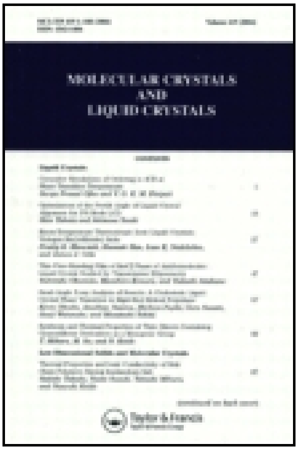

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Simulation of Energy Transfer in Photosynthetic Antenna Systems with Monolayer Assemblies

Masamichi Fujihira [a] , Masaru Sakomura [b] & Ryuji Sawada [a]

[a] Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama, 226-8501, Japan

[b] Department of Physical Chemistry, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan

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Simulation of Energy Transfer in Photosynthetic Antenna Systems with Monolayer Assemblies

MASAMICHI FUJIHIRA[a], MASARU SAKOMURA[b] and RYUJI SAWADA[a]
[a]Department of Biomolecular Engineering, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8501, Japan
[b]Department of Physical Chemistry, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

To optimize the energy transfer (ET) from a mixture of 10-(1-(8-hexyl)pyrenyl)-decanoic acid, 10-(1-(6-hexyl)-pyrenyl)decanoic acid, and 10-(1-(3-hexyl)-pyrenyl)decanoic acid (HPyDA) to a mixture of 10-(3-(9-hexyl)perylenyl)-10-oxodecanoic acid and 10-(3-(10-hexyl)perylenyl)-10-oxodecanoic acid (HPeDA) in HPyDA-HPeDA mixed monolayer assemblies, fluorescence spectra of the mixed monolayers containing various compositions of HPyDA and HPeDA were measured. Efficient ET was observed in the mixed monolayers of HPeDA:HPyDA molar ratios of 1:3 - 1:300.

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Keywords: energy transfer; monolayer assemblies; artificial photosynthesis

INTRODUCTION

We have simulated the light harvesting and the succeeding charge separation in the primary process in natural photosynthesis[1] using a monomolecular layer assembly consisting of synthetic antenna pigments and A-S-D triad molecules.[2-5] As the light-harvesting antenna, an amphiphilic pyrene derivative HPyDA (a mixture of three kinds of regioisomers, 10-(1-(8-hexyl)pyrenyl)decanoic acid, 10-(1-(6-hexyl)-pyrenyl)decanoic acid, and 10-(1-(3-hexyl)pyrenyl)-decanoic acid (Figure 1(c)) has been used, whereas the amphiphilic A-S-D triad molecule containing an acylated perylene moiety as the sensitizer (S) unit as well as a viologen and a ferrocene moiety as the electron acceptor (A) and the donor (D) unit, respectively (Figure 1(a)). To assemble these amphiphilic molecules with unidirectional orientation in the mixed monolayer, the Langmuir-Blodgett (LB) technique has been employed.[5] The fluorescence band of the antenna pyrene (Py)[6-12] overlapped with the UV absorption band of the acylated perylene moiety (Pe)[4] of A-S-D. Hence the efficient energy transfer (ET) from photo-

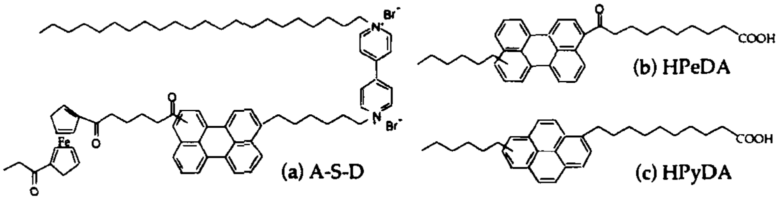

FIGURE 1 Structural formulae of amphiphilic compounds discussed in this work.

excited Py* to Pe was expected to result.[4,7,13-15] In fact, the charge separation in the A-S-D triad was observed by illumination with light whose wavelengths were in the absorption bands of Py as well as in that of Pe in A-S-D.[4]

In this work,we studied ET from the Py to the Pe moiety in their mixed monolayers. To focus only on the ET process and to avoid complication due to the succeeding charge separation process, a compound having only the S unit, i.e. a mixture of two regioisomers 10-(3-(9-hexyl)perylenyl)-10-oxodecanoic acid and 10-(3-(10-hexyl)perylenyl)-10-oxodecanoic acid (HPeDA, Figure 1(b)), was used as a substitute of A-S-D.

EXPERIMENTAL

HPyDA and HPeDA were synthesized in our laboratory.[16] The aqueous polyallylamine (PAA) solution was received by the courtesy of Nitto Boseki, Tokyo. All other chemicals were G.R.-grade and used as received.

