Electronic Supplementary Information

for

A new ratiometric ESIPT sensor for detection of palladium species in aqueous solution

Bin Liu, Hu Wang, Taisheng Wang, Yinyin Bao, Fanfan Du, Jiao Tian, Qianbiao Li, Ruke Bai*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, P. R. China 230026.

E-mail: bairk@ustc.edu.cn

Tel: 0086-551-3600722; Fax: 0086-551-3631760

Contents

1. Materials and Methods.

Preparation of parent stock palladium solutions used for this study

Entry	Reagent	Quantity	Solvent(4ml)	Concentration
A	$Pd(PPh_3)_4$	23mg	DMSO	5mM
B	$PdCl_2$	10.8mg	3:1 Brine/MeOH	15mM
C	$Pd(PPh_3)_2Cl_2$	14mg	DMSO	5mM
D	$Pd(dppf)_2Cl_2$	48.9mg	DMSO	15mM
E	K_2PdCl_6	19.9mg	3:1 Brine/MeOH	15mM

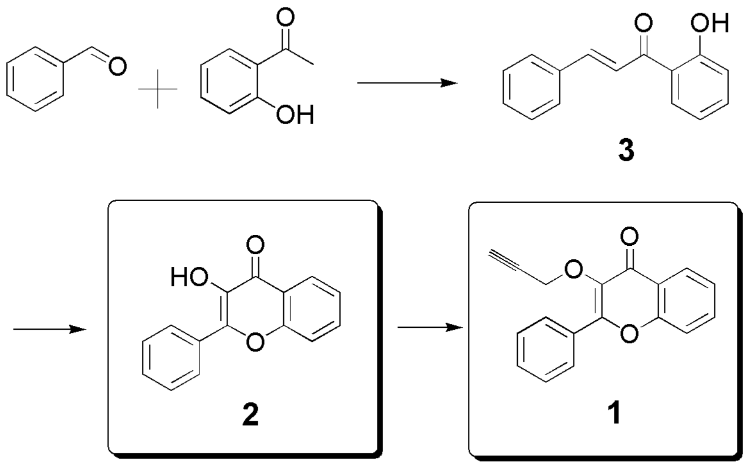
Notes: All the solutions were stored in the dark at 24 °C. A and C were freshly prepared every 1 weeks.

Each metal ion titration experiment was started with 5.0mL 1 (10μM) in CH_3CN-H_2O (1:4, v/v) solution with 10mM of HEPES buffer. Analyte solutions were prepared from $AgNO_3$, $Co(NO_3)_2$, $CdCl_2$, $MgCl_2$, $NiCl_2$, $CuCl_2 \cdot H_2O$, $ZnCl_2$, $HgCl_2$, $FeCl_3$, $CaCl_2$ (5×10^{-2} mol/L) by separately dissolved in water. All kinds of measurements were monitored after storing the mixture for 3h in room temperature.

NMR spectra were obtained using a Bruker AVANCE Ⅱ for ^{1}H NMR and ^{13}C NMR. Elemental analyses were measured by VARIO ELIII. HRMS and LC-MS spectra were obtained using a LTQ ORBITRAP XL from Thermo Scientific Company. UV-Vis spectra were recorded with Pgeneral UV-Vis TU-1901 spectrometer and fluorescence spectra were measured by RF-5301PC spectrometer. Molecular weight was determined by GPC on a Waters systems equipped with a Waters 1515 pump, a Water 2414 differential refractive index detector, and three styragel columns. THF was used as solvent and relative to polystyrene standards. All solvents and reagents were commercially available A.R. grade.

2. Synthesis

Precursors **3** and **2** were prepared according to literature procedures.[1]



Synthesis of 2′-hydroxychalcone (3)

An aqueous solution of sodium hydroxide (60%, 80 mL) was added to a methanolic solution (80 mL) of 2′-hydroxyacetophenone (40 mmol). The obtained solution was cooled to room temperature, benzaldehyde (40 mmol) was added and the reaction mixture was stirred for 12 h. After this period, the reaction mixture was poured into a mixture of water (100 mL), ice and hydrochloric acid (pH adjusted to 2). The obtained solid was filtered, taken in chloroform (200 mL) and washed with a 5% aqueous solution of sodium hydrogen carbonate (2×200 mL). The organic layer was collected, dried and evaporated to dryness. The residue was crystallized from ethanol; giving 2′-hydroxychalcone **4** (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=12.82 (s, *OH*), 7.95-7.92 (m, 2H), 7.69-7.65 (m, 3H), 7.51(t, 1H), 7.45(t, 1H), 7.05(d, 1H), 6.98(t, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) d=193.77, 163.63, 145.48, 136.41, 134.64, 130.93, 129.66, 129.07, 128.67, 120.18, 120.05, 118.86, 118.67.

