

Research Progress in the Pd Recovery by Organic Porous Materials

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Abstract. Palladium (Pd), as a strategic resource, plays an irreplaceable role in the fields of industrial catalysis, electronics manufacturing, and nuclear energy. The recovery of palladium isotopes from spent fuel not only holds significant economic value, but also represents component of the safe disposal of spent fuel. So far, porous organic polymers (POPs) have shown significant promise due to their selectivity and ability to withstand harsh conditions. Covalent organic frameworks (COFs) are also a promising porous material platform with a variety of applications, including separation and sensing. This article systematically summarizes recent advancements in selective recovery of palladium based on covalent organic frameworks and porous organic polymers, with a focus on material design strategies, adsorption mechanisms, and practical application performance.

Keywords: Pd recovery; adsorption; organic porous materials.

1. Introduction

Palladium (Pd), as an important member of platinum-group metals (PGMs), plays an irreplaceable role in fields such as automotive exhaust purification, electronics, pharmaceutical catalysis, and nuclear energy due to its excellent catalytic performance, and corrosion resistance.^[1] However, the extremely low abundance of Pd in the Earth's crust (~0.001 ppm) and the global reliance on limited mineral resources of South Africa and Russia highlight their increasing scarcity.^[2] Meanwhile, the recovery of Pd from nuclear waste, such as highly acidic extract produced during the reprocessing of spent nuclear fuel, is not only critical for sustainable utilization of resource, but also essential for reducing the risk of radioactive contamination.^{[3][4][5]} Traditional hydrometallurgical technologies face major challenges such as excessive reagent consumption, low selectivity and secondary pollution in extreme nuclear waste environments (such as strong acidity, high radiation and ion coexistence).^[6] This necessitates the development of efficient, stable and environmentally friendly adsorbents. Therefore, extracting Pd from spent fuel is regarded as a promising alternative method to obtain a large amount of Pd. However, the extractant is highly prone to decomposition under extreme conditions such as high acidity, strong radioactivity and high temperature. Furthermore, the chemical composition of UNF is extremely complex, as fresh UNF contains over 40 elements and more than 1,500 nuclides.^[7] The coexisting metal ions, especially Ni, Cd and Ag with chemical properties similar to palladium, significantly reduce the solvent extraction efficiency. Therefore, considering the integration of sufficient stability, selectivity, volume and solubility in an extractant, achieving high separation capacity is a formidable challenge.^[8]

In recent years, porous organic materials—including porous organic polymers (POPs), covalent organic frameworks (COFs)^[9], and macrocyclic polymers have emerged as research hotspots in palladium recovery. These materials, through the rational design of functional monomers, have achieved the specific recognition and efficient capture of Pd²⁺, while demonstrating outstanding chemical stability and recyclability. This paper summarizes groundbreaking advances in the field, with a focus on material design strategies, adsorption mechanisms, and performance optimization under extreme conditions, aiming to provide theoretical insights for future Pd recovery technologies.

Conventional palladium recovery methods (e.g., solvent extraction and ion exchange) are difficult to achieve in strongly acidic nuclear waste: high H⁺ concentration and competing ions (such as Ag⁺, Fe⁺) seriously interfere with adsorption; radiation causes structural degradation; the toxic emissions from chemical leaching have increased the environmental burden. In contrast, porous organic

materials exhibit unique advantages. For instance, structural tunability: precise control of pore size, surface charge and coordination environment through monomer selection and post-synthesis modification.^[10] High stability: The covalent bond framework endows it with acid resistance and radiation resistance.^[11] Multi-functionality^{[12][13][14][15]}: The integration of sensing and adsorption functions enables real-time monitoring and resource recovery. Persistent organic compounds based on pyridine, such as POP-*o*NH₂-Py developed by the Aguila team,^[16] significantly enhanced the adsorption capacity (752 mg g⁻¹) and selectivity of Pd through ortho-amino functionalization. Single crystal X-ray analysis revealed that the intramolecular hydrogen bond between the amino group and the coordinating chloride ion stabilized the Pd-N coordination and reduced the concentration of Pd²⁺ to the ppb level within 10 minutes. The electron-donating effect of the amino group further enhances the nucleophilicity of pyridine and optimizes the adsorption kinetics. These materials still maintain an efficiency of over 90% after 10 recycling cycles, highlighting their industrial potential.

