COMMUNICATION

Detection of water in organic solvents by photo-induced electron transfer method†

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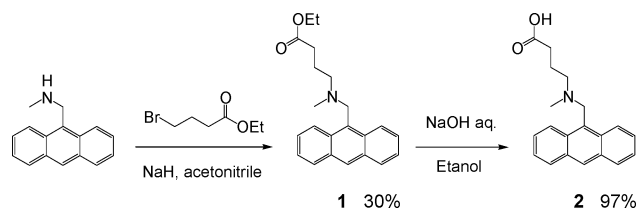
A new class of fluorescence sensor for detection of water in organic solvents based on photo-induced electron transfer (PET) of anthracene coupled with an amino acid has been designed and developed.

Chemical sensors for detection and quantification of water in organic solvents are of a fundamental interest in analytical chemistry and of a great importance in industrial applications. Water sensors based on fluorescence measurements have been developed so far.[1–5] In most of these fluorescent water sensors, however, the fluorescence intensity decreases with an increase of water in organic solvents, leading to difficulty in the determination of a trace amount of water.[4,5] In order to overcome this drawback, a new detection principle is required. In this communication, a new class of fluorescent sensor based on photo-induced electron transfer (PET) is proposed for detection of a wide concentration range of water in various organic solvents. Fluorescent PET sensors, in general, have been developed for detecting cations such as H$^+$, Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} as well as neutral organic species such as saccharides in biochemical analyses.[6–9] They are composed of a fluorophore skeleton linked to a cation binding site such as an amino moiety *via* a methylene spacer (fluorophore–spacer–receptor structure). In our PET sensor (**2**), anthracene is used as the fluorophore skeleton, a methylene unit as the spacer, and a dialkylamino group as the binding site for the cation (H$_3$O$^+$). A carboxyl group is also incorporated in the structure as the first recognition site for water molecules. Thus, the addition of water to organic solvents containing **2** may promote dissociation of the carboxyl proton of **2**, resulting in the formation of a fluorescent zwitterionic structure by the protonation of the amino group.

The synthesis of the fluorescent PET sensor (**2**) is shown in Scheme 1. The reaction of 9-(methylaminomethyl)anthracene with ethyl 4-bromobutyrate using sodium hydride yielded an ester derivative **1**. The compound **2** was obtained by hydrolysis of **1**.

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Scheme 1 Synthesis of fluorescent PET sensor (**2**).

To make sure that **2** is PET active, the fluorescence spectra of **2** were measured in aqueous solutions of different pH values (Fig. 1a and b). In the pH range from 3 to 7 (in the acidic and neutral regions), a strong fluorescence was observed. With increasing pH value from 8 to 11 (in the alkaline region), the fluorescence intensity dramatically decreased. This result demonstrates that the compound **2** has a fluorescent (PET inactive) cationic structure (**2+**) in acidic solutions and a non-fluorescent (PET active) anionic structure (**2–**) in alkaline solutions, as shown in Fig. 1c.
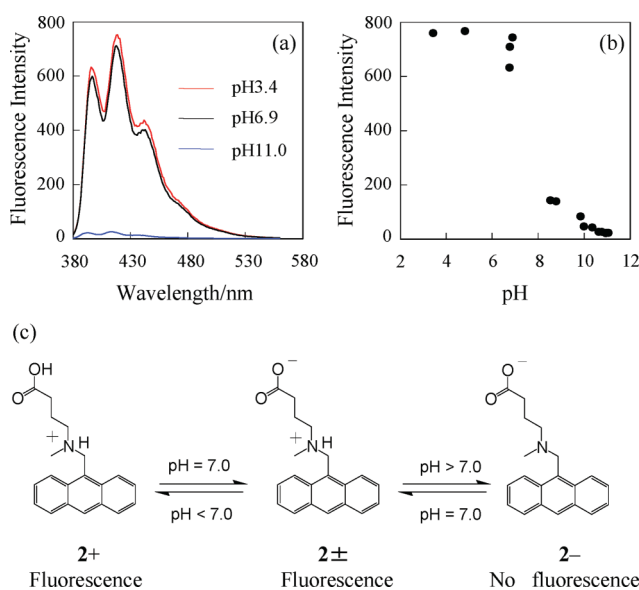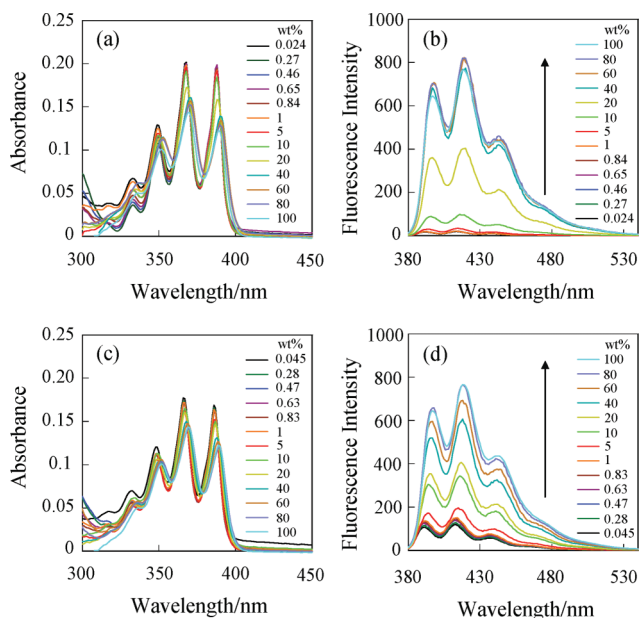

