Supporting Information

Coumarin-based Chromogenic and Ratiometric Probe for

Hydrazine

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Experimental Section

General remarks for experimental

¹H NMR, ¹³C NMR spectra were measured on a Bruker AM400 NMR spectrometer. Proton Chemical shifts of NMR spectra were given in ppm relative to internals reference TMS (1H, 0.00 ppm). ESI-MS and HRMS spectral data were recorded on a Finnigan LCQ^{DECA} and a Bruker Daltonics Bio TOF mass spectrometer, respectively. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were dried according to the standard methods prior to use. All of the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies.

Fluorescence emission spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA Jobin Yvon) at 298 K. Fluorescence emission spectra were obtained with a Xenon lamp and 1.0 cm quartz cells. Unless otherwise noted, the fluorescence data was collected after 40 min when the hydrazine added to the solution of probe **1**.



Fig. S1: Fluorescence spectra of 1 (5 μ M) with pH changing from 7.0 to 10.6 (λ_{ex} =344 nm)



Fig. S2 Fluorescence intensity of probe 1 (10 μ M) with hydrazine (50 μ M) in DMSO.



Fig. S3 Fluorescence titration of probe 1 (10 μ M) with hydrazine in DMSO.



Fig. S4 Fluorescence intensity of probe **1** (10 μ M) with hydrazine (50 μ M) in a mixture of acetate buffer (pH 4.5, 10mM) and DMSO, from left to right the proportion is 1:9, 2:8, 3:7 (v/v)



Fig. S5 Fluorescence responses of **1** (10 μ M) in a mixture of acetate buffer (pH 4.5, 10 mM) and DMSO (1:9, v/v) to various representative cations (10 μ M) including Zn²⁺, Fe²⁺, Pb²⁺, Hg²⁺, Ba²⁺, Al³⁺, Fe³⁺, Ag⁺, Co²⁺, Mg²⁺, Ca²⁺, Li⁺, Ni²⁺, Cd²⁺, Cr³⁺, Mn²⁺, K⁺, Na⁺ and contrast. ($\lambda_{ex} = 328$ nm)



Fig. S6. The color change of probe **1** (10 μ M) in a mixture of acetate buffer (pH 4.5, 10mM) and DMSO (1:9, v/v) under a UV lamp (365nm) by addition of 5 equiv. anions and primary amines (from left to right: blank, hydrazine, NH₃•H₂O, methylamine, ethylene diamine, urea, BO₃⁻, SO₃²⁻).



Fig. S7 Fluorescence titration of **2** (10 μ M) with hydrazine in a mixture of acetate buffer (pH 4.5, 10mM) and DMSO (1:9, v/v).



Fig. S8 Fluorescence responses of **2** (10 μ M) in a mixture of acetate buffer (pH 4.5, 10mM) and DMSO (1:9, v/v). From top to bottom: Hydrazine, NH₃•H₂O, methylamine, ethylene diamine and urea (10 μ M).



Fig. S9 UV-vis titration of **1** (10 μ M) with hydrazine in a mixture of acetate buffer (pH 4.5, 10 mM) and DMSO (1:9, v/v).



Fig. S10 The ESI-TOF mass spectrum of probe 1 in the presence of hydrazine (5eq.).