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# Metal-Backboned Polymers: from Synthetic Methodologies to Structure-Property Insights

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**Abstract** The polymer properties are fundamentally dictated by the chemical nature of the backbones. Metal-backboned polymers (MBPs), in which conventional non-metallic backbones are replaced by continuous chains of metal atoms linked by metal-metal bonds, open a largely unexplored dimension in polymeric materials. Their unique electronic coupling, magnetic interactions, and optical responses enable a wide range of new functionalities. Despite this promise, the development of MBPs is hindered by two intertwined challenges: the lack of robust synthetic methodologies and the absence of systematic structure-property relationships to guide predictive design. From this Perspective, we provide a systematic overview that bridges synthetic methodologies with structure-property insights for MBPs. First, we critically examined two principal synthetic strategies, direct metal-metal bonding and multidentate-ligand-assisted template synthesis, and assessed their efficiency, precision, scope, and limitations. We further discuss how metal identity, ligand architecture, and chain length affect the physicochemical properties of MBPs, revealing key structure-property relationships. Finally, we identify the major challenges and emerging opportunities to move the field from molecular construction to predictive design, including machine-learning-assisted design and single-molecule characterization. Such developments will facilitate precise and scalable synthesis, as well as quantitative structure-property studies, paving the way toward MBPs with programmable and increasingly sophisticated functions.

**Keywords** Metal-backboned polymer; Synthesis; Structure-property relationship

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## INTRODUCTION

The history of polymer science is closely associated with the continual structural evolution of the backbone. It moves from the regular, saturated C—C single bonds of polyolefin to the highly flexible, weather-resistant —Si—O— linkages of polysiloxane and further to the conductive $\pi$-conjugated double bonds of polyacetylene. Each innovation in backbone bonding has unlocked new material performance realms. Following the same logic, the latest achievement in this evolutionary trajectory is the emergence of metal-backboned polymers (MBPs), whose backbones are constructed exclusively from metal atoms linked by metal-metal bonds.[1] While coordination polymers, such as Prussian blue and its analogs, contain metal centers, these centers are predominantly connected through bridging ligands rather than continuous metal-metal bonds.[2] In contrast, MBPs are defined by consecutively bonded metal atoms that form the principal one-dimensional (1-D) polymer backbone. More importantly, MBPs exhibit polymer-typical characteristics, including chain entanglement and solution rheological behavior, which are intrinsically absent in small molecules, such as metal-chain complexes that contain only localized metal-metal bonds.[3,4] Thus, continuous metal-metal backbone connectivity and polymer-typical behavior serve as key inclusion criteria for MBPs, distinguishing them from coordination polymers and metal-chain complexes. A systematic comparison of the three classes of metal-organic compounds is summarized in Table 1. This unique long-range metallic architecture can endow MBPs with distinctive characteristics such as charge delocalization, spin coupling, and rich redox landscapes, which are unattainable in conventional polymers.[5] Consequently, MBPs hold significant promise for a range of high-impact applications including optoelectronics, thermoelectrics, microwave absorption, and catalysis.[6–9]

Despite the considerable promise of MBPs, their development is still in its infancy. On the one hand, constructing extended metal chain architectures is a formidable challenge in both physics and chemistry because metal-metal bonds are generally weaker than their C—C counterparts. This inherent weakness constitutes a core bottleneck for MBP synthesis. To address this issue, two major strategies, based on direct metal-metal bonding and multidentate ligand assistance, have delivered preliminary advances.[10,11] Nevertheless, standardized and robust synthetic methodologies for MBPs are yet to

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be established, and formidable challenges remain in controlled and scalable synthesis. On the other hand, a systematic understanding of how structural parameters such as the metal identity, ligand architecture, and chain length govern the electromagnetic, electrochemical, and optical properties of MBPs is still lacking. However, such knowledge is essential for the rational design of MBPs with diverse functionalities for practical applications. These obstacles severely hamper the targeted realization of MBPs with desirable properties.

From this Perspective, we aimed to provide a systematic overview of MBPs by connecting synthetic methodologies with their emerging structure-property relationships (Fig. 1). We critically examine two synthetic approaches, direct metal-metal bonding and multidentate-ligand-assisted template synthesis, assessing their scope, controllability, and current limitations, and propose potential extension strategies. Furthermore, the emerging structure-property relationships are comprehensively discussed in terms of metal identity, ligand structure, and chain length, paving the way for targeted material design. Finally, we summarize the remaining core challenges: controlled and scalable synthesis, as well as the establishment of quantitative structure-property relationships. Future directions include machine-learning-assisted design for controlled polymerization and single-molecule characterization of physicochemical properties toward a systematic research paradigm for MBPs.

## SYNTHETIC METHODOLOGIES FOR MBPS

Current synthetic approaches to MBPs can be broadly divided into two categories: direct metal–metal bonding and multidentate-ligand-assisted template synthesis. Their mechanisms, representative examples, and limitations are discussed below.

