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Farhana Oueslati[a]; Isabelle Dumazet-Bonnamour[a]; Roger Lamartine[a]
[a] Laboratoire d'Application de la Chimie à l'Environnement, UMR 5634, Villeurbanne Cedex, France

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New Azothiacalix[4]arenes Containing Biheterocyclic Subunits: Extraction and Complexation Properties

FARHANA OUESLATI, ISABELLE DUMAZET-BONNAMOUR* and ROGER LAMARTINE

Laboratoire d'Application de la Chimie à l'Environnement, UMR 5634, Batiment Jules Raulin, 3ème étage, 69622 Villeurbanne Cedex, France

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New thiacalix[4]arenes 2a, 3a, 4 and 5 functionalized with biheterocyclic and azophenyl groups at the lower rim and the upper rim of the macrocycle, respectively, were synthesized and their extraction properties towards Cu^{2+}, Ag^{+}, Ni^{2+} and Pb^{2+} studied. The complexation properties of the bithiazolyl receptors 2a, 4 and the bipyridyl receptors 3a, 5 were investigated by fluorescence and UV–visible titrations, respectively. The stoichiometries of the complexes were determined. A stoichiometry of 1:1 was found for the Cu-2a, Ag-3a complexes and 2:1 for the Cu_2-4, Ag_2-5 complexes as a function of the number of grafted bithiazolyl groups. The association constants for the 1:1 complexes were calculated using the Benesi–Hildebrand plot and by linear regression analysis.

Keywords: Biheterocyclic subunits; Thiacalixarenes; Conformation; Extraction; Complexation

INTRODUCTION

During the past two decades, calixarenes have attracted much attention as examples of simple or novel receptors in supramolecular chemistry [1–4]. There is increasing interest in this class of compounds because of their easy modification, the large variety of potential derivatives and their capacity to complex various metal ions [5]. The synthesis of a new type of calix[4]arene bearing four sulfur atoms instead of methylene bridges has been described recently [6–8]. These derivatives, called thiacalixarenes, show high complexation affinity towards transition metal ions [9]. The size of the cavity is enlarged and the chemical reactivity and chelating properties are modified upon the replacement of carbon by sulfur bridges [10–12]. As with the calix[4]arene, thiacalix[4]arenes can be easily functionalized at the upper or lower rim of the macrocycle, thus permitting a type of molecular engineering [13–15]. This stimulated us to design a new chromogenic thiacalix[4]arene ionophore that would be able to complex more than one transition metal cation. In recent reports [16,17], we have described the synthesis of a new class of chromoionophore sensors incorporating heterocyclic chelating agents and chromophore groups. With the aim of producing cyclic polychelating structures that can exhibit colour changes due to ionic or molecular interactions, we decided to graft phenylazo groups as a signalling device [18] at the upper rim of thiacalix[4]arene and heterocyclic chelating agents such as 2,2′-bipyridyl and 2,2′-bithiazolyl groups at the lower rim. The incorporation of biheterocyclic subunits has been chosen here because of their potential to complex various metal ions [19–24]. Thus, the presence of heteroatoms as bridging atoms in calixarene offers additional opportunities to modify the selectivity for binding ions [9]. This led us to the synthesis of four new thiacalix[4]arenes derivatives **2a**, **3a**, **4** and **5**, described here (Fig. 1). The extraction properties of thiacalixarene derivatives **2a** and **3a** towards Cu^{2+}, Ag^{+}, Ni^{2+} and Pb^{2+} were investigated by liquid–liquid extractions and their extraction efficiency compared with their analogous calix[4]arene derivatives **2b** and **3b** reported previously [17]. In addition, the complexation efficiencies of the receptors incorporating bithiazolyl units **2a** and **4** towards Cu^{+} were investigated by fluorescence titration to determine the stoichiometries of the complex species.

*Corresponding author. E-mail: i.bonnamour@cdlyon.univ-lyon1.fr

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The complexation ability towards Ag^+ of the compounds bearing bipyridyl units **3a** and **5** were also studied by UV–visible spectrophotometric titration.

