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Synthesis and complexation study of calix[4]arene diamine derivative incorporated in a polymeric backbone with chiral monomers

A. R Hajipour · S. Habibi · A. E. Ruoho

Abstract The novel chiral polymeric compounds containing more than one calix[4]arene have been synthesized by reacting a new calix[4]arene diamine derivative with two chiral monomers. These newly prepared compounds were studied by extraction of toxic heavy metal (Cu^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}), silver and alkali metal (Na^+, K^+) cations from aqueous phase. It was observed that the resulting calixarene-based polymers have a good complexing ability towards silver, alkali metal and toxic heavy metal cations.

Keywords Polymeric ionophores · Toxic heavy metals · Complexation studies · Chiral polymeric calixarenes

Introduction

Calixarenes are a well-known class of synthetic receptor molecules that possess intramolecular bow-shaped cavities capable of accommodate neutral and ionic molecular guests as well as metal ions through the establishment of selective and specific interactions of diverse origin. Their synthesis, properties and applications have been extensively reviewed [1–8]. The interesting properties shown by these cyclic oligomeric compounds have attracted in recent

years a growing interest in their use in conjunction with polymeric matrices, either covalently bounded or blended to them. A considerable amount of fundamental studies and practical applications regarding their use as sensors, selective electrodes, non-linear optics materials and devices for selective sorption of ions and neutral molecules, have been reported recently [9–13]. In particular, the chemically bounded calixarenes have been prepared by two general synthetic methods. One is based on the immobilization of the calixarene unity on an existing polymeric matrix [14–20] and the other relied on copolymerization reactions of a properly functionalized calixarene monomer, either through linear step-growth polymerization [21–26] or radical addition [27–30] reactions.

The host–guest chemistry of the calixarenes is of great interest, since the calixarenes exhibit complexing abilities towards alkali, alkaline-earth and some transition metal cations by means of functional group modification of the phenolic groups [31–33]. In particular, the easy accessibility of p-tert-butyl calix[4]arene has made this member of the series increasingly popular with ligating side-arms or podands for the reception of guest species, notably alkali, alkaline-earth and some transition metal cations [34–36].

Chiral calixarenes have attracted increasing research interest in the fields of organic, biological and medicinal chemistry. Many of the chiral calix[4]arene derivatives have shown remarkable recognition properties toward achiral cations and anions, however, more interestingly, some of them have exhibited significant chiral discrimination abilities for chiral guests such as organic ammonium salts, amino alcohols and amino acids [37–39]. Also, by immobilizing metal ions such as nickel or cobalt ions on a chiral polymer as a chiral ionophore, an affinity support that specially binds to proteins can be created. Such affinity columns are used for purification of proteins [40–42].

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On the other hand, during the last decade, resolution of racemic compounds attracted a great attention in analytical chemistry, especially in pharmaceutical analysis, because each enantiomer of the chiral drugs exhibits great differences in pharmacological, pharmacodynamic, and toxicological manners [43, 44]. High performance liquid chromatography (HPLC) using a chiral stationary phase is one of the most popular methods for the direct separation of chiral compounds [45, 46]. Hitherto, several optically active polymers have been used for enantiomeric HPLC separation as the chiral stationary phase [47, 48]. Although aromatic polyesters (PEs) and polyamides (PAs) with excellent pattern of physical and chemical properties are special candidates for chromatographic purposes, high melting or glass-transition temperatures and restricted solubility in organic solvents, due to their rigid structure, have limited their processability. In this regard, they exert a useful strategy, such as the use of monomer containing pendent groups, aimed for the improvement of solubility and processability of these polymers, without significant decrease of thermal and mechanical properties [49].

Recently, the first use of a chiral resorcinarene has been reported as a chiral stationary phase in enantioselective capillary gas chromatography [50], but until now chiral polymeric calix[4]arenes have not been synthesized and used yet and most complexation studies have been conducted with monomeric calixarenes. In this regard, given the high thermal, chemical, mechanical stability and good solubility of the polymers containing hexafluoroisopropylidene diphthalimide moieties [51] along with complexing ability of calix[4]arene based polymers, we synthesized novel chiral polymeric ionophores with complexing ability toward toxic heavy metals in a solid–liquid sorption system. We introduced chirality to the polymer backbone using aminoacids because of their biologically importance and biodegradability for enantiometric recognition of amino acid derivatives [52]. These novel chiral polymers are good candidates in chromatographic purpose for separation of chiral biological compounds like amines, amino acids and their derivatives along with organic cations such as ammonium salts.

Experimental section

Materials and instrumentation

All the chemicals were purchased from Merck. All aqueous solutions were prepared with deionized water. NMP was purified with distillation over calcium hydride under reduced pressure and stored over the molecular sieve. Dichloromethane was dried over $CaCl_2$. Reactions were monitored by TLC on silica gel. p-tert-butyl calix[4]arene were prepared as described [53].

IR spectra were recorded on a FT/IR-680 plus spectrophotometer using KBr pellets. Inherent viscosities were measured by a standard procedure using a Cannon Fenske routine viscometer at 25 °C using DMF as solvent. ^{1}H NMR spectra were recorded on 500 and 300 MHz instrument, using DMSO-d_6 as a solvent and tetra methyl silane as a chemical shift reference (tube diameter 5 mm). Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermal gravimetric analysis (TGA) was obtained by a Mettler TGA-50 under air atmosphere at a rate of 10 °C/min. Melting points were measured in open capillaries with a gallenkamp instrument.

