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Synthesis, characterization and electrochemical properties of two new calix[4]arene derivatives bearing two ferrocene imine or ferrocene amine units at the upper rim

Behrouz Shaabani *, Zohreh Shaghaghi

Research Laboratory of Synthesis of Inorganic Compounds, Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

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A novel calix[4]arene derivative with two ferrocenyl Schiff-base groups at the upper rim **3** has been synthesized from 5,17-diformyl-25,27-dipropoxy-26,28-dihydroxy calix[4]arene and 4-ferrocenylaniline via condensation reaction. Reduction of **3** with sodium borohydride led to calix[4]arene derivative **4** with two amino ferrocenyl groups at the upper rim. The ferrocenyl Schiff-base calix[4]arene and its corresponding reduced amine have been purified and characterized by elemental analysis,^{1}H NMR, FTIR, Mass and UV–vis spectral data. Electrochemical properties of compounds **3** and **4** have been investigated. Cyclic voltammograms of **3** and **4** show reversible redox couples of ferrocene/ferrocinium at $E_{1/2}$=0.401 V and 0.346 V, respectively. Electrochemical studies show these redox active compounds electrochemically recognize trivalent lanthanides La^{3+} and Ce^{3+} and divalent Pb^{2+} and Cu^{2+}cations. With ferrocenyl Schiff-base calix[4]arene **3** an anodic shift as large as 130 mV is observed on addition of one equivalent of Ce^{3+} ion. Also extraction properties of compound **4** towards some metal cations have been described. It has been observed that compound **4** has a good selectivity for metal cations Fe^{3+}, Cu^{2+}, Pb^{2+} and Cd^{2+} against Ni^{2+} and Co^{2+}.

1. Introduction

Calix[n]arenes are macrocyclic compounds in which phenolic units are linked via methylene bridging groups at their *ortho* position. The smallest in the series is where four phenolic units make up the macrocyclic backbone (n=4). Calixarenes and their derivatives can be used as synthetic receptors to selectively bind a wide variety of guest molecules/ions forming host–guest complexes or supramolecular species, and have been applied successfully to various areas of science and technology. It is also noted that the calixarene platform can be selectively functionalized both at the phenolic OH groups (lower rim or narrow rim)[1] and at the *para* positions of the phenol rings (upper rim or wide rim), which provides unique possibilities to organize several binding sites appropriately for complexation of potential guests.[2] For example, these molecules are capable of alkali, alkaline earth and heavy metal ion recognition.[3–5]

The attachment of *N*-ligating groups through imine bond formation has been successful at the upper[6] and lower[7,8] rims of calixarenes. This has resulted calix[4]arene Schiff bases, which are potential ligands for fluorescent studies[8] and for cation recognition, particularly with transition metals.[9]

Molecular sensors are required for the efficient detection of charged and neutral pollutant species within organic and aqueous effluents. Particularly, redox-active molecular receptors have been designed to sense target guest species via means of an electrochemical response. For example, ferrocene-containing ligands have previously been shown electrochemically to sense alkali, alkali-earth and transition metal ions.[10,11]

Metallocene containing calixarenes have already been studied to sense or activate molecular level processes. Beer has been a pioneer in making metallocene appended calixarene for analytical purposes and investigating electrochemical interactions between multi-redox architectures.[12–14] Tuntulani and co-workers have synthesized calix[4]arene derivatives containing amide ferrocene units at the wide rim and ethyl ester groups at the narrow rim and investigated their anion-binding and sensing properties.[15,16] Kaifer and co-workers have reported a redox controlled dissociation of a self-assembled dimer.[17] Recently Pellet and co-workers reported the syntheses and conformational analyses of similar artificial receptors associating calixarene as molecular platform and ferrocene redox-active fragments.[18]

In the present work, we report the synthesis and characterization of new calix[4]arene ligands containing two Schiff base

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* Corresponding author. Tel./fax: +98 411 3393144.
E-mail address: shaabani_b@yahoo.com (B. Shaabani).

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Table1
^{1}H NMR chemical shifts of diformylcalix[4]arene **1**, **3** and **4** (400 MHz)

No	Solvent	Lower rim				Calixarene core					Upper rim						
		OH	OPr														
			OCH_2	CH_2	CH_3	CH_2	CH_2	ArH	ArH	ArH	ArH	ArH	CHO	HCN	NH	NCH_2	ferrocene ArH
1	$CDCl_3$	9.32	4.02	2.04–2.13	1.34	4.30	3.51	6.81	6.98	7.64	—	—	9.78	—	—	—	—
3	DMSO-d_6	9.46	3.99	1.98–2.04	1.30	4.19	3.65	6.83	7.11	7.80	7.62	7.21	—	9.74	—	—	4.79,4.37,4.01
4	$CDCl_3$	—	3.98	2.04–2.13	1.33	4.32	3.38	6.79	6.95	7.07	7.32	6.59	—	—	8.52	4.54	4.23,4.15.4.03

ferrocenyl **3** and amino ferrocenyl groups **4** at the upper rim and two ether groups at the lower rim and investigate their electrochemical behaviour in the presence of La^{3+}, Ce^{3+}, Cu^{2+} and Pb^{2+} metal ions. We also report a study of extraction ability of compound **4** towards metal cations (Ni^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+} and Cd^{2+}).

