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Synthesis and Complexation Behavior of Diaza-18-crown-6 Carrying Two Pyrenylmethyl Groups

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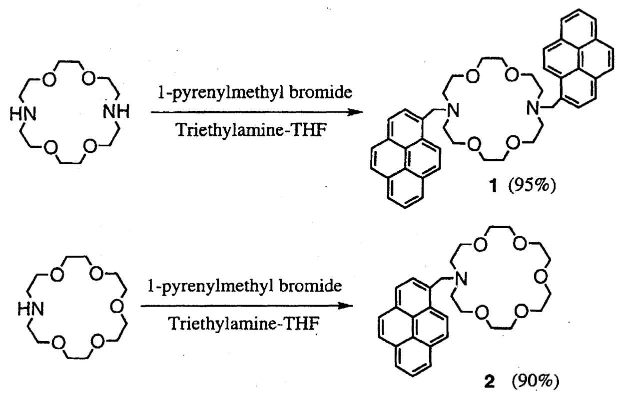
N,*N*′-Bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**1**) and *N*-(1-pyrenylmethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**2**) were synthesized and found to display unique photophysical properties in the presence of the guest-metal salts. The binding of metal ions to the diazacrown ether **1** cavity inhibited the exciplex formation and changed the distance between two pyrenyl groups. This caused not only an emission-intensity enhancement, but also a large change in the monomer/excimer fluorescence-intensity ratio. The change resulted from the coordinated structure and exchange process between the free host **1** and its metal salt complex in the ground state.

Synthetic fluoroionophores,[1)] which give rise to a specific emission spectral change upon selective complexation with cations, have attracted considerable attention as spectrophotometric analytical reagents for the detection of particular metal cations. Azacrown ethers have been important building blocks for constructing host molecules in supramoleculer chemistry.[2)]

Of particular interest, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system with an appropriate electron acceptor.[3)] The addition of metal salts enhanced the fluorescence emission intensity,[4)] while the presence of metal ions exerted a strong effect on the ratio of the monomer vs. excimer emission intensity of fluorophores containing two pyrenyl groups.[5)] By combining the exciplex and excimer forming properties, a fluoroionophore having a novel property could be produced. In this paper we report on the synthesis and fluorescence behavior of azacrown ether **1** containing two chromophoric pyrenyl pendants, as a new approach that takes advantage of the formation of both the exciplex and excimer.[6)]

Results and Discussion

Pyrene-functionalized diazacrown ether **1** and **2** were prepared by *N*-alkylation of the corresponding azacrown ethers with 1-pyrenylmethyl bromide in tetrahydrofuran-triethylamine (Scheme 1). The structure and purity of **1** and **2** were ascertained by NMR spectroscopy and elemental analysis.



Scheme 1.

In Fig. 1 is illustrated the fluorescence spectral behavior of **1** (1.0×10^{-6} M, 1.0 M = 1.0 mol dm^{-3}) and **2** (2.0×10^{-6} M) in methanol–chloroform (9 : 1 v/v) at room temperature. Fluoroionophores **1** and **2** (when excited at 342 nm) gave a broad emission band with a maximum at 464 nm in addition to monomer emission (396 nm for **1**, 378 nm for **2**). The formation of an intramolecular exciplex should be responsible for the appearance of the former emission band. The latter emission-band intensities of **2** and **1** were reduced to approximately one-20th and one-200th that of the pyrene (2.0×10^{-6} M), respectively, accompanied by the occurrence of exciplex fluorescence, indicating that the quenching of the excited pyrene chromophore by the azacrown unit proceeds by a mechanism similar to that for the classical pyrene-*N*,*N*-dimethylaniline system[7)] or a pyrene–azacrown system.[3)]

X-Ray Crystal-Structure Analysis of Diazacrown Derivative.[8)] An X-ray structural analysis of **1**, a monoclinic crystal with cell dimensions of $a = 11.503(2)$, $b = 18.218(5)$, $c = 9.305(2)$ Å, and $\beta = 110.539(5)°$ with $P2_1/a$, showed at the final stage an R factor of 0.0474 (Figs. 2 and 3). It is clear that the two pyrene units adopt an anti-conformation with the crown-ether ring. The pyrene ring of **1** is close to the N atom of the crown ether; the distance between C1 and N1 (2.505(3) Å) is shorter than the sum of their van der Waals radii [3.05 Å]. No π–π interaction is evident in the crystal packing; the distance between the pyrene planes is greater than 4.0 Å, substantially larger than that in pyrene, itself (3.53 Å).[9)] The C–N(1) bond lengths (1.464 Å) are not significantly shorter

