

Intramolecular exciplex formation and complexing behavior of 1-(2-naphthalenecarboxy)-*n*-(*p*-substituted benzenecarboxy)oxaalkanes as fluorescent chemosensors for calcium and barium ions

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Abstract

1-(2-Naphthalenecarboxy)-*n*-(*p*-substituted benzenecarboxy)oxaalkanes (2NPnX, X = H, Cl, CF₃, CN; *n* = 5, 6) as fluorescent sensors by exciplex emission for metal ions were synthesized. We investigated the relationship between the substitution effects and the metal ion recognition. Before the metal salts were added, the substitution effect was found. The fluorescence quantum yields (Φ_f) decrease as the electronegativity of the *p*-substituent of the acceptor benzoate increases. 2NPnCN (*n* = 5, 6) with the most negative free energy of electron transfer (ΔG_{ET}) showed the most efficient quenching and exciplex emission. When Li⁺, Na⁺, K⁺ and Mg²⁺ were added to the acetonitrile solution of 2NPnX (X = H, Cl, CF₃, CN; *n* = 5, 6), the shape and intensity of the fluorescence spectra did not change. However, the spectra of all the 2NPnXs significantly changed with the addition of Ca²⁺ and Ba²⁺. Especially, due to the large fluorescent enhancement factor of 2NPnCN (*n* = 5, 6) for Ca²⁺, they are well-suited for use as a fluorescent chemosensor for Ca²⁺.

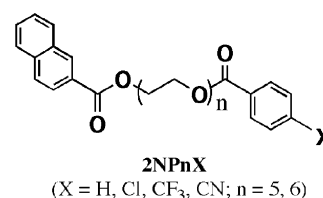
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1. Introduction

Metal ions and organic molecular recognition is a subject of considerable interest because of its implications in many fields such as biology, medicine, environmental, etc. In particular, the detection of metal cations involved in biological processes (sodium, potassium, calcium) has received considerable attention. Our aim is to design fluorescent sensors [1–3] that undergo photophysical changes as soon as possible upon cation binding. Many kinds of crown ether-type macrocyclic compounds have been used for analytical applications, such as chemical sensors and spectrophotometric analyses. In fluorometry applications, fluorescent reagents, which have two aromatic hydrocarbons at both terminals of a linear polyether as an analogue of a crown ether, have also been used [4–6]. The fluorescent aromatic hydrocarbons in these compounds are usually pyrene or anthracene [7]. The disadvantage of a pyrene or anthracene derivative is its ability to form an intermolecular excimer or exciplex even at very low

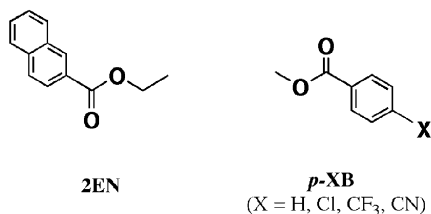
solution concentrations (10⁻⁵ mol dm⁻³) used for spectroscopic studies. It is difficult to distinguish intermolecular or intramolecular excimer or exciplex emissions at low concentrations. However, in naphthalene compounds, intermolecular interactions occur at greater than 10⁻¹ mol dm⁻³. Therefore, we have synthesized some naphthalene derivatives as fluorescent sensors for metal ions by intramolecular excimer or exciplex emission [8–12]. For example, we reported the relationship between the length of the polyether chain and metal ion recognition of 1,*n*-bis(1-naphthalenecarboxy)oxaalkanes (1NPnN, *n* = 1–6) and 1,*n*-bis(2-naphthalenecarboxy)oxaalkanes (2NPnN, *n* = 1–6) [12].



They have naphthalene rings at both termini of the linear polyether. When alkali metal salts were added to an acetonitrile solution of 1NPnN and 2NPnN (*n* = 1–6),

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the shape and intensity of the fluorescence spectra did not change, and when alkaline earth metal salts were added, changes in the fluorescence spectra of 1NP n N and 2NP n N ($n = 1$ –3) were also not observed. However, the spectra of 1NP n N and 2NP n N ($n = 4$ –6) were changed by the addition of calcium and barium salts. The value of log K for Ca²⁺ and Ba²⁺ were 2NP6N > 1NP6N > 2NP5N > 1NP5N \gg 2NP4N and 1NP4N. To attempt to construct excellent fluorescent chemosensors for metal ion recognition, better than 1NP n N and 2NP n N ($n = 5, 6$), we synthesized 1-(2-naphthalenecarboxy)- n -(p -substituted benzenecarboxy)oxaalkanes (2NP n X, X = H, Cl, CF₃, CN; $n = 5, 6$) as new fluorescent chemosensors.



2NP n X has 2-naphthalene as an electron donor (D) and p -substituted benzene as the electron acceptor (A). Especially, in the case of 2NP n CN ($n = 5, 6$) having a strong electron withdrawing group, a strong interaction can be expected between the two chromophores.

In this report, we first investigated the photophysical and photochemical properties of 2NP n X (X = H, Cl, CF₃, CN; $n = 5, 6$) before the addition of metal ions. Second, we investigated the substituent effects for metal ion recognition.

2. Experimental

2.1. General

The ¹H and ¹³C NMR spectra were recorded on a JEOL GX 270 spectrometer with TMS as the internal standard. The UV–visible absorption spectra were taken using a Hitachi U-2001 spectrometer. The fluorescence spectra were taken using a Hitachi F-4500 fluorophotometer.

Measurements of the fluorescence spectra were carried out in an acetonitrile solution of the 2NP n X (1.0×10^{-5} mol dm⁻³ where no intermolecular interaction was found) at room temperature, and alkali or alkaline earth metal salts [LiClO₄, NaClO₄, KClO₄, Mg(ClO₄)₂, Ca(ClO₄)₂ and Ba(ClO₄)₂] were added to the solution. To prevent any nonlinearity of the fluorescence intensity, 295 nm was chosen as the excitation wavelength. The fluorescence quantum yields were determined at room temperature relative to those of naphthalene (0.205 in a polar solvent) [5] for solutions of matched absorbance (0.1) at the excitation wavelength.

