

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

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## Materials and Instrumentations

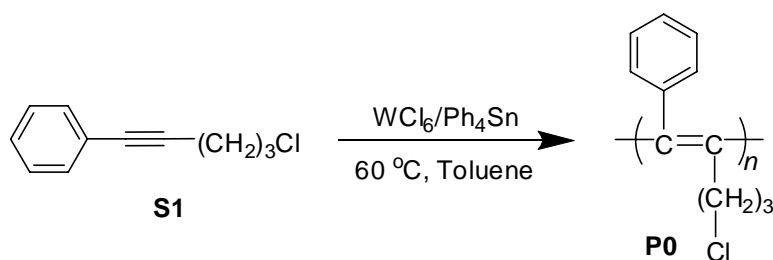
*N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH<sub>2</sub> under an atmosphere of dry nitrogen. NaNO<sub>3</sub>, KNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, AgNO<sub>3</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, FeSO<sub>4</sub>·7H<sub>2</sub>O, 3CdSO<sub>4</sub>·8H<sub>2</sub>O, MnSO<sub>4</sub>·H<sub>2</sub>O, NaCl, KBr, KI, Na<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, NaClO<sub>4</sub>, KCNS and NaF were of analytical grade, and purchased from Sinopharm Chemical Reagent Beijing Co.,Ltd.

<sup>1</sup>H-NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. Or <sup>1</sup>H and <sup>13</sup>C 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<sup>-1</sup>. 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

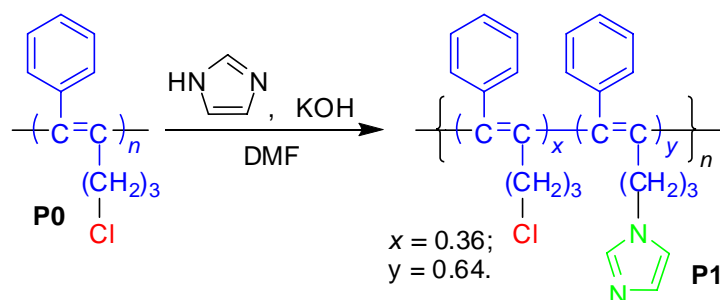
performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector.

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).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.41 (d, 2H), 7.28 (m, 3H), 3.70 (t, 2H), 2.60 (t, 2H), 2.04 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (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),  $\nu$  ( $\text{cm}^{-1}$ ): 3064 (Ar-H stretching), 2954, 2870 ( $\text{CH}_2$  stretching).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 0.8-2.6 ( $-\text{CH}_2-$ ), 2.6-3.4 ( $-\text{CH}_2-$ ), 6.5-7.8 (ArH). UV-Vis (Ethanol,  $1.06 \times 10^{-4}$  mol/L):  $\lambda_{\text{max}}$  (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%).  $^1\text{H}$  NMR ( $\text{CH}_3\text{OD}$ )  $\delta$  (ppm): 0.9-2.5 ( $-\text{CH}_2-$ ),

mol/L):  $\lambda_{\max}$  (nm): 302nm.

### Preparation of Polymer Thin Films.

The polymers were dissolved in ethanol (concentration ~3 wt %) and the solutions were filtered through syringe filters. Polymer films were spin-coated onto glass substrates, which were cleaned by *N,N*-dimethylformide, acetone, distilled water and THF sequentially in ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

### Preparation of solutions.

#### Preparation of solutions of metal ions and anions

0.2 mmol of each inorganic salt (NaNO<sub>3</sub>, 17.0 mg; KNO<sub>3</sub>, 20.2 mg; Ba(NO<sub>3</sub>)<sub>2</sub>, 52.3 mg; AgNO<sub>3</sub>, 34.0 mg; Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 80.0 mg; Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 58.2 mg; Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 47.2 mg; Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 58.2 mg; Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 59.5 mg; Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 48.3 mg; Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 75.0 mg; Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 80.8 mg; Pb(NO<sub>3</sub>)<sub>2</sub>, 66.2 mg; FeSO<sub>4</sub>·7H<sub>2</sub>O, 55.6 mg; 3CdSO<sub>4</sub>·8H<sub>2</sub>O, 51.3 mg; MnSO<sub>4</sub>·H<sub>2</sub>O, 33.8 mg; NaCl, 11.7 mg; KBr, 23.8 mg; KI, 33.2 mg; Na<sub>2</sub>SO<sub>4</sub>, 28.4 mg; K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, 53.2 mg; Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, 71.6 mg; NaClO<sub>4</sub>, 24.4 mg; KCNS, 19.4 mg; NaF, 8.4 mg) was dissolved in distilled water (10 mL) to afford 2×10<sup>-2</sup> mol/L aqueous solution. The stock solutions could be diluted to desired concentration with water when needed.

