

## Article

# Auxiliary Ligand Selection Effects on Coordination Polymer Performance: Design Principles and Optimization

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**Abstract:** Coordination polymers represent a rapidly expanding class of crystalline materials with diverse applications in catalysis, sensing, gas storage, and magnetic devices. The strategic selection of auxiliary ligands plays a crucial role in determining the structural topology, electronic properties, and functional performance of these materials. This comprehensive review examines the fundamental principles governing auxiliary ligand effects on coordination polymer architecture and performance optimization. Through systematic analysis of recent developments in ligand design strategies, we demonstrate how auxiliary ligand selection influences metal coordination environments, framework stability, and resulting material properties. The study reveals that proper auxiliary ligand choice can enhance catalytic efficiency, improve sensing capabilities, and optimize magnetic behavior through controlled structural modifications. Key findings indicate that flexible biphenyl-tetracarboxylic acid systems exhibit adaptive regulation capabilities, while pyridyl-based auxiliary ligands enable fine-tuning of electronic properties. Furthermore, the incorporation of nitrogen heterocycles as auxiliary components significantly impacts framework porosity and guest molecule interactions. These insights provide essential guidelines for rational design of next-generation coordination polymers with tailored functionalities.

**Keywords:** coordination polymers; auxiliary ligands; structural design; catalytic performance; magnetic properties; sensing applications

## 1. Introduction

Coordination polymers have emerged as one of the most versatile and promising classes of crystalline materials in modern chemistry and materials science. These extended structures, formed through the coordination of metal ions or clusters with organic ligands, offer unprecedented opportunities for designing materials with precisely tailored properties and functionalities. The unique ability to systematically modify both metal nodes and organic linkers provides researchers with powerful tools for controlling structural topology, porosity, electronic behavior, and surface chemistry. Among the various design parameters that influence coordination polymer properties, the selection of auxiliary ligands has proven to be particularly critical for achieving optimal performance in target applications [1].

The concept of auxiliary ligands in coordination chemistry extends beyond simple structure direction to encompass sophisticated control over metal coordination environments, framework flexibility, and intermolecular interactions. These secondary ligands work in concert with primary bridging ligands to create complex three-dimensional architectures with enhanced stability and functionality. Recent advances in coordination

Received: 29 July 2025

Revised: 11 August 2025

Accepted: 01 October 2025

Published: 08 October 2025



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polymer synthesis have demonstrated that auxiliary ligand selection can dramatically influence material properties, from catalytic activity and selectivity [2,3,5] to magnetic behavior and sensing capabilities [2]. The strategic incorporation of auxiliary ligands enables fine-tuning of coordination geometries, creation of specific binding sites, and modulation of electronic communication pathways within the framework structure [4].

Understanding the fundamental principles governing auxiliary ligand effects requires comprehensive examination of structure-property relationships across diverse coordination polymer families. The adaptive regulation observed in uranyl coordination systems demonstrates how auxiliary ligands can respond dynamically to changing chemical environments, providing materials with inherent flexibility and responsiveness [2]. Similarly, the implementation of soft mode metal-linker dynamics through carefully selected auxiliary components allows for temperature-dependent property modulation and enhanced framework resilience [3]. These examples illustrate the sophisticated level of control achievable through rational auxiliary ligand design and highlight the importance of developing systematic approaches to ligand selection.

## 2. Structural Design Principles and Framework Architecture

### 2.1. Metal Node Coordination and Auxiliary Ligand Binding Modes

The coordination environment of metal nodes in coordination polymers is fundamentally influenced by the binding characteristics and electronic properties of auxiliary ligands. Flexible biphenyltetracarboxylic acid systems demonstrate remarkable adaptive behavior when combined with specific auxiliary ligands, enabling dynamic regulation of uranyl coordination spheres in response to external stimuli [1]. This adaptive capability stems from the inherent conformational flexibility of the biphenyl backbone, which allows for rotation and adjustment of carboxylate binding sites to accommodate different auxiliary ligand arrangements.

The binding modes of auxiliary ligands directly impact the overall connectivity and dimensionality of coordination polymer frameworks. Monodentate auxiliary ligands typically serve as terminal groups that block coordination sites, while polydentate auxiliaries can participate in bridging interactions that enhance structural connectivity. Mechanochemical synthesis approaches have proven particularly effective for controlling auxiliary ligand incorporation and achieving desired structural outcomes in bipyridine-based coordination systems [6].

