



A versatile approach toward chemosensor for Hg^{2+} based on *para*-substituted phenylazocalix[4]arene containing mono ethyl ester unit



Serkan Elçin*, Hasalettin Deligöz

Department of Chemistry, Faculty of Science-Arts, Pamukkale University, 20017 Denizli, Turkey

ARTICLE INFO

Article history:

Received 16 January 2014

Received in revised form

21 March 2014

Accepted 2 April 2014

Available online 12 April 2014

Keywords:

Calix[n]arene

Azocalix[4]arene

Mono ester

Selective extraction

Optimized structure

Hg^{2+}

ABSTRACT

In the present study, six new azocalix[4]arenes have been synthesized by reacting calix[4]arene with *p*-substituted aniline and ethyl bromoacetate. Characterization of these compounds has been used by elemental analyses, UV–Vis, FT-IR and ^1H NMR spectroscopic studies. Their phase transfer studies have been performed by using liquid–liquid extraction procedure. With respect to the chromogenic behavior of hosts upon metal ion complexation, mono ethyl ester azocalix[4]arene derivatives have shown a significant selectivity toward Hg^{2+} and Hg^+ over many other cations. It has been deduced that these new compounds are selective ionophores toward metal cations (Na^+ , K^+ , Sr^{2+} , Ag^+ , Hg^+ , Hg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cr^{3+} , Al^{3+} and La^{3+}).

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Heavy metal contamination of water is a serious concern due to the toxic effect of heavy metal ions on the living organisms and environment [1,2]. Therefore, effective removal of heavy metal ions from water or various industrial effluents is crucially important. It has attracted considerable research and practical interest. Many methods such as chemical precipitation, ion exchange, reverse osmosis and sorption have been used to remove metal ions from various aqueous solutions [3,4]. Among the stated methods absorption has increasingly received more attention in recent years due to its relative simplicity, cost efficiency and high effectivity in removing heavy metal ions, especially at low to medium metal ion concentrations from wastewater [5,6].

The calix[n]arenes are among the most fascinating families of host compounds, and their chemistry have been significantly developed in the last 30 years [7,8]. Host–guest chemistry of the calixarenes is of great interest due to their complexing abilities toward various metal cations by means of functional group modification at the phenolic groups [9–12]. Later, it was found that calix[n]arenes can be converted into neutral ligands by converting the hydroxyl groups to esters or amides [13–17]. It has demonstrated

that the metal selectivity is based on the calix[n]arene ring size structure, for example, calix[4]aryl acetates and acetamides with a *cone* conformation show remarkably high Na^+ selectivity.

Calix[n]arene family is one of the most prominent molecular building platforms in host–guest chemistry. A new member of the calix[n]arene family is based on the replacement of the traditional methyl bridges with azo groups [18]. Up to now, azocalix[n]arenes and their binding properties were only studied by Chawla [19], Kim [20] and Lu [21].

Recently, Arnaud-Neu and co-workers [22] have studied the transport of alkaline-earth metal cations with *p*-*tert*-butylcalix[n]arene esters and amides. Reinhout and co-workers prepared 1,3-*alternate* calix[4]arene-crown-6 as a new class of cesium-selective ionophore [23]. In addition, Ungaro and co-workers have reported the synthesis, structure and complexing properties of several 1,3-dialkoxy-*p*-*tert*-butylcalix[4]arene-crown-5, a new class of potassium-selective ligands [24].

Until now, our group and co-workers have synthesized the functionalized calix[n]arene derivatives and studied their selective extraction of various transition metals [25–30]. In the course of the synthesis of new chromogenic azocalix[4]arene derivatives containing the phenolic neighboring groups at lower rim [31], we have extended our research into transition metal cations.

In the present work, we have mainly focused on the development of a new class of chromogenic azocalix[4]arene

* Corresponding author. Tel.: +90 258 296 3613; fax: +90 258 296 3593.
E-mail address: sere120@myinet.com (S. Elçin).

chemosensors (**4a–f**) as shown in Scheme 1. Then, six new compounds containing more than one tetra azo (–N=N–) groups and mono ester were synthesized, and their ion binding properties were studied.

2. Experimental

All of the chemical reagents and solvents used were of analytical grade purity and used without further purification. All aqueous solutions were prepared with deionized water purified by Human Power Plus I + UV water purification system.

p-tert-Butylcalix[4]arene, calix[4]arene, 5,11,17,23-tetrakis[(4-methoxyphenyl)azo] calix[4]arene (**3a**), 5,11,17,23-tetrakis[(4-methylphenyl)azo]calix[4]arene (**3b**), 5,11,17,23-tetrakis[(4-ethylphenyl)azo]calix[4]arene (**3c**), 5,11,17,23-tetrakis[(4-chlorophenyl)azo]calix[4]arene (**3d**), 5,11,17,23-tetrakis[(4-bromophenyl)azo]calix[4]arene (**3e**) and 5,11,17,23-tetrakis[(4-nitrophenyl)azo]calix[4]arene (**3f**) were synthesized as described previously [32–35].

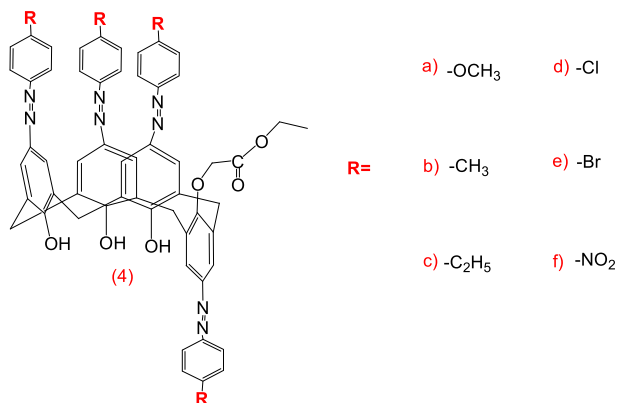
2.1. Instrumental

Melting points were measured using an Electrothermal IA9100 digital melting point apparatus with capillaries sealed under nitrogen and were uncorrected. Microwave assisted synthesis was performed using a CEM Discover synthesis unit (monomode system). ¹H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as internal standard solution and recorded on a Bruker 400 MHz spectrometer at room temperature (25 °C). IR spectra were recorded by a Mattson 1000 FTIR spectrometer as KBr pellets. UV–vis spectra were recorded by a Shimadzu 1601 UV–Visible spectrophotometer. The elemental analyses were performed in the TUBITAK (The Scientific and Technological Research Council of Turkey) Laboratories.

