Electronic Supplementary Information

for

An efficient conjugated polymer sensor based on the aggregation-induced fluorescence quenching mechanism for specific detection of palladium and platinum ions

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Contents

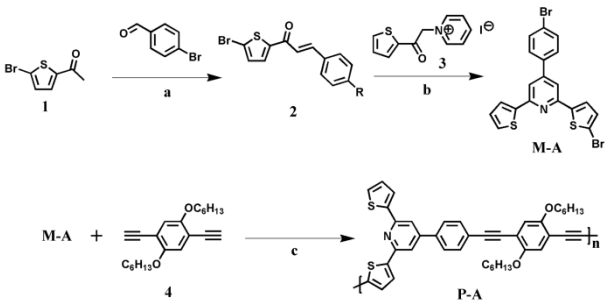
1. Materials and Methods.

Reagents and Instrumentation. All chemicals and solvents were commercially available A.R. grade. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AVANCE Ⅱ and 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 refroutive index detector, and three styragel columns and THF was used as solvent and relative to polystyrene standards. Thermogravimetric analysis (TGA) studies were carried out on a Hi-Res TGA 2950 thermogravimetric analyser (TA Instruments) with a $10^{o}C\ min^{-1}$ ramp to $700^{o}C$ under N_2.

Fluorescence Titration Procedure. Titration experiment was started with 5.0 mL polymer in THF solution with a known concentration (4.0×10^{-6}mol/L). Analyte solutions were prepared from $AgNO_3$, $Co(NO_3)_2 \cdot 6H_2O$, $CdCl_2 \cdot 1.5H_2O$, $NiCl_2 \cdot 6H_2O$, $CuAc_2 \cdot H_2O$, $ZnCl_2$, $HgCl_2$, $FeCl_3 \cdot 6H_2O$, and $CaCl_2 \cdot 2H_2O$ (4.0×10^{-3} mol/L) by dissolving in DMF respectively. 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. Polymer-metal complexes were produced by adding aliquots of a solution of the selected metal salt to a THF solution of polymer. All kinds of measurements were monitored after sonicating the mixture for 1h.

Fluorescence Anisotropy. For the fluorescence anisotropy measurements, emission and detection polarizers were incorporated into the fluorescence spectrometer. Dilute solutions of the sensing materials were excited at the peak absorption with vertically polarized excitation and the emission measured with the detection polarizer aligned for vertically (I_{VV}) and then horizontally (I_{VH}) polarized emission. The same fluorescence measurements were then repeated with horizontally polarized excitation (to give I_{HV} and I_{HH}).

2. Synthesis. The polymers **P-B** and **P-C** were prepared according to our previous works.[9r, 12]



*Synthesis of 2-acetyl-5-bromothiophene (**1**).*

2-Acetylthiophene (9 mmol) and N-bromosuccinimide (10 mmol) were dissolved in DMF (75 mL). The reaction flask was heated at 80 °C for 2 hours then cooled to room temperature. The reaction was diluted with CH_2Cl_2 (300 mL) and the mixed solution was washed with water to remove DMF. The organic phase was dried over Na_2SO_4 before concentrated. The crude product was then purified with flash chromatography (CH_2Cl_2/hexane = 1/1) to give the pure product. Yield= 70 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.41 (d, 1 H), 7.09 (d, 1 H), 2.50 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) d=189.54, 146.02, 132.48, 131.23, 122.78, 26.24.

*Synthesis of 3-(4-bromophenyl)-1-(5-bromothiophen-2-yl) prop-2-en-1-one (**2**).*

To a mixture of **1** (5 mmol) and 4-bromobenzaldehyde (5 mmol) 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 = 90%. ^{1}H NMR (400 MHz, DMSO-d6) δ=7.78 (d, 1H), 7.60 (d, 1H), 7.57 (d, 2H), 7.50 (d, 2H), 7.32 (d, 1H), 7.16 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) d=189.07, 143.94, 136.74, 133.61, 132.284, 132.00, 130.02, 129.85, 128.11, 125.08, 121.94.

