Journal of Photochemistry and Photobiology A: Chemistry 146 (2002) 163–168

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Ab initio molecular orbital study of the complexing behavior of *N*-ethyl-1-naphthalenecarboxamide as fluorescent chemosensors for alkali and alkaline earth metal ions

Jun Kawakami*, Ryo Miyamoto[1], Atsuo Fukushi, Katsuyoshi Shimozaki, Shoei Ito

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

Received 12 March 2001; received in revised form 6 August 2001; accepted 19 September 2001

Abstract

N-ethyl-1-naphthalenecarboxamide (1NEa) was synthesized as a reference compound of the 1,*n*-bis(1-naphthalenecarboxamido)oxaalkanes (1NSN and 1NLN) having two naphthalene rings as fluorescent chemosensors for metal ions using intramolecular excimer emission. However, large changes in the fluorescence spectra of 1NEa having only one naphthalene ring as well as 1NSN and 1NLN were observed with the addition of some metal ions. Therefore, the ab initio molecular orbital calculations (Gaussian 98) using both the Hartree–Fock SCF and density functional theory methods with 6-31G and 6-31 + G(d) basis sets were carried out for 1NEa and its metal complexes to investigate the complexing behavior. The results of the molecular orbital calculations suggest that 1NEa can form a complex with a metal ion by coordination with both the carbonyl oxygen of the amide group and π-electrons of the naphthalene ring. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio molecular orbital calculations; Naphthalene; Metal ion recognition; Fluorescent chemosensors

1. Introduction

Molecular recognition is a subject of considerable interest because of its implications in many fields such as 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 [1–3] that undergo photophysical changes as significant as possible upon cation binding. In 1999, we synthesized 1,*n*-bis(1-naphthalenecarboxamido)oxaalkanes (1NSN and 1NLN) (Scheme 1) [4], as fluorescent sensors for metal ions by intramolecular excimer emission. When sodium and potassium salts were added to the acetonitrile solution of 1NSN and 1NLN, the shape and intensity of the fluorescence spectra did not change. However, the spectra of 1NSN and 1NLN changed with the addition of lithium, magnesium, calcium and barium salts. The new longer wavelength emissions are due to the excited state complex formation, i.e. intramolecular excimer formation. In particular, the ratios of $\Phi_{\max}/\Phi_{\text{blank}}$ are greater for Mg^{2+} than for Li^{+}, Ca^{2+} and Ba^{2+} [4]. For *N*-ethyl-1-naphthalenecarboxamide (1NEa) (Scheme 1), which was synthesized as a reference compound, interesting results were obtained. We have thought that the shape and intensity of the fluorescence spectra of 1NEa having only one naphthalene ring did not change when metal salts were added. However, when lithium, magnesium, calcium and barium salts were added to the acetonitrile solution of 1NEa, the shape and intensity of the fluorescence spectra did change. In particular, the ratios of $\Phi_{\max}/\Phi_{\text{blank}}$ are greater for Mg^{2+} and Ca^{2+}. In esters such as ethyl 1-naphthoate (1NEe) (Scheme 1), which exchanged a nitrogen atom of 1NEa for an oxygen atom, these phenomena were not observed. Therefore, the ab initio molecular orbital calculations (Gaussian 98) using both the Hartree–Fock (HF) SCF and the density functional theory (DFT) method with 6-31G and 6-31 + G(d) basis sets were carried out for 1NEa and its metal complexes in order to investigate the complexing behavior.

2. Experimental details

2.1. Calculational procedure

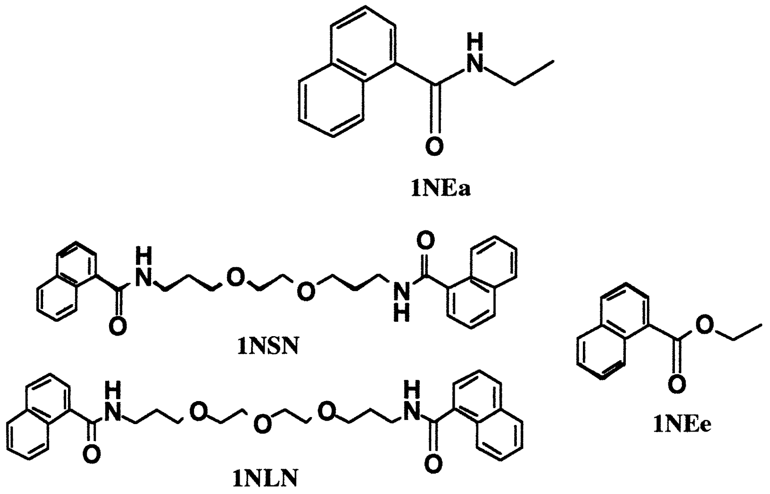
All ab initio molecular orbital calculations were carried out using Gaussian 98 [5] on an NEC TX-7/V2200

