New Calix[4]crown Diacylamides with Fluorescent Response to Complexation with Metal Ions

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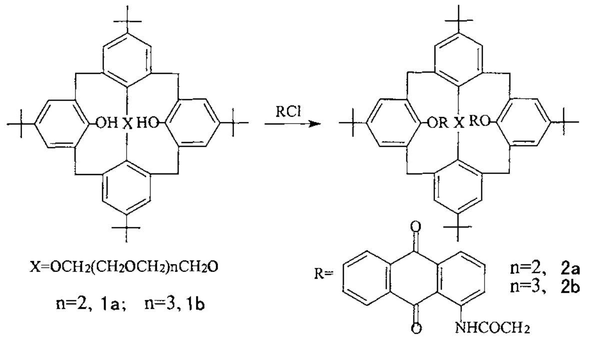
New calix[4]crowns having two acetaminoanthraquinone units at the lower rim have been synthesized; the intensity of their fluorescence spectra are markedly affected by alkali metal cation complexation.

Optical detection methods have received increasing attention for chemical trace analyses especially for selective determination of clinically important species. Spectroscopic detection of metal ions is of great importance both in the molecular design of ion sensors involving optical signal transformation and in the biochemical field. The detection of fluorescence having sensitive nature is an attractive method in a selective complexing process with metal ions.[1,2] Calixarenes are usefull building blocks in the design of novel host molecules.[3] Calix[4]arene derivatives incorporating chromogenic and fluorogenic groups at the upper or lower rim exhibit some excellent properties as receptor for metal ions or enantiomorph.[1,4-7] They can selectively complex with metal ions and selectively chiral recognize for enantiomorph, which shows a significant change on the UV-VIS absorption spectrum and fluorescence emission spectrum. Calix[4]arene crown ethers have exhibited an excellent selective complexation towards Na^+ or K^+,[8] but they have no fluorescence change on complexation because there are no fluorescence groups. This led us to prepare fluorescent calixcrowns by incorporation of fluorophores having coordination atoms into the calix[4]crown skeleton in order to observe efficiently a complexing selectivity and a concerted coordination behavior on the optical detection.

Herein, we designed and synthesized new calix[4]crown derivateves (**2a**, **2b**) appended acetaminoanthraquinone at the lower rim. The new calix[4]crown derivatives exhibit good fluorescent response in the complexation with sodium or potassium ions. We chose acetaminoanthraquinone because it is an efficient fluorophore and electroactive group.

The fluorescent calix[4]crown-4 derivative **2a** and calix[4]crown-5 derivative **2b** were synthesized by the reaction of p-tert-butylcalix[4]crown-4[8] (**1a**) or p-tert-butylcalix[4]crown-5[9] (**1b**) with 1-chloroacetamino-anthraquinone in presence of anhydrous sodium carbonate or potassium carbonate in dry toluene (Scheme 1). The purity and structure of **2a**[10] and **2b**[11] were confirmed by elemental analysis, mass specture and ^{1}HNMR spectroscopy.

The UV-VIS absorption spectra of **2a** and **2b** (2×10^{-5} mol dm^{-3}) were determined in MeOH-THF(v/v 15:1). **2a** has a maximum absorption at 401 nm and another at 336 nm; **2b** has a maximum absorption at 398 nm and another at 333 nm. After addition of NaSCN (2×10^{-5} mol dm^{-3}) in methanol, the maximum absorption of **2a** was changed from 401 nm to 380 nm, but addition of Li^+ or K^+, their absorption spectra almost were not changed. It shows that **2a** gives a selective complexation to Na^+. Addition of Li^+, Na^+ or K^+ thiocyanate (2×10^{-5} mol dm^{-3}), **2b** exhibits a selective complexation to K^+. The maximum absorption of **2b** was changed from 398 nm to 382 nm. The second absorption of **2a** or **2b** disappeared gradually as the concentration of Na^+ or K^+ was increased from 4×10^{-6} mol dm^{-3} to 2×10^{-5} mol dm^{-3}.



Scheme 1.

The fluorescence emission spectrum of **2a** or **2b** (4.0×10^{-6} mol dm^{-3} in MeOH-THF, v/v 15:1) exhibits a monomer emission characterized by a fluorescence maximum at 405 nm

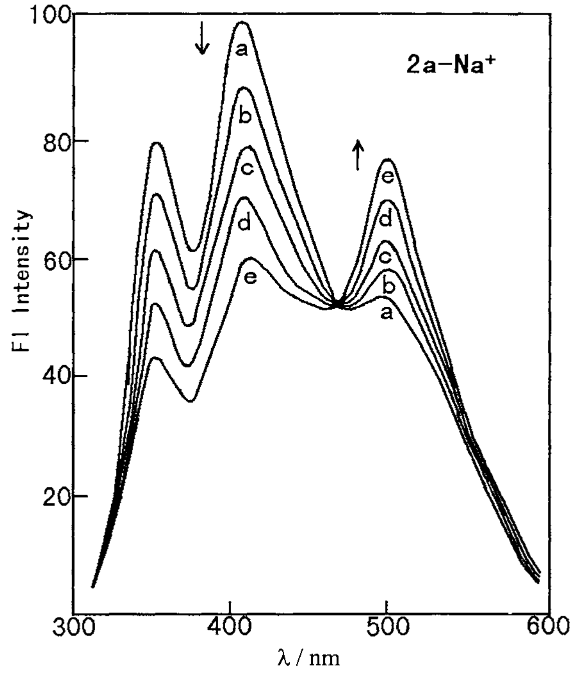


Figure 1. Fluorescence spectra of **2a** (4.0×10^{-6} mol dm^{-3}) in MeOH-THF (v/v 15:1) at different concentration of NaSCN. [Na^+]: a 0, b 1.0×10^{-6}, c 2.0×10^{-6}, d 3.0×10^{-6}, e 4.0×10^{-6} mol dm^{-3}. The spectra were measured with excitation at 314 nm.

