

Strategies for designing luminescent Metallo-supramolecular polymer networks

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ABSTRACT

Nature offers numerous examples of materials with extraordinary and multifaceted properties, like combined self-healing, stimuli-responsiveness, and luminescence. Inspired by such designs, chemists have tried to mimic such versatile properties by combining complex polymeric structures reinforced by supramolecular interactions, allowing them to perform multiple functions across various time and length scales. Among these efforts, metal coordination has emerged as a powerful tool to create dynamic, tunable systems. This review explores such innovative approaches in designing luminescent metallo-supramolecular polymer networks (MSPNs), which integrate the entanglement of polymer chains with the dynamic luminescent properties of metal-ligand junctions. Classified by the dimensionality of these junctions, from 0D, formed by single metal ion complexes, to 2D metallacycles, and 3D metallacages, MSPNs benefit from diverse functionalities of junctions, featuring the antenna effect in lanthanide-based 0D nodes and aggregation-induced emission (AIE) in 2D and 3D assemblies, on top of organic conjugated structures that can be integrated in the ligand structure. This initiative addresses the fragile nature and limited formability as one of the main classical barriers to commercialize supramolecular coordination complexes (SCCs) for real-life applications. Since developing such polymeric products requires studying material properties on a new range of time and length scales that are less frequently used by classical chemists, there is gap of knowledge that hinders development of such hybrid materials. By exploring the design strategies of this emerging class of materials, and highlighting macromolecular characteristics of such networks, this review seeks to encourage the development of further luminescent networks based on polymeric constituents, unlocking new possibilities for applications in advanced functional materials.

1. Introduction

Many biological materials consist of polymeric chains enriched by synergistic supramolecular interactions, forming hierarchical composite structures capable of performing multiple functions across varying time and length scales [1]. Examples are numerous, a simple one being the mussel's threads, which has a collagen like basis enriched with chelating ligands based on catechol and histidine. While the polymeric basis provides the integrity, the reversible dissociation of complexes formed between ligands and metal ions absorbed from seawater, provide self-healing, cohesion, and interfacial adhesion [2]. Another example is the spider silk, which features a protein-based polymeric backbone combined with hydrogen bonding and metal coordination sites, particularly involving metal ions such as zinc and calcium. The polymeric structure provides remarkable tensile strength and flexibility, while the supramolecular interactions contribute to its elasticity and toughness, enabling the material to withstand repeated mechanical stress [2]. Inspired by such sophisticated natural designs, chemists have sought to combine synthetic polymers with supramolecular interactions to impart

biomimetic properties [3]. With advances in synthetic techniques, this research is expanding to incorporate more intricate supramolecular architectures with unique functions to provide specific and tunable properties.

Among the myriads of supramolecular interactions, metal coordination is an attractive tool for forming supramolecular assemblies with defined shape, structure, and properties. The coordination driven self-assembly (CDSA) is a bottom-up approach that enables precise formation of two- and three-dimensional supramolecular coordination complexes (SCCs) with pre-designed size, shape, and geometry [4]. Among various properties that SCCs can offer, their inherent distinct and tunable luminescence has become attractive for many reasons [5–7]. The emissive properties are of particular interest since they can be tracked easily, sometimes even by the naked eye, as such, indicating the formation, destruction, or function of the supramolecular assembly. Moreover, in contrast to classic organic dyes, whose synthesis and tuning of photophysical properties require multiple steps of precise synthesis, the simple combination of predesigned building blocks, known as electron-donor and -acceptor groups, can provide novel tunable

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<https://doi.org/10.1016/j.ccr.2025.216796>

Received 4 February 2025; Accepted 4 May 2025

Available online 14 May 2025

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emission characteristics with much less trouble. On top of that, the dynamic feature of metal coordination can provide fascinating stimuli-responsiveness to their luminescence [8]. Therefore, the combination of CDSA and luminescence can pave the way not only for the design of supramolecular structures in applications that require emission, but also to facilitate understanding the kinetics and thermodynamics of CDSA and consequently the design of new SCCs.

Nevertheless, one of the classical barriers to commercialize SCCs for real-life applications is their fragile nature and limited formability. To address these limitations, incorporating SCC systems in long-chain polymers has become a promising strategy [9,10]. By embedding SCCs within a polymeric matrix, the mechanical integrity of the supramolecular structures can be significantly enhanced, providing better stability, flexibility, and processability. The polymer chains can act as a structural scaffold, offering not only improved durability but also enhanced solubility and processability, enabling SCCs to be utilized in a broader range of practical applications. Moreover, the combination of long-chain polymers with SCCs allows for the integration of additional functional properties, such as self-healing, stretchability, and stimuli responsiveness. This hybrid approach merges the precision and tunability of metal coordination with the robust and flexible characteristics of polymers, ultimately paving the way for more durable, versatile, and commercially viable materials.

Since developing polymeric products requires studying material properties on a new range of time and length scales that are less frequently used by classical chemists, specifically those focused on designing luminescent SCCs, there is a gap of knowledge that hinders development of such hybrid materials. This is unfortunate, as bridging this gap could lead to the creation of luminescent materials for a wide range of applications, including separation, delivery, sensing, catalysis, and imaging. Therefore, in this review we are focused on luminescent metallo-supramolecular polymer networks (MSPNs), where the polymeric chains maintain their structural integrity even after the dissociation of metal complexes [11]. Specifically, we classify MSPNs based on the functionality of the metal-ligand junctions into zero-, two-, and three-dimensional junctions, respectively provided by single metal ion complexes, metallacycle, and metallacages. Given the extensive research on luminescent SCCs, particularly metallacycles and metallacages, and the availability of review papers on these discrete luminescent structures [7,12,13], this review aims to highlight the less explored potential in developing hybrid materials by connecting these junctions with polymeric spacers. By advancing the understanding of such systems, we can open new avenues in the development of smart, functional materials with applications in adaptive sensing, drug delivery, energy harvesting, and beyond, thus aligning with and expanding upon current trends in both supra- and macromolecular science.

2. Luminescent constitutes and integration strategies

Luminescence encompasses a phenomenon intrinsically linked to the excitation of electroactive molecules through exposure to incident light, resulting in their subsequent emission of a diverse array of colors. This luminescence transpires as a direct consequence of the absorption of light by electrons, propelling them through transitions between distinct energy levels within the atoms of the electroactive molecule. In turn, these energetically excited electrons radiate luminescence as they return to their ground energy state. The specific color exhibited in this luminescence is intricately tied to the energy gap differentiating the ground state from the excited state of the electrons [14,15]. Luminescence phenomena have been documented across an extensive spectrum of materials, encompassing both organic and inorganic substances, as well as hybrid compounds. Among these, organic molecules constitute a substantial category. The critical determinants for observing luminescence in organic compounds hinge on three essential parameters: conjugation, electron resonance, and rigidity to avoid non-radiative decay. Furthermore, the length of conjugation and the presence of

electron-donating or -withdrawing functional groups exert a substantial influence on the excitation and emission wavelengths, and consequently, the resulting color of luminescence [15].

Organic luminescent molecules manifest two primary emission mechanisms depending on their chemical structure. The first mechanism operates in a static mode, characterized by time-independent emission, wherein luminescence is instantaneously observed upon excitation via light irradiation. This static mode becomes evident in the presence of stable electron resonance or a conjugate structure. Compounds like coumarin, rhodamine, fluorescein, anthracene, naphthalimide, cyanine, and perylene, exemplify this particular emission mode [16]. The second mechanism operates in a dynamic mode, characterized by a gradual emergence of luminescence over time in response to light irradiation. Within this category of luminescent compounds, the luminescence arises from the isomerization of the organic molecule, transitioning from a non-luminescent form to a conjugated and luminescent isomer. Notably, the intensity of this emission can be augmented upon exposure to light. Key examples of such dynamic luminescent compounds include spiropyran, spiroxazine, diarylethene, azobenzene, fulgide, viologen, and benzopyran derivatives. These compounds are renowned as photochromic or photoswitchable substances due to their capacity for dynamic transformation under the light stimulus [17,18].

Lanthanide ions, although being inherently weak light absorbers due to the Laporte-forbidden nature of the $f-f$ electronic transitions, exhibit exceptional optical properties, when combined with organic ligands in a process known as “sensitization” or the “antenna effect”. Their unique properties like sharp emission lines, long-lived excited state, and high quantum yield make these materials highly valuable for applications in display technologies, bio-imaging, and sensing. One key advantage of these lanthanide-ligand complexes is their ability to produce very narrow emission peaks with minimal spectral overlap. This property allows for precise and tunable luminescence, making them ideal for multi-color imaging and fluorescence microscopy. The long-lived excited states also enable time-resolved fluorescence, a technique that can effectively reduce background noise in biological imaging. Their practical application is, however, hampered due to low thermal stability, poor mechanical properties, low conductivity, and aggregation tendency. Nevertheless, their incorporation into long chain polymers can overcome these shortcomings [19]. Polymers can protect lanthanide ions from aggregation, maintaining their luminescent properties even under harsh conditions. Moreover, the versatility of polymer chemistry allows for the fine-tuning of optical, mechanical, and conductive properties, and even enrich them with additional stimuli-responsiveness.

2.1. Static luminescence

Static luminescence represents the instantaneous emission that occurs upon excitation by light irradiation of a specific wavelength, and this emission promptly ceases when the light source is removed. This phenomenon is typically encountered in organic molecules characterized by conjugate structures containing functional groups, which induce electron resonance upon absorbing the requisite energy from the incident light [15]. An essential determinant for static luminescent organic compounds is the excitation wavelength and the resulting emission range, both of which are notably influenced by the extent of conjugation within the aromatic structure of the luminescent compound. The incorporation of functional groups within the structure of luminescent compounds, which are able to respond to environmental alterations, provides the foundation for conferring stimuli-responsiveness. Consequently, changes in polarity, pH, and other analytes can exert a profound influence on the excitation wavelength and emission characteristics of these compounds. As such, this category of luminescent motifs presents a promising avenue to expand the utility of MSPNs as stimuli-responsive luminescent materials on top of the inherent sensitivity of metal coordination to stimuli such as pH fluctuations, redox agents, and polarity [16,20,21].

In recent years, a diverse array of organic luminescent molecules exhibiting stimuli-responsive characteristics has been developed. We can categorize them according to their utility in designing luminescent MSPNs, as shown in Fig. 1. The first group of organic luminescent compounds characterized by static emission can be directly employed as chelating ligands or incorporated in the ligand structure. Ligands with direct luminescence includes derivatives of polypyridines such as terpyridine, bipyridine, and phenanthroline. Smaller ligands such as pyridine and imidazole are not strongly luminescent, but luminescence is often observed when they are parts of larger structures that facilitate conjugation and charge transfer [11,22]. Many of the polycyclic aromatic hydrocarbons (PAHs) like naphthalene, anthracene, and pyrene are used as substitutes on the aforementioned ligands, mostly to manipulate the steric and electronic effects [23]. They can direct coordination towards selective formation of heteroleptic complexes in single metal complexes [24,25]. Moreover, in metallocycles and metallocages, they can form structural components that link the terminal ligand motifs together. These structures are often planar and highly conjugated, which contributes to their interesting electronic and optical properties. Several heterocyclic aromatic compounds, including carbazole, benzothiazole, benzoxazole, coumarin, quinoxaline, and benzimidazole exhibit luminescent properties. Many of these compounds find applications in fields like organic electronics, biosensing, fluorescent probes, and optoelectronics. Reports on their integration into metallo-supramolecular structures are rather rare, but can otherwise not only improve luminescence but also function as a potential coordination station. Integration of such luminophores in MSPNs is often prone to undesired luminescence quenching upon coordination due to aggregation-caused quenching (ACQ), particularly in the solid state, as it promotes the non-radiative decay pathways. To overcome the ACQ issue, a group of organics with static emission are developed that exhibit aggregation-induced emission (AIE), a phenomenon where certain molecules are non-emissive (or weakly emissive) in solution but exhibit strong luminescence when they aggregate [26]. These materials exhibit their unique

luminescent properties through the restriction of intramolecular motions in the aggregated state. This is the opposite of the typical behavior of many luminescent compounds, which show ACQ, due to processes like π - π stacking, which facilitates non-radiative decay pathways and suppresses luminescence. Well-known AIEgens include tetraphenylethylene (TPE) and triphenylamine derivatives. Finally, a wide array of organic luminescent compounds has emerged in recent years, designed specifically as fluorescent dyes for sensing and detection applications. Among this group, prominent compounds such as fluorescein, rhodamine, nitrobenzoxadiazolyl, and naphthalimide have been more frequently used in polymeric materials due to their high emission yields. However, the integration of such bulky aromatics in the backbone of the donor structure in SCCs can interfere with the self-assembly process. Therefore, a practical approach for the application of these dyes in MSPNs involves the integration of organic luminescent compounds into polymeric chain, normally as pendant groups. Consequently, a diverse array of organic compounds with static luminescence can be employed, as highlighted in Fig. 1, to pioneer the development of novel metallo-supramolecular structures with stimuli-responsive emission.

2.2. Dynamic luminescence

Dynamic luminescence represents a light-responsive behavior exhibited by smart molecules, which includes transitioning between two distinct states or structures, exhibiting notable disparities in terms of conjugation, polarity, and the consequent emission characteristics. This dynamic behavior is typically observed through isomerization, achieved by reversible formation of chemical bonds, often resulting in formation of a conjugated ring structure [17,27]. The isomerization can be influenced by a variety of factors, including the polarity of the surrounding medium and the presence of different analytes. Consequently, varying isomerization kinetics can be observed. Among the dynamic organic compounds, stimuli-chromic molecules including spiropyran, spirooxazine, azobenzene, and diarylethene, as shown in Fig. 2, are more often

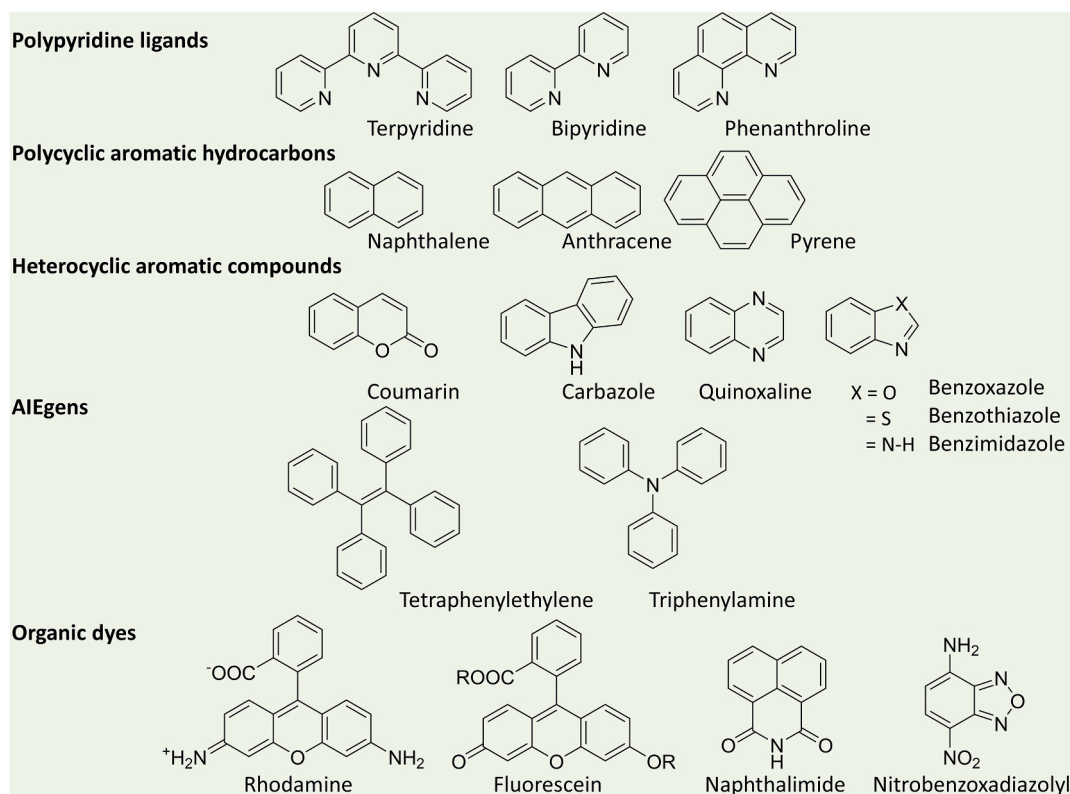


Fig. 1. The chemical structure of representative organic compounds with static luminescence for potential application in construction of MSPNs.

