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ORIGINAL ARTICLE

Synthesis of novel chromogenic azocalix[4]arenemonoquinones and their binding with alkali metal cations

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Abstract Five new chromogenic azocalix[4]arenemonoquinones have been synthesized, characterized and examined for their interaction with alkali metal cations (Li^+, Na^+, K^+, Rb^+ and Cs^+) by UV-visible spectroscopic and cyclic voltammetric techniques. It has been determined that **4a** selectively exhibits a significant bathochromic shift in its UV-visible spectrum on interaction with potassium ion in comparison to its treatment with other alkali metal cations. The binding stoichiometry of **4a** and potassium ion was established to be 1:1 with an association constant of 3.27×10^4 M^{-1}. Cyclic voltammetric experiments in 4:1 dichloromethane-acetonitrile also revealed a significant anodic shift ($\Delta E_{(1/1')} = 115$ mV) of the original redox waves of **4a** on interaction with potassium ion.

Keywords Chromogenic · Azocalix[4]arenemonoquinones · Alkali cation · Cyclic voltammetry

Introduction

The design and synthesis of abiotic host molecules for recognition of ionic and molecular species constitute important research objectives to resolve complex chemical, biological and environmental issues [1]. In this context, phenolic macrocycles represented by calix[*n*]arenes [2] occupy a special position due to their unique molecular architecture which can be suitably tailored into potential receptors by facile derivatization [3, 4]. For example, reverse Friedel-Crafts reaction of parent *p*-tert-butylcalix[4]arene with a mixture of aluminium chloride and phenol in toluene would yield a well laid out polyphenolic oligomer which on oxidation would give rise to electroactive calixquinones [5, 6] arranged in a cyclic array of *p*-quinone and aromatic units around the methylene bridges. Such molecules presumably would provide significant redox responses to ionic and molecular stimuli for various applications [7–9]. Though Beer et al. [10, 11] have reported the synthesis and electrochemical characteristics of various calix[4]quinones possessing ether, ester and amide functionalities, no work seems to have been published on calix[4]arenequinones possessing additional chromogens that can provide unique opto-electrochemical sensing properties for ionic and molecular recognition [12–14]. Accordingly, we describe herein the synthesis, characterization and evaluation of a series of chromogenic azocalix[4]arenemonoquinones in the hope to obtain new ionic filters and sensor materials for alkali metal ion recognition.

Results and discussion

Synthesis and characterization

The protocol adopted for the synthesis of new azocalix[4]arenemonoquinones (**4a–e**) is depicted in Scheme 1. The parent calix[4]arene **1** was synthesized by the method described by Gutsche et al. [15] while 1,3-disubstituted calix[4]arene derivatives **2a–e** in cone conformation were synthesized by the methods reported previously [16–20]. Oxidation of calix[4]arenes **2a–e** to calix[4]arenediquinones **3a–e** in 47–61% yields could be easily achieved by reaction with chlorine dioxide (ClO_2) in the presence of

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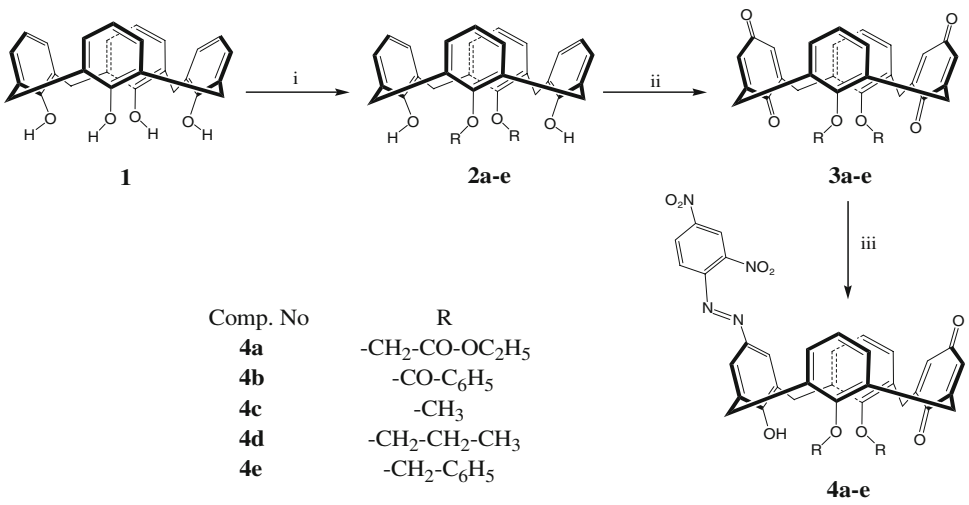

Comp. No	R
4a	$-CH_2-CO-OC_2H_5$
4b	$-CO-C_6H_5$
4c	$-CH_3$
4d	$-CH_2-CH_2-CH_3$
4e	$-CH_2-C_6H_5$

Scheme 1 (i) K_2CO_3/Na_2CO_3, RX (X = Cl, Br or I), CH_3CN, reflux; (ii) ClO_2, Phosphate Buffer (pH = 7), $(CH_3)_2CO$, r.t.; (iii) 2,4-dinitrophenylhydrazine, CH_3CH_2OH, Conc.H_2SO_4, $CHCl_3$, (−5 to −10° C)

concentrated phosphate-buffer in acetone. **3a–e** on treatment with 2,4-dinitrophenylhydrazine in a mixture of chloroform:ethanol (2:1) and concentrated H_2SO_4 at −5 to −10° C, gave 2,4-dinitrophenylazo-calix[4]arenemonoquinones (**4a–e**) in moderate yields (50–60%) as described in the experimental section.

Precursor calix[4]arenediquinones (**3a–e**) could be easily characterized by ^{1}H NMR, FT-IR and ES-mass spectrometric analysis. For example, proton NMR spectra of **3a–e** in $CDCl_3$ showed a broad singlet for the quinone protons between 6.24 and 6.60 ppm while aromatic protons belonging to calix[4]arene units appeared as multiplets at 6.53–7.16 ppm. The appearance of AB type doublets for Ar-CH_2-Q protons of **3a–e** between 3.06 and 4.01 ppm suggested their symmetrical cone conformation. The presence of quinonoid groups in **3a–e** was further confirmed by the appearance of a strong absorption band at around 1654–1657 cm^{-1} for quinone stretching frequencies while **3a** and **3b** exhibited another absorption band between 1730 and 1760 cm^{-1} for the ester carbonyl groups in their FT-IR spectra.

