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 package² employing the B3LYP³ density functional. A standardized 6-31G(d) basis set⁴ 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/H₂O (95:5 v/v).

In titration experiments of Al³⁺, 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 Al³⁺ 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 °C. ¹H NMR (CDCl₃, 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.

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$_2$O 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$_2$O 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).