

Recent Advances in Metal–Macrocycle-Based Supramolecular Polymers and Their Assemblies

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Abstract: Metal–macrocycle-based supramolecular polymers represent a frontier in smart materials, seamlessly integrating the highly tunable architectures of metal–organic macrocycles with the dynamic properties of hierarchical assemblies. This Review comprehensively evaluates recent advances in the coordination-driven synthesis and self-assembly of these tailored materials. By employing specific transition metal nodes (e.g., Pt, Pd, Fe), researchers can precisely engineer macrocyclic topologies while embedding intrinsic photophysical, electrochemical, and catalytic functionalities. We systematically analyze how secondary noncovalent interactions—such as host–guest recognition and hydrogen bonding—propel the hierarchical assembly of these building blocks from discrete molecular entities to macroscopic functional materials. Furthermore, we highlight how the dynamic nature of coordination bonds endows these assemblies with remarkable stimuli-responsiveness and self-adaptive capabilities. Finally, we discuss cutting-edge applications in biomedicine, smart sensing, and heterogeneous catalysis, alongside a critical perspective on the current bottlenecks and future directions necessary for translating these bespoke supramolecular systems into practical technologies.

Keywords: Metal–Organic Macrocycles; Supramolecular Polymers; Hierarchical Self-Assembly; Coordination-Driven Assembly; Stimuli-Responsive Materials

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1. Introduction

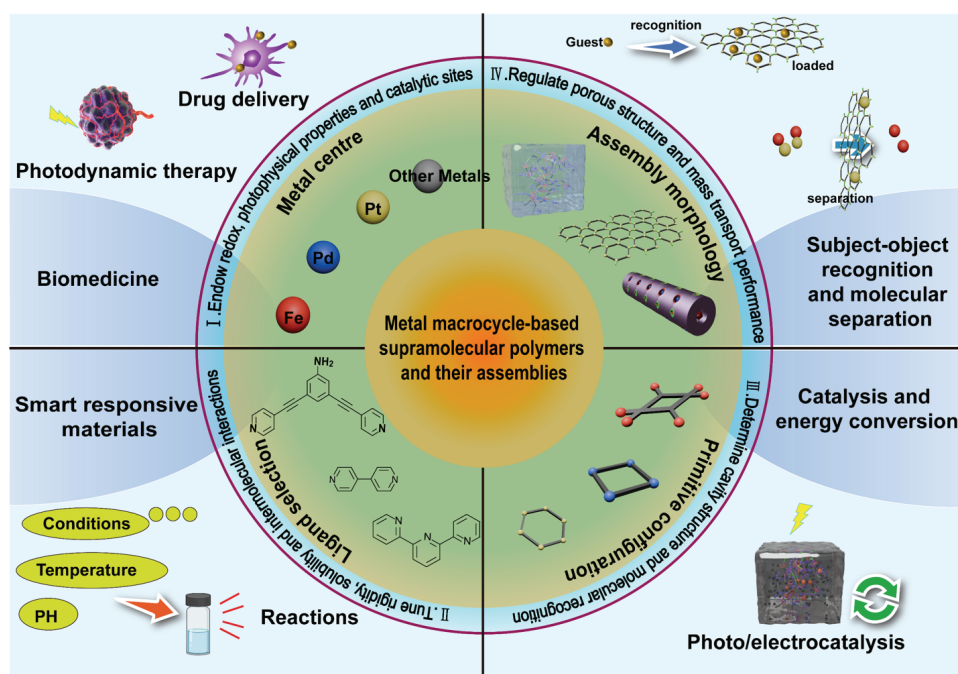
Supramolecular polymers are molecular aggregates formed by the spontaneous cross-linking of monomers bearing complementary recognition sites through reversible and highly directional noncovalent interactions, such as hydrogen bonding, host–guest recognition, metal coordination, and π – π stacking. These aggregates can further undergo hierarchical assembly into diverse macroscopic morphologies including fibers, gels, and vesicles. Compared with conventional covalent polymers, supramolecular polymers, owing to the dynamic reversibility of noncovalent bonds, combine excellent mechanical integrity with the intelligent responsiveness characteristic of supramolecular chemistry—enabling reversible depolymerization and reorganization in response to temperature, pH, or specific chemical stimuli. Among the various building blocks, macrocycle-based systems represent one of the earliest and most systematically explored classical directions,

benefiting from their well-defined cavity structures and high designability. Traditional systems predominantly employ crown ethers, cyclodextrins, calixarenes, pillararenes, and cucurbiturils as the host units, relying on molecular recognition of specific guests by the macrocyclic cavities to drive monomer polymerization. For instance, cyclodextrins, with their excellent water solubility and biocompatibility, have found prominent applications in biomedical materials; whereas crown ethers and pillararenes, owing to their precise recognition of alkali metal ions and ammonium salts, play a significant role in molecular machines and stimuli-responsive materials^{[1][2][3][4]}.

On this basis, research interest has gradually shifted toward “metal–organic macrocycle” systems constructed via coordination-driven self-assembly. The synergistic coordination between metal ions and organic ligands endows the macrocyclic building blocks with unprecedented characteristics of “structurally tunable and functionally programmable”^[5]. In terms of structural design, the diversity of metal-ion coordination geometries provides a powerful tool for precisely controlling the size, shape, and electronic distribution of the macrocycles. In terms of functionality, the introduction of metal centers directly imparts intrinsic photophysical, catalytic, and magnetic properties to the system, while the retained internal cavities still possess excellent host–guest recognition capability^[6]. By employing such metal–organic macrocycles as core nodes and triggering secondary noncovalent polymerization through peripheral functional groups, one can construct metal–macrocycle-based supramolecular polymers with highly integrated functionalities, demonstrating immense application potential in advanced functional materials^{[7][8][9]}.

Among the current metal–macrocycle assembly systems, platinum (Pt)-based systems have been the most extensively studied, with their products characterized by well-defined structures, tunable luminescent properties, and excellent biocompatibility^[10]. Palladium (Pd)-based systems are distinguished by the dynamic reversibility of their coordination bonds, endowing the assemblies with outstanding self-adaptive reconstitution ability and multi-stimuli-responsive behavior. Iron (Fe)-based systems take a unique approach, focusing on the redox reversibility and spin-crossover phenomena of the iron centers^[11]. In addition, metals such as ruthenium (Ru), iridium (Ir), and zinc (Zn) have also made significant contributions in the fields of photofunction, catalytic transformation, and fundamental theoretical research, greatly broadening the research boundaries of this field^{[8][13][14]}. On this basis, this review systematically centers on Pt-, Pd-, Fe-, and other representative metal–macrocyclic building blocks, delving into their design and synthesis strategies, morphological evolution during hierarchical assembly, and application advances in frontier areas such as biomedicine and catalysis, while also providing a perspective on future development bottlenecks and breakthrough directions.

Figure1 : Schematic illustration of the construction and regulation strategies and diversified applications of metal-macrocycle-based supramolecular polymers and their assemblies.



2. Results and Discussion

The intrinsic physicochemical properties of metal centers are the core determinants of the structure–property relationships governing both the macrocyclic building blocks and the macroscopic assemblies^{[7][15]}. Differences among various metal ions in terms of coordination kinetics, redox potential, and biocompatibility give rise to the distinct functional advantages of each metal–macrocyclic system. Therefore, a systematic review categorized by metal centers is of significant theoretical and practical importance for deeply elucidating the structure–property relationships of materials and guiding the design of tailor-made functional supramolecular systems.

2.1 Platinum (Pt)-Based Metal–Macrocyclic-Based Supramolecular Polymers

Platinum-based metal–macrocyclic systems represent one of the most well-established classical systems in the field of coordination-driven self-assembly^[16]. The Pt(II) ion exhibits a typical square-planar coordination geometry, and the Pt–N bonds formed with nitrogen-donor ligands (e.g., pyridine) combine ideal thermodynamic stability with moderate kinetic inertness. This feature endows Pt-based systems with two core advantages: first, highly predictable geometric topology, allowing researchers to precisely match the angles between acceptors and ligands through the “directional bonding” strategy to achieve rational tailoring of the macrocyclic frameworks; second, exceptional structural rigidity, which ensures that the macrocycles maintain their core frameworks without collapse during subsequent complex hierarchical assembly, thereby providing a solid foundation for the construction of higher-order supramolecular structures.

2.1.1 Construction Strategies for Pt-Based Macrocycles

The construction of Pt-based macrocycles relies primarily on coordination-driven self-assembly strategies, in which Pt(II) acceptors with specific coordination orientations and organic ligands are mixed in solution at precise stoichiometric ratios to form thermodynamically stable target macrocyclic structures through spontaneous coordination bond formation^[6]. The construction strategies can be categorized into three aspects: geometric design and multicomponent regulation, functionalization modification, and post-assembly functionalization.

