

An Imidazole-Functionalized Polyacetylene: Convenient Synthesis and Selective Chemosensor for Metal Ions and Cyanide

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Materials and Instrumentations

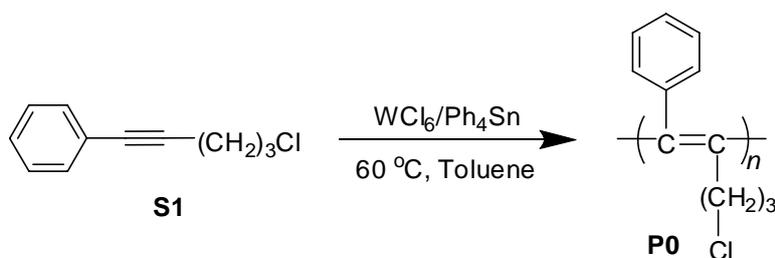
N,N-Dimethylformamide (DMF) was dried over and distilled from CaH₂ under an atmosphere of dry nitrogen. NaNO₃, KNO₃, Ba(NO₃)₂, AgNO₃, Cr(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Pb(NO₃)₂, Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Al(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O, FeSO₄·7H₂O, 3CdSO₄·8H₂O, MnSO₄·H₂O, NaCl, KBr, KI, Na₂SO₄, K₃PO₄·3H₂O, Na₂HPO₄·12H₂O, NaClO₄, KCNS and NaF were of analytical grade, and purchased from Sinopharm Chemical Reagent Beijing Co.,Ltd.

¹H-NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Or ¹H and ¹³C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm⁻¹. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Elementary analysis was taken on a Vario EL III elementary analysis instrument. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was

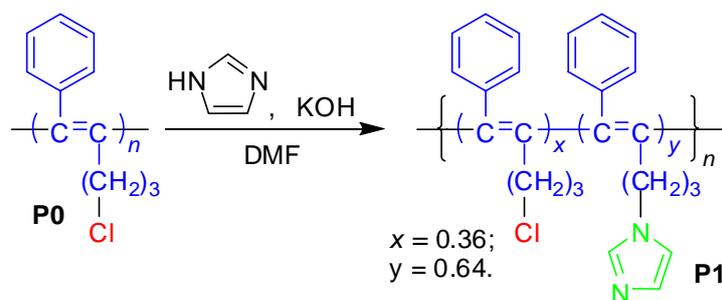
performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector.

Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer.

Scheme S1



Scheme 1



Synthesis and Characterization

Synthesis of (5-Chloro-pent-1-ynyl)-benzene (S1)

To a 250 mL flask were added 90 mg of copper (I) iodide, 180 mg of dichlorobis(triphenylphosphine)palladium and 90 mg of triphenylphosphine, in the glove box. Triethylamine (250 mL), 10.2 g of iodobenzene (50mmol) and 5.2 g of 5-chloro-1-pentyne (50mmol) were then injected. The resultant mixture was stirred at room temperature overnight. The solid was removed by filtration and the solvent was evaporated. The crude product was purified on a silica gel column using chloroform as eluent. Colorless oil of **1** was obtained in 89 % yield (7.9 g). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.41 (d, 2H), 7.28 (m, 3H), 3.70 (t, 2H), 2.60 (t, 2H), 2.04 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 131.7, 128.5, 127.7, 123.7, 88.1, 81.4, 43.7,

Synthesis of P0

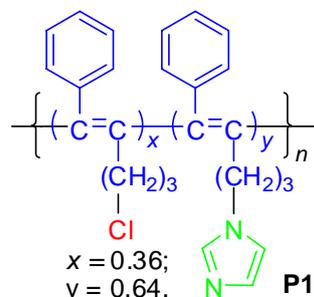
Into a baked 80-mL Schlenk tube with a stopcock in the sidearm was added 1.14 g of monomer **S1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Freshly distilled toluene (16 ml) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 127.2 mg of tungsten (VI) chloride and 137.6 mg of tetraphenyltin in 16 mL of toluene. The two tubes were aged at 60 °C for 15 min and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C for 24 hours. The resultant solution was then cooled to room temperature, diluted with 35 mL of chloroform, and added dropwise to 2500 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with methanol and dried in a vacuum oven to a constant weight, shallow green powder (0.78 g, 68.4 %). $M_w = 15700$, $M_w/M_n = 2.27$. (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3064 (Ar-H stretching), 2954, 2870 (CH_2 stretching). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 0.8-2.6 ($-\text{CH}_2-$), 2.6-3.4 ($-\text{CH}_2-$), 6.5-7.8 (ArH). UV-Vis (Ethanol, 1.06×10^{-4} mol/L): λ_{max} (nm): 302nm.

Synthesis of P1

P0 (89mg), imidazole (68 mg, 1.0 mmol), potassium hydroxide (140mg, 2.5mmol) were added to dry DMF (10 mL). After stirred at 80 °C for 3 days, the resultant mixture was filtered, then the filtrate was added to a dialyzer bag. The bag was immersed in distilled water (the water was changed every two hours) for several day to remove small molecules, such as imidazole (which would enter into water as its molecular weight is lower than 800). It was observed that some yellow precipitant yielded in the bag during the dialyzing process. The yellow powder was collected, and dried in a vacuum oven to a constant weight (47mg, 44.7%). ^1H NMR (CH_3OD) δ (ppm): 0.9-2.5 ($-\text{CH}_2-$),

P1 (1.9 mg) and imidazole (0.72 mg) were dissolved in the mixture solvent (10 mL) of ethanol and DMF (1:1) to afford the stock solution with the concentration of 1.06×10^{-3} mol/L. And this stock solution (1 mL) was diluted to 1.06×10^{-4} mol/L with ethanol.

