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Novel Fluorescent Probe Based on Anthryl Dendron Having Oligo(ethyleneoxide) Groups at the Terminals

Yutaka Takaguchi,* Yasushi Yanagimoto

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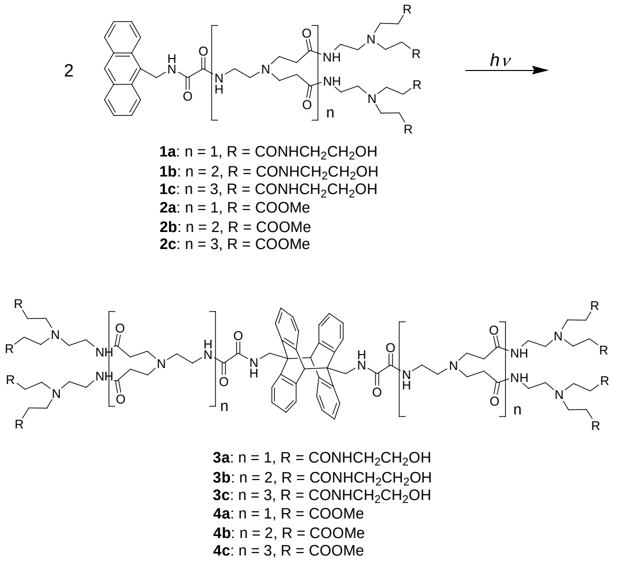
Amphiphilic anthryl dendrons **5** and **6**, which have carboxylate groups or oligo(ethyleneoxide) groups at the terminals, show solvatochromic properties. Reaction efficiency of photodimerization and dynamic light scattering (DLS) experiment of **5** and **6** reveal that formation of the aggregate of dendrons **5** or **6** plays a crucial role in this solvatochromism. Interestingly, solvatochromic property of anthryl dendron **6** was useful for determination of the ratio of methanol/water in solution as a fluorescent probe.

Key words: *dendrimer, anthracene, fluorescence, solvatochromism, water, methanol*

1 INTRODUCTION

Fluorescent organic molecules exhibit a high potential as sensor for organic and inorganic analytes and as probes and markers in biological or supramolecular systems (Desvergne et al., 1997 and De Silva et al., 1997). Among the most frequently used fluorophores in this area are anthracene derivatives, because they exhibit good emission properties with moderate to high quantum yields (Ishikawa et al., 1999, Wang et al., 1999, Ballardini et al., 1998, Hashimoto et al., 1997, Daub et al., 1996 and Vollmer et al., 1998). Meanwhile, dendrimers have received considerable attention during the past three decades due to both interesting structural properties and promising applications (Dendrimers and Other Dendritic Polymers, 2001, Dendrimers, 1998 and Dendrimers II-IV, 2000, 2001a and 2001b). In particular, the introduction of fluorophores into the dendritic macromolecules has been provided opportunities for creating new functional materials. Recently, we reported the first example of intermolecular photodimerization of a dendritic molecule having anthracene moiety at the focal point (Takaguchi et al., 2000 and 2002). Furthermore, we have found that self-organization and/or aggregate formation affect the reaction efficiency of [4+4] photocycloaddition of the



1a: n = 1, R = $CONHCH_2CH_2OH$
1b: n = 2, R = $CONHCH_2CH_2OH$
1c: n = 3, R = $CONHCH_2CH_2OH$
2a: n = 1, R = COOMe
2b: n = 2, R = COOMe
2c: n = 3, R = COOMe

3a: n = 1, R = $CONHCH_2CH_2OH$
3b: n = 2, R = $CONHCH_2CH_2OH$
3c: n = 3, R = $CONHCH_2CH_2OH$
4a: n = 1, R = COOMe
4b: n = 2, R = COOMe
4c: n = 3, R = COOMe

Scheme 1. Photodimerization of anthryl dendron **1** and **2**.

Table 1. Yields of photodimerization reactions in MeOH after 1 h.

Entry	compound	product	conversion (%)
1	**1a**	**3a**	100
2	**1b**	**3b**	100
3	**1c**	**3c**	100
4	**2a**	**4a**	76
5	**2b**	**4b**	68
6	**2c**	**4c**	51

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*Department of Material and Energy Science, Graduate School of Environmental Science, Okayama University.

