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Review Article

Structure–Activity Relationship and Stimuli-Responsiveness Behavior of Metallosupramolecular Polymers

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The widespread discourse on the circular economy has fueled a growing demand for polymeric materials characterized by mechanical robustness, sustainability, renewability, and the ability to mend defects. Such materials can be crafted using dynamic covalent bonds, albeit rarely or more efficiently through noncovalent interactions. Metal–ligand interactions, commonly employed by living organisms to adapt to environmental changes, play a pivotal role in this endeavor. Metallosupramolecular polymers (MSPs), formed through the incorporation of metal–ligand interactions, present a versatile platform for tailoring physicochemical properties. This review explores recent advancements in MSPs achieved through the assembly of (macro)monomers via reversible metal–ligand interactions. Various strategies and pathways for synthesizing these materials are discussed, along with their resulting properties. The review delves into the stimuli-responsive behavior of coordination metal–ligand polymers, shedding light on the impact of the core employed in MSPs. Additionally, it examines the influence of parameters such as solvent choice and counterions on the supramolecular assemblies. The ability of these materials to adapt their properties in response to changing environmental conditions challenges the traditional goal of creating stable materials, marking a paradigm shift in material design.

1. Introduction

Over the course of the last century, synthetic polymers have revolutionized our daily lives. The profound impact of synthetic polymers on various aspects of modern life such as medical implants [1, 2], food packaging [3, 4], coatings [5–8], automotive parts [9, 10], cosmetics [11–13], drug delivery [14, 15], and many others [16, 17], and emphasizes the growing interest in stimuli-responsive (smart) polymers. The development of stimuli-responsive (smart) polymers is of broad interest because of their ability to respond to changes in the local environment, such as light [18, 19], heat [20], pH [21–23], and mechanical force [24–26]. These polymers exhibit reversibility in either covalent or noncovalent interactions [27], with a focus on metal coordination in this review. Supramolecular chemistry, characterized by noncovalent interactions beyond traditional bonds, plays a crucial

role in the self-assembly and architecture of supramolecular polymers. The advancements in synthetic chemistry have enabled the design of supramolecular polymers (leading to the Nobel Prizes in 1987 and 2016), allowing precise control over molecular architecture, polymerization degree, and stimuli-responsive characteristics [28, 29]. The goal is to create polymers solely based on dynamic noncovalent interactions, where monomers independently self-assemble into desired structures in both solution and solid-state [30].

The specific focus of this review is on stimuli-responsive metallosupramolecular polymers (MSPs), extending the existing knowledge in supramolecular chemistry [28, 29]. The review touches upon various aspects, such as the use of hydrogen bonding [30, 31] and terpyridine ligands [32–34] in supramolecular polymers. Due to the vastness of the field, the review acknowledges the inability to provide a comprehensive account, referring readers to relevant reviews [35–38] and
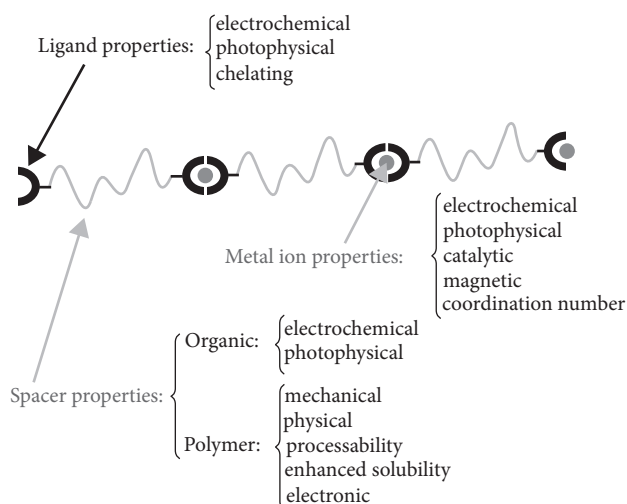
FIGURE 1: Metallosupramolecular polymers and their possible properties. Reprinted with permission from ref. [41].

books [39, 40]. The primary objective of this review is to provide an overview of MSPs categorized by noncovalent interactions, particularly metal–ligand coordination. The review also delves into the stimuli-responsive nature of these materials, detailing their responsiveness to light, heat, chemicals, and mechanical stimuli.

1.1. Supramolecular Polymers Based on Metal–Ligand Interactions. The incorporation of organometallic units into polymer structures dates back to the 1960s, but the production of well-characterized, soluble, and high molecular-weight materials has been limited despite pioneering efforts. Recently, there has been a growing interest in metal-containing polymers, particularly those where chains are grown through metal–ligand interactions. These polymers offer access to unique molecular compounds with intriguing structures and properties, opening avenues for the development of polymeric materials with diverse characteristics (Figure 1).

The first well-characterized transition-metal-based polymers, soluble at appreciable molecular weights, were reported in 1974 by Pittman et al. [42], featuring ferrocene-containing materials with organosiloxane spacers. Following this, advancements in synthetic routes, such as ring-opening polymerization, atom transfer radical polymerization (ATRP), and well-defined polycondensation via various coupling reactions (Stille, Heck, Negishi, Suzuki coupling, Sonogashira, and Mitsunobu), have enhanced the synthesis of metal-containing polymers.

A notable example is the work of Manners [43], who utilized ring-opening methods to produce high molecular weight poly(ferrocenylsilanes) with molecular weights around 10^5-10^6 g/mol. These developments showcase the evolving landscape of metal-containing polymers, with improved synthetic routes leading to materials with enhanced properties and potential applications.

The groundbreaking work of Manners [43] and other researchers has paved the way for the development of diverse metal-containing polymers, including metallocene-based polymers, nickel, and rhodium [44–48], liquid crystalline

organocobalt [49], and organochromium[50] polymers. This field has rapidly expanded, especially in the realm of materials science.

MSPs [51] represent a unique category of metal-containing polymers [52] characterized by dynamic metal–ligand coordination that facilitates reversible supramolecular polymerization [53, 54]. This hybrid material offers a broad range of ordered assemblies [55] with desirable properties, such as magnetism, optics, electricity, and catalysis, leveraging the inherent characteristics of metals. The fusion of metal complex functionalities with the advantageous features of polymers, such as processability and mechanical properties, presents a significant building block for materials science.

Metal complexes play a crucial role in the structure and function of various biopolymers like metalloproteins [56, 57], synthetic polymers such as self-healing materials [58], and adhesives [59], and many other properties [41]. The incorporation of these metal components into polymer structures opens up substantial possibilities for easily processable materials with properties distinct from traditional organic polymers (Figure 1). This convergence holds great potential for advancing the development of materials with enhanced and tailored characteristics.

The development of MSPs gives a modern measurement for an essential understanding of material science and can be used in significant applications such as electro-photochemistry, catalysis, magnetism, and thermochromism [60]. The metal–ligand complexes can be promptly tuned with the catalog of ligands that can tie in with the huge choice of metal in the Mendeleev periodic table. Other factors, such as the nature, length, and structure of the MSP core, as well as the dentricity (monodentate, bidentate, tridentate, etc.), the type and position of the ligand, the nature of the metal ion, and the counterions, allow these polymers to tailor their properties.

1.1.1. Classification of MSPs. Accurate classification of MSPs can be difficult because not all MSPs exhibit reversibility, which is a classification criterion. For instance, certain MSPs containing Ru^{2+} as aza-ligands-Ru^{2+}complexes (heterocycles with nitrogen as heteroatoms bound to Ru^{2+}) may provide a straightforward approach to prepare metalloblock copolymers and amphiphilic micelles [61, 62], despite their nondynamic nature.

Based on these observations, different criteria (coordination number, number of ligands, geometry of complex, and thermodynamic) can be used for classification (Figure 2).

(i) The coordination number allows control over the architecture, properties, and dynamic nature of supramolecular motifs. The combination of metal and ligand determines how well the pattern fits together. To make complexes with a ratio of metal to ligand 1:2, either bidentate (bipyridine, pincer) or tridentate (2,6-bis(1′-methylbenzimidazolyl)pyridine, terpyridine, etc.) ligands should be used with metal ions that have four or hexacoordinate number. Another ratio 1:3 metal:ligand could be achieved using the same ligands but coordinated
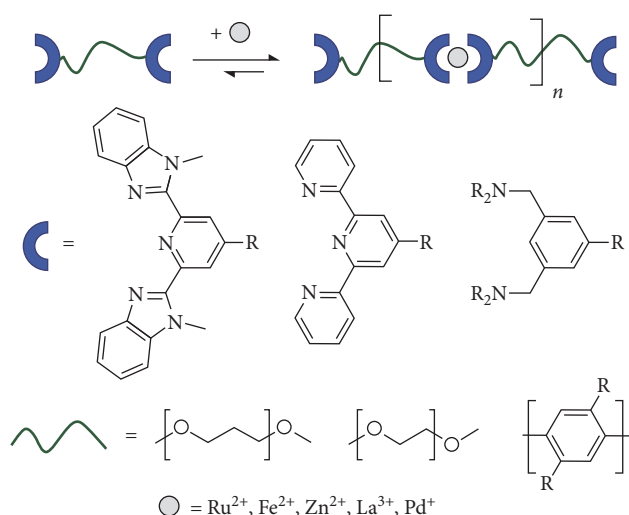
FIGURE 2: Schematic representation of the metallosupramolecular polymerization of ditopic ligands with transition metal ions.

FIGURE 3: Schematic architectures of metal transition tridentate and lanthanide tridentate ligands.

this time to hexacoordinate metal ions or lanthanide ions.

(ii) Number of ligands chelated to the metal ions. The first system is a homo-coordinate species in which one type of ligand is bound to the metal ion. The second hetero-coordinated species resulted in a combination of homo- and hetero-coordinated species.

(iii) The geometry of the complexes (e.g., octahedral, tetrahedral, square planar, etc.) depends on the choice of metal and ligand.

(iv) Reversibility is determined by the thermodynamics and kinetics of the supramolecular metal–ligand motif. These two factors are important for the structural properties of MSP. Thermodynamics controls the size of the MSPs according to the choice of metal ions and ligands. Multidentate ligands are expected to bind several orders of magnitude stronger than monodentate ligands.

In fact, the stability of the metal-to-ligand interaction can be pursued through two main strategies: employing organic ligands with high affinities for metal centers and/or utilizing ligands with an increased number of metal-binding sites, known as chelation or multidentate binding. Among these, the latter approach has been extensively explored, notably employing pyridine-type ligands. Dobrawa and Würthner [63] investigated the impact of ligand denticity on complex stability, exemplifying the chelation effect with polypyridyl ligands. For instance, a Ka value of 10^3 M^{-1} was observed for the single Zn(II)–pyridine interaction, while the Zn(II)–terpyridine system exhibited a significantly higher Ka value of 10^8 M^{-1}. Stable bis-tridentate complexes with pseudo-octahedral geometry can be formed with various transition metal ions, particularly in low oxidation states and terpyridine ligands. These complexes demonstrate exceptional stability, attributed to the dynamic chelate effect coupled with efficient metal-to-ligand d–π^* back-donation.
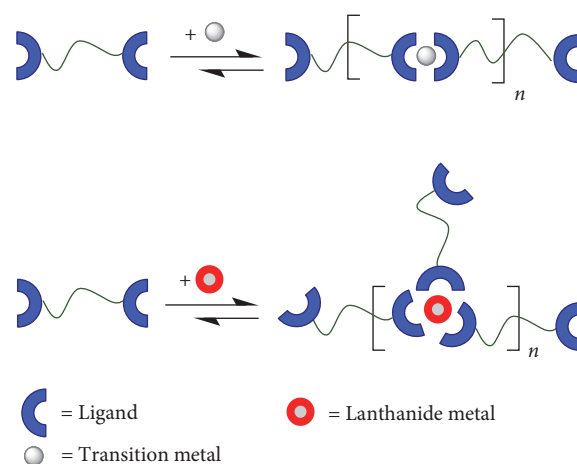
In this review, we focus on tridentate ligand (2,6-bis(1'-methylbenzimidazolyl))pyridine (Mebip) and terpyridine) in the MSP structure. For that, looking at how well the terpyridine ligand sticks to metal ions [64], it turns out that for 1:2 metal–ligand complexes, the binding strength is three-fold more important than UPy dimerization in $CHCl_3$. The decomplexation rate for the same motif complex with Co^{2+} and Fe^{2+} is about ms to 0,1 μs, respectively. A more thorough investigation of the binding strength of Mebip with metal ions (ranging from metal coordination to lanthanides) has been conducted [58] and revealed that 2,6-bis(1'-methylbenzimidazolyl) pyridine ligand Mebip exhibits similar binding behavior for metal ions, including zinc, iron, cadmium, and cobalt.

1.1.2. The Role of the Metal–Ligand Motif in the MSPs. The tridentate ligands terpyridine and Mebip can coordinate to Fe^{2+}, Co^{2+}, Zn^{2+}, and Eu^{3+}, and their dynamic nature follows the order $Fe^{2+} < Co^{2+} < Zn^{2+} < Eu^{3+}$, at least for the most stable to the most labile of this series. Additionally, Fe^{2+}, Co^{2+}, and Zn^{2+} formed a 1:2 metal:ligand ratio to form linear systems, whereas Eu^{3+} and La^{3+} had a 1:3 metal:ligand ratio, leading to a 3D network (Figure 3). The strength and color of the material changed dramatically over this series with an unassisted eye or under UV–visible spectroscopy.

