

Visualization of Molecular Length of α,ω -Diamines and Temperature by a Receptor Based on Phenolphthalein and Crown Ether

Kaoru Fuji, Kazunori Tsubaki, Kiyoshi Tanaka, Noriyuki Hayashi, Tadamune Otsubo and Takayoshi Kinoshita

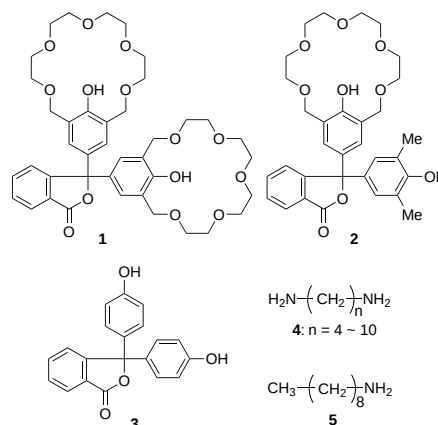
The hybrid molecule **1** consisting of phenolphthalein and crown ether moieties can discriminate the chain length of the α,ω -diamines by color change, while **2** can not. Thus, it is suggested that two crown ether part are necessary to visualize the chain length by the color. The pink color faded at 50 °C and reappeared at 20 °C, which could repeated more than 10 times.

Key words: Chromgenic receptor/ Molecular recognition/ Phenolphthalein

Supramolecular chemistry based on molecular recognition has become attractive not only for organic chemists but also for researchers in other academic fields, and remarkable progress has recently been made in this area. If the weak signals derived from such molecular interaction could be transformed into visual information, more information could be directly available. Here, we report the visual determination of the chain length of linear diamines using a functional molecule **1** consisting of phenolphthalein (**3**) and two loops of crown ether. Visualization of the “length” of a guest molecule as well as “temperature” is possible using **1** [1].

Interactions of host compounds (**1** and **2**) and phenolphthalein (**3**) with a terminal diamine **4** ($n = 8$) and nonylamine (**5**) were examined by taking UV-visible

spectra in MeOH at 25 °C (Fig. 1). While diamine **4** ($n = 8$) developed no color change with **3**, a slight color change was observed with **2**. In contrast, dramatic color change



SYNTHETIC ORGANIC CHEMISTRY — Fine Organic Synthesis —

Scope of Research

The research interests of the laboratory include the development of new synthetic methodology, molecular recognition, and total synthesis of natural products. Programs are active in the areas of use of chiral leaving groups for an asymmetric induction, asymmetric alkylation of carbonyl compounds based on “memory of chirality”, development of new type of chiral nucleophilic catalysts, utilization of 8,8'-disubstituted 1,1'-binaphthyls as a chiral controller, visualization of molecular length by functionalized phenolphthalein, use of homooxalixarene for molecular recognition, syntheses of molecular switch.



Professor
FUJI
Kaoru
(D Pharm SC)



Assoc Prof
KAWABATA
Takeo
(D Pharm SC)



Instructor
TSUBAKI
Kazunori
(D Pharm SC)



Technician
TERADA
Tomoko

Secretary:

IZAWA, Yukako

Lecturer (part-time):

BAGUL, Trusar D. (Ph. D)

Guest Research Associate:

MARX, Karsten H. (Ph. D); CHEN, Jianyong (Ph. D);

WANG, Bingui (Ph. D);

CHANCHARUNEE, Sirirat (Ph. D)

Students:

MOMOSE, Yashima (DC); OHNISHI, Hiroshi (DC);

NURUZZAMAN, Mohammad (DC);

FUJII Kunihiko (MC); HAYASHI, Noriyuki (MC);

OTSUBO, Tadamune (MC); YOSHIDA, Hiroshi (MC);

TANAKA, Hiroyuki (MC); SUZUKI, Ryutaro (MC)

MUKOYOSHI, Koichiro (MC)

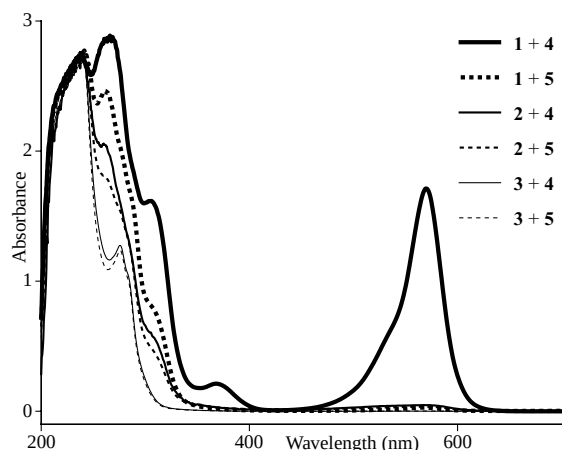


Figure 1. UV-visible spectra of **1**, **2** and **3** with the diamine **4** ($n = 8$) (solid lines) and with nonylamine (**5**) (dotted lines) in MeOH at 25 °C. The concentrations are 2.5×10^{-4} M for the hosts and 2.5×10^{-3} M for the guests.

was seen with compound **1**. The change in color depends upon the length of the diamine. The color development by **1** and amines was greatest with guest diamines of $n = 8$ and 9. Diamines shorter than 1,5-diaminopentane gave no coloration that could be detected by the naked eye.