The synthesized novel calix[4]arenemonoquinones (**4a–e**) bearing a 2,4-dinitrophenylazo unit were analyzed by a combination of ^{1}H NMR, FT-IR, UV-visible spectroscopic techniques and elemental analysis. The ^{1}H NMR spectrum of **4a** exhibited a D_2O exchangeable downfield signal at 9.49 ppm which could be assigned to the phenolic proton while the signals appearing at 8.79 (s), 8.43 (d) and 7.77 (d) ppm could be attributed to the aromatic protons of dinitrophenylazo unit present at the upper rim of **4a** (Fig. 1). The calix[4]arene ring bearing the azo group exhibited a singlet at 7.76 ppm while the unsubstituted calix[4]arene phenyl rings in **4a** gave a doublet and a triplet at 6.96 and 6.79 ppm, respectively, that could be ascribed to their aromatic protons. A singlet appearing at 6.61 ppm in the aromatic region of **4a** could be ascribed to quinone protons. Compound **4a** exhibited two pairs of doublets (1:1:1:1) at 4.29, 4.21, 3.30 and 3.22 ppm for the methylene bridge protons in its ^{1}H NMR spectrum which indicated that the compound might either be in a cone or in a partial cone conformation. Analysis of the ^{13}C NMR spectrum of **4a** revealed two distinct signals at 31.2 and 30.6 ppm for the methylene carbons which indicated its pinched cone conformation [21].

In the FT-IR spectra, the azocalix[4]arenemonoquinones (**4a–e**) exhibited strong absorptions at 3378–3502 cm^{-1} (–OH), 1585–1601 cm^{-1} (–N = N–), 1534–1540 cm^{-1} ($–NO_2$) and at 1654–1660 cm^{-1} (quinone groups). **4a** and **4b** also exhibited strong absorptions at 1759 and 1735 cm^{-1} in their IR spectra which could be attributed to the ester carbonyl stretching frequencies. Similarly, other azocalix[4]arenemonoquinones (**4b–4e**) could be characterized from their proton NMR splitting pattern, FT-IR and UV-visible spectroscopic data as summarized in Table 1.

Analysis of solvatochromism in azocalix[4]arenemonoquinones by UV-visible spectroscopy

A typical absorption spectrum of azocalix[4]arenemonoquinones (**4a–e**) exhibited strong $\pi-\pi^*$ electronic transitions at around 400–440 nm. The UV-visible spectrum of **4a** when recorded in different solvents (e.g. dimethyl sulphoxide, acetonitrile, chloroform, methanol and acetic acid) at approximate 10^{-5} M concentration (Fig. 2) revealed a significant change in the λ_{max} in comparison to its absorption spectrum recorded in chloroform. For instance, **4a** exhibited a λ_{max} at 415 nm in chloroform, 409 nm in acetic acid, 417 nm in acetonitrile, 420 nm in methanol and 438 nm in DMSO (Table 2).

From Fig. 2, it appears that proton accepting solvents (e.g., dimethyl sulphoxide, acetonitrile and methanol)

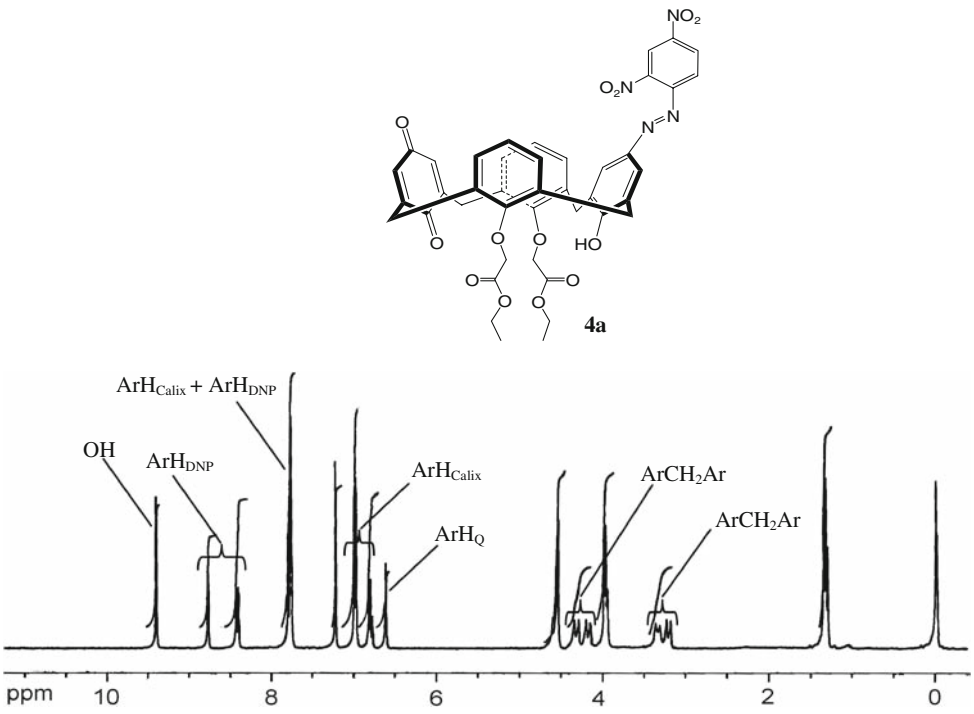

Fig. 1 Molecular structure and ^{1}H NMR spectra of 2,4-dinitrophenylazo calix[4]arenemonoquinone **4a**

Table 1 ^{1}H NMR splitting (300 MHz, 25° C), FT-IR stretching frequency (>C=O) of quinonoid ring and the UV-visible data of azocalix[4]arenemonoquinones **4a-e**

