http://dx.doi.org/10.5012/bkcs.2013.34.8.2261

# An off-on Fluorescent Sensor for Detecting a Wide Range of Water Content in Organic Solvents

**Kang-Hyeon Kim, Wan-Jin Lee, Jae Nyoung Kim,† and Hyung Jin Kim***

*School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea*
**E-mail: hyungkim@chonnam.ac.kr*
†*Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea*
*Received March 13, 2013, Accepted May 2, 2013*

This paper describes the synthesis and water sensing properties of a fluorescent photoinduced electron transfer (PET) sensor (**5**) with an extended operating sensing range. The 1,8-naphthalimide derivative (**5**) attached with a piperazine group and a carboxylic group was synthesized and applied as a fluorescent water sensor in water-miscible organic solvents. The fluorescence intensity of the dye **5** increased with increasing water content up to 80% (v/v) and the fluorescence intensities were enhanced 45-, 67- and 122-fold in aqueous EtOH, DMF and DMSO solutions, respectively. In aqueous acetone solution, the enhancement of the fluorescence intensities was somewhat lower (30-fold) but the response range was wider (0-90%, v/v).

**Key Words :** 1,8-Naphthalimide, Water sensor, Fluorescent sensor, Photoinduced electron transfer, PET

## Introduction

The control and measurement of water content are of great importance in laboratory chemistry and industrial applications because water is regarded as the most common impurity in organic solvents that affects production in various industries such as fine chemicals, food, textile and electronics.

The most popular method for the quantitative measurement of water in solvents is Karl Fisher titration[1] and gas chromatography.[2] These methods, however, have the disadvantage of requiring time-consuming sample preparation, skilled personnel and special equipment.

In recent years, fluorescence chemosensors for the detection of water based on the fluorescence intensity of a certain fluorophore have received considerable interest due to their simplicity of operation, high sensitivity and broad selection of fluorescent dyes. These fluorescence water sensors can be generally categorized into two types according to switching mode: 'on-off'[3] and 'off-on' sensors.[4] In the former case, the fluorescence intensity decreases with increasing water content in organic solvents. This type of sensor, however, is not suitable for measuring a wide concentration range of water, or for the exact determination of high water content in a solution, because the fluorescence is strongly affected by the polarity of the solution and quenched even at low water content. In the latter case, the fluorescence is enhanced with increasing water content in organic solvents, leading to the precise determination of water content. With respect to such sensors, Ooyama and coworkers[4a,4c] reported several excellent works, although the detection level of water content was limited within the range of 40-60% depending on the solvent used for measurement.

1,8-Naphthalimide derivatives have been well utilized as fluorescent chemosensors for $H^+$,[5] transition metals[6] and neutral molecules[7] because of their strong absorption and emission intensities in the visible spectral range, large Stokes' shift and the convenient step-wise introduction of appropriate functional groups leading to a number of derivatives with high sensitivity. In addition, they exhibit good fluorescence 'off-on' switching mode based on photoinduced electron transfer (PET) upon encountering a target analyte.[8]

For the development of a fluorescence water sensor possessing both high sensitivity and a wide response range for water content in organic solvents, we designed a new fluorescence sensor based on 1,8-naphthalimide as a fluorophore, which is incorporated with both a piperazine group and a carboxylic group as proton-binding and proton-donating sites. Herein, we describe its synthesis and water sensing properties in various water-miscible organic solvents.

## Experimental

**Reagents and Instrumentation.** All reagents were purchased from Aldrich Chemical Co. and used without further purification. Solvents were purchased and dried by the standard method.

The melting points were determined with a MEL-TEMP II capillary melting point apparatus and are uncorrected. The $^1$H and $^{13}$C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker ARX-R300 spectrometer and were obtained in $CDCl_3$. The mass spectral data were obtained on a Jeol JMS-700 high resolution mass spectrometer (FAB-MS). Absorption spectra were observed with a JASCO V-550 UV-VIS spectrophotometer and the fluorescence measurements were performed with a Hitachi F-4500 fluorescence spectrophotometer.

**6-Bromo-2-(5-hydroxypentyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (2).** A mixture of 4-bromo-1,8-naphthalic anhydride (1.50 g, 5.41 mmol) and 1-aminopentanol (670

mg, 6.49 mmol) in EtOH (30 mL) was refluxed for 9 h and then cooled to 25 °C. The pale yellow solid was filtered and washed with cold EtOH to afford naphthalimide **2** (1.49 g, 76%); mp 115-116 °C. $^1$H NMR δ 8.65 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.56 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.39 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.84 (t, *J* = 7.4, 1.1 Hz, 1H), 4.17 (t, *J* = 7.4 Hz, 2H), 3.66 (d, *J* = 3.4 Hz, 2H), 1.76 (m, 2H), 1.65 (m, 2H), 1.50 (m, 2H), 1.40 (s, 1H). HRMS (FAB) for $C_{17}H_{16}NO_3$: calcd 361.0314 $(M)^+$, found 361.0312 $(M)^+$.

