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# Synthesis and evaluation of a novel pyrenyl-appended triazole-based thiacalix[4]arene as a fluorescent sensor for $Ag^+$ ion

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ABSTRACT

New fluorescent chemosensors 1,3-*alternate*-**1** and **2** with pyrenyl-appended triazole-based on thiacalix[4]arene were synthesized. The fluorescence spectra changes suggested that chemosensors **1** and **2** are highly selective for $Ag^+$ over other metal ions by enhancing the monomer emission of pyrene in neutral solution. However, other heavy metal ions, such as $Cu^{2+}$, and $Hg^{2+}$ quench both the monomer and excimer emission of pyrene acutely. The $^1H$ NMR results indicated that $Ag^+$ can be selectively recognized by the triazole moieties on the receptors **1** and **2** together with the ionophoricity cavity formed by the two inverted benzene rings and sulfur atoms of the thiacalix[4]arene.



## 1. Introduction

Owing to their simplicity, high sensitivity, and high detection limits for trace chemicals in chemistry, biology, and the environment,[1] fluorescent chemosensors have received much attention in the field of supramolecular chemistry. Generally, an effective fluorescent chemosensor includes an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore), that effectively converts the information of binding recognition from the ionophore unit into an easily monitored and a highly sensitive light signal from the fluorophore. Amongst the different fluorogenic units, pyrene is one of the most useful tools due to its relatively efficient monomer and excimer emissions. The sensing mechanism of pyrene is attributable to the intensity ratio of the excimer-to-monomer emission, which is very sensitive to conformational change.[2] On the other hand, the simple, effective, and versatile chemical modifications possible for calixarenes, together with their unique topology, offer a wide range of scaffolds enabling them to be selective for many different metal ions.[3–5]

Thiacalix[4]arenes, which have received growing interest since their discovery in 1997,[6] possess additional coordination sites and have shown a more flexible structure and strong affinity for both soft and hard transition-metal ions.[7] Acetates are amongst the most versatile compounds in calixarene chemistry, because the acetate group is easily converted to carboxylic acids, amides, and other esters.[7c] Given this, one of the most interesting features of thiacalix[4]arenes is that the conformation can be controlled by the reaction with ethyl bromoacetate in the presence of alkali carbonate as base. Additionally, with the development of the electronics industry and photographic and imaging industry, more attention has been paid to the negative effect of silver ions on the environment. For example, it is believed that silver ions can bind to various metabolites and enzymes, such as in the deactivation of sulphydryl enzyme,[8] and as a consequence, many methods have been utilized to measure trace amounts of silver ion; including atomic absorption, ICP atomic emission, UV–vis absorption, and fluorescence spectroscopy. Among these approaches, fluorescence spectroscopy is widely used because of its high sensitivity and facile operation. However, due to silver belonging to heavy transition-metal ions, which usually quench fluorescence emission via enhanced spin-orbital coupling,[9] energy or electron transfer,[10] only a few fluorescent 'turn on' chemosensor for detecting silver ion have been reported at present.[11] Fluorescence quenching is not only disadvantageous for a high signal output during detection but is also undesirable for analytical purposes.[12] As a result, the development of highly selective chemosensors for the $Ag^+$ ion still remains a challenge.

With these observations in mind, we continue our studies into the design and synthesis of chemosensors for heavy metal ions.[13]

