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FULL PAPER

Heteroditopic rhenium(I) and ruthenium(II) bipyridyl calix[4]arene receptors for binding cation–anion ion pairs

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New heteroditopic ion pair receptors that contain rhenium(I) and ruthenium(II) bipyridyl amide anion recognition sites covalently linked to a lower rim calix[4]arene tetraester alkali metal cation binding site have been prepared and shown to bind alkali metal (Li^+, Na^+)–halide (Br^-, I^-) ion pair species. Proton NMR titration studies reveal the lower rim ester co-bound alkali metal cation significantly enhances the strength of bromide and iodide binding in acetonitrile solutions with the largest positive co-operative binding effect of sixtyfold observed with bromide and the lithium complex of one receptor. Solid/liquid extraction experiments show two of the receptors are capable of solubilising NaCl and NaOAc in dichloromethane solutions.

Stimulated by the need to design new selective extraction and transportation reagents for metal salt species of environmental and biological importance, ion pair recognition, the simultaneous binding of cationic and anionic guest species by ditopic receptors, is a rapidly developing new field of coordination chemistry.[1–13] Novel co-operative and allosteric metal salt complexing behaviour whereby the binding of the metal cation charged guest can enhance, through electrostatic and conformational effects, the subsequent coordination of the pairing anion has been demonstrated by a number of ditopic crown ether functionalised boron,[1] uranyl,[2] polyammonium,[3] amide,[6–12] urea[11] and amide[4,13]–urea calix[4]arene[5] based receptor systems. In addition such systems have recently been shown to solubilise and transport alkali metal salts across lipophilic membranes.[10] We have established that charged or neutral transition metal organometallic and coordination amide containing receptor systems can selectively bind and sense anions.[14] Covalently linking the known lower rim ester-functionalised calix[4]arene alkali-metal cation coordinating moiety[15] with a transition metal amide anion recognition group also at the lower rim will create new heteroditopic calix[4]arene based receptors capable of simultaneous binding of metal cation–anion ion pairs (Fig. 1). This calix[4]arene lower rim heteroditopic receptor design for ion pair recognition (Fig. 1) contrasts our recently reported heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl and ferrocene receptor molecules which were shown co-operatively to bind iodide anion at the upper rim *via* complexation of two alkali metal cations at the two lower rims.[13] We report here the syntheses and anion/cation coordination chemistry of new heteroditopic rhenium(I) and ruthenium(II) bipyridyl calix[4]arene receptors which display up to sixtyfold co-operative enhancement of halide anion binding in the presence of a co-bound alkali metal cation.

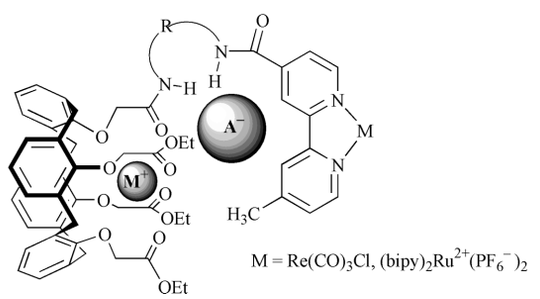

Fig. 1 Design of ion pair receptor.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on Bruker AM300 and Varian-Unity 500 instruments using the solvent deuterium signal as internal reference, fast atom bombardment (FAB) mass spectra at the EPSRC mass spectrometry service, University of Wales, Swansea. 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 and dichloromethane were distilled from calcium hydride, tetrahydrofuran was distilled from benzophenone ketyl. Unless stated otherwise, commercial grade chemicals were used without further purification. Calix[4]arene tetraester **1**,[15] Boc protected diamines[16] and 4-chlorocarbonyl-4′-methyl-2,2′-bipyridine **8**[17] were prepared according to literature procedures.

Syntheses

25-[(Carboxy)methoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 2. Calix[4]arene tetraester **1** (1 g, 1.30 mmol) was dissolved in CH_2Cl_2 (50 ml) and stirred with conc. HNO_3 (65%, 1 ml) for 3 h. Water (50 ml) was added and the mixture stirred for 15 minutes. The phases were separated and the solvent was removed under reduced pressure. The residue was stirred in diethyl ether and the solvent removed under vacuum to give the product as a white solid (0.91 g, 94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (m, 9H, OCH_2CH_3), 3.32 (d (J = 13), 2H, CCH_2C), 3.35 (d (J = 13), 2H, CCH_2C), 4.21–4.32 (m, 6H, OCH_2CH_3), 4.44 (d (J = 16), 2H, $COCH_2O$), 4.72 (s, 2H, $COCH_2O$), 4.73 (d (J = 13), 4H, CCH_2C), 4.92 (d (J = 16), 2H, $COCH_2O$), 4.95 (s, 2H, $COCH_2O$), 5.02

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(d (J = 13), 4H, CCH_2C) and 6.48–7.14 (m, 12H, ArH) Microanalysis: $C_{42}H_{44}O_{12}\cdot 0.5H_2O$ requires C 67.28, H 6.05%; found C 67.39, H 5.93%,

25-[(Chlorocarbonyl)methoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 3. Compound **2** (1.00 g, 1.35 mmol) was refluxed in oxalyl chloride for 2 hours. Excess of oxalyl chloride was removed under reduced pressure and the acid chloride used without further purification or analysis.

General synthesis of calix[4]arene protected amides: 25-[1-(*tert*-Butoxycarbonylamino)ethylcarbamoylmethoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 4a. Compound **3** (1.02 g, 1.34 mmol) was stirred in dry CH_2Cl_2 (25 ml) with an excess of dry triethylamine (1 ml) for 30 minutes. Mono-Boc protected ethylenediamine (0.5 g, 3.1 mmol, 2.2 equivalents) was added in dry CH_2Cl_2 (25 ml) and the mixture stirred overnight. 1 M HCl (25 ml) was added and the mixture stirred for 15 minutes. The phases were separated and the solvent was removed from the organic phase to give the product as a white solid (1.09 g, 91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16–1.25 (m, 9H, OCH_2CH_3), 1.33 (s, 9H, $C(CH_3)_3$), 3.19 (br d (J = 13.5), 4H, CCH_2C), 3.30–3.32 (m, 2H, $NHCH_2CH_2NH$), 3.46–3.50 (m, 2H, $NHCH_2CH_2NH$), 4.08–4.20 (m, 6H, OCH_2CH_3), 4.33 (s, 2H, $COCH_2O$), 4.46 (s, 2H, $COCH_2O$), 4.53 (d (J = 15), 2H, $COCH_2O$), 4.62 (d (J = 14), 4H, CCH_2C), 4.92 (d (J = 16), 2H, $COCH_2O$), 5.33 (br s, 1H, NHCOO), 6.21 (d (J = 7.5), 2H, *m*-H of Ar), 6.34 (d (J = 7), 2H, *m*-H of Ar), 6.44 (t (J = 7), 2H, *p*-H of Ar), 6.72 (t (J = 7), 2H, *p*-H of Ar), 6.77–6.87 (m, 4H, *m*-H of Ar), 8.45 (s, 1H, $CONHCH_2$). Microanalysis: $C_{49}H_{58}N_2O_{13}\cdot H_2O$ requires C 65.30, H 6.72, N 3.11%; found C 65.03, H 6.30, N 3.59%.

25-[1-(*tert*-Butoxycarbonylamino)propylcarbamoylmethoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 5a. Method as above Compound **3** (1.74 g, 2.29 mmol) was treated with mono-Boc protected 1,3-diaminopropane (0.8 g, 4.6 mmol, 2 equivalents) to give the product as a white solid (2.18 g, 97% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23–1.32 (m, 9H, OCH_2CH_3), 1.42 (s, 9H, $C(CH_3)_3$), 1.76–1.81 (m, 2H, $CH_2CH_2CH_2$), 3.17–3.19 (m, 2H, $NHCH_2CH_2$), 3.26 (d (J = 14), 4H, CCH_2C), 3.49–3.51 (m, 2H, CH_2CH_2NH), 4.12–4.24 (m, 6H, OCH_2CH_3), 4.36 (s, 2H, $COCH_2O$), 4.50 (s, 2H, $COCH_2O$), 4.61 (d (J = 16.5), 2H, $COCH_2O$), 4.69 (d (J = 13.5), 2H, CCH_2C), 4.71 (d (J = 13.5), 2H, CCH_2C), 4.97 (d (J = 16), 2H, $COCH_2O$), 5.41 (br s, 1H, NHCOO), 6.23 (d (J = 7.5), 2H, *m*-H of Ar), 6.35–6.38 (m, 3H, *m*-, *p*-H of Ar), 6.48 (t (J = 7), 1H, *p*-H of Ar), 6.81 (t (J = 7), 2H, *p*-H of Ar), 6.88–6.91 (m, 4H, *m*-H of Ar) and 8.39 (s, 1H, $CONHCH_2$). Microanalysis: $C_{50}H_{60}N_2O_{13}\cdot 2H_2O$ requires C 64.36, H 6.91, N 3.00%; found C 64.54, H 6.85, N 3.78%.

25-[1-(*tert*-Butoxycarbonylamino)butylcarbamoylmethoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 6a. Method as above Compound **3** (1.06 g, 1.39 mmol) was treated with mono-Boc protected 1,4-diaminobutane (0.40 g, 2.13 mmol, 1.5 equivalents). The product was purified by column chromatography on silica eluted with 1 : 1 CH_2Cl_2–ethyl acetate; after removal of the solvent this gave the product as a white solid (0.83 g, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17–1.25 (m, 9H, OCH_2CH_3), 1.35 (s, 9H, $C(CH_3)_3$), 1.44–1.50 (m, 2H, $CH_2CH_2CH_2CH_2$), 1.57–1.63 (m, 2H, $CH_2CH_2CH_2CH_2$), 3.05–3.11 (m, 2H, $NHCH_2CH_2$), 3.19 (d (J = 14), 4H, CCH_2C), 3.36–3.40 (m, 2H, CH_2CH_2NH), 4.03–4.20 (m, 6H, OCH_2CH_3), 4.29 (s, 2H, $COCH_2O$), 4.44 (s, 2H, $COCH_2O$), 4.53–4.71 (m, 7H, $COCH_2O$, CCH_2C, NHCOO), 4.90 (d (J = 16), 2H, $COCH_2O$), 6.16 (d (J = 7.5), 2H, *m*-H of Ar), 6.28–6.32 (m, 3H, *m*-, *p*-H of Ar), 6.42 (t (J = 7), 1H, *p*-H of Ar), 6.74 (t (J = 7), 2H, *p*-H of Ar), 6.81–6.85 (m, 4H, *m*-H of Ar) and 8.30 (s, 1H, $CONHCH_2$). Microanalysis: $C_{51}H_{62}N_2O_{13}$ requires C 65.92, H 6.95, N 3.02%; found C 65.86, H 7.18, N 2.93%.

