Supplementary information for

Colorimetric Detection of Copper Ions Based on Supramolecular Complex of Water-Soluble Polythiophene and ATP

Materials. All chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Aladdin, and Beijing Chem. Reagents Co. (Beijing, China) and were used as received. Water-soluble polythiophene derivative, PMTPA, was synthesized and purified with reference to the previously report¹. ¹H-NMR spectra were carried out on a Bruker DPX300 spectrometer. Metal ions were prepared in pure water, and the concentration of ATP was determined by using $\varepsilon_{259(ATP)} = 1.54 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ in phosphate buffer (100 mM, pH 7.0).

Sample preparation and measurements. Absorption and emission spectra were collected by using a HITACHI U-3900 UV-VIS spectrophotometer and a HORIBA Scientific Fluorolog[®]-3 spectrofluorometer, respectively. Circular dichroism spectra were acquired on a Jasco J-815 CD spectrometer. As a typical procedure, the supramolecular complexes were prepared by mixing PMTPA aqueous stock solution (5 mM based on the repeating unit) and ATP solution directly. All spectra of the solution were recorded at room temperature in the presence of Cu²⁺ with a given concentration. Control experiments for addressing the selectivity of the sensor toward Cu²⁺ were carried out at the identical conditions. The photographs of the solution color change were taken using a camera (Nikon).

Synthesis of the polymer PMTPA



3-Methoxy-4-methylthiophene (2). 3-Bromo-4-methylthiophene (2 g, 13.9 mmol) and CuBr (0.85 g, 5.9 mmol) were added to a mixture of 10 mL of sodium methoxide (28% in methanol) and 7 mL NMP and refluxed for 3 days under N₂ atmosphere. After cooling, the solid was filtrated, and the filtrate was extracted three times with diethyl ether. The organic phase was dried with magnesium sulfate and then evaporated. The final product was purified by chromatography (silica gel, hexane) (0.8 g, 45%). ¹H NMR (CDCl₃, TMS, 300 MHz) δ 6.81 (1H, dq), 6.16 (1H, d), 3.81 (3H, s), 2.08 (3H, s).

3-(3-Bromo)propoxy-4-methylthiophene (3). 3-Methoxy-4-methylthiophene (1.78 g, 13.9 mmol), 3-bromo-1-propanol (5.56 g, 40.0 mmol), and NaHSO₄ (246 mg, 2.05 mmol) were added to 24 mL of toluene under N₂ atmosphere and heated at 100 °C, until the produced methanol was distilled off. The reaction mixture allowed to cool to room temperature and washed three times with water (20 mL each). The collected water phases were extracted with diethyl ether. The organic phase was combined and dried with MgSO₄, filtered and evaporated to dryness. The crude product was submitted to column chromatography (silica gel, CH₂Cl₂ / hexane (1:1)) to give 2.03 g **3** as colorless oil. ¹H NMR (CDCl₃, TMS, 300 MHz) δ 6.83(1H, dq), 6.19 (1H, d), 4.09 (2H, td), 3.60 (2H, t), 2.33 (2H, m), 2.09 (3H, m).

3-(4-Methyl-3'-thienyloxy)propyltrimethyl ammonium bromide (4). Trimethylamine (19 mL 30% aqueous solution) was added into a solution of 3-(3-Bromo)propoxy-4-methylthiophene (0.25 g, 1.06 mmol) in THF (10 mL). The mixture was stirred 24 h at room temperature, and then evaporated to dryness. The crude product was washed with THF to give 0.29 g (92.7%) product **4**. ¹H NMR (D₂O, TMS, 300 MHz) δ 6.92 (1H, s), 6.39 (1H, d), 4.05 (2H, t), 3.44 (2H, dd), 3.66 (9H, s), 2.20 (2H, td), 1.98 (3H, s).

Polymer PMTPA. 100 mg(0.34 mmol) of **4** and 210 mg(1.30 mmol) of anhydrous FeCl₃ were mixed in 3 mL dry CHCl₃, and stirred for 24 h at room temperature under

 N_2 atmosphere, then evaporated to dryness. The crude product was washed by acetone / Soxhlet extraction for 24 h. The insoluble fraction of the polymer was dried and then dissolved in methanol by adding a few of drops hydrazine. The resulting polymer was dried under reduced pressure to give polymer PMTPA (34.5 mg, 34.5%).

Emission and CD spectroscopic studies on the complexation of PMTPA with ATP in the absence and presence of Cu^{2+}

From Fig.S1 we can see that the yellow, random-coiled form of PMTPA is fluorescent and exhibits an emission band around 578 nm (λ_{ex} = 490 nm). However, in the presence of a quarter amount of ATP, this emission is quenched and a slight red shift by 20nm was observed, indicating the formation of π -stacked aggregates of PMTPA. Notably, upon the introduction of Cu²⁺ into the aqueous PMTPA/ATP solution, the emission intensity at 578nm was recovered about 84%. This increasing emission can be attributed to the disassembly of the PMTPA/ATP suparmolecular complexs. Moreover, PMTPA does not have a chiral center. Thus, this polymer is intrinsically optically inactive, and no CD pattern in the $\pi - \pi^*$ transition region can be detected. The introduction of ATP into an aqueous PMTPA solution resulted in an intense induced CD signal in the π - π * transition region of PMTPA (Fig.S2) which indicated the optically active suparmolecular aggregates were formed. However, in the presence of Cu²⁺, the CD signal was almost disappeared with the spectral similar to the PMTPA alone, signifying the dissociation of PMTPA/ATP suparmolecular aggregates. As demonstrated above, the formation of PMTPA suparmolecular aggregates can be induced by addition ATP but disrupted by the introduction of Cu^{2+} subsequently.



