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N-hydroxypropyl substituted 4-hydroxynaphthalimide: Differentiation of solvents and discriminative determination of water in organic solvents

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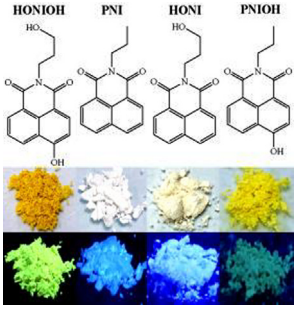
HIGHLIGHTS

- 4-hydroxynaphthalimide derivative was developed as colorimetric and fluorescent probe.
- The probe can be used to recognize DMF and differentiate methanol from ethanol.
- Distinct colors changes were observed in DMF and other organic solvents.
- The probe was successfully applied for the discriminative detection of trace water.

GRAPHICAL ABSTRACT

N-hydroxypropyl and 4-hydroxy incorporated 1,8-naphthalimide fluorescent probe, HONIOH, can be utilized to differentiate organic solvents and discriminatively detect trace water in organic solvents. Three model compounds, namely, PNI, HONI, and PNIOH were also investigated in order to demonstrate the functions of N-hydroxypropyl and 4-hydroxy groups.



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ABSTRACT

A naphthalimide-based fluorophore (HONIOH) was designed by introducing a hydroxy unit into the 4th position of the aromatic core and a hydroxypropyl unit into the N-imide site. Photophysical properties of HONIOH were highly dependent on solvents, which was ascribed to the excited state proton transfer (ESPT) coupled with intramolecular charge transfer (ICT) mechanism. Further studies demonstrated that HONIOH can be used to recognize N, N-dimethylformamide (DMF) qualitatively and differentiate methanol from ethanol. Three control compounds were synthesized, their photophysical properties were investigated in various solvents, and experimental results revealed that hydroxyl and hydroxypropyl units contribute to the solvents differentiation ability of HONIOH. In addition, HONIOH was successfully applied as a colorimetric, fluorescent probe for the discriminative detection of trace water in organic solvents, such as fluorescence turn-on response accompanied by fluorescent color changes from light yellow to purple in DMF, and fluorescence turn-off response and blue to yellow fluorescent color changes in acetonitrile, tetrahydrofuran, and acetone. We believe that N-substituted 4-hydroxynaphthalimide derivatives may find widespread applications in chemical and biochemical sensing and imaging.

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1. Introduction

Water (H_2O) is the most important component of organisms and a vital resource for all life. However, even trace amounts of H_2O are detrimental and dangerous in the chemical industry, food processing, and many other fields where H_2O is not needed [1–2]. Therefore, the development of simple, fast, and sensitive detection methods for trace water is of great demand in these fields. In recent years, considerable effort has been devoted to developing fluorescent probes for water detection due to the apparent advantages of the fluorescence method, including simple fabrication, easy operation, fast response, high selectivity, and sensitivity [2–6].

Until now, various fluorophores have been employed as the signaling unit in designing fluorescent probes [2–6], and naphthalimide (NI) fluorophore is one of the most promising candidates due to its easy functionalization and tunable photophysical properties [7–10]. The introduction of electron-donating or -withdrawing groups at the N-imide site and the 4th position of the aromatic core of the NI unit is the most common design approach [7–10]. NIs with donor groups attached to the 4th position of the aromatic core, which result in the characteristic intramolecular charge transfer (ICT)-based structures, contribute substantially to diverse chemical and biological sensing applications [7–16].

In the past 10 years, fluorophore 4-hydroxy(OH)-1,8-NI was frequently employed as the fluorescent reporter by taking advantage of its excellent ICT fluorescence properties of 4-OH-1,8-NI in alkaline environment, such as phosphate or HEPES buffer at pH 7.4, which emits green fluorescence due to the deprotonation of the OH group [17–20]. For example, by the 4-position substitution, 4-OH-1,8-NI-derived ethers [21–28] and esters [29–37] have been extensively developed as fluorescent probes (chemodosimeters) for tracing various analytes via the analyte-triggered ether or ester bond cleavage mechanism. Based on this mechanism, the inhibited ICT process of ethers and esters is effectively recovered by releasing N-substituted 4-OH-1,8-NI in the anionic forms, thus realizing the successful fluorescence determination of the analytes [21–37]. Photophysical properties of the ICT-type structure are highly solvent dependent and can be used for the determination of water content [2,9,38–40]. Moreover, 4-OH-1,8-NI can exhibit excited-state proton transfer (ESPT) because its structure contains a hydrogen bond donor (–OH) and a hydrogen bond acceptor (C=O) [18]. Photophysical properties of ESPT-type structure are also sensitive to the surrounding medium such as the solvent type [18,41–42]. However, to the best of our knowledge, only limited reports on fluorescent probes that derived N-substituted 4-OH-1,8-NI have been used for the discrimination of solvents as well as determination of water content [43].

