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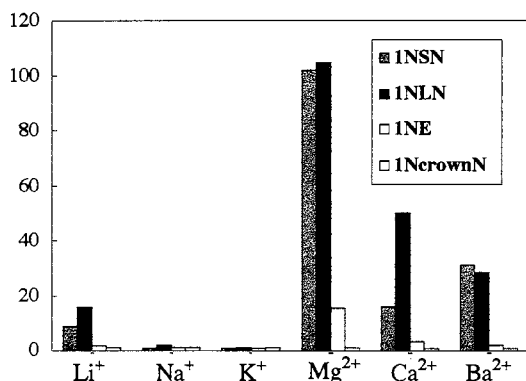


Figure 1. The ratio of $\Phi_{\text{total,max}} / \Phi_{\text{total,blank}}$ of 1NSN, 1NLN, 1NE and 1NcrownN.

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^{2+} than for Li^+ , Ca^{2+} and Ba^{2+} (Figure 1). The ionic diameters (r) of Li^+ and Mg^{2+} are ca. 0.13 nm, and those of Na^+ , K^+ , Ca^{2+} and Ba^{2+} 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^+ 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^+ and Mg^{2+} concentration. However, the peak intensity of excimer emission appeared by the addition of equimolar calcium and barium salts. We would think that Li^+ and Mg^{2+} formed 2 : 1 complex (metal ion : ligand) with 1NSN and 1NLN, and Ca^{2+} and Ba^{2+} 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^{2+} formed a 1 : 2 complex (metal ion : ligand) with 1NE. In esters such as ethyl 1-naphthoate,

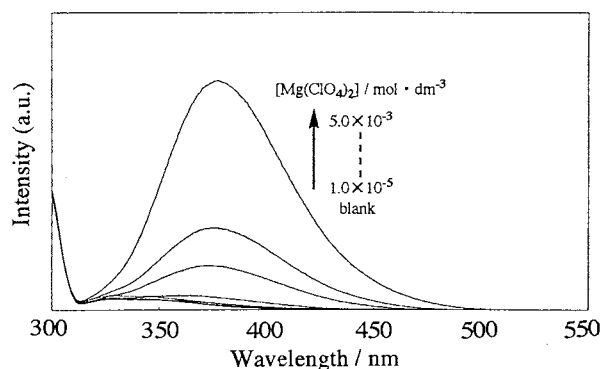


Figure 2. Fluorescence spectra of 1NE and its Mg^{2+} complexes when excited at 295 nm. $[1\text{NE}] = 1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ in MeCN at 25 °C.

these phenomena were not observed.

We think that the amide groups mainly related to the complexation of 1NSN, 1NLN and 1NE with Li^+ and Mg^{2+} , and the polyether chain mainly related to the complexation with Ca^{2+} and Ba^{2+} .

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^+), 127 (naphthalene $^+$).
 1NSN: ^1H NMR (270MHz, CDCl_3) δ 1.64 (4H, quint, $J = 5.0\text{Hz}$, CH_2), 3.36–3.47 (12H, m, NCH_2 & OCH_2), 6.50 (2H, br, NH), 7.20–8.30 (14H, m, naphthalene); ^{13}C NMR (70MHz, CDCl_3) δ 29.0 (CH_2), 38.4 (NHCH_2), 70.2, 70.3 (OCH_2), 124.7, 124.9, 125.5, 126.3, 127.0, 128.2, 130.2, 130.3, 133.7, 134.9 (naphthalene), 169.3 ($\text{C}=\text{O}$).
 1NLN: ^1H NMR (270MHz, CDCl_3) δ 1.81 (4H, quint, $J = 6.0\text{Hz}$, CH_2), 3.23 (8H, s, $\text{OCH}_2\text{CH}_2\text{O}$), 3.45 (4H, t, $J = 6.0\text{Hz}$, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 3.52–3.59 (4H, m, NCH_2), 6.60 (2H, br, NH), 7.25–8.30 (14H, m, naphthalene); ^{13}C NMR (70MHz, CDCl_3) δ 29.1 (CH_2), 38.4 (NHCH_2), 70.1, 70.3, 70.4 (OCH_2), 124.6, 124.9, 125.6, 126.3, 126.9, 128.2, 130.3, 133.7, 135.0 (naphthalene), 169.4 ($\text{C}=\text{O}$).
 1NE: ^1H NMR (270MHz, CDCl_3) δ 1.26 (3H, t, $J = 7.2\text{Hz}$, CH_3), 3.48–3.58 (2H, m, CH_2), 6.10 (1H, br, NH), 7.36–8.30 (7H, m, naphthalene); ^{13}C NMR (70MHz, CDCl_3) δ 14.9 (CH_3), 35.0 (CH_2), 124.7, 124.8, 125.4, 126.4, 127.0, 128.3, 130.2, 130.4, 137.7, 134.9 (naphthalene), 169.5 ($\text{C}=\text{O}$).
 1NcrownN: ^1H NMR (270MHz, CDCl_3) δ 3.25–3.55 (16H, m, OCH_2), 3.75–3.95 (8H, m, NH_2), 7.25–7.85 (14H, m, naphthalene); ^{13}C NMR (70MHz, CDCl_3) δ 46.1, 46.2, 49.7, 49.8 (NCH_2), 69.7, 69.8, 70.5, 70.6 (OCH_2), 123.7, 128.4, 125.1, 126.4, 127.0, 128.4, 129.0, 129.6, 133.6, 124.7 (naphthalene), 171.1 ($\text{C}=\text{O}$).