The dynamic nature of metal–ligand binding in MSPs offers a spectrum of tunable properties [65, 66], making them versatile materials. The bond strength, determined by the choice of metal and counter ions, allows modulation from weak to strong, resembling traditional polymers with covalent bonds. MSPs often exhibit phase separation between the complex and the cores, providing a mechanism to control their mechanical properties. For instance, Beck and Rowan [67] demonstrated that the glass transition temperature (T_g) of MSPs depends on the strength of the metal–ligand bond. They used poly(THF) as the core and coordinated it with Zn^{2+} ions, leading to a lamellar cross-linked segregated morphology shown by small-angle X-ray scattering (SAXS), wide-angle X-ray scattering, and dynamic
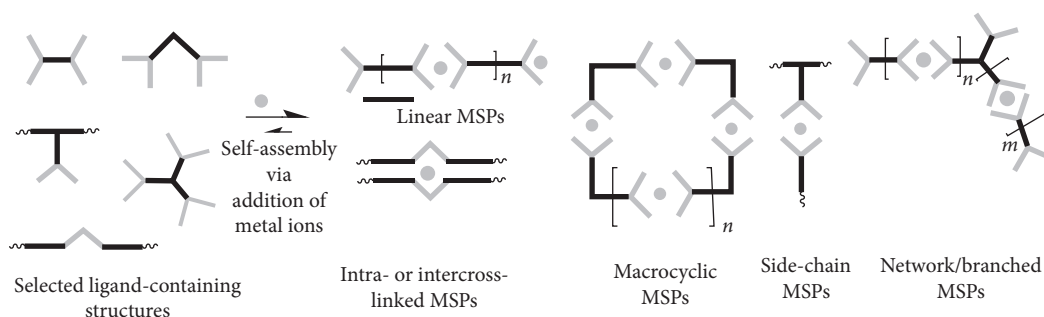
FIGURE 4: Representation of different MSPs architectures. Reprinted with permission from ref. [76].

mechanical temperature analysis (DMTA). The physical properties of the elastomeric film were significantly impacted by this system. The addition of La^{3+} or Eu^{3+} ions altered the MSP complexes, affecting their modulus and resulting in a gel-like material [67]. The choice of metal ions influences various properties, including photophysical, magnetic, electrochemical, and mechanical, while ligand selection primarily impacts optical and electrochemical properties.

The dynamic nature of MSPs was also demonstrated by Chiper et al. [68]. They explored the strength of MSPs using gel permeation chromatography (GPC). Labile MSPs, like Zn^{2+}-terpyridine systems, fractured during GPC, while kinetically inert metallopolymers, such as Ru^{2+}-terdendate ligands, passed intact. The inert nature of these polymers makes them more akin to covalent polymers than traditional MSPs. The study emphasizes the importance of metal and binding strength choices in characterizing MSPs, especially regarding techniques for determining molecular weight based on the metal–ligand motif's binding strength.

1.1.3. Type of MSPs. MSPs have been extensively explored using metallo-bipyridines [69], terpyridine [34, 70], porphyrin [71], and 2,6-bis(benzimidazolyl)pyridine (Bip) or its derivatives [72, 73], characterized both in solution and the solid state. While the coordination in these polymers can be either irreversible [74] or labile [75], the focus here is on the main chain metal–ligand interactions. MSPs exhibit various structures depending on the metal positions, including side-chain MSPs, linear MSPs (intra or intercrosslinked), and network/branched or macrocyclic MSPs (Figure 4).

In metallosupramolecular polymerizations, there exists an equilibrium process between (macro)monomer and polymeric species, influenced by the thermodynamics (K_{eq}) and kinetics (k_1 and k_{-1}) of the system. Under suitable conditions, a linear MSP with a metal can spontaneously form, leading to assemblies with few irreversible final shapes (Figure 5). The degree of polymerization (DP) is determined by the association constant (K_{eq}), (macro)monomer concentration (M), and assembly mechanism, with the relationship $DP \sim [K_{eq}(M)]^{0.5}$ generally accepted for polymers with reversible interactions [77].

This concept resembles polycondensation, where bifunctional entities assemble through their terminal ligands. The presence of even trace amounts of single-function entities significantly reduces the size of the polymers formed,
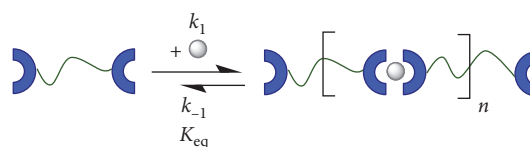

FIGURE 5: Illustration of thermodynamic and kinetic factors in linear MSP.

following the Carothers equation [78]. This insight contributes to understanding the conditions and mechanisms governing the formation of MSPs with specific properties.

1.1.4. The Role of Solvent, Concentration, and the Core Spacer in the MSPs. The choice of building block units is crucial for the conception of MSPs. We have already shown the roles of the ligand and metal, as well as the crucial role of the spacer. The conditions (solvent and concentration) for the preparation of MSPs are of paramount importance.

A pioneering study on MSPs was reported by Lahn and Rehahn [79] in which they used phenanthroline (a bidentate ligand) as end-capping of a polystyrene core with Cu+ or Ag+ ions (Figure 6). This study shows how solvent and concentration influence on the formation of MSP. The behavior (lability or stability) of metal–ligand interactions changes significantly depending on the solvent used for polymerization. The MSPs generated in uncoordinated solvents such as tetatrachloroethane-d_2 (TCE-d_2) lacked any dynamic behavior. Nonetheless, upon the utilization of acetonitrile (CH_3CN) as the coordinating solvent, the behavior of the polymer underwent a significant transformation. In CH_3CN, numerous loops are made in dilute solution, suggesting that the solvent is thought to act as a chain stopper, favoring the dissociation of the ligand metal complex. The impact of the solvent on the dynamic behavior was illustrated by blending two distinctive polymers. The blend was stable in TCE-d_2 for at slightest 3 days, with no critical compatibility within the polymer composition of the blend. However, upon the addition of CH_3CN, an exchange process occurs within the arrangement of the blend (Figure 6).

The idea is that MSPs should be made in noncoordinating solvents to avoid competition between ligands and solvents and the formation of oligomer species. Notably, a coordinating solvent can be used as a stimulus to enhance the properties of MSPs.
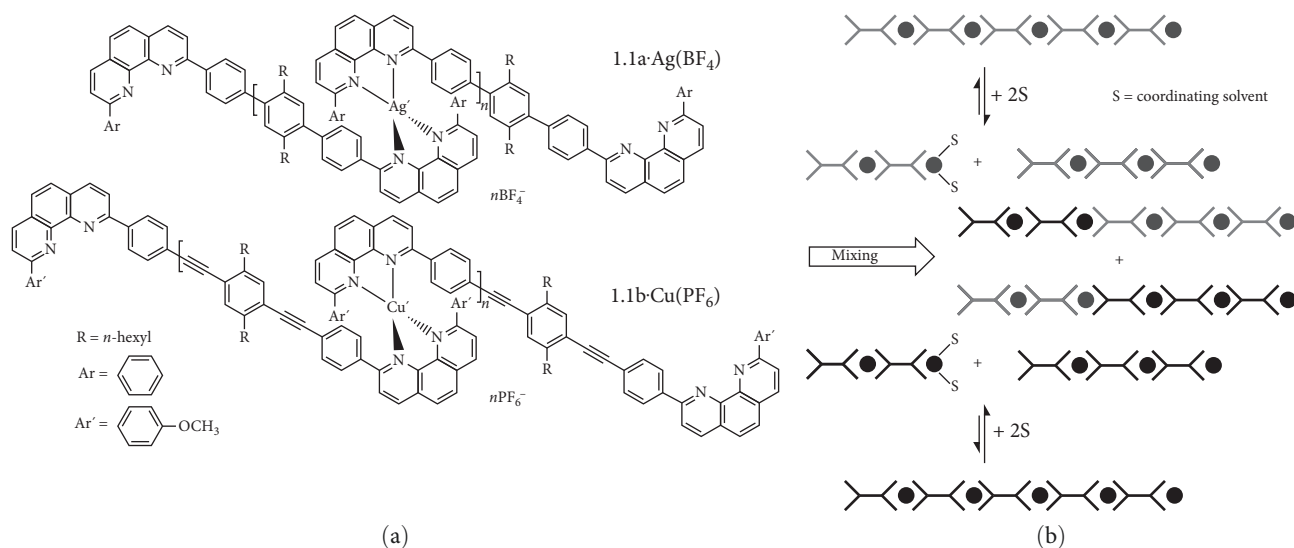
FIGURE 6: (a) MSPs with ditopic phenanthroline ligands (1a and 1b) in coordination with Ag(I) and Cu(I). (b) Schema of the coordinating solvent-switching mechanism for MSP dissociation and chain mixing. Reprinted with permission from ref. [79].

As discussed (*vide supra*), the thermodynamic variables control the size of the MSPs, depending on the choice of the metal and ligand. Moreover, according to the binding effect, the difference in size can vary by orders of magnitude from monodentate to tridentate ligands. The early 1990s saw the introduction of tridentate ligands in the production of metal-lopolymers. Constable et al. [80], first in 1995, proposed a novel approach for the utilization of terpyridine monomers to tune coordination polymers to metal ions. Since then, many studies have been done using the terpyridine motif as a ligand for making rod or linear polymers.

The same author argued that the metal ions, the structure of the core spacer, and the overall shape concentration are three variables that could be favorable thermodynamic conditions for the arrangement of a macrocycle [34, 81]. Researchers pertinently demonstrated that terminal terpyridine ligand-binding regions separated by flexible oligo(ethylene oxide) spacers end up in metallomacrocycles with Ru^{2+}, unlike labile Fe^{2+} ions finished in a linear fashion. Furthermore, diluted conditions favor the formation of these macrocycles. The formation of linear metallopolymers versus macrocycles (loops) is influenced by the length of the spacer, whether it is short or long, as well as its flexibility or rigidity. The macrocycles can be observed in rigid cores, according to Constable [34]

1.1.5. The Role of Counter-Ions.
Bode et al. [82] on the frequency-dependent oscillatory shear rheology of multisegment polymers (MSPs) based on poly(n-butylacrylate) with a terpyridine side chain cross-linked (Zn^{2+}, Ni^{2+}, Co^{2+}, or Mg^{2+}) Bode et al. [82] conducted a study *via* the frequency-dependent oscillatory shear rheology of MSPs based on poly(n-butylacrylate), with a terpyridine side chain cross-linked with various metal salts (Zn^{2+}, Ni^{2+}, Co^{2+}, or Mg^{2+}) and counterions (nitrate, acetate, or chloride). The investigation revealed no distinct patterns among MSPs. Similarly, the thermomechanical properties of MSPs derived from a

Mebip-terminated poly(butadiene) macromonomer were influenced by the choice of metal salt. Materials assembled with Eu $(NTf_2)_3$ showed varying counterions (trifluoromethanesulfonate OTf^-, perchlorate ClO_4^-, or bis(trifluoromethylsulfonyl)imide NTf_2^-), and the number-average molecular weight (Mn) of the PEB core (2,100 or 3,100 g/mol) was systematically altered. All MSPs exhibited microphase separation into lamellar or hexagonal morphologies, influenced by the geometric arrangement of metal–ligand complexes and volume fraction. The microstructure morphology, in turn, affected mechanical properties, with the nature of the metal and counterions impacting the softening temperature, notably observing a lower softening temperature for MSPs prepared with lanthanide salts.

1.1.6. Formation of MSPs.
The addition of all the following criteria: metal–ligand strength, thermodynamic and kinetic factors, solvent, concentration, and counter-ions, as previously cited, contributed to controlling the formation of MSPs, which was further demonstrated by other studies. Some of these issues are discussed in the following sections:

Vermonden et al. [83] used short spacers of ethylene oxide between pyridine-2,6-dicarboxylate (dpa) terminal groups to prepare MSPs and investigated other properties, such as the macrocycle fraction (rings) (Figure 7), effects of core length, and metal–ligand stoichiometry. Since two ligands can coordinate to one Zn^{2+} ion, it is required to have a 1 : 1 polymer: Zn^{2+} ratio in order to obtain a high-molecular-weight MSP. When this stoichiometry is off, the chain ends, and the molecular weight drops. The authors investigated the molecular weights using Jacobson and Stockmayers theoretical model and rheological studies and found that longer ethylene oxide cores promote ring formation at low concentrations.

Rowan and co-authors have shown that the use of telechelic cores (rigid or flexible) with molecular weights in the thousands can facilitate the formation of linear metallopoymers, and the resulting materials can exhibit "polymer-like" mechanical properties [84–86]. Poly(ethyleneoxide) (PEO) and poly(THF) have
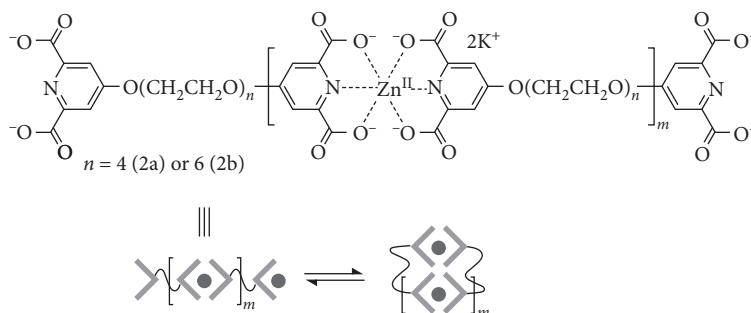
FIGURE 7: The MSPs are based on 2,6-pyridine dicarboxylate (dpa) end-capped ditopic oligo(ethylene oxide) monomers (2a and 2b) and Zn(II) ions. Formation of linear and ring MSPs. Reprinted with permission from ref. [83].

been used as the cores with low glass transition (T_g), and terminated at both ends with Mebip ligand, are capable of coordination with different metals such as Fe^{2+}, Co^{2+}, Zn^{2+} or Cd^{2+} resulting in MSPs which exhibit mechanical properties that are similar to those of poly(ethylene) [86]. The authors think that this might happen in part due to phase segregation, which results in how the core and counterion interact, as reported by Lohmeijer and Schubert [62] and also Bender et al. [87], for block copolymers containing metals.

The examples presented here clearly show that the nature of the central supramolecular motif heavily influences the properties of polymeric materials. The effect of this motif is related to its chemistry. Strength dictated by thermodynamic and kinetic factors plays a significant role in the formation of MSPs under specific concentrations and solvent conditions. All the units influence the properties of the final material. The synthesis of MSP is dictated by the properties of the final target material.

1.2. Stimuli-Responsiveness of MSPs. In this framework, MSPs are explored as systems that leverage specific intermolecular interactions to create entanglements, imparting dynamic properties to materials through supramolecular motifs. The reversibility of these interactions allows for the development of stimuli-responsive systems, where the switch between polymeric and monomeric behavior enables on-and-off states. Controlling responsiveness is achievable through synthesis and environmental factors, offering the potential to create smart materials with adjustable properties along an equilibrium state. MSPs serve as a tool to study how polymer materials respond to various stimuli, aiding in the comprehension of their dynamic behavior from the molecular to macroscopic levels (Figure 8). The main challenge lies in developing mechanically stable stimuli-responsive materials. While much work has been done in solution, the transition to the solid state poses difficulties in designing polymeric networks capable of structural changes upon stimulation while maintaining solid-state properties.

