

# Photoenergy Migration and Hole Transfer in a Bilayer Membrane Composed of Amphiphilic Compounds Carrying an *N*-Ethylcarbazolyl Group

Tomoyuki Morita, Shunsaku Kimura,\* and Yukio Imanishi

Department of Material Chemistry, Faculty of Engineering, Kyoto University, Yoshida Honmachi, Sakyo-ku, Kyoto 606-01, Japan

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Photoenergy migration and hole transfer in a bilayer membrane composed of amphiphilic compounds carrying an *N*-ethylcarbazolyl group (5Cz18) were investigated. Photoenergy migration was evaluated by fluorescence quenching of the *N*-ethylcarbazolyl (ECz) group by methyl terephthaloyldioctadecylamide mixed in the bilayer membrane. The quenching data were well simulated by taking the number of energy migrations among ECz groups to be 360 below the phase-transition temperature ( $T_c$ ) and 113 above the  $T_c$ . Two-photon excitation of the ECz group in the bilayer membrane produced a radical cation (hole). The lifetime of the cation in the bilayer membrane of 5Cz18 was 40  $\mu$ s above the  $T_c$ . It became longer below the  $T_c$  and upon dilution of the chromophores in the membrane, indicating that the rate of hole transfer is comparable to the lateral diffusion of the amphiphile in the membrane.

## Introduction

The photosynthetic process begins with photoenergy harvest and charge separation.<sup>1</sup> A bilayer membrane composed of chromophoric amphiphiles is expected to be an excellent model for a photoenergy-harvesting system because of the high density of chromophoric groups in the two-dimensional membrane. In the membrane, the probability of photoenergy transfer to an acceptor molecule should be high due to efficient photoenergy migration among the chromophores. The molecular assembly of chromophoric amphiphiles may also stabilize chemical species produced in the process of photocharge separation. For example, in anionic micelles, the radical cation is stabilized by suppression of recombination with the ejected electron by the negative charges on the micelle surface.<sup>2</sup>

We have synthesized a dialkylammonium-type amphiphile carrying L-3-(3-*N*-ethylcarbazolyl)alanine (5Cz18, *N'*,*N'*,*N'*-(trimethylaminohexanoyl)-L-3-(3-*N*-ethylcarbazolyl)alanine dioctadecylamide) (Figure 1) and reported formation of vesicular assemblies in aqueous dispersion.<sup>3</sup> The 5Cz18 bilayer membrane showed a facile energy migration among the carbazole groups, as evidenced by fluorescence quenching with acrylamide. In order to estimate the efficiency of photoenergy migration in the 5Cz18 bilayer membrane, methyl terephthaloyldioctadecylamide (Ter18, Figure 1) was mixed in the present study, and the fluorescence quenching was investigated. The quenching experiment was simulated on the basis of the electron transfer between the excited ECz (*N*-ethylcarbazolyl) group and the terephthaloyl group to determine the efficiency of photoenergy migration in the membrane.

The ECz group ejects an electron by two-photon excitation to produce a radical cation. The stability of the radical cation was investigated by transient absorption spectroscopy. The ejected electrons should be trapped by amide groups in the membrane. The radical cation might be quenched after reaching the anionic site by diffusion. The rate of hole transfer was estimated from the lifetime of the radical cation. The suitability of the chromophoric bilayer membrane for charge separation is discussed in terms of the stability of the radical cation.

## Experimental Section

**Materials.** 5Cz18 was synthesized by the method reported previously.<sup>3</sup> Dioctadecyldimethylammonium bromide (DDAB)

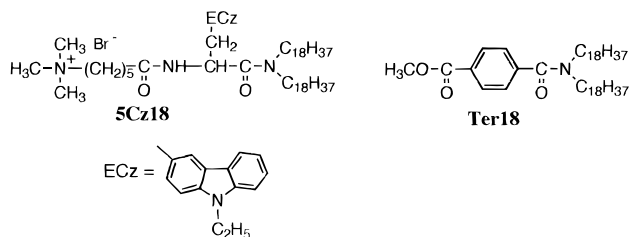


Figure 1. Molecular structure of 5Cz18 and Ter18.