COFs have ordered channels and pre-organized binding sites, providing an ideal platform for the precise capture of Pd. For example, Wang's team designed COF -TzDa, which has an adsorption capacity of 265.4 mg g⁻¹ for 3 M HNO₃ and a selectivity coefficient (*K_d*) of 10⁵ mL g⁻¹ for Ag⁺.^[17] Synchrotron X-ray studies have shown that Pd²⁺ forms a planar four-coordination geometry with the carbonyl oxygen and nitrate ions of adjacent layers, where interlayer contractions "lock" Pd²⁺, highlighting topology-driven performance modulation. Zhong's team further synthesized multi-component COFs through in-situ methods, using the steric hindrance of substituents to adjust the pore size, and achieved the uptake of 112 mg g⁻¹ Pd in 3 M hydrochloric acid. This is a new strategy for separating Pd in complex matrices.

Combining large rings such as columnar aromatics has opened up new avenues for improving selectivity and stability. Wang's research team reported that the pillar[5]arene-based covalent organic polymer (P5COP-m-BPT) has a Pd adsorption capacity of 403 mg g⁻¹ in 3 M HNO₃ and an anti-radiation capacity of up to 500 kGy.^[18] The single crystal structure confirmed that Pd²⁺ adopted a planar quadrilateral geometry with pyridine triazole groups, while the aromatics nodes of the pre-organized pillar[5]arene nodes suppress the competition of Ag⁺ (*SF*_{Pd/Ag} = 797). The dynamic column experiment verified the actual efficiency. After 10 adsorption-desorption cycles of HCl/ thiourea elution, the retention rate of was > 95%.

Therefore, porous organic materials, through precise engineering at the molecular level, are overcoming traditional limitations and providing innovative solutions for the value-added and sustainable development of nuclear waste. This article systematically reviews the recent progress to inform about future research directions and technological breakthroughs.

2. Advance in the Pd recovery by organic porous materials

In 2020, The Aguila' group designed a pyridine-based porous organic polymer (POP) nanotrap for the efficient recovery of palladium from industrial wastewater.^[16] To address the scarcity of platinum-group elements (PGEs) and the environmental burden of the traditional recycling process, they synthesized three functionalized POP materials—POP-Py (amino-free), POP-*p*NH₂-Py (para-amino-modified), and POP-*o*NH₂-Py (ortho-amino-modified)—through structural adjustment and functional group engineering. Systematic investigation into the positional effects of amino groups have revealed their critical role in Pd adsorption, providing key insights for the rational design of high-efficiency adsorbents. As shown in Figure 1, POP-*p*NH₂-Py and POP-*o*NH₂-Py can complex with palladium salt and single-crystal were obtained, named as Pd- *p*NH₂-Py and Pd- *o*NH₂-Py.

