Triazole- and azo-coupled calix[4]arene as a highly sensitive chromogenic sensor for Ca^{2+} and Pb^{2+} ions

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Abstract—A novel chromogenic calix[4]arene **3**, which has within a molecule both the triazoles and the hydroxyl azophenols as the metal-binding sites and the azophenol moiety as a coloration sites was designed and synthesized. Calix[4]arene **3** is highly sensitive to Ca^{2+} and Pb^{2+} ions, which can be detected by the naked eye. Furthermore, the association constants for the 1:1 complexes of **3**·Ca^{2+} and **3**·Pb^{2+} were determined to be 7.06×10^4 M^{-1} and 8.57×10^3 M^{-1}, respectively.
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The design and synthesis of new chemosensors for metal ions is an important subject in the field of supramolecular chemistry due to their fundamental role in biological, environmental, and chemical processes.[1] Chromogenic ionophores have been intensively investigated as a specific metal ion indicator since Vögtle reported the use of 4-(4-nitrophenyl)azo-coupled crowns and azacrowns as chromoionophores, which showed large UV/vis band shifts when cations were added.[1a]

Calix[4]arenes have been shown to be useful molecular scaffold in the development of chromoionophores, especially for metal ion recognition.[2] Shinkai and co-workers reported that calix[4]arene having a 4-(4-nitrophenyl)azophenol unit with three ethyl ester groups showed a perfect lithium ion selectivity with respect to the UV/vis band shift.[2a,b] Chang et al. reported a bathochromic shift of a *p-tert*-butylcalix[4]arene bearing a 1,3-diazophenol unit upon calcium ion complexation.[2d] Reinhoudt et al. also reported that a calix[4]arene with monoalkylated azophenol unit and triamides on the lower rim is a highly selective Pb^{2+} sensor, in which the direction of the shift was dependent on the conformation of the calix[4]arenes.[2e]

In continuation of our interests in the design and synthesis of chromogenic[3,4] and fluorogenic chemosensors,[5,6]

we report here the synthesis of a novel chromogenic calix[4]arene using the Click chemistry[7] of an azide and an alkyne to form a triazole cationic binding site.

The synthesis of host **3** is illustrated in Scheme 1. Our synthesis began with 25,27-bis(*O*-propargyl)calix[4]-arene **1**[8] followed by diazo coupling reaction using *p*-anisidine in HCl and $NaNO_2$ in acetone and pyridine gave the desired product **2** in 62% yield.[9] Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction of **2** with 1-(azido-methyl)-benzene in the Click condition afforded the 5,17-bis(*p*-methoxy-phenyl)azo-25,27-bis(1,2,3-triazole)-calix[4]arene **3** in 71% yield.[10] Control compound **4**[11] was synthesized in 79% yield using a method similar to that used in the preparation of **2**. Besides traditional organic spectroscopic identification (^1H and ^{13}C NMR, MS, and HRMS spectra) of all these calix[4]arenes, single-crystal X-ray analysis of **2** and **3** confirmed the structures to be in cone conformations (Fig. 1).[12]

The absorption maxima (λ_{max}) and molar extinction coefficients of the chromogenic calix[4]arenes and control compound synthesized in this work are summarized in Table 1. Next, we then investigated the affinities of these azo-compounds **2**–**4** for a series of groups 1A, 2A, and transition-metal ions in $MeCN/CHCl_3$ (v/v = 1000:4).

Excess perchlorate salts (10 equiv) of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Pb^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, and Zn^{2+} ions were tested to evaluate the metal

