Electronic Supplementary Material (ESI) for Chemical Communications

Highly sensitive and selective turn-on fluorescent chemosensor for palladium based on a phosphine-rhodamine conjugate

Songtao Cai,[a] Yan Lu,[a] Song He,[a] Fangfang Wei,[a] Liancheng Zhao[a,b] and Xianshun Zeng*[a]

[a] *School of Materials Science & Engineering, Tianjin University of Technology, Tianjin 300384, China..*
[b] *School of Materials Science and Engineering, Institute of Information Functional Materials& Devices, Harbin Institute of Technology, Harbin 150001, China.*

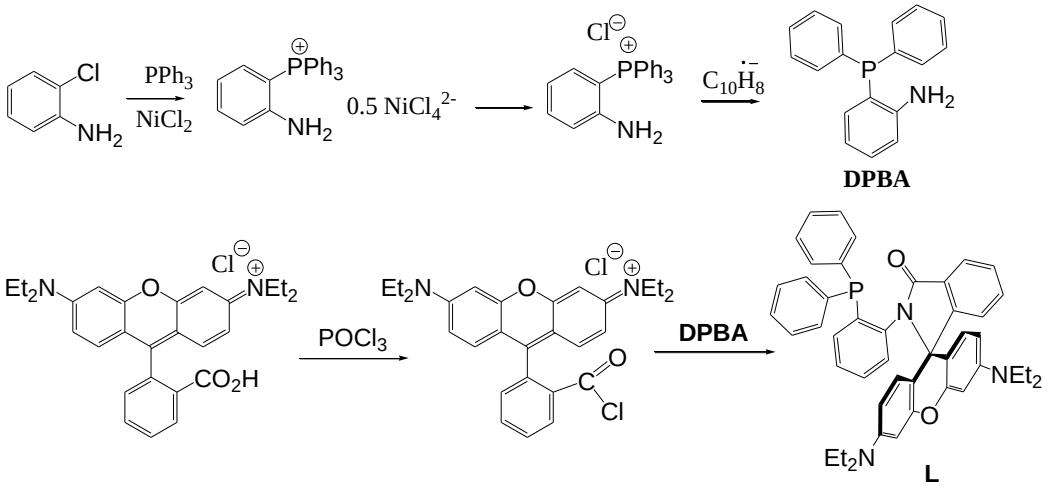
Materials and methods

1. Instruments

All solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless otherwise mentioned. NMR spectra were recorded on a Bruker spectrometer at 400 (^{1}H NMR) MHz and 100 (^{13}C NMR) MHz. Chemical shifts (δ values) were reported in ppm down field from internal Me_4Si (^{1}H and ^{13}C NMR). EI mass spectra were recorded on a VG ZAB-HS mass spectrometer (VG, U. K.). Elemental analyses were performed on a Vanio-EL elemental analyzer (Analysensysteme GmbH, Germany). UV absorption spectra were recorded on a UV-3600 UV-VIS spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed using an F-4600 fluorescence spectrophotometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). Melting points were recorded on a Boetius Block apparatus and are uncorrected.

For both UV-VIS and fluorescence measurements, the spectra were recorded in 30 min interval after the addition of Pd^{2+} to the solutions **L**.

2. Synthesis of L



2.1 Preparation of 2-(Diphenylphosphino)benzenamine (DPBA).

2-(Diphenylphosphino)benzenamine (**DPBA**) was prepared in 50% yield (based on the starting material of

triphenylphosphine) in three steps starting from 2-chlorobenzenamine and triphenylphosphine according to the known procedure.[S1]

2.2 Preparation of the chemosensor L.

To a solution of rhodamine B (479 mg, 1.0 mmol) in dry 1,2-dichloroethane (10 mL) under stirring was added phosphorus oxychloride (0.95 mL, 10.5 mmol) over a period of 10 min. After being heated to reflux for 4 h, the solvent and excess amount of phosphorus oxychloride was removed by rotary evaporation to give the corresponding acid chloride, which was dried under high vacuum and used for the next step without further purification. To a solution of the acid chloride in dry acetonitrile (5.0 mL) was added dropwise a solution of 2-(diphenylphosphino)benzenamine (**DPBA**) (333 mg, 1.2 mmol) and triethylamine (1.3 mL) in dry acetonitrile (5.0 mL), the resulting mixture was stirred for 10 h at room temperature. The reaction mixture was then concentrated under vacuum, and the residue was purified by column chromatography (ethyl acetate/dichloromethane = 1/5, v/v) to give the crude product, which was further purified by recrystallization from dichloromethane/ethyl acetate (25:1, v/v) to give a pure compound **L** as a white solid in 25 % yield (175 mg): mp = 197-198 °C; HRMS: m/z $[M + H]^+$ = 702.3253; Calcd: 702.3271; ^{1}H NMR(400 MHz, $CDCl_3$, ppm): 8.06-8.00 (m, 1.0 H), 7.56-7.71 (m, 0.3 H), 7.52-7.29 (m, 2.19 H), 7.23-7.150 (m, 1.45 H), 7.10-7.00 (m, 2.29 H), 6.77 (dd, 0.27 H, *J* = 8.8 Hz, 2.0 Hz), 6.64-6.57 (m, 0.90 H), 6.43-6.30 (m, 0.96 H), 6.16-6.02 (m, 0.40 H), 6.02 (d, 0.26 H, *J* = 2.0 Hz), 5.91 (dd, 0.15 H, *J* = 8.8 Hz, 2.0 Hz), 5.65 (dd, 0.25 H, *J* = 8.8 Hz, 2.0 Hz), 3.68 (m, 4.90 H, *J* = 7.2 Hz, CH_2), 3.39-3.31 (m, 1.68 H, CH_2), 3.19-3.12 (m, 0.55 H, CH_2), 3.04 (m, 1.0 H, *J* = 7.2 Hz, CH_2), 1.21 (t, 7.3 H, *J* = 7.2 Hz, CH_3), 1.16 (t, 2.38 H, *J* = 7.2 Hz, CH_3), 1.061 (t, 0.96 H, *J* = 7.2 Hz, CH_3), 1.01 (t, 1.60 H, *J* = 7.2 Hz, CH_3). Anal. Calcd for $C_{46}H_{44}N_3O_2P$: C 78.82, H 6.52, N 5.88; Found: C 78.72, H 6.32, N 5.99.

