

# The synthesis of some pyridyl functionalized calix[4]arenes as the sensor molecule for silver ion-selective electrodes

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Xianshun Zeng,<sup>a</sup> Linhong Weng,<sup>\*a</sup> Langxing Chen,<sup>b</sup> Xuebing Leng,<sup>b</sup> Hongfang Ju,<sup>b</sup> Xiwen He<sup>b</sup> and Zheng-Zhi Zhang<sup>\*a</sup>

<sup>a</sup> State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China

<sup>b</sup> Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China

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25,27-Bis(6-hydroxymethyl-2-pyridylmethoxy)-26,28-dipropoxycalix[4]arene **3**, its derivative **4** and 25,27-bis-(6-diphenylphosphinomethylpyridylmethoxy)-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene **6** have been synthesized and characterized by <sup>1</sup>H NMR spectroscopy and elemental analysis. The X-ray crystallographic structure was obtained for **4** and shows an infinite sheet aggregate through intermolecular hydrogen bonds and bridged methanol molecules in the solid state. Ion-selective electrodes (ISE) for Ag<sup>+</sup> containing **3**, **4** and **6** as neutral ionophores in a PVC membrane were prepared and their selectivity coefficients for Ag<sup>+</sup> ( $K_{Ag,M}^{pot}$ ) were investigated against other alkali metal, alkaline-earth metal, lead, ammonium ions and some transition metal ions using the mixed-solution method. These ISEs showed excellent Ag<sup>+</sup> selectivity towards most of the interfering cations examined, except for Hg<sup>2+</sup> which has a relatively low interference ( $\log K_{Ag,M}^{pot} \leq -1.5$ ).

## Introduction

Three dimensional molecular calixarenes have enjoyed widespread use in various areas of science and technology ever since the first efficient preparation of *p-tert*-butylcalixarenes by Gutsche.<sup>1</sup> One of their most successful applications is in analytical chemistry. Calixarenes are useful for separation, enrichment, and analyses of ionic species.<sup>2</sup> In particular, the ion-selective electrode (ISE) is the most important target in analytical applications.<sup>3,4</sup> To improve or enhance the ion selectivities of calixarenes, a great deal of effort has been devoted to the design and synthesis of novel functionalized calixarenes in recent years.<sup>5,6</sup> In fact, a number of calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been employed in the studies of ISEs sensitive to sodium ion,<sup>7–11</sup> potassium ion,<sup>12,13</sup> caesium ion,<sup>13–16</sup> thallium<sup>17</sup> and lead ion.<sup>18</sup>

For a long time, silver ion has been analyzed quantitatively by using crystal membrane Ag<sup>+</sup>-ISEs made from insoluble argentiferrous salt in water.<sup>19,20</sup> Over the past decade, increasing attention has recently been focused on neutral ionophore-type Ag<sup>+</sup>-ISEs,<sup>21–33</sup> because this type of ISE often shows better selectivity than the traditional solid-state electrode. Since thiocrown ethers were employed in the first neutral ionophore-type Ag<sup>+</sup>-ISEs which showed very high Ag<sup>+</sup>-selectivity against alkali metal ions,<sup>29</sup> thio-ethers and thio-pendant ethers have been a very important class of ionophores for Ag<sup>+</sup>-ISEs. More recently, we also demonstrated that calix[4]arene based polythia compounds showed very high Ag<sup>+</sup>-selectivities against alkali metal, alkaline-earth metal, ammonium, lead ions and most of the transition metal cations.<sup>34,35</sup> In this context, nitrogen and phosphorus atoms as soft donors are also expected to interact with soft Ag<sup>+</sup> ion selectively.

We wish to report the syntheses and characterization of 25,27-bis(6-hydroxymethyl-2-pyridylmethoxy)-26,28-dipropoxycalix[4]arene **3**, its 5,11,17,23-tetra-*tert*-butyl derivative **4** and 25,27-bis(6-diphenylphosphinomethyl-2-pyridylmethoxy)-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene **6** (Scheme 1) and their selectivity towards Ag<sup>+</sup> behavior monitored by electromotive force measurements of polymer membrane electrodes. Comparison of the ISE behavior of **3**, **4** with

**6**, together with the X-ray crystallographic structure of **4**, will serve to further our understanding of the structure–selectivity relationship in the Ag<sup>+</sup>-ISEs.

