## FOCUS REVIEW

# Network polymers derived from the integration of flexible organic polymers and rigid metal–organic frameworks

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Polymer gels, a representative state of network polymers, are a valuable and well-known class of materials with various functional and attractive properties and are thus commonly used in daily life. The properties of a polymer gel depend not only on the chemical structure of the network but also on the physical structure, including crosslinking points, polymer chains or network compositions, as demonstrated by recent studies on polymer gels with elaborate physical structures. By using a new type of porous crystal, a metal–organic framework (MOF) consisting of organic ligands and metal ions, as the key material, several research groups have developed a synthetic procedure for the formation of network polymers with highly controlled structures. This review focuses on the integration of MOFs and organic network polymers to form shaped network polymers or organic–inorganic hybrid networks through the following three methods: (1) polymerization of the organic ligands in a MOF using the guest molecules, (2) polymerization of homopolymerizable organic ligands in a MOF in the absence of guest molecules, and (3) formation of MOFs from polymeric organic ligands.

## INTRODUCTION

Polymer gels are widely known to be network polymers with a swollen three-dimensional (3D) network caused by osmosis of the solvent.[1,2] Owing to their attractive properties, such as their soft texture, volume phase transition, and high chemical stability, polymer gels have been used in many applications in our daily lives. Recently, polymer gels have been applied in more advanced functional materials, including actuators,[3–6] drug-delivery systems,[7–9] biomedical materials[10–12] and super absorbent polymers.[13–15]

To further develop the field of polymer gels, researchers have recently begun to focus their attention on designing the network structure to yield a polymer gel with a particular desired function. Several reports have demonstrated that designing the physical components of a polymer gel, such as the spatial placement of crosslinking points, the molecular weight between crosslinking points, or the branched structure, can markedly improve the properties of the gel. For example, a sliding ring gel consisting of crosslinked polyrotaxanes made up of α-cyclodextrins and poly(ethyleneglycol) can reduce stress through a topological network change involving sliding and movable crosslinking points, and results in a gel with high mechanical strength.[16,17] A double-network gel with two independent networks can also demonstrate high strength and toughness derived from the consumption of sacrificial bonds.[18,19] Nano-composite gels with inorganic clay at the crosslinking points are another example of gels with high mechanical strength.[20,21] Finally, graft gels with tethered

grafted side chains show rapid swelling–shrinking behavior.[22,23] These polymer gels with unique properties have often been referred to as 'smart gels', and highlight the importance of the network structure in polymer gels. One could imagine that the precise design of polymer gels on the macro to molecular scale could lead to exponential development in functionalized polymer gels, and thus in the field of polymer chemistry. However, such precise design of polymer gels is still highly challenging owing to the complexity and heterogeneity of conventional polymer synthesis, which produces irregular network structures depending on the random dispersion of the monomers or linear polymers.

The author and coworkers have focused on metal–organic frameworks (MOFs) as a novel molecular template for network polymer synthesis, because of the finely tuned molecular alignment derived from their crystalline nature. MOFs, or porous coordination polymers (PCPs), are microporous crystalline materials with an infinite periodic structure. This structure consists of metal ions coordinated to rigid organic ligands with two or more ligation sites that enable the formation of a robust 3D network structure.[24–27] The micropores in MOFs are usually stable, even under vacuum, owing to this robust network structure, and this enables the compound to adsorb gaseous guest molecules. Therefore, recent studies on MOFs have explored the molecular designs of the 3D network structures and their applications in areas such as catalysis,[28] storage,[29] separation[29,30] and sensors.[31] Integration of the crystallinity, porosity and structural variety of MOFs

