Thiadiazole-based turn-on fluorescent chemosensor for AcO^- and its application in environmental systems and in bioimaging

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Abstract

A novelty chemosensor **MM** to detect AcO^- was designed, synthesized and characterized. When **MM** interacted with AcO^- , it was found that the new fluorescent emission peak at 616 nm arose. Meanwhile, the color change of the solution was directly observed by the naked-eye. Interesting, other anions could not cause any interference, specially F^- , H_2PO_4^- and PO_4^{3-} . The possible interaction mode between them was confirmed based on the Job's plot, ^1H NMR titration, ESI-MS, SEM analysis and DFT calculation. And LOD (limit of detection) of **MM** toward AcO^- was 4.6 nM. Moreover, **MM** could be utilized as test strips to identify AcO^- qualitatively. It's more important that **MM** could realize to detect AcO^- in tap water quantitatively, rapidly and on-site by used of smartphone APP. Furthermore, **MM** was successfully applied to detect AcO^- in living *Caenorhabditis elegans*. And it also demonstrated its potential bioimaging in living system.

Keywords Chemosensor · Acetate ion · Test strips · Smartphone APP · Bioimaging

1 Introduction

Anion detection has become one of the most active areas of supramolecular chemistry because many anions play vital role in health, biological, medical, environmental, industrial and chemical processes [1–6]. Among the different anions, acetate anion (AcO^-) plays an enormous role in our life, such as human metabolic process, protein synthesis [7–11]. For example, the abnormal rise of AcO^- in the body could be the exogenous cause of urinary calculi [7, 12–31]. And AcO^- can also interact with Ca^{2+} to form calcium acetate, which is one of the constituents of urinary calculi [7]. Therefore, it is essential to develop some

rapid and efficient method to detect AcO^- selectively and sensitively.

Compared to other methods, chemosensors have been received more and more attentions because of their superiorities over others [12–36]. So, considerable effort has been devoted to the development of AcO^- chemosensors in recent years [6–42]. But some AcO^- chemosensors are often disturbed by the basic anions, including F^- , H_2PO_4^- and PO_4^{3-} [37–43]. Moreover, it is well-known to the fluorescent chemosensors that the ability for the long-wavelength emissions can avoid the possible influence of background fluorescence effectively, which can also improve their selectively and sensitivity [44–46]. However, only a few long-wavelength emissions fluorescent

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chemosensors for AcO^- have been reported, which greatly limit their application in practice.

In this paper, chemosensor **MM** was designed, synthesized and characterized to separate out AcO^- from other different anions. It is important that the long-wavelength fluorescence emission at 616 nm once **MM** recognized AcO^- . At the same time, the color change of the solution can be inspected by the naked-eye directly. To our surprises, other anions could not induce any interference including F^- , H_2PO_4^- and PO_4^{3-} . The interactions between them were studied by the Job's plot, ^1H NMR titration, ESI-MS, SEM analysis and DFT calculation. Furthermore, test papers were prepared and employed to identify AcO^- in aqueous solution successfully. It's more important that **MM** could realize to detect AcO^- in tap water quantitatively, rapidly and on-site by used of smartphone APP. In addition, **MM** could be used for the fluorescent imaging AcO^- in multicellular living *C. elegans*.

2 Experimental

2.1 Materials and instrumentation

All chemicals used for synthesis were procured from commercial suppliers. And all solvents were used without further purification. ^1H NMR and ^{13}C NMR spectra were detected on Bruker-AV-500 NMR spectrometer using TMS as an internal standard, $\text{DMSO}-d_6$ as the solvents. And the chemical shifts are expressed in δ ppm. UV-vis spectra and Fluorescence spectra were collected on the Shimadzu UV-1601 spectrophotometer and the Horiba Fluoromax-4-NIR spectrometer. Mass spectra were measured by Agilent 6210 ESI/TOF MS instrument. SEM measurements were obtained on a Carl Zeiss Sigma 500.

The stock solution of **MM** was prepared in HEPES buffer (0.01 M, pH 7.2)/ CH_3CN (V/V = 2:8). And the ligand concentration was kept constantly (1.0×10^{-5} M). The solutions of F^- , Cl^- , Br^- , I^- , S^{2-} , SO_4^{2-} , SO_3^{2-} , HCO_3^- , H_2PO_4^- , CO_3^{2-} , NO_3^- , NO_2^- and AcO^- were prepared from their sodium or potassium salts.

