SYNTHESIS AND COMPLEXATION BEHAVIOR OF *N,N'*-BIS(9-ANTHRYLMETHYL)-1,4,10,13-TETRAOXA-7,16-DIAZACYCLOOCTADECANE

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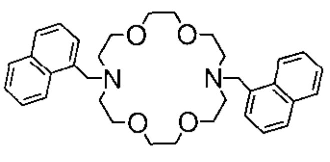
Abstract — Fluorescent photoinduced electron transfer (PET) sensor (**3**) that consists of diaza-18-crown-6 and 9-anthryl pendant shows fluorescent enhancement with various metal ions. The sensor (**3**) exhibited K^+ selectivity and in the presence of this cation the host fluorescence intensity was increased by a factor of 24.

The development of fluorescent receptors for metal cations has recently gained much attention.[1] There are extensive investigations toward the characterization of fluoroionophores including crown ether, calixarene, and cyclodextrin derivatives with naphthalene, umbelliferone, anthracene, or pyrene fluorophore.[2]
Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor.[3] The addition of metal salts enhanced the fluorescence emission intensity of *N,N'*-bis(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**1**),[4] while the presence of metal salts exerted a strong effect on the ratio of the monomer *vs.* excimer emission intensity of *N,N'*-bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**2**).[5] The azacrown ether having two pyrenyl pendants showed a strong tendency to form an inter- or an intra-molecular excimer[5] and the crown ether with naphthyl groups displayed fluorescence with a low quantum yield.[4] With this regard we report the synthesis and complexation behavior of the azacrown ether derivative (**3**) containing two chromophoric anthryl pendants.

The anthracene-functionalized diaza-crown ether (**3**) was prepared by the *N*-alkylation of 1,10-diaza-18-crown-6 with 9-chloromethylanthracene in THF-triethylamine (90% yield). The structure and purity of **3** were ascertained by ^{1}H NMR spectroscopy and elemental analysis.



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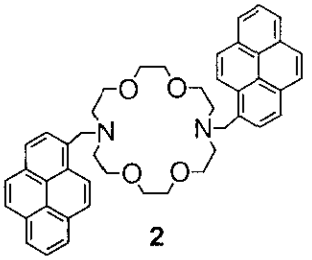

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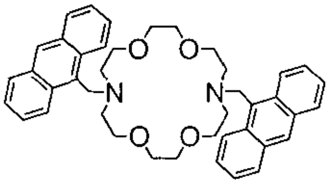

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In Figure 1 is illustrated the fluorescence spectral behavior of **3** (5.00 x 10^{-6} M, 1 M=1 mol dm^{-3}) in methanol-chloroform (9:1 *v/v*) at room temperature. A dramatic change in the emission intensity of **3** (I_3) was observed upon the addition of various amounts of metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Mg^{2+}) and NH_4^+. When the metal salts were added (10^4 molar equivalent), the relative emission intensity ratio ($I_{complex}/I_3$), being used as a measure of the molecular recognition sensing, changed from 1.2 to 24 depending on the nature of metal cations as shown in Figure 2. Figure 2 illustrates the relative emission intensity of **3** against the metal salt concentration. Clearly, the emission intensity increases with an increase in the metal ion concentration. Interestingly, the intensity ratio ($I_{complex}/I_3$) was different among

