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Synthesis, extraction and chromogenic properties of Amidoazocalix[4]arenes and their telomer derivatives

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The synthesis, extraction and chromogenic properties of calix[4]arenes, carrying phenylazo and amido groups on their *upper* and *lower* rims, respectively, are described. Novel azocalix[4]arene amides (**1a–d, 2a–d, 3a–d**) and some of their telomers (**T1a–T1d**) have been synthesised and characterised by spectroscopic methods as well as elemental analysis techniques. Compounds **1c** and **2b** were additionally characterised by two-dimensional nuclear magnetic resonance spectroscopic methods. Some of the compounds were examined by absorption spectra using different solvents. The colour changes of the resulting solutions can be observed by the 'naked eye'. Metal extraction abilities of compounds have been investigated comparatively. Telomer structures of azocalix[*n*]arenes exhibited higher extraction rates compared to those of their monomers. Products obtained under this study, especially telomers, can be used in the field of ion-selective electrodes.

Keywords: calixarene; amidoazocalix[4]arene; telomer; 2D NMR; metal extraction; absorption property

Introduction

Calix[*n*]arenes can be synthesised by base-catalysed condensation of *para*-substituted phenols with formaldehyde. They are used in designing and synthesising artificial receptors for the development of chromogenic ionophores. They are also used in the molecular recognition of ionic species of chemical and biological interest. Thus, they are regarded as an important class of building blocks, which is very well documented in supramolecular chemistry (*1*). In detection of metals, polymerised calixarenes, called telomers, can carry more metal ions than the monomer form of calixarenes. The enhancement of this binding property is mainly due to the nature of the linkers. Selective signalling of heavy metal ions is very important for detection and recognition of toxic metal ions in various systems (*2*).

Azocalix[*n*]arenes are generated by the insertion of nitrogen atoms into the *p*-positions of the calixarene structures. They have several isomers based on the position of the inserted nitrogen atoms and molecular ring size (*3*). Azo compounds are one of the most widely used classes of dyes. They are used in various fields such as the dyeing of textile fibers, colouring of differing materials, biomedical studies and advanced applications in organic synthesis (*4*). Advanced applications of azo compounds in organic synthesis include sensor molecules, metal electrodes and indicators. Moreover, calixarenes gain chromogenic activity with azo groups. These compounds are an important class of organic colourants and consist of one or more conjugated chromophore azo (—N═N—) group and two or more aromatic rings. The colour properties of organic dyes depend on their chromophore groups and some of crystalline organic dyes also depend on the crystallographic arrangement of molecules in the solid state (*5*).

For the past decade, our research group has persistently focused on mimicking the active site of mononuclear azo compounds. In our studies, calix[4 and 6]arene macrocycles are used to isolate the metal centre to prevent dimerisation and hence play the role of the host–guest complexes. The hydrophobic cavity in the azocalixarene structures provides secondary interaction between the azocalixarene molecule itself and a probable guest ion or molecule (*6*). More recently, the interest of our research group moved into developing systems that can bind two metal centres at controlled distances higher than 4 Å in order to escape the thermodynamic sink leading to the formation of bridged and electronically coupled dinuclear complexes (*7*). Indeed, many enzymes, consisting of two metal ions displaying different functions (*8*), raise interesting questions relative to selective binding of two different metal ions at two different sites. The reason for this situation is mutual structural roles, selective metal ion loading and trafficking and thus translocation processes (*9*).

So far, very few synthetic systems involving azocalix(4(arenes have been studied (*10*). Chung and co-workers have synthesised an azocalix(4(arene molecule with *bis*4-(4′-methoxyphenylazo) phenol unit and a bisallyl group on its *upper rim* (*11*). They observed a high extraction ability of the synthesised compound for particular mercury ions

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(Hg^{2+}) among various metal ions. Lu et al. have synthesised a water-soluble azocalixarene derivative and reported its application as highly selective chromogenic ionophores in recognition of chromium(III) ions (*12*). Reinhoult et al. have synthesised chromogenic azocalix[4]arene containing nitrophenylazo and amide groups and reported its high extraction ability towards Pb^{2+} among various metal ions (*13*).

Among azophenolic supramolecules, azocalix[4]arenes are unique in their efficient ionophoric properties towards some important guest ions such as Ca^{2+} or K^{+}. Azo groups, which are considered to be chromogenic centres, cannot be referred to as metal-chelating sites. Various efforts have been performed on lower rim modification of azocalix[4]arenes in order to bring metal-binding ability. But, azocalix[4]arenes without *lower rim* modifications can also bind transition metal ions effectively (*14*).

Nowadays, selective transportation of metal ions by calixarenes plays a crucial role in ion recognition for environment and biological systems. Rao and his coworkers demonstrated selective recognition of Asp, Glu and GSH by *lower rim* 1,3-diamido conjugates of calix[4]arene possessing terminal —COOH moieties by fluorescence spectroscopy (*15*).

In this study, synthesis and characterisation of novel amidoazocalix[4]arene monomers (**1a–d**, **2a–d**, **3a–d**) and telomers (**T1a–T1d**) containing different functional groups (Scheme 1) have been presented. Absorption and extraction properties of synthesised compounds have also been demonstrated in this work.

Experimental

General methods

Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column chromatography purification of products was held by using silica gel (0.040–0.063 nm). Reactions were monitored by TLC on silica gel plates and visualised by UV light.

All the solvents used were dried and distilled by the usual procedures before use. Melting points of the products were measured with Electrothermal IA9100 digital melting point apparatus in capillaries sealed under nitrogen and are uncorrected. UV–vis spectra were obtained with Shimadzu 1601 UV-Visible recording spectrophotometer (Tetra, İzmir, Turkey). IR spectra were recorded by Mattson 1000 FT-IR spectrometer (Tetra, İzmir, Turkey) with KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer (Bruker, Istanbul, Turkey) at room temperature ($CDCl_3$). 2D NMR spectra were recorded with a Bruker DPX-300 MHz spectrometer (Bruker, Istanbul, Turkey) at Ataturk University (Erzurum, Turkey).

MALDI-TOF and elemental analyses were performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).

Preparation of the ligands

p-tert-Butylcalix(4(arene (*16*), calix(4(arene (*17*), 25,27-di(ethoxycarbonylmethoxy)-26,28-hydroxycalix(4(arene, calix[4]aren(amido)mono-crown derivatives (**1–3**) (*10*) and their azo derivatives were prepared according to the procedure below.

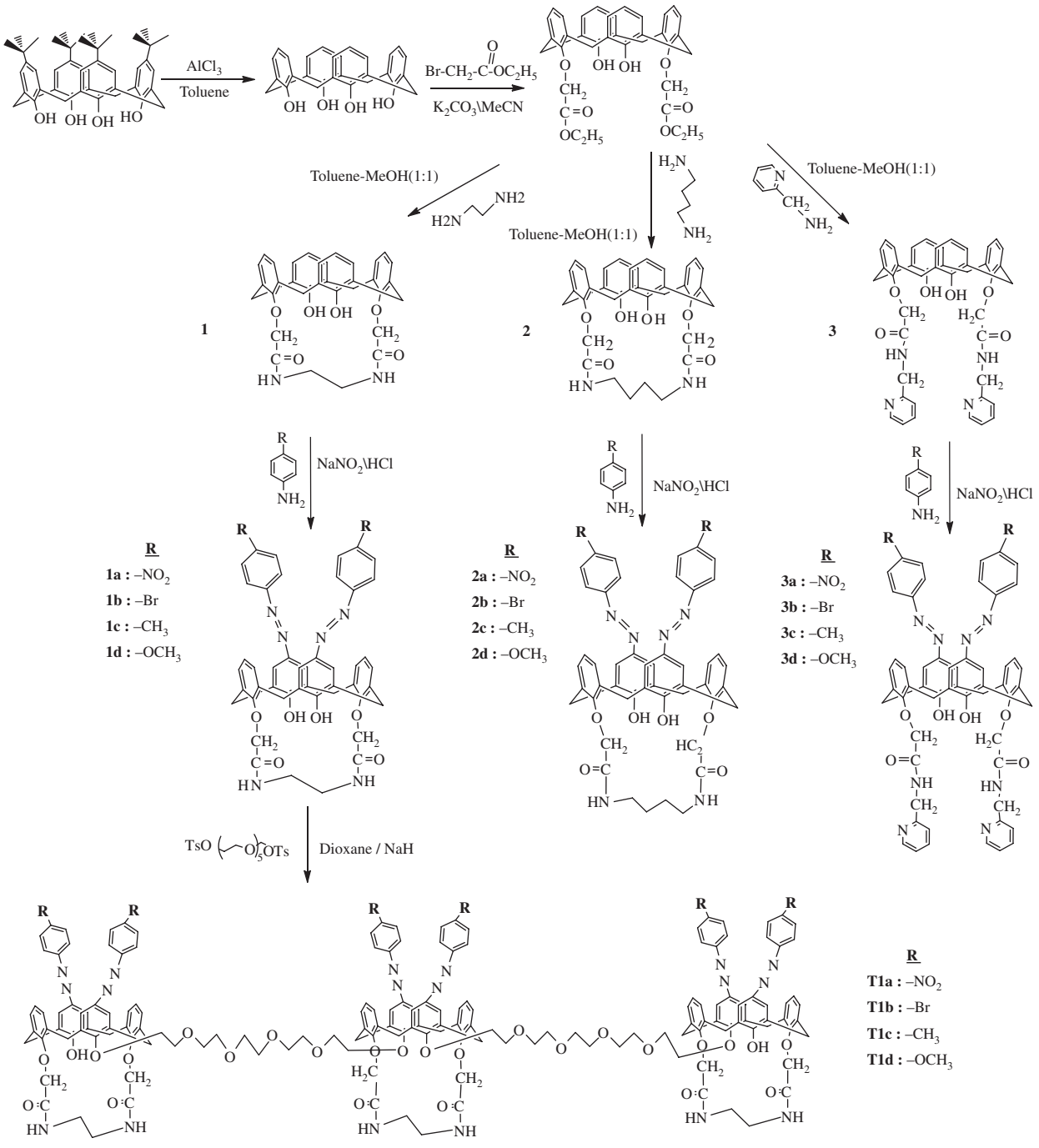
General procedure for the synthesis of amidoazocalix[4] arenes

