

Mechanochemical synthesis of pincer nanotraps for efficient rhodium recovery

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The sustainable recycling of platinum group metals (PGMs) from secondary resources requires task-specific adsorbents that offer both high extraction efficiency and environmental compatibility. However, rhodium recovery remains particularly challenging due to the high thermodynamic stability of its chloro-complexes, which hampers ligand exchange with adsorbent binding sites. Here, we report a series of porous organic polymer (POP)-based nanotraps for targeted rhodium extraction, functionalized with pincer-type chelators, whose installation was realized by mechanochemical imine bond formation in a green, solvent-free manner. Among them, POP-Py-OMe bearing electron-donating –OMe groups, exhibits the highest rhodium uptake capacity and the fastest extraction kinetics from aqueous solution, significantly outperforming its –OH and –H analogues. Furthermore, sequential breakthrough experiments employing various task-specific POPs as column packing adsorbents enable the efficient and selective separation of Pt, Pd, and Rh in sequence with high purity, highlighting a practical and modular strategy for comprehensive PGM recovery.

Rhodium (Rh), one of the rarest and most valuable platinum group metals (PGMs), plays a critical role in a variety of industrial applications, particularly as a key component in automotive catalytic converters for nitrogen oxide reduction^{1–3}. Due to its exceptional catalytic properties, Rh is also extensively used in chemical synthesis, electronics, and glass manufacturing^{4–6}. However, the global supply of rhodium is extremely limited, with production largely concentrated in a few geopolitically sensitive regions, making its market price highly volatile and supply chain vulnerable⁷. In addition, the environmental and economic costs associated with primary Rh mining are considerable, involving energy-intensive processes and significant ecological impact. Consequently, the development of efficient, selective, and sustainable strategies for Rh recovery, especially from secondary sources such as spent catalysts and electronic

waste, is of paramount importance⁸. Effective Rh recycling not only mitigates resource scarcity and reduces environmental footprint but also supports circular economy initiatives in the transition toward more sustainable industrial practices.

Significant efforts have been devoted to the uptake and recovery of PGMs using a wide range of adsorbent materials, with particular emphasis on palladium (Pd) and platinum (Pt)^{9–14}. Our group has also made substantial contributions in this area, developing task-specific adsorbents for Pd and Pt recovery and providing important insights into the design principles governing adsorbent selectivity and capacity^{15–18}. However, the efficient recovery of rhodium remains a considerable challenge in this field, primarily due to the intrinsically low affinity of Rh species for conventional adsorbents. Although traditional techniques such as precipitation¹⁹, membrane filtration²⁰ and

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solvent extraction²¹ have been explored for Rh recovery from aqueous media, adsorbent-based strategies are significantly less effective for Rh than for other PGMs^{22,23}. This disparity stems largely from the complex chemical speciation of Rh in solution. In industrial leachates and waste streams, Rh typically exists as kinetically inert and thermodynamically stable chloro-complexes (e.g., $[\text{RhCl}_6]^{3-}$), which exhibit weak interactions with most adsorbent functional groups^{2,24}. These complexes undergo ligand exchange slowly, limiting their ability to coordinate with donor atoms on the adsorbent surface^{25,26}. In addition, the strong kinetic inertness of Rh(III) severely limits ligand-exchange processes, while the highly stable $[\text{RhCl}_6]^{3-}$ chloro-complex exhibits poor ion-pair formation, collectively leading to much weaker interactions with conventional chelating adsorbents than those observed for Pd(II) and Pt(IV)²⁷. The presence of competing metal ions and high chloride concentrations in solutions can further hinder Rh adsorption due to competitive binding and ion-pairing effects^{28,29}. As a result, even advanced adsorbent materials often suffer from low Rh selectivity and limited adsorption capacity, underscoring the urgent need for new material platforms tailored specifically for Rh recovery^{30–32}.

To address these challenges, the design of highly specific coordination environments capable of overcoming the kinetic and thermodynamic barriers associated with Rh binding is essential. In this context, pincer-type chelators have emerged as a promising class of ligands due to their preorganized, rigid frameworks and multidentate binding motifs^{33,34}. By simultaneously offering two or more coordination sites in a fixed spatial arrangement, pincer chelators enable strong, directional interactions with target metal ions, even those that are otherwise reluctant to bind under mild conditions (Fig. 1). These structural features make pincer chelators particularly attractive for Rh(III) capture, as they can facilitate the activation of inert chloro-complexes through cooperative binding and promote selective coordination via tailored donor atoms^{35,36}. However, the integration of such chelating motifs into solid-state adsorbent platforms remains underexplored, largely due to synthetic complexity and limited scalability of traditional solution-phase approaches.

Herein, we present a green mechanochemical strategy for installing pincer-functionalized nanotraps, affording robust, high-surface-area adsorbents with well-defined chelating sites. Mechanochemistry, often assisted by trace liquids in liquid-assisted grinding (LAG), drives bond formation and framework construction under nearly solvent-free conditions, enhancing molecular mobility and site uniformity³⁷. This approach has been applied to organic synthesis³⁸, covalent organic frameworks (COF)^{39,40}, and porous organic polymers (POPs), such as polymers of intrinsic microporosity (PIMs)^{41,42}, facilitating the rapid, solvent-efficient construction of crystalline microporous or rigid polymer networks with high specific surface area and well-controlled porosity. By leveraging these features, the dense and homogeneous incorporation of pincer-type chelating motifs is achieved, which directly enhances Rh adsorption performance under realistic conditions. Our findings demonstrate that rationally designed pincer chelators, when combined with mechanochemical synthesis, provide a powerful platform for selective and efficient Rh recovery from complex aqueous systems.

Results

Design concept, synthesis and characterization

Porous organic polymers (POPs) represent a versatile class of advanced porous materials constructed entirely from organic building blocks^{43–46}. The modular nature of POPs allows for precise incorporation of functional groups into their frameworks, enabling the creation of tailored binding sites with task-specific affinity toward targeted metal ions^{47–51}. Our group has previously developed a series of functionalized POPs for the efficient capture and recovery of various metal ions from aqueous media, including Pd(II) and Pt(IV), demonstrating high uptake capacities and excellent selectivity^{15,16}.

Based on these successful systems, we sought to explore their potential for Rh(III) uptake. As an initial approach, three representative POPs, POP-Py¹⁵, POP-*o*NH₂-Py¹⁵, and POP-*o*2NH₂-Py¹⁶, were employed as adsorbents for the extraction of $[\text{RhCl}_6]^{3-}$ from aqueous solutions. These materials have previously exhibited strong binding affinities toward Pd(II) and Pt(IV), attributed to the presence of pyridyl and amino functionalities. However, this favorable adsorption behavior was not replicated in the case of Rh(III), which exhibited significantly lower estimated maximum uptake capacities of 150, 140, and 136 mg g⁻¹ for POP-*o*NH₂-Py, POP-*o*2NH₂-Py, and POP-Py, respectively (Supplementary Fig. 1). This discrepancy underscores a fundamental difference in binding characteristics and highlights the need for more specialized ligand environments tailored to the coordination chemistry and speciation of Rh(III).

The limited adsorption capacity of conventional monodentate-chelating POPs for Rh(III), in contrast to their strong affinity for other PGMs (Pd and Pt), underscores the distinct coordination behavior of Rh species. As previously reported, Rh(III) exists predominantly as kinetically inert chloro-complexes (e.g., $[\text{RhCl}_6]^{3-}$) in acidic aqueous environments^{2,24}, exhibiting low reactivity and weak interactions with common donor groups such as pyridyl or amino moieties. This underscores the necessity of engineering more sophisticated coordination environments with stronger and more geometrically constrained binding sites to overcome the inert nature of Rh(III) complexes. To address this challenge, we hypothesized that introducing pincer-type chelating motifs, which features preorganized, tridentate or more coordination geometries, could provide a more favorable platform for selective Rh(III) binding. Pincer ligands are known for their ability to form robust metal-ligand complexes through cooperative interactions involving multiple donor atoms, thereby offering both high thermodynamic stability and kinetic accessibility. By incorporating these motifs into the POP framework, we aimed to create localized, high-affinity binding cavities specifically tailored for Rh(III) uptake.