2.2. Solvent extraction

A solution (10 mL) of ligand (1×10^{-3} M) in chloroform and an aqueous solution (10 mL) containing 2×10^{-5} M picric acid and 1×10^{-2} M metal nitrate was stirred at 25 °C for an hour. An aliquot of the aqueous solution was withdrawn, and its UV spectrum was recorded. A similar extraction was performed in the absence of picrate ion in the aqueous solution. The extractability of the metal cations is expressed by means of the following equation:

$$\text{Extractability(\%)} = (A_0 - A)/A_0 \times 100$$



Scheme 1. Structure of azocalix[4]arene mono ester derivatives (**4a–f**).

where A and A_0 are the absorbencies with and without ligand, respectively.

2.3. Preparation of the esterification

We have followed the procedure given in Refs. [11,36] to carry out the experiment.

2.3.1. Preparation of 25-(ethoxycarbonylmethoxy)-26,27,28-trishydroxy-5,11,17,23-tetrakis[(4-methoxyphenyl)azo]calix[4]arene (**4a**)

Azocalix[4]arene **3a** (1 g, 1.04 mmol) and K_2CO_3 (1.15 g, 8.32 mmol) in dry acetonitrile (100 mL) was mixed with ethyl bromoacetate (0.36 mL, 2.19 mmol). The reaction mixture was stirred at room temperature for 4 days and then allowed to cool down to room temperature. After evaporation of the solvent with a rotary evaporator, the mixture was taken into $CHCl_3$ (100 mL). It was washed first with 0.5 N HCl (250 mL) and then with water (300 mL). The organic layer was dried over $MgSO_4$ and evaporated to half volume. The addition of ethanol yielded the pale brown product (yield, 0.92 g (84%), mp. 245–247 °C). Found: C: 68.72; H: 5.26; N: 10.73; $C_{60}H_{54}N_8O_{10}$ requires C: 68.82; H: 5.20; N: 10.70. IR (KBr) ν : 3336 cm^{-1} (–OH), 1740 cm^{-1} (–C=O), 1449 cm^{-1} (–N=N–), 1245 cm^{-1} (C–O). ¹H NMR ($CDCl_3$, 25 °C) δ_H : 1.45 (t, J = 7.14 Hz, 3H, CH_2-CH_3), 3.72 (d, J = 6.17 Hz, 2H, $ArCH_2Ar$), 3.75 (d, J = 6.09 Hz, 2H, $ArCH_2Ar$), 3.80–3.85 (m, 12H, O– CH_3), 4.40 (d, J = 13.69 Hz, 2H, $ArCH_2Ar$), 4.48 (q, J = 7.15 Hz, 2H, O– CH_2-CH_3), 4.57 (d, J = 13.61 Hz, 2H, $ArCH_2Ar$), 4.95 (s, 2H, O– $CH_2-C=O$), 6.90–6.97 (m, 8H, ArH), 7.70–7.83 (m, 16H, ArH), 9.33 (s, 2H, $ArOH$), 9.81 (s, 1H, $ArOH$).

2.3.2. Preparation of 25-(ethoxycarbonylmethoxy)-26,27,28-trishydroxy-5,11,17,23-tetrakis[(4-methylphenyl)azo]calix[4]arene (**4b**)

Azocalix[4]arene **4b** is prepared as described above, using **3b**, ethyl bromoacetate with K_2CO_3 and obtained an orange crystal product (yield, 0.89 g (81%), mp. 298–300 °C). Found: C: 73.47; H: 5.63; N: 11.43; $C_{60}H_{54}N_8O_6$ requires C: 73.30; H: 5.54; N: 11.40. IR (KBr) ν : 3324 cm^{-1} (–OH), 1742 cm^{-1} (–C=O), 1448 cm^{-1} (–N=N–), 1239 cm^{-1} (C–O). ¹H NMR ($CDCl_3$, 25 °C) δ_H : 1.45 (t, J = 7.15 Hz, 3H, CH_2-CH_3), 2.34–2.40 (m, 12H, $Ar-CH_3$), 3.74 (d, J = 6.36 Hz, 2H, $ArCH_2Ar$), 3.77 (d, J = 6.26 Hz, 2H, $ArCH_2Ar$), 4.41 (d, J = 13.75 Hz, 2H, $ArCH_2Ar$), 4.49 (q, J = 7.15 Hz, 2H, O– CH_2-CH_3), 4.59 (d, J = 13.57 Hz, 2H, $ArCH_2Ar$), 4.96 (s, 2H, O– $CH_2-C=O$), 7.19–7.27 (m, 8H, ArH), 7.67–7.80 (m, 16H, ArH), 9.40 (s, 2H, $ArOH$), 10.09 (s, 1H, $ArOH$).

2.3.3. Preparation of 25-(ethoxycarbonylmethoxy)-26,27,28-trishydroxy-5,11,17,23-tetrakis[(4-ethylphenyl)azo]calix[4]arene (**4c**)

Azocalix[4]arene **4c** is prepared as described above, using **3c**, ethyl bromoacetate with K_2CO_3 and obtained a pale orange crystal product (yield, 0.85 g (78%), mp. 268–270 °C). Found: C: 73.83; H: 5.97; N: 10.83; $C_{64}H_{62}N_8O_6$ requires C: 73.97; H: 6.01; N: 10.78. IR (KBr) ν : 3332 cm^{-1} (–OH), 1740 cm^{-1} (–C=O), 1449 cm^{-1} (–N=N–), 1238 cm^{-1} (C–O). ¹H NMR ($CDCl_3$, 25 °C) δ_H : 1.24 (t, J = 8.21 Hz, 12H, $Ar-CH_2-CH_3$), 1.46 (t, J = 7.16 Hz, 3H, CH_2-CH_3), 2.68 (q, J = 7.68 Hz, 8H, $Ar-CH_2-CH_3$), 3.74 (d, J = 6.49 Hz, 2H, $ArCH_2Ar$), 3.77 (d, J = 6.41 Hz, 2H, $ArCH_2Ar$), 4.41 (d, J = 13.90 Hz, 2H, $ArCH_2Ar$), 4.49 (q, J = 7.16 Hz, 2H, O– CH_2-CH_3), 4.59 (d, J = 13.23 Hz, 2H, $ArCH_2Ar$), 4.92 (s, 2H, O– $CH_2-C=O$), 7.24–7.29 (m, 8H, ArH), 7.71–7.79 (m, 16H, ArH), 9.40 (s, 2H, $ArOH$), 10.26 (s, 1H, $ArOH$).