Synthesis of calix[4]arene derivatives

Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-bis[(4-nitrobenzyloxy)-6,28-dihydroxy] calix [4]-arene (1)

A mixture of p-t-butyl calix[4]arene (10.0 g, 15.0 mmol), anhydrous K_2CO_3 (2.4 g, 17.6 mmol) and p-nitrobenzyl bromide (6.7 g, 30.7 mmol) in CH_3CN (80 mL) was refluxed for 20 h. The solvent was removed under reduced pressure, the mixture was treated with CH_3Cl (200 mL) and filtered. The filtrate was concentrated under reduced pressure (50 mL). Then CH_3OH (100 mL) was added and the pale yellow crystals appeared gradually. After a few hours the crystals were filtered under vacuum and washed with cold methanol to give 12.0 g (91.6%) of the pure compound 1. m.p: 148–149 °C. FTIR (KBr, cm^{-1}): 3434 (s, br), 3113 (m), 3047 (m), 2959 (s), 2906 (s), 2866 (s), 1606 (m), 1524 (s), 1483 (s), 1461 (s), 1393 (m), 1366 (s), 1348 (s), 1347 (s), 1297 (m), 1193 (s), 1123 (m), 1109 (m), 1031 (m), 946 (m), 919 (w), 824 (s), 852 (s), 819 (m), 796 (m), 780 (m), 736 (s), 699 (w), 650 (w), 629 (w), 578 (w), 552 (m), 530 (m) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ 0.96 (s, 18H), 1.29 (s, 18H), 3.34 (d, 4H, $J = 13.0$ Hz), 4.23 (d, 4H, $J = 13.0$ Hz), 5.17 (s, 4H), 6.83 (s, 4H), 7.08 (s, 4H), 7.26 (s, 2H), 7.91 (d, 4H, $J = 8.5$ Hz), 8.17 (d, 4H, $J = 8.6$ Hz). Elemental analysis: Calculated for $C_{58}H_{66}N_2O_8$: C (75.79%), H (7.24%), N (3.05%); Found: C (75.81%), H (7.23%), N (3.06%).

Reduction of compound 1 (2)

To a mixture of 1 (4.50 g, 49 mmol), Raney-Ni (5.50 g), ethyl acetate (80 mL) and MeOH (40 mL) was added gradually $N_2H_4.H_2O$ (11.5 mL). The reaction mixture was stirred at room temperature for 1 h, and was then refluxed for 2 h with continuous stirring. Then the solvent was evaporated under vacuum and Toluene (300 mL) was added and heated to its boiling point. The hot mixture was filtered and after concentrating the solvent, the white crystals appeared. The crystals were filtered and washed

with cold methanol to give 3.00 g (71.4%) of compound **2**. m.p: 278 °C. FTIR (KBr, cm^{-1}): 3551 (m), 3469 (m), 3415 (m), 3176 (m, br), 3048 (m), 3026 (m), 2954 (s), 2906 (s), 2869 (s), 1637 (m), 1617 (m), 1481 (s), 1456 (m), 1384 (m), 1361 (m), 1304 (m), 1284 (m), 1257 (w), 1250 (m), 1199 (s), 1157 (m), 1124 (m), 1102 (m), 946 (w), 889 (w), 870 (m), 815 (m), 781 (s), 729 (m), 709 (m), 695 (m), 673 (m), 619 (m), 591 (m), 552 (w), cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d$_6$, 25 °C): δ 0.91 (s, 18H), 1.16 (s, 18H), 1.8 (brs, 4H), 3.20 (d, 4H, J = 13.0 Hz), 4.18 (d, 4H, J = 13.0 Hz), 4.61 (s, 4H), 7.01–7.26 (m, 18H). Elemental analysis: Calculated for C$_{58}$H$_{70}$N$_2$O$_4$: C (81.08%), H (8.21%), N (3.26%); Found: C (80.80%), H (8.40%), N (3.00%).

Synthesis of chiral monomers

Into a 25-mL, round-bottomed flask 0.50 g (1.12 mmol) of hexafluoroisopropylidene diphthalic anhydride (**3**), 2.24 mmol of amino acids **4a** or **4b**, 10.0 mL of acetic acid and a stirring bar were placed. The mixture was stirred at room temperature overnight then was refluxed for 6 h. The solvent was removed under reduced pressure and 20 mL of cold diluted HCl (5%) was added to the residue. A white precipitate was formed, filtered off, washed with water and dried under vacuum at 100 °C to give compounds **5a**, **5b**. Recrystallization from methanol/water gave pure crystals. Then, into a 25 mL round-bottomed flask were placed 1.0 g (2.3 mmol) of compounds **5a**, **5b** and 5 mL (an excess amount) of thionyl chloride. The mixture was refluxed for 3 h. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with n-hexane, to leave diacid chlorides **6a** and **6b**.

Diacid **5a**

White crystals, yield: 94%, m.p: 176–178 °C. [α]$_D^{25}$ = −27.40° [0.050 g in 10 mL acetone]. FTIR (KBr, cm^{-1}): 3245 (m, br), 2949 (m), 1783 (s), 1719 (s), 1626 (m), 1438 (m), 1387 (s), 1300 (m), 1256 (s), 1210 (s), 1143 (m), 1095 (m), 1024 (m), 982 (m), 965 (m), 919 (m), 890 (m), 876 (m), 850 (m), 748 (m), 724 (m), 627 (m), 570 (m), 546 (w), 528 (w). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ (ppm): 1.1 (d, 6H), 4.81 (q, 2H), 7.71 (s, 2H), 7.84 (d, 2H), 8.05 (dd, 2H), 13.20 (s, 2H). Elemental analysis: calculated for C$_{25}$H$_{16}$N$_2$O$_8$F$_6$: C (51.21%), H (2.75%), N (4.78%); found C (50.90%), H (2.90%), N (4.50%).

