

Intramolecular Charge-Transfer Behavior of 1-Pyrenyl Aromatic Amides and Its Control through the Complexation with Metal Ions

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New fluorescent ionophores containing 1-pyrenyl aromatic amides based on oligoethylene oxide (**1** and **2**) have been synthesized and its photochemical behaviors have been studied. In the absence of metal ion, 1-pyrenylbenzamide moiety showed almost no fluorescence emission. However, complexation with Ca^{2+} induced a large enhancement effect on the fluorescence intensity of **1** and **2** from the pyrene ring. This behavior can be explained by in terms of the similar twisted intramolecular charge-transfer relaxation mechanism.

Photoirradiation accompanied by electron transfer between donor and acceptor subsystems in a molecule leads in the intramolecular charge transfer (ICT) state. In particular, the twisted intramolecular charge transfer (TICT) behavior of fluorophores has been a subject of interest to many photochemical researchers for years.¹ The TICT model was applied for the explanation about the photophysical property of *p*-(*N,N*-dimethylamino)benzonitrile indicating the dual fluorescence and the emission with large Stokes shift in polar solvent.² Since then, interpretation by the TICT model has been extended to other structurally related compounds showing anomalous dual fluorescence. Recently, the present authors demonstrated that 9-anthrylbenzamide derivatives show no fluorescence emission in solution through ICT relaxation pathway similar to the TICT as the most plausible explanation. On the basis of this observation, we have synthesized a new fluorescent ionophore containing 9-anthrylbenzamide based on ethyleneoxy chain. Upon complexing with metal ions, we could achieve the controlling TICT relaxation pathway with the "off-on" fluorescent signal.³

These results inspired us to examine a photochemical property of pyrenylbenzamides. Pyrene is regarded as a strong tool for high sensitive detecting probe in fluoroionophores.⁴ Although we have studied in detail about an ionophore having two of pyrenyl alliphatic amide at the terminal of polyethyleneoxide chain,⁵ we have not checked a photochemical property of pyrenyl aromatic amide yet. It is also well known that two molecules of pyrene tend to form a dimer. This may cause the difficulty for a characterization of the ICT property. To avoid this, we synthesized a new ionophore having mono fluorophore, 1-pyrenyl

aromatic amide, based on oligoethylene oxide (**1** and **2**). In this communication, we demonstrated the photochemical behaviors **1** and **2** upon the complexing with metal ions by means of fluorescence and NMR spectrometries.

Syntheses of **1** and **2** were carried out by the usual technique (Yield: 48% for **1**, 45% for **2**).^{6,7} Their structures and purities were confirmed by ¹H NMR spectra and elemental analyses. Fluorescence spectra were measured by Shimadzu RF-5300PC at 25 °C. Concentrations of fluorescent reagents were 2.5×10^{-6} mol/dm³ in purified acetonitrile. Alkaline earth metal cations were added into the solution of fluorescent reagent as perchlorate salts.

Figure 1a shows fluorescence spectra of **1** and its Ca^{2+} complexes. Fluorescence emissions from pyrene moiety in **1** were quite weak in the absence of metal ions. On the other hand, structureless broad spectra having fluorescence emission maximum (λ_{max}) around at 414 nm were observed, and fluorescence

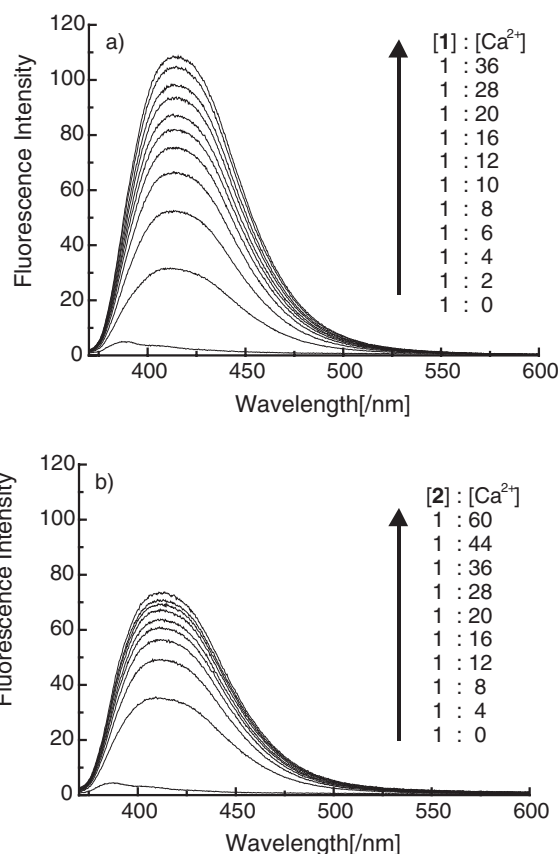
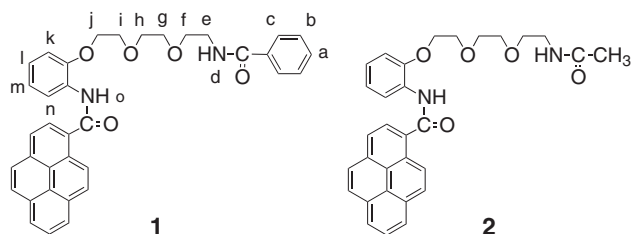


