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ADVANCED FUNCTIONALIZED COVALENT ORGANIC FRAMEWORKS FOR SUSTAINABLE AND SELECTIVE ZIRCONIUM–HAFNIUM SEPARATION

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Abstract

Zirconium (Zr) and hafnium (Hf) are two important transition metals that are widely used in nuclear energy, aerospace, and advanced materials. Although they are chemically very similar and usually found together in natural minerals, they have very different roles in nuclear applications. Zirconium is mainly used for nuclear fuel cladding because it has low neutron absorption, while hafnium is used in control rods because it can strongly absorb neutrons. Due to their almost identical chemical properties and very close ionic radii, separating Zr and Hf is very difficult. Traditional separation methods such as solvent extraction, ion exchange, fractional crystallization, and distillation of chlorides are commonly used in industry. However, these methods often require high energy, large amounts of chemicals, and produce harmful waste. In recent years, Covalent Organic Frameworks (COFs) have attracted attention as a new and promising material for metal ion separation. COFs are porous, crystalline materials made from organic building blocks linked by strong covalent bonds. They have high surface area, tunable pore size, and adjustable functional groups, which make them suitable for selective adsorption. By introducing specific functional groups such as amine, hydroxyl, and carboxyl groups into the COF structure, selective binding toward Zr^{4+} *or* Hf^{4+} *ions can be improved. This review discusses the fundamental chemistry of Zr and Hf, conventional separation methods, and the design, synthesis, and functionalization of COFs for selective Zr/Hf separation. It also explains the separation mechanisms, adsorption performance, sustainability aspects, and industrial potential. Overall, COFs offer an efficient, selective, and environmentally friendly alternative for the challenging separation of zirconium and hafnium, especially for future applications in nuclear and advanced material industries.*

1. Introduction

Zirconium (Zr) and hafnium (Hf) are two very important metals in modern science and industry (Cotton et al., 1999). They are found together in nature because they have very similar chemical properties and almost the same atomic size (Housecroft & Sharpe, 2018). Zirconium is widely used in nuclear reactors because it has a very low ability to absorb neutrons (IAEA, 2014). This property makes it highly suitable for nuclear fuel cladding (IAEA, 2014). On the other hand, hafnium has a high neutron absorption capacity, which makes it useful in nuclear control rods (Lide, 2005). Because of these opposite nuclear properties, it is extremely important to separate zirconium from hafnium before using zirconium in nuclear applications (Habashi, 1997). However, separating these two metals is very difficult (Habashi, 1997). Their chemical behavior is almost identical, and they form similar compounds in aqueous and acidic solutions (Cotton et al., 1999). Traditional separation methods are often complex, expensive, and not environmentally friendly (Ritcey & Ashbrook, 1984). These challenges have encouraged researchers to explore new and advanced materials for efficient separation (Li et al., 2016). In recent years, porous materials such as covalent organic frameworks (COFs) have gained attention as promising candidates for selective metal separation (Côté et al., 2005; Ding & Wang, 2013). This review focuses on how COFs can be designed and functionalized to achieve efficient and sustainable separation of zirconium and hafnium (Ding & Wang, 2013).

The separation of zirconium and hafnium has been studied for many decades, especially because of its importance in the nuclear industry (Habashi, 1997). Conventional separation techniques include solvent extraction, ion exchange, and fractional crystallization (Ritcey & Ashbrook, 1984). Among these, solvent extraction is the most commonly used method at the industrial level (Ritcey & Ashbrook, 1984). However, this process requires large amounts of organic solvents and strong acids, which can cause environmental pollution and increase operational costs (Ritcey & Ashbrook, 1984). In addition, these methods often involve multiple steps to achieve high purity zirconium (Habashi, 1997). The similarity in ionic radius and coordination chemistry between zirconium and hafnium makes selective separation very challenging (Cotton et al., 1999). Even small differences in process conditions can affect the separation efficiency (Ritcey & Ashbrook, 1984). Therefore, scientists are continuously searching for new materials that can provide higher selectivity, lower energy consumption, and better environmental compatibility (Li et al., 2016). Advanced porous materials have shown great potential in this area (Li et al., 2016). Materials with tunable pore sizes and functional groups can selectively bind one metal over another (Ding & Wang, 2013). Among these materials, covalent organic frameworks stand out because of their structural flexibility, high surface area, and chemical stability (Côté et al., 2005; Ding & Wang, 2013). These unique features make COFs promising candidates for the selective separation of chemically similar metal ions like zirconium and hafnium (Ding & Wang, 2013).

Covalent organic frameworks, commonly known as COFs, are a class of crystalline porous materials made entirely from light elements such as carbon, hydrogen, nitrogen, boron, and oxygen (Côté et al., 2005). They are formed through strong covalent bonds, which give them high stability and well-defined structures (Côté et al., 2005). Since their discovery in 2005, COFs have attracted significant attention in various fields, including gas storage, catalysis, sensing, drug delivery, and environmental remediation (Côté et al., 2005; Ding & Wang, 2013). One of the most attractive properties of COFs is their highly ordered pore structure (Ding & Wang, 2013). The size and shape of these pores can be carefully controlled during synthesis (Ding & Wang, 2013). In addition, different functional groups can be introduced into the framework to enhance their interaction with specific metal ions (Li et al., 2016). This tunable nature allows researchers to design COFs for targeted applications (Ding & Wang, 2013). For metal ion separation, functional groups such as amines, hydroxyls, carboxyls, and nitrogen-containing ligands can improve selectivity through coordination interactions (Li et al., 2016). Because zirconium and hafnium are hard Lewis acids, designing COFs with suitable donor atoms can enhance selective binding (Housecroft & Sharpe, 2018). These characteristics make COFs highly suitable for advanced separation technologies (Ding & Wang, 2013). As research continues to grow, COFs are becoming important materials for addressing challenges in strategic metal purification (Li et al., 2016).

The selective separation of zirconium and hafnium using COFs depends on several important factors, including pore size, surface area, type of functional groups, and chemical stability under acidic conditions (Li et al., 2016). Since industrial separation often occurs in strong acidic media, the stability of the material is very important (Ritcey & Ashbrook, 1984). Some early porous materials showed good adsorption performance but lacked long-term stability (Li et al., 2016). However, recent developments in COF chemistry have improved their resistance to heat, moisture, and harsh chemical environments (Ding & Wang, 2013). Researchers are also studying the mechanisms behind selective adsorption (Li et al., 2016). These mechanisms include coordination bonding, electrostatic interactions, and slight differences in hydration energy between zirconium and hafnium ions (Housecroft & Sharpe, 2018). Understanding these mechanisms helps in designing more efficient materials (Li et al., 2016). Advanced characterization techniques such as spectroscopy and computational modeling are also being used to study metal–framework interactions at the molecular level (Li et al., 2016). This knowledge allows scientists to improve selectivity and adsorption capacity (Li et al., 2016). By combining rational design with experimental studies, COFs can be optimized for better performance (Ding & Wang, 2013). This approach opens new possibilities for developing efficient and sustainable technologies for separating chemically similar metals (Li et al., 2016).

In recent years, sustainability has become a major concern in chemical and industrial processes (Anastas & Warner, 1998). Traditional metal separation methods often produce hazardous waste and consume large amounts of energy (Ritcey & Ashbrook, 1984). Therefore, developing greener and more efficient technologies is very important (Anastas & Warner, 1998). COFs offer several advantages in this regard (Ding & Wang, 2013). They can be synthesized using relatively mild conditions, and some methods focus on green chemistry approaches (Anastas & Warner, 1998). Their high reusability and regeneration ability also reduce operational costs and waste production (Li et al., 2016). Moreover, the development of advanced materials for strategic metal separation is highly relevant for countries like China and Pakistan, where research in nuclear energy and advanced materials is growing (IAEA, 2014). Collaborative research in this area can strengthen scientific progress and technological development (IAEA, 2014). This review aims to discuss the design strategies, functionalization methods, separation mechanisms, and sustainability aspects of COFs for zirconium and hafnium separation (Ding & Wang, 2013). It also highlights current challenges and future research directions (Li et al., 2016). By understanding recent advances, researchers can develop more efficient materials that meet industrial requirements while maintaining environmental safety (Anastas & Warner, 1998).

