

# Novel chemosensor for alkaline earth metal ion based on 9-anthryl aromatic amide using a naphthalene as a TICT control site and intramolecular energy transfer donor

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## Abstract

Novel fluorescent chemosensors **1** and **2** with two different fluorophores (naphthalene and anthracene) at the both ends of polyether was synthesized. These compounds based on 9-anthryl aromatic amide adopted a naphthalene as a TICT controller and an intramolecular energy transfer source. Compound **1** shows high fluorescence efficiency upon complexation with metal ion, and the fluorescence efficiency of **2** is regulated by metal ionic size.

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Intramolecular energy transfer (intraET) between chromophores has been a subject of considerable interest because this phenomenon is widely applicable in photochemistry and photobiology.<sup>1</sup> In recent years, Chattoraj et al.<sup>2</sup> and Speiser et al.<sup>3</sup> have studied intraET systems using bichromophoric molecules comprising two different chromophore units connected by a methylene bridge. In particular, 9-anthryl-1'-naphthyl compounds<sup>4–7</sup> have been noted for their efficiency of energy transfer by various numbers of methylene chain. Until now most frequently reported studies of intraET were in a rigid or semirigid system which defines a distance between donor and acceptor.<sup>8–10</sup> If a donor–acceptor pair is bound by a flexible chain and their distance is controlled by a guest molecule or metal ion, it is expected that the dynamic conformation can be monitored by an intraET in the system.

Recently, we have investigated behaviors of twisted intramolecular charge transfer (TICT) on linear polyether

compounds with pyrene, anthracene, or naphthalene moieties.<sup>11–14</sup> This TICT-quenching process was controlled effectively by a formation of the complex with alkaline earth metal ions. This encouraged us to develop chemosensors based on polyether, which exhibit controlling of TICT and intraET. With this in mind, we synthesized chemosensors **1** and **2**, which have a naphthalene and an anthracene group at both terminals of a polyether (Fig. 1). Naphthalene moiety of these sensors will be employed as an obstructor of TICT relaxation process and an intraET donor.

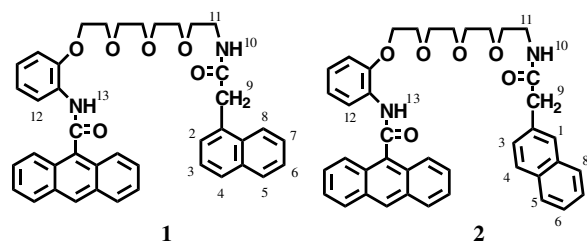


Fig. 1. Structures of **1** and **2**.

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Compounds **1** and **2** were synthesized in a usual manner (see Supplementary data). Their structures and purities were confirmed using  $^1\text{H NMR}$  spectra and elemental analyses (see Supplementary data). Fluorescence and UV–vis spectra were recorded at 25 °C using respective equipment (RF-5300PC and UV-2400PC; Shimadzu Corp.). Concentrations of the reagents were  $1 \times 10^{-5}$  mol/dm<sup>3</sup> in purified acetonitrile. For complex formation experiments, alkaline earth metal cations were added to the solution as perchlorate salts.

Figure 2 shows UV spectra of **2** and its  $\text{Ca}^{2+}$  complexes as a typical result. Almost no UV spectral changes of all complexes on the naphthalene and anthracene moieties were observed compared with that of the free compound. This observation suggests that naphthalene and anthracene rings did not interact with each other in the ground state. This phenomenon supports that the metal ions did not induce the interaction between naphthalene and anthracene. The same results were also observed in the UV spectra of **1** and its metal complexes.