Although we obtained good elemental analysis data for the chemosensor **L**, the ^{1}H NMR spectra of **L** was very complex. As can be seen from Chart S1, at least four isomers could be observed in the ratio of about 8:2.5:1:1.5 from the integration of the peaks of the ethyl groups. We rationalized that the structure of the chemosensor **L** could be converted among four steric isomers (**A**, **B**, **C** and **D**) as depicted in Inset of Chart S1. The assignment of the chemical shift of ethyls are shown in Chart S1, namely, **A**:**B**:**C**:**D** = 1:2.5:8:1.5. The protons of $\underline{CH_2}CH_3$ moieties within **C** and **D** showed stardard (n+1) splitting mode at 3.66 ppm and 3.04 ppm, respectively. With respect to isomers **A** and **B,** the protons of $\underline{CH_2}CH_3$ moieties exhbited multiplets at 3.16 ppm and 3.35 ppm, respectively, because of two phenyls restricted their free rotations. As shown in Chart S2, the assignment of the chemical shift of aromatic protons is very difficult because the peaks overlapped each other. However, a high resolute mass spectrum (HRMS) undoubtedly confirmed the structure of **L** as shown in Chart S3. The peak at m/z = 702.3253 was assigned to the mass of **L** + H^+.

[S1] M. K. Cooper, M. Downes and P. A. Duckworth, *Inorg. Synth*. 1989, **25**, 129-133.

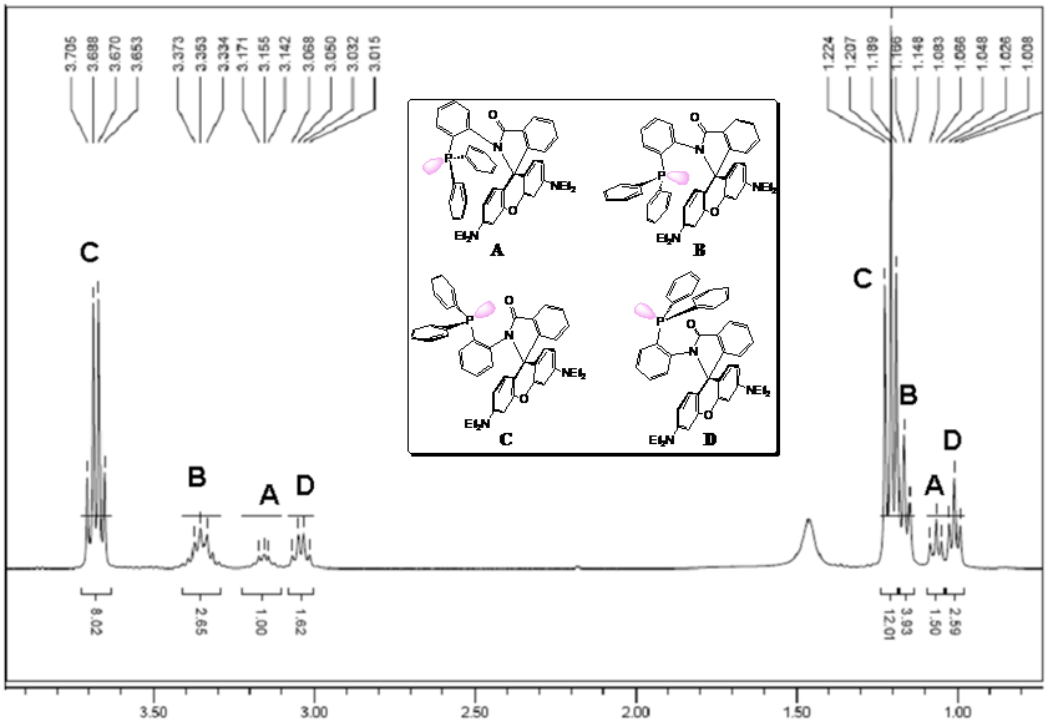


Chart S1 ^{1}H NMR of chemosensor **L** (400 MHz, $CDCl_3$) from 0-4.0 ppm. For each isomer, the assignment of the $\underline{CH_2}CH_3$ and $CH_2\underline{CH_3}$ protons were labeled **A**, **B**, **C** and **D**. Inset: possible four isomers (**A**, **B**, **C** and **D**) of **L**.