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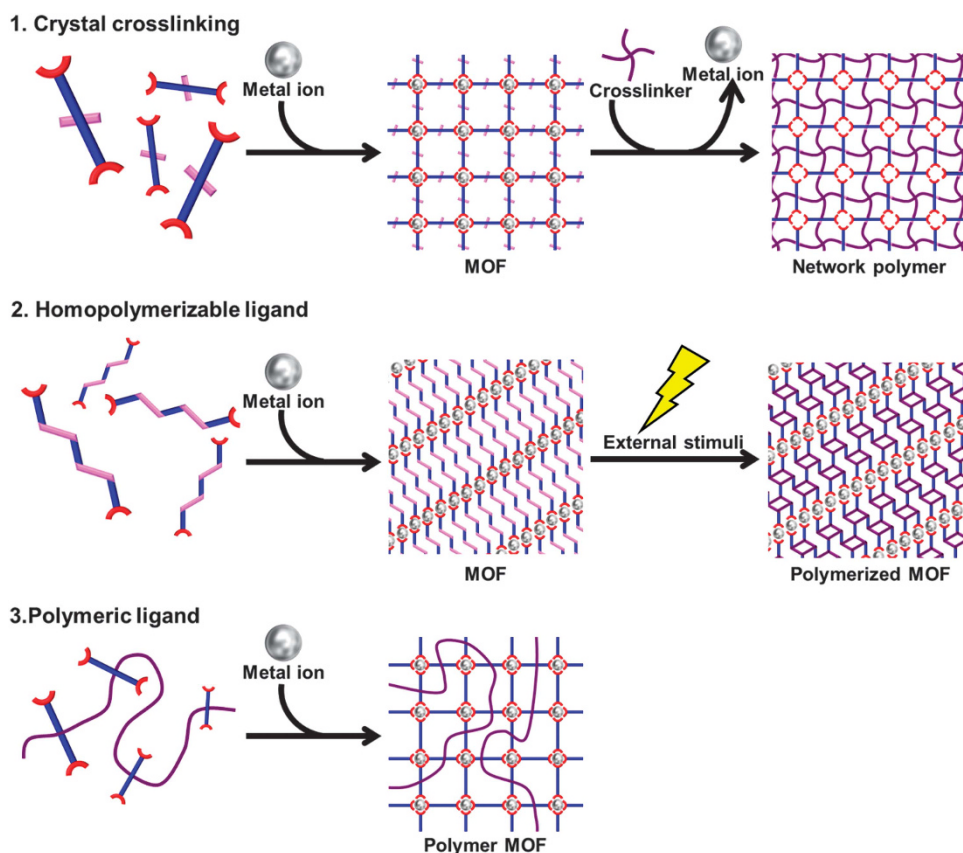E-mail: kokado@sci.hokudai.ac.jp

**Figure 1** Schematic image of the formation of network polymers from MOFs in three ways introduced in this review, (1) polymerization of the organic ligands in a MOF with the guest molecules, (2) polymerization of homopolymerizable organic ligands in a MOF in the absence of guest molecules and (3) formation of MOFs from polymeric organic ligands.

with organic network polymers is the first step toward the precise design of network polymers and polymer gels, while the molecular alignment of crystal has been never used for construction of organic network polymers. This focus review sheds light on recent developments in the integration of MOFs and organic network polymers to form shaped network polymers or organic–inorganic hybrid networks (Figure 1).

## POLYMERIZATION OF ORGANIC LIGANDS WITH THE GUEST MOLECULES IN A MOF

The author and coworkers discovered the bottom-up approach for the fabrication of polyhedral gel particles with well-defined edges and polygonal faces, known as the 'crystal crosslinking (CC) method',[32,33] by post-synthetic modification of MOFs (Figure 2a).[34,35] The crystalline nature of MOFs means that the organic ligands and metal nodes are regularly organized up to the centimeter scale. If the organic ligand is considered to be a monomer for polymerization, the monomer is highly organized and densely packed in the MOF crystal, which is in sharp contrast to conventional solution or bulk polymerization conditions. This environment thus makes it possible to prepare polymer gels with a precise network structure.

