Anion Recognition by New Acyclic Quaternary Polybipyridinium Receptors

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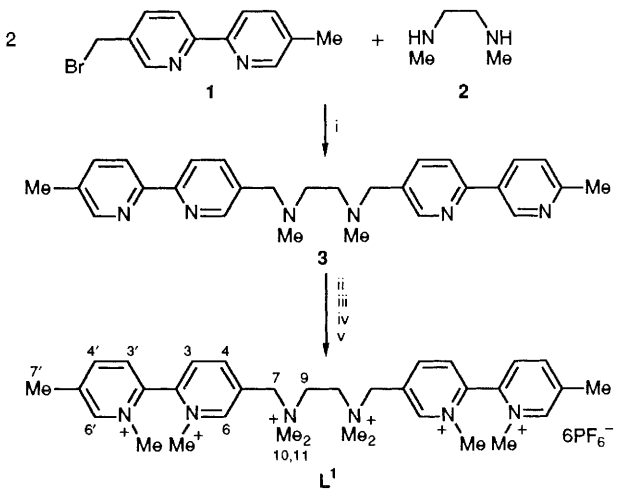
New acyclic quaternary polybipyridinium receptors L^1–L^4 containing 5,5′- and 4,4′-disubstituted-*N*,*N*′-dimethyl-2,2′-bipyridinium are prepared and shown by preliminary ^1H and ^{13}C NMR titration investigations to coordinate chloride and bromide anionic guest species.

Interest in 2,2′-bipyridine and related polypyridine derivatives has grown rapidly in recent years owing to their numerous applications in a variety of fields. Examples include their effective use as ligands for coordinating a large diversity of metal ions[1] and the versatile photoactivity of the corresponding metal complexes in electron- and energy-transfer processes.[2] One application that has yet to be exploited is to utilise the pH-independent positively charged redox-active diquaternary 2,2′-bipyridinium group[3] as a potential new class of receptor for recognising anionic guest species.[4] We describe here the syntheses and preliminary anion coordination studies of new acyclic quaternary polybipyridinium receptors containing 5,5′- and 4,4′-disubstituted-*N*,*N*′-dimethyl-2,2′-bipyridinium moieties.

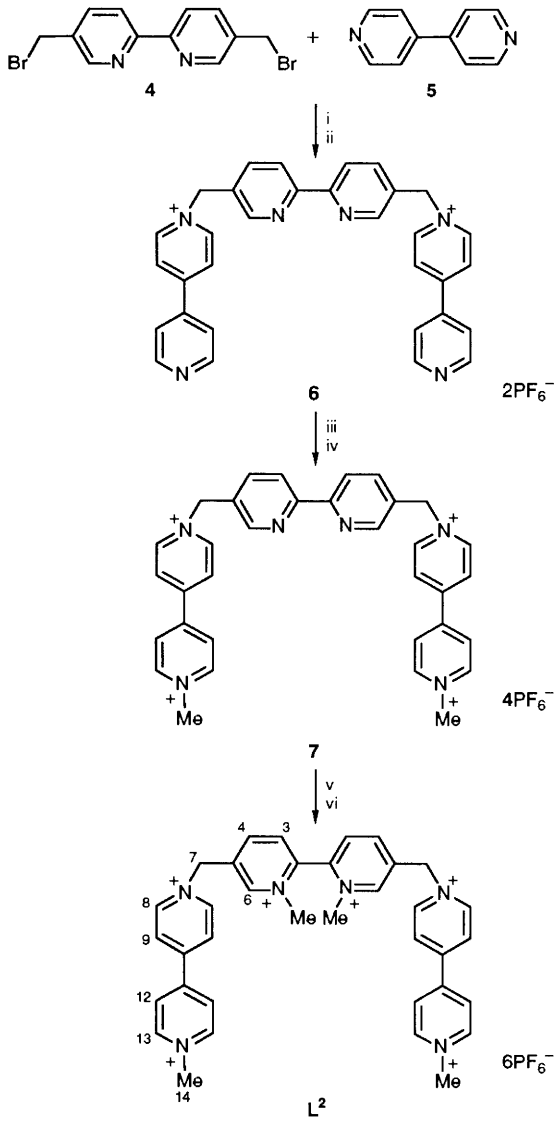
The synthesis of a molecule containing two 5,5′-disubstituted-2,2′-bipyridyl units was achieved by the reaction of two equivalents of 5-bromomethyl-5′-methyl-2,2′-bipyridine **1**[5] with *N*,*N*′-dimethylethylenediamine **2** in acetonitrile using potassium carbonate as base. Purification by column chromatography on alumina, using CH_2Cl_2–MeOH (99 : 1) as eluent, and recrystallisation from acetonitrile afforded **3** in 43% yield (Scheme 1). Treatment of **3** with dimethyl sulfate (DMS) at 75 °C for 7 days gave a mixture of products that were not fully methylated. Following conversion into the hexafluorophosphate salts, this mixture was treated further with methyl iodide in acetonitrile at reflux for 18 days. After this time the product was isolated and converted into the hexafluorophosphate salt to give L^1 in 11% overall yield (Scheme 1).