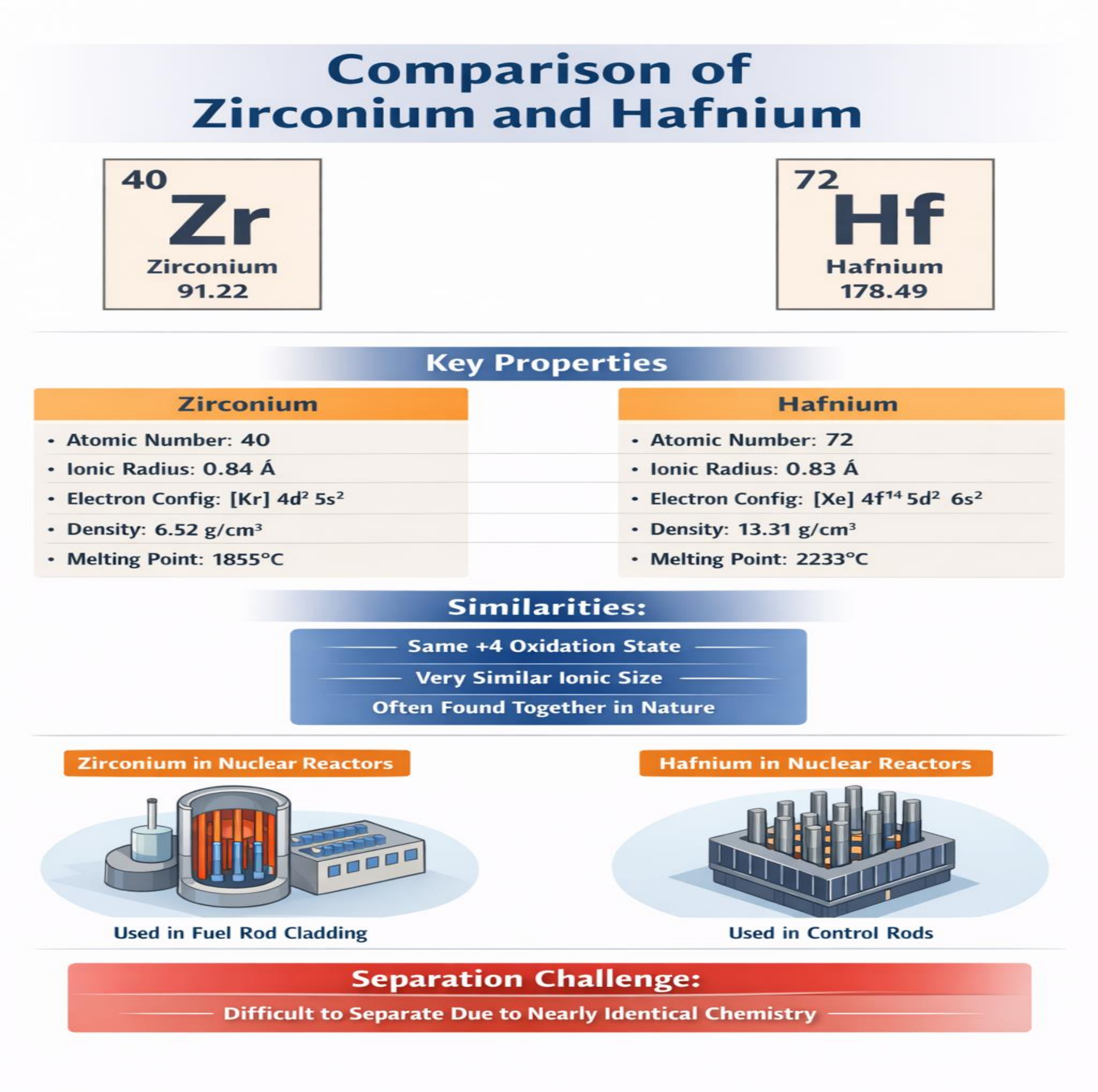
2. Fundamental Chemistry of Zirconium and Hafnium

Zirconium (Zr) and hafnium (Hf) are transition metals that belong to Group 4 of the periodic table (Housecroft & Sharpe, 2018). They are located just below titanium and share many similar chemical properties (Cotton et al., 1999). One of the main reasons for their similarity is a phenomenon called the “lanthanide contraction” (Housecroft & Sharpe, 2018). Because of this effect, the atomic radii of zirconium and hafnium are almost the same, even though hafnium has a higher atomic number (Cotton et al., 1999). This similarity in size makes their chemical behavior very close to each other (Greenwood & Earnshaw, 1997). Both metals commonly show an oxidation state of +4 in their compounds (Housecroft & Sharpe, 2018). They form stable oxides, halides, and complex ions (Greenwood & Earnshaw, 1997). Zirconium is lighter in weight compared to hafnium, but their physical appearance is similar, as both are silvery-gray metals with high melting points and good corrosion resistance (Lide, 2005). In nature, zirconium and hafnium are usually found together in the mineral zircon ($ZrSiO_4$) (Habashi, 1997). Hafnium is always present in small amounts within zirconium ores, typically around 1–3% (Habashi, 1997). Because they occur together and behave almost identically in chemical reactions, their separation becomes very difficult (Ritcey & Ashbrook, 1984). Understanding their basic chemical properties is important before designing any separation process (Cotton et al., 1999). Their electronic structure, atomic size, and oxidation behavior all play a key role in determining how they react in different chemical environments (Greenwood & Earnshaw, 1997).

Table 1 – Comparison of Zirconium and Hafnium Properties

Property	**Zirconium (Zr)**	**Hafnium (Hf)**	**Difference / Notes**
Atomic Number	40	72	Hf has more protons and electrons
Ionic Radius (Å)	0.84	0.83	Very similar, making separation difficult
Electron Configuration	[Kr] $4d^2$ $5s^2$	[Xe] $4f^{14}$ $5d^2$ $6s^2$	Hf has filled 4f orbitals
Density (g/cm³)	6.52	13.31	Hf is much denser
Melting Point (°C)	1855	2233	Hf melts at higher temperature
Coordination Number	6-8	6-8	Similar chemistry
Nuclear Application	Fuel cladding	Control rods	Zr low neutron absorption; Hf high absorption

The electronic configuration of zirconium is [Kr] $4d^2$ $5s^2$, while hafnium has the configuration [Xe] $4f^{14}$ $5d^2$ $6s^2$ (Housecroft & Sharpe, 2018). Even though hafnium contains more electrons, its outermost valence electrons are arranged in a similar way to zirconium (Cotton et al., 1999). This is one of the main reasons why they both show a +4 oxidation state in most of their stable compounds (Greenwood & Earnshaw, 1997). In aqueous solutions, Zr^{4+} and Hf^{4+} ions are highly charged and have strong attraction toward oxygen-containing ligands (Greenwood & Earnshaw, 1997). They are classified as "hard acids" according to the Hard and Soft Acids and Bases (HSAB) theory (Pearson, 1963). This means they prefer to bind with hard bases such as oxygen and nitrogen donor atoms (Pearson, 1963). Because both ions have similar charge density and ionic radii, they form similar coordination complexes (Cotton et al., 1999). Their coordination number is usually 6, 7, or 8 depending on the ligands and conditions (Greenwood & Earnshaw, 1997). The strong positive charge on Zr^{4+} and Hf^{4+} also causes them to easily hydrolyze in water (Housecroft & Sharpe, 2018). They react with water molecules and form hydroxo complexes (Greenwood & Earnshaw, 1997). This hydrolysis behavior makes their chemistry more complicated in aqueous systems (Cotton et al., 1999). As a result, their separation requires careful control of pH, ligand type, and reaction conditions (Ritcey & Ashbrook, 1984).



Comparison of Zirconium and Hafnium

Key Properties

Zirconium

- Atomic Number: 40
- Ionic Radius: 0.84 Á
- Electron Config: [Kr] $4d^2\ 5s^2$
- Density: 6.52 g/cm^3
- Melting Point: 1855°C

Hafnium

- Atomic Number: 72
- Ionic Radius: 0.83 Á
- Electron Config: [Xe] $4f^{14}\ 5d^2\ 6s^2$
- Density: 13.31 g/cm^3
- Melting Point: 2233°C

Similarities:

Same +4 Oxidation State
Very Similar Ionic Size
Often Found Together in Nature

Separation Challenge:

Difficult to Separate Due to Nearly Identical Chemistry

Figure 1 showing zirconium and hafnium in the periodic table, their atomic numbers, ionic radii, electron configurations, and key chemical properties. Include a small illustration comparing their nuclear vs industrial importance (Zr for cladding, Hf for control rods).