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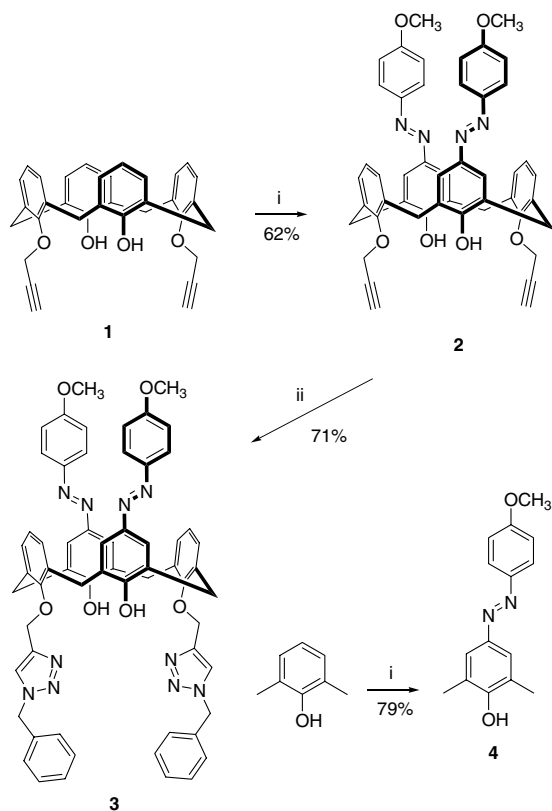
Scheme 1. Synthesis of chromogenic calix[4]arene **3**. Reagents and conditions: (i) *p*-anisidine/acetone, $NaNO_2$/4 N HCl, pyridine, 0 °C, 18 h; (ii) 1-(azidomethyl)benzene, CuI, THF/H_2O, 50 °C, 18 h.
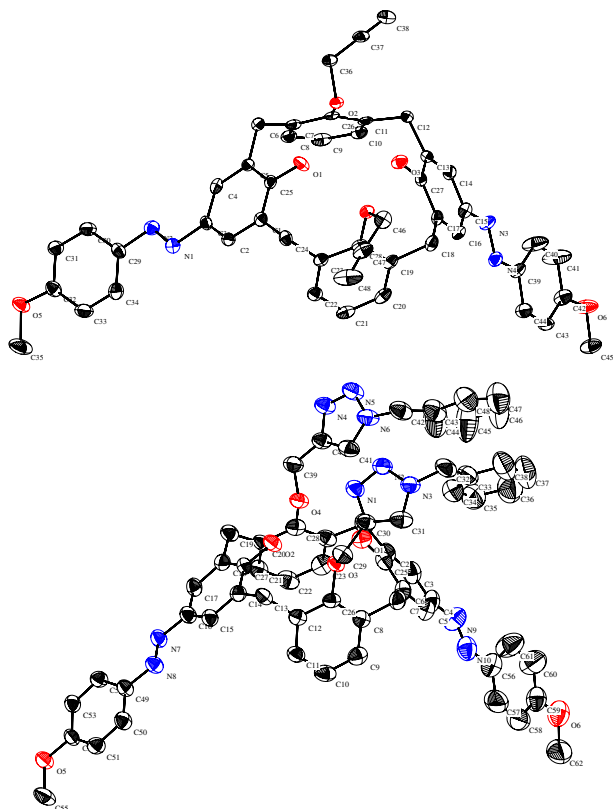
Table 1. λ_{max} and corresponding extinction coefficients of azo-compounds **2**–**4** in MeCN/CHCl$_3$ (1000:4, v/v)

| Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})
2	364	61,000
3	365	55,000
4	360	88,000

ion binding properties of **2**–**4**. Ligand concentration in all titration experiments was fixed at 10^{-5} M in MeCN/CHCl$_3$ (v/v = 1000:4). Free hosts **2**, **3**, and **4** exhibited absorption bands at 364, 365, and 360 nm in MeCN/CHCl$_3$ (v/v = 1000:4), respectively. The tri-azole–azophenol host **3**, having triazoles as the metal ligating groups, is found to exhibit remarkable selectivity toward Ca^{2+} and Pb^{2+} ions over all other metal ions. For example, the addition of 10 equiv of Ca^{2+} and Pb^{2+} ions induced a bathochromic shift of triazole ionophore **3** from λ_{max} 365 nm to 527 and 541 nm, respectively (Fig. 2). However, the UV/vis spectra of control compounds **2** and **4** showed a weak bathochromic shift to Cr^{3+} ion only, and the rest of the metal ions did not show any change (see Figs. S7 and S8).

The two triazole moieties of **3** are proven to form an efficient metal ion binding site, whereas compounds **2** and **4** are in lack of such an efficient metal ion binding site. Furthermore, the geometry of the binding site of the host, comprising the two nitrogen atoms of triazole units and two hydroxyls of the azophenol units, seems to be ideal in terms of size and arrangement for recognition of doubly charged metal cations. Of primary importance is the electrostatic interaction of metal cations with two azophenol moieties as well as the ion–dipole interaction of metal ions with the triazole unit.

