Structural Selectivity of Calix[*m*]pyrroles[*n*]furans (*m* + *n* = 4) as Ionophores in Ag(I) Ion-Selective Electrodes *

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Abstract

A series of octamethylcalix[*m*]pyrroles[*n*]furans (*m* + *n* = 4), such as *trans*-octamethylcalix[2]pyrroles[2]furans (**L₁**), *cis*-octamethylcalix[2]pyrroles[2]furans (**L₂**) and octamethylcalix[1]pyrrole[3]furans (**L₃**) have been studied as sensors in liquid membrane ion-selective electrodes for Ag(I) ion. The electrode based on **L₁**, *trans*-N_2O_2 porphyrinogen, gave the best results with a wide working concentration range of $1.0 \times 10^{-1} - 1.0 \times 10^{-5.6}$ M and a Nernstian slope of 57.0 mV/decade. This electrode exhibited a fast response time of 30 s and high selectivity over a number of mono-, di- and tri-valent cations, with only Tl(I) and Hg(II) ion interferences. The effect of anion excluders on the performance of the membrane electrodes has been also studied. The electrode based on **L₁** showed no significant potential changes in the range 2.5 < pH < 7.5. The crystal structure of **L₃**, NO_3 porphyrinogen, was determined by single crystal X-ray analysis. The crystallographic analysis of **L₃** reveals that its structure is a saddle-shaped 1,3-alternate conformation with enough space to accommodate Ag(I) in the three dimensional cavity.

Introduction

The need for the determination of Ag(I) ion in clinical analysis such as [111]Ag-based radioimmunotherapy [1] as well as in separation from natural sources or waste materials has prompted development of a number of ionophores [2, 3, 4]. The devices used in this field are mainly based on crown ethers [5, 6], calixarenes [7, 8] and podands [9, 10] having sulfur/oxygen or sulfur/nitrogen atoms which can form stable complexes with heavy metal ions according to the hard and soft acid-base concept [11].

In contrast, only a few studies have been reported on the sulfur-free nitrogen-based ionophores in Ag(I) ion-selective electrodes [12, 13]. Calix[4]pyrroles are originally fully *meso*-substituted porphyrinogens which are stable macrocyclic species composed of four pyrrole rings linked by the sp^3 *meso* carbon atom. The fully alkylated porphyrinogens which have a more rigid structure than calixarene would be better considered as calixpyrroles.

The calix[4]pyrroles have been recently exploited as strong binders of transition metals in their tetraanionic forms [14–18], and as molecular hosts for anionic species [19–21], which can form hydrogen bonding *via* NH moieties [19]. The binding properties of the calix[4]pyrroles depend on the geometrical structure, which may be conformationally mo-bile in comparison with the behavior presented by closely related calix[4]arenes. Four conformations of calix[4]arenes have been distinguished and labeled as *cone, partial cone, 1,2-alternate* and *1,3-alternate* by Gutsche *et al.* [22]. The conformational differences of calix[4]arenes may explain the origin of the structural selectivity by the discrimination of guest ion species. For example, the *cone* conformation of calix[4]pyrroles binds the anion species such as fluoride *via* hydrogen bonding [19].

Recently, we first reported that the electrode based on the *meso*-tetracyclohexylcalix[4]pyrroles exhibited excellent electrochemical response characteristics and selectivity for Ag(I) ion [13]. We believe that the calix[4]pyrroles in the 1,3-alternate conformation would be expected to form a bidentate complex with Ag(I) ion specifically *via* two nitrogen atoms.

In the extension of this work, we have utilized the calix[*m*]pyrroles[*n*]furans (*m* + *n* = 4), such as *trans*-octa-methyl-calix[2]pyrroles[2]furans (**L₁**), *cis*-octamethyl-calix[2]pyrroles[2]furans (**L₂**), and octamethyl-calix[1] pyrrole[3]furans (**L₃**) (Figure 1) as sensing materials in ion-selective electrodes to investigate the relationship between Ag(I) ion selectivity and the conformation of the porphyrinogen substituents. Undoubtedly, the cation selectivity is related to the structures of the free ligand or complexes. We have also carried out an X-ray crystal structure determination of uncomplexed **L₃** and here describe the results.

