A New Class of Fluorescent Dye for Sensing Water in Organic Solvents by Photo-induced Electron Transfer: Phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type Fluorophore with both Proton Binding and Proton Donating Sites

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A new class of fluorescent dye for sensing water in organic solvents by photo-induced electron transfer (PET), based on phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type fluorophore with both proton binding and proton donating sites, has been designed developed. The fluorophore exhibits a weak emission in organic

solvents, but a drastic enhancement in the fluorescence intensity is observed with an increase in water content in organic solvents.

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Introduction

In recent years, many fluorescent dyes that recognize protons, cations, anions, and neutral organic species such as saccharides have been developed, and their possible applications in optical, biochemical, and medical sensors and optoelectronic devices have been investigated.^[1,2] Most fluorescent sensors are composed of a binding site for the target species and a fluorescent moiety; good communication between the two sites is crucial for obtaining a guest specific fluorescent response. A fluorescent sensor for water in an organic solvent is of interest to fundamental research in analytical chemistry and important for industrial applications, especially in electronics and fine chemicals.^[3,4] Some fluorescent water-sensors have been developed, which exhibit the changes in their fluorescence lifetime and intensity with varying amounts of water in organic solvents.^[5] However, in almost all those cases, the fluorescence intensity decreases with an increase in water content in the organic solvents.^[6,7] The decrease in fluorescence intensity can be attributed to a specific water-fluorophore interaction, and also to the increase in the polarity of the solvent mixture. Therefore, exact determination of water content in a solution can be difficult using these fluorescent dyes, because the fluorescence intensity is strongly affected by the polarity of the solution. Here, we report a new class of fluorescent dye that can be used to sense water in organic solvents by photo-induced electron transfer (PET). The dye is based on substituted phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type fluorophore with both proton binding and proton donating sites. The fluorophore exhibits a weak fluorescent emission in organic solvents, but a drastic enhancement in the fluorescence intensity is observed with an increase in water content in organic solvents.

Results and Discussion

The synthesis of phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type fluorophores **2a–2e** is outlined in Scheme 1. We first prepared the starting 4-aminated-1,2-naphthoquinones **1a** and **1b** in 31% and 78% yields, respectively, by the reaction of sodium 1,2-naphthoquinone-4-sulphonate with the corresponding phenylamine in acetic acid in the presence of nickel(II) chloride, respectively. Next, the fluorophores **2a–2e** were synthesized in 14–72% yields by the reaction of *p*-substituent benzaldehyde with the corresponding the 4-aminated-1,2-naphthoquinones.

< Please insert Scheme 1 here >

Absorption and fluorescence spectral data of **2a–2e** in the solution are summarized in Table 1. The fluorophores **2a** and **2b** exhibited a weak absorption band at around 335 nm, and a single intense absorption band at around 400 nm, and a single intense fluorescence band at around 495 nm ($\Phi = 0.92–0.95$) in 1,4-dioxane (Figure 1a). The absorption maxima of **2a** and **2b** were affected slightly by changing the solvent from 1,4-dioxane to acetone, while fluorescence maxima showed a large bathochromic shift. Therefore, the Stokes shift value in polar solvents became greater than that in nonpolar solvents. Significant dependence of the fluorescence quantum yield on the solvent polarity was also observed; the Φ value of **2a** was reduced to *ca.* 4 % with an increasing polarity from 1,4-dioxane to acetone. Similar spectral changes are generally observed for most of fluorescent dyes with dipole moments in the excited state that are larger than those in the ground state.^[8]

< Please insert Table 1 here >

On the other hand, the fluorophores **2c–2e** exhibited two absorption bands at around 420 nm and 350 nm, and a weak fluorescence band at around 490 nm in 1,4-dioxane (Figure 1b). As with the fluorophores **2a** and **2b**, the dependence of the fluorescence maxima on the solvent polarity was observed; however, its dependence was smaller for **2d** and **2e**. With

increasing polarity of the solvent, Φ value of **2c**, **2d**, and **2e** was also reduced. Interestingly, in acetic acid, the fluorophores **2c–2e** exhibited a medium fluorescence intensity ($\Phi = 0.18–0.20$); however, the fluorophores **2a** and **2b** exhibited a low fluorescence intensity ($\Phi = 0.03–0.04$). The absorption bands of **2c–2e** appeared at around 385 nm, which was blue-shifted by *ca.* 30 nm, and the absorption band at around 350 nm became broader compared with that observed in 1,4-dioxane. The corresponding fluorescence maxima were observed at around 500–520 nm, which were red-shifted by 10–30 nm compared with those in 1,4-dioxane.

