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# Insoluble $\pi$ -Conjugated Polyimine as an Organic Adsorbent for Group 10 Metal Ions

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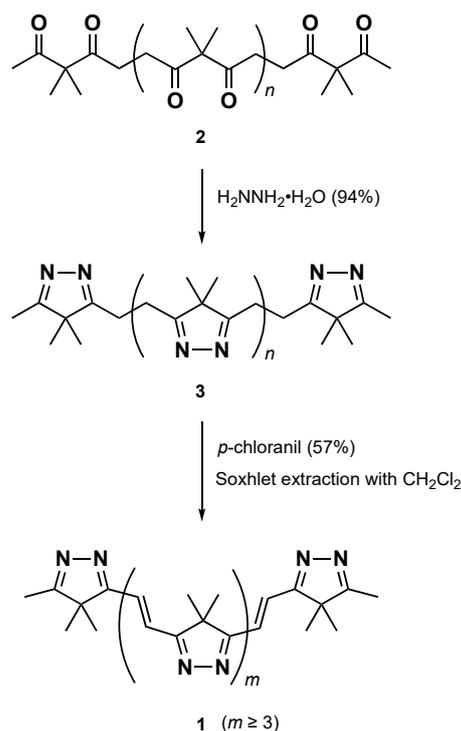
**Abstract:** Metal ion adsorbents are indispensable materials for the recovery of noble metal ions in a sustainable society. Herein, we report that poly(isopyrazole-3,5-diyl-*trans*-vinylene) (**1**) effectively adsorbed group 10 metal ions from solution in acetonitrile. Owing to its fully  $\pi$ -conjugated and rigid structure, polyimine **1** was virtually insoluble in common organic solvents and water, making it advantageous for metal ion adsorption via a solid/liquid interface. Inductively coupled plasma (ICP) analysis showed that  $\geq 90\%$  of  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Pt}^{2+}$  ions was adsorbed at a concentration of  $10\ \mu\text{M}$  (order of  $\leq 2\ \text{ppm}$ ) after stirring suspensions at room temperature. Metal ion desorption was achieved by treatment with ethylenediaminetetraacetic acid disodium salt ( $\text{EDTA}\cdot 2\text{Na}$ ), and the adsorbent was reused. Theoretical calculations supported that the desolvation energy was an important factor for effective adsorption in acetonitrile.

Metal ion adsorbents that enable the recovery and reuse of noble or hazardous metal elements have received increasing attention recently regarding a sustainable society. Owing to the degree of freedom in molecular design, various organic materials have been synthesized as effective metal ion adsorbents.<sup>[1]</sup> Among them, insoluble adsorbents that can extract specific metal ions via a solid/liquid interface are advantageous for the facile extraction of metal ions by filtration.<sup>[2]</sup> Such materials have often been generated by post-synthetic functionalization of polymer materials with metal-coordinating substituents, for example, substitution of pyridyl or imidazolyl groups onto polysaccharides.<sup>[3]</sup> However, the chemical functionalization of less-soluble polymers is not always efficient, and most of post-synthetically functionalized adsorbents have been used in their partially converted forms. Ambiguity regarding the detailed chemical structures sometimes makes further tuning and mechanistic studies difficult.

We have recently reported the post-synthetic functionalization of aliphatic polyketones<sup>[4]</sup> to give insoluble,  $\pi$ -conjugated polyimine **1**,<sup>[5]</sup> poly(isopyrazole-3,5-diyl-*trans*-vinylene). Polyimine **1** combines multiple metal-coordination sites (ketimine) and insolubility, which are essential for solid

adsorbents of metal ions. Furthermore, the post-synthetic conversion of ketone **2** to imine **3** (see Scheme 1) proceeds quantitatively without leaving unreacted ketones. The well-defined chemical structure of polyimine **1** prompted us to evaluate its metal-adsorption behavior. In this study, we focused on group 10 metal ions including noble  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  ions, for evaluation of the ion-adsorption properties of **1**, because several metal complexes of these ions with isopyrazole ligands are known.<sup>[4a,6]</sup> Herein, we report more than 90% adsorption of group 10 metal ions from acetonitrile solution with a concentration of  $10\ \mu\text{M}$  ( $\leq 2\ \text{ppm}$ ) using insoluble polyimine **1** via a solid/liquid interface. Metal ion desorption occurred when the ion-adsorbed material was treated with  $\text{EDTA}\cdot 2\text{Na}$ , demonstrating the reusability of polyimine **1**. Theoretical calculations were also performed to support the solvent-dependence of metal ion adsorption.