Calculation of x , y and molar molecular weight of **P1**



x , y was calculated according to the results of Elementary Analysis. EA: Found: C 73.09, H 6.620, N 9.015.

$$\left. \begin{aligned} (2 \times 14.01) y / (210.27 y + 178.66 x) \times 100\% &= 9.015\% \\ x + y &= 1 \end{aligned} \right\} \begin{aligned} x &= 0.36 \\ y &= 0.64 \end{aligned}$$

$$\text{Mw (per unit)} = 210.27 \times 0.64 + 178.66 \times 0.36 = 198.89$$

Fluorescence intensity changes of **P1** with metal ions

A solution of **P1** (1.06×10^{-4} mol/L) was prepared in ethanol. The solutions of metal ions (2×10^{-2} mol/L) were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the Fluorescence spectrum was recorded. The ion solution was introduced (4 μ L) and fluorescence intensity changes were recorded at room temperature every time (Excitation wavelength: 335 nm).

Fluorescence titration of **P1** with metal ions

A solution of **P1** (1.06×10^{-4} mol/L) was prepared in ethanol. The solutions of metal ions were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the Fluorescence spectrum was recorded. The ion solution was introduced in portions and fluorescence intensity changes were recorded at room temperature every time (Excitation

Ions	C (mol/L)	Total volume (μL)
Cu^{2+}	5×10^{-4}	2, 4, 6, 8, 10, 12, 16, 20, 24, 30, 40, 50, 60, 60+2 ^a
Fe^{3+}	5×10^{-4}	2, 4, 6, 10, 14, 22, 30, 40, 50, 60, 60+1 ^a , 60+2 ^a , 60+3 ^a , 60+4 ^a , 60+5 ^a
Fe^{2+}	5×10^{-4}	2, 4, 6, 8, 10, 16, 20, 24, 30, 40, 50, 60, 60+1 ^a , 60+2 ^a , 60+3 ^a , 60+4 ^a , 60+5 ^a
Co^{2+}	5×10^{-4}	2, 4, 6, 8, 10, 12, 16, 20, 24, 30, 40, 50, 60, 60+1 ^a , 60+2 ^a , 60+3 ^a , 60+4 ^a , 60+5 ^a
Ni^{2+}	2×10^{-3}	2, 4, 6, 8, 10, 12, 16, 20, 30, 40, 50, 60, 60+1 ^a , 60+2 ^a
Cr^{3+}	2×10^{-2}	2, 4, 6, 8, 12, 16, 24, 32, 48
Al^{3+}	2×10^{-2}	2, 4, 12, 20, 30, 40, 50, 60
Pb^{2+}	2×10^{-2}	2, 4, 12, 20, 30, 40, 50, 60

^a The concentration of the metal ions were changed to 2×10^{-2} mol/L.

Fluorescence intensity changes of P1 by Cu^{2+} in the presence of other metal ions

Fluorescence intensity changes were recorded after additions of $4 \mu\text{L}$ of the solutions of metal ions (Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Co^{2+} , Fe^{3+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Cr^{2+} , Ag^{2+} , Zn^{2+} , Cd^{2+} , Al^{2+} and Pb^{2+} ; the concentration of the metal ions were 2×10^{-2} mol/L) to the solution of **P1**. Then $4 \mu\text{L}$ of the solution of Cu^{2+} (2×10^{-2} mol/L) was added and fluorescence intensity changes were recorded (Excitation wavelength: 335 nm).

Fluorescence intensity changes of the mixture of P0 and imidazole with metal ions

A solution of the mixture of **P0** and imidazole (1.06×10^{-4} mol/L) was prepared in ethanol. The solutions of metal ions (2×10^{-2} mol/L) were prepared in distilled water. A solution of the mixture of **P0** and imidazole (3.0 mL) was placed in a quartz cell (10.0 mm width) and the Fluorescence spectrum was recorded. The ion solution was introduced ($4 \mu\text{L}$) and fluorescence intensity changes were recorded at room temperature every time (Excitation wavelength: 335 nm).

Fluorescence intensity changes of P1+ Cu^{2+} with CN^-

A solution of **P1** (0.528×10^{-4} mol/L) was prepared in ethanol. The solutions of NaCN (1×10^{-2} mol/L) was prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the Fluorescence spectrum was recorded. The solution of Cu^{2+} (5×10^{-4} mol/L, 40 μL) was added to quench the Fluorescence. Then NaCN solution was introduced in portions (total volume: 20, 28, 36, 44, 52, 60 μL) and fluorescence intensity changes were recorded at room temperature every time (Excitation wavelength: 335 nm).

Fluorescence intensity changes of **P1+ Cu^{2+} with other anions**

A solution of **P1** (0.528×10^{-4} mol/L) was prepared in ethanol. The solutions of anions (2×10^{-2} mol/L) were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the Fluorescence spectrum was recorded. The ion solution was introduced (10 μL) and fluorescence intensity changes were recorded at room temperature every time (Excitation wavelength: 335 nm).

Fluorescence “turn off-turn on” of polymer film by ammonia

Fluorescence intensity change was recorded after the film of **P1** immersed in aqueous $\text{Cu}(\text{NO}_3)_2$ solution (2×10^{-2} mol/L). Then the film was immersed in ammonia aqueous solution and fluorescence intensity change was recorded at room temperature (Excitation wavelength: 335 nm).