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* **Supplementary Data** related to this article are deposited with the British Library as Supplementary Publication No. SUP 82284 (43 pages).
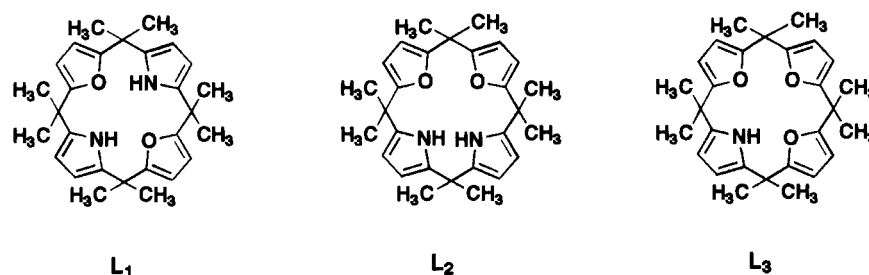
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Figure 1. The chemical structures of calix[*m*]pyrroles[*n*]furans ($m + n = 4$), **L₁**–**L₃**.

Table 1. Composition of PVC membranes and response characteristics of various types of Ag(I)-ISEs

Electrode type	Membrane mass composition/wt%				Slopes (mV/decade)	Linear region (M)	Detection limit (M)
	Plasticizer	PVC	Neutral carrier	KT*p*ClPB*			
1	NPPE (65.3)	33.3	**L₁** (1.60)	29.6	57.0	10^{-1}–10^{-5}	$10^{-5.6}$
2	NPOE (66.1)	33.6	**L₁** (1.60)	29.4	56.3	10^{-1}–10^{-5}	$10^{-5.3}$
3	TEHP (65.5)	33.5	**L₁** (1.60)	29.8	55.1	10^{-1}–10^{-4}	$10^{-4.5}$
4	BEHA (65.4)	33.5	**L₁** (1.58)	30.2	56.6	10^{-1}–10^{-5}	$10^{-5.3}$
5	NPPE (65.0)	33.4	**L₂** (1.57)	30.0	53.8	10^{-2}–10^{-6}	$10^{-6.0}$
6	NPPE (68.2)	33.6	**L₃** (1.62)	28.9	47.7	10^{-1}–10^{-5}	$10^{-5.4}$

*mole% with respect to the ionophore.

Experimental

Materials

L₁–**L₃** were prepared in 4 or 5 steps using a known procedure based on the substitution of furan by pyrrole in the octamethyl porphyrinogen skeleton [23, 24]. Poly(vinyl chloride) (PVC, secondary standard), and tris(2-ethylhexyl)phosphate (TEHP) were purchased from Aldrich, bis(2-ethylhexyl)adipate (BEHA), *o*-nitrophenyloctylether (*o*-NPOE) and 2-nitrophenyl ether (NPPE) from Eastman Kodak, and potassium tetrakis (*p*-chlophenyl)borate (KT*p*ClPB, purum p.a.) from Fluka. The electrolyte solutions for the potentiometric measurements were prepared by dissolving the nitrate salts of high purity (Merck, pro analysis) with doubly distilled water. Tetrahydrofuran was dried and purified by refluxing over sodium metal, followed by distillation under a N₂ atmosphere.

Electrode preparation and emf measurements

The electrode membranes of PVC matrix type were prepared according to the previously described procedure [25, 26]. The membrane compositions were basically 1.5–5 wt% of ionophore, ∼33 wt% of PVC, ∼65 wt% of plasticizer (NPPE, NPOE, BEHA, and TEHP) and an adequate amount of KT*p*ClPB (∼30 mol% with respect to the ionophore) was added as anionic sites.

Table 1 lists the membrane compositions with the variation of ionophore contents and plasticizers. The membrane components were dissolved in freshly distilled tetrahydrofuran which was then poured into a glass ring (d = 3.5 cm) fixed on a glass plate. After standing for 24 h, a homogeneous PVC membrane of ∼0.2 mm thickness was obtained. The prepared membranes were cut as a circle with a diameter of 3.5 mm, which were mounted in a lab-made Ag/AgCl electrode body or Philips IS-561 electrode body. After filling internal solution of 1.0×10^{-2} M AgNO₃, the electrodes were conditioned for 24 h by soaking in a 10^{-2} M AgNO₃ solution.

