Anodic Stripping Voltammetric Determination of Lead(II) Using Glassy Carbon Electrode Modified with Novel Calix[4]arene

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A new glassy carbon electrode modified with novel calix[4]-arene derivative was prepared and then applied to the selective recognition of lead ion in aqueous media by cyclic and square wave voltammtry. A new anodic stripping peak at -0.92 V (vs. Ag/Ag^+) in square wave voltammogram can be obtained by scanning the potential from -1.5 to -0.6 V, of which the peak current is proportional to the concentration of Pb^{2+}. The modified electrode in 0.1 mol/L HNO_3 solution showed a linear voltammetric response in the range of 2.0×10^{-8}—1.0×10^{-6} mol/L and a detection limit of 6.1×10^{-9} mol/L. In the modified glassy carbon electrode no significant interference occurred from alkali, alkaline and transition metal ions except Hg^{2+}, Ag^+ and Cu^{2+} ions, which can be eliminated by the addition of KSCN. The proposed method was successfully applied to determine lead in aqueous samples.

Keywords   calix[4]arene derivative, glassy carbon electrode, square wave voltammetry, lead ion

Owing to the growing awareness of lead pollution and toxicity, many techniques are currently employed for the determination of trace Pb ion in environmental samples.[1] Among them, the development of chemically modified electrodes (CMEs) and applications of anodic stripping voltammetry (ASV) have received considerable attention. CMEs are characterized by purposefully altering their surface characteristics to display new qualities that could be exploited for analytical applications. These kinds of electrodes are inexpensive and possess many advantages such as low background current, wide range of used potential, easy fabrication and rapid renewal.

For stripping voltammetric determination of Pb ion, a limited number of CMEs have been reported. Dibenzo-18-crown-6,[2] lichen,[3,4] moss,[5] benzoin oxime,[6] 1-(2-pyridylazo)-2-naphthol,[7,8] *N-p*-chlorophenylcinnamohydroxamic acid,[9] 1,4-bis(prop-2'-enyloxy)-9,10-anthraquinone,[10] and poly(ethylenimine)ethylthiourea and poly(1-vinyl-2-pyrrolidone)methylthiourea[11] were immobilized onto the electrode surface as modifier by different methods. These approaches make it possible to improve the selectivity and sensitivity of the electrochemical measurements and eliminate interferences from other components by preconcentrating Pb^{2+} from a dilute solution on the electrode surface.[12] The efficiency of the preconcentration depends obviously on the nature of modifiers, so considerable efforts have been directed torward adopting highly selective ionophore.

Calixarenes, cyclic oligomers of phenol-formaldehyde condensates, have received much attention as the basis for molecular and ionic recognition because of their conformational and structural flexibility.[13,14] Chemical modifications can be readily made on the *para*-phenolic positions, at the bridging methyl groups and at the phenolic hydrogen via OH modifications. Derivatives containing a wide range of functional groups have been synthesized and used as sensors in analytical chemistry.[15] The advantages of calixarenes inspired many electrochemists to develop new redox-active ionophores and to find their electrochemical applications. Recently, many efforts have been undertaken[16-18] and applied to the voltammetric determination of Pb^{2+} ion in aqueous media.[19]

In the past few years, we have reported the synthesis of a series of calixarenes containing sulfur atom, and their applications as ionophores for the preparation of ion-selective electrodes.[20,21] In order to enhance the selectivity of calixarenes to Pb^{2+} ions, we designed and synthesized a novel derivative containing (benzothiazolyl)thioalkoxy and quinone units in the low rim and mother nucleus of calix[4]arene. The aim of the present investigation was to develop a new glassy carbon electrode modified with a novel derivative for the selective preconcentration and quantitation of Pb^{2+} by anodic stripping voltammetry. This study has led to the development of a new voltammetric method for the determination of Pb^{2+} and has been applied to waste water samples analysis.

Experimental

Chemicals and Reagents

All membrane components, high relative molecular mass polyvinyl chloride (PVC) and *o*-nitrophenyl octyl ether (*o*-NPOE), were of selectophore grade and obtained from Fluka (Buchs, Switzerland). Analytical reagent grade tetrahydrofuran (THF, obtained from Shanghai Chemical Reagent Corporation) was used with further purification. All other chemicals used were of analytical grade and did not undergo further purification unless otherwise specified. N_2 gas was used to degas the solutions during the experiment. All solutions were prepared with doubly distilled deionized water.

