DOI: 10.1002/ejoc.200800606

A New Class of Fluorescent Dye for Sensing Water in Organic Solvents by Photo-Induced Electron Transfer – A (Phenylamino)naphtho[1,2-*d*]oxazol-2-yl-Type Fluorophore with both Proton-Binding and Proton-Donating Sites

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Keywords: Photo-induced electron transfer / Fluorescence / Water / Sensors

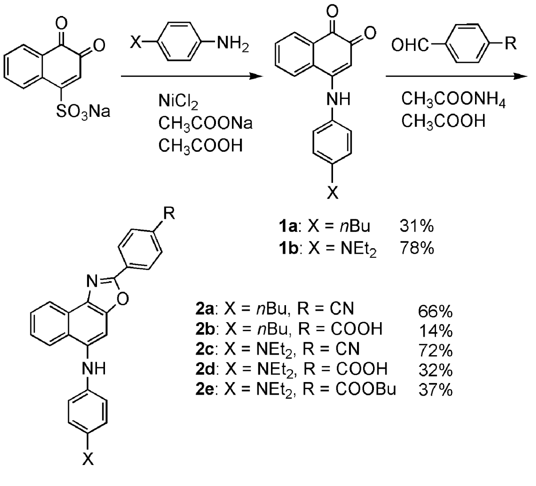
A new class of fluorescent dye for sensing water in organic solvents by photo-induced electron transfer (PET), based on a (phenylamino)naphtho[1,2-*d*]oxazol-2-yl-type fluorophore with both proton binding and proton donating sites, has been designed developed. The fluorophore exhibits a weak emission in organic solvents but a drastic enhancement in the fluorescence intensity is observed with increasing water content in organic solvents.

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 devises 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 that exhibit 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, the exact determination of water content in a solution can be difficult with these fluorescent dyes, because the fluorescence intensity is strongly affected by the polarity of the solution. Herein, 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 a substituted (phenylamino)naphtho[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 (phenylamino)naphtho[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-sulfonate with the corresponding phenylamine in acetic acid in the presence of nickel(II) chloride. Next, fluorophores **2a**–**2e** were synthesized in 14–72% yields by the reaction of *p*-substituted benzaldehydes with the 4-aminated-1,2-naphthoquinones.



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

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

Entry	Compound	Solvent	$\lambda_{max}{}^{abs}$ [nm][a] (ε_{max}/dm^3 mol^{-1} cm^{-1})	$\lambda_{max}{}^{fl}$ [nm][b]	Φ[c]
1	**2a**	benzene	406 (24300), 335 (9000)	477	0.86
2		1,4-dioxane	407 (24200), 335 (8700)	495	0.92
3		dichloromethane	408 (25400), 336 (8500)	517	0.83
4		acetone	410 (26900), 335 (9200)	545	0.04
5		ethanol	416 (24000), 334 (8500)	542	0.03
6		acetic acid	408 (25200), 334 (9200)	524	0.04
7	**2b**	1,4-dioxane	400 (20700), 336 (8600)	491	0.95
8		acetone	401 (26100), 332 (9900)	534	0.66
9		acetic acid	406 (25000), 335 (9800)	535	0.03
10	**2c**	benzene	420 (31700), 350 (18600)	485	0.001
11		1,4-dioxane	420 (25300), 350 (15500)	483	0.001
12		dichloromethane	420 (23700), 349 (14200)	498	0.002
13		acetone	420 (24200), 350 (15000)	527	0.001
14		ethanol	431 (25300), 350 (15300)	538	0.001
15		acetic acid	387 (23300), 311 (11300)	504	0.18
16	**2d**	1,4-dioxane	413 (23800), 338 (15400)	490	0.001
17		acetone	413 (21100), 338 (13600)	508	0.0003
18		ethanol	400 (20700), 328 (13400)	493	0.00006
19		acetic acid	385 (24500), 312 (12800)	520	0.20
20	**2e**	1,4-dioxane	415 (25800), 337 (15800)	500	0.002
21		acetone	417 (26000), 339 (16100)	526	0.00004
22		acetic acid	384 (24000), 312 (10000)	509	0.20

[a] $c = 2.5\times10^{-5}$ M. [b] $c = 2.5\times10^{-6}$ M. [c] The Φ value was determined with 9,10-diphenylanthracene ($\Phi = 0.67$, $\lambda_{ex} = 357$ nm) in benzene as the standard.