General synthesis of unprotected amines: 25-[(1-aminoethylcarbamoyl)methoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]-calix[4]arene 4. Compound **4a** (1.00 g, 0.97 mmol) was dissolved in CH_2Cl_2 (25 ml) and stirred with an excess of trifluoroacetic acid (TFA) (1 ml) for 1 h. HCl (1 M, 25 ml) was added and the mixture stirred for 15 minutes. The phases were separated and the CH_2Cl_2 layer was washed with water (2 × 25 ml). The phases were separated and the organic phase was dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to give the product (0.9 g, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87–1.32 (m, 9H, OCH_2CH_3), 3.24 (d (J = 14), 2H, CCH_2C), 3.26 (d (J = 13.5), 2H, CCH_2C), 3.34 (br s, 2H, $NHCH_2CH_2$), 3.75 (br s, 2H, $CH_2CH_2NH_3^+$), 4.13–4.28 (m, 6H, OCH_2CH_3), 4.36 (s, 2H, $COCH_2O$), 4.52 (s, 2H, $COCH_2O$), 4.52–4.96 (m, 6H, CCH_2C, $COCH_2O$), 4.99 (d (J = 15), 2H, $COCH_2O$), 6.25–6.87 (m, 12H, Ar H) and 8.84 (br t, 1H, NH). Microanalysis: $C_{44}H_{50}N_2O_{11}\cdot HCl\cdot CF_3CO_2H\cdot H_2O$ requires C 58.07, H 5.72, N 2.94%; found C 58.36, H 5.60, N 2.60%.

25-[(1-Aminopropylcarbamoyl)methoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 5. Compound **5a** (2.00 g, 1.92 mmol) was treated as for **4** to give the product as a white solid (1.93 g, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19–1.35 (m, 9H, OCH_2CH_3), 2.05–2.17 (m, 2H, $CH_2CH_2CH_2$), 3.03 (br s, 2H, $NHCH_2CH_2$), 3.24 (d (J = 13.5), 2H, CCH_2C), 3.25 (d (J = 14), 2H, CCH_2C), 3.57 (br q, 2H, CH_2CH_2NH), 4.11–4.26 (m, 6H, OCH_2CH_3), 4.47 (s, 2H, $COCH_2O$), 4.51 (s, 2H, $COCH_2O$), 4.53 (d (J = 16.5), 2H, $COCH_2O$), 4.62 (d (J = 14), 2H, CCH_2C), 4.65 (d (J = 14.5), 2H, CCH_2C), 4.93 (d (J = 16.5), 2H, $COCH_2O$), 6.35 (d (J = 7.5), 2H, *m*-H of Ar), 6.44–6.47 (m, 3H, *m*-, *p*-H of Ar), 6.53 (t (J = 7.5), 1H, *p*-H of Ar), 6.72 (t (J = 7.5), 2H, *p*-H of Ar), 6.76–6.79 (m, 4H, *m*-H of Ar), 8.45 (br s, 3H, NH_3^+) and 8.81 (t (J = 6.5 Hz), 1H, $CONHCH_2$). Microanalysis: $C_{45}H_{52}N_2O_{11}\cdot 2CF_3CO_2H\cdot 2H_2O$ requires C 55.40, H 5.60, N 2.64%; found C 55.35, H 5.54, N 2.89%.

25-[(1-Aminobutylcarbamoyl)methoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 6. Compound **6a** (2.00 g, 1.92 mmol) was treated as for **4** to give the product as a white solid (1.85 g, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17–1.31 (m, 9H, OCH_2CH_3), 1.70–1.73 (m, 4H, $CH_2CH_2CH_2CH_2$), 2.98–2.30 (m, 2H, $NHCH_2CH_2$), 3.23 (d (J = 14), 4H, CCH_2C), 3.41–3.42 (m, 2H, CH_2CH_2NH), 4.09–4.22 (m, 6H, OCH_2CH_3), 4.28 (s, 2H, $COCH_2O$), 4.46 (s, 2H, $COCH_2O$), 4.58 (d (J = 17), 2H, $COCH_2O$), 4.63 (d (J = 14.5), 2H, CCH_2C), 4.67 (d (J = 14.5), 2H, CCH_2C), 4.96 (d (J = 16.5), 2H, $COCH_2O$), 6.15 (d (J = 7.5), 2H, *m*-H of Ar), 6.28–6.32 (m, 3H, *m*-, *p*-H of Ar), 6.43 (t (J = 7.5), 1H, *p*-H of Ar, 6.81 (t (J = 7 Hz), 2H, *p*-H of Ar), 6.89–6.92 (m, 4H, *m*-H of Ar), 8.19 (br s, 3H, NH_3^+) and 8.58 (s, 1H, $CONHCH_2$). Microanalysis: $C_{46}H_{55}N_2O_{11}\cdot 2CF_3CO_2H\cdot 2H_2O$ requires C 55.81, H 5.71, N 2.60%; found C 55.96, H 5.24, N 3.30%.

25-[(1-Aminophenylcarbamoyl)methoxy]-26,27,28-tri[(ethoxycarbonyl)methoxy]calix[4]arene 7. 1,2-Diaminobenzene (12.85 g, 118 mmol, 100 equivalents) was dissolved in dry CH_2Cl_2 (500 ml) and stirred with an excess of NEt_3 (3 ml). Compound **3** (0.97 g, 1.18 mmol, 1 equivalent) in dry CH_2Cl_2 (250 ml) was added dropwise over 1 h. The mixture was stirred overnight. 2 M HCl (250 ml) was added and the mixture stirred for 2 h. The phases were separated and the solvent was removed from the organic phase under reduced pressure. The residue was dissolved in $CHCl_3$, filtered and the solvent removed under reduced pressure. The residue was dissolved in MeCN, filtered and the solvent removed under reduced pressure. The residue

was dissolved in Et_2O, filtered and the solvent removed under reduced pressure to give the product as a yellow powder (0.72 g, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 (t (J = 7.5), 6H, OCH_2CH_3), 1.27 (t (J = 7.5), 3H, OCH_2CH_3), 3.25 (d (J = 14), 2H, CCH_2C), 3.32 (d (J = 14), 2H, CCH_2C), 3.95–3.98 (m, 4H, OCH_2CH_3), 4.21 (q (J = 7), 2H, OCH_2CH_3), 4.57 (d (J = 16.5), 2H, $COCH_2O$), 4.60 (s, 2H, $COCH_2O$), 4.61 (s, 2H, $COCH_2O$), 4.69 (d (J = 14), 2H, CCH_2C), 4.84 (d (J = 14), 2H, CCH_2C), 4.93 (d (J = 16.5), 2H, $COCH_2O$), 6.35 (d (J = 7.5), 2H, *m*-H of Ar), 6.44–6.47 (m, 3H, *m*-, *p*-H of Ar), 6.53 (t (J = 7.5), 1H, *p*-H of Ar), 6.73–6.78 (m, 3H, *m*-, *p*-H of Ar), 6.81 (d (J = 8.5), 1H, *o*-H of Ar), 6.84 (d (J = 7.5), 4H, *m*-H of Ar), 7.08 (t (J = 7), 1H, *m*-H of Ar), 7.29 (d (J = 8 Hz), 1H, *o*-H of Ar) and 9.79 (s, 1H, CONHC). Microanalysis: $C_{48}H_{54}N_2O_{11}\cdot H_2O$ requires C 67.59, H 6.62, N 3.28%, found C 67.71, H 5.73, N 3.38%.

General synthesis of calix[4]arene bipyridyl amides: 26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-2,2′-bipyridine-4-carboxamido)ethylcarbamoylmethoxy]calix[4]arene 9. 4-Chlorocarbonyl-4′-methyl-2,2-bipyridine **8** (0.27 g, 1.17 mmol, 1.5 equivalents) was stirred in dry CH_2Cl_2 (25 ml) with dry triethylamine (1 ml) for 30 min. Compound **4** (0.64 g, 0.78 mmol) in dry CH_2Cl_2 with dry triethylamine (1 ml) was added and the mixture stirred overnight. HCl (1 M, 50 ml) was added and the mixture stirred for 15 min. The phases were separated and the organic phase was extracted with saturated K_2CO_3 solution (50 ml). The solvent was removed from the organic phase and the residue purified by silica column chromatography eluted with 10% ethyl acetate in CH_2Cl_2 to remove side products and then pure ethyl acetate to remove the product. The solvent was removed to give the product as a pale yellow solid (0.65 g, 85% yield). ^{1}H NMR (500 MHz, CD_3CN): δ 1.20 (t (J = 7), 6H, OCH_2CH_3), 1.24 (t (J = 7), 3H, OCH_2CH_3), 2.43 (s, 3H, CCH_3), 3.20 (d (J = 13.5), 2H, CCH_2C), 3.24 (d (J = 13.5), 2H, CCH_2C), 3.63 (br s, 4H, $NHCH_2CH_2NH$), 4.12–4.21 (m, 6H, OCH_2CH_3), 4.39 (s, 2H, $COCH_2O$), 4.52 (d (J = 16.5), 2H, $COCH_2O$), 4.55 (s, 2H, $COCH_2O$), 4.62 (d (J = 13.5), 2H, CCH_2C), 4.68 (d (J = 13.5), 2H, CCH_2C), 4.93 (d (J = 16), 2H, $COCH_2O$), 6.41–6.47 (m , 3H, Ar H), 6.50–6.55 (m, 3H, Ar H), 6.70 (t (J = 7.5), 2H, *p*-H of Ar), 6.76 (d (J = 7.5), 2H, *m*-H of Ar), 6.83 (d (J = 7.5), 2H, *m*-H of Ar), 7.22 (d (J = 4), 1H, bipy H), 7.66 (dd (J = 5), 1H, bipy H), 7.91 (br s, 1H, NH), 8.21 (s, 1H, bipy H^3), 8.36 (br s, 1H, NH), 8.45 (d (J = 4.5), 1H, bipy H), 8.67 (d (J = 5.5 Hz), 1H, bipy H) and 8.69 (s, 1H, bipy H^3). Microanalysis: $C_{56}H_{58}N_4O_{12}\cdot H_2O$ requires C 67.46, H 5.62, N 6.07%; found C 67.49, H 5.36, N 6.08%. FAB-MS [MH$^+$]: m/z = 979.

