

A Pyrenyl-Appended Triazole-Based Calix[4]arene as a Fluorescent Sensor for Iodide Ion[†]

Jong Seung Kim,^{*} Sun Young Park, Sang Hoon Kim, Pierre Thuéry,[‡] Rachid Souane,[#]
Susan E. Matthews,^{§,*} and Jacques Vicens^{#,*}

*Department of Chemistry, Korea University, Seoul 130-701, Korea. *E-mail: jongskim@korea.ac.kr*

[‡]CEA, IRAMIS, SCM, LCCEf (CNRS URA 331), Bât. 125, 91191 Gif-sur-Yvette, France

[§]School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, U.K

**E-mail: susan.matthews@uea.ac.uk*

*[#]IPHC-UdS-ECPM-CNRS, 25 rue Becquerel, F-67087, Strasbourg, Cédex, France. *E-mail: vicens@chimie.u-strasbg.fr*

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The synthesis and evaluation of a novel calix[4]arene-based fluorescent chemosensor **1** for the detection of I[−] is described. The fluorescent changes observed upon addition of various anions show that **1** is selective for I[−] over other anions. Addition of I[−] results in ratiometric measurements with 1 : 1 complex ratio.

Key Words: 1,2,3-Triazole, Calixarenes, Fluorescent sensors, Anion sensing, Iodide

Introduction

Iodide is recognized as an ion of significant physiological importance due to its essential role in the normal growth, development and functioning of the brain and body.¹ Any deficiency of iodide can give rise to serious diseases such as enlarged goitres or mental retardment. Iodine is a biologically essential element in seawater, where it exists predominantly as the iodide species and some organic iodine compounds. Numerous analytical methods have been developed for iodide analysis in various samples such as seawater, drinking water, milk, seaweed, and salts.¹ Since the pioneering work of Czarnik² in the detection of analytes by using fluorescent chemosensors,³ anion sensing by anion-responsive optical sensors has been developed during the last decade.⁴ With regard to the iodide ion only a few reports dealing with fluorescent sensors can be found in the literature. For instance, Singh and Jang have synthesized a neutral tripodal fluorescent receptor bearing benzimidazole motifs which exhibit a quenching of fluorescence intensity only in the presence of I[−] in acetonitrile-water mixture with no significant changes on addition of other anions such as F[−], Cl[−], Br[−], HSO₄[−], NO₃[−], CH₃COO[−], and H₂PO₄[−].⁵ Carbazole based sensors have also found favour with Ming *et al.* reporting such neutral anion receptor showing a good selectivity for I[−] which was attributed mainly to the complementarity of the geometries between the receptor and iodide ion.⁶ Similarly, Valiyaveetil and co-workers published a series of carbazole-containing conjugated copolymers as colorimetric/fluorimetric sensors for iodide ion.⁷ The UV-vis and fluorescence spectra of polymers were significantly affected by the addition of tetrabutylammonium iodide (TBI) in THF whereas changes were not observed in the presence of other anions such as fluoride, chloride, and bromide salts.⁷ Gunnlaugsson and co-workers have reported the design, synthesis and photophysical evaluation of anthracene-based photoinduced elec-

tron transfer (PET) sensors for anions.⁸ The highest affinity was observed for F[−] from a diverse series of anions and, to a lesser extent, for I[−] which was proposed to be due to the ground state interactions between the receptors and the anion.⁸ Jang and colleagues recently synthesized a Cu(II) complex of a tripodal receptor bearing an anthracene moiety on one pod as the fluorophore.⁹ The anion recognition behaviour of the Cu(II) complex was evaluated in acetonitrile-water resulting in an extremely high selectivity for iodide over other anions such as F[−], Cl[−], Br[−], NO₃[−], CH₃COO[−], and H₂PO₄[−].⁹ A fluorescence turn-on probe for iodide based on the redox reaction between cupric and iodide has been recently published by Lin and coll.¹⁰