The two-stage methylation is most likely required because the partially quaternised products are not sufficiently soluble in dimethyl sulfate to remain in solution and undergo the final quaternisation reactions. In converting the partially methylated products into the hexacationic hexafluorophosphate salts, solubility in polar solvents is conferred upon them and hence they may then undergo completion of the quaternisation procedure.

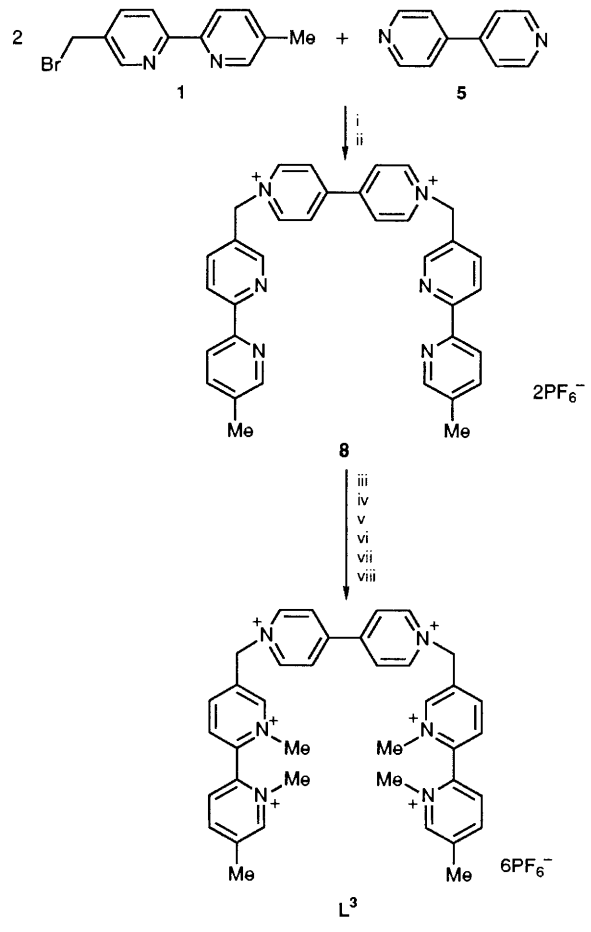
Treatment of 5,5′-bis(bromomethyl)-2,2′-bipyridine **4**[5] with a large excess of 4,4′-bipyridine **5** in acetonitrile, followed by conversion of the resultant precipitate into the hexafluorophosphate salt, gave the dicationic compound **6** in 88% yield (Scheme 2). The reaction of **6** with methyl iodide in nitromethane at reflux for 24 h produced an orange precipi-



Scheme 1 *Reagents*: i, K_2CO_3–MeCN; ii, DMS; iii, NH_4PF_6–H_2O; iv, MeI–MeCN; v, NH_4PF_6–H_2O



Scheme 2 *Reagents*: i, MeCN; ii, NH_4PF_6–H_2O; iii, MeI–$MeNO_2$; iv, NH_4PF_6–H_2O; v, DMS–MeCN; vi, NH_4PF_6–H_2O



Scheme 3 *Reagents*: i, MeCN; ii, NH_4PF_6–H_2O; iii, MeI–MeCN; iv, NH_4PF_6–H_2O; v, MeI–MeCN; vi, NH_4PF_6–H_2O; vii, DMS–MeCN; viii, NH_4PF_6–H_2O

tate, which was collected, dissolved in water, and converted into the hexafluorophosphate salt to afford the tetracationic compound **7** in 89% yield (Scheme 2). Alkylation of **7** with dimethyl sulfate in acetonitrile at reflux for 48 h gave initially a white precipitate, which was converted into the hexacationic hexafluorophosphate acyclic receptor molecule L^2 in 71% yield (Scheme 2).

4,4′-Bipyridine **5** was treated with two equivalents of 5-bromomethyl-5′-methyl-2,2′-bipyridine **1** to produce, on addition of ammonium hexafluorophosphate, the dicationic compound **8** in 78% yield (Scheme 3). Exhaustive methylation of **8** was achieved *via* alkylation reactions with methyl iodide and subsequently dimethyl sulfate followed finally by conversion into the hexafluorophosphate salt to give the desired hexacationic receptor L^3 in 44% overall yield (Scheme 3).

