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Fluorescent Change Of Pyreneamide Bearing Calix[4]crown-5: Inhibit Logic Gate In K⁺-induced Complexation

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Fluorescent Change of Pyreneamide Bearing Calix[4]crown-5: INHIBIT Logic Gate in K^+ -induced $H_2PO_4^-$ Complexation

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The fluorescence excimer emission of **1** is found to be enhanced upon the addition of K^+ ion which is due to a conformational change of the ligand to have a more efficient $\pi-\pi^*$ interaction of two pyrenes. By contrast, no fluorescence change of **1** was observed in the anion binding test with F^- , Cl^- , Br^- , I^- , $CH_3CO_2^-$, HSO_4^- , and $H_2PO_4^-$ as their tetrabutylammonium salts in MeCN. Interestingly, it was observed that the excimer emission of the two pyrenes decreases upon the addition of $CH_3CO_2^-$ or $H_2PO_4^-$ in the $1 \cdot K^+$ complex solution. This is presumably due to a conformational change of the ligand by K^+ ion binding, which induces the better conformation of two facing pyrene amides to selectively adopt $CH_3CO_2^-$ or $H_2PO_4^-$ ion. This allosterical anion complexation could be applicable for NOR and INHIBIT (INH) logic gates.

Keywords: Calixarene; Logic gate; Fluorescence; Metal ion complexation

INTRODUCTION

Anions are known to be ubiquitous throughout all biological systems [1,2]. They carry most of the genetic information (DNA or RNA) in our body and are the majority of enzyme substrates and co-factors [1,2]. For these reasons, the anion recognition has become one of the important parts in supramolecular chemistry for cation recognition [3]. For designing selective hosts for anions conformation, geometry, anion basicity, and non-covalent interaction should be considered [1–3]. The non-covalent interaction includes electrostatic interaction, hydrogen bonding, hydrophobicity, and coordination to a metal ion, etc [1,2].

Calix[4]arenes, macrocyclic molecules with almost unrestricted derivatizing potential, possess unique

three-dimensional structure with a prominent binding ability toward guest materials [4]. A number of researches with respect to cation and anion complexation in calixarene molecules have been reported [4–7]. We previously reported **1** exhibiting a blue-shifted static excimer of the two pyrenes with Cu^{2+} ion complexation [8].

In a continuation of the cation and anion complexation studies with respect to the fluorescence changes of the PCT (Photo-induced Charge Transfer)-based calixarenes **1** and **2**, we herein report an interesting observation that K^+ ion complexation to the crown loop induces the conformational change of **1**, which enables it to selectively adopt the $H_2PO_4^-$ anion in the two facing pyreneamides by strong H-bonding.

In addition, the fluorescence changes can be applicable to functions of semiconductor logic gate used in modern computing [9–16]. There are 16 different logic gate functions for the two-input system [15,16]. Some of these functions have been demonstrated where ions and molecules are used as inputs, including the AND, OR and NOT gates designed by de Silva *et al.* [17,18] and the XOR gate designed by Balzani *et al.* [19,20]. The more complicated three input integrated INH gate was also demonstrated [21]. However, there are only few examples of fundamental two-input INH gate (e.g., K^+ and $H_2PO_4^-$) [22–25].

RESULTS AND DISCUSSION

Compounds **1** [8] and **2** [26], shown in Fig. 1, were synthesized and reported by our research group

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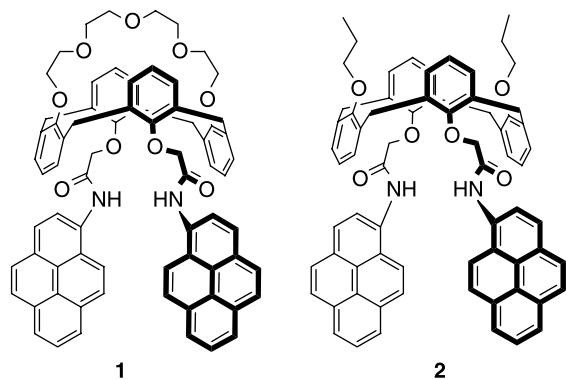


