Synthesis of Quaternary Salts from 2,3’-Bipyridine and Dibromoalkanes

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2,3’-Bipyridinium Tetraquaternary Salts, Reduction Potentials, Diradical Dications

Reaction of 2,3’-bipyridine with dibromoalkanes affords both 1’-bromoalkyl-2,3’-bipyridinium bromides and 1’,1”-(alkanediyl)-bis-2,3’-bipyridinium dibromides. The latter diquaternary salts react with dimethyl sulfate to afford 1’,1”-(alkanediyl)-bis-(1-methyl-2,3’-bipyridinium) tetraquaternary salts which are reduced to diradical dications at potentials (E0) of about —0.47 V to —0.62 V.

There has been considerable interest in the products of the reaction of 2,2’-bipyridine with dibromoalkanes. The bridged diquaternary salt (1) from 2,2’-bipyridine and 1,2-dibromoethane is the well-known herbicide diquat dibromide [1]. Similar bridged salts are obtained with 1,3-dibromopropane and 1,4-dibromobutane [2] but reaction of 2,2’-bipyridine with 1,5-dibromopentane gives instead the diquaternary salt (2) [3]. Related systems have also received attention [2]. In the 4,4’-bipyridine series, reaction of 4,4’-bipyridine with dibromoalkanes usually results in the formation of polyviologens [2, 4] or diquaternary salts such as 3 [5] depending on reaction conditions. The monoquaternary salt (4) has also been isolated, but in an impure state [6], from the reaction of 4,4’-bipyridine with 1,2-dibromoethane. We now report the results of work on the products obtained by the reaction of 2,3’-bipyridine with dibromoalkanes.

Reaction of 2,3’-bipyridine with excess of 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane in boiling ethanol afforded in each case a mixture of two products which were separated by fractional crystallisation. The predominant products (40—50% yield) comprised the 1’-bromoalkyl monoquaternary salts (5; n = 2), (5; n = 3), (5; n = 4) and (5; n = 5) respectively. The structure of these salts was confirmed by microanalyses and by their NMR spectra. The latter in each case showed a deshielded singlet at δ ~ 9.5 ppm which is attributed to the hydrogen at the 2’-position. This confirms that the nitrogen in the β-pyridyl ring and not in the α-pyridyl ring has been quaternized. This result is in accord with previous reports that 2,3’-bipyridine is preferentially quaternized at the 1’-nitrogen [2]. With the salts (5; n = 4) and (5; n = 5) the microanalyses indicated that the salts had 0.75 mole of HBr associated with them. Similar association of HBr with quaternary salts in the 2,2’-bipyridine series is well-known [1, 3]. As expected both salts (5; n = 4)

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and (5; n = 5) gave effervescence with sodium hydrogen carbonate. To verify that HBr was now no longer associated with the salts, the salt (5; n = 4) was then converted to the perchlorate which analysed correctly with no associated HBr.

The second products (35–40% yield) comprised the bis-quaternary salts (6; n = 2), (6; n = 3), (6; n = 4) and (6; n = 5) respectively. Their structure followed from microanalyses and NMR spectra. The salt (6; n = 3) which analysed as the sesquihydrate with 1.0 mole of HBr effervesced with sodium hydrogen carbonate. These four bis-quaternary salts were also obtained in ~40% yield by reaction of 2,3'-bipyridine with the appropriate dibromoalkane in 1:1 molar ratio in boiling ethanol. In these experiments no significant quantity of the 1'-bromoalkyl monoquaternary salts was formed.

In view of the recent interest in bis-quaternary salts of planar nitrogen heterocycles as bifunctional intercalators of DNA [7, 8] we extended the type of compound available for investigation by converting each of the four bis-quaternary salts (6; n = 2), (6; n = 3), (6; n = 4) and (6; n = 5) to the corresponding bis-diquaternary systems by reaction with excess dimethyl sulfate followed by conversion of the anion to perchlorate. The structure of the resulting four tetraquaternary salts (7; n = 2), (7; n = 3), (7; n = 4) and (7; n = 5) was confirmed by microanalyses and NMR spectra.

Attempts to induce intramolecular cyclisation of the 1'-bromoalkyl monoquaternary salts (5; n = 2), (5; n = 3) and (5; n = 4) to give analogues of diquat dibromide (1) by heating alone at 160–220 °C was unsuccessful. The only products isolated from the experiments were the bis-quaternary salts (6; n = 2), (6; n = 3), and (6; n = 4) as the perchlorates respectively in low yield (~20%). The formation of the bis-quaternary salts in these reactions presumably occurs by partial thermal dequaternization of the monoquaternary salts to 2,3'-bipyridine followed by reaction of the 2,3'-bipyridine with remaining monoquaternary salt. Similar results were obtained when the salts (5; n = 3) and (5; n = 4) were heated in dimethylformamide at 150 °C for several hours.

