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Visual Recognition of Triamines by Phenolphthalein Derivatives: Consideration of the Structure of the Colored Complex

Kazunori Tsubaki, Noriyuki Hayashi, Mohammad Nuruzzaman, Tomokazu Kusumoto, and Kaoru Fuji*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

fuji@scl.kyoto-u.ac.jp

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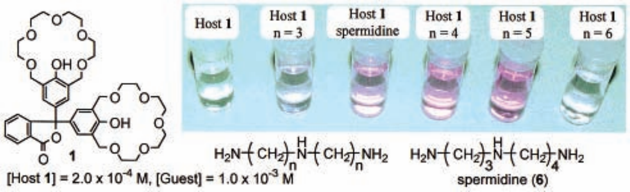
ABSTRACT



A hybrid molecule 1 consisting of phenolphthalein and two crown ether moieties can be used to discriminate the length of linear triamines strictly by color development. The purple color is developed most deeply at –10 °C and fades with either an increase or decrease in temperature.

The visualization of specific properties of a guest molecule using host−guest complexation is of significant importance in the field of supramolecular chemistry.[1] The recent progress in the visual recognition of anionic species is particularly remarkable.[2] Linear recognition (recognition of molecular length) has been reported by many researchers using ditopic receptors or cylindrical receptors.[3] We recently reported the visual recognition of α,ω-diamines using host molecule **1** composed of phenolphthalein and two crown ether moieties, although the structure of the colored complex remained obscure.[4] We observed that the ratio of the host **1** and α,ω-diamine in the colored complex shifted from 1:2 or 2:3 to 1:1 in the presence of a large excess of *N*-ethylpiperidine, which captured the carboxylate derived from ring opening of the γ-lactone of the host. In the present paper, we report the recognition of triamines using host molecule **1** and the possible structure of the colored complex (Figure 1).

Triamines such as **2**−**6** may give a colored complex with a 1:1 ratio without *N*-ethylpiperidine, because the inner imino

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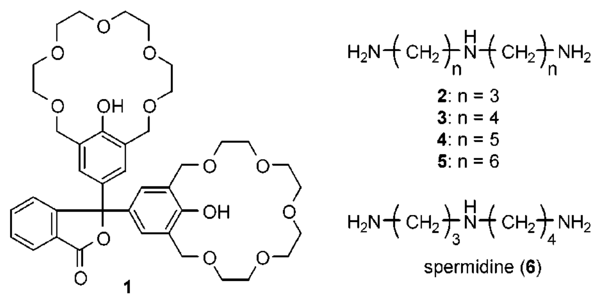

Figure 1. The structures of host **1** and guest triamines **2**−**6**.

group can capture the carboxylate. In fact, triamines **2**−**4** and spermidine (**6**) developed a bright purple color (Figure 2) due to the formation of a 1:1 complex as determined by Job plotting (Supporting Information). The association constants (K_a) as well as molar absorption coefficients (ϵ) were determined by UV−vis titration and analyzed by the Rose−Drago method.[5] The results are summarized in Table 1. Both K_a and ϵ have maximum values with triamine **4**. It is especially noteworthy that host **1** can be used to strictly discriminate **4** from **5** by color development, while general ditopic receptors bind vaguely to a guest molecule longer than the distance between two binding sites. This sharp discrimination can be ascribed to the synergistic decrease in both K_a and ϵ of triamine **5**, since the degree of color development is proportional to the product of the association constant and the molar absorption coefficient.

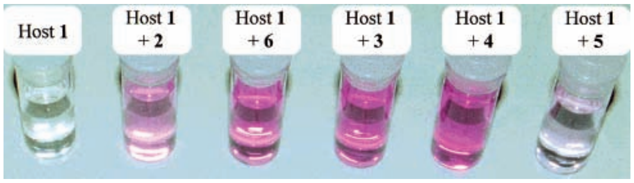

Figure 2. Color development by the host **1**. The concentrations of host **1** and guests (**2**−**6**) were 1.0 × 10^{-3} M in methanol.

Table 1. Association Constants (K_a) and Molar Absorption Coefficients (ϵ) of Complexes of the Host **1** with Triamines **2**−**6** at 25.0 °C in Methanol

entry	guest	K_a (M^{-1})	ϵ
1	**2**	720 ± 40	2250 ± 50
2	spermidine **6**	1140 ± 40	4530 ± 60
3	**3**	2270 ± 30	5080 ± 20
4	**4**	5300 ± 160	6590 ± 70
5	**5**	2360 ± 150	390 ± 10

Next, we investigated the structure and characteristics of the complex between host **1** and triamine **3**. Thermodynamic parameters ($\Delta H = -127.4 \pm 6.3$ kJ mol^{-1}, $\Delta S = -362.8 \pm 21.3$ J mol^{-1} K^{-1}) were obtained by van't Hoff plot based on the temperature dependence of the association constants ($K_a = 14870 \pm 880$ M^{-1}, $\epsilon = 5100 \pm 30$ at 15 °C; $K_a = 2270 \pm 30$ M^{-1}, $\epsilon = 5080 \pm 20$ at 25 °C; $K_a = 1090 \pm 10$ M^{-1}, $\epsilon = 4980 \pm 10$ at 30 °C). The lack of a change in ϵ indicates the formation of the same complex within the temperature range 15−30 °C. A large negative ΔS value suggests that a highly ordered complex is generated in methanol solution. Intermolecular cross-peaks between the aromatic proton of host **1** and the methylene protons adjacent to that of the imino group of triamine **3** were observed in the H−H NOESY spectrum. Figure 3 shows the proposed structure of the colored complex, where the terminal amino groups of guest **3** bridge between two phenolic crown rings of the host **1** and the protonated central imino group captures the carboxylate generated from the γ-lactone. The color

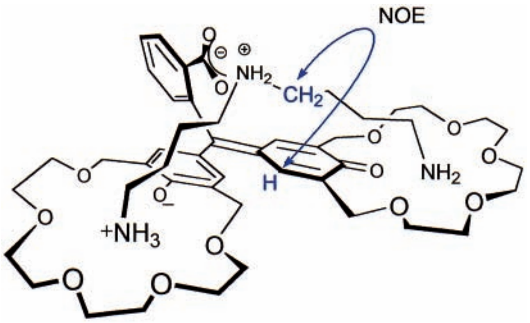

Figure 3. Proposed colored complex between host **1** and guest **3**.

