Calix[4]semitube diquinone: a potassium selective redox-active ionophore

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Oxidation of calix[4]semitube with $Tl(OCOCF_3)_3$ in TFA (trifluoroacetic acid) affords the novel redox-active ionophore calix[4]semitube diquinone. This receptor displays a remarkable selectivity preference for potassium cations over all other Group 1 metal cations, a property mirroring that of the parent calix[4]semitube, however its kinetics of complexation are relatively slow. The receptor exhibits substantial electrochemical recognition effects towards sodium and potassium cations.

Introduction

The design and synthesis of redox-active molecular receptors which are capable of selectively sensing *via* electrochemical means, charged or neutral guest species of biological and environmental importance, is an area of intense research activity.[1] In particular, the incorporation of a variety of redox-active transition metal and organic centres into macrocyclic structural frameworks based on crown ethers, cryptands and calixarenes have produced some systems which are selective and electrochemically responsive to specific alkali metal cations.[2]

We have recently reported a new class of cryptand-type ionophore, the calix[4]tube 1 and calix[4]semitube 2 (Fig. 1) both based on a bis(calix[4]arene) scaffold that display exceptional selectivity for potassium over all other Group 1 metal cations.[3] In this paper, we describe the synthesis, coordination and electrochemical properties of a novel redox-active calix[4]semitube diquinone receptor 3 which exhibits remarkable selective and redox-responsive behaviour towards potassium cations.
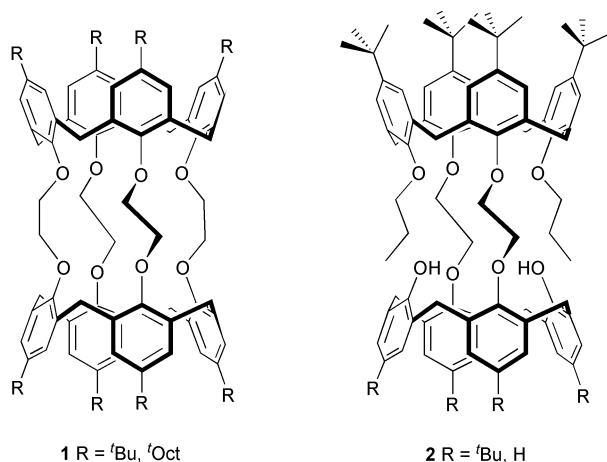

Fig. 1 Bis(calix[4]arene) frameworks designed for selective cation complexation.

Results and discussion

Synthesis

Using the reagent thallium(III) trifluoroacetate, first employed by Gutsche and co-workers for the conversion of parent calixarenes to calixquinones,[4] the calix[4]semitube ligand 2 was oxidised to the new calix[4]semitube diquinone product 3 in 53% yield (Scheme 1). The receptor was characterised by ^{1}H and ^{13}C NMR spectroscopy, electrospray mass spectrometry and elemental analysis (see Experimental section). The ^{1}H NMR
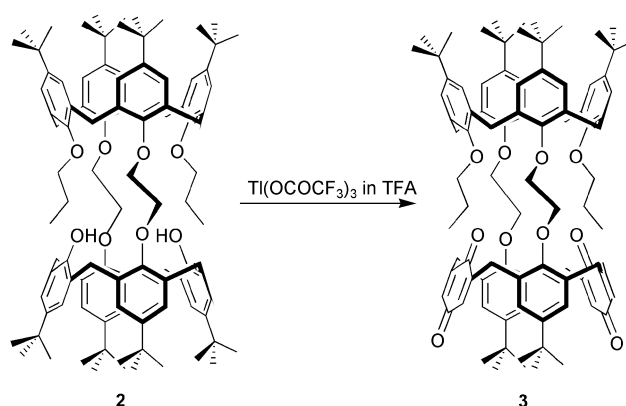
Scheme 1 Synthesis of the diquinone receptor.