RESULTS AND DISCUSSION

Synthesis and Characterization

The diazo-coupling reaction of thiacalix[4]arene with a substituted diazonium BF_4^- salt produced the *p*-tetrakis(phenylazo)thiacalix[4]arene (**1**) as described previously [25]. As there is a singlet for the aromatic protons in the ^{1}H NMR spectra at $\delta = 8.54$ ppm, and by analogy with other lower rim unsubstituted thiacalixarenes, it was presumed that **1** adopts a cone conformation in solution. Initially, we found that this system behaved very differently from azocalix[4]arene. Indeed, all our attempts to prepare disubstituted derivatives **2a** and **3a** (Fig. 1) by O-substitution using similar procedures to those reported previously [16,17] (with BaO and $Ba(OH)_2{\cdot}8H_2O$ in DMF) for the azocalix[4]arene failed. The preparation of disubstituted derivatives **2a** by direct substitution of **1** with 4-bromomethyl-4-methyl-2,2′-bithiazole [26] was therefore evaluated using various molar ratios of **1** and the base Na_2CO_3. Using an excess of 4-bromomethyl-4-methyl-2,2′-bithiazole and 5 equivalents of Na_2CO_3 in anhydrous acetone, **1** was mainly di-O-substituted to give **2a** as the major product (26% yield).

Similarly, 6-bromomethyl-6′-methyl-2,2′-bipyridine [27] was grafted onto the lower rim of **1** using 5 equivalents of Na_2CO_3 to afford compound **3a** (18% yield). The structures of 1,3-disubstituted thiacalixarene **2a** and **3a** were analysed by ^{1}H NMR spectroscopy. The spectra of **2a** and **3a** show a singlet for the O–CH_2 moieties at $\delta = 5.46$ ppm for **2a** and at 5.21 ppm for **3a**, and two singlets each integrating for four protons due to the aromatic protons of the phenolic units. The signals corresponding to the aromatic protons of the phenylazo groups and to the biheterocyclic subunits are consistent with the observed signals in calixarene analogues [16,17,28] but their conformations cannot be unambiguously established using NMR techniques [29,30]. Depending on the reaction conditions, it was found that the alkali metal cation can play an important role not only in the regioselectivity but also in the degree of O-substitution. It is also known that a contribution of Cs^+ to the template effect, that is larger than that of Na^+, can be expected [31]. We therefore used Cs_2CO_3 for the tetra-O-substitution of **1**, as for the azocalixarene derivatives [16]. The reaction of **1** with an excess of Cs_2CO_3 in dry acetone followed by the addition of 6 equivalents of 4-bromomethyl-4-methyl-2,2′-bithiazole afforded **4** in 30% yield. Compound **5** was prepared in a similar manner to that described above, by treating **1** with Cs_2CO_3 in anhydrous acetone followed by the addition of 6-bromomethyl-6′-methyl-2,2′-bipyridine. The ^{1}H NMR spectra of these new thiacalixarenes derivatives show one singlet for their O-CH_2 moieties at $\delta = 5.13$ ppm for **4** and at 5.28 ppm for **5** and only one singlet for the aromatic protons of the thiacalixarene at $\delta = 8.59$ ppm for **4** and at 8.35 ppm for **5**. The NMR spectra of **4** and **5** reflect the symmetries of the compounds, which could correspond to their being in either a cone or an 1,3-alternate conformation. Nevertheless, based on analogy with the other tetrasubstituted calix[4]-arenes and with the fact that Cs^+ generally permits the formation of 1,3-alternate conformations [32], we assume that **4** and **5** are both in 1,3-alternate conformations.

Extraction Properties

To evaluate the ability of these new thiacalixarene derivatives to bind metal ions, liquid–liquid extractions of transition metal ions were carried out. We tested the extraction abilities of thiacalixarenes **2a** and **3a**. In order to determine whether the extraction is only due to the heterocyclic chelating units or if the sulfur bridges play a role in the extractions, the extraction abilities of the corresponding azocalixarenes **2b** [16] and **3b** [17] synthesized previously

