

## 2,7-Dimethylthieno[2,3-*c*:5,4-*c'*]dipyridinium Bisperchlorate as Sensitizer for the Photoreduction of Water

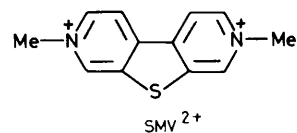
Anton Launikonis,<sup>a</sup> Albert W.-H. Mau,<sup>\*a</sup> Wolfgang H. F. Sasse,<sup>a</sup> and Lindsay A. Summers<sup>b</sup>

<sup>a</sup> CSIRO, Division of Applied Organic Chemistry, G.P.O. Box 4331, Melbourne, Victoria 3001, Australia

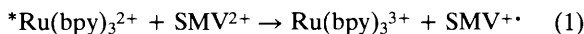
<sup>b</sup> Department of Chemistry, University of Newcastle, Newcastle, N.S.W., Australia

The title compound fluoresces strongly and acts as both photosensitizer and electron relay for the photoreduction of water.

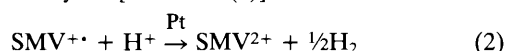
Methyl viologen (MV<sup>2+</sup>: 1,1'-dimethyl-4,4'-bipyridinium dication) is widely used as a herbicide<sup>1</sup> and as an electron relay for the reduction of water.<sup>2-5</sup> Interest in the herbicidal properties of bisquaternary pyridinium compounds has recently led to the synthesis of 2,7-dimethylthieno[2,3-



*c*:5,4-*c'*]dipyridinium (SMV<sup>2+</sup>) bisperchlorate.<sup>6</sup> In view of its structural similarity to MV<sup>2+</sup> and its ability to undergo reversible one-electron reduction,<sup>6</sup> we have now examined some of the photophysical and photochemical properties of this new dication. Initial experiments showed that SMV<sup>2+</sup>, like MV<sup>2+</sup>, quenched the trisbipyridine ruthenium dication, Ru(bpy)<sub>3</sub><sup>2+</sup>, oxidatively as shown in equation (1). Stern-Volmer plots gave  $k_q = 8.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (in acetate



buffer, pH 5) compared with  $k_q = 9.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for MV<sup>2+</sup>.<sup>4</sup> Because of its electrochemical potential  $\{E^0[\text{SMV}^{2+}/\text{SMV}^{+\cdot}] = -0.41 \text{ V vs. normal hydrogen electrode (N.H.E.)}$ , by cyclic voltammetry, acetate buffer;  $E^0[\text{MV}^{2+}/\text{MV}^{+\cdot}] = -0.44 \text{ V}$  (refs. 1–4)}, SMV<sup>2+</sup> reduces water in the presence of platinum catalysts [reaction (2)]. It is therefore not



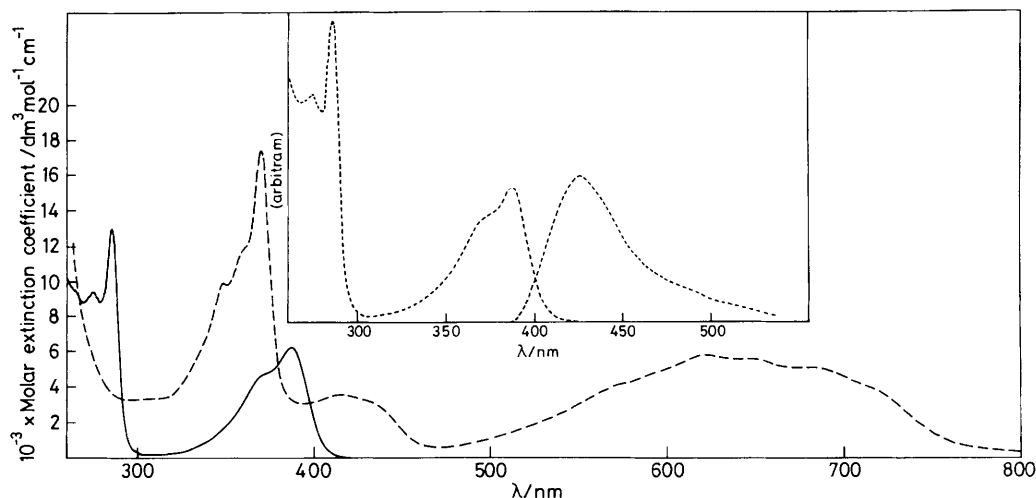
surprising that hydrogen was produced on irradiation of a solution containing SMV<sup>2+</sup> ( $2 \times 10^{-3} \text{ mol dm}^{-3}$ ), Ru(bpy)<sub>3</sub><sup>2+</sup> ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ), ethylenediaminetetracetic acid (edta,  $2 \times 10^{-2} \text{ mol dm}^{-3}$ ), and colloidal platinum in acetate buffer, pH 5.<sup>4</sup> The quantum yield of hydrogen formation,  $\Phi(460 \text{ nm}, \frac{1}{2} \text{H}_2)$ , was found to be 0.072 (*cf.*, 0.091 for MV<sup>2+</sup>, ref. 4).

