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Review

Metallo-Polyelectrolytes: Correlating Macromolecular Architectures with Properties and Applications

Tianyu Zhu,[1] Jiuyang Zhang,[2,*] and Chuanbing Tang[1,*]

Since the middle of the 20th century, metallopolymers have represented a standalone subfield with a beneficial combination of functionality from inorganic metal centers and processability from the organic polymeric frameworks. Metallo-polyelectrolytes are a new class of soft materials that showcase fundamentally different properties from neutral polymers due to their intrinsically ionic behaviors. This review describes recent trends in metallo-polyelectrolytes and discusses emerging properties and challenges, as well as future directions from a perspective of macromolecular architectures. The correlations between macromolecular architectures and properties are discussed from copolymer self-assembly, metallo-enzymes for biomedical applications, metallo-peptides for catalysis, crosslinked networks, and metallogels.

Highlights

Synthetic polyelectrolytes have found a great range of applications as functional materials. We describe the emergence of a new field of metallo-polyelectrolytes, where the cationic metal centers are generally used for building polyelectrolytes.

Numerous polymerization techniques enable the preparation of metallo-polyelectrolytes with controlled molecular weight and macromolecular architectures.

Investigation of metallo-polyelectrolytes with various compositions, properties, and architectures is essential for comprehensive understanding and further evolution of new materials in this emerging field.

Synthetic Strategies for Metallo-Polyelectrolytes with Diverse Architectures

Polyelectrolytes are ionic macromolecules (cationic, anionic, amphoteric, or zwitterionic) possessing the combined properties of electrolytes and polymers [1–4]. The past decades have witnessed pronounced development in the synthesis of polyelectrolytes and exploration of new applications. For example, luminescent azonia-containing polyelectrolytes are of interest for biological systems [5]; hydrocarbon-based polyelectrolytes with distinct microstructure are in great demand for energy devices and processes [6]; crosslinked nanofiltration membranes are appealing for selective removal of small ions [7]. Synthetic polyelectrolytes containing ionic metal centers, namely metallo-polyelectrolytes, are gaining growing attention as new polymeric materials with interesting properties (e.g., redox, magnetic, catalytic, stimulus responsiveness, optical, and electronic) that arise from unique compositions combining cationic metal centers and polymeric scaffolds. This emerging class of macromolecules is ubiquitous for a variety of utilities ranging from traditional electrolyte chemistry to biomedicals to membranes, to name just a few [8–14].

Recent synthetic developments in polymer chemistry provide polyelectrolytes ample opportunities for compositional diversity and practical relevance (Figure 1). Controlled polymerization techniques developed in the past two decades have enriched the toolbox for handling monomers in a precise fashion. Controlled radical polymerizations, including **atom transfer radical polymerization (ATRP)** (see Glossary) and **reversible addition-fragmentation chain-transfer (RAFT) polymerization**, have emerged as robust tools to control macromolecular architectures using a wide variety of monomers (e.g., acrylics, acrylamides, and styrenes) [15,16]. Ionic polymerizations propagated through reactive ionic centers may produce more precise control on chain topologies by carefully selecting charged chain ends and initiators [17]. **Ring-opening polymerization (ROP)** is also widely used to control polymeric architectures from cyclic monomers with ring strains that promote polymerization. In recent years, **ring-opening metathesis polymerization (ROMP)**, a special class of ROP for cyclic olefin derivatives, has been a highly preferred method for producing precisely controlled polymer chains with high molecular weight in a rapid manner [18–20]. Recent breakthroughs in entropy-driven ROMP and precisely controlled ROMP enable additional opportunities, such as the preparation of high molecular weight polymers from macrocycles and precise insertion of single units to polymer chains [21–24]. To date, metallo-polyelectrolytes have been prepared by many of these polymerization platforms [25]. For example, cyclic or vinyl-based monomers with metallocene cations (e.g., ferrocenium, cobaltocenium, and rhodocenium) have been used to prepare polyelectrolytes [25]. Moreover, stepwise coordination techniques are able to construct linear or branched supramolecular architectures by forming dynamic and reversible metal-ligand coordination [18,26,27].

[1]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

[2]School of Chemistry and Chemical Engineering, Jiangsu Hi-Tech Key Laboratory for Biomedical Research, Southeast University, 211189, Nanjing, PR China

*Correspondence:
jiuyang@seu.edu.cn,
tang4@mailbox.sc.edu

The physiochemical properties of metallo-polyelectrolytes are determined by both the ionic metal center and macromolecular structure. Metal cations endow optical, electronic, redox, magnetic, and catalytic properties, while counterions dictate (in part) solvophilicity and solubility of the macromolecules. The existence of metal–ligand interactions in polyelectrolytes enables them to be either physiochemically stable (based on covalent bonding) or stimuli-responsive (based on physical bonding) [8,26]. Meanwhile, macromolecular architectures and structural parameters of metallo-polyelectrolytes afford interesting features such as microphase separation, solution self-assembly, and stimuli-responsive behaviors [28–30]. While many reviews focus on the ionic metal centers [8,13,26,31,32], the architecture–property relationship in metallo-polyelectrolytes is far less discussed, partially due to the challenges in synthetic techniques to control macromolecular structures with the presence of metal units.

The aim of this short review is to illustrate a few recent advances in metallo-polyelectrolytes on macromolecular architectures, controlled polymerization, and promising applications in the hopes of shedding light on potential architecture–property relationships. Specifically, metallo-polyelectrolytes are categorized by linear (homo, random, and block) and more sophisticated (brush-like, dendritic, and interlocked) architectures containing metal moieties that are embedded into the main-chain or appended to the side-chain of polymers [13,32]. Furthermore, the correlations between macromolecular architectures and properties are discussed from the perspective of copolymer self-assembly, metallo-enzymes for biomedical applications, metallo-peptides for catalysis, crosslinked networks, and metallogels.

