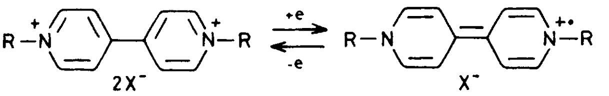
The Synthesis and Electrochemical Study of New Electrochromic Viologen-based Materials

John A. Barltrop † **and Andrew C. Jackson** *,‡
Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

A range of diquaternary salts of 4,4'-bipyridine and 3,8-phenanthroline were prepared and subsequently screened using electrochemical and spectroscopic techniques. It was determined that the stability of the radical film deposited on cathodic reduction of aqueous solutions of these salts may be strongly influenced by symmetry, steric, and electronic factors. From this basis, it was possible to design a viologen, 1,1'-bis-(2-methylbenzyl)-2-methyl-4,4'-bipyridinium dibromide (9), having electrochromic properties for electronic display applications superior to those already in existence. A radical film of mixed composition was found to be less susceptible to ageing effects than films generated from the individual dicationic salts.

In recent years there has been considerable interest in the development of a new electronic display technology based on the electrochromism of 4,4'-bipyridinium salts (more commonly termed viologens).[1] A practical electrochromic effect requires the electrochemical reduction of the colourless, aqueous solution of the dicationic salt to a highly coloured, insoluble radical ion salt that is deposited as a film on the cathode [equation (i)]. In principle, the film will remain held on the surface with the electrode isolated but may be erased rapidly by electrochemical oxidation. Attention has generally focused on the diheptyl salt [(1), $R = C_7H_{15}$, $X = Br$ or H_2PO_4], the principal drawback to which is the so-called recrystallisation effect,[2] observed following deposition of the radical ion salt film. It has been shown that films left on open-circuit gradually assume a greater degree of optical anisotropy, consistent with a reorientation of the molecules to a higher degree of ordering.[3] The formation of polycrystalline conglomerates has also been noted.[2b] In any event, the ageing process (which will be referred to as recrystallisation, regardless of whether or not an actual crystallisation is known to occur) results in a drop in erase efficiency. Jasinski [1d,2a] has reported that the physical properties of the film are dependent on the nature of the anion, and that by use of dihydrogenphosphate in place of bromide the detrimental effects of ageing are reduced. In this paper we report the influence of molecular structure on the stability of the radical ion salt film.

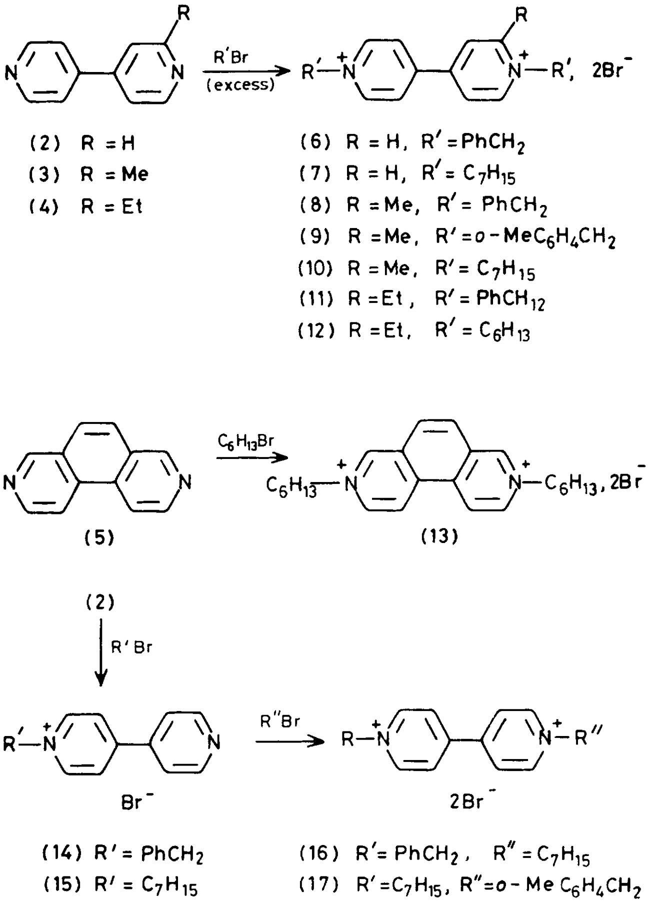


(1) (i)

Discussion

Synthesis.—Diquaternary salts having equivalent *N*-alkyl groups [(6)—(13)] were prepared simply by the reaction of the corresponding base with an excess of the appropriate alkyl bromide (Scheme). Acetonitrile was the preferred solvent owing to its high dielectric constant and reasonably high boiling point (82 °C). In general, the diquaternary salts precipitated out of solution and could be isolated by filtration. Typically, one recrystallisation was sufficient to provide a salt pure by analysis and free from any mono-quaternised impurity. In order to diquaternarise 2-substituted bipyridines it was often necessary to perform the reaction in the neat alkylating agent. The synthesis of viologens having non-equivalent *N*-alkyl groups [(16) and (17)] required isolation of the monoquaternary precursors.