### Direct Metal–Metal Bonding Strategy

Metal atoms, similar to their carbon counterparts in classical polymer backbones, feature a diverse array of valence electron configurations. Two metal centers with orbitals of compatible symmetry and energy can engage in an effective orbital overlap, thereby forming direct metal–metal bonds.[12] A key synthetic strategy for MBPs leverages such bonding interactions to directly link numerous metal atoms into a continuous backbone.

This strategy relies on a simple premise: oligonuclear metal precursors bearing labile terminal groups, typically halides, are treated with an appropriate reagent, such as $Ag^+$ to remove these moieties (Fig. 2a). This elimination affords a highly reactive metal species that subsequently forms successive metal-metal bonds *via d*-orbital overlap, ultimately producing an extended metal backbone. This process can be conceptualized as chain-growth polymerization, wherein metal precursors function as monomer units. This approach constitutes an elegant conceptual translation of classical polymerization principles into the domain of MBPs.

A representative example is the polymerization of chloride-terminated dinuclear Au(I) precursors supported by bisphosphine ligands.[11] Upon treatment with Ag(I) salts to abstract the chloride terminal groups, the resulting active species underwent chain growth to yield a gold-backboned polymer with a degree of polymerization (DP) as high as 169 (Fig. 2b). Notably, this material exhibited hallmark polymer characteristics, including a well-defined glass transition temperature, confirming its identity as a genuine polymer rather than an oligomeric aggregate.

Owing to its polymeric nature, this strategy enables the one-pot, high-efficiency synthesis of MBPs, which is crucial for the scalable production of this emerging material. However, similar to most chain growth polymerizations, this approach

**Table 1** Comparison of MBPs, coordination polymers, and metal-chain complexes.

| Feature | MBPs | Coordination polymers | Metal-chain complexes |
|---|---|---|---|
| Defining feature | Consecutively bonded metal atoms form backbone | Metal centers are linked mainly through bridging ligands | Discrete molecules containing finite metal chains |
| Connectivity | Continuous metal–metal bonds | Metal–ligand–metal linkages | Finite metal–metal bonds |
| Polymer-typical characteristics | Chain entanglement, solution rheology, glass transition temperature | Interpenetrated network topologies | None; discrete molecules without chain entanglement or extended topological structure |
| Example | Gold-based MBP[3] | Prussian blue analogues[2] | Trinuclear nickel(II) complexes[4] |