2.2. Synthesis

ω -(2-Naphthalenecarboxy)-oxaalkanol: The MS spectra of all the 2NP n Xs showed corresponding molecular ion peaks and similar fragments: 199 (naphthalene-COOC₂H₄⁺), 172 (naphthalene-CO₂H⁺), 155 (naphthalene-CO⁺), and 127 (naphthalene⁺). The preparation of 14-(2-naphthalenecarboxy)-3,6,9,12-tetraoxatetradecanol is typical for the ω -(2-naphthalenecarboxy)-oxaalkanol from 2-naphthoic acid and the corresponding polyethylene glycol. To a stirred solution of 5.00 g (21.0 mmol) of pentaerythritol, 1.81 g (10.5 mmol) of 2-naphthoic acid and 51.0 mg (0.42 mmol) of 4-dimethylaminopyridine (DMAP) in dichloromethane (15 cm³), 2.20 g (10.7 mmol) of *N,N*-dicyclohexyl carbodiimide (DCC) at 25 °C was added. The stirring was continued for 1 h at 0 °C and then overnight at room temperature. The white precipitate were filtered off and the filtrate was washed with 1 mol dm⁻³ HCl and then with saturated sodium bicarbonate. Drying over anhydrous magnesium sulfate and concentration under vacuum yielded a crude product. Chromatography on silica gel with acetone as the eluent yielded pure 14-(2-naphthalenecarboxy)-3,6,9,12-tetraoxatetradecanol (2.00 g, 48.5%). ¹H NMR (270 MHz, CDCl₃) δ 1.86 (1H, s, OH), 3.45–3.81 (16H, m, CH₂O), 3.88 (2H, t, CO₂CH₂CH₂, $J = 5.0$ Hz), 4.54 (2H, t, CO₂CH₂, $J = 5.0$ Hz), 7.49–8.66 (7H, m, naphthalene); ¹³C NMR (70 MHz, CDCl₃) δ 62.2, 64.7, 69.8, 70.8, 71.1, 71.1, 71.1, 71.2, 73.0 (OCH₂), 125.8, 127.1, 127.9, 128.2, 128.6, 128.7, 130.0, 131.6, 133.0, 136.0 (naphthalene), 167.2 (C=O).

17-(2-naphthalenecarboxy)-3,6,9,12,15-pentaoxaheptadecanol: ¹H NMR (270 MHz, CDCl₃) δ 1.87 (1H, s, OH), 3.55–3.77 (20H, m, CH₂O), 3.89 (2H, t, CO₂CH₂CH₂, $J = 5.0$ Hz), 4.54 (2H, t, CO₂CH₂, $J = 5.0$ Hz), 7.48–8.66 (7H, m, naphthalene); ¹³C NMR (70 MHz, CDCl₃) δ 61.8, 64.3, 69.3, 70.4, 70.6, 70.6, 70.7, 70.7, 72.6 (OCH₂), 125.3, 126.6, 127.5, 127.8, 128.1, 128.2, 129.4, 131.2, 132.5, 135.6 (naphthalene), 166.7 (C=O).

The 1-(2-naphthalenecarboxy)- n -(p -substituted benzenecarboxy)oxaalkanes (2NP n X, X = H, Cl, CF₃, CN, $n = 5, 6$): 2NP n Xs were prepared from the p -substituted benzoic acids and the corresponding ω -(2-naphthalenecarboxy)-oxaalkanol by the same method of preparation as the ω -(2-naphthalenecarboxy)-oxaalkanol. The MS spectra of all the 2NP n Xs showed corresponding molecular ion peaks and similar fragments: 77 (C₆H₅⁺), 199 (naphthalene-CO₂C₂H₄⁺), 172 (naphthalene-CO₂H⁺), 155 (naphthalene-CO⁺) and 127 (naphthalene⁺).

1-Benzenecarboxy-14-(2-naphthalenecarboxy)-3,6,9,12-tetraoxatetradecane (2NP5H): ¹H NMR (270 MHz, CDCl₃) δ 3.52–3.76 (12H, m, CH₂O), 3.80 (2H, t, Ph-CO₂CH₂CH₂, $J = 5.0$ Hz), 3.87 (2H, t, naphthalene-CO₂CH₂CH₂, $J = 5.0$ Hz), 4.45 (2H, t, Ph-CO₂CH₂, $J = 5.0$ Hz), 4.53 (2H, t, naphthalene-CO₂CH₂, $J = 5.0$ Hz), 7.40–8.64 (12H, m, naphthalene and Ph); ¹³C NMR (70 MHz, CDCl₃) δ 64.1, 64.3, 69.2, 69.3, 70.7, 70.7, 70.7, 70.8 (OCH₂), 125.3,

126.6, 127.5, 127.8, 128.1, 128.3, 128.3, 129.4, 131.2, 132.9, 135.6, 127.8, 129.7, 130.2, 132.5 (naphthalene and Ph), 166.8 (C=O).

1-(*p*-Chlorobenzenecarboxy)-14-(2-naphthalenecarboxy)-3,6,9,12-tetraoxatetradecane (2NP5Cl): ^1H NMR (270 MHz, CDCl_3) δ 3.40–3.75 (12H, m, CH_2O), 3.79 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.88 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.44 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.37–8.64 (11H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.7, 64.8, 69.6, 69.8, 71.1, 71.2, 71.2 (OCH_2), 125.8, 127.1, 127.9, 128.2, 128.6, 128.7, 129.2, 129.8, 131.6, 133.0, 136.1, 140.0 (naphthalene and Ph), 166.1 (C=O), 167.1 (C=O).

1-(2-Naphthalenecarboxy)-14-(*p*-trifluorobenzenecarboxy)-3,6,9,12-tetraoxatetradecane (2NP5CF₃): ^1H NMR (270 MHz, CDCl_3) δ 3.53–3.76 (12H, m, CH_2O), 3.81 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.87 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.48 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.58–8.64 (11H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.2, 64.6, 69.1, 69.3, 70.7, 70.8 (OCH_2), 121.2 (CF_3), 125.3, 125.4, 125.5, 126.6, 127.5, 127.8, 128.1, 128.3, 129.4, 130.1, 131.2, 132.5, 133.4, 135.6 (naphthalene and Ph), 165.3 (C=O), 166.7 (C=O).

