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ORIGINAL ARTICLE

Synthesis and extraction studies of polymeric phthalimido functionalized calix[4]arene

Gülderen Uysal Akkuş · Cihangir Cebeci

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Abstract The article comprises synthesis and extraction studies of polymeric calix[4]arene having phthalimide groups at the lower rim. The polymeric phthalimido functionalized calix[4]arene was synthesized via radical initiated reactions involving a vinylic monomer 5,11,17,23-tetra-*tert*-butyl-25-[4-(acrylamido)benzyloxy]-26,28-bis-(2-phthalimidoethoxy)-27-hydroxycalix[4]arene (**5**) with styrene. A five atom spacer group was incorporated between the bulky calixarene core and the acrylate moiety in order to minimize steric interactions which proved to impede the polymerization. From the liquid–liquid and solid–liquid extraction studies it has been concluded that the precursor **3** (5,11,17,23-tetra-*tert*-butyl-25-(4-nitro benzyloxy)-26,28-bis-(3-phthalimidoethoxy)-27-hydroxy-calix[4]arene) is selective for metal cations. The order of extractability of metal cations by the ligand 3 decreases in the sequence: $Hg^{2+} > Cd^{2+} > Cu^{2+} > K^{+} > Co^{2+}$ whereas its polymeric derivative is selective in the sequence: $Hg^{2+} > Cd^{2+} > K^{+} > Co^{2+} > Cu^{2+}$ for the metal cations used in the experiments.

Keywords Calixarene · Copolymer · Solvent extraction · Heavy metals · Supramolecular chemistry

Introduction

In recent years, contamination of large areas of land by heavy metals has become a major concern. It originates mainly from municipal waste incinerators, car exhausts, residues from metalliferrous mining and the smelting industry, as well as the use of urban compost, pesticides, fertilizers or sludge and sewage. From environmental and economic viewpoints, there remains a need to discover more selective and effective extractants for toxic heavy metals and anions from water and soil. The challenge is to find complexants that selectively extract those ions from mixtures then allow them to be readily released in purified form. In this respect macromolecules especially calixarenes are widely used in host–guest chemistry for the construction of various receptors for charged or neutral molecules [1]. Calix[4]arenes are macrocyclic molecules with unique three-dimensional structures. They belong to a larger family of calix[*n*]arene molecules, and are synthesized from the condensation reaction of formaldehyde and phenol [2–4]. When all four oxygen atoms point in the same direction, the macrocycle exhibits a bowl-shaped structure called the cone conformation [5]. The scaffold of calixarenes can be modified by introducing many kinds of functional groups at the “lower” rim and/or the “upper” rim. The aims of these chemical modifications are to: (i) enhance the selectivity and efficiency of their complexation properties, (ii) control their conformers, and (iii) improve their solubility [6]. Furthermore the easy derivatization of calix[4]arene together with controllable shape of its cavity make this molecule a very attractive candidate for various applications in supramolecular chemistry [7]. Therefore modified calixarenes have been used as extractants for cations, anions and neutral molecules [8–19].

During the past decades the interesting properties shown by these cyclic oligomeric compounds have stimulated a growing interest in their use in conjunction with polymeric matrices. Generally two main strategies have been followed with preparing polymeric calixarenes: One of which is based on the immobilization of the calixarene unity on

G. Uysal Akkuş (✉) · C. Cebeci
Department of Chemistry, Afyon Kocatepe University,
Afyonkarahisar 03200, Turkey
e-mail: guakkus@yahoo.com

an available polymeric matrix [20–29] and the other relies on copolymerization of the calixarene monomer with some other suitable monomer(s) either via linear step-growth polymerization or radical addition reactions [30–36]. In our previous work, we have reported new polymer-bound calix[4]arene derivative through the radical copolymerization of calix monomer with styrene [37]. Herein, we report the synthesis and extraction behavior of new styrene copolymer of calixarene derivative bearing phthalimide groups at the lower rim.

Experimental

Apparatus

Melting points were determined on a Barnsted/Electro thermal apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruke Avance DPX 400 spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer 1605 FTIR System Spectrum BX spectrometer as KBr pellets. UV–Vis spectra were obtained on a Shimadzu UV-1700 Pharma UV–Visible recording spectrophotometer. Elemental analyses were performed on a Elementar CHNS analyzer. ESI-MS spectra were taken on a Varian MAT 312 spectrometer. The molecular weight determinations were carried out by gel-permeation chromatography (GPC) in THF at 30 °C using a Agilent (HP) GPC and a refractive index detector with a solvent flow rate of 0.6 mL/min and a sample concentration of 2.0 mg/mL. The micro columns were calibrated using a set of narrow polydispersity polystyrene standards. TG–DTG thermograms were taken by a Shimadzu DTG 60 H Thermogravimetric analyzer. The sample weight was almost 10.0 mg. Analysis was performed from 0 to 600°C at a heating rate of 20°C/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min.