< Please insert Figure 1 here >

Particularly interesting are the photophysical properties of **2d** in a mixture solvent of an organic solvent and water. The absorption and fluorescence spectra undergo only small changes on changing from 1,4-dioxane to 1,4-dioxane containing 15 vol% water (Figure 2). Upon increasing the water content from 30 vol% to 45 vol%, the absorption and fluorescence spectra exhibited significant changes: the absorption band at around 410 nm was blue-shifted by 20 nm, and the absorption band at around 340 nm became broad band. In the corresponding fluorescence spectra, the fluorescence band at around 490 nm was slightly blue-shifted with the enhancement in its intensity. In 1,4-dioxane containing 45 vol% water, the fluorescence quantum yield of 0.18 was achieved (Table 2). In acetone or ethanol containing 45 vol% water, the similar absorption and fluorescence spectral changes were observed. However, such absorption and fluorescence properties were not observed in the case of **2a**, **2b**, **2c**, and **2e**. With increasing concentrations of water in 1,4-dioxane, the fluorescence intensities of **2a** and **2b** decreased dramatically and the fluorescent maxima underwent a red shift, due to the increase in the polarity of the solution. On the other hand, there are the fluorescent dyes such as the 1,8-naphthalimide derivatives, whose fluorescence efficiency in water is higher than that in organic solvents because of a change in the microscopic polarity around the fluorophore.^[9] Although the compounds **2c–2e** belong to the same category because the all of them have a diethylamino group as a proton acceptor and similar dipole moments, only **2d** with a carboxyl group as a proton donor exhibits the enhancements in the fluorescence intensity with increasing concentrations of water in 1,4-dioxane. Therefore, the enhancement of fluorescence intensity of **2d** would not be attributable to a change in the microscopic polarity around the fluorophore with increasing concentrations of water in 1,4-dioxane.

< Please insert Figure 3 on the same page with Figure 2 >

< Please insert Table 2 here >

On the bases of the above results, we considered that the absorption and fluorescence properties of **2d** in a mixture of organic solvent and water were associated with the protonation of the diethylamino group by intramolecular proton transfer from the carboxyl group, because addition of water to organic solvents promoted the dissociation of carboxyl proton of **2d**. Consequently, it was concluded that the fluorescent dye is an example of photo-induced electron transfer (PET),^[1] which in this case takes place from the diethylamino group to the naphtho[1,2-*d*]oxazole fluorophore skeleton, and can not exhibit fluorescent emission. When the diethylamino group was protonated, the structure became the zwitter-ion form, electron transfer was prevented, and a drastic fluorescence enhancement was observed (Figure 3). Thus, the fluorophores **2a** without both the carboxyl and diethylamino groups, **2b** without a diethylamino group, and **2c** and **2e** without a carboxyl group can not function as a fluorescent dye by PET. On the other hand, the fluorescence properties of **2c–2e** in acetic acid

are assumed to be caused by protonation of diethylamino group by intermolecular proton transfer from the acetic acid.

< Please insert Figure 3 here >

In order to investigate its possibility as a pH sensor, the absorption and fluorescence spectra of **2c** were investigated in acidic solutions with a range of concentrations prepared by the addition of acetic acid or trifluoroacetic acid to a 1,4-dioxane solution. When the acid/**2c** ratio is 20, the fluorescence property is weak in the case of acetic acid, but a strong fluorescence band appears at around 490 nm in the case of trifluoroacetic acid. These results demonstrated that the phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type fluorophores are promising for use as a pH sensors.

Conclusions

We have designed and developed a new class of fluorescent dye for sensing water, the phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type fluorophore with both the proton donor and acceptor sites. The photophysical properties were investigated in organic solvents as a function of water content. The fluorophore with both the carboxyl and dialkylamino groups exhibited a weak fluorescent emission in organic solvents because of PET, which takes place from the dialkylamino group to the naphtho[1,2-*d*]oxazole fluorophore skeleton. A dramatic enhancement in the fluorescence was observed with increasing concentrations of water in organic solvents, which is attributable to the suppression of PET by the intramolecular proton transfer of the carboxyl proton to the dialkylamino group. Thus, a new concept for the molecular design of a fluorescent dye for sensing water in organic solvents by PET has been demonstrated. Further studies on the fluorescent dyes with high water solubility are now in progress, and will be reported in the next paper.