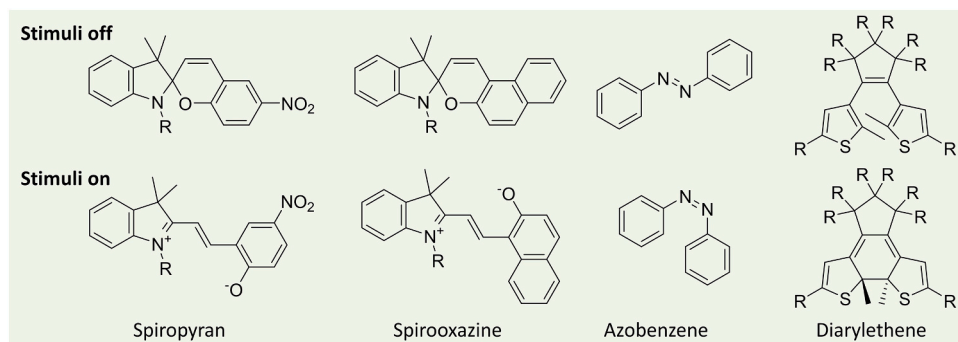


Fig. 2. The chemical structure and isomerization of representative dynamic organic luminescent compounds with potential application in construction of MSPNs.

used in construction of luminescent supramolecular polymers. Each of these molecules exhibits a wide spectrum of stimuli-responsiveness, depending on their chemical structure and the underlying mechanism of responsiveness. For instance, spiropyran and spirooxazine stand out among photochromic compounds, showcasing their reactivity to light irradiation, which enables a ring-opening reaction through reversible bond cleavage at the spiro junction. The open merocyanine form is highly conjugated and exhibits significant fluorescence, depending on the solvent and environmental conditions. Spiropyran, in particular, is a well-recognized multi-stimuli-chromic compound, exhibiting a diverse range of stimuli-responsive properties, including photochromism, solvatochromism, acidochromism, ionochromism, and mechanochromism. These stimuli-responsive traits vary depending on the specific chemical structure, and functional groups [28,29]. Azobenzene is another photochromic compound, due to its unique isomerization between *trans* and *cis* isomers, occurring around the azo bond in response to light irradiation. These two isomeric forms exhibit pronounced differences in terms of polarity, optical properties, and stereochemistry [30]. While the *trans*-isomer is non-fluorescent, the *cis*-isomer can sometimes exhibit weak fluorescence. Diarylethene is another distinct stimuli-chromic compound, which undergoes isomerization through the formation of a ring or pericyclic reaction, facilitated by an intramolecular $2n + 2$ Diels-Alder reaction in response to light irradiation [31]. In contrast to the open form, the closed form is highly conjugated, which allows for efficient fluorescence. An essential aspect of these organic compounds is their versatile functionalization capacity. For instance, spiropyran has been functionalized with hydroxyl, carboxylic acid, amines, amides, and even acrylic monomers, allowing it to be polymerized via conventional free-radical polymerization mechanisms [32]. Consequently, the integration of stimuli-chromic compounds into metallo-supramolecular structures can yield a spectrum of unique and intelligent behaviors. These behaviors are characterized by their dynamic or time-dependent nature, tunability, reversibility, and the ability to be controlled remotely. The bulky dynamic luminescent compounds can be incorporated into metallo-supramolecular structures mainly as pendant or main-chain groups within the polymer backbone. As a component of the main backbone, they can show mechanochromism, as the isomerization can be also triggered by mechanical deformation, transmitted along the backbone to the fragile nature of the dynamic structure [33,34]. Smaller dynamic luminescent components have been also incorporated as a main part of the ligand or auxiliary *endo*- or *exohedral* function [35,36].

2.3. Antenna effect in lanthanide complexes

The antenna effect is a phenomenon where a ligand absorbs light and transfers the energy to a central metal ion (often a lanthanide ion), which then emits light. This process enhances the luminescence of the metal ion by efficiently funneling energy to it, improving its overall luminescent intensity. The antenna effect is especially useful for overcoming the weak absorption of certain metal ions (such as lanthanides)

by using ligands with strong absorption capacity, provided by the bulky aromatic structure [19]. Due to conjugation, the ligand can enter the excited state upon irradiation. The energy of the excited state normally transfers to the complexed metal ion in non-radiative pathways. As such, transition metal ions normally quench the intrinsic emission of the ligand. Lanthanides, in contrast, undergo radiative decay and emit light typically in the visible or near-infrared range. They have low absorption coefficients because the Laporte-forbidden nature of *f-f* transitions, due to the shielding of inner *f*-orbitals by outer *s*- and *p*-orbitals, leads to weak light absorption. As such, their emission relies heavily on energy transfer from an efficient ligand, that is the “antenna”, to emit light. The physical and chemical properties of the organic ligand, such as their chemical structure, conjugation, electronegativity of heteroatoms, the presence of electron-donating or -withdrawing functional groups, and the polarity of the surrounding media have a significant impact on the optical characteristics of the final metal complex. Also, the diversity of ligands that can coordinate with the same metal ion in heteroleptic complexes can lead to variations in absorbance and emission wavelengths. This variation in optical properties is analogous to how the chemical structure of organic photoluminescent materials can influence their optical properties. This approach allows for the customization of optical properties, including color, intensity, brightness, and the lifetime of emission. Consequently, thanks to the antenna effect, lanthanide complexes have found applications in diverse fields such as lighting, displays, sensing, energy storage and conservation, biomedicine, anti-counterfeiting, and information encryption [37]. The primary mechanism for incorporating and assembling lanthanide complexes into supramolecular structures involves the coordination of trivalent metal ions with various multi-dentate ligands in telechelic and side-chain structures, that is, as a component of the main chain or as pendant groups, respectively. In this context, the selection of an appropriate polymer backbone and ligands for the preparation of luminescent MSPNs is critical for achieving the desired optical properties and stimuli-responsiveness.

3. Luminescent Metallo-supramolecular polymer networks

MSPNs are formed by the coordination bonds between metal ions and polymers functionalized with ligands, resulting often in percolated three-dimensional architectures. Here metal ions act as nodes and ligands serve as linkers, creating a structure where the metal-ligand complex is referred to as the “junction” or “crosslinking point”. Accordingly, such a MSPN still has a polymeric structure even after dissociation of crosslinking points. Junction dimension is a decisive factor for classifying MSPNs. Metal-ligand complexes can be an essential part of 2D (metallacycles) and 3D (metallacages) assemblies, or be 0D, including a single metal ion surrounded by coordinating ligands, as illustrated in Fig. 3a–d. While the connectivity of transient junctions in 2D and 3D structures can increase by the number of metal nodes in the assembly, it is limited to the size of the coordination sphere and

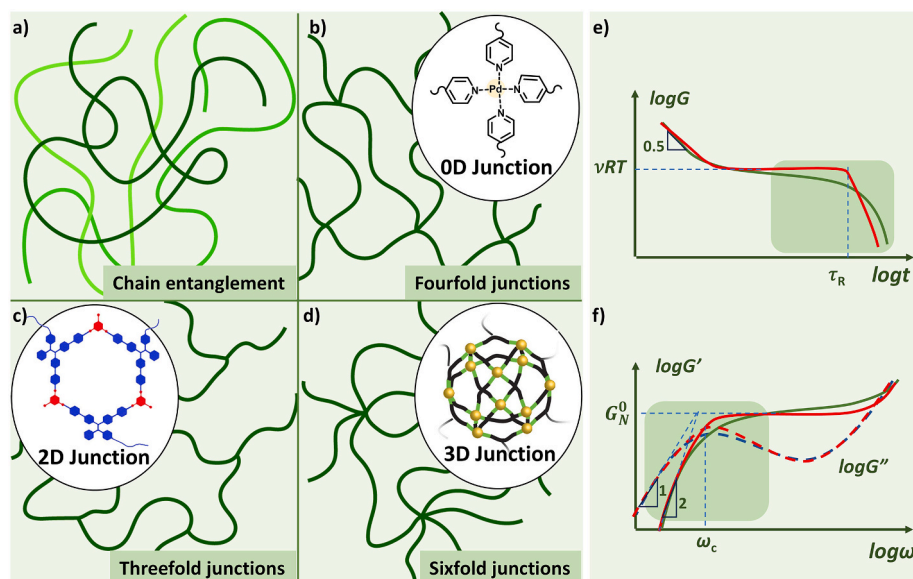


Fig. 3. Connectivity in polymer systems: a) Long chains with entanglements. Short telechelic chains with transient crosslinks: b) 0D square-planar Pd^{2+} -pyridine complexes forming fourfold junctions, c) 2D hexagonal metallacycles forming threefold junctions (in this example), d) 3D $\text{M}_{12}\text{L}_{24}$ cuboctahedral metallacycles forming sixfold junctions (only 6 out of 24 ligands are polymeryl ligands in this example). Schematic representation of dynamics of entangled systems (green curves) and telechelic MSPNs (red curves): e) relaxation modulus, $G(t)$, in time domain, and f) storage, G' , and loss, G'' , moduli in frequency domain. Time and frequency regions accessible in hydrogels are highlighted in dark boxes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

denticity of the ligand in 0D junctions. Nevertheless, the network connectivity via metal–ligand coordination also depends on the average functionality of the polymer precursor, that is, the number of ligands connected to the polymeric chain. Specifically, ligands can be incorporated at the chain ends, forming telechelic polymer precursors, or along the chain, creating side-chain systems. While the supra- and macromolecular dynamics are relatively independent in telechelic networks, they are significantly coupled in side-chain systems [38]. Therefore, we briefly compare the dynamics of entangled polymers with that of telechelic MSPNs. The dynamics of side-chain MSPNs are less studied in reports covered in this review, but interested readers can find more examples in other reviews [39].

The dynamics of polymer chains span a wide range of time and frequency, which can be studied using multiple methods like rheology, light scattering techniques, and diffusion studies [40]. Rheology is a widely used method that provides insights into the chain dynamics within a limited time and frequency window. In this approach, various types of deformations can be applied, and the material's response or relaxation is measured in either the time or frequency domain. Relaxation of entangled polymer chains (Fig. 3a), include segmental Rouse dynamics at high frequencies (slope of 0.5 in Fig. 3e). The length of relaxing segment increases by the observation time, which is ceased when it reaches the distance between two neighboring entanglements. This halts further relaxation, resulting in a plateau modulus observable in both the time and frequency domains, as illustrated in Fig. 3e and f. The relaxation continues when the entire chain moves parallel to other chains by a combination of mechanisms known as reptation, contour length fluctuations, and constraint release [40]. The terminal relaxation is characterized by the slopes of 1 and 2 for the loss and storage moduli, respectively on a double-logarithmic plot, with the relaxation time equal to the inverse of the crossover frequency ($\tau_R = 1/\omega_c$). The diversity of mechanisms coupled with the natural polydispersity of polymer chains results in relatively broad transitions. In contrast, in MSPNs, the high-frequency relaxation is mainly limited by the spacing between successive transient junctions [40,41], and the low-frequency relaxation is initiated by their reversible dissociation. Therefore, compared to entangled systems, MSPNs exhibit sharper transitions, and relatively flat

plateau modulus. Consequently, their terminal relaxation is often well-described by a single Maxwell model. According to the affine network model [40], the plateau modulus either formed by chain entanglement or transient crosslinks is defined by $G_N^0 = \nu RT$, where ν is the number of network strands per volume and RT is the thermal energy. As a distinctive feature of polymeric systems, we aim to highlight polymer dynamic data alongside the photophysical properties of MSPNs. The polymer dynamics as a function of time or frequency, are respectively reported as the shear modulus, $G(t)$ or storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, characterized by the plateau modulus, G_N^0 , and relaxation time τ_R , as illustrated in Fig. 3e and 3 f.

Unlike discrete SCCs, MSPNs develop extensive, potentially infinite network structures. This extended architecture provides MSPNs with stimuli-responsive network connectivity and mechanical properties, as crosslinking points undergo rapid response to external stimuli. Moreover, MSPNs exhibit processability due to their polymeric nature, allowing for fine-tuning of viscoelastic properties and fabrication of materials with desired shape and toughness. These qualities make MSPNs particularly suitable for applications across various fields, from tough materials to biomedicine, where the combination of durability and adaptability is essential [9–11,42].

The coordination geometry in 0D junctions is a thermodynamic property and can be adjusted by the molar fractions of the ligand and metal ions [11,43]. From the one hand, factors like the oxidation state of the metal ion and electron configuration of the metal's valence shell, as well as the steric and electronic effects of the ligands can determine the coordination geometry in a metal complex [44]. From the other hand, the synthesis procedure and preparation method, particularly the metal-to-ligand ratio (MLR), are critical in determining the connectivity of the transient 0D junction. Accordingly, while MLR is strictly fixed for 2D and 3D junctions, since under- or over-stoichiometric ratios would disintegrate the assembly [45], it is a tuning variable in 0D junction MSPNs [46]. For example, Tsvetkov and colleagues demonstrated that varying MLRs in systems containing Eu^{3+} or Pd^{2+} ions with terpyridine ligands could alter the ligand count per metal ion and thereby modulate the architecture and luminescent properties of the resultant network [47]. Besides the abovementioned MSPNs, there is another class of

metallopolymers based on mono complexes, where metal–ligand complexation does not contribute in network formation, instead, other classes of transient bonds, like hydrogen bonding, host–guest interaction, and hydrophobic association are required to induce and control the network formation.

Luminescence in MSPNs can arise from either the junctions and/or, the polymeric chain spacer, or through encapsulation of luminophores inside the empty space of 2D and 3D junction assemblies [6]. Polymers with extended conjugation along their backbone, such as poly(phenylene vinylene) or polythiophene, can exhibit luminescence. Conjugation allows delocalization of π -electrons across the structure, and upon excitation, these electrons return to the ground state, emitting photons as a result of the energy release, which leads to luminescence. Research focusing solely on metallopolymers with luminescent polymer backbones is relatively diverse. Such studies are focused on the chemical structure of the polymer constitute rather than the metal complex. For example, Schubert et al. used Zn^{2+} bis-terpyridine complexes as OD linkages to link red, green, and blue light emitting chromophores, resulting in white light emission [48]. The statistical nature of OD bis junctions allowed tuning the composition, and consequently, achieving a homogeneous luminescent color. However, no influence of the metal coordination on photophysical properties was studied. In contrast to such reports, here we place our focus on polymer networks where luminescent properties stem from metal complex junctions, or those

with both luminescent backbones and junctions.