The detection of stimuli by living organisms through the five senses (hearing, touch, sight, smell, and taste) leads to various reactions. The focus is on chemical responses involving MSPs (biological supramolecular polymers), particularly those related to muscle movement, antigen recognition by antibodies, and oxygen transport. The discussion highlights

the exploration of artificial stimuli-responsive MSPs, with specific mention of Mebip derivatives used by Rowan and Weder's groups. These derivatives have been applied in creating stimuli responsive materials [67] for chemical sensors [88], thermoplastic elastomers [41], photohealable materials [85], and dynamic polymers [54]. The research also explores the disruption of metal–ligand phases through stimuli like light, heat, mechanical stress, or chemical competition [89]. Notably, the investigations encompass solution state, gels, and the relatively rare solid state, contributing to a deeper understanding of the interplay between structural properties, stimulus-response, and the controllability of mechanical properties in MSPs.

1.2.1. Temperature-Responsive MSPs. Shunmugam and Tew [90] introduced a terpyridine-functionalized polymer based on poly(methyl methacrylate) (PMMA) through ATRP. This polymer was coordinated with lanthanide ions (Eu^{3+} and Tb^{3+}) to create MSPs with characteristic luminescence emission. Under illumination, the resultant MSPs emitted either a pink hue attributed due to Eu^{3+} or a green hue attributed to Tb^{3+}. A novel yellow emission, unique to a composite material containing Eu^{3+} and Tb^{3+} cations in a 1 : 1 ratio, was observed, creating an alloy material. Surprisingly, the emission spectrum was more intricate than anticipated, surpassing a simple superposition of Eu^{3+} and Tb^{3+} spectra (Figure 9(d)). MSPs-Eu^{3+} displayed higher emissivity than MSPs-Tb^{3+}, so the green color was dominant when they were preformed and mixed together in a 1 : 1 ratio. Notably, the emission spectrum's complexity suggested the straightforward addition of two metal ions (Figure 9(c)).

The yellow light emitted by MSPs with Eu^{3+}/Tb^{3+} in a 1 : 1 ratio was attributed to the stabilization of Eu^{2+}, producing a vivid yellow glow [90–92]. Spectral changes were linked to the optically assisted reduction of Eu^{3+} (($^5D_0 \rightarrow {}^7D_J$) luminescence due to intra 4f-transitions) to Eu^{2+}, with Eu^{2+} (originating from the 5d-4f transition) displaying a variable emission from ultraviolet to red, dependent on structural geometry and its influence on the excited state 5d. Upon heating above 50°C, the alloy polymer exhibited selective thermochromism, transitioning from yellow to orange/pink, closely resembling pure Eu^{3+} emission. This reversible thermochromism resulted from the loss of metal–metal interactions complicating room-temperature emission (Eu^{2+} emission) upon heating
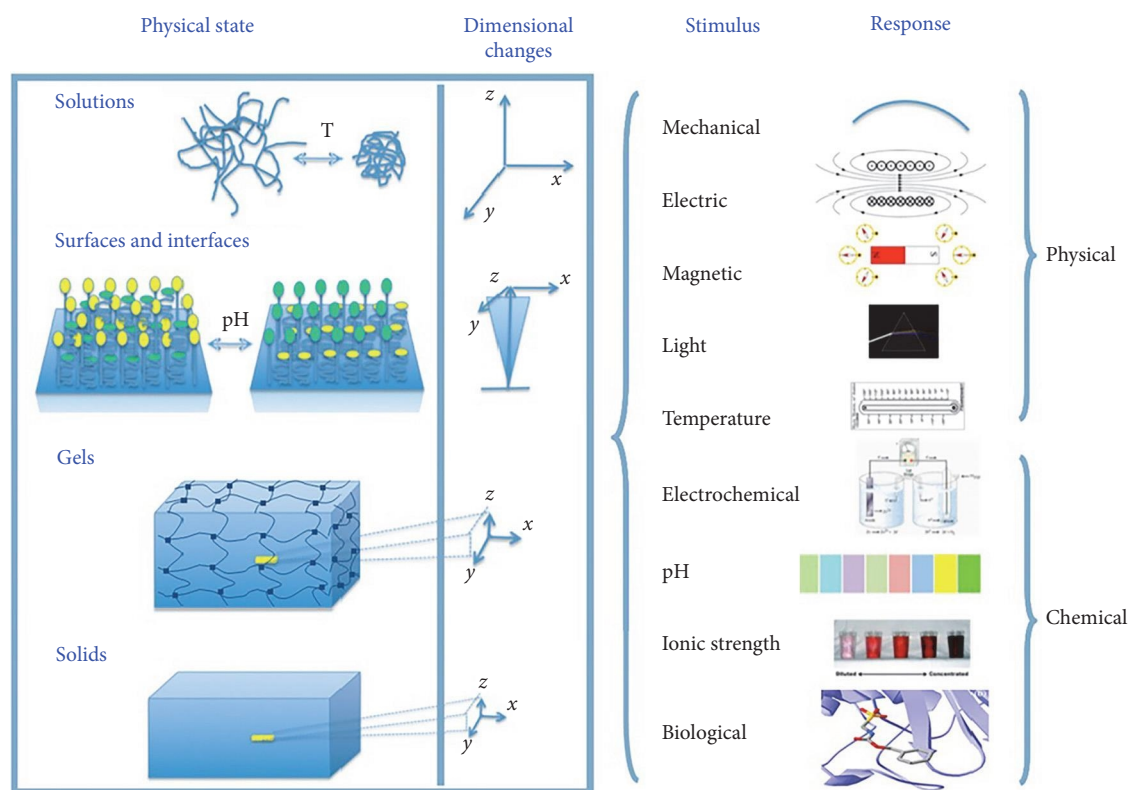
FIGURE 8: Conceptual illustration of stimuli-responsive supramolecular polymer systems. Reprinted with permission from ref. [36].

to 50°C. However, the reformed Eu3+ emission was recovered upon cooling (Figure 10). This example highlights the local thermal environment's influence on Eu^{3+} structure, enabling thermally induced changes, electron transfer processes, and a reduction in $Eu^{3+} \longrightarrow Eu^{2+}$. Subsequently, the yellow emission at room temperature reverted to red upon annealing at elevated temperatures, driven by the thermally activated detrapping of charge carriers (Figure 10).

1.2.2. Light-Responsive MSPs. Light heat conversion was used by Burnworth et al. [85] for an MSP based on telechelic poly(ethylene-*co*-butylene) (PEB) as a core with Mebip ligands as terminal units, which were polymerized with $Zn(NTf_2)_2$ and $La(NTf_2)_3$ ($NTf_2 =$ bistriflimide). This resulted in a polymer film after compression molding, and the materials exhibited appreciable mechanical properties (compared to viscous liquid PEB). Transmission electron microscopy and SAXS revealed a phase-separated lamellar morphology that governed the mechanical properties of the MSPs. Upon exposure to ultraviolet light (320–390 nm), the metal ligands are excited via $\pi–\pi^*$ transition and convert the absorbed energy into heat. This energy permits the temporary dissociation of the metal–ligand motif and liquefies the polymer, which can easily fill small defects. The increase in the chain mobility and decrease in the polymer viscosity permit healing behavior before the shift in the reaction equilibrium. The material reassembles and original mechanical properties were restored when the material was removed from the light source (Figure 11).

This healability mechanism suggests the potential mechanochemistry of this system, whereas the dynamic nature of the MSPs coordinated with La^{3+} (especially the efficient healing of La^{3+}-Mebip) is suitable for monitoring the (des) assembling/reassembling of such materials. Mechanochemistry has hitherto not been explored in the solid state or solution. This will be discussed in the next section.

1.2.3. Mechanically Responsive MSPs. Supramolecular materials depend on force, pressure, and shearing, as they depend on temperature. The application of force or stress on these materials can result in structural or conformational changes [93]. The responses of metallosupramolecular materials may be stronger than those of materials based on covalent bonds, because they are more sensitive to force or stress. For instance, ultrasonication, which results from pressure oscillations, can increase the energy, vibrate, and stress of such materials. The same counterion, trifluoromethanesulfonate (TfO−), was used by Craig teams [94–97] to synthesize a supramolecular polymer from poly(4-vinylpyridine) and bifunctional aminophenylene metal complexes (Pd or Pt) (Figure 12). These polymers have rheological properties related to the dynamic nature of supramolecular motifs [94, 95]. Metal–ligand coordination (cross-links), with its slow dynamics, displayed a higher viscoelastic response. The dissociation of cross-links determines the mechanical properties of the bulk material. Further studies [96, 97] using shear stimuli showed that above a critical shear rate, these MSPs exhibited shear thickening and thinning, which
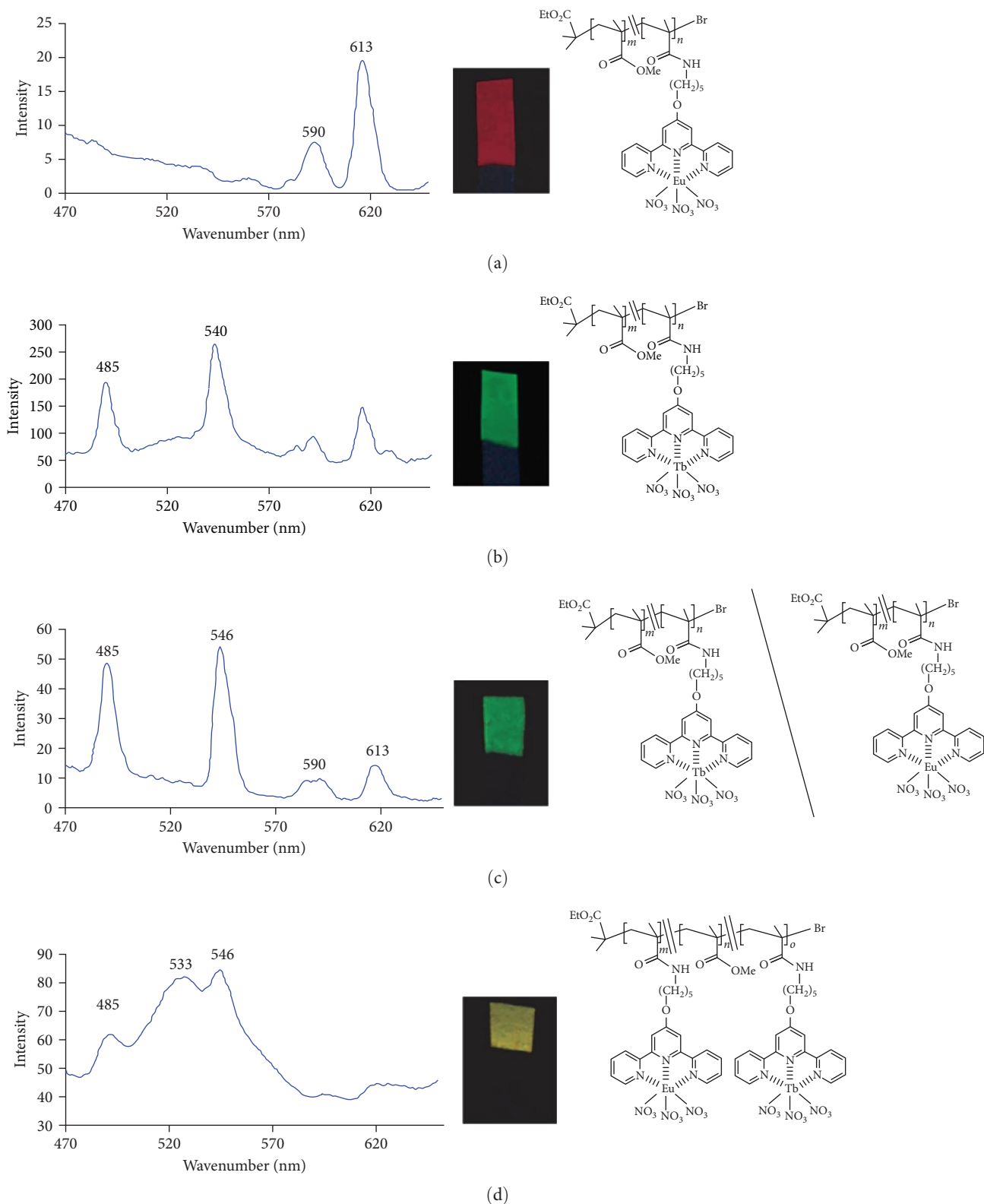
(a)

(b)

(c)

(d)

