



# Calix[4]arene containing thiourea and coumarin functionality as highly selective fluorescent and colorimetric chemosensor for fluoride ion

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## ABSTRACT

A novel calix[4]arene based chemosensor **L** which contains coumarin and thiourea group has been synthesized and characterized. Interestingly, probe **L** exhibits both fluorescent and colorimetric response to fluoride anion with high selectivity and sensitivity. The addition of F<sup>-</sup> to a solution of probe **L** resulted in obvious naked-eye color change from colorless to orange under daylight and prominent fluorescence quenching. Further studies showed that the recognition process was less affected by other anions. The binding property of **L** with F<sup>-</sup> was studied by a combination of various spectroscopic techniques, such as absorption spectra, fluorescence titration, Job's plot and <sup>1</sup>H NMR titration. We are anticipating that this architecture with functional group attached to upper rim of calix[4]arene platform may provide a new approach for the development of F<sup>-</sup> chemosensor.

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## 1. Introduction

Anions are ubiquitous throughout the biological systems and play a fundamental role in a wide range of biochemical processes. Therefore, designing chemical sensors for anion recognition has become a vital part of modern supramolecular chemistry [1–7]. Among the vast number of biological anions, the fluoride ion gains much interest due to its unique role in human health and the environment [8–12]. Fluoride ion is an indispensable element in our body, which have a significant part in regulating our body's bone growth and maintaining normal physiological function. However, excess intake of fluoride would give rise to both dental and skeletal fluorosis [13]. Thus, the development of optical sensors capable of rapidly detecting the fluoride ion has gained considerable attention due to the above mentioned reasons [14–16]. For example, Yoon and co-workers reported an elegant chemosensor bearing anthracene unit and two phenylurea group which shows fluorescence quenching behavior with fluoride ion [17]. Recently, James and co-workers reported a series of azulene boronate ester based indicators for detecting fluoride in drinking water [18].

Besides, an increasing number of fluoride chemosensors have been developed based on the highly directional hydrogen bonds between fluoride and the NH groups (ureas [17,19,20], thioureas [21,22] or amides [23,24]). In particular, thiourea serves as an excellent receptor for

fluoride ion than urea group because of its higher N-H acidities. These phenomena have been used advantageously for designing novel fluoride probes. Among various fluorophores, coumarin derivatives are often utilized in the design of synthetic molecular sensors on account of their versatility and excellent fluorescent functionality [25–30]. For instance, Huang and co-workers constructed supramolecular multicolor fluorescent gels by attaching coumarin unit to polymer backbone recently [31]. It is still striking how the receptor and fluorophore are combined in an efficient way.

Calix[n]arenes are ideal supramolecular macrocyclic platforms for the design of molecular receptors due to its unique and tunable molecular architecture together with the ease of functionalization on its lower rim and upper rim [32–37]. By attaching different pendants with sensing ability into the scaffolds, the tunable shape of the calix[4]arene cavity can adopt an elaborated organization of functional groups in a well-defined way. Compared with the lower rim, the functionalization of the upper rim is more challenging and diverse. Based on our previous studies on calix[4]arene [38,39] and fluorescent probe [40], herein we further constructed a unique structure based on calix[4]arene to recognize fluoride ion *via* quadruple hydrogen bonding of two thiourea group in a cooperative way (Fig. 1). Therefore, we have designed and synthesized a kind of architecture with coumarin and thiourea group attached to the upper rim of calix[4]arene backbone, which exhibits a prominent naked-eye-visible color change and significant selective fluorescence quenching. The interaction between probe molecules and anions was investigated by fluorescence spectroscopy, UV–visible spectroscopy and <sup>1</sup>H NMR titration.