Inspired by the investigations described above, we designed an N-hydroxypropyl and 4-hydroxy incorporated 1,8-naphthalimide fluorescent probe, HONIOH, which can be utilized to differentiate organic solvents and monitor H_2O content in organic solvents. Three model compounds, namely, PNI, HONI, and PNIOH were also synthesized for comparison (Fig. 1) to examine the effects of N-hydroxypropyl and 4-hydroxy on solvent differentiation ability. HONIOH possesses several attractive features, such as qualitative recognition of N, N-dimethylformamide (DMF), discrimination between methanol (MeOH) and ethanol (EtOH), and water-induced distinguishable fluorescent responses in organic solvents (Table S1).

2. Experimental

2.1. Materials and instruments

All chemical materials and solvents were purchased from commercial suppliers, acetonitrile (AN), ethanol (EtOH), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol (MeOH), ethyl acetate (EA) and tetrahydrofuran (THF) were distilled prior to the measurements. All other reagents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on the Bruker AVANCE III HD600 spectrometer in DMSO d_6 (chemical shifts of 2.50 ppm (^{1}H) and 39.52 ppm (^{13}C)). High Resolution mass spectra were recorded using a Thermo Fisher LCQ Fleet spectrometer. UV–visible absorption spectra were collected using a UV 1901 spectrophotometer. Fluorescence spectra were collected with a 960 MC spectrophotometer.

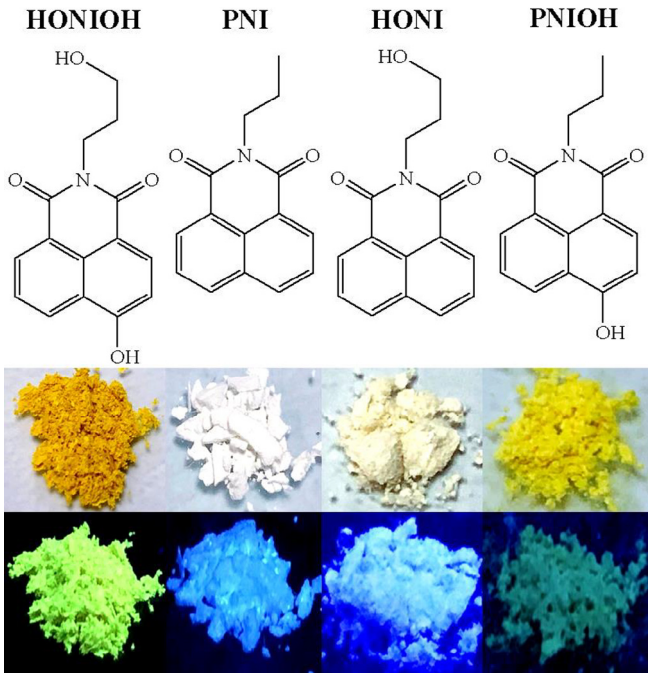


Fig. 1. Molecular structures and solid-state photographs of HONIOH, PNI, HONI, and PNIOH under day light and 365 nm UV light.