In view of our interest in the formation of radical cations by the one electron reduction of diquaternary salts of bipyridines [9–12] we investigated the polarographic behaviour of the four bis-diquaternary salts (7; n = 2), (7; n = 3), (7; n = 4) and (7; n = 5) by direct current polarography at the dropping mercury electrode with diquat dibromide (1) as reference. We included in the investigation, for comparison, 1,1'-dimethyl-2,3'-bipyridinium diperchlorate (8), which was obtained by reaction of 2,3'-bipyridine with dimethyl sulfate followed by conversion of the anion to perchlorate. 1,1'-Dimethyl-2,3'-bipyridinium di-iodide has been reported before [2]. In the pH range 7.0–11.1 1,1'-dimethyl-2,3'-bipyridinium diperchlorate (8) gave a symmetrical one electron reduction wave with a half-wave potential (E0) of ~0.80 V independent of pH attributed to the formation of the radical cation of which structure 9 is one canonical form. The corresponding diquaternary salts in the 2,2'-bipyridine and 4,4'-bipyridine series, namely 1,1'-dimethyl-2,2'-bipyridinium di-iodide and 1,1'-dimethyl-4,4'-bipyridinium dichloride (paraquat), are similarly reduced to radical cations at ~0.70 V and ~0.45 V, respectively [1]. The four bis-diquaternary salts (7; n = 2), (7; n = 3), (7; n = 4) and (7; n = 5) were investigated...
were each examined polarographically in the pH range 2.3—9.7. At higher pH values the salts tended to decompose. They each gave a symmetrical reduction wave which corresponded to the uptake of two electrons at half-wave potentials ($E_0$) of $-0.47$ V, $-0.49$ V, $-0.59$ V and $-0.62$ V respectively independent of pH and concentration attributed to the formation of diradical dications of which structures ($10; n = 2$), ($10; n = 3$), ($10; n = 4$) and ($10; n = 5$) respectively are canonical forms. It is interesting to note that the reduction potential decreases as the length of the connecting methylene bridge increases. These bis-diquaternary salts are much less easily reduced than the analogous type of salts in the 4,4'-bipyridine series. For example, the bis-diquaternary salt ($11$) in the 4,4'-bipyridine series is reduced to a diradical dication at a potential ($E_0$) of $-0.27$ V [5]. Unlike 1,1'-dimethyl-4,4'-bipyridinium dichloride (paraquat) and bis-diquaternary salts in the 4,4'-bipyridine series such as ($11$) [5] which give intense violet colorations immediately on treatment with zinc dust in aqueous solution due to the formation of a stable radical cation and diradical dications respectively, 1,1'-dimethyl-2,3'-bipyridinium diperchlorate ($8$) and the bis-diquaternary salts ($7; n = 2$), ($7; n = 3$), ($7; n = 4$) and ($7; n = 5$) gave only slight yellow colorations slowly on treatment with zinc dust in aqueous solution. This result presumably reflects the fact that the radical cation ($9$) from ($8$) and the diradical dications of type ($10$) are much less stable than their 4,4'-bipyridine analogues.

Experimental

Britton and Robinson buffers were used in the polarography experiments which were conducted at 20 °C with a standard calomel electrode and $3 \times 10^{-4}$ and $2 \times 10^{-3}$ M solutions. The solutions sometimes contained 0.2% Triton X-100 to suppress wave maxima. The half-wave potentials are given as $E_0$ values and were calculated by adding 0.25 V to the $E_{1/2}$ values. Experimental error in the half-wave potentials was ±0.02 V. Microanalyses were performed by the Australian Microanalytical Service. UV absorption measurements were taken with $2 \times 10^{-3}$ M solutions.

I’-(2-Bromoethyl)-2,3'-bipyridinium bromide ($5; n = 2$)

2,3'-Bipyridine (3 g) and 1,2-dibromoethane (15 ml) in ethanol (10 ml) were refluxed for 8 h and allowed to stand overnight at ambient temperature. A white solid separated out which was identified as ($6; n = 2$) (see below). The filtrate was evaporated and the oily residue stirred with acetone. The resultant white solid was crystallised from ethanol/acetonitrile and then from ethanol/ether to afford white crystals, m.p. 156—157 °C (yield 50%).