*Synthesis of N-[1-oxo-2-(2-thienyl)ethyl]-pyridinium iodide (**3**).*

A mixture of 2-Acetylthiophene (20 mmol) and I_2 (20 mmol) in pyridine (25 mL) was refluxed for 3 h. After cooling the mixture to 20^{o}C, the precipitate was filtered and washed with cold pyridine several times, and the product was used in the next step without further purification. Yield > 90%. ^{1}H NMR (400 MHz, $CDCl_3$) 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).

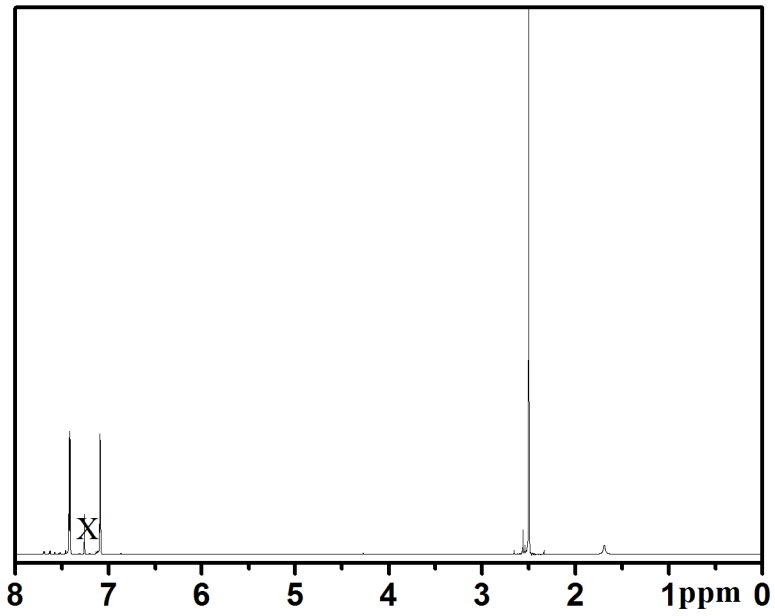
*Synthesis of 4-(4-bromophenyl)-2-(5-bromothiophen-2-yl)-6-(thiophen-2-yl) pyridine (**M-A**)*. An equimolar amount of compound **2** (4 mmol) and **3** (4 mmol) was heated under reflux for 8h in the presence of ammonium acetate (3.0 g) and glacial acetic acid (15.0 mL). After the reaction mixture was maintained at room temperature overnight, ice cold water (45.0 mL) was added to it. The precipitated was filtered, washed with methanol, dried, then purified with chromatography (CH_2Cl_2/hexane = 1/1) to give the pure product. Yield = 38%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.70 (d, 1H), 7.66-7.53 (m, 6H), 7.44 (d, 1H), 7.40 (d, 1H), 7.15 (t, 1H), 7.08 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) d=152.85, 151.92, 149.13, 146.21, 144.29, 137.28, 132.35, 130.87, 128.62, 128.21, 128.04, 125.16, 124.71, 123.71, 115.71, 114.96, 113.92.

*Synthesis of polymer **P-A***.

