

## Supporting Information

Fluorescent conjugated polymer based on  
thiocarbonyl quinacridone for sensing mercury ion  
and bioimaging

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## **Experimental Section**

### **Characterization**

The  $^1\text{H}$  NMR spectra were recorded on Bruker AM-400 spectrometers with tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were recorded on a Nicolet 380 thermo Electron corporation spectrometer. UV-vis absorption spectra were performed on a Varian Cray 500 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer. Molecular weights and polydispersity indices of the polymers were estimated in THF by a Waters Associated Gel Permeation Chromatograph (GPC) system. A set of monodisperse polystyrene standards covering the molecular weight range of  $10^3$ – $10^7$  was used for the molecular weight calibration.

### **Materials and Reagents**

Monomer **1** was synthesized according to reference.<sup>1</sup> Other chemicals and reagents were purchased from Sigma-Aldrich. All reagents were used without further purification.

### **Synthesis**

#### **Polymerization of PQA**

To a 25 mL Schelenk tube were added (**1**) (87.3 mg, 0.13 mmol), (**2**) (82.0 mg, 0.13 mmol), 2 M aqueous potassium carbonate solution (5 mL), and dry THF (10 mL) under argon. After addition of tetrakis(triphenylphosphine)palladium(0) (6.0 mg, 0.006 mmol) as a catalyst, the mixture was heated to 82 °C. The mixture was then stirred for 20 h, after it was poured into methanol-H<sub>2</sub>O (220 mL, 10/1, v/v). The precipitate was isolated by filtration and then washed

with methanol and acetone several times. The polymer was obtained after drying to yield a brick red solid of **PQA** 95 mg (77 %).

<sup>1</sup>H NMR (400 MHz , CDCl<sub>3</sub> , ppm ): δ 0.74 – 0.82 (br, -CH<sub>3</sub>), 0.89 – 0.97 (br, -CH<sub>3</sub>), 1.06 – 1.22 (br, -CH<sub>2</sub>-), 1.31 – 1.47 (br, s, -CH<sub>2</sub>-), 1.47 – 1.56 (br, -CH<sub>2</sub>-), 1.64 – 1.78 (br, CH-CH<sub>2</sub>-), 1.97 – 2.24 (br, NCH<sub>2</sub>-CH<sub>2</sub>-), 4.47 – 4.77 (br, N-CH<sub>2</sub>-), 7.63 – 7.72 (ArH) , 7.72 – 7.83 (ArH), 7.83 – 7.93 (ArH), 8.08 – 8.22 (ArH), 8.84 – 9.01 (ArH).

### **General Procedure of Thiolated Reaction Between PQA and Lawesson's Reagent.**

To a mixture of **PQA** and Lawesson's reagent with corresponding feed ratios, degassed toluene (10 mL) was added under argon. The mixture was heated to 125 °C and stirred in the dark for 2 h. After workup, the mixture was poured into methanol. The precipitated fibers were collected by filtration and then washed with methanol for four times. The polymer was purified by Soxhlet extraction in acetone for 24 h. The reprecipitation procedure in CH<sub>2</sub>Cl<sub>2</sub>/MeOH was then repeated for several times. The final product was obtained after drying in vacuum.

Polymer **PTQA1**. **PQA** (98.5 mg, 0.1 mmol), Lawesson's reagent (16.1 mg, 0.04 mmol) were used in the polymerization. Brown **PTQA1** (95.5 mg) was obtained.

Polymer **PTQA2**. **PQA** (98.5 mg, 0.1 mmol), Lawesson's reagent (24.2 mg, 0.06 mmol) were used in the polymerization. Green **PTQA2** (96.0 mg) was obtained.

