† Electronic Supplementary Information (ESI)

A colorimetric and fluorescent dual probe for palladium in aqueous medium and living cell imaging

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Materials and General Information

^{1}H and ^{13}C NMR spectra were recorded using TMS as the internal standard in $CDCl_3$ with a Bruker BioSpin GmbH spectrometer at 400 MHz and 100 MHz, respectively. High resolution mass spectra (HRMS) was taken on a Thermo-Fisher LTQ Orbitrap XL instrument. Flash column chromatography was performed with silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co. Ltd. All chemicals were purchased from commercial sources unless otherwise specified. All the solvents were of analytical reagent grade and were used without further purification.

The UV-vis absorption spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on an FL-4500 fluorescence spectrophotometer (Hitachi, Japan) equipped with quartz cell of 10.0 mm path length. Unless otherwise noted, the spectra were measured in PBS buffer solution after the mixtures were equilibrated at room temperature. The cells were imaged using a LSM 710 laser scanning confocal microscope (Carl Zeiss, Germany).

General procedure of spectral Measurements

The stock solutions of **Res-1** and $Pd(PPh_3)_4$ (10 mM) were prepared by dissolving the required amount in DMSO. $Hg(NO_3)_2$ (10 mM) was dissolved in methanol. Metal ion (Fe^{2+}, K^{+}, Co^{2+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}, Ba^{2+}) stock solutions (10 mM) were obtained by diluting the standard solutions of the corresponding nitrate salt, respectively.

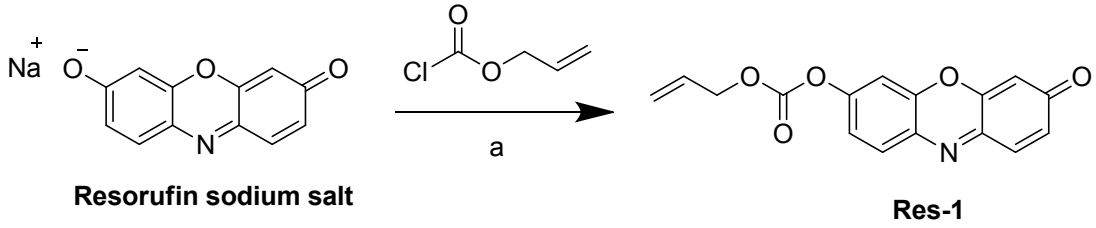
Absorption and fluorescence titrations were performed by adding small aliquots of **Res-1** and metal working solutions into a quartz cell (10.0 mm width). The fluorescence intensity was measured at the excitation wavelength of 570 nm. The excitation and emission slit width were both 5 nm.

General procedure of cell imaging

HeLa cells were grown in DMEM media containing 10% fetal bovine serum, 100 U/mL penicillin with 100 μg/mL streptomycin at 37 °C with 5% CO_2 atmosphere. The cells were seeded on a Ø 30 mm glass-bottomed dish at the density of 1×10^5 cells in a culture medium and incubated overnight for living cell imaging by confocal laser scanning microscopy (CLSM). The HeLa cells were treated with 10 μM of Hochest33342 and **Res-1**, which are prepared by diluting 2.0 μL of stock solution (10 mM in DMSO) with 2 mL of PBS solution and incubated for 30 min at 37 °C and washed with three times with PBS before imaging by CLSM. And the cells were subsequently incubated with Pd^0 (10 μM) for 30 min at 37 °C and washed three times with PBS before imaging by CLSM. The cells were imaged with a 40× objective lens. The excitation wavelengths were 405 nm for Hochest33342 and 543 nm for **Res-1**, respectively.

Synthesis and Characterization

Scheme S1. Synthesis of **Res-1**[*]