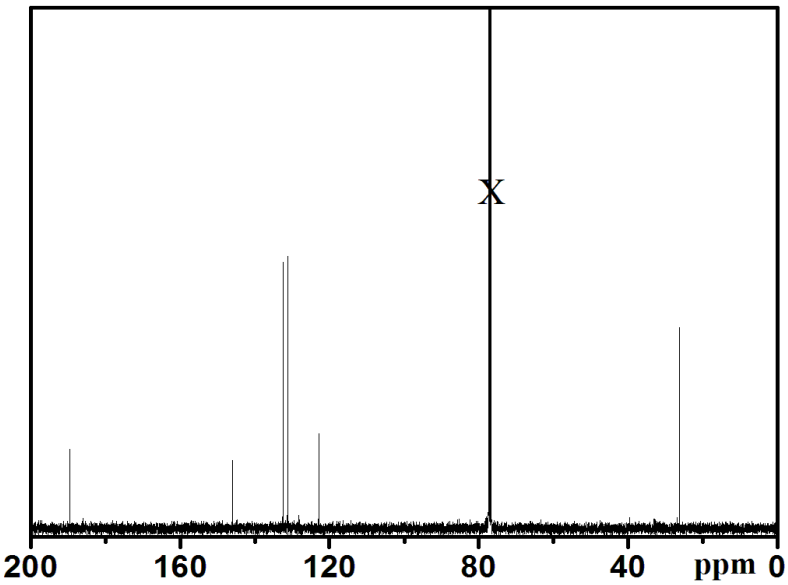
Monomer **M-A** (0.5 mmol), 1,4-bis(ethynyl)-2,5-bis(hexyloxy)benzene **4** (0.5 mmol), $Pd(PPh_3)_4$ (120mg, 0.1 mmol), and CuI (19.2mg, 0.1 mmol) were combined in dry and degassed triethylamine (5ml) and THF (10ml). The mixture was heated at 70^{o}C for 24h under argon atmosphere, and then cooled to room temperature and filtered. The filtrate was added dropwise to vigorously stirred methanol. The precipitate was centrifuged, dissolved in 10mL of THF, and then precipitated in methanol again. The final product was dried under vacuum to give polymer **P-A** as a brown solid in a yield of 46% . M_n=2960 PDI=1.52 (GPC). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.80-7.30 (11H), 6.85 (2H), 3.99 (4H), 1.80-1.50 (16H), 0.91 (6H). $(C_{41}H_{39}NO_2S_2)_n$ $(641.9)_n$: Calcd. C 76.71, H 6.12, N 2.18; Found C 75.01, H 6.44, N 2.22.

