

Electronic Supplementary Information
for
Synthesis and characterization of a fluorescent polymer
containing 2,6-bis(2-thienyl) pyridine moieties as a highly
efficient sensor for Pd²⁺ detection

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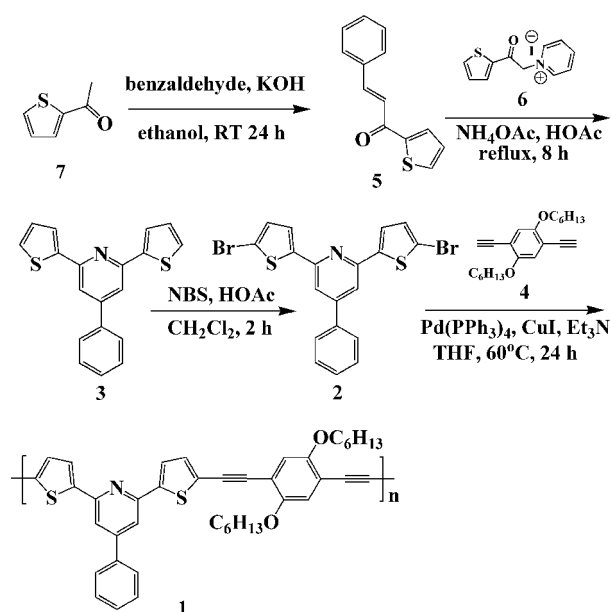
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1. Materials and Methods.

NMR spectra were obtained using a Bruker AVANCE II for ^1H NMR and ^{13}C NMR. Elemental analyses were measured by VARIO ELIII. 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.

Each metal ion titration experiment was started with 5.0mL polymer in THF solution with a known concentration (4.0×10^{-6} mol/L). Analyte solutions were prepared from AgNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 1.5\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuAc}_2 \cdot \text{H}_2\text{O}$, ZnCl_2 , HgCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (4.0×10^{-3} mol/L) by separately dissolved in DMF. The solution of Pd^{2+} and Pt^{4+} in the form of Na_2PdCl_4 and Na_2PtCl_6 (4.0×10^{-3} mol/L) was also prepared in DMF used for titration. Polymer-metal complexes were produced by adding aliquots of a solution of the selected metal salt to a THF solution of polymer 1. All kinds of measurements were monitored after sonicating the mixture for 1h.

2. Synthesis



Synthesis of 1-(thiophen-2-yl)ethanone(7)

Thiophene (25g) and acetic anhydride (25g) were added into three-neck flask and then added phosphate (2g, 85%) under stirring at 50°C. The mixture was stirred for 3 h at 100–110°C. Water was added after finishing the reaction and cooling the reactive mixture. Oil layer was washed by the Na₂CO₃ aqueous solution and water to pH at 7 and then were dried with anhydrous Na₂SO₄. After removal of the Na₂SO₄, the pure product was obtained by distilling under reduced pressure (0.91MPa) at 124–136°C. Yield=43%. ¹H NMR (400 MHz, CDCl₃) δ=7.63 (d, 1H), 7.58 (d, 1H), 7.07 (t, 1H), 2.49 (s, 3H).

Synthesis of N-[1-oxo-2-(2-thienyl)ethyl]-pyridium iodide(6)

A mixture of compound **7** (20 mmol) and I₂ (20 mmol) in pyridine (25 mL) was refluxed for 3 h. After cooling the mixture to 20°C, the precipitate was filtered and washed with cold pyridine several times, which was used in the next step without further purification. Yield>97%. ¹H NMR (400 MHz, CDCl₃) δ=9.02 (d, 2H), 8.73 (t, 1H), 8.27 (t, 2H), 8.23 (d, 1H), 7.71 (d, 1H), 7.41 (d, 1H), 6.42 (s, 2H).

