ORIGINAL PAPER

Synthesis and extraction properties of new chromogenic azo-calix[4]dibenzothiacrown ethers

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Abstract Two novel chromogenic cone calix[4]dibenzothiacrown ethers **3** and **4** in which nitrophenylazo groups attached at the phenyl ring of dibenzothiacrown unit were described. The extraction properties of **3** and **4** toward different transition metal ions have been studied using conductometric technique and found to exhibit Cu^{2+} and Hg^{2+} selectivity with very high stability constants range from log K_{assoc} = 5.19 to log K_{assoc} = 8.72.

Keywords Chromogenic ionophores · Phenylazo · Calix[4]crown ethers · Conductivity

Introduction

Recognition and sensing of heavy and transition metal ions via artificial receptors are of current interest in supramolecular chemistry because of their significant importance in chemical, biological and environmental assays. Calixarenes are ideal building blocks for the development of chromogenic receptors in molecular recognition of ionic species of chemical and biological interest [1]. The incorporation of an appropriate sensory group into the calixarene having a preorganized substrate binding site results in a tailored chromogenic receptor. A variety of chromogenic calixarenes bearing nitrophenol, nitrophenylazophenol, indoaniline, indophenol and azophenol have been synthesized and show high selectivity in recognition for cations and organic molecules [2–10]. Most of the

research on calix[4]arenes as chromogenic ionophores involves the modification of the lower rim with metal chelating groups such as acids, amides, esters, ketones or crown ethers [11–18]. Several chromogenic calix[4]crown ethers have been synthesized by incorporating the chromogenic moiety mostly into the upper rim or rarely into the periphery of crown loops.

In our recent work, we synthesized a series of calixdibenzothiacrown ethers **1–2** and studied their complexation properties with some transition metal ions [19]. As a continue to this work, we report herein the synthesis of new chromogenic ionophores **3** and **4** based on incorporating of *p*-nitrophenylazo chromogenic groups at the benzene ring of the crown loop and their cation binding ability for the transition metal ions (Scheme 1).

Experimental

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Brucker Ac-200 and Ac-50 MHz spectrometer, respectively. In all cases, samples were dissolved in $CDCl_3$ using TMS as internal standard unless otherwise noted. The mass spectrometers that used for obtaining the mass spectra is the Agilent 1100 series LCMSD, model # G1946A. All materials were analytical grade and used without further purification. For conductivity experiments, acetonitrile (HPLC grade, GCC, assay 99.8%) was dried over calcium hydride and then double-distilled fractionally to give anhydrous solvent ($<3 \times 10^{-7}$ S cm^{-1}). The following salts were obtained from the suppliers indicated: $AgNO_3$ (GCC, 99%), $Hg(ClO_4)_2 \cdot xH_2O$ (BDH, 98%), $Cu(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Zn(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Cd(ClO_4)_2$ (Aldrich), $Pb(ClO_4)_2 \cdot 3H_2O$ (Aldrich), $Co(ClO_4)_2 \cdot 6H_2O$ (Alfa).

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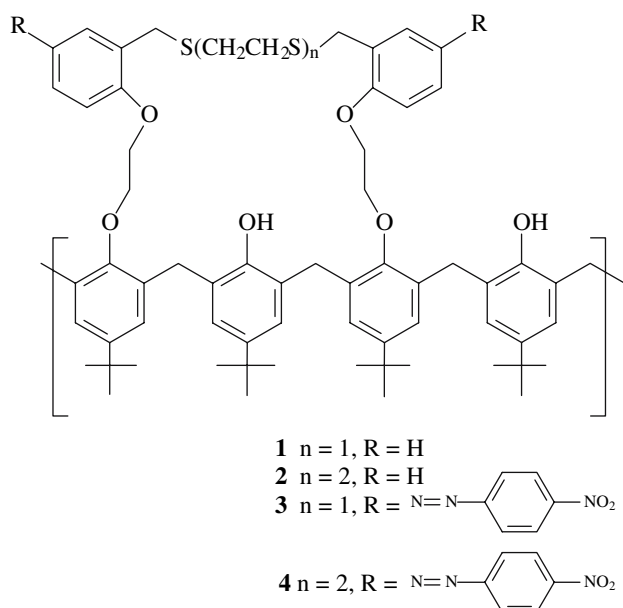
Scheme 1

Chromatographic separations were performed on silica gel columns (60–120 mesh, CDH). Thin layer chromatography (TLC) was carried out using silica gel GF$_{254}$ (Fluka). Unless otherwise noted, all reactions were carried out under dry nitrogen. The description of the conductometer and the details of the conductance measurements have been given previously [20]. Spectrophotometric measurements were carried out using Varian/Cary 2390 spectrophotometer connected to a thermostating unit (Haak Mess-Technik Gmbh U. Co. Type F3).