2. Results and discussion

2.1. Synthesis

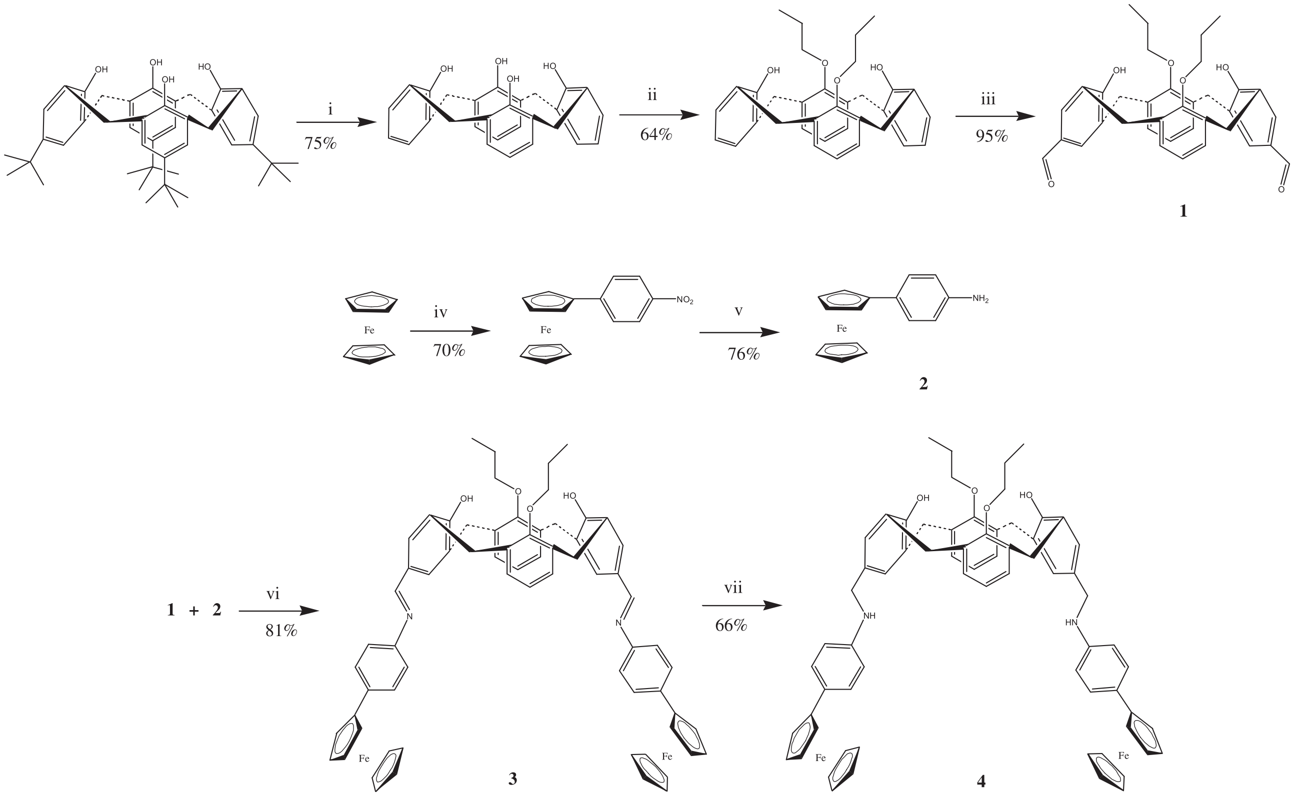
In this work, to synthesis the new compounds **3** and **4**; we used diformyl calix[4]arene **1** and 4-ferrocenylaniline **2** as the precursors. Diformyl calix[4]arene **1**[19] and 4-ferrocenylaniline[20,21] were synthesized according to the reported literature procedure. The synthetic route is shown in Scheme 1. Compound **1** was refluxed with 4-ferrocenylaniline **2** in anhydrous THF and a catalytic amount of *p*-toluenesulfonic acid to give the corresponding imine derivative of calix[4]arene **3** in 81% yield. Compound **4** was achieved by reduction of compound **3** with $NaBH_4$ in anhydrous THF in 66% yield. The new compounds **3** and **4** containing two Schiff-base and two amino groups, respectively, at the upper rim of calix[4]arene were characterized by a combination of IR, ^{1}H NMR, mass and elemental analysis and investigated with UV–vis spectrometry and cyclic voltammetry. Also we studied extraction properties of compound **4** towards some metal cations. We applied compounds **3** and **4** electrochemically for cation recognition towards some metal ions.

2.2. IR spectra

The major difference in the IR spectrum of **1** compared to **3** is the presence of an aldehyde peak at 1679 cm^{-1} in **1**. The formation of diimine derivative of calix[4]arene **3** was confirmed by the appearance of the characteristic imine peak at 1655 cm^{-1} in its IR spectra. Also, perfect reduction of compound **3** to diamine calix[4]arene derivative **4** was confirmed by the absence of the peak at 1655 cm^{-1} in its IR spectra.

