

## SYNTHESIS OF A NEW RELAY FOR PHOTOSENSITIZED HYDROGEN PRODUCTION IN BASIC AQUEOUS SiO<sub>2</sub> MEDIA

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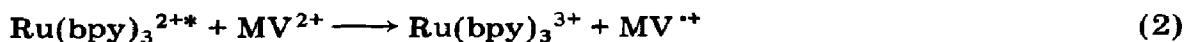
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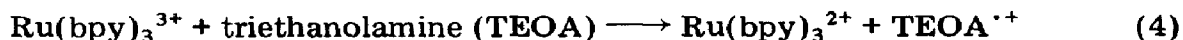
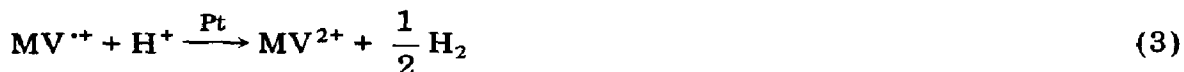
### Summary

In this paper we describe the synthesis of a new viologen with zwitterionic character, [(7,8-dihydro-6*H*-dipyrido[1,2-*a*:2,1-*c*][1,4]diazepinium)-2,12-]di-4,4'-phenethylsulphonate, which belongs to the series of bridged 2,2'-bipyridinium compounds. Its  $E_{1/2}$  value has been measured using cyclic voltammetry and it has been used in investigations of the sacrificial photo-reduction of water, either in a homogeneous phase or in the presence of colloidal SiO<sub>2</sub> as a support. This viologen has proved to be four times more efficient than those previously employed to generate hydrogen at the basic pHs needed for the use of SiO<sub>2</sub>.

### 1. Introduction

In the literature sacrificial systems for the photosensitized decomposition of water by solar radiation are frequently reported which use a relay compound to transport the electron from the photosensitizer to the platinum catalyst where water is reduced, avoiding a loss of efficiency caused by the decay of the excited photosensitizer [1, 2]. Compounds with the 4,4'-bipyridinium structure are currently being utilized, e.g. 1,1'-dimethyl-4,4'-bipyridinium chloride (methyl viologen, MV<sup>2+</sup>;  $E^\circ = -0.44$  V). These compounds should have a redox potential between that of the photosensitizer, e.g. tris(2,2'-bipyridine)ruthenium(II) chloride (Ru(bpy)<sub>3</sub><sup>3+</sup>/Ru(bpy)<sub>3</sub><sup>2+</sup>,  $E^\circ = -0.84$  V), and that of hydrogen ( $E = 0.059 \times \text{pH}$ , where  $E$  is in volts).

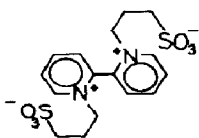




By varying the length of the 1,1'-substituents of the relay the reducing power of the corresponding radical cation is lowered [3] and this means that the splitting of water is only possible at acidic pHs.

Since charge separation of the photoproduced redox pair  $\text{Ru}(\text{bpy})_3^{3+} - \text{MV}^{\cdot+}$  is one of the crucial steps in hydrogen evolution from water, several procedures have been considered, including the use of functionalized polymers [4]. A colloidal  $\text{SiO}_2$  interface has also been introduced to control the photosensitized electron transfer reactions [5]. In this case the photosensitizer is adsorbed at basic pHs onto the negatively charged  $\text{SiO}_2$  surface and the charge separation efficiency may be increased by using a zwitterionic viologen, minimizing the thermal back recombination of the photoproducts. For this reason some neutral viologens such as *N,N*-dipropyl-4,4'-bipyridinium disulphonate [5] or *N,N*-dibenzyl-4,4'-bipyridinium disulphonate [6] have been employed. Nevertheless, at the basic conditions of pH in the experiments the redox potentials of these viologens do not allow the evolution of hydrogen from water.

