# Electronic Supplementary Information

# for

# A Simple Coumarin as turn-on fluorescence sensor for Al(III) ion

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## 1. Reagents, instruments and experimental procedures

Materials for synthesis were purchased from commercial suppliers and used without further purification. 1-Acetyl-2-naphthol was purchased from Alfa Aesar (China). Deionized water was used to prepare all aqueous solutions. Aqueous solutions of metal ions were prepared from their nitrate salts.

$^1$H NMR spectra were taken on a Bruker Avance III 400 spectrometer. Chemical shifts ($\delta$) are reported in ppm, relative to tetramethylsilane. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 6000 spectrometer. UV-vis absorption spectra were obtained with a Perkin Elmer Lambda 35 UV-vis spectrophotometer and recorded in quartz cells with 1 cm optical path length. Fluorescence spectra were recorded on a Hitachi RF-4500 fluorescence spectrophotometer. Quantum yield was measured on an Edinburgh instrument FLS920 fluorescence spectrometer and an absolute method using an integrating sphere based upon that originally developed by de Mello *et al*[1].

X-ray single crystal diffraction measurements were made on a Bruker D8 SMART APEX II Single Crystal Diffractometer equipped with graphite crystal monochromatized Mo Kα radiation ($\lambda$ = 0.71073 Å) at 296(2) K. The structure was solved by direct methods with the SHELXS-97 program, and refined anisotropically by full-matrix least-squares methods for all non-H atoms. All H atoms were added according to theoretical calculations and refined isotropically.

DFT geometry optimizations and TD-DFT excitation energy calculations of **AHMC**–Al complex was carried out with the Gaussian 09 package[2] employing the B3LYP[3] density functional. A standardized 6-31G(d) basis set[4] was used for DFT calculations.

## Procedures of metal ion sensing

The stock solutions of the metal ions were prepared in deionized water. The stock solution of **AHMC** was prepared in methanol, and then diluted to 10 μM or 50 μM with MeOH/$H_2O$ (95:5 v/v).

In titration experiments of $Al^{3+}$, each time a 2 mL solution of **AHMC** (10 μM or 50 μM) was filled in a quartz optical cell of 1 cm optical path length, and then $Al^{3+}$ stock solution was added into the cell gradually by using a microsyringe. In selectivity experiments, the test samples were prepared by placing appropriate amounts of metal ion stock solution into 2 mL solution of **AHMC** (10 μM). After 5 min of the addition, spectral data were recorded.

## 2. Synthesis and characteristic data

### 2.1 Synthesis and characterization of 8-acetyl-7-hydroxy-4-methylcoumarin

8-Acetyl-7-hydroxy-4-methylcoumarin (**AHMC**) was synthesized according to literature procedure.[5] **AHMC** are yellow needles. Melting point: 173-174 $^0$C. $^1$H NMR ($CDCl_3$, 400 MHz) δ: 2.42 (s, 3H), 2.97 (s, 3H), 6.17 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 13.59 (s, 1H). ESI-MS (m/z): 219.2 $(M+1)^+$, 241.2 $(M+Na)^+$. Colorless block single crystals of **AHMC** suitable for X-ray single crystal diffraction analysis were obtained on slow evaporation of ethanolic solution at room temperature.

### 2.2 Preparation of single crystals of 2-hydroxy-4-methoxyacetophenone–Al complex

The solution of aluminum isopropoxide in chloroform was added into methanolic solution of 2-hydroxy-4-methoxyacetophenone. After two days, colorless block single crystals of 2-hydroxy-4-methoxyacetophenone–Al complex suitable for X-ray single crystal diffraction analysis were obtained on slow evaporation at room temperature.

**[1]** de Mello, J. C.; Wittmann H. F.; Friend R. H. *Adv. Mater.*, 1997, **9**, 230.

**[2]** Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; et al. Gaussian 09, revision A.01; Gaussian, Inc.: Wallingford, CT, 2010.

**[3]** Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* 2008, **120**, 215.

**[4]** (a) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.*, 2001, **22**, 976. (b) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* 1998, **109**, 1223.

