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Invited Feature Article

# Polymerization in MOF-Confined Nanospaces: Tailored Architectures, Functions, and Applications

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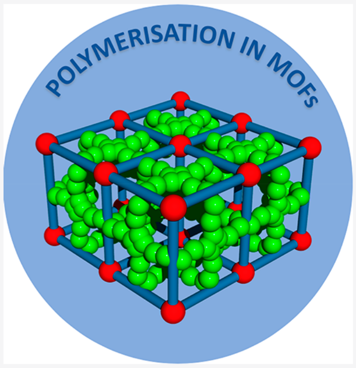
**ABSTRACT:** This feature article describes recent trends and advances in structuring network polymers using a coordination-driven metal−organic framework (MOF)-based template approach to demonstrate the concept of crystal-controlled polymerization in confined nanospaces, forming tailored architectures ranging from simple linear one-dimensional macromolecules to tunable three-dimensional cross-linked network polymers and interwoven molecular architectures. MOF-templated network polymers combine the characteristics and advantages of crystalline MOFs (high porosity, structural regularity, and designability) with the intrinsic behaviors of soft polymers (flexibility, processability, stability, or biocompatibility) with widespread application possibilities and tunable properties. The article ends with a summary of the remaining challenges to be addressed, and future research opportunities in this field are discussed.



## ■ INTRODUCTION

Nature has developed remarkable precision and exquisite control at the molecular level, thus ultimately transforming inanimate matter into biopolymers such as DNA and proteins with specific functions.[1] DNA and protein biopolymers are produced by enzymatic polymerizations within confined and organized molecular-scale spaces, which rely on certain noncovalent (e.g., hydrogen bonds) and covalent (e.g., peptide bonds) interactions. Inspired by an amazing level of control over the hierarchical organization and assembly in nature, the molecular engineering of synthetic materials with controlled arrangements has arguably been the most important objective and a long-standing aspiration.[2] Although from the perspective of complex multifunctionalities synthetic materials do not yet compare with their natural counterparts, by mimicking nature and biological principles as a model, molecular engineering allows fine control over the structure and assembly of synthetic materials on different length scales as well as tuning their molecular, nanoscopic, and macroscopic properties.[3] By assembling a vast variety of building blocks, considering precursor molecules with stereochemistry/chirality/responsiveness, the design and backbone architecture that are critical to performance and the use of innovative synthesis strategies could lead to precision materials with controlled structures/confined geometries with widespread application possibilities and tunable properties.[4]

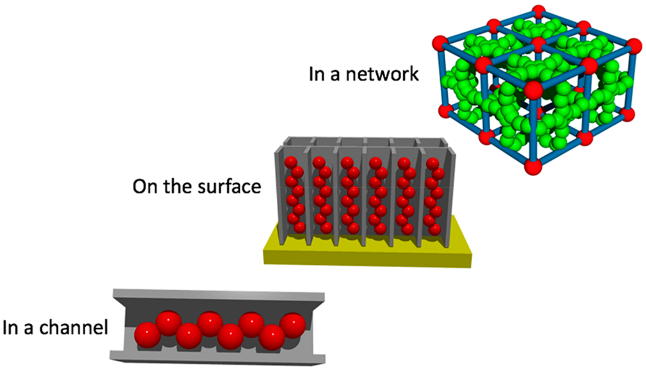


**Figure 1.** Increasing macromolecular definition along the one-dimensional chain (1D, bottom), on functionalized surfaces (center), and in three-dimensional space (3D, top).

The molecular structuring of soft materials by a dimensional organizing principle (Figure 1) (for instance, molecular arrangements "along the chain" in polymers[5] and controlled arrangements of structures on second and third dimensions "in space" forming supramolecular structures,[6] covalent/noncovalent porous crystalline networks such as metal/covalent−organic frameworks (MOFs/COFs),[7] porous organic polymers (POPs),[8] and related sophisticated architectures) has been the subject of extensive research.[9] The focus of this report is to summarize recent trends and advances in

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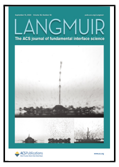

controlled arrangements of polymers using a coordination-driven metal−organic framework (MOF)-based template approach to demonstrate the concept of crystal-controlled polymerization confined in the nanospaces of MOF lattices to form tailor-made architectures ranging from simple, linear one-dimensional macromolecules to highly tunable three-dimensional cross-linked network polymers, polymeric gels, and interwoven molecular fabrics. This is a rapidly evolving research area, and summarizing each rich intellectual contribution in a single report is an immense task. We have confined this literature survey to pioneering research contributions that have facilitated the merger between the two classes (i.e., coordination-driven MOF assemblies to polymer chemistry). We summarize fundamental design principles aiming for polymerization control via defined geometries with a series of examples from literature reports as well as selective research tracing our own efforts in the past few years. The key contents are categorized as (1) the polymerization of monomers loaded inside the confined channels of MOF assemblies, thereby controlling the macromolecular growth process through the highly ordered geometry of the MOF nanospaces; (2) postsynthesis copolymerization of preorganized organic ligands in MOF with guest molecules via coupling chemistries in a step-by-step fashion to fabricate MOF-templated cross-linked porous network polymers; and (3) self-polymerization of the immobilized homopolymerizable ligands in MOF without the need for guest molecules to form polymeric interwoven molecular architectures.

This article bridges and will inspire researchers aiming to work in integrated areas of macromolecular synthesis and materials science with a particular focus on (i) the chemical synthesis of custom-made polymerizable building blocks; (ii) self-assembly and postsynthetic material fabrication; (iii) hierarchically structured assemblies from nanoarchitecture to macrostructures, and (iv) exploring advanced material applications.

**Classics of Polymerization: A Toolbox of Cross-Disciplinary Research for the Integration and Hybridization of Porous Coordination Polymers and MOFs.** The year 2020 marks 100 years of polymer science—macromolecular chemistry—since Hermann Staudinger's first landmark concept published in 1920's "Über Polymerization" that translates to "on polymerization", describing the concept of macromolecules made of repeating units linked together by covalent bonds.[10] Since Staudinger's pioneering work, much has happened in advancing synthesis and structural analysis, and several landmark discoveries in building novel structural and functional polymers have been achieved. These works have changed the landscape of macromolecular chemistry, high-tech materials, and modern key technologies which have revolutionized the way we live.[11]

The concept of structuring polymer materials is evolving beyond the conventional trends and could be implied in a new formulation. Until the mid-1990s, polymer research was dominated by established methods such as radical, ionic, and coordinative chain growth as well as step-growth polymerization, which provide polymeric materials in the bulk for diverse applications with certain tunable macroscopic properties.[12] The field of controlled polymer synthesis has also been revolutionized with the advent of new and innovative approaches, for instance, the development of reversible-deactivation radical polymerization techniques (i.e., reversible addition−fragmentation chain transfer polymerization (RAFT),[13] atom-transfer radical polymerization (ATRP),[14] and nitroxide-mediated polymerization NMP)[15] in the mid-1990s that allow radical polymerization with unprecedented control over polymer molecular weight, molecular dispersity ($Đ$), and architecture. The introduction of click-chemistry and other efficient ligation techniques to polymer science from ~2005 onward enabled the precise placement of functional groups as well as the efficient conjugation of different polymer chains.[16] Combining noncovalent or reversible covalent strategies in polymer chemistry has facilitated the merging of macromolecular chemistry to supramolecular and coordination chemistry, hence generating a new field of complex functional systems with emerging properties.[17] Employing the fundamental classics of polymerization as a toolbox in interdisciplinary research has been rewarding in countless ways to open up a new horizon for fundamental and practical explorations to a variety of application-related fields.[18] Integrating organic polymers with other emerging material classes, such as soft materials from metallopolymers and metallosupramolecular polymers[19] and coordination-driven crystalline solid-state MOF materials,[20] yields polymer@ composites with widespread application possibilities.[21]

The motivation behind the integration/hybridization of functional crystalline solid-state MOF framework materials with flexible organic polymers by employing various postsynthetic chemical modification (PSM) strategies is to combine the exceptional features of MOFs with the robustness of polymers, ultimately constructing novel composite materials with improved processability and tunability, thus taking MOFs closer to practical material applications. MOF@polymer composites have emerged as a new class of materials which exhibit innovative architectures that can be selectively tuned for diverse functions and novel material applications.[22] For the realization of MOF@polymer composites, several covalent and noncovalent or coordinative approaches, including mixed-matrix membranes, polymer-grafted MOFs, polymers templating MOFs, polymerization in MOFs, and polyMOFs have been devised, bringing MOF closer to processable useful materials (Figure 2).

A discussion of the elegant methods of synthesizing MOF@ polymer composites has been provided in a recent review.[22] This feature article, in particular, focuses on polymerization in MOF confined nanospaces after the MOF lattice is assembled.

