Heterometallic supramolecular polymers: from synthesis to properties and applications

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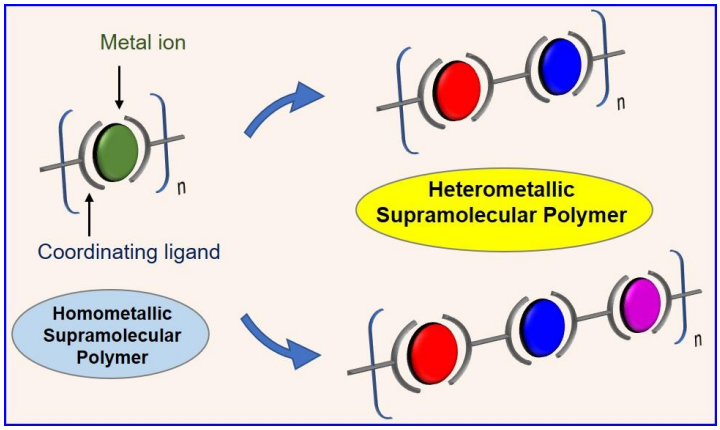
Abstract

Heterometallic supramolecular polymers (HMSPs) comprising two or more heterometal ions have drawn significant research interest in the last two decades because of their attractive properties and applications owing to the combination of organic and inorganic segments in the polymer as well as that of heterometallic complexes in the polymer chain. However, the synthesis of HMSPs is challenging because of the different stabilities of heterometallic complexes. To date, various HMSPs have been developed via one-pot or stepwise synthetic approaches, in which heterometal ions are complexed in identical or different coordination environments. The properties of this type of polymers not only depend on the heterometal ions, but also on the coordination environments of heterometal ions. In this review, we summarize the progress made in the synthesis of HMSPs and highlight their properties and applications. In the first section, we comprehensively discuss various synthetic approaches to HMSPs with all relevant reported examples. Subsequently, we highlight the properties and applications explored in different research directions. Finally, we provide a perspective on the synthetic challenges and future research prospects for HMSPs. We believe that this review will provide a roadmap for further developments in this thriving area of research to create novel functional materials.

Keywords: Heterometallic supramolecular polymer; One-pot synthesis; Stepwise synthesis; Heterometal ions; Electrochromic application

Graphical abstract



Contents

1. Introduction

Supramolecular polymers (SPs) are polymeric arrays of monomer building blocks that are connected via various noncovalent interactions, such as H-bonding, π–π stacking, host–guest interactions, van der Waals forces, hydrophobic forces, and metal–ligand coordination [1–9]. When an SP contains metal ions, it is called a metallo-supramolecular polymer (MSP) or sometime called as metallopolymers [10–16]. However, metallo-supramolecular polymers (MSPs) and metallopolymers differ. Metallopolymers are generally used for any polymer containing metal ions as an integral part of the polymer backbone (polymer main chain), or metal species attached to the side chain of the polymer, where the metal ions in the polymer are attached by covalent or noncovalent interactions [10, 11, 17–25]. Metallopolymers with covalently bonded metal ions are called organometallic polymers, and metallopolymer with metal ions bonded via metal–ligand coordination bonds are called MSPs or coordination polymers (CPs). However, the term "CP" is mostly used by inorganic chemists in a different context. Inorganic chemists generally consider 1D, 2D, and 3D coordination networks as CPs [10, 26]. However, most of these are solid crystalline materials that dissociate into individual molecular units upon dissolution. These materials are generally referred to as "metal-organic frameworks" (MOF) or "metal-organic coordination network" [27–29]. Polymer and supramolecular chemists consider CPs (or MSPs) as polymeric materials comprising metal–ligand coordination interactions, where the interactions between the metal centers and the binding sites are strong enough to keep the polymer chain intact in presence of a solvent.

Among various noncovalent interactions (H-bonding, π–π stacking, host–guest interactions, van der Waals forces, hydrophobic forces, and metal–ligand coordination) that are used for the construction of supramolecular systems, metal–ligand coordination interaction has high directionality and strength, similar to covalent bonds. Moreover, the ligand structure of metal–ligand coordination can be varied using the knowledge of organic reactions. Furthermore, the thermodynamic and kinetic stabilities of polymers containing metal–ligand coordination bonds can be fine-tuned by an appropriate combination of ligands and metal ions [16, 26]. Therefore, metal–ligand coordination provides an excellent platform for constructing well-defined 2D and 3D metallo-supramolecular architectures as well as MSPs with higher stability than other noncovalent interactions [15, 30–38]. Studies on metallo-supramolecules and MSPs (metallopolymers or metal-containing polymers) have been extensively carried out for decades owing to their fascinating features originating from the combination of conventional polymeric properties with the optical, redox, electrical, photochemical, catalytic, or magnetic properties of the metal ions. Thus, these compounds have several applications in the fields of materials science, healthcare, catalysis, energy, and the environment [39–48].

MSPs are typically synthesized by coordination–driven self-assembly of organic ligands and metal ions [10, 12, 49]. The structure of MSPs may be linear or branched, depending on the structure of the ligand and/or the type of metal ion. However, MSPs with linear structures are generally synthesized by 1:1 coordination complexation of ditopic ligands and metal ions, where the ligand molecules and metal ions are arranged in alternate sequences and connected through dative bonds. Coordinating ligands generally contain neutral donor moieties such as amines, pyridines, imines, ketones, and ethers, which form Lewis acid–base pairs with metal ions [16, 50]. Accordingly, the

binding constants for the interactions of these coordinating moieties with metal ions vary, which determines the stability of the resulting MSPs in the presence of a solvent. However, the binding constant (or stability constant) of metal–ligand interactions in MSPs can be enhanced by using donor ligands with extremely high metal–binding affinity and/or by increasing the number of neutral donor atoms in the ligand that bind the metal ion as a chelator (i.e., multidentate coordinating ligand). This strategy has been widely explored using pyridine-based coordination ligands. The chelation effect of multidentate-coordinating ligands was studied by Wurthner et al. [26]. They reported the binding constant for single Zn(II) –pyridine interaction as 10^3 M^{-1}, but the binding constant increased to 10^8 M^{-1} when Zn(II) interacted with a terpyridine (2,2′:6′,2″-terpyridine) system. Thus, polypyridyl ligands (e.g., bipyridine, phenanthroline, and terpyridine) have been observed to have high binding affinities toward various metal ions and have been extensively used to construct metallo-supramacromolecules and MSPs. Several comprehensive reviews on the synthesis, structure, properties and applications of metallo-supramacromolecules and MSPs are available in the literature, such as those by Newkome et al. [30], Schubert et al. [10, 51], Würthner et al. [26], Abd-El–Aziz et al. [40], Yang et al. [52], and Cohen et al. [15].

To date, several MSPs containing one type of metal ion (i.e., homometallic MSPs) have been developed using Cu, Ni, Zn, Fe, Ru, Os, Co, Ag, and Cd as metal ions and various pyridine-based (e.g., bipyridine, phenanthroline, and terpyridine) and non-pyridine-based (e.g., salen, catechol, and thiol) coordinating ligands. These homometallic MSPs have been extensively studied for a broad range of applications, including electrochromic displays, sensors, energy storage devices, light emitting diodes, molecular motors, memory devices, anticancer therapies, and drug delivery [13, 31, 53–72].

Schubert et al. extensively described the synthesis and characterization of homometallic and other types of MSPs [10].

The introduction of two (or more) different metal ions (heterometal ions) into a MSP chain could enable further tuning of the properties and functionalities of the polymer, owing primarily to the coupling of heterometallic segments into the polymer chain [73–75]. Mixed metal complexes in the heterometallic supramolecular polymer (HMSP) broaden the optical and electrochemical windows of the polymer, paving the way for potential optical, electro-optical, and electrochemical applications [74, 76]. For example, when Fe(II) and Eu(III) ions are alternately complexed into an SP, the resulting polymer shows on–off luminescence switching of the Eu(III)-complex moieties, triggered by their redox alteration. Again, the alternate complexation of Fe(II) and Os(II) ions into an SP chain enlarges the optical and electrochemical windows of the polymer due to the combined metal-to-ligand charge transfer (MLCT) transitions and redox characteristics of the Fe(II)- and Os(II) – complex moieties in the corresponding polymer; the resultant polymer shows potential for electro-optical applications. Over the last two decades, various types of HMSPs have been developed, and their properties and applications have been explored in different research directions.

HMSPs containing two or more heterometal ions can be synthesized in a one-pot or stepwise manner, with the heterometal ions complexed randomly or alternately throughout the polymer chain, and the coordination environments of the heterometal ions being identical or different. Generally, a one-pot reaction involves direct mixing of a ditopic ligand and two or more heterometal ions, which cannot solely produce an HMSP with the heterometal ions in alternate positions, as this process produces random polymers

[77–79]. However, the use of asymmetric ditopic ligands in a one-pot reaction can produce an HMSP with alternate alignments of the heterometal ions; however, in this case, the coordination environments of the heterometal ions are always different. On the other hand, stepwise synthetic procedures have been observed to be a successful strategy for preparing HMSPs with alternate complexation of heterometal ions, with a choice to control the coordination environments of the heterometal ions [80]. In a typical stepwise synthetic procedure, a metal–containing ditopic ligand (modified ditopic ligand) is synthesized, and the modified ditopic ligand undergoes further complexation with another heterometal ion (1:1 complexation) to form the desired HMSP. Notably, the coordination environments of the heterometal ions in an HMSP greatly determine its properties and, hence, its application. In addition to HMSPs, various structural heterometallic supramacromolecules (discrete architectures) have been mostly developed by one-pot or stepwise multicomponent self-assembly processes [30, 81–90]. However, HMSPs have several advantages over heterometallic supramacromolecules in terms of their applications; thus, HMSPs have drawn considerable attention in the last couple of years.

Although HMSPs show interesting properties and applications, their synthesis is a major challenge because of the different stabilities of the heterometallic complexes, particularly when the polymer is dissolved in a solvent. To date, success has mostly been achieved in the synthesis of HMSPs containing two heterometallic ions, that is, heterobimetallic supramolecular polymers (HBSPs). Very recently, the synthesis of HMSPs containing three heterometal ions was reported, in which three heterometal ions were introduced in the same coordination environments into a MSP chain [76]. Although the alternate complexation of three heterometal ions was not justified in the reported heterotrimetallic supramolecular polymers (HTSPs), this work enriches the portfolio of

HMSPs and opens a route to develop HMSPs with more than two heterometal ions. Therefore, we believe that a comprehensive review of the synthetic procedures, properties, applications, future opportunities, and challenges of HMSPs is necessary, which will facilitate the further development of HMSPs with a greater number of heterometallic complexes.

In this review article, we aim to provide a detailed overview of HMSPs, from their different synthetic approaches to their properties and applications. First, we describe in detail various approaches to synthesize HMSPs, and then highlight the relevant examples that have been reported in the last two decades. Subsequently, the properties and applications of HMSPs in various fields of research are discussed. There are several examples of heterometallic coordination polymers (as developed/described by inorganic chemists) that do not typically fall under the category of MSPs [91–97]. Therefore, these polymers are not considered in this review. Heterometallic polymer, a class of metallopolymers or metal-containing polymers that comprise covalent/organometallic bonds, are also excluded [98–101]. HMSPs, as covered in this review, have been defined here as polymers that contain two or more heterometal ions and that have been constructed, either partially or fully, using metal–ligand coordination interactions following the synthetic process of MSPs, that is, 1:1 complexation of ligand and metal ion.

2. Synthesis of heterometallic supramolecular polymers (HMSPs)

2.1. Synthetic approaches

Generally, bidirectional ditopic ligands are used to prepare MSPs with linear structures through coordination complexation with metal ions (with some exceptions where branched structures are formed). The same strategy can be applied to prepare HMSPs, where the metal–ligand bonds are either coordination bonds or a combination of organometallic and coordination bonds (see vide infra). However, to prepare any HMSP, metal–ligand coordination interactions must be used either partially or fully during the synthesis of the polymer. HMSPs are generally synthesized using one-pot or stepwise approaches, as discussed in detail below.

2.1.1. One-pot synthetic approach

As discussed earlier, MSPs containing one type of metal ions (i.e., homometallic MSPs) generally synthesized by 1:1 coordination complexation between ditopic ligands and metal ions in one "pot" (Fig. 1a) [10, 31]. This strategy is also utilized to prepare HMSPs by mixing : (1) a symmetric ditopic ligand (Fig. 1b) or (2) an asymmetric ditopic ligand (Fig. 1c), with heterometal ions. In Fig. 1, we consider at least two heterometal ions to represent the synthetic procedures of HMSPs.

When symmetric ditopic coordinating ligands are used to prepare HMSPs in a one-pot synthesis, the resulting HMSPs contain heterometal ions in the same coordination environment; however, the heterometal ions are usually complexed randomly throughout the polymer chain (Fig. 1b) [78, 102]. Since the reactivities of the two ends of the

symmetric ligand is the same, the ligand can undergo complexation with both heterometal ions simultaneously. Therefore, the distribution of heterometal ions in the polymer chain cannot be controlled, leading to HMSPs with a random distribution of heterometal ions.

In contrast, if asymmetric ditopic ligands are used with heterometal ions in a one-pot synthesis, the complexation of heterometal ions occurs alternately throughout the polymer chain [74, 103, 104]. As shown in Fig. 1c, the asymmetric ditopic ligand has two different reactive sites that can undergo selective complexation with two heterometallic ions. In this process, the coordination environments of the heterometallic ions in the HMSP are always different. However, this is an effective strategy for preparing HMSPs that comprise alternately occurring heterometal ions.

2.1.2. Stepwise synthetic approach

Compared with the one-pot synthetic approach, the stepwise synthetic approach has been observed to be a successful strategy for the synthesis of HMSPs [80, 105]. In the stepwise synthesis, heterometal ions are introduced by stepwise complexation. In the first step, a metal-containing ditopic ligand is prepared (see step-1 in Fig. 1d–f). In the second step, the resulting metal-containing ditopic ligand undergoes further complexation (following 1:1 coordination complexation between the ligands and metal ions) with another heterometal ion to form the desired HMSP (see step-2 in Fig. 1d–f). Depending on the type of metal complex in the modified ditopic ligand prepared in step-1, two types of HMSPs can be synthesized: (1) HMSPs with heterometal ions in identical coordination environments (Fig. 1d) [105] and (2) HMSPs with heterometal ions in different coordination environments (Fig. 1e,f) [64, 106].

The binding ability of the coordinating ligand varies from one metal ion to another. Some metal ions form strong coordination bonds with particular ligands, while others form weak coordination bonds with the same ligand [30]. Based on these strong and weak coordination metal ions, HMSPs containing heterometal ions in identical coordination environments can be synthesized by the stepwise complexation of a strong coordination metal ion followed by a weak coordination metal ion [76, 80]. The corresponding stepwise synthesis is schematically represented in Fig. 1d. In step-1, a metal-containing ditopic ligand (modified ditopic ligand) is prepared via coordination interactions between the metal ions and the ligand, where the two ends of the modified ditopic ligand are free to coordinate with another heterometal ion in step-2. Note that the modified ligand (in step-1) is synthesized in such a way that it has a symmetrical structure, and all coordinating sites (that are involved in coordination as well as those that remain free in the modified ditopic ligand) are the same. Therefore, the modified ligand underwent further coordination complexation (1:1 molar ratio of ligand to metal ion) with another heterometal ion to form HMSPs, in which the heterometal ions were bonded in identical coordination environments.

Heterometallic supramolecular polymers containing heterometal ions in different coordination environments can be synthesized in two ways following a stepwise synthetic approach, in which all metal–ligand bonds are based on either coordination linkages or a combination of organometallic and coordination linkages. As shown in Fig. 1e, metal-containing ditopic ligands are synthesized using coordination linkages, where the ligand structures (or coordination sites) involved in metal binding are not the same as those of the two terminal free ligands (or coordination sites). Therefore, when this metal containing ditopic ligand undergoes further complexation with another heterometal ion

in step-2, the resulting HMSP contains the heterometal ions in alternate fashion but the coordination environments of the heterometal ions are not identical [107, 108]. In contrast, metal-containing ditopic ligands can be synthesized using metal–ligand covalent bonds (or organometallic bonds), as shown in Fig. 1f, where the two terminal free ligands (or coordination sites) undergo further coordination complexation with another metal ion to give the desired HMSP containing heterometal ions in different coordination environments [75, 109, 110].

Using the above synthetic approaches, various HMSPs have been constructed in which heterometal ions are complexed in either identical or different coordination environments. Because the electronic environment of a metal ion in a MSP chain is greatly influenced by its coordinating ligands, the properties of individual heterometallic complexes in an HMSP chain depend on the coordination environment of the heterometal ions. Therefore, to compare the properties of each heterometallic complex in the HMSP chain, the coordination environments of the heterometal ions in the polymer chain should be identical. In contrast, when the coordination environments of heterometal ions in HMSPs are different, the properties of the heterometallic complexes also differ from one metal complex to another, and the properties of each heterometallic complex cannot be compared.