In aqueous and acidic media, zirconium and hafnium show very similar chemical behavior (Greenwood & Earnshaw, 1997). Both metals tend to form stable complexes with fluoride, chloride, sulfate, and nitrate ions (Cotton et al., 1999). Among these, fluoride complexes are particularly important in industrial separation processes (Ritcey & Ashbrook, 1984). For example, both metals can form hexafluoro complexes such as $[ZrF_6]^{2-}$ and $[HfF_6]^{2-}$ (Greenwood & Earnshaw, 1997). These complexes have very similar stability constants, which makes selective separation difficult (Ritcey & Ashbrook, 1984). In addition, both metals have a strong tendency to form polymeric and hydrolyzed species in water (Housecroft & Sharpe, 2018). When the pH increases, they start forming insoluble hydroxides like $Zr(OH)_4$ and $Hf(OH)_4$ (Greenwood & Earnshaw, 1997). These hydroxides can further convert into their respective oxides upon heating (Cotton et al., 1999). Zirconium dioxide (ZrO_2) and hafnium dioxide (HfO_2) are both highly stable and have high melting points (Lide, 2005). They are widely used in ceramics, refractories, and electronic materials (Lide, 2005). The similarity in solubility and complex formation behavior between Zr and Hf is one of the main chemical challenges in their separation (Habashi, 1997). Even slight changes in temperature, acid concentration, or ligand type can affect their distribution between phases (Ritcey & Ashbrook, 1984). Therefore, a deep understanding of their coordination chemistry and solution behavior is essential for developing advanced separation materials like COFs (Ding & Wang, 2013).

Thermodynamic and kinetic properties also play an important role in understanding zirconium and hafnium chemistry (Greenwood & Earnshaw, 1997). Thermodynamically, both metals form very stable oxide bonds due to their strong affinity for oxygen (Cotton et al., 1999). The formation of Zr–O and Hf–O bonds releases a large amount of energy, which explains why their oxides are very stable compounds (Housecroft & Sharpe, 2018). From a kinetic point of view, ligand exchange reactions involving Zr^{4+} and Hf^{4+} can be relatively slow compared to lighter metal ions (Cotton et al., 1999). This slow exchange rate sometimes allows slight differences in reaction speed to be used for selective separation (Ritcey & Ashbrook, 1984). Although their thermodynamic properties are very close, small differences in hydration energy and ionic potential may create minor selectivity under controlled conditions (Greenwood & Earnshaw, 1997). These small differences are often exploited in advanced separation systems (Ding & Wang, 2013). For example, specially designed ligands can slightly favor binding with one metal over the other (Li et al., 2016). Understanding both thermodynamic stability and reaction kinetics helps researchers design better adsorbents and separation materials (Li et al., 2016). By studying these properties, scientists can identify the key factors that influence selectivity between zirconium and hafnium in different chemical environments (Greenwood & Earnshaw, 1997).

From an industrial perspective, the chemical similarity of zirconium and hafnium creates major challenges in producing nuclear-grade zirconium (IAEA, 2014). Since hafnium strongly absorbs neutrons, even small amounts of hafnium in zirconium can affect reactor performance (IAEA, 2014). Therefore, zirconium used in nuclear reactors must contain extremely low hafnium content (IAEA, 2014). Achieving this high purity requires advanced chemical processing (Habashi, 1997). Industrial methods often involve solvent extraction using complex fluoride systems (Ritcey & Ashbrook, 1984). However, these methods consume large amounts of chemicals and generate waste (Ritcey & Ashbrook, 1984). Understanding the fundamental chemistry of zirconium and hafnium helps improve these processes and develop new alternatives (Habashi, 1997). By studying their electronic structure, coordination preferences, hydrolysis behavior, and thermodynamic properties, researchers can design more selective materials (Greenwood & Earnshaw, 1997). Modern materials like covalent organic frameworks aim to use these small chemical differences to achieve efficient separation (Ding & Wang, 2013). A clear understanding of their basic chemistry is the foundation for developing innovative, sustainable, and high-performance separation technologies in the future (Anastas & Warner, 1998).

3. Conventional Methods for Zr/Hf Separation

The separation of zirconium (Zr) and hafnium (Hf) has been a major industrial challenge for many years because of their very similar chemical properties (Habashi, 1997). Since both metals usually occur together in natural minerals, especially in zircon ore, they must be separated before being used in advanced applications (Greenwood & Earnshaw, 1997). The most important reason for this separation is nuclear technology (IAEA, 2014). Zirconium is widely used in nuclear reactors because it does not absorb neutrons easily, while hafnium absorbs neutrons very strongly (IAEA, 2014). Even a small amount of hafnium in zirconium can affect reactor performance (IAEA, 2014). Therefore, industries must reduce the hafnium content in zirconium to very low levels (IAEA, 2014). Over time, scientists and engineers have developed several conventional methods to separate these two metals (Ritcey & Ashbrook, 1984). These methods are mainly based on small differences in their chemical behavior in specific conditions (Cotton et al., 1999). However, because the differences are very small, the processes are usually long, complex, and costly (Habashi, 1997). The most common traditional techniques include solvent extraction, ion exchange, fractional crystallization, and distillation of metal chlorides (Ritcey & Ashbrook, 1984). Each method has advantages and disadvantages (Habashi, 1997). While these methods are still used at the industrial level, they often require large amounts of chemicals and energy (Ritcey & Ashbrook, 1984). Understanding these conventional techniques is important before exploring new advanced materials like COFs for improved separation (Ding & Wang, 2013).

One of the most widely used conventional methods for separating zirconium and hafnium is solvent extraction (Ritcey & Ashbrook, 1984). This method is based on the distribution of metal ions between two immiscible liquids, usually an aqueous phase and an organic phase (Ritcey & Ashbrook, 1984). In industrial processes, zirconium and hafnium are first converted into soluble fluoride or chloride complexes (Greenwood & Earnshaw, 1997). Then, an organic solvent containing specific extractants is used to selectively transfer one metal into the organic phase while the other remains in the aqueous phase (Ritcey & Ashbrook, 1984). Common extractants include organophosphorus compounds such as tributyl phosphate (TBP) (Ritcey & Ashbrook, 1984). The separation depends on slight differences in complex stability between zirconium and hafnium (Cotton et al., 1999). However, because these differences are very small, multiple extraction and back-extraction steps are required to achieve high purity (Ritcey & Ashbrook, 1984). This makes the process time-consuming and expensive (Habashi, 1997). In addition, large volumes of organic solvents and strong acids are used, which can create environmental and safety concerns (Anastas & Warner, 1998). Waste disposal and solvent recovery add extra cost to the process (Ritcey & Ashbrook, 1984). Although solvent extraction is effective at large scale, it is not considered environmentally friendly (Anastas & Warner, 1998). Therefore, researchers are looking for alternative methods that can reduce chemical consumption and improve sustainability (Ding & Wang, 2013).

Table 2 – Summary of Conventional Separation Methods

Method	Principle	Advantages	Disadvantages	Industrial Use
Solvent Extraction	Uses immiscible liquids to extract metals	Effective at large scale	High chemical consumption, organic waste	Large-scale metal purification
Ion Exchange	Adsorption of metal ions on resins	No organic solvents needed	Resin degradation, costly regeneration	Nuclear material separation
Fractional Crystallization	Exploits small solubility differences	Simple concept	Slow, labor-intensive	Laboratory purification
Distillation of Chlorides	Fractional distillation of metal chlorides	High purity achievable	High energy, sensitive to moisture	Nuclear-grade zirconium production

Another traditional method used for zirconium and hafnium separation is ion exchange (Ritcey & Ashbrook, 1984). In this technique, a solid resin material containing charged functional groups is used to selectively bind metal ions from a solution (Greenwood & Earnshaw, 1997). The metal-containing solution is passed through a column packed with ion exchange resin (Ritcey & Ashbrook, 1984). Depending on the chemical conditions, one metal ion may bind more strongly to the resin than the other (Cotton et al., 1999). By carefully controlling factors such as pH, acid concentration, and temperature, selective adsorption can be achieved (Greenwood & Earnshaw, 1997). After adsorption, the bound metal can be removed using an appropriate eluent (Ritcey & Ashbrook, 1984). Ion exchange offers better control compared to some other methods and does not always require large amounts of organic solvents (Anastas & Warner, 1998). However, because zirconium and hafnium behave so similarly, achieving high selectivity is still difficult (Habashi, 1997). The resin materials can also lose efficiency over time due to chemical degradation, especially in strong acidic conditions (Ritcey & Ashbrook, 1984). In addition, regeneration and reuse of the resin require additional chemical treatment (Anastas & Warner, 1998). While ion exchange is useful for laboratory-scale separation and purification, it may not always be the most economical option for very large industrial production (Habashi, 1997).

Figure 2. showing traditional separation techniques:

- Solvent extraction → Ion exchange → Fractional crystallization → Distillation of chlorides.
- Show pros and cons for each method briefly in boxes.