Fluorescence “turn off-turn on” of polymer film by CN^-

Fluorescence intensity change was recorded after the film of **P1** immersed in aqueous $\text{Cu}(\text{NO}_3)_2$ solution (2×10^{-2} mol/L). Then the film was immersed in NaCN aqueous solution (1.4×10^{-3} or 1.0×10^{-2} mol/L) and fluorescence intensity changes were recorded at room temperature each time (Excitation wavelength: 335 nm).

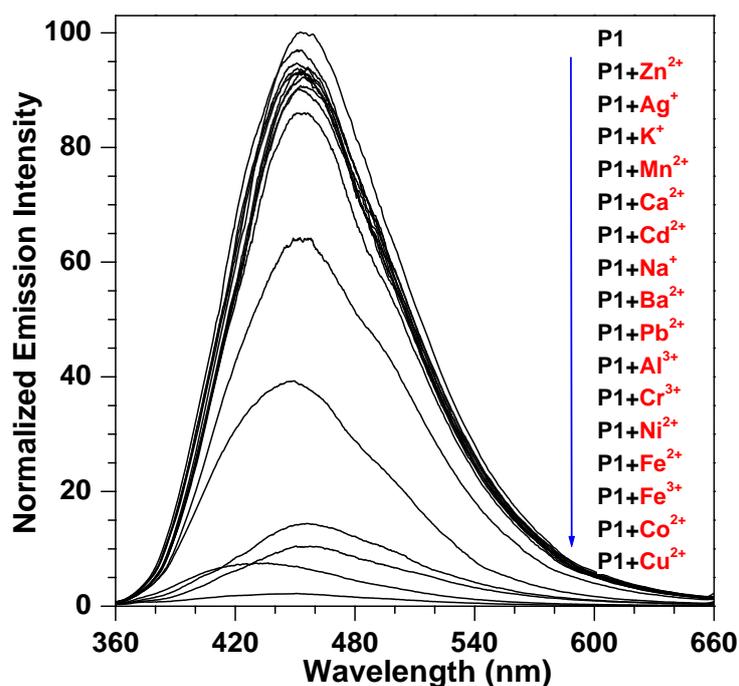


Figure S1. Emission quenching of the solution of **P1** in ethanol by different metal ions. The polymer concentration is fixed at 1.06×10^{-4} mol/L, and the concentrations of all metal ions are the same (2.67×10^{-5} mol/L), or in ppm (from Zn²⁺ to Cu²⁺): 1.74, 2.88, 1.04, 1.47, 1.07, 3.00, 0.61, 3.66, 5.53, 0.72, 1.39, 1.57, 1.49, 1.49, 1.57, 1.70. Excitation wavelength (nm): 335.

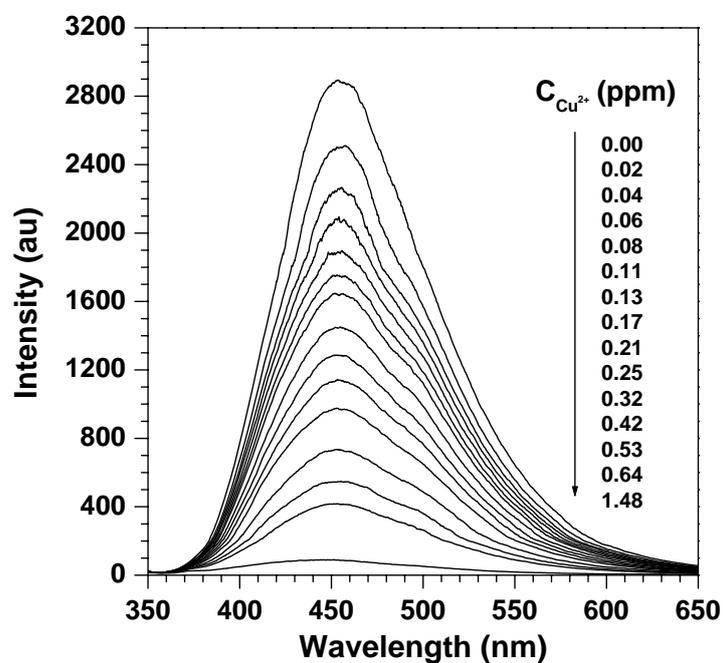


Figure S2. Emission quenching of the solution of **P1** in ethanol by Cu²⁺. Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

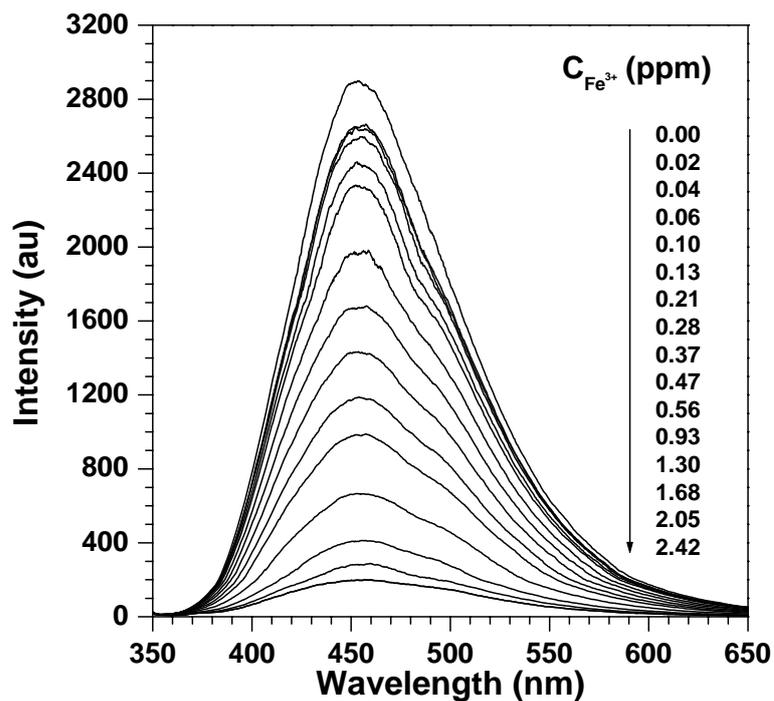


Figure S3. Emission quenching of the solution of **P1** in ethanol by Fe³⁺. Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