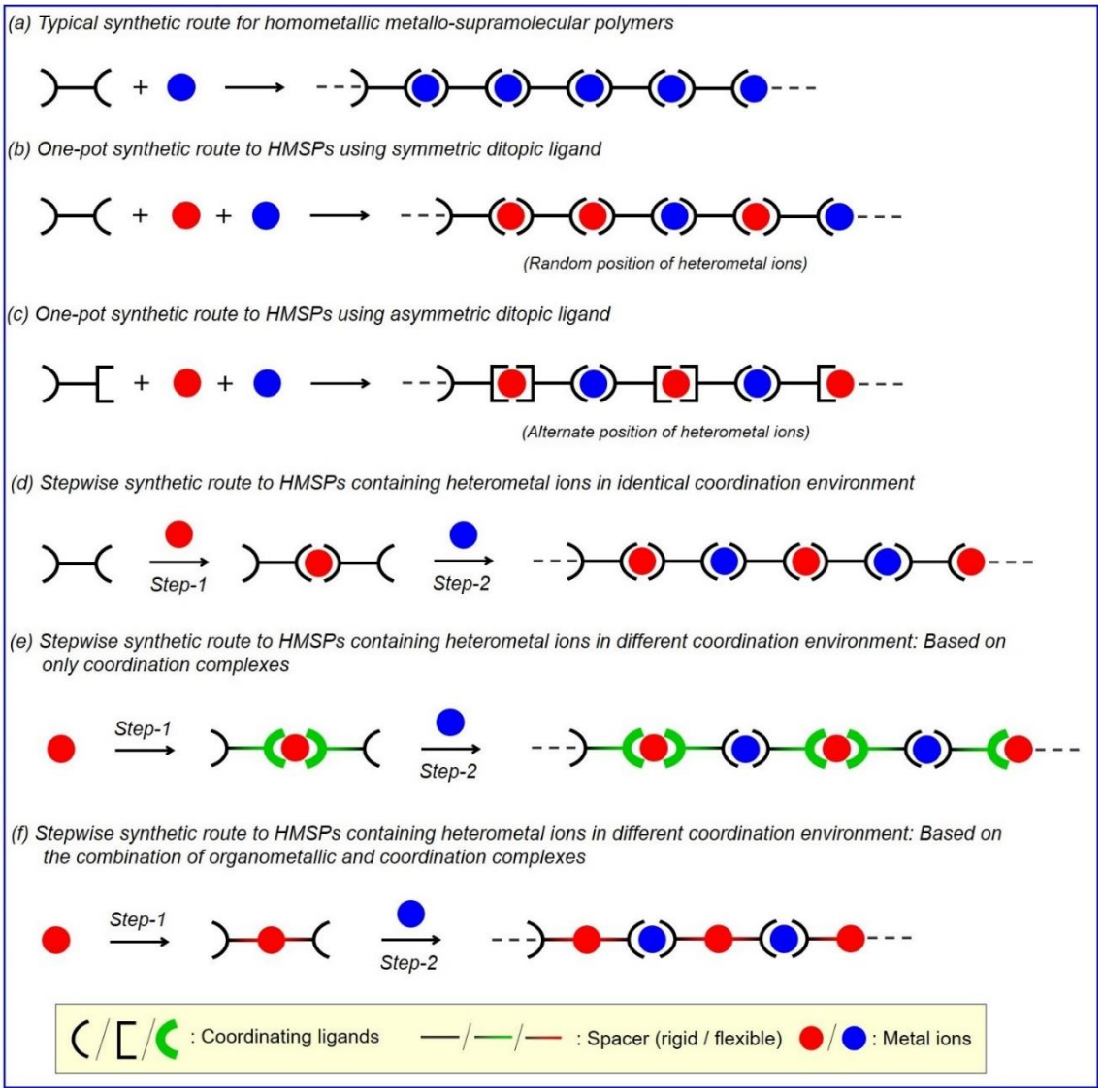


Fig. 1. *Schematic presentation of the synthesis of homometallic MSPs and HMSPs. (a) Typical synthetic route to homometallic MSPs. One-pot synthetic route to HMSPs using (b) symmetric and (c) asymmetric ditopic ligands. Stepwise synthetic route to HMSPs with (d) heterometal ions in identical coordination environments, (e) heterometal ions in different coordination environments but based on only coordination complexes, and (f) heterometal ions in different coordination environments but based on the combination of organometallic and coordination complexes. To represent the structure of HMSPs, we consider here at least two heterometal ions.*

2.2. Choice of coordinating ligands

Although various types of pyridine-based and non-pyridine-based coordinating ligands are commonly used for the synthesis of MSPs, successful synthesis of heterometallic supramolecular polymers has been achieved using polypyridyl ligands (bipyridine, phenanthroline, terpyridine, etc.). Nonpyridine-based coordinating ligands mainly produce coordination polymers (they do not fall under the category of MSPs or HMSP) [91, 93, 94, 111, 112]. For example, Maspoch et al. reported ligand L1 that is a macrocyclic linker based on 1,4,7,10-tetraazacyclododecane-1,7-bi(4-acetamidobenzoic)-4,10-diacetic acid. The L1 produces heterometallic coordination polymers in a two-step synthesis: the complexation of Ni(II) or Mn(II) ions with L1 to make metallo-macrocycles, followed by the corresponding metallo-macrocycles binding Zn(II) ions to construct Ni(II)-Zn(II) and Mn(II)-Zn(II) based HBCPs (P1, P2) (Fig. 2a) [94]. Singh *et al.* reported a maleonitrile dithiolate (mnt)-based ligand containing Ni(II) (L2), which produced bimetallic coordination polymers (P3–P5) upon complexation with Pd(II), Hg(II), and Ag(I) (Fig. 2b). Moreover, the synthesized coordination polymers are insoluble in organic solvents or water [112].

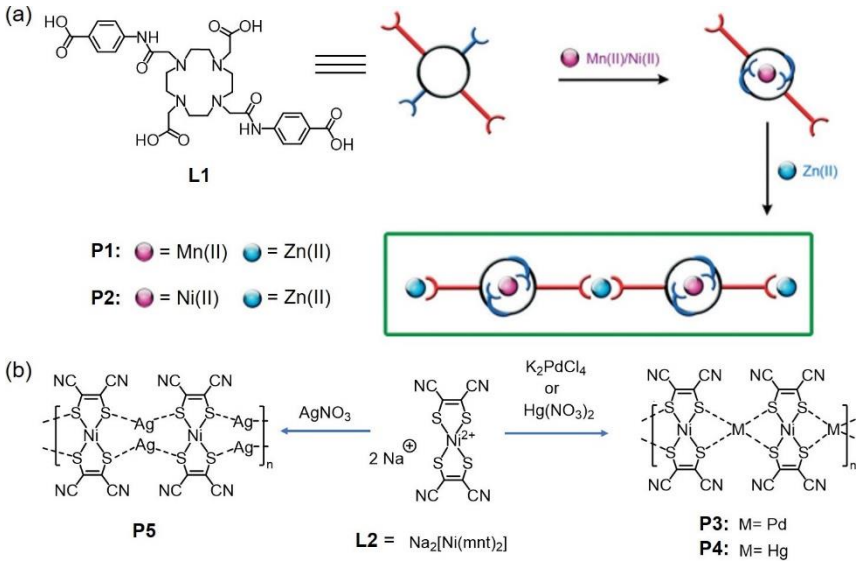


Fig. 2. *(a) Chemical structure of L1 containing Zn(II) ion and schematic view of its complexation with Ni(II) or Mn(II) to give HMSPs P1 and P2, Reproduced with permission from ref. [94]; Copyright 2016 Royal Society of Chemistry. (b) Chemical structure of L2 containing Ni(II) ion and its polymers; P3–P5.*

In contrast, pyridine-based coordinating ligands and polypyridyl ligands are useful for HMSP synthesis. However, the pyridine unit, which acts as a monodentate ligand, is not effective for preparing HMSPs. Because the binding constants of metal ions with a single pyridine moiety are very low, the metal–pyridine bonds are not strong enough to keep the HMSP chain intact in the presence of a solvent. The use of a single pyridine unit as a monodentate ligand produces coordination polymers [92, 113–115]. For example, Baudron et al. prepared dithiolene-based metalloligands (L3 and L4 in Fig. 3), which contain an Au (III) complex with free pyridine units that further bind Mn(II)/Co(II)/Cd(II) to give HBCPs [113]. Hosseini et al. synthesized Ir(III)–containing metalloligands (L5 in Fig. 3) comprising free pyridine units that underwent complexation

with Cd(II) ions to give heterometallic Ir(III)–Cd(II)-based 1D coordination polymers [92].

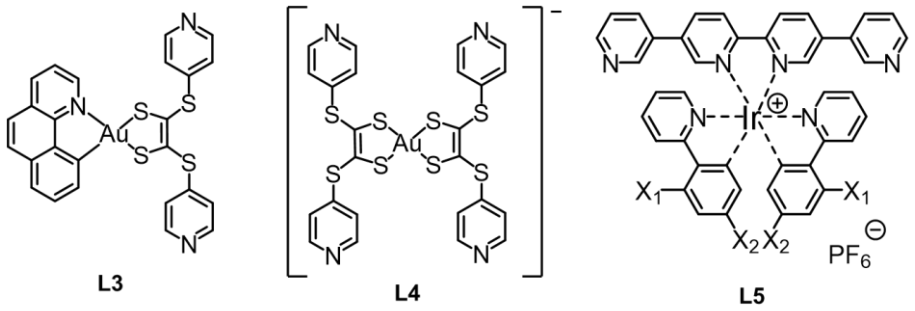


Fig. 3. *Chemical structures of the ligands L3, L4, and L5, containing free pyridine units*.

Polypyridyl ligands, such as bipyridine, phenanthroline, and terpyridine, are ideal candidates for preparing HMSPs. These ligands have high binding constants toward various metal ions and can form a variety of metal complexes with labile and nonlabile metal–ligand connectivity. However, among the polypyridyl ligands, 2,2′:6′,2″-terpyridine (tpy) based coordinating ligands are most preferrable for the synthesis of HMSPs as the terpyridine-based ligands lead MSPs having linear structure. The terpyridine unit acts as a tridentate chelating ligand and binds various metal ions through labile or nonlabile tpy-M(II)-tpy connectivity (M = Metal) [10, 30, 116]. Therefore, terpyridine-metal chemistry has been extensively used to introduce heterometal ions into MSP chains.

2.3. Examples of various HMSPs

As mentioned above, various types of HMSPs have been prepared following a one-pot or stepwise synthetic approach, where heterometal ions are bonded in identical or different coordination environments depending on the nature of the metal–ligand bonds involved in the polymer chain. The heterometal ions in the HMSP chains may be distributed randomly or alternately. In this section, we highlight the examples of HMSPs that have been developed and reported in the last two decades. The solubility and stability of HMSPs in solution are important parameters for the characterization and application of polymers. However, the noncovalent linkages between the metal and ligand in MSPs or HMSPs undergo dissociation, which hampers the stability of the polymers and makes it difficult to characterize the polymers in solution. The characterization of HMSPs is similar to that of homometallic MSPs using various analytical techniques, which have been described in detail by Schubert et al. [10]. Common analytical techniques include nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MALDI-TOF or ESI mass), size exclusion chromatography (SEC), viscometry, light scattering, scanning probe microscopy (SPM), electron microscopy, and X-ray scattering.

2.3.1. HMSPs prepared via one-pot synthetic approach

In the one-pot synthetic approach for the synthesis of HMSPs, the ditopic coordinating ligand and heterometal ions are combined under suitable reaction conditions; the metal ions are added either all at once or in a stepwise manner without isolation of the intermediate compounds. However, the coordination environments of the heterometal ions may be identical or different depending on the structure of the ditopic

coordinating ligand. The position (random versus alternate) of the heterometal ions in the polymer chain also depends on the structure of the ditopic ligand.

2.3.1.1. HMSPs based on identical coordination environments of heterometal ions

To obtain HMSPs containing heterometal ions in identical coordination environments, ditopic ligands with symmetrical structures are generally used to react with the heterometal ions in a one-pot reaction. Following this synthetic strategy, Higuchi et al. prepared a series of Fe(II)–Ru(II)-based HMSPs (the general structure of the polymer is denoted in Fig. 4 as P6) using a symmetrical ditopic ligand (L6), which contains two terpyridine units as coordinating sites in the opposite direction (Fig. 4) [78]. To prepare HMSPs, L1 was first treated with Ru-salt at 130 °C for 24 h, and then Fe-salt was added to the same reaction mixture, followed by stirring at 80 °C for 24 h. The ratio of Ru to Fe salts was varied to prepare a series of polymers. In this case, the intermediate Ru(II)complex was not isolated, producing the desired polymers with a random distribution of heterometal ions.

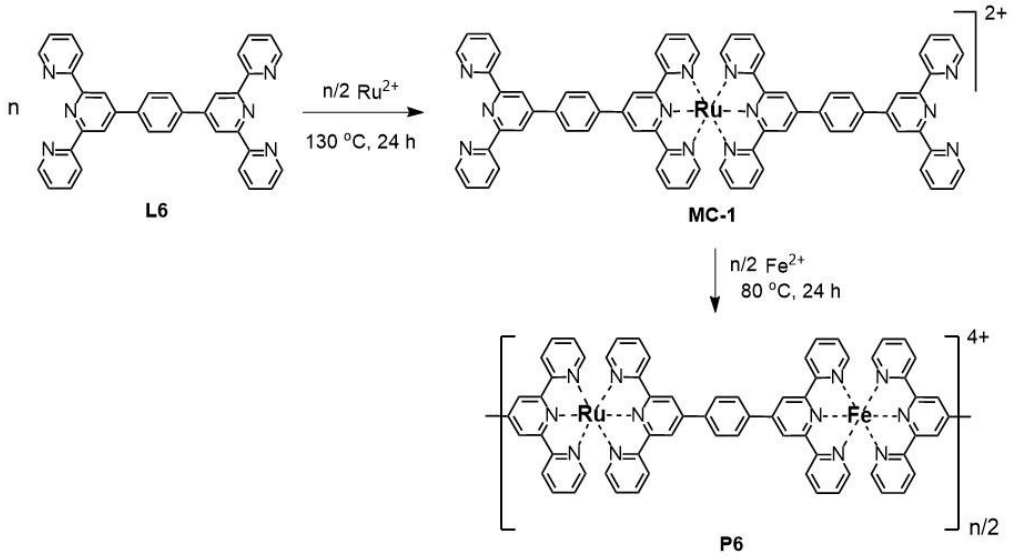


Fig. 4. *Synthetic route to P6 from the ligand L6 via one-pot reaction by stepwise addition of heterometal ions.*

Ahammad et al. synthesized a Ni(II)-Co(II)-based HMSP (P7) by treating L6 with Ni(II) and Co(II) metal salts in a ratio of 1:0.5:0.5 (for ligand:Ni:Co) in a mixture of solvents (acetic acid, acetonitrile, and methanol) at 100 °C (Fig. 5) [79]. Ni(II) and Co(II) metal ions were randomly distributed throughout the polymer chain in an octahedral coordination environment composed of two terpyridine units through tpy-M^{2+}-tpy connectivity. The successful introduction of heterometal ions (Ni and Co) was confirmed by UV–vis spectroscopy, EDS analysis, SEM, and cyclic voltammetry (CV) analysis of the polymer.

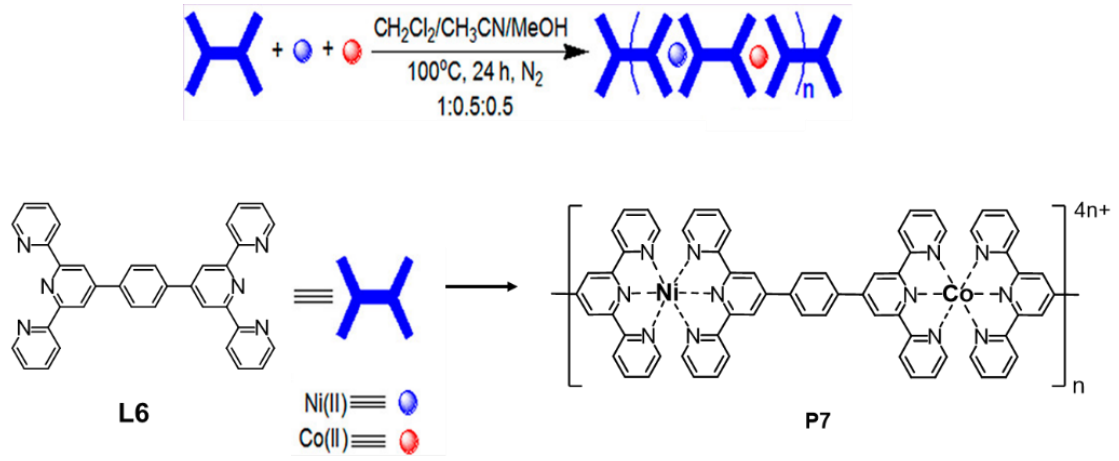


Fig. 5. *Synthetic route to P7 via a one-pot reaction between L6, Co(II), and Ni(II) ions. Adapted with permission from ref. [79], Copyright 2020 American Chemical Society.*

Another class of HMSPs was developed by Rowan et al., in which heterometal ions were incorporated into structurally different MSPs [77, 117, 118]. However, this type

of polymer has not been characterized as a typical HMSP structure owing to the formation of polymeric gels or larger architectures (e.g., linear or branched) based on the metal–ligand interactions. The metal–ligand interactions in the polymer chain are not only thermodynamically stable but also kinetically labile depending on the nature of the ligand and metal ions used. The thermodynamic stability of metal–ligand interactions generally determine the size (or degree of polymerization) of the polymer/aggregate, whereas their kinetic lability leads to dynamic polymers that always remain in equilibrium and can respond to external stimuli [119, 120]. Using these characteristics of metal-ligand bonds, stimuli-responsive metallo-supramolecular aggregates/gels were prepared using the ditopic ligand L7 and two heterometal ions, Zn(II) and La(III) [117]. L7 contains two 2,6-bis(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridine units as coordinating moieties connected via a penta-(ethylene glycol) core. The coordinating moiety, 2,6-bis(1–methyl-1*H*-benzo[*d*]imidazol–2–yl)pyridine, was introduced by the Rowan and Weder groups [121–124], and it has comparable binding strength and denticity to that of 2,2′:6′,2″-terpyridine. Using L7 and by controlling the ratio of heterometal ions as well as the nature of metal salts used, the structure of the metallo-supramolecular aggregates may be linear (where 97% Zn(II) as $Zn(ClO_4)_2$ and 2% La(III) as $La(NO_3)_3$, relative to L7; structure B in Fig. 6a) or branched (where 97% Zn(II) as $Zn(ClO_4)_2$ and 2% La(III) as $La(ClO_4)_3$, relative to L7; structure C in Fig. 6a). The same strategy was followed by Maji et al. to prepare emissive gelators based on the terpyridine-containing ditopic ligand L8 [125]. Through self-assembly, L8 formed a blue-emissive low-molecular-weight gelator containing terminal terpyridine groups, which further underwent coordination-driven self-assembly with mixed metal ions Tb(III) and Eu(III) in different stoichiometric ratios to produce coordination polymer gels (metallogels) with tunable emission from yellow

(Tb:Eu= 1:1.2) to white (Tb:Eu= 1:2) (Fig. 6b). Powder X-ray diffraction of the metallogels revealed higher-order self-assembled structures, which led to the formation of a coordination polymer network.