spectrum of 3 (Fig. 2) suggests both calix[4]arene moieties in the molecule adopt pinched cone conformations. Variable temperature ^{1}H NMR investigations of 3 in CD_2Cl_2 between 288 K and 193 K revealed the spectrum barely changed which suggests the calix[4]arene units of the diquinone ligand maintain their cone conformations over this temperature range. This observation contrasts the VT ^{1}H NMR studies of simple lower rim disubstituted calix[4]diquinone ligands where at low temperatures cone and partial cone conformers were detected.[2e,5] This was ascribed to the quinone moieties being able to freely rotate through the calixarene cavity at room temperature whilst at low temperatures this mobility is slowed on the NMR timescale and the quinones adopt fixed cone and partial cone conformations.
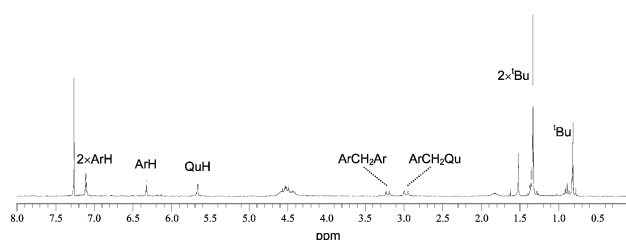

**Fig. 2** The ^{1}H NMR spectrum of 3 at 291 K (300 MHz, $CDCl_3$).

X-Ray structural investigation of 3

Crystals of 3 suitable for X-ray structural analysis were grown by layering a dichloromethane solution of the ligand with methanol. The structure (Fig. 3) reveals that the two calixarene units adopt pinched cone conformations, a fact that is in contrast to the semitube precursor which displayed one pinched cone and one regular cone conformation in the solid state. The aryl units in the quinone-containing calixarene are highly

Table 1 Stability constants and kinetic data[a] for **3** with Group 1 and ammonium cations

		Na^{+}	K^{+}	Rb^{+}	Cs^{+}	NH$_4$[+]
1 : 1 CH$_2$Cl$_2$: CH$_3$CN	$t_{1/2}$/s	150	90	>3600	[b]	>3600
	log K	2.9	>6	[c]	[b]	[c]
1 : 1 CH$_2$Cl$_2$: MeOH	$t_{1/2}$/s	[b]	465	[b]	[b]	[c]
	log K	[b]	4.7	[b]	[b]	[c]
9 : 1 CH$_2$Cl$_2$: DMSO	$t_{1/2}$/s	[b]	250	[d]	[b]	[c]
	log K	[b]	4.3	[d]	[b]	[c]
4 : 1 CHCl$_3$: DMSO	$t_{1/2}$/s	[c]	325	[c]	[c]	[c]
	log K	[c]	3.6	[c]	[c]	[c]

[a] At 291 K. The alkali metal cations were added as their perchlorate or hexafluorophosphate salts. [b] No change observed in spectrum .[c] Not assessed. [d] Very small change observed in spectrum over 90 minutes with 5 equivalents of cation.
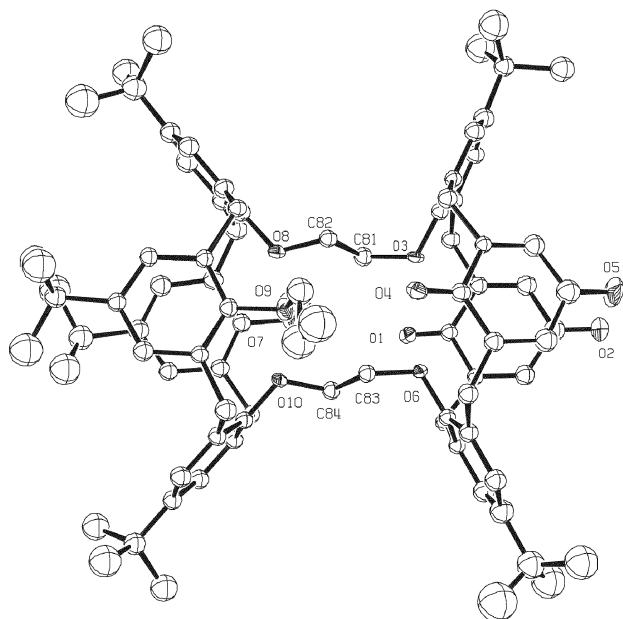
Fig. 3 Crystal structure of **3** in **3**·4CH$_2$Cl$_2$ with ellipsoids at 40% probability. The dichloromethane molecules are not shown.

flattened, the angle between their planes being 125.0°. The quinone-derivatised rings adopt an uncommon conformation with the upper rim oxygens being closer to each other than the lower rim oxygens (O(2) ⋯ O(5) = 3.39 Å, O(1) ⋯ O(4) = 6.25 Å) with the angle between their planes being 26.8°.