Fractional crystallization is another method that has been used in the past to separate zirconium and hafnium (Habashi, 1997). This technique is based on small differences in solubility between their compounds (Greenwood & Earnshaw, 1997). When a solution containing both metals is slowly evaporated or cooled, crystals of one compound may form before the other (Ritcey & Ashbrook, 1984). By repeating this process many times, partial separation can be achieved (Habashi, 1997). However, because the difference in solubility between zirconium and hafnium compounds is very small, many crystallization steps are needed (Greenwood & Earnshaw, 1997). This makes the process slow and labor-intensive (Habashi, 1997). Another classical method involves converting zirconium and hafnium into their tetrachlorides ($ZrCl_4$ and $HfCl_4$) and separating them by fractional distillation (Ritcey & Ashbrook, 1984). Since hafnium tetrachloride has a slightly higher boiling point than zirconium tetrachloride, separation can be achieved through careful temperature control (Greenwood & Earnshaw, 1997). However, this method requires very high temperatures and strict moisture-free conditions because the chlorides are highly reactive with water (Habashi, 1997). The equipment required for such processes is expensive and energy-intensive (Ritcey & Ashbrook, 1984). As a result, these methods are less commonly used today compared to solvent extraction (Habashi, 1997).

Although conventional methods have made large-scale production of nuclear-grade zirconium possible, they still have many limitations (IAEA, 2014). Most of these techniques consume high amounts of chemicals, energy, and time (Ritcey & Ashbrook, 1984). They also generate acidic and organic waste, which can harm the environment if not treated properly (Anastas & Warner, 1998). The complex multi-step procedures increase operational costs and require careful monitoring (Habashi, 1997). In addition, achieving very high purity zirconium demands repeated processing cycles (IAEA, 2014). These challenges have encouraged scientists to search for more efficient and sustainable alternatives (Ding & Wang, 2013). Modern research focuses on advanced materials that can provide higher selectivity with fewer steps (Li et al., 2016). Materials with tunable structures and functional groups may offer better control over metal binding (Ding & Wang, 2013). By understanding the strengths and weaknesses of conventional methods, researchers can design improved systems for the future (Habashi, 1997). The development of innovative materials such as covalent organic frameworks aims to overcome these traditional limitations and provide greener, more efficient solutions for zirconium and hafnium separation (Ding & Wang, 2013).

Overview of Covalent Organic Frameworks (COFs)

Covalent Organic Frameworks, commonly known as COFs, are a class of advanced porous materials made entirely from light elements such as carbon, hydrogen, nitrogen, oxygen, and boron (Ding & Wang, 2013). These materials are built through strong covalent bonds between organic building blocks (Côté et al., 2005). COFs were first reported in 2005, and since then they have attracted great attention in materials science and chemistry (Côté et al., 2005). What makes COFs special is their highly ordered and crystalline structure (Ding & Wang, 2013). Unlike many traditional polymers that are disordered, COFs form well-defined networks with repeating patterns (Ding & Wang, 2013). This ordered structure creates uniform pores throughout the material (Côté et al., 2005). These pores can store molecules or allow selective movement of ions (Ding & Wang, 2013). Because of their low density and high surface area, COFs are considered lightweight but highly functional materials (Furukawa et al., 2013). Another important feature of COFs is that their structure can be carefully designed before synthesis (Ding & Wang, 2013). Scientists choose specific organic linkers and nodes to create a targeted pore size and shape (Côté et al., 2005). This design flexibility makes COFs different from many other porous materials (Furukawa et al., 2013). Due to these properties, COFs are now being studied for various applications, including gas storage, catalysis, sensing, drug delivery, environmental cleanup, and metal ion separation (Ding & Wang, 2013; Furukawa et al., 2013).

The structure of COFs is based on the connection of small organic molecules that act as building units (Côté et al., 2005). These building units are linked together through strong covalent bonds such as imine, boronate ester, hydrazone, triazine, or amide linkages (Ding & Wang, 2013). The type of bond used in the framework affects the stability and chemical resistance of the material (Furukawa et al., 2013). For example, imine-linked COFs are widely studied because they are easier to synthesize, while other linkages may provide better stability in water or acidic conditions (Ding & Wang, 2013). COFs can be two-dimensional (2D) or three-dimensional (3D) depending on how the building blocks are arranged (Côté et al., 2005). In 2D COFs, layers are stacked on top of each other, creating channels for molecule movement (Ding & Wang, 2013). In 3D COFs, the network extends in all directions, forming interconnected pores (Furukawa et al., 2013). One of the most attractive properties of COFs is their very high surface area, which can reach more than 1000 square meters per gram (Furukawa et al., 2013). This large surface area provides many active sites for adsorption or chemical interaction (Ding & Wang, 2013). Because of their tunable pore size and functional groups, COFs can be designed for specific tasks, such as capturing certain gases or selectively binding metal ions (Ding & Wang, 2013).

Table 3 – Types of COFs and Linkages

COF Type	Linkage Type	Pore Size (nm)	Stability	Applications
Imine-linked COF	C=N	1–3	Moderate	Adsorption, catalysis
Boronate ester COF	B–O	1–2	Low	Gas storage, separation
Triazine-linked COF	C–N	1–3	High	Metal ion adsorption, catalysis
β-Ketoenamine COF	C=C–N	1–4	Very High	Metal recovery, environmental remediation

Another important advantage of COFs is their tunability (Ding & Wang, 2013). Scientists can introduce different functional groups into the framework to improve performance for a specific application (Feng et al., 2012). For example, amino, hydroxyl, carboxyl, and nitrogen-containing groups can be added to increase interaction with metal ions (Ding & Wang, 2013; Feng et al., 2012). This is especially useful for separation processes (Liu et al., 2016). The presence of these functional groups allows the framework to form coordination bonds with certain metal ions (Ding & Wang, 2013). In addition, the pore size of COFs can be adjusted by selecting longer or shorter organic linkers (Côté et al., 2005). This control over pore size helps in separating molecules or ions based on size difference (Ding & Wang, 2013). Compared to other porous materials such as metal-organic frameworks (MOFs), COFs are fully organic and often lighter in weight (Furukawa et al., 2013). They also show good thermal stability and chemical resistance, depending on the type of linkage used (Ding & Wang, 2013). Because COFs are made from organic components, they may offer better flexibility in structural design (Feng et al., 2012). This combination of structural order, chemical stability, and functional tunability makes COFs promising materials for advanced separation technologies (Ding & Wang, 2013).

The synthesis of COFs usually involves solvothermal methods, where organic building blocks react in a sealed container at controlled temperature and pressure (Côté et al., 2005). During this process, reversible reactions help in forming an ordered crystalline structure (Ding & Wang, 2013). The choice of solvent, temperature, and reaction time can affect the final structure and quality of the COF (Feng et al., 2012). In recent years, researchers have also developed other synthesis methods such as microwave-assisted synthesis, mechanochemical synthesis, and room-temperature reactions (Liu et al., 2016). Some studies focus on green synthesis approaches to reduce the use of harmful solvents (Anastas & Warner, 1998). After synthesis, COFs are characterized using different techniques such as X-ray diffraction, scanning electron microscopy, and surface area analysis (Furukawa et al., 2013). These methods help confirm the structure, crystallinity, and porosity of the material (Ding & Wang, 2013). Improving the chemical stability of COFs, especially in water and acidic conditions, is an important research area (Feng et al., 2012). For applications like metal ion separation, the material must remain stable in harsh environments (Ding & Wang, 2013). Therefore, selecting strong and stable linkages is very important in designing COFs for practical use (Furukawa et al., 2013).

