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# Complexation and Fluorescence Behavior of Tris[(1-naphthoyloxy)ethyl]amine<sup>†</sup>

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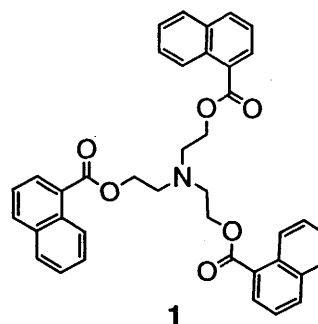
Tris[(1-naphthoyloxy)ethyl]amine (**1**) was found to display unique photophysical properties in the presence of the guest cations. The amine (**1**) revealed a broad emission band around 440 nm that is typical of a structureless emission of a naphthoyl excimer and a naphthalene-amine exciplex. From the result of X-ray analysis, the amine (**1**) adopt a tripod conformation with crystallographic *C*<sub>3</sub> symmetry. Complexation of **1** with Al<sup>3+</sup> increased the emission intensity of a factor by 5.3 in H<sub>2</sub>O-CH<sub>3</sub>OH (1:1 v/v).

## 1. Introduction

During the last decades, macrocyclic and acyclic ligands have been designed to coordinate metal ions.<sup>1,2)</sup> Polypod organic molecules containing donor atoms may be considered as non-cyclic cryptands<sup>3-5)</sup> 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.<sup>5)</sup>

Recently, a number of fluoroionophores have been designed as legards for metal ions.<sup>6-12)</sup> Some of them showed a photoinduced electron transfer (PET), exciplex, and excimer formation. De Silva *et al.*<sup>8)</sup> 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.<sup>9-12)</sup> 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.<sup>12)</sup> 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 <sup>1</sup>H, <sup>13</sup>C NMR spectroscopic data, and elemental analysis.

The fluorescence spectra of **1** (2.00 × 10<sup>-5</sup> M), (when excited at 284 nm), gave a broad emission band with a maximum at 432 nm. The formation of an intramolecular exciplex<sup>13-15)</sup> and/or excimer<sup>16,17)</sup> 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<sup>-5</sup> 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.<sup>13-25)</sup>

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<sup>†</sup>Dedicated to Professor Yukio Nishimura on the occasion of his retirement.

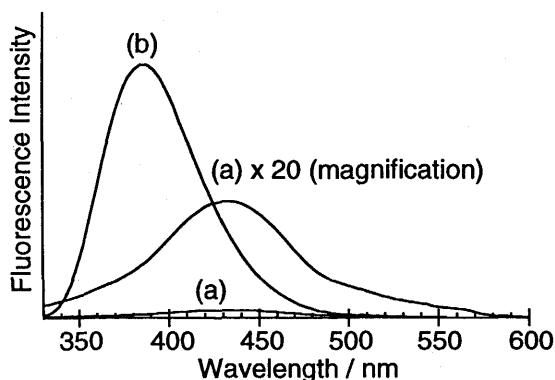


Fig. 1. Fluorescence spectra of (a) **1** ( $2.00 \times 10^{-5}$  M) and (b) 1-ethoxycarbonylnaphthalene ( $6.00 \times 10^{-5}$  M) in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  (1:1 v/v), as excited at 284 nm.

In Figure 2 is illustrated the fluorescence spectral behavior of **1** ( $2.00 \times 10^{-5}$  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 ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ). When the metal salts were added ( $2.5 \times 10^3$  molar equivalent), the relative emission intensity ( $I_{\text{complex}}/I_1$ ), 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.

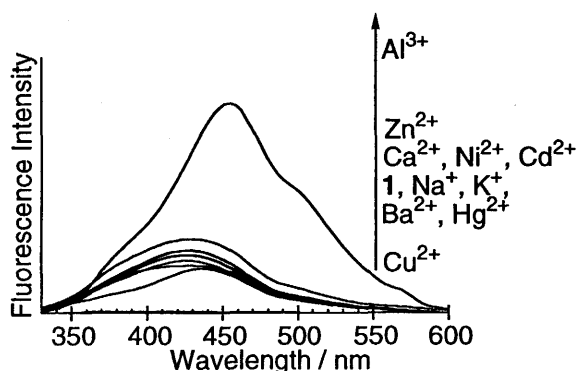


Fig. 2. Fluorescence spectra of **1** ( $2.00 \times 10^{-5}$  M) with and without various metal salts ( $5.00 \times 10^{-2}$  M) in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  (1:1 v/v), as excited at 284 nm.