2-Ethyl-4,4'-bipyridine (4) was prepared by homolytic alkylation of commercially available 4,4'-bipyridine using the procedure of Minisci *et al.*[4] Two methods were investigated for the synthesis of 2-methyl-4,4'-bipyridine (3). The route initially chosen was that described by Schmalzl and Summers,[5] involving treatment of 4,4'-bipyridine with methyl-lithium.



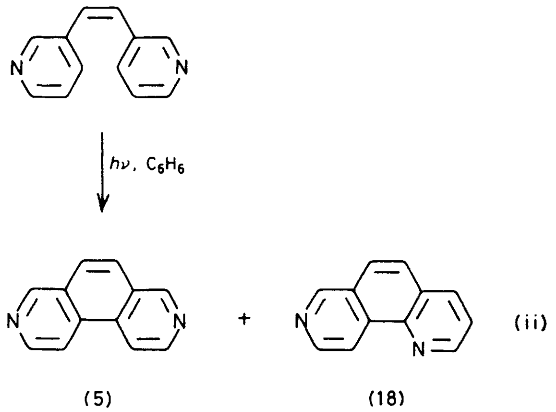
Scheme. Synthesis of diquaternary salts

---

† *Present address:* Department of Chemistry, University of South Florida, Tampa, Fl 33620, U.S.A.

‡ *Present address:* Department of Chemistry, Imperial College, London SW7 2AY.

A drawback to this method lies in the formation of a relatively large amount of tar. This is avoided using an adaptation of the Minisci procedure which affords the alkylated bipyridine, free from polymeric materials, in comparable yield. 3,8-Phenanthroline (5) was prepared using a modification of the method of Perkampus and Kassebeer [6] [equation (ii)].



(5) (18)

Electrochemical Studies.—The diquaternary salts prepared were evaluated using a microcomputer-controlled spectro-electrochemical system.[7] All tests were performed on 10mM solutions in distilled water containing 0.2M-potassium bromide as supporting electrolyte. The test solutions were continually degassed by a steady stream of argon. Cyclic voltammetry on platinum-wire working electrodes was employed for initial screening of the samples (see Table). Almost without exception, the viologens studied conformed to the expected behaviour [8] on the first potential scan. Variation away from the ideal resulted from recrystallisation effects or side reactions [9] over a large number of cycles. Such effects could be studied in more detail by appropriate modification of the voltage waveform. Viologen diffusion coefficients were estimated from peak cathodic currents.[8] The use of optically transparent Nesatron working electrodes enabled a more critical assessment of electrochromic behaviour through the acquisition of optical data. In this way it was possible to record the visible absorption spectra of a radical film at varying intervals of time following deposition or to monitor the absorbance at a selected wavelength throughout a given potential cycle.

Table. Results for cyclic voltammetry on platinum-wire working electrodes

Compd.	$-E_1$ cath.[a]/ mV	$-E_2$ cath.[a]/ mV	$\lambda_{max.}$ [b]/ nm ($V^{\cdot+}$)	ε [c]/l mol^{-1} cm^{-1} ($V^{\cdot+}$)	$D_{V^{2+}}$ [d]/ cm^2 s^{-1}
(6)	478	834	568	8 500	7.9×10^{-6}
(7)	514	850	554	11 400	7.3×10^{-6}
(8)	522	890	527	7 100	4.6×10^{-6}
(9)	510	910	538	6 900	3.8×10^{-6}
(10)	540	854	547	11 400	2.4×10^{-6}
(11)	514	812	548	7 900	4.2×10^{-6}
(12)	590	810	547	5 000	1.8×10^{-6}
(13)	534	916	576, 614	6 400	5.6×10^{-6}
(16)	504	824	549	8 900	5.2×10^{-6}
(17)	482	820	550	10 500	5.2×10^{-6}

[a] Peak potentials in mV relative to a saturated calomel electrode, measured at a scan rate of 1 V s^{-1}. [b] Measured from spectra of radical films recorded 1 s after commencement of deposition. [c] The molar decadic extinction coefficient of the radical film measured at or near the absorption maximum immediately after deposition. [d] The viologen diffusion coefficient.