Viologen salts that allow hydrogen production in a basic medium owing to their more negative redox potentials have been described previously [7 - 9] (usually 2,2'-bipyridinium chlorides). The recent papers [7] on the use of zwitterionic 2,2'-bipyridinium 1 has prompted us to report our work on a new viologen that produces good yields of hydrogen in basic aqueous media up to pH 9.



1

## 2. Experimental details

Proton magnetic resonance (pmr) and carbon magnetic resonance (cmr) spectra were obtained using a Bruker WP80SY spectrometer. UV spectra were recorded using a Perkin-Elmer 550 spectrophotometer.

### 2.1. Synthesis of 1,1'-[(2,2'-bipyridinium)-1,1'-]dipropyl-3-sulphonate (1)

A solution of 0.78 g (5 mmol) 2,2'-bipyridine and 1.83 g (15 mmol) propanesultone in 12 ml *N,N*-dimethylformamide was refluxed for 24 h. The white precipitate was filtered off and washed several times with methanol to yield 1.1 g (55%) 1. (Pmr ( $\text{D}_2\text{O}$ ):  $\delta$  values are 9.3 (d,  $J = 5$  Hz, 2H), 8.85 (t,  $J = J' = 7$  Hz, 2H), 8.6 - 8.3 (m, 4H), 5.0 - 4.2 (m, 4H), 3.0 -

2.6 (m, 4H), 2.5 - 2.0 (m, 4H); cmr (D<sub>2</sub>O):  $\delta$  values are 149.3, 149.1, 143.3, 132.8, 132.6, 59.1, 48.0 and 26.9; UV (H<sub>2</sub>O):  $\lambda_m = 272$  nm. Analysis gives C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> ·  $\frac{3}{2}$ H<sub>2</sub>O, calculated wt. %: C, 44.96; H, 5.38; N, 6.56.)

### 2.2. Synthesis of 2,12-diphenethyl-7,8-dihydro-6H-dipyrido[1,2-a:2,1-c]-[1,4]diazepinium dibromide (4)

A solution of 200 mg (0.055 mmol) 4,4'-diphenethyl-2,2'-bipyridine [10] 3 in 4 ml 1,3-dibromopropane was heated at 125 °C for 15 h with magnetic stirring. The pale yellow precipitate was filtered off and washed with pentane to yield 278 mg (91%) 4. (Pmr (d<sub>6</sub>-dimethylsulphoxide at 37 °C):  $\delta$  values are 9.43 (d,  $J = 6$  Hz, 2H), 8.66 (d,  $J = 2$  Hz, 2H), 8.33 (dd,  $J = 6$  Hz,  $J' = 2$  Hz, 2H), 7.3 (broad s, 10H), 5.3 - 4.3 (m, 4H), 3.5 - 3.0 (m, 8H), 3.0 - 2.6 (m, 2H); cmr (d<sub>6</sub>-dimethylsulphoxide):  $\delta$  values are 163.0, 146.5, 143.0, 139.8, 131.7, 129.6, 128.9, 128.3, 126.1, 54.6, 36.5, 34.5 and 30.0; UV (H<sub>2</sub>O):  $\lambda_m = 286$  nm. Analysis gives C<sub>29</sub>H<sub>30</sub>N<sub>2</sub>Br<sub>2</sub> · H<sub>2</sub>O, calculated wt. %: C, 59.58; H, 5.48; N, 4.80.)