Materials

Analytical TLC were performed on precoated silica gel plates (SiO_2, Merck PF_{254}), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. All materials and reagents were standard analytical grade, purchased from Fluka or Merck, and used without further purification. Commercial grade solvents such as acetonitrile, chloroform, ethyl acetate, and *n*-hexane were distilled and stored over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Toluene was dried with calcium hydride and stored over Na wire. CH_2Cl_2 was distilled from $CaCl_2$, MeOH was distilled over Mg and stored over molecular sieves (4 Å). The drying agent employed was anhydrous sodium sulphate. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

Synthesis

The compounds **1** and **2** were synthesized according to the literature [38, 39] procedures and the other compounds (**3–6**) employed in this work as illustrated in Scheme 1 were synthesized according to the methods given below.

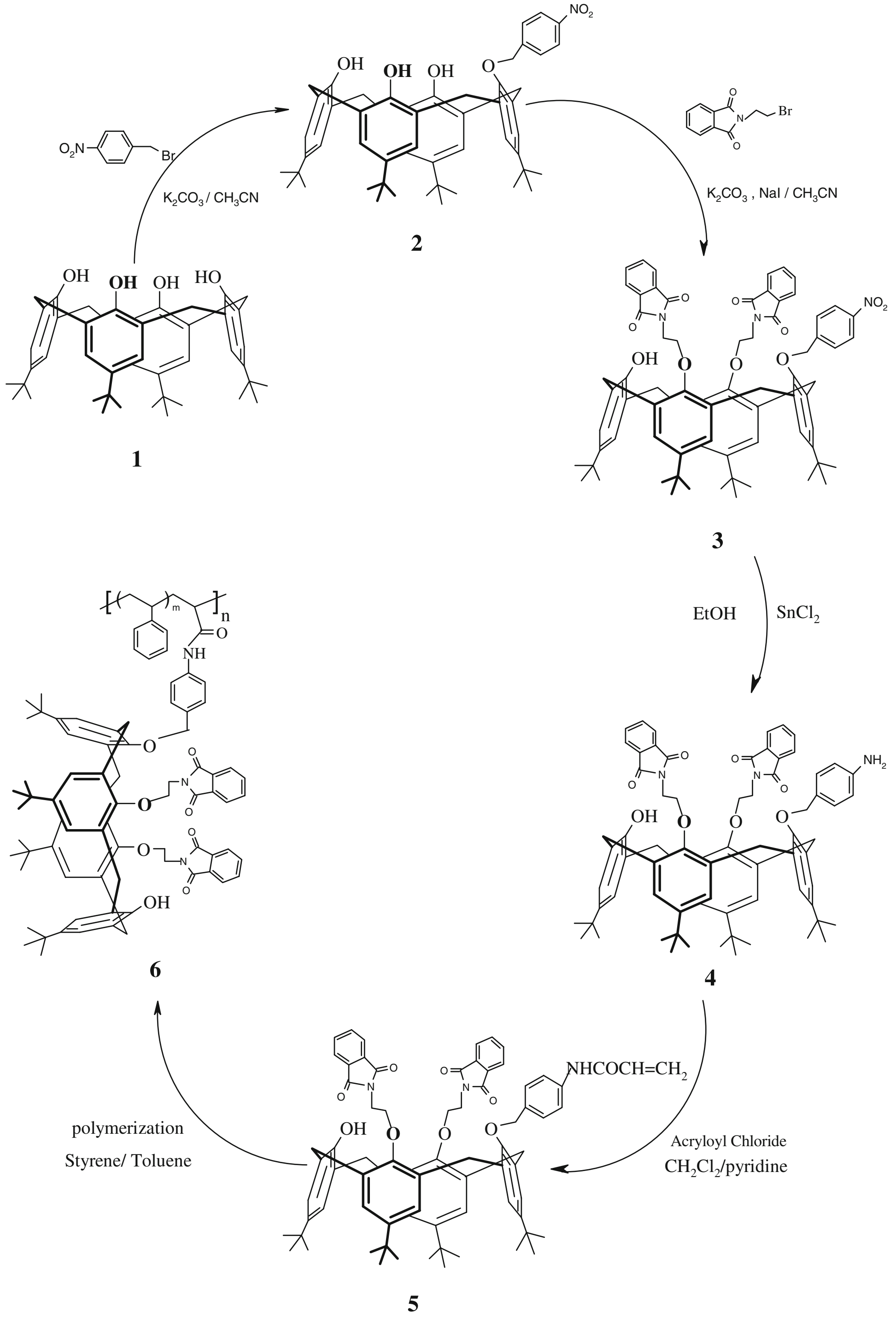
5,11,17,23-Tetra-*tert*-butyl-25,27-bis-(3-phthalimidoethoxy)-26-(4-nitrobenzyloxy)-28-hydroxy-calix[4] (**3**)

