Halide anion recognition by new acyclic quaternary polybipyridinium and polypyridinium receptors

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New acyclic quaternary polybipyridinium receptors containing 5,5'- and 4,4'-disubstituted *N,N'*-dimethyl-2,2'-bipyridinium moieties (L^1–L^6) and a polypyridinium receptor L^7 have been synthesised. ^{1}H NMR titration studies in deuteriated DMSO show these receptors complex chloride and bromide anions, with a 1:1 stoichiometric ligand:chloride stability constant evaluations suggesting the amide containing polypyridinium receptor (L^7) forms the most thermodynamically stable chloride anion complex. Square-wave voltammetric investigations showed some of the polypyridinium receptors to recognise electrochemically the chloride anion.

In recent years considerable interest has been shown in the chemistry of 2,2'-bipyridine and related polypyridine derivatives due to their numerous applications in a diversity of fields. Primary examples include their ubiquitous role as coordinating ligands for a variety of metal ions[1] and the versatile photoactivity of the corresponding metal complexes in electron- and energy-transfer processes[2] and more recently in optical chemical sensor technology.[3]

Although macropolycyclic quaternary ammonium salts have been shown to recognise anionic guest species,[4] surprisingly, to our knowledge the utilisation of the pH-independent positively charged redox-active diquaternary 2,2'-bipyridinium group[5] as a potential new class of receptor for complexing and electrochemically sensing anions has yet to be exploited. We describe here the syntheses, halide anion coordination studies and electrochemical properties of new acyclic quaternary polybipyridinium receptors[6] containing 5,5'- and 4,4'-disubstituted-*N,N'*-dimethyl-2,2'-bipyridinium moieties L^1–L^6 and a novel polypyridinium receptor L^7.

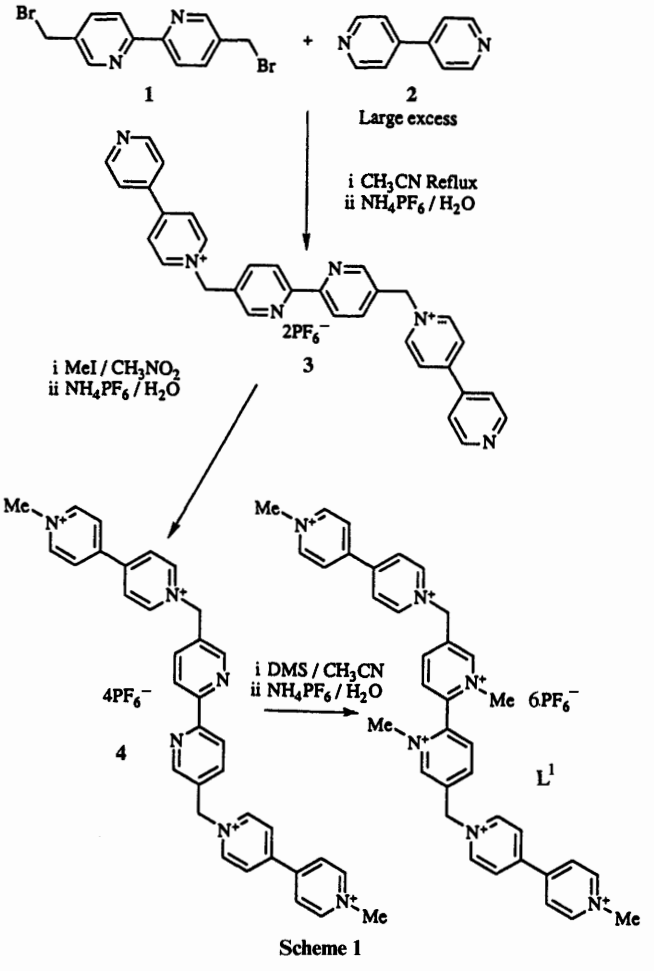
Results and discussion

Ligand syntheses

Treatment of 5,5'-bis(bromomethyl)-2,2'-bipyridine (**1**)[7] with a large excess of 4,4'-bipyridine (**2**) in acetonitrile, followed by conversion of the resultant precipitate into the hexafluorophosphate salt, gave the dicationic compound **3** in 88% yield (Scheme 1). The reaction of **3** with methyl iodide in nitromethane at reflux for 24 h produced an orange precipitate, which was collected, dissolved in water and converted into the hexafluorophosphate salt to afford the tetracationic compound **4** in 89% yield (Scheme 1). Alkylation of **4** with dimethyl sulfate in acetonitrile gave initially a white precipitate which was converted into the hexacationic hexafluorophosphate acyclic receptor molecule L^1 in 71% yield (Scheme 1).

Refluxing **1** in pyridine for 24 h gave an off-white precipitate which on conversion to the hexafluorophosphate salt produced **5** in 76% yield. This compound was further alkylated using dimethyl sulfate in acetonitrile and the hexafluorophosphate salt L^2 was isolated in 93% yield (Scheme 2).

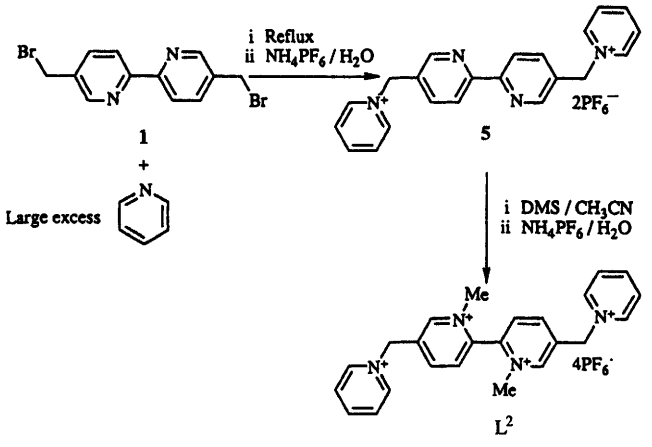
A similar synthetic procedure was used to prepare initially the dicationic derivative **6** from **1** and a large excess of nicotinamide, (Scheme 3), however attempts to quaternise **6** with dimethyl sulfate only gave intractable product materials.



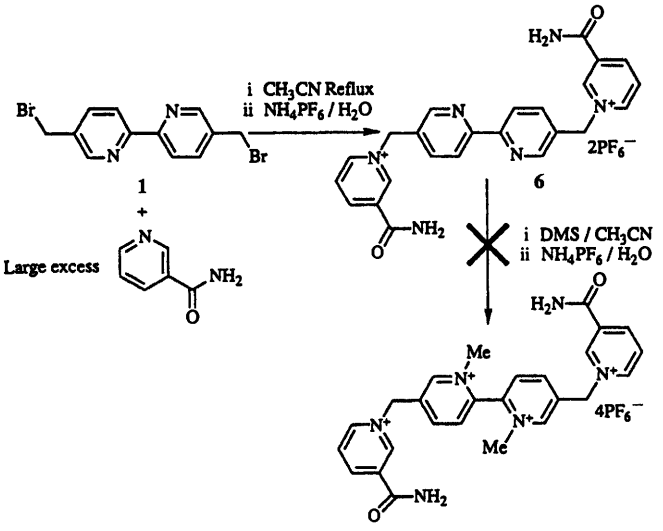
Scheme 1

4,4'-Bipyridine **2** was treated with 2 equiv. of 5-bromomethyl-2,2'-bipyridine **7**[7] to produce, on addition of NH_4PF_6, the dicationic compound **8** in 63% yield (Scheme 4). Further quaternisation with dimethyl sulfate and subsequent anion exchange produced L^3 in near quantitative yield (Scheme 4).

