

SYNTHESIS AND COMPLEXATION BEHAVIOR OF *N,N'*-Bis(1-NAPHTHYLMETHYL)-1,4,10,13-TETRAOXA-7,16-DIAZACYCLO-OCTADECANE

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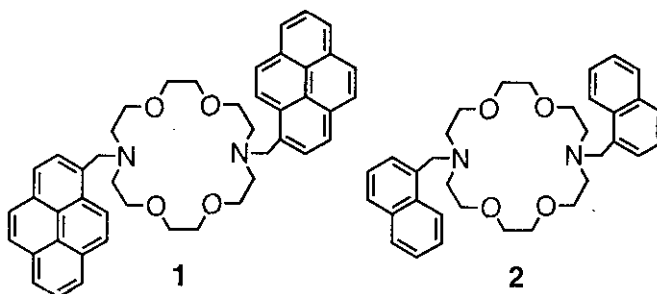
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**Abstract** — *N,N'*-Bis(1-naphthylmethyl)-4,13-diaza-18-crown-6 ether (**2**) gave intramolecular exciplex fluorescence, showing that the excited naphthalene chromophore was quenched by the azacrown unit. The azacrown ether (**2**) was found to display unique photophysical properties in the presence of metal salts. Complexation of **2** with Ba<sup>2+</sup> increased the fluorescence intensity of the host by a factor of 40. <sup>1</sup>H and <sup>13</sup>C NMR analyses of this 1:1 complexation behavior revealed that Ba<sup>2+</sup> strongly coordinates with the azacrown nitrogen to cause a dramatic decrease in an intramolecular charge-transfer character. In addition, it was suggested that not only the metal ion-dependent coordinated structure of the resulting complex but also the exchange rate between the free host (**2**) and its complex with metal ions play a role in controlling the extent of the emission-intensity enhancement that was observed in the presence of a given metal ion.

As an approach to the manipulation of an intramolecular electron transfer dynamics, photoresponsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switch.<sup>1</sup> There are extensive investigations toward the characterization of

fluoroionophores including crown ether, calixarene, and cyclodextrin derivatives with naphthalene, umbelliferone, anthracene, or pyrene fluorophore.<sup>2</sup>

Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor.<sup>3</sup> The addition of metal salts enhanced the fluorescence emission intensity of *N*-(1-pyrenylmethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane,<sup>4</sup> 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 (**1**).<sup>5</sup> The azacrown ether having two pyrenyl pendants shows a strong tendency to form an inter- or an intra-molecular excimer, whereas the ether with naphthyl groups is deemed to give no such an excimer at concentrations up to  $10^{-1}$  M ( $1\text{ M}=1\text{ mol dm}^{-3}$ ) and, thus, to render the spectroscopic analysis much easier.<sup>6</sup> With this regard we report the synthesis and properties of the azacrown ether derivative (**2**) containing two chromophoric naphthyl pendants.



The naphthalene-functionalized diaza-crown ether (**2**) was prepared by the *N*-alkylation of 1,10-diaza-18-crown-6 with 1-chloromethylnaphthalene in THF-triethylamine (90% yield). The structure and purity of **2** were ascertained by  $^1\text{H}$  NMR spectroscopy and elemental analysis.

In Figure 1 is illustrated the fluorescence spectral behavior of **2** ( $2.00 \times 10^{-5}$  M) in methanol at room temperature. Fluoroionophore (**2**), (when excited at 280 nm), gave a broad emission band with a maximum at 474 nm in addition to the monomer emission band (335 nm).

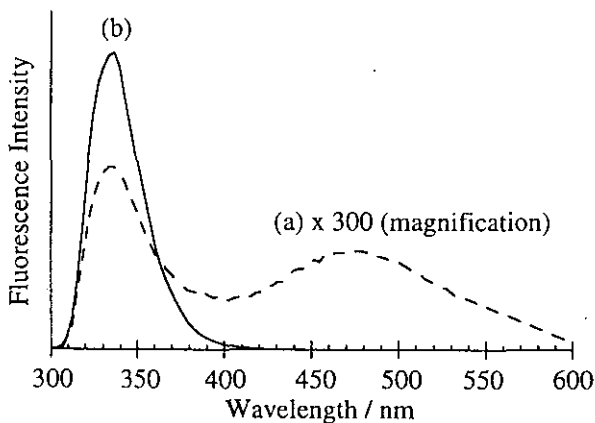


Figure 1. Fluorescence spectra of (a) **2** ( $2.00 \times 10^{-5}$  M) and (b) 1-methylnaphthalene ( $4.00 \times 10^{-5}$  M) in methanol at room temperature.

The formation of intramolecular exciplex should be responsible for the appearance of the former emission band. The latter emission-band intensity of **2** was reduced to approximately one-440th that of 1-methylnaphthalene ( $4.00 \times 10^{-5}$  M), which was accompanied by the exciplex fluorescence. This indicates that the quenching of the excited-state naphthalene chromophore by the azacrown unit proceeds in a mechanism similar to that for the classical naphthalene-aliphatic amine system.<sup>7</sup>

X-Ray structural analysis of **2**, monoclinic crystal with cell dimensions  $a=18.225$  (2),  $b=9.7912$  (11),  $c=8.582$  (2) Å, and  $\beta=90.114$  (15)° with  $P2_1/a$  (Table 1), showed at the stage of the final  $R$  factor=0.0453 that **2** is centrosymmetric and two naphthalene rings adopt *anti* conformation with respect to one another across the crown ether ring as shown in Figure 2. The naphthalene ring of **2** 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 [3.05 Å] of their van der Waals radii<sup>8</sup>. This means that intramolecular charge transfer between the naphthalene ring and the nitrogen atom can take place readily in the excited singlet state and possibly even in the ground state.

