SYNTHESIS AND PROPERTIES OF *N,N',N''*-TRIS(1-NAPHTHYLMETHYL)-1,5,9-TRIAZACYCLODODECANE

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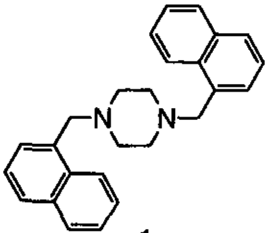
Abstract — *N,N'*-Bis(1-naphthylmethyl)piperazine and *N,N',N''*-tris(1-naphthylmethyl)-1,5,9-triazacyclododecane were found to display unique photophysical properties for the guest salts. These guest salts enhanced the host emission remarkably by the inhibition of intramolecular exciplex formation and then quenched the emission by photoinduced electron transfer from the counter anion to the naphthalene chromophore in the presence of high concentrations of the salts.

Photoresponsive ammonium ion recognition systems are of great importance particularity for their potential application to nanoscale devices for sensor and switch.[1] For example, Lehn *et al.* reported that C_3 symmetry crowns bearing ester groups form very stable complexes with primary ammonium ions.[1] Shinkai *et al.* also showed that pyrene functionalized homotrioxacalix[3]arenes selectively recognize primary ammonium ions by an intramolecular excimer fluorescence change.[2]

Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor.[3] The addition of metal salts enhanced the fluorescence emission intensity of *N*-(1-pyrenylmethy)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane, while the prescence of metal salts exerted a strong effect on the ratio of the monomer vs. excimer emission intensity of *N,N'*-bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane.[4]

As an extention of our new approach that takes advantage of intramolecular exciplex and/or excimer formation, we designed and prepared the polyazamacrocycles containing naphthylmethyl groups, hoping to develop selective ammonium ions recognition and fluorescent sensor.

The naphthalene functionalized polyazamacrocycle derivatives (**1**)[5] and (**2**) were prepared by *N*-alkylation of macrocyclic polyamines with 1-naphthylmethyl chloride in tetrahydrofuran-triethylamine (95% yield). The structure and purity of **1** and **2** were ascertained by ^{1}H NMR spectroscopy and elemental analysis.[6]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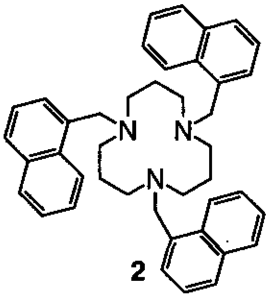
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The fluoroionophore (**2**), (2.0×10^{-5} M, 1.0 M=1.0 mol dm^{-3}, when excited at 280 nm), gave a broad emission band with a maximum at 471 nm in addition to the monomer emission (334 nm) in methanol-chloroform (9:1 v/v). The formation of intramolecular exciplex should be responsible for the former emission band. The latter emission-band intensity of **1** and **2** was reduced to approximately one-70th and 50th that of 1-methylnaphthalene (4.0×10^{-5} M for **1**, 6.0×10^{-5} M for **2**) respectively, accompaning the appearance of the exciplex fluorescence. This finding indicates that the emission quenching of the naphthalene chromophore by the azacrown unit proceeds in a mechanism similar to that for the classical naphthalene-alkylamine system.[7]

Complexation behaviors of **1** and **2** with various metal salts were analyzed by fluorescence spectroscopy. A dramatic change in the emission intensity of **1** (I_1) and **2** (I_2) was observed upon the addition of sodium, potassium and ammonium salts. When ammonium salt was added in the range of 0 to 2.0×10^{-3} M, emission intensitiy at 333 nm enhanced (Figure 1). Further addition of ammonium salt caused the emission quenching. The dependence of emission intensity at 333 nm upon the salt concentration clearly showed the inflection point around [NH_4SCN] = 2.0×10^{-3} M (Figure 2). This suggests that the observed competitive quenching is due to thiocyanate ion. A similar quenching by the thiocyanate anion was explained based on the photoinduced electron transfer from this anion to the naphthalene chromophore.[8]

It is interesting that the order of $I_{complex}/I_{free}$ for **1** and **2**, (which was being used as a measure of the molecular recognition sensing), is $NH_4^+ > Na^+ > K^+$. The ammonium sensor **1** gave a higher swich-on ability than **2**.

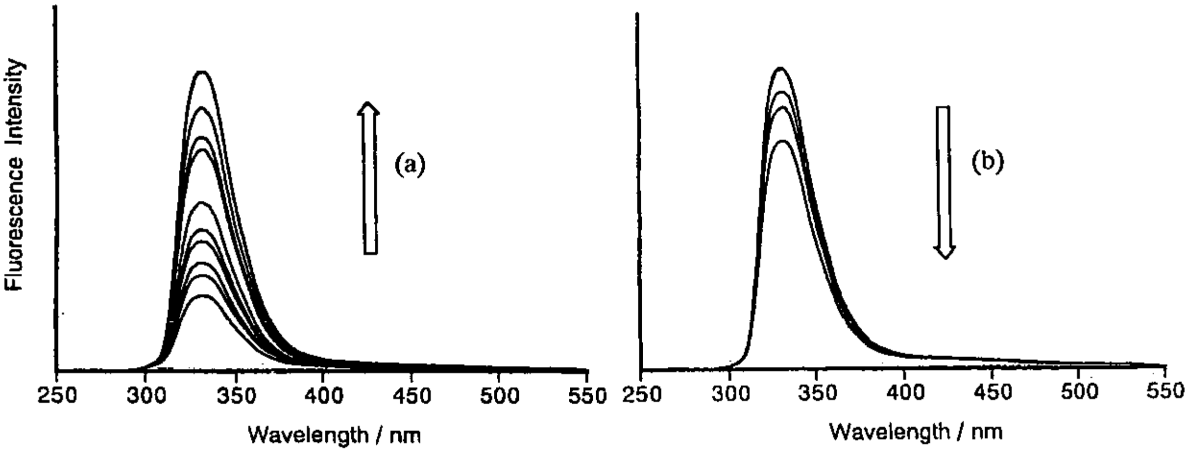

Figure 1. Fluorescence spectra of **1** (2.0×10^{-5} M) with NH_4SCN (a) 0–2.0×10^{-3} M and (b) 2.0×10^{-3}–2.0×10^{-2} M in CH_3OH-$CHCl_3$ (9:1 v/v), as excited at 282 nm.