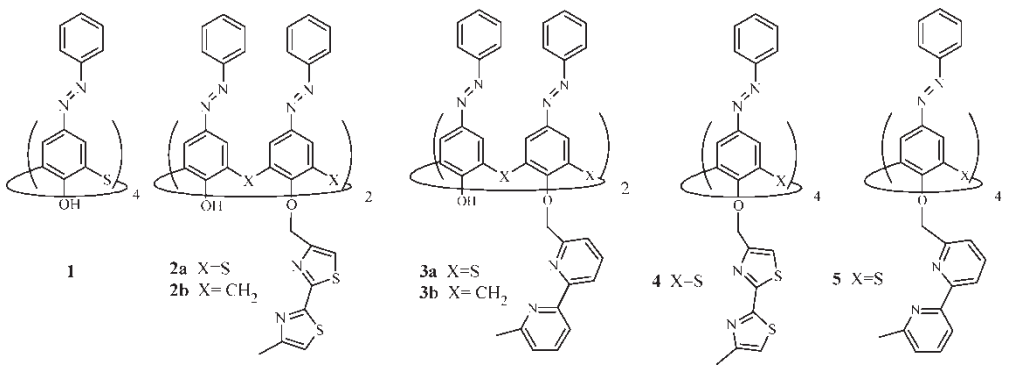

FIGURE 1 Azocalix[4]arenes incorporating 2,2′-bipyridyl or 2,2′-bithiazolyl units.

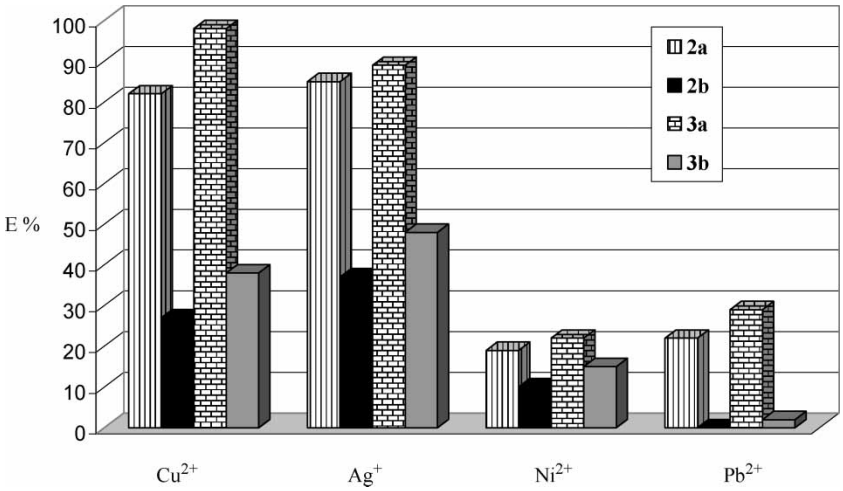

FIGURE 2 Extraction percentages of cations as a function of the nature of the ligands.

were also considered. The extraction percentages (E%) of various transition metal ions at pH 5.3 [9] were calculated (Fig. 2). We found that the thiacalixarene derivatives **2a** and **3a** have higher E% values than the corresponding calixarenes **2b** and **3b**.

Compounds **2a** and **3a** have some affinity towards all of the metal ions tested, whereas calixarene **2b** and **3b** have no affinity for Pb^{2+}. It is clear that the extractability of Pb^{2+} by **2a** and **3a** arises from the sulfur bridges in the thiacalixarene. All the ligands show higher efficiencies towards Ag^{+} and Cu^{2+}, with thiacalixarenes **2a** and **3a** being able to extract more than 80% of Cu^{2+} and Ag^{+}. This result is probably due to the presence of the bis-heterocyclic subunits, which have high affinity for Cu^{2+} and Ag^{+} [19,20]. For all of the ions, the compounds bearing bipyridyl subunits generally show greater E% than those incorporating bithiazolyl subunits.

Fluorescence Titrations

The bithiazolyl subunits [26] grafted onto the lower rim of the thiacalixarene give intrinsic blue fluorescence properties to the new thiacalixarene derivatives. Therefore, a preliminary study of the complexation of Cu^{+} by the bithiazolyl azothiacalixarene was conducted using fluorescence titrations. It has been reported [33,34] that the variation of fluorescence emission is a good method for the recognition of a metallic centre through the quenching (for transition metal ions) of the fluorescence of a light-emitting unit linked to the receptor. The fluorescence spectrum of **2a** exhibits a peak at $\lambda_{em} = 387$ nm and that of **4** exhibits a peak at $\lambda_{em} = 391$ nm. All the measurements were performed in CH_2Cl_2. In both cases, the addition of stoichiometric amounts of $[Cu^{I}(MeCN)_4]PF_6$ in CH_2Cl_2 to a solution of the ligand did not lead to any variation in the emission wavelengths, but produced a regular decrease in intensities until complete quenching. The variation in the emission maxima versus amount of added Cu^{+} salt shows that the extinction of fluorescence for receptor azothiacalixarene **2a** occurs after addition of 1 equivalent of Cu^{+} but after 2 equivalents of Cu^{+} for **4** (Fig. 3). These results suggest the formation of a 1:1 complex Cu-**2a** and a 2:1 complex Cu_2-**4**. Each solution turns from bright yellow to pale yellow upon addition of the salt, confirming the formation of the complex.