2.2 NMR titration procedure

^1H NMR titration experiments were performed in CD_3CN . The known quantity of AcO^- was added to the solution of **MM** to study the chemical shift changes of **MM**. ^1H NMR spectra of **MM** (0.5 mM) by adding AcO^- were recorded by use of the Bruker-AV-400 NMR machine.

2.3 SEM images

Samples (5 μL) of **MM** and **MM-AcO}^-, were dissolved in CH_3CN . They were left to evaporate and dry at room temperature on glass surface followed by gold plating. Then the surface was imaged using SEM technique.**

2.4 Nematode culture

The nematodes were cultured on a nematode growth medium (NGM) plate inoculated with *E. coli* strain OP50 at 20 °C. N2 young adult (3-day-old) nematodes were placed on NGM plates to lay eggs for 12 h. On the third day, imaging was performed using synchronized young adult nematodes.

2.5 Synthesis of MM

Chemosensor **MM** was synthesized as Scheme 1. 5-phenyl-1, 3, 4-thiadiazol-2-amine (177.23 mg, 1.0 mmol), 3'-formyl-4'-hydroxy-[1, 1'-biphenyl]-4-carbonitrile (223.23 mg, 1.0 mmol) and glacial acetic acid (catalyst) were dissolved in 30 mL ethanol. The solution was continually refluxed for 12 h with stirring. When the mixture was cooled to room temperature, an orange precipitate was formed. The crude product was purified by column chromatography to give the chemosensor **MM** with 65% yield. ^1H NMR (400 MHz, d_6 -DMSO) δ 11.55 (s, 1H), 9.32 (s, 1H), 8.33 (s, 1H), 7.98 (dd, J = 28.9, 16.5 Hz, 7H), 7.59 (s, 3H), 7.18 (dd, J = 14.2, 8.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.05, 166.43, 166.14, 160.90, 160.71, 143.37, 134.17, 132.88, 131.42, 129.90, 129.46, 128.41, 127.37, 126.84, 120.29, 118.86, 117.97, 109.55. HRMS (ESI) m/z : $[\text{M} + \text{H}^+]$ $^+$ Calcd for $\text{C}_{22}\text{H}_{15}\text{N}_4\text{OS}$: 383.0961; Found 383.0961.

Scheme 1 The synthetic route of chemosensor **MM**

Fig. 1 Photographs of **MM** in the presence of various anions. **a** Naked eye. **b** Visual fluorescence changes under 365 nm UV light

Fig. 2 Absorption spectra of **MM** (1.0×10^{-5} M) in the presence of various anions in HEPES buffer (0.01 M, pH 7.2)/CH₃CN (V/V = 2:8)

Fig. 3 Fluorescence spectra of **MM** (1.0×10^{-5} M) in the presence of various anions in HEPES buffer (0.01 M, pH 7.2)/CH₃CN (V/V = 2:8)

3 Results and discussion

3.1 Fluorescent and colorimetric changes of chemosensor **MM** with **AcO⁻**

When diverse anions (3 equiv. to **MM**) were added into the solution of **MM** in HEPES buffer (0.01 M, pH 7.2)/CH₃CN (V/V = 2:8), it was obvious that only **AcO⁻** could change the solution color from colorless to pink (Fig. 1a). While **AcO⁻** was added into the **MM** solution, the solution emitted orange-light under 365 nm UV-light (Fig. 1b). At the same time, a new absorption peak appeared at 520 nm, which was only caused by **AcO⁻** (Fig. 2). And the strong long-wavelength emission peak at 616 nm arose, which was excited by 520 nm (Fig. 3). It was interesting that other anions could not lead to any distinct change of the spectra, including **F⁻**, **H₂PO₄⁻** and **PO₄³⁻**.

3.2 Anti-interference experiment

To evaluate **MM** as the chemosensor for **AcO⁻**, the anti-interference experiments were carried out in presence of 3.0 equiv. of various other anions (Figs. 4, 5). The results indicated that other anions could not have any effect on chemosensor **MM** to detect **AcO⁻**. And it concluded that **MM** could recognize **AcO⁻** effectively even if co-existing anions were present.

3.3 The interaction mode between chemosensor **MM** and **AcO⁻**

In order to clarify the interaction mode, the interaction between **MM** and **AcO⁻** was investigated by the Job's plot, ¹H NMR, ESI-MS, SEM analysis and DFT calculation.

