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ANION-INDUCED FLUORESCENCE QUENCHING AND EXCIMER FORMATION OF ANTHRACENE-IMIDAZOLIUM RECEPTOR

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Abstract – New anthracene based fluorescent anion receptor bearing two imidazolium units linked by methylene spacers at 9,10-positions has been synthesized. Complexation behavior and fluorescent properties of the receptor with inorganic anions (Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, and $H_2PO_4^-$) in acetonitrile were investigated by ^{1}H NMR spectrometric and fluorimetric titrations, and fluorescence lifetime measurement. At low receptor concentration level (0.1 μM), fluorescence of the receptor was quenched by formation of 1:1 host-guest complex with the anions. At relatively higher receptor concentrations (above 1.0 μM), $H_2PO_4^-$ anion quenched the monomer emission mainly by the excimer formation due to anion-induced ground state aggregation. Fluorescence lifetime measurements revealed that quenching mechanisms are different between halide ions and oxoanions.

Complexation induced fluorescence quenching or enhancement is currently receiving a lot of attention for the detection of ionic or neutral species since it can be monitored in real time, even at very low substrate concentration levels.[1,2] During the last decade, a large number of fluorescent molecular chemosensors, which can translate a molecular recognition process into a generation of photonic signals, have been designed by linking a fluorophore to a receptor.[1-3] Luminescent signaling of anion recognition[4,5] has been achieved using a variety of chemical units including naphthalene, anthracene, pyrene, quinoxaline,

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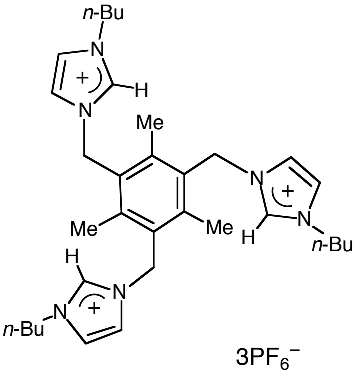
This paper is dedicated to the memory of the Emeritus Professor Kenji Koga of Tokyo University.

and porphyrin or Ru(bpy)$_3$ derivatives.[2,3] However, in contrast to the well-documented cation-sensitive sensors, the fluorosensor for anions is still relatively rare.

Recently, we have discovered that 1,3-disubstituted imidazolium group is an effective anion binding subunit utilizing both electrostatic attraction and [C-H•••X$^-$] hydrogen bonding ability, and our tripodal receptor (**1**)[6] and cyclophane (**2**)[7] form stable 1:1 host-guest complexes with small inorganic anions in acetonitrile or DMSO solutions. For the application to fluorescent anion sensing, we have now synthesized a dipodal fluorescent receptor (**3**), in which two imidazolium units are linked to a 9,10-anthracenylene fragment by methylene spacers, and we describe herein its anion binding and specific fluorescence properties of the $H_2PO_4^-$ anion complex. Although selective fluorescent sensing of $H_2PO_4^-$ anion by 1,8-isomer of **3** was recently reported by K. S. Kim *et al.*,[8] it has not been reported for the unique fluorescent behavior, i.e., the excimer formation by anion-induced assembly (*vide infra*).



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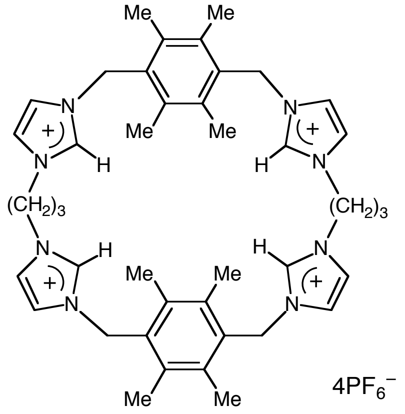

