

## SYNTHESIS, COMPLEXATION AND EMISSION BEHAVIOR OF *N,N',N'',N'''*-TETRAKIS(1-NAPHTHYLMETHYL)-1,4,8,11-TETRAAZACYCLOTETRADECANE

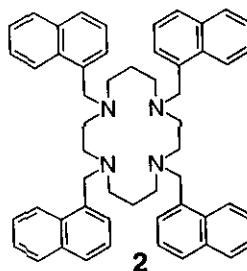
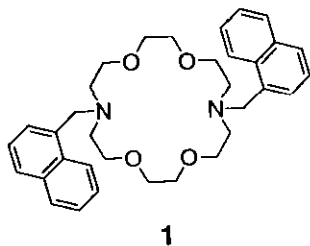
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**Abstract**—Cyclam derivative (**2**) having four naphthylmethyl pendants was found to display unique photophysical properties in the presence of the guest metal salts. The fluorescence of the cyclam (**2**) was enhanced with various metal salts. The photoinduced electron transfer (PET) sensor (**2**) exhibited high  $Zn^{2+}$  selectivity.

Azamacrocycles containing naphthyl subunits as an integral part of the macrocycle represent attractive class of synthetic receptors.<sup>1</sup> The presence of the naphthyl groups can impart some interesting properties to the resulting macrocycles. Photoresponsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switch.<sup>2</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>3,4</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>5</sup> 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**).<sup>6</sup> Thus, it is interesting to investigate the complex formation with metal salts using fluorescence spectroscopy. As an approach to the manipulation of PET sensor, we now report the fluorescence behavior of the cyclam (**2**) with four naphthyl pendants in the presence of metal salts.



The naphthalene-functionalized cyclam (**2**) was prepared by the *N*-alkylation of cyclam with 1-chloromethylnaphthalene in THF-triethylamine (49% yield). The structure and purity of **2** were ascertained by NMR spectroscopy and elemental analysis.

In Figure 1 is illustrated the fluorescence spectral behavior of **2** ( $2.00 \times 10^{-5}$  M) in methanol-chloroform (9:1 *v/v*) at room temperature. Fluoroionophore (**2**), (when excited at 282 nm), gave a broad emission band at 465 nm ( $I_{465}/I_{337}$ : 0.20) in addition to the emission band at 337 nm. 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-79th that of 1-methylnaphthalene ( $8.00 \times 10^{-5}$  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> The quenching efficiency ( $I_2/I_{1\text{-methylnaphthalene}}$ :  $1.3 \times 10^{-2}$ ) is lower than that ( $I_1/I_{1\text{-methylnaphthalene}}$ :  $2.3 \times 10^{-3}$ ) of **1**. This means the smaller macrocycle ring inhibit the PET occurring from the nitrogen atoms in the macrocycles to the naphthalene.

In Figure 2 is illustrated the fluorescence spectral behavior of **2** ( $2.00 \times 10^{-5}$  M) in methanol-chloroform (9:1 *v/v*) at room temperature. A dramatic change in the emission intensity of **2** ( $I_2$ ) was observed upon the addition of various amounts of metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mg}^{2+}$ ) and  $\text{NH}_4^+$ .

When the metal salts were added (250 molar equivalent), the relative emission intensity ( $I_{\text{complex}}/I_2$ ), being used as a measure of the molecular recognition sensing, changed from 1.3 to 8.1 depending on the nature of metal cations as shown in Figure 2.

Figure 3 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. Interestingly, the intensity ratio ( $I_{\text{complex}}/I_2$ ) was different among bound guest cations and decreased in the following order:  $\text{Zn}^{2+}$  (8.1) >

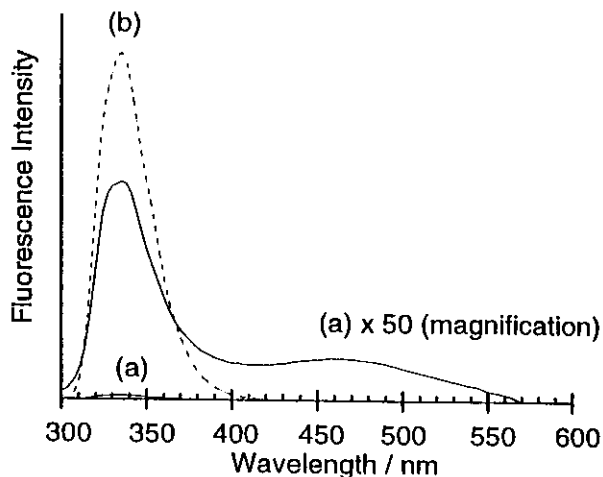


Figure 1. Fluorescence spectra of (a) **2** ( $2.00 \times 10^{-5}$  M) and (b) 1-methylnaphthalene ( $8.00 \times 10^{-5}$  M) in methanol-chloroform (9:1 *v/v*) at room temperature.