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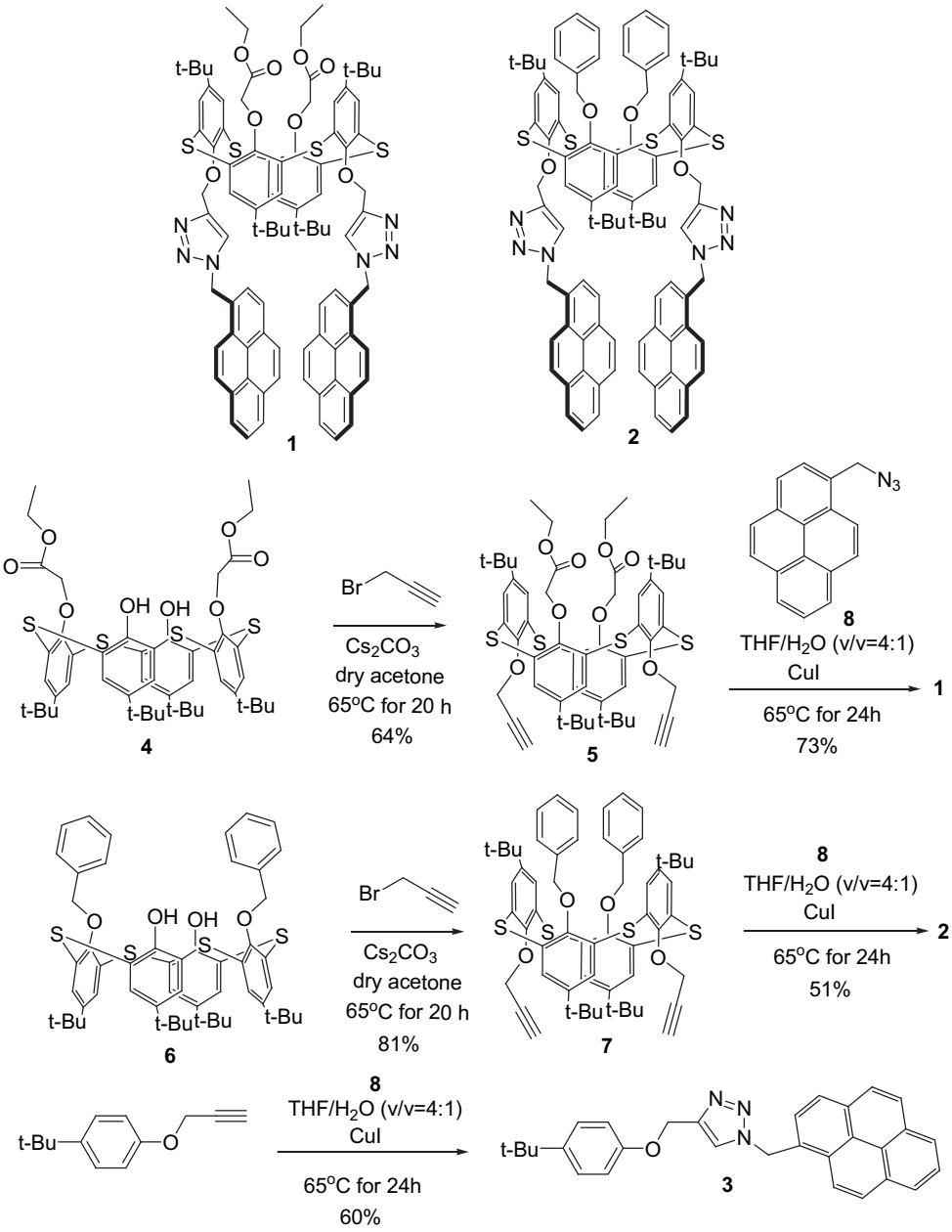
Herein, we have designed a new fluorescent sensor through pyrene-appended triazole-based thiacalix[4]arene with 1,3-*alternate* conformation. Such chemosensors display high affinity for silver ion by changing the monomer and excimer emission of the pyrene moieties.

## 2. Results and discussion

As shown in Scheme 1, compound *cone*-**4** can be obtained following the reported precedures.[14] Thus, compound 1,3-*alternate*-**5** was prepared in 64% yield by the reaction of compound *cone*-**4** with propargyl bromide in the presence of $Cs_2CO_3$ in dry acetone. Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction of compound 1,3-*alternate*-**5** with 1-azidomethylpyrene **8** under Click conditions afforded the 1,2,3-triazole thiacalix[4]arene 1,3-*alternate*-**1** in 73% yield. A similar procedure was employed in the synthesis of receptor 1,3-*alternate*-**2** with 51% yield. The reference compound **3** was prepared by *O*-propargyl $^t$Bu phenyl reactions with azide **8** through Click chemistry in a yield of 60%.