Stock solutions of 10^{-3} mol/L metal ions were prepared by dissolving the nitrate salt in water. Working solutions were prepared just before use by diluting the stock solutions in 0.1 mol/L HNO_3.

26,28-Bis(benzothiazolylthiopropoxy) calix[4]-diquinone (CAL, showed in Fig. 1) was synthesized[22] and used after purification by silica gel chromatography with CH_2Cl_2 and petroleum ether (2:1, *V*:*V*) and vacuum drying.
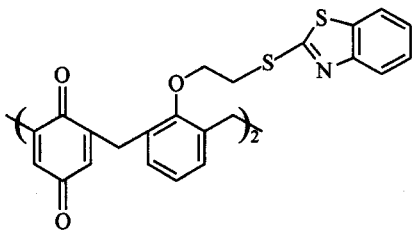

Fig. 1   Structure of calix[4]arene derivative.

Apparatus

Voltammetric measurements were carried out with a CHI Model 660 electrochemical workstation (CH Instrument Inc., USA). The three-electrode system consists of a modified glassy carbon electrode (3 mm in diameter) as working electrode, a homemade Ag|Ag$^+$ (0.01 mol/L AgNO$_3$) reference electrode, and a platinum wire counter electrode.

Preparation of the modified electrode

Glassy carbon electrode (GCE) was first hand polished on the microcloth pads and then washed with doubly distilled water. Prior to use, the GCE was ultrasonically washed with doubly distilled water and dried subsequentially in air.

In our studies, three kinds of calixarene-modified electrode were prepared as follows:

(1) 20 μL of 10 mg/mL calixarene derivative solution in THF, was pipetted directly on the GCE surface and then dried at room temperature.

(2) 20 μL of a 10 mg/mL solution (50 mg calixarene derivative, 60 mg PVC and 120 mg *o*-NPOE dissolved in 5 mL THF), was pipetted directly on the GCE surface and then dried at room temperature.

(3) 20 μL of a 10 mg/mL solution (50 mg calixarene derivative, 60 mg PVC and 120 mg *o*-NPOE dissolved in 5 mL THF), was pipetted directly on the GCE surface. After the membrane was dried at room temperature (approximately 10 min). A " # " indent was cut on the surface of CAL-GCE (PVC membrane, 1 scratch/mm) by cutter. Be careful not to scratch the surface of glassy carbon electrode!

In voltammetric experiments, we found that the voltammetric properties of the third modifing method are better than those of the others. Hence, the third modifing method was then used in the following experiments.

Procedures

A reproducible CAL-GCE response was achieved by repeating the preconcentration/voltammetric measurement/regeneration sequence three times consecutively. In the preconcentration step which was carried out in an open circuit, the lower 10 mm part of the CAL-GCE was immersed in 25 mL of a magnetically stirred solution containing Pb^{2+} ions in 0.1 mol/L HNO_3 for 1 min. After a potential of -1.5 V was applied for 4 min (while stirrer was off), the cyclic voltammograms (CVs) were run starting from -1.5 to 0.5 V and back (with a 100 mV/s scan rate), and the square wave voltammograms (SWVs) were recorded from -1.5 to -0.6 V. All experiments were carried out in N_2 atmosphere at room temperature (around 20 ℃). After each measurement, the CAL-GCE was dipped in 0.02 mol/L EDTA for 20 min, and then washed/rinsed with water.

For the quantitative determination of Pb^{2+} ion, the samples with or without known working solutions of Pb^{2+} ion were added by KSCN, and then adjusted to 0.1 mol/L HNO_3 with HNO_3. 25 mL solutions are determined by anodic stripping voltammetry applying the same scheme as that employed in the electrode conditioning.

Results and discussion

Voltammetric behaviors of CAL-GCE

The electrochemical behavior of the modified electrodes in aqueous solution was investigated in a potential range of -1.5—0.6 V using cyclic voltammetry. In the above pH = 2 B-R buffer solution, obvious peak was not observed. In the 0.05—0.25 mol/L media of HNO_3, H_2SO_4, HCl and $HClO_4$, peaks at potential of *ca*. 0 and *ca*. -1.1 V were observed. Typical voltammograms in 0.1 mol/L HNO_3 are shown in Fig. 2. As seen from Fig.