During these experiments it was observed that the solutions containing SMV<sup>2+</sup>, edta, and colloidal platinum, evolved hydrogen on irradiation (150 W xenon lamp, quartz cell) even

in the absence of Ru(bpy)<sub>3</sub><sup>2+</sup>. Under the same conditions solutions containing MV<sup>2+</sup> instead of SMV<sup>2+</sup> did not form hydrogen. That SMV<sup>2+</sup> acts as a photosensitizer and electron relay for hydrogen production prompted the following experiments.

The absorption spectra of SMV<sup>2+</sup> and of its radical cation, SMV<sup>+\cdot</sup>, are shown in Figure 1. Inspection of the absorption spectrum of SMV<sup>2+</sup> reveals a lowering of the  $\pi$ - $\pi^*$  transition compared to that of MV<sup>2+</sup> (ref. 5) by at least 1.5 eV ( $S_1 \leftrightarrow S_0$ , 3.0 eV) as a result of the conjugation between the sulphur atom and the pyridinium rings. This conjugation extends the absorption of the planar SMV<sup>2+</sup> into the visible. A somewhat smaller shift to longer wavelengths occurs with the radical cation, SMV<sup>+\cdot</sup>, but its extinction coefficient,  $\epsilon(622 \text{ nm}) = 5990 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  is about half that of MV<sup>+\cdot</sup>,  $\epsilon(605 \text{ nm}) = 14\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .<sup>7</sup>

In contrast to MV<sup>2+</sup>, which is non-fluorescent,<sup>1,5</sup> SMV<sup>2+</sup> was found to fluoresce strongly. The fluorescence spectrum of SMV<sup>2+</sup> is shown in Figure 1. The close resemblance of its photoexcitation spectrum (Figure 1, insert) and its absorption spectrum rules out the presence of emitting impurities. The quantum yield of the fluorescence,  $\Phi_f$ , was determined to be 0.29 in water ( $\Phi_f = 0.27$  for anthracene in ethanol as standard<sup>8</sup>), independent of excitation wavelength. The lifetime of the fluorescence of SMV<sup>2+</sup> was found to be 6.1 ns, *i.e.* at least three orders of magnitude longer than that of MV<sup>2+</sup>,<sup>5</sup> thus enabling \*SMV<sup>2+</sup> to undergo bimolecular reactions. The phenomenal increase in the lifetime of the S<sub>1</sub> state is clearly related to the rigidity and planarity of the new dication



**Figure 1.** Absorption spectra of SMV<sup>2+</sup> (solid line) and SMV<sup>+\cdot</sup> (dashed line) in water at pH 5; insert: photoexcitation (left) and fluorescence of SMV<sup>2+</sup> (solid line) and SMV<sup>+\cdot</sup> (dashed line). SMV<sup>+\cdot</sup> was produced by electrochemical reduction.<sup>7</sup> Admission of air regenerated SMV<sup>2+</sup> from SMV<sup>+\cdot</sup> almost quantitatively.

**Table 1.** Quantum yields of photoreduction of \*SMV<sup>2+</sup> with various donor ions.  $\Phi(\text{SMV}^{+\cdot})^a$  at pH indicated and  $\Phi(\frac{1}{2}\text{H}_2)^a$  when platinum catalyst is present (ref. 4); excitation wavelength, 400 nm;  $[\text{SMV}^{2+}] 5 \times 10^{-4} \text{ mol dm}^{-3}$ .

