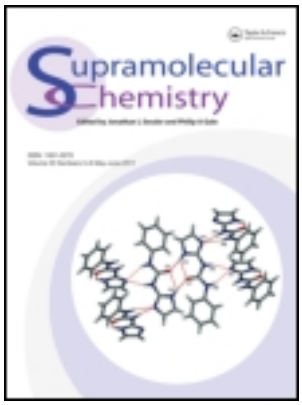

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Synthesis, crystal structure and complexation behaviour of a thiacalix[4]arene bearing 1,2,3-triazole groups

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The structure and complexation behaviour of 1,3-*alternate*-1,2,3-triazole based on thiacalix[4]arene,1,3-*alternate*-**1** and **2** have been determined by means of X-ray analysis, fluorescence and ^{1}H NMR spectroscopy. The X-ray results suggested that the nitrogen atom N3 on triazole ring can act as hydrogen bond acceptors in the self-assembly of a supramolecular structure. The fluorescence spectra changes indicated that the thiacalix[4]arene bearing 1,2,3-triazole groups were highly selective for Ag^+ in comparison with other tested metal ions by enhancement of the monomer emission of pyrene. The ^{1}H NMR results suggested that Ag^+ can be strongly bonded by the triazole groups with the cooperation of the ionophoric cavity formed by the two inverted benzene rings and the sulfur atoms of the thiacalix[4]arene.

Keywords: thiacalixarene; triazole ring; crystal structure; fluorescent sensor; silver ion

Introduction

Recently, there has been intense interest in the design and synthesis of receptors and sensors based on 1,2,3-triazole derivatives, which has resulted primarily from the studies of Meldal and co-workers (*1*) and Sharpless and co-workers (*2*) on the Cu(I) catalysis of 1,3-dipolar cycloaddition of alkynes and azides. Such 1,2,3-triazoles find potential application in organic synthesis (*3*), biological molecular systems (*4*, *5*), medical (*6*, *7*) and materials chemistry (*8–10*). The properties of the 1,2,3-triazole moiety as a linker in multivalent derivatives can be exploited for the binding of cations, typified by the accelerated catalysis of the 'click' reaction by *in situ* formation of copper complexes (*11*). The coordination chemistry of the triazole group has also been investigated through the formation of transition metal complexes of a range of bis-triazoles (*12*, *13*). Cation-binding properties of triazoles have been shown to have potential in the radiolabelling of biomolecules (*14*). At the same time, it has been shown that the polarity of neutral 1,4-disubstituted aryl-1,2,3-triazoles and of the C5—H bond can create an electropositive site that can function as an effective hydrogen bond donor for anion binding. For example, Li et al. (*15–18*) have synthesised a macrocyclic receptor that is devoid of conventional X-H hydrogen bond donors but interacts exclusively *via* C-H . . . chloride contacts.

In calixarene chemistry, a copper-catalysed 1,2,3-triazole has previously been exploited by Zhao and co-workers for the functionalisation of a calixarene scaffold (*19*). More relevant to this study have been investigations by others on the selective binding of various metal cations *via* the use of calixarene scaffolds suitably functionalised with triazoles (*20–25*). For example, Chung and co-workers have developed Ca^{2+} and Pb^{2+} chromogenic selective sensors through the introduction of triazole binding sites at the lower rim of calix[4]arene (*20*), resulting in on–off switchable fluorescent sensors (*21*).

Similarly, thiacalix[4]arenes (*26–29*) have received growing interest since their discovery in 1997, due to their novel features; their use as platforms is an emerging area. Di- or poly-topic receptors, constructed with two or more binding subunits in a single molecule, have been reported (*30*). Such systems are suitable candidates for the allosteric regulation of host–guest interactions with metal cations. In particular, the so-called 1,3-*alternate* conformation of calix[4]arene, which has D_{2h} symmetry (tube shaped) (*31–34*), can be suitably adapted for the formation of 1:1 as well as 1:2 complexes owing to its symmetrical ditopic arrangement.

In this paper, we report on the synthesis, crystal structures and complexation properties of 1,3-*alternate*-**1** and **2** based on thiacalix[4]arene scaffold.

