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ARTICLE TYPE

A simple coumarin as turn-on fluorescence sensor for Al(III) ion

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A simple Al^{3+} sensor, 8-acetyl-7-hydroxy-4-methylcoumarin (AHMC), was synthesized. It can display an excellent fluorescence “turn-on” response to Al^{3+} over other common metal ions in methanol–water media. Theoretical calculations have also been carried out to understand the configuration of AHMC–Al complex and rationalize experimental absorption data.

Aluminum is the third most abundant metal in the earth’s crust. It is widely used in our daily life, however it was found to be neurotoxic to organisms a long time ago.¹ Al^{3+} has also been linked to Alzheimer’s disease,² and it inhibits plant growth on acid soils.³ As a result of the close relationship between Al and human health and environment, it is crucial for the development of Al^{3+} sensors. Fluorescent sensors have been one of the most convenient methods to detect metal ions owing to their operational simplicity, low detection limit, realtime detection and portability.⁴ Up to now, so many fluorescent sensors for determination of Al^{3+} have been documented in literature.^{5,6,7} In general, as Al^{3+} is a hard-acid, it has been found that Al^{3+} prefers a coordination sphere containing N and O as hard-base donor sites. A large number of Schiff’s bases can be used as Al^{3+} sensors.^{5,6} On the other hand, some simple sensors for metal ions were displaying their superiority in recent years, due to good sensing performance and clear signalling mechanism.^{6,8} Getting new sensor type with simple molecular structure for Al^{3+} are fascinating and significant.

Here, we synthesized a simple chemosensor, 8-acetyl-7-hydroxy-4-methylcoumarin (AHMC, Fig. 1), for Al^{3+} . Upon binding Al^{3+} , AHMC displays a significant fluorescence enhancement in methanol–water media. To evaluate the fluorescent property of AHMC, a reference compound, 1-acetyl-2-naphthol, was used (Fig. 1). The structure of AHMC was confirmed by ¹H NMR, ESI-MS and X-ray single crystal diffraction analysis (Fig. S1, S2, and S3, ESI†).

The fluorescence intensity of AHMC in methanol–water (95:5, v/v) is very low. Upon an increase in the concentration of Al^{3+} (0–16 equ.), a strong emission band centering at 490 nm is observed (Fig. 2a). In the presence of 14 equ. Al^{3+} , the fluorescence intensity get to maximum (quantum yield, $\Phi = 0.102$), with almost 92 times enhancement compared to free AHMC. Efficient

fluorescence turn-on response to Al^{3+} and obvious blue-green emission can make naked-eye detection feasible, as can be seen in the inset photographs of Fig. 2a.

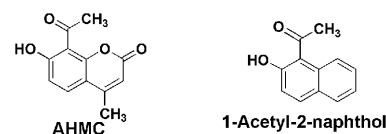


Fig. 1 Molecular structures of AHMC and 1-acetyl-2-naphthol.

There also exists a good linear relationship between the fluorescence intensity of AHMC and Al^{3+} concentration ($R^2 = 0.9655$, 0–60 μM). It is suitable for quantitative detection of Al^{3+} . From the fluorescence titration experiment, the Hill coefficient n was found to be 2.9 which indicated that the binding between AHMC and Al^{3+} should be a 3:1 stoichiometry (Fig. S4, ESI†).⁹ It was further confirmed by ESI-MS, which showed a peak at $m/z = 678.8$ assigned to $[\text{3AHMC-3H+Al}^{3+}\text{+H}]^+$ (Fig. S5, ESI†). With increasing concentration of EDTA (ethylenediaminetetraacetic acid disodium salt) to the solution of AHMC containing Al^{3+} , fluorescence intensity decreased gradually. It also indicates a reversible coordination between AHMC and Al^{3+} (Fig. S6, ESI†).

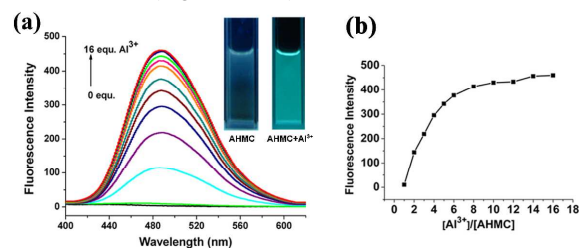


Fig. 2 (a) Fluorescence emission spectra of AHMC (10 μM) upon addition of Al^{3+} in MeOH– H_2O (95:5, v/v). The Al^{3+} concentrations are 0, 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, and 160 μM , from bottom to top. (Ex = 338 nm; slit ex = 5 nm, em = 3 nm). Inset: Photographs of AHMC upon the addition of Al^{3+} under UV irradiation (365 nm). (b) Fluorescence intensity as a function of $[\text{Al}^{3+}]/[\text{AHMC}]$.