UV–visible Titrations

A study of the complexation properties of **3a** and **5** whose podands incorporate bipyridyl subunits was undertaken with $AgPF_6$ by UV–visible titrations. The spectrophotometric measurements were carried out at 25°C in CH_2Cl_2 and the ionic strength was maintained at 0.1 mol dm^{-3} ($NaClO_4$). Ag^{+} ions are known to accept a tetrahedral geometry with 6,6′-methyl-2,2′-bipyridyl units [20]. Upon addition of

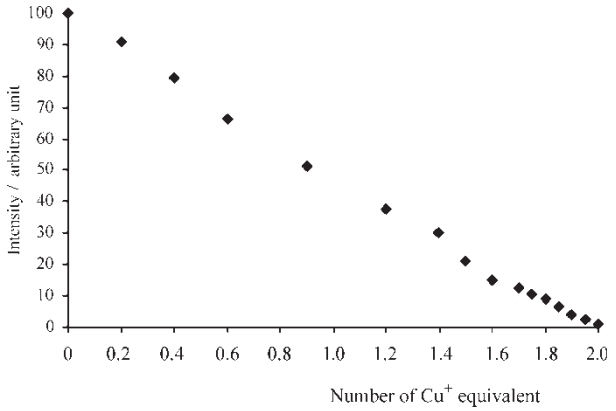

FIGURE 3 Determination of complex stoichiometry for ligand **4** via fluorescence quenching by addition of Cu^{+} salt ($\lambda_{ex} = 335$ nm, $\lambda_{em} = 391$ nm).

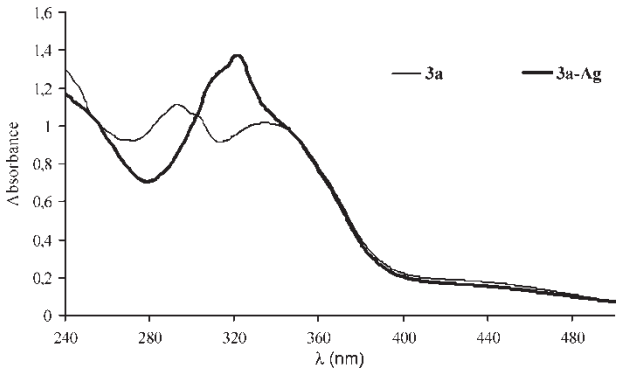

FIGURE 4 The UV–visible properties of the podand **3a** upon addition of Ag solutions.

Ag^+ solutions, the UV–visible ligand spectrum undergoes changes that indicate the formation of at least one metal complex species. The addition of aliquots of Ag^+ (from 0.1 to 1 equiv) to a solution of **3a** leads to the appearance of a new absorption band centred at 321 nm (Fig. 4). Moreover, the presence of isosbestic points indicates the existence of new species.

For compound **5**, the new absorption band appears at 330 nm and its intensity increased until exactly 2 equivalents of the metal ion were added, confirming the formation of a binuclear complex. The stoichiometries of the complexes between the metal salt and the ligand were determined by both Job's plots [35] and mole ratio [36] methods.

The two methods were used for ligand **3a** to confirm that a 1:1 Ag^+-**3a** complex was formed. The Job's plot was obtained from UV measurements at 322 nm for mixtures of **3a** and Ag^+ salt at constant total concentrations (5×10^{-5} M) (Fig. 5). For the Ag^+-**5** complex in CH_2Cl_2 a 2:1 stoichiometry was found. The stability constant, $\log K_{11}$, was calculated from Benesi–Hildebrand plots [37]. A $\log K$ value of 3.23 shows that the complexation of Ag^+ by this ligand is highly favoured, indicating the good affinity of this ligand towards the target ions.

