We recently reported the preparation of tetraquaternary salts derived from 4,4′-bipyridine of the type (1; R = Me or Et, n = 2, 3 or 4) [1], and showed that they were reversibly reduced to diradical dications (2; R = Me or Et, n = 2, 3 or 4) by the uptake of two electrons. Reversible redox systems of this type are of interest as components of electrochromic memory display devices [2–5], as bielectronic mediators [6, 7] and as components of redox active membranes [8]. In a different area of application they have very recently been found to be of great interest as intercalators of DNA [9]. We now report on an extension of this research programme involving the preparation of the two hexaquaternary salts 1,1′-bis-[2-(1′-methyl-[4,4′-bipyridinium]-1-yl)-ethyl]-4,4′-bipyridinium hexaperchlorate (3; n = 2) and 1,1′-bis-[3-(1′-methyl-[4,4′-bipyridinium]-1-yl)-propyl]-4,4′-bipyridinium hexaperchlorate (3; n = 3) and their behaviour on polarographic reduction in aqueous solution.

The hitherto unknown diquaternary salt 1,1′-bis-(2-bromoethyl)-4,4′-bipyridinium dibromide (4; n = 2, X = Br) was considered to be a suitable starting material for the synthesis of the hexaquaternary salt (3; n = 2). Reaction of 4,4′-bipyridine, however, with 1,2-dibromoethane usually results in the formation of polyviologens [10, 11] or the diquaternary salt (5) [1] depending on reaction conditions. The monoquaternary salt, 1-(2-bromoethyl)-4,4′-bipyridinium bromide (6) has also been isolated but in an impure state [12]. In our hands reaction of 4,4′-bipyridine with excess 1,2-dibromoethane under reflux produced a precipitate which proved to be a mixture of polyviologen and the monoquaternary salt (6). The latter salt was readily extracted from the crude precipitate by boiling ethanol. Attempts to convert the monoquaternary salt (6) to the diquaternary salt (4; n = 2, X = Br) by heating it with more 1,2-dibromoethane resulted in the formation of polyviologen. However, by allowing a solution of 1-(2-bromoethyl)-4,4′-bipyridinium bromide (6) in dimethyl sulfoxide and 1,2-dibromoethane to stand at ambient temperature for seven days the diquaternary salt 1,1′-bis-(2-bromoethyl)-4,4′-bipyridinium dibromide (4; n = 2, X = Br) was obtained in moderate yield. The dibromide anion of (4; n = 2, X = Br) was converted to the diperchlorate anion for the purposes of characterisation and analyses of the salt. It was subsequently ascertained that reaction of 4,4′-bipyridine with excess 1,2-dibromoethane in dimethyl sulfoxide in the same conditions gave the diquaternary salt (4; n = 2, X = Br) without isolating the intermediate monoquaternary salt (6). This route was, therefore, adopted for the preparation of 1,1′-bis-(3-bromopropyl)-4,4′-bipyridinium dibromide (4; n = 3, X = Br) by allowing 4,4′-bipyridine in dimethyl sulfoxide to react with 1,3-dibromopropene at ambient temperature for seven days. This salt too was analysed and characterised as the diperchlorate.

The diquaternary salts 1,1′-bis-(2-bromoethyl)-4,4′-bipyridinium dibromide (4; n = 2, X = Br) and 1,1′-bis-(3-bromopropyl)-4,4′-bipyridinium dibromide (4; n = 3, X = Br) were converted to the corresponding tetraquaternary salts 1,1′-bis-(2-[4,4′-bipyridinium]-1-ylethyl)-4,4′-bipyridinium tetrabromide (7; n = 2, X = Br) and 1,1′-bis-(3-[4,4′-bipyridinium]-1-ylpropyl)-4,4′-bipyridinium tetrabromide (7; n = 3, X = Br) respectively in 35–40% yield by reaction with 4,4′-bipyridine in dimethyl sulfoxide for 7–10 days at ambient temperature.
The latter salt ($7; n = 3, X = Br$) was characterised as the tetraperoxylate ($7; n = 3, X = ClO_4$).

The tetraquaternary salts ($7; n = 2, X = Br$) and ($7; n = 3, X = ClO_4$) were likewise converted to the corresponding hexaquaternary salts $1,1'$-bis-[2-(1'-methyl-[4,4'-bipyridinium]-1-yl)-ethyl]-4,4'-bipyridinium hexaperchlorate ($3; n = 2$) and $1,1'$-bis-[3-(1'-methyl-[4,4'-bipyridinium]-1-yl)-propyl]-4,4'-bipyridinium hexa-perchlorate ($3; n = 3$) respectively in 25–35% yield by reaction with dimethyl sulfate in dimethyl sulfoxide for 7 days at ambient temperature followed by conversion of the anions to perchlorate.

