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Two 8-hydroxyquinoline-based fluorescent chemosensors for ultra-fast and sensitive detection of water content in strong polar organic solvents with large Stokes shifts

Jin-Tao Wang[1,2], Ying-Ying Pei[*1,2], Shang-Feng Ren[1,2], Ming-Yue Yan[1,2], Wen Luo[1,2], Bo Zhang[1,2], Qing-Feng Li[*1,2]

[1] Henan Key Laboratory of Rare Earth Functional Materials; The Key Laboratory of Rare Earth Functional Materials and Applications, Zhoukou Normal University, Zhoukou, 466001, Henan, P. R. China.

[2] International Joint Research Laboratory for Biomedical Nanomaterials of Henan, Zhoukou Normal University, Zhoukou, 466001, Henan, P. R. China.

*Corresponding author

E-mail: peiyy0329@163.com (Y. Y. Pei); liqingf335@163.com (Q. F. Li).

Abstract

It is of great significance to detect the moisture in organic solvents before used in water-sensitive reactions. Herein, two Schiff base quinoline derivatives, 8-hydroxyquinoline-2-carboxaldehyde thiosemicarbazone (HQCT) and 8-hydroxyquinoline-2-carboxaldehyde (pyridine-2-carbonyl)-hydrazine (HQPH), were designed and synthesized by a simple one-step reaction, and used as fluorescent chemosensors for ultra-fast and sensitive detection of water content in strong polar organic solvents. Based on excited-state intramolecular proton transfer (ESIPT) process, HQCT and HQPH exhibited strong fluorescence emissions with large Stokes shifts in dimethyl sulfoxide (DMSO) and N, N-dimethylformamide (DMF) solvents compared to other various organic solvents, and their fluorescence quenching and fluorescent color changes were obviously observed with increasing water content. The experimental results revealed that the hydroxyl groups substituted at the 8-position of HQCT and HQPH played a key role in the fluorescence emission processes. Dynamic light scattering (DLS) and ^{1}H-NMR titration indicated that the sensing mechanism for the detection of water was based on inhibition of the ESIPT by H_2O via forming hydrogen bonds. In the range of 0.0-1.8 wt %, the fluorescence intensity of chemosensors changed as a linear function of water content. The detection limits of water in DMSO by HQCT and HQPH were as low as 0.0220 wt % and 0.0274 wt %, respectively. Moreover, HQCT and HQPH are successfully applied for the detection of moisture content in real commercial organic solvents.

Keywords: Fluorescent sensor; 8-hydroxyquinoline; water detection; large Stokes shift

1. Introduction

Water is of crucial importance for daily human life, but is considered as one of the most common impurities in organic solvents. For instance, the presence of trace water in organometallic reactions can decrease the reactivity of organometallic compounds and lower the yields or even bring about catastrophic events such as fire and explosion [1]. Therefore, sensitive and selective detection of water in organic solvents is of considerable significance in chemical reactions and industrial production processes. At present, Karl-Fischer method is a traditional analytical technique, and is frequently used for quantitative measurement of water content in organic solvents because of its absolute measurement, high sensitivity, wide applicability, and large dynamic range [2]. However, there are some shortcomings of requiring specialized instruments and skilled personnel, being time-consuming, using toxic reagents (e.g., I_2, and SO_2) and being unsuitable for redox-active samples [3].

Up to now, a great number of fluorescent sensors with outstanding advantages, such as operational simplicity, in-situ monitoring, rapid response and low cost, have been reported. The sensing mechanisms are mainly based on intramolecular charge transfer (ICT) [4-9], photo-induced electron transfer (PET) [10,11], solvatochromism [12-15], aggregation induced emission (AIE) [16,17] and excited state intramolecular proton transfer (ESIPT) [18,19]. In particular, ESIPT has attracted much attention for

its applications in chemosensors, biological imaging, luminescent materials and molecular logic gates, etc. [20-23] Generally, molecules can exhibit ESIPT fluorescence if their structures contain a hydrogen bond donor (-OH or NH_2) and a hydrogen bond acceptor (=N- or C=O) which can form an intramolecular hydrogen bond [24]. Large Stokes shift is one of the most significant photophysical properties of ESIPT-based chromophores compared to traditional fluorophores such as fluorescein, rhodamine, coumarin or BODIPY. It is an ideal feature for fluorophores due to the avoidance of self-absorption or inner filter effect, and the fluorescence analysis can be effectively improved by using this kind of fluorophores [25].

Although a large number of organic dye-based fluorescent chemosensors have been extensively developed for the determination of water content in organic solvents, most of the solvents tested are either non-polar or weakly polar organic solvents. Compared to other reported literatures (Table S1), few chemosensors for detection of trace water in strong polar organic solvents such as DMSO have been reported so far, and those with large Stokes shifts are even fewer.

As an ideal fluorophore and binding moiety, 8-hydroxyquinoline is one of the most useful chelating agents. Thus, various 8-hydroxyquinoline-based chemosensors have been prepared for the detection of metal cations, anions and pH [26-31]. To the best of our knowledge, only one report has been published regarding a 8-hydroxyquinoline-based fluorescent chemosensor for determination of water content in organic solvents such as acetonitrile, THF and dioxane, but stronger polar

solvents are not involved [32]. In this work, we synthesized two 8-hydroxyquinoline-based fluorescent chemosensors (HQCT and HQPH) for the detection of water content in strong polar organic solvents, (especially in DMSO and DMF), via an ESIPT mechanism with large Stokes shifts (≥ 128 nm), where the 8-hydroxyquinoline moiety acted as an ESIPT-based fluorophore. It is found that the water-sensing behaviors of HQCT and HQPH were ultra-fast and sensitive, with lower detection limits of 0.0220 wt % and 0.0274 wt % in DMSO, respectively. Based on ^{1}H-NMR titration and dynamic light scattering experiments, a plausible sensing mechanism was proposed. Finally, we successfully performed detection of water content in real samples with the chemosensors.