The monolayer LB films were formed with a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku, HBM-AP). SiO_2 substrates (micro slide glass; Matsunami Grass Ind.) were treated by chromic acid mixture. The subphase was pure water from a Mill-Q system (Millipore Ltd.) containing 0.04 mM PAA and 0.5 mM $NaHCO_3$. The temperature of the subphase was always maintained at 15°C. The monolayer was obtained by spreading a chloroform solution containing HPyDA and HPeDA. The compression speed of the monolayer was 14 cm^2 min^{-1}. The polyion-complexed monolayers were transferred to this oxidized SiO_2 substrates. The lifting speed was 2.5 mm min^{-1} and the surface pressure for deposition was 7.5 mN m^{-1}.

UV-visible absorption spectra were recorded with a Hitachi 220 A spectrometer with wavelength resolution of 2 nm. The scan speed was 60 nm min^{-1}. Absorption spectra were recorded at room temperature in air with an incident angle of 0 or 45°. The absorption spectra of the monolayers with an incident angle of 45° were recorded as follows. The UV cells were filled with pure water from Mill-Q system. A monolayer sample on the substrate was set catercornered in a cell with a square cross section. A cell for reference was filled with pure water and a substrate without LB film was set in the cell. The reflection of the incident light was reduced by filling the cell with water.

UV-visible fluorescence and excitation spectra were recorded with a Hitachi F-3000 fluorescence spectrophotometer with 5 nm wavelength resolution for excitation and emission. The spectra were recorded at room temperature under a N_2 atmosphere. To minimize photo-oxidation of HPyDA,[12,17,18] the scan speed was 240 nm min^{-1}. The response time was 0.5 s. In the present spectrophotometer, correction of the fluorescence intensity in a wavelength region longer than 600 nm could not be made. Thus, all fluorescence spectra shown in this work were recorded without correction. To enhance the absorption of aromatic hydrocarbon moieties in the monolayers, the incident angle was increased further to ca. 60° using a sample holder for emission spectra.

RESULTS AND DISCUSSION

Absorption and Fluorescence Spectra of HPeDA and HPyDA in Ethanol

In Figure 2, the UV and visible absorption (solid lines) and fluorescence spectra (dotted lines) of the HPyDA and HPeDA in ethanol (10 μM for monomer emission) are shown. The absorption band for the lowest excited state of Pe appeared in the wavelength region of 400 - 500 nm, whereas the corresponding fluorescence band of the HPyDA appeared at 370 - 450 nm. The partial overlap

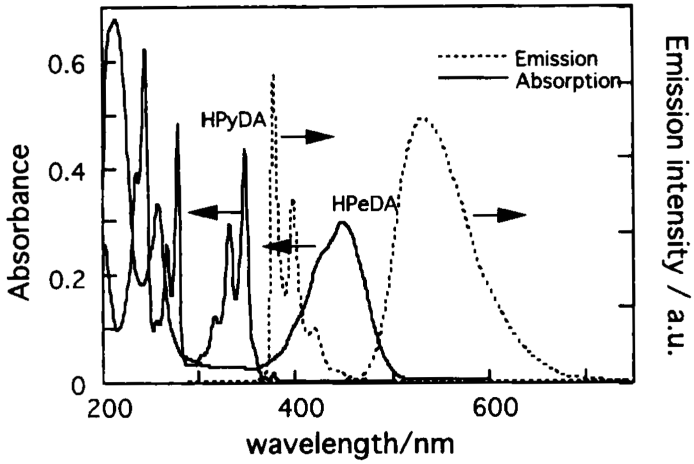

FIGURE 2 Absorption and emission spectra of HPyDA and HPeDA in ethanol.

of these bands indicates that excitation energies for Py at 300 - 380 nm, where very little absorption was observed for Pe, are transferred to Pe.

Spectra of HPeDA and HPyDA in Monolayer Assemblies

UV and visible absorption spectra of the pure HPeDA monolayer and that of HPyDA were measured (data not shown). With the 0° incident light, HPeDA exhibited the absorption bands with peaks at 205, 260 and 450 nm. With the 45° incident light, the absorption bands with peaks at 205 and 260 nm increased a little at the expense of the absorption band with a broad peak at ca. 450 nm. With the 0° incident light, HPyDA exhibited the strong absorption band at 285 nm, two broad bands at ca. 230 and 340 nm, and a sharp peak at 385 nm.[9] With the 45° incident light, absorption of the two broad band increased at the expense of the absorption peaks at 285 and 385 nm.