26,27,28-Tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-[2,2′-bipyridine-4-carboxamido)propylcarbamoylmethoxy]calix-[4]arene 10. Compound **10** was prepared by an analogous method to that for **9**. Compound **5** (2.13 g, 2.34 mmol) was treated with 4-chlorocarbonyl-4′-methyl-2,2′-bipyridine (1.10 g, 4.72 mmol) to give the product as a pale yellow solid (1.25 g, 54% yield). ^{1}H NMR (500 MHz, CD_3CN): δ 1.18 (t (J = 7.5), 6H, OCH_2CH_3), 1.23 (t (J = 7), 3H, OCH_2CH_3), 1.89 (qnt, (J = 6.5), 2H, $CH_2CH_2CH_2$), 2.44 (s, 3H, CCH_3), 3.26 (d (J = 14), 2H, CCH_2C), 3.26 (d (J = 13.5), 2H, CCH_2C), 3.47–3.51 (m, 4H, $NHCH_2CH_2CH_2NH$), 4.12–4.19 (m, 6H, OCH_2CH_3), 4.41 (s, 2H, $COCH_2O$), 4.57 (s, 2H, $COCH_2O$), 4.61 (d (J = 16.5), 2H, $COCH_2O$), 4.62 (d (J = 13.5), 2H, CCH_2C), 4.70 (d (J = 13.5), 2H, CCH_2C), 4.93 (d (J = 16), 2H, $COCH_2O$), 6.44–6.49 (m, 3H, Ar H), 6.55 (br s, 3H, Ar H), 6.74 (t (J = 7.5), 2H, *p*-H of Ar), 6.85 (d (J = 7.5), 2H, *m*-H of Ar), 6.88 (d (J = 7.5), 2H, *m*-H of Ar), 7.24 (d (J = 5), 1H, bipy H), 7.72 (d (J = 5), 1H, bipy H), 7.98 (br t, 1H, NH), 8.20 (br t, 1H, NH), 8.27 (s, 1H, bipy H^3), 8.50 (d (J = 5), 1H, bipy H), 8.74 (s, 1H, bipy H^3) and 8.75 (d (J = 5.5 Hz), 1H, bipy H). Microanalysis: $C_{57}H_{60}N_4O_{12}\cdot H_2O$ requires C 67.69, H 6.18, N 5.54%; found C 67.65, H 6.05, N 5.37%.

26,27,28-Tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-[2,2′-bipyridine-4-carboxamido)butylcarbamoylmethoxy]-c alix[4]arene 11. Prepared by an analogous method to that for compound **9**. Compound **6** (0.72 g, 8.46 mmol) was treated with 4-chlorocarbonyl-4′-methyl-2,2′-bipyridine (0.27 g, 1.17 mmol) to give the product as a pale yellow solid (0.99 g, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t (J = 7), 6H, OCH_2CH_3), 1.25 (t (J = 7), 3H, OCH_2CH_3), 1.73–1.79 (m, 4H, $CH_2CH_2CH_2CH_2$), 2.69 (s, 3H, CCH_3), 3.22 (d (J = 13.5), 2H, CCH_2C), 3.24 (d (J = 13.5), 2H, CCH_2C), 3.48 (q (J = 6.5), 2H, $NHCH_2CH_2$), 3.54 (q (J = 6.5), 2H, CH_2CH_2NH), 4.09–4.21 (m, 6H, OCH_2CH_3), 4.37 (s, 2H, $COCH_2O$), 4.48 (s, 2H, $COCH_2O$), 4.59 (d (J = 16.5), 2H, $COCH_2O$), 4.67 (d (J = 14), 4H, CCH_2C), 4.94 (d (J = 16.5), 2H, $COCH_2O$), 6.23 (d (J = 8), 2H, *m*-H of Ar), 6.36 (d (J = 8), 2H, *m*-H of Ar), 6.37 (t (J = 7.5), 1H, *p*-H of Ar), 6.47 (t (J = 8), 1H, *p*-H of Ar), 6.77 (t (J = 7.5), 2H, *p*-H of Ar), 6.84 (d (J = 6.5), 2H, *m*-H of Ar), 6.86 (d (J = 7.5), 2H, *m*-H of Ar), 7.11 (t (J = 5), 1H, bipy H), 7.29 (t (J = 5), 1H, NH), 7.77 (dd (J = 5), 1H, bipy H), 8.22 (s, 1H, bipy H^3), 8.41 (d (J = 5), 1H, bipy H), 8.44 (t (J = 6.5), 1H, NH), 8.66 (s, 1H, bipy H^3) and 8.75 (d (J = 5.5 Hz), 1H, bipy H). Microanalysis: $C_{58}H_{62}N_4O_{12}\cdot CH_3CO_2CH_2CH_3\cdot 2H_2O$ requires C 65.83, H 6.59, N 4.95%; found C 65.90, H 6.97, N 4.47%.

26,27,28-Tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-[2,2′-bipyridine-4-carboxamido)phenylcarbamoylmethoxy]-calix[4]arene 12. Prepared by an analogous method to that of compound **9**. Compound **7** (0.66 g, 0.79 mmol) was treated with 4-chlorocarbonyl-4′-methyl-2,2′-bipyridine (0.25 g, 1.08 mmol) to give the product as a pale brown solid (0.62 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09 (t (J = 7), 6H, OCH_2CH_3), 1.25 (t (J = 7), 3H, OCH_2CH_3), 2.42 (s, 3H, CCH_3), 3.23 (d (J = 14), 2H, CCH_2C), 3.24 (d (J = 14), 2H, CCH_2C), 3.87–3.98 (m, 4H, OCH_2CH_3), 4.20 (q (J = 7), 2H, OCH_2CH_3), 4.48 (s, 2H, $COCH_2O$), 4.56 (d (J = 16.5), 2H, $COCH_2O$), 4.64 (d (J = 13.5), 2H, CCH_2C), 4.69 (s, 2H, $COCH_2O$), 4.79 (d (J = 13.5), 2H, CCH_2C), 5.01 (d (J = 16.5), 2H, $COCH_2O$), 6.11 (d (J = 8), 2H, *m*-H of Ar), 6.28–6.30 (m, 3H, *m*-, *p*-H of Ar), 6.43 (t (J = 7), 1H, *p*-H of Ar), 6.81 (t (J = 7), 2H, *p*-H of Ar), 6.88 (t (J = 7), 2H, *m*-H of Ar), 6.95 (t (J = 7), 2H, *m*-H of Ar), 7.07 (d (J = 5), 1H, bipy H), 7.18 (t (J = 7.5), 1H, *m*-H of Ar), 7.37 (t (J = 7.5), 1H, *m*-H of Ar), 7.47 (d (J = 7.5), 1H, *o*-H of Ar), 7.77 (d (J = 5), 1H, bipy H), 8.12 (d (J = 8), 1H, *o*-H of Ar), 8.20 (s, 1H, bipy H^3), 8.31 (d (J = 5), 1H, bipy H), 8.78 (d (J = 5 Hz), 1H, bipy H), 8.84 (s, 1H, bipy H^3), 9.77 (s, 1H, NH) and 10.24 (s, 1H, NH). Microanalysis: $C_{60}H_{58}N_4O_{12}\cdot H_2O$ requires C 68.95, H 5.79, N 5.36%; found C 69.10, H 5.87, N 5.51%.

General synthesis of the rhenium receptors: tricarbonyl-chloro{26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-2,2′-bipyridine-4-carboxamido)ethylcarbamoyl)methoxy]-calix[4]arene} rhenium(I) L^1. Pentacarbonyl rhenium chloride (0.12 g, 0.33 mmol, 1.1 equivalents) was refluxed in dry THF (20 ml) for 30 minutes. Compound **9** (0.30 g, 0.30 mmol) was added and the mixture refluxed overnight. The solvent was removed under reduced pressure and the resulting residue purified by silica column chromatography eluting with ethyl acetate and collecting the second orange band. The solvent was removed and the residue purified by silica column chromatography eluting with THF and collecting the fraction that moved. The solvent was removed and the residue purified by silica column chromatography eluting with MeCN and collecting the orange second fraction. The solvent was removed under reduced pressure and the residue dissolved in the minimum of CH_2Cl_2. Addition of hexane resulted in a yellow precipitate which was filtered off and dried to give the product as a yellow powder (0.11 g, 28% yield). ^{1}H NMR (300 MHz, CD_3CN): δ 1.22–1.28 (m, 9H, OCH_2CH_3), 2.55 (s, 3H, CCH_3), 3.16–3.31 (m, 4H, CCH_2C), 3.67 (br s, 4H, $NHCH_2CH_2NH$),

4.16–4.24 (m, 6H, OCH_2CH_3), 4.44 (m, 10H, $COCH_2O$, CCH_2C), 4.93 (d (J = 16.5), 1H, $COCH_2O$), 4.94 (d (J = 16.5), 1H, $COCH_2O$), 6.46–6.82 (m, 12H, Ar H), 7.48 (d (J = 6), 1H, bipy H), 7.84 (d (J = 5), 1H, bipy H), 8.06 (s, 1H, NH), 8.30 (s, 1H, bipy H^3), 8.41 (s, 1H, NH), 8.66 (s, 1H, bipy H^3), 8.86 (d (J = 5.5), 1H, bipy H) and 9.02 (d (J = 5.5 Hz), 1H, bipy H). Microanalysis: $C_{59}H_{58}ClN_4O_{15}Re\cdot H_2O$ requires C 54.39, H 4.64, N 4.30%; found C 53.89, H 4.82, N 4.16%. FAB-MS: *m*/*z* 1250, $[M - Cl]^+$, 1285, $[MH]^+$, and 1308, $[M + Na]^+$.

