Donor−Sensitizer−Acceptor Triad System for Photoenergy Migration, Photoenergy Transfer, and Electron Transfer in a Bilayer Membrane

Tomoyuki Morita,[†] Shunsaku Kimura,*[,†] and Yukio Imanishi[‡]

Contribution from the Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501, Japan, and Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara 630-0101, Japan

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Abstract: A novel photoinduced electron-transfer system was constructed by using a photoenergy-harvesting bilayer membrane composed of two amphiphiles: one having an antenna group (an *N*-ethylcarbazolyl (ECz) group) and the other having a photoenergy-accepting group (anthryl group) and an electron-accepting group (viologen group). Photoenergy migration among ECz groups occurs in the membrane, and the photoenergy is transferred efficiently to the anthryl group. The excited ECz group reduces the viologen group through the excitation of the anthryl group with a quantum yield of 0.67 in the presence of 3 mol % acceptor. The photoinduced electron-transfer process was simulated successfully to determine the number of the excitation migration steps between ECz groups and the electron-transfer rate from the excited ECz group to the viologen group. Interestingly, the transient absorption spectroscopy revealed that the photooxidized chromophore decays faster than the reduced viologen, which has a lifetime longer than a millisecond, suggesting the electron donation to the oxidized chromophore by amide groups in the amphiphile molecules. This membrane is regarded as a donor-sensitizer-acceptor triad system, in which the sensitizer is coupled with two-dimensional array of photoharvesting chromophores, resulted in a more efficient electron transport system than a donor−acceptor diad system.

Introduction

In a bilayer membrane composed of chromophoric amphiphile molecules, the chromophores are two-dimensionally arranged in a high density. Effective photoenergy migration is expected to occur among the chromophores.[1] When an electron acceptor is added to the membrane, photoinduced electron transfer to the electron acceptor will also occur efficiently. We have prepared bilayer membranes composed of *N*-ethylcarbazole (ECz)-containing amphiphilic molecules and observed photoinduced electron transfer to terephthalate group.[1] The bilayer membranes containing ECz groups have an advantage over polymer systems[2−4] in preventing excimer formation, which disturbs photoenergy migration, despite a high density of chromophores.[5,6] It has been shown that effective energy migration with some hundreds of steps occurs in the monolayer or bilayer membrane.[1,7] However, the efficiency of the electron transfer to the terephthalate group in the membrane system was not so high, although the photoexcitation of a chromophore adjacent to the electron-accepting group was frequent as a result of the effective photoenergy migration. The reason for the low extent of electron transfer should be quick dissipation of photoenergy to neighboring chromophores.

To overcome this difficulty, we designed and synthesized a novel amphiphilic compound having an anthryl group (photoenergy-accepting group) and a viologen group (electron-accepting group) in one molecule (VioAnt18, Figure 1). In the bicomponent bilayer membrane of ECz-containing amphiphile (5Cz18Z, Figure 1) and VioAnt18, both ECz and anthryl groups are expected to reside in the same plane (Figure 2). The excitation of the ECz group initiates energy migration among ECz groups, and energy transfer occurs to the anthryl group from the excited ECz group near the anthryl group. The excited anthryl group, then, reduces the viologen group in the same molecule. Since the photoenergy transferred to the anthryl group is not transferred back to neighboring ECz groups, efficient photoinduced electron transfer might be realized in the membrane.

In the present study, photoinduced electron transfer in the bilayer membranes composed of 5Cz18Z and one of the viologen-containing amphiphiles (VioAnt18, VioECz18, and Vio18, Figure 1) was investigated by fluorescence quenching measurement and transient absorption spectroscopy. Furthermore, the photoinduced electron-transfer process was analyzed by computer simulation.

Experimental Section

Materials. *N*′,*N*′-Dimethyl-*N*′-carboxymethylammoniohexanoyl-L-3-[3-(*N*-ethylcarbazolyl)]alanine dioctadecylamide (5Cz18Z) and *N*′,*N*′,*N*′-trimethylammoniohexanoyl-D-3-(9-anthryl)alanine dioctadecylamide

[†] Kyoto University.
[‡] Nara Institute of Science and Technology.