2.3. ^{1}H NMR spectra

The structures of **3** and **4** were fully characterized using ^{1}H NMR spectroscopy. Table 1 shows the ^{1}H NMR chemical shifts for aromatic protons, bridging methylene protons and chain methylene and methyl proton signals for **1**, **3** and **4**. ^{1}H NMR data showed that



Scheme 1. Preparation steps of **3** and **4**. (i) $AlCl_3$/phOH, Toluene, 1 h, rt (ii) PrI, K_2CO_3, CH_3CN, Refluxed for 24 h, (iii) Cl_2CHOCH_3, $SnCl_4$, $CHCl_3$, $T=-15$ °C, (iv) 4-nitroaniline, water, concentrated hydrochloric acid, sodium nitrite, hexadecyltrimethylammonium bromide, ethyl ether, (v) palladium on charcoal, sodium borohydride, water and methanol, room temperature, 2 h, (vi) *p*-toluenesulfonic acid catalyst, THF, refluxed for 24 h, (vii) sodium borohydride, THF, Refluxed for 3 h.

compounds **3** and **4** have a cone conformation. A typical AB pattern was observed for the methylene bridge $ArCH_2Ar$ protons at 3.65 and 4.19 (J=13 Hz) for **3** and 3.38 and 4.32 (J=12.8 Hz) for **4**.

The high field doublets at 3.65 for **3** and 3.38 for **4** were assigned to the equatorial protons of methylene groups, whereas the low field signals at 4.19 for **3** and 4.32 for **4** were assigned to the axial protons.

The formation of the imine **3** was established by the loss of the signal due to the aldehyde group of **1** at 9.78 in the ^1H NMR spectra and the appearance of the signal at 9.74, depending on the substituent attached to the imine nitrogen atom. The formation of the amine **4** was determined by the loss of the signal due to the imine group of **3** at 9.74 in the ^1H NMR spectra and the appearance of the signal at 8.25 for the amine protons and 4.54 for the $–NCH_2–$ groups depending on the reduction of imino groups to the amine groups ($–HCN–$ to $–CH_2NH–$).

The aromatic proton signals of the phenyl rings of calixarene core appear as a singlet, a triplet and a doublet in the case all of the compounds **1**, **3** and **4** at δ=6.79–7.80. The aromatic proton signals of the phenyl rings attached to ferrocene appear as two doublets for compound **3** at δ=7.21 and 7.62 (J=8.4 Hz) and **4** at δ=6.59 and 7.32 (J=8.5 Hz). The ferrocene proton signals appear as three singlets in the case both compounds **3** and **4** at δ=4.01–4.79.

2.4. The UV–vis spectra

The UV–vis spectra for **3** and **4** in DMSO solvent at 200–650 nm are shown in Figure 1. Compound **3** was determined to show a strong absorption at 294 nm apparently corresponding to $\pi\rightarrow\pi^*$ transition of aromatic rings and a shoulder at 336 nm apparently corresponding to $n\rightarrow\pi^*$ transition (non-bonding electrons of nitrogen to π^* orbital of imine) and a weak band at 468 nm corresponding to the d–d transition for the iron of ferrocene. Also, compound **4** was determined to show a strong absorption at 297 nm apparently corresponding to $\pi\rightarrow\pi^*$ transition of aromatic rings and a weak band at 450 nm corresponding to the d–d transition of ferrocene. The absence of a shoulder in compound **4** compared to compound **3** was ascribed to the reduction of the imine groups and the formation of amine derivative **4** (the disappearance of π^* orbital of imine).

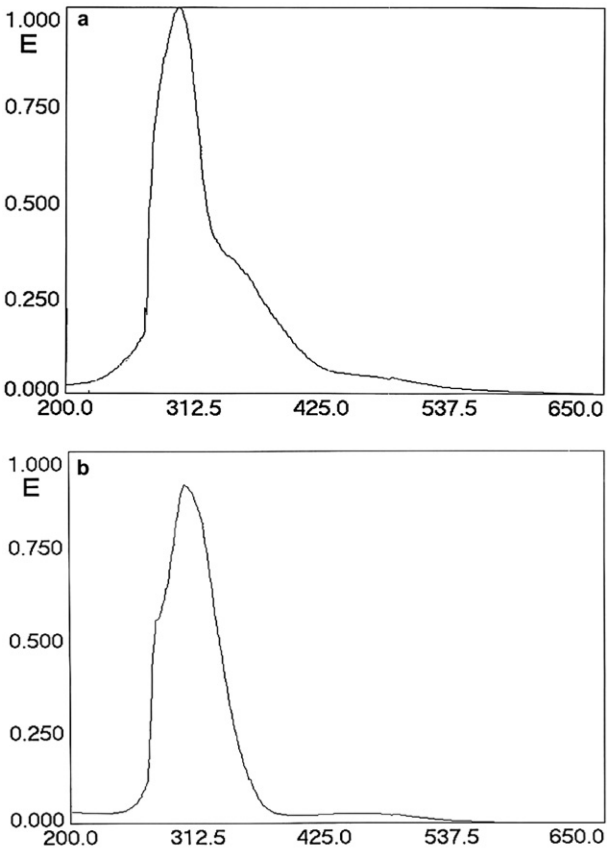


Figure 1. UV–vis spectrum of **3** (a) and **4** (b) (1×10^{-4} M in DMSO).