Synthesis of 1-phenyl-3-(2-thienyl)-1-propen-3-one(5)

To a mixture of 2-acetyl thiophene (0.03 mol) and benzaldehyde (0.03 mol) in ethanol (50 ml), a solution of potassium hydroxide (5%, 50 ml) was added slowly. The mixture was stirred for 24 h. The precipitated solid was filtered, washed with water, dried, and recrystallized from ethanol. Yield=93%. ¹H NMR (400 MHz, DMSO-d₆) δ=8.37–8.02 (m, 5H), 7.94 (dd, 1H), 7.89 (d, 1H), 7.73 (dd, 1H), 7.47 (d, 1H), 7.33 (m, 1H).

Synthesis of 2,6-bis(2-thienyl)-4-phenylpyridine(3)

An equimolar amount of compound **5** (10 mmol) and **6** (10 mmol) was heated under reflux for 8h in the presence of ammonium acetate (5.0 g) and glacial acetic acid (10.0 mL). After the reaction mixture was maintained at room temperature overnight, ice cold water (30.0 mL) was added to it. The precipitated was filtered, washed with methanol, dried, and recrystallized from appropriate solvent to afford compound **4**. Yield=31%. ¹H NMR (400 MHz, CDCl₃) δ=7.76 (d, 2H), 7.74 (d, 2H), 7.72 (s, 2H), 7.54 (m, 3H), 7.45 (d, 2H), 7.17 (t, 2H); ¹³C NMR (100 MHz, CDCl₃)

δ =152.62, 150.24, 144.84, 138.58, 129.16, 129.13, 127.97, 127.85, 127.10, 124.90, 115.15. $C_{19}H_{13}NS_2$ (319.5): Calcd. C 71.44, H 4.10, N 4.38; Found C 71.21, H 4.12, N 4.39.

Synthesis of 2,6-bis(5-bromo-2-thienyl)-4-phenylpyridine(2)

To a stirred mixture of compound **3** (2 mmol) in dichloromethane (10 mL) and acetic acid (5 mL) was slowly added NBS (4 mmol) in dichloromethane (10 mL) and acetic acid (5 mL) in half an hour, the mixture was stirred for 2 h at room temperature, and then was heated at reflux for 0.5 h. After the solution was cooled to room temperature, the white precipitates were filtered off. Dichloromethane (20 mL) was added to the solution. The organic layer was washed with NaOH solution (50 mL, 2 M) then water (50 mL) and dried over magnesium sulfate. After evaporation, the white residue was recrystallised from a chloroform–methanol solution to give **5** as white crystals. Yield=74%. 1H NMR (400 MHz, $CDCl_3$) δ =7.60 (d, 2H), 7.53 (s, 2H), 7.44 (m, 3H), 7.34 (d, 2H), 7.02 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =151.76, 150.56, 146.02, 138.19, 130.92, 129.38, 129.20, 127.06, 124.85, 115.76, 114.62. $C_{19}H_{11}NS_2Br_2$ (477.2): Calcd. C 47.82, H 2.32, N 2.93; Found C 47.77, H 2.34, N 2.91.

Synthesis of 1,4-bis(ethynyl)-2,5-bis(hexyloxy)benzene(4)

A mixture of hydroquinone (50 mmol) and 1-hexyl bromide (120 mmol) was stirred in DMF (30 ml) in the presence of K_2CO_3 (120 mmol) at 80°C under nitrogen for 1 day. The solution was poured into 300 ml of water, and extracted with chloroform (150 ml) twice. The organic layer was dried with $MgSO_4$, and filtered. The solvent was removed in vacuo, and recrystallization from methanol gave **6** as crystals. Yield=72%. 1H NMR (400 MHz, $CDCl_3$) δ =6.85 (s, 4H), 3.93 (t, 4H), 1.78 (m, 4H), 1.48 (m, 4H), 1.37 (m, 8H), 0.93 (t, 6H).

