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Complexation and Fluorescence Behavior of Tris[(1-naphthoyloxy)ethyl]amine[†]

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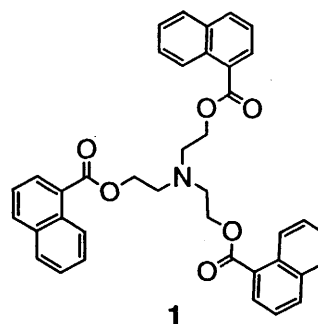
Tris[(1-naphthoyloxy)ethyl]amine (**1**) was found to display unique photophysical properties in the presence of the guest cations. The amine (**1**) revealed a broad emission band around 440 nm that is typical of a structureless emission of a naphthoyl excimer and a naphthalene-amine exciplex. From the result of X-ray analysis, the amine (**1**) adopt a tripod conformation with crystallographic C_3 symmetry. Complexation of **1** with Al^{3+} increased the emission intensity of a factor by 5.3 in H_2O-CH_3OH (1:1 v/v).

1. Introduction

During the last decades, macrocyclic and acyclic ligands have been designed to coordinate metal ions.^{1,2)} Polypod organic molecules containing donor atoms may be considered as non-cyclic cryptands³⁻⁵⁾ and indeed some of their complexes with alkali and alkali earth metal ions are more stable than the respective linear oligoether and cyclic crown ether complexes.⁵⁾

Recently, a number of fluoroionophores have been designed as legards for metal ions.⁶⁻¹²⁾ Some of them showed a photoinduced electron transfer (PET), exciplex, and excimer formation. De Silva *et al.*⁸⁾ have designed an electron donor-spacer-acceptor triad consisting of monoaza-18-crown-6 as a receptor. We have also synthesized new fluoroionophores for guest cations.⁹⁻¹²⁾ In order to design an effective PET fluoroionophore, we proposed the ionophores consisting of some donors and acceptors that interact with each other. The multi-PET system gave weak emission and high CHEF (chelation enhanced fluorescence). Furthermore, as a new approach that takes advantage of the formation of both exciplex and excimer, we have reported the synthesis and fluorescence behavior of diazacrown ether containing two fluorophoric pyrenyl pendants.¹²⁾ In this paper, we report the complexation and fluorescence behavior of

tris[(1-naphthoyloxy)ethyl]amine (**1**).



2. Results and Discussion

The naphthalene-functionalized ionophore (**1**) was prepared by the esterification of triethanolamine with 1-naphthoyl chloride (80% yield). The purity of **1** was ascertained by 1H , ^{13}C NMR spectroscopic data, and elemental analysis.

The fluorescence spectra of **1** (2.00×10^{-5} M), (when excited at 284 nm), gave a broad emission band with a maximum at 432 nm. The formation of an intramolecular exciplex¹³⁻¹⁵⁾ and/or excimer^{16,17)} should be responsible for the appearance of the emission band. The emission-band intensity of **1** was reduced to approximately one-90th of that (at 386 nm) of the standard substance (1-ethoxycarbonylnaphthalene: 6.00×10^{-5} M). The weak emission may indicate that the quenching of the naphthalene chromophore in the excited states by the triethylamine unit proceeds in a mechanism similar to that for classical fluorescent aliphatic amine systems.¹³⁻²⁵⁾

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[†]Dedicated to Professor Yukio Nishimura on the occasion of his retirement.

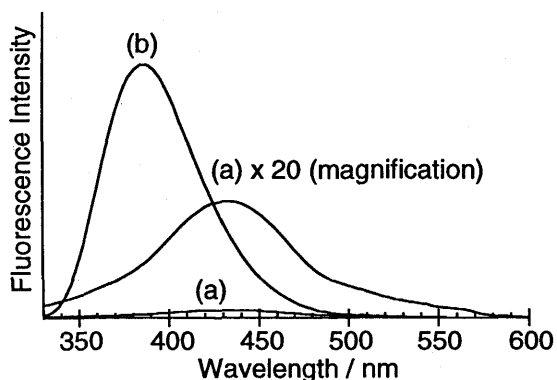


Fig. 1. Fluorescence spectra of (a) **1** (2.00×10^{-5} M) and (b) 1-ethoxycarbonylnaphthalene (6.00×10^{-5} M) in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1 v/v), as excited at 284 nm.

