Electronic Supplementary Information

Economic synthesis of functional aromatic polythioamides from KOHassisted multicomponent polymerizations of sulfur, aromatic diamines

and dialdehydes

Yang Hu,[‡] Lihui Zhang,[‡] Zhuang Wang,^a Rongrong Hu,^{*a} and Ben Zhong Tang^{*bc}

^aState Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology, Guangzhou 510640, China. E-mail: msrrhu@scut.edu.cn
^bShenzhen Institute of Aggregate Science and Technology, School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, 2001 Longxiang Boulevard, Shenzhen City 518172, China. E-mail: tangbenz@cuhk.edu.cn
^cAIE Institute, Guangzhou 510530, China.

[‡]These authors are equally contributed.

Table of Contents

Materials and instruments

Synthetic procedures and characterization data

Procedures for metal ions extraction

Fig. S1 HRMS spectrum of model compound 4.

Table S1. Crystal Data and Structure Refinement of Compounds 4

Table S2. Effect of solvent on the MCP of 1, 2a, and 5a

Table S3. Effect of temperature on the MCP of 1, 2a, and 5a

Table S4. Effect of monomer loading ratio on the MCP of 1, 2a, and 5a

Table S5. Effect of monomer concentration on the MCP of 1, 2a, and 5a

Table S6. Effect of polymerization time on the MCP of 1, 2a, and 5a

Fig. S2 GPC curves of polymers P1-P7.

Fig. S3 ¹H NMR spectra of (A) P2, (B) P3, (C) P4, (D) P5, (E) P6, and (F) P7 in DMSO-*d*6.

Fig. S4 ¹³C NMR spectra of (A) 2a, (B) 3, (C) 5a, (D) 4, and (E) P1 in DMSO-d6.

Fig. S5 ¹³C NMR spectra of (A) P2, (B) P3, (C) P4, (D) P5, (E) P6, and (F) P7 in DMSO-d6.

Fig. S6 FT-IR spectra of (A) 2a, (B) 5a, (C) 4, and (D) P1.

Fig. S7 FT-IR spectra of (A) P2, (B) P3, (C) P4, (D) P5, (E) P6, and (F) P7.

Fig. S8 S 2p XPS of elemental sulfur, model compound 4, and P1-P7.

Fig. S9 XRD patterns of solid powders of P1-P7.

Fig. S10 The extraction efficiency of different metal ions using solid powder of P1. $m_{P1} = 5$ mg, $V_{M^{n^+}} = 5$ mL, $[M^{n^+}] = 100$ mg L⁻¹. Polymer powder and the aqueous solution of metal ions were stirred at room temperature for 1 h before centrifugation.

Table S7. Gold extraction efficiencies with different amounts of polythioamides

Fig. S11 ¹H NMR spectrum of 4 in DMSO- d_6 .

Fig. S12 13 C NMR spectrum of 4 in DMSO- d_6 .

Fig. S13 ¹H NMR spectrum of P1 in DMSO- d_6 .

Fig. S14 13 C NMR spectrum of P1 in DMSO- d_6 .

Fig. S15 ¹H NMR spectrum of P2 in DMSO- d_6 .

Fig. S16 13 C NMR spectrum of P2 in DMSO- d_6 .

Fig. S17 ¹H NMR spectrum of P3 in DMSO- d_6 .

Fig. S18 13 C NMR spectrum of P3 in DMSO- d_6 .

Fig. S19 ¹H NMR spectrum of P4 in DMSO- d_6 .

Fig. S20¹³C NMR spectrum of P4 in DMSO-*d*₆.

Fig. S21 ¹H NMR spectrum of P5 in DMSO- d_6 .

Fig. S22 13 C NMR spectrum of P5 in DMSO- d_6 .

Fig. S23 ¹H NMR spectrum of P6 in DMSO- d_6 .

Fig. S24 13 C NMR spectrum of P6 in DMSO- d_6 .

Fig. S25 ¹H NMR spectrum of P7 in DMSO- d_6 .

Fig. S26 13 C NMR spectrum of P7 in DMSO- d_6 .