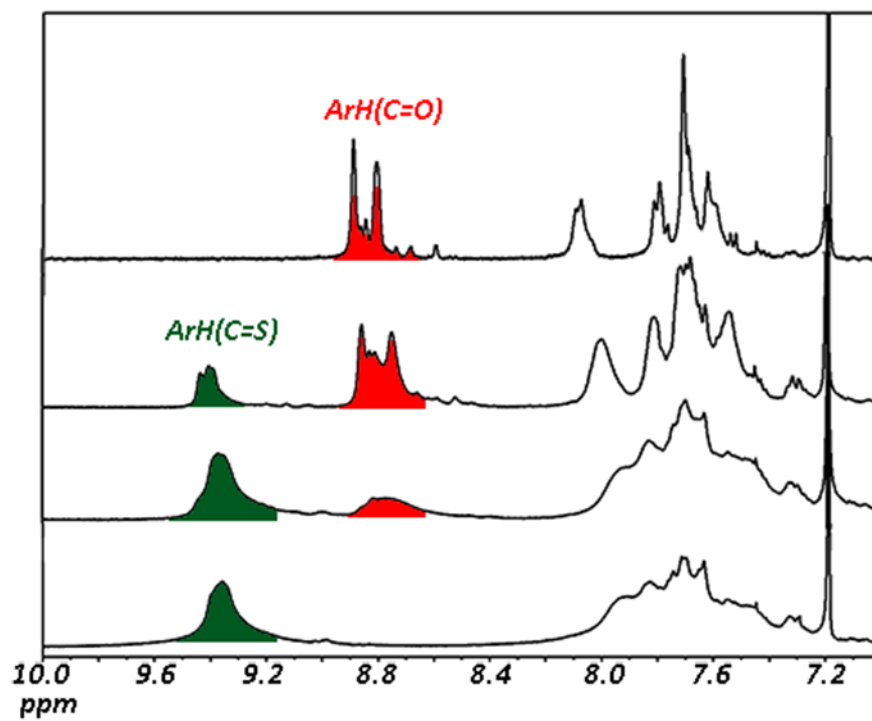
Polymer **PTQA3**. **PQA** (98.5 mg, 0.1 mmol), Lawesson's reagent (40.4 mg, 0.10 mmol) were used in the polymerization. Greenish black **PTQA3** (96.1 mg) was obtained.

**PTQA1~PTQA3** showed similar <sup>1</sup>H NMR results.

For example: **PTQA2**. <sup>1</sup>H NMR (400 MHz , CDCl<sub>3</sub> , ppm ): δ 0.62 - 0.99 (br, -CH<sub>3</sub>), 1.16 (br, -CH<sub>2</sub>-), 1.31 - 1.80 (br, -CH<sub>2</sub>-), 2.08 (br, CH-CH<sub>2</sub>- and NCH<sub>2</sub>-CH<sub>2</sub>-), 4.64 (br, N-CH<sub>2</sub>-), 7.33 - 8.18 (br, ArH), 8.87 (br, C(=O)-ArH), 9.45 (br. C(=S)-ArH).

**Fabrication of PTQA-NPs:**

The **PTQA-NPs** were prepared by a modified desolvation method. Briefly, **PTQA2** (1.0 mg) was dissolved in THF (1 mL) and stirred overnight. Then, the polymer solution (200  $\mu$ L, 50 ppm) was injected into PBS buffer (20 mL) under ultrasonication using a microtip probe sonicator. THF was evaporated by N<sub>2</sub> flow at 50 °C, and the solution was filtrated through a 0.2  $\mu$ m filter.



**Figure S1.**  $^1\text{H}$ NMR spectra of PQA and PTQA1~5 with different thiolation rate in aromatic region. (solvent:  $\text{CDCl}_3$ )

**Table S1.** Integrations of ArH adjacent to C=O and C=S moieties

No.	$\int \text{ArH}_{\text{C}=\text{S}}$	$\int \text{ArH}_{\text{C}=\text{O}}$	$\int \text{ArH}_{\text{C}=\text{S}} / (\int \text{ArH}_{\text{C}=\text{S}} + \int \text{ArH}_{\text{C}=\text{O}})$
<b>PTQA1</b>	1.0	2.8	26.3%
<b>PTQA2</b>	1.0	0.5	66.7%
<b>PTQA3</b>	1.0	0.0	100%