Poly(isopyrazole-3,5-diyl-*trans*-vinylene) (**1**) used in the adsorption study was prepared from poly(3,3-dimethylpentane-2,4-dione) (**2**) according to a reported procedure with a slight modification (Scheme 1).<sup>[5]</sup> Polyketone precursor **2** had a degree of polymerization of 5.1 and a polydispersity index of 1.24. Upon treatment with hydrazine monohydrate, polyketone **2** was quantitatively converted to polyimine **3**. Full conversion of the carbonyl groups was confirmed by the disappearance of carbonyl carbon signals at 205–210 ppm in the  $^{13}\text{C}$  NMR spectrum. During the imination process, the degree of polymerization remained unchanged. Although polyimine **3** was soluble in common organic solvents, such as chloroform and 1,4-dioxane, the solubility drastically decreased upon oxidation of the ethylene bridges using *p*-chloranil. Accordingly, conjugated polyimine **1** was obtained in 57% yield by filtration to remove soluble components, including low molecular-weight oligomers (dimer to tetramer). For adsorption experiments, as-synthesized polyimine **1** was further extracted with dichloromethane using Soxhlet apparatus. After continuous extraction for 23 h, approximately 2 wt% loss was confirmed, and the contacting solution became colorless (Figure S1 in Supporting Information).



**Scheme 1.** Post-synthetic functionalization of polyketone **2** into  $\pi$ -conjugated polyimine **1**.

Leaching tests indicated that washed polyimine **1** was virtually insoluble in common solvents including water. When polyimine **1** (10 mg) was suspended in methanol (10 mL) at room temperature, the supernatant remained transparent (Figure S2), and no absorption band was observed in the UV-Vis spectrum. Similar results were observed in leaching tests using acetonitrile, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and water.

Identification of a suitable solvent for group 10 metal ion adsorption was conducted using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solutions in various solvents (Table 1). To an acetonitrile solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (50 mL, 10.0  $\mu\text{M}$ ), polyimine **1** (10 mg, approximately 330 equiv. of imine substituents relative to total  $\text{Ni}^{2+}$  ions) was added. The suspension was vigorously stirred at room temperature for 6 h. After removal of solid materials by filtration, the  $\text{Ni}^{2+}$  ion concentration in the supernatant was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). ICP-AES analysis indicated that the  $\text{Ni}^{2+}$  ion concentration in the supernatant was 0.20  $\mu\text{M}$ , which corresponded to 98% adsorption of  $\text{Ni}^{2+}$  ions. In contrast, the adsorption amounts from other solvents were rather low, at 17, 2, and 1% in DMF, DMSO, methanol, and water, respectively. Increasing the mixing time did not improve the adsorption amounts from these solvents. Therefore, further optimization of conditions was conducted in acetonitrile. It should be noted that soluble polyimine **3** did not form precipitation upon addition to nickel salt solution, indicating the importance of insolubility of **1**.

Theoretical calculations were performed to explain the solvent dependence of  $\text{Ni}^{2+}$  ion adsorption. Assuming that  $\text{Ni}^{2+}$  ions with octahedral coordination geometry are fully coordinated by each solvent, we optimized the structures of solvated  $\text{Ni}^{2+}$

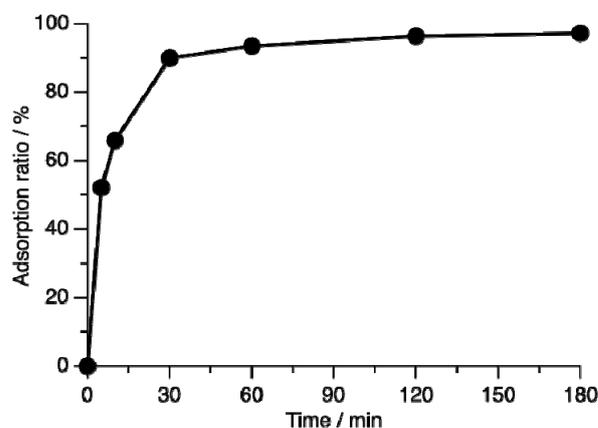
ions (Figure S4). The bond dissociation energies of each solvent were calculated to be in the order acetonitrile (20.3 kcal mol<sup>-1</sup>) < water (24.0 kcal mol<sup>-1</sup>) < methanol (26.7 kcal mol<sup>-1</sup>) < DMF (27.7 kcal mol<sup>-1</sup>) < DMSO (34.6 kcal mol<sup>-1</sup>). As the adsorption of metal ions onto polyimine **1** is a ligand exchange process, the calculation results qualitatively explain the solvent effects, and weak coordination of acetonitrile is advantageous for rapid metal ion adsorption via a solid/liquid interface.

