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New Fluorescence-Quenching Process through Resumption of PET Process Induced by Complexation of Alkali Metal Ion

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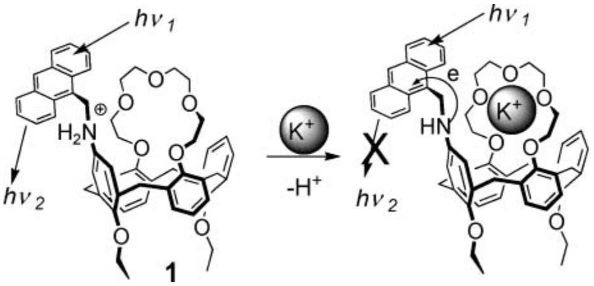
ABSTRACT



Under acidic conditions, a fluorescence-quenching process of 1 induced by selective binding of alkali metal ions was discovered. The mechanism of this new process involves alkali metal ion-induced deprotonation of the ammonium ion to trigger resumption of a fluorescence-quenching PET process.

The PET (photoinduced electron transfer) signal process has been proven to be one of the most important methods for fluorescent indication in supramolecular chemistry due to its unique advantages, “all or none” switchability, guest-induced “off−on” and “on−off” fluorescence, etc.[1] Its application in the recognition of alkali metal ions has been well-developed. One representative type of these sensors has a general unit of azacrown−spacer−fluorophore, in which a nitrogen atom acts as both the receptor in the complexation process and the electron donor in the PET process.[2] However, under acidic conditions, the signal function is invalidated due to the protonation of the amino group.[3] Inspired by the phenomenon of alkali metal-induced proton ejection,[4] we synthesized a new fluorescent chemosensor **1**, which has a classical anthracene−methylene−amine-type fluorophore, but assembled in an unique way. Its fluorescence can be selectively quenched by complexation of potassium or rubidium ion under acidic conditions. The quenching mechanism involves alkali metal ion-induced deprotonation of ammonium ion to trigger resumption of the PET process. And to the best of our knowledge, this phenomenon had never been reported before.

The synthesis of host **1** is illustrated in Scheme 1. Selective nitration of *1,3-alternate*-25,27-diethoxy-calix[4]crown-5 (**2**), an excellent K^+ ionphore,[5] with HNO_3/HOAc gave mono-

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[1] de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566.

[2] (a) de Silva, A. P.; de Silva, S. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1709−1710. (b) Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590−3593. (c) Xu, X.; Xu, H.; Ji, H.-F. *Chem. Commun.* **2001**, 2092−2093.

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[4] (a) McKervey, A.; Mulholland, L. *J. Chem. Soc., Chem. Commun.* **1977**, 438−439. (b) Cram, D. J.; Carmack, R. A.; Helgeson, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 571−577. (c) van Gent, J.; Sudhölter, E. J. R.; Lambeck, P. V.; Popma, T. J. A.; Gerritsma, G. J.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1988**, 893−895.

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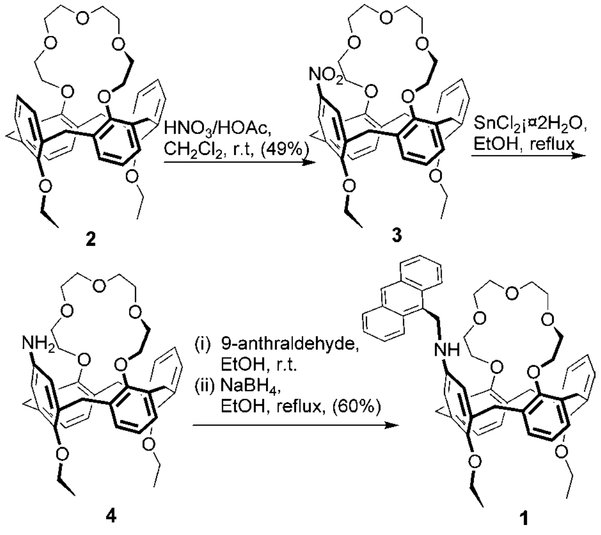
Scheme 1. Synthesis of **1**.



nitro-calix[4]crown-5 (**3**) in 49% yield. The two sets of proton NMR signals of the methyl groups at 0.79 and 0.65 ppm indicated that the nitro group was incorporated at the para position relative to one of the ethoxy groups. **3** was reduced with $SnCl_2{\cdot}2H_2O$ in ethanol and then reacted with 9-anthraldehyde to give a Schiff base. The final product **1** was obtained by $NaBH_4$-mediated reduction of the Schiff base.

