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Control between TICT and PET using chemical modification of *N*-phenyl-9-anthracenecarboxamide and its application to a crown ether type chemosensor

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ABSTRACT

Both twisted intramolecular charge transfer (TICT) and photoinduced electron transfer (PET) relaxation processes of *N*-phenyl-9-anthrylcarboxamide derivatives can be characterized by modified substitution of the phenyl group. Introduction of a methoxy group to phenyl moiety quenched fluorescence of the anthracene using TICT or PET process, and was not retrieved even using highly viscous media. The introduction of a methylene unit induced fluorescence emissions using a solvent with both viscosity and polarity. This phenomenon demonstrates that the effects of both TICT and PET are involved in this system. Based on these data, we synthesized a novel crown ether derivative **7**: its analytical usefulness as a fluorescent chemosensor for alkaline earth metal ions is reported herein.

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1. Introduction

An electron donor and acceptor system in one molecule engenders an intramolecular charge transfer state by photo-irradiation. From the perspective of the modes of charge transfer in a short range, they are classifiable into two categories: photoinduced electron transfer (PET)[1–4] and twisted intramolecular charge transfer (TICT).[5–11] The PET process depends on the distance and redox levels between the donor and acceptor. In contrast, the occurrence of TICT is expected to be governed only by redox levels. Moreover, the TICT process is expected to require the twisted motion of the donor or acceptor at the charge transfer event.

Fluorescent PET sensors have received much attention for their wide application to various analytical and chemical processes;[12] they have been used as a tool in the field of molecular switches and photonic device.[13–17] A PET sensor generally comprises a guest binding site as the receptor and fluorophore moiety. Consequently, the sensitivity is directly related to the strength of the emission signal produced after complexing of the guest molecule by the receptor.

The TICT concept, as presented by Grabowski et al.[18] has become widely recognized as an explanation of anomalous dual fluorescence emission. The TICT model is useful to describe fluorescence behavior of *N*,*N*′-dimethyl-4-aminobenzonitrile. Although numerous studies of TICT family molecules have been reported, in contrast to the PET, the use of TICT for chemosensors and signaling purposes remains limited.[19,20]

Recently, the present author reported that *N*-phenyl-9-anthracene-[21] and *N*-phenyl-1-pyrene-[22] carboxamide derivatives showed weak fluorescence emission in an acetonitrile solution through intramolecular charge transfer pathway, which is similar to TICT. Based on these results, fluoroionophores having these fluorophores and linear polyether have been synthesized. Upon complexing with alkaline earth metal ions, the absorption spectrum did not change, but a large enhancement of fluorescence intensity was obtained as a result of freezing of the twisted motion of amide bond and fluorophores by the coordination of ions. Here, the anthracene or pyrene unit acts as an acceptor; the benzene unit acts as a donor. To extend this idea, an introduction of an electron donating group, such as the methoxy unit, on the benzene ring will enhance the charge transfer characteristics.

We also reported chemosensors based on linear polyether possessing *N*-phenyl-1-naphthalenacetamide[23] or benzo-crown ether.[24] These sensors show that binding of alkaline earth metal ions signals a switching-on of the fluorescence of naphthalene. From spectroscopic data, the hybrid quenching process of TICT and PET on *N*-phenyl-1-naphthylacetamide was strongly evidenced through switching ‘Off–On’ monitoring. However, unfortunately,

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photochemical properties on its signal 'Off–On' were not elucidated in detail using spectroscopic data with model compounds.

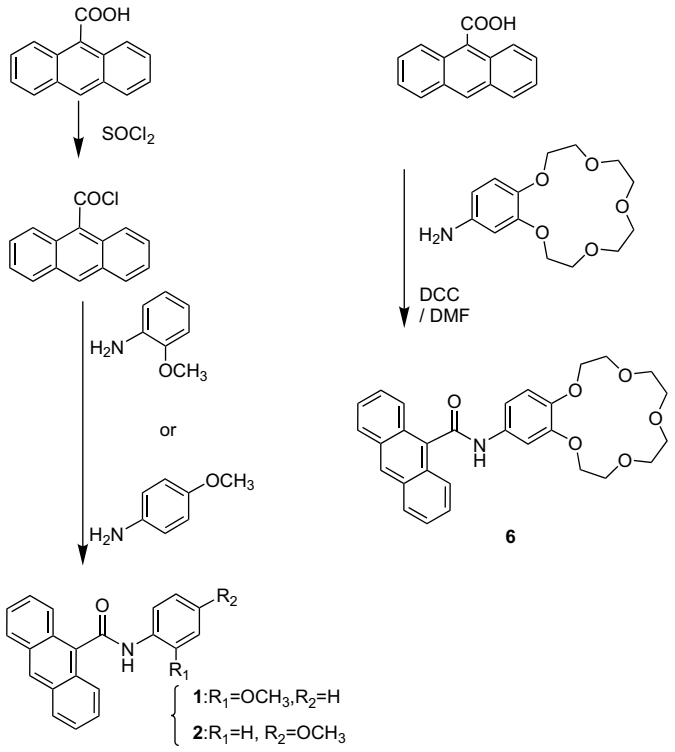
Bearing these in mind, we checked effects of a modifying substitution, which are the number and position of electron donating group (–OMe) on the benzene ring. We also report the influence of the spacer between the donor and acceptor for *N*-phenyl-9-anthraceneacetamide derivatives (Scheme 1).