**2-(5-Hydroxypentyl)-6-(piperazin-1-yl)-1*H*-benzo[*de*]-isoquinoline-1,3(2*H*)-dione (3).** A mixture of the naphthalimide **2** (1.38 g, 3.81 mmol) and piperazine (1.31 g, 15.24 mmol) dissolved in 2-methoxyethanol (30 mL) was refluxed for 2.5 h and then concentrated under reduced pressure. The residual solid was recrystallized from EtOH to afford **3** (994 mg, 71%) as a yellow solid; mg 195-195.5 °C. $^1$H NMR δ 8.56 (dd, *J* = 7.3, 1.0 Hz, 1H), 8.50 (d, *J* = 8.1 Hz, 1H), 8.41 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.68 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 4.17 (t, *J* = 7.4 Hz, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.21 (dd, *J* = 12.4, 5.7 Hz, 8H), 1.82-1.70 (m, 2H), 1.67-1.61 (m, 4H), 1.54-1.46 (m, 2H); $^{13}$C NMR δ 164.6, 164.1, 156.5, 132.6, 131.1, 130.3, 131.0, 126.3, 125.6, 123.4, 116.8, 115.0, 62.8, 54.5, 46.3, 40.1, 32.5, 27.9, 23.3, 2.8. HRMS (FAB) for $C_{21}H_{25}N_3O_3$: calcd 368.1974 $(M+H)^+$, found 368.1972 $(M+H)^+$.

**Methyl 5-(4-(2-(5-Hydroxypentyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-yl)piperazin-1-yl)pentanoate (4).** A mixture of compound **3** (800 mg, 2.16 mmol), 5-bromopentanoate (465 mg, 2.38 mmol) and $K_2CO_3$ (299 mg, 2.16 mmol) in acetone (15 mL) was refluxed for 3 h. After concentrating the mixture under reduced pressure, the resulting residue was dissolved in $CHCl_3$ and washed with water. The organic layer was dried ($MgSO_4$) and concentrated to give a crude product, which was purified by column chromatography ($SiO_2$) eluting with a mixture of $CHCl_3$/MeOH (5:1) to afford the ester **4** (797 mg, 76%) as a yellow solid; mp 108-109.5 °C. $^1$H NMR δ 8.56 (d, *J* = 7.3 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 8.39 (d, *J* = 8.4Hz, 1H), 7.67 (dd, *J* = 8.4, 7.3 Hz, 1H) 7.20 (d, *J* = 8.1 Hz, 1H), 4.17 (t, *J* = 7.17 Hz, 2H), 3.75 (s, 3H), 3.68-3.62 (m, 2H), 3.30 (d, *J* = 3.84 Hz, 4H), 2.76 (br s, 4H), 2.50 (t, *J* = 7.08 Hz, 2H), 2.38 (t, *J* = 7.02 Hz, 2H), 1.78-1.65 (m, 8H), 1.63-1.48 (m, 2H). $^{13}$C NMR δ 173.9, 164.4, 163.9, 155.9, 132.5, 130.9, 130.2, 129.8, 126.1, 125.5, 123.2, 116.6, 114.8, 62.6, 58.0, 53.2, 53.0, 51.4, 40.0, 33.8, 32.4, 27.8, 26.2, 23.2, 22.8. HRMS (FAB) for $C_{27}H_{35}N_3O_5$: calcd 482.2655 $(M+H)^+$, found 482.2656 $(M+H)^+$.

**5-(4-(2-(5-Hydroxypentyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-yl)piperazin-1-yl)pentanoic acid (5).** To a stirred solution of the ester **4** (695 mg, 1.44 mmol) in MeOH (5 mL) was added a solution of NaOH (288 mg, 7.21 mmol) in water (3 mL). After further stirring for 4 h at 25 °C, the reaction mixture was neutralized with 0.1 N HCl and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$) eluting with a mixture of $CHCl_3$/MeOH (2:1) to afford acid **5** (631 mg, 93%) as a yellow solid; mp 170-171 °C. $^1$H NMR δ 8.58 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.36 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.70 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 3.37 (s, 4H), 3.01 (s, 4H), 2.66 (s, 2H), 2.34 (br s, 2H), 1.80-1.63 (m, 9H), 1.52-1.49 (m, 2H). $^{13}$C NMR δ 174.6, 163.4, 162.8, 155.6, 132.0, 130.4, 130.3, 129.0, 125.8, 125.2, 122.4, 115.4, 114.8, 60.4, 57.3, 52.6, 33.7, 32.1, 27.4, 25.6, 23.0, 22.5. HRMS (FAB) for $C_{26}H_{33}N_3O_5$: calcd 468.2498 $(M+H)^+$, found 468.2497 $(M+H)^+$.