Tricarbonylchloro{26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-[2,2′-bipyridine-4-carboxamido)propylcarbamoylmethoxy]calix[4]arene}rhenium(I) L[2]. Prepared by an analogous method to that for L[1]. Pentacarbonyl rhenium chloride (0.27 g, 0.75 mmol) was treated with compound **10** (0.62 g, 0.63 mmol) and the products purified as for L[1]; the receptor was isolated as a yellow powder (0.16 g, 26% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.15 (t (J = 7), 6H, OCH_2CH_3), 1.20 (t (J = 7.5), 3H, OCH_2CH_3), 1.86 (qnt (J = 7.5), 2H, $CH_2CH_2CH_2$), 2.56 (s, 3H, $C(CH_3)_3$), 3.23 (d (J = 14), 4H, CCH_2C), 3.32–3.38 (m, 2H, $NHCH_2CH_2$), 3.39–3.43 (m, 2H, CH_2CH_2NH), 4.05–4.11 (m, 4H, OCH_2CH_3), 4.14 (q (J = 7), 2H, OCH_2CH_3), 4.30 (s, 2H, $COCH_2O$), 4.52 (s, 2H, $COCH_2O$), 4.60–4.68 (m, 6H, $COCH_2O$, CCH_2C), 4.91 (d (J = 16.5), 2H, $COCH_2O$), 6.30 (d (J = 7.5), 2H, *m*-H of Ar), 6.37–6.40 (m, 3H, Ar H), 6.46 (t (J = 7), 1H, *p*-H of Ar), 6.73 (t (J = 7.5), 2H, *p*-H of Ar), 6.83–6.87 (m, 4H, *m*-H of Ar), 7.61 (d (J = 5.5), 1H, bipy H), 7.99 (dd (J = 5.5), 1H, bipy H), 8.14 (t (J = 6), 1H, NH), 8.67 (s, 1H, bipy H^3), 8.86 (d (J = 5.5), 1H, bipy H), 8.93 (s, 1H, bipy H^3) and 9.10–9.13 (m, 2H, bipy H, NH). Microanalysis: $C_{60}H_{60}ClN_4O_{15}Re\cdot 4H_2O$ requires C 52.57, H 5.00, N 4.09%; found C 52.12, H 4.65, N 4.13%. ES-MS: *m*/*z* 1264, $[M - Cl]^+$; 1299, $[MH]^+$.

Tricarbonylchloro{26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-[2,2′-bipyridine-4-carboxamido)butylcarbamoylmethoxy]calix[4]arene}rhenium(I) L[3]. Prepared by an analogous method to that for L[1]. Pentacarbonyl rhenium chloride (0.23 g, 0.62 mmol) was treated with compound **11** (0.52 g, 0.52 mmol) and the products purified as for L[1]; L[3] was isolated as a yellow powder (0.10 g, 14% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.16 (t (J = 7), 6H, OCH_2CH_3), 1.22 (t (J = 7), 3H, OCH_2CH_3), 1.73–1.79 (m, 4H, $CH_2CH_2CH_2CH_2$), 2.60 (s, 3H, CCH_3), 3.23 (d (J = 13.5), 2H, CCH_2C), 3.25 (d (J = 13.5), 2H, CCH_2C), 3.50 (m, 2H, $NHCH_2CH_2$), 3.56 (m, 2H, CH_2CH_2-NH), 4.09–4.21 (m, 6H, OCH_2CH_3), 4.36 (s, 2H, $COCH_2O$), 4.48 (s, 2H, $COCH_2O$), 4.58–4.70 (m, 6H, $COCH_2O$, CCH_2C), 4.94 (d (J = 16.5), 2H, $COCH_2O$), 6.26 (d (J = 8), 2H, *m*-H of Ar), 6.35 (d (J = 8), 2H, *m*-H of Ar), 6.37 (t (J = 7.5), 1H, *p*-H of Ar), 6.44 (t (J = 8), 1H, *p*-H of Ar), 6.77 (t (J = 7.5), 2H, *p*-H of Ar), 6.83 (d (J = 6.5), 2H, *m*-H of Ar), 6.86 (d (J = 7.5), 2H, *m*-H of Ar), 7.61 (d (J = 5), 1H, bipy H), 7.97 (dd (J = 5), 1H, bipy H), 8.09 (t (J = 5), 1H, NH), 8.65 (s, 1H, bipy H^3), 8.85 (d (J = 5), 1H, bipy H), 8.95 (s, 1H, bipy H^3), 9.08 (d (J = 5.5), 1H, bipy H) and 9.14 (t (J = 6.5 Hz), 1H, NH). Microanalysis: $C_{61}H_{62}ClN_4O_{15}Re\cdot 3H_2O$ requires C 53.60, H 5.01, N 4.10%; found C 53.80, H 5.25, N 4.19%. ES-MS: *m*/*z* 1278, $[M - Cl]^+$; 1313, $[MH]^+$.

Tricarbonylchloro{26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-2,2′-bipyridine-4-carboxamido)phenylcarbamoylmethoxy]calix[4]arene}rhenium L[4]. Prepared by an analogous method to that for L[1]. Pentacarbonyl rhenium chloride (0.30 g, 0.29 mmol) was treated with compound **12** (0.15 g, 0.41 mmol). The product was isolated as a yellow powder (0.27 g, 69% yield). ^{1}H NMR (300 MHz, CD_3CN): δ 1.12–1.18 (m, 6H, OCH_2CH_3), 1.28 (t (J = 7), 3H, OCH_2CH_3), 2.59 (s, 3H, CCH_3), 3.28 (br dd, 2H, CCH_2C), 3.93–4.03 (m, 4H, OCH_2CH_3), 4.23 (q (J = 7), 2H, OCH_2CH_3), 4.53 (d (J = 16.5), 1H, $COCH_2O$), 4.57 (d (J = 16), 1H, $COCH_2O$), 4.58 (s, 2H, $COCH_2O$), 4.65 (d (J = 13.5), 2H, CCH_2C), 4.69 (s, 2H, $COCH_2O$), 4.76 (d (J = 13.5), 1H, CCH_2C), 4.78 (d (J = 13.5), 1H, CCH_2C), 4.96 (d (J = 16.5), 1H, $COCH_2O$), 4.99 (d (J = 16), 1H, $COCH_2O$), 6.26 (d (J = 7.5), 2H, *m*-H of Ar), 6.41 (t (J = 7), 1H, *p*-H of Ar), 6.45 (d (J = 8), 2H, *m*-H of Ar), 6.55 (t (J = 7.5), 1H, *p*-H of Ar), 6.74–6.87 (m, 6H, Ar H), 7.25 (t (J = 7.5), 1H, Ar H), 7.38 (d (J = 6), 1H, bipy H), 7.43 (t (J = 8), 1H, Ar H), 7.97 (d (J = 5), 1H, bipy H), 8.15 (d (J = 8.5), 1H, Ar H), 8.17 (s, 1H, bipy H^3), 8.81 (s, 1H, bipy H^3), 8.90 (d (J = 5.5), 1H, bipy H), 9.13 (d (J = 5.5 Hz), 1H, bipy H), 10.29 (s, 1H, NH) and 10.55 (s, 1H, NH). Microanalysis: $C_{63}H_{58}ClN_4O_{15}Re\cdot H_2O$ requires C 56.02, H 4.48, N 4.15; found C 55.84, H 4.61, N 4.13%. FAB-MS: *m*/*z* = 1334, M^+, 1357, $[M + Na]^+$; 1299, $[M - Cl]^+$.

General synthesis of ruthenium(II) receptors: bis(2,2′-bipyridyl){26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-[2,2′-bipyridine-4-carboxamido)ethylcarbamoylmethoxy]calix[4]arene}ruthenium(II) L[5]. Bis(2,2′-bipyridyl)ruthenium(II) dichloride (0.17 g, 0.33 mmol) was dissolved in 1:1 water–ethanol (10 ml) and stirred for 30 min before being brought to reflux for 1 h. Compound **9** (0.30 g, 0.31 mmol) in ethanol (10 ml) was added and the mixture refluxed overnight. The solvent was removed and the residue purified by column chromatography on Sephadex LH-20® eluted with acetonitrile. The last bright red fraction was collected and the solvent removed. The residue was stirred in water (20 ml) and an excess of ammonium hexafluorophosphate (0.5 g, 1.8 mmol). The resulting precipitate was filtered off, washed with copious water to remove excess of ammonium hexafluorophosphate and dried to give the product as an orange powder (0.08 g, 26% yield). ^{1}H NMR (500 MHz, CD_3CN): δ 1.17–1.21 (m, 6H, OCH_2CH_3), 1.23 (t (J = 7), 3H, OCH_2CH_3), 2.53 (s, 3H, $C(CH_3)_3$), 3.18 (d (J = 13.5), 1H, CCH_2C), 3.19 (d (J = 13.5), 1H, CCH_2C), 3.28 (d (J = 13.5), 2H, CCH_2C), 3.63–3.64 (m, 4H, $NHCH_2$-CH_2NH), 4.09–4.14 (m, 4H, OCH_2CH_3), 4.18 (q (J = 7), 2H, OCH_2CH_3), 4.48 (s, 2H, $COCH_2O$), 4.50 (d (J = 12.5), 1H, CCH_2C), 4.53 (d (J = 12.5), 1H, CCH_2C), 4.61 (s, 2H, $COCH_2O$), 4.65 (d (J = 13.5), H, CCH_2C), 4.67 (d (J = 16.5), 2H, $COCH_2O$), 4.88 (d (J = 16.5), 2H, $COCH_2O$), 6.44–6.49 (m, 4H, Ar H), 6.60–6.76 (m, 8H, Ar H), 7.26 (d (J = 6), 1H, bipy H), 7.33–7.41 (m, 4H, bipy H), 7.54 (d (J = 5.5), 1H, bipy H), 7.58 (d (J = 5.5), 1H, bipy H), 7.69–7.71 (m, 3H, bipy H), 7.79 (d (J = 6), 1H, bipy H), 8.01–8.08 (m, 4H, bipy H), 8.09 (s, 1H, NH), 8.39 (s, 1H, NH), 8.43 (s, 1H, bipy H^3), 8.48 (m, 5H, bipy H) and 8.75 (s, 1H, bipy H^3). Microanalysis: $C_{76}H_{74}F_{12}$-$N_8O_{12}P_2Ru\cdot 2H_2O$ requires C 53.12, H 4.57, N 6.52%; found C 53.00, H 5.18, N 6.36%. FAB-MS: *m*/*z* 1537, $[M - PF_6]^+$; 1392, $[M^+ - 2PF_6]^+$.