Materials and instruments

Sublimed sulfur **1** was purchased from Guangzhou Chemical Reagent Factory; diamines **2a**, **2c**, dialdehydes **5a**, **5b**, **5d**, KF, KOH, CoCl₂, CuCl₂, NiCl₂·6H₂O, FeCl₃, and Pb(NO₃)₂ were purchased from Energy Chemical; K₂CO₃, Na₂CO₃, Cs₂CO₃, CsF, and diamine **2b** were purchased from TCI; **5c** was purchased from Bidepharm; MnCl₂ was purchased from Aladdin; gold standard solution ($[Au^{3+}] = 1000 \text{ mg/L}$, [HCl] = 1.5 mol/L, with trace amount of HNO₃) was purchased from Meryer; CdCl₂ was purchased from 3A Chemicals; tetrahydrofuran (THF), dichloromethane (DCM), methanol (MeOH) and ethyl acetate were purchased from Guangzhou Chemical Reagent Factory. All reactants and reagents were used without further purification.

¹H and ¹³C NMR spectra were measured on a Brucker Avance 400 or 500 MHz NMR spectrometer using deuterated dimethyl sulfoxide (DMSO-d₆) as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal reference. FT-IR spectra were determined on a Bruker Vector 33 FT-IR spectrometer. High resolution mass spectra measurement was carried out on a Bruker maxis impact mass spectrometer. The number- (M_n) and weight- (M_w) average molecular weights and polydispersity indices (PDI = M_w/M_n) of the polymers were estimated by a Waters 1515 gel permeation chromatography system. DMF/LiBr solution (0.05 M of LiBr) was used as eluent at a flow rate of 1 mL/min. A set of monodispersed polymethyl methacrylate (PMMA), covering the $M_{\rm w}$ range of 10³-10⁷ g/mol, were utilized as standards for molecular weight calibration. Thermogravimetric analysis was carried out on Netzsch TG 209 F3 under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Single crystal X-ray diffraction patterns were measured by an X'Pert Pro Panalytical X-ray diffractometer at an incident angle ranging from 5 to 50°. X-ray photoelectron spectroscopy was performed using a Kratos Axis Ultra DLD spectrometer with a monochromated Al K α X-ray source at a residual pressure of 5 \times 10⁻⁹ torr. X-ray diffraction patterns of polymer product were measured by an X'Pert Powder at an incident angle ranging from 5 to 60°. The concentrations of metal ions were measured by Z-2000 atomic absorption spectrophotometer (AAS). Refractive indices of the polymer film were determined by a J. A. Woolam V-VASE spectroscopic ellipsometer with a wavelength range of 400~1700 nm.

Synthetic procedures and characterization data

Aromatic thioamide model compound 4: Into a 10 mL flask equipped with a magnetic stir bar were added elemental sulfur (1, 128.0 mg, 4 mmol), 4,4'-methylenedianiline (2a, 198.0 mg, 1 mmol) and KOH (112.2 mg, 2 mmol) under nitrogen atmosphere. *p*-Tolualdehyde (3, 0.35 mL, 3 mmol) and 2 mL of pyridine were then injected into the tube by syringe. After stirring at 105 °C for 24 h, 20 mL of water was added after the reaction solution cooled to room temperature, and the reaction mixture was extracted with dichloromethane for three times (3 × 50 mL). The organic phases were combined and the solvent was removed under reduced pressure to afford the crude product, which was then purified by column chromatography on silica gel using dichloromethane/ethyl acetate mixture (99/1, v/v) as eluent. A light yellow solid was obtained in 72% yield. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 11.59 (s, 2H, HN-C=S), 7.75-7.72 (m, 4H), 7.31-7.26 (m, 8H), 3.98 (s, 2H), 2.36 (s, 6H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 197.01 (C=S), 140.82, 139.79, 139.15, 138.18, 128.65, 128.49, 127.51, 124.37, 20.90. IR (KBr disk), v (cm⁻¹): 3170, 1601, 1514, 1410, 1347, 1213, 991.