1,4-bis(hexyloxy)benzene (16 mmol) was dissolved in CCl_4 (30 ml) and stirred at 0°C. To the solution was added dropwise 2.0 ml (40 mol) of bromine over the course of 2 h. The resulting solution was stirred overnight. The remaining bromine was quenched by the addition of Na_2SO_3 aq., then the organic layer was extracted with dichloromethane (50 ml) twice, washed with water (150 ml), dried with $MgSO_4$, and

filtered. The solvent was removed in vacuo, and the residue was recrystallized from dichloromethane–ethanol to give **7** as crystals. Yield=88%. ^1H NMR (400 MHz, CDCl_3) δ =7.11 (s, 2H), 3.97 (t, 4H), 1.82 (m, 4H), 1.51 (m, 4H), 1.37 (m, 8H), 0.93 (t, 6H).

1,4-bis(hexyloxy)-2,5-dibromobenzene (10 mmol), CuI (0.1 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.1 mmol) were added to a mixture of 10 mL THF and 5 mL triethylamine, followed by the addition of ethynyltrimethylsilane (22 mmol). The mixture was degassed by several freeze-thaw cycles, and flushed with argon. The reaction mixture was refluxed for 3 h at 110 °C under an argon atmosphere. After cooling to room temperature the precipitated salt was filtered off and washed with triethylamine. The filtrate was evaporated and 150 mL of water were added. The mixture was extracted with diethyl ether until the aqueous phase was colorless. The combined organic phases were dried over MgSO_4 , and the solvent was evaporated. The residue was recrystallized from hexane to give **8** as crystals. Yield=75%. ^1H NMR (400 MHz, CDCl_3) δ =6.89 (s, 2H), 3.94 (t, 4H), 1.78 (m, 4H), 1.50 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H), 0.25 (s, 18H).

Mixture of methanol (30 mL) and K_2CO_3 (2 mL, 5 N) was added to the solution of 1,4-bis[(trimethylsilyl)ethynyl]-2,5-bis(hexyloxy)benzene in THF (20 mL). Stir for 8 h, then the solvent was evaporated, and the residue was poured into 100 mL of water and extracted with hexane twice. The combined hexane layer was washed with water and brine and dried over anhydrous magnesium sulfate. The pale yellow solid **9** was obtained after the solvent was removed. Yield>95%. ^1H NMR (400 MHz, CDCl_3) δ =6.95 (s, 2H), 3.97 (t, 4H), 3.33 (s, 2H), 1.77 (m, 4H), 1.50 (m, 4H), 1.33 (m, 8H), 0.90 (t, 6H).

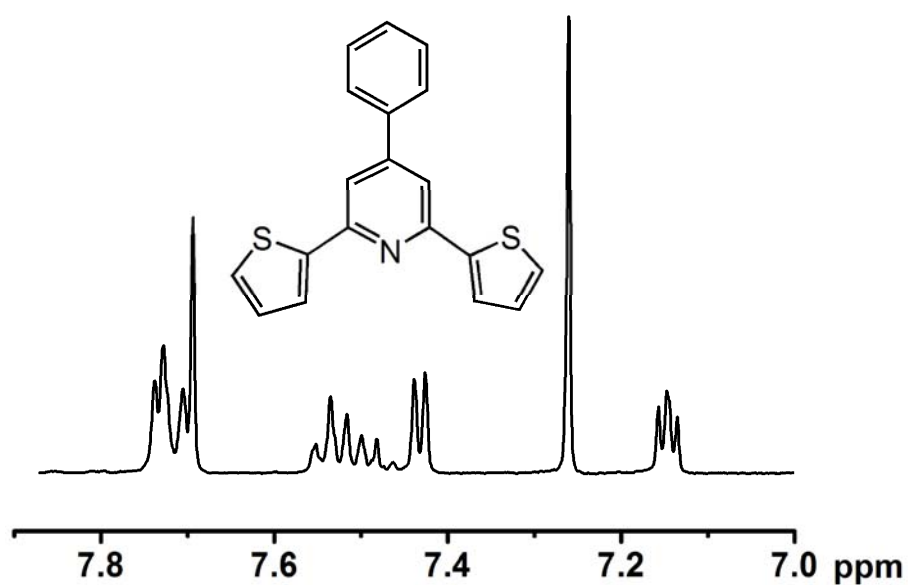
Synthesis of Polymer (**1**)