An azide-functionalized terphenyl dicarboxylic acid derivative (**1**, Figure 2b) was selected as the organic ligand for the platform MOF for the CC method.[35] A cubic crystal of **AzM** with sharp edges was obtained after heating $Zn(NO_3)_2 \cdot 6H_2O$ and **1** in N,N-diethyl formamide (DEF) at 80 °C for 3 days. This crystal showed an identical X-ray diffraction (XRD) pattern to that of IRMOF-15, which consists

of Zn(II) and terphenyl dicarboxylic acid.[27] Then, the azide group on the organic ligand was subjected to Cu(I)-catalyzed alkyne–azide cycloaddition (CuAAC), a typical click reaction,[36,37] with a tetra-alkynyl crosslinker (**3**, Figure 2b) to achieve the crosslinked MOF (**CLM**, Figure 2a). The progress of the reaction was followed by the disappearance of the stretching vibration peak of the azide group ($\nu_{N3}$, 2094 cm$^{-1}$) in the Fourier transform infrared (FT-IR) spectrum. Even after the crosslinking reaction, the XRD pattern remained identical to that of the original MOF, which means that the crosslinking reaction did not affect the crystallinity of the MOF at all. Hydrolysis of the **CLM** under acidic conditions provided a soft network polymer that retained its cubic shape but had a slightly expanded size; this was denoted a MOF-templated polymer (**MTP**, Figure 2a). The availability of the CC method was thus clarified, and XRD measurements showed that the crystallinity originating from the **AzM** or **CLM** was lost. A simultaneous click reaction of **1** and **3** during crystallization of the **AzM** produced only amorphous powder. The use of a dialkynyl reagent in place of **3** resulted in the dissolution of the **CLM** owing to the lack of crosslinking. The Zn(II) ion included in the tetrahedral secondary building unit (SBU) in the **AzM** was eliminated to the solution in the hydrolysis. The removal of the Zn(II) ions was confirmed by analysis of the solution using inductively coupled plasma atomic emission spectroscopy (ICP-AES), which showed that more than 90% of the original Zn(II) ions were present in the solution. The obtained cubic polymer gel, **MTP**, was swollen in aprotic polar solvents such as DMF, DEF and DMSO, and collapsed in water, acetonitrile, and low or nonpolar solvents such as acetone,
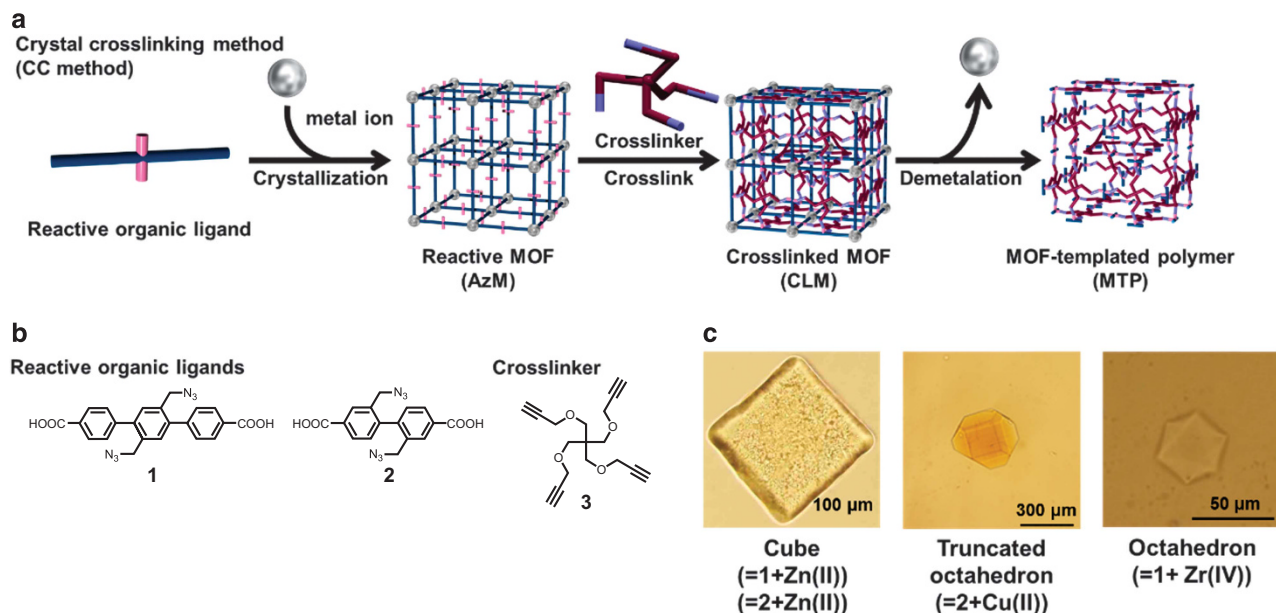
**Figure 2** (**a**) Schematic image of the crystal crosslinking (CC) method. (**b**) Chemical structures of reactive organic ligands (**1** and **2**) and a crosslinker (**3**). (**c**) Photographs of resulting MOF-templated polymers (**MTP**) from various combinations of organic ligands and metal ions. Adapted with permission from ref. 32. Copyright 2013 American Chemical Society.
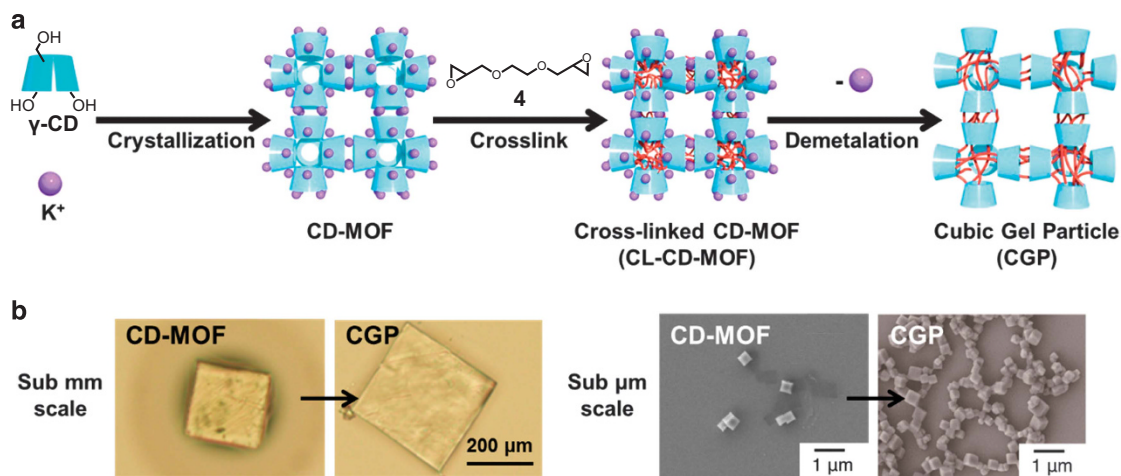