As the basis for investigation, we considered that a recrystallisation process involving a molecular reorientation to a more highly ordered structure should be disfavoured by the removal of symmetry from the viologen. Electrochemical tests performed on benzyl heptyl viologen (16) reinforced this hypothesis. In the case of diheptyl viologen, the absorption band of the radical film was seen to have developed a shoulder, attributable to a recrystallisation process,[7] within 0.5 s of deposition. Under comparable conditions, the absorption spectrum of the benzyl heptyl radical film revealed a band with a maximum at 549 nm but with no shoulder. However, with the film held on the isolated electrode a shoulder was seen to develop within 60 s, gradually gaining in prominence with time. Voltammetric tests performed on platinum electrodes confirmed the presence of a second electroactive species formed on a time-scale of several seconds following film deposition. Once the recrystallisation process was allowed to occur, however, the film exhibited a poor erase behaviour relative to diheptyl viologen; such an apparent stabilising effect of an *N*-benzyl group has been noted previously.[7] In an independent study, Barna and Fish [10] have shown benzyl heptyl viologen dihydrogenphosphate to have a superior long-term performance to the corresponding diheptyl salt. A steric effect of the benzyl moiety, rather than the use of symmetry arguments, was invoked by these authors to explain the improved behaviour.

Evidence that steric effects might indeed play an important role in the recrystallisation process was afforded through a comparison between the properties of benzyl heptyl viologen (16) with those of the salt (17), which differs only in the presence of a methyl substituent in the *ortho*-position of the phenyl ring. It became clear that the effect of the methyl substituent was to improve significantly the erase behaviour of the recrystallised radical film; presumably, in this case, the substituent acts to destabilise a more highly ordered arrangement of the radical ion salt molecules. We will describe the use of other unsymmetrical diquaternary salts of 4,4′-bipyridine in a later publication.[11]

The potential for influencing electrochromic performance through symmetry and steric modifications led us to examine the dibenzyl 2-methyl salt (8). It was found that the introduction of the methyl substituent on the bipyridine nucleus had a marked effect in delaying recrystallisation of the radical ion salt film; indeed, thick films (*ca*. 9 mC cm^{-2}) showed no evidence of change over periods of up to 300 s hold on open circuit. Absorption spectra of the film showed little variation until after a time of 10—15 min had elapsed; this compares with a time-scale of 0.5 s or less in the case of either diheptyl or dibenzyl viologen. Although considerations of symmetry cannot be ignored, it is logical to suppose that the delay in recrystallisation is primarily a consequence of steric interactions. We suggest that the methyl substituent operates by imposing a constraint on the orientation of the benzyl group relative to the bipyridine nucleus. In this event, conformations in which the phenyl ring lies well out of the plane of the nucleus will be favoured, and a higher barrier to reorientation must result. Unfortunately, the high stability to electrochemical oxidation of the recrystallised film renders this material unsuitable for display applications.

It is interesting to note that radical films derived from diheptyl 2-methyl viologen (10) begin to undergo an ageing process within 0.5 s of deposition, as judged from absorption spectra. Such a result is consistent with the above argument, as the heptyl chain must barely be susceptible to steric interaction with the 2-methyl substituent. It was, however, surprising to learn that recrystallised radical films of this viologen were less readily erased than those of the unsubstituted salt (7); the effect is presumably due to an electronic influence of the methyl substituent.

The concept that steric resistance to a reorientation process results from an interaction between a substituent on the pyridine ring and an *N*-benzyl group implies that such a resistance might be sharply increased by the presence of an *ortho*-substituent on the phenyl ring. Evaluation of bis-(2-methylbenzyl) 2-methyl viologen (9) lent reinforcement to this argument. Thus, the absorption spectrum of the corresponding radical film ($\lambda_{max.}$ 539 nm) remained essentially unchanged over open-circuit hold periods of as long as 25 min. In contrast to dibenzyl 2-methyl viologen (8), radical films allowed to stand over such a period of time could still be quantitatively and rapidly erased by electrochemical oxidation. On testing the modified viologen under practical conditions by pulse-driving the system at 0.5 Hz (1 s at 0 V, 1 s at −800 mV) using a Nesatron working electrode, it was found that the change in absorbance at 540 nm, on depositing the radical film, remained constant over 20 000 cycles with no significant increase in background absorbance. This compares with tests performed under comparable conditions on diheptyl viologen (7) in which breakdown occurred within 5 000—10 000 cycles. At this concentration (10 mM) there is no doubt that the electrochromic properties of this modified salt are markedly superior to those of diheptyl viologen.

We examined the viologen salts (11) and (12), based on 2-ethyl-4,4′-bipyridine, in the expectation that the bulkier 2-substituent would further disfavour a recrystallisation process. This proved to be the case. For example, absorption spectra recorded of dibenzyl 2-ethyl viologen radical films held on open-circuit for as long as 18 min showed no variation in form, and consisted of a broad, featureless band with a maximum at 548 nm. However, these systems were not tested exhaustively owing to the narrow separation of the first and second reduction potentials, attributable in part to the fact that donating groups should stabilise the parent dication.