2. Experimental Section

2.1. Materials and methods

Unless otherwise stated, all chemicals and reagents were purchased from commercial suppliers (Heowns, Aldrich, Energy Chemical) and used without further purification. All solvents (i.e., DMSO, DMF, acetonitrile, tetrahydrofuran, dichloromethane, ethanol, ethyl acetate and 1,4-dioxane) for spectral analysis were dried by standard methods before using. Ultrapure water from a Millipore Milli-Q purification system was used for the titration. ^{1}H and ^{13}C-NMR spectra were collected on a Bruker Avance III 600 MHz instrument. Mass spectrometry was recorded on an Agilent 6520 Q-TOF mass spectrometer. UV-vis spectra were collected on a Lambda

35 (PerkinElmer) spectrometer using a quartz cell of 1 cm path length. The fluorescence spectra were recorded on an Edinburgh FLS920 spectrometer.

2.2. Synthesis and characterization of HQCT and HQPH

8-Hydroxyquinoline-2-carboxaldehyde (302.2 mg, 1.75 mmol) and thiosemicarbazide (192.5 mg, 2.11 mmol) were dissolved in 20 mL of absolute ethanol, and the solution was heated under reflux for 5 h. After cooling to room temperature, the resulting precipitate was collected by filtration and washed three times with cold absolute ethanol; then, the product was dried under vacuum at 45 °C for 48 h to produce 0.34 g of HQCT (79% yield) as pale yellow powder. m.p. 249 °C. ^{1}H NMR (600 MHz, DMSO-d_6, Fig. S1), δ (ppm): 11.81 (s, 1H, -N*H*-), 9.81 (s, 1H, -O*H*), 8.39 (d, 1H, Ar*H*), 8.38 (s, 1H, -NH_2), 8.28 (s, 1H, -NH_2), 8.23 (d, 1H, Ar*H*), 8.22 (s, 1H, -C*H*=N), 7.39 (t, 1H, Ar*H*), 7.33 (d, 1H, Ar*H*), 7.05 (d, 1H, Ar*H*). ^{13}C NMR (150 MHz, DMSO-d_6, Fig. S2), δ (ppm): 179.30, 153.89, 152.36, 142.97, 138.71, 136.66, 129.29, 128.59, 118.99, 118.28, 112.54. MS (ESI, Fig. S3): m/z $[M+H]^+$ calcd. for $C_{11}H_{11}N_4OS$: 247.06, found: 247.04.

8-Hydroxyquinoline-2-carboxaldehyde (302.2 mg, 1.75 mmol) and 2-picolinyl hydrazide (263.2 mg, 1.92 mmol) were dissolved in 20 mL of absolute ethanol, and the solution was heated to reflux and stirred for 4 h. After cooling to room temperature, the resulting precipitate was collected by filtration and washed three times with cold absolute ethanol; then, the product was dried under vacuum at 45 °C for 48 h to produce 0.42 g of HQPH (82% yield) as white solid. m.p. 226 °C. ^{1}H NMR

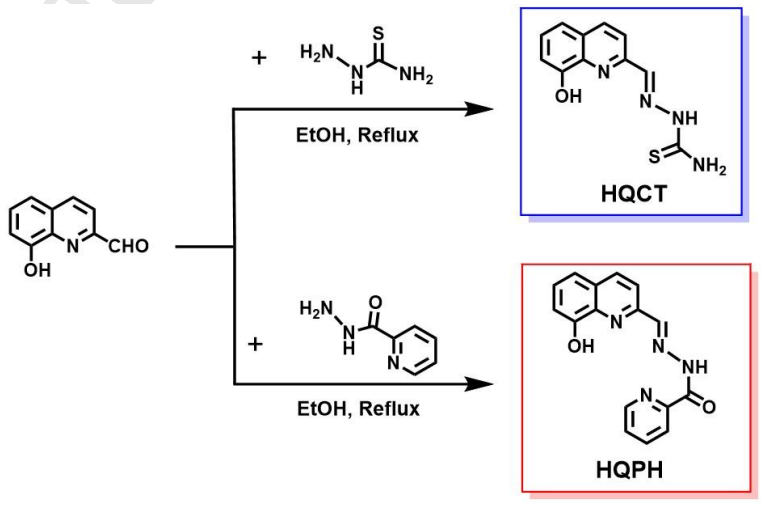
(600 MHz, DMSO-d_6, Fig. S4), δ (ppm): 12.69 (s, 1H, -N*H*-), 9.88 (s, 1H, -O*H*), 8.83 (s, 1H, -C*H*=N), 8.77 (d, 1H, Ar*H*), 8.35 (d, 1H, Ar*H*), 8.17 (d, 1H, Ar*H*), 8.13 (d, 1H, Ar*H*), 8.09 (t, 1H, Ar*H*), 7.71 (t, 1H, Ar*H*), 7.47 (t, 1H, Ar*H*), 7.42 (d, 1H, Ar*H*), 7.14 (d, 1H, Ar*H*). ^{13}C NMR (150 MHz, DMSO-d_6, Fig. S5), δ (ppm): 161.57, 153.97, 152.49, 150.12, 149.67, 149.10, 138.79, 138.53, 137.06, 129.44, 128.80, 127.64, 123.46, 118.41, 112.69. MS (ESI, Fig. S6): m/z $[M+H]^+$ calcd. for $C_{16}H_{13}N_4O_2$: 293.10, found: 293.10.

2.3. The detection limit

The detection limit was calculated based on the following equation: DL = 3σ/|k|, where σ is the standard deviation of the blank measurements and k is the slope between fluorescence intensity versus water content.

3. Results and discussion

3.1. Synthesis and characterizations



Scheme 1. Synthetic routes of HQCT and HQPH.

The synthetic routes of HQCT and HQPH are shown in Scheme 1. According to the literatures [33-36], HQCT and HQPH were successfully prepared by a simple condensation reaction of 8-hydroxyquinoline-2-carboxaldehyde with thiosemicarbazide or 2-picolinyl hydrazide in absolute ethanol under reflux conditions. The structures of HQCT and HQPH were confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy (MS) (see supporting information, Fig. S1-S6). The spectral data are in good agreement with the expected structures.