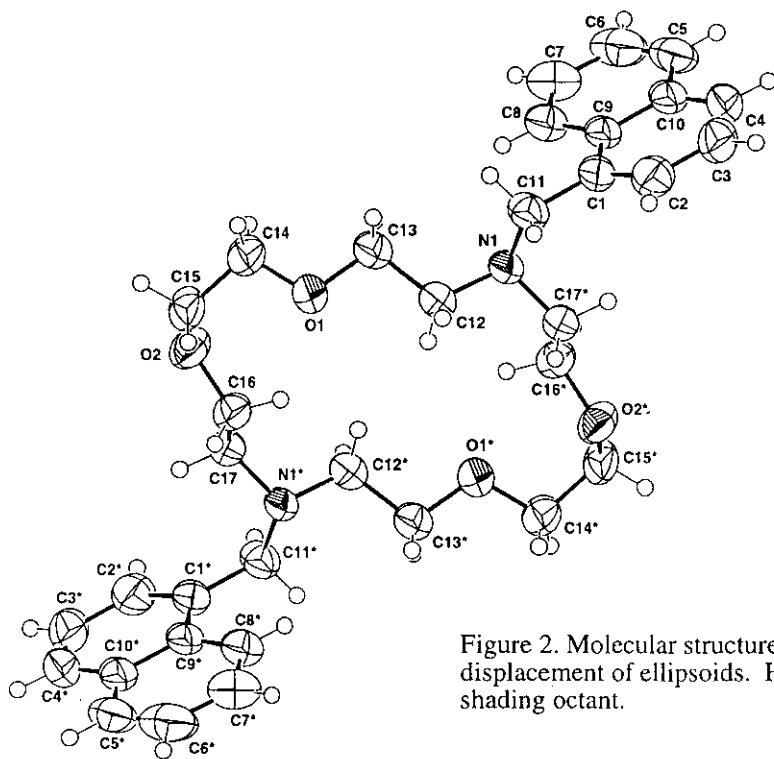


Figure 2. Molecular structure of **2** showing 50% probability displacement of ellipsoids. Hetero atoms are shown with shading octant.

Table 1. Crystal data, data collection, and refinement of **2**

<i>Crystal data</i>	<i>Data collection</i>	<i>Refinement</i>
$C_{34}H_{42}N_2O_4$	Enraf-Nonius FR590	Refinement on $F^2$
$M_r = 542.72$	diffractometer	$R[F^2 > 2\sigma(F^2)] = 0.0453$
Monoclinic	$\omega$ - $2\theta$ scans	$wR(F^2) = 0.1339$
$P2_1/a$	empirical via $\psi$ scans <sup>9</sup>	$S = 1.038$
$a = 18.225(2) \text{ \AA}$	$T_{\min} = 0.9520, T_{\max} = 0.9993$	3125 reflections
$b = 9.7912(11) \text{ \AA}$	3228 measured reflections	182 parameters
$c = 8.582(2) \text{ \AA}$	3125 independent reflections	riding
$\beta = 90.114(15)^\circ$	2510 reflections with $I > 2\sigma(I)$	$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2 + 0.3989P]$
$V = 1531.4(4) \text{ \AA}^3$	$R_{\text{int}} = 0.0278$	where $P = (F_o^2 + 2F_c^2) / 3$
$Z = 2$	$\theta_{\max} = 74.29^\circ$	$(\Delta / \sigma)_{\max} = -0.000$
$D_x = 1.177 \text{ Mg m}^{-3}$	$h = -22 \rightarrow 0$	$\Delta\rho_{\max} = 0.213 \text{ e \AA}^{-3}$
$D_m$ not measured	$k = -12 \rightarrow 0$	$\Delta\rho_{\min} = -0.193 \text{ e \AA}^{-3}$
Cu $K\alpha$ radiation	$l = -10 \rightarrow 10$	Extinction correction:
$\lambda = 1.54184 \text{ \AA}$	3 standard reflections	<i>SHELXL</i>
Cell parameters from 25 reflections	frequency: 120 min	Extinction coefficient: 0.0033
$\theta = 40.1\text{--}46.0^\circ$	intensity decay: $-0.2\%$	(4)
$\mu = 0.607 \text{ mm}^{-1}$		Scattering factors from
$T = 296(2) \text{ K}$		<i>International Tables for</i>
Spherical		<i>Crystallography</i> (Vol. C)
$\rho = 0.19 \text{ mm}$		
Colorless		

A dramatic change in the emission intensity of **2** (**I**<sub>2</sub>) was observed upon the addition of various amounts of metal cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Zn<sup>2+</sup>, and Mg<sup>2+</sup>) and NH<sub>4</sub><sup>+</sup>. When the metal salts were added (500 molar equivalent), the relative emission intensity ratio (*I*<sub>complex</sub>/*I*<sub>2</sub>), being used as a measure of the molecular recognition sensing, changed from 1.1 to 41 depending on the nature of metal cations as shown in Figure 3. Figure 4 illustrates the relative emission intensity of **2** against the metal salt concentration. Clearly, the emission intensity increases with an increase in the metal ion concentration.