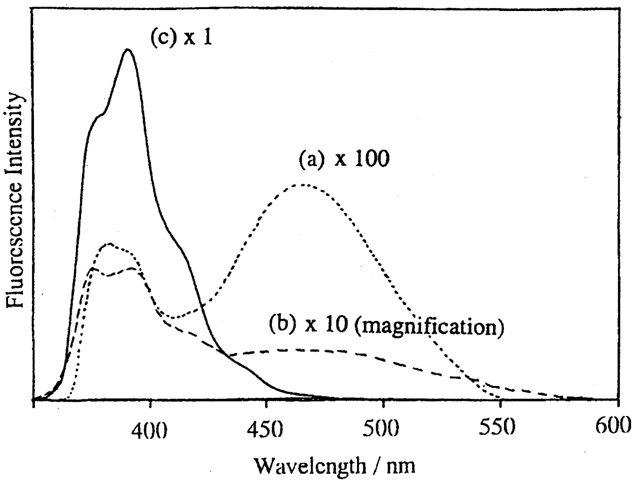


Fig. 1. Fluorescence spectra of (a) **1** (1.0×10^{-6} M), (b) **2** (2.0×10^{-6} M), and (c) pyrene (2×10^{-6} M) in methanol–chloroform (9 : 1 v/v) at room temperature.

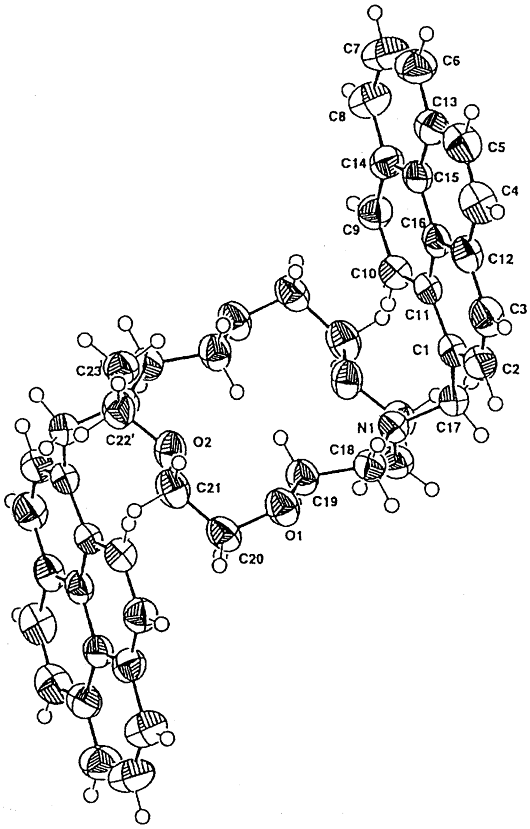


Fig. 2. Molecular structure showing 50% probability displacement ellipsoids.

than the single C–N bond length [1.472(5) Å].[10] This means that an intramolecular charge transfer can readily take place between the pyrene and the nitrogen atom in the ground state as well as in the excited singlet state.

Complex Formation with Various Metal Salts. A dramatic change in the monomer emission intensity of **1** (I_1) and **2** (I_2) was observed upon the addition of various amounts of metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, $NH_4{}^+$, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Mg^{2+}). When metal salts were added (10^4 molar equivalent), the relative emission intensity ratio ($I_{complex}/I_2$), being used as a measure of molecular-recognition sensing, changed from 0.5 to 13, depending on the nature of the metal cations, as illustrated in Fig. 4. It is clearly seen from Fig. 4 that the emission intensity increased along with an increase in the concentration of the metal ion, except for Na^+. The observed enhancement indicates the inhibition of exciplex formation by complexation with a metal salt. Futhermore, it is noteworthy that the **2**–NaSCN complex exhibited a decrease in its monomer emission intensity relative to that of **2**, itself. This suggests that the observed quenching is due to the presence of thiocyanate ion. A similar quenching by the thiocyanate anion was explained based on the photoinduced electron transfer from this anion to the pyrene chromophore.[11]