3.2. Spectral characteristics in different solvents

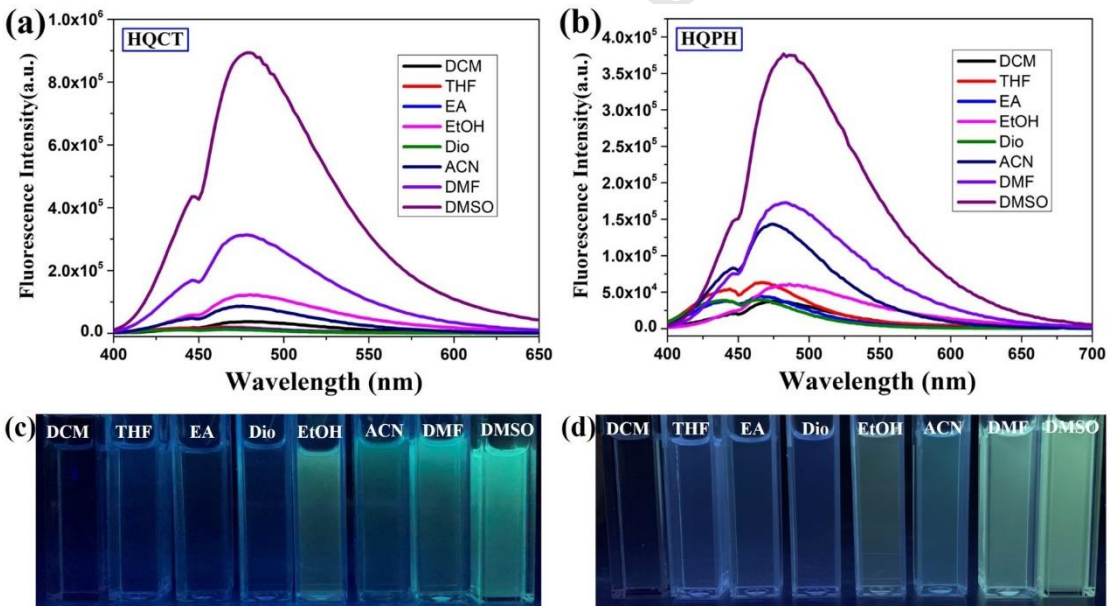


Fig. 1. (a) Fluorescence spectra of HQCT (20 μM) in different solvents, λ_{ex} = 350 nm. (b) Fluorescence spectra of HQPH (20 μM) in different solvents, λ_{ex} = 340 nm. Photographs of HQCT (c) and HQPH (d) in different solvents under a 365 nm UV lamp.

With the chemosensors in hand, the fluorescence and absorption spectra of HQCT and HQPH at a concentration of 20 μM were investigated in a variety of organic

solvents including dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (EA), ethanol (EtOH), dioxane (Dio), acetonitrile (ACN), N, N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The absorption spectra of HQCT and HQPH in different pure organic solvents were first investigated. As can be seen from Fig. S13, HQCT and HQPH displayed two major bands in the range of 290-310 nm and 330-360 nm, which can be attributed to π-π* and n-π* transitions [26].

Moreover, studies on the fluorescence of HQCT and HQPH in different organic solvents were also performed, the corresponding photophysical data are summarized in Table S2. The fluorescence spectra of HQCT showed a major emission peak around 480 nm with a shoulder peak at 445 nm (Fig. 1a). On the other hand, the HQPH exhibited a maximum emission peak around 486 nm with a shoulder peak at 450 nm (Fig. 1b). The emission peaks at 445 nm and 450 nm are assigned to the enol form, and the emission bands at 480 nm and 486 nm are attributed to the keto tautomer, produced by the ESIPT process [24]. The Stokes shifts of HQCT and HQPH in DMSO are 130 and 146 nm, respectively. The above large Stokes shifts can be attributed to the ESIPT [25]. Noticeably, there are slight changes of the absorption spectra in all the evaluated solvents. In contrast, the type of solvent has a significant effect on the fluorescence emission intensity of HQCT and HQPH. As shown in Fig. 1a and 1b, as the polarity of solvents increased from DCM to DMSO, the emission intensity changed significantly. For instance, the HQCT and HQPH in strong polar organic solvents such as DMSO and DMF exhibited strong fluorescence emissions. In contrast, in weakly polar organic solvents such as DCM, THF, EA and Dio, the

fluorescence intensity was very weak, which may be attributed to the formation of hydrogen bonds between high electronegativity oxygen atoms in solvent molecules and -OH in HQCT or HQPH, resulting in inhibition of the ESIPT process. Fig. 1c and 1d show the pictures of HQCT and HQPH in different organic solvents under illumination of 365 nm UV light. Obviously, the HQCT and HQPH in DMSO or DMF displayed strong blue-green fluorescence, but caused weak or no fluorescence in DCM, THF, EA and Dio under identical conditions. These experimental results are good consistent with the spectral data.

3.3. The fluorescence response to water content

It is found that the HQCT and HQPH emitted bright blue-green fluorescence in strong polar organic solvents, especially in DMSO and DMF, while their fluorescence was strongly quenched by the addition of water. Therefore, this phenomenon inspires us to detect water content in strong polar water-miscible organic solvents using HQCT or HQPH as a fluorescence sensor.

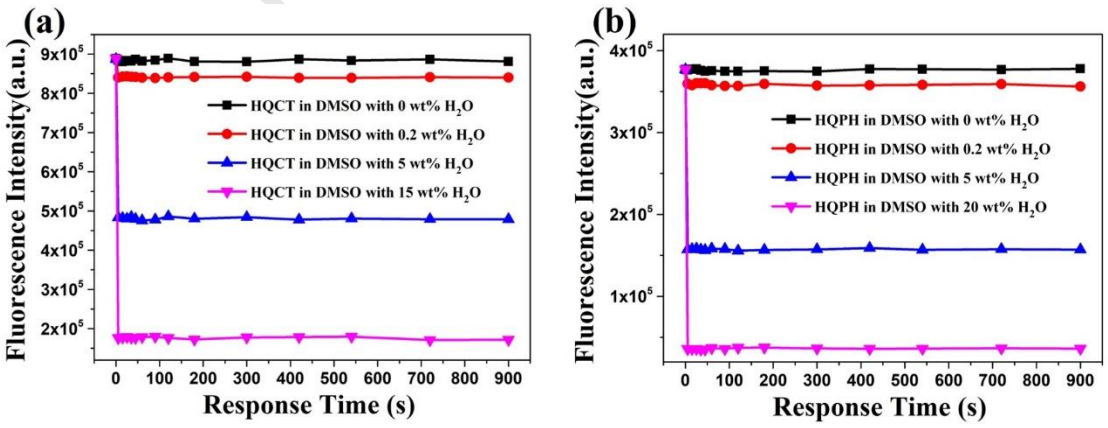


Fig. 2. (a) Fluorescence intensities at 480 nm of HQCT (20 μM) after addition of 0, 0.2, 5, 15 wt % water to DMSO as a function of time. (b) Fluorescence intensities at

486 nm of HQPH (20 μM) after addition of 0, 0.2, 5, 20 wt % water to DMSO as a function of time.