Figure 3 depicts fluorescence spectra of **1** and **2**, and their  $\text{Ca}^{2+}$  complexes when naphthalene moieties were excited. The excitation wavelength was set to 281 nm, which is the absorption maximum of the compounds and attributed to a naphthalene moiety. In the absence of metal ion, weak fluorescence from naphthalene moiety was observed at around 330 nm, and also weak fluorescence from anthracene moiety was observed at 440 nm. After the addition of  $\text{Ca}^{2+}$ , a structureless broad emission at around 440 nm increased remarkably, but the emission at around 330 nm, which was attributed to naphthalene, did not change. These results show that an intraET from the naphthalene to the anthracene occurred. The fluorescence maxima ( $\lambda_{\text{max}} = 440$  nm) of **1** and **2** are similar to that of 9-anthracenecarboxamide. Therefore, anthracene and naphthalene groups did not show any  $\pi$ – $\pi$  interaction such as an exciplex.<sup>13</sup> These observations underline that the TICT quenching processes of free **1** and **2** occurred in the anthracenecarboxamide, as reported previously,<sup>13,15</sup> and were controlled by the formation of  $\text{Ca}^{2+}$  complexes. Sim-

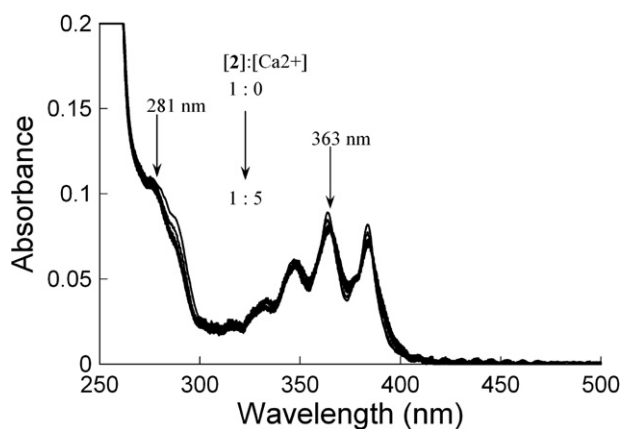


Fig. 2. UV spectra of **2** and its  $\text{Ca}^{2+}$  complex in acetonitrile at 25 °C.  $[\mathbf{2}] = 1 \times 10^{-5}$  M.  $[\text{Ca}^{2+}] = 0, 0.25, 0.5, 0.75, 1, 2, 3, 4, 5$ .

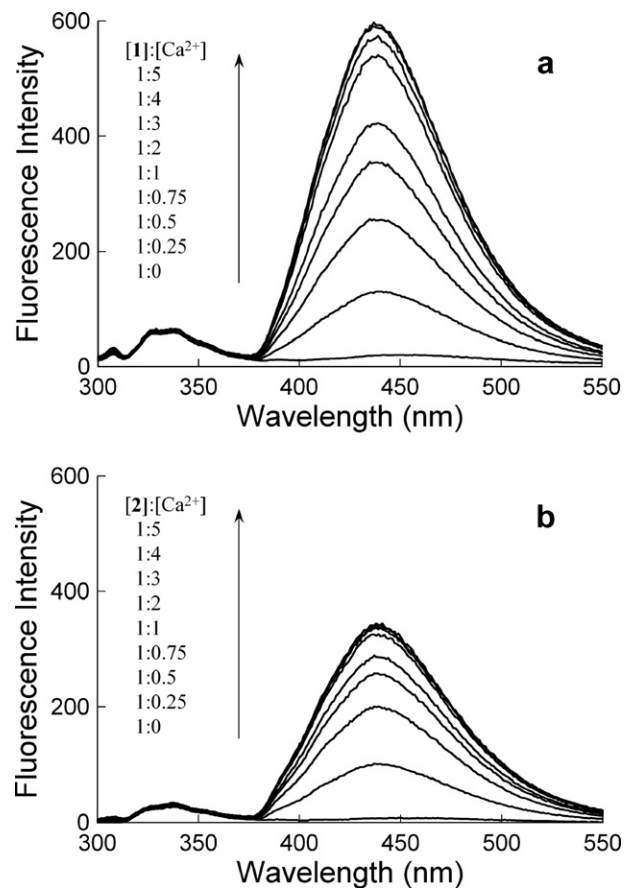


Fig. 3. Fluorescence spectra of **1** (a) and **2** (b) and its  $\text{Ca}^{2+}$  complexes in acetonitrile at 25 °C. The excitation wavelength is 281 nm.  $[\mathbf{1}] = [\mathbf{2}] = 1 \times 10^{-5}$  M.

ilar ‘Off–On’ behavior was observed in the presence of  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ . On the other hand, intermolecular energy transfer was ruled out by the observation of fluorescence spectra of model solution, which is a mixture of 1-naphthaleneacetamide and 9-anthryl aromatic amide (see Supplementary data).