Synthesis

5-(4-nitrophenylazo)-2-hydroxybenzylalcohol (7)

To a 500-mL E-flask, *p*-nitroaniline (9.83 g, 0.071 mol) was added which contained a solution of 1:1 THF:H$_2$O (150 ml) and NaNO$_2$ (5.02 g, 0.072 mol). To the solution, which was being stirred at 0 °C, HCl (8.55 mL, 12 M), was slowly added. This solution was added drop wise to 500-mL single neck R.B.F which contained 2-hydroxybenzyl alcohol **6** (8.0 g, 0.065 mol) in a solution of 1:1 THF:H$_2$O (150 mL) at 0 °C. The final solution was stirred at 0 °C for 45 min. The resulting dark red solution was extracted with diethyl ether (500 mL). The organic layers were dried over anhydrous MgSO$_4$, filtered and the filtrate reduced to give dark red solid. The crude product was treated with CHCl$_3$ or diethyl ether, filtered and washed with CHCl$_3$ to give dark red-brown solid **7** (5.6 g, 32%); mp 165–166 °C; ^{1}H NMR δ_H (CDCl$_3$): 5.30 (d, J = 6 Hz, 2H), 7.40

(d, J = 6 Hz, 2H), 7.75 (d, J = 4 Hz, 1H), 7.90 (br, 1H), 7.98 (d, J = 8 Hz, 2H), 8.12, (s, 1H), 8.38 (d, J = 8 Hz, 2H); ^{13}C NMR δ_c (acetone-d_6): 60.1, 116.1, 124.0, 124.3, 126.0, 126.1, 130.1, 147.6, 150.0, 157.1, 161.0; MS *m/z*: 273 (M$^+$, 27), 208 (4), 149 (26), 123 (54), 105 (88).

5-(4-nitrophenylazo)-2-(2-bromoethoxy)benzylalcohol (8)

In a 250 mL one-necked R. B. flask equipped with a magnetic stirrer bar and a reflux condenser, compound **7** (2.0 g, 7.2 mmol), 1, 2-dibromoethane (13.6 g, 72 mmol) and anhydrous K$_2$CO$_3$ (1.0 g, 7.2 mmol) were mixed with anhydrous CH$_3$CN (150 mL). The mixture was refluxed for 24 h and then cooled to room temperature, filtered and the solid was washed with CH$_3$CN. The filtrate was evaporated to dryness to give crude dark brown solid which was washed with diethyl ether to give **8** (2.55 g, 92%); mp 75–76 °C; ^{1}H NMR δ_H (CDCl$_3$): 3.76 (t, J = 4 Hz, 2H), 4.45 (t, J = 4 Hz, 2H), 4.83 (d, J = 6 Hz, 2H), 7.0 (d, J = 6 Hz, 1H), 7.98 (br, 1H), 8.0 (s, 1H), 8.10 (d, J = 8 Hz, 2H), 8.40 (d, J = 8 Hz, 2H); ^{13}C NMR δ_c(CDCl$_3$): 29.2, 61.9, 66.2, 110.8, 122.3, 122.4, 122.7, 124.6; MS *m/z*: 271 (M$^+$-CH$_2$CH$_2$Br, 37), 149 (72), 121 (100), 93 (41), 75 (24), 65 (71).

25, 27-O-Bis[2-hydroxymethyl-5-(4-nitrophenylazo)phenoxyethyl]-p-tert-butyl calix[4]arene (9)