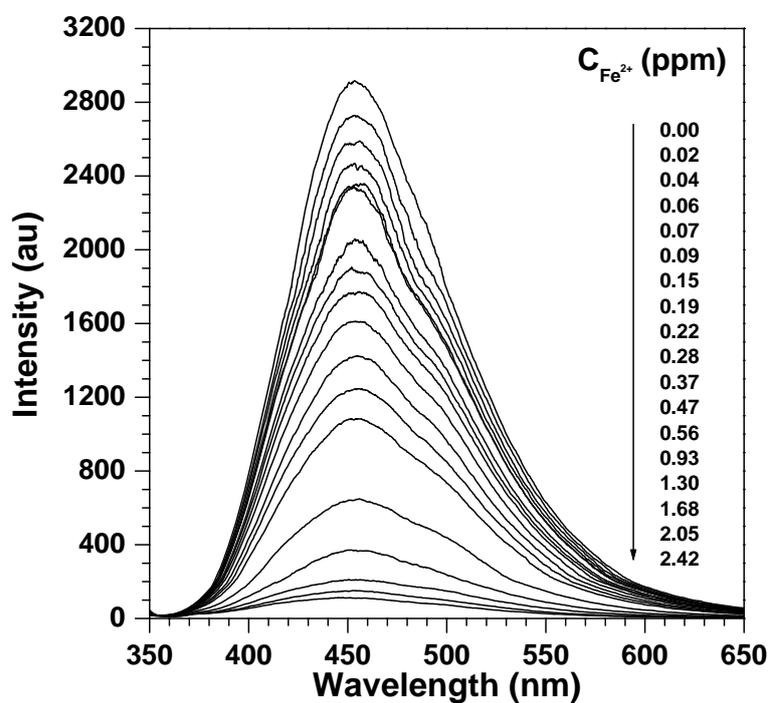


Figure S4. Emission quenching of the solution of **P1** in ethanol by Fe²⁺. Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

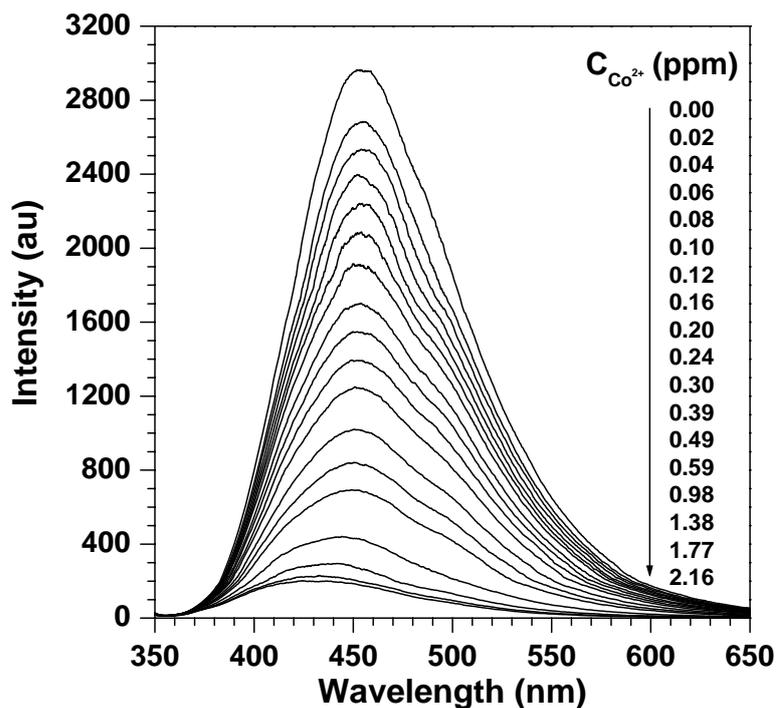


Figure S5. Emission quenching of the solution of **P1** in ethanol by Co^{2+} . Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