**[5]** Russell, A.; Frye, J. R. *Org. Synth.*, 1941, **21**, 22.

## 3. Supplementary spectra data

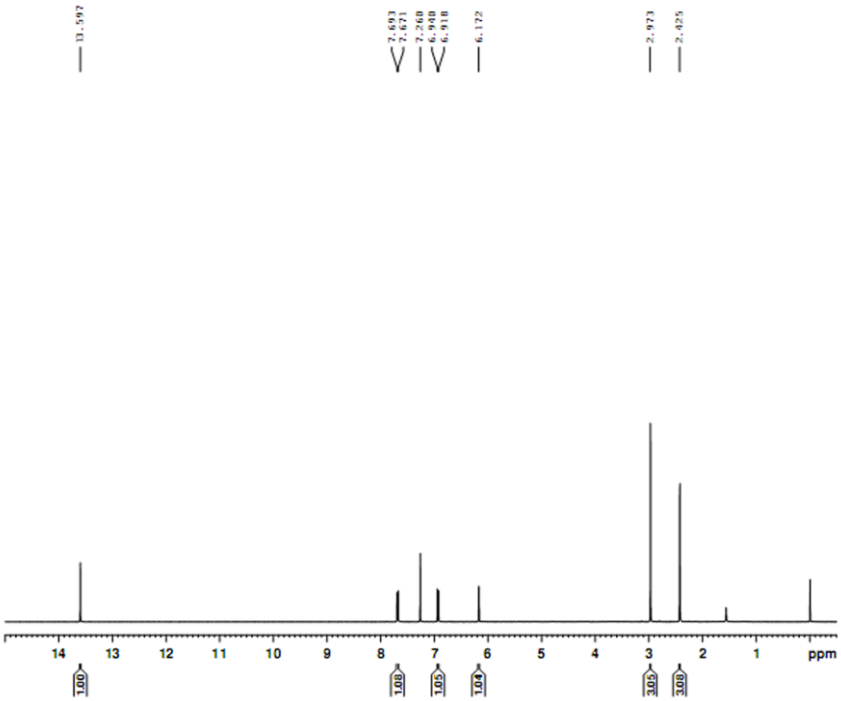


**Fig. S1** $^{1}$H NMR ($CDCl_3$, 400 MHz) spectrum of **AHMC**.

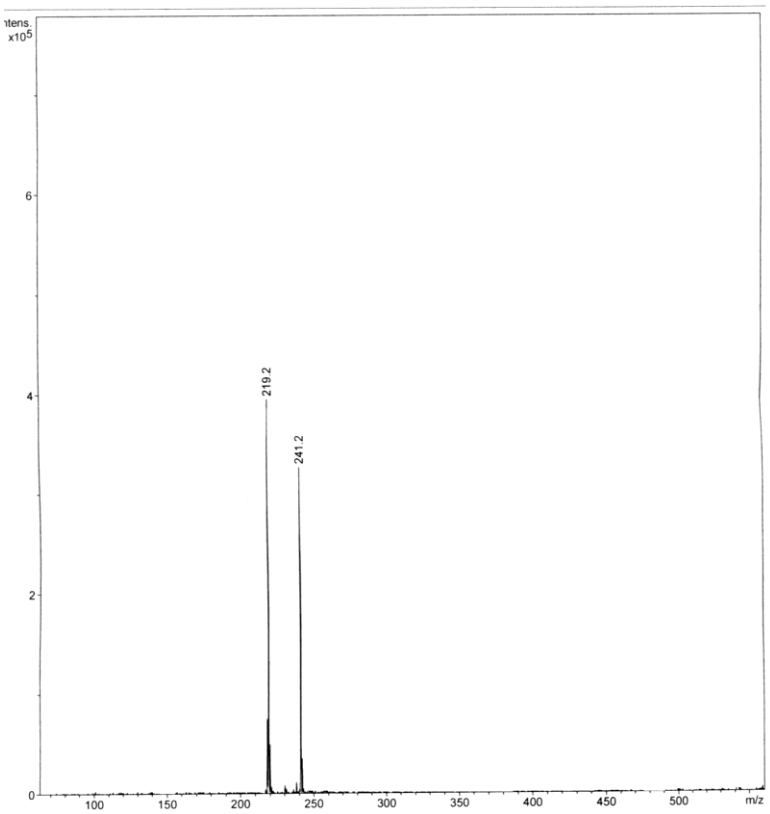


**Fig. S2** ESI-MS spectrum of **AHMC**.

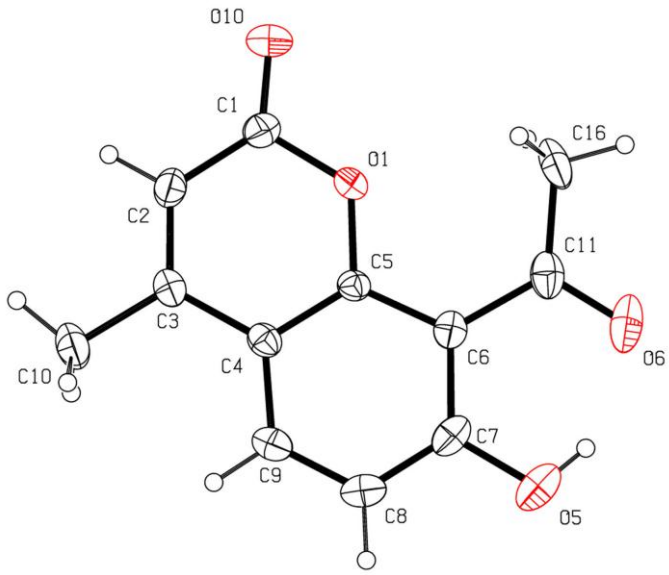


**Fig. S3** X-ray crystal structure of **AHMC** (30% probability level for the thermal ellipsoids).

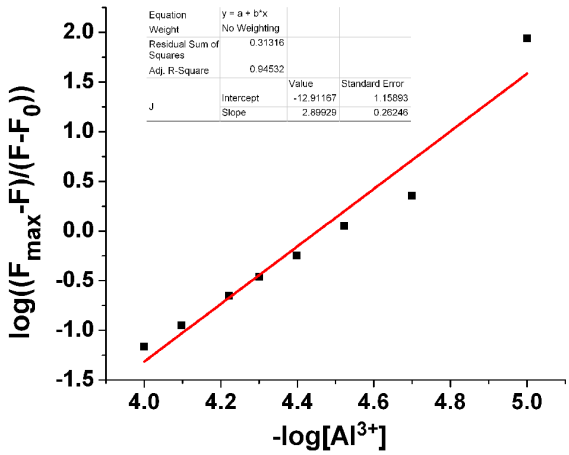