## DESIGN CONCEPT OF ORGANIZED ASSEMBLIES AND POLYMERIZATION IN CONFINED SPACES

Under the confined environment, molecular orientation, chemical interactions, and the properties of the molecular systems can be modulated, which in turn results in divergent reactivity and selectivity.[23] Understanding the design principles of confined spaces/assemblies and studying their effects on particular chemical reactivity is essential to creating novel molecular systems with tailored properties, functions, and chemical reactivity.[24] Molecular systems bearing discrete confined inner cavities, such as crown ethers, cryptands, molecular boxes, pillararenes, cucurbiturils, cavitands, and other macrocycles display specific chemical reactivity, recognition, and complexation properties owing to confined spaces.[25] Porous network materials, for instance, inorganic crystalline zeolites,[26] and hybrid MOFs,[27] exhibit regular extended structures and bear confined pores and channels which can be tailored to serve as molecular-level flasks for

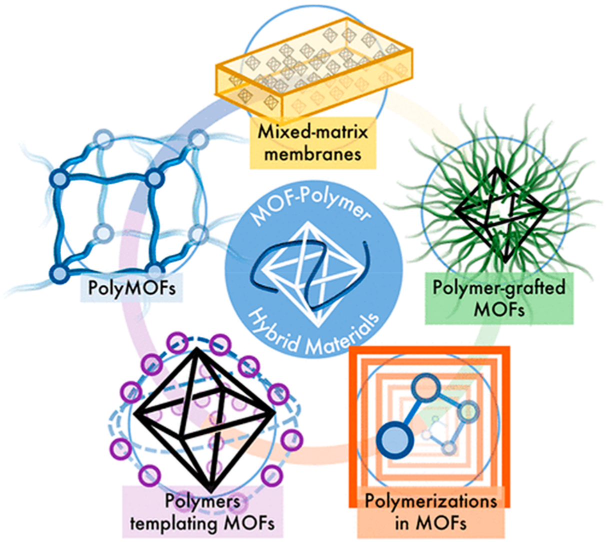

**Figure 2.** Overview of MOF@polymer composite materials. The depiction is reproduced with permission from ref 22. Copyright 2020 American Chemical Society.

chemical reactions.[28] Zeolites, classic porous materials, are crystalline aluminosilicates constructed from regular networks made up of metal oxide bonds and have been largely studied as shape-selective catalysts with confined chemical reactivity and have been proposed as a confined polymerization environment to construct zeolite-templated composites.[29] However, owing to certain limitations with respect to the pore size and structural tunability of the pore sizes and surfaces of zeolites, controlled polymerization of monomers with larger molecular sizes could be restricted.[30] MOFs are synthetic three-dimensional porous hybrid materials composed of inorganic metal nodes or polynuclear metal-containing clusters (referred to as secondary building units or SBU) and bridging organic blocks.[31] By varying the metal nodes (metal types, oxidation states, and coordination capabilities),[32] in combination with the possibility to select from the vast variety of organic building blocks,[33] the precise engineering of MOF nanospaces and channels with tailored 3D geometries (pore size, shapes, and functional groups) can be achieved that ultimately enable the modulation of their chemical reactivity and specific behaviors.[34] One of the distinctive features of the MOFs, compared to other porous materials, is their postsynthetic chemical modification, a fruitful way to introduce useful functional moieties post-synthetically with the preservation of the lattice structure. The postsynthetic tunability of the MOF pore spaces and nanochannels, modulated through organic or inorganic blocks, for instance, by introducing specific functional groups via covalent modification and coordinative modifications at SBU, led to tailored chemical and physical functions.[35]

Owing to fascinating structural attributes, MOFs have been demonstrated to be an excellent host for the confinement of heterogeneous catalysts,[36] which have been extensively investigated in adsorption (separation),[37] molecular recognition,[38] and other emerging areas which have been the subject of inspiring articles and excellent focused reviews.[39] MOFs can host various nanoentities including inorganic nanoparticles,[40] quantum dots,[41] polyoxometalates,[42] biomolecules, enzymes, or therapeutics[43] and form various composite nanomaterials.[44] The chemical environment control, for instance, tuning the strong or weak acidity of nanocrystalline MOF materials by incorporating sulfonic acid or ammonium functionalities, plays a critical role in product selectivity and reactivity in the gas-phase conversion of methylcyclopentane to an acyclic isomer, olefins, cyclohexane, and benzene.[45] The next section highlights the utility of MOFs confined pores and channels as hosts for the encapsulation of nanoentities and polymerization control via MOF defined geometries as sacrificial templates, where pore dimensionality can facilitate the formation of tailored polymers. For simplicity and clarity, we have used the term metal−organic frameworks (MOFs) in this article. In the material science community, however, other terminology for this class of materials is also being used, such as porous coordination polymers (PCP), coordination networks (CN), and organic−inorganic hybrid framework materials.[46] To describe the organic bridging cores, in the literature different terms such as organic building blocks, ligands, linkers, tectons, and struts have been coined.

**Polymerization of Monomers Inside MOF Confined Nanospaces.** MOFs offer well-ordered confined pore spaces that can be precisely tuned to be used as tailored templates, and their confinement effect can control the orientation and

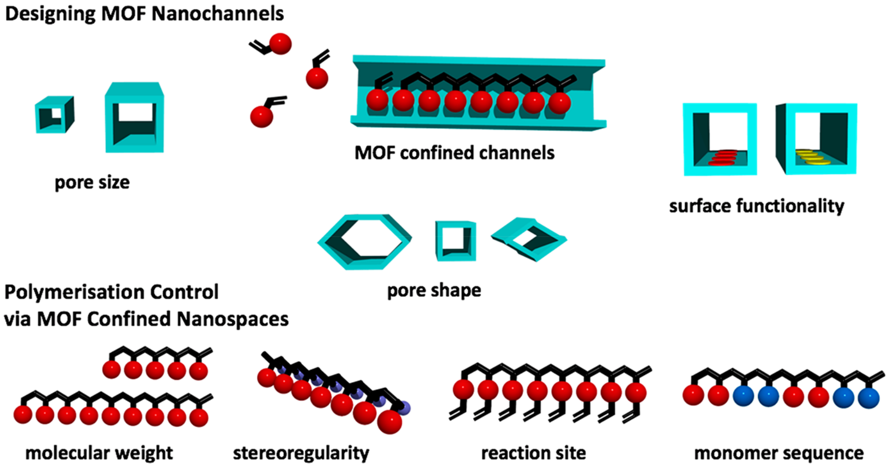

**Figure 3.** Schematic illustration of the environment and polymerization control via predesigned MOF nanospaces (tailor-made size, shape, and surface functionality). Adapted with permission from ref 50. Copyright 2018 Royal Society of Chemistry.

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conformational arrangements for controlled polymerization on the encapsulation of monomer (guest) molecules.[47] The confinement effects of pores can be considered to be a stabilization effect, which enables the preparation of an ordered array of molecules that is not stable as bulk fluids, which is called a space effect.[48] MOF confined pore spaces and channels can prevent the entanglement of polymer chains and provide control over the polymer primary architecture in contrast to other bulk system polymerization processes, typically performed in organic solutions or aqueous emulsions.[49] Using specifically designed MOF nanochannels (size, shape and surface functionalities of the pores as well as channel dimensionality)[50] affects the morphogenesis and creates polymers with controlled molecular weight, stereoregularity, and polymer composition different than those prepared in bulk (Figure 3).

Kitagawa, Uemura, and co-workers in their pioneering research have demonstrated the utility of the MOF confined geometries and nanochannels in the controlled free-radical polymerization of styrene using $[M_2(bdc)_2(dabco)]_n$ (M = $Zn^{2+}$ or $Cu^{2+}$) (bdc = benzenedicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane).[51] On encapsulation of the monomers together with the initiator in MOF channels, polymerization with high conversion (71%) was observed without the collapse of the channel structures. The resultant polystyrene remained encapsulated within the MOF channels and on dissolution yielded an MOF-templated polymer with a lower dispersity (1.6 versus 4.6) compared to that of bulk synthesis. With the advent of pioneering studies on the polymerization of styrene and acrylate monomers encapsulated inside host MOF confined one-dimensional nanochannels, a living radical nature was further demonstrated using electron spin resonance because the propagating radical due to its effective protection in the nanochannels is free from side reactions. The chemistry of the coordination spaces affects the stability and reactivity of the radical, hence leading to controlled smaller polydispersities compared to polymerization in the bulk.[52] In the radical polymerization of vinyl monomers using MOFs, it has been observed that the nanochannel size can have a strong influence on the reactivity, molecular weight, and stereostructure.[53] Similarly, channel surface modification by incorporating functional moieties such as nitro-, hydroxyl-, and carbonyl groups influences the (MOF) chemistry inside the nanochannels, which has a direct influence on stereoregularity and conversion.[54] Chemical reactions within the MOF tuning multiple specific interaction sites using a series of metal nodes [M(btb)] (M = $Al^{3+}$, $Tb^{3+}$, $La^{3+}$, $Y^{3+}$, $Nd^{3+}$, and $Eu^{3+}$; $btb^{3-}$ = 1,3,5-benzenetribenzoate) have been investigated to understand their effects on the net outcome and control over tacticity in the polymerization process.

