Polymer metal-organic cage gels based on Cu₂₄L₂₄ cuboctahedra: design, synthesis, and additive manufacturing enabled by three-state photoswitching

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Abstract: The merger of conformationally flexible macromolecules with the programmed self-assembly of metal-organic cages (MOCs) has enabled the design of hybrid polymer networks with properties that cannot be replicated in traditional gels/elastomers or crystalline frameworks alone. Herein, we report a new class of supramolecular polymer metal-organic cage (polyMOC) gels based on the assembly of $\text{Cu}_{24}\text{L}_{24}$ cuboctahedra. Leveraging the modularity of their high branch functionality junctions, and the photoredox chemistry of Cu(II) paddlewheel complexes, we demonstrate how these polyMOCs can be reversibly photoswitched between three oxidation states (Cu(II), Cu(I), and Cu(0)) that each give rise to unique mechanical, optical, and catalytic properties: the Cu(II) state is a high branch functionality, robust polyMOC with fast network dynamics, the Cu(I) state is a catalytically active fluid, and the Cu(0) state generates a copper suspension that can deposit metallic films. Reversible switching between these states allows their individual properties to be combined in a spatiotemporally patterned multi-material to achieve unprecedented functions. For example, extrusion of the Cu(II) polyMOC in the presence of polymeric azides and alkynes, where the mechanically robust polyMOC serves to hold the solution of azides and alkynes in a printed shape, followed by photoswitching to the Cu(I) state and subsequent re-oxidation provides 3D-printed MOC-interpenetrating networks (MINs) with >100-fold enhanced toughness compared to either parent network. Such complex functions, which cannot be accessed in traditional polymer networks, arise from synergistic interactions between three independent and reversible material states, highlighting the unique capabilities of state-switchable polyMOCs.

Keywords: Gels, State-switching, Multi-material, PolyMOCs, stimuli responsive

Introduction: Unlike traditional synthetic materials, biological materials are active chemical systems in which molecular-level responses lead to reversible switching between multiple states, resulting in adaptive properties that exceed the limitations of their abiological counterparts. For example, during the healing of a fractured bone, a soft hematoma provides initial structure supporting the growth of spongy bone and new vasculature, which in turn enables further calcification and ultimately returns the material (bone) to its initial state.¹ Inspiration from biological tissues has led to the advent of many advanced synthetic material properties such as self-healing and enhanced toughness.^{2–5} To achieve these properties on demand, materials chemists have relied on the incorporation of dynamic bonds that can be controlled through a specific external stimulus (*e.g.*, light, force, heat, electricity) to give rise to a host of novel “stimuli-responsive” materials with properties that could be altered to achieve a desired function.^{5–20} These dynamic bonds, however, are often binarily actuated by this stimulus, resulting in two-state materials that return to the initial state upon the removal of the stimulus. Recently, a new concept has emerged for polymer network design wherein supramolecular interactions are leveraged to produce materials that reversibly switch topological structure in response to a given set of stimuli and that are subsequently stable in each state upon removal of the stimulus.^{21,22} For example, by using photo-switchable dithienylethene-based polymer ligands to link Pd-based metal-organic cages (MOCs), a “polyMOC” material capable of alternating between Pd₃L₆ and Pd₂₄L₄₈ topological states with different static and dynamic mechanical properties was reported.²² Nevertheless, the scope of accessible properties with two-state switchable materials is limited and leveraging topologically switchable materials to control advanced properties such as catalysis in a single state has not yet been demonstrated.

Seeking to find a new supramolecular system that is capable of achieving several complementary and useful states, we hypothesized that leveraging a photo-redox process in a polyMOC could allow access to several oxidation states where, in each state, a diverse range of chemical and physical properties would be available. We identified the photoswitchable redox states of Cu(II)-based MOCs as a promising starting point.²³ Despite the fact there are examples of copper based polyMOCs used in the dry state for gas sorption,^{24,25} such assemblies have not, to our knowledge, been used to generate copper-based dynamic polyMOC gels that can be leveraged for applications such as catalysis, additive manufacturing, etc. Herein, we introduce polyMOC gels derived from Cu(II) and polymer strands with *m*-benzenedicarboxylate (*m*-BDC = L) termini (*e.g.*,

