

Tetrahedral Anions Selective Fluorescent Calix[6]arene Receptor Containing Urea and Pyrene Moieties

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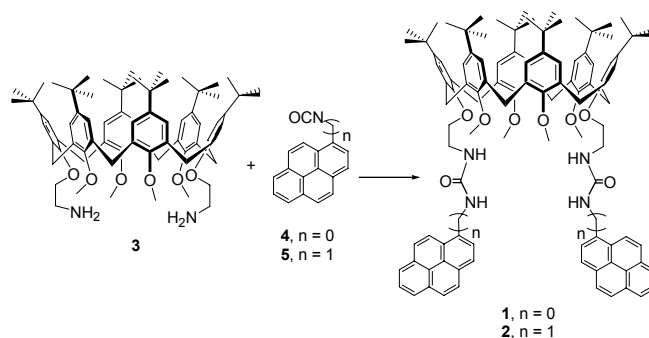
The design of supramolecules as specific chemosensors has been focused upon the design of supramolecules which have the ability to selectively recognize and sense analytes through the naked eye, electrochemical, and optical responses.^{1,2} On account of its simplicity and high sensitivity, fluorescence is becoming of increasing importance for chemical trace detection.³

Selective binding of ions is an important aspect of ion detection and ion transport. Selective complexation of anions is more demanding than that of cations due to low charge density and strong solvation. Furthermore, it has to be kept in mind that anions are subject to pH-dependent acid-base equilibria.^{4,5} Sulfate and phosphate binding proteins are very important receptors for the active transport systems in the cell. It is known, that sulfate binding proteins can bind anions with high selectivity, exclusively by the formation of hydrogen bonds.⁶ Anion recognition is a growing field of research and there are good introductory texts and reviews available on the subject.⁷⁻¹⁴ Adding hydrogen bond donor groups to organic hosts has been a key tool in providing recognition for specific anion geometries.¹⁵ The urea and thiourea functional groups provide such effective and directional H-bonds for anion recognition. There are many examples of hosts that incorporate one or more urea group for anion binding, offering diverse binding geometries. Examples include open chain chelators or acyclic tweezers, tripodal, and tetrapodal hosts. The structural design criteria for hosts in light of these geometries have been examined recently. Kim and coworkers reported¹⁶ the several anion selective calix[4]arene complex with pyrene, but calix[6]arene pyrene complex was not reported yet, presumably due to the difficulties of modifying of calix[6]arene. Incorporating of anion binding urea and fluorescence pyrene moieties into the calix[6]arene framework, we synthesized two urea derivatives of calix[6]arene **1** and **2** and studied the fluorescence emission behavior. This novel neutral anion receptor **1** binds anions through hydrogen bonding.

Results and Discussion

Pyrene urea derivatives calix[6]arene **1** and **2** were obtained successfully by the reaction of aminocalix[6]arene **3**¹⁶ with 1-pyrenylisocyanate and 1-pyrenylmethylisocyanate which were prepared by treating 1-aminopyrene and 1-aminomethylpyrene with triphosgene.¹⁷ ¹H and ¹³C NMR spectra are proposed structure **1** and **2**.

The excitation spectrum of **1** and **2** revealed a λ_{max} of 343 nm



Scheme 1. Synthetic routes to fluorescent chemosensors **1** and **2**

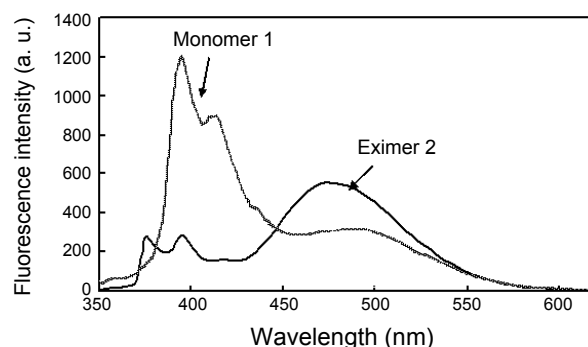


Figure 1. Emission spectra of **1** and **2** (1×10^{-6} M) in acetonitrile showed monomer and excimer emission (The excitation wavelength is 343 nm).

as an ideal excitation wavelength. Figure 1 shows the emission spectrum of **1** and **2** in acetonitrile. Chemosensor **1** shows a little broad excimer emission and large broad monomer emission band at 392 nm and 410 nm. But, chemosensor **2** shows the monomer emissions as well as a much larger broad emission band at 472 nm (λ_{max}) due to the excimer formation. We first probed the anion binding abilities of **1** and **2** based on fluorescence changes of their MeCN solutions produced by addition of tetrabutylammonium salts of the anions. The change in excimer and monomer emission was monitored. Remarkably hydrogen sulfate and phosphate caused the dramatic change in the emission spectrum of **1**. The addition of HSO_4^- , H_2PO_4^- decline in excimer emission with a corresponding increase in monomer emission. This observation suggest that hydrogen sulfate and phosphate anions appear to selectively coordinate with the urea