2. Experimental section

2.1. Materials

*2.1.1. N-(2-Methoxy or 4-methoxyphenyl)-9-anthracenecarboxmide (**1** or **2**)*

A solution of 9-anthracenecarboxylic acid (9-anthroic acid) (2.22 g, 0.01 mol) in 30 mL of $SOCl_2$ was refluxed for 1.5 h. Excess $SOCl_2$ was distilled off in vacuo and completely evaporated after addition of 10 mL of benzene three times. This obtained acid chloride was dissolved in 80 mL of THF. To this solution was added each 2-anisidine (0.28 g, 0.02 mol) or 4-anisidine (0.28 g, 0.02 mol) dissolved dropwise in 20 mL of THF at room temperature. The mixture was stirred for 1 day; a small amount of 2-aminophenol hydrochloride salt was precipitated. The solution was filtered. Then the precipitate was washed with 30 mL of water, EtOH, and $CHCl_3$, successively, and dried in vacuo. Compounds **1** and **2** were purified by recrystallization from ethanol (Scheme 2).



Scheme 2.

*2.1.2. N-(2-Methoxy-, 4-methoxy-, or 3,4-dimethoxy-phenyl)-9-anthraceneacetamide (**3**, **4**, or **5**)*

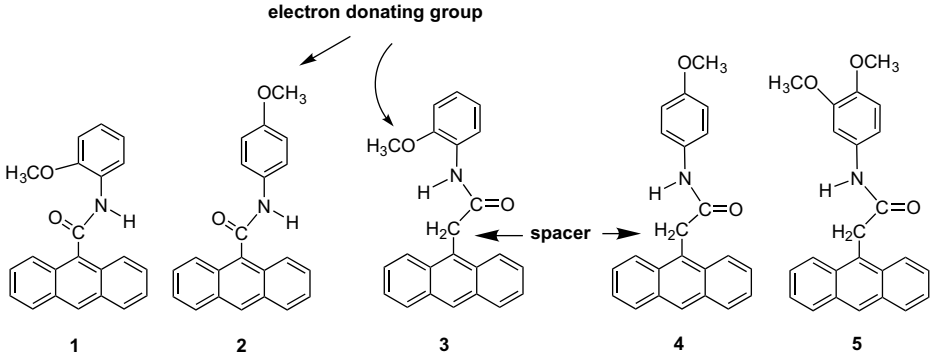
9-Anthracenemethanol (5 g, 0.024 mol) in 1,4-dioxane (50 mL) was refluxed for 2 h with the addition of $SOCl_2$ (1.15 mL, 0.026 mol). The solution was cooled to room temperature. The crude chlorinated methyl anthracene was precipitated in H_2O and dried at room temperature. The residue was dissolved in acetonitrile (50 mL) and refluxed with the addition of NaCN (2.45 g, 0.05 mol). The reaction mixture was filtered. Then, the acetonitrile mixture was added to water (100 mL). After the precipitate was filtered, the residue (4.17 g, 0.02 mol) in acetic acid (150 mL) was refluxed carefully for 5 h with the addition of HCl (50 mL). The solution was cooled and precipitated in water. The crude product was dissolved in 20% NaOH aqueous solution and filtered. Subsequently, HCl (20 mL) was added to the solution and a yellow solid (9-anthraceneacetic acid) was precipitated. The filtered 9-anthraceneacetic acid (4.28 g, 0.018 mol) and HOBt (2.4 g, 0.018 mol) were dissolved in 50 mL of DMF; then 2-anisidine (2.21 g, 0.018 mol), 4-anisidine (2.21 g, 0.018 mol), or 3,4-dimethoxyaniline (2.75 g, 0.018 mol) was added. The solution was treated with dicyclohexylcarbodiimide (3.71 g, 0.018 mol) under stirring for 1 day at 0 °C. After the solvent was evaporated under reduced pressure, a crude compound was obtained. Compound **3**, **4**, or **5** was purified by recrystallization from acetic acid.