The following procedure was used to transform amidocalix[4]arenes (**1**,**2**,**3**) in to the corresponding azo series.

A solution of *p*-substituted phenyldiazonium chloride was prepared from *p*-substituted aniline (1.84 mmol), sodium nitrite (2.76 mmol) and conc. HCl (9.24 mmol) in water (2 mL). The resulting solution was added slowly to a solution of cold (5°C) amidocalix[4]arene (0.5 g, 0.88 mmol) and sodium acetate trihydrate (9.36 mmol) in DMF/MeOH (13 mL, 8:5, v/v). The resulting yellow suspension was kept between 0 and 5°C for 10 h. Then, the suspension was brought to room temperature before acidifying with aqueous HCl (60 mL, 4 N). The resulting mixture was firstly warmed up to 60°C and kept at that temperature for 30 min to give an *amidoazocalix[4]arene* residue. After filtering and washing with water, the solid residue was purified by column chromatography with hexane and ethyl acetate as an eluent.

Compound 1a: The solid was eluted with hexane/ethyl acetate (3:1,v/v) and gave 0.45 g (60%) of a red powder, mp.: 315°C (dec): ^{1}H NMR ($CDCl_3$) δ: 3.70 (d, $J = 13.42$ Hz, 4H, Ar**CH$_2$**Ar), 3.76 (s, 4H, amido-**CH$_2$**), 4.21 (d, $J = 13.32$ Hz, 4H, Ar**CH$_2$**Ar), 4.62 (s, 4H, O-**CH$_2$**), 7.00 (t, 2H, Ar**H**-calix), 7.20 (d, 4H, Ar**H**-calix), 7.62 (d, 4H, Ar**H**—N═N), 7.77 (d, 4H, Ar**H**—N═N), 7.79 (s, 4H, Ar**H**-calix), 8.40 (s, 2H, N**H**), 8.88 (s, 2H, Ar**OH**). ^{13}C NMR (75 MHz $CDCl_3$): 167.7, 151.9, 148.9, 133.0, 132.1, 129.3, 129.2, 127.4, 127.1, 125.0, 124.7, 123.1, 120.7, 74.7, 39.3, 31.4. Anal. calcd for $C_{46}H_{38}N_8O_{10}$: C, 64.03; H, 4.44; N, 12.99. Found: C, 64.28; H, 4.63; N, 12.77.

Compound 1b: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.42 g (%52) of an orange powder, mp.: 270°C. ^{1}H NMR ($CDCl_3$) δ: 3.69 (d, $J = 13.49$ Hz, 4H, Ar**CH$_2$**Ar), 3.74 (s, 4H, amido-**CH$_2$**), 4.22 (d, $J = 13.41$ Hz, 4H, Ar**CH$_2$**Ar), 4.63 (s, 4H, O—**CH$_2$**), 6.95 (t, 2H, Ar**H**-calix), 7.16 (d, 4H, Ar**H**-calix), 7.63 (d, 4H, Ar**H**—N═N), 7.74 (d, 4H, Ar**H**—N═N), 7.78 (s, 4H, Ar**H**-calix), 8.38 (s, 2H, N**H**), 8.86 (s, 2H, Ar**OH**). ^{13}C NMR (75 MHz $CDCl_3$): 167.2, 155.2, 151.5, 149.0, 146.4, 132.3, 132.3, 130.1,



Scheme 1. Synthesis of amidoazocalix(4(arenes and telomers.

128.0, 127.2, 124.7, 124.4, 124.0, 74.9, 39.2, 31.4.Anal. calcd for $C_{46}H_{38}Br_2N_6O_6$: C, 59.37; H, 4.12; N, 9.03. Found: C, 59.68; H, 4.43; N, 9.28.

Compound 1c: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.40 g (%58) of a yellow powder, mp: > 320°C (dec): ^{1}H NMR ($CDCl_3$) δ: 2.45 (s, 3H, Ar—**CH_3**), 3.71 (d, $J = 13.48$ Hz, 4H, Ar**CH_2**Ar), 3.76 (s, 4H, amido-**CH_2**), 4.24 (d, $J = 13.38$ Hz, 4H, Ar**CH_2**Ar), 4.66 (s, 4H, O-**CH_2**), 6.96 (t, 2H, Ar**H**-calix), 7.19 (d, 4H, Ar**H**-calix), 7.32 (d, 4H, Ar**H**—N═N), 7.78 (s, 4H, Ar**H**-calix), 7.80 (d, 4H, Ar**H**—N═N), 8.45 (s, 2H, **NH**), 8.82 (s, 2H, Ar**OH**). ^{13}C NMR (75 MHz $CDCl_3$): 167.3, 154.7, 150.8, 148.9, 146.6, 140.9, 132.4, 130.1, 129.7, 127.9, 127.2, 124.1, 122.5, 74.8, 39.3, 31.5, 21.5. Anal. calcd for $C_{48}H_{44}N_6O_6$: C, 71.98; H, 5.54; N, 10.49. Found: C, 71.68; H, 5.88; N, 10.62.

Compound 1d: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.42 g (58%) of a dark

yellow powder, mp**:** 312°C (dec): ^{1}H NMR ($CDCl_3$) δ: 3.73 (d, $J = 13$ Hz, 4H, Ar**CH$_2$**Ar), 3.77 (s, 4H, amido-**CH$_2$**), 3.92 (s, 6H, O**CH$_3$**), 4.25 (d, $J = 13$ Hz, 4H, Ar**CH$_2$**Ar), 4.67 (s, 4H, O-**CH$_2$**), 6.98 (t, 2H, Ar**H**-calix), 7.03 (d, 4H, Ar**H**—N═N), 7.20 (d, 4H, Ar**H**-calix), 7.76 (s, 4H, Ar**H**-calix), 7.90 (d, 4H, Ar**H**—N═N), 8.47 (s, 2H, **NH**), 8.80 (s, 2H, Ar**OH**). ^{13}C NMR (75 MHz $CDCl_3$): 167.3, 161.6, 154.3, 148.9, 147.0, 146.6, 132.4, 130.0, 127.8, 127.2, 124.3, 123.9, 114.2, 74.7, 55.5, 39.3, 31.4. Anal. calcd for $C_{48}H_{44}N_6O_8$: C, 69.22; H, 5.32; N, 10.09. Found: C, 68.99; H, 5.44; N, 10.20.

Compound 2a: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.48 g (64%) of a yellow powder, mp: 232 °C (dec): ^{1}H NMR ($CDCl_3$) δ: 1.81 (s, 4H, amido-**CH$_2$**), 3.66 (d, $J = 13.68$ Hz, 4H, Ar**CH$_2$**-Ar), 3.68 (s, 4H, amido-**CH$_2$**), 4.25 (d, $J = 13.56$ Hz, 4H, Ar**CH$_2$**Ar), 4.59 (s, 4H, O-**CH$_2$**), 6.86 (t, 2H, Ar**H**-calix), 7.02 (d, 4H, Ar**H**), 7.50 (s, 2H, **NH**), 7.85 (s, 2H, Ar**OH**), 7.87 (s, 4H, Ar**H**-calix), 8.01 (d, 4H, Ar**H**—N═N—), 8.38 (d, 4H, Ar**H**—N═N). ^{13}C NMR (75 MHz $CDCl_3$): 167.8, 152.2, 150.4, 148.3, 146.4, 132.2, 131.3, 129.6, 127.6, 126.6, 124.9, 123.1, 120.7, 75.1, 37.7, 31.2, 25.2. Anal. calcd for $C_{48}H_{42}N_8O_{10}$: C, 64.71; H, 4.75; N, 12.58. Found: C, 64.98; H, 4.88; N, 12.73.