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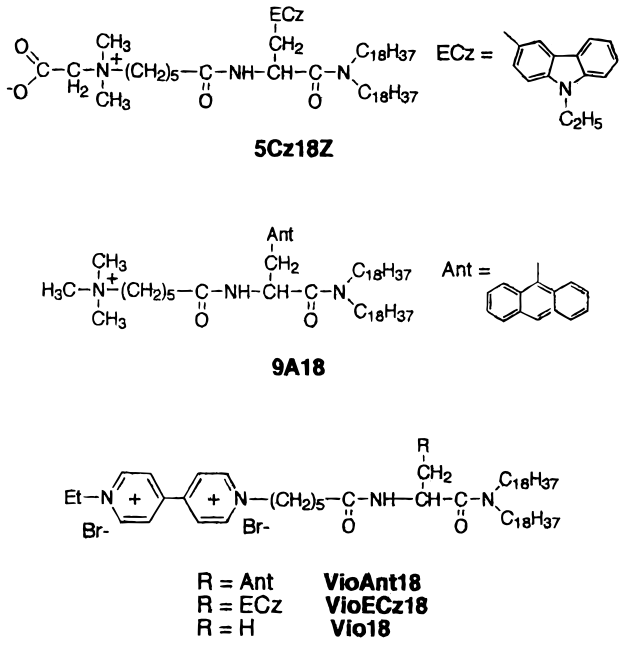

Figure 1. Molecular structures of 5Cz18Z, novel electron acceptors (VioAnt18, VioECz18, and Vio18), and energy acceptor 9A18.

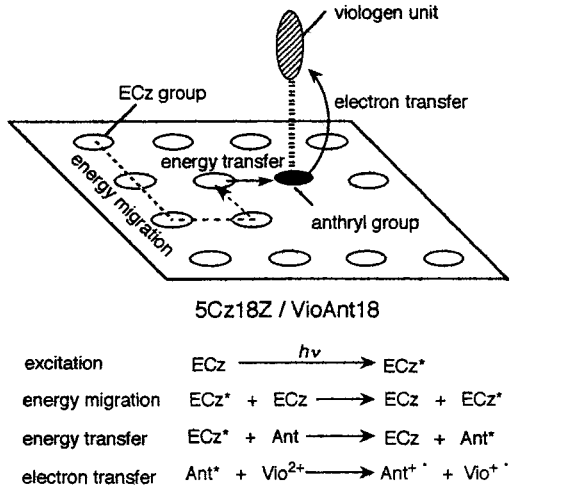

Figure 2. Schematic representation for the photoenergy harvest and photoinduced electron transfer in the 5Cz18Z/VioAnt18 bilayer membrane.

bromide (9A18, Figure 1) were synthesized by the method reported previously.[7,8] Ethylcarbazole and dimethyl terephthalate were purchased from Tokyo Kasei, Ltd. (Japan) and recrystallized from ethyl acetate before use. *N*,*N*-Dimethylacetamide was purchased from Nacalai Tesque, Ltd. (Japan), and used without further purification. Novel amphiphilic acceptors, VioAnt18, VioECz18, and Vio18, were synthesized according to Scheme 1. The syntheses of **1a** and **1b** have been reported.[6,8] **1c** was synthesized by a similar procedure. All intermediates were identified by ^{1}H NMR (270 MHz), and the final products were identified by ^{1}H NMR and mass spectroscopy. The purity was checked by thin-layer chromatography (TLC).

Membrane Preparation. A chloroform solution of 5Cz18Z (0.2 mg) and electron acceptor (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 40 °C for 1 min and a probe-type sonicator at 45 °C for 2 min under N_2 atmosphere.

