

Bidirectional and Colorimetric Recognition of Sodium and Potassium Ions

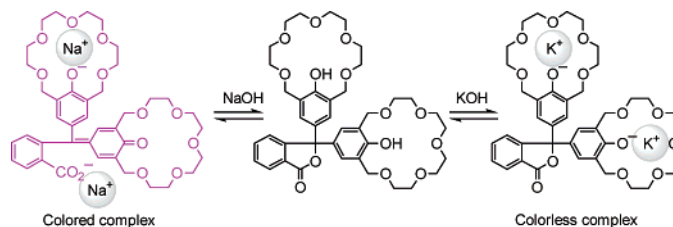
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ABSTRACT



Host **1** based on the phenolphthalein skeleton and two crown ether moieties demonstrated opposite behaviors toward sodium and potassium cations caused by bidirectional complexation.

In living organisms, sodium and potassium ions play important and opposite roles in the maintenance of homeostasis.¹ Studies of functional molecules that can selectively capture metal cations were the dawn of host–guest chemistry or supramolecular chemistry.² Numerous host molecules that interact with metal cations have been reported, and host molecules that can discriminate among metal cations by changing color have been investigated.³ These host molecules change color due to differences in their ability to recognize various cations. To the best of our knowledge, there have

been no reports on a functional molecule that can exhibit opposite behaviors toward two kinds of cations. We have reported that host **1** and its related compounds could recognize various properties, such as the length of guest molecules,^{4a,b} sequences of dipeptides,^{4c} and chiralities,^{4d,e} by developing color. In this paper, we report that host **1** exhibits fascinating and opposite behavior toward sodium and potassium accompanied by temperature change.⁵

Variable-temperature UV–vis spectra and photographs of host **1** and sodium or potassium are shown in Figure 1. The absorbance at around 565 nm caused by the interaction of **1** and NaOH increased as the temperature decreased (Figure

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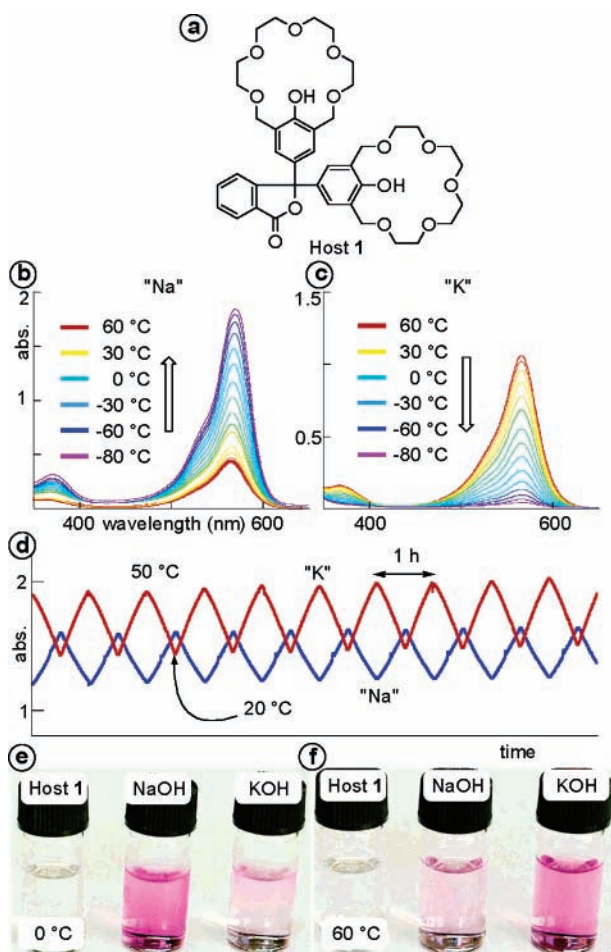
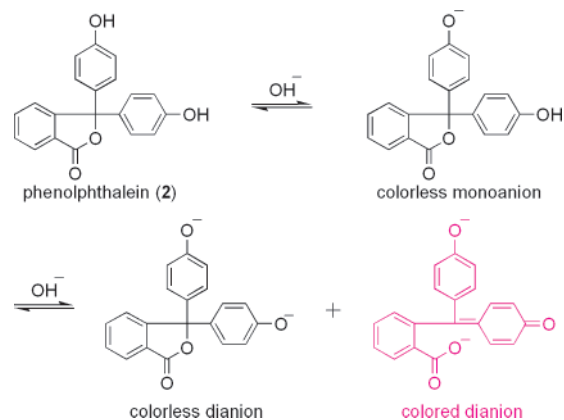