PL, Fig. 1a). A combination of small/wide-angle X-ray scattering (SAXS/WAXS), UV-vis absorption, rheology, and simulation experiments supported a polyMOC network structure composed of high branch functionality MOC junctions interconnected by flexible polymer strands. In particular, the high branch functionality of these polyMOCs leads to mechanically robust materials with MOC junctions that can be modularly functionalized without impacting the mechanical properties of the material. Leveraging this unique aspect of the polyMOC topology,²⁶ we demonstrate the installation of coumarin-based *m*-BDC ligands (**CL**) that, in the presence of a photosensitizer and a hydrogen atom donor, facilitate controlled reduction of the Cu centers within the MOC junctions of the material, thereby enabling photoswitching between three distinct redox states (Cu(II), Cu(I), and Cu(0)) that each display dramatically different mechanical, optical, catalytic, and electronic properties (Fig. 1b). The mechanism of this unprecedented three-state photoswitching process within a polyMOC is studied using a range of control experiments and density functional theory calculations, which highlight the key role of the polyMOC topology. We utilize this material to introduce a fundamentally new way to form interpenetrating networks, in this case a “metal-organic cage interpenetrating networks” (MINs), by leveraging the Cu(I) polyMOC functional state to catalyze the formation of a covalent network and subsequent switching back to the Cu(II) state to reform a polyMOC. The resulting MIN has >100-fold increased toughness compared to the polyMOC and the covalent network alone. Moreover, because this process is photoinduced, we can leverage the mechanical robustness and dynamics of the polyMOC to 3D pattern and print MINs of arbitrary shape, addressing a major challenge in the field of 3D printing of gels. This work significantly expands the scope of polyMOCs and their photochemistry, as well as the emerging paradigm of state-switchable materials, showing for the first time how the properties of three states can be leveraged within one material to achieve complex functions similar to biological materials.

Results and Discussion. Though we have previously established that star polymers with suitable ligands attached to their termini enable the synthesis of robust, defect-tolerant Pd-based polyMOCs,^{26,27} there are no analogous examples, to our knowledge, of using this concept for the formation of Cu-based polymer networks. Thus, we first focused on the synthesis and properties of Cu-based polyMOCs lacking photochemically active junctions as a proof-of-concept. When **PL** was combined with *m*-BDC in a 1:3 ratio with respect to *m*-BDC groups (each **PL** contributes 4 *m*-BDC groups) and mixed with a dimethylformamide (DMF) solution of Cu(II) acetate (Note: 5.3

wt. % polymer was used for these studies; polymer concentrations as low as 2 wt. %, however, still formed robust gels) (Fig. 2a). Gelation occurred immediately; annealing for 4 h at 60 °C provided a translucent blue gel (*s*-Gel) with a maximum absorption (λ_{max}) at 724 nm (Fig. 2b), which is diagnostic of the paddlewheel complexes in the desired *m*-BDC-based Cu₂₄L₂₄ MOCs.²⁸ The small- and wide-angle X-ray scattering (SAXS/WAXS) curve (Fig. 2c) for *s*-Gel displayed two peaks: one in the high *q* region (0.47 Å⁻¹) that corresponds to the form factor of a ~2.7 nm spherical particle, which agrees well with the size of the cuboctahedral Cu₂₄L₂₄ MOC,²⁹ and a broad peak at low *q* (~0.07 Å⁻¹) that provides the average distance between the MOC junctions (~9 nm; see supplemental text section I for details). These two peaks, which are unique to the spherical shape of the MOC and the predictable inter-MOC distance within the network, respectively, are strong indicators of the presence of nanoscale MOCs within the material. In oscillatory rheology frequency sweep studies, *s*-Gel behaved as an elastic solid ($G' > G''$) at all measured frequencies (0.1 to 100 rad/s) with $G' = 6.6$ kPa @ 10 rad/s (Fig. 2d). This modulus value is consistent with the presence of high branch functionality junctions as expected for the proposed polyMOC structure. Cu₂₄L₂₄ MOCs are known to undergo rapid ligand exchange in solution,^{28,30} which in the case of *s*-Gel could provide a mechanism for stress relaxation. Indeed, *s*-Gel relaxes stress (Fig. 2e) with a characteristic relaxation time (τ) of 132 ± 5 s at room temperature, which is ~100-fold less than previously reported polyMOCs with cuboctahedral Pd₁₂L₂₄ MOC junctions at 55 °C.²⁶ As expected given its highly dynamic nature, *s*-Gel can readily heal when damaged (Fig. 2f). In addition to these studies using star polymer **PL**, we note that *m*-BDC-terminated linear polymers also formed robust Cu₂₄L₂₄ polyMOCs with similar properties to *s*-Gel (supplemental text section II, Fig. S1-S2), suggesting that the MOC junctions of *s*-Gel are serving as cross-linkers in addition to **PL**. Such a result would not be possible with small paddlewheel clusters, thus strongly motivating the use of high junction functionality MOCs to obtain mechanically robust materials. These findings are further supported by simulations of networks of four-arm star polymers (e.g., **PL**) and model Cu₂₄L₂₄ MOCs, which reveal that a significant fraction of the arms of each **PL** ligand are bridging across two different Cu₂₄L₂₄ MOCs to provide a high crosslinking density (Fig. S3).