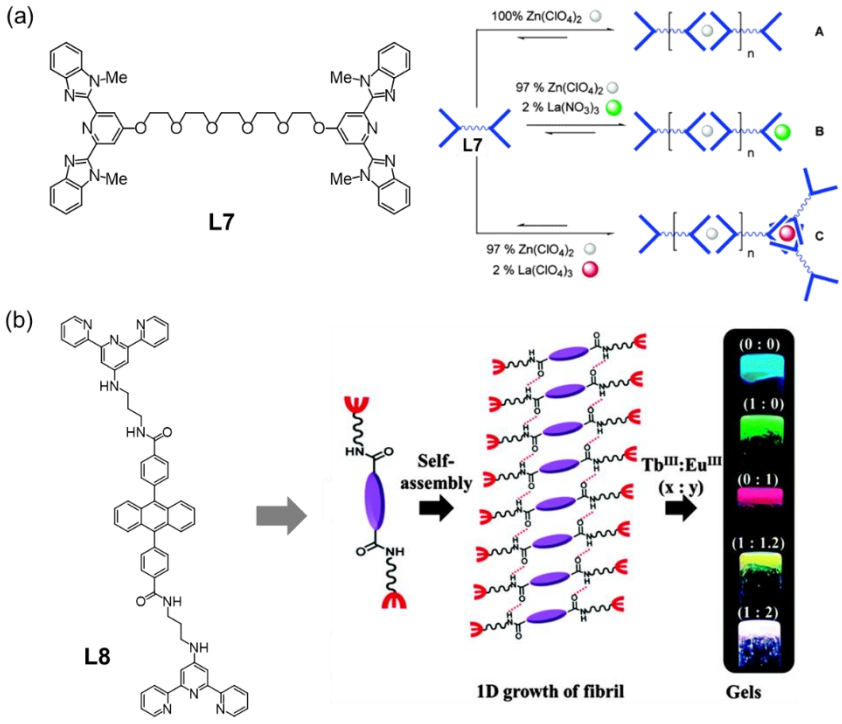


Fig. 6. *(a) Chemical structure of ligand L7 and schematic view of various structural metallo-supramolecular aggregates upon complexation of L7 with Zn an La. Adapted with permission from ref. [117], Copyright 2006 American Chemical Society. (b) Chemical structure of ligand L8 and its self-assembled structure with mixed metal ions showing tunable emission. Adapted with permission from ref. [125], Copyright 2015 Royal Society of Chemistry.*

2.3.1.2. HMSPs based on different coordination environments of heterometal ions

In one-pot synthesis, alternating heterometallic (heterobimetallic) SPs can be prepared using a ditopic ligand with an asymmetrical structure and two heterometal ions. The two ends of the ditopic ligand contained two different coordinating units that underwent selective complexation, with two different heterometal ions arranged alternately throughout the polymer chain. In this case, the coordination environments of the heterometal ions are not identical. Following this strategy, Higuchi et al. synthesized an asymmetrical bisterpyridine ligand (L9) via Suzuki coupling, which was used to prepare an Eu(III)-Fe(II)-based HBSP (P8, Fig. 7). P8 was prepared via a one-pot synthesis by addition of 0.5 equiv. of $Eu(NO_3)_3$ with L9, followed by the addition of 0.5 equiv. of $Fe(BF_4)_2$ in the presence of tridodecylamine [74]. L9 contains an unsubstituted terpyridine (tpy) and a dicarboxylate-substituted terpyridine (ctpy), which bind Eu(III) ions through two ctpy units and Fe(II) ions through two tpy units to form a HBSP with alternating complexation of heterometal ions. Tridodecylamine deprotonates the -COOH groups of L4 to form complexes with Eu(III) ions. Although the synthesis of P8 was one-pot, the order of the heterometal-ions addition is important to obtain the desired polymer, that is, Eu(III) (as $Eu(NO_3)_3$ salt) should be added first, followed by Fe(II) [as $Fe(BF_4)_2$ salt]. This is because the Fe(II) ions tend to bind to both tpy and ctpy, and the binding constant of Fe(II) with ctpy is higher than that with tpy. Therefore, if Fe(II) was added first to L9, the desired polymer did not form, as Fe(II) first underwent 1:1 complexation with one ctpy unit (not 1:2 complexation), and the bulky dicarboxylate groups of ctpy prevented further complexation with another ctpy unit. As a result, polymer chain formation did not proceed upon further addition of Eu(III) ions, as confirmed by UV–vis titration experiments.

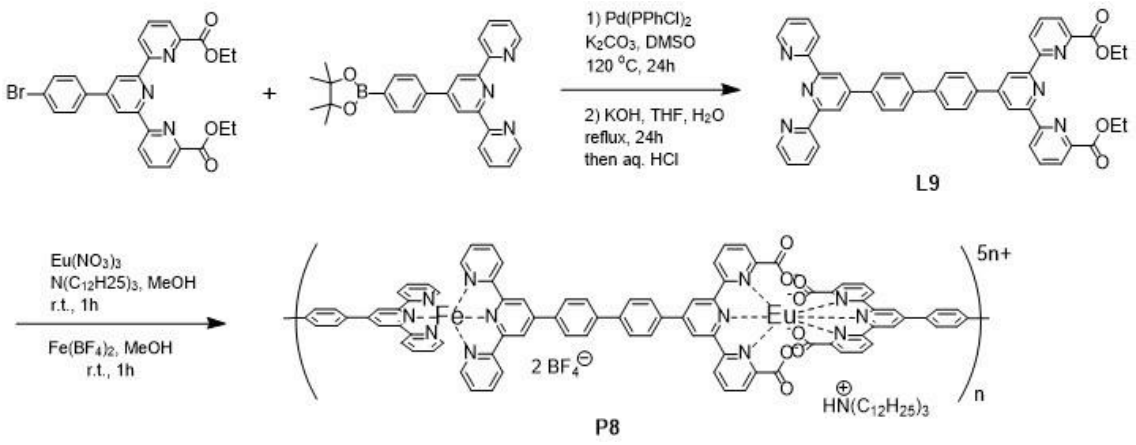


Fig. 7. *Synthetic route to P8 from the asymmetric ligand L9.*

L9 was also used to prepare Eu(III)–Zn(II) containing a HBSP (P9) through one-pot synthesis by mixing L9, $Eu(NO_3)_3$, and $Zn(ClO_4)_2$ in a molar ratio of 1:0.5:0.5, in the presence of tridodecylamine (Fig. 8) [104]. Eu(III) and Zn(II) ions were introduced alternately throughout the polymer chain via a tpy-Zn(II)-tpy-ctpy-Eu(III)-ctpy connectivity. Generally, the bonds in tpy-Zn(II)-tpy-type complexes are labile in nature; thus, when competitive metal ions are present in a system containing tpy-Zn(II)-tpy-type complexes, the exchange of Zn(II) ions with these competitive metal ions is possible. However, in the case of P9, the exchange of Zn(II) ions in the presence of excess Eu(III) ions occurred because of the different coordination environments of Zn(II) and Eu(III) ions, as confirmed by UV–vis titration. When 0.5 equivalent of $Eu(NO_3)_3$ was added to L1 in methanol (in the presence of tridodecylamine), the absorbance at 345 nm increased linearly owing to the formation of a 1:2 complex (L1-Eu-L1). Subsequent addition of $Zn(ClO_4)_2$ (up to 0.5 eq) resulted in a steady increase in absorption at 340 nm, which was unchanged upon further addition of Zn salt, demonstrating 1:1 complexation between

Zn(II) and L1-Eu-L1, leading to the formation of P9. Again, the addition of $Eu(NO_3)_3$ to the resulting solution containing the as-prepared P9 did not change the spectral behavior, indicating no exchange between Zn(II) and Eu(III) ions.

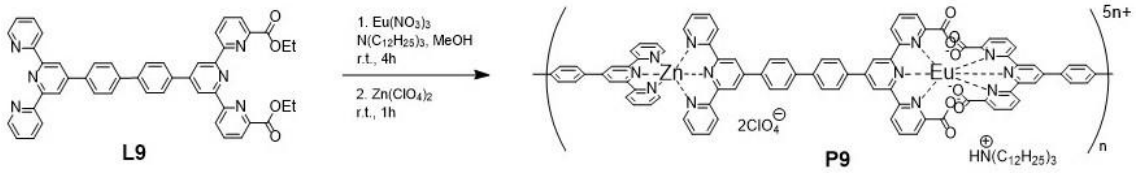


Fig. 8. *Synthetic route to P9 from the asymmetric ligand L9.*

An asymmetrical ditopic ligand (L10) containing phenanthroline and terpyridine moieties as the coordination sites was developed to prepare a Cu(I)–Fe(II)-based HBSP (P10) [103]. P10 was obtained by the one-step complexation of L10 with Cu(I) and Fe(II) ions in a molar ratio of 1:0.5:0.5, where the ligand underwent selective complexation with Cu(I) and Fe(II) to maintain these two heterometal ions in alternate positions throughout the polymer chain (Fig. 9). The coordination environments of Cu(I) and Fe(II) in P10 were different: Cu(I) ions preferentially formed tetrahedral complexes with two bidentate phenanthroline moieties, while Fe(II) formed octahedral complexes with tridentate terpyridine moieties. Interestingly, the selective binding of Cu(I) and Fe(II) ions in an alternating fashion by ligand L10 did not depend on the order of addition of metal salts during the synthesis of P10. Two different metal salts were added simultaneously to L10 to obtain the desired HMSP with alternate complexation of Cu(I) and Fe(II) ions. The presence of Cu(I) and Fe(II) ions in P4 was confirmed by CV and the alternate alignment in P4 was confirmed by ESI-MS. Fragment peaks were observed in the ESI mass

spectrum of P10, equivalent to the calculated mass of the L10-Cu-L10-Fe-L10 fragment. This finding suggests an alternating alignment of Cu(I) and Fe(II) ions in P10.

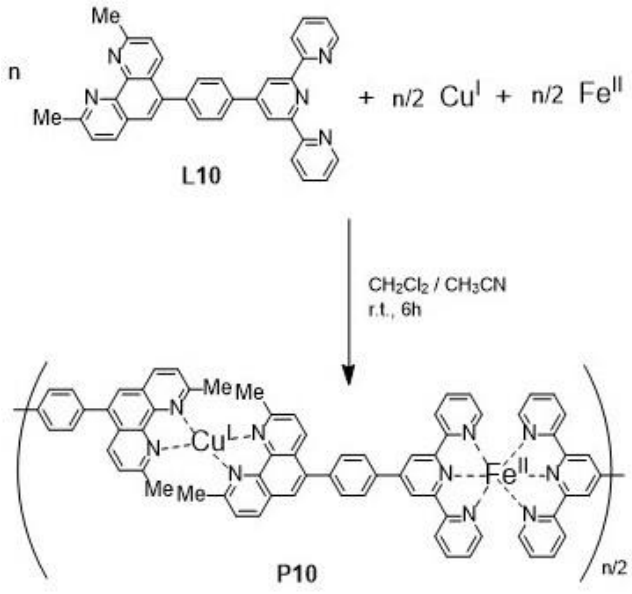


Fig. 9. *Synthetic route to P10 from the asymmetric ligand L10.*

Recently, another asymmetrical ditopic ligand (L11) containing dicarboxylate-substituted terpyridine and phenanthroline as coordinating moieties was used to prepare Eu(III)–Fe(II)-based HMSPs (P11) [126]. In this case, the structure of P11 was 3D-hyperbranched, instead of linear (Fig. 10). The synthesis of P11 was one-pot using L11, Eu(III), and Fe(II) ions, where two dicarboxylate-substituted terpyridine units bind Eu(III) ions, and three phenanthroline units bind Fe(II) ions to create a hyperbranched structure. The presence of Fe(II) and Eu(III) ions in P5 was confirmed using CV, fluorescence, and XPS analyses.

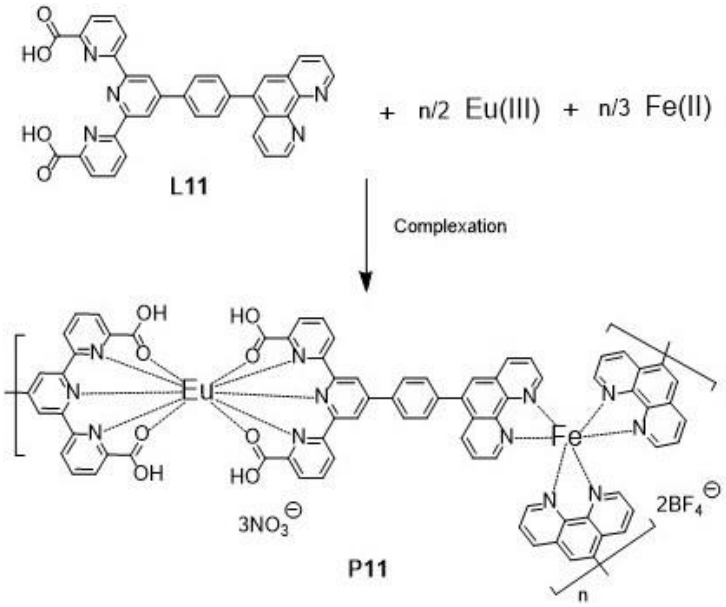


Fig. 10. *Synthetic route to P11 from the asymmetric ligand L11.*

2.3.2. HMSPs prepared via stepwise synthetic approach

In a stepwise synthetic approach, a metal-containing ditopic ligand is first prepared, isolated, and characterized and then used for further complexation with other heterometal ions to obtain an HMSP. Depending on the type of ligand used in the different steps of the process, the coordination environments of the heterometal ions in the HMSPs may be identical or different. Using this process, HMSP with alternately complexed heterometal ions were easily prepared.

2.3.2.1. HMSPs based on identical coordination environments of heterometal ions

To prepare HMSPs containing heterometal ions in identical coordination environments following a stepwise synthetic process, only one type of coordinating ligand (or binding site) is typically used for polymer synthesis. Higuchi et al. developed

this type of polymer by designing a stepwise synthetic route schematically shown in section 2.1 (Fig. 1c) [76, 80, 105]. Two as well as three heterometal ions were successfully introduced into the MSP chain. A series of HBSPs and HTSPs were similarly developed, in which the metal ions were coordinated by two terpyridine (tpy) units through tpy-M(II)-tpy connectivity.

2.3.2.1.1. Heterobimetallic supramolecular polymers (HBSPs)

As shown in Fig. 4, Ru(II)/Fe(II)-containing alternating HBSPs were synthesized using a one-pot approach; however, the intermediate Ru(II)-containing ditopic ligand (MC-1) was not isolated during the synthesis [78]. Therefore, this process does not confirm the complexation of MC-1 with Fe(II) ions in an alternate fashion, because the complexation of Ru(II) ions with the symmetrical ditopic ligand L6 does not proceed in a controlled manner. Because the reactivity of both ends of L6 is the same, both ends can bind Ru(II). Therefore, the production of MC-1 is always associated with some oligomeric products that create difficulty in separating MC-1 from the oligomeric mixtures. At this stage, the isolation of MC-1 from oligomeric mixtures is very difficult. Moreover, the addition of Fe(II) ions to these oligomeric mixtures led to the formation of various polymeric chains with a random distribution of heterometal ions.

The above synthetic problem was solved by designing a stepwise complexation route in which the intermediate metal-containing ditopic ligand was separated by column chromatography, and the process did not lead to the formation of any undesired oligomers.

The isolated metal-containing ditopic ligand can then undergo 1:1 complexation with any heterometal ion to produce alternating linear HMSPs. The idea behind The development of a stepwise complexation route was based on the complexation of strong-coordination metal ions, followed by weak/moderate-coordination metal ions. Based on this strategy, an alternating Fe(II)–Os(II)-based HBSP (P12) was synthesized using a terpyridine-based ligand, where Os(II) is considered a strong coordination metal ion and Fe(II) is considered a weak coordination metal ion (Fig. 11a) [80]. Starting from 4′-bromo-2,2′:6′,2″-terpyridine, Os(II) containing ditopic ligand was synthesized in two steps and the ligand was isolated and characterized by NMR and mass spectrometry and analyses. A clear distinction between the coordinated and free terpyridine units in MC-2 was highlighted in the ^{1}H NMR study, as shown in Fig. 11b. The Os(II)-containing ditopic ligand then underwent 1:1 complexation (confirmed by UV-spectroscopic titration of the ligand with Fe salt) with Fe(II) ions to give P12. The presence of Os(II) and Fe(II) ions in P12 was further confirmed using CV and XPS analyses. Using the same synthetic strategy, Bera et al. synthesized an Os(II)–Ru(II)-based HBSP (P13) by the complexation of MC-2 with Ru(II) ions (Fig. 11a), where both metal ions are strongly coordinated and complexed in the same coordination environments [127].