Diacid **5b**

White crystals, yield: 95%, m.p: 194–195 °C. [α]$_D^{25}$ = −80.96° [0.050 g in 10 mL acetone]. FTIR (KBr): 3240 (m, br), 3063 (m), 2927 (m), 1780(s), 1719 (s), 1673 (m), 1620 (m), 1601 (m), 1497 (m), 1455 (s), 1427 (m), 1384

(s), 1344 (m), 1295 (m), 1249 (s), 1182 (s), 1159 (m), 1106 (m), 1029 (m), 978 (m), 948 (m), 917 (m), 870 (m), 747 (m), 726 (m), 700 (w), 623 (m), 550 (w). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ (ppm): 3.08 (dd, 2H), 3.48 (dd, 2H), 5.13 (m, 2H), 7.17 (m, 10H), 7.80 (m, 2H), 7.98 (s, 2H), 8.01 (dd, 2H), 13.33 (s, 2H). Elemental analysis: Calculated for C$_{37}$H$_{24}$N$_2$O$_8$F$_6$: C (60.17%), H (3.27%), N (3.79%); found C (59.70%), H (3.60%), N (3.30%).

Diacid chloride **6a**

White powder, yield: 93%, mp: 154–155 °C. [α]$_D^{25}$ = −26.82° [0.050 g in 10 mL acetone]. FTIR (KBr, cm^{-1}): 2948 (m), 2874 (m), 1798 (s), 1784 (s), 1725 (s), 1626 (m), 1540 (w), 1489 (m), 1438 (m), 1381 (s), 1299 (m), 1256 (s), 1211 (s), 1191 (s), 1143 (m), 1105 (m), 1022 (m), 983 (m), 965 (m), 945 (m), 890 (m), 850 (m), 750 (m), 722 (m), 691 (m), 647 (m), 609 (w), 572 (m), 545 (w), 528 (w). Elemental analysis: Calculated for C$_{25}$H$_{14}$N$_2$O$_6$F$_6$Cl$_2$: C (48.18%), H (2.26%), N (4.49%); found C (47.80%), H (2.50%), N (3.90%).

Diacid chloride **6b**

White powder, yield: 89%, mp: 141–143 °C. [α]$_D^{25}$ = −78.31° [0.050 g in 10 mL acetone]. FTIR (KBr): 2925 (m), 2875 (m), 1798 (s), 1783 (s), 1723 (s), 1624 (m), 1490 (m), 1445 (m), 1427 (m), 1382 (s), 1298 (m), 1254 (s), 1210 (s), 1144 (m), 1105 (m), 1023 (m), 980 (m), 891 (w), 787 (m), 748 (m), 692 (m), 568 (w). Elemental analysis: Calculated for C$_{37}$H$_{22}$N$_2$O$_6$F$_6$Cl$_2$: C (57.31%), H (2.86%), N (3.61%); found C (56.80%), H (3.20%), N (3.10%).

Synthesis of polymeric calixarenes

Method 1: polymerization under microwave irradiation

Into a porcelain dish were placed 0.233 mmol of diacid chloride **6a** or **6b** and 0.200 g (0.233 mmol) of diamine **2**. After the reagents were completely ground for 5 min, 0.3 mL of NMP as a solvent was added and the mixture was ground for 5 min. The reaction mixture was irradiated in the microwave oven for 7 min at 100% power. The resulting polymer film was isolated by addition of 20 mL of methanol/water (10/1) and trituration; it was then filtered and dried at 80 °C for 10 h in vacuo.

PA **7a**

FTIR (KBr): 3162 (m, br), 3064 (m), 2955 (s), 2868 (m), 1781 (s), 1721 (s), 1695 (s), 1603 (m), 1482 (s), 1462 (m), 1385 (s), 1362 (m), 1286 (m), 1257 (m), 1242 (m), 1200 (s), 1158 (m), 1123 (m), 1103 (m), 1027 (m), 982 (m), 946

(m), 916 (m), 889 (m), 872 (m), 816 (m), 782 (m), 738 (m), 728 (m), 710 (m), 675 (m), 619 (m), 592 (w), 570 (w), 553 (w). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ (ppm) 1.1 (s, 18H), 1.34 (s, 18H), 1.51 (d, 6H), 3.38 (d, 4H), 4.21 (d, 4H), 4.82 (q, 2H), 5.24 (s, 2H), 7.02–7.34 (m, 18H), 7.6 (s, br, 2H), 7.71 (s, 2H), 7.82 (d, 2H), 8.03 (m, 2H).

PA 7b

FTIR (KBr): 3171 (m, br), 2956 (m), 2868 (m), 2284 (m), 1782 (m), 1723 (s), 1696 (s), 1604 (m), 1482 (s), 1462 (m), 1383 (s), 1362 (m), 1302 (m), 1256 (m), 1202 (s), 1143 (m), 1110 (m), 981 (m), 947 (m), 914 (m), 871 (m), 847 (m), 817 (m), 782 (m), 744 (m), 724 (m), 709 (m), 675 (m), 619 (m), 592 (m), 570 (m), 554 (m), 524 (w), 512 (w). ^{1}H NMR (300 MHz, DMSO-d$_6$, 25 °C): δ (ppm) 0.91 (s, 18H), 1.20 (s, 18H), 3.01–3.11 (m, 4H), 3.27–3.40 (m, 4H), 3.96–4.00 (m, 4H), 4.81–4.86 (m, 4H), 5.11–5.18 (m, 2H), 6.89 (s, 10H), 7.04–7.28 (m, 18H), 8.03–8.23 (m, 8H).

Method 2: solution polycondensation

In a suspension of compound **2** (0.2 g, 0.233 mmol) in dry CH$_2$Cl$_2$ (5 mL) in the presence of TEA (0.2 mL, 1.44 mmol) was added drop wise a solution of diacid chloride **6a** or **6b** (0.233 mmol) in dry CH$_2$Cl$_2$ (5 mL) at room temperature. The solution was stirred at room temperature for 30 min and then was refluxed for 1 h. During this time the polymer precipitate was appeared. The solvent was evaporated and methanol/water (10/1) (20 mL) was added. The polymer powder was filtered and washed with methanol/water (10/1) (10 mL) and vacuum dried.