## Results and discussion

### Syntheses

The syntheses of calix[4]arenes **3**, **4**, and **6** were accomplished in several steps from the known compounds **1** and **2** (Scheme 1). Treatment of **1** and **2** with 6-hydroxymethyl-2-bromomethylpyridine in the presence of NaH in THF–DMF afforded **3** and **4** in isolated yields of 68 and 81%, respectively. Compound **4** reacted with SOCl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature to give **5** in 91% yield. Reaction of **5** with Ph<sub>2</sub>PLi in THF at –5 °C yielded compound **6**. Compounds **3–6** were conventionally characterized by <sup>1</sup>H NMR spectra. Compounds **3–6** each have two doublets assigned to ArCH<sub>2</sub>Ar protons at *ca.* 4.30 and 3.10 ppm proving that they adopt cone conformations.

### Ag<sup>+</sup> selectivity

The Ag<sup>+</sup> selectivities of compounds **3**, **4** and **6** were evaluated by the potentiometric selectivity coefficients ( $K_{Ag,M}^{pot}$ ) determined for polymer membranes containing these ionophores. The polymer membrane was composed of PVC as the matrix, dibutyl phosphate (DBP) as the membrane solvent, and 6-substituted pyridyl functionalized calix[4]arene as the ionophore. The membranes also contained 100 mol% potassium tetrakis(*p*-chlorophenyl)borate (KTCIPB) relative to the ionophore for the purpose of reducing membrane resistance and suppressing permeation of counteranions in the aqueous phase into the membrane phase. The potentiometric selectivity coefficients for Ag<sup>+</sup>, which were determined by a mixed solution method or for strong interfering ions by the solution separation method, are illustrated in Table 1. The selectivity coefficient ( $K_{Ag,M}^{pot}$ ) represents the preference of the ISE (or PVC membrane) containing the pyridyl functionalized calix[4]arene for Ag<sup>+</sup> over the other cations. Thus, the coefficient  $K_{I,J}^{pot}$  defines the ability of an ISE (or membrane) to distinguish different ions

**Table 1** Selectivity coefficient ( $\log K_{I,J}^{\text{pot}}$ ,  $I = \text{Ag}^+$ ) of the electrodes based on ionophores **3**, **4** and **6**

Ion	$K_{I,J}^{\text{pot}}$		
	<b>6</b>	<b>4</b>	<b>3</b>
$\text{Ag}^+$	0	0	0
$\text{Na}^+$	-4.3	-4.0	-3.9
$\text{K}^+$	-4.3	-4.1	-4.0
$\text{NH}_4^+$	-4.2	-4.0	-4.0
$\text{Ca}^{2+}$	-4.5	-4.5	-4.5
$\text{Mg}^{2+}$	-4.5	-4.4	-4.5
$\text{Cu}^{2+}$	-4.6	-4.5	-4.6
$\text{Zn}^{2+}$	-4.5	-4.4	-4.5
$\text{Ni}^{2+}$	-4.4	-4.5	-4.5
$\text{Cd}^{2+}$	-4.5	-4.4	-4.4
$\text{Pb}^{2+}$	-3.5	-3.4	-3.4
$\text{Hg}^{2+}$	-1.8	-1.6	-1.5

under the same conditions. The smaller the  $K_{I,J}^{\text{pot}}$  value, the greater the electrode preference for the primary ion ( $I^+$ ) over the interfering ion ( $J^+$ ).