It is clearly seen from Figure 3 that the emission intensity of **1** is enhanced with an increase in concentration of  $\text{Al}^{3+}$  and reduced with an increase in concentration of  $\text{Cu}^{2+}$ . The emission enhancement means that the complexation with  $\text{Al}^{3+}$  or  $\text{HCl}$  (generated from  $\text{AlCl}_3$  in water) inhibits the PET from the nitrogen atom to the naphthalene ring and promotes

the formation of an intramolecular naphthoyl excimer.

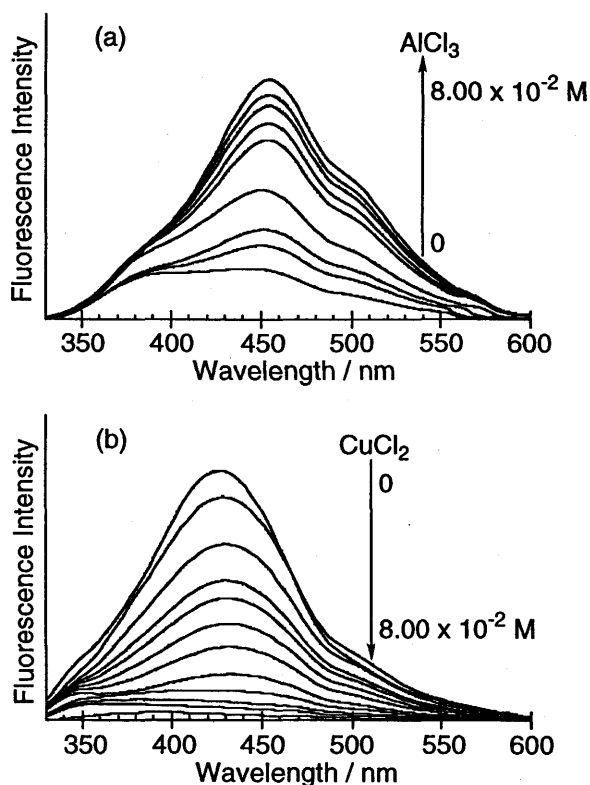


Fig. 3. Fluorescence spectra of **1** ( $2.00 \times 10^{-5}$  M) with (a)  $\text{AlCl}_3$  (0– $8.00 \times 10^{-2}$  M) and (b)  $\text{CuCl}_2$  (0– $8.00 \times 10^{-2}$  M) in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  (1:1 v/v), as excited at 284 nm.

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

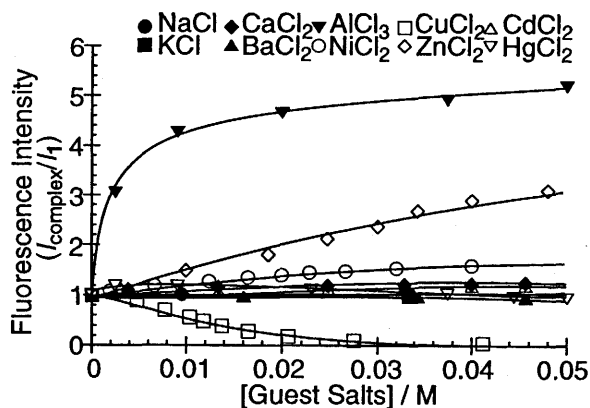


Fig. 4. Dependence of fluorescence intensities of **1** ( $2.00 \times 10^{-5}$  M) on the concentration of various metal salts in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  (1:1 v/v), as excited at 284 nm.

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  $\text{Na}^+$ , 0.08 for  $\text{K}^+$ , 0.11 for  $\text{Ca}^{2+}$ , 0.08 for  $\text{Ba}^{2+}$ , 0.47 for  $\text{Al}^{3+}$ , 0.14 for  $\text{Ni}^{2+}$ , 0.004 for  $\text{Cu}^{2+}$ , 0.30 for  $\text{Zn}^{2+}$ , 0.11 for  $\text{Cd}^{2+}$  and 0.08 for  $\text{Hg}^{2+}$ . The fluorescence intensity of **1**- $\text{Al}^{3+}$  complex was approximately half of that of 1-ECN. This means that **1** has a high fluorescence switch-on ability as an  $\text{Al}^{3+}$  sensing fluoroionophore. Furthermore, the emission intensity of **1** decreases with an increase in concentration of the quenching metal cation ( $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ ).<sup>18)</sup>