The fluorescence spectra of 1,3-*alternate*-**1** and **2** appeared with a typical intramolecular excimer emission around 485 nm and monomer emissions around 378 and 396 nm in organic solution, and a typical monomer emission appeared for reference compound **3** (excitation at 343 nm) in $CH_3CN/CH_2Cl_2$ (1000:1, v/v) (Fig. 1). The excimer emission band was attributed to the interaction of two pyrene units forming an intramolecular $\pi\cdots\pi$ stacking, which was fixed by the thiacalix[4]arene scaffold.[15] The cation-binding properties of receptors **1**–**3** were then investigated by fluorescence spectroscopy. The fluorescence intensity changes upon addition of various perchlorate salts, such as $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Zn^{2+}$, $Pb^{2+}$, $Ag^+$, $Cu^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Cr^{3+}$ in aqueous solution, are depicted in Fig. 1. It was observed that both the excimer and monomer emissions of receptor 1,3-*alternate*-**1** were strongly quenched by $Hg^{2+}$, and $Cu^{2+}$. By contrast, upon addition of $Ag^+$ ion into the solution of receptor **1**, an obvious enhancement of the




**Scheme 1.**

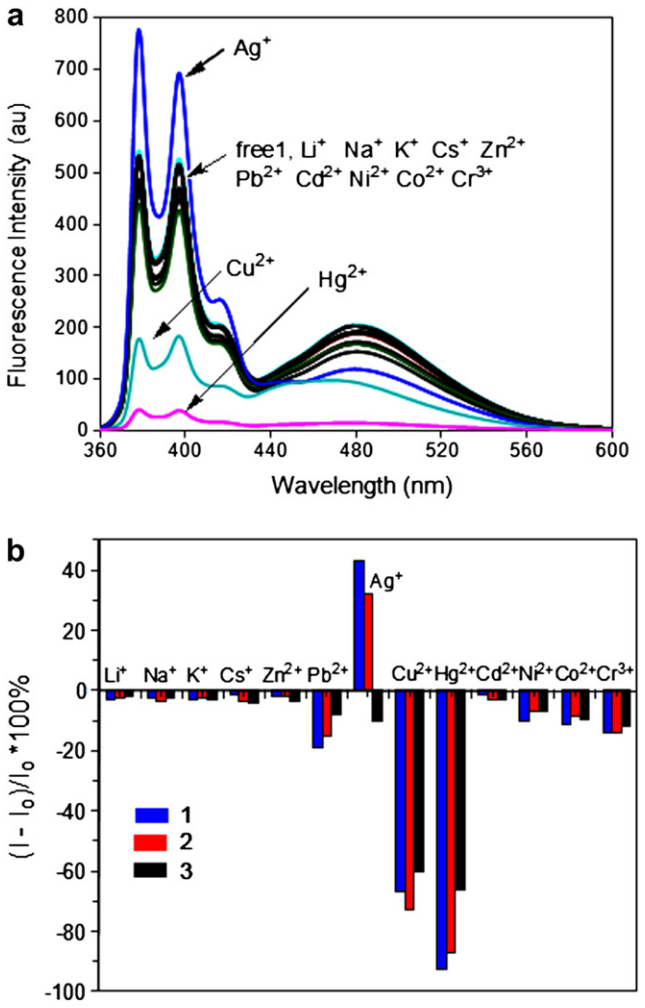



**Fig. 1.** Fluorescence spectra of the receptor **1** (5.0 μM) (a) and relative fluorescence intensity changes of the receptors **1**–**3** (each of 5.0 μM) (b) in $CH_3CN/CH_2Cl_2$ (1000:1, v/v) at 298 K upon addition of various metal ions (100 μM) as their aqueous solution. $I_o$ is fluorescent emission intensity at 378 nm for free receptors, and $I$ is the fluorescent intensity after adding metal cations with an excitation at 343 nm.