Results and discussion

*Syntheses of compounds 1,3-*alternate-*1 and 2*

The syntheses of 1,3-*alternate*-**1** and **2** are shown in Scheme 1.

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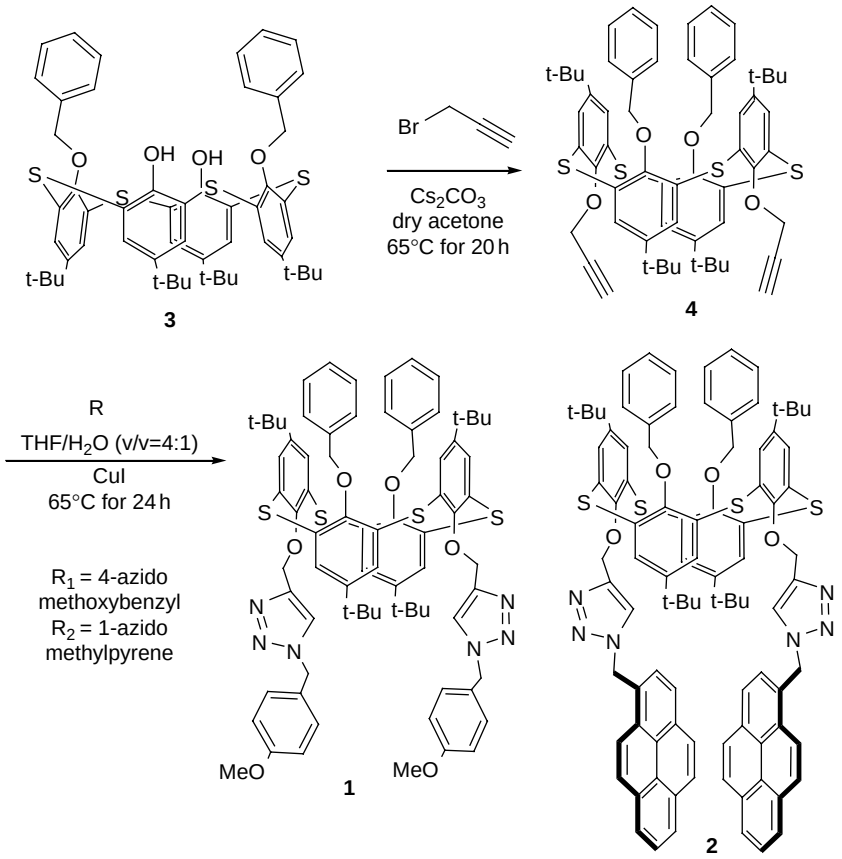

Scheme 1. The synthetic route of receptors 1,3-*alternate*-**1** and **2**.

In our previous study, we regioselectively synthesised thiacalix[4]arene derivatives with the controlled conformation by a protection–deprotection method using benzyl groups as a protecting group, and the result demonstrated that solid superacid (Nafion-H) is a good catalyst for the present deprotection of benzyl group (*28*). Hence, the *O*-alkylation of thiacalix[4]arene was carried out with 10 equiv. of benzyl bromide in the presence of 10 equiv. of Na_2CO_3 according to the reported procedure (*28*) to afford *distal*-**3** in 93% yield. Compound **4** was prepared by the reaction of *distal*-**3** with propargyl bromide in the presence of 10 equiv. of Cs_2CO_3 in dry acetone in 81% yield. The Cu(I)-catalysed 1,3-dipolar-cycloaddition reaction of 1,3-*alternate*-**4** with 4-azidomethoxybenzyl under Click conditions afforded 1,3-*alternate*-**1** in a yield of 74%. The latter procedure was also used in the synthesis of 1,3-*alternate*-**2** from the reaction with 1-azidomethylpyrene giving a yield of 51%. The product structures were supported by their spectroscopic and analytical data. For example, the ^{1}H NMR spectrum of 1,3-*alternate*-**1** shows two singlets for the *tert*-butyl protons at δ 0.79 and 1.13 ppm; the former peak is observed at a higher field due to the ring current effect arising from the two inverted benzene rings of benzyl groups. Other signals in the ^{1}H NMR spectrum may correspond to either the *cone* or 1,3-*alternate* conformer which differ only slightly in their observed chemical shifts (*35*). Fortunately, the 1,3-*alternate* conformation of compound 1,3-*alternate*-**1** was also confirmed by a single crystal X-ray diffraction study, and the structure is shown in Figure 1.