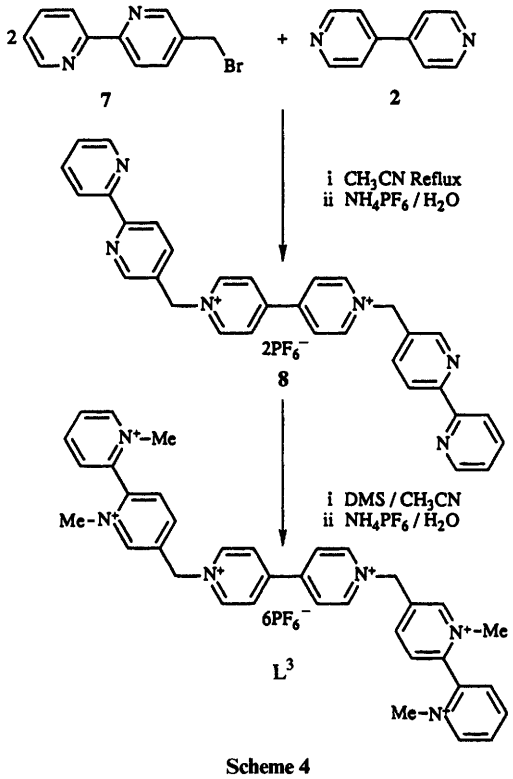
Compound **9** was prepared in 41% yield by reacting two equivalents of **7** with **3** and conversion to the hexafluorophosphate salt (Scheme 5). The usual synthetic dimethyl sulfate



Scheme 2

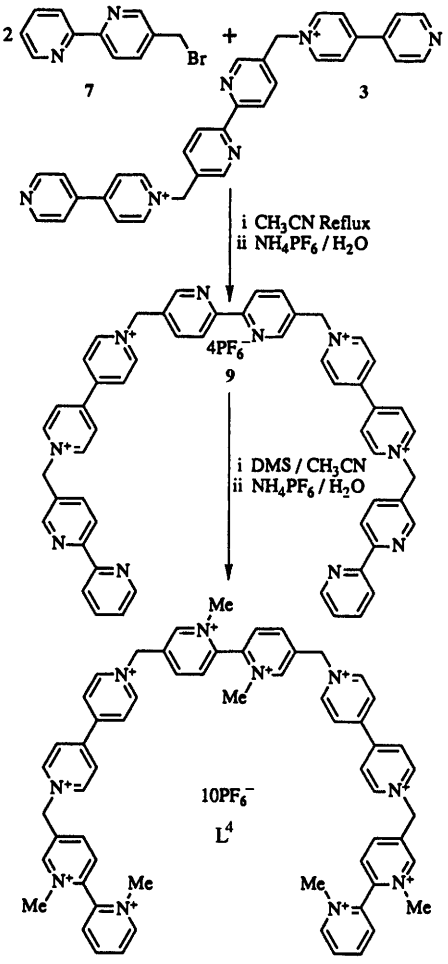


Scheme 3



Scheme 4

quaternisation method was used to produce the new decacationic ligand L^4 in 91% yield (Scheme 5).



Scheme 5

The vinyl linked quaternary polypyridinium receptors L^5 and L^6 were prepared *via* stoichiometric lithiation reactions,[8] using lithium diisopropylamide (LDA), of 4,4-dimethyl-2,2′-bipyridine **10** and reaction with pyridine-4-carboxaldehyde **11** followed by exhaustive methylation with dimethyl sulfate (Scheme 6).

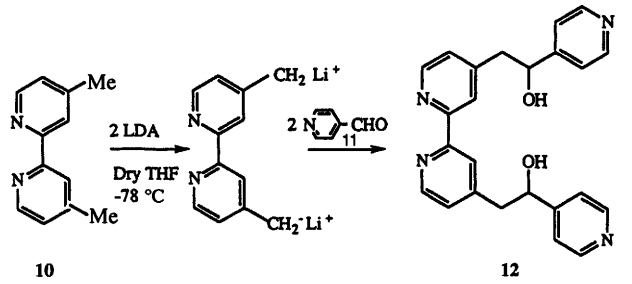
A new tripodal amide linked trispyridinium receptor L^7 was synthesised by the condensation reaction of benzene-1,3,5-tricarbonyl trichloride **14** and 3 equivs. of 4-(methylamino)pyridine **15**. Quaternisation of the pyridine moieties of **16** was effected through exhaustive methylation with methyl iodide and addition of excess NH_4PF_6 produced L^7 in good yields (Scheme 7). All these new acyclic receptors gave spectroscopic and analytical data in accordance with assigned structures (see Experimental section).

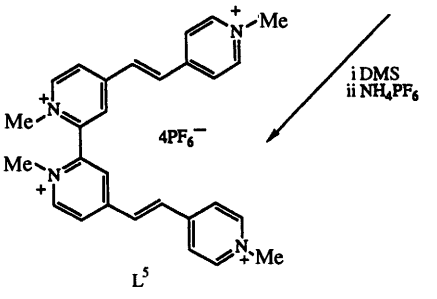
Halide anion coordination studies

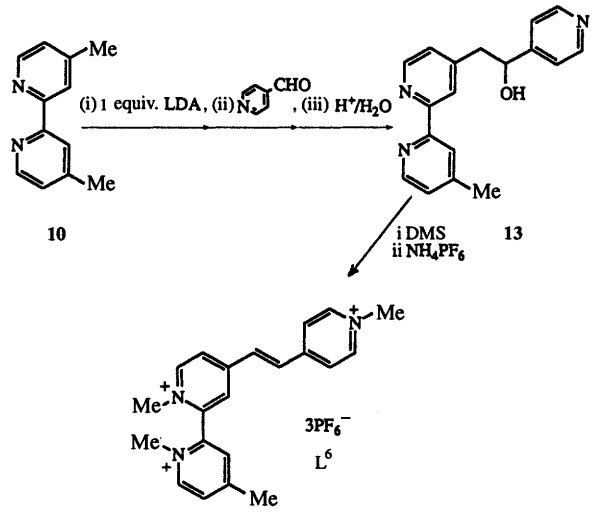
The combination of ^1H NMR spectroscopy and electrochemical cyclic and square wave voltammetric experiments were used to investigate the anion coordination chemistry of L^1–L^7 with halide anions.

^1H NMR anion titration investigations

In a typical ^1H NMR titration experiment the addition of 1 equiv. of tetrabutyl ammonium chloride or bromide to respective deuteriated DMSO solutions of L^1–L^7 led to significant shifts of the receptor's proton signals. For example with L^1 and chloride anion the largest downfield shifts are seen for protons H-3 ($\Delta\delta$ 0.1), H-4 ($\Delta\delta$ 0.1), H-6 ($\Delta\delta$ 0.28), H-7 ($\Delta\delta$ 0.1) and H-8 ($\Delta\delta$ 0.2). Interestingly with L^1 there are no shifts seen for the signals corresponding to the protons H-13 and H-14, and the perturbations for the protons H-9 and H-12 are very small, ($\Delta\delta \leqslant 0.04$) suggesting that the interaction with







Scheme 6

the chloride guest anion is primarily taking place close to the central *N,N'*-dimethyl-2,2'-bipyridinium unit. This is perhaps 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. With L^4 generally smaller ($\Delta\delta$ max 0.1) proton perturbations were observed and disappointingly precipitation problems with both halide anions gave inconclusive results. With L^5 the largest observed proton shifts were for the H-3,3'-bipyridine ($\Delta\delta$ 0.35) and vinyl protons ($\Delta\delta$ 0.2). As no hydrogen-bonding interactions are expected for the quaternary polypyridinium receptors L^1–L^6, these shifts may be attributed to the proximity of the halide anionic guest perturbing the electrostatic environment of the receptor and also causing alterations to its solution conformation.

