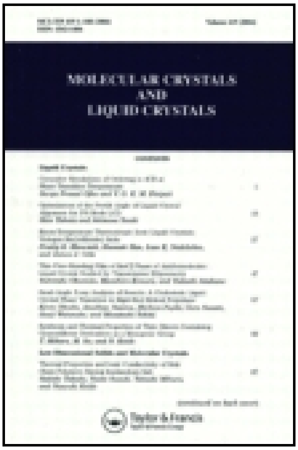

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External Electric Field Effect on Photoinduced Electron Transfer from Monomer and Dimer of Oxacarbocyanine in Langmuir-Blodgett Films

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External Electric Field Effect on Photoinduced Electron Transfer from Monomer and Dimer of Oxacarbocyanine in Langmuir-Blodgett Films

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Interlayer vectorial electron transfer from the excited state of oxacarbocyanine (OCC) to viologen (VIO) occurs in a molecular assembly composed of a mixed LB monolayer of OCC and a mixed LB monolayer of VIO separated by a spacer layer of a fatty acid. Fluorescence quantum yield of OCC in this system is changed by an external electric field, indicating that the photoinduced electron transfer rate is affected by an electric field. The rate is depressed or enhanced by an electric field, depending on the direction of the applied electric field. It was also found that monomer and dimer of OCC show different field effects on the electron transfer from each other in LB films.

Keyword: electric field effect; LB film; fluorescence; oxacarbocyanine; photoinduced electron transfer

INTRODUCTION

Intra- or intermolecular dynamics such as a photoinduced electron transfer may be affected by an external electric field[1], but the number of research works of the field effects on excitation dynamics is very limited.

In a homogeneous system where electron donor and acceptor molecules are uniformly distributed, the analysis of the field effect on the electron transfer process will be very complicated, even if the field effect exists, since different pairs of donor and acceptor will show different magnitudes of the field effect from each other. If the electron donor and acceptor are arranged with a well defined molecular order and photoinduced electron transfer can be induced with a definite direction, the elucidation both of the mechanism of electron transfer and of the field effect on the dynamics seems to be developed extremely well. The Langmuir-Blodgett (LB) technique is one of the excellent methods to prepare such a molecular assembly[2,3].

In the present study, external electric field effects on interlayer vectorial electron transfer from photoexcited molecules of oxacarbocyanine have been examined, based on the field effects on absorption and fluorescence spectra.

EXPERIMENTAL

A mixture of arachidic acid (AA) and methyl arachidate (MA) whose ratio is 1:1, denoted by AA/MA, was used as a matrix of a mixed LB monolayer film of N,N'-dioctadecyloxacarbocyanine perchrolate, denoted by OCC, and of N,N'-dioctadecyl-4,4'-bipyridinium dibromide, denoted by VIO. A mixing fraction of OCC to AA/MA was 0.5 mol% or 20 mol%, and a fraction of VIO to AA/MA was 10 mol%. Two kinds of stacked multilayer films were prepared: one includes VIO (sample(I)), and the other doesn't include VIO (sample(II)). Sample(II) was prepared as follows: at first, seven layers of AA were deposited on the quartz substrate coated by a semi-transparent aluminum film; the plural number of mixed monolayers composed of OCC and AA/MA were deposited with a spacer composed of four layers of AA between the adjacent mixed layers; 10 layers of AA were post-coated: a semi-transparent aluminum film was again coated with evaporation. In sample(I), the monolayer film of AA deposited following the deposition of OCC mixed monolayer and one AA monolayer was replaced by a monolayer film of VIO. A schematic illustration

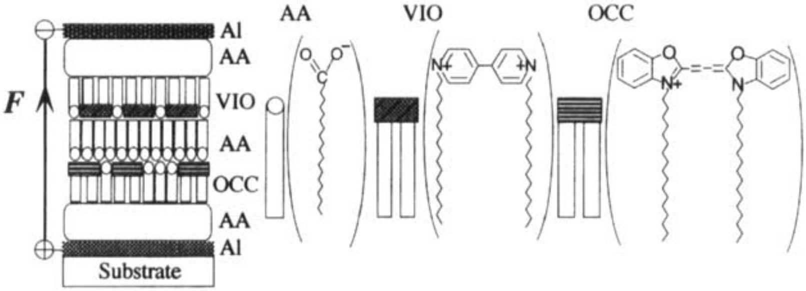

FIGURE 1 Molecular structures and schematic illustration of stacking multilayer LB films of OCC and VIO with a spacer layer of AA.

of sample(I) is shown in Fig. 1. The aluminum films were used as electrodes. The thickness of each layer was assumed to be 27.3 Å[4], and the applied electric field was estimated with an applied voltage divided by the film thickness.