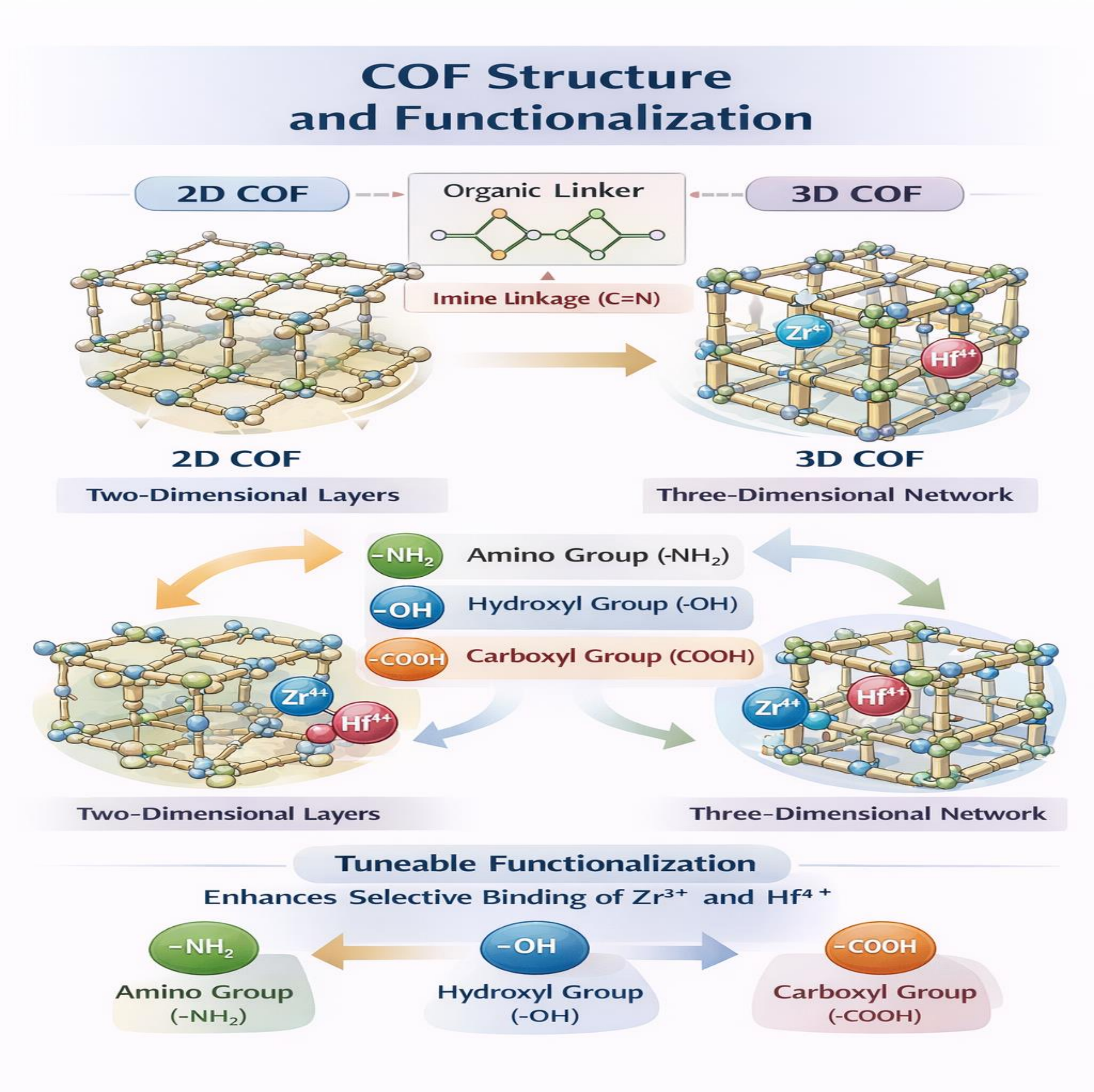


Figure 3. A schematic of a 2D COF and 3D COF, showing pores, nodes, linkers, and functional groups (amine, hydroxyl, carboxyl). Include arrows showing where metal ions (Zr^{4+}, Hf^{4+}) can coordinate inside the pores.

Due to their unique properties, COFs have been explored in many fields of science and technology (Ding & Wang, 2013; Furukawa et al., 2013). In gas storage, they are used to capture hydrogen, carbon dioxide, and methane (Furukawa et al., 2013). In catalysis, they provide a stable platform for hosting active catalytic sites (Ding & Wang, 2013). In environmental applications, COFs are studied for removing pollutants, dyes, and heavy metals from water (Liu et al., 2016). Recently, their potential in selective metal ion separation has gained attention (Ding & Wang, 2013; Liu et al., 2016). Because zirconium and hafnium are chemically very similar, materials with precise control over pore environment and functional groups are needed (Feng et al., 2012). COFs offer this level of control (Ding & Wang, 2013). Their ordered pores and customizable surface chemistry allow researchers to design frameworks that slightly favor one metal over another (Liu et al., 2016). Although research on COFs is still developing compared to older materials, their flexibility and performance show great promise (Ding & Wang, 2013). With continuous improvement in synthesis and stability, COFs may become key materials for sustainable and efficient separation technologies in the future (Furukawa et al., 2013).

Synthesis and Functionalization of COFs

The synthesis of Covalent Organic Frameworks (COFs) is an important step because the final structure and performance of the material depend strongly on how it is prepared (Ding & Wang, 2013; Côté et al., 2005). COFs are usually formed by connecting small organic molecules through strong covalent bonds (Côté et al., 2005). These organic molecules act as building blocks, and they are carefully selected before the reaction begins (Feng et al., 2012). Most commonly, COFs are synthesized using a method called solvothermal synthesis (Ding & Wang, 2013). In this method, the building blocks are dissolved in a suitable solvent and then heated in a sealed container for several hours or even days (Côté et al., 2005). The heat helps the molecules react slowly and form an ordered crystalline network (Ding & Wang, 2013). The reaction conditions such as temperature, solvent type, concentration, and reaction time play a very important role in determining the final structure (Feng et al., 2012). If the conditions are not controlled properly, the material may become amorphous instead of crystalline (Ding & Wang, 2013). The reversible nature of some chemical bonds, such as imine bonds, allows the framework to correct errors during formation and create a more ordered structure (Feng et al., 2012). This process is often called dynamic covalent chemistry (Ding & Wang, 2013). Proper synthesis is essential because high crystallinity and porosity are necessary for good adsorption and separation performance (Furukawa et al., 2013).

Besides the solvothermal method, researchers have developed other techniques to synthesize COFs in a more efficient or environmentally friendly way (Liu et al., 2016). One such method is microwave-assisted synthesis (Liu et al., 2016). In this technique, microwave radiation is used to heat the reaction mixture quickly and uniformly (Liu et al., 2016). This reduces the reaction time from days to just a few hours or even minutes (Liu et al., 2016). Another approach is mechanochemical synthesis, where solid reactants are ground together without using large amounts of solvent (Feng et al., 2012). This method supports green chemistry because it reduces solvent waste (Anastas & Warner, 1998). Some researchers also use room-temperature synthesis or interfacial polymerization techniques (Ding & Wang, 2013). These methods aim to simplify the process and lower energy consumption (Feng et al., 2012). Each synthesis method has its own advantages and limitations (Ding & Wang, 2013). For example, some methods may produce higher crystallinity, while others may be faster or more environmentally friendly (Feng et al., 2012). The choice of method depends on the desired application (Ding & Wang, 2013). For metal ion separation, it is important that the COF has strong chemical stability and well-defined pores (Liu et al., 2016). Therefore, selecting the right synthesis strategy is a key step in developing effective COF materials (Ding & Wang, 2013).

After synthesis, functionalization of COFs is often carried out to improve their performance (Ding & Wang, 2013). Functionalization means introducing specific chemical groups into the framework to give it special properties (Feng et al., 2012). This can be done in two main ways: direct synthesis and post-synthetic modification (Ding & Wang, 2013). In direct synthesis, functional groups are included in the building blocks before the framework is formed (Feng et al., 2012). This method ensures that the functional groups are evenly distributed throughout the structure (Ding & Wang, 2013). In post-synthetic modification, the already-formed COF is chemically treated to attach new functional groups (Liu et al., 2016). This approach allows more flexibility because the base structure remains the same while the surface properties are adjusted (Feng et al., 2012). Functional groups such as amine (-NH_2), hydroxyl (-OH), carboxyl (-COOH), and nitrogen-containing ligands are commonly introduced for metal ion adsorption (Ding & Wang, 2013; Liu et al., 2016). These groups can form coordination bonds with metal ions, improving selectivity and adsorption capacity (Feng et al., 2012). For separating zirconium and hafnium, functional groups that interact strongly with hard metal ions are especially useful (Ding & Wang, 2013). Proper functionalization increases the efficiency and specificity of COFs in separation processes (Liu et al., 2016).

Improving the chemical and thermal stability of COFs is another important part of their synthesis and functionalization (Furukawa et al., 2013). Early COFs sometimes showed limited stability in water or acidic conditions, which restricted their practical applications (Feng et al., 2012). However, researchers have developed new types of linkages that provide stronger resistance to harsh environments (Ding & Wang, 2013). For example, β-ketoenamine and triazine-linked COFs show better stability in acidic and basic solutions (Feng et al., 2012; Ding & Wang, 2013). Stability is especially important for industrial metal separation because the process often occurs in strong acid solutions (Liu et al., 2016). If the framework breaks down, it cannot be reused (Furukawa et al., 2013). Therefore, selecting strong covalent bonds and stable building blocks is essential (Ding & Wang, 2013). In addition, surface modification techniques can improve resistance to moisture and heat (Feng et al., 2012). Researchers also test stability through repeated adsorption and regeneration cycles (Liu et al., 2016). A stable COF should maintain its structure and performance after multiple uses (Furukawa et al., 2013). By focusing on stability during synthesis, scientists can design materials that are not only effective but also durable for long-term industrial applications (Ding & Wang, 2013).