Metallo-Polyelectrolytes with Linear Architectures

Homopolymers

The most common metallo-polyelectrolytes are homopolymers with a linear architecture, which is convenient for synthesis. Homopolymers with metal centers could possess some intrinsic properties that are beneficial for studying more complex architectures. They are usually prepared by controlled polymerization techniques, including ROP and RAFT. Based on the location of metal centers, these homopolymers can be categorized into main-chain (Figure 2A–C) and side-chain (Figure 2D–F) topologies. Main-chain metallopolymers prepared by ROP of metallocenophane (Fe, Co, Ni) monomers have been extensively explored over the past decades [19]. Manners and colleagues reported the synthesis of main-chain cobaltocenium-containing homopolymers via thermal ROP or anionic polymerization of an *ansa*-cobaltocene monomer ([2]cobaltocenophanes) followed by oxidation reactions [33]. These poly(cobaltocenylethylene) (PCE) homopolymers are water-soluble and redox-active (Figure 2A). Besides, ROP of sila[1]ferrocenophanes and subsequent side group modification enabled the preparation of water-soluble polyferrocenylsilane (PFS) polyelectrolytes with anionic or cationic pendant groups attached to the silicon centers (Figure 2B) [34,35]. Owing to the robust redox property of ferrocene units in the main-chain, PFS polyions can be reversibly reduced and oxidized under chemical or electrochemical stimuli.

Compared with main-chain metallo-polyelectrolytes having a stretched chain conformation and high Kuhn length, side-chain polymers are usually more flexible by placing the rigid metal moiety away from the polymer backbones. This could offer side-chain polyelectrolytes better solution and thermal processability. There have been many techniques for the synthesis of side-chain metallo-polyelectrolytes. Tang and coworkers explored a series of side-chain metallocenium-containing (cobaltocenium and rhodocenium) homopolymers [36–38]. Owing to the diverse chemistry involving carboxylic and ethynyl groups, metallocenium derivatives have been used to prepare (meth)acrylate and norbornene based monomers by esterification, amidation, or azide-alkyne cycloaddition reactions [25]. Further free radical polymerization, or RAFT or ROMP, gave metallocenium-containing polyelectrolytes (Figure 2D). It is worth noting that homopolymers with high molecular weight (~167 kg/mol) can be achieved with high yields under open air conditions by this synthetic strategy [36].

The use of metal–ligand interactions is another method to construct main-chain and side-chain metallo-polyelectrolytes. Schubert and colleagues focused on the synthesis of water-soluble

Glossary

Atom transfer radical polymerization (ATRP): a reversible-deactivation radical polymerization method to achieve uniform polymer chain growth with a transition metal catalyst.
Reversible addition-fragmentation chain-transfer (RAFT) polymerization: a reversible-deactivation radical polymerization method that makes use of a chain transfer agent in the form of a thiocarbonylthio compound to afford control over the molecular weight and polydispersity.
Ring-expansion metathesis polymerization (REMP): a type of olefin metathesis chain-growth polymerization to form cyclic polymers with a cyclic metal-alkylidene catalyst.
Ring-opening metathesis polymerization (ROMP): a type of olefin metathesis chain-growth polymerization driven by the relief of ring strain of cyclic olefins (e.g., norbornene or cyclopentene).
Ring-opening polymerization (ROP): a type of chain-growth polymerization to form longer polymer chains by attacking cyclic monomers with the reactive chain end.

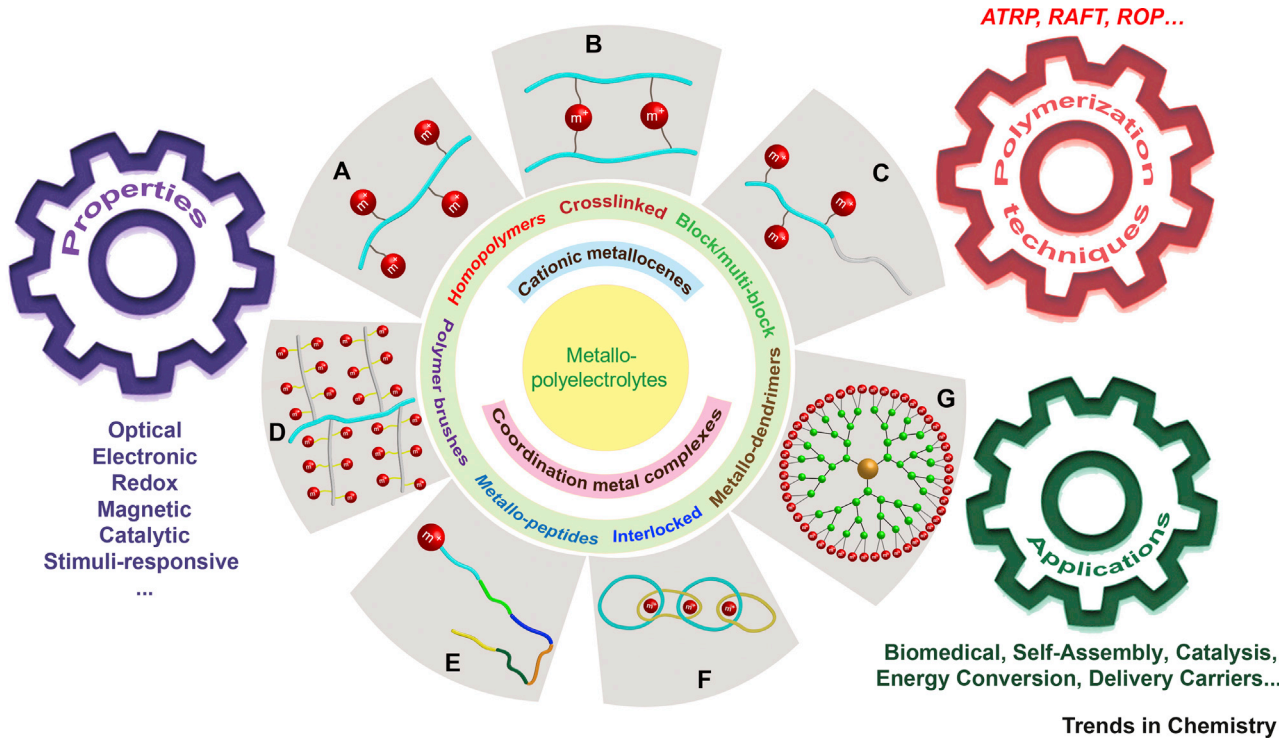

Figure 1. Illustration of Diverse Macromolecular Architectures, Polymerization Techniques, Properties, and Applications of Metallo-Polyelectrolytes.