To address the challenge of Rh(III) recovery, we developed a solvent-free mechanochemical strategy for the modular synthesis of pincer-functionalized POPs (p-POPs) using POP-*o*2NH₂-Py as a precursor. This polymer offers two ortho-positioned amino groups on each pyridyl unit, serving as reactive sites for covalent post-modification and pincer ligand installation. The resulting materials feature high specific surface area, well-defined porosity, and a dense distribution of pincer coordination sites. Compared to unmodified POPs, the pincer-functionalized adsorbents exhibited markedly improved Rh(III) uptake capacity and selectivity, underscoring the importance of multidentate chelation in overcoming the inert coordination behavior of Rh species. These results provide valuable insights for designing next-generation adsorbents for efficient and selective Rh recovery from complex aqueous environments.

POP-*o*2NH₂-Py was prepared via free-radical polymerization of 3,5-divinylpyridin-2,6-diamine using azobisisobutyronitrile (AIBN) as the initiator. The amino-functionalized precursor was then converted into pincer-functionalized POPs through a green, solvent-free mechanochemical Schiff base reaction, in which ortho-substituted benzaldehydes with diverse functionalities were installed via imine bond formation (Fig. 2a). This process afforded three distinct p-POPs, namely POP-Py-H, POP-Py-OH, and POP-Py-OMe, featuring different ortho substituents on the newly formed Schiff base linkages (Fig. 2b). In contrast, solution-based functionalization was attempted by refluxing 2 equivalents of the respective benzaldehyde with POP-*o*2NH₂-Py in ethanol using acetic acid as catalyst. Even after 12 h, residual amino groups remained, indicating incomplete reaction (Supplementary Fig. 2).

To optimize the ball-milling duration for efficient conversion, Fourier transform infrared spectroscopy (FT-IR) was used to monitor the consumption of amino groups. During the synthesis of POP-Py-H,

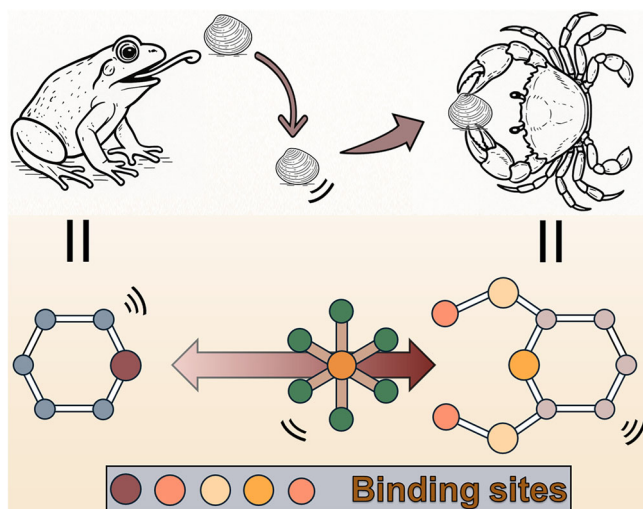


Fig. 1 | Schematic view of metal coordination with pincer ligand vs. monodentate ligand. Pincer ligands coordinate to the metal center through multiple donor atoms simultaneously, forming chelating coordination that results in stronger binding affinity and higher complex stability compared to monodentate ligands, which bind through only a single donor atom and are more prone to ligand exchange or dissociation. The rigid and preorganized geometry of the pincer ligand enforces an optimal spatial arrangement of donor atoms for metal coordination, enhancing metal–ligand interaction strength, reducing structural flexibility, and improving both thermodynamic stability and resistance to competitive coordination.

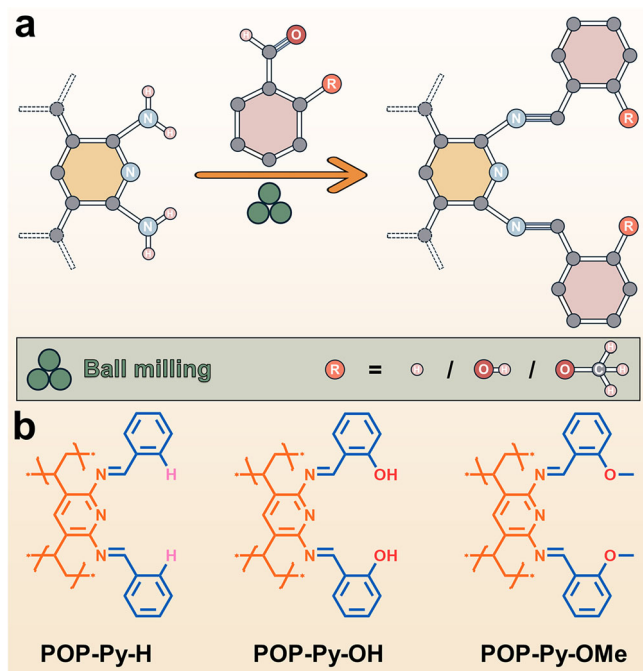


Fig. 2 | Preparation of the pincer nanotraps for rhodium recovery. **a** Schematic illustration of the solvent-free mechanochemical synthesis used to incorporate pincer-type chelators into POPs. **b** Representation of the porous frameworks functionalized with rhodium-specific pincer ligands, along with the molecular structures of the resulting pincer-functionalized POPs investigated in this study.

samples were withdrawn from the milling jar at 5, 15, 30, and 60 min, thoroughly washed with dry ethanol, and vacuum-dried at 70 °C for 24 h. FT-IR analysis showed a rapid attenuation of the primary amine stretching bands ($\nu_{\text{N-H}}$ = between $\sim 3518\text{ cm}^{-1}$ to 3224 cm^{-1}) together with the corresponding bending vibration ($\delta_{\text{N-H}}$ = $\sim 1660\text{ cm}^{-1}$) of POP-

$\text{o}2\text{NH}_2\text{-Py}$ during the initial 30 min of mechanochemical milling, indicating fast consumption of amine groups, with no appreciable changes detected upon further milling up to 60 min (Supplementary Fig. 3). This indicates that the conversion of amino groups to imine bonds was completed within 30 min. Furthermore, the FT-IR spectra confirmed the successful transformation of aminopyridine moieties into pincer-functionalized groups in all three p-POPs, each displaying characteristic vibrational features corresponding to their respective pincer substituents (Supplementary Fig. 4). The successful incorporation of pincer sites was further corroborated by the solid-state ^{13}C nuclear magnetic resonance (SS ^{13}C NMR) spectra. All three p-POPs exhibited broad peaks in the range of 127–133 ppm, which are characteristic of aromatic carbons associated with framework formation through imine condensation. In addition, sharp signals at 162 and 56 ppm were observed, corresponding to $-\text{C}-\text{OH}$ and $-\text{C}-\text{OCH}_3$ groups in POP-Py-OH and POP-Py-OMe, respectively (Supplementary Fig. 5). X-ray photoelectron spectroscopy (XPS) analysis further confirmed the formation of imine bonds. In the high-resolution N 1s spectra, the dominant nitrogen signal corresponding to amine groups ($-\text{NH}_2$, 399.4 eV) in pristine POP- $\text{o}2\text{NH}_2\text{-Py}$ markedly decreased after modification, while a new peak emerged at lower binding energy (398.5–398.6 eV), assignable to imine nitrogen ($\text{C}=\text{N}$) (Supplementary Figs. 6–8). These changes collectively indicate the successful transformation of amino groups into imine linkages, consistent with the observations from FT-IR and solid-state ^{13}C NMR analyses.