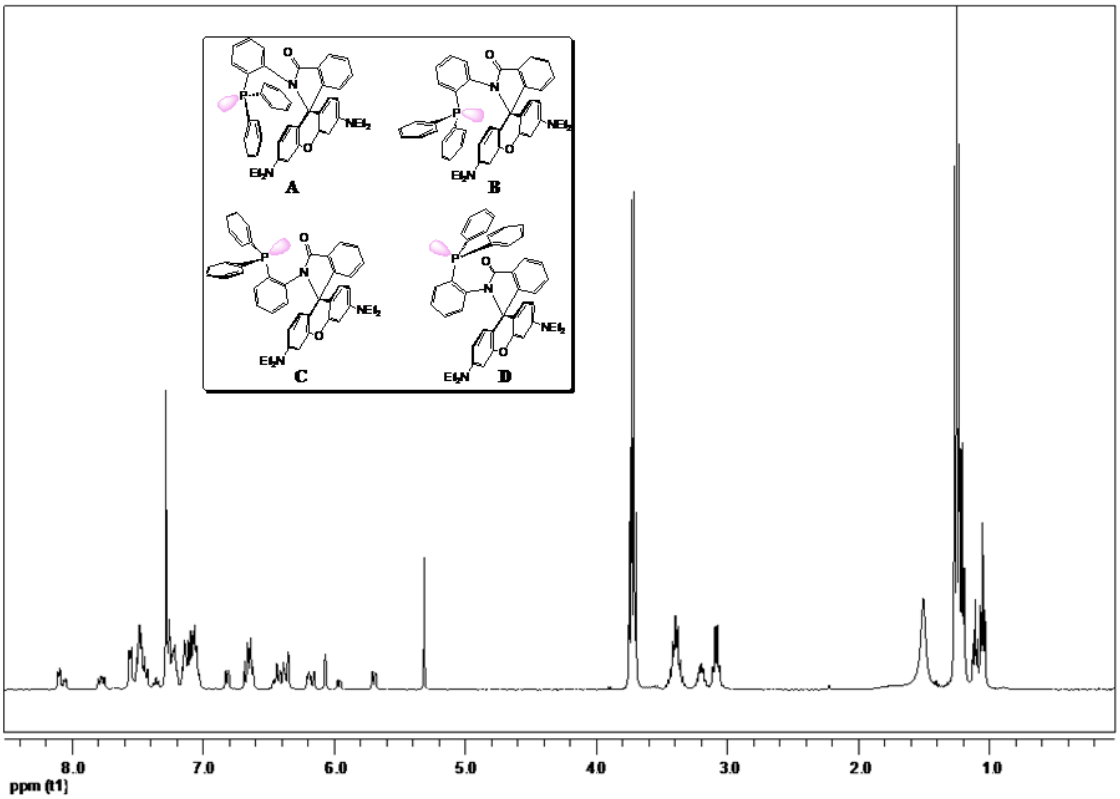


Chart S2 ^{1}H NMR of chemosensor **L** (400 MHz, $CDCl_3$). Inset: possible four isomers (**A**, **B**, **C** and **D**) of **L**.

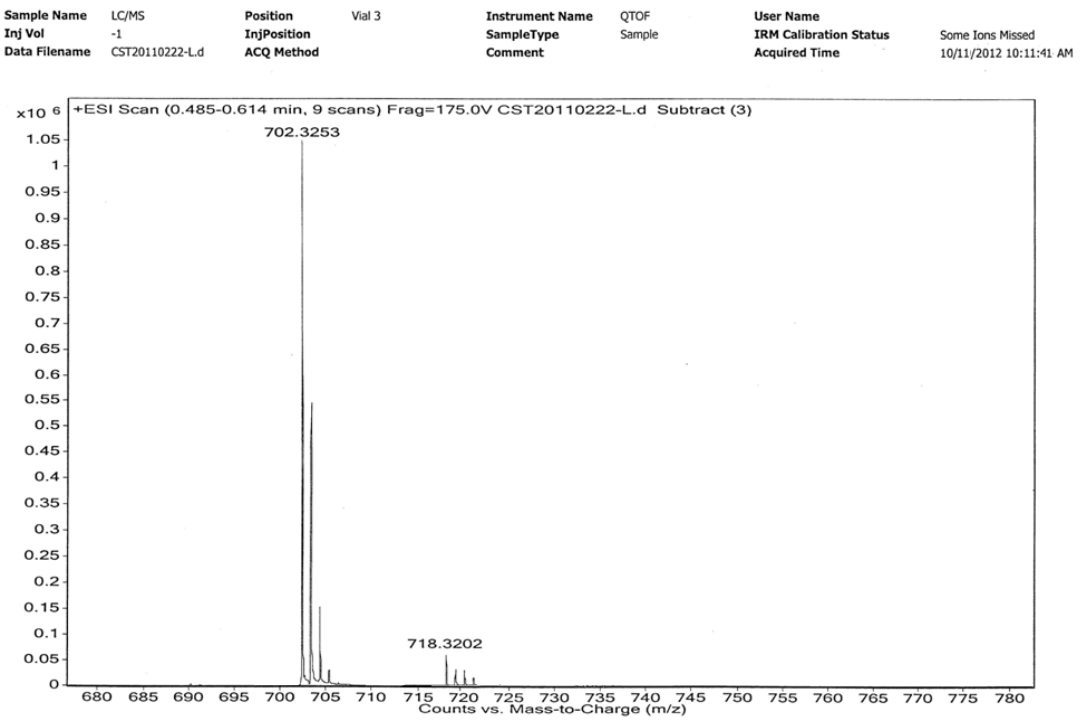


Chart S3 HRMS (LC/MS) spectra of **L**. The peak at m/z = 702.3253 was assigned to the mass of **L**+H^+.