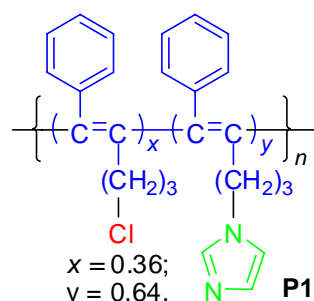
#### Preparation of polymer solutions

**P1** (2.1 mg) was dissolved in ethanol to afford the stock solution with the concentration of 1.06×10<sup>-3</sup> mol/L. This stock solution was diluted to 1.06×10<sup>-4</sup> mol/L and 0.528×10<sup>-4</sup> mol/L with ethanol.

**P0** (1.9 mg) was 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<sup>-3</sup> mol/L. And this stock solution (1 mL) was diluted to 1.06×10<sup>-4</sup> mol/L with ethanol.

**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  $1.06 \times 10^{-3}$  mol/L. And this stock solution (1 mL) was diluted to  $1.06 \times 10^{-4}$  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** ( $1.06 \times 10^{-4}$  mol/L) was prepared in ethanol. The solutions of metal ions ( $2 \times 10^{-2}$  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  $\mu$ 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** ( $1.06 \times 10^{-4}$  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 ( $\mu\text{L}$ )
$\text{Cu}^{2+}$	$5 \times 10^{-4}$	2, 4, 6, 8, 10, 12, 16, 20, 24, 30, 40, 50, 60, 60+2 <sup>a</sup>
$\text{Fe}^{3+}$	$5 \times 10^{-4}$	2, 4, 6, 10, 14, 22, 30, 40, 50, 60, 60+1 <sup>a</sup> , 60+2 <sup>a</sup> , 60+3 <sup>a</sup> , 60+4 <sup>a</sup> , 60+5 <sup>a</sup>
$\text{Fe}^{2+}$	$5 \times 10^{-4}$	2, 4, 6, 8, 10, 16, 20, 24, 30, 40, 50, 60, 60+1 <sup>a</sup> , 60+2 <sup>a</sup> , 60+3 <sup>a</sup> , 60+4 <sup>a</sup> , 60+5 <sup>a</sup>
$\text{Co}^{2+}$	$5 \times 10^{-4}$	2, 4, 6, 8, 10, 12, 16, 20, 24, 30, 40, 50, 60, 60+1 <sup>a</sup> , 60+2 <sup>a</sup> , 60+3 <sup>a</sup> , 60+4 <sup>a</sup> , 60+5 <sup>a</sup>
$\text{Ni}^{2+}$	$2 \times 10^{-3}$	2, 4, 6, 8, 10, 12, 16, 20, 30, 40, 50, 60, 60+1 <sup>a</sup> , 60+2 <sup>a</sup>
$\text{Cr}^{3+}$	$2 \times 10^{-2}$	2, 4, 6, 8, 12, 16, 24, 32, 48
$\text{Al}^{3+}$	$2 \times 10^{-2}$	2, 4, 12, 20, 30, 40, 50, 60
$\text{Pb}^{2+}$	$2 \times 10^{-2}$	2, 4, 12, 20, 30, 40, 50, 60

<sup>a</sup> The concentration of the metal ions were changed to  $2 \times 10^{-2}$  mol/L.

#### Fluorescence intensity changes of P1 by $\text{Cu}^{2+}$ 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 ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Ag}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{2+}$  and  $\text{Pb}^{2+}$ ; the concentration of the metal ions were  $2 \times 10^{-2}$  mol/L) to the solution of **P1**. Then  $4 \mu\text{L}$  of the solution of  $\text{Cu}^{2+}$  ( $2 \times 10^{-2}$  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 ( $1.06 \times 10^{-4}$  mol/L) was prepared in ethanol. The solutions of metal ions ( $2 \times 10^{-2}$  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+ $\text{Cu}^{2+}$ with $\text{CN}^-$





