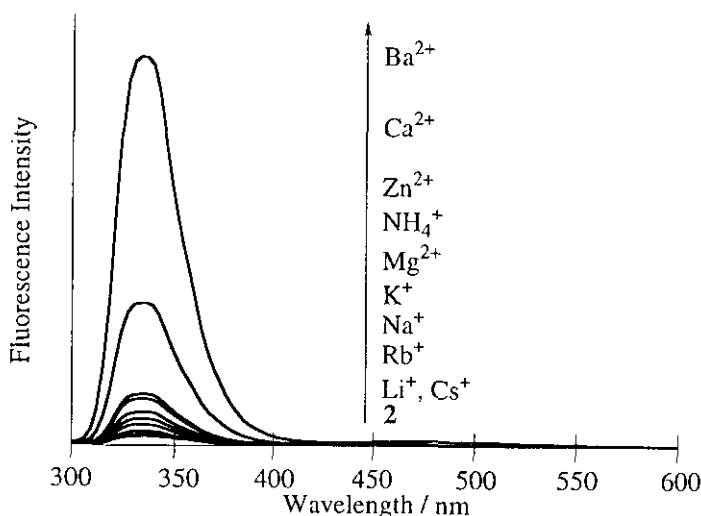


Figure 3. Fluorescence spectra of **2** ( $2.00 \times 10^{-5}$  M) with and without various metal cations ( $1.00 \times 10^{-2}$  M) in methanol, as excited at 280 nm.

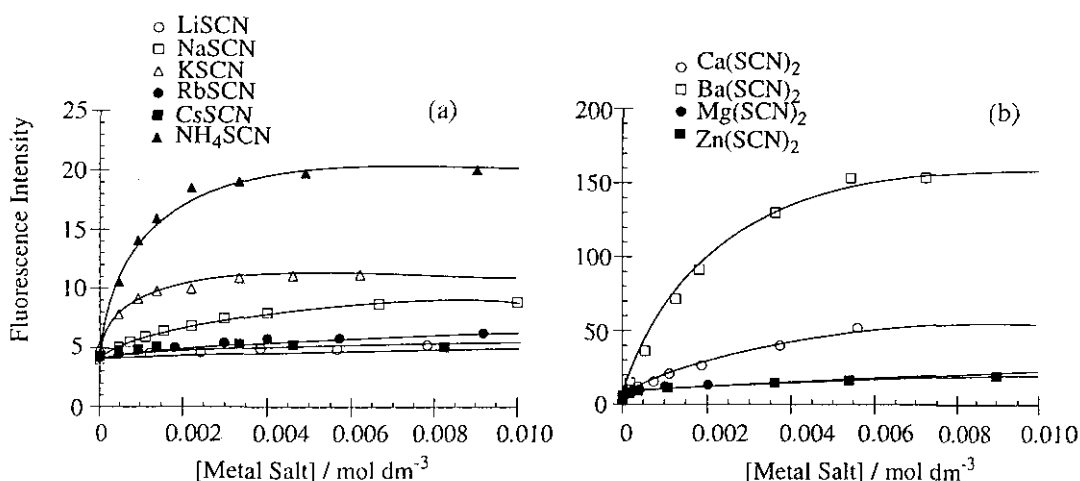


Figure 4. Dependence of fluorescence intensities of **2** ((a)  $2.00 \times 10^{-4}$  M, (b)  $2.00 \times 10^{-5}$  M) at 333 nm on the concentration of various metal cations (added as thiocyanate salts) in methanol.

Interestingly, the intensity ratio ( $I_{\text{complex}}/I_2$ ) was different among bound metal ions and was decreased in the following order:  $\text{Ba}^{2+}$  (41) >  $\text{Ca}^{2+}$  (15) >  $\text{Zn}^{2+}$  (5.4) >  $\text{NH}_4^+$  (4.9) >  $\text{Mg}^{2+}$  (3.5) >  $\text{K}^+$  (2.8) >  $\text{Na}^+$  (2.2) >  $\text{Rb}^+$  (1.5) >  $\text{Li}^+$  (1.2) and  $\text{Cs}^+$  (1.2). The larger  $I_{\text{complex}}/I_2$  value for bivalent metal ions than for monovalent ions suggests that the coordinated structure of bivalent metal ions differs from that of the alkali metal ions. The nitrogen atom is very likely to prefer coordination with bivalent metal ions. From the relative emission-intensity ratio ( $I_{\text{complex}}/I_2$ ), 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 (Figures 3 and 4) allowed us to determine the association constants ( $K$ ) by the non-linear curve-fitting method<sup>10</sup> (Table 2). The  $K$  values of **2** for  $K^+$  are almost similar to those of **1**, indicating that the two naphthalene rings substantially inhibit the complexation with metal ions.<sup>5</sup>

Table 2. Association constants ( $K$ , mol dm<sup>-3</sup>) of **1** and **2** for metal salts in methanol and methanol-chloroform (9:1 v/v)

	<b>1</b> $K$ (M <sup>-1</sup> )	<b>2</b> $K$ (M <sup>-1</sup> )	
	CH <sub>3</sub> OH:CHCl <sub>3</sub> (9:1 v/v)	CH <sub>3</sub> OH:CHCl <sub>3</sub> (9:1 v/v)	CH <sub>3</sub> OH
LiSCN	3 ± 0.4		27 ± 5
NaSCN	389 ± 37		123 ± 9
KSCN	2400 ± 23	2800 ± 140	1850 ± 320
RbSCN	345 ± 22		305 ± 26
CsSCN	117 ± 3		97 ± 30
NH <sub>4</sub> SCN	50 ± 4		1490 ± 165
Ca(SCN) <sub>2</sub>	145 ± 14		61 ± 4
Ba(SCN) <sub>2</sub>	142 ± 17		710 ± 114
Zn(SCN) <sub>2</sub>	7 ± 1		126 ± 13
Mg(SCN) <sub>2</sub>	1410 ± 139		3240 ± 200