In the other calixarene moiety, the aryl groups bearing the propyl chains are near parallel, their planes being offset by 3.5° while the other two aryl rings are flattened with an angle of 95.3° between them. This double pinched cone conformation of the calixarene units results in the cavity, defined by the eight central oxygen atoms, being asymmetric (O(7) ⋯ O(9) = 5.92 Å, O(8) ⋯ O(10) = 3.42 Å). The two ethylene linkers adopt *anti* conformations with torsion angles for O(3)–C(81)–C(82)–O(8) and O(6)–C(83)–C(84)–O(10) of 165.8° and 166.6°, respectively. Overall, the two calixarene units within the molecule are approximately parallel, there only being an angle of 1.9° between the planes created by their respective methylene bridges.

Alkali metal coordination studies

UV/Vis binding studies. UV/Vis titration experiments were undertaken by monitoring the perturbation of the n ⟶ π* electronic transition of the quinone moiety of **3** on addition of alkali metal cation guest. Preliminary titration results in a range of polar organic solvent mixtures revealed slow kinetics of alkali metal complexation. By monitoring the change in absorbance at 350 nm over time on the addition of one equivalent of alkali metal cation to 1 : 1 CH$_2$Cl$_2$: CH$_3$CN, 1 : 1 CH$_2$Cl$_2$: MeOH, 9 : 1 CH$_2$Cl$_2$: DMSO and 4 : 1 CHCl$_3$:

DMSO solvent mixtures of **3**, $t_{1/2}$ values, the time taken to reach 50% equilibrium conversion were calculated. Stability constant values for 1 : 1 complexes were determined subsequently using the SPECFIT program[6] by leaving the solutions to equilibrate for a time corresponding to five times the $t_{1/2}$ value (Table 1).

The most salient feature of the data in Table 1 is that ligand **3** does indeed display high K^{+} selectivity and also slow kinetics of complexation. In the weakly competitive solvent mixture 1 : 1 CH$_2$Cl$_2$: CH$_3$CN, **3** shows uptake of Na^{+}, K^{+}, Rb^{+} and NH$_4$[+] cations, but not Cs^{+} which is presumably too large for the cavity. K^{+} is taken up at a slightly faster rate than Na^{+} but both exhibit very rapid kinetics in comparison to Rb^{+} and NH$_4$[+] cations; in fact, the values of $t_{1/2}$ quoted for these two cations are lower limits as the spectra were still changing at the end of the predetermined time period for the experiment. The reason for such slow uptake of Rb^{+} may be due to its slightly larger diameter compared to K^{+} resulting in a higher energy barrier for entry into the cavity. The slow kinetics of NH$_4$[+], on the other hand, may be a consequence of hydrogen bonding effects between the cation and quinone oxygen atoms. In 1 : 1 CH$_2$Cl$_2$: MeOH, there was no evidence for metal cation uptake of either Na^{+}, Rb^{+} or Cs^{+}, even after the addition of five equivalents of cation and the solution being left for 1 hour. This implies that binding is either exceptionally slow, very weak and slow, or it does not occur. Potassium cation addition did produce large changes in the spectrum but $t_{1/2}$ was quite long being almost 8 minutes.

In 9 : 1 CH$_2$Cl$_2$: DMSO, only K^{+} was unequivocally being complexed amongst the Group 1 cations (there was no change with five equivalents of Na^{+} or Cs^{+} over 90 minutes and only a very small change with Rb^{+}). Group 2 (Ca^{2+}, Sr^{2+}, Ba^{2+}) binding was also examined in 9 : 1 CH$_2$Cl$_2$: DMSO, however, interestingly no change was observed in any of the spectra even after 45 minutes in the presence of five equivalents of cation. Stronger solvation of these cations may be responsible for either extremely slow kinetics of complexation or no binding at all in this solvent mixture.

As regards stability constant data, K^{+} forms a very stable complex with **3** in 1 : 1 CH$_2$Cl$_2$: CH$_3$CN. Sodium, on the other hand, only binds weakly to the receptor, indicating a poor fit of the cation within the cavity. Interestingly, Rb^{+} and NH$_4$[+] do form fairly strong complexes with **3** in this solvent mixture (determined by ^{1}H NMR, see next section) despite having very slow kinetics of complexation and this probably reflects their reasonably good size match with the cavity of **3**. In other solvent mixtures used, K^{+} still formed a moderately strong complex even in 4 : 1 CHCl$_3$: DMSO, however, none of the other cations tested showed any conclusive evidence for complexation. It is noteworthy that the stability constant magnitudes are in accordance with the relative competitiveness of the solvent mixtures used for cation and cavity, the least competitive 1 : 1 CH$_2$Cl$_2$: CH$_3$CN giving the highest log K value and the most competitive 4 : 1 CHCl$_3$: DMSO giving the lowest log K value.