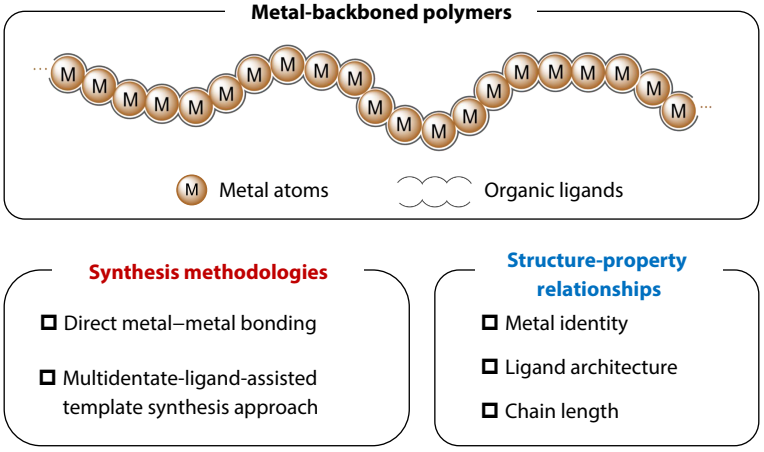


**Fig. 1** Overview of synthetic methodologies and structure-property insights for MBPs.

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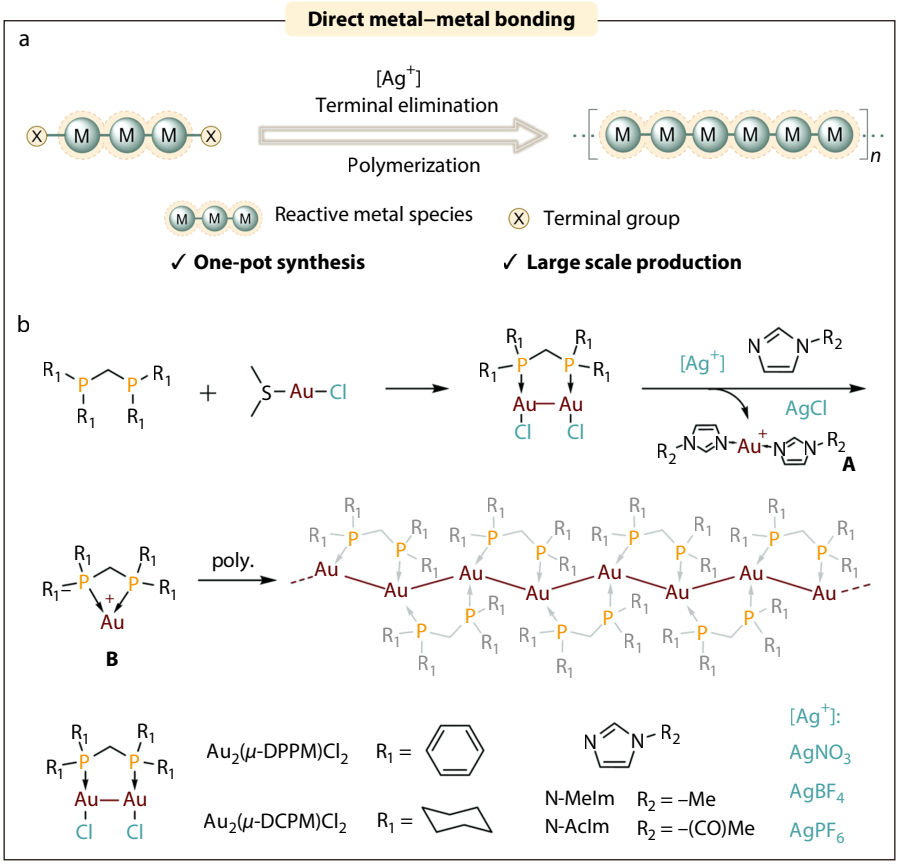


**Fig. 2** (a) Schematic of the direct metal-metal bonding strategy for MBP synthesis; (b) Schematic of the formation of a gold-backboned polymer with DP=169 (Reproduced with permission from Ref. [11]; Copyright (2026), Springer Nature).

currently suffers from limited controllability over the polymerization process. The resulting MBPs often exhibit broad molecular weight distributions, potentially compromising batch-to-batch uniformity in material properties. Hence, based on these preliminary successes, it is important to gain a deeper mechanistic understanding of polymerization kinetics and thermodynamics. Such insights would facilitate the rational design of metal precursors and optimization of reaction conditions, potentially enabling the efficient synthesis of MBPs with high molecular weights and narrow dispersity. Additionally, second- and third-row transition metals (*e.g.*, Re, Ru, and Os) are known for their ability to form three or more metal–metal bonds in polynuclear clusters.[13] Therefore, designing precursors that incorporate these metal atoms may introduce branching sites along the linear backbone, ultimately affording star- or comb-like topologies analogous to those in classical branched polymers.

The conceptual framework of step-growth polymerization presents another promising avenue for the construction of MBPs. By designing metal precursors bearing complementary reactive groups at opposite termini (*e.g.*, a halide and a metal carbonyl anion), mutual reactions between these groups can drive end-group elimination and metal–metal bond formation.[14] This enables backbone extension in a manner analogous to classical polycondensation. Thus, this step-growth strategy complements its chain-growth counterpart while offering additional leverage over sequence control and molecular weight. In particular, the polycondensation of different metal precursors can afford heterometallic backbones, while stoichiometric control provides a handle for tuning the molecular weight and its distribution. In addition, drawing on the classical strategy of using highly dilute monomers to suppress interchain coupling and favor intrachain cyclization in step-growth polymerization, this approach can be extended to the construction of cyclic MBPs. This would diversify the topology of this emerging class of polymers.

## Multidentate-ligand-assisted Template Synthesis Approach

Although the direct metal-metal bonding strategy provides a one-pot, highly efficient route to MBPs, its chain-growth polymerization mechanism intrinsically leads to products with broad molecular weight distributions.

To address this challenge, multidentate ligand-assisted template synthesis is a viable alternative. The underlying concept involves a multiarm rigid scaffold (such as 4-tert-butylcalix[4]arene) as the initiating platform.[10] A multidentate-ligand chain containing multiple coordination sites extends from each arm, giving rise to a multidentate ligand template. Representative multidentate ligands that can fulfill this templating role include polyaminopyridine and its derivatives, multidentate phosphines, and conjugated polyenes.[5] The preorganized ligand template then directs the metal atoms into a linear array through cooperative coordination, thereby

constructing the resulting metal backbone (Fig. 3a).[10]

The most distinctive advantage of this approach is its precise control over the length of the backbone. Because the number of metal atoms incorporated is governed by the coordination sites within the template, synthesizing a template of a given length affords MBPs with a precisely corresponding number of metal atoms. This one-to-one correspondence naturally endows the products with a monodisperse molecular weight distribution, a hallmark that is exceptionally difficult to achieve using conventional polymerization methods. Based on this strategy, MBP containing up to 28 nickel atoms was synthesized (Fig. 3b).[15] Another merit of this method is that, enabled by the stabilization of the ligand template, many metal species that might otherwise form only weak metal–metal bonds can form stable backbones, potentially expanding the range of accessible metals to cobalt, copper, manganese, and beyond.[6] Furthermore, the templating scaffold facilitates post-synthetic modifications. For example, partial replacement of coordinated metal atoms through metal replacement reactions could afford heterometallic MBPs with tunable sequences and compositions, thereby greatly expanding the chemical diversity of the metal backbone.[16]