In Figure 2 is illustrated the fluorescence spectral behavior of **1** (2.00×10^{-5} M) in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1 v/v) at room temperature. A dramatic change in the emission intensity of **1** (I_1) was observed upon the addition of various amounts of metal cations (Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Al^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+}). When the metal salts were added (2.5×10^3 molar equivalent), the relative emission intensity (I_{complex}/I_1), being used as a measure of the molecular recognition, changed from 0.04 to 5 depending on the nature of metal cations as shown in Figure 2.

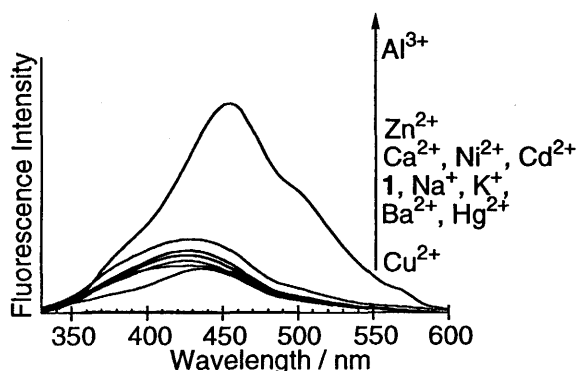


Fig. 2. Fluorescence spectra of **1** (2.00×10^{-5} M) with and without various metal salts (5.00×10^{-2} M) in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1 v/v), as excited at 284 nm.

It is clearly seen from Figure 3 that the emission intensity of **1** is enhanced with an increase in concentration of Al^{3+} and reduced with an increase in concentration of Cu^{2+} . The emission enhancement means that the complexation with Al^{3+} or HCl (generated from AlCl_3 in water) inhibits the PET from the nitrogen atom to the naphthalene ring and promotes

the formation of an intramolecular naphthoyl excimer.

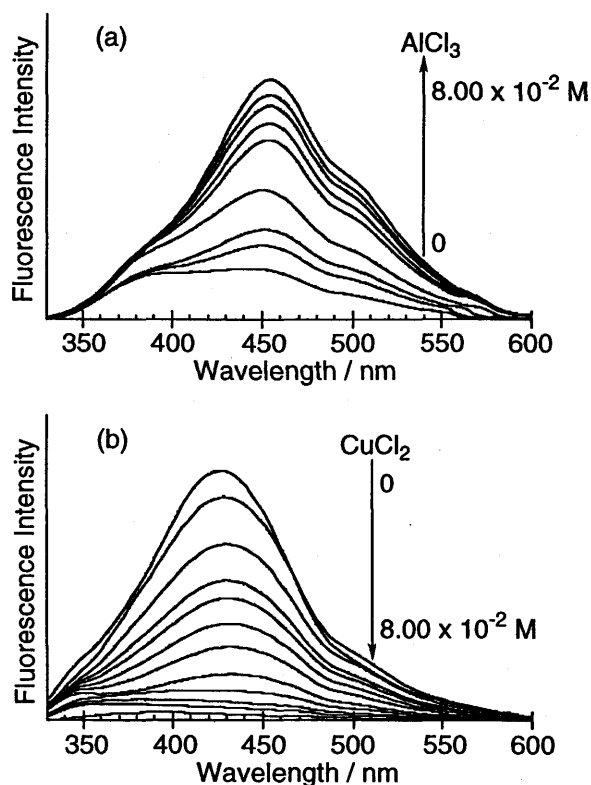


Fig. 3. Fluorescence spectra of **1** (2.00×10^{-5} M) with (a) AlCl_3 (0– 8.00×10^{-2} M) and (b) CuCl_2 (0– 8.00×10^{-2} M) in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1 v/v), as excited at 284 nm.

Figure 4 illustrates the relative emission intensity of **1** versus the metal salt concentration. The intensity ratio (I_{complex}/I_1) depends on liganded metal ions and decreases in the following order: Al^{3+} (5.3) > Zn^{2+} (3.4) > Ni^{2+} (1.6) > Ca^{2+} , Cd^{2+} (1.2) > Na^+ , K^+ , Ba^{2+} , Hg^{2+} (0.9) > Cu^{2+} (0.04).

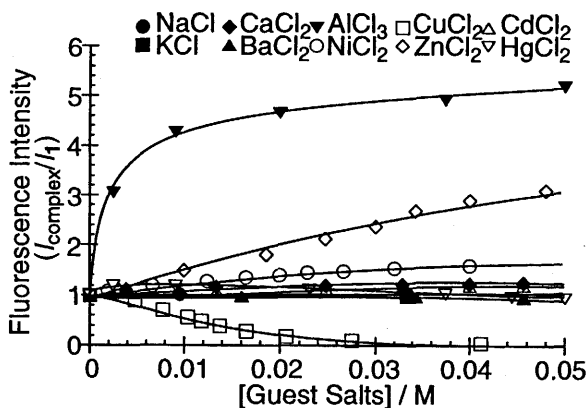


Fig. 4. Dependence of fluorescence intensities of **1** (2.00×10^{-5} M) on the concentration of various metal salts in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1 v/v), as excited at 284 nm.

