Amphiphilic Pyranines: Chromophore Wrapped in a Hydrophobic Alkyl Chain and Micelle Formation Induced by Complexation with Methylviologen

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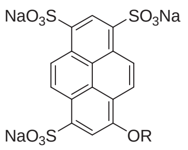
Amphiphilic pyranines POC*n* ($n = 8$, 12, and 16) were synthesized, and their aggregation behaviors were investigated in water. ^{1}H NMR studies implied that POC16 existed in the conformation of the pyranine chromophore wrapped with a hexadecyl methylene chain, which showed no indication of aggregation at the concentration up to 10^{-4} M. However, the formation of micelles was readily induced by the addition of methylviologen (MV^{2+}) to a POC16 solution, which was responsible for an apparent large complexation constant of ca. 10^6 M^{-1}.

Supramolecular assembly systems composed of molecules having chromophores have attracted much attention in recent years from the viewpoint of mimicking natural light-harvesting complexes.[1] Membranes and micelles formed through a hydrophobic interaction of amphiphiles in water are one of the most fascinating systems for the aggregation of chromophores. In the course of our studies on the artificial photosynthesis employing pyrenes as chromophores,[2] we have investigated the aggregation behaviors of amphiphilic pyrenes in water and their usefulness for artificial light-harvesting systems. One of the molecular designs for amphiphilic pyrenes is an introduction of a hydrophobic alkyl group into a water-soluble pyrene derivative such as trisodium 8-hydroxypyrene-1,3,6-trisulfonate (pyranine, POH). In this paper, we report the aggregation behaviors of pyranines attached to a long alkyl chain in water, where a unique structure of these amphiphiles in dilute solutions, as well as a novel complexation-induced micelle formation, is demonstrated.

Three amphiphilic pyranines,[3] in which an acidic hydrogen of POH was replaced by octyl, dodecyl, and hexadecyl groups, were synthesized by the treatment of POH with corresponding bromides in the presence of *N*,*N*-diisopropylethylamine in methanol. They are referred to in this paper as POC*n* ($n = 8$, 12, and 16, respectively) (Chart 1).

All POC*n*'s were well soluble in water and practically exhibited the same UV–vis absorption and fluorescence spectra (λ_{ex} 350 nm) at the concentration up to 10^{-4} M. Thus, it is found that POC*n*'s show no indication of aggregation even in the molecule having a long alkyl chain ($n = 16$) and at 10^{-4} M concentration. However, the fluorescence maximum of POC16 was shifted from 433 to 445 nm at the concentration going from 1.2×10^{-4} to 1.4×10^{-3} M, indicating a sign of aggregation of the chromophores. In the fluorescence spectrum of an aqueous POC16 solution (1.8×10^{-2} M) prepared by sonication in the presence of Nile Red, the fluorescence due to Nile Red appeared at 644 nm on the excitation of 520 nm. This observation suggests that POC16 molecules aggregate in water with a critical micelle concentration (CMC) of 10^{-2} M to form a hydrophobic domain in which the hydrophobic dye is incorporated. Judging from the maximal wavelength of Nile Red emission, the hydrophobicity of the aggregate interior is comparable to that of the micelles composed of sodium dodecyl sulfate.[4]



R = $(CH_2)_7CH_3$; POC8
R = $(CH_2)_{11}CH_3$; POC12
R = $(CH_2)_{15}CH_3$; POC16

Chart 1.

The information as to a structure of POC*n*'s in dilute aqueous solutions is obtained by NMR studies. The ^{1}H NMR spectra of all POC*n*'s recorded in D_2O at 1.0×10^{-3} M concentration showed sharp signals, indicating the absence of large intermolecular interaction among POC*n* molecules. In the ^{1}H NMR spectrum of POC16, it should be pointed out that the multiplet signals having the intensity of eight protons appeared at higher chemical shift values than the triplet signal assigned to a terminal methyl group (δ 0.51 ppm) (Figure 1). Although a detailed assignment of these signals could not be achieved even by the aid of ^{1}H–^{1}H COSY spectrum, the methylene protons connected to the carbons from the 10 to 14 position of the 1-hexadecyl group of POC16 could be responsible for the multiplet signals. The extremely upfield shift of the methylene signals is interpreted by considering the ring current effect of the pyranine ring. Thus, it is proposed that POC16 exists in the conformation of the pyranine nucleus wrapped with a hexadecyl methylene chain, in which the methylene protons near a terminal methyl group are located in the shielding zone of the pyranine ring (Figure 1). This compact structure reduces the surface area of POC16 molecule to minimize an unfavorable interaction with water.