*2.1.3. 4′-(9-Anthracencarboxamido)benzo-15-crown-5 (**6**)*

9-Anthracenecarboxylic acid (9-anthroic acid) (2.22 g, 0.01 mol) and HOBt (1.53 g, 0.01 mol) were dissolved in 50 mL of DMF, and 4′-aminobenzo-15-crown-5-ether (3.1 g, 0.01 mol) was added. The solution was treated with dicyclohexylcarbodiimide (2.6 g, 0.01 mol) under stirring for 1 day at 0 °C. The solvent was evaporated under reduced pressure, and the crude compound was obtained. Compound **6** was recrystallized from acetic acid.

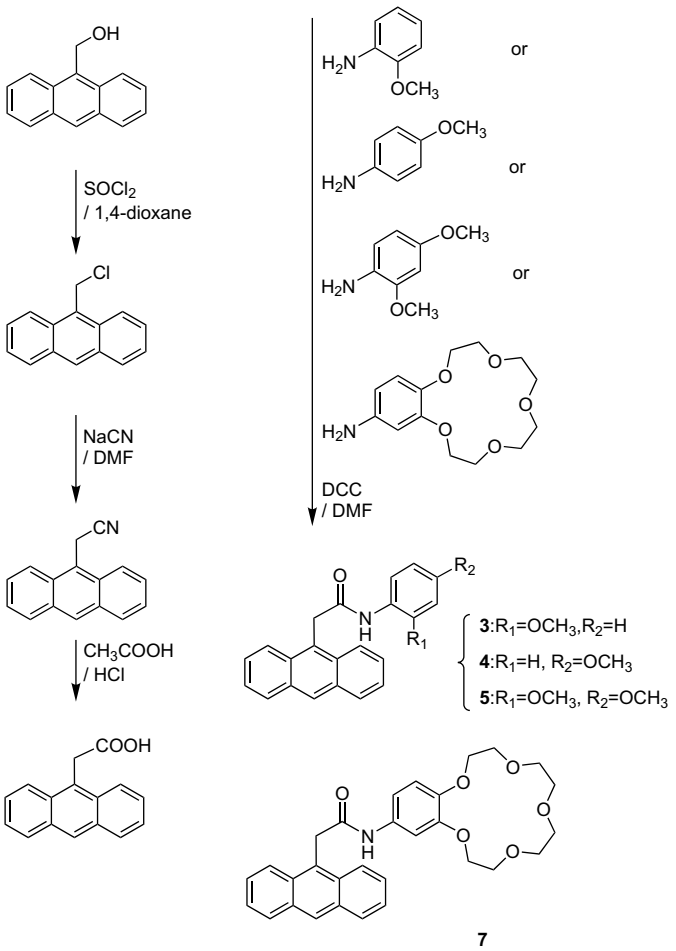
*2.1.4. 4′-(9-Anthraceneacetamido)benzo-15-crown-5 (**7**)*

9-Anthraceneacetic acid (2.35 g, 0.01 mol) and HOBt (1.53 g, 0.01 mol) were dissolved in 50 mL of DMF; then 4′-aminobenzo-15-crown-5-ether (5.1 g, 0.018 mol) was added. The solution was treated using dicyclohexylcarbodiimide (3.4 g, 0.018 mol) under stirring for 1 day at 0 °C. The solvent was evaporated under reduced



Scheme 1.

pressure. Thereby, a crude compound was obtained. Compound **7** was recrystallized from acetic acid (Scheme 3).



Scheme 3.

*2.1.5. N-(2-Methoxyphenyl)-9-anthracenecarboxamide (**1**)*

Yield 73%; pale yellow solid; mp 164–166 °C; ^{1}H NMR ($CDCl_3$) δ=3.74 (–OCH_3, s, 3H), 6.92 (aromatic, d, 1H), 7.14 (aromatic, m, 2H), 7.49 (aromatic, m, 4H), 8.03 (aromatic, d, 2H), 8.18 (aromatic, d, 2H), 8.31 (NH, s, 1H), 8.53 (aromatic, s, 1H), 8.85 (aromatic, d, 1H). Anal. Found: C, 80.14; H, 5.23; N, 4.23. Calcd for $C_{22}H_{17}NO_2\cdot 1/5H_2O$: C, 80.27; H, 5.27; N, 4.26.

*2.1.6. N-(4-Methoxyphenyl)-9-anthracenecarboxamide (**2**)*

Yield 75%; pale yellow solid; mp 168–170 °C; ^{1}H NMR ($CDCl_3$) δ=3.84 (–OCH_3, s, 3H), 6.96 (aromatic, d, 2H), 7.48–52 (aromatic, m, 4H), 7.59 (NH, s, 1H), 7.67 (aromatic, d, 2H), 8.01 (aromatic, d, 2H), 8.16 (aromatic, d, 2H), 8.52 (aromatic, s, 1H). Anal. Found: C, 80.56; H, 5.25; N, 4.29. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28.

