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A general strategy for in situ generation of coumarin-Cu²⁺ complex for fluorescent water sensing

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ABSTRACT: Detection of moisture in organic solvents is very important before they are used in water sensitive reactions. Herein, we report that coumarins **D1** and **D2** were able to generate corresponding water sensitive copper complexes **D1-Cu** and **D2-Cu** in common organic solvents, which can be used as efficient fluorescent turn-on sensors for water. Single crystal diffraction analysis of the reaction product indicated that the sensing mechanism is based on the formation of water bridged 3D supramolecular hydrogen bonding network. We demonstrated that the hydroxyl or amine group substituted at the 7-position of the coumarin framework played a key role in the water sensing performance of **D1-Cu** and **D2-Cu**, by acting as a hydrogen bond acceptor in the supramolecular network. This provided a general strategy for designing such coumarin based copper complexes for fluorescent water sensing. The water sensing behavior of **D1-Cu** and **D2-Cu** were determined to be fast, pH tolerant and sensitive. As low as 0.0525 wt % of water in methanol can be detected using **D1-Cu** as the sensor. Moreover, **D1-Cu** was successfully used for moisture sensing in real commercial products.

INTRODUCTION

Water is an essential substance of life, but is also considered as an impurity in organic solvents.¹ The presence of even trace of water in organometallic reactions may lead to quenching of the reaction or even catastrophic incidents such as fire and explosion.² Therefore, it is of great importance to detect moisture in organic solvents before performing chemical reactions and industrial production processes.³⁻⁴ Moreover, sensing of relative humidity is also very important for instrument maintenance and storage of many water sensitive chemicals and commercial products.⁵⁻⁶

To date, various analytical methods have been developed for water detection. A classical method is the Karl Fischer titration, which is determined to be accurate and selective.⁷ However, this method is time-consuming and requires toxic reagents such as SO₂, and it is unsuitable for redox-active samples.⁸ The development of novel convenient and reliable methods for water detection is still a hot research topic.⁹⁻¹² In recent years, chromatography, electrochemical analysis and spectroscopic technique based methods have been reported for water sensing.¹³⁻¹⁶ Among them, small molecule based optical sensors with distinct color and/or fluorescence changes attracted our attention.¹⁷⁻¹⁹ These molecular sensors are easy to operate, sensitive and even allow water detection with naked eyes. For example, by assembling AIE-active molecular rotors and poly(acrylic acid), AIE sensors were reported by Tang group for fast, sensitive, quantitative and high spatial-temporal resolution visualization of relative humidity.²⁰ Kim, Lee and their co-workers reported a series of coumarin based Schiff bases for sensitive water detection based on a hydrolysis

reaction mechanism.²¹ These exciting results suggest that fluorescent molecular sensor can be considered as an excellent tool for water sensing.

A commonly used strategy for designing fluorescent molecular sensors is to introduce a specific reaction unit for the target analyte into the chosen fluorophore.²²⁻²⁸ However, this strategy is not ideal for designing practical fluorescent sensors for water. Because both of the synthesis and storage of a water sensitive compound are not convenient, which require a highly dry atmosphere. It is more reasonable that a water sensitive material is generated "in situ" when water detection is needed. A representative example is the benzophenonesodium system, which is widely used in many labs for organic solvent drving.²⁹ In this system, benzophenone is reduced by sodium to afford a water sensitive, deeply blue colored radical anion, saying diphenylketyl, to report whether the solvent is dry enough. This suggests that the strategy of "in situ" generation of the water sensitive material is ideal for the design of practicable fluorescent sensor for water.

In this paper, we report that coumarins **D1** and **D2** were able to generate corresponding water sensitive copper complexes in common organic solvents (Scheme 1). The addition of Cu^{2+} into the organic solution of **D1** and **D2** afforded complexes **D1-Cu** and **D2-Cu** respectively, both of which were almost non-fluorescent in dry organic solvents but show bright fluorescence emission in the presence of trace water. The sensing mechanism was carefully investigated by X-ray single crystal diffraction analysis, UV-Vis spectroscopy, fluorescence spectroscopy and NMR studies. It was demonstrated that the formation of a water bridged 3D