3.1. Polymer networks with luminescent OD junctions

There are some reports on the enhanced luminescence of polymer networks upon the introduction of metal ions and formation of metal complexes. The strong coordination between metal ions and the nitrogen/oxygen donor sites of the ligands, can lead to rigidity, as such, suppression of non-radiative decay, and possible chelation-enhanced fluorescence effects [49]. These factors collectively enhance the luminescence of the system by favoring radiative pathways and reducing energy loss via non-radiative mechanisms. For instance, Qu and colleagues synthesized a multifunctional metallo-hydrogel through the terpolymerization of acrylic acid, acrylamide, and a hydrophobic methylacrylamide arylhydrazone-based ligand (1). This polymerization resulted in a random poly(acrylic acid-co-acrylamide) copolymer with integrated arylhydrazone-based ligands along the backbone accompanied by hydrogen bonding between carboxylic acid moieties. The incorporation of Al^{3+} ions, at various ratios, yielded a MSPN (2) based on tris metal complexes. The addition of Al^{3+} significantly enhanced the fluorescence properties of the hydrogel. The study also explored mixed-metal MSPNs by incorporating Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , or Fe^{3+} along with Al^{3+} . Among these, Zn^{2+} and Ni^{2+} demonstrated superior luminescence compared to Fe^{3+} and Cu^{2+} , while the luminescence

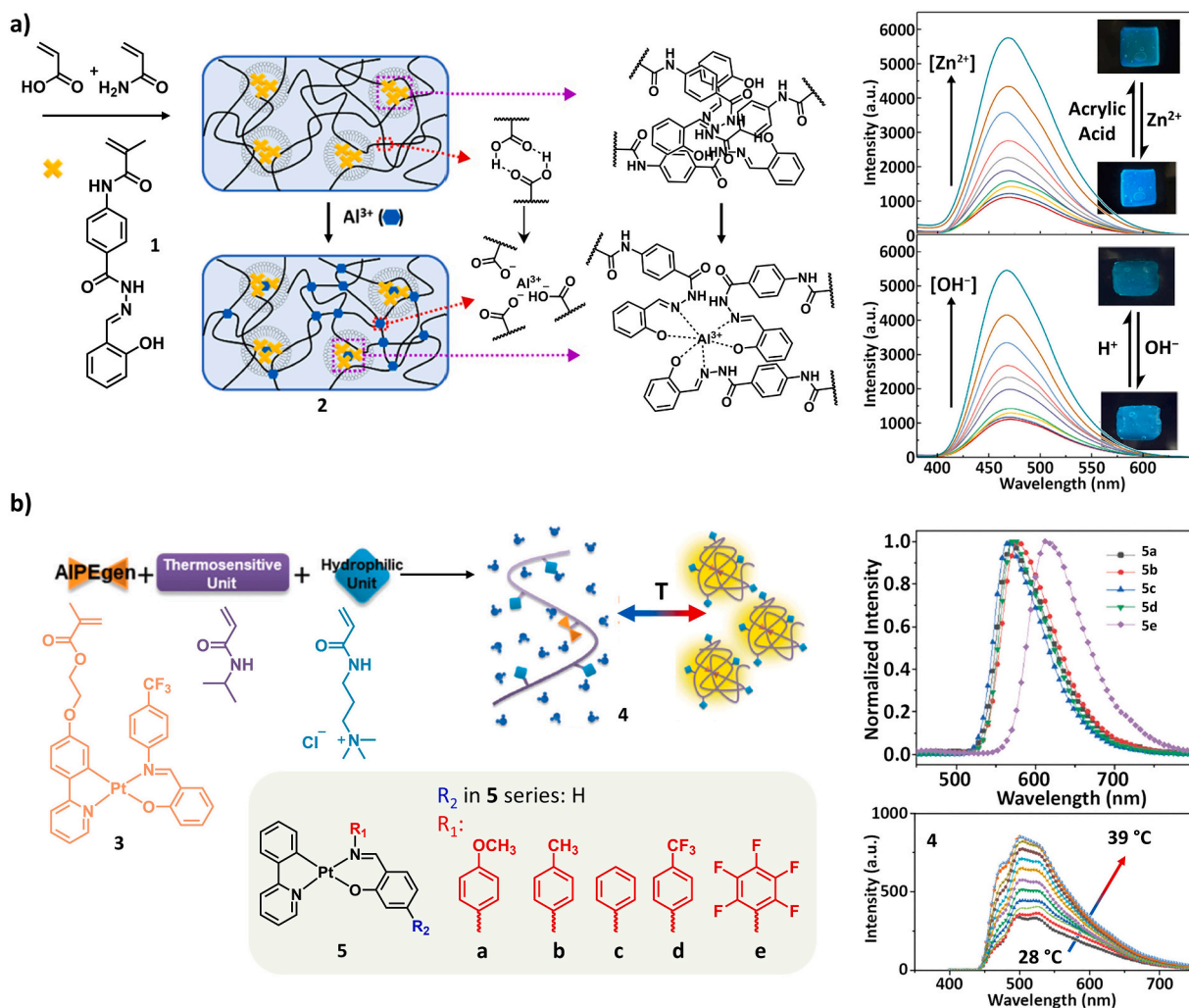


Fig. 4. Diverse mechanisms of emission in polymer systems: a) Enhanced emission of 2 upon deprotonation and coordination of ligands. [50], Copyright 2019. Reproduced with permission from ACS. b) Emission spectra of complexes made by ligand series 5 in the solid state, and effect of temperature on AIE of polymer network 4. [57], Copyright 2019. Reproduced with permission from RSC.

remained almost unchanged with the addition of Mn^{2+} and Co^{2+} . The superiority of Zn^{2+} is attributed to the ability of Zn^{2+} to enhance the rigidity of the polymer backbone by coordinating two arylhydrazone ligands, thereby improving fluorescence quantum yields. Additionally, the luminescence intensity of **2** can be tuned by varying the $\text{OH}^-:\text{H}^+$ ratio, achieving up to a 500 % enhancement with 0.1 M OH^- , due to stronger association of deprotonated ligands, as shown in Fig. 4a. The hydrogel also exhibited excellent mechanical properties, including elongation, shape-memory capability, and self-healing characteristics, making it highly suitable for applications in information transmission, wearable devices, and flexible sensors [50].

Many of the ligands used in MSPNs have intrinsic luminescence that may be enhanced or quenched upon complexation with metal ions. Accordingly, Olsen et al. have used the emission of terpyridine and phenanthroline ligands to study the origin of shear thinning. They formed MSPNs upon complexation of telechelic ligand-functionalized four-arm poly(ethylene glycol) (tetraPEG). The emission is quenched when these ligands associate with Ni^{2+} , therefore, emission intensity reflects the number of unassociated ligands during deformation [51,52]. Similarly, Kurth et al. have reported that while the emission of terpyridine is quenched upon complexation with most of transition metal ions, it is retained when complexed with Zn^{2+} [53,54]. The retained luminescence in the presence of Zn^{2+} is attributed to the completely filled *d*-orbitals. This makes Zn^{2+} a closed-shell ion that does not participate in non-radiative decay pathways associated with *d-d* transitions, which helps preserve the luminescence. In contrast, metal ions with partially filled *d*-orbitals participate in *d-d* transitions, therefore, the excited-state energy can be dissipated through non-radiative pathways rather than being released as luminescence [55]. In a related research, Bu and co-workers synthesized telechelic oligomers containing two terpyridine and two crown ether ring groups. The addition of Zn^{2+} ions led to the formation of linear polymer chains based on bis metal complexes. Introducing a bisammonium salt induced host-guest interactions between the crown ether hosts, resulting in the formation of a percolated network. The fluorescence band and emission intensity could be modulated by changing the concentration of Zn^{2+} and the ammonium guest [56].

Examples on the utility of AIE in OD junction MSPNs are surprisingly rare. In one example, Huang et al. investigated an AIE-active Pt^{2+} complex with tunable photophysical properties, where each Pt^{2+} ion was coordinated with a Schiff base ligand. They employed a random free radical terpolymerization, incorporating a methacrylate-linked Pt-Schiff base AIEgen complex (**3**), along with N-isopropylacrylamide, and (3-Acrylamidopropyl)trimethylammonium chloride. The metal ion was introduced at the MLR of 1:1 to create linear polymer chains decorated with the AIEgen. Due to the inability of mono metal complexes to form junctions, N-isopropylacrylamide units served as the primary intermolecular hydrophobic interaction to form the network **4**. The phosphorescent AIE was enhanced upon aggregation of **3**, triggered by temperature as the external stimulus, as demonstrated in Fig. 4b. By modulating the Schiff base structure (**5**) and incorporating various functionalities, they achieved tunable emission properties. The introduction of electron-withdrawing or -donating groups into the aniline structure caused a subtle red shift in the solid-state emission spectra, whereas electron-donating groups in the o-hydroxybenzaldehyde moiety induced a significant blue shift. The hydrogel's responsiveness to temperature fluctuations enabled its utility as a thermosensitive probe [57].

Lanthanides are commonly used to provide luminescence in OD junction MSPNs because of their unique optical properties, which make them highly attractive for applications in light-emitting materials [19,58]. Particularly trivalent lanthanide ions like Eu^{3+} and Tb^{3+} exhibit sharp and characteristic emission lines due to the transitions within their 4*f* orbitals [59]. These transitions are minimally affected by the surrounding environment because 4*f* electrons are shielded by the 5*s* and 5*p* orbitals, leading to well-defined and highly specific emission

peaks. Lanthanides themselves have weak absorption in the visible region, but their luminescence can be significantly enhanced through the antenna effect. This process enhances the overall luminescence efficiency and allows for the design of materials with tailored emission properties. Lanthanides typically exhibit coordination numbers between 7 and 12 due to their large ionic radii and their tendency to form complexes with multiple donor atoms. When complexed with tridentate ligands, they typically form bis complexes, while the remaining orbitals are filled with solvent molecules or small counterion molecules. If the spatial hindrance allows, even tris complexes can be made by tridentate ligands, which makes lanthanides attractive to form percolated transient networks, as explained in the following examples.

For instance, Holten-Andersen and coworkers achieved white light emitting hydrogels by developing luminescent MSPNs crosslinked by lanthanide-terpyridyl coordination complexes. A telechelic tetraPEG, with arms terminated by terpyridine ligands was coordinated to different lanthanide ions (**6-Ln**). They were able to tune the emission properties across a broad spectrum, including white light, by adjusting the stoichiometry of lanthanide metal ions, as demonstrated in Fig. 5a. The dynamic nature of the lanthanide-nitrogen coordination bonds allowed the materials to exhibit reversible stimuli-responsive behavior (mechano-, vapo-, thermo-, and chemochromism), enabling applications in both sol-gel systems and solid thin films. This approach not only enabled full-spectrum light emission but also showed potential for creating smart materials that respond to environmental changes and feature optomechanically coupled sol-gel transitions, useful for real-time monitoring and self-healing properties [60].

Li and co-workers developed another highly stretchable and fast self-healing luminescent network crosslinked with complexes of Ln ions (Eu^{3+} , Tb^{3+} , Yb^{3+} , or Nd^{3+}) and terpyridine ligand. The synthesis involved polycondensation of bifunctional isocyanate-terminated- (**7**) with trifunctional amine-terminated polypropylene glycol (**8**) and an amine functionalized terpyridine ligand (**9**), yielding poly(urea-propylene glycol) with an architecture ranging from three-arm to hyper-branched, featuring arms terminated with terpyridine. The MSPN (**10**) is formed upon adding Ln metal ions at the MLR of 1:2, which results in prevalent formation of bis complexes. Urea groups form additional hydrogen bonds, which enhances the mechanical properties of the network. These materials exhibited exceptional luminescent properties due to the antenna effect in Ln-terpyridine coordination complexes, including visible (Eu^{3+} and Tb^{3+}) and near-infrared (Yb^{3+} and Nd^{3+}) luminescence. By altering $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio they managed to achieve color-tunable emission. This makes them highly suitable for applications in wearable electronics and flexible displays. In addition to their luminescent properties, these materials displayed excellent mechanical properties, such as high stretchability and rapid self-healing at ambient conditions, as demonstrated in Fig. 5b. Remarkably, the healing process remains effective despite surface aging and exposure to atmospheric moisture [61].

Mebip is another tridentate ligand that in contrast to many terpyridine ligands, is reported to absorb UV light and transform it into heat, which destabilizes complexes and can be harnessed to provoke light-driven self-healing [62]. Mebip is also reported to form tris complexes with lanthanide ions but bis complexes with divalent transition metal ions. Accordingly, researchers have employed Mebip in combination with multiple metal ions to control and tune the architecture, and consequently, the mechanical and luminescent properties of MSPNs. Specifically, Beck and Rowan employed Mebip-terminated PEG oligomers to form luminescent network in the presence of mixed lanthanide and transition metal ions (3 % Ln), and the overall MLR of 1:1. They incorporated La^{3+} and Eu^{3+} lanthanide ions, and Zn^{2+} and Co^{2+} as transition metal ions. The Zn/Eu system exhibited characteristic emission bands of Eu^{3+} . In contrast, other combination of metal ions exhibited poor luminescence intensities [20]. Extending on this research idea, they utilized Mebip terminated poly(tetrahydrofuran) (PTHF) (**11**) to form MSPNs (**12**) with Eu^{3+} as the Ln and Zn^{2+} as the transition metal,

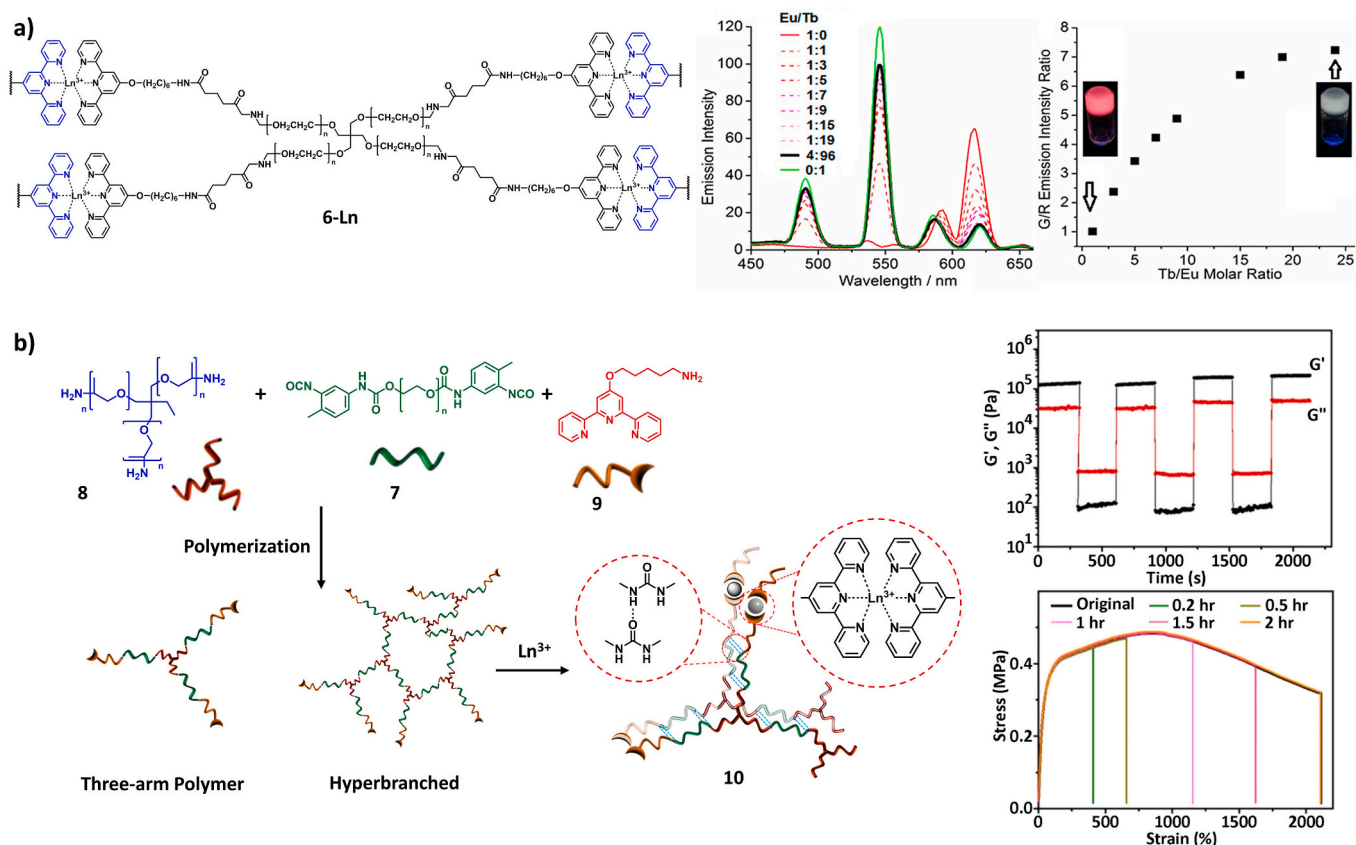


Fig. 5. Terpyridine-Ln complexed MSPNs: a) Emission spectra of 6-Ln at varying MLR. [60], Copyright 2015. Reproduced with permission from ACS. b) Different structures of poly(urea-propylene glycol); tensile curves of networks healed for varying times; and dynamic moduli at high and low oscillation amplitudes, demonstrating instantaneous self-healing. [61], Copyright 2020. Reproduced with permission from ACS.

investigating the effect of varying the metal ion composition at constant overall MLR of 4.35:9. By varying the $\text{Zn}^{2+}:\text{Eu}^{3+}$ ratio, they observed significant changes in the material's characteristics. A higher concentration of Eu^{3+} resulted in a more pronounced luminescence due to the antenna effect, with distinct emission bands at 581, 594, 616, and 652 nm. Conversely, increasing the Zn^{2+} content enhanced the network's mechanical robustness, while Zn^{2+} ions act as relatively more stable chain extender, improving material's tensile strength and elasticity. The optimal balance was found at a $\text{Zn}^{2+}:\text{Eu}^{3+}$ ratio around 1:1, which provided both strong luminescence and desirable mechanical properties. Additionally, the $\text{Zn}^{2+}:\text{Eu}^{3+}$ ratio influenced the emission color, with higher Eu^{3+} concentrations yielding a more intense red emission, while higher Zn^{2+} concentrations shifted the emission towards a fainter blue hue, as shown in Fig. 6a. These studies highlight the potential of tuning metal composition in tailoring properties of MSPNs for applications in smart materials and advanced photonic devices [63].