The fluorescence spectra of 1,3-*alternate*-**1** at various concentrations of $Ag^+$ ion are shown in Fig. 2. As can be seen, the fluorescence intensity of the monomer emission of receptor **1** gradually increased on increasing concentrations of $Ag^+$ ion from 0 to 100 μM and was accompanied by a concomitant decrease in the excimer emission. A discernible isoemissive point appeared at 430 nm. On the basis of the fluorescence titration experiments, the association constant ($K_a$)[18] for **1**·$Ag^+$ was determined to be $1.33\times10^5$ $M^{-1}$, and a job plot[19] for the complexation showed a 1:1 stoichiometry (Fig. 2). Similar fluorescence titration behavior was also evaluated in the case of receptors **1** and **2** with related metal ions (Figs. S3–S7). From these observations, the association constants for complexation were calculated to be: **1**·$Hg^{2+}$= $4.24\times10^4$ $M^{-1}$, **1**·$Cu^{2+}$= $3.97\times10^4$ $M^{-1}$, **2**·$Ag^+$= $5.40\times10^4$ $M^{-1}$, **2**·$Hg^{2+}$= $2.46\times10^4$ $M^{-1}$, **2**·$Cu^{2+}$= $5.39\times10^4$ $M^{-1}$, respectively.

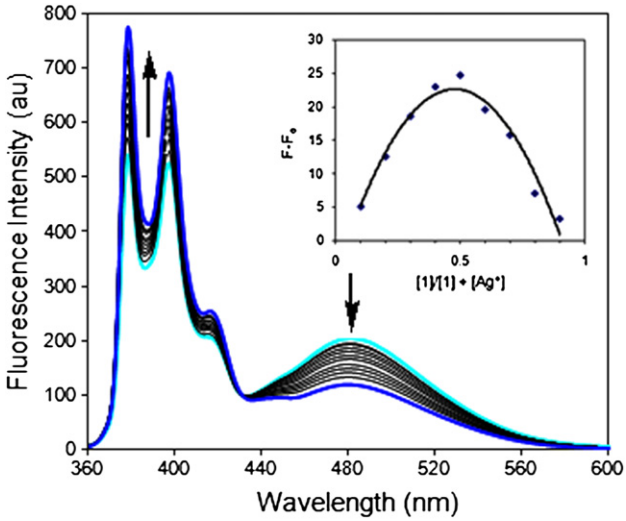



**Fig. 2.** Changes in the fluorescence emission spectra of **1** (5.0 μM) upon addition of increasing concentrations of $Ag^+$ ion in aqueous solution (0–100 μM) at 298 K in $CH_3CN/CH_2Cl_2$ (1000:1, v/v) with an excitation at 343 nm. Inset: Job's plot showing a 1:1 stoichiometry.

monomer emission occurred, whilst the accompanying excimer emission declined (Fig. 1a). Much weaker responses for fluorescence emissions of the monomer and excimer quenching were given by addition of $Pb^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Cr^{3+}$ ions, and no significant fluorescence intensity changes were observed upon addition of alkali metal ions. Similar selective fluorescent behavior caused by metal ions was also observed for receptor **2** (Fig. 1b and Fig. S1). However, under the same analytical conditions, the fluorescent intensity of compound **3** (Fig. 1b and Fig. S2) was not obviously changed upon addition of $Ag^+$ ion and other metal ions, except in the cases of $Hg^{2+}$ and $Cu^{2+}$ ions, where acute quenching was observed. These results indicated that the fluorescent sensitive and selective binding of $Ag^+$ ion requires the coordination of two triazole rings of receptors **1** and **2**. Generally, the fluorescence of monomer emission quenching by heavy atoms, such as $Hg^{2+}$ and $Cu^{2+}$ in the chemosensors **1**–**3** can be attributed to the reverse PET (photon electron transfer)[16] from the pyrene unit to the nitrogen atoms of triazole ring or a heavy atom effect.[17] The excimer quenching is a result of a conformational change, which occurs during the binding of the targeted metal ions with the nitrogen atoms on the triazole ring. In this procedure, the coordination forces make the pyrene groups move far away from each other and inhibits the π···π stacking for generating excimer emission.

