

Supporting information for

**An intramolecular charge transfer(ICT)-based dual emission fluorescent probe
for ratiometric detection of gold ions**

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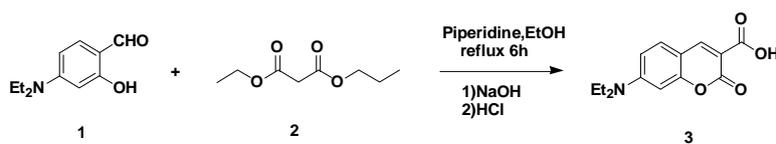
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Materials and instruments

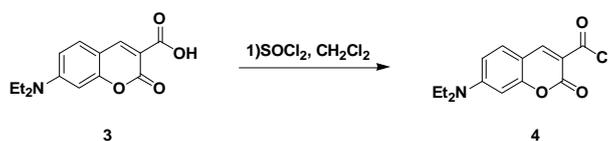
Unless otherwise stated, all the solvents and chemicals were of analytical grade and purchased from commercial suppliers and used without further purification. Highly pure water (sterile Minipore water, 18.3 M Ω) was used throughout all experiments. Nuclear magnetic resonance spectra were recorded at 400 MHz and carbon spectra were recorded at 100 MHz on an Invoa-400 (Invoa 400) spectrometer. All the chemical shifts (δ) are reported in ppm using the deuterated solvent and tetramethylsilane as the internal reference. High-resolution mass spectra were obtained on LCQ/Advantage HPLC-Mass Spectrometer. TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200-300), both of which were obtained from Qingdao Ocean Chemicals. UV-vis absorption spectra were recorded in 1 cm path length quartz cuvettes on a Hitachi U-4100 UV/vis spectrophotometer (Kyoto, Japan). Fluorescence emission spectra were obtained at room temperature on a PTI QM4 Fluorescence System (Photo Technology International, Birmingham, NJ) with the excitation and emission slit widths at 5.0 and 5.0 nm respectively. Fluorescence emission spectra were collected using a bandwidth of 5 nm and 0.2 \times 1cm² quartz cuvettes containing 600 μ L of solution. The pH measurements were carried out on a Mettler-Toledo Delta 320 pH meter. Data processing was performed on a personal computer with Sigmaplot version 2.0.

Synthesis



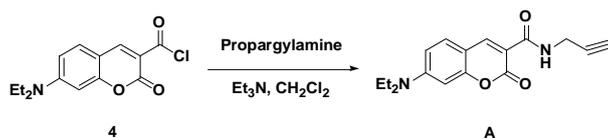
Synthesis of compound 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylic acid (3):

7-diethylamino-2-oxo-2H-chromen-3-carboxylic acid (3) was synthesized according to the literature method¹⁰. 4-Diethylaminosalicylaldehyde (1.93 g, 0.01 mol), diethylmalonate (3.2 g, 0.02 mol) and piperidine (1 mL) were combined in absolute ethanol (30 mL) and stirred for 6 hours under reflux conditions. Then 10% NaOH (30 mL) solution was added and the mixture was refluxed for 15 min. The reaction was cooled to room temperature and acidification to pH 2 using concentrated hydrochloric acid under ice bath gave a crystalline deposit which was filtered, washed with water, dried, then recrystallized with ethanol to give a pink needle crystal 3 (1.96 g, 74.93%).



Synthesis of compound 7-diethylamino-2-oxo-2H-chromene-3-carbonyl chloride (4):

Compound (4) was synthesized according to the literature method^{S1}. Under nitrogen, 3 (1.31 g, 0.005 mol) was added to dry SOCl₂ solution (10 mL) and the suspension was stirred at room temperature for 3 hours. Then the mixture was filtered. The deposit was washed with ether to afford 0.92 g of yellow solid 4 (65%), which was taken forward in the synthesis immediately.