The two diquaternary salts ($4; n = 2, X = ClO_4$) and ($4; n = 3, X = ClO_4$), the two tetraquaternary salts ($7; n = 2, X = Br$) and ($7; n = 3, X = ClO_4$) and the two hexaquaternary salts ($3; n = 2$) and ($3; n = 3$) were each examined by direct current polarography at the dropping mercury electrode in aqueous buffer solutions with diquat dibromide ($8$) as reference. Diquat dibromide is well-known [13] to be reduced by two distinct one electron reduction steps to give firstly the radical cation ($9$) at $E_0 = -0.35$ V and then the neutral species ($10$) at about $E_0 = -0.75$ V. The former reduction potential is pH independent and the latter pH dependent. In the pH range 2.6–10.2 the diquaternary salts ($4; n = 2, X = ClO_4$) and ($4; n = 3, X = ClO_4$) each gave a one-electron reduction wave at half-wave potentials ($E_0$) of $-0.30$ V and $-0.35$ V respectively independent of pH and concentration due to the formation of the radical cations ($11; n = 2$) and ($11; n = 3$). It is interesting to note that these reduction potentials
are higher than that of the paraquat di-cation (13) (£0 = −0.45 V) [13] but are close to the value reported (£0 = −0.335 V) for the 1,1′-bis-(2-chloroethyl)-4,4′-bipyridinium dication [13]. Both diquaternary salts (4; n = 2, X = ClO4) and (4; n = 3, X = ClO4) gave a second one-electron reduction step at a half-wave potential (£0) of about −0.60 V presumably due to the formation of the neutral species of type (12).

In the pH range 2.6–8.5 the two hexaquaternary salts (3; n = 2) and (3; n = 3) each gave a reduction wave which corresponded to the uptake of three electrons at a half-wave potential (£0) of −0.24 V independent of pH and concentration clearly due to the formation of the novel triradical trications (14; n = 2) and (14; n = 3) respectively. At lower potential (£0 ∼ −0.70 V) there were indications of a second reduction wave probably due to the formation of neutral species of type (15) but this wave was not always distinct. It is interesting to note that the formation of the triradical trications occurs at a potential slightly higher than the potential of £0 = −0.27 V obtained for the reduction of (1; R = CH3, n = 2) to the diradical dication (2; R = CH3; a = 2) [1].

Like paraquat (13), the two diquaternary salts (4; n = 2, X = ClO4) and (4; n = 3, X = ClO4) and the two hexaquaternary salts (3; n = 2) and (3; n = 3) gave intense violet colorations in aqueous solution on treatment with zinc dust due to the formation of the radical species (11) and (14). When the reducing agent was removed and the solutions were shaken in air the deep colorations disappeared. If the solutions were then again treated with zinc dust the violet colorations returned suggesting that the one-electron transfer from 4 to 11 and the three-electron transfer from 3 to 14 are reversible.

The two tetraquaternary salts (7; n = 2, X = Br) and (7; n = 3, X = ClO4) on polarographic examina-
tion in the pH range 2.6–4.1 also gave a reduction wave which corresponded to the uptake of three electrons at a half-wave potential (E₀) of about -0.26 V independent of pH and concentration due to the formation of triradical trications of type (14; H for CH₃) since at these pH values the end nitrogen atoms of (7; n = 2, X = Br) and (7; n = 3, X = ClO₄⁻) are protonated. At higher pH values however the polarograms were difficult to interpret. The salts decomposed above about pH 8.5.

**Experimental**

Microanalyses were performed by the Australian Microanalytical Service. UV absorption measurements were taken with 1×10⁻³ M solutions. NMR spectra (60 MHz) were determined in either D₂O or trifluoroacetic acid. Britton and Robinson aqueous buffer solutions were used in the polarography experiments which were conducted at 20 °C with a standard calomel electrode and 3×10⁻⁴ and 2×10⁻⁴ M solutions. Half-wave potentials are assumed to be E₀ values and were calculated by adding 0.25 V to the E₁/₂ values. Experimental error in the half-wave potentials was ±0.02 V.

1-(2-Bromoethyl)-4,4′-bipyridinium bromide (6)

4,4′-Bipyridine (5 g) was refluxed with 1,2-dibromoethane (30 ml) for 0.75 h. The brown precipitate was collected and exhaustively extracted with boiling ethanol. The mixture was filtered to remove insoluble polyviologen. A yellow precipitate separated from the filtrate. It was crystallised from ethanol, m.p. (decomp.) 280 °C (yield 25%).