The photo-induced reduction of Cu(II) complexes in the presence of benzophenone and hydrogen donors is well-known.^{31–34} Recently, Park and coworkers²³ applied this strategy to the photoreduction of Cu₂₄*m*-BDC₂₄ MOCs bearing exohedral coumarin ligands, the latter of which

were required for accessing the Cu(I) state in a controlled manner (as opposed to rapid reduction to Cu(0)). A distinguishing feature of polyMOCs is their ability to be modularly functionalized by the addition of small molecule ligands²⁶ into the network junctions without affecting their mechanical properties, which is not possible in traditional supramolecular networks based on point metal-ligand complexes as junctions. Here, we leverage this capability for the installation of coumarin-based *m*-BDC into the junctions of *s*-Gel (providing “*c*-Gel”), enabling controlled photoreduction of the network junctions from Cu(II) to Cu(I). It was hypothesized that such a photoreduction would disrupt the paddlewheel complexes within these Cu₂₄L₂₄ MOCs and induce a corresponding change in the network topology. Density functional theory (DFT) calculations of a model bis-Cu(II) paddlewheel complex supported this hypothesis (Fig. S4). Moreover, selective access to a catalytically active species (here, Cu(I)) could enable the chemical remodeling of the material in a way that creates new multi-material properties, for example through the polymerization of polymeric azides and alkynes (*vide infra*).

To prepare coumarin functionalized Cu₂₄L₂₄ polyMOCs (*c*-Gel), **PL** was combined with **CL**²³ in a 1:3 ratio with respect to *m*-BDC groups and Cu(II) acetate (6.6 wt. % polymer) (Fig. 1). Park and coworkers²³ reported on the use of a mixture of benzophenone, *N,N*-dimethylformamide, and methanol or THF to achieve controlled photoreduction of discrete coumarin-based MOCs in solution. Searching for conditions to achieve a similar photoreduction in the context of materials, where solvent evaporation and long-term storage stability are concerns, we screened several alternatives and identified ethyl-4-(dimethylamino)benzoate (EDMAB) as a suitable H-donor to achieve, in combination with benzophenone, controlled photoreduction of our polyMOCs. Thus, EDMAB (3 equiv relative to Cu) and benzophenone (0.5 equiv relative to Cu) were added and the mixture was annealed for 4 h at 60 °C. The resulting material, *c*-Gel, displayed the characteristic $\lambda_{\text{max}} = 724$ nm of Cu(II) paddlewheel complexes (Fig. 3a) while the SAXS/WAXS (Fig. 3b) and frequency sweep rheology (Fig. 3c) results were similar to those of *s*-Gel, suggesting that, as expected for the unique high branch functionality polyMOC topology, coumarin incorporation and the presence of EDMAB and benzophenone have little effect on the structure and topology of the polyMOC network. Strikingly, when *c*-Gel was exposed to 368 nm light (FL8BLB-368 8W bulb) under N₂ atmosphere, it converted over the course of 2 h into a transparent green liquid (Fig. 3d). This solid-to-liquid phase transition along with disappearance of the 724 nm absorbance peak (red line, Fig. 3a) are consistent with photoinduced reduction of the Cu(II) polyMOC to a primarily

Cu(I) state. The material was stable in this state indefinitely under N₂ atmosphere, while exposure to 368 nm light for an additional 2 h produced an opaque brown liquid (Fig. 3a) with $\lambda_{\text{max}} = 580$ nm (grey line, Fig. 3a), which is consistent with the formation of Cu(0)³⁵. Once again, the material was indefinitely stable in this state under N₂ atmosphere. Exposing either the primarily Cu(I) or Cu(0) solutions to ambient air, however, led to their slow conversion back to Cu(II) *c*-Gel with $\lambda_{\text{max}} = 724$ nm (blue line, Fig. 3a; Fig. 3d, supplementary video S1), an identical SAXS/WAXS profile (red line, Fig. 3b), and a similar G' value compared to *c*-Gel (red line, Fig. 3c) (10.3 kPa vs 13.1 kPa @ 10 rad/s before and after photoreduction/re-oxidation, respectively; the increase in G' is attributed to solvent evaporation during the re-oxidation process). This switching between the primarily Cu(II), Cu(I), Cu(0) and back to Cu(II) states was repeated for 4 cycles without the addition of any new reagents, which corresponds to 12 separate state transformations for a single sample (Fig. 3d). We note that the photoreduction required a longer irradiation time with subsequent cycles (~4 h for the fourth cycle compared to ~2 h for the first cycle) likely due to the consumption of EDMAB during each photoreduction step; more EDMAB can be added to the material to enable further switching if desired.