¹H NMR binding studies. In order to further investigate the complexation process of **3** with Group 1 cations, ¹H NMR spectroscopy was used. The complexation of Na⁺ and K⁺ cations by **3** was investigated in 1 : 1 CDCl₃ : CD₃CN. Both complexation reactions displayed slow kinetics of uptake, reaching equilibrium in ≤15 minutes, with the addition of one equivalent of Na⁺ and K⁺ cations giving percentage complexes with **3** of 10 and 100%, respectively. The addition of a further four equivalents of Na⁺ cation resulted in a 40% complex of **3**. These results are in agreement with those found in the UV/Vis studies conducted in 1 : 1 CH₂Cl₂ : CH₃CN.

The very slow complexation of NH₄⁺ and Rb⁺ by **3** in 1 : 1 CH₂Cl₂ : CH₃CN, as observed in UV/Vis experiments, was also investigated by ¹H NMR. In each case, one mole equivalent of the respective cation was added to a separate NMR tube containing a 7×10^{-4} M solution of **3** in 1 : 1 CD₂Cl₂ : CD₃CN and the spectrum recorded at intervals over the course of 7 days. The percentage complex formation *versus* time for each is displayed in Fig. 4.
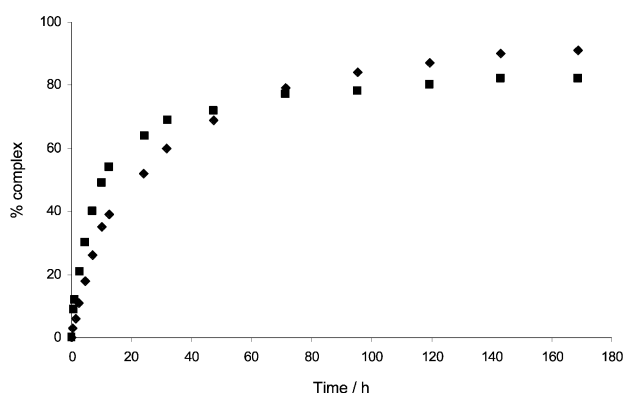
Fig. 4 Complexation profiles of **3** with Rb⁺ (◆) and NH₄⁺ (■) cations in 1 : 1 CD₂Cl₂ : CD₃CN.

The values of $t_{1/2}$ for NH₄⁺ and Rb⁺, interpolated from the graph in Fig. 4, are 2.6×10^4 and 6.3×10^4 seconds, respectively, indicating extremely slow cation uptake of these cations by **3**. Equilibrium is estimated to be reached in around 150 hours for NH₄⁺ and between 160–200 hours for Rb⁺. It should be noted however that the values determined for $t_{1/2}$ by this method are not comparable with those from UV/Vis due to different concentrations being used.

Fig. 5 shows the changes in the ¹H NMR spectrum of **3** at 0, 4.6, 10, 47.3 and 169 hours after the initial addition of Rb⁺ cations. The new resonances formed are entirely consistent with the cation being bound inside the cavity, in particular, the four
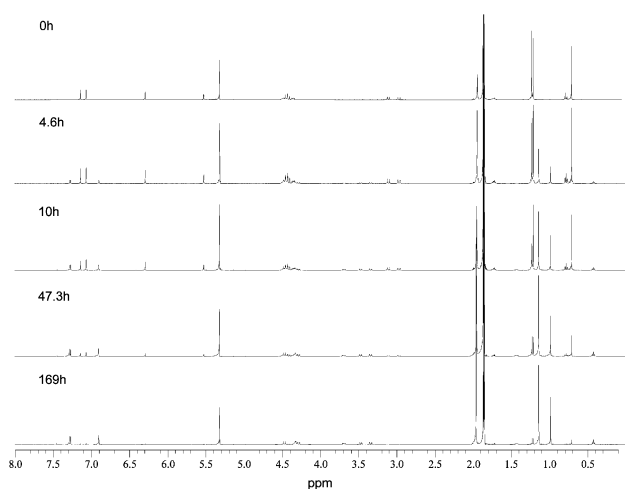
Fig. 5 ¹H NMR spectra of **3**, free and in the presence of one equivalent of Rb⁺ cations after various times in 1 : 1 CD₂Cl₂ : CD₃CN.

