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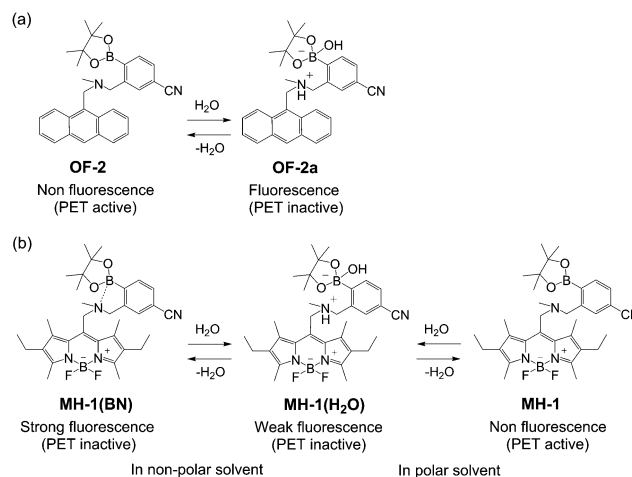
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A BODIPY sensor for water based on a photo-induced electron transfer method with fluorescence enhancement and attenuation systems†

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It was found that BODIPY MH-1 can act as a dual function-based fluorescent sensor for trace amounts of water possessing fluorescence intensity and fluorescence quantum yield as a function of water detection based on the PET (photo-induced electron transfer) method with fluorescence enhancement and attenuation systems.

The development of fluorescence sensing methods for the detection and quantification of a trace amount of water in solutions, solids, the atmosphere and products has received considerable attention in recent years from the viewpoint of fundamental study in analytical chemistry and photochemistry, and is eagerly anticipated in industry because of their potential applications in environmental and quality control monitoring systems, and sanitary and medical materials.^{1–4} Most of fluorescent sensors for a trace amount of water developed so far, including conjugated polymer and organic fluorescent dyes, are based on fluorescence quenching systems, that is, the fluorescence intensity of the sensor decreases as a function of water content in organic solvents.^{5–8} This feature can be attributed to the solvatochromic properties of sensors,⁵ the aggregation of sensors⁶ or the formation of hydrogen bonding⁷ between the sensor and water molecules with the increase in the water content. However, this fluorescence quenching system makes it difficult to detect trace amounts of water. Therefore, in our previous work, as a new approach for improving the detection limit of water, we have devised the fluorescence enhancement system based on PET (photo-induced electron transfer),⁹ that is, anthracene-aminomethyl-phenylboronic acid pinacol ester (PhenylBPin) **OF-2** was designed and synthesized as a fluorescent PET sensor for a trace amount of water (Scheme 1a).^{10a} In the low water content region below 1.0 wt%, the addition of water to organic solvents containing **OF-2** causes an efficient



Scheme 1 Proposed mechanisms of fluorescent sensors: (a) **OF-2** and (b) **MH-1** with a PET (photo-induced electron transfer) structure for the detection of water in non-polar solvent and polar solvent.

formation of fluorescent ionic structure **OF-2a** with a protonated tertiary amino group, resulting in the occurrence of fluorescence by the suppression of the PET process from the electron-donating tertiary amino group to the photoexcited anthracene fluorophore due to the lowering of the HOMO level of the tertiary amino group. The detection limits (DLs) were as low as 0.009 wt% for water in acetonitrile. Thus, we demonstrated that the fluorescence enhancement system based on the PET method is useful for the detection and quantification of a trace amount of water in organic solvents.¹⁰ On the other hand, as another fluorescence enhancement system for the detection of water, an AIE (aggregation-induced emission)-based fluorescent sensor is attributed to the emission enhancement induced by aggregate formation upon addition of large amounts of water (over 40 wt% in almost every case) into the solution, leading to restricted intramolecular rotation (RIR) in the molecular structure, that is, the aggregation can restrict the intramolecular

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free rotation, resulting in the elimination of radiationless (non-emissive) relaxation of the photoexcited fluorophore.^{11–14} Meanwhile, in some cases, the fluorescence attenuation with the increase in the water content was observed in the low water content region below 1.0–2.0 wt% due to the increase in polarity of the solution.^{13,14} However, the fluorescence enhancement system based on the AIE sensors developed so far is not sufficient for the detection of a trace amount of water because the addition of large amounts of water into the solution is necessary for being AIE active.