The azacrown (**2**) showed the following cation selectivity:  $Li^+ < Ca^{2+} < Cs^+ < Na^+ < Zn^{2+} < Rb^+ < Ba^{2+} < NH_4^+ < K^+ < Mg^{2+}$ . This selectivity order is distinct from that for 18-crown-6 ( $K$ :  $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+ < Ba^{2+}$ )<sup>1</sup> and **1** ( $K$ :  $Li^+ < Zn^{2+} < NH_4^+ < Cs^+ < Ba^{2+} < Ca^{2+} < Rb^+ < Na^+ < Mg^{2+} < K^+$ ). In spite of the small association constant for **2** in methanol, the emission intensity of this host was greatly enhanced in the presence of metal salts, establishing that **2** has a high fluorescence switch-on ability for complexation with various metal ions.

Binding interactions of the host (**2**) with alkali metal and bivalent metal ions were examined using <sup>1</sup>H NMR spectroscopy. When alkali metal salts were added, each resonance peak was shifted to downfield or upfield

depending on the nature of added metal cations (Figure 5), while the addition of bivalent metal ions decreased the original-signal intensities with an increase in new-signal intensities (Figure 6).

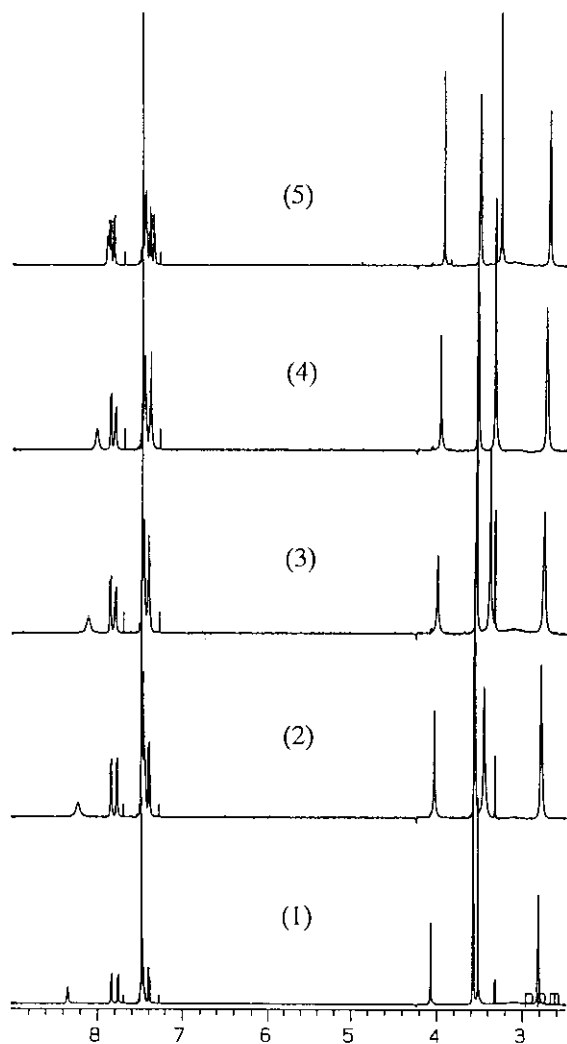


Figure 5.  $^1\text{H}$  NMR spectral changes of **2** ( $8.0 \times 10^{-4}$  M) with KSCN in  $\text{CD}_3\text{CN}-\text{CDCl}_3$  (1:1 v/v) at 298 K. Concentration of KSCN: (1) 0, (2)  $2.3 \times 10^{-4}$ , (3)  $2.6 \times 10^{-4}$ , (4)  $6.4 \times 10^{-4}$ , and (5)  $1.4 \times 10^{-3}$  M.