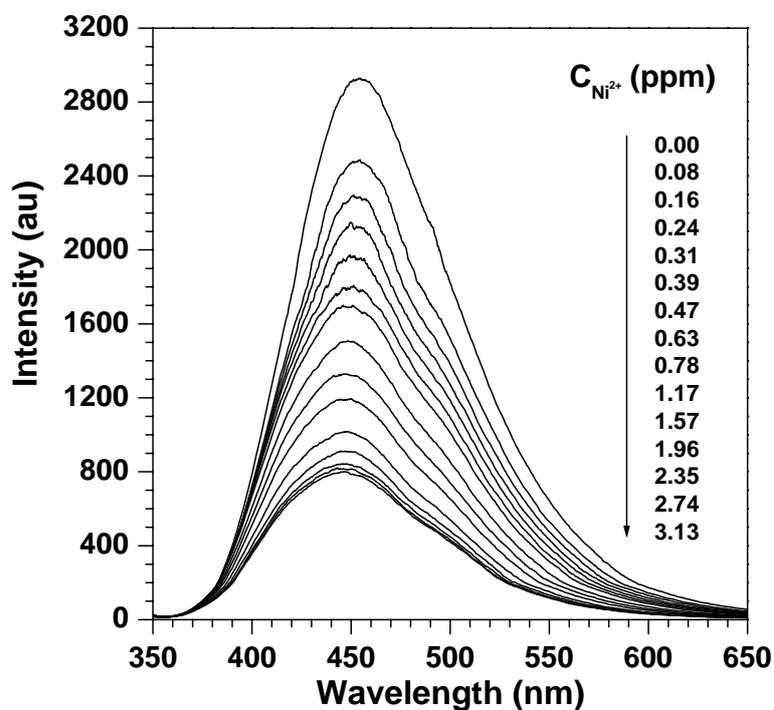


Figure S6. Emission quenching of the solution of **P1** in ethanol by Ni^{2+} . Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

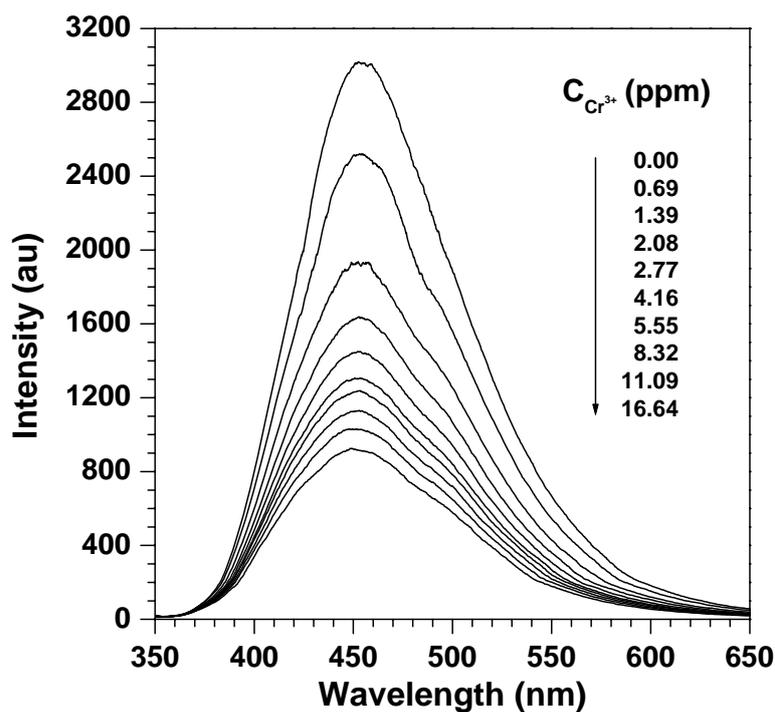


Figure S7. Emission quenching of the solution of **P1** in ethanol by Cr³⁺. Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

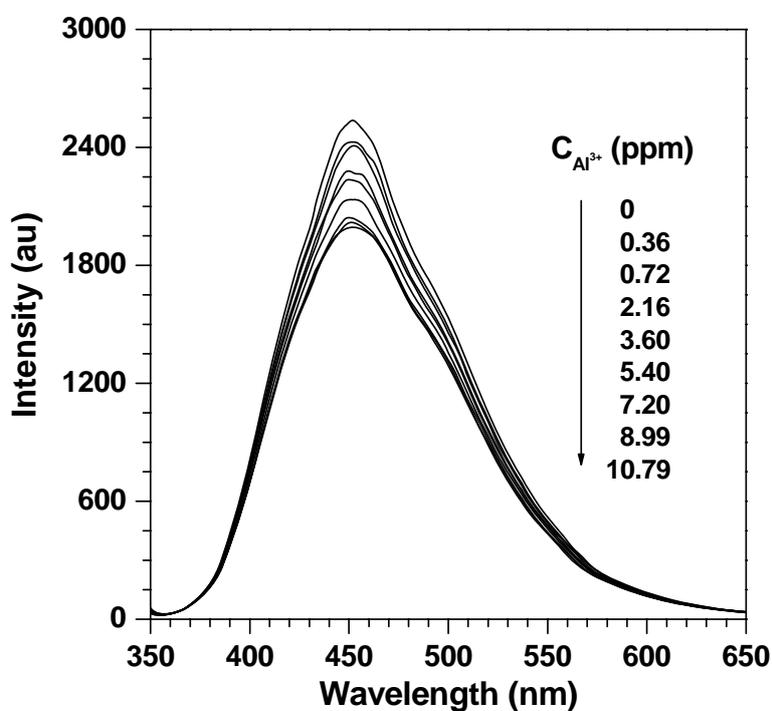


Figure S8. Emission quenching of the solution of **P1** in ethanol by Al³⁺. Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

