Electronic Supplementary Information

for

Utilizing modified flavonoids to construct a chemodosimeter array for discrimination of different palladium species by using principal component analysis

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1. Materials and Methods

General Information

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 spectra were obtained using a LTQ ORBITRAP XL from Thermo Scientific Company. Fluorescence spectra were measured by RF-5301PC spectrometer. All solvents and reagents were commercially available A.R. grade.

Preparation of metal ions

Table S1 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

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

Synthesis of HF, POF and AOF

3-hydroxyflavone (**HF**) was prepared according to literature procedures.[1]

3-(prop-2-ynyloxy) flavone **(POF)**. 3-hydroxyflavone (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 **POF** (53%) as yellow powder. ^1H 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-allyloxy flavone **(AOF).** 3-hydroxyflavone (150mg, 0.63 mmol) was dissolved in 20mL of dry acetone and 1mL 3-chloroprop-1-ene was added. The mixture was stirred at room temperature for 15 min, followed by addition of 150mg potassium carbonate. The mixture was stirred at 60℃ 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 = 9:1) to give probe **AOF** (37%) as yellow-green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.26 (d, 1H), 8.11 (d, 2H), 7.67 (t, 1H), 7.54-7.49 (m, 4H), 7.41 (t, 1H), 5.93 (m, 1H), 5.26(d, 1H), 5.15 (d, 1H), 4.64 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) d=175.18, 156.05, 155.30, 140.00, 133.56, 133.43, 131.08, 130.68, 128.74, 128.40, 125.83, 124.68, 124.20, 118.51, 118.00, 69.50. HRMS: *m/z* calcd. for $C_{18}H_{15}O_3$ $(M + H)^+$ 279.1021 found 279.1016.

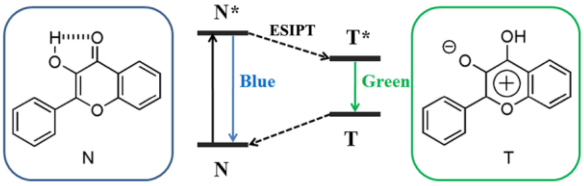
General procedure for metal ion-sensing properties

The fluorescence sensing behavior of **POF** toward metal ions was investigated using a 10 μM solution of **POF** in CH_3CN-H_2O (1:4, v/v) solution buffered at pH 7.0 (HEPES, 10mM). The fluorescence sensing behavior of **AOF** toward metal ions was investigated using a solution containing 10 μM **AOF,** 0.25 mM PPh_3 and 1 mM $NaBH_4$ in CH_3CN-H_2O (4:1, v/v) solution buffered at pH 7.0 (HEPES, 10mM). The fluorescence sensing behavior of **HF** toward metal ions was investigated using a 10μM solution of **HF** in CH_3CN-H_2O (1:4, v/v) solution buffered at pH 7.0 (HEPES, 10mM). Each metal ion titration experiment was started with 5.0 mL prepared sensor solution. All kinds of measurements were monitored after storing the mixture of sensor and metal ions for 3 hours in room temperature.

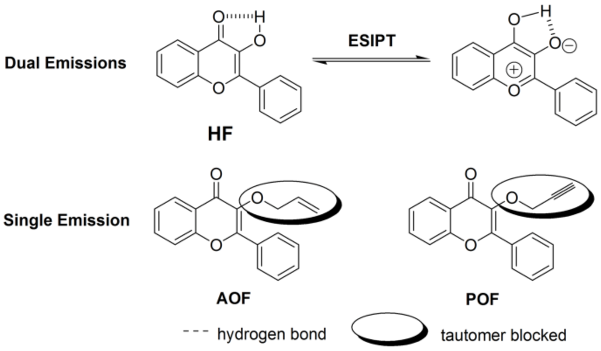
Discrimination of palladium species with flavonoids dosimeter array

The fluorescence data for the discrimination of palladium species were obtained at 0 and 0.1 mM five different palladium species, following the optimal concentrations of **POF**, **AOF** and **HF** solutions. The differences in fluorescence intensities of the assay mixture with and without palladium species at Npeak and Tpeak (Npeak: fluorescence intensity at normal isomer peak=402 nm, Tpeak: fluorescence intensity at tautomer peak=515 nm) were calculated. Six repetitions were done. The fluorescence data and fluorescent intensity ratios (Tpeak/Npeak) were then analyzed by PCA.

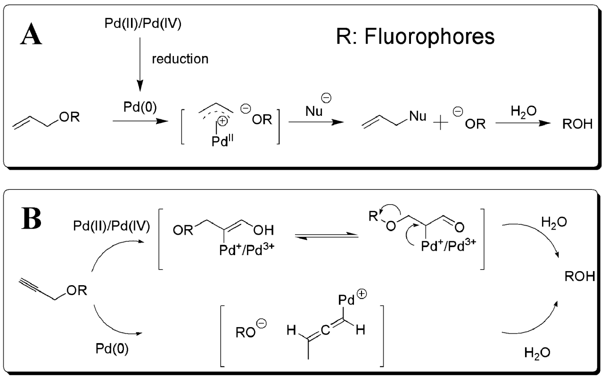
2. Additional spectroscopic data



Scheme S1 General mechanism of ESIPT process and chemical structures of normal isomer (**N**) and the tautomer (**T**) in the ESIPT process of **HF**.