Figure 1. Fluorescence spectra of **1** and its Ca^{2+} complex (a), **2** and its Ca^{2+} complex (b) in acetonitrile at 25 °C. Excitation wavelength: 350 nm. $[\mathbf{1}] = [\mathbf{2}] = 2.5 \times 10^{-6}$ mol/dm³.



Scheme 1.

intensity increased upon the addition of Ca^{2+} . The disappearance of vibrational structure in the spectra also suggests that the emitted species has a somewhat charge-transfer character. To obtain further information on the emitted chemical species, we prepared **2** containing an acetamide group which shows no π - π interaction with the pyrene ring.

Figure 1b also demonstrates fluorescence spectra of **2** and its Ca^{2+} complexes. Although increase of fluorescence intensity was small compared with that of **1**, fluorescence emission maximum (λ_{max}) and shape were quite similar to that of $\mathbf{1}\cdot\text{Ca}^{2+}$. The emitted chemical species can be concluded to be the pyrene ring. These results strongly suggested that pyrenyl aromatic amide also showed like TICT relaxation process for fluorescence quenching as the same as 9-anthrylbenzamide.

The successive increase in monomer emission with the addition of metal ions will finally cause an inhibition of ICT quenching. The degree of increase of monomer emission clearly depended on the concentrations of metal ions. The fluorescence intensity of **1** and **2** at 414 nm was plotted against the ratio of $[\text{M}^{2+}]/[\mathbf{1}$ or $\mathbf{2}]$. The obtained titration curve clearly indicates the formation of a 1:1 complex with Ca^{2+} . The complex formation constant (K) was determined from the curve by means of a nonlinear least-square curve fitting method (Marquardt's method).⁸ The fluoroionophores **1** and **2** did not respond to Ba^{2+} and Mg^{2+} whereas Sr^{2+} induced a moderate inhibition effect for the TICT compared with that of Ca^{2+} . (**1** and **2**) (Table 1).

Table 1. Complex formation constants and fluorescent response of **1** and **2** for various metal ions in acetonitrile at 25 °C

Fluoro-ionophore	$\log K (I_{\text{max}}/I_{\text{max}})$			
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	—	5.65 (37.1)	4.94 (20.6)	—
2	—	5.98 (30.6)	4.97 (7.0)	—

The fluorescence spectral data evidently showed the structural changes of **1** and **2** upon complexation with metal ions. To clarify these changes of complexes in detail, an ^1H NMR study of **1** was carried out in the absence and presence of Ca^{2+} in acetonitrile- d_3 at 30 °C as a typical result. Peak assignments were made by ^1H - ^1H COSY and NOESY spectra except for peaks of pyrene which were too complicated to assign individually. In $\mathbf{1}\cdot\text{Ca}^{2+}$ complex (refer to the scheme for peak assignments), oxyethylene proton peaks (e, f, g, h, and j) shifted to low magnetic field ($\Delta\delta = 0.26, 0.26, 0.25, 0.31,$ and 0.28 ppm, respectively). The proton (i) could not be assigned because of overlapped of the H_2O peak. Two peaks of amide protons (d and o) also showed large lower magnetic field shift changes ($\Delta\delta = 1.15$ and 0.70 ppm, respectively). These indicated that **1** binds Ca^{2+} with the ethyleneoxy moiety and carbonyl oxygen in both of amide groups cooperatively. Benzene protons (k, l and m) shifted to low magnetic field ($\Delta\delta \approx 0.1$ ppm) whereas the proton (n) indicated unusual high magnetic field shift ($\Delta\delta = -1.12$ ppm). It is reasonable that a steric hindrance arises between carbonyl group and the oxyethylene chain. To avoid this, these two groups must take a trans-molecular geometry, and the proton (n) have to stand