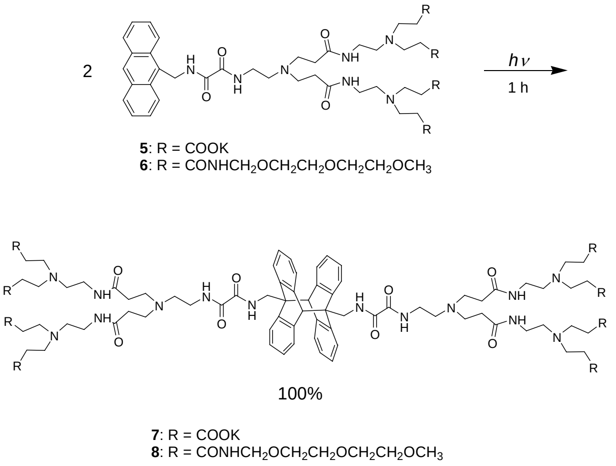
anthryl groups (Yanagimoto et al., 2006a-c, and Takaguchi et al., 2003). Interestingly, anthryl dendrons **1a-c** having hydroxyl groups at the terminals, show higher efficiency of the photodimerization reaction in methanol than the anthryl dendrons **2a-c** having methyl ester groups at the terminals because of the aggregate formation of dendrons **1a-c** in methanol as shown in Scheme 1 and Table 1 (Takaguchi, 2007). During our studies on the photochemistry of anthryl dendrons, we found that fluorescent intensity of the anthryl dendron largely depend on solvent polarity.

This paper describes the solvatochromic property of amphiphilic anthryl dendron, which has oligo(ethyleneoxide) groups or carboxylate groups at the terminals. Furthermore, application to the fluorescence probe for determination of the ratio of methanol/water in solution was described.

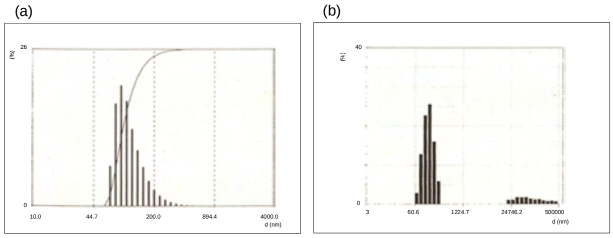
2 RESULTS AND DISCUSSION

The amphiphilic dendrons **5** and **6** were synthesized according to the previously reported method (Yanagimoto et al., 2006a and Hirano et al., 2005). In order to clarify the photoreactivity of anthracene moieties, the dendrons **5** and **6** in water were irradiated with a high-pressure mercury lamp (λ > 300 nm) for 1 h at room temperature. The [4+4] photodimerizations of anthracene moiety quantitatively proceeded to afford photodimers **7** and **8** (Scheme 2). This high reaction efficiency might arise from aggregates formation in the solution of **5** or **6**. The structures of photodimers **7** and **8** were confirmed by the ^{1}H NMR spectroscopies.

In order to check the aggregate formation, aqueous solutions of the dendrons **5** and **6** were investigated by the use of dynamic light scattering (DLS). Several solutions showed aggregates, of which average particle diameters were around one hundred nanometers as shown in Figure 1.



Scheme 2. Photodimerization of anthryl dendron **5** and **6**.



average particle diameter 114 nm

average particle diameter 133 nm

Figure 1. Size distribution of the aggregates of (a) dendron **5** and (b) dendron **6**, measured by DLS.