2.5. Electrochemical analysis

The electrochemical properties of compounds **3** and **4** were studied by cyclic voltammetry. Cyclic voltammetry (CV) was performed using solutions of **3** and **4** (1×10^{-3} M) prepared in DMSO with 0.1 M $LiClO_4$ as a supporting electrolyte and using a glassy carbon working electrode, a Hg/Hg_2^{2+} reference electrode, and a Pt wire counter electrode. The potential was scanned in the range of 1 to −1 V at 100 mV/s potential scan rate. Cyclic voltammograms of **3** and **4** showed reversible redox couples of ferrocene/ferricinium at $E_{1/2}$=0.401 V and 0.346 V, respectively, as shown in Figure 2 and Table 2. The observation of only one redox wave for both iron centers in compounds **3** and **4** indicates no interaction between the ferrocene units.

In the next step, cyclic voltammetry was used to investigate the electrochemical response of the ferrocene units in compounds **3** and **4** in the presence of varying concentrations from 0.1 (1×10^{-4} M) to 2.0 equiv (2×10^{-3} M in DMSO) of metal ions (La^{3+}, Ce^{3+}, Cu^{2+} and Pb^{2+}). Table 3 shows that in all cases addition of metal ions (La^{3+}, Ce^{3+} and Pb^{2+}) cause significant anodic shifts in the respective ferrocene-ferrocenium redox couple of **3** and **4**, addition of Cu^{2+} cation causes a cathodic shift in the respective ferrocene-ferrocenium redox couple of **3**, and for **4**, after adding 1 equiv of Cu^{2+} cation, disappear oxidation and reduction waves (Figs. 3 and 4). For metal ions (La^{3+}, Ce^{3+} and Pb^{2+}) Schiff-base ligand **3** shows greater potential shifts than compound **4**. Thus compound **3** exhibits generally greater anodic perturbations (Table 3). Compound **3** and **4** give a shift increasing from 125 mV for La, to 130 mV for Ce and 20 mV for La, to 64 mV for Ce, respectively. The smaller, more charge dense Ce^{3+} cation, perturbs the ferrocene oxidation more than the La^{3+} ion (Table 3).

Titration of **3** and **4** with metal ions (La^{3+}, Ce^{3+} and Pb^{2+}) display a progressive appearance of a new reduction wave at the less positive potential and a progressive disappearance of the initial reduction (after adding 0.1 equiv of La^{3+} ion, ligand **4** only shows

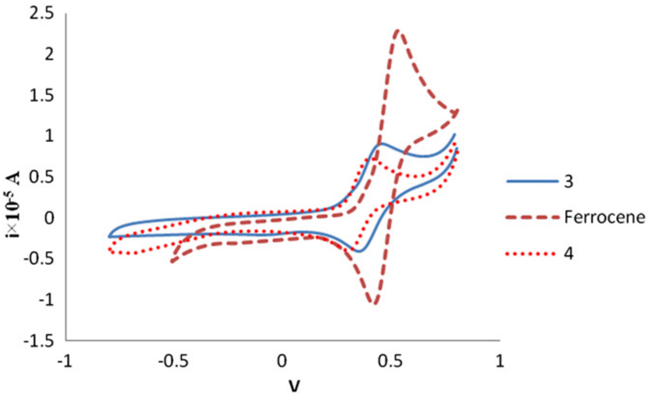


Figure 2. Cyclic voltammogram of ferrocene, compounds **3** and **4** (1×10^{-3} M in DMSO).

Table 2
Electrochemical data recorded by cyclic voltammetry for ferrocene, **3** and **4** dissolved in DMSO

	E_{pa}(mV)	E_{pc}(mV)	$E_{1/2}$(mV)	ΔE_p(mV)	$\Delta E_{p/2}$(mV)
Ferrocene	528	417	472	111	55.5
3	457	346	401	111	55.5
4	397	296	346	101	50.5

E_{pa} (anodic peak potential), E_{pc} (cathodic peak potential), $E_{1/2}=(E_{pa}+E_{pc})/2$, $\Delta E_p=E_{pa}-E_{pc}$.

Table 3
Electrochemical data and metal ions electrochemical recognition results

Compound	$E^a_{1/2}$	$\Delta E^b_{1/2}$			
		La^{3+}	Ce^{3+}	Pb^{2+}	Cu^{2+}
3	401	125, 115	130, 125	124, 119	45, 45
4	346	20, 20	64, 59	9, 53	The disappearance of oxidation and reduction wave

[a] Obtained in DMSO solution with $LiClO_4$.

[b] Anodic shifts (for Cu^{2+}, cathodic shift) of respective ferrocene/ferrocenium couple produced by 1 and 2 equiv of metal cations.

a potential shift of initial reduction wave) and a potential shift of oxidation wave (with Ce^{3+} ion, compound **3** shows a progressive appearance of a new oxidation wave at a less positive potential and a progressive decreasing of the initial oxidation wave). Titration of **3** and **4** with Cu^{2+} cation reveal a potential shift of oxidation and reduction wave with a progressive decreasing of intensity of the oxidation and reduction wave (for compound **4**, after 1 equiv addition of cation disappear oxidation and reduction wave) (Figs. 3d and 4d).

2.6. Two phase solvent extraction

The extraction data with diferrocenylamine calix[4]arene derivative **4** has been investigated for various cations and compared with **2** (a simple non-calixarene compound) in Table 4 and Figure 5.