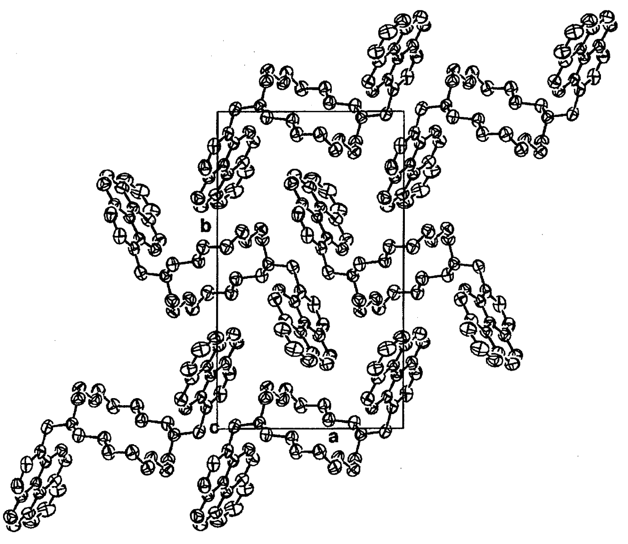


Fig. 3. Packing diagram of **1** viewed down the *c* axis.

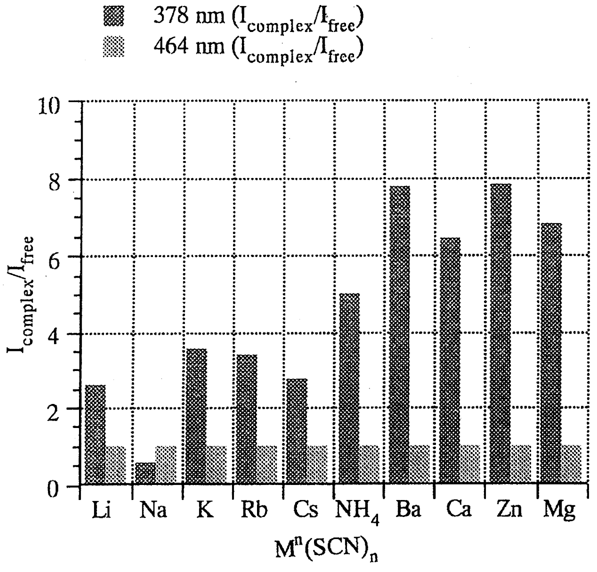


Fig. 4. The influence of various metal cations (added as thiocyanate salts) on the emission-intensity ratio ($I_{complex}/I_2$); [**2**] = 2.0×10^{-6}, [Metal salts] = 2.0×10^{-2} M, excitation at 341 nm.

Surprisingly, when the metal salts were added (2×10^4 molar equivalent), the emission-intensity ratio (I_{complex}/I_1, which was being used as a measure of the molecular recognition sensing), changed from 2 to 32 at 397 nm (monomer emission) and from 1 to 13 at 464 nm (excimer emission), depending on the nature of the added metal cations, as demonstrated in Fig. 5. It is interesting that the ratio ($I_{\mathrm{ex}}/I_{\mathrm{m}}$) of the excimer- ($I_{\mathrm{ex}}$) to monomer- ($I_{\mathrm{m}}$) emission intensities are different among bound metal ions. The order of this ratio was Na^+ (1.89) > K^+ (0.66) > Li^+ (0.65) > Rb^+ (0.49) > Cs^+ (0.34). This result indicates that the binding of bigger alkali metal ions to the azacrown ether hinders excimer formation to a greater extent. The smaller $I_{\mathrm{ex}}/I_{\mathrm{m}}$ values for Li^+ and bivalent metal ions imply that the coordinated structure of these ions differs from that of the other alkali metal ions. From the intensity ratio of the monomer- and excimer- fluorescences of the pyrene pendant, one can estimate the size and the valence of metal ions that were incorporated into the host **1**.