**Figure 3** (**a**) Schematic image for the CC method using CD-MOF to obtain a cubic gel particle (**CGP**). (**b**) Conversion of CD-MOF to the **CGP** on various size scales. Adapted with permission from ref. 33. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

dichloromethane, tetrahydrofuran, ethyl acetate, chloroform and toluene, because of the coexistence of hydrophilic carboxylic acid and hydrophobic terphenyl groups. The carboxylic acid group gave the **MTP** pH-dependent swelling behavior; it was swollen in basic conditions (pH > 10.5) and collapsed in acidic conditions (pH < 4.5). This behavior is similar to that of conventional poly (acrylic acid) gels and due to the dissociation of the carboxylic acid groups, which induces electrostatic repulsion and osmotic pressure, and leads to osmosis. FT-IR spectroscopy revealed that the **MTP** could entrap added metal ions such as Zn(II), Eu(III) or Cu(II) ions; however, once broken, the SBU and crystallinity were not regenerated, even on addition of Zn(II) ions. To demonstrate the generality of the CC method, the use of other MOFs with various shapes was also examined by changing the combination of metal ions (Zn(II), Cu(II), Zr(IV)) and organic ligands (**1** and **2**). The combination of Zn(II) and **2** provided a colorless cubic crystal,[27] Cu(II) and **2** provided a green