To a stirred mixture of compound **2** (1.8 g, 2.35 mmol) in 30 ml of dry acetonitrile were added *N*-(3-bromoethyl)-phthalimide (1.25 g, 4.94 mmol), K_2CO_3 (0.39 g, 2.82 mmol) and a catalytic amount of KI. The reaction mixture was refluxed under nitrogen for 60 h and then the solvent was removed under reduced pressure. The residue was dissolved in CH_2CI_2 (100 mL) and this solution washed with a 1 N NH_4CI aqueous solution (3 × 30 mL). The organic phase was dried over $MgSO_4$, the solvent was removed at the Rotavapor, and the compound **3** was obtained as a white powder by treatment with acetonitrile/methanol. Yield: 55%, mp: 143 °C. IR(KBr): 3420 cm^{-1} (OH), 1660 cm^{-1} (C=O), 1528 cm^{-1}(NO_2). ^{1}H NMR ($CDCl_3$), δ: 0.92 (s, 9H, Bu^t), 1.14 (s, 18H, Bu^t), 1.51 (s, 9H, Bu^t), 3.32 (d, 4H, $J = 13.0$ Hz, $ArCH_2Ar$), 4.18 (d, 4H, $J = 13.0$ Hz, $ArCH_2Ar$), 4.28 (t, 4H $J = 6.7$ Hz, OCH_2 and NCH_2), 4.51 (t, 4H, $J = 6.7$ Hz, OCH_2 and NCH_2), 4.98 (s, 2H, OCH_2Ar), 6.65–6.71 (m, 4H, ArH), 6.79–6.83 (m, 2H, ArH), 6.85 (s, 1H, ArOH), 7.01 (s, 2H, ArH), 7.49–7.54 (m, 4H, Phth–H), 7.67–7.71 (m, 4H, Phth–H), 7.78 (d, 2H, ArH, $J = 13.2$ Hz, 4-nitrophenyl), 7.92 (d, 2H, ArH, $J = 13.2$ Hz, 4-nitrophenyl). ^{13}C NMR ($CDCl_3$): δ 168.9 (CO); 134.1, 132.0, 123.4, 123.3, (ArC); 77.3, 77.2, 77.0, 76.7 (OCH_2); 59.0 (OCH_2Ar); 31.3, 30.0 ($ArCH_2Ar$). ESI-MS *m/z*: 1131.3 $[M + H]^+$. Anal. calculated for $C_{71}H_{75}N_3O_{10}$ (1130.3); C, 75.44; H, 6.69; N, 3.72. Found: C, 75.61; H, 6.93; N, 3.65.

Reduction of compound **3** (**4**)

A solution of **3** (3.0 g, 2.65 mmol) and $SnCl_2$ (10.83 g, 48 mmol) in ethanol (120 mL) was refluxed for 4 h. Then the reaction mixture was cooled, added in ice-cold water, neutralized with NaOH (pH: 7–8) and extracted twice with dichloromethane. The organic phase was washed with brine, dried with anhydrous Na_2SO_4 and evaporated until brownish-solid residue. Then triturated with MeOH and finally recrystallization was performed in isopropanol.

Scheme 1 Schematic representation of the synthesis of copolymer 6



Yield: 72%, m.p: 168 °C. IR(KBr): 3374 (OH, NH$_2$), 1668 (C=O). ^{1}H NMR (CDCl$_3$): δ 0.87 (s, 9H, Bu^t), 1.21 (s, 9H, Bu^t), 1.47 (s, 18H, Bu^t), 1.75–1.98 (brs, 2H, NH$_2$), 3.12 (d, 4H, $J = 13.0$ Hz, ArCH$_2$Ar), 4.15–4.29 (brm, 4H, ArCH$_2$Ar), 4.34 (t, 4H, $J = 7.0$ Hz, NCH$_2$), 4.57 (t, 4H, $J = 7.0$ Hz, OCH$_2$), 4.73 (s, 2H, OCH$_2$Ar), 6.59 (s, 4H, ArH), 6.84 (s, 2H, ArH), 6.89 (s, 1H, ArOH), 7.12–7.20 (m, 2H, ArH), 7.34–7.46 (m, 4H, ArH), 7.51–7.60 (m, 8H, Phth–H). ^{13}C NMR (CDCl$_3$): δ 168.3, 168.2 (CO); 150.7, 149.8, 148.5, 146.8, 146.6, 144.3, 143.0, 141.2, 133.9, 133.8, 133.7, 133.4, 132.5, 132.1, 128.2, 127.9, 127.7, 127.6, 127.5, 126.4, 125.9, 125.7, 125.6, 125.5, 125.0, 123.3, 123.1 (ArC); 77.3, 77.2, (OCH$_2$); 76.7, 74.2 (OCH$_2$Ar); 31.8, 31.7 (ArCH$_2$Ar). ESI-MS *m/z*: 1101.4 $[M + H]^+$. Anal. calculated for $C_{71}H_{77}O_8N_3$ (1100.4); C, 77.49; H, 7.05; N, 3.83. Found: C, 77.72; H, 6.89; N, 3.68.