Compound **2**(62.0mg, 0.13mmol), compound **4**(42.4mg, 0.13mmol), $\text{Pd}(\text{PPh}_3)_4$ (120mg, 0.1mmol), and CuI(19.2mg, 0.1mmol) were combined in dry and degassed triethylamine (5ml) and THF (5ml). The mixture was heated at 60°C for 24h under argon atmosphere, and then cooled to room temperature and filtered. The filtrate was added dropwise to vigorously stirred methanol. The precipitate was centrifuged and

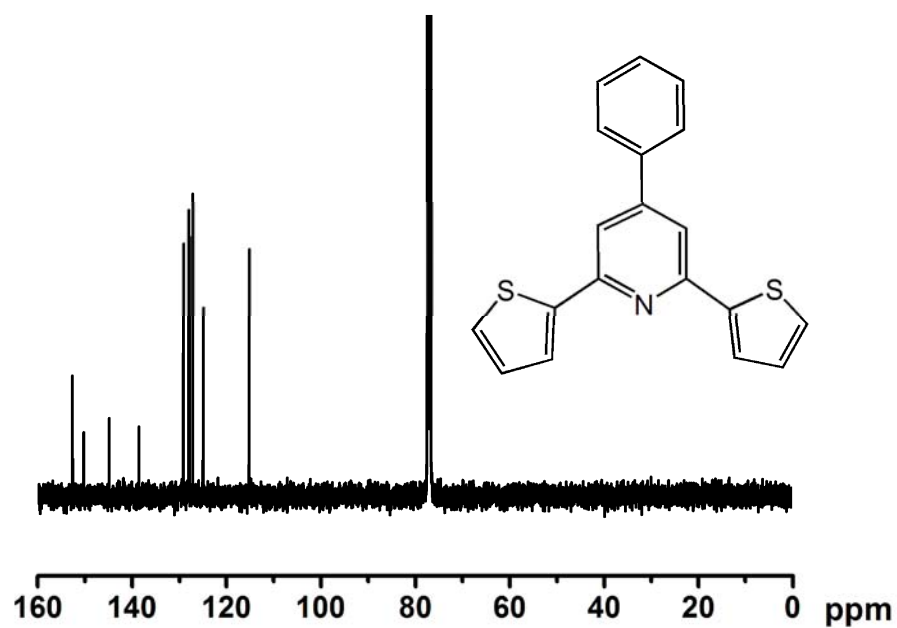
dissolved in 3mL of THF, then precipitated in methanol again. The final product was dried under vacuum to give polymer **1** as a brown solid with 65% yield. $M_n=3500$ PDI=2.24 (GPC). ^1H NMR (400 MHz, CDCl_3) δ = 7.70-6.80 (13H), 3.96 (t, 4H), 1.61-1.49 (m, 6H), 1.36 (m, 8H), 0.91 (t, 6H). $(\text{C}_{41}\text{H}_{39}\text{NO}_2\text{S}_2)_n$ (641.9) $_n$: Calcd. C 76.71, H 6.12, N 2.18; Found C 75.07, H 6.24, N 2.17.