2.2. Synthesis of 4-hydroxy-N-(3-hydroxypropyl)-1,8-naphthalimide (HONIOH)

A mixture of 4-bromo-1,8-naphthalic anhydride (l.050 g, 3.79 mmol) and 3-aminopropan-1-ol (0.3102 g, 4.13 mmol) were dissolved in EtOH (25 mL) and then heated at 85 °C for 15 h. After cooling the mixture, the precipitate was collected and washed with H_2O (3 × 15 mL) to give compound **1**. Compound **1** (0.2000 g, 0.60 mmol) and K_2CO_3 (0.1650 g, 1.2 mmol) were dissolved DMF/H_2O (1:1, 12 mL) and then heated at 120 °C for 6 h. Upon cooling down, the reaction mixture was diluted with H_2O (60 mL). Dichloroform (3 × 50 mL) was used to extract the aqueous phase, sodium chloride solution (3 × 20 mL) was used to wash the combined organic layer. After drying with anhydrous $MgSO_4$ and removing the solvent, **HONIOH** was obtained as a yellow powder (0.142 g, 87.3%). ^{1}H NMR: 1.77 (m, 2H), 3.49 (t, 2H), 4.08 (m, 2H), 4.50 (s, 1H), 7.16 (d, 1H), 7.77 (dd, 1H), 8.37 (d, 1H), 8.51 (ddd, 2H), 11.87 (s, 1H) (Fig. S1 in the ESI†); ^{13}C NMR: 164.19, 163.53, 160.68, 134.01, 131.58, 129.64, 129.34, 126.08, 122.84, 122.32, 113.14, 110.42, 59.49, 39.49, 30.29 (Fig. S2 in the ESI†); mass spectra (*m*/*z*): calculated for $C_{15}H_{13}NO_4$ $[M - H]^-$ 270.27, Found 270.14 (Fig. S3 in the ESI†).

2.3. Synthesis of N-propyl-1,8-naphthalimide (PNI)

A mixture of 1,8-naphthalic anhydride (0.3944 g, 2.0 mmol) and aminopropane (0.3 mL, 3.6 mmol) were dissolved in EtOH (25 mL) and then heated at 85 °C for 0.5 h. After cooling down, the precipitate was collected and washed with cold ethanol to give **PNI** as a white powder (0.3648 g, 76%). ^{1}H NMR: 0.94 (t, 3H), 1.67 (m, 2H), 4.03 (m, 2H), 7.89 (dd, 2H), 8.48 (dd, 2H), 8.52 (dd, 2H) (Fig. S4 in the ESI†); mass spectra (*m*/*z*): calculated for $C_{15}H_{13}NO_2$ $[M+H]^+$ 240.09, Found 240.18 (Fig. S5 in the ESI†).

2.4. Synthesis of 4-hydroxy-N-(3-hydroxypropyl)-naphthalimide (HONI)

A mixture of 1,8-naphthalic anhydride (0.8043 g, 3.79 mmol) and 3-aminopropan-1-ol (0.3102 g, 4.13 mmol) were dissolved in EtOH (25 mL) and then heated at 85 °C for 15 h. After cooling the mixture to room temperature, glacial water (50 mL) was added. Then, the precipitate was collected and washed with H_2O (3 × 15 mL) to give **HONI** as a brown powder (0.76 g, 78.6%). ^{1}H NMR: 1.81 (m, 2H), 3.51 (td, 2H), 4.12 (m, 2H), 7.89 (dd, 2H), 8.50 (m, 4H) (Fig. S6 in the ESI†); ^{13}C NMR: 163.86, 134.69, 131.72, 131.11, 127.76, 127.64, 122.53, 59.49, 38.04, 31.47 (Fig. S7 in the ESI†); mass spectra (*m*/*z*): calculated for $C_{15}H_{13}NO_3$ $[M + H]^+$ 256.27, Found 256.06 (Fig. S8 in the ESI†).

2.5. Synthesis of 4-hydroxy-N-propyl-1,8-naphthalimide (PNIOH)

A mixture of 4-bromo-1,8-naphthalic anhydride (0.5541 g, 2.0 mmol) and aminopropane (0.2 mL, 3.0 mmol) were dissolved in EtOH (25 mL) and then heated at 85 °C for 0.5 h. After cooling the mixture, the precipitate was collected and washed with H_2O (3 × 15 mL) to obtain compound **2**. Compound **2** (0.1900 g, 0.60 mmol) and K_2CO_3 (0.1650 g, 1.2 mmol) were dissolved in DMF/H_2O (1:1, 12 mL) and then heated at 120 °C for 6 h. Upon cooling the reaction mixture, H_2O (60 mL) was added. Ddichloroform (3 × 50 mL) was used to extract the aqueous phase, then the organic layer was combined and washed with sodium chloride solution (3 × 20 mL). After drying with anhydrous $MgSO_4$, the solvent was then removed under vacuum and **PNIOH** was obtained as a yellow powder (0.142 g, 92.8%). ^{1}H NMR: 0.92 (t, 3H), 1.69 (tq, 2H), 3.88 (t, 2H), 7.10 (dd, 1H), 7.38 (t, 1H), 8.02 (d, 1H), 8.14 (dd, 1H), 8.20 (ddd, 1H) (Fig. S9 in the ESI†); mass spectra (*m*/*z*): calculated for $C_{15}H_{13}NO_3$ $[M-H]^-$ 254.1, Found 254.22 (Fig. S10 in the ESI†).

