

## A two-dimensional mechanically interlocked polymer crosslinked by [c2]daisy chains

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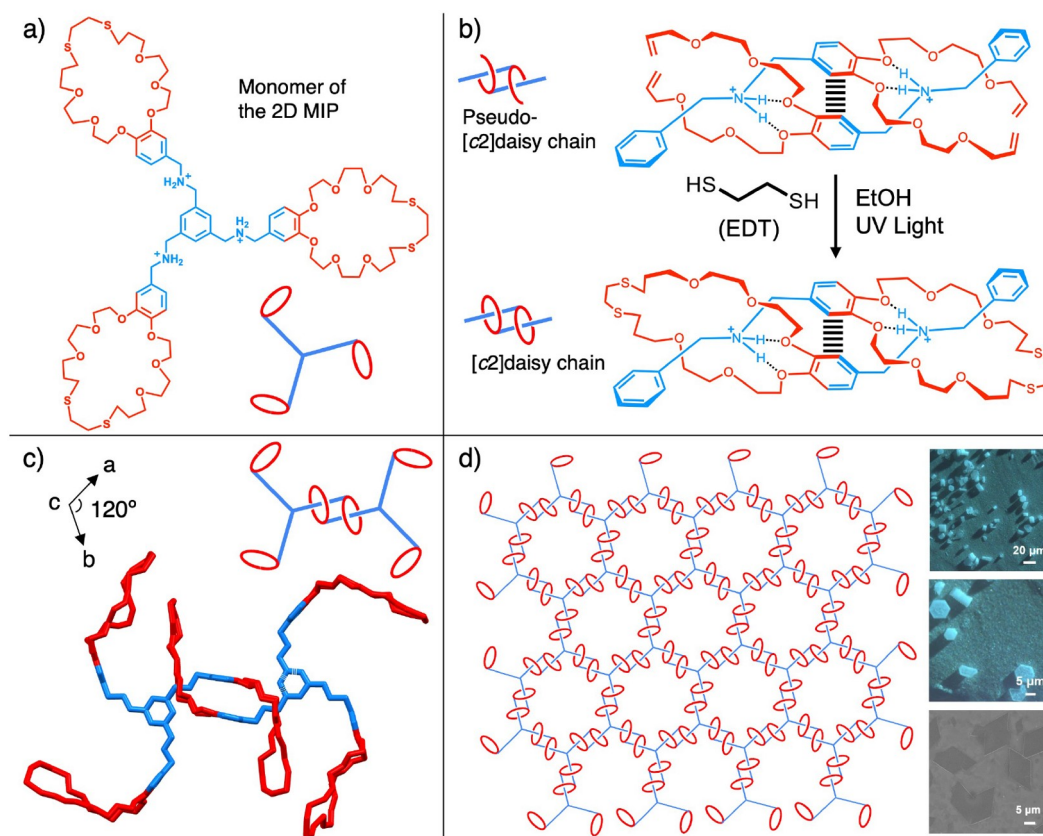
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The design and synthesis of two-dimensional (2D) polymers have received notable attention over the past two decades because of their unique structural properties and wide range of applications, such as molecular separation, nanoelectronics, sensing, and optoelectronics [1]. The regularity of 2D polymeric networks, especially when high crystallinity is formed, allows them to control their pore sizes, surface areas, and mechanical properties, keeping them at the forefront of materials chemistry and nanotechnology [2,3]. Instead of crosslinking by covalent bonds, a new class of polymers, namely mechanically interlocked polymers (MIPs), adopt mechanical bonds to allow relative motion between components [3–6]. Using that advantage, MIPs that include polyrotaxanes, polycatenanes, and daisy chain polymers have been recently developed in the field of dynamic and stimulus-responsive materials [7]. MIPs often incorporate flexible units as linkers to enhance molecular mobility, but this typically results in amorphous gel-like materials that struggle to balance flexibility with mechanical strength [5]. Consequently, introducing rigid units can improve strength but compromise selectivity in synthesis by limiting chain mobility [8]. The flexibility in the building blocks is crucial to form mechanical bonds, whereas the rigidity of the structure is required for crystallinity [9]. To overcome the contradiction between flexibility and rigidity, researchers have utilized supramolecular preorganization to yield well-ordered superstructures, followed by the single-crystal-to-

single-crystal (SCSC) transformation to form the mechanical bond at the designated position. Enabling the precise synthesis of purely organic, crystalline 2D MIPs remain a critical scientific goal in this field.