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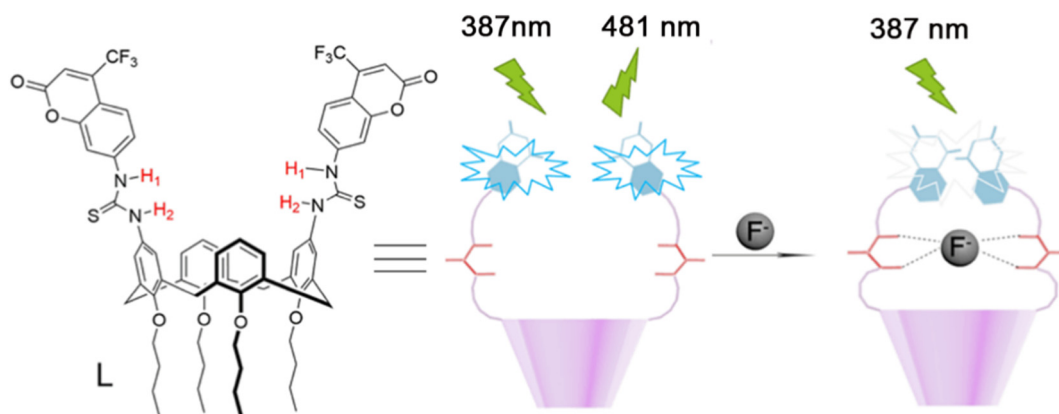


Fig. 1. Design of calix[4]arene receptor **L** with upper rim functionalization for fluoride sensing.

## 2. Experimental Section

### 2.1. Materials and Apparatus

DMSO was dried using calcium hydride and distilled under vacuum prior to use. Unless special annotation, all the reagents were purchased from commercial sources. NMR spectra were recorded on a BRUCKER ARX-300 MHz with chemical shifts reported as ppm (in CDCl<sub>3</sub> or DMSO *d*<sub>6</sub>, with TMS as internal standard). HRMS were obtained on a 6540 UHD Accurate-Mass Q-TOF LC/MS. Absorption spectra were measured on a UV-1700 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on an Agilent Cary Eclipse spectrofluorometer.

### 2.2. General Procedure for the Spectroscopic Studies

The tetrabutylammonium (TBA) salts (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) solutions were prepared at the concentration of 0.1 M in DMSO. Different equivalents of TBA salts were added to the probe solution and their corresponding UV-vis and fluorescence spectra were recorded at 25 °C. For <sup>1</sup>H NMR titrations, the solution of **L** was titrated with fluoride anion (as TBA salt) by addition of increasing equivalents of F<sup>-</sup> in DMSO *d*<sub>6</sub>.

The 0.1 M anions solution were prepared by using DMSO. The probe **L** (2 × 10<sup>-4</sup> M) stock solution was prepared in DMSO and protected from light for 24 h before using DMSO as solvent. Microsyringe was utilized to transfer **L** (1 mL) and anions (0.2 mL) stock solution to 10 mL volumetric flask and dissolved in DMSO to make a solution to 10 mL accurately. So the concentration diluted to 2.0 × 10<sup>-5</sup> M. For each mixture the fluorescence response was measured after 30 min mixed. The fluorescence emission intensity was quenched when F<sup>-</sup> was added and other anions showed no change in the fluorescence intensity.

### 2.3. Synthesis of Probe **L**

#### 2.3.1. Synthesis of Compound **3**

To a solution of **2** (1.40 g, 6.11 mmol), in 20 mL CH<sub>2</sub>Cl<sub>2</sub> was added triethylamine (1.78 mL, 12.81 mmol) and the solution was stirred at 35 °C for 20 min. After cooling the system to room temperature, thiophosgene (1.40 mL, 18.37 mmol) was added dropwise and the mixture was stirred at 35 °C for 20 min. The reaction was completed after 20 min, as indicated by TLC (Hexanes:EtOAc = 8:1). Excess of CS<sub>2</sub> was removed by distillation in high vacuum. The orange precipitate was dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through silica gel for the removal of triethylamine hydrochloride, washed with 10 mL dichloromethane, and dried in high vacuum to yield 1.37 g (83.0%) of product as a light orange solid.