*2.1.7. N-(2-Methoxyphenyl)-9-anthraceneacetamide (**3**)*

Yield 81%; pale yellow solid; mp 182–184 °C; ^{1}H NMR ($CDCl_3$) δ=3.70 (–OCH_3, s, 3H), 4.76 (–CO–CH_2, s, 2H), 6.65 (aromatic, d, 1H), 6.72 (NH, s, 1H), 6.79 (aromatic, d, 1H), 7.01 (aromatic, m, 2H), 7.56–7.60 (aromatic, m, 4H), 8.09 (aromatic, d, 2H), 8.30 (aromatic, d, 2H), 8.65 (aromatic, d, 1H). Anal. Found: C, 80.69; H, 5.73; N, 4.04. Calcd for $C_{23}H_{19}O_2N\cdot 1/5H_2O$: C, 80.49; H, 5.64; N, 4.08.

*2.1.8. N-(4-Methoxyphenyl)-9-anthraceneacetamide (**4**)*

Yield 83%; pale yellow solid; mp 185–187 °C; ^{1}H NMR ($CDCl_3$) δ=3.71 (–OCH_3, s, 3H), 4.73 (–C–CH_2, s, 2H), 6.70 (aromatic, d, 2H), 6.76 (NH, s, 1H), 7.08 (aromatic, d, 2H), 7.56–7.62 (aromatic, m, 4H), 8.13 (aromatic, d, 2H), 8.35 (aromatic, d, 2H), 8.57 (aromatic, s, 1H). Anal. Found: C, 80.01; H, 5.64; N, 4.03. Calcd for $C_{23}H_{19}O_2N\cdot 1/4H_2O$: C, 79.86; H, 5.68; N, 4.05.

*2.1.9. N-(3,4-Methoxyphenyl)-9-anthraceneacetamide (**5**)*

Yield 81%; pale yellow solid; mp 178–180 °C; ^{1}H NMR ($CDCl_3$) δ=3.76 (–OCH_3, s, 6H), 4.73 (–C–CH_2, s, 2H), 6.45 (aromatic, d, 1H), 6.61 (aromatic, d, 2H), 6.77 (NH, s, 1H), 7.07 (aromatic, s, 1H), 7.51–7.57 (aromatic, m, 4H), 8.08 (aromatic, d, 2H), 8.26 (aromatic, d, 2H), 8.52 (aromatic, s, 1H). Anal. Found: C, 77.26; H, 5.70; N, 3.77. Calcd for $C_{24}H_{21}NO_3$: C, 77.16; H, 5.71; N, 3.78.

*2.1.10. 4′-(9-Anthracenecarboxamido)benzo-15-crown-5 (**6**)*

Yield 78%; pale yellow solid; mp 167–169 °C; ^{1}H NMR ($CDCl_3$) δ=3.72 (–O–CH_2, m, 8H), 3.88 (–O–CH_2, m, 4H), 4.12 (–O–CH_2, t, 2H), 4.19 (–O–CH_2, t, 2H), 6.85 (aromatic, d, 1H), 7.04 (aromatic, d, 1H), 7.47–51 (aromatic, m, 4H), 7.60 (aromatic, s, 1H), 7.73 (NH, s, 1H), 8.01 (aromatic, d, 2H), 8.12 (aromatic, d, 2H), 8.49 (aromatic, s, 1H). Anal. Found: C, 70.55; H, 6.03; N, 2.80. Calcd for $C_{29}H_{29}O_6N\cdot 1/4H_2O$: C, 70.79; H, 6.04; N, 2.85.

*2.1.11. 4′-(9-Anthraceneacetamido)benzo-15-crown-5 (**7**)*

Yield 74%; pale yellow solid; mp 163–165 °C; ^{1}H NMR ($CDCl_3$) δ=3.70 (–O–CH_2, m, 8H), 3.83 (–O–CH_2, m, 4H), 4.02 (–O–CH_2, m, 4H), 4.71 (C–CH_2, s, 2H), 6.45 (aromatic, d, 1H), 6.63 (aromatic, d, 1H), 6.76 (NH, s, 1H), 7.03 (aromatic, s, 1H), 7.52 (aromatic, t, 2H), 7.59 (aromatic, t, 2H), 8.07 (aromatic, d, 2H), 8.23 (aromatic, d, 2H), 8.51 (aromatic, s, 1H). Anal. Found: C, 71.53; H, 6.22; N, 2.79. Calcd for $C_{30}H_{31}O_6N$: C, 71.84; H, 6.23; N, 2.79.

2.2. Measurement of fluorescence and UV spectra

Fluorescence spectra were measured using a spectrometer (RF-5300PC; Shimadzu Corp.) at 25 °C. The excitation wavelength was 363 nm. Concentrations of the fluorescent reagents were 1×10^{-5} mol/dm^3 in purified acetonitrile. Alkaline earth metal cations were added to the solution of fluorescent reagent as perchlorate salts. The UV spectra were recorded using a spectrometer (UV-2400; Shimadzu Corp.) with an equipment of temperature controller in spectral grade acetonitrile.