Figure 1. (a) Structure of host **1**. The variable-temperature UV-vis spectra of host **1** with (b) NaOH and (c) KOH in methanol: [host **1**] = 1.7×10^{-4} M; [metal-OH] = 6.7×10^{-4} M. (d) Temperature dependence of the absorbance of host **1** with NaOH (blue line) and KOH (red line) at 566 nm in methanol: [host **1**] = 2.8×10^{-4} M; [metal-OH] = 1.0×10^{-3} M. The temperature of the mixture was decreased gradually from 50 °C to 20 °C over 30 min and then increased back to 50 °C over an additional 30 min. This temperature program was repeated several times and followed by UV-visible spectroscopy. Color development by host **1** with NaOH and KOH at (e) 0 °C and (f) 60 °C: [host **1**] = 1.3×10^{-4} M; [metal-OH] = 5.0×10^{-4} M.

1b). In contrast, coloration decreased as the temperature decreased for **1** and KOH (Figure 1c). The reversibility and reproducibility of these changes were confirmed (Figure 1d), and these phenomena could be detected by the naked eye (Figures 1e and 1f).

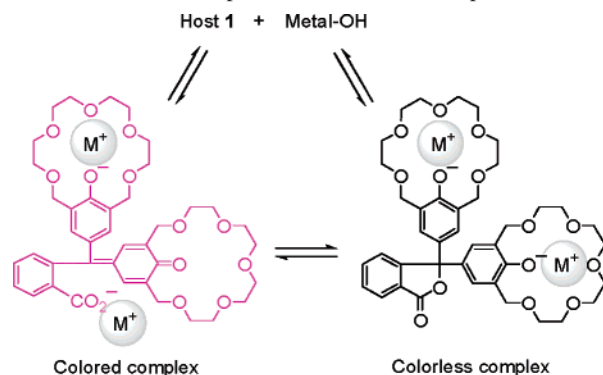
Because this observation was entirely unexpected and was the first example of sodium and potassium ions playing opposite roles in an artificial molecular recognition system, we further elucidated the mechanism. In previous studies of phenolphthalein (**2**) reported by Taguchi^{6a} and Tamura,^{6b} two types of dianions (colored carboxylate form and colorless lactone form) were shown to play important roles in color

Scheme 1. Acid Dissociation Equilibria of Phenolphthalein^{6b}



development (Scheme 1). Host **1** derived from the phenolphthalein skeleton inherits this property. We assumed that the different behaviors of host **1** with NaOH and KOH were caused by bidirectional complexation. Thus, complexation between host **1** and NaOH preferentially gives the colored carboxylate complex and that between host **1** and KOH leads to the colorless lactone complex (Scheme 2). To verify this

Scheme 2. Proposed Bidirectional Complexation



hypothesis, IR measurements were performed (Figure 2).

Host **1** shows lactone carbonyl absorption at around 1755 cm^{-1} . As metal hydroxide was added, a new absorption at around 1665 cm^{-1} increased; this new absorption was assigned to the colored carboxylate carbonyl (Figures 2a and 2b). Next, variable-temperature IR spectra were measured. In Figure 2c, in the presence of NaOH, the absorption (around 1655 cm^{-1}) corresponding to the carboxylate carbonyl group increased relative to that of the lactone carbonyl (1755 cm^{-1}) as the temperature decreased. This spectral behavior can be ascribed to the equilibrium moving from the colorless lactone complex to the colored carboxylate complex. The opposite behavior was observed for host **1** and KOH.