In a 500 mL one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, compound **8** (4.2 g, 11.1 mmol), *p-tert*-butylcalix[4]arene (3.60 g, 5.55 mmol), and anhydrous K$_2$CO$_3$ (4.6 g, 5.55 mmol) were mixed with anhydrous CH$_3$CN (400 mL) and refluxed for 6 days. The mixture was filtered and the solid was washed with CH$_3$CN. The combined filtrate was evaporated to dryness. The crude product was purified by flash chromatography using ethyl acetate:hexane (3:7) to give **9** as red solid (3.65 g, 53%); mp 123–125 °C ^{1}H NMR δ_H(CDCl$_3$): 1.11 (s, 18H, *t*-But), 1.26 (s, 18H, *t*-But), 3.42 (d, J = 16 Hz, 4H, Ar*CH$_2$*Ar), 4.33 (d, J = 16 Hz, 4H, Ar*CH$_2$*Ar), 4.30 + 4.50 (br, 8H, O*CH$_2$CH$_2$*O), 4.70 (d, J = 4 Hz, 4H, *CH$_2$*OH), 4.96 (t, J = 2 Hz, CH$_2$*OH*), 6.68 (d, J = 4 Hz, 2H), 7.00 (s, 4H), 7.06 (s, 4H), 7.63 (d, J = 3 Hz, 2H), 7.94 (s, 2H), 7.98 (d, J = 10 Hz, 4H), 8.35 (d, J = 10 Hz, 4H), 8.70 (s, 2H, OH); ^{13}C NMR δ_c(CDCl$_3$): 31.0, 31.5, 32.0, 34.0, 34.1, 60.8, 67.5, 74.6, 111.0, 123.1, 124.8, 125.5, 127.0, 127.6, 128.0, 131.0, 133.2, 143.0, 146.6, 148.2, 148.3, 149.2, 156.0, 160.4; +APCI HRMS calcd for C$_{74}$H$_{82}$N$_6$O$_{12}$ (M+1)$^+$ 1247.6, found 1247.5.

25, 27-O-Bis[2-chloromethyl-5-(4-nitrophenylazo)phenoxyethyl]-p-tert-butylcalix[4]arene (10)

To a solution of **9** (1.0 g, 0.8 mmol) in anhydrous CH_2Cl_2 (100 mL) was added freshly distilled $SOCl_2$ (0.49 mL, 6.4 mmol) at room temperature. The reaction was stirred for 6 h and then cold water was added. The organic layer was separated and washed with water, dried and evaporated to give **10** as dark red solid (0.95 g, 92%). Sample was further purified for analysis by TLC using ethyl acetate:hexane (3:7); mp 118–120 °C (decomp.); ^1H NMR δ_H(CDCl$_3$):1.05 (s, 18H, t-But), 1.30 (s, 18H, t-But), 3.20 (d, J = 18 Hz, 4H, ArCH_2Ar), 4.55–4.28 (m, 12H, OCH_2CH_2O and ArCH_2Ar), 4.72 (s, 4H, CH_2Cl), 6.86 (s, 4H), 7.00 (J = 3 Hz, 2H), 7.04 (s, 4H), 7.50 (s, 2H), 8.10–7.88 (m, 6H), 8.31 (d, J = 10 Hz, 4H); ^{13}C NMR δ_c(CDCl$_3$): 30.5, 31.4, 34.0, 41.5, 67.9, 73.6, 111.5, 123.5, 124.5, 124.7, 125.1, 125.6, 126.0, 127.5, 128.0, 132.6, 142.1, 146.5, 147.8, 148.6, 149.5, 150.5, 155.6, 159.0; +APCI HRMS calcd for $C_{74}H_{80}Cl_2N_6O_{10}$ (M+1)$^+$ 1283.5, found 1283.4.

General procedure for the synthesis of Azocalix[4]dibenzothiacrown Ethers 3 and 4

Macrocycles **3** and **4** were synthesized under high dilution conditions. In a 250 mL two-necked flask equipped with a magnetic stirrer bar and a reflux condenser and a gas line to maintain a nitrogen atmosphere, anhydrous K_2CO_3 (0.11 g, 0.39 mmol) was suspended in anhydrous CH_3CN (100 mL). To this well-stirred solution at reflux temperature was added a solution containing dithiol [HS(CH$_2$CH$_2$S)$_n$H, n = 1, 2] and dichloride **10** (0.39 mmol) in anhydrous CH_3CN (100 mL) dropwise over a period of 10–12 h. The reaction mixture was further refluxed with stirring for another 12 h. The reaction mixture was filtered and the filtrate was evaporated. The residue was dissolved in CHCl$_3$ (100 mL) and washed with H$_2$O. The organic layer was dried over anhydrous MgSO$_4$ and then evaporated. The purification was carried out as indicated by the entries below for the separate compounds.