Firstly, DMSO is one of the most commonly used aprotic organic solvents in organic synthesis with strong polarity, which is often used as a solvent to dissolve water-insoluble compounds. DMSO has a very strong affinity for water. Once exposed to air, pure DMSO will soon be diluted with water [37]. To evaluate the practicality of HQCT and HQPH for water sensing, a variety of experiments were carried out to measure the response time. As shown in Fig. 2, upon adding a certain amount of H_2O to DMSO, the fluorescence intensity of HQCT and HQPH decreased immediately in less than 5 s and remained stable over a period of 15 min, indicating that both HQCT and HQPH show a fast response toward water and can be used for practical applications.

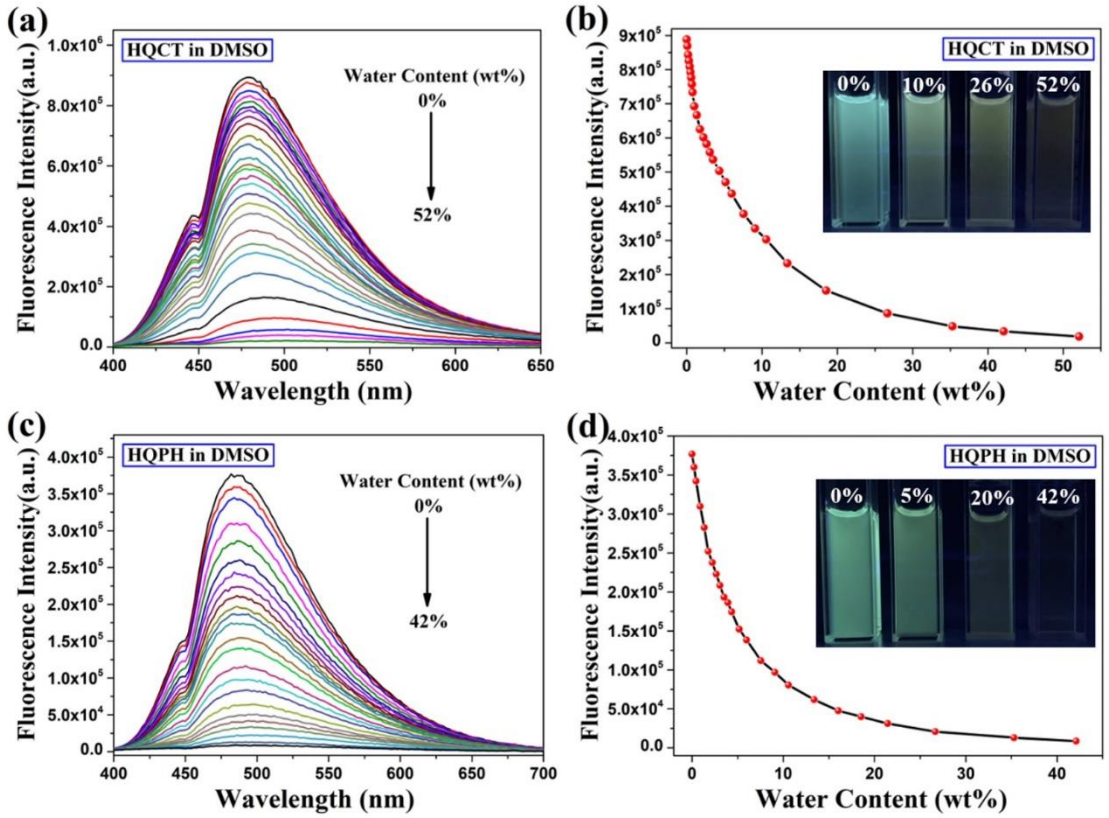


Fig. 3. Fluorescence spectra (a) and changes in fluorescence intensity at 480 nm (b) of HQCT (20 μM) in DMSO with increasing water content, λ_{ex} = 350 nm. Inset: photographs of HQCT in DMSO with increasing water content under a 365 nm lamp. Fluorescence spectra (c) and changes in fluorescence intensity at 486 nm (d) of HQPH (20 μM) in DMSO with increasing water content, λ_{ex} = 340 nm. Inset: photographs of HQPH in DMSO with increasing water content under a 365 nm lamp.

Fig. 3a and 3c display the fluorescence responses of HQCT and HQPH with the addition of water to anhydrous DMSO. With the increase of water content (0-15 wt% for HQCT and 0-10 wt% for HQPH, respectively), the fluorescence intensity of chemosensors (20 μM) was drastically decreased, and then decreased slightly with further increase of water content (15-52 wt% for HQCT and 10-42 wt% for HQPH, respectively). In addition, with gradual increase of water content in DMSO, obvious

color changes from intense blue-green to weak yellow-green, to colorless were easily observed by the naked eye under UV 365 nm excitation (insets in Fig. 3b and 3d), suggesting that HQCT and HQPH can be used for qualitative analysis of water content in organic solvents. Moreover, as seen from Fig. S14, with increasing water content in DMSO, the normalized fluorescence emission peak showed a slight bathochromic shift from 480 to 502 nm for HQCT, from 486 to 498 nm for HQPH, respectively. The red-shift of emission peak can be attributed to the solvatochromic emission property of chemosensors in DMSO/H_2O mixtures, which is induced by a progressively increasing portion of the more polar water [38]. These results are in accordance with the photos taken under a 365 nm UV lamp (insets in Fig. 3b and 3d).