Upon interaction with Ca(ClO$_4$)$_2$, the chromogenic sensor **3** in MeCN/CHCl$_3$ (v/v = 1000:4) solution experienced a marked bathochromic shift in its λ_{max} as shown in Figure 3. The absorption maximum at 365 nm gradually decreased in intensity with the formation of a new absorption band at ca. 527 nm ($\Delta\lambda_{max}$ = 162 nm). Three isosbestic points are 270, 305,

Figure 1. X-ray single-crystal structures of **2** and **3**.
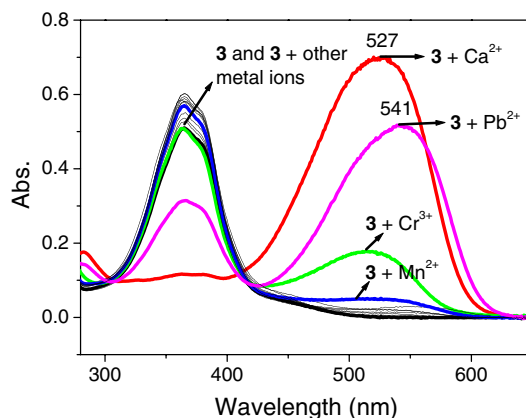
Figure 2. UV/vis spectra of **3** (10 μM) before and after adding 100 μM concentration of various metal perchlorates in MeCN/CHCl$_3$ (1000:4, v/v).
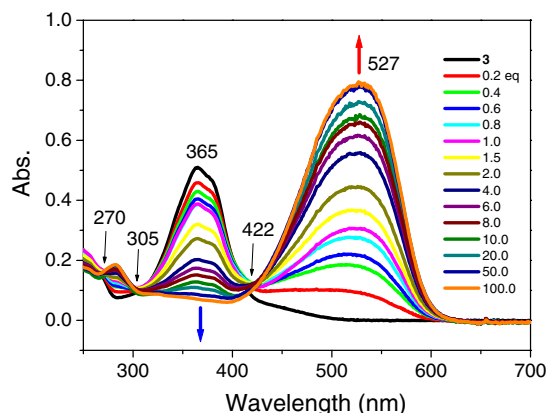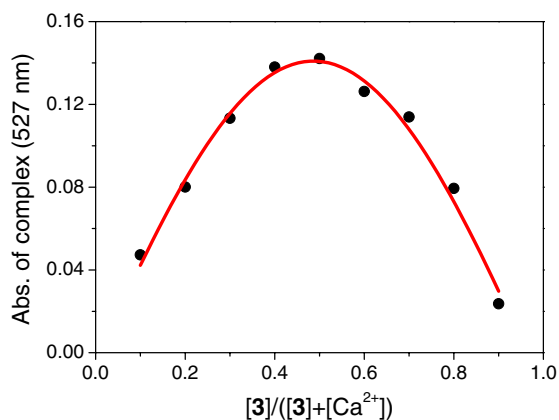
Figure 3. UV/vis spectra of **3** (10 μM) upon titration by various equivalents of $Ca(ClO_4)_2$ in MeCN/CHCl$_3$ (1000:4, v/v).

Figure 5. Benesi–Hilderbrand plot of **3** with $Ca(ClO_4)_2$.
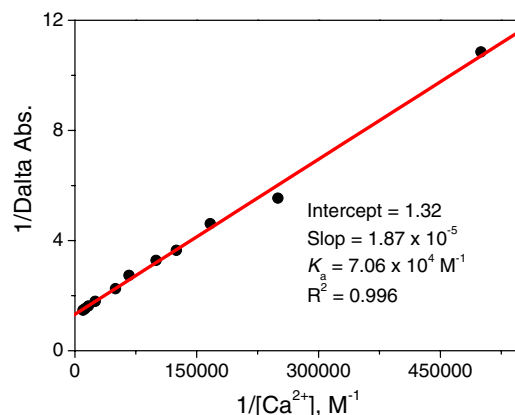
and 422 nm for the titration spectra of **3** by $Ca(ClO_4)_2$. The spectral features in Figure 3 are consistent with a 1:1 binding ratio between calix[4]arene **3** with Ca^{2+} ion. Further support of the 1:1 binding ratio comes from a Job plot experiment,[13] where the absorptions of the complex at 527 nm were plotted against molar fractions of **3** under the conditions of an invariant total concentration. As a result, the concentration of $\mathbf{3}\cdot Ca^{2+}$ complex approached a maximum when the molar fraction of [**3**]/ ([**3**] + [Ca^{2+}]) was about 0.5 (see Fig. 4).