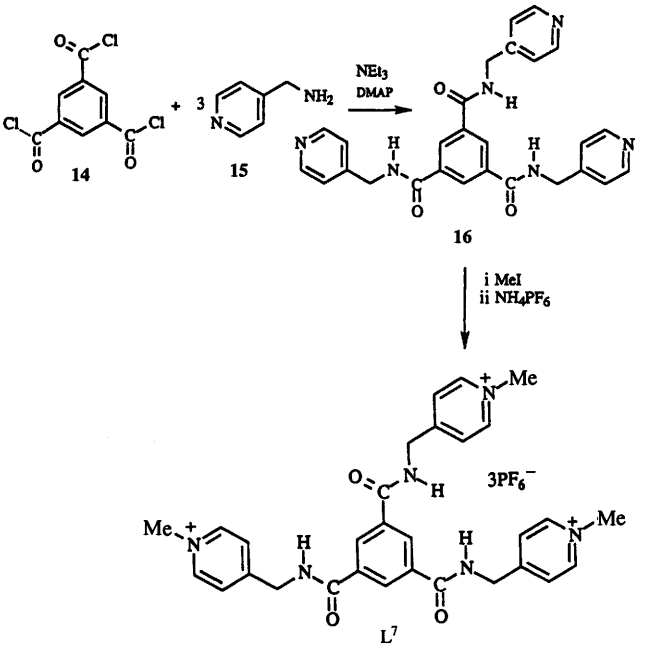
Under identical experimental conditions no significant shifts ($\Delta\delta \leqslant 0.01$) in the respective ^{1}H NMR spectra of 'model' compounds **17** and **18** were observed on addition of halide anions, implying that no anion complexation takes place and that simple anion exchange is not responsible for these $\Delta\delta$ observations with L^1–L^7 and halide anion.

In some cases it was possible to analyse the resulting titration curves (Fig. 1) using the computer program EQNMR [9] and to evaluate stability constants for the receptor–halide anion 1:1 solution stoichiometric complexes. Table 1 shows that L^1–L^3 receptors exhibit similar magnitudes of stability constant for chloride, which presumably reflects their similar structural

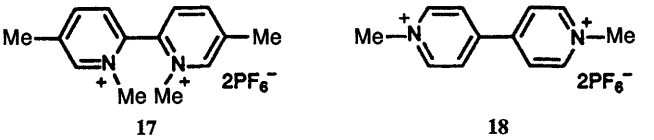
Table 1 Stability constant data with halide anions in $(CD_3)_2SO$

Receptor	Anion	K[a]/dm^3 mol^{-1}
L^1	Cl^-	40
L^2	Cl^-	30
L^3	Cl^-	30
L^7	Cl^-	110
L^7	Br^-	50

[a] Errors estimated to be $\leqslant 10\%$.



Scheme 7



frameworks. It is noteworthy that L^7 displays the largest thermodynamic stability for chloride and this most likely reflects the importance of additional favourable amide (CO–NH)···anion hydrogen bonding to the overall anion complexation process, a feature noticed with other classes of anion receptor.[10] Fig. 1 shows the amide protons of L^7 are significantly perturbed in the presence of chloride. Receptor L^7 does exhibit a degree of selectivity for Cl^- over Br^- (Table 1) and unfortunately EQNMR analyses of the bromide titration curves with L^1–L^3 failed to produce any meaningful quantitative data.

Electrochemical anion recognition investigations

Methyl viologen or paraquat **18** is a well known redox-active moiety [5] which exhibits two one-electron reversible reduction waves in acetonitrile at -0.40 and -0.82 V, respectively (*versus* Ag/Ag^+ reference electrode). Several of the new acyclic receptors contain this redox-active subunit and consequently the electrochemical behaviour of these systems in the absence and presence of chloride ions was investigated by cyclic and square-wave voltammetry. Table 2 summarises the electrochemical properties of the receptors and, for example, Fig. 2 shows the CV and SW voltammograms of L^1. The 4,4'-bipyridinium redox-active moiety present in receptors L^1, L^3 and L^4 undergoes its usual reversible two wave reduction process. In contrast the electrochemical reversibility of the 2,2'-bipyridinium and pyridinium moieties depends on the structure of the

Table 2 Electrochemical data[a]

Receptor	E_1/V[b]	E_2/V[b]	E_3/V[b]	E_4/V[b]
L^1	−0.685	−0.975	−1.210[c]	
L^2	−1.195[c]	−1.545[c]		
L^3	−0.560	−0.870	−1.170	−1.285[c]
L^4	−0.660[d]	−1.025[d]	−1.145	−1.535[c]
L^5	−0.620	−0.730	−0.90	−1.00
L^6	−0.430[e]	−0.570[e]	−0.700[c,e]	
L^7	—	—	—	−1.50[c]

[a] Obtained in acetonitrile solution using Bu_4NPF_6 as supporting electrolyte, Ag/AgCl reference electrode. [b] Reduction potential obtained from square wave voltammograms with compounds at concentration of 1×10^{-4} M. [c] Irreversible process. [d] Two electron reduction process. [e] Obtained in DMSO solution.

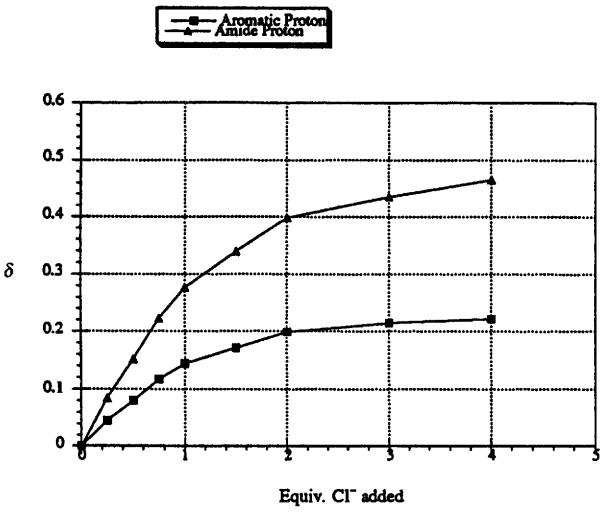


Fig. 1 ^{1}H NMR titration of L^7 and chloride anions in $(CD_3)_2SO$

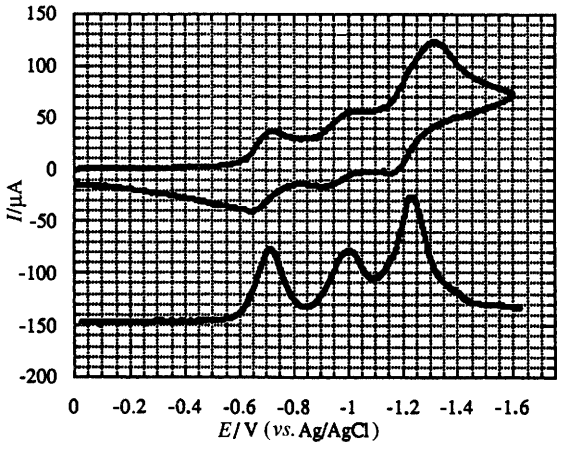


Fig. 2 Cyclic and square wave voltammograms of L^1 in acetonitrile

receptor. For example, L^2 exhibits two irreversible reduction waves, whereas L^5 displays four reversible reduction processes. The irreversible redox behaviour of simple *N,N'*-dialkyl-2,2-bipyridinium molecules[5] has previously been attributed to the reduced species possessing a non-planar conformation which can undergo an intramolecular chemical reaction. Electrochemical chloride anion recognition studies were initially attempted using cyclic voltammetry, however, precipitation problems thwarted any anion induced perturbations of the respective receptor redox waves being observed. However at lower receptor concentrations (10^{-4} M) the monitoring of square wave voltammograms after the progressive addition of stoichiometric equivalents of chloride anion to electrochemical solutions of receptor was successful and the results are summarised in Table 3.