The electrochemical cell for the EMF measurements was as follows:

Ag;AgCl/3M KCl/0.3M NH₄NO₃/sample solution/ membrane/10^{-2}M AgNO₃/AgCl;Ag
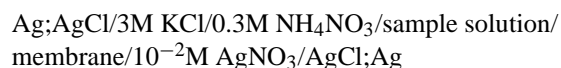
EMF was measured relative to a Ag–AgCl double-junction reference electrode (Orion 90-02-00) using a digital pH/potentiometer (Orion 720A). All measurements were carried out at 25.0 ± 0.1 °C. Potentiometric selectivity coefficients ($K_{\text{Ag/M}}^{\text{pot}}$) were determined by the separate solution method recommended by IUPAC with 10^{-2} M aqueous solutions of the nitrates using the Nicolsky–Eisenman equation [27].

X-ray crystallography

A crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated MoK$_\alpha$ (λ = 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. Data collection was performed at room temperature. The two-dimensional diffraction images were collected, each of which was measured for 30 s. The frame data were processed to give structure factors using the program SAINT [28]. Crystallographic data and additional details of the data collection and refinement are summarized in Table 2. The structure was solved by direct methods and refined by full matrix least squares against F^2 for all data using SHELXTL software [29]. All non-H atoms were refined with anisotropic displacement parameters.
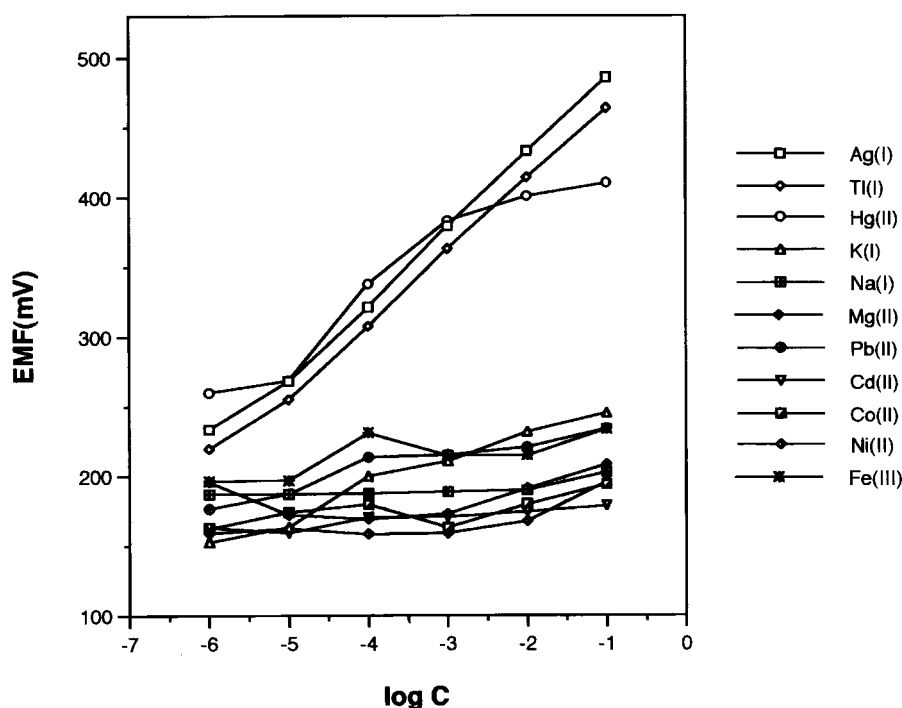
Figure 2. Calibration curves for the Ag(I)-ISE based on L_1 in PVC/NPPE membrane with KTpClPB (electrode type **1**).
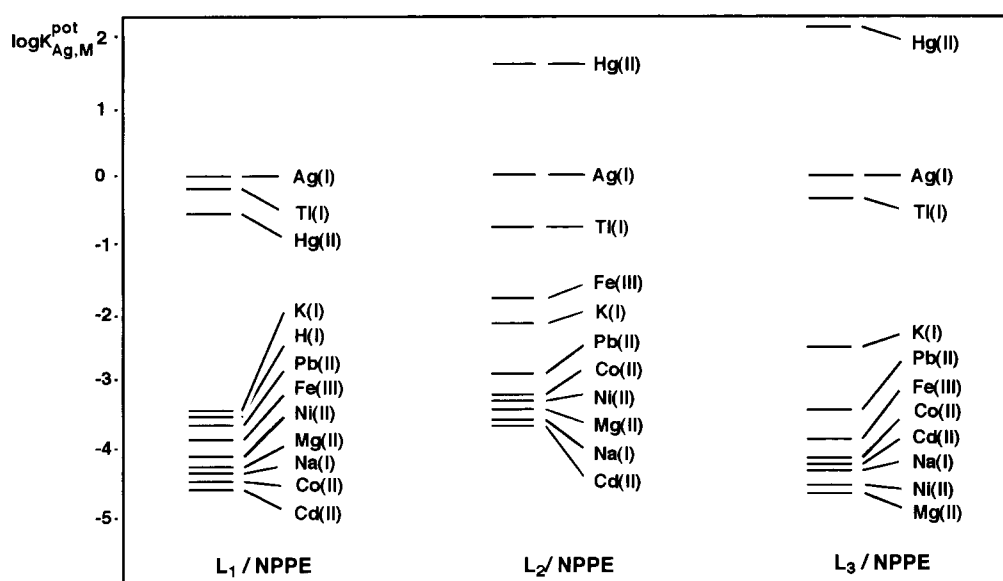