3.The NMR data

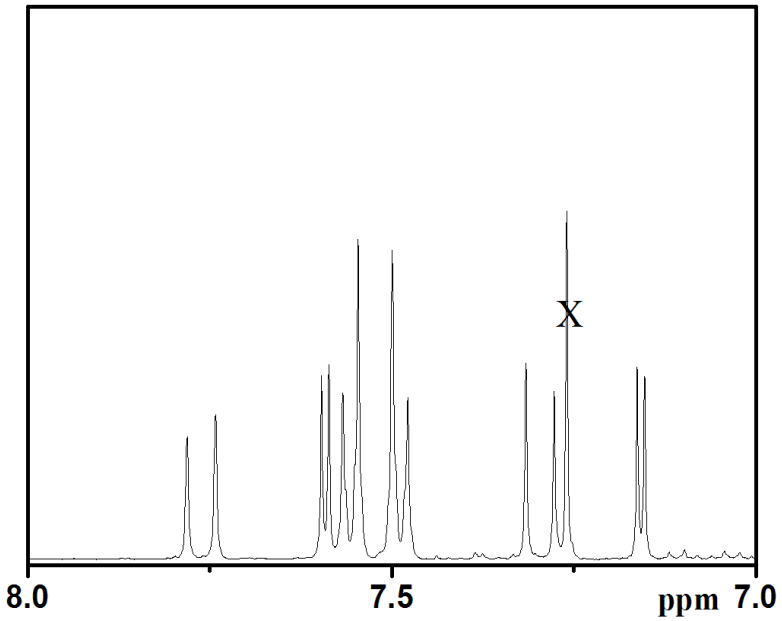
^{1}H NMR of compound 1



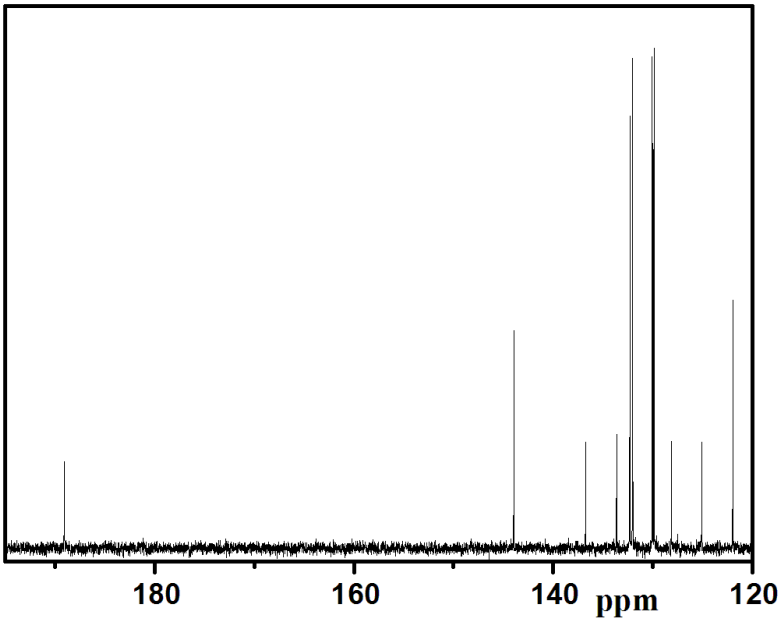
^{13}C NMR of compound 1



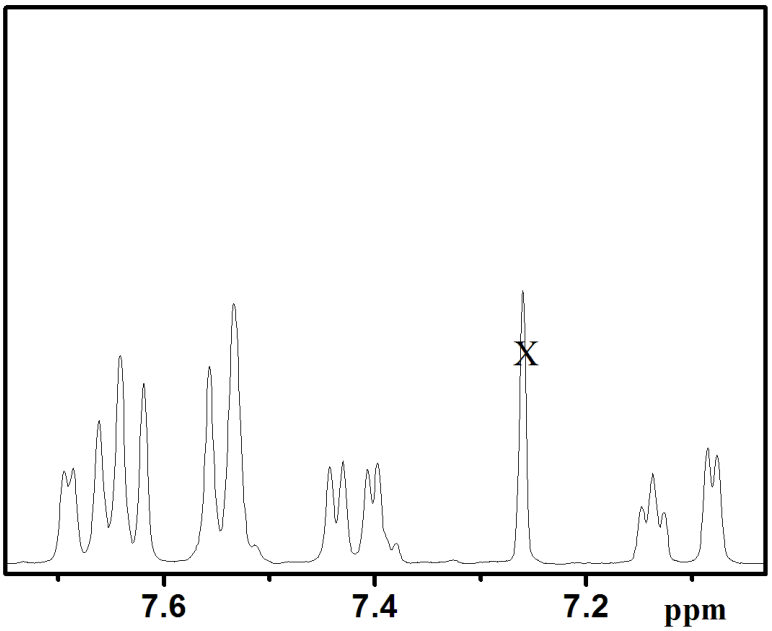
^{1}H NMR of compound 2



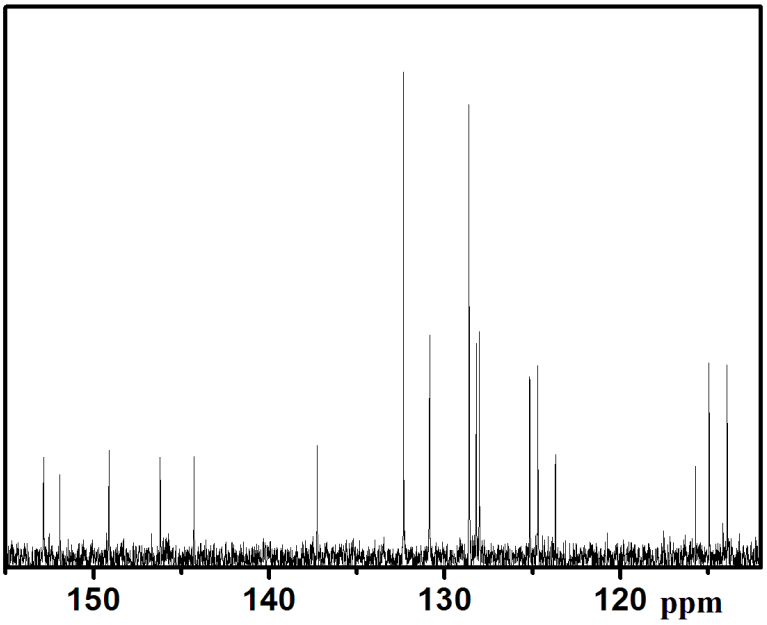
^{13}C NMR of compound 2



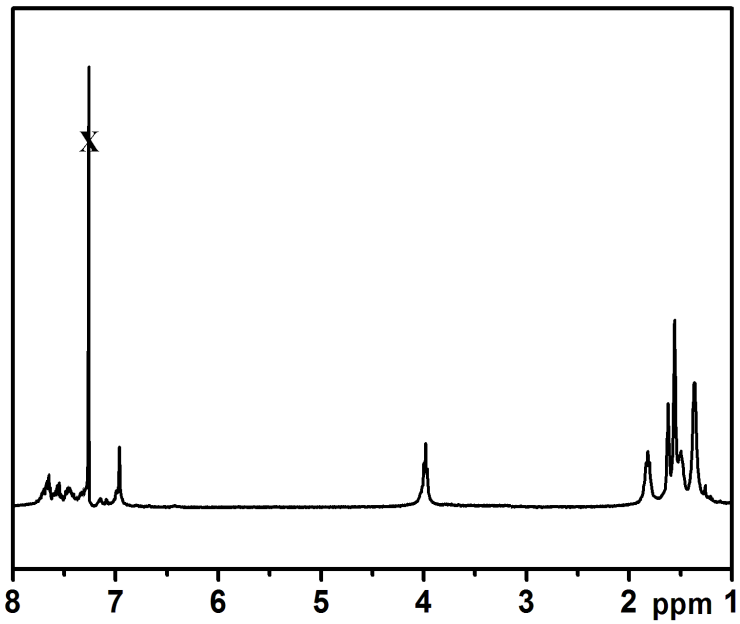
^{1}H NMR of compound 4



^{13}C NMR of compound 4



^{1}H NMR of polymer P-A



4. Optical properties

Table S1. Optical properties of compounds TPP, M-A, M-B, M-C, P-A, P-B and P-C.

