

## Anion Recognition by Novel Ruthenium(II) Bipyridyl Calix[4]arene Receptor Molecules

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Exotic calix[4]arene mono- and di-topic anion receptors containing one and two ruthenium(II) bipyridyl moieties have been prepared and shown by <sup>1</sup>H NMR and CV to bind and electrochemically recognise halide, dihydrogen phosphate and hydrogen sulphate anions. The monotopic calix[4]arene anion receptor **8** selectively electrochemically recognises H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in the presence of tenfold excess amounts of HSO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup>.

Anions are known to play many ubiquitous roles in chemical and biochemical processes and some are presently of great environmental and medical concern.<sup>1</sup> Consequently, the molecular recognition of anionic guest species by positively charged<sup>2</sup> or electron deficient neutral<sup>3</sup> abiotic organic receptor molecules is an area of intense current interest. As part of a research programme aimed at designing new spectroelectrochemical sensory reagents for anions, we have recently reported new classes of anion receptor that contain positively charged<sup>4</sup> or neutral<sup>5</sup> organometallic and coordination transition metal Lewis acidic binding sites in combination with amide N-H groups. The Lewis acidic redox- and photo-active ruthenium(II) bipyridyl moiety<sup>6</sup> and calixarene host molecules<sup>7</sup> are attractive building blocks to use for the design and construction of novel calix[4]arene anion receptors which are extremely rare.<sup>8</sup>

Here we report the synthesis, anion coordination chemistry and electrochemical investigations of novel redox-active mono- and bis-[ruthenium(II) bipyridyl]-calix[4]arene receptor molecules that complex and electrochemically recognise halide, hydrogen sulfate and dihydrogen phosphate anionic guest species.

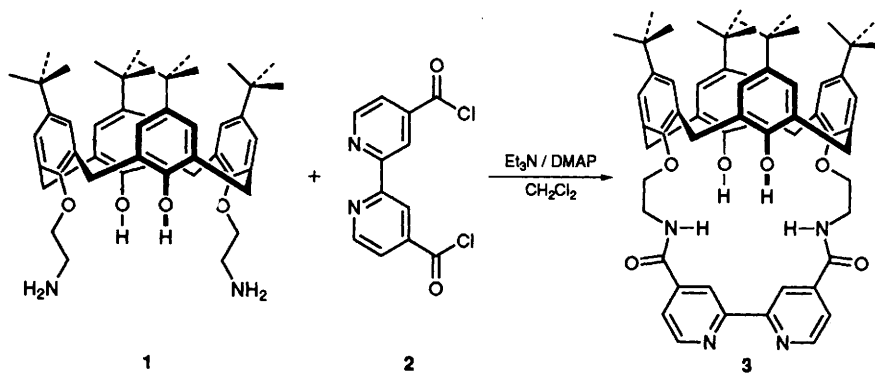
Condensation of the 1,3-distally substituted calix[4]arene amine **1**<sup>9</sup> and 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine **2**<sup>10</sup> under high dilution conditions in the presence of triethylamine gave the novel lower rim 2,2'-bipyridyl functionalised calix[4]arene

receptor **3** as a white powder, 55% yield (Scheme 1). The new upper rim bis(2,2'-bipyridyl) functionalised calix[4]arene receptor **6** was synthesised in 75% yield via the condensation of **4**<sup>8a</sup> with 2 equiv. of 4-chlorocarbonyl-2,2'-bipyridine **5** (Scheme 2).<sup>†</sup>

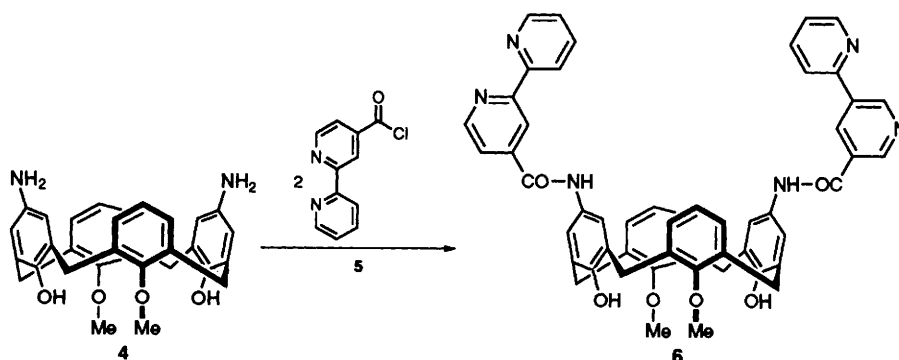
A new 4,4'-amide disubstituted bipyridine ligand **7** was prepared in high yields via a condensation reaction of **2** with the appropriate primary alkyl amine.

