Electron Transport across Vesicle Bilayers Sensitized by Pyrenes: Design and Syntheses of Unsymmetrically Substituted Bifunctional Pyrenes Acting as Excellent Sensitizers

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An electron transport from an electron donor entrapped into inner waterpool to an electron acceptor in outer aqueous solution across vesicle bilayers was sensitized by pyrene derivatives incorporated in the vesicle walls, although the sensitizer ability was very dependent on the substituent group on the pyrenyl ring. The newly designed pyrenes having both a hydrophilic group linked by short methylene chain and a hydrophobic long alkyl group were found to act as excellent sensitizers.

Photoinduced electron transport across vesicle bilayers has been of great interest in view of not only the construction of models to understand better the natural photosynthetic system, but the production of artificial systems to convert light energy into chemical potential. Although a number of systems reported so far have revealed the usefulness of vesicle bilayers for an efficient charge separation,[1] further investigation is required to achieve the final goals. Recently, we have found that pyrene derivatives incorporated into the bilayer of phosphatidylcholine (pc) vesicles can sensitize transport of electrons from ascorbate (asc^-) entrapped into inner waterpool to methylviologen (mv^{2+}) present in outer aqueous solution without any additional components acting as electron carriers.[2] The mechanism of the electron transport, as well as the enhancement of its efficiency, of this system merits a detailed study for the following three reasons. First, the overall process of this electron transport proceeds with a gain in free energy, transducing light energy into chemical potential.[3] Secondly, the spatial separation of asc^- and mv^{2+} with the vesicle walls plays an essential role in the formation of long-lived charge separation state, in contrast to the photochemical accumulation of reduced mv^{2+} ($mv^{+\bullet}$) using an efficient sacrificial donor such as EDTA. Finally, the use of pyrene derivatives as a sensitizer enables us to study the electron transport mechanism systematically owing to the ease of preparation of a wide variety of derivatives and the facile spectroscopic detection of short-lived reactive species which would intervene in the electron transport. Here, we report the remarkable dependence of the ability to sensitize an electron transport on the substituent group introduced into the pyrene nucleus, and propose an optimal structure of pyrene derivatives which can be employed as sensitizers.

The vesicle solution was prepared as follows; a suspension of (1-pyrenyl)acetic acid (**1a**) and pc from egg yolks (3 mM) in a 1.0 M tris(hydroxymethyl)aminomethane–HCl buffer (pH 7.5) containing ascNa (1.0 M) was sonicated under argon for 60 min at 45 °C. The suspension was run through a column with Sephadex G-50 equilibrated with a buffer solution containing NaCl (1.0 M) to remove the electron donor and the sensitizer outside the vesicle, and then $mvCl_2 \cdot 3H_2O$ was added to give a vesicle solution with mv^{2+} (10 mM) in an outer aqueous phase. Irradiation of the degassed vesicle solution with a 500-W xenon arc lamp through a band-pass filter (360 ± 20 nm) at 24 °C resulted in the formation of $mv^{+\bullet}$, which was identified by its characteristic absorption with maximum at 396 and 604 nm.[4]

On the basis of the following three experimental results, we believe that the production of $mv^{+\bullet}$ proceeds through an electron transport from asc^- to mv^{2+} across the vesicle bilayers sensitized by **1a** incorporated in the vesicle walls. First, the initial rate of the $mv^{+\cdot}$ formation (v_i) was reduced to less than 5% with the addition of surfactant (Triton X-100, 18 mM) to the vesicle solution, indicating that the spatial separation of the electron donor and acceptor with the vesicle walls plays an essential role in the accumulation of $mv^{+\bullet}$. Secondly, although the formation of $mv^{+\bullet}$ was observed by the irradiation even in the absence of asc^- due to the pyrene-sensitized charge separation at the bilayer–water interface,[5] v_i was increased 4.1-fold with the addition of asc^- in an inner waterpool of the vesicle. Finally, by employing the fact that the vibronic fine structure of the fluorescence of pyrene derivatives is very sensitive to solvent polarities,[6] it was confirmed that the sensitizer existed not in an aqueous phase but in a slightly hydrophobic region of the vesicle.[7]