As can be seen from Table 1, the polymer membranes containing **3**, **4** and **6** gave good selectivity for  $\text{Ag}^+$  ( $\log K_{I,M}^{\text{pot}} \leq -3.4$ ) against most of the interfering cations examined (*i.e.*,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$ ), except for  $\text{Hg}^{2+}$ . It is interesting to note that, despite the incorporation of different heteroatoms, ionophores **3**-, **4**- and **6**-based ISEs showed similar characteristic ion selectivity tendencies. The performance of the ISEs discussed here is generally superior to that displayed by the conventional  $\text{Ag}_2\text{S}$ -based electrode and they are satisfactory for use as  $\text{Ag}^+$ -ISEs. The fact that the polymer membrane containing **6** gave lower  $\log K_{\text{Ag},M}^{\text{pot}}$  values against  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{Hg}^{2+}$  than those of **3**- and **4**-based ISEs and similar  $\log K_{\text{Ag},M}^{\text{pot}}$  values against  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  means that **6**-based ISE primarily possesses high  $\text{Ag}^+$  selectivity and only weakly responds to alkaline-earth metal ions (*i.e.*,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$ ). One possible explanation is that hard divalent cations possessing high hydration energies cannot interact strongly with nitrogen moieties in the ionophore, while less heavily hydrated soft cations *e.g.*  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  coordinate to soft nitrogen donors. Similarly, the soft phosphorus donors may assist the interaction with  $\text{Ag}^+$ , thus enhancing the  $\text{Ag}^+$  selectivity. This is proved by the small low field shift observed in  $^{31}\text{P}$  NMR spectra. In the  $^{31}\text{P}$  NMR spectra, the chemical shift of free ligand **6** is at 28.95 ppm, while for **6** coordinated with  $\text{Ag}^+$ , the  $^{31}\text{P}$  NMR signal is at 29.75 ppm under the same conditions. On the other hand, the hydroxys in **3** and **4** act as hard donors which may enhance the ability of ionophores **3** and **4** to coordinate to hard cations, which leads to the  $\log K$  values of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  being slightly higher than those of **6**-based ISEs. The oxygen atoms acting as hard donors to  $\text{Na}^+$  and  $\text{K}^+$  can also be explained by results given in the literature.<sup>25</sup> These results show that for ionophores containing sulfur atoms, the presence of ester groups close to sulfur donors greatly enhances the interference of  $\text{Na}^+$  and  $\text{K}^+$

towards  $\text{Ag}^+$  in the ISEs. In contrast, ionophores usually gave fairly good  $\text{Ag}^+$ -selectivity over  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  in the absence of oxygen atoms close to sulfur or nitrogen atom donors.<sup>26,34</sup>

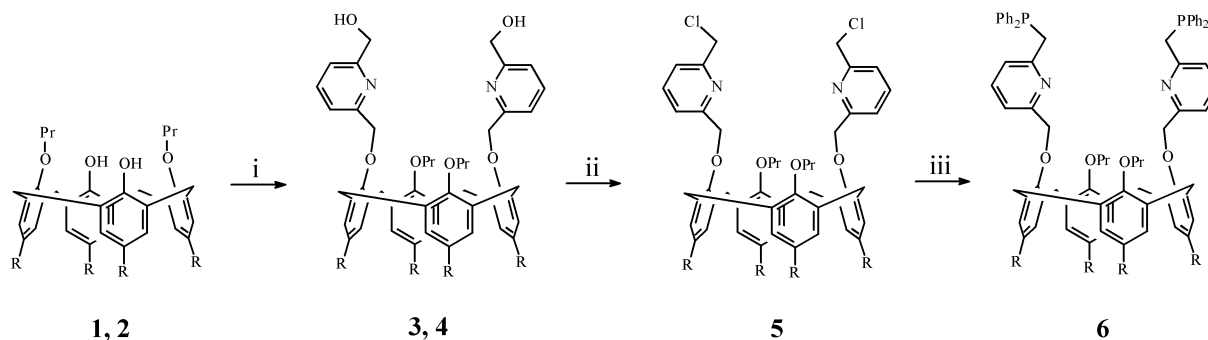
Generally speaking, free  $\text{Hg}^{2+}$  only exists in strong acidified aqueous solution ( $\text{pH} < 2$ ), while at  $\text{pH} > 2$ ,  $\text{Hg}^{2+}$  usually exists in the form of  $\text{Hg}(\text{OH})^+$ . The oxygen atoms located close to the coordinating atoms may assist the ligation of coordinating atoms with  $\text{Hg}(\text{OH})^+$  through  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. This might be the primary reason why  $\text{Hg}^{2+}$  usually shows some interference towards  $\text{Ag}^+$  in the ionophore-based ISEs. The four oxygen atoms on the lower rim of **3**, **4** and **6** and the two hydroxy oxygen atoms in **3** and **4** are close to the coordinating nitrogen atoms and might enhance the ligation of ionophores **3** and **4** towards  $\text{Hg}(\text{OH})^+$ . With the displacement of the two hydroxy groups by two diphenylphosphino groups in **6**, the interference of  $\text{Hg}(\text{OH})^+$  towards  $\text{Ag}^+$  was reduced in the ISEs. This hypothesis can also be proven by results given in the literature. These results show that for ionophores with ester groups close to sulfur donors the interference of  $\text{Hg}(\text{OH})^+$  towards  $\text{Ag}^+$  in the ISEs is significantly enhanced. Those ionophores without oxygen atoms close to the sulfur or nitrogen donors can greatly reduce this interference.<sup>26,34</sup>