By incorporating radically active bifunctional divinyl moieties (2,5-divinyl-terephthalate) as an organic polymerizable ligand into an MOF and subsequent radical polymerization with an adsorbed styrene monomer inside their channels (host–guest polymerization), highly ordered cross-linked polymeric materials were achieved that exhibit a crystalline arrangement and improved mechanical and thermal properties.[55] Sequence-regulated vinyl copolymer, based on periodic covalent positioning of the monomers along one-dimensional nanochannels, has also been described to control the copolymer sequence via the transcription of MOF periodicity at the molecular level.[56]

Oxidative polymerization methods are often employed to engineer conjugated polymers. Using MOF as a template, oxidative polymerization yields a highly ordered chain alignment of unsubstituted polythiophene (PT) inside the nanopores of $[La(BTB)]_n$ (BTB = 1,3,5-benzenetrisbenzoate).[57,58] The same group has reported a series of conductive porous composites by the polymerization of 3,4-ethylenedioxythiophene in MOFs.[59] Later on, polythiophene (PT) and poly(3,4-ethylenedioxythiophene) (PEDOT) were also synthesized using SURMOF thin films together with oxidizing agents.[60]

The concept of the electropolymerization of monosubstituted acetylene, namely, 1-hexyne confined in nanochannels of SURMOF-2, has also been demonstrated.[61] Schmidt and co-workers have investigated combining MOF $[Zn_2(bdc)_2ted]_n$ (bdc = benzene-1,4-dicarboxylic acid and ted = triethylenediamine) confined environment with free radical and RAFT polymerization techniques using various vinyl esters with different monomer dimensions for the synthesis of highly isotactic poly(vinyl ester)s with a controlled narrow molecular weight distribution and stereocontrolled architectures.[62] $Zn_2$(benzene-1,4-dicarboxylate)$_2$-(1,4-diazabicyclo[2.2.2]octane) confined nanochannels enable surface-initiated ARGET (activators regenerated by electron transfer) atom-transfer radical polymerization to achieve strict control over dispersity, chain-end functionalities, and tacticity by employing various precursor monomers including methyl, ethyl, benzyl, and isobornyl methacrylate.[63] This approach of combining MOFs and ARGET ATRP is a promising methodology for structuring polymers that exhibit defined uniformity in chain length, microstructure, and preserved chain-end functionality.

The MOF-templated self-polymerization of *p*-phenylenediamines (pPD) can create a hollow box-assembled spherical polymer (poly pPD) through simple carbonization.[64] In a rather different investigation via carbonization, it was observed that the critical environment of MOF nanospaces as a host compared to the bulk state could suppress the self-catalyzed or other side reactions in polyacrylonitrile chains, hence leading to the formation of a ladder polymer with an extended conjugated backbone.[65] The formation of electron-rich polymer/interpenetrated MOFs by vinylcarbazole monomer impregnation[66] and a few other reactions inside MOFs such as cationic polymerization and coordination ring-opening polymerization has also been demonstrated.[67] Recent progress in the functions and applications of the MOF@polymer composites is the subject of a recent focused review article.[68]

**Postsynthetic Copolymerization of the Immobilized Organic Ligands in MOF Crystals with Guest Molecules via Coupling.** MOFs are amenable to PSM with the preservation of the lattice structure.[69] Amide coupling reactions, isocyanate condensations, and click chemistry including azide–alkyne and thiol–ene click modifications and Glaser–Hay coupling mechanisms, are compatible for the realization of postsynthetic cross-linking polymerization.[70] Postsynthetic polymerization of the organic ligands, preorganized in the framework of the MOF "in space", is driven by the need for a specific molecular design of building blocks (i.e., the immobilized monomers with specific or required distances of the polymerizable functionalities that could be used in later-stage cross-coupling, after the formation of the MOF assemblies).[71] The modular synthesis approach in the design and optimization of polymerizable modular building

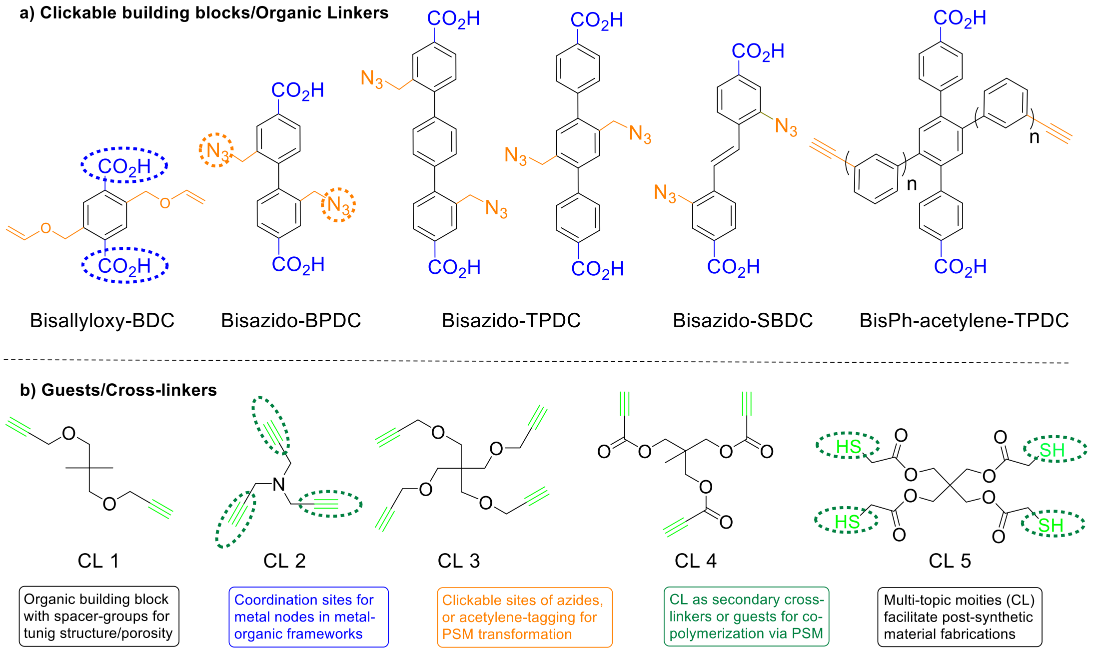

**Figure 4.** (a) Some representative customized most prevalent organic clickable building blocks employed in MOFs and postsynthetic polymerization. (b) Thiol- or alkyne-tagged molecules used as secondary cross-linkers (CL).

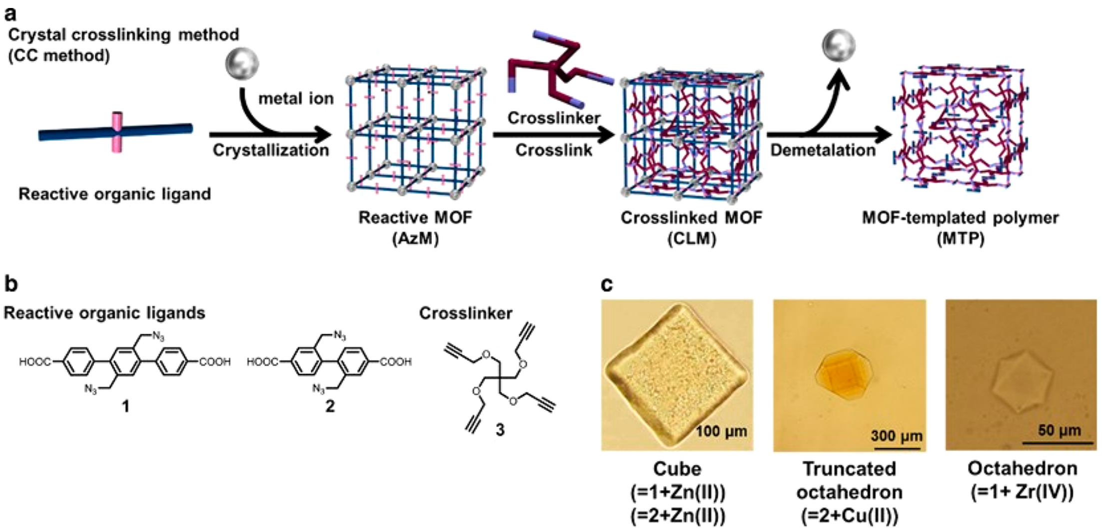

**Figure 5.** Schematic representation of the MOF-to-network polymers via covalently interconnecting the MOF structure by the postsynthetic polymerization process. Reproduced with permission from the ref 74. Copyright 2013 American Chemical Society.

blocks (MBBs) is of utmost relevance. For instance, arene derivatives and their extended systems equipped with coordination-capable carboxylic acid moieties at peripheries to enable the formation of MOF structures while adding functional components (azides, alkynes, thiols, allyloxys, etc.) can covalently interconnect the preassembled MOF crystals into cross-linked covalent networks using secondary cross-linkers (guest molecules) via a postsynthetic azide−alkyne "click" reaction, a photoinduced thiol−ene reaction, or other covalent approaches (Figure 4). The judicious selection of the cross-linker molecules (with proper dimensions) for encapsulation within MOF pores is a prerequisite. If both the primary organic ligands preassembled in MOF and the secondary cross-linker (clickable guest molecules) are ditopic, then this can yield linear polymer chains. If one of the two primary building blocks or secondary linkers is tri- or multitopic, then this would result in the formation of cross-linked network polymers.[72]

