

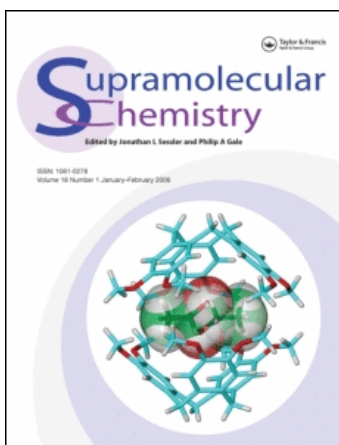
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Bichromophoric Naphthalene Derivatives of Ethylenediaminetetraacetate: Fluorescence from Intramolecular Excimer, Protonation and Complexation with Zn^{2+} and Cd^{2+}

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Chelating water-soluble bichromophoric compounds were designed by linking two naphthalene rings with an ethylenediaminetetraacetate (edta) chain through amide linkages, and characterized by fluorescence and NMR spectroscopies: the bichromophores studied were 1,4-bis(methylenecarboxy)-1,4-bis(*N*-1-naphthylacetamide)-1,4-diazabutane, abbreviated as (edta1nap) H_2 , and the corresponding 2-naphthylacetamide, abbreviated as (edta2nap) H_2 . Completely deprotonated species M^{2-} that formed in basic solution exhibited an intense emission from intramolecular excimer at 440 nm for (edta1nap) $^{2-}$ and 404 nm for (edta2nap) $^{2-}$, while emission from monomeric naphthyl group was comparatively very weak. Geometry optimization based on Density Functional Theory showed that two naphthyl groups in an M^{2-} molecule faced each other in such a way that an intramolecular excimer was readily formed by light excitation. Protonation on amino nitrogen affected monomer–excimer interconversion in different modes for the two compounds: the excimer emission was strengthened in the resulting (edta1nap) H^- , but was weakened in (edta2nap) H^- . Upon coordination with Zn^{2+} , the excimer band of (edta1nap) $^{2-}$ as well as (edta2nap) $^{2-}$ was strengthened in a linear manner with $[Zn]/[L]$; concurrently monomer emission was weakened. Coordination of (edta2nap) $^{2-}$ with Cd^{2+} resulted in a large decrease in the excimer emission, while the emission of (edta1nap) $^{2-}$ was almost unchanged. The formation of intramolecular excimer, which is highly sensitive to protonation and complexation, is due to the strictly defined molecular conformation.

Keywords: Fluorescent chemosensors; Naphthalene derivatives; Metal ion recognition; Excimer emission

INTRODUCTION

Some chromophores including highly conjugated hydrocarbons can form excimers as a result of collision between an excited molecule and an unexcited identical molecule, and exhibit fluorescence from excimers in addition to emission from monomeric (or isolated) molecules [1]. When two identical chromophoric groups are linked by a short flexible chain, the resulting bichromophoric molecule is capable of forming an intramolecular excimer when the interlinking chain is appropriately designed. Convincing evidence for the formation of intramolecular excimers has been given by studies of naphthalene-based bichromophores [2–10]. In a series of 1,*n*-bis(1-naphthyl)alkanes (where $n = 1–4$) and the corresponding 2-naphthyl derivatives, for example, only the propane derivatives ($n = 3$) exhibit an intramolecular excimer band at approximately 400 nm and the others show only a monomeric naphthalene band at 335 nm; only when $n = 3$, two naphthalene rings in a molecule are permitted to adapt to a parallel stack required for singlet-excimer formation, while the other alkyl chains hinder such adaptation because of the steric constraints [3,4]. In 1,*n*-bis(naphthalenecarboxy)oxaalkanes in acetonitrile, intramolecular excimers are formed as a result of a conformational equilibrium between the “extended” and “folded” species, and the excimer formation is most efficient for chain

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length of $n = 5$ [2]. These studies have clearly demonstrated that the formation of intramolecular excimer requires a preorganized structure in which two chromophores can approach each other close enough to form a face-to-face stack during the excited-state lifetime. Since the binding force in intramolecular excimers is very weak, excimer formation is highly sensitive to the environment. A bichromophoric compound of naphthalene linked by polyamine, for example, forms excimer solely in basic media; in acidic media the interlinking polyamine chain is fully protonated, and the resulting positive charges on the chain mutually have a large electrostatic repulsion to obstruct a bending movement required for excimer formation [5]. Thus, bichromophoric naphthalene derivatives provide interesting systems for studying weak non-covalent binding forces, which are essential in supramolecular assemblies. For bichromophoric naphthalene compounds bearing metal-binding sites in the interlinking chains, the excimer fluorescence was reported to be strongly influenced by complexation with metal ions in acetonitrile [2,11,12]. Such bichromophores are expected to provide a new type of fluorescent chemosensors based on monomer–excimer interconversion, with a high sensitivity toward specific metal ions. The majority of bichromophoric naphthalene compounds reported already are insoluble in water because of the hydrophobicity of chromophoric groups, except a family of polyamine derivatives [5,13,14]. Our special interest is directed to water-soluble bichromophores because a variety of forces related to hydrophobic interaction (or solvent-exclusion effect) and protonation are operative in aqueous systems and because molecular sensors functioning in aqueous systems are of obvious importance. In this work, we have designed bichromophores **1** and **2** shown in Scheme 1, abbreviated as (edta1nap) H_2 and (edta2nap) H_2 , respectively, with acidic protons; in each compound, two naphthalene units are linked by amide bonds to an ethylenediaminetetraacetate (edta) chain, which contains amino nitrogen atoms as electron-donating sites. The amide

groups are predicted to define the effective length and conformation of the interlinking chain because of their planarity [15,16]. As a result of the combined effects of these functional groups, two naphthyl groups in a molecule are expected to have a mutual geometrical relation favorable for forming an excimer under specific conditions. Carboxylate groups endow the compounds with water solubility, and also enhance the complexation capacity to form stable metal complexes over a wide pH range. This paper reports the syntheses of these amide-based bichromophoric naphthalene compounds (Scheme 1) and their emission properties; the slight difference between the structures of the isomers results in their quite distinctive spectroscopic properties, which are highly sensitive to protonation and complexation with Zn^{2+} and Cd^{2+} .