C$_{13}$H$_{12}$Br$_2$N$_2$
Calcd C 41.9 H 3.5 N 8.1 Br(ionic) 23.2,
Found C 41.6 H 3.4 N 8.0 Br 46.1 Br(ionic) 22.9.

NMR spectrum (CF$_3$COOD): $\delta = 3.60$—3.78 (m, 2H, CH$_2$Br); 4.83—5.01 (m, 2H, N—CH$_2$); 7.80—8.90 (m, 7H, 3,4,5,6,4',5',6'-aromatic); 9.32 (s, 1H, 2'-aromatic) [ppm].

UV spectrum (H$_2$O, pH 8.2): $\lambda_{max}$ 209, 230, 276 (log $e$ 4.17, 4.16, 4.04) [nm].

I’-(3-Bromopropyl)-2,3'-bipyridinium bromide ($5; n = 3$)

This salt was obtained similarly using 1,3-dibromopropane and was separated from ($6; n = 3$) (see below). It crystallised from ethanol as off-white crystals, m.p. 172—174 °C (yield 47%).

C$_{13}$H$_{14}$Br$_2$N$_2$
Calcd C 43.6 H 3.9 N 7.8 Br(ionic) 22.3,
Found C 43.4 H 3.8 N 7.7 Br(ionic) 22.3.

NMR spectrum (CH$_3$COOD): $\delta = 2.12$—2.55 (m, 2H, central CH$_2$); 3.00—3.20 (t, 2H, CH$_2$Br); 4.55—4.78 (t, 2H, N—CH$_2$); 7.75—8.89 (m, 7H, 3,4,5,6,4',5',6'-aromatic); 9.28 (s, 1H, 2'-aromatic) [ppm].

UV spectrum (H$_2$O, pH 8.2): $\lambda_{max}$ 210, 229, 276 (log $e$ 4.18, 4.17, 4.04) [nm].
1'-((4-Bromobutyl)-2,3'-bipyridinium bromide (5; \(n = 4\))

This salt was obtained similarly using 1,4-dibromobutane and was separated from (6; \(n = 4\)) (see below). It crystallised from ethanol (twice) as white crystals, m.p. 216 °C (yield 44%). The analyses indicated that 0.75 mole HBr was associated with the salt.

\[
\text{C}_{14}\text{H}_{10}\text{Br}_{2}\text{N}_{2}, 0.75 \text{ HBr}
\]

Calcd C 38.85 H 3.9 N 6.5 Br(total) 50.7,

Found C 38.60 H 3.8 N 6.2 Br(total) 50.7.

NMR spectrum (CF\(_3\)COOD): \(\delta = 1.75-2.55\) (m, 4H, central CH\(_2\)); 3.30–3.50 (t, 2H, CH\(_2\)Br); 4.75-5.00 (t, 2H, N–CH\(_2\)); 8.15–9.25 (m, 7H, 3,4,5,6,4',5',6'-aromatic); 9.72 (s, 1H, 1'-aromatic) [ppm].

UV spectrum (H\(_2\)O, pH 8.2): \(\lambda_{\text{max}}\) 210, 229, 276 (log \(\varepsilon\) 4.20, 4.12, 4.02) [nm].

The bromide salt was converted to the perchlorate by dissolving it in the minimum volume of water. Solid sodium hydrogen carbonate was added until effervescence ceased and then excess solid lithium perchlorate. White crystals of the perchlorate salt formed on standing. It crystallised from aqueous ethanol, m.p. 88–90 °C (yield 90%).

\[
\text{C}_{14}\text{H}_{10}\text{BrClNO}_{4}
\]

Calcd C 42.9 H 4.1 N 7.15,

Found C 43.3 H 4.3 N 7.2.

NMR spectrum (CF\(_3\)COOD): \(\delta = 1.5–2.25\) (m, 4H, central CH\(_2\)); 3.01–3.22 (t, 2H, CH\(_2\)); 4.55-4.80 (t, 2H, N–CH\(_2\)); 7.95-9.05 (m, 7H, 3,4,5,6,4',5',6'-aromatic); 3.30-3.50 (t, 2H, CH:Br); [ppm].

UV spectrum (H\(_2\)O, pH 8.2): \(\lambda_{\text{max}}\) 210, 229, 276 (log \(\varepsilon\) 4.22, 4.15, 4.05) [nm].