**Fluorescence Measurements.** The solvents for spectral analysis were dried by the standard method and kept with molecular sieve (4 Å) prior to use. Stock solutions with the same concentration ($1.0 \times 10^{-5}$ M) of the dye **5** were firstly prepared in dry organic solvents and in pure water. Sample solutions (10 mL) containing different amounts of water were prepared by mixing each of the above stock solutions together in various volumetric ratios to give a water content ranging from 0% to 100% (v/v).

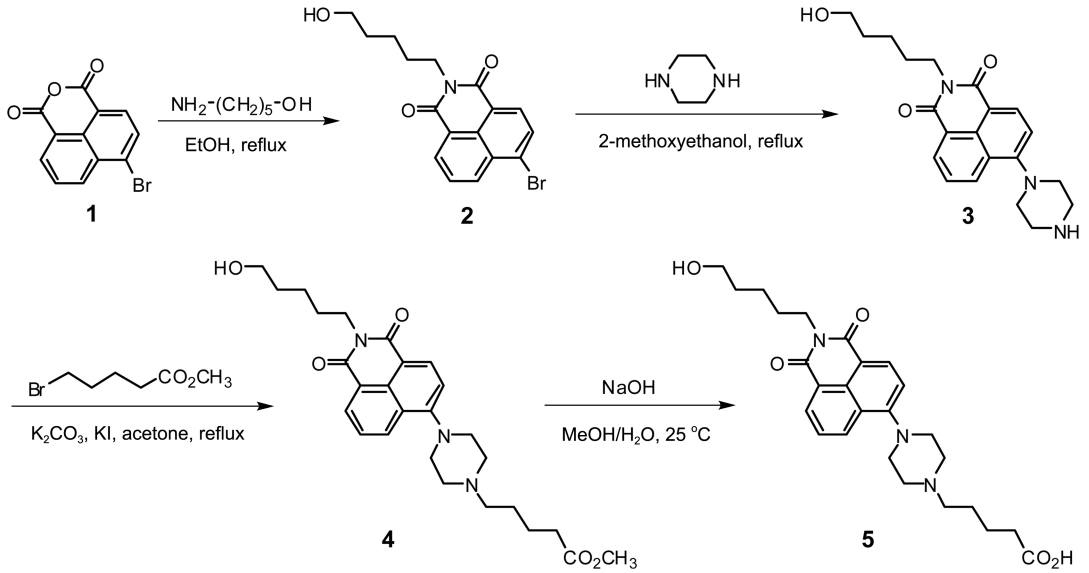
Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra using coumarin 153 ($\Phi_F = 0.38$ in ethanol) as the standard.[9]

## Results and Discussion

**Design and Synthesis of the Fluorescent Water Sensor.** To develop an "off-on" fluorescent water sensor **5**, we utilized the PET system with a 'fluorophore-spacer-receptor' skeleton. Thus, 4-substituted 1,8-naphthalimide was selected as a fluorophore. As the spacer-receptor part, the piperazinyl pentanoic acid moiety was attached to the 4-position of 1,8-naphthalimide for the easy zwitterion formation (**5a**) by proton transfer from the carboxyl group to the piperazine nitrogen. The lone-pair electrons of the piperazine nitrogen quenched the fluorescence of the excited fluorophore 4-aminonaphthalimide by the PET mechanism (off-state), whereas in the case that the electron-donating piperazine nitrogen was protonated, the PET process was inhibited and the fluorescence with high quantum yield was reproduced (on-state). In addition, the 5-hydroxypentyl group was attached to the nitrogen atom on the imide moiety to provide the sensor **5** with better water solubility.

The synthesis of the sensor **5** was efficiently performed as described in Scheme 1. It began with the reaction of 4-bromo-1,8-naphthalic anhydride **1** with 5-hydroxypentanol to give 1,8-naphthalimide derivative **2**. The compound **3** was obtained by the substitution reaction of the 4-bromo-1,8-naphthalimide **2** with piperazine, which further reacted with 5-bromopentanoate to afford **4** in good yield. The fluorescent dye **5** was produced as a yellow solid by hydrolysis of **4** in basic condition and subsequent neutralization. The formation of the dye **5** was confirmed by the presence of resonance peaks ($^{13}$C NMR) for $CO_2H$ at 174.6 ppm, $CH_2OH$ at 62.6, all methylene carbons and aromatic carbons, as well as an indicative molecular ion peak (HRMS) at *m/z* 482.2656 $(M+H)^+$.