In order to optimize the structure of pyrenes employed as sensitizers for an electron transport across vesicle bilayers, we have investigated the dependence of the sensitizer ability, which is evaluated with v_i and the maximal concentration of accumulated $mv^{+\bullet}$ (c_{max}), on the substituent group at the 1-position of the pyrene nucleus. Since highly hydrophilic pyrenes such as 1-pyrenylcarboxylic acid cannot be incorporated into the bilayer of pc vesicles, we have examined the pyrenes having the structure of $Py(CH_2)_nX$ (Py = 1-pyrenyl, X = H or substituent group). The results are summarized in Table 1, which shows that the sensitizer ability is very dependent on the substituent group. It should be noted that a hydrophilic functional group is indispensable for pyrene derivatives to act as sensitizers for the electron transport. Thus, 1-alkylpyrenes **4a** and **4b**, as well as parent pyrene, are found to be completely unavailable for a sensitizer. Moreover, the effectiveness of the hydrophilic group decreases significantly as the length of methylene groups linking the hydrophilic group with the pyrene nucleus is increased. This drastic dependence of the sensitizer ability on the substituent of the pyrenyl ring is interpreted in terms of the position of the sensitizer in the pc vesicle. It is reasonable to think that the sensitizers having a hydrophilic group connected with a pyrene nucleus by short methylene chain are anchored at the bilayer–water interface, facilitating an electron transfer process which occurs at the interface. On the other hand, the hydrophobic sensitizers are incorporated in the interior of the vesicle, although an increase in the hydrophobicity of the sensitizer is favorable for an increase in

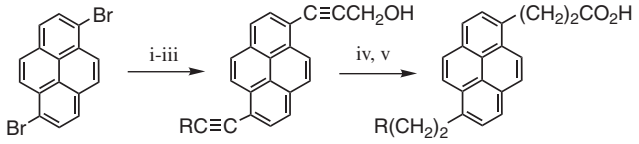
Table 1. Dependence of the ability to sensitize an electron transport across vesicle bilayers on the substituent group at the 1-position of the pyrene nucleus

Substituent group		v_i[a] (10^{-7} M min^{-1})	c_{max}[b] (μM)	c_s[c] (μM)
CH_2CO_2H	(**1a**)	18.0	17.4	5.4
$(CH_2)_2CO_2H$	(**1b**)	9.1	11.0	5.7
$(CH_2)_3CO_2H$	(**1c**)	2.5	3.0	30
CH_2NH_2	(**2a**)	53.5	30.8	35
$(CH_2)_2NH_2$	(**2b**)	5.9	5.0	72
CH_2OH	(**3a**)	44.9	16.5	66
$(CH_2)_2OH$	(**3b**)	16.2	9.6	70
CH_2CH_3	(**4a**)	<0.1	<0.1	68
$(CH_2)_7CH_3$	(**4b**)	<0.1	<0.1	71

[a]Initial rate of the $mv^{+\cdot}$ formation evaluated by an increase in the absorption at 604 nm ($\varepsilon = 12,400\ M^{-1}cm^{-1}$)[8] at 24 °C which obeyed good first-order kinetics. [b]Maximal concentration of accumulated $mv^{+\cdot}$. [c]Concentration of sensitizer in the vesicle solution evaluated by its UV absorption.

its solubility in the vesicle (Table 1).

Furthermore, on the basis of the results obtained above, we have designed novel unsymmetrically substituted bifunctional pyrenes **5a**[9] and **5b**[10] having both a carboxylic acid group linked by short methylene chain and a hydrophobic long alkyl group, which are expected to act as more effective sensitizers. The synthetic route used to prepare these pyrene derivatives is summarized in Scheme 1. The production of $mv^{+\cdot}$ by irradiation of the vesicle solution containing **5a** and **5b** under conditions identical to those described above is illustrated in Figure 1, compared with that observed by using 3-(1-pyrenyl)propionic acid (**1b**) as a sensitizer. As shown in the figure, v_i, as well as c_{max}, has jumped up enormously by the introduction of long alkyl group into the pyrene nucleus; v_i (10^{-7} M min^{-1}) and c_{max} (μM) are 57.9 and 38.7 for **5a**, and 46.2 and 29.0 for **5b**, respectively. The significant increase in the sensitizer ability is thought to be attributed to not only a retention of high efficiency of **1b** for an electron transfer process occurring at the bilayer–water interface, but an increase in the solubility in the vesicle with the aid of long alkyl chain; concentration of sensitizer in the vesicle solution (c_s, μM) is 64 and 74 for **5a** and **5b**, respectively.