FIGURE 1 Receptors 1 and 2.

earlier. Both compounds bear activated pyreneamides for hydrogen bonding interaction with anions. In the fluorescent changes of pyrene (Py) excimer at about 480 nm, **2** as a reference showed F^- ion selectivity [26], whereas **1** gave no response to any anions tested (Fig. 2a). This is probably because the crown loop of **1** has something to do with a conformational distortion of the two facing pyreneamides for the anion complexation. For cation binding, we also reported that the polyether ring of **1** plays an important role in the change of the excimer emission of pyrenes. Upon addition of K^+ ion which is suitable for calix[4]crown-5 of **1**,

the excimer emission of pyrene unit increases because the K^+ ion complexation induces the conformational change of the two pyrene amides to enhance the π - π interaction [8,26–28].

Interestingly, however, we found that the excimer emission of **1** declines for $H_2PO_4^-$ ion in the presence of K^+ ion as shown in Fig. 2. The excimer quenching due to a PET (Photo-induced Electron Transfer) effect [29,30] was shown only in the case of $H_2PO_4^-$ ion complexation. It is noteworthy that the H-bonding based $H_2PO_4^-$ ion complexation is enhanced not only by an allosterical conformational change induced by K^+ ion complexation in the crown-5 loop but also by more efficient ion-pairing electrostatic interaction between K^+ and $H_2PO_4^-$. For the latter ion, it is in good agreement with the report from Beer and co-workers that the anion binding ability is enhanced in the presence of a suitable cation, so called ion-pair recognition [2,31–33]. Figure 3 indicated excimer emission changes of $1 \cdot K^+$ by the titration of $H_2PO_4^-$ ion in CH_3CN . When the K^+ ion was added, the excimer emission of **1** enhanced by allosterical conformational change of the pyreneamide part to give the more prominent π - π interaction (HOMO–LUMO) between two pyrenes [8,26]. Upon the addition of $H_2PO_4^-$ to this $1 \cdot K^+$ complex, the excimer emission gradually declined.