Reports on bulk powder azide-MOF "Clickable MOF" by Sada and co-workers[73] and later on postsynthetic click chemistry by copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC) as a synthesis tool for the transformation of azide−MOF to a polymer gel by crystal-controlled cross-linking of the organic ligands preorganized in MOF with acetylene-tagged molecules encapsulated (as a guest/secondary cross-linkers) in the nanopores have opened up a new platform for the exploration of MOF-templated network structures.[74] After covalent cross-coupling of the MOF organic backbone, the metal ions can be removed by dissolution, hence the cross-linked MOF is converted to metal-free, hierarchically structured, entirely organic cross-linked networks (Figure 5). This novel class of network polymers combines the advantages

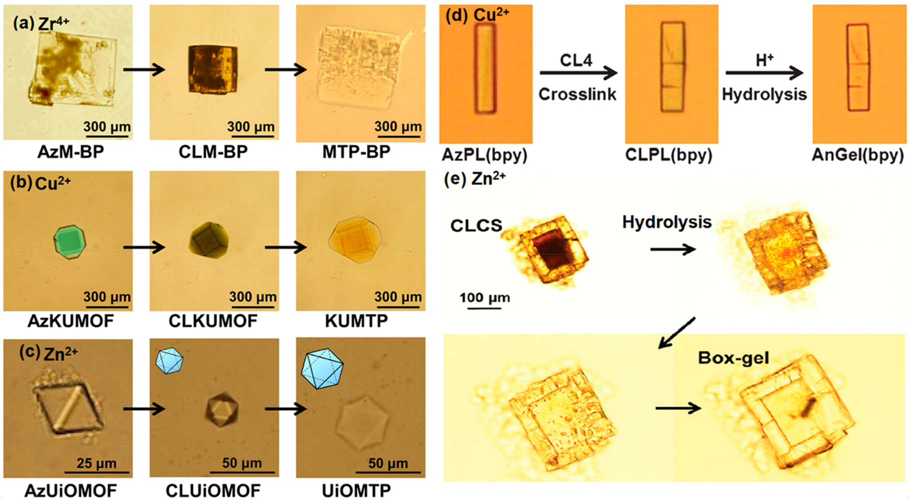

**Figure 6.** Shape-controlled nanoarchitecture: transformation of MOFs to AzoMOF (AzM) network polymers to cross-linked MOF (CLM) and finally to MOF-templated polymer (MTP). Reproduced with permission from refs 74, 76, and 78. Copyright 2013 American Chemical Society, 2017 Wiley-VCH, and 2018 Royal Society of Chemistry, respectively.

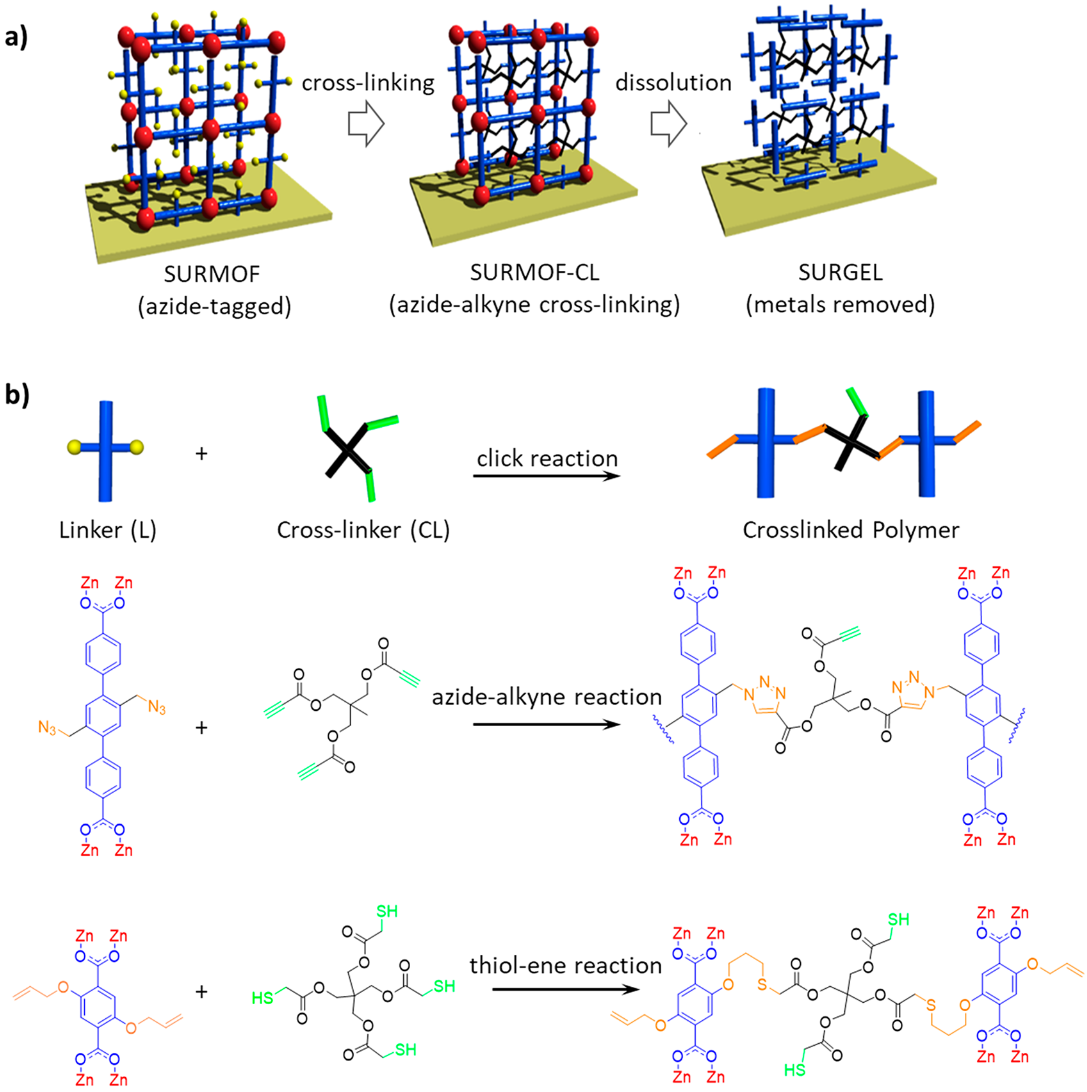

**Figure 7.** (a) Schematic of the SURMOF-to-SURGEL postsynthetic polymerization process. Reproduced with permission from ref 81. Copyright 2013 American Chemical Society. (b) Orthogonal functional sites, such as azides and alkoxys within the linker−backbone interacting with CL molecules to covalently interconnect the MOF structure via click reaction mechanisms.

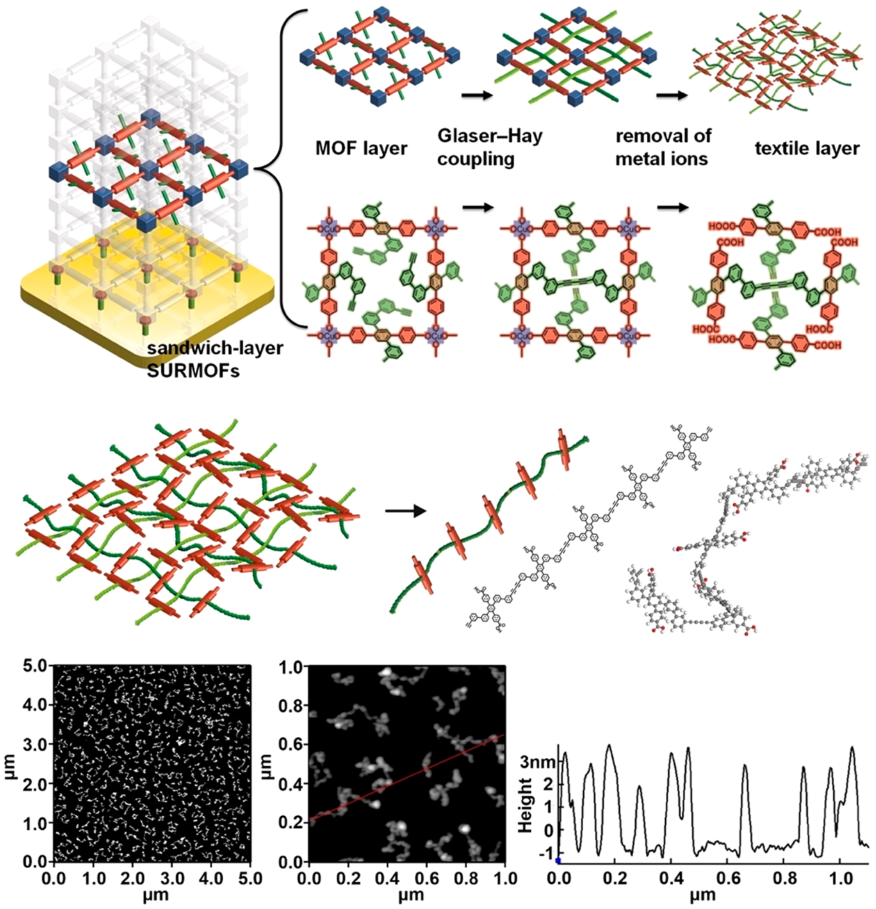

**Figure 8.** Schematic illustration of the heteroepitaxial surface-anchored SURMOF system and formation of woven molecular textiles. Reproduced with permission from ref 83. Copyright 2017 Nature Publishing Group.