An evaluation of the phenanthrolinium salt (13) was prompted by the potential for a particularly strong delocalisation of the unpaired electron in the radical ion. Hexyl was adopted as the *N*-alkyl group so as to maintain solubility characteristics similar to those of diheptyl viologen. In practice, the electrochemical properties of the two salts were comparable, which in turn suggested the use of an active medium comprising a combination of the two salts to generate a radical film of mixed composition. The disorder introduced into the film is expected to provide a barrier to the attainment of an ordered crystalline structure. Tests were performed on a solution containing equimolar amounts of both electroactive components. The mixed composition of a radical film deposited at −800 mV was evident on comparing the absorption spectrum with those derived from the pure components under identical conditions. Specifically, when compared with spectra of diheptyl viologen radical films, the absorption band showed a marked extension to longer wavelengths, while maintaining the extinction coefficient at the absorption maximum (557 nm). The effect of the mixed composition of the film was found not to be to delay a recrystallisation, but to lower the activation barrier to reoxidation of the recrystallised form. Thus, although changes in the light absorbing properties of films held on open-circuit were consistent with the occurrence of a rapid recrystallisation process, in strong contrast to diheptyl viologen radical films this was not accompanied by any loss in erase efficiency.

In conclusion, we have demonstrated how symmetry, steric, and electronic factors can influence the stability of a viologen radical ion salt film. Our studies have led to the design of a viologen (9) which we believe to show superior electrochromic behaviour to salts hitherto proposed for display applications. Further, we have shown that viologen solutions of mixed composition may be used to advantage.

Experimental

Electrochemical Studies.—The viologens tested were dissolved in distilled water containing potassium bromide (0.2M). Solutions were continually degassed by the passage of a steady stream of argon. The three-compartment electrochemical cell consisted of a working electrode, a platinum counter electrode, and a saturated calomel reference electrode, (SCE). Cyclic voltammograms were recorded using a platinum-wire working electrode. The provision of two quartz windows allowed the spectroscopic study of films deposited on to the surface of an optically transparent electrode (OTE). The OTEs used consisted of tin-doped indium-oxide-coated glass (Nesatron) of sheet resistance 27Ω/□ and were cleaned before use [12] by treatment with 30% potassium hydroxide in ethanol–water (1 : 1). The generation of selected electrical waveforms and the acquisition and storage of data was microcomputer controlled.[7] Optical data were accumulated using a Pye Unicam SP 1800 spectrophotometer interfaced to the computer.

Chemical Synthesis.—Melting points were determined on a Kofler block and are uncorrected. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R32 spectrometer operating at 90 MHz, using Me_4Si as the standard. U.v. spectra were obtained on a Perkin-Elmer 555 spectrophotometer. Mass spectra were recorded using a VG-ZAB-1F instrument. Microanalyses were carried out under the supervision of Dr. F. B. Strauss.

Acetonitrile was dried (CaH_2) and redistilled before use. Alkyl bromides used for quaternisations were dried ($MgSO_4$) and redistilled. The boiling range of the light petroleum was 40—60 °C. 1,1′-Diheptyl- and 1,1′-dibenzyl-4,4′-bipyridinium dibromide were prepared as reported previously.[7]

1-*Benzyl*-4-(4-*pyridyl*)*pyridinium bromide* (14). A solution of 4,4′-bipyridine (2.0 g, 13 mmol) and benzyl bromide (1.71 g, 10 mmol) in dry acetone (100 ml) was heated at reflux for 1 h. The solvent was evaporated *in vacuo* down to a volume of *ca.* 10 ml from which the precipitated salt was collected then washed with ether. Recrystallisation from ethanol–ether gave the *monoquaternary salt* which was dried *in vacuo* (1.71 g, 52%); m.p. 239—241.5 °C; ^{1}H n.m.r., δ (CF_3CO_2H) 6.0 (s, 2 H), 7.5 (s, 5 H), 8.6 (d, 4 H), and 9.1 (m, 4 H); $\lambda_{max.}$ (H_2O) 260 nm (log ε 4.33) (Found: C, 62.19; H, 4.67; N, 8.44. $C_{17}H_{15}N_2Br$ requires C, 62.40; H, 4.62; N, 8.56%).