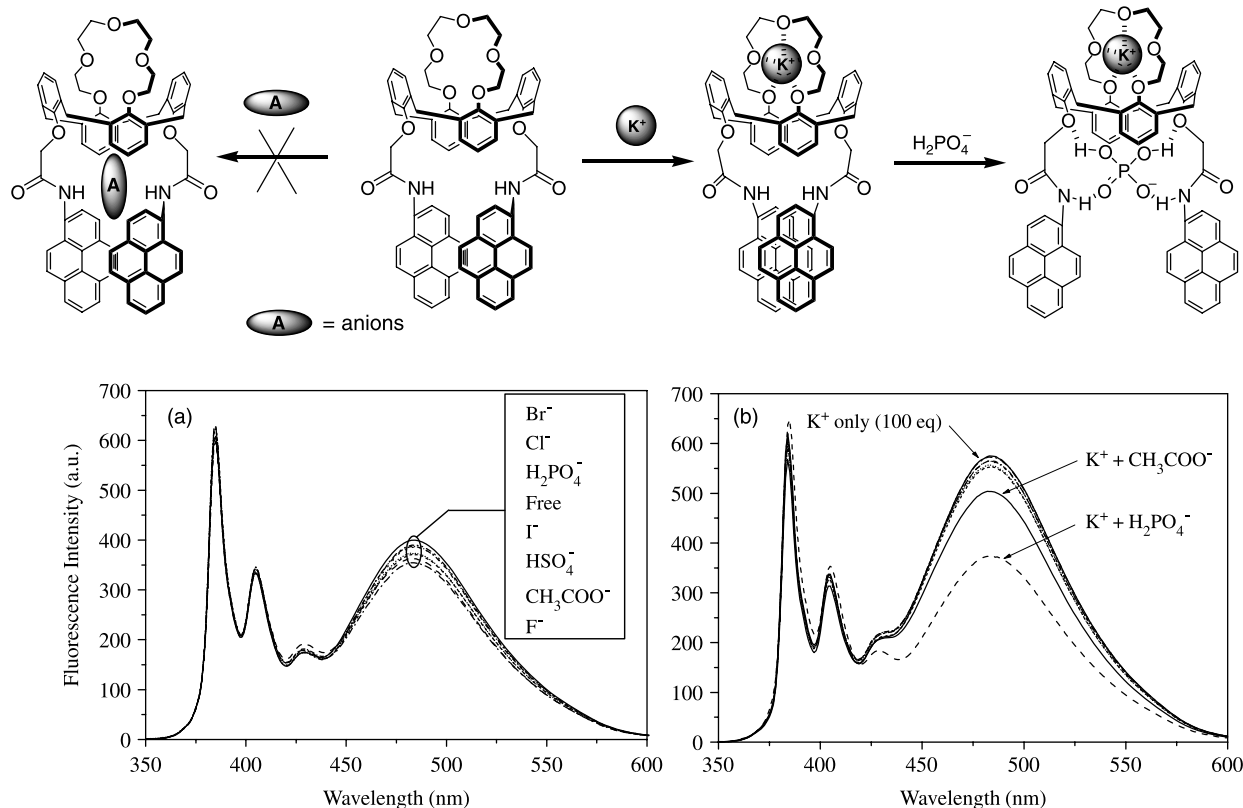


FIGURE 2 (a) Fluorescence changes of **1** (6.0 μ M) in CH_3CN upon the addition of various anions (1,000 equiv). (b) Fluorescence changes of $1 \cdot K^+$ (6.0 μ M) in CH_3CN upon the addition of various anions (1,000 equiv). The excitation wavelength is 343 nm.

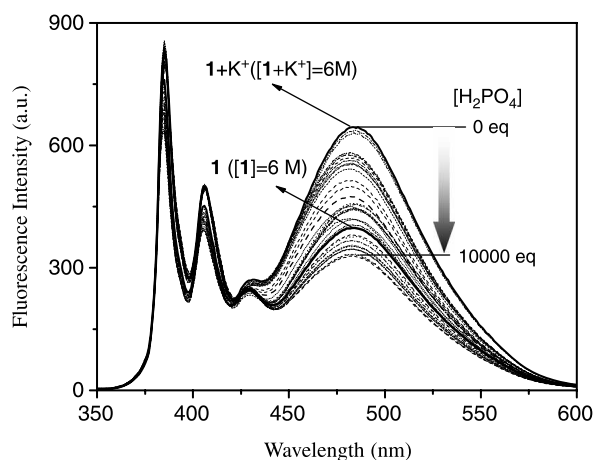


FIGURE 3 Fluorescence emission change of the $1\cdot K^+$ complex in CH_3CN upon the addition of $H_2PO_4^-$. The excitation wavelength is 343 nm.

The 1H NMR experiment (Fig. 4) was performed to clarify the binding mode of K^+ and $H_2PO_4^-$. Upon adding 5 equiv. of $KClO_4$ into a chloroform- d solution of the receptor **1**, we observed an up-field shift of the $N-H$ of pyrene unit. This is because the initial strong H-bonding between the $C=O$ and $N-H$ of two pyrenes of **1** is interrupted by the K^+ ion complexation in the crown unit. Subsequently, addition of $n-Bu_4NH_2PO_4$ to the solution causes the peak of amide to down-field shift by the H-bonding interaction.

As a consequence of the excimer emission behavior of the **1** in the presence of K^+ or $H_2PO_4^-$,