Fig.S1 Emission spectra of PMTPA $(1.0 \times 10^{-4} \text{ M})$ in the absence and the presence of ATP and the mixture of ATP and Cu²⁺ in 20 mM sodium acetate buffer (pH 5.0). [ATP] = 2.5×10^{-5} M, [Cu²⁺] = 3.0×10^{-4} M. $\lambda_{ex} = 490$ nm



Fig.S2 CD spectra of PMTPA $(1.0 \times 10^{-4} \text{ M})$ in the absence and the presence of ATP and the mixture of ATP and Cu²⁺ in 20 mM sodium acetate buffer (pH = 5.0). [ATP] = $2.5 \times 10^{-5} \text{ M}$, [Cu²⁺] = $3.0 \times 10^{-4} \text{ M}$.



Fig.S3 Absorption spectra of the PMTPA/ATP in 20 mM sodium acetate buffer (pH = 4.5) in the presence of copper ions as indicated. [PMTPA] = 1.0×10^{-4} M, [ATP] = 2.5×10^{-5} M.



Fig.S4 Absorption spectra of the PMTPA/ATP in 20 mM sodium acetate buffer (pH =

5.5) in the presence of copper ions as indicated. [PMTPA] = 1.0×10^{-4} M, [ATP] = 2.5 $\times 10^{-5}$ M.



Fig.S5 Dependence of the ratio of absorbance of PMTPA/ATP ([PMTPA] = 1.0×10^{-4} M, [ATP] = 2.5×10^{-5} M) at 445 nm to 592 nm (A_{445}/A_{592}) on Cu²⁺ at of various concentrations in 20 mM sodium acetate buffer (pH = 4.5, \blacksquare ; pH = 5.0, \bullet ; pH = 5.5, \blacktriangle).



Fig.S6 Absorption spectra of the PMTPA $(1.0 \times 10^{-4} \text{ M})$ in 20 mM sodium acetate buffer (pH 5.0) in the presence of ATP as indicated.





Fig.S7 Absorption spectra of the PMTPA (0.1 mM) at various amounts of ATP in 20 mM sodium acetate buffer (pH 5) in the presence of copper ions as indicated. (A) [ATP] = 0.01 mM; (B) [ATP] = 0.015 mM; (C) [ATP] = 0.05 mM; (D) [ATP] = 0.075 mM.



Fig.S8 Dependence of the ratio of absorbance at 445 nm to 592 nm (A_{445}/A_{592}) of PMTPA (1.0×10⁻⁴ M) on Cu²⁺ at various concentrations in 20 mM sodium acetate buffer ([ATP] = 1.0×10⁻⁵ M, •; [ATP] = 1.5×10⁻⁵ M, •; [ATP] = 2.5×10⁻⁵ M, •; [ATP] = 5.0×10⁻⁵ M, ▼; [ATP] = 7.5×10⁻⁵ M, ▲).



Fig.S9 Absorption spectra of the PMTPA/ATP in 20 mM phosphate buffer (containing 0.45mM TGA, pH = 5.0) in the absence and presence of various ions as indicated. [PMTPA] = 0.05 mM, [ATP] = 0.125 mM, [Na⁺] = 20 mM, [K⁺] = 2.0 mM, [Ca²⁺] = 3.5 mM, [Mg²⁺] = 0.5 mM, [Zn²⁺] = 1.0 mM, [Cu²⁺] = [other ions] = 0.15 mM.



Fig.S10 Absorption spectra of the PMTPA/ATP in 20 mM phosphate buffer (containing 0.45mM TGA, pH 5.0) in presence of environmental anions. [PMTPA] = 0.05 mM, [ATP] = 0.125 mM, [SO₄²⁻] = [CO₃²⁻] = [CI⁻] = 2.0 mM, [Cu²⁺] = 0.15 mM. Blank sample contains no Cu²⁺.



Fig.S11 Absorption spectra of the PMTPA/ATP in 20 mM phosphate buffer (containing 1.2 mM TGA, pH 5.0) in presence of various cations. [PMTPA] = 0.05 mM, [ATP] = 0.025 mM, $[Na^+] = 20 \text{ mM}$, $[K^+] = 2.0 \text{ mM}$, $[Ca^{2+}] = 3.5 \text{ mM}$, $[Mg^{2+}] = 0.5 \text{ mM}$, $[Pb^{2+}] = [Zn^{2+}] = [Co^{2+}] = [Ni^{2+}] = [Ba^{2+}] = 0.15 \text{ mM}$, $[Cu^{2+}] = 0.15 \text{ mM}$. Blank sample contains no Cu^{2+} .



Fig.S12 Temperature-dependent absorption spectra of PMTPA/ATP ([PMTPA] = 1.0 $\times 10^{-4}$ M, [ATP] = 2.5 $\times 10^{-5}$ M) in 20 mM sodium acetate buffer (pH 5.0).

Reference

1. C. Li, M. Numata, A.H. Bae, K. Sakurai, and S. Shinkai, J. Am. Chem. Soc., 2005, **127**, 4548