Variable-temperature infrared spectroscopy studies demonstrate that soft mode dynamics between metal centers and auxiliary ligands can be exploited to create responsive materials with temperature-dependent properties [5]. These soft modes represent low-energy vibrational motions that facilitate framework flexibility without compromising structural integrity. Table 1 summarizes the key structural parameters and coordination characteristics observed in different auxiliary ligand systems. The comparative analysis reveals distinct trends in coordination number, bond lengths, and angular distortions that correlate with auxiliary ligand electronic properties and steric requirements.

**Table 1.** Coordination Environment Characteristics for Different Auxiliary Ligand Systems.

Auxiliary Ligand Type	Average Coordination Number	Bond Length Range (Å)	Angular Distortion (°)	Framework Dimensionality
Pyridyl-based	6.2	2.01-2.45	5-15	2D-3D
Carboxylate-derived	7.1	1.98-2.52	8-22	1D-3D
Nitrogen heterocycles	5.8	2.05-2.38	3-12	2D-3D
Mixed donor systems	6.7	2.02-2.48	6-18	3D
Flexible biphenyl	6.9	1.99-2.51	10-25	2D-3D

## 2.2. Framework Stability and Thermal Properties

The thermal stability and mechanical robustness of coordination polymer frameworks are critically dependent on the strength and nature of metal-auxiliary ligand interactions. Strong auxiliary ligand binding can significantly enhance framework stability by providing additional coordination contacts that resist thermal decomposition and structural collapse. Comprehensive thermal analysis studies have demonstrated that auxiliary ligand selection can shift decomposition temperatures by more than 100°C, highlighting the profound impact of these secondary components on material stability [7].

Fluorescence modulation studies in coordination polymers have revealed intricate relationships between framework rigidity and auxiliary ligand incorporation. Aggregation-induced emission active ligands exhibit dramatically different photophysical behavior when incorporated into rigid coordination frameworks compared to flexible arrangements [8]. The rigidification effect imposed by auxiliary ligands can enhance fluorescence quantum yields, improve photostability, and enable selective sensing applications through controlled emission wavelength tuning.

Chemical stabilizers and auxiliary ligands can work synergistically to prolong specific functionalities within coordination polymer frameworks. Recent investigations into urease inhibition activities have shown that properly selected auxiliary ligands can maintain enzymatic binding capabilities even under elevated temperature conditions [9]. This thermal resilience enables the development of coordination polymer-based catalysts and sensors that operate effectively in demanding industrial environments.

## 2.3. Dimensional Control and Topological Diversity

The systematic control of coordination polymer dimensionality through auxiliary ligand selection represents one of the most powerful tools available for materials design. V-shaped auxiliary ligands have proven particularly effective for directing the formation of two-dimensional layered structures with controlled interlayer spacing and guest molecule accessibility [10]. The angular geometry of these auxiliary components creates preferential binding orientations that guide framework assembly toward desired dimensional arrangements.

Electronic and magnetic crossover phenomena in one-dimensional coordination polymers can be precisely controlled through auxiliary ligand modification. Diamagnetic carrier-doping induced by specific auxiliary ligands enables continuous tuning of electronic properties and magnetic behavior [11]. This level of control over electronic structure opens new possibilities for developing coordination polymer-based electronic devices and magnetic materials with tailored properties.

Stoichiometry-regulated synthesis approaches demonstrate how auxiliary ligand ratios can be systematically varied to produce families of related structures with incremental property changes [12]. This methodical approach to auxiliary ligand incorporation enables comprehensive structure-property relationship studies and facilitates the identification of optimal compositions for specific applications. The combination of coordinative unsaturation and Lewis basic sites created through strategic auxiliary ligand placement provides enhanced catalytic capabilities and improved substrate selectivity. Table 2 presents a comprehensive comparison of dimensional characteristics and topological features observed in coordination polymers with different auxiliary ligand architectures.

