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A novel caesium selective fluorescent chemosensor

Wen-Sheng Xia, Russell H. Schmehl* and Chao-Jun Li*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA.
E-mail: cjli@mailhost.tcs.tulane.edu

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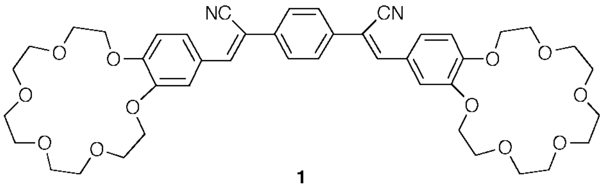
A novel caesium selective fluorescent chemosensor has been designed and synthesized; the chemosensor exhibited a selective fluorescent enhancement in the presence of other alkali metal ions.

The rapid and selective measurement of trace ions *in situ* has significant environmental and biological applications.[1] The selective sensing of trace amounts of caesium is important in detecting leaks from nuclear waste storage tanks (^{137}Cs in particular), which may cause serious problems to the environment.[2] Currently, there is no method available for *in situ* quantitative determination of Cs^+ in nuclear solutions. Very recently, Dabestani and coworkers developed a first-generation caesium selective fluorescent chemosensor based on a calix[4]arene derivative.[3] Nevertheless, it is still necessary to develop more sophisticated and more selective caesium chemosensors that can be easily handled.

Recently, we reported a highly selective fluorescent chemosensor for potassium, a dicyano-substituted distyrylbenzene derivative containing two 15-crown-5 rings which has a low emission quantum yield in acetonitrile ($\phi = 0.001$).[4] Studies showed that the high potassium selectivity of the sensor upon the complexation of potassium ions results from formation of a sandwich complex between the 15-crown-5 and a potassium ion that leads to a large enhancement of the fluorescence of the disytrylbenzene derivative. We have denoted this type of fluorescence enhancement Self-Assembling Fluorescent Enhancement (SAFE) since the luminescence is believed to result from formation of a structure in which each crown of the fluorophore is part of a sandwich complex.[5] Herein, we report a novel caesium-selective fluorescent chemosensor **1** that consists of a dicyano-substituted distyrylbenzene derivative and two 18-crown-6 rings.[6]



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In acetone solution, **1** shows a broad absorption at 380 nm. With the addition of Cs^+ ion [$Cs(CF_3CO_2)$ in acetonitrile], a slight decrease of the absorption is observed. However, a significant change is observed in fluorescence spectra of **1** when Cs^+ ions are added as shown in Fig. 1. The fluorescence intensity is enhanced significantly and the fluorescent peak red-shifts from 482 to 526 nm. The insert in Fig. 1 shows the titration curve of **1** with Cs^+. Stoichiometry studies indicate that **1** forms a 1 : 1 complex with caesium ion, indicating that each Cs^+ ion coordinates to two 18-crown-6 moieties. At saturation in acetone solution the maximum fluorescence intensity of **1** complexed with Cs^+ is about 20 times that of free **1**. Other alkali metal ions such as Li^+, Na^+ and K^+ were also examined. No significant fluorescent enhancement was observed with any of these, even though 18-crown-6 is known to bind K^+ strongly.[7] The results strongly suggest the formation of a sandwich complex consisting of two 18-crown-6 substituents and Cs^+. A similar fluorescence enhancement of *ca.* 12–15 times was also observed when CsF was used as a cation source. Stability constants, expressed as log *K*, determined assuming 1 : 1 complex formation are 4.3 in acetone and 5.7 M^{-1} in chloroform–acetonitrile (9 : 1, v/v).