The results of extraction show that compound **4** presents a low affinity towards Fe^{3+}, Pb^{2+}, Cu^{2+} and Cd^{2+} and no affinity for Ni^{2+} and Co^{2+}, when the concentration of **4** and the concentration of cation are same([ligand]/[cation]=1). But, when the concentration of **4** to the concentration of metal cation solution increases ten times, it presents a good affinity towards Fe^{3+}, Pb^{2+}, Cu^{2+} and Cd^{2+} and no affinity for Ni^{2+} and Co^{2+}. In this case, compound **4** presents a very good selectivity for Fe^{3+}, Pb^{2+}, Cu^{2+} and Cd^{2+} in the comparison with Ni^{2+} and Co^{2+}. Thus, when large amount of compound **4** contributes in the extraction, the extractabilities for Fe^{3+}, 7.6, Pb^{2+}, 4.27, Cd^{2+}, 2.5 and Cu^{2+}, 3.5 times increase and affinity for Ni^{2+} and Co^{2+} does not change. While, in the same conditions (when large amount of non-calix[4]arene compound **2** contributes in the extraction) affinity for Fe^{3+}, Cu^{2+} and Ni^{2+} does not increase, for Cd^{2+} and Co^{2+} shows minor increase and for Pb^{2+} is similar to compound **4** (Fig. 5 and Table 4).

Generally, the extractability of **4** for Fe^{3+}, Cu^{2+} and Cd^{2+} is six, four and near to two times greater than **2**, respectively. The affinity of **4** for Pb^{2+} is 48.78, that is, a little more in the comparison with **2**, the extraction properties of compounds **2** and **4** are similar for Ni^{2+} and finally unlike ligand **4**, **2** shows approximately a good affinity for Co^{2+} (Fig. 5b).

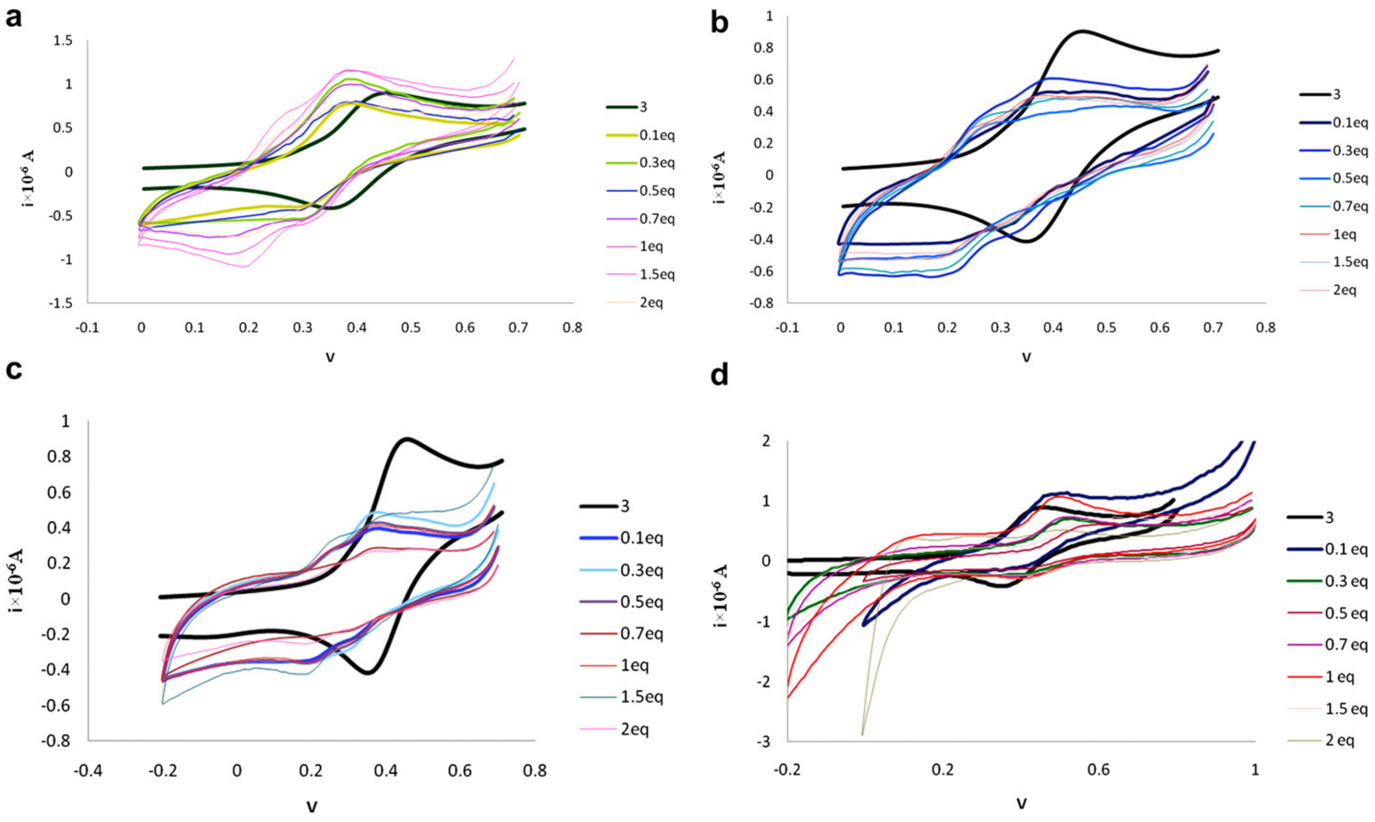


Figure 3. Titration of **3** and metal ions (La^{3+}, Ce^{3+}, Cu^{2+} and Pb^{2+}) in DMSO with 0.1 M $LiClO_4$ and a scan rate of 100 m V/s: (a) La^{3+}, (b) Ce^{3+}, (c) Pb^{2+}, (d) Cu^{2+}.

