Photochemistry of a Surfactant Derivative of Tris(2,2′-bipyridyl)ruthenium(II)

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Summary Contrary to a previous report, it has been found that surfactant derivatives of tris(2,2′-bipyridyl)-ruthenium(II) (**2**) do not sensitise the photodissociation of water into its elements.

A POTENTIALLY important method for storage of solar energy is the photochemical formation of a useful chemical product. An ideal system would enable catalytic dissociation of water into its elements using visible light excitation and a recent paper[1] reported that surfactant derivatives of tris(2,2′-bipyridyl)ruthenium(II) (**2**) acted as sensitisers for such a reaction. However, this finding has been questioned by Gaines and Valenty[2] who described the difficulties associated with the preparation of the complex. We have prepared samples of the surfactant complex (**1**) by replacing a single 2,2′-bipyridyl ligand in (**2**) with 2,2′-di(4-carboxyoctadecylpyridine). The complex (**1**) gave satisfactory elemental analysis but h.p.l.c., using conditions described previously,[2] showed the presence of two impurities, (**4**) (2 mol %) and (**5**) (3 mol %). The mixed esters were caused by impurities in the octadecanol used for the

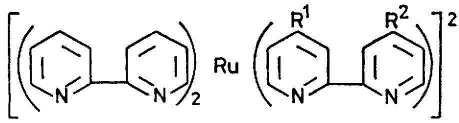
TABLE. Photophysical properties of the surfactant and two water-soluble ruthenium(II) complexes.

Compound	Solvent	λ_{max} (absorption) nm	λ_{max} (emission) nm	τ_L ns	ϕ_L
(1)	$CHCl_3$	482	668	900	0·180
(2)	H_2O	453	608	685	0·055
	EtOH	449	603	900	0·078
	Et_2O-n-C_5H_{12}–EtOH	446	601	945	0·130
(3)	H_2O	475	660	615	0·045

esterification. When spread on to a clean water surface, dilute chloroform solutions of (**1**) gave stable monomolecular films showing a surface area of 80 $Å^2$ mol^{-1} at a pressure of 3 N m^{-2}. The spectral properties, luminescence quantum yield (ϕ_L), and lifetime (τ_L) of (**1**) are similar to those of the unsubstituted complex (**2**) and the water-soluble 2,2′-di(carboxymethylpyridine) complex (**3**) although there is a strong solvent dependence (Table).

When a monolayer assembly of (**1**), either coated on to glass or on to six layers of cadmium arachidate, is immersed in water the luminescence intensity is reduced by *ca.* 40—80%. However, we have not found that the luminescence is 'almost entirely quenched' as reported previously[1] and, in fact, the reduction observed is only of the same magnitude as the solvent dependence exhibited by (**2**).

Outgassed aqueous solutions of (**2**) and (**3**) were irradiated with light of $\lambda > 360$ nm but there was no change in concentration or composition. Using an oxygen-sensitive electrode, we were not able to detect oxygen as a photoproduct during these experiments. Also, irradiation of (**1**) in dioxan–water or in a micelle system did not result in formation of oxygen. Furthermore, the vapour pressure over a frozen, outgassed solution of (**1**), (**2**), or (**3**) was not increased by irradiation of the thawed solution. Typical irradiation times were about 10 h and each experiment was repeated many times.



(**1**) R^1=R^2=$CO_2C_{18}H_{37}$
(**2**) R^1=R^2=H
(**3**) R^1=R^2=CO_2Me
(**4**) R^1=$CO_2C_{18}H_{37}$, R^2=$CO_2C_{16}H_{33}$
(**5**) R^1=$CO_2C_{18}H_{37}$, R^2=$CO_2C_{20}H_{41}$

A set of glass slides was prepared containing one outermost layer of (**1**) deposited on to six layers of cadmium arachidate. Ten slides were irradiated in a specially constructed cell filled with water (5 ml), designed to detect a small pressure change within the system due to any evolved gas. However, no gaseous products were detected during 48 h irradiation periods. In conclusion, we find that monomolecular assemblies of pure surfactant ruthenium(II) complexes do not sensitise the photodissociation of water into hydrogen and oxygen. This finding raises the possibility that the previously reported results[1] were obtained with a synergistic mixture of surfactant complexes.

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[1] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1976, **98**, 2337.
[2] G. L. Gaines and S. J. Valenty, *J. Amer. Chem. Soc.*, 1977, **99**, 1285.