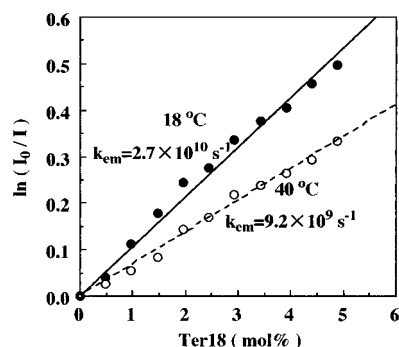
was purchased from Tokyo Kasei, Ltd., and was recrystallized from ethyl acetate before use. Ter18 was synthesized by coupling dioctadecylamine with terephthaloylchloride monomethyl ester. The product was recrystallized successively from methanol and ethanol. Elemental analysis: Anal. Calcd for C<sub>45</sub>H<sub>81</sub>NO<sub>3</sub>: C, 79.00; H, 11.93; N, 2.05. Found: C, 78.84; H, 11.99; N, 1.83.

**Membrane Preparation.** A chloroform solution of 5Cz18 (0.2 mg) and Ter18 (0–5 mol%) was evaporated to form a thin film. The film was dried under vacuum and was dispersed in water (6 mL) by using a bath-type sonicator at 30 °C for 1 h and a probe-type sonicator at 40 °C for 2 min under N<sub>2</sub> atmosphere. The mixed membrane of 5Cz18 and DDAB was prepared in a similar way, too.

**Measurement.** UV and fluorescence spectra were recorded on a Jasco Ubest-50 spectrometer and a Hitachi MPF-4 fluorometer, respectively. Transient absorption spectra were recorded on an Otsuka Electronics IMUC-7000. The excimer-laser photolysis experiment was carried out after passing Ar gas through the sample solution for 30 min. The sample was photoexcited by a focused light pulse (351 nm, 54 mJ) from a XeF excimer laser (Lambda Physik, LPX-105). The time response of the apparatus is 1.0  $\mu$ s, which is the gate width of the multichannel photodiode array with the image-intensifier tube. A single-photon-counting method was used for the measurement of fluorescence decay curves. Details of the apparatus for measurements have been described before except with a Spectra-Physics Ti:S laser (Tsunami Model 3950).<sup>4</sup> The full-width at half-maximum of the overall excitation pulse was 600 ps.

The molecular area of 5Cz18 in the monolayer was determined as follows. 5Cz18 was dissolved in chloroform at the concentration of  $7.2 \times 10^{-4}$  M. The  $\pi$ -A isotherm was

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**Figure 2.** Perrin plot of the fluorescence quenching of the 5Cz18 bilayer membrane with Ter18. The experimental data at 18 °C (●) and 40 °C (○) are shown together with the result of computer simulations by taking  $k_{em}$  to be  $2.7 \times 10^{10} \text{ s}^{-1}$  (—) and  $9.2 \times 10^9 \text{ s}^{-1}$  (---).

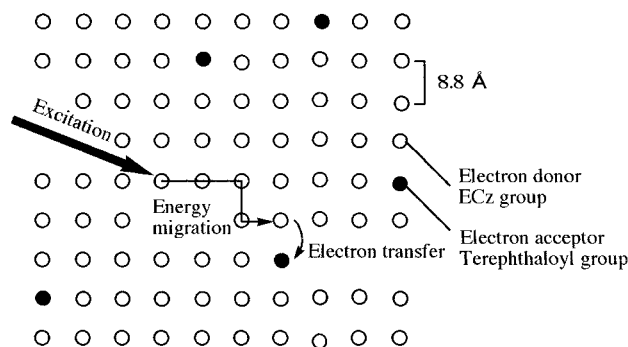
recorded at a constant rate of reducing area of  $5 \text{ cm}^2/\text{s}$  with a USI Langmuir trough. The 5Cz18 solution was spread on the aqueous phase by using a microsyringe and equilibrated for 10 min before compression. The inflection point in the isotherm was determined from the differential of the curve.