Bis(2,2′-bipyridyl){26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-2,2′-bipyridine-4-carboxamido)propylcarbamoylmethoxy]calix[4]arene}ruthenium(II) L[6]. Prepared by an analogous method to that for L[5]. Bis(2,2′-bipyridyl)-ruthenium(II) dichloride (0.25 g, 0.48 mmol) was treated with compound **10** (0.40 g, 0.40 mmol). The initial reaction product was purified by chromatography on Sephadex LH-20® eluted with acetonitrile. The solvent was removed and the residue redissolved in the minimum of CH_2Cl_2. Addition of diethyl ether (100 ml) resulted in a precipitate, which was filtered off and dried to give the product as the chloride salt, an orange powder (0.35 g, 57% yield). ^{1}H NMR (500 MHz, CD_3CN): δ 1.12–1.14 (m, 6H, OCH_2CH_3), 1.21 (t (J = 7), 3H, OCH_2CH_3), 2.53 (s, 3H, $C(CH_3)_3$), 3.24 (d (J = 13.5), 4H, CCH_2C), 3.40–3.52 (m, 4H, $NHCH_2CH_2CH_2NH$), 4.04–4.10 (m, 4H, OCH_2CH_3), 4.17 (q (J = 7), 2H, OCH_2CH_3), 4.33 (s, 2H, $COCH_2O$), 4.53 (s, 2H, $COCH_2O$), 4.62–4.70 (m, 4H, $COCH_2O$, CCH_2C), 4.74 (d (J = 13.5), 2H, CCH_2C), 4.96 (d (J = 16), 2H, $COCH_2O$), 6.35–6.40 (m , 3H, Ar H), 6.46–6.48 (m, 3H, Ar H), 6.75 (t (J = 7), 2H, *p*-H of Ar), 6.87–6.91 (m, 4H, *m*-H of Ar), 7.23 (d (J = 6), 1H, bipy H), 7.33–7.40 (m, 4H, bipy H), 7.51 (d (J = 5), 1H, bipy H), 7.70–7.74 (m, 5H, bipy H),

7.83 (d (J = 5), 1H, bipy H), 8.01–8.07 (m, 4H, bipy H), 8.20 (br s, 1H, NH), 8.58–8.60 (m, 4H, bipy H), 9.47 (s, 1H, bipy H^3), 10.08 (s, 1H, bipy H^3) and 10.19 (br s, 1H, NH). Microanalysis: $C_{77}H_{76}Cl_2N_8O_{12}Ru\cdot 6H_2O$ requires C 58.33, H 5.55, N 7.07%; found C 58.57, H 5.23, N 7.09%.

The chloride salt (0.14 g, 0.09 mmol) was stirred in water (20 ml) and an excess of ammonium hexafluorophosphate (0.5 g, 1.8 mmol). The resulting precipitate was filtered off, washed with copious water to remove excess of ammonium hexafluorophosphate and dried to give the product as an orange powder (0.16 g, 98% yield) ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.10–1.13 (m, 6H, OCH_2CH_3), 1.19 (t (J = 7), 3H, OCH_2CH_3), 1.82 (qnt (J = 7), 2H, $CH_2CH_2CH_2$), 2.54 (s, 3H, $C(CH_3)_3$), 3.24 (br d (J = 14), 4H, CCH_2C), 3.32–3.35 (m, 2H, $NHCH_2CH_2$), 3.39 (q (J = 6), 2H, CH_2CH_2NH), 4.04–4.09 (m, 4H, OCH_2CH_3), 4.14 (q (J = 7), 2H, OCH_2CH_3), 4.29 (s, 2H, $COCH_2O$), 4.52 (s, 2H, $COCH_2O$), 4.59–4.69 (m, 6H, $COCH_2O$, CCH_2C), 4.89 (d (J = 16.5), 2H, $COCH_2O$), 6.30 (d (J = 7.5), 2H, *m*-H of Ar), 6.37–6.40 (m, 3H, Ar H), 6.47 (t (J = 7), 1H, *p*-H of Ar), 6.73 (t (J = 7.5), 2H, *p*-H of Ar), 7.40 (d (J = 5.5), 1H, bipy H), 7.47–7.53 (m, 4H, bipy H), 7.57 (d (J = 5.5), 1H, bipy H), 7.69–7.77 (m, 4H, bipy H), 7.85 (d (J = 6), 1H, bipy H), 8.12–8.18 (m, 5H, bipy H, NH), 8.76 (s, 1H, bipy H^3), 8.83 (br d (J = 7.5), 4H, bipy H), 9.00 (br t (J = 5.5 Hz), 1H, N*H*) and 9.04 (s, 1H, bipy H^3). Microanalysis: $C_{77}H_{76}F_{12}N_8O_{12}P_2Ru\cdot 3H_2O$ requires C 52.83, H 4.72, N 6.40%; found C 52.61, H 4.47, N 6.39%. FAB-MS; m/z 1551, $[M - PF_6]^+$; 1406, $[M - 2PF_6]^+$.

Bis(2,2′-bipyridyl){26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-2,2′-bipyridine-4-carboxamido)butylcarbamoylmethoxy]calix[4]arene}ruthenium(II) hexafluorophosphate L^7. Prepared by an analogous method to that for L^5. Bis(2,2′-bipyridyl)ruthenium(II) dichloride (0.15 g, 0.29 mmol) was treated with compound **11** (0.20 g, 0.20 mmol) to give the product as (the hexafluorophosphate salt) an orange powder (0.07 g, 27% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.16 (t (J = 7), 6H, OCH_2CH_3), 1.20 (t (J = 7), 3H, OCH_2CH_3), 1.58 (br s, 4H, $CH_2CH_2CH_2CH_2$), 2.53 (s, 3H, $C(CH_3)_3$), 3.23 (br d (J = 14), 4H, CCH_2C), 3.28–3.30 (m, 2H, CH_2CH_2NH), 4.07–4.10 (m, 4H, OCH_2CH_3), 4.14 (q (J = 7), 2H, OCH_2CH_3), 4.27 (s, 2H, $COCH_2O$), 4.52 (s, 2H, $COCH_2O$), 4.61 (d (J = 16.5), 2H, $COCH_2O$), 6.64 (d (J = 13), 4H, CCH_2C), 4.87 (d (J = 16.5), 2H, $COCH_2O$), 6.32 (d (J = 7.5), 2H, *m*-H of Ar), 6.38–6.42 (m , 3H, Ar H), 6.48 (t (J = 7.5), 1H, *p*-H of Ar), 6.70 (t (J = 7.5), 2H, *p*-H of Ar), 6.80 (d (J = 7.5), 2H, *m*-H of Ar), 6.83 (d (J = 7.5), 2H, *m*-H of Ar), 7.40 (d (J = 6), 1H, bipy H), 7.46–7.54 (m, 4H, bipy H), 7.57 (d (J = 6), 1H, bipy H), 7.69–7.72 (m, 3H, bipy H), 7.75 (d (J = 5), 1H, bipy H), 7.81 (d (J = 6), 1H, bipy H), 8.08 (t (J = 6), 1H, NH), 8.13–8.19 (m, 4H, bipy H), 8.75 (s, 1H, bipy H^3), 8.83–8.85 (m, 4H, bipy H), 8.98 (t (J = 6 Hz), 1H, NH) and 9.04 (s, 1H, bipy H^3). Microanalysis: $C_{78}H_{78}F_{12}N_8O_{12}P_2Ru\cdot 2H_2O$ requires C 53.64, H 4.73, N 6.42%; found C 53.44, H 4.61, N 6.37%. FAB-MS: m/z 1565, $[M - PF_6]^+$, 711, $[M - 2PF_6]^{2+}$.

