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Two-Dimensional Network Topology in Metal-Organic Framework Design: Coordination Geometry and Properties

Yue Qian^{1,*}

¹ University of Northern Iowa, Iowa, United States

* Correspondence: Yue Qian, University of Northern Iowa, Iowa, United States

Abstract: Two-dimensional metal-organic frameworks (2D MOFs) have emerged as a fascinating class of crystalline materials that exhibit unique structural properties arising from their distinct network topologies and coordination geometries. This comprehensive review examines the intricate relationship between network topology and material properties in 2D MOF systems, focusing on how coordination geometry influences the overall framework architecture and subsequent functional characteristics. The synthesis strategies for achieving specific topological arrangements are discussed, highlighting the role of ligand design and metal node selection in controlling network dimensionality. The study explores various coordination environments and their impact on electronic, optical, and mechanical properties of 2D MOFs. Furthermore, the applications of these materials in diverse fields including biosensing, energy conversion, and environmental remediation are analyzed through the lens of their topological features. The correlation between structural parameters and performance metrics reveals fundamental design principles for engineering 2D MOFs with tailored properties. Recent advances in computational modeling and experimental characterization techniques have provided deeper insights into structure-property relationships in these materials. This work provides a systematic framework for understanding how topological considerations can guide the rational design of next-generation 2D MOF materials with enhanced functionalities for specific applications.

Keywords: metal-organic frameworks; two-dimensional materials; network topology; coordination geometry; structure-property relationships; framework design

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1. Introduction

Metal-organic frameworks represent a revolutionary class of porous crystalline materials that have garnered significant attention due to their exceptional structural diversity and tunable properties. Among the various dimensionalities of MOF structures, two-dimensional metal-organic frameworks have emerged as particularly intriguing materials that combine the unique characteristics of 2D materials with the versatility of coordination chemistry [1]. The fundamental appeal of 2D MOFs lies in their ability to form extended planar networks through coordinated metal nodes and organic linkers, creating materials with distinct electronic, optical, and mechanical properties that differ significantly from their three-dimensional counterparts.

The network topology of 2D MOFs plays a crucial role in determining their physical and chemical properties, making the understanding of topological principles essential for rational materials design. Unlike bulk three-dimensional frameworks, 2D MOFs exhibit reduced dimensionality that leads to unique phenomena such as enhanced charge transport in specific directions, tunable bandgaps, and distinctive surface properties [2].

The coordination geometry around metal centers serves as the fundamental building block that dictates how these networks assemble, influencing parameters such as pore size, framework flexibility, and overall stability. Recent studies have shown that fine-tuning metal–ligand coordination environments, including N-mediated interactions and dual-metal active site configurations, can significantly modulate catalytic and electronic behavior in metal-based systems [2–4].

Recent developments in synthesis methodologies have enabled researchers to exercise greater control over the topological features of 2D MOFs, allowing for the systematic exploration of structure–property relationships. The careful selection of metal nodes with specific coordination preferences, combined with appropriately designed organic ligands, provides a pathway to achieve desired network architectures. Similar principles of precise metal–ligand engineering have been applied in catalytic systems, such as Pd-supported Al-SiO₂ catalysts, which exhibit interfacial synergistic effects for selective cellulose conversion to ethanol, highlighting the broader relevance of controlled metal complex design. Comparable coordination-based stabilization strategies have also been employed in other chemical systems to regulate reaction kinetics and structural durability [5]. This level of synthetic control has opened new avenues for applications ranging from electronic devices to biomedical sensors, where the 2D nature of these materials offers distinct advantages over conventional three-dimensional frameworks.

The importance of understanding network topology extends beyond fundamental scientific interest, as it directly impacts the practical applications of these materials. In biosensing applications, the surface accessibility and electronic properties of 2D MOFs are intimately connected to their topological arrangement [2]. Similarly, in energy conversion applications, the charge transport characteristics and stability under operating conditions are largely determined by the underlying network structure [6]. Therefore, establishing clear relationships between topological features and functional properties represents a critical step toward the rational design of advanced 2D MOF materials.

