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A Supramolecular Fluorescent Probe, Activated by Protons To Detect Cesium and Potassium Ions, Mimics the Function of a Logic Gate

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The design and synthesis of molecular electronics and photonics for molecular-scale information processing has become an active area of research.[1] Molecular devices which function as wires,[2−5] switches,[6−12] diodes,[13,14] and logic gates[15−21] have been reported. Five basic logic gates, YES, NOT, AND, OR, and XOR, have been documented in recent years.[15−21] Two integrated logic functions, OR NOT and AND NOT, based on a photoinduced electron transfer (PET) process have been recently described.[22,23] Fluorescent PET sensors have also received much attention in recent years for their wide application in various chemical and biological processes.[24] In general, a PET sensor consists of a guest binding site as the receptor and a photointeraction site (fluorophore) for signal transduction.[24] Many of the receptor (host) and fluorophore (reporter) molecules reported to date are connected with a short spacer molecule.[24,25] The sensing phenomenon observed in such systems results from the change in emission intensity of the reporter molecule upon accommodation of a guest molecule within the host cavity.[24] Thus, the sensitivity is proportional to the strength of the emission signal produced after complexation of the guest molecule by the receptor. Aza crown ethers have been utilized as the metal ion receptor in PET sensors because the lone pair electrons of the nitrogen atom in the crown moiety can act as an electron donor to quench the emission of many fluorophores.[24] Protonation or participation of the lone pair electrons on the nitrogen atom upon metal ion complexation diminishes the PET effect, causing an enhancement in the fluorophore's emission intensity (fluorescence turn-on). The combination of these two effects could be used as a concept to design molecular probes for sensing two metal ions. In this paper, we report the emission properties of a supramolecular assembly, **1**, whose synthesis was based on the above conceptual approach.[26] Our fluorescence data indicate that **1** acts as a cesium sensor in an acidic environment and as a potassium sensor in an alkaline environment. Furthermore, the fluorescence behavior of **1** mimics the function of a logic gate.

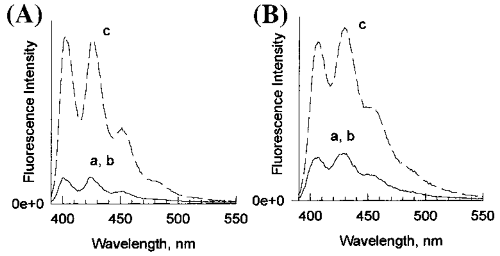
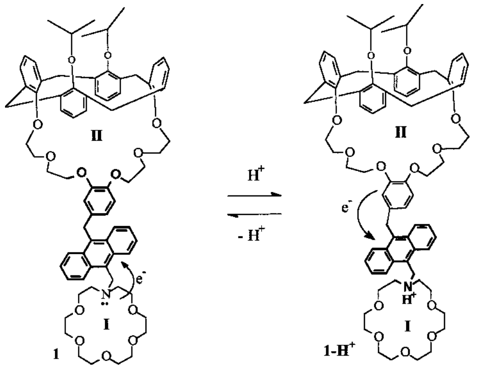


Figure 1. (A) Fluorescence spectra of **1** (1×10^{-6} M) in methanol under basic conditions (curve a) using trimethylbenzylammonium hydroxide,1 $\times$ 10^{-2} M, as proton scavenger in the presence of Cs^+ (1×10^{-4} M) and K^+ (1×10^{-4} M) ions (curves b and c, respectively). (B) Fluorescence spectra of **1**-H^+ (1×10^{-6} M) in methanol (1×10^{-2} M HCl) without (curve a) and with K^+ (2×10^{-6} M) and Cs^+ (2×10^{-6} M) ions present (curves b and c, respectively). Excitation at the isosbestic point for both **1** and **1**-H^+ was at 376 nm.