In another study, Schrettl, Weder, and coworkers coordinated a telchelic Mebip terminated poly(ethylene-co-butylene) (13) to Eu^{3+} and Tb^{3+} ions at an MLR of 1:3, forming tris complexes with the tridentate ligand. The luminescence of Eu^{3+} and Tb^{3+} based networks was employed to study the welding kinetics. UV irradiation led to a decrease in luminescence intensity at the welded area, indicating successful welding through photothermal effects, as illustrated in Fig. 6b. Mechanical properties of polymers were evaluated before and after self-healing, revealing that the materials retained their mechanical integrity after healing, showcasing their potential as reprocessable networks, being suitable where durability, reparability, and mechanical strength are essential [64].

Weder et al. also utilized telechelic poly(ethylene-butadiene) copolymers terminated with either Mebip (13) or dipicolinate ligands

(14), to form MSPNs based on tris complexes with Eu^{3+} at the MLR of 1:3. The Eu^{3+} based MSPNs exhibited sharp red emission attributed to the $5\text{D}_0 \rightarrow 7\text{F}$ transitions, confirming the successful incorporation of Eu^{3+} ions into the polymer network. Doping the MSPN network with Fe^{2+} ions, specifically using Mebip functionalized precursors, resulted in a mechanochromic MSPN. This system displayed reversible photoluminescence color changes from red to blue upon ultrasonication, demonstrating its dynamic mechanoresponsive nature. The mechanochromic response was due to the disruption and reformation of coordination bonds between Fe^{2+} and Mebip ligands in 13-based MSPN under sonication, leading to changes in the local environment of the Eu^{3+} ions, and consequently, their emission properties, as demonstrated in Fig. 6c. 14-based MSPN, in contrast, provided a less pronounced mechanochromic effect. This difference is attributed to the distinct coordination environments and binding affinities of the two ligands with Fe^{2+} and Eu^{3+} ions. The Mebip ligand forms weaker and less stable coordination bonds with metal ions, resulting in a more sensitive mechanochromic response. This example highlights the role of ligand in tuning emission properties of OD junction MSPNs, with potential applications in optical sensing, where real-time monitoring of mechanical stress and damage is essential [65].

Bidentate ligands are even more effective than tridentate ligands in forming percolated luminescent network in combination with lanthanides due to the accommodation of more ligands in the complex. For instance, Li and coworkers synthesized luminescent self-healing polyurethane elastomers by polycondensation of PTHF with 4-methylenedicyclohexyl diisocyanate, followed by the incorporation of [2,2'-bipyridine]-4,4'-dimethanol to introduce multiple bipyridine ligands along polyurethane chains (15). They achieved percolated networks by introducing Ln ions (Eu^{3+} and Tb^{3+}), and forming tri-functional

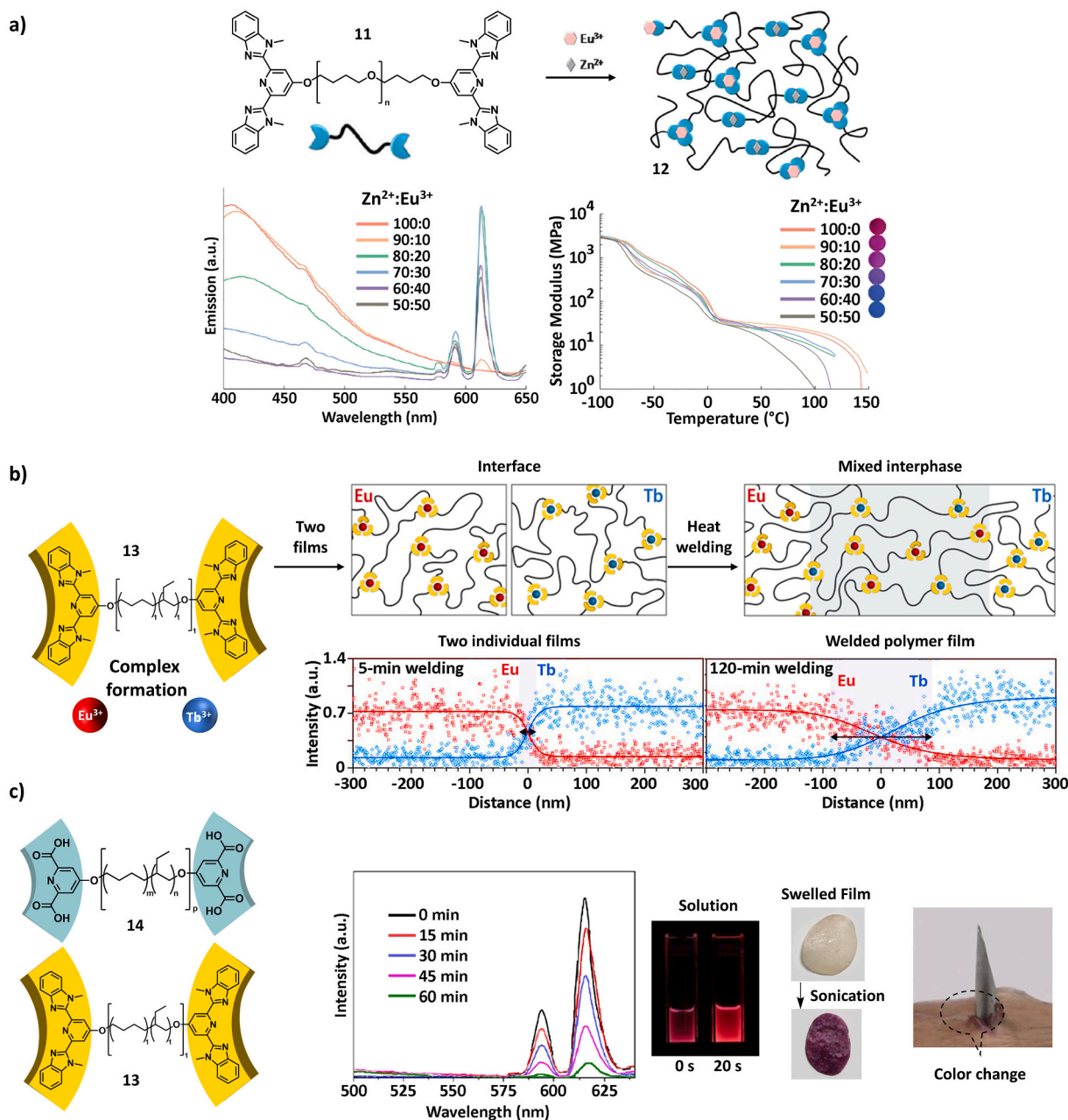


Fig. 6. Mebip-Ln complexed MSPNs: a) Emission spectra and dynamic mechanical thermal analysis of 12 at different $\text{Zn}^{2+}:\text{Eu}^{3+}$ ratios. [63], Copyright 2010. Reproduced with permission from RSC. b) Time-evolution of the interphase composition in Eu- and Tb-crosslinked 13 upon UV-induced self-healing. [64], Copyright 2021. Reproduced with permission from American Association for the Advancement of Science. c) Emission spectra of 13 network as a function of sonication time in $\text{Fe}(\text{ClO}_4)_2$ solution; Images of solution and swelled film before and after sonication, and demonstration of mechanochromism in punctured swelled film. [65], Copyright 2014. Reproduced with permission from ACS.

junctions at MLR of 1:3. The resulting elastomers exhibited tunable luminescent properties due to the antenna effect of Ln-bipyridine, similar to complexes formed by terpyridine, with the $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio allowing precise control over the emission color, as shown in Fig. 7a. Additionally, these materials demonstrated high tensile strength and elasticity, enhanced by hydrogen bonding interactions and the dynamic nature of the Ln-bipyridine coordination bonds. This combination of self-healing and luminescence, makes them suitable for advanced applications in smart coatings and wearable devices [66].

Wang et al. developed stimuli-responsive, self-healing, luminescent materials by employing a three-step polymerization process including: I) polycondensation of diol-terminated poly(dimethylsiloxane) (PDMS) (16) and diol-terminated polycaprolactone (17) with different

diisocyanates (4,4'-dicyclohexylmethane diisocyanate, hexamethylene diisocyanate, or isophorone diisocyanate), II) adding [2,2'-bipyridine]-4,4'-diol to the reaction mixture, and finally III) adding 1,4-butanediol. The resulting linear poly(dimethylsiloxane-caprolactone-urethane) (18), featured bipyridine and urethane moieties along the chain. The urethane groups facilitate hydrogen bonding, whereas the incorporation of Ln ions (Eu^{3+} and Tb^{3+}) with a MLR of 1:3 forms a percolated network based on tris Ln-bipyridine complexes (19-Ln). The Ln-bipyridine coordination exhibited an antenna effect, enhancing luminescence due to the broad and intense absorption peak of bipyridine in the excitation spectra of 19-Eu and 19-Tb. These MSPNs demonstrated exceptional self-healing properties due to the dynamic nature of available transient bonds. The best self-healing performance was achieved in the presence

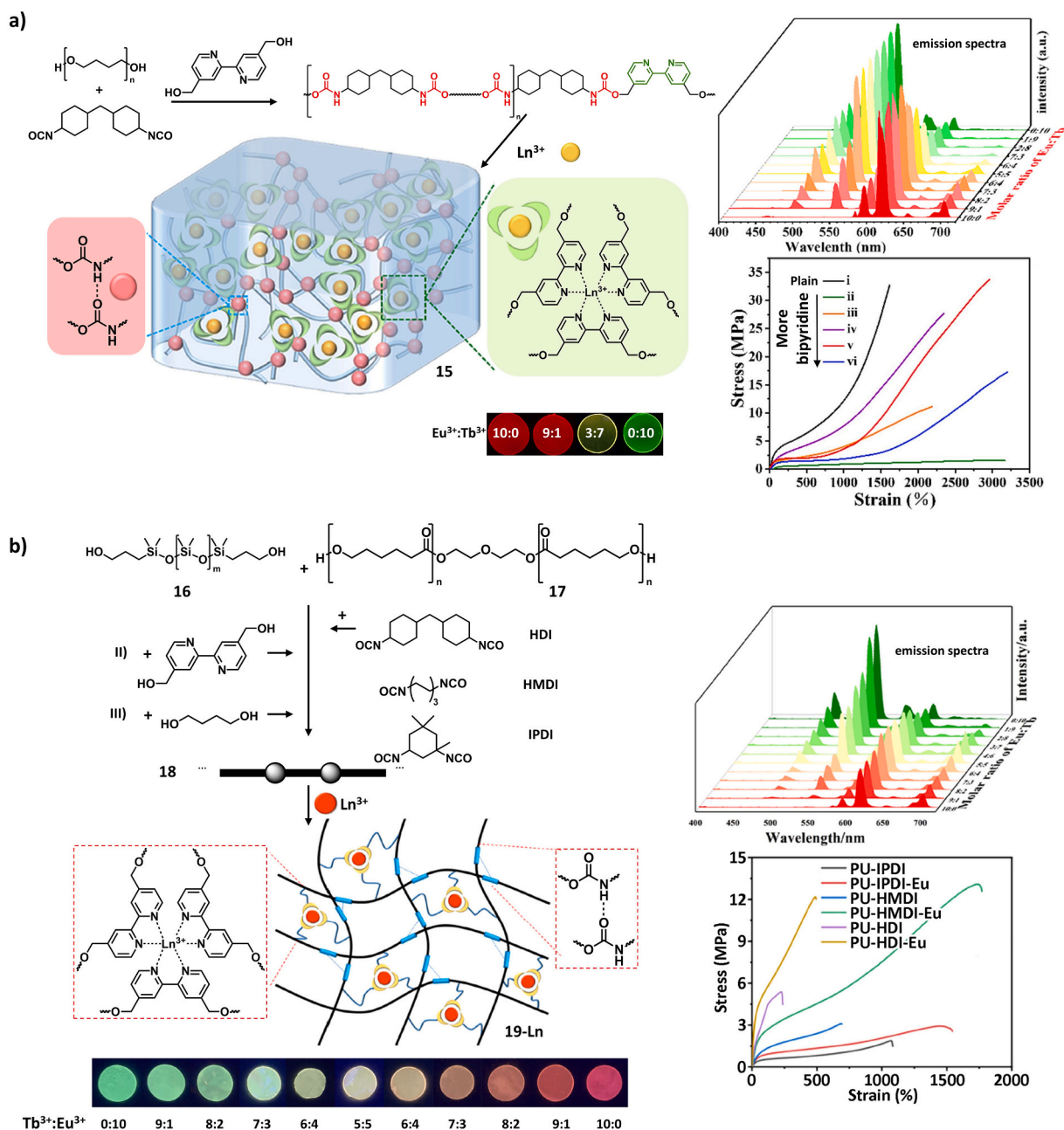


Fig. 7. Bipyridine-Ln complexed MSPNs: a) Tensile profiles of 15 at various contents of OD junctions, and emission spectra at various $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratios. [66], Copyright 2024. Reproduced with permission from Elsevier. b) Tensile properties of 18 and 19-Eu samples with different isocyanates, and emission spectra of 19 (with HMDI) at various $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratios. [67], Copyright 2023. Reproduced with permission from ACS.

of hexamethylene diisocyanate. The $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio was crucial for tuning the luminescent properties, with Eu^{3+} emitting red and Tb^{3+} emitting green light. The mechanical properties of the polymer, such as tensile strength and elasticity, were significantly improved in the presence of Ln ions, resulting in a robust network structure, as demonstrated in Fig. 7b. The combination of luminescent properties and self-healing capabilities positions these materials as promising candidates for applications where both luminescence and mechanical resilience are essential, as in smart coatings and wearable sensors [67].

Pyridine dicarboxylate ligands are also very effective in sensitizing luminescence due to the combined effects of strong nitrogen coordination and relatively weaker carboxylate chelation [68]. Indeed, the luminescence efficiency of a ligand is determined by various factors, particularly the alignment of the ligand's energy levels with the excited states of the lanthanide and the stability of the resulting complex. In a

study conducted by Wang et al., extra ionic interactions were leveraged to enhance the mechanical strength of MSPNs, resulting in the coacervation of an anionic lanthanide coordination polymer with a cationic polyelectrolyte. The synthesis involved preparing a ditopic ligand (20), where two pyridinedicarboxylic acids (PDCAs) were covalently bonded to a tetra(ethylene oxide) spacer. By introducing Ln ions in the aqueous medium, a MSPN was formed based on tris complexes. The addition of the cationic poly(3-(methacryloylamino)propyl-trimethylammonium chloride) (21) further enhanced the network's mechanical strength through ionic bonds bridging the PDCA ligands to the cationic polymer, thereby creating a coacervative network (22). The conetwork demonstrated increased toughness and elasticity due to the dynamic nature of ionic bonds, and excellent self-healing properties at room temperature, attributed to the reversibility of transient interactions. In terms of luminescence, they showed tunable emission properties, with the color

adjustable by varying the $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio. Tb^{3+} provided a prominent green emission around 545 nm, while Eu^{3+} exhibited red emission at approximately 615 nm. This system also exploits antenna effect since excitation mainly happens through PDCA groups rather than the intra- $4f^6$ transition of Eu^{3+} or Tb^{3+} . The viscoelasticity of **22** hydrogels was found to be thermo-rheologically simple, therefore, following the time-temperature superposition principle, master-curves of the storage and loss moduli were built. An Arrhenius equation was used to fit the plots of shift factors against inverse temperature, providing an apparent

activation energy, E_a , of 55 kJ mol^{-1} . This relatively low activation energy indicates the energetic barrier against both supra- and macro-molecular dynamics. Moreover, charge-driven assemblies were found to be responsive not only to temperature but also to ionic strength, therefore, the crossover frequency, ω_c , was shifted to higher frequencies with increasing NaCl concentration. This indicates that higher salt concentrations can decrease the interaction between the polycation and the carboxyl groups of the PDCA ligand, as such, decreasing the mechanical strength of the hydrogel. Accordingly, a master-curve was built based on