RESULTS AND DISCUSSION

1H NMR: Identification of Species Formed in Aqueous Media

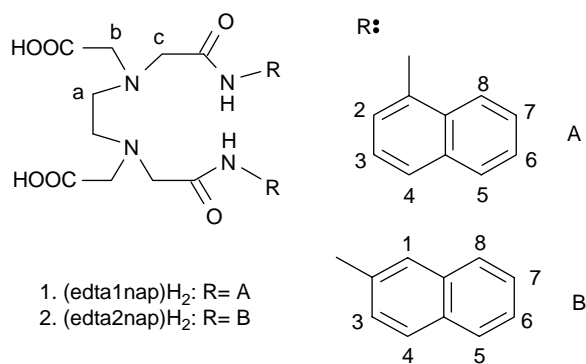
The formation of the bis(naphthylamide) derivatives shown in Scheme 1 has been confirmed by 1H NMR and electrospray mass spectroscopy, as described in Experimental. The pD dependences of the 1H NMR chemical shifts observed for (edta1nap) H_2 and (edta2nap) H_2 are shown in Figs. 1 and 2, respectively. In both compounds, the aliphatic protons *a*, *b* and *c* (labeled as shown in Scheme 1) shifted downfield with decreasing pD in the range 5–9, indicating that the amino nitrogen atoms were protonated prior to the carboxylate oxygen atoms. The shift of proton *i* upon protonation is given by the following function of pD [15]:

$$\delta_i(pD) = \{\delta_{0,i} + \delta_{1,i}K_D[D^+]\}/\{1 + K_D[D^+]\} \quad (1)$$

Here K_D is the protonation constant in D_2O media, $[D^+]$ is D^+ concentration given by 10^{-pD} , and $\delta_{0,i}$ is the chemical shift of proton *i* in the completely deprotonated species M^{2-} , and $\delta_{1,i}$ is the δ_i values of the protonated species MH^- . The shifts of all proton signals were well reproduced by Eq. (1) with $\log K_D$ values given in the figure captions of Figs. 1 and 2. The $\log K_D$ is the logarithmic constant of equilibrium between M^{2-} and MH^- species; in the latter species the amino nitrogen is protonated. A small downfield shift was observed for proton (labeled *b*) in $-CH_2CO_2^-$ groups for the 1-naphthyl derivative at pD below ca. 5.5. In such a low pD region, protonation occurs on the carboxylate oxygen, resulting in the formation of MH_2 species.

Fluorescence Spectra and Protonation

Figure 3 shows that the two naphthyl derivatives exhibit quite different emission spectra with



SCHEME 1

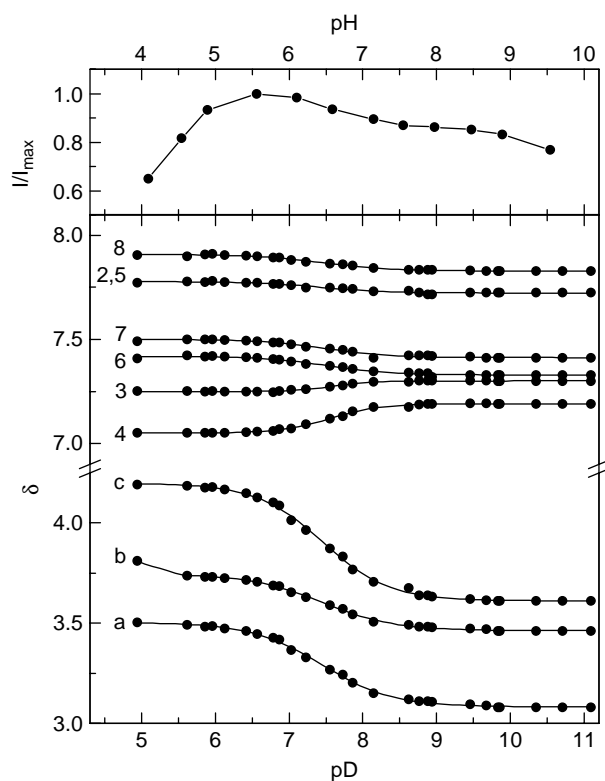


FIGURE 1 (Top) pH dependence of emission intensity at 440 nm ($\lambda_{\text{exc}} = 330$ nm) for $(\text{edta1nap})\text{H}_2$; the data points are normalized to the intensity (I_{max}) at pH = 5.6. (Bottom) pD dependence of ^1H NMR chemical shifts (referenced to DSS) of $(\text{edta1nap})\text{H}_2$; for labeling see Scheme 1. The solid lines were calculated by Eq. (1) with $\log K_D = 7.45$. The pD and pH axes are displaced by one unit for the aid of comparison of NMR and fluorescence data, because the $\log K$ in $\text{H}_2\text{O}-d_2$ is ca. 0.9 higher than in H_2O as reported for other weak acids [17].