Treatment of compound **4** with acryloyl chloride (**5**)

To a solution of compound **4** (1.10 g, 1.00 mmol) and pyridine (0.5 mL) in $CHCl_3$ (50 mL) was added acryloyl chloride (0.10 mL, 1.20 mmol) in $CHCl_3$ (5 mL) from a dropping funnel at 0 °C with continuous stirring. The stirring was continued for 1 h at 0 °C and then 24 h at room temperature. The reaction mixture was extracted with $CHCl_3$. The organic phase was washed with cold dilute NaOH aqueous solution and then with distilled water. Finally dried (Na_2SO_4), filtered, and concentrated in vacuo. The product was purified by passed through a silica gel gravity column using $CHCl_3$ and *n*-hexane (1:5) as eluent for **5**, Yield 79%. IR(KBr): 3470 (OH, NH), 1679 (C=O). ^{1}H NMR ($CDCl_3$): δ 0.91 (s, 9H, Bu^t), 1.32 (s, 9H, Bu^t), 1.43 (s, 18H, Bu^t), 3.17 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 4.31 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 4.41–4.57 (m, 8H, OCH_2 and NCH_2), 4.92 (s, 2H, OCH_2Ar), 6.51–6.77 (m, 4H, $HC{=}CH_2$, OH), 7.19–7.65 (m, 13H, ArH and NH), 7.71–7.97 (m, 8H, Phth–H). ^{13}C NMR ($CDCl_3$): δ 168.3, 168.2 (CO); 150.8, 149.8, 148.5, 146.8, 146.6, 144.3, 143.0, 133.9, 133.7, 133.4, 132.5, 132.1, 128.2, 127.9, 127.7, 127.5, 126.5, 125.9, 125.7, 125.6, 125.5, 125.0, 123.3, 123.1 (ArC); 77.3, 77.0 (OCH_2); 76.7, 74.2 (OCH_2Ar); 31.8, 31.7, 31.5 ($ArCH_2Ar$). ESI-MS *m/z*: 1155.4 $[M + H]^+$. Calculated for $C_{74}H_{79}N_3O_9$ (1154.4); C, 77.49; H, 7.05; N, 3.83. Found: C, 77.72; H, 6.89; N, 3.68.

Copolymerization of compound **5** (**6**)

The monomer **5** (0.45 g, 0.385 mmol), toluene (1 mL), benzoyl peroxide (12.5 mg) and styrene (0.22 mL, 1.925 mmol) were placed in a vial and flushed for 30 min with purified nitrogen with stirring. After that the vial was degassed and sealed under vacuum. The vial was heated at 80 °C for 12 h. The product was then precipitated in methanol. The crude product was purified by several precipitations from chloroform solution in methanol. The precipitated polymer was filtered and dried in vacuum. Yield 75%. IR (KBr): 3418 cm^{-1} (OH, NH), and 1672 cm^{-1} (CONH). ^{1}H-NMR ($CDCl_3$): δ 0.93 (s, 36H, Bu^t), 1.37 − 1.75 (brs, 38H, CH_2–C and CH–C); 3.80 (brd, 4H, Ar–CH_2–Ar); 4.21–4.54 (brm, 5H, Ar–CH_2–Ar and CH–C); 5.12–5.36 (brm, 10H, CH_2O, CH_2N); 6.85 (brs, 37H, ArH); 7.13–7.32 (brm, 8H, Ar–H); 7.42–7.89 (brm, 35H, Ar–H, NH, OH).

Analytical procedure

Liquid–liquid extraction

Picrate extraction experiments were performed following Pedersen's procedure [40]. A 10 mL of 2.0×10^{-5} M aqueous picrate and 10 mL of 1×10^{-3} M solution of calixarene (**2–4**) or a 1×10^{-3} M solution of calix[4]arene unit/g polymeric resin (**6**) in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with mechanical shaker for 2 min, then magnetically stirred in a thermostated water-bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The percent extraction (*E*%) has been calculated as:

$$E\% = (A_0 - A)/A_0 \times 100$$

where A_0 and A are initial and final concentrations of metal picrate before and after the extraction, respectively. The metal picrates were prepared according to previous studies [41, 42].

Solid–liquid extraction

About 25 mg of the copolymer (**6**) was shaken with a 10 mL of aqueous solution containing about 2.5×10^{-5} M metal picrate in a 50 mL stoppered glass flask immersed in a thermostated water bath maintained at 25 °C for 1 h and finally filtered off. The concentration of picrate ion remaining in the aqueous phase after the adsorption was then determined spectrophotometrically [43].

Results and discussion

The preparation of the calixarene monomer (**5**) and its styrene copolymer (**6**) are presented in Scheme 1. The synthesis of *p-tert*-butylcalix[4]arene (**1**) and *p-tert*-butyl-25,27,28-trihydroxy-26-(4-nitrobenzyloxy)calix[4]arene (**2**) were based on previously published procedure [38, 39]. *p-tert*-Butyl-25,27-bis-(3-phthalimidoethoxy)-26-(4-nitrobenzyloxy)-28-hydroxycalix[4] arene (**3**) was synthesized by refluxing compound **2** with *N*-(3-bromoethyl)-phthalimide in acetonitrile in the presence of K_2CO_3 in % 55 yield. The IR spectra of compound **3** shows an amide band at 1660 cm^{-1}. The ^{1}H NMR spectrum of **3** has a typical AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 3.32 and 4.18 ppm ($J = 13.0$ Hz) indicating that the compound **3** exist in cone conformation. The nitro group of **3** then underwent reduction with Sn(II)Cl_2 in ethanol to give the amino derivative **4** in 72% yield. Completion of this reaction was followed by the IR spectroscopy indicating the disappearance of the band due to the nitro groups at 1528 cm^{-1}. The monomer **5** is derived from **4** by coupling the extended aminobenzyl group of **4** with acryloyl chloride in the presence of pyridine. After purification by column chromatography ($CHCl_3$: *n*-hexane, 1:4) **5** is obtained in 79% yield.

