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Development of fluorescent sensors based on a combination of PET (photo-induced electron transfer) and FRET (Förster resonance energy transfer) for detection of water

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Fluorescent sensors DJ-1 and DJ-2 with large Stokes shift (SS) based on a combination of PET (photo-induced electron transfer) and FRET (Förster resonance energy transfer) have been developed for the detection of water in organic solvents. DJ-1 is composed of anthracene-(aminomethyl)phenylboronic acid ester as a PET-type donor fluorophore and BODIPY skeleton as an acceptor fluorophore in the FRET process. In contrast, DJ-2 is composed of anthracene skeleton as a donor fluorophore and BODIPY-(aminomethyl)phenylboronic acid ester skeleton as a PET-type acceptor fluorophore in the FRET process. In fact, the addition of water to organic solvents containing DJ-1 or DJ-2 caused both the PET suppression and the energy transfer from the donor fluorophore to the acceptor fluorophore through the FRET process, resulting in the enhancement of the fluorescence band originating from BODIPY skeleton. In addition, the pseudo-SS values of DJ-1 and DJ-2 between the photoabsorption maximum of the anthracene fluorophore and the fluorescence maximum of the BODIPY fluorophore are 7563 cm⁻¹ (141 nm) and 8017 cm⁻¹ (153 nm), respectively, which are significantly higher than those of a typical PET-based fluorescent sensors. It was found that the FRET efficiency for DJ-1 is quantitative, but that for DJ-2 is estimated to be ca. 50% based on time-resolved fluorescence lifetime measurements. Moreover, the detection limit of DJ-1 for water is superior to that of DJ-2. Based on the fluorescence sensing mechanism of DJ-1 and DJ-2 for water, we propose that a combination of a PET-type donor fluorophore and an acceptor fluorophore in the FRET process is one of the most promising molecular design to create an efficient fluorescent sensor for water in organic solvents.

Introduction

The visualization as well as detection and quantification of water in samples and products, such as solutions, solids, and gas or water on the surface of a substrate, are doubtless significant in not only fundamental study in photochemistry, photophysics and analytical chemistry, but also their potential applications to environmental and quality control monitoring systems and industry.¹,² As a common and classical method for the determination of water content, Karl Fischer titration method, which utilizes coulometric or volumetric titration to determine amounts of water (0.001-100 wt%) in sample such as solution and solid, is widely used in laboratory and industry. The coulometric titration is suitable for determination of low amount of water below 0.1 wt% and based on the Karl Fischer reaction (eqn (1) I₂ + SO₂ + 3Base + ROH + H₂O → 2Base HI + Base·HSO₃R and eqn (2) 2I⁻ – 2e⁻ → I₂), that is, 1 mole of water will react with 1 mole of iodine generated electrolytically by eqn (2), so that the electricity for 1 milligram of water is equivalent to 10.71 coulombs. Therefore, the Karl Fischer titration method has sufficient accuracy, but is batch (ex situ) analysis, which leads to time-consuming measurement as well as inability of real-time monitoring and flow (in situ) analysis of the water content. On the other hand, optical method utilizing colorimetric and fluorescent sensors for water is of considerable scientific and practical concern in recent years, because it allows the visualization, detection and quantification of water in samples and products by highly sensitive and quick flow analysis based on the changes in wavelength, intensity and lifetime of photoabsorption and photoluminescence depending on the water content. In fact, to date, some kinds of organic fluorescent sensors and polymers for water based on ICT (intramolecular charge transfer),³,⁴ PET (photo-induced electron transfer),⁵,⁶ ESIP (excited state intramolecular proton transfer),⁷ or solvatochromic property⁸ have been designed and synthesized. The optical sensing properties of these fluorescent sensors for the detection and quantification of water were investigated from the viewpoints of the relationship between ICT, PET, or ESIP characteristics and the intermolecular interaction of the sensor with water molecules. As the results, it was found that most of previous fluorescent sensors for water, including conjugated polymer and organic fluorescent dyes with ICT and ESIP characteristics are based on fluorescence quenching (turn-off) system, that is, the fluorescence intensity of sensor decreases as a function of water content in organic solvents. However, this fluorescence quenching system makes it difficult to detect a trace amount of water. In contrast, fluorescence enhancement (turn-on) system with increase in water content in organic solvents is