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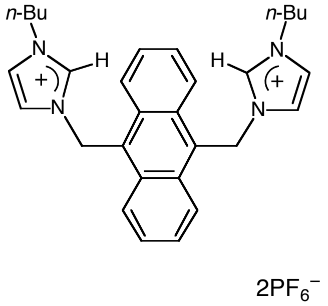
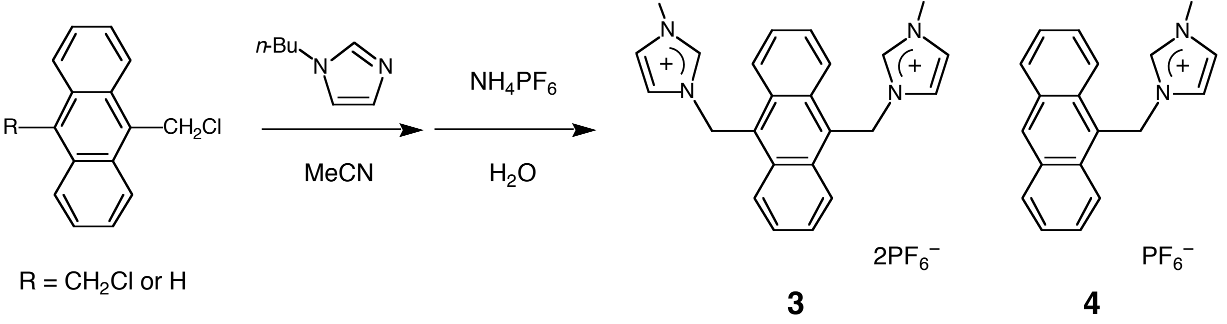


3

Receptor (**3**) was prepared by the reaction of 1-*n*-butylimidazole with 9,10-bis(chloromethyl)anthracene in acetonitrile. After counter ion exchange into hexafluorophosphate salts by NH_4PF_6/H_2O, **3** was purified by recrystallization from acetonitrile-ethanol (72% yield).[9] Monoimidazolium receptor (**4**)[10] was also synthesized from 1-*n*-butylimidazole and 9-chloromethylanthracene (66% yield).



Scheme 1

The anion complexation ability of the receptors was initially studied by ^{1}H NMR titration techniques. Addition of tetrabutylammonium salts *n*-$Bu_4N^+X^-$ (X^- = Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, and ClO_4^-) to a CD_3CN solution of **3** or **4** (0.5 mM) produced a significant downfield shifts (up to 1.1 ppm) of the imidazolium C(2)-H proton due to the formation of [C-H•••X^-] hydrogen bonds[6] (Figure 1). On the addition of $H_2PO_4^-$ ion to the receptor (**3**), the downfield shifts were observed but precipitation occurred during titration. The binding constant of **3** and $H_2PO_4^-$ was determined in DMSO-d_6. Analysis of the titration data using a nonlinear least-squares curve-fitting[11] afforded the binding constants for 1:1 stoichiometric complexes as shown in Table 1. The receptors (**3**) and (**4**) have a similar guest selectivity, but the bidentate receptor (**3**) has higher affinity than the mono-imidazolium receptor (**4**) probably due to two-point recognition.