1-(*p*-Cyanobenzenecarboxy)-14-(2-naphthalenecarboxy)-3,6,9,12-tetraoxatetradecane (2NP5CN): ^1H NMR (270 MHz, CDCl_3) δ 3.41–3.76 (12H, m, CH_2O), 3.80 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.88 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.48 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.48–8.65 (11H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.5, 65.1, 69.3, 69.6, 70.7, 70.9, 71.0, 71.3 (OCH_2), 116.8 (CN), 118.2, 125.6, 126.9, 127.7, 128.2, 128.4, 128.5, 129.6, 130.5, 131.4, 132.4, 132.8, 134.3, 135.9 (naphthalene and Ph), 165.2 (C=O), 166.9 (C=O).

1-Benzenecarboxy-17-(2-naphthalenecarboxy)-3,6,9,12,15-pentaoxaheptadecane (2NP6H): ^1H NMR (270 MHz, CDCl_3) δ 3.30–3.75 (16H, m, CH_2O), 3.81 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.88 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.46 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.49–8.65 (12H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.4, 64.5, 69.5, 69.6, 70.9, 70.9, 71.0, 71.0, 71.0 (OCH_2), 125.6, 126.9, 127.7, 128.0, 128.4, 128.5, 128.6, 129.6, 130.0, 130.5, 131.4, 132.8, 133.2, 135.9 (naphthalene and Ph), 166.8 (C=O), 167.0 (C=O).

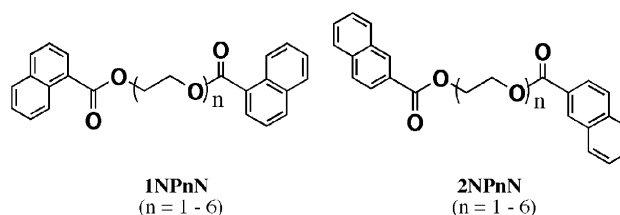
1-(*p*-Chlorobenzenecarboxy)-17-(2-naphthalenecarboxy)-3,6,9,12,15-pentaoxaheptadecane (2NP6Cl): ^1H NMR (270 MHz, CDCl_3) δ 3.46–3.75 (16H, m, CH_2O), 3.80 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.88 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.45 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.38–8.64 (11H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.2, 64.3, 69.2, 69.3, 70.6, 70.7, 70.7, 70.8 (OCH_2), 125.3, 126.6, 127.5, 127.8, 128.1,

128.2, 128.7, 129.4, 131.1, 131.2, 132.5, 135.6, 139.4 (naphthalene and Ph), 166.7 (C=O).

1-(2-Naphthalenecarboxy)-17-(*p*-trifluorobenzenecarboxy)-3,6,9,12-pentaoxa heptadecane (2NP6CF₃): ^1H NMR (270 MHz, CDCl_3) δ 3.52–3.76 (16H, m, CH_2O), 3.82 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.88 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.49 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.48–8.64 (11H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.7, 65.1, 69.6, 69.8, 71.1, 71.1, 71.2, 71.2 (OCH_2), 121.2 (CF_3), 125.8, 125.9, 127.1, 127.9, 128.2, 128.6, 128.7, 130.6, 133.0, 133.9, 136.1 (naphthalene and Ph), 166.8 (C=O), 167.2 (C=O).

1-(*p*-Cyanobenzenecarboxy)-17-(2-naphthalenecarboxy)-3,6,9,12,15-pentaoxa heptadecane (2NP6CN): ^1H NMR (270 MHz, CDCl_3) δ 3.40–3.76 (16H, m, CH_2O), 3.81 (2H, t, $\text{Ph-CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 3.88 (2H, t, naphthalene- $\text{CO}_2\text{CH}_2\text{CH}_2$, $J = 5.0$ Hz), 4.49 (2H, t, $\text{Ph-CO}_2\text{CH}_2$, $J = 5.0$ Hz), 4.54 (2H, t, naphthalene- CO_2CH_2 , $J = 5.0$ Hz), 7.48–8.64 (11H, m, naphthalene and Ph); ^{13}C NMR (70 MHz, CDCl_3) δ 64.5, 65.1, 69.3, 69.6, 70.9, 70.9, 71.0, 71.0 (OCH_2), 116.8 (CN), 118.2, 125.6, 126.9, 127.7, 128.0, 128.4, 128.5, 129.6, 130.5, 131.4, 132.4, 132.8, 134.3, 135.9 (naphthalene and Ph), 165.2 (C=O), 166.9 (C=O).

The methyl *p*-substituted benzoate (*p*-XB; X = H, Cl, CF₃, CN) was prepared from the corresponding *p*-substituted benzoic acid and methanol by the same method for the preparation of 2NPnX. The physical data for these compounds were identical with the literature values. The preparation of ethyl 2-naphthoate (2EN) was reported in [12].



3. Results and discussion

3.1. Absorption spectra and emission spectra

The UV absorption spectra of 2NPnX (X = H, Cl, CF₃, CN; $n = 5, 6$) are essentially identical with an equimolar mixture of 2EN and *p*-XB. Fig. 1 shows the spectra of 2NP5CN, 2NP6CN and an equimolar mixture of 2EN and *p*-CNB as a typical example. The ground state intramolecular interactions, such as charge transfer (CT), were excluded by the absence of a new band at a longer wavelength for 2NPnX.