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PET takes place from the nitrogen atom of amino moiety to the ester (for applications in biochemistry and leading to the fluorescence quenching. The addition of water to the photoexcited fluorophore skeleton in the absence of water, Förster resonance energy transfer (FRET)-based sensor is useful causes a drastic and linear enhancement of fluorescence emission organic solvents containing the PET-based fluorescent sensor usually has the disadvantage of very protonated or strongly interacts with water molecule, leading to PET method makes it possible to visualize, detect and determine the fluorescence enhancement system for low water content. On the other hand, AIE (aggregation-induced emission enhancement) of organic fluorophores in the aggregation state has been reported as fluorescence enhancement system for high water content, that is, AIE dye such as tetraphenylethene (TPE) and its derivatives exhibits the emission enhancement due to the restricted intramolecular rotation (RIR) in the molecular structures induced by the formation aggregation upon addition of large amounts of water (over 40 wt% in almost every case) into the solution. In particular, the fluorescence enhancement system based on the PET-type fluorescent sensor for water can detect a reversible change in its immediate environment due to the reversible intermolecular interaction between the sensor and water molecules. Actually, in our previous work, anthracene-(aminomethyl)phenylboronic acid pinacol esters (OM-1, OF-1 and OF-2) and BODIPY-(aminomethyl)phenylboronic acid ester (MH-1) were designed and synthesized as PET-based fluorescent sensors for a trace amount of water (Fig. 1a, b). The PET takes place from the nitrogen atom of amino moiety to the photoexcited fluorophore skeleton in the absence of water, leading to the fluorescence quenching. The addition of water to organic solvents containing the PET-based fluorescent sensor causes a drastic and linear enhancement of fluorescence emission as a function of the water content, which is attributed to the suppression of PET. The nitrogen atom of amino moiety is protonated or strongly interacts with water molecule, leading to the formation of PET inactive species such as OM-1a. Thus, the PET method makes it possible to visualize, detect and determine a trace amount of water in organic solvents. However, the PET-based fluorescent sensor usually has the disadvantage of very small Stokes shift (SS), causing serious self-quenching and fluorescence detection errors due to photoexcitation and scattering lights from the excitation source; SS is the difference in wavelength or frequency units between the maxima of the first photoabsorption band and fluorescence band. On the other hand, Förster resonance energy transfer (FRET)-based sensor is useful for applications in biochemistry and environmental research such as nucleic acid and ion analysis, signal transduction, and light harvesting, as well as for designing ratiometric fluorescent sensors. FRET is well described as an energy transfer process between an excited-state donor fluorophore and a ground-state acceptor fluorophore linked together by a non-conjugated spacer, and as the result, the fluorescence spectrum from acceptor fluorophore is observed. In order to achieve an effective FRET, a strong spectral overlap between the donor fluorescence and the acceptor photoabsorption is required. Consequently, the pseudo-SS between the maxima of donor photoabsorption band and acceptor fluorescence band of FRET-based sensor is larger than the SS of either the donor or acceptor fluorophore, leading to an effective avoidance of the self-quenching and fluorescence detection errors. Thus, in our previous work, in order to develop a fluorescent sensor possessing large SS for detection of water in solvents, we have designed and synthesized a PET/FRET-based fluorescent sensor DJ-1 composed of anthracene-(aminomethyl)phenylboronic acid ester as a donor fluorophore with PET characteristics and BODIPY skeleton as an acceptor fluorophore in the FRET process (Fig. 1c). In fact, the enhancement of fluorescence band originating from the BODIPY skeleton was observed upon addition of water to the acetonicrile solution of DJ-1 due to both the suppression of PET in the donor fluorophore (anthracene-(aminomethyl)phenylboronic acid ester) and the occurrence of FRET from the excited-state donor fluorophore to the ground-state acceptor fluorophore (BODIPY skeleton) (Fig. 2a). It was found that the PET/FRET-based fluorescent dye composed of the PET-type donor fluorophore and the acceptor fluorophore in FRET process can act as a fluorescent sensor with large SS for the detection of a trace amount of water in solvents. Thus, it is expected that the development of PET/FRET-based fluorescent sensor allows creation of fluorescent sensor system with large SS for the detection of water in solvents, that is, the PET/FRET-based fluorescent sensor has the advantage over PET-based fluorescent sensor with very small SS.

Fig. 1 Proposed mechanisms of PET-type fluorescent sensors (a) OM-1, OF-1, OF-2 and (b) MH-1 for the detection of water in solvent. Chemical structures of (c) PET/FRET-type fluorescent sensors DJ-1 and DJ-2, (c) BODIPY derivative B-1, PET-type BODIPY MH-2 and anthracene derivative A-1.

In this work, in order to provide a direction in molecular design toward creating a highly efficient PET/FRET-based fluorescent sensor for water in organic solvents, we have newly designed and synthesized a PET/FRET-based fluorescent sensor DJ-2, where the anthracene skeleton and BODIPY-(aminomethyl)phenylboronic acid ester skeleton are the donor fluorophore and the PET-type acceptor fluorophore in the FRET process, respectively (Fig. 1c). It is expected that for DJ-2 in absolute solvents the FRET takes place from the excited-state donor fluorophore (anthracene skeleton) to the ground-state acceptor fluorophore (BODIPY skeleton), but fluorescence emission originating from the acceptor fluorophore is not
observed due to the occurrence of PET in BODIPY-(aminomethyl)phenylboronic acid ester skeleton (Fig. 2b). On the other hand, as with the case of DJ-1, the addition of water to organic solvents containing DJ-2 causes both the PET suppression and the energy transfer from the anthracene to the BODIPY skeleton through the FRET process, thus resulting in the enhancement of the fluorescence band originating from BODIPY skeleton. Based on the obtained results and the fluorescence sensing mechanism of DJ-1 and DJ-2 for water, we propose a molecular design to create an efficient PET/FRET-based fluorescent sensor for water in organic solvents.