Association Constants (*K*). Metal-ion concentration dependence of the emission intensity (Fig. 6) allowed us to determine the association constants (*K*) by a nonlinear curve-fitting method[12] (Table 1). The *K* values of **2** were in reasonable agreement with those available for the parent macrocycles, indicating that the pyrenyl moiety may not block the incorporation of metal ions into a macrocycle in **2**.[1] The *K* values of **1** were smaller than those of **2**. This suggests that the two large pyrene rings of **1** substantially inhibit complexation with metal ions, expect for Mg^{2+}. The azacrown **1** showed metallic cation selectivity: $\mathrm{Li}^+ < \mathrm{Zn}^{2+} < \mathrm{NH_4}^+ < \mathrm{Cs}^+ < \mathrm{Ba}^{2+} < \mathrm{Ca}^{2+} < \mathrm{Rb}^+ < \mathrm{Na}^+ < \mathrm{Mg}^{2+} < \mathrm{K}^+$. This selectivity pattern is distinct from that of 18-crown-6. Compared with 18-crown-6, different features are simply noted as follows: (i) a larger *K* value for K^+ complexation than for Ba^{2+} and (ii) a larger *K* value for Na^+ than for Rb^+ and Cs^+. These differences may be explained by the idea that two large pyrene rings of **1** suppress complexation with larger metal cations (Rb^+ and Cs^+) than Na^+. In spite of the small association constant for **1** in methanol–chloroform, the enhancement of the monomer and/or excimer emission intensity of this host **1** by bound metal salts establishes that **1** has a high fluorescence switch-on ability for complexation with various metal ions.

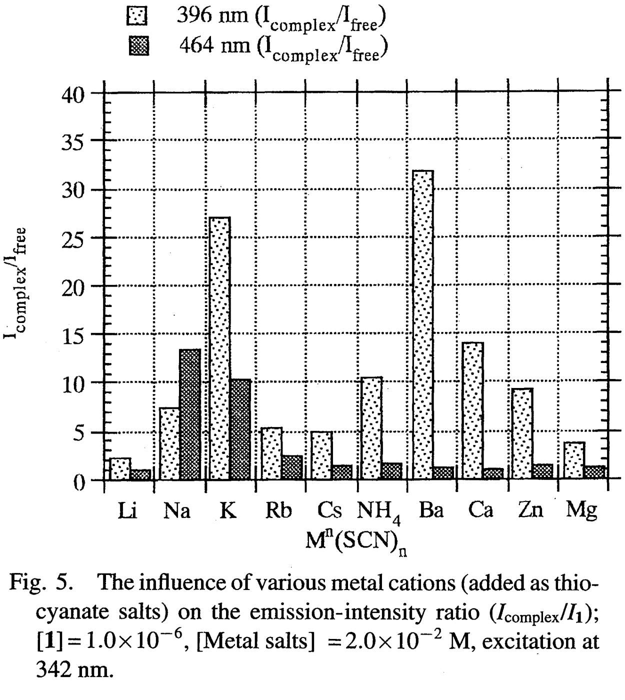


Fig. 5. The influence of various metal cations (added as thiocyanate salts) on the emission-intensity ratio (I_{complex}/I_1); $[\mathbf{1}] = 1.0\times10^{-6}$, [Metal salts] $= 2.0\times10^{-2}$ M, excitation at 342 nm.

Table 1. Association Constants (K/M^{-1}) of **1** and **2** for Metal Salts in Methanol–Chloroform (9 : 1 v/v)

	K (M^{-1})	
	1	**2**
LiSCN	3±0.4	48±3
NaSCN	389±37	1010±60
KSCN	2400±23	56200±2470
RbSCN	345±22	15100±780
CsSCN	117±3	4630±280
$\mathrm{NH_4SCN}$	50±4	2530±80
$\mathrm{Ca(SCN)_2}$	145±14	847±74
$\mathrm{Ba(SCN)_2}$	142±17	22300±400
$\mathrm{Zn(SCN)_2}$	7±1	158±14
$\mathrm{Mg(SCN)_2}$	1410±139	513±19

NMR Spectral Analysis. Binding interactions of the host **1** with alkali metal and bivalent metal ions were examined using ^{1}H NMR spectroscopy. When alkali metal salts were added, the resonance peaks shifted downfield or upfield, depending on the nature of the added metal cations (Figs. 7b and 7c). However, the addition of bivalent metal ions decreased the original peak intensities, accompanied by an increase in new resonance-peak intensities (Figs. 7d and 7e). These spectral changes mean that the exchange rates are different between the alkali-metal and bivalent-metal ions. The gradual upfield shift of the proton signal of the azacrown unit with added KSCN (Figs. 7b and 7c) indicates that the exchange process between a free host and its potassiun complex is rapid compared to the NMR time scale: Time-averaged NMR shifts are observed depending upon the guest concentrations. On the other hand, the original (free host, **1**) signal intensities decreased, and new resonance-peak intensities (the corresponding complex, [**1**–Ba^{2+}]) at 3.90 and 4.84 ppm increased as the $\mathrm{Ba(SCN)_2}$ concentration was increased (Figs. 7d and 7e). This finding indicates that the exchange process is slow enough even at room temperature, compared with the NMR time scale, to give a new signal corresponding to the barium complex ([**1**–Ba^{2+}]). The difference in the exchange rates between K^+ and Ba^{2+} should be responsible for the large difference in the monomer/excimer fluorescence-intensity ratio for there metal ions (Fig. 5).