FIGURE 9: Emission spectra of solid-state (a) polymer-Eu^{3+}, (b) polymer-Tb^{3+}, (c) a mixture of 1 : 1 polymer-Eu^{3+} and polymer-Tb^{3+}, (d) a polymer-Eu^{3+}/Tb^{3+} alloy. Spectra d showed only one new emission band at 533 nm, which was assigned to metastable Eu^{2+}. Excitation at 350 nm is required. Reprinted with permission from ref. [90].
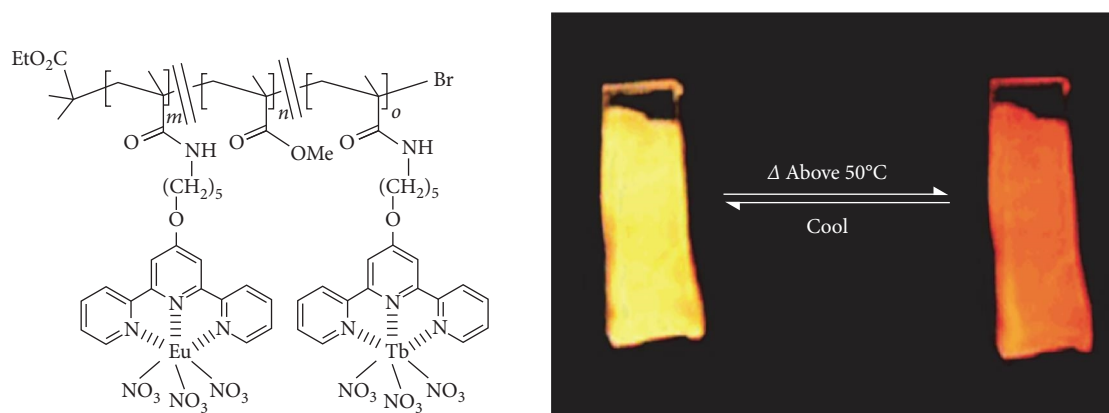
FIGURE 10: Schematic structure of the polymer-Eu^{3+}/Tb^{3+} alloy (left) and the alloy film (yellow). It turned orange when heated above 50°C and yellow when cooled. Reprinted with permission from ref. [90].
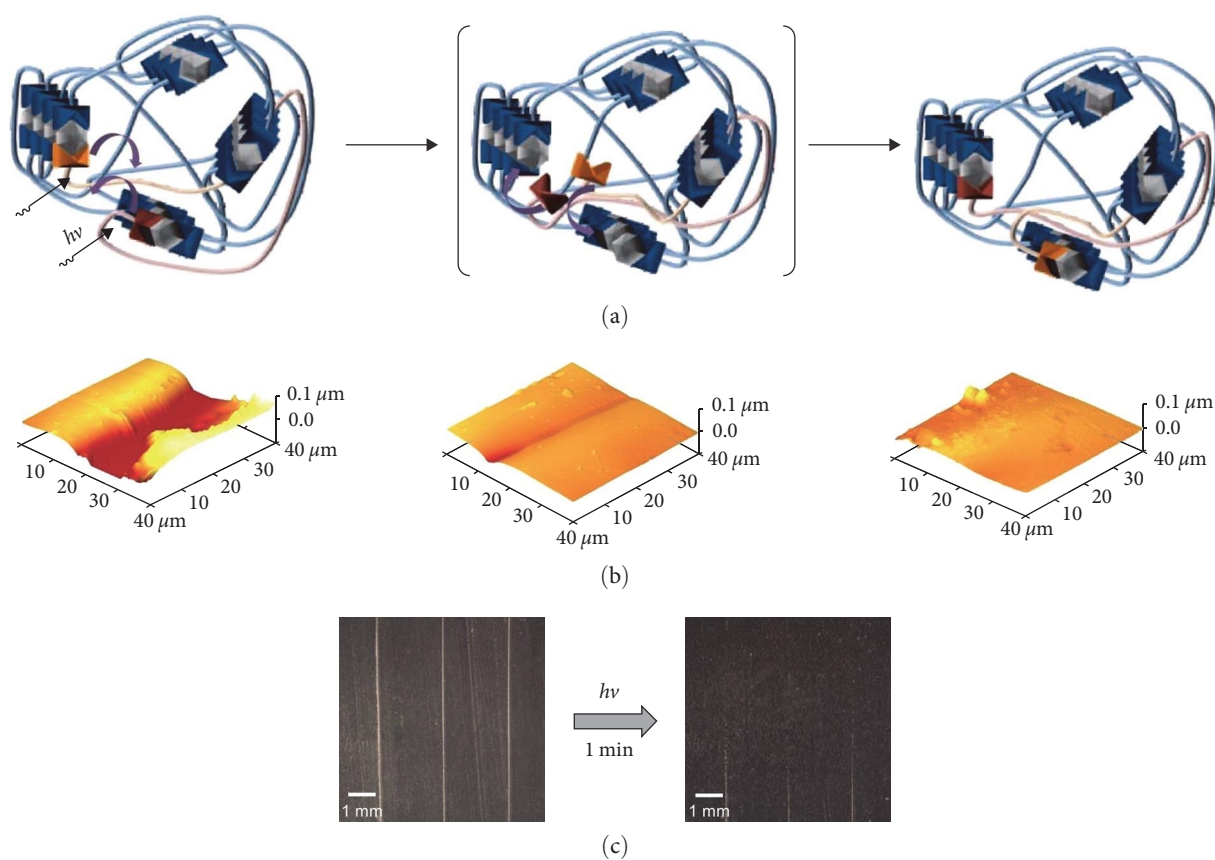

(a)

(b)

(c)

FIGURE 11: (a) Scheme of the optical healing mechanism of phase-separated MSP. (b) The height images (AFM) of a film that has been damaged and treated with 100% La^{3+} are depicted, displaying the film's conditions prior to healing (left), subsequent to partial healing (middle), and finally complete healing (right). (c) Images of how UV light was used to repair a polymer film prepared with 70% Zn^{2+} using UV light (320–390 nm). Reprinted with permission from ref. [85].

experimentally correlated with the lifetime of metal–ligand interactions. The onset and magnitude of shear thickening depend on the number of added cross-linkers. The lifetime of network relaxation increases during shear thickening, which is in contrast to the behavior of most transient networks.

Zhao et al. [98] also reported a shear-responsive metallo-supramolecular gel from the telechelic polymers polyethylene glycol (PEG) terminated with the tridentate Mebip ligand and coordinated as chain extender with Zn^{2+} metal transition or as cross-linker with lanthanide ions La^{3+}. The mixture of 3 mol% La^{3+} salt of the Mebip–PEG–Mebip macromonomer followed by 97 mol% Zn^{2+} salt in a solution of CHCl$_3$/CH$_3$CN resulted in spontaneous gelation (Figure 13).

The rheological modulus decreased rapidly to 200 Pa with increasing shear stress. This suggests that the network structure collapsed owing to the disassembly (or splitting) of
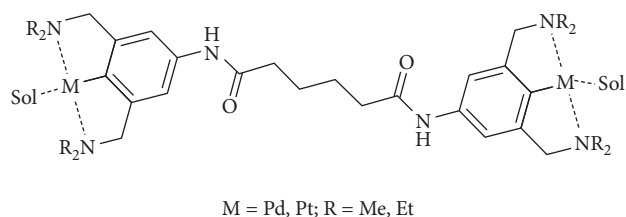
M = Pd, Pt; R = Me, Et

FIGURE 12: Supramolecular polymer gels were formed using poly(4-vinylpyridine) (PVP) and bifunctional aminophenylene metal complexes. Sol represents solvent.

the metal–ligand interactions. The network loss was caused by the formation of dangling ends instead of cross-links due to exposure to a large sol fraction. The sol phase can contain free Mebip ligands and/or more complex self-assembled structures. It took 18 min to gradually restore the network structure, during which the dangling ends were bound back to their original state. Network reconstruction in the gel phase was a stepwise process. Initially, network loss occurred *via* the formation of 2:1 Mebip: La^{3+} or Mebip: Zn^{2+} complexes with many dangling chain ends. In the final step, the 2:1 Mebip: La^{3+} complexes are transformed into 3:1 Mebip: La^{3+} cross-linked complexes and/or 2:1 Mebip: Zn^{2+} complexes that connect the loose chain ends. An alternative mechanism might involve hierarchical cross-linking species through the metal-ion-induced self-assembly of Mebip-PEG-Mebip, followed by aggregation and subsequent gelation. The elastic modulus of the fully reconstituted gel is slightly higher than that of the newly formed gel.

There's also ultrasonication of supramolecular coordination polymers of poly(THF) with diphenylphosphine or dicyclohexylphosphine and Pd^{2+} ions as the terminal units reported by Paulusse et al. [99, 100] The GPC investigation revealed that the supramolecular coordination polymer molecular weight decreased following several hours of ultrasonication, indicating that the coordination bonds had been broken. In initial studies [99], phosphine-free chain ends triggered a series of ligand-exchange reactions terminated by chain-end recombination. Therefore, the sonication process only results in redistribution and does not lead to chain reduction (especially molecular weight, Mw), as expected. The stable fragments observed by GPC analysis were assigned to the ring species (macrocycles). In a second study [100], it was easier to quantify the reduction in the DP and Mw observed by GPC, because the coordination polymer was kinetically inert and did not re-equilibrate during the experiment. The efficiency of sonication was much higher in the early stages, when longer chains were still present, than in the final hours. These results demonstrate a chain-length dependence of cleavage rates, consistent with longer chains being more susceptible to cleavage. Paulusse et al. [101] further studied sonication-responsive supramolecular coordination polymers. The network was shaped from poly(THF) carrying diphenylphosphine units coordinated to rhodium (Rh^I) and iridium (Ir^I) metal ions, leading to stable gels at RhI and IrI concentrations above 50 and 30 g/L, respectively. Studies of both coordination networks (100 g/L) revealed that the elastic
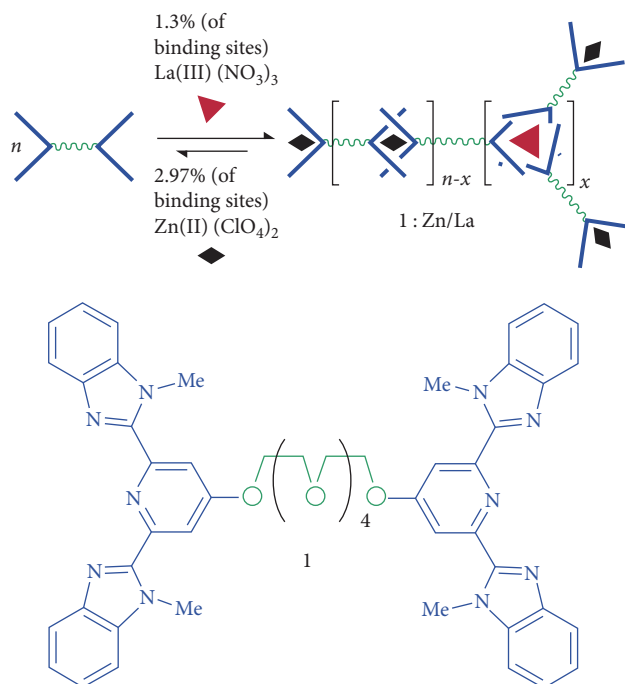

1 : Zn/La

FIGURE 13: Schematic representation of MSP gel-like material formation using a combination of lanthanides and transition-metal ions mixed with macromonomer 1. Reprinted with permission from ref. [100].

moduli remained constant over a broad frequency range, indicating a similarity to the gel. The iridium gel system had an elastic modulus of 28 hPa, which was higher than that of the rhodium gel system (10 hPa). The iridium gel underwent gel-to-sol transition upon ultrasonication over a time gap of 3 min.

After the sonication was stopped, the mixture turned into a gel. The rhodium gel was restored faster (1 min) than the iridium gel (1.5 hr) at room temperature and within 10 days at −20°C. The results of ^{31}P NMR measurements revealed that the re-gel of iridium complexes a considerable amount of time in comparison to the rhodium complexes, corresponding to their trends on ligand exchange kinetics. This difference was attributed to the lower ligand exchange rates when moving from the second row of d-block metals (rhodium) to the third row (iridium).

Sonication-induced gelation of solutions has also been used by Naota et al. [102, 103]. They reported lower-Mw binuclear Pd(II) complexes in various organic solvents made from Pd(II) acetate and N,N'-bis(salicylidene)-1, n-alkanediamine (n = 5–8) [103]. Among these binuclear complexes, solutions of the anticomplex (n = 5) in acetone (12 mM) gelled after sonication (0.45 W/cm^2, 40 KHz) at 20°C for 3 s. Gelation occurs in other solvents, such as TCE, dioxane, and ethyl acetate, at different concentrations and longer times (10 s). The solution remained stable at room temperature without sonication. Heating these gels resulted in the initial sol state, because these transitions (gel to sol and *vice versa*) were fully reversible. In contrast, brief sonication induced the interaction of the appropriate anti-complex to form linear MSPs through π–π stacking interactions, resulting in gelling. The anticomplex adopts a conformation similar to a
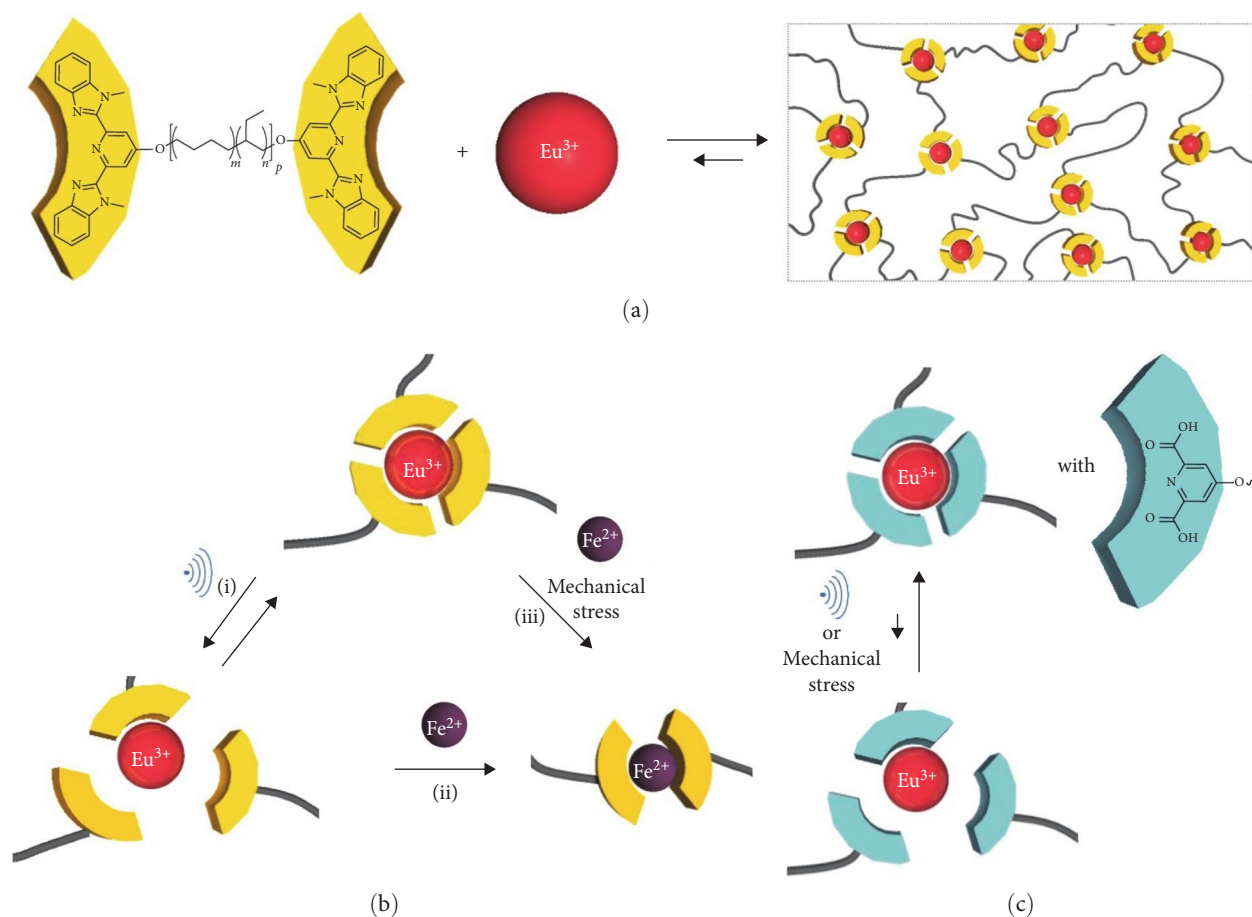
FIGURE 14: (a) Formation of MSP networks $[Eu(BKB)_{1.5}](ClO_4)_3$. Reversible dissociation reaction of Eu^{3+}ligand complexes in $[Eu(BKB)_{1.5}]$ $(ClO_4)_3$ upon ultrasonication to the MSP illustrated in (b); irreversible metal exchange with Fe^{2+} ions in films of $[Eu(BKB)_{1.5}](ClO_4)_3$ by (ii) ultrasonication, or (iii) puncture application. (c) Dipicolinic acid (dpa) ligands deprotonated bind strongly to Eu^{3+}, and the metallosupramolecular networks with the formula $[Eu(DKD)_{1.5}](NHEt_3)_3$. Reprinted with permission from ref. [104].

clothespin, which prevents aggregation without sonication. Sonication causes a self-locking conformation, which results in an unprecedented assembly of polymeric aggregates.