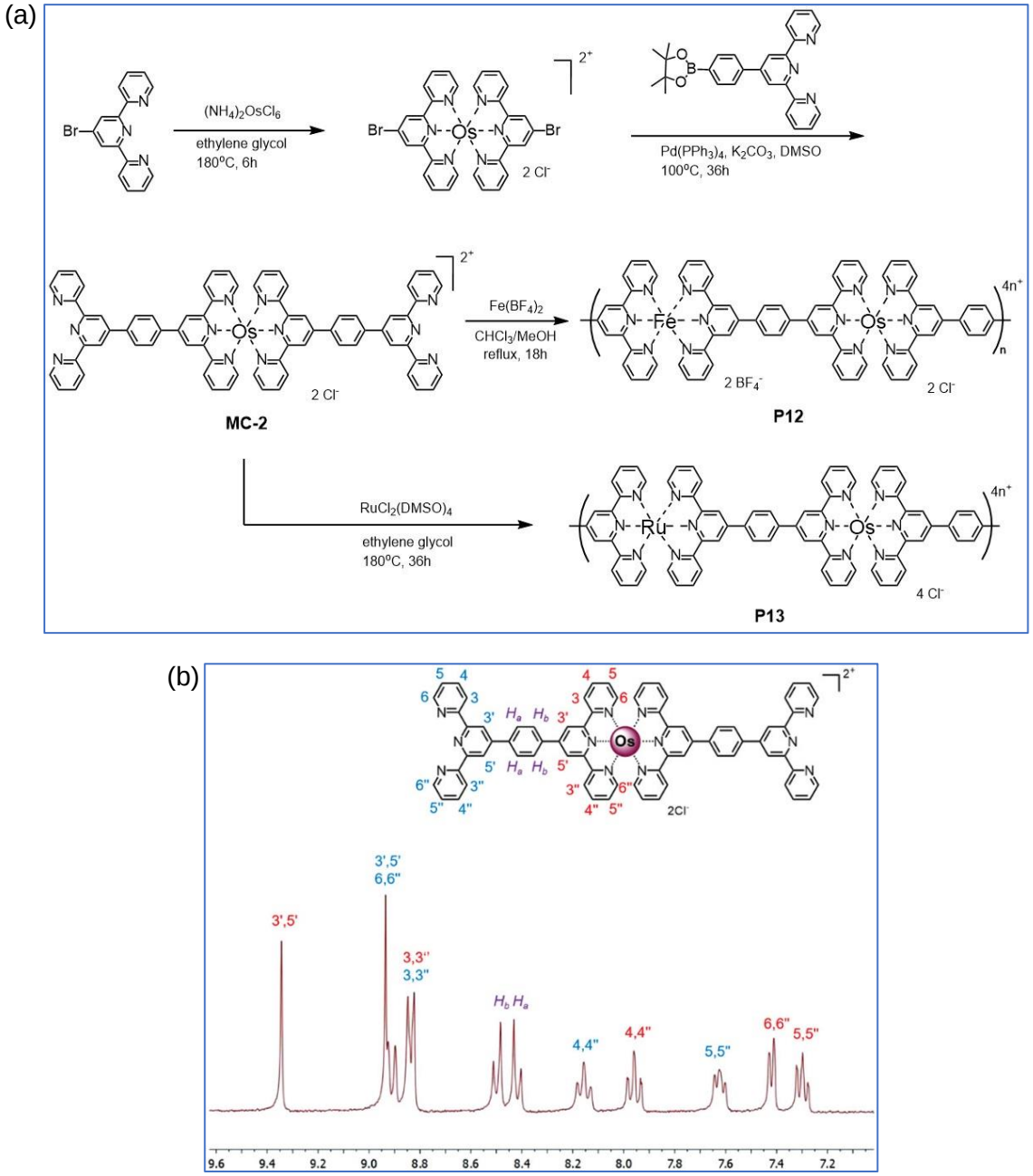


Fig. 11. *(a) Synthetic route to P12 and P13. (b) Partial ^{1}H NMR spectrum of MC-2. Adapted with permission from ref. [80], Copyright 2020 Wiley-VCH.*

Following the same strategy, a HBSP (P14) containing alternately complexed Ru(II) and Fe(II) ions was prepared by the stepwise complexation of strongly coordinated

Ru(II) ions and weakly coordinated Fe(II) ions (Fig. 12) [105]. Using terpyridine as the coordinating moiety, a ditopic ligand containing Ru(II) ions was prepared, which was then reacted with the Fe salt to obtain P14. The combination of the two redox-active metal ions in P12, P13, and P14 produced a broad optical and electrochemical window, which was confirmed through UV–vis and CV studies.

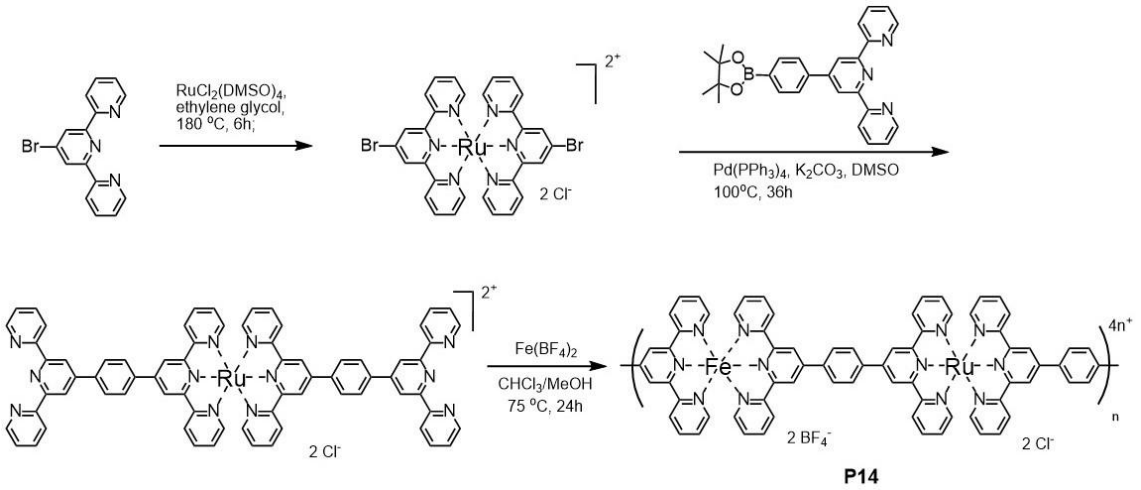


Fig. 12. *Synthetic route to P14.*

2.3.2.1.2. Heterotrimetallic supramolecular polymers (HTSPs)

This stepwise synthetic route can also be used to prepare HTSP, that is, three heterometal ions can be introduced into a linear MSP chain where the heterometal ions are in identical coordination environments. Employing the concept of strong, moderate and weak coordination metal ions, a series of HTSP (P15–P17) were prepared using Os(II)-Ru(II)-Fe(II), Os(II)-Ru(II)-Co(II), and Os(II)-Ru(II)-Zn(II), respectively, as the heterometal-ions triad and terpyridine (tpy) as the coordinating ligand (Fig. 13) [76]. The strong coordination of metal ions reflects the binding strength of the tpy-M(II)-tpy

connectivity. Generally, the binding strengths of tpy-Os(II)-tpy and tpy-Ru(II)tpy connectivities are higher than those of other tpy-M(II)-tpy connectivities, where M = Fe/Co/Zn [128, 129]. In addition, the reaction conditions of the heterometal ions toward particular ligands varied. For example, Os(II) ions undergo complexation with tpy at high temperatures, Ru(II) ions at moderate to high temperatures, and Fe(II), Co(II), or Zn(II) ions at moderate to room temperatures. Considering these parameters, a stepwise synthetic route was developed to synthesize the polymers. The steps were as follows: (1) an Os(II) complex was prepared, (2) complexation of Os(II) complex with Ru(II) ion to construct an Os(II)-Ru(II) containing ditopic ligand, and (3) the Os(II)-Ru(II) containing ditopic ligand undergoes further complexation with Fe(II) or Co(II) of Zn(II) to give the desired HTSPs. The intermediate metal complexes were characterized by NMR and mass spectrometry. The introduction of the three heterometal ions into the polymer was confirmed by optical, CV, and XPS analyses.

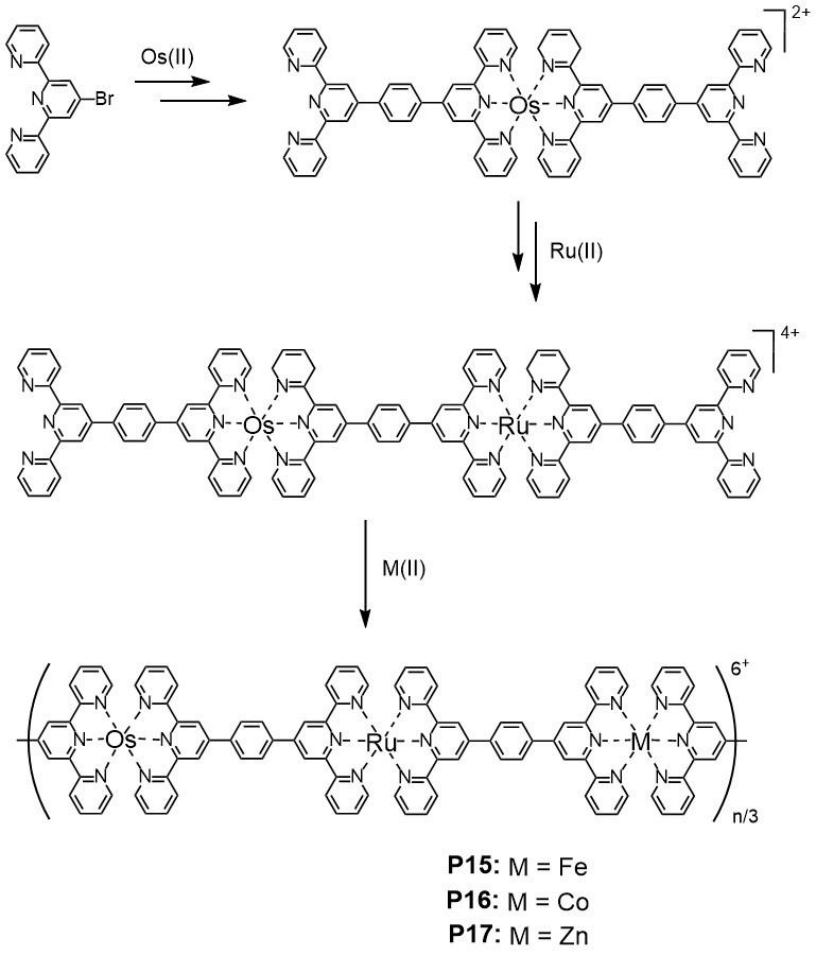


Fig. 13. *Synthetic route to P15–P17.*

2.3.2.2. HMSPs based on different coordination environments heterometal ions

During the stepwise synthesis of HMSPs, the coordination environment of the heterometal ions in the resulting polymer may vary with the type of ligand are used to bind the metal ions. As different ligands form different types of metal–ligand bonds, the resulting polymers may be based on either (i) only coordination complexes or (ii) the combination of organometallic and coordination complexes. Examples of such polymers are highlighted in the following sections.

2.3.2.2.1. Polymers with only coordination complexes

The introduction of a spacer between the two coordinating sites of a ditopic ligand may introduce great diversity in the structural arrangements and/or physicochemical properties, such as viscosity, mechanical properties, and optical properties, of the target MSP [130, 131]. However, the use of a complexing spacer in a ditopic ligand allows the introduction of heterometal ions into the MSP. Using this concept, Royal et al. developed a multitopic cyclam bis-terpyridine platform for the synthesis of various homo- and hetero-MSP because two different types of metal ions can be introduced using terpyridine units and the macrocyclic framework of the cyclam bis-terpyridine system [107, 132-135]. A representative example is bis(terpyridine)dioxocyclam (dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-5,7-dione) ligand L12 which was used to prepared a series of soluble homo- and hetero-MSP (P18–P21) containing the metal-ion pair Cu(II)-M(II); M = Fe(II)/Cu(II)/Co(II)/Ni(II) in a two-step procedure (Fig. 14) [134]. L12 can selectively bind Cu(II) inside its macrocyclic framework when metalation is performed in the presence of a mild base such as K_2CO_3. Therefore, a stable mononuclear Cu(II) complex was prepared, and the free terpyridine units of the Cu(II) complex were further complexed with another metal ion, M(II): M = Fe(II)/Cu(II)/Co(II)/Ni(II), to produce homo- and hetero-MSP. Various redox-responsive polymeric gels based on the cyclam bis-terpyridine system were developed [107].

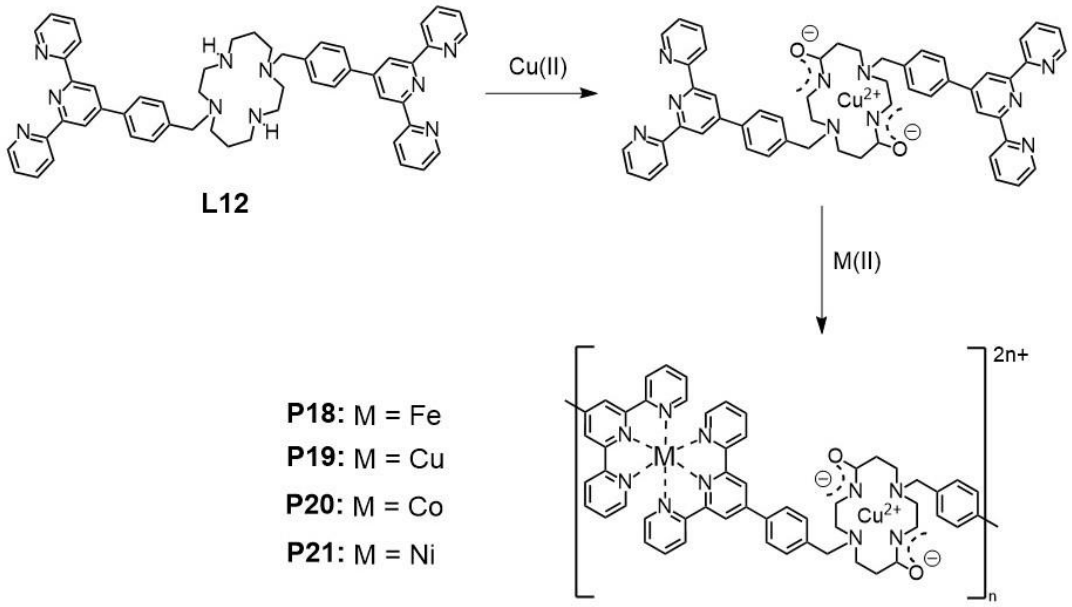


Fig. 14. *Synthetic route to P18–P21.*

This metalloligand design strategy was further modified by Chauvin et al. to achieve efficient photoinduced electron transfer reactions. To achieve this goal, they combined Ru (II)-tris (bipyridine), a photoredox sensitizer with a bis-terpyridine framework. As a photoredox sensitizer, the Ru(II)-tris(bipyridine) system is more convenient to use than the Ru(II)-bis(terpyridine) system in terms of the lifetime of its excited state [136]. Therefore, a heteroditopic ligand (L13) containing one 2,2′-bipyridine and two terpyridine units was designed and a Ru(II)-tris(bipyridine)-like complex (Ru-L13) was prepared. Ru-L13 contains two free terpyridine units that can bind another heterometal ion to yield a HBSP. Two alternating HMSPs (P22 and P23) based on Ru(II)-M(II) [where M = Fe(II), Zn(II)] were synthesized via coordination complexation between Ru-L13 and Fe(II) or Zn (II) ions (Fig. 15) [106]. The formation of HMSPs was confirmed using MALDI-TOF mass spectroscopy. The Ru(II-Fe(II)-containing polymer showed an m/z range of 3000–12000, which corresponds to the mass of five repeated Ru-

Fe monomeric units (oligomer structure). The formation of macrocyclic species always competes against that of linear polymers when an angular bis-terpyridine ligand is complexed with metal ions [10, 137]. Because Ru-L13 has a structure similar to that of angular bis-terpyridine units, it is expected to tend to form cyclic structures alongside linear polymers. This may explain why long-chain linear polymers were not obtained, as reflected in the MALDI-TOF mass spectrometry study [138].

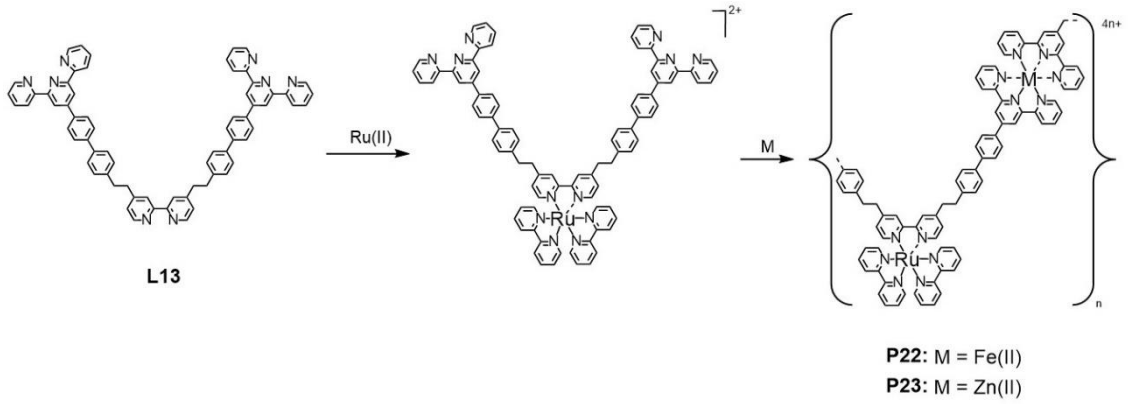


Fig. 15. *Synthesis of P22 and P23 from an angular ligand L13.*

However, the formation of small cyclic oligomers can be restricted by replacing the angular bis-terpyridine ligand with a linear ligand, which can produce more tailored 1D polymers. The same group (Chauvin et al.) demonstrated this strategy by designing and synthesizing a linear Ru(II)-containing ligand, L14, which contains two free terpyridine units aligned in opposite directions. This linear ditopic ligand was further complexed with Fe(II) to synthesize the HBSP P24 (Fig. 16) [108]. The molecular weight of P10 was determined using MALDI-TOF mass spectrometry, which revealed an m/z

range between 3000 and 18000, with a pattern consistent with the mass of ten repeating units of the Ru-Fe segment.