Through our continuing efforts to gain insight into the molecular design toward developing a high-sensitivity optical sensor for water based on the PET method, we found that boron-dipyrromethene (BODIPY) **MH-1** with a PhenylBPin unit can act as a fluorescent sensor for trace amounts of water based on the PET method with both fluorescence enhancement and attenuation systems (Scheme 1b). Herein, we report that **MH-1** is a dual function-based fluorescent sensor possessing fluorescence intensity and fluorescence quantum yield (Φ_F) as a function of detection of water.

BODIPY **MH-1** studied in this work was synthesized according to a stepwise synthetic protocol (Scheme S1, ESI†). We first prepared 2,6-diethyl-8-(bromomethyl)-1,3,5,7-tetramethyl BODIPY **1** via the reaction of 3-ethyl-2,4-dimethylpyrrole with bromoacetyl chloride followed by treatment with $\text{BF}_3 \cdot \text{OEt}_2$. Subsequently, BODIPY **1** was reacted with methyl amine to give 2,6-diethyl-8-[[N-methylamino)methyl]-1,3,5,7-tetramethyl BODIPY **2**. We obtained **MH-1** with PhenylBPin via the reaction of **2** with 2-bromomethyl-4-cyanophenylboronic acid.

The absorption and fluorescence spectra of **MH-1** in THF and various solvents are shown in Fig. 1a and Fig. S1 (ESI†), respectively, and their optical data in various solvents are summarized in Table 1. In all the solvents, the absorption maximum wavelength (λ_{abs}) of **MH-1** was observed at around 535 nm, which is assigned to the $S_0 \rightarrow S_1$ transition of the BODIPY core. The molar extinction coefficient (ϵ) at λ_{abs} is 67 000–78 000 $\text{M}^{-1} \text{cm}^{-1}$. The corresponding fluorescence maximum wavelength (λ_{fl}) appeared at around 550 nm, which arises from the BODIPY locally excited (LE) state. It is worth mentioning here that a significant dependence of Φ_F value on the solvent polarity was observed (Fig. 1b), that is, the Φ_F value significantly decreases with increasing the empirical solvent

Table 1 Optical data of **MH-1** in various solvents

Solvent	E_T^N ^a	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{fl}}/\text{nm}$	Φ_F ^b
Toluene	0.099	540	77 500	556	62
1,4-Dioxane	0.164	537	72 500	552	51
THF	0.207	537	69 300	552	27
Acetone	0.355	534	67 500	549	4
Acetonitrile	0.460	534	68 000	548	2

^a Empirical solvent polarity parameter (ref. 19). ^b Fluorescence quantum yields (Φ_F) were determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 490 \text{ nm}$).

polarity parameter (E_T^N) from toluene ($E_T^N = 0.099$, $\Phi_F = 62\%$) to acetonitrile ($E_T^N = 0.460$, $\Phi_F = 2\%$). Thus, on the basis of the fact that there is no change in λ_{fl} by changing the solvent polarity, which reveals the decrease in Φ_F value with increasing the solvent polarity is not attributed to the intramolecular charge transfer (ICT) properties and the change of photoexcited state,¹⁵ this result indicates that in non-polar solvents such as toluene and 1,4-dioxane the formation of strong boron–nitrogen (B–N) interaction¹⁶ between BPin and a tertiary amino group in **MH-1(BN)** can lead to the suppression of the PET process from the electron-donating tertiary amino group to the photoexcited BODIPY core due to the lowering of the HOMO levels of the tertiary amino group, resulting in a high Φ_F value (Scheme 1b). Moreover, it is revealed by the fact that 2,6-diethyl-1,3,5,7-tetramethyl-8-[[N,N-dimethylamino)methyl] BODIPY ($\Phi_F = 5\%$ in THF)¹⁷ suffers from a drastic fluorescence attenuation due to the PET process from the electron-donating tertiary amino group to the photoexcited BODIPY core when compared to the corresponding 1,3,5,7,8-pentamethyl-2,6-diethyl BODIPY (**PM567**) without the amino group ($\Phi_F = 75\%$ in THF).¹⁸ On the other hand, in polar solvents such as acetone and acetonitrile the weakened B–N interaction accompanied with the promotion of intramolecular rotation of PhenylBPin in **MH-1** due to the polar environment can lead to the activation of the PET process, resulting in a low Φ_F value.