The calixarene monomer **5** has been copolymerized with styrene (1:5 ratio) in sealed vials using degassed toluene as the solvent and benzoyl peroxide as the radical initiator gives the copolymer **6** in 75% yield. The ^{1}H NMR spectrum of **6** indicates that both monomers (**5** and styrene) have been incorporated into the repeating units, since signals unique to both monomers are observed in **6**. The molecular weight for **6** has been determined by GPC in THF against polystyrene standards. The average molecular weight (M_n) for the copolymer **6** was found 5765 g/mol. The percent composition of the copolymer **6** is determined from integration of signals unique to each monomer (**5** and styrene) in the ^{1}H NMR spectra. From integration ratios between the signals of the *tert*-butyl protons of the calixarene (δ 0.93), and the methylene protons of the styrene units (δ 1.37–1.75), the copolymer composition (n/m) of **6** is 1/12. This n/m value shows that in **6** the styrene monomer is predominant and the calixarene units are randomly distributed along the chain. This result was obtained presumably due to the steric hindrances exhibited by bulky calixarene moieties.

The thermogravimetric analysis (TGA) of **6** was determined and its TG and DTG curves presented in Fig. 1, as well as thermal behavior and decomposition temperatures of the copolymer **6** are given in Table 1. As seen in Fig 1, initial weight loss of mass 4.13% occurs at 280 °C, maximum weight loss is occurred at 453 °C, up to 500 °C temperature the remaining of 3.75 of polymer without decomposed.

Extraction studies

The ion recognition properties of *p-tert*-butylcalixarene bearing phthalimido groups (**3**) on lower rim and its polymeric analogue (**6**) were studied by liquid–liquid and solid–liquid extraction experiments. The liquid–liquid extraction was performed with selected alkali and transition metal (Na^+, K^+, Cs^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+} and Cd^{2+}) picrates and the results are summarized in Table 2. These data were obtained by using dichloromethane solutions of the ligands to extract metal picrates from aqueous solution. The equilibrium concentration of picrate in aqueous phase was then determined spectrophotometrically.

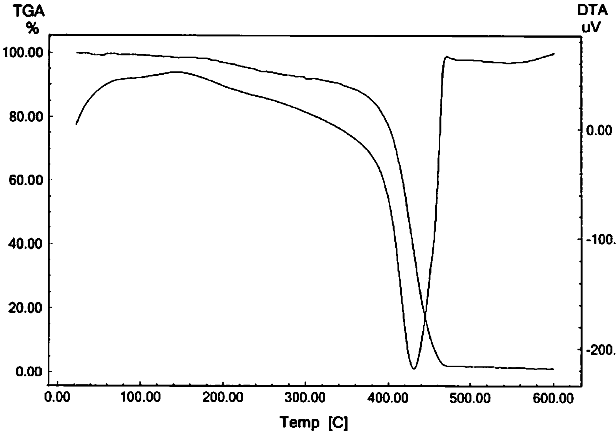


Fig. 1 TG and DTG curves of copolymer **6**

Table 1 Thermogravimetric analysis results of copolymer **6**[a,b]

IDT (°C)[c]	The temperature (°C) for a weight loss (%)				The residue (%) at 500 °C
	20	40	60	80	
280	311	394	409	417	3.75

[a] The sample weight was almost 10 mg

[b] Analysis was performed from 0 to 600 °C at a heating rate of 20 °C/min in a nitrogen atmosphere with a glass flow rate of 40 mL/min

[c] Initial decomposition temperature

From the extraction data given in Table 2, it was observed that **2** extracts neither alkali nor transition metal ions into organic phase from aqueous phase. But its phthalimido derivative (**3**) shows significant extraction of metal cations, with the relative order $Hg^{2+} > Cd^{2+} > Cu^{2+} > K^+ > Co^{2+}$ being observed. It is apparent that this compound is more efficient extractant for mercury(II) in selected metal ions. This is because mercury has a more soft nature as compared to competing cations. The effectiveness in transferring these cations by **3** indicates that the binding ability towards metal cations belongs to soft acids and bases in Pearson's classification [44, 45]. This is consistent with the SHAB principle because the π-electrons (C=O) is polarizable. When the nitro group is reduced to amino group, the decrease in extraction is probably due to intramolecular hydrogen bonding between N–H and facing oxygen atoms of the phthalimido group, which decreases the metal ion complexing ability [46]. To compare the extraction characteristics of the calixarene loaded polymeric ionophore **6** with the monomers **3** and **4**, comparable

Table 2 Liquid–liquid extraction of metal cations with ligands[a]