Results and discussion

The PET/FRET-based fluorescent sensors DJ-1 and DJ-2 were synthesized according to a stepwise synthetic protocol. The synthesis of DJ-1, which is composed of anthracene-(aminomethyl)phenylboronic acid ester as a PET-type donor fluorophore and BODIPY skeleton as an acceptor fluorophore in the FRET process, as well as PET-based fluorescent sensor OM-1 and B-1 as reference to DJ-1 (Fig. 1d), has been reported elsewhere. The synthetic pathway of DJ-2, which is composed of anthracene skeleton as a donor fluorophore and BODIPY-(aminomethyl)phenylboronic acid ester skeleton as a PET-type acceptor fluorophore in the FRET process, is shown in Scheme 1. We first prepared BODIPY 1 by the reaction of 2,4-dimethylpyrrole with bromoacetyl chloride followed by treatment with BF₃·OEt₂. The BODIPY 1 was reacted with methyl amine to give BODIPY 2. The reaction of 2 with 2-(4-Bromo-3-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in the presence of N,N-diisopropylethylamine yielded compound 3. PET/FRET-based derivative 4 was prepared by Suzuki coupling of 9-(4-iodophenyl)anthracene (see Scheme S1 for the synthesis, ESI†) with the compound 3. Finally, we obtained DJ-2 from the compound 4 with bis(pinacolato)diboron via the Miyaura boronation reaction. As reference to DJ-2, the anthracene derivative A-1 was prepared by Suzuki coupling of 9-(4-iodophenyl)anthracene with phenylboronic acid (Fig. 1d, see Scheme S2 for the synthesis, ESI†). Also, we prepared PET-based fluorescent sensor MH-2 by the reaction of 2 with 2-(2-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Fig. 1d, see Scheme S3 for the synthesis, ESI†).