Nitrogen sorption isotherms collected at 77 K revealed that the resulting p-POPs possessed hierarchical porosity, comprising both micro- and mesopores (Supplementary Figs. 9–11). A steep nitrogen uptake at low relative pressure ($P/P_0 < 0.1$) indicated the presence of micropores, while the emergence of a hysteresis loop at higher pressures was characteristic of mesoporous structures^{52,53}. The Brunauer–Emmett–Teller (BET) surface areas were calculated to be $351\text{ m}^2\text{ g}^{-1}$, $357\text{ m}^2\text{ g}^{-1}$, and $373\text{ m}^2\text{ g}^{-1}$ for POP-Py-H, POP-Py-OH, and POP-Py-OMe, respectively. Powder X-ray diffraction (PXRD) patterns confirmed the amorphous nature of all p-POP samples, which is characteristic of such porous organic polymers (Supplementary Fig. 12). Scanning electron microscopy (SEM) revealed that these materials were composed of nanoscale primary particles aggregated into microscale clusters, in contrast to their precursor POP- $\text{o}2\text{NH}_2\text{-Py}$, which exhibited predominantly nanoscale aggregates (Supplementary Fig. 13). Elemental mapping further confirmed the successful incorporation of functional groups: a clear oxygen signal was detected in POP-Py-OH and POP-Py-OMe, while it was negligible in POP-Py-H (Supplementary Figs. 14–17). This observation indicates the successful introduction of phenolic and methoxy groups into POP-Py-OH and POP-Py-OMe, respectively. Furthermore, high-resolution transmission electron microscopy (HR-TEM) confirmed that all three p-POPs exhibited similar nanoscale morphology, characterized by irregular agglomeration, an intrinsically amorphous nature, and hierarchical porous architectures (Supplementary Fig. 18). In this structure, meso- and macropores facilitated efficient mass transport, whereas the micropores acted as confinement sites that concentrated the chelating groups, thereby enhancing adsorption performance. Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of all three p-POPs after activation at 100 °C for 24 h, revealing that they remained thermodynamically stable at temperatures up to at least 326 °C under a nitrogen atmosphere (Supplementary Figs. 19).

Rhodium sorption studies

Given the potential instability of imine bonds in acidic aqueous environments⁵⁴, adsorption experiments were conducted using 400 ppm Rh solutions over a pH range of 1–7, adjusted with either an inorganic acid (HCl) or an organic acid (CH_3COOH)⁵⁵, to systematically evaluate the stability and adsorption performance of p-POPs under acidic conditions. The results show that the adsorption performance

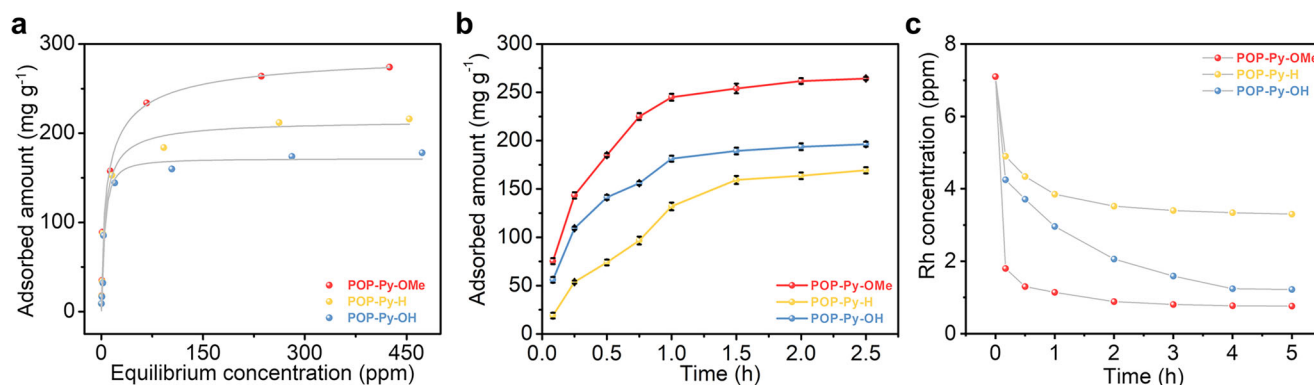


Fig. 3 | Rhodium adsorption isotherms and kinetics investigations. **a** Rhodium adsorption isotherms of p-POP-based adsorbents fitted with the Langmuir model; all fittings yielded R^2 values above 0.99, indicating excellent model agreement. **b** Adsorption kinetics of rhodium from aqueous solution (initial concentration: 20

ppm, volume: 400 mL) using 5 mg of adsorbent. The error bars represent the standard deviation (SD) from three independent experiments. **c** Rhodium removal kinetics at an initial concentration of 7.1 ppm at a V/m ratio of 10,000 mL g⁻¹.

of all three materials remains relatively stable between pH 3 and 7 (Supplementary Fig. 20). At pH 1–2, POP-Py-OMe and POP-Py-H lose their adsorption capacity, indicating partial hydrolysis of the imine linkages, likely accompanied by protonation of amino groups and pyridine. In contrast, POP-Py-OH retains considerable adsorption ability under these highly acidic conditions, suggesting that hydrogen bonding between the hydroxyl groups and imine linkages provides partial stabilization of the imine bonds. Additionally, each p-POP sample was immersed in HCl solution at pH 4 at room temperature under continuous stirring for 4 h, followed by filtration. After vacuum drying, the treated samples were subjected to FT-IR analysis to monitor potential changes in their chemical structure. The spectra revealed no discernible differences between the freshly synthesized and acid-treated materials, indicating that both the adsorption performance and FT-IR analysis confirm the structural integrity and chemical stability of the p-POPs at pH $\geq$ 4 (Supplementary Figs. 21–23). In addition, storage stability tests were performed on all three p-POPs, and FT-IR analysis revealed no detectable changes in the chemical structure. The results demonstrated that after three months of storage under ambient conditions, the adsorbents retained both their chemical structure and adsorption performance (Supplementary Fig. 24).

The Rh(III) adsorption performance of the three p-POPs was subsequently evaluated through batch adsorption experiments. Equilibrium isotherms were obtained by varying the initial Rh(III) concentrations from 10 to 600 ppm at pH $\sim$ 7, with a contact time of 4 h to ensure adsorption equilibrium, and the resulting uptake capacities are plotted in Fig. 3. Among the three materials, POP-Py-OMe exhibited the highest Rh(III) sorption capacity, followed by POP-Py-H and POP-Py-OH. The maximum equilibrium uptake capacities were estimated to be 274, 216, and 178 mg g⁻¹ for POP-Py-OMe, POP-Py-H, and POP-Py-OH, respectively, at an equilibrium concentration of $\sim$ 400 ppm (Supplementary Tables 1–3), comparable to those of state-of-the-art adsorbents (Supplementary Table 4). The adsorption isotherms were well described by the Langmuir model, suggesting monolayer adsorption on homogeneous sites (Supplementary Fig. 25).