(A) Homopolymers; (B) crosslinked networks; (C) block and multiblock copolymers; (D) polymer brushes; (E) metallo-peptides; (F) interlocked macrocycles; and (G) metallo-dendrimers. Abbreviations: ATRP, Atom transfer radical polymerization; RAFT, reversible addition-fragmentation chain-transfer; ROP, ring-opening polymerization.

coordination polymers on the basis of terpyridine-functionalized ligand and iron(II) chloride [39]. The reversible formation of the iron–ligand bond was investigated by addition of the strong chelating ligand in aqueous solution (Figure 2C). Weck and colleagues reported the preparation of side-chain homopolymers containing iridium complexes by ROMP (Figure 2E) [40]. These polymeric materials feature phosphorescent properties in both solution and solid state owing to the pendant iridium complexes.

Copolymers and Block Copolymers

Compared with simple homopolymers, random and block copolymers bring more structural and compositional diversity. Co-monomers and their distribution within the chain could afford access to additional polymer behavior, including bulk microphase separation, solution self-assembly, and macroscopic mechanical performance. Random copolymers of metallo-polyelectrolytes are typically prepared by copolymerization with different monomers. For example, Zhu and colleagues reported a class of cobaltocenium-containing polyelectrolytes with polyethylene-like frameworks by ROMP of two *cis*-cyclooctene-based monomers [41]. These copolymers were then fabricated into mechanically robust membranes for anion-exchange applications. It should be mentioned that the random topology is critical for tuning mechanical properties and microphase separation by preventing aggregation of ionic domains [42]. Hydrocarbon backbones phase separate into hydrophobic domains, while the hydrophilic metallo-moieties facilitate the formation of ion conducting channels and thus improve ion-transport properties of polyelectrolyte membranes [41].

Furthermore, block copolymers bring more possibilities that homopolymers and other copolymers cannot access, especially because of their ability to self-assemble into more defined nanostructures

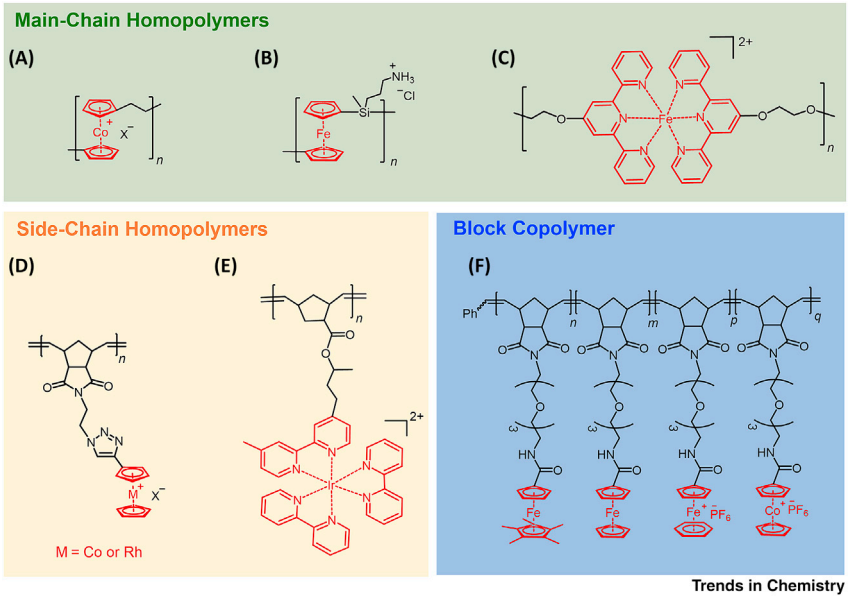

Figure 2. Molecular Structures of Linear Metallo-Polyelectrolytes.
(A,B) Main-chain homopolymers based on covalent bonding; (C) main-chain homopolymer based on physical bonding; (D) side-chain homopolymer based on covalent bonding; (E) side-chain homopolymer based on physical bonding; and (F) side-chain tetrablock copolymer.

in the solid state or solution [43–45], as discussed in the following section. Block copolymers of metallo-polyelectrolytes are typically synthesized by controlled polymerization techniques, for example, ROMP. Norbornenes with pendant metallocene-containing chains are predominantly used as monomers to construct block copolymers of metallo-polyelectrolytes for their high reactivity, absence of secondary metathesis, and simple functionalization. The Astruc group systematically studied redox properties of a series of block metallopolymers containing ferrocenyl, pentamethyl-ferrocenyl hexafluorophosphate salts of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$ complex, and cobaltocenium [46,47]. Triblock and tetrablock metallopolymers with 25 metallo-units in each block were prepared via living ROMP of norbornene derivatives [48,49]. Four distinct electroactive redox centers in the tetrablock copolymers provided electrochemical redox cascades and rich electrochromic properties (Figure 2F).

Metallo-Polyelectrolytes with More Sophisticated Architectures

Polyelectrolyte Brushes

Polyelectrolyte brushes constitute a class of polymeric materials with defined molecular architectures and unique physiochemical properties. The high density of grafted chains usually leads to an extended conformation of polymer brushes that occupy a large volume. As a result, the giant molecular size and unique 1D structure, together with a high amount of ionic metal centers, provide many special functionalities that have not been observed in other metallo-polyelectrolytes. For example, cationic polymer brushes are especially effective in combating biofouling and biocorrosion [50]. With the development of controlled polymerization techniques, simple and efficient methods for preparing metal-containing brushes with high grafting density have been achieved. Tew and coworkers demonstrated the first topology of metallo-supramolecular cyclic brushes (Figure 3A) [51]. The cyclic polymer template was prepared by **ring-expansion metathesis polymerization (REMP)** and then metal-containing polyelectrolytes were formed by metallo-supramolecular interactions between terpyridine ligands and transition metal ions. Direct imaging of single polymer chains of metallo-polyelectrolyte brushes by transmission electron microscopy is shown in Figure 3C. Zhang and colleagues designed and prepared the first cobaltocenium-containing molecular brushes via a 'graft from'