**Table 1.** Adsorption ratios of  $\text{Ni}^{2+}$  ions onto polyimine **1** in various solvents.<sup>[a]</sup>

solvent	acetonitrile	DMF	DMSO	methanol	water
adsorption ratio (%)	98	17	2	2	1

[a] Initial  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  concentration, 10.0  $\mu\text{M}$ ; polyimine **1**, 10.0 mg; final  $\text{Ni}^{2+}$  ion concentration was analyzed using ICP-AES analysis after stirring at room temperature for 6 h.

Time-dependent analysis showed that 90% of  $\text{Ni}^{2+}$  ions was adsorbed by polyimine **1** after 30 min at a concentration of 10  $\mu\text{M}$  (Figure 1). Remarkably, more than 50% of  $\text{Ni}^{2+}$  ions was rapidly adsorbed during the initial 5 min. After stirring for 1 h, changes in the adsorption amount became trivial (94, 96, and 97% adsorption after 1, 2, and 3 h, respectively), suggesting that the total adsorption amount reached saturation after approximately 2 h.



**Figure 1.** Time-dependence of  $\text{Ni}^{2+}$  ion adsorption ratios (initial concentration, 10.0  $\mu\text{M}$ ) using 330 equiv. of polyimine **1** in acetonitrile.

Next, the stoichiometry of polyimine **1** was optimized for effective  $\text{Ni}^{2+}$  ion adsorption in acetonitrile. When the amount of adsorbent **1** was decreased from 330 to 200 equiv., no significant drop in adsorption ratio was observed. However, only 70 and 42% of  $\text{Ni}^{2+}$  ions were extracted from 10.0  $\mu\text{M}$  solutions using 100 and 50 equiv. of polyimine **1**, respectively (Table 2). Therefore, subsequent analysis of the adsorption of group 10 metal ions was conducted in the presence of 200 equiv. of polyimine **1**.

**Table 2.** Adsorption ratio of Ni<sup>2+</sup> ions using various equivalents of polyimine **1**.<sup>[a]</sup>

stoichiometry of imine units relative to Ni <sup>2+</sup> ions	330 eq.	200 eq.	100 eq.	50 eq.
adsorption ratio (%)	96	93	70	42

[a] Initial Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O concentration, 10.0 μM; polyimine **1**, 10.0 mg; final Ni<sup>2+</sup> ion concentration was analyzed using ICP-AES analysis after stirring at room temperature for 2 h.

Using the optimized conditions, polyimine **1** effectively adsorbed group 10 metal ions at ppm to sub-ppm levels in acetonitrile (Table 3). The adsorption amount gradually decreased upon dilution of the initial Ni<sup>2+</sup> ion solution (entries 1 to 3). Nonetheless, 58% of Ni<sup>2+</sup> ions was captured from 1 μM (0.06 ppm) solution using the simple mixing and filtration process. When Pd<sup>2+</sup> and Pt<sup>2+</sup> ions were examined as their nitrate salts at a concentration of 10 μM (1.1 and 2.0 ppm) in the presence of 200 equiv. of polyimine **1**, the adsorption ratios were determined to be 90 and 92%, respectively, which were comparable to Ni<sup>2+</sup> ion adsorption.

**Table 3.** Adsorption ratio of group 10 metal ions by polyimine **1**.<sup>[a]</sup>

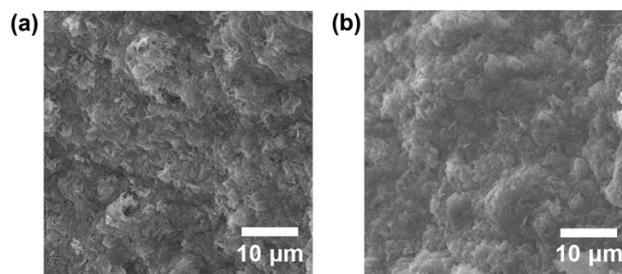
entry	metal salt	initial concentration (μM) [ppm]	adsorption ratio (%)
1	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	10 [0.59]	93
2	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5 [0.29]	78
3	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	1 [0.06]	58
4	Pd(NO <sub>3</sub> ) <sub>2</sub>	10 [1.1]	90
5	Pt(NO <sub>3</sub> ) <sub>2</sub>	10 [2.0]	92

[a] Polyimine **1** (200 equiv.) was added to each acetonitrile solution and vigorously stirred at room temperature for 2 h. Final concentrations of metal ions were determined by ICP-AES analysis.