2.3.4. Preparation of 25-(ethoxycarbonylmethoxy)-26,27,28-trishydroxy-5,11,17,23-tetrakis[(4-chlorophenyl)azo]calix[4]arene (4d)

Azocalix[4]arene **4d** is prepared as described above, using **3d**, ethyl bromoacetate with K_2CO_3 and obtained a dark orange crystal product (yield, 0.73 g (67%), mp. 307–308 °C). Found: C: 63.29; H: 4.02; N: 10.47; $C_{56}H_{42}Cl_4N_8O_6$ requires C: 63.17; H: 3.98; N: 10.52. IR (KBr) ν : 3303 cm^{-1} (–OH), 1733 cm^{-1} (–C=O), 1467 cm^{-1} (–N=N–), 1273 cm^{-1} (C–O). 1H NMR ($CDCl_3$, 25 °C) δ_H : 1.43 (t, J = 7.16 Hz, 3H, CH_2-CH_3), 3.74 (d, J = 5.37 Hz, 2H, $ArCH_2Ar$), 3.78 (d, J = 5.29 Hz, 2H, $ArCH_2Ar$), 4.41 (d, J = 13.98 Hz, 2H, $ArCH_2Ar$), 4.50 (q, J = 7.14 Hz, 2H, $O-CH_2-CH_3$), 4.60 (d, J = 13.28 Hz, 2H, $ArCH_2Ar$), 4.98 (s, 2H, $O-CH_2-C=O$), 7.39–7.45 (m, 8H, ArH), 7.72–7.80 (m, 16H, ArH), 9.50 (s, 2H, $ArOH$), 9.92 (s, 1H, $ArOH$).

2.3.5. Preparation of 25-(ethoxycarbonylmethoxy)-26,27,28-trishydroxy-5,11,17,23-tetrakis[(4-bromophenyl)azo]calix[4]arene (4e)

Azocalix[4]arene **4e** is prepared as described above, using **3e**, ethyl bromoacetate with K_2CO_3 and obtained an orange crystal product (yield, 0.67 g (62%), mp. 283–285 °C). Found: C: 54.24; H: 3.37; N: 9.09; $C_{56}H_{42}Br_4N_8O_6$ requires C: 54.13; H: 3.41; N: 9.02. IR (KBr) ν : 3309 cm^{-1} (–OH), 1742 cm^{-1} (–C=O), 1467 cm^{-1} (–N=N–), 1270 cm^{-1} (C–O). 1H NMR ($CDCl_3$, 25 °C) δ_H : 1.45 (t, J = 7.16 Hz, 3H, CH_2-CH_3), 3.73 (d, J = 5.28 Hz, 2H, $ArCH_2Ar$), 3.77 (d, J = 5.19 Hz, 2H, $ArCH_2Ar$), 4.41 (d, J = 13.96 Hz, 2H, $ArCH_2Ar$), 4.49 (q, J = 7.15 Hz, 2H, $O-CH_2-CH_3$), 4.59 (d, J = 13.27 Hz, 2H, $ArCH_2Ar$), 4.97 (s, 2H, $O-CH_2-C=O$), 7.54–7.80 (m, 24, ArH), 9.40 (s, 2H, $ArOH$), 9.80 (s, 1H, $ArOH$).

2.3.6. Preparation of 25-(ethoxycarbonylmethoxy)-26,27,28-trishydroxy-5,11,17,23-tetrakis[(4-nitrophenyl)azo]calix[4]arene (4f)

Azocalix[4]arene **4f** is prepared as described above, using **3f**, ethyl bromoacetate with K_2CO_3 and obtained an orange crystal

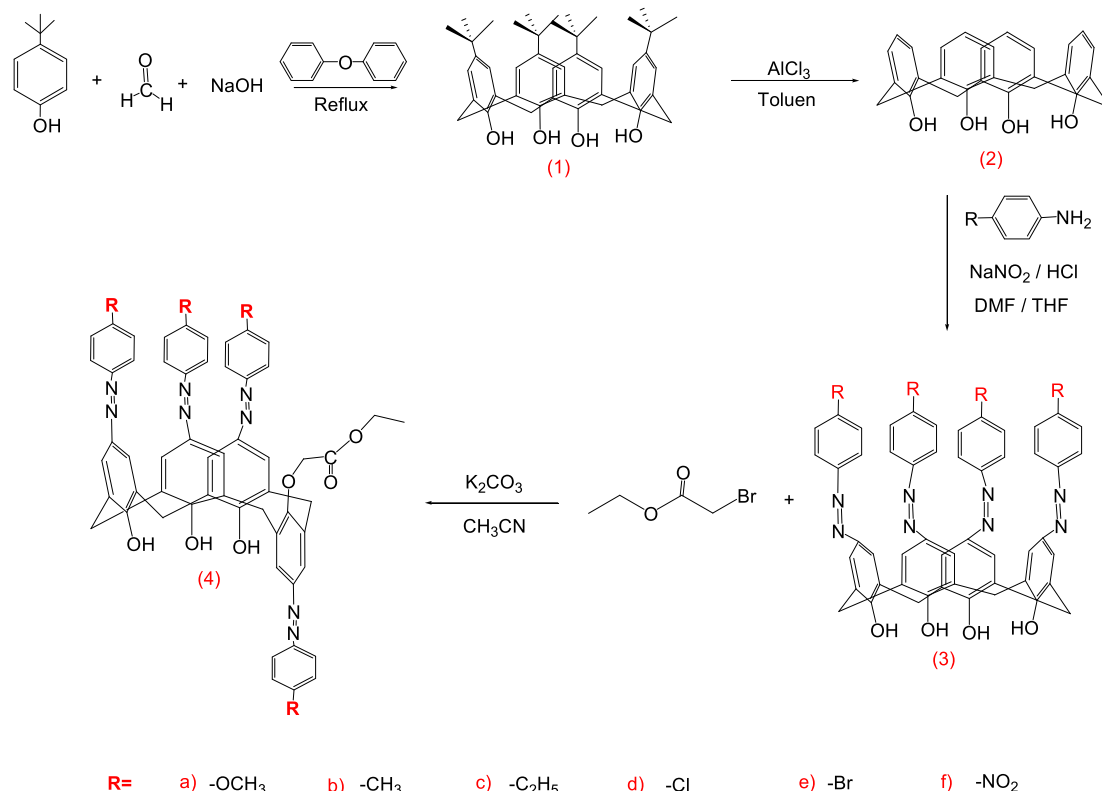
product (yield, 0.59 g (54%), mp. 292–294 °C). Found: C: 60.88; H: 3.77; N: 15.11; $C_{56}H_{42}N_{12}O_{14}$ requires C: 60.76; H: 3.82; N: 15.18. IR (KBr) ν : 3302 cm^{-1} (–OH), 1754 cm^{-1} (–C=O), 1466 cm^{-1} (–N=N–), 1278 cm^{-1} (C–O). 1H NMR ($CDCl_3$, 25 °C) δ_H : 1.43 (t, J = 7.16 Hz, 3H, CH_2-CH_3), 3.74 (d, J = 5.41 Hz, 2H, $ArCH_2Ar$), 3.78 (d, J = 5.32 Hz, 2H, $ArCH_2Ar$), 4.41 (d, J = 13.98 Hz, 2H, $ArCH_2Ar$), 4.50 (q, J = 7.15 Hz, 2H, $O-CH_2-CH_3$), 4.60 (d, J = 13.29 Hz, 2H, $ArCH_2Ar$), 4.99 (s, 2H, $O-CH_2-C=O$), 7.62–7.96 (m, 24, ArH), 9.42 (s, 2H, $ArOH$), 10.12 (s, 1H, $ArOH$).

