Intramolecular Exciplex Formation and Metal Ion Recognition in 1-(1-Naphthalenecarboxy)-*n*-(*p*-substituted benzenecarboxy)oxaalkanes

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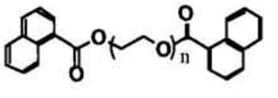
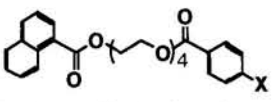
1-(1-naphthalenecarboxy) - *n* - (*p* -cyano benzenecarboxy) oxaalkanes (**1NPnCN**, n = 1 - 6) as fluorescent sensors by exciplex emission for metal ions were synthesized. we investigated the relationship between the length of the polyether chain and the metal ion recognition of **1NPnCN** (n = 1 - 6). Changes in the fluorescence spectra of **1NPnCN** (n = 1 - 4) were not observed by the addition of calcium and barium salts. However, the spectra of **1NPnCN** (n = 5, 6) were changed.

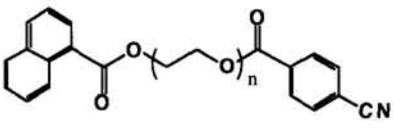
Many kinds of crown ether type macrocyclic compounds have been used for analytical application such as chemical sensor[1] and spectrophotometries.[2] In the application for fluorimetry, fluorescent reagents, which have two aromatic hydrocarbons at both terminals of a linear polyether as an analogue of a crown ether, also have been used.[3] In 1996, we synthesized 1,*n*-Bis(1-naphthalenecarboxy)oxaalkanes (**1NPnN**, n = 1 - 6) as fluorescent sensors by excimer emission for metal ions and investigated the relationship between the length of the polyether chain and metal ion recognition of **1NPnN**.[4] When alkali metal salts were added in an acetonitrile solution of **1NPnN** (n = 1 - 6), the shape and intensity of the fluorescence spectra were not changed, and when alkaline earth metal salts were added, changes in the fluorescence spectra of **1NPnN** (n = 1 - 3) were also not observed. However, the spectra of **1NPnN** (n = 4,5,6) were changed by the addition of calcium and barium salts.[4] In **1NPnN** (n = 4,5,6), the complex formation constants (K) obtained by fluorescent changes were 3.63 - 4.82 (= log K). We attempted to construct excellent fluorescent chemosensors for ion recognition, better than **1NPnN** (n = 4,5,6).



1NPnN(n = 1 - 6)



1NP4X(X = H, Cl, CF_3, CN, NO_2)



1NPnCN(n = 1 - 6)

We synthesized a D-A system having 1-naphthoic acid and *p*-substituted benzoic acid at both terminals of the linear polyether. First, we investigated substitution effects by means of 1-(1-naphthalenecarboxy) - 14 - (*p*-substituted benzenecarboxy) oxa alkanes (**1NP4X**, X = H, Cl, CF_3, CN, NO_2). Next, we investigated the relationship between the length of the polyether chain and the metal ion recognition of 1-(1-naphthalenecarboxy) -*n* -(*p*-cyanobenzenecarboxy)oxaalkanes (**1NPnCN**, n = 1 - 6) observed exciplex emission. **1NP4X** (X = H, Cl, CF_3, CN, NO_2) and **1NPnCN** (n = 1 - 6) were prepared by the same methods as those of **1NPnN** (n = 1 - 6)[4], which was the condensation between 1-naphthoic acid or *p*-substituted benzoic acid and the corresponding polyethleneglycols using *N*, *N* -dicyclohexyl carbodiimide (DCC).