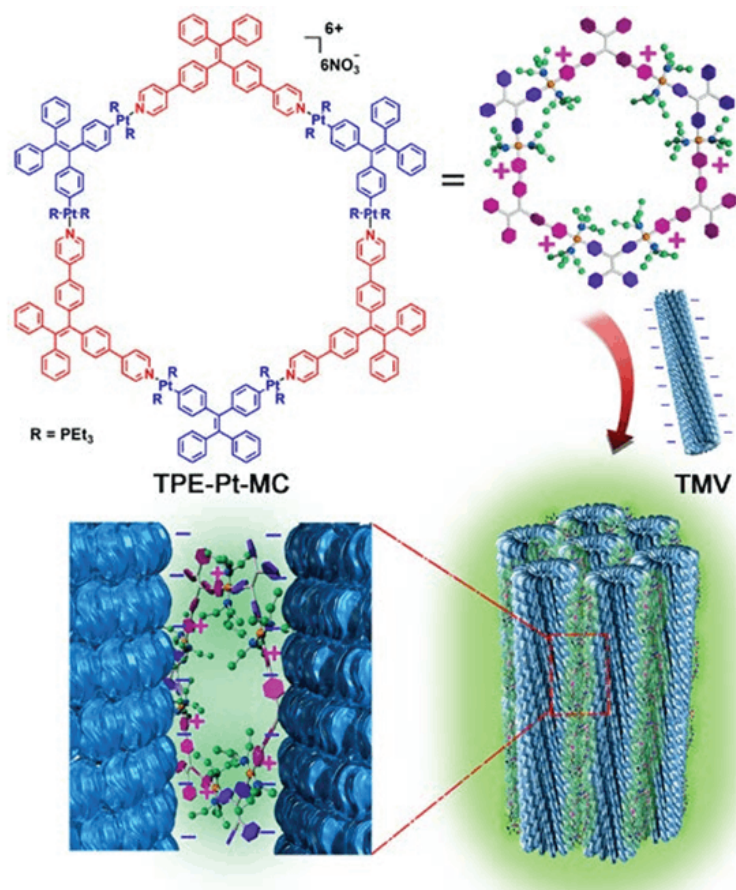
The topological shape of Pt-based macrocycles is predominantly governed by the “angle complementarity” principle: the sum of the directional angles of the donors and acceptors defines the polygonal geometry of the closed ring. For example, the combination of a 60° Pt(II) acceptor with a 120° bipyridyl ligand generates a rhomboidal macrocycle; the combination of a 120° acceptor with a 120° ligand yields a hexagonal macrocycle; whereas the combination of a 90° acceptor with a 180° linear ligand produces a square macrocycle^[10]. To date, researchers have successfully developed a variety of two-dimensional polygons ranging from triangles to hexagons, as well as sophisticated three-dimensional structures such as prisms and cages via extension with three-dimensional ligands. In addition, by adjusting the stoichiometric ratios of multicomponent mixtures or introducing asymmetric bifunctional ligands, the systems exhibit excellent “self-error-correction” mechanisms and self-sorting behaviors, thereby enabling the high-purity acquisition of complex yet single isomeric macrocycles^[17].

Under the premise of preserving the integrity of the macrocyclic framework, specific functional units can be conveniently introduced into Pt-based macrocycles through rational design of the organic ligand functionalities. For instance, incorporating aggregation-induced emission (AIE) moieties such as tetraphenylethylene (TPE) into platinum rings not only effectively restricts the single-bond rotation of TPE via the confinement effect of the rigid macrocyclic framework, but also significantly enhances the radiative transition after hierarchical assembly, laying the foundation for the design of highly sensitive fluorescent probes^[18]. Similarly, the introduction of large π -conjugated systems such as phenazine, through modulation of ligand substitution and conjugation degree, enables tunable emission from blue to yellow-green^[19]. Furthermore, to avoid interference of complex functional groups with the thermodynamic equilibrium of self-assembly, post-assembly modification strategies have been developed. Stang innovatively introduced copper-free strain-promoted azide–alkyne cycloaddition (SPAAC) reactions^[36], by pre-assembling cyclooctyne groups onto rhomboidal or hexagonal platinum rings and subsequently performing mild [3+2] cycloaddition with azides, this approach achieves flexible functional module incorporation while perfectly circumventing the risk of traditional copper catalysts displacing the Pt–N framework or metal centers, thereby providing a powerful tool for the construction of multifunctional Pt-based supramolecular materials.

2.1.2 Advances in the Applications of Pt-Based Macrocycle-Based Supramolecular Polymers and Their Assemblies

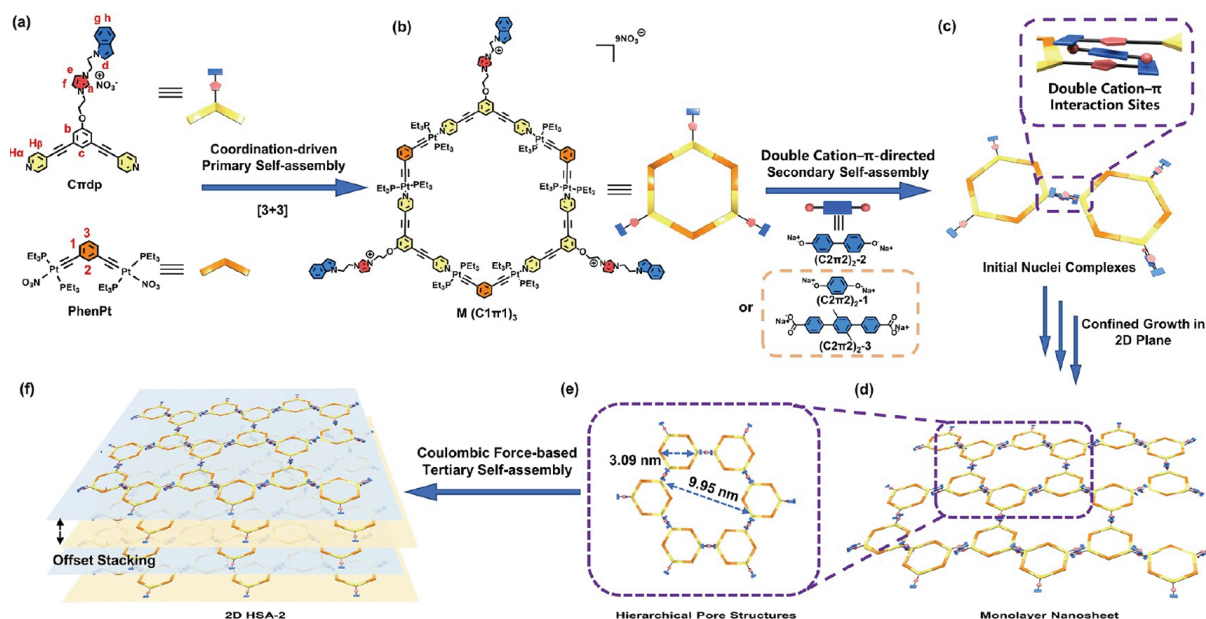
Constructing supramolecular polymers using platinum-based metal–macrocyclic building blocks enables the seamless integration of the intrinsic functions of platinum macrocycles with the macroscopic properties of supramolecular materials^{[9][15]}.

Figure 2. Electrostatically triggered hierarchical co-assembly between cationic TPE-functionalized platinum metallacycles (TPE-Pt-MC) and tobacco mosaic virus (TMV). Size-matched oppositely charged building blocks form three-dimensional bundled microscale superstructures. Confinement inhibits intramolecular rotation of TPE groups, activates aggregation-induced emission (AIE), and enhances fluorescence. Reprinted with permission from Tian et al., J. Am. Chem. Soc., 2016, 138, 11348–11351. Copyright 2016 American Chemical Society.



Hierarchical assembly strategies provide an important pathway for the functional applications of metal–macrocycle assemblies. Tian et al.^[18] developed cationic platinum metallacycles containing tetraphenylethylene (TPE), the size of which matches well with that of tobacco mosaic virus (TMV). Through electrostatic interactions, the two components undergo hierarchical assembly into three-dimensional micron-scale bundle-like superstructures. Meanwhile, the intramolecular rotation of the TPE units is restricted by steric hindrance effects within the assembled architectures, activating the AIE effect and resulting in significantly enhanced fluorescence. The resulting supramolecular assemblies can also be disassembled upon the addition of a competing reagent (e.g., TBABr), which disrupts the Pt–N coordination and leads to the dissociation of the structures. This process relieves the restriction on TPE intramolecular rotation, inducing the aggregation-caused quenching (ACQ) effect and enabling on-demand release of TMV. This reversible metallacycle–virus assembly strategy based on electrostatic recognition provides new insights for the development of biosensors with fluorescence-traced functions, intelligent drug delivery vehicles, and tissue engineering scaffold materials. On this basis, researchers can track the assembly process in real time, facilitating the visualized fabrication of biohybrid materials. Notably, this strategy is also applicable to other negatively charged protein-based nanoparticles, such as bacteriophage M13 and ferritin, demonstrating excellent platform versatility.