3. Results and discussion

3.1. Photochemical properties of model compounds 1–5

To study effects of molecular motions on charge transfer (CT) at an excited state, the solvent dependence on fluorescence intensities was assessed using model compounds **1**–**5**, as shown in Scheme 1. Compounds **1** and **2**, respectively, show 2-methoxy and 4-methoxy groups on anthracene aromatic amide; compounds **3** and **4** have a methylene group between anthracene and amide moieties based on compounds **1** and **2**. Compound **5** possesses two methoxy groups at 3 and 4 substitution positions of the benzene ring. Modification studies of the methoxy group on anthracene aromatic amide donate a foundation of the benzo-crown ether compound, as explained below.

Three polar solvents were used: acetonitrile, methanol, and glycerin. Polarities (dielectric constants) of these solvents are almost equal (ε_0=37.5 for acetonitrile, 33.7 for methanol, and 42.5 for glycerin), but their viscosities (μ) mutually differ (μ=0.34 mPa s for acetonitrile, 0.58 mPa s for methanol and 1490 mPa s for glycerin at 20 °C).[25]

Figure 1 presents fluorescence spectra of **1** and **2** as a function of solvents. In acetonitrile or methanol, the fluorescence emissions from **1** or **2** are weak. These spectroscopic data indicate that fluorescence emissions **1** and **2** were quenched by charge separation at the excited state, where high polarity of the solvent stabilized the charge-separated state. A glycerin solution of **1** provided a stronger fluorescence emission than other solvents, whereas that of **2** gave weak emission equal to that of acetonitrile and methanol solution. A clear difference existed in the charge transfer mode between **1** and **2**. Glycerin has three hydroxyl groups. For that reason, it forms a strong hydrogen bond network in a solution, which causes high viscosity. The molecular motion is expected to be suppressed when substances are dissolved in such a viscous environment. The molecular motion of **1**, which includes a rotation of the benzene ring around C–N, was frozen by the high viscosity of glycerin. This phenomenon indicates that fluorescence properties are governed by the TICT relaxation process. A glycerin solution of **2** did not impart a considerable fluorescence enhancement as that in the acetonitrile and methanol solution did, which indicates that the quenching of **2** occurs in any molecular geometry such as that of PET. In other words, the formation of the charge-separated state of **1** necessitates a change of molecular motion, whereas that of **2** does not. Consequently, it can be concluded that an excited state of **1** decays through the TICT process, whereas that of **2** reverts to the ground state via the PET process rather than TICT.

According to the OMe group position (*ortho* and *para*), the HOMO energy level of phenyl moiety might be disparate because free rotation of benzene ring with *ortho*-OMe group is restrained using a steric repulsion of amide moiety in contrast to that of *para* position. The difference of the charge transfer property should result from a geometric structure of the substituent if the electron donating capabilities of OMe group in **1** and **2** are almost equal. The occurrence of CT requires a change of conformation to be a suitable configuration (e.g., all-planar molecular geometry). The fluorescence quenching properties of **1** and **2** revealed the two mechanisms, TICT and PET, by the substitution position of OMe group.

We investigated the effects on the CT of an introduction of a spacer, $-CH_2-$, between the donor (methoxy-benzene and amide groups) and the acceptor (anthracene moiety). Figure 2 portrays