These studies showed changes in the viscoelastic properties and sol–gel as a response (*vide supra*), but this time with MSPs. The viscoelastic properties of solutions strongly depend on the strength of the metal–ligand motif, which closely depends on the kinetics and dynamics of this interaction.

Our work by Balkenende et al. [104], published in the *Journal of the American Chemical Society*, details the creation of a mechanically sensitive MSP. When combined with europium perchlorate $(Eu(ClO_4)_3)$, BKB resulted in a mechanically mechanical triggered MSP (Figure 14(a)) with the formula $[Eu(BKB)_{1.5}](ClO_4)_3$.

The rationale behind the design of the MSPs was influenced by the fragile and dynamic nature of Eu^{3+}-Mebip complexes. These complexes served as supramolecular mechanophores and internal optical probes to measure the assembly of dynamic binding motifs. Ultrasound sonication of the MSP in a dilute solution led to changes in the photoluminescence of the Eu^{3+}: Mebip complex, ranging from red to bluish. The reversible nature of this change, observed within minutes of stopping sonication, indicated the disassembly and reassembly of the Eu^{3+}-Mebip complex, following first-order kinetics. The time associated with the pulse corresponds to a percentage of assembly, and the reassembly or recovery followed this time of ultrasonication (Figure 15 (b)). By the way, the ultrasonication of a low-molecular-weight model complex $[Eu(MebipC_{12}H_{25})_{1.5}]$ $(ClO_4)_3$ between monotopic $MebipC_{12}H_{25}$ and Eu^{3+} resulted either in no change of emission, neither in disassembly (Figure 15(e)). The dodecane chain was too small to generate the ultrasound-induced mechanochemical force required for ligand dissociation, which supports the conclusion that ultrasound-induced dissociation of the Eu^{3+}-Mebip complex is indeed driven only by mechanochemical transduction.

Mechanochemical transduction was explored in the solid state, demonstrating the potential for healing or repairing damaged objects through exposure to ultrasound. Additionally, mechanical stimuli induced a color change in the MSP film when swelled with a Fe^{2+} salt. Despite the film not changing color until reaching equilibrium after 5 days, mechanical force, such as puncturing with a needle, caused a rapid shift to a deep purple hue characteristic of the Fe^{2+}-MeBip complex. This change was accompanied by the switching off of Eu-based fluorescence, indicating the irreversible mechanically induced exchange of the Eu^{3+} complex with Fe^{2+} (Figure 16).
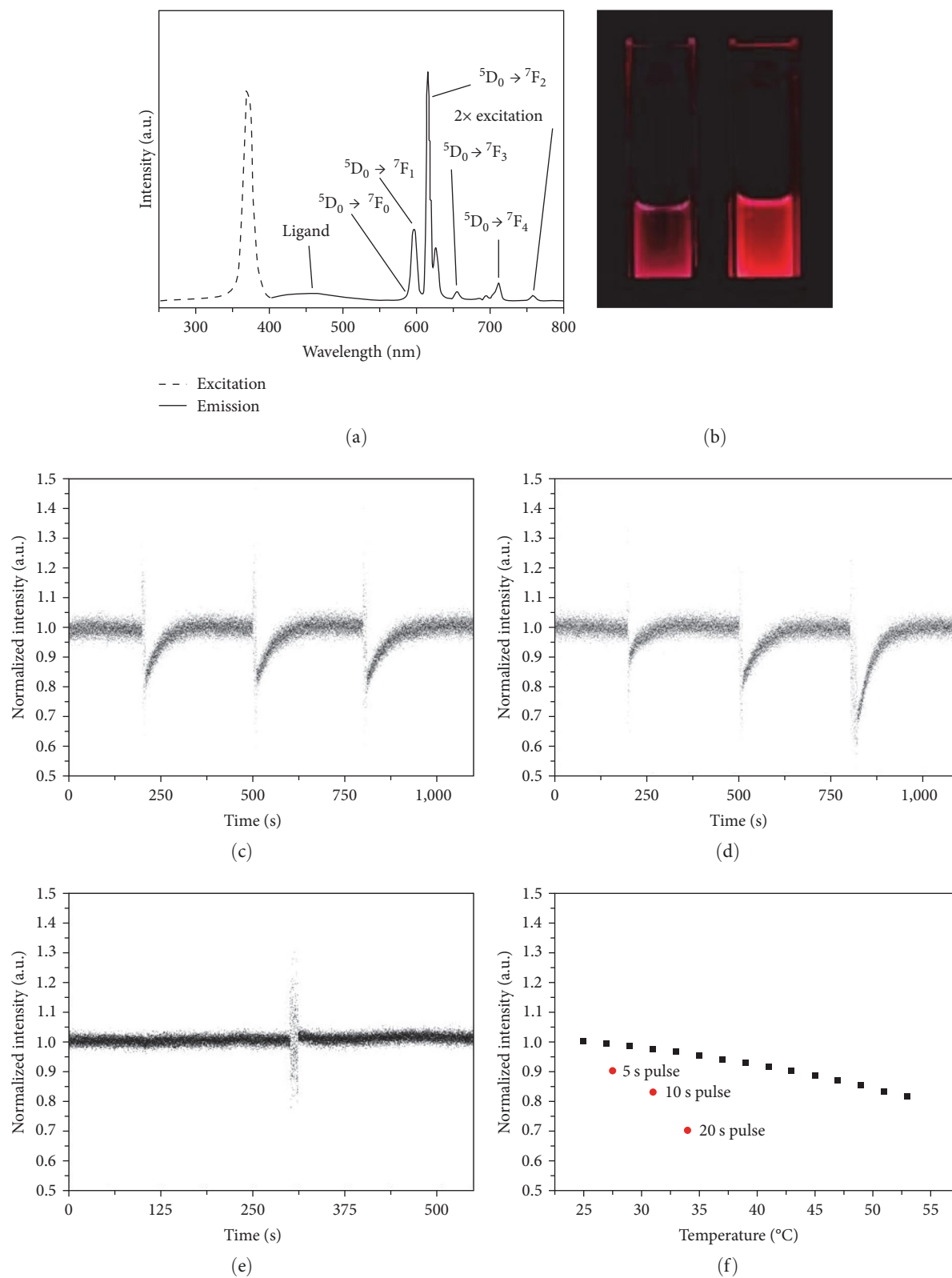
(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 15: Photoluminescence spectroscopy was used to monitor the dynamics of dissociation of metallosupramolecular polymers by ultrasound. Reprinted with permission from ref. [104].
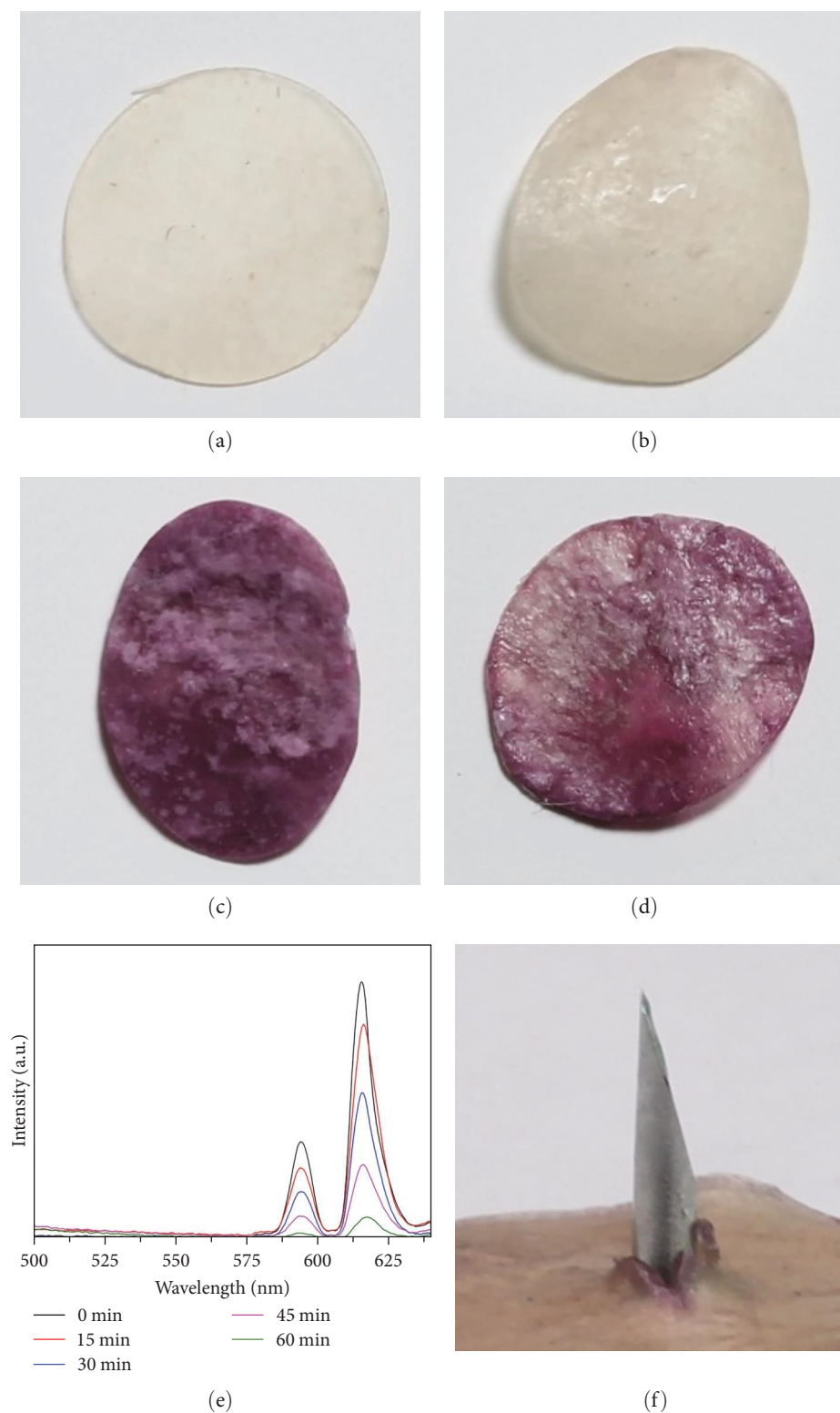
Figure 16: Mechanically induced metal exchange occurs in $[Eu(BKB)_{1.5}](ClO_4)_3$ films. Photos of $[Eu(BKB)_{1.5}](ClO_4)_3$ films before (a) and after (b) swelling in an iron solution in acetonitrile for 5 days. (c) The image depicted here is of a film that underwent the same process as in (b) and then subjected to ultrasonication for 45 min in iron solution. (d) Same process such in (c) with 60 min ultrasonication. (e) When ultrasonication was performed in iron solution, the emission spectra of the $Eu(BKB)_{1.5})(ClO_4)_3$ film changed over time using a fiber-optic cable and excited at 365 nm. (f) Image of a $[Eu(BKB)_{1.5}](ClO_4)_3$ film (bottom) swollen in a $Fe(ClO_4)_2$ solution for 24 hr and then punctured with a needle. Reprinted with permission from ref. [104].
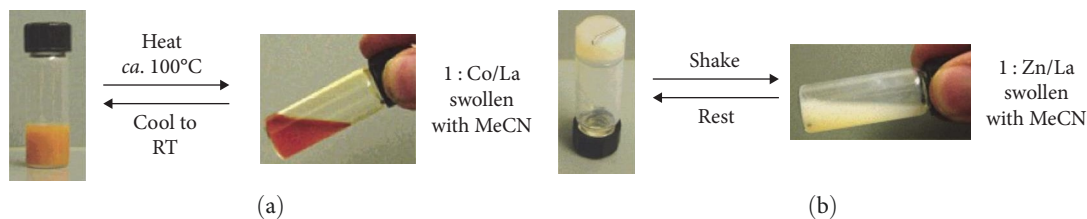
1.2.4. Multistimuli-Responsive MSPs. Several works on MSPs focus on a single specific activity responding to a particular stimulus (Figure 17). However, biological systems are designed in such a way that very often require multistimuli with multi-responsive (MSMR) materials. It is more difficult to find materials that respond to two or even several stimuli in an orthogonal way. The idea of specifically designing MSPs with MSMR has gained significant attention in recent years. The aim is to mimic biological systems that have evolved to adapt and respond in complex ways to various environmental stimuli exhibiting a wide range of complex properties and functions.

(1) Multistimuli-Responsive Metallosupramolecular Gels. Supramolecular polymer materials that respond to two or more stimuli are important components in the field of smart materials. Most examples published on this topic address the combinations of temperature and other stimuli. Almost all supramolecular interactions are temperature-sensitive (*vide supra*). Temperature is the most widely used stimulus among all stimuli. To yield multistimuli and/or multiresponsive supramolecular polymers, research has focused on thermo-pH-responsive [105, 106], thermochemically responsive [107, 108], thermo-photo responsive [109, 110] and thermo-redox responsive [111] systems.

