Complexation and Fluorescence Behavior of Diaza-15-crown-5 Carrying Two Naphthyl Pendants

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Complexation and Fluorescence Behavior of Diaza-15-crown-5 Carrying Two Naphthyl Pendants[†]

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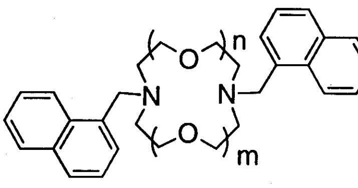
N,N'-Bis(1-naphthylmethyl)-4,10-diaza-15-crown-5 (**1b**) was found to display unique photophysical properties in the presence of the guest metal salts. The diaza-15-crown-5 (**1b**) exhibited high Zn^{2+} enhancement selectivity and in the presence of this cation the host fluorescence intensity was increased by a factor of 8.3.

1. Introduction

The development of photoinduced electron transfer (PET) systems for guest cations has gained much attention for their potential application to nanoscale devices for cation sensor and switch.[1] There are extensive investigations toward the characterization of PET fluoroionophores including crown ether derivatives with naphthalene, umbelliferone, anthracene, or pyrene fluorophore.[2,3]

Recently, it was found that the diazacrown ether derivatives having two naphthylmethyl groups act as effective PET fluoroionophores.[4] The addition of guest salts enhanced the fluorescence emission intensity of the diazacrown ethers (**1a**, **c**).[5,6] Thus, it is interesting to investigate the complex formation of various PET fluoroionophores with guest salts using fluorescence spectroscopy. As an approach to the manipulation of PET fluoroionophore, we now report the complexation and fluorescence behavior of the diazacrown ethers (**1a**–**c**) containing two naphthyl pendants.



1a (n=1, m=1)
1b (n=1, m=2)
1c (n=2, m=2)

2. Results and Discussion

The naphthalene-functionalized azacrown ether (**1b**)[7] was prepared by *N*-alkylation of 1,7-diaza-15-crown-5 with 1-chloromethylnaphthalene in toluene-THF-triethylamine (90% yield).

Figure 1 illustrates the fluorescence spectral behavior of **1a**–**c** (2.00 x 10^{-5} M) in methanol at room temperature. The diazacrown (**1b**), when excited at 280 nm, gave a broad emission band with a maximum at 476 nm in addition to the emission band at 335 nm. The formation of intramolecular exciplex should be responsible for the appearance of the former emission band. The emission-band intensity at 335 nm of **1b** was reduced to approximately one-331th that of 1-methylnaphthalene (1-MN, 4.00 x 10^{-5} M), which was accompanied by the exciplex fluorescence. This indicates that the quenching of the excited naphthalene chromophore by the amino unit proceeds in a mechanism similar to that for the classical naphthalene-aliphatic amine system.[8]

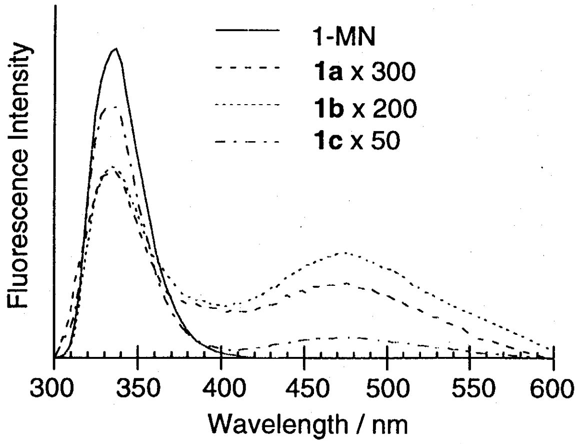


Fig. 1 Fluorescence spectra of 1-methylnaphthalene (4.00 x 10^{-5} M) and **1a**–**c** (2.00 x 10^{-5} M) in methanol, as excited at 280 nm.

The formation of the intramolecular exciplex is very likely to be responsible for the observed emission

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quenching. The order of the quenching efficiency ($I/I_{1\text{-}MN}$) is **1a** (1.7 x 10^{-2})[6] > **1b** (3.0 x 10^{-3}) > **1c** (2.3 x 10^{-3})[5]. This means steric hinderence 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 **1b** (I_{1b}) was observed upon the addition of various amounts of guest cations (Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+}). When the guest cations were added (500 molar equivalent), the relative emission intensity ratio ($I_{complex}/I_{1b}$), being used as a measure of the molecular recognition sensing, changed from 8.3 to 0.5 depending on the nature of metal cations as shown in Figure 2.

