

## Complexing Behavior of New Naphthalene Derivatives Having Amide Groups as Fluorescent Chemosensors for Alkali and Alkaline Earth Metal Ions

Jun Kawakami,\* Atsuo Fukushi, and Shoei Ito

Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University,  
3 Bunkyo-cho, Hirosaki, Aomori 036-8561

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New naphthalene derivatives (**1NSN**, **1NLN**, **1NE** and **1NcrownN**) as fluorescent chemosensors for metal ions using excimer emission were synthesized. We investigated the metal ion recognition of **1NSN**, **1NLN**, **1NE** and **1NcrownN**. Large changes in the fluorescence spectra of not only **1NSN** and **1NLN** but also **1NE** were observed with the addition of magnesium ion. However, changes in the fluorescence spectra of **1NcrownN** were not observed with the addition of alkali and alkaline earth metal ions.

Molecular recognition is a subject of considerable interest because of its implications in many fields: biology, medicine, environment, etc. In particular, the detection of metal cations involved in biological processes (e.g. calcium, magnesium) has received considerable attention. Our aim is to design fluorescent sensors<sup>1</sup> that undergo photophysical changes as marked as possible upon cation binding. In 1996 and 1998, we synthesized compounds having ester groups, 1, *n*-bis(1-naphthalenecarboxy)oxaalkanes (**1NPnN**, *n* = 1 - 6)<sup>2</sup> and 1- (1-naphthalenecarboxy) - *n* - (*p*-cyanobenzene carboxy)oxaalkanes (**1NPnCN**, *n* = 1 - 6),<sup>3</sup> as fluorescent sensors for metal ions by intramolecular excimer or exciplex emission. When alkali metal salts were added to an acetonitrile solution of **1NPnN** and **1NPnCN** (*n* = 1 - 6), the shape and intensity of the fluorescence spectra did not change, but when alkaline earth metal salts were added, the spectra of **1NPnN** (*n* = 4,5,6) and **1NPnCN** (*n* = 5,6) changed with the addition of calcium and barium salts. We attempted to develop new fluorescent chemosensors for magnesium ion. It is known that some noncyclic amide ionophores is good magnesium sensors.<sup>1b)</sup> Therefore, we synthesized compounds having amide groups, **1NSN**, **1NLN**, **1NE** and **1NcrownN**, and investigated the alkali and alkaline earth metal ion recognition. We now wish to report the

preliminary results of our study on the metal ion recognition by **1NSN**, **1NLN**, **1NE** and **1NcrownN**.

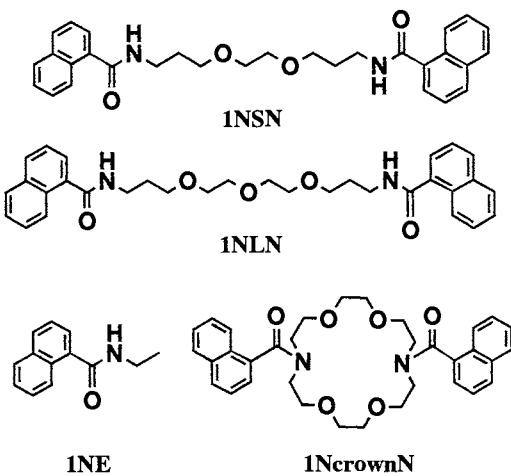
**1NSN**, **1NLN**, **1NE** and **1NcrownN** were prepared from 1-naphthoic acid and the corresponding ethyleneglycol bis(3-aminopropyl)ether, diethyleneglycol bis(3-aminopropyl)ether, ethylamine or 4,13-diaza-18-crown 6-ether in the presence of *N,N*-dicyclohexyl carbodiimide and 4-dimethylaminopyridine in dichloromethane.<sup>4</sup> Measurements of the fluorescence spectra were carried out in an acetonitrile solution of the **1NSN**, **1NLN**, **1NE** and **1NcrownN** ( $1.0 \times 10^{-5}$  mol dm<sup>-3</sup>) at room temperature, and alkali or alkaline earth metal salts ( $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Ca}(\text{SCN})_2$  and  $\text{Ba}(\text{ClO}_4)_2$ ) were added to the solution. To prevent any nonlinearity of the fluorescence intensity, the isosbestic points (295 nm) of the absorption spectra of **1NSN**, **1NLN**, **1NE** and **1NcrownN** were chosen as the excitation wavelengths.

The absorption and excitation spectra of **1NSN**, **1NLN**, **1NE** and **1NcrownN** are essentially identical. The ground state intramolecular interaction, such as charge transfer (CT), was excluded by the absence of a new band at a longer wavelength for **1NSN**, **1NLN**, **1NE** and **1NcrownN**.

Fluorescence quantum yields ( $\Phi$ ) in acetonitrile obtained relative to naphthalene are reported in Table 1, in which  $\Phi_{\text{total}}$  is the quantum yield for total emission,  $\Phi_{\text{LE}}$  is that of a locally excited emission and  $\Phi_{\text{EX}}$  is that of the excimer emission.