According to the absorption spectra and the fluorescence emission spectra, it was clear from the Job's plot that

Fig. 4 Absorption responses of **MM** (1.0×10^{-5} M) at 520 nm in the present of 5 equiv. of AcO^- and other common anions in HEPES buffer (0.01 M, pH 7.2)/ CH_3CN (V/V = 2:8) solution. (1–14: F^- , Cl^- , Br^- , I^- , SO_4^{2-} , SO_3^{2-} , S^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , CO_3^{2-} , HCO_3^- , AcO^- , H_2PO_4^-)

Fig. 5 Fluorescence responses of **MM** (1.0×10^{-5} M) at 616 nm in the present of 5 equiv. of AcO^- and other common anions in HEPES buffer (0.01 M, pH 7.2)/ CH_3CN (V/V = 2:8) solution. (1–14: F^- , Cl^- , Br^- , I^- , SO_4^{2-} , SO_3^{2-} , S^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , CO_3^{2-} , HCO_3^- , AcO^- , H_2PO_4^-)

the stoichiometric ratio was 1:2 when **MM** distinguished AcO^- (Figs. 6, 7, Fig. S5 and S6). And it was important that the result founded on the Job's plot was also supported by ESI-MS. From the ESI-MS, the ion peak was detected at m/z 500.1125 which was consistent with $[\text{MM} + 2\text{AcO}^-]^+$ (Fig. S4). Moreover, the ^1H NMR titration was applied to seek out the interaction site, where **MM** interacted with AcO^- . When AcO^- was added gradually, the chemical shift assigned to hydrogen atoms in hydroxyl groups at 11.00 ppm was disappeared. And the signal at 5.83 ppm assigned to the hydrogen atoms in $-\text{HC}=\text{N}-$ protons

Fig. 6 Job's plot for the interaction between **MM** and AcO^- based on the absorption spectra

Fig. 7 Job's plot for the interaction between **MM** and AcO^- based on the fluorescent spectra

shifted to the downfield slightly (Fig. 8). The data proved that **MM** might interact with AcO^- by hydrogen bonds (Scheme 2) [9].

To discuss the aggregation change of **MM**, SEM analysis was launched (Fig. 9). From the SEM image, it was apparent that the aggregation of **MM** was transformed from the "wood stick" rod aggregation to the "petal" sheet-like structure. And the DFT calculations were developed to understand the combination between **MM** and AcO^- further (Fig. 10). It was palpable for chemosensor **MM** that the electron distribution of LUMO was distributed over the entire molecule, where the HOMO was mainly concentrated in the five-membered heterocyclic ring and a part of $\text{C}=\text{N}$ bond. However, it was also clear for **MM**- AcO^- that the electron distribution of HOMO was distributed over

Fig. 8 ^1H NMR spectra of **MM** in CD_3CN upon addition of AcO^- (0–2.5 equiv.) at 400 MHz

Scheme 2 The proposed interaction mode between chemosensor **MM** and AcO^-

Fig. 9 SEM micrographs of **MM** (a) and **MM-AcO⁻** complex (b)

Fig. 10 Energy level diagram of the HOMOs and LUMOs of **MM** and **MM-AcO⁻**

the -OH group, which resulted in the fluorescence enhancement. Moreover, the HOMO–LUMO energy gap of **MM** and **MM-AcO⁻** was calculated to be 3.2342 eV and 2.3927 eV, respectively. The result indicated that the difference in electron distribution in **MM** and **MM-AcO⁻** led to the change of their fluorescent properties. Therefore, all the results could fully demonstrate that **MM** could distinguish AcO^- from other anions selectively and sensitively by hydrogen bonds.

Besides, the LOD of **MM** toward AcO^- was calculated to be 4.6×10^{-9} M (4.6 nM) on basis of $3\delta/K$ (Figure S7) [47,

48], which had advantages over some other chemosensors (Table 1). And the association constant (K_s) was also calculated by use of the Benesi-Hildebrand plot (Figure S8) [49]. From the obtained linear relationship, K_s was calculated to be $2.522 \times 10^9 \text{ M}^{-2}$ [49].