## Results and Discussion

**Excitation Energy Migration in the Bilayer Membrane of 5Cz18.** 5Cz18 has been shown to take a vesicular structure with a diameter of 20–80 nm in water.<sup>3</sup> The vesicles have a skin of bilayer membrane, where the ground-state interaction of ECz groups is prohibited. A mixed membrane of 5Cz18 and Ter18 (95/5 mol/mol) showed an UV spectrum similar to the 5Cz18 membrane, suggesting that the Ter18 mixing does not influence the bilayer structure.

Fluorescence spectra of 5Cz18 in water were measured with varying concentrations of Ter18 and at two different temperatures. The fluorescence quenching of 5Cz18 with Ter18 is shown in the form of the Perrin plot in Figure 2. The quenching data were nearly on a straight line in the Perrin plot, which is reasonable because the diffusion of the amphiphiles in the membrane is severely restricted even at the higher temperature (less than  $0.1 \text{ Å}$  during the lifetime of ECz group). Notably, the quenching rate at a temperature (18 °C) below the phase-transition temperature ( $T_c$ ) of  $25.4 \text{ °C}$ <sup>3</sup> is higher than that above the  $T_c$  (40 °C). The quenching rate in the bilayer membrane is high because of facile energy migration. Therefore, the high quenching rate in a gel-state membrane may be due to easy migration of excitation energy among chromophores suitably fixed in the membrane.

**Simulation of the Fluorescence Quenching.** Simulation of the fluorescence quenching process in the mixed membrane of 5Cz18 and Ter18 was carried out under an assumption that ECz groups and terephthaloyl groups are placed on a square lattice with a spacing of  $8.8 \text{ Å}$  (Figure 3), which is taken from the molecular area at the inflection point in the  $\pi$ -A isotherm of 5Cz18 spread on the water subphase. The surface pressure at the inflection point was  $43 \text{ mN/m}$ . The ECz groups and the terephthaloyl groups were distributed randomly on 900 lattice points. The decay curve of the monomer fluorescence of the 5Cz18 membrane was measured and fitted to a two-exponential function. The decay times (their weights) are 1.25 ns (0.82) and 10.8 ns (0.18) (average = 2.98 ns) at 18 °C and 1.23 ns (0.84) and 10.5 ns (0.16) (average = 2.71 ns) at 40 °C. Since the quantum yield was 0.22 at 18 °C,  $k_f$  (the radiative transition probability) and  $k_{nr}$  (the nonradiative transition probability) are calculated to be  $7.35 \times 10^7 \text{ s}^{-1}$  and  $2.62 \times 10^8 \text{ s}^{-1}$ , respectively. Similarly, the quantum yield of 0.19 at 40 °C gives  $6.90 \times 10^7 \text{ s}^{-1}$  for  $k_f$  and  $3.00 \times 10^8 \text{ s}^{-1}$  for  $k_{nr}$ . The electron transfer rate from the ECz group to the terephthaloyl group ( $k_{et}$ ) was



**Figure 3.** Schematic representation for the computer simulation of the energy migration and the electron transfer in the 5Cz18/Ter18 bicomponent bilayer membrane.