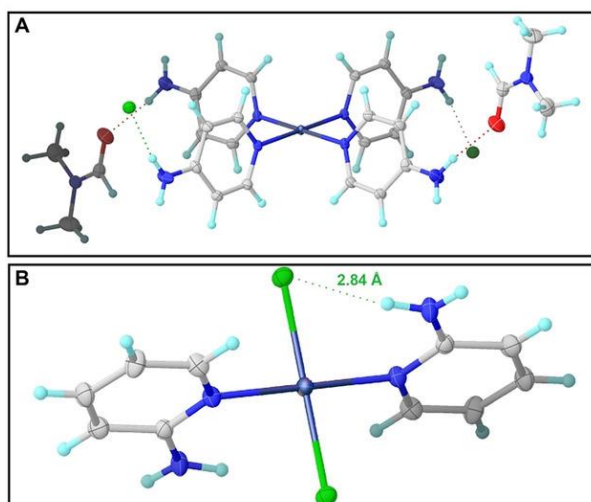


Figure 1. Single-crystal structures of A) Pd-*p*NH₂-Py and B) Pd-*o*NH₂-Py

The POP material was prepared via free radical polymerization, and amino groups were introduced to regulate the electronic properties of the pyridine unit. The nitrogen adsorption experiments show that the specific surface areas of POP-Py, POP-*p*NH₂-Py and POP-*o*NH₂-Py are 979, 536 and 359 m²/g, respectively. Although the ortho-amino-modified POP-*o*NH₂-Py reduced the surface area due to amino functionalization, it still exhibited excellent Pd adsorption performance: a record-breaking high capacity of 752 mg/g, exceeding traditional adsorbents (such as silicon-based materials, metal-organic frameworks). The Pd concentration was rapidly reduced from 5 ppm to 0.29 ppb within 10 minutes, fitting the quasi-second-order kinetic model ($R^2 > 0.99$), indicating that chemical adsorption is the rate-limiting step. Mechanism analysis indicates that the electron-donating effect of the amino group enhances the nucleophilicity of pyridine nitrogen, while the ortho amino group stabilizes the Pd-Cl complex through intramolecular hydrogen bonds. Single crystal X-ray data confirmed shorter Pd-Cl bond lengths (2.25 Å vs. 2.29 Å para-amino analogues), verifying the structural stability induced by hydrogen bonds. In the mixed solution containing competing ions (Fe²⁺, Zn²⁺, Pb²⁺, etc., each at 5 ppm), the selectivity of POP-*o*NH₂-Py for Pd reached 99.9%, with a residual concentration of 1.02 ppb, which was significantly better than that of POP-*p*NH₂-Py (188 ppb). The thiourea/hydrochloric acid elution and regeneration test indicated that the adsorption capacity of POP-*o*NH₂-Py was completely restored (residual Pd: 0.1 ppb), while the performance of POP-*p*NH₂-Py declined due to its weak coordination stability (residual Pd: 29 ppb). XPS analysis confirmed reversible Pd-N coordination. The peak of n1s shifted from 399.3 eV (original) to 399.6 eV (Pd loaded) and recovered after regeneration. EDX plotting and FTIR spectroscopy further verified the uniform distribution of Pd-n bonding. Furthermore, this material still maintained a high adsorption efficiency under extreme pH conditions (pH 3 and pH 10). The residual Pd concentrations after soaking for 3 days were 2.08 ppb and 6.14 ppb, respectively, demonstrating good chemical stability.

Single-crystal and extended X-ray absorption fine structure (EXAFS) analyses revealed that ortho-amino groups stabilized Pd's tetrahedral coordination geometry (Pd-N₂Cl₂) via hydrogen bonding, while para-amino groups reduced coordination numbers due to steric hindrance. This structural distinction enhanced adsorption kinetics, capacity, and selectivity in complex systems. Dynamic column experiments further validated POP-*o*NH₂-Py's practical potential in continuous-flow systems, achieving a breakthrough capacity of 680 mg/g with no significant performance loss over five cycles. This design strategy is extendable to other PGEs (e.g., Pt, Rh), offering a novel approach to alleviate resource scarcity and advance green metallurgy. Future work will focus on scalable synthesis, mechanical strength optimization, and long-term stability testing under real industrial wastewater conditions.

In 2021, Yue's group designed a new bifunctional sp² carbon conjugated covalent organic framework (PY-SE-COF), which was synthesized through the Knoevenagel condensation of selenium-containing diazole monomers (TFPPY and SEA), achieving highly sensitive fluorescence

detection, efficient adsorption and palladium ion (Pd^{2+}) recovery.^[19] Figure 2 shows how PY-SE-COF was synthesized. This material features high crystallinity, large specific surface area ($998.03 \text{ m}^2\text{g}^{-1}$), ordered channels (pore size 2.64 nm), and excellent chemical stability under harsh conditions (pH 2-12, temperature up to $350 \text{ }^\circ\text{C}$). The fluorescence sensing experiment shows that under the excitation of 420 nm, PY-SE-COF can emit strong fluorescence at 575 nm. Pd^{2+} has high selectivity, with a detection limit of $0.45 \text{ }\mu\text{M}$, and the interference of other metal ions (dual concentrations) can be ignored. XPS analysis confirmed that Pd^{2+} coordinated with the Se and N atoms in the selenodiazole structure, inducing electron transfer and dynamic fluorescence quenching. In terms of adsorption performance, the removal of Pd^{2+} follows the quasi-second-order kinetic model ($R^2 > 0.9999$) and the Freundlich isothermal model ($R^2 = 0.9727$), with a maximum adsorption capacity of 4578.6 mg g^{-1} , which is significantly better than materials such as MOF-808 (163.9 mg g^{-1}). Selectivity stems from the specific coordination of the selenodiazole group with Pd^{2+} . It is notable that the adsorbed Pd^{2+} can be effectively recovered by HCl-thiourea solution, and the removal rate remains above 95% after 10 consecutive cycles. PXRD and FT-IR confirmed the integrity of the structure after regeneration. This work was the first to integrate the selenodiazole functional group into sp^2 carbon-conjugated COFs, achieving the integrated "detection-removal-recovery" function. It provides an innovative strategy for the synchronous monitoring and remediation of heavy metal pollutants in complex environments, and simultaneously expands the application potential of sp^2 carbon conjugated materials in environmental remediation.