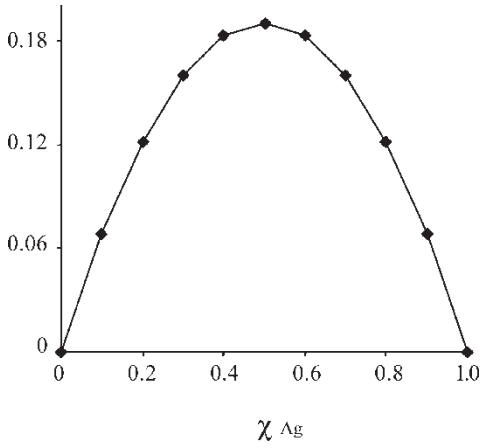

FIGURE 5 Job's plot for the mixture of **3a** and Ag^+.

The yellow colour of this new complex is also advantageous because Ag complexes are generally colourless.

CONCLUSIONS

The present paper describes for the first time the syntheses of new thiacalixarenes bearing both phenylazo and biheterocyclic groups. The results of extraction show that the replacement of methylene bridges by epithio groups in calix[4]arene affects its extraction ability and permits the more effective extraction of metal ions. The disubstituted thiacalixarenes **2a** and **3a** exhibit efficiency for the extraction and complexation of Cu^{2+} and/or Ag^+. This indicates some interesting features relating to the use of calixarenes. The complexation and fluorescence properties of these compounds with others metals ions are under investigation.

EXPERIMENTAL

Spectroscopic Measurements

UV–visible titrations were carried at 25°C in CH_2Cl_2 using a Shimadzu UV-2401 PC spectrophotometer. Titrations were performed in a spectrophotometric cell: typically, to record a spectrum, the reagent was delivered by a precision syringe (Halminton, 50 μL) and the solution allowed to equilibrate for 3 min. Usually aliquots (10 μL) of a metal cation solution (5×10^{-4} mol L^{-1}) were added to a host solution (1 mL; 5×10^{-5} mol L^{-1}). The spectrophotometric data were collected over the range 220–600 nm for all the podands investigated.

The fluorescence measurements were recorded at 25°C with a xenon lamp. Titrations were performed in a spectrophotometric cell using the procedure described above with a 7×10^{-5} mol L^{-1} solution of metal cation and a 7×10^{-6} mol L^{-1} solution of the host (1 mL). The spectrophotometric data were collected over the range 330–600 nm for all the podands investigated.

Extraction Studies

The extraction of metals (Ag^+, Cu^{2+}, Ni^{2+} and Pb^{2+}) by **2a**, **2b**, **3a** and **3b** ligands was investigated using acetate and nitrate salts. The organic solutions were prepared by dissolving a weighed amount of the ligand in dichoromethane. The aqueous solution was buffered to pH 5.3 with CH_3COOH (99%) (1.8×10^{-3} M) and CH_3COONa (99%) (8.2×10^{-3} M) and the ionic strength was maintained at $\mu = 0.1$ with KCl (98%). Liquid–liquid extraction experiments were carried out in a flask by shaking for 12 h in a thermostatted bath (30°C) 25 mL of an aqueous phase containing

metal salt (1.06×10^{-4} M) and 5 mL of organic phase containing ligand (5.3×10^{-4} M). The aqueous phase was separated, centrifuged, and then 1% of HNO_3 was added to these solutions and analysed by atomic absorption spectrometry (Perkin Elmer 3110) with an air-acetylene flame, the measurements being carried out using standard conditions calibration. The percentages of extraction (E%) were determined from Eq. (1) [38].

$$E\% = \left([M]_{blank} - [M]_{final}\right) \times 100/[M]_{blank} \quad (1)$$

where $[M]_{blank}$ and $[M]_{final}$ represent the metal concentration in the aqueous phase extracted with pure dichloromethane and with the dichloromethane solutions containing ligands, respectively.

General Experimental Methods

Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column chromatography was performed with silica gel 60 (0.040–0.063 mm). Melting points were recorded on a capillary apparatus and were uncorrected. UV measurements were recorded on a Shimadzu UV-2401 PC spectrophotometer (λ_{max} in nm; ε in mol dm^{-3} cm^{-1}). Fluorescence measurements were recorded at 25°C with a xenon lamp. Infrared measurements were performed (ν in cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded (300.13 and 75 MHz) (chemical shifts in ppm, J in Hertz). Mass spectra were obtained by the electrospray technique (positive mode) (HP 5989, S.C.A., CNRS, Solaize).