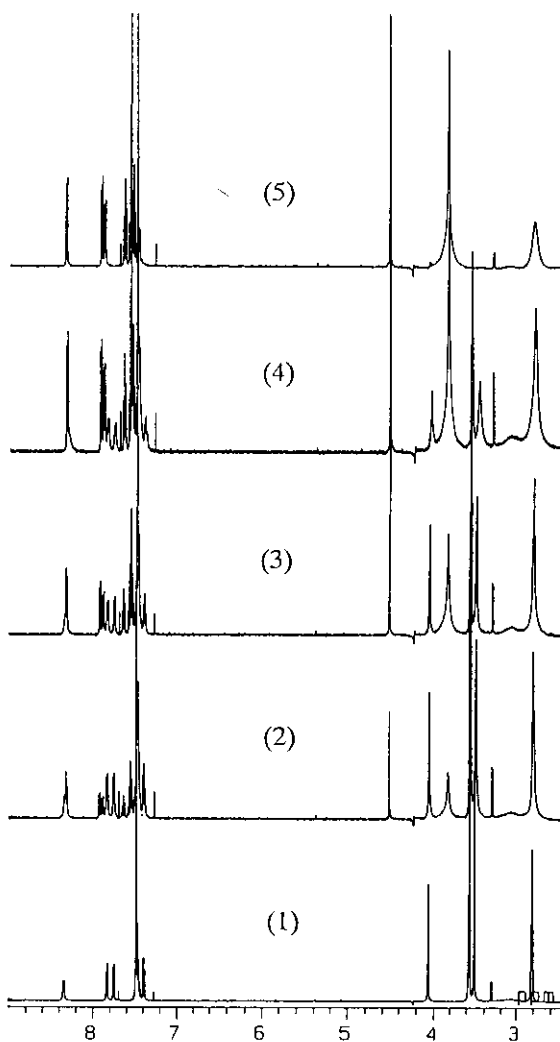


Figure 6.  $^1\text{H}$  NMR spectral changes of **2** ( $8.0 \times 10^{-4}$  M) with  $\text{Ba}(\text{SCN})_2$  in  $\text{CD}_3\text{CN}-\text{CDCl}_3$  (1:1 v/v) at 298 K. Concentration of  $\text{Ba}(\text{SCN})_2$ : (1) 0, (2)  $2.3 \times 10^{-4}$ , (3)  $2.6 \times 10^{-4}$ , (4)  $6.4 \times 10^{-4}$ , and (5)  $1.4 \times 10^{-3}$  M.

These spectral changes confirm that the exchange rates are different between alkali metal and bivalent metal ions. The gradual upfield shift of proton signal in the azacrown unit with added KSCN (Figure 5) shows that the exchange process between free host and its potassium complex is rapid as 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, **2**) signal intensities decreased and the intensities of new signals (of the corresponding complex **2**-Ba<sup>2+</sup>) appeared at 3.86 and 4.55 ppm increased as the Ba(SCN)<sub>2</sub> concentration was increased (Figure 6). Thus, the exchange process for this complex is slow enough even at room temperature, compared with the NMR time scale, to give new signal corresponding to the barium complex (**2**-Ba<sup>2+</sup>). The difference in exchange rate between K<sup>+</sup> and Ba<sup>2+</sup> should be responsible for a large difference in the relative emission-intensity ratio for these metal ions (Figure 4).

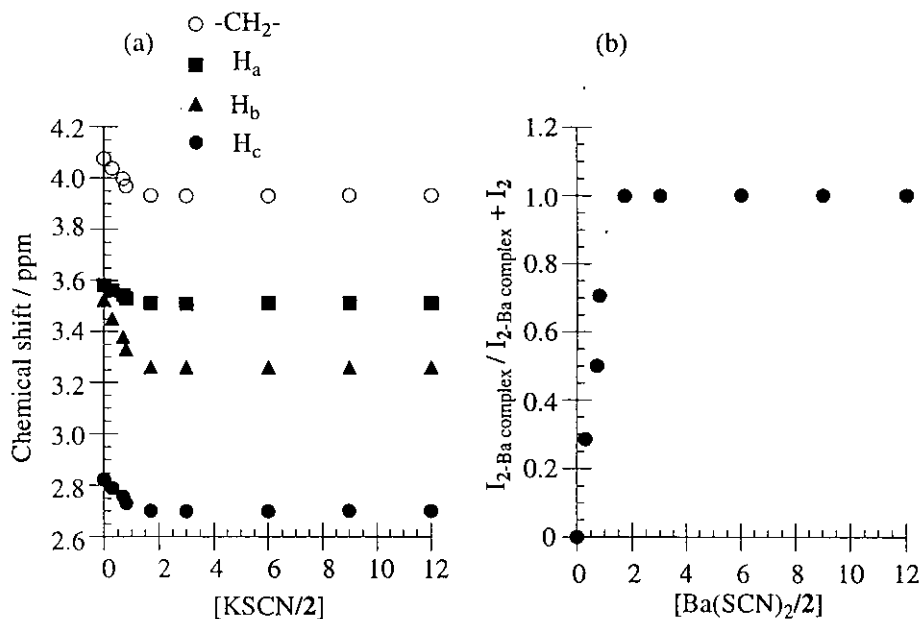


Figure 7. <sup>1</sup>H NMR spectral changes of **2** ( $8.0 \times 10^{-4}$  M) with KSCN and Ba(SCN)<sub>2</sub> in CDCl<sub>3</sub>-CD<sub>3</sub>CN (1:1 v/v); I<sub>2</sub>: Integral ratio of free(**2**), I<sub>2-Ba complex</sub>: Integral ratio of **2**-Ba(SCN)<sub>2</sub> complex.

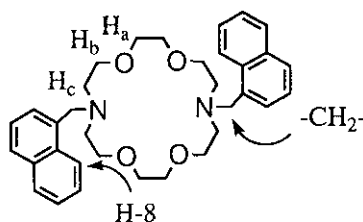
In all the complexation systems examined, the composition of the complexes (**2**-metal cations) could be determined by the use of <sup>1</sup>H NMR titration curves. Figure 7a shows a plot of the induced shift of each signal versus the molar concentration ratio of metal ion to **2**. The stoichiometry of the complexation between the host (**2**) and the guest K<sup>+</sup> was confirmed as 1:1, at least, in chloroform-*d*<sub>3</sub> and acetonitrile-*d*<sub>3</sub> (1:1 v/v) mixture. Similarly, the composition of the **2**-Ba<sup>2+</sup> complex was determined to be 1:1 by the molar ratio method (Figure 7b).