Synthesis of probe 7-(diethylamino)-2-oxo-N-(prop-2-yn-1-yl)-2H-chromene-3-carboxamide

(A):

Under nitrogen, a solution of 4 (0.57 g, 1.25 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (0.21 mL, 1.50 mmol) and a solution of propargylamine (103 μL , 1.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise to the solution with stirring. And then stays overnight at room temperature. The solvent was removed under reduced pressure. The crude product was purified by silica-gel column chromatography (petroleum ether: ethyl acetate=8: 1) to afford 0.28 g of yellow solid A in 63% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.01 (s, 1H), 8.71 (s, 1H), 7.43 (d, $J = 9.0$ Hz, 1H), 6.65 (d, $J = 6.5$ Hz, 1H), 6.50 (s, 1H), 4.24 (s, 2H), 3.45 (d, $J = 14.3$ Hz, 4H), 2.24 (s, 1H), 1.24 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.82, 162.43, 157.55, 152.48, 148.24, 131.06, 109.85, 109.52, 108.15, 96.44, 79.58, 70.99, 44.95, 29.01, 12.24; MS (ESI): m/z : 299.0 [$\text{M}^+\text{+H}$].

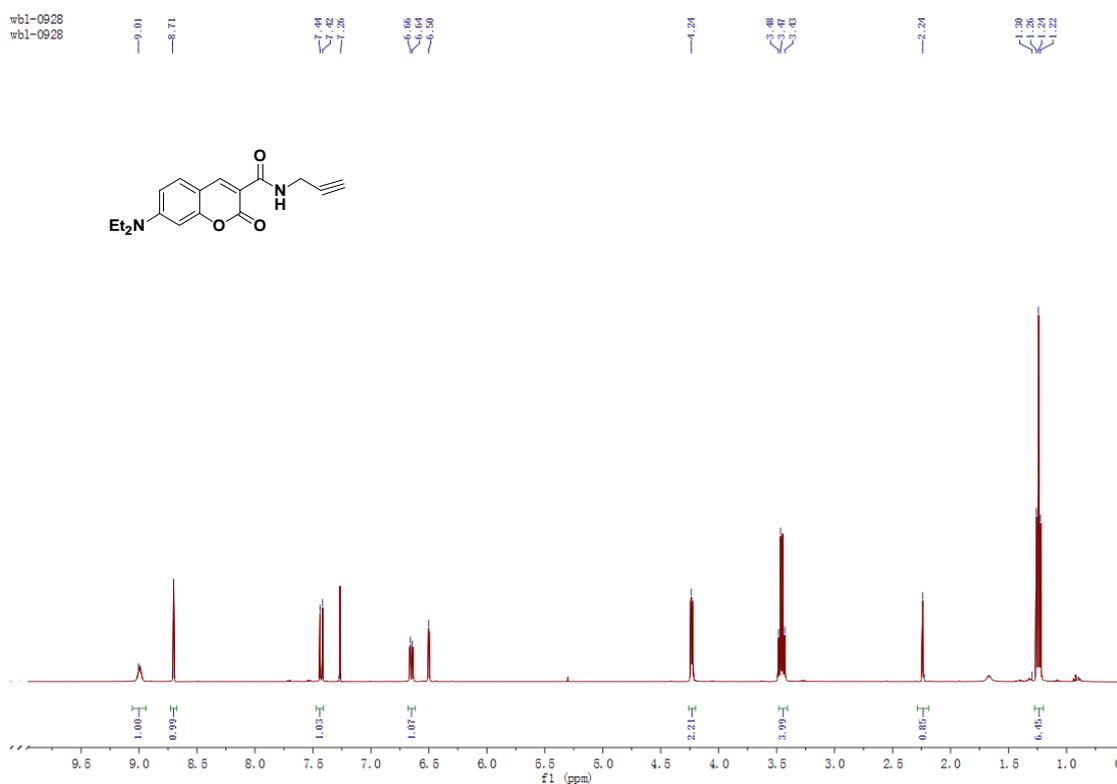


Figure S1. ^1H NMR spectrum of compound A.