Figure 3. Schematic illustration of the multistage hierarchical self-assembly route toward porous Pt(II)-based metallacycle two-dimensional supramolecular nanosheets that serve as dual-functional heterogeneous catalytic platforms. Reprinted with permission from Chen et al., *Journal of the American Chemical Society*, 2023, 145, 19746–19758. Copyright 2023 American Chemical Society.

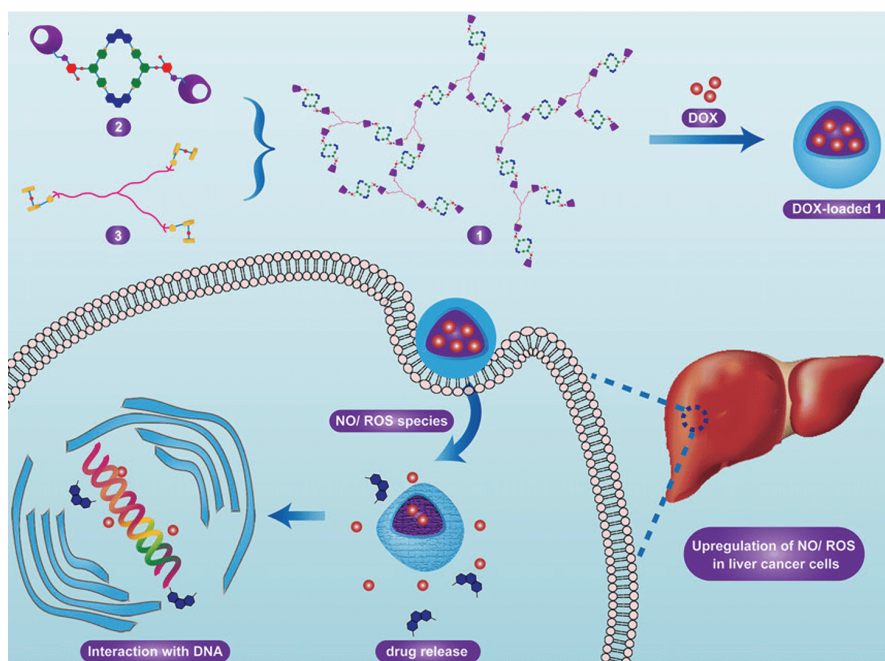


In addition, Tian and Chen et al.^[20] introduced dication- π interactions to achieve the directional and continuous growth of platinum rings in two dimensions, thereby constructing two-pore supramolecular nanosheets capable of loading dual nanocatalysts. This work broadens the application scope of Pt-based assemblies in heterogeneous cooperative catalysis. Notably, this study not only opens up a new direction for Pt-based metal-macrocylic systems in the field of heterogeneous catalysis, but also provides a general strategy for regulating the two-dimensional self-assembly pathways of metallacycles.

Figure 4. Schematic of NO/redox dual-responsive Pt metallacycle nanocarriers for synergistic liver cancer chemotherapy. β -CD-modified metallacycles self-assemble with ferrocene guests to construct DOX-loaded nanoparticles. Intracellular NO/ROS triggers carrier disassembly, enabling combined anti-tumor therapy via synergistic DNA-targeting of Pt metallacycles.

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In the frontier field of biomedicine, Pt-based macrocycle-based supramolecular polymers and their assemblies have become one of the important research directions for precision drug delivery platforms, leveraging their synergistic advantages of structural tunability, stimuli-responsiveness, and the intrinsic anticancer activity of platinum centers. Tian and Chen et al.^[21] successfully constructed a supramolecular drug delivery assembly with dual responsiveness to both nitric oxide (NO) and redox stimuli, featuring a β -cyclodextrin-modified rhomboidal Pt(II) metallacycle as the core, through an orthogonal self-assembly strategy. In this system, the β -cyclodextrin-functionalized platinum-based metallacycle serves as the host unit, which further assembles with a redox-responsive three-arm PEGylated ferrocene guest via host–guest recognition to form spherical nanoparticles with hyperbranched topological architecture. Benefiting from the extremely low critical aggregation concentration of the assemblies, the hydrophobic anticancer drug doxorubicin (DOX) can be efficiently encapsulated within their hydrophobic cavities. In the hepatocellular carcinoma cellular microenvironment, endogenous NO triggers the cleavage of the amide-functionalized o-phenylenediamine units on the metallacycles, while oxidative stimuli drive the dissociation of ferrocene from the cyclodextrin cavities. The synergistic action of these two stimuli induces a morphological transformation of the assemblies and enables the controlled release of DOX. Concurrently, the Pt(II) acceptor itself possesses intrinsic anticancer activity, working synergistically with the encapsulated DOX to achieve a chemotherapeutic combination effect. In vitro experiments demonstrated that the drug-loaded assemblies exhibited superior growth inhibition against HepG2 hepatocellular carcinoma cells compared with free DOX, confirming the feasibility of this system for precision drug delivery and synergistic therapy through dual-responsive mechanisms. This work provides new perspectives for the application of platinum-based metallacycle-based supramolecular polymers in precision therapy of hepatocellular carcinoma.

Figure 5. Structure of naphthalene-functionalized Pt(II)-based metallamacrocyclic. (a) Schematic cartoon representation and chemical structure of metallacycle monomer 1. (b) Top and side views of the single-crystal molecular conformation of metallacycle 1. Reprinted with permission from Chen et al., *J. Am. Chem. Soc.*, 2019, 141, 13338–13343. Copyright 2019 American Chemical Society.

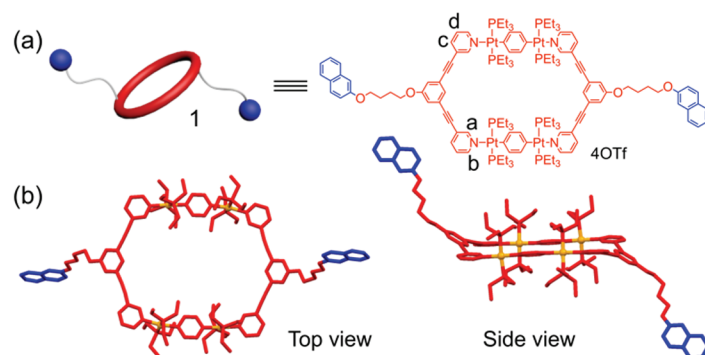
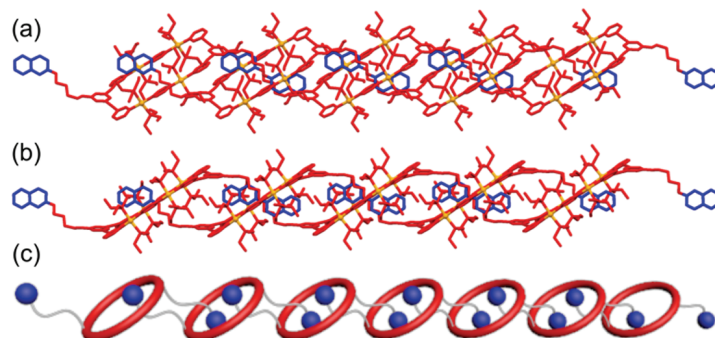


Figure 6. Hierarchical self-assembly of metallacycle 1 into linear supramolecular polymers. (a) Crystal packing view of the one-dimensional supramolecular chain driven by intermolecular naphthalene–naphthalene stacking interactions. (b) Simplified side view of the assembled polymeric chain. (c) Cartoon schematic illustrating the formation of linear supramolecular polymer. Reprinted with permission from Chen et al., *J. Am. Chem. Soc.*, 2019, 141, 13338–13343. Copyright 2019 American Chemical Society.



The unique electroactivity, photoluminescence, and dynamic nature of coordination bonds associated with platinum centers make them ideal candidates for constructing stimuli-responsive supramolecular materials. In addition to the aforementioned host–guest competitive response and electrostatic shielding response, Pt-based macrocyclic assemblies can also respond to redox environments, pH changes, and light irradiation. Sun, Chen, and Stang^[15] systematically summarized the research progress on supramolecular polymers and their hierarchical assemblies with diverse superstructures constructed via self-assembly of metal–organic complexes, including gels, vesicles, nanotubes, and nanosheets. Shi et al.^[22] constructed a class of linear supramolecular polymers based on the host–guest recognition between the cavities of Pt(II) metallacycles and the naphthyl groups pendant at their vertices. In this system, each metallacyclic monomer simultaneously plays the dual roles of both host and guest, with the naphthyl groups embedded into the cavities of adjacent metallacycles to form multiple C–H $\cdots\pi$ weak bonding interactions, which effectively suppress the kinetic exchange at the metallacyclic coordination centers and thereby drive the spontaneous growth of one-dimensional chains. Benefiting from this dynamic noncovalent cross-linking mechanism, the resulting supramolecular polymers exhibit favorable thermoresponsiveness—temperature elevation triggers a reversible gel–sol transition—as well as sensitive responsiveness to exogenous anions (e.g., Br[−]), which can competitively coordinate to disrupt the metallacyclic frameworks and induce structural depolymerization. Such metallacycle-based dynamic supramolecular materials hold promising application prospects in smart soft materials, including self-healing, shape memory, and drug-controlled release.

