Supporting Information

A LONG-WAVELENGTH EMISSION FLUORESCENT PROBE BASED ON TCF DERIVATIVES FOR HIGH-SENSITIVITY DETECTION OF Hg^{2+}

Yuan Sun,[a] Keli Zhong,[a] Lijun Tang,[a,c,*] and Xiaomei Yan [b,*]

[a] College of Chemistry and Materials Engineering, Bohai University, Jinzhou 121013, China. E-mail: ljtang@bhu.edu.cn (L. Tang)

[b] College of Laboratory Medicine, Dalian Medical University, Dalian, 116044, China. E-mail: xmyan1978@sina.com (X. Yan)

[c] Department of Chemistry, National Demonstration Centre for Experimental Chemistry Education, Yanbian University, Yanji 133002, China.

Table of Contents

EXPERIMENTAL SECTION

Unless otherwise specified, solvents and reagents are analytical grade products provided by commercial suppliers and used directly. Compound **2** was synthesized according to literature method.[1] ^{1}H NMR and ^{13}C NMR are measured on an Agilent 400-MR nuclear magnetic resonance instrument. High-resolution mass spectrometry (HRMS) were recorded on a mass spectrometer (Bruker, microTOF-Q). the fluorescence spectra were measured with F-4700 fluorescence spectrophotometer (Hitachi, Japan). Cell imaging were performed under the Leica SP2 (Germany Leica) laser confocal scanning microscope.

Double distilled water was used throughout the experiment, prepare a stock solution of probe **1** (1.0 mM) in DMSO, The stock solution was further diluted with a mixed solution of MeOH/Tris (1:1, v/v, Tris 20 mM, pH = 7.4) to obtain a test solution (10 μM). Metal ions (with the corresponding nitrate or chloride, 10 mM) are prepared with deionized water for titration experiments. Measure and record the fluorescence spectra and ultraviolet spectra with a quartz cuvette with an optical path of 10 mm at 25 °C. (λ_{ex}= 465 nm, λ_{em} = 625 nm).

MCF-7 (human breast carcinoma) cells were obtained from Institute of Basic Medical Sciences (IBMS) of Chinese Academy of Medical Sciences (CAMS), MCF-7 cells were cultured in Dulbecco's modified Eagle's medium (DMEM, Invitrogen) supplemented with 10% FBS (fetal bovine serum) in an atmosphere of 5% CO_2 and 95% air at 37 °C. Grow MCF-7 cells in the exponential phase of growth on 35-mm glass-bottom culture dishes (Φ 20 mm) for 1-2 days to reach 70-90% confluence, remove the medium, and wash the cells 3 times with PBS buffer (pH = 7.4). Then incubate the cells with probe **1** (10 μM) for a further 30 min at 37 °C, after washing 3 times with PBS buffer, cell imaging was conducted. In order to evaluate the ability of probe **1** for sensing Hg^{2+} in living cells, the probe **1** treated live MCF-7 cells were in situ incubated with different concentrations of Hg^{2+} for 30 min at 37 °C, and then the same group of cells was used for fluorescence imaging measuring.

Synthesis of Probe 1. Compound **2** (0.706 g, 2.0 mmol) was dissolved in dry CH_2Cl_2 (30 mL) at 0 °C, and triethylamine (0.54 mL, 4.0 mmol) was added to the solution, after stirring for 30 min, phenyl thiochloroformate (0.517 g, 3 mmol) was add dropwise, and the resultant was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure, the crude product was purified by silica gel column chromatography (CH_2Cl_2 as eluent) to give yellow powder (0.685 g, 70%). mp 243.8-244.9 °C ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 1H), 8.19-8.12 (m, 2H), 8.10-8.04 (m, 2H), 7.95 (d, J = 1.5 Hz, 1H), 7.61 (dd, J = 8.9, 2.0 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.37 (dd, J = 12.3, 5.9 Hz, 4H), 1.82 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.51, 177.60, 175.36, 153.60, 152.77, 147.30, 135.44, 132.94, 132.46, 131.77, 131.56, 130.41, 129.29, 127.53, 125.30, 122.94, 122.18, 119.61, 116.45, 113.13, 112.30, 111.39, 100.00, 55.00, 25.50. HRMS (ESI-): Calcd for $C_{29}H_{18}N_3O_3S$ $[M-H]^-$ 488.1074; found: 488.1093.