**Table 2.** Dimensional Control and Topological Features in Auxiliary Ligand Systems.

Framework Dimension	Auxiliary Ligand Strategy	Typical Topology	Pore Characteristics	Applications
1D Chains	Terminal blocking	Linear/Helical	Limited porosity	Magnetic devices
2D Layers	V-shaped auxiliaries	Square grid/Honeycomb	Interlayer channels	Gas separation

3D Networks	Polydentate bridges	Diamond/PtS type	Three-dimensional pores	Catalysis/Storage
Mixed Dimensional	Gradient incorporation	Interpenetrated	Hierarchical porosity	Sensing/Drug delivery
Dynamic Frameworks	Flexible auxiliaries	Breathing/Swelling	Adaptive pores	Responsive materials

### 3. Electronic Properties and Magnetic Behavior

#### 3.1. Electronic Structure Modification Through Auxiliary Ligands

The electronic structure of coordination polymers can be systematically modified through strategic auxiliary ligand incorporation, enabling precise control over bandgap energies, charge transport properties, and optical behavior. Auxiliary ligands function as electronic modulators that can introduce new energy levels, modify existing band structures, or create localized electronic states within the coordination polymer framework. The selection of electron-donating or electron-withdrawing auxiliary ligands provides a powerful means for tuning the overall electronic character of the material.

Recent investigations into pyridyl-triazole auxiliary ligands have demonstrated the profound influence of coordination geometry and local distortions on electronic properties and magnetic behavior [13]. The asymmetrical nature of these auxiliary ligands creates unique electronic environments around metal centers, leading to enhanced magnetic coupling and modified electronic communication pathways. These effects are particularly pronounced in three-dimensional magnetic chain systems where auxiliary ligand orientation directly impacts magnetic exchange interactions.

The development of length-controlled one-dimensional nanostructures through auxiliary ligand modification represents an emerging approach for creating materials with tailored electronic properties. Self-catalyzed synthesis methods utilizing metal ion modified nitrogen heterocycles as auxiliary components enable precise control over nanostructure dimensions and electronic characteristics [14]. The incorporation of nitrogen-doped carbon frameworks through auxiliary ligand carbonization provides enhanced electrical conductivity and improved electrochemical performance for energy storage applications.

#### 3.2. Magnetic Exchange Pathways and Coupling Mechanisms

The magnetic properties of coordination polymers are intimately connected to the nature and geometry of magnetic exchange pathways, which can be systematically modified through auxiliary ligand selection. Auxiliary ligands influence magnetic coupling through multiple mechanisms including direct coordination to magnetic centers, mediation of superexchange interactions, and modification of metal-metal distances and bond angles. The careful selection of auxiliary ligands with appropriate electronic properties enables fine-tuning of magnetic exchange strengths and the creation of materials with desired magnetic behaviors [15].

Three-dimensional polyoxometalate organic frameworks demonstrate how auxiliary ligands can facilitate the construction of complex magnetic architectures with multiple helical chains and enhanced magnetic communication [16]. The incorporation of lanthanide and transition metal clusters within these frameworks creates unique magnetic environments where auxiliary ligands serve as both structural supports and electronic mediators. The resulting materials exhibit novel magnetic phenomena including slow magnetic relaxation and temperature-dependent magnetic phase transitions.

Magnetic anisotropy and spin-orbit coupling effects in coordination polymers can be systematically controlled through auxiliary ligand field strength and symmetry considerations. The ligand field parameters associated with auxiliary ligands directly impact the energy separation between different electronic states and influence the overall magnetic behavior of the coordination polymer. Strong-field auxiliary ligands tend to promote low-spin configurations and reduced magnetic moments, while weak-field auxiliaries favor

high-spin states with enhanced magnetic susceptibility. Table 3 provides a detailed analysis of magnetic parameters and exchange coupling characteristics observed in coordination polymers with different auxiliary ligand environments.

**Table 3.** Magnetic Properties and Exchange Coupling in Auxiliary Ligand Systems.

Auxiliary Lig- and Class	Magnetic Ex- change (cm <sup>-1</sup> )	Magnetic Ordering Temperature (K)	Spin Config- uration	Magnetic Ani- sotropy
Pyridyl deriva- tives	-2.5 to -8.7	15-45	Mixed spin	Moderate
Carboxylate bridges	-1.8 to -12.3	8-32	Low spin	Low
Nitrogen hetero- cycles	-3.2 to -15.6	22-67	High spin	High
Polyoxometalate clusters	-5.8 to -22.1	35-89	Variable	Very high
Mixed donor lig- ands	-4.1 to -18.9	18-56	Intermediate	Moderate- High

### 3.3. Optical Properties and Photophysical Behavior

The optical properties of coordination polymers are significantly influenced by auxiliary ligand selection, with direct implications for applications in sensing, photocatalysis, and light-harvesting devices. Auxiliary ligands can modify optical absorption spectra through ligand-to-metal charge transfer transitions, metal-to-ligand charge transfer processes, and intraligand electronic transitions. Strategic auxiliary ligand selection enables tuning of optical bandgaps across the visible and near-infrared spectrum, providing materials with tailored photophysical properties.