1-*Benzyl*-1′-*heptyl*-4,4′-*bipyridinium dibromide* (16). A suspension of 1-benzyl-4-(4′-pyridyl)pyridinium bromide (1.70 g, 5 mmol) in acetonitrile (20 ml) was treated with 1-bromoheptane (3.0 g) and the mixture heated at reflux, with stirring, for 48 h. The precipitated salt was collected and washed with acetonitrile and ether. Recrystallisation from ethanol gave the *dibromide* as bright yellow plates that were dried *in vacuo* (0.60 g, 23%); m.p. 215—219 °C; ^{1}H n.m.r., δ (CF_3CO_2D) 0.8—2.5 (m, 13 H), 4.79 (t, 2 H, *J* 8 Hz), 5.96 (s, 2 H), 7.65 (s, 5 H), 8.67 (d, 4 H), and 9.1 (m, 4 H); $\lambda_{max.}$ (H_2O) 260 nm (log ε 4.38) (Found: C, 56.94; H, 6.26; Br, 31.76; N, 5.29. $C_{24}H_{30}Br_2N_2$ requires C, 56.93; H, 5.97; Br, 31.56; N, 5.53%).

1-*Heptyl*-4-(4-*pyridyl*)*pyridinium bromide* [13] (15). 4,4′-Bipyridine (6.25 g, 40 mmol) and 1-bromoheptane (4.0 ml, 25 mmol) were heated together in a sealed glass tube at 80—90 °C for 20 h. After cooling, the tube was opened and the yellow crystalline material extracted and washed well with ether. The product was transferred into a Soxhlet thimble and extracted with dry acetone (200 ml) over several hours. Material remaining in the thimble (1.22 g) was recrystallised from ethanol to give bright yellow plates of 1,1′-diheptyl-4,4′-bipyridinium dibromide (0.94 g, 14%); m.p. 293 °C. On cooling the acetone extract to −20 °C, pale yellow crystals separated, which were collected and washed with a little cold acetone followed by ether. Recrystallisation from acetone gave cream-coloured crystals of the monoquaternary salt which were dried *in vacuo* (2.96 g); m.p. 123—124 °C. A further recrystallisation gave the pure material (2.23 g, 26%); m.p. 123.5—125 °C (lit.,[13] 89—91 °C); ^{1}H n.m.r., δ (CF_3CO_2D) 0.8—2.5 (m, 13 H), 4.82 (t, 2 H, *J* 8 Hz), 8.63 (d, 4 H, *J* 6 Hz), and 9.17 (m, 4 H).

1-*Heptyl*-1′-(2-*methylbenzyl*)-4,4′-*bipyridinium dibromide* (17). A solution of 1-heptyl-4-(4′-pyridyl)pyridinium bromide (1.01 g, 3 mmol) and 2-methylbenzyl bromide (0.6 g) in acetonitrile (20 ml) was heated at reflux, with stirring, for 5 h. The precipitated salt was collected and washed with acetonitrile and ether. Recrystallisation from ethanol gave the *dibromide* as bright yellow crystals, which were dried *in vacuo* (1.09 g, 70%); m.p. 217—219 °C; ^{1}H n.m.r., δ (CF_3CO_2D) 0.8—2.5 (m, 13 H), 2.34 (s, 3 H), 4.80 (t, 2 H, *J* 8 Hz), 6.02 (s, 2 H), 7.43 (s, 4 H), 8.6—8.9 (m, 4 H), and 8.9—9.2 (m, 4 H); $\lambda_{max.}$ (H_2O) 260 nm (log ε 4.35) (Found: C, 57.70; H, 6.12; Br, 30.60; N, 5.39. $C_{25}H_{32}Br_2N_2$ requires C, 57.71; H, 6.20; Br, 30.71; N, 5.38%).

2-*Ethyl*-4,4′-*bipyridine*[4] (4). 4,4′-Bipyridine (15.62 g, 0.1 mol) was dissolved in a solution of 98% sulphuric acid (5.3 ml) in water (70 ml). To this was added propionic acid (37.0 g, 0.5 (mol) and a solution of silver nitrate (1.70 g, 0.01 mmol) in water (20 ml). The resultant mixture was heated to 80 °C and maintained at that temperature for 30 min, at which point ammonium persulphate (22.82 g, 0.1 mol) was added, portionwise, as a solid. After vigorous evolution of carbon dioxide had ceased, the solution was heated at reflux for a further 30 min, allowed to cool, made alkaline by addition of 0.880 ammonia, then extracted with ether (8 × 150 ml). The extracts were dried ($CaCl_2$) and evaporated *in vacuo*, and the residue introduced as a solution in chloroform on to a column of alumina packed in petroleum. Elution with 2% ethyl acetate in ether gave first 2,2′,6-*triethyl*-4,4′-*bipyridine* as a colourless oil (80 mg); ^{1}H n.m.r., δ ($CDCl_3$) 1.32 (t, 6 H, *J* 7 Hz), 1.34 (t, 3 H, *J* 7 Hz), 2.86 (q, 4 H, *J* 7 Hz), 2.89 (q, 2 H, *J* 7 Hz), 7.15—7.4 (m, 4 H), and 8.59 (d, 1 H, *J* 5 Hz); $\lambda_{max.}$ (EtOH) 236 (log ε 4.06) and 273 nm (3.67); *m*/*z* 240 (M^+, 86), 239 (100), 224 (10), 212 (19), and 119 (14) (Found: C, 78.88; H, 8.39; N, 11.76. $C_{16}H_{20}N_2$ requires C, 79.96; H, 8.39; N, 11.66%).

