

Notes

Chromoionophoric Recognition of Alkylamines by Nitro Derivative of Calix[4]arene-crown-5 Ether

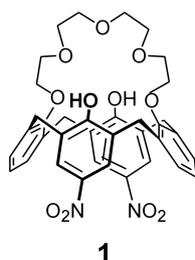
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The molecular design of efficient and selective chromogenic and fluorogenic ionophore systems for the sensing of chemically and biologically important ionic guests has attracted much attention in the past decade.^{1,2} Many of the compounds are based on the well-known molecular framework of crown ethers, calixarenes, and other EDTA type efficient chelating compounds.³ Among them the calix[4]arenes are particularly attractive for their selective ionophoric properties toward many of interesting organic ammonium guests.⁴ Particularly, the calix[4]arene-crown ethers are known to have unique binding properties toward some of alkali, alkaline earth metal ions, and biogenic amines.⁵ Many of the chromogenic sensing materials are developed by conjugating molecular framework of calix[4]arene-crown ethers with suitable signaling functions of azophenols,⁶ thiazoles,⁷ and indophenols.⁸ Quite unexpectedly, however, the ionophoric properties of simple nitro derivative of calix[4]arene-crown ethers were not reported, except for the closely related structure having ester-ether functions in crown moiety,^{9,10} in spite of their synthetically easy availability and expectedly efficient ionophoric properties toward organic amine guests. In this paper, we report the ionophoric properties of dinitro derivative of calix[4]arene-crown-5 ether **1** toward representative alkylammonium ions aiming for the development of efficient and selective chromogenic sensing material for the biologically important organic amine guests. The Ba²⁺-selective chromogenic behavior of **1** over the representative alkali and alkaline earth metal ions has been reported earlier.¹¹



Dinitro derivative **1** was prepared by the selective nitration of calix[4]arene-crown-5 ether¹² with HNO₃ (HOAc, CH₂Cl₂) in good yield following the reported procedure.¹¹ The molecular recognition properties of **1** were investigated by the UV-Vis spectroscopy. Preliminarily, we measured the absorption behavior of the host **1** in common organic solvents. In chloroform, the ionophore showed a broad absorption band around 331 nm which is characteristic of *p*-nitrophenol moiety. However, in more polar solvents of methanol and its aqueous solution, the ionophore exhibited some chromogenic behavior even without any guests by showing absorbance at 428 nm due to the absorption of ionized phenoxide form of **1**. So, we investigated molecular discrimination behavior of **1** toward alkylamines in chromogenically least interfering solvent of chloroform.

First, the discrimination behavior of **1** between the representative amines of primary, secondary, and tertiary amines (*n*-butyl, diethyl, and triethylamine) were tested. Addition of 1000 equiv of amine guests resulted in the appearance of a new band due to the formation of nitrophenoxide form of ionophore^{9,10,13} around 428 nm with concomitant decrease in 331 nm band ([**1**] = 5 × 10⁻⁵ M) (Figure 1). The ionophore **1** showed a pronouncedly selective chromogenic behavior toward primary amine of *n*-

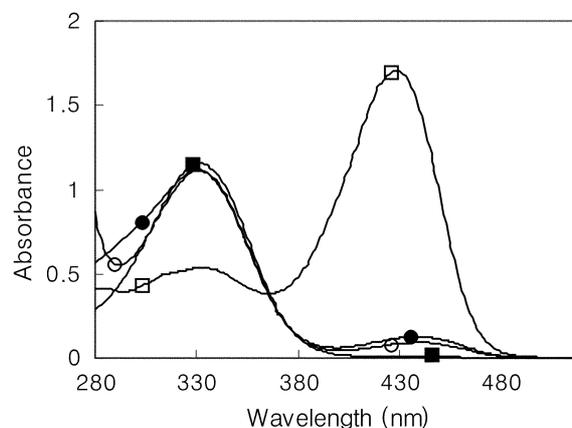


Figure 1. The UV-Vis spectra of **1** (■) and **1** in the presence of *n*-butylamine (□), diethylamine (●), and triethylamine (○). [**1**] = 5 × 10⁻⁵ M, [amine] = 5 × 10⁻² M in CHCl₃.