### 2.3. Synthesis of [(7,8-dihydro-6H-dipyrido[1,2-a:2,1-c][1,4]diazepinium)-2,12-di-4,4'-phenethylsulphonate (2)

1.5 ml concentrated sulphuric acid were added to 325 mg (0.574 mmol) diazepinium dibromide 4 and HBr evolution was immediately observed. When this ceased, the diazepinium salt was dissolved and the solution heated at 100 °C for 25 min with magnetic stirring. The crude material was poured into ice-water and NaHCO<sub>3</sub> was added at 0 °C to give pH 2 - 3. An oil formed which was separated from the aqueous solution and washed with water. This oil was dried under vacuum to yield 226 mg (70%) yellow solid 2. (Pmr (D<sub>2</sub>O + KCl):  $\delta$  values are 9.21 (d,  $J = 6$  Hz, 2H), 8.3 (dd,  $J = 6$  Hz,  $J' = 2$  Hz, 2H), 7.95 (d,  $J = 2$  Hz, 2H), 7.92, 7.82, 7.60 and 7.50 (AA'BB' system, 8H), 5.1 - 4.6 (m, 4H), 3.7 - 3.2 (m, 8H) and 3.2 - 2.9 (m, 2H); UV (H<sub>2</sub>O):  $\lambda_m = 286$  nm.)

### 2.4. Synthesis of 2,12-dimethyl-7,8-dihydro-6H-dipyrido[1,2-a:2,1-c][1,4]-diazepinium dibromide (5)

The procedure described by Homer and Tomlinson [11] was modified as follows. A solution of 5 ml 1,2-dibromopropane containing 368 mg (2 mmol) 4,4'-dimethyl-2,2'-bipyridine [12] was heated at 125 °C for 24 h with magnetic stirring. The white precipitate was filtered off and washed with acetone and pentane to yield 733 mg (95%) 5.

### 2.5. Irradiation conditions

All experiments were performed twice. 40 ml of solution was irradiated at 30 °C in an argon atmosphere with two 150 W halogen lamps utilizing a Wratten gelatin filter (Kodak CAT 149 5431) to cut off the radiation below 400 nm. Solution strengths were  $5 \times 10^{-5}$  M Ru(bpy)<sub>3</sub><sup>2+</sup>,  $10^{-3}$  M viologen,  $3 \times 10^{-5}$  M colloidal platinum and  $4 \times 10^{-2}$  M TEOA below pH 8 and  $10^{-2}$  M TEOA above pH 8.

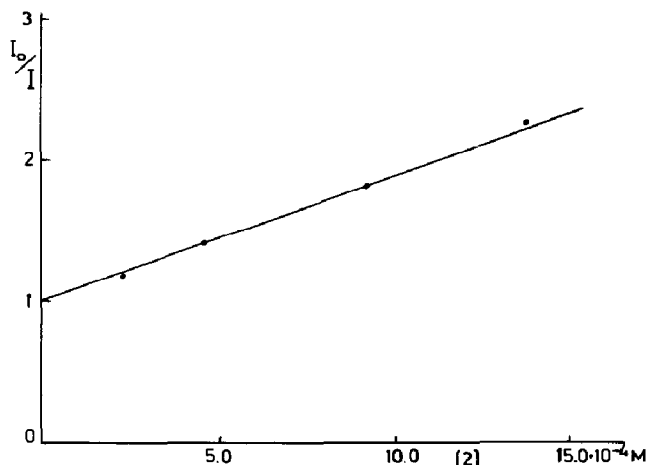


Fig. 1. Stern-Volmer plot of the quenching of the luminescence of  $\text{Ru}(\text{bpy})_3^{2+*}$  by 2 in water.

In the homogeneous solution experiments the hydrogen evolution stopped after 8 - 10 h irradiation; in heterogeneous systems it stopped after 12 - 14 h.

The solutions at pH 7 were buffered with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ . The pH of the basic solutions was controlled by adding the required quantities of 4 M HCl to the TEOA solutions. After the irradiation experiments the pH values of the solutions did not vary by more than  $\pm 0.1$  pH unit.

The actinometry was carried out with potassium ferrioxalate following the procedure described by J. G. Calvert [13].