The second band gave 2,2′-diethyl-4,4′-bipyridine as a colourless oil (0.70 g, 3%); ^{1}H n.m.r., δ ($CDCl_3$) 1.35 (t, 6 H, *J* 8 Hz), 2.90 (q, 4 H, *J* 8 Hz), 7.25—7.4 (m, 4 H), and 8.62 (d, 2 H, *J* 5 Hz); *m*/*z* 212 (M^+, 94), 211 (100), 184 (23), 105 (19), and 83 (25).

The third band gave 2-ethyl-4,4′-bipyridine as a colourless oil (2.86 g, 16%); ^{1}H n.m.r., δ ($CDCl_3$) 1.34 (t, 3 H, *J* 8 Hz), 2.91 (q, 2 H, *J* 8 Hz), 7.25—7.6 (m, 4 H), and 8.6—8.8 (m, 3 H); $\lambda_{max.}$ (EtOH) 239 nm (log ε 4.03); *m*/*z* 184 (M^+, 79), 183 (100), 156 (19), 155 (12), 83 (15), and 51 (11). Unreacted 4,4′-bipyridine was eluted later.

2-*Methyl*-4,4′-*bipyridine* (3). 2-Methyl-4,4′-bipyridine was obtained by a similar procedure to that detailed above, using acetic acid in place of propionic acid.

Chromatography gave trace amounts of 2,2′,6-*trimethyl*-4,4′-*bipyridine* first as a white crystalline solid; ^{1}H n.m.r., δ ($CDCl_3$) 2.61 (s, 6 H), 2.63 (s, 3 H), 7.18 (s, 2 H), 7.26 (s, 1 H), 7.36 (br, 1 H), and 8.59 (d, 1 H, *J* 5 Hz).

The second band gave 2,2′-dimethyl-4,4′-bipyridine (0.34 g, 2%); m.p. 81—83 °C (lit.,[14] 81—83 °C).

The third band gave 2-methyl-4,4′-bipyridine (2.71 g, 16%) which crystallised from ether–light petroleum (1.83 g, 11%); m.p. 92—93 °C (lit.,[5] 93 °C). Unreacted 4,4′-bipyridine was eluted later.

1,1′-*Dibenzyl*-2-*methyl*-4,4′-*bipyridinium dibromide* (8). A solution of 2-methyl-4,4′-bipyridine (0.34 g, 2 mmol) and benzyl bromide (1.03 g, 6 mmol) in acetonitrile (20 ml) was heated at reflux, with stirring, for 2 days. The precipitated salt was collected and washed with acetonitrile and ether. Recrystallisation from ethanol gave the *dibromide* as bright yellow plates, which were dried *in vacuo* (0.62 g, 61%); m.p. 253—255 °C (decomp.); ^{1}H n.m.r., δ(CF_3CO_2H) 3.02 (s, 3 H), 5.84 (s, 2 H), 5.89 (s, 2 H), 7.2—7.6 (m, 10 H), 8.2—8.7 (m, 4 H), 8.87 (d, 1 H, *J* 6 Hz), and 9.07 (d, 2 H, *J* 6 Hz); $\lambda_{max.}$ (H_2O) 257 nm (log ε 4.34) (Found: C, 58.32; H, 4.79; Br, 31.42; N, 5.57. $C_{25}H_{24}Br_2N_2$ requires C, 58.61; H, 4.72; Br, 31.20; N, 5.47%).

1,1′-*Bis*-(2-*methylbenzyl*)-2-*methyl*-4,4′-*bipyridinium dibromide* (9). A solution of 2-methyl-4,4′-bipyridine (0.43 g, 2.5 mmol) and 2-methylbenzyl bromide (1.48 g, 8 mmol) in acetonitrile (20 ml) was heated at reflux, with stirring, for 4 days. The precipitated salt was collected and washed with acetonitrile and ether. Recrystallisation from ethanol–methanol (5 : 1) gave the *dibromide* as bright yellow crystals, which were dried *in vacuo* (0.98 g, 72%); m.p. 295—299 °C (decomp.); ^{1}H n.m.r., δ (CF_3CO_2D) 2.34 (s, 3 H), 2.37 (s, 3 H), 3.10 (s, 3 H), 5.87 (s, 2 H), 6.01 (s, 2 H), 6.9—7.6 (m, 8 H), 8.3—8.5 (m, 1 H), 8.5—8.8 (m, 4 H), and 9.03 (d, 2 H, *J* 6 Hz); $\lambda_{max.}$ (H_2O) 258 nm (log ε 4.43) (Found: C, 60.21; H, 5.30; Br, 29.86; N, 5.29. $C_{27}H_{28}Br_2N_2$ requires C, 60.02; H, 5.22; Br, 29.58; N, 5.18%).