Table 2 Percentage complex formation and equilibrium times[a] from ¹H NMR for **3** with Group 1 cations

Cation	1 : 1 CDCl₃ : CD₃OD		4 : 1 CDCl₃ : DMSO-d₆[b]	
	% Complex	t_{eq}/h	% Complex	t_{eq}/h
Na⁺	6[b]	[e]	0	–
K⁺	80[c]	0.6	40	0.5
Rb⁺	13[b]	70	2	[e]
Cs⁺	[d]	[d]	0	–

[a] Cations added as their perchlorate or hexafluorophosphate salts. [b] 5 equivalents cation added. [c] 1 equivalent cation added. [d] Not determined. [e] Uncertain.

ArH and quinone (QuH) protons are all shifted upon complexation indicating cation binding with both calixarene units. The positioning of these new ArH and QuH resonances implies that the complex adopts a double regular cone conformation for the calixarene units as opposed to a double pinched cone in the free ligand. The spectrum of **3**·NH₄⁺ is essentially the same as that of the **3**·Rb⁺ complex. From the relative integrations of the *tert*-butyl resonances in the equilibrated mixtures of **3** with NH₄⁺ and Rb⁺, stability constants of 3×10^4 and 2×10^5 M⁻¹, respectively, have been estimated.

As the results from UV/Vis were not entirely conclusive about uptake of some of the cations in the more competitive solvent mixtures, these systems were also examined by ¹H NMR. Experiments were set up in which a specific number of equivalents of Group 1 cation were added to separate NMR tubes containing **3** in 1 : 1 CDCl₃ : CD₃OD and 4 : 1 CDCl₃ : DMSO-d₆. Complex formation for each was followed at regular intervals. The results, including approximate equilibrium times, are summarised in Table 2.

Contrasting the ¹H NMR results in 1 : 1 CDCl₃ : CD₃OD with those from UV/Vis in 1 : 1 CH₂Cl₂ : CH₃OH (CDCl₃ was used in NMR because **3** was of insufficient solubility in 1 : 1 CD₂Cl₂ : CD₃OD), a good agreement can be seen after noting that K⁺ forms a strong complex with only one equivalent of cation whereas Na⁺ and Rb⁺ require five equivalents of cation just to form very weak complexes. In addition, for Rb⁺ at least, equilibrium is not attained for several days. In 4 : 1 CDCl₃ : DMSO-d₆, Rb⁺ evidently forms a very weak complex with **3** however, again, equilibration was slow. In comparison, K⁺ formed a moderately strong complex in around 30 minutes.

In summary, taking into account both the UV/Vis and ¹H NMR results, ligand **3** displays a very high kinetic selectivity for K⁺ over the other Group 1 cations (except Na⁺ in 1 : 1 CH₂Cl₂ : CH₃CN) and NH₄⁺ cation in both weakly and strongly competitive solvent mixtures. The thermodynamic stability of **3**·K⁺ is much greater than that of **3**·Na⁺ in all of the solvent mixtures used, and **3**·K⁺ has been found to be much more stable than all of the other Group 1 cation complexes in the more polar systems of 1 : 1 CHCl₃ : CH₃OH and 4 : 1 CHCl₃ : DMSO. The complexation of Ca²⁺, Sr²⁺ and Ba²⁺ cations by **3** was not seen to occur in 9 : 1 CH₂Cl₂ : DMSO even after exposure to five equivalents of cation for 45 minutes.

Electrochemical studies

There have been several studies on the redox properties of calixquinones[2e,5] and their recognition of cations[7] and anions.[8] Calix[4]diquinones can in theory accept a total of four electrons to become a tetraanion. For such species, three redox processes are generally observed in their cyclic (CV) and square wave (SWV) voltammograms. The first two couples occur at similar potential and are assigned to one-electron transfers to each of the quinone units, giving semiquinone species. The precise potential of these two couples depends on the donor ability of the appended group on the aromatic rings while their difference in potential reflects the interaction energy between the two