truncated octahedral crystal,[38] and Zr(IV) and **1** gave a colorless octahedral crystal.[39] XRD analysis indicated that these crystals had the same crystal structures as the corresponding MOFs without the incorporated azide groups. The three MOFs were also crosslinked in a CuAAC reaction with **3** and demetalated under acidic conditions. As expected, all crystals were successfully transformed into polymer gels with the same shape as the corresponding MOF, signifying that the CC method is widely applicable and independent of the shape of the MOF (Figure 2c).

In the CC method, a crystal is used as the template for a network polymer with a polyhedral shape; thus, the size of the final network polymer reflects the size of the original crystal. The size of a crystal usually depends on the preparation conditions, and can be varied from the nanometer to the centimeter scale. Even if a small-sized crystal is used in the CC method, the resulting network polymer should have a size that reflects the original crystal. To confirm this hypothesis,

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various sized MOF crystals were used in the CC method. **CD-MOF**, which consists of γ-cyclodextrin (γ-CD) and alkali metal ions,[40] was used as the template MOF for this experiment. In this MOF, the abundant hydroxyl groups on the saccharide can be regarded as reactive functional groups for crosslinking (Figure 3a). Ethylene glycol diglycidyl ether (**4**), which undergoes a facile ring-opening addition reaction with nucleophiles, was employed as the crosslinker. When **CD-MOF** was prepared by methanol vapor diffusion into an aqueous solution of γ-CD containing KOH, cubic crystals with sides of 50–500 μm were formed. Further addition of the poor solvent (methanol) or cetyltrimethylammonium bromide (CTAB), a crystallization retarder, to the supernatant resulted in the successful preparation of other cubic crystals with sizes of 10 μm (**CD-MOF-Micro1**), 1 μm (**CD-MOF-Micro2**) or 100 nm (**CD-MOF-Nano**) depending on the crystallization time. The crosslinking reaction of the γ-CD moieties in the different sized **CD-MOFs** was then performed by treatment with **4** in ethanol at 65 °C for 3 days to yield crosslinked **CD-MOFs** (**CL-CD-MOF**). Removal of the potassium ions by immersion of **CL-CD-MOF** in aqueous ethanol solution resulted in a cubic gel particle (**CGP**) with the same cubic shape as the original **CD-MOF** for all of the examined sizes (Figure 3b). XRD measurement showed that the crosslinking reaction did not affect the crystallinity of **CD-MOF**, but the crystallinity was completely lost after the demetalation reaction, analogous to the CuAAC case. This result clearly leads us to two conclusions: (1) the CC method functions irrelevant of the size of the original porous crystal and (2) addition reactions other than CuAAC are applicable in the CC method.