Experimental Section

IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer for samples in KBr pellet form. Absorption spectra were observed with a JASCO U-best30 spectrophotometer. For the measurement of the emission spectra, a JASCO FP-777 spectrometer was used. In Table 1, the fluorescence quantum yields (Φ) were determined using 9,10-diphenylanthracene ($\Phi = 0.67$, $\lambda_{ex} = 357$ nm) in benzene as the standard. In Table 2, the fluorescence quantum yields (Φ) were determined by using a calibrated integrating sphere system ($\lambda_{ex} = 325$ nm). Elemental analyses were recorded on a Perkin Elmer 2400 II CHN analyzer. ¹H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral).

Synthesis of 4-(4-butyl-phenylamino)-[1,2]naphthoquinone (1a): A solution of 1,2-naphthoquinone-4-sulfonic acid sodium salt (25 g, 96.1 mmol), *p*-butylaniline (14.3 g, 96.1 mmol), sodium acetate (7.88 g, 96.1 mmol), and NiCl₂ (12.45 g, 96.1 mmol) in acetic acid (150 ml) was stirred at room temperature for 5 days. The solution was neutralized with aq. Na₂CO₃ and the resulting precipitate was filtered. The resulting precipitate was extracted with CH₂Cl₂. The organic extract was washed with water. The CH₂Cl₂ extract was evaporated and the residue was chromatographed on silica gel (CH₂Cl₂: ethyl acetate = 5 : 1 as eluent) to give **1a** (8.91 g, yield 31 %) as a red powder: m.p. 234–236 °C; ¹H NMR (400 MHz, [D₆]acetone, TMS): δ = 0.95 (t, 3H), 1.34–1.44 (m, 2H), 1.61–1.68 (m, 2H), 2.67 (t, 2H), 6.14 (s, 1H), 7.14 (br, 2H), 7.33 (d, *J* = 8.28 Hz, 2H), 7.73–

7.77 (m, 1H), 7.84-7.88 (m, 1H), 8.02 (dd, $J = 1.44$ and 7.89 Hz, 1H), 8.34 (br, 1H); IR (KBr): $\tilde{\nu} = 3222, 1606, 1579$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{19}\text{NO}_2$ (305.37): C 78.66, H 6.27, N, 4.59; found: C 78.94, H 6.25, N 4.56.

Synthesis of 4-[(4-diethylamino)phenylamino]-[1,2]naphthoquinone (1b): To a solution of 1,2-naphthoquinone-4-sulfonic acid sodium salt (9.48 g, 36.4 mmol), sodium acetate (9.91 g, 72.8 mmol), and NiCl_2 (4.72 g, 36.4 mmol) in acetic acid (25 ml) was added dropwise a solution of N,N -diethyl-1,4-phenylenediamine dihydrochloride (8.64 g, 36.4 mmol) in acetic acid (25 ml) with stirring at room temperature. After further stirring for 3 h, the reaction mixture was poured into water. The solution was neutralized with aq. Na_2CO_3 and the resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2 : ethyl acetate = 3 : 1 as eluent) to give **1b** (9.10 g, yield 78 %) as a blue solid: 229-231 °C (decomposition); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 1.11$ (t, 6H), 3.42 (q, 4H), 5.63 (s, 1H), 6.75 (d, $J = 8.05$ Hz, 2H), 7.14 (d, $J = 8.05$ Hz, 2H), 7.70-7.72 (m, 1H), 7.83-7.85 (m, 1H), 8.02 (d, 1H), 8.29 (d, 1H), 9.77 (s, 1H); IR (KBr): $\tilde{\nu} = 3219, 1593, 1568$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$ (320.39): C 74.98, H 6.29, N, 8.74; found: C 74.77, H 6.11, N 8.87.