Table 3 Chloride anion induced cathodic shifts in reduction potentials of receptors

Receptor	ΔE_1/mV[a]	ΔE_2/mV[a]	ΔE_3/mV[a]	ΔE_4/mV[a]
L^1	50	10	≤5	—
L^2	50	10	≤5	—
L^3	130	10	≤5	—
L^5	30	30	≤5	≤5

[a] Obtained in acetonitrile solution using Bu_4NPF_6 as supporting electrolyte; ΔE_n refers to cathodic shift in reduction potential produced by the presence of tetrabutylammonium chloride (10 equiv.).

With L^1–L^3 significant cathodic shifts of the first reduction wave was observed, with L^3 displaying the largest ΔE value of 130 mV. The complexed chloride anion effectively stabilises the overall positive charge of the receptor. Surprisingly insignificant perturbations ($\Delta E \leqslant 10$ mV) of the more cathodic waves of L^1–L^3 were observed even in the presence of excess amounts of chloride.

In contrast with L^5 cathodic perturbations were observed for more than one of the reduction couples (Table 3). Precipitation problems with L^4, L^6 and L^7 meant ΔE data for these receptors could not be determined. Analogous electrochemical chloride anion recognition studies with model compounds **17** and **18** gave no perturbations of the respective redox couples.

Conclusions

New acyclic quaternary polybipyridinium receptors containing 5,5'- and 4,4'-disubstituted-*N,N'*-dimethyl-2,2'-bipyridinium moieties (L^1–L^6) and a polypyridinium receptor L^7 have been prepared. ^{1}H NMR titration studies in deuteriated DMSO have shown these receptors to complex chloride and bromide anions, with comparative 1:1 stoichiometric ligand:chloride anion stability constant evaluations, (L^1–L^3, K = 30–40 dm^3 mol^{-1} *versus* L^7, K = 110 dm^3 mol^{-1}) highlighting the importance of amide CO–NH • • • anion hydrogen-bonding interactions to the overall anion complexation process.[11] Electrochemical investigations reveal L^1–L^3 and L^5 can electrochemically recognise the chloride anion *via* significant cathodic perturbations of up to ΔE = 130 mV of their respective least cathodic reduction couple.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on a Bruker AM300 instrument using the solvent deuterium signal as internal reference (*J* values are given in Hz). Fast atom bombardment mass spectrometry (FABMS) was performed by the SERC mass spectrometry service at University College, Swansea. Electrochemical measurements were carried out using an E.G. and G. Princeton Applied Research 362 scanning potentiostat. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford.

Solvent and reagent pretreatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was pre-dried over class 4 Å molecular sieves (4–8 mesh) and then distilled from calcium hydride. Unless stated to the contrary commercial grade chemicals were used without further purification. 5,5'-Bis(bromomethyl)-2,2'-bipyridine **1** and 5-bromomethyl-2,2'-bipyridine **7** were prepared according to literature procedures.[7]

Syntheses

5,5'-Bis(4,4'-bipyridin-1-ium-1-ylmethyl)-2,2'-bipyridine bis(hexafluorophosphate) (3). 4,4'-Bipyridine (**2**) (4.20 g, 26.1

mmol) was dissolved in dry acetonitrile (400 ml) and heated to reflux. A solution of 5,5′-bis(bromomethyl)-2,2-bipyridine (**1**) (1.00 g, 2.92 mmol) in acetonitrile (200 ml) was added dropwise over 1 h and the resultant solution refluxed for 20 h giving a brown precipitate. The mixture was cooled to room temperature and the volume of the solvent reduced to *ca.* 400 ml. The brown solid was collected by filtration, washed with acetonitrile (3 × 50 ml) and dried *in vacuo*. The solid was dissolved in water (200 ml) at 50 °C and filtered through Celite®. A saturated aqueous solution of ammonium hexafluorophosphate was added until no further precipitation occurred. The mixture was cooled to 0 °C ensuring complete precipitation of the product. The pale cream precipitate was collected by filtration, washed with water (3 × 20 ml) and dried *in vacuo*. Yield 1.49 g, 65.0%, mp > 300 °C. $\delta_H[(CD_3)_2SO]$ 6.00 (4 H, s, CH_2), 8.02 (4 H, d, *J* 6.1, 4,4′$H^{3'}$), 8.15 (2 H, dd, *J* 8.3 and 2.0, bipyH^4), 8.45 (2 H, d, *J* 8.3, bipyH^3), 8.67 (4 H, d, *J* 6.7, 4,4′H^3), 8.87 (4 H, d, *J* 6.1, 4,4′$H^{2'}$), 8.95 (2 H, d, *J* 2.0, bipyH^6) and 9.40 (4 H, d, *J* 6.7, 4,4′H^2); $\delta_C[(CD_3)_2SO]$ 60.3 (CH_2), 120.8, 125.9, 130.7, 138.0, 140.8, 145.5, 149.6, 151.0, 153.0 and 155.3 (bipy *C*) (Calc. for $C_{32}H_{26}F_{12}N_6P_2$: C, 49.0; H, 3.3; N, 10.7. Found: C, 48.8; H, 3.4; N, 10.6%); FABMS $[M - PF_6]^+$ 639.

5,5′-Bis(1′-methyl-4,4′-bipyridine-1,1′-dium-1-ylmethyl)-2,2′-bipyridine tetrakis(hexafluorophosphate) (4). The synthon **3** (0.13 g, 0.16 mmol) was dissolved in nitromethane (10 ml) with stirring. To this was added methyl iodide (10 ml) and the resultant solution heated to reflux for 23 h. After cooling to room temperature the orange precipitate was collected by filtration, washed with nitromethane (3 × 5 ml) and dried under vacuum. The solid was then dissolved in water (75 ml) with warming and a saturated aqueous solution of ammonium hexafluorophosphate added until no further precipitation occurred and allowed to stand overnight at 4 °C. The solid was collected by filtration, washed with water (2 × 10 ml) and dried under vacuum to give a white solid of **4**. Yield 0.18 g, 98.3%, mp > 300 °C. $\delta_H[(CD_3)_2SO]$ 4.43 (6 H, s, 4,4′N^+–CH_3), 6.05 (4 H, s, bipyCH_2), 8.16 (2 H, dd, *J* 8.3 and 2.2, bipyH^4), 8.45 (2 H, d, *J* 8.3, bipyH^3), 8.71 (4 H, d, *J* 6.9, 4,4′$H^{3'}$), 8.79 (4 H, d, *J* 6.9, 4,4′H^3), 8.95 (2 H, s, bipyH^6), 9.26 (4 H, d, *J* 6.9, 4,4′$H^{2'}$) and 9.54 (4 H, d, *J* 6.9, 4,4′H^2) (Calc. for $C_{34}H_{32}F_{24}N_6P_4$: C, 37.0; H, 2.9; N, 7.6. Found: C, 36.8; H, 2.8; N, 7.3%).