Comp. No.	^{1}H NMR values (δ) and splitting patterns (300 MHz, 25°C)				IR $\nu_{c=o}$ (cm^{-1}) quinone	UV (λ_{max}) (nm)
	Phenolic –OH	Calixarene protons attached to azo group	Quinone protons (2H)	Methylene bridge protons (8 H) Ar–CH_2–Q		
4a	9.49 (s)	7.76 (m, 3H)	6.61 (s)	4.29 (d), 4.21 (d), 3.30 (d), 3.22 (d)	1657	422
4b	9.41 (s)	7.81–7.77 (m, 5H)	6.37 (s)	4.18 (d), 3.50 (d), 3.39 (d)	1654	420
4c	9.21 (s)	7.76–7.71 (m, 3H)	6.44 (s)	4.26 (d), 4.16 (d), 3.38 (d), 3.30 (d)	1656	421
4d	9.31 (s)	7.78–7.72 (m, 3H)	6.47 (s)	4.39 (d), 4.31 (d), 3.28 (d), 3.20 (d)	1655	422
4e	9.27 (s)	7.70 (s. 2H)	6.46 (s)	4.15 (d), 4.09 (d), 3.11 (d)	1660	419

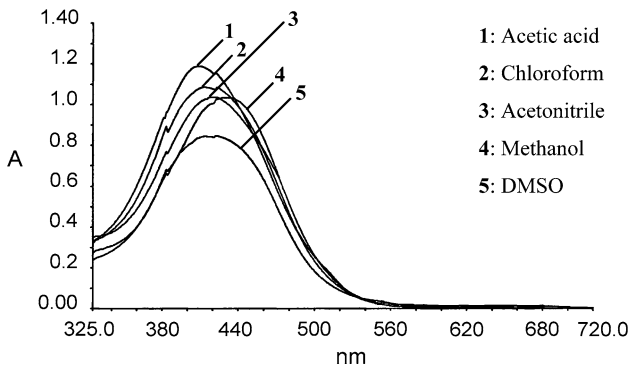

Fig. 2 Absorption spectra of azocalix[4]arenemonoquinone **4a** in various solvents

Table 2 Influence of solvent on λ_{max} (nm) of azocalix[4]arenemonoquinone **4a**

Solvent	λ_{max} of **4a** (in nm)	
	Concentrated ($\sim 10^{-1}$ M)	Diluted ($\sim 10^{-5}$ M)
Chloroform	414	415
Methanol	420	420
Acetonitrile	418	417
Dimethyl sulphoxide (DMSO)	436	438
Acetic acid	408	409

allow **4a** to display a red shift in its λ_{max} while proton donating solvents (e.g., acetic acid) cause a blue shift in the λ_{max} of **4a** in comparison to its absorption spectrum recorded in chloroform. Such changes in the absorption spectrum of **4a** with solvents of different polarities are in consonance with earlier observations [22, 23] but the change in absorption maximum was not in a linear

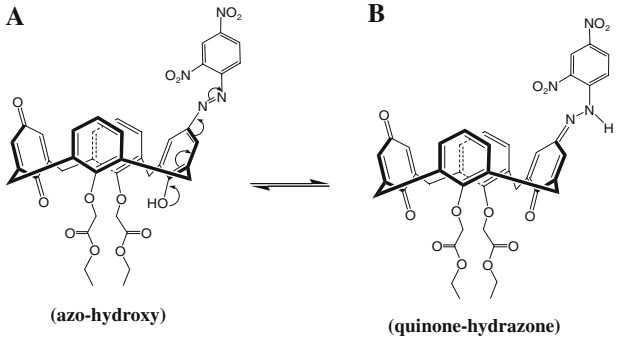

Fig. 3 The possible tautomeric forms of azocalix[4]arenemonoquinone **4a**

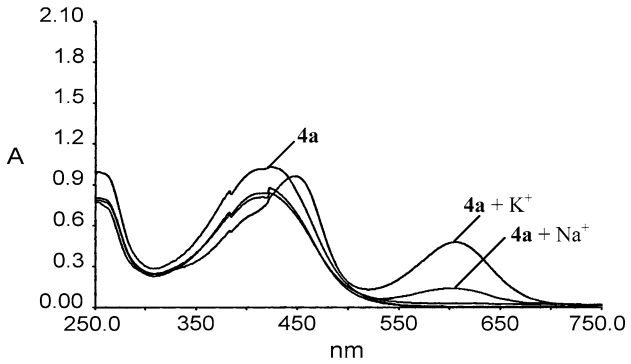

Fig. 4 UV-visible spectra of **4a** and shifts in its λ_{max} upon the addition of alkali metal cations

relationship with solvent polarity. The complexity of effect of polar and nonpolar solvents observed on the λ_{max} of **4a** could possibly be ascribed to an equilibrium between two tautometric forms of the azo group [24] present in the calix[4]arene derivative as shown in Fig. 3 in accordance with the observations reported by Kishimoto et al. [25]. This was confirmed by the fact that the equilibrium was markedly affected by the basicity or acidity of the solvent used. For example, **4a** showed a bathochromic shift (+23 nm) in basic dimethyl sulphoxide (pKa = −1.80) and a hypsochromic shift (−06 nm) in acetic acid (pKa = 4.76) when compared to its λ_{max} in chloroform.

The effect of concentration of the compound on the absorption maxima of **4a** when examined spectrophotometrically (Table 2) revealed no significant change in its λ_{max} with increase in the concentration of **4a** indicating that the azocalix[4]arene (**4a**) possibly exists in its tautomeric forms in all solvents used.

Binding characteristics of azocalix[4]arenemonoquinones **4a–e**

UV-visible studies

The synthesized azocalix[4]arenemonoquinones **4a–e** were examined for their interaction with alkali metal ions (Li^+, Na^+, K^+ as perchlorate salts and Rb^+ and Cs^+ as carbonate salts) by UV-visible spectroscopy using chloroform:methanol (1:1 v/v) as the solvent. When 10 μM solution of **4a** was treated with alkali metal cations, a significant bathochromic shift ($\Delta\lambda_{max}$) was observed in its absorption maxima. The absorption peak at 422 nm shifted bathochromically in the presence of Na^+ and K^+ ions with concurrent appearance of a new absorption band at 604 nm (with $\Delta\lambda_{max}$ of 182 nm) while addition of Li^+, Rb^+ and Cs^+ ions did not exhibit any significant shift in the absorption maximum of **4a** (Fig. 4).