Figure 3. Comparison of selectivity coefficients for Ag(I)-ISEs based on L_1–L_3 with NPPE as plasticizer.

Results and discussion

Silver(I) ion-selective electrodes

The electrochemical properties of PVC membrane Ag(I) ion-selective electrodes (electrode type **1–6**) based on L_1–L_3 were tested as a function of membrane composition and the results are compiled in Table 1. As shown in Table 1, the effect of variation of ionophores on the electrode performance was significant. The order of ionophores drawn from the Nernstian slopes and the range of linearity including detection limit of the electrodes was $L_1 > L_2 > L_3$. The electrode type **1** incorporating L_1 gave the best response of 57.0 mV/dec in the limited range of 10^{-1}–$10^{-5.6}$

M, while L_2 and L_3 exhibited sub-Nernstian responses of 53.8 and 47.7 mV/decade over a narrow or similar working concentration range of 10^{-2}–$10^{-6.0}$ M and 10^{-1}–$10^{-5.4}$ M, respectively. This order is in agreement with the solvent extraction data using 1,2-dichloromethane as the extracting solvents reported by us [30].

In Figure 2, the potential responses of electrode type **1** as a function of concentration for a wide variety of ions, including alkali, alkaline earth, transition, and heavy metal are shown. All of the ions under investigation except Ag(I), Hg(II) and Tl(I) show negligible responses.

