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COOPERATIVE SENSITIZATION IN PHOTOREDUCTION OF VIOLOGENS BY METAL COMPLEXES AND CHARGE-TRANSFER COMPLEXES ON AMPHIPATHIC VIOLOGEN MICELLES[1)]

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Amphipathic viologens having alkyl chain with a naphthyloxy group formed micelles and showed charge-transfer (CT) absorption. The quantum yield of photoreduction of viologens sensitized by metal complex in these micelles was about twice of the sum of those sensitized by metal complex in micelle without CT and by CT-complex alone. These results strongly indicated the cooperative action between CT- and metal complexes.

Photosensitized reduction of viologens has recently called much attention, since most viologen cation radicals can reduce protons at neutral or slightly acidic conditions.[2)] Especially, methylviologen has proved to be an effective electron mediator in photogeneration of hydrogen from water in the presence of appropriate sacrificial electron donor and colloidal platinum.[3)] In order to improve the efficiency of photoreduction of viologens, some amphipathic viologens have recently been prepared.[4-6)] Grätzel et al.[7)] reported that the reverse electron transfer from cation radicals of amphipathic viologens to oxidized photosensitizers was suppressed by a factor of 500. The effect was ascribed to rapid solubilization of the amphipathic viologen cation radical into cationic micellar surface, where electrostatic field prevents the approach of oxidized photosensitizer. The present authors found efficient electron exchange interactions between viologen groups aligned at the interface of amphipathic viologen micelles. Such electron exchange interactions also were able to improve the efficiencies of photoreduction of viologens or hydrogen production in micelles, bilayer membranes, and polymers.[8,9)]

In the present communication, the photoreduction of viologens sensitized by amphipathic metal complexes in molecular assemblies composed of a series of new amphipathic viologens containing a 6-substituted-2-naphthyloxy group as a part of molecular structure will be reported. The CT-complex formed between naphthyloxy group as a donor and viologen as an acceptor in these micelles was found to cooperatively assist the sensitized reduction of viologens by metal complexes.

The molecular structure of amphiphiles and photosensitizers employed in the present experiments is shown in Fig. 1. The details of synthetic procedures and self-assembling properties of amphipathic viologens will be reported elsewhere.[10)]

The absorption spectra of amphiphiles in micellar solution are shown in Fig. 2. CT-absorptions are evident, especially in 2 and 3, at above 380 nm.

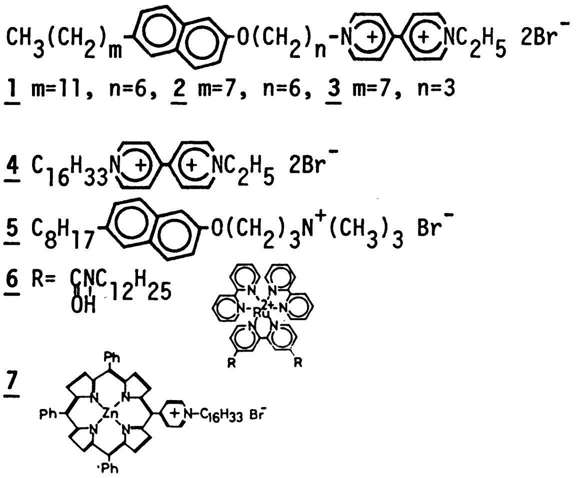


Fig. 1. Structure and abbreviation of amphiphiles and photosensitizers.

Table 1. Photoreduction of viologens sensitized by ruthenium and/or CT-complexes in various micelles of amphipathic viologen.

System	Ru complex	Viologen	A	Φ_{rel}	Φ_{cal}
1	6	4	55.4	100	---
2	6	1	69.9	76.5	79.3
3	6	2	104.8	143.4	65.1
4	6	3	106.7	127.9	70.5
5	--	3	51.3	38.6	---
6	--	2	49.4	26.0	---
7	--	1	14.5	0	---

[6]= 20 μM, [EDTA]= 1.0 mM, [1, 2, 3, 4]= 2.0 mM, L-42 filter (λ> 405 nm), at 25 °C. System 1 was used as a reference (Φ_{rel}=100). See text for the definition of A, Φ_{rel}, and Φ_{cal}.

Similar CT-absorptions with much less intensities were observed in homogeneous methanol solutions of 2 or 3, which suggests the formation of intramolecular CT-complexes. Intermolecular CT-complex formation was also confirmed with a mixture of ammonium amphiphile having naphthyloxy group (5) and usual amphipathic viologen (4) as shown in Fig. 2.