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

On the other hand, 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 1, b). As with fluorophores **2a** and **2b**, a dependence of the fluorescence maxima on the solvent polarity was observed. However, the dependence was smaller for **2d** and **2e**. With increasing polarity of the solvent, the Φ value of **2c**, **2d**, and **2e** were also reduced. Interestingly, in acetic acid, fluorophores **2c**–**2e** exhibited a medium fluorescence intensity (Φ = 0.18–0.20), while fluorophores **2a** and **2b** exhibited a low fluorescence intensity (Φ = 0.03–0.04). The absorption bands of **2c**–**2e** appeared at around 385 nm, which was blue-shifted by about 30 nm, and the absorption bands at around 350 nm became broader than those 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.

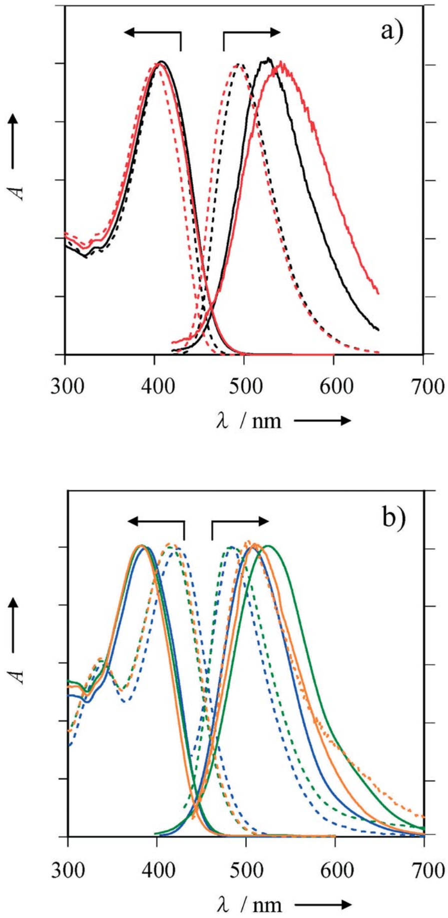

Figure 1. Absorption and fluorescence spectra in 1,4-dioxane (dotted line) and acetic acid (solid line): a) **2a** (black), **2b** (red); b) **2c** (blue), **2d** (green), and **2e** (orange).

The photophysical properties of **2d** in a mixture of organic solvent and water were particularly interesting. The absorption and fluorescence spectra underwent 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 broadened. 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, a fluorescence quantum yield of 0.18 was achieved (Table 2). In acetone or ethanol containing 45 vol.-% water, similar absorption and fluorescence 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 fluorescence 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 they all contain a diethylamino group as a proton acceptor and similar dipole moments, only **2d**, with a carboxyl group as a proton donor, exhibited 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.

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 the addition of water to organic solvents promoted the dissociation of the carboxyl proton of **2d**. Consequently, we concluded that