---

* Corresponding author. Tel.: +81-172-39-3570/3564; fax: +81-172-39-3541.
E-mail addresses: jun@cc.hirosaki-u.ac.jp (J. Kawakami), rmiya@cc.hirosaki-u.ac.jp (R. Miyamoto).

[1] Co-corresponding author.

PII: S1010-6030(01)00596-2



Scheme 1.

(HP-UX 11.0) at the computer center of Hirosaki University. Conformation search was performed as follows: Mg(II) ion was placed near the 1NEa and 1NEe in the π-form or in the bidentate form, if necessary. Initial geometries of the flexible *N*-ethylcarboxyamide chain and ethylcarboxylate group were determined by the so-called 3^n algorithm. There found lots of the local minimum structures as the optimized geometries of the conformers of 1NEa and 1NEe and their magnesium(II) complexes, which were obtained using the HF SCF calculation with the 6-31G basis set. Total energies were also obtained using the larger basis set of 6-31+G(d), and the DFT method of B3LYP, as a single-point energy calculation. The transition energies of these compounds were also calculated by ZINDO with the optimized molecular structures which was obtained by HF/6-31G calculations described above.

2.2. Measurements

The UV–visible absorption spectra were taken on a Hitachi U-2001 spectrometer. The fluorescence spectra were taken on a Hitachi F-4500 fluorophotometer. The fluorescence spectra measurements were carried out in an acetonitrile solution of the 1NEa ($<10^{-4}$ mol dm^{-3} where no intermolecular interaction was found) at room temperature, and alkali or alkaline earth metal salts ($LiClO_4$, $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$ and $Ba(ClO_4)_2$) were added to the solution. To prevent any nonlinearity of the fluorescence intensity, 295 nm was chosen as the excitation wavelength.

2.3. Synthesis

1NEa was prepared from 1-naphthoic acid and ethylamine in the presence of *N*,*N*-dicyclohexyl carbodiimide and 4-dimethylaminopyridine in dichloromethane. The material data of 1NEa was reported in Ref. [4].

3. Results and discussion

3.1. Absorption and emission spectra

The measurement of the absorption spectra was carried out in an acetonitrile solution of 1NEa at room temperature, and alkali or alkaline earth metal salts ($LiClO_4$, $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Ca(SCN)_2$ and $Ba(ClO_4)_2$) were added to the solution. When lithium, sodium, potassium and barium salts were added to the acetonitrile solution of 1NEa, the absorption spectra in the absence and presence of the metal salts were identical. Fig. 1 shows the absorption spectra of 1NEa in the absence and presence of the sodium salts as a typical example. When magnesium and calcium salts were added to an acetonitrile solution of 1NEa, the isosbestic points were observed. Fig. 2 shows the absorption spectra of 1NEa in the absence and presence of calcium salts as a typical example. Next, we investigated the fluorescence spectra of 1NEa. When sodium and potassium salts were added to an acetonitrile solution of 1NEa, the shape and intensity of

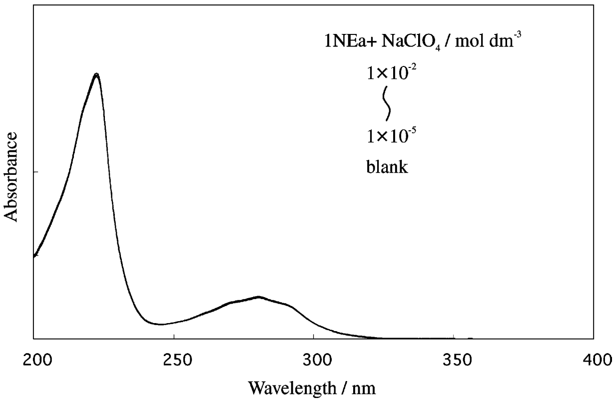


Fig. 1. Absorption spectra of 1NEa (1×10^{-5} mol dm^{-3}) before and after the incremental addition of $NaClO_4$.