Azocalix[4]dibenzothiacrown ethers (3)

The crude product was purified by column chromatography using ethyl acetate/hexane (3:7) as eluent to give **3** as dark red solid (0.11 g, 20%); mp 165–167 °C, (decomp); ^1H NMR δ_H(CDCl$_3$): 0.95 (s, 18H, t-But), 1.30 (s, 18H, t-But), 2.68 (s, 4H), 3.32 (d, J =14 Hz, 4H, ArCH_2Ar), 4.01 (s, 4H),4.56–4.30 (br,12H), 6.76 (s, 4H), 6.95 (s, 2H), 8.03–7.85 (br, 6H), 8.30 (d, J = 6 Hz, 4H); ^{13}C NMR

δ_c(CDCl$_3$): 30.0, 31.1, 31.5, 31.8, 32.0, 34.1, 67.1, 74.1, 111.2, 123.7, 125.0, 125.2, 126.0, 128.1, 129.8, 132.8, 141.8, 147.0, 147.6, 148.2, 149.8, 150.6, 155.8, 159.8; +APCI HRMS calcd for $C_{76}H_{84}N_6O_{10}S_2$ (M+1)$^+$1305.5, found 1305.3.

Azocalix[4]dibenzothiacrown ethers (4)

The crude product was purified by TLC using ethyl acetate/hexane (3:7) as eluent to give **4** as red solid (0.12 g, 23%); mp 152–155 °C (decomp); ^1H NMR δ_H(CDCl$_3$): 0.92 (s, 18H, t-But), 1.31 (s, 18H, t-But), 2.59 (br, 8H), 3.35 (d, J =12 Hz, 4H, ArCH_2Ar), 3.95 (s, 4H), 4.48 (br,12H), 6.76 (s, 4H), 6.95 (s, 2H), 7.02 (d, J =3 Hz, 2H), 7.10 (s, 4H), 8.02–7.82 (m, 6H), 8.32 (d, d, J = 4 Hz, 4H); ^{13}C NMR δ_c(CDCl$_3$): 30.1, 31.2, 31.3, 32.0, 32.6, 34.0, 67.5, 74.5, 111.2, 123.2, 124.9, 125.0, 125.1, 125.2, 125.4, 128.0, 128.9 132.5, 141.9, 147.2, 147.5, 148.5, 149.6, 150.5, 156.0, 159.8; +APCI HRMS calcd for $C_{78}H_{88}N_6O_{10}S_3$ (M+1)$^+$1365.5, found 1365.4.