Figure 3 illustrates the relative emission intensity of **1b** against the guest salt concentration. It is clearly seen from Figure 3 that the emission intensity increased along with an increase in the concentration of the guest cations, except for Rb^+. The observed enhancement indicates the inhibition of exciplex formation by complexation with a metal salt. Furthermore, it is noteworthy that the **1b**-rubidium thiocyanate complex exhibited a decrease in its monomer emission intensity relative to that of **1b**,

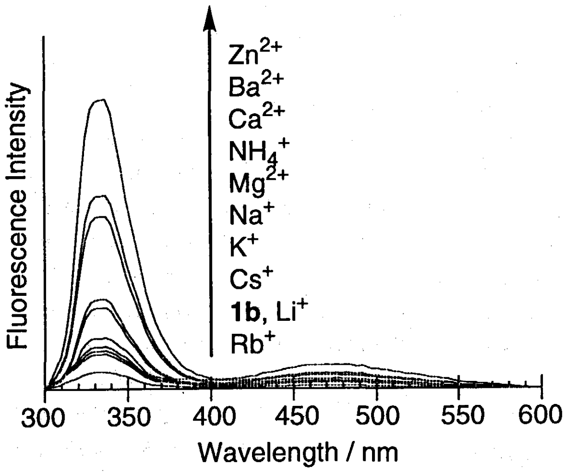

Fig. 2 Fluorescence spectral changes of **1b** (2.00 x 10^{-5} M) with and without various guest salts (1.00 x 10^{-2} M) in methanol, as excited at 280 nm.

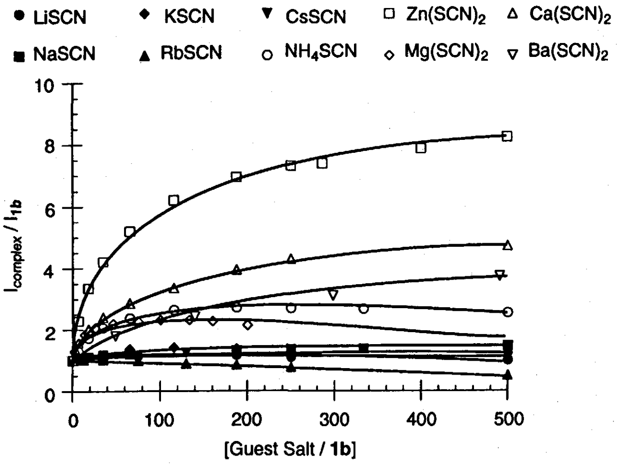

Fig. 3 Dependence of fluorescence intensities of **1b** (2.00 x 10^{-5} M) at 335 nm on the concentration of various guest salts in methanol.

Table 1. Fluorescence intensity ratio ($I_{complex}/I_1$ and $I_{complex}/I_{1\text{-}MN}$) of guest cation complexes of **1** for 1-methylnaphthalene (1-MN)

	$I_{1a}/I_{1\text{-}MN}$	$I_{complex}/I_{1a}$	$I_{1b}/I_{1\text{-}MN}$	$I_{complex}/I_{1b}$	$I_{1c}/I_{1\text{-}MN}$	$I_{complex}/I_{1c}$
Free	1.7 x 10^{-2}	-	3.0 x 10^{-3}	-	2.3 x 10^{-3}	-
LiSCN	1.9 x 10^{-2}	1.1	3.0 x 10^{-3}	1.0	2.7 x 10^{-3}	1.2
NaSCN	2.0 x 10^{-2}	1.2	4.5 x 10^{-3}	1.5	5.0 x 10^{-3}	2.2
KSCN	2.0 x 10^{-2}	1.2	3.6 x 10^{-3}	1.2	6.4 x 10^{-3}	2.8
RbSCN	1.7 x 10^{-2}	1.0	1.5 x 10^{-3}	0.5	3.4 x 10^{-3}	1.5
CsSCN	2.0 x 10^{-2}	1.2	3.3 x 10^{-3}	1.1	2.7 x 10^{-3}	1.2
NH_4SCN	2.9 x 10^{-2}	1.7	7.5 x 10^{-2}	2.5	1.1 x 10^{-2}	4.9
$Zn(SCN)_2$	0.73	43	2.5 x 10^{-2}	8.3	1.2 x 10^{-2}	5.4
$Mg(SCN)_2$	2.7 x 10^{-3}	1.6	7.0 x 10^{-3}	2.3	8.0 x 10^{-3}	3.5
$Ca(SCN)_2$	2.7 x 10^{-2}	1.6	1.5 x 10^{-2}	4.9	3.4 x 10^{-2}	15
$Ba(SCN)_2$	2.2 x 10^{-2}	1.3	1.7 x 10^{-2}	5.5	9.3 x 10^{-2}	41