As part of our on-going studies on simple and easy-to-make fluorescent sensors for anion recognition,¹¹ we present here the synthesis and anion binding studies of a pyrenyl-appended triazole-based calix[4]arenes as fluorescent sensors for anions.¹²

The development of the Cu(I)-catalysed 1,3-dipolar cycloaddition of alkynes and azides by Meldal¹³ and Sharpless¹⁴ from the original thermal reaction of Huisgen¹⁵ has provided a straightforward molecular linking strategy which has been adopted in a wide range of applications.¹⁶ In addition, it has also been demonstrated that the triazoles formed during the coupling reaction are themselves excellent cation binding motifs¹⁷ and if suitably arranged can act cooperatively to provide receptors and sensors.¹⁸ Recently we¹⁹ and others²⁰ have shown that when such arrays are incorporated onto a tailored calixarene scaffold can be useful for the selective binding of Cd²⁺, Ca²⁺, Pb²⁺, and Zn²⁺.

More recently it has been shown that triazole units can act as an amide mimics enabling protein folding by virtue of the polarized strong C-H hydrogen bond donors.²¹ This result has additionally opened up the potential of triazoles to act as anion binding motifs through C-H hydrogen bond donation. Thus, single triazoles,²² bistriazoles,²²⁻²⁴ rigid tetrameric triazole macrocycles,²⁵ and triazole linked dendrimers²⁶ have all been demonstrated to bind a range of anions including halides and phosphates. In this report we describe the synthesis, *via* the click reac-

[†]This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

tion, of two new calixarenes derivatives featuring pyrene reporting units and investigate their ability, along with previously prepared derivatives to act as fluorescent anion sensors.

Results and Discussion

Three potential fluorescent anion sensors were investigated in this study. We have synthesized a series of *p*-*tert*-butylcalix[4]arenes appending pyrene fluorophores **1–3** (Chart 1) incorporated into a 1,2,3-triazole spacer *via* the ‘click’ reaction and measured their optical properties and fluorescence changes upon anion binding.

According to scheme 1, compound **1** was prepared in a short synthetic sequence from the known^{27,28} dipropargyl derivative of *p*-*tert*-butylcalix[4]arene (**4**). Firstly, the two ester binding moieties were introduced through exhaustive alkylation with methyl bromoacetate in the presence of NaH to give the tetrafunctionalised calix[4]arene (**5**) in 74% yield. The fluorescent

pyrene reporting units were then incorporated using our previously developed conditions¹⁹ for the Cu(I)-catalysed 1,3-dipolar cycloaddition of calix[4]arene alkynes and azides, namely reaction of **5** with 1-azidomethyl pyrene (**6**) in the presence of CuI in DMF for 2 h at 90 °C.

We have previously described the synthesis of **2**, the mono ester mono pyrene receptor, through a cycloaddition between **7** and **6**.¹⁹ The synthesis of **8** from the common precursor **7** was achieved through the introduction of the amine binding group on treatment with commercial dimethylethyleneamine. The importance of amine binding in enhancing Cu(I) mediated click reactions was verified through the observation that introduction of the pyrene reporting unit to prepare sensor **3** proceeded swiftly at room temperature in this case which can be proposed to be due to intra/intermolecular formation of amine copper complexes.

The conservation of the original fixed cone conformation of the calix[4]arene was confirmed by the presence of doublets for