3. The characterization data of compound 1, 2, 3

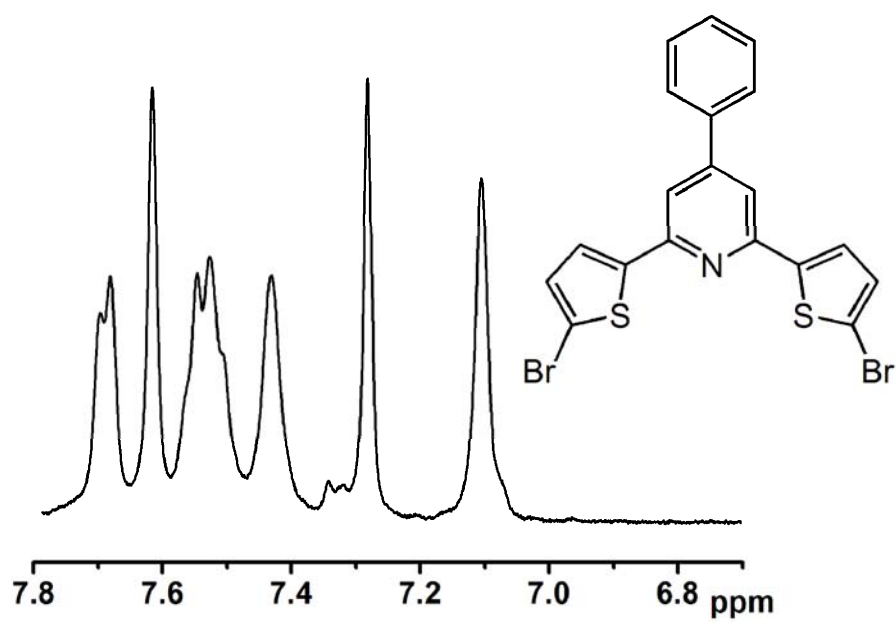
^1H NMR spectra of **3**



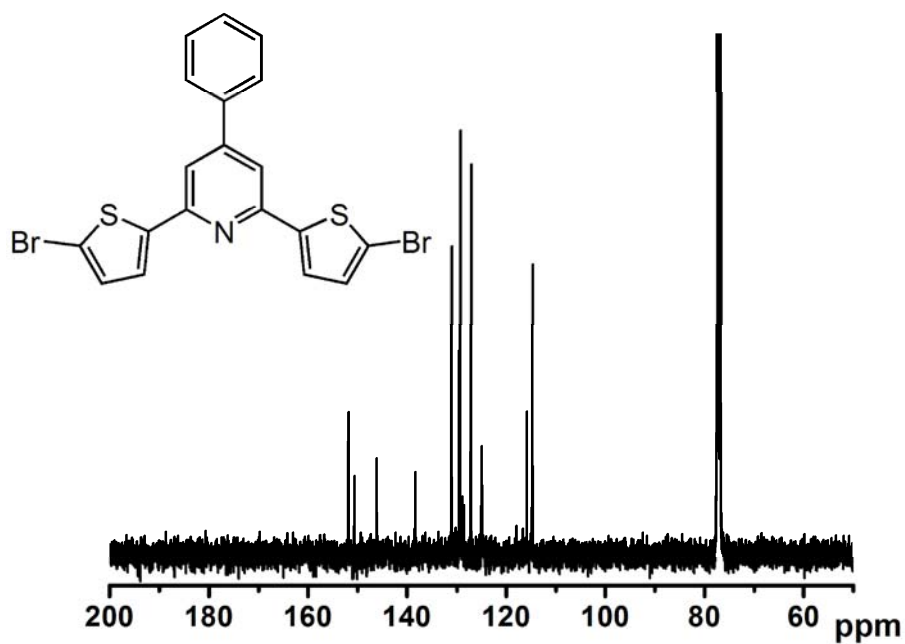
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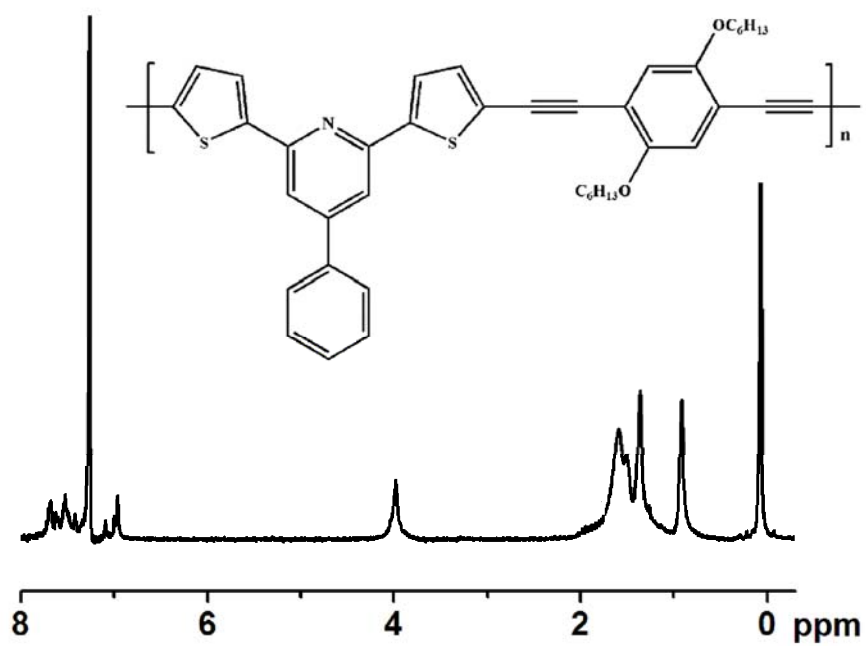
¹H NMR spectra of **2**



