ChemComm

Cite this: Chem. Commun., 2011, 47, 4448-4450

www.rsc.org/chemcomm

COMMUNICATION

Fluorescence PET (photo-induced electron transfer) sensors for water based on anthracene-boronic acid ester[†]

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Received 24th January 2011, Accepted 17th February 2011 DOI: 10.1039/c1cc10470e

Anthracene-boronic acid ester as a new class of fluorescence PET sensors for detection of a trace amount of water in organic solvents has been designed and developed.

Sensing water in organic solvents is of a practical importance as well as of a keen interest in fundamental analytical chemistry. Water sensors based on fluorescence measurements have been developed so far.^{1–5} In most of these fluorescence water sensors, however, the fluorescence intensity decreases with an increase of water in organic solvents and this feature makes it difficult to detect a trace amount of water. Thus, a new detection principle is required for improving sensitivities of fluorescence water sensors. Quite recently, we have proposed a new class of a fluorescence water sensor based on PET (photo-induced electron transfer).⁶ An anthracene– amino acid 1 newly designed and synthesized acts as a fluorescence PET sensor for detection of water in organic solvents (Scheme 1a).⁷ In the fluorescence water sensor 1,



Scheme 1 Mechanisms of fluorescence PET sensors (a) 1 and (b) 2 for detection of water in organic solvents.

the addition of water to organic solvents containing 1 promotes dissociation of the carboxyl proton of 1, followed by the formation of fluorescent zwitterionic structure 1a through the protonation of the amino group. As a result, the intramolecular proton transfer of the carboxyl proton to the amino group suppresses PET and thus fluorescence is enhanced with increasing water content in various organic solvents. The detection limit (DL) and quantitation limit (QL) are, respectively, 0.1 and 0.4 wt% for acetonitrile and 0.1 and 0.2 wt% for ethanol. However, with the anthracene-amino acid structure, the DL and QL in less polar organic solvents are lower than those in polar organic solvents due, most likely. to poor dissociation of the carboxyl proton in the former solvents. In order to overcome the drawback of 1, we conceived an idea of applying an anthracene-boronic acid ester 2 as a new fluorescence PET sensor for water (Scheme 1b). An anthracene-boronic acid system developed by Shinkai group has been used as a fluorescence PET sensor for saccharides.⁸ In our fluorescence PET sensor 2, we expect that boronic ester enhances the Lewis acidity of a boron atom and solubility of the sensor dye in organic solvents.^{8–11} The addition of water to organic solvents containing 2 may cause the formation of fluorescent ionic structure 2a by hydrolysis, independent of the kind of solvents (polar, nonpolar, protic and aprotic). Herein, we report the high-sensitive detection of a trace amount of water in various organic solvents based on the PET characteristics of the anthracene–boronic acid ester.

Anthracene–boronic acid ester 2 was synthesized by reaction of 9-(methylaminomethyl)anthracene with 2-bromomethylphenylboronic acid pinacol ester in the presence of sodium hydride (Scheme 2).

Absorption and fluorescence spectra of **2** were measured in 1,4-dioxane, THF, acetonitrile and ethanol containing various



Scheme 2 Synthesis of fluorescence PET sensor 2.

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Fig. 1 (a) Absorption and (b) fluorescence spectra ($\lambda_{ex} = 366$ nm) of **2** ($c = 2.0 \times 10^{-5}$ M) in 1,4-dioxane containing water (0.084–40 wt%). (c) Absorption and (d) fluorescence spectra ($\lambda_{ex} = 366$ nm) of **2** ($c = 2.0 \times 10^{-5}$ M) in acetonitrile containing water (0.046–40 wt%).

concentrations of water. As shown typically in Fig. 1a and c for 1,4-dioxane and acetonitrile, in all the four solvents the absorption spectra of 2 underwent no appreciable changes in intensity and shape upon addition of water. In contrast, the corresponding fluorescence spectra exhibited significant changes in intensity with a negligible change in their spectral shapes (Fig. 1b and d). The changes in the fluorescence peak intensity are plotted in Fig. 2a-d against water fraction in these four organic solvents. In the low water content region below 1.3 wt%, as shown in Fig. 2e, the fluorescence intensities are increased almost linearly with the increase in the water content, although the slopes for 1,4-dioxane and THF are smaller than those for acetonitrile and ethanol. Surprisingly, the plots for THF and acetonitrile fit straight lines passing through the origin. When the water content ranges between 1 and 5 wt%, the fluorescence intensity is increased gradually in acetonitrile and ethanol (Fig. 2c and d), while in 1,4-dioxane and THF (Fig. 2a and b) the fluorescence intensity is increased dramatically. As in the fluorescence PET sensor 1, the fluorescence enhancement of 2 with the increase in the water content is attributable to suppression of PET due to the formation of 2a with a fluorescent ionic structure by hydrolysis of 2.