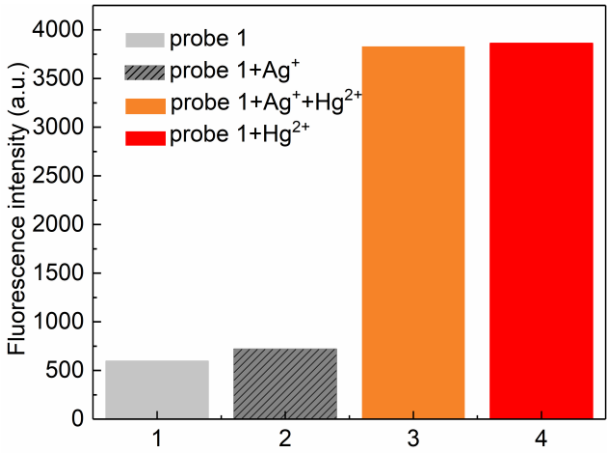

Figure S1. Fluorescence intensity changes of probe **1** toward Ag^+ and Hg^{2+} in MeOH/Tris (1:1, v/v, Tris 20 mM, pH = 7.4 NaCl = 154 mM) solution.

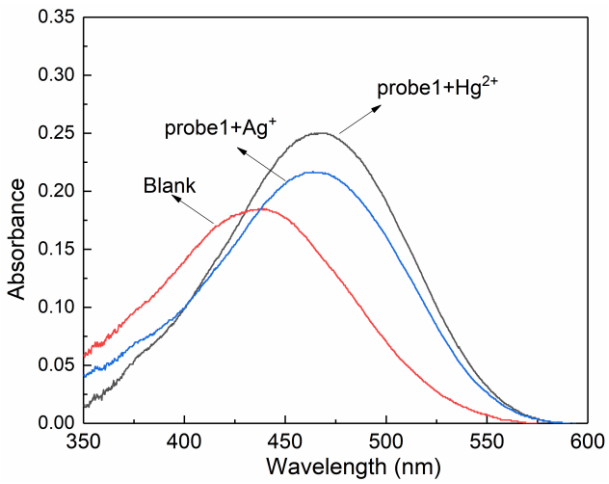

Figure S2. Changes in UV-vis absorption spectra of probe 1 (10 μM) in MeOH/Tris (1:1, v/v, Tris 20 mM, pH = 7.4) on addition of Ag^{+} and Hg^{2+} (30 μM of each)

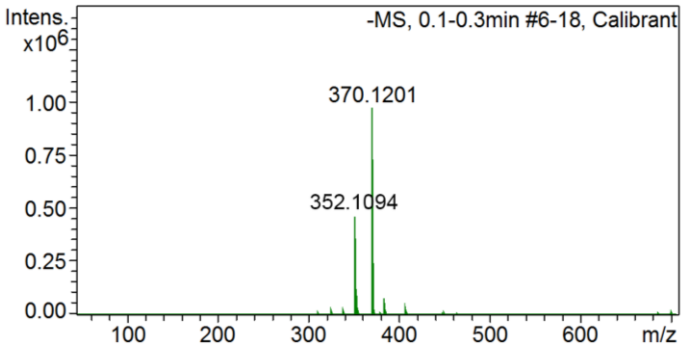

Figure S3. HRMS (ESI^{-}) spectra of probe **1** in the presence of 30 μM of Hg^{2+}

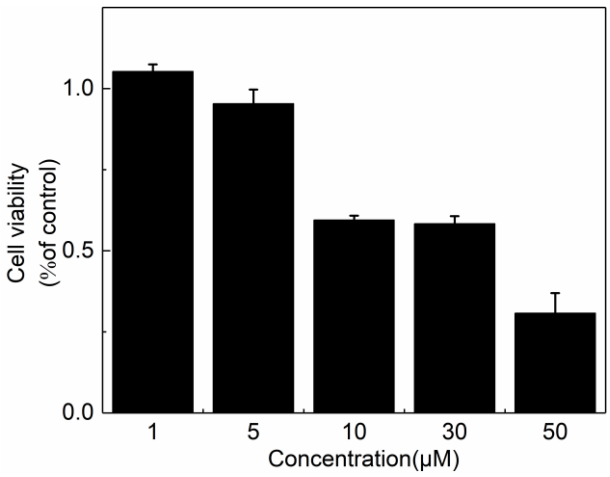

Figure S4. Cell viability values (%) evaluated by CCK-8 analysis after culturing MCF-7 cells in the presence of probe **1** at different concentrations (1, 5, 10, 30, and 50 μM) for 24 hours at 37 ºC.