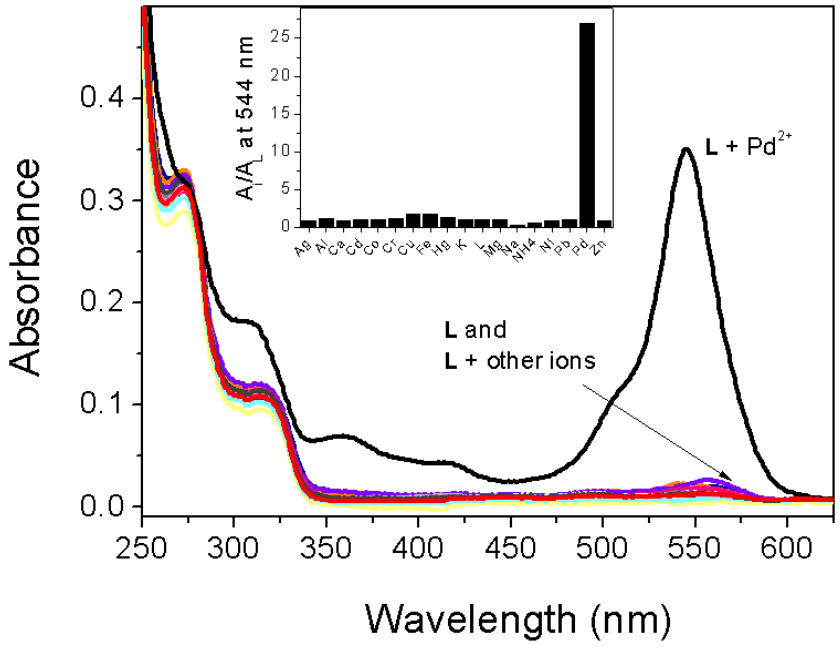


Figure S1 UV-vis spectra of chemosensor **L** (10 μM) in the presence of nitrate salts (1.0 equiv) of Na^+, K^+, NH_4^+, Ag^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+} and 1.0 equiv of $PdCl_2$ in ethanol/H_2O (4:1, v/v). Inset: Histogram representing the absorbance enhancement (A_i/A_L) of **L** at 544 nm in the present of 1.0 equiv of metal ions.

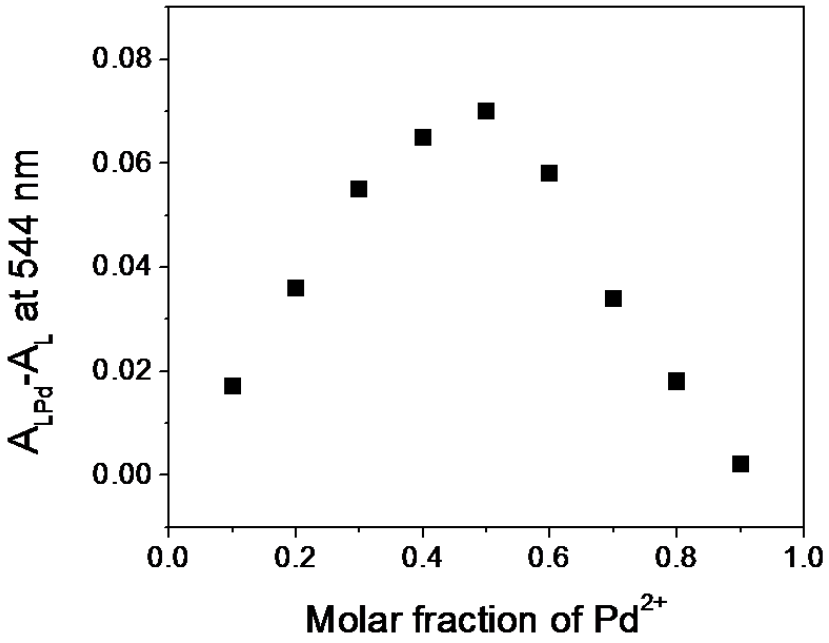


Figure S2 Job's plot of **L** in EtOH/water (v/v, 4:1) showing the 1:1 stoichiometry of the complex between Pd^{2+} ion and **L**. The total of the chemosensor and Pd^{2+} is 10 μM. Absorbance is recorded at 544 nm.

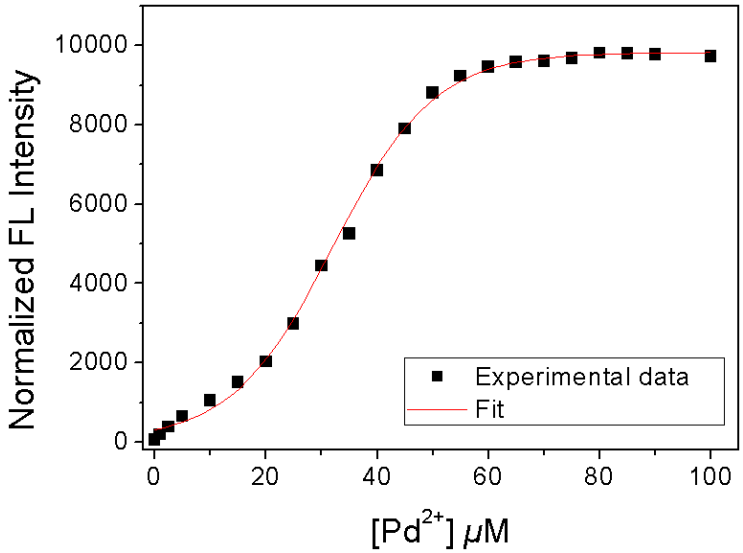


Figure S3. Measurement of the fluorescence turn-on constant ($K_{turn\text{-}on}$) of **L**.[S2]

[S2] P. Du and S. J. Lippard, *Inorg. Chem.* 2010, **49**, 10753.

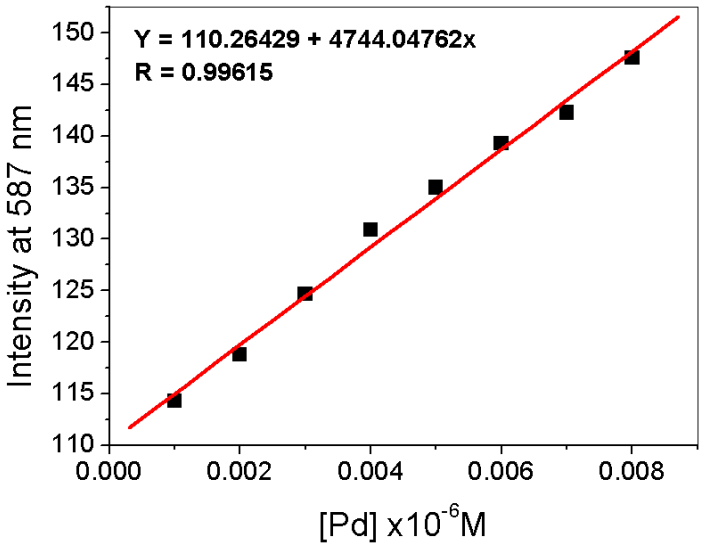


Figure S4 Emission (at 587 nm) of **L** at different concentrations of Pd^{2+} (0.001, 0.002, 0.003, 0.004, 0.005, 0.006, 0.007, 0.008 μM) added. A good linear relationship between the fluorescence intensity and the Pd^{2+} concentration could be obtained in the 0-0.008 μM concentration range (R^2 = 0.996). The detection limit was then calculated with the equation: detection limit = $3\sigma_{bi}/m$, where σ_{bi} is the standard deviation of blank measurements (σ_{bi} = 2.3636, derived from eight measurements), *m* is the slope between intensity *versus* sample concentration. The detection limit was measured to be 1.49×10^{-9} M. λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.

