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Editorial

Highly robust supramolecular polymer networks crosslinked by metallacycles

Supramolecular polymer networks (SPNs), which integrate principles from both supramolecular chemistry and traditional polymer science, offer a multitude of advantages, including dynamic, reversible, recoverable, and stimuli-responsive characteristics [1,2]. These unique attributes render them exceedingly appealing as prospective adaptive materials. Nonetheless, owing to the utilization of relatively weak non-covalent bonds, supramolecular polymers often exhibit weaker mechanical properties when compared with their covalent counterparts. Addressing this challenge necessitates the incorporation of multiple and robust non-covalent interactions within the crosslinkers. For instance, Huang and co-workers engineered highly compressible glass-like SPNs by leveraging CB[8]-enhanced phenyl-perfluorophenyl polar–π interactions [3]. Similarly, Yan and co-workers recently demonstrated the synthesis of exceptionally robust and resilient SPNs through cryptand-based host-guest recognition as crosslinkers [4]. Noteworthy is the observation that achieving substantial mechanical strength typically mandates a significant proportion of supramolecular units (~10 mol% or more) within the network to ensure robust crosslinking. However, the excessive inclusion of supramolecular crosslinking units can impede chain segment mobility, rendering the material brittle and diminishing its stretchability and practical utility. Consequently, there is a pressing need to optimize the quantity of supramolecular units utilized to address this challenge.

Very recently, Shijun Li, Peter Stang, Feihe Huang, Jianying Huang and co-workers reported highly robust SPNs crosslinked by a tiny amount of metallacycles based on metal-coordination interactions [5]. As depicted in Fig. 1, a norbornene monomer (**M-1**) featuring a 120° dipyridine group was synthesized. The self-assembly of **M-1** with the 60° Pt(II)-based acceptor **7** in a 1:1 molar ratio yielded a [2 + 2] Pt(II)-coordinated rhomboid (**9**), whereas the self-assembly of **M-1** with the 120° Pt(II)-based acceptor **8** resulted in a [3 + 3] hexagonal metallacycle (**10**). These metallacycles underwent characterization through $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and single crystal X-ray analysis. Copolymerization of **M-1** with a diester-derived norbornene monomer, **M-2**, yielded covalent copolymers (**CP**s) with feed ratios of **M-1**/**M-2** = 1:60 for **CP-1**, 1:180 for **CP-2**, 1:360 for **CP-3**, and 1:600 for **CP-4**, respectively. Subsequently, coordination-driven self-assemblies of **CP**s were conducted by mixing the **CP**s with **7** and **8**, respectively, in THF to generate the corresponding metallacycle-crosslinked polymer networks (**MCPN**s). Due to the robust crosslinking of metallacycles, **MCPN**s derived from **CP-1** (containing 1.64 mol% dipyridine units) and **CP-2** (0.55 mol%) rapidly transformed into gels, while **MCPN**s (**CP-3R**, **CP-3H**, **CP-4R**, and **CP-4H**) originating from **CP-3** (0.28 mol%) and **CP-4** (0.17 mol%) remained soluble but exhibited substantially elevated viscosities.

Tensile tests were employed to evaluate the mechanical performance of **MCPN**s and **CP-3**. As illustrated in Figs. 2a and b, the tensile strengths and Young's moduli of **MCPN**s surpassed 15 MPa and 350 MPa, respectively, significantly outperforming those of **CP-3**. Moreover, the toughness of **CP-3R** and **CP-3H** markedly increased from less than 50 MJ/m³ for **CP-3** to over 150 MJ/m³. These findings underscored substantial enhancements in the mechanical properties of the polymers following crosslinking by the metallacycles, notwithstanding the utilization of minute amounts of crosslinkers. Additionally, the Young's modulus of **CP-3R** surpassed that of **CP-3H**, indicative of the superior stability of the rhomboid metallacycle crosslinked network. Scanning electron microscopy (SEM) was further employed to scrutinize the improvement in mechanical properties by examining the fracture surface. Consequently, the cryo-fractured surface of **CP-3** appeared relatively smooth, whereas those of **CP-3R** and **CP-3H** exhibited a more rugged appearance, attributable to the disruption of robust metallacycle networks dispersed within the polymers during the fracture process.

The intrinsic dynamic nature of coordination interaction imparts attractive dynamic properties to **MCPN**s. The energy dissipation capacities of **CP-3R** and **CP-3H** were evaluated through cyclic tensile tests. With the gradual increase in strain, they both exhibited substantial hysteresis loops accompanied by higher residual strains. This demonstrated that **CP-3R** and **CP-3H** maintained consistently high damping capacities of approximately 80% at elevated strains, indicating their effective energy dissipation capabilities. Furthermore, the dynamic nature of the metallacycles endow the materials with stimuli-responsive properties. As shown in Fig. 3, the addition of TBABr disrupted the Pt–N bonds, resulting in the partial decomposition of the **MCPN**s and a drastic decline in mechanical properties (including tensile strength, Young's moduli, and toughness). Subsequently introducing AgOTf into the solutions partially restored the corresponding tensile strength and Young's moduli. The results suggest that Pt(II) metallacycle-based supramolecular crosslinking is amenable to modulation by external stimuli, thereby imbuing the **MCPN**s with stimuli-responsiveness.