The shapes and intensities of the emission spectra of 2NPnX (X = H, Cl, CF₃; $n = 5, 6$) are essentially identical with the reference compound 2EN. In contrast, the emission

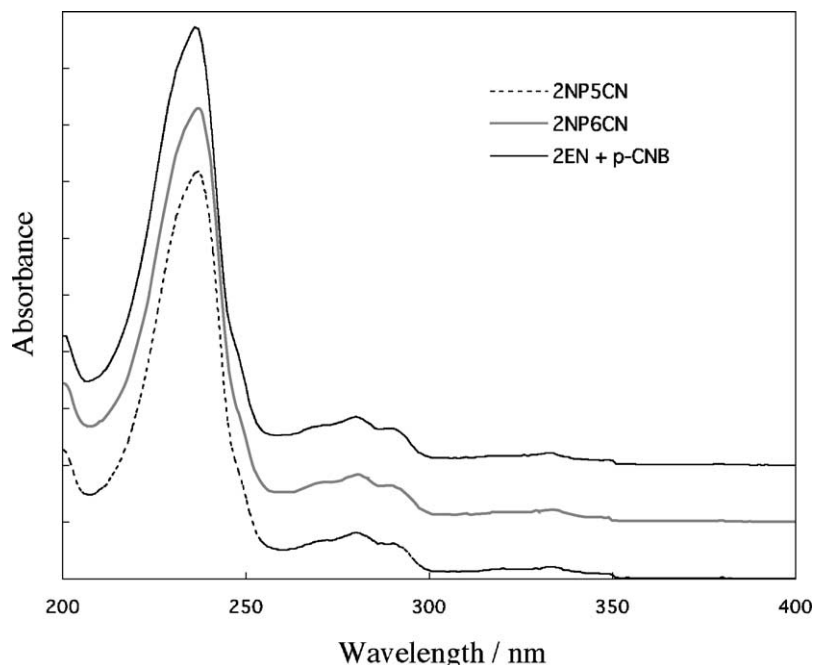


Fig. 1. UV absorption spectra of 2NP5CN, 2NP6CN and an equimolar mixture of 2EN and *p*-CNB in acetonitrile at room temperature.

spectra of 2NP n CN ($n = 5, 6$) showed differences from that of the reference compound 2EN. Although 2NP n X (X = H, Cl, CF₃; $n = 5, 6$) and 2EN showed only emission from the naphthalene chromophore in acetonitrile, structureless broad emissions were observed in the longer wavelength region for 2NP n CN ($n = 5, 6$). For example, the fluorescence spectra of 2NP5CN in acetonitrile at room temperature are shown in Fig. 2. The excitation spectra of 2NP n CN ($n = 5, 6$) observed at 360 nm are identical with the absorption spectra, indicating that these new longer wavelength emis-

sions are due to the excited state complex formation; that is, intramolecular exciplex formation.

It is known that electron transfer and exciplex formation are possible for a system with a negative free energy of electron transfer (ΔG_{ET}) value, given by the Rehm–Weller equation [13]:

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

where IP_D is the ionization potential of a donor, EA_A the electron affinity of an acceptor, E_{00} the excitation energy of

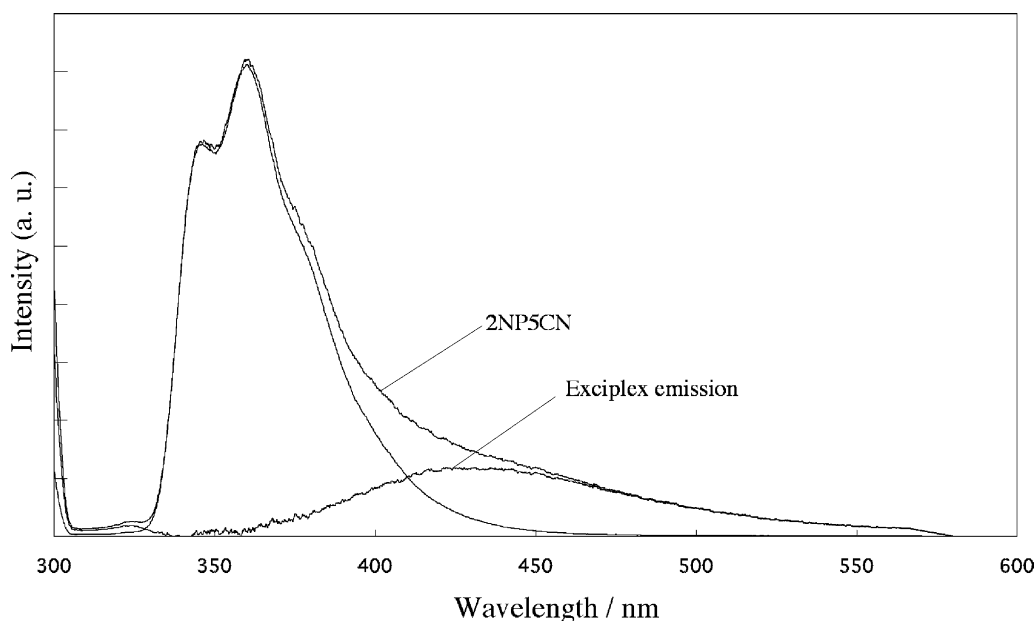


Fig. 2. Fluorescence spectra of 2NP5CN in acetonitrile at room temperature.

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 using the equation [14]:

$$\Delta G_{\text{ET}} (\text{eV}) = E_{(\text{D}/\text{D}^+)} - E_{(\text{A}^-/\text{A})} - E_{00} - \left[\frac{e^2}{\epsilon \rho} \right] - \left[\left(\frac{e^2}{r} \right) \left(\frac{1}{36.2} - \frac{1}{\epsilon} \right) \right] \quad (2)$$