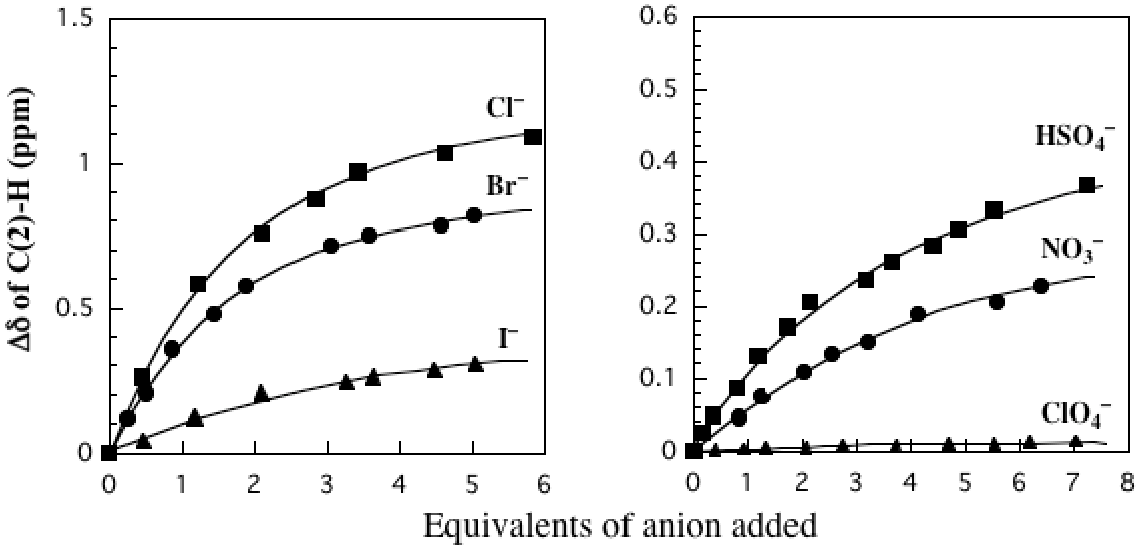


Figure 1. ^{1}H NMR titration curves of the receptor **3** (0.5 mM in CD_3CN) with halide ions (left) and oxoanions (right), respectively.

Table 1. Binding constants $\boldsymbol{K_a}$ for 1:1 complexes of receptors (**3** and **4**) with various anions (as tetrabutylammonium salts) determined by ^{1}H NMR titration (0.5 mM) in CD_3CN at 298 K.

	K_a[a] / M^{-1}						
Receptor	Cl^-	Br^-	I^-	NO_3^-	HSO_4^-	$H_2PO_4^-$	ClO_4^-
3	1900	1500	520	610	240	-[b] (3400)[c]	-[d]
4	280	230	140	250	45	770 (670)[c]	-[d]

[a] Errors are estimated to be <10%. [b] Precipitation occurred during titration. [c] In DMSO-d_6. [d] No significant shift was observed.

The fluorescence (1.0 μM, λ_{ex} = 335 nm) spectra of **3** and **4** in acetonitrile exhibit a set of structured bands assigned to monomeric anthracene emission. Quenching of anthracene fluorescence by covalently attached cationic heterocycles such as pyridinium groups is a well-known phenomenon, for example, fluorescence of pyridinium analogues of **3** and **4** is completely quenched by intramolecular photo-induced electron transfer (PET) from excited anthracene to ground state pyridinium groups.[12] Relative fluorescence quantum yields (Φ_f) of **3** and **4**, determined based on parent anthracene as a standard (Φ_f = 0.27 in EtOH[13]), are 0.49 and 0.37, respectively. These high quantum yields indicate no effective charge transfer to the imidazolium unit can occur. The difference between the imidazolium and pyridinium derivatives was already ascribed to the electron accepting ability of the two heterocycles[14] by Blackburn *el al.*[12b]

As shown in Figure 2, the strong fluorescence emission of **3** (1.0 μM in MeCN) considerably decreased by the addition of tetrabutylammonium salts of $H_2PO_4^-$ while only little changes in the absorption spectrum of **3** took place. In the case of Cl^-, Br^-, I^-, NO_3^-, and HSO_4^-, small decrease in the fluorescence intensity of **3** are observed even in the presence of large excess of the anions (up to 150-200 equiv.).