To investigate the roles of benzophenone and coumarin in this system, a sample of *s*-Gel (Fig. 2a, lacking coumarin ligand CL) was prepared in the presence of benzophenone and EDMAB and irradiated with 368 nm light. Regardless of the light intensity used, the material immediately converted to a brown fluid indicative of the Cu(0) state, confirming that coumarin is necessary for controlled access to the Cu(I) state (Fig. S5). In addition, when *c*-Gel (with coumarin) was irradiated for 24 h in the absence of benzophenone, no detectable changes were observed, which suggests that direct photoexcitation of coumarin does not induce to Cu(II) reduction (Fig. S6). Finally, when coumarin is not covalently attached to the MOC and is simply added into solution the material rapidly reduces directly to Cu(0). To rationalize these results, DFT calculations of a model system were conducted (supplementary text section III, Fig. S7), showing that triplet-state coumarin, which can be generated via energy transfer from triplet benzophenone, is thermodynamically capable of reducing Cu(II) to Cu(I) but not Cu(I) to Cu(0). Thus, we suggest that when a photoexcited triplet benzophenone approaches the MOC junctions within *c*-Gel, its energy is transferred to the coumarin groups covalently attached to the junctions, and the resulting triplet state coumarin can reduce Cu(II) to Cu(I) but not Cu(I) to Cu(0). As the sample approaches complete reduction to Cu(I), in contrast to what was proposed by Park et al. for solution-state

MOCs,²³ the MOC topology changes (as evidenced by the gel-to-sol transition and DFT calculations, Fig. S4) allowing for direct approach of photoexcited benzophenone to copper centers and further reduction of Cu(I) to Cu(0) (Fig. S8). These results highlight the synergistic interplay between the properties of each state of *c*-Gel and the critical role of the self-assembled MOC junctions to control reduction in a useful manner.

Inspired by Park and coworkers,²³ who used photoreduction of discrete Cu₂₄L₂₄ MOCs in solution to induce a Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) between small molecule reactants, we anticipated that reduction of *c*-Gel could be used to create new material functionality. Specifically, we envisioned that the Cu(I) functional state of *c*-Gel could serve as a catalyst for the formation of a covalent polymer network via copper-catalyzed azide-alkyne cycloaddition (CuAAC) of suitable polymeric azides and alkynes. Then, re-oxidation to the Cu(II) state would provide a MIN that is composed of both the Cu₂₄L₂₄ polyMOC and a secondary covalent network. Related interpenetrating networks featuring energy dissipating supramolecular networks and ductile covalent networks have received extensive attention due to their similarity to biological tissues and their outstanding toughness;^{36–39} the use of a primary supramolecular network, however, to catalyze the formation of a reinforcing secondary covalent network represents, to our knowledge, a fundamentally new way to generate such materials.

To confirm that *c*-Gel in its Cu(I) state could catalyze CuAAC,²³ benzyl azide and tetrakis(prop-2-ynyloxymethyl)methane were added during formation of *c*-Gel and the mixture was exposed to 368 nm light for 4 h. After re-oxidation the CuAAC triazole product was isolated from *c*-Gel in 85% yield (supplementary text section IV). Notably, incubation of these starting materials with *c*-Gel in the absence of light did not provide any detectable product. Building on these results, α,ω -azide-terminated PEG ($M_n = 2.0$ kDa) (A₂) and tetrakis(prop-2-ynyloxymethyl)methane (B₄) were included (2:1 ratio of A₂:B₄, 13 wt. % of A₂) during the formation of *c*-Gel as precursors to covalent A₂ + B₄ covalent networks (Fig. 4a). The mixture was annealed into a sheet, which was cut into uniform strips and placed in nitrogen-purged vials (Fig. 4a, i). The strips were then irradiated with 368 nm light for 4 h to achieve switching throughout the sample (Fig. 4a, ii). In contrast to *c*-Gel alone, which converts into a fluid upon switching (Fig. 3a), the material prepared in the presence of A₂ and B₄ retained its solid form hinting at the creation of a new covalent network. UV-vis analysis after irradiation showed complete disappearance of

the characteristic 724 nm absorbance associated with the Cu(II) paddlewheel complex; re-oxidation by air provided the desired MIN (*min*-Gel, Fig. 4a, iii) with the original blue color and $\lambda_{\text{max}} = 724$ nm. Notably, the SAXS/WAXS scattering profile (Fig. S9) for *min*-Gel was identical before and after irradiation, indicating that formation of an interpenetrating covalent network does not significantly alter the structure of the polyMOC network (Fig. 4b). Thus, though a new covalent network is formed irreversibly in this process, the polyMOC network is able to reversibly switch between states (*e.g.*, from Cu(I) back to Cu(II)) within the MIN, making it available to catalyze subsequent reactions if desired.