Synthesis of 4-[5-(4-butyl-phenylamino)-naphtho[1,2-d]oxazol-2-yl]-benzonitrile (2a): A solution of the compound **1a** (2.00 g, 6.55 mmol), p -cyanobenzaldehyde (0.86 g, 6.55 mmol), and ammonium acetate (10.1 g, 0.13 mol) in acetic acid (150 ml) was stirred for 2 h at 90 °C. After concentrating under reduced pressure, the resulting residue was neutralized with aq. Na_2CO_3 and the product was extracted with CH_2Cl_2 . The organic extract was washed with water and evaporated. Then the residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **2a** (1.80 g, yield 66 %) as a yellow powder: m.p. 189-191 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$, TMS): $\delta = 0.96$ (t, 3H), 1.36-1.43 (m, 2H), 1.60-1.68 (m, 2H), 2.63 (t, 2H), 7.21-7.27 (m, 4H), 7.53 (s, 1H), 7.59-7.64 (m, 1H), 7.74-7.79 (m, 1H), 7.83 (br, -NH), 8.01 (d, $J = 8.8$ Hz, 1H), 8.40-8.44 (m, 3H), 8.52-8.54 (m, 1H); IR (KBr): $\tilde{\nu} = 3377, 2230$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}$ (417.50): C 80.55, H 5.55, N, 10.06; found: C 80.52, H 5.53, N 10.03.

Synthesis of 4-[5-(4-butyl-phenylamino)-naphtho[1,2-d]oxazol-2-yl]-benzoic acid (2b): A solution of the compound **1a** (3.00 g, 9.83 mmol), p -carboxybenzaldehyde (1.48 g, 9.83 mmol), and ammonium acetate (15.16 g, 0.20 mol) in acetic acid (250 ml) was stirred for 2 h at 90 °C. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 , and washed with water. The organic extract was evaporated. Then the residue was chromatographed on silica gel (CH_2Cl_2 : ethyl acetate = 3 : 1 as eluent) to give **2b** (0.62 g, yield 14 %) as a yellow powder: m.p. 251-252 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$, TMS): $\delta = 0.96$ (t, 3H), 1.36-1.43 (m, 2H), 1.60-1.68 (m, 2H), 2.62 (t, 2H), 7.21-7.25 (m, 4H), 7.56 (s, 1H), 7.59-7.63 (m, 1H), 7.75-7.79 (m, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 8.37-8.41 (m, 3H), 8.54-8.56 (m, 1H); IR (KBr): $\tilde{\nu} = 3387, 1686$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_3$ (436.50): C 77.04, H 5.54, N, 6.42; found: C 77.34, H 5.54, N 6.37.

Synthesis of 4-[5-(4-diethylamino-phenylamino)-naphtho[1,2-d]oxazol-2-yl]-benzonitrile (2c): To a solution of the compound **1b** (5.00 g, 15.6 mmol) and ammonium acetate (24.05 g, 0.31 mol) in acetic acid (170 ml) was added dropwise a solution of p -cyanobenzaldehyde (2.05 g, 15.6 mmol) in acetic acid (100 ml) with stirring at 90 °C. After further stirring for 3 h, the reaction mixture was neutralized with aq. Na_2CO_3 and the product was extracted with CH_2Cl_2 . The organic extract was washed with water and evaporated. Then the residue was chromatographed on silica gel (CH_2Cl_2 : ethyl acetate = 10 : 1 as eluent) to give **2c** (4.86 g, yield 72 %) as a yellow powder: m.p. 205-206 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 1.11$ (t, 6H), 3.35 (q, 4H), 6.76 (d, $J = 9.03$ Hz, 2H), 6.99 (s, 1H), 7.16 (d, 2H), 7.76 (t, 1H), 7.74 (t, 1H), 8.02 (d, 2H), 8.26-8.28 (m, 2H),

8.31 (s, 1H), 8.39 (d, $J = 8.29$ Hz, 1H), 8.48 (d, $J = 8.29$ Hz, 1H); IR (KBr): $\tilde{\nu} = 3404, 2224$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{24}\text{N}_4\text{O}$ (432.52): C 77.75, H 5.59, N, 12.95; found: C 77.74, H 5.59, N 12.98.