In order to investigate the sensing ability of **MH-1** for water in solvents, the absorption and fluorescence spectra of **MH-1** were measured in 1,4-dioxane, THF, acetone and acetonitrile that contained various concentrations of water (Fig. 2 for 1,4-dioxane and acetonitrile, Fig. S2, ESI†). In the water content region below 20 wt% for all the four solvents, the absorption spectra of **MH-1** did not undergo appreciable changes upon addition of water to the solution. On the other hand, for 1,4-dioxane and THF the fluorescence spectra of **MH-1** underwent a decrease in fluorescence intensity with a slight red-shift (ca. 5 nm) of the fluorescence peak wavelength at 552 nm upon addition of water to the solution. The decrease in fluorescence peak intensity levels off in the water content region greater than 4.0–5.0 wt%. In contrast, for acetone and acetonitrile the fluorescence spectra exhibited an enhancement of fluorescence intensity with a slight red-shift (ca. 8 nm) of the fluorescence peak wavelength at around 548 nm upon addition of water to acetone or acetonitrile solution (Fig. 2d). The enhancement of the fluorescence peak intensity levels off in the water content region greater than 2.0–5.0 wt%. These results indicate that the addition of water to a polar solvent

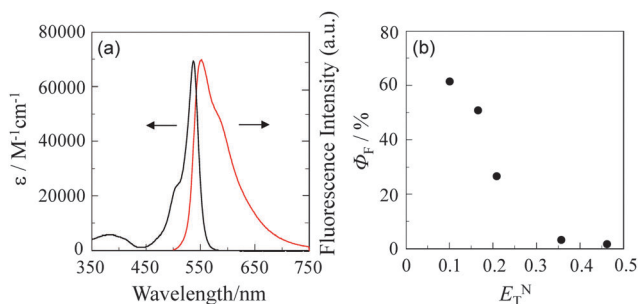


Fig. 1 (a) Absorption and fluorescence spectra ($\lambda_{\text{ex}} = 490 \text{ nm}$) of **MH-1** in THF. (b) Correlation between Φ_F and E_T^N (0.099, 0.164, 0.207, 0.355 and 0.460 for toluene, 1,4-dioxane, THF, acetone and acetonitrile, respectively).