Plots of the electric field induced change in absorption intensity or in fluorescence intensity as a function of wavelength, i.e., the so-called electroabsorption or electrofluorescence (E-F) spectra, were obtained using field modulation spectroscopy with the same apparatus as described elsewhere[5,6]. The field induced change in transmitted excitation light intensity or emission intensity was detected with a lock-in amplifier. External electric field, denoted by F, was applied up to 1.0 MVcm^{-1} in rms.

RESULTS AND DISCUSSION

In mixed LB monolayer films of OCC, monomer and dimer of OCC dye chromophores are considered to be in equilibrium[2,7]. The absorption spectrum of OCC at 0.5 mol% is nearly the same as the spectrum in diluted solution with a peak at 495 nm, and the dimer formation at 20 mol% is known by a reduction in intensity of the absorption maximum at 495 nm and the appearance of a new maximum at 460 nm. Thus, monomer is dominant at 0.5 mol%, whereas a large part of the absorption intensity is attributed to dimer at 20 mol%. It is noted that the absorption spectra of OCC are not affected by a VIO layer; samples(I) and (II) give essentially the same absorption spectra at 0.5 mol% and at 20 mol%, indicating that the interaction between OCC and VIO with a spacer layer of AA is negligibly small in the ground state.

Fluorescence spectra and E-F spectra of OCC at 0.5 mol% observed in the absence and in the presence of VIO are shown in Fig. 2, together with the first derivatives of the fluorescence spectrum. The E-F spectra were detected at the first harmonic (1F) of the modulation frequency (typically 20 Hz). These spectra were obtained with excitation at 441 nm, where the field induced change in absorption intensity is negligibly small. Fluorescence spectra at 0.5 mol%, which are very similar to a diluted-solution spectrum of OCC irrespective of the presence of VIO, are regarded as the OCC monomer spectra. It is worth mentioning that fluorescence is reduced in the presence of VIO, as a result of photoinduced interlayer electron transfer from OCC to VIO.

The 1F E-F spectrum of monomer observed at 0.5 mol% in the absence of VIO is nearly the same in shape as the first derivative spectrum of fluorescence, indicating that the electric field effect comes from only the first Stark shift resulting from the difference in electric dipole moment between the fluorescent state and the ground state ($\Delta\mu_F$). In the presence of VIO, on the other hand, the 1F E-F spectrum is rather close in shape to the fluorescence spectrum (see Fig. 2), indicating that fluorescence quantum yield (Φ_F) is changed by ***F***. Actually, the observed spectrum in sample(I) could be simulated by a linear combination of the fluorescence spectrum with its first derivative spectrum, i.e., both the field induced change in Φ_F, i.e., $\Delta\Phi_F$, and the Stark shift resulting from $\Delta\mu_F$ are observed in the presence of VIO. $\Delta\Phi_F$ relative to Φ_F is estimated to be ~ 2 x 10^3 at 1 MVcm^{-1}. Note that $\Delta\Phi_F/\Phi_F$ is proportional to the field strength. The E-F spectra shown in Fig. 2, which were obtained with the field direction given in Fig. 1, indicate that fluorescence is enhanced by ***F***. When the field direction was inverted, the spectral shape and the magnitude of the field-induced change in fluorescence intensity were essentially the same, but the sign of the spectra changed. Thus, Φ_F is increased by ***F*** with the field

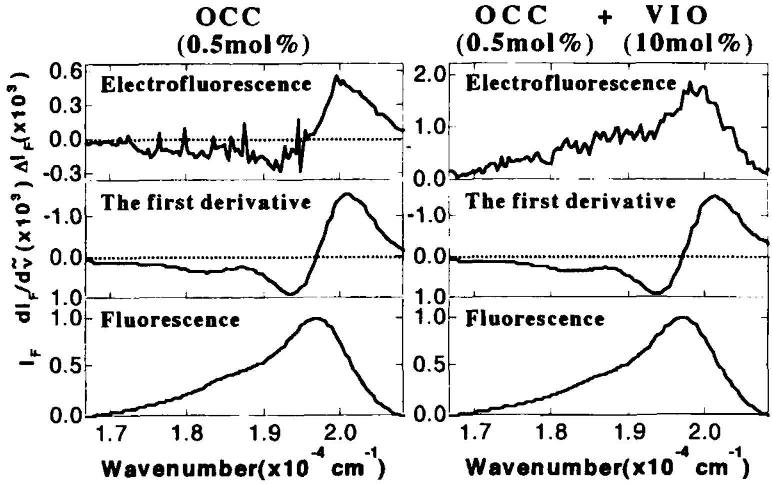

FIGURE 2 Fluorescence spectrum of OCC at 0.5 mol% (bottom), its first derivative spectrum (middle) and 1F E-F spectrum at 1.0 MVcm^{-1} (top) in the absence of VIO (left) and in the presence of VIO (right).

direction given in Fig.1, but Φ_F is decreased by $\boldsymbol{F}$ with the opposite field direction.