Besides the differences described above, there are also small differences in the Nernstian slopes of **3**-, **4**- and **6**-based PVC membrane electrodes. The Nernstian slope of **6** ( $52.5 \text{ mV decade}^{-1}$ ) is higher than those of **3** ( $49.2 \text{ mV decade}^{-1}$ ) and **4** ( $49.8 \text{ mV decade}^{-1}$ ). This can be attributed to the limited participation of phosphorus atoms in the ligation of  $\text{Ag}^+$  in ionophore **6**.

The steric effect of the propyl groups in **4** may be evaluated approximately by the X-ray crystallographic structure shown in Fig. 1. Although the propyl groups in close proximity to the nitrogen donors cause some steric hindrance to the ligation with  $\text{Ag}^+$ , there is enough space around the nitrogen atoms to accommodate  $\text{Ag}^+$  and indeed good  $K_{\text{Ag},M}^{\text{pot}}$  values were obtained in the ISE experiments described above. Because the propyl group is hydrophobic, it may also enhance the  $\text{Ag}^+$ -selectivity over other highly hydrated interfering cations. Furthermore, if the propyl group strongly sterically hinders the interaction of nitrogen donors with the  $\text{Ag}^+$  cation, the other interfering cations would also experience similar unfavorable steric hindrance and so the net effect would be negligible. Taking into account the tendency of  $\text{Ag}^+$  to form 2–6 coordinate complexes,<sup>37</sup> the two nitrogen atoms must adopt a face-to-face orientation to coordinate with  $\text{Ag}^+$  in solution although the two nitrogen atoms are in a nearly opposite orientation in the solid state.

#### X-Ray structure of **4**

As can be seen from Fig. 2, the crystal structure of compound **4** is a unique infinite sheet aggregate formed *via* intermolecular  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds and bridged methanol molecules. Compound **4** adopts a pinched cone conformation (Fig. 1). The



**Scheme 1** Reagents and conditions: i, NaH, THF–DMF, 2-bromomethyl-6-hydroxypyridine, 80 °C; ii,  $\text{SOCl}_2$ ,  $\text{CH}_2\text{Cl}_2$ , rt; iii,  $\text{Ph}_2\text{PLi}$ , THF,  $-5^\circ\text{C}$ .

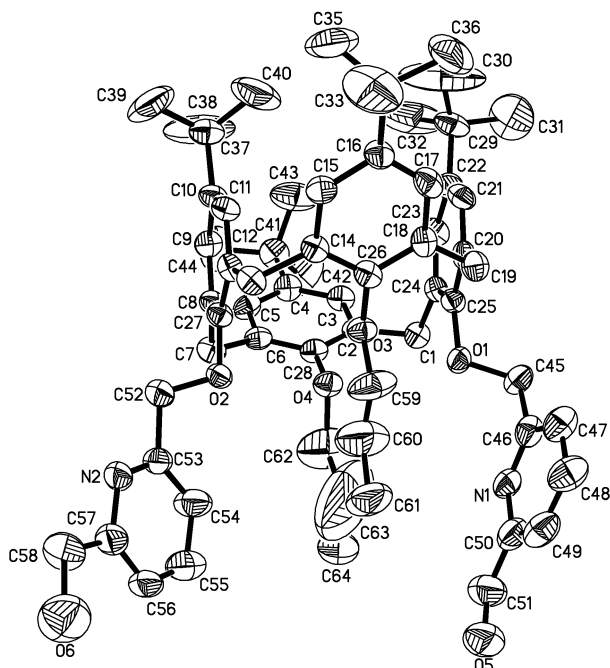


Fig. 1 The structure of compound 4.