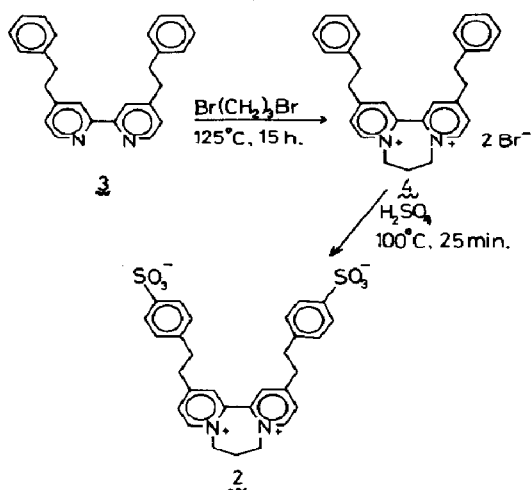
### 2.6. Quenching measurements

The samples for the quenching measurements in  $\text{H}_2\text{O}$  contained  $3.2 \times 10^{-6}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  with the appropriate concentration of added quencher (1, 2 or 4) and with enough  $[\text{N}(\text{C}_4\text{H}_9)_4]\text{Cl}$  to maintain the ionic strength at 0.1 M. In a typical experiment, solutions containing different concentrations of quencher were placed in quartz tubes and were degassed by bubbling through oxygen-free argon for 15 - 30 min. The samples were thermostatted at  $25 \pm 0.5$  °C and the emission measurements were made using a Perkin-Elmer 650-40 fluorescence spectrophotometer. The  $k_q$  values were calculated from the Stern-Volmer plots using  $\tau_0 = 0.58 \times 10^{-6}$  s for  $\text{Ru}(\text{bpy})_3^{2+*}$  in water [14].

## 3. Results and discussion

In order to design a good relay for use in  $\text{SiO}_2$  systems, a viologen with a reduction potential between about  $-0.7$  and  $-0.6$  V is needed, with sulphonate groups present to provide negative charges. 2,2'-Bipyridinium

salts are suitable for this purpose, although they cannot be sulphonated directly. This can only be achieved by quaternization of the nitrogens with sulphonated aliphatic hydrocarbon chains (as in Willner's viologen 1) or by introducing supplementary aromatic rings for further sulphonation. We have followed this second alternative and have quaternized the nitrogens with a hydrocarbon chain, thus compensating for the raising of the reduction potential on introducing alkyl groups into the bipyridine system (*cf.* the values of the reduction potentials for viologens given in ref. 9). Viologen 2 has thus been synthesized by nitrogen quaternization with 1,3-dibromopropane and subsequent sulphonation with concentrated sulphuric acid (the reverse sequence did not work) of the previously prepared [10] 4,4'-diphenethyl-2,2'-bipyridine 3.



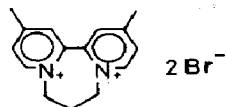
Scheme 1.

Viologen 2 has  $E_{1/2} = -0.65$  V versus normal hydrogen electrode (NHE) measured using cyclic voltammetry, while we have found using the same technique that viologen 1 has  $E_{1/2} = -0.63$  V (literature value [7],  $E^\circ = -0.75$  V). Moreover, our viologen shows completely reversible waves at  $100\text{ mV s}^{-1}$ ; this behaviour is not observed with viologen 1.

The constants  $k_q$  for the quenching of the  $\text{Ru}(\text{bpy})_3^{2+}$  luminescence by viologens 1, 2 and 4 were calculated from Stern-Volmer plots. In a homogeneous aqueous solution the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by viologen 2 ( $k_q = 1.52 \times 10^9\text{ l mol}^{-1}\text{ s}^{-1}$ ) is more effective than by methyl viologen (literature value [2],  $k_q = 1.03 \times 10^9\text{ l mol}^{-1}\text{ s}^{-1}$ ), by viologen 1 (literature value [7],  $k_q = 5.9 \times 10^8\text{ l mol}^{-1}\text{ s}^{-1}$ , in this study,  $k_q = 6.1 \times 10^8\text{ l mol}^{-1}\text{ s}^{-1}$ ) or by viologen 4 ( $k_q = 1.29 \times 10^9\text{ l mol}^{-1}\text{ s}^{-1}$ ). This behaviour has allowed us to work with low concentrations of viologen in our investigations of the photosensitized formation of hydrogen using colloidal platinum stabilized with poly(vinyl alcohol) [15] as a catalyst and  $\text{Ru}(\text{bpy})_3^{2+}$  as a photosensitizer.