*Crystal structures of 1,3-*alternate-*1*

Compound 1,3-*alternate*-**1** adopts a '1,3-*alternate* conformation', with the four sulfur atoms forming an almost square plane (S_4 plane) (Figure 1); the dihedral angles between the S_4 plane and substituted phenyl rings are 76.45(3)° and 79.19(3)° (1,2,3-triazole substituted) and 87.50(3)° and 72.61(3)° (benzyl substituted), respectively. The distances between the centres of opposite calix benzene rings of the calixarene are 6.013 and 5.733 Å, respectively.

Ghadiri and co-workers (*36*) have shown that triazole units can act as amide mimics enabling protein folding by virtue of the strongly polarised C5—H bond of the triazole ring acting as a hydrogen bond donor and the N3 atom acting as a hydrogen bond acceptor: an amide/peptide bond mimic. This result demonstrated the unique properties of the 1,4-disubstituted 1,2,3-triazole ring in terms of its ability to participate in hydrogen bonding and

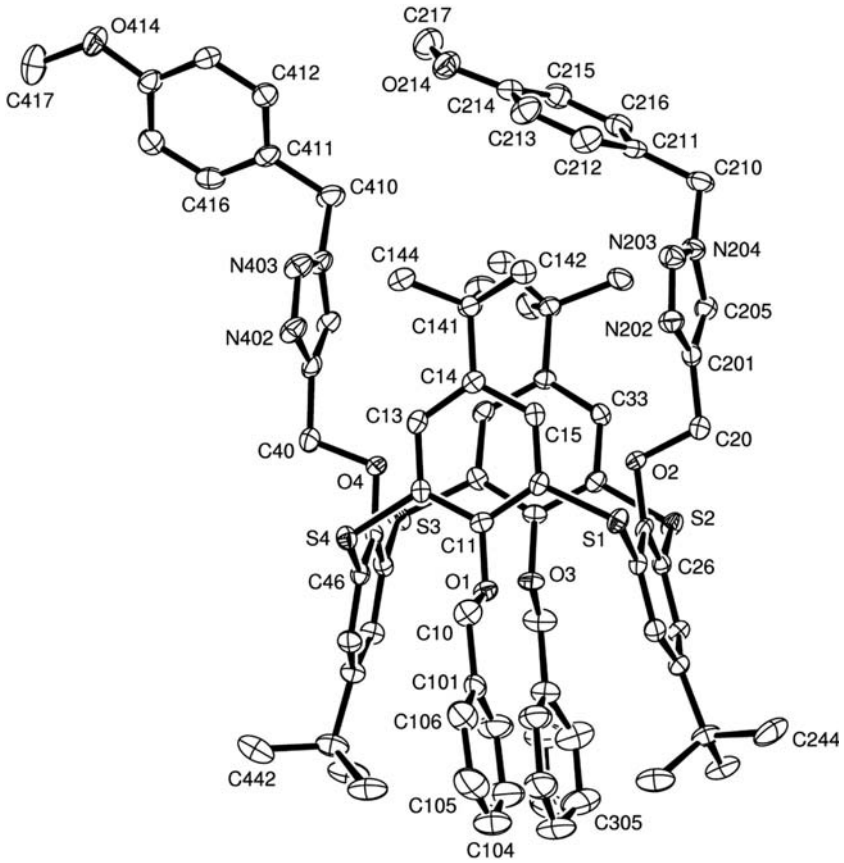

Figure 1. X-ray structure of 1,3-*alternate*-**1**. The thermal ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity.