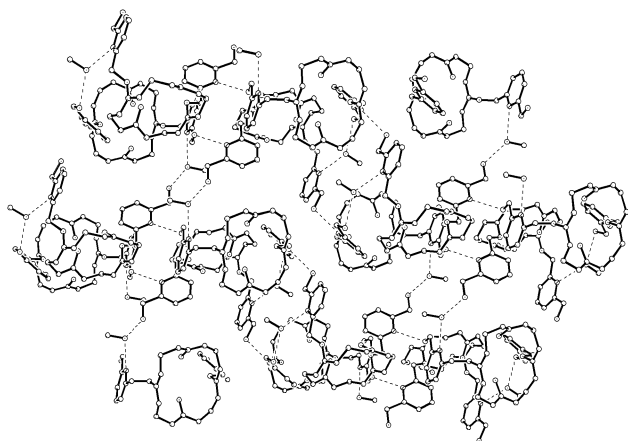


Fig. 2 The infinite sheet aggregate profile of 4·CH<sub>3</sub>OH. For clarity, C(3)–C(5), C(9)–C(11), C(15)–C(17), C(21)–C(23), C(29)–C(44) and all hydrogens have been omitted.

angles between the planes of the adjacent four arenes are 95.0, 95.4, 85.4 and 85.7°, respectively. The two opposite rings that are bonded to the pyridylmethoxy groups are almost parallel with an interplanar angle of 0.5°, while the other two rings tilt away from the calixarene cavity with an interplanar angle of 86.5°. This conformation causes O···O separations of 5.577 Å between O(1) and O(2), and 3.583 Å between O(3) and O(4). The O···O distances between adjacent phenolic oxygens are between 3.152 and 3.496 Å. The interplanar angle between the pyridine planes is 118.0°. The torsion angles of C(25)–O(1)–C(45)–C(46), O(1)–C(45)–C(46)–N(1), N(1)–C(50)–C(51)–O(5), C(27)–O(2)–C(52)–C(53), O(2)–C(52)–C(53)–N(2), N(2)–C(57)–C(58)–O(6) are 155.4, 79.2, 167.5, 179.0, 145.8 and 172.7°, respectively. The described geometric conformation of 4 and the intermolecular tail-to-tail O–H···N hydrogen bonds cause 4 to adopt a wave-like infinite linear aggregate along the *c* axis (Fig. 2). Further linear aggregates are assembled by bridging methanol molecules along the *b* axis which causes an infinite sheet aggregate of the calix[4]arene. The distances of O(5)···N(2), H(5B)···N(2), O(7)···N(1), O(6)···O(7), H(45B)···O(7) and H(6A)···O(7) are 2.770, 2.535, 2.905, 2.882, 2.895 and 2.078 Å respectively, which indicate that the intermolecular hydrogen bonds are fairly strong.

## Conclusions

25,27-Bis(6-hydroxymethyl-2-pyridylmethoxy)-26,28-dipropoxy-calix[4]arene 3, its tetra-*tert*-butyl derivative 4 and 25,27-bis(6-diphenylphosphinomethyl-2-pyridylmethoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene 6 have been synthesized as sensor molecules for the Ag<sup>+</sup>-selective electrode. The polymer membranes containing 3, 4 and 6 gave good selectivity for Ag<sup>+</sup> (log  $K_{Ag,M}^{pot} \leq -3.4$ ) against most of the interfering cations examined (*i.e.*, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Pb<sup>2+</sup>), except for Hg<sup>2+</sup>. Of the three investigated ionophore-based ISEs, 6 gave the best selectivity and sensitivity of Ag<sup>+</sup> against interfering cations. The performance of the ISEs studied in this work is superior to that displayed by the traditional Ag<sub>2</sub>S-based electrode and is satisfactory for use as Ag<sup>+</sup>-ISEs. All in all, nitrogen- and phosphorus-containing multi-receptors are suitable for Ag<sup>+</sup>-selective ionophores in ISEs. A unique infinite sheet aggregate structure of 4 was determined by X-ray structure analysis in the solid state.