Ligand	Picrate salt extracted (%)							
	Na^+	K^+	Cs^+	Cu^{2+}	Cd^{2+}	Ni^{2+}	Hg^{2+}	Co^{2+}
2	13.7	24.7	31.5	12.3	21.6	23.6	40.0	19.7
3	9.8	28.5	11.9	34.8	42.3	13.5	68.3	23.1
4	19.5	32.6	31.0	30.4	43.1	17.3	47.7	16.3
6	23.8	61.7	28.9	32.0	65.5	21.4	66.8	36.6
6[b]	–	47.3	–	–	32.6	–	53.0	–

[a] Aqueous phase [metal picrate] = 2.0×10^{-5} M; organic phase. dichloromethane [ligand] = 1×10^{-3} M or 1×10^{-3} M solution of calix[4]arene unit/g resin for oligomer at 25 °C for 1 h

[b] Solid–solid batch wise adsorption extraction experiments

extractions have been performed. It is observed that **6** is selective in sequence: $Hg^{2+} > Cd^{2+} > K^{+} > Co^{2+} > Cu^{2+}$ for the metal cations used in the experiments.

The solid–liquid batchwise adsorption extraction experiments of copolymer **6** were performed into the aqueous solutions of selected metal picrates (K^+, Cd^{2+} and Hg^{2+}) at 25 °C for 1 h. Table 2 shows the extractability behavior of the copolymer **6**. From the data given in Table 2 it has been observed that there is a significant decrease in the extraction ability of the copolymer **6** and a little binding evidence, which means that binding ability is weak in solid state, but showed more or less the same affinity toward the metal cations.

Conclusion

In this study new calix[4]arene (**3**) containing phthalimido groups at the lower rim and its copolymer (**6**) have been synthesized. Copolymer has been synthesized by radical initiated reactions from monomer **5** and styrene. The liquid–liquid extraction studies of **3**, **4** and its corresponding polymer **6** have been performed. At the same time the solid–liquid extraction study of polymer **6** has been fulfilled. It has been observed that the precursor **3** shows a good selectivity towards Hg^{2+} cation. But the polymer (**6**) extracts all of the metals from aqueous phase to the organic phase showing no selectivity. As a result, it can be concluded that the metal transfer ability of ionophores depends upon the nature of binding sites and conformation of calixarene units in the polymeric skeleton. The easy process ability and good properties of **3** enhances its utility in phase-transfer reactions, as adsorbent, or potential candidate material for fabricating membranes and sensors.