1,1′-Dimethyl-5,5′-bis(1′-methyl-4,4′-bipyridine-1,1′-diium-1-ylmethyl)-2,2′-bipyridine-1,1′-diium hexakis(hexafluorophosphate) L¹. The synthon **4** (0.15 g, 0.20 mmol) was dissolved in acetonitrile (10 ml). To this was added dimethyl sulfate (3 ml) and the resultant solution was refluxed under nitrogen for 6 days giving a dark red solid. Water (200 ml) was added to dissolve the oily product and the volume reduced to 50 ml at reduced pressure to give an orange solution. A large excess of ammonium hexafluorophosphate (2.0 g) was added in the minimum volume of water (3 ml) resulting in the formation of a cream precipitate which was collected by vacuum filtration, washed with water (2 × 10 ml), and dried *in vacuo* to give a white solid of L^1. Yield 0.34 g, 70.4%, mp > 300 °C. $\delta_H[(CD_3)_2SO]$ 4.12 (6 H, s, 4,4′N^+–CH_3), 4.44 (6 H, s, bipyN^+–CH_3), 6.29 (4 H, s, bipyCH_2), 8.45 (2 H, d, *J* 8.1, bipyH^4), 8.72 (4 H, d, *J* 6.4, 4,4′$H^{3'}$), 8.88 (4 H, d, *J* 6.4, 4,4′H^3), 9.07 (2 H, d, *J* 8.1, bipyH^3), 9.27 (4 H, d, *J* 6.4, 4,4′$H^{2'}$), 9.47 (4 H, d, *J* 6.4, 4,4′H^2) and 9.66 (2 H, s, bipyH^6); $\delta_C[(CD_3)_2SO]$ 47.8 and 48.1 (bipyN^+–CH_3 and 4,4′N^+–CH_3), 59.1 (bipyCH_2), 126.1, 126.9, 130.6, 135.9, 142.7, 146.6, 146.7, 147.4, 147.7, 149.8 and 150.0 (bipy*C*) (Calc. for $C_{36}H_{38}F_{36}N_6P_6$: C, 30.3; H, 2.7; N, 5.9. Found: C, 29.8; H, 3.2; N, 6.0%).

5,5′-Bis(pyridin-1-ium-1-ylmethyl)-2,2′-bipyridine bis(hexafluorophosphate) (5). A solution of 5,5′-bis(bromomethyl)-2,2′-bipyridine (**1**) (0.10 g, 0.29 mmol) in acetonitrile (50 ml) was added dropwise over 1 h to pyridine (75 ml) and the resultant solution refluxed for 18 h giving a brown precipitate. The mixture was cooled to 0 °C and the brown solid was collected by filtration, washed with acetonitrile (2 × 10 ml) and dried *in vacuo*. The solid was dissolved in water (50 ml) at 50 °C and filtered to remove dark coloured impurities. A saturated aqueous solution of ammonium hexafluorophosphate was added until no further precipitation occurred. The mixture was stored overnight at 4 °C to ensure complete precipitation of the product. The pale cream precipitate was collected by filtration, washed with water (3 × 10 ml) and dried *in vacuo*. Yield 0.14 g, 76.0%, mp > 300 °C; $\delta_H[(CD_3)_2SO]$ 5.97 (4 H, s, CH_2), 8.09 (2 H, dd, *J* 8.2 and 2.0, bipyH^4), 8.21 (4 H, tm, *J* 7.0, pyH^3), 8.43 (2 H, d, *J* 8.2, bipyH^3), 8.65 (2 H, t, *J* 7.8, pyH^4), 8.90 (2 H, d, *J* 2.0, bipyH^6) and 9.25 (4 H, d, *J* 6.7, pyH^2); $\delta_C[(CD_3)_2SO]$ 60.6 (CH_2), 120.9, 128.6, 130.6, 138.0, 138.2, 145.5, 146.2 and 149.8 (bipy*C*) (Calc. for $C_{22}H_{20}F_{12}N_4P_2$: C, 41.9: H, 3.2; N, 8.9. Found: C, 41.5; H, 3.2; N, 8.5%). FABMS $[M - PF_6]^+$ 485.

1,1′-Dimethyl-5,5′-bis(pyridin-1-ium-1-ylmethyl)-2,2′-bipyridine-1,1′-diium tetrakis(hexafluorophosphate) L². The synthon **5** (0.10 g, 0.16 mmol) was dissolved in acetonitrile (5 ml). To this was added dimethyl sulfate (1 ml) and the resultant yellow solution was refluxed under nitrogen for 6 days giving a dark red solid. Water (200 ml) was added to dissolve the oily product and the volume of the orange solution was reduced to 50 ml at reduced pressure. A large excess of ammonium hexafluorophosphate (1.5 g) was added in the minimum volume of water (2 ml) resulting in the formation of a cream precipitate, which was collected by vacuum filtration, washed with water (2 × 10 ml), and dried *in vacuo* to furnish a cream solid of L^2. Yield 0.14 g, 92.9%, mp > 300 °C; $\delta_H[(CD_3)_2SO]$ 4.10 (6 H, s, bipyN^+–CH_3), 6.20 (4 H, s, bipyCH_2), 8.29 (4 H, tm, *J* 6.5, pyH^3), 8.43 (2 H, d, *J* 8.1, bipyH^4), 8.73 (2 H, t, *J* 7.4, pyH^4), 9.02 (2 H, d, *J* 8.1, bipyH^3), 9.2 (4 H, d, *J* 6.2, pyH^2) and 99.59 (2 H, s, bipyH^6); $\delta_C[(CD_3)_2SO]$ 47.8 (bipyN^+–CH_3), 59.1 (bipyCH_2), 128.7, 130.1, 136.1, 142.8, 145.4, 146.9, 147.2 and 149.8 (bipy*C*) (Calc. for $C_{24}H_{26}F_{24}N_4P_4 \cdot H_2O$: C, 29.8; H, 2.9; N, 5.8. Found: C, 29.5; H, 2.9; N, 5.7%); FABMS $[M - PF_6]^+$ 805.

5,5′-Bis[3-(aminocarbonyl)pyridin-1-ium-1-ylmethyl]-2,2′-bipyridine bis(hexafluorophosphate) (6). A solution of 5,5′-bis(bromomethyl)-2,2-bipyridyl (**1**) (0.15 g, 0.44 mmol) and nicotinamide (1.40 g, 11.5 mmol) were refluxed for 20 h in acetonitrile (250 ml) giving a brown precipitate. The mixture was stored overnight at 4 °C and subsequently the brown solid was collected by filtration, washed with acetonitrile (2 × 20 ml) and dried *in vacuo*. The solid was dissolved in water (100 ml) to which ammonium hexafluorophosphate (1.00 g) was added in water (3 ml) giving a white precipitate. The mixture was stored overnight at 4 °C to ensure complete precipitation of the product. The white solid was collected by filtration, washed with water (3 × 10 ml) and dried in an oven (60 °C). Yield 0.29 g, 92.3%, mp > 300 °C; $\delta_H[(CD_3)_2SO]$ 6.03 (4 H, s, CH_2), 8.14 (2 H, d, *J* 8.4, bipyH^4), 8.19 (2 H, s, NH_2), 8.31 (2 H, tm, *J* 7.0, NicH^5), 8.44 (2 H, d, *J* 8.4, bipyH^3), 8.57 (2 H, s, NH_2), 8.93 (2 H, s, bipyH^6), 8.97 (2 H, d, *J* 8.5, NicH^4), 9.34 (2 H, d, *J* 6.2, NicH^6) and 9.65 (2 H, s, NicH^2); $\delta_C[(CD_3)_2SO]$ 61.0 (CH_2), 120.8, 128.2, 128.4, 134.3, 138.2, 143.9, 145.2, 146.5, 150.0, 155.3 and 162.7 (bipy*C*) (Calc. for $C_{24}H_{22}F_{12}N_6O_2P_2 \cdot 2H_2O$: C, 38.3; H, 3.5; N, 11.2. Found: C, 38.0; H, 3.4; N, 11.0%); FABMS $[M - PF_6]^+$ 571.