A  $10^{-3}$  M solution of 2 quenches the fluorescence of  $\text{Ru}(\text{bpy})_3^{2+}$  with approximately the same efficiency as a  $10^{-2}$  M solution of 1, when these are adsorbed onto  $\text{SiO}_2$ .

Table 1 compares the quantum yields of hydrogen production (and actual volumes of hydrogen evolved per hour) using viologen 2 at different pHs in homogeneous solutions with the data we have obtained utilizing the other viologens 1 and 5.



5

It can be observed clearly that viologen 2 is as effective as the bridged viologen 5 which has been the most effective described up till now at pH 7. The greater effectiveness of viologens 2 and 5 compared with viologen 1 may

TABLE 1

Quantum yields and hydrogen production in homogeneous solutions

pH	$\Phi$			Hydrogen production (ml h <sup>-1</sup> )		
	1	2	5	1	2	5
7		$4 \times 10^{-2}$	$4 \times 10^{-2}$		2	2
8	$6 \times 10^{-3}$	$2.3 \times 10^{-2}$		0.3	1.15	
8.8		$2.4 \times 10^{-3}$			0.12	
9.1	$1.4 \times 10^{-3}$	$1.8 \times 10^{-3}$		0.07	0.09	

[ $\text{Ru}(\text{bpy})_3$ ]<sup>2+</sup> =  $5 \times 10^{-5}$  M; [viologen] =  $10^{-3}$  M; [Pt] =  $3 \times 10^{-5}$  M; [TEOA] =  $4 \times 10^{-2}$  M at pH 8 or below; [TEOA] =  $10^{-2}$  M above pH 8.

TABLE 2

Quantum yields and hydrogen production using  $\text{SiO}_2$  particles of diameter 120 Å (0.5% w/v colloidal system (i.e. a 0.5% slurry suspension of silica in water))

pH	$\Phi$			Hydrogen production (ml h <sup>-1</sup> )		
	1	1 <sup>a</sup>	2	1	1 <sup>a</sup>	2
8	$2.6 \times 10^{-3}$		$1 \times 10^{-2}$	0.13		0.5
8.5		$2.2 \times 10^{-3}$				
8.8			$1.2 \times 10^{-2}$			0.6
9.1	$1.2 \times 10^{-3}$		$6.4 \times 10^{-3}$	0.06		0.32
9.2		$1.4 \times 10^{-3}$				

[ $\text{Ru}(\text{bpy})_3$ ]<sup>2+</sup> =  $5 \times 10^{-5}$  M; [viologen] =  $10^{-3}$  M; [Pt] =  $3 \times 10^{-5}$  M; [TEOA] =  $4 \times 10^{-2}$  M at pH 8; [TEOA] =  $10^{-2}$  M above pH 8.

<sup>a</sup>Data from ref. 7.