## Experimental

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on Bruker AC-P200 spectrometer at 200 MHz in CDCl<sub>3</sub> solution. Tetramethylsilane was used as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. FAB-MS spectra were obtained on a Zabspec spectrometer. All solvents were purified by standard procedures. Compounds 1, 2<sup>38</sup> and 2-bromomethyl-6-hydroxymethylpyridine<sup>39</sup> were prepared according to the literature procedures.

### 25,27-Bis(6-hydroxymethyl-2-pyridylmethoxy)-2,4-dipropoxy-calix[4]arene 3 and 25,27-bis(6-hydroxymethyl-2-pyridylmethoxy)-2,4-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene 4. General procedure

A suspension of dihydroxydipropoxy-calix[4]arene 1 or 2 (7.5 mmol) and NaH [0.45 g, 18.75 mmol, freed from mineral oil by washing with *n*-hexane (3 × 20 mL) and THF (2 × 20 mL)] in THF (100 mL) and DMF (50 mL) was stirred for 1 h at room temperature. Subsequently, 2-hydroxymethyl-6-bromomethylpyridine (3.03 g, 15 mmol) was added, and the mixture was stirred overnight at 85 °C. The solvent was removed under vacuum, and the residue was dissolved in CHCl<sub>3</sub> (50 mL), washed with water (2 × 100 mL) and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a sticky liquid, which was purified by column chromatography (petroleum ether–ethyl acetate = 4:1). Calixarenes 3 and 4 were obtained in 68 and 81% yields, respectively.

**Compound 3.** This was obtained as a white powder, mp 140–142 °C. <sup>1</sup>H NMR: 7.68 (t, 2H, *J* = 7.3 Hz, Py-H), 7.51 (d, 2H, *J* = 7.8 Hz, Py-H), 7.15 (d, 2H, *J* = 7.3 Hz, Py-H), 6.67 (m, 6H, Ar-H), 6.51 (s, 6H, Ar-H), 5.08 (s, 4H, PyCH<sub>2</sub>OH), 4.72 (s, 4H, PyCH<sub>2</sub>O), 4.38 (d, 4H, *J* = 13.5 Hz, ArCH<sub>2</sub>Ar), 3.76 (t, 4H, *J* = 7.8 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.13 (d, 4H, *J* = 13.5 Hz, ArCH<sub>2</sub>Ar), 1.67 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.74 (t, 6H, *J* = 7.6 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>48</sub>H<sub>50</sub>N<sub>2</sub>O<sub>6</sub>: C, 76.78; H, 6.71; N, 3.73. Found: C, 76.70; H, 6.49; N, 3.71%.

**Compound 4.** Compound 4 was obtained as a white powder, mp 163–164 °C. IR (cm<sup>-1</sup>): 3419.2, 3067.0, 3038.0, 2961.0, 2870.0, 1595.0, 1480.9, 1361.5. <sup>1</sup>H NMR: 7.68 (t, 2H, *J* = 7.3 Hz, Py-H), 7.56 (d, 2H, *J* = 8.3 Hz, Py-H), 7.17 (d, 2H, *J* = 7.4 Hz, Py-H), 6.97 (s, 4H, Ar-H), 6.57 (s, 4H, Ar-H), 4.90 (s, 4H, PyCH<sub>2</sub>OH), 4.73 (s, 4H, PyCH<sub>2</sub>O), 4.40 (d, 4H, *J* = 12.4 Hz, ArCH<sub>2</sub>Ar), 3.69 (t, 4H, *J* = 7.9 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>),

3.09 (d, 4H,  $J = 12.4$  Hz, ArCH<sub>2</sub>Ar), 1.67 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>-CH<sub>3</sub>), 1.22 (s, 18H, *t*-Bu-H), 0.91 (s, 18H, *t*-Bu-H), 0.57 (t, 6H,  $J = 7.1$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>64</sub>H<sub>82</sub>N<sub>2</sub>O<sub>6</sub>: C, 78.81; H, 8.47; N, 2.87. Found: C, 78.97; H, 8.46; N, 3.05%.