3. Results and discussion

The binding ability of the azocalix[4]arenes depends on the macrocyclic ring sizes, their conformations and the nature of the functional groups [18]. All these six new compounds (**4a–f**) took *partial cone* conformation in solution. The presence of tetra azo (–N=N–) groups and mono ester in the azocalix[4]arenes were observed to play an important role in cation complexation with corresponding azocalix[4]arene derivatives.

The selectivity of azocalix[4]arene derivatives toward transition metal cations has been reported in the literature [25]. Bingol et al. reported the selectivity of a novel benzothiazole based azocalix[4]arene toward selected metal cations, particularly Hg^{2+} [37].

In this work, it was aimed to synthesize azocalix[4]arenes containing mono ester groups which are suitable for Hg^{2+} metal complexation. 5,11,17,23-tetrakis[(4-methoxy phenyl)azo]calix[4]arene (**3a**) was obtained by the diazo-coupling reaction. The esterification reaction of 5,11,17,23-tetrakis[(4-substituephenyl)azo]calix[4]arene (**3a–f**) were performed with the presence of K_2CO_3 and ethyl bromoacetate in dry acetonitrile at room temperature for 4 days. Other azocalix[4]arene derivatives (**4a–f**) were also synthesized in a similar manner but their yields were lower as compared to (**3a–f**). The obtained azocalix[4]arenes (**4a–f**) were further purified by recrystallization, and



Scheme 2. Synthesized of azocalix[4]arene mono ester derivatives (**4a–f**).

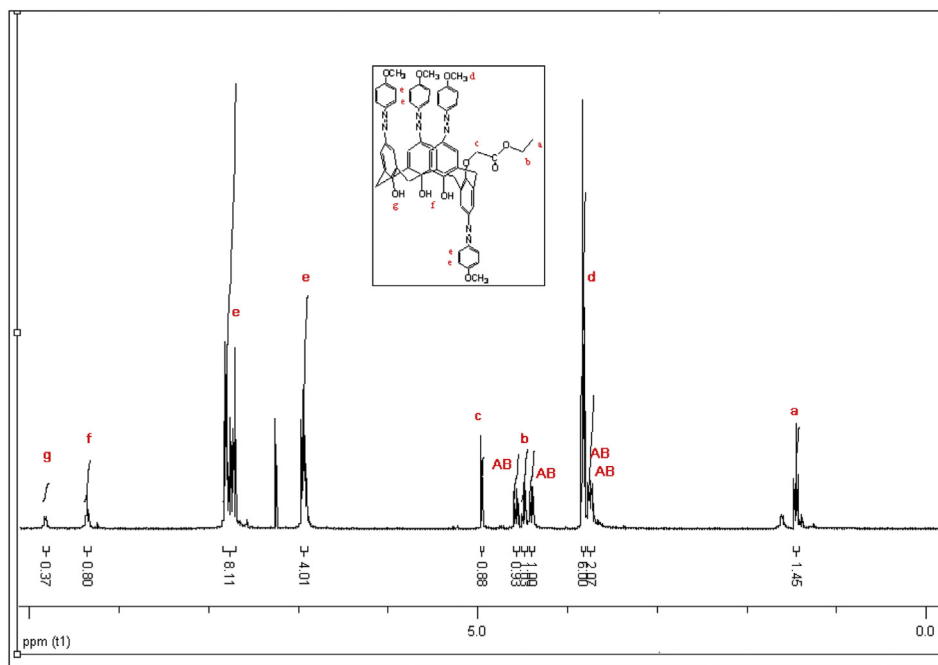


Fig. 1. ^1H NMR spectra of azocalix[4]arene mono ester derivative (**4a**).

their purity was examined by thin-layer chromatography (Scheme 2).

The IR and NMR spectra of the azocalix[4]arenes were recorded. The IR spectra of the azocalix[4]arenes exhibited absorption between 1467 and 1448 cm^{-1} , which is characteristic for $-\text{N}=\text{N}-$ vibration mode. Analysis of the IR spectra have revealed that these compounds (**4a–f**) were attached to each consecutive ($-\text{N}=\text{N}-$) groups in a regular array.

The ^1H NMR spectra of compound **4a** exhibited rather broad signals for all protons, with each peak for the methyl (**a**) (t, 1.45), for the methoxy (**b**) (m, 3.80–3.85), for the methylene (**c**) OCH_2CO (d, 4.95) and for the aromatic (**e**) (m, 6.90–6.97 and 7.70–7.83) residues. The proton of the AB system, characteristic of the bridging methylene protons in tetramers in the *partial cone* conformation, partly obscured by four doublets at 3.72, 3.75, 4.40 and 4.57 ppm. Among all of the proton chemical shifts in the azocalix[4]arene, the two largest are those of the axial proton in methylene bridges of the azocalix[4]arene in the *partial cone* conformation (0.10–0.30 ppm upfield) and the aromatic protons (0.20 ppm downfield) (Fig. 1).