1,1′-Bis(2,2′-bipyridin-5-ylmethyl)-4,4′-bipyridine-1,1′-diium bis(hexafluorophosphate) (8). 5-Bromomethyl-2,2′-bipyridine (**7**) (0.80 g, 3.21 mmol) and 4,4′-bipyridyl (**2**) (0.20 g, 1.28 mmol) were dissolved in acetonitrile (80 ml). The solution was then heated to reflux for 24 h giving a yellow precipitate. After cooling to 0 °C, the solid was collected by filtration, washed with acetonitrile (2 × 10 ml) and dried under vacuum. It was then dissolved in water (75 ml) and ammonium hexafluorophosphate (1.0 g) in water (2 ml) added furnishing a cream precipitate. The solid was collected by filtration, washed with water (2 × 10 ml) and dried in an oven (60 °C). Yield 0.63 g, 62.7%, mp > 300 °C. $\delta_H[(CD_3)_2SO]$ 6.05 (4 H, s, bipyCH_2),

7.48 (2 H, dd, *J* 4.9 and 7.1, bipy$H^{5'}$), 7.97 (2 H, t m, *J* 65, bipy$H^{4'}$), 8.15 (2 H, d, *J* 8.2, bipyH^{4}), 8.38 (2 H, d, *J* 7.9, bipy$H^{3'}$), 8.45 (2 H, d, *J* 8.2, bipyH^{3}), 8.69 (2 H, d, *J* 4.1, bipy$H^{6'}$), 8.74 (4 H, d, *J* 6.7, 4,4′H^{3}), 8.94 (2 H, s, bipyH^{6}) and 9.52 (4 H, d, *J* 6.7, 4,4″H^{2}); δ_C[$(CD_3)_2SO$] 61.0 (bipyCH_2), 120.7, 120.8, 124.7, 127.2, 2 × 129.9, 137.6, 138.0, 145.9, 149.4, 149.8, 154.4 and 156.1 (bipy*C*) (Calc. for $C_{32}H_{26}F_{12}N_6P_2$: C, 48.9; H, 3.3; N, 10.7. Found: C, 48.1; H, 3.2; N, 10.4%); FABMS [M − PF_6]$^+$ 639.

1,1′-Bis(1,1′-dimethyl-2,2′-bipyridine-1,1′-diium-5-ylmethyl)-4,4′-bipyridine-1,1′-diium hexakis(hexafluorophosphate) L³. The compound (**8**) (0.20 g, 0.253 mmol) was dissolved in acetonitrile (15 ml) under nitrogen. To this was added dimethyl sulfate (5 ml) and the resultant solution heated at reflux for 6 days. After cooling to room temperature, water (300 ml) was added to the oily red residue that remained and stirred for 18 h. The volume of solvent was reduced to *ca.* 30 ml and an aqueous solution of ammonium hexafluorophosphate (2.0 g in 3 ml) was added giving a cream precipitate. The solid was collected by filtration, washed with water (2 × 10 ml) and dried under vacuum giving compound L³. Yield 0.36 g, 99.0%, mp > 300 °C; δ_H[$(CD_3)_2SO$] 4.10 (6 H, s, bipyN′CH_3), 4.18 (6 H, s, bipyNCH_3), 6.30 (4 H, s, bipyCH_2), 8.37 (2 H, d, *J* 7.9, bipy$H^{3'}$), 8.51 (2 H, m, bipy$H^{5'}$), 8.56 (2 H, d, *J* 8.1, bipyH^{3}), 8.89 (4 H, d, *J* 6.3, 4,4′H^{3}), 8.90 (2 H, m, bipy$H^{4'}$), 9.07 (2 H, d, *J* 8.4, bipyH^{4}), 9.41 (2 H, d, *J* 5.3, bipy$H^{6'}$), 9.51 (4 H, d, *J* 6.1, 4,4′H^{2}) and 9.67 (2 H, s, bipyH^{6}); δ_C[$(CD_3)_2SO$] 47.4 and 47.9 (bipyN^+–CH_3), 59.2 (bipyCH_2), 126.9, 2 × 130.4, 130.7, 135.5, 142.4, 143.5, 3 × 146.75, 147.2, 149.3 and 150.1 (bipy*C*) (Calc. for $C_{36}H_{38}F_{36}N_6P_6 \cdot H_2O$: C, 30.0; H, 2.8; N, 5.8. Found: C, 29.9; H, 2.9; N, 5.9%); FABMS [M − PF_6]$^+$ 1279.

5,5′-Bis[1′-(2,2′-bipyridin-5-ylmethyl)-4,4′-bipyridine-1,1′-diium-1-ylmethyl]-2,2′-bipyridine tetrakis(hexafluorophosphate) (9). The synthon **3** (0.70 g, 0.89 mmol) and 5-bromomethyl-2,2′-bipyridine (**7**) (0.56 g, 2.25 mmol) were dissolved in acetonitrile (40 ml) under nitrogen and heated to reflux for 24 h. After cooling to 0 °C, the yellow precipitate was collected by filtration and washed with cold acetonitrile (2 × 10 ml). The solid was dissolved in water (400 ml) with warming and filtered. An aqueous solution of ammonium hexafluorophosphate (1.0 g in 10 ml) was added and the mixture cooled giving a cream precipitate. The solid was collected by filtration, washed with water (2 × 10 ml) and dried *in vacuo* to give a pale solid of **9**. Yield 0.52 g, 41.2%, mp > 300 °C; δ_H[$(CD_3)_2SO$] 6.07 (8 H, s, bipyCH_2), 7.51 (2 H, m, bipy$H^{5''}$), 8.00 (2 H, m, bipy$H^{4''}$), 8.17 (4 H, d, *J* 8.0, bipyH^{4} and $^{4'}$), 8.42 (2 H, d, *J* 8.1, bipy$H^{3''}$), 8.47 (4 H, d, *J* 8.0, bipyH^{3} and $^{3'}$), 8.72 (2 H, d br, bipy$H^{6''}$), 8.77 (8 H, d, *J* 5.3, 4,4′H^{3} and $^{3'}$), 8.97 (4 H, 2 s, bipyH^{6} and $^{6'}$) and 9.55 (8 H, d, *J* 5.3, 4,4′H^{2} and $^{2'}$); δ_C[$(CD_3)_2SO$] 2 × 60.9 (bipyCH_2), 120.7, 2 × 120.9, 124.7, 2 × 127.2, 2 × 130.4, 2 × 130.6, 137.7, 138.0, 138.1, 2 × 146.0, 149.3, 149.8, 154.2, 155.3 and 155.9 (bipyC) (Calc. for $C_{54}H_{44}F_{24}N_{10}P_4$: C, 45.9; H, 3.1; N, 9.9. Found: C, 45.1; H, 3.0; N, 9.3%); FABMS [M − PF_6]$^+$ 1267.