The relative quantum yield of sensitized reduction of viologens in the presence of EDTA was estimated from the initial rate of reduction. The relative number of photons absorbed by metal and/or CT-complexes was evaluated as the A-value taking intensities of light source and absorptions by sensitizers into account.11) The luminescence quenching efficiency of ruthenium complexes by viologens was almost the same (94-98%) for Systems 1 - 4 in Table 1, where the relative quantum yield normalized by absorbed photons is shown together with A-values. The Φ_{cal}-value in Table 1 was calculated from Φ_{rel}- and A- values of corresponding system with CT- or metal complex alone (Systems 5-7 and System 1).12) The Φ_{rel}-value was found to be increased by 30 - 40% in micelles with strong CT-absorption (Systems 3, 4) compared with usual viologen micelles without it (System 1), whereas the Φ_{rel}-value in micelle with very weak CT-absorption was decreased by about 25% (System 2).

Photodissociation from excited CT-state of amphipathic viologen with naphthyloxy group was confirmed by pico- and nano-second laser flash photolysis.13) A part of viologen cation radicals was found to survive for relatively long time (more than a few microseconds) due probably to Coulombic repulsion between the positively charged micellar interface and naphthyloxy cation radicals. Steady state illumination of CT-absorption alone in the presence of EDTA was also found to generate viologen cation radicals as shown in Table 1 for Systems 5 and 6. The quantum yield in these systems without metal complex was about 30% of that in System 1. The coexistence of CT- and metal complexes, however, was found to considerably improve the quantum yield of photoreduction as shown by comparison of Φ_{rel}- and Φ_{cal}-values. These values for System 2, where only very weak CT-absorption exists, coincided within experimental errors. This result indi-

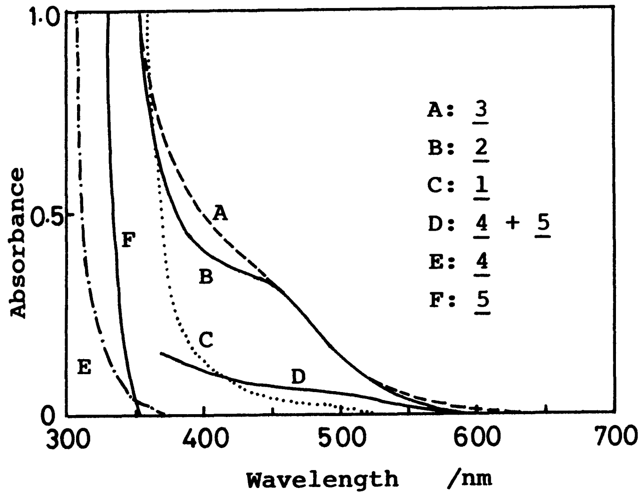


Fig. 2. Absorption spectra of amphiphiles in aqueous solutions. (A) [3]= 3.0, (B) [2]= 3.0, (C) [1]=2.0, (D) [4]=1.5 and [5]= 1.5, (E) [4]= 3.0, (F) [5]= 3.0 mM.

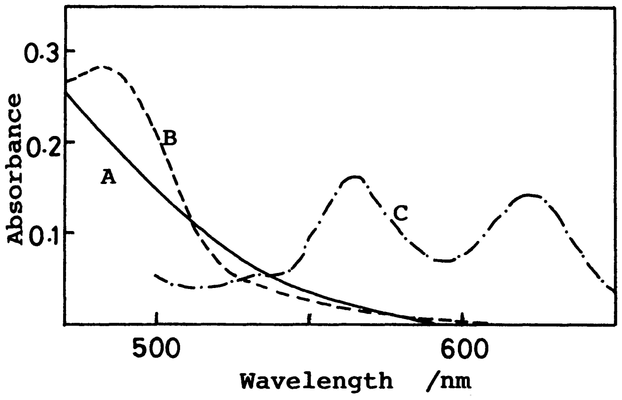


Fig. 3. Absorption spectra of amphipathic metal complexes and viologens. (A) [2]= 3.0 mM, (B) [6]= 20 μM, (C) [7]= 10 μM. 6 and 7 are solubilized in 10 mM aqueous solutions of 4.