It is known that the fluorescence of POH is effectively quenched with methylviologen (MV^{2+}) in water by the forma-

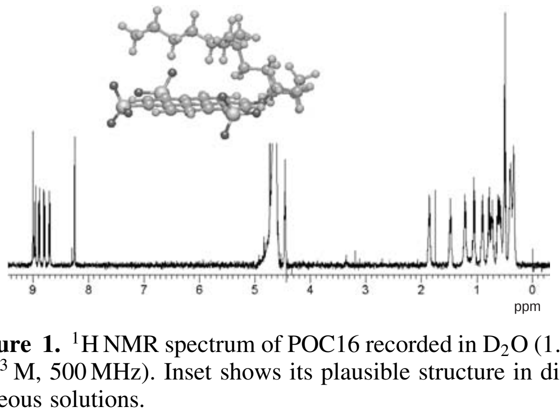


Figure 1. ^{1}H NMR spectrum of POC16 recorded in D_2O (1.0×10^{-3} M, 500 MHz). Inset shows its plausible structure in dilute aqueous solutions.

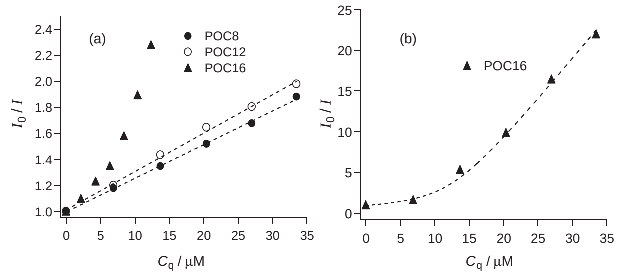


Figure 2. (a) Stern–Volmer plots for the fluorescence quenching of POC*n* by MV^{2+} in water. (b) Stern–Volmer plot for POC16 at MV^{2+} concentration up to 35 µM and the curve fitted to the experimental data according to eq 1.

tion of an electrostatic complex.[5,6] Thus, the effect of a hydrophobic alkyl chain on the POH/MV^{2+} complexation was examined next. An addition of $MV{\bullet}Cl_2$ to an aqueous solution of POC*n* (1×10^{-5} M) caused a decrease in the intensity of the fluorescence of POC*n*. As shown in Figure 2a, Stern–Volmer treatment of the quenching data for POC8 and POC12 resulted in a regular linear relationship between I_0/I and total concentration of MV^{2+} added in the solution (C_q) to afford quenching constants (K_q) of 2.6×10^4 and $2.9 \times 10^4\,M^{-1}$, respectively. The intensity of the absorption of POC*n* also decreased by the addition of MV^{2+}. The Benesi–Hildebrand analyses[5] of the absorption suppression data gave linear plots, indicating the formation of the complex having a 1:1 stoichiometry [POC*n*•MV^{2+}]. The calculated complexation constants (K_s) of 2.5×10^4 and $3.4 \times 10^4\,M^{-1}$ for POC8 and POC12, respectively, were in fair agreement with the K_q values, suggesting that the fluorescence quenching occurs by a static mechanism. These K_s values for the formation of [POC*n*•MV^{2+}] are in consistent with that reported for the complexation of POH with MV^{2+} in acidic media.[5]