2A, obvious anodic peak at potential of about − 0.02 V was observed. The anodic peak may be due to the oxidation of S atom in the derivative.[23,24] The derivative has two quinone moieties and is expected to exhibit almost the same voltammetric behavior as that of several calix[4]-arene-diquinones.[25,26] As expected, Fig. 2A shows that an obvious cathodic peak is observed with a peak potential of about − 1.1 V, which is attributed to the electrochemical reduction of quinone, and the result is similar to those of reported calix[4]arene-diquinones. Square-wave voltammograms of CAL-GCE (Fig. 2B) confirmed the presence of redox peaks and indicated that cathodic peak at about − 1.1 V is an irreversible reduction, and there is a pair of reversible peaks at about 0 V.
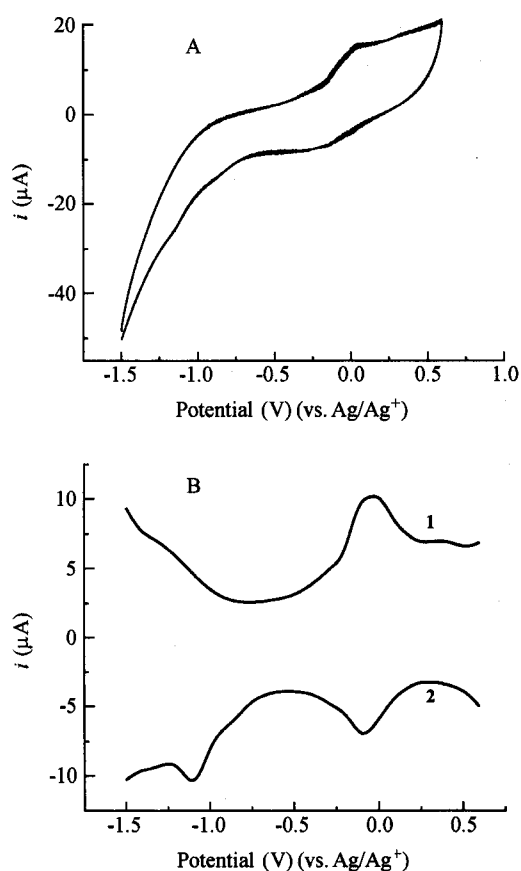

Fig. 2 (A) Cyclic voltammogram of CAL-GCE at scan rate of 100 mV/s. (B) Square-wave voltammogram of CAL-GCE at frequency of 60 Hz. Medium: 0.1 mol/L HNO$_3$. Potential scan: **1** from − 1.5 V to 0.4 V, **2** from 0.4 V to − 1.5 V.

Voltammetric behaviors of Pb^{2+} *on the* CAL-GCE

Fig. 3 displays typical voltammograms obtained for the CAL-GCE in the presence of 4 × 10^{-7} mol/L Pb^{2+}. As seen from Fig. 3A, a new anodic peak at − 1.1 V was observed. In square-wave voltammogram (Fig. 3B), the anodic peak at − 0.92 V was also observed, while the original peaks of the derivative remained. The property of

the anodic peak at *ca*. − 0.92 V was also investigated by cyclic and square-wave voltammetry. The experimental data indicated that the relationships of peak potential with scan rate, peak current with frequency and peak potential with logarithm of frequency have the characteristic of adsorbsion mode. The peak current, moreover, increases linearly in the low concentration and i_p is proportional to the concentration of Pb^{2+} in the solution, but it gradually reaches a maximum value. This result reflects that the entrapment of Pb^{2+} ion into the derivative on the electrode follows the Langmuir isotherm.
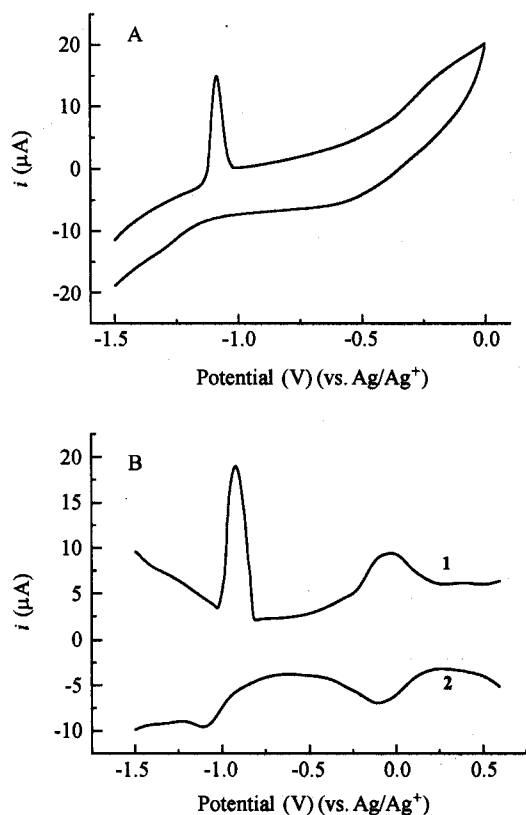