Instead of the emission quantum yield, a measure of the guest cation-induced fluorescence recovery is the emission intensity ratio ($I_{\text{complex}}/I_{\text{standard substance}}$) of the guest cation complexes for the corresponding standard substance (1-ECN). The guest cation-induced fluorescence recoveries ($I_{1-\text{guest cation complexes}}/I_{1-\text{ECN}}$) of **1** were 0.08 for Na^+ , 0.08 for K^+ , 0.11 for Ca^{2+} , 0.08 for Ba^{2+} , 0.47 for Al^{3+} , 0.14 for Ni^{2+} , 0.004 for Cu^{2+} , 0.30 for Zn^{2+} , 0.11 for Cd^{2+} and 0.08 for Hg^{2+} . The fluorescence intensity of **1**- Al^{3+} complex was approximately half of that of 1-ECN. This means that **1** has a high fluorescence switch-on ability as an Al^{3+} sensing fluoroionophore. Furthermore, the emission intensity of **1** decreases with an increase in concentration of the quenching metal cation (Cu^{2+} and Hg^{2+}).¹⁸⁾

The metal-ion concentration dependence of the emission intensity (Figure 4) allowed us to determine the association constants (K / M^{-1}) by a non-linear curve-fitting method.^{13,14)} The sensor (**1**) showed the following cation selectivity: Na^+ , K^+ , Ba^{2+} , Hg^{2+} (< 1) $<$ Zn^{2+} (5 ± 2) $<$ Cd^{2+} (12 ± 2) $<$ Ca^{2+} (16 ± 2) $<$ Ni^{2+} (45 ± 3) $<$ Cu^{2+} (66 ± 16) $<$ Al^{3+} (204 ± 7). In spite of the small association constant for **1** in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1 v/v), the emission intensity of this host was enhanced in the presence of Al^{3+} , establishing that **1** has a high fluorescence switch-on ability for complexation within a wide concentration range.

To obtain a better understanding of the complexation behavior of **1**, the crystal structure of **1** was elucidated by X-ray analyses. The amine (**1**) adopts a tripod conformation with crystallographic C_3 symmetry as shown in Figure 5.

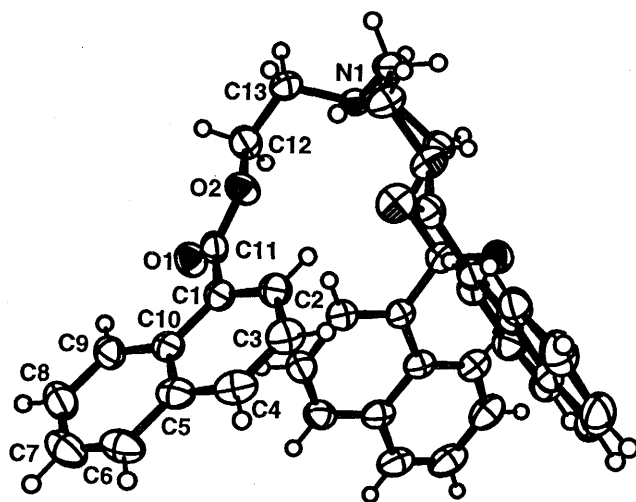


Fig. 5. Molecular structure of **1** showing 50% probability displacement ellipsoids.

The intramolecular distance between the

naphthalene rings is 3.812 Å for C1–C2ⁱ (i: symmetry codes $-x+y$, $-x$, z). The value is close to the range associated with π - π interaction (3.3–3.8 Å).^{25–29)} This means that intramolecular excimer formation can take place in the excited state. In conclusion, the fluoroionophore (**1**) could be utilized as a fluorescent sensing ionophore for Al^{3+} .

3. 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 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 spectrofluorometer. Mass spectra were measured with a JEOL 01SG-2 spectrometer.