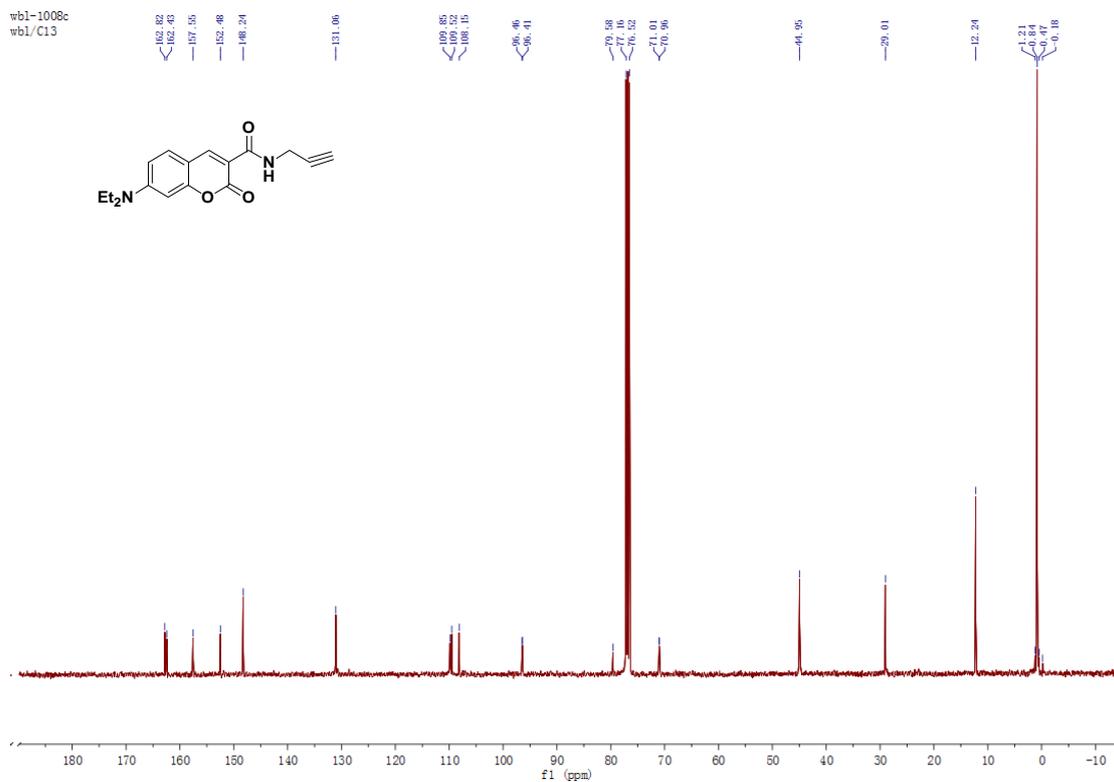


Figure S2. ^{13}C NMR spectrum of compound A.