Fig. 3 (A) Cyclic voltammogram at scan rate of 100 mV/s. (B) Square-wave voltammogram at frequency of 60 Hz. Conditions: concentration of lead ion, 4 × 10^{-7} mol/L; medium, 0.1 mol/L HNO$_3$ solutions; accumulation potential, − 1.5 V; accumulation time, 4 min; amplitude, 50 mV. Potential scan: **1** from − 1.5 V to 0.4 V, **2** from 0.4 V to − 1.5 V.

According to the experimental data, we propose that the total reaction involves the chelating of metal ions from bulk solution onto the surface of CAL-GCE, the reducing of accumulated metal ions and the electrochemical stripping the reductive material back into solution. The recognition process is suggested as follows:

1. Preconcentration step, complex formation at open circuit.

$$\text{Pb}^{2+}_{aq} + \text{CAL}_{mem} \longrightarrow [\text{Pb}^{2+}\text{-CAL}]_{mem} \qquad (1)$$
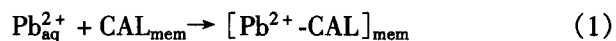
2. Reduction step, at closed circuit under a potential

of -1.5 V.

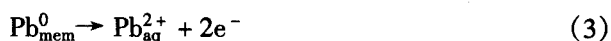$$[Pb^{2+}\text{-CAL}]_{mem} + 2e^- \rightarrow Pb^0_{mem} + CAL_{mem} \qquad (2)$$
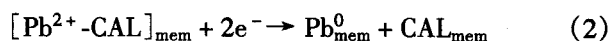
3. Stripping step, at closed circuit under a positive scan from -1.5 to -0.6 V.

$$Pb^0_{mem} \rightarrow Pb^{2+}_{aq} + 2e^- \qquad (3)$$

In the past few years, we have synthesized a number of tweezer derivatives containing bi-(benzothiazolyl) thio-alkoxy units in the low rim of calix[4]arene, evaluated their performances as ionophores using ionic-selective electrodes (ISEs) and studied the structure of the complexes of calix[4]arenes with silver ion by crystallograms. We found that ISEs based on these calix[4]arene derivatives exhibited excellent silver selectivity against other interfering ions. Silver ion are encircled in the cavity inclosed by the sulfur atoms (as soft binding sites) of the tweezer in calix[4]arene.[27] In this paper, two phenolic units of calix[4]arene are oxidized to quinones. The recognition of lead ion by calix[4]arene might be caused by the quinone units which make the sulfur atoms more rigid. The profound reason is under investigation.

Optimization of voltammetric conditions

The parameters of anodic stripping voltammetry were optimized, such as the supporting electrolyte, the accumulation potential and time, and the pulse amplitude and frequency. These parameters are interrelated and have a combined effect on the response but only the general trends will be examined.

Influence of medium and its concentration   Several acidic solutions, namely HNO_3, H_2SO_4, HCl and $HClO_4$, were tested. The experimental results showed that the peak current of Pb^{2+} in HNO_3 system was much higher than that in other systems. The effect of nitric acid concentration on the peak current of a 5.0×10^{-7} mol/L Pb^{2+} solution was then investigated in the range of 0.05—0.5 mol/L. The maximum peak current was observed for 0.1 mol/L solution, after which the net peak current decreased because of the influence of proton reduction on the base of the peak. Therefore, 0.1 mol/L HNO_3 was used for the open-circuit preconcentration and voltammetric measurements of Pb^{2+} ions.