(excitation 314 nm) and two bands at 346 nm and 496 nm. The effect of lithium, sodium or potassium thiocyanate in MeOH to fluorescence emission spectra of **2a** and **2b** was determined.[5] When Na^+ was added to **2a**, the fluorescence intensities of maximum emission at 405 nm and the emission at 346 nm decrease markedly and that of the emission at 496 nm increases markedly with increasing Na^+ concentration, in the range of 1.0×10^{-6} mol dm^{-3}–4.0×10^{-6} mol dm^{-3}, with an isoemissive point at 463 nm (Figure 1). However, when Li^+ or K^+(4.0×10^{-6} mol dm^{-3}) is added to solution of **2a**, there is no obvious change in fluorescence emission spectra. The addition of K^+ (1.0×10^{-6} mol dm^{-3}–4.0×10^{-6} mol dm^{-3}) to the solution of **2b** causes significant changes in fluorescence emission spectra with an isoemissive point at 464 nm (Figure 2). But when Li^+ or Na^+ (4.0×10^{-6} mol dm^{-3}) is added to the solution of **2b**, there is no change in their fluorescence emission spectra. This change in fluorescence emission spectra of **2a** or **2b** on complexation with Na^+ or K^+ can be due to the change in the relative configuration of the two anthraquinone moieties, which is induced by the reorientation of two carbonyl groups of **2a** or **2b** to concertedly bind Na^+ or K^+ ion.[6] This obvious selectivity of **2a** or **2b** for Na^+ or K^+ and their fluorescence characteristics in complexation towards metal ions indicate that acetaminoanthraquinone and original calix[4]crowns possess a concerted coordination behavior, and **2a** or **2b** could be utilized to selectively determine Na^+ or K^+ by fluorescence emission spectra in nonaqueous solution.

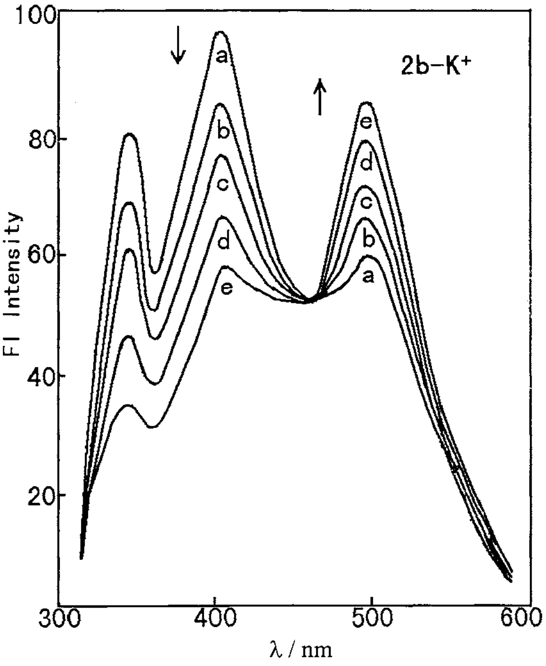


Figure 2. Fluorescence spectra of **2b** (4.0×10^{-6} mol dm^{-3}) in MeOH-THF(v/v 15:1) at different concentrations of KSCN. [K^+]: a 0, b 1.0×10^{-6}, c 2.0×10^{-6}, d 3.0×10^{-6}, e 4.0×10^{-6} mol dm^{-3}. The spectra were measured with excitation at 314 nm.

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References and Notes

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10 **2a:** Yield: 85%, m.p. 206-208 °C; Anal. Calcd for $C_{82}H_{84}N_2O_{12}$: C, 76.36; H, 6.58; N, 2.17%. Fouund: C, 76.12; H, 6.48; N, 2.15%. MS (FAB, *RI*): m/z 1288(20, M^+). ^{1}HNMR($CDCl_3$): δ 0.89, 1.20 (s, 18H each, $ArCMe_3$), 3.28 (d, 4H, J=12.7 Hz, H_A, $ArCH_2Ar$), 3.75-3.95 (m, 4H, OCH_2CH_2O), 4.28-4.41 (m, 8H, OCH_2CH_2O), 4.64 (d, 4H, J=12.7 Hz, H_B, $ArCH_2Ar$), 4.98 (s, 4H, OCH_2CO), 6.72, 7.01 (s, 4H each, ArH), 7.65-8.24(m, 14H, AqH), 12.03 (s, 2H, NH).
11 **2b:** Yield: 90%, m.p. 196-198 °C; Anal. Calcd for $C_{84}H_{88}N_2O_{13}$: C, 75.64; H, 6.66; N, 2.10%. Fouund: C, 75.31; H, 6.58; N, 2.09%. MS (FAB, *RI*): m/z 1332(30, M^+). ^{1}HNMR($CDCl_3$): δ 0.96, 1.18 (s, 18H each, $ArCMe_3$), 3.28 (d, 4H, J=12.7 Hz, H_A, $ArCH_2Ar$), 3.27, 3.53 (sb, 4H each, OCH_2CH_2O), 4.30, 4.40 (t, 4H each, OCH_2CH_2O), 4.73 (d, 4H, J=12.7 Hz, H_B, $ArCH_2Ar$), 5.0 (s, 4H OCH_2CO), 6.68, 6.96 (s, 4H each, ArH), 7.71-8.05 (m, 14H, AqH), 12.03 (s, 2H, NH).