2.6. Determination of the fluorescence quantum yields

The fluorescence quantum yields (Φ) of HONIOH, PNI, HONI, and PNIOH were determined in acetonitrile using rhodamine B as standard (Φ = 0.89 in ethanol) [21]. All compounds were excited at 360 nm and the area under each emission spectrum integrated. The quantum yields for all compounds were obtained using the following equation (1) [35,44].

$$\Phi_1 = \Phi_B \frac{I_1 A_B \lambda_{exB} \eta_{acetonitrile}}{I_B A_1 \lambda_{ex1} \eta_{ethanol}} \quad (1)$$

Φ is the quantum yield; I is the area under the emission spectra; A is the absorbance at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the refractive index of the solution; the subscripts 1 and B refer to HONIOH (or PNI, or HONI, or PNIOH) and the standard, respectively.

3. Results and discussion

The synthesis and characterization of naphthalimide-based compounds HONIOH, PNI, HONI, and PNIOH are provided in the experimental section and the Supporting Information (Figs. S1-S10). In the solid state, HONIOH, PNI, HONI, and PNIOH showed orange-yellow, white, light yellow, and yellow color under daylight and green, blue, blue, and blue-green color when exposed to 365 nm UV light, respectively (Fig. 1).

3.1. Differentiation of solvents

HONIOH is an NI derivative with N-hydroxypropyl and 4-hydroxy substitutions. Photophysical properties of HONIOH dispersed in different solvents were investigated (Fig. 2, Fig. 3 and Table S2). In AN, CH_2Cl_2, $CHCl_3$, acetone, EA, toluene, and THF, HONIOH (Φ = 0.67) showed blue emission color and one fluorescence emission band at around 436–453 nm (Fig. 2), and one absorption band at around 365–370 nm (Fig. 3), indicating that HONIOH exists as neutral forms in the excited state and the ground state in these solvents [18–19]. In EtOH, DMF, DMSO, and MeOH, HONIOH showed yellow or faint yellow emission color and two fluorescence emission bands at approximately 450 and 550 nm, which are assigned to the excited neutral species and anionic species, respectively, indicating that HONIOH undergoes ESPT actions efficiently in EtOH, DMF, DMSO, and MeOH [41] (Fig. 2 and Fig. S11). When the hydroxy group was replaced by a negative oxygen moiety, HONIOH existed in the anionic species, which facilitated the ICT process owing to the stronger electron-donor ability of the oxygen anions, with the appearance of fluorescence emission peak centered at approximately 550 nm [17–37]. In MeOH, neutral species and anionic species existed in the ground state, and two absorption bands centered at 377 and 452 nm (Fig. 3). In DMF, HONIOH predominately existed as anionic forms with an absorption band of 480 nm in the ground state (Fig. 3) due to the strong basicity of DMF [41]. In EtOH and DMSO, only one absorption band appeared at 377 nm (Fig. 3), which is attributed to the neutral species [18]. In aqueous solution, HONIOH

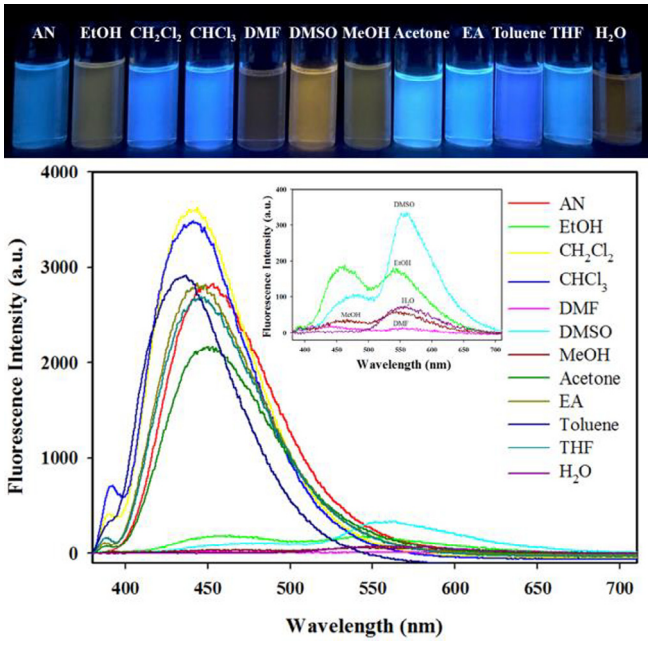


Fig. 2. Fluorescence spectra of HONIOH (20 μM) in various solvents. The photos were taken under 365 nm UV light irradiation. Inset: Magnification.