using the oxidation and reduction potentials [$E_{(\text{D}/\text{D}^+)}$ and $E_{(\text{A}^-/\text{A})}$] of a donor and an acceptor separated by ρ with the 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 ($\epsilon = 36.2$). In order to evaluate the free energy of electron transfer in the 2NPnX series, the oxidation potential of naphthalene and the reduction potentials of p -XB ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}$) were compared. The oxidation potential of naphthalene [$E_{(\text{D}/\text{D}^+)}$] was 1.26 V vs. Ag/Ag^+ in acetonitrile at room temperature [15]. The reduction potentials [$E_{(\text{A}^-/\text{A})}$] of p -XB carrying p -H, p -Cl, p -CF₃ and p -CN were -2.63 , -2.47 , -2.19 and -2.11 V vs. Ag/Ag^+ in acetonitrile at room temperature, respectively [16]. If we assume that the donor and acceptor parts of 2NPnX in the extended conformation are separated by a distance of 28 Å obtained from the molecular model, ΔG_{ET} is calculated from Eq. (2) (ionic radii are assumed to be 4.3 Å) using the 0–0 transition energy for naphthalene $E_{00} = 98$ eV determined from the absorption and fluorescence spectra. ΔG_{ET} for the folded conformation is also calculated using 4 Å as the minimum value for the distance between the donor and acceptor. As shown in Table 1, the values of ΔG_{ET} for the folded conformation (4 Å) are greater than that for the extended conformation (28 Å). ΔG_{ET} decreases as the electronegativity of the p -substituents of the acceptor benzoate increases. The combination of naphthalene (D) with p -H, p -Cl, p -CF₃ and p -CN benzoate (A) gives a negative ΔG_{ET} , indicating that both the exciplex formation and electron transfer are possible for these systems [17,18].

The fluorescence quantum yields (Φ) relative to that of naphthalene of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3; n = 5, 6$) in acetonitrile are given in Table 2, in which Φ_{total} is the quantum yield for the total emission, Φ_{LE} is that of a locally excited emission and Φ_{EX} is that of the exciplex emission. The emission spectra of the exciplex were obtained by subtraction of

Table 1
Free energy of electron transfer (ΔG_{ET}) between naphthalene and p -XB ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}$) in acetonitrile

D–A	σ_p^a	ΔG_{ET} (eV mol ⁻¹)	
		$\rho = 28 \text{ \AA}$	$\rho = 4 \text{ \AA}$
Naphthalene– p -HB	0.00	–0.10	–0.19
Naphthalene– p -ClB	0.23	–0.26	–0.35
Naphthalene– p -CF ₃ B	0.54	–0.54	–0.63
Naphthalene– p -CNB	0.66	–0.62	–0.71

^a Hammett σ values for p -substituents.

Table 2
Fluorescence quantum yields of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}; n = 5, 6$) in acetonitrile ($\epsilon = 36.2$) at 25 °C

Quantum yield	2NP5H	2NP5Cl	2NP5CF ₃	2NP5CN
Φ_{total}	0.19	0.21	0.18	0.047
Φ_{LE}	0.19	0.21	0.18	0.040
Φ_{EX}	^a	^a	^a	0.007
	2NP6H	2NP6Cl	2NP6CF ₃	2NP6CN
Φ_{total}	0.22	0.22	0.24	0.067
Φ_{LE}	0.22	0.22	0.24	0.056
Φ_{EX}	^a	^a	^a	0.011

^a Not detected.

the spectra of 2EN from those of 2NPnX after normalization at the peak wavelength of naphthalene. That is to say, $\Phi_{\text{EX}} = \Phi_{\text{total}} - \Phi_{\text{LE}}$. Φ_{total} decreases as the electronegativity of the p -substituent of the acceptor benzoate increases. 2NPnCN ($n = 5, 6$), with the most negative ΔG_{ET} , show the most efficient quenching. In 2NPnCN ($n = 5, 6$), the intramolecular exciplex emission is observed, but not observed in 1NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3; n = 5, 6$). An exciplex emission requires a strong interaction of the two chromophores.

3.2. Absorption studies for metal ion recognition

We examined the change in the absorption spectra when adding LiClO_4 , NaClO_4 , KClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ to the solution of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}; n = 5, 6; 1.0 \times 10^{-5} \text{ mol dm}^{-3}$). The addition of Li^+ , Na^+ , K^+ and Mg^{2+} resulted in no observable changes in the absorption spectra of 2NPnX. However, Ca^{2+} or Ba^{2+} added to 2NPnX resulted in a red shift of the naphthalene absorption and isosbestic points were observed (e.g., Fig. 3 shows the absorption spectra of 2NP5CN in the absence and presence of Ca^{2+}). The absorption spectra of 2NPnX in the presence of Ca^{2+} or Ba^{2+} suggested that the calcium or barium complexes formed in the ground state. This behavior was not observed in case of Li^+ , Na^+ , K^+ and Mg^{2+} .

3.3. Fluorescence studies for metal ion recognition

Measurement of the fluorescence spectra was carried out in the acetonitrile solution of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}; n = 5, 6; 1.0 \times 10^{-5} \text{ mol dm}^{-3}$) at room temperature, and alkali or alkaline earth metal salts [LiClO_4 , NaClO_4 , KClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$] were added to the solution. To prevent nonlinearity of the fluorescence intensity, 295 nm was chosen as the excitation wavelength of 2NPnX.

When lithium, sodium, potassium, and magnesium salts were added to an acetonitrile solution of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}; n = 5, 6$), the shape and intensity of the fluorescence spectra did not change. However, when calcium and barium salts were added, the spectra of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}; n = 5, 6$) changed and exciplex emissions were