Electrospray mass spectrometry also supports the formation of complex $\mathbf{3}\cdot Ca^{2+}$ and $\mathbf{3}\cdot Pb^{2+}$, where a peak at $m/z = 1173.6$ corresponding to the mass of [$\mathbf{3} + Ca + ClO_4$]$^+$ and a double charged peak at $m/z = 537.4$ which corresponds to [$\mathbf{3} + Ca$]$^{2+}$ were observed. Furthermore, a peak at $m/z = 1241.6$ corresponding to the mass of [$\mathbf{3} + Pb - H$]$^+$ and a double charged peak at $m/z = 621.2$ which corresponds to [$\mathbf{3} + Pb$]$^{2+}$ were also observed (see Figs. S9 and S10 for detail).

The association constant for $\mathbf{3}\cdot Ca^{2+}$ in MeCN/CHCl$_3$ (1000:4, v/v) was determined to be 7.06×10^4 M^{-1} by Benesi–Hilderbrand plot[14] (Fig. 5). Similar UV/vis titration behavior and 1:1 binding stoichiometry was also

observed in the case of **3** with Pb^{2+} (see Figs. S11–S13 for details); and its association constant was estimated to be 8.57×10^3 M^{-1}.

Metal ion-induced chemical shift changes in the ^{1}H NMR (in CD$_3$CN) spectra support that Ca^{2+} is bound to the two nitrogen atoms of the triazole units and the two hydroxyl azophenol groups of **3** (see Fig. 6). In the presence of 10.0 equiv of Ca^{2+}, chemical shifts of protons H$_a$–H$_e$ on the azophenol unit of **3** changed significantly; the peaks of H$_a$–H$_c$ were upfield shifted by 0.18, 0.17, and 0.42 ppm, respectively, but the peak of H$_e$ was downfield shifted by 2.74 nm. In particular, the peak of H$_d$ was split into two peaks, one was upfield shifted by 0.23 ppm and the other was downfield shifted by 0.03 ppm. However, the peaks of H$_g$ and H$_h$ were each split into two sets of signals and upfield shifted.
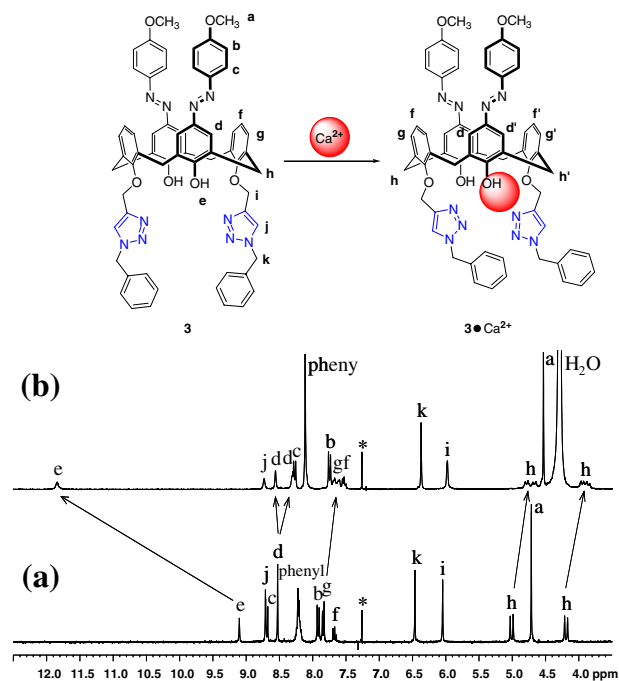

Figure 4. Job plot of a 1:1 complex of **3** and Ca^{2+} ion, where the absorption at 527 nm was plotted against the mole fraction of **3** at invariant total concentration of 10 μM in MeCN/CHCl$_3$ (1000:4, v/v).

Figure 6. ^{1}H NMR spectra of **3** (2.5 mM) in CD$_3$CN (a) and in the presence of 25 mM (10.0 equiv) of $Ca(ClO_4)_2$ (b), where ∗ denotes an external standard CHCl$_3$.

The protons H_i, H_j, and H_k were little influenced. Furthermore, ^{13}C NMR spectroscopy proved that ionophore **3** forms a complex with Ca^{2+} in a cone conformation. The methylene carbon atoms bridging the aromatic rings appear at δ 31.2 and 32.1, which are typical resonances for a cone conformation of calix[4]arenes[15] (see Fig. S14). These results suggest that Ca^{2+} ion not only is bound by triazole–azophenol host **3**, it also breaks the symmetry of the host molecule after complexation.