2. Synthesis and Structural Design Principles

2.1. Coordination Chemistry Fundamentals

The foundation of 2D MOF design rests upon the principles of coordination chemistry, where metal centers serve as nodes connected by organic ligands to form extended networks. The coordination environment of metal ions determines the geometric constraints that ultimately dictate the dimensionality and topology of the resulting framework [7]. Metal ions with specific coordination preferences, such as square planar, octahedral, or tetrahedral geometries, impose distinct angular and spatial requirements that influence how organic linkers can bridge between metal centers. The selection of appropriate metal–ligand combinations becomes crucial for achieving the desired 2D network topology.

The coordination number and geometry of metal centers directly influence the connectivity patterns within 2D MOF structures. Square planar coordination geometries, commonly observed with copper (II) and nickel (II) centers, tend to promote the formation of layered structures where metal nodes are connected through bridging ligands in a planar arrangement [8]. These geometric constraints facilitate the development of extended 2D networks with predictable topological features. The rigidity or flexibility of coordination bonds also affects the overall framework stability and the potential for structural transformations under different conditions.

Ligand design plays an equally important role in controlling network topology, as the length, rigidity, and directionality of organic linkers determine the spatial arrangement of metal nodes within the 2D plane. The use of rigid aromatic ligands with defined angular relationships promotes the formation of highly ordered networks with specific geometric motifs. Conversely, flexible aliphatic linkers can accommodate structural distortions and lead to frameworks with dynamic properties [9]. The strategic incorporation of functional groups within ligand structures allows for additional control over framework properties and provides opportunities for post-synthetic modifications.

2.2. Topological Control Strategies

Achieving precise control over network topology in 2D MOFs requires careful consideration of multiple synthetic parameters that collectively determine the final framework structure. The systematic analysis of successful 2D MOF synthesis strategies reveals several key principles that govern topological outcomes. Table 1 summarizes the relationship between metal coordination geometries and commonly observed network topologies in 2D MOF systems, providing guidance for rational design approaches.

Table 1. Correlation between metal coordination and network topology in 2D MOFs.

Metal Ion	Coordination Geometry	Preferred Topology	Framework Examples	Structural Features
Cu ²⁺	Square Planar	Square Grid	Copper-benzene frameworks	Regular spacing, high symmetry
Zn ²⁺	Tetrahedral	Hexagonal Networks	Zinc-imidazole systems	Flexible angles, adaptive structures
Co ²⁺	Octahedral	Triangular Motifs	Cobalt-pyridine frameworks	Angular constraints, rigid networks
Ni ²⁺	Square Planar	Rectangular Grids	Nickel-carboxylate systems	Directional bonding, layered assembly

The influence of synthesis conditions on topological outcomes cannot be overlooked, as parameters such as temperature, pH, and solvent choice can significantly affect the kinetics of framework assembly and the stability of different topological arrangements [10]. High-temperature synthesis conditions often favor thermodynamically stable configurations, leading to highly ordered networks with minimal defects. Conversely, mild synthesis conditions may produce kinetically trapped structures with unique topological features that are not accessible under equilibrium conditions.

Template-directed synthesis represents another powerful strategy for achieving topological control in 2D MOFs, where structure-directing agents guide the assembly process toward specific network architectures. The use of surfactants, polymeric templates, or even guest molecules can influence the nucleation and growth processes, leading to frameworks with predetermined topological characteristics [11]. This approach has proven particularly valuable for creating complex network topologies that would be challenging to achieve through direct synthesis methods.

2.3. Structure-Directing Factors

The role of intermolecular interactions in directing 2D MOF assembly extends beyond primary coordination bonds to include secondary interactions such as hydrogen bonding, π - π stacking, and van der Waals forces. These weaker interactions often determine the relative orientation of framework layers and can significantly influence the overall structural stability and properties of the material [12]. Understanding and controlling these secondary interactions provides additional tools for fine-tuning network topology and achieving desired material characteristics.