Uniaxial tensile testing (Fig. 4c) and oscillatory rheology (Fig. S10) experiments were conducted using *min*-Gel and several control samples (see table S1 for values of toughness, Young's moduli (E), extensibility, and ultimate strength). Remarkably, *min*-Gel had ~150-fold enhanced toughness (black line, Fig. 4c) and increased moduli compared to both *c*-Gel with A₂ and B₄ in solution in the absence of irradiation (blue line, Fig. 4c) and *c*-Gel irradiated and re-oxidized in the absence of A₂ and B₄ (red line, Fig. 4c). Following irradiation, the polyMOC network of *min*-Gel could be extracted from the MIN with an aqueous ethylene diamine solution (10% v/v) (Fig. S11) providing a colorless covalent PEG-based gel with much lower toughness (green line, Fig. 4c). All of these data support the notion that *min*-Gel is composed of interpenetrating supramolecular (polyMOC) and covalent (PEG) networks and that the state switching capability of the Cu₂₄L₂₄ polyMOC enables photoredox-catalyzed formation of MINs.

Further mechanical testing revealed that τ was 2460 ± 35 s for *min*-Gel (Fig. S12), while hysteresis experiments demonstrated that *min*-Gel dissipated stress as seen by the area between extension and relaxation (red line, Fig. 4d); in repeated extensions, the material recovered a majority of its toughness despite a small amount of plastic deformation. The recovery of toughness on the timescale of the tensile testing experiment is likely due to the fast relaxation time of the polyMOC network within *min*-Gel. Compressive testing corroborated these tensile testing results, showing that *min*-Gel displayed significantly enhanced toughness compared to its component networks (Fig. S13). In addition, a strain rate dependence is observed, as expected due to the fast relaxation time of the polyMOC network. Compression analysis of an irradiated sample before re-

oxidation showed lower toughness than the oxidized *min*-Gel, which further demonstrates that an intact polyMOC network is necessary for the enhanced properties of this material.

In optimized interpenetrating networks, such as double networks and related systems, the secondary network typically comprises highly extensible, high molecular weight, lightly crosslinked polymers.^{36,40} To probe the composition and topology of the covalent network of *min*-Gel, Fourier-transform infrared spectroscopy (FTIR) and network disassembly spectrometry (NDS) experiments were employed (Fig. S14).^{41–45} FTIR and NDS showed the presence of unreacted azides within the covalent network, while NDS revealed that the average number of primary loops per B₄ junction was ~0.6, which is near the limiting sol-gel threshold for tetra-functional end-linked networks.⁴² These factors significantly lower the crosslinking density of the covalent network and influence the properties of the resulting MIN. The modular construction of this material system lends itself to further optimization and tuning for enhanced properties in the future. Along those lines, to our knowledge, there have been no precise measurements of loop content in interpenetrating networks; the loop fraction result presented here should spur further investigations into the topology of such systems more generally.⁴⁶ Lastly, a *min*-Gel sample was prepared using a 20 kDa PEG bis-azide (13 wt. %), which afforded a more extensible material with a lower ultimate stress (Fig. S15).

We reasoned that by leveraging the light-induced state-switching properties of *c*-Gel it should be possible to spatiotemporally control MIN fabrication. To demonstrate this concept, a fish-shaped slab (Fig. 4e, i) of *c*-Gel containing A₂ and B₄ was covered by a fish skeleton-shaped photomask (Fig. 4e, ii). After exposure to 368 nm light for 8 h, the Cu(I) functional state could be readily observed in the pattern set by the photomask (Fig. 4e, iii). Re-oxidation provided a fish with a soft polyMOC body and a tough MIN skeleton, the covalent component of which could be isolated by dissolving away the polyMOC component with ethylene diamine (Fig. 4e, iv), supplementary video S2). Notably, the isolated fish skeleton is composed of a covalent, end-linked PEG network; given the liquid-like nature of the PEG network components this shape could only otherwise be generated using a fish skeleton-shaped mold or complex viscosity modification/processing techniques. Our approach provides a way to utilize the dynamic polyMOC as a scaffold to hold the liquid PEG components in place for subsequent covalent

crosslinking. Given that covalent PEG gels of defined shapes are widely used as biomaterials,^{13,47} the approach described here could find broad applications in 3D bioprinting and related fields.

