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Review

Functional Coordination Polymers with Dual Catalytic Applications

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Abstract: Functional coordination polymers have emerged as remarkable materials exhibiting dual catalytic capabilities that enable simultaneous or sequential transformations in complex reaction systems. These crystalline porous materials, constructed from metal ions or clusters connected by organic linkers, possess unique structural features including high surface areas, tunable pore environments, and diverse metal coordination sites that facilitate multiple catalytic functions. The integration of different catalytic functionalities within a single framework enables cascade reactions, tandem transformations, and multifunctional catalytic processes that would be difficult to achieve using conventional catalysts. This review examines the design principles underlying dual-functional coordination polymers, emphasizing how structural architecture, metal center selection, and ligand design contribute to multifunctional catalytic behavior. The synthetic strategies for creating coordination polymers with controlled dual functionalities are discussed, along with characterization approaches that reveal structure-activity relationships. Applications in various catalytic processes including organic transformations, environmental remediation, electrochemical reactions, and biomimetic catalysis are comprehensively analyzed. Special attention is given to systems demonstrating synergistic effects where dual functionalities enhance overall catalytic performance beyond simple additive contributions. The challenges associated with maintaining structural stability during catalytic processes and strategies for optimizing dual catalytic activities are addressed. This comprehensive analysis demonstrates that functional coordination polymers represent a powerful platform for developing advanced catalytic systems with multiple integrated functionalities.

Keywords: coordination polymers; dual catalysis; metal-organic frameworks; heterogeneous catalysis; multifunctional materials; tandem reactions

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1. Introduction

The development of catalytic materials capable of performing multiple functions within a single framework represents a significant advancement in modern catalysis research. Traditional catalytic systems typically focus on optimizing a single transformation, necessitating multiple reactors and separation steps for complex synthetic sequences. Functional coordination polymers have emerged as sophisticated materials that address this limitation by incorporating multiple catalytic sites within their crystalline structures, enabling dual or even multiple catalytic applications simultaneously [1]. These materials combine the advantages of heterogeneous catalysis, including ease of separation and recyclability, with the versatility of homogeneous systems through their well-defined active sites and tunable chemical environments.

Coordination polymers, particularly metal-organic frameworks, possess several structural features that make them ideal platforms for dual catalytic applications. The regular arrangement of metal nodes and organic linkers creates uniform pore environments where different catalytic functionalities can be strategically positioned [2, 3]. The high surface areas characteristic of these materials ensure excellent accessibility of reactants to active sites, while the crystalline nature facilitates structural characterization and rational design. Moreover, the modular construction of coordination polymers allows independent manipulation of metal centers and organic components, providing unprecedented control over catalytic properties. This design flexibility enables the creation of materials where acid-base, redox, and coordination catalysis can coexist within a single framework [4, 5].

Recent advances in synthesis methodologies have enabled the preparation of increasingly sophisticated coordination polymers with precisely controlled dual functionalities. Post-synthetic modification techniques allow introduction of secondary catalytic sites without disrupting the parent framework structure, while mixed-metal and mixed-ligand approaches create materials with inherent multifunctionality. The emergence of computational tools has accelerated catalyst design by predicting optimal combinations of metals and linkers for specific dual catalytic applications [6, 7]. These developments have led to coordination polymers exhibiting remarkable performance in cascade reactions, tandem transformations, and processes requiring cooperative activation of multiple substrates, demonstrating the potential of these materials to revolutionize catalytic chemistry.

2. Design Principles and Structural Considerations

2.1. Metal Center Engineering for Dual Functionality

The selection and arrangement of metal centers within coordination polymer frameworks fundamentally determine their dual catalytic capabilities. Different metal ions exhibit distinct catalytic properties based on their electronic configurations, coordination geometries, and redox potentials, enabling diverse reaction pathways when incorporated into the same structure. Copper-based coordination polymers have demonstrated exceptional versatility in dual catalytic applications due to copper's ability to participate in both redox processes and coordination-mediated transformations [8]. The oxidation state flexibility of copper allows it to function in electron transfer reactions while simultaneously serving as a Lewis acid for substrate activation. Mixed-metal frameworks incorporating copper alongside secondary metals such as zinc or manganese create systems where each metal contributes distinct catalytic functionality, enabling cooperative substrate activation and transformation.

