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Electronic Supplementary Information Efficient recovery of precious metal based on Au-S bond and electrostatic interaction

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 $PEI-NH_2 \xrightarrow{\bigvee C_{S}} PEI^{H} H$

Scheme S1 Synthesis routes of TPs.

Notes ^a	Feeding molar ratio of MTC/CH ₂ CH ₂ N of PEI	Resultant molar ratio of MTU/CH ₂ CH ₂ N of PEI ^b	Yield	Resultant MTU content ^c (mmol g ⁻¹)	Solubility in HCl aq. (pH 1.0)
TP2.8	15%	15.3%	95.3%	2.8	soluble
TP4.5	30%	28.9%	93.6%	4.5	soluble
TP5.4	45%	39.2%	89.1%	5.4	soluble
TP6.4	60%	52.3%	92.4%	6.4	partly soluble



Fig. S1 SEM image of (A) TP5.4 and (B) precipitate.



Fig. S2 Recovery rate and adsorption efficiency of Au^{III} by TP5.4 at different time points. The HCl aqueous solution (0.1 mol L⁻¹) of Au^{III} (1.5 g L⁻¹, 1.0 mL) and TP5.4 (0.5 g L⁻¹, 1.0 mL) were mixed at room temperature.



Fig. S3 Recovery rate and adsorption efficiency of Au^{III} by TP5.4 at different pH values. The HCl aqueous solution of Au^{III} (1.5 g L⁻¹, 1.0 mL) and TP5.4 (0.5 g L⁻¹, 1.0 mL) were mixed at room temperature for 30 min.

Table S2 Comparison of maximum adsorption efficiency of Au ^{III} by several reported adsorbents						
Note	Adsorbents	Maximum adsorption efficiency (mmol _{Au} g _{polymer} ⁻¹)	Reference			
1	Thiourea-modified polyethylenimine	16.0	Present work			
2	Chitosan derivative	8.32	1			
3	Alkoxycarbonyl thiourea resin	4.65	2			
4	Cross-linked cellulose gel	7.57	3			
5	Cross-linked dextran gel	7.20	3			
6	Chestnut pellicle	10.6	4			
7	Lysine-modified crosslinked chitosan	0.36	5			
8	Thiourea modified polyallylamine	3.06	6			
9	Cross-linked paper gel	6.21	7			
10	Chemically modified chitosan with magnetic	3.43	8			



Fig. S4 TGA of precipitate. The HCl aqueous solution (0.1 mol L^{-1}) of Au^{III} (1.5 g L^{-1} , 1.0 mL) and TP5.4 (0.5 g L^{-1} , 1.0 mL) were mixed at room temperature for 2 h. The precipitate was resuspended by distilled water and centrifuged (1000 g). The resultant precipitate was dried under vacuum before TGA analysis.



Fig. S5 XPS of precipitate (S 2p).

Materials. Polyethylenimine (PEI, number-average molecule weight = 10 kDa, weight-average molecule weight = 25 kDa) was purchased from Aldrich (St. Louis, MO, USA). Methyl isothiocyanate (MTC) was purchased from Tianjin Heowns Biochemical Technology Co., Ltd (Tianjin, China). Gold (III) trichloride hydrochloride (AuCl₃·HCl·4H₂O) was provided by Shanghai Chemical Reagent Co. Ltd.

Synthesis and characterization of TP. The synthesis of TPs was previously reported.⁹ Briefly, PEI was first dissolved in absolute methanol (10.0 mL). Different masses of MTC in methanol (5.0 mL) were added dropwise to the above PEI solution. The resultant solution was stirred for another 2 h at room temperature, and the solvent was removed using a rotary evaporator at 40 °C. The thiourea content of the resulting copolymer was calculated through the S content measured by elemental analysis (Vario EL III, Germany).

Precious metal recovery by TP (Typical procedure). An HCl aqueous solution of TP (0.5 g L^{-1} , 1.0 mL, pH 1.0) was added into the HCl aqueous solution of HAuCl₄ (pH 1.0) at different aurum concentrations with continuous stirring for 30 min. Then the solution was filtered and the resultant precipitate and supernatant were harvested. The Au and S content in the solution and precipitate were measured by inductively coupled plasma-mass spectrometry (ICP-MS).

Preparation and characterization of precipitate. A HCl aqueous solution of TP (0.5 g L⁻¹, 10.0 mL, pH 1.0) was added into the HCl aqueous solution of Au^{III} (1.5 g_{Au} L⁻¹, 10.0 mL, pH 1.0) and remained stirring for 30 min. The solution was filtered and the precipitate was resuspended by distilled water and centrifuged (1000 g). The resultant precipitate was dried under vacuum. FT-IR spectra were recorded on a Bio-Rad Win-IR instrument on potassium bromide (KBr) pellets. Raman spectroscopy was recorded by a confocal microprobe spectrometer (LabRam I from Dilor, France). The excitation wavelength was 632.8 nm from an inner air-cooled He-Ne laser with a power of 10 mW and a spot of size 3 µm at the sample surface. The used slit and pinhole were 200 and 800 µm, respectively. The acquisition time was 10 s and the accumulation was four times for each spectrum. X-ray photoelectron spectroscopy (XPS) was performed with Thermo ESCALAB 250 (Thermo Electron Corporation, U.K.) at room temperature by using an Al Ka X-ray source (*hv* = 1486.6 eV). The main chamber of the XPS instrument was maintained at 10⁻⁹ Torr. Pass energies of 50 and 20 eV were used to obtain the survey scan spectra and high-resolution spectra, respectively. Thermal gravity analysis (TGA) was performed by a TGA-Q50 Thermo Gravimetric Analyzer from room temperature to 900 °C by 10 °C min⁻¹.

Environment scanning electron microscopy (ESEM) was performed on an XL 30 scanning electron microscope (Micrion FEI PHILIPS).

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