1'-((5-Bromopentyl)-2,3'-bipyridinium bromide (5; \(n = 5\))

This salt was obtained similarly using 1,5-dibromopentane and was separated from (6; \(n = 5\)) (see below). It crystallised from ethanol (twice) as white crystals, m.p. 186–188 °C (yield 38%). The analysis indicated that 0.75 mole HBr was associated with the salt.

\[
\text{C}_{14}\text{H}_{10}\text{Br}_{2}\text{N}_{2}, 0.75 \text{ HBr}
\]

Calcd C 40.3 H 4.2 N 6.3 Br(ionic) 32.7 Br(total) 49.2,

Found C 40.0 H 4.0 N 6.4 Br(ionic) 32.7 Br(total) 49.4.

NMR spectrum (CF\(_3\)COOD): \(\delta = 1.30–2.30\) (m, 6H, central CH\(_2\)); 3.10–3.30 (t, 2H, CH\(_2\)Br); 4.55-4.80 (t, 2H, N–CH\(_2\)); 7.95-9.05 (m, 7H, 3,4,5,6,4',5',6'-aromatic); 9.55 (s, 1H, 1'-aromatic) [ppm].

UV spectrum (H\(_2\)O, pH 8.2): \(\lambda_{\text{max}}\) 210, 229, 276 (log \(\varepsilon\) 4.22, 4.15, 4.05) [nm].

1',1''-(1,2-Ethanediyl)-bis-2,3'-bipyridinium dibromide (6; \(n = 2\))

(a) 2,3'-Bipyridine (3 g) and 1,2-dibromoethane (1.7 ml) in ethanol (10 ml) were refluxed for 6 h and left to stand overnight at ambient temperature. A white solid separated out which was washed with acetone and crystallised from ethanol (twice) to afford white crystals, m.p. 278 °C (dec.) (yield 38%).

\[
\text{C}_{22}\text{H}_{15}\text{Br}_{2}\text{N}_{4}
\]

Calcd C 52.8 H 4.0 N 11.2 Br 31.9,

Found C 52.6 H 3.8 N 11.0 Br 31.9.

NMR spectrum (D\(_2\)O): \(\delta = 5.60\) (s, 4H, CH\(_2\)); 7.45–9.30 (m, 14H, aromatic); 9.55 (s, 2H, 2',2''-aromatic) [ppm].

UV spectrum (H\(_2\)O, pH 8.2): \(\lambda_{\text{max}}\) 209, 232, 278 (log \(\varepsilon\) 4.38, 4.37, 4.26) [nm].

(b) The salt was obtained in 40% yield as co-product from the preparation of (5; \(n = 2\)) (see above).

1',1''-(1,2-Ethanediyl)-bis-2,3'-bipyridinium diperchlorate

1'-((2-Bromoethyl)-2,3'-bipyridinium bromide (5; \(n = 2\)) (4 g) was heated in a flask to 160 °C for 7 h and then cooled. The solid which remained, effervesced with sodium hydrogen carbonate. It was dissolved in water. The solution was treated with solid sodium hydrogen carbonate until effervescence ceased followed by the addition of lithium perchlorate. The solid was crystallised from aqueous ethanol to afford white crystals, m.p. 296–298 °C (yield 18%) of 1',1''-(1,2-ethanediyl)-bis-2,3'-bipyridinium diperchlorate.

\[
\text{C}_{22}\text{H}_{15}\text{Cl}_{2}\text{N}_{4}\text{O}_{8}, 0.25 \text{ H}_{2}\text{O}
\]

Calcd C 48.6 H 3.8 N 10.3,

Found C 48.3 H 3.5 N 10.1.

NMR spectrum (DMSO): \(\delta = 5.45\) (s, 4H, CH\(_2\)); 7.40–9.30 (m, 14H, aromatic); 9.70 (s, 2H, 2',2''-aromatic) [ppm].

The diperchlorate salt was identical to a sample prepared from the dibromide (6; \(n = 2\)) by dissolving the latter in water and treating it with lithium perchlorate.

1'',1''-(1,3-Propanediyl)-bis-2,3'-bipyridinium dibromide (6; \(n = 3\))

(a) 2,3'-Bipyridine (3 g) and 1,3-dibromopropane (1.9 ml) in ethanol (10 ml) were refluxed for 12 h and left to stand overnight at ambient temperature. The solvent was partly evaporated and the mixture diluted with acetone whereupon a white solid precipitated. It was crystallised from ethanol/acetone twice to afford white crystals, m.p. 216–218 °C
(yield 36%). The salt effervesced with sodium hydrogen carbonate and the analyses showed that it was a sesquihydrate with which 1 mole HBr was associated.