Measurement. Fluorescence spectra were recorded on a Hitachi F-4010 or a Hitachi MPF-4 fluorometer. Transient absorption spectra were recorded on an Otsuka Electronics IMUC-7000. The excimer-laser photolysis experiment was carried out after passing argon through the sample solution for 30 min. The sample was photoexcited by a focused light pulse (351 nm, 56 mJ) from a XeF excimer laser (Lambda Physik, LPX-105). The time response of the apparatus is 0.90 μs (for the aqueous dispersion) and 0.35 μs (for the acetonitrile solution), which is the gate width of the multichannel photodiode array with the image-intensifier tube. The molecular area of 5Cz18Z in the monolayer was determined as follows. 5Cz18Z was dissolved in chloroform at the concentration of 9.5×10^{-4} M. The $\pi-A$ isotherm was recorded at a constant rate of reducing area of 5 cm^2/min with a USI Langmuir trough. The 5Cz18Z 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 curve.

Results and Discussion

Fluorescence Quenching of the ECz Group in Bilayer Membranes. A transmission electron micrograph observation and dynamic light scattering measurement revealed that the 5Cz18Z formed a spherical molecular assembly in aqueous dispersion. Differential scanning calorimetry showed the presence of a bilayer membrane with a phase-transition temperature of 27.6 °C. Therefore, 5Cz18Z formed liposome in water as reported with similar amphiphiles.[1,6,9]

Fluorescence quenching of the ECz group in the 5Cz18Z membrane was investigated by using viologen-containing amiphiphiles. Figure 3 shows the fluorescence spectra of the 5Cz18Z/VioAnt18 bilayer membrane with varying molar ratios at 17 °C, which is below the phase-transition temperature of the membrane. In the absence of the acceptor, only monomer emission of the ECz group (362, 378 nm) was observed. The fluorescence intensity decreased with increasing addition of the acceptor. Weak peaks at 397, 423, and 446 nm are assigned to emission from the anthryl group. The fluorescence quenching of the ECz group by different electron acceptors is summarized in Figure 4 in the form of a Perrin plot. The quenching rate increases in the following order: Vio18 < VioECz18 < VioAnt18. This order is consistent with the theoretical consideration that the intramolecular quenching by VioECz18 in the membrane occurs more easily than the intermolecular quenching by Vio18 on the basis of the distance between the ECz group and the viologen group. On the other hand, the high quenching rate of VioAnt18 (3 mol % VioAnt18 quenches about 70% of ECz emission) indicates that the anthryl group efficiently accepts the excitation photoenergy that should migrate among ECz groups in the membrane.[1,7,8] In the fluorescence spectra of the 5Cz18Z/VioAnt18 bilayer membrane the emission intensity of the anthryl group was weak (Figure 3), which indicates the excited anthryl group is quenched photooxidatively by the viologen group. The quantum yield of the electron transfer from the excited anthryl group to the viologen group was determined by fluorescence quenching of the anthryl group with the viologen group as follows. The fluorescence quenching of the ECz group in the 5Cz18Z membrane was measured by using two kinds of quencher, VioAnt18 and 9A18 (Figure 1). 9A18 in the 5Cz18Z/9A18 bilayer membrane quenches ECz emission to the same extent as VioAnt18 quenches, indicating photoenergy transfer from the ECz group to the anthryl group occurs to nearly the same extent in the two membrane systems (Figure 5). On the other hand, the anthryl emission in the 5Cz18Z/VioAnt18 bilayer membrane is quenched more significantly than that in the 5Cz18Z/9A18 bilayer membrane (Figure 6). This significant quenching should be due to electron transfer from

