Fluorescence Spectrophotometric Determination of Ca^{2+} and Ba^{2+} Based on 1, *n*-Bis(1-naphthylcarboxy)oxaalkanes

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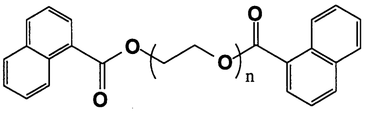
1,*n* -Bis(1-naphthylcarboxy)oxaalkanes (**1NPnN**, n = 1, 2, 3, 4, 5, 6) as fluorescent sensors by excimer emission for metal ions were synthesized, and the complexation of **1NPnN** with alkali and alkaline earth metal ions in acetonitrile was investigated. Alkaline earth metal cations suppress or enhance the fluorescence remarkably, depending on the cation size and the length of polyether chain.

Many kinds of crown ether type macrocyclic compounds have been used for analytical application such as chemical sensor,[1] and spectrophotometries.[2] In the application for fluorimetry, fluorescent reagents, which have two aromatic hydrocarbons at both terminals of linear polyether as an analogue of a crown ether, also have been used.[3] However, there are few studies of the relation between the length of polyether chain and metal ion recognition, and fluorescent aromatic hydrocarbons in these compounds are usually pyrene and anthracene.[4] The disadvantage of pyrene and anthracene is its ability to form an intermolecular excimer even at very low concentration of the solutions (10^{-5}M, 1M = 1mol dm^{-3}) for spectroscopic studies. It is difficult to distinguish inter- or intramolecular excimer in low concentrations. On the other side, in naphtharene, intermolecular interaction is found more than 10^{-1}M. Therefore, we synthesized 1,*n* -Bis(1-naphthylcarboxy)oxaalkanes (**1NPnN**, n = 1, 2, 3, 4, 5, 6). We wish to report here preliminary results of our study on the relation between the length of polyether chain and metal ion recognition of **1NPnN**.



1NPnN (n = 1,2,3,4,5,6)

1NPnN (n = 1,2,3,4,5,6) were prepared from the corresponding polyethyleneglycols and 1-naphthoic acid in the presence of N,N-dicyclohexyl carbodiimide and 4-dimethylamino pyridine in dichloromethane. The products were separated through a silica gel column and purified by repeated flush column chromatography on silica gel.[5] Measurements of fluorescence spectra were carried out in acetonitrile solution of the **1NPnN** (1.0 x 10^{-5}M) at room temperature, and alkali or alkaline earth metal salts ($LiClO_4$, $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$ and $Ca(SCN)_2$) were added to the solution. To prevent a non-linearity of the fluorescence intensity, isosbestic points (295 nm) of absorption spectra of **1NPnN** were chosen as excitation wavelength, respectively.

When lithium, sodium, potassium, and magnesium salts were added in acetonitrile solution of **1NPnN** (n = 1 - 6), shape and intensity of fluorescence spectra was not changed, and when calcium and barium salts were added, changes of fluorescence spectra of **1NPnN** (n = 1 - 3) were not observed, too. However, the spectra of **1NPnN** (n = 4,5,6) changed by addition of calcium and barium salts. These results suggest that the complexation abilities of these reagents to Ca^{2+} and Ba^{2+} are large. ^1H NMR spectra in acetonitrile-*d* 3 gave information to structures of the complexes.[6] When **1NPnN** (n = 4,5,6) complexed with Ca^{2+} and Ba^{2+}, all peaks of the polyether chain protons shifted to lower magnetic field. Etherial proton shifts to downfield, since the electron density of the oxygen atoms is reduced by the coordinated cation. H-4 proton of naphthalene ring shifted to lower magnetic field, too. Its downfield shift of the aromatic proton should be attributed to the ring current effect of the each aromatic unit.

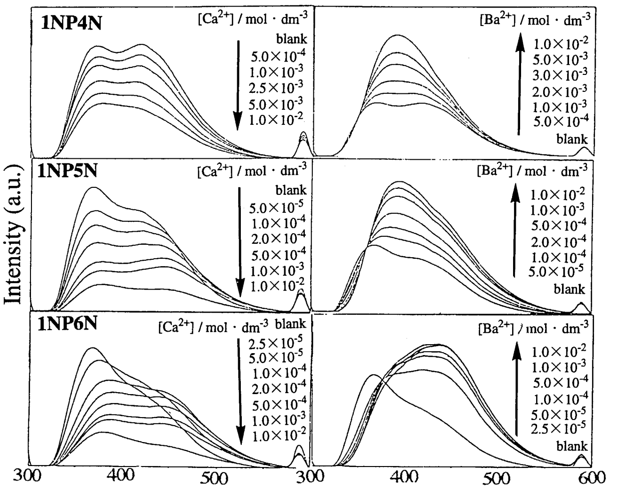


Figure 1. Fluorescence spectra of **1NPnN** (n = 4,5,6) and its Ca^{2+} and Ba^{2+} complexes, as excited at 295 nm. [**1NPnN** (n = 4,5,6)] = 1×10^{-5} mol · dm^{-3} in MeCN at 25 ℃.