supramolecular hydrogen bonding network was responsible for the fluorescence enhancement. Moreover, we discovered that the hydroxyl or amine group substituted at the 7-position of the coumarin framework played a key role in the water sensing performance of D1-Cu and D2-Cu by acting as a hydrogen bond acceptor. As the copper complex of the control molecule **D3** showed negligible fluorescence response towards water (Scheme 1). Therefore, D1-Cu and D2-Cu were successfully used as an "in situ" generated agent for water detection in a fluorescence turn on manner in various common organic solvents, including acetonitrile, methanol, ethanol, DMF and THF. The water sensing behavior of D1-Cu and D2-Cu was determined to be fast, pH tolerant and sensitive, with a lowest detection limit of 0.0525 wt % in methanol. The promising sensing performance even allowed D1-Cu to be used for moisture measurement in real commercial products such as NaOH, dextrin and potato starch.

Scheme1. Chemical structure of coumarins D1-D3.



EXPERIMENTAL SECTION

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Materials and Instrument. All reagents were of analytical grade and were used as received. The water used was deionized water. UV-Visible absorption spectra were recorded on a SHIMADZU UV-2600 Spectrophotometer. Fluorescence titration experiments were performed on a Horiba Fluoromax-4 fluorescence Spectrophotometer with a quartz cuvette (path length = 1 cm).

General synthetic procedure for D1-D3. Compounds D1-D3 were synthesized according to the literature methods and characterized by NMR and HRMS (Figures S1-6).³⁰⁻³² Generally, 1 mmol of salicylaldehyde or its derivatives (4-Diethylamino-salicylaldehyde for synthesis of D1; 2,4-Dihydroxybenzaldehyde for synthesis of D2; Salicylaldehyde for synthesis of D3), Meldrum's acid (144 mg, 1 mmol) and K₂CO₃ (28 mg, 0.2 mmol) were added into distilled water (5 mL). Then, the mixture was stirred vigorously at room temperature for 24 h to complete the reaction. The resulting solution was acidified with hydrochloric acid. The precipitate was collected by filtration and washed with water for several times to obtain pure D1-D3.

D1 (orange solid, yield: 96%): ¹H NMR (400 MHz, DMSOd6) δ 12.52 (s, 1H), 8.58 (s, 1H), 7.63 (d, 1H, J = 8.8 Hz), 6.79 (d, 1H, J = 8.8 Hz), 6.57 (s, 1H), 3.49 (m, 4H), 1.14 (t, 6H, J = 6.8 Hz). HRMS: observed: 262.1075, calculated for C₁₄H₁₆NO₄ ([M+H]⁺): 262.1079.

D2 (white solid, yield: 96%): ¹H NMR (400 MHz, DMSOd6) δ 8.69 (s, 1H), 7.75 (d, 1H, J = 8.8 Hz), 6.85 (m, 1H), 6.74 (d, 1H, J = 2.4 Hz). HRMS: observed: 207.0293, calculated for C₁₀H₇O₅ ([M + H]⁺) 207.0293.

D3 (white solid, yield: 95%): ¹H NMR (400 MHz, Acetoned6) δ 12.14 (s, 1H), 8.98 (s, 1H), 8.06 (m, 1H), 7.89 (m, 1H), 7.57 (m, 2H). HRMS: observed: 191.0342, calculated for $C_{10}H_6O_4$ ([M + H]⁺) 191.0344.

UV/Vis Absorption and Fluorescence Spectrum Measurements. Both of the absorption and fluorescence emission spectra were measured at room temperature. Stock

solutions of **D1** and **D2** (2 mM) were freshly prepared with dry solvents (acetonitrile, methanol, ethanol, THF and DMF) and diluted to 10 μ M before all absorption and fluorescence measurements. Cu²⁺ was added as cupric acetate monohydrate or cupric sulphate pentahydrate dissolved in corresponding dry solvents. Deionized water was used for the water titration study. The slit width for fluorescence emission spectral measurements was set at 3 nm.