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References

1. Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J. (eds.): Calixarenes 2001. Kluwer Academic Publishers, Dordrecht (2001)
2. Gutsche, C.D.: Calixarenes Revisited. The Royal Society of Chemistry, Cambridge (1998)
3. Böhmer, V., Vicens, J. (eds.): Calixarenes: A Versatile Class of Macrocyclic Compounds. Kluwer Academic Publishers, Dordrecht (1991)
4. Atwood, J.L., Bott, S.G.: Water Soluble Calixarene Salts. A Class of Compounds with Solid State Structures Resembling Those of Clays in Calixarenes: A Versatile Class of Macrocyclic Compounds. Kluwer, Dordrecht (1991)
5. Creaven, B.S., Gernon, T.L., McGinley, J., Moorea, A.-M., Toftlund, H.: Wide- and narrow-rim functionalised calix[4]arenes: synthesis and characterization. Tetrahedron **62**, 9066–9071 (2006). doi:10.1016/j.tet.2006.06.096
6. Shimojo, K., Oshima, T., Goto, M.: Calix[6]arene acetic acid extraction behavior and specificity with respect to nucleobases. Anal. Chim. Acta **521**, 163–171 (2004). doi:10.1016/j.aca.2004.06.015
7. Sykora, J., Himl, M., Stibor, I., Cisarova, I., Lhotak, P.: Unique self-assembly patterns based on thiacalix[4]arene-silver interactions. Tetrahedron **63**, 2244–2248 (2007). doi:10.1016/j.tet.2006.12.070
8. Talanov, V.S., Roper, E.D., Buie, N.M., Talanova, G.G.: A new fluorogenic mono-ionizable calix[4]arene dansylcarboxamide as a selective chemosensor of soft metal ions, Tl^+ and Hg^{2+}. Tetrahedron Lett. **48**, 8022–8025 (2007). doi:10.1016/j.tetlet.2007.09.043
9. Tu, C., Surowiec, K., Bartsch, R.A.: Efficient divalent metal cation extractions with di-ionizable calix[4]arene-1, 2-crown-4 compounds. Tetrahedron **63**, 4184–4189 (2007). doi:10.1016/j.tet.2007.02.105
10. Mohapatra, P.K., Ansari, S.A., Sarkar, A., Bhattacharyya, A., Manchanda, V.K.: Evaluation of calix-crown ionophores for selective separation of radio-cesium from acidic nuclear waste solution. Anal. Chim Acta **571**, 308–314 (2006). doi:10.1016/j.aca.2006.05.006
11. Zhoua, X., Li, X., Zenga, Z.: Solid-phase microextraction coupled with capillary lectrophoresis for the determination of propranolol enantiomers in urine using a sol–gel derived calix[4]arene fiber. J. Chromatogr. A **1104**, 359–365 (2006). doi:10.1016/j.chroma.2005.11.126
12. Agrawal, Y.K., Sharma, K.R.: Speciation, liquid–liquid extraction, sequential separation, preconcentration, transport and ICP-AES determination of Cr(III), Mo(VI) and W(VI) with calix-crown hydroxamic acid in high purity grade materials and environmental samples. Talanta **67**, 112–120 (2005). doi:10.1016/j.talanta.2005.02.015
13. Li, X., Zeng, Z., Chen, Y., Xub, Y.: Determination of phthalate acid esters plasticizers in plastic by ultrasonic solvent extraction combined with solid-phase microextraction using calix[4]arene fiber. Talanta **63**, 1013–1019 (2004). doi:10.1016/j.talanta.2004.01.006
14. Boulet, B., Bouvier-Capely, C., Cote, G., Poriel, L., Cossonnet, C.: Selective extraction of Pu(IV) by a calix[6]arene bearing hydroxamic groups. Application to bioassays. J. Alloy. Comp. **444**, 526–528 (2007). doi:10.1016/j.jallcom.2006.12.038
15. Karakucuk, A., Durmaz, M., Sirit, A., Yilmaz, M., Demir, A.S.: Synthesis and chiral recognition properties of two novel chiral calix[4]arene tartaric ester derivatives. Tetrahedron Asymmetry **17**, 1963–1968 (2006). doi:10.1016/j.tetasy.2006.07.011
16. Tilki, T., Sener, I., Karcı, F., Gulce, A., Deligoz, H.: An approach to the synthesis of chemically modified bisazocalix[4]arenes and their extraction properties. Tetrahedron **61**, 9624–9629 (2005). doi:10.1016/j.tet.2005.07.078
17. Saf, A.O., Alpaydin, S., Sirit, A.: Transport kinetics of chromium(VI) ions through a bulk liquid membrane containing *p-tert*-butyl calix[4]arene 3-morpholino propyl daimide derivative. J. Membr. Sci. **283**, 448–455 (2006). doi:10.1016/j.memsci.2006.07.023
18. Tabakci, M., Memon, S., Yilmaz, M.: Synthesis and extraction properties of new 'proton-switchable' tri- and tetra-substituted calix[4]arene derivatives bearing pyridinium units. Tetrahedron **63**, 6861–6865 (2007). doi:10.1016/j.tet.2007.04.060
19. Uysal Akkus, G., Memon, S., Gürkas, D.E., Aslan, S., Yilmaz, M.: The synthesis and metal cation extraction studies of novel polymer-bound calix(aza)crowns. React. Funct. Polym. **68**(1), 125–132 (2008). doi:10.1016/j.reactfunctpolym.2007.10.005
20. Tabakci, M., Erdemir, S., Yilmaz, M.: Preparation, characterization of cellulose-grafted with calix[4]arene polymers for the adsorption of heavy metals and dichromate anions. J. Hazard. Mater. **148**, 428–435 (2007). doi:10.1016/j.jhazmat.2007.02.057