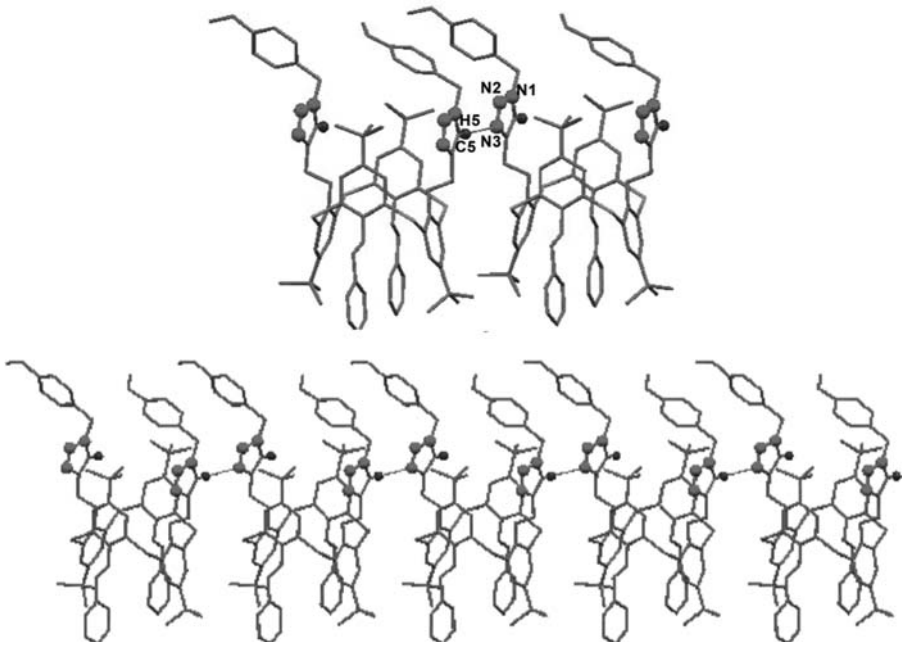

Figure 2. C—H . . . N hydrogen bonding: between N3 and C5–H in 1,3-*alternate*-**1** and 1D supramolecular chains constructed through C—H . . . N interactions in 1,3-*alternate*-**1**. Other hydrogen atoms are omitted for clarity.

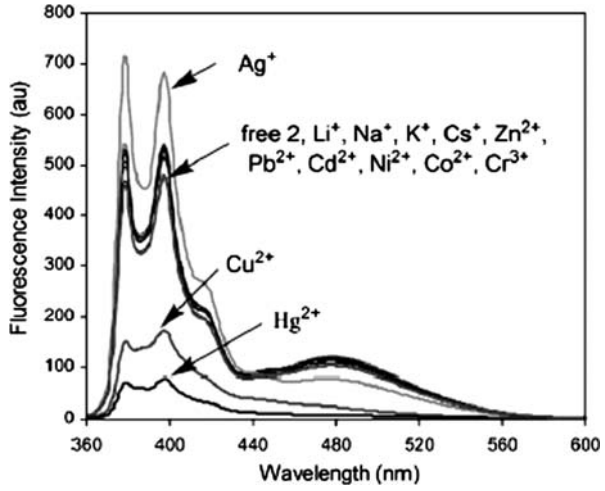

Figure 3. Fluorescence spectra of receptor **2** (5.0 μM) in $CH_3CN-CH_2Cl_2$ (1000:1, v/v) at 298 K upon addition of various metal ions (100 μM) as their aqueous solution.