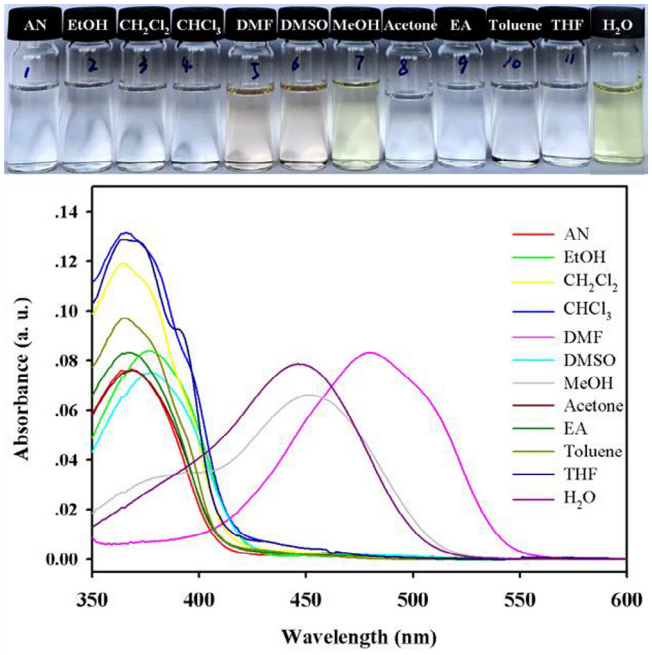


Fig. 3. UV–vis absorption spectra of HONIOH (20 μM) in various solvents. The photos were taken under day light.

existed as anionic species in the ground state and excited state, with an absorption band at 447 nm (Fig. 3) and a fluorescence emission band at 552 nm (Fig. 2) [18–19].

According to the above experimental results, solvent-dependent spectral changes in HONIOH were further analyzed. First, HONIOH classified the investigated solvents into yellow emission group and blue emission group through the fluorescence channel (Fig. 2 and Fig. S11). Next, DMF and H_2O could be selectively recognized by monitoring the absorbance at 480 and ~450 nm, respectively, by taking advantage of the UV–vis channel (Fig. 3). MeOH and EtOH could be discriminated by monitoring the absorbance at 377 and ~450 nm (Scheme 1).

Photophysical properties of three model NI derivatives (Fig. 1), namely, PNI (Φ = 0.025), HONI (Φ = 0.014), and PNIOH (Φ = 0.063), in various solvents, were investigated to gain a better insight into the solvents' differentiation ability for HONIOH. Of these three derivatives, PNI and HONI possess N-propyl and N-hydroxypropyl substitution, respectively; PNIOH possesses a 4-hydroxy group as in the case of HONIOH, whereas N-hydroxypropyl is replaced with the N-propyl functionality. Fluorescent emission wavelengths and emission colors of PNI and HONI have a slight solvent dependence (Figs. S12 and S13), confirming the important role of the 4-hydroxy group. The solvents were categorized into two groups through the FL channel by observing the distinct emission wavelengths and colors of PNIOH (Fig. S14 and Table S3), which are ascribed to efficient ESPT in AN, EtOH, MeOH, DMF, DMSO, and H_2O in the excited state [2,41,45]. However, in the case of PNIOH, qualitative recognition of DMF and differentiation of solvents having similar physicochemical properties, such as MeOH and EtOH, were not achieved by utilizing the UV–vis channel (Figs. S15 and Scheme S1), confirming the important role of the N-hydroxypropyl group. Compared with PNI, HONI, and PNIOH, HONIOH possesses desirable abilities for solvent differentiation, which should be attributed to the synergy of N-hydroxypropyl and 4-hydroxy groups.