added electrons in the diametrical quinone rings. This interaction energy strongly depends on the conformational properties of the ligand in solution. The third more negative wave is believed to be due to the third and fourth electron transfers. Casnati and co-workers suggested that the irreversibility of this wave could be due to the formation of insoluble hydroquinone species.[5] The electrochemical properties of **3** were investigated using both cyclic and square wave voltammetric techniques. Fig. 6 shows the CVs of **3** in 1 : 1 CH_2Cl_2 : CH_3CN at various scan rates. The voltammograms indicate that the electrochemical characteristics of **3** are analogous to those just described for a simple calix[4]diquinone. The occurrence of wave 3″ has been previously attributed to incompletely protonated quinone dianion species.[7c]
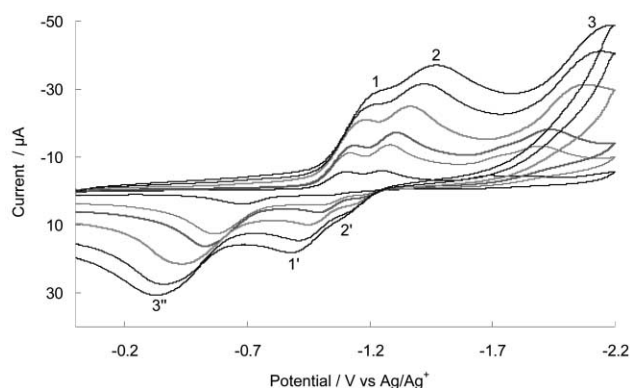
Fig. 6 The CVs of **3** at various scan rates (in order of increasing amplitude of current: 20, 50, 100, 200, 400, 600 mV s^{-1}) in 1 : 1 CH_2Cl_2 : CH_3CN.

Electrochemical recognition experiments were conducted between **3** and Na$^+$ and K$^+$ cations. In each case, voltammograms were only recorded after the respective **3**/cation system had been left to equilibrate for around 10 minutes. The addition of KSCN to an electrochemical solution of **3** resulted in the appearance of anodically shifted waves. With 0.5 equivalent of K$^+$ cations, the original couples 1/1′ and 2/2′ decreased in intensity and two new reversible couples 4/4′ and 5/5′ replacing them emerged such that the heights of the two sets of couples were approximately equal. The addition of a further 0.5 equivalents of K$^+$ cations resulted in the disappearance of the original waves and the maximisation of the new waves (Fig. 7). The original irreversible wave 3 also disappeared giving another anodically shifted wave 6.

The addition of NaClO$_4$ to an electrochemical solution of **3** also resulted in the emergence of new anodically shifted waves. However, unlike for K$^+$, the original wave couples 1/1′ and 2/2′ did not disappear, even in the presence of five equivalents of Na$^+$. In fact, with this amount of cation, the two original and two new wave couples were of approximate equal height. This voltammetric behaviour may reflect the weak binding properties of Na$^+$ by **3**, as seen in the UV/Vis experiments. As expected, however, Na$^+$ produced a larger anodic shift of the new waves due to its larger charge to radius ratio. A summary of the voltammetric properties of **3** with Na$^+$ and K$^+$ cations is displayed in Table 3.

Conclusion

Modification of the established calix[4]semitube design through oxidation of its free phenol rings has yielded a quinone-derivatised, redox-active ionophore. UV/Vis titrations and ^{1}H NMR experiments in solvent mixtures of varying polarity revealed that this receptor displays a remarkable selectivity preference for potassium cation amongst Group 1 and ammonium cations thus mirroring the properties of the parent semitube **2**.[3c] The kinetics of cation uptake of **3** were relatively slow

Table 3 The voltammetric properties^a of receptor **3** in 4 : 1 CH_2Cl_2 : CH_3CN

$E_{1/2}$ (1/1′)/ V	−1.05
$E_{1/2}$ (2/2′)/ V	−1.21
E_{pc} (3/3′)/ V	−1.94
ΔE (Na$^+$)/ mV^b	420
	270
ΔE (K$^+$)/ mV^b	340
	170