Furthermore, organic ligands offer versatile platforms for functionalization. Incorporating reactive handles such as azide, halogen, and amino groups into the ligand skeleton is expected to yield MBPs bearing functional sites. These sites can be covalently attached to functional molecules or substrates, thereby broadening their application scope as functional materials. However, this precision comes at cost. The construction of multidentate ligand templates requires multi-step organic synthesis, and the synthetic complexity increases sharply as the target chain length increases. Moreover, once the number of coordination sites exceeds a critical threshold (*e.g.*, 50 sites), the coordination of metal atoms to a highly flexible ligand chain results in a substantial loss of conformational entropy.[17] This entropic penalty increases the risk of miscoordination, leading to a marked decline in yield. Thus, although the template synthesis strategy excels in precision, its scalability is inherently constrained by the entropic cost associated with the coordination process.[14] Future work should focus on developing strategies such as stepwise coordination, chemical confinement, or physical confinement in nanoscale reactors, which can mitigate the entropic penalty associated with the final metalation step.[18–20] Achieving this target would allow the template approach to produce MBPs with genuinely high molecular weights and exceptional structural uniformity, combining the precision of molecular design with the scalability required for material applications.

Overall, the two synthetic approaches exhibit complementary strengths and limitations in terms of chain length control, structural precision, synthetic efficiency, and scalability. The direct metal–metal bonding strategy generally enables one-pot polymerization and produces MBPs with high DPs, making it more favorable for synthetic efficiency and scalability. However, limited understanding and insufficient control of the polymerization process often leads to broad dispersity and relatively low structural precision. In contrast, the multidentate-ligand-assisted template synthesis approach allows precise control over the chain length and structural precision, as these features are predetermined by the number of coordi-

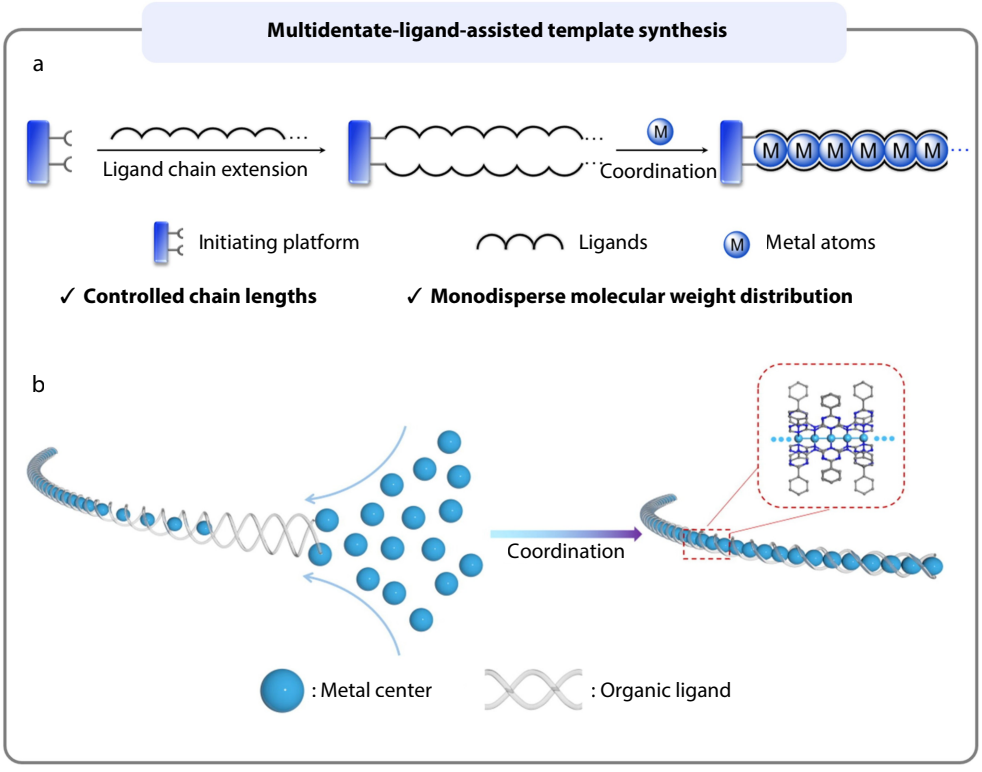


**Fig. 3** (a) Schematic of the multidentate-ligand-assisted template synthesis approach for MBP synthesis; (b) Schematic of the formation of an MBP containing 28 nickel atoms (Reproduced with permission from Ref. [15]; Copyright (2025), Elsevier).

nation sites. Nevertheless, the required multistep ligand synthesis and increasing entropic penalty associated with longer ligand chains reduce the overall synthetic efficiency and scalability.