Table 1. Fluorescence quantum yields of **1NSN**, **1NLN**, **1NE** and **1NcrownN** in acetonitrile at 25 °C

	<b>1NSN</b>	<b>1NLN</b>	<b>1NE</b>	<b>1NcrownN</b>
$\Phi_{\text{total}}$	0.012	0.011	0.0036	0.0083
$\Phi_{\text{LE}}$	0.0034	0.0046	0.0036	0.0083
$\Phi_{\text{EX}}$	0.0083	0.0060	0.0000	0.0000
$\Phi_{\text{EX}} / \Phi_{\text{LE}}$	2.4	1.3	0.0	0.0



All compounds studied have smaller  $\Phi_{\text{LE}}$  values than that of naphthalene ( $\Phi_{\text{naph}} \approx 0.2$ ). The fluorescence of these compounds having amide groups is assumed to be strongly quenched by intersystem crossing to a triplet state. Intramolecular excimer emission were observed in the flexible compounds, **1NSN** and **1NLN**, but not observed in the rigid compounds such as **1NcrownN**. The ratio of  $\Phi_{\text{EX}} / \Phi_{\text{LE}}$  for **1NSN** is larger than that of **1NLN**. The reason for these results is that overlapping of the two naphthalene rings of **1NSN** having the short spacer is better than that of **1NLN** having a long spacer, and **1NcrownN** as a rigid compound could not overlap the two chromophores.

When sodium and potassium salts were added to the acetonitrile solution of **1NSN** and **1NLN**, the shape and intensity of the fluorescence spectra were not changed.

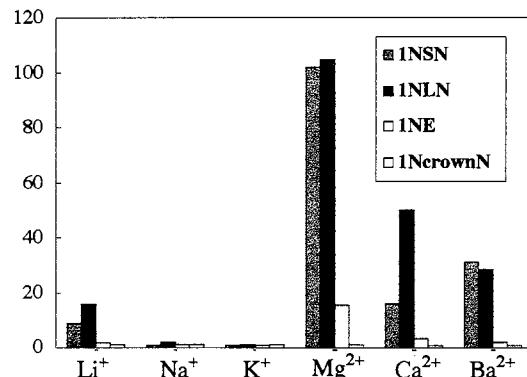


Figure 1. The ratio of  $\Phi_{\text{total,max}} / \Phi_{\text{total,blank}}$  of **1NSN**, **1NLN**, **1NE** and **1NcrownN**.

However, the spectra of **1NSN** and **1NLN** changed with the addition of lithium, magnesium, calcium and barium salts. New longer wavelength emissions are due to the excited state complex formation, i.e., intramolecular excimer formation. In particular, the ratio of  $\Phi_{\text{total,max}} / \Phi_{\text{total,blank}}$  is larger in the case of Mg<sup>2+</sup> than for Li<sup>+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> (Figure 1). The ionic diameters (r) of Li<sup>+</sup> and Mg<sup>2+</sup> are ca. 0.13 nm, and those of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> are r > 0.19 nm. These results showed that **1NSN** and **1NLN** formed a more stable complex with the divalent metal ions than with the monovalent metal ions, and the desirable size of metal ionic diameters to form a complex was ca. 0.13 nm. The lithium ion is monovalent, but **1NSN** and **1NLN** would form complex with Li<sup>+</sup> having desirable ionic diameters, that is, ca. 0.13 nm. We derived interesting results in change of fluorescent spectra. The peak intensity of excimer emission (ca. 400 nm) did not appear by the addition of equimolar lithium and magnesium salts. Then, a peak of excimer emission appeared on the further addition of lithium and magnesium salts, and the intensity increased with Li<sup>+</sup> and Mg<sup>2+</sup> concentration. However, the peak intensity of excimer emission appeared by the addition of equimolar calcium and barium salts. We would think that Li<sup>+</sup> and Mg<sup>2+</sup> formed 2 : 1 complex (metal ion : ligand) with **1NSN** and **1NLN**, and Ca<sup>2+</sup> and Ba<sup>2+</sup> formed 1 : 1 complex. On the other hand, when lithium, sodium, potassium magnesium, barium and calcium salts were added to the acetonitrile solution of **1NcrownN**, the shape and intensity of the fluorescence spectra did not change. The reason for these results is that **1NcrownN** as a rigid compound could not form an intramolecular excimer which required actual overlapping of the two naphthalene rings. In the case of **1NE**, which was synthesized as a reference compound, interesting results were obtained. We have thought that the shape and intensity of the fluorescence spectra of **1NE** having only one naphthalene ring did not change when metal salts were added. However, when magnesium salts were added to the acetonitrile solution of **1NE**, the shape and intensity of the fluorescence spectra did change as shown in Figure 2. These new longer wavelength emissions may be due to intermolecular excimer formation. That is to say, Mg<sup>2+</sup> formed a 1:2 complex (metal ion : ligand) with **1NE**. In esters such as ethyl 1-naphthoate,