**Absorption Spectroscopic Properties.** The absorption spectra of the dye **5** were obtained in various water-miscible




**Scheme 1.** Synthesis of the fluorescent sensor (**5**).

**Table 1.** Absorption spectroscopic data of the dye **5** ($2.5 \times 10^{-5}$ M) in water-miscible organic solvents

| Solvent | Dielectric constant | $\lambda_{max}$ (nm) | ε (L/mol·cm) |
|---|---|---|---|
| Acetone | 21 | 375 | $5.4 \times 10^3$ |
| EtOH | 24.5 | 400 | $8.6 \times 10^3$ |
| MeOH | 33 | 398 | $9.6 \times 10^3$ |
| $CH_3CN$ | 37.5 | 398 | $4.3 \times 10^3$ |
| DMF | 38 | 403 | $8.2 \times 10^3$ |
| DMSO | 46.7 | 409 | $7.9 \times 10^3$ |

organic solvents and are summarized in Table 1. The absorption maxima of **5** were observed in the visible region at around 400 nm and were not greatly affected by the polarity of the solvent, while the absorption maximum in acetone showed a hypsochromic shift. In order to observe the effect of water on the absorption spectrum of the dye **5**, the absorption spectra were measured in ethanol with increasing water content. As shown in Figure 1, the absorption spectral

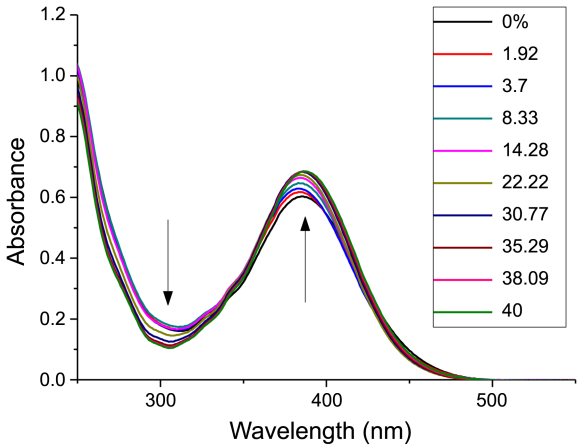



**Figure 1.** Absorption spectra of the dye **5** ($5.0 \times 10^{-5}$) in the presence of an increasing amount of water (0-40%) in EtOH.

**Table 2.** Fluorescence characteristics of the dye **5** ($1.0 \times 10^{-5}$ M) in various solvents

| Solvent | $\lambda_A$ (nm) | $\lambda_F$ (nm) | $\nu_A$-$\nu_F$ ($cm^{-1}$) | $\Phi_F$ |
|---|---|---|---|---|
| Acetone | 415 | 510 | 4489 | 0.017 |
| EtOH | 400 | 520 | 5769 | 0.006 |
| MeOH | 400 | 525 | 5952 | 0.003 |
| $CH_3CN$ | 410 | 510 | 4782 | 0.011 |
| DMF | 400 | 520 | 5769 | 0.005 |
| DMSO | 400 | 520 | 5769 | 0.066 |
| Water | 400 | 528 | 6061 | 0.158 |

change of **5** in the presence of increasing water was negligible in shape and exhibited only small changes in intensity.

**Fluorescence Spectroscopic and Water Sensing Properties.** Fluorescence spectroscopic data of the dye **5** in the representative water-miscible organic solvents are summarized in Table 2. The dye **5** exhibited weak emission bands at around 520 nm in all organic solvents, such as a very weak fluorescence band ($\Phi_F = 0.006$) at 520 nm when excited by radiation of 400 nm. In water, however, the fluorescence of **5** was dramatically increased ($\Phi_F = 0.158$), while the fluorescence maxima was slightly red shifted within 8 nm. We also observed the similar emissive properties for **5** in acetone, methanol, acetonitrile, *N,N*-dimethyl formamide and dimethyl sulfoxide.

To investigate the responses of the dye **5** to the change of water content in organic solvent, the fluorescence spectra of **5** were measured in the presence of increasing water content in ethanol, acetone, *N,N*-dimethyl formamide and dimethyl sulfoxide. As shown in Figure 2(a), the fluorescence intensities greatly increased as the water content increased in ethanol. The changes in the fluorescence peak intensity at 520 nm are plotted against water content in ethanol in Figure 3. The peak intensity was enhanced about 45-fold when the