The photoabsorption and fluorescence spectra of OM-1, MH-2, A-1, B-1, DJ-1 and DJ-2 in acetonitrile are shown in Fig. 3. OM-1 and B-1, which are structural components for DJ-1, show photoabsorption bands in the ranges of 300 nm to 400 nm and 420 nm to 520 nm originating from the anthracene skeleton and the BODIPY skeleton, respectively (Fig. 3a). In addition, for B-1, a feeble and broad photoabsorption band was observed in the range of 300 nm to 400 nm. The molar extinction coefficient ($\varepsilon_{\text{max}}$) for the photoabsorption maximum ($\lambda_{\text{abs,max}}$ = 498 nm) of B-1 is 72 600 M⁻¹ cm⁻¹, which is significantly higher than that ($\lambda_{\text{abs,max}}$ = 366 nm, $\varepsilon_{\text{max}}$ = 6800 M⁻¹ cm⁻¹) of OM-1. On the other hand, DJ-1 shows two photoabsorption bands in the ranges of 300 nm to 400 nm ($\lambda_{\text{abs,max}}$ = 367 nm, $\varepsilon_{\text{max}}$ = 14 200 M⁻¹ cm⁻¹) and 420 nm to 520 nm ($\lambda_{\text{abs,max}}$ = 498 nm, $\varepsilon_{\text{max}}$ = 72 200 M⁻¹ cm⁻¹), which are assigned to the anthracene skeleton and the BODIPY skeleton, respectively. MH-2 and A-1, which are structural components for DJ-2, show photoabsorption bands in the ranges of 430 nm to 540 nm and 300 nm to 400 nm originating from the BODIPY skeleton and the anthracene skeleton, respectively (Fig. 3c). As with the case of B-1, for MH-2, a feeble and broad photoabsorption band was observed in the range of 300 nm to 400 nm. The $\varepsilon_{\text{max}}$ value for the $\lambda_{\text{abs,max}}$ at 510 nm of MH-2 is 82 900 M⁻¹ cm⁻¹, which is significantly higher than that ($\lambda_{\text{abs,max}}$ = 367 nm, $\varepsilon_{\text{max}}$ = 11 100 M⁻¹ cm⁻¹) of A-1. In addition, as with the case of DJ-1, DJ-2 shows two photoabsorption bands in the ranges of 300 nm to 400 nm ($\lambda_{\text{abs,max}}$ = 367 nm, $\varepsilon_{\text{max}}$ = 14 800 M⁻¹ cm⁻¹) and 430 nm to 540 nm ($\lambda_{\text{abs,max}}$ = 511 nm, $\varepsilon_{\text{max}}$ = 61 300 M⁻¹ cm⁻¹) originating from the anthracene skeleton and the BODIPY skeleton, respectively. In the corresponding fluorescence spectra, OM-1 and B-1 exhibit a fluorescence maximum ($\lambda_{\text{em,max}}$) at 412 nm and 507 nm by the photoexcitation ($\lambda_{\text{exc}}$) at 366 nm and 367 nm, respectively (Fig. 3b). It is worth mentioning here that the edge for the fluorescence band of OM-
I reached 500 nm, that is, the photoabsorption spectrum originating from the BODIPY skeleton of B-1 has spectral overlap with the fluorescence spectrum originating from the anthracene skeleton of OM-1. This result suggests that for DJ-1, the FRET from the anthracene skeleton as the donor fluorophore to the BODIPY skeleton as the acceptor fluorophore occurs by the photoexcitation of the anthracene skeleton. In fact, DJ-1 exhibits an only fluorescence band with the \( \lambda_{\text{max}} \) at 508 nm in the range of 480 nm to 600 nm originating from the BODIPY skeleton by the photoexcitation (\( \lambda_{\text{ex}} = 367 \) nm) of the anthracene skeleton, as well as the photoexcitation (\( \lambda_{\text{ex}} = 472 \) nm) of the BODIPY skeleton (Fig. S10, ESI†). On the other hand, by the photoexcitation (\( \lambda_{\text{ex}} = 367 \) nm, MH-2 exhibits a feeble fluorescence band with the \( \lambda_{\text{max}} \) at 520 nm, whereas A-I exhibits an intense fluorescence band (fluorescence quantum yield (\( \Phi_{\text{f}} \)) = 57%) with the \( \lambda_{\text{max}} \) at 404 nm and the edge of the fluorescence band reached 530 nm (Fig. 3d). Therefore, the photoabsorption spectrum originating from the BODIPY skeleton of MH-2 has spectral overlap with the fluorescence spectrum originating from the anthracene skeleton of A-I, indicating the occurrence of FRET in DJ-2 from the anthracene skeleton to the BODIPY skeleton by the photoexcitation of the anthracene skeleton. However, in contrast to the case of DJ-1, DJ-2 exhibits two fluorescence bands with the \( \lambda_{\text{max}} \) at 407 nm and the \( \lambda_{\text{max}} \) at 520 nm originating from the anthracene skeleton and the BODIPY skeleton, respectively, by the photoexcitation (\( \lambda_{\text{ex}} = 367 \) nm) of the anthracene skeleton, although DJ-2 shows an only fluorescence band with the \( \lambda_{\text{max}} \) at 520 nm originating from the BODIPY skeleton by the photoexcitation (\( \lambda_{\text{ex}} = 486 \) nm) of the BODIPY skeleton (Fig. S12, ESI†). Thus, we considered the difference in fluorescence properties between DJ-1 and DJ-2 based on the FRET efficiency. Obviously, in absolute acetone solution, the FRET efficiency for DJ-1 is quantitative by the fact that no fluorescence band originating from the anthracene skeleton is observed. In contrast, the FRET efficiency for DJ-2 is estimated to be 53% from the equation \( E_{\text{FRET}} = 1 - (\tau_{\text{D}}/\tau_{\text{A}}) \) based on time-resolved fluorescence lifetime measurements, where \( \tau_{\text{A}} \) and \( \tau_{\text{D}} \) are the donor fluorescence lifetimes in the presence and absence of an acceptor, that is, \( \tau_{\text{A}} \) and \( \tau_{\text{D}} \) are the fluorescence lifetimes of DJ-2 (2.0 ns) and A-I (4.2 ns), respectively. Indeed, this result indicates that the FRET efficiency for DJ-1 is higher than that for DJ-2. The reason for the inferior \( E_{\text{FRET}} \) value of DJ-2 might be not only intense fluorescence emission originating from the anthracene skeleton (actually, the \( \Phi_{\text{f}} \) value of A-I is 57%) that is too strong for the BODIPY skeleton to well absorb the energy, but also poor overlap integral of the donor fluorescence spectrum with the acceptor photoabsorption spectrum, compared to the overlap integral in DJ-1, although DJ-1 and DJ-2 have the same spatial distance between the donor and the acceptor fluorophores. Nevertheless, based on the photoabsorption and fluorescence properties of OM-1, MH-2, A-I, B-1, DJ-1 and DJ-2, it is expected that the addition of water to organic solvents containing DJ-1 or DJ-2 causes both the PET suppression in the anthracene- or BODIPY-(aminomethyl)phenylboronic acid ester and the energy transfer from anthracene skeleton to BODIPY skeleton through the FRET process, thus resulting in the enhancement of the fluorescence band originating from BODIPY skeleton.

In addition, it was found that the pseudo-SS value of DJ-1 and DJ-2 between the \( \lambda_{\text{abs max}} \) of the anthracene skeleton and the \( \lambda_{\text{max}} \) of the BODIPY skeleton is 7563 cm\(^{-1}\) (141 nm) and 8017 cm\(^{-1}\) (153 nm), respectively, which are significantly higher than those of OM-1 (395 cm\(^{-1}\)) and B-1 (356 cm\(^{-1}\)), and those of MH-2 (377 cm\(^{-1}\)) and A-I (1222 cm\(^{-1}\)), respectively.