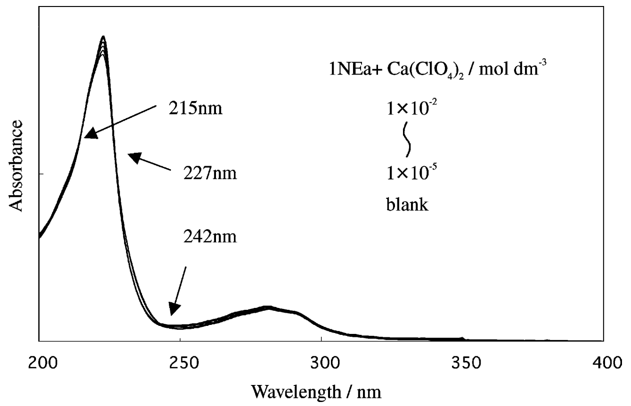


Fig. 2. Absorption spectra of 1NEa ($1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$) before and after the incremental addition of $Ca(ClO_4)_2$.

Table 1
The association constants (K) of 1NEa

	$\log K$	
	Mg^{2+}	Ca^{2+}
1NEa	2.7	2.6

the fluorescence spectra did not vary. For the lithium and barium salts, the shape and intensity of the fluorescence spectra varied only slightly. However, when magnesium and calcium salts were added to an acetonitrile solution of 1NEa, the shape and intensity of the fluorescence spectra varied significantly as shown in Fig. 3. These results are interesting. We have postulated that the shape and intensity of the fluorescence spectra of 1NEa did not change when metal salts were added, because 1NEa having only one naphthalene ring will not be able to form an intramolecular exciplex. However, when lithium, magnesium, calcium and barium salts were added to the acetonitrile solution of 1NEa, the shape and intensity of the fluorescence spectra did change. In esters such as 1NEe, which exchanged a nitrogen atom of 1NEa for an oxygen atom, these phenomena were not observed. The $\log K$ values of 1NEa are reported in Table 1.[2] When the lithium and barium salts were added to an acetonitrile solution of 1NEa, the shape and intensity of the fluorescence spectra varied only slightly, and the values of $\log K$ for Li^+ and Ba^{2+} were low ($\log K < 2$). However, for Mg^{2+} and Ca^{2+}, the shape and intensity of the fluorescence spectra clearly varied. The $\log K$ values for Mg^{2+} and Ca^{2+} were 2.7 and 2.6, respectively.

In the absence of metal salts, the fluorescence quantum yield of 1NEa ($\Phi_\mathrm{f} = 0.0036$ [4]) was much smaller than that of 1NEe. The fluorescence quantum yield of 1NEe was the same value as naphthalene, namely ca. 0.20. The 1-naphthalene-amide moiety in 1NEa exhibited the twisted intramolecular charge transfer (TICT) relaxation through the excited rotation around three bonds, which were the naphthalene–CO, OC–NH and N–CH_2 bonds, in acetonitrile solution. In the 9-anthracenecarboxamide derivative, the same phenomenon was reported by Morozumi and Nakamura [6]. The 1-naphthalene-ester moiety of 1NEe did not exhibit a TICT relaxation, and naphthalene–CO would form in conjugation with the coplanar naphthalene ring. With respect to the ability of binding with metal ions, 1NEa would be excellent and better than 1NEe, as shown