Crystallography. Single crystal suitable for X-ray analysis of Cu(D2)2.4H2O was obtained by slow evaporation of the acetonitrile/H₂O solution of D2-Cu at room temperature. Crystal data for $Cu(D2)_2 \cdot 4H_2O$: $C_{20}H_{18}CuO_{14}$, $M_w = 545.88$, $0.15 \times 0.12 \times 0.10$ mm³, Monoclinic, C2/c, a = 24.606(6) Å, b = 6.6699(16) Å, c = 13.439(3) Å, α = 90°, β = 113.247(7)°, γ = 90°, V = 2026.6(9) Å³, F(000) = 1116, $\rho_{calcd} = 1.789$ Mg/m³, μ (Mo K α) = 1.160 mm⁻¹, T = 296(2) K, 7748 data measured on a Bruker SMART Apex diffractometer, 2289 of which were unique ($R_{int} = 0.0280$), 161 parameters refined against F_{02} (all data), final wR2 = 0.1185, S = 1.047, R1 (I > $2\sigma(I)$) = 0.0452, largest final difference peak/hole +1.827/-0.528 e Å⁻³, structure solution by direct methods and full-matrix least squares refinement against F2 (all data). CCDC 1881528 (Cu(D2)₂·4H₂O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

RESULTS AND DISCUSSION

During the investigation on coumarin based fluorescent sensors, our group found that the metal complex of a very simple coumarin could exhibit interesting fluorescence properties and be developed as fluorescent sensor for metal ions or anions.³³⁻³⁴ In the structures of **D1** and **D2**, the carboxyl group was designed as a metal chelation site, which enabled their ability to coordinate with metal ions. During the investigation of the optical response of D1 and D2 towards various metal ions, we found that the most significant fluorescence quenching was observed when Cu2+ was added (Figure S7). Importantly, in the coexistence of other metal ions, the successive addition of Cu²⁺ strongly quenched the fluorescence to an extent almost equal to that with only Cu²⁺, indicating that D1 and D2 show high binding affinity towards Cu²⁺ to generate corresponding non-fluorescent copper complexes as D1-Cu and D2-Cu. Unexpectedly, we then discovered that the non-fluorescent organic solution of D1-Cu and D2-Cu becomes highly fluorescent in the presence of water. This phenomenon urged us to further investigate its deep mechanism and potential application in water sensing.

We first investigated the ability of **D1** and **D2** to form corresponding Cu^{2+} complexes in dry organic solvents such as acetonitrile, methanol, ethanol, THF and DMF. In dry methanol, **D1** (10 µM) displayed two strong absorption bands at ~260 nm and ~427 nm (Figure 1a). The addition of Cu^{2+} to the solution induced vivid spectral changes, as the original absorption peaks at 260 and 427 nm became much stronger, while the absorption band at ~378 nm gradually decreased. Two isobestic points were found at ~352 and ~402 nm during the titration process, indicating that a new complex **D1-Cu** was formed. The formation of the **D1-Cu** complex was also observed during the fluorescence titration experiments. As shown in Figure 1b, **D1** was highly fluorescent in methanol with a strong emission peak at ~453 nm. The fluorescence

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intensity decreased significantly during the addition 0-1.4 equiv. of Cu²⁺. This result was not surprising as Cu²⁺ complexes of fluorescent ligands are usually non-fluorescent due to the paramagnetic property of Cu²⁺. Similar Cu²⁺ binding induced absorption changes and fluorescence quenching of D1 were also observed when other solvents such as acetonitrile, ethanol and DMF were used (Figures S8-S10). Besides, the binding of Cu²⁺ to **D2** was also determined by UV-Vis and fluorescence spectral changes in acetonitrile, methanol, ethanol and THF (Figures S11-S14). Moreover, binding of Cu²⁺ to **D1** and **D2** was confirmed by the broad NMR signal of the complex (Figures S15-S16). These results indicated that both of D1 and D2 were able to form corresponding nonfluorescent Cu²⁺ complexes in common dry organic solvents. The binding stoichiometry between **D1** and **D2** with Cu^{2+} was determined to be 2:1 (ligand:metal) according to the Job Plot data (Figure S17), which is in accordance with the X-ray single crystal analysis data (vide infra).



Figure 1. a) UV-Vis absorption spectral changes of **D1** (10 μ M) upon titration with 0-1.4 equiv. of Cu²⁺ in dry methanol; b) Corresponding fluorescence emission spectral changes. λ_{ex} =402 nm.

