Anion recognition and luminescent sensing by new ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors

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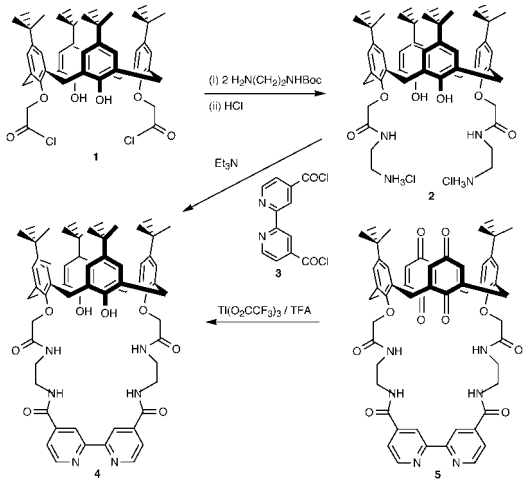
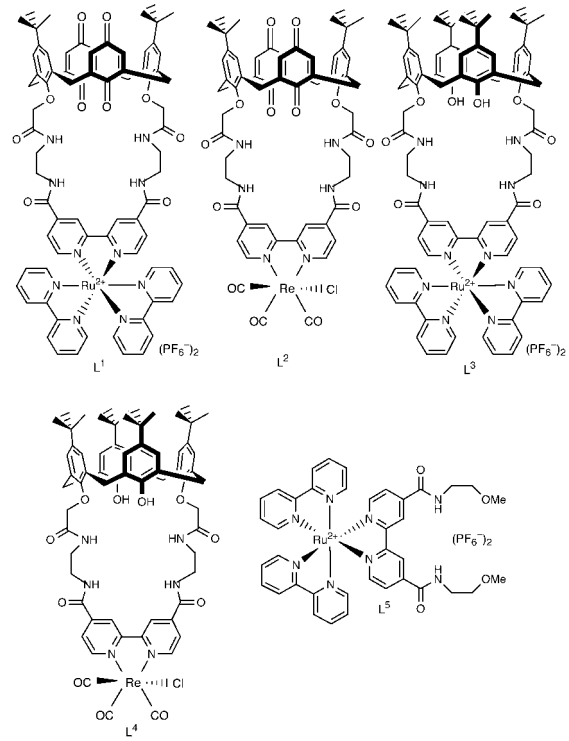
New ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors have been prepared and shown to selectively bind and sense acetate anions *via* remarkable luminescent emission intensity retrieval effects.

Anionic species are well known to play numerous fundamental roles in biological and chemical processes and their detrimental effects as environmental pollutants is of growing concern.[1] In view of this there is intense current interest being shown in the design and syntheses of receptors that are proficient at detecting anions in solution.[2] By incorporating redox- and photo-active transition metal inorganic signalling probes into various acyclic, macrocyclic and calixarene ligand frameworks we have produced a series of selective spectral and electrochemical responsive reagents for anions.[2a,3] For example, using the ruthenium(II) bipyridyl luminescent reporter moiety the selective sensing of dihydrogen phosphate has been demonstrated with lower[4] and upper rim[5] ruthenium(II) bipyridyl calix[4]arene receptor systems. In an effort to construct a novel type of switchable and selective luminescent sensitive receptor for anions we report here the synthesis of new ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors which selectively bind and sense acetate anions *via* remarkable emission intensity retrieval effects.

The condensation of the lower rim 1,3-bis(chlorocarbonyl) substituted *p-tert*-butylcalix[4]arene **1**[6] with 2 equiv. of mono-Boc protected 1,2-diaminoethane[7] followed by HCl gave **2** in 68% yield. The reaction of **3**[8] with **2** in the presence of Et_3N in dry CH_2Cl_2 under high dilution conditions afforded the [1 + 1] product **4** in 44% yield together with the [2 + 2] dimer in 20% yield. $Tl(O_2CCF_3)_3$ in TFA[9] was used to oxidise **4** and produce the new bipyridyl bridged calix[4]arene-diquinone **5** in 68% yield (Scheme 1). Complexation reactions with $(bipy)_2RuCl_2{\cdot}2H_2O$ followed by NH_4PF_6, and $Re(CO)_5Cl$ gave the new receptors L^1 and L^2 in 81 and 79% respective yields. Analogous high yielding complexation reactions with **4** produced the new lower rim calix[4]arene derivatives L^3 and L^4.