Since self-quenching effect of the aggregate of anthryl dendron should affect fluorescence properties of dendrons **5** and **6**, fluorescence spectra of **5** and **6** were observed. All solutions prepared were 1.0 mM and were measured by means of the fluorescent spectrometer upon excitation at 370 nm under the room temperature. Figure 2(a) shows emission fluorescence spectra of dendron **5** in methanol and water. In case of the water solution, fluorescence was not detected although, in case of the methanol solution, specific fluorescence of anthracene with an emission maximum at 413 nm was observed. This result indicated that self-quenching of fluorescence of the anthryl dendron, which might be cause of its aggregation promoted by the hydrophobic anthracene moiety, occurred in water. Furthermore, fluorescence spectra of the dendron **6** that can dissolve in water or conventional organic solvent were examined in water, methanol, and chloroform as show in Figure 2(b). The spectra in methanol and chloroform showed the emission attributed to the fluorescence of anthracene moiety. However, in case of the water solution, its

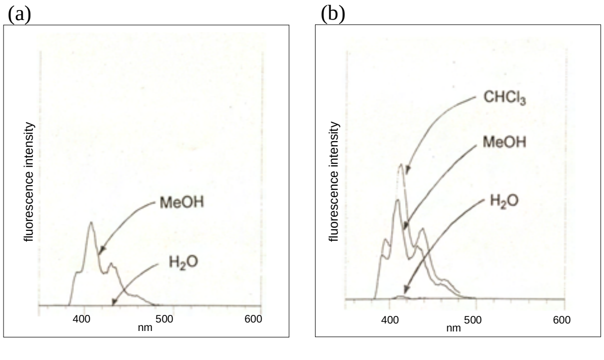


Figure 2. Fluorescence spectra of (a) dendron **5** and (b) dendron **6**, upon excitation at 370 nm.

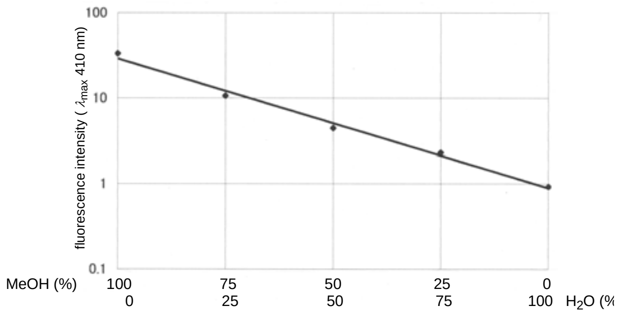


Figure 3. Fluorescence intensity at emission λ_{max} = 410 nm of **6** in methanol, water, and mixtures of these two solvents.

intensity is very low due to the self-quenching for the same reason. In comparison with the chloroform solution, the methanol solution showed rather weak fluorescence. These results imply that the self-quenching caused by its aggregation in solution might be well affected by polarity of the environment.

Interestingly, we found that the solvatochromic property of anthryl dendron **6** was useful for determination of the ratio of methanol/water in solution as the fluorescence probe. Figure 3 shows intensities of fluorescence at 410 nm of **6** in methanol, water, and mixtures of these two solvents at different compositions. As expected, when the increases of the amount of water in the mixture, intensities of the fluorescence was decreased. Interestingly, when a logarithmic scale was applied for the intensity as vertical axis, a linear relationship appears to exist between the intensity and ratio of the two solvents. Although the reason of this linear relationship is still not clear, this phenomena is useful for determination of the amount of water contaminating in methanol.

3 CONCLUSION

In this paper, we described that the high reaction efficiency of the amphiphilic anthryl dendrons **5** and **6** arisen from their self-organizations induced by hydrophobic interactions of anthracene moiety. Self-quenching effect of fluorescence spectra and DLS experiment revealed the aggregates formation in water and/or methanol. Furthermore, we found that the solvatochromic property of anthryl dendron **6** was useful for determination of the ratio of methanol/water solution as the fluorescence probe. To our knowledge, this is the first example of a fluorescence probe for determination of the ratio of water to methanol.

4 EXPERIMENTAL

UV/vis spectra (λ_{max} in nm (ε)) were measured on a HITACH U-3210 spectrophotometer. Fluorescent spectra was measured on a SIMADZU RF-500 spectrophotometer. Dynamic Light Scattering (DLS) were measured on a Photal DLS-7000. Photoirradiation was carried out in a Pyrex reactor. A 500 W high-pressure mercury lamp was used as the light source.

The reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., Kanto Kagaku Co., Ltd., or Aldrich Chemical Co. All chemicals were used as received without further purification. Ion-exchange water was used throughout the experiment.

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