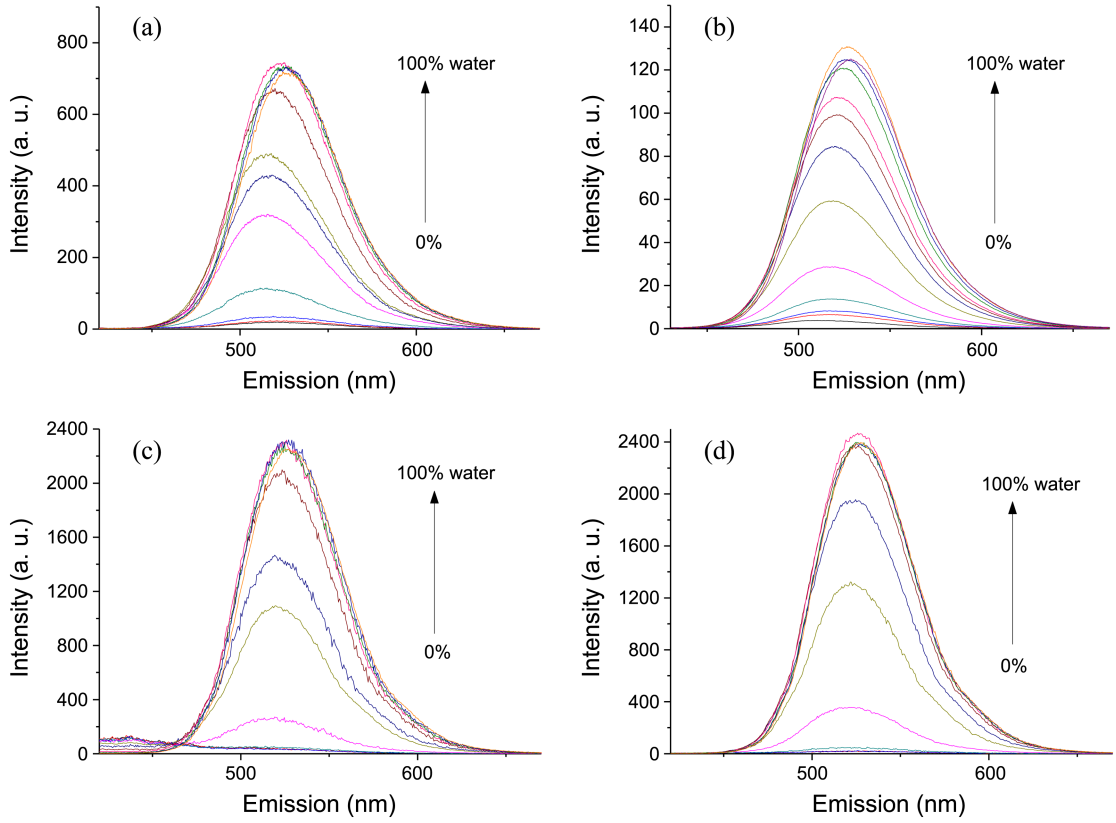



**Figure 2.** Changes in the fluorescence spectra of the dye **5** ($1.0 \times 10^{-5}$ M) in the presence of an increasing amount of water (0-100%) in the following solvents: (a) EtOH, (b) acetone, (c) DMF and (d) DMSO.