Overall, the synthesis and functionalization of COFs require careful planning and design (Ding & Wang, 2013). The selection of building blocks, reaction conditions, and functional groups all influence the final properties of the material (Feng et al., 2012). For metal ion separation, it is not enough to have a porous structure; the framework must also have suitable chemical groups that can selectively interact with target ions (Liu et al., 2016). In the case of zirconium and hafnium separation, small differences in coordination behavior must be carefully used to achieve selectivity (Ding & Wang, 2013). Functionalized COFs can provide specific binding sites that slightly favor one ion over the other (Feng et al., 2012). In addition, developing greener synthesis methods supports sustainable chemistry and reduces environmental impact (Anastas & Warner, 1998). As research continues, scientists are working to make COF synthesis faster, cheaper, and more scalable (Liu et al., 2016). With proper functionalization and improved stability, COFs have strong potential to become advanced materials for efficient and sustainable separation technologies in the future (Ding & Wang, 2013).

Mechanisms of Selective Zr/Hf Separation in COFs

The separation of zirconium (Zr) and hafnium (Hf) using covalent organic frameworks (COFs) depends on understanding the small chemical differences between these two metals (Ding & Wang, 2013; Liu et al., 2016). Since both metals have almost the same ionic size and the same +4 oxidation state, separating them is very challenging (Cotton et al., 1999). However, even small differences in their chemical behavior can be used to achieve selective separation (Ding & Wang, 2013). One important mechanism is coordination interaction. Both Zr^{4+} and Hf^{4+} ions prefer to bind with oxygen- and nitrogen-containing groups because they are hard Lewis acids (Pearson, 1963; Cotton et al., 1999). If a COF contains carefully designed functional groups, it can create a slightly stronger interaction with one ion compared to the other (Liu et al., 2016). This small difference in binding strength can lead to selective adsorption (Ding & Wang, 2013). The structure of the COF also plays a role. The pore size and shape can influence how easily metal ions enter and interact with active sites (Feng et al., 2012). Even minor differences in hydration energy and coordination environment may affect how the ions behave inside the pores (Cotton et al., 1999). By controlling these structural and chemical factors, COFs can create a selective environment (Liu et al., 2016). Although the difference between zirconium and hafnium is very small, advanced material design allows researchers to take advantage of these subtle variations for effective separation (Ding & Wang, 2013).

Another important mechanism involved in selective separation is based on the Hard and Soft Acids and Bases (HSAB) theory (Pearson, 1963). According to this theory, hard acids prefer to bind with hard bases. Zirconium and hafnium are both hard acids, but there may be slight differences in their charge density and ionic potential (Cotton et al., 1999). When a COF is functionalized with hard donor atoms such as oxygen or nitrogen, it creates strong coordination bonds with these metal ions (Ding & Wang, 2013; Liu et al., 2016). By carefully selecting the type and arrangement of these donor atoms, researchers can slightly favor the binding of one metal over the other (Feng et al., 2012). For example, differences in bond length and bond strength between metal–ligand interactions may result in different adsorption energies (Cotton et al., 1999). Computational studies and experimental measurements often help in identifying these small differences (Liu et al., 2016). In addition, the arrangement of functional groups inside the pores can create a specific coordination geometry. If the geometry is more suitable for one ion, selectivity increases (Ding & Wang, 2013). Therefore, the HSAB principle provides a theoretical foundation for designing COFs with improved separation performance (Pearson, 1963). Understanding this concept helps researchers create materials that use chemical preferences to achieve better selectivity (Liu et al., 2016).

Size exclusion and pore confinement effects also contribute to the separation mechanism (Ding & Wang, 2013). Although zirconium and hafnium have almost identical ionic radii, their hydrated forms in solution may have slightly different effective sizes (Cotton et al., 1999). Inside the narrow and well-defined pores of a COF, even small size differences can influence diffusion and adsorption behavior (Liu et al., 2016). The pore environment can also create spatial restrictions that favor one ion's coordination structure over the other (Ding & Wang, 2013). In some cases, the movement of ions inside the pores is controlled by diffusion rates (Feng et al., 2012). If one ion diffuses slightly faster or interacts more quickly with active sites, selective adsorption may occur (Liu et al., 2016). Additionally, electrostatic interactions between the positively charged metal ions and the functional groups in the framework can affect separation (Ding & Wang, 2013). Surface charge distribution inside the COF pores may influence how strongly each ion is attracted (Liu et al., 2016). These physical factors, combined with chemical interactions, create a selective environment (Ding & Wang, 2013). Although size exclusion alone may not be enough for complete separation, when combined with coordination and electrostatic effects, it enhances overall selectivity (Feng et al., 2012).

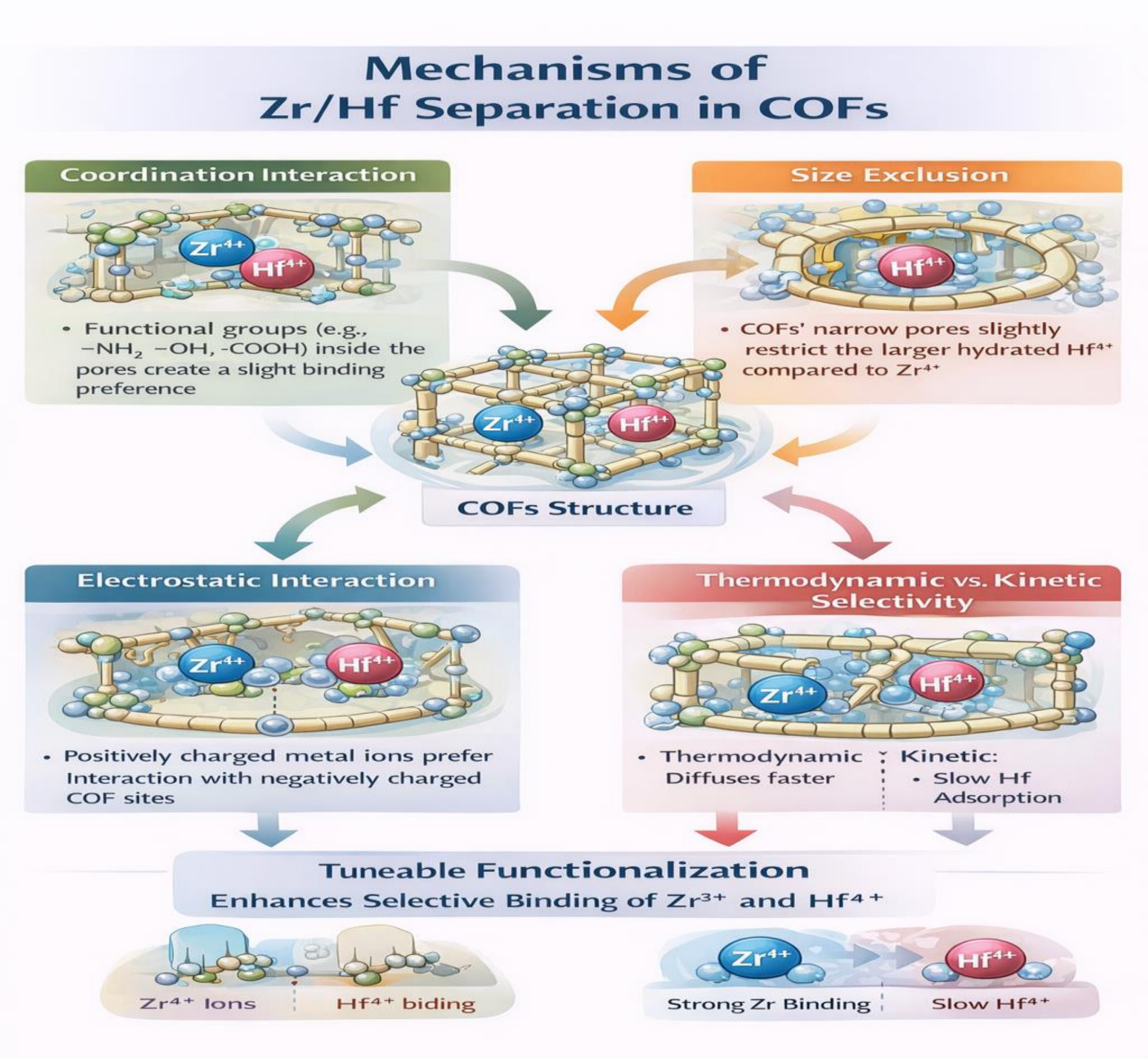


Figure 4. A schematic showing:

- Coordination interaction
- Size exclusion
- Electrostatic interactions
- Thermodynamic vs kinetic selectivity
  Use arrows and labels to indicate selective binding inside COF pores.

