

Manuscript for Supporting Information

## **A Facile and High-Recovery Material for Rare Metals Based on a Water-Soluble Polyallylamine with Side-Chain Thiourea Groups**

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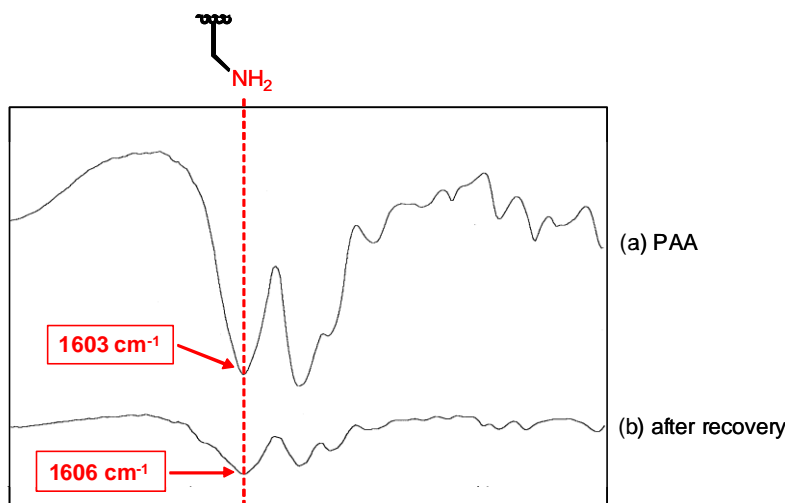
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**Table S1.** Reaction of PAA with methyl isothiocyanate.<sup>[a]</sup>

entry	feed amount of methyl isothiocyanate (mol% to repeat units)	copolymer composition (mol%) <sup>[b]</sup>		Yield (%) <sup>[c]</sup>	solubility in 1.0 M HCl aq. <sup>[d]</sup>
		thiourea units	amine units		
1	2.5	4	96	92	○
2	10	12	88	95	○
3	20	28	72	92	△
4	100	99	1	90	×

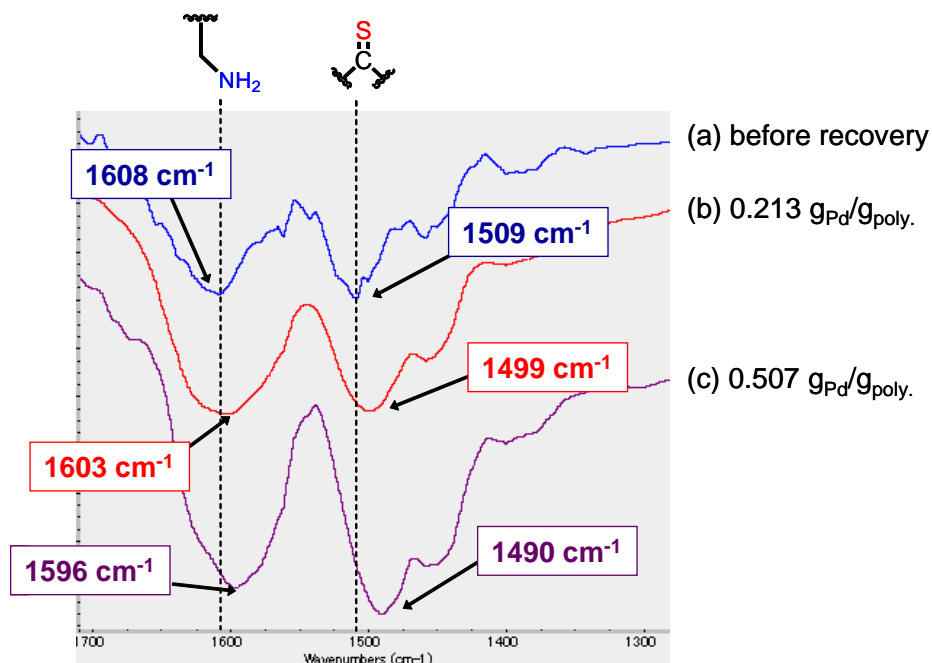
[a] Conditions:  $[PAA]_0 = 0.44$  M, 30 °C, 48 h. [b] Calculated on the basis of elemental analysis. [c] Diethyl ether-insoluble parts. [d] 50 mg of the polymer was added to 1.0 mL of 1.0 M HCl aq: (○) soluble; (△) partially soluble; (×) insoluble.

**Fig. S1** IR spectra of polyallylamine (a) before and (b) after recovery.



Because the complexation amount of  $Pd^{II}$  onto PAA could not be measured by atomic absorption spectrometry (AAS), IR spectroscopic analysis was carried out before and after the experiment (Fig. S1). An absorption peak at  $1603\text{ cm}^{-1}$ , corresponding to NH-bending of the allylamine moieties in PAA, was found to have hardly shifted after the experiment. This indicates that the complexation amount of  $Pd^{II}$  was very low, with no formation of cross-linking precipitates.