Mono- and bis-ruthenium(II) bipyridyl calix[4]arene complexes **8** and **9** were prepared by refluxing one and two equivalents of (bipy)<sub>2</sub>RuCl<sub>2</sub>·2H<sub>2</sub>O with the respective calix[4]arene receptor in ethanol, followed by purification on a Sephadex LH30 column and precipitation of the hexafluorophosphate complexes on addition of NH<sub>4</sub>PF<sub>6</sub>. Analogous reaction conditions were used to prepare the ruthenium complex **10**.

Evidence for anion recognition initially came from <sup>1</sup>H NMR titration studies. The addition of tetrabutylammonium halides, hydrogen sulphate and dihydrogen phosphate to deuterated acetonitrile <sup>1</sup>H NMR solutions of **8** and **9** resulted in remarkable perturbations of the respective receptor's protons. For example with Cl<sup>-</sup> in acetonitrile the respective amide protons of **8** and **9** shifted downfield by Δδ 1.5 and 3.0 respectively. In addition the 3,3'-bipyridyl protons of each receptor are perturbed by up to Δδ 1.7 with **9**. With **8** the calix[4]arene attached OCH<sub>2</sub> and hydroxy protons are also



Scheme 1



Scheme 2

significantly perturbed by the anionic guest species (by up to  $\Delta\delta$  0.2 with  $\text{HSO}_4^-$ ) suggesting anion complexation takes place at the calix[4]arene lower rim-amide bipyridyl recognition site. In contrast, the upper rim aryl protons of the calix[4]arene structural framework of **9** are shifted downfield in the presence of anions ( $\Delta\delta$  0.6 with  $\text{Cl}^-$ ) indicating guest anion binding in this vicinity of the receptor. The resulting titration curves indicate **8** to form 1:1 and **9** 1:2X<sup>-</sup> stoichiometric solution anion complexes suggesting **8** is a monotopic anion receptor whereas **9** exhibits ditopic behavi-

our. The  $^1\text{H}$  NMR anion titration results with the simple acyclic ruthenium(II) bipyridyl derivative **10** imply this receptor forms 1:1 complexes. $\ddagger$

CV was used to investigate the electrochemical anion recognition properties of the receptors and the results are summarised in Table 1. With reference to the known electrochemical properties of  $[(\text{bipy})_3\text{Ru}](\text{PF}_6)_2$  the respective reversible oxidation and reduction couples exhibited by the ruthenium(II) bipyridyl receptors can be assigned to the metal centred oxidation (1.3–1.2 V) and three bipyridyl ligand centred reductions in the range (-1.2 to -2.0 V). Because of the electron-withdrawing nature of the carbonyl amide moieties the least cathodic bipyridyl ligand centred reduction couple can be assigned to the amide substituted bipyridyl group present in each receptor. It is this reduction couple that exclusively undergoes significant cathodic perturbations on addition of anionic guest species (Fig. 1), suggesting, in agreement with  $^1\text{H}$  NMR titration studies, that anion recognition takes place in the amide-bipyridyl vicinity of the respective receptor. $\S$