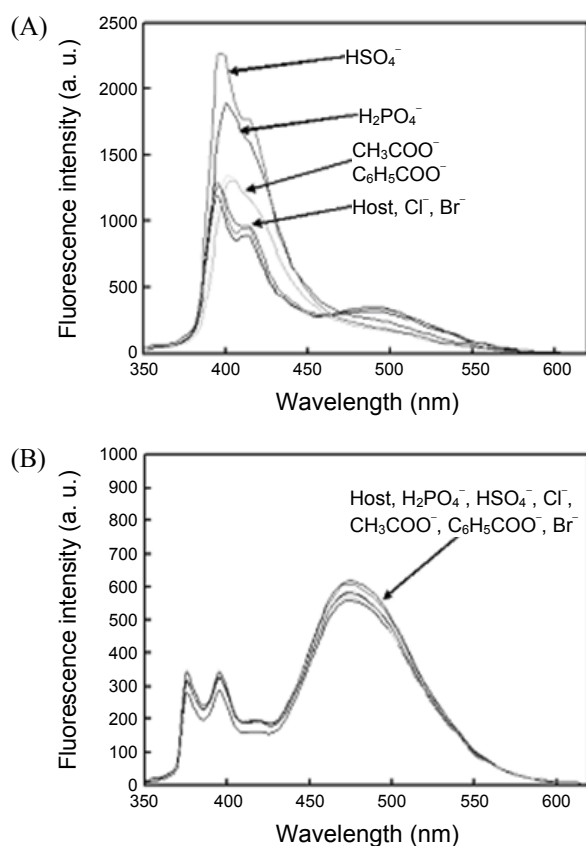


Figure 2. Emission spectra of **1**(A) and **2**(B) (1.0 μM) upon the addition of anions to 1000eq in acetonitrile (The excitation wavelength is 343 nm).

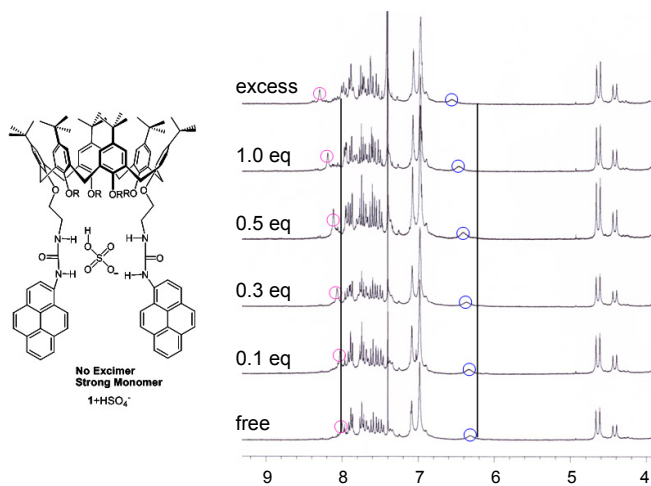


Figure 3. Partial ¹H NMR spectra of chemosensor **1** with tetrabutylammonium hydrogensulfate in CD₃CN : CDCl₃ = 1 : 1.

protons in the cavity of **1** so as to disrupt the facing π - π stacked pyrenes. Also, ¹H NMR titration is supported that tetrahedral anions coordinate with urea protons (Figure 3). But, no emission change was observed in chemosensor **2** in the presence of various anions. Probably, due to the strong intramolecular hydrogen bonding of urea and oxygen, fluorescence intensity not changed with various anions.

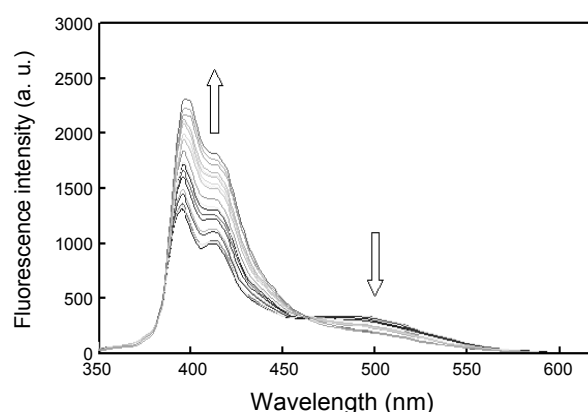


Figure 4. Emission spectra of **1** (1.0 μM) upon the addition of hydrogen sulfate from 0 eq to 1000 eq in acetonitrile (The excitation wavelength is 343 nm).