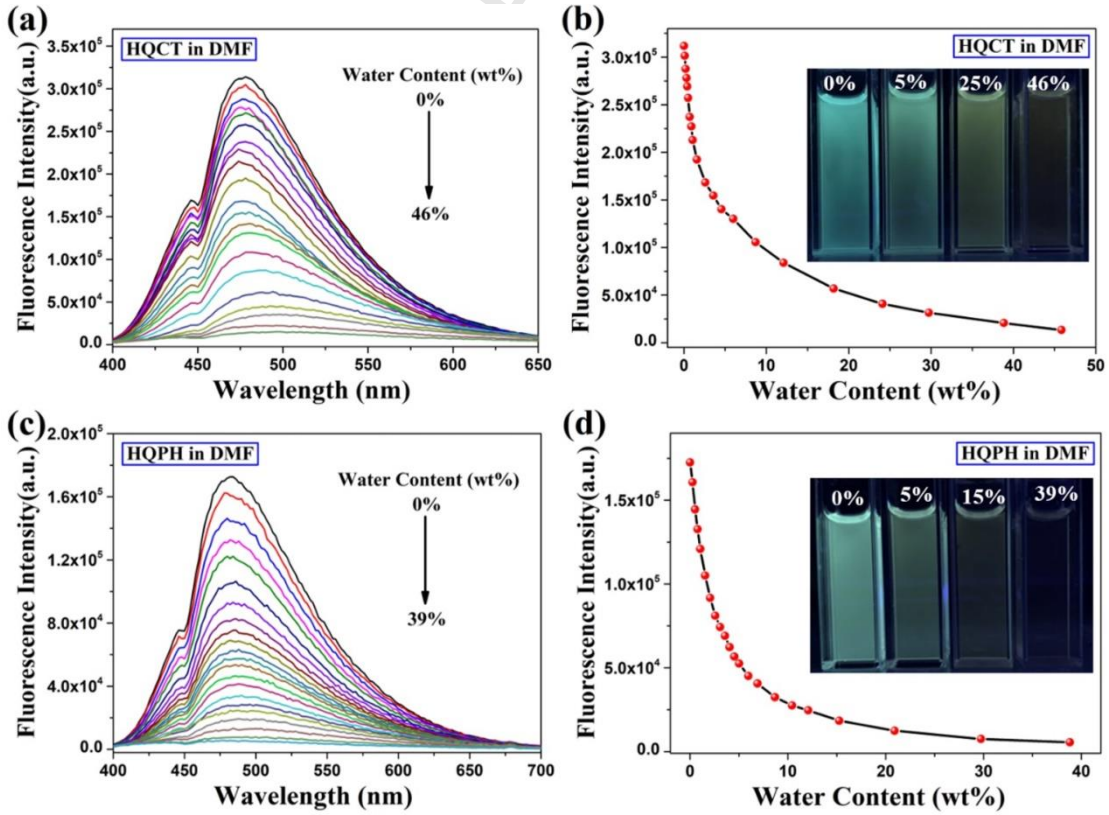


Fig. 4. Fluorescence spectra (a) and changes in fluorescence intensity at 478 nm (b) of HQCT (20 μM) in DMF with increasing water content, λ_{ex} = 350 nm. Inset:

photographs of HQCT in DMF with increasing water content under a 365 nm lamp. Fluorescence spectra (c) and changes in fluorescence intensity at 484 nm (d) of HQPH (20 μM) in DMF with increasing water content, λ_{ex} = 340 nm. Inset: photographs of HQPH in DMF with increasing water content under a 365 nm lamp.

DMF is not only an excellent polar solvent for various compounds, but also can react as a chemical reagent [39]. Hence, we further tested the fluorescence emission behaviors of HQCT and HQPH in DMF. Fig. 4 shows the fluorescence changes of HQCT and HQPH after adding different amounts of water to anhydrous DMF. It is clear that the maximum emission of HQCT and HQPH in DMF is more sensitive to a low-level water content. As the water content increased from 0 to 5 wt %, the fluorescence intensity of HQCT and HQPH in DMF was reduced by 55% and 70%, respectively, compared to 47% and 58% decreased in DMSO, respectively. In addition to this, other spectral behaviors including a decrease in fluorescence intensity (Fig. 4a and 4c) and a slight bathochromic shift with increasing water content in DMF were similar to those observed in DMSO. In detail, as the water content increased from 0 to 46 wt %, the emission peak of HQCT at 478 nm was gradually red shifted to 498 nm (Fig. S15a), while the emission peak of HQPH at 484 nm was progressively red shifted to 494 nm with increasing water content from 0 to 39 wt % (Fig. S15b). Furthermore, as shown in the insets of Fig. 4b and 4d, HQCT and HQPH exhibited apparent fluorescent color variations from intense blue-green to weak yellow-green, to colorless under UV irradiation (365 nm). Finally, we evaluated the fluorescence responses of chemosensors in dry ACN and EtOH. As shown in Fig. S16 and S17, the changes in fluorescence intensity of HQCT and HQPH in response to

increasing water content in ACN and EtOH solvents followed a similar trend with that in DMSO and DMF under the same conditions, but with relatively weaker fluorescence intensity and lower fluorescence quenching percentage.