The potentiometric selectivity coefficients for Ag(I) with respect to other cations are given in Figure 3. Consequently,
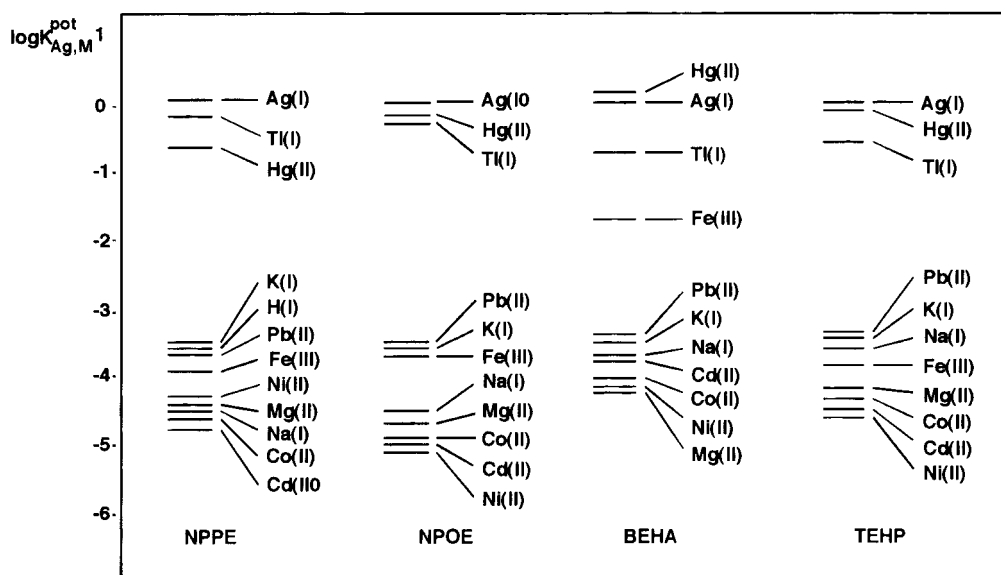
$$logK^{pot}_{Ag,M}$$

Figure 4. Effect of plasticizers on Ag(I)-selectivity for L_1-based PVC membrane electrodes.
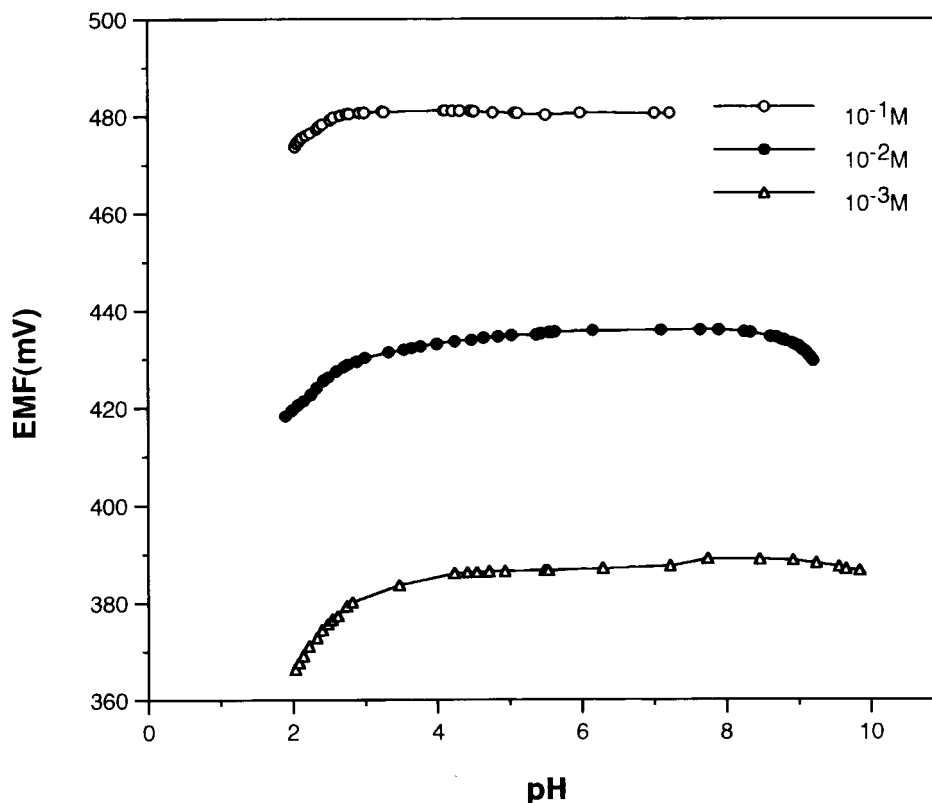

Figure 5. Effect of pH on the EMF response for Ag(I)-ISE based L_1 (electrode type 1). HNO_3 and KOH were used to change the pH value.

L_1 was demonstrated to show excellent selectivity towards Ag(I) over a number of metal ions except Tl(I) and Hg(II). However, it was found that the electrode using L_2, the *cis*-type isomer of L_1, exhibited worse selectivity than the electrode using L_1 or L_3.