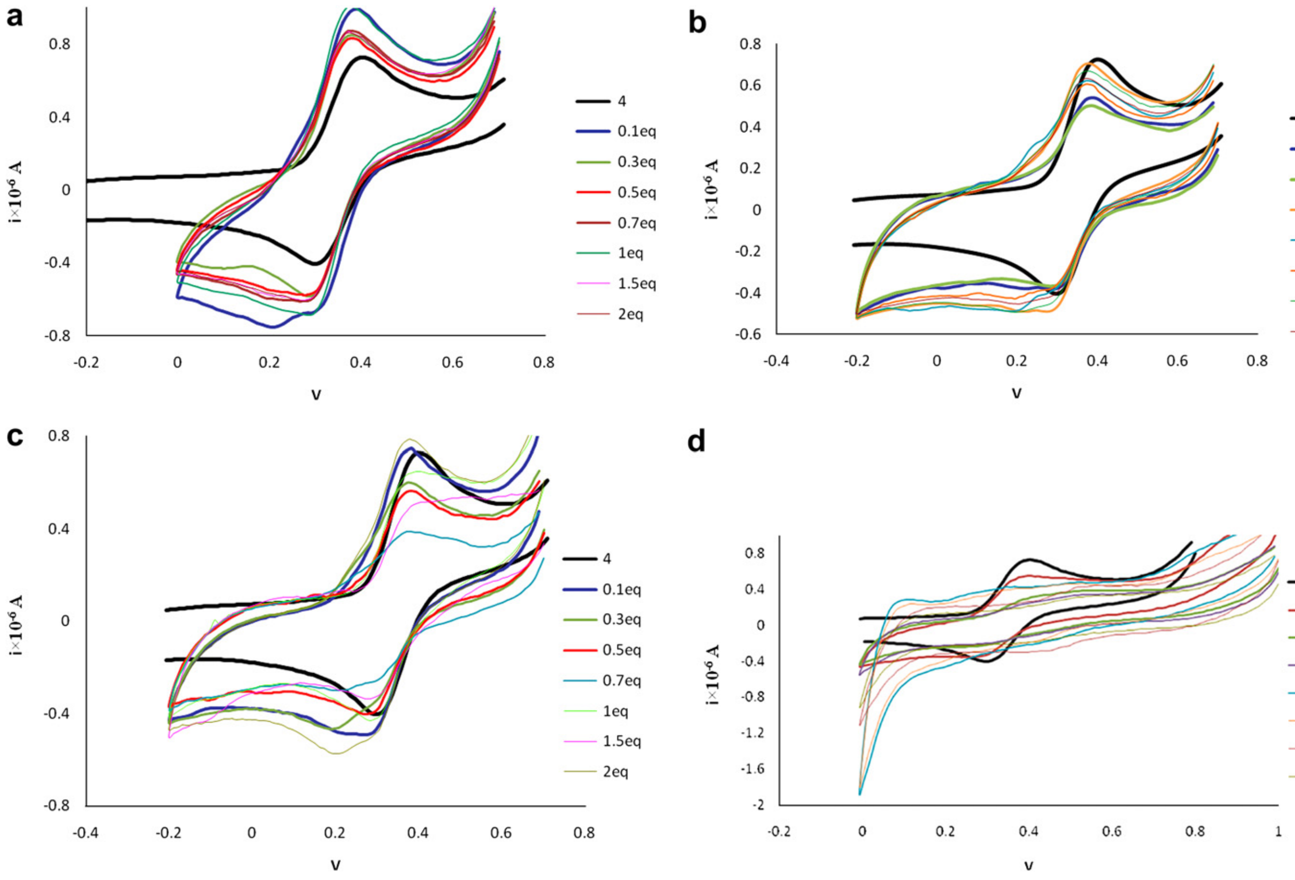


Figure 4. Titration of **4** and metal ions (La^{3+}, Ce^{3+}, Cu^{2+} and Pb^{2+}) in DMSO with 0.1 M $LiClO_4$ and a scan rate of 100 m V/s: (a) La^{3+}, (b) Ce^{3+}, (c) Pb^{2+}, (d) Cu^{2+}.