**Fig. S4** Hill plot from the spectrophotometric titration (fluorescence intensity of **AHMC** at 490 nm were used).

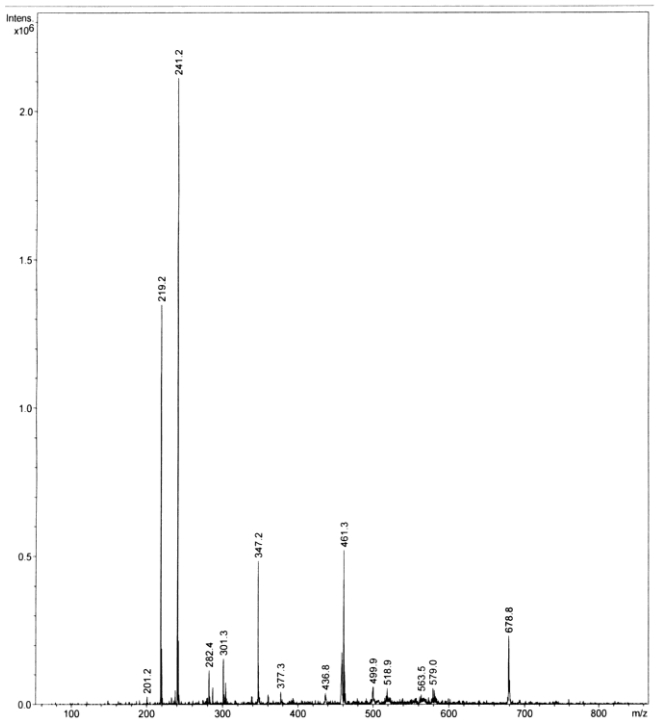


**Fig. S5** ESI–MS spectrum of **AHMC**–$Al^{3+}$.

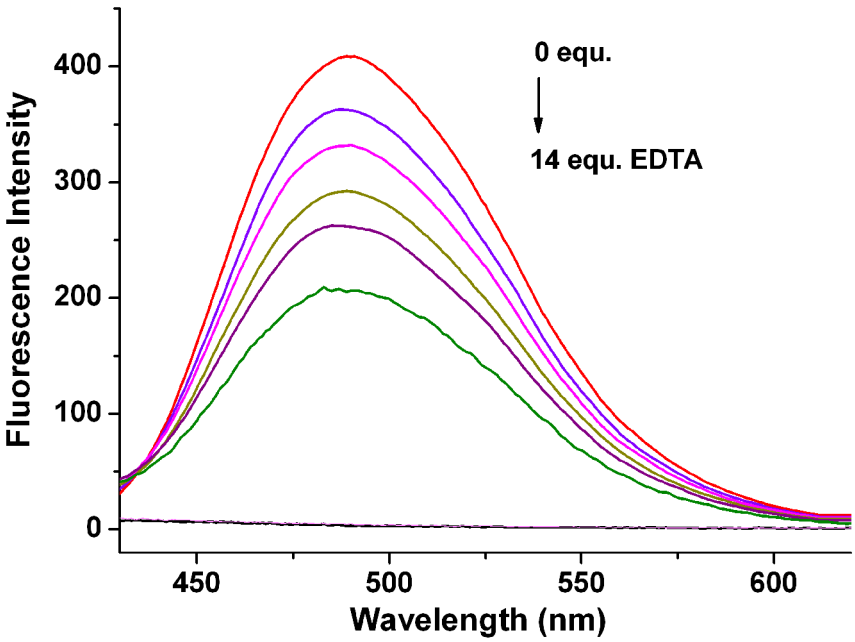


**Fig. S6** Fluorescence spectra of **AHMC** with 14 equ. of $Al^{3+}$ related to the number of equivalents of **EDTA** added (From top to bottom: 0, 2, 4, 6, 8, 10, 12 and 14 equ. of **EDTA**; Ex = 338 nm).

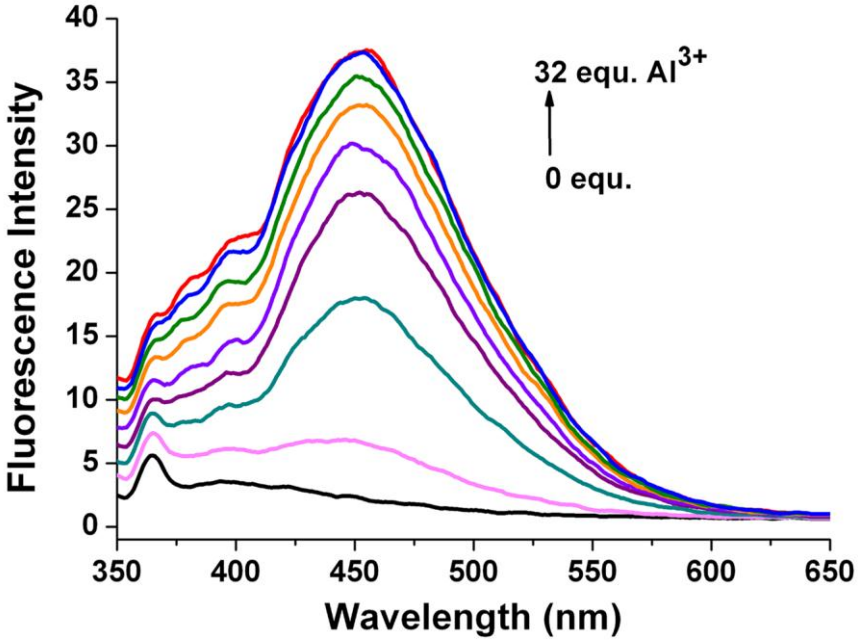


**Fig. S7** Fluorescence emission spectra of 1-acetyl-2-naphthol **(**10 μM**)** upon addition of $Al^{3+}$ in MeOH−$H_2O$ mixture (95:5, v/v). The $Al^{3+}$ concentrations are 0, 40, 80, 120, 160, 200, 240, 280, and 320 μM, from bottom to top. (Ex = 329 nm; slit ex = 5 nm, em = 3 nm).