PE 7a′

FTIR (KBr): 3568 (m), 3521 (m), 3161 (m), 2961 (m), 2869 (m), 1766 (s), 1730 (s), 1724 (s), 1603 (m), 1603 (m), 1483 (s), 1382 (s), 1363 (m), 1301 (m), 1256 (m), 1203 (s), 1143

(m), 1101 (m), 1072 (m), 1023 (m), 981 (m), 917 (m), 873 (m), 847 (m), 817 (m), 782 (m), 743 (m), 724 (m), 711 (w), 676 (m), 620 (m), 592 (m), 570 (m), 554 (w), 513 (w). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ (ppm) 1.16 (s, 18H), 1.38 (s, 18H), 1.42 (d, 6H), 1.82 (s, br, 4H), 3.43 (m, 4H), 4.00 (m, 4H), 5.09 (m, 2H), 5.60 (s, 4H), 6.72–7.31 (m, 16H), 7.74 (m, 2H), 7.86 (m, 2H), 8.09 (m, 2H).

PE 7b′

FTIR (KBr): 3567 (m), 3526 (m), 3168 (m), 2961 (m), 2870 (m), 1768 (s), 1731 (s), 1727 (s), 1626 (m), 1602 (m), 1483 (s), 1462 (m), 1383 (s), 1301 (m), 1256 (m), 1206 (s), 1142 (m), 1100 (m), 1070 (m), 1022 (m), 981 (m), 918 (m), 873 (m), 847 (m), 817 (m), 782 (m), 743 (m), 724 (m), 675 (m), 621 (w), 592 (m), 570 (m), 553 (w), 526 (w). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ (ppm) 0.94 (s, 18H), 1.20 (s, 18H), 1.87 (s, br, 4H), 3.00-3.12 (m, 4H), 3.25–3.45 (m, 4H), 4.10–4.30 (m, 4H), 5.18 (s, 4H), 5.97–6.09 (m, 2H), 6.60–7.40 (m, 26H), 7.98–8.18 (m, 6H).

Complexation studies

Picrate extraction experiments were performed following the Cram procedure [54, 55]: 0.01 g of polymer was mixed with 10 mL of an aqueous solution containing 2.5×10^{-5} M of picric acid (2,4,6-trinitrophenol) and 10^{-3} M of an alkali and transition metal salt MNO$_3$, M(NO$_3$)$_2$ and was shaken at room temperature for 20 min in a stoppered glass flask. The sorbent was removed by filtration before measurements. The concentration of the picrate remaining in aqueous phase after the sorption was determined spectrophotometrically using a Perkin-Elmer Lambda 6 spectrophotometer equipped with integrating sphere. The salts used for the extraction, NaNO$_3$, KNO$_3$, CsNO$_3$, AgNO$_3$, Cu(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Co(NO$_3$)$_2$ and Hg(NO$_3$)$_2$ were reagent grade. The alkali picrates were made by preparing an aqueous solution containing 2.5×10^{-5} M of picric
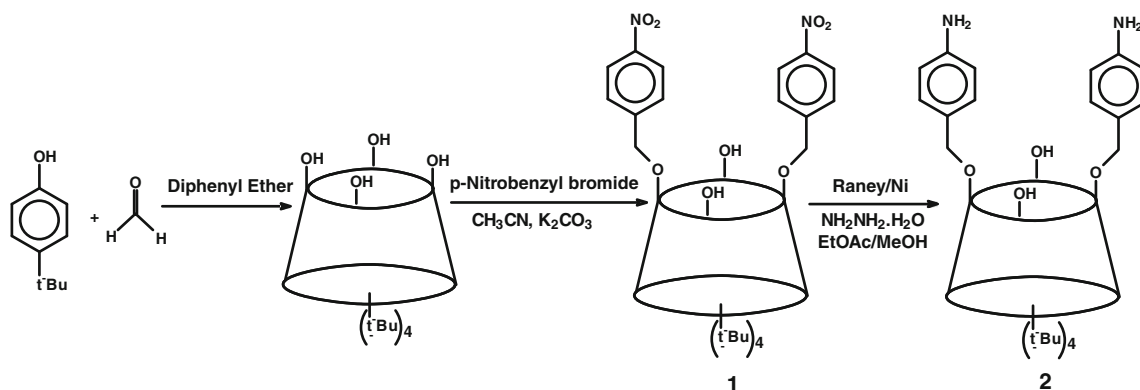
Scheme 1 Synthesis of *p*-tert-butyl-calix[4]arene diamine derivative (**2**)
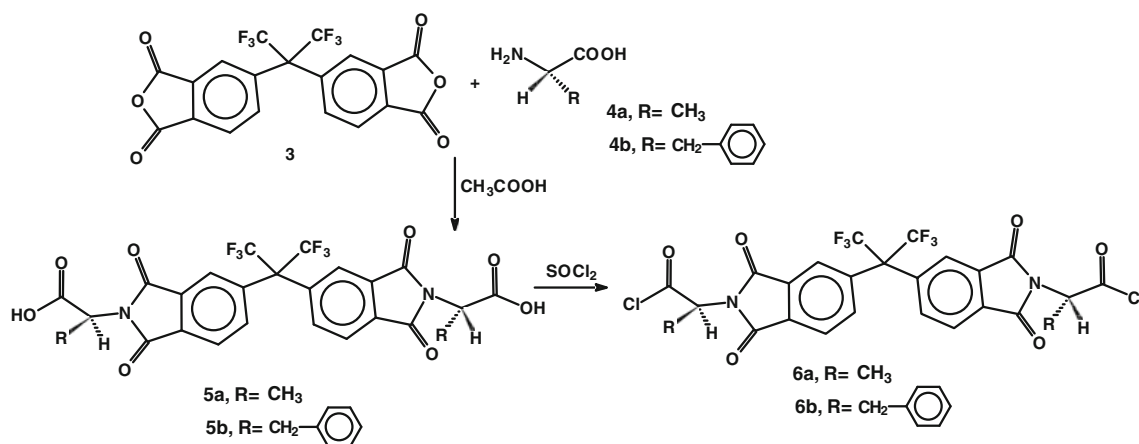
Scheme 2 Synthesis of chiral monomers **6a**, **6b**
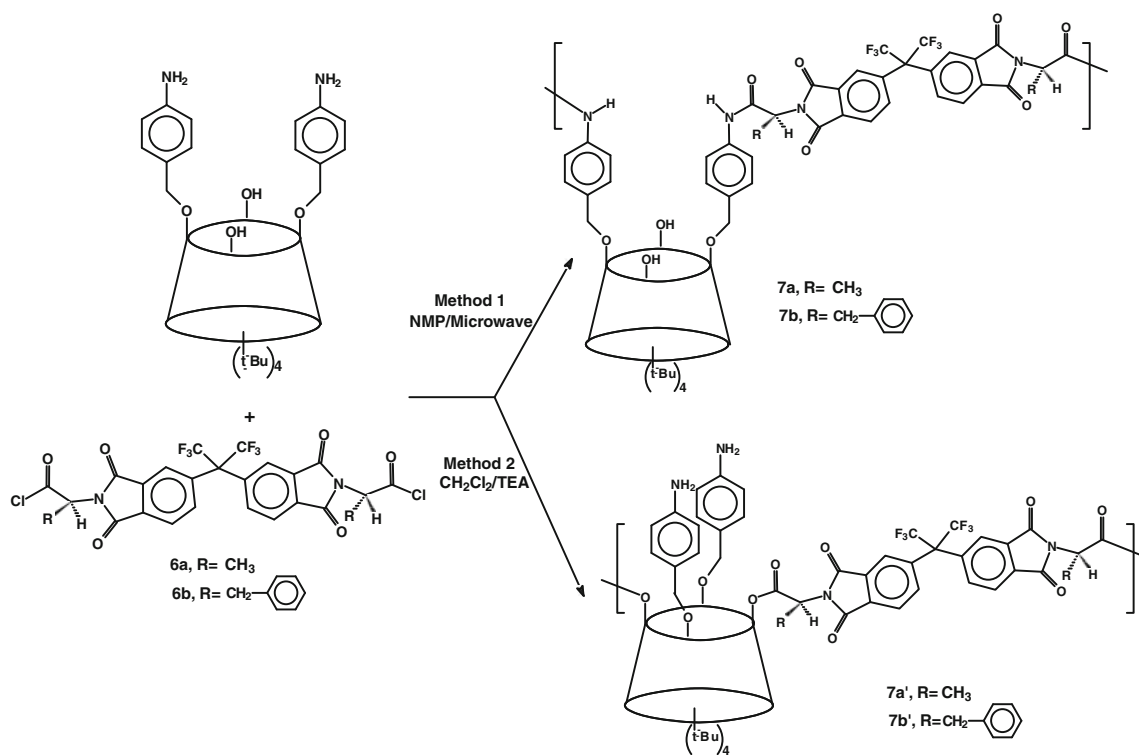
Scheme 3 Synthesis of chiral polymeric calixarenes **7a–7b′**