The absorption spectrum of AHMC in methanol–water (95:5, v/v) shows maximum absorption bands at 269 nm and 311 nm, with molar absorption coefficient of 9580 and 10540 $\text{M}^{-1}\text{cm}^{-1}$, respectively. Upon addition of Al^{3+} , these two bands shift to 281 nm and 325 nm gradually, at the same time a weak band

centering at 380 nm appeared (Fig. 3). The clear isosbestic points at 270, 301, and 345 nm indicate between free and complexed **AHMC** only a single equilibrium occurs during the titration.¹⁰

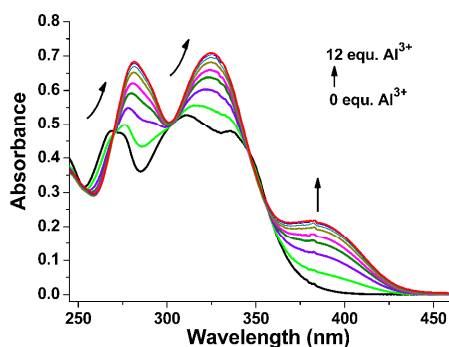


Fig. 3 UV-vis absorption spectra of **AHMC** (50 μM) to titration of Al^{3+} in $\text{MeOH-H}_2\text{O}$ (95:5, v/v). The Al^{3+} concentrations are 0, 25, 50, 100, 200, 300, 400, 500, and 600 μM , from bottom to top.

The fluorometric behaviour of **AHMC** to other metal ions was also studied. As shown in Fig. 4a, no significant spectral changes of **AHMC** occurred in the presence of 14 equ. of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Cr^{3+} or Fe^{3+} . However, only the addition of Al^{3+} resulted in a significant enhancement of the emission intensity positioned at 490 nm under the identical condition. Moreover, as shown in Fig. 4b, in the presence of miscellaneous competitive cations, it showed that Al^{3+} could also result in the enhancement of fluorescence intensity. All these results indicate that the selectivity of **AHMC** for Al^{3+} over other competitive cations is remarkably high. Although the molecular structure of **AHMC** is simple, by contrast with other reported Al^{3+} fluorescent chemosensors (Shiff's based type^{5,6} or non-Shiff's based type⁷), **AHMC** is very competitive and somewhere better than others in respect of some features like high fluorescent enhancement efficiency and good selectivity.

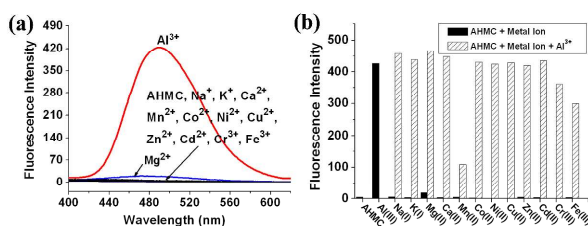


Fig. 4 In $\text{MeOH-H}_2\text{O}$ (95:5, v/v), **(a)** Fluorescence spectra of **AHMC** (10 μM) in the presence of 14 equ. of metal ions. **(b)** Fluorescence intensities of **AHMC** (10 μM) at 490 nm. Black bars: fluorescence intensity of **AHMC** with the addition of the respective cations (14 equ.). Sparse bars: fluorescence intensity of **AHMC** with the addition of the respective competing cations (14 equ.) and Al^{3+} (14 equ.).

Selective fluorescence enhancement by Al^{3+} could be due to the effective coordination of Al^{3+} with **AHMC** over other metal ions. Coordination of Al^{3+} to oxygen atoms on *o*-acetylphenol moiety suppressed photoinduced electron transfer (PET) quenching process, thus enhances the fluorescence output of **AHMC** via chelation-enhanced fluorescence (CHEF) effect.¹¹

As a control, fluorescence titration experiment shows the fluorescence intensity of 1-acetyl-2-naphthol in methanol-water (95:5, v/v) is low. Upon an increase in the concentration of Al^{3+} (0–28 equ.), an emission band centering at 453 nm is observed, but only almost 17 times enhancement (Fig. S7, ESI†). Quantum yield, $\Phi = 0.0154$. Upon addition of Al^{3+} , similar shift and clear isosbestic points were also shown on the absorption spectrum of 1-acetyl-2-naphthol (Fig. S8, ESI†). It suggests that *o*-acetylphenol moiety could provide suitable coordination environment for Al^{3+} , but coumarin framework showed better fluorescence property. Notably, a simple molecule, 2-hydroxy-1-naphthaldehyde reported by Wu and co-workers, can also be an Al^{3+} sensitive turn-on fluorescent probe.^{7c} In that molecule, *o*-hydroxyl benzaldehyde moiety can provide a similar coordination ability to Al^{3+} .