Wöll and coworkers have reported the use of the CC method for a MOF crystal grown on a gold substrate;[41] this MOF was denoted **SURMOF** (surface MOF, Figure 4a).[42] This group employed diazidostilbene dicarboxylic acid (**5**, Figure 4b) as the organic ligand and Cu(II) as the metal ion, and **SURMOF** was grown on a self-assembled monolayer (SAM)-coated gold substrate using 11-mercaptoundecanoic acid or 16-mercaptohexadecanoic acid. Tri(propionyloxymethyl)ethane (**6**) was added to this substrate to react without a catalyst. After the removal of Cu(II) using aqueous ethylenediaminetetraacetic acid (EDTA) solution, a thin gel film, denoted **SURGEL**, was obtained. The formation of **SURGEL** and **SURMOF** was confirmed by XRD measurements and FT-IR spectroscopy. **SURGEL** was amorphous and therefore had no XRD pattern, but a peak shift was observed in the FT-IR spectrum. Patterning of the resulting **SURGEL** was also possible if a patterned SAM substrate was used (Figure 4c). Because the obtained **SURGEL** showed high stability, even under physiological conditions, it could be used as a cell culture substratum. The ingestion of arabinose by bacteria was illustrated in a cell culture using **SURGEL** containing arabinose, and thus the possibility of using **SURGEL** for the specific manipulation of the adhered cell in substrate biotransformations or biomedical applications has been suggested.

The same group subsequently reported the introduction of an electrochemical probe into **SURGEL** with the aim of investigating the inside of the gel film.[43] 6-(Ferrocenyl)-hexanethiol was selected as the electrochemical probe, and it was attached to the excess azide groups in a thiol–yne reaction mediated by 254 nm UV irradiation under argon. The reaction progress was followed by FT-IR and X-ray photoelectron spectroscopy. The ferrocene-modified **SURGEL** showed redox behavior in cyclic voltammetry (CV), with the oxidation peak at 0.12 V and reduction peak at 0.07 V versus a Pt electrode; the separation between the peaks was thus only 45 mV. The current density was also smaller than expected, meaning that only the ferrocene moieties close to the SAM–**SURGEL** interface were involved

in the redox process. This behavior contrasts with that of a SAM of ferrocene thiols, which exhibited no separation of the redox peaks owing to the well-defined positions of the electroactive groups. The redox behavior of the ferrocene-modified **SURGEL** is therefore attributed to the noncrystalline and flexible nature of the gel film and the high mobility of the covalently attached ferrocenyl groups. Surprisingly, addition of bare ferrocene molecules to the external solution of ferrocene-modified **SURGEL** caused the redox peaks to shift to 0.18 V (ox) and 0.104 V (red) with 76 mV separation, which is close to the theoretical value for a Nernstian diffusion-limited process. The relationship between the current density and scan rate showed that the diffusion of charge in **SURGEL** governed the redox process, meaning that the film was permeable to the ferrocene guest molecules and that charge hopping involving the immobilized ferrocenyl groups occurred.

The concept was then extended to cover the surface of micro- or nanometer-sized magnetite particles with a crosslinkable MOF (**magMOF**).[44] The compound **1** was used as the crosslinkable organic ligand and Cu(II) as the metal ion, and the MOF was grown by repeated immersion of the COOH-terminated magnetic particles in solutions of the organic ligand and metal ions. A multi-shell structure could also be constructed by changing the organic ligand to one without crosslinking ability (terphenyl dicarboxylic acid). The obtained multi-shell structure could be observed when the azide group was modified with red or blue dyes possessing an alkynyl group. After formation of the MOF, the crosslinking reaction was carried out with **6**, and the reaction progress was followed by the decrease in the intensity of the azide stretching band in the FT-IR spectrum. Treatment with chelating EDTA solution readily extracted terphenyl dicarboxylic acid and the Cu(II) ions, yielding **SURGEL** on the magnetic particle (**magGEL**). Increasing the number of immersion cycles increased the shell thickness of the gel layer; this was observed in transmission electron microscopy (TEM) images. Post-synthetic modification with dye molecules was also possible using strain-promoted azide–alkyne cycloaddition (SPAAC) of cyclooctyne derivatives.[45,46] The unreacted dye molecules included in the gel could be released by increasing the pH, and the release was completed after 120 min.