Scheme 1



The addition of Bu_4NOAc, Bu_4NCl and $Bu_4N(H_2PO_4)$ to DMSO-d_6 ^{1}H NMR solutions of L^1–L^4 resulted in significant perturbations of most notably the respective amide and 3,3′-bipyridyl receptor protons by up to $\Delta\delta$ = 0.95 ppm. The resulting titration curves all suggested a 1:1 receptor:anion stoichiometry. The computer program EQNMR[10] was used to determine the stability constants from the ^{1}H NMR titration data, and the results are summarised in Table 1, which includes for comparison purposes stability constant data for acyclic receptor L^5.[13] It is evident that the topological nature of a receptor's calix[4]arene/calix[4]diquinone cavity and the bipyridyl coordinated charged ruthenium(II)/neutral rhenium(I) transition metal centre have a major effect on the anion thermodynamic stability and on the selectivity preference that a particular receptor exhibits. Compared to acyclic receptor L^5, L^1–L^4 form significantly stronger anion complexes with AcO^- and Cl^-, and

Table 1 Stability constants of receptors with anions in DMSO-d_6

	K^a/M^{-1}		
Receptor	Cl^-	AcO^-	$H_2PO_4^-$
L^1	1050	9990	215
L^2	255	1790	160
L^3	840	4060	240
L^4	435	760	185
L^5	150	350	1300

[a] Errors < 10%; T = 298 K.

weaker complexes with $H_2PO_4^-$. The AcO^- > Cl^- > $H_2PO_4^-$ selectivity trend displayed by L^1–L^4 contrasts acyclic L^5 selectivity preference $H_2PO_4^-$ > AcO^- > Cl^-. It is noteworthy that the AcO^- stability constant magnitudes are significantly larger for the calix[4]diquinone-containing receptors L^1 and L^2 when compared to the calix[4] arene receptors L^3 and L^4. Electrostatic considerations can account for the neutral rhenium(I) receptors forming relatively weaker anion complexes in contrast to the charged ruthenium(II) analogues.

Preliminary absorption and emission investigations displayed in Table 2, reveal that these receptors behave like the parent $[Ru(bpy)_3]^{2+}$ and $[Re(bpy)(CO)_3Cl]$ complexes.

As expected,[11,12] the heteroleptic nature of the ruthenium receptors leads to two metal–ligand charge transfer (MLCT) transitions, Ru→bpy-macrocycle and Ru→bpy; the former lies at slightly lower energy than the Ru→bpy ones because of the presence of the electron-withdrawing carbonyl amide substituents on the bpy-macrocycle ligand. As a consequence, for L^1 and L^3 the absorption band around 450 nm is broader and the emission band is red-shifted compared to that of $Ru(bpy)_3^{2+}$. The low emission yield exhibited by L^1 is expected since it is well known that quinones efficiently quench the luminescence emission of $Ru(bpy)_3^{2+}$ *via* an oxidative (intramolecular[13] or intermolecular[14]) electron transfer mechanism. In our case an intermolecular quenching process can be ruled out because of the low receptor concentration used; thus an intramolecular quenching mechanism is operative and a rate constant of 3×10^7 s^{-1} can be calculated on the basis of the lifetimes of Ru–calix[4]arene L^3 and Ru–calix[4]diquinone L^1.