Fig. 1 (a) pH dependence of fluorescence spectra (λ_{ex} = 366 nm) of **2** in aqueous solutions and (b) plot of fluorescence peak intensity at around 417 nm *vs*. pH, and (c) ionic structures of **2** in acidic and alkaline solutions.

The detection of water in 1,4-dioxane and acetonitrile was attempted by measuring the absorption and fluorescence spectra of **2**. As shown in Fig. 2a and c, the absorption spectra of **2** undergo only small changes in intensity and shape by increasing a water content in both 1,4-dioxane and acetonitrile. On the other hand, the corresponding fluorescence spectra exhibit significant changes in intensity with a negligible change in the main fluorescence peak wavelength (Fig. 2b and d). Similar trends of absorption and fluorescence spectral changes of **2** upon addition of water were observed also in THF and ethanol. The changes in the fluorescence peak intensity are plotted in Fig. 3a–d against water fraction in these four organic solvents. It is seen in the lowest water content limit that the fluorescence intensities are higher in polar solvents (acetonitrile and ethanol) than in less polar solvents (1,4-dioxane and THF). In the region of low water content below 1.2 wt%, the fluorescence intensities in 1,4-dioxane and THF exhibit only slight enhancement, while a drastic fluorescence enhancement is observed in acetonitrile and ethanol (Fig. 3e). When the water content lies between 5 and 40 wt%, the fluorescence intensity is increased dramatically in 1,4-dioxane and THF solution, but is increased gradually in acetonitrile and ethanol. The fluorescence intensity shows a saturation at 60 wt% for 1,4-dioxane and THF, and at 80 wt% for acetonitrile and ethanol. It is worthy of note here that such a fluorescence change was not observed in mixtures of organic solvents and water when ester **1** is used, demonstrating that the carboxyl group in **2** is essential to the current water sensor.
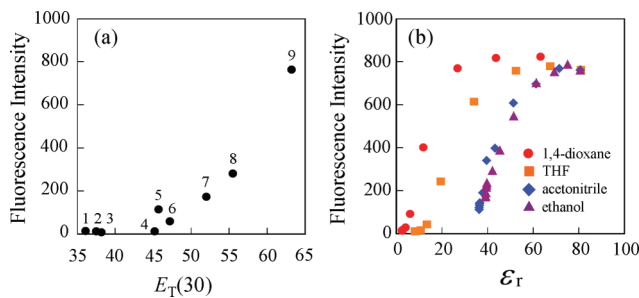

Fig. 3 Fluorescence peak intensity at around 417 nm (λ_{ex} = 366 nm) of **2** as a function of water content in (a) 1,4-dioxane, (b) THF, (c) acetonitrile, and (d) ethanol. (e) Fluorescence peak intensity of **2** in 1,4-dioxane, THF, acetonitrile, and ethanol solutions in the low water content region below 1.2 wt%.

Fig. 2 (a) Absorption and (b) fluorescence spectra (λ_{ex} = 366 nm) of **2** ($c = 2.2 \times 10^{-5}$ M) in 1,4-dioxane containing water (0.024–100 wt%). (c) Absorption and (d) fluorescence spectra (λ_{ex} = 366 nm) of **2** ($c = 2.1 \times 10^{-5}$ M) in acetonitrile containing water (0.045–100 wt%).