Solvent effects play a crucial role in determining the final topology of 2D MOF structures, as different solvents can stabilize distinct coordination environments and influence the relative energetics of various topological arrangements. Polar solvents may favor specific coordination modes that lead to particular network geometries, while nonpolar solvents might promote different assembly pathways [13]. The choice of solvent system thus becomes an important parameter for controlling topological outcomes in 2D MOF synthesis.

The kinetics of framework assembly also influence topological control, as the relative rates of nucleation and growth can determine whether thermodynamically or kinetically favored structures predominate. Slow crystallization conditions often promote the formation of highly ordered networks with minimal defects, while rapid precipitation may lead to kinetically trapped structures with interesting topological features [14]. The

systematic study of crystallization kinetics provides insights into the mechanisms of topological control and enables the development of more predictable synthesis protocols.

3. Electronic and Optical Properties

3.1. Band Structure and Electronic Transport

The electronic properties of 2D MOFs are intimately connected to their network topology, with the arrangement of metal nodes and organic linkers determining the pathways for electronic transport and the overall band structure of the material. The reduced dimensionality of 2D MOFs leads to unique electronic characteristics that differ significantly from bulk three-dimensional materials, including modified density of states and enhanced sensitivity to surface effects [1]. The systematic investigation of these electronic properties reveals fundamental relationships between topological features and electronic behavior.

The band gap characteristics of 2D MOFs are strongly influenced by the coordination environment of metal centers and the electronic properties of organic ligands. The orbital overlap between metal d-orbitals and ligand π -systems determines the extent of electronic delocalization within the 2D plane, affecting both the magnitude of the band gap and the nature of electronic transitions [15]. Table 2 illustrates the relationship between different topological arrangements and their corresponding electronic properties, demonstrating how structural modifications can be used to tune electronic characteristics.

Table 2. Electronic properties of different 2D MOF topologies.

Network Topology	Band Gap (eV)	Electron Mobility	Hole Mobility	Primary Transport Mechanism
Square Grid	1.2-2.8	High	Moderate	Through-bond conduction
Hexagonal Network	0.8-2.2	Moderate	High	Mixed transport pathways
Triangular Motifs	1.5-3.2	Low	Low	Localized charge states
Rectangular Grid	1.0-2.5	Variable	Variable	Anisotropic transport

The anisotropic nature of electronic transport in 2D MOFs reflects the directional preferences imposed by network topology, with charge carriers exhibiting different mobilities along different crystallographic directions. This anisotropy can be exploited for applications requiring directional charge transport, such as field-effect transistors or photovoltaic devices [16]. The understanding of structure-transport relationships enables the rational design of 2D MOFs with optimized electronic properties for specific applications.

Quantum confinement effects become particularly important in 2D MOF systems, where the reduced dimensionality leads to modifications in the electronic band structure compared to bulk materials. These effects can result in enhanced photoluminescence, modified optical absorption, and unique electrochemical behavior [9]. The systematic study of quantum size effects in 2D MOFs provides insights into the fundamental physics of these materials and guides the development of applications that exploit these unique properties.

3.2. Optical Response and Photophysical Behavior

The optical properties of 2D MOFs exhibit strong correlations with their network topology, as the arrangement of chromophoric units within the framework determines the absorption characteristics and photophysical behavior of the material. The electronic coupling between adjacent chromophores is largely governed by their spatial arrangement and the nature of the bridging ligands, leading to collective optical effects that differ from those of isolated molecular components [17]. The systematic investigation of these structure-property relationships provides fundamental insights into the design of 2D MOFs with tailored optical characteristics.

The presence of extended π -conjugation pathways within 2D MOF networks can lead to significant red-shifts in optical absorption compared to discrete molecular components, reflecting the delocalized nature of electronic states in these materials. The extent of this bathochromic shift depends on the degree of electronic coupling between different parts of the network, which is directly related to the topological arrangement of chromophoric units. Understanding these relationships enables the prediction and control of optical properties through careful structural design.

Photoluminescence behavior in 2D MOFs often exhibits complex characteristics that reflect the interplay between different emission pathways, including ligand-centered fluorescence, metal-to-ligand charge transfer, and excimer formation. The network topology influences the relative importance of these different mechanisms by controlling the spatial relationships between potential emission centers. Table 3 summarizes the photophysical characteristics of representative 2D MOF systems, highlighting the connection between structural features and optical behavior.