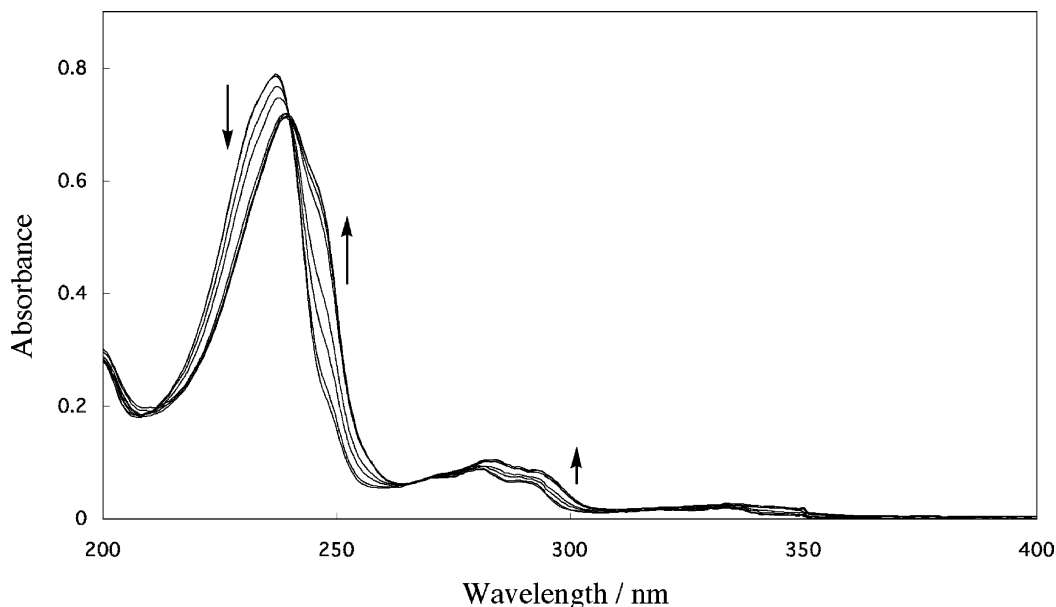
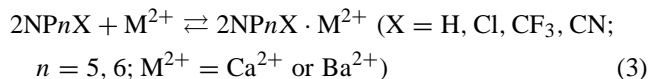


Fig. 3. Spectra changes in the UV absorption of 2NP5CN ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$) upon the addition of Ca^{2+} (0, 1.0×10^{-5} , 5.0×10^{-5} , 1.0×10^{-4} , 1.0×10^{-3} , 5.0×10^{-3} , $1.0 \times 10^{-2} \text{ mol dm}^{-3}$) in acetonitrile.

observed. The fluorescence spectra of 2NP5H in the presence of several concentrations of LiClO_4 , NaClO_4 , KClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ are shown in Fig. 4 as typical examples.

To study the complexation behavior of 2NP n X (X = H, Cl, CF_3 , CN; $n = 5, 6$) with Ca^{2+} and Ba^{2+} , the measurement of the fluorescence was carried out in detail. The fluorescence spectra of 2NP n X (X = H, Cl, CF_3 , CN) in the presence of several concentrations of $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ are shown in Fig. 5 as typical examples. We separated the emission spectra of 2NP n X in the presence of several concentrations of Ca^{2+} and Ba^{2+} by the emission spectra of the reference compounds 2EN, and we obtained locally excited emission (LE) and exciplex emission (EX) spectra of 2NP n X. In both cases of $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$, the LE emission decreased by the addition of the metal salt, and the EX emission increased. The fluorescence enhancement factors (FEFs) for Ca^{2+} and Ba^{2+} at exciplex emission maxima are shown in Table 3. FEF is calculated as a ratio of the fluorescence of the metal complex and the uncomplexed ligand. In all the 2NP n Xs, the FEFs for Ca^{2+} were greater than that for Ba^{2+} . The FEFs for Ca^{2+} were 5.2, 4.6, 4.5, 4.6, 5.0, 4.0, 11 and 12 for 2NP5H, 2NP6H, 2NP5Cl, 2NP6Cl, 2NP5CF $_3$, 2NP6CF $_3$, 2NP5CN and 2NP6CN, and the FEFs for Ba^{2+} were 2.7, 2.2, 2.4, 2.1, 2.0, 1.9, 2.5 and 4.8 for 2NP5H, 2NP6H, 2NP5Cl, 2NP6Cl, 2NP5CF $_3$, 2NP6CF $_3$, 2NP5CN and 2NP6CN, respectively. Especially, the large values of 2NP5CN (FEF = 11) and 2NP6CN (FEF = 12) for Ca^{2+} are remarkable. Next, we calculated the association constants (K). Even though the solvent takes part in the association interaction, the solvent concentration is virtually unaffected. Therefore, we express the interaction of

the metal salts in terms of the equilibrium [19]:



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

$$K = \frac{[2\text{NP}n\text{X} \cdot \text{M}^{2+}]}{[2\text{NP}n\text{X}][\text{M}^{2+}]} \\ = \frac{[2\text{NP}n\text{X} \cdot \text{M}^{2+}]}{\{([2\text{NP}n\text{X}]_0 - [2\text{NP}n\text{X} \cdot \text{M}^{2+}]) \\ \times ([\text{M}^{2+}]_0 - [2\text{NP}n\text{X} \cdot \text{M}^{2+}])\}} \quad (4)$$

$$[2\text{NP}n\text{X} \cdot \text{M}^{2+}] = a[2\text{NP}n\text{X}]_0 = \left\{ \frac{I - I_0}{I_{\text{max}} - I_0} \right\} [2\text{NP}n\text{X}]_0 \quad (5)$$

Table 3
The FEFs^a of 2NP n X (X = H, Cl, CF_3 , CN; $n = 5, 6$) at exciplex emission maxima

	Ca^{2+}	Ba^{2+}
2NP5H	5.2	2.7
2NP6H	4.6	2.2
2NP5Cl	4.5	2.4
2NP6Cl	4.6	2.1
2NP5CF $_3$	5.0	2.0
2NP6CF $_3$	4.0	1.9
2NP5CN	11	2.5
2NP6CN	12	4.8

^a The enhancement factor is the ratio of the fluorescence intensity of a complex divided by the fluorescence intensity of the uncomplexed ionophore.