¹³C NMR spectra of **2**



^1H NMR spectra of **1**



4. Photographs.

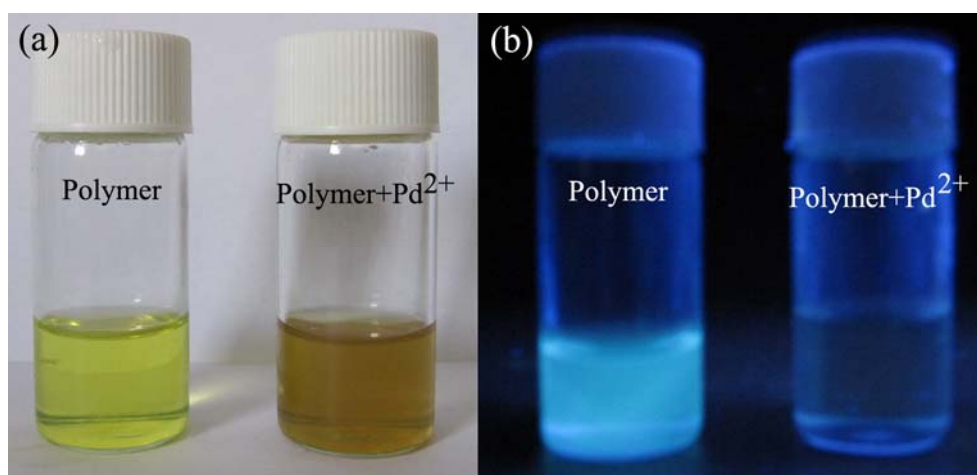


Fig. S1. Visible emission observed in the presence of Pd²⁺ (a) without excitation and (b) with 440nm excitation.

5. The Stern-Volmer data.

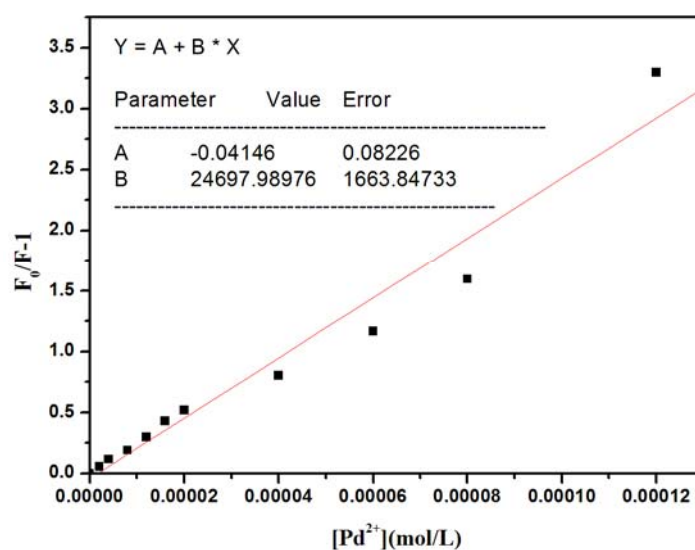


Fig. S2a. Fluorescence quenching of polymer 1 by various concentration of palladium, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the analyte, respectively. $K_{SV} = (F_0/F - 1)/[Pd^{2+}]$.