Beyond these two synthetic strategies, insights from related metal-organic systems can further inform the development of MBPs in terms of design, synthesis, and characterization. For instance, metal-chain complexes offer well-established libraries of matching relationships between metal types and ligand structures, which can guide the selection of appropriate metal-ligand combinations in MBP design. In addition, the synthesis of 1-D coordination architectures relies on multidentate ligands to pre-organize metal centers in an ordered manner, a principle that closely parallels the template synthesis approach for MBPs. Furthermore, metal-cluster polymers contain diverse metal-metal bonds, and the experimental methods developed for their characterization, such as Raman spectroscopy and multinuclear NMR, are expected to provide valuable references for MBPs research.[21] However, despite these valuable references, the distinctive combination of long-range, continuous metal–metal bonds and polymer-typical behavior fundamentally sets MBPs apart from other metal-organic compounds in terms of structure and function, positioning them as a novel class of materials with unique promise.

## EMERGING STRUCTURE-PROPERTY RELATIONSHIPS IN MBPS

Beyond the challenge of synthesizing MBPs, it is important to understand how their structure dictates their physicochemical properties. MBPs have three primary structural parameters: metal identity, ligand architecture, and chain length. Along the 1-D metal backbone, the effects of these three parameters are expected to amplify, ultimately culminating in emergent properties. This section examines these parameters in sequence, elucidating their underlying mechanisms and projecting the property landscapes that they may unlock (Fig. 4).

### Metal Identity

The metal atoms that constitute the backbone represent the most critical structural parameters, which directly dictate the intrinsic electronic structure of MBPs. Different metal atoms possess distinct *d*-orbital electron configurations, resulting in varying degrees of $d_z^2$ orbital overlap once a backbone is formed. Upon reaching the polymeric length scale, localized *d* orbitals are expected to evolve through long-range delocalization into a continuous 1-D band structure.[10] In this regime, the degree of *d*-orbital overlap, which is inherently metal-specific, directly governs both the bandwidth and occupancy of electronic states near the Fermi level.[22]

For heavy metals with substantial *d*-orbital overlap, such as Pd ($4d^8$) and Pt ($5d^8$), the resulting 1-D band is broadened into a wide conduction band, which is expected to exhibit a conductivity approaching that of metallic materials. Therefore, MBPs constructed from these metals are expected to combine the efficient charge transport characteristics of metals with the processability of polymers, making them promising candidates for flexible electronic materials.