Surprisingly, the fluorescence quenching of POC16 by MV^{2+} occurred much more effectively compared with that of POC8 and POC12. Moreover, the Stern–Volmer plot gave a curve deviating extremely upward from a straight line (Figure 2). An apparent K_q for the fluorescence quenching of POC16 was estimated to be $9.8 \times 10^5\,M^{-1}$. A clue to understanding the observed dramatic dependence of K_q on the length of the alkyl chain attached to the pyranine nucleus was obtained by ^{1}H NMR and dynamic light scattering (DLS) studies. In the ^{1}H NMR spectra of a 1:1 mixture of POC*n* (*n* = 8 and 12) and $MV{\bullet}Cl_2$ in D_2O at 1.0×10^{-4} M concentration, all signals were observed but slightly broadened, and the chemical shifts of pyranine and MV^{2+} aromatic protons were upfield shifted compared with those recorded in an independent solution of POC*n* and $MV{\bullet}Cl_2$ in D_2O. On the other hand, no signals assigned to the POC16 and MV^{2+} protons were detected in the ^{1}H NMR spectrum of a 1:1 mixture of POC16 and MV^{2+} owing to the extreme broadening of signals. This observation suggests that the motions of POC16 and MV^{2+} molecules are enormously restricted by the formation of aggregates of the complex [POC16•MV^{2+}]. This assumption was confirmed by the DLS studies, which revealed the formation of micelle-size particles with hydrodynamic diameters of ca. 5.5 nm in an aqueous solution of a 1:1 mixture of POC16 and MV^{2+} at 1.0×10^{-3} M concentration.

Thus, we propose the following scenario for the observed effective fluorescence quenching of POC16 by MV^{2+}: upon addition of MV^{2+} to a solution of POC16, π-stacking and electrostatic interactions cause the complexation to form [POC16•MV^{2+}]. In the complex, a long hexadecyl chain is unwrapped from the pyranine nucleus, and an electrostatic repulsion of a polar head group is considerably reduced compared with POC16. Thus, a hydrophobic interaction among long alkyl chains of the complex [POC16•MV^{2+}] operates to induce the aggregate formation, which shifts the equilibrium to the direction of the complexation of POC16 with MV^{2+}.

$$\mathrm{POC16} + \mathrm{MV}^{2+} \overset{K_s}{\rightleftharpoons} [\mathrm{POC16{\bullet}MV}^{2+}] \rightarrow [\mathrm{POC16{\bullet}MV}^{2+}]\mathrm{micelle} \qquad (1)$$

Assuming that only POC16 molecules free from the complexation fluoresce and the concentration of free complex [POC16•MV^{2+}] is kept constant at CMC (S_c), the relationship between I_0/I, which is equal to S_0/S (S_0 and S stand for the concentrations of POC16 free from the complexation in the absence and presence of MV^{2+}, respectively; $S_0 = 1.23 \times 10^{-5}$ M), and a total MV^{2+} concentration (C_q) is given by eq 2, where K_s represents a complexation constant for [POC16•MV^{2+}].

$$\frac{I_0}{I} = \frac{S_0}{2}\frac{K_s}{S_c}\left(C_q - S_0 + \sqrt{(C_q - S_0)^2 + \frac{4S_c}{K_s}}\right) \qquad (2)$$

The nonlinear least-squares analysis revealed that the Stern–Volmer plot for POC16 was reproduced by eq 2 with $K_s/S_c = 8.4 \times 10^{10}\,M^{-2}$, as shown with a broken line in Figure 2b. It is reasonable to think that the K_s value of POC16 is comparable with that of POC*n* (*n* = 8 and 12), because an electronic property of the pyranine chromophore of POC16 seems to be identical with that of other POC*n*'s. Thus, by assuming $K_s = 3.0 \times 10^4\,M^{-1}$, CMC of the complex [POC16•MV^{2+}] (S_c) is estimated to be 3.6×10^{-7} M.

In conclusion, we demonstrated that although CMC of POC16 in water was not more than 10^{-2} M, the formation of micelles was readily induced by the addition of MV^{2+}. It is likely that the conformational change of a long hexadecyl chain and the reduction of electrostatic repulsion caused by the complexation are responsible for the facile micellization of the complex [POC16•MV^{2+}]. It is expected that in the micelles the charge separation state [$POC16^{+\bullet}{\bullet}MV^{+\bullet}$] formed by a photoinduced electron transfer from POC16 to MV^{2+} would have a long lifetime owing to charge delocalization. Studies are in progress to elucidate photophysical and photochemical properties of the micelles consisting of the complex [POC16•MV^{2+}], as well as the POC16 aggregates.

References and Notes

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