Of particular relevance to the future design of ampero-

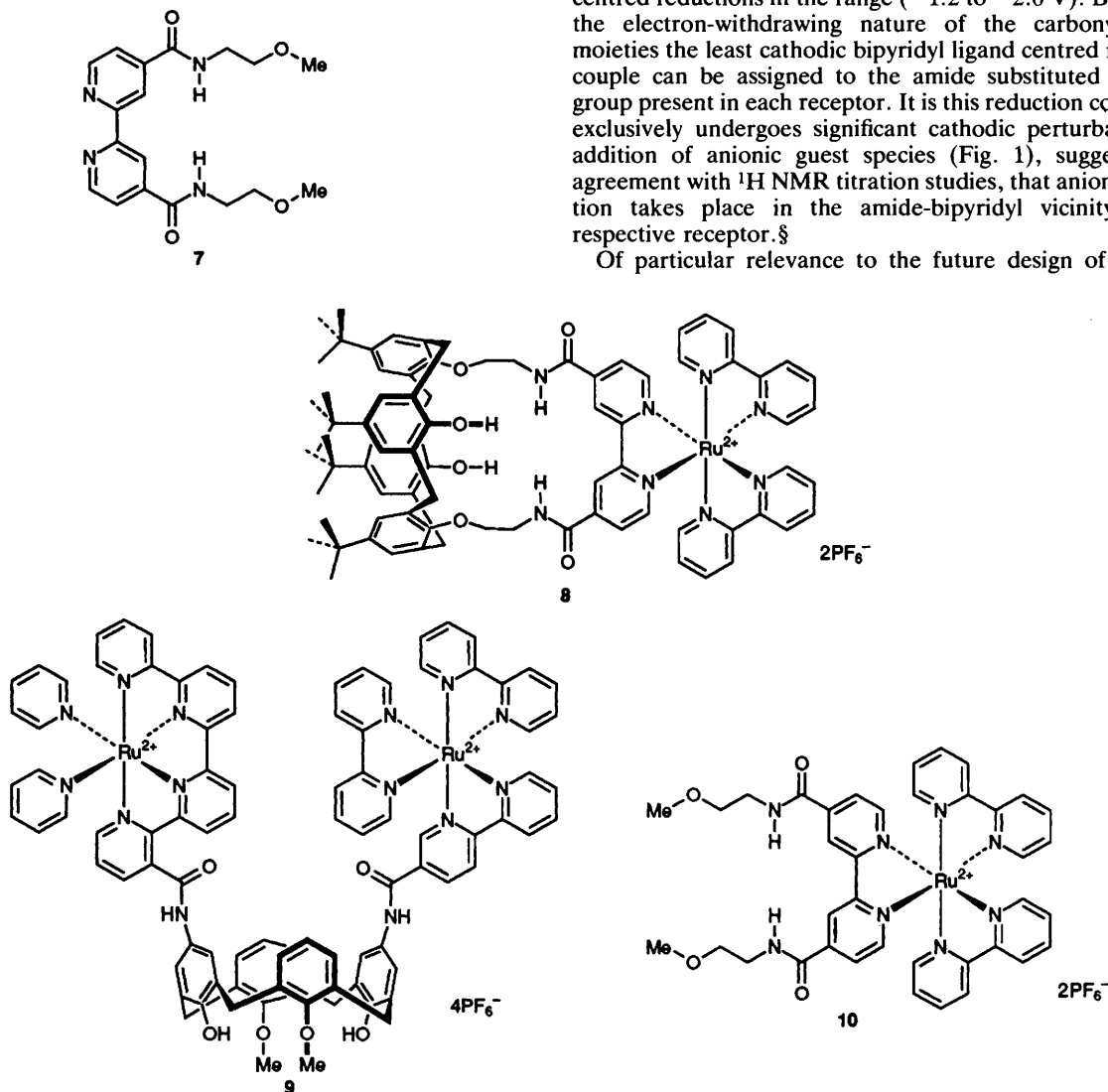


Table 1 Electrochemical data

Receptor	8			9			10					
Redox couple	+3/+2 <sup>d</sup>	+2/+1 <sup>e</sup>	+1/0 <sup>e</sup>	0/-1 <sup>e</sup>	+3/+2 <sup>d</sup>	+2/+1 <sup>e</sup>	+1/0 <sup>e</sup>	0/-1 <sup>e</sup>	+3/+2 <sup>d</sup>	+2/+1 <sup>e</sup>	+1/0 <sup>e</sup>	0/-1 <sup>e</sup>
$E_{1/2}(\text{free}, \text{V})^a$	1.12	-1.40	-1.80	-2.01	1.16	-1.38	-1.71 <sup>f</sup>	-2.0 <sup>f</sup>	1.12	-1.44	-1.80	-2.01
$\Delta E(\text{H}_2\text{PO}_4^-, \text{mV})^{b,c}$	—	175	<5	<5	—	30	30	10	—	130	<5	<5
$\Delta E(\text{HSO}_4^-, \text{mV})^b$	—	15	<5	<5	—	<5	<i>f</i>	<i>f</i>	—	15	<5	<5
$\Delta E(\text{Cl}^-, \text{mV})^b$	—	70	<5	<5	—	30	<5	<5	—	65	<5	<5
$\Delta E(\text{Br}^-, \text{mV})^b$	—	60	<5	<5	—	15	<5	<5	—	60	<5	<5
$\Delta E(\text{I}^-, \text{mV})^b$	—	40	<5	<5	—	—	—	—	—	10	<5	<5