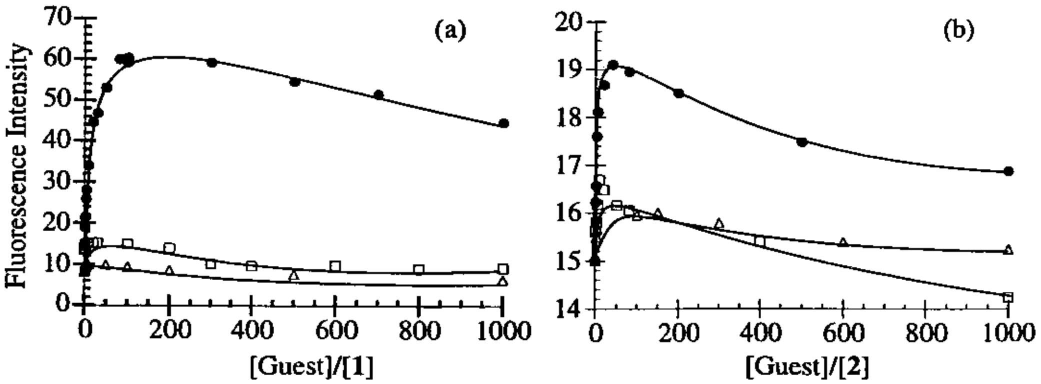

Figure 2. Dependence of fluorescence intensities at 333 nm of (a) **1** and (b) **2** on the concentration of (□) NaSCN, (△) KSCN and (●) NH_4SCN.

Using changes in the emission intensity as well as in the metal salt concentration, the association constants (K_1 and K_2)[9] were determined by the curve-fitting method[10] (Table 1).

The fluoroionophore (**2**) exhibits NH_4^+ selectivity. The fluorescence titration of **1** with different metal salts in chloroform-methanol confirms that **1** has a high fluorescence swich-on ability for the complexation with ammonium salt despite the low association constant of this system.

Table 1. Association constants (K_1, K_2 / M^{-1})for NaSCN, KSCN and NH_4SCN complexes of **1** and **2** in CH_3OH-$CHCl_3$ (9:1 v/v)

	1		**2**	
	K_1	K_2	K_1	K_2
NaSCN	4770	282	4840	361
KSCN	18600	187	3460	45
NH_4SCN	2410	27	14200	104

In conclusion, the macrocycles examined in this study have the following properties: This might be due to 1) Ammonium ion recognition by fluorescence quenching *via* intramoleculer electron transfer between naphthyl group and donor atom in macrocycles; 2) Selective recognition of ammonium ion by polyazamacrocycles with C_3 symmetry. In addition, introduction of three fluorophores into polyazamacrocycles have been demostrated to allow us to develope new fluorescence sensing sensor for ammonium ion.

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6. **1**: colorless crystals, mp 162.0–163.0 °C, ^{1}H NMR (500 MHz in $CDCl_3$) δ=2.52 (8H, br s), 3.89 (4H, s), 7.38 (2H, ddd, *J*=7.9, 7.0, 1.4 Hz), 7.42 (2H, d, *J*=7.0 Hz), 7.46 (2H, ddd, *J*=7.9, 6.7, 1.4 Hz), 7.50 (2H, ddd, *J*=8.2, 6.7, 1.4 Hz), 7.75 (2H, d, *J*=7.9 Hz), 7.83 (2H, d, *J*=7.9 Hz), 8.30 (2H, d, *J*=8.2 Hz); ^{13}C NMR($CDCl_3$) δ=53.5 (4C), 61.0 (2C), 124.8 (2C), 125.1 (2C), 125.5 (2C), 125.7 (2C), 127.3 (2C), 127.8 (2C), 128.3 (2C), 132.6 (2C), 133.8 (2C), 134.3 (2C). Anal. Calcd for $C_{26}H_{26}N_2$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.02; H, 7.36; N, 7.41.

   2: colorless crystals, mp 119.0–121.0 °C, ^{1}H NMR (500 MHz in $CDCl_3$) δ=1.73 (6H, t, J=6.1 Hz), 2.51 (12H, t, *J*=6.1 Hz), 3.85 (6H, s), 7.34 (3H, dd, *J*=7.9, 7.0 Hz), 7.39(3H, d, *J*=7.0 Hz), 7.46 (3H, ddd, *J*=7.9, 7.0, 1.0 Hz), 7.48 (3H, ddd, *J*=7.9, 7.0, 1.0 Hz), 7.71(3H, d, *J*=7.9 Hz), 7.82 (3H, d, *J*=7.9Hz), 8.22 (3H, d, *J*=7.9Hz); ^{13}C NMR($CDCl_3$) δ=21.7 (3C), 50.0 (6C), 57.7 (3C), 124.5 (3C), 125.2 (3C), 125.4 (3C), 125.5 (3C), 127.2 (3C), 127.5 (3C), 128.4 (3C), 132.4 (3C), 133.8 (3C), 135.4 (3C). Anal. Calcd for $C_{42}H_{45}N_3$: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.93; H, 7.98; N, 6.94.

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