Receptors **4b–e** did not exhibit any significant change in their absorption maxima when interacted with alkali metal cations (Li^+, Na^+, K^+, Rb^+ and Cs^+) under similar experimental conditions indicating that the functionality tethered to the lower rim of **4a–e** played an important role in the binding of alkali metal cations. In the case of **4a**, the carbonyl groups of ester units possibly provided the complementary binding sites [26] in addition to the preorganised calix[4]arene cavity which resulted in a significant binding affinity towards Na^+ and K^+ ions while **4b** with identical carbonyl functions could not induce a similar effect (Fig. 4). The difference in intensity of the new absorption band appearing at 604 nm on addition of sodium and potassium ions (Fig. 4) indicated that the interaction of K^+ ions with **4a** was more significant than that with Na^+ ions possibly due to appropriate cavity size for K^+ binding.

It was observed that addition of potassium ions to a 10^{-5} M solution of **4a** in a gradual manner led to a continuous decrease in the intensity of the absorption band centered at 422 nm while the intensity of **4a**/K^+ complex absorption band at 604 nm increased with each addition of potassium ion from 10^{-5} to 10^{-3} M solutions (Fig. 5). At concentration ratio of 100:1 (K^+: **4a**), the original absorption at 422 nm disappeared completely with the appearance of absorption at 604 nm with an isobestic point at 481 nm. The bathochromic shift observed in the absorption of **4a** on addition of potassium ion could possibly be ascribed to a change in dipole moment of the chromophore through possible charge transfer induced by potassium binding via lower rim oxygen atoms and ester carbonyl groups [27, 28].

Quantitative analysis of the binding characteristics of **4a** with potassium ions when determined by Job's continuous variation plots revealed a maximum absorbance at 0.5 mole fraction of ligand to indicate a 1:1 binding stoichiometry for the interaction between **4a** and potassium ions (Fig. 5b). A plot of measured absorbance $[1/(A - A_0)]$ at 604 nm versus $1/[K^+]$ revealed a linear relationship ($R = 0.99639$) which further indicated a 1:1 complex stoichiometry between **4a**

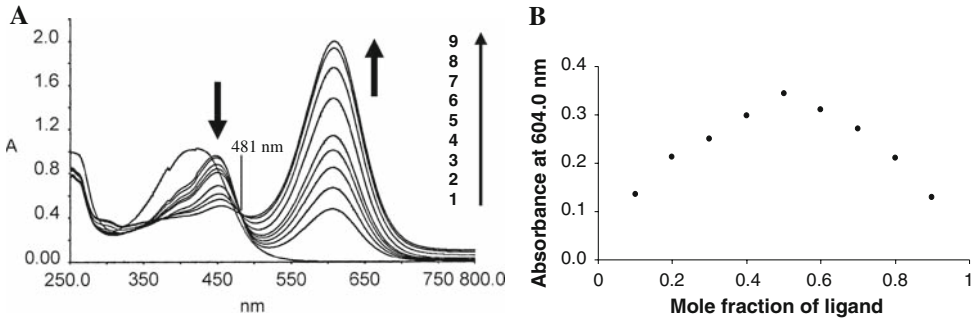

Fig. 5 (**a**) changes in the UV-visible spectra of **4a** (1×10^{-5} M) upon titration by potassium salt in methanol as a solvent where the concentration (M) of potassium salt (1) 1×10^{-5} (2) 3×10^{-5} (3) 5×10^{-5} (4) 7×10^{-5} (5) 9×10^{-5} (6) 2×10^{-4} (7) 5×10^{-4} (8) 7×10^{-4} (9) 1×10^{-3}; (**b**) Job's continuous variation plot indicating 1:1 complex stoichiometry between **4a** and K^+

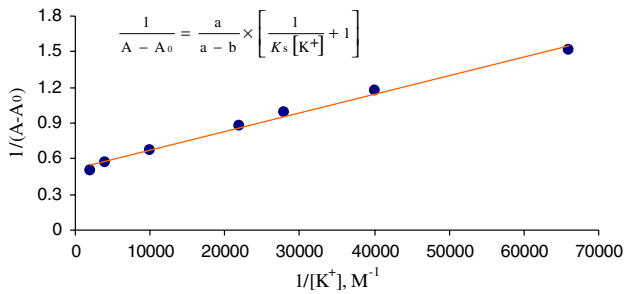

Fig. 6 Benesi-Hildebrand plot of **4a** with K^+

and K^+ ion (Fig. 6) [29]. The association constant (K_s) of **4a** in the presence of K^+ ion was determined from the UV-visible titration data in chloroform-methanol (Fig. 5a) as 3.27×10^4 M^{-1} (Fig. 6).

Electrochemical studies

The electrochemical behavior of the azocalix[4]arene-monoquinones **4a–e** was investigated by cyclic and squarewave voltammetry at glassy carbon electrode using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte in 4:1 dichloromethane:acetonitrile (CH_2Cl_2:CH_3CN). A solution of 1 mM concentration of **4a** when examined voltammetrically, gave two redox waves in the potential range of 0 to −2.0 V (Fig. 7) in consonance with the previous electrochemical studies on calix[4]arenemonoquinones [30]. Two cathodic waves observed at −1.117 V and −1.781 V could be assigned as 1/1′ and 2, respectively for one and two electron transfer processes in the quinone moiety [30]. A third wave (3) observed at a more positive potential of −0.751 V could be ascribed to the reduction of nitro substituents present in the 2,4-dinitrophenylazo unit. Likewise the receptors **4b–e** also showed a very similar electrochemical response and exhibited two redox waves in their voltammograms for quinone moiety as summarized in Table 3.