Probable three-dimensional structure of the (**4b**) molecule, was drawn with GaussView 5.0 molecular imaging program [38] and space settlements of atoms were determined. All theoretical calculations were performed by Gaussian 09 W package program [39]. Shown in Fig. 2 the crystal structure of azocalix[4]arene ester derivative (**4b**) exhibited as *partial cone* conformation.

The coloring ability of azocalix[4]arenes **4a–f** in acetonitrile, acetic acid, chloroform, DMF, DMSO and methanol solvents was detected by either *naked eye* (visual) or UV–Vis absorption (optical) methods. The solution of the compounds **4a–f** showed dramatic color changes from light orange to red in above solvents. The absorption spectrum of the compounds **4a–f** has a maximum absorption peak at 369 nm, corresponding to $\pi-\pi^*$ transitions of the $-\text{N}=\text{N}-$ bond. When **4a–f** (4×10^{-5} M) were treated with a series of above solvents (2×10^{-4} M), bathochromic shifts were observed only for DMF and DMSO. On the other hand, no significant change was observed upon the addition of the other solvents. The results can be attributed to the more suitable interaction between solvent polarities and negative charge center in **4a–f** (Fig. 3) (Table 1).

As shown in Table 1, when the compounds **4a–f** were dissolved in methanol plus acid or base, significant changes at the peak values were observed with the spectroscopic measurements (Fig. 4).

The stability constant value of the Hg^{2+} with the compounds **4a–f** demonstrates that they exhibit good Hg^{2+} recognition properties, most probably due to having a more complementary structure as compared to other heavy metal ions. Moreover, the compounds **4a–f** have a higher association constant value for Hg^{2+} than the other chemosensors reported in the literature [37].

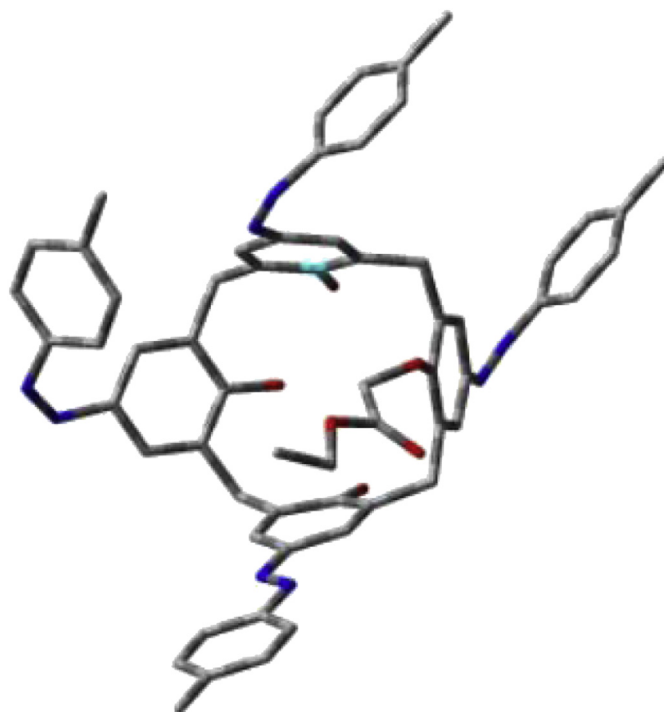


Fig. 2. The optimized structure of (**4b**) molecule.