In summary, this work reported the design and fabrication of resilient SPNs crosslinked by a minute quantity of metallacycles. A norbornene monomer, substituted with a 120° dipyridine ligand, was copolymerized with a diester-derived norbornene monomer,

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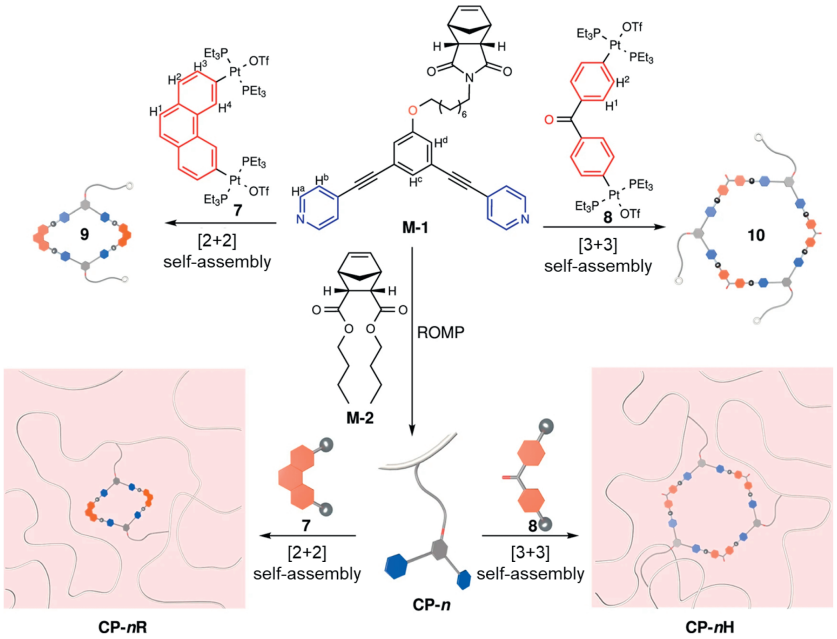

Fig. 1. Schematic illustration of preparation of the metallacycle-crosslinked polymer networks. Reproduced with permission [5]. Copyright 2024, Nature Publishing Group.

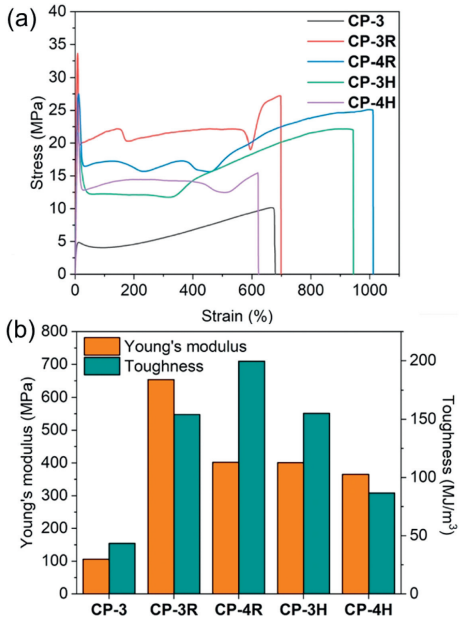

Fig. 2. (a) Stress–strain curves of **CP-3** and **MCPN**s recorded with a deformation rate of 100 mm/min. (b) Young's moduli and toughness of **CP-3** and **MCPN**s calculated from their stress–strain curves. Reproduced with permission [5]. Copyright 2024, Nature Publishing Group.

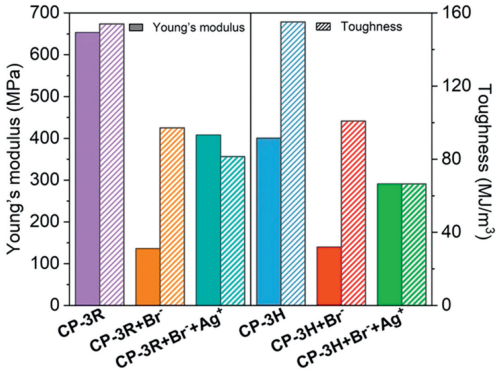

Fig. 3. Young's moduli and toughness of **CP-3R**, **CP-3R** + Br^-, **CP-3R** + Br^- + Ag^+, **CP-3H**, **CP-3H** + Br^-, and **CP-3H** + Br^- + Ag^+. Reproduced with permission [5]. Copyright 2024, Nature Publishing Group.

yielding the corresponding covalent polymers (CPs). Subsequently, the copolymers underwent self-assembly with Pt(II) acceptors to construct metallacycle-crosslinked polymer networks. Despite employing only 0.28 mol% or less pendant dipyridine units, the mechanical properties of the materials experienced a significant enhancement. Particularly noteworthy is the preservation of good stimuli-responsiveness in these robust materials, attributed to their intrinsic dynamic properties.

This study presents a promising approach to developing robust and stimuli-responsive SPNs through the incorporation of a tiny amount of metallacycles as crosslinkers. Although supramolecular polymers exhibit unique dynamic properties, their mechanical strength often proves insufficient due to weak non-covalent interactions. Through the strategic incorporation of metallacycles, the authors achieved significant enhancements in mechanical properties while preserving stimuli responsiveness. Future research directions may delve into exploring the versatility of metallacycle-based crosslinking across diverse polymer systems and elucidating the intricate relationship between structure, properties, and performance in these materials. Overall, this study lays the groundwork for designing advanced adaptive materials with tailored properties suited for various applications, offering novel insights to the materials science community.

Declaration of competing interest

On the behalf of all co-authors and myself here, I declare that we have no any known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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