Compound 2b: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.48 g (60%) of an orange powder, mp: 240°C (dec): ^{1}H NMR ($CDCl_3$) δ: 1,73 (s, 4H, amido-**CH$_2$**), 3.57 (s, 4H, amido-**CH$_2$**), 3.61 (d, $J = 13.59$ Hz, 4H, Ar**CH$_2$**Ar), 4.15 (d, $J = 13.56$ Hz, 4H, Ar**CH$_2$**Ar), 4.50 (s, 4H, O-**CH$_2$**), 6.76 (t, 2H, Ar**H**-calix), 6.93 (d, 4H, Ar**H**-calix), 7.47 (s, 2H, **NH**), 7.57 (d, 4H, Ar**H**—N═N—), 7.60 (s, 2H, Ar**OH**), 7.70 (d, 4H, Ar**H**—N═N—), 7.74 (d, 4H, Ar**H**-calix). ^{13}C NMR (75 MHz $CDCl_3$): 167.7, 155.4, 151.5, 150.5, 146.2, 132.3, 131.6, 130.0, 128.2, 126.7, 124.8, 124.2, 124.1, 75.1, 37.7, 31.2, 25.2.Anal. calcd for $C_{48}H_{42}Br_2N_6O_6$: C, 60.14; H, 4.42; N, 8.77.Found: C, 60.39; H, 4.60; N, 8.48.

Compound 2c: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.47 g (67%) of a yellow powder, mp**:** 294 °C (dec): ^{1}H NMR ($CDCl_3$) δ: 1,83 (s, 4H, amido-**CH$_2$**), 2.48 (s, 6H, Ar—**CH$_3$**), 3.66 (s, 4H, amido-**CH$_2$**), 3.69 (d, $J = 13.61$ Hz, 4H, Ar**CH$_2$**Ar), 4.25 (d, $J = 13.55$ Hz, 4H, Ar**CH$_2$**Ar), 4.60 (s, 4H, O-**CH$_2$**), 6.87 (t, 2H, Ar**H**-calix), 7.04 (d, 4H, Ar**H**-calix), 7.35 (d, 4H, Ar**H**N = N—), 7.58 (s, 2H, Ar**OH**), 7.60 (s, 2H, **NH**), 7.82 (s, 4H, ArH-calix), 7.84(d, 4H, Ar**H**—N═N—). ^{13}C NMR (75 MHz $CDCl_3$): 167.8, 154.8, 151.5, 150.8, 150.5, 146.9, 141.0, 131.7, 129.7, 128.1, 126.6, 123.9, 122.6, 124.2, 75.1, 37.7, 31.2, 25.2, 21.5. Anal. calcd for $C_{50}H_{48}N_6O_6$: C, 72.45; H, 5.84; N, 10.14. Found: C, 71.67; H, 5.70; N, 9.97.

Compound 2d: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.49 g (68%) of an orange powder, mp: >256°C (dec): ^{1}H NMR ($CDCl_3$) δ: 1,7 (s, 4H, amido-**CH$_2$**), 3.41 (d, $J = 13.52$ Hz, 4H, Ar**CH$_2$**-Ar), 3.58 (s, 4H, amido-**CH$_2$**), 3.80 (s, 6H, O—**CH$_3$**), 4.18 (d, $J = 13.47$ Hz, 4H, Ar**CH$_2$**Ar), 4.45 (s, 4H, O-**CH$_2$**), 6.60 (t, 2H, Ar**H**-calix), 6.78 (d, 4H, Ar**H**-calix), 6.95 (d, 4H, Ar**H**—N═N—), 7.15 (s, 4H, Ar**H**-calix), 7.55 (s, 1H, **NH**), 7.65 (s, 1H, **NH**), 7.70 (s, 2H, Ar**OH**), 7.65 (d, 4H, Ar**H**—N═N—). ^{13}C NMR (75 MHz $CDCl_3$): 168.1, 154,7 152.2, 150.4, 132.1, 129.6, 129.2, 128.2, 127.7, 126,5, 124.3, 120.6, 114.2, 75.0, 55.6, 37.7, 31.2, 25.1. Anal. calcd for $C_{50}H_{48}N_6O_8$: C, 69.75; H, 5.62; N, 9.76. Found: C, 69.92; H, 5.78; N, 9.83.

Compound 3a: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.51 g (70%) of an orange powder, mp**:** 240°C (dec): ^{1}H NMR ($CDCl_3$) δ: 3.42 (dd, $J = 13.19$ Hz, 4H, Ar**CH$_2$**Ar), 3,62 (s, 4H, Ar**CH$_2$**Ar), 4.20 (d, 2H, amido-**CH$_2$**), 4.30 (d, 2H, Amido-**CH$_2$**), 4.48 (s, 2H, O—**CH$_2$**), 4.63 (s, 2H, O—**CH$_2$**), 6.68 (t, 2H, Ar**H**-calix), 6.80 (t, 2H, Ar**H**-pyridyl), 6.90 (d, 2H, Ar**H**-pyridyl), 7.10 (d, 4H, Ar**H**-calix), 7.50 (d, 2H, Ar**H**-pyridyl), 7.65 (d, 2H, Ar**H**-pyridyl), 7.80 (d, 4H, Ar**H**—N═N—), 8.00 (s, 4H, Ar**H**-calix), 8.38 (d, 4H, Ar**H**—N═N—), 8.52 (s, 2H, Ar**OH**), 9.11 (s, 1H, **NH**), 9.20 (s, 1H, **NH**). ^{13}C NMR (75 MHz $CDCl_3$): 169.0, 158.9, 152.7, 149.0, 146.0, 136.5, 132.9, 132.0, 130.0, 129.5, 128.8, 127.5, 126.3, 124.7, 123.0, 121.7, 120.6, 119.6, 71.8, 44.8, 31.5. Anal. calcd for $C_{56}H_{46}N_{10}O_{10}$: C, 66.00; H, 4.55; N, 13.75. Found: C, 66.29; H, 4.64; N, 13.89.

Compound 3b: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.52 g (68%) of a brown powder, mp**:** 150°C (dec): ^{1}H NMR ($CDCl_3$) δ: 3.62 (d, $J = 13$ Hz, 4H, Ar**CH$_2$**Ar), 4.15 (d, $J = 13$ Hz, 4H, Ar**CH$_2$**Ar), 4.55 (s, 4H, NH—**CH$_2$**) 4.70 (s, 4H, O-**CH$_2$**) 6.76 (t, 2H, Ar**H**-calix), 6.95 (d, 4H, Ar**H**-calix), 6.80 (t, 2H, Ar**H**-pyridyl), 7.32 (d, 2H, Ar**H**-pyridyl), 7.58 (d, 2H, Ar**H**-pyridyl), 7.65 (d, 4H, Ar**H**—N═N—), 7.75 (d, 4H, Ar**H**—N═N—), 7.70 (s, 4H, Ar**H**-calix), 8.21(d, 2H, Ar**H**-pyridyl), 8.22 (s, 2H, Ar**OH**), 8.85 (s, 1H, **NH**), 8.95 (s, 1H, **NH**). ^{13}C NMR (75 MHz $CDCl_3$): 167.9, 156.5, 155.6, 151.1, 149.3, 146.0, 136.7, 132.6, 132.3, 131.9, 130.0, 129.7, 128.9, 127.8, 127.1, 126.5, 124.0, 122.4, 74.7, 45.4, 31.6. Anal. calcd for $C_{56}H_{46}Br_2N_8O_6$: C, 61.89; H, 4.27; N, 10.31. Found: C, 62.50; H, 4.05; N, 10.48.

Compound 3c: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.50 g (73%) of a brown powder, mp**:** 215°C (dec). ^{1}H NMR ($CDCl_3$) δ: 2.43 (s, 6H Ar—**CH$_3$**), 3.58 (d, $J = 13.51$ Hz, 4H, Ar**CH$_2$**Ar), 4.10 (d, $J = 13.50$ Hz, 4H, Ar**CH$_2$**Ar), 4.57 (s, 4H, O-**CH$_2$**), 4.73 (s, 4H, NH—**CH$_2$**), 6.83 (t, 2H, Ar**H**-calix), 7,01 (d, 4H, Ar**H**-calix), 7.07 (m, 2H, Ar**H**-pyridyl), 7.30 (d, 4H, Ar**H**—N═N), 7.35 (d, 2H, Ar**H**-pyridyl), 7.60 (t, 2H, Ar**H**-pyridyl), 7.73 (s, 4H, Ar**H**-calix), 7.78 (d, 4H, Ar**H**—N═N), 8.05 (s, 2H, Ar**OH**), 8.28 (d, 2H, Ar**H**-pyridyl) 8.92 (s, 2H, **NH**). ^{13}C NMR (75 MHz $CDCl_3$): 167.9, 156.5, 155.1, 151.1, 150.9, 149.4, 146.2, 140.9, 136.7, 131.9, 130.1, 129.9, 129.8, 127.7, 126.6, 123.8,

122.5, 74.7, 45.3, 31.6, 29.7, 21.5. Anal. calcd for $C_{58}H_{52}N_8O_6$: C, 72.79; H, 5.48; N, 11.71. Found: C, 72.97; H, 5.59; N, 11.98.