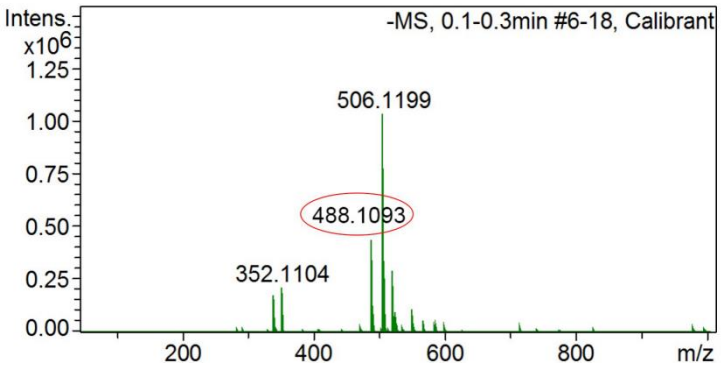

Figure S5. HRMS (ESI^-) spectra of probe **1**

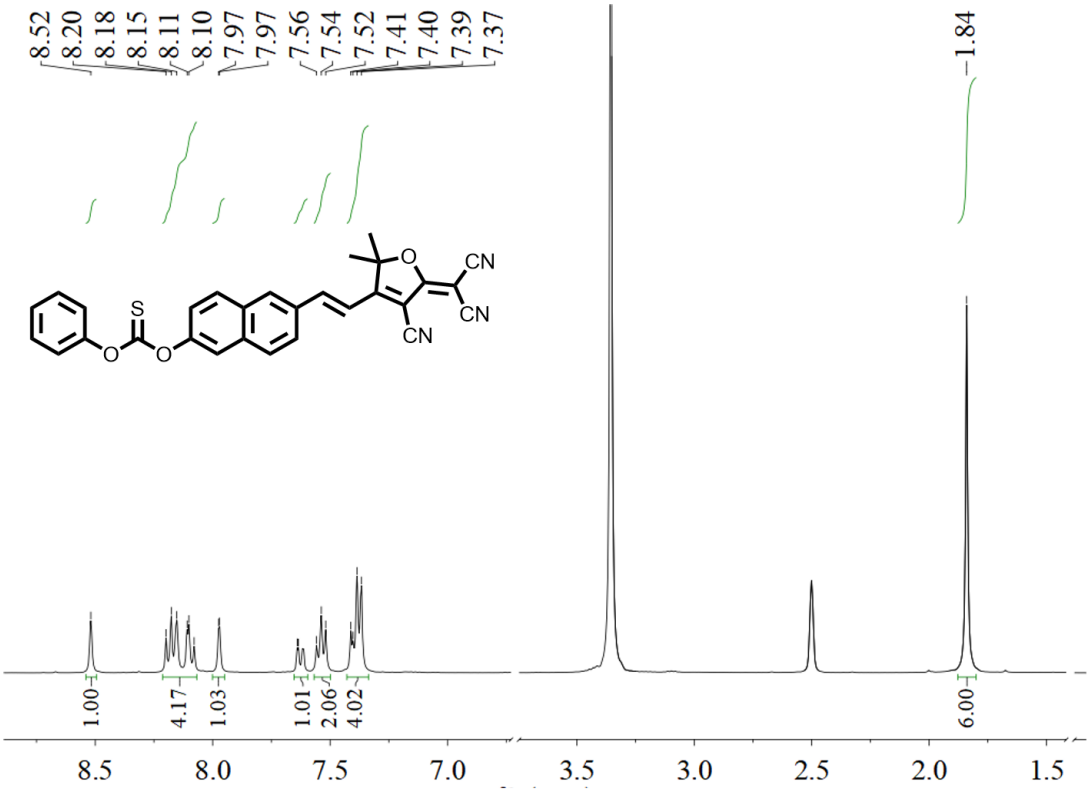