3.2. Determination of trace water in organic solvents

The above results reveal that the fluorescence emission properties of HONIOH in H_2O are distinct from organic solvents, such as DMF, AN, THF, and acetone (Fig. 2 and Fig. S11). Therefore, it is predicted that the presence of trace amounts of H_2O in these solvents would result in fluorescence alteration.

Trace amounts of H_2O in organic solvents were determined to evaluate the accuracy of HONIOH as a water probe. As shown in

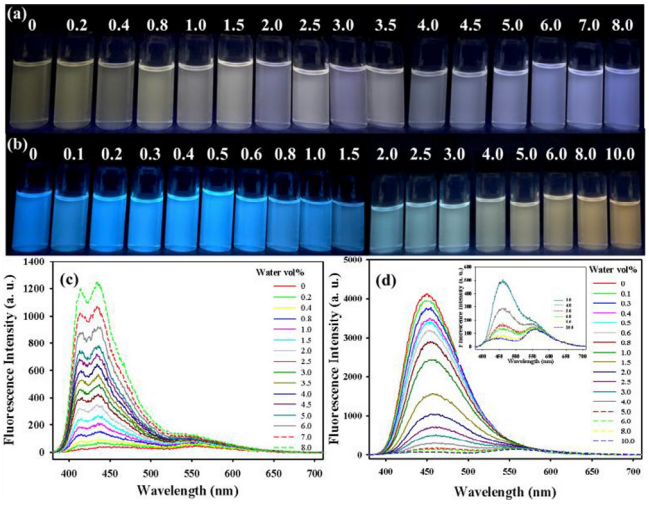
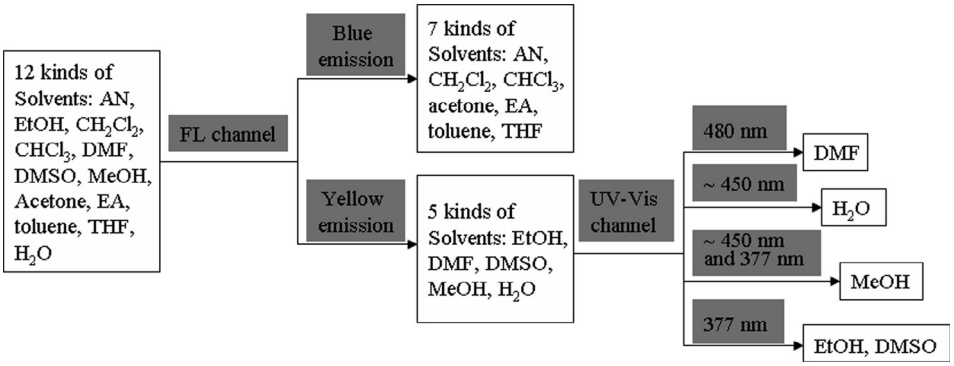


Fig. 4. Color changes of HONIOH in DMF solution (a) and AN solution (b) with different water fractions (%) under 365 nm UV light; and fluorescence spectra of HONIOH in DMF solution (c) and AN solution (d) with increasing amounts of water. Concentration of HONIOH: 30 μM; excitation wavelength: 350 nm.



Scheme 1. Schematic representation of the two-step approach used to discriminate 12 kinds of solvents by HONIOH.