Considering that Rh(III) readily forms multiple chloro-complex species in chloride-containing solutions, chloride ions are expected to play a critical role in governing its adsorption behavior. To isolate the influence of Cl⁻, the best-performance adsorbent, POP-Py-OMe, was systematically evaluated in the presence of increasing concentrations of LiCl, NaCl, and NH₄Cl, while minimizing changes in solution acidity⁵⁵. As the chloride concentration increased, a gradual decrease in Rh adsorption capacity was observed for all three chloride salts, indicating that elevated Cl⁻ levels adversely affect Rh(III) uptake (Supplementary Fig. 26). Notably, for LiCl and NaCl

systems, the adsorption loss remained relatively limited when the chloride concentration was below 1 mol L⁻¹, suggesting that POP-Py-OMe maintains a reasonable degree of adsorption stability under moderate chloride conditions. In contrast, a much more pronounced decline was observed in NH₄Cl containing systems at comparable chloride concentrations. This behavior is plausibly attributed to the enhanced formation of stable chloro-complexes, such as (NH₄)₃[RhCl₆] complex, which reduces the availability of adsorbable Rh species and weakens their coordination interaction with the pincer-type chelating sites of POP-Py-OMe⁵⁵.

Notably, the p-POPs also demonstrated rapid adsorption kinetics at low Rh concentrations. As shown in Fig. 3b, $\sim$ 90% of the final uptake capacity was reached within 1 h for all three materials when exposed to a 20 ppm Rh(III) solution (Supplementary Tables 5–7). However, a discrepancy was observed between experimental and theoretical capacities. Based on a 1:1 stoichiometry between the pincer sites and Rh(III) chloride complexes, calculated using the assumed polymer monomer containing one pincer site per repeating unit, the theoretical maximum capacities were calculated to be 259, 305, and 279 mg g⁻¹ for POP-Py-OMe, POP-Py-H, and POP-Py-OH, respectively. The slightly higher experimental uptake (2.0% higher) observed for POP-Py-OMe is attributed to additional interactions beyond the idealized pincer sites (Supplementary Table 7), including cooperative binding by neighboring multidentate ligands and minor electrostatic adsorption within the microporous environment. This interpretation is further supported by subsequent mechanistic studies of Rh adsorption.

To investigate the rhodium removal kinetics, 20 mg of each p-POP was dispersed in 200 mL of 7.1 ppm Rh(III) solution. At predetermined intervals, 3 mL aliquots were withdrawn, filtered, and analyzed by ICP-MS to quantify the remaining Rh(III). The kinetic data revealed that POP-Py-OMe removed nearly 90% of Rh within 5 h, whereas POP-Py-H and POP-Py-OH removed approximately 80% and 54%, respectively, under identical conditions (Fig. 3c and Supplementary Table 8). The significantly enhanced sorption rate of POP-Py-OMe highlights the beneficial role of the methoxy group in improving Rh(III) coordination kinetics, potentially by providing additional oxygen donor sites that complement the nitrogen-based pincer framework. Interestingly, despite its comparable theoretical uptake capacity, POP-Py-OH exhibited the lowest Rh(III) adsorption performance. This result may be attributed to the competitive hydration and reduced donor ability of the phenol group. In aqueous media, the -OH moieties can form strong hydrogen bonds with surrounding water molecules⁵⁶, potentially shielding nearby pincer sites and decreasing their accessibility to [RhCl₆]³⁻. Moreover, the weaker electron-donating character of -OH , compared to -OCH_3 , may reduce the overall Lewis basicity of the

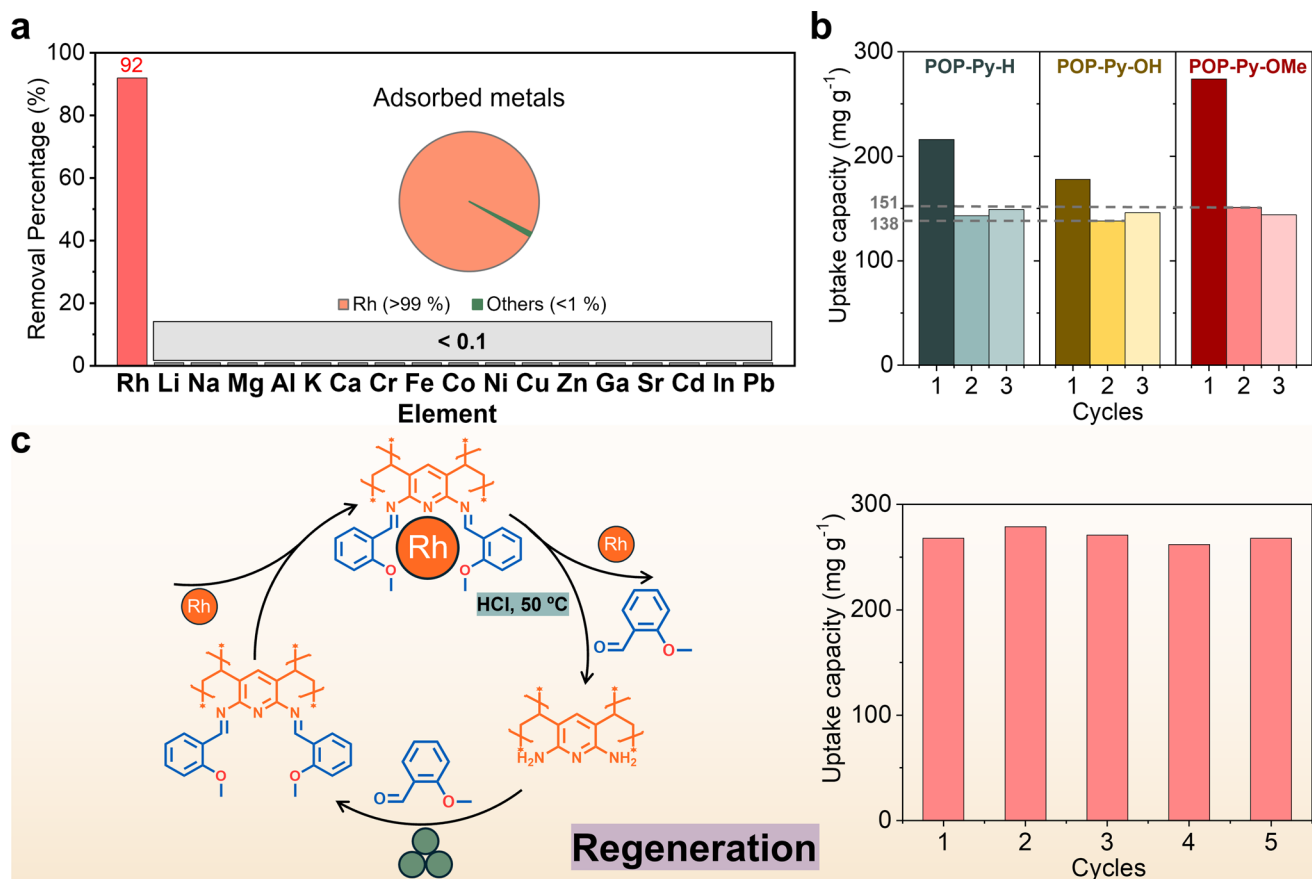


Fig. 4 | Selectivity and recyclability evaluation of pincer-functionalized POPs. **a** Selective extraction of Rh(III) by POP-Py-OMe from a mixture containing equal concentrations of various competing metal ions. **b** Recyclability of p-POP

adsorbents after treatment with 1 M HCl aqueous solution. **c** Schematic illustration of Rh(III) release and regeneration of POP-Py-OMe, along with its recyclability performance after multiple regeneration cycles.

pincer framework, thereby impairing its coordination affinity toward Rh(III). These effects collectively diminish the sorption efficiency of POP-Py-OH relative to the other two analogs.

To further quantify the affinity of these materials toward Rh(III), the distribution coefficient (K_d) was calculated from equilibrium data. POP-Py-OMe exhibited the highest K_d value of $8.1 \times 10^4 \text{ mL g}^{-1}$, compared to $4.8 \times 10^4 \text{ mL g}^{-1}$ and $1.2 \times 10^4 \text{ mL g}^{-1}$ for POP-Py-H and POP-Py-OH, respectively. These results underscore the importance of fine-tuning the chemical environment of pincer sites by incorporating electron-donating substituents, such as $-\text{OCH}_3$, to enhance both the binding strength and uptake kinetics of Rh(III), thereby advancing the rational design of high-performance adsorbents for precious metal recovery.