The spatial distribution of metal centers within the framework architecture significantly influences dual catalytic performance. Frameworks with metal clusters positioned at nodes provide high local concentrations of catalytic sites that facilitate cooperative substrate binding and activation. The distance between different metal types affects the efficiency of tandem reactions, as intermediate transfer between catalytic sites depends on spatial proximity. Frameworks designed with alternating metal centers create environments conducive to sequential transformations where products from one catalytic site serve as substrates for adjacent sites [9]. Advanced synthetic strategies including layer-by-layer assembly and controlled nucleation enable precise control over metal distribution, facilitating optimization of dual catalytic systems for specific applications.

The coordination environment surrounding metal centers modulates their catalytic properties through electronic and steric effects. Organic linkers directly coordinated to metals influence electron density at the metal center, affecting its Lewis acidity and redox potential. Auxiliary ligands introduced through post-synthetic modification can fine-tune metal properties without altering the overall framework structure. The incorporation of pendant functional groups near metal sites creates secondary catalytic functionalities that complement the intrinsic activity of the metal center [10, 11]. Table 1 summarizes the relationship between metal center properties and dual catalytic capabilities in representative coordination polymer systems.

Table 1. Metal centers and their dual catalytic functionalities in coordination polymers.

Metal Center	Primary Function	Secondary Function	Coordination Geometry	Electronic Configuration	Representative Application
Copper (II)	Lewis acid	Redox catalysis	Square planar	d^9	Oxidative coupling
Manganese (II)	Coordination	Magnetic property	Octahedral	d^5	Dielectric switching
Zinc (II)	Lewis acid	Framework stability	Tetrahedral	d^{10}	Henry reactions
Iron (III)	Redox catalysis	Magnetic ordering	Octahedral	d^5	Biomimetic oxidation
Cobalt (II)	Coordination	Electron transfer	Octahedral	d^7	Electrochemical reactions

2.2. Ligand Design and Functional Group Integration

The organic linkers connecting metal centers in coordination polymers provide opportunities for introducing additional catalytic functionalities beyond those inherent to the metal sites. Ligands featuring basic groups such as amines or imidazoles create Bronsted base sites that complement the Lewis acidity of metal centers, enabling acid-base bifunctional catalysis. The strategic positioning of functional groups along ligand backbones allows control over substrate orientation and reaction selectivity [12]. V-shaped auxiliary ligands have proven particularly effective in modulating framework properties and introducing secondary functionalities, as their geometry influences pore structure and creates distinct microenvironments within the material [13].

The length and rigidity of organic linkers significantly affect the catalytic performance of dual-functional coordination polymers. Longer linkers create larger pores that accommodate bulkier substrates and facilitate mass transfer, while shorter linkers produce more compact structures with higher volumetric densities of active sites. Rigid aromatic linkers maintain structural integrity under catalytic conditions, preventing framework collapse that could eliminate dual functionality. Flexible linkers enable dynamic structural responses to substrate binding, potentially enhancing selectivity through induced-fit mechanisms. The combination of multiple linker types within a single framework creates hierarchical pore structures that optimize both accessibility and site density [1, 2].

Post-synthetic modification of ligands represents a powerful approach for introducing dual catalytic functionalities into existing coordination polymer frameworks. Chemical transformations of pendant groups on linkers can install catalytic sites without disrupting the metal-ligand connectivity that maintains framework integrity. This strategy allows sequential optimization of different catalytic functions, as each modification step can be independently controlled and characterized. Grafting of organocatalytic moieties onto framework linkers creates hybrid systems combining metal-based and organic catalytic functionalities [6, 7]. Table 2 illustrates various ligand design strategies and their contributions to dual catalytic systems.

Table 2. Ligand design strategies for dual-functional coordination polymers.

