

Synthesis and Complexation Behavior of 2-[N, N-Bis (1-naphthylmethyl)-aminomethyl]-18-crown-6

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Synthesis and Complexation Behavior of 2-[*N,N*-Bis(1-naphthylmethyl)-aminomethyl]-18-crown-6

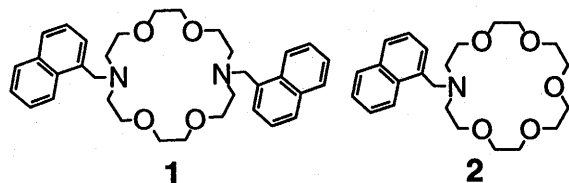
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2-[*N,N*-Bis(1-naphthylmethyl)-aminomethyl]-18-crown-6 (**3**) gave intramolecular exciplex fluorescence, showing that the excited naphthalene chromophore was quenched by the nitrogen atom in the armed crown unit. The armed crown ether (**3**) was found to display unique photophysical properties in the presence of metal salts. Complexation of **3** with Zn^{2+} increased the fluorescence intensity of the host by a factor of 2.4. ^1H and ^{13}C NMR analyses of this complexation behavior revealed that Zn^{2+} strongly coordinates with the armed crown nitrogen to cause a dramatic decrease in an intramolecular charge-transfer character.

1. Introduction

As an approach to the manipulation of an intramolecular electron transfer dynamics, photo-responsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switch.¹⁾ There are extensive investigations toward the characterization of photoinduced electron transfer (PET) fluoroionophores including crown ether derivatives with naphthalene, umbelliferone, anthracene, or pyrene fluorophore.^{2,3)}

Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor.⁴⁾ The addition of metal salts enhanced the fluorescence emission intensity of *N,N'*-bis(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-azacyclooctadecane(**1**).⁵⁾ While, *N*-(1-naphthylmethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**2**) showed fluorescence increase with divalent metal cations and fluorescence decrease with monovalent metal cations.

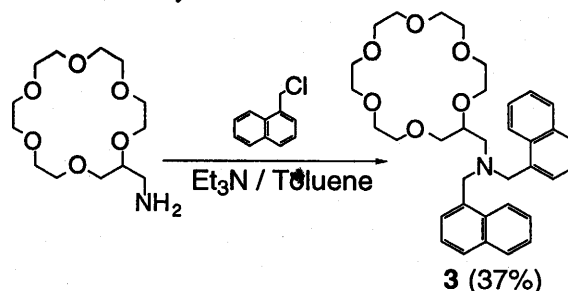


Thus, it is interesting to investigate the complex formation of various PET fluoroionophores with metal

salts using fluorescence spectroscopy. We now report the synthesis and fluorescence behavior of the armed crown ether (**3**) containing two chromophoric naphthyl pendants.

2. Results and Discussion

The naphthalene-functionalized armed crown ether (**3**) was prepared by *N*-alkylation of 2-aminomethyl-18-crown-6 with 1-chloromethylnaphthalene in toluene-triethylamine (37% yield). The structure and purity of **3** were ascertained by NMR spectroscopy and elemental analysis.



Scheme 1

Figure 1 is illustrated the fluorescence spectral behavior of **3** (2.00×10^{-5} M) in methanol at room temperature. Fluoroionophore (**3**), when excited at 281 nm, gave a broad emission band with a maximum at 460 nm in addition to the monomer emission band (334 nm).

The formation of intramolecular exciplex should be responsible for the appearance of the former emission band. The latter emission-band intensity of **3** was reduced to approximately one-270th that of 1-methylnaphthalene (4.00×10^{-5} M), which was accompanied by the exciplex fluorescence. This

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indicates that the quenching of the excited-state naphthalene chromophore by the amino unit proceeds in a mechanism similar to that for the classical naphthalene-aliphatic amine system.⁷⁾

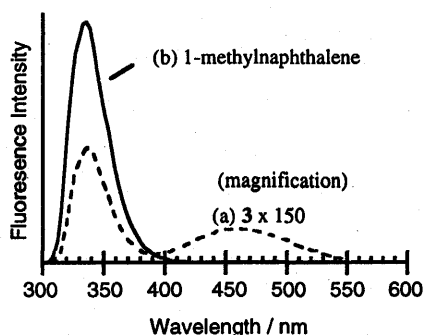


Fig. 1 Fluorescence spectrum of (a) **3** (2.00×10^{-5} M) and (b) 1-methylnaphthalene (4.00×10^{-5} M) in methanol, as excited at 281 nm.