Synthesis of aromatic polythioamides P1 and P2. The synthesis of P1 was given below as an example. Into a 10 mL Schlenk tube equipped with a magnetic stir bar were added elemental sulfur (1, 72.0 mg, 2.25 mmol), 4,4'-methylenedianiline (2a, 99.1 mg, 0.5 mmol), *m*-phthalaldehyde (5a, 134.1 mg, 1.0 mmol), and KOH (56.1 mg, 1.0 mmol) under nitrogen atmosphere. Pyridine (0.63 mL) was then injected by a syringe to dissolve the monomers, and the polymerization solution was stirred at 110 °C for 8 h. Afterwards, the polymerization mixture was precipitated by dropping it into 100 mL of methanol through a cotton filter. The precipitate was filtered and washed with methanol (3×30 mL), which was then dried under vacuum at 40 °C to a constant weight.

P1 was obtained as a yellow solid in 94% yield. $M_{\rm w} = 54\ 700\ {\rm g\ mol^{-1}}, M_{\rm w}/M_{\rm n} = 2.99$. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 11.84 (s, 2H, HN-C=S), 8.19 (s, 1H), 7.96-7.95 (d, 2H), 7.78-7.76 (d, 4H), 7.55-7.52 (t, 1H), 7.33-7.31 (d, 4H), 3.99 (s, 2H). ¹³C NMR (125 MHz,

DMSO-*d*₆), δ (TMS, ppm): 196.33 (C=S), 142.19, 139.30, 138.01, 129.78, 128.74, 127.86, 125.97, 124.17. IR (KBr disk), *ν* (cm⁻¹): 3230, 1595, 1513, 1359, 1179, 1018, 805.

P2 was obtained as a yellowish brown solid in 92% yield. $M_w = 25\ 300\ \text{g mol}^{-1}$, $M_w/M_n = 2.20$. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 11.90 (2H, HN-C=S), 8.23 (1H), 8.00-7.98 (2H), 7.89-7.87 (4H), 7.58-7.55 (1H), 7.14-7.12 (4H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 196.37 (C=S), 154.38, 142.14, 135.54, 129.83, 128.28, 127.92, 125.93, 118.55. IR (KBr disk), ν (cm⁻¹): 3192, 1598, 1495, 1354, 1236, 833.

Synthesis of aromatic polythioamide P3. Elemental sulfur (1, 72.0 mg, 2.25 mmol), *p*-phenylenediamine (2c, 54.1 mg, 0.5 mmol), *m*-phthalaldehyde (5a, 134.1 mg, 1.0 mmol), and KOH (56.1 mg, 1.0 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. Pyridine (1.0 mL) was then injected by a syringe to dissolve the monomers and stirred at 110 °C for 12 h. Afterwards, the polymerization mixture was precipitated by dropping it into 100 mL of methanol through a cotton filter. The precipitate was filtered and washed with methanol (3 × 30 mL), which was then dried under vacuum at 40 °C to a constant weight. P3 was obtained as a yellow solid in 93% yield. $M_w = 14\ 200\ \text{g mol}^{-1}$, $M_w/M_n = 1.67$. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 11.98 (s, 2H, HN-C=S), 8.25 (s, 1H), 8.01 (2H), 7.94 (4H), 7.59-7.57 (t, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 196.51 (C=S), 142.19, 137.70, 129.97, 127.98, 125.04, 124.10. IR (KBr disk), ν (cm⁻¹): 3196, 1605, 1513, 1426, 1349, 1175, 989.

Synthesis of aromatic polythioamide P4 and P7. The synthesis of P4 was given below as an example. Elemental sulfur (1, 72.0 mg, 2.25 mmol), 4,4'-methylenedianiline (2a, 99.1 mg, 0.5 mmol), *p*-phthalaldehyde (5b, 120.7 mg, 0.9 mmol), and KOH (56.1 mg, 1.0 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. Pyridine (1.0 mL) was then injected by a syringe to dissolve the monomers and stirred at 110 °C for 12 h. Afterwards, the polymerization mixture was precipitated by dropping it into 100 mL of methanol through a cotton filter. The precipitate was filtered and washed with methanol (3 × 30 mL), which was then dried under vacuum at 40 °C to a constant weight. P4 was obtained as a yellow solid in 96% yield. $M_w = 11\ 800\ \text{g mol}^{-1}$, $M_w/M_n = 1.54$. ¹H NMR (400 MHz, DMSO-