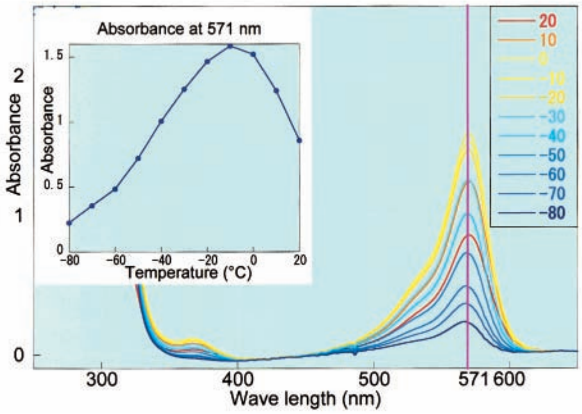

Figure 4. The variable-temperature UV−vis spectra of host **1** with guest **3**. The concentrations of host **1** and guest **3** were 3.1 × 10^{-4} M in methanol.

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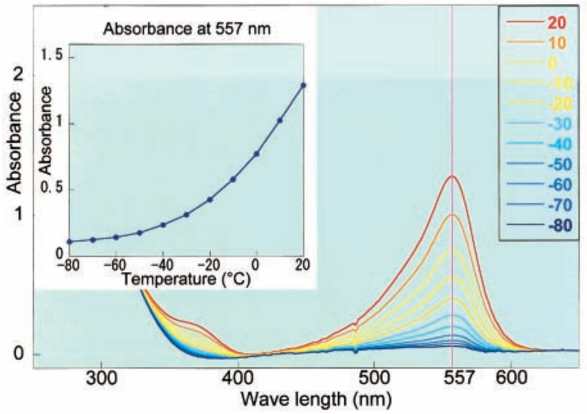

Figure 5. The variable-temperature UV−vis spectra of host **1** with NaOH. The concentration of host **1** was 8.3 × 10^{-5} M, and that of NaOH was 5.2 × 10^{-3} M in methanol.

development increases with a decrease in temperature, as observed for diamines as guest molecules.[4] This observation is ascribed to the large negative ΔS value. However, the degree of color development gradually decreases as the temperature decreases further from −10 °C (Figure 4).[6] This behavior turned out to be general for the phenolphthalein framework, since a similar temperature dependence was observed for the combination of host **1** and sodium hydroxide, as well as with phenolphthalein itself and sodium hydroxide (Figures 5 and 6). The disappearance of the color reflects deconjugation of the π-system spread over the two phenolic rings. The wavelength of maximal absorption ($\lambda_{\max}$) did not change at any temperature, which means that the color disappearance is not the result of distortion of the two conjugated rings but rather is due to the generation of a new colorless complex. We propose a structure for the colorless complex, although there are still some key aspects of this interesting observation that need to be explored further (Figure 7).

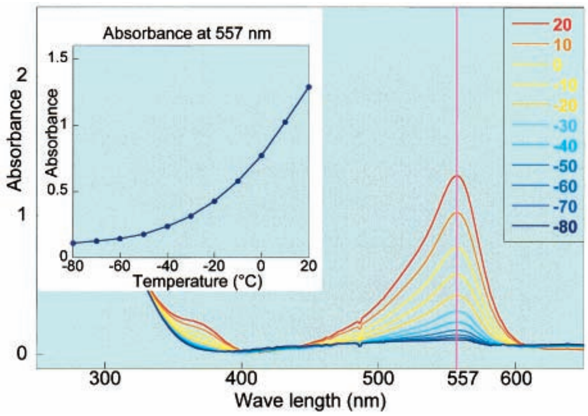

Figure 6. The variable-temperature UV−vis spectra of phenolphthalein with NaOH. The concentration of phenolphthalein was 7.3 × 10^{-4} M, and that of NaOH was 2.7 × 10^{-2} M in methanol.

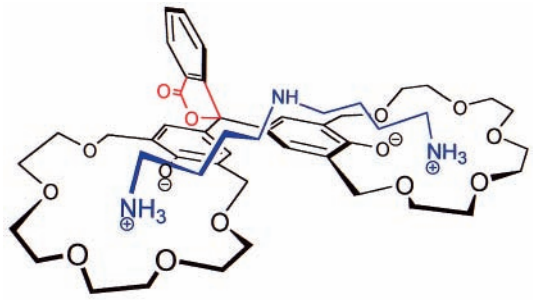

Figure 7. Proposed colorless complex between host **1** and guest **3**.

In conclusion, we demonstrated that host **1** can strictly recognize the length of a linear triamine by developing a purple color due to the synergistic cooperation of K_a and ϵ. This color develops in a limited temperature range and therefore can be used as a visible index of temperature.

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Supporting Information Available: Job plot between host **1** and triamines. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) For a recent review for temperature effect on the selectivity, see: Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Esser, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 477−515.