The formation of the intramolecular exciplex is very likely to be responsible for the observed emission quenching. However, the quenching efficiency (I_3/I_1 , methylnaphthalene: 3.7×10^{-3}) is lower than that (I_1/I_1 , methylnaphthalene: 2.3×10^{-3})⁵⁾ of **1**. This means steric hindrance between the macrocycle ring and two naphthalene rings inhibit the PET occurring from the nitrogen atoms in the macrocycles to the naphthalene.

A dramatic change in the emission intensity of **3** (I_3) was observed upon the addition of various amounts of guest cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Ba^{2+} , Zn^{2+} , and Mg^{2+}) and NH_4^+ . When the guest cations were added (50 molar equivalent), the relative emission intensity ratio (I_{complex}/I_3), being used as a measure of the molecular recognition sensing, changed from 2.4 to 1.2 depending on the nature of metal cations as shown in Figure 2.

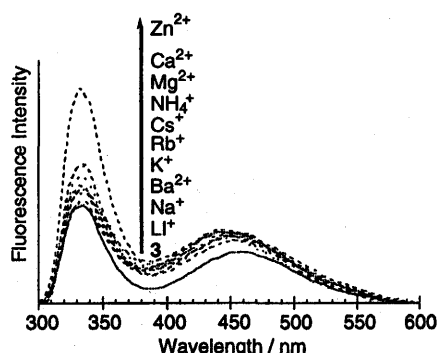


Fig. 2 Fluorescence spectral changes of **3** (2.00×10^{-5} M) with and without various metal salts (1.00×10^{-3} M) in methanol, as excited at 281 nm.

Figure 3 illustrates the relative emission intensity of **3** against the guest 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 bound metal ions and decreased in the following order: Zn^{2+} (2.4) > Ca^{2+} , Mg^{2+} (1.6) > NH_4^+ , Cs^+ (1.4) > Rb^+ , K^+ (1.3) > Ba^{2+} , Na^+ , Li^+ (1.2). The order of I_{complex}/I_2 differs from that of I_{complex}/I_3 (Ba^{2+} (41) > Ca^{2+} (15) > Zn^{2+} (5.4) > NH_4^+ (4.9) > Mg^{2+} (3.5) > K^+ (2.8) > Na^+ (2.2) > Rb^+ (1.5) > Li^+ (1.2) and Cs^+ (1.2))⁵⁾. Zinc ion binding can then cause high fluorescence recovery. This recovery is due to coordination from the nitrogen atoms of the armed crown to the zinc ion. The strength of this binding interaction modulates the PET from the amine to naphthalene. However, the recovery of the armed crown (**3**) is lower than that of the azamacrocycles (**1**, **2**)^{5,6)}.

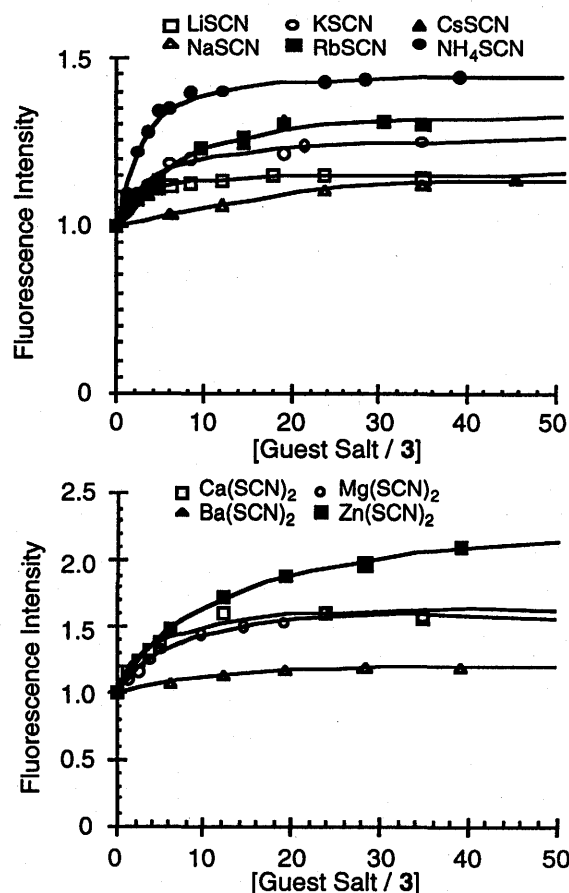


Fig. 3 Dependence of fluorescence intensities of **3** (2.00×10^{-5} M) at 334 nm on the concentration of various metal salts in methanol.

Metal-ion concentration dependence of the emission intensity (Figure 3) allowed us to determine the association constants (K) by the non-linear curve-fitting

method⁸⁾ (Table 1).