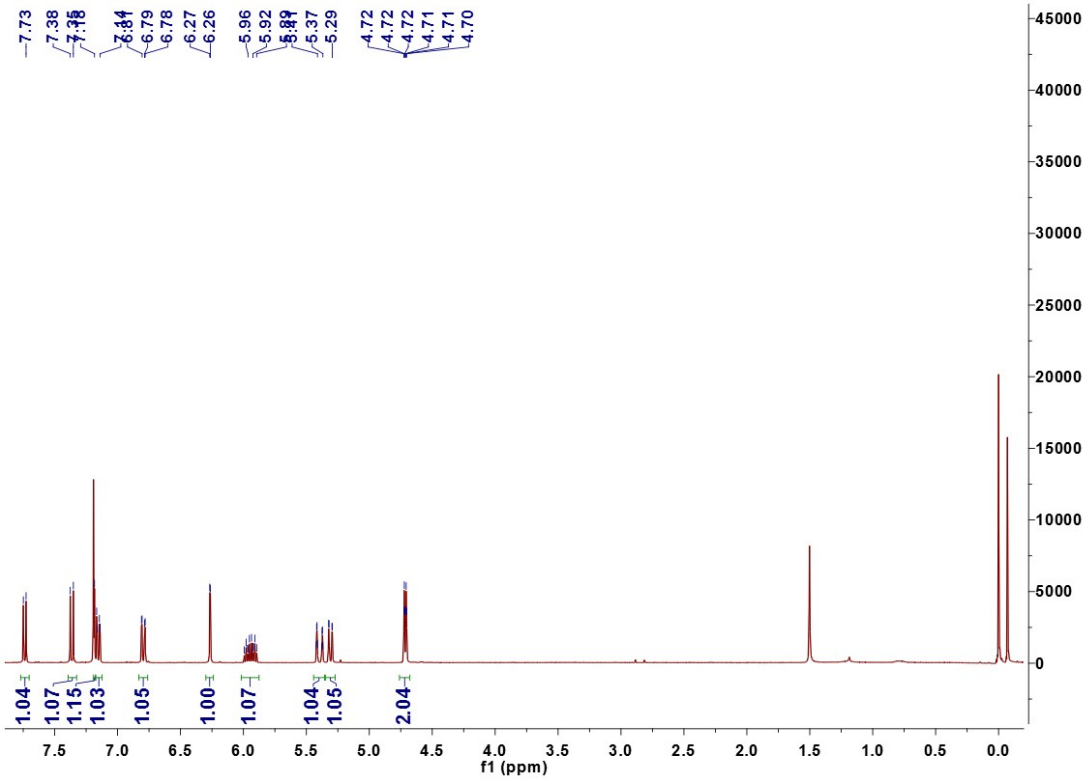


Resorufin sodium salt **Res-1**

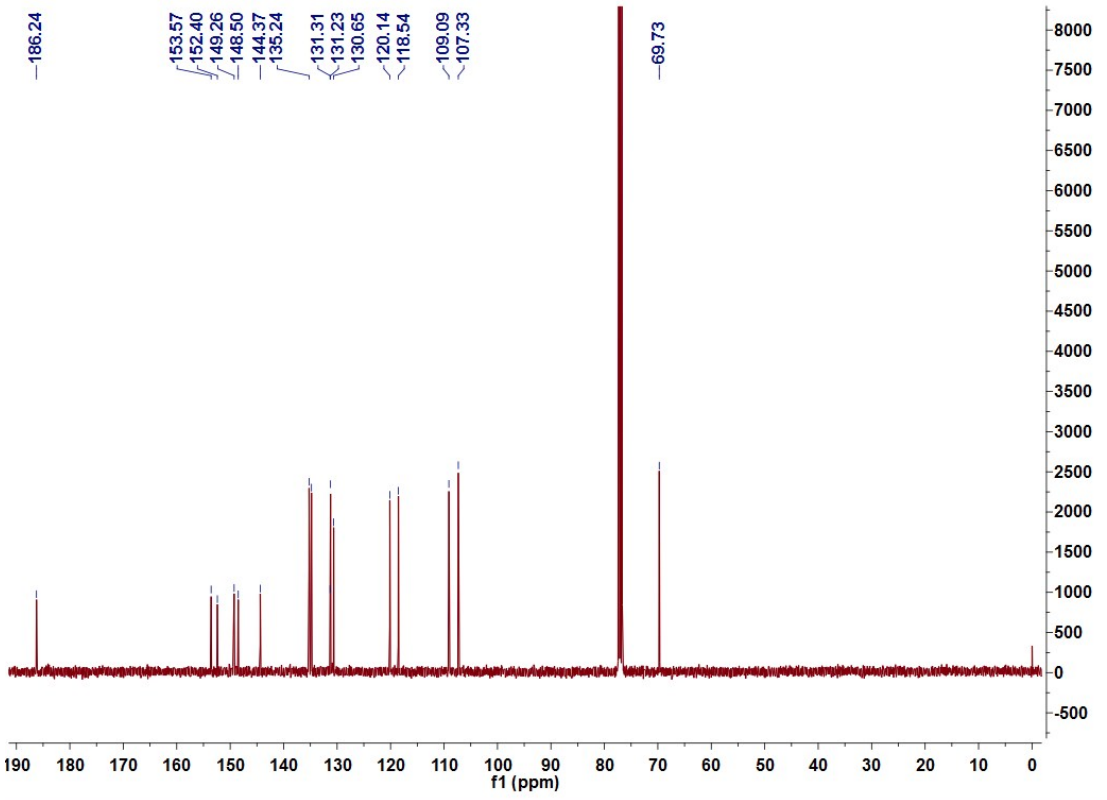
[*] Reagents and conditions: (a) DMF, Et_3N, RT, overnight.