For instance, Beck and Rowan [67] reported multistimulus, multiresponsive MSPs based on a combination of metal transitions and lanthanide ions combined with the Mebip ligand as termini with PEB core. These MSPs gel-like materials prepared with Mebip-PEG-Mebip mixed with Co^{2+}/La^{3+}, Zn^{2+}/La^{3+}, Co^{2+}/Eu^{3+}, and Zn^{2+}/Eu^{3+} showed thermoresponsive behavior. For example, Mebip-PEG-Mebip:Co^{2+}/La^{3+} resulted in a reversible gel–sol transition at approximately 100°C after heating. When bound to Co^{2+}, Mebip–PEG–Mebip gave an orange emission, whereas when bound to Zn^{2+}, the gel was slightly colorless. But when the temperature got higher, the orange color of Mebip–PEG–Mebip:Co^{2+}/La^{3+} stayed in the solution. This means that only the La^{3+}–Mebip interactions were broken.

The mechano-responsive (thixotropy) behavior in this material was also shown; when shaken, Mebip–PEG–Mebip:Zn^{2+}/La^{3+} turns into a flowing liquid, and the material regelled after about 20 s. The photoresponsiveness of these materials was investigated by examining the "antenna effect" of the Mebip ligand for Eu^{3+} ions, which exhibited a significant luminescence in the presence of a suitable UV wavelength. As expected, Mebip–PEG–Mebip:Zn^{2+}/La^{3+} displayed only a metal-bound ligand-based emission (397 nm). The low-energy metal-centered levels [112], which aid the decay processes, are likely to cause Mebip–PEG–Mebip:Co^{2+}/Eu^{3+} to exhibit no

luminescence. The nature of the metal can be controlled through the photoresponsive behavior of these materials.

Furthermore, the chemo-responsiveness of the MSP Mebip–PEG–Mebip Zn^{2+}/Eu^{3+} was demonstrated. The affinity of lanthanides for binding strongly to carboxylic acids is well-known. Hence, the addition of 0.85 weight% formic acid (HCOOH) to Mebip–PEG–Mebip Zn^{2+}/Eu^{3+} results in the loss of gel mechanical stability, while simultaneously causing the quenching of the Eu^{3+} emission. $HCOO^-$ moves the Mebip ligand away from the Eu^{3+} ions, which turns off the "antenna effect" of Mebip. The process is reversible, just by drying the material in *vacuo* at 40°C for 8 hr, and an increase in Eu^{3+} emission was observed upon inflating the material with acetonitrile.

Weng et al. [113] used the same metal–ligand interaction to make a Mebip unit attached to the end of a penta(ethylene glycol) (PEG) core, themselves. The macromonomer generated gels in the presence of only Zn^{2+} or Zn^{2+} with a small amount of La^{3+}. The resulting materials displayed remarkable reversible responses to various environmental conditions, including heat, pressure, and chemical stimuli. An examination of the MSP revealed that there was a formation of crystals and phase separation during gelation. Spherulite particles that emerged were frail and highly sensitive to mechanical changes, resulting in a thixotropic behavior. Although the gel condition was restored after shearing, the particles slowly broke into smaller particles as a function of mechanical stress. Once the stress was eliminated, the gel strength increased significantly. The gels that were generated through sonication exhibited the highest resistance, which was attributed to the interactions between the particles resulting from increased contact with the surface. The metal salts used to shape the gels can be adjusted to make them more sensitive. When using gels with noncoordinating counterions like perchlorate, they tend to exhibit lower yield stress than gels made with lanthanide salts that have competing counterions like nitrate or gels made only with metal transition Zn^{2+} salts. The formation of Mebip:La^{3+} complexes with a 3:1 ratio led to branching or cross-linking sites and a subsequent decrease in crystallinity in the supramolecular species.

Similar multistimuli-responsive MSP gels based on a binaphthylbisbipyridine-Cu(I) complex were reported by He et al. [112]. This novel class of chiral MSP organogels was achieved in hot $CH_3CN–CH_2Cl_2$ (1:1 v/v), followed by cooling to room temperature with a minimum gel concentration of 10 mM. The formation of a red gel was solely

feasible through the utilization of equimolar molar ratios between the ligand and $Cu(CH_3CN)_4BF_4$. Another crucial aspect was the nature of the counterion, wherein triflate (TfO^-) and iodine ions (I^-) produced either a solution or a precipitate, respectively. The length of the spacer unit between the bipyridine and binaphthyl rings in the ligand had an impact on gelation as well. The gelation process takes longer when the spacer is longer.

(2) Multistimuli-Responsive MSPs in Solid State. Kumpfer and Rowan [73] prepared and studied a series of films that respond to stimuli based on MSPs. The MSPs were prepared using Mebip ditopic end-capped poly(THF) with different ratios of Zn^{2+} and Eu^{3+}. The optical properties of the Eu^{3+} complex and its more labile nature have led to the development of highly multistimuli-responsive materials. The onset of a temperature or exposure to compounds such as triethyl phosphate, which resembles to organophosphate pesticides and nerve gas agents, results in a noticeable optical response in MSP films containing Eu^{3+}. An analysis of the thermomechanical properties of the MSP films was performed to investigate the effects of varying the $Zn^{2+}:Eu^{3+}$ ratio. The results were achieved by performing a DMTA on various films ranging from $Zn^{2+}:Eu^{3+}$ 100:0 to $Zn^{2+}:Eu^{3+}$ 50:50. Before cooling, the films were annealed at $-35°C$ for 1 hr in order to avoid cold crystallization of the poly(THF) cores. Two additional transitions were observed: T_g ca. $-80°C$ (attributed to the T_g of poly(THF) in the soft phase) and the melting temperature (T_m) of the low-molecular-weight poly(THF) segment, which occurs around $0°C$ (attributed to the hard-phase metal ligand complexes). Higher temperatures revealed temperature-dependent thermomechanical properties of these films. Most films that are more sensitive to heat have less $Zn^{2+}:Eu^{3+}$. The trend toward thermally responsive Eu^{3+}-containing films can be explained by different factors. The strength of binding between Eu^{3+} and Zn^{2+} is the first. As previously demonstrated, Eu^{3+} binds weaker to Mebip than Zn^{2+} ions. As a result, films with a high proportion of Eu^{3+} are expected to exhibit a more robust thermal response. In this regard, it appears that the mechanical characteristics of these films are correlated with phase separation between the metal complexes and core (*vide supra*).

Heating the 70:30 $(Zn^{2+}:Eu^{3+})$ film to around $120°C$ caused a shift in luminescence emission from pink to blue, as observed in Figure 18. Photoluminescence studies confirmed that the temperature increase led to the disappearance of Eu^{3+}-based emission, indicating greater thermomechanical sensitivity due to thermally sensitive Eu^{3+} complexes. Upon removal of the light source, the reappearance of a pink color suggested the recomplexation of Eu^{3+} to Mebip ligands. The material demonstrated potential as a chemical sensor, particularly in detecting nerve gas agent mimics such as triethyl phosphate [88]. Exposure to triethyl phosphate quenched the Eu^{3+}-based luminescence, and the removal of the agent resulted in the reversible return of red luminescence, showing the reversibility of the process.

Similarly, Kumpfer and Rowan [89] developed multiresponsive shape-memory films using poly(butadiene) end-capped with Mebip and coordinated with a metal salt.

They employed a tetra-functional thiol for covalent cross-linking of the films [89]. The poly(butadiene) soft phase underwent cross-linking through a thiol-ene reaction, facilitated by low-intensity light in the range of 320–390 nm, as illustrated in Figure 19.

The study investigated the impact of cross-link density and metal salt nature on the shape-memory properties of films through standard memory shape tests (Figure 20). The metal–ligand hard phase played a crucial role in temporary shape fixation and release. Thermal shape-memory studies using DMA revealed that warming the sample above $50°C$ induced shape memory. After heating to $100°C$ and applying a force of 0.5 N, the sample exhibited a fixed shape, with subsequent heating and cooling recovering the strain. Films showed high initial strain fixing values (R_f) and recovery values (R_r) above 90%. UV light, used to remotely activate shape-memory properties, caused localized heating and uncoordination of Eu^{3+}, turning the film blue. Removal of the light source led to the return of red emission. Shape-memory responses under DMTA and light irradiation were similar to nonirradiated controls, indicating light-heat conversion induced the observed behavior. SAXS revealed structural effects, with the permanent shape having a peak at 8.6 nm. Light exposure caused a peak shift to 9.8 nm during strain fixing, and 8.7 nm was recovered after light exposure.

Films incorporating diverse metals or counterions were prepared, specifically $Zn(NTf_2)_2$ and $Zn(OTf)_2$, and compared to $Eu(NTf_2)_3$ films. Shape-memory tests revealed that both the metal and counterions were unaffected by shape-memory recovery. Notably, changing the counterion from bistriflimide (NTf_2^-) to triflate (OTf^-) resulted in a significant decrease in fixed values, with a 16% reduction observed for $Zn(OTf)_2$ films compared to $Zn(NTf_2)_2$, and a 21% decrease compared to $Eu(NTf_2)_3$ films. This decrease was more pronounced after 1 hr, with $Zn(OTf)_2$ exhibiting a fixing value of only 40%. The shift to a triflate counterion required higher temperatures to disrupt phase separation in the "hard" metal–ligand phase.

Investigation of the mechanical properties of noncross-linked films with different metal salts showed distinct thermal behaviors. The films' modulus values, T_g (or T_m), and/or order–disorder transition was attributed to variations in the thermal stability induced by different metal salts. The $Zn(OTf)_2$ film, with lower modulus values, demonstrated mechanically stable qualities above $150°C$, requiring substantially higher temperatures to disrupt phase separation compared to the $Eu(NTf_2)_3$ film.

Additionally, the chemo-responsive shape-memory effect was explored by examining the recovery of the permanent form under the influence of solvents such as methanol. Results indicated that methanol plasticizes the metal–ligand (hard phase), inducing shape-memory qualities without competitive binding. This study provides insights into the role of metal salts in shaping the mechanical and shape-memory properties of polymer films [114].

MSPs that exhibit structural or conformational changes in response to various stimuli, either in solution or in the solid state, are very important. These changes represent
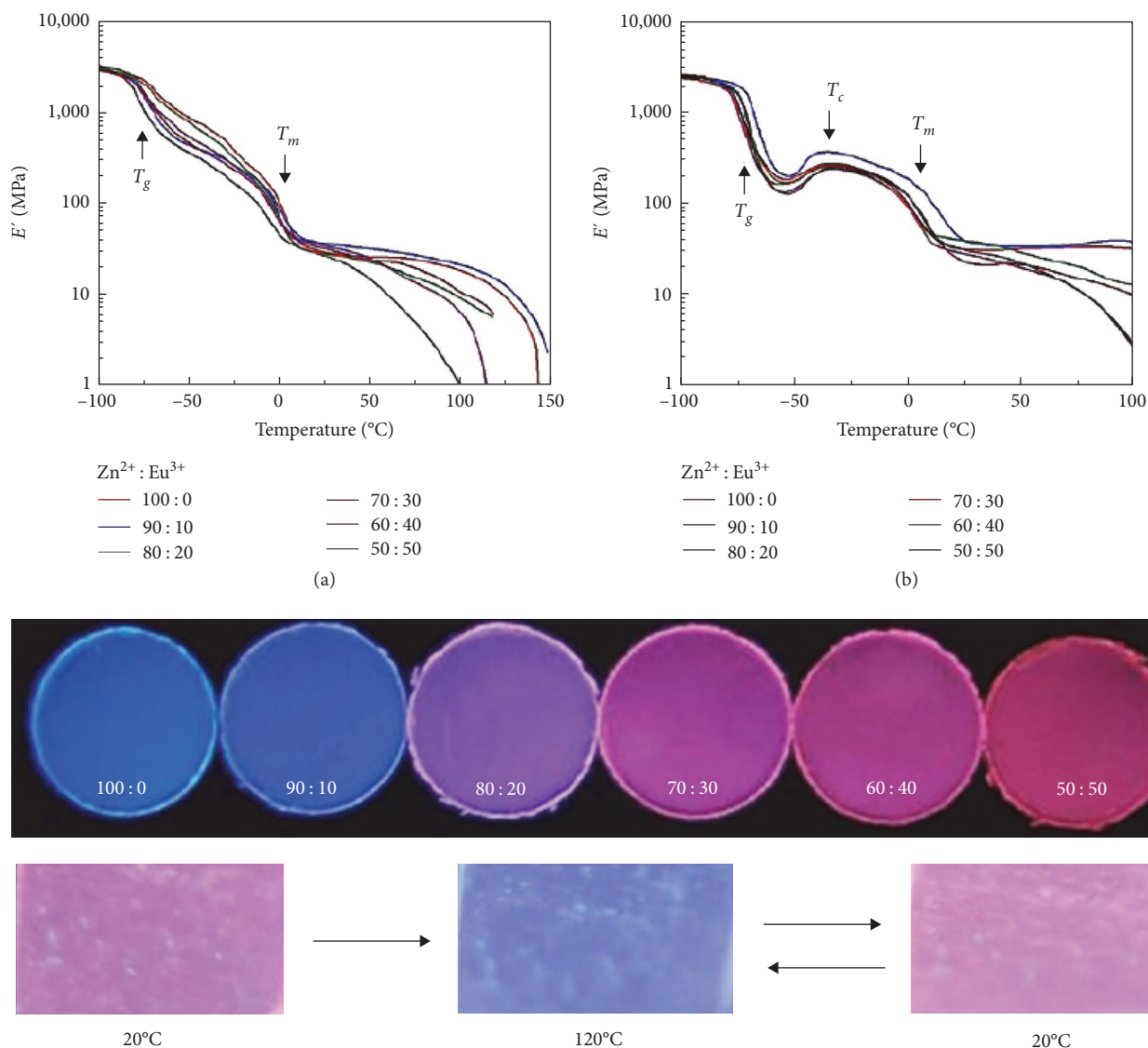
FIGURE 18: (a) A DMTA of solution-cast films with $Zn^{2+} : Eu^{3+}$ ratios ranging from $100 : 0$ to $50 : 50$ is shown in the top image. Prior to testing, samples were annealed at $-35°C$. (b) Samples were cooled directly to $-110°C$ at room temperature. In the middle, images of solution-cast films with different $Zn^{2+} : Eu^{3+}$ ratios ($100 : 0$ to $50 : 50$) show different luminescence colors between blue and red-pink under UV light (365 nm). (Below) Photographs of film luminescence under UV light (365 nm). Reprinted with permission from ref. [88].

macroscopic responses resulting from microscopic chemical events. While significant progress has been made in this field, there is still much work to be done, especially in developing highly functional materials, such as stimuli-responsive biological supramolecular systems. The emphasis is on the need for further advancements in constructing complex materials with specific responsiveness.