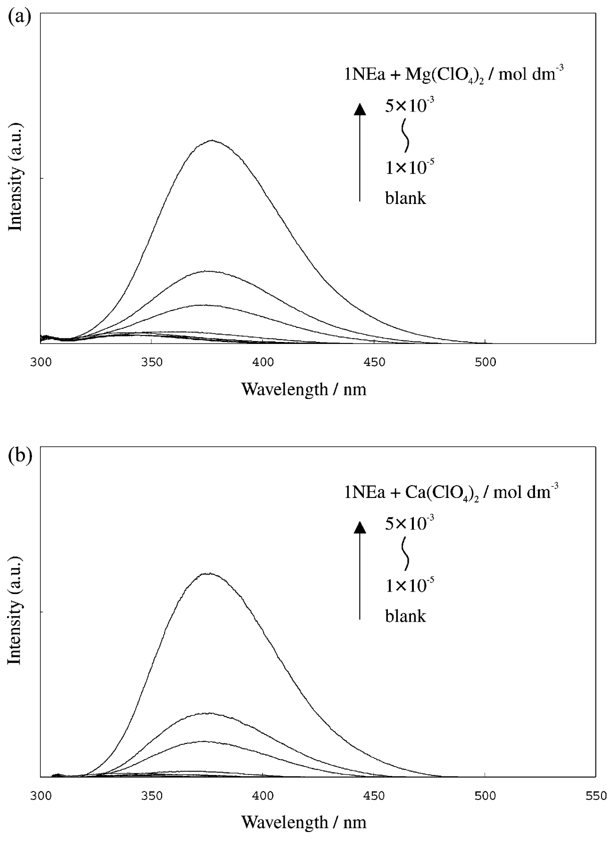


Fig. 3. Fluorescence spectra of 1NEa ($1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$) before and after the incremental addition of: (a) $Mg(ClO_4)_2$; (b) $Ca(ClO_4)_2$.

---

[2] We express the metal salt interactions in terms of the equilibrium

$$\mathrm{1NEa} + \mathrm{M} \rightleftarrows \mathrm{1NEa} \cdot \mathrm{M} \quad (\mathrm{M} = \text{metal ions}) \tag{1}$$

Also, the association constants (K) should be expected as follows:

$$K = \frac{[\mathrm{1NEa} \cdot \mathrm{M}]}{[\mathrm{1NEa}][\mathrm{M}]} = \frac{[\mathrm{1NEa} \cdot \mathrm{M}]}{([\mathrm{1NEa}]_0 - [\mathrm{1NEa} \cdot \mathrm{M}])([\mathrm{M}]_0 - [\mathrm{1NEa} \cdot \mathrm{M}])} \tag{2}$$

where

$$[\mathrm{1NEa} \cdot \mathrm{M}] = a[\mathrm{1NEa}]_0 = \frac{I - I_0}{I_\mathrm{max} - I_0}[\mathrm{1NEa}]_0 \tag{3}$$

From Eqs. (2) and (3), the following equation could be derived:

$$[\mathrm{M}]_0 = \frac{a}{K(1-a)} + a[\mathrm{1NEa}]_0 \tag{4}$$

where $[\mathrm{1NEa}]_0$ and $[\mathrm{M}]_0$ are the initial concentrations of 1NEa and the metal salts, respectively, I and I_0 the observed locally excited emission intensities of the 1NEa in the presence and absence of the metal ion, respectively, and I_max the observed locally excited emission intensity of the 1NEa and metal ion complex. A self-written nonlinear curve-fitting computer program (Eq. (4)) was used to fit the experimental titration curves. The association constant was determined from the emission–intensity changes at the emission maxima using the equation.

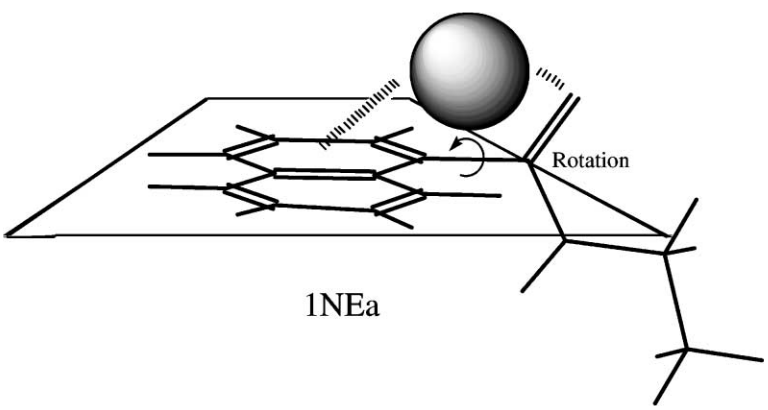


Fig. 4. The binding model with metal ion in TICT state.

in Fig. 4. Therefore, the ab initio molecular orbital calculations (Gaussian 98) using both the HF SCF and DFT methods with 6-31G and 6-31+G(d) basis sets were carried out for 1NEa and its metal complexes in order to investigate the complexing behavior. In the next section, we discuss the results of the ab initio molecular orbital calculations.