Fluorescence and Excitation Spectra of HPeDA and HPyDA Mixed Monolayers

In Figure 3, the emission spectra of mixed monolayers containing various molar ratios of HPeDA and HPyDA measured with an excitation wavelength of 335 nm are shown. Except for a 1:1 mixed monolayer, the intensity of emission at around 485 - 700 nm is stronger than those of the pure monolayers, while the emission intensities of the mixed monolayers are lower than that of the pure HPyDA at a shorter wavelength region than 485 nm. The latter wavelength region overlaps with the absorption band of HPeDA. Therefore, it can be said that the following process occurred in these mixed monolayers. First, incident light was absorbed by the Py moieties in HPyDA. Next, energy migration among the Py moieties could occur. The migrating excited energy of Py* would be transferred to the Pe moiety. Finally, the fluorescence emitted from the Pe* moiety. The observed emission spectra were superposition of the emission from

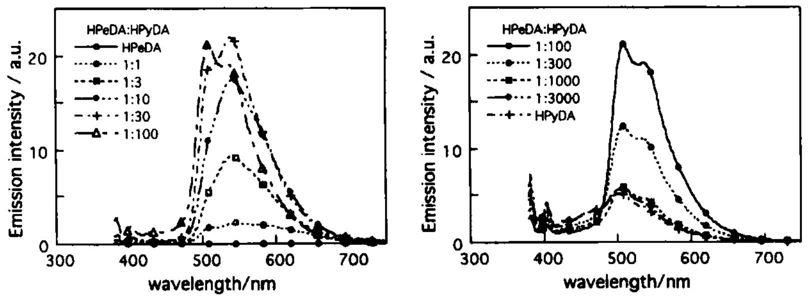

FIGURE 3 Observed emission spectra of the mixed monolayers containing various molar ratios of HPeDA to HPyDA excited at a wavelength of 335 nm.

Pe* and the emission from Py*. The intensity change as a function of the composition will be described in the next section.Excitation spectra of these mixed monolayers were measured (data not shown). The excitation spectra at an emission wavelength of 385 nm (monomer emission from HPyDA) were the same as the absorption spectrum of HPyDA, but the intensity of the spectra was negligible in the presence of sufficient HPeDA concentrations. Excitation spectra at emission wavelengths of 550 and 650 nm (emissions from HPeDA and aggregated HPyDA[7,8,17]) were also the same as the absorption spectrum of HPyDA except for the mixed monolayers with high concentrations of HPeDA. These results support the efficient ET from the HPyDA antenna molecules to the HPeDA energy acceptor.

Estimation of Optimized Molar Ratios between HPeDA and HPyDA for Effective ET

An emission peak wavelength of HPeDA in the monolayers was *ca.* 530 nm. But aggregated HPyDA in the monolayers also emitted at this wavelength.[7,8,17] Therefore, the emission from the aggregated HPyDA was subtracted to measure ET from HPyDA to HPeDA. Figure 4. shows the corrected emission intensity at a wavelength of 540 nm as a function of the molar ratio of HPeDA to HPyDA. The corrected emission intensity I was calculated by the following equation:

$$I = I_{mix} - I_{Py} R / (1 + R) \qquad (1)$$

where I_{mix}, I_{Py} and R denote the measured emission intensity of the mixed monolayer, the measured intensity of the pure HPyDA monolayer, and the inverse of the molar ratio, respectively. Emission from HPeDA due to absorp-

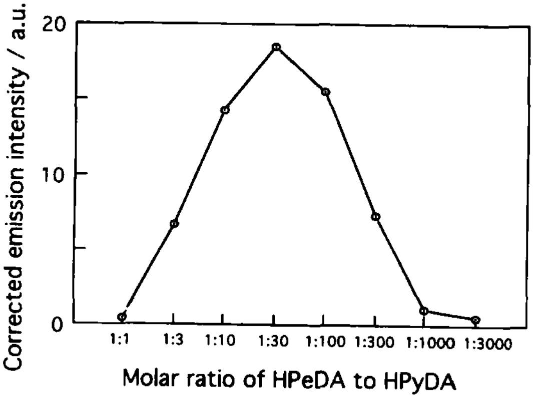

FIGURE 4 The emission intensity at a wavelength of 540 nm corrected by Eq. (1) as a function of the molar ratio of HPeDA to HPyDA.

tion by itself was negligible because of the weakness of the absorption at 335 nm. It can be concluded from the result shown in Figure 4 that the efficient ET proceeded in the mixed monolayer of the molar ratios between 1:3 - 1:300 with an optimized molar ratio of 1:30.

CONCLUSIONS

The efficient ET from the antenna HPyDA to the energy acceptor HPeDA in the mixed monolayers were confirmed. It was found that the optimized molar ratio of HPeDA to HPyDA of 1:30 for the ET.

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