Ligand Type	Structural Feature	Primary Contribution	Secondary Contribution	Synthesis Approach	Stability Factor
Carboxylate	Rigid aromatic	Metal coordination	Framework rigidity	Direct synthesis	Excellent
Nitrogen heterocycle	Basic sites	Bronsted base	Substrate orientation	Mixed ligand	Very good
Functionalized aromatic	Pendant groups	Organocatalysis	Hydrophobicity control	Post-modification	Good
V-shaped linker	Angular geometry	Pore engineering	Dielectric modulation	Auxiliary ligand	Very good
Bipyridine	Chelating ability	Metal stabilization	Electron transfer	Direct synthesis	Excellent

2.3. Pore Engineering and Microenvironment Control

The porous nature of coordination polymers provides unique opportunities for creating specialized microenvironments that enhance dual catalytic performance through confinement effects and selective substrate access. Pore size distribution determines which substrates can access catalytic sites, enabling size-selective catalysis where only molecules below certain dimensions undergo transformation. The chemical nature of pore walls influences substrate adsorption and orientation, affecting reaction selectivity and kinetics [3]. Hydrophobic pores preferentially adsorb organic substrates, while hydrophilic environments favor polar molecules, allowing tuning of substrate selectivity in competitive reaction systems.

The hierarchical organization of pores at multiple length scales optimizes mass transfer while maintaining high surface areas. Micropores provide high densities of catalytic sites and strong confinement effects that can stabilize reactive intermediates, while mesopores facilitate substrate diffusion and product removal. Frameworks designed with interconnected pore networks ensure efficient transport throughout the material, preventing diffusion limitations that could diminish catalytic activity [5]. The strategic placement of different catalytic functionalities within distinct pore regions enables spatial separation of incompatible catalytic sites, allowing them to function independently without mutual deactivation.

The local chemical environment within pores can be engineered to promote specific reaction pathways through electronic and steric effects. The presence of charged species or polar groups in pore walls creates electric fields that stabilize transition states or intermediates, lowering activation barriers for desired transformations. Confinement within nanoscale pores can alter the thermodynamics and kinetics of reactions compared to bulk solution, potentially enabling transformations that are unfavorable under normal conditions [9, 10]. Table 3 demonstrates how pore characteristics influence dual catalytic performance in various coordination polymer systems.

Table 3. Pore characteristics and their influence on dual catalytic applications.

Pore Size Range	Surface Area	Wall Chemistry	Confinement Effect	Substrate Selectivity	Typical Application
Microporous (<2 nm)	1200-1800 m²/g	Hydrophobic	Strong stabilization	Size-selective	Small molecule activation
Mesoporous (2-50 nm)	600-1200 m²/g	Amphiphilic	Moderate orientation	Shape-selective	Bulky substrate conversion
Hierarchical	1500-2500 m²/g	Mixed character	Variable control	Multiscale access	Complex transformations

Ultramicroporous (<0.7 nm)	1800-2400 m²/g	Highly polar	Maximum confinement	Molecular sieving	Gas separation catalysis
Large pore (>5 nm)	400-800 m²/g	Tunable	Minimal restriction	Low selectivity	Biomolecule catalysis

3. Synthetic Strategies and Characterization

3.1. Direct Synthesis and Mixed-Component Approaches

The direct synthesis of dual-functional coordination polymers involves combining metal precursors with multiple types of organic linkers under controlled conditions to produce frameworks with integrated functionalities. Solvothermal synthesis remains the most widely employed method, offering precise control over crystallization kinetics and framework topology through manipulation of temperature, solvent composition, and reactant concentrations [1, 2]. The selection of metal salts and their counterions influences the coordination geometry and oxidation states of metal centers in the resulting framework. Modulator molecules added to synthesis mixtures control crystal growth rates and morphologies, affecting the accessibility of catalytic sites and overall material performance.

Mixed-ligand synthesis strategies enable the incorporation of different organic linkers within a single framework, creating materials with complementary catalytic functionalities. The relative ratios of linker types determine the distribution of different functional groups throughout the structure, affecting the balance between various catalytic activities. Careful selection of linkers with compatible coordination modes ensures successful framework formation without phase separation or preferential incorporation of one linker type. The use of auxiliary ligands alongside primary structural linkers introduces additional functionalities without disrupting the main framework architecture [8, 13]. This approach has proven particularly effective for creating coordination polymers with both structural stability and high catalytic versatility.

Room-temperature and mechanochemical synthesis methods offer advantages for incorporating thermally sensitive functional groups that might decompose under solvothermal conditions. Grinding or ball-milling mixtures of metal precursors and ligands produces coordination polymers with reduced crystallinity but potentially enhanced surface areas and defect densities that benefit catalytic applications. The absence of solvents in mechanochemical approaches aligns with green chemistry principles and simplifies purification procedures. Microwave-assisted synthesis accelerates framework formation while maintaining control over structural features, enabling rapid screening of synthetic conditions for optimizing dual catalytic performance [3, 5]. Table 4 compares different synthetic approaches for dual-functional coordination polymer preparation.