Bis(2,2′-bipyridyl){26,27,28-tri[(ethoxycarbonyl)methoxy]-25-[1-(4′-methyl-2,2′-bipyridine-4-carboxamido)phenylcarbamoylmethoxy]calix[4]arene}ruthenium(II) hexafluorophosphate L^8. Prepared by an analogous method to that for L^5. Bis(2,2′-bipyridyl)ruthenium(II) dichloride (0.10 g, 0.19 mmol) was treated with compound **12** (0.10 g, 0.97 mmol) to give the product as an orange powder (0.08 g, 46% yield). ^{1}H NMR (500 MHz, CD_3CN): δ 1.04–1.08 (m, 6H, OCH_2CH_3), 1.22 (t (J = 7), 3H, OCH_2CH_3), 2.50 (s, 3H, CCH_3), 3.14 (d (J = 13.5), 2H, CCH_2C), 3.28 (d (J = 13.5), 2H, CCH_2C), 3.87–3.96 (m, 4H, OCH_2CH_3), 4.17 (q (J = 7), 2H, OCH_2CH_3), 4.47 (d (J = 16.5), 1H, $COCH_2O$), 4.52 (d (J = 16.5), 1H, $COCH_2O$), 4.58–4.61 (m, 4H, $COCH_2O$, CCH_2C), 4.68 (s, 2H, $COCH_2O$), 4.73 (d (J = 13.5), 1H, CCH_2C), 4.74 (d (J = 13.5), 1H, CCH_2C), 4.85–4.91 (m, 2H, $COCH_2O$), 6.24–6.32 (m, 3H, Ar H), 6.58 (br s, 3H, Ar H), 6.65–6.72 (m, 4H, *m*-H of Ar), 6.83–6.86 (m, 2H, *p*-H of Ar), 7.27 (d (J = 5.5), 1H, bipy H), 7.31–7.44 (m, 6H, Ar*H*, bipy H), 7.54–7.56 (m, 2H, Ar H), 7.65 (d (J = 5), 1H, bipy H), 7.67–7.74 (m, 4H, bipy H), 7.87 (d (J = 5), 1H, bipy H), 7.99–8.08 (m, 5H, bipy H), 8.40 (s, 1H, bipy H^3), 8.47–8.50 (m, 4H, bipy H), 8.87 (s, 1H, bipy H^3), 9.84 (s, 1H, NH) and 9.91 (s, 1H, NH). Microanalysis: $C_{80}H_{74}F_{12}N_8O_{12}P_2Ru\cdot 2H_2O$ requires C 54.39, H 4.45, N 6.34%; found C 54.66, H 4.24, N 6.16%. FAB-MS: m/z 1585, $[M - PF_6]^+$; 1440, $[M^+ - 2PF_6]^+$.

Crystallography

Crystal data for L^4. $C_{63}H_{58}ClN_4O_{15}Re$, M = 1332.78, monoclinic, space group $P2_1/a$, Z = 4, a = 15.947(17), b = 23.90(3), c = 16.640(19) Å, β = 96.77(1)°, U = 6298 Å^3, 17787 reflections (10509) independent, R(int) = 0.0649 collected with Mo-Kα radiation using the MARresearch Image Plate System at room temperature. Data analysis was carried out with the XDS program.[18] The structure was solved using direct methods with SHELXS 86.[19] The non-hydrogen atoms were refined with anisotropic thermal parameters apart from a few carbon atoms in CO_2Et groups which had high thermal motion and for which dimensions were constrained. Hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using SHELXL[20] with 733 parameters to R1 0.0961, $wR2$ 0.2500 for 4314 data with $I > 2\sigma(I)$ and R1 0.2151, $wR2$ 0.3055 for all data.

CCDC reference number 186/2309.

See http://www.rsc.org/suppdata/dt/b0/b008576f/ for crystallographic files in .cif format.

^{1}H NMR titrations

A solution of the receptor (500 μl) was prepared at a concentration typically of the order of 0.01 mol dm^{-3} in deuteriated acetonitrile. The initial ^{1}H NMR spectrum was recorded and aliquots of anion were added by gas-tight syringe from a solution made such that 1 mol equivalent was added in 20 μl. After each addition and mixing the spectrum was recorded again and changes in the chemical shift of certain protons were noted. The result of the experiment was a plot of displacement in chemical shift as a function of the amount of added anion, which was subjected to analysis by curve-fitting since the shape is indicative of the stability constant for the complex. The computer program EQNMR[21] was used which requires the concentration of each component and the observed chemical shift (or its displacement) for each data point. Typically these titration experiments were repeated three times with at least fifteen data points in each experiment.

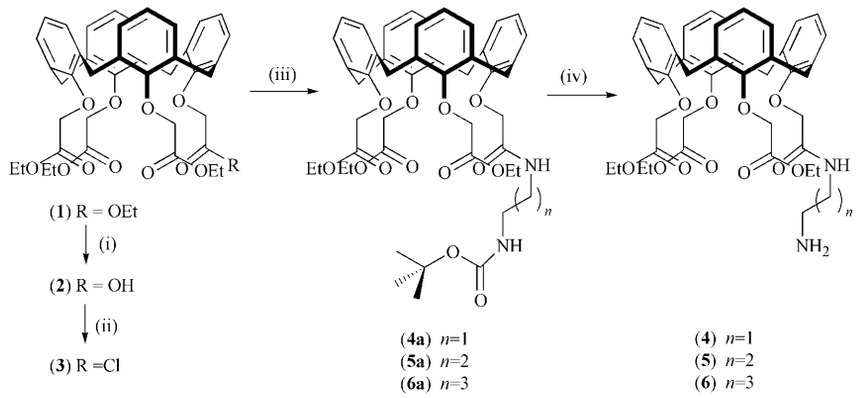
Results and discussion

Syntheses of lower rim mono-amine calix[4]arene synthons

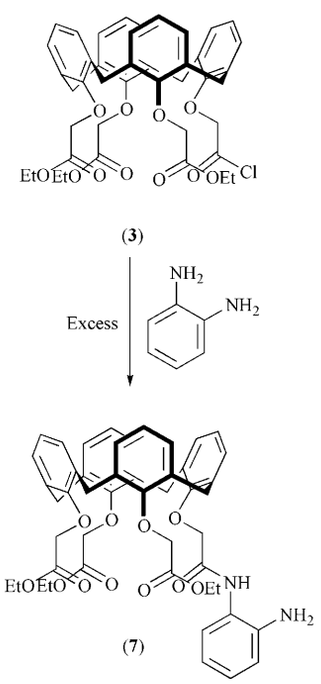
The new lower rim mono-amine ester substituted calix[4]arene derivatives **4–7** were prepared according to Scheme 1. The reaction of the tetraester **1**[15] with 65% HNO_3 in dichloromethane led to selective hydrolysis of one of the esters to give the monoacid **2** in almost quantitative yield. Refluxing **2** with oxalyl chloride produced the triester monoacid chloride **3** which on condensation with the appropriate Boc protected alkyl diamine[16] followed by addition of trifluoroacetic acid in dichloromethane gave the new lower rim mono-amine calix[4]arene synthons **4–6** in very good yields (Scheme 1). The addition of a large excess of 1,2-diaminobenzene to **3** in dichloromethane afforded the calix[4]arene aryl linked amine **7** in 69% yield (Scheme 2).

Receptor syntheses and characterisation

Condensation reactions of the appropriate lower rim mono-



Scheme 1



Scheme 2

amine calix[4]arene derivative with 4-chlorocarbonyl-4′-methyl-2,2′-bipyridine **8** [17] gave the ethyl **9**, propyl **10**, butyl **11** and aryl **12** linked compounds in 85%, 54%, 84% and 80% yields respectively (Scheme 3). Complexation reactions with $Re(CO)_5Cl$ in THF produced the new rhenium(I) bipyridyl calix[4]arene receptors L^1–L^4 as orange-yellow solids. The ruthenium(II) bipyridyl calix[4]arene receptors L^5–L^8 were prepared by reaction of the bipyridyl calix[4]arene derivatives with $Ru(bipy)_2Cl_2$ in aqueous ethanol solution followed by addition of an excess of ammonium hexafluorophosphate (Scheme 3). All these new receptors were characterised by ^{1}H NMR spectroscopy, FAB mass spectrometry and elemental analysis (see Experimental section).

It is noteworthy that the ^{1}H NMR spectra of L^1–L^8 in CD_3CN gave evidence for the existence of intramolecular hydrogen bonds between the carbonyl oxygens and amide-NH groups of the lower rim substituents. For example Fig. 2 displays a comparison of the ^{1}H NMR spectra of the methylene proton region for compound **9** and L^5. **9** exhibits the expected splitting pattern, four pairs of doublets, for the calixarene methylene protons. The spectrum for L^5 contains six pairs of doublets, H_{1a} and H_{1b}, H_{3a} and H_{3b} being no longer equivalent. This is consistent with a lowering of symmetry involving the ruthenium(II) bipyridyl amide substituent being held asymmetrically by intramolecular hydrogen bonds with respect to the symmetry plane. Interestingly in the more polar solvent DMSO-d_6 this asymmetry is removed indicating that hydrogen bonding has been disrupted. Evidence for intramolecular hydrogen bonding occurring in the solid state is discussed below with the X-ray structural investigation of L^4.

X-Ray structural investigation of receptor L^4

Crystals of L^4 suitable for structural determination were grown from dilute acetonitrile solutions of the receptor. The structure is shown in Fig. 3 together with the atomic numbering scheme. The Re atom has a distorted octahedral environment being bonded to three mutually *cis* carbonyl groups (1.92(2)–1.99(2) Å), two nitrogen atoms of a substituted bipyridyl (Re–N(l) 2.138(10), 2.179(12) Å) and a chlorine atom (Re–Cl 2.438(5) Å). The bipyridyl group is linked to a calix[4]arene by a diamide linkage whose conformation is fixed *via* an intramolecular hydrogen bond between N(161)–H and O(153) of 2.726 Å. The conformation of the calix[4]arene is a C_2 distorted cone. The four phenyl rings intersect the plane of the four methylene groups at angles of 103.3, 36.5, 105.2 and 36.1°. As can be seen clearly in the Figure rings 1 and 3 are tilted so that the atoms at the top of the cone C(13) and C(33) are closer together than atoms at the bottom rim C(16) and C(36). The position of the calix[4]arene is adjacent to the diamide linkage to facilitate an intramolecular hydrogen bond between N(154)–H and O(253) of 2.938 Å. N(154) is also in close proximity to O(150) at 2.669 Å. There is an additional intermolecular hydrogen bond in the unit cell, between N(154) and O(100) ($0.5 - x$, $-0.5 + y$, $-z$) at 3.059 Å.