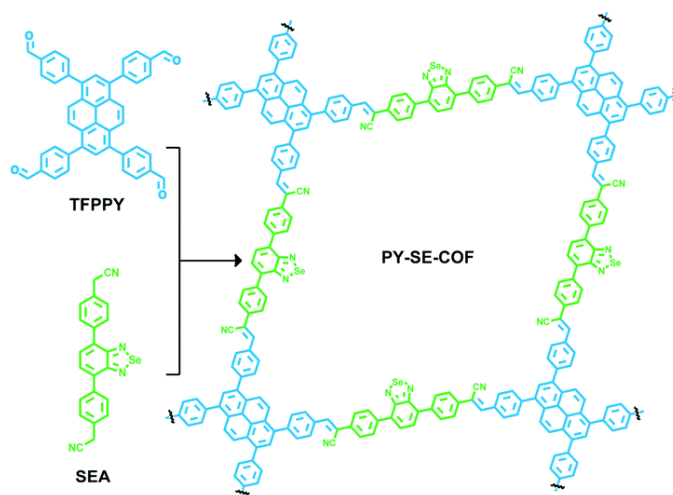


Figure 2. The synthesis route of PY-SE-COF

In 2022, to address the challenges of Pd recovery under harsh conditions (high acidity, strong radioactivity, and coexisting interfering ions), Yuan's group developed a two-dimensional covalent organic framework (COF TzDa). As seen in Figure 3, which is the top and side views of COF-TzDa. This material utilizes the cooperative coordination strategy of salicylaldehyde diamine functional groups and the adaptive interlayer π - π interaction to achieve the precise identification and efficient adsorption of Pd^{2+} .^[17] The experimental results show that it has excellent performance in 1 M HNO_3 : a removal efficiency of 99.8%, rapid equilibrium (120 min), and a maximum adsorption capacity of 265.4 mg/g (close to the theoretical value of 290.5 mg/g). This material exhibits significant stability under acidic conditions, β -ray irradiation and repeated cycles (with relatively small capacity loss after four adsorption-desorption cycles). The dynamic column separation experiment further verified the practicability of this method. Theoretical calculations show that Pd^{2+} (two carbonyl oxygen and two nitrate oxygen from adjacent layers) presents a planar four-coordination geometry, and the interlayer spacing decreases from 3.67 \AA to 2.96 \AA , enhancing the binding selectivity. This work provides a new strategy for recovering high-value metals from nuclear waste, which can be extended to other radionuclides or scarce elements.

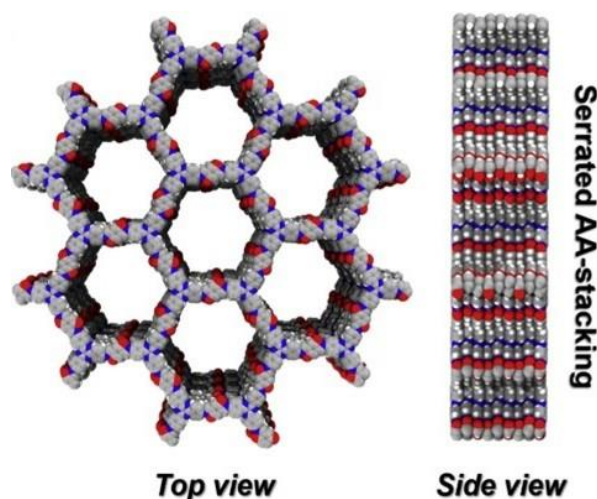


Figure 3. Top and side views of COF-TzDa

In the same year, Bai and her team successfully developed a new type of covalent organic framework (COF) -based material,^[8] COF-TzDa, which was designed for the efficient and selective adsorption of palladium (Pd^{2+}) from nuclear waste under strongly acidic conditions. Through its unique interlayer synergistic chelation mechanism, COF-TzDa breaks through the limitations of traditional solvent extraction methods, such as poor stability and selectivity of the extractant. Figure 4 shows why this material can exceptionally select Pd^{2+} and guarantee stability at the same time.