Building on this success, we further evaluated the performance of POP-Py-OMe under more challenging conditions by testing its ability to selectively capture rhodium in the presence of various competing ions, including Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ga^{3+} , Sr^{2+} , Cd^{2+} , In^{3+} , and Pb^{2+} . Adsorption experiments were conducted using an aqueous solution containing Rh(III) and the aforementioned ions at approximately equal concentrations (10 ppm each). Remarkably, POP-Py-OMe achieved over 90% Rh(III) removal efficiency within 3 h at a phase ratio of $10,000 \text{ mL g}^{-1}$, while the uptake of competing metal ions remained negligible (Fig. 4a). Following adsorption, the loaded POP-Py-OMe was digested with aqua regia to recover the sorbed metals. ICP-MS analysis revealed that more than 99% of the total metal content recovered from the adsorbent was Rh, confirming the material's exceptional selectivity for Rh(III) over a wide range of potential interferents. To assess the applicability of POP-Py-OMe for Rh recovery under realistic conditions, recovery experiment

was conducted using a simulated aqueous solution present in three-way catalysts (TWC)⁵⁷. The solution contained Rh^{3+} (2.57 ppm), along with background metal ions Pd^{2+} (13.64 ppm), Pt^{4+} (7.54 ppm), Mg^{2+} (851 ppm), Al^{3+} (7430 ppm), Ca^{2+} (116 ppm), Fe^{3+} (488 ppm), Zn^{2+} (33 ppm), Ba^{2+} (77 ppm), and Cr^{3+} (160 ppm), reflecting the composition of typical spent catalytic converter ceramic honeycombs. Other experimental conditions were consistent with those described above. Under these conditions, POP-Py-OMe was able to recover more than 99% of Rh(III), demonstrating its high selectivity and efficiency even in the presence of a complex mixture of competing metal ions (Supplementary Fig. 27).

The ability to completely recover and recycle adsorbents is essential for their practical deployment, especially when the materials involved are of high cost. Efficient regeneration not only improves sustainability but also ensures economic feasibility in large-scale applications. To this end, we first attempted to elute the Rh(III)-loaded adsorbents using an aqueous solution of 0.2 M thiourea, a method previously proven effective for desorbing Pd(II) and Pt(IV) from pyridyl-based polymeric adsorbents^{15,16}. However, the strong coordination affinity between the Rh(III) chloro-complexes and the pincer chelating sites significantly impeded Rh desorption, rendering this approach ineffective. Given this limitation, we explored a degradation-regeneration strategy based on the dynamic nature of the imine bonds. The Rh(III)-loaded p-POPs were treated in 1 M HCl aqueous solution at 50°C for 1 h to hydrolyze the imine-linked pincer sites and release the coordinated Rh(III) species into solution. Subsequently, the materials were filtered and neutralized with 0.1 M Na_2CO_3 solution to remove residual acid. The resulting recycled materials exhibited moderate Rh uptake capacities ($138\text{--}151 \text{ mg g}^{-1}$), which were comparable to that of

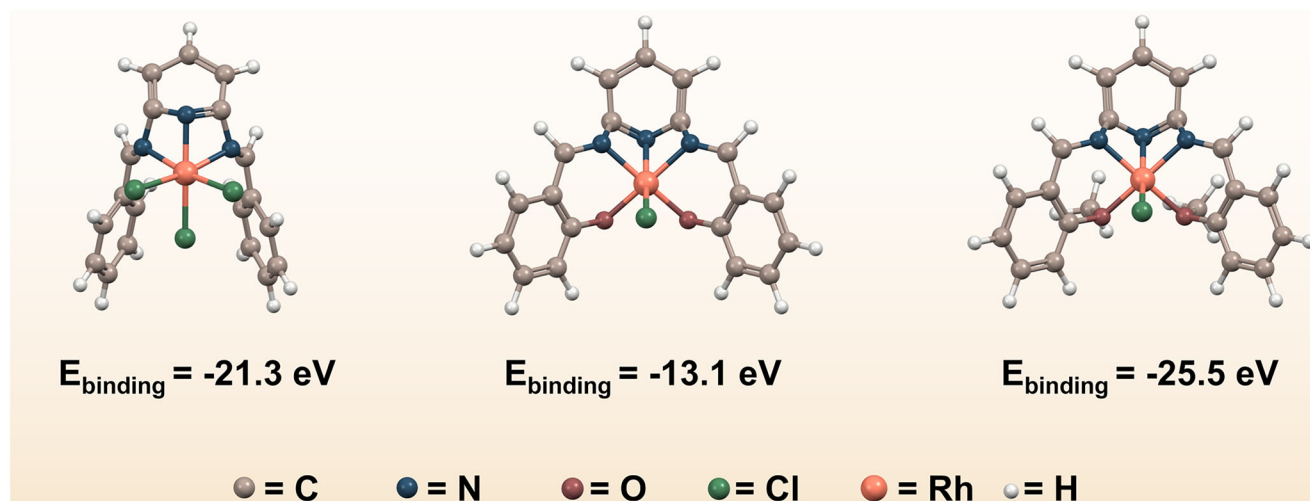


Fig. 5 | DFT optimized structures of rhodium complexes. DFT optimized structure of Rh@Py-H, Rh@Py-OH, and Rh@Py-OMe, along with their corresponding calculated binding energies, computed using the PBE0 functional with the def2-SVP basis set.

the precursor POP-*o*2NH₂-Py (140 mg g⁻¹), as shown in Fig. 4b. FT-IR analysis confirmed that all p-POPs were structurally converted back to the parent POP-*o*2NH₂-Py after acid treatment, verifying the successful cleavage of the pincer framework and the feasibility of adsorbent recovery (Supplementary Figs. 28–30).

Building on this, we developed a regeneration route for POP-Py-OMe (Fig. 4c). After releasing Rh(III) via acid hydrolysis, the resulting POP-*o*2NH₂-Py reacted with 2-methoxybenzaldehyde and catalytic acetic acid under mechanochemical milling to restore POP-Py-OMe. The regenerated material exhibited the same chemical structure as the original POP-Py-OMe and maintained its Rh(III) uptake performance over at least five regeneration cycles (Fig. 4c and Supplementary Figs. 28–30). This solvent-free, rapid, and sustainable approach offers an effective route for Rh(III) recovery and adsorbent reuse.

Binding mechanism investigation

To elucidate the interaction mechanism between Rh(III) and the p-POPs, FT-IR spectroscopy was performed on both pristine and Rh-loaded samples. All Rh-loaded materials, Rh@POP-Py-H, Rh@POP-Py-OH, and Rh@POP-Py-OMe, exhibited a new absorption peak around 1572 cm⁻¹, corresponding to the C=N stretching region, along with enhanced aromatic ring vibrations in the 1445–1450 cm⁻¹ range (Supplementary Figs. 31–33). These spectral features suggest the formation of Rh–N coordination bonds and indicate a denser material structure, consistent with coordination-driven packing behavior between Rh(III) and the pincer chelators. Further insights into the structural and morphological changes upon Rh(III) binding were obtained from SEM and TEM imaging (Supplementary Figs. 34–35), which confirmed that the overall framework integrity of the p-POPs was preserved after interaction with [RhCl₆]³⁻. Additionally, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), coupled with energy-dispersive X-ray spectroscopy (EDX), revealed a uniform distribution of Rh throughout the polymer matrix (Supplementary Figs. 36–38). This homogeneous dispersion of Rh(III) ions provides direct evidence for strong and well-dispersed binding interactions between the metal ions and the pincer-functionalized adsorbents.