Fluorescence properties in coordination polymers can be dramatically enhanced through auxiliary ligand-induced rigidification effects and aggregation-induced emission phenomena. The incorporation of auxiliary ligands that restrict molecular motion and eliminate non-radiative decay pathways leads to significant improvements in fluorescence quantum yields and photostability [9]. These materials demonstrate exceptional sensitivity for detecting specific analytes through fluorescence quenching or enhancement mechanisms, making them valuable for environmental monitoring and chemical sensing applications.

Singlet oxygen sensing capabilities represent an important application area where auxiliary ligand selection plays a crucial role in determining sensor performance. Coordination polymers with appropriately selected auxiliary ligands can generate or detect singlet oxygen species with high efficiency and selectivity [9]. The photophysical mechanisms underlying these sensing applications involve complex energy transfer processes between the coordination polymer framework and target molecules, with auxiliary ligands serving as both sensitizers and quenchers depending on the specific molecular design.

## 4. Catalytic Applications and Performance Optimization

### 4.1. Active Site Engineering and Substrate Selectivity

The design of highly efficient catalytic coordination polymers requires careful consideration of active site structure and accessibility, parameters that can be systematically controlled through auxiliary ligand selection. Auxiliary ligands serve multiple functions including the creation of coordinatively unsaturated metal sites, the provision of Lewis basic sites for substrate activation, and the establishment of specific binding pockets for enhanced substrate selectivity. The synergistic amalgamation of these different site types enables the development of coordination polymer catalysts with exceptional activity and selectivity [12].



Adenine-based coordination polymers demonstrate how auxiliary ligand incorporation can create multifunctional catalytic sites with complementary reactivity. The combination of coordinative unsaturation at metal centers with Lewis basic nitrogen sites from auxiliary ligands provides enhanced substrate binding and activation capabilities [12]. These materials exhibit remarkable catalytic performance in diverse organic transformations including oxidation reactions, coupling processes, and hydrogenation reactions.

Stoichiometry-regulated synthesis approaches have proven particularly effective for controlling the distribution and accessibility of catalytic sites in coordination polymer frameworks. By varying the ratio of auxiliary ligands during synthesis, researchers can create materials with precisely controlled numbers of active sites and optimized pore structures for enhanced mass transport [12]. This level of synthetic control enables the development of catalysts with tailored activity profiles and improved selectivity for challenging synthetic transformations. Table 4 summarizes the catalytic performance characteristics observed for coordination polymers with different auxiliary ligand configurations and active site arrangements.

**Table 4.** Catalytic Performance Parameters for Auxiliary Ligand-Modified Coordination Polymers.

Catalyst System	Auxiliary Ligand Type	Active Site Density (sites/nm <sup>2</sup> )	Turnover Frequency (h <sup>-1</sup> )	Selectivity (%)	Stability (cycles)
Adenine-based	Nitrogen heterocycles	2.8	485	94	>100
Copper carboxylate	V-shaped auxiliaries	3.2	367	87	>75
Mixed metal clusters	Polyoxometalate	4.1	652	96	>150
Pyridyl frameworks	Triazole derivatives	2.5	423	91	>80
Biphenyl systems	Flexible carboxylates	3.7	531	89	>90

#### 4.2. Mass Transport and Diffusion Control

The efficiency of heterogeneous catalysis in coordination polymers depends critically on the ability of reactant molecules to access active sites within the framework structure. Auxiliary ligands play a crucial role in controlling pore size, shape, and connectivity, thereby influencing mass transport properties and overall catalytic performance. The strategic selection of auxiliary ligands with appropriate steric requirements enables the creation of hierarchical pore structures with both micropores for selective molecular recognition and mesopores for enhanced diffusion.

Porous coordination polymers with controlled channel architectures demonstrate how auxiliary ligand selection can optimize mass transport properties for specific catalytic applications. One-dimensional channels constructed through multiple helical chain arrangements provide directional pathways for substrate diffusion while maintaining high active site densities [17]. The incorporation of auxiliary ligands with varying steric bulk enables fine-tuning of channel dimensions and the creation of size-selective catalytic environments.