Synthesis of 3-hydroxyflavone (2)

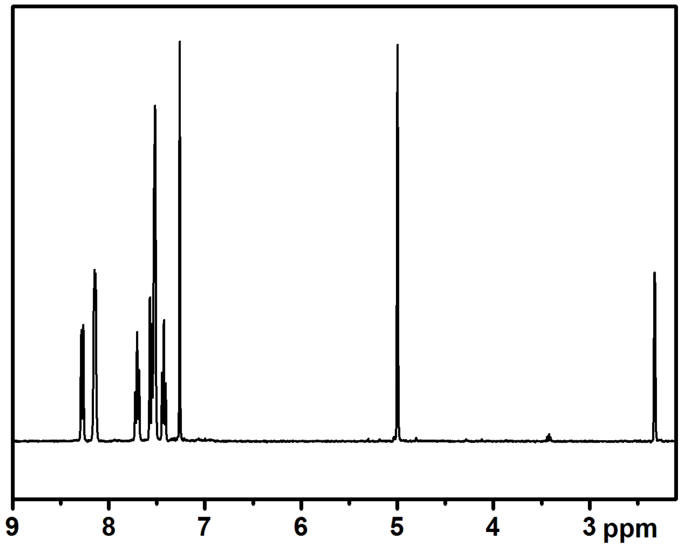
Compound **4** (3.0 mmol) and 4mL of 20% NaOH solution were dissolved in 20mL of CH_3OH. The reaction mixture was placed in an ice-water bath and 3mL of 30% H_2O_2 solution was slowly added, and then the resulting mixture was stirred at room temperature for another 7 h with the gradual formation of precipitation. The collected precipitation was dried and the crude product was used for the next step without further purification. Yield=43%. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.28-8.26 (d, 3H), 7.74 (t, 1H), 7.62 (d, 1H), 7.57(t, 2H), 7.50 (d, 1H), 7.45(t, 1H), 7.02(t, *OH*).

Synthesis of 3-(prop-2-ynyloxy)-hydroxyflavone (1)

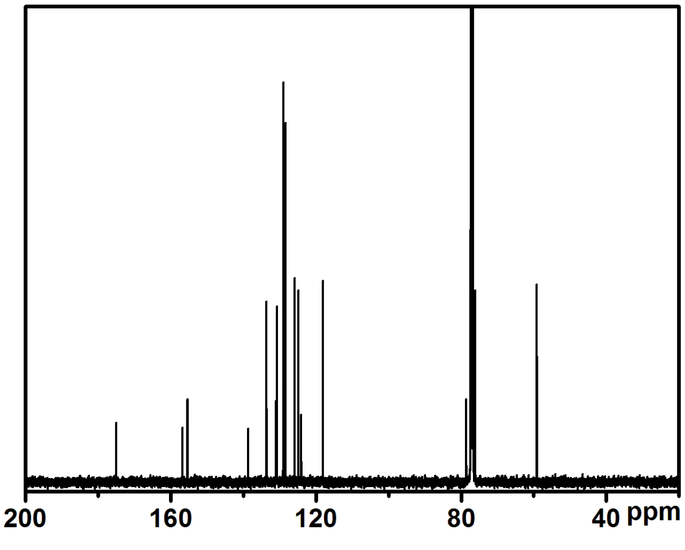
Compound 3 (100mg, 0.42 mmol) was dissolved in 20mL of dry acetone and 0.5mL 3-Bromo-1-propyne (0.63mM) was added. The mixture was stirred at room temperature for 15 min, followed by addition of potassium carbonate (87mg, 0.63mM). The mixture was stirred at 65℃ for 12 h. Then 40ml CH_2Cl_2 was added into the reaction mixture and washed with brine and water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to give probe **1** (53%) as yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.26 (d, 1H), 8.15 (d, 2H), 7.70 (t, 1H), 7.57(d, 1H), 7.53-7.51 (m, 3H), 7.45(t, 1H), 5.00(s, 2H), 2.32(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) d=174.97, 156.60, 155.34, 138.62, 133.60, 130.97, 130.80, 128.97, 128.38, 125.84, 124.84, 124.05, 118.06, 78.60, 76.14, 59.18. HRMS: *m/z* calcd. for $C_{18}H_{13}O_3$ $(M + H)^+$ 277.0859 found 277.0758.