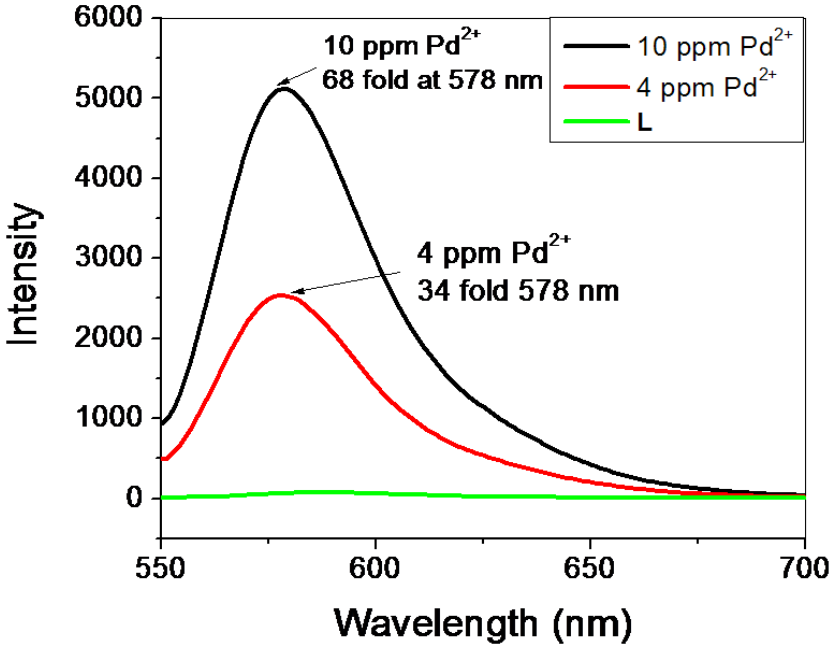


Figure S5 Fluorescence spectra of the chemosensor **L** (1 μM) in the absence and in those spiked with 4.7×10^{-5} M (5 ppm) and 9.4×10^{-5} M (10 ppm) of the Pd^{2+} ions in EtOH/water (v/v, 4:1) to assay the WHO limit for palladium content in drug chemicals, indicating that **L** met the limit for the threshold for palladium in drug chemicals (5-10 ppm). λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.

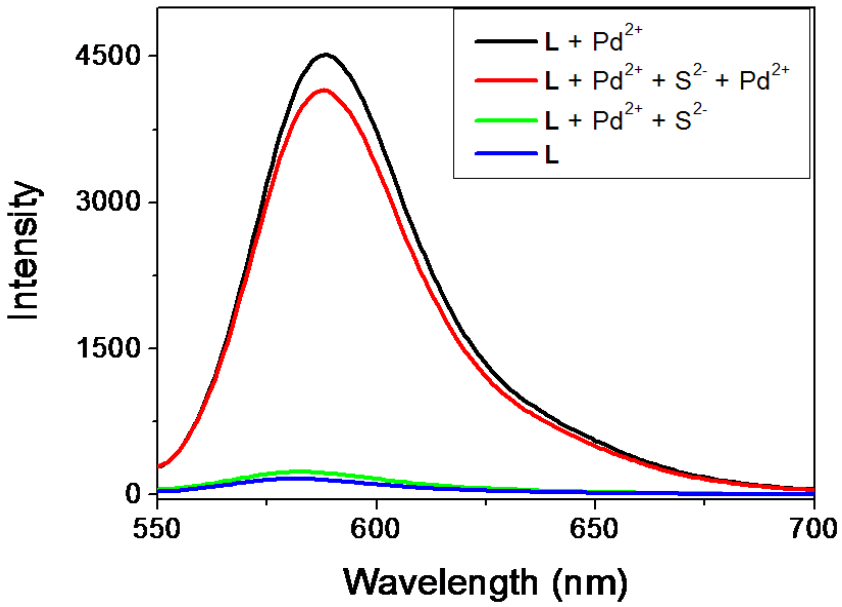


Figure S6. Fluorescence spectra of **L** (1 μM) upon the addition of 35 equivalents of Pd^{2+} in ethanol/H_2O (4:1, v/v). Na_2S (35 equiv) was added to **L**+Pd^{2+} mixture to show the reversible binding nature of Pd^{2+} with **L.**