**Fig. S2** IR spectra of **P12** (a) before recovery; (b) after recovery (recovery amount: 0.213 g<sub>Pd</sub>/g<sub>poly.</sub>); (c) after recovery (recovery amount: 0.506 g<sub>Pd</sub>/g<sub>poly.</sub>).



## References of 11. in Main Text

- (a) D. Parajuli, H. Kawakita, K. Inoue, and M. Funaoka, *Ind. Eng. Chem. Res.*, 2006, **45**, 6405; (b) E. Birinci, M. Gulfen, and A. O. Aydin, *Hydrometallurgy*, 2009, **95**, 15; (c) C. Park, J. S. Chung, and K. W. Cha, *Bull. Korean Chem. Soc.*, 2000, **21**, 121; (d) K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa, and K. Ueda, *J. Hazard. Mater.*, 2007, **146**, 39; (e) M. Ruiz, A. M. Sastre, and E. Guibal, *React. Funct. Polym.*, 2000, **45**, 155; (f) C. R. Adhikari, D. Parajuli, H. Kawakita, K. Inoue, K. Ohto, and H. Harada, *Environ. Sci. Technol.*, 2008, **42**, 5486; (g) E. Guibal, N. Von Offenbergs Sweeney, T. Vincent, and J. M. Tobin, *React. Funct. Polym.*, 2002, **50**, 149; (h) D. Jermakowicz-Bartkowiak, B. N. Kolarz, and A. Serwin, *React. Funct. Polym.*, 2005, **65**, 135-142.

**Table S2.** Recovery ( $g_{\text{metal}}/g_{\text{poly.}}$ ) of various metal ions by **P12** <sup>[a]</sup>

Mn <sup>II</sup> ×	Fe <sup>III</sup> ×	Co <sup>II</sup> ×	Ni <sup>II</sup> ×	Cu <sup>II</sup> ×
	Ru <sup>III</sup> 0.709	Rh <sup>III</sup> 0.523	Pd <sup>II</sup> 0.508	Ag <sup>I</sup> ×
	Os <sup>III</sup> 0.338	Ir <sup>III</sup> 0.957	Pt <sup>IV</sup> 0.588	Au <sup>III</sup> 0.603

[a] Conditions: Aqueous HCl solution of metal ion: 5 mL (metal concentration: 1300 mg/L); aqueous HCl solution of polymer: 5 mL (0.2 wt%); temperature: 25°C; reaction time: 2h.

**Table S3.** Desorption of Pd<sup>II</sup> from the **P12**.<sup>a</sup>

entry	desorption solution	desorption efficiency/%
1	1.0 M NaOH aq.	2
2	3.0 M NaOH aq.	2
3	5.0 M NaOH aq.	2
4	2.0 M HNO <sub>3</sub> aq.	93
5	4.0 M HNO <sub>3</sub> aq.	>99

<sup>a</sup>Conditions: polymer 20 mg, desorption agent 20 mL,

room temperature, 24 h.

**Materials.** Polyallylamine (PAA, 10.4 wt % aqueous solution,  $M_w = 25000$ ) was supplied by Nitto Boseki Co., Ltd. (sample code PAA-25). Methyl isothiocyanate (Tokyo Kasei Kogyo, >98.0 %) was distilled prior to use. *N,N*-Dimethylformamide (Wako Pure Chemical, >99.5 %) was dried and distilled over  $\text{CaH}_2$ . Sodium tetrachloropalladate (II) ( $\text{Na}_2\text{PdCl}_4$ , Tokyo Kasei Kogyo, >98.0 %), manganese (II) chloride tetrahydrate (Kanto Chemical, >99.0 %), iron (III) chloride hexahydrate (Wako Pure Chemical, >99.0 %), cobalt (II) chloride hexahydrate (Kanto Chemical, >99.0 %), nickel (II) chloride hexahydrate (Kanto Chemical, >98.0 %), copper (II) chloride (Wako Pure Chemical, >95.0 %), ruthenium (III) chloride trihydrate (Kanto Chemical, >98.0 %), rhodium (III) chloride hydrate (Aldrich, >99.9 %), silver (I) nitrate (Kanto Chemical, >99.8 %), osmium (III) chloride hydrate (Alfa Aesar, 99.99 %), iridium (III) chloride trihydrate, (Aldrich, >99.9 %), hydrogen hexachloroplatinate (IV) (Wako Pure Chemical, >98.5 %), and sodium tetrachloroaurate (III) dihydrate (Wako Pure Chemical, >95.0 %) were commercially available and used as received.