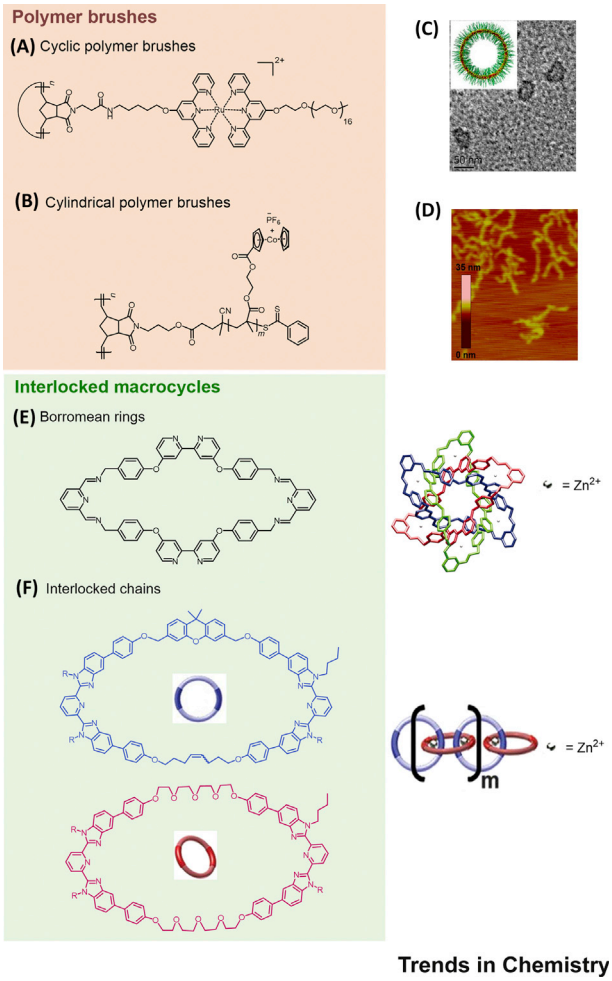

Figure 3. Metallo-Polyelectrolytes with More Sophisticated Architectures.
(A) Cyclic and (B) cylindrical polyelectrolyte brushes; (C) transmission electron microscopy image of a cyclic polymer brush; (D) atomic force microscopy height image of cylindrical polymer brushes; (E) Borromean rings; and (F) interlocked polymer chains. (C–F) Adapted from [51,52,54,55], with permission, respectively.

technique by a combination of ROMP and RAFT techniques (Figure 3B) [52]. Tapping-mode atomic force microscopy was used to image the morphologies of these cylindrical metallo-polyelectrolyte brushes (Figure 3D). The cylindrical polymer brushes were used for the preparation of cobalt-based nanoparticles and nanowires and also applied to qualitatively analyze the counterion exchange effect on macromolecular conformations [53]. In particular, this quantitative approach is of utmost importance for the understanding of inter/intramolecular interactions of these charged macromolecules and also for other charged biomolecules.

Interlocked Macrocycles

The cyclic topology and interlocked structures are of great interest in many aspects, including rheological behaviors and mechanical performance, but they are also more synthetically challenging. Metal–ligand coordination interactions (noncovalent bonds) between pyridine ligands and metal ions are usually dynamic and reversible, which can be used to construct polymeric materials with more sophisticated cyclic architectures. The Stoddart group reported the construction of Borromean rings by a strict self-assembly protocol to bring three rings together in one step [54].

The self-assembly process was achieved by using kinetically labile zinc(II) ions as crossover points to preferentially bound to bipyridyl and diiminopyridyl ligand (Figure 3E). More recently, Rowan and coworkers reported the synthesis of mechanically interlocked polymers poly[*n*]catenanes by ring closing of a metallo-supramolecular polymer as a template [55]. The alternating supramolecular copolymer was firstly formed based on macrocycle and threading molecules by metal–ligand coordination between a terdentate ligand [2,6-bis(*N*-alkyl-benzimidazolyl)pyridine] and Zn(II) ions (Figure 3F). These interlocked metallopolymers exhibited stimuli-responsive properties in both solution and bulk, and the isolated poly[*n*]catenane molecules held potential for molecular machines, catalysis, and drug delivery.

Metallo-Dendrimers and Nanocomposites

Metallo-dendrimers are highly distinguished from other metallo-polyelectrolytes in the aspects of branched structures, high local concentration of metal ions, and symmetric molecular geometries, which have attracted growing interest because of their redox, magnetic, catalytic, transport, and photo-optical properties [56–60]. In early 2000, Losada and coworkers reported the synthesis of several families of silicon- and nitrogen-based dendritic metallo-polyelectrolytes with both ferrocene and cobaltocenium moieties (Figure 4A) [61]. One remarkable feature of these organometallic dendrimers is their ability to modify electrode surfaces. Cyclic voltammetry scans can be carried out hundreds of times with no loss of electroactivity. The Astruc group also designed and prepared series of polycationic metallo-dendrimers with various organometallic complexes onto the periphery of dendrimers [62]. Wang and colleagues synthesized metallo-dendrimers with two electronically communicating iron centers in three oxidation states ($Fe^{II}Fe^{II}$, $Fe^{II}Fe^{III}$, $Fe^{III}Fe^{III}$) by the Sonogashira coupling reaction (Figure 4B). These cationic metallo-dendrimers were demonstrated to stabilize and isolate gold nanoparticles (AuNP) by AuNP-triazole or interdendritic interactions [63].

Nanomaterials are one of the most important discoveries in the 20th century. Fabrication of new nanocomposites based on conventional materials provides some unexpected properties [59]. Vancso and colleagues fabricated PFS capsules by an electrostatic layer-by-layer assembly of PFS polycation and polyanion onto a colloidal template [64]. The permeability of capsule wall can be controlled by the concentration of oxidants and number of polyion bilayers. Song and colleagues reported the preparation of PFS polyelectrolytes for the decoration of AuNP (Figure 4C). Incorporation of these PFS polyions allowed exploration of the redox-responsive property of the nanocomposites. Changing the redox state of the localized surface plasmon resonance nanostructures resulted in a switchable color tuning, which could be used for the colorimetric sensing of oxidation or reduction partners [65]. Tang and colleagues recently reported a few surface-grafted cobaltocenium-containing nanoparticles (Figure 4D) [66–68]. For example, cobaltocenium-containing silica nanoparticles were prepared by surface-initiated RAFT polymerization of a cobaltocenium-containing methacrylate monomer from silica nanoparticles [66]. These nanoparticles were then bioconjugated with β-lactam antibiotic penicillin-G based on electrostatic interactions between the cationic cobaltocenium moiety and anionic antibiotic. The formed cationic nanoparticles were demonstrated to provide more active sites to contact the membranes of bacteria, improve the vitality of penicillin-G, and kill bacteria more effectively. Similar methodologies were used for other nano-objects, including AuNP [67] and magnetic iron oxide nanoparticles [68].