*d*₆), δ (TMS, ppm): 11.84 (s, 2H, HN-C=S), 7.85 (4H), 7.79-7.78 (4H), 7.34-7.32 (4H), 4.00 (s, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 196.14 (C=S), 144.09, 139.17, 137.98, 128.73, 127.04, 124.16. IR (KBr disk), υ (cm⁻¹):3218, 1597, 1511, 1407, 1359, 1210, 988.848. P7 was obtained as a brown solid in 69% yield. $M_{\rm w} = 14\ 800\ {\rm g}\ {\rm mol}^{-1}$, $M_{\rm w}/M_{\rm n} = 1.48$. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 12.40 (2H, HN-C=S), 8.81-8.79 (2H), 8.21-8.18 (1H), 7.64 (4H), 7.36 (4H), 4.02 (2H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 189.13 (C=S), 149.76, 140.18, 137.27, 129.22, 128.89, 127.59, 125.86, 125.62. IR (KBr disk), υ (cm⁻¹): 3177, 1606, 1511, 1424, 1346, 1130, 991.

Synthesis of aromatic polythioamide P5. Elemental sulfur (1, 72.0 mg, 2.25 mmol), 4,4'oxydianiline (2b, 100.1 mg, 0.5 mmol), *p*-phthalaldehyde (5b, 120.7 mg, 0.9 mmol), and KOH (56.1 mg, 1.0 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. Pyridine (1.25 mL) was then injected by a syringe to dissolve the monomers and stirred at 110 °C for 12 h. Afterwards, the polymerization mixture was precipitated by dropping it into 100 mL of methanol through a cotton filter. The precipitate was filtered and washed with methanol (3 × 30 mL), which was then dried under vacuum at 40 °C to a constant weight. P5 was obtained as a yellow solid in 88% yield. $M_w = 9 100$ g mol⁻¹, $M_w/M_n = 1.33$. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 11.91(s, 2H, HN-C=S), 7.89 (8H), 7.14 (4H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 196.20 (C=S), 154.36, 139.29, 135.52, 129.03, 127.54, 127.10, 125.93, 118.54. IR (KBr disk), v (cm⁻¹): 3359, 3036, 1619, 1497, 1408, 1360, 1243, 843.

Synthesis of aromatic polythioamide P6. Elemental sulfur (1, 72.0 mg, 2.25 mmol), 4,4'methylenedianiline (2a, 99.1 mg, 0.5 mmol), 4-(4-formylphenoxy)benzaldehyde (5c, 169.7 mg, 0.75 mmol), and KOH (56.1 mg, 1.0 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. Pyridine (1.0 mL) was then injected by a syringe to dissolve the monomers and stirred at 110 °C for 12 h. Afterwards, the polymerization mixture was precipitated by dropping it into 100 mL of methanol through a cotton filter. The precipitate was filtered and washed with methanol (3 × 30 mL), which was then dried under vacuum at 40 °C to a constant weight. P6 was obtained as a yellow solid in 42% yield. $M_w = 5\,900$ g mol⁻ ¹, $M_w/M_n = 1.20$. ¹H NMR (400 MHz, DMSO-*d*₆), δ (TMS, ppm): 11.67-11.65 (2H, HN-C=S), 7.94-7.92 (4H), 7.75-7.73 (4H), 7.32-7.30 (4H), 7.15-7.13 (4H), 3.99 (2H). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (TMS, ppm): 195.87 (C=S), 158.20, 139.19, 138.87, 138.16, 137.98, 129.80, 128.67, 128.10, 124.29, 118.31, 118.01, 117.83, 43.98, 42.98. IR (KBr disk), ν (cm⁻¹): 3225, 3032, 1588, 1497, 1356, 1242, 1168, 989, 835.

Procedures for metal ions extraction

Selectivity test with different metal ions. Into 5 mL aqueous solutions of $MnCl_2$, FeCl₃, CoCl₂, CuCl₂, NiCl₂·6H₂O, CdCl₂, Pb(NO₃)₂, and AuCl₃ ([M^{n+}]₀ = 100 mg L⁻¹) were added 5 mg solid powder of P1, respectively. After the mixtures were stirred at room temperature for 1 h, the suspensions were centrifuged for 15 min with the spin rate of 8000 r min⁻¹ and the solid was filtered by a filter membrane with an aperture of 0.22 µm. The remaining concentration of metal ions in the supernatant was then measured by AAS.

