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# New Fluorescence from Molecular Aggregates of 10-(1-Pyrenyl)decanoic Acid

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In addition to the normal monomer and excimer fluorescence, vacuum-deposited, cast and their laser-irradiated films of 10-(1-pyrenyl)decanoic acid showed three kinds of fluorescence bands. Similar new fluorescence bands were also observed in its aqueous solution. These emissions were due to meta-stable aggregates of pyrenyl chromophores whose structures were ascribed to molecular interactions operating during the processes of film preparation.

Pyrene is the most representative conjugated hydrocarbon which forms excimer in concentrated solutions and molecular assemblies such as micelles and liposomes. Recently, we found that vacuum-deposited films of ω-(1-pyrenyl)alkanoic acid did not show an excimer emission as a main component at any delay times.1,2) Instead, we observed new fluorescence spectra: a band around 420 nm and a structured fluorescence band in the same wavelength region as that of excimer. The former looks like the bands observed for liquid pyrene at high temperature3) and for Langmuir-Blodgett film,4) while the latter structured emission has never been reported in the long history of pyrene excimer. In the present work, we demonstrate a variety of fluorescence spectrum of 10-(1-pyrenyl)decanoic acid by changing experimental conditions.

10-(1-Pyrenyl)decanoic acid was prepared by Friedel-Craft reaction of pyrene with sebacic acid monoethyl ester followed by Wolf-Kischner reduction. The crude product was purified by silica gel column chromatography (hexane-chloroform) and recrystallization from hexane-chloroform mixture (mp 111 °C).

A preparation method of vacuum-deposited film was the same as mentioned before.1,2) A cast film was prepared by evacuating the solvent from benzene solution in a few minutes. Both films were transparent and stable at room temperature. An effect of laser irradiation upon fluorescence spectra of films was investigated by using a Lumonix TE 430T-2 excimer laser (308 nm, 6 ns). Excitation intensity was adjusted to be $3 \times 10^{18}$ photons·cm$^{-2}$·pulse$^{-1}$.

Fluorescence spectrum of the deposited film consists of a monomer fluorescence, a band at 420 nm and a band with peaks around 450, 480,and 520 nm. On the other band, the cast film gave a monomer fluorescence, the band with shoulders at 440 and 470 nm and a descending long tail up to 550 nm (see the spectra before irradiation in Figs. 2 and 3). This result is identical with the result on 12-(1-pyrenyl)dodecanoic acid.[1,2] Their excitation spectra monitored at different fluorescence bands were broad and similar to the absorption spectra below 400 nm,[1,2] as shown in Fig. 1. A large difference between these films is that an additional excitation band at 420 nm was detected only for the deposited film when monitored beyond 440 nm. This indicates that the structured emission is due to an aggregate formed only in the deposited film.

The vacuum-deposited film was irradiated by an excimer laser, which resulted in an interesting behavior summarized in Fig. 2. Fluorescence intensity was reduced of a few shots of irradiation laser, and further irradiation leads to an increase of a new structured emission and a disappearance of the 420 nm band. The former is similar to the original one, but blue-shifted. In the later stages of irradiation all emissions lost their intensity, while their relative rate is different from each other.

A laser-induced fluorescence spectral change was also observed for the cast film, which is given in Fig. 3. At first, monomer fluorescence was weakened and a broad emission with a maximum at 470 nm was enhanced. This change was observed only by a few shots of laser pulse. This emission is identified as an excimer since its spectral shape and the maximum wavelength were similar to the characteristics of typical pyrene excimer. Increasing the shot number, both monomer and excimer emissions were decreased, while no further spectral change was observed. During laser irradiation, no absorption spectral change was detected.

Fluorescence spectra of the present molecule in aqueous solution are shown in Fig. 4. Although this molecule does not dissolve in water at lower pH, while its solubility increases at higher pH. Actually, fluorescence and excitation spectra at pH 9 are very close to those of 1-substituted pyrene in organic solvents. At pH 7, a structured fluorescence with peaks at 460 and 490 nm and the 420 nm band was observed in addition to the monomer fluorescence. In accordance with this spectral change, excitation spectra became broad, and some bands were measured beyond 400 nm, as reported in Fig. 1 (A). This means that an association of pyrenyl chromophores is induced in water. A further decrease of pH resulted in the blue-shifted emission with peaks 420 and 435 nm.

It was confirmed that the present molecule gives some new fluorescence bands together with monomer and excimer emissions, depending on the experimental conditions. The structured band in the longer wavelength region is a quite new emission and has never been observed for any kinds of pyrene aggregates and for dipyrenyl model compounds.[5,6] It is worth noting that the structured emission was obtained not only in the deposited film but also in the aqueous solution. This result denies completely a possibility that the structured emission in deposited films is due to impurity formed during sublimation process. Furthermore, it is surprising that the structured emission is modified and the 420 mn band changes to an excimer-like band by an irradiation with an excimer laser. This behavior indicates that the present new fluorescence bands are due to meta-stable species.