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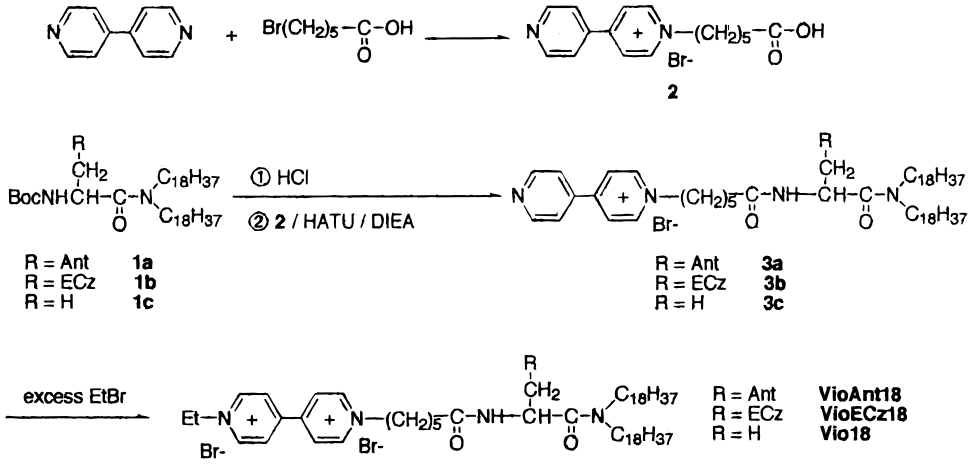
Scheme 1. Synthetic Schemes of the Electron Acceptors, VioAnt18, VioECz18, and Vio18



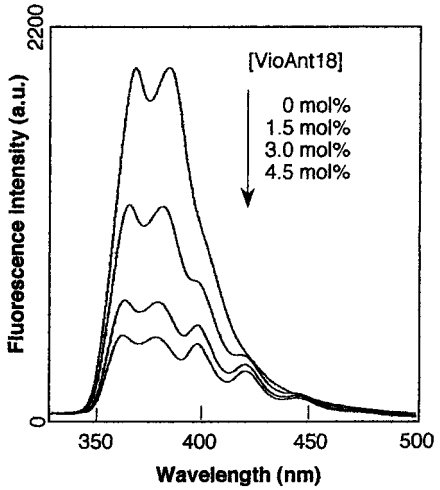


Figure 3. Fluorescence spectra of the 5Cz18Z/VioAnt18 bilayer membrane containing various amounts of VioAnt18 at 17 °C (excitation at 299 nm).

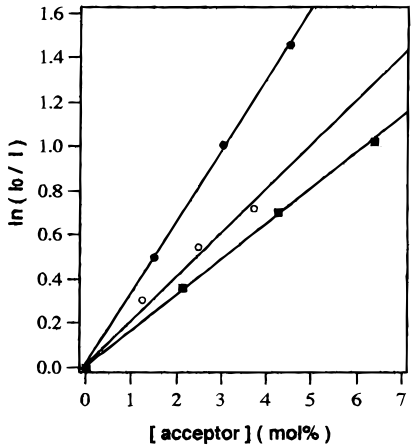


Figure 4. Perrin plot of the fluorescence quenching of the ECz group in the 5C18Z membrane with the electron acceptors: VioAnt18 (●), VioECz18 (○), and Vio18 (■).

the excited anthryl group to the viologen group. The quantum yield for the electron transfer is 0.95 in the VioAnt18 molecule, which is obtained by calculating $1 - I/I_0$, where I_0 and I represent the emission intensity of the anthryl group in the 5Cz18Z/9A18 membrane and that in the 5Cz18Z/VioAnt18 membrane, respectively. In the membrane containing 3 mol % VioAnt18, the anthryl group accepts about 70% of the excitation

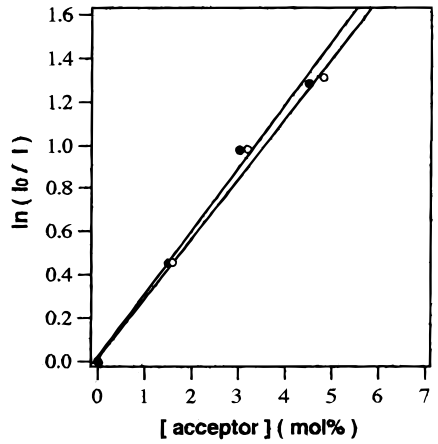


Figure 5. Perrin plot of the fluorescence quenching of the ECz group in the 5Cz18Z membrane with VioAnt18 (●) and 9A18 (○).