3. Conclusion

Two new calix[4]arene derivatives containing ferrocenyl units **3** and **4** have been prepared and characterized. These compounds studied with cyclic voltammetry. Cyclic voltammograms of **3** and **4** showed reversible redox couples of ferrocene/ferrocenium at $E_{1/2}$=0.401 V and 0.346 V, respectively. The observation of only one redox wave for both iron centers in compounds **3** and **4** indicates no interaction between the ferrocene units. Electrochemical studies show these redox-active ligands electrochemically recognize trivalent lanthanide ($La^{3+}$and Ce^{3+}), and divalent Pb^{2+} and Cu^{2+} ions. According to CV data Schiff-base ligand **3** shows greater potential shifts than compound **4**. With ferrocenyl Schiff-base calix[4]arene **3** an anodic shift as large as 124–130 mV is observed on addition of one equivalent of La^{3+} and Pb^{2+} ions. Compound **3** shows a cathodic shift for Cu^{2+} cation and for ligand **4**, after adding 1 equiv of Cu^{2+} cation, anodic and cathodic waves disappear. Also the investigation of extraction properties of compound **4** towards some metal cations show that compound **4** has a good selectivity for metal cations Cu^{2+}, Fe^{3+}, Pb^{2+} and Cd^{2+} against Ni^{2+} and Co^{2+}. Extraction data comparison of **4** with **2**, a simple non-calixarene compound, reveals grater extractability of **4** for Cu^{2+}, Fe^{3+}, Pb^{2+} and Cd^{2+}.

4. Experimental

4.1. General

5,17-Diformyl-25,27-dipropoxy-26,28-dihydroxy calix[4]arene **1**[19] and 4-ferrocenylaniline [20,21] were prepared according to literature methods. Starting materials were all purchased commercially and used without further purifications. THF solvent was distilled and dried before use and other solvents were used without purifications. All operations were performed under an oxygen free dry dinitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on Bruker Avance 400 in $CDCl_3$ and DMSO-d_6 solvent with $SiMe_4$ as internal standard at room temperature. Elemental analyses were performed on Elementar Vario EL III. IR spectra were recorded on a FT-IR Spectrometer Bruker Tensor 27 in the region 4000–400 cm^{-1} using KBr pellets. Electronic absorption spectra in the UV–vis region were recorded with an Analytick Jena Spectrod 40. Mass spectrometries were performed on LC/MS 500 ion trap Varian at Klinikum rechts der Isar, Technische Universität München, Department of Nuclear Medicine. Melting points were obtained with an Electrothermal 9100 and are uncorrected.

4.2. Synthesis of 5,17-bis(4-iminophenylferrocne)-25,27-dipropoxy-26,28-dihydroxy calix[4]arene 3

4-Ferrocenylaniline **2** (0.39 g, 1.42 mmol) in THF (30 ml) was added drop wise, over one hour, to a THF solution (150 ml) of 5,17-diformyl-25,27-dipropoxy-26,28-dihydroxy calix[4]arene **1** (0.4 g, 0.71 mmol) and a catalytic amount of *p*-toluenesulfonic acid, immediately the colour of solution changed to dark-violet and precipitation was formed. The mixture was refluxed for 24 h, then the mixture was filtrated and residue solid was washed with dry THF twice and dried in vacuum. Yield: 0.626 g (81%). IR (KBr, cm^{-1}) 3422b, 1655vs, 1603vs, 1526m, 1484w, 1431m, 1314m, 1277m, 1174s, 1032m, 910m, 816s, 771s. ^{1}H NMR (400 MHz, DMSO-d_6): 9.74 (s, 2H, –HC=N–), 9.46 (s, 2H, –OH), 7.80 (s, 4H, ArH of calixarene core), 7.62 (d, 4H, *J*=8.42 Hz, ArH), 7.21 (d, *J*=8.42 Hz, 4H, ArH), 7.11 (d,

Table 4
Extraction percentage of metal nitrates by **2** and **4**

No	[L]/[cation]	Ni^{2+}	Co^{2+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Cd^{2+}
2	1	4.46	16.48	5.81	8.88	11.77	8.75
	10	1.27	23.52	5.24	44.2	11.77	29.88
4	1	<1	<1	3.96	10.44	13.47	15.88
	10	<1	<1	30.47	48.78	47.37	40.12

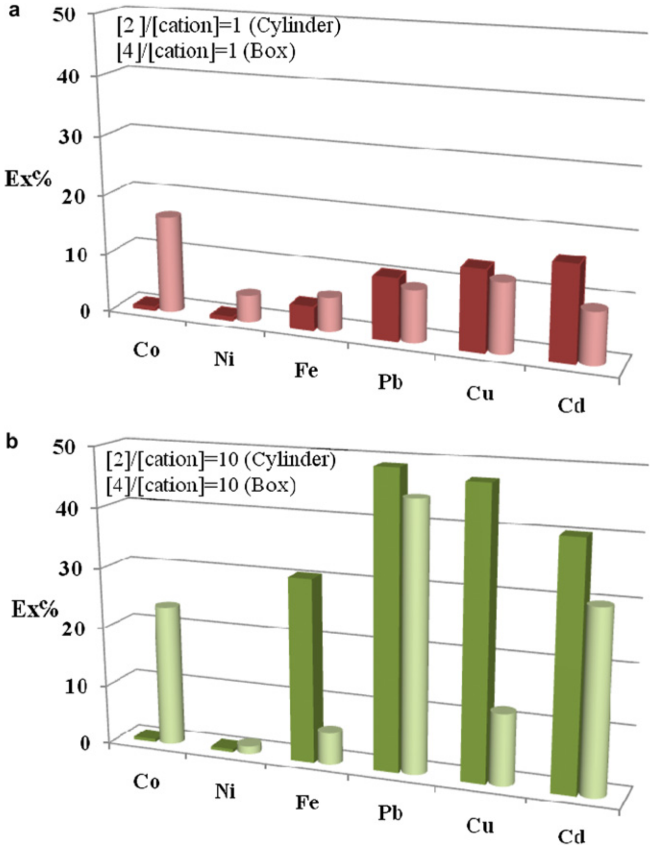


Figure 5. Extraction percentage of the metal nitrates with **2** and **4** at 25 °C: (a) [L]/[cation]=1, (b) [L]/[cation]=10 (L=**2** and **4**).