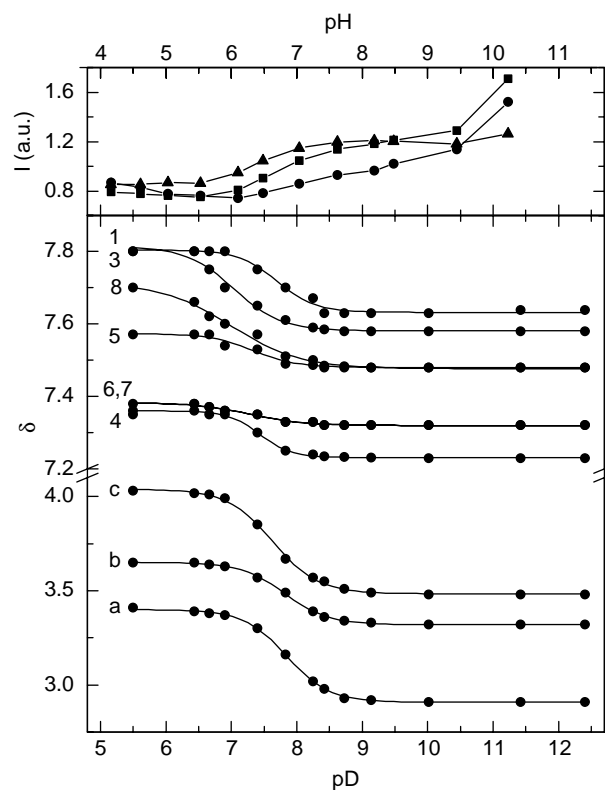


FIGURE 2 (Top) pH dependence of the emission intensity (a.u.) for $(\text{edta2nap})\text{H}_2$: circle, excimer-to-monomer intensity ratio, I_E/I_M ; square, excimer intensity, I_E ; triangle, monomer intensity, I_M . I_E and I_M are intensities at 404 nm and 355 nm, respectively. (Bottom) pD dependence of ^1H NMR chemical shifts (referenced to DSS) of $(\text{edta2nap})\text{H}_2$; for labeling see Scheme 1. The solid lines were calculated by Eq. (1) with $\log K_D = 7.84$. The pD and pH axes are displaced by one unit for the aid of comparison of NMR and fluorescence data [17].

different pH dependences in aqueous solutions. The 2-aminonaphthyl derivative, $(\text{edta2nap})\text{H}_2$, exhibits an intense structureless band at 404 nm, and a shoulder at about 350 nm in strongly basic solutions. The shape and the position of the major band agree with those reported for the excimer band of naphthalene, and the shoulder corresponds to the emission band of monomeric (or isolated) naphthalene [5,13,14]. The excimer band is assignable to an intramolecular excimer rather than an intermolecular excimer, because the concentration, 5×10^{-5} M, is low enough to suppress the formation of the latter [2]. The intensities of the excimer (I_E) and the monomer (I_M) bands are plotted as functions of pH in Fig. 2; the pH and pD axes are displaced by one unit for the aid of comparison of fluorescence and NMR data, because the $\log K$ in $\text{H}_2\text{O}-d_2$ is ca. 0.9 higher than in H_2O as reported for other weak acids [17]. The ratio I_E/I_M was largest at pH 10, and was decreased with decreasing pH down to pH \approx 6. Below this pH, the spectral pattern was unchanged, and the I_E/I_M value remained constant (Fig. 2). The pH dependence of the emission spectrum is well correlated with the species identified by NMR:

the completely deprotonated species M^{2-} is capable of forming the intramolecular excimer more readily than the partially protonated species MH^- .

The emission spectrum of $(\text{edta1nap})\text{H}_2$ in basic solutions showed a broad intense band assignable to an intramolecular excimer at 440 nm, and a monomer band located at 360 nm was so weak as to be almost buried in the slope of the excimer band (Fig. 3). The wavelength of the excimer band is longer than that of the excimer band of $(\text{edta2nap})\text{H}_2$, and is close to 430 nm reported for 1,*n*-bis(naphthalenecarboxy)oxaalkanes in acetonitrile [2]. Similar difference ascribable to the substituent positions has been reported for 1,3-dinaphthylpropanes [3,4]. The excimer emission of $(\text{edta1nap})\text{H}_2$ was strengthened gradually with decreasing pH until pH 5.5, as shown in Fig. 1. With the further decrease of pH, the band was weakened rapidly to disappear at pH below 2.0. The comparison of this pH dependence with the pD dependence of NMR shifts (Fig. 1) suggests that: (1) the MH^- species forms the excimer more readily than M^{2-} , contrary to the pH dependence of excimer formation in the 2-naphthyl derivative; (2) the further protonation that occurs on carboxylate oxygen causes a

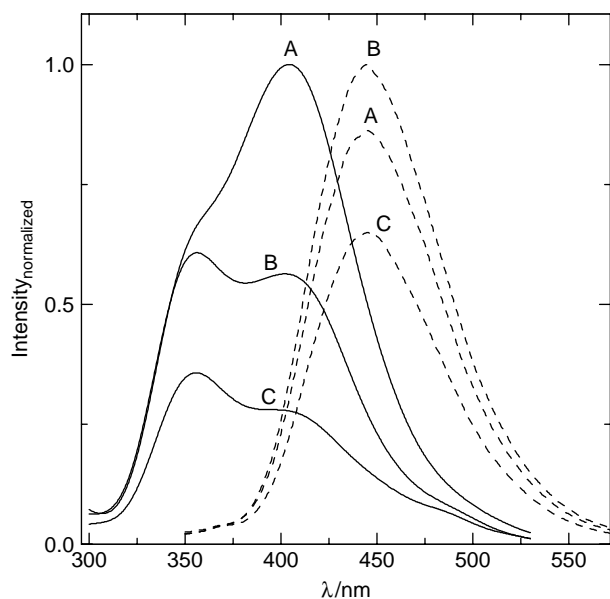


FIGURE 3 Emission spectra of (edta1nap) H_2 (broken line) and (edta2nap) H_2 (solid line) in aqueous solution at selected pH values: for (edta1nap) H_2 , (A) pH = 8.0, (B) 5.6 and (C) 4.1; for (edta2nap) H_2 , (A) 10.2, (B) 7.6 and (C) 5.0. The spectral intensities are normalized to the peak maximum of the most intense spectrum of each compound. $\lambda_{exc} = 330$ nm for (edta1nap) H_2 and 280 nm for (edta2nap) H_2 . Concentration = 1×10^{-4} M for (edta1nap) H_2 and 5×10^{-5} M for (edta2nap) H_2 .