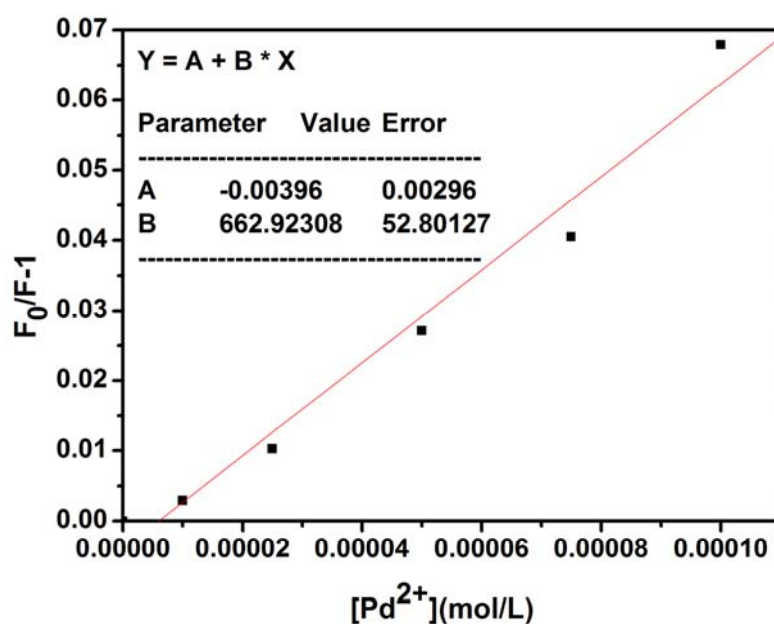


Fig. S2b. Fluorescence quenching of compound 2 by various concentration of palladium, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the palladium ions, respectively. $K_{SV}=(F/F_0-1)/[Pd^{2+}]$. The excitation wavelength is 347nm. The emission wavelength is 390nm.

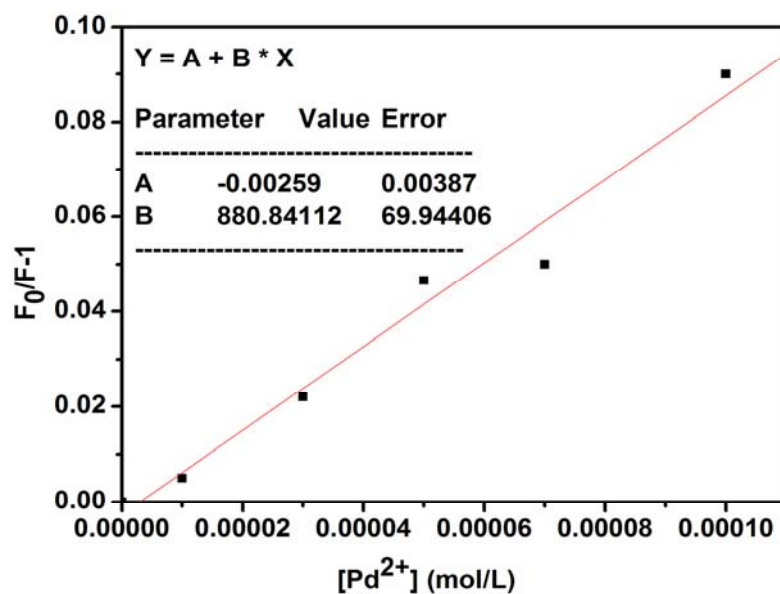


Fig. S2c. Fluorescence quenching of compound 3(TPT) by various concentration of palladium, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the palladium ions, respectively. $K_{SV}=(F/F_0-1)/[Pd^{2+}]$. The excitation wavelength is 346nm. The emission wavelength is 385nm.