To better investigate the practical applicability of the receptors **1** and **2** as $Ag^+$ ion selective fluorescent sensor, competitive experiments were carried out in the presence of $Ag^+$ ion (100 μM) mixed with $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Zn^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Cr^{3+}$ at 100 μM; as shown in Fig. 3 and Fig. S8, no significant interference in detection of $Ag^+$ with receptors **1** and **2** was observed in the presence of most other competitive metal ions except for the $Hg^{2+}$ ion, for which interference with the detection signal abolished the ratiometric effect on binding of $Ag^+$ ion. Accordingly, these observations suggested that receptors **1** and **2** can be used as selective fluorescent sensors for $Ag^+$ ion in the presence of most completive metal ions.

In order to obtain detailed information on the complexation structure of receptors **1** and **2** with $Ag^+$ ion, $^1H$ NMR titration experiments in $CDCl_3/CD_3CN$ (10:1, v/v) were carried out. The partial spectral changes are shown in Fig. 4. Upon addition of 1.0 equiv of $Ag^+$ ion to the solution of 1,3-*alternate*-**1**, as expected, the chemical shift of proton $H_b$ on the triazole ring exhibited a significant downfield shift by $\Delta\delta$ 0.45 ppm from $\delta$ 7.29 ppm. The peak of $H_c$ on the O$CH_2$-triazole unit and $H_f$ also demonstrated a similar but smaller downfield shift from $\delta$ 4.87 to 5.06 ppm and $\delta$ 4.42 to 4.58 ppm, respectively, whereas the peaks of the protons on the ester moieties were little affected. Additionally, similar coordination behavior was observed for the complexation **2**·$Ag^+$ (Fig. S12). These

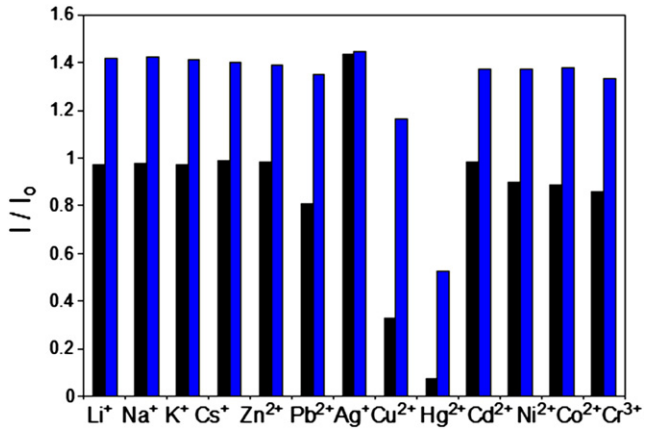



**Fig. 3.** Fluorescence response of **1** (5.0 μM) in $CH_3CN/CH_2Cl_2$ (1000:1, v/v) to 100 μM various tested metal ions (black bar) and to the mixture of 100 μM tested metal ions with 100 μM $Ag^+$ ion (blue bar) at 298 K. $I_0$ is the fluorescence intensity at 378 nm for free **1**, and $I$ is the fluorescence intensity after adding metal ions with an excitation at 343 nm.