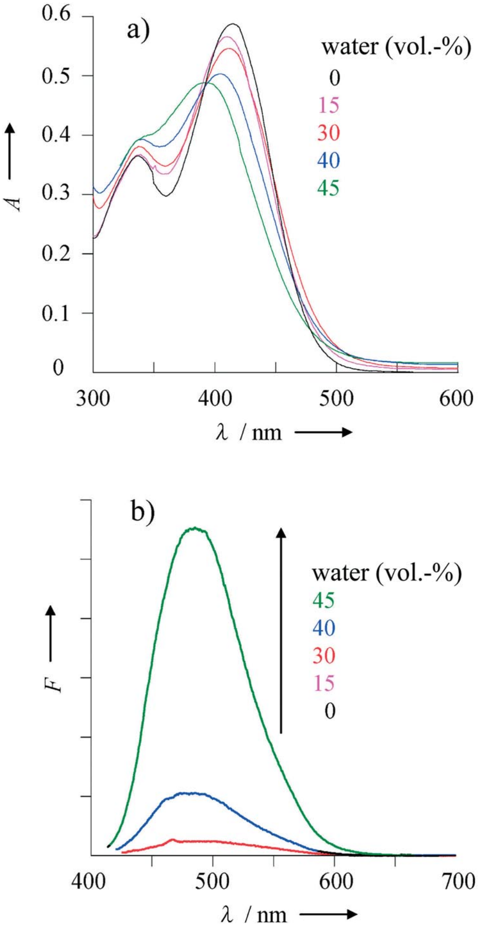

Figure 2. a) Absorption and b) fluorescence spectra of **2d** in water/1,4-dioxane with different volume fractions of water ([**2d**] = 2.5×10^{-5} M).

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

Entry	Compound	Solvent	λ_{max}^{abs} [nm][a] (ε_{max}/dm^3 mol^{-1} cm^{-1})	λ_{max}^{fl} [nm][b]	Φ[c]
1	**2a**	1,4-dioxane (water-free)	407 (24200), 335 (8700)	495	0.92
2		1,4-dioxane/water (45 vol.-%)	414 (21900), 334 (8300)	548	0.02
3	**2b**	1,4-dioxane (water-free)	400 (20700), 336 (8600)	491	0.95
4		1,4-dioxane/water (45 vol.-%)	396 (22700), 335 (10800)	508	0.04
5	**2c**	1,4-dioxane (water-free)	420 (25300), 350 (15500)	483	–[d]
6		1,4-dioxane/water (45 vol.-%)	426 (21200), 340 (14000)	534	0.02
7	**2d**	1,4-dioxane (water-free)	413 (23800), 338 (15400)	490	–[d]
8		1,4-dioxane/water (15 vol.-%)	413 (23300), 338 (15400)	490	–[d]
9		1,4-dioxane/water (30 vol.-%)	411 (21900), 338 (15600)	490	0.02
10		1,4-dioxane/water (40 vol.-%)	404 (20100), 338 (15800)	487	0.03
11		1,4-dioxane/water (45 vol.-%)	392 (19800), 338 (15900)	486	0.18
12		acetone (water-free)	413 (21100), 338 (13600)	508	–[d]
13		acetone/water (45 vol.-%)	396 (–)[e], 337 (–)[e]	495	0.08
14		ethanol (water-free)	400 (20700), 328 (13400)	493	–[d]
15		ethanol/water (45 vol.-%)	390 (–)[e], 325 (–)[e]	495	0.17
16	**2e**	1,4-dioxane (water-free)	415 (25800), 337 (15800)	500	–[d]
17		1,4-dioxane/water (45 vol.-%)	419 (–)[e], 338 (–)[e]	541	–[d]

[a] $c = 2.5\times10^{-5}$ M. [b] $c = 2.5\times10^{-6}$ M. [c] The Φ values were determined with a calibrated integrating sphere system (λ_{ex} = 325 nm). [d] Too weak ($\Phi \leq\leq 0.01$) to be measured. [e] Poor solubility.

this fluorescent dye exhibits 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 zwitterionic form, electron transfer was prevented, and a drastic fluorescence enhancement was observed (Figure 3). Thus, fluorophores **2a** (without both the carboxyl and diethylamino groups), **2b** (without a diethylamino group), and **2c** and **2e** (without a carboxyl group) cannot function as fluorescent dye by PET. Instead, the fluorescence properties of **2c**–**2e** in acetic acid are assumed to be caused by protonation of the diethylamino group by acetic acid.