#### 25,27-Bis(6-chloromethyl-2-pyridylmethoxy)-2,4-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix-[4]arene (5)

Compound **4** (4.02 g, 3.84 mmol) was dissolved in CHCl<sub>3</sub> (50 mL), and the solution was cooled in an ice bath to 0 °C. Thionyl chloride (2.75 mL) was added to the above solution, and stirring was continued for 1 h at room temperature. Solvent and excess thionyl chloride were removed under vacuum. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with 1 M sodium carbonate (2 × 50 mL). The organic layer was dried over magnesium sulfate and filtered, and the solvent was removed to yield a yellowish solid product. This product is pure enough for analysis and for use in further reactions. Compound **5** was obtained in 91% yield (3.75 g), mp 170–171 °C. IR (cm<sup>-1</sup>): 3061.0, 3030.0, 2961.0, 2869.0, 1594.7, 1480.2, 1361.2. <sup>1</sup>H NMR: 7.95 (s br, 2H, Py-H), 7.85 (s br, 2H, Py-H), 7.50 (d, 2H,  $J = 7.0$  Hz, Py-H), 6.84 (s, 4H, Ar-H), 6.75 (s, 4H, Ar-H), 5.05 (s, 4H, PyCH<sub>2</sub>Cl), 4.78 (s, 4H, PyCH<sub>2</sub>O), 4.34 (d, 4H,  $J = 12.5$  Hz, ArCH<sub>2</sub>Ar), 3.09 (d, 4H,  $J = 12.5$  Hz, ArCH<sub>2</sub>Ar), 3.64 (t, 4H,  $J = 7.6$  Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.56 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>), 1.09 (s, 18H, *t*-Bu-H), 1.04 (s, 18H, *t*-Bu-H), 0.61 (t, 6H,  $J = 7.2$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>64</sub>H<sub>82</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 75.94; H, 7.97; N, 2.77. Found: C, 75.66; H, 8.17; N, 3.05%.

#### 25,27-Bis(6-diphenylphosphinomethyl-2-pyridylmethoxy)-2,4-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene (6)

To a 250 mL Schlenk reactor, was added **5** (3.65 g, 3.61 mmol) and THF (40 mL). The solution was cooled in an ice bath. After degassing, the solution was treated dropwise with a solution of diphenylphosphinolium (prepared from Ph<sub>2</sub>P<sup>+</sup>H (1.61 g, 8.66 mmol) with BuLi (8.66 mmol)) in THF (30 mL). The solution was stirred at -10 to -5 °C for 2 h and allowed to stand for 10 h at room temperature. Then the reaction was quenched with water (40 mL). The upper layer was collected by separation. The water layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The organic layers were combined and dried over magnesium sulfate. After the mixture was filtered and condensed to dryness, the residue was purified by column chromatography (petroleum ether–ethyl acetate = 4:1). 4.25 g of **6** was obtained as a white foam in 90% yield. IR (cm<sup>-1</sup>): 3062.0, 2960.9, 1593.2, 1479.6, 1364.0. <sup>1</sup>H NMR: 8.43 (m, 2H, Py-H), 8.01 (m, 12H, PPh-H, Py-H), 7.85 (m, 12H, PPh-H, Py-H), 7.46 (m, 10H, Ph-H), 6.82 (s, 4H, Ar-H), 6.72 (s, 4H, Ar-H), 5.41 (s, 4H, PyCH<sub>2</sub>O), 4.63 (d, 4H,  $J = 14.6$  Hz, PyCH<sub>2</sub>P), 4.19 (d, 4H,  $J = 13.6$  Hz, ArCH<sub>2</sub>Ar), 3.74 (t, 4H,  $J = 8.3$  Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.16 (d, 4H,  $J = 13.6$  Hz, ArCH<sub>2</sub>Ar), 1.63 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.11 (s, 18H, *t*-Bu-H), 1.01 (s, 18H, *t*-Bu-H), 0.73 (t, 6H,  $J = 7.3$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 81 MHz): 28.96. FAB<sup>+</sup>-MS: *m/z* 1311.6. Anal. Calcd. for C<sub>88</sub>H<sub>100</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C, 80.58; H, 7.68; N, 2.14. Found: C, 80.93; H, 7.36; N, 1.98%.