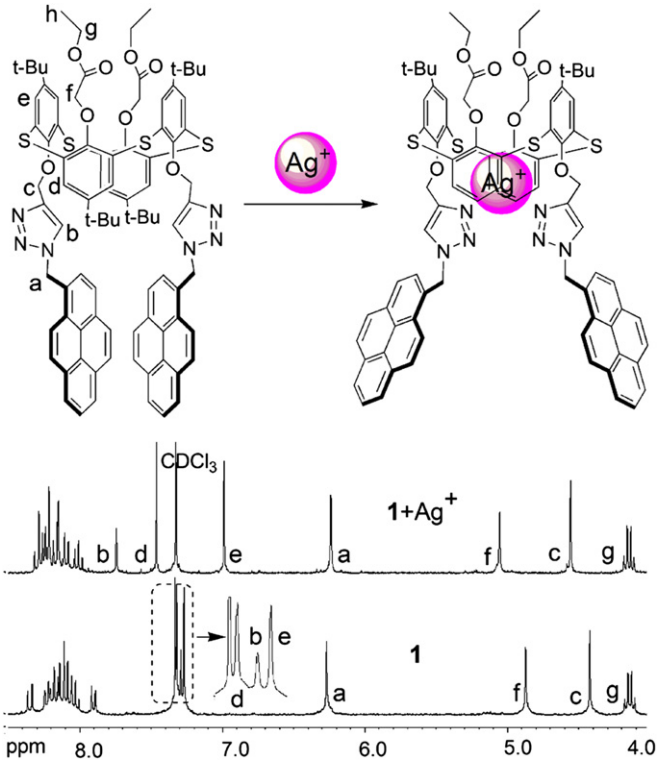



**Fig. 4.** Plausible complexation structure of receptor **1** for $Ag^+$ ion, and partial $^1H$ NMR spectra of **1** (5.0 mM) in $CDCl_3/CD_3CN$ (10:1, v/v) upon addition of 1.0 equiv $Ag^+$ ion at 298 K; (partial *tert*-butyl moieties are omitted for clarity).

spectral changes suggested that $Ag^+$ ion can be selectively bound by the nitrogen atoms on the triazole rings. On the other hand, it should be noted that the protons of $H_d$ and $H_e$ on the phenol 1,3-*alternate* thiacalix[4]arene also experienced a downfield shift from $\delta$ 7.32 to 7.50 ppm and an upfield shift from $\delta$ 7.26 to 6.98 ppm, respectively. These data further indicated that there must be a conformational change for receptor **1** in the presence of $Ag^+$ ion. As a matter of fact, it is believed that the conformation of thiacalix[4]arene can be preorganized for the binding of $Ag^+$ ion in solution in a manner, that is, similar to an example described by Shinkai and coworkers.[20] In that case, the X-ray structure clearly demonstrated that $Ag^+$ ion was included in the π-basic benzene cavity at the lower rim, where the two distal benzene rings were being flattened and the residual two benzene rings were standing upright for binding $Ag^+$ ion. Thus, we conclude that the two triazole groups and the ionophoricity cavity, formed by the two inverted benzene rings with the sulfur atoms framework based on thiacalix[4]arene, are all involved in the complexation with the $Ag^+$ ion.[21]

## 3. Conclusion

In conclusion, we have synthesized a new type of fluorescent sensor having triazole rings as cation-binding sites on the lower rim of a thiacalix[4]arene scaffold with 1,3-*alternate* conformation. The selective binding behavior of receptors **1** and **2** has been evaluated by fluorescence spectra and $^1H$ NMR analysis. All the results suggested that the triazole moieties on the receptors **1** and **2** are highly sensitive and selective for $Ag^+$. This is due to cooperative coordination by the ionophoricity cavity, formed by the two inverted benzene rings and the sulfur atoms of the thiacalix[4]arene, by enhancement of the monomer emission of pyrene.

## 4. Experimental section

### 4.1. General

All melting points (Yanagimoto MP-S1) are uncorrected. NMR spectra were determined at 300 MHz with a Nippon Denshi JEOL FT-300 spectrometer with $Me_4Si$ as an internal reference: $J$ values are given in hertz. IR spectra were measured for samples as KBr pellets in a JASCO FT/IR 4200. All the fluorescence spectra were recorded on a JASCO FP-6200 spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by Yanaco MT-5.

### 4.2. Materials

Compounds **4**,[14] **6**,[22] and **8**[15b] were prepared following the reported procedure.