In all of the complexation systems, the examined composition of the complexes [**1**–metal cation] could fortunately be determined by using the ^{1}H NMR titration curve. Fig. 8 shows a plot of the induced shift of each signal versus the molar composition of **1** and the metal. The stoichiometry of the complexation between the host **1** and the guest K^+ was

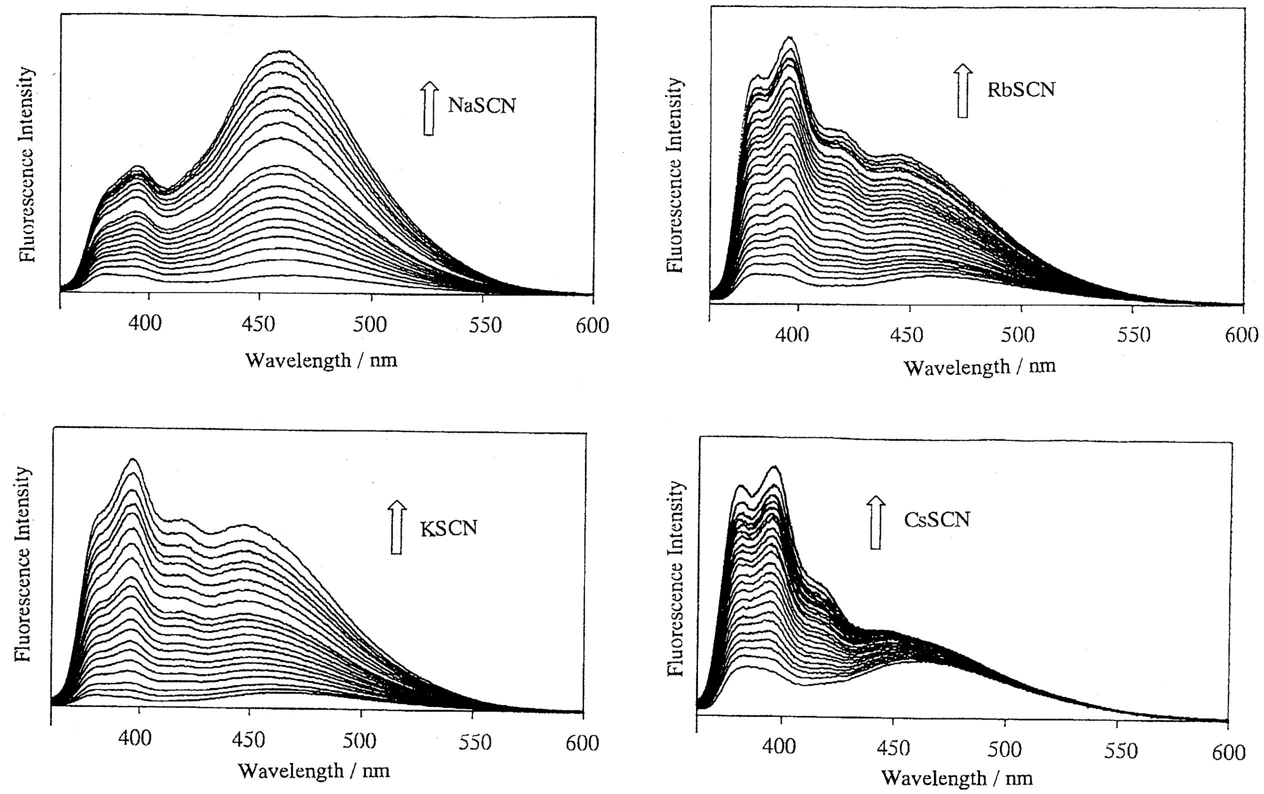


Fig. 6. Fluorescence spectral changes of **1** (1.0×10^{-6} M) with different concentrations of (a) NaSCN, (b) KSCN, (c) RbSCN, and (d) CsSCN in methanol : chloroform (9 : 1 v/v) mixture; excitation at 342 nm.