Correlating Metallo-Polyelectrolyte Architectures with Properties and Applications

Self-Assembly

Self-assembly is an autonomous process to build organized structures, which is common throughout nature from molecular to planetary scales [69]. For metallo-polyelectrolytes, the different crystallinity and flexibility of chain segments also lead to varied self-assembly behaviors in solution [70]. For example, main-chain PCE homopolymer can self-assemble into helical structures at a scale of micrometers, which could pave new synthetic routes for chiral macromolecular systems (Figure 5A) [71]. Manners and colleagues established the introduction of chirality in a metallo-polyelectrolyte for the first time using DNA as an anionic template [72]. Later, they further realized the transmission of

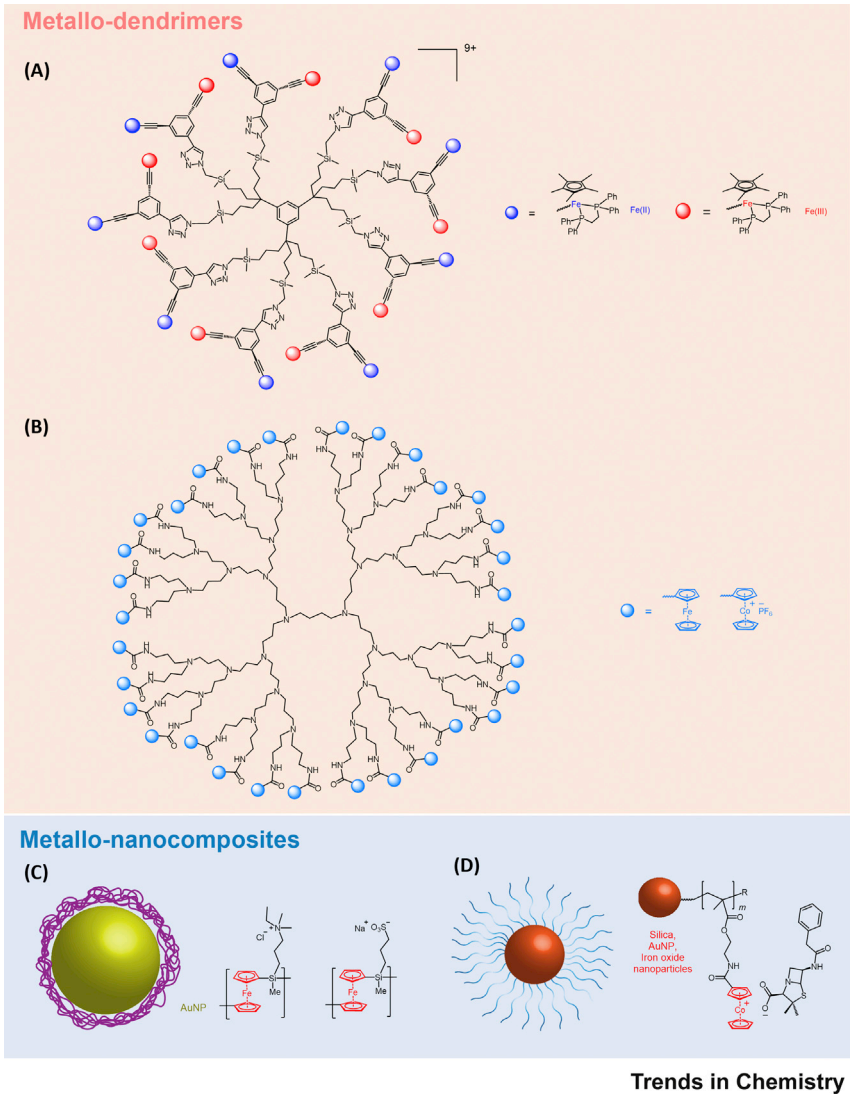

Figure 4. Molecular Structures of Metallo-Dendrimers and Nanocomposites.
(A,B) Metallo-dendrimers with different ionic moieties; (C) Au nanoparticles (NPs) coated with polyferrocenylsilane (PFS) polyelectrolytes; and (D) NPs grafted with cobaltocenium-containing polyelectrolytes.

chirality from chiral surfactant counteranions to the micrometer length scale through ion-pairing. In both cases, the induction of chirality was thought to be facilitated by the location of the positive charges and the structural flexibility of PCE homopolymer (Figure 5E).

Compared with homopolymers and random copolymers, Flory-Huggins parameter (χ) between different blocks should be sufficiently high to induce phase segregation of block copolymers with diverse morphologies in both solution and bulk self-assembly. Specifically, solution self-assembly of block copolymers in selective solvents comprising a crystalline core-forming block and a solubilizing cationic block has been carried out. Gilroy and colleagues reported the preparation of heterobimetallic block copolymers by ROP of strained sila[1]ferrocenophanes and dicarba[2]cobaltocenophane monomers (Figure 5B) [73]. These block copolymers (PFS_{50}-*b*-[PCE][OTf]) showed interesting redox properties and self-assembly behavior originating from the ferrocene and cobaltocenium units. Due to the crystallization of the core-forming poly(ferrocenyldimethylsilane) block, a