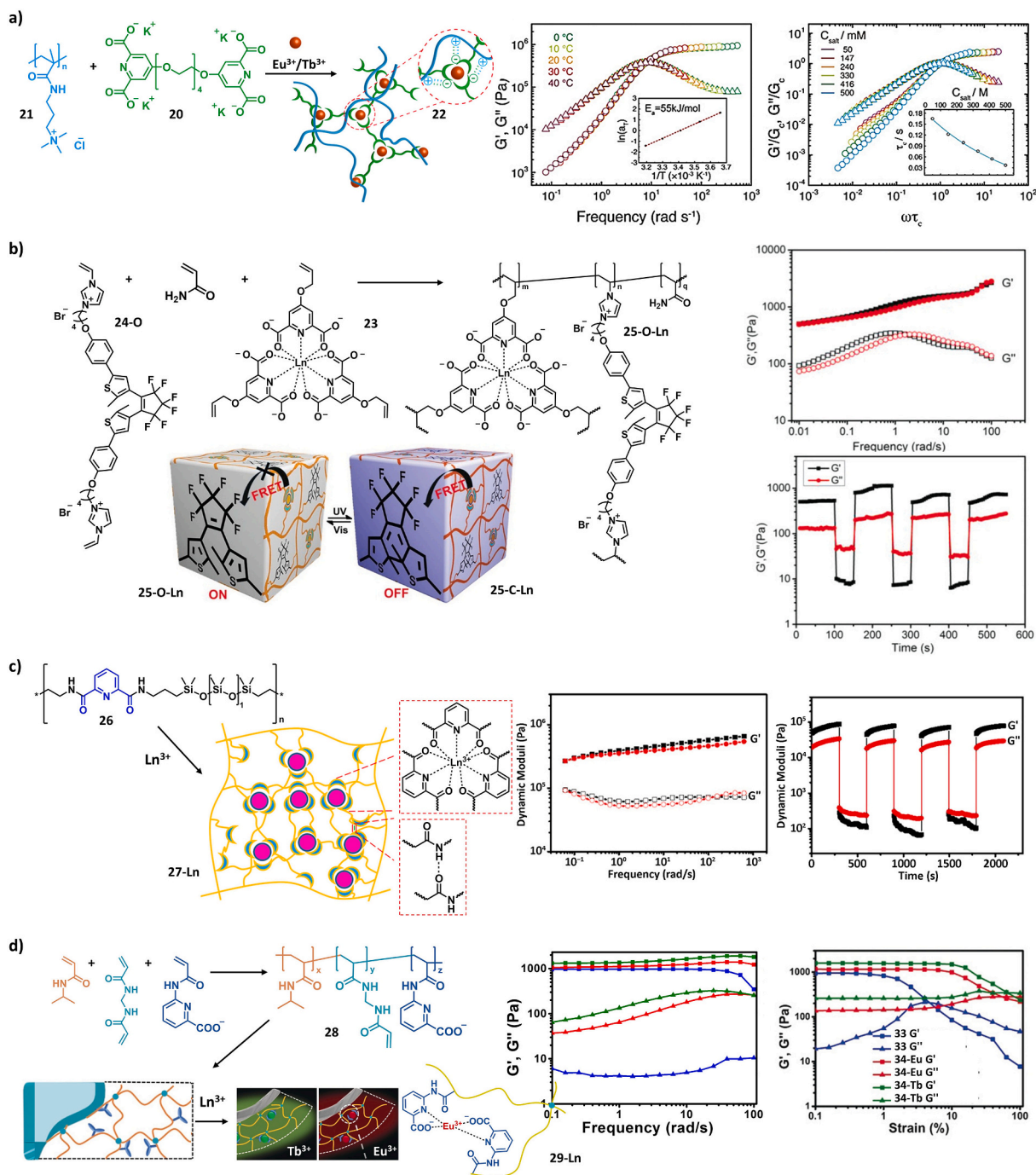


Fig. 8. PDCA-Ln complexed MSPNs: a) Two-step formation of the **22** coacervative network and the corresponding temperature and salt concentration master-curves, with insets describing the exponential decay of shift factors. [69], Copyright 2019. Reproduced with permission from ACS. b) Reversible isomerization of **25** and the corresponding change in dynamic moduli of **25-O-Ln** (black symbols) and **25-C-Ln** (red symbols) and self-healing behavior. [70], Copyright 2019. Reproduced with permission from Wiley. c) Dynamic moduli of **27-Ln** before (black symbols) and after (red symbols) self-healing at room temperature along with self-healing tests. [72], Copyright 2020. Reproduced with permission from ACS. d) Frequency and amplitude sweep measurements of **28** and **29-Ln**. [73], Copyright 2019. Reproduced with permission from Wiley. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

time–salt concentration superposition by horizontally shifting the dynamic moduli according to their crossover frequency. Interestingly, they found that the calculated relaxation times followed an exponential decay with increasing the salt concentration, as demonstrated in Fig. 8a. Such polyelectrolyte hydrogels with tunable luminescence and mechanical properties are promising for applications in stimuli-responsive, self-healing, and smart devices [69].

Zhao et al. terpolymerized a propylene-terminated PDCA complexed with Eu^{3+} and/or Tb^{3+} with MLR of 1:3 (23), a vinyl imidazolium salt modified diarylethene (24-O), and acrylamide, resulting in a MSPN (25-O-Ln) based on tris complexes. The reversible closed (24-C and 25-C-Ln) and open (24-O and 25-O-Ln) isomerization of the diarylethene units was respectively achieved upon irradiation with 300 nm UV light and visible light (>450 nm). This photoresponsive behavior plays a crucial role in controlling the luminescent properties of the material. The antenna effect is enabled between the PDCA ligand and Ln, as demonstrated in their excitation spectra. However, the emission band of the Ln-PDCA complex overlaps with the absorption band of the closed state of the diarylethene units in 25-C-Ln, enabling efficient fluorescence resonance energy transfer (FRET), leading to invisible emission of 25-C-Ln under UV light. In contrast, 25-O-Ln shows strong emission in the visible wavelength region. So basically, these MSPNs can be used as on and off photoswitches (off under UV: 25-C-Ln, and on under natural light: 25-O-Ln). The emission color was finely tunable from green to red by altering the $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio. These transparent and self-standing luminescent hydrogels exhibited remarkable mechanical properties, as well. Specifically, they showed fracture stress up to 80 kPa and elongation at break exceeding five times their original length. Notably, no significant differences in mechanical properties were observed between the open and closed network isomers, indicating that the isomerization process does not affect the hydrogel network's connectivity and structural integrity. The dynamic moduli demonstrated a gel-like behavior with storage modulus outweighing the loss modulus across all measured frequencies. Interestingly, local maxima were obtained in the loss modulus around 1 rad/s, as shown in Fig. 8b, which can be associated with supramolecular dynamics and dissociation of the metal coordinative bonds. Moreover, sequential high and low-amplitude oscillatory deformation demonstrated very fast recovery of the network structure after breakage at deformations beyond the linear viscoelastic regime. The tunable emission colors, mechanical robustness, and self-healing characteristics of hydrogels make them promising candidates for intelligent security protection, smart anti-counterfeiting materials, and advanced wearable sensors. Moreover, the $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio provides a virtually limitless range of information-rich codes for advanced encryption applications [70]. In a similar study, a FRET-active MSPN was developed based on ionic bonds interacting with metal–ligand complexes based on PDCA ligands and Ln ions. Similar to the previous example, the diarylethene unit undergoes reversible photoisomerization, as such, enabling a FRET process between Eu^{3+} complexes and the closed isomer of diarylethene, and quenching the emission. The produced hydrogel offers promising candidate for reversible on-off photoswitch applications [71].

In another study by the same group, a linear polymer was synthesized by polycondensation of a bifunctional amine-terminated PDMS and 2,6-pyridinedicarboxamide dichloride in the presence of triethylamine at mild basic conditions, resulting in a linear PDMS covalently extended with PDCA ligands along the backbone (26). The addition of Eu^{3+} and Tb^{3+} , at MLR of 1:3, yielded a MSPN (27-Ln) due to the formation of tris complexes. The dynamicity of Ln-ligand complexes and hydrogen bonding of secondary amide groups conferred the material with high toughness, stretchability, and self-healing capabilities at room temperature, in the solid state. The minimal self-absorption of Eu^{3+} in the excitation spectrum of 27-Eu indicates that the metal ions are primarily excited through the PDCA group rather. Similarly, the faint absorptions of Tb^{3+} and intensive absorption of PDCA in 27-Tb suggest efficient energy transfer from the ligand to Tb^{3+} . These results indicate

that the antenna effect is present between the Ln ions and PDCA. The material exhibited tunable luminescence, with emission color modulated by varying the $\text{Eu}^{3+}:\text{Tb}^{3+}$ ratio or excitation wavelength. Additionally, a reversible luminescence switch was achieved through alternating exposure to acid and base vapors, enabled secure data protection via reversible information encryption and decryption. Moreover, rheological studies, as shown in Fig. 8c, demonstrated the formation of a percolated network with two relaxation modes, associated with dissociation of transient bonds based on metal coordination and hydrogen bonding. Besides, remarkable self-healing behavior was obtained in the film state. These attributes rendered the material suitable for optical devices, advanced sensors, anti-counterfeiting measures, and innovative LED technologies that may require adjustable/reversible luminescence besides self-healing and high mechanical properties [72].

In another study, Chen et al. developed a novel class of bioinspired polymeric hydrogel actuators that exhibit synergistic fluorescence color-switching and shape-morphing capabilities, enabled by dynamic metal–ligand coordination. A poly(N-Isopropylacrylamid)-K6APA (28) hydrogel was prepared by photoinduced radical polymerization of N-Isopropylacrylamid (NIPAM), methylenebisacrylamide (MBAA) cross-linker, and K6APA, which is the potassium salt of a ligand monomer 6-acrylamidopicolinic acid that was synthesized by the amidation reaction of methyl 6-aminopyridine-2-carboxylate and acryloyl chloride and subsequent hydrolysis of the methyl ester. The as-prepared hydrogel was transparent and nonfluorescent. However, red- and green-light-emitting hydrogels (29-Ln) were produced by immersing 28 hydrogels into aqueous solutions of Eu^{3+} and Tb^{3+} . The formation of additional transient crosslinks based on metal coordination, on top of hydrophobic association of NIPAM units, resulted in enhanced storage modulus, specifically at the high-frequency region, as shown in Fig. 8d. The reversible dissociation of metal complexes also shifted the onset of non-linear viscoelasticity to larger deformation. That means the fast formation of transient crosslinks based on metal complexes keeps the integrity of the network and postpones the structure breakage to larger deformations. The hydrogel emission color could be modulated by varying the metal ion molar ratio of the mixed solutions. Subsequently, anisotropic bilayer actuators were prepared, using these fluorescent MSPNs as the actuating layer and pan paper as a passive layer, where the large mismatch in modulus and swelling capacity of these two layers induced anisotropic actuation motion. Accordingly, the synergetic color-changing and shape-morphing functions of some natural flowers and animals in response to subtle environmental stimuli like temperature and acidity/alkalinity could be mimicked. This was obtained by the change in luminescence along with association affinity of metal complexes in response to employed external stimuli. These soft actuators hold promise for biomimetic soft robotics, biological sensors, camouflage, and visual display technologies [73].

The incorporation of multiple fluorophores in MSPNs can enable development of multi-color switchable stimuli-responsive polymer networks. For instance, Chen et al. have recently integrated organic dyes and lanthanide complexes in separate polymer chains that form a percolated single network. The fluorescence intensity of each fluorophore could be controlled independently by different external stimuli, which provides multi-stimuli responsive multicolor fluorescence characteristics. Briefly, a vinyl substituted naphthalimide dye (4-phenoxy-N-allyl-1,8-naphthalimide (PhAN)) was first covalently introduced into the linear thermo-responsive polymer chain through terpolymerization with NIPAM and hydroxyethyl methacrylate (HEMA), yielding poly(PhAN-NIPAM-HEMA) (30). Desired hydrogels (31) were synthesized by copolymerization of K6APA ligand and N-acryloyl glycineamide (NAGA) yielding poly(K6APA-NAGA) in the presence of various concentrations of 30. Multicolor fluorescent (32-Ln) was achieved in the presence of the blue light emitting 30 and introduction of a combination of red and green light emitting Eu^{3+} and Tb^{3+} metal ions. Besides the temperature sensitivity of the NIPAM associations, NAGA is well-known hydrogen bonding motif. Therefore, robust dynamic crosslinks were formed based

on a combination of hydrophobic association, hydrogen bonding, and metal coordination. Rheological studies demonstrated a surprisingly higher plateau modulus upon the introduction metal ions, as demonstrated in Fig. 9a. Moreover, fluorescence studies confirmed stable red, green, and blue fluorescence bands, as covalent bonding of fluorophores avoids any leakage when responding to external stimuli. The emission color was tuned upon varying either the $\text{Tb}^{3+}/\text{Eu}^{3+}$ ratios or the concentration of **30**. Furthermore, remarkable fluorescence color changes were achieved by independently regulating the fluorescence intensities of fluorophores in response to different external stimuli. Accordingly, such soft biomimetic color-changing skins can have promising applications in fields like optical sensing, soft camouflaging robots, and visual human-machine interaction technology [74].

Using a similar approach, the same group has recently developed fluorescent hydrogel actuators that can simultaneously change their emission and perform origami-like 3D shape deformation. As illustrated in Fig. 9b, a red-light-emitting Eu^{3+} coordinated hydrogel (**33**) was synthesized by terpolymerization of K6APA ligand, acrylamide, and the MBAA crosslinker. New information was written by the red fluorescent carbon dots, which was invisible in the alkaline environment due to the pH sensitivity of the CD ink. Subsequently, a temperature-responsive blue fluorescent hydrogel was introduced as the top layer, by the in-situ terpolymerization of the naphthalimide functionalized monomer with NIPAM, and MBAA (**34**). The temperature-sensitivity of the second layer enabled temperature-responsive change in swelling and mechanical properties along with a luminescence band different from the first layer, which results not only in color change but deformation in response to temperature. Finally, a third layer was introduced by the in-situ terpolymerization of a vinyl substituted pH-sensitive naphthalimide dye with dimethyl aminoethyl acrylate and MBAA (**35**), providing additional mode of color change and anisotropic deformation in response to pH. This study offers a new approach for the development of new kinds of smart actuating and information encryption systems with

programmable responsiveness [75].

3.2. Polymer networks with luminescent 2D junctions

In the past decade, MSPNs crosslinked by 2D metallacycles and 3D metallacages have emerged at the interface of coordination chemistry and polymer science. The primary motivation has been to enhance the processability of inherently fragile and brittle inorganic structures by incorporating entangled long chains. However, the rich functionality and stimuli-responsiveness of SCCs have played a significant role in the development of innovative polymeric materials [9,76]. In contrast to luminescent MSPNs with 0D junction, which are mainly developed based on lanthanide ions and the antenna effect, luminescent networks with junctions comprising 2D and 3D assemblies are mainly developed based on the AIE effect [13]. First examples were focused on connecting SCCs with other transient bonds like host-guest interactions. For instance, Yin and coworkers prepared a ditopic ligand (**36-R**) containing a terpyridine group and a 120° dipyrindyl ligand, where the central phenyl group was functionalized either with primary amine (**36-NH₂**), hydroxyl (**36-OH**), methoxy (**36-OCH₃**), or left unfunctionalized (**36-H**). These ligands were first coordinated with a 60° benzo-21-crown-7 modified di- Pt^{2+} acceptor (**37**) to form rhombohedral metallacyclic SCCs (**38-R**). Subsequent addition of Zn^{2+} ions to **38-R** led to the formation of linear metallo-supramolecular polymers (**39-R**) through formation of bis terpyridine complexes, and thanks to stability of Pt^{2+} -pyridine complexes. The introduction of a bisammonium salt (**40**) establishes host-guest interactions with crown ethers and forms percolated networks (**41-R**). The luminescent properties of **38-R** were significantly influenced by the electron-donating ability of the functional groups on the dipyrindyl moiety. Specifically, **38-NH₂** exhibited the broadest emission spectra (400–750 nm) with the most significant red-shift due to its strong electron-donating effects. The methoxy and hydroxy variants also contributed to red-shifts, but to a lower extent.