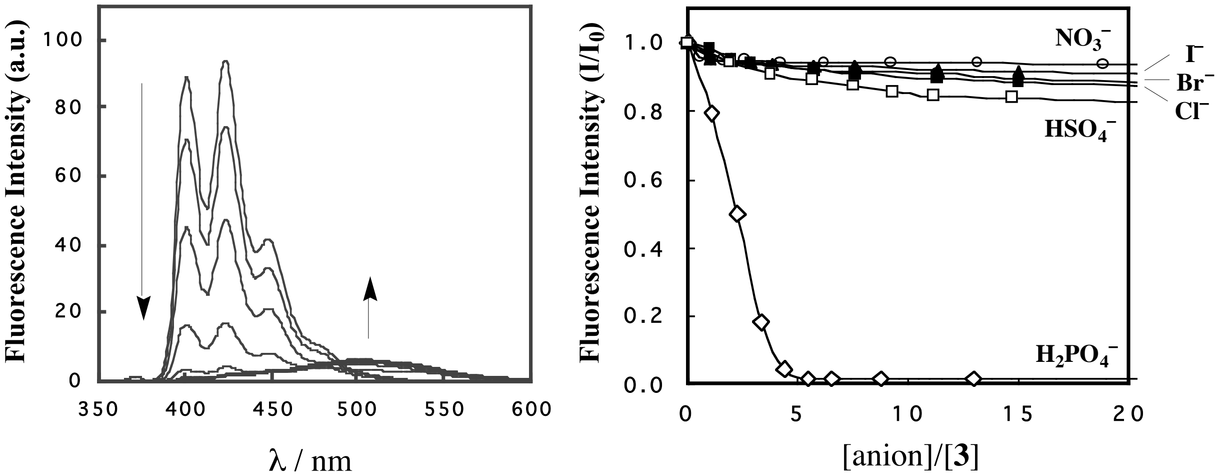


Figure 2. Fluorescence (1.0 μM, excited at 335 nm) spectra of **3** in MeCN for varying $n\text{-}Bu_4N^+H_2PO_4^-$ concentration (left). Fluorescence intensity dependence of **3** (423 nm) in CH_3CN upon addition of various anions (right). [receptor] = 1.0 μM, [guest anion] = 0-20 μM, excitation at 335 nm.

These titration results clearly show that $H_2PO_4^-$ anion quenches the monomer fluorescence of receptor (**3**) efficiently. However, the titration curve for $H_2PO_4^-$ monitored at 423 nm shows non-single equilibrium and a new broad band of emission centered around 502 nm was observed only when $H_2PO_4^-$ anion was added. The new longer wavelength emission band can be assigned to the excimer emission band compared with the literature data of the compounds of covalently linked two anthracene units.[15] Although similar spectral features were observed in addition of the anions to the monoimidazolium receptor (**4**), fluorescence spectral changes were relatively small and no excimer emission was observed.

The appearance of the excimer emission in the presence of $H_2PO_4^-$ was sensitive to the absolute concentration of the receptor (**3**). At relatively lower concentration (0.1 μM) of **3**, the fluorescence emission decreased in almost single equilibrium (but the excimer still formed in the presence of 50 equiv. $H_2PO_4^-$). On the other hand, at the relatively higher concentration (10 μM), the characteristic monomer emission was completely eliminated and the broad emission band centered at 503 nm appeared by the addition of 2.5 equiv. of $H_2PO_4^-$ (Figure 3 right). The UV-vis absorption spectrum became also considerably broad and red-shifted with isosbestic points along with the addition of $H_2PO_4^-$ anion (Figure 3 left). These spectral changes are ascribed to the ground state interactions between the anthracene chromophores upon aggregation induced by the multiple intermolecular hydrogen bondings between the imidazolium units and $H_2PO_4^-$ anions.