Until now the molecular structure of L_1 or L_2 was not known. In this work, we reveal the molecular structure of L_3 which should be similar to L_1 or L_2. The crystal structure of L_3 shown in Figure 5 (see the later discussion), exhibits a saddle-shaped 1,3-alternate conformation wherein adjacent heterocycle rings are oriented in opposite directions. As a hypothesis we can assume that similar structures would be true for L_1 and L_2. The electrode behaviors described could be explained by the difference of the structural arrangement of the donor atoms in each ionophore. It is known that the Ag(I) ion exhibits strong affinity toward nitrogen or sulfur atoms and shows a remarkable preference for linear coordination. Therefore, the Ag(I) ion would be in an advantageous linear coordination environment of two nitrogen atom in the
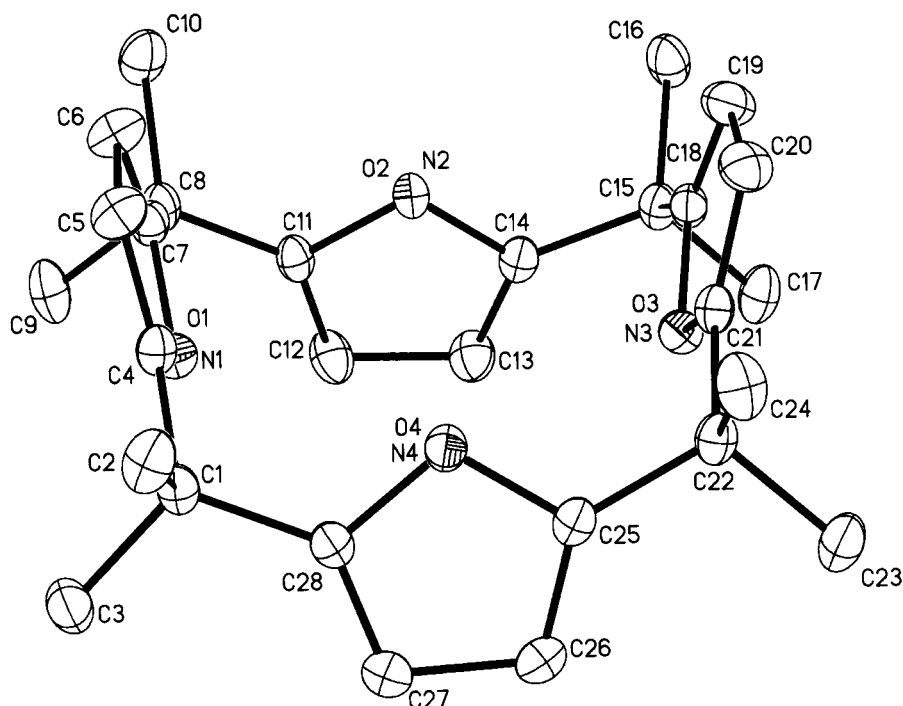
Figure 6. ORTEP plot of **L₃**.

Table 2. Crystal data and structure refinement for **L₃**

Formula	$C_{28}H_{33}NO_3$
M	431.55
T, K	296(2)
Crystal system,	Tetragonal
space group	P4₃
a/Å	10.0823(9)
b/Å	10.0823(9)
c/Å	24.318(3)
V/Å^3	2472.0(4)
Z	4
Dc/g cm^{-3}	1.160
μ/mm^{-1}	0.074
F(000)	928
Crystal size, mm	$0.06 \times 0.18 \times 0.26$
Theta range for data collection, deg	2.02 to 28.29
Limiting indices	$-8 \leq h \leq 13$
	$-12 \leq k \leq 13$
	$-31 \leq l \leq 32$
Reflections collected	16356
Independent reflections	5865 (R_{int} = 0.0404)
Completeness to theta, %	99.2 (=28.29°)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5865/1/289
GOF on F^2	1.021
Final R_1, wR_2	
indices [$I > 2\sigma(I)$]	0.0484, 0.1161
(all data)	0.0781, 0.1295
Largest diff. peak and hole/e Å^3	0.164, −0.169