The chemical ( $\delta$ ) and induced ( $\Delta\delta$ ) shifts of the host (**2**) with and without metal cations are summarized in Table 3. The presence of Ba<sup>2+</sup> and Ca<sup>2+</sup> induced a dramatic downfield shift ( $\Delta\delta = 0.47$  for Ba<sup>2+</sup> and 0.79 for Ca<sup>2+</sup>) of the methylene proton signal of 1-naphthylmethyl group. There was also a significant downfield shift ( $\Delta\delta = 0.34$  for Ba<sup>2+</sup> and 0.32 for Ca<sup>2+</sup>) of the H<sub>b</sub> signal of azacrown unit. These

downfield shifts may be due to the strong interaction of the cations with the azacrown nitrogen. On the other hand,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  caused distinct upfield shifts of the H signal of azacrown unit as well as the methylene proton signal of 1-naphthylmethyl group. Ring-current effects of the naphthalene rings must be responsible for these upfield shifts.

Table 3. Changes of  $^1\text{H}$  NMR chemical shifts of **2** ( $1.0 \times 10^{-2}$  M) with various metal salts ( $1.0 \times 10^{-2}$  M) in  $\text{CD}_3\text{CN}-\text{CDCl}_3$  (1:1 v/v)

	Naphthylmethyl unit		Azacrown unit		
	H-8	$-\text{CH}_2-$	$\text{H}_a$	$\text{H}_b$	$\text{H}_c$
<b>2</b>	8.35	4.08	3.58	3.52	2.82
$\text{LiSCN}$	8.24 (-0.11)	4.12 (+0.04)	3.61 (+0.03)	3.55 (+0.03)	2.81 (-0.01)
$\text{NaSCN}$	7.95 (-0.40)	3.89 (-0.19)	3.49 (-0.09)	3.16 (-0.36)	2.66 (-0.16)
$\text{KSCN}$	7.93 (-0.42)	3.94 (-0.14)	3.51 (-0.07)	3.26 (-0.26)	2.70 (-0.12)
$\text{RbSCN}$	8.08 (-0.27)	3.98 (-0.10)	3.53 (-0.05)	3.34 (-0.18)	2.73 (-0.09)
$\text{CsSCN}$	8.24 (-0.11)	4.03 (-0.05)	3.56 (-0.02)	3.46 (-0.06)	2.78 (-0.04)
$\text{NH}_4\text{SCN}$	8.14 (-0.21)	4.05 (-0.03)	3.56 (-0.02)	3.32 (-0.20)	2.79 (-0.03)
$\text{Ca}(\text{SCN})_2$	8.55 (+0.20)	4.87 (+0.79)	3.84 (+0.26)	3.84 (+0.32)	2.85 (+0.03)
$\text{Ba}(\text{SCN})_2$	8.35 (0.00)	4.55 (+0.47)	3.86 (+0.28)	3.86 (+0.34)	2.82 (0.00)
$\text{Mg}(\text{SCN})_2$	8.24 (-0.11)	4.39 (+0.31)	3.63 (+0.05)	3.41 (-0.11)	3.06 (+0.24)
$\text{Zn}(\text{SCN})_2$	8.29 (-0.06)	4.27 (+0.19)	3.60 (+0.02)	3.43 (-0.09)	2.97 (+0.15)



Further detailed information on the cation binding behavior for **2** was obtained by  $^{13}\text{C}$  NMR spectroscopy in chloroform- $d_3$  and acetonitrile- $d_3$  (1:1 v/v) mixture. Table 4 summarizes the cation-induced shifts of the selected carbon signals of **2**. In order to assign the carbon signals of **2** in the absence and presence of the guest cation, H-H and C-H COSY experiments were performed for the free host as well as for each of the complexes (Figure 8).

Table 4. Changes of  $^{13}\text{C}$  NMR chemical shifts of **2** ( $1.0 \times 10^{-2}$  M) with various metal salts ( $1.0 \times 10^{-2}$  M) in  $\text{CD}_3\text{CN}-\text{CDCl}_3$  (1:1 v/v)

	-CH <sub>2</sub> -	Azacrown unit		
		C <sub>a</sub>	C <sub>b</sub>	C <sub>c</sub>
<b>2</b>	58.8	71.0	70.2	54.6
LiSCN	57.5 (-1.3)	69.5 (-1.5)	69.4 (-0.8)	53.5 (-1.1)
NaSCN	56.9 (-1.9)	68.6 (-2.4)	67.7 (-2.5)	53.3 (-1.3)
KSCN	56.9 (-1.9)	69.8 (-1.2)	68.0 (-2.2)	55.7 (+1.1)
RbSCN	57.1 (-1.7)	70.1 (-0.9)	68.5 (-1.7)	55.5 (+0.9)
CsSCN	58.1 (-0.7)	70.6 (-0.4)	69.5 (-0.7)	55.0 (+0.4)
NH <sub>4</sub> SCN	55.2 (-3.6)	68.9 (-2.1)	66.9 (-3.3)	55.1 (+0.5)
Ca(SCN) <sub>2</sub>	53.4 (-5.4)	70.3 (-0.7)	69.6 (-0.6)	51.0 (-3.6)
Ba(SCN) <sub>2</sub>	49.7 (-9.1)	70.9 (-0.1)	68.4 (-1.8)	53.3 (-1.3)
Mg(SCN) <sub>2</sub>	55.2 (-3.6)	68.9 (-2.1)	65.9 (-4.3)	54.1 (-0.5)
Zn(SCN) <sub>2</sub>	57.3 (-1.5)	70.5 (-0.5)	67.7 (-2.5)	55.3 (+0.7)