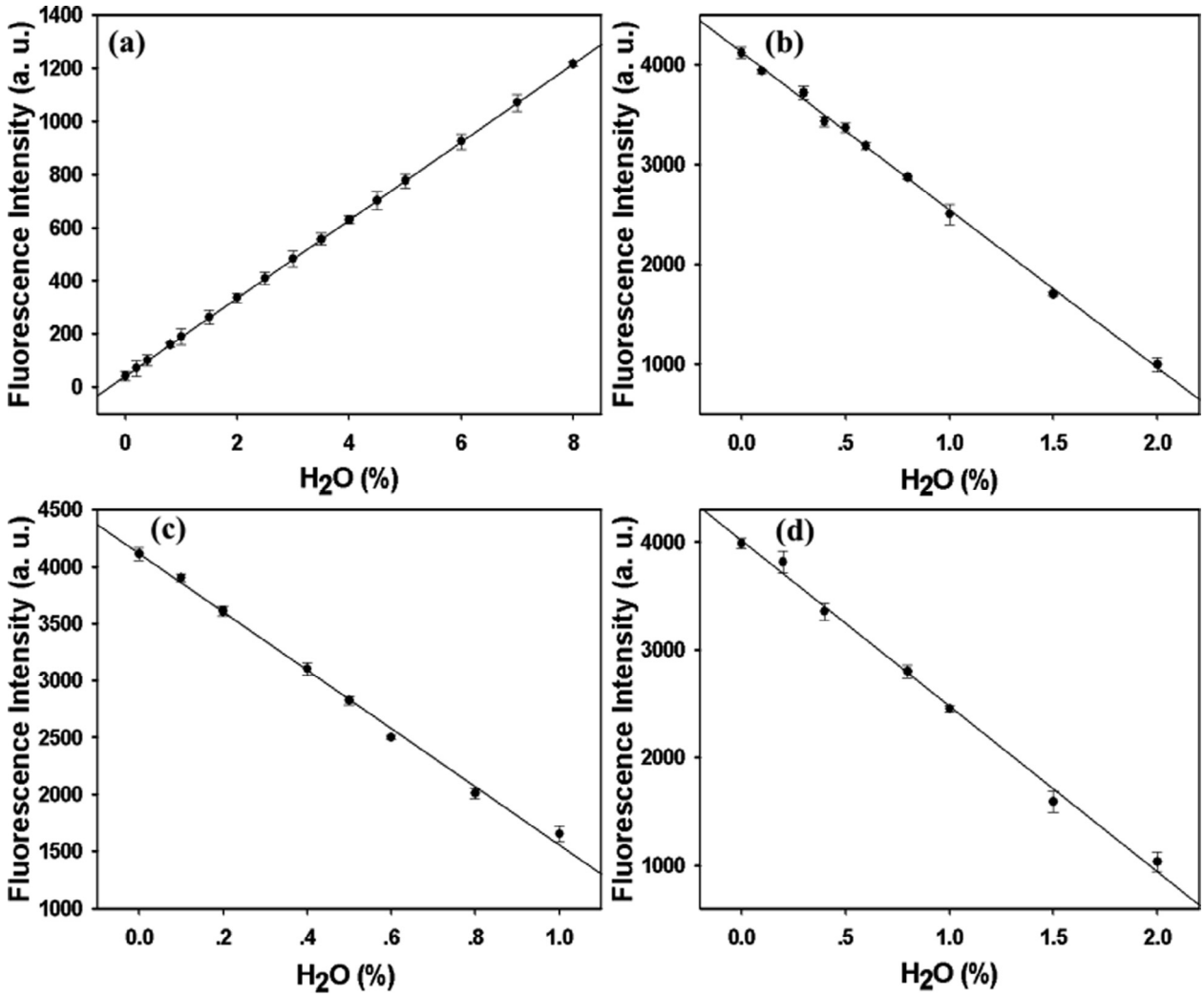


Fig. 5. Plot of fluorescence intensity of HONIOH at 436 nm in DMF solution (a), 450 nm in AN solution (b), 444 nm in THF solution (c), and 447 nm in acetone solution (d) as a function of H_2O contents (v%). Concentration of HONIOH: 30 μM; excitation wavelength: 350 nm.

Table 1
Summary of the water sensing performance of HONIOH.

Solvent	R^2	Calibration equation	Linear range/v%	DL/v%
DMF	0.9992	$F = 146.8390[H_2O] + 41.4453$	0.2–8.0	0.0817
AN	0.9941	$F = -1585.9767[H_2O] + 4116.2646$	0.1–2.0	0.0315
THF	0.9955	$F = -2665.2865[H_2O] + 4123.7600$	0.06–1.0	0.0186
Acetone	0.9942	$F = -1553.1011[H_2O] + 4032.0730$	0.3–2.0	0.0925

F: fluorescence peak intensity; DL: Detection limit.

Table 2
Determination of H_2O in practical DMF samples (n = 3).

Samples	Water content[a] (%)	Spiked (%)	Found (%)	Recovery (%)
1	2.5	2.0	4.45	98.9
2	2.5	4.0	6.61	101.7
3	2.5	6.0	8.54	100.5

[a] Water content measured in practical DMF using the proposed probe HONIOH.

