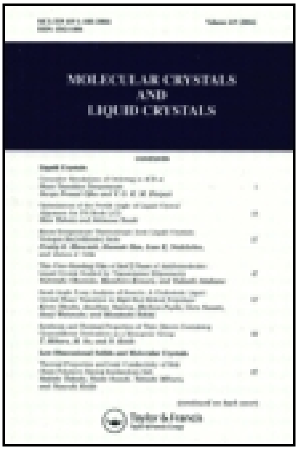

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Effect of Polynucleotides on Fluorescence Quenching in Monolayers at the Air-Water Interface

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Effect of Polynucleotides on Fluorescence Quenching in Monolayers at the Air-Water Interface

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Fluorescence quenching of an amphiphilic intercalator (an electron donor, $C_{18}AO^+$) by an amphiphilic viologen (an electron acceptor, $C_{12}BhpC_5V^{2+}$) in a cationic monolayer of $2C_{18}N^+2C_1$ was enhanced when the monolayer formed polyion complexes with double-stranded polynucleotides at the air-water interface. Fluorescence intensity and quenching efficiency were strongly depended on structure of polynucleotides.

Keywords: fluorescence quenching; photoinduced electron transfer; monolayer; DNA; polynucleotide; polyion-complex; intercalation

INTRODUCTION

Recently, DNA has attracted a great deal of attention as a molecular wire based on the stacked π-electron array of nucleo bases through the inside of the double strand. Enhanced photoinduced electron transfer between electron donors and acceptors covalently bound to oligo or polynucleotides have been reported[1]. We have already succeeded in preparing DNA-octadecyl acridine orange ($C_{18}AO^+$) complex monolayers at the air-water interface and Langmuir-Blodgett films[2]. In this report, cationic monolayers containing an amphiphilic electron donor ($C_{18}AO^+$, **1**) and acceptor ($C_{12}BphC_5V^{2+}$, **3**) were prepared to investigate effect of polynucleotides on fluorescence quenching caused by electron transfer from **1** to **3** along the monolayer (Fig. 1).

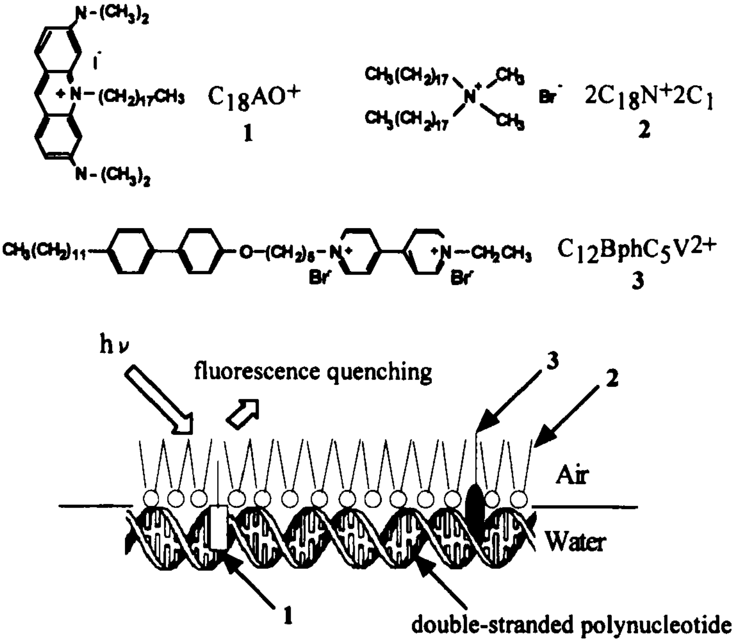

FIGURE 1 Chemical formulae of cationic amphiphiles and schematic representation of the donor-acceptor monolayer complexed with double-stranded DNA at the air-water interface.

RESULT AND DISCUSSION

Binary (**1** and **2**; molar ratio 1:9) and ternary (**1**, **2** and **3**; molar ratio 1:8:1) component monolayers were prepared on a pure water subphase and aqueous polynucleotides solutions, respectively.

Fluorescence spectra of the binary- and ternary component monolayers on various subphases were measured by a fiber-optics fluorescence spectrometer (Hamamatsu; PMA-11) through an epifluorescence microscope attached to a Langmuir trough (USI-System; FSD-50)[3]. Table I shows the relative fluorescence intensities, I_b and I_t at 560 nm when the monolayers were excited at 480 nm. On the subphases of DNA and RNA (polyA•polyU, polyI•polyC), I_b were higher than that on the pure water subphase. The fluorescence enhancement can be ascribable to the microenvironment effects caused by intercalation of **1** into the stacked base-pairs of polynucleotides. PolyG•polyC strongly quenched fluorescence of **1** because the guanine base is known to be photochemically oxidized by some intercalators[4].

TABLE I Relative fluorescence intensities at 530nm[a] and quenching efficiencies of the binary- and ternary component monolayers on the various subphases

	I_b	I_t	$(I_b-I_t)/I_bI_t$
pure water	1.0	0.86	0.16
DNA	1.5	0.78	0.61
polyA·polyU	4.2	1.0	0.76
polyI·polyC	3.8	1.5	0.40
polyG·polyC	0.88	0.67	0.36
CMC[b]	1.8	1.6	0.07

[a]Blue excitation (480nm).
[b]carboxymethylcellulose. [polymer]=10mg/l

Viologens are well known strong electron acceptors of the photoexcited states of acridine orange derivatives and can quench their fluorescence emission[5]. Addition of the amphiphile **3**, which has a viologen unit as a hydrophilic part, in the binary monolayer reduced I_t to 86% of the binary monolayer on pure water. Since the quencher molecules were spatially separated from excited donors in the matrix amphiphile **2**, fluorescence quenching was not so efficient. If I_b is proportional to the fluorescence life time (τ) of **1**, Stern-Volmer equation can be described as following,

$$\frac{I_b - I_t}{I_b I_t} \propto k_q[Q] \qquad (1)$$

where k_q is quencing rate constant and [Q] is quencher concentration. Since [Q] was constant in the ternary monolayers, the value of $(I_b - I_t)/I_b I_t$ is representative to the relative quenching efficiency (Table I). The quenching efficiency largely depends on the chemical structure of nucleobases. PolyA•polyU is most effective for the fluorescence quenching, although the pressure-area isotherms of the complexed monolayers were almost identical, that means the average distance between the donor and acceptor is almost same. DNA shows smaller values of quenching efficiency than those of polyA•polyU and polyI•polyC. Although polyG•polyC already quenched the fluorescence in the binary monolayer, the quenching efficiency reached to 0.36, which was two times higher than that on pure water. CMC, which complexed with the monolayer, shows no effect on the quenching efficiency. This strongly supports that the stacked π-electron array of base-pairs in polynucleotides can promote the photoinduced electron transfer in the monolayer assemblies. Structure and sequence of the bases are considerably important for the DNA-mediated electron transfer.

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