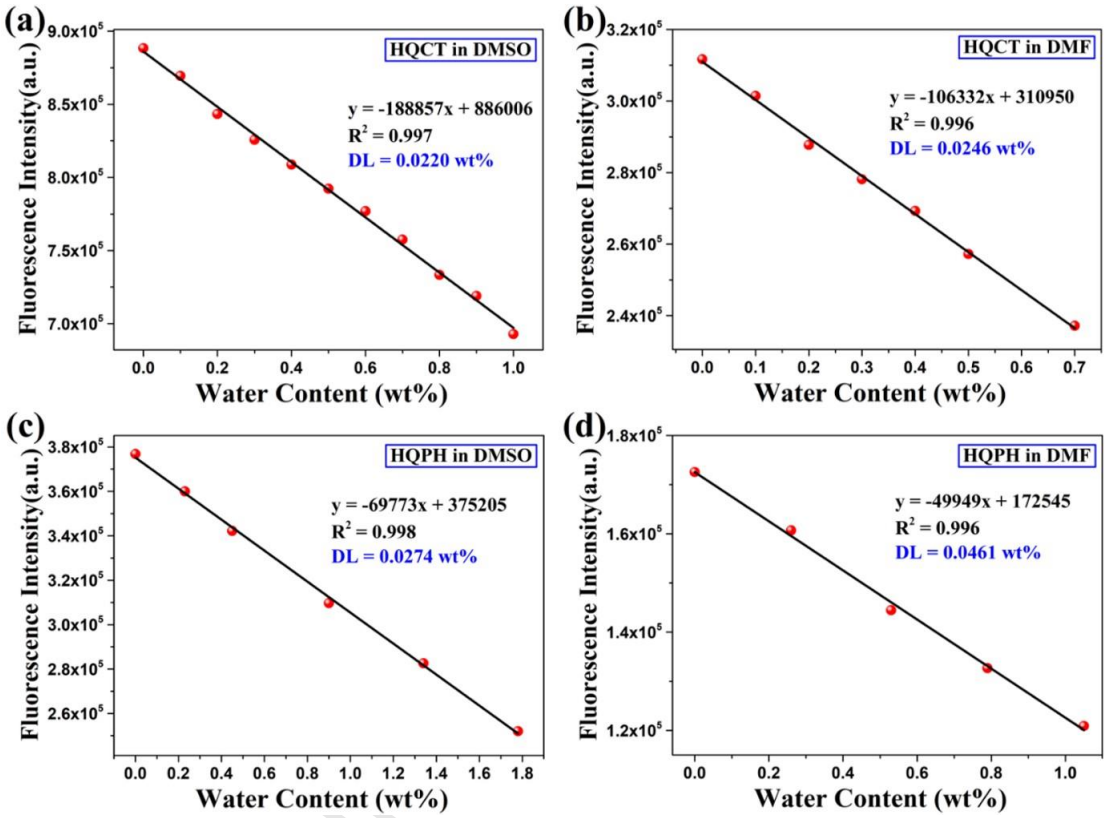


Fig. 5. Plot of the fluorescence intensity of HQCT (20 μM) *vs*. water content in DMSO (a) and DMF (b). Plot of the fluorescence intensity of HQPH (20 μM) *vs*. water content in DMSO (c) and DMF (d).

In order to assess the possibility of quantitative detection of trace water, we investigated the sensing performance of chemosensors in different dry organic solvents (i.e., DMSO, DMF, ACN and EtOH). Fig. 5 and S18 show that the plots of the fluorescence intensity of HQCT and HQPH versus the water content (wt %) exhibit good linearity over a range of different water contents, with a correlation coefficient (R^2) of 0.997, 0.996, 0.995, 0.996, 0.998, 0.996, 0.993 and 0.994 for

HQCT/DMSO, HQCT/DMF, HQCT/ACN, HQCT/EtOH, HQPH/DMSO, HQPH/DMF, HQPH/ACN and HQPH/EtOH systems, respectively. Furthermore, detection limits were calculated based on the 3σ/|k| method. The detection limits (DLs) of HQCT for water content were calculated to be 0.0220 wt %, 0.0246 wt %, 0.1404 wt %, and 0.1513 wt % in DMSO, DMF, ACN, and EtOH, respectively. While the DL (wt %) values of HQPH for water content in DMSO, DMF, ACN, and EtOH were determined to be 0.0274, 0.0461, 0.0221, and 0.0595, respectively. It is noteworthy that the water-sensing performance of HQCT and HQPH slightly depends on the examined solvent. HQCT displayed the highest sensitivity toward water in DMSO, followed by DMF, ACN, and EtOH. However, the lowest detection limit for HQPH was achieved in ACN, followed by DMSO, DMF, and EtOH. Compared to previously reported chemosensors based on organic dyes (Table S1), the lower detection limits of HQCT and HQPH for water content in DMSO are observed. These results indicate that HQCT and HQPH can be used as fluorescent sensors to quantify and accurately analyze the water content of some organic solvents, especially in strong polar organic solvents such as DMSO and DMF.

3.4. The detection mechanism toward water

In order to find out the cause of water-induced fluorescence quenching in organic solvents, the aggregation states of HQCT and HQPH were first investigated by dynamic light scattering (DLS). As shown in Fig. S19, when adding 6 wt % water to HQCT or 35 wt % water to HQPH in DMSO, the hydrodynamic diameter was below

2 nm, implying no aggregation formation in the solution. In contrast, significant fluorescence quenching of chemosensors was observed under the same conditions. The above results indicate that there is no direct causal relationship between fluorescence quenching and aggregation, so the aggregation-caused quenching (ACQ) can be ruled out.

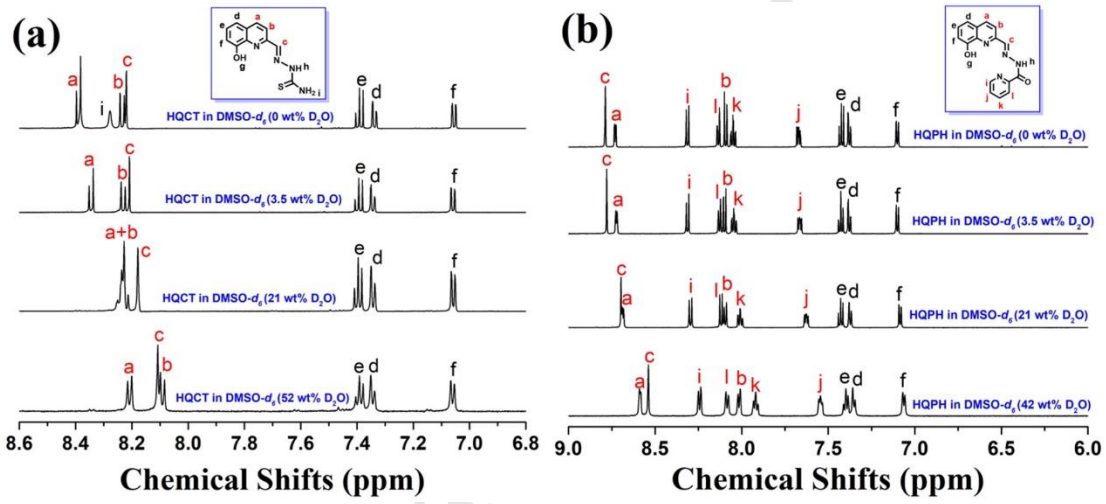
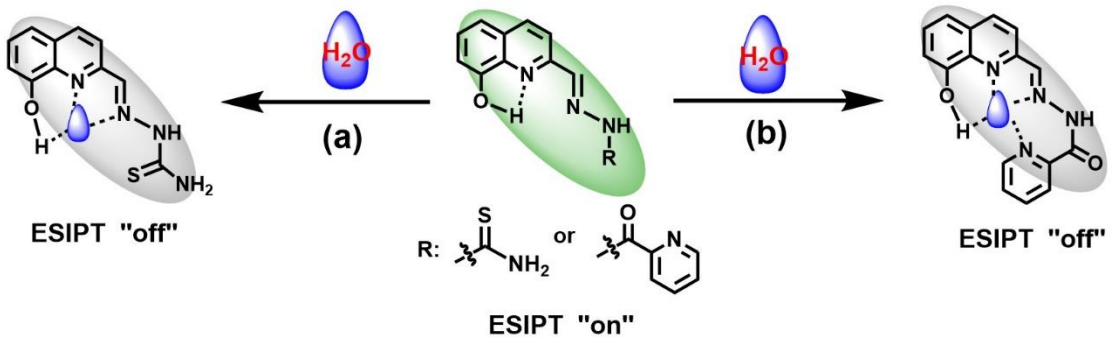


Fig. 6. Partial ^{1}H-NMR spectra of HQCT (a) and HQPH (b) in DMSO-d_6 containing different amounts of D_2O.