Compound	λab[a]	λex[b]	λem[c]	ϕ[d]
TPP	Nd	345	385	Nd
M-A	348	309,353	394	Nd
M-B	Nd	350	390	Nd
M-C	Nd	327	365	Nd
P-A	442	442	476	0.27
P-B	436	423	472	0.24
P-C	406	400	467	0.22

[a] Absorption maximum (nm). [b] Excitation wavelength (nm). [c] Emission maximum (nm). [d] Ratio of fluorescence quantum yields. Nd: Not determined

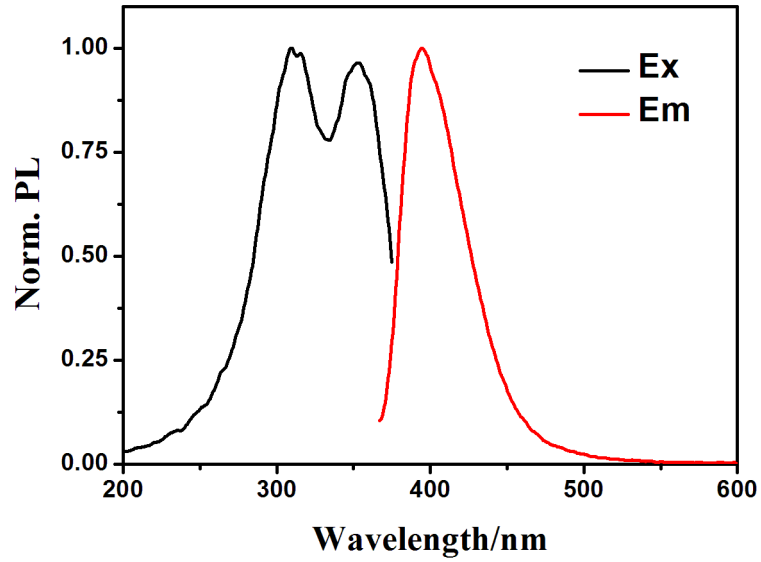


Fig. S1. Normalized excitation and emission spectra of compound **M-A** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

