New fluorescent probes for the detection of mixed sodium and potassium metal ions

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A new fluorescent probe 2 is developed that is capable of measuring the concentration of a mixture of sodium and potassium ions in the solution. This probe contains a fluorophore that is utilized in two ways depending on the pH of the solution.

A large family of the fluorescent chemical sensors is based on photo-induced electron transfer quenching (PET) of the fluorophore by the receptor.1–4 Most of the current PET fluorescent probes are designed for only one species. A multicolor labeling experiment entails the deliberate introduction of two or more probes to monitor simultaneously different species. This technique has major applications in flow cytometry, DNA sequencing, in situ hybridization, etc. However, only a few such two or multicolor systems have been studied because of the strict prerequisites of this technique, including absorption at a coincident excitation wavelength and well-separated emission spectra of two or more fluorophores,5 no energy transfer between two fluorophores, no transient excited-state collisional quenching, and no excited state dimer, etc. These prerequisites increase the barrier in the development of multicolor sensors.

Recently,6 we designed and synthesized one novel fluorescent probe 1. Our results have shown that this molecule can be used to detect caesium ions in acid conditions, but potassium ions in basic solutions. Based on the same design, we synthesized another probe 2. Logically, 2 would be a potential sensor in basic solution and a sodium sensor in acidic solution. In this paper, we report the fluorescence-sensing behavior of probe 2. Furthermore, the unique fluorescence behaviors of 1 and 2 suggest that another approach for a mixture of dual component sensing is feasible. We also report here that probe 2 could be a potential sensor for a mixture of sodium and potassium ions.

In molecule 2, two receptors are connected with the anthracene. One receptor is benzo-15-crown-5, which is a good host for sodium ions.7 Another is aza-crown-6-ether (ring I). The lone-pair electrons on nitrogen in ring I quench the fluorescence of anthracene. Addition of K+ in the solution causes an enhancement in the fluorophore’s emission due to the formation of the K+–2 complex as shown in Fig. 1. The complexations of ring I with other alkali metal ions are weaker than ring I with K+ and only cause weak fluorescence enhancement of 2. Meanwhile, since the crown ring II has no contribution to the PET process, the complexation of alkali metals by the crown ring II under basic conditions has no effect on the fluorophore’s emission.

In an acidic environment, where the nitrogen atom of azacrown ring I of 2 is protonated (hereafter referred as 2-H+), the PET fluorophore–receptor pair is switched to anthrylmethylammonium and benzo group in benzo-15-crown-5. The low fluorescence quantum yield of 2-H+ is similar to that of 2 in basic solution. The diminished emission intensity of anthrylmethylammonium is due to PET quenching of the fluorophore by the dialkoxybenzene moiety of crown ring II. The driving force, ΔG, is calculated to be −0.1 eV.9 Addition of Na+ to the solution results in an enhancement of fluorescence intensity of 2-H+ because the complexation between Na+ and benzo-15-crown-5 (ring II) inhibits the PET process from benzo to anthrylmethylammonium. The complexation constants of ring

![Image](https://example.com/image.png)

**Fig. 1** (A) Changes in the fluorescence intensity (λ_em = 426 nm) of 2 (1 × 10^{-6} M) in basic methanol (morpholine, 1 × 10^{-2} M as proton scavenger) as a function of concentration of various alkali metal ions. (B) Change in the emission intensity (λ_em = 425 nm) of 2-H+ (1 × 10^{-6} M) in acidic methanol (1 × 10^{-5} M HCl) as a function of concentrations of various alkali metal ions. Excitation at the isosbestic point for both 2 and 2-H+ is at 376 nm.
Table I The maximum fluorescence quantum yield ($\Phi$) and complexation constants, $K$, for the complexation of various alkali metal ions by 2 and 2-H$^+$ (1 $\times$ 10$^{-6}$ mol L$^{-1}$) in CH$_3$OH. $\lambda_{max}$ = 376 nm at the isosbestic point for both 2 and 2-H$^+$. The quantum yields were determined relative to 9,10-diphenylanthracene in MeOH, $\Phi_0$ = 0.94$^6$

<table>
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<tr>
<th>Metal ion</th>
<th>M$^+$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_{max}$ of 2</td>
<td>0.048</td>
<td>0.060</td>
<td>0.053</td>
<td>0.39</td>
<td>0.31</td>
<td>0.12</td>
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<td>$K$ of aza-crown in 2 with ions</td>
<td>—</td>
<td>10</td>
<td>$7.4 \times 10^2$</td>
<td>$6.30 \times 10^4$</td>
<td>$1.26 \times 10^4$</td>
<td>$2.82 \times 10^3$</td>
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<tr>
<td>$\Phi_{max}$ of 2-H$^+$</td>
<td>0.060</td>
<td>0.098</td>
<td>0.55</td>
<td>0.26</td>
<td>0.22</td>
<td>0.15</td>
</tr>
<tr>
<td>$K$ of 2-H$^+$</td>
<td>—</td>
<td>65</td>
<td>$6.2 \times 10^2$</td>
<td>$6.0 \times 10^2$</td>
<td>$3.9 \times 10^3$</td>
<td>$1.5 \times 10^2$</td>
</tr>
</tbody>
</table>

Notes and references