21. Oshima, T., Sato, M., Shikaze, Y., Ohto, K.: Enzymatic polymerization of o-phenylendiamine with cytochrome c activated by a calixarene derivative in organic media. Biochem. Eng. J. **35**, 66–70 (2007). doi:10.1016/j.bej.2006.12.023
22. Valente, A.J.M., Jime'nez, A., Simoes, A.C., Burrows, H.D., Polishchuk, A.Y., Lobo, V.M.M.: Transport of solutes through calix[4]pyrrole-containing cellulose acetate films. Eur. Polym. J. **43**, 2433–2442 (2007). doi:10.1016/j.eurpolymj.2007.03.047
23. Ulewicz, M., Lesinska, U., Bochenska, M., Walkowiak, W.: Facilitated transport of Zn(II), Cd(II) and Pb(II) ions through polymer inclusion membranes with calix[4]-crown-6 derivatives. Sep. Purif. Technol. **54**, 299–305 (2007). doi:10.1016/j.seppur.2006.09.018
24. Memon, S., Tabakci, M., Roundhill, D.M., Yilmaz, M.: Synthesis and evaluation of the Cr(VI) extraction ability of amino/nitrile calix[4]arenes immobilized onto a polymer backbone. React. Funct. Polym. **66**, 1342–1349 (2006). doi:10.1016/j.reactfunctpolym.2006.03.017
25. Ana, R., Mendes, G., Carla, C., Barata, D., Patricia, A., Costa, I., et al.: Linear and crosslinked copolymers of *p-tert*-butylcalix[4]arene derivatives and styrene: new synthetic approaches to polymer-bound calix[4]arenes. React. Funct. Polym. **65**, 9–21 (2005). doi:10.1016/j.reactfunctpolym.2005.01.006
26. Bergougnant, R.D., Robin, A.Y., Fromm, K.M.: From simple rings to one-dimensional channels with calix[8]arenes, water clusters, and alkali metal ions. Tetrahedron **63**, 10751–10757 (2007). doi:10.1016/j.tet.2007.07.048
27. Gungor, O., Memon, S., Yilmaz, M., Roundhill, D.M.: Synthesis of alkyl nitrile and alkyl benzonitrile derivatives of calix[4]arene and their polymer supported analogues: a comparative study in two-phase extraction systems. React. Funct. Polym. **63**, 1–9 (2005). doi:10.1016/j.reactfunctpolym.2005.02.004
28. Barata, P.D., Costa, A.I., Granja, P., Prata, J.: The synthesis of novel polymer-bound calix[4]arenes. React. Funct. Polym. **61**, 147–151 (2004). doi:10.1016/j.reactfunctpolym.2004.04.005
29. Tabakci, B., Beduk, A.D., Tabakci, M., Yilmaz, M.: Synthesis and binding properties of two polymeric thiacalix[4]arenes. React. Funct. Polym. **66**(3), 379–386 (2006). doi:10.1016/j.reactfunctpolym.2005.08.013
30. Memon, S., Yilmaz, A., Yilmaz, M.: Synthesis and comparative complexation studies of schiff base derivatives of *p-tert* butylcalix[4]arene copolymers. J. Macromol. Sci. Part A Pure Appl. Chem. **37**(8), 865–879 (2000). doi:10.1081/MA-100101128
31. Yang, F., Guo, H., Cai, X., Chen, X.: Syntheses and adsorption properties of novel calixarene polymers: calix[6]-1,4-crown-4-based netty polymers. React. Funct. Polym. **64**, 163–168 (2005). doi:10.1016/j.reactfunctpolym.2005.05.012
32. Trivedi, U.V., Menon, S.K., Agrawal, Y.K.: Polymer supported calix[6]arene hydroxamic acid, a novel chelating resin. React. Funct. Polym. **50**, 205–216 (2002). doi:10.1016/S1381-5148(01)00106-7
33. Alexandratos, S.D., Natesan, S.: Synthesis and ion-binding affinities of calix[4]arenes immobilized on cross-linked polystyrene. Macromolecules **34**, 206–210 (2001). doi:10.1021/ma0012550
34. Deligöz, H., Tavasli, M., Yilmaz, M.: Selective extraction of Fe^{3+} by a polymeric calix[4]arene. J. Polym. Sci. Part Polym. Chem. **32**, 2961–2964 (1994). doi:10.1002/pola.1994.080321518
35. Gravett, D.M., Guillet, J.E.: Synthesis and photophysical properties of a novel water-soluble, calixarene-containing polymers. Macromolecules **29**(2), 617–624 (1996). doi:10.1021/ma950870e
36. Deligöz, H., Yilmaz, M.: Synthesis of polymer-supported calix[4]arene and selective extraction of Fe^{3+}. React. Funct. Polym. **31**(2), 81–88 (1996). doi:10.1016/1381-5148(96)00030-2
37. Uysal, G., Memon, S., Yilmaz, M.: Synthesis and binding properties of polymeric calix[4]arene nitriles. React. Funct. Polym. **50**(1), 77–84 (2001). doi:10.1016/S1381-5148(01)00099-2
38. Gutsche, M., Iqbal, M.: *p-tert*-Butylcalix[4]arene. Org. Synth. **68**, 234–235 (1990)
39. Tabakci, M., Memon, S., Sap, B., Roundhill, D.M., Yilmaz, M.: A calix[4]arene derived dibenzonitrile receptor modified at its lower rim by a polymerizable group. J. Macromol. Sci. Part A Pure Appl. Chem. **41**(8), 811–825 (2004). doi:10.1081/MA-120037344
40. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. J. Am. Chem. Soc. **89**(26), 7017–7036 (1967). doi:10.1021/ja01002a035
41. Memon, S., Uysal, G., Yilmaz, M.: Selective complexation of Hg^{2+} by biscalix[4]arene nitriles. Sep. Sci. Technol. **35**(8), 1247–1256 (2000). doi:10.1081/SS-100100223
42. Memon, S., Tabakci, M., Roundhill, D.M., Yilmaz, M.: A useful approach toward the synthesis and metal extractions with polymer appended thioalkyl calix[4]arenes. Polymer (Guildf.) **46**, 1553–1560 (2005). doi:10.1016/j.polymer.2004.12.019
43. Memon, S., Uysal, G., Yilmaz, M.: Syntheses and binding properties of polymeric calix[4]crown-4. React. Funct. Polym. **47**, 165–174 (2001). doi:10.1016/S1381-5148(01)00029-3
44. Pearson, R.G.: Hard and soft acids and bases. J. Am. Chem. Soc. **85**(22), 3533–3534 (1963). doi:10.1021/ja00905a001
45. Yordanov, A.T., Roundhill, D.M.: Chemically modified calix[4]-arenes as selective complexants for heavy metal ions, comparison with crowns and thiacrowns and oxyion salts. N. J. Chem. **20**, 447–451 (1996)
46. Gorbunova, M.G., Bonnesen, P.V., Engle, N.L., Bazelaire, E., Delmau, L.H., Moyer, B.A.: New amino-functionalized 1,3-alternate calix[4]arene bis- and mono-(benzo-crown-6 ethers) for pH-switched cesium nitrate extraction. Tetrahedron Lett. **44**(29), 5397–5401 (2003). doi:10.1016/S0040-4039(03)01310-8