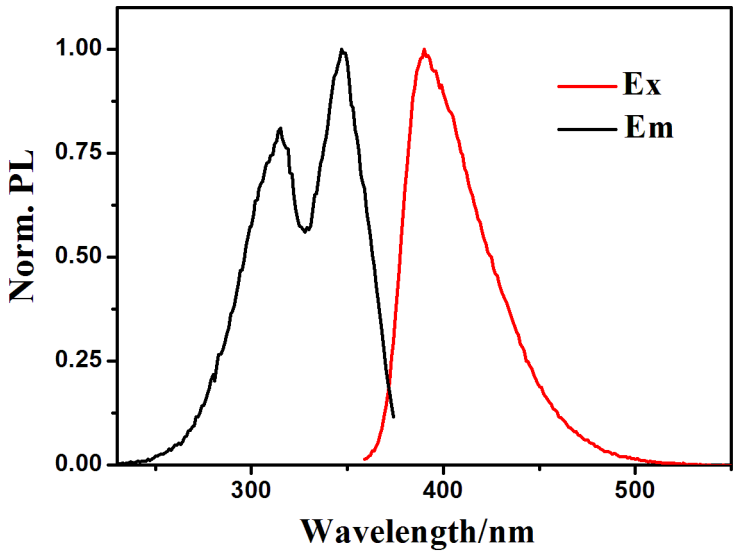


Fig. S2. Normalized excitation and emission spectra of compound **M-B** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

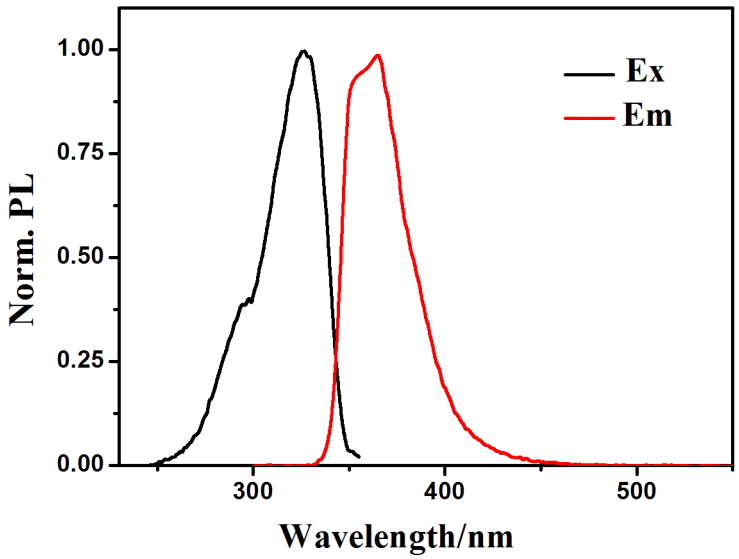


Fig. S3. Normalized excitation and emission spectra of compound **M-C** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

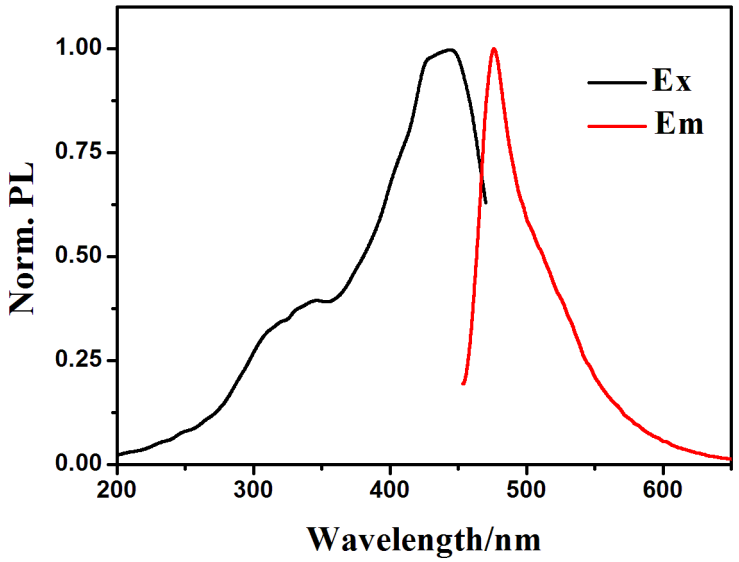


Fig. S4. Normalized excitation and emission spectra of polymer **P-A** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