acid and 10^{-3} M of an alkali nitrates. Transition metal picrates were prepared by stepwise addition of a 1.0×10^{-3} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at room temperature for 1 h.

The percent sorption of ion ($S\%$) has been calculated as

$$S(\%) = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \qquad (1)$$

where C_i and C_e are the initial and final concentrations of metal picrate before and after sorption, respectively.

Results and discussion

In this work, the extraction properties of a diamine derivative of *p*-tert-butyl calix[4]arene and its polymers has been investigated and compared. Also we introduced amino acid moiety to induce chirality to the polymers. *p*-tert-butylcalix[4]arene was treated with *p*-nitrobenzyl bromide in dry acetonitrile in the presence of potassium carbonate to obtain the cone conformer of **1** in 91.6% yield (Scheme 1). The IR spectrum of **1** displays the nitro group absorptions at 1524 and 1348 cm^{-1} and the ^{1}H NMR
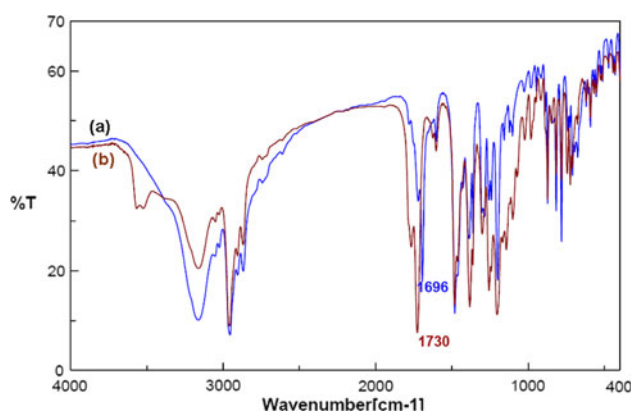
Fig. 1 FTIR spectra of **a** polymer **7a** and **b** polymer **7a′**

spectrum of this compound has a typical AB system for the methylene bridge protons (ArCH$_2$Ar) of the calixarene moiety at δ 3.34 and 4.23 ($J = 13.0$ Hz), the aromatic meta protons at δ 7.91 ($J = 8.5$ Hz), and ortho protons at δ 8.17 ($J = 8.6$ Hz) which indicated that the substitution of p-nitrobenzyl bromide had occurred. A reduction of the nitro groups of **1** by Raney-Ni/N$_2$H$_4$.H$_2$O gave the amino derivative **2** in 71.4% yield (Scheme 1). Completion of the reaction was followed by IR spectroscopy, which showed the disappearance of the band because of the nitro groups at 1524 and 1348 cm^{-1} and appearance of the new bands at 3551 and 3469 cm^{-1} for the amine groups.