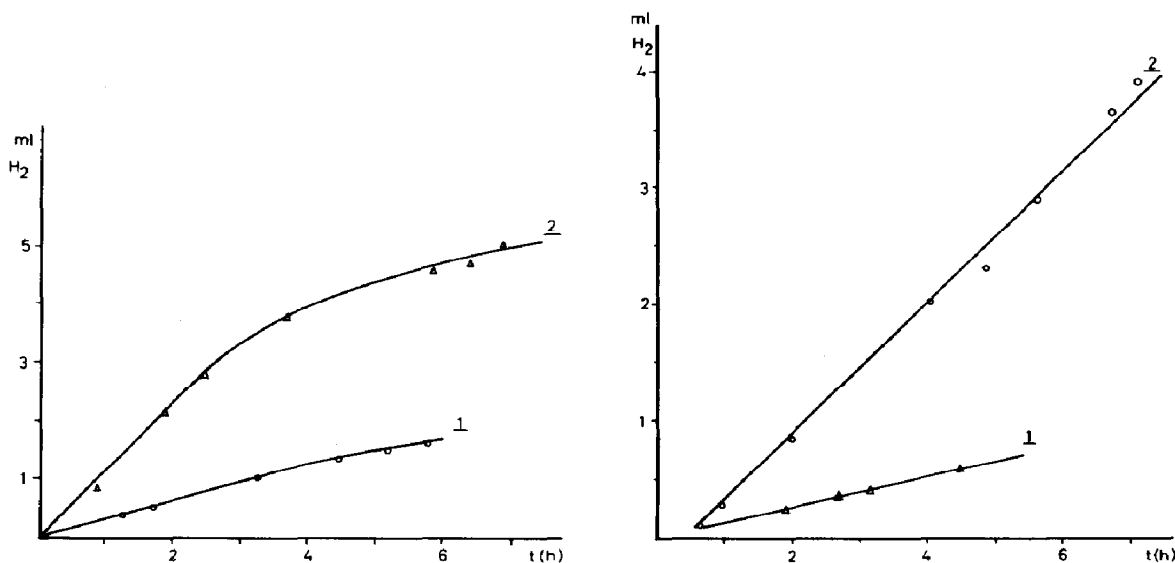


Fig. 2. Hydrogen production in homogeneous solutions at pH 8:  $[\text{Ru}(\text{bpy})_3]^{2+} = 5 \times 10^{-5} \text{ M}$ ;  $[\text{viologen}] = 10^{-3} \text{ M}$ ;  $[\text{Pt}] = 3 \times 10^{-5} \text{ M}$ ;  $[\text{TEOA}] = 4 \times 10^{-2} \text{ M}$ .

Fig. 3. Hydrogen production using  $\text{SiO}_2$  particles of 120 Å diameter (0.5% w/v colloidal system) at pH 8:  $[\text{Ru}(\text{bpy})_3]^{2+} = 5 \times 10^{-5} \text{ M}$ ;  $[\text{viologen}] = 10^{-3} \text{ M}$ ;  $[\text{Pt}] = 3 \times 10^{-5} \text{ M}$ ;  $[\text{TEOA}] = 4 \times 10^{-2} \text{ M}$ .

be due to structural effects (the hydrocarbon bridge forces the bipyridinium system to be more coplanar). In spite of Willner's results we do observe some hydrogen formation both in using our viologen and in using 1 at pH 9.

While viologen 5 is not suitable for use in heterogeneous  $\text{SiO}_2$  systems (diameter of  $\text{SiO}_2$  particles, 120 Å), both 2 and 1 are appropriate since the reduced form (radical anion) is ejected from the negative  $\text{SiO}_2$  surface, especially in basic aqueous media. However, our viologen is more effective than 1 for hydrogen evolution, as shown in Table 2.

At pH 8.0, 2 gives a quantum yield  $\Phi$  of hydrogen formation of  $1 \times 10^{-2}$  while we have found that 1 gives  $\Phi = 2.6 \times 10^{-3}$ ; a fourfold increase in quantum yield is thus obtained with viologen 2.

The yield of hydrogen at higher pHs is of more interest, where the  $\text{SiO}_2$  is ionized. Thus at pH 8.8 2 gives  $\Phi = 1.2 \times 10^{-2}$ , while Willner reported  $\Phi = 2.2 \times 10^{-3}$  for 1 at pH 8.5. Our viologen is still five times more effective at pH 9.1.

This difference in effectiveness could be due to the higher efficiency of viologen 2 in quenching  $\text{Ru}(\text{bpy})_3^{2+*}$  and to the higher degree of reversibility of 2 in the redox processes which gives a higher turnover number than viologen 1.

In conclusion, we have presented herein the synthesis of a new viologen (2) that is very effective in photosensitized hydrogen evolution, not only since it can be used at very low concentrations but also since it functions in basic solutions with  $\text{SiO}_2$  present.

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