X-ray photoelectron spectroscopy (XPS) profiles were collected to examine the rhodium binding environments in the adsorbents. The Rh 3*d* XPS spectra of NaRhCl₆ before and after adsorption are shown in Supplementary Figs. 39–41. For the pristine NaRhCl₆, the Rh 3*d*_{5/2} and 3*d*_{3/2} peaks appear at -310.1 eV and -314.9 eV, respectively, consistent with Rh³⁺ in a chloride-coordinated environment. Upon adsorption by the p-POPs, both Rh 3*d* peaks shift toward lower binding energies,

indicating increased electron density at the Rh centers. This shift arises from partial electron donation from the coordinating sites, which lowers the effective oxidation state of Rh³⁺ and enhances the stability of the resulting metal–ligand complexes. The magnitude of the shift further reflects the strong coordination between the Rh centers and the chelating groups of the adsorbates. Consistently, the N 1*s* peaks in all samples shift toward higher binding energies upon Rh coordination, with the largest shift observed for POP-Py-OMe (from 398.5 to 399.4 eV), indicating stronger coordination interactions between the nitrogen donor sites and Rh centers. Meanwhile, the O 1*s* peaks in POP-Py-OH and POP-Py-OMe shift to lower binding energies upon adsorption, with POP-Py-OMe exhibiting a more pronounced shift (from 532.8 to 531.7 eV) compared to POP-Py-OH (from 532.1 to 531.8 eV). These downward shifts suggest additional electron donation from the oxygen-containing functional groups to the Rh centers, which increases the electron density around the metal and stabilizes the resulting complexes. The larger shifts in POP-Py-OMe indicate that its methoxy substituents enhance electron donation, leading to stronger Rh–ligand interactions relative to POP-Py-OH. Overall, these XPS observations are in line with previous studies on N, O-donor Rh complexes⁵⁸, which demonstrated that strong donor ligands enhance Rh electron density and stabilize high oxidation states. The characteristic spectroscopic signatures in such systems highlight the importance of donor strength and geometry in tuning Rh–ligand interactions. Similarly, the shifts in Rh 3*d*, N 1*s*, and O 1*s* binding energies in our p-POPs reflect variations in ligand-to-metal electron donation, with methoxy-substituted POP-Py-OMe providing the strongest stabilizing environment.

To gain deeper insight into the local coordination environment of Rh within the adsorbents, X-ray absorption fine structure (XAFS) spectroscopy was conducted. The extended X-ray absorption fine structure (EXAFS) spectra were fitted using theoretical scattering paths calculated by FEFF 6, based on structural models derived from small molecule analogs shown in Fig. 5 (Supplementary Fig. 42 and Supplementary Table 9). EXAFS fitting results consistently indicate that Rh is three-fold coordinated to nitrogen atoms in all samples, in agreement with the XPS observation of N 1*s* shifts, which reflect active participation of nitrogen donor sites. In Rh@POP-Py-H, Rh is three-fold coordinated to chlorine atoms, whereas in Rh@POP-Py-OH and Rh@POP-Py-OMe, Rh exhibits one-fold coordination to chlorine and two-fold coordination to oxygen atoms from the functionalized groups. These variations in the coordination sphere are consistent with the XPS-derived binding energy shifts, where stronger electron donation from oxygen atoms in POP-Py-OMe corresponds to more

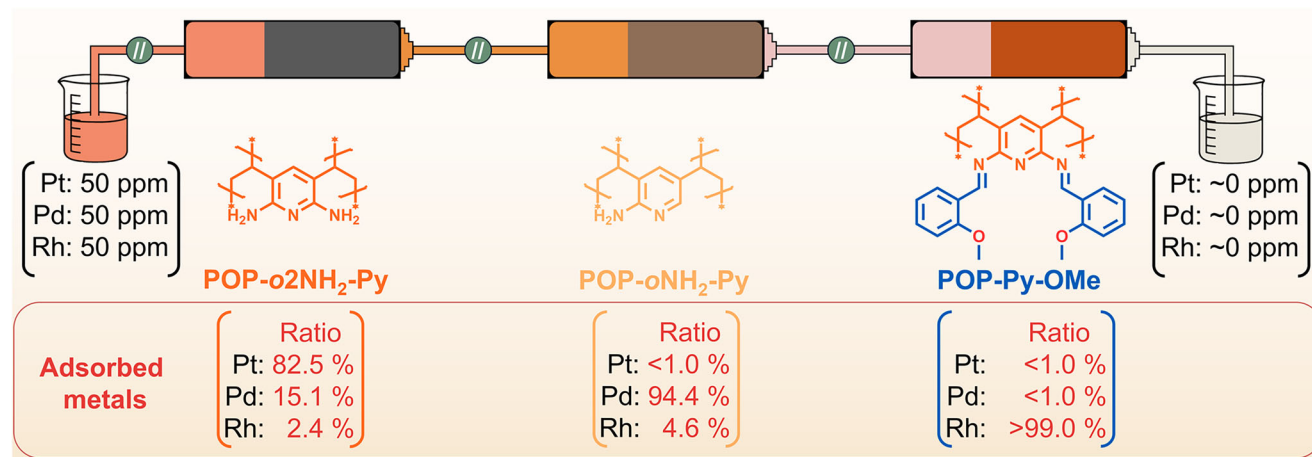


Fig. 6 | Sequential recovery of the three major PGMs (Pd, Pt, and Rh). Breakthrough experiment setup employing three syringes packed in series with POP-o2NH₂-Py, POP-oNH₂-Py, and POP-Py-OMe, enabling the sequential separation and recovery of Pt, Pd, and Rh.

pronounced stabilization of the Rh centers. Minor features at higher *R* values in the EXAFS spectra further indicate contributions from longer-range scattering. The refined coordination numbers corroborate a local Rh(III) environment comprising a mixed coordination sphere of N, Cl, and O atoms. Collectively, these findings reveal distinct Rh(III) binding modes in different p-POPs and highlight the role of functional groups in modulating the Rh coordination environment, which ultimately governs adsorption performance.

Density functional theory (DFT) calculations were conducted to explore how ortho-substituents on the aryl ring influence [RhCl₆]³⁻ binding in pincer-based nanotraps. The calculated binding energies showed a clear trend, with Rh@Py-OMe (−25.5 eV) exhibiting the strongest binding, followed by Rh@Py-H (−21.3 eV), and then Rh@Py-OH (−13.1 eV) (Fig. 5). The enhanced [RhCl₆]³⁻ affinity of POP-Py-OMe is attributed to the electron-donating −OMe group, which increases electron density at the imine nitrogen, thereby strengthening coordination. In contrast, the −OH group in POP-Py-OH, although potentially electron-donating, tends to form intramolecular hydrogen bonding with the adjacent imine nitrogen⁵⁹. This interaction, together with possible solvation effects in aqueous media, reduces the availability of the donor site for Rh binding and weakens the overall coordination strength. These findings underscore the importance of ortho-substituent effects in modulating the local electronic environment of pincer ligands and optimizing metal sorption performance.

Selective separation of PGMs

Based on these experimental results, we systematically evaluated the separation performance of platinum-group metals (PGMs) using the p-POP materials. We first investigated the Pd and Pt uptake capacities of all three p-POPs through batch adsorption experiments. POP-Py-OMe exhibited competitive sorption capacities compared with our previously reported POP-based adsorbents, achieving Pd and Pt uptakes of 729 mg g^{−1} and 369 mg g^{−1}, respectively¹⁶ (Supplementary Figs. 43–44), indicating a strong affinity of the pincer-coordinated sites toward PGMs. Subsequently, a bench-scale breakthrough experiment was conducted using POP-Py-OMe as the column filler to assess its ability to separate Pd, Pt, and Rh, which are commonly present in TWC⁵⁷. Analysis of the collected effluent fractions showed that Pd, Pt, and Rh were eluted within a narrow and overlapping time window, insufficient for effective separation or obtaining individual metals in high purity (Supplementary Fig. 45).