It is known that electron transfer and exciplex formation are possible for a system with a negative value of the free energy of electron transfer (ΔG_{ET}), given by the Rehm-Weller equation[5]:

$$\Delta G_{ET} = IP_D - EA_A - E_{00} - C + \Delta G_{solv} \qquad (1)$$

where IP_D is the ionization potential of a donor, EA_A is the electron affinity of an acceptor, E_{00} is the excitation energy of the excited molecule, and C and ΔG_{solv} are the Coulombic energy and solvation of ion pairs, respectively. A fairly accurate value of ΔG_{ET} can be calculated with the equation[6]

$$\Delta G_{ET}\,(eV) = E_{(D/D+)} - E_{(A-/A)} - E_{00} - [e^2/\varepsilon\rho] - [(e^2/r)(1 - 1/\varepsilon)] \qquad (2)$$

using the oxidation and reduction potentials [$E_{(D/D+)}$ and $E_{(A-/A)}$] of a donor and an acceptor separated by ρ with average individual ionic radii r in a solvent with dielectric constant ε when the redox potentials of the donor and the acceptor were determined in acetonitrile solution (ε = 36.2). In order to evaluate the free energy of electron transfer in the **1NP4X** series, the oxidation potential of naphthalene and the reduction potentials of methyl *p*-substituted benzoate were compared. The oxidation potential of naphthalene [$E_{(D/D+)}$] was 1.26 V vs Ag/Ag^+ in acetonitrile at room temperature.[7] The reduction potentials [$E_{(A-/A)}$] of methyl benzoate carrying *p*-H, *p*-Cl, *p*-CF_3, *p*-CN and *p*-NO_2 were -2.63, - 2.47, - 2.19, - 2.11 and - 1.97 V vs Ag/Ag^+ in acetonitrile at room temperature, respectively.[8] If we assume that the donor and acceptor parts of **1NPnX** in the folded conformation are separated by a distance between 4 Å to form exciplex, ΔG_{ET} is calculated from equation (2) (ionic radii are assumed to be 4.3 Å) using the 0-0 transition energy for naphthalene E_{00} = 3.98eV determined from the absorption and fluorescence spectra. As shown Table 1, ΔG_{ET} decreases as the electronegativity of the *p*-substitutents of the acceptor benzoate increases. Combination of naphthalene (D) with *p*-H, *p*-Cl, *p*-CF_3, *p*-CN and *p*-NO_2 benzoate (A) gives negative ΔG_{ET}, indicating that both exciplex formation and electron transfer are possible for these systems.[9]

The absorption and excitation spectra of **1NP4X** (X = H, Cl, CF_3, CN, NO_2) are essentially identical with equimolar mixtures of Ethyl 1-naphtoate and the corresponding methyl *p*-substituted benzoates. The ground state intramolecular interaction, such as charge transfer (CT) between D and A, was excluded by the absence of new band at longer wavelength for **1NP4X** (X = H, Cl, CF_3, CN, NO_2).

Fluorescence quantum yields (Φ) in acetonitrile obtained relative to naphthalene are reported in Table 2, in which Φ_{total} is the quantum yield for total emission, Φ_{LE} is that of a locally excited emission and Φ_{EX} is that of the exciplex emission.

Table 1. Free energy of electron transfer (ΔG_{ET})[a] between naphthalene (Naph) and *p*-substituted benzoate (*p*-H, *p*-Cl, *p*-CF$_3$, *p*-CN, *p*-NO$_2$) in acetonitrile

D - A	σ_p [a]	ΔG_{ET} / eV mol^{-1} $\rho = 4$ Å
Naph - *p*-H	0.00	- 0.19
Naph - *p*-Cl	0.23	- 0.35
Naph - *p*-CF$_3$	0.54	- 0.63
Naph - *p*-CN	0.66	- 0.71
Naph - *p*-NO$_2$	0.78	- 0.85

[a] Hammett's values for *p*-substituents.

Table 2. Fluorescence Quantum Yields of **1NP4X** (X = H, Cl, CF$_3$, CN, NO$_2$) in acetonitrile at 25 ℃

	1NP4X				
Φ\X	**H**	**Cl**	**CF$_3$**	**CN**	**NO$_2$**
Φ_{total}	0.25	0.24	0.24	0.075	0.062
Φ_{LE}	0.25	0.24	0.24	0.060	0.062
Φ_{EX}	0.00	0.00	0.00	0.015	0.000

Φ_{total} decreases as the electronegativity of the *p*-substituent of the acceptor benzoate increases. (Table 2)
1NP4CN and **1NP4NO$_2$**, with the most negative ΔG_{ET}, show the most efficient quenching. In **1NP4CN**, exciplex emission is observed, but not observed in **1NP4X** (X = H, Cl, CF$_3$, NO$_2$).