Synthesis of allyl (3-oxo-3H-phenoxazin-7-yl) carbonate (Res-1). Allyl chloroformate (0.144g, 1.2 mmol) was added to a solution of Resorufin sodium salt (0.235 g, 1.0 mmol) and triethylamine (0.120 g, 1.2 mmol) in 10 mL DMF. The reaction mixture was stirred overnight at room temperature, and the resulting solution was treated with water and CH_2Cl_2. The organic phase was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford **Res-1** (0.204 g, 68.7%) as an orange colored solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.7 Hz, 1H), 7.36 (d, J = 9.8 Hz, 1H), 7.18 (s, 1H), 7.15 (dd, J = 8.7, 2.5 Hz, 1H), 6.80 (dd, J = 9.8, 2.0 Hz, 1H), 6.27 (d, J = 2.0 Hz, 1H), 6.02-5.88 (m, 1H), 5.44-5.36 (m, 1H), 5.31 (dd, J = 10.4, 1.1 Hz, 1H), 4.71 (dt, J = 5.9, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.24, 153.57, 152.40, 149.26, 148.50, 144.37, 135.24, 134.80, 131.31, 131.23, 130.65, 120.14, 118.54, 109.09, 107.33, 69.73. HRMS (ESI): calcd for $(M+Na)^+$ ($C_{16}H_{11}O_5NNa^+$) 320.0529, found 320.0541.

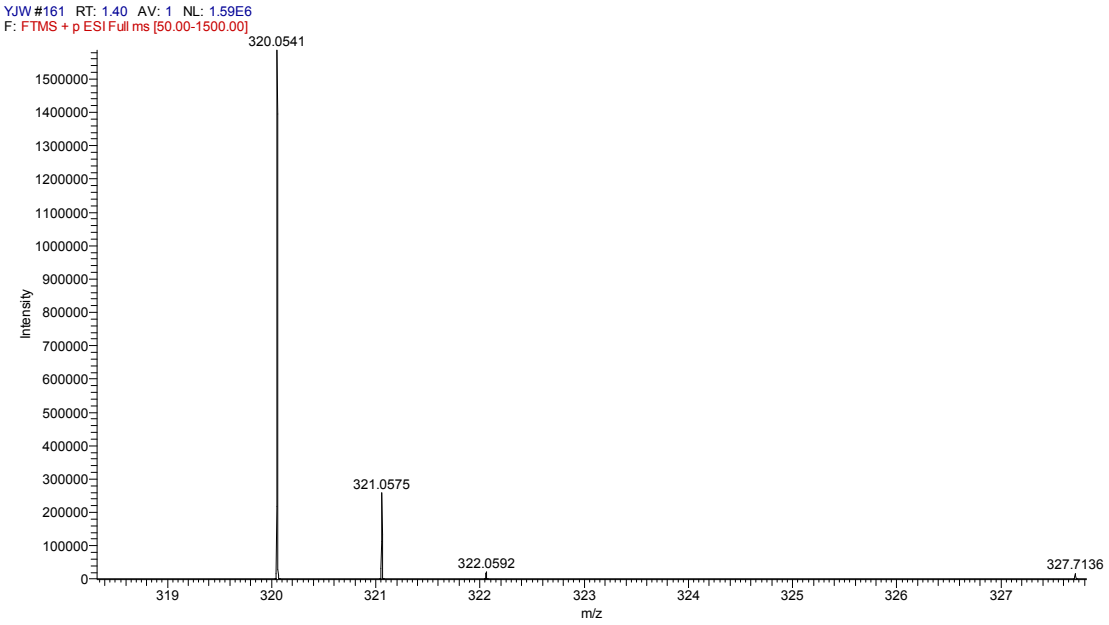
^{1}H NMR, ^{13}C NMR, and HRMS spectra of compound Res-1.