Under both neutral and basic conditions, the fluorescence spectra of **1** were almost identical, and the fluorescence intensity was very weak due to the fluorescence-quenching PET process between the anthracene and the nitrogen atom. Unlike the azacrown−spacer−fluorophore-type fluoroionphore,[2] the addition of alkali metal ions had hardly any effect on the fluorescence of **1** under basic conditions, even after the concentration of alkali metal ions reached 100 equiv. The reason might be that the nonbonded lone pair electrons of the nitrogen atom could not participate in complexing the metal ion as in the azacrown.

In contrast, the fluorescence intensity of **1** was found to be much higher under acidic conditions, since the protonation of the nitrogen atom of amino group prevented the fluorescence-quenching PET process. It was remarkable that the fluorescence of $\mathbf{1}{\cdot}H^+$ could be quenched significantly by addition of K^+ under these conditions. When the concentration of K^+ reached 100 equiv, the fluorescence intensity was only 1/7 of the initial value (Figure 1).

Apart from K^+, 100 equiv of Rb^+ could also quench the fluorescence intensity to 1/7 that of $\mathbf{1}{\cdot}H^+$. However, there was no obvious spectral change upon addition of same amount Li^+, Na^+, or Cs^+ under the same conditions. These results were consistent with the binding selectivity of *1,3-alternate*-25,27-diethoxycalix[4]-crown-5 to alkali metal ions, i.e., a good ionphore for K^+ and Rb^+.[5,6]

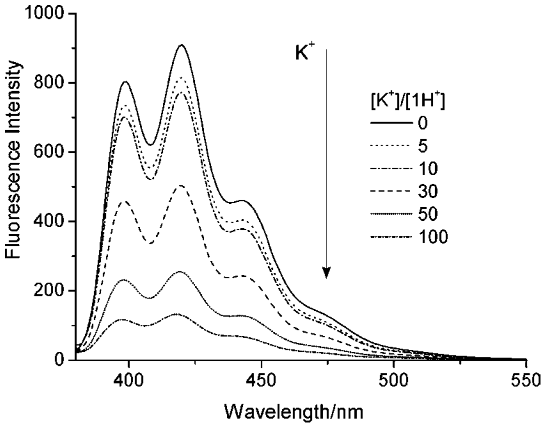


Figure 1. Fluorescence spectra of $\mathbf{1}{\cdot}H^+$ upon addition of K^+ ($[\mathbf{1}{\cdot}H^+] = 2.5 \times 10^{-5}$ mol L^{-1}, in $MeCN/H_2O$ = 99/1 (v/v) with 1.0×10^{-2} mol L^{-1} HCl, λ_{ex} = 369 nm).

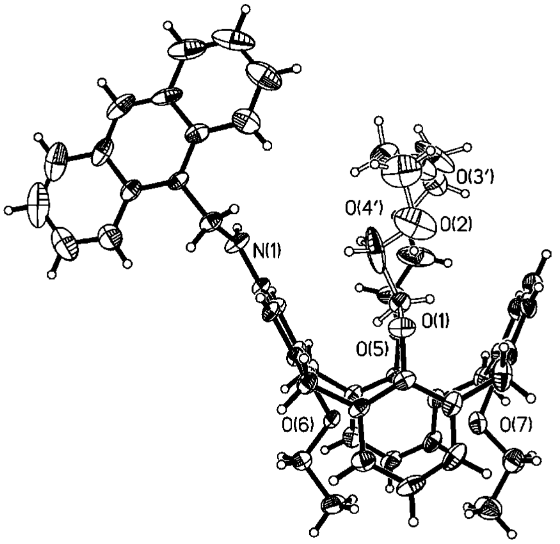


Figure 2. X-ray structure of **1**.

It is well-known that the two ethoxy-containing benzene rings facing the crown ether of the *1,3-alternate* calixcrown can participate in complexing metal ions through cation−π interactions.[7] From the X-ray structure of **1** (Figure 2),[8] it can be seen that the atomic distances between “the ethoxy benzene ring and the crown ether ring” as well as “the crown ether ring and the nitrogen atom” are similar. In addition,

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(7) Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102−3110.

(8) Crystal data for **1**: $C_{55}H_{57}NO_7$; $M = 844.02$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.815(4)$ Å, $b = 30.518(9)$ Å, and $c = 11.346(4)$ Å, $\beta = 109.457(6)°$, $V = 4510(2)$ Å^3, $\rho_c = 1.243$ g/cm^3. Data were taken using Mo Kα radiation at 293 K; 7960 independent reflections were measured on a sealed tube using ϕ and ω scan technique. The structure was determined by direct methods using Shelxtl. Final R indices $[I > 2\sigma]$ $R_1 = 0.0794$, $wR_2 = 0.1723$.