The field effect on Φ_F in the presence of VIO can be interpreted in terms of the field effect on the photoinduced electron transfer from OCC to VIO; the electron transfer rate is considered to be decreased by $\boldsymbol{F}$ with the field direction given in Fig. 1, whereas the rate is increased by $\boldsymbol{F}$ with the opposite field direction.

Fluorescence spectrum at 20 mol% can be regarded as a mixture of the monomer spectrum and the dimer spectrum, as is shown in Fig. 3. The 1F E-F spectrum at 20 mol% observed in the absence of VIO is simulated well by a linear combination of the dimer fluorescence spectrum with the first derivative spectra of the monomer and dimer fluorescence spectra. These results indicate that excitation dynamics of dimer is affected by $\boldsymbol{F}$ even in the absence of VIO. With the field direction given in Fig. 1, Φ_F of dimer is decreased by $\boldsymbol{F}$, indicating that the nonradiative rate of the excited dimer is enhanced by $\boldsymbol{F}$. When the field direction was inverted, the spectral shape and the magnitude of

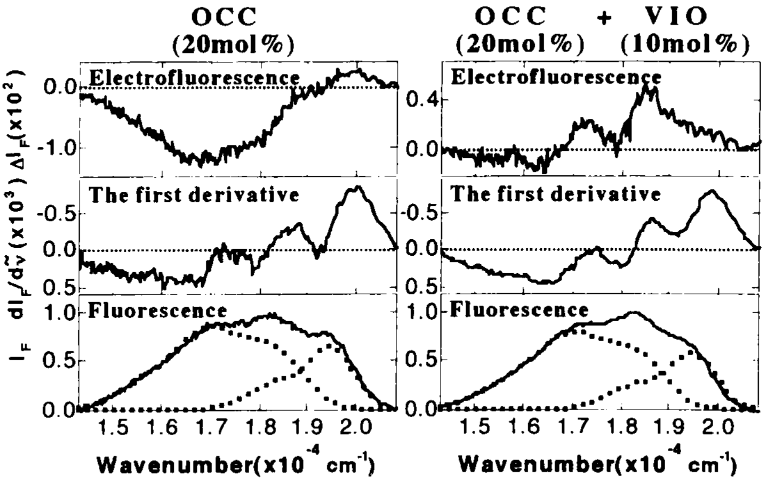

FIGURE 3 Fluorescence spectrum of OCC at 20 mol% (bottom), its first derivative spectrum (middle) and 1F E-F spectrum at 1.0 MVcm^{-1} (top) in the absence of VIO (left) and in the presence of VIO (right). Each of monomer and dimer fluorescence spectra is also shown by a dotted line.

the field induced change in fluorescence intensity were essentially the same, but the sign changed. Then, the excitation dynamics of dimer which is affected by ***F*** is regarded as a vectorial process along the normal to the surface. This process may be attributed to the electron transfer between the excited state of OCC dimer and the fatty acid deposited in contact with each other (see Fig. 1).

In the presence of VIO, the 1F E-F spectrum at 20 mol% is rather close in shape to the first derivative spectrum in the low frequency region (see Fig. 3), indicating that the magnitude of $\Delta\Phi_F$ becomes smaller in the presence of VIO, and the first Stark effect resulting from $\Delta\mu_F$ is exaggerated. These results imply that the rate of the photoinduced electron transfer from OCC dimer to VIO is decreased by ***F*** and that the fluorescence quenched by the photoinduced electron transfer is recovered by ***F***. Note that the E-F spectra in Fig. 3 were obtained with the same field direction as in Fig. 1. When the field direction was inverted, the shape and the magnitude of the E-F spectra are essentially the same, but the sign changed, indicating that the photoinduced electron transfer from OCC dimer to VIO is enhanced by ***F*** with the opposite direction, as in the case of monomer. Thus, photoinduced electron transfer from OCC to VIO is affected by ***F*** both in monomer and in dimer, and the field effect depends on the direction of the applied electric field in the present LB films.

Acknowledgments

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