Using addition polymerization, Uemura, Kitagawa and coworkers have reported a method to connect organic ligands in a MOF with each other.[47] They used terephthalic acid, divinyl terephthalic acid (1–20 mol% with respect to terephthalic acid), and 1,4-diazabicyclooctane as the organic ligands and Cu(II) as the metal ion. In this system, divinyl terephthalic acid acted as a polymerizable organic ligand after adsorption of polymerizable guest molecules such as styrene or methyl methacrylate in the micropores of the MOF. Heating at 70 °C under nitrogen atmosphere initiated the addition polymerization. Extraction of the metal ions using aqueous EDTA solution produced a cubic polymer particle derived from the original MOF; this was revealed by scanning electron microscopy (SEM) observation. XRD measurements of the obtained polymer particle remarkably contained a sharp reflection at $2\theta = 18.0°$, which indicated that the molecular orientation derived from the crystal structure of the original MOF was retained even after removal of the MOF skeleton. High resolution TEM (HRTEM) directly demonstrated the 4.9 Å interplanar *d*-spacing between the polymer chains. This high-order molecular orientation resulted in the high stability of the polymer particle on thermal or solvent treatment, and this method can thus be expected to be suitable for the development of plastic materials with high mechanical strength.
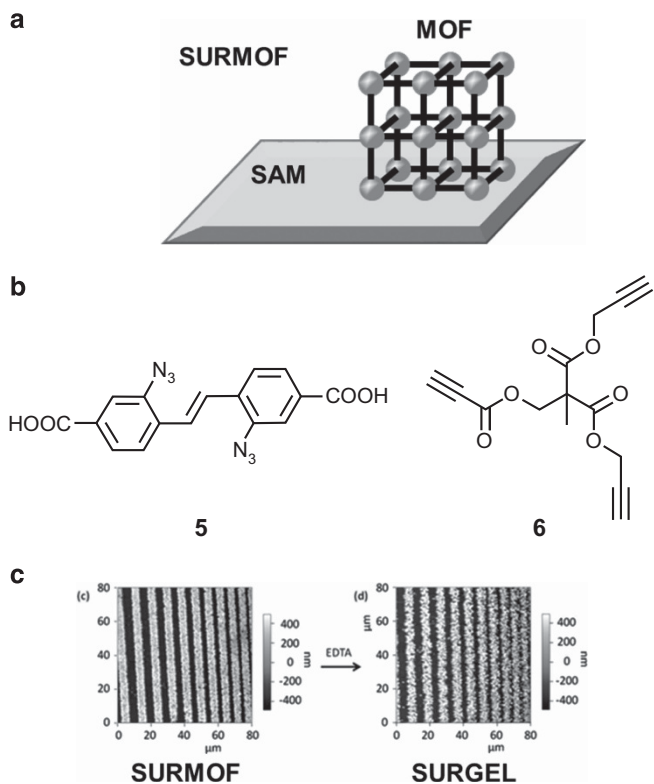
**Figure 4** (**a**) Schematic representation of a surface MOF (**SURMOF**). (**b**) Chemical structures of the ligand **5** and the crosslinker **6** used to form the thin gel film **SURGEL**. (**c**) AFM observation of **SURMOF** and **SURGEL** grown on a patterned self-assembled monolayer (SAM) substrate. Adapted with permission from ref. 41. Copyright 2014 American Chemical Society. A full color version of this figure is available at the *Polymer Journal* journal online.