J=7.6 Hz, 4H, ArH of calixarene core), 6.83 (t, *J*=7.6 Hz, 2H, ArH of calixarene core), 4.79 (s, 4H, HFc), 4.37 (s, 4H, HFc), 4.19 (d, *J*=13 Hz, 4H, $ArCH_2Ar$), 4.01 (s, 10H, HFc), 3.99 (d, *J*=6.2 Hz, 4H, $-OCH_2-$),3.65 (d, *J*=13 Hz, 4H, $ArCH_2Ar$), 1.98–2.04 (m, 4H, $-OCH_2CH_2-$), 1.30 (t, *J*=7.28 Hz, 6H, $-OCH_2CH_2CH_3$). Elem. Anal. Calcd for $C_{68}H_{62}O_4N_2Fe_2\cdot 3CHCl_3$: C, 59.14; H, 4.51; N, 1.94. Found: C, 58.83; H, 5.01; N, 2.26. ESIMS: *m*/*z* 1083.2. Decomp.: 235 °C.

4.3. Synthesis of 5,17-bis(4-aminophenylferrocne)-25,27-dipropoxy-26,28-dihydroxy calix[4]arene 4

To a stirred suspension of compound **3** (0.700 g, 0.646 mmol) in THF (250 ml) under dry N_2 gas was added $NaBH_4$ (0.123 g, 3.23 mmol) in three steps at room temperature. Then, the reaction mixture was refluxed for 3 h. During the reflux, the colour of **3** disappeared slowly and finally an orange solution was obtained. The solution was filtrated and the filtrate was evaporated under reduce pressure. The residue was dissolved in CH_2Cl_2 (50 ml) and to the solution was added NaOH 1 M. The organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent, the crude product was recrystalized in MeOH–CH_2Cl_2 and an orange product was obtained. Yield: 0.467 g (66%). IR (KBr, cm^{-1}) 3382b, 3086w, 2960w, 1612s, 1530s, 1459s, 1315w, 1259s, 1200w, 1090s, 809 Vs, 488s. ^1H NMR ($CDCl_3$, 400 MHz) 8.52 (s, 2H, –NH–), 7.32 (d, *J*=8.5 Hz, 4H, Ar–H), 7.07 (s, 4H, Ar–H of calixarene core), 6.95 (d, *J*=7.5 Hz, 4H, Ar–H of calixarene core), 6.79 (t, *J*=7.5 Hz, 2H, Ar–H of calixarene core), 6.59 (d, *J*=8.5 Hz, 4H, Ar–H), 4.54 (s, 4H, $-CH_2-NH-$), 4.32 (d, *J*=12.8 Hz, 4H, $ArCH_2Ar$), 4.23 (s, 4H, HFc), 4.15 (s, 4H, HFc), 4.03 (s, 10H, HFc), 3.98 (t, *J*=6.2 Hz, 4H, $-OCH_2-$), 3.38 (d, *J*=12.8 Hz, 4H, $ArCH_2Ar$), 2.04–2.13 (m, 4H, $-OCH_2CH_2-$), 1.33 (t, *J*=7.4 Hz, 6H, $-OCH_2CH_2CH_3$). Elem. Anal. Calcd for $C_{68}H_{66}O_4N_2Fe_2\cdot 1.5CH_2Cl_2$: C, 68.73; H, 5.68; N, 2.31. Found: C, 68.67; H, 5.84; N, 2.76. ESIMS: *m*/*z* 1086.3. Decomp.: 215 °C.

4.4. Solvent extraction

A solution of compound **4** (2.5 ml, 1×10^{-3} M) in CH_2Cl_2 and an aqueous solution containing nitrate salt of metal cations Cu^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+} and Co^{2+} (5 ml, 1×10^{-3} M) were mixed and shaken in a stoppered glass tube with a magnetically stirred in a thermostatic water bath at 25 °C for 2 h and finally left standing for an additional 15 min. Then, the aqueous phase was separated and the concentration of metal ion remaining in the aqueous phase was determined by atomic absorption. The extraction percentage (*E*%) was calculated by the following expression:

$$(E\%) = \frac{A_0 - A}{A_0} \times 100$$

where A_0 and A are the initial and final absorbance of the metal ion before and after the extraction in aqueous phase, respectively. The extraction was repeated with compound **4** (3×10^{-3} M) in CH_2Cl_2 (2 ml) and 10 ml aqueous solution containing 3×10^{-4} M nitrate salts of metal Cations Cu^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+} and Co^{2+}.

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References and notes

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