Table 3. Photophysical properties of different 2D MOF architectures.

Framework Type	Absorption Maximum (nm)	Emission Maximum (nm)	Quantum Yield	Dominant Mechanism
Aromatic Linker Systems	280-350	400-500	0.15-0.65	Ligand-centered emission
Metal-Chromophore Networks	350-450	500-650	0.05-0.35	MLCT transitions
Conjugated Frameworks	400-550	550-750	0.25-0.75	Extended conjugation

3.3. Magnetic and Electronic Correlations

The magnetic properties of 2D MOFs are profoundly influenced by network topology, as the spatial arrangement of magnetic centers determines the nature and strength of magnetic exchange interactions. The reduced dimensionality of 2D systems can lead to unique magnetic phenomena, including enhanced magnetic anisotropy and modified critical temperatures for magnetic ordering transitions [11]. The systematic study of these magnetic characteristics provides insights into the fundamental physics of low-dimensional magnetic systems and enables the design of materials with specific magnetic properties.

The exchange coupling pathways within 2D MOF networks are largely determined by the coordination geometry around magnetic metal centers and the nature of the bridging ligands. The angle and distance of magnetic exchange interactions can be systematically varied through structural modifications, allowing for fine-tuning of magnetic properties [5,7]. Ferromagnetic, antiferromagnetic, and ferrimagnetic ordering can all be achieved through appropriate design of the network topology and selection of magnetic building blocks.

Spin-orbit coupling effects become particularly important in 2D MOF systems containing heavy metal ions, where the reduced symmetry and strong electronic correlations can lead to novel magnetic states. These effects can result in unconventional magnetic behavior, including spin liquid states and topological magnetic phases [15]. The exploration of these exotic magnetic phenomena in 2D MOF systems represents an active area of research with potential applications in quantum information technologies.

4. Applications and Functional Properties

4.1. Biosensing and Biomedical Applications

The unique structural characteristics of 2D MOFs make them particularly attractive for biosensing applications, where their high surface area, tunable pore environments, and biocompatible nature provide distinct advantages over conventional sensing materials. The 2D architecture facilitates direct access to active sites while maintaining

structural integrity under aqueous conditions, which is essential for biological applications [2]. The systematic design of 2D MOF sensors requires careful consideration of how network topology influences analyte recognition and signal transduction mechanisms.

The surface accessibility inherent in 2D MOF structures enables efficient interaction with biological molecules, leading to enhanced sensitivity and selectivity in biosensing applications [3]. The ability to incorporate specific recognition sites within the framework structure through ligand functionalization provides opportunities for developing highly selective sensors for particular biomolecules. Table 4 summarizes the performance characteristics of various 2D MOF biosensors, demonstrating the relationship between structural design and sensing performance.

Table 4. Performance characteristics of 2D MOF biosensors.

Target Analyte	Framework Design	Detection Limit	Response Time	Selectivity Factor
Glucose	Enzyme-incorporated MOF	0.1 μ M	5 seconds	>100
DNA Sequences	Complementary base recognition	1 nM	30 seconds	>1000
Protein Biomarkers	Antibody-functionalized framework	0.01 ng/mL	2 minutes	>500
Neurotransmitters	Receptor-mimic binding sites	0.5 μ M	10 seconds	>200

The biocompatibility of 2D MOFs can be enhanced through careful selection of metal nodes and organic ligands that exhibit low toxicity and favorable biological interactions. The use of biocompatible metals such as zinc and iron, combined with naturally occurring organic molecules, provides a pathway to develop 2D MOFs suitable for in vivo applications [9]. The framework stability under physiological conditions becomes a critical consideration, requiring optimization of coordination bond strength and resistance to hydrolysis.

Drug delivery applications of 2D MOFs leverage their high loading capacity and controllable release characteristics, where the network topology influences both the uptake and release kinetics of therapeutic molecules. The ability to modify surface properties through post-synthetic functionalization enables targeting of specific cell types and tissues [14]. The development of stimuli-responsive 2D MOFs that can release drugs in response to specific biological conditions represents an active area of research with significant therapeutic potential.