Polymeric calixarenes are potentially capable of forming stable complexes with many metal ions. In recent years a large amount of work has been reported in the literature related to the functionalization of the calixarenes. However, investigations of chiral polymeric macro structures containing more than one compound are quite limited. In the present work, because of the high chemical, mechanical and thermal character of the imide groups along with biodegradability of amino acids and their biological properties, we envisioned the introduction of imide moieties in distal calix[4]arenes derivative **2** as an entry to a new class of chiral receptors for metal cations. Hence, condensation reactions of dianhydride **3** with two moles of chiral amino acids L-alanine (**4a**) and L-phenylalanine (**4b**) in acetic acid afforded the corresponding chiral imide-diacids (**5a**, **5b**). The diacids were converted into the corresponding diacid chlorides (**6a**, **6b**) by reaction with thionyl chloride (Scheme 2). The subsequent polymerization reactions of **2** with **6a** and **6b** were carried out using two methods: polymerization under microwave irradiation in NMP as a solvent and solution polycondensation in the presence of triethyl amine (TEA) as a catalyst and dichloromethane as a solvent. All polymers were characterized by a combination of FTIR, ^{1}H NMR and elemental analysis. Since the compound **2** has two functionalities (NH$_2$ and OH groups),

surprisingly we observed the evidences of polyamide formation (**7a**, **7b**) in the first method and polyester formation (**7a′**, **7b′**) in the second method (Scheme 3). The NH$_2$ groups in calix diamine derivative are more reactive towards carbonyl groups in the acid chloride, but the OH groups are acidic and buried in the calix cavity, so in the microwave irradiation method, where no catalyst is used, NH$_2$ groups react with acid chlorides and the amide linkages are formed. In the second polycondensation method where triethyl amine is used as a catalyst and an acid scavenger, the acidic protons of phenolic groups in the calix derivative are removed and phenolate ions which are more reactive towards acid chloride, reacted and the ester linkages are formed. The introduction of the monomeric calix derivative **2** as a bulky group in the polymer backbone, reduce the molecular weight of the resulted polymers. It is worth knowing that using triethyl amine as a catalyst and an acid scavenger with aliphatic acid chlorides with alpha hydrogen can cause ketene formation which causes racemization at the chiral center and reduces the optical rotation. The FTIR spectra of polymers **7a** and **7b** showed an amide band at 1695–1696 cm^{-1} and a broad band at 3162–3171 cm^{-1} for the hydroxyl group (OH), but for polymers **7a′** and **7b′** it was shown an ester band at 1730-1731 cm^{-1} and two absorption bands in the region of 3521–3568 cm^{-1} for NH$_2$ groups and a broad band at around 3160 cm^{-1} for OH (Fig. 1). Also the ^{1}H NMR spectra of these polymers verify this evidence (Fig. 2). Examination of the ^{1}H NMR spectra of the polymers suggests the existence of the cone conformation of the macrocyclic molecules in the polymer chain.

Some physical properties of these chiral polymers are listed in Table 1. The inherent viscosities of the resulting polymers under optimized condition were in the range of 0.22–0.26 dL g^{-1} and the yields were 84–87%.

All polymers were optically active and soluble in polar aprotic solvents such as DMF, DMSO, DMAc, NMP but insoluble in solvents such as water, CH$_3$OH, CH$_2$Cl$_2$, CHCl$_3$ and nonpolar organic solvents. The elemental analysis of all polymers has been shown in Table 2.

Thermal properties

The thermal properties of polymers **7b** and **7b′** was evaluated by means of TGA/DTG in a nitrogen atmosphere at a heating rate of 10 °C/min. Both polymers exhibited good resistance to thermal decomposition up to 200 °C and began to decompose gradually above those temperatures. The temperature of 5 and 10% weight loss together with char yield at 600 °C have been calculated by means of thermograms, and used as criterion for evaluation of thermal stability of the polymers. The thermoanalysis data of these polymers are summarized in Table 3. It is interesting

to note that $T_{10\%}$ weight loss for the polymer **7b′** is 400 °C that shows the high thermal stability of this polymer.

Evaluation of extraction capabilities

Polymeric calixarenes have been employed widely in the formation of metal complexes and in the study of inclusion phenomena due to their relatively easy preparation, remarkable stability and high versatility [56, 57]. The molecular recognition properties of *p-tert*-butyl calix[4] diamine (**2**) and its polymeric derivatives (**7a–7b′**) were studied by solid–liquid extraction experiments. The solid–liquid extraction was performed with alkali and transition metal picrates such as Na^+, K^+, Cs^+, Cu^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+} and Ag^+ from aqueous solutions. The ionophoric calixarenes were subjected to comparative study. The sorption percentages ($S\%$) were calculated according to the Eq. 1 and given in Tables 4 and 5. These data were obtained by using the solid ligands to extract metal ions from aqueous picrate solutions. The equilibrium concentration of metal ions was then determined spectrophotometrically.