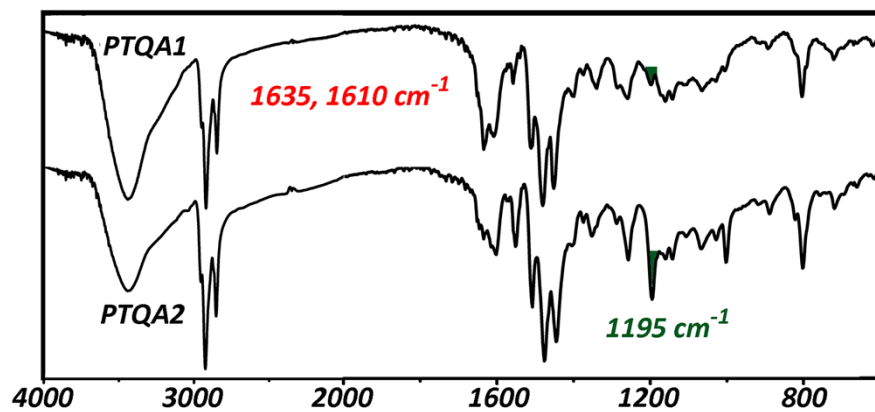
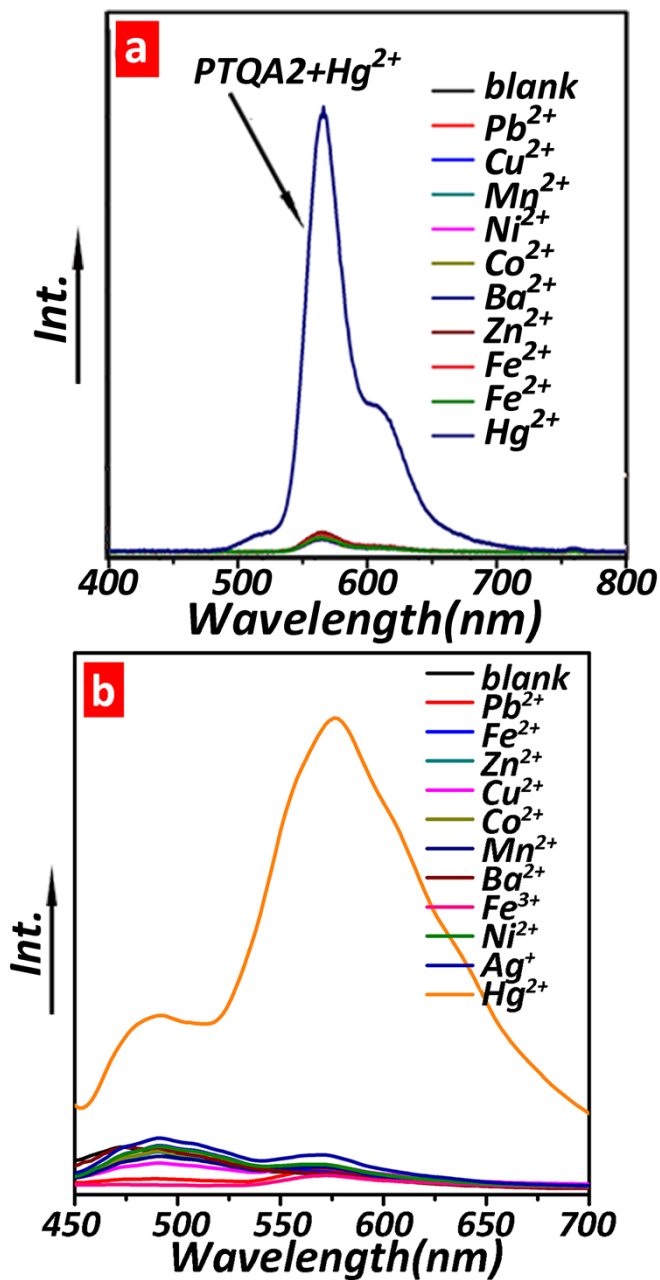


Figure S2. FT-IR spectra of PTQA1 and PTQA2.

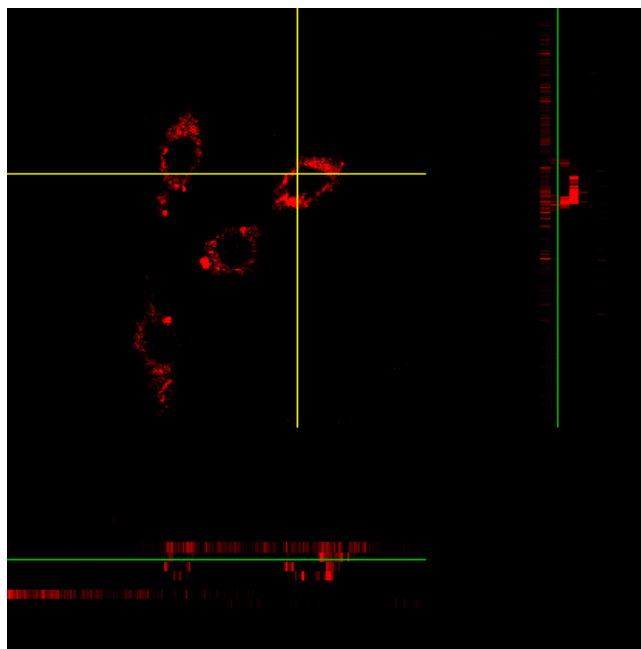
**Table S2.** GPC data of polymers **PQA** and **PTQA1~3**

No.	$M_n$	$M_w$	PDI
<b>PQA</b>	4849	5674	1.17
<b>PTQA1</b>	4038	5106	1.26
<b>PTQA2</b>	3979	5147	1.29
<b>PTQA3</b>	4168	5888	1.41



**Figure S3.** (a) Emission spectra of PTQA2 upon addition of different metal ions in chloroform ([PTQA2]= 10  $\mu\text{g/mL}$ ) (b) Emission spectra of PTQA-NPs upon addition of different metal ions in PBS solutions ([PTQA-NPs]=10  $\mu\text{g/mL}$ ).





**Figure S4.** The Z-scan confocal image of the living HeLa cells incubated with **PTQA-NPs** (10 µg/mL)