Rather than re-oxidizing the material after covalent network formation, further photoreduction using a 365 nm UV LED light source enabled the deposition of Cu(0) in irradiated regions (Fig. S16 and S17). We reasoned that this phenomenon could provide a novel way to pattern metallic copper onto soft materials. To demonstrate this concept (supplementary text section V), a 2.1 cm square slab of *c*-Gel containing A₂ and B₄ (Fig. 4f, i) was switched to the Cu(I) state to form a covalent network. A photomask was applied (Fig. 4f, ii) and the sample was exposed to the UV-LED until a metallic pattern was apparent (~2 h, Fig. 4f, iii). Removal of the polyMOC provided a covalent PEG network with a film of Cu(0) in a circuit-shaped pattern embedded on its surface (Fig. 4f, iv). Notably, the resistance of the Cu(0) regions of this material was ~1000-fold lower than in non-irradiated regions. Though this work serves as a proof-of-principle, we believe that with further engineering and optimization the switchability of *c*-Gel could open new avenues for the fabrication of integrated soft-material circuits that could have applications in biometrics, sensing, and soft robotics.^{48,49}

The results provided above represent, to our knowledge, the first examples of a multi-state switchable material capable of catalyzing a self-reinforcing reaction (MIN formation) and deposition of metal on a soft material in response to an external stimulus. Thus, the properties of each state of this material can be leveraged to create a complex object (*i.e.*, a soft circuit board) using a simple apparatus (a UV lamp or LED and a photomask). Seeking further applications that highlight the synergistic interplay between redox states in the material, we were drawn to MIN additive manufacturing. The fabrication of soft gels that can be extruded without damage due to shear forces while simultaneously possessing sufficient mechanical strength to maintain an intended geometry remains a challenge.^{50–55} Given its rapid stress relaxation, we surmised that *c*-Gel could be extruded to form filaments that, in the presence of A₂ and B₄ (or any suitable CuAAC reactants), could be converted to MINs of a desired geometry following irradiation. As a proof-of-principle demonstration of this concept, we examined extrusion of *c*-Gel using an inexpensive (~\$200) custom-built 3D printer with an attached syringe pump and heating element (Fig. S18, supplementary text section VI). *c*-Gel was extruded at a rate of 0.06 cm³/s at 60 °C to provide uniform 2 mm diameter filaments (Fig. 5a, i). A multi-layered structure was created by overlapping filaments of *c*-Gel that fused together over the course of 2 h at room temperature (Fig. 5a, ii and

iii). Using this approach, a raft-shaped object was printed (Fig. 5b, i), irradiated, and re-oxidized to provide a MIN of the same shape (Fig. 5b, ii). Extraction of the polyMOC provided a raft-shaped covalent PEG gel (Fig. 5b, iii), demonstrating that *c*-Gel can support printing a mixture of A₂ and B₄ monomers and then, upon irradiation, it can catalyze their conversion to a covalent network.

A longstanding challenge in the field of additive manufacturing, particularly of soft gel materials, is the production of overhanging or bridging regions.^{50–55} The state switching capability of *c*-Gel can overcome this challenge. By alternating filaments of *c*-Gel with and without A₂ and B₄ (Fig. 5c), a lattice with several overhangs and bridges was produced (Fig. 5d, i). Photoswitching to the Cu(I) state led to covalent network formation only in the filaments containing A₂ and B₄. Extraction of the polyMOC components provided a covalent PEG lattice with the overhang and bridging regions preserved (Fig. 5d, ii). This process was repeated with a second lattice featuring fewer overhangs (Fig. 5d, iii and iv). It should be noted that in these examples, (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide) (TPO) was used as a photoinitiator rather than benzophenone. We found that TPO can be used to access the Cu(I) state of *c*-Gel without further reduction to Cu(0), which allows for the use of excess initiator, reducing the light-induced switching and CuAAC reaction time to as little as 30 min.⁵⁶ This rapid CuAAC reaction precluded diffusion of the A₂ and B₄ components across filaments allowing access to well-resolved bridges and overhangs. Despite this advantage for covalent gel patterning, it should be noted that TPO-induced switching was not reversible (*i.e.*, the polyMOC could not be reformed to generate a MIN after TPO-initiated photoreduction). The origin of this difference is the subject of ongoing investigations. Nevertheless, these results demonstrate that the unique state-switching of *c*-Gel can provide facile access to 3D printed gel geometries with overhangs and bridges, thus providing a complementary strategy for soft material and composite additive manufacturing.