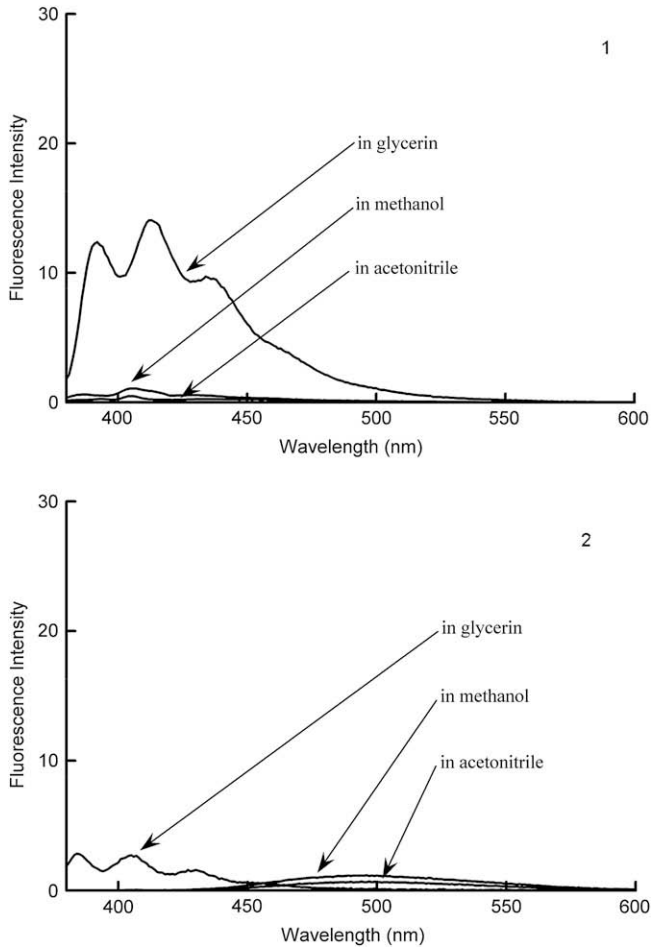


Figure 1. Fluorescence spectra of **1** and **2** in various solvents at 25 °C; [L]=1×10^{-5} mol/dm^3; excitation wavelength: 364 nm; slit width: 3 nm.

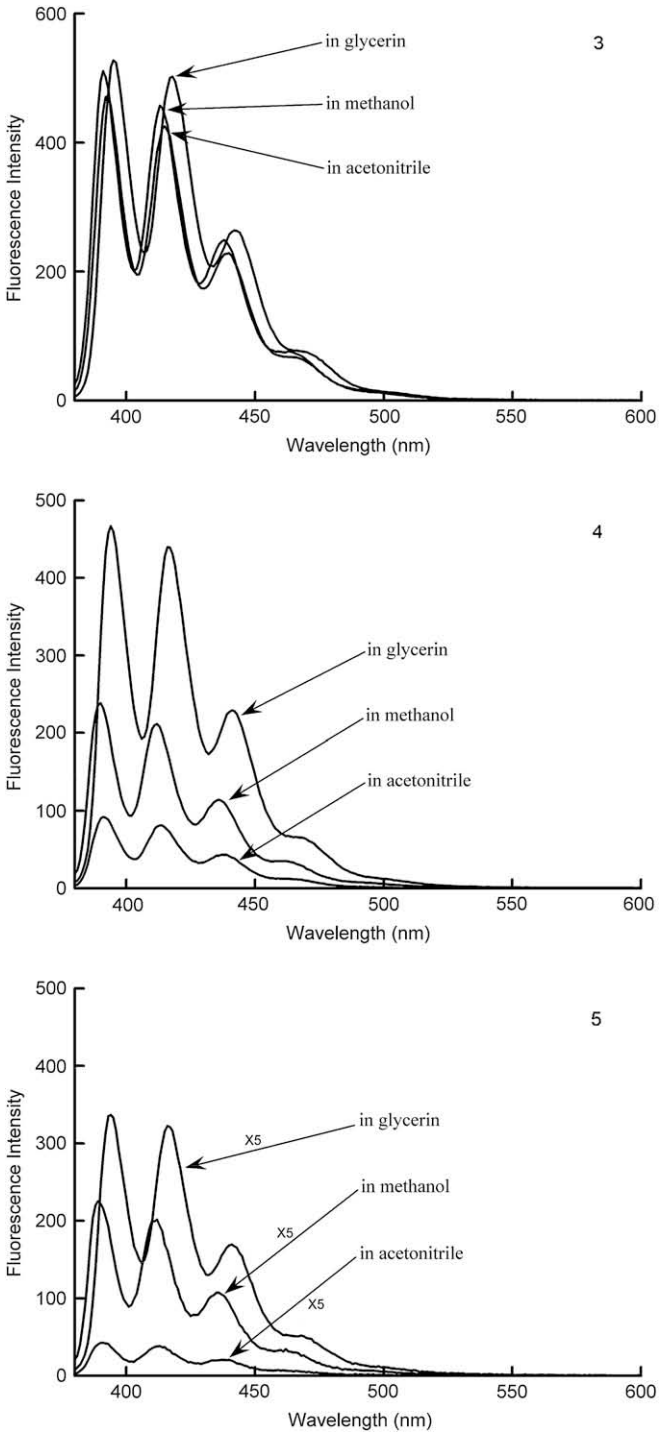
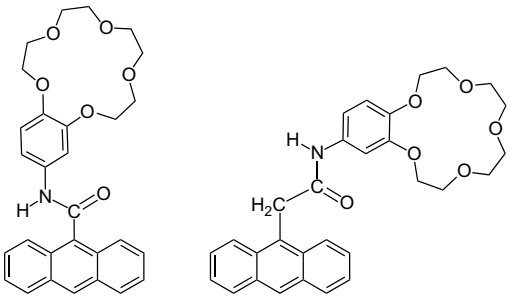


Figure 2. Fluorescence spectra of **3**, **4**, and **5** in various solvents at 25 °C; [L]=1×10^{-5} mol/dm^3; excitation wavelength: 364 nm; slit width: 3 nm.

