Remarkably Slow Aggregation of a Styrylpyrazine Amphiphile in Aqueous Dispersion

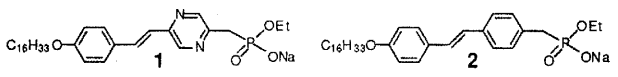
Jong-mok Park, Wanbin Zhang, Yohji Nakatsuji, Tetsuro Majima,† and Isao Ikeda*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871
†*The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047*

(Received November 5, 1999; CL-990947)

Styrylpyrazine amphiphile **1** in aqueous dispersion showed a remarkably slow aggregation process. Evidence supporting the "translation" layered structure of **1** having face-to-face stacking in the aggregate was obtained by the blue-shifted fluorescence spectra by the aggregation in contrast with the red-shift for stilbene amphiphile **2**.

The photochemistry and photophysics of a chromophore embedded in a hydrophobic chain of an amphiphile in organized assemblies such as Langmuir-Blodgett films, supported multilayers, and bilayer membranes have attracted much attention due to their potential widespread applications.[1] It is well known that the photochemistry and photophysics of these aggregates are very different from those of a monomeric species in homogeneous solution, and are dependent on the molecular-orientation of the chromophore and its physical environment in the aggregate.[2] Therefore, for artificial manipulation of the photochemistry and photophysics of the chromophore in the aggregate, it is very important to understand the molecular-orientation of the chromophore in the aggregate and the aggregation process of the amphiphile containing the chromophore. The aggregation process, however, is generally too fast to allow investigation without fast time-resolved spectroscopic measurements.

Recently, we found that styrylpyrazine amphiphile **1** formed a unique aggregate with a "translation" structure having face-to-face stacking, through a study on the photodimerization reactivities in aqueous dispersion[3a] and in the bilayer matrix of L-α-dipalmitoyl phosphatidylcholine.[3b] During the study on the photophysics of this aggregate, we found that the aggregation process of **1** in water was quite slow enough to be observable with usually available UV and fluorescence spectrometers. In this paper, we describe this unique aggregation behavior of **1** in aqueous dispersion disclosed by investigating the change in UV-vis absorption and fluorescence spectra, the lifetime of fluorescence, the size of aggregate, and the initial rate of [2+2] cycloaddition in the time course of storage at 25 °C.



The absorption and fluorescence spectra of **1** in aqueous dispersion were obtained at the concentration of 5.0×10^{-5} M and 5.0×10^{-6} M, respectively. The sample solutions were prepared just before the measurement by dilution of a portion of an aqueous stock solution (5.0×10^{-4} M) prepared by sonication. The stock solution was purged with Ar gas, sealed completely, and stored in darkness through the whole experiment. Immediately after sonication, the aqueous dispersion of **1** showed a similar absorption spectrum (Figure 1A-a, λ_{max} = 344 nm) to that in methanol solution (λ_{max} = 348 nm). However, the absorption λ_{max} was gradually blue-shifted to b after 5 h, to c after 48 h, and then finally to d after 72 h from sonication at 25 °C. The spectrum d (λ_{max} = 283 nm) was essentially unchanged at 25 °C at even longer storage time. The λ_{max} at 283 nm of the resultant spectrum (A-d) indicates 65 nm blue-shift from 348 nm of the spectrum in methanol. The large blue-shift of the absorption spectra in the bilayer assembly may be explained by considering the card-packed orientation ("H" aggregation) of the styrylpyrazine chromophores along the long axis of the molecule based on the extended dipole model proposed by Kuhn et al.[2a,b] The gradual blue-shift of the absorption spectrum is attributed to the slow "H" aggregation of **1** in water. The slow aggregation suggests that two nitrogen atoms of styrylpyrazine would be strongly hydrated in aqueous dispersion, and the dehydration energy may be necessary for the aggregation. In comparison, the absorption spectrum of stilbene analogue **2** in aqueous dispersion showed a 39 nm blue-shift immediately after sonication from that in methanol solution and was essentially unchanged even after 1 week.

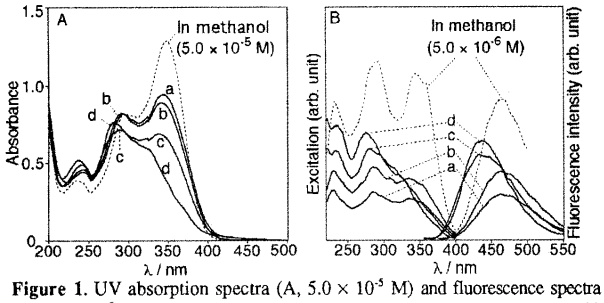


Figure 1. UV absorption spectra (A, 5.0×10^{-5} M) and fluorescence spectra (B, 5.0×10^{-6} M) of **1** in aqueous dispersion in the time course of storage: (a) immediately after sonication; (b) after 5 h; (c) after 48 h; (d) after 72 h at 25 °C. For methanol solution, the excitation spectrum was monitored by emission at λ_{em} 468 nm, while the emission spectrum was monitored by excitation at λ_{ex} 294 nm. For aqueous dispersion, the emission spectra were monitored by excitation at λ_{ex} 280 nm, while the excitation spectra were monitored by emission at λ_{em} 464 nm in the cases of A-a and A-b and at λ_{em} 434 nm in the cases of A-c and A-d.