Ion pair binding studies

Receptors L^1–L^8 are designed simultaneously to bind a cation and anion ion pair such that the presence of a co-bound alkali metal cation would enhance the strength of anion binding *via* favourable electrostatic interactions and preorganisation effects. The difficulty with investigating simultaneous cation and anion binding is that there are many competing equilibria processes involved (Fig. 4). The number of equilibria shown in Fig. 4 can be simplified and reduced if the following assumptions and considerations of choice of metal salt, ion pair guest species and solvent medium are taken into account. The anion stability constant K_2 of the receptor can be determined independently and the titration experiment repeated in the presence of a

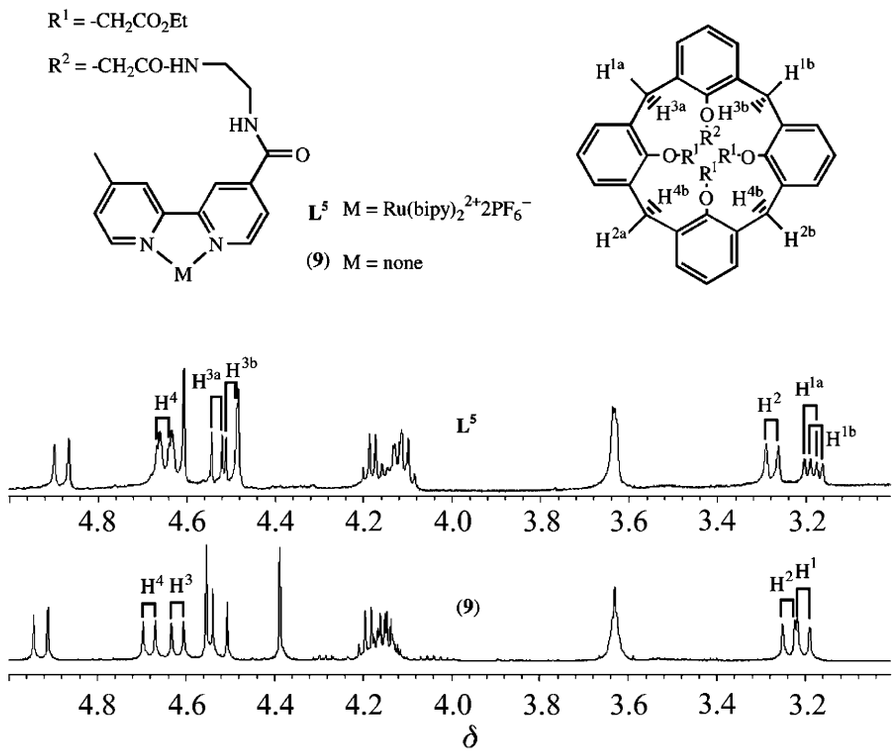
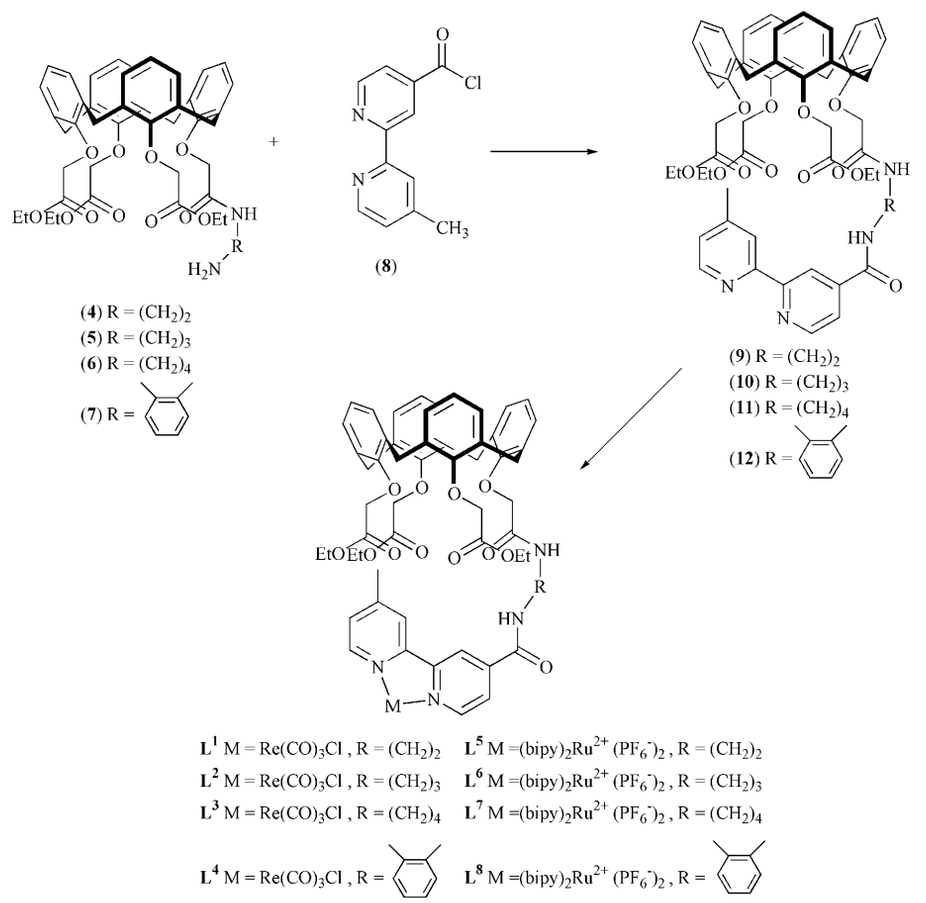


Fig. 2 Comparison of the ^{1}H NMR methylene region for compound **9** and L^5 in CD_3CN solution.



Scheme 3

stoichiometric amount of metal cation. If it is assumed that any metal cation present in solution is fully bound to the receptor, K_5 can then be determined. Comparison of K_2 and K_5 therefore gives the enhancement of anion binding as a consequence of the co-bound metal cation. However, consideration must also be given to both the competing process of ion pairing in solution K_3 and precipitation of the salt K_1. The assumption that the metal cation is fully bound by the receptor ignores these competing equilibria which will be responsible for any apparent decreases in strength of anion binding when the 'free' metal cation is present in solution. Precipitation of the ion pair salt (K_1) is of particular concern and it is therefore prudent to

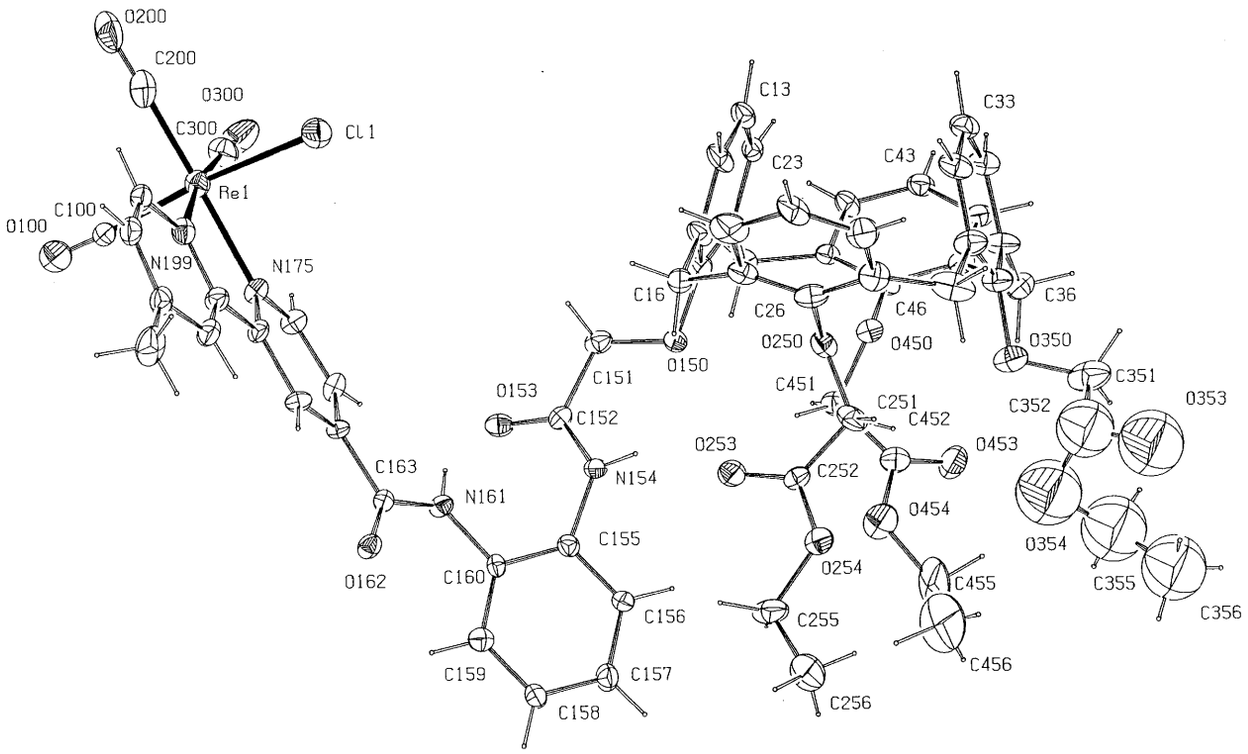


Fig. 3 The structure of L^4 with ellipsoids at 20% probability.

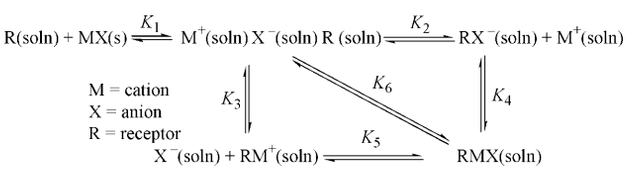


Fig. 4 Equilibria involved in ion pair binding.