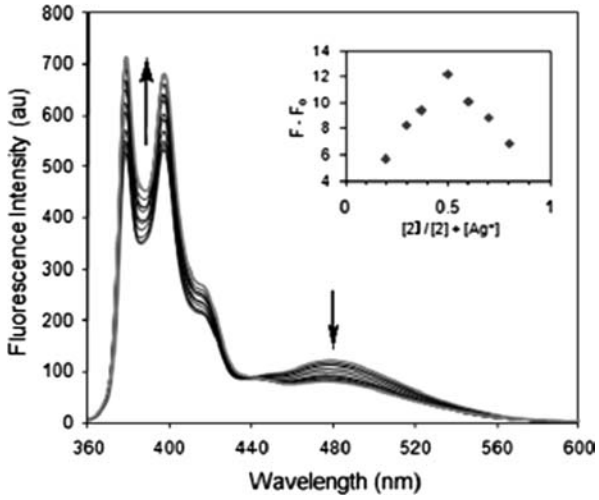

Figure 4. Fluorescence intensity changes of **2** (5.0 μM) upon addition of increasing concentrations of Ag^+ in aqueous solution (0–100 μM) at 298 K in $CH_3CN-CH_2Cl_2$ (1000:1, v/v) with an excitation at 343 nm. Inset: Job's plot showing a 1:1 stoichiometry.

dipole–dipole interactions. As shown in Figure 1, in the crystal structure of 1,3-*alternate*-**1**, the thiacalix[4]arene unit contains two nearly parallel 1,2,3-triazole groups functionalised with the 4-methoxybenzene moiety. It is clearly shown, Figure 2, that the N3 atom, N(402), of one 1,2,3-triazole tethered to a thiacalix[4]arene also acts as acceptor of an intermolecular hydrogen bond from the C5—H, C(205)—H(205) group of an adjacent molecule, with an H…N distance of 2.40 Å; thus, molecules are linked in chains.

Fluorescence spectroscopy studies

To better evaluate the recognition properties of 1,2,3-triazole groups based on thiacalix[4]arene, are synthesised 1,3-*alternate*-**2** (*37*), in which the methoxybenzyl unit of 1,3-*alternate*-**1** was replaced by the pyrene moiety as a fluorophore (*38–41*). Consequently, the binding behaviour of 1,2,3-triazole moieties based on thiacalix[4]arene towards different metal cations can be readily investigated by fluorescence spectroscopy. As shown in Figure 3, the fluorescence spectra of 1,3-*alternate*-**2** displayed a typical excimer emission around 485 nm and monomer emissions around 378 and 396 nm in $CH_3CN-CH_2Cl_2$ (1000:1, v/v) with excitation wavelength at 343 nm. The effect of addition of various metal ions such as Li^+, Na^+, K^+, Cs^+, Zn^{2+}, Pb^{2+}, Ag^+, Cu^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} as their perchlorate salts in the aqueous solution has been studied. As can be seen, when upon addition of Ag^+ into the solution of receptor **2**, an obvious enhancement of the monomer emission occurred, whilst the accompanying excimer emission decreased. On the other hand, both the excimer and monomer emissions of 1,3-*alternate*-**2** were acutely quenched by Cu^{2+} and Hg^{2+}, and much weaker fluorescence quenching was observed by addition of Pb^{2+}, Ni^{2+}, Co^{2+} and Cr^{3+} ions than by addition of Cu^{2+} and Hg^{2+}. No significant fluorescence intensity changes were shown upon the addition of alkali metal ions. Basically, the quenching in excimer emission of receptor **2** is due to a conformational change that occurred during the complexation of related metal ions with the nitrogen atoms on the triazole rings, which shows that it is not possible for the pyrene moieties to stack together for excimer emission, whereas the quenching in monomer emission of receptor **2** maybe attributed to reverse PET from pyrene groups to the nitrogen atom of the triazole units (*42*) or a heavy atom effect (*43*).

Figure 4 shows the fluorescence spectra of receptor **2** at various concentrations of Ag^+; upon addition of increasing

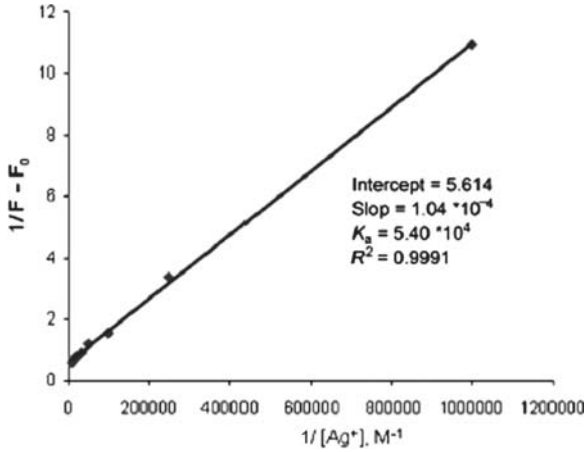

Figure 5. Benesi–Hildebrand plot of **2** with $AgClO_4$.