of solid-state MOFs (precisely controlled structure, high porosity, and structural diversity) with the intrinsic behavior of soft polymers (flexibility, improved stability, and biocompatibility under physiological conditions).[75]

These porous network polymers allow for fine control over molecular architecture. The morphology and structural regularity of the parent MOF are preserved and can be transferred into the newly transformed network nanostructure to obtain octahedra, cubes, and truncated octahedra using various azido-MOF assemblies (Figure 6a–c). The same group has reported a postsynthetic crystal cross-linking of a pillared-layer MOF (AzPLMOF).[76] The AzPLMOF crystals on cross-linking inherit the parent crystal rectangular prism shape and size. Upon solvent impregnation, the network polymer gel materials exhibited an anisotropic swelling phenomenon (Figure 6d). Employing similar PSM approaches, crystal cross-linked gels with stimuli-responsive photoluminescence behavior[77] and box-like, well-defined hollow gel capsules with a cubic shape reflecting heterostructures based on core–shell MOF crystals were also examined (Figure 6e).[78] For the preparation of box-like hollow gel capsules, the epitaxial growth of two isostructural MOFs and a postsynthetic crystal cross-linking technique were applied, reflecting the parent crystals' shape. Postsynthetic polymerization via the crystal cross-linking method of MOF allows control over architecture on different length scales; for instance, the fabrication of nano- and microsized gel particles with a cubic shape from cyclodextrin MOFs has been achieved.[79]

We extended the postsynthetic polymerization approach to epitaxially grown surface-anchored MOF (SURMOF) thin films[80] employing diazidostilbene dicarboxylic acid as an organic ligand and Cu(II) as a metal ion source on a self-assembled monolayer (SAM)-coated gold substrate functionalized with 11-mercaptoundecanoic acid or 16-mercaptohexadecanoic acid.[81] Cross-linking SURMOF using tri(propionyloxymethyl)ethane by copper-free click modifications and subsequent metal ion extraction yields a metal-free, homogeneous, entirely organic polymer thin film called SURGEL (Figure 7). Surface-anchored MOF thin film synthesis methods add the possibility to epitaxially grow MOF crystals on a wide range of functionalized substrates (such as glass, silicon wafers, copper, gold, silver, metal oxides, etc.) that direct the nucleation site, orientation, and structure of the deposited SURMOF.[82] Combining a layer-by-layer (LBL) liquid-phase epitaxy (LPE) approach using repetitive, sequential immersion and then rinsing on each reactant exposure (using two solutions of the metal precursor and organic building block) controls the growth and thickness of the SURMOF thin films by choosing the number of deposition cycles. These SURMOFs are homogeneous in thickness and orientation and can be prepared with a very small number of defect densities, thus offer advantages as well as new opportunities compared with randomly oriented bulk system deposition methods.

**Self-Polymerization of the Immobilized Organic Ligands in MOF.** A new concept of covalent cross-linking without the need for secondary linkers or guest molecules to achieve interwoven network polymer architecture "molecular weaving" has been developed.[83] In this case, SURMOF crystals, with the ditopic primary organic linker (bis-(acetylene-biphenyl)-terphenyl dicarboxylic acid), were assembled via metal nodes. The acetylene-tagged "arms" of the primary organic linker were made long enough for the homocoupling reaction. Subsequently, by directly homocoupling the docking sites, the primary linkers were combined to yield long polymer strands. The length of the arms was longer than the MOF unit cell, hence resulting in shaped bows, and ultimately interwoven polymer chains, such as weft and warp in a textile woven with a loom, were obtained (Figure 8).

By sandwiching these "active" linkers between two MOFs thin films (shown in light gray), multiheteroepitaxial crystalline systems were obtained. The preorganized terphenyl primary linkers bearing bis(acetylene-biphenyl) as docking sites could be polymerized via Glaser-Hay coupling to yield linear and interwoven polymer chains. X-ray diffraction revealed that this topochemical reaction retains the MOF backbone fully intact. On dissolution and removal of the metal ions, the textile sheets were imaged using scanning electron microscopy and atomic force microscopy (AFM). The individual polymer strands forming the two-dimensional textiles have lengths on the order of 200 nm, as determined from the AFM images recorded for the disassembled textiles (Figure 8, bottom). The chain lengths of the obtained polymer strands correspond to about 100 monomers (i.e., about 100 unit cells of the original MOF were cross-linked). This approach of molecular weaving in crystals aiming for functional properties would need detailed exploration.

Using a rather different strategy, photocontrolled [2 + 2] cycloaddition has also been found to be suitable for the reversible structural transformation of metal−organopolymeric hybrid framework dynamic assemblies through the construction of reversible covalent linkages that operate under specific physical or chemical environments.[84] Photodriven solid-state multiple [2 + 2] cycloaddition strategies can be performed with high precision under a solvent-free environment, constructing polycyclobutane derivatives without generating biproducts, and are considered to be highly sustainable (i.e., green chemistry) processes.[85] A large number of photoactive MOFs have been constructed, and their [2 + 2] cycloaddition polymerization reactions have been investigated, mostly demonstrating photo- and thermal reversibility (depolymerization by cleavage of the polycyclobutane rings).[86] MOF transformation by a UV-induced [2 + 2] cycloaddition reaction (between the neighboring double bonds) forming a metal−organopolymeric hybrid structure containing cyclobutanes separated by phenylenes with 2,4-pyridyl pendants has been successfully demonstrated (Figure 9).[87] The reversible nature of the cyclobutane rings was achieved by depolymerization through cleavage. On heating at 250 °C for 3 h, the structure reverted to the original parent MOF assembly, hence demonstrating a single-crystal to single-crystal (SCSC) transformation. Upon photopolymerization, the microporosity of these polymer materials was retained, thus demonstrating their diverse application possibilities.

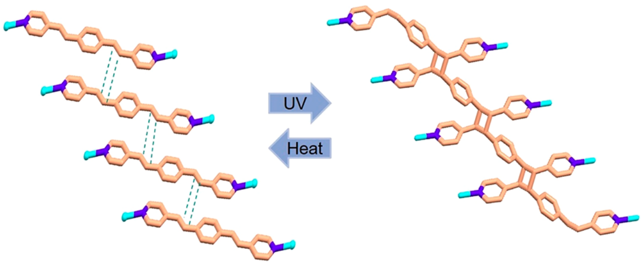

**Figure 9.** Reversible polymerization by the photocontrolled [2 + 2] cycloaddition of slip-stacked olefinic ligands in MOF and depolymerization by cleavage of the polycyclobutanes. Both processes occur through SCSC transformations. Adapted with permission from ref 87. Copyright 2014 Wiley-VCH Verlag, Weinheim, Germany.

A recent investigation of photopolymerization by [2 + 2] cycloaddition inside the channels of a photoreactive MOF with guest photoreactive molecules to form a cross-linked network demonstrated a strong coupling and feedback mechanism among the photocenters moderated by the coordination backbone.[88] The presence or absence of guest molecules (for instance, solvents) modulates [2 + 2] cycloaddition and also the final positioning of the newly formed cyclobutanes, resulting in different chemical patterns.[89] The photopolymerization by [2 + 2] cycloaddition methodology could be extended to the design and synthesis of a range of new metal−organopolymeric materials. Photochemical cycloaddition causes changes in the MOF nanospaces and ultimately impacts material properties, for instance, sorption behavior using light stimulation.[90] However, metal-coordination dissolution and network polymer fabrication possibilities of such assemblies have not been explored so far.

## ■ FUNCTIONS AND APPLICATIONS OF MOF-TEMPLATED POLYMERIC NETWORKS

MOF confined spaces not only allow multilevel control of the polymerization but also enable the fabrication of next-generation nanomaterials. We envisioned SURGEL-derived material applications and the development of new functional materials. After transforming SURMOFs via covalent cross-linking and metal ion extraction, the obtained nanoporous SURGEL polymer films retain the ordered network structure of the parent crystals, bearing regularly spaced free carboxylic acid groups which were found to exhibit proton conductivity of 0.1 S $cm^{-1}$ at 30 °C and 100% relative humidity with high ductility and pronounced water stability compared to conventional ion-conductive polymers.[91] The conductivities of the SURGEL membrane were calculated from the SURGEL film resistance $R_b$, which was determined by fitting Nyquist diagrams (Figure 10, top) using the equivalent circuit shown. The conductivity increased from 0.10 to 0.36 S $cm^{-1}$ upon increasing the temperature from 303 to 353 K. The value of 0.36 S $cm^{-1}$ exceeds that of conventional proton-conductive perfluorosulfonic acid polymers such as a commercial Nafion@211 membrane (0.13 S $cm^{-1}$ at 353 K and 95% RH).[92]

In a separate setup, the SURGEL network polymer has been demonstrated for potential applications in the separation of eight gases with different kinetic diameters.[93] This study paves the way for the creation of more complex SURGEL membranes, including vertically organized pore geometries as well as the incorporation of functional groups to tune the permeance and selectivity for applications in liquid and gas separation (Figure 10, bottom).