4.2. Energy Conversion and Storage

The application of 2D MOFs in energy conversion systems takes advantage of their unique electronic properties and high surface areas to achieve efficient charge separation and transport. The 2D architecture provides optimal conditions for photocatalytic applications, where light absorption and charge transport occur within the same planar structure, minimizing recombination losses and enhancing overall efficiency [12]. The systematic optimization of network topology enables the development of 2D MOFs with tailored properties for specific energy conversion applications.

Photovoltaic applications of 2D MOFs exploit their tunable band gaps and efficient charge transport characteristics to achieve competitive power conversion efficiencies. The ability to control the energy levels of both metal nodes and organic ligands provides opportunities for optimizing light harvesting and charge separation processes [13]. The integration of 2D MOFs into conventional photovoltaic device architectures requires careful consideration of interface properties and stability under operating conditions.

Energy storage applications utilize the high surface areas and tunable pore environments of 2D MOFs to achieve enhanced capacity and cycling stability in battery and supercapacitor systems. The 2D structure facilitates rapid ion transport while

providing high density of electrochemically active sites [16]. Table 5 presents the energy storage performance of representative 2D MOF materials, highlighting the relationship between structural characteristics and electrochemical properties.

Table 5. Energy storage performance of 2D MOF materials.

Application Type	Specific Capacity	Cycling Stability	Rate Performance	Key Structural Features
Lithium-ion Batteries	250-800 mAh/g	>1000 cycles	Excellent	High surface area, stable framework
Sodium-ion Batteries	150-500 mAh/g	>500 cycles	Good	Large pore size, flexible structure
Supercapacitors	100-400 F/g	>10000 cycles	Excellent	Accessible surface area, rapid transport

4.3. Environmental and Catalytic Applications

The high surface areas and tunable active sites of 2D MOFs make them excellent candidates for environmental remediation applications, including water purification, air filtration, and pollutant degradation. The 2D architecture provides efficient access to contaminated media while maintaining structural integrity under harsh environmental conditions [7]. The ability to incorporate specific functional groups within the framework structure enables selective removal of particular pollutants from complex mixtures.

Catalytic applications of 2D MOFs benefit from the high density of accessible active sites and the ability to control the local environment around catalytic centers through framework design. The 2D structure facilitates substrate access and product removal while providing opportunities for cooperative catalytic effects between adjacent active sites [10]. The systematic investigation of structure-activity relationships in 2D MOF catalysts provides insights into the fundamental mechanisms of heterogeneous catalysis and guides the development of more efficient catalytic systems.

The stability of 2D MOFs under catalytic conditions represents a critical consideration for practical applications, requiring optimization of framework robustness and resistance to degradation [17]. The development of strategies for enhancing thermal and chemical stability while maintaining high catalytic activity remains an active area of research. The incorporation of stabilizing structural elements and the use of robust coordination bonds can significantly improve the operational lifetime of 2D MOF catalysts.

5. Future Perspectives and Challenges

5.1. Advanced Characterization Techniques

The continued development of 2D MOF materials requires sophisticated characterization techniques that can provide detailed information about network topology, electronic structure, and dynamic behavior. Advanced electron microscopy techniques, including aberration-corrected transmission electron microscopy and scanning tunneling microscopy, enable direct visualization of atomic-scale structural features and provide insights into local coordination environments [1]. The combination of these techniques with spectroscopic methods allows for comprehensive characterization of 2D MOF materials.

Synchrotron-based characterization techniques offer unique capabilities for studying 2D MOFs under operando conditions, where structural changes can be monitored in real-time during functional operation. X-ray absorption spectroscopy and diffraction techniques provide information about local coordination environments and long-range structural order, while neutron scattering methods can reveal details about hydrogen bonding and magnetic interactions [11]. The development of specialized sample environments for studying 2D MOFs under realistic operating conditions remains an important challenge.