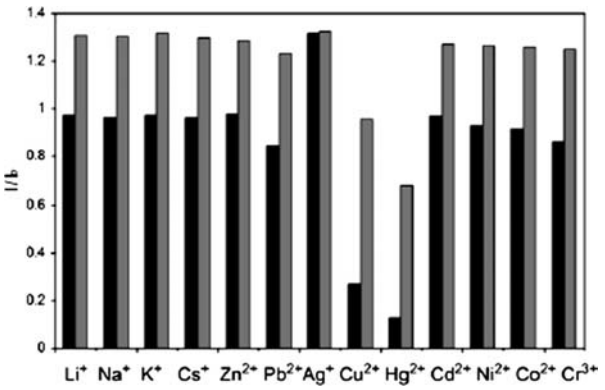

Figure 6. Fluorescence response of **2** (5.0 μM) in CH_3CN–CH_2Cl_2 (1000:1, v/v) to 100 μM various tested metal ions (black bar) and to the mixture of 100 μM tested metal ions with 100 μM Ag^+ (grey bar) at 298 K. I_0 is the fluorescence intensity at 378 nm for free **2**, and I is the fluorescence intensity after adding metal ions with an excitation at 343 nm.

amounts of Ag^+ as its perchlorate salt from 1 to 100 μM to the solution of receptor **2**, there was a significant enhancing monomer emission at 378 nm and an accompanying excimer emission decreasing at 485 nm was observed. On the basis of the titration experiments data, the association constant (K_a) for **2**·Ag^+ was thus calculated to be $5.40 \times 10^4\,M^{-1}$ by a Benesi–Hildebrand plot (Figure 5) (*44*). In the job pot (inset of Figure 4) (*45*), a maximum fluorescence intensity change appeared at 0.5 in the molar fraction of receptor **2** versus Ag^+, which clearly indicated a 1:1 complex of receptor **2** with Ag^+.

The practical applicability of receptor **2** as a selective chemosensor to Ag^+ was evaluated by a competitive experiment. As shown in Figure 6, the fluorescence intensity was almost identical to that obtained in the absence of other cations suggesting that no obvious interference to the selective response of receptor **2** to Ag^+ in the presence of most competitive metal ions except for the Hg^{2+} ion, for which interference with the detection signal abolished the ratiometric effect on complexation of Ag^+.

Proton NMR studies

The complexation modes of receptor **2** with Ag^+ were also investigated by ^{1}H NMR spectroscopy. Figure 7 shows the partial ^{1}H NMR spectra of receptor **2** in the absence and presence of Ag^+ in a mixture solution of $CDCl_3$–CD_3CN (10:1, v/v). Upon addition of 1.0 equiv. of Ag^+ to the solution of receptor **2**, some significant chemical shift changes are observed in the ^{1}H NMR spectra. For example, the proton H_b on the triazole ring undergoes a significant downfield chemical shift from δ 7.47 to 7.79 ppm ($\Delta\delta = 0.32$), and the proton H_c on the O–CH_2-triazole also moves downfield from δ 4.61 to 5.01 ppm, whereas the peaks of protons H_a and H_d have not undergone any obvious changes in the presence of Ag^+. These results strongly suggested that Ag^+ can be selectivity bound by