5a; R = $CH_3(CH_2)_5$
5b; R = $CH_3(CH_2)_9$

Scheme 1. Reagents and conditions: i, H–C≡C–R, $PdCl_2(PPh_3)_2$, CuI, morpholine; ii, H–C≡C–CH_2OTHP, $PdCl_2(PPh_3)_2$, CuI, morpholine; iii, pyridinium *p*-toluenesulfonate, EtOH–CH_2Cl_2; iv, H_2, PtO_2, THF; v, pyridinium dichromate, DMF.

In conclusion, we have found strategies to design pyrene derivatives employed as excellent sensitizers for an electron transport across vesicle bilayers. At the present stage we assume that the electron transport proceeds by a mechanism involving

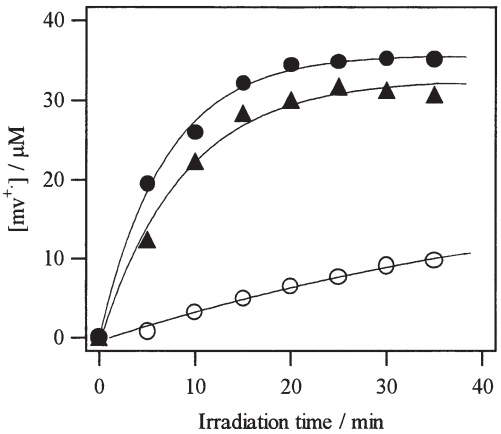


Figure 1. Production of $mv^{+\cdot}$ sensitized by **5a** (●), **5b** (▲), and **1b** (◯) as a function of irradition time (360 ± 20 nm).

electron exchange between pyrene derivatives located at the inner and outer interface across the bilayer.[1,11] Work is in progress to elucidate the mechanism of the electron transport and to enhance its efficiency.

References and Notes

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4 The quantum yield for the initial rate of the $mv^{+\cdot}$ formation sensitized by 1-(aminomethyl)pyrene (**2a**) in the vesicle solution was determined to be 0.10 using a photon counter under irradiation with light of 365 nm of a 500-W extra-high pressure mercury lamp.
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7 For example, the value of *Py*, which is defined as the ratio of the intensity of the 0–0 band of pyrene fluorescence observed in the range of 370–400 nm to that of the 0–2 band, is evaluated to be 2.19 for **2a** in the vesicle solution prepared in the manner described in the text. The values of *Py* of **2a** are 2.87, 2.29, 1.97, and 1.86 in water, acetonitrile, methanol, and chloroform, respectively.
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9 Light brown granules: mp 169–172 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 7.0 Hz), 1.27–1.31 (6H, m), 1.37 (2H, quintet, J = 7.4 Hz), 1.48 (2H, quintet, J = 7.4 Hz), 1.84 (2H, quintet, J = 7.7 Hz), 2.92 (2H, t, J = 8.1 Hz), 3.32 (2H, t, J = 7.8 Hz), 3.70 (2H, t, J = 8.0 Hz), 7.86 (1H, d, J = 7.8 Hz), 7.89 (1H, d, J = 7.8 Hz), 8.05 (1H, d, J = 9.2 Hz), 8.08–8.11 (3H, m), 8.20 (1H, d, J = 9.4 Hz), 8.24 (1H, d, J = 9.4 Hz).
10 Light brown granules: mp 171–175 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.9 Hz), 0.99–1.34 (14H, m), 1.36–1.39 (2H, m), 1.48 (2H, quintet, J = 7.6 Hz), 1.85 (2H, quintet, J = 7.5 Hz), 2.93 (2H, t, J = 7.9 Hz), 3.34 (2H, t, J = 7.8 Hz), 3.71 (2H, t, J = 7.9 Hz), 7.87 (1H, d, J = 8.0 Hz), 7.90 (1H, d, J = 8.0 Hz), 8.06 (1H, d, J = 9.2 Hz), 8.09–8.12 (3H, m), 8.21 (1H, d, J = 8.9 Hz), 8.25 (1H, d, J = 9.2 Hz).
11 The Stern–Volmer constants for the quenching of fluorescence of **1a** in the vesicle solution by asc^- and mv^{2+} were determined under air to be 3.1 and 16.9 M^{-1}, respectively, suggesting that the electron transport was initiated by a reductive quenching of singlet excited **1a** by asc^- (1.0 M).