Fig. 4 and Figs. S16-S18, water induced the fluorescence turn-on response property of HONIOH in DMF and the fluorescence turn-off response property of HONIOH in AN, THF, and acetone. The changes of water content (0–8%) in DMF of HONIOH induced fluorescence color variations from light yellow to purple (Fig. 4a), accompanied by an increased fluorescence emission intensity at 414, 430, and 551 nm (Fig. 4c and Fig. S16). HONIOH showed one fluorescence emission band at 450 nm and emitted blue colors in AN, the fluorescence intensity at 450 nm gradually decreased upon increasing the water concentration (0–10%), and one new emission centered at approximately 550 nm emerged (Fig. 4d), thus leading to continuous emission color shifts from blue to yel-

low (Fig. 4b). Similar to the fluorescence response of HONIOH in AN, the fluorescence emission intensity of HONIOH at 444 and 447 nm enhanced gradually in THF and acetone, respectively, with increasing amounts of H_2O (0–10%), and one new emission appeared at approximately 550 nm as in the case of AN (Fig. S17 and Fig. S18).

Good linear relationships were observed between water content and fluorescence emission intensity at 436, 450, 444, and 447 nm in DMF, AN, THF, and acetone, respectively, and the corresponding linear ranges were the H_2O content of 0.2%–8%, 0.1%–2%, 0.06%–1%, and 0.3%–2%, respectively (Fig. 5 and Table 1). The detection limit of HONIOH to trace H_2O in DMF, AN, THF and acetone was calculated to be 0.0817% (v/v), 0.0315% (v/v), 0.0186% (v/v) and 0.0925% (v/v), respectively (Table 1). Moreover, the plot of I/I_0 versus [H_2O] in DMF, and the Stern – Volmer plots of I_0/I versus [H_2O] in AN, THF, and acetone displayed good linear relationships (Fig. S19), where I_0 and I represent the fluorescence intensity of HONIOH in the absence and presence of water concentration, respectively.

Compared with the previously reported fluorescent probes for determination of the water content in organic solvents (Table S1), the most valuable performance of the present work is that HONIOH can discriminatively detect the water content with distinguishable fluorescence emission profile and emission color changes, such as fluorescence "turn-on" mode in DMF and "turn-off" mode in AN, THF, and acetone (Figs. S16-S18); and light yellow to purple color changes in DMF and blue to yellow color changes in AN, THF, and acetone (Fig. 4).

The water-induced fluorescent response of HONIOH in DMF is distinct from that of other organic solvents. Thus, HONIOH was applied to the determination of water in practical DMF samples based on the calibration curve of Fig. 5a. As shown in Table 2, satisfactory recovery values of the DMF samples that ranged from 98.9% to 101.7% were obtained, indicating that the present method can be used to determine trace water in real samples.

4. Conclusions

In summary, 4-hydroxy and N-hydroxypropyl functionalized 1,8-naphthalimide, HONIOH, and three 1,8-naphthalimide-based control molecules, PNI, HONI, and PNIOH, were synthesized, and their photophysical properties were investigated in various solvents. UV – vis absorption and fluorescence measurements showed that 4-hydroxynaphthalimide-derived HONIOH and PNIOH possess tunable fluorescence emission wavelength and color in different solvents due to the ESPT and ICT process, whereas only HONIOH displayed effective solvent differentiation ability, which is attributed to the synergy of 4-hydroxy and N-hydroxypropyl substitutions. Additionally, HONIOH was developed as a colorimetric, fluorescent probe for trace water in organic solvents. HONIOH exhibited different fluorescence changes in different solvents with increasing water contents, such as turn-on response in DMF, and turn-off response in AN, THF, and acetone. The fluorescent color of HONIOH changed from light yellow to purple in DMF and from blue to yellow in AN, THF, and acetone, which could be clearly observed by the naked eyes. The low detection limits of HONIOH to trace H_2O in DMF, AN, THF, and acetone were 0.0817% (v/v), 0.0315% (v/v), 0.0186% (v/v), and 0.0925% (v/v), respectively. We hope that the application of N-substituted 4-hydroxynaphthalimide reported in this work would provide positive instructions for future research.

CRediT authorship contribution statement

Jing Huang: Software, Validation, Formal analysis, Investigation, Data curation. **Yuehui Liang:** Software, Validation, Conceptualization, Investigation. **Hai-Bo Liu:** Supervision, Writing - review & editing, Funding acquisition. **Xiangmin Zhang:** Formal analysis, Investigation. **Jing Wang:** Conceptualization, Methodology, Writing - original draft, Resources, Visualization, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2021.119559.

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