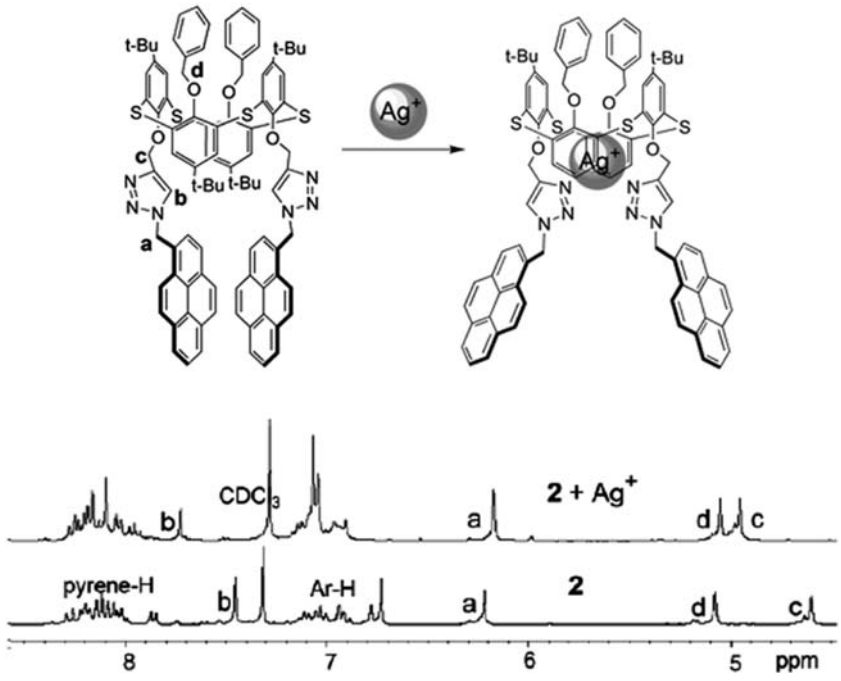

Figure 7. Proposed structure for 1,3-*alternate*-**2** on complexation with Ag^+ and ^{1}H NMR spectra of 1,3-*alternate*-**2** in $CDCl_3$–CD_3CN (10:1) and in the presence of 1.0 equiv. of $AgClO_4$ at 298 K (partial *tert*-Butyl moieties are omitted for clarity).

the nitrogen atoms of the triazole rings. On the other hand, the chemical shift changes of protons on the phenol of thiacalix[4]arene scaffold indicated that the ionophoric cavity, which was formed by the two inverted benzene rings with sulfur atoms framework based on thiacalix[4]-arene, is also involved in binding with Ag^+ (*46–48*).

Conclusion

In summary, the synthesis, structure and complexation behaviour of 1,2,3-triazole ring based on 1,3-*alternate*-thiacalix[4]arene have been investigated by X-ray analysis, fluorescence and ^{1}H NMR spectroscopy. These experimental results suggested that the nitrogen atoms on the triazole moiety of a thiacalix[4]arene have a strong binding affinity for Ag^+. We expect the novel electronic properties of triazole ring; such as the large dipole moment and electropositive C5–H group will lead to their increasing use as valuable design tools for self-assembly of supramolecular chemistry and cation-binding sites of receptors. Further investigation of 1,2,3-triazole-based calixarenes is currently ongoing.

Experimental

General

All melting points (Yanagimoto MP-S1) are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz using a Nippon Denshi JEOL FT-300 NMR spectrometer with $SiMe_4$ as an internal reference: *J* values are given in Hz. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct-inlet system through GLC. Elemental analysis: Yanaco MT-5.

Materials

5,11,17,23-Tetra-*tert*-butyl-25,27-dibenzyloxy-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene **3** was prepared according to the reported procedure (*28*).

5,11,17,23-Tetra-tert-butyl-25,27-dibenzyloxy-26,28-[bis(propargyloxy)]-2,8,14,20-tetrathiacalix[4]arene (4)