C₂₂H₂₆Br₂N₄, 1.5 H₂O, HBr  
Caled  C 44.4  H 4.0  N 9.0  Br (ionic) 38.5  Br (total) 38.5,  
Found  C 44.4  H 4.1  N 9.4  Br (ionic) 38.4  Br (total) 38.5.

NMR spectrum (CF₃COOD): \( \delta = 2.95-3.50 \) (m, 2H, central CH₂); 4.90-5.30 (t, 4H, N-CH₂); 7.95-9.25 (m, 14H, aromatic); 9.12 (s, 2H, 2',2''-aromatic) [ppm].

UV spectrum (H₂O, pH 8.2): \( \lambda_{max} 209, 230, 277 \) (log ε 4.42, 4.39, 4.28) [nm].

(b) The salt was also obtained in 45% yield as co-product from the preparation of (5; \( n = 4 \)) (see above).

I',1''-(1,3-PropanediyI)-bis-2,3'-bipyridinium diperchlorate

I',(3-Bromopropyl)-2,3'-bipyridinium dibromide (5; \( n = 3 \)) (4 g) was heated in a flask at 170 °C for 2.5 h and then cooled. The salt which remained effervesced with sodium hydrogen carbonate. It was dissolved in water. The solution was treated with solid sodium hydrogen carbonate until effervescence ceased followed by the addition of lithium perchlorate. The brownish solid was crystallised from aqueous ethanol (twice) to give light brown crystals, m.p. 226–228 °C (yield 17%) of I',1''-(1,3-propanediyl)-bis-2,3'-bipyridinium diperchlorate.

C₂₃H₂₇Cl₂N₂O₈  
Caled  C 49.9  H 4.0  N 10.1,  
Found  C 49.9  H 4.2  N 10.1.

NMR spectrum (CF₃COOD): \( \delta = 2.86-3.46 \) (m, 2H, central CH₂); 4.86-5.36 (t, 4H, N-CH₂); 8.11-9.21 (m, 14H, aromatic); 9.15 (s, 2H, 2',2''-aromatic) [ppm].

The diperchlorate salt was identical to a sample prepared from the dibromide (6; \( n = 3 \)) by dissolving the latter in water, adding excess sodium hydrogen carbonate, and treating the solution with lithium perchlorate.

I',1''-(1,4-Butanediyl)-bis-2,3'-bipyridinium dibromide (6; \( n = 4 \))

(a) 2,3'-Bipyridine (3 g) and 1,4-dibromobutane (2.3 ml) in ethanol (10 ml) were refluxed for 12 h and left to stand overnight at ambient temperature. A white solid separated out which was washed with acetone and crystallised from ethanol/acetone (twice) to afford white crystals, m.p. 250 °C (yield 38%).

C₂₄H₂₅Br₂N₄  
Caled  C 54.3  H 4.5  N 10.3  Br (ionic) 30.25  Br (total) 30.25,  
Found  C 54.3  H 4.5  N 10.3  Br (ionic) 30.1  Br (total) 30.0.

NMR spectrum (D₂O): \( \delta = 2.40-2.67 \) (m, 4H, central CH₂); 4.92-5.22 (m, 4H, N-CH₂); 7.52-9.32 (m, 14H, aromatic); 9.64 (s, 2H, 2',2''-aromatic) [ppm].

UV spectrum (H₂O, pH 8.2): \( \lambda_{max} 210, 230, 277 \) (log ε 4.34, 4.39, 4.29) [nm].

(b) The salt was also obtained in 46% yield as co-product from the preparation of (5; \( n = 5 \)) (see above).

I',1''-(1,5-Pentanediyl)-bis-2,3'-bipyridinium dibromide (6; \( n = 5 \))

(a) 2,3'-Bipyridine (3 g) and 1,5-dibromopentane (2.6 mol) in ethanol (10 ml) were refluxed for 12 h and left to stand overnight at ambient temperature. The solvent was partly evaporated and the mixture diluted with acetone whereupon a white solid precipitated. It crystallised from aqueous acetone to afford white crystals, m.p. 74 °C (yield 35%).

C₂₅H₃₀Br₂N₄  
Caled  C 55.4  H 4.8  N 10.2  Br 29.5,  
Found  C 55.4  H 4.8  N 10.2  Br 29.2.