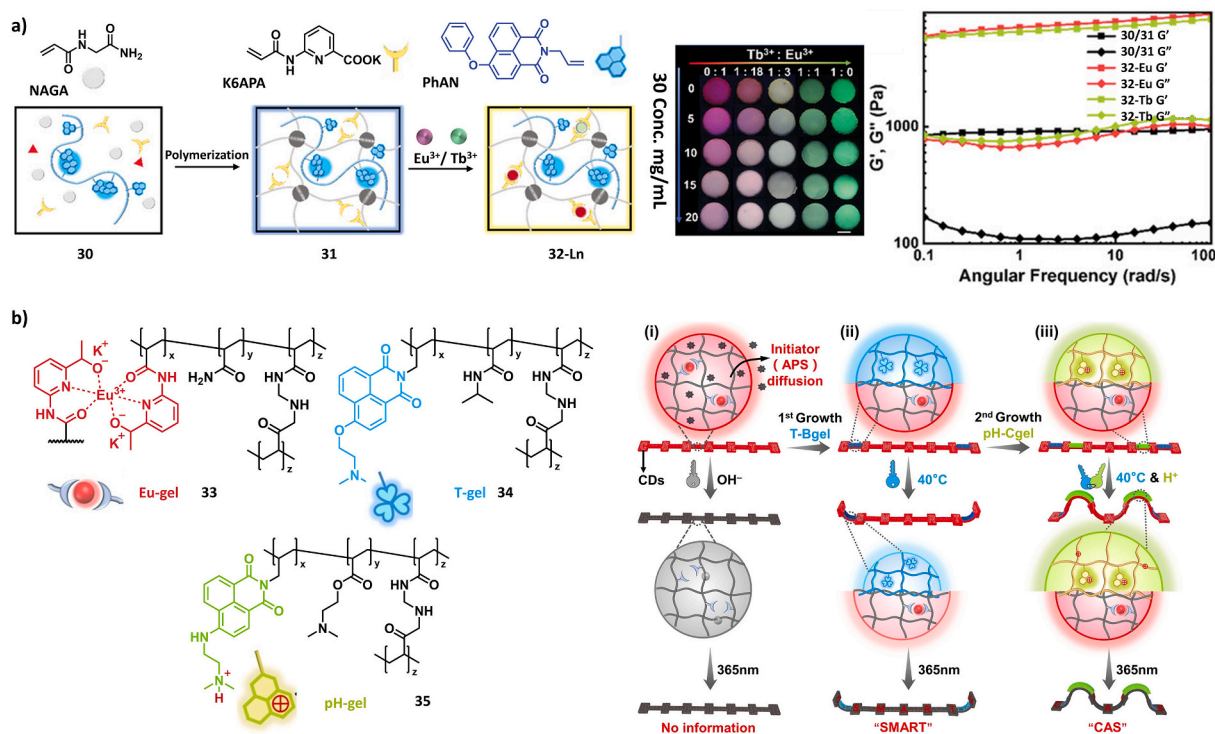


Fig. 9. Multi-color switchable MSPNs: a) Fluorescent photos MSPN 37 at different $\text{Eu}:\text{Tb}$ ratios and 30 contents, and dynamic moduli of the polymer before and after adding Ln ions. [74], Copyright 2022. Reproduced with permission from Wiley. b) Chemical structure of polymer precursors and multicolor fluorescent MSPN; Illustration of the stepwise structure-editing process to produce diverse adaptive actuating states in response to environmental changes. [75], Copyright 2023. Reproduced with permission from Wiley.

The red-shifts were further enhanced by the extended conjugation from the Zn^{2+} – terpyridine coordination in **39-R** and **41-R**. The **41-R** network exhibited gel-like behavior with storage modulus outweighing loss modulus across the measured frequency range, as shown in Fig. 10a. Specifically, the network demonstrated no relaxation, as comprehended from the steady loss modulus and lack of crossover between dynamic moduli. Moreover, the material had notable self-healing properties, resulting from the dynamic metal–ligand coordination and reversible host–guest interactions [77]. Despite by our definition, this example does not represent a MSPN, as no polymeric chain was involved, this combination of metal complexation and host–guest interaction formed the basis for the development of several metallacycle crosslinked luminescent MSPNs.

For instance, the same group synthesized a 120° pyridinedione boron difluoride donor (**42**), which is a derivative of TPE AIEgen bonded to boron difluoride and 1,3-bis(pyridin-4-ylethynyl)benzene. By introducing **37**, complexation happened with bipyridine units of **42**, resulting in the formation of a rhombohedral metallacyclic SCC (**43**). This time, they synthesized a random copolymer of styrene and benzyl chloride ammonium salt (**44**) to provide the network forming guest molecule. Introducing this copolymer to **43** enabled host–guest interactions between the ammonium salt and the crown ether, leading to the formation of a MSPN (**45**) with 2D rhombohedral junctions. **45** exhibited notable mechanical properties, including good flexibility and recyclability. Rheological measurements indicated a higher storage- than loss

modulus, indicative of a stable supramolecular gel, with excellent self-healing properties, allowing it to repeatedly repair fracture under alternating large and small strains. Additionally, **45** could undergo a reversible sol–gel transition at 50 °C, demonstrating thermal responsiveness. In parallel, emission wavelength of **45** shifted from 690 nm to 660 nm under acidic conditions, which was reversed upon neutralization, demonstrating a sensitive and reversible emissive response to pH changes, as shown in Fig. 10b. This pH-sensitive luminescence makes the MSPN a promising candidate for detecting even slightly acidic environments with visible fluorescence changes [78].

The 2D junction MSPNs with covalently linked metallacycle cross-links can be formed following two different approaches; I) connecting SCCs after assembly by polymer strands or II) assembling polymeric donor/acceptor constitutes [9]. The first approach may use click reactions to connect the pre-assembled SCCs with preformed polymeric spacers, or use the SCCs as a comonomer, initiator, or chain transfer agent to grow polymer chains in a polymerization reaction. Therefore, the first approach may have the risk of destructing the SCC structure under the conditions required for the click reaction or polymerization, although it benefits from well-defined pre-organized SCCs junctions. Moreover, radical polymerization in the presence of high functionality SCCs may result in the undesired radical coupling reaction. In the second approach, in contrast, the formation of well-defined SCCs is hindered by the steric hindrance, specifically when the polymer concentration and the functionality of the SCC increase [79].

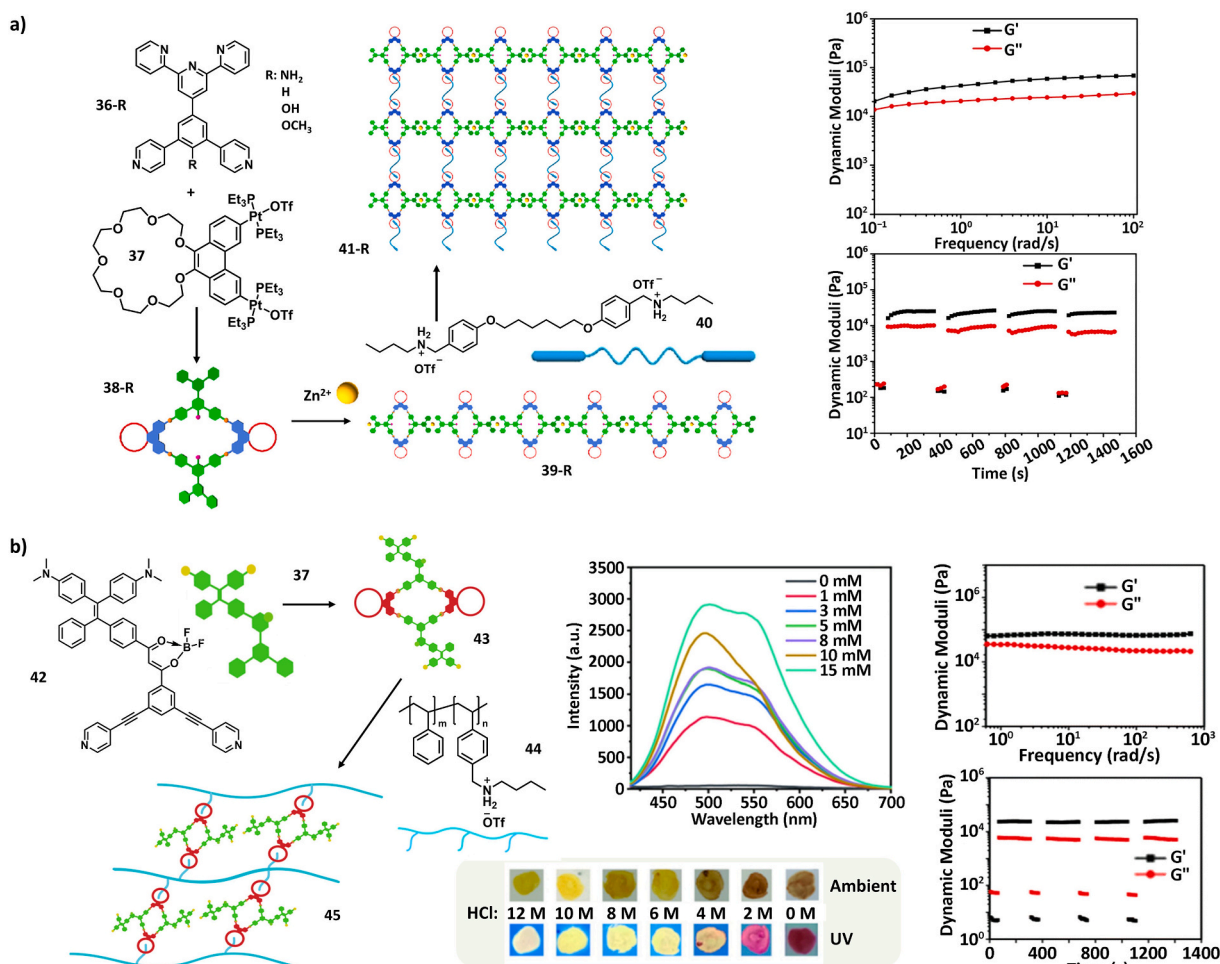


Fig. 10. MSPNs with physically bound 2D junctions: a) Dynamic moduli of 41-NH₂ as a function of oscillation frequency and alternating high and low oscillation amplitudes. [77], Copyright 2019. Reproduced with permission from ACS. b) Emission spectra of 45 at different concentrations of trifluoroacetic acid; and rheological measurements demonstrating gel-like behavior in frequency-sweep and self-healing in alternating high and low deformations. [78], Copyright 2022. Reproduced with permission from RSC.

Following a post-assembly click reaction, Zhang and coworkers synthesized a rhombohedral metallacycle (**48**) by adding a 120° amine-functionalized 4-methyl-*N,N*-bis(4-(pyridin-4-yl)phenyl)aniline donor (**46**) to a 60° di-Pt²⁺ acceptor (**47**). Simultaneously, they synthesized a propiolate terminated tetraPEG (**49-n**). A subsequent “amino-yne” click reaction was performed between the propiolate groups of the tetraPEG

and the amine groups of **48**, forming MSPNs with 2D rhombohedral junctions (**50-n**). Two tetraPEGs with different molar masses were used, resulting in two distinct MSPNs, with short (**50-11**) and long strands (**50-111**). The rheological properties of **50-n** were assessed, revealing a gel-like behavior with no sign of any relaxation, indicative of the stability of the formed metallacycles, due to the robust Pt²⁺-pyridine

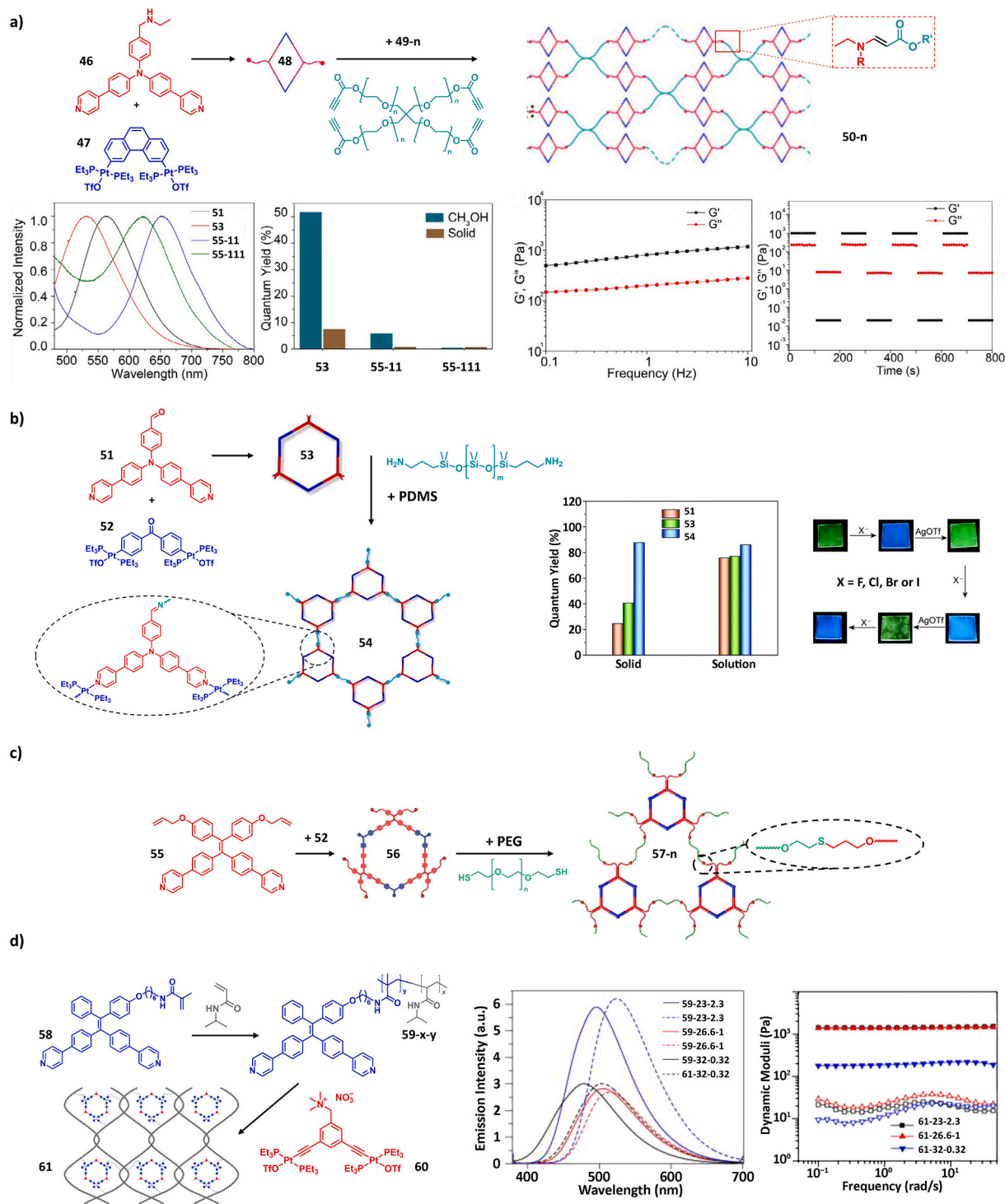


Fig. 11. Post-assembly connecting metallacycles: a) Normalized emission spectra and quantum yield of **50-n** MSPNs and their precursors in the solid-state and solution; Frequency sweep of **50-11** and self-healing. [80], Copyright 2020. Reproduced with permission from Wiley. b) Solution and solid-state quantum yield of **54** and its precursors; Fluorescence photographs of **54** in response to different halogens with reversibility. [81], Copyright 2020. Reproduced with permission from RSC. c) Post-assembly connection of metallacycle **56** through click reaction. [82], Copyright 2021. Reproduced with permission from RSC. d) Assembly of polymeric donor and acceptor: emission spectra of **61** with different chemical compositions and the corresponding dynamic moduli. [86], Copyright 2020. Reproduced with permission from Wiley.

complexes. As **50–11** had a higher crosslink density, it exhibited a ten times higher storage modulus (~ 1 kPa) compared to **50–111** (~ 0.1 kPa), as shown in Fig. 11a. Moreover, Both MSPNs demonstrated self-healing, recovering their mechanical properties after damage due to the dynamic and reversible nature of coordination bonds. The luminescent properties were also notable; **50-n** exhibited red-shifted emission bands, with **50–11** and **50–111** respectively emitting at 513 nm and 532 nm in methanol, which shifted to 650 nm and 622 nm in the solid state. The solid-state quantum yields were reduced due to ACQ, where the dense molecular packing leads to a non-radiative energy loss. These properties enable the potential application of these MSPNs as reversible and emissive supramolecular adhesives, with strong adhesion strength, self-healing properties, thermo-responsiveness, and the unique functionality of visualizing the adhesion process [80].

In a related study, the same group synthesized a hexagonal metallacycle (**53**) by combining a 120° donor, namely 4-(bis(4-(pyridin-4-yl)phenyl)amino)benzaldehyde (**51**) with a 120° di- Pt^{2+} acceptor (**52**). The **53** metallacycle was then transformed into a 2D junction MSPN (**54**) upon introducing amine-terminated PDMS into the medium, which underwent condensation with the carbonyl groups of metallacycles. **54** exhibited bright green emission, an enhanced quantum yield in the solid state, and a red-shifted emission compared to **51** and **53**, attributed to the AIE behavior of the triphenylamine units. The luminescence of the network could be selectively quenched by adding halogen ions or picric acid, indicating its potential use in detecting such substances, as demonstrated in Fig. 11b. Accordingly, **54** shows promise for sensing applications, particularly as radiometric sensors for halogen ions and chemo-sensors for nitroaromatic explosives [81].