The syntheses of **2b** [16] and **3b** [17] have been reported previously.

5,11,17,23-Tetra(phenylazo)-25,27-di[(4-methyl-2,2′-bithiazolyl-4′-yl)methoxy]-26,28-di(hydroxy) thiacalix[4]arene (2a)

p-Tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene [25] (0.15 g, 0.16 mmol) and Na_2CO_3 (0.08 g, 0.8 mmol) were stirred in refluxing acetone (30 mL) under nitrogen for 1 h. After addition of 4-bromomethyl-4-methyl-2,2′-bithiazole (0.35 g, 1.28 mmol), the mixture was stirred at room temperature for 36 h. Then the solvent was removed and the residue was dissolved in CH_2Cl_2 (30 mL). The resulting solution was filtered using Celite®. The filtrate was washed with HCl (0.1 N) and water (2 × 15 mL). The organic phase was dried over Na_2SO_4. After concentration, MeOH was added and the precipitate was filtered off. Evaporation of the solvent gave a residue that was submitted to column chromatography on silica gel (petroleum ether/AcOEt, 70/30) to give **2a** as a red powder (0.055 g, 26%): $Rf = 0.64$. mp 283–284°C. ^{1}H NMR (CD_2Cl_2): 2.55 (s, 6H); 5.46 (s, 4H); 7.18 (s, 2H); 7.32–7.43 (m, 12H); 7.75–7.81 (m, 8H); 7.98 (s, 4H); 8.24 (s, 2H); 8.51 (s, 4H). ^{13}C NMR (CD_2Cl_2): 17.19, 75.26, 123.43, 123.35, 125.18, 133.56, 135.36, 150.39, 124.01, 124.52, 134.98, 135.36, 135.98, 136.01, 149.67, 144.65, 148.43, 156.45, 168.15. ES-MS m/z: 1302.1 $[M + H]^+$ (calcd 1302.6). $C_{64}H_{44}N_{12}O_4S_8$ (1301.64): calcd C 59.06, H 3.41, N 12.91; found C 59.42, H 3.01, N 12.88. UV (CH_2Cl_2): 331 (19 640); 434 (696). IR: 3233 (stretching, OH); 3068 (CH_3-*btz*); 1583, 1560, 1468, 1446 (C═C, N═N); 1404 (C–S); 905, 800 (*btz*C-H).

5,11,17,23-Tetra(phenylazo)-25,27-di[(6-(6′-methyl-2,2′-bipiridyl)yl)methoxy]-26,28-di(hydroxy) thiacalix[4]arene (3a)

p-Tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (0.15 g, 0.16 mmol), Na_2CO_3 (0.084 g, 0.8 mmol) and 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.33 g, 1.28 mmol) were stirred in refluxing acetone (30 mL) under nitrogen for 48 h. The product was purified by chromatography column on silica gel (petroleum ether/AcOEt: 70/30) to give **3a** as a red powder (0.038 g, 18%): $Rf = 0.64$. mp 278–279°C. ^{1}H NMR (CD_2Cl_2): 2.64 (s, 6H); 5.21 (s, 4H); 7.10 (d, $J = 7.6$, 2H); 7.21–7.24 (m, 2H); 7.42–7.51 (m, 12H); 7.64 (m, 2H); 7.84–7.89 (m, 8H); 8.07 (m, 2H); 8.24 (s, 4H); 8.31 (d, $J = 7.7$, 2H); 8.45 (s, 4H); 8.52 (d, $J = 7.7$, 2H). ^{13}C NMR (CD_2Cl_2): 24.71, 77.64, 122.69, 122.91, 123.11, 125.04, 125.33, 126.35, 129.37, 130.41, 133.65, 134.19, 134.80, 136.20, 147.95, 148.24, 148.81, 152.95, 153.45, 159.80, 167.18, 167.81, 168.91. ES-MS m/z: 1277.4 $[M + H]^+$ (calcd 1277.5), 1300.1 $[M + Na]^+$ (calcd 1300.5). $C_{72}H_{52}N_{12}O_4S_4$ (1277.5): calcd C 67.69, H 4.10, N 13.16; found C 67.35, H 3.97, N 13.10. UV (CH_2Cl_2): 292 (22 354); 301 (21 264); 332 (21 206); 426 (2654). IR: 3361 (elongation, OH); 3104 (Csp^2-H); 2922 (Csp^3-H); 1508, 1472 (C═C); 1591 (C═N).