Compound 3d: The solid was eluted with hexane/ethyl acetate (3:1, v/v) and gave 0.46 g (65%) of a brown powder, mp**:** 155°C (dec): ^{1}H NMR ($CDCl_3$) δ: 3.60 (d, $J = 13.54$ Hz, 4H, Ar**CH$_2$**Ar), 3.93 (s, 6H O-**CH$_3$**), 4.12 (d, $J = 13.50$ Hz, 4H, Ar**CH$_2$**Ar), 4.58 (s, 4H, NH—**CH$_2$**), 4.77 (s, 4H, O-**CH$_2$**), 6.87 (t, 2H, Ar**H**-calix), 7.03 (d, 4H, Ar**H**-calix), 7.04 (d, 4H, Ar**H**—N═N), 7.11 (t, 2H, Ar**H**-pyridyl), 7.38 (d, 2H, Ar**H**-pyridyl), 7.63 (m, 2H, Ar**H**-pyridyl), 7.73 (s, 4H, Ar**H**-calix), 7.91 (d, 4H, Ar**H**—N═N), 8.05 (s, 2H, Ar**OH**), 8.32 (s, 2H, Ar**H**-pyridyl), 9.00 (s, 2H, **NH**). ^{13}C NMR (75 MHz $CDCl_3$): 168.2, 162.6, 156.9, 155.2, 151.8, 149.7, 147.5, 146.8, 136.8, 133.3, 132.6, 130.1, 128.2, 127.6, 124.1, 123.5, 122.2, 114.1, 74.9, 56.1, 45.9, 31.2.Anal. calcd for $C_{58}H_{52}N_8O_8$ Found: C, 70.43; H, 5.30; N, 11.33.Found: C, 70.25; H, 5.24; N, 11.16.

General procedure for the synthesis of telomers

Compound **1a** 0.25 g (0.28 mmol) was dissolved in 20 mL dioxane. Pentaethyleneglycol ditosylate (0.45 mmol) was added to resulting solution. Ninety-five percent NaH (0.34 g, 15 mmol) was added slowly while the solution was stirring at room temparature for 30 min. The reaction mixture was followed with TLC and stirring has continued for 4 days. After evaporating, the solvent dried residue was washed with petroleum ether and ethanol before acidifying with 0.1 M HCl. Finally, the precipitated residue was washed with water and dried in an oven. The solid residue was purified by column chromatography with ethyl acetate-methanol as an eluent.

Telomer T1a: The solid was eluted with ethyl acetate/methanol (9:1, v/v) and gave 0.1 g (15%) of a red powder, mp: 120–130°C. MS (MALDI-TOF): *m/z* 2833 $[M + H]^+$.

Telomer T1b: The solid was eluted with ethyl acetate/methanol (9:1, v/v) and gave 0.08 g (10%) of an orange powder, mp: 140°C. MS (MALDI-TOF): *m/z* 3143 $[M + H]^+$.

Telomer T1c: The solid was eluted with ethyl acetate/methanol (9:1, v/v) and gave 0.05 g (10%) of an orange powder, mp: 205°C. MS (MALDI-TOF): *m/z* 2839 $[M + H]^+$.

Telomer T1d: The solid was eluted with ethyl acetate/methanol (9:1, v/v) and gave 0.15 g (10%) of an orange powder, mp: 190°C. MS (MALDI-TOF): *m/z* 2903 $[M + H]^+$.

Solvent extraction

A solution (10 mL) of ligand (1×10^{-3} M) in chloroform and an aqueous solution (10 mL) of 1×10^{-2} M metal nitrate in 2×10^{-5} M picric acid were vigorously shaken at 25°C for an hour. After the completion of phase separation, an aliquot of the was withdrawn to record its UV spectrum. A similar extraction was performed in the absence of picrate ion in the aqueous solution. Absorbance values have been measured three times at 354 nm (λ_{max}) spectrophotometrically. The extractability of the metal cations is expressed by means of the following equation:

$$\text{extractability}(\%) = \frac{A0 - A}{A0} \times 100,$$

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

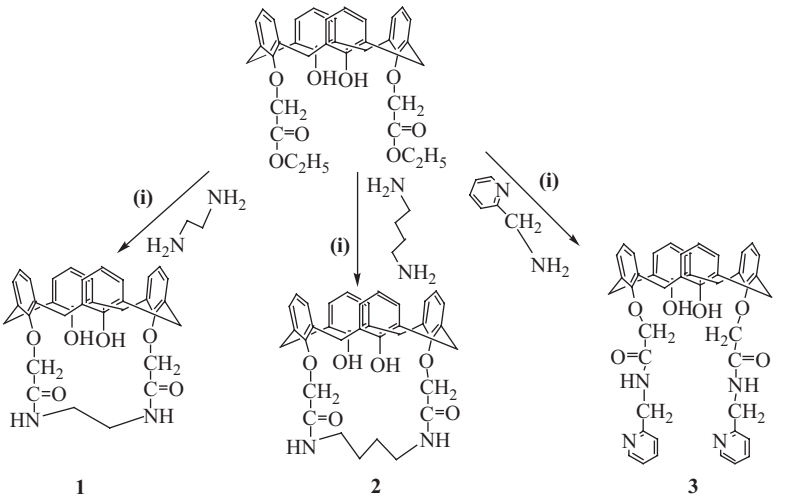
Results and discussion

Synthesis and characterisation

Previously, our research group investigated azo coupling reactions of diketonecalix[4]arenes and triestercalix[4]arenes with substituted benzene diazonium chlorides (*18*). In this study, 12 amidoazocalix[4]arenes have been synthesised from amido derivatives according to the method described by Morita et al. (*19*). Subsequently, their four telomers were prepared by the synthetic routes depicted in Scheme 1. All synthesised compounds were characterised by UV–vis, FT-IR, ^{1}H and ^{13}C NMR spectroscopic methods as well as elemental analysis techniques. Some of the compounds were characterised by 2D NMR technique (COSY, HMQC, HMBC, NOESY) additionally.

Amidocalix[4]arenes (**1**–**3**) were synthesised by the reaction of calix[4]arene diethyl ester and primer aliphatic amines in toluene/methanol (1:1) under reflux conditions (Scheme 2). They were characterised by FT-IR, ^{1}H and ^{13}C NMR spectroscopic techniques. Characteristic amido C = O stretching bands were observed around 1690 cm^{-1} frequency in FT-IR spectra. The doublet pairs representing $ArCH_2Ar$ protons appeared around 3.5 and 4.2 ppm of H NMR spectra separately. These peaks confirm the symmetrical *cone* conformation amidocalix[4]arenes in solution. Amido −NH protons of compounds **1**, **2** and **3** were appeared as separate singlet peaks at 8.50, 7.75 and 9.10 ppm on the H NMR spectra, respectively.