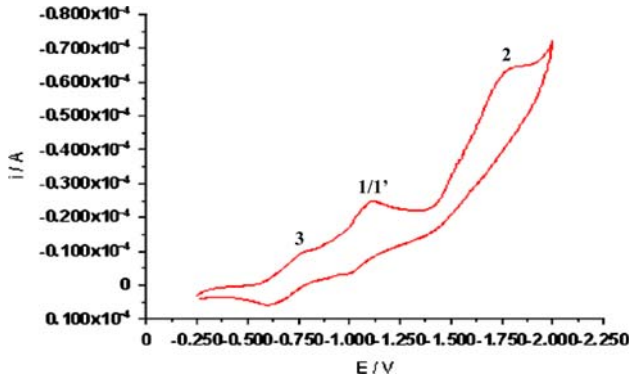

Fig. 7 Cyclic voltammogram of 0.001 M solution of receptor **4a** at scan rate 50 mVs^{-1} in 4:1 CH_2Cl_2:CH_3CN solvent system. Supporting electrolyte; 0.1 M $TBAPF_6$. All potentials are referenced to $Ag|Ag^+$ electrode

Table 3 Electrochemical data of the synthesized azocalix[4]arene-monoquinones **4a-e** at glassy carbon electrode[a]

Compound No.	Redox couple or wave			
	1/1′		2	
	i_{pc} (μA)[b]	$E_{1/2}$ (V)[c]	i_{pc} (μA)[d]	E_{pc} (V)[e]
4a	14	−1.117	44	−1.781
4b	15	−1.115	43	−1.780
4c	14	−1.118	45	−1.785
4d	13	−1.114	44	−1.790
4e	15	−1.117	43	−1.788

[a] The solution was 0.1 M $TBAPF_6$ in 4:1 CH_2Cl_2:CH_3CN

[b] Cathodic peak current measured using extrapolation of decreasing current of wave 3 as base line

[c] $E_{1/2}$ value is the cathodic peak potential of the described couple referenced to an $Ag|Ag^+$ electrode at 298 K

[d] Cathodic peak current measured using extrapolation of decreasing current of wave 1 as base line

[e] E_{pc} is the cathodic peak potential of wave 2, which is irreversible

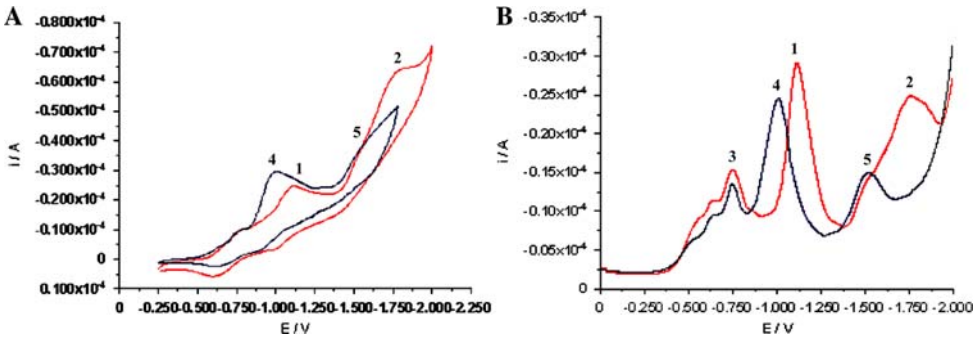

Fig. 8 (**a**) Cyclic voltammograms (**b**) Square wave voltammograms (at 10 Hz) of free **4a**, and in presence of 1.0 equiv of K^+ cations in 4:1 CH_2Cl_2:CH_3CN solvents system. Supporting electrolyte; 0.1 M $TBAPF_6$. All potentials are referenced to $Ag|Ag^+$ electrode. Red line (**4a**) and blue line (**4a** + 1 equivalent K^+)

It was observed that gradual addition of potassium ions to an electrochemical solution of **4a** in the presence of 0.1 M $TBAPF_6$ revealed a continuous decrease in the cathodic current of waves 1/1′ and 2 with increase in the potassium ion concentration. Addition of one equivalent of potassium ion resulted in the disappearance of redox waves at −1.117 V (1/1′) and −1.781 V (2) with concomitant appearance of new anodically shifted waves 4/4′ and 5 at −1.002 and −1.541 V, respectively (Fig. 8). Square wave voltammetric experiments with **4a** in the presence of one equivalent of potassium ion correspondingly exhibited an anodic shift in waves 1 and 2, respectively to −1.002 V and −1.541 V (Fig. 8b) with $\Delta E_{(1/1')}$ of 115 mV for wave 1/1′. The anodic shifts observed in the redox couples of **4a** on addition of potassium ions could possibly be ascribed to easier reduction of quinone units through extra stabilization of the reduced quinone species in the presence of positively charged metal ions.

In conclusion, we have synthesized five novel chromogenic azocalix[4]arenemonoquinones (**4a–e**) and have examined their interaction with alkali metal cations (Li^+, Na^+, K^+, Rb^+ and Cs^+). It has been observed that **4a** significantly and selectively interacts with potassium ion in preference to other alkali metal cations and exhibits a bathochromic shift in the absorption maxima of **4a** in the UV-visible and anodic shift in the original redox waves in the cyclic voltammetric experiments. Quantitative studies on the binding characteristics of **4a** with K^+ ions through Job's continuous variation plots revealed a 1:1 binding stoichiometry with an association constant of 3.27×10^4 M^{-1}. These studies may be helpful in the design of novel opto-electrochemical sensory devices for ionic and molecular recognition.