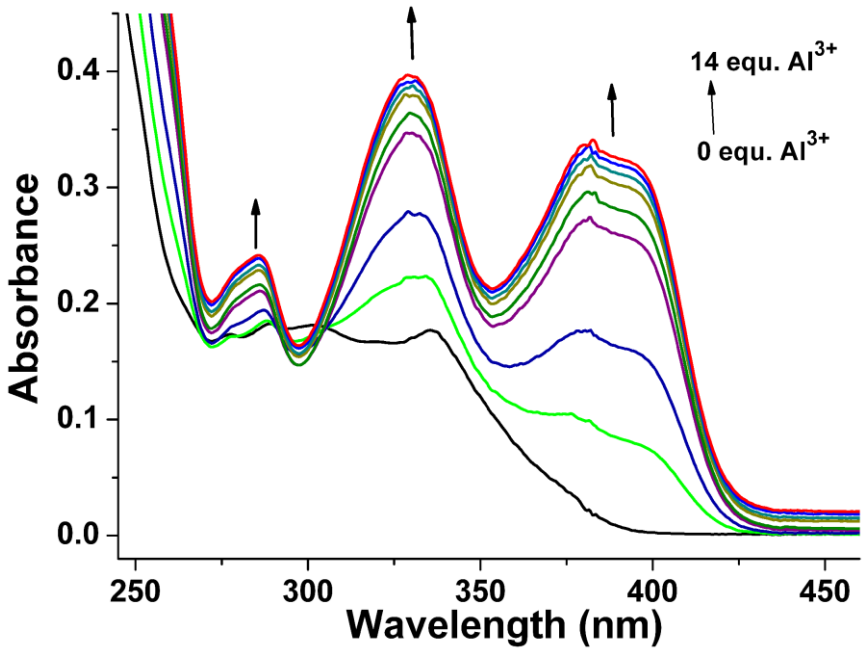


**Fig. S8** UV-vis absorption spectra of 1-acetyl-2-naphthol (50 μM) to titration of $Al^{3+}$ in MeOH−$H_2O$ mixture (95:5, v/v). The $Al^{3+}$ concentrations are 0, 25, 50, 100, 200, 300, 400, 500, 600, and 700 μM, from bottom to top.

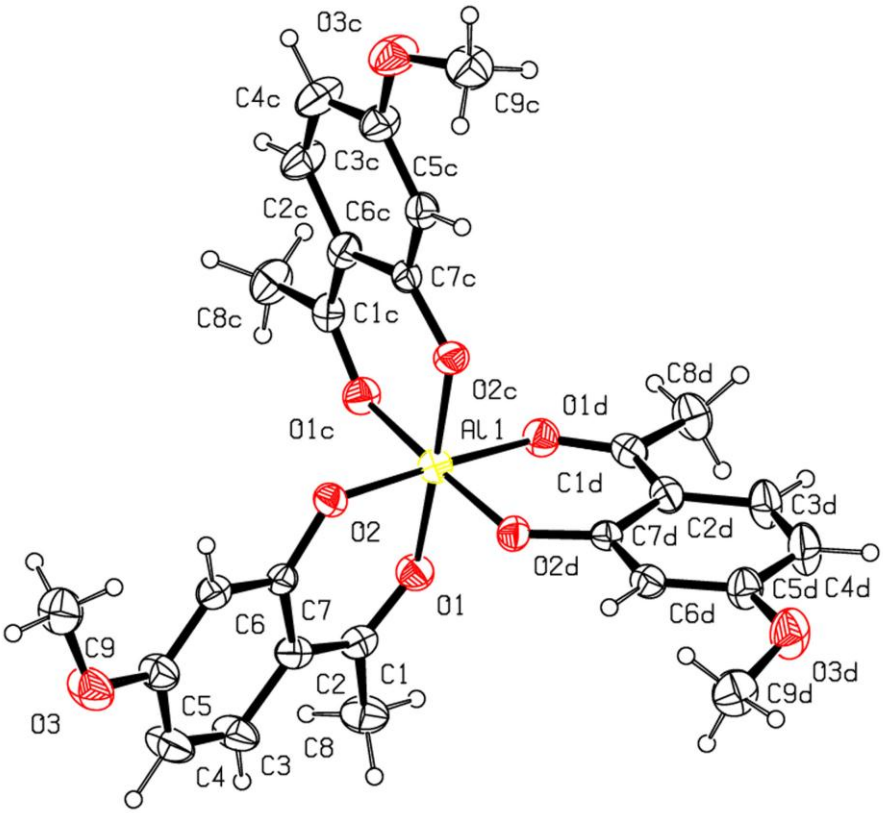


**Fig. S9** X-ray crystal structure of 2-hydroxy-4-methoxyacetophenone–Al complex (30% probability level for the thermal ellipsoids).