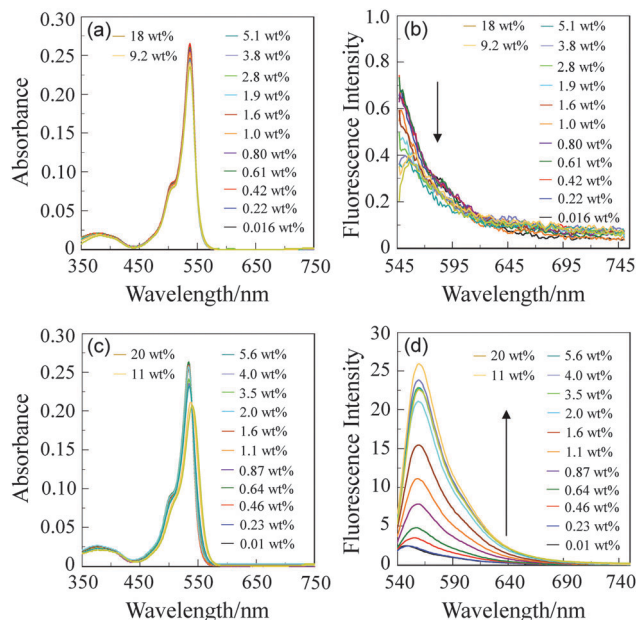


Fig. 2 (a) Absorption and (b) fluorescence spectra ($\lambda_{\text{ex}} = 537$ nm, slit: 1.0 nm) of **MH-1** ($c = 4.0 \times 10^{-6}$ M) in 1,4-dioxane containing water (0.016–18 wt%). (c) Absorption and (d) fluorescence spectra ($\lambda_{\text{ex}} = 534$ nm, slit: 2.5 nm) of **MH-1** ($c = 4.0 \times 10^{-6}$ M) in acetonitrile containing water (0.01–20 wt%).

(acetone or acetonitrile) containing **MH-1** causes the efficient formation of the fluorescent ionic structure. Thus, as shown in Scheme 1b, **MH-1(H₂O)** with a stable fluorescent ionic structure between the protonated tertiary amino group and the hydroxylated PhenylBPIn by the addition of water molecules is stably formed in a polar solvent, because, as described in an earlier **MH-1**, the weakened B–N interaction can facilitate the formation of **MH-1(H₂O)** in the polar envelopment. Consequently, for polar solvents such as acetone and acetonitrile the fluorescence enhancement of **MH-1** with increasing water content in the solution can be attributed to the suppression of the PET process by the efficient formation of **MH-1(H₂O)**, which is due to the lowering of the HOMO level of tertiary amino group by the addition of water molecules, as with the case of anthracene-based sensor **OF-2**. On the other hand, for non-polar solvents such as 1,4-dioxane or THF the decrease in fluorescence intensity upon addition of water to the solution is attributed to the disruption of B–N interaction in **MH-1(BN)** associated with the formation of ionic species **MH-1(H₂O)** in the solvent/water mixture.²⁰ Therefore, this work reveals that for **MH-1** the formation of B–N interaction can effectively inactivate the PET process, rather than the formation of an ionic structure between the protonated tertiary amino group and the hydroxylated PhenylBPIn, that is, the HOMO level of the tertiary amino group in **MH-1(BN)** due to the B–N interaction is lower than that in **MH-1(H₂O)**. Consequently, this work demonstrates that **MH-1** can act as a fluorescent sensor for trace amounts of water based on the PET method with both fluorescence enhancement and attenuation systems.

To estimate the sensitivity and accuracy characteristics of **MH-1** for the detection of water in the low water content region,

the changes in fluorescence intensity (at *ca.* 550 nm) and Φ_F value are plotted against the water fraction in these four organic solvents (Fig. 3 for 1,4-dioxane and acetonitrile, and Fig. S3 (ESI[†]) for THF and acetone). These plots demonstrated that for 1,4-dioxane and THF the fluorescence intensity and Φ_F value decreased almost linearly as a function of the water content, but for acetone and acetonitrile the fluorescence intensity and Φ_F value increased linearly as a function of the water content. Moreover, it is worth mentioning here that the Φ_F value levels off at 20–30% in the water content region greater than 2.0–5.0 wt% for all the four solvents, that is, this result strongly indicates the formation of **MH-1(H₂O)** upon addition of water to all the four solvents. The DL determined from the plot of the fluorescence intensity as a function of the water content is 0.3 wt% for acetonitrile and over 1.0 wt% for 1,4-dioxane, respectively (DL = $3.3\sigma/m_s$, where σ is the standard deviation of the blank sample and m_s is the slope of the calibration curve in the low water content region below 5.0 wt% for 1,4-dioxane and 2.0 wt% for acetonitrile, respectively). Therefore, this work indicates that the fluorescence behavior of **MH-1** for the detection of water based on the PET method with both fluorescence enhancement and attenuation systems exhibited a good linear response in the low water content region, indicating that BODIPY **MH-1** with a PET structure can act as a dual function-based fluorescent sensor for trace amounts of water possessing fluorescence intensity and Φ_F value as a function of detection of water, although the DL for water based on the PET characteristics of **MH-1** is not superior to that based on the PET method in our previous work.⁹