1,1′-*Diheptyl*-2-*methyl*-4,4′-*bipyridinium dibromide* (10). A solution of 2-methyl-4,4′-bipyridine (0.68 g, 4 mmol) in 1-bromoheptane (15 ml) was heated at 100 °C, with stirring, for 7 days. The precipitated salt was collected and washed with acetone and ether. Recrystallisation from ethanol–ethyl acetate gave the *dibromide* as a yellow microcrystalline powder, which was dried *in vacuo* (0.87 g, 41%); m.p. 270 °C (decomp.); ^{1}H n.m.r., δ (CF_3CO_2H) 0.7—2.4 (m, 26 H), 3.04 (s, 3 H), 4.5—4.9 (m, 4 H), 8.4—8.8 (m, 4 H), and 8.9—9.2 (m, 3 H); $\lambda_{max.}$ (H_2O) 261 nm (log ε 4.29) (Found: C, 56.59; H, 7.50; N,5. 34; Br, 29.85. $C_{25}H_{40}N_2Br_2$ requires C, 56.83; H, 7.63; N, 5.30; Br, 30.24%).

1,1′-*Dibenzyl*-2-*ethyl*-4,4′-*bipyridinium dibromide* (11). A solution of 2-ethyl-4,4′-bipyridine (0.50 g, 2.7 mmol) and benzyl bromide (1.54 g, 9 mmol) in acetonitrile (20 ml) was heated at reflux, with stirring, for 4 days. The precipitated salt was collected and washed with acetonitrile and ether. Recrystallisation from ethanol–acetone (1 : 1) gave the *dibromide* as bright yellow crystals, which were dried *in vacuo* (0.53 g, 36%); m.p. 187—190 °C; ^{1}H n.m.r., δ(CF_3CO_2D) 1.48 (t, 3 H, *J* 7 Hz), 3.34 (q, 2 H, *J* 7 Hz), 5.88 (s, 2 H), 5.90 (s, 2 H), 7.15—7.6 (m, 10 H), 8.3—8.5 (m, 2 H), 8.62 (d, 2 H, *J* 6 Hz), 8.89 (d, 1 H, *J* 6 Hz), and 9.09 (d, 2 H, *J* 6 Hz); $\lambda_{max.}$ (H_2O) 257 nm (log ε 4.33) (Found: C, 57.59; H, 5.36; Br, 29.55; N, 4.99. $C_{26}H_{26}Br_2N_2,2H_2O$ requires C, 57.37; H, 5.18; Br, 29.36; N, 5.15%).

1,1′-*Dihexyl*-2-*ethyl*-4,4′-*bipyridinium dibromide* (12). A solution of 2-ethyl-4,4′-bipyridine (0.84 g, 4.5 mmol) in 1-bromohexane (15 ml) was heated at 90 °C, with stirring, for 7 days. The precipitated salt was collected and washed with acetone and ether. Recrystallisation from ethanol–ethyl acetate gave the *dibromide* as a bright yellow microcrystalline powder, which was dried *in vacuo* (0.79 g, 31%); m.p. 218—222 °C; ^{1}H n.m.r., δ (CF_3CO_2D) 0.8—2.4 (m, 25 H), 3.46 (q, 2 H, *J* 7 Hz), 4.6—4.9 (m, 4 H), 8.4—8.55 (m, 2 H), 8.6—8.8 (m, 2 H), and 8.9—9.2 (m, 3 H); $\lambda_{max.}$ (H_2O) 260 nm (log ε 4.22) (Found: C, 52.47; H, 7.70; Br, 28.79; N, 5.05. $C_{24}H_{38}Br_2N_2,2H_2O$ requires C, 52.37; H, 7.69; Br, 29.03; N, 5.09%).

3,8-*Phenanthroline* (5). The method used was a modification of that of Perkampus and Kassebeer.[6]