Effect of preconcentration time   The dependence of the anodic peak current on the preconcentration time for two different Pb^{2+} concentrations was studied. The peak current was found to increase with increasing preconcentration time, indicating an enhancement of Pb^{2+} uptake at the electrode surface. Normally, the increase in the response current continus until a maximum signal level (presumably corresponding to either a saturation or an equilibrium surface coverage) is attained. Thus, the results obtained indicate that the attainment of a steady-state accumulation level of Pb^{2+} at the electrode surface requires an exposure time of 30 s for 5.0×10^{-7} mol/L Pb^{2+} and 50 s for 5.0×10^{-8} mol/L Pb^{2+}. Hence, a 1 min preconcentration time was employed in all subsequent experiments.

Influence of accumulation potential and time   In the SWV method, the potential applied on the modified electrodes affects the efficiency of the accumulation during the reduction step as a result of columbic effects and competitive accumulation.[28] The influence of reduction potential on the anodic peak current of Pb^{2+} was studied by varying the reduction potential from -0.9 to -2.0 V. When the potential was increased to -1.5 V, a well-defined peak with the highest peak current was obtained. Further increase in the accumulation potential led to decreased peak currents. Hence, -1.5 V was employed as an optimum reduction potential for further studies.

The relationship between the peak current of Pb^{2+} and the accumulation time (t_{acc}) was studied. The anodic peak current for Pb^{2+} was found to increase gradually with increasing accumulation time up to 3.5 min, and remained constant after 3.5 min. Therefore, a 4 min accumulation time was used for all subsequent measurements.

Effect of instrumental parameters   Different pulse amplitudes (10—100 mV) showed that there was a magnification of peak intensity when the pulse amplitude increased from 10 to 50 mV. For the larger pulse, the peak-width increased and amplitude of 50 mV was used for further studies. The peak intensity increased linearly with increase of frequency in the range of 5—60 Hz, and then remained unchanged with larger frequency. So, a value of 60 Hz was chosen for the rest of experiment.

Interference

In voltammetric determinations of trace metals involving preconcentration of the analyte at chemically modified electrodes, coexisting metal ions that exhibit affinity for the modifier can interfere, whether they are electroactive or not. The voltammetric signal of the analyte might be affected by an overlapping response, by competition on binding sites, or by both phenomena. Hence, the effect of other metal ions on both the voltammetric behavior of CAL-GCE and response of Pb^{2+} ion was investigated.

The effect of various metal ions on the voltammetric behavior of CAL-GCE in 0.1 mol/L HNO_3 solution was examined by the standard addition method. The results show that 10^{-4} mol/L common ions such as Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} do not interfere with voltammetric behavior of Pb^{2+}. While Ag^+, Fe^{3+}, Fe^{2+}, Cu^{2+} and Hg^{2+} ions also give rise to new peaks at -0.15, -0.65, -0.65, -0.45 and -0.30 V, respectively. Among these ions, Hg^{2+} yields more sensitive peak, while other peaks are with much lower sensitivity.

For determination of 5.0×10^{-7} mol/L Pb^{2+} ion, an equimolar amount of Hg^{2+} decreased obviously the current of the peak at -0.92 V, while a 100-fold molar excess of Fe^{3+} and Fe^{2+} only resulted in increase of baseline cur-

rent, and a 50-fold molar excess of Cu^{2+} or Ag^+, or the presence of 1000 times of other metal ions mentioned above did not interfere. The influence of anions was also investigated by the standard addition method. The results show that up to 1000-fold molar excess of SCN^-, F^- and ClO_4^-, or 50-fold molar excess of Cl^-, Br^-, I^-, SO_4^{2-} and acetate have only negligible effect.

The experiments indicated that the interfering effect of Hg^{2+}, and the influence of other weakly interfering ions such as Ag^+, Fe^{3+}, Fe^{2+} and Cu^{2+} were eliminated by the addition of KSCN. After adding 0.001 mol/L KSCN, The 100-fold molar excess of Hg^{2+}, Ag^+, Fe^{3+}, Fe^{2+} and Cu^{2+} did not affect the determination of 5.0×10^{-7} mol/L Pb^{2+} ion.