Due to the poor solubility of complex **3**·Pb^{2+} in CD_3CN, the following titration was in $CDCl_3/CD_3CN$ (v/v = 3:1) co-solvent system. Upon adding 10.0 equiv of Pb^{2+} to the solution of **3** (see Fig. S15 for detail), the peak of H_d was downfield shifted by 0.21 ppm, but did not split. The peaks of H_g and H_h stayed intact. The peak of H_j on the triazole unit of **3** was downfield shifted by 0.24 ppm, and the peaks of H_i and H_k were also downfield shifted by 0.08 and 0.12 ppm. Interestingly, the peak of H_e was upfield shifted by 3.58 ppm. These results suggest that Pb^{2+} ion can also be bound by host **3**, but was forming a symmetrical metal ion complex.[16]

In conclusion, we have developed a new calix[4]arene sensor with bistriazoles and azophenols as the metal ion binding sites and azo groups as the signal transduction unit, which showed selective coloration of Ca^{2+} and Pb^{2+} ions.[16] The Ca^{2+} and Pb^{2+} ion detection gives rise to a large bathochromic shift in the absorption spectrum (from light yellow to red), which is clearly visible to the naked eye.

Acknowledgements

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.08.045.

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9. *Compound* **2**: To an ice cold solution of 0.07 g (1.00 mmol) of $NaNO_2$ in 6 mL of 4 N HCl was added a solution of 0.06 g (0.50 mmol) of *p*-anisidine in 3 mL of acetone, and the mixture was stirred for 30 s. The combined solution was then added to another ice cold solution of 0.10 g (0.20 mmol) of 25,27-dipropargyloxy-26,28-dihydroxy-calix[4]arene **1** in 12 mL of pyridine to produce a colored solution. The reaction mixture was stirred for 18 h at 0 °C and then treated with 50 mL of 4 N HCl to give a colored precipitate. The solid residue was recrystallized from CH_2Cl_2/methanol mixture to give 0.095 g (62%) of **2** as a red solid; mp 226–228 °C; $R_f = 0.5$ (hexane/EtOAc = 3:1); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.87 (d, $J = 8.9$ Hz, 4H), 7.73 (s, 4H), 7.62 (s, 2H), 7.00 (d, $J = 8.9$ Hz, 4H), 6.96 (d, $J = 7.6$ Hz, 4H), 6.76 (t, $J = 7.6$ Hz, 2H), 4.84 (d, $J = 2.3$ Hz, 4H), 4.46 (d, $J = 13.5$ Hz, 4H), 3.87 (s, 6H), 3.57 (d, $J = 13.5$ Hz, 4H), 2.63 (t, $J = 2.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 161.3 (Cq), 155.8 (Cq), 151.3 (Cq), 147.2 (Cq), 145.7 (Cq), 132.7 (Cq), 129.4 (CH), 128.5 (Cq), 125.9 (CH), 124.1 (CH), 123.4 (CH), 114.1 (CH), 78.0 (Cq), 63.6 (CH_2), 55.5 (CH_3), 31.8 (CH_2); FABMS *m/z* 770 (M^++1, 2), 769 (M^+, 2), 460 (6), 307 (100); HR FABMS Calcd for $C_{48}H_{40}N_4O_6$ 768.2948. Found 768.2936.

10. *Compound* **3**: To a mixture of **2** (0.20 g, 0.26 mmol) and 9-(azidomethyl)benzene (0.084 g, 0.63 mmol) in THF and water (v/v = 2:1, 30.0 mL) was added CuI (about 1 mg, 0.005 mmol). The heterogeneous mixture was stirred vigorously at 50 °C for 24 h. The mixture was extracted thrice with chloroform. The chloroform solution was dried over $MgSO_4$ and evaporated to give the solid crude product. Chromatography on silica gel eluting with hexane/ethyl acetate (v/v = 1:1) gave 0.19 g (71%) of **3** as an orange solid; mp 179–181 °C; $R_f = 0.3$ (hexane/EtOAc = 1:1); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.04 (s, 2H), 7.87 (d, $J = 9.0$ Hz, 4H), 7.73 (s, 2H), 7.67 (s, 4H), 7.35–7.27 (m, 10H), 6.98 (d, $J = 9.0$ Hz, 4H), 6.93 (d, $J = 7.6$ Hz, 4H), 6.70 (t, $J = 7.6$ Hz, 2H), 5.58 (s, 4H), 5.17 (s, 4H), 4.22 (d, $J = 13.2$ Hz, 4H), 3.83 (s, 6H), 3.37