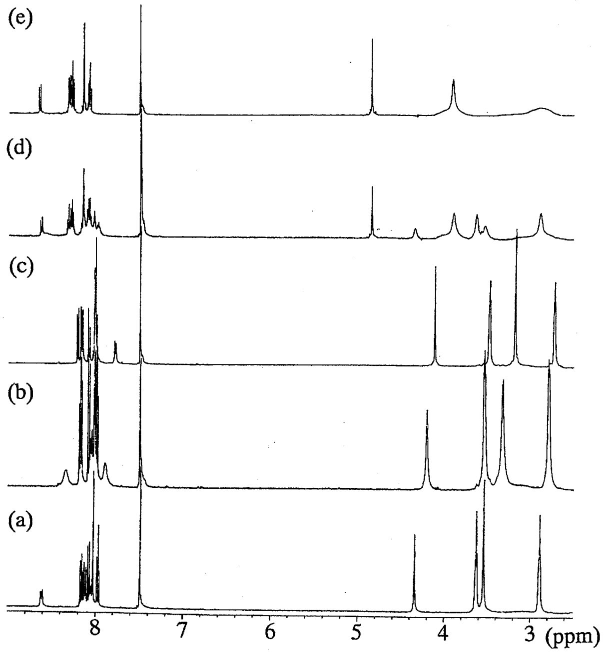


Fig. 7. ^{1}H NMR spectral changes of **1** (8.0×10^{-4} M) with KSCN and $Ba(SCN)_2$ in CD_3CN–$CDCl_3$ (1 : 1 v/v) at 298 K. Concentration of metal salts: (a) 0, (b) [KSCN] = 2.6×10^{-4}, (c) [KSCN] = 1.4×10^{-3}, (d) $[Ba(SCN)_2]$ = 2.6×10^{-4}, (e) $[Ba(SCN)_2]$ = 1.4×10^{-3} M.

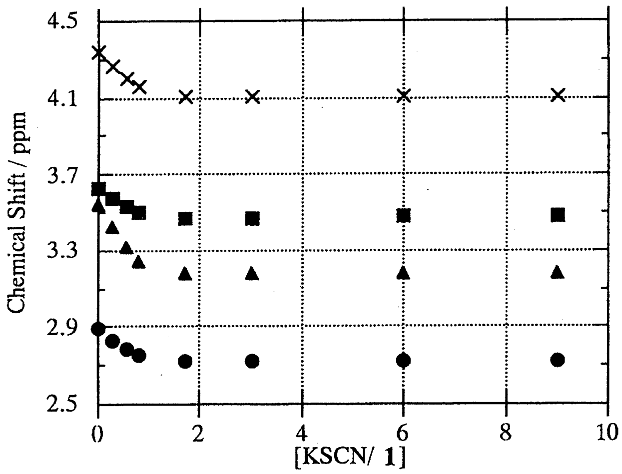


Fig. 8. ^{1}H NMR titration curves for complexation between diazacrown ether and KSCN.

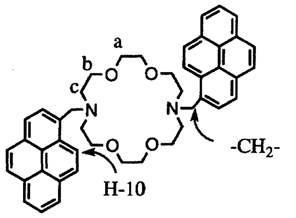
confirmed to be 1 : 1, at least, in a chloroform-d_3 and acetonitrile-d_3 (1 : 1 v/v) mixture. Similarly, the composition of the **1**–metal ion complexes (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}) was determined as 1 : 1 by the molar ratio.

The chemical shifts (δ) and induced shifts ($\Delta\delta$) of the host **1** with and without a metal cation are summarized in Table 2. The presence of Ba^{2+} and Ca^{2+} induced a dramatic downfield shift ($\Delta\delta = 0.49$ and 0.76) of the methylene proton signal of the 1-pyrenylmethyl group. There was also a significant downfield shift ($\Delta\delta = 0.36$) of the H_b signal of the azacrown unit. This downfield shift was due to an interaction with a metal cation.