^{1}H NMR spectrum of **Res-1**



^{13}C NMR spectrum of **Res-1**



HRMS spectrum of **Res-1**

A **B**

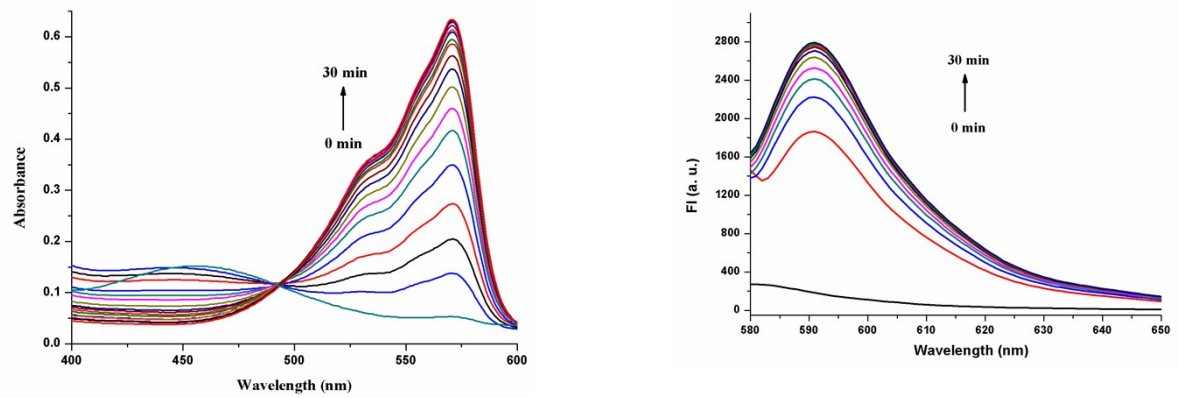


Fig. S1. UV-vis spectral changes (A) and fluorescence spectral changes (B) of **Res-1** (10 μM and 0.5 μM, respectively) against time in the presence of $Pd(PPh_3)_4$ (3 equiv) in PBS buffer at 25 °C.

A **B**

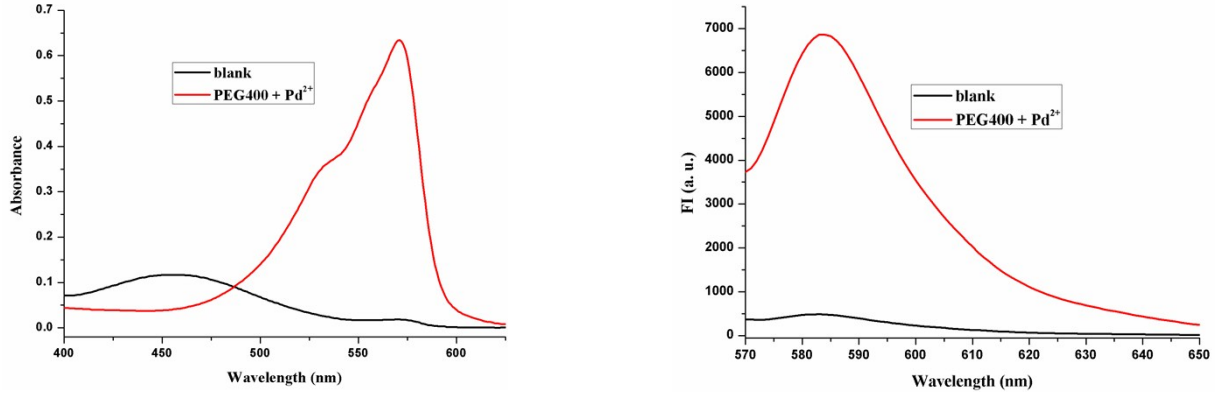


Fig. S2. UV-vis spectral changes (A) and fluorescence spectral changes (B) of **Res-1** (10 μM and 0.5 μM, respectively) in the presence of $PdCl_2$ (3 equiv) in PEG400-PBS solution (1:1, v/v) at 25 °C.