Gold extraction with different amounts of polythioamides. Into 10 mL aqueous solution of Au³⁺ with a concentration of 100 mg L⁻¹ (the gold standard solution with the concentration of 1000 mg L⁻¹ was diluted with 5 *wt*% HCl solution to furnish the resultant solution) was added 0, 1, 2, 5, and 10 mg solid powders of P1-P7, respectively. After the mixtures were stirred at room temperature for 1 h, the suspensions were centrifuged for 15 min with the spin rate of 8000 r/min and the solid was filtered by a filter membrane with an aperture of 0.22 µm. The remaining concentration of Au³⁺ in the supernatant was then measured by AAS to calculate the extraction efficiency. The extraction efficiency of polymers was calculated to be $\eta = ([M^{n+}]_0 - [M^{n+}])/[M^{n+}]_0 \times 100\%$, where $[M^{n+}]_0$ is the initial concentration of metal ion, and $[M^{n+}]$ is the remaining concentration of metal ion. The extraction capacity of polymers was calculated to be $V_M \times [M^{n+}]_0 \times \eta / m_p$, where V_M is the volume of the gold solution, m_p is the weight of the polymer.



Fig. S1 HRMS spectrum of model compound 4.

Table ST. Crystal Data and Structure Refinement of Combound	ructure Refinement of Compour	unds
--	-------------------------------	------

Crystal	4			
CCDC number	2225162			
Empirical formula	$C_{29}H_{26}N_2S_2$			
Formula weight (g mol ⁻¹)	466.15			
Temperature (K)	150(10)			
Wavelength (Å)	1.54184			
Absorption correction	multi-scan			
Crystal system, space group	Monoclinic, P 1 21/n 1			
	a = 33.855(2) Å, b = 8.1449(5) Å, c = 17.6248(10) Å			
Unit cell dimensions	$\alpha = 90, \beta = 96.650(5), \gamma = 90$			
Volume (Å ³)	4827.2(5)			
Z, Calculated density (g cm ⁻³)	8, 1.302			
Absorption coefficient (mm ⁻¹)	2.275			
<i>F</i> (000)	1993			
Crystal size (mm ³)	0.25 imes 0.03 imes 0.02			
Theta range for data collection (°)	2.628 to 73.863			
Index ranges	$-41 \le h \le 37, -5 \le k \le 9, -21 \le 1 \le 21$			
Reflections collected	28605			
Independent reflections	9419 [R(int) = 0.0901]			
completeness to theta	99.19 %, 66.97°			
Max. and min. transmission	1.00000 and 0.75824			
Data / restraints / parameters	9419 /0/599			
Goodness-of-fit on F ²	1.376			
Final <i>R</i> indices [I > 2sigma(I)]	R1 = 0.1658, wR2 = 0.3803			
R indices (all data)	R1 = 0.2085, wR2 = 0.4115			
Largest diff. peak and hole	3.047 and -0.517 e.Å ⁻³			

entry	solvent	yield (%)	$M_{\rm w}({ m g\ mol}^{-1})^b$	$M_{ m w}/{M_{ m n}}^b$	solubility
1	pyridine	68	10 300	1.36	\checkmark
2	DMAc	42	6 800	1.21	\checkmark
3	DMF	30	5 200	1.14	\checkmark

Table S2. Effect of solvent on the MCP of 1, 2a, and $5a^a$

^{*a*}Carried out at 105 °C under nitrogen for 12 h and the yield was calculated based on **2a**, $[2a] = 0.4 \text{ M}, 1/8[S_8]$: [2a]: [5a]: [KOH] = 4.0: 1.0: 1.5: 2.0. ^{*b*} M_w and M_n were determined by GPC in DMF based on PMMA standard samples. $\sqrt{}$: the product is completely soluble.