To further elucidate the mechanism for the detection of water, ^{1}H NMR spectral measurements of HQCT and HQPH in DMSO-d_6/D_2O mixtures at different contents of D_2O were performed. As shown in Fig. S1, the ^{1}H NMR spectrum of HQCT in DMSO-d_6 without adding D_2O were in good consistent with its structure. Upon addition of D_2O, the signals at 11.81 ppm (the peak h), 9.81 ppm (the peak g), 8.38 ppm (the peak i) and 8.28 ppm (the peak i) representing the protons of -OH, -NH-, and -NH_2 disappeared completely owing to fast hydrogen/deuterium exchange (Fig.

S20a) [40]. At the same time, in a magnified view (Fig. 6a), most of the proton signals were shifted to the high field with increasing water content, especially the peaks a, b and c from the quinoline ring and -CH=N-, indicating that the chemical environment of protons has changed. Similar results were also observed in the ^{1}H NMR titration experiments of HQPH in DMSO-d_6 with D_2O (Fig. 6b and S20b). The only difference was that the proton signals (the peaks i, j, k and l) on the pyridine ring also moved to the high field, which means that the nitrogen atom on the pyridine ring are also involved in the interaction with water.

In addition to the above phenomena, we also note that the hydroxyl groups substituted at the 8-position of HQCT and HQPH are likely to play an important role in the fluorescence emission processes. Therefore, two control compounds (QCT and QPH) without hydroxyl groups substituted at the 8-position were designed to confirm this hypothesis. The synthetic routes of QCT and QPH are shown in Scheme S1. Detailed synthesis procedures can be found in the supporting information. The chemical structures of QCT and QPH were well characterized using ^{1}H NMR, ^{13}C NMR and mass spectroscopy (MS) (Fig. S7-S12). As expected, QCT and QPH had no fluorescence emission in DMSO, while HQCT and HQPH exhibited strong fluorescence (Fig. S21).



Scheme 2. Proposed detection mechanisms of HQCT (a) and HQPH (b) toward H_2O.

Based on the above experimental results, the sensing mechanisms of HQCT and HQPH for the detection of water in DMSO are proposed as depicted in Scheme 2. When trace amounts of water are added to HQCT/DMSO or HQPH/DMSO solution, the intramolecular hydrogen bonding (-OH---N-) needed for the ESIPT process is inhibited by H_2O via forming hydrogen bonds with -OH and N atoms, which can result in fluorescence "turn off".

3.5. Interference studies from pH and metal ions

The influence of pH value of water in DMSO and DMF on fluorescence emission intensity of HQCT and HQPH was investigated with a wide range of pH (pH 1.0-14.0). As shown in Fig. 7, after adding water (5 wt %) with different pH values, the fluorescence intensity of HQCT and HQPH in DMSO and DMF was quite stable below pH 10.0, which indicated a wide range of practical usability of HQCT and HQPH in sensing water. When the pH value was raised above 10.0, the fluorescence intensity of HQCT and HQPH decreased sharply. This is likely because the hydroxyl

group of HQCT and HQPH was deprotonated under high alkaline conditions, resulting in the disruption of the ESIPT process.

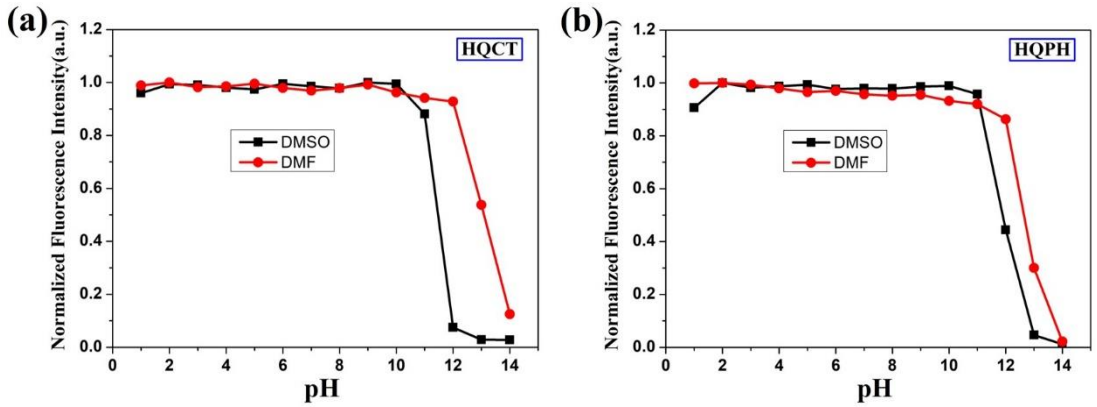


Fig. 7. Fluorescence intensity changes of HQCT (20 μM) (a) and HQPH (20 μM) (b) in DMSO and DMF after adding water (5 wt %) with different pH values.

The practicability of HQCT and HQPH for detecting water in organic solvent was verified by fluorescence interference experiment, possible interference ions (Zn^{2+}, Cd^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Pb^{2+}, K^{+}, Li^{+}, Na^{+}, Al^{3+}, Cr^{3+}, Hg^{2+}) were tested. First, the metal ions were separately added to the system containing only HQCT or HQPH, and the fluorescence emission spectral data were collected after being mixed. Then the water was added to the above system, and the fluorescence spectrum was taken. As shown in Fig. 8, the results showed that the water-sensing behaviors of HQCT and HQPH in DMSO were not obviously interfered by the coexistent metal ions (1.0 equiv.), except for Cu^{2+}. The interference of Cu^{2+} may be related to its strong fluorescence quenching characteristics [41].