The analytical usefulness is assessed, respectively, using low and high emission intensities of the free reagent and the complexes. The ‘Off–On’ responses were evaluated as  $I_{\text{max}}/I_0$  values. Here,  $I_0$  is the fluorescence intensity of free **1** or **2**, and  $I_{\text{max}}$  is that of the complex **1** or **2** at the same condition. The fluorescence intensity will also change according to the absorbance at the excitation wavelength, if it is changed by the complexation. This effect does not come from the change of quenching process. To distinguish this effect, the emission intensity should be normalized by the absorbance; alternatively, an isosbestic point should be excited. In these experiments, the excitation wavelengths were adjusted to the isosbestic points (Fig. 2).

The  $I_{\text{max}}/I_0$  values are independent on the excitation wavelength if the ‘Off–On’ phenomenon is controlled by TICT alone. However, the values of **1** on excitation at 281 nm are 10–20% larger than those of anthracene excitation for all metal cations (Table 1). This result indicates

Table 1  
Fluorescence 'Off-On' response ( $I_{\max}/I_0$ ) and excitation wavelength dependence

Fluoroionophores		$I_{\max}/I_0$ ( $\lambda_{\max}$ )			
<b>1</b>		$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Sr}^{2+}$	$\text{Ba}^{2+}$
Excitation wavelength	281 nm	15.2 (413)	32.7 (439)	10.6 (439)	5.1 (440)
	363 nm	13.8 (413)	28.1 (439)	8.9 (439)	4.6 (440)
$\{I_{\max}/I_0$ (281 nm)/ $I_{\max}/I_0$ (363 nm) $\}$		1.10	1.16	1.19	1.10
<b>2</b>		$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Sr}^{2+}$	$\text{Ba}^{2+}$
Excitation wavelength	281 nm	12.7 (413)	36.5 (439)	9.8 (439)	3.9 (440)
	363 nm	14.3 (413)	37.8 (439)	13.6 (439)	6.3 (440)
$\{I_{\max}/I_0$ (281 nm)/ $I_{\max}/I_0$ (363 nm) $\}$		0.88	0.96	0.72	0.62

that the efficiency of intraET from naphthalene to anthracene in **1** was increased by complexation with metal ions. This effect was also observed in excitation spectra. Excitation spectra of **1** and **1**· $\text{Ca}^{2+}$  complex normalized at 363 nm is shown in Figure 4. The excitation intensity of the complex around at 281 nm is ca. 16% larger than that of **1**. On the other hand,  $I_{\max}/I_0$  values of **2** are of the order of  $\text{Ca}^{2+}$  (96%) >  $\text{Mg}^{2+}$  (88%) >  $\text{Sr}^{2+}$  (72%) >  $\text{Ba}^{2+}$  (62%) (Table 1). Moreover, they are smaller than 100%. The

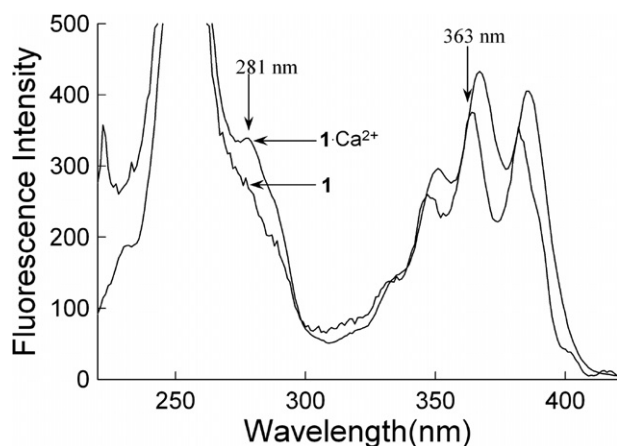


Fig. 4. Excitation spectra of **1** and its  $\text{Ca}^{2+}$  complex normalized at 363 nm in acetonitrile- $d_3$ .  $[\mathbf{1}] = 1 \times 10^{-5}$  mol/dm $^3$ .