^{a} 0.1 M TBABF$_4$ (Bu$_4$NBF$_4$) was added as the supporting electrolyte. The receptor concentration was approximately 1×10^{-3} M. $E_{1/2}$ values are the averages of the cathodic and anodic peak potentials of the described couple referenced to an Ag/Ag$^+$ electrode at 298 K. E_{pc} is the cathodic peak potential of wave 3, which is irreversible. ^{b} Anodic shifts of the new couples 4/4′ and 5/5′ relative to the couple 1/1′. Voltammograms of **3** in the presence of cations were recorded around 10 minutes after the cation addition.
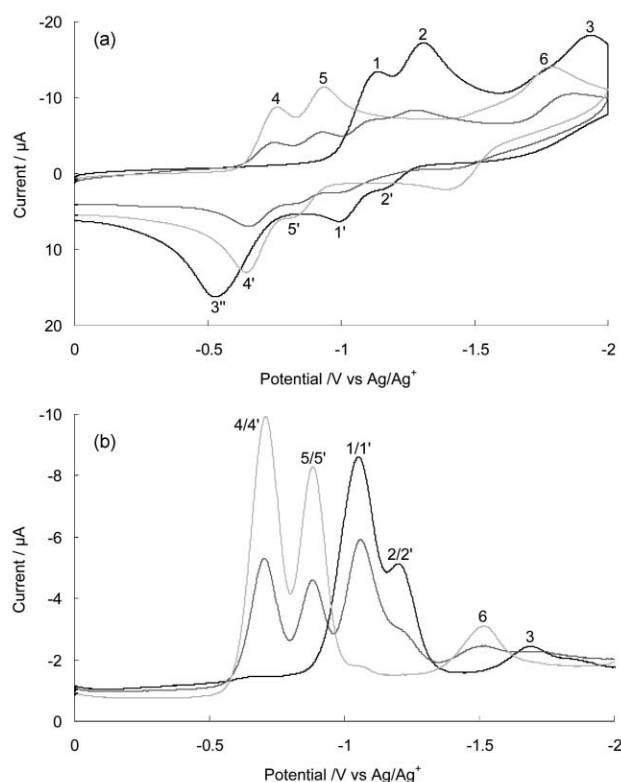
Fig. 7 The CVs (100 mV s^{-1}) (top) and SWVs (5 Hz) (bottom) of **3**, free (black line) and in the presence of 0.5 equiv. K$^+$ cations (grey line) and 1.0 equiv. K$^+$ cations (pale grey line) in 4 : 1 CH_2Cl_2 : CH_3CN.

compared to **2**, however equilibrium was attained generally at a faster rate with potassium cation than with the other Group 1 cations. This redox-active receptor exhibits substantial electrochemical recognition effects towards sodium and potassium cations.

Experimental

General

All chemicals were commercial grade and used without further purification unless otherwise stated. Solvents were predried, purified by distillation and stored under nitrogen where appropriate.

Nuclear magnetic resonance spectra were recorded using either a 300 MHz Varian VXWorks spectrometer or a 500 MHz Varian Unity spectrometer. Electrospray mass spectra were recorded using Micromass LCT equipment. Microanalyses were obtained on an elementar vario EL and were performed by the Inorganic Chemistry Laboratory, University of Oxford.[9]

Electrochemical measurements were carried out using an EG&G Princeton Applied Research 273 potentiostat/galvanostat. All reported voltammograms were recorded on the first potential sweep. The electrochemical cell was an unsealed one compartment cell with a glassy carbon working electrode, an Ag/Ag$^+$ reference electrode (0.33 V ± 10 mV vs. SCE) and a Pt wire coil counter electrode. The reference contained an internal solution of 0.01 M AgNO$_3$ and 0.1 M TBABF$_4$ in acetonitrile and was incorporated with a salt bridge containing 0.1 M TBABF$_4$ in the respective solvent. All electrochemical solutions were degassed with argon and maintained under an argon atmosphere for the duration of the experiment. Kemet diamond sprays (1 μm and 0.25 μm) were used to polish the working electrode. UV/Vis spectra were obtained using a PC-controlled Perkin-Elmer Lambda 6 spectrometer. *tert*-Butyl ethylsemitube **2** was prepared according to a previously described method.[3c]

Crystal structure determination of 3

Single crystals of compound **3** were obtained by layering a dichloromethane solution of the ligand with methanol. A suitable crystal was mounted using perfluoropolyether oil and cooled to 150 K in a stream of N$_2$. Intensity data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K$_a$ radiation (λ = 0.71037 Å). Due to the poor quality of the crystal, it was not possible to measure meaningful data with θ > 23.2°. As a result there were insufficient independent observed data to permit refinement of anisotropic thermal parameters of any C atoms.