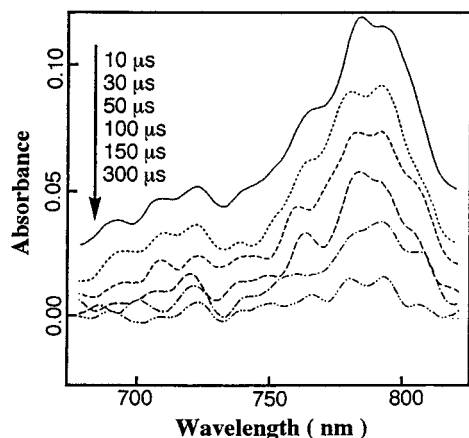
estimated from the quenching of *N*-ethylcarbazole by dimethyl terephthalate in the poly(methyl methacrylate) matrix.<sup>5</sup> The Perrin plot of the quenching was replotted by  $k_{et}$  vs  $r$  (the average distance between *N*-ethylcarbazole and the quencher), which was well fitted by  $k_{et} = 4.5 \times 10^{14} \times \exp(-1.55r)$ . The excited ECz group may lose excitation energy either by fluorescence emission (radiative deactivation), by internal quenching (nonradiative deactivation), or by quenching with the terephthaloyl group. The frequency of emission was calculated for  $10^5$  different distributions of 5Cz18 and Ter18 on the square lattice. The simulation was done by setting the value of  $k_{em}$  (the rate of the excited energy migration between the ECz groups) and using  $k_f$ ,  $k_{nr}$ , and  $k_{et}$  described above. The results of the simulation are shown in Figure 2. The experimental points fall exactly on the simulation curves by taking values of  $k_{em}$  at  $2.7 \times 10^{10} \text{ s}^{-1}$  at 18 °C and  $9.2 \times 10^9 \text{ s}^{-1}$  at 40 °C. Thus, the number of energy migrations during the lifetime of the excited ECz group is 360 at 18 °C and 113 at 40 °C.

**Comparison of the  $k_{em}$  with the Expected Value.** The rate of energy migration between ECz groups in the membrane ( $k'_{em}$ ) was calculated by using the Förster's equation (1).<sup>6</sup>

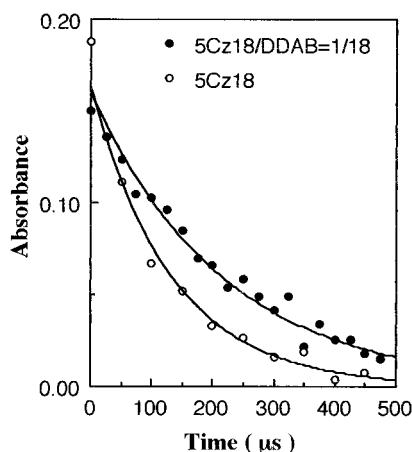
$$k'_{em} = 9000\kappa^2(\ln 10)Jk_f/(128\pi^5n^4NR^6) \quad (1)$$

where  $\kappa^2$ ,  $J$ ,  $n$ ,  $N$ , and  $R$  represent the orientation factor, the overlap integral of the fluorescence spectrum and the absorption spectrum of 5Cz18, the refractive index, the Avogadro number, and the distance between ECz groups in the membrane, respectively. The orientation factor and the quantum yield at 18 °C are taken to be  $2/3$ <sup>7</sup> and 0.22, respectively. The  $k'_{em}$  value at 18 °C was  $1.9 \times 10^{10} \text{ s}^{-1}$ , which agrees with the experimental value of  $k_{em}$  ( $2.7 \times 10^{10} \text{ s}^{-1}$ ). The slight difference between  $k'_{em}$  and  $k_{em}$  may be due to the orientation factor of random orientation for the calculation. The ECz groups should be packed tightly in the membrane below the phase-transition temperature, where the rotational mobility as well as the translational diffusion is hindered. Therefore,  $\kappa^2$  may be larger than  $2/3$  in the membrane.<sup>8,9</sup> In the present case, a  $\kappa^2$  of 0.95 yields the coincidence of  $k'_{em}$  and  $k_{em}$ . It is thus considered that the simulation was carried out under consistent conditions, the square lattice with a spacing of  $8.8 \text{ Å}$ , the expression of  $k_{et}$ , etc. In addition, the bilayer membrane of 5Cz18 should have a regular structure even in the presence of Ter18, probably because 5Cz18 and Ter18 are the same dialkyl-type amphiphiles. The number of energy migrations of 360 at 18 °C should mean an efficient photoharvesting system of the 5Cz18 membrane.