Figure S6. ^1H NMR spectra of probe **1** in DMSO-d_6

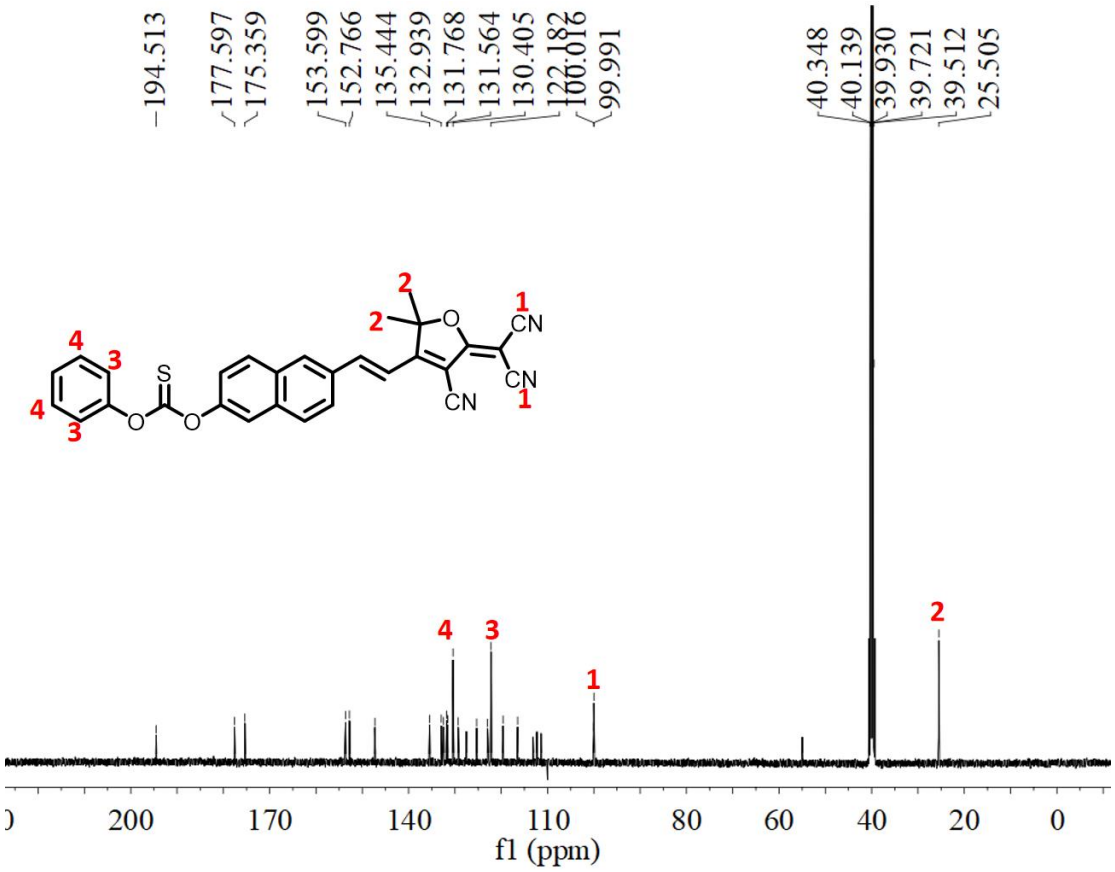

Figure S7. ^{13}C NMR spectra of probe **1** in DMSO-d_6.