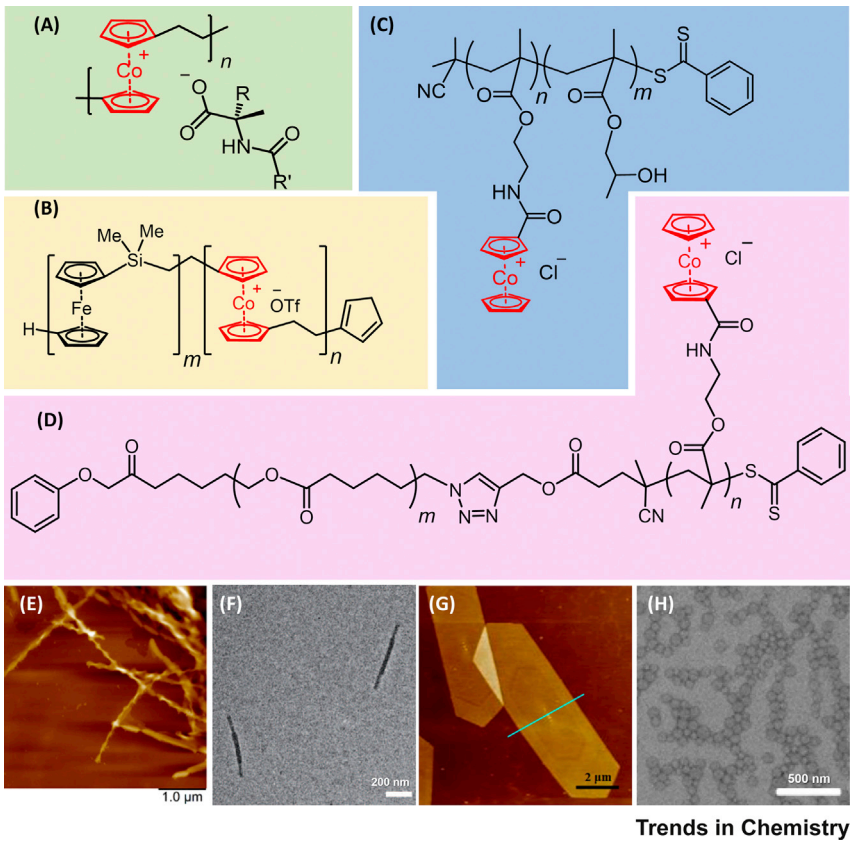

Figure 5. Self-Assembly of Metallo-Polyelectrolyte Homopolymers and Block Copolymers.
Molecular structures of (A) main-chain poly(cobaltocenylethylene) (PCE) homopolymer with chiral anionic surfactant; (B) main-chain polyferrocenylsilane (PFS)-*b*-PCE block copolymer; (C) side-chain cobaltocenium-containing PCoAEMACl-*b*-PHPMA block copolymer; (D) side-chain polycaprolactone $(PCL)_{61}$-*b*-$PCoAEMA_{58}$ block copolymer; (E) atomic force microscopy (AFM) height images of $[PCE][C_{16\text{-}L}\text{-Ala}]_n$ on a carbon-coated copper grid; (F) bright-field transmission electron microscopy image of cylindrical micelles resulting from the addition of PFS_{50}-*b*-$([PCE][OTf])_{50}$ to PFS_{34}-*b*-$P2VP_{272}$ seed micelles; (G) AFM height image of PCL_{61}-*b*-$PCoAEMA_{58}$; and (H) TEM image of $PCoAEMACl_{26}$-*b*-$PHPMA_{250}$. (E–H) Adapted from [44,45,71,73], with permission.

'dumbbell-shaped' central portion of micelles was observed by adding the cationic block copolymer into the solution of cylindrical seed micelles of poly(ferrocenyldimethylsilane)-*b*-poly(2-vinylpyridine) (PFS-*b*-P2VP) (Figure 5F). Similarly, a series of side-chain cobaltocenium-containing block copolymers with polycaprolactone (PCL) as the core-forming block was reported recently by Tang and Manners (Figure 5D) [44]. Driven by the crystallization of PCL and the electrostatic interactions within charged polycobaltocenium segments (PCoAEMA), block copolymer PCL-*b*-PCoAEMA can self-assemble into various 2D platelet morphologies in selective solvents with PCL as the core block and cobaltocenium as the corona block. These copolymers showed unique crystallization-driven self-assembly behavior to form various 2D platelet structures (like hexagons and diamonds) in polar protic solvents (Figure 5G). Polymerization-induced self-assembly (PISA) has emerged as another powerful approach to preparing nano-objects with a variety of morphologies. PISA of diblock copolymers with poly(2-hydroxypropyl methacrylate) (PHPMA) as the core-forming block and poly(2-cobaltocenium amidoethyl methacrylate chloride) (PCoAEMACl) as the soluble stabilizer block was recently reported (Figure 5C) [45]. Spherical nanoparticles of PCoAEMACl-*b*-PHPMA with controllable hydrodynamic diameters were formed by the PISA process (Figure 5H). The size of particles was observed to increase when extending the length of the core-forming block or increasing the charge density of polyelectrolytes.

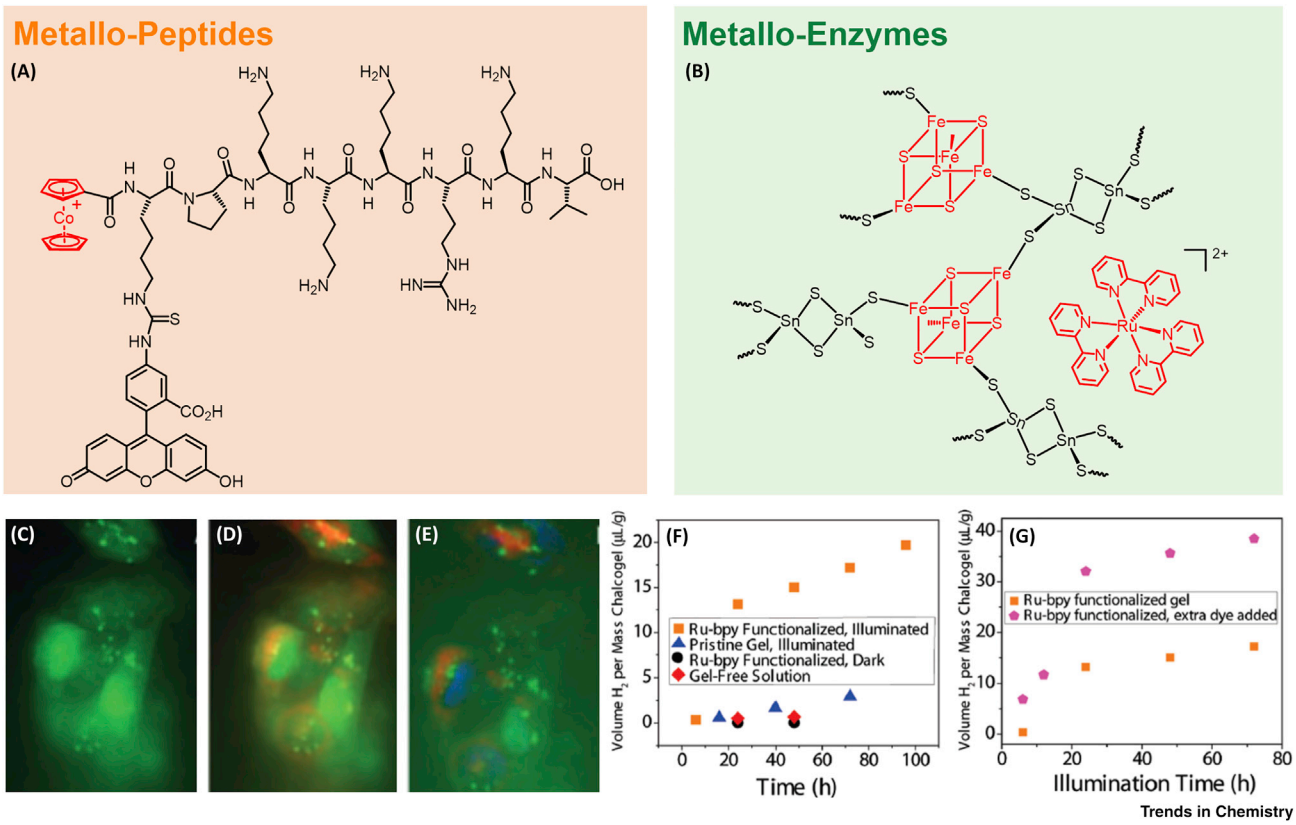

Figure 6. Metallo-Peptides and Metallo-Enzymes.