The fluorescence behavior of **1** in the presence of Cs^+ is strongly dependent on solvent. In acetonitrile, sensor **1** shows a similar fluorescent enhancement when Cs^+ ions are added, but the enhancement is significantly lower than that in acetone. The saturation enhancement is only a factor of 4 in acetonitrile. The diminished enhancement could be due to a variety of factors such as differences in the emission quantum yield of the $Cs(\mathbf{1})_2$ sandwich complex in the two solvents or competitive formation of other $Cs^+/\mathbf{1}$ complexes involving acetonitrile displacement of a crown [*i.e.* formation of $Cs(\mathbf{1})(MeCN)_n$ complexes]. The use of mixed solvents containing chloroform and a small amount of acetonitrile (9 : 1, v/v) results in a much larger fluorescence enhancement than observed in pure acetonitrile. The titration curve, monitoring emission at 512 nm, is shown in Fig. 2. An enhancement of a factor of 20 is observed when two equivalents of Cs^+ ion are added to solutions containing 20 μM **1**. However, the luminescence intensity *decreases* with increasing Cs^+ concentration above $Cs^+/\mathbf{1}$ ratios of 2 (no new emission with a different maximum is observed). The decrease may result from break-up of the sandwich structure to form 1:1 (Cs^+ : 18-crown-6) complexes with the excess Cs^+ present. Results from ^{1}H NMR measurements support this hypothesis.[8] It should be noted that the fluorescence enhancement observed in acetone in greatly diminished upon addition of water as a cosolvent. For instance, acetone–water (9 : 1, v/v) little change in luminescence occurs with less than a ten-fold excess of Cs^+ and the maximum enhancement observed is only a factor of 3.5.

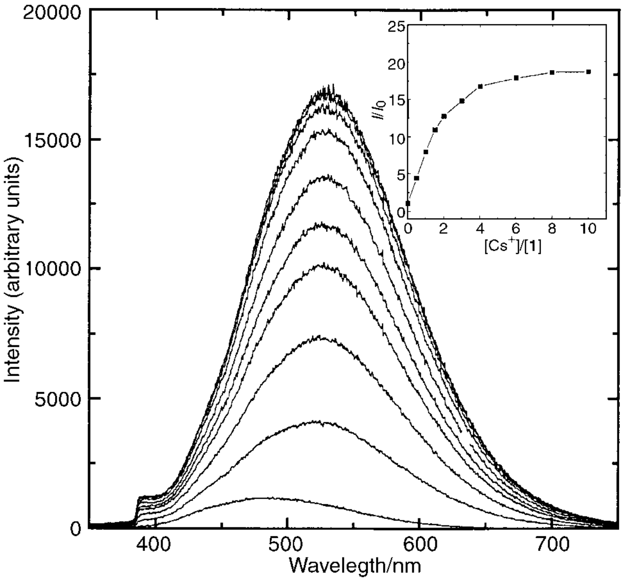

Fig. 1 Fuorescence spectral change upon the addition of caesium ions in acetone, [**1**] = 2 × 10^{-5} M. The insert shows the titration curve of Cs^+ in acetone (monitored at 526 nm, excited at 350 nm).

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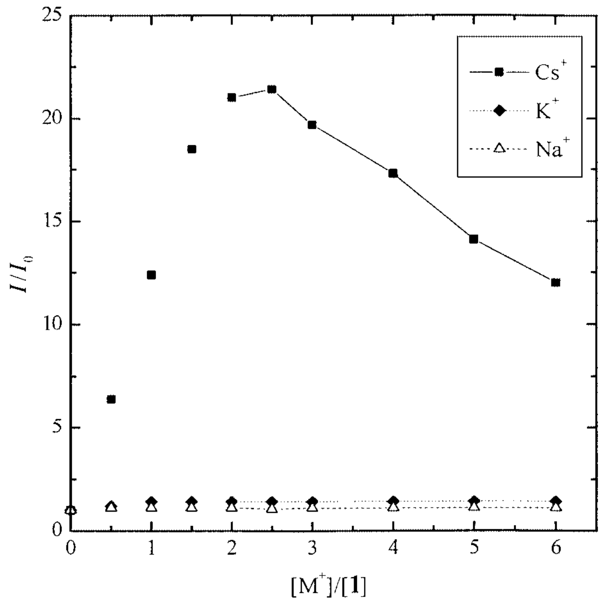

Fig. 2 Titration curve of **1** with metal ions ([**1**] = 2×10^{-5} M) monitored at 512 nm.