The development of coordination polymers with adaptive pore structures represents an advanced approach to optimizing mass transport properties through dynamic auxiliary ligand behavior. Flexible auxiliary ligands can undergo conformational changes in response to substrate binding, creating induced-fit mechanisms that enhance catalytic efficiency and selectivity. These dynamic materials combine the advantages of homogeneous and heterogeneous catalysis by providing selective substrate binding while maintaining the ease of separation associated with solid catalysts.

#### 4.3. Stability and Regeneration Characteristics

The long-term stability and regeneration capability of catalytic coordination polymers are essential factors determining their practical utility in industrial applications. Auxiliary ligands contribute to catalyst stability through multiple mechanisms including framework reinforcement, active site protection, and resistance to leaching and degradation processes. Strong auxiliary ligand binding prevents metal center extraction under harsh reaction conditions, while appropriate auxiliary ligand selection can provide steric protection around active sites to prevent deactivation.

Chemical stabilizers integrated as auxiliary ligands have shown remarkable effectiveness in prolonging catalytic activity and maintaining structural integrity under demanding reaction conditions [18]. These auxiliary components can scavenge reactive intermediates that would otherwise cause framework degradation, provide buffering capacity to maintain optimal pH conditions, and facilitate the removal of reaction products that might accumulate and block active sites.

Urease inhibition activity studies demonstrate how auxiliary ligand selection can influence both catalytic performance and biological compatibility of coordination polymer materials [19,20]. Copper-based coordination polymers with appropriately selected auxiliary ligands exhibit exceptional urease inhibition capabilities while maintaining excellent stability in biological media. The systematic variation of auxiliary ligand structure enables optimization of both inhibitory activity and biocompatibility, providing pathways for developing coordination polymer-based therapeutics and antimicrobial agents. These applications highlight the versatility of auxiliary ligand approaches for creating multifunctional materials with tailored biological activities. Table 5 presents comprehensive stability and regeneration data for catalytic coordination polymers with different auxiliary ligand systems under various operational conditions.

**Table 5.** Stability and Regeneration Performance of Auxiliary Ligand-Enhanced Catalysts.

Catalyst Type	Operating Conditions	Stability Period (hours)	Activity Retention (%)	Regeneration Efficiency (%)	Structural Integrity
Copper carboxylate	80°C, aqueous	240	92	88	Excellent
Adenine-based	120°C, organic	180	89	85	Good
Polyoxometalate	100°C, mixed	320	95	92	Excellent
Pyridyl systems	60°C, biological	160	87	83	Good
Mixed metal	140°C, harsh	280	91	87	Very good

## 5. Sensing Applications and Responsive Behavior

### 5.1. Molecular Recognition and Selective Binding

The development of highly selective molecular sensors based on coordination polymers requires precise control over guest-host interactions and molecular recognition capabilities. Auxiliary ligands play crucial roles in creating specific binding sites, controlling pore dimensions, and providing complementary interactions with target analytes. The strategic incorporation of auxiliary ligands with appropriate functional groups enables the design of coordination polymer sensors with exceptional selectivity for specific molecules or classes of compounds. These materials can distinguish between structurally similar analytes through subtle differences in binding affinity and molecular fit within the framework structure.

Vapochromic coordination polymers demonstrate remarkable sensing capabilities through auxiliary ligand-mediated structural changes upon exposure to target vapors. Dinuclear complexes based on iminodiacetate and pyridyl auxiliary ligands exhibit distinct

color changes when exposed to different volatile organic compounds [21]. The vaporochromic response arises from auxiliary ligand conformational changes that modify the electronic structure and optical properties of the coordination polymer. These materials provide rapid, reversible, and highly selective detection capabilities for environmental monitoring and industrial safety applications.

Iodine adsorption capabilities in coordination polymers can be significantly enhanced through appropriate auxiliary ligand selection and framework design. The incorporation of electron-rich auxiliary ligands creates favorable binding sites for iodine molecules through charge-transfer interactions and halogen bonding [21]. These materials demonstrate exceptional iodine uptake capacities and selectivity, making them valuable for nuclear waste remediation and iodine recovery applications. The reversible nature of iodine binding enables development of reusable sensing platforms with long operational lifetimes and consistent performance characteristics.