1,1′-Dimethyl-5,5′-bis[1′-(1,1′-dimethyl-2,2′-bipyridine-1,1′-diium-5-ylmethyl)-4,4′-bipyridine-1,1′-diium-1-ylmethyl]-2,2′-bipyridine-1,1′-diium decakis(hexafluorophosphate) L⁴. The compound (**9**) (0.130 g, 0.092 mmol) was dissolved in acetonitrile (15 ml) under nitrogen. To this was added dimethyl sulfate (5 ml) and the resultant solution heated at reflux for 6 days. After cooling to room temperature, water (25 ml) was added to the black oily residue that remained and stirred for 18 h at 60 °C. The volume was increased with water (100 ml) and stirred for a further 2 h. The quantity of solvent was reduced to *ca.* 30 ml and an aqueous solution of ammonium hexafluorophosphate (2.0 g in 3 ml) was added giving a cream precipitate. The solid was collected by filtration, washed with water (2 × 10 ml) and dried under vacuum giving compound L⁴. Yield 0.198 g, 91.0%, mp > 300 °C; δ_H[$(CD_3)_2SO$] 4.11 (6 H, s, bipy$N''CH_3$), 4.15 (6 H, s, bipy$N'CH_3$), 4.18 (6 H, s, bipyNCH_3), 6.31 (8 H, s, bipyCH_2), 8.37 (2 H, d, *J* 7.6, bipy$H^{3''}$), 8.48 (2 H, d, *J* 7.7, bipy$H^{3'}$), 8.49 (2 H, m, bipy$H^{5''}$), 8.56 (2 H, d, *J* 8.0, bipyH^{3}), 8.89 (8 H, d, *J* 6.2, 4,4′H^{3} and $^{3'}$), 8.90 (2 H, m, bipy$H^{4''}$), 9.08 (2 H, d, *J* 7.9, bipy$H^{4'}$), 9.11 (2 H, d, *J* 7.6, bipyH^{4}), 9.53 (8 H, d, *J* 6.7, 4,4′H^{2} and $^{2'}$), 9.41 (2 H, d, *J* 6.0, bipy$H^{6''}$), 9.69 (2 H, s, bipy$H^{6'}$) and 9.72 (2 H, s, bipyH^{6}); δ_C[$(CD_3)_2SO$] 47.4, 47.8 and 47.8 (bipyN^+–CH_3), 59.1 (bipyCH_2), 2 × 127.0, 2 × 130.4, 2 × 130.7, 135.5, 135.8, 142.4, 3 × 142.8, 143.5, 2 × 146.7, 147.3, 2 × 147.5, 149.3 and 2 × 150.1 (bipy*C*) (Calc. for $C_{60}H_{62}F_{60}N_{10}P_{10}$: C, 30.4; H, 2.6; N, 5.9. Found: C, 30.5; H, 2.8; N, 5.9%).

4,4′-Bis[2-(4-pyridyl)-2-hydroxyethyl]-2,2′-bipyridine (12). Into a three-necked flask equipped with a septum cap and pressure-equalised dropping funnel was placed dry diisopropylamine (4.56 ml, 33 mmol) in dry tetrahydrofuran (20 ml). After cooling to −75 °C with an acetone–solid CO_2 bath, butyllithium (1.6 M solution in hexanes, 20.47 ml, 33 mmol) was added *via* a syringe. The resultant pale yellow solution was then stirred for 30 min at −75 °C, and a solution of 4,4′-dimethyl-2,2′-bipyridine (**10**) (2.00 g, 11 mmol) in dry tetrahydrofuran (100 ml) was added *via* a dropping funnel to give a red solution. The acetone–CO_2 bath was then replaced by an ice–water bath and the mixture stirred at 0 °C for 1 h. A solution of pyridine-4-carboxaldehyde (**11**) (2.32 g, 22 mmol) was then added in one portion to give a pale green solution. The mixture was stirred at this temperature for 1 h and then at room temperature for a further 5 h. It was then quenched with methanol (2 ml) and water (100 ml) and stirred overnight to give a brown–yellow solution containing a yellow precipitate. On extraction with chloroform, this precipitate did not dissolve. It was collected by filtration, dried and recrystallised from hot methanol to give an off-white crystalline solid (needles). Yield 1.80 g, 42%, mp 215–218 °C; δ_H[$(CD_3)_2SO$] 2.88–3.08 (4 H, m, –CH_2), 3.90 (2 H, t, –CH–), 5.68 (2 H, d, *J* 5.0, –OH), 7.27 (2 H, d, ^3J 4.6, $H^{5,5'}$-bipy), 7.39 (4 H, d, ^3J 5.5, $H^{3,5}$-pyr), 8.29 (2 H, s, $H^{3,3'}$-bipy), 8.49 (4 H, d, ^3J 5.6, $H^{2,6'}$-pyr) and 8.52 (2 H, d, ^3J 4.9, $H^{6,6'}$-bipy); δ_C[$(CD_3)_2SO$] 44.02 (–CH_2), 71.30 (CH), 121.08, 121.79, 125.26, 148.55, 148.61, 149.32, 153.79 and 155.05 (aromatic Cs) (Calc. for $C_{24}H_{22}N_4O_2$: C, 14.07; H, 5.52; N, 72.36. Found: C, 13.89; H, 5.51; N, 72.18%).

4-[2-(4-Pyridyl)-2-hydroxyethyl]-4′-methyl-2,2′-bipyridine (13). This compound was prepared by a method analogous to that for **11** using 4,4′-dimethyl-2,2′-bipyridine (**10**) (2 g, 11 mmol), BuLi (7.43 cm^3, 12 mmol, 1.6 M solution in hexane), diisopropylamine (1.66 cm^3, 12 mmol) and pyridine-4-carboxaldehyde (1.16 g, 11 mmol). The solution was only stirred at room temperature for 3 h and after quenching the solution was extracted with three 50 cm^3 portions of chloroform. After removal of the solvent *in vacuo*, the residual solid was washed with a small portion of cold dichloromethane (10–15 cm^3) leaving the desired product. Yield 1.70 g, 53%, mp 161–163 °C; FABMS *m*/*z* 292; δ_H[$(CD_3)_2SO$] 2.40 (3 H, s, –CH_3), 2.88–3.10 (2 H, m, –CH_2–), 4.91 (1 H, tm, –CH–), 5.66 (1 H, d, *J* 5.0, –OH), 7.27 (2 H, m, $H^{5,5'}$-bipy), 7.39 (2 H, ^3J 5.7, $H^{3,5}$-pyr), 8.22 and 8.29 (2 H, 2 s, $H^{3,3'}$-bipy), 8.49 (2 H, d, ^3J 5.9, $H^{2,6}$-pyr) and 8.52 (2 H, m, $H^{6,6'}$-bipy); δ_C[$(CD_3)_2SO$] 20.65 (–CH_3), 40.03 (–CH_2–), 71.33 (–CH–), 121.07, 121.24, 121.81, 124.77, 125.27, 147.78 (q), 148.55, 148.62 (q), 148.65, 149.29, 153.83 (q), 154.99 (q) and 155.23 (q) (Calc. for $C_{18}H_{17}N_3O \cdot \frac{1}{2}H_2O$: C, 71.90; H, 6.04; N, 13.99. Found: C, 72.39; H, 5.73; N, 14.05%).