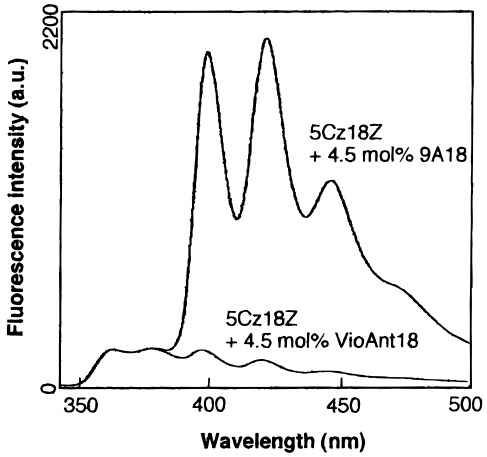


Figure 6. Fluorescence spectra of the 5Cz18Z/VioAnt18 bilayer membrane and the 5Cz18Z/9A18 bilayer membrane at 17 °C (excitation at 299 nm).

energy of the ECz group, thus the overall quantum yield for the photoinduced electron transfer is 0.67 in the membrane.

Photoinduced Electron Transfer to the Viologen Group and Back Electron Transfer. The photoreduction of the viologen group and the back electron transfer were investigated by transient absorption spectroscopy. Figure 7 shows the transient absorption spectra of the 5Cz18Z-containing single-component or bicomponent bilayer membranes at 500 ns after laser irradiation. In the case of the 5Cz18Z bilayer membrane, the ECz radical cation ($ECz^{+\bullet}$; 790 nm) was generated by two-

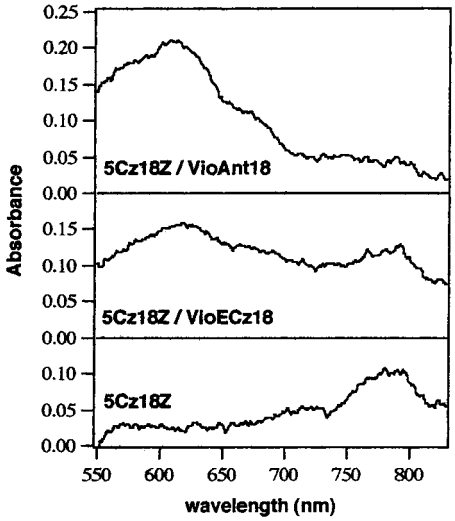


Figure 7. Transient absorption spectra of the 5Cz18Z bilayer membrane without electron acceptor and 10 mol % VioAnt18 or 10 mol % VioECz18 at 17 °C at 500 ns after laser irradiation.

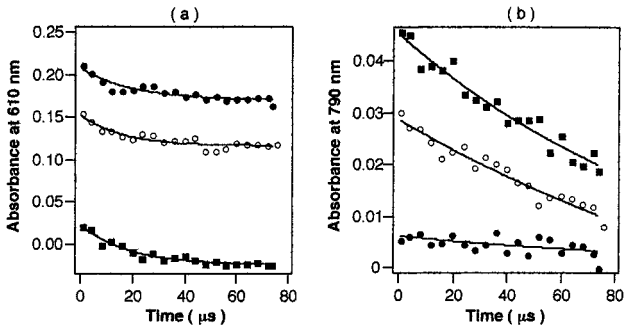


Figure 8. Decay profiles of the transient absorption at 610 (a) and 790 nm (b) of the 5Cz18Z (■), the 5Cz18Z/VioAnt18 (●), and the 5Cz18Z/VioECz18 (○) bilayer membranes on laser photolysis at 17 °C.

photon absorption. When VioECz18 was added in the 5Cz18Z bilayer membrane, the reduced viologen ($V^{+\bullet}$; 610 nm) as well as $ECz^{+\bullet}$ was formed, indicating the photoinduced electron transfer from the ECz group to the viologen group. In contrast to these bilayer membranes, only $V^{+\bullet}$ was formed in the 5Cz18Z/VioAnt18 bilayer membrane, suggesting the absence of $ECz^{+\bullet}$ production or rapid consumption of $ECz^{+\bullet}$. The difference between the two systems exists in the presence of the anthryl group in the 5Cz18Z/VioAnt18 bilayer membrane. The absence of $ECz^{+\bullet}$ formation seems to be real, because the excitation energy of the ECz group (one-photon absorption) might be transferred quickly to the anthryl group to suppress two-photon absorption of the ECz group.