C₁₂H₁₂Br₂N₂
Calcd C 41.9 H 3.5 N 8.1,
Found C 41.7 H 3.8 N 8.0.

NMR spectrum (D₂O): δ = 4.10–4.30 (t, 2H, CH₂–Br); 5.16–5.36 (t, 2H, CH₂–N); 7.93–8.03 (d, 2H, 3′,5′-aromatic); 8.50–8.90 (m, 4H, 3,5,2′,6′-aromatic); 9.15–9.25 (d, 2H, 2,6-aromatic) [ppm].

1,1′-Bis-(2-bromoethyl)-4,4′-bipyridinium dichloride (4; n = 2, X = ClO₄⁻)

A solution of 1-(2-bromoethyl)-4,4′-bipyridinium bromide (6) (20 g) and 1,2-dibromoethane (33 ml) in dimethyl sulfoxide (350 ml) was allowed to stand for 7 days at ambient temperature. The cloudy solution was filtered and the filtrate diluted with acetone (400 ml) to precipitate the crude product, which was dissolved in a 5% aqueous solution of lithium perchlorate. The diquaternary salt precipitated as the diperchlorate. It was crystallised from water to afford pale brown crystals, m.p. 220–222 °C (yield 32%).

C₁₄H₁₄Br₂Cl₂N₂O₄
Calcd C 29.4 H 2.8 N 4.9,
Found C 29.2 H 3.1 N 5.0.

NMR spectrum (CF₃COOH – D₂O): δ = 3.95–4.15 (t, 4H, CH₂–Br); 5.16–5.35 (t, 4H, CH₂–N); 8.60–8.70 (d, 4H, 3,3′,5,5′-aromatic); 9.20–9.30 (d, 4H, 2,2′,6,6′-aromatic) [ppm].

UV spectrum (H₂O): λmax 274 (log ε 4.46) [nm].

1,1′-Bis-(3-bromopropyl)-4,4′-bipyridinium diperchlorate (4; n = 3, X = ClO₄⁻)

A solution of 4,4′-bipyridine (10 g) and 1,3-dibromopropane (65 ml) in dimethyl sulfoxide (50 ml) was allowed to stand for 7 days at ambient temperature. The cloudy solution was filtered and the filtrate diluted with acetone (50 ml) to precipitate the crude product, which was dissolved in a 5% aqueous solution of lithium perchlorate. The diquaternary salt precipitated as the diperchlorate. It was crystallised from water to afford cream crystals, m.p. 210–212 °C (yield 44%).

C₁₆H₁₄Br₂Cl₂N₂O₆
Calcd C 32.1 H 3.4 N 4.7,
Found C 31.8 H 3.3 N 4.7.

NMR spectrum (CF₃COOH): δ = 2.50–2.90 (m, 4H, central CH₂); 3.35–3.55 (t, 4H, CH₂–Br); 4.85–5.10 (t, 4H, CH₂–N); 8.50–8.65 (d, 4H, 3,3′,5,5′-aromatic); 9.00–9.15 (d, 4H, 2,2′,6,6′-aromatic) [ppm].

UV spectrum (H₂O): λmax 274 (log ε 4.38) [nm].

1,1′-Bis-((2,4,4′-bipyridinium)-1-ylethyl)-4,4′-bipyridinium tetrabromide (7; n = 2, X = Br)

A solution of the diquaternary dibromide salt (4; n = 2, X = Br) (10 g) and 4,4′-bipyridine (29 g) in dimethyl sulfoxide (180 ml) was allowed to stand for 10 days at ambient temperature. The cloudy solution was filtered and the filtrate diluted with acetone (200 ml) to precipitate the crude product. It was crystallised from water to afford brown crystals, m.p. >360 °C (yield 34%).

C₃₄H₃₂Br₂N₆
Calcd C 48.3 H 3.8 N 9.95,
Found C 48.0 H 3.55 N 10.00.

NMR spectrum (D₂O): δ = 5.70 (s, 8H, CH₂); 8.20–8.30 (d, 4H, aromatic protons meta to nitrogen atoms in unquaternised rings); 8.65–9.05 (m, 12H, 8 protons meta to nitrogen atoms in quaternised rings and 4 protons ortho to nitrogen atoms in
unquaternised rings); 9.25—9.50 (m, 8H, aromatic protons ortho to nitrogen atoms in quaternised rings).

UV spectrum (H$_2$O): $\lambda_{max}$ 274 (log $\varepsilon$ 4.70) [nm].