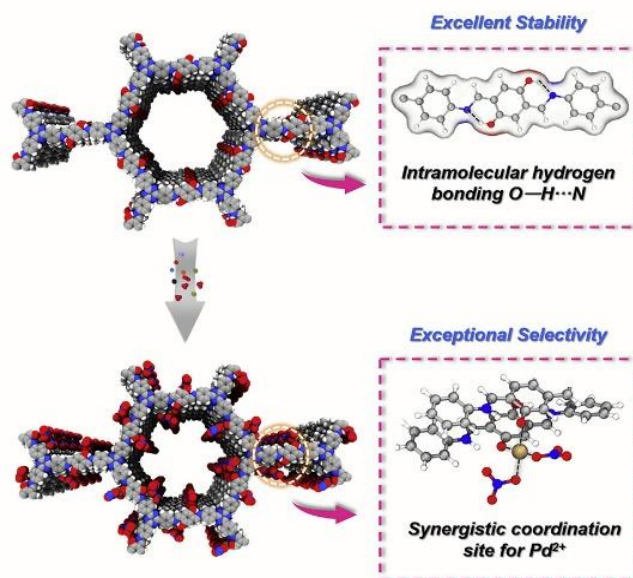


Figure 4. Stability and selectivity of COF-TzDa

Constructed through the Schieff base reaction between triazinyl monomer (Tz) and 2,5-dihydroxyterephthalic acid (Da), this material features high crystallinity, large specific surface area ($1426 \text{ m}^2/\text{g}$), and excellent acid resistance (tolerance to 1 M HNO_3). The innovation lies in the use of interlayer π - π stacking to form a rigid framework with local flexibility, and the planar four-tooth coordination of Pd^{2+} is achieved through the oxygen suppliers and free nitrate ions of adjacent layers. The experimental results show that COF-TzDa achieves 99.8% Pd removal within 30 minutes, and the maximum adsorption capacity in 1 M HNO_3 is 265.4 mg/g (close to the theoretical value of 290.5 mg/g), exceeding the existing adsorbents. In the dynamic column experiment simulating high-level waste liquid (HLLW, containing 17 competing ions), COF-TzDa achieved single-round Pd^{2+} enrichment with a capacity of 255.8 mg/g . The use of thiourea can achieve efficient regeneration (with a desorption efficiency of 98.48%), and the material still maintains an adsorption capacity of

84% after 4 cycles. It is notable that it can still maintain structural integrity and performance under a radiation dose of up to 1,000 kGy. Mechanism studies have shown that Pd^{2+} adsorption triggers the tautomerism from enols to ketones and enhances coordination through oxygen suppliers. XPS and DFT calculations confirmed a planar coordination model involving two oxygen atoms and two nitrate ions in adjacent layers, with the layer spacing adaptively adjusted to 2.96 Å. The PXRD simulation was consistent with the experimental data, verifying the ordered distribution of Pd^{2+} in the pore channels. This work not only provides a powerful strategy for recovering palladium from nuclear waste, but also highlights the potential of interlayer synergy in selective metal ion capture, offering new approaches for environmental remediation and resource extraction in complex matrices.

In 2023, Wang's group designed a macrocyclic nitrogen-rich covalent organic polymer (COP) material containing pillar[5]arene for the super-selective and efficient capture of palladium (Pd(II)) from highly acidic and highly radioactive waste liquid (HLLW).^[18] By integrating the pyridinyl and triazole functional groups into the macrocyclic framework, three COP materials (P5COP-m-BPT, P5COP-o-BPT and P5COP-BP) were designed and synthesized as shown in Figure 5a.