The reaction of 4,4′-dimethyl-2,2′-bipyridine **9** with two equivalents of lithium diisopropylamide followed by two equivalents of 4-formylpyridine **10** gave the bis(hydroxy) compound **11** in 42% yield. Exhaustive alkylation of **11** in refluxing dimethyl sulfate also led to concomitant dehydration, and subsequent addition of an excess of ammonium hexafluorophosphate produced L^4 in 60% yield as an off-white powdery solid (Scheme 4). All these new acyclic receptors gave spectroscopic and analytical data in accordance with assigned structures.†

The combination of ^1H and ^{13}C NMR spectroscopy together with electrochemical cyclic voltammetric experiments were used to investigate the preliminary anion coordination chemistry of the new acyclic polybipyridinium receptors L^1–L^4 and simple model bipyridinium compounds, **12**, **13**, with halide anions.

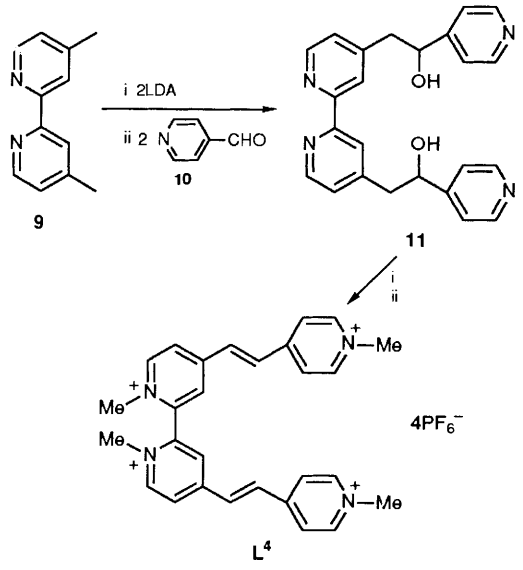
In a typical ^1H NMR titration experiment the addition of one equivalent of tetrabutylammonium chloride to respective [$^2H_6$]dimethyl sulfoxide (DMSO) solutions of L^1–L^4 led to

† *Selected spectral data for* L^1: MS (FAB)[*m*/*z* $-PF_6$]$^+$ 1267. ^1H NMR (DMSO, 400 MHz) δ: 2.68 (6H, s, bipy CH_3), 3.21 and 3.24 [12H, 2s, bipy$CH_2N^+(CH_3)_2$], 4.14 and 4.24 (12H, 2s, bipyN^+-CH_3), 4.27 (4H, s, bipyCH_2) 5.02 (4H, s, bipyCH_2), 8.19 (2H, d, ^3J 8.1 Hz, bipyH_4′), 8.63 (2H, d, ^3J 8.1 Hz, bipyH_4) 8.79 (2H, d, ^3J 8.1 Hz, bipyH_3′), 9.07 (2H, d, ^3J 8.1 Hz, bipyH_3), 9.42 (2H, s, bipyH_6′), 9.53 (2H, s, bipyH_6).

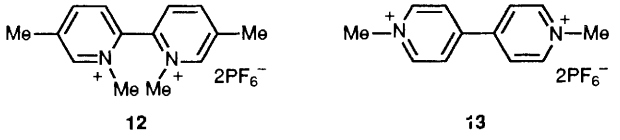
^{13}C NMR (DMSO 100.6 MHz) δ: 18.12 (bipyCH_3), 47.42 and 48.11 (bipyN^+-CH_3), 49.58 and 49.74 [bipy$CH_2N^+(CH_3)_2$] 57.98 (bipy$CH_2N^+CH_2$), 62.60 (bipyCH_2), 129.47, 129.70, 131.22, 139.78, 141.63, 144.67, 146.72, 149.14, 151.00 and 152.09.

For L^3: MS (FAB) [*m*/*z* − ZPF_6]$^+$1161. ^1H NMR (DMSO, 400 MHz) δ: 2.64 (6H, s, bipyCH_3), 4.05/4.16 (12H, 2s, bipyN^+-CH_3), 6.29 (4H, s, bipyCH_2), 8.25 (2H, d, ^3J 8.1 Hz, bipyH_4′), 8.52 (2H, d, ^3J 8.2 Hz, bipyH_4), 8.74 (2H, d, ^3J 8.1-Hz, bipyH_3′), 8.89 (4H, d, ^3J 6.4 Hz, 4, 4′H_3), 9.06 (2H, d, ^3J 8.1 Hz, bipyH_3), 9.36 (2H, s, bipyH_6′), 9.52 (4H, d, ^3J 6.3 Hz, 4,4′H_2), 9.67 (2H, s, bipyH_6).