To understand the optimized configuration of **AHMC**- Al complex, density functional theory (DFT) calculations were performed. As shown in Fig. 5, an Al^{3+} ion binds to three **AHMC** very well through six coordination sites. Al-O bond lengths are 1.86 Å (Al-hydroxyoxygen) and 1.92 Å (Al-carbonyloxygen). They are comparable to the corresponding lengths found in related complexes.¹² This calculated structure was also supported by the similar crystal structure of 2-hydroxy-4-methoxyacetophenone- Al complex gained in this paper (Fig. S9, ESI†).

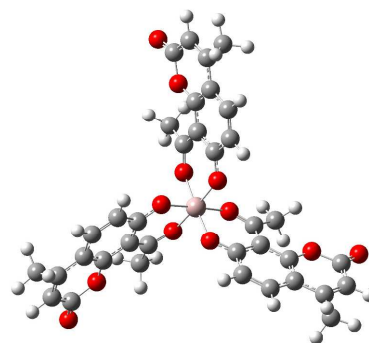


Fig. 5 DFT-calculated structure of **AHMC**- Al complex (pink, red, dark gray, and light gray spheres refer to Al, O, C, and H atoms respectively).

Three bands were shown in the experimental absorption curve of **AHMC** during the titration with Al^{3+} . To rationalize the experimental attributions of the absorption data, time dependent-density functional theory (TD-DFT) calculations were carried out, on the basis of the above optimized ground-state geometry. The calculated dominant frontier molecular orbitals (MOs) of **AHMC**- Al complex are depicted in Fig. 6. It can be seen that the highest occupied molecular orbital (HOMO) consists of two degenerate orbitals MO175 and MO176. Two calculated lower-energy absorption bands are at 376 nm and 311 nm (experimental value found at 380 nm and 325 nm, respectively), and contributed to the transition of HOMO (MO176) \rightarrow LUMO (oscillator strength $f = 0.080$) and HOMO (MO175) \rightarrow LUMO+2 ($f = 0.487$), respectively. Both of them are reasonable to assign to $\pi \rightarrow \pi^*$ charge transfer. The higher energy band calculated at 270 nm (experimental value found at 281 nm) is originated in HOMO-1 \rightarrow LUMO+1 transition ($f = 0.101$), which is described as ligand-to-ligand charge transfer.

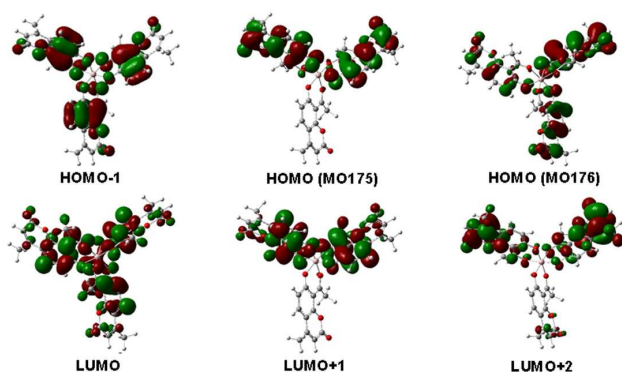


Fig. 6 The contours of molecular orbitals of AHMC–Al complex involved in dominant transitions.

Conclusions

In summary, a simple compound, 8-acetyl-7-hydroxy-4-methylcoumarin AHMC, shows excellent fluorescent performance toward Al^{3+} in methanol–water media. The results showed AHMC could be used as a turn-on fluorescence sensor for Al^{3+} . The configuration of AHMC–Al complex was illustrated by DFT calculations and supported by the similar single crystal structure of 2-hydroxy-4-methoxyacetophenone–Al complex. TD–DFT calculations could also rationalize the experimental attributions of the absorption data well.

Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures and additional spectroscopic data. See DOI: 10.1039/b000000x/. CCDC reference numbers are 957277 for AHMC, and 971189 for 2-hydroxy-4-methoxyacetophenone–Al complex.

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A simple non-Shiff's base type molecule serves as selective chemosensor for Al^{3+} based on chelation-enhanced fluorescence (**CHEF**) effect.