Table 1 Association constants (K / M^{-1}) of 1-3 for various metal salts in methanol

| | 1 | 2 | 3 |
|----------------------|------------|---------------|--------------|
| LISCN | 27 ± 5 | 2400 ± 310 | - |
| NaSCN | 123 ± 9 | 3890 ± 300 | - |
| KSCN | 1850 ± 320 | 98200 ± 10500 | - |
| RbSCN | 305 ± 26 | 51400 ± 4500 | 8500 ± 690 |
| CsSCN | 97 ± 30 | 6260 ± 750 | 990 ± 580 |
| NH ₄ SCN | 1490 ± 165 | 15800 ± 1300 | 19000 ± 6400 |
| Ca(SCN) ₂ | 61 ± 4 | 7100 ± 700 | 10100 ± 2500 |
| Ba(SCN) ₂ | 710 ± 114 | 51300 ± 19600 | - |
| Mg(SCN) ₂ | 3240 ± 200 | 29600 ± 1700 | 6500 ± 800 |
| Zn(SCN) ₂ | 126 ± 13 | 1300 ± 120 | 3600 ± 400 |

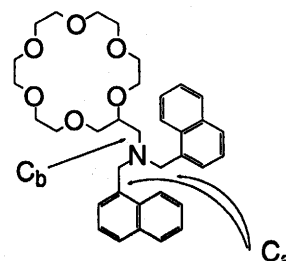
The armed crown (3) showed the following cation selectivity: $Cs^+ < Zn^{2+} < Mg^{2+} < Rb^+ < Ca^{2+} < NH_4^+$. This selectivity order is distinct from that for 1 ($K: Li^+ < Ca^{2+} < Cs^+ < Na^+ < Zn^{2+} < Rb^+ < Ba^{2+} < NH_4^+ < K^+ < Mg^{2+}$)⁵⁾ and 2 ($K: Zn^{2+} < Li^+ < Na^+ < Cs^+ < Ca^{2+} < NH_4^+ < Mg^{2+} < Ba^{2+} < Rb^+ < K^+$)⁶⁾. The association constants of 1-3 for various metal ions are depending upon the nature of ionophore properties.

Further detailed information on the cation binding behavior for 3 was obtained by ¹H and ¹³C NMR spectroscopy. The chemical (δ) and induced ($\Delta\delta$) shifts of the selected proton and carbon signals of the host (3) with and without metal cations are summarized in Table 2. Interestingly, Zn^{2+} produced even more remarkable chemical-shift change and peak splitting for the methylene proton and carbon signal of naphthylmethyl group. The induced shift was clearly demonstrating that the nitrogen atom in the armed crown (3) has a propensity to strongly coordinate with Zn^{2+} . As already mentioned, the binding of guest cations to the armed crown (3) caused an emission-intensity enhancement. The change is considered to result from the guest cation-dependent coordinated structure and the stretch of coordination between nitrogen atoms and guest 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 armed-crown ring, and the cation binding to the host armed crown results in an emission-intensity enhancement; 2) the metal cation-induced emission-intensity enhancement originates from the affinity of the nitrogen atom in the armed crown ether for cations; 3) the armed crown ether having two 1-naphthyl pendants may be utilized as a new fluorescent sensor for metal cations.

Table 2 Changes of ¹H and ¹³C NMR chemical shifts (δ) and induced shifts ($\delta_{\text{complex}} - \delta_3$) of 3 (1.0×10^{-2} M) with various metal salts (1.0×10^{-2} M) in CD₃CN-CDCl₃ (1:1 v/v)

| | Naphthylmethyl Group -CH ₂ - | | | |
|----------------------|--|-----------------|------------------|------------------|
| | H _A | H _B | C _a | C _b |
| 3 | 3.96 | 4.13 | 59.58 | 54.50 |
| LiSCN | 3.93 (-0.03) | 4.21 (+0.08) | 59.79 (+0.21) | 53.35 (-1.19) |
| NaSCN | 3.93 (-0.03) | 4.20 (+0.07) | 59.83 (+0.25) | 53.61 (-0.91) |
| KSCN | 3.89 (-0.07) | 4.22 (+0.09) | 59.82 (+0.24) | 52.78 (-1.76) |
| RbSCN | 3.95 (-0.01) | 4.18 (+0.05) | 59.74 (+0.16) | 53.43 (-1.11) |
| CsSCN | 3.98 (+0.02) | 4.14 (+0.01) | 59.69 (+0.11) | 53.77 (-0.77) |
| NH ₄ SCN | 3.93 (-0.03) | 4.20 (+0.07) | 59.78 (+0.20) | 53.06 (-1.48) |
| Ca(SCN) ₂ | 3.86 (-0.10) | 4.33 (+0.20) | 59.67 (+0.09) | 52.35 (-2.19) |
| Ba(SCN) ₂ | 3.89 (-0.07) | 4.30 (+0.17) | 59.79 (+0.21) | 52.41 (-2.13) |
| Mg(SCN) ₂ | 3.97 (+0.01) | 4.24 (+0.11) | 59.86 (+0.28) | 54.23 (-0.31) |
| Zn(SCN) ₂ | 4.45 | 4.82 | 4.95 | 5.74 |
| | | | 59.41 | 57.97 |
| | | | | 56.69 |