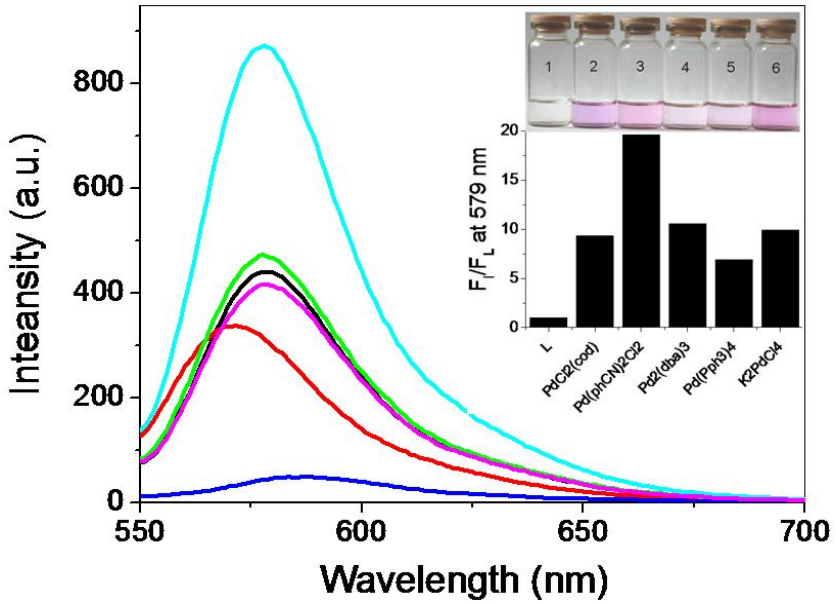


Figure S7 Fluorescence intensity changes and color changes (Inset) of **L** (1 μM) in the presence of commonly found palladium complexes (1 equivalent) in H_2O-EtOH (4:1, v/v) solutions. Inset: color changes in the presence of palladium complexes (top), from left to right: 1. **L**; 2. **L** + $PdCl_2$(cod); 3. **L** + $Pd(PhCN)_2Cl_2$; 4. **L** + $Pd_2(dba)_3$; 5. **L** + $Pd(PPh_3)_4$; 6. **L** + K_2PdCl_4. Histogram representing the fluorescence enhancement ($F_i/F_{L)}$ of **L** at 579 nm in the presence of palladium complexes (bottom). λ_{ex} = 530 nm. λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.

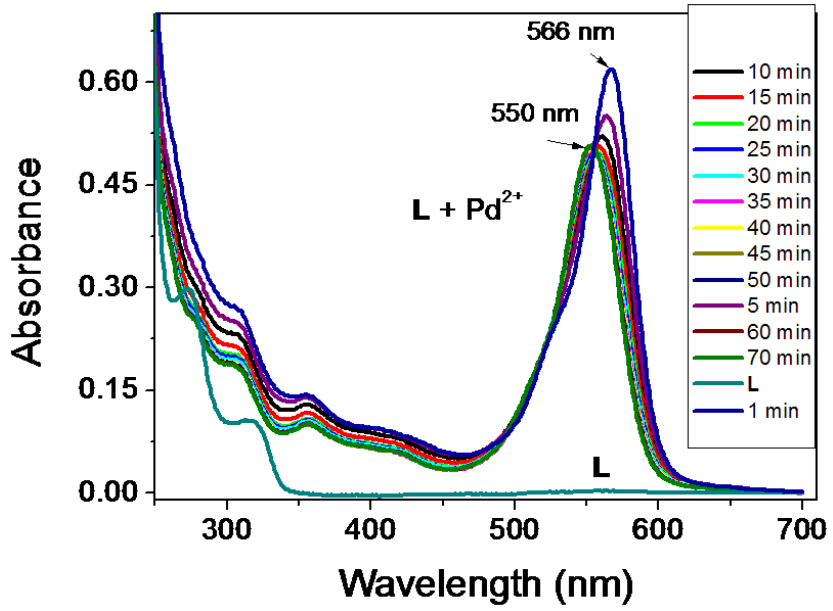


Figure S8. Absorption changes against time for **L** (10 μm) upon addition of Pd^{2+} (2 equivalents) in EtOH/water (v/v, 4:1). Upon addition 2 equiv. of Pd^{2+}, the maximum absorbance at 566 nm produced immediately, and then it was gradually converted to a new one at 550 nm within 30 min. During the conversion process, the appearance of isosbestic point at 555 nm indicated the chelating mode of **L**•Pd^{2+} converted from one to another.

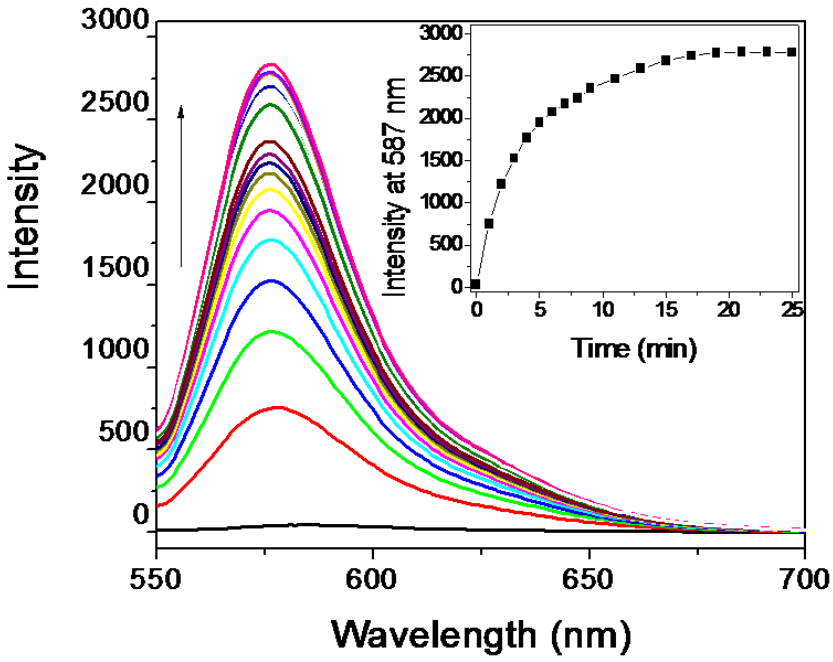


Figure S9. Fluorescence changes against time for **L** (1 μm) upon addition of Pd^{2+} (30 equivalents) in EtOH/water (v/v, 4:1). Inset: the fluorescence at 587 nm of **L** as a function of the reaction time. λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.