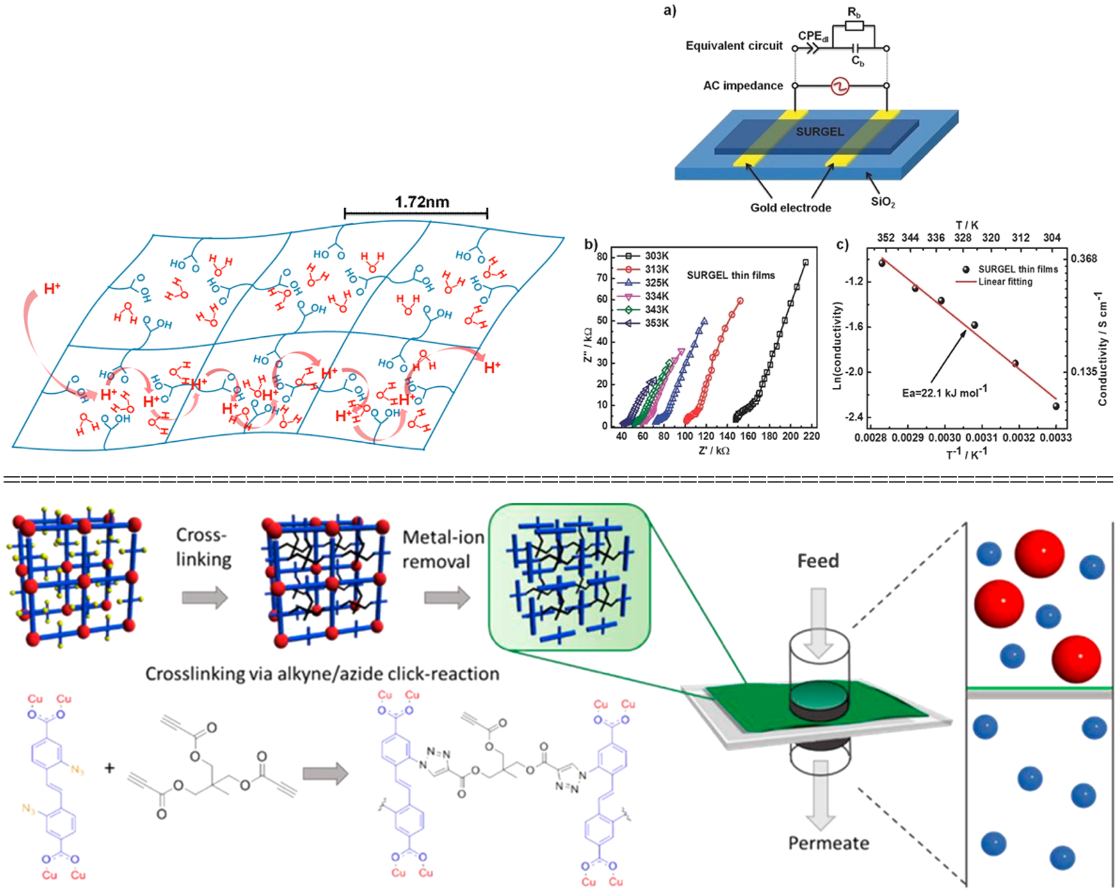

**Figure 10.** Schematic illustration of the highly organized polymer network in the SURGELs (top). The channels required for Grotthuß-type (proton hopping) transport consist of the carboxylic acid groups (spacing 1.72 nm) and $H_2O$ molecules embedded in the film. (a) Illustration of the AC impedance measurement of the SURGELs. In the equivalent circuit model, $R_b$ is the resistance of SURGELs, $C_b$ is the capacitance of SURGELs, and CPEdl is the capacitance of the SURGELs/electrode interfaces. (b) Temperature-dependent Nyquist diagrams of SURGEL at 100% RH. (c) Arrhenius plots of the proton conductivity of SURGELs. Reproduced with permission from ref 91. Copyright 2018 Wiley-VCH. Gas-separation characteristics of SURGEL polymer membranes (bottom). Reproduced with permission from ref 93. Copyright 2019 MDPI.

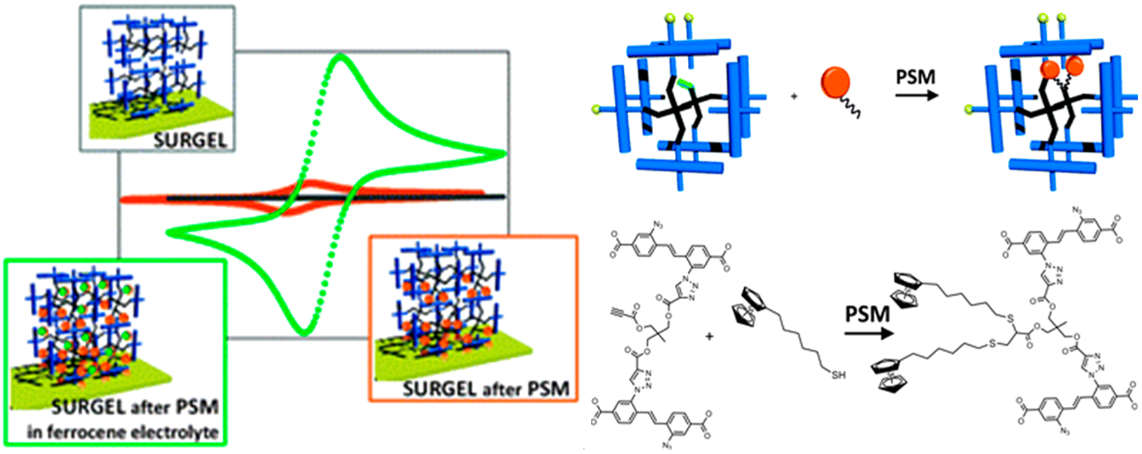

**Figure 11.** Schematic 3D representation of the cross-linked SURGEL unit cell and the cross-linking of the ferrocenyl derivative (top, left). Chemical structure of the cross-linked SURGEL tecton and the ferrocenyl derivative. Reproduced with permission from ref 94. Copyright 2014 Royal Society of Chemistry.

Under controlled cross-linking polymerization, not all of the polymerizable (azides) moieties of the organic ligands immobilized in SURMOF can couple to the alkyne moieties of the secondary cross-linker due to the spatial and sterical constraints. The unreacted alkyne groups within cross-linked assemblies can also be utilized for the incorporation of new chemical functionalities. To demonstrate the generality of this approach, we prepared different types of SURGELs-derived materials. For instance, we investigated the covalent insertion of a 6-(ferrocenyl)hexanethiol into the pore walls of the

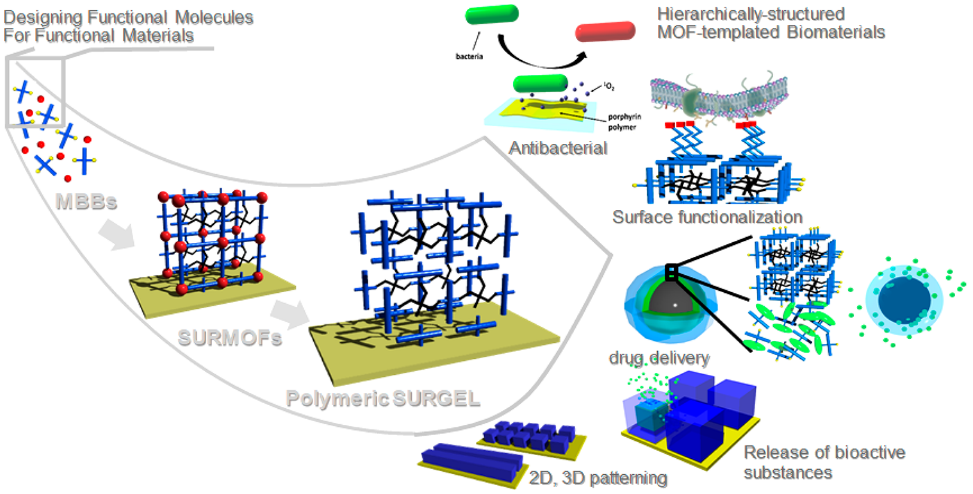

**Figure 12.** Depiction of function-inspired hierarchically structured MOF-templated biomaterials via postsynthetic polymerization and materials fabrication in confined nanospaces. Adapted with permission from ref 96. Copyright 2016 Wiley-VCH Verlag, Weinheim, Germany. Adopted with permission from refs 97−99. Copyrights 2015, 2017, and 2018 American Chemical Society.