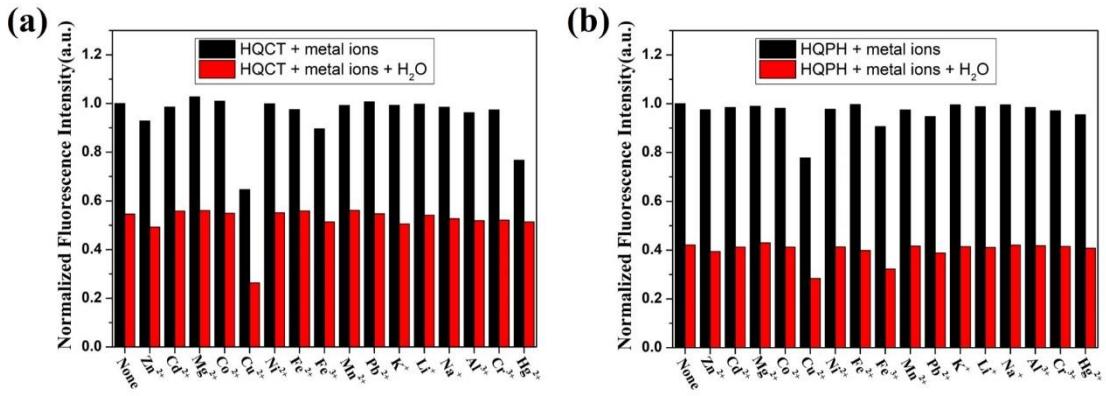


Fig. 8. The fluorescent intensity of HQCT (20 μM) (a) and HQPH (20 μM) (b) in DMSO with 1.0 equiv. of various metal ions, and then added 5 wt % water.

3.6. Fluorescence detection of water content in real samples

Table 1. Determination of water content in real organic solvent samples.

Chemosensors	Samples	Water content (wt %)	Added (wt %)	Found (wt %)	Recovery (%)
HQCT	DMSO	≤ 0.005	0.230	0.237 ± 0.012	103
	DMF	≤ 0.005	0.320	0.316 ± 0.023	99
	ACN	≤ 0.005	0.750	0.730 ± 0.041	97
	EtOH	≤ 0.005	0.750	0.712 ± 0.033	95
HQPH	DMSO	≤ 0.005	0.900	0.885 ± 0.016	98
	DMF	≤ 0.005	0.500	0.524 ± 0.029	105
	ACN	≤ 0.005	0.370	0.365 ± 0.021	99
	EtOH	≤ 0.005	0.750	0.727 ± 0.037	97

To explore the practical application of chemosensors to measure trace water in real samples, four commercial solvents (DMSO, DMF, ACN and EtOH. Extra dry, with molecular sieves, water ≤ 50 ppm) purchased from Energy Chemical were employed to measure the recovery of water using standard addition method. The values of water content derived from calibration equation and the recoveries were summarized in Table 1. Seen from Table 1, the reasonable spiked recoveries were obtained both for HQCT and HQPH, indicating that the present method can be used in real organic solvent samples.

4. Conclusions

In summary, two 8-hydroxyquinoline-based fluorescent chemosensors (HQCT and HQPH) were designed and successfully synthesized. The fluorescence emission intensity of chemosensors strongly depends on the solvent polarity. Specifically, the chemosensors in strong polar organic solvents such as DMSO and DMF exhibited strong fluorescence emission with large Stokes shifts, while displaying weak or no fluorescence emission in weakly polar organic solvents. Furthermore, as the water content increased in four water-miscible organic solvents, the pronounced fluorescence quenching and color changes could be observed due to the inhibition of ESIPT process. In addition, the low limit of detection allows HQCT and HQPH to be utilized as ultra-sensitive water chemosensors for the quantitative detection of low-level water in organic solvents (DMSO, DMF, ACN, and EtOH). We expect that

the work in this paper will expand the scope of research and application of water-sensitive sensors in organic solvents.

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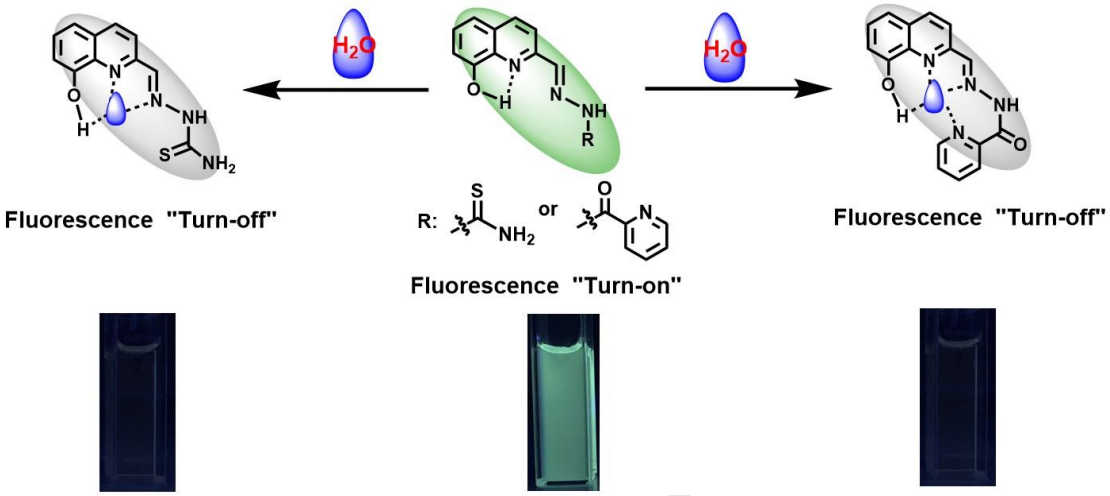
Graphical abstract



Highlights

- The two 8-hydroxyquinoline based fluorescent chemosensors (HQCT and HQPH) were designed and successfully synthesized by a simple condensation reaction.
- The chemosensors are especially responsive to water in strong polar organic solvents such as DMSO and DMF with large Stokes shifts ($\geq$ 128 nm).
- The chemosensors can quickly (less than 5 s) detect H_2O in DMSO with low detection limits.
- The chemosensors were successfully applied for the detection and quantitation of trace water in real organic solvent samples.

Author Contributions

J. T. Wang, Y. Y. Pei and Q. F. Li conceived, designed and supervised the experiments and wrote the paper. J. T. Wang, Y. Y. Pei, S. F. Ren, M. Y. Yan, W. Luo, and B. Zhang performed the experiments and analyzed the data. All authors reviewed the manuscript.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: