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 napthylmethyl 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 Zn²⁺ selectivity.

Azamacrocycles containing naphtyl subunits as an integral part of the macrocycle represent attractive class of synthetic receptors.¹ The presence of the naphtyl 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.² There are extensive investigations toward the characterization of fluorophorophores including crown ether, calixarene, and cyclodextrin derivatives with napthalene, umbelliferone, anthracene, or pyrene fluorophore.³,⁴ Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor.⁵ The addition of metal salts enhanced the fluorescence emission intensity of N,N'-bis(1-napthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1).⁶ 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 napthyl pendants in the presence of metal salts.

![Diagram of compounds 1 and 2]
The naphthalene-functionalized cyclam (2) was prepared by the N-alkylation of cyclam with 1-chloro-
methylnaphthalene 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 x 10^{-4} 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 x
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.\(^7\) The quenching efficiency (I_{2}/I_{1-methylnaphthalene}; 1.3 x 10^{-2}) is lower than that (I_{2}/I_{1-methylnaphthalene}; 2.3 x 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 x 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 (Li\(^+\), Na\(^+\), K\(^+\),
Rb\(^+\), Cs\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), Zn\(^{2+}\), and Mg\(^{2+}\)) and NH\(_4^+\).
When the metal salts were added (250 molar equivalent), the relative emission intensity (I_{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_{complex}/I_{2}) was different among bound guest cations and decreased in the following order: Zn\(^{2+}\) (8.1) >
$\text{NH}_4^+ \text{*(2.7)} > \text{Rb}^+ \text{*(2.3)} > \text{Mg}^{2+} \text{*(2.1)} > \text{Ca}^{2+} \text{*(2.0)} > \text{Li}^+, \text{Na}^+ \text{*(1.8)} > \text{Ba}^{2+}, \text{Cs}^+ \text{*(1.6)} > \text{K}^+ \text{*(1.3)}. \text{The order of} I_{\text{complex}}/I_0 \text{differs from that of} I_{\text{complex}}/I_0 \text{(*)} (\text{Ba}^{2+} \text{*(4.1)} > \text{Ca}^{2+} \text{*(15.4)} > \text{Zn}^{2+} \text{*(5.4)} > \text{NH}_4^+ \text{*(4.9)} > \text{Mg}^{2+} \text{*(3.5)} > \text{K}^+ \text{*(2.8)} > \text{Na}^+ \text{*(2.2)} > \text{Rb}^+ \text{*(1.5)} > \text{Li}^+ \text{*(1.2)} > \text{Cs}^+ \text{*(1.2)}^6). \text{The sensor (2) exhibited Zn}^{2+} \text{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^8 (Table I). The association constants (K) were calculated within the metal ion concentration range with the emission intensity increase.}

- \text{Figure 3. Dependence of fluorescence intensities of} 2 \text{ (2.00 x 10}^{-5} \text{ M)} \text{ 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, M\textsuperscript{-1}) of 1 and 2 for metal salts in methanol and methanol-chloroform (9:1 v/v)

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

\text{The azacrown (2) showed the following cation selectivity: Li}^+ < \text{Cs}^+ < \text{Rb}^+ < \text{NH}_4^+ < \text{Zn}^{2+} < \text{Na}^+ < \text{Ba}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{K}^+. \text{This selectivity order is distinct from that for} 1 \text{ (K: Li}^+ < \text{Ca}^{2+} < \text{Cs}^+ < \text{Na}^+ < \text{Zn}^{2+} < \text{Rb}^+ < \text{Ba}^{2+} < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{2+})^6. \text{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 \( I_{\text{complex}}/I_1 \) for 2 in the presence of metal salts. This result is similar to 1. The host (2) has a fluorescence swich-on ability for complexation with various metal ions.

In conclusion, the PET sensor (2) that showed 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 CDCl\(_3\); the chemical shifts are expressed by a \( \delta \) 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 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, \(^1\)H NMR (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); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta = 24.5 \) (2C), 50.6 (4C), 51.7 (4C), 58.0 (4C), 125.0 (4C), 125.3 (4C), 125.4 (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 cm\(^{-1}\); UV (CHCl\(_3\)) \( \lambda_{\text{max}} \) (nm) = 273.3 (e=22200, sh), 283.8 (25700), and 295.1 (18200, sh); Anal. Calcd for C\(_{54}H\(_{56}\)N\(_4\): H\(_2\)O: C, 83.25; H, 7.50; N, 7.19. Found: C, 83.01; H, 7.28; N, 7.11.

**REFERENCES AND NOTES**


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