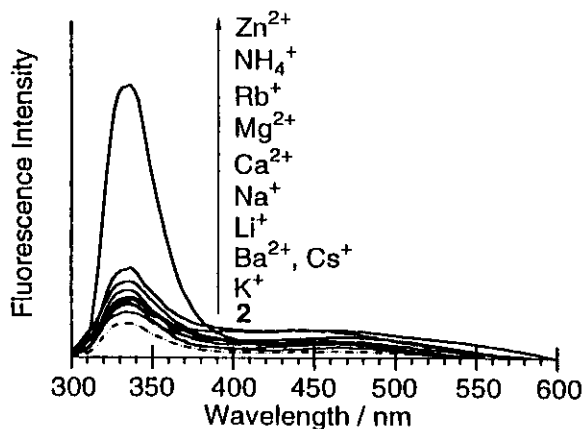


Figure 2. Fluorescence spectra of **2** ( $2.00 \times 10^{-5}$  M) with and without various metal cations ( $5.00 \times 10^{-3}$  M) in methanol-chloroform (9:1 *v/v*), as excited at 282 nm.

$\text{NH}_4^+$  (2.7) >  $\text{Rb}^+$  (2.3) >  $\text{Mg}^{2+}$  (2.1) >  $\text{Ca}^{2+}$  (2.0) >  $\text{Li}^+$ ,  $\text{Na}^+$  (1.8) >  $\text{Ba}^{2+}$ ,  $\text{Cs}^+$  (1.6) >  $\text{K}^+$  (1.3). The order of  $I_{\text{complex}}/I_2$  differs from that of  $I_{\text{complex}}/I_1$  ( $\text{Ba}^{2+}$  (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))<sup>6</sup>. The sensor (2) exhibited  $\text{Zn}^{2+}$  selectivity.

Metal-ion concentration dependence of the emission intensity (Figure 3) allowed us to determine the association constants ( $K$ ) by the non-linear curve-fitting method<sup>8</sup> (Table 1). The association constants ( $K$ ) were calculated within the metal ion concentration range with the emission intensity increase.

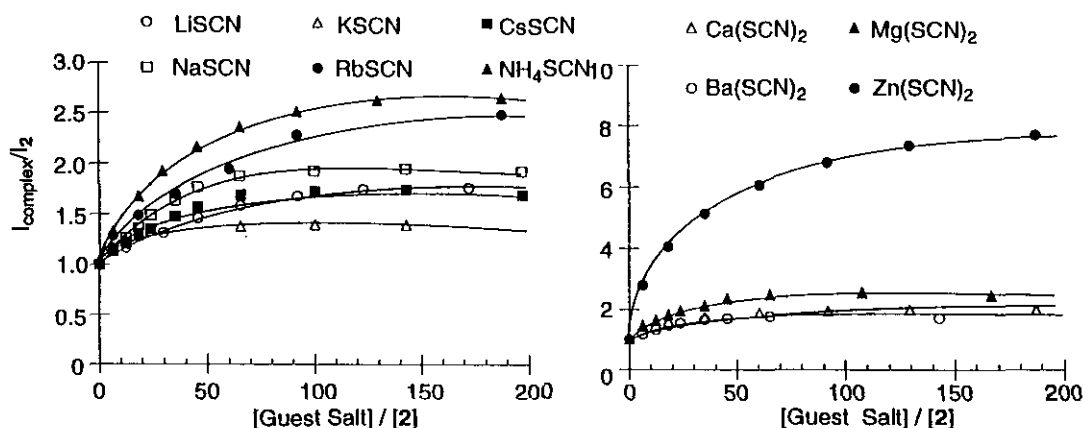


Figure 3. Dependence of fluorescence intensities of 2 ( $2.00 \times 10^{-5}$  M) at 337 nm on the concentration of various guest cations (added as thiocyanate salts) in methanol-chloroform (9:1 v/v).