3.2. The ab initio molecular orbital calculations

The flexibilities of the *N*-ethylcarboxyamide group for 1NEa and ethylcarboxylate group for 1NEe are able to have some conformers in solution. Our MO calculations were then performed for the conformers given by the so-called 3^n algorithm in order to find the most stable conformers (Fig. 5). Both 1NEa and 1NEe have formed stable complexes with the magnesium(II) ion in an 1:1 ratio. Many local minimum or optimized structures of the 1NEa and their Mg(II) complexes and so the 1NEe could be obtained. The structures of the conformers were different in the metal binding site as well as in the alkyl chain. The obtained structures of the magnesium–1NEa complexes were classified into two types: (a) both N and O of the 1NEa bind with Mg^{2+} to make a four-membered chelate ring; (b) either N or O of the 1NEa coordinate to the ion with the π-electrons of the naphthalene chromophore. It was found in the latter that binding by the carbonyl oxygen was more energetically stable than that by the amide nitrogen. Furthermore, the π-complex form is estimated to be more stable than the bidentate form in ca. $100\,\mathrm{kJ\,mol^{-1}}$ from DFT calculation. This is because the π-electrons are able to capture the magnesium(II) ion and may contribute to neutralizing the positive charges on the cation (Table 2). The net charges on the Mg^{2+} were diminished by the larger basis set with a polarized and diffused function. The electron correlation also decreased the positive charges. The conformers of the Mg–1NEe complexes have essentially taken the same classification. The complex formation energy (ΔE) was estimated by the following equation, where the E_{complex}, E_{1NEa} and $E_{\mathrm{Mg}^{2+}}$ are the total energy of the most stable conformer of the complex, 1NEa and Mg^{2+}, respectively

$$\Delta E = E_{\mathrm{complex}} - E_{\mathrm{1NEa}} - E_{\mathrm{Mg}^{2+}}$$

The resulting ΔE's are also summarized in Table 2. It is important to point out that E_{1NEa} is the total energy of the 1NEa alone in the most stable conformation; so ΔE includes the energy for the conformational change of 1NEa to make the magnesium complexes. From these values, it seems that the expansion of the basis function did not affect the complex formation, even in the π-complex. On the other hand, the use of the DFT method makes the formation energy (ΔE) slightly larger. The effect of the electron correlation

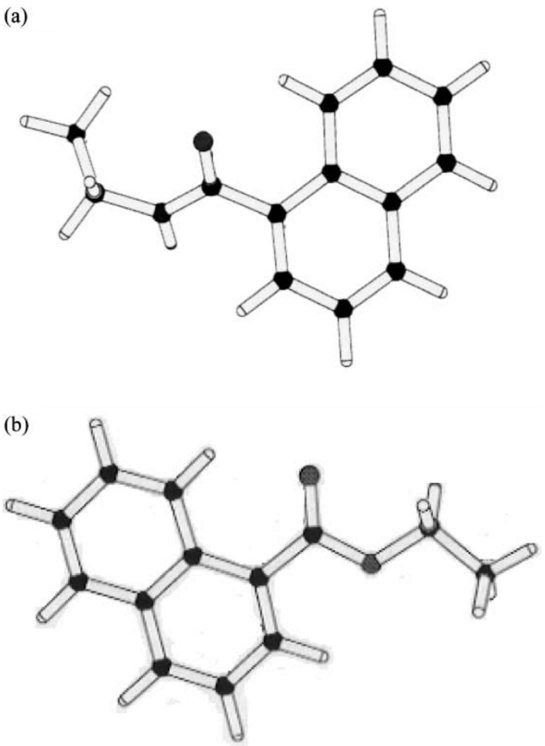


Fig. 5. The most stable conformer of: (a) 1NEa; (b) 1NEe.