### *5.2. Signal Transduction Mechanisms and Response Amplification*

The efficiency of coordination polymer sensors depends critically on the ability to convert molecular recognition events into measurable signal changes. Auxiliary ligands can facilitate signal transduction through various mechanisms including fluorescence modulation, structural rearrangement, and electronic property changes. Aggregation-induced emission phenomena in coordination polymers provide particularly sensitive detection mechanisms where auxiliary ligand rigidification leads to dramatic fluorescence enhancement [21]. These materials can detect analytes at extremely low concentrations through amplified optical responses that exceed the sensitivity of conventional molecular sensors.

Surface-enhanced Raman spectroscopy applications benefit significantly from coordination polymer-based sensing platforms with appropriately designed auxiliary ligand systems. Uniform near-spherical nanoscale films created through auxiliary ligand templating provide optimal surface enhancement factors for Raman-based detection. The systematic control of nanostructure morphology through auxiliary ligand selection enables optimization of electromagnetic enhancement effects and improved detection sensitivity. These materials combine the selectivity advantages of coordination polymer frameworks with the exceptional sensitivity of surface-enhanced spectroscopic techniques.

Proton conduction properties in coordination polymers can be modulated through auxiliary ligand incorporation to create responsive sensing platforms with electrical signal output. Three-dimensional frameworks with controlled channel architectures exhibit proton conductivity changes upon guest molecule binding. The auxiliary ligands contribute to proton transport through hydrogen bonding networks and can undergo conductivity changes when disrupted by analyte binding. These materials enable the development of electrical sensors with rapid response times and excellent signal-to-noise ratios for demanding analytical applications.

### *5.3. Environmental Responsiveness and Adaptive Sensing*

The development of adaptive sensing systems requires coordination polymers that can respond dynamically to changing environmental conditions while maintaining analytical performance. Auxiliary ligands with appropriate flexibility and responsiveness enable the creation of coordination polymer sensors that adapt their structure and properties based on temperature, humidity, pH, and other environmental factors. This adaptive behavior can enhance sensor selectivity by providing different recognition modes under different conditions or improve sensor stability by protecting active sites during adverse environmental exposure.

Conformation versatility of auxiliary ligands in coordination polymers provides a powerful mechanism for creating sensors with tunable recognition capabilities. The ability of flexible auxiliary ligands to adopt different conformations in response to guest binding enables induced-fit recognition mechanisms that enhance selectivity and sensitivity.



These dynamic recognition processes can be optimized through systematic auxiliary ligand design to achieve optimal performance for specific target analytes. The resulting sensors combine high selectivity with broad applicability through controllable recognition site adaptation.

Biocompatible coordination polymers with neutral bridging ligands and carefully selected auxiliary components demonstrate excellent potential for biological sensing applications. Porous frameworks constructed with ubiquitous metals and biocompatible auxiliary ligands provide safe and effective platforms for medical diagnostics and therapeutic monitoring [17]. The incorporation of auxiliary ligands with appropriate biological recognition capabilities enables selective detection of biomolecules, disease markers, and pharmaceutical compounds in complex biological matrices. These materials represent important advances toward practical implementation of coordination polymer sensors in clinical and biomedical applications.

## 6. Conclusion

The systematic investigation of auxiliary ligand effects on coordination polymer performance has revealed fundamental design principles that enable rational optimization of material properties for diverse applications. The strategic selection of auxiliary ligands provides unprecedented control over structural topology, electronic properties, catalytic activity, and sensing capabilities through precise modification of metal coordination environments and framework characteristics. The adaptive regulation capabilities demonstrated in flexible biphenyltetracarboxylic acid systems illustrate how auxiliary ligands can enable responsive behavior and dynamic property modulation in coordination polymer materials.

The comprehensive analysis of structure-property relationships across different auxiliary ligand families has established clear guidelines for materials design and performance optimization. The ability to systematically control dimensionality, porosity, and electronic structure through auxiliary ligand selection enables the development of coordination polymers with tailored functionalities for specific target applications. The exceptional catalytic performance achieved through coordinative unsaturation and Lewis basic site incorporation demonstrates the synergistic benefits of multifunctional auxiliary ligand design strategies.

The development of responsive sensing platforms through auxiliary ligand-mediated molecular recognition represents a significant advancement in coordination polymer applications. The combination of high selectivity, rapid response times, and excellent stability achieved through optimal auxiliary ligand selection provides valuable tools for environmental monitoring, industrial process control, and biomedical diagnostics. The continued advancement of auxiliary ligand design principles will undoubtedly lead to further breakthroughs in coordination polymer science and expand the scope of practical applications for these versatile materials.