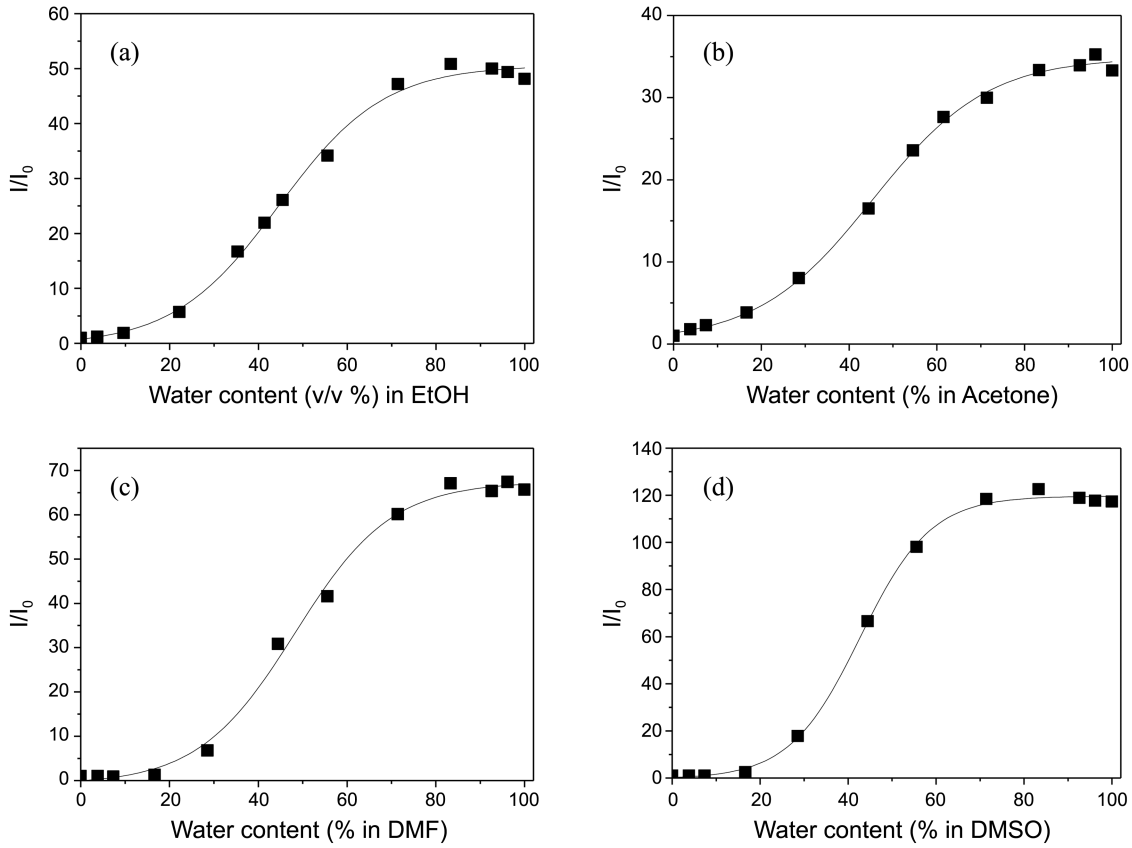
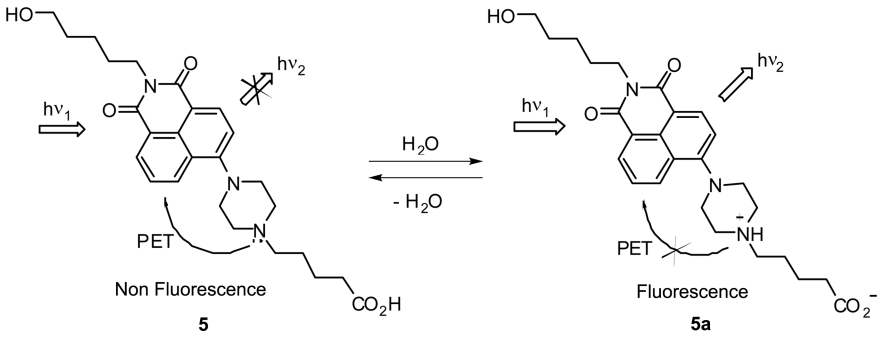



**Figure 3.** Relative fluorescence intensity of the dye **5** as a function of the water content in the following solvents: (a) EtOH, (b) acetone, (c) DMF and (d) DMSO.




**Scheme 2.** Representative scheme explaining the changes in fluorescence for the detection of water.

water content reached 80%. This phenomenon in which **5** exhibited a fluorescence change with varying water content is related to the equilibrium between the neutral structure (**5**) and the zwitterionic structure (**5a**), as mentioned by Ooyama *et al.*[4d] In dry ethanol, the fluorescent dye exists mainly in the form of the neutral structure (**5**) to allow the PET process from the piperazine to the fluorophore leading to non fluorescence ($\Phi_F = 0.006$), while this dye exists predominantly in the zwitterionic form (**5a**) in the presence of water in ethanol. The protonation on the piperazine nitrogen atom prevents PET, which restores the fluorescence ($\Phi_F = 0.086$) from the 1,8-naphthalimide moiety. In an acetone-water mixture, a similar tendency of fluorescence spectral changes of **5** was observed (Figure 3(b)). The response range for the fluorescent signaling of water content was somewhat wider; the fluorescence intensity increased with increasing water content up to 90%, but the fluorescence enhancement was rather lower (30-fold) than that in ethanol. In DMF-water and DMSO-water mixtures (Figure 3(c) and 3(d)), the fluorescence intensities exhibited significant enhancement as the water content was increased from 18% to 80%. In these cases, the enhancements of the peak intensity were much greater (67- and 122-fold, respectively) than that in ethanol-water mixture. However, the fluorescence of **5** was less sensitive to a water content below 18%.

In order to determine the dependence of pH on the fluorescence and the p$K_a$ value of the dye **5**, the fluorescence spectra were measured in buffer solutions of different pHs. As expected, the dye **5** showed a remarkable change in the fluorescence between pH 5-9. In acidic solution for **5** a strong fluorescence was observed. Upon increasing pH, how-