To clarify the nature of this bidirectional coloration, the interaction of host **1** and metal hydroxide was divided into two stages: deprotonation of the phenolic hydroxyl groups

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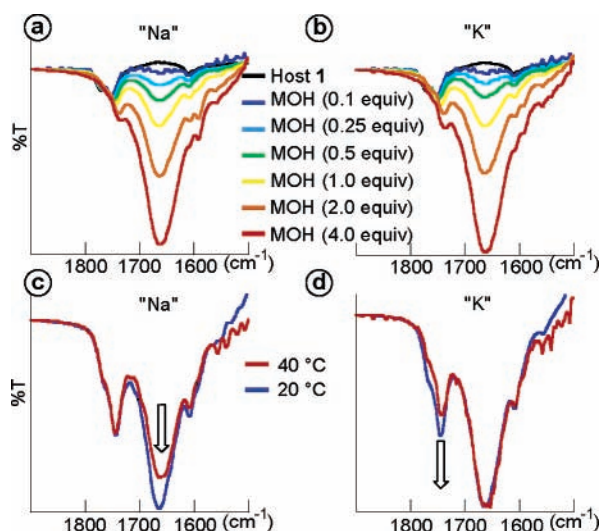
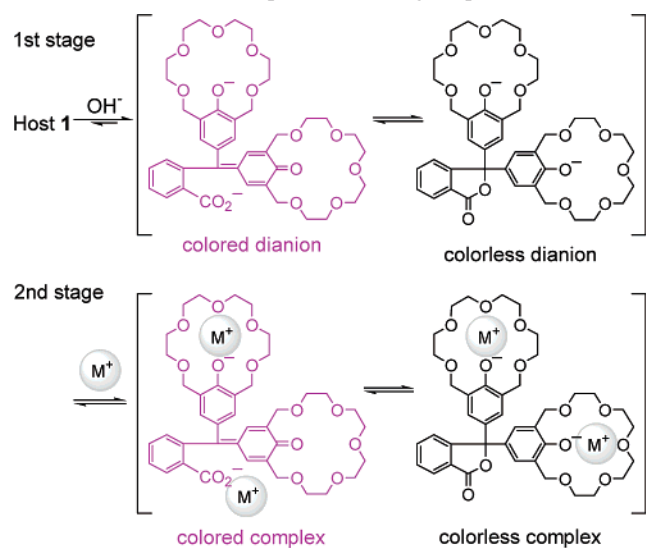


Figure 2. IR spectra of host **1** in the presence of metal-OH (NaOH for (a) and KOH for (b)) in methanol at 20 °C: [host **1**] = 1.5×10^{-2} M; [metal-OH] = 0 ~ 6.0×10^{-2} M. Variable-temperature IR spectra of host **1** and metal-OH (NaOH for (c) and KOH for (d)) in methanol: [host **1**] = [metal-OH] = 1.5×10^{-2} M. CaF₂ liquid cell. Light path length = 0.025 mm (GL Science).

of host **1** by hydroxide anions derived from the metal hydroxide and complexation between the phenolate crown-rings (or the carboxylate) and the metal cations (Scheme 3).

Scheme 3. Proposed Two-Stage Equilibrium



Because the counter cation of the base may be too bulky to interact with the phenolate ion of host **1**, tetra-*n*-butylammonium hydroxide (TBA-OH) was selected for the first stage. When excess TBA-OH was added to the host **1** solution, the color of the solution changed from colorless to magenta. A sodium or potassium ion was then added to the magenta solution. Strong bleaching was observed with the