the half thickness of the benzene π-electron cloud (1.70 Å)[9] is also similar to the radius of the ammonium ion. In this regard, under acidic conditions, the complexed metal ion and the protonated amino group would become very close to each other. To lessen the unfavorable electronic repulsion between the two positive charges, either cation decomplexation[10] or ammonium ion deprotonation would occur. Thus, the relative values of the log K_{a_M} of the metal ion with the calixcrown as well as the pK_a of the amino group would determine the occurrence of either cation decomplexation or ammonium ion deprotonation. In this case, the pK_a of the amino group is about 5.1 (estimated from the fluorescence change of **1** after addition of a different concentration of HCl),[11] and the typical value of log Ka_M of a *1,3-alternate*-calix[4]crown-5 with K^+ or Rb^+ is much larger than 5,[5,6] therefore ammonium ion deprotonation occurred and led to fluorescence quenching. However, the log K_{a_M} values of other alkali metal ions are smaller than 5. Thus, cation decomplexation occurred and hence no fluorescence quenching was observed.

To validate the above hypothesis, the ^{1}H NMR spectral changes of **1** were monitored by addition of DCl/D_2O and then $KClO_4/D_2O$ (Figure 3). Most of the proton signals of **1** shifted downfield after addition of DCl/D_2O (acidic conditions), especially for the methylene and the ortho aromatic proton adjacent to the ammonium group. However, after K^+ was added, the proton signals almost shifted back to their original positions, indicating the deprotonation of the ammonium group.

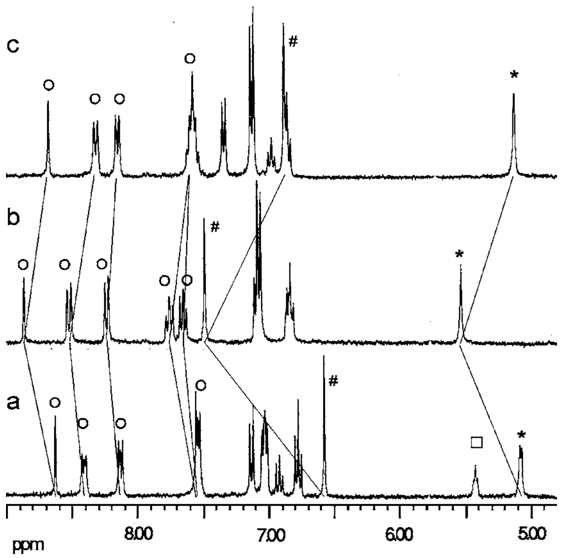

Figure 3. ^{1}H NMR spectra of (a) **1** (5×10^{-4} mol L^{-1}), (b) **1** (5×10^{-4} mol L^{-1}) with 0.1 mol L^{-1} DCl, and (c) b with 0.05 mol L^{-1} $KClO_4$ in DMSO-d_6. ((*) NH−CH_2−; (#) *ortho*-Ar*H* to nitrogen atom; (○) anthracene *H*; (□) −N*H*−).

From the experiments, we could deduce that there was an equilibrium (eq 1) in the solution.

$$[\mathbf{1}\cdot H^+] + M^+ \leftrightarrows [\mathbf{1}\cdot M^+] + H^+ \qquad (1)$$

And the equilibrium constant (K) could be obtained by an alternate form of the Stern−Volmer function (2).

$$\frac{F_0}{F} = \frac{[M^+]}{[H^+]}\cdot K + 1 \qquad (2)$$

Then, the association constant of **1** with alkali metal ions could be calculated from eq 3,[12]

$$\log K_{a_M} = \log K + pK_a \qquad (3)$$

and the values were 4.98, 5.12, 6.72, 6.55, and 5.10 for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively.

The fluorescence quantum yields for $\mathbf{1}\cdot H^+$ ($\Phi_f = 0.086$) complexed with different ions were calculated relative to that of 9,10-diphenylanthracene in cyclohexane ($\Phi_f = 1.0$).[13] After adding 100 equiv of K^+ or Rb^+ to $\mathbf{1}\cdot H^+$, the fluorescence quantum yields reduce to 0.011 and 0.012, respectively, a little higher than that of **1** ($\Phi_f = 0.002$). Addition of the same amount of other alkali metal ions, Li^+, Na^+, or Cs^+, have very little effect on the fluorescent quantum yields of $\mathbf{1}\cdot H^+$, and the values were found to be 0.086, 0.085, and 0.096, respectively.

It is envisioned that **1** could act as a logic gate with logic formula $F = H^+\cdot\overline{K^+}$. It is an INH-type logic gate,[14] and the output signal can be inhibited by K^+.

In conclusion, the fluorescence of $\mathbf{1}\cdot H^+$ could be quenched selectively by potassium and rubidium ion under acidic conditions through the "alkali metal ion induced" deprotonation of ammonium and the consequent resumption of the PET process. In addition, it may provide a new method for the design of fluoroionphore and molecular logic gate.

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Supporting Information Available: Deduction of eq 2, experimental procedures and characterization for compounds **1** and **3**, and crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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