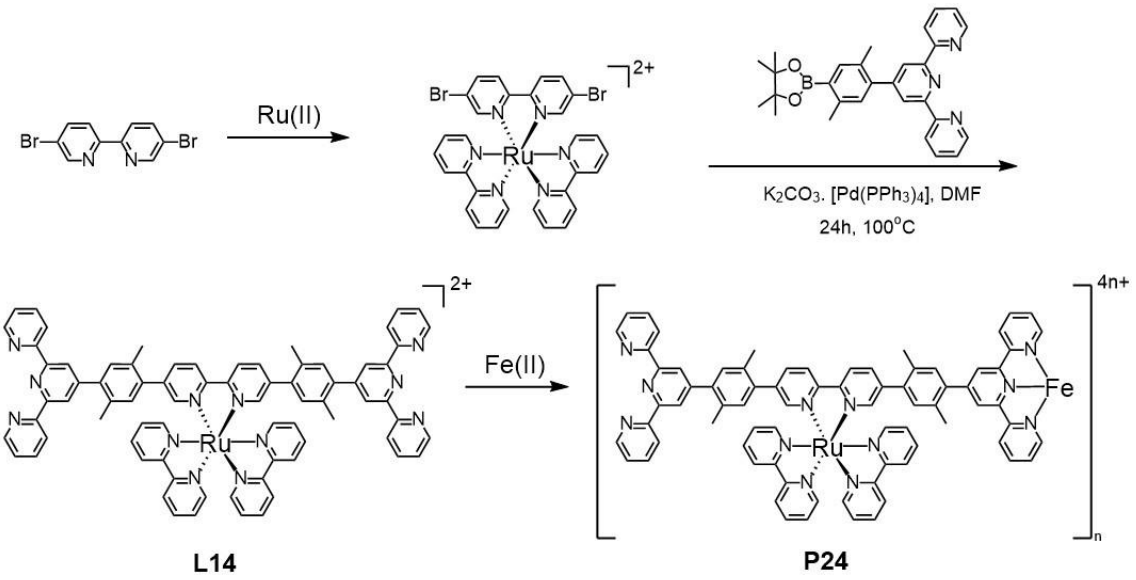


Fig. 16. *Synthesis of P24.*

In addition to the above linear HMSPs, the construction of an HMSP network was demonstrated by Tian et al., in which two different heterometal ions were introduced into a SP network in different coordination environments. In this case, the structure of the polymer was not linear; rather, a network structure was formed (2D type structure). A homoditopic ligand, L15, was synthesized, which contained two free terpyridine units at the terminals and two 1,2,3-triazole units in the spacer between the two terpyridine units (Fig. 17) [139]. Upon addition of Fe(II) to L15, a linear MSP was formed, which self-assembled into a network structure in the presence of Pd(II) ions. The Pd(II) ions were coordinated through the two 1,2,3-triazole units present in the ligand of the linear polymer

chain. Various metal-organic assemblies based on heterometallic coordination interactions have been reported, which do not fall under the category of MSP [140-144]. Therefore, these examples are not discussed herein.

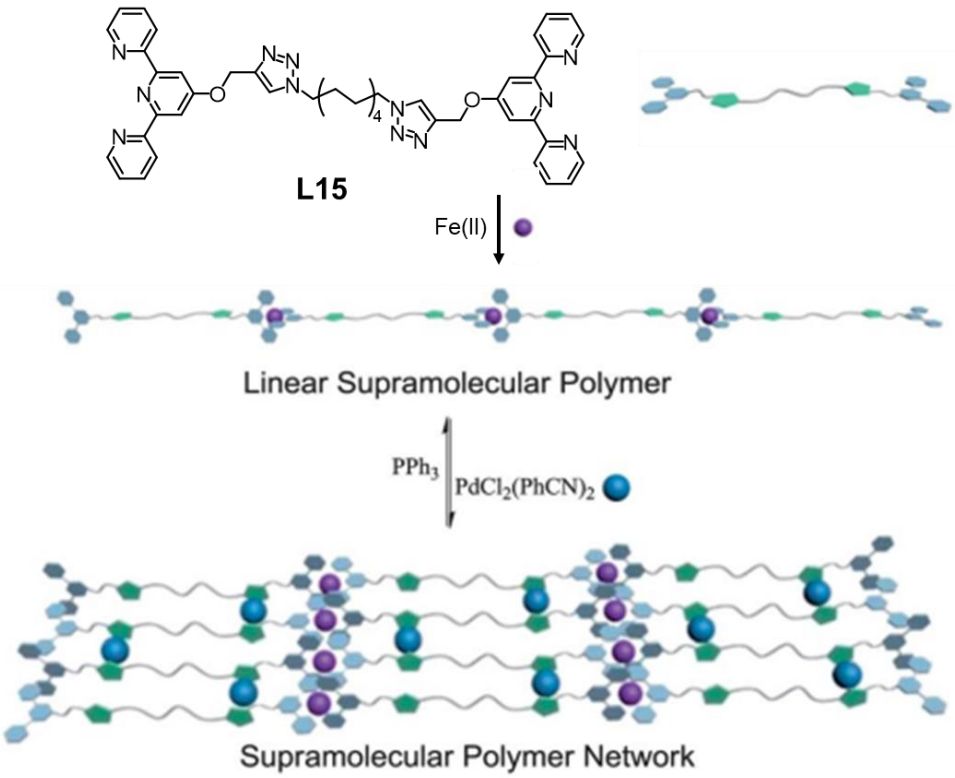


Fig. 17. *Synthetic route to heterometallic supramolecular polymer network. Adapted with permission from ref. [139], Copyright 2013 Royal Society of Chemistry*.

2.3.2.2.2. Polymers with the combination of organometallic and coordination complexes

In a stepwise synthesis process, when a metal-containing ditopic ligand is synthesized based on an organometallic bond (metal–carbon bond), the organometallic ditopic ligand can bind to another metal ion through coordination (1:1 complexation) to produce an HMSP. Higuchi et al. synthesized HMSPs (P25 and P26) by alternately

introducing Pt (II) and Fe (II) ions, where Pt(II) ions were complexed through organometallic bonds, and Fe(II) ions were complexed through coordination bonds (Fig. 18) [109]. Platinum(II) acetylide-based derivatives (small molecules, oligomers, and polymers) have intriguing photophysical properties that originate from the overlap of the d-orbitals of metals with the p-orbitals of alkyne ligands [145–147]. Therefore, the combination of a platinum (II) acetylide unit with other metal ions in the polymer chain can produce additional polymer features. To achieve this, bis-terpyridine organo-Pt(II) ligands with *trans*- and *cis*-conformations (L16 and L17) were synthesized via the reaction of 4′-(4-Ethynylphenyl)-2,2′:6′,2″-terpyridine with *trans*-dichlorobis(triphenylphosphine)platinum(II) and *cis*-dichlorobis(triphenylphosphine)platinum(II), respectively. Finally, P25 and P26 were prepared through the 1:1 complexation of L16 and L17 with Fe(II) ions. The molecular weights (M_w) of the synthesized polymers were observed to be 2.27×10^4 Da for P24 and 2.22×10^4 Da for P25, as determined by the SEC-Viscometry/RALLS method.

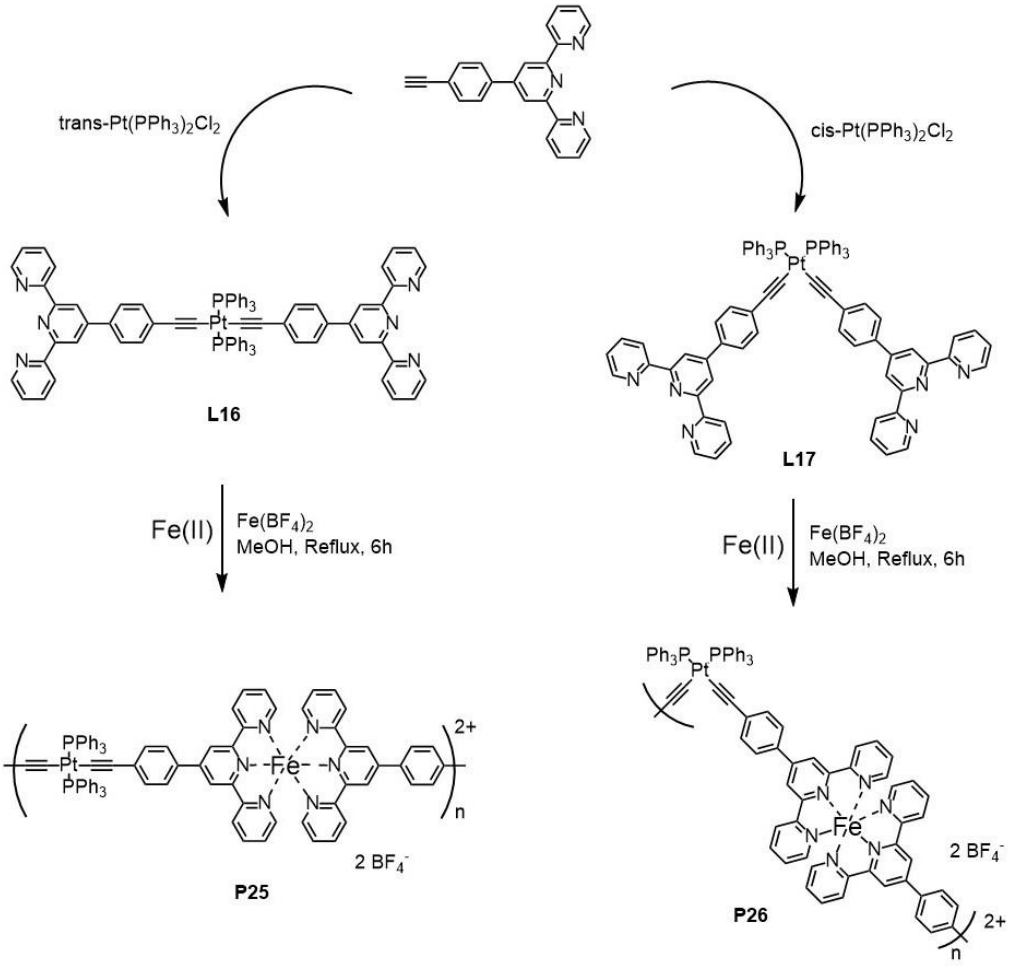


Fig. 18. *Synthetic route to P25 and P26.*

Another bis-terpyridine ditopic ligand (L18) containing a rigid benzothiadiazole-functionalized dinuclear platinum(II) acetylide unit as a spacer was developed by Tian et al [148]. L18 was used for the synthesis of a Pt(II)–Zn(II)-based heterometallic supramolecular polymer (P27) via coordination complexation with Zn(II) ions (Fig. 19). The dinuclear platinum (II) acetylide unit was introduced into the polymer chain to achieve a low critical polymerization concentration (CPC) to expedite the supramolecular polymerization, which enabled the formation of rigid SPs with useful optical and electrochromic properties. In this case, the heterometal ions are not in alternate positions

in the polymer chain because L18 contains two Pt (II) ions. Viscosity measurements revealed the formation of a high molecular weight SP.

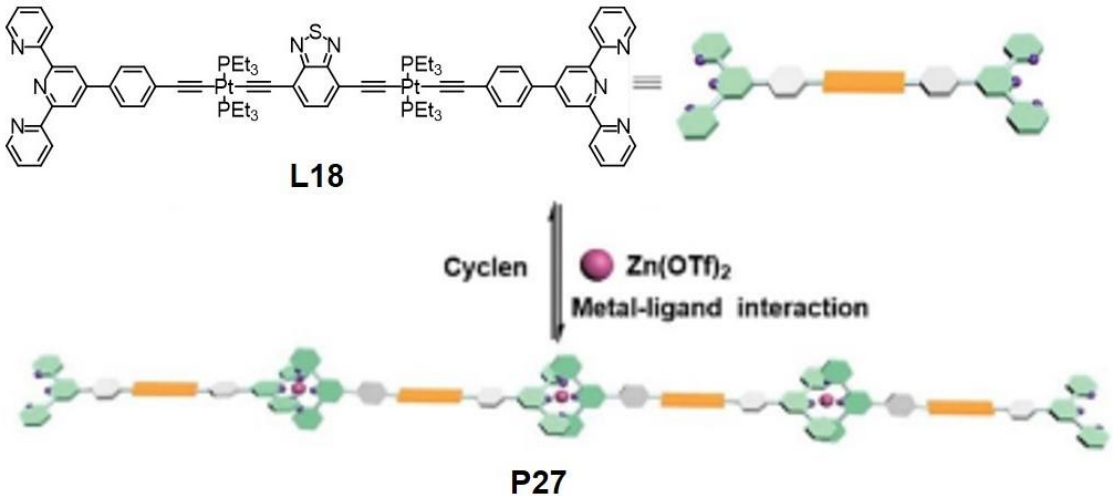


Fig. 19. *Synthetic route to P27. Adapted with permission from ref. [148], Copyright 2018 Royal Society of Chemistry.*

Stang et al. synthesized a series of linear HMSPs based on Pt(II) and Zn(II) ions [75]. First, ditopic ligands with a terpyridine unit on one side and a 120° dipyridine fragment on the other side containing different substituents were synthesized. Rhomboidal metallacycles were then constructed via a coordination-driven self-assembly of platinum(II) with a 120° dipyridine fragment; organometallic bonds were formed. Rhomboidal metallacycles (L19) contain terminal terpyridine units that undergo complexation with Zn(II) ions to produce HMSPs (P28) (Fig. 20). The resultant HMSPs were used to create supramolecular polymer network gels by adding a suitable crosslinker. The formation of the linear heterometallic SPs was confirmed by UV–vis, NMR, and

DLS analyses. The high molecular weight of the linear SPs was directly supported by the SEM study, which revealed a rod-like fiber structure.

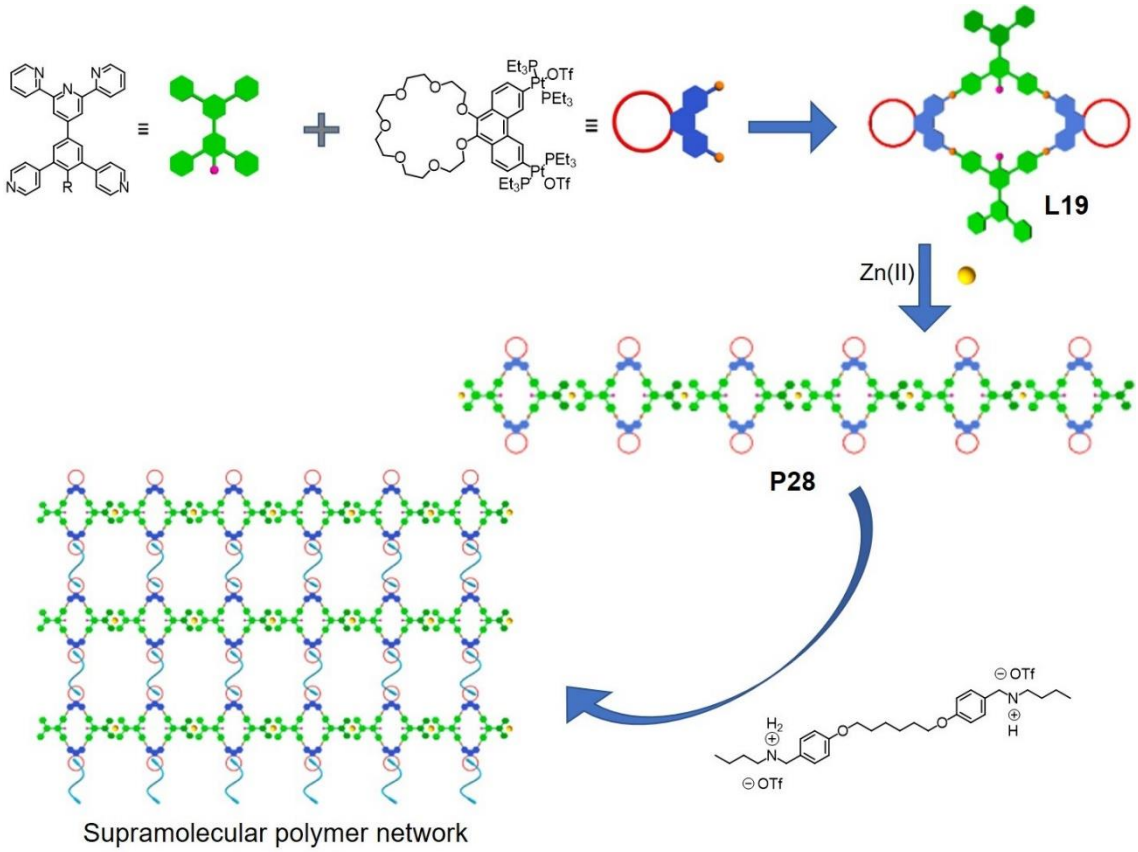


Fig. 20. *Schematic presentation of the synthesis of homometallic MSPs and heterometallic supramolecular polymers. Adapted with permission from ref. [75], Copyright 2019 American Chemical Society.*

3. Properties of HMSPs

The combination of heterometallic complexes with HMSPs leads to various interesting properties that are not observed in homometallic SPs. The properties of HMSPs typically depend on the characteristics of their metal centers. In addition, the solubility of HMSPs is an important parameter that affects their processability. In

particular, HMSPs soluble in low-boiling solvents are highly preferable for easy and quick deposition in thin-film form on any desired substrate by spin or spray-coating processes. In this section, we discuss the common properties of HMSPs.