Experimental

General

All the reagents used in the study were purchased from Sigma-Aldrich or Merck and were considered chemically pure. Solvents used were predried and purified by distillation as recommended in the literature [31]. Column chromatography was performed on silica gel (60–120 mesh) obtained from Merck. Melting points were recorded on an electric melting point apparatus (Toshniwal, India) and are uncorrected. FT-IR spectra were recorded on a Nicolet Protégé 460 spectrometer using KBr discs while CHN analysis were taken on a Perkin-Elmer 240C elemental analyzer. ^1H NMR spectra were recorded on a 300 MHz Bruker DPX 300 instrument at room temperature using tetramethyl silane (TMS) as an internal standard. The electrochemical measurements were performed on an AUTOLAB PG-STAT 100 cyclic voltammeter (Metrohm Ltd. Switzerland). The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass spectrometer/Data System using Argon/Xenon (6 kV, 10 mA) as the FAB gas while the ESI mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer setting the ESI capillary at 3.5 kV and the cone voltage at 40 V.

Preparation of the starting materials

Calix[4]arene **1** and calix[4]arene derivatives **2a–2e** were synthesized as reported previously [15–20]. The analytical data of the compounds **2a–e** were found to be same as reported in earlier references.

Preparation of reagent and buffer solutions

Chlorine dioxide (ClO_2) reagent solution was obtained by mixing equal volumes of $NaClO_2 \cdot 2H_2O$ solution (31.60 g in 500 mL Milli Q water) and $Na_2S_2O_8$ solution (29.70 g in 500 mL Milli Q water). The mixture was then stored overnight in a dark coloured bottle at 0 °C to get the yellowish chlorine dioxide solution. Concentrated aqueous buffer solution was prepared by dissolving 4.36 g of $Na_2HPO_4 \cdot 2H_2O$ and 2.42 g of $NaH_2PO_4 \cdot 2H_2O$ in 100 mL of Milli Q water. A pH ~7.0 buffer solution was obtained when the concentrated solution was diluted to five times in volume.

Synthesis of calix[4]arenediquinones (**3a–3e**)

A slurry of 2.00 g of compound (**2a–e**) was dissolved in 170 mL of acetone and 70 mL of concentrated phosphate buffer. A portion of 150 mL of chlorine dioxide (ClO_2) solution was then added and the reaction mixture was stirred at room temperature for 48 h. The reaction was monitored by TLC and the mixture was evaporated in vacuo at the completion of the reaction to yield a yellow precipitate. The precipitate was extracted by chloroform (3 × 50 mL) and washed with water three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated on a rotary evaporator to yield a sticky yellow product which was further triturated with methanol to yield **3a–e** as bright yellow solids.

Compound 3a: Yellow powder, yield: 57% (1.21 g), mp = 237°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 1760, 1655. ^1H NMR (300 MHz, $CDCl_3$) δ_H 6.71 (br s, 4H, ArH); 6.60 (s, 4H, QuH); 6.53 (br s, 2H, ArH); 4.39 (s, 4H, –OCH_2); 4.17 (q, J = 6.9 Hz, 4H, –CH_2–CH_3); 3.90 (d, J = 13.2 Hz, 4H, Ar–CH_2–Qu), 3.25 (d, J = 13.2 Hz, 4H, Ar–CH_2–Qu), 1.22 (t, J = 6.9 Hz, 6H, –CH_2–CH_3). ES MS m/z: 624 (M^+). Anal. Calcd for $C_{36}H_{32}O_{10}$: C, 69.22; H, 5.16. Found: C, 69.16; H, 5.13.

Compound 3b: Bright yellow solid, yield: 61% (1.27 g), mp = 254°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 1732, 1656. ^1H NMR (300 MHz, $CDCl_3$) δ_H 8.20 (br s, 4H, $ArH_{benzoyl}$); 7.73 (t, J = 6.6 Hz, 2H, $ArH_{benzoyl}$); 7.56 (t, J = 6.9 Hz, 4H, $ArH_{benzoyl}$); 7.02 (br s, 4H, ArH_{calix}); 6.91 (m, 2H, ArH_{calix}); 6.29 (s, 4H, QuH); 3.42 (br s, 8H, Ar–CH_2–Qu). ES MS m/z: 660 (M^+). Anal. Calcd for $C_{42}H_{28}O_8$: C, 76.35; H, 4.27. Found: C, 76.30; H, 4.23.

Compound 3c: Yellow powder, yield: 53% (1.14 g), mp = 255°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 1654, 1611. ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.16 (br s, 4H, ArH); 6.92 (br s, 2H, ArH); 6.24 (s, 4H, QuH); 3.70 (s, 6H, –OCH_3); 3.28 (br s, 4H, Ar–CH_2–Qu); 3.06 (br s, 4H, Ar–CH_2–Qu). ES MS m/z: 480 (M^+). Anal. Calcd for $C_{30}H_{24}O_6$: C, 74.99; H, 5.03. Found: C, 74.83; H, 5.01.

Compound 3d: Yellow powder, yield: 47% (0.99 g), mp = 249°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 1657, 1611. ^1H NMR (300 MHz, $CDCl_3$) δ_H 6.73 (m, 4H, ArH); 6.57 (m, 2H, ArH); 6.52 (s, 4H, QuH); 4.01 (d, J = 13.2 Hz, 4H, Ar–CH_2–Qu); 3.59 (t, J = 6.9 Hz, 4H, –OCH_2–CH_2–CH_3); 3.26 (d, J = 13.2 Hz, 4H, Ar–CH_2–Qu); 1.77 (m, 4H, –OCH_2–CH_2–CH_3); 0.95 (m, 6H, –OCH_2–CH_2–CH_3). ES MS m/z: 536 (M^+). Anal. Calcd for $C_{34}H_{32}O_6$: C, 76.10; H, 6.01. Found: C, 76.06; H, 5.98.

Compound 3e: Yellow solid, yield: 55% (1.15 g), mp = 241° C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 1655, 1617. ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.27 (m, 10H, ArH_{benzyl}); 6.73 (d, J = 6.6 Hz, 4H, ArH_{calix}); 6.60 (m, 2H, ArH_{calix}); 6.39 (s, 4H, QuH); 4.72 (s, 4H, –OCH_2–Ar); 3.57 (d, J = 13.1 Hz, 4H, Ar–CH_2–Qu); 3.10 (d, J = 13.1 Hz, 4H, Ar–CH_2–Qu). ES MS m/z: 632 (M^+). Anal. Calcd for $C_{42}H_{32}O_6$: C, 79.73; H, 5.10. Found: C, 79.69; H, 5.11.