Table 2. Association constants (K / M^{-1}) of **1a**–**1c** for guest salts in methanol

	1a	**1b**	**1c**
LiSCN	27 ± 5	-	13100 ± 3300
NaSCN	123 ± 9	246 ± 37	9390 ± 610
KSCN	1850 ± 320	-	9320 ± 1600
RbSCN	305 ± 26	-	5120 ± 2210
CsSCN	97 ± 30	-	4940 ± 960
NH_4SCN	1490 ± 165	2210 ± 420	4670 ± 180
$Zn(SCN)_2$	126 ± 13	597 ± 56	190000 ± 10000
$Mg(SCN)_2$	3240 ± 200	4620 ± 460	10200 ± 400
$Ca(SCN)_2$	61 ± 4	794 ± 54	21300 ± 1100
$Ba(SCN)_2$	710 ± 114	106 ± 5	11100 ± 3900

itself. This suggests that the observed quenching is due to the presence of thiocyanate ion. A similar quenching by the thiocyanate anion was explained based on the photoinduced electron transfer from this anion to the naphthalene chromophore.$^{9)}$

Interestingly, the intensity ratio ($I_{complex}/I_{1b}$) was different among bound metal ions and decreased in the following order: Zn^{2+} (8.3) > Ba^{2+} (5.5) > Ca^{2+} (4.9) > NH_4^+ (2.5) > Mg^{2+} (2.3) > Na^+ (1.5) > K^+ (1.2) > Cs^+ (1.1) > Li^+ (1.0) > Rb^+ (0.5). The order of $I_{complex}/I_{1b}$ differs from that of $I_{complex}/I_{1a}$$^{6)}$ and $I_{complex}/I_{1c}$$^{5)}$ (Table 1). Zinc ion binding can then cause high fluorescence recovery. This recovery is due to coordination from the nitrogen atoms of the diazacrown to the zinc ion. The strength of this binding interaction modulates the PET from the amine to naphthalene. However, the recovery of the diaza-15-crown-5 (**1b**) is lower than that of the diaza-12-crown-4 (**1a**)$^{6)}$.

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$^{10)}$ (Table 2). The diazacrown (**1b**) showed the following cation selectivity: Ba^{2+} < Na^+ < Zn^{2+} < Ca^{2+} < NH_4^+ < Mg^{2+}. This selectivity order is distinct from that for **1a** and **1c**$^{5,6)}$. The association constants of **1a–c** for various metal ions are depending upon the nature of ionophore properties.

In conclusion, the guest cation-induced emision-intensity enhancement and association constants of **1a–c** originates from the nature of ionophore properties and the affinity of the nitrogen atom in the diazacrown ether for cations. The diazacrown ether having two 1-naphthyl pendants may be utilized as a model of PET fluorescent cation sensor.

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7. **1b**; pale yellow oils, ^{1}H-NMR: δ=2.82 (4H, t, J=5.2 Hz), 2.89 (4H, t, J=6.1 Hz), 3.54 (4H, s), 3.55 (4H, t, J=5.2 Hz), 3.59 (4H, t, J=6.1 Hz), 4.05 (4H, s), 7.37 (2H, dd, J=7.3, 8.2 Hz), 7.45 (4H, ddd, J=1.8, 6.7, 7.3 Hz), 7.48 (2H, d, J=6.7 Hz), 7.73 (2H, d, J=8.2 Hz), 7.81 (2H, dd, J=1.8, 7.3 Hz), and 8.34 (2H, d, J=7.3 Hz); ^{13}C-NMR: δ=54.45 (2C), 54.80 (2C), 59.12 (2C), 69.38 (2C), 70.49 (2C), 70.62 (2C), 124.82 (2C), 125.18 (2C), 125.49 (2C), 125.61 (2C), 127.14 (2C), 127.74 (2C), 128.30 (2C), 132.47 (2C), 133.81 (2C), and 135.29 (2C); IR: ν (NaCl) 770, 1116, 1258, 1292, 1352, 1444, 1594, and 2852 cm^{-1} HR-MS (FAB): *m/z* 499.2961. Calcd for $C_{32}H_{39}N_2O_3$: 499.2960.
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