2.2 Palladium (Pd)-Based Metal–Macrocyclic-Based Supramolecular Polymers

Palladium-based metal–macrocyclic systems represent another widely studied class of coordination-driven self-assembly systems following the Pt-based counterparts. Similar to Pt(II), the Pd(II) ion also adopts a square-planar coordination geometry; however, the kinetic exchange rate of the Pd–N bond is substantially higher than that of the Pt–N bond (typically by 10⁴–10⁶ orders of magnitude). This pronounced kinetic lability endows Pd-based macrocycles with unparalleled “self-correction” capability and high sensitivity to environmental stimuli. The trade-off for such dynamic behavior is that the solution stability of Pd-based macrocycles is generally lower than that of their Pt-based analogues. Nevertheless, this very characteristic provides a unique chemical basis for the construction of stimuli-responsive supramolecular materials, complex interlocked topological structures, and adaptive dynamic systems^{[23][24]}.

2.2.1 Construction Strategies for Pd-Based Macrocycles

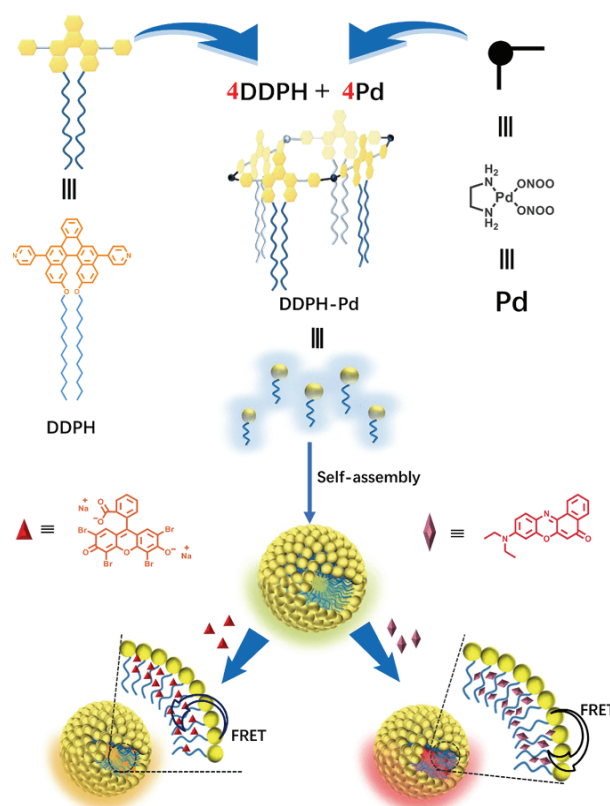
The construction of Pd-based macrocycles similarly relies on coordination-driven self-assembly as the core strategy, wherein Pd(II) acceptors with specific coordination orientations are mixed with organic ligands in solution at stoichiometric ratios to obtain the target macrocyclic structures through Pd–N coordination bond formation. Compared with Pt-based systems, the construction strategies for Pd-based macrocycles exhibit the following distinctive features.

The geometric configuration of Pd-based macrocycles is co-determined by the coordination angles of the Pd(II) acceptors and the bond angles of the organic ligands. The most commonly employed cis-protected Pd(II) acceptors provide a 90° coordination angle, which, when combined with bidentate ligands of varying angles and lengths, affords two-dimensional structures such as rectangles and parallelograms^[23]. In contrast to Pt-based systems, the choice of ligands in Pd-based systems is considerably more diverse. In addition to classical pyridine-type ligands, N-heterocyclic carbenes (NHCs), serving as strong σ -donor ligands that form stable Pd–C bonds with Pd(II), have been successfully utilized as “corner” ligands for Pd-based macrocycles^[25]. Zhou et al.^[26] exploited the Pd $\cdots$ Pd metal–metal interactions between cyclometalated palladium complexes to drive their spontaneous assembly into supramolecular nanostructures under physiological conditions, extending the applications of palladium complexes in the field of self-assembled nanomedicines. In recent years, 2-pyridyl-1,2,3-triazole chelating ligands have also been introduced into Pd-based supramolecular polymer systems, leveraging the high selectivity of the triazole moiety toward Pd(II) coordination to achieve selective capture of Pd(II) from mixed solutions containing multiple metal ions including Pt, Ni, Fe, Co, and Zn^[27].

Thermodynamically controlled topological dynamic interconversion represents the most distinctive feature of Pd-based macrocycles^{[23][24]}. By adjusting environmental parameters (concentration, temperature, solvent polarity) or introducing guest templates, the system can be readily driven to undergo reversible switching between macrocycles of different nuclearities.

Poole et al.^[23] conducted in-depth thermodynamic studies that transcended the traditional perception of purely “enthalpy-driven” assembly, revealing the dominant roles of solvent release entropy and conformational entropy of flexible ligands in determining the product distribution between Pd(II) high-nuclearity macrocycles and cage-like products, thereby providing a novel theoretical framework for the precise prediction of complex dynamic assemblies. By varying concentration, temperature, or solvent polarity, reversible interconversion between macrocycles of different nuclearities can be achieved within the same system. For example, the self-assembly of pyridine-containing ligand systems with Pd(II) acceptors can be switched between the $[\text{Pd}_2\text{L}_2]^{6+}$ metallacycle and the $[\text{Pd}_4\text{L}_4]^{12+}$ “ring-in-ring” structure via external stimuli—the former being favored at low concentrations and elevated temperatures, while the latter is more stable at high concentrations and low temperatures^[28]. Additionally, the introduction of aromatic guest molecules can also modulate the species distribution; for instance, the addition of large π -planar molecules such as pyrene can stabilize the larger cavity structures, shifting the self-assembly equilibrium toward higher-nuclearity metallacycles. Sharma, Sarkar, and Chand^[24] systematically summarized the structural diversity, solution dynamics, and intermolecular interactions of coordination cages with Pd(II) vertices in both bridged and non-bridged configurations, pointing out that the dynamic nature of Pd–N bonds provides a unique chemical tool for constructing programmable supramolecular systems. More importantly, Poole et al.^[23] thoroughly investigated the directing role of entropy in the self-assembly of Pd(II) coordination macrocycles and cages. They found that the release entropy of solvent molecules and the conformational entropy of polydentate ligands play critical roles in determining product distribution—when flexible long-chain ligands are employed, the contribution of conformational entropy increases significantly, stabilizing thermodynamically favored products with higher nuclearities. This discovery reveals that, in addition to the enthalpy-driven formation of coordination bonds, entropic effects are equally non-negligible in palladium-based supramolecular self-assembly, offering a more comprehensive thermodynamic framework for the precise prediction and control of assembly outcomes.

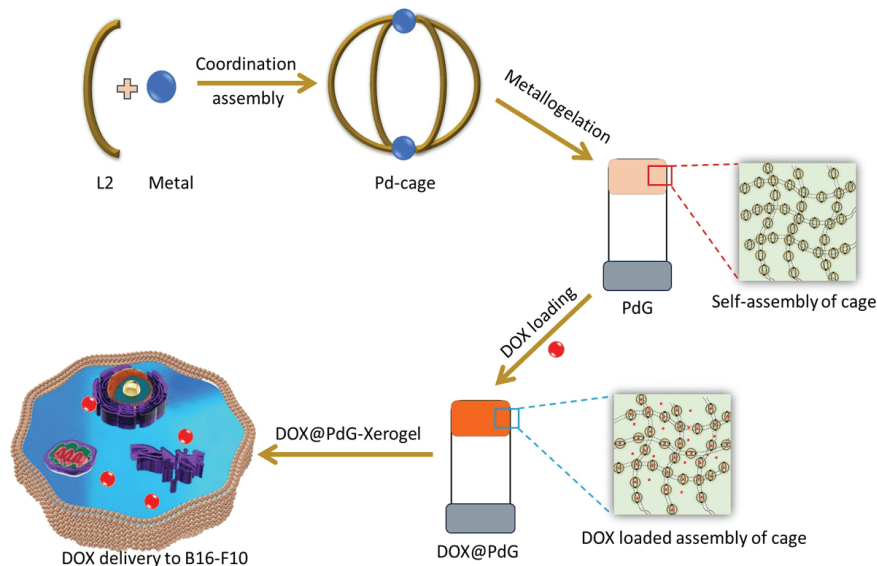
Figure 7. Helicene-based Pd(II) metallacycles as aqueous artificial light-harvesting platforms. Amphipathic DDPH-Pd metallacycles self-assemble from DDPH ligands and Pd(II) complexes, and further aggregate into water-soluble nanospheres. Fluorescent acceptors are encapsulated inside the nanoscopic cavities, achieving efficient FRET energy transfer between metallacycle donors and guest dyes. Reprinted with permission from Ref. ^[28]. Copyright 2022 Elsevier Ltd.