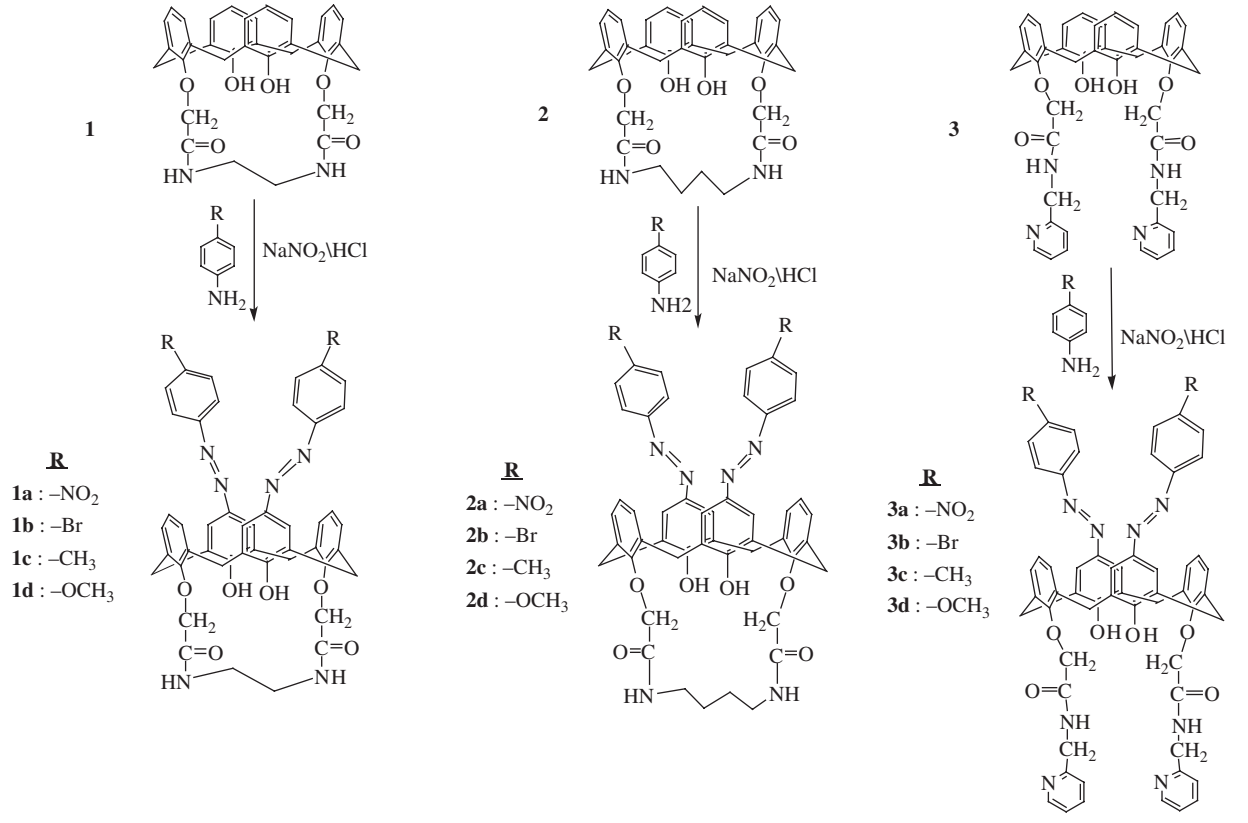
The amidoazocalix[4]arene derivatives were gathered by a coupling reaction of amidocalix[4] arenes (**1**–**3**) and diazotized carbocyclic amines in $NaNO_2$/HCl (Scheme 3). Each coupling has been selectively accomplished at the *p*-position of each calix[4]arene ring to give compounds in moderate to excellent yields (60–80%). These results are in accordance with the greater nucleophilicity of the carbocyclic amine ring The schemed structures of amidoazocalix[4]arenes were unambiguously confirmed by their analytical and spectral data.



Scheme 2. Synthesis of amidocalix(4(arenes. (i) Toluene/MeOH (1:1).

The infrared spectrum of each synthesised amidoazocalix[4]arene compound presented a strong band at 1495–1480 cm^{-1} referring to —N═N—. The other υ_{max} value around 1268–1250 cm^{-1} can be assigned to for υC–O. The ^{1}H NMR spectrum of each compound measured in DMSO-d_6 at 25°C showed a pair of doublets between 7.9 and 6.9 ppm for substituted aromatic protons (ArH-X), triplet, doublet and singlet peaks between 7.9 and 7.0 ppm for calix[4]arene aromatic protons (Ar–H), a broad peak between 8.1 and 7.5 ppm for hydroxyl protons (—OH).

COSY, HMQC, HMBC and NOESY correlations of some compounds were examined by 2D NMR technique. Analyses of these correlations also provided important results about the configuration of compounds.



Scheme 3. Synthesis of amidoazocalix(4(arenes.

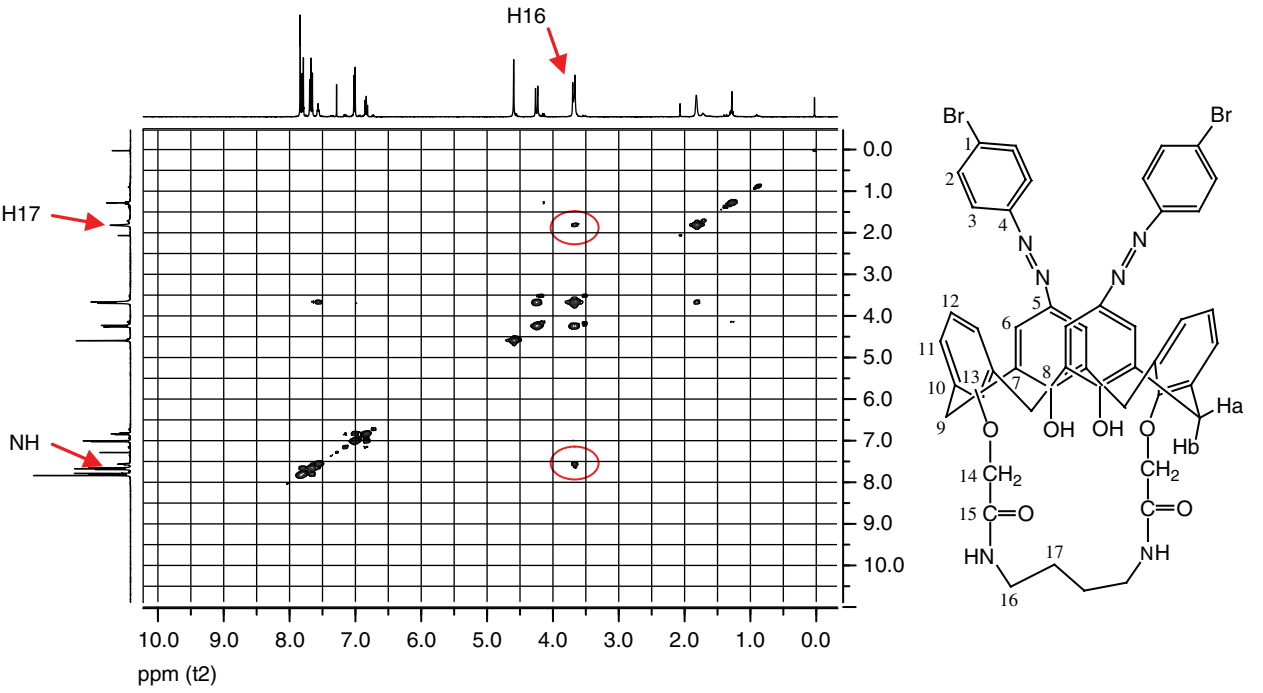


Figure 1. (Colour online) COSY spectrum of amidoazocalix[4]arene **2b**.

The COSY spectrum of **2b** revealed two noteworthy cross peaks. One of them can be referred to the interaction between H16 and H17 protons. While the other one can be assigned to the interaction between NH and H16 protons (Figure 1).

It is not possible to elucidate the connection between aromatic rings according to COSY experiment results. Therefore, construction of the carbon framework was made possible by the interpretation of a series of selective INEPT experiments.

The most important finding about the conformation of amidoazocalix[4]arene **1c** was obtained by NOESY spectra. 2D NOESY spectrum of *p*-methyphenylazo substituted amidocalix[4]arene (**1c**) is presented in Figure 2. Expanded NOESY spectrum showed that Hb and OH protons are in the same space because of their interaction. In the same way, Ha and H12 protons are in the same space (Figure 2). As a result, we can easily say that the compound is in *cone* conformation in solution.

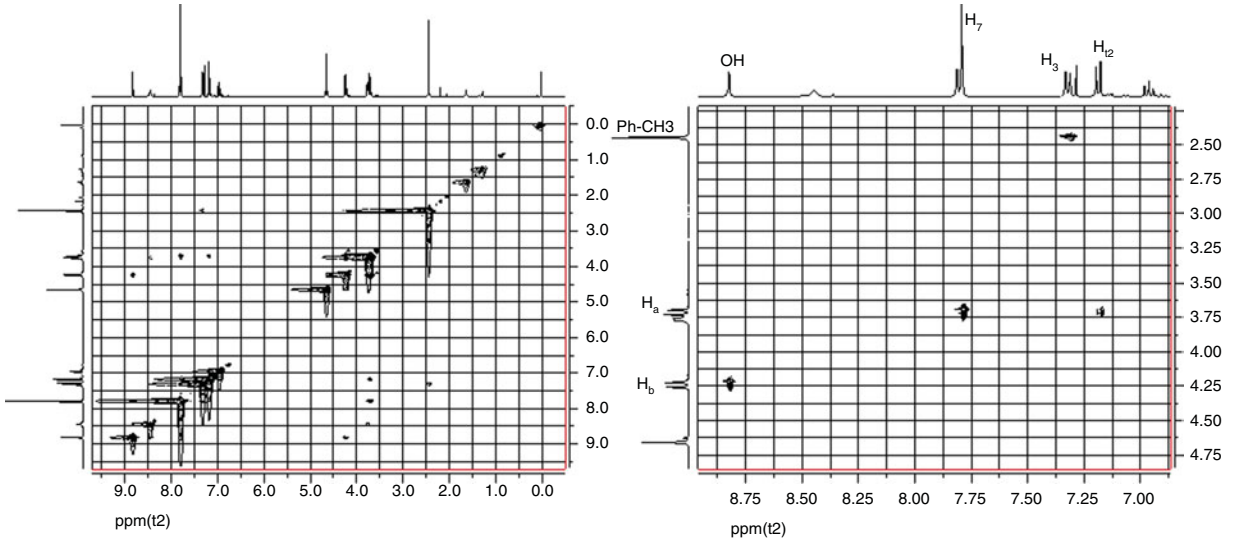
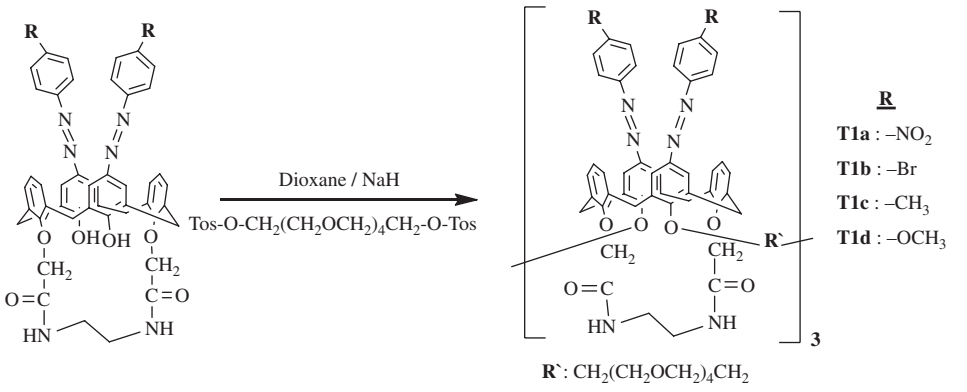


Figure 2. (Colour online) NOESY and expanded NOESY spectra for amidoazocalix[4]arene **1c**.