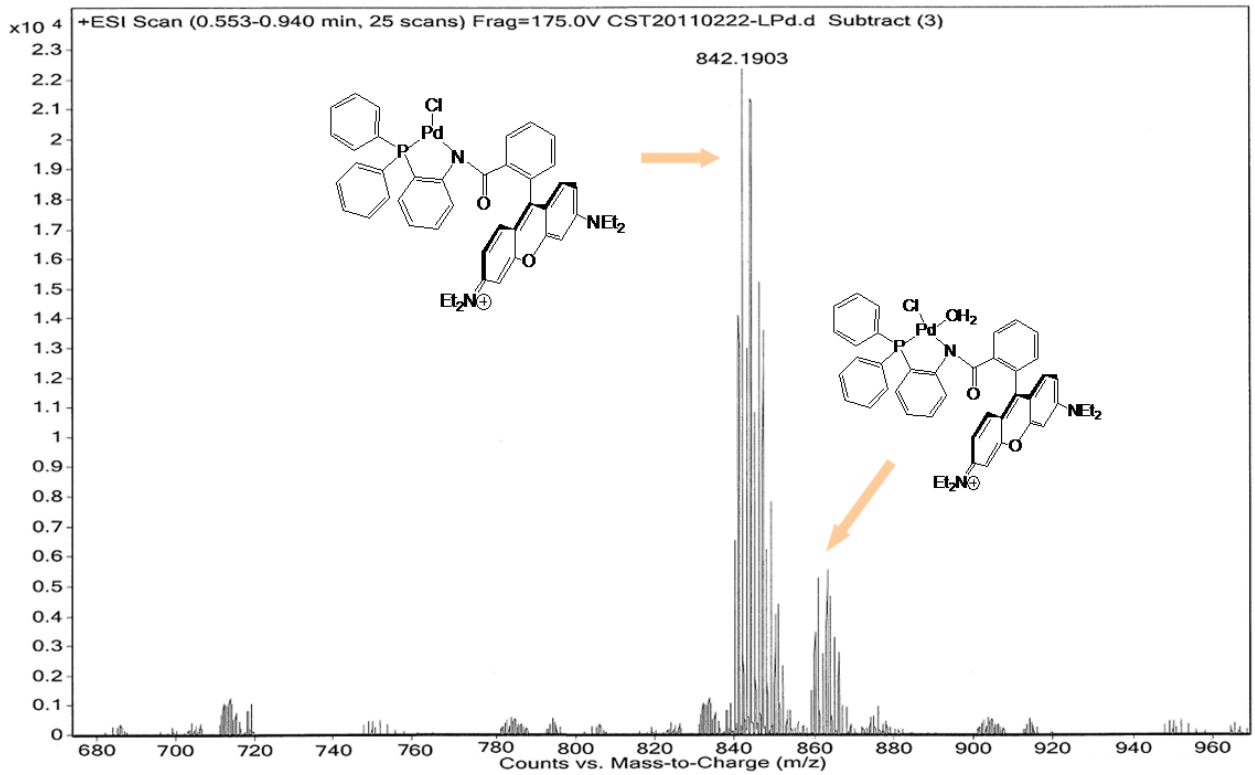


Figure S10. HRMS spectra of the reaction mixture of **L** with Pd^{2+}. The peak (m/z) at 842.1903 corresponds to the ring-opened form of [**L**•PdCl]$^{+}$ ion.

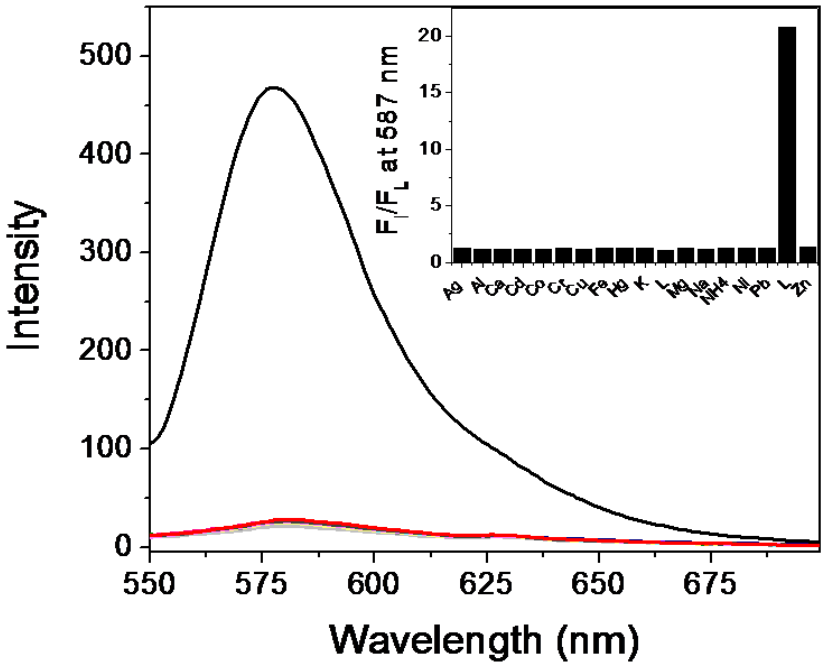


Figure S11 Fluorescence spectra of **L** (1 μM) upon the addition of the nitrate salts (2 equiv.) of Na^{+}, K^{+}, NH_4^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+} and 2 equiv of $PdCl_2$ in ethanol/H_2O (4:1, v/v). Inset: histogram representing the fluorescence enhancement of **L** in the presence of metal ions. λ_{ex} =

530 nm. λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.