In addition to homometallic MBPs, incorporating distinct

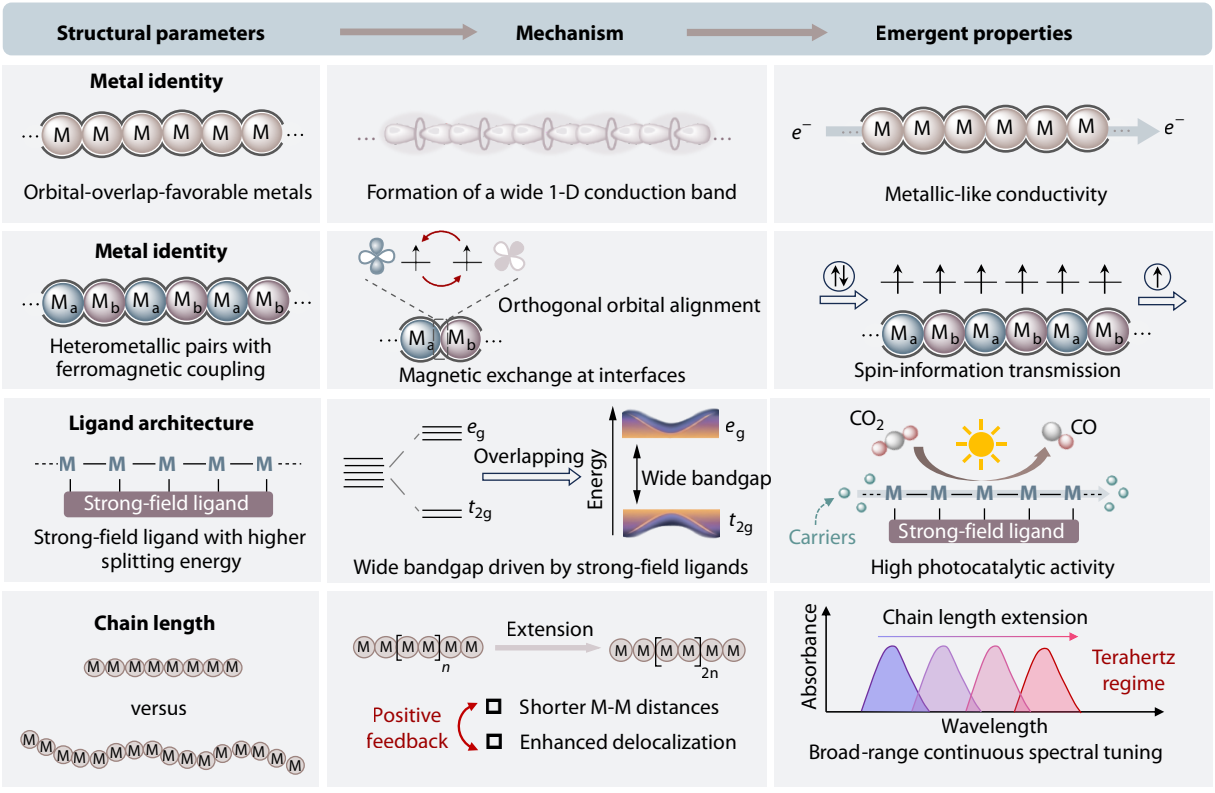


**Fig. 4** Overview of structure-property relationships in MBPs. Key structural parameters—metal identity, ligand architecture, and chain length—and their respective effects on physicochemical properties of MBPs are illustrated.

metal species into the backbone affords heterometallic MBPs. Metal identity also plays a decisive role in determining the properties of heterometallic MBPs. This influence originates from the differences in *d*-orbital symmetry and electronegativity of the constituent metal atoms.[23] This gives rise to unique magnetic exchange interactions at the heterointerfaces, which are expected to accumulate and propagate along the backbone as a result of its extended electronic delocalization. For instance, in the "Cu—Pd" heterobimetallic building block, orthogonal orbital alignment at the interface between two metals induces strong ferromagnetic coupling, resulting in the parallel alignment of adjacent metal spins.[23] When periodically repeating such a sequence along a long polymer chain, this ferromagnetic coupling is expected to propagate over the entire backbone, extending the spin alignment from a localized motif to a chain-wide phenomenon. This propagation enables spin information transmission along the backbone without charge migration, thereby circumventing the Joule heating inherent in conventional electron-based transport. Such a mechanism could provide a structural platform for low-power spintronic devices, a domain in which traditional materials are fundamentally limited by energy dissipation.

Overall, metal identity influences the electromagnetic properties of MBPs through two primary channels: the orbital overlap governing band formation and the interfacial exchange interactions determining the magnetic ordering. The deliberate selection of metal identities based on their *d*-orbital overlap and interfacial coupling characteristics enables the customization of electronic and spintronic properties for specific applications. This level of control is not attainable with conventional polymers or metals alone.

## Ligand Architecture

In addition to metal identities along the backbone, peripheral organic ligands constitute an integral structural element of MBPs. These ligands serve a dual role, providing the scaffolding necessary to stabilize the metal backbone while also acting as independent parameters that modulate the electronic structure and energy level. Owing to the structural support and electronic modulation provided by the ligands, MBPs adopt thermodynamically stable coordination configurations that enable excellent environmental resistance, solubility, and processability. For instance, a nickel-based MBP containing 21 nickel atoms exhibited a thermal decomposition temperature of 380 °C and good solubility in dichloromethane and tetrahydrofuran, demonstrating its potential for solution processing.[10]

Ligands regulate the properties of MBPs *via* two distinct mechanisms. The first is electronic: the electron-donating or electron-withdrawing nature of the ligand modifies the charge density and energy levels of the metal centers *via* inductive and conjugative effects, analogous to the substituent effects in classical polymers. Furthermore, this substituent effect can be leveraged to tune the conventional polymeric properties of MBPs. For example, replacing the pyridine unit in the ligand skeleton with a more electron-deficient pyrazine unit elevates the oxidation potential of the system.[24] This modification is expected to enhance the oxidative stability of MBPs, thereby contributing to their environmental resistance. In addition, introducing hydrophobic groups, such as ethyl groups, into the ligand framework could suppress interchain aggregation and further improve solubility. This enhanced solubility facilitates their processing through widely adopted solution-based techniques, such as spin-coating and dip-coating.[15,25] Even more significantly, the second is structural; the ligand field strength imposed by the ligand framework directly alters the electronic configuration of the metal centers. Strong-field ligands (such as phosphines and cyanides) can substantially split the metal *d* orbitals, widening the energy gap between the bonding and antibonding states.[26] When extended to polymer systems, this ligand-field effect is expected to amplify and effectively counteract the bandgap narrowing that typically accompanies long-range delocalization, thereby preserving a wide intrinsic bandgap. This suggests that MBPs bearing strong-field ligands, such as cyanides, could leverage their wide intrinsic bandgap to endow photogenerated carriers with a high thermodynamic driving force for photocatalysis. With this thermodynamic advantage, the 1-D metal backbone facilitates rapid carrier migration, synergistically promoting the photocatalytic reduction of $CO_2$ and water.[9]

Conversely, weak-field ligands (such as oxygen donors) exert a smaller splitting energy, tending to preserve unpaired electrons on the metal centers, thus promoting a high-spin configuration.[27] At the polymeric scale, these unpaired electrons could interact along the backbone to form a 1-D spin-chain structure that may give rise to spin-polarized bands. This provides a structural foundation for macroscopic spin-polarized transport. Concurrently, weak-field ligands promote high-spin configurations of metal centers, whereas heterometallic backbones enable long-range spin alignment. Their combination could provide a material platform for information processing based on 1-D solid-state qubit arrays.