2.2.2 Advances in the Applications of Pd-Based Macrocyclic-Based Supramolecular Polymers and Their Assemblies

In the field of photofunctional materials, the abundant discrete cavities of Pd-based macrocycles enable the precise anchoring of fluorescent donor–acceptor pairs for the efficient construction of artificial light-harvesting systems. In a typical design, fluorescent donor molecules are encapsulated within the metallacyclic cavities or anchored onto the cyclic frameworks via coordination bonds, while acceptor molecules are connected to the periphery of the macrocycles through host–guest recognition or coordination interactions. By precisely regulating the spatial distance and orientation between donors and acceptors, efficient Förster resonance energy transfer (FRET) can be achieved^[28]. Since changes in optical signals can report molecular recognition or chemical reaction events occurring within the system in real time, such systems also hold application potential in catalysis, guest encapsulation, proton conduction, and explosive detection.

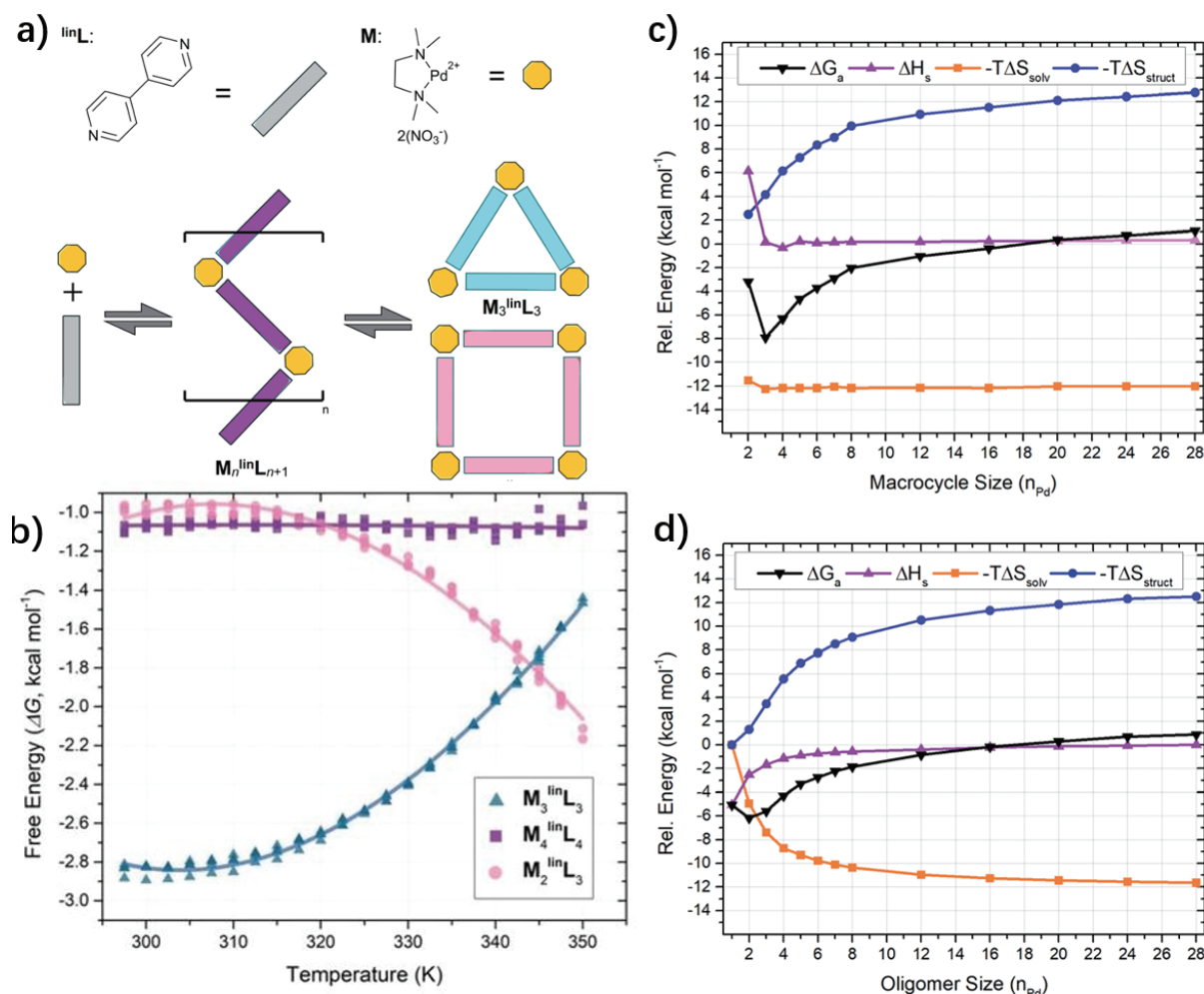
Figure 8. Pd₂L₄ metallacage-based supramolecular metallogels as carriers for tumor drug delivery. Ligand L2 coordinates Pd(II) to form Pd₂L₄ metallacages, which further self-assemble into PdG metallogels driven by hydrogen bonding and π – π stacking. The metallacage cavities encapsulate doxorubicin (DOX). Owing to the dual confinement effect of cage cavities and gel networks, sustained drug release is achieved for DOX delivery to B16-F10 melanoma cells. Reprinted with permission from Ref. ^[29]. Copyright 2024 Wiley-VCH GmbH.



Bera et al.^[29] developed supramolecular metallogels based on Pd₂L₄ metal–organic cages. In this system, the metal–organic cages, formed by the self-assembly of bipyridyl bisamide ligands with Pd(II), serve dual functions—the amide groups and aromatic rings on the cage periphery cooperatively drive the formation of three-dimensional fibrous networks through hydrogen bonding and π – π stacking interactions, thereby achieving gelation, while the internal molecular cavities of the cages remain intact and accessible in the gel state, providing molecular-level inclusion sites for doxorubicin. The dual confinement spaces constituted by the gel network and the cage cavities collectively endow the loaded drug with sustained release behavior, while the thixotropic and self-healing properties of the gel itself facilitate practical applications. In vitro experiments demonstrated that the doxorubicin-loaded metallogels exhibited significant anticancer activity against B16-F10 melanoma cells, whereas the blank gel exhibited low cytotoxicity toward normal cells. This work showcases the design strategy of integrating the molecular cavities of discrete metal–organic cages with the hierarchical confinement effects of three-dimensional gel networks, providing a valuable paradigm for the application of Pd-based supramolecular materials in drug delivery. Zhou et al.^[26] constructed supramolecular nanoassemblies with photodynamic therapy functionality by exploiting Pd···Pd metal–metal interactions to drive the spontaneous self-assembly of cyclometalated palladium complexes under physiological conditions, expanding the application scope of palladium complexes in the field of self-assembled nanomedicines. This work reveals that metal–metal interactions represent an effective strategy for driving the in vivo self-assembly of anticancer agents into nanoscale delivery systems, offering valuable insights for the application of Pd-based

supramolecular assemblies in cancer photodynamic therapy.

Figure 9. Dynamic coordination-driven self-assembly of linear bipyridyl ligand linL with Pd(II) and quantitative thermodynamic analysis. (a) Schematic illustration of assembly pathway: Pd(II) ions and linear bipyridyl ligands initially produce open-chain oligomeric intermediates $M_n\text{linL}_{n+1}$, which undergo reversible cyclization to competitively yield triangular $M_3\text{linL}_3$ and square $M_4\text{linL}_4$ macrocycles. (b) Temperature-dependent free energy curves of distinct assembled species. (c,d) Theoretical simulations deconvolute the energetic contributions from enthalpy, conformational entropy and solvation entropy during the assembly of cyclic macrocycles and open-chain oligomers. The results reveal that solvation entropy acts as the dominant thermodynamic driving force for ring closure and governs the equilibrium distribution of multiple supramolecular species. Adapted from Poole III et al., *Chem. Sci.*, 2022, 13, 10141, licensed under CC BY 3.0 Unported licence.