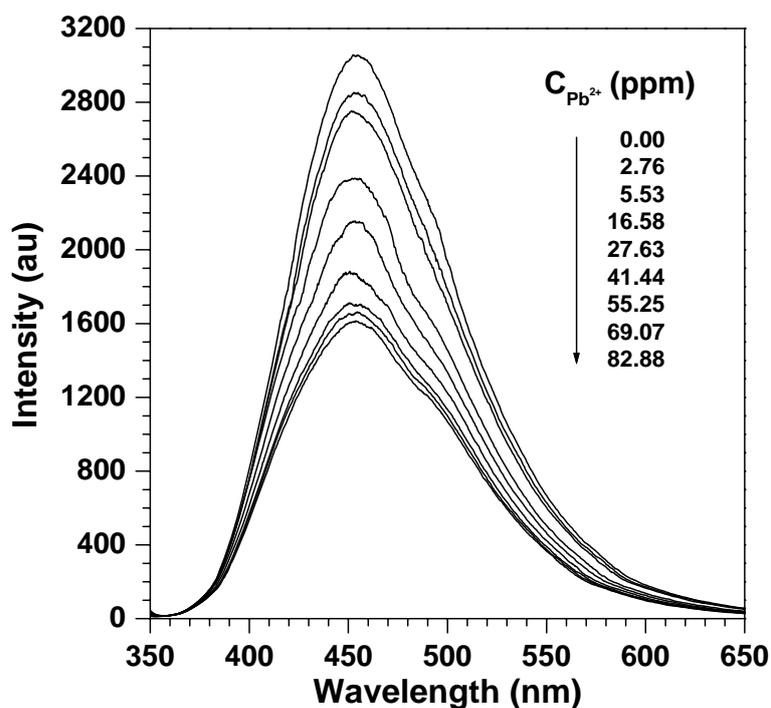


Figure S9. Emission quenching of the solution of **P1** in ethanol by Pb^{2+} . Concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

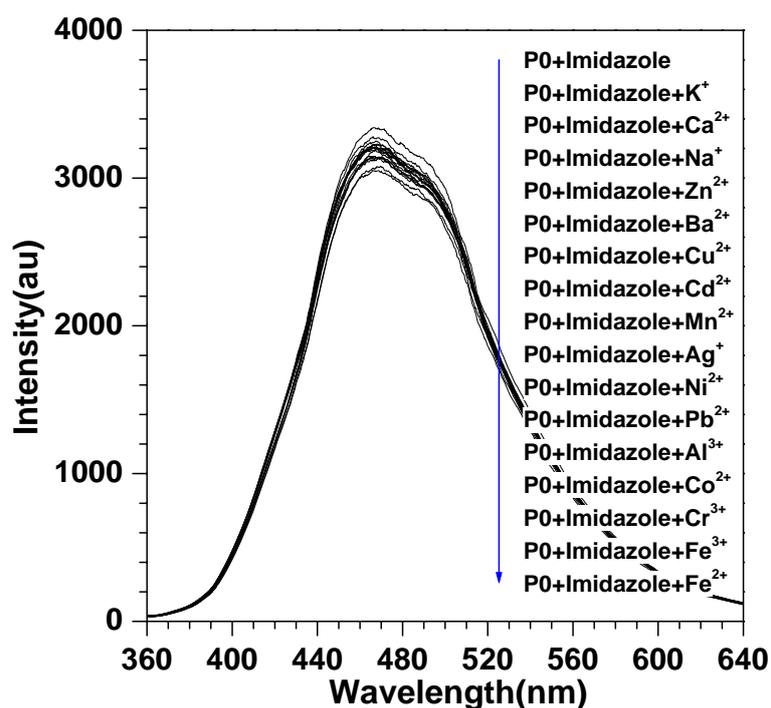


Figure S10. Emission quenching of the solution of the mixture of **P0** and Imidazole in ethanol by different metal ions. The polymer concentration is fixed at 1.06×10^{-4} mol/L, and the concentrations of all metal ions are the same (2.67×10^{-5} mol/L), or in ppm (from K^+ to Fe^{2+}): 1.04, 1.07, 0.61, 1.74, 3.66, 1.70, 3.00, 1.47, 2.88, 1.57, 5.53, 0.72, 1.57, 1.39, 1.49, 1.49. Excitation wavelength (nm): 335.

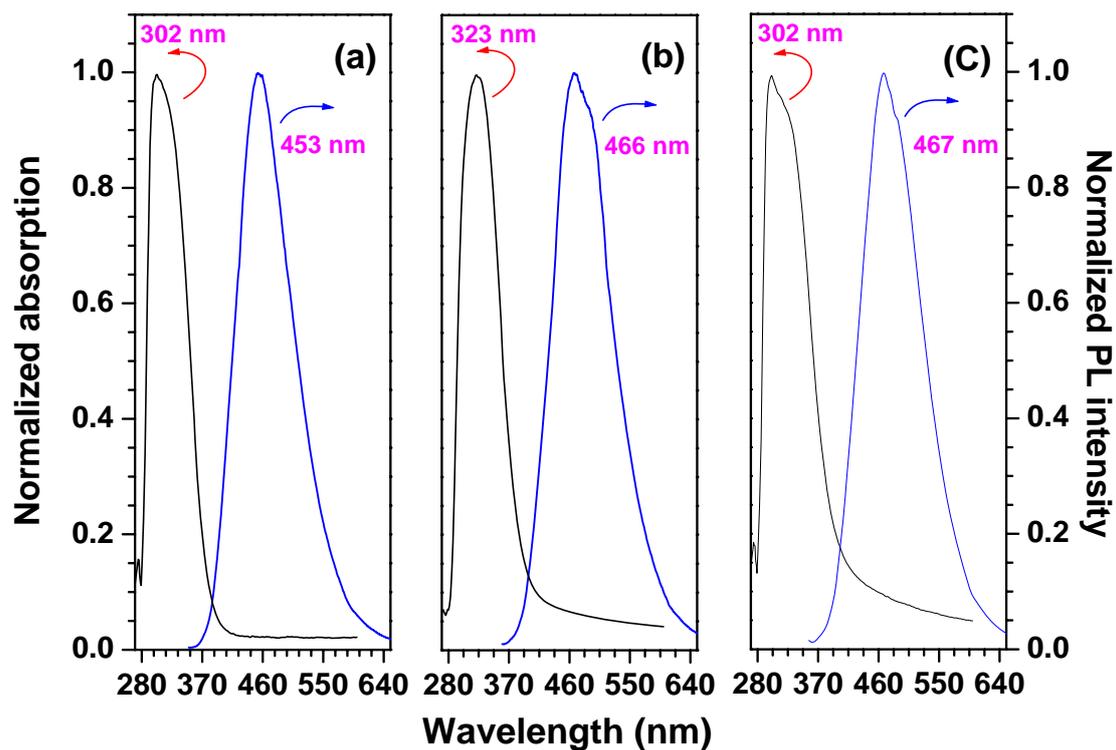


Figure S11. The UV-vis absorption and fluorescence spectra of **P1** (a), the mixture of **P0** and imidazole (b) and **P0** (c) in ethanol. The polymer concentration is 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