A suspension of *distal*-**3** (300 mg, 0.333 mmol) and Cs_2CO_3 (1.085 g, 3.33 mmol) was refluxed for 1 h in dry acetone (15 ml). A solution of 3-bromo-1-propyne [propargyl bromide (396 mg, 3.33 mmol)] in dry acetone (10 ml) was added and the mixture refluxed for 20 h. The solvents were evaporated and the residue partitioned between 10% HCl and CH_2Cl_2. The organic layer was dried ($MgSO_4$) and evaporated. The residue was recrystallised from $CHCl_3$–hexane (1:3, v/v) to afford the desired product **4** as colourless prisms with a yield of 81% (263.5 mg). Mp 180–182°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60, 0.85, 0.98, 1.11, 1.31 (each s, 36H, *t*Bu), 2.20–2.51, 4.41–5.08 (m, 10H, acetylene-*H*, ArO–CH_2-acetylene and ArO–CH_2-Ph) and 7.0–8.8 (18H, m, Ar*H*). FAB-MS: *m/z* 977.4 (M^+). Anal. calcd for $C_{60}H_{64}O_4S_4$ (977.42): C, 73.74; H, 6.61. Found: C, 74.10; H, 6.67. The splitting pattern in ^{1}H NMR shows that the isolated compound is a mixture of *cone*- and *partial-cone*-**4**. Compound **4** was not further isolated and directly used for the next reaction.

5,11,17,23-Tetra-tert-butyl-25,27-dibenzyloxy-26,28-bis{[1H-(4-methoxybenzyl)-(1,2,3-triazolyl)]-4-methoxy}-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate-1)

Copper iodide (5 mg) was added to compound **4** (112 mg, 0.12 mmol) and 4-methoxybenzyl azide (58 mg, 0.36 mmol) in 40 ml mixture of THF–H_2O (v/v = 4:1) and the mixture was heated at 65°C for 24 h. The resulting solution was cooled and extracted thrice with $CHCl_3$. The organic layer was separated and dried ($MgSO_4$) and evaporated to give the solid crude product. The residue was eluted from a chromatographic column of silica gel with hexane–ethyl acetate (v/v = 1:1) to give the desired product 1,3-*alternate*-**1** (112 mg, 74%). Recrystallisation from $CHCl_3$–hexane afforded X-ray quality colourless crystals. Mp 180–182°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (s, 18H, *t*Bu), 1.13 (s, 18H, *t*Bu), 3.78 (s, 6H, OMe), 4.89 (s, 4H, CH_2), 5.16 (s, 4H, CH_2), 5.46 (s, 4H, CH_2), 6.82 (s, 4H, ArH), 6.85 (d, *J* = 8.4 Hz, 4H, ArH), 7.23–7.02 (m, 14H, ArH), 7.34 (s, 4H, ArH) and 7.40 (s, 2H, Triazole-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.69, 30.76, 33.74, 34.09, 53.37, 55.23, 62.93, 72.10, 114.26, 122.84, 126.83, 127.25, 127.98, 128.02, 129.41, 129.47, 129.62, 131.56, 137.82, 144.04, 145.94, 146.18, 155.67, 157.61 and 159.68. FAB-MS: *m/z* 1303.50 (M^+). Anal. calcd for $C_{76}H_{82}N_6O_6S_4$ (1303.76): C, 70.01; H, 6.34; N, 6.45. Found: C, 69.71; H, 6.35; N, 6.37.

Crystallography

Crystallographic data for 1,3-alternate-1

Recrystallised from $CHCl_3$–hexane (1:3). Crystal data: $C_{76}H_{82}O_6N_6S_4$; $M = 1303.7$; crystal system: triclinic; space group: $P-1$; $a = 10.5587(2)$ Å, $b = 11.2767(2)$ Å, $c = 29.5518(5)$ Å; $\alpha = 90.906(2)°$, $\beta = 93.0121(14)°$, $\gamma = 101.166(2)°$, $V = 3446.06(11)$ Å^3; $Z = 2$; $D_c = 1.256$ g cm^{-3}; $R_{int} = 0.060$, $R\ [I > 2\sigma(I)]^a = 0.038$, $wR\ [I > 2\sigma(I)]^b = 0.078$ for 15,794 unique reflections. The intensity data of the compound 1,3-*alternate*-**1** were measured on an Oxford Diffraction Xcalibur-3/Sapphire 3 CCD diffractometer. Structural solution was obtained by direct methods using the SHELXS program, and refinement was done by full-matrix least-squares methods

on F^2 in the SHELXL program (*49*). All the non-hydrogen atoms in structure were refined anisotropically. The hydrogen atoms were generated geometrically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC–786359. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223/336 033; deposit@ccdc.cam.ac.uk).

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