3.1. Solubility

Although HMSPs are synthesized using organic ligands that are hydrophobic in nature, they are generally soluble in polar solvents, such as water, methanol, ethanol, ethylene glycol, water, DMSO, and DMF, owing to the hydrophilic characteristics of the metal-complex moieties present in the polymer [12]. Generally, in MSPs, the positive charges of the metal ions are neutralized by counter anions. Owing to the high charge density of MSPs, their solubility is significantly influenced by counter anions [149]. The exchange of counter anions in MSPs is also possible using a counter-anion exchange strategy [150, 151]. In the counter-anion exchange strategy, a MSP containing one type of counter anion is dissolved in a minimum volume of the desired solvent, and then, the solution is added to a large volume of another solution containing the metal salt of other types of anions to precipitate the target polymer with the exchanged counter anions.

Similar to homometallic MSPs, the solubility of HMSPs also depends on the counter anions. Moreover, homometallic supramolecular polymers contain mainly one type of counter anion, whereas HMSPs contain different types of counter anions in different metal complexes. As a result of this, solubility of HMSPs is determined by the presence of different counter anions. For example, when P12 was synthesized using a combination of the counter anions Cl^- and BF_4^-, the resulting polymer was soluble in DMSO and DMF [73]. When the counter anions of P12 were changed to only Cl^- through

counter-anion exchange using $FeCl_2$, P12 was soluble in only DMSO and DMF. Again, the replacement of the counter anions in P12 by PF_6^- led to partial solubility of the polymer in acetonitrile. However, the use of a combination of Cl^- and OAc^- as counter anions made the polymer soluble in methanol (Fig. 21). These observations reveal that the counter anions of HMSPs play a significant role in controlling the solubility of the polymers. A similar strategy was adopted to tune the solubility of heterotrimetallic supramolecular polymer (P15) and enhance its processability [76].

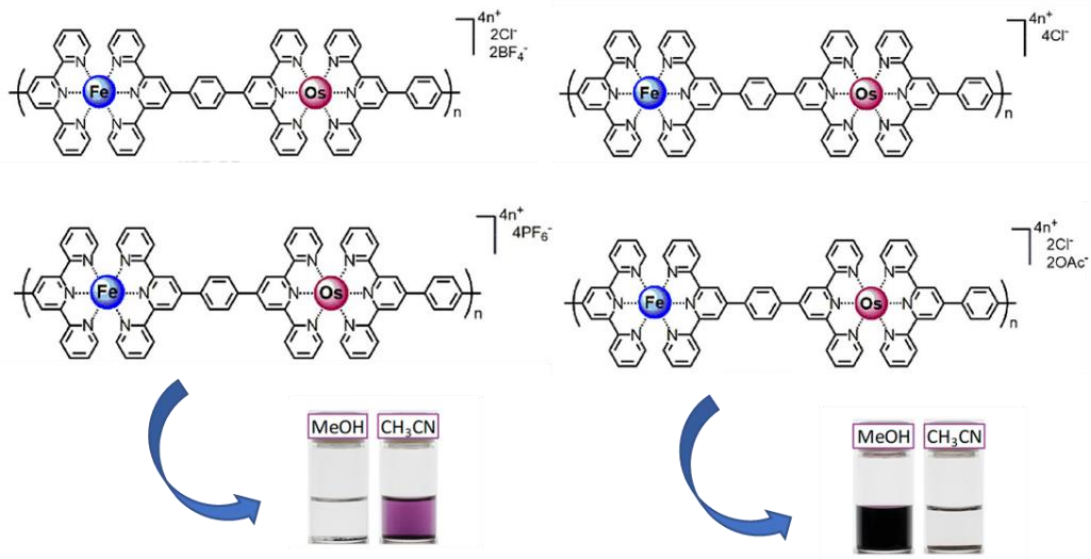


Fig. 21. *Tenable solubility of P12 in different solvents using different counter anions. Adapted with permission from ref. [73], Copyright 2020 American Chemical Society.*

3.2. Optical properties

Metal-containing polymers or MSPs generally exhibit the combined optical properties (absorption or emission) of organic ligands and metal complexes. The organic parts mainly contribute for π–π* transition, whereas the metal parts (or complex parts)

contribute through MLCT transitions. in the HMSPs, heterometallic complexes contribute more to different MLCT transitions. As a result, the HMSPs exhibit a broad optical window. For example, the combination of Fe(II)- and Ru(II)-complexes in P6, P14, and P22, gave broad absorption bands that comes from π–π* transitions and MLCT transition of heterometallic complexes [78, 105, 106, 108]. As shown in Fig. 22a, the individual complexation of Ru(II) and Fe(II) in P14 was indicated by their respective visual color changes in solution and gradual broadening in the optical window. For 1-Ru, an MLCT was observed near 495 nm, whereas upon the addition of Fe(II), an additional MLCT appeared near 577 nm. Similarly, the combination of Fe(II)- and Os(II)-complexes in P12 produced a broad absorption from 450 to 700 nm because of the combination of the MLCT band of the Fe(II)-complex and the singlet and triplet MLCT bands of the Os(II)-complex [80]. In P15, the combined MLCT transitions of three heterometallic complexes [Fe(II), Os(II), and Ru(II)] also gave a broad absorption window [76]. The stepwise complexation of the three heterometal ions was confirmed by the gradual addition of the MLCT absorption bands corresponding to the heterometallic complexes. As presented in Fig. 22b, the Os(II)complex (denoted by Os) shows singlet and triplet MLCT bands at ~492 and 669 nm, respectively, whereas the addition of Ru(II) shows the MLCT of the Ru(II)complex (denoted by Os-Ru); as a result, a broad peak is observed at 500 nm. Further addition of Fe(II) led to polymer P15 with an additional MLCT of the Fe(II)complexes at 575 nm.

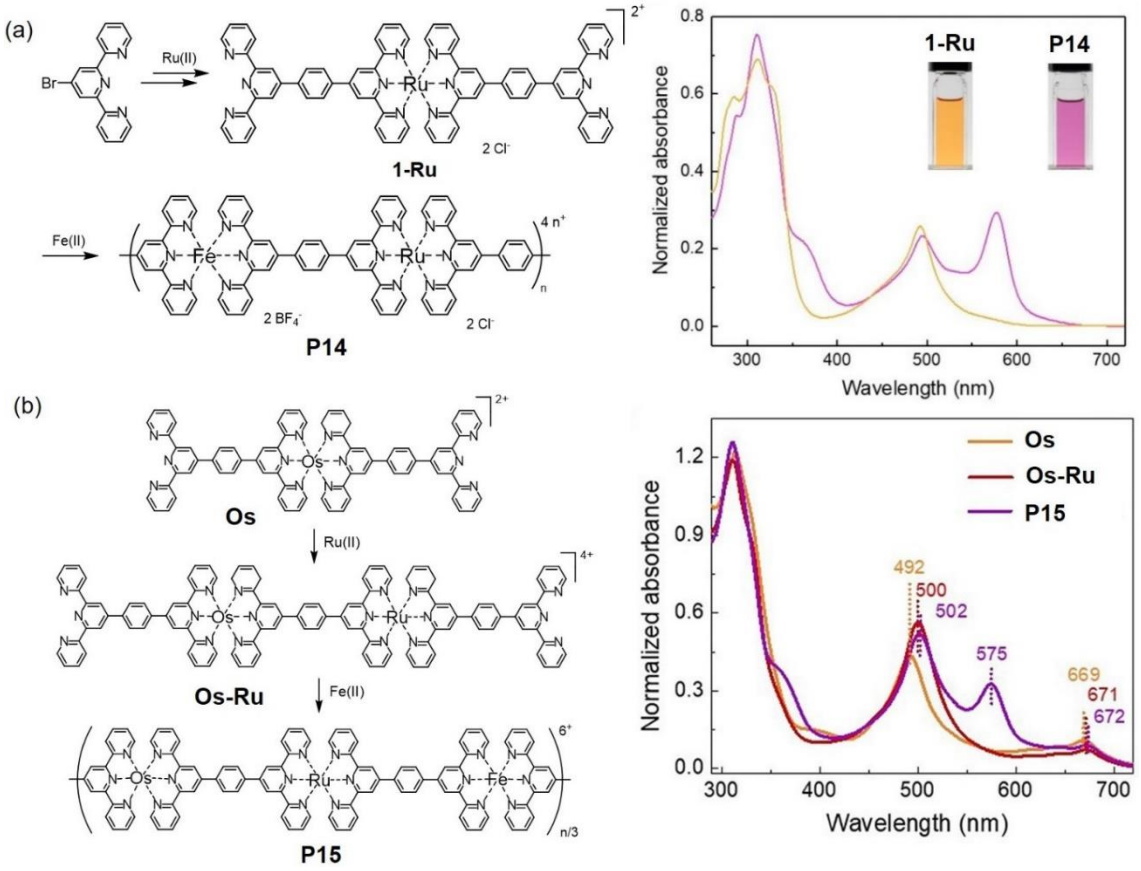


Fig. 22. *Absorption spectra of (a) P14; Adapted with permission from ref. [105], Copyright 2020 MDPI. and (b) P15. Adapted with permission from ref. [76], Copyright 2021 Nature Portfolio.*

The absorption and emission of each heterometallic complex in the HMSPs were combined to create new emission characteristics. For example, P9 exhibits white emission because of the combination of Zn(II) and Eu(III)complexes in the polymer (Fig. 23a) [104]. Polymers based only on Zn(II) ions (PolyZn) show blue emission with a 439 nm emission maximum, whereas Eu(III)-containing polymers (PolyEu) exhibit red emission with an emission maximum of 613 nm. However, P9, which is composed of both Zn(II) and Eu(III), shows emission maxima for the combination of heterometallic complexes with emission maxima at 446 and 613 nm, which combine with white emission (Fig. 23b).

Maji et al. demonstrated a similar strategy for white light generation by controlling the mixing of ligands L8, Tb(III), and Eu(III) ions (Fig. 23c) [125]. If L8 is combined with only Tb(III) ions or only Eu(III), the resulting gels show green or red emissions, with characteristic emission peaks in the region between 400 and 700 nm. However, when Tb(III) and Eu(III) ions were mixed at a ratio of 1:2 with L8, the heterobimetallic gel displayed white emission. The emission spectrum of Tb(III)-L8 ranges from 400 to 600 nm, in which the blue and green parts are the major components, and the introduction of Eu(III) as a red component covers the entire visible spectrum (400-800 nm) to produce white light. HMSP (P28) prepared from L19 also showed broad emission ranging from 400 to 750 nm owing to the combination of Pt(II) and Zn(II) complexes [75].

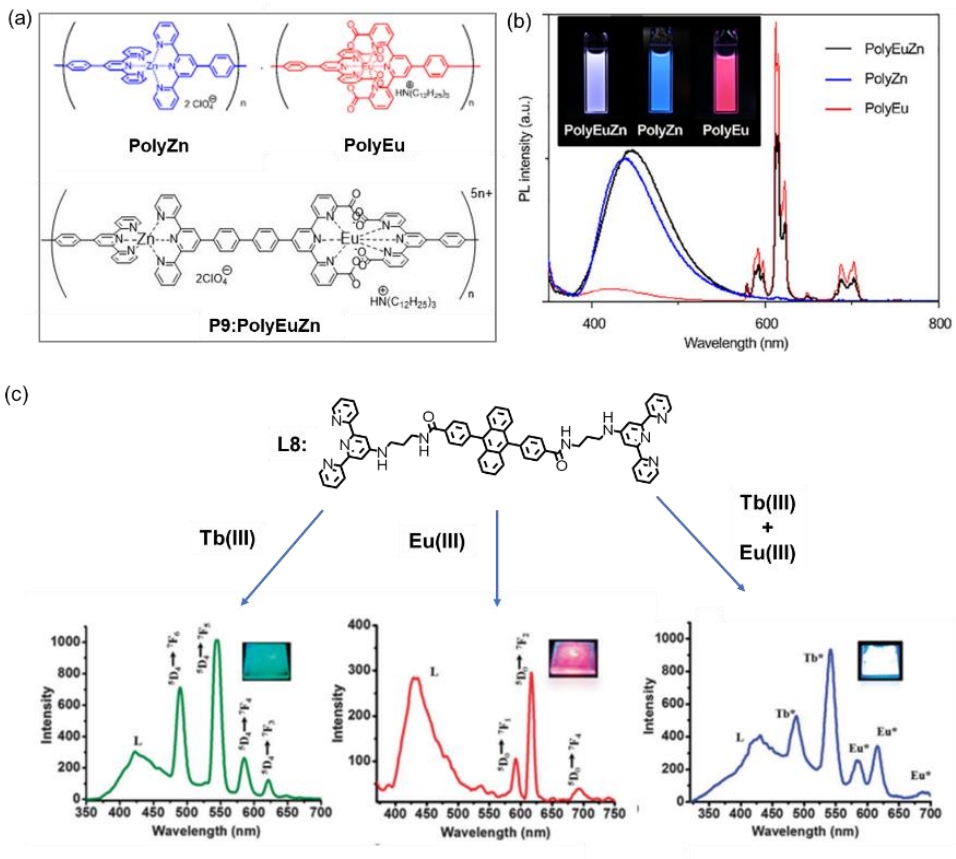


Fig. 23. *(a) Chemical structure and (b) emission spectra (inset: color of respective solution under 365 nm UV lamp) of PolyZn, PolyEu, and P9. Adapted with permission from ref. [104], Copyright 2019 Elsevier. (b) Emission spectra of L8 with Tb(III), Eu(III), and mixture of Tb(III) & Eu(III) (inset: color of gel under UV light). Adapted with permission from ref. [125], Copyright 2015 Royal Society of Chemistry.*

3.3. Electrochemical properties

If HMSPs contain one or more redox-active metal ions, the polymers exhibit electrochemical activity by changing the redox state of the metal ions upon the application of voltage. Electrochemical property of HMSPs is studied with the help of cyclic voltammetry (CV) experiment. The redox-active metal ions in the HMSP show redox changes from one state to another through oxidation (or reduction) upon application of a bias voltage and return to the initial state through reduction (or oxidation) upon application of an opposite bias voltage. If HMSPs contain two or more redox-active metal ions, the resulting polymers generally show multiple oxidation and reduction waves with a broadening of the potential window. For example, the redox-active Fe(II) and Ru(II) ions in P14, P22, and P24 exhibited broad electrochemical windows with two distinct reversible redox waves of Fe(II)/Fe(III) and Ru(II)/Ru(III) redox pairs, respectively [78, 106]. The polymer P14 displays the dual redox characteristic with $E_{1/2}$ (with half-wave redox potential; vs. Ag/Ag^{+}; scan rate: 50 mV/s) of 0.77 and 0.93 V, for Fe(II) and Ru(II)-complex parts, respectively. Similarly, Os(II)-Fe(II) based P12 also shows reversible dual redox nature of Os(II)/Os(III) and Fe(II)/Fe(III) redox pairs with $E_{1/2}$ (vs. Ag/Ag^{+}; scan rate: 50 mV/s) of 0.55 and 0.72 V, for Os(II) and Fe(II)-complex parts, respectively. Co(II)–Ni(II)-based polymer P7 showed a broad CV spectrum with six different (I–VI) peak current characteristics [79]. The CV plot for P7 is shown in Fig. 24a (2 mM P7 in 0.1 M TBAP/DMF in GCE; scan rate: 50 mV/s). These peaks were attributed to the (I)

reduction of Co(II) to Co(I), as denoted by I (quasi-reversible redox feature); oxidation of Co(II) to Co(III), as denoted by VI; reduction of Ni(II) to Ni(I), as denoted by II (irreversible peak); Ni- and Co-centered ligand-based one-electron redox processes as denoted by III and IV (reversible in nature); overpotential for ligand-based reduction phenomenon, as denoted by V.

The electrochemical window was further broadened using three redox-active metal centers in the HMSP chain. As shown in the structures of P15 and P16, the heterotrimetallic supramolecular polymers contain three redox-active metal ions: Fe(II)/Os(II)/Ru(II) in P15 and Co(II)/Os(II)/Ru(II) in P16 (Fig. 13) [76]. P15 shows three distinct reversible redox features for the Os(II)/Os(III), Fe(II)/Fe(III), and Ru(II)/Ru(III) redox pairs, with $E_{1/2}$ (vs. Ag/Ag^{+}) of 0.58, 0.76, and 0.92 V, respectively. In case of P16, reversible redox features for Os(II)/Os(III), Ru(II)/Ru(III), and Co(II)/Co(I) redox pairs with $E_{1/2}$ (vs. Ag/Ag^{+}) of 0.58, 0.91, and −1.29 V were observed (Fig. 24b). The multiple and broad electrochemical natures of P15 and P16 demonstrate the potential of these polymers for various electrochemical and electro-optical applications.