Thermodynamic and kinetic factors also play a key role in the separation process (Liu et al., 2016; Ding & Wang, 2013). Thermodynamically, the ion that forms the more stable complex with the functional groups inside the COF will be preferentially adsorbed (Pearson, 1963; Cotton et al., 1999). Even small differences in binding energy can lead to measurable selectivity over time (Ding & Wang, 2013). Researchers often calculate adsorption energies using computational chemistry methods to predict which ion will bind more strongly (Liu et al., 2016). On the other hand, kinetic factors refer to the speed at which adsorption and desorption occur (Ding & Wang, 2013). In some systems, one ion may bind faster than the other, leading to kinetic selectivity (Liu et al., 2016). For example, slight differences in ligand exchange rates or hydration shell removal may influence how quickly the ion attaches to the framework (Cotton et al., 1999). By controlling contact time, temperature, and concentration, it is sometimes possible to enhance this kinetic advantage (Ding & Wang, 2013). Therefore, both thermodynamic stability and reaction speed must be considered when designing COFs for zirconium and hafnium separation (Liu et al., 2016). A good separation material should combine favorable binding strength with controlled adsorption kinetics (Feng et al., 2012).

Modern research also uses advanced tools to better understand separation mechanisms in COFs (Ding & Wang, 2013; Liu et al., 2016). Techniques such as spectroscopy, X-ray analysis, and electron microscopy help scientists study how metal ions interact with the framework at the molecular level (Furukawa et al., 2013). Computational modeling and density functional theory (DFT) calculations are often used to predict binding sites and adsorption energies (Liu et al., 2016). These methods provide detailed information about metal–ligand interactions and help explain experimental results (Ding & Wang, 2013). By combining theoretical and experimental studies, researchers can improve material design step by step (Feng et al., 2012). The goal is to create a COF structure where small chemical differences between zirconium and hafnium become more noticeable inside the confined pore environment (Liu et al., 2016). Although the challenge is significant due to their strong similarity, careful control of functional groups, pore structure, and reaction conditions can lead to selective separation (Ding & Wang, 2013). Understanding these mechanisms deeply is essential for developing efficient, stable, and sustainable COF-based separation systems in the future (Furukawa et al., 2013).

Adsorption Performance and Separation Efficiency

Adsorption performance is one of the most important factors when evaluating covalent organic frameworks (COFs) for zirconium (Zr) and hafnium (Hf) separation (Ding & Wang, 2013; Liu et al., 2016). Adsorption refers to the ability of a material to capture and hold metal ions on its surface or inside its pores (Feng et al., 2012). For effective separation, a COF must have high adsorption capacity and good selectivity (Liu et al., 2016). Adsorption capacity means how much metal ion the material can capture per unit weight, usually measured in milligrams of metal per gram of adsorbent (Ding & Wang, 2013). A high surface area and well-defined pore structure help increase adsorption capacity because they provide more active sites for metal binding (Feng et al., 2012). However, capacity alone is not enough. The material must also show preference for one metal over the other. In the case of Zr and Hf, the difference in chemical properties is very small, so achieving high selectivity is challenging (Cotton et al., 1999). Researchers test adsorption performance by placing the COF in a solution containing both metal ions and measuring how much of each ion is removed (Liu et al., 2016). These experiments help determine whether the material can effectively separate the two metals under controlled conditions (Ding & Wang, 2013).

To understand adsorption behavior in detail, scientists often use adsorption isotherm models (Feng et al., 2012). These models describe how metal ions interact with the surface of the adsorbent at equilibrium. Two common models are the Langmuir and Freundlich isotherms. The Langmuir model assumes that adsorption occurs on a uniform surface with a limited number of identical sites and that once a site is filled, no further adsorption can occur at that site (Liu et al., 2016). This model helps estimate the maximum adsorption capacity of the material. The Freundlich model, on the other hand, assumes that the surface is heterogeneous and contains different types of binding sites (Ding & Wang, 2013). By comparing experimental data with these models, researchers can better understand how zirconium and hafnium interact with COFs (Liu et al., 2016). In addition to equilibrium studies, adsorption kinetics are also important. Kinetic studies show how fast the adsorption process takes place (Feng et al., 2012). Faster adsorption rates are beneficial for industrial applications because they reduce processing time. Therefore, both equilibrium capacity and adsorption speed are important when evaluating separation performance (Liu et al., 2016).

Separation efficiency is usually measured using a parameter called the selectivity coefficient or separation factor (Ding & Wang, 2013). This value indicates how strongly the COF prefers one metal ion over the other. A higher selectivity coefficient means better separation performance. In experiments, researchers prepare mixed solutions containing both zirconium and hafnium ions in known concentrations. After adsorption, the remaining concentration of each ion in the solution is measured using analytical techniques such as atomic absorption spectroscopy or inductively coupled plasma analysis (Liu et al., 2016). From these results, the separation factor can be calculated. Even small differences in adsorption percentage can lead to meaningful separation if the process is repeated multiple times (Ding & Wang, 2013). Reusability is another important factor. A good COF should maintain its adsorption capacity and selectivity after several cycles of use. After each cycle, the adsorbed metal ions are removed using a suitable eluent, and the material is reused (Liu et al., 2016). Stable and reusable materials are more economical and environmentally friendly for long-term industrial use (Feng et al., 2012).

Another important aspect of adsorption performance is stability under real operating conditions (Ding & Wang, 2013). In industrial processes, zirconium and hafnium separation often takes place in acidic environments. Therefore, the COF must remain stable in strong acid solutions (Liu et al., 2016). If the framework structure breaks down, its adsorption performance will decrease. Researchers test chemical stability by exposing the material to acidic or high-temperature conditions and then analyzing its structure (Feng et al., 2012). Thermal stability is also important because some industrial processes involve elevated temperatures (Liu et al., 2016). In addition, the effect of competing ions must be considered. In real solutions, other metal ions or impurities may be present. These competing ions can reduce selectivity by occupying active sites in the COF (Ding & Wang, 2013). Therefore, performance tests are often carried out in complex solutions to simulate real industrial conditions. A material that performs well only in simple laboratory solutions may not work effectively in practical applications (Liu et al., 2016). Comprehensive performance testing ensures that the COF is suitable for real-world separation challenges (Feng et al., 2012).

Comparing COFs with traditional adsorbents helps evaluate their overall efficiency (Ding & Wang, 2013). Conventional materials such as ion exchange resins or activated carbon may have good adsorption capacity, but they often lack high selectivity for zirconium and hafnium (Cotton et al., 1999). COFs offer advantages such as tunable pore size, adjustable functional groups, and high surface area (Liu et al., 2016). These features allow better control over metal–framework interactions (Feng et al., 2012). However, challenges still remain, such as large-scale production and long-term stability (Ding & Wang, 2013). To move toward industrial application, researchers are also studying pilot-scale experiments and cost analysis (Liu et al., 2016). Improving adsorption capacity, selectivity, and regeneration efficiency are key goals in current research (Feng et al., 2012). By carefully optimizing structure and functionalization, COFs have the potential to achieve higher separation efficiency than conventional methods (Ding & Wang, 2013). Continued research in this area will help develop more reliable and sustainable technologies for zirconium and hafnium separation in the future (Liu et al., 2016).

Sustainable and Industrial Applications

Covalent Organic Frameworks (COFs) have shown great potential for sustainable and industrial applications due to their unique properties (Ding & Wang, 2013; Feng et al., 2012). Sustainability in modern chemistry means reducing energy use, minimizing waste, and designing materials that can be reused (Liu et al., 2016). Traditional methods for separating zirconium (Zr) and hafnium (Hf), such as solvent extraction or ion exchange, often use large amounts of toxic chemicals and generate hazardous waste (Cotton et al., 1999). COFs, on the other hand, can be designed to selectively capture metal ions with minimal chemical input (Ding & Wang, 2013). Their high surface area, ordered pores, and functional groups allow efficient adsorption, reducing the number of separation steps required (Feng et al., 2012). Furthermore, COFs can be regenerated and reused multiple times without losing performance (Liu et al., 2016). This reusability significantly decreases waste and operational costs. In addition, COFs can be synthesized using green chemistry approaches, such as mechanochemical synthesis or room-temperature reactions, which reduce energy consumption and avoid harmful solvents (Ding & Wang, 2013). By combining efficiency, selectivity, and low environmental impact, COFs offer a more sustainable alternative for industrial separation processes (Feng et al., 2012). Their application is not limited to laboratory scale; they have strong potential for large-scale use in nuclear, chemical, and environmental industries (Liu et al., 2016).