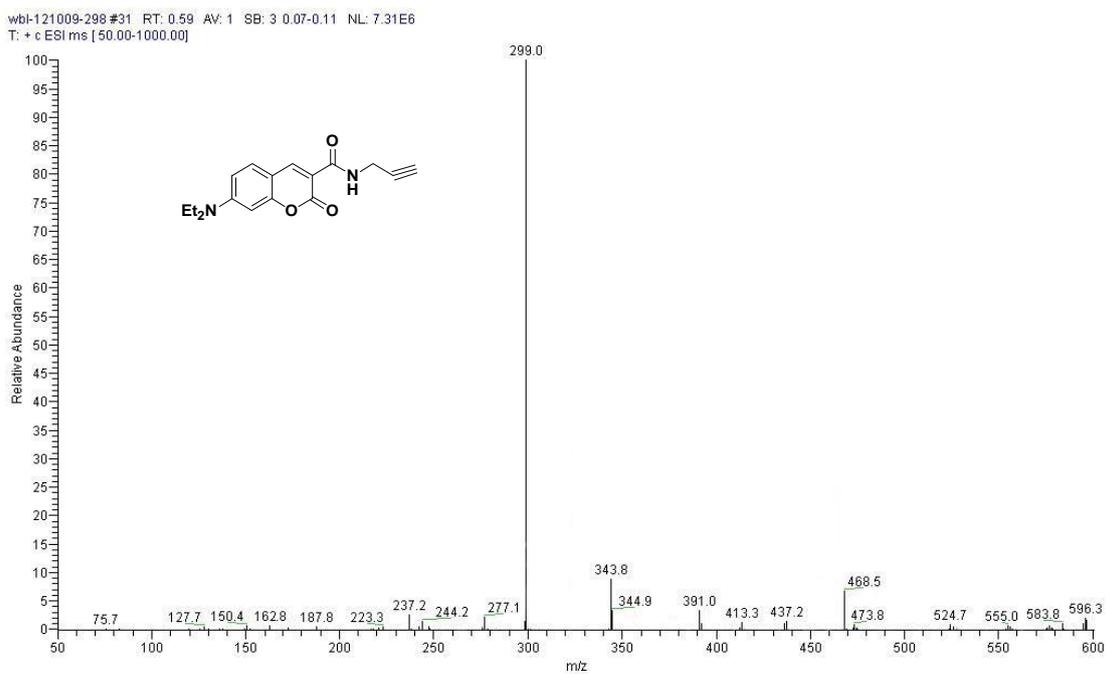


Figure S3. HRMS spectrum of compound A.

wbl-121011-313 #33 RT: 0.63 AV:1 NL: 4.11E5

100^+ c ESI Full ms [310.00-315.00]