Scheme S2. The ESIPT blocking process of **POF**, **AOF**.



Scheme S3 The mechanism of palladium species catalytic reactions of (A) **AOF** and (B) **POF**.

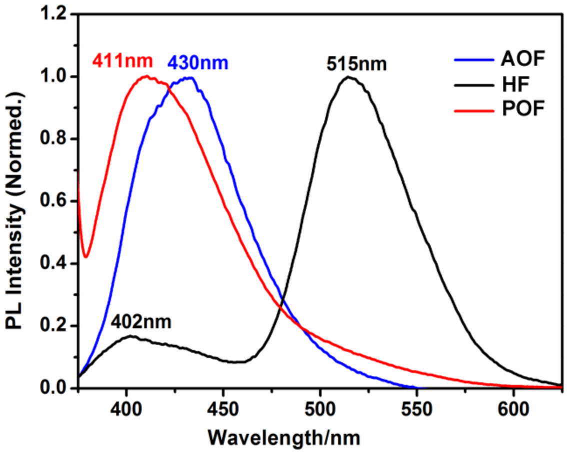


Fig. S1. Normalized emission spectra of **POF**, **AOF** and **HF**. The excitation wavelength is 350nm.

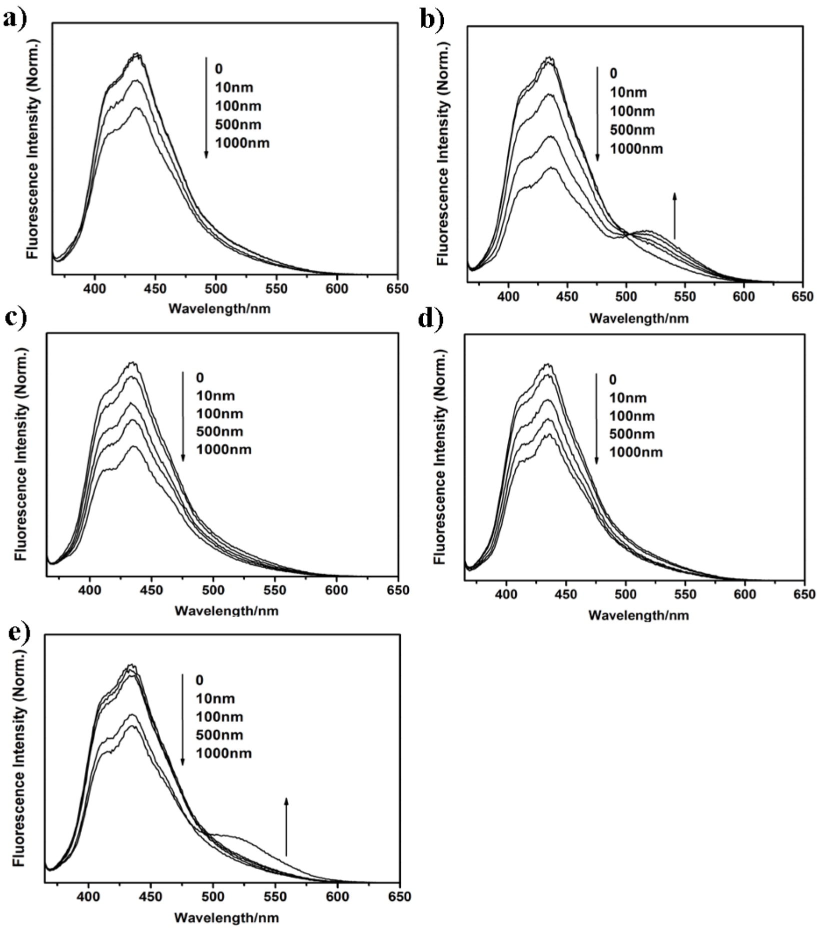


Fig. S2 Fluorescence spectra changes of the sensors **AOF** upon addition of different palladium species (0-1 μM): (a) $Pd(PPh_3)_4$; (b) $PdCl_2$; (c) $PdCl_2(dppf)_2$; (d) $Pd(PPh_3)_2Cl_2$; (e) K_2PdCl_6. [**AOF**]=2.5 μM, Solvents: 1 mM HEPES buffered CH_3CN:H2O=1:1 (v/v), $[PPh_3]$=50 μM, $[NaBH_4]$=100 μM.