(d, $J = 13.2$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ 61.2 (Cq), 155.7 (Cq), 151.3 (Cq), 147.1 (Cq), 145.7 (Cq), 143.6 (Cq), 134.9 (Cq), 132.6 (Cq), 129.4 (CH), 129.0 (CH), 128.7 (CH), 128.2 (Cq), 127.9 (CH), 125.8 (CH), 124.1 (CH), 123.5 (CH), 123.4 (CH), 114.1 (CH), 69.6 (CH$_2$), 55.4 (CH$_3$), 54.1 (CH$_2$), 31.4 (CH$_2$); FABMS *m/z* 1035 (M$^+$, 9), 91 (100); HR FABMS Calcd for C$_{62}$H$_{54}$N$_{10}$O$_6$ 1034.4228. Found 1034.4221.

11. *Compound* **4**: To an ice cold solution of 1.40 g (20.3 mmol) of NaNO$_2$ in 10 mL of 4 N HCl was added a solution of 1.50 g (12.2 mmol) of *p*-anisidine in 15 mL of acetone, and the mixture was stirred for 30 s. The combined solution was then added to another ice cold solution of 0.50 g (4.1 mmol) of 2,6-dimethylphenol in 20 mL of pyridine to produce a colored solution. The reaction mixture was stirred for 18 h at 0 °C and then treated with 100 mL of 4 N HCl to give a colored precipitate. The solid residue was purified by column chromatography with hexane/ethyl acetate (v/v = 3:1) to give 0.83 g (79 %) of **4** as an orange solid; mp 120–122 °C; $R_f = 0.6$ (hexane/EtOAc = 3:1); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.86 (d, $J = 9$ Hz, 2H), 7.59 (s, 2H), 7.00 (d, $J = 9$ Hz, 2H), 4.98 (s, 1H), 3.88 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (CD$_3$CN, 75.4 MHz) δ 162.6 (Cq), 156.6 (Cq), 147.7 (Cq), 146.9 (Cq), 125.4 (Cq), 124.9 (CH), 123.9 (CH), 115.3 (CH), 56.3 (CH$_3$), 16.6 (CH$_3$); FABMS *m/z* 257 (M$^+$+1, 100), 256 (M$^+$, 85), 136 (55), 121 (45); HR FABMS Calcd for C$_{15}$H$_{16}$N$_2$O$_2$ 256.1212. Found 256.1206.

12. *Crystal structure data for* **2**: C$_{50}$H$_{40}$Cl$_6$N$_4$O$_6$, $M = 1005.56$, Triclinic, $a = 13.5391(6)$ Å, $\alpha = 74.752(1)°$, $b = 14.2081(7)$ Å, $\beta = 65.904(1)°$, $c = 14.2656(7)$ Å, $\gamma = 72.891(1)°$, $V = 2361.89(19)$ Å^3, $T = 150(1)$ K, space group *P*-1, $Z = 2$, $\mu = 0.418$ mm^{-1}, 25,311 reflections collected ($R_1 = 0.0918$, $wR_2 = 0.2296$), 8313 independent reflections (R(int) = 0.0433, $R_1 = 0.1094$, $wR_2 = 0.2435$). Crystal structure data for **3**: C$_{63}$H$_{57}$Cl$_3$N$_{10}$O$_6$, $M = 1156.54$, Monoclinic, $a = 25.3068(11)$ Å, $\alpha = 90°$, $b = 10.5670(4)$ Å, $\beta = 101.372(3)°$, $c = 21.5706(13)$ Å, $\gamma = 90°$, $V = 5655.1(5)$ Å^3, $T = 150(2)$ K, space group *P*2(1)/c, $Z = 4$, $\mu = 0.225$ mm^{-1}, 23,719 reflections collected ($R_1 = 0.1076$, $wR_2 = 0.2617$), 9868 independent reflections (R(int) = 0.0822, $R_1 = 0.2174$, $wR_2 = 0.3089$). Crystallographic data for the two structures in this letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Their CCDC numbers are **2** (CCDC 652909), **3** (CCDC 652910), respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033, e-mail: data_request@ccdc.ca-m.ac.uk.

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16. Based on the results of different metal ion-induced chemical shift changes in the ^{1}H NMR of ionophore **3**, one may infer that the binding modes for **3**·Ca^{2+} and **3**·Pb^{2+} are different; that is, the Ca^{2+} is bound to one of the two triazole units and the two hydroxyl azophenol groups, whereas Pb^{2+} is bound to both the two triazole units and the two hydroxyl azophenol groups of **3**.