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butylamine over other employed amines. Upon addition of *n*-butylamine, nearly 80-fold increase in absorbance at 428 nm was observed. The color of solution transformed from almost colorless of **1** into intense yellow one, which can be detected visually without any difficulty. Secondary and tertiary amines exhibited much smaller responses than *n*-butylamine: *n*-butylamine \gg diethylamine $>$ triethylamine. The selectivity toward *n*-butylamine over diethylamine and triethylamine, estimated from the ratio of absorbances induced by the added amines at 428 nm, was found to be 18 and 27, respectively.

Next, the chromogenic responses of **1** toward various isomers of primary butylamine (*n*-Bu, *iso*-Bu, *sec*-Bu, and *tert*-Bu) were investigated. Within various isomers of butylamines, nitro derivative showed the most pronounced response toward *n*-butylamine that might be due to the steric interaction between the benzene ring of the ionophore and the alkyl groups of complexed amine guests. The response generally decreases as the bulkiness of the alkyl group increases as expectedly in the order of *n*-Bu \gg *iso*-Bu $>$ *sec*-Bu $>$ *tert*-Bu. This observation is in line with the reported molecular recognition properties of *p*-*tert*-butylcalix[4]-arene-crown-5 ethers.¹⁴ Here, also the selectivity toward *n*-butylamine over other isomeric amines was estimated from the ratio of the absorbance changes at 428 nm induced by the addition of the amine guests and found to be 11.4 (*iso*-Bu), 41.7 (*sec*-Bu), and 52.7 (*tert*-Bu), respectively. The observed discrimination efficiency suggests that the calix-crown compound **1** can be used as a selective chromogenic probe for the sensing of *n*-alkylamine and related structures.

The binding constant for the **1**-*n*-butylamine system was determined from the UV-Vis titration data. The linear relationship obtained by the plot of $1/\Delta\text{Abs}$ versus $[\textit{n}\text{-butylamine}]^{-2}$ supports the formation of complexes in 1 : 2 (**1** : *n*-butylamine) stoichiometry.⁹ The binding constant was obtained by the non-linear curve fitting procedure¹⁵ for the formation of complexes in 1 : 2 stoichiometry and found to be $1.41 \times 10^3 \text{ M}^{-2}$. On the other hand, the detection limit¹⁶

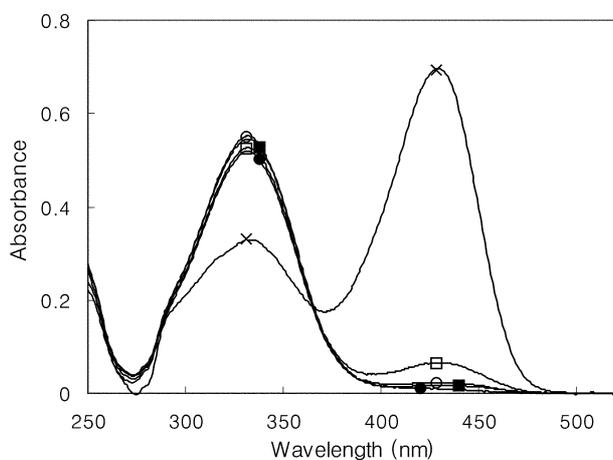


Figure 2. UV-Vis absorption spectra of **1** in the absence (■) and presence of *n*-Bu (×), *iso*-Bu (□), *sec*-Bu (○), and *tert*-Bu amines (●) in chloroform. $[\mathbf{1}] = 2.5 \times 10^{-5} \text{ M}$. $[\textit{Butylamine}] = 2.5 \times 10^{-2} \text{ M}$.