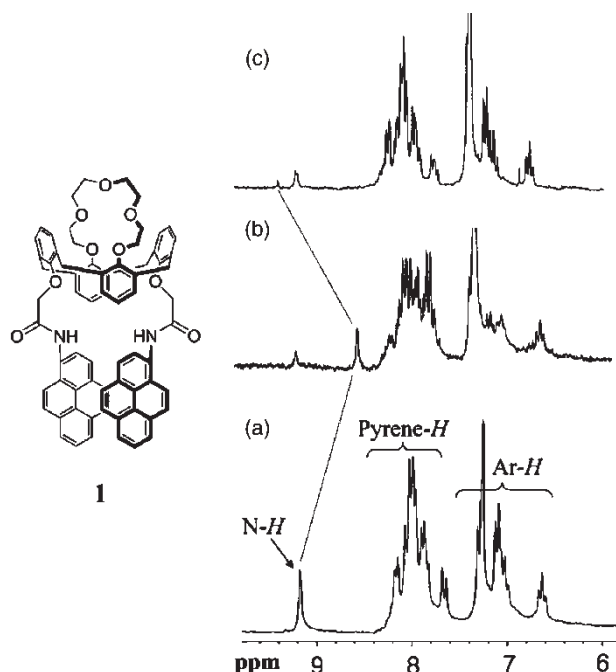


FIGURE 4 Partial 1H NMR spectra (200 MHz) in $CDCl_3$: (a) free **1** (0.03 mM); (b) **1** with $KClO_4$ (5 equiv); (c) $1\cdot K^+$ with $n-Bu_4NH_2PO_4$ (10 equiv).

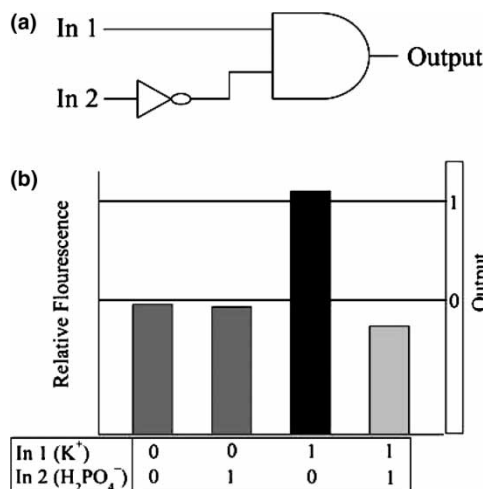


FIGURE 5 (a) The INH gate represented using a conventional gate notation; (b) Bar representation of INHIBIT gate at 483 nm upon irradiation at 343 nm. Output of **1** was inhibited by combination of two inputs (K^+ and $H_2PO_4^-$).

this probe molecule mimics a function of logic gate. The fluorescence logic gate for **1** was operated by a combination of inputs of K^+ and $H_2PO_4^-$ as input signals. As shown in Fig. 5, we constructed a logic circuit along with the truth table for the fluorescence on-off behavior of **1** upon addition of two sets of inputs. The excimer emission at 483 nm is Switched-off without any inputs (none of K^+ and $H_2PO_4^-$). In **1** (K^+) is operated to signal the excimer emission enhanced (Output = $0 \rightarrow 1$) while In **2** ($H_2PO_4^-$) as an inhibitor is executed to provide the excimer emission quenched (Output = $1 \rightarrow 0$). This progress is referred to as the INH logic function which can interpret a particular integration of an AND and a NOT logic function, where the output signal is inhibited by one of the active inputs [15,16,21].

In conclusion, free **1** having two pyreneamide groups and crown-ether ring was found to be unable to encapsulate any anions. K^+ ion complexation to the crown-5 ring of **1** induced an allosteric effect to result in the better interaction of HOMO and LUMO of the $Py-Py^*$ to give rise to a strong excimer emission. $1\cdot K^+$ executed an allosteric effect on conformational change of the two amides group to preferentially adopt the $H_2PO_4^-$ ion. Hence, regarding excimer emission of **1**, it was fluorescence-On with K^+ and fluorescence-Off with two combinational inputs (K^+ and $H_2PO_4^-$ ions), mimicking the function of the 2-bit INHIBIT logic gate.

EXPERIMENTAL SECTION

Synthesis

Compound **1** [8] and **2** [26] were prepared following the literature procedures.

General Procedures for Fluorescence Study

Fluorescence spectra were recorded with a RF-5301PC spectrofluoro-photometer. Stock solutions (1.00 mM) of the metal perchlorate salts were prepared in CHCl_3 . Stock solutions (0.06 mM) of **1** and **2** were prepared in CHCl_3 . For all measurements, excitation was made at 343 nm and emission slit width was 3 nm.

Acknowledgement

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