The metal-ion concentration dependence of the emission intensity (Figure 4) allowed us to determine the association constants ( $K / \text{M}^{-1}$ ) by a non-linear curve-fitting method.<sup>13,14)</sup> The sensor (**1**) showed the following cation selectivity:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Hg}^{2+}$  ( $< 1$ )  $<$   $\text{Zn}^{2+}$  ( $5 \pm 2$ )  $<$   $\text{Cd}^{2+}$  ( $12 \pm 2$ )  $<$   $\text{Ca}^{2+}$  ( $16 \pm 2$ )  $<$   $\text{Ni}^{2+}$  ( $45 \pm 3$ )  $<$   $\text{Cu}^{2+}$  ( $66 \pm 16$ )  $<$   $\text{Al}^{3+}$  ( $204 \pm 7$ ). 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  $\text{Al}^{3+}$ , 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.

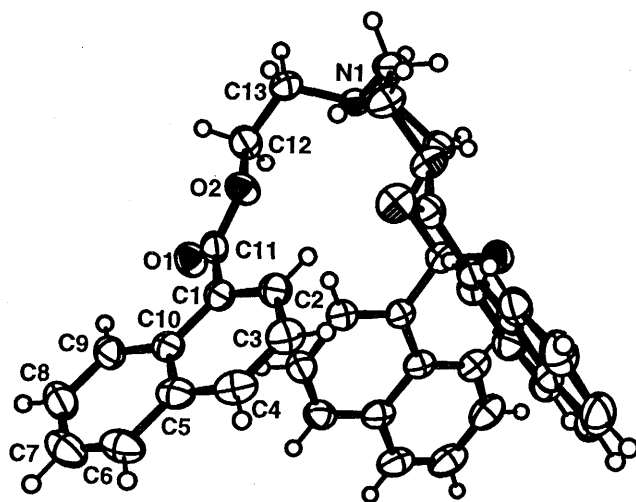


Fig. 5. Molecular structure of **1** showing 50% probability displacement ellipsoids.

The intramolecular distance between the

naphthalene rings is 3.812 Å for C1–C2<sup>i</sup> (i: symmetry codes -x+y, -x, z). The value is close to the range associated with  $\pi$ - $\pi$  interaction (3.3–3.8 Å).<sup>25–29)</sup> 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  $\text{Al}^{3+}$ .

### 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  $\text{CDCl}_3$ ; 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 spectrofluorometer. Mass spectra were measured with a JEOL 01SG-2 spectrometer.

**3.1. Preparations of Tris[(1-naphthoyloxy)ethyl]amine (**1**) and 1-ethoxycarbonylnaphthalene (1-ECN).** A tetrahydrofuran-triethylamine mixture solution (2+2  $\text{cm}^3$ ) 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  $\text{cm}^3$ ). Recrystallization from ethyl acetate gave analytically pure sample (489 mg, 80%) with the following physical and spectroscopic properties. colorless crystals, mp 73–74 °C,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ ) = 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  $\text{cm}^{-1}$ . UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  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-ECN<sup>24)</sup> was prepared by esterification of ethanol with 1-naphthoyl chloride.

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

Fluorescence intensities of **1** ( $2.00 \times 10^{-5}$  M,  $1 \text{ M} = 1 \text{ mol l}^{-1}$ ) and 1-ECN ( $6.00 \times 10^{-5}$  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 ( $2.0 \text{ cm}^3$ ) containing metal salts ( $0-2.00 \times 10^{-1}$  M NaCl, KCl,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ , and  $\text{HgCl}_2$  in  $\text{H}_2\text{O}$ ,  $1 \text{ M} = 1 \text{ mol dm}^{-3}$ ), to a cuvette containing  $2.0 \text{ cm}^3$  of the fluoroionophore solution ( $4.00 \times 10^{-5}$  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.<sup>25,26)</sup>

### 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*.<sup>27)</sup> Structure solution: *SIR92*.<sup>28)</sup> Refinement: *SHELXL97*.<sup>29)</sup>

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  $P31c$ ,  $Z = 2$ ,  $D_x = 1.311 \text{ Mg m}^{-3}$ . The final  $wR(F^2)$  was 0.0966 (all data).

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