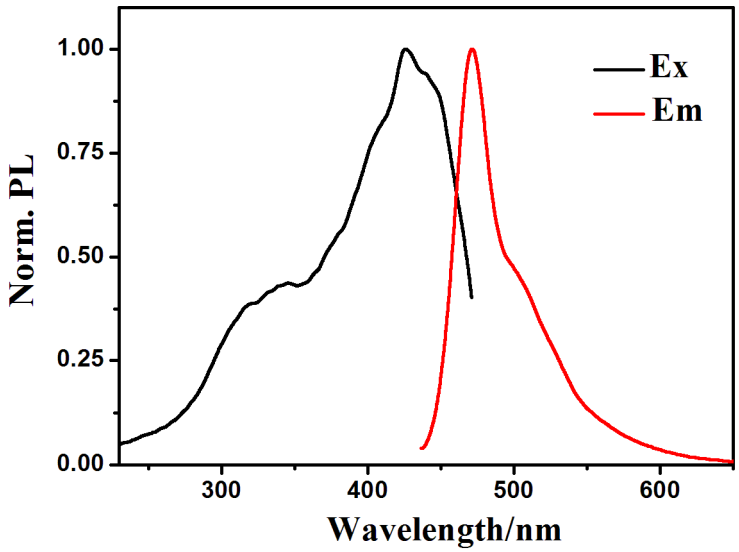


Fig. S5. Normalized excitation and emission spectra of polymer **P-B** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

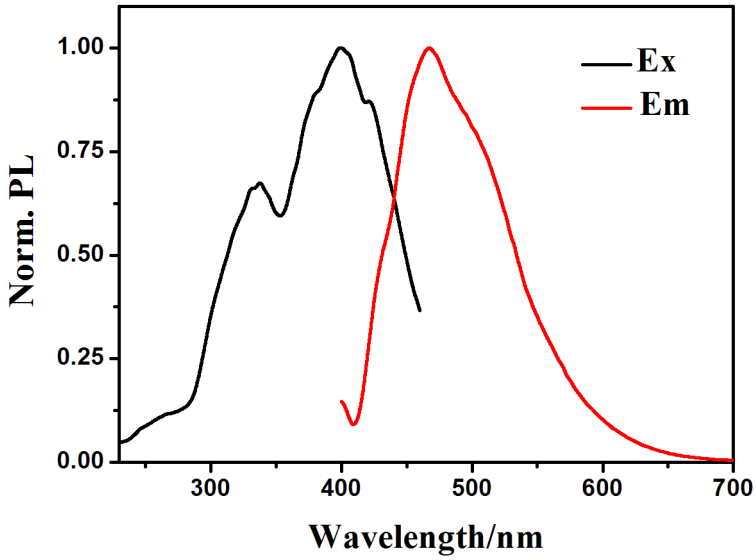


Fig. S6. Normalized excitation and emission spectra of polymer **P-C** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

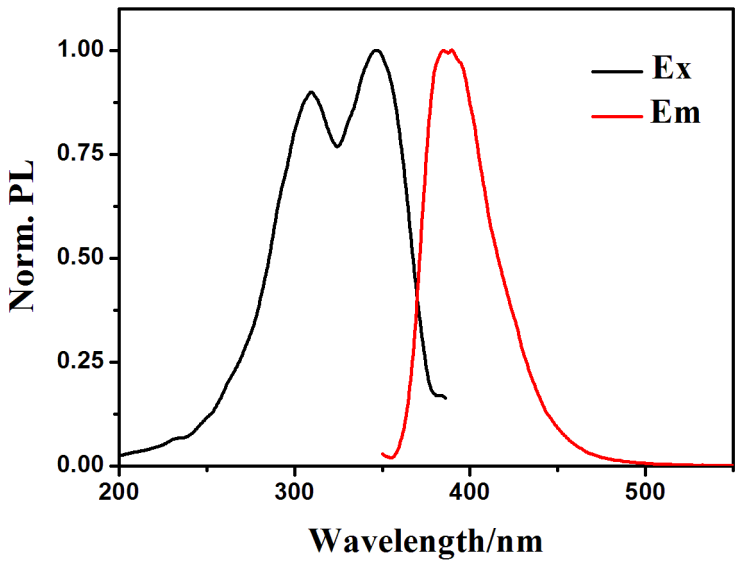


Fig. S7. Normalized excitation and emission spectra of compound **TPP** in THF. The dash line is excitation spectra and the solid line is emission spectra, respectively.