The fluorescence peak intensities for almost dry organic solvents are plotted in Fig. 3 against the solvent polarity parameter, $E_{\rm T}(30)$.¹² Interestingly, the fluorescence intensities are almost zero for the solvents with the $E_{\rm T}(30)$ values below 46 except 1,4-dioxane ($E_{\rm T}(30) = 36$), whereas it increases with the increase in $E_{\rm T}(30)$ beyond 47. It has been reported in the early fluorescence PET sensor study that the fluorescence intensity decreases monotonously as the solvent polarity increases, showing that quenching of the excited state by PET responsible for the fluorescence decrease is more efficient in polar solvents than in less polar solvents.¹³ In our PET sensor, on the contrary, fluorescence is enhanced in polar



Fig. 2 Fluorescence peak intensity of 2 at around 415 nm ($\lambda_{ex} = 366$ nm) 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 in the low water content region below 1.3 wt%.



Fig. 3 Fluorescence peak intensity of **2** at around 415 nm $(\lambda_{ex} = 366 \text{ nm})$ plotted against $E_T(30)$ of solvents. The numbers 1–13 correspond to 1,4-dioxane, THF, ethyl acetate, DMSO, acetonitrile, 2-butanol, 2-propanol, ethyl acetoacetate, 1-butanol, 1-propanol, 2-ethoxyethanol, ethanol, and methanol, respectively.

solvents as is shown in Fig. 3. It may attribute to that the suppression of PET by the formation of acid(boronic ester)–base(amino group) interaction in the ground state or the excited state is more efficient in polar solvents than in less polar solvents. Obviously, suppression of fluorescence in dry organic solvents is of a crucial importance for improving further sensing abilities of the new class of water sensors.

Table 1 DL and QL of 1 and 2 for water determination in various solvents

Compound	Solvent	DL	QL
1	Acetonitrile	0.1 wt%	0.4 wt%
	Ethanol	0.1 wt%	0.2 wt%
2	1,4-Dioxane	0.2 wt%	0.7 wt%
	THF	0.2 wt%	0.5 wt%
	Acetonitrile	0.04 wt%	0.1 wt%
	Ethanol	0.04 wt%	0.1 wt%

Clarification of detailed mechanisms of the PET and hydrolysis processes is required to design more efficient fluorescent dyes for the water sensor based on PET.

We estimated the detection limit (DL) and quantitation limit (QL) based on the following equations: $DL = 3.3\sigma/m_{sl}$ and QL = $10\sigma/m_{\rm sl}$, where σ is the standard deviation of the blank sample and $m_{\rm sl}$ is the slope of the calibration curve in the region of the low water content (below 1.0 wt%), respectively (Table 1). The DL and QL of anthracene-boronic acid ester 2 are, respectively, 0.2 and 0.7 wt% for 1,4-dioxane, 0.2 and 0.5 wt% for THF, 0.04 and 0.1 wt% for acetonitrile and 0.04 and 0.1 wt% for ethanol, which are much higher than those of anthracene-amino acid 1. Furthermore, the addition of 1 wt% ethanol to acetonitrile solution of 2 or the addition of 1 wt% acetonitrile to THF solution of 2 caused no change in the fluorescence intensity, which is indicative of high selectivity of 2 for sensing water. These results show that anthraceneboronic acid ester 2 acts as a highly efficient fluorescence PET sensor for the detection of a trace amount of water in polar, less polar, protic and aprotic solvents.

In conclusion, we have designed and synthesized anthraceneboronic acid ester to develop a new class of fluorescence PET sensors for detection of water in organic solvents. An enhancement in fluorescence is observed with increasing water content in various organic solvents, which is attributable to the suppression of PET by the formation of the fluorescent ionic structure by hydrolysis. The DL and QL of anthracene-boronic acid ester in various solvents are higher than those of anthraceneamino acid. The fluorophore-boronic acid ester system is one of the most promising classes of fluorescence PET sensors for detection of a trace amount of water. Further studies on development of the polymer film containing fluorescence PET sensors for detection of water in organic solvents and in the atmosphere are now in progress and will be reported in a subsequent paper.

This work was supported by A Research for Promoting Technological Seeds from Japan Science and Technology Agency (JST), and by the Ogasawara Foundation for the Promotion of Science & Engineering.

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