Poole et al.^[23] systematically investigated the thermodynamic contributions in Pd-based coordination self-assembly, revealing the dominant role of entropy in driving the formation of macrocycles and cages. Conventional wisdom holds that the cumulative enthalpy change associated with coordination bond formation is the primary driving force for self-assembly. However, through variable-temperature NMR experiments, the authors found that the M_2L_3 -type open-ring intermediates formed by the self-assembly of 4,4'-bipyridine with palladium acceptors exhibit lower enthalpy than the M_3L_3 triangular and M_4L_4 square products, yet their entropic penalty is significantly higher, which renders the closed macrocyclic products more favorable in terms of total free energy. Molecular dynamics simulations further revealed that this entropic penalty primarily originates from the loss of solvation entropy—the open-ring intermediates possess a larger solvent-accessible surface area, leading to greater restriction of solvent molecules, whereas the closed macrocycles release more solvent molecules by reducing the surface area exposed to the solvent, thereby gaining a substantial solvation entropy benefit that ultimately drives the evolution of the self-assembly from open intermediates to closed macrocyclic products. Upon extending this computational approach to the self-assembly system of $\text{Pd}_{12}L_{24}$ -type dodecanuclear coordination cages, the authors

further verified that solvation entropy similarly dominates the formation pathway of cage products and can differentiate thermodynamically stable products from kinetically trapped intermediates. This work elucidates the critical contribution of entropic effects in coordination self-assembly, enriches the conventional understanding of thermodynamic driving forces in self-assembly, clarifies the key role of solvation entropy in constructing highly ordered supramolecular structures, and provides an important theoretical foundation for the rational design of self-assembly systems.

2.3 Iron (Fe)-Based Metal–Macrocycle-Based Supramolecular Polymers

The research focus of Fe-based macrocycles extends beyond kinetic regulation and is instead highly centered on the octahedral stereochemistry of Fe(II), the rich redox interconversion between Fe²⁺ and Fe³⁺, and spin-state modulation^{[11][12]}. In contrast to the square-planar nodes of platinum and palladium, the Fe(II)–terpyridine (tpy) system not only offers richer three-dimensional topological possibilities but also endows the assemblies with unique intelligent attributes of magnetic and redox responsiveness^{[30][31][32]}.

2.3.1 Construction Strategies for Fe-Based Macrocycles

The construction of Fe-based macrocycles primarily relies on the coordination-driven self-assembly of Fe(II) with multidentate nitrogen-donor ligands, particularly terpyridine ligands^[33]. In contrast to the Pt and Pd systems, which typically employ bidentate pyridine ligands and bimetallic acceptors as the core building mode, Fe-based macrocycles generally adopt a “ligand–metal–ligand” linear connectivity pattern—each Fe(II) ion coordinates with two terpyridine ligands to form an octahedral [Fe(tpy)₂]²⁺ node, which can serve as a rigid connecting unit for further participation in macrocycle construction^[30]. Fe-based macrocycles typically adopt a “ligand–metal–ligand” linear connectivity mode, forming octahedral [Fe(tpy)₂]²⁺ rigid nodes^{[30][33]}. Through precise design of the angles (e.g., 60°, 120°) and bridging arm lengths of polytopic terpyridine ligands, systematic self-assembly can afford polygonal macrocycles ranging from trinuclear to hexanuclear species^{[33][31]}. Newkome et al.^[33] pioneeringly compared the “direct self-assembly” and “stepwise unilateral metallation assembly” pathways, finding that the latter could more effectively circumvent kinetic traps to obtain high-purity hexagonal macrocyclic products. The Fe-based system distinguishes itself in terms of sophisticated functionalization and heterometallic cooperative construction. Wang et al.^[34] grafted bulky dendritic macromolecules onto the ligand periphery, which not only significantly improved the solubility and processability of the system but also enabled modulation of photophysical conformations through steric effects. By exploiting the “chemical orthogonality” between Fe(II)-tridentate coordination and Pt(II)-bidentate coordination, researchers have successfully constructed structurally elaborate Fe–Pt heterometallic bicyclic supramolecules, seamlessly integrating two distinctly different geometric configurations within a single molecular framework. Furthermore, the introduction of novel chelating ligands such as bispyrazolylmethane has further expanded the chemical construction space of the Fe-based system^[35].

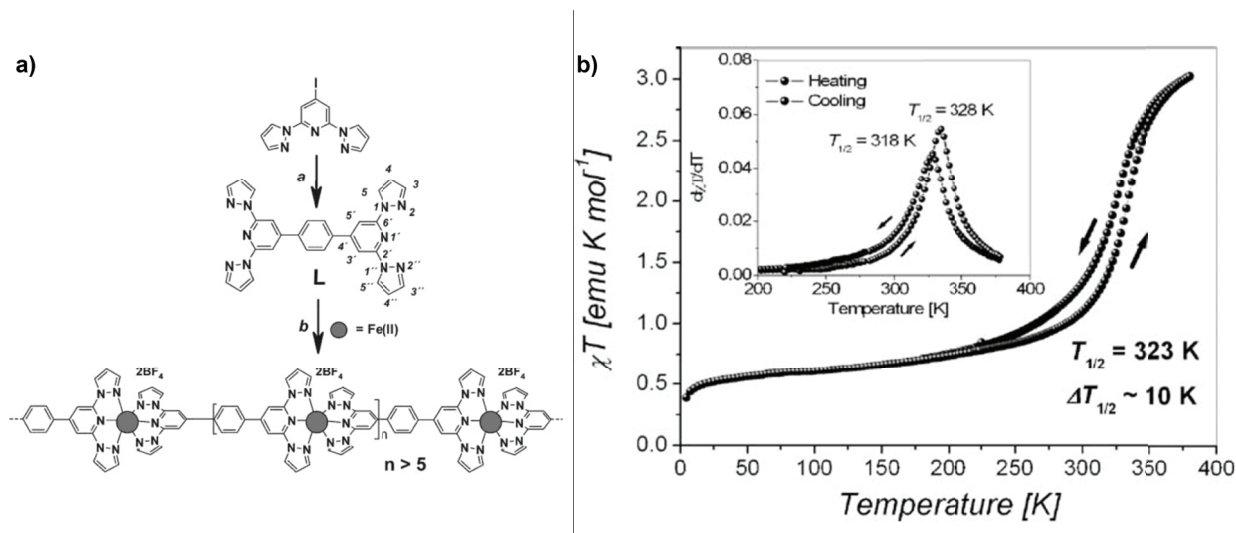
2.3.2 Advances in the Applications of Fe-Based Macrocycle-Based Supramolecular Polymers and Their Assemblies

Fe-based macrocycles and their assemblies, leveraging the intrinsic advantages of iron centers such as rich valence states, redox activity, and biocompatibility, exhibit unique development potential in the construction of supramolecular polymers and functional assemblies. Although research in this field is currently less mature than that of Pt and Pd systems, several pioneering studies have laid important foundations^{[12][32][37]}.

The redox reversibility of Fe-based macrocycles serves as a powerful tool for constructing intelligent responsive receptors. The introduction of ferrocene units into the Fe-based macrocyclic structures or their use as guest molecules to drive assembly represents a core strategy for constructing redox-responsive supramolecular polymers. Ferrocene can reversibly interconvert between the hydrophobic neutral Fc form and the hydrophilic cationic Fc⁺ form under electrochemical stimulation, a property that has been widely exploited to modulate host–guest recognition^[11]. For example, upon covalently attaching Fc units to the periphery of macrocyclic ligands, the resulting macrocycle can serve as a guest to be recognized by macrocyclic hosts such as cucurbit^[19]uril or pillararenes—exhibiting tight binding in the reduced state (Fc) and being released from the host cavities upon oxidation (Fc⁺) due to the enhanced hydrophilicity. Leveraging this principle, researchers have successfully constructed redox-reversible intelligent molecular receptors and supramolecular polymers. Furthermore, Guchhait et al.^[11] pointed out that

the vertical distance between the two cyclopentadienyl rings of ferrocene (ca. 3.3 Å) and its nearly frictionless “ball-bearing” rotational characteristics are also conducive to the formation of intramolecular π - π stacking, hydrogen bonding, and metal–metal interactions, thereby providing additional structural stabilizing factors for supramolecular assemblies.

Figure 10. One-dimensional Fe(II) spin-crossover coordination polymer based on bis-tridentate ligand. (a) Synthetic pathway for linear metallo-supramolecular Fe(II) chain; (b) Temperature-dependent magnetic curves show distinct hysteresis loop with $T_{1/2} = 323$ K and a hysteresis width $\Delta T_{1/2} \approx 10$ K. Adapted with permission from Rajadurai et al., *Chem. Commun.*, 2007, 2636–2638. Copyright 2007 Royal Society.