conformational change and quenches the excimer emission in the MH_2 species.

Interannular Interaction at Different pH Values: UV and NMR Spectra

In an intramolecular excimer, two aromatic groups are commonly stacked face-to-face, and hence the formation of the excimer is facilitated by a preorganized structure in which the two aromatic groups approach close each other in the ground state [2–5]. Such geometrical features are supposed to exist in the M^{2-} and MH^- species of the 1-naphthyl and 2-naphthyl derivatives. The NMR δ values of the aromatic protons were changed in the pD region in which equilibrium occurred between the M^{2-} and MH^- species (Figs. 1 and 2). On the other hand, the electronic absorption spectra of the two derivatives did not show a significant change with pH: the electronic absorption spectrum of (edta1nap) $^{2-}$ exhibited a broad band at 280 nm with $\epsilon 1.5 \times 10^4$ $M^{-1} cm^{-1}$ (for each molecule containing two chromophores) independently of pH; (edta2nap) $^{2-}$ showed an absorption band at 280 nm ($\epsilon 1.5 \times 10^4$ $M^{-1} cm^{-1}$) and a shoulder at 290 nm throughout the pH range studied. These pH-independent UV spectra show that the interannular interaction is too weak to be detected as a change in the electronic structure of the ground state. The NMR shifts observed for the

aromatic protons can be interpreted by the ring current effect, which results in interannular interaction through space without causing a significant change in the electronic structure of the aromatic group; the ring current of an aromatic group induces angular-dependent magnetic field around the group, and leads to a decrease in δ for a proton existing above the molecular face of the group, and an increase in δ for a proton residing on the molecular plane of the group [18].

For (edta2nap) H_2 , the δ values of all aromatic protons in the M^{2-} species are smaller than the corresponding values in the MH^- species (Fig. 2). This observation suggests that the overlap of two aromatic groups in the M^{2-} species is larger than that in the MH^- species. One of major forces for intramolecular stacking of hydrophobic groups arises from the so-called hydrophobic interaction (or solvent exclusion effect) in aqueous media [19,20]. This effect is operative more efficiently when the interlinking chain is more flexible and adaptable to a close stack of the aromatic groups. In the MH^- species, the added proton is supposed to be rapidly exchanged between two equivalent amino nitrogen atoms in the edta chain, because the ethylene protons show a single NMR signal. The resulting intramolecular hydrogen bonding makes the edta chain so rigid as to define the molecular conformation in the MH^- species probably in such a manner that two naphthyl groups are slipped away less favorably for the excimer formation, and the inflexibility of the chain opposes the hydrophobic interaction. The M^{2-} species does not involve hydrogen bonding, and hence the edta chain may be flexible enough to allow hydrophobic interaction effective; the geometrical relation between two naphthyl groups in the ground state of the M^{2-} species can be preorganized favorably for the formation of the intramolecular excimer in aqueous media. Thus, the pH dependence of the excimer emission can be interpreted consistently by the pD dependence of δ of aromatic protons.

In the NMR of (edta1nap) $^{2-}$, protons 3 and 4 shifted upfield with $\Delta\delta = -0.05$ and -0.1 , respectively, upon protonation, while the other protons shifted downfield ($\Delta\delta \approx 0.05$). The absolute values of $\Delta\delta$ are much smaller than those in (edta2nap) $^{2-}$, and more importantly there are two types of proton signals that shift in opposite directions. These NMR shifts suggest that two aromatic groups are reoriented by protonation on the amino nitrogen but the overall stacking mode is not significantly altered. Consequently, fluorescence is dominated by excimer rather than monomer throughout the pH region studied, and the quantum yield is increased by enhancement of the molecular rigidity in the protonated species. These properties are quite different from those of the 2-naphthyl derivative.

DFT (Density Functional Theory) Calculation: Molecular Conformation and Role of Amide Group

With the objective of comparing the orientations of naphthyl groups in the two compounds, geometry optimizations were carried out on the basis of Density Functional Theory (DFT) by using program Gaussian 98 [21] on a Compaq Tru64 UNIX V5.1 computer. The hybrid B3LYP [22,23] in conjunction with the 3-21G* basis set [24] was applied for optimization of all stationary points in the gas phase. All geometry optimizations were followed by frequency calculations at the same level of the theory in order that the stationary points were characterized as true minima. Carboxymethyl groups were excluded in the geometry optimizations so that the true geometries were obtained readily and unequivocally for the conformations of the naphthyl-interlink-naphthyl systems; otherwise, various orientations of carboxymethyl arms obtained with small energy differences led to ambiguity in the geometry of the interlinking system. The optimized model molecules were 1,4-bis(*N*-1-naphthylacetamide)-1,4-diazabutane (abbreviated as 1napazb) and the corresponding 2-naphthylacetamide (abbreviated as 2napazb), and their optimized geometries represent the conformations of the most important species M^{2-} in which the amino nitrogen atoms are neutral without being protonated. Figure 4 displays the obtained structures; each structure has a C_2 symmetry.