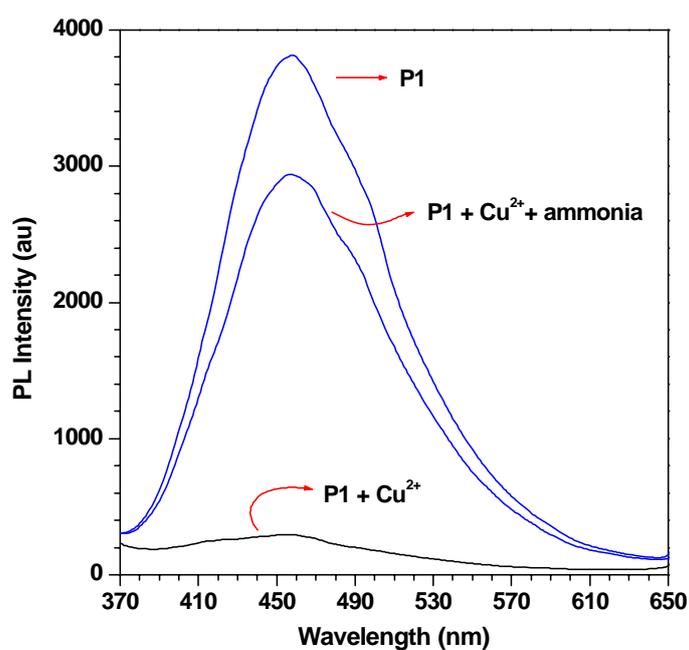
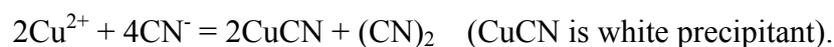
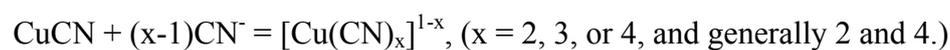


Figure S12. Fluorescence emission spectra **P1** in solid states on a glass plate before immersion in Cu²⁺ aqueous solution, after immersion in Cu²⁺ aqueous solution, and after immersion in ammonia aqueous solution.

Equation S1: the reaction between Cu^{2+} and CN^-



Equation S2: the reaction between CuCN and CN^-



The stability constants (K), $[\text{Cu}(\text{CN})_2]^-$: $K = 1.00 \times 10^{24}$; $[\text{Cu}(\text{CN})_4]^{3-}$: $K = 2.00 \times 10^{30}$.

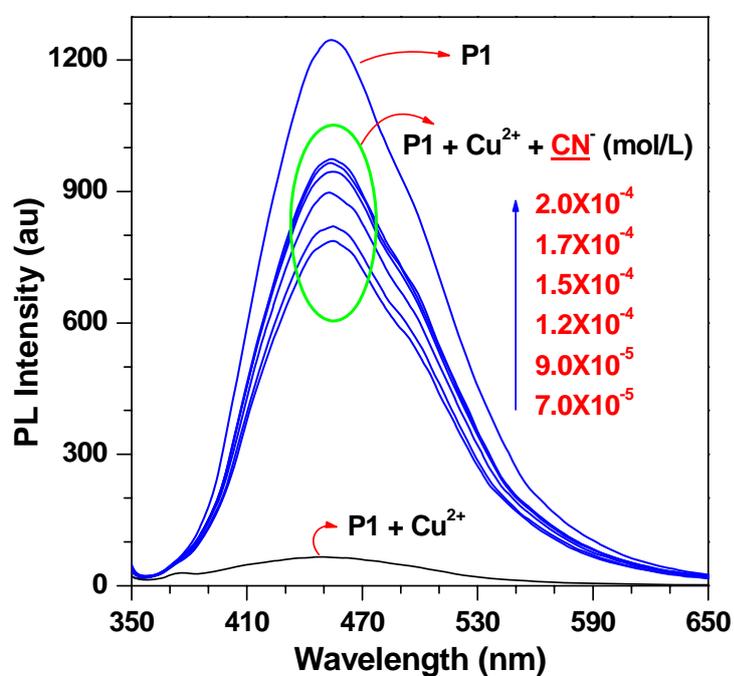


Figure S13. Fluorescence emission spectra **P1** in ethanol before added Cu^{2+} , after added Cu^{2+} , and turned on by CN^- . The polymer concentration is fixed at 0.528×10^{-4} mol/L. Excitation wavelength (nm): 335.