Analytical performance

Under the optimized conditions, a series of Pb^{2+} standard solutions was tested to determine the linearity for Pb^{2+} ion at the modified electrode. Fig. 4 showed the effect of the concentration of Pb^{2+} ion. The anodic peak (at -0.92 V) current increases linearly as the concentration of Pb^{2+} ion increases in a wide concentration range from 2.0×10^{-8} to 1.0×10^{-6} mol/L, and the calibration equation is $i_p(\mu A) = 1.90 + 3.09 \times 10^7 \times c_{Pb}$, with a linear correlation coefficient (R) of 0.9996. However it gradually reaches a maximum and remains unchanged. The detection limit $(S/N = 3)$ turned out to be 6.1×10^{-9} mol/L. The standard deviation for 10 determinations using a 5.0×10^{-7} mol/L lead containing solution is 4.6%.

Table 1 compares the characteristic of the present work with the methods reported. It is clear that the detect limit and precision of the present system are significantly better than those reported with modified GCE.
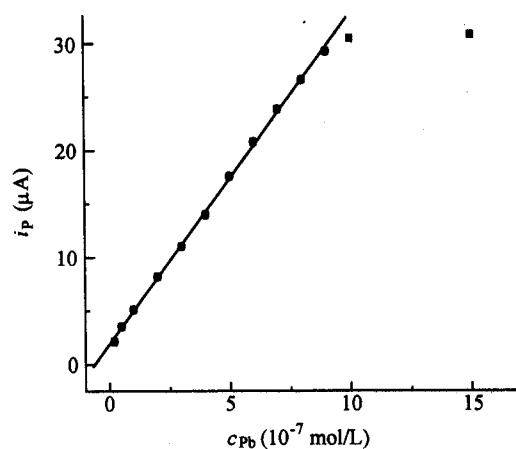

Fig. 4 Calibration plot of Pb^{2+} concentration. Other conditions are the same as those in Fig. 3.

Applications

To assess the applicability of the modified electrode to real samples, five replicate determinations of Pb^{2+} in spiked and unspiked water samples were carried out using standard addition method. The detected values and recoveries generated from five replicate determinations are summarized in Table 2. These data indicate that the proposed method holds promise for determing water samples containing concentrations of Pb^{2+} examined in this study.

Conclusions

In this work, we prepared a new chemically modified glassy carbon electrode based on the calixarene derivative. It was found that the CAL-GCE recognizes selectively Pb^{2+} ion in aqueous solution by anodic stripping voltammetry. The recognition mechanism of Pb^{2+} ion in aqueous

Table 1 Comparison of the characteristic of the present work with the methods reported

	Ref. 3	Ref. 5	Ref. 9	Ref. 29	This work
Detection limit (mol/L)	1×10^{-9}	9.7×10^{-9}	1×10^{-8}	8×10^{-8}	6.1×10^{-9}
Linear range (mol/L)	2×10^{-9}—1×10^{-5}	2.4×10^{-8}—4.8×10^{-6}	2×10^{-8}—2.4×10^{-5}	1×10^{-7}—1×10^{-6}	2×10^{-8}—1×10^{-6}
RSD (%)	3.7	4.8	5.3	5.8	4.6

Table 2 Analytical results of water samples by the proposed method[a]

Sample	Original conc. (10^{-7} mol/L)	Added (10^{-7} mol/L)	Found (10^{-7} mol/L)	Recovery (%)
Lake water	ND[b]	5.00	5.20	104.0
Waste water	1.21	5.00	5.93	94.4
Synthetic solution	1.00	5.00	5.99	99.8
	4.00	5.00	8.76	95.2

[a] Average of five determinations; [b] ND: not detected.

solution and some experimental parameters were discussed in detail. The linear range for Pb^{2+} determination lies between 2.0×10^{-8} and 1.0×10^{-6} mol/L. A detection limit of 6.1×10^{-9} mol/L for an accumulation time of 4 min shows the sensitivity of the measurements by this modified electrode. The good qualities of the CAL-GCE electrode and the sensitivity of the lead measurements make them suitable for analysis of real samples. The results would prompt us to further synthesize functionalized calixarenes and exploit their applications in analytical chemistry.

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