In the optimized structures, two naphthyl groups basically face each other; the angles between the molecular planes of two naphthyl groups are 27° and 20° in 1napazb and 2napazb, respectively. The distance between the molecular centers of two naphthyl groups is 7.630 Å in 1napazb and 8.160 Å in 2napazb. These distances are much longer than 3.4 Å predicted for the van der Waals contact of aromatic molecules. In aqueous media, however, the two aromatic groups may approach closer due to the hydrophobic effect. Thus, the naphthyl groups can orient favorably for the formation of a parallel

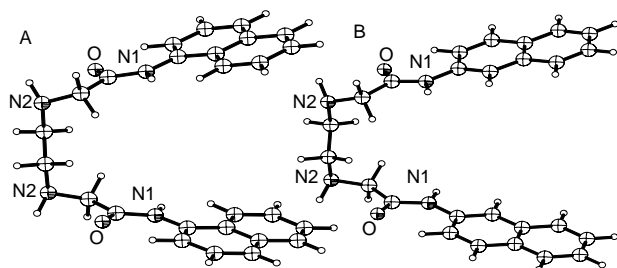


FIGURE 4 Geometries optimized by DFT (B3LYP/3-21G*) for naphthyl-interlink-naphthyl systems in the M^{2-} species of (A) (edta1nap) H_2 and (B) (edta2nap) H_2 . Carboxymethyl groups were excluded in the optimization for simplicity: the optimized model molecules are (A) 1,4-bis(*N*-1-naphthylacetamide)-1,4-diazabutane and the corresponding (B) 2-naphthylacetamide derivative.

stack upon light excitation; this is consistent with the observation of the strong intramolecular excimer bands for (edta1nap) $^{2-}$ and (edta2nap) $^{2-}$ in basic solutions. The naphthyl groups are slightly closer in 1napazb than in 2napazb, although the angle between the molecular planes is slightly larger in the former than in the latter. The angle between the naphthyl molecular plane and a vector connecting two naphthyl molecular centers is 75° in 1napazb and 80° in 2napazb; two aromatic rings are less slipped away in the former. On the whole, the geometry in 1-napazb is more favorable for the formation of face-to-face stack upon excitation. These structural features consistently explain the reason why (edta1nap) $^{2-}$ more readily forms intramolecular excimers with a longer emission wavelength than (edta2nap) $^{2-}$.

The interlinking chain of edta is apparently much longer than the chain lengths that have been claimed to be advantageous to intramolecular excimer formation [2-5]. The incorporation of rigid amide groups in the interlinking chain, however, shortens the effective length, and leads to conformation that are favorably preorganized for the intramolecular excimer formation in (edta1nap) $^{2-}$ and (edta2nap) $^{2-}$. In addition, the combined effects of the rigidity of amide groups and the protonation on amino groups result in the novel pH dependence of the emission spectra.

Fluorescence Spectra and Complexation With Zn^{2+} And Cd^{2+}

In buffer solutions used for studying complex formation, the intensity ratios of the monomer and excimer emissions observed for uncoordinated ligands were slightly different from the corresponding values observed in the experiments of pH dependence, probably owing to the nature of the coexisting electrolytes. The difference was, however, so small that the essential features of the emission spectra were identical.

As $[Zn]/[L]$ increased, the excimer band of (edta1nap) $^{2-}$ was rapidly intensified and shifted to shorter wavelengths, as shown in Fig. 5; the weak monomer band observed for the free ligand was buried in the slope of the excimer band at high Zn concentrations. In correlation with the blue shift in the emission band, the absorption band of (edta1nap) $^{2-}$ showed a 10 nm red-shift and a slight decrease in molar absorptivity upon coordination with Zn: at $[Zn]/[L] = 0$, $\lambda_{max} = 282$ nm, $\epsilon = 1.0 \times 10^4$ M $^{-1}$ cm $^{-1}$ in an NaOH/NaHCO $_3$ (pH 10) buffer solution; at $[Zn]/[L] = 1$, $\lambda_{max} = 292$ nm, $\epsilon = 0.8 \times 10^4$ M $^{-1}$ cm $^{-1}$. This red shift in the UV spectrum is ascribable to the perturbation of the conjugated system by the coordination of amide oxygen with a Zn^{2+} ion; this effect results in the blue shift of the emission band. In the Cd-(edta1nap) $^{2-}$ system, both the

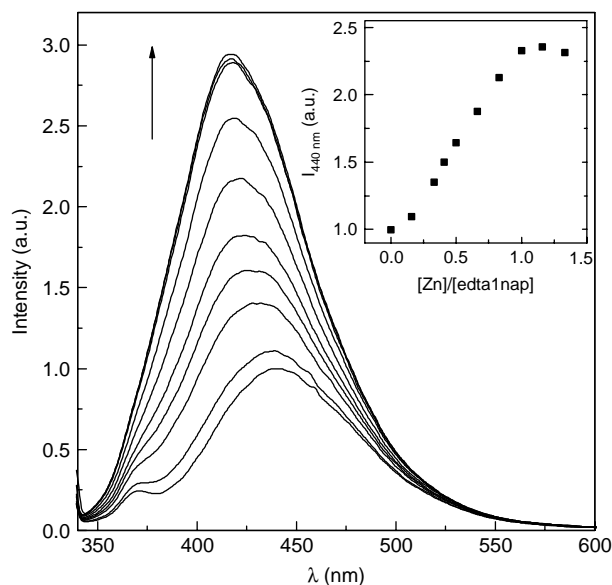


FIGURE 5 Fluorescence spectra of $(\text{edta1nap})\text{H}_2$ in the presence of Zn^{2+} at different $[\text{Zn}]/[(\text{edta1nap})\text{H}_2]$ ratios 0 to 1.33, in buffer solution at pH = 10 (0.1 M NaOH/0.05 M NaHCO_3); concentration of $(\text{edta1nap})\text{H}_2 = 5 \times 10^{-5}$ M. Inset: Intensity of emission (a.u.) at 440 nm as a function of $[\text{Zn}]/[(\text{edta1nap})\text{H}_2]$.