5,11,17,23-Tetra(phenylazo)-25,26,27,28-tetra[(4-methyl-2,2′-bithiazolyl-4′-yl) methoxy]thiacalix[4]arene (4)

p-Tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (0.10 g, 0.109 mmol) and Cs_2CO_3 (0.357 g, 1.09 mmol) in acetone (30 mL) was stirred under nitrogen at 60°C. 4-Bromomethyl-4-methyl-2,2′-bithiazole (0.179 g, 0.65 mmol) was added after 1 h. The reaction was heated at reflux for 4 days. The solvent was removed and the residue was dissolved in CH_2Cl_2 and the resulting precipitate was filtered using Celite®. The filtrate was washed with water (2 × 30 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent removed by evaporation. The product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH; 99/1) to give **4** as an orange powder (0.056 g, 30%):

Rf = 0.25. mp 289-290°C. ^{1}H NMR ($CDCl_3$): 2.47 (s, 12H); 5.13 (s, 8H); 6.84 (s, 4H); 7.12 (s, 4H); 7.38 (t, 4H); 7.45–7.52 (m, 8H); 7.99 (d, *J* = 7.3, 8H); 8.59 (s, 8H). ^{13}C NMR ($CDCl_3$): 17.60; 67.80; 115.78, 118.02, 123.24, 129.03, 130.25, 131.12, 128.37, 148.55, 152.36, 160.64, 153.01, 154.30, 160.71, 161.37. ES-MS *m/z*: 1690.1 $[M + H]^+$ (calcd 1690.2), 1713.1 $[M + Na]^+$ (calcd 1713.2). $C_{80}H_{56}N_{16}O_4S_{12}$ (1690.2): calcd C 56.85, H 3.34, N 13.26; found C 56.50, H 3.01, N 13.42. UV (CH_2Cl_2): 333 (61852); 440 (10220). IR: 3109, 3060 (C–H); 2921 (C–H); 1510, 142 (C═C); 1550 (C N); 1403 (C–S).

5,11,17,23-Tetra(phenylazo)-25,26,27,28-tetra [(6-(6′-methyl-2,2′-bipyridyl)yl) methoxy]thiacalix[4]arene (5)

As described for **4**, compound **1** (0.10 g, 0.109 mmol), Cs_2CO_3 (0.35 g, 1.09 mmol) and 6-bromomethyl-6′-methyl-2,2′-bipyridine (0.17 g, 0.65 mmol) were stirred in refluxing acetone (25 mL) under nitrogen for 4 days. Purification followed by recrystallization in CH_2Cl_2/MeOH (3/2) affording an orange powder (0.038 g, 21%). *Rf* = 0.27. mp 282–283°C. ^{1}H NMR ($CDCl_3$): 2.61 (s, 12H); 5.28 (s, 8H); 7.12–7.19 (m, 8H); 7.48–7.85 (m, 4H); 7.64–7.71 (m, 12H); 7.85 (m, 4H); 7.92–7.96 (m, 8H); 8.26 (d, *J* = 7.6, 4H); 8.35 (s, 8H); 8.50 (d, *J* = 7.7, 4H). ^{13}C NMR ($CDCl_3$): 28.17, 74.06, 120.07, 122.83, 124.37, 126.43, 129.14, 129.20, 129.44, 129.81, 129.99, 130.55, 128.19, 128.73, 132.70, 133.45, 134.59, 146.33, 153.31, 156.56. ES-MS *m/z*: 1642.6 $[M + H]^+$ (calcd 1642.0). $C_{96}H_{72}N_{16}O_4S_4$ (1641.9): calcd C 70.22, H 4.42, N 13.65; found C 69.95, H 4.08, N 13.78. UV (CH_2Cl_2): 293 (66792); 303 (66796); 331 (69904). IR: 3103 (C–H); 2923 (C–H); 1518, 1456 (C═C); 1589 (C═N).

Acknowledgements

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