We consider that a long chain of aliphatic acid of 10-(1-pyrenyl)decanoic acid plays an important role in forming meta-stable aggregation structures. In the case

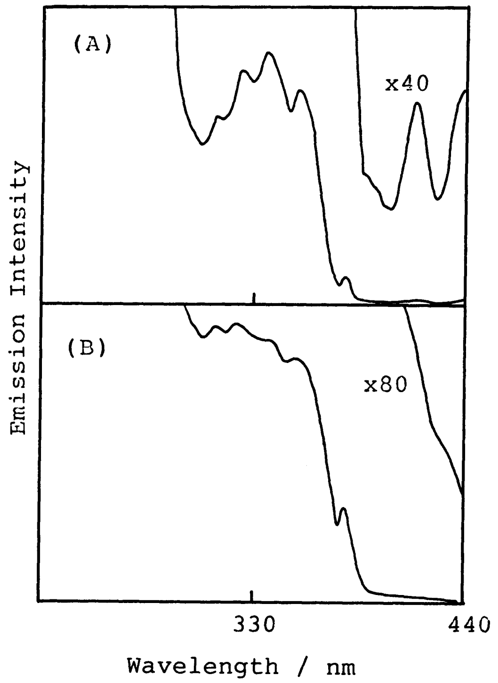

Fig. 1. (A) Excitation spectra of a deposited film of 10-(1-pyrenyl)-decanoic acid monitored at 480 nm. (B) Excitation spectra of a cast film of 10-(1-pyrenyl)decanoic acid monitored at 480 nm.

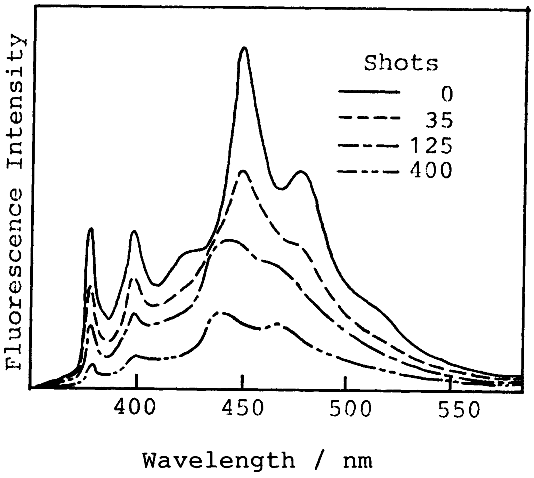

Fig. 2. Fluorescence spectral change of a vacuum-deposited film of 10-(1-pyrenyl)decanoic acid, induced by an excimer laser irradiation. The shot number of irradiation pulse is given in the figure.

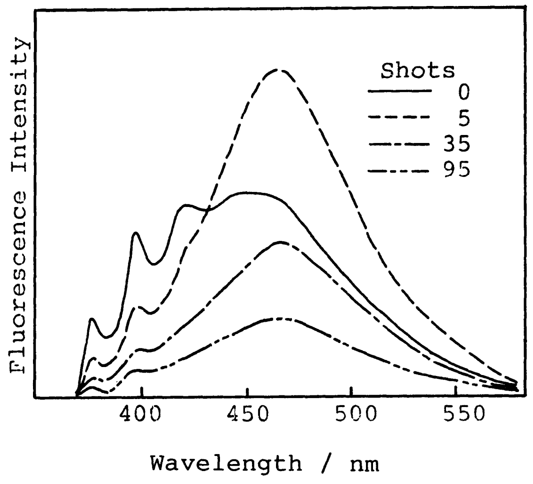

Fig. 3. Fluorescence spectral change of a cast film of 10-(1-pyrenyl)-decanoic acid, induced by an excimer laser irradiation. The shot number of irradiation pulse is given in the figure.

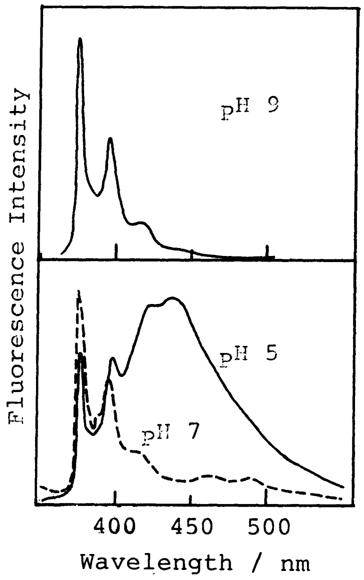

Fig. 4. Fluorescence spectra of $1\times10^{-6}$ mol $dm^{-3}$ aqueous solution of 10-(1-pyrenyl)decanoic acid. The pH value is given in the figure.

of the cast film, an intermolecular interaction in concentrated benzene solution may be responsible for the structure formation, while hydrophobic interaction should have an important role in aqueous solutions. On the other hand, a successive intermolecular interaction in the slow deposition processes and an interaction with a quartz plate may form a unique structure of deposited film. All these structures are considered to be meta-stable which can be changed by laser irradiation. Molecular aspects of aggregates considered and their structural change will be elucidated shortly.

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