Unexpectedly, we found that if water was added into the organic solution of **D1-Cu** and **D2-Cu**, a bright fluorescence "turn on" was observed by the naked eyes (Figure S18). Water titration experiments were then carried out to investigate the moisture sensing ability of **D1-Cu** and **D2-Cu** in common organic solvents including acetonitrile, methanol, ethanol, DMF and THF. These solvents were selected for the test because they are miscible with water and easily contaminated by it. As shown in Figure 2a-2d, vivid fluorescence enhancement was observed during gradual addition of water into the dry organic solution of **D1-Cu** in acetonitrile, methanol, ethanol and DMF. While **D2-Cu** showed fluorescence turn on response towards water in acetonitrile, methanol, ethanol and THF (Figure S19). Analysis of the

titration data revealed the relationship between emission intensity and water content of D1-Cu and D2-Cu in tested solvents (Figure 2e and 2f). It can be seen that **D1-Cu** showed the sharpest fluorescence turn on response towards water in methanol, while **D2-Cu** showed the best performance in THF. The linear response range and linear fit of D1-Cu and D2-Cu for water were summarized in Table 1. The detection limits (DL) of D1-Cu and D2-Cu for water were calculated based on the IUPAC $3\sigma/s$ definition, where the σ is the standard deviation of blank samples and s is the slope of the calibration curve (Figures S20-S21, Table 1). The DL (wt %) of D1-Cu for water in acetonitrile, methanol, ethanol and DMF were determined to be 0.0749, 0.0525, 0.2364 and 0.2716, respectively. The DL (wt %) of D2-Cu for water in acetonitrile, methanol, ethanol and THF were found to be 0.3313, 0.1856, 0.1560 and 0.0745, respectively. We noticed that the water sensing performance of **D1-Cu** and **D2-Cu** were slightly dependent on the solvent tested. D1-Cu showed the highest sensitivity towards water in methanol, followed by acetonitrile, ethanol, and then DMF. While for D2-Cu, the lowest detection limit was achieved in THF, followed by ethanol, methanol and acetonitrile. The achieved water detection limits of D1-Cu and D2-Cu were comparable to literature reports (Table S1). Further considering the facile synthetic chemistry and stability of D1 and D2, and their ability for in situ generation of corresponding water sensitive copper complexes, strong practicability of D1-Cu and D2-Cu for water detection in commercial organic solvents could be expected.

The promising moisture sensing ability of D1-Cu and D2-Cu urged us to investigate the deep mechanisms. It was firstly confirmed that **D1** and **D2** showed no spectral response towards water, indicating that formation of the Cu²⁺ complex is responsible for their moisture sensing ability (Figure S22). We initially envisioned that the presence of water may decompose complexes D1-Cu and D2-Cu and regenerate D1 and **D2**. However, this hypothesis was proven to be incorrect by UV-Vis, fluorescence, NMR, and single crystal data. Firstly, the addition of water to the dry solution of **D1-Cu** and D2-Cu has not fully recovered the original fluorescence. For example, the addition of water to D1-Cu in dry acetonitrile generated an emission peak at 459 nm, while the original emission peak of **D1** in dry acetonitrile was centered at 471 nm (Figures 2a and S8b). A blue shift of 12 nm indicated the possibility of the formation of a new species but not regeneration of the original compound. Moreover, NMR studies also suggested that addition of water to D1-Cu and D2-Cu failed to regenerate compounds D1 and D2 (Figures S15-S16). To further elucidate the deep sensing mechanism, we tried to grow the single crystal of the reaction products of D1-Cu and D2-Cu with water. Luckily, single crystals of D2-Cu with water in acetonitrile were successfully obtained and analyzed as Cu(D2)₂·4H₂O. This crystal structure further confirmed that the **D2-Cu** have not decompose in the presence of water, and D2 was indeed coordinated with Cu2+ in a 2:1 (ligand:metal) ratio through its carboxyl group (vide supra). In this structure, the Cu²⁺ ion was coordinated with two carboxyl oxygen atoms and four water molecules in a common octahedral geometry (Figure 3a). Two coumarin ligands were parallel to each other with a dihedral angle of 0° (Figure 3b). The bond lengths of Cu1-O2 and Cu1-O6 was determined to be 1.939 (2) and 1.977(2) Å respectively, while the bond length of Cu1-O7 was found to be 2.485(2) Å. The distance

between O7 and Cu1 was obviously larger than that of O6 and Cu1. In fact, three hydrogen bonds were found between the axial water molecule and three other adjacent D2-Cu molecules. Also, intramolecular hydrogen bond was found between H6 and O3 with a length of 1.914 Å. Therefore, the presence of water generated a water molecule bridged supramolecular network in the structure of Cu(D2)₂·4H₂O (Figure 3c). These data indicated that addition of water to the dry organic solution of D1-Cu and D2-Cu resulted in the formation of a water bridged supramolecular hydrogen bonding network, and this unique structure influenced the electronic states of the complex, resulting in fluorescence emission changes.³⁵⁻³⁷ Further considering that both compounds D1 and D2 bear a push-pull electronic system, with carboxyl group acts as the electron acceptor and amine or hydroxyl group as the electron donor. Thus intramolecular charge transfer (ICT) should occur in molecules **D1** and **D2**. The coordination of Cu^{2+} with the carboxyl group of **D1** and