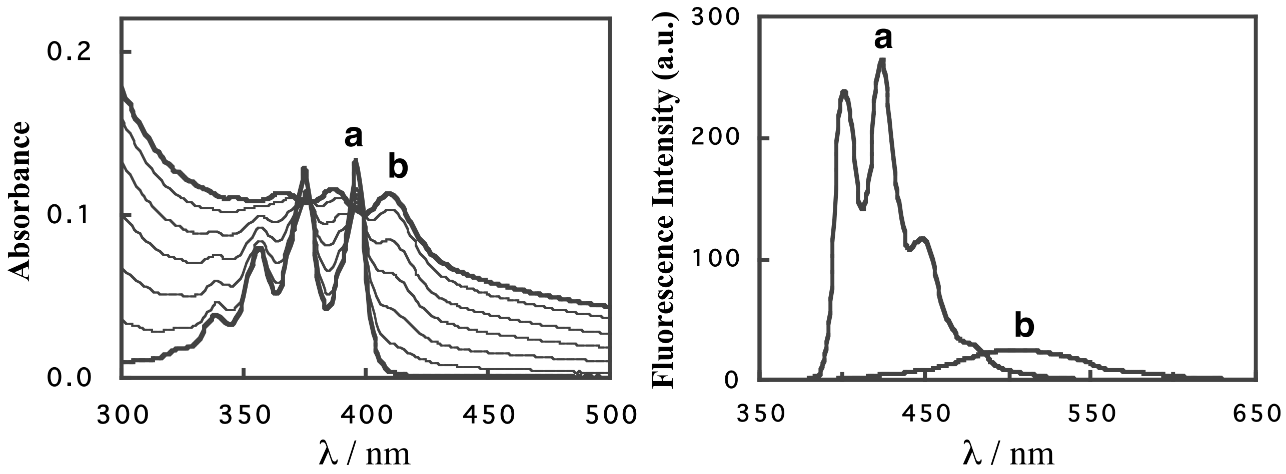


Figure 3. Absorption (10 μM) and fluorescence (10 μM, excited at 335 nm) spectra of **3** in MeCN without $n\text{-}Bu_4N^+H_2PO_4^-$ (a) and with 2.5 equiv. of $n\text{-}Bu_4N^+H_2PO_4^-$ (b), respectively.

The excitation spectra provided further evidence for the excimer formation. The excitation spectrum of **3** without $H_2PO_4^-$, monitored at 448 nm (Figure 4 (a)), is similar to the absorption spectrum of **3** (Figure 3 left (a)). In the presence of $H_2PO_4^-$, the excitation spectrum monitored at 503 nm (Figure 4 (b)) is similar to its absorption spectrum (Figure 3 left (b)). These results support the ground state aggregation of **3** by the interaction with $H_2PO_4^-$ ions.

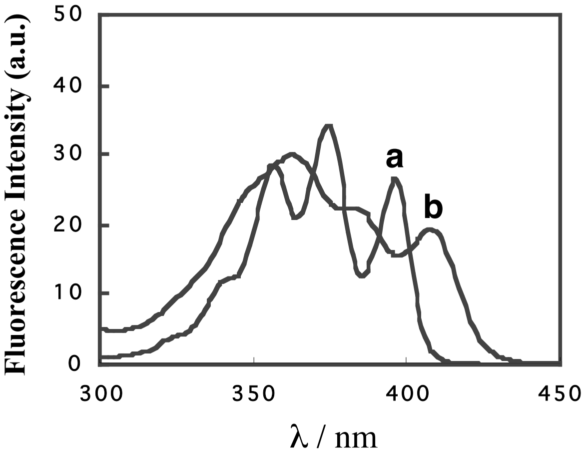


Figure 4. Excitation spectra (10 μM) of **3** in MeCN without *n*-$Bu_4N^+H_2PO_4^-$ monitored at 448 nm (a) and with 2.5 equiv. of *n*-$Bu_4N^+H_2PO_4^-$ monitored at 503 nm (b), respectively.

The fluorescent lifetime measurements gave an important information for the different fluorescent quenching properties of halide ions and oxoanions. While fluorescence of **3** decayed in a clean single exponential to give the lifetime τ = 7.4 (±0.1) ns, the decay curves for halide ion complexes showed double exponential profiles to give two lifetimes (τ_1 and τ_2) as shown in Table 2. The constant lifetime τ_1 must come from the decay of singlet excited state anthracene of the guest-free receptor. The other component τ_2 should be static quenching of the halide ion complex by photo-induced electron transfer processes from bonded electron-donative halide ion to excited anthracene chromophore. On the other hand, in the presence of NO_3^- and HSO_4^- anions, the fluorescent lifetime did not change (τ = 7.4 ±0.1 ns), indicating the formation of non-emissive host-guest complex. In the case of $H_2PO_4^-$ anion, the fluorescent lifetime of monomer emission was similarly constant, and thus the formation of non-emissive complex is also considered for $H_2PO_4^-$ anion.