excimer and monomer bands were weakened with increasing $[\text{Cd}]/[\text{L}]$, and the intensity change was very small as it might partially include effect of a slight variation in the ligand concentration (Fig. 6). For $(\text{edta2nap})^{2-}$, the excimer emission was strengthened while the monomer band was weakened with increasing $[\text{Zn}]/[\text{L}]$ (Fig. 7). In contrast, complexation with Cd weakened both the excimer and the

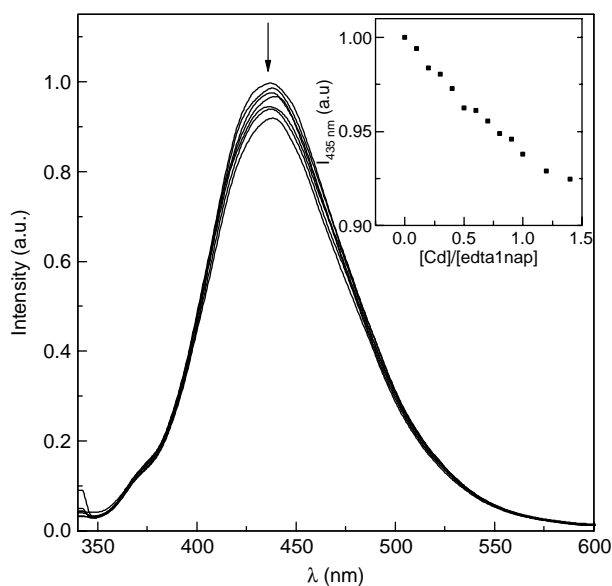


FIGURE 6 Fluorescence spectra of $(\text{edta1nap})\text{H}_2$ in the presence of Cd^{2+} in the concentration range 0 to 1.4 equiv., in buffer solution at pH = 10 (0.1 M NaOH/0.05 M NaHCO_3). Concentration of $(\text{edta1nap})\text{H}_2 = 5 \times 10^{-5}$ M. Inset: Intensity of emission (a.u.) at 435 nm as a function of $[\text{Cd}]/[(\text{edta1nap})\text{H}_2]$.

monomer emission (Fig. 8); the degree of the change was much larger than that observed for $\text{Cd}(\text{edta1nap})^{2-}$.

All spectral changes described above were obtained at pH 10, at which the emission spectrum of every system was highly reproducible and gave reliable results. The NMR shifts indicate that the ligands are almost deprotonated at pH 8, and hence the metal complexes are supposed to be readily formed at the lower pH. The spectral changes observed for $(\text{edta1nap})^{2-}$ at pH 8.5 were essentially identical with those at pH 10. For $(\text{edta2nap})^{2-}$, the relative intensities of the monomer and the excimer band of the uncoordinated ligand were sharply altered around pH 8 (Fig. 3), and consequently the spectral pattern observed for the metal complexes at pH 8.5 was not well reproduced. Tendency of changes in emission intensity with $[\text{M}]/[\text{L}]$ was, however, similar to that observed at pH 10. The emission intensity of every metal–ligand system was changed in a linear manner with $[\text{M}]/[\text{L}]$ ratio up to 1.0, and remained constant above this ratio at both pH 8.5 and 10 (Figs. 5–8). This discontinuity at $[\text{M}]/[\text{L}] = 1$ indicates the formation of 1:1 complexes. X-ray studies of Zn^{2+} and Cd^{2+} complexes of amide-based aza-macrocycles with pendant carboxylate arms have shown that the metal complexes commonly have a distorted octahedral coordination which consists of two carboxylate oxygen atoms, two amino nitrogen atoms and one amide oxygen atom from a single ligand molecule, the sixth coordination site being occupied by an oxygen atom

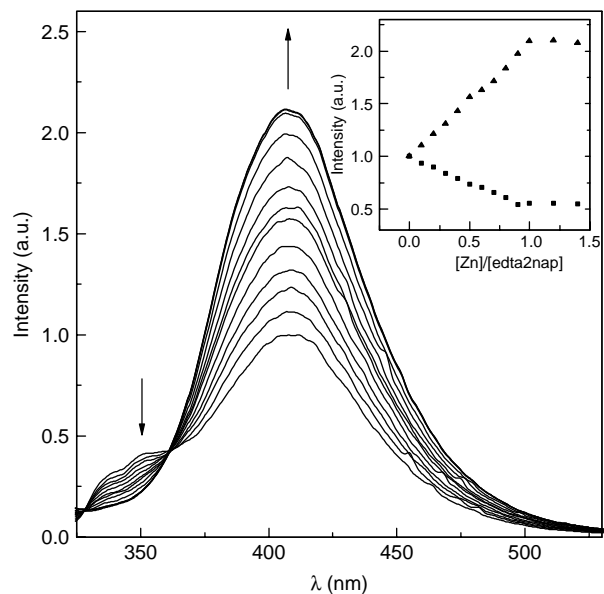


FIGURE 7 Fluorescence spectra of $(\text{edta2nap})\text{H}_2$ in the presence of Zn^{2+} in the concentration range 0 to 1.4 equiv., in buffer solution at pH = 10 (0.1 M NaOH/0.05 M NaHCO_3). Concentration of $(\text{edta2nap})\text{H}_2 = 1 \times 10^{-5}$ M. Inset: Intensity of emission (a.u.) as a function of $[\text{Zn}]/[(\text{edta2nap})\text{H}_2]$: triangle, at $\lambda_{\text{em}} 410$ nm; square, at $\lambda_{\text{em}} 350$ nm.

