# Use of Synthetic Surfactant Vesicles as Electron Storage Systems

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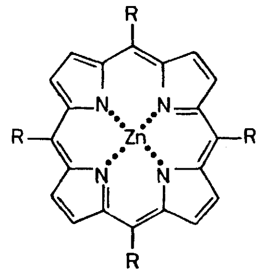
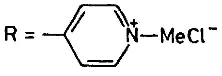
*Summary* The use of dioctadecyldimethylammonium chloride, a cationic surfactant vesicle, to facilitate charge separation and electron storage was investigated using $Ru(bipy)_3{}^{2+}$ (bipy = 2,2′-bipyridyl) and zinc tetramethylpyridyl porphyrin as sensitizers and an alkyl-substituted methylviologen as an electron relay.

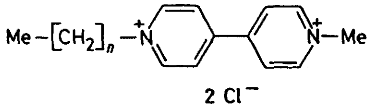
The separation and storage of charges produced in the photoredox reaction (1) where S = sensitizer and R = electron relay is a topic of high priority in light energy conversion studies.[1] Recently we reported on the successful prevention of the back-electron transfer between $R^-$ and $S^+$ by employing surfactant viologens as electron acceptors.[2] While hydrophilic in the oxidized state, these species acquire strongly hydrophobic properties once reduced to the monocation by a suitable sensitizer. The reduced form is readily entrapped into cationic micelles which, through electrostatic repulsion of the sensitizer cation, provide an effective electrostatic barrier for the back reaction.[3]

$$\mathrm{S} + \mathrm{R} \underset{\text{Heat}}{\overset{h\nu}{\rightleftharpoons}} \mathrm{S}^+ + \mathrm{R}^- \tag{1}$$

The present work is concerned with the use of cationic vesicles to induce charge separation and storage effects. Vesicles have the advantage over conventional micelles that they are formed at much lower surfactant concentrations. Moreover, they provide compartmented systems allowing for the local separation of fuel generating processes such as hydrogen and oxygen formation from water.[4] We have now demonstrated their suitability for the storage of reduction equivalents produced in light-driven electron transfer reactions.



(1) 



(2)

The system investigated consisted of an aqueous solution containing dioctadecyldimethylammonium chloride (DODAC) as a vesicle-forming agent (*ca.* spherical aggregates, mean hydrodynamic radius of 309 Å),† the ruthenium complex $Ru(bipy)_3^{2+}$ (bipy = 2,2′-bipyridyl) or the porphyrin (**1**), and the amphiphilic viologen deriva-

† The radius was determined by the quasi-elastic light scattering technique.

tive (**2**). The latter functions as an electron relay which is reduced by the excited state of the sensitizer [equation (2), MV = methylviologen]. The reduced form is readily

$$S + C_{14}MV^{2+} \xrightarrow{h\nu} S^{+} + C_{14}MV^{+} \tag{2}$$

entrapped in the interior of the DODAC aggregates. Laser photolysis studies showed that the back reaction between $S^+$ and $C_{14}MV^+$ in the presence of $10^{-4}$ M DODAC is at least 50 times slower than in vesicle-free solution. The increased lifetime of the oxidized sensitizer $S^+$ in such a system allows for the ready back conversion into the original state S through reduction by an electron donor such as EDTA ($H_4EDTA$ = ethylenediaminetetra-acetic acid). The formation and fate of $C_{14}MV^+$ produced under continuous illumination was then examined.

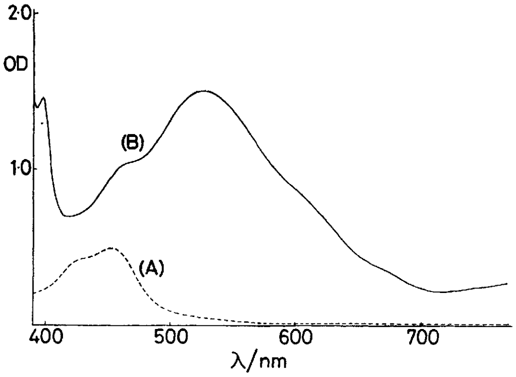


FIGURE 1. Absorption spectra of the Ru(bipy)$_3{}^{2+}$–$C_{14}MV^{2+}$–DODAC–EDTA system before (A) and after (B) irradiation.