More notably, the thermally induced spin-crossover (SCO) behavior of Fe(II) centers under specific ligand fields endows the assemblies with remarkable magneto–thermal–mechanical multi-responsive functionality. Octahedrally coordinated Fe(II) ions tend to adopt a low-spin state ($S = 0$, diamagnetic) in strong ligand fields (e.g., tpy) and a high-spin state ($S = 2$, paramagnetic) in weak ligand fields. For systems with intermediate ligand-field strengths, temperature variation can induce reversible switching between the low-spin and high-spin states, a phenomenon known as spin-crossover (SCO). Rajadurai et al.^[32] reported a Fe(II)–terpyridine-based supramolecular coordination oligomer/polymer system, in which the Fe(II) centers, upon coordination with the tridentate units at both ends, have their intermetallic distances locked by the rigid ligands, thereby establishing long-range cooperative interactions along the entire chain. Magnetic measurements revealed that this coordination chain undergoes spin transition around 323 K, accompanied by a hysteresis loop of approximately 10 K in width, with the transition temperature significantly higher than that of the corresponding zero-dimensional monomeric complex (259 K), and the hysteresis width markedly broadened from 3 K to 10 K. Mössbauer spectroscopy further confirmed the temperature-dependent ratio variation between the low-spin and high-spin states. Upon the transition of Fe(II) from the low-spin to the high-spin state, the metal–ligand bond lengths increase (by ca. 0.2 Å), accompanied by a color change (from dark purple to pale yellow) and a significant enhancement of magnetic susceptibility. Incorporating such SCO-active [Fe(tpy)₂]²⁺ nodes into metal–macrocyclic frameworks, followed by network formation through supramolecular polymerization, is expected to yield intelligent soft materials with magneto–thermal–mechanical multi-responsive characteristics. The expansion effect associated with the thermally induced high-spin state can be coupled to the volume phase transition of gels, offering possibilities for the construction of artificial muscles and thermally responsive actuators. In addition, Fe-based macrocyclic carbonyl cluster compounds, designed by drawing inspiration from the structures of natural enzymes, can serve as efficient catalytic centers, playing a key role in photocatalytic or electrocatalytic hydrogen evolution and energy conversion^[37].

2.4 Other Metal–Macrocyclic-Based Supramolecular Polymers

In addition to the three major systems of Pt, Pd, and Fe, metals such as ruthenium (Ru), iridium (Ir), and zinc (Zn), as well as multimetallic hybrid systems, also occupy important positions in the field of coordination-driven self-assembly. These systems either excel in their superior photophysical and photochemical properties (e.g., Ru, Ir), or are distinguished by their

diverse coordination modes and fluorescence sensing capabilities (e.g., Zn), or open up new avenues for the development of functionally integrated supramolecular materials through multimetallic synergy.

2.4.1 Construction Strategies for Other Metal–Macrocyclic-Based Supramolecular Polymers

The construction of Ru-based macrocycles relies on the coordination-driven self-assembly of Ru(II) with terpyridine ligands. Through the design of bis-terpyridine ligands with varied angles, the nuclearity and geometric configuration of the macrocycles can be systematically regulated, and can be achieved via both “self-assembly” and “stepwise assembly” pathways, with the latter effectively avoiding kinetic traps and enabling the formation of heterometallic hexanuclear macrocycles with Fe(II)^{[33][38]}.

The construction of Ir-based macrocycles can be achieved through supramolecular assembly driven by noncovalent interactions between cyclometalated Ir(III) complexes, or by integrating them as building units into coordination assembly systems^{[13][39]}. Cyclometalated Ir(III) complexes exhibit excellent stability and their emission colors can be tuned across the full visible spectrum. In recent years, living supramolecular polymerization techniques have been successfully extended to this system; by introducing amide groups capable of directional hydrogen bonding and long alkyl chains that facilitate π – π stacking, living supramolecular polymerization of Ir(III) complexes has been realized, yielding well-defined luminescent block copolymeric supramolecular polymers^[40].

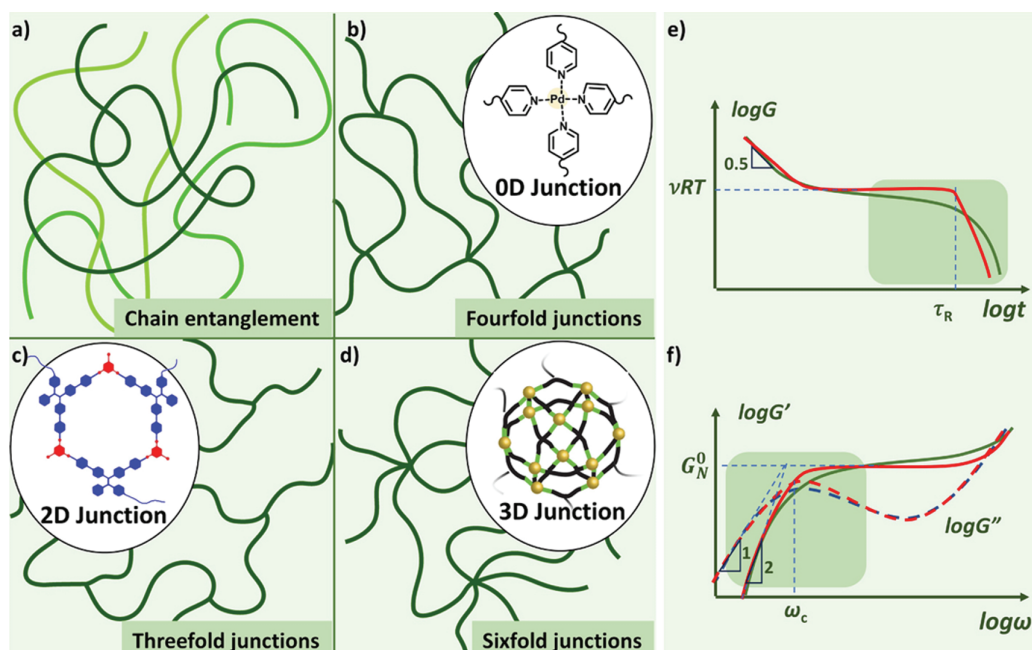
The construction of Zn-based macrocycles relies on the coordination-driven self-assembly of Zn(II) with terpyridine ligands. Through the design of bis-terpyridine ligands with varied angles, the nuclearity and geometric configuration of the macrocycles can be systematically regulated^[41]. The d^{10} configuration of Zn(II) ions endows the complexes with excellent optical transparency and strong fluorescence emission^[42], and this system can be extended to the directional synthesis of heterometallic macrocycles with divalent metal ions such as Ni(II), Cd(II), and Fe(II)^[30].

The synthesis of heterometallic macrocycles and supramolecular polymers faces challenges such as coordination competition and ligand exchange. Li et al.^[43] summarized strategies for multicomponent coordination-driven self-assembly toward heterometallic macrocycles and cages, including the hard and soft acid–base strategy, steric regulation strategy, (semi-) macrocycle stabilization strategy, and chelation-enhanced directing strategy. Leveraging the chemical orthogonality between Fe(II)–terpyridine nodes and Pt(II)–pyridine coordination modes, researchers have successfully constructed Fe–Pt heterometallic bicyclic supramolecules through multicomponent self-assembly^[36]. Kurpik et al.^[14] reviewed the application of pyridyl- β -diketone ligands in the construction of functional nanostructures; such ligands can simultaneously provide hard O,O-chelating sites and soft N-coordination sites, offering a versatile platform for the construction of various homonuclear and heteronuclear coordination assemblies.

2.4.2 Advances in the Applications of Other Metal–Macrocyclic-Based Supramolecular Polymers

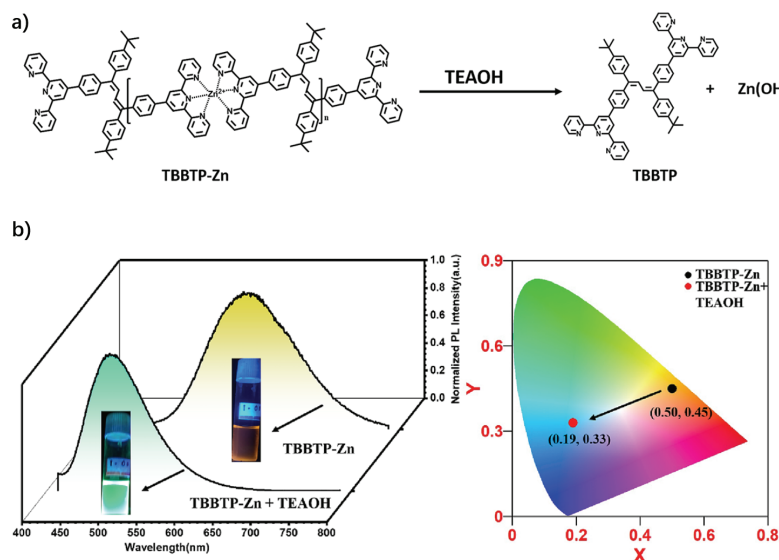
Ru-based macrocycles and their supramolecular assemblies exhibit outstanding application value in photocatalytic redox reactions. Polypyridine Ru(II) complexes, with their strong visible-light absorption, long excited-state lifetimes (typically hundreds of nanoseconds to microseconds), and appropriate redox potentials, serve as highly efficient photosensitizers for photocatalytic redox reactions. Li et al.^[13] systematically reviewed the applications of polypyridine Ru(II)- or cyclometalated Ir(III)-functionalized assemblies in photocatalysis, including photocatalytic water splitting for hydrogen evolution, CO₂ reduction, organic pollutant degradation, and light-driven organic synthesis. By co-assembling Ru(II) photosensitizers and catalytic active centers (such as Pt or Co nanoparticles or molecular catalysts) within the same supramolecular polymer framework, the spatial distance and electronic coupling between the photosensitizer and the catalyst can be precisely regulated, enabling efficient intramolecular photoinduced electron transfer and thus enhancing catalytic efficiency.