It is notable that $V^{+\bullet}$ in the 5Cz18Z/VioECz18 bilayer membrane has a lifetime longer than a millisecond (Figure 8a). However, the lifetime does not agree with 150 μs for $ECz^{+\bullet}$ (Figure 8b), indicating that the decay of $V^{+\bullet}$ and $ECz^{+\bullet}$ is not attributed to their recombination. $ECz^{+\bullet}$ should be reduced possibly by a certain electron donor in the system, not via the back electron transfer from $V^{+\bullet}$. Similarly, the lifetime of $V^{+\bullet}$ in the 5Cz18Z/VioAnt18 bilayer membrane was longer than a millisecond although the oxidized anthryl group ($Ant^{+\bullet}$) was not clearly observed. This point is referred in the following section.

Electron Transfer from the Amide Group to the Photooxidized Chromophore. It is considered that the photooxidized chromophores, $ECz^{+\bullet}$ and $Ant^{+\bullet}$, should be reduced before the recombination reaction by a functional group in the membrane other than $V^{+\bullet}$. A possible candidate is an amide group involved in the amphiphile. This possibility was investigated by using *N*,*N*-dimethylacetamide as a model of an electron donor.

Table 1. Lifetimes of the Ethylcarbazole Radical Cation and Dimethyl Terephthalate (DMTP) Radical Anion Generated on Laser Photolysis with Various Amounts of *N*,*N*-Dimethylacetamide (DMAA) in Acetonitrile Solution

	radical cation (μs)	radical anion (μs)
ECz + DMTP	4.14 ± 0.07	5.10 ± 0.03
ECz + DMTP + 0.1 M DMAA	3.50 ± 0.01	5.21 ± 0.05
ECz + DMTP + 1.0 M DMAA	3.00 ± 0.03	5.43 ± 0.02

Table 2. Lifetimes of the Anthracene (Ant) Radical Cation and Dimethyl Terephthalate (DMTP) Radical Anion Generated on Laser Photolysis with Various Amounts of *N*,*N*-Dimethylacetamide (DMAA) in Acetonitrile Solution

	radical cation (μs)	radical anion (μs)
Ant + DMTP	2.12 ± 0.01	2.50 ± 0.03
Ant + DMTP + 0.1 M DMAA	1.73 ± 0.05	2.99 ± 0.08
Ant + DMTP + 1.0 M DMAA	1.18 ± 0.02	4.09 ± 0.06

$ECz^{+\bullet}$ was produced in an acetonitrile solution of *N*-ethylcarbazole and dimethyl terephthalate by laser irradiation. Lifetimes of $ECz^{+\bullet}$ under varying concentrations of *N*,*N*-dimethylacetamide were determined and are summarized in Table 1 together with those of the terephthalate radical anion. The lifetime of the radical cation becomes shorter with the addition of acetamide, while that of the radical anion becomes longer, indicating that acetamide donates an electron to the radical cation. Similarly, $Ant^{+\bullet}$ was produced in an acetonitrile solution of anthracene and dimethyl terephthalate, and lifetimes under varying concentrations of *N*,*N*-dimethylacetamide were determined (Table 2). Acetamide is also shown to reduce the anthracene radical cation. These results suggest that the amide group close to the chromophore in the molecule may become an electron donor to the oxidized chromophore. Therefore, the oxidized anthryl group might be instantly reduced by an amide group located nearby in the membrane. This reduction may be the reason the oxidized anthryl group was not clearly observed in the 5Cz18Z/VioAnt18 membrane.