Building on these results and our previous success in selectively separating Pd and Pt, we further explored a sequential extraction strategy. A breakthrough experiment was conducted using three

syringes packed in series with POP-o2NH₂-Py, POP-oNH₂-Py, and POP-Py-OMe (Fig. 6), enabling stepwise selective capture. This sequence was guided by adsorption isotherm studies, which showed that POP-o2NH₂-Py and POP-oNH₂-Py have weaker affinity for Rh than for Pd and Pt (Supplementary Fig. 1), with POP-oNH₂-Py favoring Pd over Pt and POP-o2NH₂-Py exhibiting the opposite selectivity¹⁶, reflecting the influence of their coordination environments and stabilizing interactions. POP-Py-OMe, bearing a pincer-type chelator, binds all three PGMs strongly but shows a distinctive preference for Rh, whereas hydrogen-bond stabilization in POP-o2NH₂-Py enhances its selectivity for Pt over Pd. These complementary behaviors support their ordered arrangement for efficient stepwise separation of Pd, Pt, and Rh. ICP-MS analysis of the final filtrate showed that over 99.99% of the metals were effectively captured. Subsequent digestion and analysis of each adsorbent revealed distinct separation efficiencies: POP-o2NH₂-Py retained 82.5% of Pt, 15.1% of Pd, and 2.4% of Rh; POP-oNH₂-Py captured 94.4% of Pd, less than 1.0% of Pt, and 4.6% of Rh; and POP-Py-OMe finally retained over 99.0% of Rh, with only trace Pt and Pd detected. This stepwise approach demonstrates effective, sequential separation and recovery of Pt, Pd, and Rh, building upon our prior work in Pd and Pt selective recovery and extending it to a comprehensive multi-metal extraction system.

Discussion

In summary, we developed a series of p-POP-based adsorbents incorporating pincer-type chelators, designed to achieve highly efficient and selective uptake of Rh(III) ions even from complex leachate solutions, owing to their superior binding affinity toward [RhCl₆]³⁻ compared to conventional monodentate-chelating adsorbents. These pincer-functionalized nanotraps were installed via a green, solvent-free mechanochemical strategy, providing a scalable and sustainable platform for advanced sorbent construction, while also enabling facile release of sorbed Rh(III) and regeneration of the p-POPs. Importantly, the material cost can be maintained below \$40 g^{−1}, and each regeneration needs only ~\$5, offering a highly favorable cost-to-performance ratio given the value of Rh captured per cycle (Supplementary Table 10). This combination of high efficiency, selectivity, and economic feasibility highlights the practical potential of the system for industrial recovery of PGMs, and ongoing advances in synthetic strategies and material design are expected to further enhance scalability and cost-effectiveness. Among them, POP-Py-OMe, bearing electron-donating −OMe substituents, demonstrated both high uptake capacity and rapid sequestration kinetics for Rh(III) from aqueous solutions. The underlying reasons for this superior performance were elucidated

through a combination of morphological and structural characterizations, spectroscopic analysis, and DFT calculations, which revealed enhanced Rh–ligand interactions facilitated by the electronic environment of the pincer site. Building on our previous success in achieving selective separation and recovery of Pd and Pt, this study puts the final piece of the puzzle into place by demonstrating the selective capture of Rh(III), thereby completing a modular strategy for recycling all three major platinum group metals (PGMs) from spent TWC leaching solution. This proof-of-concept work provides a practical and versatile platform for the design of next-generation POP-based adsorbents aimed at sustainable PGM recovery from industrial leachates and waste streams.

Methods

Materials and measurements

Solvents and other commercially available reagents were purchased from Fisher Scientific and Sigma-Aldrich and used without further purification. The Rh(III) stock solution was prepared by dissolving the appropriate amount of Na_3RhCl_6 in deionized water. Deionized water used in all of the experiments was obtained from a Milli-Q water purification system. Nitrogen sorption isotherms at 77 K were measured using Micromeritics ASAP 2020 M and Tristar system. The samples were outgassed for 12 h at 373 K before the measurements. The Powder X-ray diffraction (PXRD) data were collected on a PANalytical Empyrean diffractometer (40 kV, 40 mA) using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. FT-IR spectra were recorded on a Nicolet Nexus iS50 ATR-IR instrument. Thermogravimetric analysis (TGA) measurements were taken under a nitrogen atmosphere with a ramping rate of $10^\circ\text{C min}^{-1}$ from 25°C to 800°C by using a TGA Q50 thermogravimetric analyzer. Scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) studies were performed at a Zeiss Auriga Crossbeam FIB-SEM. Transmission electron microscopy (TEM) images and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected on a Fisher Scientific Spectra 300. X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with Al $\text{K}\alpha$ irradiation at $\theta = 90^\circ$ for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV . Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a Perkin-Elmer Elan DRC II Quadrupole Inductively Coupled Plasma Mass Spectrometer. ^{13}C (125 MHz) cross-polarization magic-angle spinning (CP-MAS) was recorded on a Bruker Avance 500 spectrometer equipped with a magic-angle spin probe in a 4-mm (^{13}C) ZrO_2 rotor. ^1H NMR (400 MHz) spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts are expressed in ppm downfield from TMS at $\delta = 0 \text{ ppm}$, and J values are given in Hz. X-ray absorption fine structure (XAFS) experiments were performed at Sector 10 on the insertion device line operated by the Materials Research Collaborative Access Team (MRCAT)⁶⁰. Measurements were performed in transmission on pure materials in Kapton tape. XAFS data processing and analysis were done using the IFEFFIT suite of programs⁶¹. Initial estimates of the threshold energy values (E_0) were obtained via the inflection point in the normalized absorption edges. A Hanning window was applied to a selected k -range ($3\text{--}10.8 \text{ \AA}^{-1}$) to obtain the Fourier transformed extended XAFS (EXAFS) data.

Synthesis of 3,5-divinylpyridin-2,6-amine. To a solution of 2,6-diaminopyridine (10.9 g, 100 mmol) in glacial acetic acid (200 mL), bromine (11.4 mL) was added dropwise at 0°C . After stirring at room temperature for 5 h, the reaction mixture was treated with an aqueous Na_2SO_3 solution to quench excess bromine. The resulting mixture was neutralized to pH 8–9 using NaOH, followed by filtration, washing, and drying to afford 3,5-dibromo-2,6-pyridinediamine as a light white powder. Next, 3,5-dibromo-2,6-pyridinediamine (1.068 g, 4 mmol), potassium vinyltrifluoroborate (1.32 g, 9.6 mmol), K_2CO_3 (1.6 g,

12 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.116 g, 0.1 mmol) were dissolved in a mixture of 1,4-dioxane (40 mL) and H_2O (10 mL). The reaction mixture was refluxed at 100°C under a nitrogen atmosphere for 48 h. Upon completion, the reaction was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure to afford the crude product. The product was purified by flash chromatography using hexane/ethyl acetate (2:1, v/v) containing 1% triethylamine as eluent to yield the title compound as a yellow powder (1.23 g, 84%). ^1H NMR (400 MHz, DMSO-d_6 , 298 K, TMS): 7.56 (s, 1H), 6.67–6.73 (m, 2H), 5.68 (m, 4H), 5.39–5.43 (m, 2H), 4.89–4.91 (m, 2H) ppm (Supplementary Fig. 46).