**Hole Transfer among ECz Groups.** When the bilayer membrane is irradiated by an excimer-laser beam, a radical cation ( $\text{ECz}^{\bullet+}$ ) may be yielded by a biphotonic ejection of an electron. The hole produced hops among the ECz groups under Coulombic force of a radical anion which is produced by



**Figure 4.** Transient absorption spectra of the 5Cz18 bilayer membrane at 18 °C at different time lapses after laser irradiation.



**Figure 5.** Decay profiles of transient absorption at 790 nm of the 5Cz18 bilayer membrane or the 5Cz18/DDAB bicomponent bilayer membrane on laser photolysis at 18 °C.

**TABLE 1: Lifetimes of ECz<sup>•+</sup> Generated on Laser Photolysis of the 5Cz18 Bilayer Membrane or the 5Cz18/DDAB (1/18 mol/mol) Bicomponent Bilayer Membrane at Various Temperatures**

	5Cz18 (μs)	5Cz18/DDAB (μs)
18 °C	130	200
50 °C	40	60

trapping the electron ejected from the ECz group. The position of the geminate electron has been reported to be about 20 Å apart from the parent radical cation.<sup>10</sup>

Figure 4 shows transient absorption spectra of the 5Cz18 bilayer membrane at 18 °C. The time-dependent change of the 790-nm absorbance (Figure 5) was fitted by a single-exponential curve to obtain a lifetime of 130 μs for ECz<sup>•+</sup> (Table 1). The lifetimes are longer than a few microseconds of the ECz group in a bilayer membrane reported by Nakamura et al.<sup>11</sup> A possible reason may be the existence of carbonyl groups in the present system. The electron ejected from the ECz group may first become a solvated electron and then be stabilized by trapping by the carbonyl group. On the other hand, the lifetime of ECz<sup>•+</sup> was 40 μs at 50 °C (Table 1). The decreasing lifetime above  $T_c$  may be due to lateral diffusion of amphiphiles in the bilayer membrane, which facilitates encounter of ECz<sup>•+</sup> with a radical anion.

The hole transfer among ECz groups was examined with a mixed membrane of 5Cz18 and DDAB. 5Cz18 and DDAB are the same type of cationic amphiphiles having a dioctadecyl

group in the molecule. Therefore, a discrete phase separation of the mixed membrane should not occur. The decay of transient absorption at 790 nm of the mixed membrane with time was followed, and the results are shown in Figure 5. The lifetime of ECz<sup>•+</sup> in the mixed membrane is significantly longer than that in the bilayer membrane of 5Cz18 (Table 1). The hole transfer in the mixed membrane must be hindered by separation of ECz groups by DDAB amphiphiles, resulting in suppression of recombination of ECz<sup>•+</sup> and the radical anion. The different lifetimes for the 5Cz18 membrane and the mixed membrane below the  $T_c$  should be due to the faster hole transfer in the former membrane. The different lifetimes at the different temperatures should be due to the facilitated lateral diffusion of the amphiphiles in the liquid-crystalline membrane. The difference of lifetimes of the radical cation in the 5Cz18 membrane at different temperatures is nearly the same as the difference of lifetimes of the radical cation in the 5Cz18 membrane and in the 5Cz18/DDAB mixed membrane at 18 °C (Table 1), suggesting that the rate of hole transfer in the bilayer membrane of 5Cz18 is comparable to the rate of lateral diffusion of the amphiphile in the membrane ( $10^{-8}$  cm<sup>2</sup>/s).<sup>12</sup>

The rate of hole transfer in the poly(vinylcarbazole) film has been reported to be  $10^{-5}$  cm<sup>2</sup>/s.<sup>13</sup> Thus, the rate of the hole transfer in the bilayer membrane is considered to be remarkably low. ECz<sup>•+</sup> in the bilayer membrane may be surrounded by ECz groups and be stabilized due to a specific interaction between them. For example, the radical cationic carbazole group of poly(*N*-vinylcarbazole) was found to be stabilized by multichromophoric interaction.<sup>14</sup> Especially, ECz<sup>•+</sup> in the membrane is located in a spatially regular arrangement of ECz groups, which may contribute significantly to the stabilization.

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