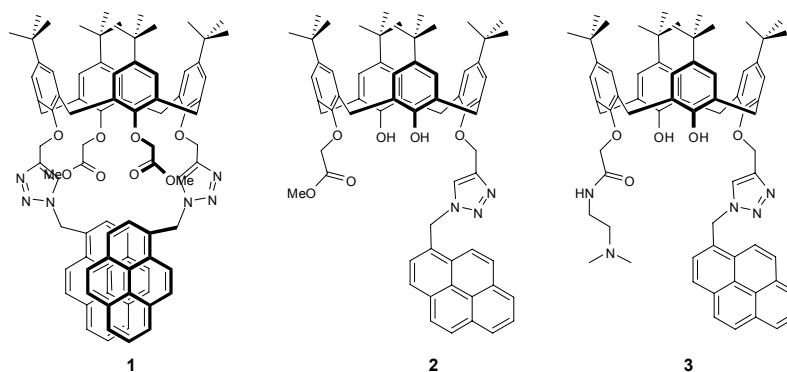
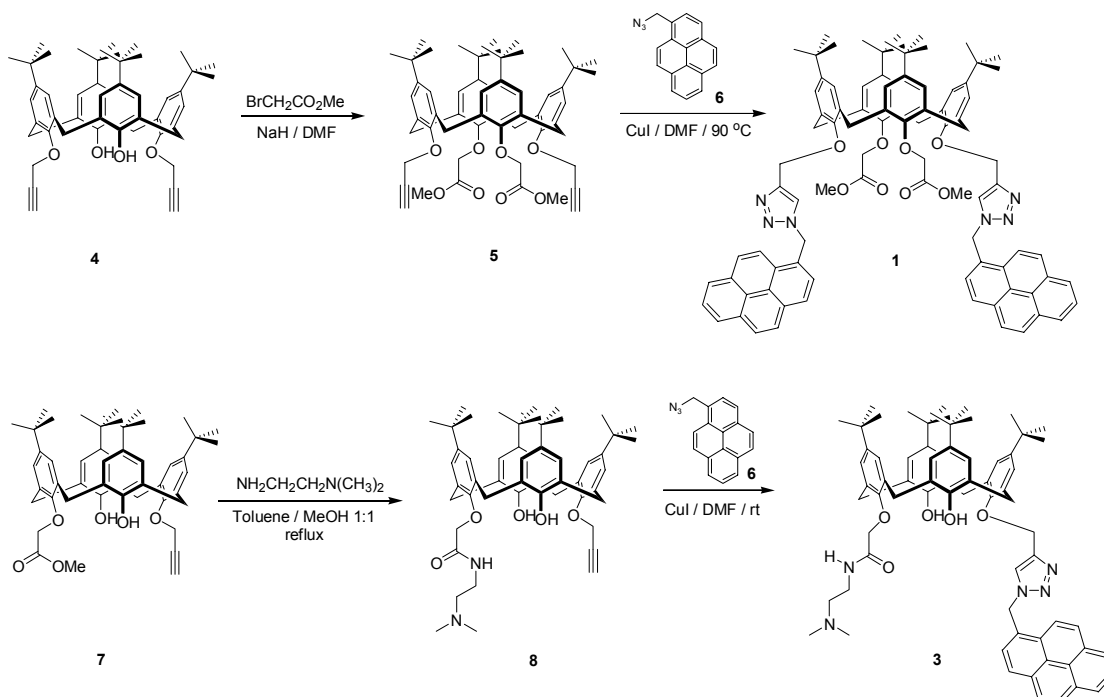


Chart 1. Structures of fluorescent sensors **1–3**



Scheme 1. Synthesis of **1**, **3**, **5**, and **8**

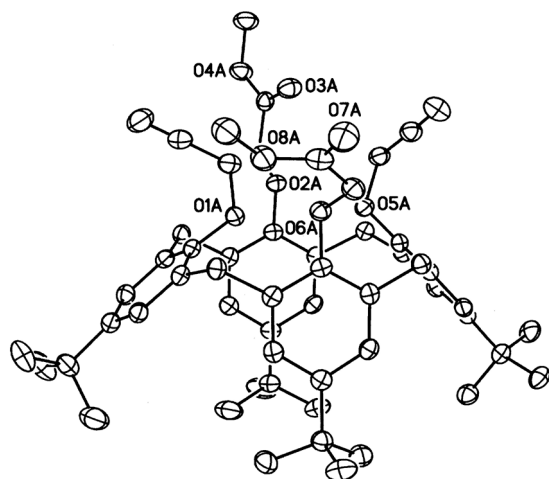


Figure 1. ORTEP view of **5**. Hydrogen atoms are omitted for clarity.

the ArCH_2Ar protons at ~ 3 and 4 ppm. The formation of the 1,2,3-triazole rings was shown from appearance of the triazole- H signal as a singlet within the range at 7.52 ppm for **1** and 7.88 ppm for **3** and the down-field shift of the OCH_2 -triazole linker. All analytical data of **1**, **3**, **5**, and **8** are given in the experimental section. The cone conformation of **5** was also confirmed by the determination of its crystal structure (Figure 1).