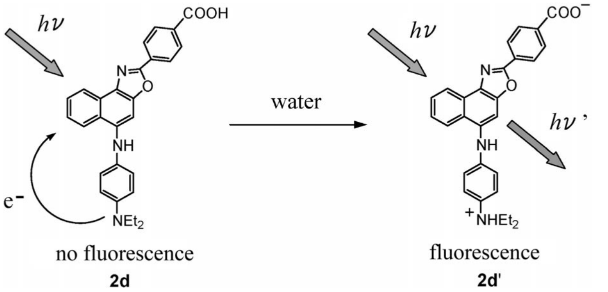

Figure 3. Proposed mechanism for the fluorescent water-sensor **2d** by PET.

In order to investigate its possibility as a pH sensor, the absorption and fluorescence spectra of **2c** were investigated in solutions of varying acidity, prepared by the addition of acetic acid or trifluoroacetic acid to a 1,4-dioxane solution. When the acid/**2c** ratio was 20, the fluorescence was weak in acetic acid, but a strong fluorescence band appeared at around 490 nm in trifluoroacetic acid. These results demonstrated that the (phenylamino)naphtho[1,2-*d*]oxazol-2-yl-type fluorophores are promising for use as pH sensors.

Conclusions

We have designed and developed a new class of fluorescent dye for sensing water, a (phenylamino)naphtho[1,2-*d*]-oxazol-2-yl-type fluorophore with both proton donor and acceptor sites. The photophysical properties were investigated in organic solvents as a function of water content. The fluorophore with both a carboxyl and dialkylamino group 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 fluorescent dyes with high water solubility are now in progress and will be reported in the next paper.

Experimental Section

General: IR spectra were recorded with 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 with 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 with a calibrated integrating sphere system ($\lambda_{ex} = 325$ nm). Elemental analyses were recorded with a Perkin–Elmer 2400 II CHN analyzer. ^{1}H NMR spectra were recorded with a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Column chromatography was performed with silica gel (KANTO CHEMICAL, 60 N, spherical, neutral).

4-[(4-Butylphenyl)amino]-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 $NiCl_2$ (12.45 g, 96.1 mmol) in acetic acid (150 mL) was stirred at room temperature for 5 d. The solution was neutralized with aqueous Na_2CO_3, and the resulting precipitate was filtered. The resulting precipitate was extracted with CH_2Cl_2. The organic extract was washed with water. The CH_2Cl_2 extract was concentrated, and the residue was chromatographed on silica gel (CH_2Cl_2/ethyl acetate, 5:1 as the eluent) to give **1a** (8.91 g, 31%) as a red powder; m.p. 234–236 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): $\delta = 0.95$ (t, 3 H), 1.34–1.44 (m, 2 H), 1.61–1.68 (m, 2 H), 2.67 (t, 2 H), 6.14 (s, 1 H), 7.14 (br., 2 H), 7.33 (d, $J = 8.28$ Hz, 2 H), 7.73–7.77 (m, 1 H), 7.84–7.88 (m, 1 H), 8.02 (dd, $J = 1.44$, 7.89 Hz, 1 H), 8.34 (br., 1 H) ppm. IR (KBr): $\tilde{\nu} = 3222$, 1606, 1579 cm^{-1}. $C_{20}H_{19}NO_2$ (305.37): calcd. C 78.66, H 6.27, N 4.59; found C 78.94, H 6.25, N 4.56.