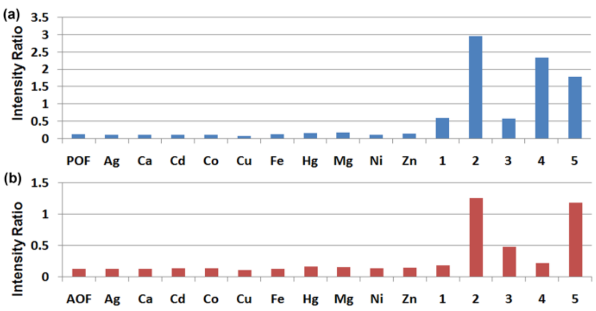


Fig. S3 Fluorescence intensity ratios (Tpeak/Npeak) of the dosimeters (a) **POF**, (b) **AOF** upon addition of different transition metal ions (10 equiv.) Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, and palladium species: 1, $Pd(PPh_3)_4$; 2, $PdCl_2$; 3, $PdCl_2(dppf)_2$; 4, $Pd(PPh_3)_2Cl_2$; 5, K_2PdCl_6.

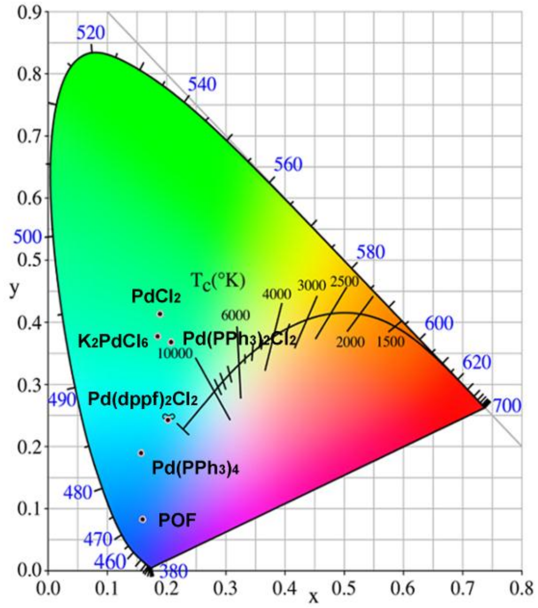


Fig. S4 CIE 1931 (x,y) chromaticity diagram of sensor **POF** for the detection of different palladium species derived from fluorescence spectra.

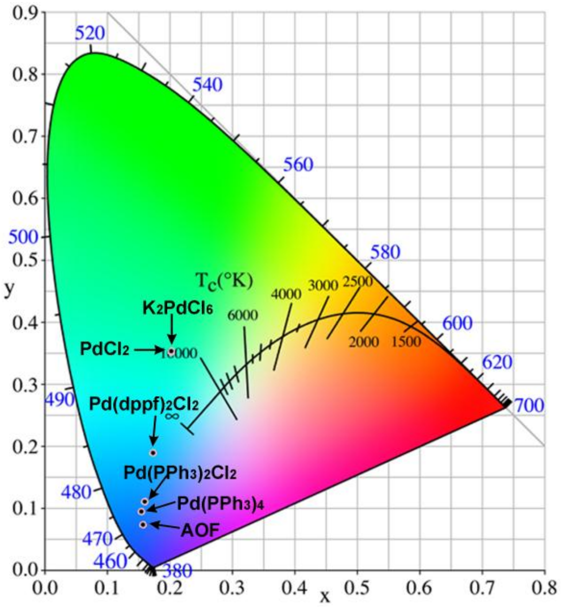


Fig. S5 CIE 1931 (x,y) chromaticity diagram of sensor **AOF** for the detection of different palladium species derived from fluorescence spectra.

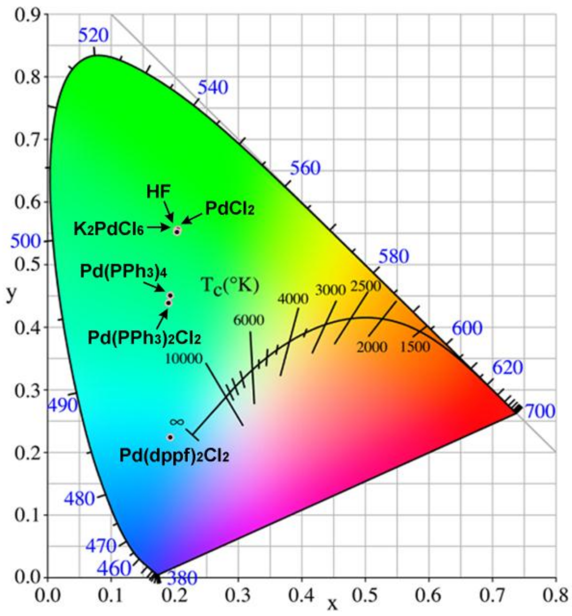


Fig. S6 CIE 1931 (x,y) chromaticity diagram of sensor **HF** for the detection of different palladium species derived from fluorescence spectra.

References

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