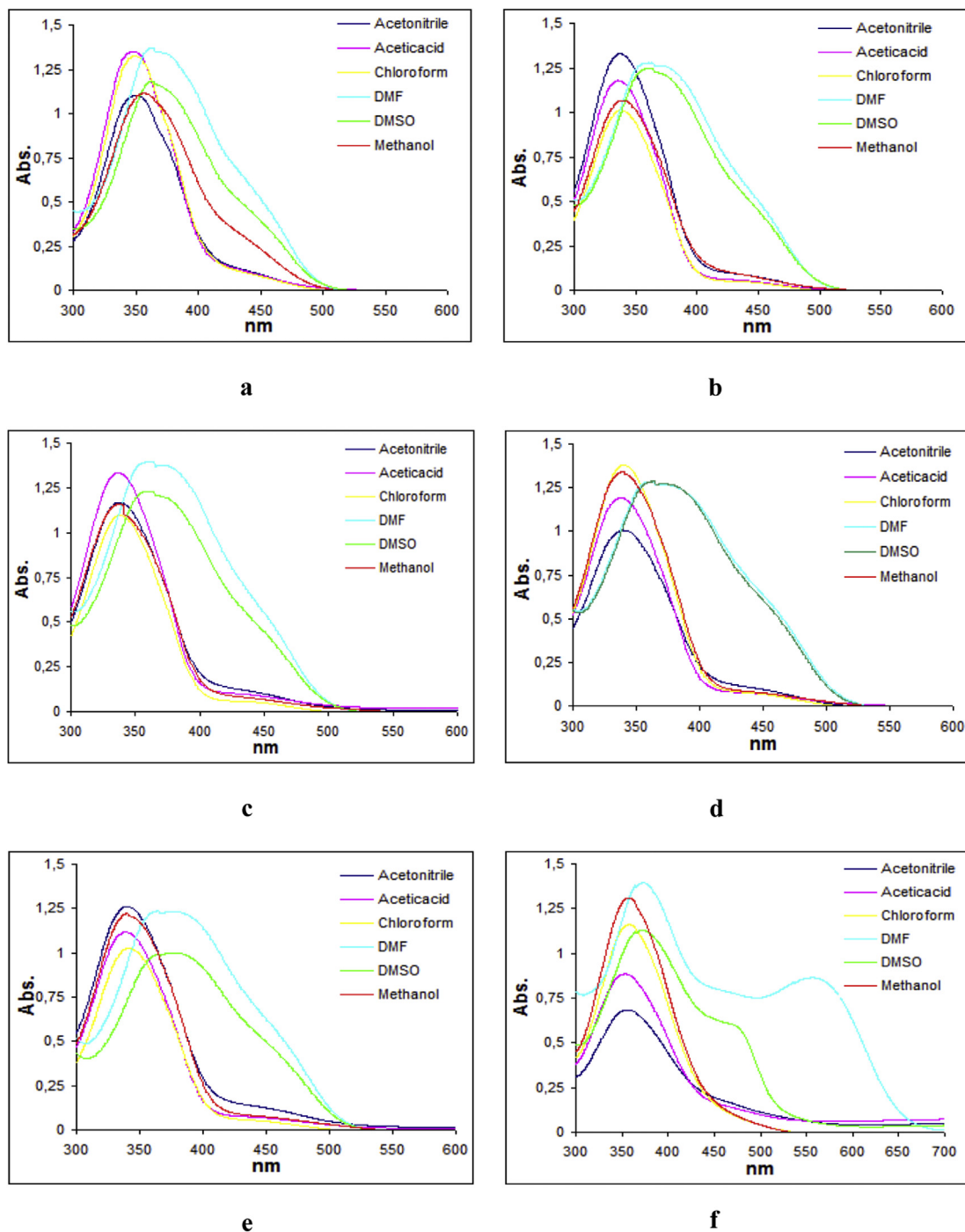


Fig. 3. Absorption spectra of azocalix[4]arene (**4a–f**).

Solvent extraction experiments have been performed to ascertain the effectiveness of the compounds **4a–f** in transferring the metal cations, such as Na^+ , K^+ , Sr^{2+} , Ag^+ , Hg^+ , Hg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cr^{3+} , Al^{3+} and La^{3+} from the aqueous phase into the organic phase. The results of the metal picrate extractions with azocalix[4]arene derivatives **4a–f** are summarized in Table 2 and are depicted in Fig. 5. It is obvious that the compounds **4a–f** are more effective in transferring $\text{Hg}^+/\text{Hg}^{2+}$ than the other cations. However, this conclusion has been reported in the literature previously [8].

This phenomenon can be explained by the hard-soft acid–base principle (HSAB). The $-\text{N}=\text{N}-$ groups are a soft base and show a

stronger affinity toward soft basic metal cations than toward hard metal cations. In this case, the strong participation of the $-\text{N}=\text{N}-$ groups in the host–guest complexation was further confirmed by the extraction results of azocalix[4]arenes (**4a–f**). The extraction values given in Table 2 clearly show that the $-\text{N}=\text{N}-$ groups certainly play a decisive role in the extraction of Hg^{2+} due to its contribution to cation– π interaction. This cation– π interaction can not be explained by the ionic radius of Hg^{2+} since the Co^{2+} having a closely similar ionic radius with Hg^{2+} could not be extracted as effectively as Hg^{2+} . No simple explanation for this difference is apparent at this time, but the cavity size, polarizability effects, the number and type of the donor atoms, and conformational aspects

Table 1
Influence of solvent on $\lambda_{\max}$ (nm) of azocalix[4]arenes (**4a–f**).

Ligands	MeCN	AcOH	CHCl ₃	DMF	DMSO	MeOH	MeOH + HCl	MeOH + KOH
4a	347	350	349	363	364	356	352	361
4b	336	335	339	367	359	339	499	353
4c	338	336	338	371	358	338	338	357
4d	339	336	340	362	370	339	472	352
4e	339	338	341	377	378	340	341	372
4f	357	352	358	377	372	357	348	343
				564	474		358	433

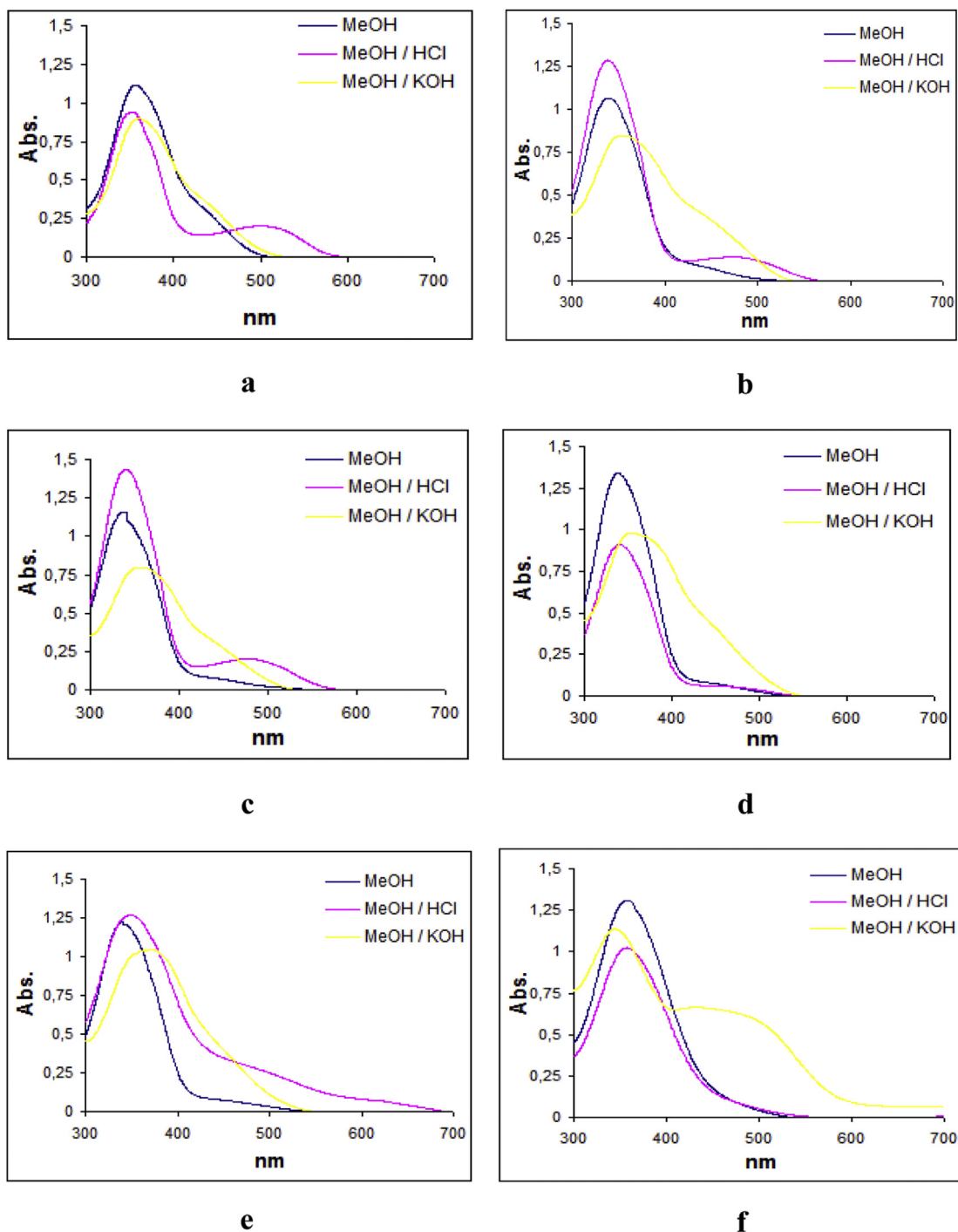


Fig. 4. Effect of acid and base absorption spectra of azocalix[4]arenes (**4a–f**).