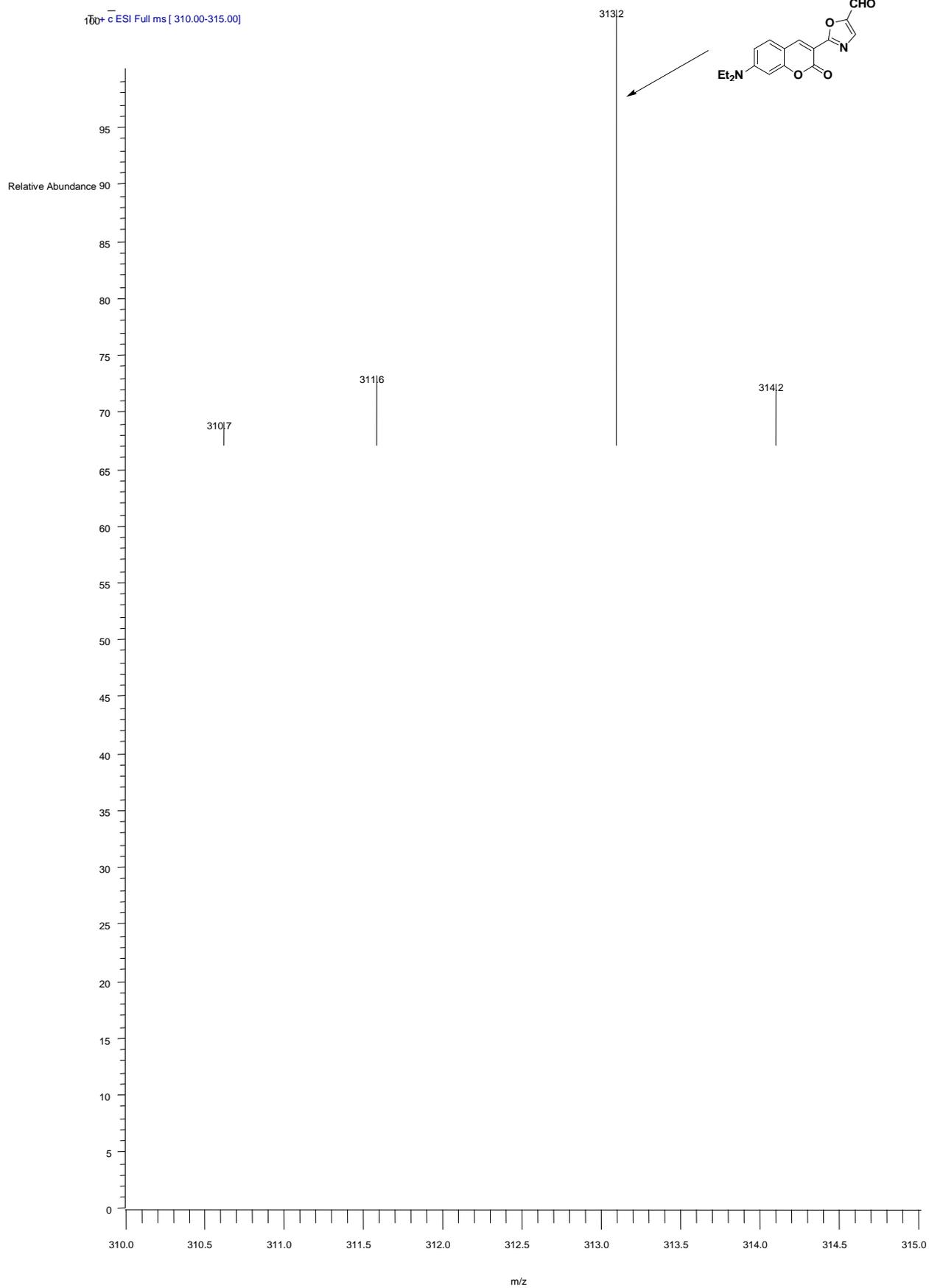


Figure S4. Mass spectrum of probe A (3 μM) with 4 equiv. of Au^{3+} ions in HEPES buffer at pH 7.4 /DMF (4:6).

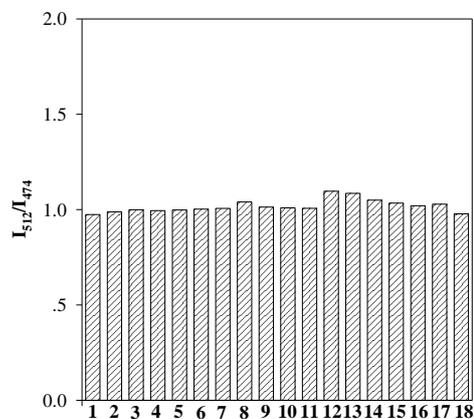


Figure S5 Fluorescent ratiometric response of probe Ratio-Au (500 nM) to the various metal ions (2000 equiv. for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , 2 equiv for Au^{3+} , 4 equiv. for other tested metal ions) in 10mM HEPES buffer at pH 7.4/DMF(4:6): 1. $\text{Ag}^+ + \text{Au}^{3+}$; 2: $\text{Cu}^{2+} + \text{Au}^{3+}$; 3: $\text{Cd}^{2+} + \text{Au}^{3+}$; 4: $\text{Pb}^{2+} + \text{Au}^{3+}$; 5 : $\text{Ca}^{2+} + \text{Au}^{3+}$; 6: $\text{Ba}^{2+} + \text{Au}^{3+}$; 7: $\text{Mn}^{2+} + \text{Au}^{3+}$; 8: $\text{Mg}^{2+} + \text{Au}^{3+}$; 9: $\text{Zn}^{2+} + \text{Au}^{3+}$; 10: $\text{Al}^{3+} + \text{Au}^{3+}$; 11: $\text{Fe}^{3+} + \text{Au}^{3+}$; 12: $\text{Fe}^{2+} + \text{Au}^{3+}$; 13: $\text{Hg}^{2+} + \text{Au}^{3+}$; 14: $\text{K}^+ + \text{Au}^{3+}$; 15: $\text{Na}^+ + \text{Au}^{3+}$; 16: $\text{Ni}^{2+} + \text{Au}^{3+}$; 17: $\text{Co}^{2+} + \text{Au}^{3+}$, 18: Au^{3+} .

References:

(S1) G. He, D. Guo, C. He, X. Zhang, X. Zhao, and C. Duan, *Angew. Chem. Int. Ed.* 2009, 48, 6132–6135.