4-{[4-(Diethylamino)phenyl]amino}-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 a solution of *N*,*N*-diethyl-1,4-phenylenediamine dihydrochloride (8.64 g, 36.4 mmol) in acetic acid (25 mL) dropwise with stirring at room temperature. After additional stirring for 3 h, the reaction mixture was poured into water. The solution was neutralized with aqueous 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 the eluent) to give **1b** (9.10 g, 78%) as a blue solid; m.p. 229–231 °C (dec.). ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): $\delta = 1.11$ (t, 6 H), 3.42 (q, 4 H), 5.63 (s, 1 H), 6.75 (d, $J = 8.05$ Hz, 2 H), 7.14 (d, $J = 8.05$ Hz, 2 H), 7.70–7.72 (m, 1 H), 7.83–7.85 (m, 1 H), 8.02 (d, 1 H), 8.29 (d, 1 H), 9.77 (s, 1 H) ppm. IR (KBr): $\tilde{\nu} = 3219$, 1593, 1568 cm^{-1}. $C_{20}H_{20}N_2O_2$ (320.39): calcd. C 74.98, H 6.29, N 8.74; found C 74.77, H 6.11, N 8.87.

4-{5-[(4-Butylphenyl)amino]naphtho[1,2-*d*]oxazol-2-yl}benzonitrile (2a): A solution of 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 the mixture under reduced pressure, the resulting residue was neutralized with aqueous Na_2CO_3, and the product was extracted with CH_2Cl_2. The organic extract was washed with water, and the solvents were evaporated. The residue was then chromatographed on silica gel (CH_2Cl_2 as the eluent) to give **2a** (1.80 g, 66%) as an yellow powder; m.p. 189–191 °C. ^{1}H NMR (400 MHz, [D$_6$]-acetone, TMS): $\delta = 0.96$ (t, 3 H), 1.36–1.43 (m, 2 H), 1.60–1.68 (m, 2 H), 2.63 (t, 2 H), 7.21–7.27 (m, 4 H), 7.53 (s, 1 H), 7.59–7.64 (m, 1 H), 7.74–7.79 (m, 1 H), 7.83 (br., -NH), 8.01 (d, $J = 8.8$ Hz, 1

H), 8.40–8.44 (m, 3 H), 8.52–8.54 (m, 1 H) ppm. IR (KBr): ṽ = 3377, 2230 cm^{-1}. $C_{28}H_{23}N_3O$ (417.50): calcd. C 80.55, H 5.55, N 10.06; found C 80.52, H 5.53, N 10.03.

4-{5-(4-Butylphenyl)amino]naphtho[1,2-*d*]oxazol-2-yl}benzoic Acid (2b): 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) were stirred for 2 h at 90 °C. After concentrating the mixture under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 and washed with water. The organic extract was concentrated. The residue was then chromatographed on silica gel (CH_2Cl_2/ethyl acetate, 3:1 as the eluent) to give **2b** (0.62 g, 14%) as a yellow powder; m.p. 251–252 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 0.96 (t, 3 H), 1.36–1.43 (m, 2 H), 1.60–1.68 (m, 2 H), 2.62 (t, 2 H), 7.21–7.25 (m, 4 H), 7.56 (s, 1 H), 7.59–7.63 (m, 1 H), 7.75–7.79 (m, 1 H), 8.25 (d, J = 8.8 Hz, 1 H), 8.37–8.41 (m, 3 H), 8.54–8.56 (m, 1 H) ppm. IR (KBr): ṽ = 3387, 1686 cm^{-1}. $C_{28}H_{24}N_2O_3$ (436.50): calcd. C 77.04, H 5.54, N 6.42; found C 77.34, H 5.54, N 6.37.

4-{5-[4-(Diethylamino)phenylamino]naphtho[1,2-*d*]oxazol-2-yl}-benzonitrile (2c): To a solution of 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 additional stirring for 3 h, the reaction mixture was neutralized with aqueous Na_2CO_3, and the product was extracted with CH_2Cl_2. The organic extract was washed with water, and the solvents were evaporated. The residue was then chromatographed on silica gel (CH_2Cl_2/ethyl acetate, 10:1 as the eluent) to give **2c** (4.86 g, 72%) as a yellow powder; m.p. 205–206 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 1.11 (t, 6 H), 3.35 (q, 4 H), 6.76 (d, J = 9.03 Hz, 2 H), 6.99 (s, 1 H), 7.16 (d, 2 H), 7.76 (t, 1 H), 7.74 (t, 1 H), 8.02 (d, 2 H), 8.26–8.28 (m, 2 H), 8.31 (s, 1 H), 8.39 (d, J = 8.29 Hz, 1 H), 8.48 (d, J = 8.29 Hz, 1 H) ppm. IR (KBr): ṽ = 3404, 2224 cm^{-1}. $C_{28}H_{24}N_4O$ (432.52): calcd. C 77.75, H 5.59, N 12.95; found C 77.74, H 5.59, N 12.98.