Similarly, a hexagonal metallacycle (**56**) was formed by coordinating a TPE derivative, 120° allyl-functionalized bispyridyl donor (**55**) to a 120° di- Pt^{2+} acceptor (**52**). **56** was subsequently mixed with two equivalents of telechelic thiol-terminated linear PEG, with varying lengths. As a result, 2D junction MSPNs (**57-n**) were formed following a “thiol-ene” click reaction between the allyl groups of **56** and the thiol groups of PEG. Shorter PEG spacers led to denser networks with stronger luminescence, as the higher crosslink density promotes aggregation of TPE units and AIE properties, thereby, intensifying the emission, as shown in Fig. 11c. The fluorescence intensity was responsive to environmental factors, such as solvent polarity [82]. Such examples on the extension of preformed metallacycles based on AIEgens through click reactions or transient bonding with polymeric/oligomeric spacers, to form luminescent and stimuli-responsive MSPNs are frequent [83–85]. In contrast, reports on the formation of metallacycle crosslinked MSPNs based on the assembly of polymeric doner/acceptor constituents are relatively rare.

Accordingly, Zhang et al. synthesized donor polymeric chains (**59**) by copolymerizing NIPAM and a methacrylamide derivative of a 120° TPE bispyridyl ligand (**58**). They used different molar ratios of NIPAM and **58** (x and y) to create **59-x-y** copolymers. The formation of MSPNs (**61-x-y**) with different crosslink densities ($y:x$ ratio) occurred upon the addition of a stoichiometric amount of the 120° di- Pt^{2+} acceptor (**60**), resulting in the establishment of 2D hexagonal metallacyclic junctions within the network. **61-x-y** demonstrated notable mechanical properties, including significant flexibility and structural rigidity, attributed to the dynamic network junctions. Rheological studies demonstrated a larger plateau modulus for networks with more junctions, as demonstrated in Fig. 11d. Besides a high-frequency peak in the loss modulus, which can be attributed to the relaxation of free polymeric chains, no crossover between the storage and loss moduli was observed, which stems from the stability of junctions formed by metallacycles. The luminescent properties were significantly influenced by the inherent AIE effect of TPE units. Moreover, the crosslinking density greatly influenced the extent of TPE aggregation and increased the emission intensity and its thermo-responsiveness. The water solubility of MSPNs along with their luminescence and mechanical attributes, make them useful in applications like biomedical engineering [86].

One of the attractive applications of luminescent MSPNs is in the development of light-harvesting systems (LHSs), which are designed to mimic the natural process of photosynthesis, efficiently capturing, transferring, and storing the light energy. LHSs are composed of multiple donor chromophores and one or more acceptor chromophores that work together to collect light energy and transfer it to a reaction center, where it is converted into chemical energy or other useful forms. This mirrors the function of chloroplast pigments in nature, which capture, transmit, and store light energy [87]. By incorporating various chromophores with different absorption-emission spectra, these systems can improve light absorption and extend the range from UV to visible light through the FRET process. While many artificial LHSs rely on a single-step FRET, the most effective natural systems utilize multi-step sequential FRET processes [88]. This multi-step FRET process, referred to as the LHS antenna effect, is distinctly different from the antenna effect observed in lanthanide-ligand complexes. In lanthanide complexes, the antenna effect involves a single-step FRET process in which a strongly absorbing organic ligand transfers energy directly to a lanthanide ion, thereby compensating for the ion's inherently low absorption efficiency. In contrast, the LHS antenna effect relies on a multi-step sequential FRET process among multiple chromophores. This cascade mechanism not only enhances the overall energy transfer efficiency by channeling energy through a series of donor-to-acceptor transfers but also broadens the system's absorption spectrum, enabling the capture of a wider range of light wavelengths. Although both mechanisms employ FRET to enhance luminescence and energy transfer, they are tailored to meet different functional demands and operate within distinct structural frameworks. 2D and 3D junction MSPNs are excellent candidates for LHS application due to their capability to incorporate multiple donor and acceptor units, precise adjustments of their ratio, and control over the overall structure to optimize performance. Moreover, the noncovalent self-assembly of MSPNs simplifies the construction of LHSs, making it more scalable and straightforward compared to traditional methods that involve complex and multistep syntheses [89–91]. To the best of our knowledge, however, MSPNs with polymeric constituents are not yet employed in development of LHSs, therefore, here we briefly review relevant supramolecular networks with 2D junctions, which can inspire the substitution of polymeric constituents.

Accordingly, Stang et al. conducted a study where a 120° bis(4-(pyridin-4-yl)phenyl)amine donor functionalized with a cyanostilbene group was synthesized, with each cyanostilbene being connected to an oligomeric alkyl chain terminated with a phenyl group (**62**). Using 120° (**63**) and 180° (**64**) di- Pt^{2+} acceptors, they created two distinct hexagonal metallacycles. **65** formed by **63** was smaller compared to **66** made by **64**, due to the smaller bent angle of the **63** acceptor. Networks were created by the subsequent host-guest interaction and π - π stacking between the end-phenyl groups of the donor and the metallacyclic assemblies [92,93]. The luminescent properties of both networks were enhanced due to the AIE effect of cyanostilbene. Spherical nanoparticles were formed, as confirmed by transmission electron microscopy (TEM) and dynamic light scattering (DLS), with high quantum yields in solution. The hydrodynamic diameters of the aggregates were found to be around 250 nm and 174 nm for **65** and **66** respectively. The subsequent addition of Eosin Y fluorescent dye into these networks facilitated FRET, due to the overlap between the absorption spectrum of Eosin Y and the emission spectra of metallacycles, thereby enabling LHS characteristics, as shown in Fig. 12a. The energy transfer for the Eosin Y-doped networks was higher for the network with smaller metallacycles [89].

In a similar study by Yang and coworkers, a TPE derivative 120° bispyridyl donor was functionalized with nitrile-terminated alkyl chains (**67**). The subsequent addition of a 120° di- Pt^{2+} acceptor (**52**) led to the formation of a hexagonal metallacycle (**68**). This SCC was then mixed with mono-pillar[5]arene-modified boron-dipyrromethene (BODIPY) (**69**) or 9,10-distyrylanthracene (DSA) modified with two pillar[5]arene functionalities (**70**), resulting in distinct SCCs. The mono-pillar[5]arene-modified BODIPY led to the formation of a 6-arm star-shaped metallo-

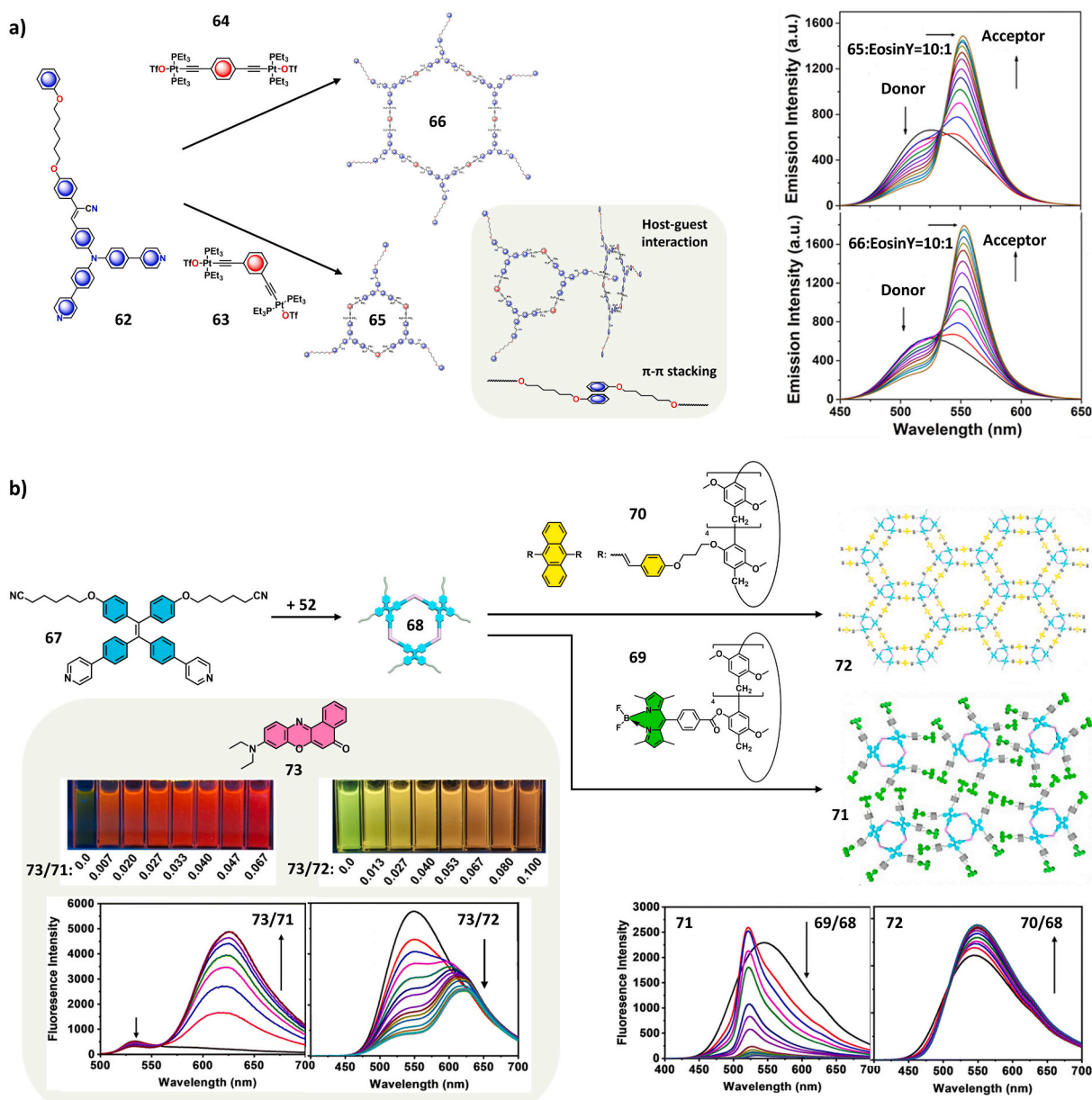


Fig. 12. Metallacycle crosslinked LHSs: a) Transformation of emission spectra of 65 and 66 in the presence of Eosin Y due to FRET. [89], Copyright 2019. Reproduced with permission from ACS. b) Variation of emission spectra of 71 and 72 solutions (two graphs on left) with changing 68:69 and 68:70 ratios, and the addition of 78 (two graphs on right). [91], Copyright 2023. Reproduced with permission from RSC.

supramolecular polymer (71), while the di-pillar[5]arene-modified DSA formed a percolated network (72). Notably, 71 exhibited ACQ behavior, while 72 demonstrated AIE properties due to the copresence of TPE and DSA units. AIE-FRET and ACQ-FRET effects were evident in the emission spectra; higher 68:69 ratios in 71 led to weaker emission and peak shifts, whereas higher ratios resulted in stronger emission with slight peak repositioning in 72. The addition and encapsulation of Nile Red dye (73) enabled an additional FRET process, as shown in Fig. 12b, due to the overlap of 73 absorption with emission bands of both 71 and 72. Nanoparticle with high quantum yields were obtained in aqueous medium, as confirmed by TEM and DLS, yielding particles with mean diameters of 104 nm for 71 and 239 nm for 72 [91]. Despite these examples are not MSPNs by our definition, as no polymer chain is involved, they highlight the significant potential of MSPNs in LHS applications, especially in cases requiring processability on top of accurate energy transfer and customizable luminescence.

3.3. Polymer networks with luminescent 3D junctions

Compared to the vast structural diversity and luminescent properties of metallacycles [13,94], luminescent MSPNs based on 3D cage junctions are significantly under-developed. Considering the functionality and application of metallacycles and processability of polymers, such networks could have broad potential across multiple high-tech fields due to their unique combination of luminescence, structural diversity, chemical tunability, and responsiveness to stimuli. Just like 2D junction networks, the first examples tried to connect preformed cages by host-guest interactions. In a study by Zhang, Yin, Stang, and coworkers, a ditopic 2,7-di(pyridin-4-yl)phenanthrene modified with a 21-crown-7 moiety (74), a tetratopic TPE-based sodium benzoate (75), and *cis*-Pt(PeEt₃)₂(OTf)₂ were used to form a tetragonal prismatic metallacycle (76). This metallacycle was further developed into a 3D network (77) through the addition of a bisammonium salt (40), facilitating host-guest interaction with the crown ether hosts. 77 exhibited remarkable

luminescent and mechanical properties, responsive to multiple external stimuli. Notably, when temperature of the network solution in acetone was increased, the emission intensity diminished due to the enhanced solubility, which disrupts aggregated clusters. The material also demonstrated reversible sol-gel transition when exposed to potassium ions/18-crown-6, due to disassembly and reassembly of the network

crosslinks, as illustrated in Fig. 13a, showcasing its dynamic emission and mechanical properties. These unique features make **77** suitable for a variety of applications, including optical sensing, actuating, and potentially biomedical engineering, combining fluorescence, stimuli-responsiveness, and self-healing capabilities [95].

Extending on these results, Zhang et al. modified a ditopic

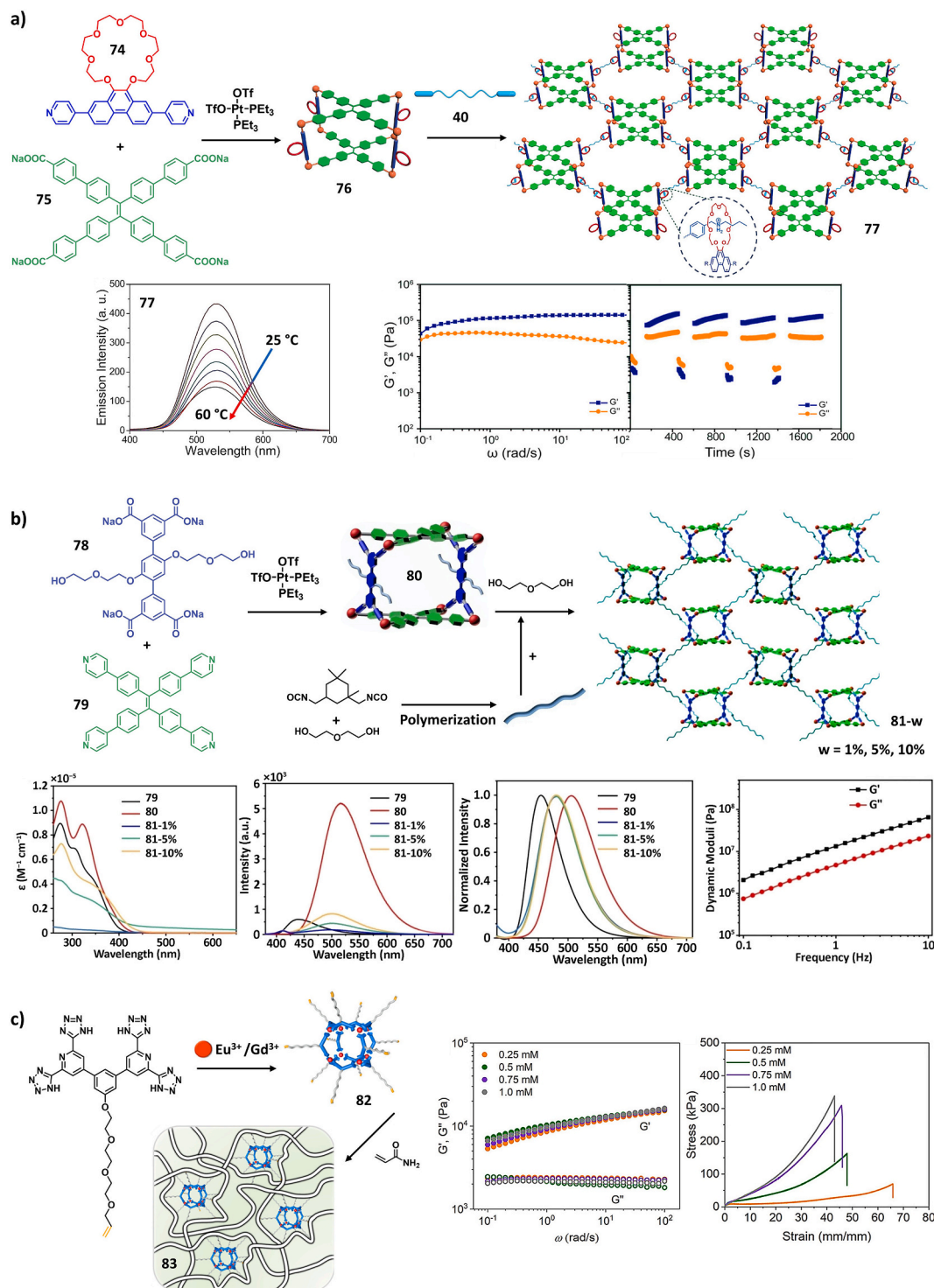


Fig. 13. Post-assembly connecting metallages: a) Temperature-dependent emission spectra of **77** solutions, and the corresponding dynamic moduli and self-healing measurements. [95], Copyright 2018. Reproduced with permission from ACS. b) Absorption (left) and emission (left-middle) spectra of the **81** network and precursors, and their normalized solid-state emission spectra (right-middle); Dynamic moduli of 91–1 %. [97], Copyright 2022. Reproduced with permission from Wiley. c) Ln-cage crosslinked MSPNs demonstrating slightly enhanced storage modulus, but significantly superior mechanical properties upon increasing the cage content. [98], Copyright 2024. Reproduced with permission from ACS.