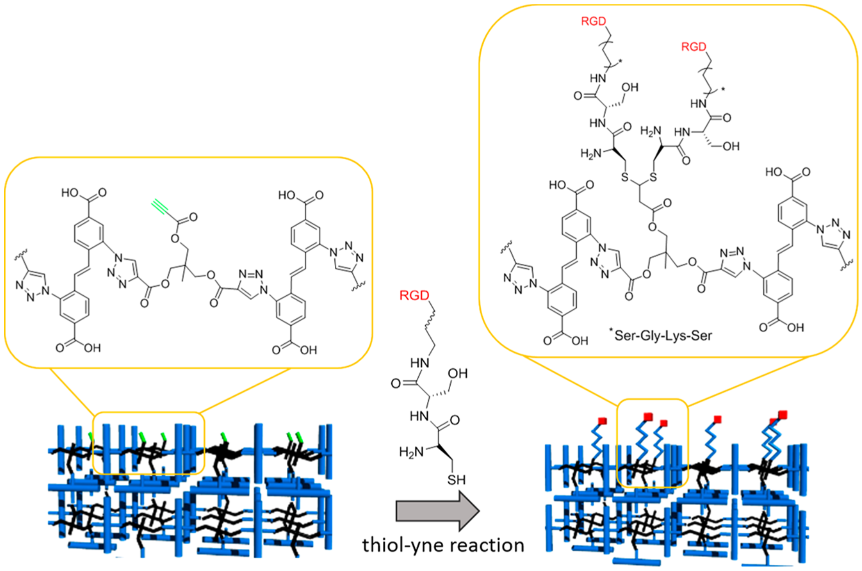

**Figure 13.** Grafting RGD-containing oligopeptide onto a SURGEL via photoinduced thiol−yne click chemistry. (Left) Scheme of the SURGEL framework. Organic linkers (blue) connect through the multifunctional cross-linking molecules (black) with remaining alkyne moieties (green). (Right) Surface-modified SURGEL via the thiol−yne click reaction. Adapted with permission from ref 96. Copyright 2016 Wiley.

porous polymer SURGELs using thiol−yne postsynthetic modification induced by 254 nm UV irradiation, aimed at electrochemical applications (Figure 11).[94] By cyclic voltammetry, the resulting electrochemical properties were demonstrated, and it was shown that the ferrocene-functionalized SURGELs can be reversibly reduced and oxidized, with the oxidation peak at 0.12 V and the reduction peak at 0.07 V versus a Pt electrode; the separation between the peaks was thus only 45 mV. By adding ferrocene as an electrolyte, a Nernstian diffusion-limited process was observed, which can be presumed to be due to the high permeability of the modified SURGELs for ferrocene molecules after the postsynthetic modification.

Merging SURGELs with biology-relevant molecules leads to engineered MOF-templated materials with tailored biofunctions.[95] These SURGEL-derived cross-linked polymeric biomaterials are persistent under physiological conditions and overcome some of the main drawbacks of the parent SURMOFs. For instance, their instability and potential to release toxic metal ions can be overcome, which are substantial problems for applications in life sciences. As a proof-of-principle for the biofunctionalization of the SURGEL, different biofunctions have been demonstrated as depicted in Figure 12.

While tuning cell adhesion by surface biofunctionalization of the SURGEL-derived cross-linked network, we inserted a short peptide of arginine−glycine−aspartic acid (RGD).[96] Cell adhesion can be tuned via a specific interaction with the integrin receptors of the cell membrane. RGD is known for inducing the adhesion of osteoblasts onto implanted surfaces. The proof of concept was performed *in vitro* using the osteoblast-like CAL72 cell line. The linker is incorporated into the peptide to enhance its solubility in water and to increase the distance between the bioactive sequence RGD and the functionalized surface to improve the accessibility of the RGD peptide for cells (Figure 13).

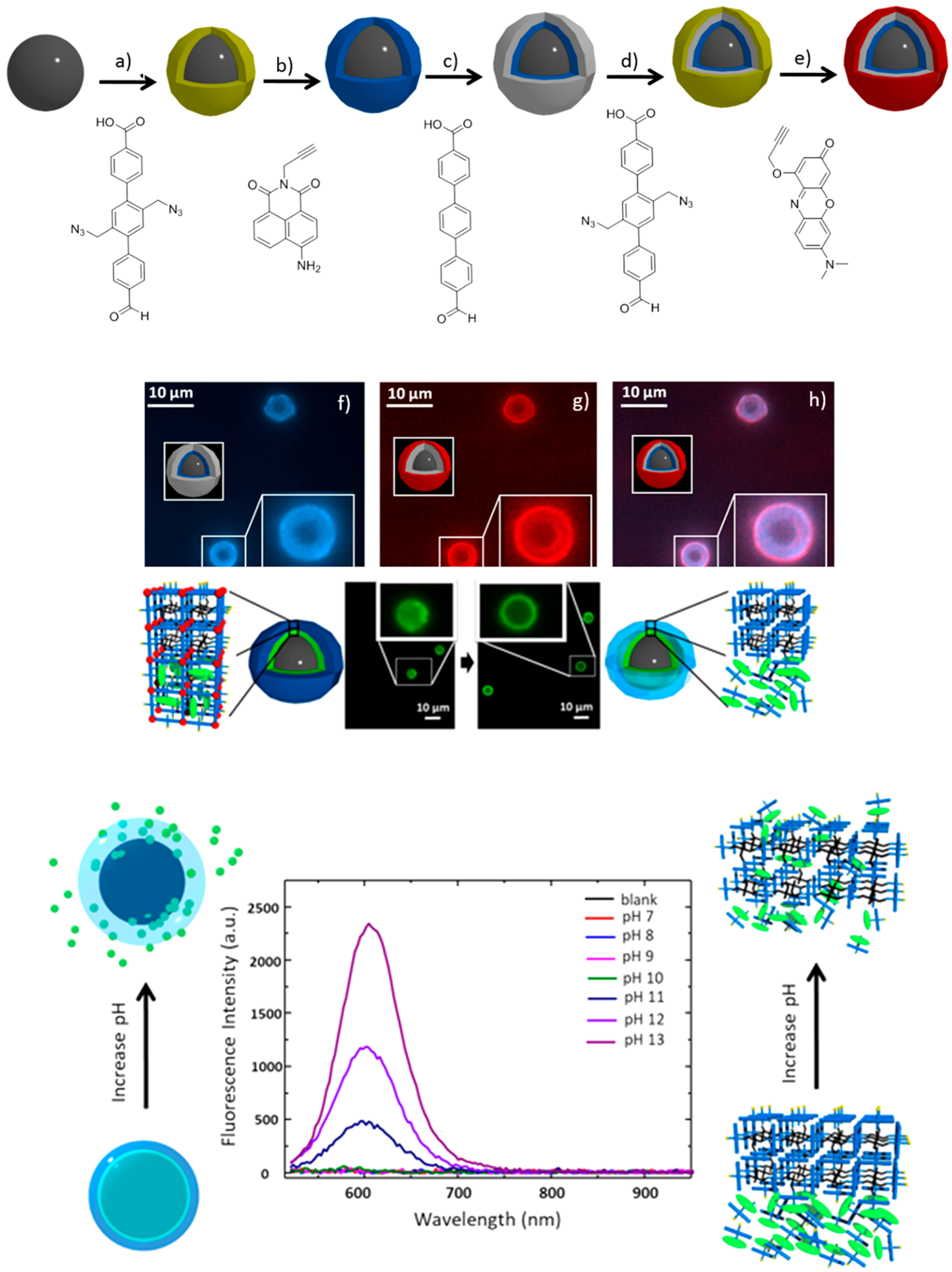

**Figure 14.** (Top left) Schematic design of MOF growth around magnetic core particles (MagMOF) via layer-by-layer heteroepitaxy. (a) MOF growth of Cu(BA-TPDC); (b) loading of blue dye molecules via the click reaction; (c) MOF growth of Cu(TPDC); (d) MOF growth of Cu(BA-TPDC); and (e) loading of red dye molecules via the click reaction. (Bottom left) Confocal microscope images of the dye-functionalized multishell MOF coated nanoparticles using different filters: (f) blue channel, (g) red channel, and (h) overlay of the red/blue channel. (Right) Depiction of the pH-triggered swelling and release of dye from the magGel capsule as confirmed by emission spectra. Adapted with permission from ref 97. Copyright 2015 American Chemical Society.

The influence of the RGD functionalization was determined by comparing the adhesion and spreading behavior of CAL72 cells on the SURGEL surfaces. The number of cells adhering to the RGD-modified substrates was substantially larger than the number adhering to the pristine SURGEL substrates. In addition, the mean cell area (i.e., the cell spreading) was significantly larger on the functionalized SURGELs. Consistent with these experiments, we could show in microfluidic shear force assays that the cells' attachment is already moderate on the pristine SURGEL but increases significantly with the RGD biofunctionalization. Our investigations show no cytotoxic effects of the SURGEL and efficient mediation of the adhesion of osteoblast-like cells.

The sequential use of differently functionalized organic linkers employing a layer-by-layer (LBL) approach in combination with postsynthetic polymerization, enables the surface coating of COOH-bearing magnetic particles with a uniform cross-linkable MOF multishell, referred to as the MagMOF system. MagMOF in combination with LBL approaches allows the selective functionalization of a particular layer in the core−shell system.[97] For instance, alkyne-tagged dyes (or potential drug molecules) can be selectively incorporated to construct smart capsule systems for application possibilities in an advanced delivery system. The inner shell serves as a reservoir for guest molecules/potential drugs, and the outer shell is selectively transformed into a network polymer form. External stimuli such as varying the pH, leading to swelling of the gel shell and hence the permeability of the outer shell as a porous membrane, can be tuned. The synthesis strategy and chemistry of these MagMOF core−multishell particles are depicted in Figure 14. The multishell particles can be visualized by confocal microscopy by tagging the inner blue and the outer red dyes.