Scheme 4. Synthesis of telomers.

After the synthesis of amidoazocalix[4]arenes, telomer derivatives of **1a**, **1b**, **1c** and **1d** were synthesized (Scheme 4). These telomers (**T1a**–**T1d**) were obtained by reacting **1a**, **1b**, **1c** and **1d** with pentaethyleneglycol ditosylate in dioxane and 95% NaH at room temperature. Pentaethyleneglycol ditosylate was used for this polymerisation reaction because it can easily link bulky azocalix[4]arene molecules with each other.

Polymerisation reactions were monitored by TLC. The resulting product mixtures were separated by column chromatography. The molecular weight data for the resulting polymers were measured by mass spectrum analysis. Analysis of the mass spectra showed that each telomer molecule consists of three calixarene units.

Mass spectrum of telomer **T1b** is seen in Figure 3. Its calculated molecular weight is 3188 g/mol and its molecular ion peak is observed as 3143 g/mol. Hence, this result refers to a telomer molecule with three calixarene units.

Absorption properties

The absorption spectra of amidoazocalix[4]arenes (**1a**–**d**, **2a**–**d**, **3a**–**d**) were recorded in various solvents at concentrations between 10^{-6} and 10^{-8} M. The solvents have been chosen according to their polarities. The visible absorption spectra of these dyes were found to exhibit strong solvent dependency in case of the polarity of the solvents.

The azocalix[4]arene derivatives (**1a**–**d**, **2a**–**d**, **3a**–**d**) showed characteristic absorption patterns. The appearance of the amidoazocalix[4]arene absorption band at a relatively high wavelength may be attributed to the presence of an electron-withdrawing group such as nitro and bromo groups. The absorption spectrum of some amidoazocalix[4]arene derivatives exhibited a single absorption band between 300 and 400 nm and single shoulder between 400 and 550 nm corresponding to $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively. This result is in

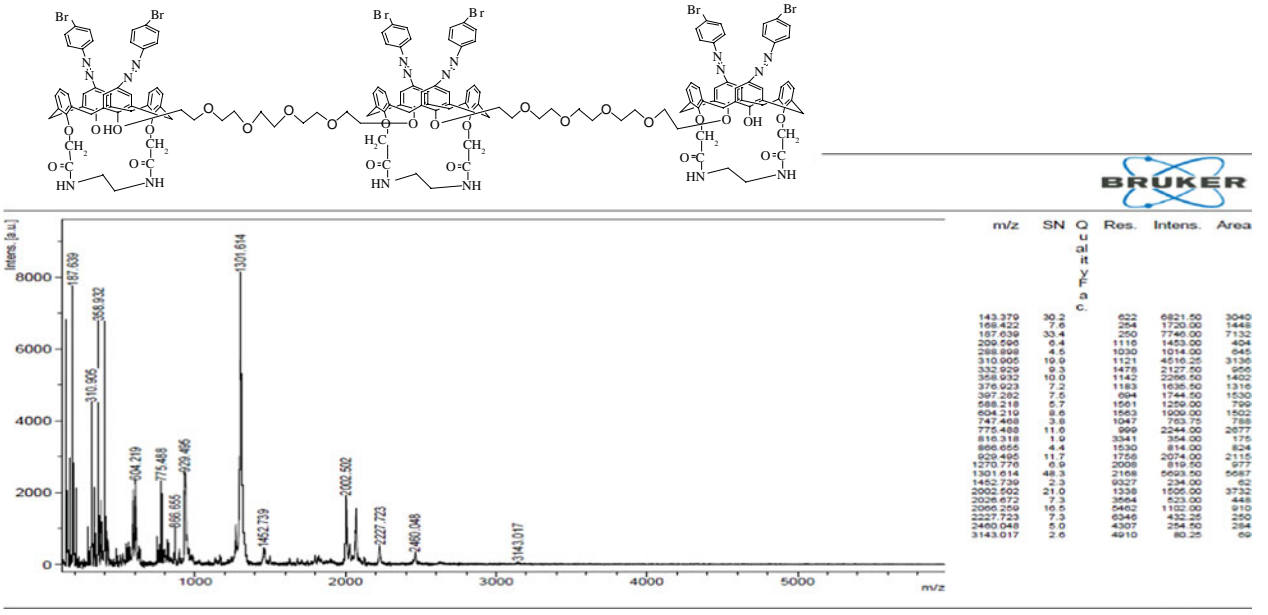


Figure 3. (Colour online) MALDI TOF spectrum for telomer **T1b**.

Table 1. Absorption maxima (nm) of some compounds in different solutions.

Compound	DMSO	DMF	MeCN	MeOH	MeOH + KOH	MeOH + HCl	AcOH	$CHCl_3$
1a	395	393, 603	382	381	304, 547	382	378	381
1c	361	358	354	354	470	355	353	355
2a	400	398, 619	382	382	304, 550	387	379	382
3d	369	367	362	381	459	363, 508	382	364

accordance with previous diazo calix[4]arene spectra measured before.

Solvent effect

Absorption spectra of amidoazocalix[4]arenes were recorded in six different solvents (DMSO, DMF, MeCN, $CHCl_3$, MeOH and AcOH). Their maximum absorption values were noted in Table 1. Compounds **1a, 1c** and **2a** exhibited similar absorption spectra in acetonitrile, chloroform, methanol and acetic acid solvents. A new band was observed in DMF on absorption spectra of these compounds. Bathochromic shifts on the absorption spectra of these compounds were also observed in DMSO (Figure 4(a)–(c)).

Although the maximum absorption value values belonging to absorption spectra of compound **3d** in acetonitrile and chloroform are found to be close, λ_{max} on the spectrum of same compound in MeOH is observed in longer wavelength values. Spectra of compound **3d** in DMF and DMSO lacks this shift observed in MeOH.

pH effect

The spectra of compounds **1a, 1c**, **2a** and **3d** in acidic and basic solutions were recorded by the addition of KOH and HCl in methanol separately. As expected, there were bathochromic shifts of maximum absorption values when KOH was added to the amidoazocalixarenes **1a, 1c**, **2a** and