The fluorescence properties of **1-3** were investigated in acetonitrile (Figure 2). On excitation at 343 nm, the maximum absorption wavelength of the pyrene, **1** displays monomer and excimer bands at 395 and 475 nm, respectively, whereas **2** and **3** both exhibit only the monomer band at 395 nm. Compared with **2**, **3** shows a relatively weaker emission, which is attributable to the fact that the pendent amide group ($-\text{CH}_2\text{CONH}-$) takes part in a PET (photo-induced electron transfer) process: an electron transfer from a lone-pair electron of the nitrogen atom (HOMO) to the pyrene unit of **3** (LUMO).

UV/vis absorption and fluorescence changes have been investigated on the addition of tetrabutylammonium (Bu_4N^+) salts of F^- , Cl^- , Br^- , I^- , CH_3CO_2^- , OH^- , HSO_4^- , and H_2PO_4^- to CH_3CN solutions of **1-3**. From UV/vis and fluorescence spectral changes of **1-3** (Figure 3), we found that only **1** exhibits I^- selectivity over the other anions tested. Addition of I^- to the CH_3CN solution of **1** induced a marked ratiometry where the monomer emission of **1** increases as its excimer emission concomitantly declines (Figure 4 (a)). In contrast, **2** and **3** bearing only one pyrene unit, show no significant spectral changes upon addition of any anions.

Figure 4 shows the titration profiles of **1** on I^- addition. When the concentration of I^- ion is increased up to 1.2×10^{-4} M, the intensity is decreased by 6.2-fold in excimer emission. Addition of more than 200 equiv of I^- to **1** resulted in both the monomer and excimer emission becoming quenched, due to the heavy atom effect imparted by I^- . The association constant (K_a) of **1** with I^- was determined to be 979.25 M^{-1} for a 1 : 1 complex. The quantum yields (Φ_f) of **1**, and **1-I}^-**, referenced to anthracene, were also determined and found to be 0.176, and 0.074, respectively.

The 1 : 1 stoichiometry was confirmed by the MALDI-TOF

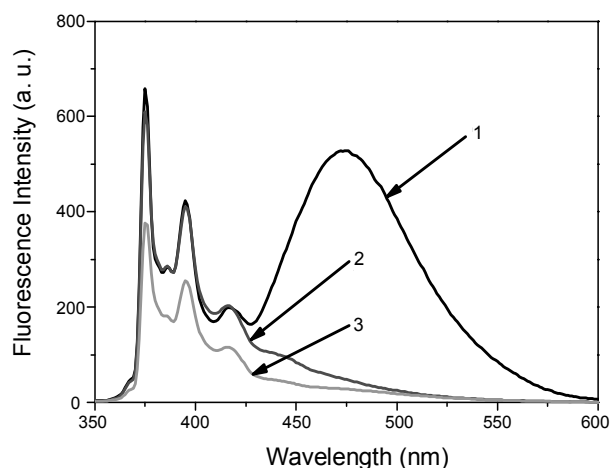


Figure 2. Fluorescence spectra of **1-3** (6.0 μM) in CH_3CN . The excitation wavelength is 343 nm.