Synthesis of 4-[5-(4-diethylamino-phenylamino)-naphtho[1,2-d]oxazol-2-yl]-benzoic acid (2d): To a solution of the compound **1b** (4.00 g, 12.5 mmol) and ammonium acetate (15.4 g, 0.20 mol) in acetic acid (150 ml) was added dropwise a solution of p -carboxybenzaldehyde (1.88 g, 12.5 mmol) in acetic acid (100 ml) with stirring at 90 °C for 8 h. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 , and washed with water. The organic extract was evaporated. Then the residue was chromatographed on silica gel (ethyl acetate as eluent) to give **2d** (1.80 g, yield 32 %) as a red powder: 268-271 °C (decomposition); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 1.11$ (t, 6H), 3.33-3.36 (m, 4H), 6.57 (d, $J = 9.00$ Hz, 2H), 7.01 (s, 1H), 7.15 (d, $J = 9.00$ Hz, 2H), 7.58 (t, 1H), 7.74 (t, 1H), 8.10 (d, $J = 8.54$ Hz, 2H), 8.22 (s, 1H), 8.28 (d, $J = 8.54$ Hz, 2H), 8.39 (d, $J = 7.56$ Hz, 1H); IR (KBr): $\tilde{\nu} = 3410, 1589$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{O}_3$ (451.52): C 74.48, H 5.58, N, 9.31; found: C 74.44, H 5.55, N 9.24.

Synthesis of 4-[5-(4-diethylamino-phenylamino)-naphtho[1,2-d]oxazol-2-yl]-benzoic acid butyl ether (2e): A solution of the compound **1b** (1.00 g, 3.12 mmol), 4-formyl-benzoic acid butyl ester (0.64 g, 3.12 mmol), and ammonium acetate (4.8 g, 0.06 mol) in acetic acid (100 ml) was stirred for 5 h at 90 °C. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 , and washed with water. The organic extract was evaporated. Then the residue was chromatographed on silica gel (CH_2Cl_2 : ethyl acetate = 10 : 1 as eluent) to give **2e** (0.59 g, yield 37 %) as a red powder: m.p. 170-172 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$, TMS): $\delta = 1.00$ (t, 3H), 1.11 (t, 6H), 1.47-1.57 (m, 2H), 1.76-1.82 (m, 2H), 3.40-3.46 (m, 4H), 4.36 (t, 2H), 6.82 (d, $J = 9.04$ Hz, 2H), 7.12 (s, 1H), 7.21 (d, $J = 9.04$ Hz, 2H), 7.55-7.61 (m, 2H), 7.72-7.76 (m, 1H), 8.19 (d, $J = 8.76$ Hz, 2H), 8.33 (d, $J = 8.8$ Hz, 2H), 8.44 (d, $J = 8.52$ Hz, 1H), 8.50 (d, $J = 9.04$ Hz, 1H); IR (KBr): $\tilde{\nu} = 3359, 1592$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{33}\text{N}_3\text{O}_3$ (507.62): C 75.71, H 6.55, N, 8.28; found: C 75.43, H 6.49, N 8.17.

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Layout 2:

A new class of fluorescent dye for sensing water in organic solvents by photo-induced electron transfer (PET), which based on phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type fluorophore with both proton binding and proton donating sites, has been designed and developed.

Fluorescent Sensor for Water

Yousuke Ooyama,* Haruka Egawa,
and Katsuhira Yoshida* Page
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A New Class of Fluorescent Dye for Sensing Water in Organic Solvents by using Photo-induced Electron Transfer: Phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type Fluorophore with both Proton Binding and Proton Donating Sites

Keywords: Photo-induced electron transfer / Fluorescence / Zwitter-ion form / Fluorescent sensor / Water