entry	<i>T</i> (°C)	yield (%)	$M_{\rm w}({ m g\ mol}^{-1})^b$	$M_{ m w}/M_{ m n}{}^b$	solubility
1	90	59	6 700	1.22	
2	100	66	9 800	1.30	\checkmark
3 ^c	105	68	10 300	1.36	\checkmark
4	110	68	10 600	1.34	\checkmark
5	115	62	9 700	1.31	\checkmark

Table S3. Effect of temperature on the MCP of 1, 2a, and $5a^a$

^{*a*}Carried out under nitrogen in pyridine for 12 h and the yield was calculated based on **2a**, **[2a]** = 0.4 M, $1/8[S_8]$: **[2a]**: **[5a]**: **[KOH]** = 4.0: 1.0: 1.5: 2.0. ^{*b*} M_w and M_n were determined by GPC in DMF based on PMMA standard samples. ^{*c*}Data were taken from Table S2, entry 1. $\sqrt{}$: the product is completely soluble.

entry	1/8[S ₈]: [2a]: [5a]: [KOH]	yield (%)	$M_{ m w}({ m g\ mol}^{-1})^b$	$M_{ m w}/M_{ m n}{}^b$	solubility
1	4.0: 1.0: 0.8: 2.0	29	5 700	1.20	
2	4.0: 1.0: 1.0: 2.0	28	5 500	1.18	
3	4.0: 1.0: 1.2: 2.0	37	6 900	1.24	
4 ^{<i>c</i>}	4.0: 1.0: 1.5: 2.0	68	10 600	1.34	
5	4.0: 1.0: 1.8: 2.0	78	17 400	1.74	
6	4.0: 1.0: 2.0: 2.0	80	19 000	1.86	
7	4.0: 1.0: 2.2: 2.0	69	19 800	2.13	gel
8	3.0: 1.0: 2.0: 2.0	51	5 900	1.20	
9	3.5: 1.0: 2.0: 2.0	62	10 200	1.50	
10	4.5: 1.0: 2.0: 2.0	81	34 300	2.79	
11	5.0: 1.0: 2.0: 2.0	95	25 300	2.20	
12	4.5: 1.0: 2.0: 1.0	34	3 800	1.08	Δ
13	4.5: 1.0: 2.0: 3.0	25	5 200	1.10	\checkmark

Table S4. Effect of monomer loading ratio on the MCP of 1, 2a, and $5a^{a}$

^{*a*}Carried out at 110 °C under nitrogen in pyridine for 12 h and the yield was calculated based on **2a**, [2a] = 0.4 M. ^{*b*} M_w and M_n were determined by GPC in DMF based on PMMA standard samples. ^{*c*}Data were taken from Table S3, entry 4. $\sqrt{}$: the product is completely soluble, Δ : the product is partially soluble.

entry	[2a] (M)	yield (%)	$M_{\rm w}({\rm g\ mol}^{-1})^b$	$M_{ m w}/M_{ m n}{}^b$	solubility
1	0.2	74	5 800	1.24	\checkmark
2	0.3	79	13 400	1.81	\checkmark
3^c	0.4	81	34 300	2.79	\checkmark
4	0.5	83	36 500	2.57	\checkmark
5	0.8	87	41 700	2.53	\checkmark
6	1.0	-	-	-	gel

Table S5. Effect of monomer concentration on the MCP of 1, 2a, and $5a^{a}$

^{*a*}Carried out at 110 °C under nitrogen in pyridine for 12 h and the yield was calculated based on **2a**, $1/8[S_8]$: **[2a]**: **[5a]**: **[KOH]** = 4.5: 1.0: 2.0: 2.0. ^{*b*} M_w and M_n were determined by GPC in DMF based on PMMA standard samples. ^{*c*}Data were taken from Table S4, entry 10. $\sqrt{}$: the product is completely soluble.

Table S6. Effect of polymerization time on the MCP of 1, 2a, and $5a^{a}$

entry	<i>t</i> (h)	yield (%)	$M_{\rm w}({\rm g\ mol}^{-1})^b$	$M_{ m w}/M_{ m n}{}^b$	solubility
1	4	74	31 600	2.43	\checkmark
2	8	94	54 700	2.99	\checkmark
3^c	12	87	41 700	2.53	\checkmark
4	16	65	34 400	2.14	\checkmark

^{*a*}Carried out at 110 °C under nitrogen in pyridine and the yield was calculated based on **2a**, **[2a]** = 0.8 M, $1/8[S_8]$: **[2a]**: **[5a]**: **[KOH]** = 4.5: 1.0: 2.0: 2.0. ^{*b*} M_w and M_n were determined by GPC in DMF based on PMMA standard samples. ^{*c*}Data were taken from Table S5, entry 5. $\sqrt{}$: the product is completely soluble.



