

論文内容の要旨

論文題目 A Study on Syntheses, Aggregation Behaviors, and Photochemical Properties
of Amphiphilic Pyrene Derivatives

両親媒性ピレン誘導体の合成、集合化挙動、および光化学的性質に関する研究

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In this dissertation, the author reports several novel results found out in the course of the investigations on artificial photosynthetic systems using molecular assembly composed of the amphiphilic compounds including pyrene derivatives: (i) possibility of dispersing hydrophobic compounds monomerically; (ii) facile micelle formation induced by charge-transfer interaction; (iii) a development of superior sensitizers for an electron transport system as a primitive model of the natural light-energy conversion systems. The abstract is described as follows.

(i) Possibility of dispersing hydrophobic compounds monomerically

To construct artificial light-harvesting systems, pyranine (**1**), a commercially available hydrophilic pyrene derivative absorbing longer wavelength UV light than pyrene due to π conjugation between substituents and a pyrenyl ring, was used as a chromophore. Four amphiphilic pyranines in which the acidic hydrogen of **1** was replaced by an octyl, dodecyl, hexadecyl, and eicosyl group, (**2**, **3**, **4**, and **5**, respectively), were prepared, and their spectroscopic properties and aggregation behaviors in water were investigated. The critical micelle concentration (CMC) of the amphiphilic pyranines was found to be relatively large even in **5** having a long hydrophobic alkyl chain (ca. 3×10^{-3} M). This observation was due to a large electrostatic repulsion derived from triple negative charges, and indicated that the amphiphilic pyranines were not suitable for an antenna system to harvest and transfer light energy in high efficiency disappointingly. However, ^1H NMR studies revealed interesting

phenomena that **4** and **5** exist in the compact structure with the pyranine nucleus wrapped with a long methylene chain in water (Figure 1). This observation implies a significant strategy in interface science: introduction of several charges with the same sign to a hydrophobic compound enables the compound to be dissolved monomerically in relatively high concentrations (\sim mM) which is necessary for the studies on the conformation of hydrophobic compounds in water.

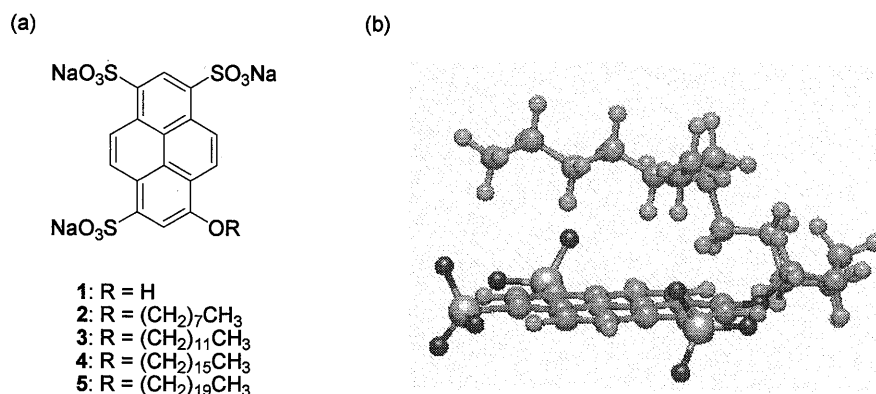
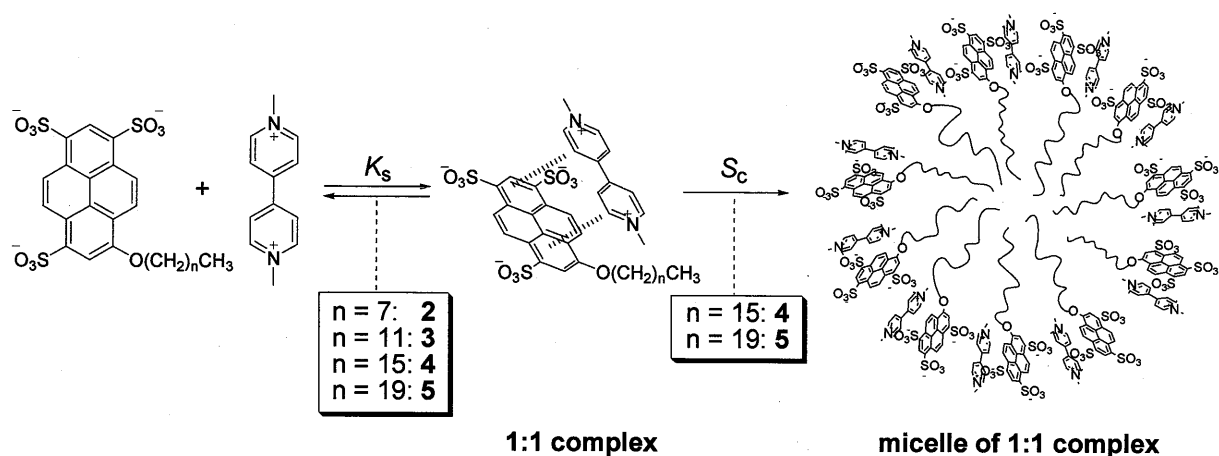


Figure 1. (a) Chemical structures of pyranine and its amphiphilic derivatives. (b) plausible conformation of **4** in water: the pyranine nucleus is wrapped with a long methylene chain.