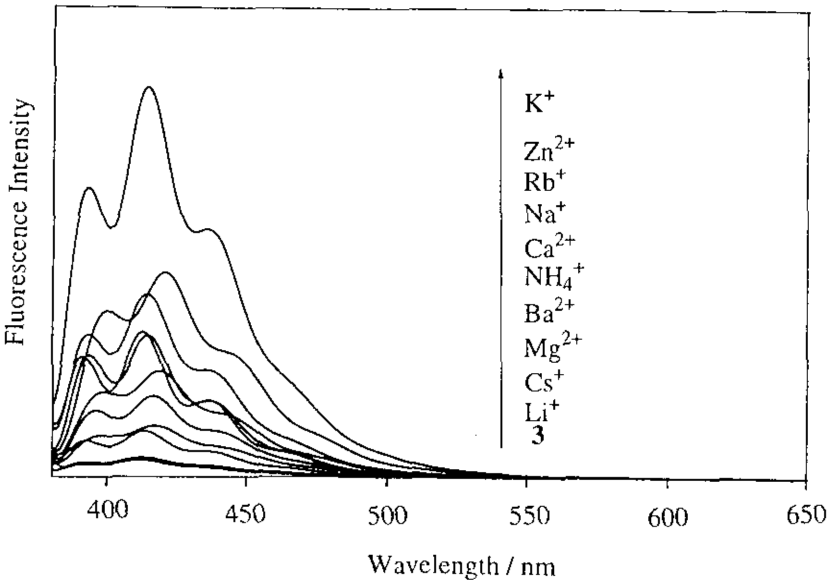

Figure 1. Fluorescence spectra of **3** (5.00 x 10^{-6} M) with and without various metal cations (5.00 x 10^{-2} M) in methanol-chloroform (9:1 *v/v*), as excited at 366 nm.

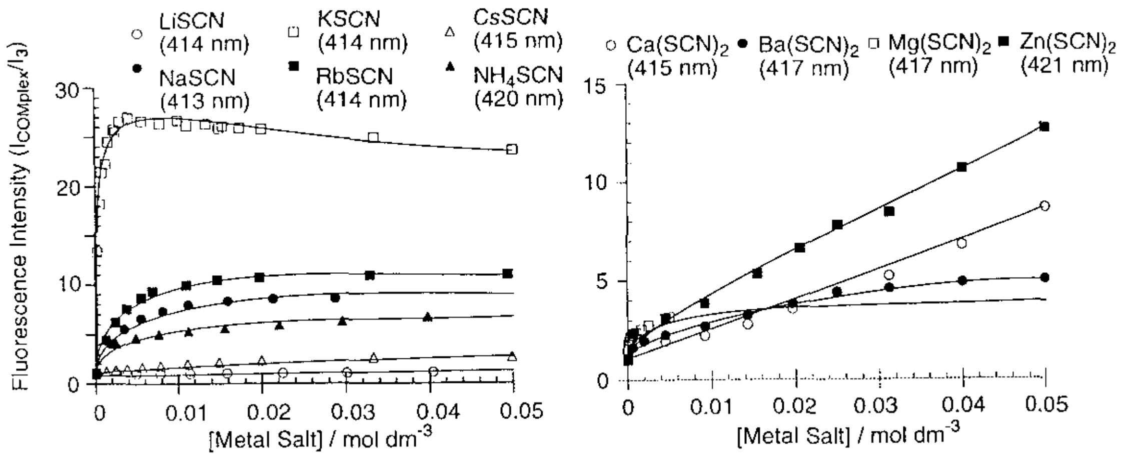

Figure 2. Dependence of fluorescence intensities of **3** (5.00×10^{-6} M) at observed wavelength (414–421 nm) on the concentration of various metal cations (added as thiocyanate salts) in methanol.

bound metal ions and decreased in the following order: K^+ (24) > Zn^{2+} (13) > Rb^+ (11) > Na^+ (8.5) > Ca^{2+} (8.7) > NH_4^+ (7.0) > Ba^{2+} (5.0) > Mg^{2+} (3.2) > Cs^+ (2.7) > Li^+ (1.2). The order of $I_{complex}/I_3$ differs from that of $I_{complex}/I_1$. From the relative emission-intensity ratio ($I_{complex}/I_3$), one can estimate the size and the valence of metal ions that were incorporated into the host cavity. Metal-ion concentration dependence of the emission intensity (Figure 2) allowed us to determine the association constants (K) by the non-linear curve-fitting method[5,6] (Table 1). The order of K values for K^+ is **3** < **2** < **1**, indicating that the two anthracene rings inhibit the complexation with metal ions to some extent.[5]

Table 1. Association constants (K, M^{-1}) of **1**, **2**, and **3** for metal salts in methanol and methanol-chloroform (9:1 *v/v*)

	K (M^{-1}) CH_3OH	K (M^{-1}) $CH_3OH:CHCl_3$ (9:1 *v/v*)		
	1	**1**	**2**	**3**
LiSCN	27 ± 5		3 ± 0.4	6 ± 1
NaSCN	123 ± 9		389 ± 37	500 ± 100
KSCN	1850 ± 320	2800 ± 140	2400 ± 23	1970 ± 660*
RbSCN	305 ± 26		345 ± 22	450 ± 50
CsSCN	97 ± 30		117 ± 3	130 ± 9
NH_4SCN	1490 ± 165		50 ± 4	120 ± 10
$Ca(SCN)_2$	61 ± 4		145 ± 14	3 ± 1
$Ba(SCN)_2$	710 ± 114		142 ± 17	59 ± 8
$Zn(SCN)_2$	126 ± 13		7 ± 1	7 ± 2
$Mg(SCN)_2$	3240 ± 200		1410 ± 140	1180 ± 200

*The association constant was determined in metal-salt concentration from 0 to 0.005 M.