3.1. Preparations of Tris[(1-naphthoxy)ethyl]amine (**1**) and 1-ethoxycarbonylnaphthalene (1-ECN). A tetrahydrofuran-triethylamine mixture solution (2+2 cm^3) of triethanolamine (149 mg, 1.0 mmol) and 1-naphthoyl chloride (953 mg, 5.0 mmol) was refluxed for 6 h. Cooling the mixture solution afforded the precipitate. The precipitate was filtered and washed with an water (5 cm^3). Recrystallization from ethyl acetate gave analytically pure sample (489 mg, 80%) with the following physical and spectroscopic properties. colorless crystals, mp 73–74 °C, ^1H NMR (500 MHz, CDCl_3): δ = 3.22 (3H, t, $J=6.2$ Hz), 4.57 (3H, t, $J=6.2$ Hz), 7.30 (3H, dd, $J=8.2$, 7.3 Hz), 7.48 (3H, ddd, $J=8.6$, 7.0, 1.2 Hz), 7.55 (3H, ddd, $J=8.5$, 7.0, 1.2 Hz), 7.80 (3H, d, $J=8.6$ Hz), 7.90 (3H, d, $J=8.2$ Hz), 8.11 (3H, d, $J=7.3$ Hz), and 8.89 (3H, d, $J=8.5$ Hz); ^{13}C NMR (125.7 MHz, CDCl_3) = 53.6 (3C), 63.1 (3C), 124.4 (3C), 125.8 (3C), 126.1 (3C), 126.9 (3C), 127.7 (3C), 128.5 (3C), 130.2 (3C), 131.4 (3C), 133.3 (3C), 133.8 (3C), and 167.4 (3C). IR (KBr): 774, 920, 1012, 1136, 1196, 1242, 1276, 1358, 1442, 1502, 1590, 1700, 2824 and 2952 cm^{-1} . UV (CH_3OH) λ_{max} 210.6 ($\epsilon=10000$), 216.3 (10000), 233.4 (5800, sh), 296.6 (1700), and 323.8 (700, sh) nm. FAB-MS (M+H) 612. Anal. Calcd for $\text{C}_{39}\text{H}_{33}\text{N}_1\text{O}_6$: C, 76.58; H, 5.44; N, 2.29. Found: C, 76.47; H, 5.45; N, 2.33.

1-ECN²⁴⁾ was prepared by esterification of ethanol with 1-naphthoyl chloride.

3.2. Fluorescence Measurement of **1** and Its Complexes.

Fluorescence intensities of **1** (2.00×10^{-5} M, $1 \text{ M} = 1 \text{ mol l}^{-1}$) and 1-ECN (6.00×10^{-5} M) excited at 284 nm, measured in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1 v/v) under nitrogen at room temperature, as shown in Figure 1.

The titrations were conducted by adding a solution (2.0 cm^3) containing metal salts ($0-2.00 \times 10^{-1}$ M NaCl, KCl, CaCl_2 , BaCl_2 , AlCl_3 , NiCl_2 , CuCl_2 , ZnCl_2 , CdCl_2 , and HgCl_2 in H_2O , $1 \text{ M} = 1 \text{ mol dm}^{-3}$), to a cuvette containing 2.0 cm^3 of the fluoroionophore solution (4.00×10^{-5} M for **1** in methanol). The solutions were homogenized by ultrasonication for 10 min. A spectrum was recorded after each addition. The equivalents of the cation added were then plotted against the emission-intensity change at 399-455 nm (excited at 284 nm). The association constants (K) were determined by a curve-fitting method as described in previous studies.^{25,26)}

3.3. X-Ray crystallographic analysis of **1**.

A colorless crystal of $\text{C}_{39}\text{H}_{33}\text{N}_1\text{O}_6$ having approximate dimensions of $0.60 \times 0.50 \times 0.50 \text{ mm}$ was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) on a Rigaku RAXIS-RAPID equipped with an imaging plate. Data collection and cell refinement: MSC/AFC diffractometer control. Data reduction: *teXsan for windows version 1.06*.²⁷⁾ Structure solution: *SIR92*.²⁸⁾ Refinement: *SHELXL97*.²⁹⁾

Crystal data for **1**: $\text{C}_{39}\text{H}_{33}\text{NO}_6$, $M = 611.67$, Trigonal, $a = 14.3418 (5) \text{ \AA}$, $b = 14.3418 (5) \text{ \AA}$, $c = 8.6968 (2) \text{ \AA}$, $V = 1549.16 (7) \text{ \AA}^3$, $T = 296 \text{ K}$, space group $P31c$, $Z = 2$, $D_x = 1.311 \text{ Mgm}^{-3}$. The final $wR(F^2)$ was 0.0966 (all data).

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