*4.2.1. 5,11,17,23-Tetra-tert-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-[bis(propargyloxy)]-tetrathiacalix[4]arene (1,3-alternate-**5**). Cone-***4*** (300 mg, 0.34 mmol) and $Cs_2CO_3$ (1.085 g, 3.33 mmol) were refluxed for 1 h in dry acetone (15 mL). 3-Bromo-1-propyne [propargyl bromide (396 mg, 3.33 mmol)] and 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 separated and dried ($MgSO_4$) and the solvents were evaporated. The residue was recrystallized from $CHCl_3$/hexane (3:1) to afford 1,3-*alternate*-5 (210 mg, 64%) as prisms. Mp 223–225 °C. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.06 (18H, s, $^t$Bu), 1.28 (6H, m, $CH_2CH_3$), 1.40 (18H, s, $^t$Bu), 2.10 (1H, t, $J$=3.0 Hz, acetylene-H), 2.44 (1H, m, acetylene-H), 4.25 (4H, q, $J$=7.1 Hz, $CH_2CH_3$), 4.61 (4H, s, $CH_2$), 4.83 (4H, s, $CH_2$), 7.46 (4H, s, ArH), 7.59 (4H, s, ArH). IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 3309, 2958, 1768, 1575, 1440, 1367, 1268, 1193, 1085, 1010. FABMS: $m/z$ 969.39 ($M^+$). Anal. Calcd for $C_{54}H_{64}O_8S_4$ (969.35): C, 66.91; H, 6.66. Found: C, 67.09; H, 6.70.

*4.2.2. 5,11,17,23-Tetra-tert-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-bis[1H-(1-pyrenylmethyl-(1,2,3-triazolyl)-4-methoxy)]-tetrathiacalix[4]arene (1,3-alternate-**1**).* Copper iodide (20 mg) was added to a solution of 1,3-*alternate*-**5** (174 mg, 0.18 mmol) and 1-(azidemethyl)pyrene **8** (139 mg, 0.54 mmol) in 20 mL THF/$H_2O$ (4:1) and the mixture was heated at 65 °C for 24 h. The resulting solution was cooled and diluted with water and extracted thrice with $CH_2Cl_2$. The organic layer was separated and dried ($MgSO_4$)

and evaporated to give the solid crude product. The residue eluted from a column chromatography of silica gel with hexane/ethyl acetate (v/v=4:1) to give the desired product 1,3-*alternate*-**1** (194 mg, 73%) as colorless prisms. Mp 154–156 °C. $^1$H NMR (300 Hz, $CDCl_3$) $\delta$ 0.88 (18H, s, $^t$Bu), 1.08 (18H, s, $^t$Bu), 1.22 (6H, t, $J$=7.1 Hz, $CH_2CH_3$), 4.15 (4H, q, $J$=7.1 Hz, $CH_2CH_3$), 4.45 (4H, s, $CH_2$), 4.84 (4H, s, $CH_2$), 6.28 (4H, s, $CH_2$), 7.24 (4H, s, ArH), 7.28 (2H, s, Triazole-H), 7.33 (4H, s, ArH), 7.88 (2H, d, $J$=9.0 Hz, Pyrene-H), 7.99–8.23 (14H, m, Pyrene-H), 8.34 (2H, d, $J$=9.0 Hz, Pyrene-H). $^{13}$C NMR (75 MHz, $CDCl_3$): 14.07, 22.59, 31.01, 33.82, 52.08, 60.43, 64.85, 67.60, 122.18, 123.22, 124.45, 124.85, 124.94, 125.62, 125.71, 126.21, 127.18, 127.25, 128.04, 128.23, 128.79, 129.07, 130.54, 131.13, 131.84, 131.96, 133.15, 144.59, 145.97, 146.00, 156.51, 157.20, 167.91. IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 2960, 2360, 1768, 1442, 1380, 1265, 1190, 1045. FABMS: $m/z$ 1483.42 ($M^+$). Anal. Calcd for $C_{88}H_{86}N_6O_8S_4$ (1483.92): C, 71.23; H, 5.84; N, 5.66. Found: C, 71.09; H, 5.70; N, 5.64.

*4.2.3. 5,11,17,23-Tetra-tert-butyl-25,27-dibenzyloxy-26,28-[bis-(propargyloxy)]-tetrathiacalix[4]arene (**7**).* A suspension of compound **6** (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 recrystallized from $CHCl_3$/hexane (1:3, v/v) to afford the desired product **7** as colorless prisms with a yield of 81% (263.5 mg). Mp 180–182 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 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, ArH). IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 3307, 2960, 1575, 1432, 1367, 1265, 1085, 1008. FABMS: $m/z$ 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*-**7**.