Fig. 3 (a) Photoabsorption and (b) fluorescence (\( \lambda_{\text{ex}} = 366 \) nm for OM-1 and 367 nm for B-1 and DJ-1) spectra of OM-1 (\( c = 2.0 \times 10^{-5} \) M), B-1 (\( c = 4.0 \times 10^{-6} \) M), and DJ-1 (\( c = 4.0 \times 10^{-6} \) M) in acetonitrile. (c) Photoabsorption and (d) fluorescence (\( \lambda_{\text{ex}} = 367 \) nm for MH-2 and 366 nm for A-I) spectra of MH-2 (\( c = 4.0 \times 10^{-6} \) M), A-I (\( c = 2.0 \times 10^{-5} \) M), and DJ-2 (\( c = 4.0 \times 10^{-6} \) M) in acetonitrile.

In order to investigate the optical sensing ability of DJ-1 for water in acetone-tertile, the photoabsorption and fluorescence spectra of OM-1 and B-1 were measured in acetone-tertile that contained various concentrations of water, prior to DJ-1 (Fig. 4). The photoabsorption spectra of OM-1 did not undergo appreciable changes upon addition of water to the acetone-tertile solution (Fig. 4a), but the fluorescence spectra of OM-1 underwent an increase in fluorescence intensity at around 415 nm with the increase in the water content, which is attributed to the fluorescence emission originating from the anthracene skeleton due to the suppression of PET (Fig. 4b). On the other hand, the photoabsorption and fluorescence spectra of B-1 did not undergo appreciable changes upon the addition of water to the acetone-tertile solution (Fig. 4c, d, and S11, ESI†). As with the case of OM-1, the photoabsorption spectra of DJ-1 show unnoticeable changes upon addition of water to the acetone-tertile solution (Fig. 4c). However, for the corresponding fluorescence spectra, it is worth mentioning here that DJ-1 exhibits an enhancement of fluorescence band at 508 nm originating from the BODIPY skeleton by the photoexcitation (\( \lambda_{\text{ex}} = 367 \) nm) of
the anthracene skeleton upon addition of water to the acetonitrile solution (Fig. 4f). The enhancement of the fluorescence band levels off when the water content becomes 5.0 wt% as with the case of OM-1. This result indicates that the enhancement of fluorescence band originating from the BODIPY skeleton is attributed to both the suppression of PET in the anthracene-(aminomethyl)phenylboronic acid ester and the occurrence of FRET from the excited-state anthracene fluorophore to the ground-state BODIPY fluorophore upon addition of water to the acetonitrile solution. As an additional evidence for the FRET process in DJ-1, the fluorescence spectra of DJ-1 by the photoexcitation ($\lambda_{ex}$ = 472 nm) of the BODIPY skeleton did not undergo appreciable changes in intensity and shape of the fluorescence band originating from BODIPY skeleton upon addition of water to the acetonitrile solution (Fig. S10, ESI†). Consequently, as shown in Fig. 2a, these facts strongly propose that for DJ-1, the enhancement of the fluorescence band upon addition of water to the solution is due to both the suppression of PET and the occurrence of FRET in the PET/FRET-based fluorescence system. As with the case of DJ-1, the optical sensing ability of DJ-2 for water was investigated by the photoabsorption and fluorescence spectral measurement as well as MH-2 and A-1 in acetonitrile that contained various concentrations of water (Fig. 5). The photoabsorption spectra of MH-2 did not undergo appreciable changes upon addition of water to the acetonitrile solution (Fig. 5a). On the other hand, the fluorescence spectra of MH-2 by the photoexcitation ($\lambda_{ex}$ = 367 nm) underwent an increase in the intensity with a red-shift (ca. 15 nm) of fluorescence peak wavelength at 520 nm in the water content region greater than 5.0 wt%, which is attributed to the fluorescence emission originating from the BODIPY skeleton due to the suppression of PET (Fig. 5b). Similar result was also obtained in the fluorescence spectra of MH-2 by the photoexcitation ($\lambda_{ex}$ = 485 nm) of BODIPY skeleton (Fig. S12, ESI†). On the other hand, the photoabsorption and fluorescence spectra of A-1 did not undergo appreciable changes upon addition of water to the acetonitrile solution (Fig. 5c, d, and S13, ESI†). As with the case of MH-2, the photoabsorption spectra of DJ-2 show unnoticeable changes upon addition of water to the acetonitrile solution (Fig. 5e). In addition, DJ-2 exhibits an enhancement and red-shift (ca. 15 nm) of fluorescence band at 520 nm originating from the BODIPY skeleton by the photoexcitation ($\lambda_{ex}$ = 367 nm) of the anthracene skeleton in the water content region greater than 5.0 wt% (Fig. 5f), but the fluorescence band at around 410 nm origination from the anthracene skeleton does not undergo appreciable changes upon the addition of water to the acetonitrile solution, which might be attributed to the low FRET efficiency. This result indicates that the enhancement of fluorescence band originating from the BODIPY skeleton is attributed to both the PET suppression in the BODIPY-(aminomethyl)phenylboronic acid ester and the FRET process from the excited-state anthracene fluorophore to the ground-state BODIPY fluorophore upon addition of water to the acetonitrile solution. As an additional evidence for the suppression of PET in DJ-2 upon the addition of water to the acetonitrile solution, the fluorescence spectra of DJ-2 by the photoexcitation ($\lambda_{ex}$ = 486 nm) of the BODIPY skeleton showed similar changes with the case of the photoexcitation ($\lambda_{ex}$ = 367 nm) of the anthracene skeleton (Fig. S14, ESI†) as well as the case of MH-2. As shown in Fig. 2b, these facts strongly indicate that for DJ-2 in absolute solvent, the FRET takes place from the excited-state donor fluorophore (anthracene skeleton) to the ground-state acceptor fluorophore (BODIPY skeleton), although the fluorescence emission originating from the acceptor fluorophore is not observed due to the PET in BODIPY-(aminomethyl)phenylboronic acid ester skeleton. On the other hand, the addition of water to acetonitrile solution containing DJ-2 causes both the PET suppression and the energy transfer from anthracene to BODIPY skeleton through the FRET process, thus resulting in the enhancement of the fluorescence band originating from BODIPY skeleton. For both DJ-1 and DJ-2, the similar results were obtained in the case of THF.