Synthesis of 2,4-dinitrophenylazo calix[4]arenemonoquinones (**4a–e**)

To a solution of calix[4]arenediquinone **3a–e** (100 mg) in chloroform (20 mL), was added absolute ethanol (10 mL), 2,4-dintrophenylhydrazine (1.1 equiv), and concentrated H_2SO_4 (10 drops) in sequence. The reaction mixture was stirred for 2 h at temperature −5 to −10° C and treated with ice cold water and extracted with chloroform. The organic phase was separated and dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to give a residue which was purified through column chromatography using 9.5:0.5 chloroform:ethylacetae solvent system. Further recrystalization in chloroform and methanol gave the products **4a–e** as orange-red powders.

Compound 4a: Orange solid. Yield: 57% (73.0 mg), mp > 280°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3496, 1759, 1657, 1598, 1537, 1461. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.49 (s, 1H, OH, D_2O exchangeable); 8.79 (s, 1H, ArH_{DNP}); 8.43 (d, J = 6.6 Hz, 1H, ArH_{DNP}); 7.77–7.76 (m, 3H, ArH_{DNP} + –N = N–ArH_{calix}); 6.96 (d, J = 7.5 Hz, 4H, ArH_{calix}); 6.79 (t, J = 7.5 Hz, 2H, ArH_{calix}); 6.61 (s, 2H, QuH); 4.55 (s, 4H, –OCH_2–); 4.29 (d, J = 12.9 Hz, 2H, Ar–CH_2–Ar); 4.21 (d, J = 13.0 Hz, 2H, Ar–CH_2–Ar); 4.01 (q, J = 6.3 Hz, 4H, –CH_2–CH_3); 3.30 (d, J = 12.9 Hz, 2H, Ar–CH_2–Ar); 3.22 (d, J = 13.0 Hz, 2H, Ar–CH_2–Ar); 1.32 (t, J = 7.2 Hz, 6H, –CH_2–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 188.5, 185.1, 169.9, 159.3, 150.8, 149.4, 149.2, 146.9, 146.8, 146.6, 132.3, 129.8, 127.7, 126.8, 125.9, 120.2, 120.0, 72.3, 61.7, 31.2, 30.6, 14.3. FAB MS m/z: 805 (M^++1). Anal. Calcd for $C_{42}H_{36}N_4O_{13}$: C, 62.68; H, 4.51; N, 6.96. Found: C, 62.61; H, 4.55; N, 6.99. UV (λ_{max}, MeOH/$CHCl_3$): 422 nm.

Compound 4b: Orange solid. Yield: 50% (64.1 mg), mp > 255°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3502, 1735, 1654, 1585, 1534. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.41 (s, 1H, OH, D_2O exchangeable); 8.85 (s, 1H, ArH_{DNP}); 8.45–8.19 (m, 5H, ArH_{DNP} + $ArH_{benzoyl}$); 7.81–7.77 (m, 5H, ArH_{DNP} + $ArH_{benzoyl}$ + ArH_{calix}); 7.63 (m, 4H, $ArH_{benzoyl}$); 7.02 (d, J = 7.5 Hz, 4H, ArH_{calix}); 6.85 (t, J = 7.5 Hz, 2H, ArH_{calix}); 6.37 (s, 2H, QuH); 4.18 (d, 4H, J = 13.1, Ar–CH_2–Ar); 3.50 (d, 2H, J = 12.6, Ar–CH_2–Ar); 3.39 (d, 2H, J = 12.6, Ar–CH_2–Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 187.6, 185.9, 164.1, 159.6, 147.7, 143.6, 142.9, 142.6, 139.9, 135.2, 134.4, 133.9, 132.9, 132.3, 130.5, 130.1, 129.0, 128.8, 128.6, 127.5, 125.6, 124.0, 122.8, 118.2, 116.5, 30.8, 29.9. FAB MS m/z: 842 (M^++2). Anal. Calcd for $C_{48}H_{32}N_4O_{11}$: C, 68.57; H, 3.84;

N, 6.66. Found: C, 68.51; H, 3.85; N, 6.63. UV (λ_{max}, MeOH/$CHCl_3$): 420 nm.

Compound 4c: Red solid. Yield: 55% (75.6 mg), mp > 285°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3413, 1656, 1601, 1535, 1458. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.21 (s, 1H, OH, D_2O exchangeable); 8.65 (s, 1H, ArH_{DNP}); 8.44 (d, J = 6.6 Hz, 1H, ArH_{DNP}); 7.76–7.71 (m, 3H, –N = N–ArH + ArH_{DNP}), 6.98 (d, J = 7.5 Hz, 4H, ArH_{calix}); 6.76 (t, J = 7.5 Hz, 2H, ArH_{calix}); 6.44 (s, 2H, QuH); 4.26 (d, J = 13.2 Hz, 2H, Ar–CH_2–Ar); 4.16 (d, J = 13.1 Hz, 2H, Ar–CH_2–Ar); 3.75 (s, 6H, –O–CH_3); 3.38 (d, J = 12.9 Hz, 2H, Ar–CH_2–Ar); 3.30 (d, J = 12.9 Hz, 2H, Ar–CH_2–Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 188.3, 186.0, 158.9, 156.7, 154.1, 148.9, 148.3, 147.6, 146.1, 143.4, 142.3. 133.1, 130.0, 128.1, 127.3, 126.9, 125.2, 122.2, 120.6, 63.5, 31.8, 30.9. FAB MS m/z: 661 (M^++1). Anal. Calcd for $C_{36}H_{28}N_4O_9$: C, 65.45; H, 4.27; N, 8.48. Found: C, 65.46; H, 4.22; N, 8.50. UV (λ_{max}, MeOH/$CHCl_3$): 421 nm.