Conclusion. This work describes the first examples of Cu-based polyMOC gels, significantly expanding the scope of this emerging class of hybrid materials. In addition, by leveraging the unique topology of polyMOCs and the photoredox behavior of Cu(II) paddlewheel complexes, we demonstrate the synthesis of a polyMOC that is capable of switching between three distinct physicochemical states in response to light. Similar to biological materials that can toughen in response to external stimuli (*e.g.*, the healing of a bone), the properties of each state could be leveraged synergistically to enable unique applications: the Cu(II) functional state allows for the

formation of robust extrusion-printable supramolecular networks with modular sites for functionalization and fast network dynamics, the Cu(I) functional state provides a liquid that catalyzes azide-alkyne cycloaddition reactions that can be used for tough MIN fabrication, and the Cu(0) functional state leads to the formation of metallic copper, which can be photopatterned onto a soft gel network. In combination with the spatiotemporal control provided by light as an external stimulus, these capabilities could be leveraged for biomaterial printing, soft circuit fabrication for bioelectronics, heterogeneous catalysis, and a range of other potential applications. The ability to achieve all of these functions within a single material is unprecedented, highlighting the power of multi-state switchable polyMOCs. These results should motivate the continued development of materials that are not confined to a single set of physical and chemical properties and that can potentially address the growing breadth and complexity of modern material needs and applications. In addition, it should be noted that the structures and topologies of these polyMOCs and MINs are complex and were largely optimized empirically; future studies aimed toward probing the impact of loops, numbers of coumarins per cage, cage density, etc. will further improve the properties of these systems and enable the rational design of next-generation state-switchable materials.

Associated Content: All data is available in the main text or the supplementary materials

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Abbreviations: MOC, metal organic cage; polyMOC, polymer metal organic cage network; MIN, MOC interpenetrating network; UV-LED, ultra-violet light emitting diode; FTIR, Fourier transform infrared spectroscopy; NDS, network disassembly spectroscopy; PEG, polyethylene glycol; SAXS, small angle x-ray scattering; WAXS, wide angle x-ray scattering; CuAAC, copper catalyzed alkyne azide cycloaddition; EDMAB, ethyl-4-(dimethylamino)benzoate; DFT, density functional theory; PL, polymer ligand; CL, coumarin ligand; DMF, dimethylformamide; *m*-BDC, meta-benzene dicarboxylic acid.

Competing interests: Authors declare no competing interests

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Fig. 1 | Design of Cu₂₄L₂₄-based polyMOCs featuring coumarin-functionalized junctions. **a**, Readily accessible *m*-BDC-functionalized PEG star polymer **PL** and coumarin-functionalized *m*-BDC (**CL**) are combined with Cu(OAc)₂. Annealing provides coumarin-functionalized polyMOC *c*-Gel, which is comprised of Cu₂₄L₂₄ junctions densely functionalized with coumarins and polymer strands from **CL** and **PL**, respectively. The Cu(II) state of this material provides its deep

blue color. **b**, Combining this material with suitable reagents and exposing it to light or oxygen enables its reversible interconversion between primarily Cu(II), Cu(I), and Cu(0) functional states. The properties of each state can be used alone or the different states can be leveraged against one another for more advanced functions.

Fig. 2 | Synthesis and characterization of star polymer-based $\text{Cu}_{24}\text{L}_{24}$ polyMOC *s*-Gel. **a**, Synthesis and schematic representation of *s*-Gel. DMF = *N,N*-dimethylformamide. **b**, UV-vis spectrum of *s*-Gel network (black line) showing the red-shifting of λ_{max} to 724 nm compared to copper acetate (red line). This red shift is indicative of the formation of Cu-*m*-BDC paddlewheel complexes. **c**, SAXS/WAXS curve depicting the spacing between $\text{Cu}_{24}\text{L}_{24}$ MOCs within *s*-Gel as well as the form factor of the individual MOCs. **d**,

Frequency sweep rheology curve for *s*-Gel (5.3 wt. %) swollen to equilibrium in DMF. **e**, Stress relaxation curve for *s*-Gel. The red line corresponds to fitting of the data using the Kohlrausch stretched exponential model, which provide the characteristic relaxation time τ . Inset: Image of *s*-Gel mashed into several pieces (left). Placing the mashed sample in a mold and applying pressure leads to complete healing (right).