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D2 could enhance the ICT process, while further binding of water to Cu²⁺ of **D1-Cu** and **D2-Cu** may result in decrease in the ICT efficiency in the complexes. As we know, decrease in the ICT process is always accompanied with blue shifts in the UV-Vis absorbance and fluorescence emission wavelengths. Similar with the above mentioned blue shift in fluorescence data upon water addition, blue shift in the absorbance spectrum was also observed when titrating D1-Cu and D2-Cu with water (Figure S23). Particularly, a clear isobestic point at 303 nm was observed when titrating **D2-Cu** with water in dry THF, with a new absorption peak developed at 294 nm (Figure S23b). This new isobestic point and absorption peak again confirmed the generation of a new structure rather than removal of Cu²⁺. Based on these results, it can be concluded that the formation of a water bridged hydrogen bonding network and the decreased ICT process upon water binding with D1-Cu and D2-Cu should be responsible for the fluorescence changes.



Figure 2. a-d) Fluorescence emission spectral changes of **D1-Cu** (10 μ M) upon titration with water in dry a) acetonitrile; b) methanol; c) ethanol and d) DMF. e) Calibration curves of **D1-Cu** (10 μ M) in acetonitrile, methanol, ethanol and DMF with increasing water content; f) Calibration curves of **D2-Cu** (10 μ M) in acetonitrile, methanol, ethanol and THF with increasing water content.

We also noticed that the hydroxyl group substituted at the 7position of **D2** acted as both of the hydrogen bond donor and acceptor to form the supramolecular network in the single crystal structure of $Cu(D2)_2$ ·4H₂O. Further considering that

there is also an amine nitrogen substituted at the 7-position in **D1**, which can be used as a hydrogen bond acceptor, we proposed that the presence of a hydrogen bond acceptor at the 7-position of 3-carboxyl coumarins is essential for designing such water sensitive Cu^{2+} complexes. Therefore, a control compound **D3** was synthesized to confirm this hypothesis. In the structure of **D3**, the incorporation of a carboxyl group at the 3-position ensured its coordination with Cu^{2+} . The fluorescence quenching behavior of **D3** upon addition of Cu^{2+} indicated the formation of corresponding Cu^{2+} complex **D3**-

Cu (Figure S24a). However, the titration of D3-Cu with water resulted in negligible fluorescence changes (Figure S24b). This result further demonstrated that the fluorescent turn-on sensing behavior of D1-Cu and D2-Cu was based on the formation of a water bridged hydrogen bonding network. Moreover, this result also provided a general strategy for designing coumarin based Cu^{2+} complex for water sensing by incorporating a metal binding site at the 3-position and a hydrogen bond acceptor at the 7-position of the coumarin framework.



Figure 3. Single crystal structure of $Cu(D2)_2 \cdot 4H_2O$ in acetonitrile with water. a) top view; b) side view; c) supramolecular hydrogen bonding network with water as the bridge.

Fable	1.	Summary of	the water	sensing pe	erformance o	f D)1-(Cu and	D2-	-Cu
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Material	Solvent	Function ^a	R	Linear range (wt%)	DL (wt %)
D1-Cu	Acetonitrile	$F = 7.00 \times 10^5 \times [H_2O] + 4.27 \times 10^4$	0.996	1.24-8.07	0.0749
	Methanol	$F=2.18\times10^{6}\times[H_{2}O]+1.74\times10^{6}$	0.992	0-2.46	0.0525
	Ethanol	$F=3.82{\times}10^{5}{\times}[H_{2}O]+1.44{\times}10^{6}$	0.998	0-8.05	0.2364
	DMF	$F=1.55\times10^{5}\times[H_{2}O]+9.32\times10^{5}$	0.998	0-4.03	0.2716
D2-Cu	Acetonitrile	$F = 4.75 \times 10^5 \times [H_2O] + 1.90 \times 10^6$	0.995	0-8.08	0.3313
	Methanol	$F = 5.50 \times 10^5 \times [H_2O] + 1.67 \times 10^6$	0.992	0-3.03	0.1856
	Ethanol	$F = 7.03 \times 10^5 \times [H_2O] + 3.20 \times 10^6$	0.983	0-1.85	0.1560
	THF	$F=1.05{\times}10^{6}{\times}[H_{2}O]+5.45{\times}10^{5}$	0.999	0-3.24	0.0745

^aF represents the fluorescence peak intensity.