**Fig. 4** (a) Photoabsorption and (b) fluorescence spectra ($\lambda_{ex}$ = 366 nm) of OM-1 ($c$ = 2.0×10–5 M) in acetonitrile containing water (0.046–40 wt%). (c) Photoabsorption and (d) fluorescence spectra ($\lambda_{ex}$ = 367 nm) of B-1 ($c$ = 4.0×10–6 M) in acetonitrile containing water (0.0042–39 wt%). (e) Photoabsorption and (f) fluorescence spectra ($\lambda_{ex}$ = 367 nm) of DJ-1 ($c$ = 4.0×10–6 M) in acetonitrile containing water (0.0070–39 wt%).
On the basis of the above results, we considered the optical sensing ability of DJ-1 and DJ-2 for water in a solvent. Evidently, the FRET efficiency for DJ-1 in acetonitrile solution containing water is quantitative by the fact that no fluorescence band originating from the anthracene skeleton is observed as a function of the water content. On the other hand, the plots of MH-2 and DJ-2 in the low water content region below 1.0 wt% showed the good linearity with the R² values of 0.99 for MH-2 and 0.96 for DJ-2, that is, the fluorescence peak intensity at 520-535 nm increased linearly as a function of the water content (Fig. 7). In addition, we performed the measurement of Φₘ for DJ-1 in the acetonitrile solution with various water contents. Indeed, these Φₘ values are in good agreement with the intensity of the fluorescence spectra (Fig. 8). Such a relationship between the Φₘ value and the fluorescence intensity was also observed in the case of DJ-2, although the Φₘ value is estimated from the fluorescence bands originating from both the anthracene skeleton and the BODIPY scaffold. (Fig. S15, ES†). These facts also indicate that the fluorescence sensing mechanism of the PET/FRET-based fluorescent sensors for water is based on the suppression of PET and occurrence of FRET by water molecules for DJ-1 and the suppression of PET and the utilization of FRET by water molecules for DJ-2, respectively (Fig. 2). Thus, the detection limit (DL) of DJ-1 was determined from the plot of the fluorescence intensity at 508 nm versus the water fraction in the low water content region below 1.0 wt% (DL = 3.3σ/mᵑ, where σ is the standard deviation of the blank sample and mᵑ is the slope of the calibration curve). The mᵑ and DL values of DJ-1 are 13 and 0.25 wt%, which are inferior to those (mᵑ = 67, DL = 0.04 wt%) of the PET-based fluorescent sensor OM-1 (Fig. 6). The mᵑ and DL values of PET/FRET-based fluorescent sensor may be dependent on the non-conjugated spacer between the donor fluorophore and the acceptor fluorophore, that is, the substituent on the phenylboronic acid pinacol ester. In fact, the mᵑ value (55) and DL value (0.06 wt%) of OF-1 having a methoxy group as an electron-donating substituent are inferior to those of OM-1, but the mᵑ value (382) and DL value (0.009 wt%) of OF-2 having a cyano group as an electron-withdrawing substituent are superior to those of OM-1 and OF-1. On the other hand, the DL values of MH-2 (mᵑ = 0.16) and DJ-2 (mᵑ = 0.24) determined from the plots of the fluorescence intensity at 520-535 nm versus the water fraction below 40 wt% are over 10 wt% (Fig. 7), which are much inferior to those of OM-1 and DJ-1. The inferior DL values of MH-2 and DJ-2 might be attributed to the highly active PET characteristics in BODIPY-(aminomethyl)phenylboronic acid ester skeleton, compared to anthracene-(aminomethyl)phenylboronic acid ester skeleton in OM-1 and DJ-1. These results suggest that the mᵑ and DL values of PET/FRET-based fluorescent sensor for the detection of water can be improved by not only modifying the non-conjugated spacer between the donor fluorophore and the acceptor.
fluorophore, but also the selecting the PET-type fluorophore. Consequently, this work reveals that DJ-1 composed of a PET-type donor fluorophore and an acceptor fluorophore in the FRET process can act as an efficient PET/FRET-based fluorescent sensor for water, compared with DJ-2 composed of a donor fluorophore and a PET-type acceptor fluorophore in the FRET process.