^{13}C NMR (DMSO, 100.6 MHz) δ: 18.18 (bipyCH_3), 47.38 (bipyN^+ CH_3), 59.42 (bipyCH_2), 127.15, 129.80, 131.03, 135.62, 139.94, 141.69, 143.75, 146.72, 146.91, 147.40, 149.11, 149.54 and 150.25 (aromatic C).



Scheme 4 *Reagents*: i, DMS; ii, NH_4PF_6–H_2O



substantial shifts of the receptor's proton signals. For example, with L^1 the largest downfield shifts are seen for protons H-3 ($\Delta\delta$ 0.1 ppm), H-6 ($\Delta\delta$ 0.38 ppm), H-4′ ($\Delta\delta$ 0.15 ppm), H-7 ($\Delta\delta$ 0.16 ppm) and H-10,11 ($\Delta\delta$ 0.12 ppm). As no hydrogen-bonding interactions are expected for the quaternary bipyridinium receptors, these shifts may be attributed to the proximity of the anionic guest perturbing the electrostatic environment of the receptor and also causing alterations to its solution conformation.

Under identical experimental conditions no significant shifts ($\Delta\delta \leqslant 0.01$ ppm) in the respective ^{1}H NMR spectra of model compounds **12** and **13** were observed on addition of chloride anions, implying that no anion complexation takes place and that simple anion exchange is not responsible for these $\Delta\delta$ observations with L^1 and chloride anion.

A noteworthy feature of the ^{1}H NMR spectrum of the complex formed between L^1 and the chloride anion is that protons H-7, which appear as a sharp singlet in the spectrum of the free receptor are observed as an AB system. Clearly this implies that some conformational restrictions have been imposed upon the host, causing the two H-7 protons to exist in differing chemical environments, and is further evidence for the formation of a host–guest species. Fig. 1 shows a possible structure of the chloride complex of L^1 with the anionic guest in close proximity to the protons of the host that undergo the largest shifts in the ^{1}H NMR spectrum.

Chloride anion addition to ^{1}H NMR solutions of receptor L^2 results in significant shifts of some of the host's protons. Interestingly there are no shifts seen for the signals corresponding to the protons H-13 and H-14, and the shifts for the protons H-9 and H-12 are very small, ($\Delta\delta \leqslant 0.04$ ppm) suggesting that the interaction with the guest anion is primarily taking place close to the central *N*,*N*′-dimethyl-2,2′-bipyridinium unit. This is to be expected as in this region the positive charge density is highest, especially if the molecule can arrange itself in a U-shaped conformation.

Although ^{1}H NMR chloride and bromide titration experiments in [$^2H_6$]DMSO with L^1 and L^2 have been thwarted by precipitation problems titration curves with L^3 and L^4 suggest respective 1 : 1 and 1 : 2 stoichiometric complexes with these halide anions.

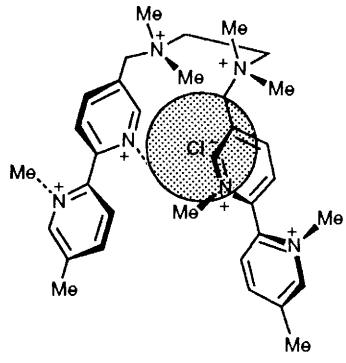


Fig. 1 A possible form for the chloride complex of the receptor L^1

Analogous anion complexation results were observed with ^{13}C NMR titration studies. Significant shifts of the respective carbon resonances of L^1, L^2, L^3, of up to 1.11 ppm were seen on addition of chloride anions to [$^2H_6$]DMSO solutions of all three receptors. No shifts were observed with model compounds **12**, **13** in agreement with ^{1}H NMR titration investigations described previously.

The electrochemical properties of L^1, L^2, L^3 were investigated using cyclic voltammetry and coulometry. Each compound exhibited reversible reduction waves in the −0.3 to −0.8 V region [*vs.* saturated calomel electrode (SCE)]. At more cathodic potentials the ligands exhibited additional irreversible redox behaviour attributed to the respective second reduction redox process of the *N*,*N*′-dimethyl-2,2′-bipyridinium moiety.[3]

Preliminary electrochemical anion recognition[6] investigations revealed that the addition of chloride anions to electrochemical DMSO solutions of L^1–L^3 disappointingly had only small effects on the respective reduction waves. Perturbations of $\Delta E \leqslant 10$ mV were observed suggesting under these experimental conditions these redox-active hosts are not sensitive enough to recognise electrochemically the chloride anionic guest.

In conclusion, novel acyclic polybipyridinium receptors containing the 5,5′- and 4,4′-disubstituted-*N*,*N*′-dimethyl-2,2′-bipyridinium moieties have been prepared and shown from ^{1}H and ^{13}C NMR titration studies to complex chloride and bromide guest anions. Thus, they represent a new class of anion receptor the coordination chemistry of which towards anions of medical and environmental importance is currently being investigated.

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