To evaluate the practicability of **D1-Cu** and **D2-Cu** for water sensing, the fluorescence response speed of **D1-Cu** and **D2-Cu** towards water was then investigated. It was determined that the sensing behavior completed within ~ 2 min (Figures S25). This indicated that both **D1-Cu** and **D2-Cu** showed fast response towards water. To further confirm

whether D1-Cu and D2-Cu can be used for moisture sensing in complicated solvent systems, influence of pH on the sensing behavior was also checked (Figure S26). We found that the water sensing performance of D1-Cu was not interfered by pH fluctuations in a wide range of 4-12, suggesting that D1-Cu is a practical fluorescent sensor for moisture sensing. However, the fluorescence of D2-Cu was sensitive to pH changes in a range of 2-8, and became stable within a pH range of 8-12. Reason for **D2-Cu**'s broad pH sensitivity may be ascribed to the easily occurred protonation/deprotonation reaction at the hydroxyl group in compound **D2** (the phenol OH has a pK_a) value about 9.9).³⁸ While for D1-Cu, its amine nitrogen can only be protonated in a strong acidic condition (the pK_a of aromatic ammonium is about 4.6). These results indicated that D1-Cu can be considered as a fast response and pH tolerant fluorescent sensor for water, urging us to investigate its practicability in sensing water in real commercial samples.

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As we know, moisture level affects the quality of the product during storage, especially for some water sensitive chemicals. To confirm the moisture sensing practicability of this material, we tried to detect moisture in real commercial products with our fluorescent sensor. In this experiment, NaOH, dextrin and potato starch were selected for the test as they may represent inorganic salt, organic polymer and food. Since D1-Cu showed the highest sensitivity towards water in methanol, moisture level of these commercial samples was measured using D1-Cu in dry methanol. By adding 200 mg of above products into the D1-Cu solution and then treated via ultrasonic and centrifugation, the clear solution was taken for fluorescence measurements. The emission intensities were collected as shown in Figure 4. It can be seen that the oven dried samples showed weaker fluorescence than that of the original ones. Especially for potato starch, vivid fluorescence enhancement was observed for the original sample. These result indicated that D1-Cu bears the ability of moisture sensing in real commercial products.



Figure 4. Emission intensity changes of D1-Cu ($10 \mu M$) in dry methanol after addition of 200 mg of oven dried and original NaOH, dextrin and potato starch, respectively (parallel test three times).

CONCLUSIONS

In conclusion, the in situ generated copper complexes **D1**-**Cu** and **D2-Cu** showed fast, pH tolerant, sensitive and fluorescent turn-on water sensing ability in common organic solvents. **D1-Cu** was able to detect 0.0525 wt % water in methanol and its sensing behavior was not interfered by pH fluctuations in a wide range of 4-12. Single crystal analysis, fluorescence, UV-Vis and NMR data indicated that the sensing mechanism is based on the formation of the water bridged 3D supramolecular hydrogen bonding network, but not decomposition of the copper complex. Moreover, it was found that the incorporation of a hydrogen bond acceptor unit at the 7-position of 3-carboxyl coumarin is essential for the water sensing ability. This suggested a general strategy for designing coumarin based copper complexes for water sensing by incorporation of a metal binding site at the 3-position and a hydrogen bond acceptor at the 7-position.

ASSOCIATED CONTENT

Supporting Information

NMR and HRMS characterization data for **D1-D3**, UV-Vis, fluorescence spectral data, NMR studies, crystal data, Figures S1-S26 and Tables S1-S4. CCDC 1881528. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): Y. D., W. C. and W. Z. are inventors on a patent application at the China patent office.

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Analytical Chemistry

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- $\begin{array}{ccc} (38) \text{ The mentioned } pK_a \text{ data was obtained from the Bordwell } pKa \\ \hline Table & with & a & substructure: \\ http://www.chem.wisc.edu/areas/reich/pkatable/index.htm. \end{array}$