The fluorescence intensity of **1** in aqueous dispersion (5.0×10^{-6} M) immediately after sonication was much weaker than that in methanol solution of the same concentration. However, it increased gradually along with the progression of aggregation as shown in Figure 1B. The λ_{max} at 464 nm of the fluorescence spectra of aqueous dispersion of **1** at the initial stage was similar to that of the methanol solution. However, it was strongly blue-shifted to 434 nm after 48 h (B-c). The blue-shift of the fluorescence spectra of **1** by aggregation is very unique, because the aggregate of **2**, *trans*-stilbene,[4a] 1,2-diphenylethyne,[4b] and styrylthiophene[2d] showed the red-shift of the fluorescence spectra compared to their homogeneous solution. The unique fluorescence phenomenon of **1** in aqueous

dispersion can be understood qualitatively by considering the excited state decay model proposed by Lapouyade et al.[5] According to this model, electron donor-acceptor substituted stilbene derivatives show a larger Stokes shift[6] in a polar solvent than the non-substituted analogue because the emissive excited state of the former can be more stabilized by twisting around the single bond between the double bond and the phenyl group than the latter. Therefore, the much larger Stokes shift value (120 nm) of **1** than that (46 nm) of **2** in methanol is not surprising. The strong face-to-face stacking of the styrylpyrazine units like a crystal in a bilayer membrane, however, may suppress the twisting around the single bond which is free in solution. This suppression may contribute to the unusual blue-shifted fluorescence because the stabilization of the emissive excited state by twisting around the single bond is not involved in this case. In fact, the Stokes shift of benzofuran-2-pyrazine, in which the twisting is blocked around the double bond and one single bond, was 44 nm smaller than that of 2-hydroxy styrylpyrazine in which the twisting is not blocked.[7] Therefore, the face-to-face stacking of **1** in aqueous dispersion proposed by us[3] would be supported by this unusual blue-shifted fluorescence spectra.

The changes in the superficial size of the aggregate also support the slow aggregation of **1** in water. The weight average diameters of aggregates in aqueous dispersions of **1** and **2** (5.0×10^{-4} M) prepared by sonication were determined at 25 °C by the laser light scattering method. The size of the aggregate of **1** was too small to be detected by this method till 5 h after sonication. However, the weight average diameter of the aggregate of **1** increased gradually to 514 nm after 24 h, 1133 nm after 48 h, and 2026 nm after 72 h, as shown in Figure 2A. On the other hand, the aggregate size of stilbene analogue **2** was 232 nm immediately after sonication, and was almost constant even after 1 week (348 nm). The slow aggregation of **1** is also supported by the observation of the slow increase of content (%) of the excimer-fluorescence (Figure 2A).[8]

The photochemical reactivity of **1** in aqueous dispersion (5.0×10^{-5} M) with irradiation at above 300 nm in the time course of storage was examined by UV-vis spectroscopy. Surprisingly, the photodimerization progressed rapidly (the initial second-order rate constant, $k_2 = 1740$ $M^{-1}s^{-1}$) as indicated in Figure 2B.[3a] In methanol solution, only *trans-cis* isomerization was observed. The fluorescence lifetime ($\tau = 0.758$ ns) in aqueous dispersion was also much shorter than $\tau = 1.27$ ns in methanol solution. After 5 h, the k_2 increased to 3500 $M^{-1}s^{-1}$ and τ decreased to 0.589 ns. These observations suggest

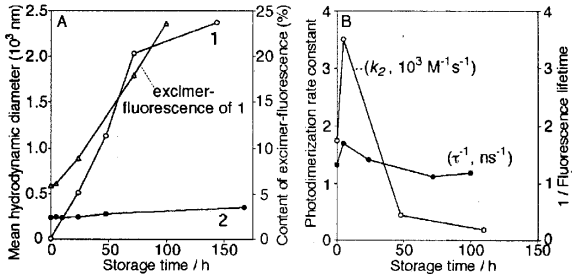
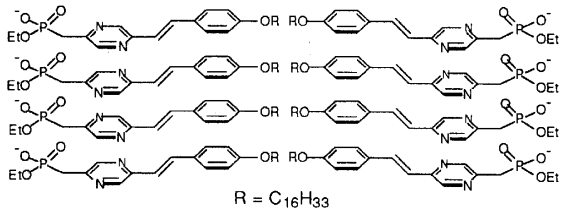


Figure 2. Mean hydrodynamic diameters of aggregates of **1** and **2** (5.0×10^{-4} M) and content of excimer-fluorescence of **1** (5.0×10^{-5} M) in aqueous dispersion (A), and photodimerization rate constant (k_2) and inverse of lifetime of fluorescence (τ^{-1}) of **1** (5.0×10^{-5} M) in aqueous dispersion (B) as a function of storage time at 25 °C.

that **1** forms an aggregate in water even immediately after sonication, in spite of the similarity of the UV absorption spectrum with that in methanol. The k_2 then drastically decreased to 430 $M^{-1}s^{-1}$ after 48 h, 170 $M^{-1}s^{-1}$ after 110 h. Also, the τ changed to 0.705 ns after 24 h, 0.891 ns after 72 h, and 0.846 ns after 102 h. The dependence of k_2 on the storage time is well related with that of τ^{-1} concerning **1** in aqueous dispersion as shown in Figure 2B.



Scheme 1.

Experimental results suggest that aggregation of **1** progressed to give large clusters of the closely face-to-face packed styrylpyrazine units of which the pyrazine is stacked alternately through the multipole-multipole interaction as shown in Scheme 1. The decrease of k_2 at a later stage of the aggregation process can be explained by considering the excitation energy migration and delocalization within the clusters[9] and the reduction of absorption at above 300 nm by the blue-shift. Since the cyclobutane structure adopts a puckered conformation, the transformation of monomer to the cyclobutane dimer should break the planarity of the monomer molecule and induce considerable distortion. In a large aggregate, this distortion may be constrained by the lattice of the aggregate. This, also, may be an important factor to reduce k_2 at a later stage of aggregation.

In conclusion, we have found that the aggregation of the amphiphile **1** was very different from that of the stilbene amphiphile **2** due to the multipole character of the pyrazine group induced by introducing two electronegative nitrogen atoms into one of the two benzene rings of stilbene.

References and Notes

1 a) D. G. Whitten, *Acc. Chem. Res.*, **26**, 502 (1993). b) A. Yabe, Y. Kawabata, A. Ouchi, and M. Tanaka, *Langmuir*, **3**, 405 (1987). c) W. Li, V. Lynch, H. Thompson, and M. A. Fox, *J. Am. Chem. Soc.*, **119**, 7211 (1997).
2 a) V. Czikkely, H. D. Forsterling, and H. Kuhn, *Chem. Phys. Lett.*, **6**, 207 (1970). b) V. Czikkely, H. D. Forsterling, and H. Kuhn, *Chem. Phys. Lett.*, **6**, 11 (1970). c) M. Kasha, *Radiat. Res.*, **20**, 55 (1963). d) X. Song, J. Perlstein, and D. G. Whitten, *J. Phys. Chem. A*, **102**, 5440 (1998).
3 a) J. Park, W. Zhang, Y. Nakatsuji, T. Majima, and I. Ikeda, *Chem. Lett.*, **1999**, 1309. b) J. Park, S. Aoyama, W. Zhang, Y. Nakatsuji, and I. Ikeda, *Chem. Commun.*, in press.
4 a) X. Song, C. Geiger, U. Leinhos, J. Perlstein, and D. G. Whitten, *J. Am. Chem. Soc.*, **116**, 10340 (1994). b) S. Vaday, H. C. Geiger, B. Cleary, J. Perlstein, and D. G. Whitten, *J. Phys. Chem. B*, **101**, 321 (1997). c) C. W. Farahat, T. L. Penner, A. Ulman, and D. G. Whitten, *J. Phys. Chem.*, **100**, 12616 (1996).
5 R. Lapouyade, K. Czeschka, W. Majenz, W. Rittig, E. Gilabert, and C. Rulliere, *J. Phys. Chem.*, **96**, 9643 (1992).
6 W. Rittig and W. Majenz, *Chem. Phys. Lett.*, **154**, 335 (1989).
7 L. Zemin and W. Shikang, *J. Fluoresc.*, **7**, 237 (1997).
8 Two components of fluorescence having lifetimes of 0.7-0.9 ns (monomer fluorescence) and 3-6 ns, respectively, were involved in each spectrum of Figure 1B. The excimer fluorescence is corresponding to the latter.
9 W. F. Mooney, P. E. Brown, J. C. Russel, S. B. Costa, L. G. Pedersen, and D. G. Whitten, *J. Am. Chem. Soc.*, **106**, 5659 (1984).