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 CDCl₃; the chemical shifts were expressed by an δ 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.

Synthesis of 2-[N,N-Bis(1-naphthylmethyl)-amino-methyl]-1,4,7,10,13,16-hexaoxacyclooctadecane (3).

A toluene solution (10 mL) of 2-(aminomethyl)-

18-crown-6 (0.147g, 0.5 mmol), triethylamine (1.0 mL, 7.2 mmol), 1-chloromethylnaphthalene (0.618 g, 3.5 mmol) was refluxed for 6 h. The mixture was then diluted with 1M NH₃ (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.

3 (colorless oil); ¹H-NMR: δ 2.64 (1H, dd, J=13.4, 5.5 Hz), 2.69 (1H, dd, J=13.4, 6.4 Hz), 3.07-3.18 (4H, m), 3.43 (2H, ddd, J=5.5, 3.7, 1.2 Hz), 3.51-3.68 (17H, m), 3.99 (2H, d, J=12.8 Hz), 4.11 (2H, d, J=12.8 Hz), 7.19 (2H, ddd, J=8.6, 7.0, 1.2 Hz), 7.36 (2H, dd, J=8.2, 7.0 Hz), 7.40 (2H, ddd, J=8.2, 7.0, 1.2 Hz), 7.45 (2H, d, J=7.0 Hz), 7.73 (2H, d, J=8.2 Hz), 7.78 (2H, d, J=8.2 Hz), and 7.98 (2H, d, J=8.6 Hz); ¹³C-NMR: δ 55.26, 59.17(2C), 69.18, 70.33, 70.50(2C), 70.53, 70.55, 70.67, 70.72, 70.73, 70.78, 72.71, 77.63, 125.02 (2C), 125.33 (2C), 125.48 (2C), 125.51 (2C), 128.10 (2C), 128.16 (2C), 128.33 (2C), 132.53 (2C), 133.82 (2C), and 134.97 (2C); IR: ν (NaCl) 951, 1116, 1287, 1350, 1449, 1596, 2860, and 3040 cm⁻¹; EA: Found C 71.43, H 7.27, N 2.21, Calcd for C₃₅H₄₃NO₆·H₂O C 71.04, H 7.67, N 2.37.

Determination of Association Constants (K).

The titrations were conducted by adding a crown ether solution (2.00 × 10⁻⁵ M) for **3** in methanol progressively containing excess metal salts, using a 0.25 cm³ syringe, to a cuvette containing 2 cm³ of the crown ether solution (2.00 × 10⁻⁵ M in methanol). The solutions were kept for 30 min. The spectrum was recorded after each addition. The added equivalents of the cation were then plotted against the emission-intensity change at 334 nm, as shown Figure 2. Even though the solvent takes part in the association interaction, the solvent concentration is virtually unaffected. Therefore, we expressed the interaction of metal salts in terms of the equilibrium.⁸⁾



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

$$K = [\text{CE} \cdot \text{M}] / [\text{CE}] [\text{M}]$$

$$= [\text{CE} \cdot \text{M}] / ([\text{CE}_0] - [\text{CE} \cdot \text{M}])([\text{M}_0] - [\text{CE} \cdot \text{M}]) \quad (\text{eq } 2)$$

$$[\text{CE} \cdot \text{M}] = a[\text{CE}_0] = (I - I_0 [\text{CE}_0]) / (I_{\text{CE} \cdot \text{M}} - I_0) \quad (\text{eq } 3)$$

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

$$[\text{M}_0] = a / K(1-a) + a[\text{CE}_0], \quad (\text{eq } 4)$$

where [CE₀] and [M₀] are the initial concentrations of the crown ether and the metal salt, I and I₀ are the observed emission intensities of the crown ethers in the presence and in the absence of the metal ion and I_{CE·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 334 nm using the equation as given in Table 1.

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