A light-induced metal-free thiol−ene click reaction, in combination with photomasks or other photopatterning techniques, allows locally confined MOF conversion and thereby enables the structuring of a network polymer on a macroscopic level.[98] To examine the possibility to incorporate functional molecules within the pores of the gel networks, rhodamine-B fluorescent dye incorporation and triggered release from the gel networks on swelling were demonstrated. The immobilization of certain biorelevant or naturally occurring core-like porphyrins into SURGEL polymer thin films and the probing of their visible-light-promoted singlet $O_2$ generation using cultures of Gram-negative *Escherichia coli* (*E. coli*) as a model organism have shown antibacterial activity against pathogens.[99]

We add that SURGEL polymer thin films do not have to be limited to the above-mentioned few selected demonstrations. There could be other diverse conventional/nonconventional cores that could be incorporated into the SURGEL inner pores or at external surfaces exploring new efficient functional materials. Other elegant ways of synthesizing MOF@polymer hybrid composites have also been reported,[100] including grafting polymers to construct MOFs, and the bottom-up synthesis of polyMOFs has been demonstrated.[101] The polyMOFs framework is composed of polymer (instead of molecular organic ligands) and bears aromatic dicarboxylic acids in the backbone function as a polymeric ligand. This concept has been applied in combination with isoreticular chemistry approaches for the fabrication of polyIRMOF series.[102]

## CONCLUSIONS AND FUTURE PERSPECTIVES

In this report, we provide an overview of polymerization control using MOF confined nanospaces to design MOF-templated polymeric network materials with defined morphologies and tailored functionalities. MOF-templated network polymers combine the advantages of two material classes (i.e., solid-state crystalline MOFs with the intrinsic behavior of soft polymers with widespread application possibilities and tunable properties). Although most of the pioneering research on MOF-templated network polymers has been of fundamental understanding in bridging coordination-driven MOF assemblies with polymeric chemistry, recent interest is largely centered on emerging applications.

We emphasize a few points: (1) Despite the progress in structuring MOF-templated polymeric network materials, certain challenges remain. For instance, scalability and processability that limit their practical and translational potential need to be addressed. Polymerization in MOF pores, from the perspective of scalability, does not yet compare with conventional polymerization in the bulk performed on the industrial level. Sustainable, rapid, low-cost, efficient protocols that could generate a significant number of MOFs as well as MOF-templated polymers that could enable large-scale production for practical material applications are still lacking. Addressing certain limitations, automated synthesis approaches could assist in scaling up for practical applications.

(2) In combination with in-silico theoretical studies, recently more insights about the distinct polymerization and degrees of cross-linking in solid-state MOFs crystals compared to those of solution polymerization have been described.[103]

(3) The need for enhanced sequence control and understanding the in-depth mechanism of polymerization in MOF nanospaces will likely be a crucial focus in the future for material applications.

(4) Considering the confined environment, the pore-functionalization chemistry stands at the very center addressing MOF pore nanospaces to be used as tailored templates for specific chemical reactivity or selectivity and applications.[104] Advanced multiscale simulations and modeling approaches could predict and assist in the synthetic planning of optimally performing molecular building blocks, desired chemical functionalities, and right pore chemistry which offer distinct features and spatial properties.[105]

(5) Employing MOFs as hosts can serve as sacrificial templates, which, after the polymerization of the encapsulated monomers inside the channels, are dissolved to yield polymer structures. The dissolved components can be recrystallized, hence enabling their recyclability and reusability in MOF reconstruction, which in terms of the green-sustainable chemistry perspective has important environmental and economical implications. The concept of orthogonal cross-linking via click chemistry approaches is also compatible with a complex system, for instance, modular programming of hierarchy and structural diversity, creating multivariate hierarchical MOF@polymer composites with tailored properties and behaviors, while such tunability is hard to achieve through traditional synthesis.[106] Like the alkyne−azide or thiol−ene click chemistry approaches used in postsynthetic polymerization mentioned above, other potential synthesis strategies, for instance, incorporating dynamic reversible covalent linkages of nitroxide-mediated polymerization processes, could also be introduced for the formation of covalently cross-linked dynamic polymer networks that could be repeatedly assembled and disassembled by modulating the reaction equilibrium.[107] Considering the labile and highly dynamic nature of the nitroxide-mediated process in polymerization, the degree of cross-linking can be controlled thermodynamically, hence ultimately enable network fabrication dynamically.[108] Exploiting the dynamic nature of the nitroxide-mediated process in polymerization, and depolymerization/degradation with the possibility of recyclability/reusability of these materials is the focus of our ongoing research.

(6) In addition to the above-mentioned different polymerization methods reported for preparing MOF-templated materials, where each polymerization method has certain limitations such as the requirement of a specific catalyst or initiator, solvent, temperature, and long reaction time limiting its applicability, Lahann and co-workers envisioned a conceptually novel, initiator- and solvent-free cyclophane-based chemical vapor deposition (CVD) polymerization method to template parylenes into liquid-crystalline films.[109] This strategy also enables a general and simple protocol for the preparation of MOF@polymer composites.

(7) Structuring framework materials across nano-, meso-, and bulk regimes is the most important step.[110] From the perspective of synthetic planning and materials engineering at a molecular level, introducing modular building blocks with distinct ambitious features, for instance, switchability, responsiveness to stimuli,[111] chiral $\pi$-stacked conjugated molecular components,[112] struts bearing macrocyclic components as recognition modules,[113] integrating interlocked dynamic mechanical bonds,[114] and molecular knots,[115] is of utmost relevance because these molecular functions could be inherited once assembled into materials. Smart and dynamic building blocks, once incorporated into materials, can be further modulated in response to different stimuli such as radiation, hence enabling remotely controlled material modulation in a noninvasive way by using light radiation. Ensuing interdisciplinary research (by combining insights from organic synthesis, polymers, and MOF materials chemistry aided by computational theory and simulations), one of our ongoing focuses under the umbrella of the Cluster of Excellence 3D Matter Made to Order jointly at the Karlsruhe Institute of Technology and the University of Heidelberg, involves exploring and developing advanced technologies employing lithography techniques for polymerization using hierarchical assemblies to engineer a new form of matter made to order. By capitalizing on interdisciplinary research efforts, we are looking forward to exciting new tailored architectures, functions, and material applications.

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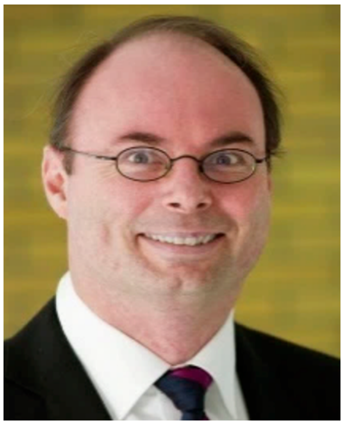
### Notes

The authors declare no competing financial interest.

### Biographies

Salma Begum studied at the Leipzig School of Natural Sciences − Building with Molecules and Nano-objects (BuildMoNa) at the University of Leipzig (H. Krautscheid) and the Institute for Integrated Cell-Material Sciences (WPI-iCeMS) with S. Kitagawa at Kyoto University, Japan. After receiving her Ph.D. in 2015, she moved to the Institute of Functional Interfaces (IFG) at Karlsruhe Institute of Technology (KIT) as a postdoctoral associate. She was a KHYS Fellow at the CAMD Research Centre UNSW, Sydney (M. Stenzel) in 2019. Her research interest centers on the synthetic assembly of nanoscale objects, porous polymers, thin films, and MOF-templated bionanomaterials.

Zahid Hassan studied chemistry at the HEJ Research Institute of Chemistry (M. Phil.) and at Leibniz University of Hannover and received his Ph.D. at the Institute of Chemistry, Leibniz-Institute for Catalysis, University of Rostock. After an IBS Fellowship at the Centre for Self-Assembly and Complexity POSTECH, in 2014 he started his independent career and held a faculty position at the University of Nizwa. Since 2017, he has been associated with the IOC with AKBräse at KIT and has led the paracyclophane chemistry and synthetic materials team. His research interests include transition-metal catalysts and their applications in the synthesis and design of materials.



Stefan Bräse is a professor of chemistry (IOC) and Director of the Institute of Biological and Chemical Systems (IBCS-FMS) at the Karlsruhe Institute of Technology (KIT). He studied in Göttingen, Bangor (U.K.) and Marseille and received his Ph.D. in 1995. After postdoctoral appointments at Uppsala University and Scripps Research Institute, he began his independent research career at the RWTH Aachen in 1997. After habilitation in 2001, he moved to the University of Bonn as a professor of organic chemistry, and since 2003, he has been a professor at the Institute for Chemistry at the KIT. His research interests include asymmetric processes, combinatorial methods, the synthesis of natural products (on solid supports), and synthetic functional materials.

Manuel Tsotsalas leads a Helmholtz young investigator group, hosted at the Institute of Functional Interfaces (IFG) and the Institute of Organic Chemistry (IOC), and has been a PI of SFB 1176 “Molecularly Structuring of Soft Matter” at Karlsruhe Institute of Technology. He studied chemistry and obtained his Ph.D. at the University of Münster. After a postdoctoral stay at Kyoto University, he joined at the Institute of Functional Interfaces (IFG) at Karlsruhe Institute of Technology (KIT), where he received his habilitation in 2019. His research interests focus on the interfacial synthesis and hierarchical structuring of porous polymers and their application as novel nanomembranes and bioactive surface coatings.

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