The degree of color development by **1** and diamines **4** is quite sensitive to temperature. The absorbance at 571 nm by the complex of **1** and diamine **4** ($n = 9$) decreases with a rise in temperature. The reversibility and reproducibility of this change were confirmed as follows. The temperature of the mixture was gradually increased from 20 °C to 50 °C over 30 min and then dropped to 20 °C over another 30 min. This temperature profile was repeated more than 10 times while monitoring the UV-visible spectrum at 571 nm (Fig. 2). In the ^1H NMR spectrum of the complex, the signal of the α -methylene of the diamine at δ 2.47 ppm was broad at 22 °C, but sharpened to a triplet at 60 °C. These experiments show that the diamine **4** ($n = 9$) dissociates from the host molecule **1** to show free rotation at a higher temperature. Thus, color development due to complex formation reflects changes in temperature.

To better understand the above phenomena, the structure of the colored complex of **1** and diamine **4** ($n = 9$) was investigated in detail. The values of $\text{p}K_{\text{a}1'}$ and $\text{p}K_{\text{a}2'}$ in 50% aqueous methanol at 30 °C were 10.4 and 11.1 for **1**, and 9.6 and 11.3 for **3**. These data suggest that there is no correlation between the coloration of **1** and the difference in $\text{p}K_{\text{a}}$ values. Tamura and his coworkers reported that the colored complex of phenolphthalein (**3**) exists in a dianionic form [2]. The colored complex of **1** and diamines is also considered a dianion. A Job plot using UV-visible spectra suggested that the host-guest ratio in the colored complex of **1** and diamine **4** ($n = 9$) was not 1:1, but rather 1:2, 2:3, or some intermediate ratio. These findings indicate that one molecule of the diamine is

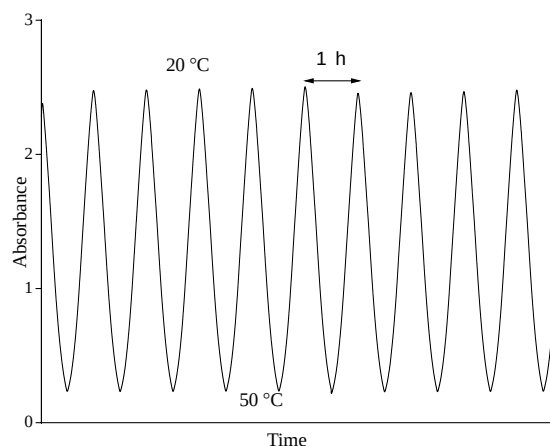


Figure 2. Temperature dependence of the absorbance of **1** (5.0×10^{-4} M) in the presence of **4** ($n = 9$, 1.0×10^{-3} M).

Table 1. The Apparent Association Constant (K') of the complexes of **1** with diamines **4** and Molar Absorption Coefficients (ϵ).

diamine 4	$K' (\text{M}^{-1})$	ϵ
$n = 7$	910 ± 60	5830 ± 120
$n = 8$	1270 ± 50	8930 ± 100
$n = 9$	2020 ± 100	7940 ± 130
$n = 10$	1370 ± 80	5280 ± 70

bridged between two crown rings and the other serves as a counter cation of the carboxylate, derived from ring-opening of the γ -lactone of **1**. Therefore, a new system was designed in which a large excess of *N*-ethylpiperidine exists together with the diamine to act as a counter cation for the carboxylate anion. *N*-Ethylpiperidine itself gave no color without a diamine. The Job plot of **1** and diamines **4** ($n = 7$ -10) in the presence of *N*-ethylpiperidine clearly showed a 1:1 correlation between them. Thus, the colored complex consists of **1**, diamine and *N*-ethylpiperidine in the ratio of 1:1:1 in this system. The apparent association constant (K') of the complexes and molar absorption coefficients (ϵ) were determined by UV-visible titration. The results listed in Table 1 show that the degree of coloration caused by the interaction between **1** and diamines depends not only on the apparent association constants but also molar absorption coefficients.

References

- Fuji, K.; Tsubaki, K.; Tanaka, K.; Hayashi, N.; Otsubo, T.; Kinoshita, T. *J. Am. Chem. Soc.*, **1999**, *121*, 3807.
- Tamura, Z.; Abe, S. Ito, K.; Maeda, M. *Anal. Sci.*, **1996**, *12*, 927.