fluorescence spectra of **3**, **4**, and **5** as a function of solvents. Compound **3** gave strong emissions from anthracene moiety in all solvents, with almost identical fluorescence intensities (Fig. 2), which shows that the CH_2 group in **3** inhibited the charge transfer interaction between a donor and an acceptor. Figure 2 shows that quenching efficiencies of these compounds were markedly lower than those of **1** and **2**. The fluorescence spectra of **4** exhibited weaker emission than that of **3** in acetonitrile, which is expected to result from charge transfer beyond the CH_2 group. In methanol, compound **4** formed a hydrogen bond between the amide moiety of **4** and the solvent. These conditions induced the suppression of internal molecular motion of **4**; moreover, a slight fluorescence enhancement effect was observed. In glycerin, a large enhancement of fluorescence intensity of **4** was obtained (Fig. 2). This solvent dependence of **4** closely resembled that of **1**, and can be interpreted by the relaxation mechanism as TICT. The fluorescence intensity of **5**, which has two OMe groups, was faint compared to that of **4** in all solvents (Fig. 2), which indicated that the addition of an OMe group showed increased electron donating capability, and the PET process became predominant. Model studies using **3**–**5** are summarized as follows. (1) The introduction of a spacer greatly decreased of the CT efficiency; the electron donating ability of the benzene moiety, which is adjustable through introduction of OMe group, played an important role in both TICT and PET over the spacer. (2) These CT behaviors were determined by the substituent position and number of the OMe group. (3) The *para*-OMe group enhanced TICT of **4**, although the *ortho*-OMe substituent in **3** did not increase the CT character. (4) Two OMe groups emphasized PET character in **5**. As described above, controlling TICT and PET on *N*-phenyl-9-anthracenecarboxamide derivatives can be achieved through appropriate selection for introduction of OMe group and the spacer. Based on the model study, we synthesized novel benzo-crown ethers having 9-anthracencarboxamide (**6**) and 9-anthraceneacetamide (**7**) (Scheme 4).



6 **7**

Scheme 4.

3.2. Photochemical properties of chemosensors 6 and 7

Although it is identifiable from ^{1}H NMR data that the crown ether moiety of **6** formed a complexation with metal ions, the fluorescence emission was not increased by the presence of any alkaline earth metal ion. This phenomenon indicates that excited **6** is relaxed to the ground state with the PET mechanism just as **2**, which could not break the charge transfer pathway. These results suggest that the coordination of cations on the benzo-crown ether moiety and the carboxyl group connected to anthracene ring was insufficient to intercept a conjugation system between the donor and the acceptor.

Figure 3 displays fluorescence spectra of **7** and its Mg^{2+} complexes in acetonitrile at 25 °C. The weak emission of free **7** was attributed to the PET action as an analogy of model study using **5**.

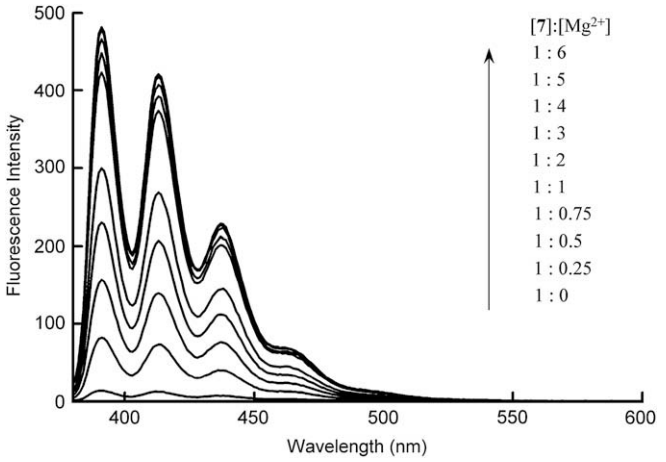


Figure 3. Fluorescence spectra of **7** and its Mg^{2+} complex in acetonitrile at 25 °C; [L]=1×10^{-5} mol/dm^3; excitation wavelength: 364 nm; slit width: 3 nm.

The addition of Mg^{2+} induced considerably large enhancement of the fluorescence intensity of **7**. This fluorescence enhancement is clearly induced by complexation. The shape and region of fluorescence of **7**·Mg^{2+} were featurized by anthracene emission, which indicated that **7**·Mg^{2+} had no CT interaction between the anthracene and benzo-crown moieties. It is acceptable that cooperative binding of Mg^{2+} with a crown ether moiety and a carbonyl group in **7** formed a bending structure.[25]