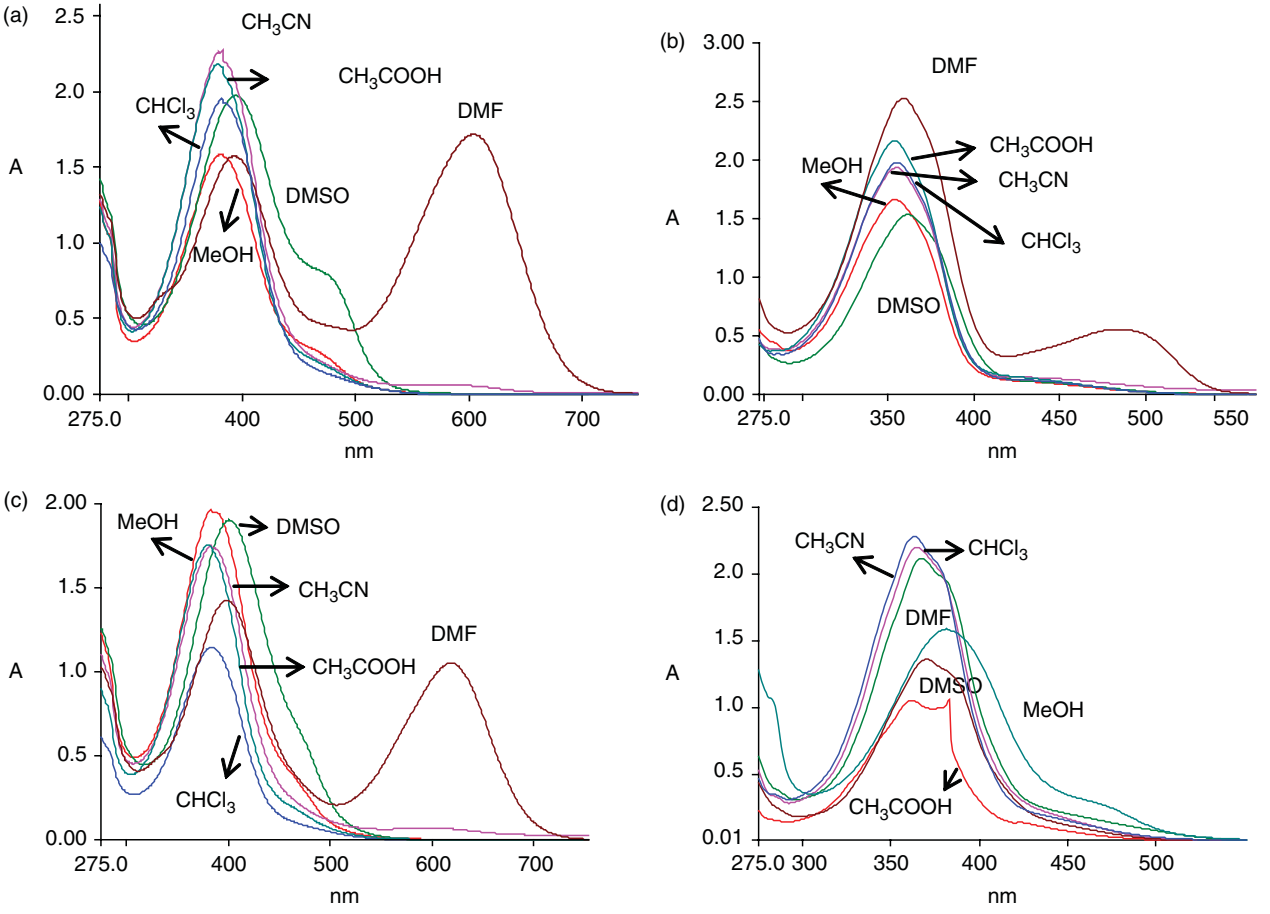


Figure 4. (Colour online) UV spectra of amidoazocalix[4]arenes in different solvents: (a) **1a,** (b) **1c,** (c) **2a** (d) and **3d**.

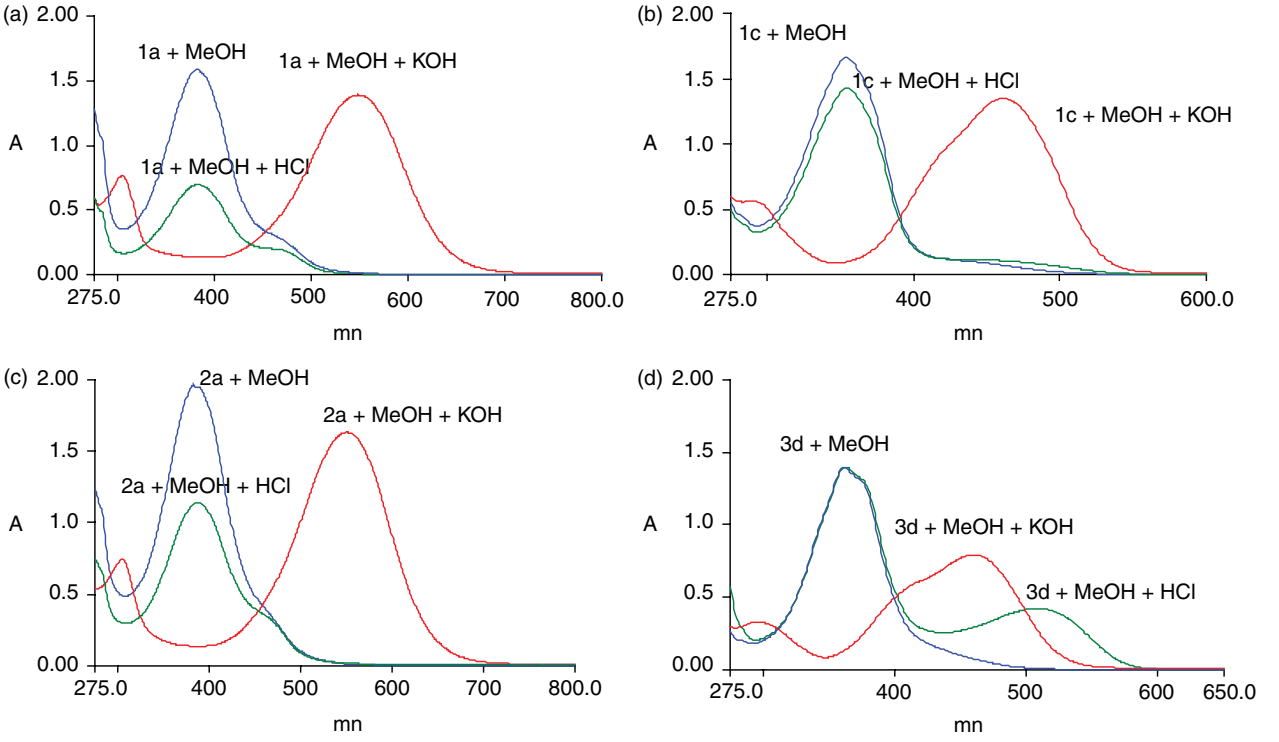
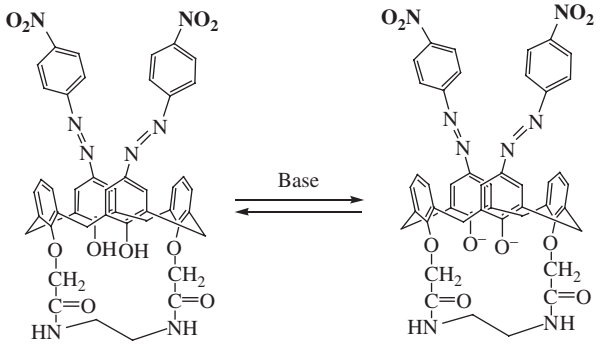


Figure 5. (Colour online) **UV** spectra of amidoazocalix[4]arenes in acidic and basic solvents: (a) **1a,** (b) **1c,** (c) **2a** (d) and **3d**.

3d (Figure 5(a)–(d)). This is due to the easiness in deprotonation of the *lower rim* hydroxyl groups by the basic solvent. This deprotonation phenomenon is showed in Scheme 5. No shift on the absorption spectra of the compounds **1a, 1c** and **2a** was observed when HCl was added to methanol. However, compound **3d** exhibited two absorption bands at 363 and 508 nm when HCl was added in methanol controversially. This extra absorption band appearing at a longer wavelength can be explained by the protonation of the nitrogen atom on the pyridyl ring.

The results of pH effect experiments were observed as colour changes on the solutions of compounds in different pH by the 'naked eye'. The yellow colour of compound **2a** turned into purple at pH 10 as expected. The colour changes have been observed on compound **3d** solutions at pH 1 and pH 14 (Figures 6 and 7).



Scheme 5. Ionisation equilibrium of the compound **1a** in basic solution.

Extraction properties

Transportation experiments with metal picrate salts were carried out with a H_2O—$CHCl_3$ liquid–liquid phase transfer system using the amidoazocalix[4]arenes as cation carriers. The results of the cation transportation experiments are in harmony with those of the two-phase extraction measurements.

The ionophoric properties of azo compounds (**1a–d**, **2a–d**, **3a–d**) and telomer derivatives (**T1a–T1d)** towards the alkaline (Na^+, K^+), alkaline-earth (Sr^{2+}) and the transition metal cations (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Cr^{3+} and Al^{3+}) were initially investigated by the picrate extraction method (*20*). The results are expressed in units of percentages of cation extracted (*E%*)and presented in Tables 2 and 3 and Figures 8 and 9.

According to the results, Ag^+, Hg^+, Hg^{2+} and Cr^{3+} metal cations were transported with high efficiency by synthesised compounds. Extraction reactions of telomer structures took place with higher efficiency rates with respect to those of monomer structures. Memon and coworkers also studied metal extraction of calixarene monomers and telomers. They observed selectivity for

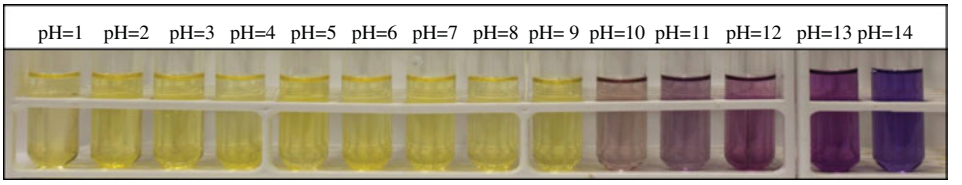


Figure 6. (Colour online) Solutions of compound **2a** in different pH.