$I_{\max}/I_0$  values of **2** can be ordered by the metal ionic size, except for  $\text{Mg}^{2+}$ , but they are smaller than those of **1**. This finding manifested that the efficiency of energy transfer in **2** is governed by the fitness between the pseudo-polyether cavity and the sizes of metal ions. These phenomena of **1** and **2** occur because of the geometric structure of naphthalene moiety by the difference of substitution position.

Fluorescence spectral data suggested a structural change in **1** and **2** upon complexation with metal cations. To clarify the effect of complexation with metal cations,  $^1\text{H}$  NMR measurements of **1** and **2** were carried out in the absence and the presence of metal cations in acetonitrile- $d_3$  at 30 °C. The chemical shifts of **1**, **2** and their changes at the formation of complexes with various metal ions are shown in Table 2. The peaks were assigned using H–H COSY and NOESY spectra. The addition of  $\text{Ca}^{2+}$  to the solution of **1** or **2** induced low magnetic field shifts for protons 13 and 10 ( $\Delta\delta = 0.61$ – $0.67$  ppm and  $0.74$ – $0.77$  ppm, respectively). This indicates that **1** or **2** formed  $\text{Ca}^{2+}$  complexes cooperatively with the carbonyl oxygen atom in both amide groups. Before the addition of  $\text{Ca}^{2+}$ , proton 12 of **1** or **2** exhibited an unusual lower chemical shift (8.47 and 8.45 ppm, respectively). However, a large higher magnetic chemical shift change ( $\Delta\delta = -1.06$  and  $-1.08$  ppm, respectively) was observed in complexation with  $\text{Ca}^{2+}$ . This fact indicates that the benzene proton 12 existed on a deshielding zone of the carbonyl group, and that the carbonyl moiety is reversed by complexation with

Table 2  
Chemical shifts ( $\delta$ , ppm) of **1** and **2**, and their changes upon complexation with various cations<sup>a</sup>

	Metal ion	1	2	3	4	5	6	7	8	9	10	11	12	13
<b>1</b>	Blank		7.35	7.40	7.77	7.86	7.47	7.48	7.94	3.84	6.35	3.12	8.47	8.81
	$\text{Mg}^{2+}$		-0.05	-0.01	0.02	-0.02	-0.01	-0.02	-0.21	0.01	1.18	0.02	-0.83	0.68
	$\text{Ca}^{2+}$		-0.02	-0.08	-0.03	-0.04	-0.10	-0.11	-0.35	-0.54	0.77	-0.57	-1.06	0.61
	$\text{Sr}^{2+}$		-0.08	-0.06	-0.01	-0.07	-0.06	-0.07	-0.22	-0.39	0.68	-0.33	-0.93	0.44
	$\text{Ba}^{2+}$		-0.05	-0.04	0.00	-0.03	-0.02	-0.03	-0.11	-0.09	0.63	-0.09	-0.97	0.33
<b>2</b>	Blank		7.67	7.36	7.78	7.80	7.44	7.44	7.81	3.53	6.51	3.17	8.45	8.86
	$\text{Mg}^{2+}$		-0.05	0.02	0.01	0.00	0.01	0.01	0.02	0.02	1.05	0.01	-0.88	0.69
	$\text{Ca}^{2+}$		-0.12	-0.21	0.01	0.02	0.02	0.02	-0.03	-0.34	0.74	-0.47	-1.08	0.67
	$\text{Sr}^{2+}$		-0.09	-0.16	0.00	-0.01	0.02	0.02	-0.02	-0.27	0.69	-0.25	-1.07	0.52
	$\text{Ba}^{2+}$		-0.07	0.00	0.02	-0.06	0.01	0.01	-0.07	-0.05	0.63	-0.06	-1.00	0.37

<sup>a</sup> Positive values show lower field shifts, negative values show higher field shifts. The 'blank' values indicate chemical shifts ( $\delta$ , ppm, from TMS) of protons in acetonitrile- $d_3$  at 30 °C. Other protons were omitted because significant chemical shift changes were not observed.