Molecular structures of (A) metallo-peptides; (B) metallo-enzymes; (C) localization of fluorescent-labeled cobaltocenium-NLS bioconjugate in living HepG2 cells; (D) colocalization of bioconjugate and endosome marker (FM 4-64); (E) colocalization of bioconjugate, FM 4-64, and Hoechst 33342 dye; (F) hydrogen evolution of a variety of gels and conditions; and (G) hydrogen evolution of Ru-bpy functionalized gel with dye. (C–E), (F,G) adapted from [74,78], with permission, respectively.

Metallo-Peptides for Biomedical Applications

Metallo-peptides are a class of bioconjugates containing transition metals that could be used for biological and catalytic systems. Metzler-Nolte and coworkers reported a series of cobaltocenium bioconjugates prepared by solid-phase peptide synthesis (Figure 6A) [74]. Taking advantage of the exceedingly high stability of cobaltocenium moiety under physiological conditions, these metallo-peptides demonstrated directed nuclear delivery of an organometallic compound. Figure 6C–E depicts the intracellular localization of metallo-peptides and colocalization with an endosome marker and a fluorescence dye. Further study showed that the cationic metallocene provides a hydrophobic handle and helps a nuclear localization sequence to gain entry into cells [75]. Compared with neutral ferrocene counterparts, the cobaltocenium conjugates exhibited greater robustness, redox inactivity, and low toxicity.

Metallo-Enzymes for Electrocatalysis

Enzymes are the most efficient catalysts, which exist in almost all organisms and function under physiological conditions. Developing polymer-supported artificial metallo-enzymes to mimic the features of naturally occurring enzymes is essential for many catalysis, biomedical, and sustainable energy applications [76,77]. In 2011, Kanatzidis and colleagues reported a chalcogenide framework containing immobilized redox-active Fe_4S_4 clusters and light-harvesting dye molecules for solar energy conversion (Figure 6B) [78]. Photochemical hydrogen evolution experiments (Figure 6F,G) demonstrated the

photocatalytic capability of this metallo-enzyme to produce H_2 in the presence of photoredox dye. Very recently, Pyun and coworkers conceptualized a metallopolymer-supported catalyst system with [2Fe-2S] clusters for hydrogen evolution reactions [79]. Macromolecular engineering of the chemical environment around the [2Fe-2S] clusters and polymer composition enables solubility and catalysis in various milieu, as well as enhanced charge and ion transport for catalysis.

Crosslinked Networks and Metallogels

Crosslinking is largely used in polymer chemistry and engineering to improve the physiochemical stability, solvent tolerance, and mechanical properties of polymeric materials. Crosslinking can extremely broaden the practical applications of metallo-polyelectrolytes via addressing issues on mechanical performance, permeability, self-healing property, and durability. In addition to conventional crosslinking methods (i.e., the formation of covalent linkage), a special type of crosslinking through metal–ligand coordination, which is typically dynamic and reversible, is widely employed in metallo-polyelectrolyte systems [26,80]. The metal–ligand interaction can also enhance the performance of conventional materials, such as toughness, adhesion, and self-healing. For example, Hickner, Tew, and coworkers reported the first metal-cation-based polyelectrolyte for anion-conducting applications, which was prepared by copolymerization of bis(terpyridine)Ru(II) complex-functionalized norbornene with dicyclopentadiene as a crosslinkable comonomer (Figure 7A). By tuning the molar ratios of comonomers in the crosslinks, optimal polymer membranes exhibited excellent mechanical properties, ionic conductivity, and methanol tolerance [81]. No significant increase in swelling ratios was observed for the membranes in aqueous methanol solution (2 M, 6 M, 10 M), largely due to their densely crosslinked hydrophobic network (Figure 7D). More recently, the same group further developed nickel-, cobalt-, and ruthenium-containing polyelectrolytes, using metal complexes as both ion conductor and crosslinker. Related results revealed the counterion association thermodynamics to be a key parameter for understanding cation behavior and for designing advanced ion-exchange membranes [82,83]. Beyond that, crosslinking can also be achieved by many other metal–ligand coordination interactions between metal ions and functional groups having lone pair electrons. For example, Zhang and coworkers prepared a series of organometallic polymers with copper complex crosslinker [$CuBr(PPh_3)_2$(4-MePy)] via a facile mechanosynthetic route (Figure 7B) [84]. The metal–ligand coordination between the PPh_3 ligand and Cu(I) not only enhanced the mechanical properties, but also granted luminescent properties to these hybrid materials. These crosslinked membranes were tested for more than four vapoluminescence-recovery cycles without any loss of photoluminescence intensity (Figure 7E), indicating their high chemical stability and good processability.

Introduction of metal ions is also an effective way to enhance inter- and intramolecular interactions and consequently trigger the formation of metallogels [31,85]. Zhang and colleagues prepared a series of supramolecular hydrogels using ultrafast complexation between a native biopolymer, chitosan, and transition metal ions (Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pd^{2+}) (Figure 7C,F) at appropriate pH levels [86]. Specifically, chitosan and Ag^+-based hydrogel (denoted as CS-Ag) exhibited good mechanical properties and rapid responsiveness to a variety of external stimuli. Thus, metallogels with interwoven networks and dynamic metal–ligand interaction are appealing for a variety of practical applications, such as flexible electronic devices, actuators for controlled release, electrocatalysis and sensing, and antibacterial membranes [87].