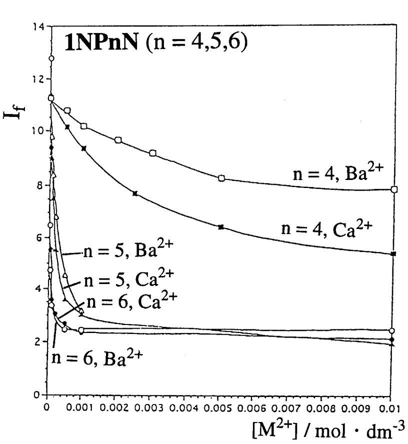


Figure 2. Dependence of fluorescence intensities at 368 nm on the concentration of Ca^{2+} and Ba^{2+}. Conditions were the same as Figure 1.

To study the complexation behavior of **1NPnN** (n = 4,5,6) with Ca^{2+} and Ba^{2+} ions, the measurements of the fluorescence were carried out in detail. The fluorescence spectra of **1NPnN** (n = 4,5,6) in the presence of several concentration of Ca^{2+} and Ba^{2+} ions were shown in Figure 1. The peak intensty of the naphtharene monomer (368 nm) decrased by the addition of Ca^{2+} and Ba^{2+} respectively (Figure 2). The complex formation constants (K) and the fluorescence intensities of the complexes (I_{ML}) were evaluated from these intensities, using equation (1).[7] The fluorescence intensities at 368 nm were used for calculation.

$$(I_f - I_{f,max}) / (I_{f,max} - I_f) = K[M] \qquad (1)$$

Table 1. The complex formation constants (K) of **1NPnN** (n = 4,5,6)

Metal ion	log K **1NP4N**	 **1NP5N**	 **1NP6N**
Ca^{2+}	3.63	4.48	4.82
Ba^{2+}	3.78	4.72	4.15

Solvent : acetonitrile at 25 ℃.

[**1NPnN** (n = 4,5,6)] = 1.0×10^{-5} mol · dm^{-3}.

As shown in Table 1, the order of the formation constants (K) of **1NPnN** for Ca^{2+} is **1NP6N** > **1NP5N** > **1NP4N**, and for Ba^{2+} is **1NP5N** > **1NP6N** > **1NP4N**. **1NP4N** formed the most unstable complex with Ca^{2+} and Ba^{2+}. This may be due to the short polyether chain to enclose on matal ions. **1NP5N** formed the most stable complex with Ba^{2+}. **1NP6N** formed the most stable complex with Ca^{2+}. These show that the complexing ability was mostly determined by the polyether chain length. In **1NPnN** (n = 4,5,6), there is the ability of distinctions between Ca^{2+} and Ba^{2+} by changes of fluorescence spectra. That is to say, the total fluorescence quantum yield ($\Phi_{f,total}$) decreased by the addition of Ca^{2+}, while increased by the addition of Ba^{2+} respectively as shown Figure 1. It is interesting to note this result and further studies are in progress.