The electron donation by an amide group, however, can only account for the fast disappearance of the photooxidized chromophore, but cannot explain entirely the reason for the long lifetime of $V^{+\bullet}$. The production of $V^{+\bullet}$ with a lifetime longer than a millisecond has been reported with the micellar system.[10−12] The lifetime became longer in the micelles because the back electron transfer is suppressed due to low concentration of $V^{+\bullet}$ in micelles, which results from electrostatic repulsion between $V^{+\bullet}$ and the micellar surface. In the present case, however, the electron donor and the electron acceptor are immobilized in the membrane, bringing forth a situation different from the micellar system. Currently, this long lifetime is considered to be due to the electron migration among viologen groups in the membrane, which should suppress the back electron transfer because of large separation of the hole and electron.[13] However, this point needs to be investigated further.

Computer Simulation of the Photoenergy Harvest in the Bilayer Membrane. To estimate the contribution of energy

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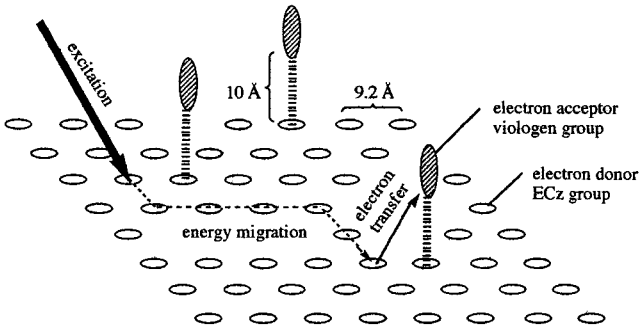

Figure 9. Schematic representation for the computer simulation of the energy migration and the energy transfer in the 5Cz18Z/VioECz18 bilayer membrane.

migration to the photoenergy harvest in the 5Cz18Z/VioECz18 or 5Cz18Z/Vio18 bilayer membranes, a computer simulation was carried out under an assumption that ECz groups are placed on a square lattice with a spacing of 9.2 Å (Figure 9). The 9.2 Å space was taken from the molecular area at the inflection point in the $\pi-A$ isotherm of 5Cz18Z spread on the water subphase.[7] The surface pressure at the inflection point was 45 mN/m. The ECz groups were distributed randomly on 900 lattice points. Since the fluorescent lifetime of the ECz group is 7.93 ns and the quantum yield of the ECz emission is 0.0913 at 17 °C, the rate constants of k_f (the radiative transition rate) and k_{nr} (the nonradiative transition rate) are 1.15×10^7 and 1.14×10^8 s^{-1}, respectively. The rate constant of photoinduced electron transfer from the ECz group to the viologen group (k_{et}) is expressed by eq 1,

$$k_{et} = k_{et}' \exp\{-\alpha (r - r_0)\} \quad (1)$$

where r represent the donor−acceptor distance and k_{et}' is k_{et} at $r = r_0$. α is the tunneling parameter that is determined by the electronic properties of the medium that lies between the donor and acceptor. r_0 and k_{et}' are evaluated by using molecular and fluorescent parameters of 5Cz18Z and VioECz18 in methanol as follows. r_0 is estimated to be 10 Å by assuming the extended chain conformation about the linker part between the ECz group and the viologen group of VioECz18. k_{et}' is obtained by comparing quantum yields of 5Cz18Z and VioECz18. Since the fluorescent lifetime of the ECz group of 5Cz18Z is 8.92 ns, $k_f + k_{nr}$ is 1.12×10^8 s^{-1} in methanol. The quantum yields of ECz emission of 5Cz18Z and VioECz18 are 0.196 and 0.0101, respectively, in methanol. The small quantum yield of the latter is due to photoinduced electron transfer from the ECz group to the viologen group. Taking these three values for calculation, the rate of electron-transfer is 2.17×10^9 s^{-1}. This value is taken as k_{et}' at $r_0 = 10$ Å.