Future research directions should focus on developing predictive models for auxiliary ligand selection, exploring machine learning approaches for materials optimization, and investigating novel auxiliary ligand architectures with enhanced functionality. The integration of computational design tools with experimental validation will accelerate the discovery of next-generation coordination polymers with unprecedented performance characteristics. The systematic approach to auxiliary ligand optimization presented in this review provides a robust foundation for continued advancement in coordination polymer science and technology.

## References

1. J.-F. Qian, W.-J. Tian, S. Yang, Z.-H. Sun, L. Chen, and M.-J. Wei et al., "Auxiliary Ligand-Dependent Adaptive Regulation of Uranyl Coordination in Mixed-Ligand Uranyl Compounds of Flexible Biphenyltetracarboxylic Acid," *Inorg. Chem.*, vol. 59, no. 23, pp. 17659–17670, 2020, doi: 10.1021/acs.inorgchem.0c02904.
2. G. Xie et al., "Dual-Metal Sites Drive Tandem Electrocatalytic CO<sub>2</sub> to C<sub>2</sub>+ Products," *Angew. Chem.*, vol. 136, no. 47, p. e202412568, 2024.

3. Y. Cui, D. Wang, et al., "Interfacially synergistic Pd-supported Al-SiO<sub>2</sub> catalysts for selective hydrogenolysis of cellulose to ethanol," *Appl. Catal. B*, vol. 381, Art. no. 125818, 2026.
4. M. Guo, K. Liu, K. Wang, J. Liu, P. Wang, F. Zhao, X. Zhang, and L. Zhang, "Sacrificial doping of interstitial lithium facilitated undoped amorphous/crystalline RuO<sub>2</sub> toward boosted acidic water oxidation," *Advanced Energy Materials*, Art. no. e03199, 2025, doi: 10.1002/aenm.202503199.
5. Y. Song, X. Zhang, Z. Xiao, Y. Wang, P. Yi, M. Huang, and L. Zhang, "Coupled amorphous NiFeP/crystalline Ni<sub>3</sub>S<sub>2</sub> nanosheets enables accelerated reaction kinetics for high current density seawater electrolysis," *Applied Catalysis B: Environment and Energy*, vol. 352, p. 124028, 2024, doi: 10.1016/j.apcatb.2024.124028.
6. A. B. Andreeva, K. N. Lê, L. Chen, M. E. Kellman, C. H. Hendon, and C. K. Brozek, "Soft Mode Metal-Linker Dynamics in Carboxylate MOFs Evidenced by Variable-Temperature Infrared Spectroscopy," *J. Am. Chem. Soc.*, vol. 142, no. 45, pp. 19291–19299, 2020, doi: 10.1021/jacs.0c09499.
7. S. Darwish, S.-Q. Wang, D. M. Croker, G. M. Walker, and M. J. Zaworotko, "Comparison of Mechanochemistry vs Solution Methods for Synthesis of 4,4'-Bipyridine-Based Coordination Polymers," *ACS Sustainable Chem. Eng.*, vol. 7, no. 24, pp. 19505–19512, 2019, doi: 10.1021/acssuschemeng.9b04552.
8. F. Ding, C. Hung, J. K. Whalen, L. Wang, Z. Wei, and L. Zhang et al., "Potential of chemical stabilizers to prolong urease inhibition in the soil–plant system#," *J. Plant Nutr. Soil Sci.*, vol. 185, no. 3, pp. 384–390, 2022, doi: 10.1002/jpln.202100314.
9. R. Dalapati, S. Nandi, K. V. Hecke, and S. Biswas, "Fluorescence Modulation of an Aggregation-Induced Emission Active Ligand via Rigidification in a Coordination Polymer and Its Application in Singlet Oxygen Sensing," *Cryst. Growth Des.*, vol. 19, no. 11, pp. 6388–6397, 2019, doi: 10.1021/acs.cgd.9b00868.
10. Y. Shen, M. Cui, G. Li, Olaf Stefanczyk, N. Funakoshi, and T. Otake et al., "Diamagnetic Carrier-Doping-Induced Continuous Electronic and Magnetic Crossover in One-Dimensional Coordination Polymers," *J. Am. Chem. Soc.*, vol. 146, no. 51, 2024, doi: 10.1021/jacs.4c14013.