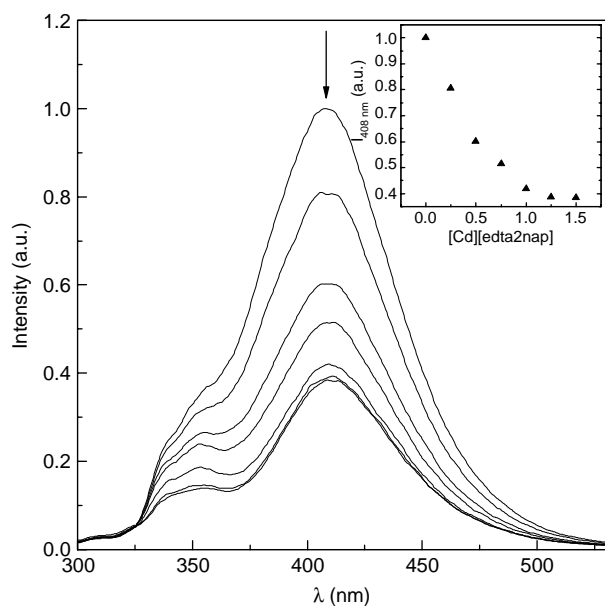


FIGURE 8 Fluorescence spectra of (edta2nap) H_2 in the presence of Cd^{2+} in the concentration range 0 to 1.5 equiv., in buffer solution at pH = 10 (0.1 M NaOH/0.05 M $NaHCO_3$). Concentration of (edta2nap) H_2 = 1×10^{-4} M. Inset: Intensity of emission (a.u.) at 408 nm as a function of $[Cd]/[(edta2nap)H_2]$.

from a water molecule [15,25,26]. A similar coordination mode is expected to be formed in the metal complexes studied in this work. The coordination of amide oxygen in Zn-(edta1nap) is evidenced by the red shift observed for the absorption band, as described above. For Zn-(edta2nap), no significant change in the absorption and emission wavelengths was observed, suggesting that none of amide oxygen atoms occupies the first coordination sphere probably for steric reason, and instead the coordination of two water oxygen atoms complete a six-coordination. Thus, the two Zn^{2+} complexes are formulated as $[ML(H_2O)_n]^0$ ($n = 1$ or 2), which is the major species around pH 8.5. At pH 10, $[ML(H_2O)_n]^0$ may be converted in part to a hydroxo-complex. However, the spectral changes observed at pH 8.5 and 10 are identical. This observation suggests that OH group is merely substituted for water molecule without exerting a significant influence on the conformation as well as the coordination mode of the bichromophoric ligand; consequently the high emission efficiency is maintained even at the higher pH. A hydroxo-complex in which a coordinated donor atom of the ligand is substituted by OH group would be less emissive, but such a substitution is supposed to hardly occur at pH 10 in the complexes.

In a molecule of the uncoordinated compounds, two naphthyl groups face each other so as to form excimer readily upon photoexcitation, as evidenced by the DFT calculation. A similar structure is supposed to be more strictly defined by coordinate bonds in the metal complexes. When a chelating fluorescent molecule is coordinated to a metal ion, generally two

opposing effects are operative; (1) the structural rigidity of the complex molecule increases the quantum efficiency for fluorescence, and (2) the so-called heavy atom effect decreases the efficiency [27]. Usually the former fluorescence enhancement is more effective for Zn complexes than for the corresponding Cd complexes, and the latter quenching effect is more pronounced in Cd complexes [15,28]. This common tendency was also observed for the excimer emission of the chelating bichromophores studied. In addition to these metal effects, the excimer emission is naturally dependent on the molecular conformation of the metal complexes. In fact, the decrease in the monomer-emission intensity in the Zn-(edta2nap) $^{2-}$ system occurs concurrently with the increase in the excimer emission intensity, suggesting that the conversion of the monomer to the excimer is facilitated, probably as a result of a closer approach of two naphthyl groups in the Zn complex. The large spectral changes observed for the excimer emission suggest that the chelating bichromophoric compounds (edta1nap) H_2 and (edta2nap) H_2 are potential molecular sensors based on monomer–excimer interconversion; the origin of this sensing capability is different from that reported already for monochromophoric sensors in which a change in fluorescence is caused by a direct protonation on the conjugated system or by a photo-induced electron transfer (PET) between protonation and emission sites [29–34].

CONCLUSION

The chelating bichromophoric compounds synthesized in this work form intramolecular excimer in a highly efficient monomer–excimer interconversion, and fluorescence emission from the intramolecular excimer is strongly dependent on protonation and coordination with metal ions. The slight structural difference between the isomers results in the quite distinctive spectroscopic properties. These characters are due to the preorganized structures in which two naphthyl groups basically face each other, as a result of the molecular conformation of the interlinking chain that is strictly defined by the planarity of amide group. Such a feature is more pronounced by coordination with metal ions, to suggest a metal-sensing capacity, especially toward Zn^{2+} .