3. The characterization data of compound 1

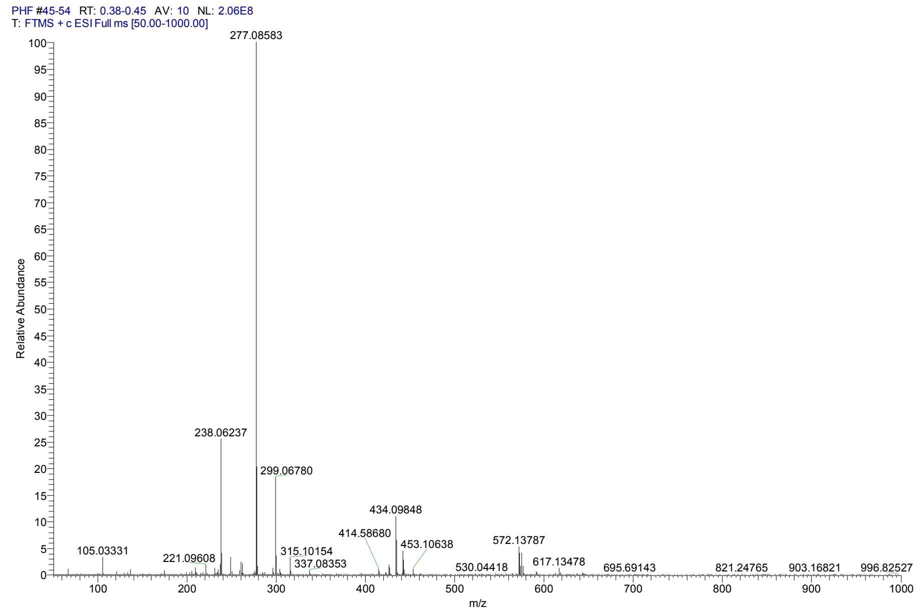
^{1}H NMR spectra of **1**



^{13}C NMR spectra of **1**



HRMS of **1**



4. Additional Spectra

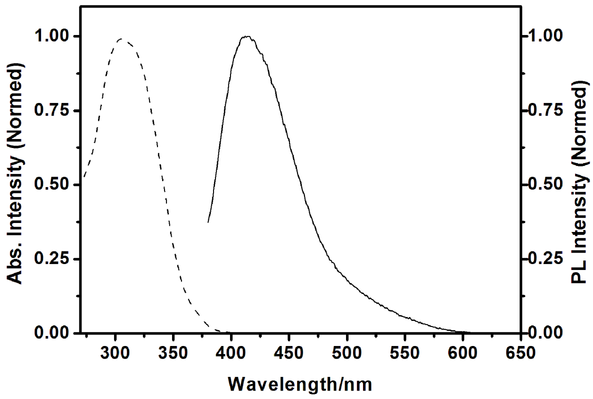


Fig. S1. Normalized UV-Vis absorption and emission spectra of **1**. The excitation wavelength is 360nm. The dash line is absorption spectra and the solid line is emission spectra, respectively.

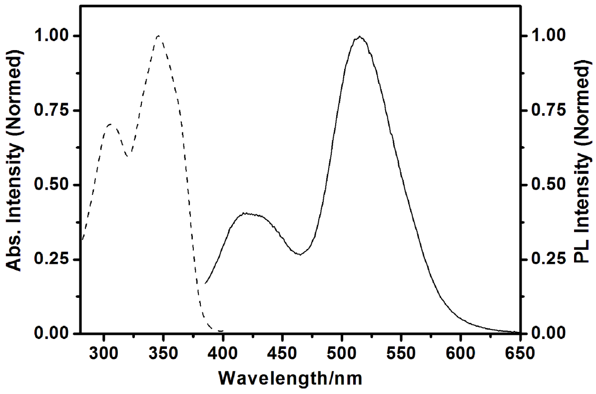
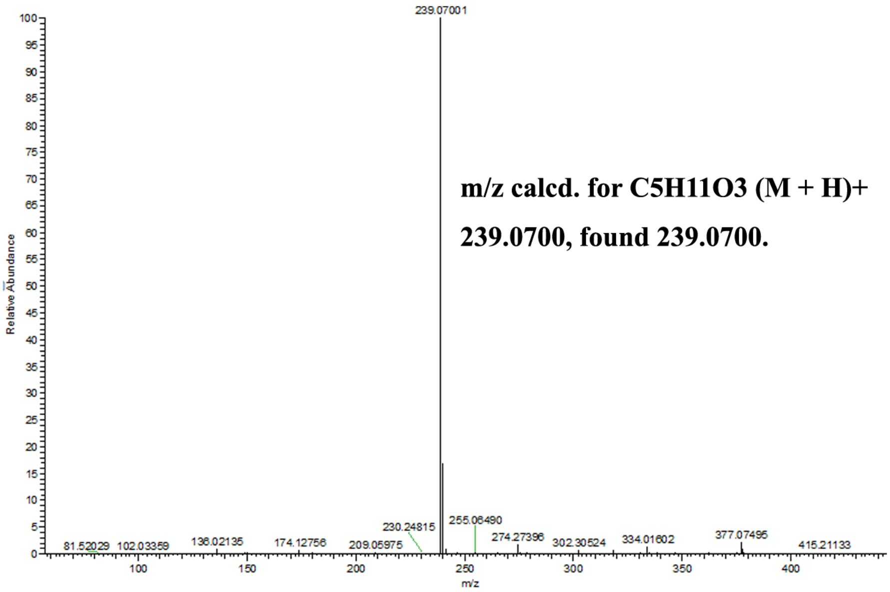