(3) Multistimuli-Responsive MSPs with Other Interactions that Closely Mimic Biological Systems. Until this section, the review highlighted systems featured a single type of noncovalent interaction. In contrast, biological systems employ a diverse array of noncovalent interactions, such as hydrogen bonding, metal coordination, and hydrophobic interactions, simultaneously or independently. These interactions contribute to the functionality, diversity, and complexity of biological

systems. Supramolecular polymers, influenced by spontaneous self-assemblies, play a crucial role, demanding various functions, well-defined structures, and controlled features for advanced applications. The advantages of these materials include rapid optimization through reversible functionalization, leading to highly advanced features responsive to external stimuli. The goal is to develop dynamic and optimized "smart" materials. Achieving this involves creating polymers with multiple noncovalent interactions that can be produced, deformed, and reversed predictably and controllably. This strategy allows tailoring material properties by leveraging changes in the nature of reversible interactions and multifunctionalization. However, a key challenge lies in ensuring the orthogonality of these interactions, where each noncovalent interaction should be independent or have a sufficiently slow effect on the same timescale as others
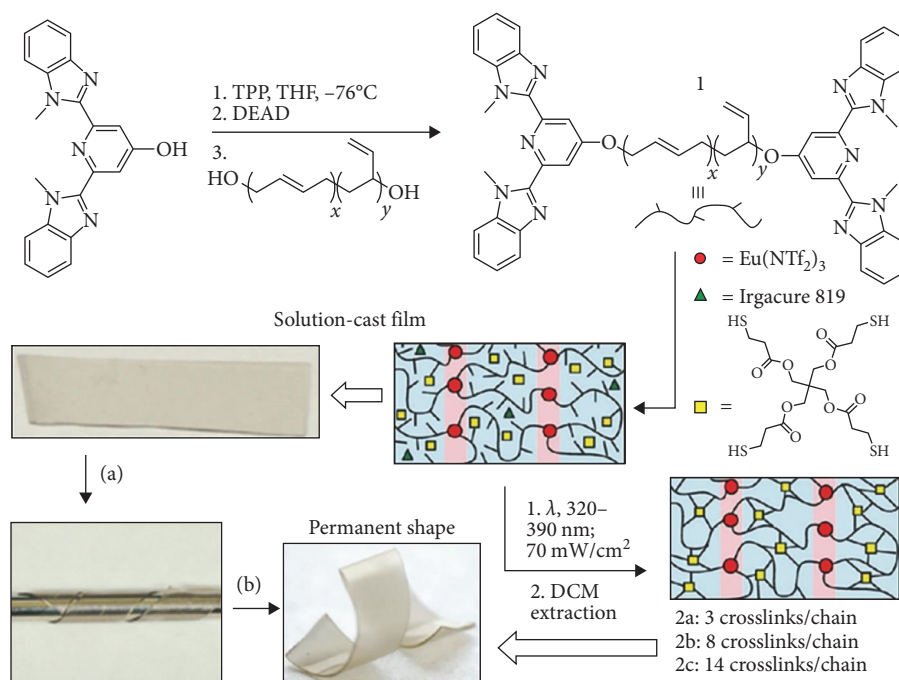
FIGURE 19: Synthesis of poly(butadiene) macromonomers with tetrathiol crosslinker and photoinitiator end-capped with metal ligands. Reprinted with permission from ref. [89].

[115]. While the dynamic nature of supramolecular properties is intriguing for stimuli-responsive systems, managing orthogonal functioning poses a considerable challenge.

South et al. [116] developed a modular polymer multifunctionalization method using pre-existing polymeric scaffolds featuring pendant units for hydrogen bonding, metal coordination, and coulombic interactions. The researchers demonstrated the creation of a range of materials derived from a common polymer backbone. They employed an orthogonal self-assembly strategy to achieve quantitative synthesis while ensuring the desired properties of the resulting materials.

Pollino et al. [117, 118] demonstrated the quantitative synthesis of a family of materials derived from a single polymer backbone through an orthogonal self-assembly procedure. They were the first to show the arrangement of hydrogen bonds and metal coordination in side-chain polymers in a straight line. The polymers were constructed around three-point hydrogen-bonded complexes of 2,6-diamino pyridine and N-butylthymine, as well as metal coordination based on a palladium bond. The orthogonality of these noncovalent interactions was confirmed through thorough investigations of hydrogen bonding strength using 1H-NMR spectroscopy or isothermal calorimetric titration. The key finding was that the strength of hydrogen-bonding interactions remained independent of the presence or absence of metal coordination sites. In a subsequent study, Pollino et al. [118] explored the impact of the polymer backbone structure on the orthogonality of these noncovalent interactions, creating block copolymers through ring-opening metathesis polymerization with each block functionalized by either hydrogen bonding or metal-coordinating moieties (Figure 21).

Along the side chains of the polymeric scaffolds, block copolymer 1 comprised 2,6-diaminopyridine and a palladated SCS pincer moiety with N-butylthymine and pyridine as complementary recognition moieties, respectively. Block copolymer 2 employs thymine and nitrile functional moieties as complementary recognition moieties covalently bonded to polymer side chains with the same moieties, such as polymer 1. There was no influence on the strength of the hydrogen-bonding interactions along the polymer backbones regardless of the DP, block copolymer composition, and metal coordination.

This shows that metal–ligand coordination and hydrogen bonding are orthogonal to each other in the block copolymers. They also reported that the position of the hydrogen-bonding connections (covalently connected to the backbone or as a complementary recognition moiety) had a minimal impact on both the strength of the hydrogen-bonding interactions and the solubility of the copolymers. Despite the inclusion of ADA–DAD units in both block copolymers, the 2,6-diaminopyrimidine in block 1 exhibits a low tendency for dimerization, resulting in higher association constants than thymine in block 2, which dimerizes and contributes to lower association constants (∼10%–30%). Furthermore, the effect of metal location on the copolymers was investigated. The use of a suitable solvent resulted in quantitative metal coordination, which did not interfere with or interact with hydrogen bonds during the coordination step. These investigations revealed that the strength of the hydrogen-bonding interactions was slightly influenced by the location of the functional groups covalently attached to the polymer. The polymer composition and structure were not affected by the alignment of these phenomena. Both hydrogen
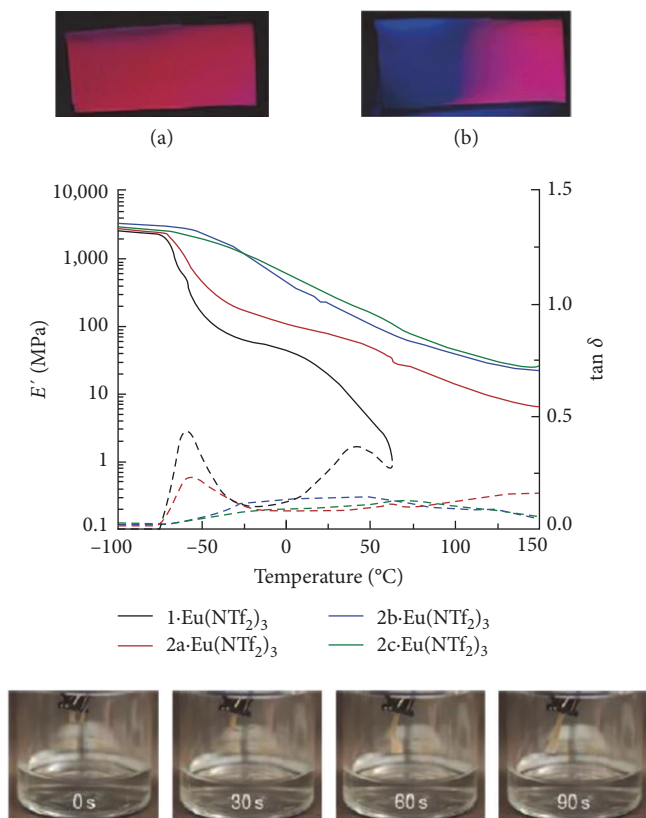
FIGURE 20: (Top) Cross-linked film image 2b. Eu(NTf$_2$)$_3$ in its permanent shape (a) under low-intensity (70 mW/cm^2) UV light and (b) under high-intensity (1,000 mW/cm^2) UV light selectively irradiated the left side of the film. (Middle) DMTA of unrelated films 1. Eu(NTf$_2$)$_3$ with cross-linking 2a–c. Eu(NTf$_2$)$_3$. Enhancement of the mechanical properties beyond 40°C, at which time the uncrosslinked film flows. Increasing cross-linking suppresses T_g. (Below) Photo depicted the chemo-responsive shape-memory behavior of 2b. Eu(NTf$_2$)$_3$ films prepared in methanol. Reprinted with permission from ref. [114].

bonding and metal coordination interactions are, in the end, orthogonal.

Furthermore, work done by Hofmeier et al. [120] used 2-ureido-4[1H]-ureidopyrimidone (UPy) as molecules containing quadruple hydrogen bonds, and metal complexes with terpyridine units were designed and assembled to form a supramolecular polymer, where both interactions were present in the main chain of poly(ε-caprolactone). Solid-like behavior was observed at room temperature. The dynamics of the metal–ligand interactions are responsible for the abrupt drop in melt viscosity at temperatures ranging from 100 to 127°C. The temperature of this transition was reduced to 70–80°C when iron was replaced with a zinc salt.

Other examples of H bonds and coordination interactions have been used in dendritic systems [113], Hamilton receptor and terpyridine motif polymers [120], or in triblock polymers [121].

Therefore, it is critical to investigate the response of these polymers to diverse stimuli. Some stimuli employed in this study have been shown to exhibit unexpected behavior in solution or solid form, and a thorough analysis should be conducted to explain or rationalize their behavior.

The following section discusses the exploration of materials inspired by nature, involving the combination of MSP (multistimuli-responsive polymers) and other noncovalent interactions. This approach aims to integrate orthogonal features, leading to the development of smart materials. The focus is on the emerging field of multistimuli-responsiveness, where materials exhibit responsiveness to multiple stimuli due to the incorporation of different supramolecular interactions. While initial experiments were mainly conducted in solutions, the section highlights the rarity of examples involving solid materials with various supramolecular interactions that offer orthogonal responses to stimuli. The Weder group has reported two types of new material platforms featuring two orthogonally bound supramolecular networks [59, 122].

Coulibaly et al. [59] showed supramolecular polymer blends by combining two supramolecular polymers with the same poly (ethylene-co-butylene) core. These blends incorporated "orthogonal" noncovalent binding motifs, specifically hydrogen bonding and metal–ligand coordination. Through careful selection of components, we achieved orthogonal binding and multistimulus responsiveness. The degree of orthogonality was investigated using techniques such as SAXS and DMTA. In the solid state, the blends exhibited microphase-separated lamellar morphologies, with two hard phases formed by UPy stacks and metal–ligand motifs. DMTA experiments revealed distinct melting and disassembly temperatures for the two hard phases, highlighting the successful development of materials with differentiated responses to stimuli.

In an extensive study, Sautaux et al. [122] explored the utilization of the same binding motifs in orthogonally coupled supramolecular polymer networks, based on trifunctional poly(propylene oxide) with terminal 2,6-bis(1$'$-methylbenzimidazolyl)pyridine (Mebip) ligands or 2-ureido−4[1H]pyrimidinone (UPy) groups. The orthogonal binding of the metal–ligand complex and hydrogen-bonding motifs was confirmed through DMTA traces. The study found that the homopolymer networks (neat) were qualitatively identical, with differences in rubbery plateaus and failure temperatures (Figure 22(b)). The presence of a stable rubbery plateau in both materials was attributed to the hard-crystalline phase cross-linking of the PPO matrix. Higher binding motif content consistently resulted in higher E' (modulus). The DMTA trace of the blend $(M1)_2 − (M2 \cdot Zn(NTf_2)_2)1$, derived from the parent homopolymers, exhibited two distinct rubbery plateaus and sharp drops in modulus, supporting transitions observed by DSC (Figure 22(a)).

The DSC and DMTA data provided confirmation of the orthogonality of supramolecular bonds, affirming the capacity to selectively activate them through heat above their transition temperatures. This capability was leveraged to observe shape memory and selective healing behavior, where the dissociation of metal–ligand complexes or UPy dimers could be independently triggered either chemically or thermally.