1,1'-Bis-[3-[4,4'-bipyridinium]-1-ylpropyl]-4,4'-bipyridinium tetraphenyltricarboxylate (7; $n = 3$; $X = $ ClO$_4$)

A solution of the diquaternary dibromide salt ($4; n = 3$, $X = $ Br) (10 g) and 4,4'-bipyridine (17 g) in dimethyl sulfoxide (200 ml) was allowed to stand for 7 days at ambient temperature. The cloudy solution was filtered and the filtrate diluted with acetone (200 ml) to precipitate the crude product which was dissolved in a 5% aqueous solution of lithium perchlorate. The tetraquaternary salt precipitated as the hexaperchlorate. It was crystallised from water to afford cream crystals, m.p. 268—270 °C (yield 38%).

C$_{38}$H$_{42}$Cl$_4$N$_6$O$_{16}$, 2 H$_2$O
Calcd C 43.8 H 4.1 N 8.5.
Found C 43.9 H 3.9 N 8.3.

NMR spectrum (CF$_3$COOH—D$_2$O): $\delta = $ 2.80—3.30 (m, 4H, central CH$_2$); 4.95—5.35 (m, 8H, CH$_2$—N); 7.95—8.05 (d, 4H, aromatic protons meta to nitrogen atoms in unquaternised rings); 8.50—8.85 (m, 12H, 8 protons meta to nitrogen atoms in quaternised rings and 4 protons ortho to nitrogen atoms in unquaternised rings); 9.20—9.45 (m, 8H aromatic protons ortho to nitrogen atoms in quaternised rings).

UV spectrum (H$_2$O): $\lambda_{max}$ 274 (log $\varepsilon$ 4.75) [nm].

1,1'-Bis-[2-(l'-methyl-[4,4'-bipyridinium]-1-yl)ethyl]-4,4'-bipyridinium hexaphenyltricarboxylate (3; $n = 2$)

A solution of the tetraquaternary tetrabromide salt (7; $n = 2$, $X = $ Br) (5 g) and dimethyl sulfate (5.5 ml) in dimethyl sulfoxide (100 ml) was allowed to stand for 7 days at ambient temperature. The cloudy solution was filtered and the filtrate diluted with acetone (100 ml) to precipitate the crude product which was dissolved in a 5% aqueous solution of lithium perchlorate. The hexaquaternary salt precipitated as the hexaperchlorate. It was crystallised from water to afford brown crystals, m.p. >360 °C (yield 37%).

C$_{36}$H$_{36}$Cl$_6$N$_6$O$_{24}$
Calcd C 37.5 H 3.3 N 7.1.
Found C 37.3 H 3.6 N 7.1.

NMR spectrum (CF$_3$COOH—D$_2$O): $\delta = $ 4.60 (s, 6H, CH$_3$); 5.65 (s, 8H, CH$_2$); 8.55—8.80 (m, 12H, protons meta to nitrogen atoms); 9.10—9.60 (m, 12H, protons ortho to nitrogen atoms).

UV spectrum (H$_2$O): $\lambda_{max}$ 274 (log $\varepsilon$ 4.71) [nm].

1,1'-Bis-[3-(l'-methyl-[4,4'-bipyridinium]-1-yl)propyl]-4,4'-bipyridinium hexaphenyltricarboxylate (3; $n = 3$)

A solution of the tetraquaternary tetrabromide salt (7; $n = 3$, $X = $ ClO$_4$) (5 g) and dimethyl sulfate (5.5 ml) in dimethyl sulfoxide (100 ml) was allowed to stand for 7 days at ambient temperature. The cloudy solution was filtered and the filtrate diluted with acetone (100 ml) to precipitate the crude product which was dissolved in a 5% aqueous solution of lithium perchlorate. The hexaquaternary salt precipitated as the hexaperchlorate. It was crystallised from water to afford cream crystals of the dihydrate, m.p. >360 °C (yield 24%).

C$_{36}$H$_{42}$Cl$_6$N$_6$O$_{24}$, 2 H$_2$O
Calcd C 37.5 H 3.8 N 6.9.
Found C 37.2 H 3.4 N 6.7.

NMR spectrum (CF$_3$COOH—D$_2$O): $\delta = $ 2.75—3.30 (m, 4H, central CH$_2$); 4.60 (s, 6H, CH$_3$); 4.95—5.35 (m, 8H, CH$_2$—N); 8.50—8.75 (m, 12H, protons meta to nitrogen atoms); 9.05—9.35 (m, 12H, protons ortho to nitrogen atoms).

UV spectrum (H$_2$O): $\lambda_{max}$ 274 (log $\varepsilon$ 4.74) [nm].