*4.2.4. 5,11,17,23-Tetra-tert-butyl-25,27-bisbenzyl-26,28-bis[1H-(1-pyrenylmethyl-(1,2,3-triazolyl)-4-methoxy)]-tetrathiacalix[4]arene (1,3-alternate-**2**).* Copper iodide (20 mg) was added to compound **7** (112 mg, 0.12 mmol) and azide **8** (92 mg, 0.36 mmol) in 20 mL THF/$H_2O$ (4:1) and the mixture was heated at 65 °C for 24 h. The resulting solution was cooled and diluted with water and extracted thrice with $CH_2Cl_2$. The organic layer was separated and dried ($MgSO_4$) and evaporated to give the solid crude product. The residue eluted from a column chromatography of silica gel with hexane/$CH_2Cl_2$ (1:1, v/v) to give the desired product (92 mg, 51%). Mp 134–136 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.46 (18H, s, $^t$Bu), 1.14 (18H, s, $^t$Bu), 4.64 (4H, s, $CH_2$–Triazole), 5.08 (4H, s, $CH_2$Ph), 6.24 (4H, $CH_2$–Pyrene), 6.74 (4H, s, ArH), 7.11–6.9 (14H, m, Ph–H), 7.45 (2H, s, Triazole–H) 7.86–8.28 (18H, m, Pyrene–H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 30.38, 31.25, 33.41, 34.15, 52.26, 63.93, 72.69, 122.29, 123.29, 124.52, 124.84, 125.01, 125.75, 125.79, 126.29, 126.83, 126.97, 127.23, 127.29, 127.34, 127.41, 127.85, 127.99, 128.16, 128.98, 129.24, 129.69, 129.76, 130.62, 131.22, 131.98, 132.98, 137.86, 143.99, 145.58, 146.01, 155.56, 158.09. IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 2960, 2364, 1646, 1434, 1375, 1265, 1083. FABMS: $m/z$ 1491.23 ($M^+$). Anal. Calcd for $C_{94}H_{86}N_6O_4S_4$ (1491.99): C, 75.67; H, 5.81; N, 5.63. Found: C, 75.35; H, 5.67; N, 5.54.

*4.2.5. 4-tert-Butyl-[1H-(1-pyrenylmethyl-(1,2,3-triazolyl)-4-methoxy)] benzene (**3**).* A mixture of 4-*tert*-butyl-1-(propargyloxy) benzene (95 mg, 0.5 mmol) and **8** (140 mg, 1.1 mmol) in 20 mL THF/$H_2O$ (4:1) and the mixture was heated at 65 °C for 24 h at the presence of CuI as catalyst. The resulting solution was cooled and diluted with water and extracted thrice with $CH_2Cl_2$. The organic layer was separated and dried ($MgSO_4$) and evaporated to give the solid crude product. The residue eluted from a column chromatography of silica gel with hexane/ethyl acetate (6:1, v/v) to give the desired product **3** (134 mg, 60%) as pale yellow prisms. Mp 147–149 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.24 (9H, s, $^t$Bu), 5.07 (2H, s, $CH_2$), 6.25 (2H, s, $CH_2$), 6.82 (2H, d, $J$=5.4 Hz, ArH), 7.22 (2H, d, $J$=5.4 Hz, ArH), 7.37 (1H, s, Triazole-H), 7.94–8.25 (9H, m, Pyrene-H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 31.41, 33.98, 52.42, 62.10, 114.19, 121.85, 124.42, 124.88, 125.02, 125.79, 125.90, 126.15, 126.35, 126.61, 127.15, 127.62, 128.27, 129.03, 129.26, 130.51, 131.12, 132.10, 143.84, 155.88. IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 2954, 2360, 1768, 1442, 1380, 1265, 1190, 1045. FABMS: $m/z$ 445.26 ($M^+$). Anal. calcd for $C_{30}H_{27}N_3O$ (445.57): C, 80.87; H, 6.11; N, 9.43. Found: C, 80.62; H, 6.03; N, 9.36.

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## Supplementary data

Experimental procedures, $^1$H and $^{13}$C NMR spectral data, fluorescence and $^1$H NMR titration spectra data are available. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.03.008.

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