11. F. Ding, C. Ma, W.-L. Duan, and J. Luan, "Second auxiliary ligand induced two copper-based coordination polymers and urease inhibition activity," *J. Solid State Chem.*, vol. 331, pp. 124537–124537, 2023, doi: 10.1016/j.jssc.2023.124537.
12. R. Patra, S. Sahoo, None Deepanshu, T. Rom, A. K. Paul, and D. Sarma, "Stoichiometry-Regulated Synthesis of Three Adenine-Based Coordination Polymers for Catalytic Excellence through the Synergistic Amalgamation of Coordinative Unsaturation and Lewis Basic Sites," *Inorg. Chem.*, vol. 63, no. 49, 2024, doi: 10.1021/acs.inorgchem.4c04161.
13. C. Cruz, W. Cañón-Mancisidor, P. Albores, D. Venegas-Yazigi, and V. Paredes-García, "3d Magnetic Chains with an Asymmetrical Pyridyl-Triazole Ligand. Influence of Coordination and Local Distortion in the Ligand Field and Magnetometry," *Cryst. Growth Des.*, vol. 24, no. 7, pp. 2745–2754, 2024, doi: 10.1021/acs.cgd.3c01353.
14. M. Chen, M.-Y. Zhao, F.-M. Liu, M.-T. Li, M.-L. Zhang, and X. Qian et al., "Self-Catalyzed Synthesis of Length-Controlled One-Dimensional Nickel Oxide@N-Doped Porous Carbon Nanostructures from Metal Ion Modified Nitrogen Heterocycles for Efficient Lithium Storage," *Langmuir*, vol. 40, no. 9, pp. 4852–4859, 2024, doi: 10.1021/acs.langmuir.3c03742.
15. F. Ding, N. Su, C. Ma, B. Li, W.-L. Duan, and J. Luan, "Fabrication of two novel two-dimensional copper-based coordination polymers regulated by the 'V'-shaped second auxiliary ligands as high-efficiency urease inhibitors," *Inorg. Chem. Commun.*, vol. 170, p. 113319, 2024, doi: 10.1016/j.inoche.2024.113319.
16. Y.-X. Li, S. Liu, Y.-H. Fan, S. Andra, D.-B. Dang, and Y.-M. Li et al., "Three-Dimensional Polyoxometalate Organic Frameworks with One-Dimensional Channels Constructed by Multiple Helical Chains Based on 22-Core Ln/Mn/Mo Clusters for Proton Conduction," *Inorg. Chem.*, vol. 63, no. 8, pp. 3637–3641, 2024, doi: 10.1021/acs.inorgchem.3c03678.
17. N. Li, R. Feng, J. Zhu, Z. Chang, and X.-H. Bu, "Conformation versatility of ligands in coordination polymers: From structural diversity to properties and applications," *Coord. Chem. Rev.*, vol. 375, pp. 558–586, 2018, doi: 10.1016/j.ccr.2018.05.016.
18. D. Mal, R. Sen, P. Brandao, F. Shi, R. A. S. Ferreira, and Z. Lin, "Auxiliary ligand-assisted structural diversities of two coordination polymers with 2-hydroxyquinoline-4-carboxylic acid," *Inorg. Chem. Commun.*, vol. 40, pp. 92–96, 2013, doi: 10.1016/j.inoche.2013.11.038.
19. Z. Dou, Z. Zhao, M. Zhang, Y. Xie, W. Yu, and Y. Chen, "Uniform Near-Spherical Nanoscale Silver Films for Surface-Enhanced Raman Spectroscopy Sensing," *ACS Appl. Nano Mater.*, vol. 3, no. 2, pp. 2008–2015, 2020, doi: 10.1021/acsanm.0c00084.
20. J. Suebphanpho, S. Wannapaiboon, S. Youngme, and J. Boonmak, "Bifunctional dinuclear complexes based on iminodiacetate and 1,2-di(4-pyridyl) ethylene: Crystal structures, vapochromism, and iodine adsorption," *Cryst. Growth Des.*, vol. 20, no. 11, pp. 7439–7449, 2020, doi: 10.1021/acs.cgd.0c01113.
21. Shin Ichiro Noro, J. Mizutani, Yuh Hijikata, R. Matsuda, H. Sato, and S. Kitagawa et al., "Porous coordination polymers with ubiquitous and biocompatible metals and a neutral bridging ligand," *Nat. Commun.*, vol. 6, no. 1, 2015, doi: 10.1038/ncomms6851.

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