Fig. S2. Normalized UV-Vis absorption and emission spectra of **2**. The excitation wavelength is 360nm. The dash line is absorption spectra and the solid line is emission spectra, respectively.[a]

a: The fluorescent intensity at λ=412 nm isn't very stable, this may be because the intensity of the 412 nm band is greatly affected by the hydrogen bond donating ability of the solvent molecules, which is instable under tiny environment changes.[2] In order to eliminate the impact of errors, all fluorescence data were repeated 3 times.



m/z calcd. for C5H11O3 (M + H)+

239.0700, found 239.0700.

Fig. S3 LC-MS of reaction product of chemosensor **1** with $PdCl_2$.

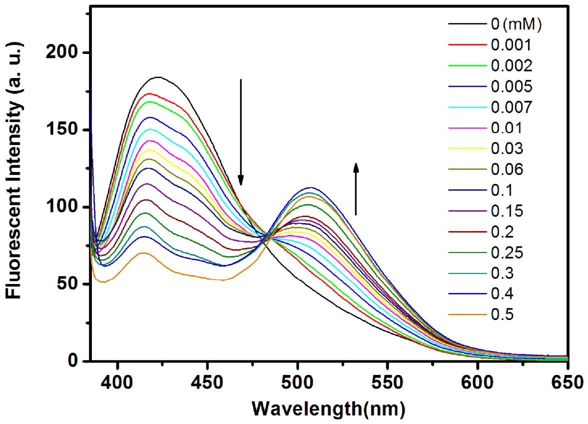


Fig. S4 Fluorescence spectra changes of **1** (10μM) in the presence of increasing concentrations of $PdCl_2$ in pure water with HEPES buffer (10mM). (Containing <0.3% CH_3CN to dissolve the sensor **1**)

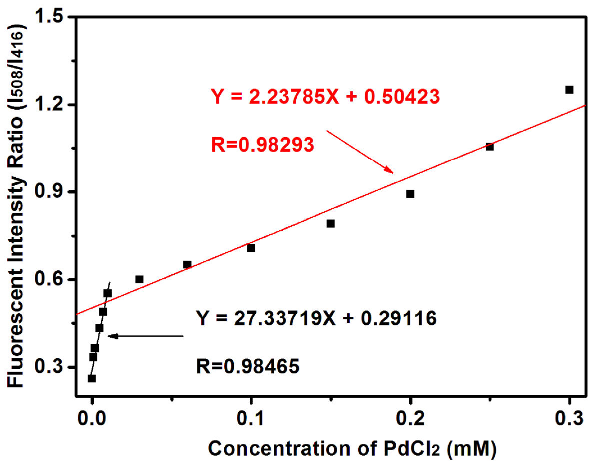


Fig. S5 The fluorescence intensities ratio (I_{517}/I_{412}) of **1** (10μM) in the presence of increasing concentrations of $PdCl_2$ in pure water with HEPES buffer (10mM). (Containing <0.3% CH_3CN to dissolve the sensor **1**)

References:

1 X. Liu, H. Liu, X. Shen, B. Song, P. S. Bhadury, H. Zhu, J. Liu, X. Qi, Bioorg. *Med. Chem. Lett.*, 2010, **20**, 4163

2 K. M. Prasun, S. Anunay, *J. Phys. Chem. A* 2003, **107**, 6334.