Figure 11. Classification and viscoelastic behavior of luminescent metallo-supramolecular polymer networks (MSPNs). (a–d) Four types of network architectures with different crosslinking motifs; (e,f) Rheological curves comparing pure entangled polymers and metal-crosslinked MSPNs. Ir(III) monometallic 0D crosslinks impart self-healing and mechano-luminescent responsiveness to networks via reversible metal–ligand coordination interactions. Adapted from Hassanian-Moghaddam et al., Coordination Chemistry Reviews, 2025, 540, 216796, licensed under CC BY 4.0.



Ir-based supramolecular polymers and their assemblies exhibit outstanding performance in self-healing luminescent elastomers, stimuli-responsive luminescent gels, and solid-state lighting. Hassanian-Moghaddam et al.^[8] systematically summarized the design strategies for luminescent metallosupramolecular polymer networks, highlighting the unique advantages of Ir-based systems in the construction of self-healing luminescent elastomers and stimuli-responsive luminescent gels. In a typical design, Ir(III) complexes modified with bis-terpyridine or bisphenylpyridine moieties serve as luminescent cross-linking points, connecting to polymer chains through metal–ligand coordination to form dynamic networks. Upon mechanical damage, the reversible cleavage and recombination of coordination bonds drive the autonomous healing of the network, while the luminescent signals can report the damage and repair states of the material. Furthermore, Ir-based supramolecular assemblies also demonstrate significant application prospects in sensing, bioimaging, photoredox catalysis, and solid-state lighting^[39]. Leveraging living supramolecular polymerization strategies, Ir-based supramolecular copolymers with well-defined block architectures can be prepared, enabling advanced functions such as spatial encoding of emission colors and optical information encryption^[40].

Figure 12. Reversible luminochromic stimuli-response of Zn-containing AIE metallo-supramolecular polymers. (a) Schematic depolymerization mechanism triggered by competitive TEOH coordination; (b) Fluorescence spectra, CIE coordinates and UV photographs illustrate reversible emission color transition from yellow (polymer) to cyan-green (free ligand) upon disassembly. Adapted from Pal et al., *European Polymer Journal*, 2023, 194, 112115, licensed under CC BY 4.0.



The applications of Zn-based macrocycles and their supramolecular polymers are primarily focused on the fields of fluorescent materials and sensing. The d^{10} electronic configuration of Zn(II) ions endows their complexes with excellent fluorescence properties—since there are no low-energy d–d states to quench the excited states, the ligand-centered emission can be efficiently preserved. Pal et al.^[44] rationally designed bis-terpyridine ligands with aggregation-induced emission (AIE) activity (aryl-substituted derivatives containing a buta-1,3-diene core) and obtained solid-state emissive Zn-based metallosupramolecular polymers through self-assembly with Zn(II). In dilute solution, the rotation of the phenyl rings in the ligands leads to nonradiative deactivation; whereas in the solid state or aggregated state, the restricted intramolecular rotation activates radiative transitions, resulting in intense solid-state fluorescence. Such materials also exhibit significant potential in stimuli-responsive luminochromism—by altering the solvent, temperature, or applying mechanical force, the aggregation state and intermolecular packing mode of the polymer chains can be modulated, thereby enabling reversible switching of the emission colors. In addition, Zn-based macrocycles also hold broad application prospects in the construction of supramolecular libraries, host–guest chemistry, and heterometallic supramolecular assemblies^[42].

Heterometallic supramolecular polymers, by integrating different metal centers within the same framework, can achieve multifunctional integration that is difficult to obtain in single-metal systems, demonstrating unique advantages in fields such as electrochromism, magnetic materials, biomedicine, and catalysis. In electrochromism, heterometallic supramolecular polymers containing Fe(II) and Ru(II) can exhibit multicolor electrochromic behavior—different metal centers undergo redox reactions at different voltages, producing a rich variety of color changes. In magnetic materials, heterometallic assemblies containing Fe(II) and Co(II) can display complex magnetic coupling and spin-state modulation behavior^[45]. In biomedicine, heterometallic supramolecular polymers containing Gd(III) and Pt(II) can simultaneously enable MRI imaging and chemotherapy, providing a platform for theranostic applications. In catalysis, Li et al.^[43] pointed out that heterometallic macrocycles possess unique advantages in enzyme-mimetic catalysis—by introducing two different metal ions (e.g., Fe and Zn, Cu and Zn, etc.) into the same macrocyclic framework, the catalytic functions of different metal centers in natural metalloenzymes can be mimicked separately to achieve cooperative catalysis. For example, one metal center activates the electrophilic substrate while the other activates the nucleophile, and the spatial proximity of the two centers significantly enhances the catalytic efficiency. Furthermore, Kurpik et al.^[14] reviewed the potential applications of heterometallic nanostructures constructed from pyridyl- β -diketone ligands in molecular sensing, gas adsorption, and catalysis, pointing out that the structural diversity and metal-combination flexibility of such systems open up new avenues for the development of next-generation multifunctional supramolecular materials.

3. Conclusions and Outlook

In summary, this review systematically elucidates the evolution of metal–macrocyclic supramolecular polymers from discrete molecular building blocks to macroscopic smart functional materials, a progression that has profoundly reshaped our understanding of coordination-driven self-assembly. By precisely tuning the characteristics of specific transition metal nodes—such as the kinetic inertness of Pt(II) versus the kinetic lability of Pd(II)—and strategically introducing secondary noncovalent interactions (e.g., host–guest recognition and hydrogen bonding), researchers have successfully imbued these hierarchical assemblies with unprecedented stimuli-responsiveness and self-adaptive capabilities. Consequently, these tailored materials have demonstrated immense potential across frontier fields, including biomedicine, smart sensing, and heterogeneous catalysis.

However, despite these remarkable breakthroughs, the translation of metal–macrocyclic supramolecular materials from fundamental laboratory research to practical technological implementation remains hindered by three critical bottlenecks: First, balancing processability with mechanical integrity. Currently, the vast majority of metal–macrocyclic assemblies exhibit high brittleness in the solid state, alongside poor solubility and an inherent lack of melt or solution processability. To overcome these limitations, future research must transcend the constraints of purely rigid frameworks. Strategically embedding flexible polymer segments or dynamic covalent networks into the metal–macrocyclic architectures will be essential to fundamentally improve thermal processability, mechanical flexibility, and interfacial adhesion, thereby meeting the stringent manufacturing requirements for thin films, flexible wearables, and solid-state devices. Second, bridging the gap

between scale-up synthesis and structural fidelity. The construction of highly complex supramolecular topologies currently relies heavily on stringently controlled, highly dilute solution conditions. This sensitivity to concentration and solvent polarity makes it incredibly difficult to maintain structural uniformity during scale-up. Developing robust, high-yielding “one-pot” synthetic strategies, or even exploring solvent-free mechanochemical synthesis, will be crucial to bypassing the current barriers to mass production while maintaining batch-to-batch reproducibility. Third, shifting the paradigm from empirical “trial-and-error” to predictive design. As evidenced by the decisive role of solvation entropy in dictating Pd-based assembly pathways, coordination-driven self-assembly is governed by highly complex thermodynamic and kinetic factors. The current fragmentation of structure–property mapping hinders rational design. The future of this field lies in data-driven science: by deeply integrating high-throughput automated synthesis with machine learning (ML) and coarse-grained theoretical calculations, researchers can enable the *de novo* design and reverse-prediction of specific assembly pathways, topological structures, and targeted macroscopic properties.

Ultimately, metal–macrocylic supramolecular systems represent not only a captivating class of next-generation smart soft materials but also an ideal physicochemical platform for investigating the synergistic effects of hierarchical interactions. With the continuous refinement of synthetic methodologies and the integration of computational materials science, these coordination-driven supramolecular materials are poised to catalyze disruptive technological advancements in advanced manufacturing, life sciences, and green energy.

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Conflict of Interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

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