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Anion sensing by a donor–spacer–acceptor system: an intramolecular exciplex emission enhanced by hydrogen bond-mediated complexation

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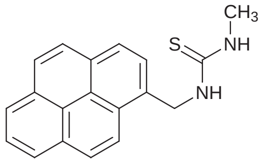
A new donor–spacer–acceptor system, 1 shows monomer emission quenching followed by intramolecular exciplex emission upon hydrogen bond-mediated complexation of anions.

Due to many possible applications in analytical chemistry and biomedical research, the development of fluoroionophores has attracted much attention.[1] One of the recent approaches to the design of fluorescent signaling systems relies on the exploitation of photoinduced electron transfer (PET) in fluorophore–spacer–receptor (donor–spacer–acceptor) systems,[2] where the PET process is suppressed or enhanced by the introduction of a substrate into the receptor, exhibiting a fluorescent signal. A large number of fluorescent sensors based on the PET process have been developed for protons and metal ions as well as sugars.[1–3] In contrast, the number of probes for biologically important anions is still very limited.[4–7a,8c] The first and only example of a fluorescent anion sensing system utilizing the PET process has been described by Czarnik *et al.*[5] They have reported that anthrylpolyamines can be used in aqueous solution at pH 6–7 for detecting anions such as phosphate and pyrophosphate.

As a new fluorescent signaling system for anions based on the PET process, we here report a donor–spacer–acceptor system **1**, in which pyrene (Py) as an electron acceptor is linked to thiourea (TU) as an electron donor *via* a methylene spacer.† In this system, the formation of an intramolecular exciplex between the excited Py and TU was found to be controlled by anion binding such as $CH_3CO_2^-$ and $H_2PO_4^-$ in non-aqueous media, resulting in the spectral responses to allow analytically useful ratiometric measurements, *i.e.*, a ratio of the exciplex emission to the monomer emission can be used for calibration. Such a change in the shape of the fluorescence emission spectrum is one of the essential requirements for fluoroionophores,[7] but very few ratiometric anion indicators have been reported so far.[7a] To the best of our knowledge, this is the first report to describe the design concept of ratiometric anion indicators based on the control of the intramolecular exciplex formation.



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Compound **1** was synthesized in one step by reacting 1-pyrenemethylamine with methyl isothiocyanate in THF–triethylamine, and purified three times by recrystallization from chloroform.‡

It has been demonstrated that simple thiourea binds $CH_3CO_2^-$ selectively over various monovalent anions ($CH_3CO_2^- > H_2PO_4^- > Cl^- > HSO_4^- \gg ClO_4^-$) in non-aqueous solvents.[8] Binding studies of **1** were first carried out in acetonitrile using $CH_3CO_2^-$ as $N(C_4H_9)_4^+$ salt. ^1H NMR spectra of **1** (2.0 mM) in CD_3CN showed a large downfield shift (> 3 ppm) of both TU hydrogens upon addition of 2 equiv. of $CH_3CO_2^-$, revealing the formation of hydrogen bonds between TU and this anion. Determination of the stability of the complex was however impossible because the NH signals became too broad upon complexation. Fig. 1b shows fluorescence spectra of **1** in CH_3CN as a function of $CH_3CO_2^-$ concentration, when excited at 314 nm (isosbestic point in absorption spectra of **1**). Upon addition of $CH_3CO_2^-$, the monomer emission of **1** was significantly quenched, whereas the absorption spectra showed only a slight change in the presence and absence of $CH_3CO_2^-$ (Fig. 1a). The Benesi–Hildebrand plot of **1** with $CH_3CO_2^-$ looking at the fluorescence intensity change at 396 nm is linear, indicating a 1 : 1 complex formation. The association constant K_{11} calculated from the plot is 5.7×10^3 dm^3 mol^{-1}, which is in agreement with K_{11} (5.1×10^3 dm^3 mol^{-1}) as obtained by UV–VIS