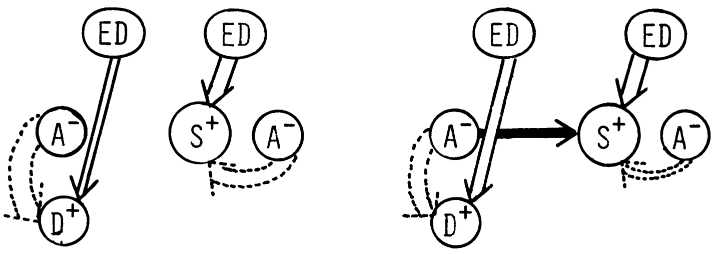
Table 2. Difference in the relative quantum yield of photosensitized reduction of viologens by amphipathic zinc porphyrin 7 in micelles with CT-absorption (2) and without it (4).

System	Viologen	Relative quantum yield under illumination through following filter Y-48	O-57	Y-48(without 7)
8	2	160a)	36b)	7c)
9	4	100b)	40b)	0

[2, 4]= 3.0 mM, [7]= 10 μM, [EDTA]= 1.0 mM, at 25 °C. These values are relative to that (100) for System 9 with a Y-48 filter. a) Both 7 and CT-complexes are excited. b) Only 7 is excited. c) Only CT-complex is excited. See text for details.

cates that CT-absorption simply acted as a filter to reduce photons. Meanwhile, Φ_{rel}-values are about twice of Φ_{cal}-values for Systems 3 and 4 which showed relatively strong CT-absorption. These results strongly suggest the presence of cooperative action between metal complex and CT-complex in these micelles.

Due to the spectral overlapping, it was impossible to excite ruthenium complex and CT-complex separately. In the case of amphipathic zinc porphyrin (7), however, selective excitation was possible as it is obvious from the absorption spectra shown in Fig. 3. Results from selective excitation of 7 using an O-57 filter (λ> 550 nm) and simultaneous excitation of 7 and CT-complex with a Y-48 filter (λ> 470 nm) are summarized in Table 2.14) The micellar system of 4 was chosen as a reference without CT-absorption.15) There is no difference in yields between Systems 8 and 9 in the case of selective excitation of 7 alone. The simultaneous exciatation through a Y-48 filter, however, brought the significant increase in the yield for System 8, which is about 1.6 times larger than the sum of yields for the corresponding individual excitation of 7 and CT-complex under the same condition. These results clearly demonstrate the cooperative sensitization by 7 and CT-complex in amphipathic viologen micelles containing naphthyloxy group. This will also be the case for amphipathic ruthenium complex and CT-complex (Systems 3 and 4 in Table 1).



(a) Independent system (b) Cooperatively coupled system

Fig. 4. Schematic representation of cooperative sensitization of photoreduction of viologens by metal and CT-complexes on amphipathic viologen micelle. The size of an arrow indicates the probability of electron transfer reaction concerned. A: viologen group, D: naphthyloxy group, S: metal complex, ED: EDTA.

The details of the cooperative sensitization are not fully resolved at present. The following mechanism will be most feasible. In the case of viologen micelles with naphthyloxy group, photodissociation from excited CT-state was found to result in relatively long-lived radical pairs as mentioned above. A part of naphthyloxy cation radicals was reduced by EDTA to leave viologen cation radicals. The rest of photogenerated radical pairs will return to the original state by reverse electron transfer reactions. If metal complexes are incorporated in micelles of amphipathic viologens with CT-absorptions, however, these otherwise wasted viologen cation radicals from excited CT-state are assumed to reduce the oxidized metal complex as additional sacrificial reducing agents as schematically shown in Fig. 4. Such cooperative coupling between charge-separated states of CT- and metal complexes is presumed to become possible only through efficient electron exchange interactions between viologen groups aligned at the micellar interface.[6)]

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11) The emissions from a 500 W superhigh pressure mercury lamp (Ushio USH-500D) at 404.7/407.8 and 434.8/435.8 nm are responsible for excitation of the present system. The relative intensities of these emissions through an L-42 filter are 20 and 100, respectively. The A-value was defined as follows; $A=(1 - T_{405})x20 + (1 - T_{435})x100$, where T_{405} and T_{435} are transmittance at 405 and 435 nm, respectively.
12) $\Phi_{cal}=(\Phi^M_{rel} \times A^M + \Phi^{CT}_{rel} \times A^{CT})/(A^M + A^{CT})$, where the superscripts, M and CT, stand for metal and CT-complexes, respectively.
13) T. Nagamura, N. Takeyama, M. Sumitani, K. Yoshihara, and T. Matsuo, to be submitted to J. Phys. Chem.
14) The emissions at 577.0/579.1 nm and 546.1 nm are responsible for excitation.
15) There is a weak CT-interaction between counter ions (Br^-) and viologen groups in a micellar system of 4. The CT-absorption due to this interaction is, however, negligible at the present experimental condition as shown in Fig. 2.

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