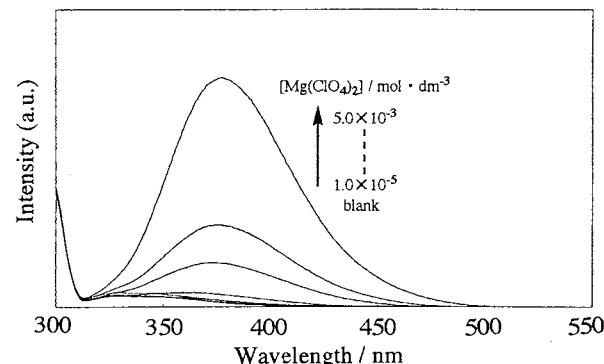


Figure 2. Fluorescence spectra of **1NE** and its Mg<sup>2+</sup> complexes when excited at 295 nm.  
[**1NE**] =  $1 \times 10^{-5}$  mol · dm<sup>-3</sup> in MeCN at 25 °C.

these phenomena were not observed.

We think that the amide groups mainly related to the complexation of **1NSN**, **1NLN** and **1NE** with Li<sup>+</sup> and Mg<sup>2+</sup>, and the polyether chain mainly related to the complexation with Ca<sup>2+</sup> and Ba<sup>2+</sup>.

We reported here the preliminary results of our studies of the metal ion recognition of compounds having amide groups, i.e., **1NSN**, **1NLN**, **1NE** and **1NcrownN**. Further studies are now in progress.

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#### References and Notes

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- 4 The MS spectra of all compounds showed corresponding molecular ion peaks and similar fragments: 155 (naphthalene-CO<sup>+</sup>), 127 (naphthalene<sup>+</sup>).
- 1NSN:** <sup>1</sup>H NMR (270MHz, CDCl<sub>3</sub>) δ 1.64 (4H, quint, *J* = 5.0Hz, CH<sub>2</sub>), 3.36 – 3.47 (12H, m, NCH<sub>2</sub> & OCH<sub>2</sub>), 6.50 (2H, br, NH), 7.20 – 8.30 (14H, m, naphthalene); <sup>13</sup>C NMR (70MHz, CDCl<sub>3</sub>) δ 29.0 (CH<sub>2</sub>), 38.4 (NHCH<sub>2</sub>), 70.2, 70.3 (OCH<sub>2</sub>), 124.7, 124.9, 125.5, 126.3, 127.0, 128.2, 130.2, 130.3, 133.7, 134.9 (naphthalene), 169.3 (C=O).
- 1NLN:** <sup>1</sup>H NMR (270MHz, CDCl<sub>3</sub>) δ 1.81 (4H, quint, *J* = 6.0Hz, CH<sub>2</sub>), 3.23 (8H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 3.45 (4H, t, *J* = 6.0Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.52 – 3.59 (4H, m, NCH<sub>2</sub>), 6.60 (2H, br, NH), 7.25 – 8.30 (14H, m, naphthalene); <sup>13</sup>C NMR (70MHz, CDCl<sub>3</sub>) δ 29.1 (CH<sub>2</sub>), 38.4 (NHCH<sub>2</sub>), 70.1, 70.3, 70.4 (OCH<sub>2</sub>), 124.6, 124.9, 125.6, 126.3, 126.9, 128.2, 130.3, 133.7, 135.0 (naphthalene), 169.4 (C=O).
- 1NE:** <sup>1</sup>H NMR (270MHz, CDCl<sub>3</sub>) δ 1.26 (3H, t, *J* = 7.2Hz, CH<sub>3</sub>), 3.48 – 3.58 (2H, m, CH<sub>2</sub>), 6.10 (1H, br, NH) 7.36 – 8.30 (7H, m, naphthalene); <sup>13</sup>C NMR (70MHz, CDCl<sub>3</sub>) δ 14.9 (CH<sub>3</sub>), 35.0 (CH<sub>2</sub>), 124.7, 124.8, 125.4, 126.4, 127.0, 128.3, 130.2, 130.4, 137.7, 134.9 (naphthalene), 169.5 (C=O).
- 1NcrownN:** <sup>1</sup>H NMR (270MHz, CDCl<sub>3</sub>) δ 3.25 – 3.55 (16H, m, OCH<sub>2</sub>), 3.75 – 3.95 (8H, m, NH<sub>2</sub>), 7.25 – 7.85 (14H, m, naphthalene); <sup>13</sup>C NMR (70MHz, CDCl<sub>3</sub>) δ 46.1, 46.2, 49.7, 49.8 (NCH<sub>2</sub>), 69.7, 69.8, 70.5, 70.6 (OCH<sub>2</sub>), 123.7, 128.4, 125.1, 126.4, 127.0, 128.4, 129.0, 129.6, 133.6, 124.7 (naphthalene), 171.1 (C=O).