With all ligands substituted with more than one calix[4]arenes 6.75–46.61% extraction was accomplished for toxic heavy metals and 17.47–53.04% for alkali metal

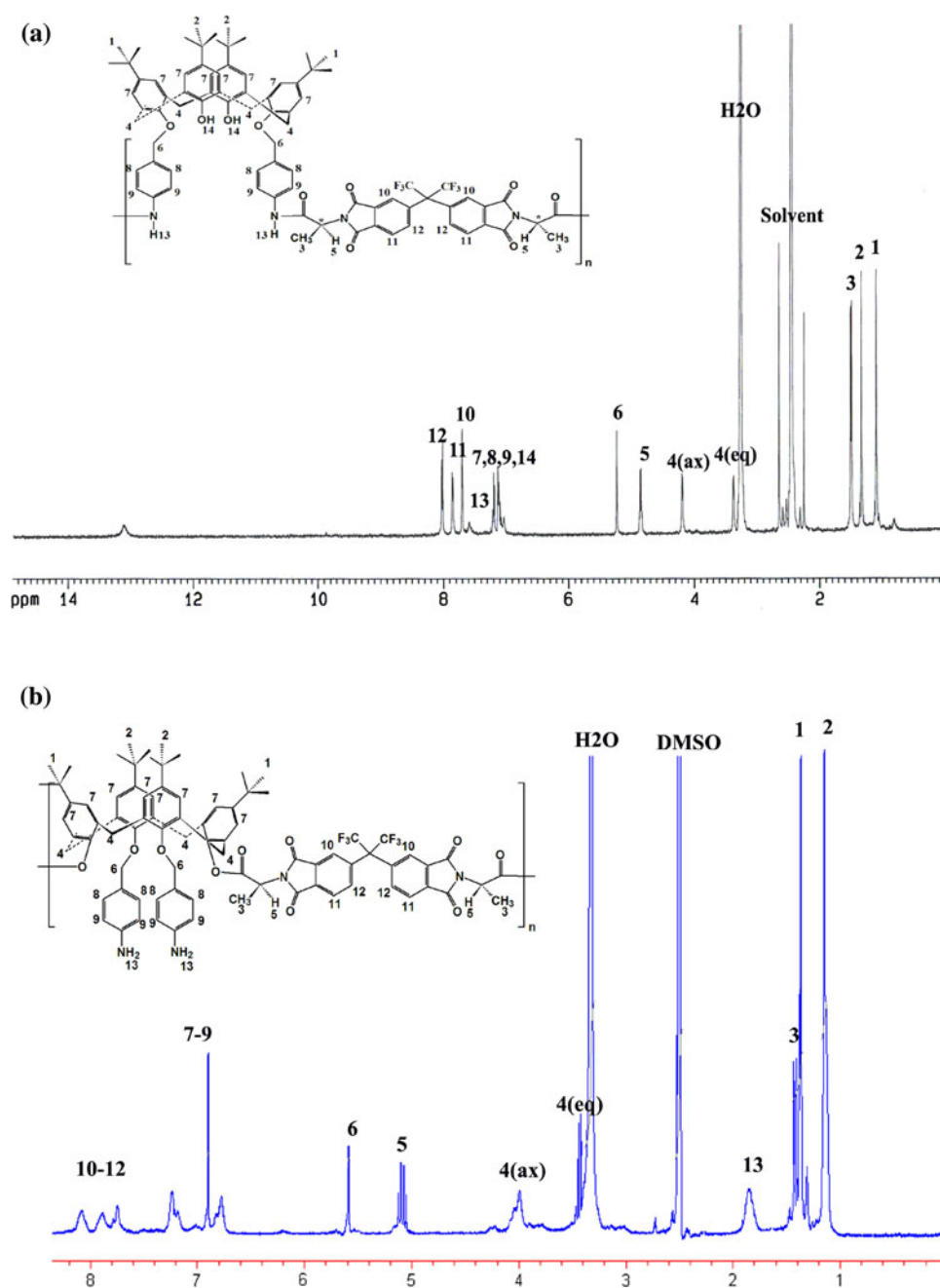**Fig. 2** ^{1}H NMR spectra of **a** polymer **7a** and **b** polymer **7a′**

Table 1 Some physical properties of polymers **7a–7b″**

Monomer	Polymer				
	Polymer	Yield (%)	$\eta_{(inh}(dL/g)^a$	$[\alpha]_D^{25\,b}$	Color[c]
6a	**7a**	86.1	0.24	−5.74	OW
	7a′	83.7	0.23	−4.72	OW
6b	**7b**	87.2	0.26	−31.60	PY
	7b′	84.3	0.22	−1.10	Y

[a] Measured at a concentration of 0.5 g/dL in DMF at 25 °C

[b] Measured at a concentration of 0.5 g/dL in DMF at 25 °C

[c] *Y* Yellow, *PY* Pale Yellow, *OW* Off-White

Table 2 Elemental analysis of polymers **7a–7b′**

Polymer	Formula		C (%)	H (%)	N (%)
7a	$(C_{83}H_{81}N_4O_{10}F_6)_n$ (1409)$_n$	Calcd	70.77	5.80	3.98
		Found	70.90	5.70	4.10
7b		Calcd	73.11	5.75	3.59
		Found	73.00	6.00	3.50
7a′		Calcd	70.77	5.80	3.98
		Found	70.60	6.10	3.70
7b′		Calcd	73.11	5.75	3.59
		Found	73.30	5.90	4.10

Table 3 Some thermogravimetric analysis results of polymers **7b** and **7b′**

Polymer	$T_{5\%}$ (°C)[a]	$T_{10\%}$ (°C)[b]	Char yield (%)[c]
7b	200	281	21.4
7b′	271	400	29.2

[a] Temperature at which 5% weight loss was recorded by TG at heating rate of 10 °C/min in N_2

[b] Temperature at which 10% weight loss was recorded by TG at heating rate of 10 °C/min in N_2

[c] Percentage weight of material left undecomposed after TG analysis at maximum temperature 600 °C in N_2

Table 4 Sorption percentages (S%) of toxic heavy metal ions by monomer **2** and polymers **7a–7b′**

Ligand[a]	Metal ions			
	Cu^{2+}	Cd^{2+}	Co^{2+}	Hg^{2+}
7a	36.64	17.36	14.53	40.55
7b	9.91	8.26	11.81	19.07
7a′	14.22	33.06	44.02	46.61
7b′	4.31	28.10	6.75	45.76
2	43.96	18.80	18.37	28.11