#### Silver selectivity evaluated by potentiometric selectivity coefficients. Membrane electrode

The typical procedure for membrane preparation is as follows: poly(vinyl chloride) (PVC) (132 mg, 33%), dibutyl phosphate (DBP) (264 mg, 66%), benzothiazolyl functionalized calix[4]arene (4 mg, 1%), potassium tetrakis(*p*-chlorophenyl)-borate (KTClPB) (100 mol% relative to the ionophore) were dissolved in 5 mL of THF. This solution was then poured into a flat-bottomed petri dish of 32 mm inner diameter and 50 mm height. Gradual evaporation of the solvent at room temperature gave a transparent, flexible membrane of about

**Table 2** Crystal data and data collection parameters

Data	4
Formula	C <sub>64</sub> H <sub>82</sub> N <sub>2</sub> O <sub>6</sub> ·CH <sub>3</sub> OH
Formula wt/g mol <sup>-1</sup>	1007.36
<i>T</i> /K	298(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2(1) <i>c</i>
<i>a</i> /Å	21.401 (17)
<i>b</i> /Å	13.436 (10)
<i>c</i> /Å	22.040 (18)
$\beta$ /deg	95.396 (16)
<i>V</i> /Å <sup>3</sup>	6309 (9)
<i>Z</i>	4
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.061
<i>F</i> (000)	2184
Crystal size/mm	0.20 × 0.25 × 0.30
$\theta$ range/deg	1.78 to 25.03
Reflns collected	21932
Independent reflns	10972
Data/restraints	10972/2
Parameters	668
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.895
<i>R</i> <sub>1</sub>	0.0834
<i>wR</i> <sub>2</sub>	0.1870

0.3 mm thickness. A disk of 7 mm in diameter was cut from the PVC membrane and incorporated into the PVC tube tip with 5% THF solution in water. After injection of 0.01 M aqueous solution of AgNO<sub>3</sub> as the internal solution, the electrode was conditioned by soaking in 0.01 M aqueous solution of AgNO<sub>3</sub> for 2 h. The external reference electrode is a double junction type Ag/AgCl glass electrode. The composition of the electrochemical cell is given as Ag|AgCl|0.01 M AgNO<sub>3</sub> || PVC membrane || sample solution|3 M KNO<sub>3</sub>|saturated KCl|Hg<sub>2</sub>Cl<sub>2</sub>|Hg.

#### EMF measurements

All EMF (electromotive force) measurements were made at 25 ± 0.1 °C, using a pH/mV meter. Sample solutions were magnetically stirred and kept in a thermostated water bath. The EMF values were corrected by subtracting the liquid-junction potential between the external reference electrode and the sample solution at high Ag<sup>+</sup> concentration.

#### Selectivity coefficients

The potentiometric selectivity coefficients,  $K_{Ag,M}^{pot}$ , determined here are defined by the Nicolsky–Eisenman equation [eqn. (1)],

$$E = E^0 + \frac{2.303 RT}{F} \log [a_{Ag} + K_{Ag,M}^{pot} (a_M)^{1/Z_M}] \quad (1)$$

where *E* represents the experimentally observed potential, *R* the gas constant, *T* the thermodynamic temperature in K, *F* the Faraday constant, *a*<sub>Ag</sub> the Ag<sup>+</sup> activity, *a*<sub>M</sub> the activity of the interfering cation, and *Z*<sub>M</sub> the charge of the interfering cation. The selectivity coefficients were determined by a mixed-solution method. In order to evaluate the selectivity of the Ag<sup>+</sup> over other cations, the mixed-solution method was employed.<sup>36</sup> According to this method, the potentiometric selectivity coefficients,  $K_{Ag,M}^{pot}$ , can be evaluated from the potential measurements on solutions containing a fixed concentration of the interfering ions (M<sup>*n*+</sup>) and varying the concentration of Ag<sup>+</sup> ion using eqn. (2).

$$K_{Ag,M}^{pot} = a_{Ag} / (a_M)^{1/Z_M} \quad (2)$$

The resulting log  $K_{Ag,M}^{pot}$  values are summarized in Table 1.

### Crystallographic structural determination †

Crystals of **4** suitable for X-ray crystallography were grown by slow evaporation from a CH<sub>2</sub>Cl<sub>2</sub>–MeOH solution of **4**. X-Ray crystallographic data were obtained on a Bruker Smart 1000 instrument. The data collection and refinement parameters are given in Table 2.

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† CCDC reference number 188/285. See <http://www.rsc.org/suppdata/p2/b0/b008114k/> for crystallographic files in .cif format.

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