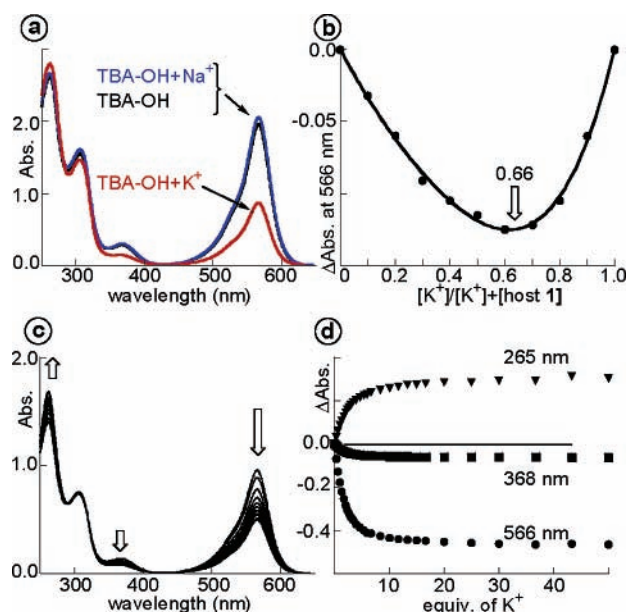


Figure 3. (a) UV-vis spectra of host **1** with Na⁺ and K⁺ in the presence of TBA-OH. Conditions: [host **1**] = 1.5×10^{-4} M, [metal-OH] = 6.0×10^{-4} M, [TBA-OH] = 7.5×10^{-2} M; solvent, MeOH; temp = 10 °C. (b) Job's plot of host **1** and K⁺: [host **1**] + [KOH] = 1.5×10^{-4} M, [TBA-OH] = 7.5×10^{-2} M; solvent, MeOH; temp = 25 °C. (c) UV-vis spectra of host **1** with various amounts of KOH in the presence of TBA-OH. Conditions: [host **1**]₀ = 7.5×10^{-5} M, [TBA-OH] = 3.8×10^{-2} M; solvent, MeOH; temp = 25 °C. (d) Three titration curves at different wavelengths (265, 368, and 566 nm).

addition of K⁺, whereas almost no color change was observed with Na⁺ (Figure 3a). It suggests that the colorless lactone complex formed with K⁺ and host **1** is generated in preference to the colored carboxylate complex. Next, the stoichiometry of the colorless complex was determined by a Job's plot under a large excess of TBA-OH (Figure 3b).⁷ The minimum of the Job's plot is at around 0.66, which indicates a 1:2 host-guest ratio for the colorless complex. The apparent association constants (K_1 and K_2) were determined by titration. The changes in the UV-vis spectra of host **1** upon the addition of K⁺ in the presence of a large excess of TBA-OH were measured (Figure 3c). The three titration curves at different wavelengths (265, 368, and 566 nm) were analyzed with an equation for 1:2 complex formation (Figure 3d).⁸ The association constants are: $K_1 = (15.7 \pm 1.1) \times 10^3$ (M⁻¹) and $K_2 = (2.7 \pm 0.3) \times 10^3$ (M⁻¹). In the case of Na⁺, the spectral changes were too small to calculate the corresponding association constants.

Why does the colorless lactone complex dominate in the case of host **1** and K⁺, whereas the colored carboxylate complex prevails with host **1** and Na⁺? One possible

(7) Because $\Delta\text{Abs} = \text{Abs}(\text{host } \mathbf{1} + \text{TBA-OH} + \text{K}^+) - \text{Abs}(\text{host } \mathbf{1} + \text{TBA-OH})$ is plotted on the ordinate, the amount of the change is negative.

(8) Determination of the apparent association constants (K_1 and K_2); see Supporting Information.

explanation is that the potassium ion is strongly inclined to occupy the seat of the pseudo phenol 18-crown-6 rings.⁹ This interaction is likely due to the fact that potassium has a suitable ionic radius relative to the diameter of the ring and to the resulting release of many solvated methanol molecules.¹⁰ Occupation of the seat of the ring is favored relative to cutting the long conjugated system between the two phenol crown rings.

In conclusion, we have found the first artificial recognition system in which sodium and potassium ions show opposite behaviors. These phenomena were caused by a complicated equilibrium among the host molecule, a colored complex,

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and a colorless complex. A membrane containing host **1** may be a useful tool for controlling flow between a Na⁺-rich layer and a K⁺-rich layer by using a temperature switch.

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Supporting Information Available: Variable-temperature ¹H NMR for host **1** with NaOH/KOH (SI Figures 1–3) and determination of the apparent association constants (K_1 and K_2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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