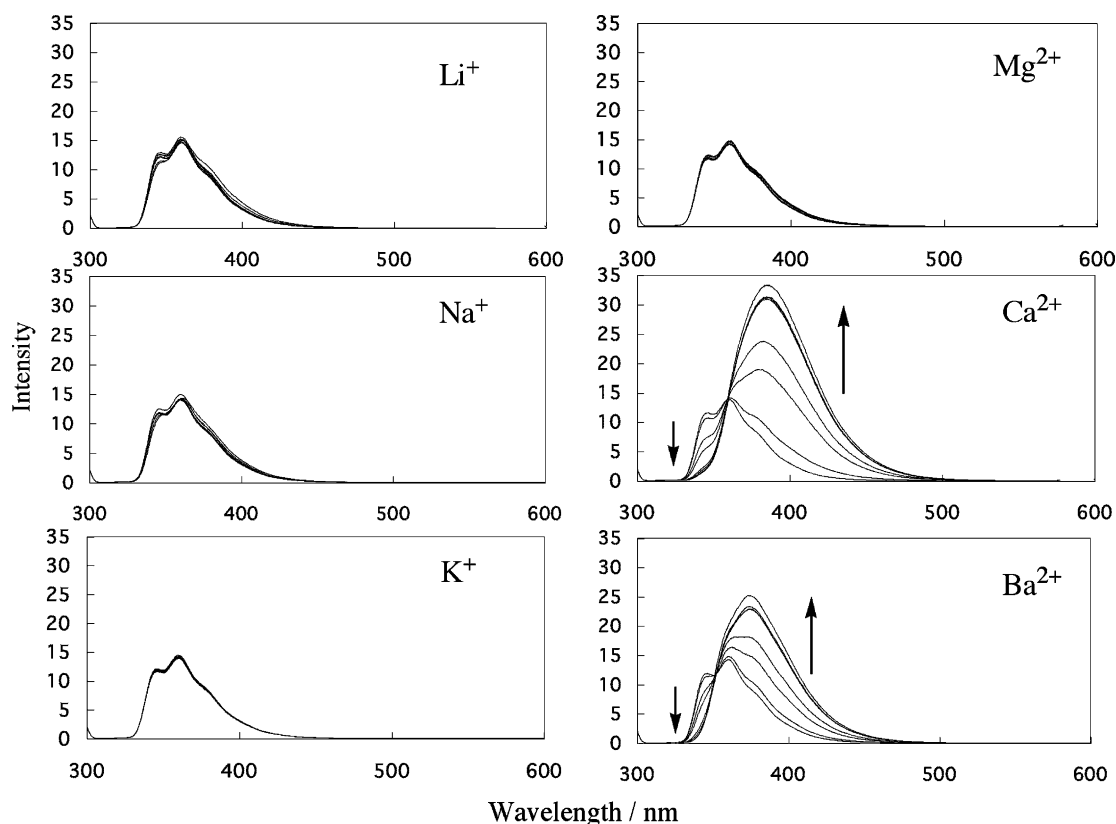


Fig. 4. Fluorescence spectra of 2NP5H with Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} or Ba^{2+} ($[\text{2NP5H}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile, $[\text{LiClO}_4]$, $[\text{NaClO}_4]$, $[\text{KClO}_4]$, $[\text{Mg}(\text{ClO}_4)_2]$, $[\text{Ca}(\text{ClO}_4)_2]$ or $[\text{Ba}(\text{ClO}_4)_2] = 0, 1.0 \times 10^{-5}, 5.0 \times 10^{-5}, 1.0 \times 10^{-4}, 1.0 \times 10^{-3}, 5.0 \times 10^{-3}, 1.0 \times 10^{-2} \text{ mol dm}^{-3}$).

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

$$[\text{M}^{2+}]_0 = \frac{a}{K(1-a)} + a[\text{2NPnX}]_0 \quad (6)$$

where $[\text{2NPnX}]_0$ and $[\text{M}^{2+}]_0$ are the initial concentrations of 2NPnX and the metal salts, I and I_{max} are the observed locally excited emission intensities of the 2NPnX in the presence and in the absence of the metal ion, respectively, and I_0 is the observed locally excited emission intensity of the complex of the 2NPnX and the metal ion. A self-written nonlinear curve-fitting computer program (Eq. (6)) was used to fit the experimental titration curves. The association constants were determined from the emission-intensity changes at the exciplex emission maxima for 2NPnX using this equation. The values of $\log K$ of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}$; $n = 5, 6$) are reported in Table 4. In all the 2NPnXs, the values of $\log K$ for $n = 6$ ($\log K = \text{ca. } 5$) were greater than $n = 5$ ($\log K = \text{ca. } 4$). Because oxygen atoms of the polyether chain are necessary to bind metal ions, in the case of $n = 6$ with many oxygen atoms, the complexation ability for metal ions would be increased. Actually, 2NPnX ($n < 4$) having a shorter polyether chain could not form complexes with the metal ions. The complexing ability will be mostly determined by the polyether chain length. The order of the $\log K$ values for Ca^{2+} was $2\text{NPnCN} > 2\text{NPnCl} > 2\text{NPnH} > 2\text{NPnCF}_3$ ($n = 5, 6$), and the order of the $\log K$

values for Ba^{2+} was $2\text{NPnCl} > 2\text{NPnCN} > 2\text{NPnH} > 2\text{NPnCF}_3$ ($n = 5, 6$). For the same length of the polyether chain, the $\log K$ values of 2NPnCF₃ were the lowest. We do not know that reason precisely. But, probably, the reason for the low the $\log K$ values is because it will be difficult to form the complex by the bulk of the trifluoromethyl group. For the each 2NPnXs, the values of $\log K$ for Ca^{2+} and Ba^{2+} were almost same. For example, the values of $\log K$ of 2NP5CN are 4.4 for Ca^{2+} and 4.3 for Ba^{2+} , respectively. This means that the complexing ability for Ca^{2+} and Ba^{2+} is same. On the other hand, in all the 2NPnXs, the FEFs for Ca^{2+} were greater than that for Ba^{2+} . Though the association constants (K) depend on $(I - I_0)/(I_{\text{max}} - I_0)$, the FEFs do not depend on it. The FEFs are I_{max}/I_0 , and those

Table 4
The association constants (K) of 2NPnX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}$; $n = 5, 6$)

	$\log K$	
	Ca^{2+}	Ba^{2+}
2NP5H	4.0	4.1
2NP5Cl	4.3	4.4
2NP5CF ₃	3.7	3.6
2NP5CN	4.4	4.3
2NP6H	5.0	4.7
2NP6Cl	5.1	5.2
2NP6CF ₃	4.7	4.6
2NP6CN	5.1	5.1