To summarize, peripheral ligands modulate the intrinsic bandgap and spin states of MBPs through their electronic properties and imposed ligand field strength. Through rational ligand design, ligand-field effects can be synergistically coupled with the intrinsic properties imparted by metal identity, greatly expanding the engineering design space for this emerging class of polymers.

## Chain Length

Chain length, or the DP, is one of the most fundamental attributes of polymeric systems, directly defining its molecular weight regime. For MBPs, the chain length plays an equally decisive role, serving as a key parameter that bridges the molecular-scale electronic structure and bulk properties.

Experimental evidence from a series of nickel-based MBPs with different chain lengths corroborated the clear correlation between the chain length and electronic properties. As the number of Ni atoms increased from 3 to 21, the system exhibited progressive bandgap narrowing, accompanied by a continuous red shift in the optical absorption.[10] This observation clearly indicates that, as the chain extends, electron delocalization is significantly enhanced, which is similar to that of conventional conjugated polymers. However, the electronic communication in MBPs mainly arises from axial $d_z^2$ orbital overlap, which is far less sensitive to conformational distortions than the $\pi$-$\pi$ overlap in classical organic systems. Therefore, even at higher DPs, the delocalization channel re-

mains intact, ensuring that the degree of delocalization continued to increase with chain length over a much broader range.

Remarkably, MBPs exhibit an unusual positive feedback effect between chain elongation and electronic delocalization, which is a phenomenon with no analog in classical conjugated polymers. As the chain length increased, the average metal-metal bond length along the backbone anomalously shortened progressively.[10] This contraction, in turn, enhances the orbital overlap between adjacent metal centers, thereby further reinforcing electronic delocalization. Notably, the metal-metal bond contraction observed in nickel-based MBPs with increasing chain lengths has also been observed in gold- and cobalt-based systems.[9,28] This suggests that the effect may be general across different metal centers, potentially including Pd, and is likely to extend to heterometallic MBPs. Consequently, systematic variation of chain length over a wide range would enable continuous bandgap tuning from the visible well into the near-infrared and potentially the terahertz regime.

Overall, metal identity determines the intrinsic 1-D band structure, ligand architecture governs the charge density and crystal-field splitting of the metal backbone, and the chain length provides a broad approach for modulating the degree of delocalization. By leveraging the modulation of conductivity, spin state distribution, and delocalization extent through these three parameters, MBPs are expected to serve as an ideal research platform for frontier physical problems, such as superconductivity. Understanding the structure-property relationships of each parameter enables their synergistic combination. This integrated approach facilitates the rational design and synthesis of MBPs with tailored electronic, magnetic, and optical characteristics, thereby positioning them to address emerging demands in flexible electronics, quantum information processing, and beyond.

## SUMMARY AND PROSPECTS

Recent years have witnessed notable preliminary advances in both synthesis methodologies and structural regulation of MBPs. Representative MBPs are compared in Table 2 according to the metal type, synthetic method, chain length, and key properties. These systems, including nickel-, cobalt-, and gold-based MBPs prepared through direct metal-metal bonding or ligand-assisted template strategies, exhibit diverse thermoelectric, electronic, catalytic, and optical properties.[7,8,9,15,28]

Existing studies have established several viable synthetic strategies and have revealed that metal identity, ligand architecture, and backbone length would all influence physicochemical properties. Nevertheless, the field remains in its early stage, with two critical bottlenecks yet to be overcome. First, synthetic routes that enable scalable, high-efficiency production of MBPs with sufficiently long chain lengths and low-molecular-weight dispersity remain underdeveloped. Second, quantitative structure-property relationships are largely absent. Although valuable empirical and qualitative guidelines have been established, these have not yet reached the level of truly predictive design rules. Addressing these challenges will be essential for advancing MBPs from structurally intriguing systems to broadly useful material platforms.

A key direction is to leverage machine learning to accelerate the study of the polymerization mechanisms and kinetic processes in MBPs. The aim is to identify precursor structural features and reaction conditions that favor controlled synthesis. The polymerization mechanisms of MBPs differ substantially from those of classical polymer chemistry, posing a significant challenge for rational optimization. Machine learning is a powerful tool to bridge this gap. In a machine-learning workflow, precursor features (*e.g.*, metal valence states, ligand Hammett constants, and leaving group types) and reaction parameters (*e.g.*, solvent polarity, temperature, and concentration) are encoded as input descriptors. For example, training a model on approximately 30–50 datasets obtained under varied conditions allows the identification of feature importance for the DP and dispersity. This information can help identify whether chain propagation or chain initiation is rate-determining, or how the valence states of metals and ligand structures influence the control over the DP, thereby offering chemically interpretable hypotheses for mechanistic studies.[29] Such a data-driven approach can rapidly identify the key factors governing product properties from finite experimental datasets, which accelerates the development of synthetic protocols that afford MBPs with defined molecular weights and narrow dispersity.