Table 1. Spectroscopic properties of **2a–2e** in solution

	Solvent	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}^{[a]}$	$\lambda_{\text{max}}^{\text{fl}}/\text{nm}^{[b]}$	$\Phi^{[c]}$
		$[\epsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}]$		
2a	benzene	406 (24300), 335 (9000)	477	0.86
	1,4-dioxane	407 (24200), 335 (8700)	495	0.92
	dichloromethane	408 (25400), 336 (8500)	517	0.83
	acetone	410 (26900), 335 (9200)	545	0.04
	ethanol	416 (24000), 334 (8500)	542	0.03
	acetic acid	408 (25200), 334 (9200)	524	0.04
2b	1,4-dioxane	400 (20700), 336 (8600)	491	0.95
	acetone	401 (26100), 332 (9900)	534	0.66
	acetic acid	406 (25000), 335 (9800)	535	0.03
2c	benzene	420 (31700), 350 (18600)	485	0.001
	1,4-dioxane	420 (25300), 350 (15500)	483	0.001
	dichloromethane	420 (23700), 349 (14200)	498	0.002
	acetone	420 (24200), 350 (15000)	527	0.001
	ethanol	431 (25300), 350 (15300)	538	0.001
	acetic acid	387 (23300), 311 (11300)	504	0.18
2d	1,4-dioxane	413 (23800), 338 (15400)	490	0.001
	acetone	413 (21100), 338 (13600)	508	0.0003
	ethanol	400 (20700), 328 (13400)	493	0.00006
	acetic acid	385 (24500), 312 (12800)	520	0.20
2e	1,4-dioxane	415 (25800), 337 (15800)	500	0.002
	acetone	417 (26000), 339 (16100)	526	0.00004
	acetic acid	384 (24000), 312 (10000)	509	0.20

[a] 2.5×10^{-5} M. [b] 2.5×10^{-6} M. [c] The Φ value were determined using using 9,10-diphenylanthracene ($\Phi = 0.67$, $\lambda_{\text{ex}} = 357$ nm) in benzene as the standard.

Table 2. Spectroscopic properties of **2a–2e** in solvent-water

	Solvent	$\lambda_{\max}^{\text{abs}}/\text{nm}^{[\text{a}]}$ [$\epsilon_{\max}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$]	$\lambda_{\max}^{\text{fl}}/\text{nm}^{[\text{b}]}$	$\Phi^{[\text{c}]}$
2a	1,4-dioxane (water free)	407 (24200), 335 (8700)	495	0.92
	1,4-dioxane-water (45 vol%)	414 (21900), 334 (8300)	548	0.02
2b	1,4-dioxane (water free)	400 (20700), 336 (8600)	491	0.95
	1,4-dioxane-water (45 vol%)	396 (22700), 335 (10800)	508	0.04
2c	1,4-dioxane (water free)	420 (25300), 350 (15500)	483	— ^[d]
	1,4-dioxane-water (45 vol%)	426 (21200), 340 (14000)	534	0.02
2d	1,4-dioxane (water free)	413 (23800), 338 (15400)	490	— ^[d]
	1,4-dioxane-water (15 vol%)	413 (23300), 338 (15400)	490	— ^[d]
	1,4-dioxane-water (30 vol%)	411 (21900), 338 (15600)	490	0.02
	1,4-dioxane-water (40 vol%)	404 (20100), 338 (15800)	487	0.03
	1,4-dioxane-water (45 vol%)	392 (19800), 338 (15900)	486	0.18
	acetone (water free)	413 (21100), 338 (13600)	508	— ^[d]
	acetone-water (45 vol%)	396 (—) ^[e] , 337 (—) ^[e]	495	0.08
	ethanol (water free)	400 (20700), 328 (13400)	493	— ^[d]
	ethanol-water (45 vol%)	390 (—) ^[e] , 325 (—) ^[e]	495	0.17
2e	1,4-dioxane (water free)	415 (25800), 337 (15800)	500	— ^[d]
	1,4-dioxane-water (45 vol%)	419 (—) ^[e] , 338 (—) ^[e]	541	— ^[d]

[a] 2.5×10^{-5} M. [b] 2.5×10^{-6} M. [c] The Φ values were determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 325$ nm). [d] too weak ($\Phi \ll 0.01$). [e] poor solubility.

Figure and Scheme captions

Scheme 1. Syntheses of the fluorophores **2a–2e**.

Figure 1. Absorption and fluorescence spectra of a) **2a** (black), **2b** (red), b) **2c** (blue), **2d** (green), and **2e** (orange) in 1,4-dioxane (dotted line) and acetic acid (solid line).

Figure 2. a) Absorption and b) fluorescence spectra of **2d** in water/1,4-dioxane mixture with different volume fractions of water ($[\mathbf{2d}] = 2.5 \times 10^{-5} \text{ M}$), respectively.

Figure 3. Proposed mechanism for fluorescent water–sensor **2d** by PET.

Scheme 1

Figure 1

Figure 2

Figure 3