Compound 4d: Orange solid. Yield: 60% (80.1 mg), mp > 265°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3393, 1655, 1599, 1538, 1465. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.31 (s, 1H, OH, D_2O exchangeable); 8.68 (s, 1H, ArH_{DNP}); 8.42 (d, J = 6.6 Hz, 1H, ArH_{DNP}); 7.78–7.72 (m, 3H, –N = N–ArH + ArH_{DNP}), 7.01 (d, J = 7.5 Hz, 4H, ArH_{calix}); 6.78 (t, J = 7.5 Hz, 2H, ArH_{calix}); 6.47 (s, 2H, QuH); 4.39 (d, J = 12.9 Hz, 2H, Ar–CH_2–Ar); 4.31 (d, J = 12.9 Hz, 2H, Ar–CH_2–Ar); 3.99 (t, J = 6.3 Hz, 4H, –O–CH_2–CH_2–CH_3); 3.28 (d, J = 13.1 Hz, 2H, Ar–CH_2–Ar); 3.20 (d, J = 13.0 Hz, 2H, Ar–CH_2–Ar); 2.12 (m, 4H, –O–CH_2–CH_2–CH_3); 1.29 (t, J = 7.2 Hz, 6H, –O–CH_2–CH_2–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 188.2, 185.7, 159.8, 156.3, 154.4, 149.1, 147.9, 145.7, 142.1. 132.4, 129.9, 127.5, 126.6, 125.5, 123.2, 119.9, 73.7, 31.6, 30.8, 23.5, 10.5. FAB MS m/z: 717 (M^++1). Anal. Calcd for $C_{40}H_{36}N_4O_9$: C, 67.03; H, 5.06; N, 7.82. Found: C, 66.99; H, 5.02; N, 7.84. UV (λ_{max}, MeOH/$CHCl_3$): 422 nm.

Compound 4e: Red solid. Yield: 56% (72.0 mg), mp > 280°C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3378, 1660, 1588, 1540. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.27 (s, 1H, OH, D_2O exchangeable); 8.71 (s, 1H, ArH_{DNP}); 8.44 (d, J = 6.3 Hz, 1H, ArH_{DNP}); 7.80 (d, J = 6.3 Hz, 1H, ArH_{DNP}); 7.70 (s, 2H, –N = N–ArH_{calix}); 7.31 (m, 10H, ArH_{benzyl}); 6.75 (m, 4H, ArH_{calix}); 6.62 (m, 2H, ArH_{calix}); 6.46 (s, 2H, QuH); 4.89 (s, 4H, –O–CH_2); 4.15 (d, J = 13.6 Hz, 2H, Ar–CH_2–Ar); 4.09 (d, J = 13.6 Hz, 2H, Ar–CH_2–Ar); 3.11 (d, J = 13.2 Hz, 4H, Ar–CH_2–Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 187.9, 185.3, 158.8, 157.4, 154.6, 149.3, 148.1, 147.2, 146.1 145.5, 143.5, 142.9, 140.9, 132.5, 127.7, 127.3, 124.8, 123.5, 122.8, 120.7, 119.6, 118.7, 115.2, 112.3, 78.2, 31.9, 30.2 FAB MS m/z: 812 (M^+). Anal. Calcd for $C_{48}H_{36}N_4O_9$: C, 70.93; H, 4.46; N, 6.89. Found: C, 70.89; H, 4.49; N, 6.90. UV (λ_{max}, MeOH/$CHCl_3$): 419 nm.

Analytical procedure

Procedure for electrochemical experiments

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed on an AUTOLAB PG-STAT 100 with three electrodes consisting of a glassy carbon working electrode with a conducting area of 3 mm diameter, a platinum wire counter electrode, and an $Ag|Ag^+$ reference electrode. All cyclic voltammetric (CV) measurements were digitized by using the GPES software (version 4.9.005). Unless otherwise indicated, all experiments were carried out in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in 20% acetonitrile in dichloromethane. All CV and SWV measurements were carried out in a cell compartment enclosed with a built-in Teflon cap. To avoid interference from oxygen, all solutions were bubbled with nitrogen at least for 5 min before each measurement. Typically, a solution of 0.001 M of a ligand (5×10^{-6} mol) and $TBAPF_6$ (5×10^{-4} mol) in 5 mL of 20% acetonitrile in dichloromethane was prepared in a volumetric flask. A mixture of potassium salt ($KClO_4$) (5×10^{-4} mol) and $TBAPF_6$ (5×10^{-4} mol) in 5 mL of acetonitrile was prepared in a volumetric flask. All the solutions were sonicated for 10 min before use. The solution of the potassium ion was added directly to the cell by a microsyringe to have desired cation/ligand ratios. Redox currents were determined from CV scans of the complex solutions at a scan rate of 50 mVs^{-1}.

Procedure for UV-visible experiments

Unless otherwise specified, all UV-visible experiments reported in this work were carried out in methanol/chloroform (1:1). Perchlorate salts of Li^+, Na^+, K^+ and carbonate salts of Rb^+ and Cs^+ were used for UV-visible spectrophotometeric experiments.

Job's plot experiment

Stock solutions of compound **4a** (10^{-5} M) and metal salt (e.g., $KClO_4$) (10^{-5} M) in chloroform-methanol (1:1) were prepared and the concentrations of each solution was varied with their total volume fixed at 5.0 mL. The mixture was shaken for 2 min and the UV-visible absorbance at 604 nm was recorded in each case. Assuming that only one

complex (ML_n) was formed at equilibrium; the value of 'n' could be calculated from the plot of χ_{max} [mole fraction of the ligand (χ_L) at maximum absorption] by the following relationship, $n = \chi_{max}/1 - \chi_{max}$. The value of χ_{max} was noted from the plot of absorbance vs χ_L.

Determination of the association constants

The association constant (K_s) of **4a**/K^+ complex was determined from the following Benesi-Hildebrand equation [29]:

$$\frac{1}{A - A_0} = \frac{a}{a - b} \times \left[\frac{1}{K_s[M]} + 1\right]$$

where K_s = Association constant; A_0 = The observed absorption in the absence of cation; A = The observed absorption after cation addition; [M] = The concentration of the cation-added; a and b are constants, the association constant value K_s was evaluated graphically by plotting 1/ΔA against 1/[M].

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