Table 4. Synthetic methods for dual-functional coordination polymer fabrication.

Synthesis Method	Temperature Range	Reaction Time	Crystallinity	Functional Group Tolerance	Scalability Potential
Solvothermal	80-200°C	12-72 hours	Excellent	Moderate	Good
Hydrothermal	100-220°C	24-96 hours	Excellent	Limited	Excellent
Room temperature	20-40°C	24-168 hours	Good	High	Moderate
Mechanochemical	Ambient	0.5-4 hours	Poor to moderate	Very high	Excellent

Microwave-assisted	80-180°C	0.5-3 hours	Good to excellent	Moderate	Moderate

3.2. Post-Synthetic Modification and Functionalization

Post-synthetic modification represents a versatile strategy for introducing secondary catalytic functionalities into pre-formed coordination polymer frameworks without disrupting their structural integrity. This approach allows sequential optimization of different functional aspects, as the initial framework provides a stable platform for subsequent chemical transformations. Covalent modification of organic linkers through reactions with pendant functional groups enables attachment of organocatalytic moieties, creating hybrid systems that combine metal-based and organic catalytic activities. The accessibility of modification sites depends on pore structure and the size of reagents used, with smaller molecules more readily penetrating the framework interior [6, 7].

Metal exchange processes allow replacement of original metal centers with alternative metals possessing different catalytic properties, enabling fine-tuning of framework reactivity. Partial exchange creates mixed-metal systems where the original and introduced metals provide distinct catalytic functionalities. The kinetics of metal exchange depend on the lability of metal-ligand bonds and the relative binding affinities of different metals for the linker coordination sites. Careful control of exchange conditions prevents framework degradation while achieving desired metal compositions [9]. Doping with additional metal species through impregnation or chemical vapor deposition introduces catalytic sites in pores without altering the framework structure, though the distribution and stability of these species require careful optimization.

The incorporation of guests or encapsulated species within coordination polymer pores provides another avenue for creating dual-functional catalytic systems. Molecules possessing catalytic activity can be loaded into pores through soaking procedures, where their retention depends on size-exclusion effects and favorable interactions with the framework. Polymerization within pores creates organic phases with distinct catalytic properties that complement the framework's intrinsic activity. The stability of guest species during catalytic operations requires consideration, as leaching can diminish dual functionality over time [11, 12]. Strategies such as covalent tethering or electrostatic interactions enhance guest retention, maintaining dual catalytic capabilities through multiple reaction cycles.

3.3. Structural Characterization and Performance Evaluation

Comprehensive characterization of dual-functional coordination polymers requires multiple complementary techniques to establish relationships between structure and catalytic performance. X-ray diffraction provides fundamental information about framework topology, unit cell parameters, and crystallinity, allowing confirmation of phase purity and structural integrity before and after catalytic applications. Single-crystal diffraction offers the most detailed structural information, revealing precise positions of metal centers, ligands, and guest molecules, though obtaining suitable crystals can be challenging for some systems [1, 14]. Powder diffraction suffices for phase identification and monitoring structural changes during synthesis or catalytic processes, with Rietveld refinement enabling detailed structural analysis when single crystals are unavailable.

Spectroscopic techniques probe the chemical nature and coordination environment of catalytic sites within frameworks. Infrared spectroscopy identifies functional groups and can track their transformation during post-synthetic modifications or catalytic reactions. X-ray photoelectron spectroscopy determines metal oxidation states and surface compositions, providing insights into the distribution of different metal types in mixed-metal systems. Nuclear magnetic resonance spectroscopy characterizes organic linkers and can detect framework dynamics or substrate interactions in certain cases [15]. Electron paramagnetic resonance reveals information about paramagnetic metal centers and radical intermediates formed during catalytic processes, elucidating mechanistic details of dual catalytic systems.