Table 2
Net charges on the Mg^{2+} (upper) and the formation energies (lower, ΔE (kJ mol^{-1})) of the complexes

	Calculation methods			
	HF/6-31G	HF/6-31+G(d)	B3LYP/6-31G	B3LYP/6-31+G(d)
1NEa				
Bidentate	1.59	1.32	1.35	1.17
	−659	−647	−735	−718
π-Complex	1.55	1.26	1.34	1.09
	−797	−772	−834	−811
1NEe				
Bidentate	1.68	1.38	1.47	1.21
	−651	−610	−707	−674
π-Complex	1.55	1.25	1.35	1.09
	−737	−717	−775	−758

was larger during the formation of the bidentate complex than for the monodentate π-complex. In any case, it is considered that the 1NEa makes a stable complex with the magnesium(II) ion in the π-complex form, and not in the (N, O)-bidentate form. The complex formation energy ($\Delta E = E_{\mathrm{complex}} - E_{\mathrm{1NEe}} - E_{\mathrm{Mg^{2+}}}$) for the magnesium–1NEe system is shown in Table 2, which is not so different from that for the 1NEa. These calculated results of the energy cannot explain the experimental results that the fluorescence spectra of the 1NEe did not change with addition of the cations, while that of the 1NEa changed. However, it can be explained from the difference in the conformational structures of 1NEa and 1NEe. The most stable form of the 1NEa has a twisted configuration at the carboxamide group, while in the 1NEe, the carboxylate group takes coplanar conformation with respect to the naphthalene moiety to make a π-conjugated system. These structures suggest that there is much larger activation energy being required for 1NEe to make the π-complex with the metal ion than that for 1NEa. Thus, the 1NEe may be hard to make a complex with Mg^{2+}.

The transition energies and their oscillator strengths of 1NEa obtained from the ZINDO calculations were selected and listed in Table 3, and the stick spectra of 1NEa and its Mg^{2+} complexes are shown in Fig. 6. All the magnesium(II) complexes had transitions in the visible region, ca. 450 nm. These transitions are assigned as the ligand-to-metal charge-transfer (LMCT) band, because the major component of their transitions are calculated to be ones from the π-orbital of the naphthalene moiety to the metal s-orbital. Furthermore, it is remarkable that the other transitions of the Mg^{2+} complexes involved the LMCT character, even if the transitions were associated with that of the ligand itself. The observed behavior in the absorption band at ca. 220 and 280 nm, that move to the lower energy side with the addition of cations, was reproduced by the calculated results of forming the magnesium(II) complex. In other words, the transition energies of the n–π* and the π–π* of the organic compounds decreased by the interaction with the metal ion. The ZINDO calculation for the bidentate

Table 3
Calculated transition energies and their oscillator strengths (Mg^{2+} π-complex)[a]

Mg^{2+} π-complex, λ (nm)	Oscillator strengths
453.81	0.0562
303.86	0.1178
301.55	0.1693
281.95	0.1218
239.24	0.0877
228.26	0.9859

[a] Only the transition with a large oscillator strength are included, though all peaks are drawn in Fig. 6.

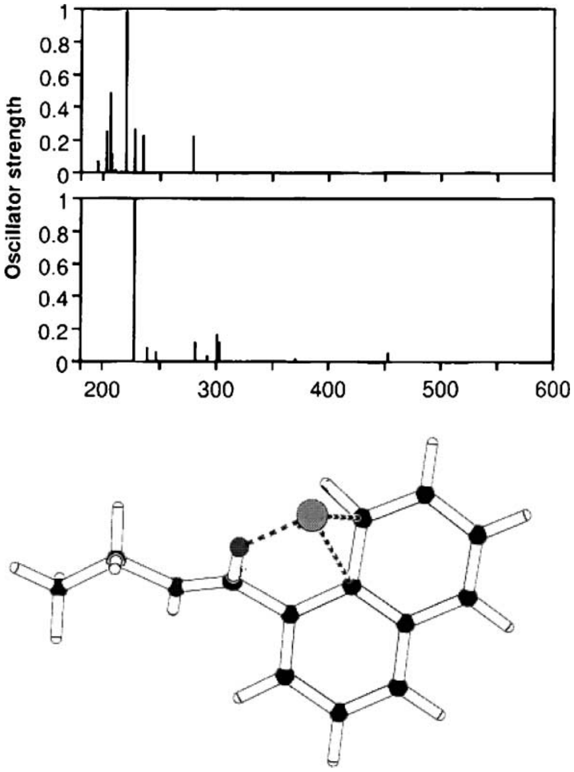


Fig. 6. The calculated spectra of a) 1NEa, b) 1NEa–Mg^{2+} π-complex and the optimized geometry of 1NEa–Mg^{2+} π-complex.