Table 2. Fluorescence lifetime of receptor (**3**) (1.0 μM, excited at 335 nm) and its complexes with various anions (as tetrabutylammonium salts) in MeCN.

	lifetime[a] / ns							
	3	Cl^-	Br^-	I^-	NO_3^-	HSO_4^-	$H_2PO_4^-$	
	monomer			monomer			monomer	excimer
$\boldsymbol{\tau_1}$	7.4	7.4	7.4	7.4	7.4	7.5	7.3	0.5-1
$\boldsymbol{\tau_2}$	-	6.8	5.6	5.4	-	-	-	>80

[a] Errors are estimated to be ±0.1 ns.

From these results, the efficient fluorescent quenching of **3** by $H_2PO_4^-$ anion might be caused by not only the excimer formation but also the formation of non-emissive complex. To confirm the specific quenching by $H_2PO_4^-$ anion, we prepared a bis(trimethylammonium) derivative (**5**)[16] and the fluorescence spectral change by addition of $H_2PO_4^-$ was studied. The fluorescence of **5** (1.3 μM in MeCN) was also quenched in the presence of $H_2PO_4^-$ but no excimer emission was observed (Figure 5). Fluorescent lifetime of **5** (6.6 ns) did not change before and after addition of $H_2PO_4^-$. These results indicated that the fluorescence of anthracene chromophore is effectively quenched by $H_2PO_4^-$ anion by the formation of a non-fluorescent complex without excimer formation.

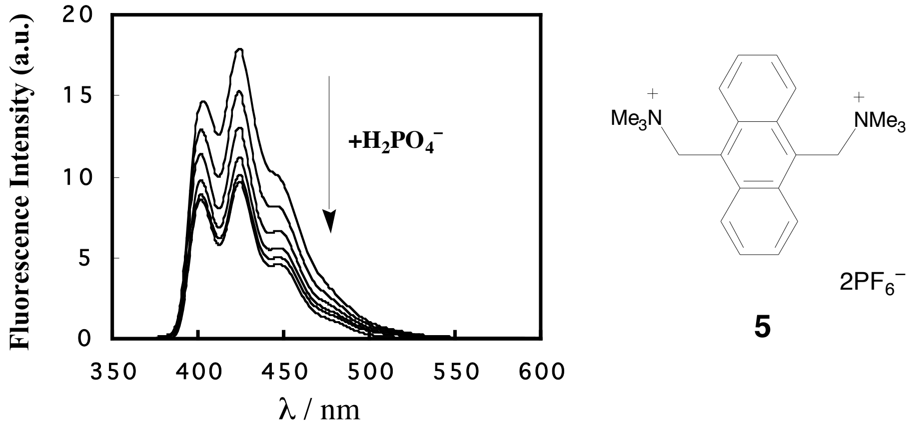


Figure 5. Fluorescence (1.3 μM, excited at 330 nm) spectra of **5** in MeCN for varying *n*-$Bu_4N^+H_2PO_4^-$ concentration (0-100 μM).

In summary, the fluorescence of imidazolium-anthracene linked receptor (**3**) is quenched in the presence of halide ions and oxoanions, in particular, $H_2PO_4^-$ anion significantly affected. Fluorescence quenching of aromatic hydrocarbons by anions has been explained by several mechanisms but they are still not completely elucidated. The fluorescence lifetime measurements, however, revealed that the quenching in halide ion complexes occurred by photo-induced electron transfer from halide anion to the excited anthracene chromophore, whereas in the case of oxoanions non-emissive host-guest complexes were formed. The $H_2PO_4^-$ complex exhibits a concentration-dependent quenching properties and at relatively higher concentration of **3** (>1 μM) the monomer emission was efficiently quenched by excimer formation.[17] We propose that the multiple inter-molecular interactions between $H_2PO_4^-$ anions and the imidazolium moieties were formed at relatively higher concentrations. The formation of the excimer by complexation with $H_2PO_4^-$ anion without covalent bridging is an attractive feature for the supramolecular and analytical chemistries.[18,19]

ACKNOWLEDGEMENTS

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