Table 2
Extraction of metal picrates with azocalix[4]arene derivatives **4a–f**.^a

Ligands	Picrate salt extracted (%)												
	Na ⁺	K ⁺	Sr ²⁺	Ag ⁺	Hg ⁺	Hg ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cr ³⁺	Al ³⁺	La ³⁺
4a	<3	<3	<3	<3	20.9	21.7	<3	<3	<3	<3	4.2	<3	<3
4b	<3	<3	<3	3.6	17.6	21.4	<3	<3	<3	<3	4.2	<3	<3
4c	<3	<3	<3	<3	8.6	21.7	<3	<3	<3	<3	<3	<3	<3
4d	<3	<3	<3	<3	9.6	16.0	<3	<3	<3	<3	3.6	<3	<3
4e	<3	<3	<3	<3	9.6	22.3	<3	<3	<3	<3	4.5	<3	<3
4f	<3	<3	<3	<3	13.3	21.4	<3	<3	<3	<3	<3	<3	<3

^a H₂O/CHCl₃ = 10/10 mL (v/v); [picric acid] = 2×10^{-5} M, [ligand] = 1×10^{-3} M, [metal nitrate] = 1×10^{-2} M; 298 K, 1 h contact time. $\alpha \leq \pm 2\%$.

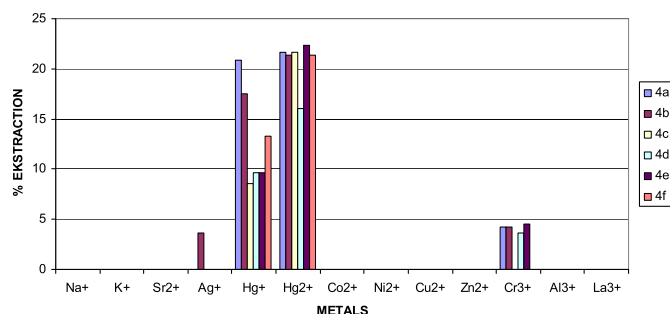


Fig. 5. Extraction percentages of azocalix[4]arene derivatives (**4a–f**).

of the azocalix[4]arenes are all likely to be important factors in selectivity.

Since azocalix[4]arenes are easily available in larger quantities and also amenable to nearly unlimited chemical modifications, it can be expected that even better extractants or ion carriers can be obtained on the basis of the calix[4]arenes. It is hoped that the selectivity of certain ligands toward Hg²⁺ can be further improved.

In conclusion, we have synthesized new azocalix[4]arene based chemosensors that are particularly selective for Hg²⁺. due to presence of azo groups at the *upper rim* as the metal binding sites. It is believed that these compounds could be applied for the selective extraction of Hg²⁺ ions from particular samples such as environmental surface waters or industrial effluents.

Acknowledgments

This work is supported in part by a grant from the Scientific and Technical Research Council of Turkey (TUBITAK, 112T028). The authors would like to thank Prof. Dr. Alaattin SEN for his invaluable and constructive comments on the manuscript.