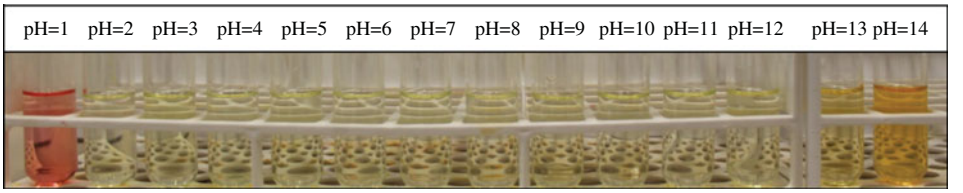


Figure 7. (Colour online) Solutions of compound **3d** in different pH.

Table 2. Extraction of metal picrates with ethylene amidoazocalix[4]arenes and their telomer derivatives[a].

	Picrate salt extracted (%)												
	Na^+	K^+	Sr^{2+}	Ag^+	Hg^+	Hg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cr^{3+}	Al^{3+}
1a	0.0	0.0	08	10.3	25.1	24.2	1.5	2.8	1.5	2.1	3.2	11.0	6.3
1b	0.0	0.0	4.7	41.6	41.4	46.9	12.5	3.2	10.7	6.5	19.0	33.7	24.4
1c	5.5	7.5	19.9	40.1	42.3	47.7	22.5	10.6	24.0	19.5	26.1	33.2	33.0
1d	47.5	44.6	41.4	54.1	56.6	63.2	31.2	29.5	43.5	45.9	49.5	52.1	51.5
T1a	17.5	15.3	14.6	36.2	89.3	85.8	22.5	11.6	21.4	17.5	14.2	47.4	23.4
T1b	25.3	14.2	26.6	61.9	87.9	89.9	27.3	24.1	33.5	27.9	34.6	65.2	35.2
T1c	28.2	21.6	44.8	86.1	94.7	96.2	38.1	34.7	47.2	37.5	38.7	76.6	51.5
T1d	55.6	51.6	53.2	95.7	95.3	92.5	43.6	33.0	53.8	42.5	57.02	84.2	57.3

Note: [a]$H_2O/CHCl_3$ = 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. $\alpha \leq \pm 2\%$.

Hg^{2+}, Cd^{2+} and Pb^{2+} in different molecules. Results of this study are in consistent with those of interested study (*21*).

Cations are believed to hold an encapsulation into the cavity defined by the conjugated chromophore azo (—N═N—) groups. *p*- Interactions may play important role in complexation with amidoazocalix[*n*]arenes. Results of this study have shown that interested compounds bear hard nitrogen donor atoms. Although they display a weak affinity towards soft metal cations such as Ag^+, they exhibit respectively higher affinity towards Hg^{2+} cation.

Compounds **2a**–**d** and **3a**–**d** were synthesised with 1,4-diaminobutane and 2-amino-methylpyridine, respectively, to determine the effect of cyclic and free amide

Table 3. Extraction of metal picrates with amidoazocalix[4]arenes[a].

	Picrate salt extracted (%)												
	Na^+	$K^{b>+}$	Sr^{2+}	Ag^+	Hg^+	Hg^{2+}	Co^{2+}	$Ni^{b>2+}$	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cr^{3+}	Al^{3+}
2a	0.0	0.0	0.0	4.6	19.2	24.8	0.9	1.2	2.0	0.6	6.1	10.6	8.8
2b	5.5	2.1	1.9	3.4	18.6	24.5	1.5	3.6	4.0	2.9	6.9	12.2	11.9
2c	42.1	4.9	6.8	4.7	19.4	29.5	5.1	4.3	5.9	5.7	9.0	13.7	11.5
2d	1.6	41.5	30.4	54.3	55.3	76.4	28.4	33.2	44.7	37.2	37.8	63.6	51.0
3a	0.5	0.9	1.5	19.6	37.7	34.6	1.5	2.1	12.4	5.6	15.4	13.4	20.1
3b	6.1	1.8	1.6	92.3	63.8	88.6	1.9	2.5	30.8	3.4	13.7	39.0	21.8
3c	4.2	6.9	6.7	93.9	66.0	93.2	6.4	6.6	33.1	8.1	11.2	30.4	16.0
3d	3.8	3.0	3.2	91.0	60.0	93.0	1.3	1.4	10.3	3.9	15.2	30.8	14.4

Note: [a]$H_2O/CHCl_3$ = 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. $\alpha \leq \pm 2\%$.

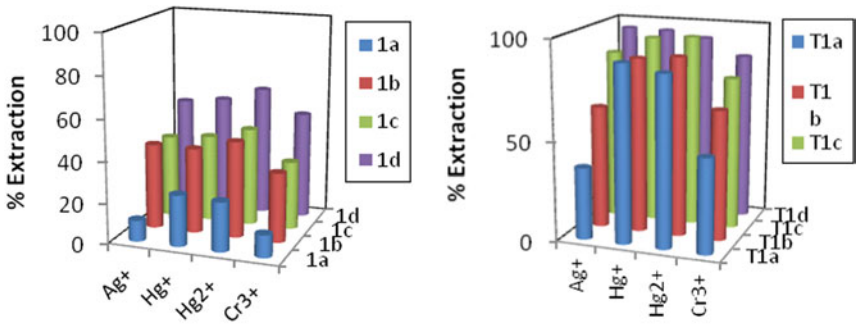


Figure 8. (Colour online) Extraction percentages of monomers and telomers.

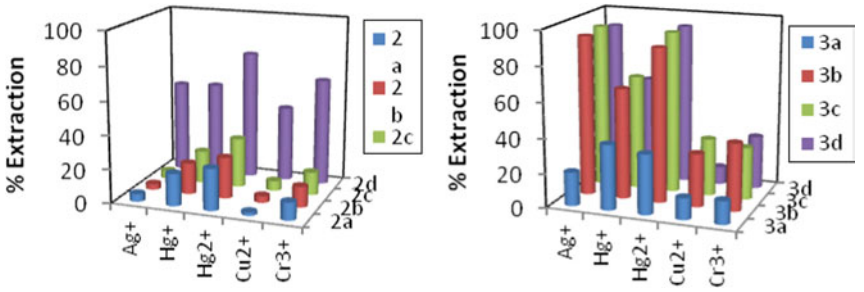


Figure 9. (Colour online) Extraction percentages of butyl and pyridyl amidoazocalix[4]arenes.

groups on the extraction phenomenon. Their extraction efficiencies were noted in Table 3.

Extraction efficiencies of butylene amido compounds (**2a**–**2d**) and pyridyl amido compounds (**3a**–**3d**) were also graphed in Figure 9. The extraction efficiencies of telomers **T1a**–**T1d** were found to be more than twice of those of monomers **1a**–**d,** respectively. The extraction efficiencies of cyclic amido derivatives (**2a**–**2d**) were observed to be less than those of amido pyridyl derivatives (**3a**–**3d**). This result can be explained by two features. It may be resulted from the space of calix[4]arene moiety. It also may be resulted from the electron density of the pyridyl group and its flexibility. The second feature ends up with a significant contribution for extraction.

Conclusion

The 12 novel amidoazocalix[4]arene (**1a**–**d**, **2a**–**d**, **3a**–**d**) compounds and some of their telomer derivatives were synthesised and characterised. Absorption and extraction properties of synthesised compounds were investigated.

Amidoazocalix[4]arene compounds **1a**, **1c**, **2a** and **3d** exhibited great binding abilities to various bases (MeOH + KOH) in an equivalent stoichiometry with colorimetric changes. The binding feature of synthesised compounds can be assigned to hydrogen bonding and deprotonation of the interested compounds. The binding phenomenon did not take place until high base concentrations are reached. The colour change of compound **2a** at pH 10 and that of compound **3d** at pH 1 and 14 are clearly visible to the 'naked eye'. This allowed us to use the interested compounds as indicators.

Extraction studies of amidoazocalix[4]arene compounds **1a**, **2a** and **3a** exhibited poor binding abilities towards metal cations. This feature may result from the strong electron withdrawing properties of the substituted nitro groups. Pyridylamido group containing amidoazocalix[4]arene compounds **3b**, **3c** and **3d** exhibited high extraction efficiencies towards heavy metal ions (**Ag^+**, **Hg^+**, **Hg^{2+}**). This result can be explained with high electron density of substituted pyridyl groups and their elastic structure in solution. Extraction results of this study indicate that the mechanism of complexation depends on the interaction between metal cations and both amido and azo groups of the calix[4]arene units.

The selective tendencies of synthesised compounds **3b**, **3c** and **3d** through complexation with heavy metal ions (**Ag^+**, **Hg^+**, **Hg^{2+}**) may be of considerable importance for the future design of novel calix[*n*]arene based receptors, carriers or supramolecular structures. The results of the ongoing research studies orienting chemosensation and dyeing properties of these new amidoazocalix[4]arenes will be presented in the future.

Supporting Information ^{1}H and ^{13}C NMR spectra for the compounds prepared.

Acknowledgements

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Note

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