Results and discussion

Synthesis

Azocalix[4]dibenzothiacrown ethers **3** and **4** were synthesized using a method almost similar to that used in the preparation of **1–2** (Scheme 2) [19]. Salicylaldehyde was envisioned as being suitable precursor to condense with p-nitrodiazonium salt. However all attempts to synthesize the p-nitroazoaldehyde **5** were failed. This can be ascribed to the deactivating effect of the formyl group which deactivate the coupling reaction of the arenedizonium salt with the aromatic ring. Fortunately, condensation of 2-hydroxybenzylalcohol **6** with the diazonium salt produced the target compound **7** as dark orange solid in good yield which shorting the route by one step. Alkylation of compound **7** with an excess of 1, 2-dibromoethane in presence of two equivalents of anhydrous K_2CO_3 in refluxing anhydrous CH_3CN afforded, after washing the crude product with diethyl ether, compound **8** in 92% yield as dark brown solid. Compound **9** was prepared by condensation of p-tert-butylcalix[4]arene with two equivalents of compound **8** in refluxing anhydrous CH_3CN containing two equivalents of anhydrous K_2CO_3. Compound **9** was formed as red solid in 53% after purifying the crude product by flash chromatography using ethylacetate:hexane (3:7). Treatment of **9** with fresh distilled $SOCl_2$ at room temperature in anhydrous CH_2Cl_2 for 6 h produced compound **10** as dark red solid in 92% yield. Base mediated coupling of equimolar amounts of ethane 1, 2-dithiol or
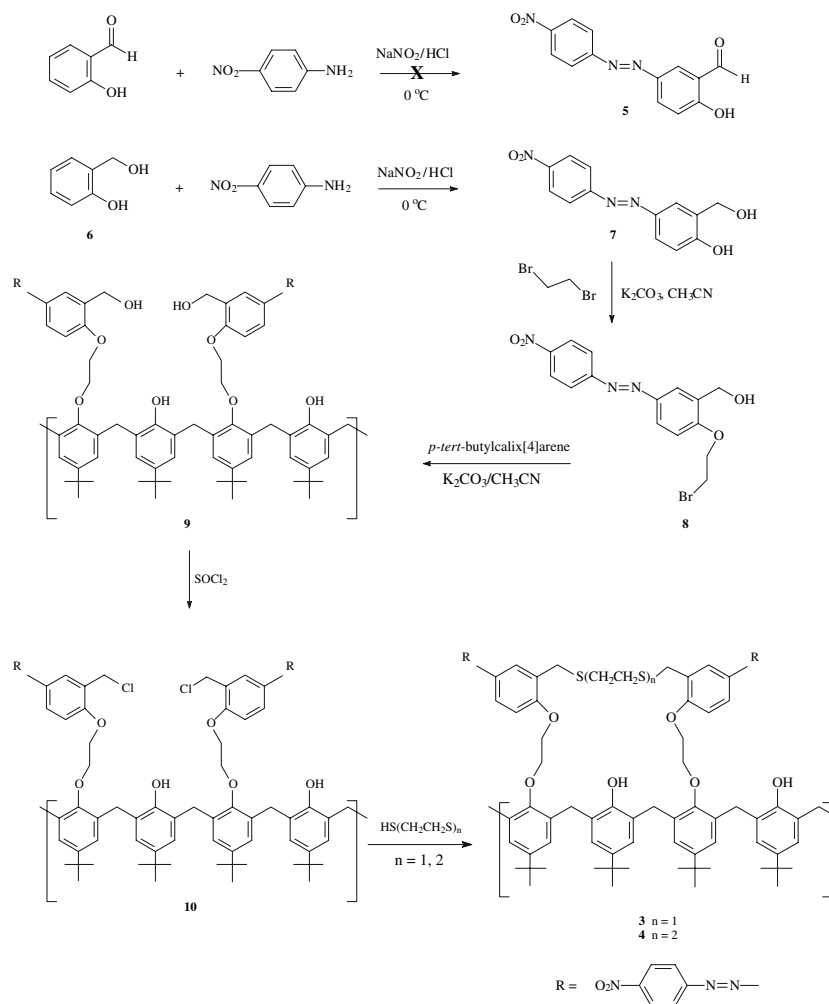
Scheme 2

bis(mercaptoethyl)sulfide and **10** afforded crude products of **3** and **4**. Each of the resulting reaction products was purified by column chromatography to give **3** and **4** as orange solid in 20 and 23% yield, respectively. Compounds **3** and **4** were fully characterized and established to be in cone conformation by the presence of two sets of doublet signals in their ^{1}H NMR spectra at δ 3.29 and 4.30 ppm and at δ 3.31 and 4.45 ppm, respectively due to the methylene bridge protons as well as by presence of two singlet signals due to the *tert*-butyl groups at δ 0.96 and 1.30 ppm, and at δ 0.93 and 1.31 ppm respectively.

Complexation studies

UV-vis spectral titrations

Upon addition of acetonitrile solution of Cu^{2+} or Hg^{2+} to acetonitrile solutions of either hosts **3** or **4**, no distinct color change was observed. But UV-vis spectra of hosts **3** or **4** in

presence of various concentrations of Cu^{2+} are shown in Figs. 1 and 2, respectively as typical example.

Although no presence of significant changes in the position of the absorption maxima, it can be seen that the
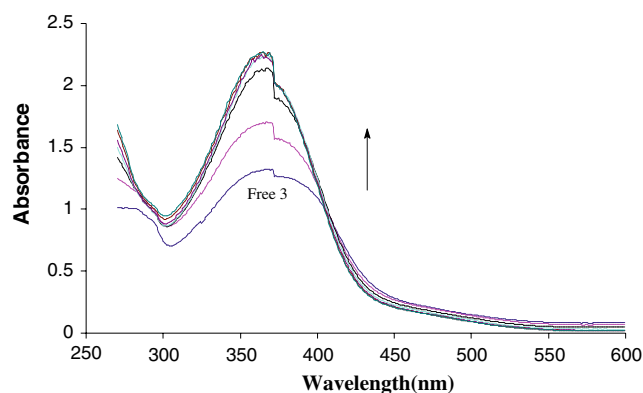