References

- [1] Ko DCK, Porter JF, McKay G. Mass transport model for the fixed bed sorption of metal ions on bone char. *Ind Eng Chem Res* 2003;42:3458–69.
- [2] Meena AK, Mishra GK, Rai PK, Rajagopal C, Nagar PN. Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. *J Hazard Mater* 2005;122:161–70.
- [3] Memon S, Yilmaz M. An excellent approach towards the designing of a Schiff-base type oligocalix[4]arene, selective for the toxic metal ions. *J Macromol Sci Part A – Pure Appl Chem* 2002;39:63–73.
- [4] Raut DR, Mohapatra PK, Ansari SA, Sakar A, Manchanda VK. Selective transport of radio-caesium by supported liquid membranes containing calix[4]crown-6 ligands as the mobile carrier. *Desalination* 2008;232:262–71.
- [5] Hajipour AR, Habibi S, Ruoho AE. Synthesis and characterization of new optically active polymers carrying calix[4]arene and amino acid units in the main chain and their binding properties towards toxic heavy metals. *Polym Int* 2009;58:630–9.
- [6] Tabakci M, Yilmaz M. Sorption characteristics of Cu(II) ions onto silica gel-immobilized calix[4]arene polymer in aqueous solutions: batch and column studies. *J Hazard Mater* 2009;151:331–8.
- [7] Gutsche CD. In: Stoddart FJ, editor. *Calixarenes, revisited*. Cambridge: Royal Society of Chemistry; 1989.
- [8] Vicens J, Böhmer V, editors. *Calixarenes: a versatile class of macrocyclic compounds*. Dordrecht, The Netherlands: Kluwer Academic Publishers; 1991.
- [9] Kubo Y, Hamaguchi S, Niimi A, Yosida K, Tokita S. Synthesis of a 1,3-bis(indoaniline)-derived calix[4]arene as an optical sensor for calcium ion. *J Chem Soc Chem Commun*; 1993:305–7.
- [10] Arnaud-Neu F, Schwing-Weill MJ, Ziat K, Cremin S, Harris SJ, McKevey MA. Selective alkali and alkaline earth cation complexation by calixarene amides. *New J Chem* 1991;15:33–7.
- [11] Arnaud-Neu F, Collins EM, Deasy M, Ferguson G, Harris SJ, Kaitner B, et al. Synthesis, X-ray crystal structures, and cation-binding properties of alkyl calixaryl esters and ketones, a new family of macrocyclic molecular receptors. *J Am Chem Soc* 1989;111:8681–91.
- [12] Matsumoto H, Shinkai S. Metal-induced conformational change in pyrene-appended calix[4]crown-4 which is useful for metal sensing and guest tweezing. *Tetrahedron Lett* 1996;37:77–80.
- [13] Arduini A, Ghidini E, Pochini A, Ungaro R, Andreotti GD, Calestani G, et al. *p*-*t*-Butylcalix[4]arene tetra-acetamide: a new strong receptor for alkali cations. *J Incl Phenom* 1998;6:119–34.
- [14] McKevey MA, Seward EM, Ferguson G, Ruhl B, Harris SJ. Synthesis, X-ray crystal structures, and cation transfer properties of alkyl calixaryl acetates, a new series of molecular receptors. *J Chem Soc Chem Commun*; 1985:388–90.
- [15] Chang SK, Cho I. New metal cation-selective ionophores derived from calixarenes: their syntheses and ion-binding properties. *J Chem Soc Perkin Trans* 1986;1:211–4.
- [16] Shinkai S, Shirahama Y, Satoh H, Manabe O, Arimura T, Fujimoto K, et al. Selective extraction and transport of UO₂²⁺ with calixarene-based uranophiles. *J Chem Soc Perkin Trans* 1989;2:1167–71.
- [17] Iwamoto K, Shinkai S. Synthesis and ion selectivity of all conformational isomers of tetrakis(ethoxycarbonyl)methoxy-calix[4]arene. *J Org Chem* 1992;57:7066–73.
- [18] Deligöz H. Azocalixarenes: synthesis, characterization, complexation, extraction, absorption properties and thermal behaviours. *J Incl Phenom Macrocycl Chem* 2006;55:197–218.
- [19] Chakrabarti A, Chawla HM, Francis T, Pant N, Upreti S. Synthesis and cation binding properties of new arylazo- and heteroarylazotetraphthalcalix[4]arenes. *Tetrahedron* 2006;62:1150–7.
- [20] Kim TH, Kim SH, Tan LV, Dong Y, Kim H, Kim JS. Diazo-coupled calix[4]arenes for qualitative analytical screening of metal ions. *Talanta* 2008;74:1654–8.
- [21] Lu L, Zhu S, Liu X, Xie Z, Yan X. Highly selective chromogenic ionophores for the recognition of chromium(III) based on a water-soluble azocalixarene derivative. *Anal Chim Acta* 2005;535:183–7.
- [22] Arnaud-Neu F, Fanni S, Guerra L, Megregor W, Ziat K, Schwingweill MJ, et al. Cation complexation by chemically-modified calixarenes .7. Transport of alkali cations by *p*-tert-butylcalix-[*n*]arene esters and amides. *J Chem Soc Perkin Trans* 1995;2:113–8.
- [23] Casnati A, Pochini A, Ungaro R, Uggozoli F, Arnaud F, Fanni S, et al. Synthesis, complexation and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: a new class of cesium-selective ionophores. *J Am Chem Soc* 1995;117:2767–77.
- [24] Ghidini E, Uggozoli F, Ungaro R, Harkema S, El-Fadl AA, Reinholt DN. Complexation of alkali metal cations by conformationally rigid, stereoisomeric calix[4]arene crown ethers: a quantitative evaluation of preorganization. *J Am Chem Soc* 1990;112:6979–85.
- [25] Ak M, Taban D, Deligöz H. Transition metal cations extraction by ester and ketone derivatives of chromogenic azocalix[4]arenes. *J Hazard Mater* 2008;154:51–4.
- [26] Alpoğuz HK, Kaya A, Deligöz H. Liquid membrane transport of Hg(II) by an azocalix[4]arene derivative. *Sep Sci Technol* 2006;41:1155–67.
- [27] Elçin S, Deligöz H. Di-substituted azocalix[4]arenes containing chromogenic groups: synthesis, characterization, extraction, and thermal behavior. *Tetrahedron* 2013;69:6832–8.
- [28] Tilki T, Şener İ, Karci F, Gülce A, Deligöz H. An approach to the synthesis of chemically modified bisazocalix[4]arenes and their extraction properties. *Tetrahedron* 2005;61:9624–9.
- [29] Akdoğan A, Tavashli MD, Cebecioglu S, Şen A, Deligöz H. Liquid-liquid extraction of transition metal cations by nine new azo derivatives calix[*n*]arene. *Sep Sci Technol* 2002;37:973–80.
- [30] Deligöz H, Yilmaz M. Liquid-liquid extraction of transition metal cation by calixarenes-based cyclic ligands. *Solvent Extr Ion Exch* 1995;13:19–26.

- [31] Ak MS, Deligöz H. Azocalixarenes. 6: synthesis, complexation, extraction and thermal behaviour of four new azocalix[4]arenes. *J Incl Phenom Macrocycl Chem* 2007;59:115–23.
- [32] Gutsche CD, Iqbal M. Para-*tert*-butylcalix[4]arene. *Org Synth* 1990;68:234–7.
- [33] Gutsche CD, Iqbal M, Stewart D. Calixarenes.18. Synthesis procedures for para-*tert*-butylcalix[4]arene. *J Org Chem* 1986;51:742–5.
- [34] Karakuş ÖÖ, Deligöz H. Azocalixarenes.7: synthesis and study of the absorption properties of novel mono-azo substituted chromogenic calix[4]arenes. *Turk J Chem* 2011;35:87–98.
- [35] Karakuş ÖÖ, Deligöz H. Azocalixarenes.8: synthesis and investigation of the absorption spectra of *di*-substituted azocalix[4]arenes containing chromogenic groups. *J Incl Phenom Macrocycl Chem* 2008;61:289–96.
- [36] Lang K, Proskova P, Kroupa J, Moravek J, Stibor I, Pojarova M, et al. The synthesis and complexation of novel azosubstituted calix[4]arenes and thiacalix[4]arenes. *Dyes Pigments* 2008;77:646–52.
- [37] Bingol H, Kocabas E, Zor E, Coskun A. A novel benzothiazole based azocalix[4]arene as a highly selective chromogenic chemosensor for Hg^{2+} ion: a rapid test application in aqueous environment. *Talanta* 2010;82:1538–42.
- [38] Dennington R, Keith T, Millam J. GaussView, version 5. Shawnee Mission KS, USA: Semichem Inc.; 2009.
- [39] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, revision A.1. Wallingford CT: Gaussian, Inc.; 2009.