The desorption of metal ions adsorbed on polyimine **1** was achieved by treatment with a metal chelator. When Ni<sup>2+</sup> ion-adsorbed polyimine **1** (approx. 100 mg) obtained from entry 1 in Table 3 was suspended in ethylenediaminetetraacetic acid disodium salt (EDTA·2Na)<sup>[7]</sup> solution (0.36 mM) of in acetonitrile/water (1/1, v/v), 86% of Ni<sup>2+</sup> ions were eluted out to the contacting solution. Notably, other desorption methods, such as addition of hydrochloric acid<sup>[8]</sup> or continuous washing with acetonitrile, were not as successful, with no more than 50% of Ni<sup>2+</sup> ions eluted.

After desorption with EDTA·2Na, polyimine **1** was reused for further Ni<sup>2+</sup> ion adsorption. The adsorption performance of **1** was recovered after washing the material with acetonitrile and subsequently drying. With recovered material **1**, 72% of Ni<sup>2+</sup> ions was again adsorbed under the same conditions as entry 1 in Table 3. Chemical stability of the adsorbent is also an important factor for sustainability. Unlike common ketimines, polyimine **1**

hardly undergoes hydrolysis of the imine subunits, owing to the π-conjugated and cyclic structure. During the metal ion adsorption process, signals assignable to carbonyl stretching band were not observed in the IR spectrum of polyimine **1**.

**Figure 2.** SEM images of polyimine **1** (a) before and (b) after Ni<sup>2+</sup> ion adsorption under the conditions shown in entry 1 of Table 3.

Scanning electron microscopy (SEM) measurements showed that polyimine **1** had an uneven surface (Figure 2). The surface morphology remained intact after Ni<sup>2+</sup> ion adsorption. Powder X-ray diffraction (PXRD) analysis of **1** before and after Ni<sup>2+</sup> ion adsorption showed no diffraction, indicating that the adsorbent was an amorphous material. Ni<sup>2+</sup> ion adsorption on the surface of polyimine **1** was confirmed by high-resolution X-ray photoemission spectroscopy (XPS). While as-synthesized **1** showed no signal in the Ni (2p) core level region,<sup>[9]</sup> a peak for Ni (2p<sub>3/2</sub>) appeared at 856 eV after contact with the Ni<sup>2+</sup> ion solution (Table 3, entry 1).

In conclusion, we have demonstrated that insoluble, π-conjugated polyimine **1** reversibly adsorbed group 10 metal ions through a simple mixing and filtration process. More than 90% adsorption occurred by simple mixing of polyimine **1** with acetonitrile solutions of group 10 metal nitrate salts on a ppm to sub-ppm level. As polyimine **1** remained intact during metal ion adsorption, it could be reused as an adsorbent after desorption with EDTA·2Na, demonstrating its sustainability. Detailed analysis using SEM, XPS, and theoretical calculations also supported the rapid adsorption of metal ions via a solid/liquid interface. As isopyrazole ligands are known to form complexes with Zn<sup>2+</sup> [4a] and Cd<sup>2+</sup> [5] ions as well as group 10 metal ions, polyimine **1** would be applicable for adsorption of other metal ions with non-specificity. Although the solvent scope was limited, our results demonstrated a new post-synthetic approach to an insoluble metal ion adsorbent from a soluble polyketone precursor. Key points include the quantitative formation of isopyrazole rings at the 1,3-diketone subunits and the drastic change in solubility upon elongation of π-conjugation. As the parent polyketone is capable of elongation and substitution on the main carbon chain, our approach will lead to a new class of solid metal ion adsorbents derivatized from polyketones.

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**Keywords:** Adsorbent • Polyimine • Polyketone • Adsorption • Transition metals

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## Entry for the Table of Contents



Insoluble organic metal ion adsorbent, poly(isopyrazole-3,5-diyl-*trans*-vinylene), was generated from a soluble polyketone precursor by post-synthetic functionalization, including quantitative imination and a solubility change upon  $\pi$ -conjugation formation. This material adsorbed more than 90% of group 10 metal ions ( $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Pt}^{2+}$ ) from their dilute acetonitrile solutions ( $\leq 2$  ppm).