Table 3. Selected bond lengths [Å], bond angles [°], and dihedral angles [°] for **L₃**

Bond lengths			
O(1)–C(4)	1.376(2)	O(1)–C(7)	1.380(2)
C(7)–C(8)	1.510(3)	C(8)–C(11)	1.503(3)
O(2)–C(11)	1.380(2)	O(2)–C(14)	1.377(2)
C(14)–C(15)	1.506(3)	C(15)–C(18)	1.507(3)
O(3)–C(18)	1.381(2)	O(3)–C(21)	1.376(2)
C(21)–C(22)	1.502(3)	C(22)–C(25)	1.504(3)
O(4)–C(25)	1.374(2)	O(4)–C(28)	1.376(2)
C(1)–C(28)	1.511(3)	C(1)–C(4)	1.503(3)

Bond angles			
C(4)–O(1)–C(7)	107.75(17)	C(11)–C(8)–C(7)	110.11(18)
C(14)–O(2)–C(11)	107.68(17)	C(14)–C(15)–C(18)	110.22(17)
C(21)–O(3)-C(18)	108.13(17)	C(21)–C(22)–C(25)	110.56(17)
C(25)–O(4)–C(28)	108.15(17)	C(4)–C(1)–C(28)	110.21(17)

Dihedral angles		
dihedral angles between NO₃ core		
and the A, B, C, D ring	A	102.4
	B	78.7
	C	104.7
	D	74.1
dihedral angle between AB		87.5
dihedral angle between AD		93.1
dihedral angle between BC		92.9
dihedral angle between CD		95.8

A, B, C, and D define the furan and pyrrole rings containing O(1), N(1); O(2), N(2); O(3), N(3); and O(4), N(4) atoms, respectively.

trans-pyrrole ring of **L₁**, while the two oxygen atoms in the furan ring would have the role of weakly binding spectators.

The poor sensitivity or selectivity of **L₂** or **L₃** toward Ag(I) ion could be explained because only one strong bind-

ing is available between Ag(I) and nitrogen. Hg(II) gives the most severe interference for the membrane electrodes based on L_1–L_3 as well as the thia crown ether reported previously [5–8].

In addition, the 1,3-alternate conformation seems particularly appropriate for excluding other transition metal ions with higher coordination numbers in the presence of weakly binding electron-poor oxygens in the furan ring [31]. In fact, the metal ions larger (Tl(I), K(I), Pb(II) and Sr(II)) or smaller (Na(I), Hg(II), Ca(II), Cd(II), Zn(II), Cu(II), Mg(II), Co(II) and Ni(II)) [32] than Ag(I) (r_{ion}; 1.29 Å) [32] in terms of ionic radii exhibit very weak or almost no affinity, except for Hg(II), and Tl(I) as shown in Figure 3. These results strongly suggest that the selectivity for Ag(I) ion is not a matter of the cavity size of the calix[4]pyrroles/furans macrocycles because there is enough space to accommodate any of the metal ions tested in this study, but depends on the structural arrangement of appropriate donor atoms, such as nitrogen to form the linear coordination.

An investigation of the effect of variation of plasticizers in ion-selective electrodes incorporating L_1 was accomplished and the results are summarized in Figure 4. Since the nature of plasticizers affects the dielectric constant of the membrane phase, the ability to form complexes, and the mobility of the ligands and their complexes, the role of plasticizers is important in determining the electrochemical characteristics and selectivity of the membrane electrodes [33]. It was found that the membrane electrode based on NPPE or NPOE ($\epsilon = 24$; ϵ is the dielectric constant), which have relatively high dielectric constants, enhanced selectivity over Hg(II) and provided a better Nernstein slope and linear range than those of BEHA and TEHP ($\epsilon = 4$). As seen in Table 1 and Figure 4, the electrode based on L_1/NPPE membrane provided the best result.

The influence of pH on the response of the electrode based on L_1 was examined in three different Ag(I) concentration of 10^{-1}, 10^{-2}, and 10^{-3}M over a pH range from 2.0 to 10.0. The response remained constant from pH 2.5 to 7.5, but the response was reduced at pH below 2.5 (Figure 5). At lower pH, the decrease of complexing ability due to the protonation of the ionophore may cause the lower response, while a precipitate was formed at pH > 7.5.