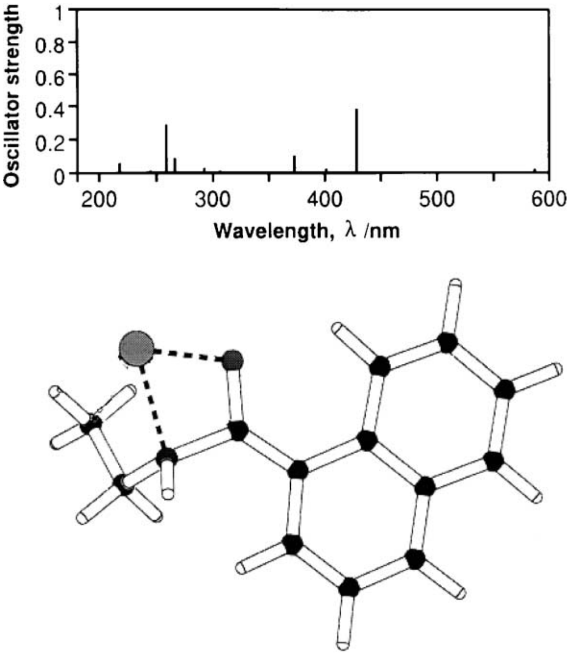


Fig. 7. The calculated spectra of 1NEa–Mg^{2+} bidentate complex and the optimized geometry of 1NEa–Mg^{2+} bidentate complex.

complex form of 1NEa with Mg^{2+} gives a very different spectra as shown in Fig. 7. There is no transition around 230 nm, while the prominent peak is at ca. 430 nm which is assigned as a ligand to metal transition. The experimental spectra show the absorption band at ca. 220 nm for 1NEa even with and without cations, therefore, the results suggest that the magnesium(II) ion is interacting with 1NEa not in the bidentate form but in the π-complex form.

As we have shown in the fluorescence spectra of 1NEa with alkali and alkali earth ions, the broad and intense emissions appeared at ca. 370 nm. Though these emissions seem to be very similar to that of 1NSN and 1NLN with a cation [4], the fluorescence of 1NEa with Mg^{2+} and Ca^{2+} (Fig. 3) must not be coming from an intermolecular excimer because of our experimental conditions of low concentration. The second possibility for that emission is a TICT, which causes a large Stokes shift. (The emission spectrum of 1NEa itself is shown as the cation free spectrum at Fig. 3.) The π-complex formation with a metal ion may make it easier to twist the carboxyamide group at the excited state so that the TICT emission has appeared. The results of the ZINDO calculation suggested another possible interpretation, i.e. the emission from the LMCT state for luminescence of 1NEa. Note that the ZINDO calculation is assuming the conformation of the excited state being the same as that of the ground state. The third possibility does not exclude the second one. We can then form the picture of the emission from the excited state which may be the twisted carbonyl conformation having some metal character to the ground state of the π-complex form.

4. Conclusion

Although 1NEa has only one naphthalene ring, new longer wavelength emissions, i.e. excimer-like emissions, appeared by the addition of Mg^{2+} and Ca^{2+}. Therefore, the ab initio molecular orbital calculations (Gaussian 98) using both the HF SCF and DFT methods with 6-31G and 6-31+G(d) basis sets were carried out for 1NEa to investigate the cause of these new longer wavelength emissions. For the metal complex of 1NEa, a new transition band at the longer wavelength was obtained by the molecular orbital calculations. This transition band would correspond to the absorption band of the new longer wavelength emission.

Acknowledgements

This present work was supported by a Grant-in-aid for Encouragement of Young Scientists, Nos. 07740536 and 11740405, from the Ministry of Education, Science and Culture.

References

[1] A.P. De Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.

[2] P. Buhlmann, E. Pretsch, E. Bakker, Chem. Rev. 98 (1998) 1593.

[3] Y. Suzuki, T. Morozumi, H. Nakamura, M. Shimomura, T. Hayashita, R.A. Bartsh, J. Phys. Chem. B 102 (1998) 7910.

[4] J. Kawakami, A. Fukushi, S. Ito, Chem. Lett. (1999) 955.

[5] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.6, Gaussian, Inc., Pittsburgh, PA, 1998.

[6] T. Morozumi, H. Nakamura, Photochemistry 31 (2000) 108.