tetracarboxylate with diethylene glycol side chains (**78**) to form tetragonal prismatic metallacage assemblies (**80**) in combination with tetrapotic tetra-(4-pyridylphenyl)ethylene (**79**) and *cis*-Pt(PEt_3)₂(OTf)₂. Subsequently, prepolymers made by polycondensation of isophorone diisocyanate and diethylene glycol were extended to networks (**81-w**, w being the weight percent of metallacage) in the presence of the cage **80** as the junction, as demonstrated in Fig. 13b [96]. Along with the crosslink density, the modulus of MSPNs increased, while the elongation at break decreased, reflecting enhanced mechanical strength but reduced flexibility. The rheological data represent a gel-like behavior, with storage modulus surpassing the loss modulus over all measured frequency range, however, the decaying behavior of the dynamic moduli towards lower frequencies demonstrates the significant relaxation of free complexed chains. This suggests that the network structure contains many defects like loops and dangling ends and is not as ordered as expected. The MSPNs also exhibited self-healing capacity and notable shape memory characteristics, particularly at high crosslink densities, which allowed materials to return to their original shape after deformation when subjected to appropriate stimuli, such as heat. In terms of luminescence, MSPNs with the higher crosslink density exhibited more intense AIE, as the denser network restricts the molecular motion more effectively, and therefore, promotes efficient aggregation of TPE units. Accordingly, the sustained luminescence of these MSPNs, combined with their mechanical strength, makes them ideal for optoelectronics and wearable devices [97].

More recently, Liang et al. presented a novel approach to developing highly stretchable hydrogels by incorporating a minimal amount of

lanthanide-based metallacages as crosslinkers. Specifically, a bipyridyl bis-tetrazole ligand functionalized with a vinyl group was coordinated with lanthanide ions (Eu^{3+} and Gd^{3+}) to form metallacages (**82**). This complex was then used as a multi-functional comonomer in free radical polymerization of acrylamide (**83**), at concentrations ranging from 0.0083 % to 0.033 %. The resulting hydrogels demonstrated exceptional mechanical properties, achieving stretchability beyond 4200 % and tensile stress over 400 kPa at a strain rate of 100 mm/min. This remarkable performance was attributed to the high functionality and dynamic nature of the metal coordination bonds in lanthanide cages, enabling efficient energy dissipation during stretching. Dynamic moduli demonstrated a gel-like behavior across the measured frequency range, while stress-relaxation measurements revealed relaxation times of 10 and 100 s for networks made by Eu^{3+} and Gd^{3+} , respectively, as shown in Fig. 13c. Additionally, hydrogels demonstrated enhanced luminescent and magnetic properties. Eu^{3+} cages endowed the hydrogels with high luminescence quantum yields, while Gd^{3+} equivalents facilitated fast magnetic resonance relaxation. The heterometallic cages, formed by co-assembly of Eu^{3+} and Gd^{3+} ions, rendered the hydrogels with both superior luminescence and fast T1 relaxation, making them highly suitable for biomedical applications in luminescent and magnetic resonance imaging [98].

In contrast to metallacycle crosslinked MSPNs, cage crosslinked polymer networks are developed more based on the assembly of macromolecular ligands rather than connecting preformed cages. In a pioneering work, Johnson's group developed a percolated MSPN using telechelic bispyridyl-terminated PEG and naked Pd^{2+} metal ions. The

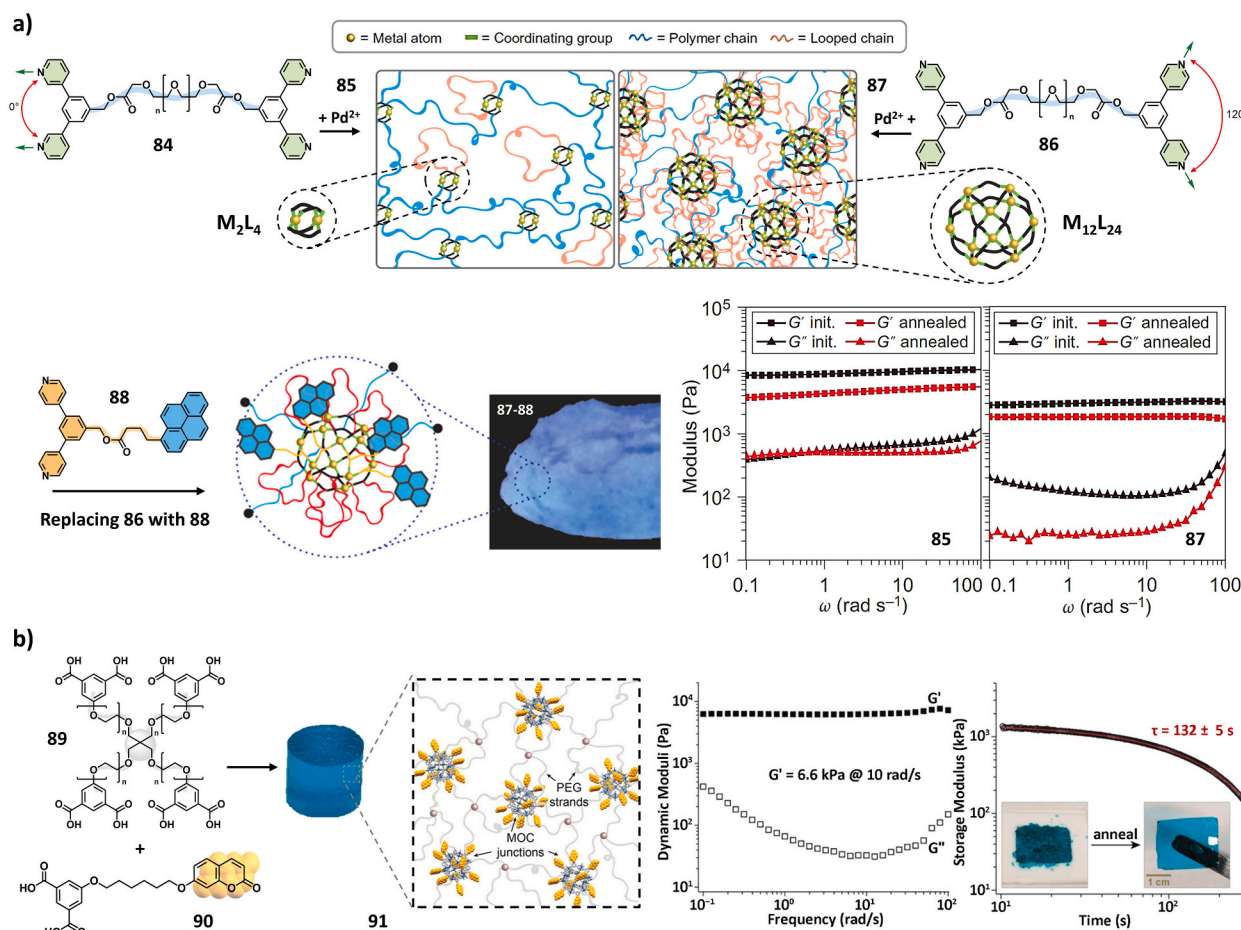


Fig. 14. Assembly of polymeric donor and acceptor: a) Network connectivity as a function of cage size and replacing a fraction of ditopic PEG precursors with monotopic pyrene; Dynamic moduli of MSPNs before and after annealing. [36], Copyright 2018. Reproduced with permission Springer Nature. b) Dynamic moduli and stress relaxation of MSPNs formed by dye-decorated cage junctions. [100], Copyright 2020. Reproduced with permission from Wiley.

bispyridyl (**84**) with 0° bent angle promoted the formation of paddle-wheel M_2L_4 metallacage MSPNs (**85**), while the bispyridyl equivalent with 120° bent angle (**86**) led to the formation of cuboctahedral $M_{12}L_{24}$ metallacage MSPNs (**87**), as demonstrated in Fig. 14a. Surprisingly, the network based on the smaller cage, with junctions of the functionality of four showed a higher plateau modulus compared to the one based on the bigger cage and junctions with functionality of 24, even after annealing. This is in contrast to the expectation based on affine or phantom network models, correlating modulus with density and functionality of crosslinks [43]. This discrepancy was associated with the fact that due to the steric hindrance in crowded crosslinks, polymer spacers would form elastically inactive intramolecular loops rather than connecting different cages. By replacing some of the bridging PEG chains with the pyrene substituted bispyridyl ligands (**88**), they managed to create luminescent 3D MSPNs (**87–88**) at the expense of network connectivity [99]. More recently, they expanded their research by integrating the photoresponsive diarylethene group with dynamic luminescence into the bispyridyl ligand structure. This allowed them to alter the network topology in response to irradiation, triggered by irradiation induced change in ligand's bent angle from 62° to 138° . As a result, the cage structure shifted from small Pd_3L_3 rings to large $Pd_{24}L_{48}$ rhombicuboctahedra, which resulted in profound increase in plateau modulus. Nevertheless, they did not study the simultaneous change in luminescent properties [36].

In another recent example, Johnson's group developed a luminescent MSPN with $Cu_{12}L_{24}$ polyhedra junctions (**91**) formed upon complexation of terminal benzenedicarboxylate ligands of tetraPEG precursors (**89**) with Cu^{2+} . Rheological studies revealed a gel-like behavior with a plateau modulus of 6.6 kPa at the polymer concentration of 5.3 wt%. The storage and loss moduli indicated a relaxation process below the measurable frequency range, whose specific timescale was determined by stress relaxation measurement to be 132 s, indicative of a rather fast dynamics for $Cu_{12}L_{24}$ metallacages compared to those formed by Pd^{2+} or Pt^{2+} with bispyridyl-based ligands. Replacing a fraction of tetraPEG precursors with monotopic benzenedicarboxylate ligands functionalized with coumarin (**90**), they could tune the junction functionality and of course luminescence (**91**), as demonstrated in Fig. 14b. Exposure to 368 nm light under nitrogen caused the metallacage to break down due to the photoreduction of Cu^{2+} to Cu^+ , resulting in deconstruction of junctions and transition from gel to a clear green liquid. Further irradiation for two hours produced a brown liquid, due to the formation of Cu(0) nanoparticles. When both, the green and the brown liquids, were exposed to air, the initial gel state was retrieved. This entire irradiation process enabled reversible sol-gel transitions through the redox manipulation of copper metal centers. The presence of coumarin in the vicinity of metallacage junctions was found to be necessary to avoid over-reduction. As such, the redox induced formation of Cu^+ was utilized to catalyze the azide-alkyne cycloaddition reaction. Specifically, they formed an interpenetrating double network consisting of the metallacage crosslinked polymer network alongside a secondary covalent network formed through reaction of azide terminated PEG chains and tetrakis-(prop-2-ynyloxymethyl)methane [100].

In summary, classifying polymer networks by the dimensionality or nuclearity of their transient junctions provides a clear framework for understanding the mechanisms of luminescence in different MSPNs. This classification also correlates with distinct material characteristics, such as mechanical properties and specific functionalities. While detailed synthetic strategies for creating networks with various junction types, and the resulting effects on material properties and functionalities, lie beyond the scope of this study, they have been thoroughly reviewed elsewhere [9,76]. Accordingly, we can briefly list these distinct properties, as shown in Table 1.

4. Conclusions and outlook

In summary, luminescent metallo-supramolecular polymer networks represent a promising class of materials that combine the dynamic

Table 1

General classification of luminescence mechanisms and material properties in MSPNs with various types of junctions.

Type of Junction	Luminescence Mechanism	Mechanical Properties	Pros and cons
0D	Antenna effect	Low elasticity Low damping Short relaxation time Moderate elasticity	Limited but predictable network connectivity Fast stimuli-responsiveness
2D	AIE	Moderate damping Long relaxation time	Functionalities like host-guest interaction
3D	AIE	High elasticity High damping Long relaxation time	Functionalities like host-guest interaction and catalysis Widely tunable network connectivity Annealing might be required for optimal cage formation

properties of supramolecular chemistry with the structural integrity and processability of entangled polymers. By incorporating metal coordination junctions, MSPNs can achieve not only adaptive mechanical properties, but tunable luminescence and responsiveness to external stimuli. This review has classified different strategies used so far in development of luminescent MSPNs, based on junction functionality, highlighting how dimensionality of junctions can bring unique advantages, from the antenna effect in 0D junction lanthanide complexes to AIE in 2D and 3D metallacycles and metallacages. While significant progress has been made, especially with 0D systems based on lanthanide complexes, there remains untapped potential in the further integration of more complex supramolecular architectures in polymeric networks. The development of these hybrid materials could enable a wide range of applications, from bioimaging to energy harvesting.

Looking forward, several areas remain underexplored in the field of luminescent MSPNs. First, the use of AIE effects in 0D junction MSPNs could significantly broaden the design possibilities of these systems, offering a novel approach to enhance their luminescence and responsiveness. At the same time, incorporating lanthanides in 2D and 3D crosslinked networks remains largely unexplored. Given the excellent luminescent properties of lanthanides and their versatility in coordination chemistry, this could pave the way for multifunctional networks with enhanced performance in both luminescence and stimuli-responsiveness. A crucial future direction is the transition from material development to practical applications. The potential of MSPNs in areas like FRET-based light harvesting, catalysis, drug delivery, and bioimaging is immense but requires more focused research to realize these capabilities. Furthermore, although metallacages hold great promise due to their high functionality and tunability, examples of MSPNs based on 3D crosslinks are still scarce. Considering the extensive potential of metallacages for functional applications, expanding the study of cage-crosslinked MSPNs could open new horizons in the design of next-generation smart materials. A concerted effort in addressing these gaps could significantly advance the field, leading to a new wave of innovations in material science. However, realizing this potential is not without challenges. Specifically, we elaborate here on several synthetic and structural limitations that must be addressed to move the field forward.

Achieving AIE in 0D junction-based systems faces several challenges. One major challenge is the limited availability of aggregation-compatible ligands that simultaneously offer suitable coordination sites and desirable photophysical properties. Nonetheless, this remains a highly promising direction. The incorporation of AIE-active motifs may not only enhance emission efficiency but also provide new tools for probing supramolecular dynamics, including bonding kinetics and macromolecular dynamics.

Incorporating lanthanide ions into 2D and 3D supramolecular junctions also presents considerable hurdles, particularly related to coordination geometry control and solubility of precursors. The majority of well-defined metallacycles and metallacages to date are constructed using Pd^{2+} and Pt^{2+} ions, due to their predictable square-planar coordination geometries, which offer a reliable balance between steric hindrance and coordination affinity. In contrast, lanthanides often display flexible and unpredictable coordination behavior, making it difficult to construct structurally precise supramolecular junctions. Addressing this limitation will require the development of new ligand designs—such as pre-organized multidentate ligands, rigid frameworks, or heteroleptic coordination strategies—that can impose greater control over coordination geometry and improve the structural stability of lanthanide-based architectures.

Moreover, supramolecular networks crosslinked through purely non-covalent interactions—particularly those incorporating lanthanide-based junctions—tend to form soft gels with limited mechanical robustness, which constrains their applicability. To overcome this, future research should explore parallel incorporation of reversible or permanent covalent crosslinks, as well as the use of reinforcing polymers beyond the commonly used PEG. These strategies could enhance mechanical strength while preserving the dynamic and stimuli-responsive features of the networks.

By addressing these synthetic and structural challenges, the field of luminescent metallo-supramolecular polymer networks can move closer to realizing its full potential in both fundamental research and practical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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