3.4 Practical application

To investigate the application of chemosensor **MM** to detect AcO^- , test strips where **MM** (100 μM , CH_3CN) has been coated were prepared and dried in the dry watch-glass. After AcO^- (5 equiv.) was added in the aqueous solution, the significant color change of test strips could be inspected under visible light. Meanwhile, the color also changed under the 365 nm UV light (Fig. 11). It showed that good application future for **MM** in the detection of AcO^- qualitatively.

In order to realize the quantitative detection of AcO^- in water on-site, the widespread use of smartphones have aroused our interests [53, 54]. Based on the good bare-eye recognition properties of **MM** towards AcO^- , Color Assist (the APP within iPhone X) was used to determine the color changes in the RGB (red, green, blue) values of **MM** solutions. The R/B ratios for **MM** were plotted against the different concentrations of AcO^- . And the curve was revealed good linearity ranges ($R^2 = 0.98902$) (Fig. 12a). To prove the accuracy of the way, the tap water contaminated with AcO^- was tested quantitatively by the APP and an ultraviolet–visible spectrophotometer, respectively. As the result, the R/B value of the contaminated tap water

Table 1 Comparison of different LOD between **MM** and previously reported chemosensors for sensing AcO^-

Chemosensors	LOD	Solvent	References
	4.00×10^{-7} M	DMSO	[9]
	0.91×10^{-6} M	Ethanol/ H_2O (v/v, 1:1)	[50]
	2.50×10^{-6} M	DMSO/ H_2O (v/v, 1:1)	[51]
	140.00×10^{-6} M	DMSO/bis-tris buffer (8:2)	[52]
	2.05×10^{-7} M	$\text{CH}_3\text{CN-H}_2\text{O}$ (v/v, 1:1).	[8]
MM	4.6×10^{-9} M	In HEPES buffer (0.01 M, pH 7.2)/ CH_3CN (V/V = 2:8)	Present work

Fig. 11 The photographs of test strips upon addition of AcO^-

obtained by the APP was 1.39, which the concentration of AcO^- should be $15.28 \mu\text{M}$ (Fig. 12a). Correspondingly, the concentration of AcO^- obtained by the spectroscopic instrument was $14.51 \mu\text{M}$ (Fig. 12b). The concentration error between the two methods was only 5.31%. It implied that smartphone APP could provide the low cost, convenient and on-the-spot approaches for the detection of AcO^- in tap water quantitatively.

It's well-known that *C. elegans* was the valuable model organism for the study of bioimaging. So the ability of **MM** to track AcO^- in living *C. elegans* to inspect **MM** the bioimaging of AcO^- in biological systems. It's clear that the nematodes cultured without AcO^- displayed weak blue fluorescent intensity (Fig. 13b, e). But the intensity enhanced distinctly when the nematodes were treated with $40 \mu\text{M}$ AcO^- (Fig. 13c, f). The data proved that **MM** could recognize AcO^- in living *C. elegans* effectively.

4 Conclusions

In summary, chemosensor **MM** was designed, synthesized and characterized. And **MM** possesses high selectivity and good sensitivity for AcO^- , which the LOD was 4.6 nM . When **MM** interacted with AcO^- , the new absorption peak at 520 nm arose. Meanwhile, the color change was observed directly by the naked-eye. And the fluorescent emission peak at 616 nm appeared when it was excited at 520 nm . It was interesting that other anions could not cause any interference, particularly F^- , H_2PO_4^- and PO_4^{3-} . The data confirmed that stoichiometric ratio between **MM** and AcO^- was 1:2. And **MM** combined with AcO^- by hydrogen bonds. Furthermore, test strips coated chemosensor **MM** showed excellent application prospect for detecting

Fig. 12 **a** Smartphone-assisted RGB responses for the determination of AcO^- . **b** Spectrophotometer for the determination of AcO^- , at 520 nm

Fig. 13 In vivo imaging of living *C. elegans* (**a, d**); **a, d** images of *C. elegans* pretreated with **MM** (20 μ M, DMSO/H₂O, v/v, 40/60) for 30 min; **c, f** images of *C. elegans* pretreated with **MM** (20 μ M, DMSO/H₂O, v/v, 40/60) and AcO[−] (40 μ M) for 30 min

AcO[−] qualitatively. The APP was used to achieve quantitative detection of AcO[−] in tap water simply, efficiently and on-site. Furthermore, **MM** could be applied for imaging AcO[−] in living *C. elegans*. And it indicated that **MM** has promising potential application in living system.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interests.

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