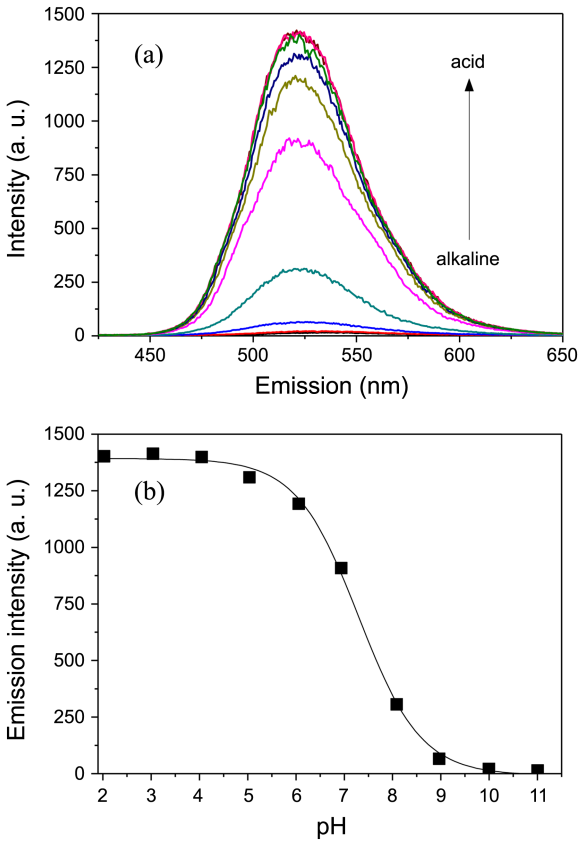
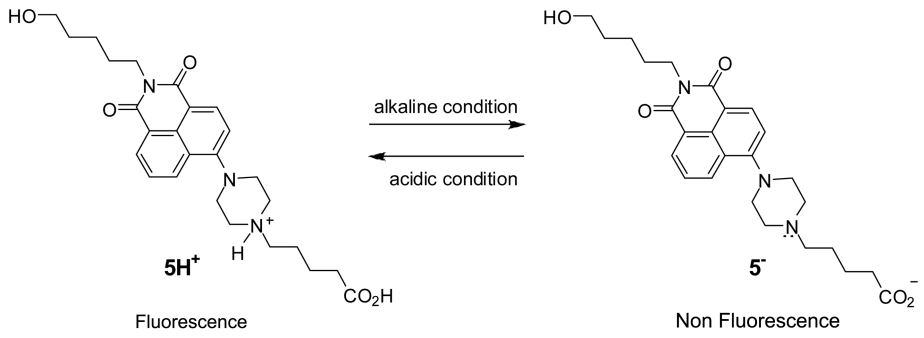



**Figure 4.** (a) Emission spectra changes of the fluorescent dye **5** ($6.6 \times 10^{-5}$ M) in buffer solutions between pH 11 and 2 at 25 °C when irradiated at 410 nm. (b) Effect of pH on the fluorescence intensity ($\lambda_{em} = 530$ nm) of **5**.




**Scheme 3**. Chemical structures of the dye **5** in equilibrium in acidic and alkaline solutions.

ever, the fluorescence was gradually reduced, as demonstrated in Figure 4. This change was attributed to the protonation-deprotonation equilibrium of the dye **5** depending on pH (Scheme 3). The protonated compound (**5H**$^+$) in acidic solution inhibits PET, giving rise to the strong fluorescence, whereas the deprotonated one (**5**$^-$) in alkaline solution enhances PET. The p$K_a$ value of 7.29 was determined by fluorescence titration *via* the following equation: $\log[(I_{Fmax} - I_F)/(I_F - I_{Fmax})] = pH - pK_a$.[10]

## Conclusions

The water-soluble fluorescent 1,8-naphthalimide derivative (**5**) possessing a piperazine group and a carboxylic group was synthesized and its ability to be used for the quantitative determination of water was investigated in various organic solvents. This dye displayed the fluorescence "off-on" detection for water over a wider operating sensing range. The fluorescence intensities of **5** dramatically increased with increasing water content in water-miscible organic solvents such as acetone, ethanol, DMF and DMSO. The enhancements of the fluorescence intensities in acetone, ethanol, DMF and DMSO were 30-, 45-, 67- and 122-fold, respectively. The response ranges were over a wide range of water content from 0% to ~80% (v/v) for ethanol, DMF and DMSO, and from 0% to ~90% (v/v) for acetone. This fluorescence enhancement was attributed to the inhibition of PET of the zwitterionic form by the protonation on the piperazine nitrogen in the presence of water in organic solvents, leading to restoration of the fluorescence. These results support the potential for the fluorescence dye **5** to act as a highly efficient optical water sensor with a wide response range.