On the other hand, Na^+, K^+, Rb^+, and Cs^+ induced dis-

Table 2. Changes of ^{1}H NMR Chemical Shifts of **1** (8.0×10^{-4} M) with Various Metal Salts (1.4×10^{-3} M)

	Pyrenyl group		Azacrown unit		
	H-10	$-CH_2-$	a	b	c
1	8.61	4.35	3.63	3.54	2.89
LiSCN	8.38 (−0.23)	4.32 (−0.03)	3.65 (+0.02)	3.33 (−0.21)	2.82 (−0.07)
NaSCN	8.08 (−0.53)	4.04 (−0.31)	3.36 (−0.27)	3.06 (−0.48)	2.65 (−0.24)
KSCN	8.22 (−0.39)	4.11 (−0.24)	3.47 (−0.06)	3.18 (−0.36)	2.72 (−0.27)
RbSCN	8.34 (−0.27)	4.21 (−0.14)	3.53 (−0.10)	3.28 (−0.26)	2.78 (−0.11)
CsSCN	8.38 (−0.23)	4.23 (−0.12)	3.55 (−0.08)	3.35 (−0.19)	2.80 (−0.09)
$Ca(SCN)_2$	8.85 (+0.24)	5.21 (+0.76)	3.90 (+0.27)	3.90 (+0.36)	3.09 (+0.20)
$Ba(SCN)_2$	8.66 (+0.05)	4.84 (+0.49)	3.90 (+0.27)	3.90 (+0.36)	2.87 (−0.02)
$Mg(SCN)_2$	8.43 (−0.18)	4.67 (+0.32)	3.65 (+0.02)	3.41 (−0.13)	3.09 (+0.20)
$Zn(SCN)_2$	8.46 (−0.15)	4.67 (+0.32)	3.63 (0.00)	3.38 (−0.16)	3.32 (+0.43)



tinct upfield shifts of the H signal of the azacrown unit as well as the methylene proton signal of the 1-pyrenylmethyl group. This upfield shift must be due to ring-current effects of the pyrene rings. Interestingly, there were also upfield shifts ($\Delta\delta = -0.23$ — -0.53) of the H-10 signal of the 1-pyrenyl group, suggesting that an intramolecular interaction between two pyrene rings takes place. As already mentioned, the binding of metal ions to the diazacrown ether caused an emission-intensity enhancement and a large change in the monomer/excimer fluorescence-intensity ratio. The change in the monomer/excimer fluorescence-intensity ratio is considered to result from the metal ion-dependent coordinated structure and exchange rate between the free host **1** and its metal salt complex in the ground state.

In conclusion, the diazacrown ether **1** has the following properties: 1) fluorescence quenching via an intramoleculer electron transfer between the pyrenyl group and the nitrogen atom in the crown ring and cation recognition by emission-intensity enhancement; 2) fluorescence sensing of the alkali metal (I) ions using the monomer/excimer emission-intensity ratio. The diazacrown ether, having two 1-pyrenyl pendants, may be utilized as a new fluorescent sensor for metal ions and chiral compounds.

Experimental

Elemental analyses were performed using a Perkin–Elmer PE2400 series II CHNS/O analyzer. The melting points were obtained with a Yanagimoto Micro Melting Point Apparatus and were uncorrected. The NMR spectra were measured on a JEOL JNM-500 Model spectrometer in $CDCl_3$; the chemical shifts were expressed by a δ unit using tetramethylsilane as an internal standard. The IR spectra were recorded on a Hitachi Model 270-30 infrared spectrometer. The UV spectra were measured using a Shimadzu Model UV-2200 spectrophotometer. The fluorescence spectra were measured with a Hitachi Model F-4500 spectrofluorimeter. The stationary phase for the column chromatography was Merck silica gel, and the eluant was a mixture of methanol, ethyl acetate, chloroform, and hexane.

Preparation of *N*,*N*′-Bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1): After a tetrahydrofuran–toluene solution (10 cm^3, 1 : 1 v/v) of diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, 0.026 g, 0.1 mmol), triethylamine (0.5 cm^3), 1-(bromomethyl)pyrene (0.174 g, 0.6 mmol) was refluxed for 12 h, it was filtrated to remove any insolube triethylamine hydrobromide. 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 ethanol gave analytically pure samples with the following physical properties: Yellow prisms, mp 149—150 °C; ^{1}H NMR $\delta = 3.60$ (8H, t, $J = 5.8$ Hz), 3.67 (8H, s), 3.95 (8H, t, $J = 5.8$ Hz), 4.37 (4H, s), 7.96 (2H, t, $J = 7.6$ Hz), 8.01 (4H, s), 8.04 (2H, d, $J = 7.9$ Hz), 8.08 (2H, d, $J = 9.2$ Hz), 8.09 (2H, d, $J = 7.9$ Hz), 8.14 (2H, d, $J = 7.6$ Hz), 8.15 (2H, d, $J = 7.6$ Hz), and 8.58 (2H, d, $J = 9.2$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 54.32$ (4C), 58.60 (2C), 70.21 (4C), 70.80 (4C), 124.44 (2C), 124.73 (2C), 124.82 (2C), 124.87 (2C), 124.92 (2C),125.01 (2C), 125.78 (2C), 126.96 (2C), 127.03 (2C), 127.46 (2C), 128.08(2C), 129.83 (2C), 130.66 (2C), 130.94 (2C), 131.33 (2C), and 133.36 (2C). IR (KBr) ν 927, 984, 1068, 1113, 1257, 1284, 1353, 1376, 1452, 1476, 1587, 2788, 2866 cm^{-1}. Found: C, 79.89; H, 6.67; N, 3.95%. Calcd for $C_{46}H_{46}N_2O_4$: C, 79.97; H, 6.71; N, 4.05%.