All of the electrodes under investigation exhibited a fast response time of 30 s. The membrane could be used repeatedly within at least two weeks if stored in distilled water and kept free of contamination. After lengthy storage, the electrode was reconditioned in 10^{-2} M Ag(I) solution for 1 day before use. After two weeks, the slope was decreased gradually.

It can be concluded that the selectivity towards Ag(I) exhibited by the calix[*m*]pyrroles[*n*]furans is not due to the size of the cavity, but depends on the geometrical arrangement of the nitrogen coordination centers in the porphyrinogen skeleton and to its tendency for linear coordination. From this point of view, the best selectivity and sensitivity of the calix[2]pyrroles[2]furans (L_1)-based membrane electrode for Ag(I) among its derivatives examined can be well understood.

X-ray crystal structure of L_3

The cation selectivity seems to be related to the structures of the free ligands or complexes, and the crystal structure determination was undertaken as a part of understanding of the sensing system. Recently the crystal structures of the calix[4]pyrroles, N_4 derivatives of L_1–L_3, with the 1,3-alternate conformation as well as the anion complexes were reported [19]. The Li(I) and Na(I) complex of L_2 [34] were known to be flatted partial cone or chair conformation. But the crystal structures of L_1–L_3 and their Ag(I) complexes have not been reported to our knowledge.

The crystals of L_3 suitable for X-ray study were grown by slow evaporation of an acetone/dichloromethane solution. The ligand L_3 crystallizes in the tetragonal space group P4$_3$. The representative bond lengths, bond angles, and dihedral angles for L_3 are compiled in Table 3. Since the individual identifications of the N and O atoms in the pyrrole and furan rings were not possible in this case, these four hetero atoms were treated as disordered with occupancies of 0.25 and 0.75, respectively, in accordance with the atomic fraction of NO_3.

The crystallographic analysis of L_3 reveals that its structure is a saddle-shaped 1,3-alternate conformation; the hetero rings are tilted up and down alternatively relative to the NO_3 core (Figure 6). The NO_3 core forms a square plane and the average displacement of the core atoms from the mean plane is *ca.* 0.14 Å. The cross section of the cavity measures about 25 Å^2, and there is enough space to accommodate a Ag(I) in the three dimensional cavity. A, B, C, and D define the furan and pyrrole rings containing O(1), N(1); O(2), N(2); O(3), N(3); and O(4), N(4) atoms, respectively. Two rings A and C on the same side are slightly out of perpendicular with respect to the NO_3 core plane (dihedral angle 102.4° and 104.7°), while the B and D rings in the opposite direction form dihedral angles of 78.7° and 74.1°, respectively. So, the two pairs of hetero atoms on both sides direct towards the inside of cavity obliquely.

The structural features of L_3, such as the 1,3-alternate conformation are very similar to those found in the calix[4]pyrroles previously reported [19]. We attempted to obtain crystals of L_1, L_2 and Ag(I) complexes with L_1–L_3 but without success.

Supplementary material deposited comprises atomic and thermal parameters, interatomic distances and angles, torsional angles, stereo view and structure factors.

Conclusions

Polymeric liquid membrane electrodes based on octamethylcalix[*m*]pyrroles[*n*]furans ($m + n = 4$), such as trans-octamethylcalix[2]pyrroles[2]furans (L_1), *cis*-octamethylcalix[2]pyrroles[2]furans (L_2) and octamethylcalix[1]pyrrole[3]furans (L_3) were prepared and the characteristics of the electrodes were tested towards silver(I) ion sensing. The electrode based on L_1, *trans*-N_2O_2 porphyrinogen, gave the best results in terms of the working concentration range, Nernstian slope and selectivity towards

interfering ions. The best performance of the **L₁**-based electrode can be understood since the selectivity towards Ag(I) exhibited depends strongly on the geometrical arrangement of the nitrogen coordination centers in the porphyrinogen skeleton and to its tendency for linear coordination.

Acknowledgement

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