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References and Notes

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5 The QMS spectra of all the **1NPnN** (n = 1,2,3,4,5,6) showed corresponding molecular ion peaks and similar fragments: 199 (naphthalene-$COOC_2H_4^+$), 172 (naphthalene-CO_2H^+), 155 (naphthalene-CO^+), 127 (naphthalene$^+$).
1NP1N : ^{1}H NMR (270MHz, $CDCl_3$) δ 4.81 (4H, s, $C\underline{H}_2$), 7.42-8.98 (14H, m, naphthalene); ^{13}C NMR (70MHz, $CDCl_3$) δ 62.80 ($\underline{C}H_2$), 124.50, 125.80, 126.30, 126.70, 127.80, 128.30, 130.50, 131.40, 133.60, 133.80 (naphthalene), 167.30 ($\underline{C}$=O).
1NP2N : ^{1}H NMR (270MHz, $CDCl_3$) δ 3.97 (4H, t, *J* = 5.0Hz, $C\underline{H}_2O$), 4.61 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.31 - 8.95 (14H, m, naphthalene); ^{13}C NMR (70MHz, $CDCl_3$) δ 64.03 ($\underline{C}H_2O$), 69.27 ($COO\underline{C}H_2$), 124.40, 125.80, 126.20, 127.00, 127.70, 128.30, 130.30, 131.40, 133.40, 133.80 (naphthalene), 167.50 ($\underline{C}$=O).
1NP3N : ^{1}H NMR (270MHz, $CDCl_3$) δ 3.76 (4H, s, $C\underline{H}_2O$), 3.90 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.55 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.40 - 8.95 (14H, m, naphthalene); ^{13}C NMR (70MHz, $CDCl_3$) δ 64.15 ($\underline{C}H_2O$), 69.40 ($COOCH_2\underline{C}H_2$), 70.80 ($COO\underline{C}H_2$), 124.50, 125.90, 126.20, 127.20, 127.70, 128.40, 130.30, 131.40, 133.40, 133.90 (naphthalene), 167.45 ($\underline{C}$=O).
1NP4N : ^{1}H NMR (270MHz, $CDCl_3$) δ 3.70 (8H, s, $C\underline{H}_2O$), 3.87 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.55 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.41 - 8.95 (14H, m, naphthalene); ^{13}C NMR (70MHz, $CDCl_3$) δ 64.08, 69.25 ($\underline{C}H_2O$), 70.71 ($COOCH_2\underline{C}H_2$), 70.76 ($COO\underline{C}H_2$) 124.50, 125.80, 126.20, 127.10, 127.70, 130.30, 131.40, 133.40, 133.80 (naphthalene), 167.50 ($\underline{C}$=O).
1NP5N : ^{1}H NMR (270MHz, $CDCl_3$) δ 3.59 - 3.73 (12H, m, $C\underline{H}_2O$), 3.86 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.56 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.43 - 8.96 (14H, m, naphthalene); ^{13}C NMR (70MHz, $CDCl_3$) δ 64.02, 69.27 ($\underline{C}H_2O$), 70.67 ($COOCH_2\underline{C}H_2$), 70.70 ($COO\underline{C}H_2$), 124.50, 125.90, 126.20, 127.80, 130.40, 131.40, 133.40 (naphthalene), 167.00 ($\underline{C}$=O).
1NP6N : ^{1}H NMR (270MHz, $CDCl_3$) δ 3.54 - 3.74 (16H, m, $C\underline{H}_2O$), 3.97 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.56 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$) 7.42 - 8.95 (14H, m, naphthalene); ^{13}C NMR (70MHz, $CDCl_3$) δ 64.15, 69.30, 70.63 ($\underline{C}H_2O$), 70.70 ($COOCH_2\underline{C}H_2$), 70.76 ($COO\underline{C}H_2$), 124.50, 125.90, 126.20, 127.80, 128.30, 130.30, 131.40, 133.30, 133.90 (naphthalene), 167.00 ($\underline{C}$=O).

6 For example: **1NP5N** : ^{1}H NMR (270MHz, CD_3CN) δ 3.48 - 3.62 (12H, m, $C\underline{H}_2O$), 3.79 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.49 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.50 - 7.67 (6H, m, naphthalene H-3, H-6, H-7), 7.94 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-5), 8.09 (2H, d, *J* = 8.0Hz, naphthalene H-8), 8.14 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-4), 8.80 (2H, d, *J* = 9Hz, naphthalene H-2). Ba^{2+} complex of **1NP5N**: ^{1}H NMR (270MHz, CD_3CN) δ 3.65 - 3.85 (12H, m, $C\underline{H}_2O$), 4.04 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.77 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.47 - 7.61 (6H, m, naphthalene H-3, H-6, H-7), 7.96 (2H, m, naphthalene H-5), 8.14 (2H, d, *J* = 8.0Hz, naphthalene H-8), 8.25 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-4), 8.74 (2H, m, naphthalene H-2). **1NP6N** : ^{1}H NMR (270MHz, CD_3CN) δ 3.40 - 3.65 (12H, m, $C\underline{H}_2O$), 3.81 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.50 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.50 - 7.67 (6H, m, naphthalene H-3, H-6, H-7), 7.95 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-5), 8.10 (2H, d, *J* = 8.0Hz, naphthalene H-8), 8.14 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-4), 8.80 (2H, d, *J* = 9Hz, naphthalene H-2). Ca^{2+} complex of **1NP6N**: ^{1}H NMR (270MHz, CD_3CN) δ 3.65 - 3.93 (12H, m, $C\underline{H}_2O$), 4.04 (4H, t, *J* = 5.0Hz, $COOCH_2C\underline{H}_2$), 4.61 (4H, t, *J* = 5.0Hz, $COOC\underline{H}_2$), 7.53 - 7.70 (6H, m, naphthalene H-3, H-6, H-7), 7.96 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-5), 8.11 (2H, d, *J* = 8.0Hz, naphthalene H-8), 8.22 (2H, dd, *J* = 8.0Hz, *J* = 1.5Hz, naphthalene H-4), 8.80 (2H, m, naphthalene H-2).

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