Surface area and porosity measurements through gas adsorption experiments quantify the accessibility of catalytic sites and reveal how framework modifications affect pore structures. Nitrogen adsorption isotherms at cryogenic temperatures provide accurate surface area values and pore size distributions, while carbon dioxide adsorption at ambient temperature probes ultramicropore regions more effectively. The evolution of porosity during activation procedures and catalytic operations indicates structural stability and potential framework changes. Microscopy techniques including scanning and transmission electron microscopy visualize crystal morphologies, particle sizes, and the distribution of different components in composite materials [2, 3]. Table 5 summarizes key characterization techniques and the structural information they provide for dual-functional coordination polymers.

Table 5. Characterization techniques for dual-functional coordination polymers.

Technique	Information Obtained	Resolution	Sample Requirement	Application Stage	Complementary Method
X-ray diffraction	Crystal structure	Atomic scale	Crystalline powder	Synthesis verification	Spectroscopy
Gas adsorption	Surface area, porosity	Nanoscale	Activated sample	Performance prediction	Microscopy
Infrared spectroscopy	Functional groups	Molecular	Minimal	Synthesis monitoring	NMR
Electron microscopy	Morphology, composition	Nanoscale	Stable under vacuum	Quality assessment	Diffraction
Thermal analysis	Stability, composition	Bulk	Few milligrams	Stability evaluation	Spectroscopy

4. Catalytic Applications and Performance

4.1. Organic Transformations and Cascade Reactions

Dual-functional coordination polymers have demonstrated exceptional performance in complex organic transformations requiring multiple catalytic steps, particularly cascade reactions where products from one transformation serve as substrates for subsequent reactions. The integration of acid-base bifunctional sites within frameworks enables tandem processes such as aldol condensation followed by Michael addition, eliminating the need for intermediate isolation and purification. Metal centers provide Lewis acid activation of carbonyl groups while basic sites on organic linkers deprotonate nucleophiles, creating systems where both reaction partners are simultaneously activated for efficient bond formation [6, 7]. The spatial organization of catalytic sites within the framework influences reaction selectivity by controlling substrate orientation and intermediate transfer between sites.

Henry reactions between nitroalkanes and aldehydes represent important carbon-carbon bond forming processes that benefit from dual-functional catalysis. Coordination polymers featuring both metal Lewis acid sites and basic functional groups catalyze these transformations with enhanced rates and selectivities compared to single-function catalysts. The metal centers activate aldehydes through coordination while basic sites facilitate nitroalkane deprotonation, creating a cooperative activation mechanism that lowers overall activation barriers [10]. The porous structure allows substrates to access both types of sites efficiently, while product molecules rapidly diffuse away, preventing undesired secondary reactions. This dual functionality enables operation under mild conditions with excellent atom economy and minimal waste generation.

Oxidation reactions coupled with other transformations demonstrate the versatility of dual-functional coordination polymers in complex synthetic sequences. Frameworks incorporating redox-active metal centers alongside coordination or acid-base sites enable oxidative coupling reactions where substrate oxidation and subsequent bond formation occur within the same material. The electron-transfer capabilities of certain metal centers facilitate oxidation steps, while additional catalytic sites promote coupling reactions between oxidized intermediates [4, 9]. The containment of these processes within the framework microenvironment prevents side reactions and improves selectivity toward desired products. Applications in fine chemical synthesis and pharmaceutical intermediate production benefit from the high selectivity and recyclability of these heterogeneous dual-functional catalysts.

4.2. Environmental and Electrochemical Applications

The unique properties of dual-functional coordination polymers make them valuable for environmental remediation applications where simultaneous pollutant capture and catalytic degradation enhance overall efficiency. Frameworks designed with high adsorption capacities for organic pollutants combined with catalytic sites for their degradation create self-contained systems that eliminate the need for separate adsorption and treatment steps. The porous structure facilitates pollutant diffusion to catalytic sites while the framework's chemical stability ensures performance in harsh aqueous environments [5]. Metal centers catalyze oxidative degradation of organic contaminants while functional groups on linkers provide selective binding sites that concentrate pollutants near catalytic centers, enhancing degradation rates through proximity effects.

Dual-functional coordination polymers incorporating both catalytic and sensing capabilities enable real-time monitoring of catalytic processes or environmental contaminants. Fluorescent ligands or metal centers provide optical signals that change upon substrate binding or product formation, allowing in-situ detection of reaction progress or pollutant concentrations. This combination of catalytic activity with sensing functionality finds applications in environmental monitoring systems where simultaneous detection and remediation of contaminants are desired [14, 15]. The integration of these functions within a single material simplifies system design and reduces costs compared to separate detection and treatment components.