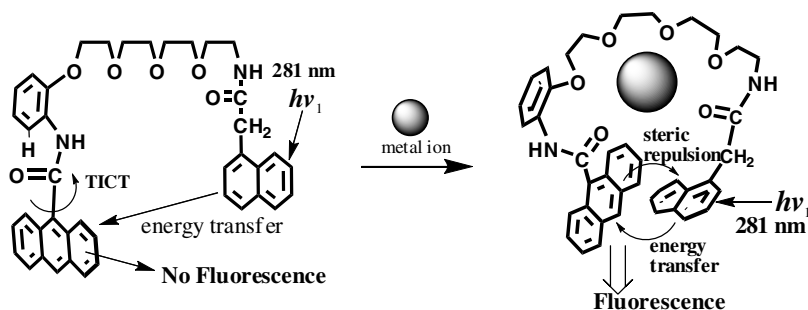


Fig. 5. Fluorescence emissions mechanism of **1** before and after addition of  $M^{2+}$  in the ground state.

Table 3  
Complex formation constants (log  $K$ )

	$Mg^{2+}$	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$
<b>1</b>	4.74	5.75	5.22	5.11
<b>2</b>	4.71	5.96	5.43	4.99

$Ca^{2+}$ , and that the chemical shift returned to a normal value through complexation.

It is noteworthy that two methylene proton peaks 11 and 9 of **1** or **2** shifted to a higher magnetic field (proton 11:  $\Delta\delta = -0.57$  and  $-0.47$  ppm; proton 9:  $\Delta\delta = -0.54$  and  $-0.34$  ppm, respectively) at complexation with  $Ca^{2+}$ . In addition, the proton 8 in **1** showed high-magnetic chemical shift changes ( $\Delta\delta = -0.35$  to  $-0.11$  ppm), although that in **2** showed almost no chemical shift changes ( $\Delta\delta = -0.07$  to  $0.02$  ppm). These chemical shift changes are explained as follows: In the naphthaleneacetamide group, methylene moiety is located in an opposite direction to the carbonyl group that will bind to the metal ion. The naphthalene ring is, therefore, positioned toward the anthracene ring because the methylene moiety induces a steric hindrance for the hydrogen atom (e.g., proton 8 for **1**) of the *peri*-position of the naphthalene ring. The phenomenon in the free rotation range of naphthalene ring should be more restricted in **1** on the geometric structure.

Protons 8, 9, and 11 of **1** showed higher chemical shift changes than in **2**. This phenomenon showed that they are attributable to a shielding effect of the anthracene ring in the complex. This result shows that the complex structure of **1** takes an effective obstacle conformation to the TICT relaxation process, which is a reason for higher fluorescence intensity. No other protons of anthracene and naphthalene indicated significant chemical shift changes before or after complexation with all metal ions. This result shows that anthracene and naphthalene moieties did not take a so-closed structure, and did not give  $\pi$ - $\pi$  interactions. On the bases of fluorescence and  $^1H$  NMR studies, a plausible complex structure of  $1 \cdot M^{2+}$  on the ground state is depicted in Figure 5.

The complex formation constants (log  $K$ ) were evaluated using the titration curve of fluorescence intensity versus  $[M^{2+}]$  with a nonlinear least-squares curve fitting method

(Marquardt's method),<sup>15</sup> as summarized in Table 3. The complex formation constants (log  $K$ ) of chemosensors **1** and **2** showed the best affinity for  $Ca^{2+}$ , which shows that the ionic diameter of  $Ca^{2+}$  resembles the size of the pseudocavity formed by polyoxyethylene group and carbonyl oxygens. In both cases, the order of log  $K$  is  $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$ .

In conclusion, **1** and **2** exhibited different fluorescence responses to metal ions by excitation moieties (281 and 363 nm). However, the mechanism of the difference of the responses in intraET is not elucidated. Further studies are in progress.

#### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.01.085.

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