A significant breakthrough was reported in *Nature Synthesis* by Tang *et al.* [10], demonstrating a combined method to create a crystalline 2D MIP based on [c2]daisy chains. The building block of this MIP is a  $C_3$ -symmetric monomer (Figure 1a), which contains three dibenzylammonium ( $\text{DBA}^+$ ) cores (blue) adjacent to a dithiol-inserted pseudo-benzo-18-crown-6 (B18C6) ring (red) at the end of each branch. Driven by the hydrogen bonding and  $[\pi \cdots \pi]$  stacking between the pseudo-B18C6 host and the  $\text{DBA}^+$  guest, each of the two monomers can crosslink through a mechanical bond to form a [c2]daisy chain. Following the rational design of the tripod-shaped monomer, each one connects to three counterparts with  $120^\circ$  interval angles, organizing into a 2D honeycomb polymeric network. The precursor of the monomer exhibits a similar backbone, except that the pseudo-B18C6 rings are not closed as a loop. Each of the three claw-shaped termini contains a pair of allylic substituents while maintaining the oligoethylene glycol hydrogen bonding acceptors. Driven by multiple noncovalent intermolecular interactions,  $\text{DBA}^+$  units were captured by the “claws” to form thermodynamically stable pseudo-[c2]daisy chains, yielding colorless and transparent single crystals. The successful 2D supramolecular preorganization was confirmed by single-crystal X-ray diffraction (SCXRD), high-angle annular dark-field scanning transmission electron

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**Figure 1** (Color online) (a) Chemical structural formula of the monomer that forms the two-dimensional (2D) mechanically interlocked polymer (MIP). (b) Schematic representation of the supramolecular preorganization driven by the interaction between a dibenzylammonium (blue) unit and a dithiol-inserted pseudo-benzo-18-crown-6 (red) ring and the ring closure through the UV-triggered thiol-ene click reaction. (c) Single-crystal X-ray diffraction (SC-XRD) structure of a [c2]daisy chain between two monomers. (d) Graphical representation, optical and scanning electron micrographs of the honeycomb-like 2D MIP network.

microscopy (HAADF-STEM), high-resolution transmission electron microscopy (HRTEM), and energy dispersive spectroscopy (EDS). The pseudo-[c2]daisy chain MIP crystal then underwent the ultraviolet (UV)-triggered thiol-ene click reaction (Figure 1b) between allylic groups and 1,2-ethanedithiol (EDT) in EtOH, leading to the pseudo-B18C6 ring closure. The SCSC transformation resulted in the formation of [c2]daisy chains (Figure 1c) between monomers, providing strong crosslinks in the polymer by the mechanical bond. The well-constructed single crystal was confirmed (Figure 1d) by SCXRD and optical microscopy. It is worth highlighting that the mechanical stiffness of the crystalline polymer can be enhanced by exfoliating it into nanosheets. By co-solvent exfoliation in EtOH and trifluoroacetic acid (TFA), a trilayer stacking nanosheet with a thickness of 3.9 nm was obtained. Scanning electron microscopy (SEM) illustrated the retention of hexagonal prism morphology in the MIP nanosheet. Structural information of the 2D MIP was further examined by HAADF-STEM, HRTEM, and EDS, respectively. Measured by atomic force microscopy (AFM), Young's modulus ( $E$ ) value of thinner layers with a height of 120 nm shows up to 4.23 GPa, which

is 47-fold greater than the bulky crystal ( $E = 0.09$  GPa).

The success of the preorganization-directed synthesis, crystallization, and exfoliation of the 2D MIP crosslinked by [c2]daisy chains provides a new synthetic pathway for functional materials. The chemical and structural design of this project inspires researchers to incorporate metal-free host-guest templation (e.g., crown ether and ammonium) as the driving force of supramolecular preorganization. The introduction of UV-triggered thiol-ene click chemistry in the ring closure yielded effective SCSC transformation. These techniques can be used to construct various complex molecular nanotopologies to synthesize crystalline MIPs [11]. It is well-recognized that polycatenated materials [12] can achieve important functions in the macroscopic world. For example, the medieval chain mail can effectively protect the body by its robustness, without hindering movement by its flexibility. This 2D MIP has provided insight into stimuli-responsive and mechanically adaptive materials, leading to applications in the fields of biomaterials, electronic products, and protective equipment. Moreover, we are looking forward to seeing high-dimensional MIPs with unique building blocks and complex nanotopologies to be designed and synthesized in the future.

**Conflict of interest** The authors declare no conflict of interest.

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