Fig. S2 GPC curves of polymers P1-P7.



Fig. S3 ¹H NMR spectra of (A) P2, (B) P3, (C) P4, (D) P5, (E) P6, and (F) P7 in DMSO-*d*6. The solvent peaks were marked with asterisks.



Fig. S4 ¹³C NMR spectra of (A) 2a, (B) 3, (C) 5a, (D) 4, and (E) P1 in DMSO-*d*₆. The solvent peaks were marked with asterisks.



Fig. S5 ¹³C NMR spectra of (A) P2, (B) P3, (C) P4, (D) P5, (E) P6, and (F) P7 in DMSO-*d*₆. The solvent peaks were marked with asterisks.



Fig. S6 FT-IR spectra of (A) 2a, (B) 5a, (C) 4, and (D) P1.



Fig. S7 FT-IR spectra of (A) P2, (B) P3, (C) P4, (D) P5, (E) P6, and (F) P7.



Fig. S8 S 2p XPS of elemental sulfur, model compound 4, and P1-P7.



Fig. S9 XRD patterns of solid powders of P1-P7.



Fig. S10 The extraction efficiency of different metal ions using solid powder of P1. $m_{P1} = 5$ mg, $V_{M^{n+}} = 5$ mL, $[M^{n+}] = 100$ mg L⁻¹. Polymer powder and the aqueous solution of metal ions were stirred at room temperature for 1 h before centrifugation.

entry	$m_{\rm p}({\rm mg})$	P1	P 2	P 3	P 4	P 5	P 6	P 7
1	1	38.42%	25.03%	40.42%	55.91%	26.72%	59.38%	78.75%
2	2	56.42%	49.30%	60.02%	73.91%	49.01%	80.31%	89.06%
3	5	99.88%	78.09%	98.00%	99.95%	99.85%	98.63%	99.25%
4	10	99.98%	99.99%	99.95%	99.99%	99.99%	99.99%	99.99%

Table S7. Gold extraction efficiencies with different amounts of polythioamides^a

 ${}^{a}m_{P}$ (mg): the amount of polymer powder. $[Au^{3+}]_{0} = 100 \text{ mg } \text{L}^{-1}$, $V_{Au^{3+}} = 10 \text{ mL}$. Polymer powder and the aqueous solution of Au^{3+} were stirred at room temperature for 1 h before centrifugation.



Fig. S11 ¹H NMR spectrum of 4 in DMSO- d_6 .



Fig. S12 13 C NMR spectrum of 4 in DMSO- d_6 .



Fig. S13 ¹H NMR spectrum of P1 in DMSO- d_6 .





Fig. S14¹³C NMR spectrum of P1 in DMSO-*d*₆.



Fig. S15 ¹H NMR spectrum of P2 in DMSO- d_6 .



Fig. S16 13 C NMR spectrum of P2 in DMSO- d_6 .



Fig. S17 ¹H NMR spectrum of P3 in DMSO- d_6 .



Fig. S18 13 C NMR spectrum of P3 in DMSO- d_6 .



Fig. S19 ¹H NMR spectrum of P4 in DMSO- d_6 .



200 190 180 170 fl (ppm)

Fig. S20 13 C NMR spectrum of P4 in DMSO- d_6 .



Fig. S21 ¹H NMR spectrum of P5 in DMSO- d_6 .



f1 (ppm)

Fig. S22 13 C NMR spectrum of P5 in DMSO- d_6 .



Fig. S23 ¹H NMR spectrum of P6 in DMSO- d_6 .



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Fig. S24 ¹³C NMR spectrum of P6 in DMSO-*d*₆.



Fig. S25 ¹H NMR spectrum of P7 in DMSO- d_6 .



Fig. S26 13 C NMR spectrum of P7 in DMSO- d_6 .