The bending motion around the amide bond will engender the breakdown of π-conjugation between the benzene ring and the carbonyl group. The shutting off of the π-conjugation corresponds with the great enhancement of fluorescence intensity. A similar result was also obtained with a similar fluorescence enhancement effect for **7**·Ca^{2+}. Regarding **7**·Sr^{2+}, a unique feature in the fluorescence spectra was observed, as portrayed in Figure 4. A broad excimer-like emission at 450–550 nm was obtained. With increasing Sr^{2+} concentration, the fluorescence emission intensity increased to an approximately 1:1 molar ratio (L/M^{2+}), and then decreased at greater ratios. This phenomenon is explained using the formation of a 2:1 (L/M^{2+}) complex prior to a 1:1 complex. The same result was observed for **7**·Ba^{2+}. However, these observations were not obtained in Mg^{2+} and Ca^{2+}. This result is explainable by the fact that Mg^{2+} and Ca^{2+}, which have small ionic size, form only 1:1 complex in the inside of the crown ether cavity. However, large

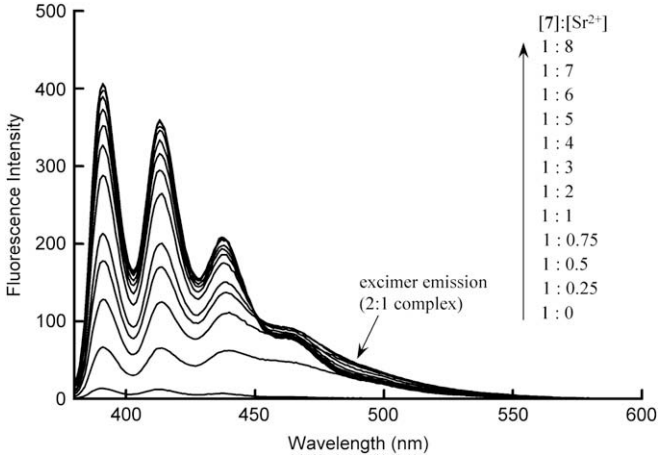


Figure 4. Fluorescence spectra of **7** and its Sr^{2+} complex in acetonitrile at 25 °C; [L]=1×10^{-5} mol/dm^3; excitation wavelength: 364 nm; slit width: 3 nm.

Table 1
Wavelength of fluorescence maxima (λ_{max}), fluorescence intensity ratios (I_{max}/I_0) at λ_{max} and complex formation constants (log K) of **7**[a]

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
λ_{max} (nm)	391	391	391	391
I_{max}/I_0	37.1	34.5	30.8	25.8
log K (1:1)	5.86	5.79	4.21	4.25
(1:2)	—	—	6.09	6.20

[a] Fluorescence spectra of **7** was measured in acetonitrile at 25 °C; [**7**]=1×10^{-5} mol/dm^3; excitation wavelength: 364 nm; K (1:1)=[ML^{2+}]/[M^{2+}][L], K (1:2)=[ML_2^{2+}]/[ML^{2+}][L].

Sr^{2+} and Ba^{2+} formed 2:1 complexes with a sandwich-type structure.[26,27] In general, benzo-15-crown-5 derivatives[28–33] having fluorophores are known to have high sensitivity and selectivity for alkali metal cations. However, fluorescence responses to Li^+, Na^+, and K^+ were not observed in this work.

The fluorescence response ratios of **7**, expressed as I_{max}/I_0 values for metal cations, are presented in Table 1. The order of I_{max}/I_0 was Mg^{2+} (37.1)>Ca^{2+} (34.5)>Sr^{2+} (30.8)>Ba^{2+} (25.8). This shows large PET control ability of the crown ether moiety for Mg^{2+} compared to that of other metal cations. The binding constant (log K) of the complex was also evaluated from the fluorescence intensities using a nonlinear least-squares curve fitting method.[34] For complexes formed with 1:1 stoichiometry, Mg^{2+} and Ca^{2+} showed larger affinity than either Sr^{2+} or Ba^{2+} (Table 1); 1:2 complexes in Sr^{2+} and Ba^{2+} gave larger log K values than 1:1 complexes.

The introduction of a spacer in **7** decreased the CT efficiency and increased molecular flexibility compared to that of **6**. The addition of flexibility for the molecular motion induced breakage of π-conjugation in **7** upon complexation with alkaline earth metal ions, which results in a large fluorescence enhancement.

4. Conclusions

The control of TICT and PET on *N*-phenyl-9-anthracenecarboxamide derivatives can be carried out by an appropriate introduction of combination of OMe group and the spacer. The substitution position of the electron donating OMe group played an important role for both TICT and PET. The CT behavior can be controlled through formation of complexation with metal ions. The novel fluorescent crown ether **7** exhibits a high response ability (I_{max}/I_0=37.1) for Mg^{2+}. Our future efforts will specifically elucidate photochemical behavior of donor–acceptor systems linked by amide bonds and develop the use of CT action for fluorescent chemosensors, molecular switches, photonic devices, and other photo-active materials.

References and notes

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