4-{5-[4-(Diethylamino)phenylamino]naphtho[1,2-*d*]oxazol-2-yl}-benzoic Acid (2d): To a solution of 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 4-formylbenzoic acid (1.88 g, 12.5 mmol) in acetic acid (100 mL) with stirring at 90 °C for 8 h. After concentrating the mixture under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 and washed with water. The organic extract was concentrated. The residue was then chromatographed on silica gel (ethyl acetate as the eluent) to give **2d** (1.80 g, 32%) as a red powder; m.p. 268–271 °C (dec.). ^{1}H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 1.11 (t, 6 H), 3.33–3.36 (m, 4 H), 6.57 (d, J = 9.00 Hz, 2 H), 7.01 (s, 1 H), 7.15 (d, J = 9.00 Hz, 2 H), 7.58 (t, 1 H), 7.74 (t, 1 H), 8.10 (d, J = 8.54 Hz, 2 H), 8.22 (s, 1 H), 8.28 (d, J = 8.54 Hz, 2 H), 8.39 (d, J = 7.56 Hz, 1 H) ppm. IR (KBr): ṽ = 3410, 1589 cm^{-1}. $C_{28}H_{25}N_3O_3$ (451.52): calcd. C 74.48, H 5.58, N 9.31; found C 74.44, H 5.55, N 9.24.

Butyl 4-{5-[4-(Diethylamino)phenylamino]naphtho[1,2-*d*]oxazol-2-yl}benzoate (2e): Compound **1b** (1.00 g, 3.12 mmol), butyl 4-formylbenzoate (0.64 g, 3.12 mmol), and ammonium acetate (4.8 g, 0.06 mol) in acetic acid (100 mL) were stirred for 5 h at 90 °C. After concentrating the mixture under reduced pressure, the resulting residue was dissolved in CH_2Cl_2, and washed with water. The organic extract was concentrated. The residue was then chromatographed on silica gel (CH_2Cl_2/ethyl acetate, 10: 1 as the eluent) to give **2e** (0.59 g, 37%) as a red powder; m.p. 170–172 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 1.00 (t, 3 H), 1.11 (t, 6 H), 1.47–1.57 (m, 2 H), 1.76–1.82 (m, 2 H), 3.40–3.46 (m, 4 H), 4.36 (t, 2 H), 6.82 (d, J = 9.04 Hz, 2 H), 7.12 (s, 1 H), 7.21 (d, J = 9.04 Hz, 2 H), 7.55–7.61 (m, 2 H), 7.72–7.76 (m, 1 H), 8.19 (d, J = 8.76 Hz, 2 H), 8.33 (d, J = 8.8 Hz, 2 H), 8.44 (d, J = 8.52 Hz, 1 H), 8.50 (d, J = 9.04 Hz, 1 H) ppm. IR (KBr): ṽ = 3359, 1592 cm^{-1}. $C_{32}H_{33}N_3O_3$ (507.62): calcd. C 75.71, H 6.55, N 8.28; found C 75.43, H 6.49, N 8.17.

Acknowledgments

This work was partially supported by a Grant-in-Aid for Science and Research from the Ministry of Education, Science, Sport and Culture of Japan (Grant 18350100) and by a Special Research Grant for Green Science from Kochi University.

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Received: June 21, 2008