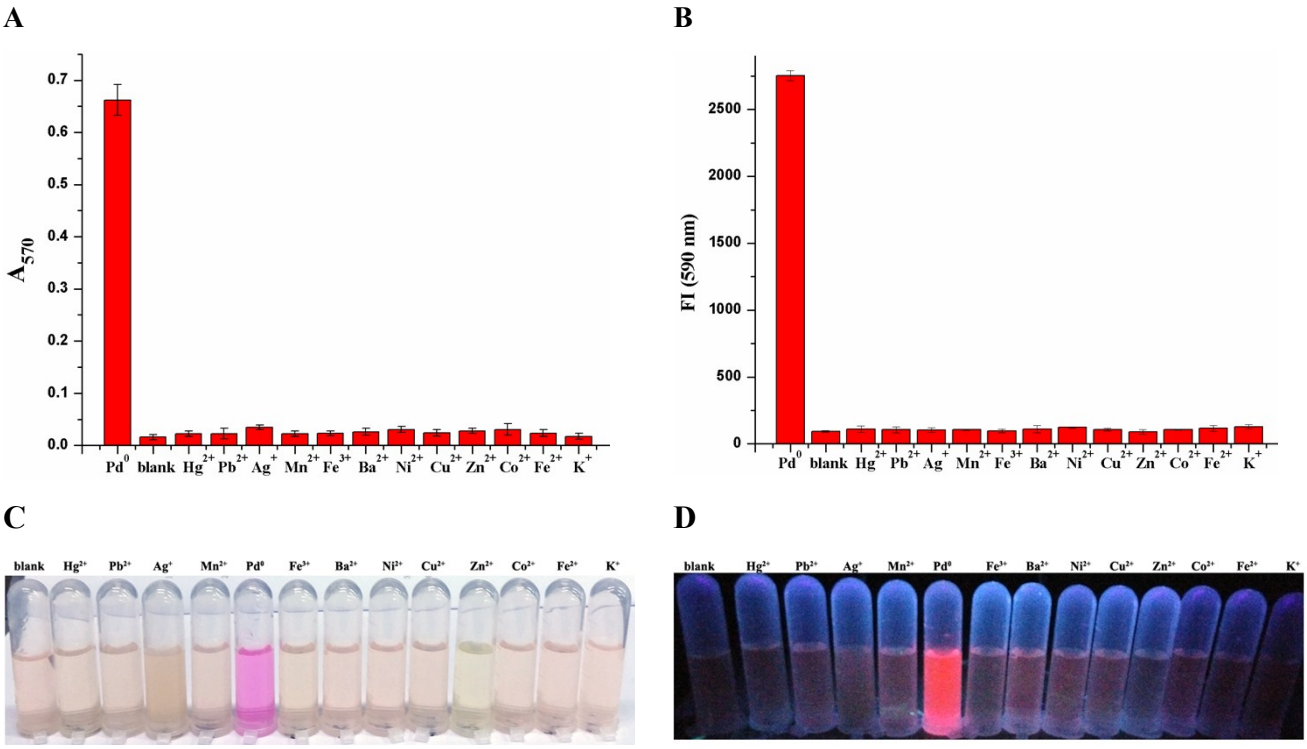


Fig. S3. Absorbance at 570 nm (A), fluorescence intensity at 590 nm (B), color changes (C) and emission changes (D) of **Res-1** (10 μM, 0.5 μM, 10 μM and 0.5 μM, respectively) in the presence of $Pd(PPh_3)_4$ (3 equiv) and the excess of representative metal ions (100 equiv) in PBS buffer at 25 °C. Each spectrum was acquired 30 min after mixing.

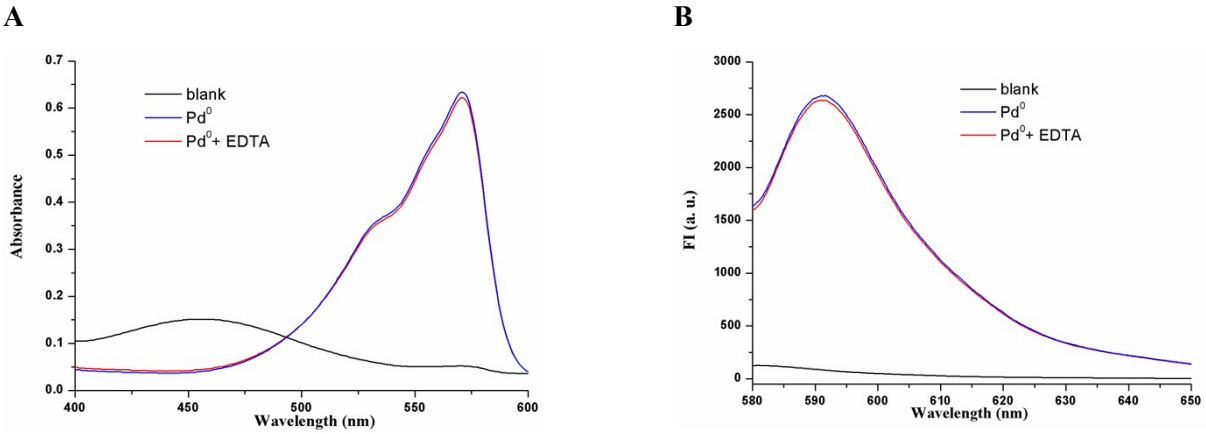


Fig. S4. UV-vis spectral changes (A) and fluorescence spectral changes (B) of **Res-1** (10 μM and 0.5 μM, respectively) in the presence of $Pd(PPh_3)_4$ (3 equiv), with or without EDTA (3 equiv) at 25 °C.