(ii) Facile micelle formation induced by charge-transfer interaction

To evaluate the effect of introduction of a hydrophobic substituent on the charge-transfer interaction between pyranine (**1**) and methylviologen (MV^{2+}), photochemical properties such as UV-vis absorption and fluorescence were studied. As in the case of parent compound **1**, the addition of MV^{2+} to an aqueous solution of the amphiphilic pyranines **2-5** resulted in the absorption spectral change and efficient quenching of the pyranine's fluorescence. In the case of **2** and **3**, these spectral changes induced by the MV^{2+} addition were thoroughly explained in terms of the formation of the electrostatic complex **2**/ MV^{2+} or **3**/ MV^{2+} with a complexation constant of $\sim 3 \times 10^4 M^{-1}$. On the other hand, an unexpectedly large dependence of the absorption spectral change, as well as fluorescence quenching, on the total concentration of MV^{2+} was observed in **4** and **5**. The Stern-Volmer plot for quenching of the fluorescence of **4** and **5** gave a curve deviating largely upward from a straight line. The plot was successfully analyzed by the equation induced by assuming the aggregate formation of the complex **4**/ MV^{2+} or **5**/ MV^{2+} (Scheme 1 and Eq. 1), which revealed the considerably small CMCs of the complex; 3.6×10^{-7} and 3.6×10^{-8} M for **4**/ MV^{2+} and **5**/ MV^{2+} , respectively. Experimental evidence in support of the aggregate formation was obtained by 1H NMR and dynamic light scattering studies.



Scheme 1. Mechanism of the interaction between **2-5** and MV^{2+} : complexation between amphiphilic pyranines **2-5** and MV^{2+} , followed by micelle formation (**4**/ MV^{2+} and **5**/ MV^{2+}).

$$\frac{I_0}{I} = \frac{S_0}{2} \cdot \frac{K_s}{S_c} \left(C_q - S_0 + \sqrt{(C_q - S_0)^2 + \frac{4S_c}{K_s}} \right) \quad (1)$$

I_0 : fluorescence intensity in the absence of quencher (MV^{2+})

I : fluorescence intensity in the presence of quencher (MV^{2+})

S_0 : the initial concentration of the derivative (**4** or **5**)

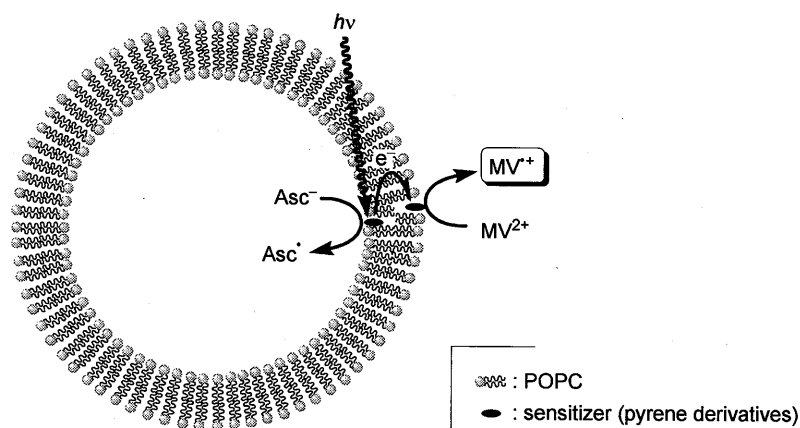
K_s : the complexation constant between the derivative (**4** or **5**) and MV^{2+}

S_c : the CMC of one-to-one complex (**4**/ MV^{2+} or **5**/ MV^{2+})

C_q : the total concentration of quencher (MV^{2+})

(iii) A development of superior sensitizers for an electron transport system as a primitive model of the natural light-energy conversion systems

Endoergic electron transport across vesicle bilayers from ascorbate (Asc^-) in the inner waterpool to MV^{2+} in the outer aqueous solution was driven by the irradiation of pyrene derivatives embedded in the vesicle bilayers (Figure 2). To develop utility sensitizers for the photoinduced electron transport reaction as a primitive model of the natural light-energy conversion system, the amphiphilic 1-pyrenecarboxylic acids **6-8** were newly designed and synthesized (Figure 3). All these derivatives had a high fluorescence quantum yield. It was disappointing that **6-8** were not suitable for light-harvesting systems in water because they showed extremely low solubility and dispersibility in water. It was revealed, however, that **6-8** could be excellent sensitizers for the photoinduced electron transport reaction by analyzing their photochemical properties and membrane affinity compared with those of $PyCH_2OH$ used previously as a general sensitizer which afforded relatively good results in this system.



Total reaction

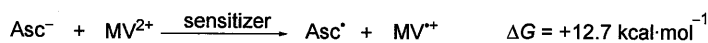
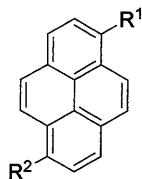


Figure 2. Schematic illustration of the photoinduced electron transport across vesicle bilayers using the amphiphilic pyrene derivative.



- 1-(hydroxymethyl)pyrene: $R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{H}$
- 1-pyrenecarboxylic acid: $R^1 = \text{COOH}$, $R^2 = \text{H}$
- 6**: $R^1 = \text{COOH}$, $R^2 = \text{C}\equiv\text{C}(\text{CH}_2)_5\text{CH}_3$
- 7**: $R^1 = \text{COOH}$, $R^2 = (\text{CH}_2)_7\text{CH}_3$
- 8**: $R^1 = \text{COOH}$, $R^2 = (\text{CH}_2)\text{CHO}(\text{CH}_2)_{11}\text{CH}_3$
 $\text{CH}_2\text{O}(\text{CH}_2)_{11}\text{CH}_3$

Ability of sensitizer

- (i) efficiency of the electron transport: **6, 7, 8** > PyCH_2OH
- (ii) membrane affinity: **6, 7, 8** \geq PyCH_2OH

Figure 3. Chemical structures of PyCH_2OH , PyCOOH and **6-8**, and the qualitative comparison of the results of **6-8** with those of PyCH_2OH as a sensitizer for the photoinduced electron transport across vesicle bilayers.