**Instruments.**  $^1\text{H}$  NMR spectra were recorded with a JEOL JNM- $\lambda$ 500 using 35 % deuterium chloride solution in  $\text{D}_2\text{O}$  as a solvent; the  $\delta$  values are given in parts per million (ppm). IR spectra were recorded with a Jasco FT/IR-5000 spectrometer and the values were given in  $\text{cm}^{-1}$ . Flame atomic absorption spectrometry was carried out using a Hitachi polarized zeeman atomic absorption spectrometer (AAS) Z-2310.

**Synthesis of polyallylamine with thiocarbonyl groups (Typical procedure).** A DMF solution (12.0 mL) of methyl isothiocyanate (76.8 mg, 1.05 mmol, 10 mol% with respect to repeating unit of PAA) was added to a DMF solution (24 mL) of PAA (0.600 g, 10.5 mmol of repeating unit) at  $0^\circ\text{C}$ . The reaction mixture was stirred at  $30^\circ\text{C}$  for 48 h. The resulting mixture was poured into diethylether (200

mL), and the precipitate was collected by filtration with suction and dried under vacuum to obtain **P12** of thiourea unit (0.657 g, 95%) as a white powder.

$^1\text{H}$  NMR (500 MHz, 35 wt% DCl in  $\text{D}_2\text{O}$ ,  $\delta$ , at  $60^\circ\text{C}$ ): 2.29–3.20 (br,  $0.12 \times 2\text{H} + 0.88 \times 2\text{H}$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{NH}_2)-$ ), 3.20–3.74 (br,  $0.12 \times 1\text{H} + 0.88 \times 1\text{H}$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{NH}_2)-$ ), 3.97 (s,  $0.12 \times 3\text{H}$ ,  $-\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3$ ), 4.10–4.51 (br,  $0.88 \times 2\text{H}$ ,  $-\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3$ ), 4.51–4.98 (br,  $0.88 \times 2\text{H}$ ,  $-\text{CH}_2\text{NH}_2$ ); IR (KBr):  $1468\text{ cm}^{-1}$  ( $-\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3$ ),  $1509\text{ cm}^{-1}$  ( $-\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3$ ),  $1608\text{ cm}^{-1}$  ( $-\text{CH}_2\text{NH}_2$ ),  $3420\text{ cm}^{-1}$  ( $-\text{CH}_2\text{NH}_2$ ,  $-\text{CH}_2\text{HN}-\text{C}=\text{S}-\text{NHCH}_3$ ); Elemental analysis of sulfur: **P4**; 2.16 %, **P12**; 5.85 %, **P99**; 24.53 %.

**Metal recovery (Typical procedure):** A 1.00 M aqueous HCl solution of **P12** (5.00 mL, 0.200 wt%, 10.0 mg) was added to a 1.00 M aqueous HCl solution of the appropriate metal concentration (5.00 mL, metal concentration: 130–1500 mg/L), and the mixture was stirred at  $25^\circ\text{C}$  for 2 h. The resulting precipitate was separated by filtration (pore size of filter;  $0.45\ \mu\text{m}$ ), and an aliquot (0.250 mL) of the filtrate was removed for sampling. After appropriate dilution, the metal concentration in the solution was determined by AAS. The recovery amount was calculated based on the following equation:

Recovery amount ( $\text{g}_{\text{metal}}/\text{g}_{\text{poly.}}$ ) = M of metal  $\times$  recovery amount (mmol)/weight of polymer used (g).

**Desorption of  $\text{Pd}^{\text{II}}$  from the polymer (Typical procedure):** To examine the desorption of  $\text{Pd}^{\text{II}}$  from **P12**, recovery experiments were first conducted. A 1.00 M aqueous HCl solution of PAA (15.0 mL, 0.200 wt%, 30.0 mg) was added to a 1.00 M aqueous HCl solution of  $\text{Na}_2\text{PdCl}_4$  (15.0 mL,  $\text{Pd}^{\text{II}}$  concentration: 450 mg/L), and the mixture was stirred at  $25^\circ\text{C}$  for 2 h. The resulting precipitate was separated by filtration and the concentration of  $\text{Pd}^{\text{II}}$  in the filtrate was measured by AAS to determine the recovery amount (mmol). The precipitate was washed with distilled water and samples were added to 30

mL portions of various concentrations of HNO<sub>3</sub> and aqueous NaOH in flasks. The contents of the flasks were stirred at 200 rpm at 25°C for 24 h, and the polymers were separated by filtration (in the case of desorption in aqueous HNO<sub>3</sub>, the pH of the solution was adjusted using aqueous NaOH to precipitate the polymers). The concentration of Pd<sup>II</sup> in the filtrate was measured by AAS to determine the amount desorbed (mmol). The desorption efficiency was calculated using the following equation:

$$\text{Desorption efficiency (\%)} = \text{desorption amount (mmol)} / \text{recovery amount (mmol)} \times 100. \quad (5)$$

The polymers were washed with 3.0 wt% aqueous KOH to regenerate the free amino groups and washed with distilled water. The resulting polymers were freeze-dried and reused in the next recovery experiment.