Li et al. [123] developed a straightforward and efficient method for creating multistimulant intelligent gels, specifically
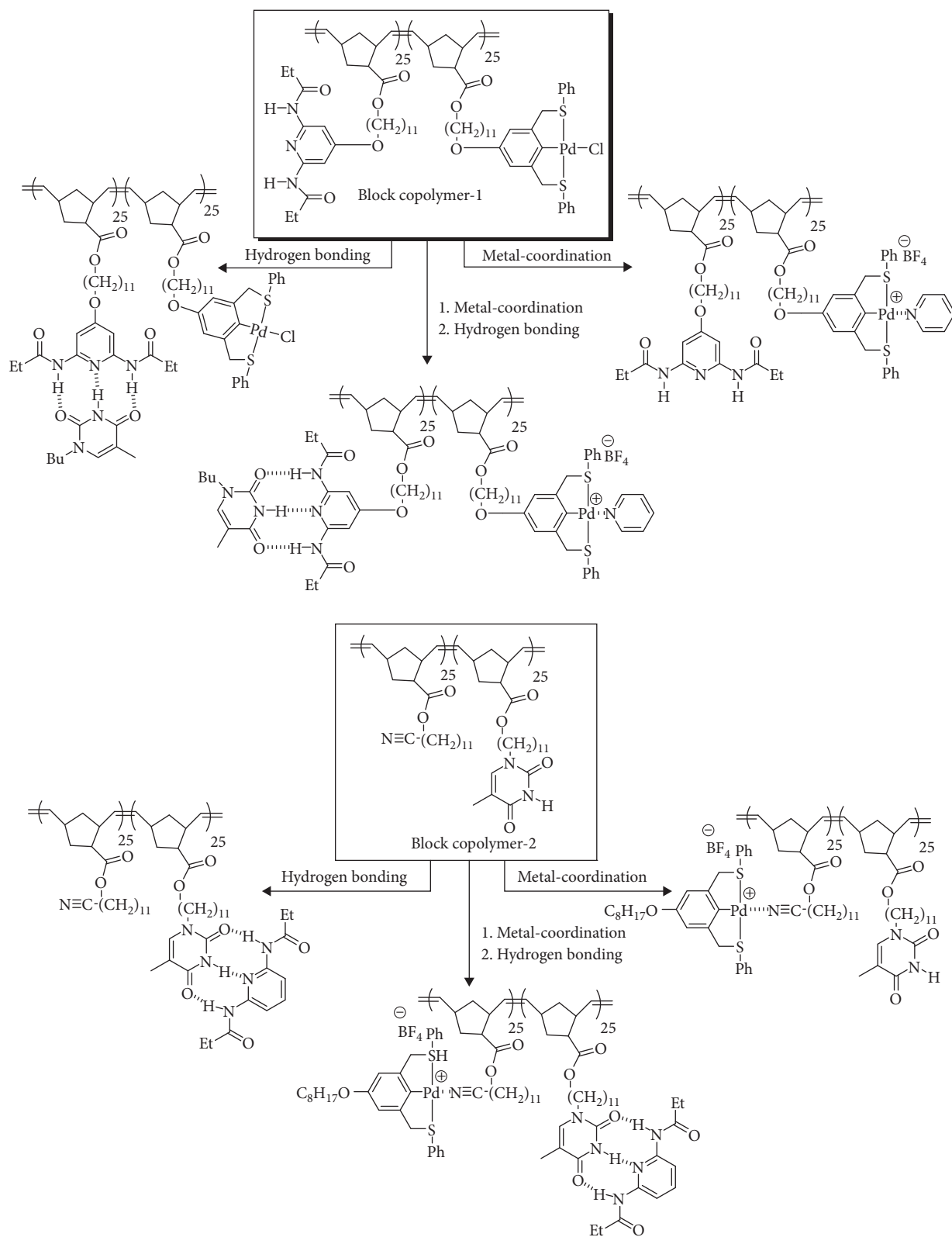
FIGURE 21: Illustration of side chain functionalization of diblock copolymers 1 and 2 using a dual combination of hydrogen bonding and metal coordination. Reprinted with permission from ref. [119].
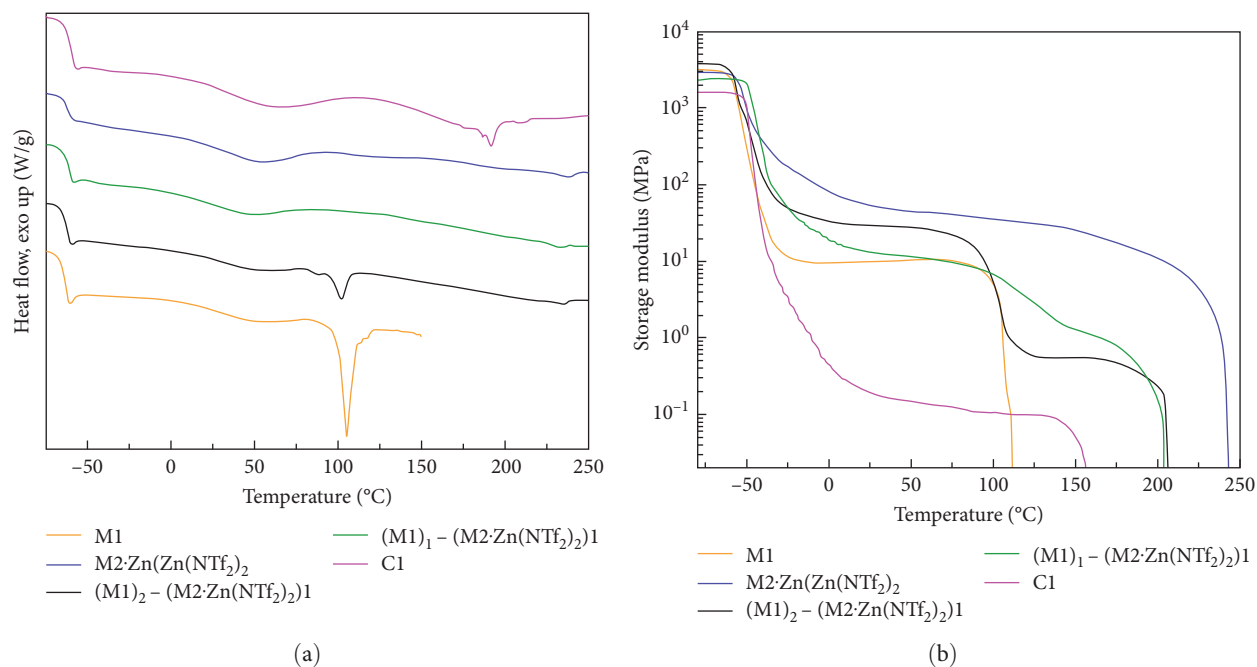
(a)

(b)

FIGURE 22: Depicts (a) differential scanning calorimetry (DSC) traces (first heating, 10°C/min) and (b) dynamic mechanical analysis (DMA, 5°C/min) traces of networks (Individual M1 and M2·Zn(NTf$_2$)$_2$), mixtures of M1 and M2· Zn(NTf$_2$)$_2$, and the covalent reference network C1. Reprinted with permission from ref. [122].

DSPy SHP5@Zn. This innovation broadens the range of intelligent supramolecular materials. The synthesis involved a double-arm pill[5]arene, SHP5, and a ditopic DSPy-invited molecule assembled to form the DSPy SHP5 structure. Characterization through various techniques, including ^{1}H and ^{13}C NMR, mass spectrometry, and FT-IR spectroscopy, confirmed the formation of intermolecular hydrogen bonds (−N–H… O = C−) between adjacent host-guest inclusion complexes [124] (Figure 23).

Dynamic light scattering (DLS) measurements showed that DSPy SHP5 had a mean hydrodynamic diameter of 295 nm, larger than free SHP5 and DSPy, indicating the assembly of monomers into large structures. To construct DSPy SHP5@Zn, a method by Ding et al. [125] was employed, involving the binding of a hydrazine derivative to Zn^{2+} and the assembly into a metallosupramolecular polypseudorotaxane. The stoichiometry of SHP5 and Zn^{2+} bonds was determined through the Job-plot method [126] based on ^{1}H NMR experiments.

Furthermore, the average diffusion coefficients by weight (D) increased from 8.55×10^{-11} (DSPy SHP5) to 7.44×10^{-11} m^2/s (DSPy SHP5@Zn), as indicated in Figure 23(c). DSPy SHP5@Zn exhibited a wider and larger distribution band centered at 4,150 nm, characteristic of the Tyndall effect [127], indicating the formation of large aggregates (Figure 23(d)). This work showcases a novel approach to constructing intelligent gels with potential applications in supramolecular materials.

Herbert et al. [128] dedicated a review focus on MSMR polymers, which are materials capable of responding to multiple and various stimuli in several and distinctive ways. Somewhat akin to living systems, they have evolved to adapt

and respond in complex ways to different environmental cues. Reports on MSMR polymers have been devoted to the investigation and perspective focus on solid materials.

2. Future Work

MSPs represent a promising class of materials with unique properties and functionalities. Despite considerable advancements in understanding the interplay between the configuration and functionality of these molecular self-assembled systems, a multitude of obstacles and prospects persist, thereby stimulating further avenues of investigation. Augmenting the steadfastness and resilience of molecular self-assembled systems assumes paramount importance in their pragmatic utilization across diverse environmental circumstances. Future investigations could concentrate on devising strategies to bolster their stability, particularly under extreme temperatures [129, 130], pH variations, and mechanical stresses, thereby unlocking their full potential across diverse settings. The dynamic nature of MSPs offers immense potential for stimuli-responsive behavior, yet there is room for exploring novel mechanisms and design principles to broaden their responsiveness to environmental cues. Research efforts could delve into identifying new stimuli-responsive mechanisms, including biological cues or specific chemical signals, expanding the utility of MSPs in dynamic material systems. Moreover, while MSPs hold promise across an array of applications such as electro-photochemistry [131], catalysis, magnetism, and thermochromism, translating these materials into practical applications necessitates further investigation. Future studies might explore uncharted territories, such as their utilization in biomedical devices [132], environmental remediation, or
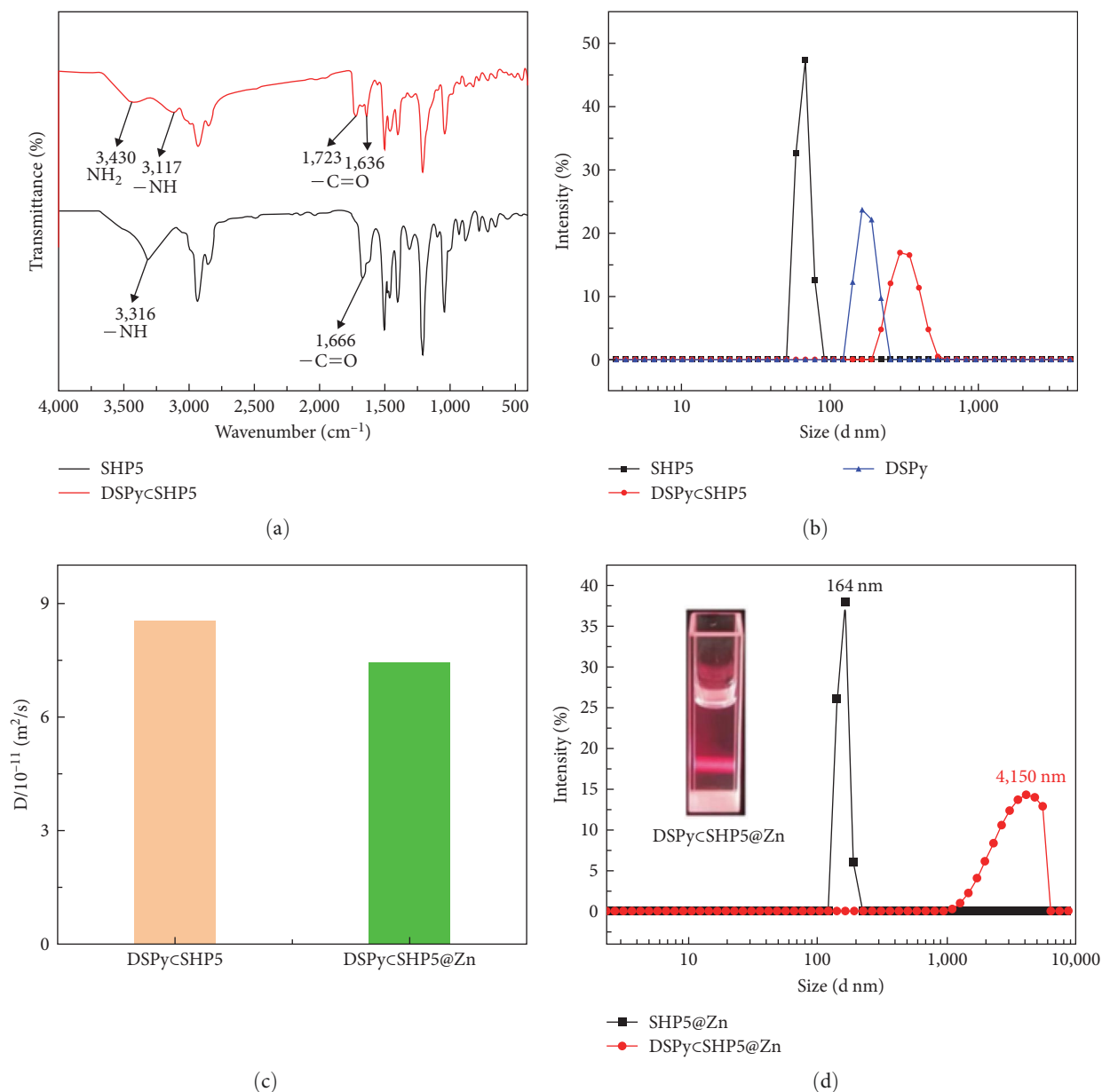
FIGURE 23: (a) FT-IR characterization of the host–guest assembly DSPy⊂SHP5. (b) DLS characterization of the host–guest complexation of SHP5 and DSPy. (c) Diffusion moyens en poids (*D*) du (DSPy⊂SHP5) et du (DSPy⊂SHP5@Zn). (d) Profiles of the SHP5@Zn and metallosupramolecular polymer network DSPy⊂SHP5@Zn. Reprinted with permission from ref. [123].

as components of advanced functional materials [133], thereby broadening the horizon of MSP applications. As the demand for sustainable materials continues to grow, future research on MSPs should also consider their environmental impact and sustainability. This could involve the development of MSPs from renewable resources, as well as the investigation of environmentally friendly synthesis routes and end-of-life considerations.

3. Conclusion

A considerable understanding of the fundamentals of supramolecular processes has been achieved, and the fruits of particular realizations, such as the assembly of large assemblies in supramolecular polymers, particularly MSPs, are truly impressive. Indeed, in the overall field, MSPs have used the metal centers as the structural element and the center of the functionality, with increasing emphasis on other interactions such as hydrogen bonding or π–π interactions. A key step is the differentiation between labile and kinetically inert metal centers, particularly the recognition that labile centers can be used to assemble thermodynamic MSPs, whereas inert centers can be used to obtain pseudocovalent polymers. The labile aspect, which was initially seen as a major disadvantage in obtaining materials with good physical properties, has become an enormous advantage, leading to stimuli-responsive materials (self-healing, shape-memory, sol–gel, adhesive, and generally) to adaptive

materials. Indeed, the use of (multi)stimuli to play on the thermodynamic equilibrium developed the degree of their functionality and their use as stimuli-responsive or "smart" materials. Currently, it is useful to develop synthetic supramolecular materials that are capable of mimicking the high complexity of supramolecular biological systems with multifunctionality.

Data Availability

The majority of data in this review are datasets under publications currently in journal articles cited in the review and also our own research published there. The list of structural databases provided in this guide are those that are recommended by major countries by journal publishers.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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