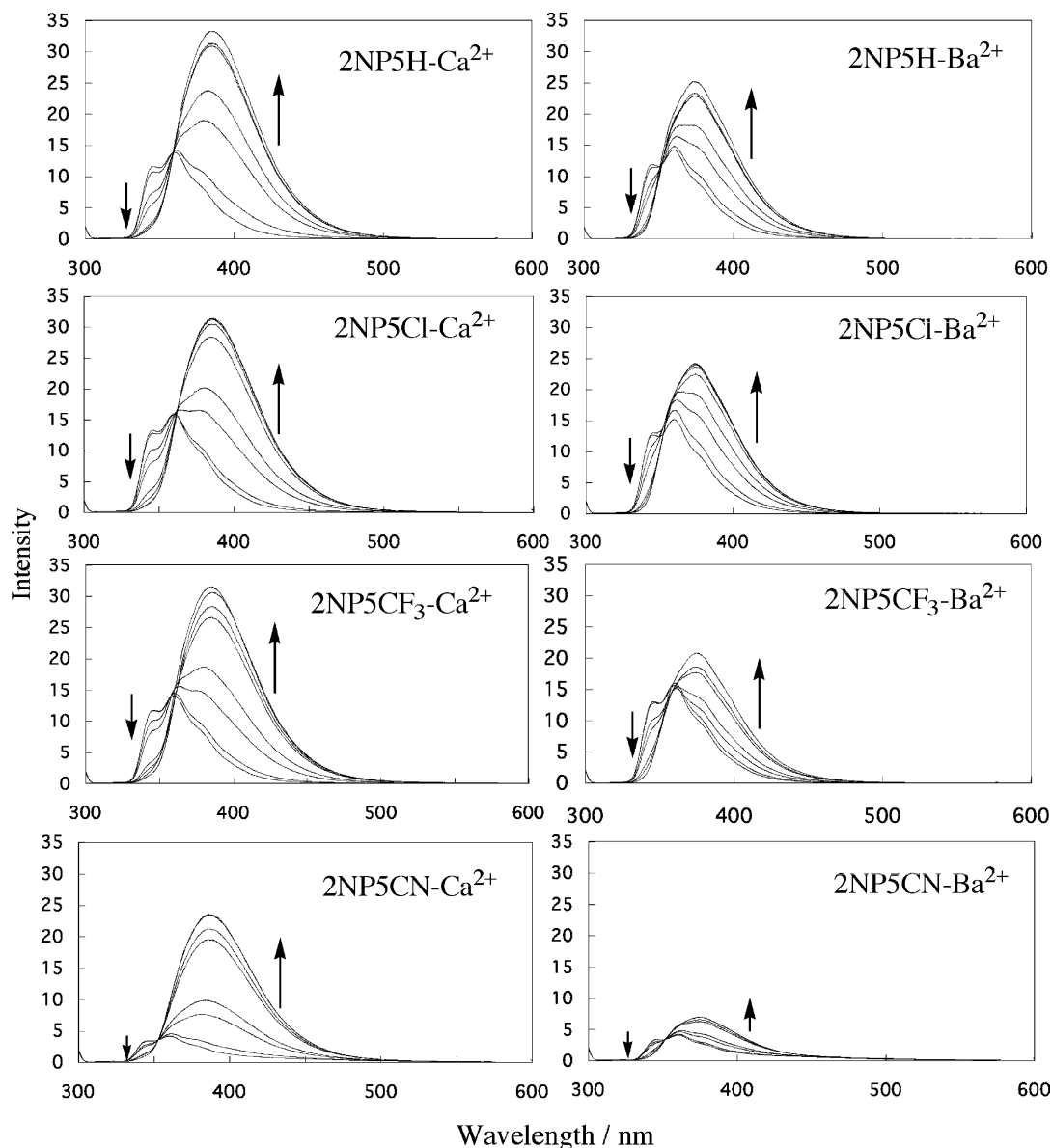


Fig. 5. Fluorescence spectra of 2NP5X ($X = \text{H, Cl, CF}_3, \text{CN}$) and their Ca^{2+} and Ba^{2+} complexes ($[\text{2NP5X}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile, $[\text{Ca}(\text{ClO}_4)_2]$ or $[\text{Ba}(\text{ClO}_4)_2] = 0, 1.0 \times 10^{-5}, 5.0 \times 10^{-5}, 1.0 \times 10^{-4}, 1.0 \times 10^{-3}, 5.0 \times 10^{-3}, 1.0 \times 10^{-2} \text{ mol dm}^{-3}$).

are often more important than the association constants as fluorescent chemosensors. We think that the calcium complex showed the strong fluorescence by forming the stable exciplex further than barium complex.

These results suggest that 2NP n X ($X = \text{H, Cl, CF}_3, \text{CN}$; $n = 5, 6$) is an excellent fluorescent chemosensor for Ca^{2+} and Ba^{2+} . Especially, 2NP5CN and 2NP6CN have the largest FEF values, and 2NP5CN is also good for the selectivity of Ca^{2+} (FEF = 11) and Ba^{2+} (FEF = 2.5).

4. Conclusion

Whereas the intramolecular interaction in the ground state is not observed in any 2NP n X ($X = \text{H, Cl, CF}_3, \text{CN}$; $n = 5,$

6), their spectroscopic features in the excited state depend on the p -substituents of the benzoate. In the absence of metal salts, 2NP n CN ($n = 5, 6$) with the most negative free energy of electron transfer (ΔG_{ET}) showed the most efficient quenching and exciplex emission. The exciplex formation of 2NP n X ($X = \text{H, Cl, CF}_3$; $n = 5, 6$) is not easier than for 2NP n CN ($n = 5, 6$), because the two chromophores cannot easily approach close enough to interact. However, in the presence of calcium and barium salts, all the 2NP n Xs formed an exciplex, and showed exciplex emission. 2NP n X ($X = \text{H, Cl, CF}_3, \text{CN}$; $n = 5, 6$) is an excellent fluorescent chemosensor for Ca^{2+} and Ba^{2+} . Especially, due to the large fluorescent enhancement factor of 2NP n CN ($n = 5, 6$) for Ca^{2+} , they are well-suited for use as a fluorescent chemosensor for Ca^{2+} .

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