Scheme 1. Molecular Structure of **1** and **1**-H^+



The emission behavior of **1** (1×10^{-6} M) in MeOH under basic and acidic conditions is shown in Figure 1. Under basic conditions, a weak emission from **1** is observed (curve a in Figure 1A) owing to the quenching of anthracene fluorescence by the aminomethyl moiety in the crown ring I (Scheme 1). The emission intensity is not altered upon addition of Cs^+ ions (1×10^{-4} M, curve b in Figure 1A) that could potentially complex with either

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crown rings I or II (Scheme 1). Complexation of alkali metal ions by the crown ring II under basic conditions will have no effect on the fluorophor's emission because the unprotonated aminomethyl group in I acts as a donor[17] in the PET process. Thus, the emission of I is insensitive to Cs$^+$ ions due to weak complexation between crown ring I and Cs$^+$. This is also supported by the observation that the addition of K$^+$ ions (1×10^{-4} M), which can strongly complex with crown ring I, causes a 7-fold enhancement in the fluorophore emission (curve c, Figure 1A).

In acidic media, where the nitrogen atom of aza-crown ring I is protonated, **1**-H$^+$ exhibits an emission that is only slightly higher in intensity than that of the unprotonated **1** (curve a, Figure 1B). In the absence of alkali metal ions, this diminished emission intensity is due to PET quenching of the fluorophore by the dialkoxybenzene moiety of crown ring II, which is activated upon protonation of the amino group.[17] Protonation of the amine changes the energetics of the fluorophore so that the dialkoxybenzene can quench the fluorescence. This emission is unchanged upon addition of K$^+$ ions (2×10^{-6} M) because of the low affinity of the crown ring II for K$^+$ complexation (curve b, Figure 1B). However, addition of Cs$^+$ (2×10^{-6} M) to the solution containing **1**-H$^+$ causes a 4-fold increase in the fluorophore emission (curve c, Figure 1B). This observation is consistent with the large complexation constant reported for Cs$^+$ binding compared to that for K$^+$ binding for crown ring II.[27]

The effects of various alkali metal ions on the emission of **1** in MeOH, studied under basic and acidic conditions, are shown in Figure 2. Neither Li$^+$ nor Na$^+$ ions (up to 10^{-2} M) exert any effect on the emission behavior of **1** under either acidic or basic conditions. Complexation of Cs$^+$ (onset at 5×10^{-4} M) and Rb$^+$ (onset at 5×10^{-4} M) ions induces 2.5- and 5.2-fold enhancement in the emission of **1** under basic conditions (Figure 2A). In contrast, K$^+$ ion complexation under basic conditions promotes an emission enhancement of 6.4-fold with an onset at 10^{-6} M (Figure 2A). Both crown rings I and II present in **1** can bind alkali metal ions. However, the emission of **1** is quenched by a free amine group,[17] suggesting that the observed enhancement is due to complexation of the ions by aza-crown ring I. This is consistent with reports that aza-18-crown-6 is a good K$^+$ receptor.[24,28]

Under acidic conditions, complexation of K$^+$ and Rb$^+$ ions induces 2.9- and 3.3-fold enhancement in the emission of **1**-H$^+$ with onsets at 10^{-5} and 10^{-7} M concentration of each ion, respectively (Figure 2B). A 3.8-fold enhancement in the emission behavior of **1**-H$^+$ is observed for Cs$^+$ ions (onset at 10^{-8} M, Figure 2B). The 1,3-alternate calix[4]crown-6 has been shown to have a large complexation constant for Cs$^+$ binding.[27] Comparison of the emission behavior of **1** under basic and acidic conditions clearly shows the dual function of this probe for detecting both potassium and cesium ions in the same solution.