<sup>a</sup> Obtained in acetonitrile solution containing 0.1 mol dm<sup>-3</sup>  $[\text{Bu}_4\text{N}]\text{PF}_6$  as supporting electrolyte. Solutions were ca.  $5 \times 10^{-4}$  mol dm<sup>-3</sup> in compound and potentials were determined with reference to a  $\text{Ag}^+/\text{Ag}$  electrode ( $330 \pm 5$  mV vs. SCE) at  $21 \pm 1$  °C at 50 mV s<sup>-1</sup> scan rate. <sup>b</sup> Cathodic shifts of reduction potential produced by presence of anions (up to 10 equiv.) added as their tetrabutyl ammonium salts. <sup>c</sup> DMSO was added (up to 50% v/v) before the addition of  $\text{H}_2\text{PO}_4^-$  to prevent precipitation of complex. <sup>d</sup> Metal centred oxidation. <sup>e</sup> Ligand centred reduction. <sup>f</sup> Adsorption and depletion were observed during the redox reactions of +1/0 and 0/-1 for **9** when using pure acetonitrile as solvent. These disappeared when  $\text{HSO}_4^-$  was added but the corresponding current waves became broad and assignment of peaks was difficult.

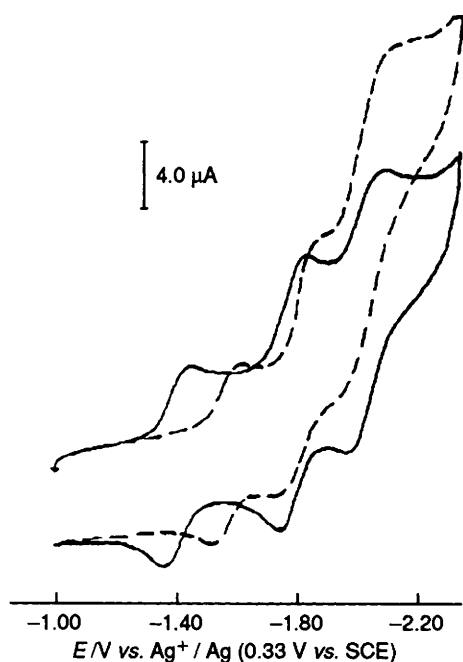


Fig. 1 CVs of **8** in MeCN, in the absence (solid line) and presence (dashed line) of 4 equiv. of  $\text{H}_2\text{PO}_4^-$

metric chemical sensors were the novel results of electrochemical competition experiments with receptor **8**. When an ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ) equimolar mixture of  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$  and  $\text{Cl}^-$  was added to an acetonitrile electrochemical solution of **8** ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ) the bipyridyl ligand centred reduction couple shifted cathodically by an amount approximately the same ( $\Delta E = 175 \text{ mV}$ ) as that induced by the  $\text{H}_2\text{PO}_4^-$  anion alone. The same result was even obtained when  $\text{HSO}_4^-$  and  $\text{Cl}^-$  anions were in tenfold excess concentrations ( $5 \times 10^{-3} \text{ mol dm}^{-3}$ ) over  $\text{H}_2\text{PO}_4^-$  ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ). This result suggests **8** is a first generation prototype dihydrogen phosphate-selective amperometric sensor<sup>¶</sup> and the synthesis of other anion selective Lewis acid-amine calix[4]arene receptor molecules is currently under investigation.<sup>||</sup>

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### Footnotes

† All new compounds were fully characterised by elemental analyses,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and FABMS.

‡  $^1\text{H}$  NMR anion titration experiments with  $\text{Ru}(\text{bipy})_3(\text{PF}_6)_2$  gave no evidence of anion recognition.

§ Analogous electrochemical anion recognition experiments with  $\text{Ru}(\text{bipy})_3(\text{PF}_6)_2$  gave no evidence of anion complexation.

¶ Square wave voltammetry, suitable for low concentration investigations, was used to undertake an electrochemical competition experiment in acetonitrile using an equimolar mixture of receptors **8** and **10** ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) and subsequent addition of this solution to an equivalent concentration ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) of  $\text{H}_2\text{PO}_4^-$ . A perturbation of the +2/+1 redox couple of **8** was only observed, suggesting, qualitatively, this calixarene containing receptor exhibits a higher affinity for  $\text{H}_2\text{PO}_4^-$  than receptor **10** which does not contain a calix[4]arene structure.

|| Note added in proof. Stability constant determinations have confirmed **8** is a superior anion receptor to **10**.

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