Crystal data. C$_{94}$H$_{116}$Cl$_8$O$_{10}$, M = 1689.58, triclinic, a = 14.2466(3), b = 17.7148(4), c = 19.4627(5) Å, a = 104.454(1)°, β = 93.398(1)°, γ = 105.952(1)°, U = 4529.9 Å^3, T = 150 K, space group $P\bar{1}$, Z = 2, μ(Mo-K$_a$) = 0.305 mm^{-1}, 36466 reflections measured, 12811 unique (R_{int} = 0.087) which were used in all calculations. The final $wR(F)$ was 0.1395 (observed data with I>3σ).

CCDC reference number 214710.

See http://www.rsc.org/suppdata/dt/b3/b307419f/ for crystallographic data in CIF or other electronic format.

Syntheses

***tert*-Butyl ethylsemitubediquinone 3.** *tert*-Butyl ethylsemitube (0.6 g, 0.42 mmol) was stirred in Tl(OCOCF$_3$)$_3$/TFA (trifluoroacetic acid) solution (2.9 ml, 2.5 mmol) for 2 hours in the dark. Approximately 75% of the TFA was removed *in vacuo* and the remainder poured into iced water (70 ml). The product was extracted with CHCl$_3$ (2 × 75 ml) and the combined organic extracts washed with water (200 ml). After drying the organic layer (MgSO$_4$), the solvent was removed *in vacuo*. Pure **3** was isolated by recrystallisation of the residue from CHCl$_3$/MeOH *via* slow evaporation as bright orange needles (0.30 g, 53%) (Found: C, 76.20; H, 8.05%. C$_{90}$H$_{108}$O$_{10}$· 2/3(CHCl$_3$) requires C, 76.18; H, 7.66%); δ_H(300 MHz, CDCl$_3$) 0.82 (18H, s, (CH_3)$_3$C), 0.90 (6H, t, ^3J = 7.5 Hz, OCH$_2$-CH$_2$CH_3), 1.34 (18H, s, (CH_3)$_3$C), 1.34 (18H, s, (CH_3)$_3$C), 1.84 (4H, m, OCH$_2$CH_2CH$_3$), 2.98 (4H, d, ^2J = 15.3 Hz, ArCH_2Qu), 3.21 (4H, d, ^2J = 12.9 Hz, ArCH_2Ar), 4.44 (4H, t, ^3J = 7.8 Hz, OCH_2CH$_2$CH$_3$), 4.52 (4H, d, ^2J = 12.9 Hz, ArCH_2Ar), 4.55 (4H, d, ^2J = 14.7 Hz, ArCH_2Qu), 4.55 (4H, t, ^3J = 8.0 Hz, ROCH_2CH$_2$OR′), 4.59 (4H, t, ^3J = 8.0 Hz, ROCH$_2$CH_2OR′), 5.67 (4H, s, QuH), 6.33 (4H, s, ArH), 7.11 (4H, s, ArH), 7.12 (4H, s, ArH); δ_C(75 MHz, CDCl$_3$) 10.15 (OCH$_2$CH$_2$$CH_3$),

22.29 (OC$H_2$$CH_2CH_3$), 29.65 (ArC$H_2$Qu), 31.18, 31.57 and 31.67 ((CH_3)$_3$C), 32.03 (ArCH_2Ar), 33.57, 34.02 and 34.33 ((CH$_3$)$_3$$C$), 71.46, 73.73 and 77.20 (ROCH$_2$CH$_2$OR′, ROCH$_2$-CH$_2$OR′ and OCH$_2$CH$_2$CH$_3$), 123.80, 125.79, 126.54, 131.34, 132.54, 134.56, 135.29, 143.65, 144.81, 146.82, 151.00, 153.12, 154.69 and 155.74 (Ar, Qu), 185.27, (C=O), 187.20 (C=O); MS (ES): *m/z* 1373 (M + Na$^+$), 1389 (M + K$^+$).

Determination of stability constants and kinetics of cation uptake

In UV/Vis studies, $t_{1/2}$ values (the time taken to reach 50% equilibrium conversion) were assessed through adding 1 mole equivalent of cation to the receptor and then recording the spectrum of absorbance *versus* time. Equilibrium was assumed to have been reached when the absorbance reading had become constant. Stability constants were determined by titration experiments. After each cation addition, solutions were left to equilibrate for a time corresponding to five times the $t_{1/2}$ value of that system. A minimum of 15 data points were recorded for each titration. Stability constant values were calculated using the SPECFIT program.

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