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

	1 $K$ ( $\text{M}^{-1}$ )		2 $K$ ( $\text{M}^{-1}$ )
	$\text{CH}_3\text{OH}$	$\text{CH}_3\text{OH}:\text{CHCl}_3$ (9:1 v/v)	$\text{CH}_3\text{OH}:\text{CHCl}_3$ (9:1 v/v)
LiSCN	$27 \pm 5$		$733 \pm 68$
NaSCN	$123 \pm 9$		$1800 \pm 390$
KSCN	$1850 \pm 320$	$2800 \pm 140$	$3740 \pm 1000$
RbSCN	$305 \pm 26$		$1050 \pm 180$
CsSCN	$97 \pm 30$		$760 \pm 50$
$\text{NH}_4\text{SCN}$	$1490 \pm 165$		$1300 \pm 30$
$\text{Zn}(\text{SCN})_2$	$126 \pm 13$		$1350 \pm 80$
$\text{Mg}(\text{SCN})_2$	$3240 \pm 200$		$3190 \pm 860$
$\text{Ca}(\text{SCN})_2$	$61 \pm 4$		$3520 \pm 400$
$\text{Ba}(\text{SCN})_2$	$710 \pm 114$		$2400 \pm 200$

The azacrown (2) showed the following cation selectivity:  $\text{Li}^+ < \text{Cs}^+ < \text{Rb}^+ < \text{NH}_4^+ < \text{Zn}^{2+} < \text{Na}^+ < \text{Ba}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{K}^+$ . This selectivity order is distinct from that for 1 ( $K$ :  $\text{Li}^+ < \text{Ca}^{2+} < \text{Cs}^+ < \text{Na}^+ < \text{Zn}^{2+} < \text{Rb}^+ < \text{Ba}^{2+} < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{2+}$ )<sup>6</sup>. Comparison of the selectivity order for 1 and 2 confirms that the size and

electronic property of ionophore attached with aromatic pendants may control the selectivity of the host toward metal cations in a delicate manner. Interestingly, the order of the association constant ( $K$ ) of **2** differ from that of the emission-intensity enhancement ( $I_{\text{complex}}/I_2$ ) for **2** in the presence of metal salts. This result is similar to **1**. The host (**2**) has a fluorescence switch-on ability for complexation with various metal ions. In conclusion, the PET sensor (**2**) that showed  $\text{Zn}^{2+}$  selectivity 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 are uncorrected. NMR spectra were measured on a JEOL JNM-500 Model spectrometer in  $\text{CDCl}_3$ ; the chemical shifts are 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.

### *N,N',N'',N'''*-Tetrakis(1-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane (**2**).

A THF solution (10 mL) of cyclam (1,4,8,11-tetraazacyclotetradecane, 0.10 g, 0.5 mmol), triethylamine (1.53 g, 15.1 mmol), and 1-chloromethylnaphthalene (1.53 g, 8.7 mmol) was refluxed for 9 h. The solvent was evaporated and the residue was washed with 1 M  $\text{NH}_3$  (10 mL) and methanol (30 mL). Recrystallization from chloroform gave analytically pure sample with the following physical and spectroscopic properties.

**2**: colorless crystals, mp 185–187°C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 1.91 (4H, qui,  $J=7.0$  Hz), 2.38 (8H, t,  $J=7.0$  Hz), 2.62 (8H, s), 3.67 (8H, s), 7.25–7.31 (12H, m), 7.36 (4H, dd,  $J=7.9, 7.0$  Hz), 7.69 (4H, d,  $J=7.9$  Hz), 7.76 (4H, d,  $J=7.9$  Hz), and 8.49 (4H, d,  $J=8.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 24.5 (2C), 50.6 (4C), 51.7 (4C), 58.0 (4C), 125.0 (4C), 125.3 (4C), 125.4 (4C), 125.7 (4C), 127.4 (4C), 127.5 (4C), 128.0 (4C), 132.5 (4C), 133.7 (4C), and 135.6 (4C). IR  $\nu_{\text{max}}$  KBr 770, 958, 1114, 1222, 1274, 1364, 1498, 1590, 2788, and 2944  $\text{cm}^{-1}$ ; UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  (nm) = 273.3 ( $\epsilon=22200$ , sh), 283.8 (25700), and 295.1 (18200, sh); Anal. Calcd for  $\text{C}_{54}\text{H}_{56}\text{N}_4 \cdot \text{H}_2\text{O}$ : C, 83.25; H, 7.50; N, 7.19. Found: C, 83.01; H, 7.28; N, 7.11.

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