singlet excited state of the core but affects the energy transfer efficiency from the dendron to the core. In other words, added KCl should affect the folding of the dendrimer. However, the reason why KCl should cause folding of the dendrimer is still under investigation.

In summary, added KCl to the solutions of water-soluble stilbene dendrimers **2** and **3** affected the fluorescence and fluorescence excitation spectral changes due to diminishing the interaction between the core of the dendrimers and water. The 2nd generation dendrimer **2** could transfer excited energy from the dendron to the core most efficiently probably because the dendron subunit was folded up by the effect of added salt. The results obtained indicate the energy transfer efficiency from the dendron to the core is simply dependent on the generation or distance between the core and the outermost aryl groups. This is the first direct observation of the control of the hydrophobic properties in water-soluble dendritic molecules in water achieved simply by added salt.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) and the 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government and by the Asahi Glass Foundation.

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