mass spectrometry technique. The MALDI-TOF mass spectrum of a mixture of **1** with an excess of I^- as its Bu_4N^+ salt showed the formation of **1-Bu}_4\text{N}^+ complex with a peak at $m/z = 1624.0202$ for a calculated molecular weight = 1626.18 (Figure 4 (b)). This may correspond to the detection of **1-Bu}_4\text{N}^+\text{I}^- in which iodide is not seen. To compare a similar experiment was done with $\text{Bu}_4\text{N}^+\text{X}^-$ ($\text{X} = \text{F}^-$, Cl^- , Br^-) which were shown to not induce fluorescent changes. And indeed no detection was made of the presence of **1-Bu}_4\text{N}^+ complex evidencing the complexation of I^- and not of other halide anions by **1**. This suggested the fluorescence changes of **1** upon addition of I^- to be due partly due to complexation.******

In conclusion, new fluorogenic calix[4]arene (**1**) bearing two methyl ester and two pyrene triazole groups in opposite dispositions has been prepared. It was shown to be selective for the binding of I^- . When I^- is bound to **1**, the pyrene monomer emission increased while the excimer emission declined in a ratiometric manner. This ratiometric change is probably due to the encapsulation of I^- in the cavity, delineated by the ester and triazole functionality, to form a 1 : 1 complex. This encapsulation induces conformational changes of the frame which removes one pyrene residue from the other. The 1 : 1 stoichiometry of the complex was confirmed by mass spectrometry.

Experimental Section

5,11,17,23-Tetra-*tert*-butyl-25,26-dihydroxy-27,28-dipropargylcalix[4]arene (**4**)^{27,28} and 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26-methylacetate-28-propargylcalix[4]arene (**7**)¹⁹ are known compounds.

Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-dimethylacetate-26,28-di(1,2,3-triazol-1-methyl pyrene) calix[4]arene (1**).** Copper iodide (10 mg) was added to **5** (505 mg, 0.59 mmol) and **6** (300 mg, 1.18 mmol) in DMF (6 mL) and the mixture heated at 90 °C for 2 h. The resulting solution was cooled and diluted with water. The mixture was filtered, the residue washed with water and then taken up in dichloromethane and dried. The desired material was isolated as a pale cream solid following precipitation from dichloromethane / acetone (370 mg, 46%). mp