Data obtained with aqueous solutions ($10^{-2}$ M acetate buffer, pH 4·7) of Ru(bipy)$_3^{2+}$ (4·2 × $10^{-5}$ M), $C_{14}MV^{2+}$ (1·38 × $10^{-3}$ M), DODAC (2·75 × $10^{-4}$ M), and EDTA (1·3 × $10^{-3}$ M) are presented in Figure 1. Exposure of these solutions to light (450 W Xe-lamp, beam passed through a 15 cm water jacket and a 400 nm cut-off filter, 5 × $10^{16}$ photons min$^{-1}$) produced an intense purple colour. The absorption maximum shifted to 520 nm, curve (B), where the absorbance of a 1 cm cell is 1·37 after 5 min of illumination.

An even more remarkable photochromic effect was observed in the presence of the porphyrin ZnTMPyP$^{4+}$ (**1**) (2 × $10^{-5}$ M) as a sensitizing agent. (Figure 2, concentrations of other components as for Figure 1). Illumination immediately produced an intense purple colour; after 1 min of exposure the optical density at 520 nm had already reached a value of 4·5. Interestingly, with both sensitizers the formation of the purple colour was readily observed in aerated solution also where it appeared after an induction period of *ca.* 50 s. Continued exposure to air resulted in very slow fading of the colour.

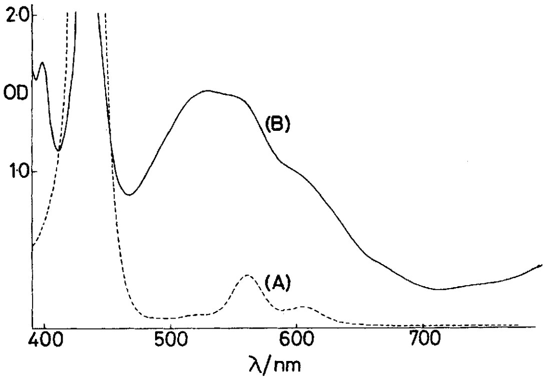


FIGURE 2. Absorption spectra of the Zn porphyrin–$C_{14}MV^{2+}$–DODAC–EDTA system before (A) and after (B) irradiation.

The species absorbing at 520 nm can be identified as a multimer form of the reduced viologen $C_{14}MV^+$. Published data on related symmetrical dialkylviologens[5] indicate that the absorption maxima of such multimers are located around 530 nm. It was found that vesicles are required to obtain the multimer form. If, *e.g.*, micelles were used as hosts for the reduced viologen $C_{14}MV^+$ then the latter was preserved in the monomer state. This was checked by illuminating solutions containing cetyltrimethylammonium chloride, CTAC ($10^{-2}$ M), instead of DODAC vesicles, under otherwise identical conditions. Here, light exposure produced a blue species whose spectrum exhibited a maximum at 603 nm, typical for the monomer form of $C_{14}MV^+$. The latter was much more sensitive to oxygen than the multimer form. Thus in a vessel exposed to air hardly any colour change was produced under illumination owing to the immediate reoxidation of the $C_{14}MV^+$ radical by oxygen.

In conclusion, it appears that cationic vesicles, apart from retarding the back electron transfer between oxidized sensitizer and $C_{14}MV^+$, favour the association of the latter to yield multimers of surprisingly low reactivity towards oxygen. Consequently, in these systems vesicles can serve to store reduction equivalents. A crucial point is whether electrons stored in this form can be used in subsequent redox processes such as the reduction of water to hydrogen. This was tested by adding to the vesicle solution after light exposure a very active Pt-catalyst (30—40 Å particle diameter, protected by Carbowax 20-M, Pt concentration 20 mg/l). The catalyst caused the disappearance of the violet colour and a concomitant generation of hydrogen, thus indicating that the transformation shown in equation (3) is mediated by the Pt solution. The reaction is completed within 2 to 3 h. Though considerably slower than the Pt-mediated reduction of water by monomer viologen, this process is of considerable interest as it shows a method for coupling the photoredox and charge storage events in a fuel generating reaction.

$$(C_{14}MV^{+})_n + nH_2O \rightarrow 0{\cdot}5\,n\,H_2 + nOH^{-} + nC_{14}MV^{2+} \tag{3}$$

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