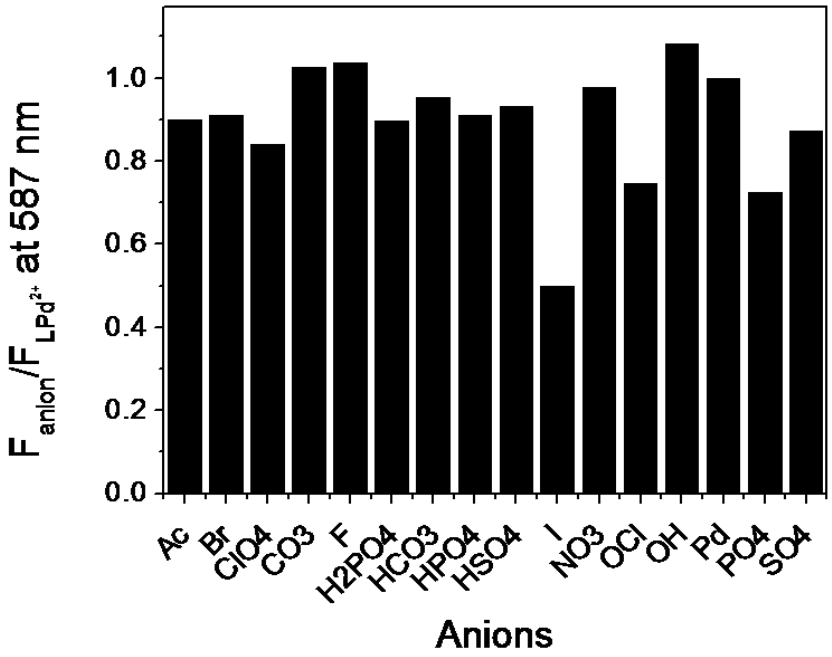


Figure S12. The emission spectra of **L** with Pd^{2+} salts with different counteranions (AcO^-, Br^-, ClO_4^-, CO_3^{2-}, F^-, $H_2PO_4^-$, HCO_3^-, HPO_4^{2-}, HSO_4^-, I^-, NO_3^-, ClO^-, OH^-, PO_4^{3-}, and SO_4^{2-}). λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.

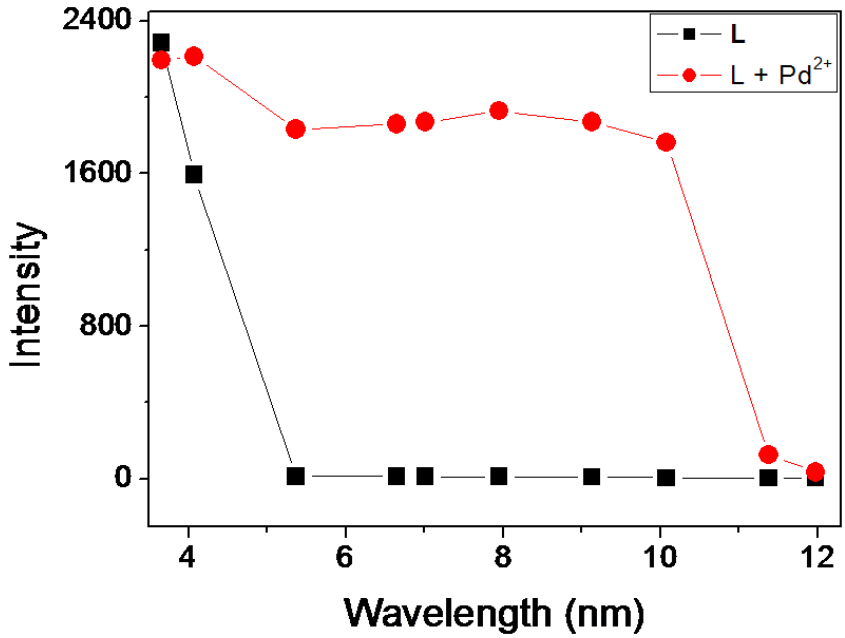


Figure S13. Profile of pH dependence of the fluorescence intensity of **L** (1 μM) at 587 nm in the absence and presence of Pd^{2+} (10.0 equiv.) in ethanol/H_2O (4:1, v/v).

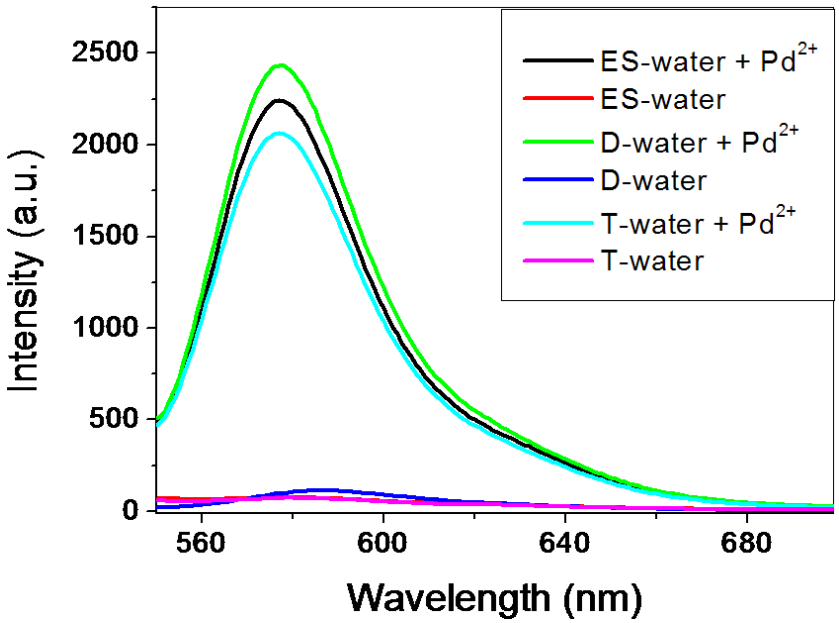


Figure S14 Fluorescence spectra of the chemosensor **L** (1 μM) in the absence of Pd^{2+} ions and in those spiked with 20 equivalents of the Pd^{2+} ions in distilled water (D-water), tap water (T-water), and earth-soaked water (ES-water). λ_{ex} = 530 nm, Slit: 5.0 nm; 10.0 nm.