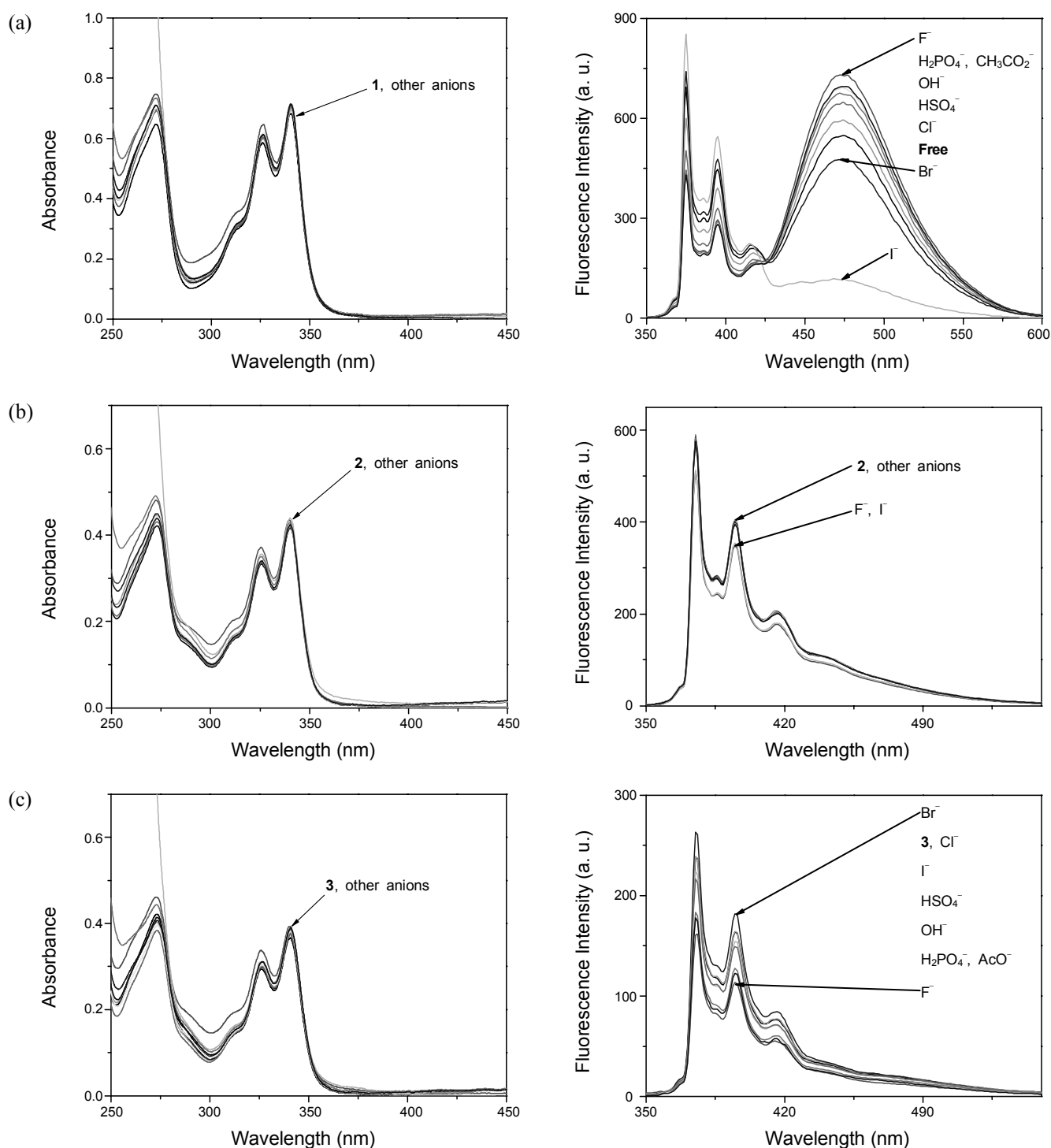


Figure 3. UV/vis and fluorescence spectra of (a) **1**, (b) **2**, and (c) **3** (absorption: 15 μ M, emission: 6 μ M) in CH_3CN in the presence of various anions, including F^- , Cl^- , Br^- , I^- , OH^- , CH_3COO^- , HSO_4^- , and H_2PO_4^- (200 equiv, as Bu_4N^+ salts).

153 - 155 $^\circ\text{C}$. ^1H NMR (300 MHz) δ 7.85-8.29 (9H, m), 7.59 (2H, s), 6.71 (4H, s), 6.45 (4H, s), 6.10 (4H, s), 5.08 (4H, s), 4.44 (4H, s), 4.29 (4H, d, $J=12$ Hz), 3.45 (6H, s), 2.88 (2H, d, $J=12$ Hz), 1.05 (18H, s), 0.87 (18H, s). ^{13}C NMR (400 MHz) δ 31.2, 31.3, 31.6, 31.8, 33.8, 34.0, 51.6, 52.0, 66.0, 71.7, 94.5, 122.3, 124.6, 124.7, 125.0, 125.3, 125.8, 125.9, 126.4, 127.4, 127.4, 127.8, 128.0, 128.9, 129.2, 130.7, 131.3, 131.9, 132.4, 135.2, 144.8, 145.2, 145.5, 152.6, 153.0, 171.0. IR ν = 2953, 1752, 1735,

1479, 1439, 1360, 1300, 1196, 1123 cm^{-1} . MALDI-TOF MS ($\text{CHON}=1383.71$) 1406.68 [$\text{M} + \text{Na}^+$]. Anal. Calcd for $\text{C}_{90}\text{H}_{90}\text{N}_6\text{O}_8$: C, 78.12; H, 6.56; N, 6.07. Found: C, 72.33; H, 6.15; N, 5.70.

Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26-dimethylethylenamine-28-(1,2,3-triazol-1-methyl)pyrene calix[4]arene (3**).** Copper iodide (10 mg) was added to **8** (200 mg, 0.24 mmol) and **6** (157 mg, 0.61 mmol) in DMF (6 mL) and

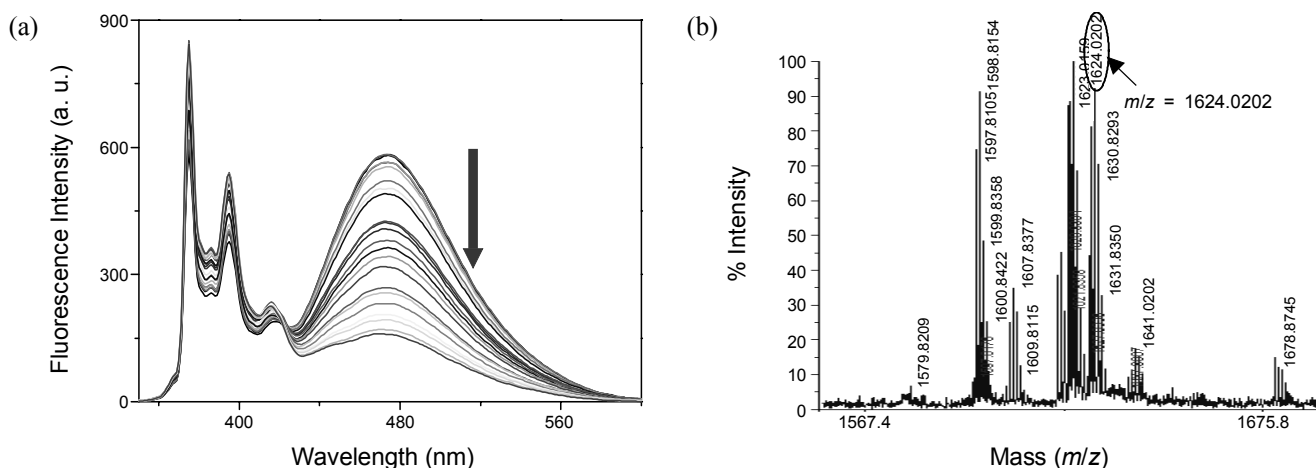


Figure 4. (a) Fluorescence spectra of **1** (6 μ M) in CH_3CN upon addition of increasing concentrations of I^- (0 - 200 equiv, as Bu_4N^+ salts) with an excitation at 343 nm. (b) MALDI-TOF Mass Spectrum of $1\cdot\text{Bu}_4\text{N}^+\text{I}^-$.

the mixture stirred at room temperature for 2 h. The resulting solution was cooled and diluted with water. The mixture was filtered, the residue washed with water and then taken up in dichloromethane and dried. The desired material was isolated as a buff solid following column chromatography in dichloromethane : acetone = 5 : 1 (178 mg, 68%). mp 147 - 149 $^\circ\text{C}$. ^1H NMR (300 MHz) δ 8.53 (1H, t, J = 6 Hz), 7.98-8.29 (9H, m), 7.88 (1H, s), 7.02 (2H, br s), 6.90 (4H, s), 6.75 (2H, s), 6.66 (2H, s), 6.34 (2H, s), 5.17 (2H, s), 4.35 (2H, s), 4.03 (2H, d, J = 12 Hz), 3.75 (2H, d, J = 12 Hz), 3.36 (2H, m), 3.12 (4H, d, J = 12 Hz), 2.43 (2H, br t), 2.17 (6H, s), 1.25 (18H, s), 0.94 (9H, s), 0.86 (9H, s). ^{13}C NMR (75 MHz) δ 30.8, 30.9, 31.6, 31.7, 33.8, 33.9, 33.9, 45.0, 52.7, 57.8, 70.1, 74.3, 121.9, 125.0, 125.1, 125.2, 125.7, 125.8, 125.9, 125.92, 126.3, 127.1, 127.3, 127.4, 128.1, 128.4, 129.0, 132.2, 132.5, 142.1, 149.0, 149.1, 149.7, 168.6. IR ν = 3364, 2952, 2857, 1736, 1672, 1539, 1481, 1460, 1431, 1360, 1282, 1190, 1123 cm^{-1} . MALDI-TOF MS (CHON = 1072.42) 1073.1 [$\text{M} + \text{H}$]. Anal. Calcd for $\text{C}_{70}\text{H}_{81}\text{N}_5\text{O}_5$: C, 78.40; H, 7.61; N, 6.53. Found: C, 76.21; H, 7.50; N, 6.38.

Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,26-dimethylacetate-28,27-dipropargylcalix[4]arene (5). A suspension of sodium hydride (95%, 790 mg, 32.92 mmol) and **4** (4.00 g, 5.41 mmol) in DMF (80 mL) was stirred at room temperature for 1 h. Methyl bromoacetate (5.07 g, 33.2 mmol) was added and the suspension stirred for a further 18 h. Water (50 mL) was added and the resulting precipitate collected and dissolved in dichloromethane (50 mL). The organic solution was washed with 10% HCl and brine then dried with magnesium sulphate. Evaporation of the solvent gave a crude white solid which on precipitation from dichloromethane-methanol yielded the title compound (3.58 g, 74%). mp 173 - 175 $^\circ\text{C}$. ^1H NMR (300 MHz) δ 7.02 (4H, s), 6.39 (4H, s), 5.07 (2H, d, J = 2.5 Hz), 4.54 (4H, d, J = 13 Hz), 4.42 (4H, s), 3.76 (6H, s), 3.08 (4H, d, J = 13 Hz), 2.29 (1H, t, J = 2.5 Hz), 1.23 (18H, s), 0.74 (18H, s). ^{13}C NMR (100 MHz) δ 31.2, 31.9, 32.1, 33.8, 34.4, 52.0, 60.2, 72.1, 74.2, 82.3, 124.9, 125.6, 132.0, 136.4, 145.3, 146.0, 152.3, 152.9, 170.44. IR ν = 3285, 2954, 2909, 2868, 1756, 1479, 1435, 1362, 1300, 1196, 1125, 1071, 1009 cm^{-1} .

Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26-

dimethylethylenamine-28-propargylcalix[4]arene (8). Dimethylethylenamine (296 mg, 3.40 mmol) was added to a solution of **7** (1.27 g, 1.70 mmol) in toluene / methanol 1 : 1 (30 mL) and the resulting mixture stirred at reflux for 18 h. The solvent was evaporated and the residue subjected to column chromatography (dichloromethane : methanol 20 : 1) to yield the desired compound as a white foam (233 mg, 68%). mp 108 - 110 $^\circ\text{C}$. ^1H NMR (300 MHz) δ 8.71 (1H, br s), 7.10 (4H, m), 7.02 (2H, s), 6.84 (2H, s), 6.82 (2H, s), 4.78 (2H, d, J = 2.5 Hz), 4.53 (2H, s), 4.37 (2H, d, J = 14 Hz), 4.14 (2H, d, J = 14 Hz), 3.72 (2H, br s), 3.41 (2H, d, J = 13 Hz), 3.37 (2H, d, J = 14 Hz), 2.89 (1H, br t), 2.81 (2H, br s), 2.45 (6H, br s), 1.31 (18H, s), 0.99 (9H, s), 0.96 (9H, s). ^{13}C NMR (75 MHz) δ 30.9, 31.7, 31.9, 32.1, 33.9, 34.0, 96.1, 125.3, 125.9, 127.4, 127.9, 132.2, 132.6, 142.4, 150.0. IR ν = 3359, 2952, 1676, 1540, 1480, 1359, 1299, 1192 cm^{-1} . GC MS (CHON = 815.13) 815.0 [M^+]. Anal. Calcd for $\text{C}_{53}\text{H}_{70}\text{N}_2\text{O}_5$: C, 78.09; H, 8.66; N, 3.44. Found: C, 75.86; H, 8.48; N, 3.46.

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