NMR spectrum (CF₃COOD): \( \delta = 1.65-2.75 \) (m, 6H, central CH₂); 4.75-5.20 (m, 4H, N-CH₂); 8.10-9.20 (m, 14H, aromatic); 9.80 (s, 2H, 2',2''-aromatic) [ppm].

UV spectrum (H₂O, pH 8.2): \( \lambda_{max} 210, 229, 276 \) (log ε 4.40, 4.38, 4.28) [nm].

(b) The salt was also obtained in 46% yield as co-product from the preparation of (5; \( n = 5 \)) (see above).

I',1''-(1,2-Ethanediyl)-bis-(1-methyl-2,3'-bipyridinium) tetrapерchlorate (7; \( n = 2 \))

1',1''-(1,2-Ethanediyl)-bis-2,3'-bipyridinium dibromide (6; \( n = 2 \)) (5 g) and dimethyl sulfate (10 ml) were heated at 160 °C for 7 h and left to stand overnight at ambient temperature. The solution was diluted with acetone whereupon a white solid precipitated. The solid was dissolved in water and lithium perchlorate added. The solid which precipitated was crystallised twice from aqueous ethanol to give pale brown needles, m.p. > 300 °C (yield 78%).

C₂₅H₃₀Cl₄N₄O₁₆  
Caled  C 37.5  H 3.4  N 7.3,  
Found  C 37.9  H 3.4  N 7.4.
NMR spectrum (DMSO): δ = 4.26 (s, 6 H, CH₃); 5.43 (s, 4 H, CH₂); 8.05–9.50 (m, 16 H, aromatic) [ppm].

UV spectrum (H₂O, pH 2.3): λ_max 208, 273 (log ε 4.40, 4.41) [nm].

1',1''-(1,3-Propanediyl)-bis-(1-methyl-2,3'-bipyridinium) tetraperchlorate (7; n = 3)

This salt was obtained similarly from 1',1''-(1,3-propanediyl)-bis-2,3'-bipyridinium dibromide and dimethyl sulfite. It crystallised from aqueous ethanol as white crystals, m.p. 220–222 °C (yield 68%).

C₂₅H₃₂Cl₄N₄O₆
Calcd C 38.4 H 3.6 N 7.2, Found C 38.2 H 3.4 N 7.2.

NMR spectrum (DMSO): δ = 2.75–3.05 (m, 2 H, central CH₂); 4.30 (s, 6 H, CH₃); 4.70–5.10 (t, 4 H, N—CH₂); 8.40–9.75 (m, 16 H, aromatic) [ppm].

UV spectrum (H₂O, pH 2.3): λ_max 206, 271 (log ε 4.47, 4.42) [nm].

1',1''-(1,4-Butanediyl)-bis-(1-methyl-2,3'-bipyridinium) tetraperchlorate (7; n = 4)

This salt was obtained similarly from 1',1''-(1,4-butanediyl)-bis-2,3'-bipyridinium dibromide and dimethyl sulfate. It crystallised from aqueous ethanol as light brown crystals, m.p. 308 °C (dec.) (yield 76%).

C₂₆H₃₀Cl₄N₄O₆
Calcd C 39.2 H 3.8 N 7.0, Found C 39.5 H 3.7 N 7.1.

NMR spectrum (DMSO): δ = 1.95–2.40 (m, 4 H, central CH₂); 4.22 (s, 6 H, CH₃); 4.55–4.95 (m, 4 H, N—CH₂); 8.10–9.45 (m, 16 H, aromatic) [ppm].

UV spectrum (H₂O, pH 2.3): λ_max 206, 271 (log ε 4.49, 4.44) [nm].

1,1'-Dimethyl-2,3'-bipyridinium diperchlorate
2,3'-Bipyridine (1.2 g) was heated with dimethyl sulfate (10 ml) at 135 °C for 2 h. After cooling the mixture was diluted with acetone. The solid which precipitated was dissolved in water and lithium perchlorate was added to the solution. The white diperchlorate salt which precipitated was crystallised from aqueous ethanol, m.p. 280 °C (yield 38%).

C₁₂H₁₄Cl₂N₂O₆
Calcd C 37.4 H 3.7 N 7.3, Found C 37.25 H 3.6 N 7.3.

NMR spectrum (D₂O): δ = 4.29 (s, 3 H, α-N—CH₃); ~4.59 (s, 3 H, β-N—CH₂); 8.10–9.29 (m, 8 H, aromatic) [ppm].

UV spectrum (H₂O, pH 8.2): λ_max 202, 270 (log ε 4.18, 4.10) [nm].