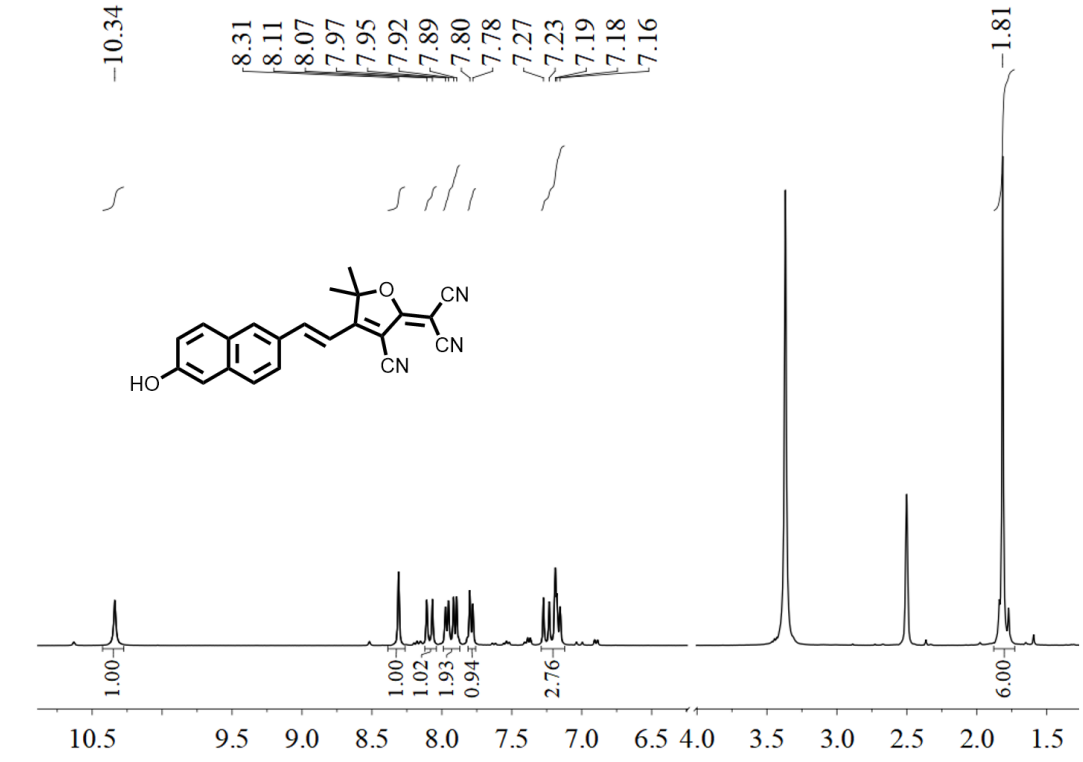

Figure S8. ^{1}H NMR spectra of probe **1**+Hg^{2+} in DMSO-d_6.

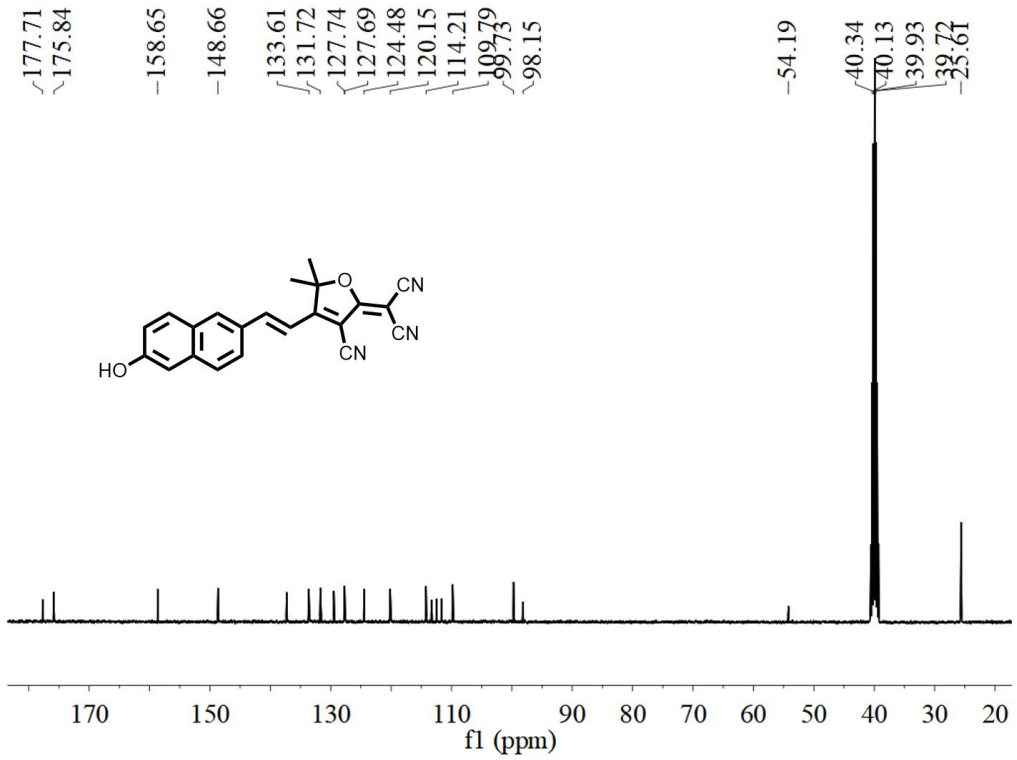

Figure S9. ^{13}C NMR spectra of probe **1**+Hg^{2+} in DMSO-d_6.

References

1. I. Martin, C. Billon, G. Micouin, et al . *Org. Biomol. Chem*, 2014, **12**, 3641.