A stirred solution of (*Z*)-3,3′-(1,2-ethenediyl)bipyridine [15] (1.17 g, 6.4 mmol) in thiophene-free benzene (1 000 ml) was irradiated in a quartz immersion well apparatus fitted with a 125 W medium-pressure mercury lamp for 36 h. Throughout the photolysis a steady stream of oxygen through the solution was maintained. After removal of a small amount of precipitated polymeric material, the solution was concentrated *in vacuo* to yield a residual oil, which was dissolved in chloroform (*ca.* 30 ml) and introduced on to a column of alumina packed in light petroleum. Elution with 2% ethyl acetate in ether gave, first, 1,8-phenanthroline (18) as a pale yellow oil that crystallised (282 mg, 24%); m.p. 110—113.5 °C (lit.,[6] 100—104 °C); ^{1}H n.m.r. δ ($CDCl_3$) 7.5—7.9 (m, 3 H), 8.17 (dd, 1 H), 8.75—9.05 (m, 3 H), and 9.26 (s, 1 H). Later fractions gave pure 3,8-phenanthroline (5) as a white crystalline solid (195 mg, 17%); m.p. 145—149 °C (lit.,[6] 139—141 °C); ^{1}H n.m.r., δ ($CDCl_3$) 7.89 (s, 2 H), 8.35 (d, 2 H, *J* 6 Hz), 8.83 (d, 2 H, *J* 6 Hz), and 9.30 (s, 2 H).

3,8-*Dihexyl*-3,8-*phenanthrolinium dibromide* (13). A solution of 3,8-phenanthroline (0.19 g, 1.05 mmol) and 1-bromohexane (3.3 g, 20 mmol) in acetonitrile (10 ml) was heated at reflux, with stirring, for 3 days. The precipitated salt was collected and washed with acetonitrile and ether. Recrystallisation from methanol–ether gave the *dibromide* as a pale yellow microcrystalline powder, which was dried *in vacuo* (0.33 g, 61%); m.p. > 300 °C; ^{1}H n.m.r., δ (CF_3CO_2D) 0.8—2.5 (m, 22 H), 5.01 (t, 4 H, *J* 8 Hz), 8.72 (s, 2 H), 9.13 (d, 2 H, *J* 6 Hz), 9.64 (d, 2 H, *J* 6 Hz), and 9.98 (s, 2 H); $\lambda_{max.}$ (H_2O) 250 nm (log ε 4.73) (Found: C, 56.26; H, 6.72; Br, 31.41; N, 5.53. $C_{24}H_{34}Br_2N_2$ requires C, 56.48; H, 6.71; Br, 31.31; N, 5.49%).

Acknowledgements

We thank Dr. Nicholas J. Goddard and Mark G. S. R. Thomas for valuable assistance.

References

1 See for example: (*a*) J. G. Kenworthy, B.P. 1314049/1973; (*b*) C. J. Schoot, J. J. Ponjee, H. T. van Dam, R. A. van Doorn, and P. T. Bolwijn, *Appl. Phys. Lett.*, 1973, **23**, 64; (*c*) J. J. Ponjee, H. T. van Dam, and C. J. Schoot, U.S.P. 3912368/1975; (*d*) R. J. Jasinski, U.S.P. 3961842/1976; (*e*) J. J. Ponjee and J. Bruinink, U.S.P. 4116535/1978; (*f*) D. J. Barclay, Europ. P. Appl. 0001 912/1979; (*g*) D. J. Barclay, C. L. Bird, and D. H. Martin, *J. Electron. Mater.*, 1979, **8**, 311.

2 (*a*) R. J. Jasinski, *J. Electrochem. Soc.*, 1977, **124**, 637; (*b*) J. Bruinink, C. G. A. Kregting, and J. J. Ponjee, *ibid.*, p. 1854.

3 G. G. Barna, *J. Electrochem. Soc.*, 1980, **127**, 1317.

4 F. Minisci, F. Bertini, R. Galli, and A. Quilico, Ger. Offen. 2 153 234/1972.

5 K. J. Schmalzl and L. A. Summers, *Chem. Ind.* (*London*), 1975, **15**, 652; *Aust. J. Chem.*, 1977, **30**, 657.

6 H.-H. Perkampus and G. Kassebeer, *Justus Liebigs Ann. Chem.*, 1966, **696**, 1.

7 N. J. Goddard, D. Phil. Thesis, University of Oxford, 1980.

8 J. Bruinink and C. G. A. Kregting, *J. Electrochem. Soc.*, 1978, **125**, 1397.

9 A. C. Jackson, D. Phil. Thesis, University of Oxford, 1982; R. D. Balanson, M. E. Oxsen, and Y. Y. Cheng, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2704.

10 G. G. Barna and J. G. Fish, *J. Electrochem. Soc.*, 1981, **128**, 1290.

11 J. A. Barltrop, N. J. Goddard, and M. S. G. R. Thomas, in preparation.

12 R. J. Jasinski, *J. Electrochem. Soc.*, 1978, **125**, 1619.

13 B. A. Khaskin, I. V. Sablina, N. N. Mel'nikov, and G. S. Supin, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1972, **42**, 2057.

14 A. Heuser and C. Stoehr, *J. Prakt. Chem.*, 1890, **42**, 429.

15 P. Y. White and L. A. Summers, *Aust. J. Chem.*, 1977, **30**, 1153.

Received 4*th May* 1983; *Paper* 3/711