**Acknowledgments.** This study was financially supported by Chonnam National University, 2011.

## References

1. (a) Fischer, K. *Angew. Chem*. **1935**, *48*, 394-396. (b) Liang, Y. Y. *Anal. Chem.* **1990**, *62*, 2504. (c) Oraedd, C.; Cedergren, A. *Anal. Chem.* **1995**, *67*, 999.
2. Oguchi, R.; Yamaguchi, K.; Shibamoto, T. *J. Chromatogr. Sci.* **1988**, *26*, 588.
3. (a) Kim, J. S.; Choi, M. G.; Huh, Y.; Kim, M. H.; Kim, S. H.; Wang, S. Y.; Chang, S.-K. *Bull. Korean Chem. Soc*. **2006**, *27*, 2058. (b) Li, Z.; Yang, Q.; Chang, R.; Ma, G.; Chen, M.; Zhang, W. *Dyes Pigments* **2011**, *88*, 307. (c) Citterio, D.; Minamihashi, K.; Kuniyoshi, Y.; Hisamoto, H.; Sasaki, S.; Suzuki, K. *Anal. Chem.* **2001**, *73*, 5339. (d) Niu, C.-G.; Guan, A.-L.; Zeng, G.-M.; Liu, Y.-G.; Li, Z.-W. *Anal. Chim. Acta* **2006**, *577*, 264. (e) Niu, C.-G.; Qin, P.-Z.; Zeng, G.-M.; Gui, X.-Q.; Guan, A.-L. *Anal. Bioanal. Chem.* **2007**, *387*, 1067. (f) Orellana, G.; Gomez-Carneros, A. M.; de Dios, C.; Garcia-Martinez, A. A.; Moreno-Bondi, M. C. *Anal. Chem.* **1995**, *67*, 2231.
4. (a) Ooyama, Y.; Matsugasako, A.; Nagono, T.; Oka, K.; Kushimoto, K.; Komaguchi, K.; Imae, I.; Harima, Y. *J. Photochem. Photobiol. A: Chem.* **2011**, *222*, 52. (b) Ooyama, Y.; Matsugasako, A.; Oka, K.; Nagono, T.; Sumomogi, M.; Komaguchi, K.; Imae, I.; Harima, Y. *Chem. Commun.* **2011**, *47*, 4448. (c) Ooyama, Y.; Egawa, H.; Yoshida, K. *Dyes Pigments* **2009**, *82*, 58. (d) Ooyama, Y.; Sumomogi, M.; Nagano, T.; Kushimoto, K.; Komaguchi, K.; Imea, I.; Harima, Y. *Org. Biomol. Chem.* **2011**, *9*, 1314.
5. Georgiev, N. I.; Bojinov, V. B.; Nikolov, P. S. *Dyes Pigments* **2011**, *88*, 350.
6. He, H.; Mortellaro, M. A.; Leiner, M. J. P.; Young, S. T.; Fraatz, R. J.; Tusa, J. K. *Anal. Chem.* **2003**, *75*, 549.
7. (a) Zeng, X.; Zhang, X.; Zhu, B.; Jia, H.; Li, Y. *Dyes Pigments* **2012**, *94*, 10. (b) Trupp, S.; Schweitzer, A.; Mohr, G. J. *Org. Biomol. Chem.* **2006**, *4*, 2965.
8. (a) He, H.; Mortellaro, M. A.; Leiner, M. J. P.; Young, S. T.; Fraatz, R. J.; Tusa, J. K. *Anal. Chem.* **2003**, *75*, 549. (b) Tian, H.; Gan, J.; Chen, K.; He, J.; Song, Q. L.; Hou, X. Y. *J. Mater. Chem.* **2002**, *12*, 1262. (c) de Silva, A. P.; Rice, T. E. *Chem. Commun*. **1999**, 163. (d) Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Biomol. Chem.* **2003**, *1*, 3265. (e) Guo, X.; Qian, X.; Jia, L. *J. Am. Chem. Soc*. **2004**, *126*, 2272. (f) Grabchev, I.; Chovelon, J.-M.; Qian, X. *New J. Chem*. **2003**, *27*, 337. (g) Jia, L.; Zhang, Y.; Guo, X.; Qian, X. *Tetrahedron Lett.* **2004**, *45*, 3969. (h) Wang, J.; Xiao, Y.; Zhang, Z.; Qian, X.; Yanga, Y.; Xua, Q. *J. Mater. Chem.* **2005**, *15*, 2836. (i) Xu, Z.; Han, S. J.; Lee, C.; Yoon, J.; Spring, D. R. *Chem. Commun*. **2010**, *46*, 1679. (j) Poteau, X.; Brown, A. I.; Brown, R. G.; Holmes, C.; Matthew, D. *Dyes Pigments* **2000**, *47*, 91. (k) Gan, J.; Chen, K.; Chang, C.-P.; Tian, H. *Dyes Pigments* **2003**, *57*, 21. (l) de Silva, A. P.; Goligher, A.; Gunaratne, H. Q. N.; Rice, T. E. *ARKIVOC* **2003**, *7*, 229.
9. Brouwer, A. M. *Pure Appl. Chem*. **2011**, *83*, 2213.
10. de Silva, A. P.; Goligher, A.; Gunaratne, H. Q. N.; Rice, T. E. *ARKIVOC* **2003**, (*vii*), 229.