Electrochemical applications of dual-functional coordination polymers leverage their electrical conductivity and catalytic properties for energy conversion and storage processes. Frameworks incorporating redox-active metal centers alongside conductive organic linkers or guest molecules exhibit enhanced electron transfer rates that benefit electrocatalytic reactions. The dual functionality of these materials in electrochemical carbon dioxide reduction enables both efficient electron transfer and selective product formation through cooperative mechanisms between different metal sites [4]. The porous structure facilitates mass transport of reactants and products while providing high densities of catalytic sites. Applications in fuel cells, batteries, and electrochemical synthesis benefit from the combination of conductivity, stability, and catalytic activity that dual-functional coordination polymers provide.

4.3. Biomimetic and Specialized Catalytic Systems

Coordination polymers designed to mimic the dual functionalities of metalloenzymes represent an exciting frontier in biomimetic catalysis, where synthetic materials replicate the sophisticated catalytic mechanisms found in biological systems. Natural enzymes achieve remarkable selectivity through precise positioning of multiple catalytic residues within protein active sites, creating microenvironments that facilitate specific reaction pathways. Synthetic coordination polymers can replicate these principles by positioning different metal centers or functional groups at controlled distances, enabling cooperative substrate activation reminiscent of enzymatic mechanisms [8, 13].

The rigid framework structure maintains optimal spatial relationships between catalytic sites, unlike homogeneous catalysts where conformational flexibility can reduce efficiency.

Urease inhibition represents a specialized application where coordination polymers demonstrate dual functionality by both binding to enzyme active sites and disrupting catalytic mechanisms. Copper-based coordination polymers featuring auxiliary ligands exhibit high efficiency in inhibiting urease activity through mechanisms involving metal coordination to enzyme residues and structural interference with substrate access. The dual action of metal-based coordination and steric blocking creates synergistic inhibition effects superior to single-mechanism inhibitors [8, 13]. This approach finds applications in agricultural systems where urease inhibition prevents rapid urea decomposition, improving nitrogen utilization efficiency and reducing environmental nitrogen losses.

Specialized applications including dielectric switching coupled with catalytic activity demonstrate the expanding scope of dual-functional coordination polymers beyond traditional catalysis. Manganese coordination polymers exhibiting both tunable dielectric properties and selective catalytic activity enable materials that respond to external stimuli while maintaining catalytic functionality. The polar solvent-responsive behavior of these materials creates opportunities for switchable catalysis where activity can be modulated through environmental changes [11]. This combination of physical and chemical functionalities opens new applications in smart materials and responsive catalytic systems. The multifunctional nature of these coordination polymers positions them as versatile platforms for developing integrated materials with multiple operational capabilities.

5. Conclusion

Functional coordination polymers with dual catalytic applications represent a sophisticated class of materials that integrate multiple catalytic functionalities within crystalline porous frameworks, enabling complex transformations unattainable with conventional single-function catalysts. The strategic combination of different metal centers, functional organic linkers, and engineered pore environments creates systems capable of performing cascade reactions, tandem transformations, and processes requiring cooperative substrate activation. The modular construction of coordination polymers allows independent optimization of different catalytic functions through careful selection of metals, linkers, and synthesis conditions, providing unprecedented control over catalytic properties. Advanced synthetic strategies including mixed-component approaches and post-synthetic modifications enable precise tailoring of dual functionalities for specific applications.

The applications of dual-functional coordination polymers span diverse fields including organic synthesis, environmental remediation, electrochemical energy conversion, and biomimetic catalysis. Their performance in complex organic transformations demonstrates advantages in selectivity, efficiency, and sustainability compared to traditional catalytic systems. The combination of catalytic activity with additional functionalities such as sensing or dielectric properties expands their utility beyond conventional catalysis. Despite remarkable progress, challenges remain in areas including long-term stability under harsh catalytic conditions, scalability of synthesis methods, and complete mechanistic understanding of cooperative catalytic processes. Future developments will likely focus on creating increasingly sophisticated systems with multiple integrated functionalities, potentially incorporating dynamic responsiveness and self-healing capabilities. The continued advancement of dual-functional coordination polymers promises to establish them as essential materials for sustainable chemical processes and advanced technological applications.

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