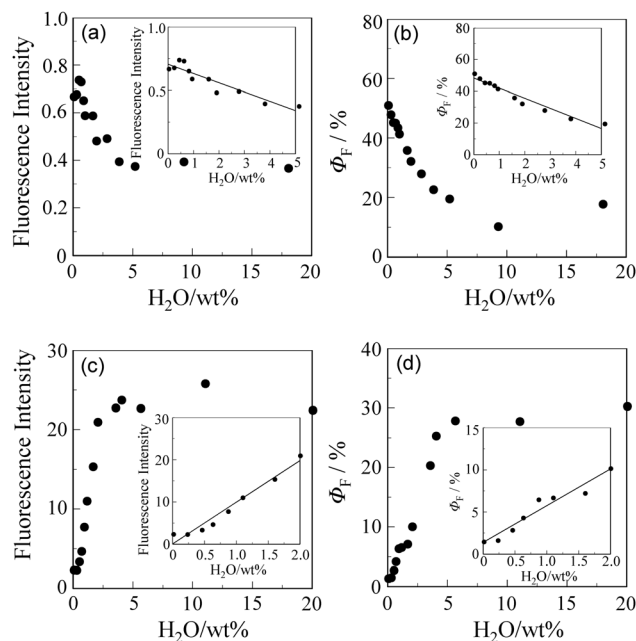


Fig. 3 (a) Fluorescence peak intensity at around 550 nm ($\lambda_{\text{ex}} = 537$ nm, slit: 1.0 nm) and (b) Φ_F of **MH-1** as a function of water content in 1,4-dioxane in a water-content region below 20 wt%. (c) Fluorescence peak intensity at around 550 nm ($\lambda_{\text{ex}} = 534$ nm, slit: 2.5 nm) and (d) Φ_F of **MH-1** as a function of water content in acetonitrile in a water-content region below 20 wt%; inset: the fluorescence peak intensity and Φ_F of **MH-1** in a low water-content region below 5.0 wt% for 1,4-dioxane and 2.0 wt% for acetonitrile, respectively.



In conclusion, we revealed that BODIPY **MH-1** with a PET structure can act as a dual function-based fluorescent sensor possessing fluorescence intensity and Φ_F value as a function of detection of trace amounts of water. It was found that the fluorescence enhancement of **MH-1** with increasing water content in a polar solvent can be attributed to the suppression of the PET process associated with the formation of fluorescent ionic species **MH-1(H₂O)** by the addition of water molecules. In contrast, the fluorescence attenuation of **MH-1** with increasing water content in a non-polar solvent can be attributed to the disruption of boron–nitrogen (B–N) interaction between BPin and a tertiary amino group in **MH-1(BN)** associated with the formation of **MH-1(H₂O)** by the addition of water molecules. We propose that this organic fluorescent dye with a PET structure which is capable of efficiently forming the fluorescence ionic structure by the addition of water molecules could be a promising candidate as a fluorescent sensor for a trace amount of water based on the PET method. Consequently, this work provides new insight into the molecular design for the development of high-sensitivity and -accuracy optical sensors for water based on the PET method with both fluorescence enhancement and attenuation systems.

The absorption spectra were recorded using a Shimadzu UV-2910 spectrophotometer. The fluorescence spectra were recorded using a Hitachi F-4500 spectrophotometer. The addition of water to organic solvents containing **MH-1** was made in terms of weight percent (wt%). The determination of water in 1,4-dioxane, THF, acetone and acetonitrile was done using a MKC-610 and MKA-610 Karl Fischer moisture titrator (Kyoto Electronics manufacturing Co., Ltd) based on Karl Fischer coulometric titration for below 1.0 wt% and volumetric titration for above 1.0 wt%, respectively.

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