One of the most important industrial applications of COFs is in nuclear material purification. Zirconium used in nuclear reactors must have extremely low hafnium content because hafnium absorbs neutrons strongly (Cotton et al., 1999). COFs can be designed to selectively remove hafnium from zirconium solutions, ensuring high-purity zirconium suitable for reactor use (Ding & Wang, 2013). Traditional methods for this separation are energy-intensive and require multiple extraction cycles (Liu et al., 2016). COFs offer a more controlled and potentially faster approach due to their tunable pores and functionalized surfaces (Feng et al., 2012). Moreover, they are resistant to harsh acidic conditions, which is often required during nuclear-grade metal processing (Ding & Wang, 2013). Beyond nuclear materials, COFs can also be used in strategic metal recovery, where valuable metals need to be selectively separated from waste streams or ores (Liu et al., 2016). By designing frameworks with appropriate chemical groups, COFs can target specific metals, reducing the need for broad chemical treatment and lowering environmental impact (Feng et al., 2012). This precision makes COFs suitable for high-value industrial applications where both efficiency and sustainability are critical (Ding & Wang, 2013).

COFs also have potential in environmental and chemical industries for sustainable metal separation (Liu et al., 2016). Many industrial processes generate wastewater containing metals and chemical residues. Using COFs to capture and recycle valuable or hazardous metals can help reduce pollution and recover resources (Feng et al., 2012). For example, heavy metals, rare earth elements, and strategic metals can be selectively removed from industrial effluents using COFs (Ding & Wang, 2013). Their tunable pore size and functional groups allow customization for specific metal ions (Liu et al., 2016). Unlike traditional adsorbents, COFs can withstand repeated use in harsh chemical environments (Feng et al., 2012). They can be regenerated through mild washing or chemical treatment, making them a cost-effective and eco-friendly solution (Ding & Wang, 2013). Additionally, COFs can reduce the overall chemical consumption during separation, which decreases waste generation and energy use (Liu et al., 2016). This makes them highly attractive for industries that aim to comply with environmental regulations while maintaining high operational efficiency (Feng et al., 2012). By integrating COFs into industrial workflows, companies can adopt greener processes without sacrificing performance (Ding & Wang, 2013).

The scalability and practical use of COFs are also being explored in pilot-scale and industrial settings (Liu et al., 2016). While laboratory studies have shown excellent performance, challenges remain for large-scale production. Scientists are working to develop synthesis methods that are cost-effective, reproducible, and environmentally friendly (Feng et al., 2012). Techniques such as mechanochemical synthesis or continuous flow reactions could make large-scale COF production feasible (Ding & Wang, 2013). In addition, pilot-scale studies help optimize COF performance under realistic industrial conditions, including variations in metal concentration, temperature, and acidity (Liu et al., 2016). These studies also evaluate regeneration and long-term stability. The ability to maintain high adsorption capacity and selectivity over multiple cycles is essential for industrial adoption (Feng et al., 2012). Once these challenges are addressed, COFs could replace or supplement traditional separation methods in industries such as nuclear material processing, metal recovery, and chemical manufacturing (Ding & Wang, 2013). Their combination of high performance, sustainability, and tunability makes COFs promising candidates for modern industrial processes (Liu et al., 2016).

COFs also promote international scientific collaboration in sustainable technologies (Feng et al., 2012). For countries like China and Pakistan, where research in nuclear energy, advanced materials, and environmental chemistry is growing, COFs offer opportunities for joint research and industrial innovation (Ding & Wang, 2013). Developing COF-based separation systems can strengthen technological capabilities while maintaining environmentally friendly practices (Liu et al., 2016). The use of COFs supports sustainable development goals by reducing chemical waste, saving energy, and promoting material reuse (Feng et al., 2012). In addition, their application is not limited to metals; COFs can also be used in gas storage, catalysis, and environmental remediation (Ding & Wang, 2013). By integrating COFs into industrial workflows, industries can improve efficiency, reduce costs, and minimize environmental impact (Liu et al., 2016). Continued research in this area will likely expand the applications of COFs, making them a key material for sustainable and high-performance industrial processes in the future (Feng et al., 2012).

Challenges, Future Perspectives, and Research Directions

Although covalent organic frameworks (COFs) show great promise for separating zirconium (Zr) and hafnium (Hf), several challenges must be addressed before they can be widely applied in industrial processes (Ding & Wang, 2013; Liu et al., 2016). One of the main challenges is scalability. Most COFs are still synthesized in small laboratory quantities, and producing large amounts for industrial use is difficult. The synthesis often requires precise control of temperature, solvent, and reaction time to achieve high crystallinity and uniform pore structure (Feng et al., 2012). Small deviations can result in lower-quality materials with reduced adsorption performance. Another challenge is cost. Some of the building blocks and functionalized linkers used to make COFs are expensive, which increases overall production costs (Liu et al., 2016). Additionally, not all COFs have strong stability in harsh chemical environments. Industrial processes often involve strong acids, high temperatures, or multiple adsorption–desorption cycles. If the COF structure degrades under these conditions, its efficiency decreases. Finally, although COFs can show high selectivity in controlled laboratory solutions, real industrial solutions may contain other metal ions or impurities that compete for adsorption sites, reducing separation efficiency. Addressing these challenges is critical for turning COFs into practical industrial materials (Ding & Wang, 2013).

Optimizing selectivity and adsorption efficiency is another key challenge. Zirconium and hafnium are chemically very similar, so COFs must be carefully designed to exploit even small differences in their coordination behavior (Feng et al., 2012). This requires precise functionalization of the framework and careful control of pore size and surface chemistry. Achieving the ideal combination of pore structure and functional groups is not easy, as small design changes can significantly affect adsorption performance. Researchers must also consider adsorption kinetics and regeneration ability. Even if a COF shows high adsorption capacity, slow adsorption rates or poor reusability can limit industrial use. Repeated adsorption and desorption cycles may weaken the framework over time. Therefore, COFs must be designed not only for high selectivity but also for durability and rapid performance. Achieving a balance between selectivity, efficiency, and stability remains one of the most important research challenges (Liu et al., 2016).

Despite these challenges, the future of COFs in metal separation is promising. Advances in computational chemistry and molecular modeling allow scientists to predict optimal COF structures and functional groups for selective zirconium and hafnium separation (Ding & Wang, 2013). Simulations can identify how small differences in ion size, hydration, or coordination chemistry can be exploited within COF pores. Combining computational predictions with experimental synthesis accelerates the development of high-performance COFs. Hybrid materials that combine COFs with other porous materials, such as metal-organic frameworks (MOFs) or nanoparticles, are also being explored, offering improved stability, selectivity, and adsorption capacity (Feng et al., 2012). Researchers are further investigating green synthesis methods, such as mechanochemical approaches or room-temperature reactions, to reduce chemical waste and energy consumption (Liu et al., 2016). These innovations make COFs more sustainable and suitable for industrial applications in the future.

Future research should focus on practical industrial applications. Pilot-scale studies are needed to test COFs under real-world conditions, including variable metal concentrations, competing ions, and continuous operation over multiple cycles (Ding & Wang, 2013). These studies can identify potential limitations and optimize COF properties for large-scale processes. Life-cycle assessments and cost analysis are also important to evaluate economic feasibility. Multifunctional COFs capable of capturing multiple metals or pollutants simultaneously represent another promising direction, increasing the versatility and efficiency of separation systems (Liu et al., 2016). Bridging the gap between laboratory research and industrial application remains a key priority.

Conclusion

In conclusion, COFs offer a promising solution for selective zirconium and hafnium separation, but challenges such as scaling up synthesis, reducing costs, improving stability, and optimizing selectivity and adsorption efficiency remain (Feng et al., 2012). Future work will likely focus on combining computational design, hybrid materials, and green synthesis approaches to create robust and sustainable COFs. Pilot-scale testing and life-cycle analysis will help determine industrial feasibility. Addressing these challenges will enable COFs to become a key technology for sustainable, efficient, and high-performance separation of critical metals. The ongoing development of COFs also opens opportunities for international collaboration, particularly in countries like China and Pakistan, where nuclear energy and advanced materials research are growing. With continued innovation, COFs may play an important role in metal separation, environmental protection, and sustainable industrial processes.

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