The fluorescence peak intensities for almost dry organic solvents are plotted in Fig. 4a against the solvent polarity parameter, $E_T(30)$. The florescence intensity is almost zero for the solvents of the $E_T(30)$ values below 40, whereas it starts to increase when the $E_T(30)$ increases beyond 45. This shows that the PET activity is affected by the solvent polarity as well. The influence of the relative permittivity (ε_r)[10,11] of a solution on the fluorescence intensity is

Fig. 4 (a) Fluorescence peak intensity at around 417 nm (λ_{ex} = 366 nm) of **2** plotted against (a) $E_T(30)$ of solvents and (b) ε_r of organic solvent–water mixtures. The numbers 1–9 in (a) correspond to 1,4-dioxane, THF, ethyl acetate, DMSO, acetonitrile, 2-butanol, ethanol, methanol, and water, respectively.

also studied by plotting the fluorescence peak intensity *vs.* ε_r of mixtures of water and organic solvents (Fig. 4b). The plots show that the effect of water on the fluorescence intensity is larger than the solvent polarity, *i.e.*, the fluorescence intensity (*ca.* 800) at 60 wt% of 1,4-dioxane solution is much higher than that (*ca.* 400) at 20 wt% of acetonitrile, although the ε_r values for both the solutions are *ca.* 43. On this basis, in dry organic solvents the fluorescent zwitterionic structure (**2±**) with the protonated

amino group is favored in highly polar solvents such as acetonitrile and ethanol (Fig. 5), responsible for the increased fluorescence compared with those in 1,4-dioxane and THF. Namely, the fluorescent zwitterionic structure (2±) is dominant in highly polar solvents, while the neutral structure (2) is dominant in less polar solvents. Upon increasing the water content in organic solvents, the dissociation of the carboxyl proton of 2 is promoted, and as a result the fluorescent zwitterionic structure (2±) tends to be formed by the protonation of the amino group by the dissociated proton. The equilibrium constant (K_a) increases in the order of K_a (in less polar solvent) < K_a (in highly polar solvent) ≪ K_a (in water). This result demonstrates that a drastic fluorescence enhancement of 2 with increase in water content is attributable to suppression of PET by the intramolecular proton transfer of the carboxyl proton to the amino group.
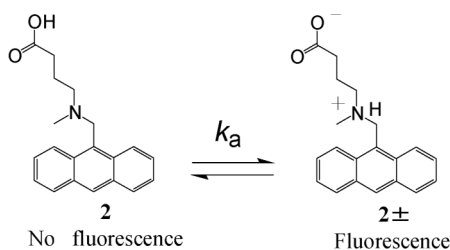
$$K_a \text{ (in less polar solvent)} < K_a \text{ (in highly polar solvent)} \ll K_a \text{ (in water)}$$

Fig. 5 Mechanism of fluorescence of PET sensor for detection of water in organic solvents.

We estimated the detection limit (DL) and quantitation limit (QL) by the following equations: $DL = 3.3\sigma/m_{sl}$ and $QL = 10\sigma/m_{sl}$, where σ is the standard deviation of blank sample and m_{sl} is the slope of the calibration curve in the region of the low water content (below 1.0 wt%), respectively. The DL and QL are, respectively, 0.1 and 0.3 wt% for 1,4-dioxane, 0.1 and 0.4 wt% for THF, 0.001 and 0.004 wt% for acetonitrile and 0.001 and 0.002 wt% for ethanol, which are comparable to those of the traditional fluorescent sensors[4b].

In conclusion, we have designed and synthesized an anthracene molecule with an amino acid-type structure to develop a new class of fluorescent PET sensor for detection of water in organic solvents. An enhancement in fluorescence is observed with increasing water content in polar and less polar organic solvents, which is attributable to the suppression of PET by the intramolecular proton transfer of the carboxyl proton to the amino group, providing a new concept in molecular design for a fluorescent water sensor based on PET. In order to improve the DL and QL and to be a usable fluorescent PET sensor for detection of water in a wide pH range, further studies on development of the fluorescent PET sensors with proton donating sites such as dicarboxyl groups, sulfonic acid groups, and boronic acid groups are now in progress and will be reported in a subsequent paper.

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1316 | *Org. Biomol. Chem.*, 2011, **9**, 1314–1316

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