The azacrown (**3**) showed the following cation selectivity: $Ca^{2+} < Li^+ < Zn^{2+} < Ba^{2+} < NH_4^+ < Cs^+ < Rb^+ < Na^+ < Mg^{2+} < K^+$. This selectivity order is distinct from that for **1** (K: $Li^+ < Ca^{2+} < Cs^+ < Na^+ < Zn^{2+} < Rb^+ < Ba^{2+} < NH_4^+ < K^+ < Mg^{2+}$)[4] and **2** ($K$: $Li^+ < Zn^{2+} < NH_4^+ < Cs^+ < Ba^{2+} < Ca^{2+} < Rb^+ < Na^+ < Mg^{2+} < K^+$).[5] Comparison of the selectivity order for **1–3** confirms that the size and electronic property of the aromatic pendants attached to the azacrown nitrogen atoms may control the selectivity of the host toward metal cations in a delicate manner. In spite of the small association constant for **3** in methanol-chloroform (9:1 *v/v*), the emission intensity of this host was greatly enhanced in the presence of metal salts, establishing that **3** has a high fluorescence switch-on ability for complexation with various metal ions.

In conclusion, the PET sensor (**3**) that showed K^+ selectivity may be utilized as a new fluorescent sensor for metal cations.

EXPERIMAENTAL

Elemental analyses were performed by Perkin Elmer PE2400 series II CHNS/O analyzer. Melting points were obtained with a Yanagimoto Micro Melting Point Apparatus and were uncorrected. NMR spectra were measured on a JEOL JNM-500 Model spectrometer in $CDCl_3$; the chemical shifts were expressd by an δ unit using tetramethylsilane as an internal standard. IR spectra were recorded on a Hitachi Model 270-30 infrared spectrophotometer. Fluorescence spectra were measured with a Hitachi Model F-4500 spectrofluorimeter. The stationary phase for the column chromatography was Merck and the eluant was a mixture of methanol, ethyl acetate, chloroform, and hexane.

***N,N'*-Bis(9-anthrylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (3).**

A tetrahydrofuran solution (10 mL) of diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, 0.13 g, 0.50 mmol), triethylamine (0.5 mL, 3.6 mmol), and 9-chloromethylanthracene (0.68 g, 3.0 mmol) was refluxed for 12 h. The mixture was then diluted with 1M NH_3 (10 mL) and extracted with chloroform. The solvent was evaporated and the residue was purified by column chromatography over silica gel (70–230 mesh, Merck) using hexane and ethyl acetate as the eluent. Recrystallization from chloroform gave analytically pure sample with the following physical and spectroscopic properties.

3: yellow needles, mp 189–190°C, ^1H NMR ($CDCl_3$) δ= 2.91 (8H, t, J= 5.8 Hz), 3.52 (8H, s), 3.58 (8H, t, J= 5.8 Hz), 4.60 (4H, s), 7.43 (4H, ddd, J= 8.2, 6.7, 1.2 Hz), 7.47 (4H, ddd, J= 9.2, 6.7, 1.2 Hz), 7.98 (4H, d, J= 8.2 Hz), 8.39 (2H, s), 8.55 (4H, d, J= 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ= 52.1 (2C), 54.0 (4C), 70.2(4C), 70.6 (4C), 124.8 (4C), 125.3 (4C), 125.5 (4C), 127.4 (2C), 128.9 (4C), 130.6 (2C), 131.4 (4C), 131.5 (4C). IR ν_{max} KBr 711, 1032, 1065, 1110, 1251, 1290, 1332, 1356, 1443, and 2895 cm^{-1}; Anal. Calcd for $C_{42}H_{46}N_2O_4$: C, 78.47 ; H, 7.21 ; N, 4.36. Found: C, 78.03 ; H, 7.24 ; N, 4.09.

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Received, 11th November, 1997