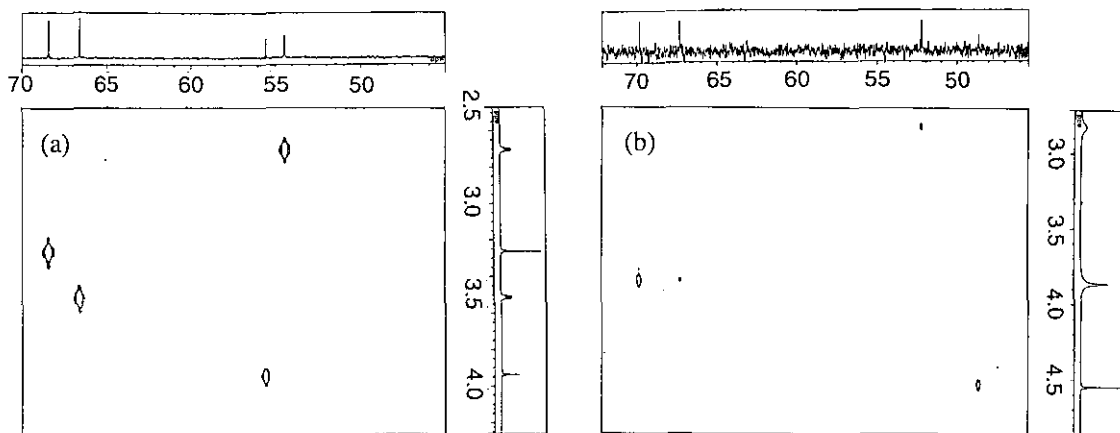
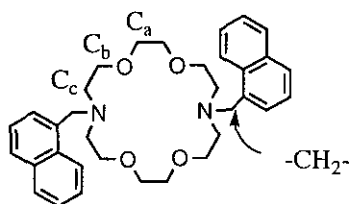


Figure 8. C-H COSY spectra of (a) **2**-KSCN and (b) **2**-Ba(SCN)<sub>2</sub> complex.

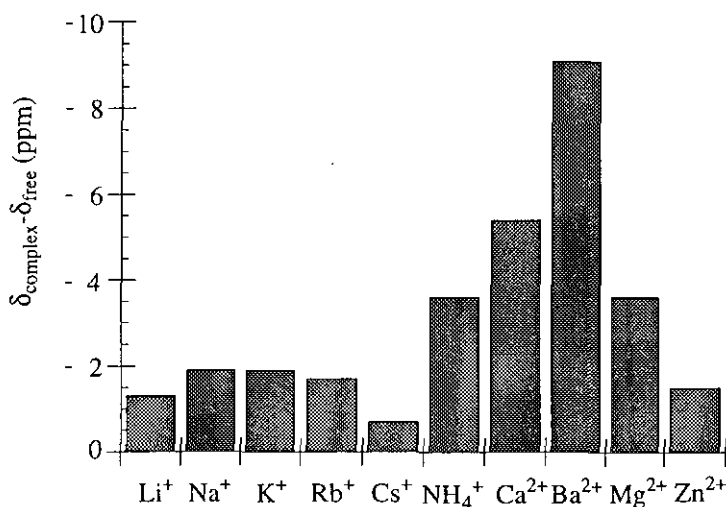


Figure 9. Metal-induced changes in  $^{13}\text{C}$  NMR chemical shift of methylene carbon of naphthylmethyl group.

Interestingly,  $\text{Ba}^{2+}$  produced even more remarkable chemical-shift change for the methylene carbon signal (Figure 9). The magnitude of metal ion-induced shift for this carbon signal decreased in the following order:  $\text{Ba}^{2+}$  (-9.1) >  $\text{Ca}^{2+}$  (-5.4) >  $\text{NH}_4^+$  (-3.6) >  $\text{Mg}^{2+}$  (-3.6) >  $\text{K}^+$  (-1.9) >  $\text{Na}^+$  (-1.9) >  $\text{Zn}^{2+}$  (-1.5) >  $\text{Rb}^+$  (-1.7) >  $\text{Li}^+$  (-1.3),  $\text{Cs}^+$  (-0.7), clearly demonstrating that the nitrogen atom in the azacrown ether has a propensity to strongly coordinate with bivalent cations.

In conclusion, 1) the fluorescence quenching of the host itself occurs by intramolecular electron transfer between the naphthyl group and the nitrogen atom in the crown ring, and the cation binding to the host azacrown results in an emission-intensity enhancement; 2) the metal cation-induced emission-intensity enhancement originates from the affinity of the nitrogen atom in the azacrown ether for cations; 3) the diazacrown ether having two 1-naphthyl pendants may be utilized as a new fluorescent sensor for metal cations.

## EXPERIMENTAL

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  $\text{CDCl}_3$ ; the chemical shifts were expressed by an  $\delta$  unit using tetramethylsilane as an internal standard. IR spectra were recorded on a Hitachi Model 270-30

infrared spectrophotometer. UV spectra were measured using a Shimadzu Model UV-2200 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(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2).**

A tetrahydrofuran solution (10 mL) of diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, 0.262 g, 1.0 mmol), triethylamine (0.5 mL, 3.6 mmol), 1-chloromethylnaphthalene (1.767 g, 10.0 mmol) was refluxed for 12 h. The mixture was then diluted with 1M NH<sub>3</sub> (10 mL), extracted with EtOAc. The solvent was evaporated and the residue was purified by column chromatography over silica gel (70–230 mesh, Merck) using hexane and ethyl acetate (3:1 v/v) as the eluent. Recrystallization from ethanol gave analytically pure samples with the following physical properties.