The fluorescence quantum yields for **1** ($\Phi_f = 0.061$) and **1**-H$^+$ ($\Phi_f = 0.094$) complexed with different alkali metal ions were calculated relative to that of 9,10-diphenylanthracene in MeOH, $\Phi_f = 0.94$.[29] Under basic conditions, K$^+$ ions (10^{-4} M) induce a 7-fold increase in the emission of **1** ($\Phi_f = 0.41$ for **1**-K$^+$ complex), while the same concentration of Cs$^+$ ions (10^{-4} M) exerts no effect ($\Phi_f = 0.061$ for **1**-Cs$^+$ complex). In acidic media, on the other hand, a 10^{-6} M solution of Cs$^+$ ions induces about a 4-fold enhancement in the emission of **1**-H$^+$ ($\Phi_f = 0.36$), while the same concentration of K$^+$ ions shows no significant change in emission intensity.

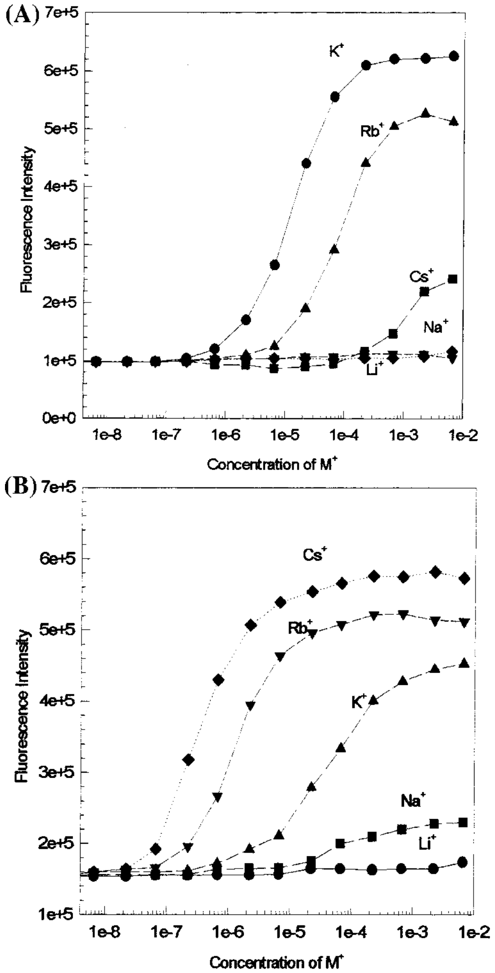

Figure 2. (A) Changes in the emission intensity ($\lambda_{em} = 429$ nm) of **1** (1×10^{-6} M) in basic methanol (trimethylbenzylammonium hydroxide, 1×10^{-2} M, was used as proton cavenger) as a function of concentration of various alkali metal ions, $\lambda_{ex} = 376$ nm and $\lambda_{em} = 427$ nm. (B) Changes in the emission intensity ($\lambda_{em} = 429$ nm) of **1**-H$^+$ (1×10^{-6} M) in acidic methanol (1×10^{-2} M HCl) as a function of concentration of metal ions. Excitation at the isosbestic point for both **1** and **1**-H$^+$ was at 376 nm.

Probe molecule **1** provides an example of a single fluorescent reporter group that is influenced by two different ion receptors. Experimental observations suggest that in unprotonated **1**, the observed PET effect results from communication between the fluorophore and crown ring I under circumstances in which crown ring II is inactive. In contrast, protonated form **1**-H$^+$ allows communication to be established between the fluorophore and crown II while disabling crown I from participation in the PET process.

As a consequence of the emission behavior of probe molecule **1** in the presence of K$^+$, H$^+$, and Cs$^+$ in solution, this probe molecule mimics the function of a logic gate. The emission profile of **1** as the concentrations of the above species are varied resembles a combination of simple logic gates. Although **1** may not be suitable for computing applications, a clever design based on this kind of switchable behavior will allow a single system to predict levels of several species in a complex solution mixture. We are currently investigating the fluorescent (and logic-gating) response of **1** and related molecules, immobilized in an organic matrix (e.g., a polymer inclusion membrane) to various alkali metal ions in aqueous solution.

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