Additionally, a mechanistic understanding of structure-property relationships requires collecting extensive electromagnetic, optical, and other property data from samples with various structures, an endeavor currently constrained by the immature synthesis of MBPs. Traditional bulk characterization of polymers often requires large amounts of high-purity samples, which is particularly challenging for MBPs at their current synthetic stage. Single-molecule break-junction techniques provide a powerful platform for quantitatively probing the charge and spin transport through individual MBP chains.[30] By forming hundreds to thousands of molecular

**Table 2** Comparison of representative MBPs by metal type, synthetic method, chain length, and key property.

| Representative MBP | Metal type | Synthetic method | Chain length | Key property |
|---|---|---|---|---|
| $Ni_{21}BP$[7] | Ni | Multidentate-ligand-assisted template synthesis | 21 Ni atoms | High Seebeck coefficient (76.3 $\mu V \cdot K^{-1}$, thermoelectrics) |
| $Ni_{28}BP$[15] | Ni | Multidentate-ligand-assisted template synthesis | 28 Ni atoms | Semiconducting with bandgap (2.66 eV) |
| $Co_{13}BP$[9] | Co | Multidentate-ligand-assisted template synthesis | 13 Co atoms | Photocatalytic $CO_2$-to-ethanol (497 $\mu mol \cdot g^{-1} \cdot h^{-1}$) |
| $Au_{50}BP$[28] | Au | Direct metal-metal bonding | About 50 Au atoms (DP ≈ 50) | Photoluminescence (130 $cd \cdot m^{-2}$) |

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junctions within a short time, these techniques generate statistically robust conductance data and enable direct correlations between transport properties and molecular parameters, such as chain length, metal identity, sequence, and ligand structure. Their application generally requires suitable anchoring groups, including thiol, amino, or cyano groups, to establish reliable electrode contacts. By further introducing external stimuli, such as temperature, magnetic fields, and gate voltages, single-molecule devices can reveal transport mechanisms and electromagnetic and spintronic properties at the molecular level. More importantly, the resulting high-dimensional datasets can be integrated with machine-learning methods to identify the structural descriptors that most strongly govern charge and spin transport, thereby enabling quantitative structure-property relationships and guiding the rational design of MBPs. Such structure-transport correlations at the single-molecule level can inform the rational construction and performance optimization of MBP-based materials for macroscopic devices.

In summary, preliminary progress has been made in synthetic methodologies and structural modulation, but controlled and scalable production, as well as predictive structure-property relationships, remain unresolved. Overcoming these challenges will require the close integration of polymer chemistry, quantum transport, and machine-learning-driven discovery. Such advances may establish MBPs as versatile platforms for flexible electronics, spintronics, 1-D quantum systems, and other applications.

## BIOGRAPHIES

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## Conflict of Interests

Huisheng Peng is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. The authors declare no conflict of interest.

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## Graphical Abstract

### Metal-Backboned Polymers: from Synthetic Methodologies to Structure-Property Insights

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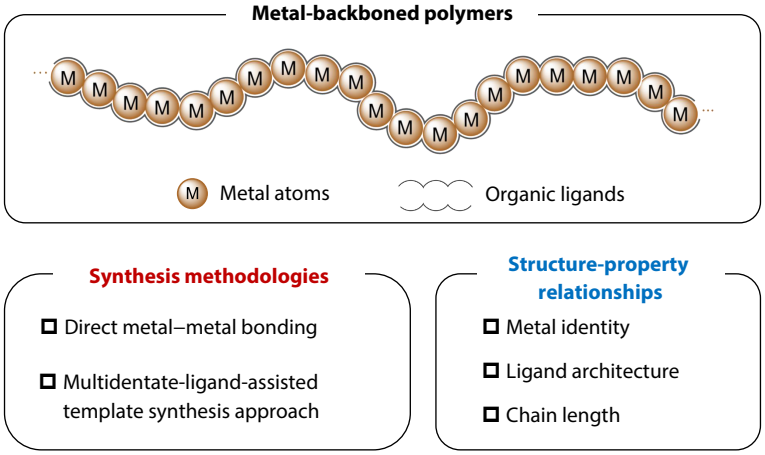
This study surveys synthetic methodologies to metal-backboned polymers (MBPs) and reveals how metal type, ligand architecture, and chain length modulate their properties, offering a roadmap for function-oriented design and scalable synthesis.

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