The rate constant of energy migration among the ECz groups (k_{em}) is expressed according to Förster's equation,[14]

$$k_{em} = \frac{9000\kappa^2(\ln 10)k_f J}{128\pi 5 n^4 N r^6} \quad (2)$$

where k^2, J, n, N, and r represent the orientation factor, the overlap integral of the fluorescence spectrum and the absorption spectrum of the ECz group, the refractive index, the Avogadro number, and the distance between the energy donor and acceptor, respectively. The orientation factor and the quantum yield are taken to be 0.667[15] and 0.0913, respectively. The k_{em} values for the energy migration between the nearest ECz groups orthogonally and diagonally in the lattice are, then, 2.19×10^9 and 2.75×10^8 s^{-1}, respectively. The excited ECz group follows any of the following processes of donating the excitation energy to the neighboring ECz group, fluorescence emission, nonradiative deactivation, or quenching by the viologen group. Therefore, only the tunneling parameter, α, is a variable parameter for the simulation of the present membrane system.

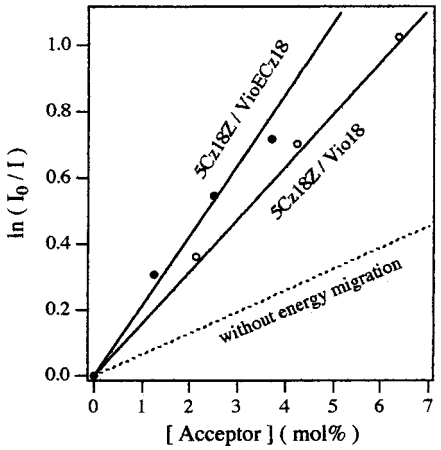

Figure 10. The computer simulation of the fluorescence quenching in the 5Cz18Z/VioECz18 or 5Cz18Z/Vio18 membrane. The simulation curves with considering the theoretical energy migration (solid line) or without energy migration (dotted line) are shown together with the experimental data: 5Cz18Z/VioECz18 (●) and 5Cz18/Vio18 (○). The tunneling parameter, α, is taken as 0.32 Å^{-1}.

The quenching by VioECz18 or Vio18 was simulated by producing 10^5 different distributions of 5Cz18Z and VioECz18 or Vio18 on the square lattice with counting emission frequency. Varying values of the tunneling parameter, α, at the simulation, experimental data of both 5Cz18Z/VioECz18 and 5Cz18Z/Vio18 membranes meet exactly on the simulation curves when α is taken as 0.32 Å^{-1} (Figure 10). α values for typical donor−acceptor pairs separated by aliphatic spacers are reported to be greater than 1 Å^{-1},[16,17] but the α value will become smaller in the presence of functional groups which have available electronic states for the electron transfer between the donor−acceptor pair due to the electronic coupling.[18] Since a few amide groups are located in the space between the ECz group and the viologen group in the membrane, they might serve to reduce the α value.[19] It is also reported that α tends to become small for reactions where excited states of chromophores are involved.[20]

The number of energy migration steps within the fluorescent lifetime is calculated to be 78 from the simulation. A simulation curve without energy migration in the 5Cz18Z/VioECz18 membrane is shown in Figure 10, which is far below the experimental data, indicating that the high quenching rate of the present systems is due to the energy migration.

Conclusion

An efficient photoenergy-harvest and electron-transfer system was formed by a bilayer membrane composed of amphiphiles

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carrying an ECz group and an anthryl and/or a viologen group. About 70% of the photoexcitation energy which was harvested by ECz groups in the membrane was transferred efficiently to VioAnt18 at 3 mol % concentration, and the excited anthryl group effectively reduced the viologen group with a quantum yield of 0.95. It was shown that the photooxidized chromophore decays much faster than the photoreduced viologen group which has a lifetime over a millisecond in the bilayer membrane, suggesting that an amide group in the membrane should donate an electron to the photooxidized chromophore and electron migration among viologen groups might suppress the back electron transfer. By utilizing such a long-lived reductant, an efficient reduction reaction will be possible. Since the viologen group is located at the membrane surface, the system is suitable for construction of an electron-relay system especially with an electron acceptor in the water phase.

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Supporting Information Available: Synthetic procedures and characterization for **2**, **3a**, VioAnt18, **3b**, VioECz18, **3c**, and Vio18 (2 pages, PDF). See any current masthead page for Web access instructions.

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