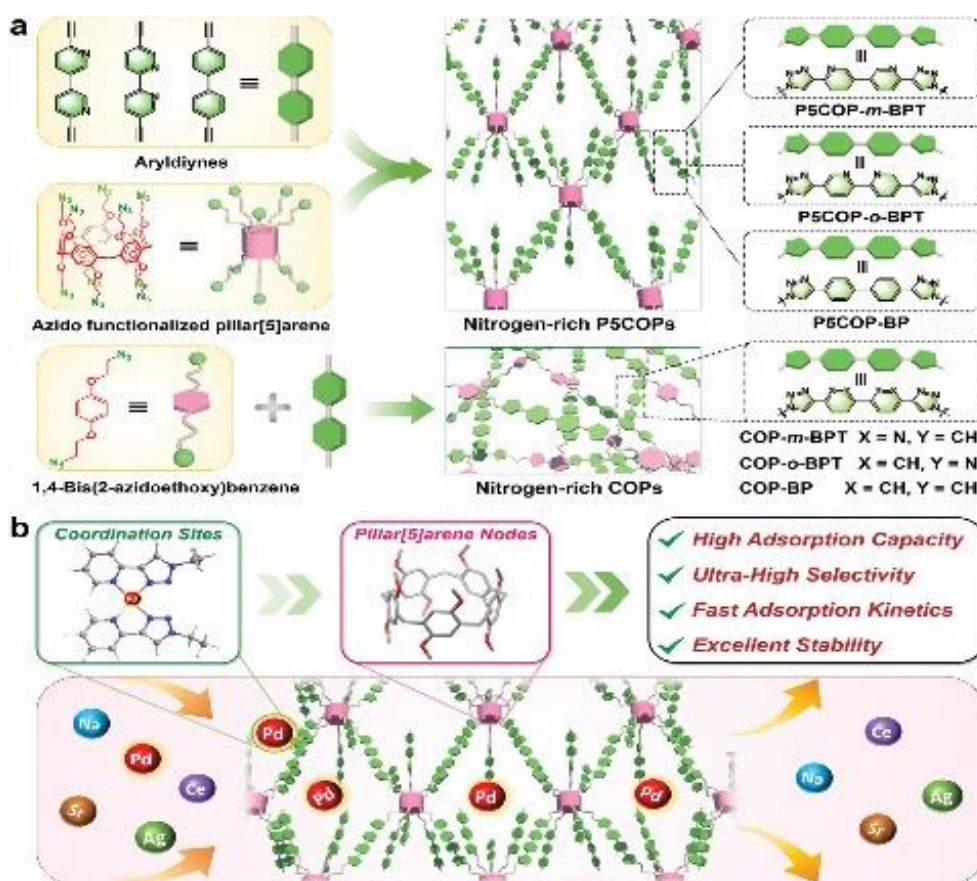


Figure 5. a) Synthesis diagram of COP and b) the selective adsorption of Pd (II) by P5COP-m-BPT

Among them, P5COP-m-BPT demonstrated outstanding performance, achieving a record-breaking high Pd (II) adsorption capacity of 403 mg g^{-1} in 3 M HNO_3 , while maintaining structural stability under extreme conditions, including gamma radiation of 500 kGy. In Figure 5b, we can see how P5COP-m-BPT adsorb Pd. Kinetic studies demonstrated rapid adsorption kinetics, removing 95% of Pd(II) within 2 minutes and reaching equilibrium within 7 minutes, significantly outperforming traditional adsorbents. P5COP-m-BPT shows extremely high selectivity for Pd(II) in the simulated HLLW containing 17 cations and 6 anions. Its distribution coefficient (K_d) is $2.01 \times 10^5 \text{ mL g}^{-1}$, and the selectivity factor ($\text{SF}_{\{\text{Pd}/\text{Ag}\}}$) of Pd(II)/Ag(I) is 797. It far exceeds the control polymer COP-m-BPT ($\text{SF}_{\{\text{Pd}/\text{Ag}\}} = 42$). Single crystal X-ray diffraction and EXAFS analysis indicated that Pd (II) formed a square-plane coordination complex with the pyridine-triazole group, while Ag(I) caused adsorption inhibition due to geometric mismatch. FT-IR and XPS confirmed the stability of the

material under harsh conditions. It maintained an adsorption efficiency of 98% in 6 M HNO₃ and did not degrade after 9 adsorption-desorption cycles. The dynamic column experiment further verified its practical applicability. The absorption of 320.8 mg g⁻¹ Pd (II) was achieved in the continuous flow system, and the interference of coexisting ions was minimal. By taking advantage of the pre-organization effect of pillar[5]arene and nitrogen-rich coordination, this study addressed the key challenges in recovering Pd (II) from high-waste liquids, including high acidity, radiation resistance and multi-ion interference. It represents the first application of cop based on large rings in metal ion separation, providing a new strategy for designing advanced adsorbents to support sustainable nuclear energy development and resource recovery.