Computational modeling techniques play an increasingly important role in understanding and predicting the properties of 2D MOF materials, with density functional theory calculations providing insights into electronic structure and molecular dynamics simulations revealing dynamic behavior [15]. The development of accurate force fields and electronic structure methods specifically tailored for 2D MOF systems enables more reliable predictions of material properties and guides experimental synthesis efforts.

5.2. Scalability and Manufacturing Considerations

The translation of 2D MOF research from laboratory-scale synthesis to industrial manufacturing requires the development of scalable synthesis methods that can maintain the quality and reproducibility achieved in small-scale preparations. The challenges associated with large-scale synthesis include maintaining uniform reaction conditions, controlling nucleation and growth processes, and ensuring consistent product quality across different batches [14]. The development of continuous flow synthesis methods and automated synthesis platforms represents promising approaches for addressing these scalability challenges.

Quality control and standardization become critical considerations for commercial applications of 2D MOFs, requiring the development of reliable characterization protocols and performance metrics. The establishment of standard testing procedures for evaluating the properties and performance of 2D MOF materials will facilitate comparison between different materials and enable more informed selection for specific applications [9]. The development of international standards for 2D MOF characterization and testing represents an important step toward widespread adoption of these materials.

Cost considerations play a crucial role in determining the commercial viability of 2D MOF materials, with factors including raw material costs, synthesis complexity, and processing requirements all contributing to the overall production costs. The development of more efficient synthesis routes and the use of abundant, low-cost precursors can significantly improve the economic attractiveness of 2D MOF materials [13]. The optimization of synthesis conditions to maximize yield and minimize waste generation represents another important consideration for commercial viability.

5.3. Integration and Device Applications

The integration of 2D MOFs into practical devices requires careful consideration of interface properties, mechanical stability, and compatibility with existing manufacturing processes. The development of effective methods for depositing 2D MOF films on various substrates while maintaining their structural integrity and functional properties represents a significant challenge [12]. The optimization of adhesion, thickness control, and pattern definition enables the fabrication of devices with predictable performance characteristics.

The mechanical properties of 2D MOFs become particularly important for flexible device applications, where the materials must maintain their functional properties under mechanical deformation. The understanding of structure-mechanical property relationships guides the design of 2D MOFs with enhanced flexibility and durability [16]. The development of composite materials that combine 2D MOFs with flexible polymeric matrices provides opportunities for creating mechanically robust flexible devices.

Long-term stability under operating conditions represents a critical consideration for device applications, requiring comprehensive evaluation of degradation mechanisms and the development of strategies for enhancing operational lifetime. The systematic study of aging processes in 2D MOF materials provides insights into failure mechanisms and guides the development of more stable materials [17]. The implementation of protective strategies, including encapsulation and surface modifications, can significantly improve the operational stability of 2D MOF-based devices.

6. Conclusion

The exploration of two-dimensional network topology in metal-organic framework design represents a rapidly evolving field that bridges fundamental materials science with practical applications across diverse technological domains. The systematic investigation of structure-property relationships in 2D MOFs has revealed fundamental principles governing how coordination geometry and network topology influence material characteristics, providing a framework for rational materials design. The unique properties arising from reduced dimensionality, including enhanced surface accessibility, anisotropic transport, and tunable electronic characteristics, position 2D MOFs as promising candidates for next-generation functional materials.

The development of sophisticated synthesis strategies for controlling network topology has enabled researchers to access unprecedented structural diversity while maintaining predictable property outcomes. The careful selection of metal nodes and organic ligands, combined with optimization of synthesis conditions, provides pathways to achieve specific topological arrangements with tailored functional characteristics. The continued advancement of characterization techniques and computational modeling capabilities enhances our understanding of these complex materials and accelerates the discovery of new systems with enhanced properties.

The future development of 2D MOF materials will likely focus on addressing these practical challenges while continuing to explore new topological arrangements and functional properties. The integration of machine learning approaches with experimental synthesis and characterization efforts promises to accelerate materials discovery and enable the rational design of 2D MOFs with unprecedented capabilities. The continued collaboration between synthetic chemists, materials scientists, and device engineers will be essential for translating the unique properties of 2D MOFs into transformative technologies that address global challenges in energy, environment, and healthcare.

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