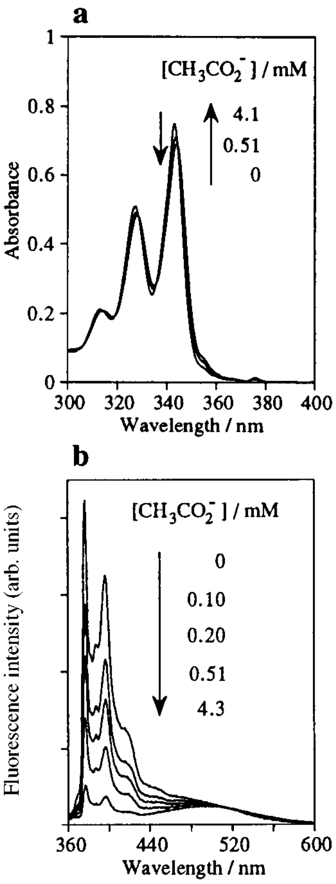

Fig. 1 Effect of acetate (as $N(C_4H_9)_4^+$ salt) concentration on (a) absorption and (b) emission spectra of **1** in acetonitrile. [**1**] = 1.4×10^{-5} M and 1.1×10^{-6} M for absorption and fluorescence spectra, respectively. Excitation wavelength: 314 nm.

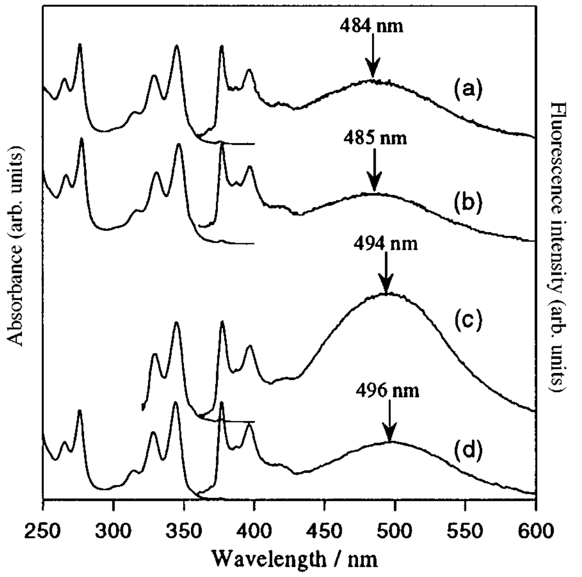

Fig. 2 Absorption (left half) and fluorescence (right half) spectra of **1** in the presence of 5.0 mM acetate (as $N(C_4H_9)_4^+$ salt) in (a) EtOAc, (b) THF, (c) acetone and (d) CH_3CN. [**1**] = 1.5×10^{-5} M and 2.0×10^{-6} M for absorption and fluorescence spectra, respectively. Excitation wavelength (nm): EtOAc, 315; THF, 317; acetone, 345; CH_3CN, 314.

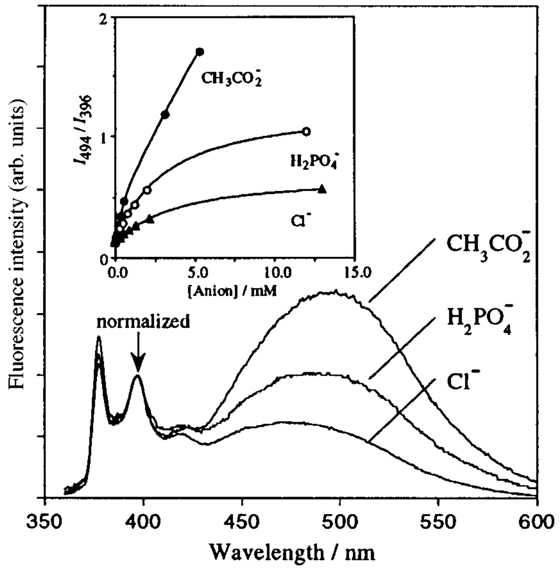

Fig. 3 Effect of anion species (as $N(C_4H_9)_4^+$ salt) on emission spectra of **1** in acetone. [**1**] = 2.0×10^{-6} M; $[CH_3CO_2^-] = 5.3$ mM; $[H_2PO_4^-] = 12$ mM; $[Cl^-] = 13$ mM. Excitation wavelength: 345 nm. Inset: plot of the ratio of fluorescence intensity at 494 nm (I_{494}) to that at 396 nm (I_{396}) *vs.* anion concentration.

spectroscopy. In contrast, no quenching was observed for a solution of 1-methylpyrene and $CH_3CO_2^-$. These results indicate that the emission quenching takes place *via* complexation of **1** with $CH_3CO_2^-$.