2: colorless prism, mp 95.0–96.0°C, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ= 2.88 (8H, t, J=5.8 Hz), 3.56 (8H, s), 3.62 (8H, t, J=5.8 Hz), 4.09 (4H, s), 7.38 (2H, dd, J=8.2, 7.0 Hz), 7.43–7.49 (6H, m), 7.74 (2H, d, J=8.2 Hz), 7.82 (2H, dd, J=7.6, 1.5 Hz), 8.34 (2H, dd, J=7.9, 1.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ=54.2 (4C), 58.6 (2C), 70.1(4C), 70.7 (4C), 124.8 (2C), 125.2 (2C), 125.5 (2C), 125.6 (2C), 127.2 (2C), 127.7 (2C), 128.3 (2C), 132.5 (2C), 133.8 (2C), 135.4 (2C). IR ν<sub>max</sub> KBr 789, 930, 987, 106, 1110, 1140, 1257, 1353, 1374, 1440, 1479, 1596, and 2794 cm<sup>-1</sup>; Anal. Calcd for C<sub>34</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>: C, 75.25 ; H, 7.80 ; N, 5.16. Found: C, 75.47 ; H, 8.06 ; N, 5.16.

**X-Ray Analysis of Diazacrown (2)**

All H atoms were located at ideal positions and were included in refinement, but restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.2 times *U*<sub>eq</sub> of the riding atoms.

Data collection: *CAD-4 Software*.<sup>11</sup> Cell refinement: *CAD-4 Software*. Data reduction: *MolEN*.<sup>12</sup>

Program used to solve structure: *SIR92*.<sup>13</sup> Program used to refine structure: *SHELXL93*.<sup>14</sup> Molecular graphics: *Xtal GX*.<sup>15</sup> Software used to prepare material for publication: *SHELXL93*.

The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 5. The selected bond lengths and angles are summarized in Table 6.

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) of 2

	x	y	z	$U_{eq}$
O1	-0.12394(6)	0.03636(13)	0.6927(2)	0.0658(4)
O2	-0.20541(6)	-0.06674(14)	0.42534(13)	0.0646(4)
N1	0.04819(7)	0.21022(13)	0.77952(15)	0.0501(3)
C1	0.09192(9)	0.3951(2)	0.9568(2)	0.0570(4)
C2	0.14079(11)	0.3913(2)	1.0777(2)	0.0762(6)
C3	0.18973(12)	0.5014(3)	1.1063(3)	0.0901(8)
C4	0.18952(11)	0.6112(3)	1.0126(3)	0.0900(8)
C5	0.13709(13)	0.7397(2)	0.7938(3)	0.0874(7)
C6	0.0878(2)	0.7514(2)	0.6785(3)	0.0945(8)
C7	0.03824(14)	0.6461(2)	0.6484(3)	0.0845(6)
C8	0.03951(10)	0.5292(2)	0.7366(2)	0.0656(5)
C9	0.09004(8)	0.5128(2)	0.8595(2)	0.0557(4)
C10	0.14014(9)	0.6225(2)	0.8884(3)	0.0707(6)
C11	0.03997(9)	0.2773(2)	0.9323(2)	0.0595(4)
C12	-0.00488(9)	0.0996(2)	0.7629(2)	0.0584(4)
C13	-0.08339(9)	0.1463(2)	0.7544(2)	0.0636(5)
C14	-0.19878(9)	0.0659(2)	0.6646(2)	0.0654(5)
C15	-0.23237(8)	-0.0511(2)	0.5794(2)	0.0643(5)
C16	-0.14127(8)	-0.1468(2)	0.4120(2)	0.0579(4)
C17	-0.12238(8)	-0.1572(2)	0.2423(2)	0.0544(4)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 6. Selected bond lengths ( $\text{\AA}$ ), angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) for 2

O1—C13	1.409(2)	C1—C2	1.367(3)	C5—C10	1.407(3)
O1—C14	1.414(2)	C1—C9	1.424(3)	C6—C7	1.394(3)
O2—C16	1.412(2)	C1—C11	1.506(2)	C7—C8	1.372(3)
O2—C15	1.419(2)	C2—C3	1.420(3)	C8—C9	1.408(3)
N1—C12	1.459(2)	C3—C4	1.342(4)	C9—C10	1.431(2)
N1—C17 <sup>i</sup>	1.461(2)	C4—C10	1.398(3)		
N1—C11	1.474(2)	C5—C6	1.340(4)		
C13—O1—C14	114.39(13)	C12—N1—C11—C1	-178.70(14)		
C16—O2—C15	115.06(13)	C17 <sup>i</sup> —N1—C11—C1	59.0(2)		
C12—N1—C17 <sup>i</sup>	109.72(12)	C17 <sup>i</sup> —N1—C12—C13	-169.56(14)		
C12—N1—C11	110.43(13)	C11—N1—C12—C13	67.0(2)		
C17 <sup>i</sup> —N1—C11	111.59(12)	N1—C12—C13—O1	162.66(14)		
N1—C11—C1	113.58(13)	O1—C14—C15—O2	-67.9(2)		
N1—C12—C13	114.16(14)	O2—C16—C17—N1 <sup>i</sup>	66.58(13)		

symmetry code (i);  $-x, -y, 1-z$

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