5. Additional fluorescence spectra

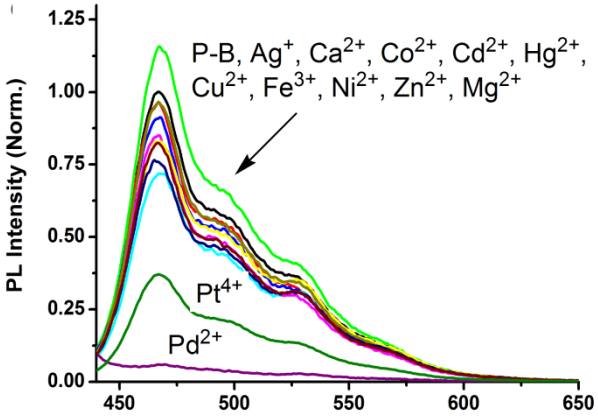


Fig. S8. Emission spectra of **P-B** (1×10^{-6} M in repeat units) upon addition of different metal cations (0.1mM of Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{4+} and Zn^{2+}) in THF-H_2O (1:1, v/v) solution with HEPES buffer (10mM).

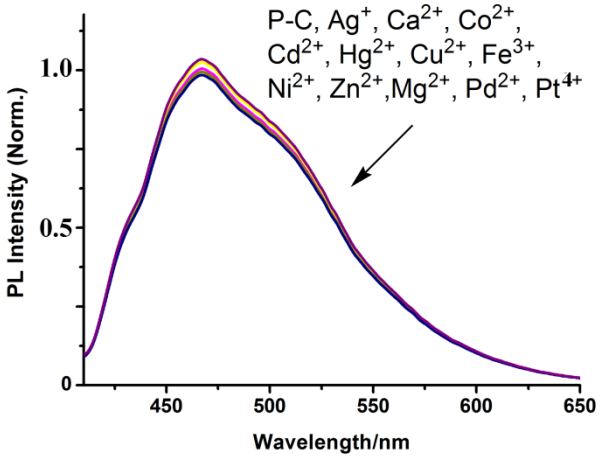


Fig. S9. Emission spectra of **P-C** (1×10^{-6} M in repeat units) upon addition of different metal cations (0.1mM of Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{4+} and Zn^{2+}) in THF-H_2O (1:1, v/v) solution with HEPES buffer (10mM).

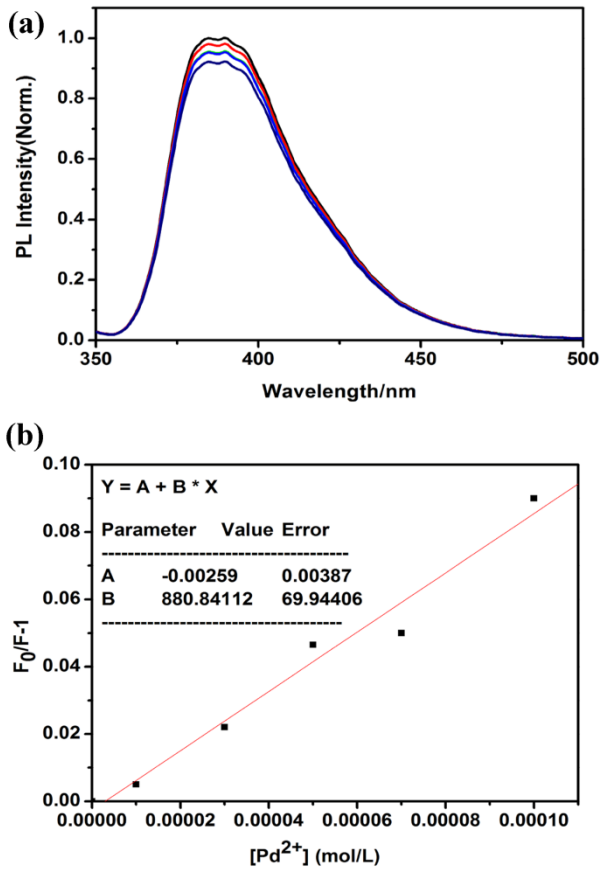


Fig. S10.(a)Fluorescent emission spectra of **TPP** in the presence of different concentrations of Pd^{2+} ions from 0 to 1.0×10^{-4} M; (b)Fluorescence quenching of compound **TPP** by various concentration of palladium, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and

presence of the palladium ions, respectively. $K_{SV}=(F_0/F -1)/[Pd^{2+}]$.