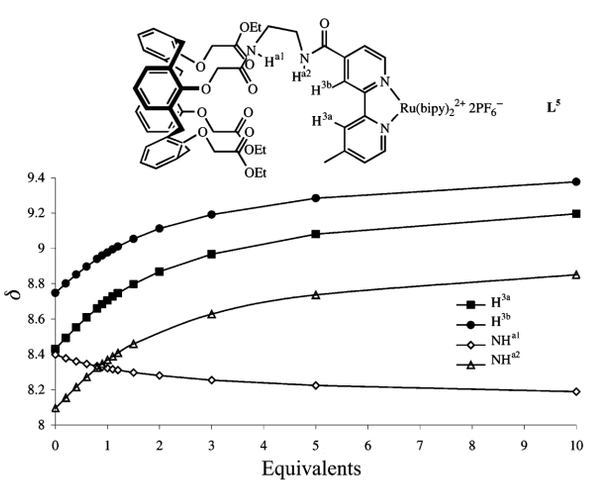


Fig. 5 Proton NMR titration curves of L^5 with I^- in CD_3CN.

ensure the metal salt itself is soluble in the chosen solvent medium. As a consequence solution ion pairing will then be the only major equilibrium process to compete with anion binding by the metal bound receptor.

Proton NMR alkali metal cation and halide anion binding studies

Taking into account the above, the knowledge that lower rim ester functionalised calix[4]arenes are known strongly to complex alkali metal cations,[15] which will minimise competing ion pairing interactions, and receptor–alkali metal salt solubility properties, the lithium, sodium cation and bromide, iodide anion coordination properties of L^1–L^8 were investigated by ^{1}H NMR titration experiments in CD_3CN solution. The addition of tetrabutylammonium bromide and iodide salts to CD_3CN solutions of the receptors resulted in significant downfield perturbations of the bipy H^{3a}, H^{3b} and amide NH^{a2} protons whereas those of NH^{a1}, were observed to move marginally upfield (Fig. 5), which indicates that anion binding is occurring near the bipyridyl group involving amide NH^{a2} but not NH^{a1} which perhaps continues to form an intramolecular hydrogen bond with a carboxyl ester group of the lower rim. EQNMR [21] analysis of the resulting titration curves (*e.g.* Fig. 5) gave stability constant values for 1 : 1 solution anion complexes shown in Tables 1 and 2. All the receptors complex bromide anion more strongly than iodide and as a consequence of the positively charged ruthenium(II) metal centre, which leads to additional attractive electrostatic interactions with the bromide anion, L^5–L^8 display larger magnitudes of halide stability constants in comparison to those of the neutral rhenium receptors L^1–L^4.

The addition of $LiClO_4$ and $NaClO_4$ to L^1–L^8 caused the lower rim calixarene ester methylene receptors protons to broaden initially and sharpen again after one equivalent suggesting strong complexes of 1 : 1 stoichiometry are being formed in solution. Interestingly significant upfield shifts of up to $\Delta\delta = 1.5$ ppm were also observed for both the amide protons on alkali metal cation addition which indicates that lower rim metal cation binding disrupts the amide–carbonyl ester intramolecular hydrogen bonding interactions noted previously. Repeating the bromide and iodide ^{1}H NMR titrations in the presence of one equivalent of lithium or sodium alkali metal cation caused all four amide and bipy H^3 proton resonances of the respective receptors to be significantly shifted downfield and the EQNMR determined stability constant values are also presented in Tables 1 and 2. Clearly both Tables show that with all receptors there is a significant increase in the strength of bromide and iodide binding when the alkali metal is co-bound with the largest anion enhancement of sixtyfold being exhibited by L^4Li^+ and bromide (Table 1). This positive co-operative binding of halide anion may be attributed to mutual electrostatic alkali metal cation–anion attraction, preorganisation effects and increased strength of hydrogen bonding to the bound anion as

Table 1 Stability constants for bromide and iodide binding in the presence and absence of alkali metal cations by rhenium receptors L^1–L^4 in CD_3CN

Receptor	Anion	Metal cation[a]	K^b/M^{-1}	Relative enhancement[c]
L^1	I^-	None	15	
L^1	I^-	Li^+	200	13.3
L^1	I^-	Na^+	215	14.3
L^1	Br^-	None	50	
L^1	Br^-	Li^+	1110	22.2
L^2	I^-	None	[d]	
L^2	I^-	Li^+	220	
L^2	I^-	Na^+	280	
L^2	Br^-	None	[d]	
L^2	Br^-	Li^+	1185	
L^3	I^-	None	[d]	
L^3	I^-	Li^+	[e]	
L^3	Br^-	None	[d]	
L^3	Br^-	Li^+	[e]	
L^4	I^-	None	10	
L^4	I^-	Li^+	205	20.5
L^4	I^-	Na^+	220	22.0
L^4	Br^-	None	40	
L^4	Br^-	Li^+	2400	60.0

[a] Titration carried out in the presence of one equivalent of alkali metal perchlorate salt. [b] Determined at 298 K; errors estimated to be $\leqslant 5\%$. [c] Relative anion binding enhancement, $K(M^+)/K$ (free receptor). [d] EQNMR could not determine a stability constant from the titration data. [e] Partial precipitation prevented a stability constant from being determined.

Table 2 Stability constants for bromide and iodide binding in the presence and absence of alkali metal cations by ruthenium receptors L^5–L^8 in CD_3CN

Receptor	Anion	Metal cation[a]	K^b/M^{-1}	Relative enhancement[c]
L^5	I^-	None	60	
L^5	I^-	Li^+	310	5.2
L^5	I^-	Na^+	335	5.6
L^5	Br^-	None	230	
L^5	Br^-	Li^+	1260	5.5
L^6	I^-	None	65	
L^6	I^-	Li^+	350	5.4
L^6	I^-	Na^+	460	7.1
L^6	Br^-	None	250	
L^6	Br^-	Li^+	2410	9.6
L^7	I^-	None	75	
L^7	I^-	Li^+	175	2.3
L^7	I^-	Na^+	270	3.6
L^7	Br^-	None	275	
L^7	Br^-	Li^+	620	2.3
L^8	I^-	None	20	
L^8	I^-	Li^+	170	8.5
L^8	I^-	Na^+	270	13.5
L^8	Br^-	None	130	
L^8	Br^-	Li^+	1540	11.8

[a] Titration carried out in the presence of one equivalent of alkali metal perchlorate salt. [b] Determined at 298 K; errors estimated to be $\leqslant 5\%$. [c] Relative anion binding enhancement, $K(M^+)/K$ (free receptor).

a result of metal cation complexation removing lower rim ester–amide intramolecular hydrogen bonding. Interestingly the degree of enhancement of iodide binding for all receptors is greatest in the presence of co-bound sodium which correlates with this metal cation being known to form highly stable and selective complexes with lower rim tetrasubstituted ethyl ester calix[4]arenes.[15] It is also noteworthy that when comparing Tables 1 and 2 the degree of halide binding enhancements for the neutral rhenium receptors are much larger than for the charged ruthenium receptors. This may be rationalised by considering the relative charge increases of the rhenium *versus* ruthenium receptors on alkali metal cation binding. In the presence of alkali metal cation the relative increase of charge is larger for the neutral rhenium receptors (neutral to +1) compared to the dicationic ruthenium systems (+2 to +3). Alternatively, the positive charge on the ruthenium receptor may *via* unfavourable electrostatic interactions disfavour lower rim ester alkali metal cation binding, thus a relatively greater proportion of unbound metal cations is present in solution to compete with anion binding by ion pairing, reducing the enhancement of anion complexation. Tables 1 and 2 also reveal that alkyl chain length variation has little effect on the strength of halide anion binding. However, the enhancement of anion binding with a co-bound cation for the ruthenium receptors in particular (Table 2) is dependent on the alkyl spacer being greatest for the propyl linked receptor L^6 with the butyl linked receptor L^7 exhibiting the lowest enhancement values. Moreover, although the rigid aryl linked receptors L^4, L^8 form comparatively weaker halide complexes than the alkyl linked analogues, alkali metal coordination leads to the largest co-operative amplifications of anion binding of up to sixtyfold for L^4 with co-bound lithium cation and bromide anion guest. This may be a consequence of co-bound alkali metal cation induced aryl linked receptor preorganisation and intramolecular hydrogen bond disruption which especially favours subsequent halide anion complexation.

Alkali metal salt extraction experiments

Having demonstrated that these ditopic receptors with a co-bound metal cation co-operatively bind anions in solution, it was of interest to investigate whether solid alkali metal salts could be extracted and solubilised into organic solvents. Alkali metal salt solid/liquid extraction experiments were performed with rhenium receptor L^1 and ruthenium receptor L^6. Each receptor was dissolved in CD_2Cl_2 and stirred with an excess of solid NaCl and NaOAc for 12 hours. After filtration the ^1H NMR spectra revealed two sets of resonances which corresponded to the salt complex and free receptor. The salt complex resonances were characterised notably by significant downfield perturbations of the bipy H^3 and amide NH^a protons, and by perturbations of the calixarene aromatic and lower rim ester protons. The percentage extraction was determined by relative integration of equivalent protons and revealed L^1 extracted 60% and L^6 55% of both sodium salts. It is noteworthy that on repeating the extraction experiments with NH_4OAc no significant changes were observed in the ^1H NMR spectra suggesting the metal cation binding ability of the heteroditopic receptor is of paramount importance in the alkali metal salt extraction process.

Conclusions

A series of new heteroditopic rhenium(I) and ruthenium(II) bipyridyl calix[4]arene receptors that simultaneously complex alkali metal cation–anion ion pairs at the calixarene lower rim have been synthesized. Proton NMR halide anion titration investigations in the absence and presence of lithium and sodium cations reveal the lower rim ester co-bound alkali metal cation significantly enhances the strength of bromide and iodide binding, with the largest positive co-operative anion binding effect of sixtyfold being displayed by $[LiL^4]^+$ and bromide. It is noteworthy that with iodide the greatest enhancement of binding for all receptors is with the co-bound sodium cation which correlates with the known selectivity preference of lower rim tetrasubstituted ethyl ester for this alkali metal cation. Interestingly the degree of halide binding enhancement for the neutral rhenium(I) receptors L^1–L^4 is considerably larger than for the charged ruthenium(II) receptors L^5–L^8 which may be attributable to unfavourable electrostatic effects leading to a relatively higher proportion of 'free' metal cations being available in solution to compete with anion binding *via* ion

pairing. Alkali metal salt solid/liquid extraction experiments reveal L^1 and L^6 to solubilise NaCl and NaOAc by up to 60% in dichloromethane solutions.

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