1,1′-Dimethyl-4,4′-bis[1-methylpyridin-1-ium-4-ylvinyl]-2,2′-bipyridine-1,1′-diium tetrakis(hexafluorophosphate) L⁵. 4,4′-Bis-[2-(4-pyridyl)-2-hydroxyethyl]-2,2′-bipyridine (**12**) (0.4 g, 1 mmol) was dissolved in methyl iodide (20 cm^3) and gently refluxed under nitrogen for seven days. The yellow precipitate which formed was collected by filtration and dissolved in water (20 ml). A saturated solution of ammonium hexafluorophosphate in water was then added dropwise to yield a cream precipitate which quickly became brown and oily. This was collected and dried to give a brown powder. Analysis by ^{1}H

NMR spectroscopy (CD_3CN) suggested it was a mixture of products. It was then dissolved in 10 ml of dimethyl sulfate and gently heated overnight. To this cooled solution was added dichloromethane to precipitate an oily, brown solid which was collected by filtration. After dissolution in 20 ml of water, addition of saturated, aqueous ammonium hexafluorophosphate solution gave an off-white precipitate. This was collected by filtration, washed with water (2 × 5 ml portions) and dried under vacuum. Yield 0.53 g, 53%, FABMS *m/z* 857 ($M - PF_6^-$); $\delta_H(CD_3CN)$ 2.30 (H_2O), 4.14 (6 H, s, N^+–CH_3), 4.30 (6 H, s, N^+–CH_3), 7.91 (4 H, s, –CH=CH–), 8.18 (4 H, d, ^3J 6.6, $H^{3,5}$-pyridines), 8.45 (2 H, d, ^3J 6.5, $H^{5,5'}$-bipy), 8.48 (2 H, s, $H^{3,3'}$-bipy), 8.65 (2 H, d, ^3J 6.6, $H^{2,6}$-pyridines) and 9.00 (2 H, d, ^3J 6.3, $H^{6,6'}$-bipy); $\delta_C(CD_3CN)$ 48.08, 48.95 (N–CH_3), 126.74, 129.05, 129.53, 133.78, 136.66, 144.06, 146.69, 150.37, 151.25 and 153.77 (Calc. for $C_{28}H_{30}N_4P_4F_{24}\cdot H_2O$: C, 32.96; H, 3.16; N, 5.39. Found: C, 32.84; H, 3.00; N, 5.49%).

1,1′-Dimethyl-4-[1-methylpyridin-1-ium-4-ylvinyl]-4′-methyl-2,2′-bipyridine-1,1′-diium tris(hexafluorophosphate) L⁶. To 0.30 g (1.03 mmol) of 4-[2-(4-pyridyl)-2-hydroxyethyl]-4′-methyl-2,2′-bipyridine (**13**) was added dimethyl sulfate (15 ml). The mixture was heated at 80 °C for three days to give a pale amber solution. Addition of dichloromethane caused precipitation of an off-white solid. This was collected by filtration and washed and dissolved in 10 ml of water. Addition of saturated, aqueous ammonium hexafluorophosphate gave a white precipitate which was collected by filtration and washed with two 10 ml portions of water. This was dried under vacuum to give a white solid product. Yield 0.43 g, 55%, FABMS *m/z* 608 ($M - PF_6^-$); $\delta_H(CD_3CN)$ 2.30 (H_2O), 2.76 (3 H, s, $-CH_3$), 4.05–4.07 (6 H, 2 s, N^+–CH_3), 4.30 (3 H, s, N^+–CH_3), 7.86 (2 H, s, H–C=C–H), 8.02 (1 H, d, ^4J 1.7, H^3-bipy), 8.14 (1 H, d, H^5-bipy), 8.16 (2 H, d, ^3J 6.7, $H^{3,5}$-py), 8.35 (1 H, d, ^4J 2.0, $H^{3'}$-bipy), 8.41 (1 H, dd, ^3J 6.4, ^4J 2.0, $H^{5'}$-bipy), 8.65 (1 H, d, ^3J 6.7, $H^{2,6}$-py), 8.82 (1 H, d, ^3J 6.4, H^6-bipy) and 8.96 (1 H, d, ^3J 6.5, $H^{6'}$-bipy); $\delta_C(CD_3CN)$ 47.66, 48.01, 48.95 (N–CH_3), 126.73, 128.89, 129.41, 131.61, 132.74, 133.79, 136.59, 142.63, 146.69, 148.85, 150.24, 151.25, 153.70 and 163.31 (aromatic and vinylic) (Calc. for $C_{21}H_{24}N_3P_3F_{18}\cdot 2H_2O$: C, 31.95; H, 3.35; N, 5.32. Found: C, 31.80; H, 3.35; N, 5.29%).

***N,N′,N″*-Tris(4-pyridylmethyl)benzene-1,3,5-tricarboxamide (16).** To a large excess of 4-(aminomethyl)pyridine (**15**) (5 g, 47 mmol) and triethylamine (0.91 g, 9 mmol) was added a solution of benzene-1,3,5-tricarbonyl trichloride (**14**) (0.795 g, 3 mmol) in dry dichloromethane over 30 min with cooling. After stirring under nitrogen for 1 h at room temperature water was added. The immiscible mixture was then transferred to a separating funnel, shaken vigorously and the dichloromethane decanted off. Dilute hydrochloric acid was then added to the aqueous layer and the pH adjusted to approximately 7, whereupon a precipitate formed. This was collected by filtration and washed with water. A second crop of product also precipitated from the filtrate. This was also collected by filtration and the two samples dried under vacuum. Yield 0.87 g, 60%; $\delta_H[(CD_3)_2SO]$ 3.47 (H_2O), 4.55 (6 H, d, $-CH_2-$), 7.35 (6 H, d, ^3J 4.3, $H^{3,5}$-pyr), 8.52 (6 H, d, ^3J 4.1, $H^{2,6}$-pyr), 8.63 (3 H, s, benz) and 9.49 (3 H, t, N–H); $\delta_C(CD_3OD)$ 43.28 ($-CH_2-$), 123.60, 130.04, 136.06 (q), 149.75, 150.29 (q) and 168.34 (–C=O); IR (KBr)/cm^{-1}: 3232, 3062 (secondary amide), 1638 (amide, –C=O stretch), 1604 (aromatic) and 1558 (amide) (Calc. for $C_{27}H_{24}N_6O_3\cdot 2H_2O$: C, 62.78; H, 5.46; N, 16.27. Found: C, 61.56; H, 5.36; N, 16.58%).

Tripodal receptor L⁷. Compound **16** (0.5 g, 1.04 mmol), was heated to gentle reflux overnight in 20 ml methyl iodide. The resulting light brown precipitate was collected by filtration and dissolved in water to give a pale brown solution. Dropwise addition of saturated aqueous ammonium hexafluorophosphate solution gave a cream precipitate which was collected by filtration and dried under vacuum. Yield 0.81 g, 81%, FABMS *m/z* 983 (M + Na), 815 ($M - PF_6^-$); $\delta_H(CD_3CN)$ 2.30 (H_2O), 4.27 (9 H, s, N–CH_3), 4.62 (6 H, d, ^3J 5.6, $-CH_2-$), 7.95 (6 H, d, ^3J 6.3, $H^{3,5}$-pyr), 8.11 (3 H, t, N–H), 8.53 (6 H, d, ^3J 6.6, $H^{2,6}$-pyr) and 8.54 (3 H, s, benz); $\delta_C(CD_3CN)$ 42.34 ($-CH_2-$), 47.39 (N^+–CH_3), 125.31, 129.45, 134.24, 145.12, 158.74 (aromatic) and 165.86 (–C=O); IR (KBr)/cm^{-1} 3248, 3048 (secondary amide), 1653 (amide, – C=O stretch), 1566 (aromatic), 1522 (amide) (Calc. for $C_{30}H_{33}N_6O_3P_3F_{18}\cdot H_2O$: C, 36.82; H, 3.60; N, 8.58. Found: C, 36.56; H, 3.38; N, 8.58%).

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