We investigated the complexing ability of **1NPnCN** (n = 1- 6) with Ca^{2+} and Ba^{2+} in order to compare that of **1NPnN**, because, in **1NPnCN**, it is easy to detect exciplex emission. Measurements of fluorescence spectra were carried out in an acetonitrile solution of the **1NPnCN** (1.0 x 10^{-5} mol dm^{-3}) at room temperature, and Ca(SCN)$_2$ and Ba(ClO$_4$)$_2$ were added to the solution. To prevent a nonlinearity of the fluorescence intensity, isosbestic points (295 nm) of the absorption spectra of **1NPnCN** were chosen as excitation wavelength, respectively. When calcium and barium salts were added in the acetonitrile solution of **1NPnCN** (n = 1 - 4), shape and intensity of the fluorescence spectra were not changed. However, the spectra of **1NPnCN** (n = 5 and 6) were changed. To study the complexation behavior of **1NPnCN** (n = 5 and 6) with Ca^{2+} and Ba^{2+}, the measurements of the fluorescence were carried out in detail . For example, the fluorescence spectra of **1NP5CN** in the presence of several concentrations of Ba^{2+} are shown in Figure 1. The peak intensity of the naphthalene monomer (368 nm) was decreased by the addition of Ca^{2+} and Ba^{2+}; respectively. The peak intensity of the exciplex (the longer wavelength region) was also decreased by the addition of Ca^{2+}. However, when Ba^{2+} was added, the peak intensity of exciplex emission was increased. The complex formation constants (K) and the fluorescence intensities of the complexes (I_{ML}) were evaluated from these intensities, using equation 1.[10] The fluorescence intensities at 368 nm[11] were used for calculation.

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

As shown in Table 3, the order of the formation constants (K) of **1NP5CN** for Ca^{2+} and Ba^{2+} is Ba^{2+} > Ca^{2+}, and of **1NP6CN** for Ca^{2+} and Ba^{2+} is Ca^{2+} > Ba^{2+}.

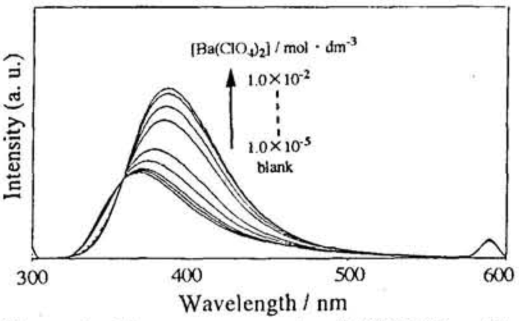


Figure 1. Fluorescence spectra of **1NP5CN** and its Ba^{2+} complexes, as excited at 295 nm.
[**1NP5CN**] = 1×10^{-5} mol · dm^{-3} in MeCN at 25 ℃.

Table 3. The complex formation constants (K) of **1NPnCN** (n = 5 and 6)

	log K	
	1NP5CN	**1NP6CN**
Ca^{+}	5.54	5.46
Ba^{+}	5.65	4.57

Solvent : acetonitrile at 25 ℃.
[**1NPnCN** (n = 5,6)] = 1.0×10^{-5} mol · dm^{-3}.

These results were the same as the results of **1NPnN** (n = 4 - 6). However, the value of the complex formation constants (K) for **1NPnCN** was greater than that for **1NPnN**.[4] These results suggested that **1NPnCN** (n = 5 and 6) were excellent fluorescent chemosensors for ion recognition, better than **1NPnN** (n = 4,5,6).

We reported here preliminary results of our studies on the relationship between the length of the polyether chain and the metal ion recognition of **1NPnCN**. Further studies are in progress.

References and Notes

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11 368 nm is the peak of the naphthalene monomer emission.