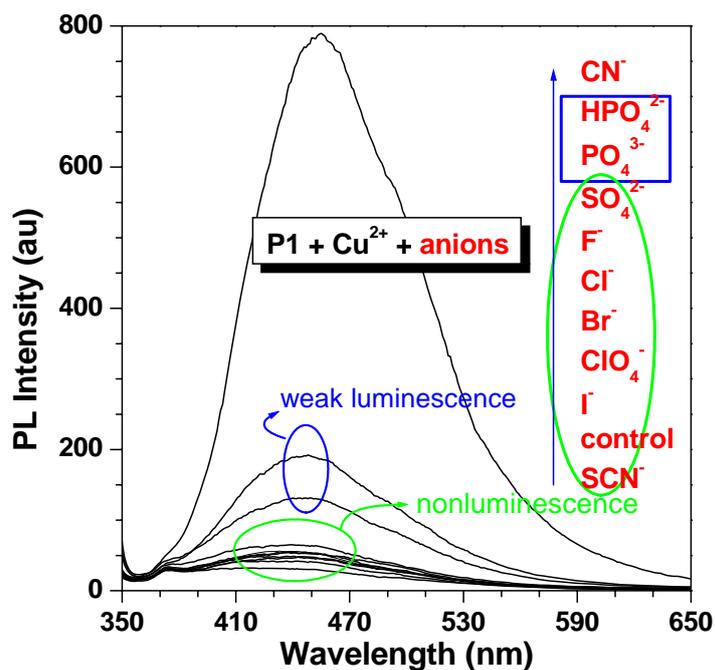


Figure S14. Fluorescence emission spectra **P1** in ethanol after added Cu^{2+} , and turned on by CN^- and other anions. The polymer concentration is fixed at 0.528×10^{-4} mol/L, and concentration of all anions is 7.0×10^{-5} mol/L. Excitation wavelength (nm): 335.

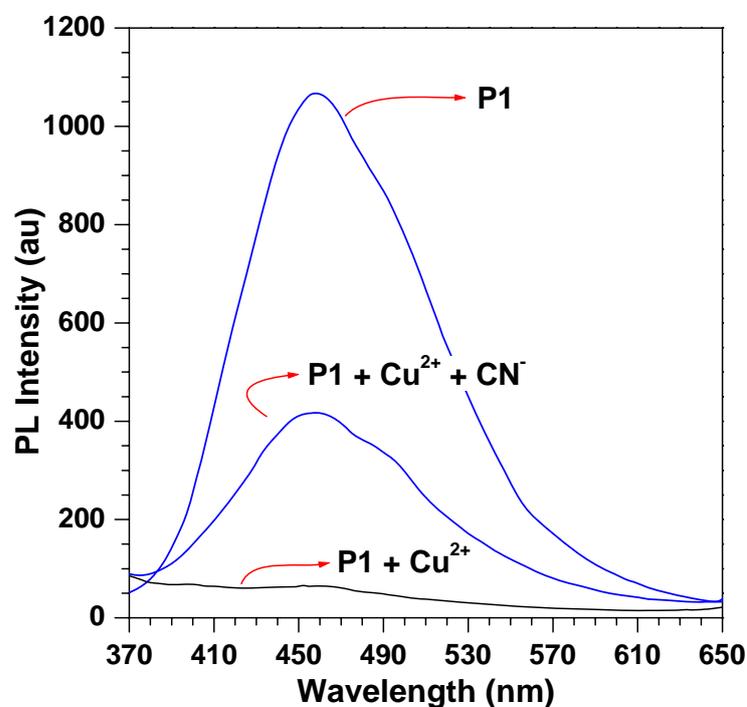


Figure S15. Fluorescence emission spectra **P1** in solid states on a glass plate before immersion in Cu^{2+} aqueous solution, after immersion in Cu^{2+} aqueous solution, and after immersion in sodium cyanide aqueous solution (1.4×10^{-3} mol/L).

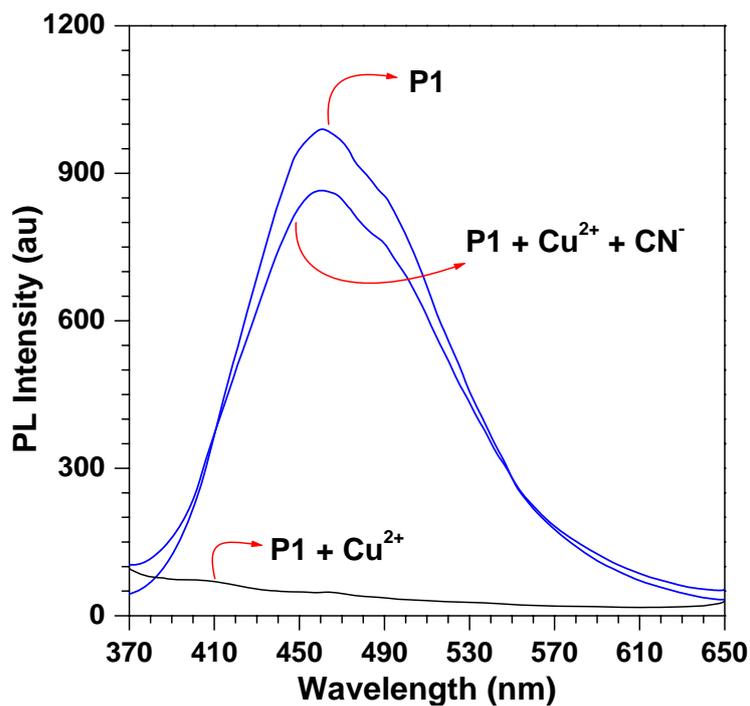


Figure S16. Fluorescence emission spectra **P1** in solid states on a glass plate before immersion in Cu^{2+} aqueous solutions, after immersion in Cu^{2+} aqueous solutions, and after immersion in sodium cyanide aqueous solutions (1.0×10^{-2} mol/L).