in deshielding area of the carbonyl group showing an unusual low chemical shift value (8.46 ppm). Upon complexing with Ca^{2+} , the geometry changed to a cis-form, and the proton (n) comes out of this area showing normal chemical shift value (7.34 ppm). It is also noted that benzene protons (a, b and c) indicated higher magnetic field shifts ($\Delta\delta = -0.18, -0.40$ and -0.18 ppm, respectively). This suggested that these protons stand in the magnetically shielding region of the pyrene ring, and the benzene moiety can work as an obstacle to the rotation along pyrene-CO bond.

On the basis of fluorescence and ^1H NMR studies, an expected structural change of **1** before and after the addition of Ca^{2+} on the ground state is illustrated in the graphical abstract. It has been clear that carbonyl group and ethyleneoxy moiety were provided cooperative strong binding site, and the benzene and acetyl groups induced inhibition of the rotation around amide bond in both of the ground and excited states resulting the inhibition of TICT relaxation process. Thus, the fluorescence emission from pyrene of $\text{Ca}^{2+}\cdot(\mathbf{1}$ and $\mathbf{2})$ can be observed.

In the case of larger ionic radii than Ca^{2+} such as Ba^{2+} , the oxyethylene chain lengths of **1** and **2** are too short to surround. The phenyl and acetyl groups could not be the obstacles for the excited rotation around the pyrenyl aromatic amide moiety. These complexes did not exhibit the enhancement effect on the fluorescence intensity. On the other hand, **1** and **2** could not bind Mg^{2+} with oxyethylene and carbonyl moieties cooperatively resulting no enhance effect of the fluorescence intensity.

The detailed observation for complex structure is now underway. We believe that present fluorophores **1** and **2** will be available as photodetecting system for analytical use with "off-on" fluorescent signaling character.

References and Notes

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- 6 1-[2-(1-pyrenecarboxamido)phenoxy]-8-(benzamido)-3,6-dioxaoctane(**1**): white solid, mp 123–124 °C (from ethanol). ^1H NMR (CDCl_3) $\delta = 3.03$ (C-CH₂-O, t, 2H), 3.12 (C-CH₂-O, t, 2H), 3.30 (C-CH₂-O, t, 2H), 3.34 (C-CH₂-O, t, 2H), 3.70 (C-CH₂-O, t, 2H), 4.16 (C-CH₂-O, t, 2H), 6.30 (NH, m, 1H), 6.96 (aromatic, d, 2H), 7.13 (aromatic, q, 2H), 7.31 (aromatic, t, 2H), 7.40 (aromatic, t, 1H), 7.63 (aromatic, d, 2H), 8.04–8.23 (aromatic, m, 8H), 8.72 (aromatic, d, 1H), 8.72 (NH, m, 1H). Found: C, 75.38; H, 5.66; N, 4.83%. Calcd. for $\text{C}_{36}\text{H}_{32}\text{O}_5\text{N}_2$: C, 75.51; H, 5.63; N, 4.89%.
- 7 1-[2-(1-pyrenecarboxamido)phenoxy]-8-(acetamido)-3,6-dioxaoctane(**2**): white solid, mp 81–82 °C (from benzene). ^1H NMR (CDCl_3) $\delta = 1.81$ (CH₃), 3.02 (C-CH₂-O, t, 4H), 3.09 (C-CH₂-O, t, 2H), 3.34 (C-CH₂-O, t, 2H), 3.73 (C-CH₂-O, t, 2H), 4.21 (C-CH₂-O, t, 2H), 5.60 (NH, m, 1H), 6.96 (aromatic, d, 2H), 7.13 (aromatic, q, 2H), 8.05–8.31 (aromatic, m, 8H), 8.73 (aromatic, d, 1H), 8.73 (NH, m, 1H). Found: C, 73.06; H, 5.94; N, 5.26%. Calcd. for $\text{C}_{31}\text{H}_{30}\text{O}_5\text{N}_2$: C, 72.92; H, 5.92; N, 5.49%.
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