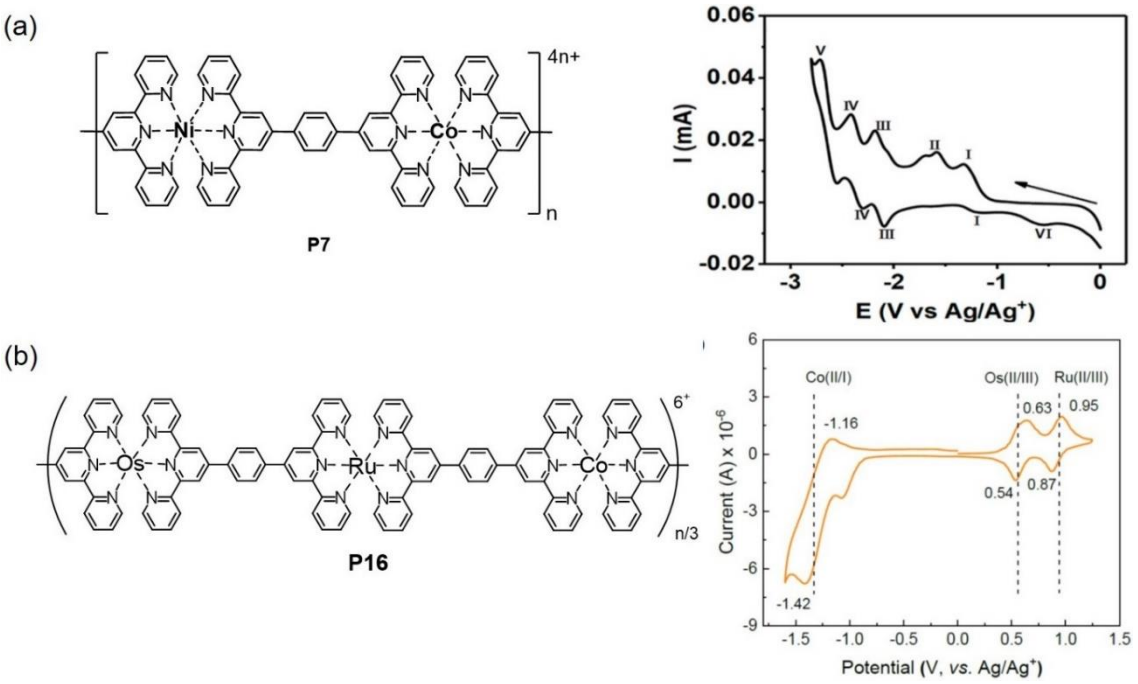


Fig. 24. *Cyclic voltammograms of (a) P7; Adapted with permission from ref. [79], Copyright 2020 American Chemical Society. and (b) P16. Adapted with permission from ref. [76], Copyright 2021 Nature Portfolio.*

3.4. Stimuli responsive properties

If an HMSP contains one or more metal ions that are responsive to external stimuli, the properties of the resulting polymers can be altered by applying external stimuli. For example, P8 contains redox-active Fe(II) and emissive Eu(III)complexes (Fig. 25a). The oxidation state of the Fe centers can be altered by an electrical stimulus, which further leads to the reversible optical switching of P8 [74]. As shown in Fig. 25b,c, Fe(II) can be reversibly oxidized to Fe(III) by altering the voltage between 0 and 2 V, depending on which absorption or emission of P8 (emission comes from the Eu-center) can be reversibly switched. Again, the optical color (as well as transmittance) of multi redox active HMSP can be altered by stepwise redox state alternation of the heterometal ions. For example, P7, P12, and P15 show an optical color change with alteration of the

transmittance of the HMSPs by a stepwise redox state change of the heterometal ions upon stepwise application of different voltages. This electro-optical feature of HMSPs leads to the use of polymers for electrochromic applications (see vide infra for a detailed discussion) [76, 106].

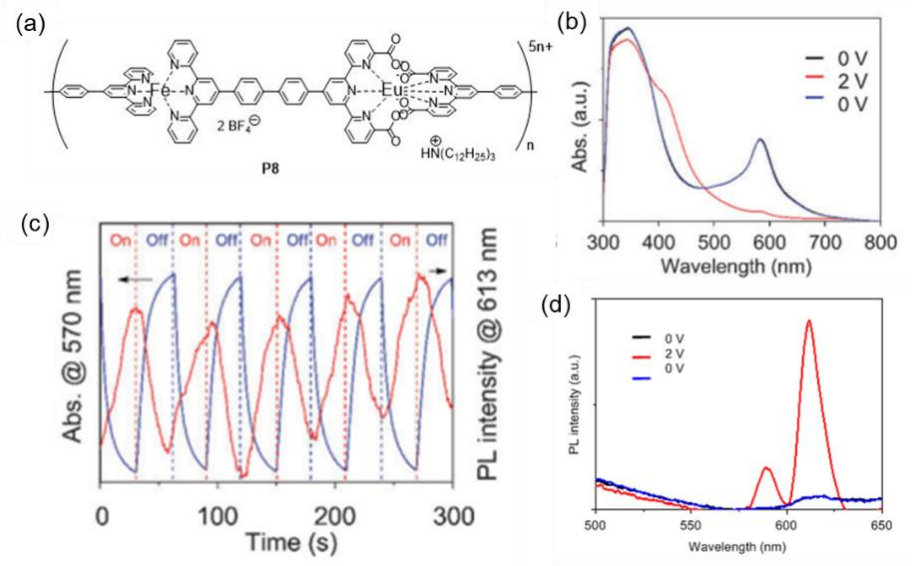


Fig. 25. *Redox induced absorption and emission spectra change of P8. Adapted with permission from ref. [74], Copyright 2013 Royal Society of Chemistry.*

Rowan et al. developed thermoresponsive heterometallic supramolecular assemblies using La(III) and Co(II) with ligand L7 [77]. The formed heterometallic gel exhibited a gel-sol transition upon periodic heating at 100 °C and cooling to room temperature. At 100 °C, La(III)-ligand interactions are broken, whereas Co(II)-interactions persist as observed by orange color of the solution (Fig. 26a). Stang et al. prepared a supramolecular network that formed a gel using the linear heterometallic polymer P28 [75]. The prepared supramolecular gel also showed a reversible gel-sol transition upon the alternating addition of cyclen (1,4,7,10-tetraazacyclododecane) and

Zn^{2+}. The addition of cyclen to the gel weakened the interactions between the terpyridine units and Zn^{2+} ions, resulting in gel degradation. The gel was reformed by the addition of Zn^{2+} (Fig. 26b). This gel-sol transition was also achieved by heating and cooling, for which a different mechanism was explained.

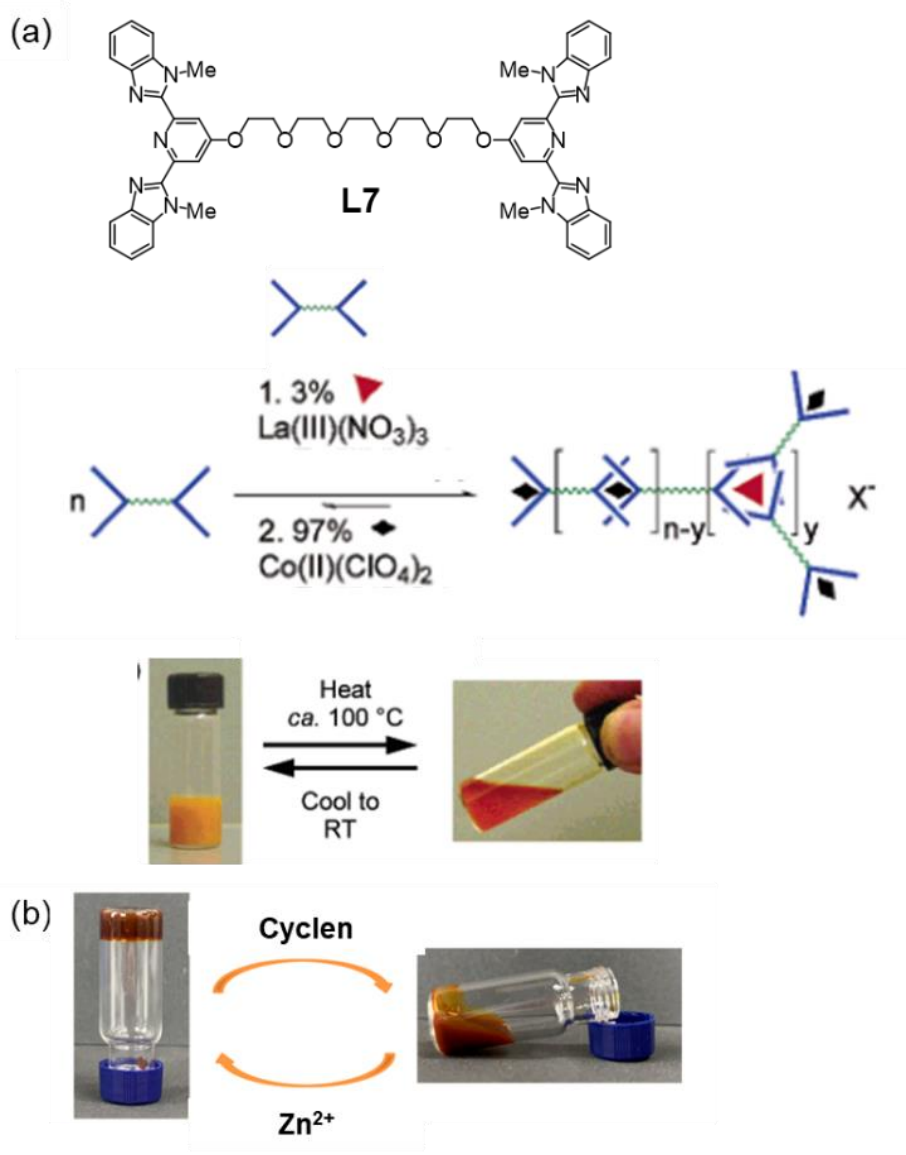


Fig. 26. *(a) La(III)-Co(II) based heterometallic supramolecular assemblies prepared from L7 shows thermoresponsive behavior. Adapted with permission from ref. [77], Copyright 2003 American Chemical Society. (b) Supramolecular assemblies prepared*

from P28 shows reversible gel-sol transition upon addition of cyclen and Zn^{2+}, respectively. Adapted with permission from ref. [75], Copyright 2019 American Chemical Society.

4. Applications of HMSPs

As discussed above, HMSPs exhibit interesting properties owing to the combination of heterometallic complexes in the polymer chain, which have been utilized for various applications including electrochromism, anticancer drugs, and electrochemical sensors. In this section, we briefly highlight applications of HMSPs.

4.1. Electrochromism

Electrochromism refers to the optical color change of a material under an applied voltage. To date, a range of materials has been used for electrochromic applications [32, 68, 152-164]. Among the various types of electrochromic (EC) materials, MSPs (monometallic) are attractive EC materials due of their wide color variation, first EC color switching, and easy processability. Unlike homometallic MSPs, which generally show electrochromism between two color states, if two or more redox-active metal ions are present in the HMSPs, the resulting polymers show promising multicolor EC behavior [73]. Such multicolor electrochromism is preferred for fabricating voltage-tunable multicolor EC devices (ECDs) and camouflage devices.

If the HMSPs contain two redox-active heterometal ions, the EC color of the resulting polymer can be switched between three color states. For example, the heterobimetallic polymer P6 has been synthesized using redox active Fe(II) and Ru(II) ions, which shows multicolor electrochromism (dark purple ↔ orange ↔ light green)

upon oxidation of Fe(II) and Ru(II)-complexes 0.9 and at 1.2 V, respectively (Fig. 27a) [102]. The corresponding absorption spectra of P6 show two distinct MLCT bands for the Fe(II) and Ru(II)complexes at 580 and 503 nm, respectively. When a voltage of 0.9 V (vs. Ag/Ag^{+}) is applied on the film of P6 on indium tin oxide coated glass substrate (ITO) in 0.1 M $NaClO_4$/acetone, the MLCT at 580 nm is disappeared due to oxidation of Fe(II) to Fe(III) and when the applied voltage is further increased to 1.2 V, the MLCT at 503 nm disappeared due to oxidation of Ru(II) to Ru(III). Similarly, Fe(II)-Ru(II) based another HBSP P22 shows similar multicolor EC characteristic (reddish brown ↔ orange-yellow ↔ pale green), but the MLCTs of Fe(II) and Ru(II)-complexes are observed at 573 and 450 nm, respectively (Fig. 27b) [106]. The MLCT bands of P22 were different from those of P6 because of the use of different coordinating ligands (terpyridine vs. bipyridine) in the polymers. The heterobimetallic P12 (with Cl^{-} and AcO^{-} counter anions) contains Fe(II) and Os(II), which also shows multicolor electrochromism (purple ↔ violet ↔ greenish yellow) upon stepwise oxidation of Os(II)- and Fe(II)-complexes in P12 at 0.7 and 1.0 V. P12 exhibited excellent EC switching stability over more than 10000 EC switching cycles (measured in a three-electrode system vs. Ag/Ag^{+}). A voltage-tunable multicolor ECD was constructed by integrating P12 into a patterned solid-state device (Fig. 27c) [73]. The P13 containing Os(II) and Ru(II)-complexes displays multicolor electrochromism (brown-red ↔ yellow ↔ green) upon stepwise oxidation of Os(II)- and Ru(II)-complex parts, that is also applicable to fabrication of camouflage devices (Fig. 27d) [127].

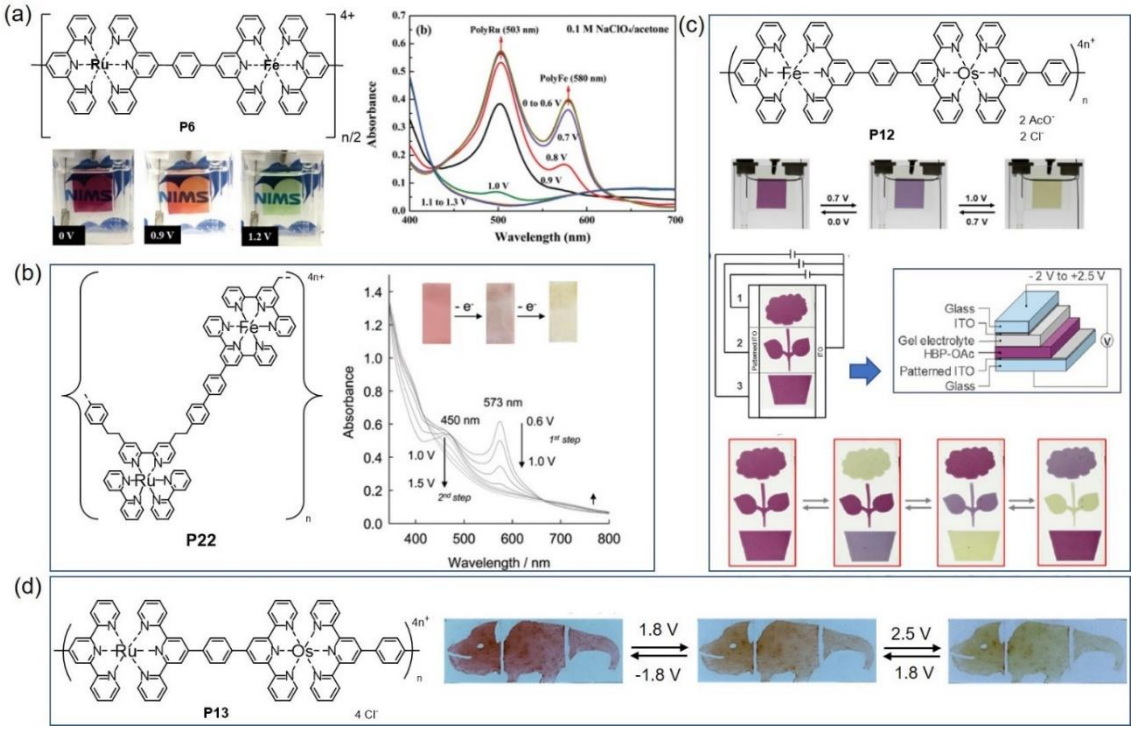


Fig. 27. *(a) Chemical structure of P6 with the electrochromic (EC) color of its thin film on ITO in a three-electrode system and corresponding change in the absorption spectra at different voltages. Adapted with permission from ref. [102], Copyright 2019 Royal Society of Chemistry. (b) Chemical structure of P22 with the EC color of its thin film on ITO in a three-electrode system and corresponding change in the absorption spectra at different voltages. Adapted with permission from ref. [106], Copyright 2014 Royal Society of Chemistry. (c) Chemical structure of P12 with the EC color of its thin film on ITO in a three-electrode system at different voltages and structure of solid-state voltage-tunable multicolor patterned ECD that produces multicolor displays upon application of different voltages in different segments (1,2, and 3) of the device. Adapted with permission from ref. [73], Copyright 2020 American Chemical Society. (d) Chemical structure of P13 with fabricated camouflage device that showing different color at different voltages. Adapted with permission from ref. [127], Copyright 2023 American Chemical Society.*

If three redox-active metal centers are present in an HMSP, the resulting polymer can exhibit quad-color electrochromism. For example, P15 contains redox active Fe(II), Ru(II), and Os(II) ions and shows reversible quad-color electrochromism (magenta ↔

brown ↔ yellow ↔ green; measured in a three-electrode system vs. Ag/Ag^{+}) upon stepwise oxidation of the heterometal ions (Fig. 28a–c) [76]. The initial color of the film (on ITO) of P15 was magenta, showing major MLCT absorption bands at 502 and 574 nm for the combined singlet MLCT of Os(II)- and MLCT of Ru(II)-complex parts and for Fe(II)-complex parts, respectively [54, 105]. At 0.7 V, oxidation of Os(II) ions occurs and the corresponding MLCT bands (singlet and triplet) for the Os(II)-complex parts disappear. The color of the film becomes brown, which changes to yellow at 0.85 V for the oxidation of Fe(II) ions with the disappearance of the MLCT band corresponding to Fe(II)-complex parts. At an applied voltage of 1.20 V, the color of the film changed to green owing to the oxidation of Ru(II) ions to P14, with the disappearance of the MLCT band for the Ru(II)-complex parts (Fig. 28d). Therefore, an increase in the number of heterometallic complexes in a MSP chain could yield multicolor EC materials with greater color variation.