Fig. 1 Spectral changes of **3** (5×10^{-5}M, CH$_3$CN) upon addition of various amounts of Cu^{2+}; Cu(ClO$_4$)$_2$·6H$_2$O equivalents: 0, 5, 10, 15, 20, 25 and 30
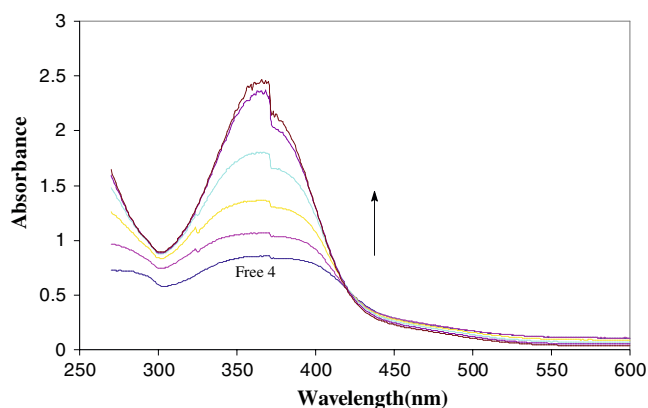
Fig. 2 Spectral changes of **4** (5×10^{-5}M, CH$_3$CN) upon addition of various amounts of Cu^{2+}; Cu(ClO$_4$)$_2$·6H$_2$O equivalents: 0, 5, 10, 15, 20 and 25

Fig. 3 Conductance versus [L]$_T$/[M]$_T$ for compound **3** with Hg^{2+} and Cu^{2+} in CH$_3$CN at 25 °C

Fig. 4 Conductance versus [L]$_T$/[M]$_T$ of compound **4** with Hg^{2+} and Cu^{2+} in CH$_3$CN at 25 °C

Fig. 5 Conductance versus [L]$_T$/[M]$_T$ of compound **4** with Ag$^+$, Cd^{2+}, Pb^{2+} and Zn^{2+} in CH$_3$CN at 25 °C

absorbance in both figures increased continually upon addition of Cu^{2+}. This change in absorption intensity indicates presence of a complexation taking place between Cu^{2+} and either hosts **3** or **4**. Furthermore, it is noteworthy that the presence of isosbestic point at about 410 nm implies that two species, the host and host-Cu^{2+} complex, are present in equilibrium. Upon increasing equivalent numbers of Cu^{2+} (up to 15 equiv in Fig. 1 and up to 20 equiv. in Fig. 2), changes in the UV-vis spectra were only minor for both compounds **3** and **4** which imply that the complexes reached the saturation limit. Therefore, addition of greater than 15 or 20 equiv. of Cu^{2+} would not give any further significant spectral changes. The presence of the complexation between **3** or **4** and either Cu^{2+} or Hg^{2+} was confirmed also by a conductometric titration experiments as shown below.

Conductometric Titration:

In present complexation study, the conductometric method is used to evaluate both the stability constants of the complexes and the stoichiometry of the ligand:metal ratio.