Synthesis of POP-o2NH₂-Py. 3,5-Divinylpyridin-2,6-amine (1.0 g) was dissolved in DMF (10 mL), followed by the addition of the free radical initiator azobisisobutyronitrile (AIBN, 0.025 g). The resulting mixture was transferred to an autoclave and heated at 100°C for 24 h. After cooling, the polymer was isolated as a brown solid in nearly quantitative yield by extracting the DMF with ethanol and subsequently drying under vacuum at 50°C for 24 h.

Synthesis of p-POPs. Three p-POPs were synthesized by mechanochemical condensation of POP-o2NH₂-Py (200 mg, containing 2.48 mmol of $-\text{NH}_2$ groups) with various aldehydes. The POP-o2NH₂-Py was loaded into a 10 mL zirconia milling jar with three zirconia balls (10 mm diameter, ~3 g), followed by the addition of an excess of benzaldehyde (526.4 mg, 4.96 mmol), 2-hydroxybenzaldehyde (605.7 mg, 4.96 mmol), or 2-methoxybenzaldehyde (675.3 mg, 4.96 mmol). 20 μL glacial acetic acid was added as a catalyst, and the mixture was milled at 25 Hz for 30 min (Retsch MM 400 Mixer Mill)⁶². The polymer was isolated, washed with ethanol, and dried under vacuum at 50°C for 24 h, affording three distinct p-POPs: POP-Py-H, POP-Py-OH, and POP-Py-OMe.

Rhodium sorption experiments. Aqueous solutions with varying rhodium concentrations were prepared by diluting a stock Na_3RhCl_6 solution with appropriate amounts of distilled water, unless otherwise specified. All sorbents were activated by heat under vacuum prior to the adsorption experiments. Rhodium concentrations in all experiments were determined using ICP-MS. All adsorption experiments were conducted under ambient conditions. For each sorption experiment, the rhodium concentration in the absence of sorbent material was measured and used as a negative control.

Rhodium sorption isotherms. To obtain Rh(III) adsorption isotherms for various adsorbents, 5 mg of each sorbent material was added to 10 mL of aqueous Rh(III) solutions with concentrations ranging from 10 to 600 ppm. The suspensions were briefly sonicated to ensure uniform dispersion of the adsorbents, followed by vigorous stirring to allow the adsorption process to reach equilibrium. After a 4 h contact time to reach equilibrium, the mixtures were filtered through a 0.45 μm membrane filter, and the supernatants were analyzed by ICP-MS to determine the remaining Rh(III) concentrations. The adsorbed amount at equilibrium (q_e , mg g^{-1}) was calculated by:

$$q_e(\text{mg g}^{-1}) = (C_i - C_e) \times V / m \quad (1)$$

where V is the volume of the treated solution (mL) and m is the amount of used adsorbent (mg), and C_i and C_e are the initial concentration and the final equilibrium concentration of rhodium, respectively.

Rhodium sorption kinetics from distilled water. Rhodium aqueous solution (400 mL, 20 ppm) and adsorbents (5 mg) were added to an Erlenmeyer flask equipped with a magnetic stir bar. The mixture was stirred at room temperature for 2.5 h. At appropriate time intervals, 5 mL aliquots were withdrawn and immediately filtered through a

0.45 μm membrane syringe filter to separate the adsorbent. The rhodium concentrations in the filtrates were analyzed by ICP-MS. The adsorption capacity at each time point was calculated using the following equation:

$$\text{Adsorption capacity (mg g}^{-1}\text{)} = (C_i - C_t) \times V/m \quad (2)$$

where V is the volume of the treated solution (mL) and m is the amount of used adsorbent (mg), and C_i and C_t are the initial concentration and the concentration of rhodium at t (h), respectively.

Rhodium removal kinetics

An Rh(III) aqueous solution (200 mL, 7.1 ppm) and adsorbent (20 mg) were added to an Erlenmeyer flask and stirred continuously. At pre-determined time intervals, 3 mL aliquots were withdrawn and filtered through a 0.45 μm syringe filter to remove the adsorbent. The Rh(III) concentrations in the filtrates were then analyzed by ICP-MS. The removal efficiency and adsorption capacity of Rh(III) were calculated as follows:

$$\text{Removal percentage (\%)} = 100 \times (C_i - C_t)/C_i \quad (3)$$

$$\text{Adsorption capacity (mg g}^{-1}\text{)} = (C_i - C_t) \times V/m \quad (4)$$

where V is the volume of the treated solution (mL) and m is the amount of used adsorbent (mg), and C_i and C_t are the initial concentration and the concentration of rhodium at t (h), respectively.

K_d value calculation. The distribution coefficient (K_d) value as used for the determination of the affinity of sorbents for Rh(III), is given by the equation:

$$K_d = \left(\frac{C_0 - C_e}{C_e} \right) \times \frac{V}{m} \quad (5)$$

where V is the volume of the treated solution (mL), m is the amount of adsorbent (g), C_0 is the initial concentration of rhodium, and C_e is the equilibrium concentration of rhodium.

Selectivity tests. To a 100 mL of distilled water spiked with $[\text{RhCl}_6]^{3-}$, Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ga^{3+} , Sr^{2+} , Cd^{2+} , In^{3+} , and Pb^{2+} at approximately 10 ppm each, various sorbent materials (10 mg) were added in an Erlenmeyer flask equipped with a magnetic stir bar. The mixture was stirred at room temperature for 6 h. Afterward, aliquots were withdrawn and filtered through a 0.45 μm syringe filter to remove the sorbent. The concentrations of metal ions in the filtrates were analyzed by ICP-MS.

Regeneration of POP-Py-OMe. The Rh-loaded POP-Py-OMe (Rh@POP-Py-OMe) was treated with 1 M HCl aqueous solution at 50 $^\circ\text{C}$ for 1 h to hydrolyze the imine-linked pincer sites and release the coordinated Rh(III) species into solution. The resulting solid was then filtered and neutralized with 0.1 M Na_2CO_3 solution to remove residual acid. The recovered POP-*o*- 2NH_2 -Py was subsequently reacted with an excess of 2-methoxybenzaldehyde and a catalytic amount of acetic acid under mechanochemical milling to regenerate POP-Py-OMe.

Breakthrough test. To simulate a flow-through system, 100 mg each of POP-*o*- 2NH_2 -Py, POP-*o*- NH_2 -Py, and POP-Py-OMe were individually packed into separate 1 mL syringes to form sequential separation columns. A 50 mL ternary metal solution containing 50 ppm each of Pt, Pd, and Rh was passed through the first syringe using a syringe pump at a flow rate of 50 mL h^{-1} . The filtrate from the first syringe was

subsequently passed through the second syringe and finally through the third syringe. This sequential setup enabled the stepwise separation and recovery of Pt, Pd, and Rh.

DFT calculation

The geometries of $[\text{RhCl}_6]^{3-}$ and the pincer-functionalized ligand complexes were optimized using density functional theory (DFT) with the PBE0 functional⁶³. The def2-SVP basis set⁶⁴ was employed for light atoms, while the Stuttgart-Dresden (SDD) effective core potential⁶⁵ was applied to account for the outer-shell orbitals and relativistic effects of the Rh atom. All DFT calculations were carried out using the Gaussian 16 software package.

Data availability

The authors declare that all the data supporting the findings of this study are available within the article (and Supplementary Information files). Additional data are available from the corresponding author upon request. Source Data are provided with this manuscript. Source data are provided with this paper.

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Author contributions

Y.S., N.W., and S.M. conceived and designed the research. Y.S., J.R., H.W., W.F., and T.A. carried out material synthesis, characterization, and adsorption experiments. Y.S. also performed density functional theory (DFT) calculations. J.T.W. and R.W.M. performed the XAFS

measurements and data analysis. All authors participated in drafting the paper and gave approval to the final version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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