Fig. 3 | Multi-state switching of *c*-Gel in the presence of benzophenone and EDMAB. **a**, UV-vis spectra of the material (6.6 wt. %) before UV exposure (black line), in the Cu (I) state (red line), in the Cu (0) state (gray line), and after oxidation via exposure to air (blue line). **b**, SAXS/WAXS curves for *c*-Gel before (black) and after UV exposure and re-oxidation (red). The structure of the Cu(II) *c*-Gel is restored upon re-oxidation. **c**, Frequency sweep rheology curves for *c*-Gel before (black) and after UV exposure and re-oxidation (red). The slight increases in the storage and loss moduli are attributed to a small amount of solvent evaporation during the course of the

switching and re-oxidation processes. **d**, Images of *c*-Gel as it proceeds through a full switching cycle. After 2 h of UV exposure the gel converts into a green fluid, which further converts into a brown opaque liquid after 2 additional hours of UV exposure. 16 h after exposure to air the blue Cu(II) *c*-Gel is re-formed. **e**, Switching of *c*-Gel through 4 complete cycles (12 total state conversions) as monitored by UV-vis spectroscopy. The blue circles represent absorbance at 724 corresponding to the Cu (II) state, while the brown squares represent absorbance at 580 corresponding to the Cu(0) state. Dashed lines are drawn between points to aid the viewer; they are not mathematical fits or actual data. *Note*: oxidation labels indicate the primary functional oxidation state of the material; they are not intended to imply that 100% of the Cu centers have a given oxidation state.

Fig. 4 | Metal-organic cage interpenetrating network (MIN) fabrication enabled by photo-induced switching of *c*-Gel. **a**, Synthesis of *c*-Gel (6.6 wt. %) in the presence of 2 kDa bis-azido-PEG A_2 and tetrakis-alkyne B_4 . Images of the material immediately after annealing (i), after irradiation with UV light to induce the CuAAC reaction (ii), and re-oxidation (iii) to provide a MIN *min*-Gel. In case ii, some dark regions of Cu(0) were observed, which had no apparent effect on the subsequent MIN formation. **b**, Schematic depiction of the interpenetrating polyMOC and PEG supramolecular and covalent networks, respectively, within *min*-Gel. The covalent PEG network consists of linear strands (green) that can connect two junctions (green spheres) or be connected to the same junction. The latter “primary loop” defects reduce the network connectivity

giving rise to double-network-like properties. **c**, Stress-strain plot from tensile testing showing the increased toughness of *min*-Gel compared to control samples. The observed enhancement of toughness is attributed to the IPN effect. **d**, Stress-strain curves showing hysteresis of *min*-Gel over 4 cycles. Strain rate = 1 mm/min; sample length = 5 mm. There was no resting period between cycles. **e**, A fish-shaped sample of *c*-Gel with A₂ and B₄ (*i*) is covered with an aluminum foil photomask (*ii*). Irradiation of the sample with a 365 nm UV lamp for 8 h leads to the formation of Cu(I) in irradiated regions (*iii*). Washing the sample with aqueous ethylene diamine allows for isolation of the newly formed PEG-based covalent network (*iv*). **f**, A rectangular sample of *c*-Gel (*i*) was first switched to the Cu(I) state to induce covalent network formation throughout the sample. Then, a photomask in the shape of a circuit was placed over the sample (*ii*), and the material was irradiated with a 365 nm UV LED to deposit Cu(0) in irradiated regions (*iii*). Washing the material with aqueous ethylene diamine allowed for isolation of the PEG covalent network with patterned Cu(0) regions (*iv*). *Note*: oxidation labels indicate the primary functional oxidation state of the material; they are not intended to imply that 100% of the Cu centers have a given oxidation state.

Fig. 5 | *c*-Gel-mediated additive manufacturing. **a**, *c*-Gel (6.6 wt. %) can be extruded to form a single uniform 2 mm diameter filaments (*i* and *ii*). Over the course of hours, the filaments fuse together generating a slab of material (*iii*). **b**, By overlaying filaments, *c*-Gel objects containing A_2 and B_4 can be fabricated (*i*). Irradiation of the resulting object induces covalent network formation; re-oxidation converts the object into a dimensionally stable *min*-Gel (*ii*). Then, the

polyMOC component of the newly fabricated object can be removed with aqueous ethylene diamine, yielding an entirely covalent network with the same shape as the printed *c*-Gel (*iii*). **c**, Schematic of lattice structures that can be fabricated by alternating *c*-Gel with and without A₂ and B₄ components. **d**, Images of *c*-Gel lattices before (*i* and *iii*) and after (*ii* and *iv*) extraction of the polyMOC components. The resulting covalent PEG networks preserve the overhanging and bridging regions of the 3D printed lattice.