![Image](https://via.placeholder.com/150)

**Fig. 6** Fluorescence peak intensity at (a) around 415 nm of OM-1 ($\lambda_{ex} = 366$ nm) and (b) 508 nm of DJ-1 ($\lambda_{ex} = 367$ nm) as a function of water content below 40 wt% in acetonitrile. Inset in (a): fluorescence peak intensity at around 415 nm of OM-1 ($\lambda_{ex} = 366$ nm) as a function of water content below 1.3 wt% in acetonitrile. Inset in (b): fluorescence peak intensity at 508 nm of DJ-1 ($\lambda_{ex} = 367$ nm) as a function of water content below 1.0 wt% in acetonitrile.

![Image](https://via.placeholder.com/150)

**Fig. 7** Fluorescence peak intensity at 520-535 nm of (a) MH-2 ($\lambda_{ex} = 367$ nm) and (b) DJ-2 ($\lambda_{ex} = 367$ nm) as a function of water content below 40 wt% in acetonitrile.

![Image](https://via.placeholder.com/150)

**Fig. 8** Fluorescence quantum yield of DJ-1 by photoexcitation at 367 nm as a function of water content (a) below 20 wt% and (b) 1.0 wt% in acetonitrile.

**Conclusions**

We have designed and developed two different-types of PET/FRET-based fluorescent sensors (DJ-1 and DJ-2) possessing large SS for visualization, detection and quantification of water in solvents. DJ-1 is composed of a PET-type donor fluorophore (anthracene-(aminomethyl)phenylboronic acid ester) and an acceptor fluorophore (BODIPY skeleton) in the FRET process, but DJ-2 is composed of a donor fluorophore (anthracene skeleton) and a PET-type acceptor fluorophore (BODIPY-(aminomethyl)phenylboronic acid ester) in the FRET process. This work demonstrated that that the FRET efficiency for DJ-1 is quantitative, but that for DJ-2 is estimated to be ca. 50% based on time-resolved fluorescence lifetime measurements. Moreover, it was found that the detection limit of DJ-1 for water is superior to that of DJ-2. Based on the fluorescence sensing mechanism of DJ-1 and DJ-2 for water, we propose that a combination of a PET-type donor fluorophore and an acceptor fluorophore in the FRET process is one of the most promising molecular design to create an efficient fluorescent sensor for water in organic solvents.

**Experimental**

**General**

Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using ATR method. 1H and 13C NMR spectra were recorded on a Varian-500 (500 MHz) FT NMR spectrometer. High-resolution mass spectral data by ESI and GC-FI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL and JEOL JMS-T100 GCV 4G, respectively. Photoabsorption spectra were observed with a SHIMADZU UV-3150 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields were determined by a HORIBA FluoroMax-4 spectrofluorometer by using a calibrated integrating sphere system. Fluorescence decay measurements were performed on a HORIBA DeltaFlex modular fluorescence lifetime system, using a Nano LED pulsed diode excitation source (370 nm).

**Synthesis**

10-(Bromomethyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-44,54-dipyrrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (1). A solution of 2,4-dimethylpyrrrole (2.0 mL, 19 mmol) and bromoacetyl chloride (0.84 mL, 10 mmol) in dichloromethane (100 mL) was refluxed for 1.5 h under a nitrogen atmosphere. To
the reaction mixture under a nitrogen atmosphere was added triethylamine (7.0 mL, 50.0 mmol) and stirred for 10 min at room temperature. Next, BF3·OEt2 (26 mL, 100 mmol) was added dropwise and the solution was refluxed for 22 h. The reaction mixture was washed with water and extracted with dichloromethane. The organic extract was dried over anhydrous MgSO4, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane : hexane = 1:2 as eluent) to give 1 (0.46 g, 14 % yield) as a red solid; FT-IR (ATR): ν = 2960, 1556, 1504, 1195, 1159, 1066, 1022, 989 cm⁻¹; ¹H NMR (500 MHz, CDCl3): δ = 2.54 (s, 12H), 4.79 (s, 2H), 6.10 (s, 2H) ppm; ¹³C NMR (125 MHz, CDCl3) δ = 14.84, 15.68, 37.30, 122.42, 131.50, 136.07, 141.26, 156.79 ppm; HRMS (ESI): m/z (%): [M+Na⁺] calc for C16H12N2BrF2Na, 363.0452; found 363.0450.