EXPERIMENTAL

Syntheses

1,4-bis(methylenecarboxy)-1,4-bis(N-1-naphthyl acetamide)-1,4-diazabutane, (edta1nap) H_2 , 1

(Edta1nap) H_2 was synthesized by a method similar to that reported for dtpa-bis(ethylamide)

(dtpa: diethylenetriaminepentaacetate) [35]: edta dianhydride (1.3 g, 5.0 mmol) was added little by little through a powder dispensing funnel to 1-aminonaphthalene (3.3 g, 17 mmol) dissolved in DMF (20 mL), with stirring at room temperature. After the resulting reaction mixture was left to stand overnight, any solid present was removed by filtration and the filtrate was concentrated to a viscous liquid. Addition of water (20 mL) to the liquid, followed by adjusting pH to 2 with conc. HCl, gave a pale pink solid. The solid was recrystallized repeatedly from hot ethanol until colorless crystals of **1** were obtained (1.3 g, 50%). ^1H NMR (400 MHz, D_2O - Na_2CO_3 , pD = 8.2, DSS): δ = 3.20 (s, 4H, assigned to H_a in **1**), 3.55 (s, 4H, H_b), 3.76 (s, 4H, H_c), 7.20 (d, 2H, J = 7 Hz, H_4), 7.30 (t, 2H, J = 7 Hz, H_3), 7.33 (t, 2H, J = 8 Hz, H_6), 7.42 (t, 2H, J = 8 Hz, H_7), 7.72 (d, 4H, J = 7 Hz, H_5), 7.73 (d, 2H, J = 8 Hz, H_2), 7.83 (d, 2H, J = 8 Hz, H_8); MS (ESI): m/z (%): 543.1 (100) [$(M + \text{H})^+$]; elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{30}\text{O}_6\text{N}_4\cdot 2\text{C}_2\text{H}_6\text{O} \cdot 4\text{H}_2\text{O}$: C, 57.87, H, 6.95, N, 7.94; found: C, 57.65, H, 6.89, N, 7.89.

1,4-bis(methylenecarboxy)-1,4-bis(N-2-naphthyl acetamide)-1,4-diazabutane (edta2nap) H_2 , **2**

(Edta2nap) H_2 was synthesized by a method similar to that for (edta1nap) H_2 . To 2-aminonaphthalene (0.50 g, 3.5 mmol) dissolved in DMF (20 mL) was added edta dianhydride (0.35 g, 1.4 mmol) at room temperature. After the resulting reaction mixture was left to stand overnight, any solid present was removed by filtration and the filtrate was concentrated to a viscous liquid. Addition of water (20 mL) to the liquid, followed by adjusting pH to 2 with conc. HCl, gave a colorless solid. The solid was washed with water and then ethanol to give **2** (0.58 g, 54%); the product in its acid form was very slightly soluble in water, while in the anionic form was readily soluble. ^1H NMR (400 MHz, D_2O - Na_2CO_3 , pD = 10.0, DSS): δ = 2.90 (s, 4H, H_a), 3.32 (s, 4H, H_b), 3.47 (s, 4H, H_c), 7.64 (s, 2H, H_1), 7.57 (d, 2H, H_3), 7.47 (tt, 4H, H_6 and H_7), 7.32 (d, 2H, J = 7 Hz, H_5), 7.31 (d, 2H, J = 7 Hz, H_8), 7.22 (d, 2H, J = 8 Hz, H_4); MS (ESI): m/z (%): 543.1 (100) [$(M + \text{H})^+$]; elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{30}\text{O}_6\text{N}_4$: C, 66.16, H, 5.55, N, 10.28; found: C, 66.59, H, 5.66, N, 10.28.

Spectroscopic Measurements

The ^1H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer for H_2O - d_2 solutions at a probe temperature of approximately 23°C. The internal reference was sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). For the studies of pD dependence, a minimum quantity of a dilute KOH-d or HCl-d solution was used for adjusting the pD of the sample solutions. The pH value of each sample

solution was measured with a long-stem combination electrode inserted into the NMR tube after NMR experiments. The electrode was calibrated with standard aqueous buffers, and the measured pH values were converted to the pD values by the relation $\text{pD} = \text{pH}_{\text{meas}} + 0.45$ [36].

Luminescence spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer. For experiments of pH dependence, sample compounds were dissolved in 0.01 M NaCl solution by adding an equimolar amount of solid Na_2CO_3 , and the pH values of the sample solutions were adjusted by using 0.01 M HCl and 0.01 M NaOH so that the ionic strength was kept constant. For studies of metal complexation, stock solutions of the ligands were prepared by dissolving a suitable amount of the appropriate ligands in a 0.1 M NaOH/0.05 M NaHCO_3 buffer solution at pH 10 or in tris buffer at pH 8.5; the concentration of the sample solution was 10^{-5} – 10^{-4} M for which the spectrum intensity was in a suitable range and the formation of intermolecular excimer was suppressed. Stock solutions of Zn and Cd were prepared from the appropriate chlorides so that the concentration was about 30 times that of the stock solution of a ligand studied. Into a quartz fluorimeter cuvette, three mL of the stock solution of a ligand was admitted, and then about 10 μL aliquots of a metal stock solution were added with a calibrated micropipette so that the $[\text{Zn}]/[\text{L}]$ ratio was in a desired range. The resulting sample solution was shaken thoroughly for 3 min, and the emission spectrum was confirmed to be unchanged with time.

Absorption spectra were obtained with a Perkin-Elmer Lambda 20 UV-Vis spectrometer. Sample solutions were prepared by the same procedure as for the fluorescence measurements. The mass spectra were obtained for NH_3 -methanol solutions at the University of Arizona Mass Spectroscopy Facility (Tucson, AZ, USA). The elemental analyses were performed by Desert Analytics (Tucson, AZ, USA).

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