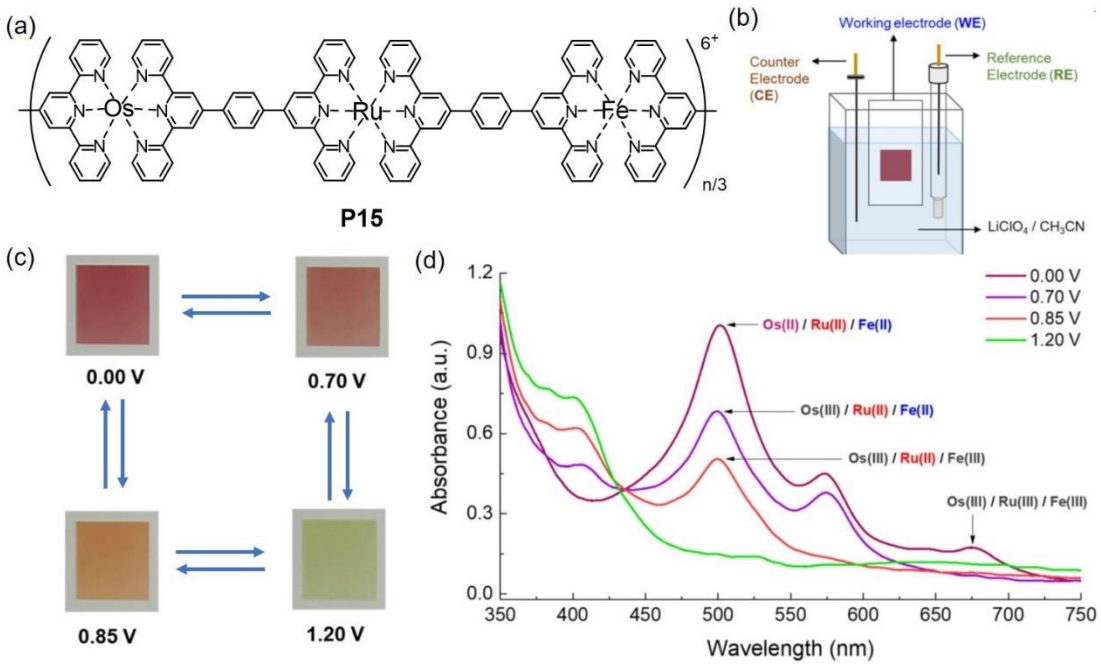


Fig. 28. *(a) Chemical structure of P15. (b) Three-electrode electrochemical cell for electrochromic (EC) property analysis of P15 film on ITO. (c) EC color of the film at different voltages. (d) Change in the absorption at different voltages. Adapted with permission from ref. [76], Copyright 2021 Nature Portfolio.*

4.2. Anticancer drug

Anticancer drugs are widely used to treat cancer, a disease that causes numerous deaths worldwide. Anticancer drug therapy is primarily based on DNA-binding affinity, which occurs in two ways: groove binding and intercalation. Groove binding of anticancer drugs is considered to be more effective in increasing the DNA-binding affinity [165]. MSPs show strong groove binding activity toward DNA and higher cytotoxicity for cancer cells, which arises from the positive metal ions in the polymer chain [61, 166]. Because metal ions have a positive charge, MSPs can be treated as polycations that can interact with the phosphate anions of DNA. In addition to homometallic MSPs, heterometallic complexes, and HMSPs containing different cytotoxic metals are promising candidates for anticancer drug applications. Most anticancer drugs, such as cisplatin, oxaliplatin, and carboplatin, are based on Pt complexes [167]. Therefore, Ru/Pt-based heterobimetallic supramolecular complexes have been found to show excellent anticancer activity [168, 169]. Heterometal ions with different coordination environments multiply their interaction with biological targets and simultaneously enhance their anticancer activity (Fig. 29a,b) [170, 171]. The HBSP P25 contains alternating Pt(II) and Fe(II) complexes in different coordination environments, which exhibit excellent anticancer activity [110]. Fe(II) ions show good antitumor activity with few side effects, and Pt(II)complexes (organometallic Pt complexes) serve as good anticancer agents. The anticancer activity of P25 was tested in human-lung-cancer cells

(A549) using the CCK-8 assay, and cell viability decreased with increasing concentration of P25 (Fig. 29c). The two heterometallic complexes in P25 enhance its binding affinity to DNA and cytotoxicity, which reflects the potential of P25 as an anticancer drug.

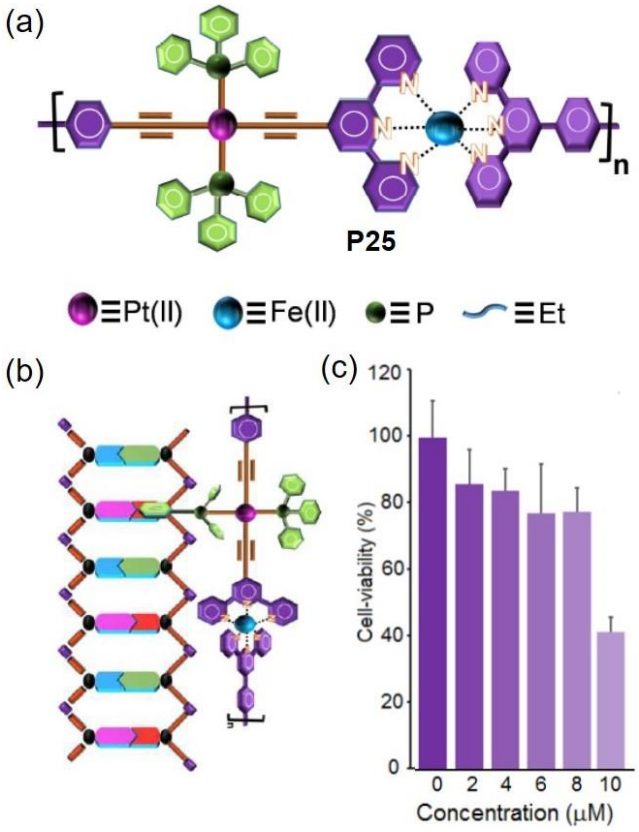


Fig. 29. *(a) Chemical structure of P25. (b) Possible structure of the conjugate of P25 with B-DNA. (c) Cell viability test with P25. Adapted with permission from ref. [110], Copyright 2019 Elsevier.*

4.3. Electrochemical sensor

In the field of electrochemistry, making of new electrocatalyst to develop electrochemical sensor, has drawn significant research interest [79, 172, 173]. Similar to other established electrocatalytic systems, HMSP exhibit electrocatalytic activity as an electrochemical sensor. Since Ni- and Co-based systems exhibit excellent electrocatalytic

performance [174, 175], Ahammad et al. developed randomly distributed Ni(II) and Co(II) ion-based HBSPs (P7) [176] and used them as organometallic electrocatalysts to electrochemically detect nitrite species [79]. The heterometal ions in P7 are complexed in an octahedral environment composed of terpyridine units. The use of such HMSPs as electrocatalysts helps to enhance the electroactive properties via the metal–metal interactions utilizing coordination bonding and to form a low-spin complex due to the same octahedral environments in both metal complexes [177, 178]. P7 exhibited excellent electrochemical activity as an effective nitrite sensor, as confirmed by both CV and amperometric analyses. Amperometry revealed a limit of detection (LOD) of 0.45 μM for nitrite. P7 promotes irreversible oxidation of nitrite, which has been proven both experimentally and theoretically. In addition, both the heterometallic centers in P7 were found to be electroactive; the flexible metal–ligand bond in P7 provides facile electron transfer during the catalytic process (Fig. 30).

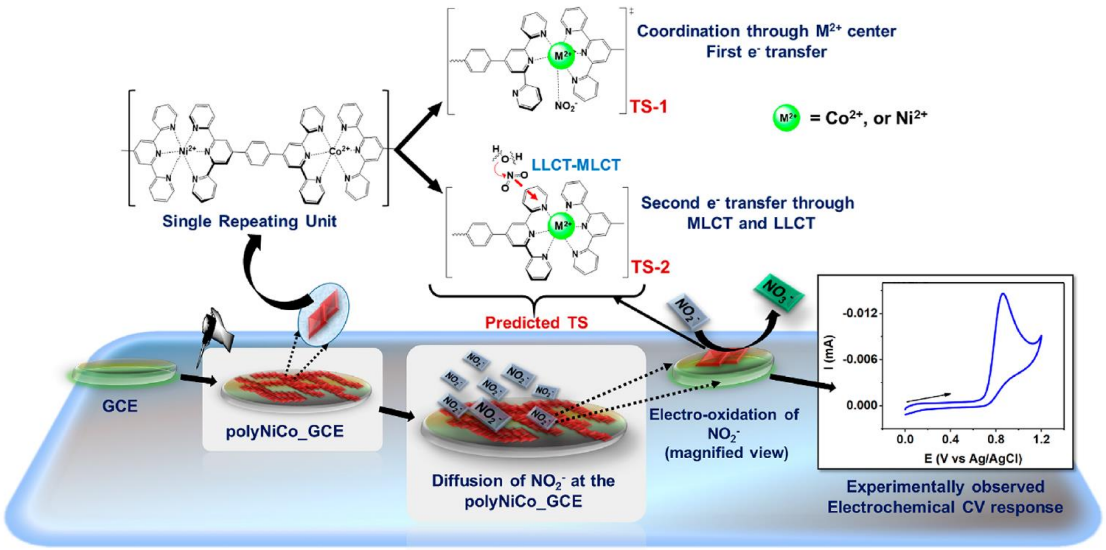


Fig. 30. *(a) Proposed reaction mechanism process of P7 for irreversible oxidation of nitrite. Adapted with permission from ref. [79], Copyright 2020 American Chemical Society.*

4.4. Other applications

HMSPs have also been used for enhancing proton conductivity [126] and for photoelectric conversion [108]. P11 contains Eu(III) and Fe(II) ions and has a hyperbranched structure; it exhibits excellent proton conductivity of 2.36×10^{-4} S/cm at room temperature (25 °C) with a relative humidity of 95% [126]. The proton conductivity becomes higher with increase in temperature and it reaches 2.1×10^{-3} S/cm at 90 °C with a relative humidity of 95%. The Ru(II)/Fe(II)-based HBSP, P24, is also useful for photoelectric conversion. The P24 deposited on ITO acted as a photocathode in the presence of a sacrificial electron acceptor (aromatic diazonium ArN_2^+ salt) at 0.4 V [108].

5. Conclusions and perspectives

The development of heterometallic supramolecular polymers (HMSPs) is comprehensively summarized in this review, which includes descriptions of various synthetic approaches and their properties and applications. HMSPs can be synthesized using either a one-pot or stepwise synthetic route. Furthermore, the coordination environments of the heterometal ions in HMSPs may be identical or different. Moreover, the distribution of heterometallic ions may be random or alternating throughout the HMSP chain. All reported examples of HMSPs developed over the last two decades are highlighted. Depending on the synthesis procedures (one-pot vs. stepwise) and ligand structures, the resulting HMSPs are formed as gels or solid products, where the structures of HMSPs are mostly linear. It has also been observed that stepwise syntheses are suitable

for preparing HMSPs containing heterometallic ions in an alternate fashion. Among the reported HMSPs, most of the polymers have been constructed with two heterometal ions. The stabilities of heterometallic complexes are different, making it difficult to stabilize various heterometallic complexes in a MSP chain. Therefore, introducing more than two heterometallic ions into a polymer chain is challenging. However, attempts have been made to introduce three heterometal ions into the polymer chain (P15–P17) through stepwise complexation of the three heterometal ions using the concept of strong and weak coordination metal ions.

The properties of HMSPs depend on the polymer structure, counter anions attached to the polymer, and coordination environment of the heterometallic complexes in the polymer. HMSPs generally show broad absorption owing to a combination of metal-to-ligand charge-transfer (MLCT) transitions in various heterometallic complexes. Moreover, if HMSPs contain two or more redox-active heterometal ions, the resultant polymers exhibit a broad electrochemical window, which has several potential optoelectronic applications. The counter anions attached to an HMSP plays a crucial role in the solubility of the polymer. Counter anions can be changed, as shown for P12 and P15, to tune the solubility of the polymer in various solvents, which facilitates the processability of the polymer. Depending on the characteristics of the metal centers, HMSPs show various stimuli-responsive properties such as redox-induced optical property changes and thermoresponsive behaviors. The combination of various heterometallic complexes with HMSPs chains enables various interesting applications of HMSPs in the fields of electrochromism, anticancer drugs, electrochemical sensors, and proton conduction. Multi-redox responsive HMSPs are promising multicolor EC materials for the fabrication of voltage-tunable multicolor ECDs and displays.

Although various HMSPs have been developed, their applications have not been extensively explored. Further studies on HMSPs should be conducted to explore their diverse applications. Again, most HMSPs have been developed using only two heterometal ions, and the introduction of more than two heterometal ions into a polymer chain has been only limitedly successful. Thus, several opportunities and challenges exist in the development of HMSPs with a large number of heterometal ions. The development and synthesis of HMSPs may lead to novel properties and exciting applications stemming from the combination of heterometallic segments into the polymer chain. Herein, we provide a perspective on the challenges and opportunities in the field of HMSPs that will guide researchers in this field.

A major limitation in the synthesis of HMSPs is the choice of ligand structure. Terpyridine-based coordinating ligands have been mostly used for the successful synthesis of HMSPs because terpyridine-metal complexes lead to SPs rather than coordination polymers, whereas the use of non-pyridine-based ligands mostly produces coordination polymers. However, various nonpyridine- and pyridine-based ligands may be used to prepare new HMSPs. Since the pyridine unit mainly leads to coordination polymers, pyridine cannot be used as the coordinating ligand. Therefore, we need to focus on other polypyridyl ligands, such as bipyridine, phenanthroline, and quarterpyridines [10, 179]. Close examination of the structure of P10 revealed that the polymer was synthesized using a ditopic ligand containing phenanthroline and terpyridine units. Compound P11 was constructed using phenanthroline-based ligands. In P11, the Fe(II) metal ions bind to three phenanthroline units to form a network structure, whereas in P10, the Cu(I) ions bind to two phenanthroline units to produce a linear HMSP. Therefore, by selecting appropriate metal ions and ligand structures, HMSPs with different structures can be

developed. In this context, linear HMSPs have greater advantages in terms of solubility, processability, characterization, and application than network-structured HMSPs. The HMSPs, P18–P21 were constructed using cyclam and terpyridine units, where cyclam can bind Cu(II) ions. Therefore, the use of cyclam-and phenanthroline/bipyridine-based ditopic ligands facilitates the introduction of heterometal ions into a linear HMSP chain.

The stepwise and controlled complexation of strong-coordination and weak-coordination metal ions led to the successful synthesis of HMSPs (P15–P17) containing three heterometal ions. In these HMSPs, a benzene ring was used as the spacer between the heterometallic complexes. Introducing an organometallic complex or a cyclam unit as a spacer in the above heterotrimetallic supramolecular systems can pave the way for introducing four heterometallic complexes into a MSP chain. Therefore, a suitable ligand design as well as the choice of metal complex could offer several approaches of preparing novel HMSPs.

The counter anions were found to play an important role in the solubility of HMSPs. Polymers comprising Fe(II)-bisterpyridine complexes with BF_4^- counter anions are soluble in DMSO or DMF, whereas those comprising Fe(II)-bisterpyridine complexes with AcO^- counter anions are soluble in methanol. Polymers with PF_6^- counter anions are soluble in acetonitrile, whereas those containing Ru(II) ions with Cl^- counter anions are soluble in methanol. Therefore, during the synthesis of HMSPs, attention must be paid to the choice of the metal salt, since it determines the overall solubility of the resulting polymer.

Compared to the methods of HMSP synthesis, the properties and applications of HMSPs have been less explored, which also provides a vast opportunity for further

investigation. Various metal complexes exhibit catalytic activity (as electrocatalysts or photocatalysts); therefore, the introduction of heterometallic complexes into an HMSP chain enhances the catalytic effect by combining the effects of the heterometallic segments. Based on these assumptions, P7 was constructed using Co(II) and Ni(II) ions and showed excellent electrocatalytic activity. Recently, Gong et al. developed Ru-based MSPs as heterogeneous catalysts for the hydrogenation of carbonyl compounds [56]. Maji et al. introduced dual metalation (Ni/Ir) into a 2D covalent organic framework, which was used for photocatalytic applications [47]. Therefore, these structural metal complexes can be introduced into HMSP chains to create novel HMSPs that are useful for various catalytic applications. In addition to the above-mentioned applications, HMSPs should also be explored in biological, luminescent, and energy-related applications.

HMSPs have attracted significant attention over the years owing to their structural diversity, attractive properties, and applications. However, the synthesis, properties, and applications of HMSPs have not been explored extensively, which warrants greater attention toward their study. By introducing various ligands and different metal ions as well as different metal salts, the structure, and properties of HMSPs can be tuned, that will be find various applications. This review provides a roadmap for readers and researchers for further developments in this research area.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that may have influenced the work reported in this study.

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