The quenching observed with $CH_3CO_2^-$ can be rationalized in terms of the change in the redox properties of TU. The fluorescence intensity at 396 nm of **1** in CH_3CN was found to be reduced to *ca.* one-fifth relative to that of 1-methylpyrene, while the absorption spectrum of **1** was almost equal to the sum of those of 1-methylpyrene and TU. This can be explained by the fact that the TU moiety acts as an electron donor to quench the excited Py and thus, binding of TU with $CH_3CO_2^-$ lowers its oxidation potential strongly[6a,12] so that complexed TU can quench the excited Py more effectively than free TU.

It is worth noting that as a result of the monomer emission quenching, a structureless red-shifted band became prominent as compared to the monomer emission. It is well known that the Py excimer shows a long-wavelength emission and the λ_{max} of the emission is independent of the solvent polarity.[13] As shown in Fig. 2, the fluorescence maximum of the long-wavelength emission was red-shifted with increasing solvent polarity, while the absorption spectra showed little dependence on the solvent polarity. This is evidence for the charge-transfer nature of the emission[10,13] which is assigned to an intramolecular exciplex formed between Py and TU.§

The effect of other anions (used as the $N(C_4H_9)_4^+$ salt) on the fluorescence spectra of **1** was examined in acetone, because the intramolecular exciplex emission was the most prominent in this solvent. The monomer emission was also quenched with $H_2PO_4^-$ and Cl^-, but the degree of the quenching depended on the anion. The magnitude of the quenching efficiency (Φ_Q)¶ follows the order of $CH_3CO_2^-$ (0.97) > $H_2PO_4^-$ (0.90) > Cl^- (0.83), reflecting the stabilities of the complexes [K_{11} (dm^3 mol^{-1}): $CH_3CO_2^-$, 7.0×10^3; $H_2PO_4^-$, 5.2×10^3; Cl^-, 1.0×10^3]. This result can be explained by the complexation-induced change in the donor ability of TU. The binding of **1** with $CH_3CO_2^-$ caused a negative shift for TU oxidation potential most effectively, and consequently the strongest quenching was observed with $CH_3CO_2^-$. This interpretation is also consistent with the largest Stokes' shift of the exciplex emission observed with $CH_3CO_2^-$ [Fig. 3, λ_{max} (nm): $CH_3CO_2^-$, 494; $H_2PO_4^-$, 486; Cl^-, 472].[14] Finally, it is worth noting that ratiometric measurements are possible using a ratio of the fluorescence intensities measured at 396 and 494 nm (inset in Fig. 3).

In summary, we have demonstrated that hydrogen bond-mediated complexation of anions by **1** results in monomer emission quenching followed by intramolecular exciplex emission. Although the spectral responses of **1** to anions are still moderate for practical use such as sensor applications, further systematic survey of a series of donor–spacer–acceptor systems would be promising for the fabrication of novel ratiometric anion indicators based on the control of the intramolecular exciplex emission.

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Notes and references

† The feasibility of PET within this system was roughly assessed according to the Rehm–Weller equation: $\Delta G(\text{kcal mol}^{-1}) = 23.06\ [E_{ox}(D) - E_{red}(A)] - w_p - \Delta G_{00}(A)$ where $E_{ox}(D)$, $E_{red}(A)$, w_p, and $G_{00}(A)$ are the oxidation potential of a donor, the reduction potential of an acceptor, the ion-pairing energy, and the excitation energy of the acceptor, respectively.[9–11] $E_{red}(Py)$[11] = −2.09 V in DMF *vs.* SCE, and $\Delta G_{00}(Py)$[9] = 77 kcal mol^{-1}. $E_{ox}(TU)$ = *ca.* −0.09 V *vs.* Ag/Ag$^+$ electrode, which was measured in 0.1 M $N(C_4H_9)_4ClO_4$ acetonitrile solution by cyclic voltammetry. An Au wire electrode was used as a working electrode. The free energy change, ΔG, of electron transfer within the present system calculated from these values is negative. However, an accurate determination of the ΔG was impossible because the oxidation of TU was found to be an irreversible process.[11]

‡ Compound **1** was characterised by elemental analyses and ^1H and ^{13}C NMR spectra.

§ The intermolecular exciplex formation was effectively negligible under the present conditions ([**1**] = 1.1–2.0 × 10^{-6} M).

¶ The quenching efficiencies were obtained by the equation: $\Phi_Q = (I_{host} - I_{complex})/I_{host}$, where I_{host} and $I_{complex}$ are the fluorescence intensities (396 nm) of **1** and its complex, respectively.

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