Concentration: 1.0×10^{-2} M of metal nitrate salts in aqueous solution containing 2.0×10^{-5} M of picric acid
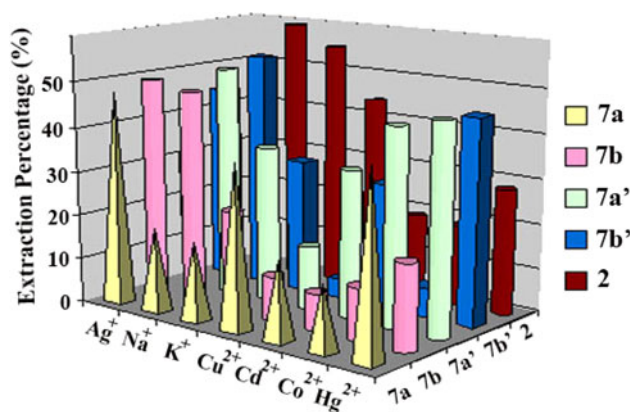
[a] 10 mg of ligand in 10 mL of aqueous metal picrate solution (aqueous phase) was shaken at 25 °C for 20 min

Table 5 Sorption percentages (S%) of toxic heavy metal ions by monomer **2** and polymers **7a–7b′**

Ligand[a]	Metal ions			
	Ag^+	Na^+	K^+	Cs^+
7a	47.58	18.55	17.47	0.0
7b	49.19	47.54	22.60	0.0
7a′	30.64	51.30	34.93	0.0
7b′	44.09	53.04	30.14	0.0
2	42.74	59.42	55.14	0.0

Concentration: 1.0×10^{-2} M of metal nitrate salts in aqueous solution containing 2.0×10^{-5} M of picric acid

[a] 10 mg of ligand in 10 mL of aqueous metal picrate solution (aqueous phase) was shaken at 25 °C for 20 min

Fig. 3 Sorption percentage of the polymers **7a–7b′** and calix diamine derivative **2**

ions. Most of the polymeric ligands had good sorption capacity for toxic heavy metals. Also all of them extracted silver and alkali metal ions but Cs^+. Monomer **2** had the highest sorption ability for Na^+, K^+ and Cu^{2+}. But the polymers extracted Ag^+, Na^+ and Hg^{2+} better than the other metal ions. The extraction value of the polymers for toxic heavy metals is higher than the value of the monomeric ligand. These results indicate that the existence of more than one calix[4]arene in the polymeric compounds and imide groups in the polymer backbone play important roles in the extraction process. Also all of the polymers and calix[4]arene diamine derivative (**2**) had no extraction ability towards Cs^+ ion. This result showed that

the binding ability of the compound (**2**) and the polymers is related to the macrocycle ring and metal ion size. The extraction percentages of the compound **2** and the polymeric ligands **7a–7b′** were illustrated in Fig. 3. As an
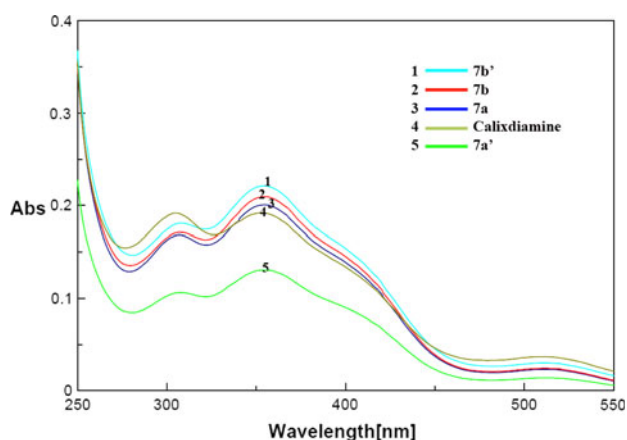
Fig. 4 UV curves of the aqueous cobalt picrate solutions after sorption by **7a**–**7b′** and **2**

example, the UV spectra of aqueous solutions of cobalt picrate after sorption by **7a**–**7b′** and **2** were demonstrated in Fig. 4.

From various studies [58, 59], it was deduced that amine and amide derivatized calixarenes are effective sorbents for these cations. Because NHC=O group is preferable to complex the more polarizable transition metal ions especially Hg due to cation–π interactions. The phenomenon may also reflect the "principle of hard and soft acids and bases" introduced by Pearson [60]. The detailed sorption mechanism has been explained in our published paper [61] and literature [62].

It should be noted that the results of our study on these optically active polymeric ionophores and the experiments in chiral media showed that the optical activity of the polymers didn't have influence on their sorption ability toward metal ions, but this approach is the subject of further investigation. Here, we studied the efficiency of the new polymeric calix[4]arenes towards silver, alkali and toxic heavy metal cations especially Hg^{2+}. The main advantage of these polymers is their insolubility in water and easy workup (unlike some sorbents such as polyelectrolytes), and the ease of large-scale preparation. On the other hand, unlike the other calix[4]arenes with this sorption efficiency, our functionalized calix[4]arene was prepared via simple two-stage synthetic route. We are investigating the enantiomeric discrimination and separation of chiral amine derivatives.

Conclusion

We have demonstrated that the macrocycles, such as *p-tert*-butyl calix[4]arene diamine derivative **2** can be polymerized with chiral imide containing monomers to give chiral polymeric ionophores. The main goal of this work is introducing calix[4]arene into the chiral polymer chain and giving the complexing properties to these polymers. The different polymerization methods influenced the chemical and physical properties of the corresponding polymeric ligands. We synthesized a new class of chiral polymers as good polymeric ionophores for sorption of alkali and toxic heavy metal ions. These polymers can be a choice for chiral recognition in the fields of organic, biological and medicinal chemistry.

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