In 2023, Zhong's team developed an innovative strategy for constructing multiple-component covalent organic frameworks (COFs) via an in-situ approach and demonstrates their exceptional performance in palladium (Pd) recovery from strong acidic environments.^[20] Conventional COFs are typically synthesized through binary condensation of two monomers, whereas multiple-component COFs, despite their structural complexity and functional versatility, remain underexplored due to reliance on ternary condensation systems. This study breaks new ground by utilizing a binary condensation system to achieve in-situ formation of linkers through substituent-induced effects, enabling the preparation of multi-component COFs with diverse topologies and simplifying synthetic pathways.

The research team employed 2,3,5,6-tetramethylpyrazine (TMP, C₄ symmetry monomer) and reacted it with C₂ symmetry terephthalaldehyde (TPA) and its ethylene-substituted derivative (DTPA), as well as C₃ symmetry benzene-1,3,5-tricarbaldehyde (BTA) and its hydroxyl-substituted analogue (HBTA). Through powder X-ray diffraction (PXRD), Brunauer–Emmett–Teller (BET) surface area analysis, and theoretical calculations, the steric hindrance effects of substituents on COF topology were elucidated. For instance, in the C₄+C₂ system, ethylene substitution in DTPA induced in-situ formation of a bidentate TMP mode, converting the original two-component sql topology into a three-component sql-defect structure (ECUT-COF-34) with an enlarged pore size of 1.7 nm. In the C₄ + C₃ system, hydroxyl substitution in HBTA transformed a three-component 3,4-connected network (ECUT-COF-35) into a two-component hcb-defect topology (ECUT-COF-36) with a 1.4 nm pore aperture. These findings highlight that substituents not only modulate pore size but also drive dynamic interconversion between component numbers via topological isomerization.

This study not only demonstrates a simplified in-situ strategy for synthesizing multiple-component COFs but also establishes a structure–function relationship linking substituents, topology, pore size, and performance. The findings provide theoretical guidance for designing high-performance adsorbents and offer a groundbreaking solution for noble metal recovery in extreme environments, advancing both synthetic methodology and resource recycling applications.

3. Conclusion

This review collectively demonstrate that significant progress has been made in the design and application of porous organic materials,^[6] including covalent organic frameworks (COFs), porous organic polymers (pops), and macrocyclic polymers, which can effectively recover palladium under extreme conditions. These materials utilize customized functional groups (such as pyridine groups, selenodiazole, amino groups) and hierarchical pore structures to achieve outstanding Pd²⁺ selectivity, adsorption capacity and stability in highly acidic (up to 3-6 M HNO₃) and radioactive environments. The key breakthroughs include the development of PY-SE-COF, which integrates fluorescence sensing and a record 4578.6 mg g⁻¹ Pd, as well as P5COP-m-BPT, which has radiation resistance (500 kGy) and ultra-high selectivity (SF_{Pd/Ag} ≈ 797). Meanwhile, the studies of POP-*o*NH₂-Py and COF-TzDa have shown that intramolecular hydrogen bonds and interlayer π - π interactions play a key role in improving the coordination stability and dynamics of Pd. It is worth noting that the multi-component COFs synthesized through in-situ strategies further expand the pore tunability and solve the mass transfer limitations in complex matrices. Despite these achievements, there are still

challenges in scaling up these materials for industrial deployment. Firstly, the long-term durability under harsher conditions (e.g., >6 M HNO_3 , prolonged irradiation) requires a deeper understanding of the bond's stability and defect tolerance. Secondly, most of the research focuses on static adsorption, and dynamic column experiments are needed to optimize the flow rate and regeneration scheme. Thirdly, cost-effective synthetic routes are crucial for reducing reliance on precious metal precursors and complex procedures. The future direction should prioritize AI-guided material design for multi-functional integration (for example, simultaneous detection and recycling), green solvent-based manufacturing, and hybrid systems that combine membranes or electrocatalysts for closed-loop resource recycling. By combining molecular-level precision with engineering scalability, porous organic materials have transformative potential in sustainable Pd recycling, advancing nuclear waste management, and achieving circular economy goals.

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