Table 2 also shows that the rhenium receptors exhibit red-shifts of the lowest energy absorption and emission bands compared to the reference $[Re(bpy)(CO)_3Cl]$ complex.[15] Again the carbonyl amide substituents on the bpy-macrocycle ligand can explain the energy decrease of the MLCT excited state involved in the absorption (^{1}MLCT) or in the emission (^{3}MLCT) process. An excited state quenching process *via* intramolecular electron transfer is also expected for the Re–calix[4]diquinone receptor L^2 since the redox properties[15] of the excited Re^I moiety are quite similar to those of the excited Ru^{II} complexes. On the basis of the luminescence lieftimes of Re–calix[4]arene L^4 and Re–calix[4]diquinone L^2 a value of 7×10^7 s^{-1} can be calculated for the rate constant of the intramolecular quenching.

The addition of Bu_4NOAc and Bu_4NCl was found to dramatically affect the luminescence spectrum of all the receptors, the only exception being an insensitive response with L^2 and Cl^- in DMSO solution. While the Ru–calix[4]arene receptor L^3 exhibits an emission decrease, the other receptors L^1, L^2 and L^4 display a marked emission retrieval upon anion addition. In particular, AcO^- addition to MeCN solutions of L^1 caused a remarkable intensity increase of up to 500% concomitant with a slight blue shift of the emission maximum (Fig. 1). A notable 60% intensity increase was observed on Cl^- addition

Table 2 Absorption and emission data of the four receptors and of the reference compounds

	Absorption[a]		Emission[a]		
Compound	λ/nm[b]	ε/dm^3 mol^{-1} cm^{-1}	λ/nm[c]	τ/ns[d]	Φ_{em}[e]/10^{-3}
$[Ru(bpy)_3]^{2+}$	452	14 000	615	180	—
L^3	472	9 300	654	510	30
L^1	475	11 000	660	30[f]	1.0
$[Re(CO)_3bpyCl]$[g]	384		615	50	—
L^4[h]	393	4 200	675	21	2.0
L^2[h]	385	4 600	685	8.5	0.5

[a] Room temperature, air equilibrated MeCN solutions, unless otherwise noted. [b] Wavelength of the lowest energy absorption band. [c] Corrected wavelength of the emission band. [d] Luminescence emission lifetime values (±10%). [e] Luminescence emission quantum yield values (±30%). [f] A longer decay is also present as a minority component (see ref. 13). [g] CH_2Cl_2, ref. 15. [h] DMSO.

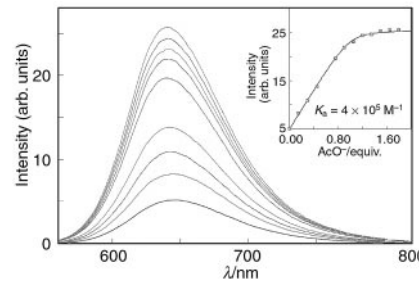


Fig. 1 Emission spectral variations upon titration of MeCN solution of L^1 (1.1×10^{-4} M) with Bu_4NOAc.

to L^1. Results obtained from Cl^- and AcO^- titrations of L^1 and L^3 in CD_3CN are consistent with a receptor–anion complex of 1:1 stoichiometry with stability constant magnitudes $>10^4$ M^{-1}, larger than the ^{1}H NMR determined values in DMSO-d_6, reflecting the less competitive CD_3CN solvent medium. The anion induced enhancement of the luminescence intensity in the case of Ru–calix[4]diquinone complex L^1 is clearly due to a significant decrease in the electron transfer rate constant, indicating that the anion binding decreases the interaction between the ruthenium(II) bipyridyl centre and the quinone moieties. In the case of Cl^- addition to Ru–calix[4]arene L^3 the intensity decrease matches the decrease in the emission lifetime (−25%) indicating that, at least in this case, anion binding favours the non-radiative decay processes.†

In summary the new ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors selectively bind and optically sense AcO^- anions by overcoming intramolecular quenched luminescence and retrieving an anion induced emission.

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Notes and references

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