Table 1. OR logic gate behavior of **1** toward Ca^{2+} and *n*-butylamine

Chemical input ^a		Absorbance at 428 nm
Ca^{2+}	<i>n</i> -butylamine	
X	X	0.02 (OFF, 0)
O	X	0.79 (ON, 1)
X	O	0.84 (ON, 1)
O	O	0.86 (ON, 1)

^a'O' and 'X' denote the absence and the presence of chemical stimuli, respectively. $[\mathbf{1}] = 2 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 2 \times 10^{-3} \text{ M}$, and $[\textit{n}\text{-butylamine}] = 2 \times 10^{-2} \text{ M}$ in a mixed solvent of $\text{CHCl}_3\text{-MeOH}$ (1 : 1, v/v).

for the sensing of *n*-butylamine was estimated from the plot of the changes in absorbance at 428 nm as a function of the concentration of added butylamine and found to be about 1 mM in chloroform solution. The obtained binding constant and detection limit suggest that the compound **1** is suitable for the determination of millimolar concentration range of *n*-alkylamines in organic solvent systems.

We also tried to discriminate biologically important structure of isomeric phenethylamines. As can be easily understood from the steric requirements for the complex formation, the ionophore showed much larger chromogenic response toward less bulkier 2-phenethylamine than 1-phenethylamine. The selectivity ratio estimated from the respective absorbances at 426 nm for the discrimination of 2-phenethylamine/1-phenethylamine was found to be 7.7.

Finally, the selective responses of **1** toward Ca^{2+} and *n*-butylamine were utilized for the construction of molecular logic gate. The changes in absorbance of **1** at 428 nm upon the treatment of physiologically important chemical stimuli of Ca^{2+} and *n*-butylamine which is a representative of many biogenic amines were a typical behavior of OR logic gate.¹⁷ As can be seen from the Table 1, the ionophore **1** showed low absorbance at 428 nm but exhibited high absorbances in the presence of individual chemical stimulus of Ca^{2+} and *n*-butylamine or both of the chemical inputs at 428 nm.

In conclusion, simple nitro derivative of calix[4]arene-crown-5 ether showed a selective molecular recognition behavior toward primary alkylamine over other isomeric amines. The prepared nitro derivative can be used as a selective chromogenic sensor for the determination of biologically important amine guests. Furthermore, a simple OR logic gate could be constructed by utilizing selective responses of nitro derivative toward Ca^{2+} and *n*-butylamine.

Experimental Section

UV-Vis spectra were obtained with a Jasco V-550 spectrophotometer. Calix[4]arene-crown-5 ether and its nitro derivative were prepared by the reported procedure.¹¹

UV-Vis measurements: Stock solutions of ionophore **1** ($5 \times 10^{-5} \text{ M}$) was prepared in chloroform. The stock solutions of alkylamines ($5 \times 10^{-2} \text{ M}$) were prepared by dissolving calculated amounts of alkylamine in the stock solution of ionophore **1** ($5 \times 10^{-5} \text{ M}$) in chloroform. The two stock solutions were mixed or diluted to give a series of solutions

of [amine]/[1] ratio in between 0 and 1000.

OR logic gate behavior: The UV-Vis spectral responses of **1** were obtained in the absence of any added chemical stimuli and the presence of 100 equiv of $\text{Ca}(\text{ClO}_4)_2$, 1000 equiv of *n*-butylamine, or both of 100 equiv of $\text{Ca}(\text{ClO}_4)_2$ and 1000 equiv of *n*-butylamine in chloroform-MeOH (1 : 1, v/v) solution. The measurements were performed by the addition of aliquots of chemical stimuli to the chloroform solution of **1** (5×10^{-5} M, 2 mL). Due to the limited solubility of $\text{Ca}(\text{ClO}_4)_2$ in chloroform, stock solution of $\text{Ca}(\text{ClO}_4)_2$ in MeOH was used. For the compensation of any chromogenic responses due to the added MeOH, other measurements also were performed by the addition of aliquots of MeOH to make the constant solution composition of chloroform-MeOH (4 mL, 1 : 1, v/v). The absorbance changes of **1** at 428 nm were monitored and the truth table for OR logic gate was constructed.

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