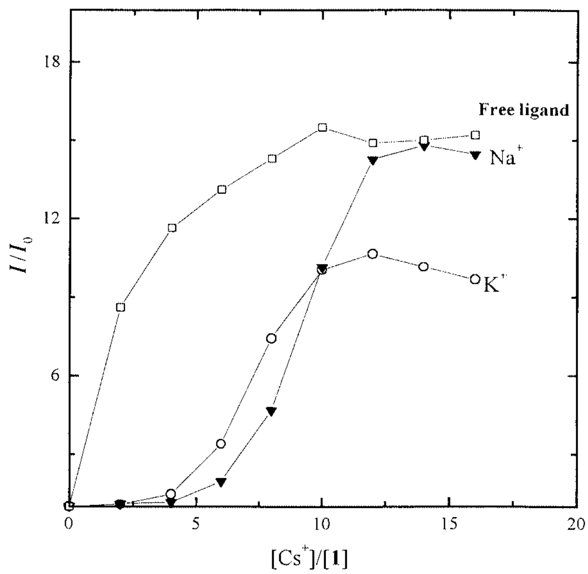

Fig. 3 The fluorescence intensity change upon the addition of Cs^+ ion in acetone in the presence of K^+ and Na^+ ($[K^+]$ = 3.75×10^{-4} M, $[Na^+]$ = 3.75×10^{-4} M). The intensity was monitored at 526 nm; [**1**] = 2×10^{-5} M.

The selectivity of this novel sensor for Cs^+ was also examined by competition experiments. Fig. 3 shows fluorescence intensity changes upon addition of Cs^+ when either K^+ or Na^+ is also present. Although K^+ and Na^+ each cause some interference to the fluorescence response at the beginning stage of the addition of Cs^+ ions, the fluorescence is turned on when $[Cs^+]/[K^+]$ or $[Cs^+]/[Na^+]$ reaches *ca.* 1:4. Further increases in the Cs^+ ion concentration lead to increases in the fluorescence intensity until a plateau in the emission is reached at $[Cs^+]/[M^+]$ and $[Cs^+]/[\mathbf{1}]$ ratios of 1:3 and 5:1, respectively. Competition studies between the Cs^+ ion and K^+ or Na^+ ions are also consistent with the assumption that only the formation of a sandwich structure will result in the turn-on of the fluorescence.

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Notes and references

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3 H.-F. Ji, G. M. Brown and R. Dabestani, *Chem. Commun.*, 1999, 609.

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5 Results from MALDI-TOF mass spectrometry and ^1H NMR suggest a 2:2 complex is formed.

6 Sensor **1** was synthesized by the following procedure: a mixture of 4′-formyl-benzo-18-crown-6 (100 mg), 1,4-phenyldiacetonitrile (22 mg) and three drops of tetrabutylammonium hydroxide in methanol was refluxed for 12 h. The reaction mixture was then filtered hot, and the recovered yellow solid was washed with ethanol several times. Further purification by recrystallization from a mixture of chloroform and methanol (2:8) gave **1** (100 mg, 40%) as yellow solid. $\delta_H(CDCl_3)$ 7.71(m, 3H), 7.49 (s, 1H), 7.4 (m, 1H), 6.92 (d, 1H, J = 12 Hz), 4.27 (m, 4H), 3.97 (m, 4H), 3.83–3.67 (m, 12H). $\delta_C(CDCl_3)$ 151.9, 149.8, 135.5, 127.7, 126.6, 125.3, 118.7, 113.8, 113.5, 108.1, 71.4, 71.2, 71.1, 69.9, 69.8, 69.6, 69.4. Elemental analysis. Calc. for $C_{44}H_{52}N_2O_{12}$: C, 66.00; H, 6.50; N, 3.50. Found: C, 65.46; H, 6.56; N, 3.39%.

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8 ^1H NMR titration of caesium trifluoroacetate in CD_3CN and **1** in $CDCl_3$–CD_3CN (9:1, v/v) shows that with the addition of caesium ions, the chemical shift first shifts upfield and then shifts downfield when the ratio of caesium to **1** is *ca.* 2:1.