***N*-(1-Pyrenylmethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (2):** ^{1}H NMR $\delta = 2.92$ (4H, t, $J = 5.8$ Hz), 3.60—3.70 (20H, m), 4.37 (2H, s), 7.99 (1H, t, $J = 7.6$ Hz), 8.03 (2H, s), 8.04 (1H, d, $J = 7.9$ Hz), 8.10 (1H, d, $J = 9.2$ Hz), 8.11 (1H, d, $J = 7.9$ Hz), 8.16 (1H, d, $J = 7.6$ Hz), 8.17 (1H, d, $J = 7.6$ Hz), and 8.60 (1H, d, $J = 9.2$ Hz); ^{13}C NMR $\delta = 54.33$ (2C), 58.70, 70.16 (2C), 70.41 (2C), 70.83 (2C), 70.87 (2C), 70.97 (2C), 124.32, 124.45, 124.85, 124.88, 124.92, 125.04, 125.79, 126.99, 127.02, 127.49, 128.12, 129.87, 130.68, 130.97, 131.36, and 133.43. IR (NaCl) ν 846, 1116, 1293, 1358, 1449, 1587, 2854 cm^{-1}. Found: C, 72.79; H, 7.69; N, 2.63%. Calcd for $C_{29}H_{35}NO_5$: C, 72.93; H, 7.39; N, 2.93%.

Determination of Association Constants (*K*). The titrations were conducted by adding a crown-ether solution (1.0×10^{-6} for **1**, 2.0×10^{-6} M for **2** in methanol–chloroform (9 : 1, v/v)) progressively containing excess metal salts, using a 250 cm^3 syringe, to a cuvette containing 2 cm^3 of the crown-ether solution (1.0×10^{-6} for **1**, 2.0×10^{-6} M for **2** in methanol–chloroform (9 : 1, v/v)). The solutions were homogenized by ultrasonic waves for 5 min. The spectrum was recorded after each addition, as shown Fig. 6. The added equivalents of the cation were then plotted against the emission-intensity change at 397 nm. Even though the solvent takes part in the association interaction, the solvent concentration is virtually unaffected. Therefore, we express the interaction of metal salts in terms of the equilibrium:[12)]

$$\mathrm{CE}+\mathrm{M}\rightleftarrows\mathrm{CE{\cdot}M} \tag{1}$$

Also, the association constants (K) should be expressed as follows:

$$\begin{aligned}K&=[\mathrm{CE{\cdot}M}]/[\mathrm{CE}][\mathrm{M}]\\&=[\mathrm{CE{\cdot}M}]/([\mathrm{CE_0}]-[\mathrm{CE{\cdot}M}])([\mathrm{M_0}]-[\mathrm{CE{\cdot}M}])\end{aligned} \tag{2}$$

$$[\mathrm{CE{\cdot}M}]=a[\mathrm{CE_0}]=(I-I_0[\mathrm{CE_0}])/(I_{\mathrm{CE{\cdot}M}}-I_0) \tag{3}$$

From the Eqs. 2 and 3, the following equation could be derived:

$$[\mathrm{M_0}]=a/K(1-a)+a[\mathrm{CE_0}], \tag{4}$$

where $[\mathrm{CE_0}]$ and $[\mathrm{M_0}]$ are the initial concentrations of the crown ether and the metal salt, I and I_0 are the observed emission intensities of the crown ethers in the presence and in the absence of the metal ion and $I_{\mathrm{CE{\cdot}M}}$ is the observed emission intensity of the complex of the crown ether and the metal ion.

A self-written nonlinear curve-fitting computer program (Eq. 4) was used to fit the experimental titration curves. The association constants were determined from the emission-intensity changes at 397 nm using the equation as given in Table 1.

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