1-(5,5-Difluoro-1,3,7,9-tetramethyl-5H-4/4,4/4-dipyrrrolo[1,2-c;2',1'-f][1,3,2]diazaborinin-10-yl)-N-methylmethanaminne (2). To a solution of 1 (0.077 g, 0.23 mmol) in THF (4 mL) was added methyl amine (0.24 mL, 0.46 mmol) and was refluxed for 1 h. The reaction mixture was washed with water and extracted with dichloromethane. The organic extract was dried over anhydrous MgSO4, filtrated, and concentrated. The residue was chromatographed on silica gel (ethyl acetate : hexane = 1:3 as eluent) to give 2 (0.048 g, 72 % yield) as an orange solid; m.p. 188–189 °C; FT-IR (ATR): ν = 2951, 1544, 1508, 1305, 1193, 1157, 1058, 1024, 968 cm⁻¹; ¹H NMR (500 MHz, CDCl3): δ = 2.47 (s, 6H), 2.51 (s, 6H), 2.56 (s, 3H), 3.89 (s, 2H), 6.06 (s, 2H) ppm; ¹³C NMR (125 MHz, CDCl3) δ = 14.68, 15.38, 36.80, 48.60, 121.89, 132.38, 140.40, 141.28, 155.22 ppm; HRMS (ESI): m/z (%): [M+H⁺] calc for C13H10F2N2BrF2, 292.1791; found 292.1790.

N-(2-Bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4/4,4/4-dipyrrrolo[1,2-c;2',1'-f][1,3,2]diazaborinin-10-yl)-N-methylmethanaminne (3). A solution of 2 (0.046 g, 0.16 mmol), 2-(4-bromo-3-(bromomethyl)phenyl)amine-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.059 g, 0.16 mmol), N,N-diisopropylethylamine (0.11 mL, 0.64 mmol), and acetonitrile (6 mL) was refluxed for 3 h under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was dried over anhydrous MgSO4, filtrated on celite, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate : hexane = 1:3 as eluent) to give 3 (0.064 g, 68 % yield) as an orange solid; m.p. 222–224 °C; FT-IR (ATR): ν = 2974, 1546, 1508, 1344, 1195, 1159, 1141, 1060, 1016, 964 cm⁻¹; ¹H NMR (500 MHz, CDCl3): δ = 2.41 (s, 3H), 2.51 (s, 6H), 2.59 (s, 6H), 3.86 (s, 2H), 4.03 (s, 2H), 6.09 (s, 2H), 7.36–7.40 (m, 2H), 7.47–7.50 (m, 5H), 7.61 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 8.53 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl3) δ = 14.75, 17.58, 42.26, 52.20, 59.18, 122.39, 125.29, 125.59, 126.86, 127.11, 127.88, 128.51, 130.36, 131.50, 131.89, 133.16, 133.41, 136.58, 138.27, 139.01, 139.93, 140.13, 140.46, 142.22, 155.18 ppm (one aromatic carbon signal was not observed owing to overlapping resonances); HRMS (ESI): m/z (%): [M+H⁺] calc for C25H18BrF2N2BrF2, 712.2304; found 712.2306.

1’-((Anthracen-9-yl)-4’-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1’-biphenyl]-3-yl)-N-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4/4,4/4-dipyrrrolo[1,2-c;2',1'-f][1,3,2]diazaborinin-10-yl)-N-methylmethanaminne (DJ-2). A solution of 4 (0.071 g, 0.10 mmol), bis(pinacolato)diboron (0.041 g, 0.16 mmol), PdCl2(dppf)·CH2Cl2 (0.009 g, 0.011 mmol), and KOAc (0.031 g, 0.32 mmol) in 1,4-dioxane (3 mL) was refluxed for 2 h under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The dichloromethane extract was dried over anhydrous MgSO4, filtrated on celite, and evaporated under reduced pressure. The residue was dissolved in toluene, and HPLC was performed to give DJ-2 (0.015 g, 19 % yield) as a reddish brown solid; m.p. 147–150 °C; FT-IR (ATR): ν = 2972, 1544, 1508, 1344, 1305, 1193, 1157, 1072, 975 cm⁻¹; ¹H NMR (500 MHz, CDCl3): δ = 1.37 (s, 12H), 2.35 (s, 3H), 2.51 (s, 6H), 2.58 (s, 6H), 3.98 (s, 2H), 4.14 (s, 2H), 6.07 (s, 2H), 7.17–7.19 (m, 1H), 7.37–7.40 (m, 2H), 7.47–7.51 (m, 4H), 7.63 (d, J = 7.8 Hz, 1H), 7.73–7.78 (m, 4H), 7.91 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 8.52 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl3) δ = 14.73, 17.49, 24.73, 25.12, 41.51, 51.86, 58.47, 83.79, 122.23, 124.70, 125.28, 125.54, 126.78, 126.99, 127.10, 127.85, 128.51, 130.36, 131.51, 131.80, 133.44, 136.59, 136.80, 138.18, 139.96, 141.28, 142.36, 142.93, 145.91, 154.91 ppm (one aromatic carbon signal was not observed owing to overlapping resonances); HRMS (ESI): m/z (%): [M+H⁺] calc for C35H22BrF2N2BrF2, 760.4051; found 760.4061.

Conflicts of interest

This is an Accepted Manuscript. The final published version may differ.
There are no conflicts to declare.

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