Concluding Remarks

Although only a small selection of the recent developments on metallo-polyelectrolytes is included in this short review, it is clear that the presence of cationic metal centers with a wide range of polymer architectures can confer a variety of polymeric materials with new properties and broad applications. The emerging polymerization techniques may bring many benefits to the development of metallo-polyelectrolytes. The rapid expansion of controlled radical polymerization provides much more efficient and convenient methods to prepare metallo-polyelectrolytes, such as photocontrolled/air-friendly ATRP and RAFT techniques [88,89]. Iterative polymerization provides a numeric growth of chain ends for initiation, highly suitable to produce branched polymers and

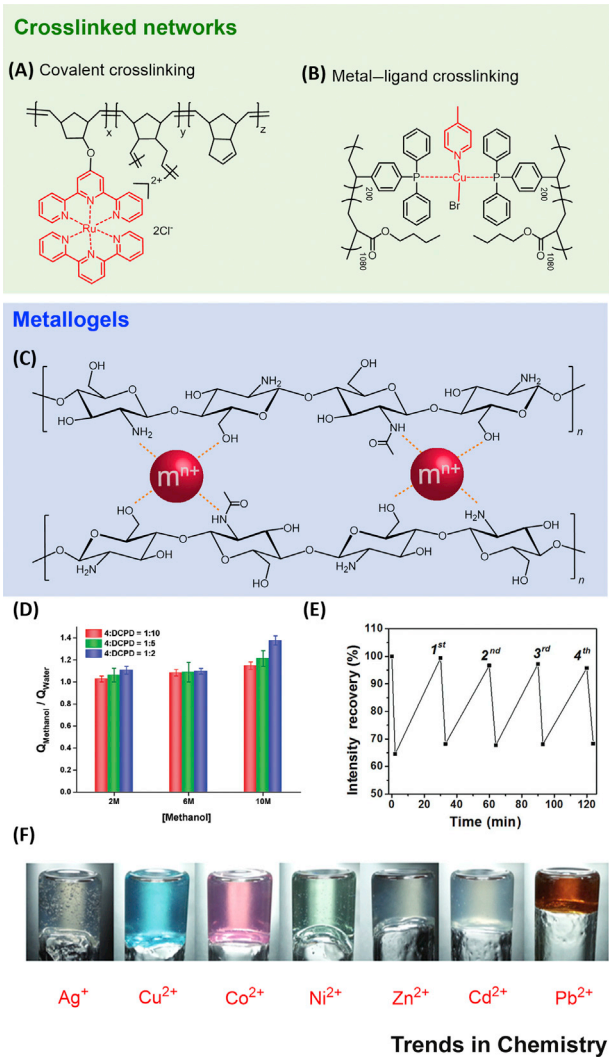

Figure 7. Crosslinked Networks and Metallogels.
Crosslinked networks of metallo-polyelectrolytes based on: (A) covalent crosslinking, (B) metal–ligand crosslinking, and (C) metallogels formed by the complexation between transition metal ions and functional groups in the chitosan; (D) methanol tolerance of metal-cation-based polyelectrolyte membranes as evaluated by the volume swelling ratio; (E) four vapoluminescence-recovery cycles of the organometallic copper polymer; and (F) images of metallogels formed by chitosan and a variety of metal ions. (D–F) Adapted from [81,84,86], with permission, respectively.

dendrimers [90]. Multicomponent polymerization and tandem polymerization with advantages in green chemistry are also excellent techniques to prepare alternative or random copolymers with metal units in the polymer chains [91,92]. Elemental sulfur-based ROP with divinyl monomers developed by the Pyun group is promising for preparing metal-containing polymers to generate crosslinked composites with the merits of abundant sulfurs [93]. Thus, through the judicious choice of synthetic techniques, polymeric framework, transition metal and ligands, and macromolecular architectures, it is conceivable to design materials with tailored electrochemical, magnetic, self-assembly, and photophysical properties [37].

While we have highlighted several examples of how macromolecular architectures impact physiochemical properties for metallo-polyelectrolytes, the nature of interactions between metal moieties

and organic scaffolds and the phase behaviors of these polyelectrolytes remain elusive (see Outstanding Questions). To date, the development of metallo-polyelectrolytes is largely based on some serendipitously experimental outcomes, rather than following a guided rationale of design. This may be attributed to an insufficient understanding of structure–property relationships. For example, although many block copolymers with metal ions are reported, the phase behaviors are far less investigated and no Flory-Huggins parameters related with metal-containing monomers have been quantified. The theoretical prediction of phase segregation is not available in either solution or bulk self-assembly, which limits advanced utilization of metallo-polyelectrolytes. Thus, elucidating the structure–property relationships from experimental results and developing new theoretical models for these metal-containing polyelectrolyte systems are in great demand. In addition, most of current applications in metallo-polyelectrolytes are focused on the solution state. However, bulk polymers like membranes, adhesives, powders, and plastics are preferred in engineering applications. The limited knowledge on chemical stability, mechanical durability, and toughness, related with structure–property relationships, still heavily hinders the applications of metallo-polyelectrolytes.

The selection of metal ions and complexes is not limited to the examples highlighted in this short review. It can be expected that in the future a wider range of new metallo-cations will be investigated to make metallo-polyelectrolytes. Current synthetic methods to incorporate metal-cations or metal-complexes into polymeric materials are relatively limited, providing more opportunities for synthetic organic and polymer chemistry to broaden the scope in this area.

Outstanding Questions

Metallo-polyelectrolytes are largely dictated by the presence of metal building blocks, synthesis of which often involves oxygen- or moisture-sensitive reactions with tedious purification. How is the recent progress in synthetic chemistry interrogated toward readily accessible and structurally diverse organometallic moieties for controlled polymerization? How are properties interfaced with macromolecular compositions and architectures?

How can quantitative ionic binding and theoretical modelling on metallo-polyelectrolytes be advanced? Current understanding on metallo-polyelectrolytes is mostly qualitative, especially regarding interactions with different substrates (from small molecules to macromolecules to cell membranes). Can we use existing theoretical models for organo-polyelectrolytes to predict critical parameters (e.g., topology, charge density, chain length) on properties of metallo-polyelectrolytes? Can we establish phase diagrams for metallo-polyelectrolytes and correlate with traditional organo-polyelectrolytes?

How can real applications of metallo-polyelectrolytes be achieved in a scalable and economically viable pathway? Although earlier work has demonstrated the great potential of metallo-polyelectrolytes for various applications (e.g., biomedical, self-assembly, energy storage), a more comprehensive understanding on customized functions and mechanisms is required to direct the future design of metal complexes and macromolecular architectures.

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