According to the strength of complexation between the ligand and the metal cation, plot of molar conductance Λ_m (S cm^2 mol^{-1}) against [L]$_T$/[M$^+$]$_T$ show three different patterns for strong (two straight lines with a sharp break at the reaction stoichiometry), moderate (broad break in the curvature so the composition of the complex is determined by extrapolating the lines prior to and after the end-point of the titration), and weak (slight or nonexisting changes in the slope) complexes. Among the cations investigated in acetonitrile (Cu^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ag$^+$), the complexation of Cu^{2+} with **3** and **4** led to titration curves which are the result of a combination of two straight lines intersecting at the reaction stoichiometry of 1:2, while for Hg^{2+} the intersecting of the two straight lines occurs at the reaction stoichiometry of 1:1 as shown in Figs. 3 and 4.
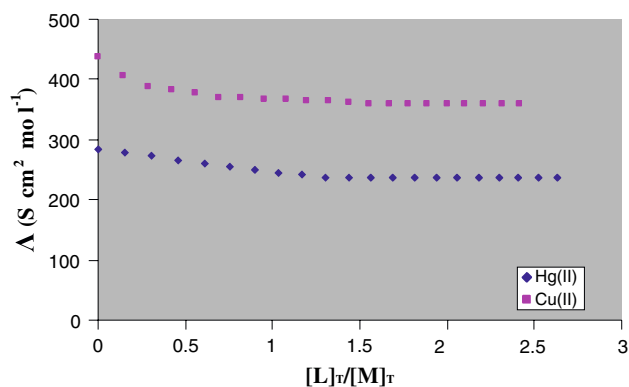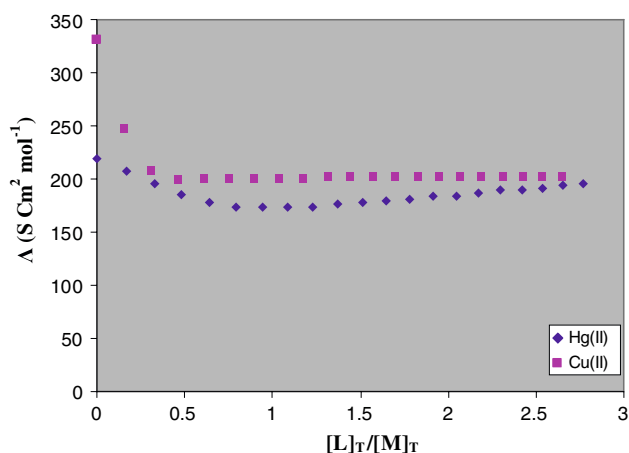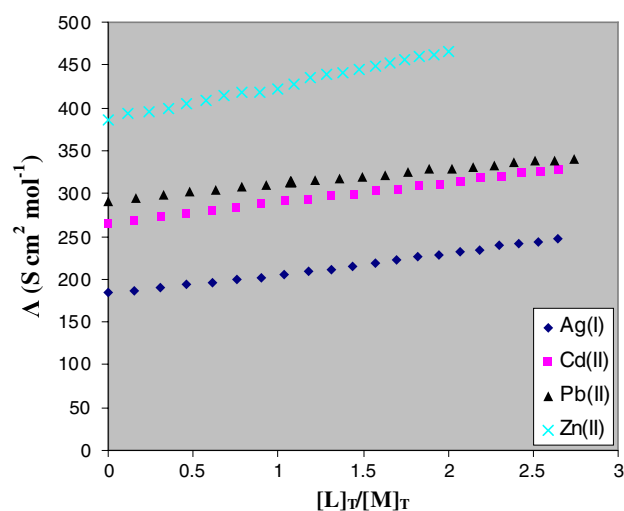
Table 1 log K_{assoc} (dm^3 mol^{-1}) for complexations of some transition metal cations with **3** and **4** in acetonitrile at 25 °C

Compound#	Cu^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Ag$^+$
3	6.62 ± 0.31	5.19 ± 0.25	–	–	–	–
4	8.53 ± 0.43	8.72 ± 0.41	2.52 ± 0.12	2.86 ± 0.14	1.43 ± 0.07	1.12 ± 0.06

These finding indicate the formation of highly stable complexes between **3** or **4** and Cu^{2+} and Hg^{2+} cations in acetonitrile.

It is obvious, from Figs. 3 and 4, addition of ligands **3** or **4** to solutions of Cu^{2+} or Hg^{2+} results in a decrease in molar conductivity of the resulting solutions. This indicates that the resulting complexes are less mobile than free solvated Cu^{2+} or Hg^{2+}. On the other hand, as shown in Fig. 5, addition of ligand **4** to solutions of Zn^{2+}, Cd^{2+}, Pb^{2+} or Ag$^+$ results in an increase in molar conductivity of the resulting solutions. This indicates that the resulting complexes are more mobile than free solvated metal cations alone.

No detectible changes in molar conductances were found when a solution of **3** was added to metal solutions of Zn^{2+}, Cd^{2+}, Pb^{2+} or Ag$^+$ (Figure not shown). This conclude that ligand **3** is more selective than ligand **4** toward the metal ions under investigation. The stability constants of the **3**-M^{2+} and **4**-M^{2+} complexes at 25 °C were calculated from variation of molar conductance as a function of [L]$_T$/[M]$_T$ molar ratio using a nonlinear least-square program "simplex" reported elsewhere [21]. The stability constants (log K_{assoc}) for the complexes are listed in Table 1. As shown in Table 1, it is obvious that the stability constants of **4**-Cu^{2+} and **4**-Hg^{2+} complexes are higher than those of **3**. This is may due to the larger cavity size of crown loop of **4** than the crown loop of **3** which match the diameter of both Cu^{2+} and Hg^{2+} metal cations.

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