The association constant for HSO₄⁻ and H₂PO₄⁻ complexation with **1** in MeCN was calculated to be 3.5×10^4 and $3.0 \times 10^4 \text{ M}^{-1}$ from the resulting titration curves using ENZFITTER program.¹⁷ The highest binding affinity for HSO₄⁻ was observed for the ligand **1** expected from the fluorescence spectra.

In conclusion, calix[6]arene pyrene urea derivatives **1** and **2** have been synthesized by **3** and their corresponding isocyanates. When hydrogen sulfate and phosphate ions are bound, chemosensor **1** ratiometry of monomer increased and excimer decreased due to the effective intramolecular hydrogen bonding between receptor **1** and hydrogen sulfate and phosphate ions causing the separation of pyrene π - π stacking.

Experimental

5,11,17,23,29,35-Hexa-tert-butyl-37,40-bis(1-pyreneuredo-2-ethoxy)-38,39,41,42-tetramethoxycalix[6]arene (1). To a solution 0.145 g (0.13 mmol) of 5,11,17,23,29,35-Hexa-tert-butyl-37,40-bis(aminoethoxy)-38,39,41,42-tetramethoxycalix[6]arene **3** in 10 mL dioxane was added with 0.06 g (0.26 mmol) of 1-pyrene isocyanate which was prepared from reaction of 1-aminopyrene and triphosgene and the reaction mixture was stirred for 4 hour under the nitrogen atmosphere. The crude product was purified by chromatography on silica gel with CHCl₃ as to give a 70 mg (34%) yield of **1** as a brown solid; ¹H NMR (CDCl₃) δ 7.97 and 6.20 (two s, 4H, NH), 7.84-7.36 (m, 18H, PyH), 7.08 and 6.97 (two s, 12H, ArH), 4.65, 4.31, 3.57 and 3.46 (two pair of d, 12H, ArCH₂Ar), 3.70 (br s, 4H, -OCH₂-, $J = 4.6$ Hz), 3.70 (br s, 4H, -CH₂N), 3.17 (s, 6H, -OCH₃), 1.17 and 1.11 (two s, 54H, -C(CH₃)₃). ¹³C NMR (CDCl₃) δ 157.97 (-CO-), 153.92, 151.98, 146.24, 146.73, 133.60, 133.61, 132.76, 130.91, 130.50, 126.74, 126.37, 125.90, 124.59, 124.40, 124.16, 123.87 and 120.95 (Ar), 72.45 (-OCH₂-), 60.56 (-OCH₃), (-CH₂N-), 40.92, 34.19, 31.35 and 29.19 (ArCH₂Ar, -CH₂N- and -C(CH₃)₃).

5,11,17,23,29,35-Hexa-tert-butyl-37,40-bis(1-pyrenemethyluredo-2-ethoxy)-38,39,41,42-tetramethoxycalix[6]arene (2). To a solution 0.145 g (0.13 mmol) of 5,11,17,23,29,35-Hexa-tert-butyl-37,40-bis(aminoethoxy)-38,39,41,42-tetramethoxycalix[6]arene **3** in 10 mL dioxane was added with 0.066 g (0.26 mmol) of 1-pyrenemethyl isocyanate which was

prepared from reaction of 1-aminomethylpyrene and triphosgene and the reaction mixture was stirred for 4 hour under the nitrogen atmosphere. The crude product was purified by chromatography on silica gel with CHCl_3 as to give a 60 mg (28%) yield of **2** as a yellow solid; ^1H NMR (CDCl_3) δ 7.80-7.47 (m, 18H, PyH), 6.92 and 6.80 (two s, 12H, ArH), 6.27 and 5.71 (two s, 4H, NH), 4.56 (br s, 4H, $-\text{CH}_2\text{Py}$), 4.35, 3.66, 3.38 and 2.95 (two pair of d, 12H, ArCH_2Ar), 3.72 (br s, 4H, $-\text{OCH}_2-$, $J=4.6$ Hz), 3.60 (br s, 4H, $-\text{CH}_2\text{N}$), 2.61 (s, 6H, $-\text{OCH}_3$), 1.07 and 1.05 (two s, 54H, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3) δ 158.97 ($-\text{CO}-$), 153.62, 151.78, 146.10, 145.73, 133.67, 132.81, 132.36, 132.03, 130.74, 130.38, 130.32, 128.49, 127.14, 126.97, 126.46, 125.81, 125.58, 125.17, 124.58, 124.37, 124.26, 124.17, and 123.07 (Ar), 72.34 ($-\text{OCH}_2-$), 59.85 ($-\text{OCH}_3$), ($-\text{CH}_2\text{N}-$), 42.76, 40.79, 34.08, 31.31 and 29.54 (ArCH_2Ar , $-\text{NCH}_2\text{Ar}$, $-\text{CH}_2\text{N}$ - and $-\text{C}(\text{CH}_3)_3$).

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