mp: 119.7–120.8 °C. <sup>1</sup>H NMR (300 MHz, DMSO *d*<sub>6</sub>): δ (ppm) = 7.73–7.76 (m, 1H, ArH), 7.71 (d, 1H, *J* = 2.1 Hz, ArH), 7.50 (dd, 1H, *J*<sub>1</sub> = 2.1 Hz, *J*<sub>2</sub> = 8.7 Hz, ArH), 7.12 (s, 1H, C-CH-C=O). <sup>13</sup>C NMR (75 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 158.45, 154.83, 139.03, 138.59, 136.87, 134.37, 126.56, 123.65, 118.29, 115.13, 113.00. <sup>19</sup>F NMR (282 MHz, DMSO *d*<sub>6</sub>) δ (ppm): -63.42. HR-ESI-MS (C<sub>11</sub>H<sub>4</sub>F<sub>3</sub>NO<sub>2</sub>S): *m/z* calcd for [M + H]<sup>+</sup> = 271.9993, found = 271.9987.

#### 2.3.2. Synthesis of Compound **L**

To a solution of **1** (1.00 g, 1.47 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added solution of **3** (1.00 g, 3.69 mmol). The reaction mixture was stirred at the room temperature for 2 h. The CH<sub>2</sub>Cl<sub>2</sub> was removed by vacuum. The resulting residue was purified by silica column chromatography (ethyl acetate/petroleum ether 1:10) to give **L** (1.46 g, 81.3%) as a yellow solid.

mp: 185.4–186.3 °C. <sup>1</sup>H NMR (300 MHz, DMSO *d*<sub>6</sub>): δ (ppm) = 10.01 (s, 2H, NH), 9.70 (s, 2H, NH), 7.94 (d, 2H, *J* = 1.8 Hz, ArH), 7.53 (d, 2H, *J* = 7.5 Hz, ArH), 7.38 (dd, 2H, *J*<sub>1</sub> = 2.1 Hz, *J*<sub>2</sub> = 8.7 Hz, ArH), 6.87 (s, 2H, C-CH-C=O), 6.83 (s, 4H, ArH), 6.65 (d, 4H, *J* = 7.5 Hz, ArH), 6.54 (t, 2H, *J* = 13.2 Hz, ArH), 4.33 (d, 4H, *J* = 12.9 Hz, ArCH<sub>2</sub>Ar), 3.80–3.87 (m, 8H, ArOCH<sub>2</sub>), 3.17 (d, 4H, *J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 1.84–1.91 (m, 8H, CH<sub>2</sub>), 1.41–1.49 (m, 8H, CH<sub>2</sub>), 0.95–1.01 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 178.83, 159.08, 156.58, 154.66, 154.08, 144.85, 135.20, 134.80, 132.94, 128.60, 128.46, 125.16, 124.05, 122.35, 120.33, 118.95, 114.60, 108.72, 108.60, 74.98, 74.84, 46.12, 32.30, 30.70, 19.34, 14.35. <sup>19</sup>F NMR (282 MHz, DMSO *d*<sub>6</sub>) δ (ppm): -63.63. HR-ESI-MS (C<sub>66</sub>H<sub>66</sub>F<sub>6</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>): *m/z* calcd for [M + H]<sup>+</sup> = 1221.4305, found = 1221.4301.

## 3. Results and Discussion

### 3.1. Design and Synthesis of Probe **L**

Probe **L** was prepared by simple modification of amino-functionalized calix[4]arene as shown in Scheme 1. Firstly, compound **1** was prepared from dinitrocalix[4]arene which can be reduced by Raney nickel and hydrazine hydrate in refluxing methanol according to our previous report [41]. Meanwhile, compound **2** was converted into compound **3** in dichloromethane solution by using thiophosgene. After that, compound **1** was easily reacted with compound **3** under mild condition, which could afford the target compound **L** in good yield. These compounds were well characterized by NMR and MS analyses (shown in the Electronic Supplementary information Fig. S8–S13).

### 3.2. Spectral Properties of **L** Toward Fluoride Anion

Initially, the fluorescence response of probe **L** toward various anions in DMSO were studied using emission spectroscopy. As shown in Fig. 2a,

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