[Electron donor]/mol dm <sup>-3</sup>	Oxalate (pH 4)			edta (pH 5)		Acetate (pH 5)
	$\Phi(\text{SMV}^{+\cdot})^b$ (calc.)	$\Phi(\text{SMV}^{+\cdot})$	$\Phi(\frac{1}{2}\text{H}_2)$	$\Phi(\text{SMV}^{+\cdot})$	$\Phi(\frac{1}{2}\text{H}_2)$	$\Phi(\frac{1}{2}\text{H}_2)$
$1 \times 10^{-3}$	0.17	—	0.02	—	—	—
$5 \times 10^{-3}$	0.51	0.04	0.04	—	0.01	—
$1 \times 10^{-2}$	0.67	0.07	0.06	0.02	0.02	0.02
0.1	0.94	0.14	0.13	0.05	0.05	0.04

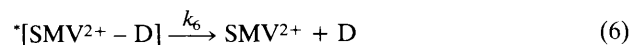
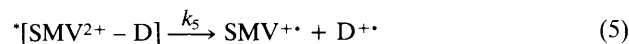
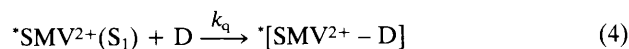
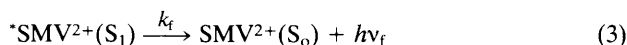
<sup>a</sup> Error in measurement  $\pm 10\%$ . <sup>b</sup> Calculated value, assuming excited singlet reaction, according to  $k_q[\text{donor}]/(k_f + k_q[\text{donor}])$ , where  $k_f = 1.64 \times 10^8 \text{ s}^{-1}$ ,  $k_q = 3.4 \times 10^{10}$  for oxalate,  $3.1 \times 10^{10}$  for edta and  $2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for acetate.

(SMV<sup>2+</sup>). Enhancement of fluorescence intensity often follows an increase in molecular rigidity and is well documented in the literature.<sup>8</sup>

From the phosphorescence of SMV<sup>2+</sup> which was observed in water at 77 K the triplet energy of 2.7 eV and lifetime,  $\tau_p$ , of 0.7 s were obtained. Measurements of its excitation energies and its ground state reduction potentials allow us to estimate the oxidation potentials of the S<sub>1</sub> and T<sub>1</sub> states of SMV<sup>2+</sup> to be 2.6 and 2.3 V respectively. Hence both states are potent oxidants and in fact <sup>\*</sup>SMV<sup>2+</sup> is reduced by oxalate, edta, and acetate (Table 1).

The involvement of S<sub>1</sub> of SMV<sup>2+</sup> in these reactions was demonstrated as follows. Quenching of its fluorescence by edta ( $2 \times 10^{-3}$  to 0.1 mol dm<sup>-3</sup>, pH 5, 295 K) gave linear Stern–Volmer plots, indicating a solely dynamic process, in which we obtained  $K_{SV} = 192$  dm<sup>3</sup> mol<sup>-1</sup> and  $k_q = 3.1 \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Quenching constants with other substrates are also listed in Table 1. At these donor concentrations, ground state complex formation was not observed. In all cases, the formation of SMV<sup>++</sup> increases with the substrate concentration. Laser flash photolysis<sup>5</sup> of SMV<sup>2+</sup> ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) in the presence of oxalate and edta ( $2 \times 10^{-3}$  to 0.1 mol dm<sup>-3</sup>) generated SMV<sup>++</sup> with its formation instantaneous with the rise of the laser pulse (337 nm, 4 ns risetime). The formation of SMV<sup>++</sup> occurs therefore in the same timescale as the fluorescence lifetime of SMV<sup>2+</sup> (6.1 ns).

Table 1 shows that oxalate is a better donor than edta or acetate ions. The measured values for  $\Phi$ (SMV<sup>++</sup>) and  $\Phi$ (<sup>1/2</sup>H<sub>2</sub>) are, however, about ten times lower than those calculated assuming 100% cage escape yield.<sup>2</sup> The present results can be represented by equations (3)–(6), where D is oxalate, edta, or acetate. The experimental results show that only about 10% of the encounter complex <sup>\*</sup>[SMV<sup>2+</sup> – oxalate] yields product ions [ $k_5/(k_5 + k_6) \sim 0.1$ ]. As  $\Phi$ (SMV<sup>++</sup>) and  $\Phi$ (<sup>1/2</sup>H<sub>2</sub>) are essentially identical (Table 1) it follows that the re-oxidation of SMV<sup>++</sup> (equation 2) is almost 100% effective.



It is of particular interest that the photo-oxidation of acetate ion gave, besides hydrogen, similar yields of methane and ethane. This shows that the 'photo-Kolbe' reaction can follow a bimolecular one-electron pathway using visible light and SMV<sup>2+</sup> as homogeneous photocatalyst. By contrast, earlier examples of photo-Kolbe reactions reported by Bard,<sup>9</sup> involved the use of semiconductor materials such as TiO<sub>2</sub> and near-u.v. light to decompose acetate.

The photophysics and photochemistry of SMV<sup>2+</sup> and related viologens with long singlet state lifetimes are potentially valuable in the design of solar energy conversion systems and may contribute to the understanding of their herbicidal activities. Such relationships are being explored.

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