## POLYMERIZATION OF MOFS CONTAINING POLYMERIZABLE ORGANIC LIGANDS IN THE ABSENCE OF GUEST MOLECULES

Zaworotko, Vittal, and coworkers have reported the only example of the transformation of a MOF to a network polymer and a network polymer to a MOF without using any guest monomers.[48] They used **7** and **8** as the organic ligands and Zn(II) as the metal ion, and synthesized a MOF with six-fold interpenetration (Figure 5a). In the MOF, two molecules of each ligand (**7** and **8**) are coordinated to each Zn(II) ion, and the coordination network has a diamondoid topology (Figure 5b). The single crystal structure showed that **7** is slip-stacked and the distance between adjacent C=C bonds is 3.68 Å. The yellow single crystal was irradiated for 2 h with 365 nm light from a xenon lamp to yield a pale yellow crystal. X-ray crystallographic analysis revealed the quantitative [2+2] cyclization reaction between the C=C bonds in adjacent **7** ligands to form a linear polymer (**9**). This MOF can thus form two network structures, that of a MOF and that of an organic polymer, without the addition of guest crosslinkers (Figure 5c). Moreover, the organic polymer chain could be reversibly decomposed by thermal treatment at 250 °C for 3 h through retrocyclization of the cyclobutane ring. This was confirmed by XRD measurement (Figure 5d). The insoluble pale yellow crystal obtained after light irradiation was transformed into a soluble brown crystal after heat treatment, and the ^{1}H NMR spectrum after digestion of the brown crystal also confirmed the regeneration of the cyclobutane ring. The infinite slip-stacked structure of organic ligands that can undergo cycloaddition with each other was the key to success in this case; this structure resulted

from the particular characteristics of MOFs, which allow the incorporation of various components in a highly ordered alignment.

The above polymerization occurred in an isotactic manner. In contrast, Vittal and coworkers[49] recently presented the syndiotactic formation of **9** from the same homopolymerizable ligand (**7**) by changing the carboxylate ligand to 4,4-oxybis(benzoic acid) but keeping the metal ion the same (Zn(II)). The MOF crystal showed a three-fold interpenetrated structure. By varying the included solvents, the conformation of **7** was readily shifted, and the polymerization was carried out by UV irradiation. Before the UV irradiation, the distance between the C=C double bond in two adjacent **7** ligands was around 4.7 Å and the conformation was *trans,trans,trans*. This conformation should lead to isotactic polymerization, which means that a pedal motion to form the *trans,cis,trans* conformation took place upon UV irradiation.

## FORMATION OF MOFS FROM POLYMERIC ORGANIC LIGANDS

The preparation of MOFs from polymeric ligands is an important topic in this field. Cohen and coworkers have extensively investigated the construction of hybrid networks of MOFs and organic polymers using multiple covalently linked organic ligands.[50–53] In their first report, they prepared MOFs from telechelic organic ligands synthesized from aminoterephthalic acid and alkyl dicarboxylic acids and Zn(II) ions.[50] A crystalline powder was obtained using all the organic ligands, and the XRD patterns were identical to that of the parent MOF, which contains a free aniline group.[27] Although the exact structure of the alkyl chains in the MOF was not determined from the XRD study, elemental analysis and nitrogen adsorption measurements indicated that the two terephthalic acid groups at the chain ends coordinated to Zn(II) and there were no or very few dangling chains. Interestingly, the sample obtained from adipic acid ($n = 4$) exhibited a variable specific surface area depending on the temperature of the heat treatment used to prepare the MOF; the sample treated at higher temperature (150 °C) had a 10% larger specific surface area than that treated at lower temperature (105 °C).

The same group synthesized a polymeric organic ligand with terephthalic acid groups not only at the chain ends but also in the middle of the chain. To do this, they condensed hydroxyterephthalic acid with α,α′-dibromoxylene or dibromoalkane. The MOFs formed from these ligands had identical XRD patterns to that of the parent MOF.[27] All of the obtained MOFs showed an increase in the specific surface area of up to three times after heat treatment at high temperatures.[51]

A further increase in the number of terephthalic acid groups in the organic ligand was recently reported by the same group.[52] The organic ligand was synthesized by polycondensation of dibromoalkanes and 1,4-dihydroxyterephthalic acid (see also Figure 6a), and the number average molecular weight was found to be 10–20 kDa by size-exclusion chromatography (SEC). Surprisingly, and except for the ligand prepared from dibromohexane, crystalline powders were obtained by simply mixing the ligands with Zn(II) at 100 °C. These were denoted polymer MOFs (polyMOFs). The XRD patterns were identical to that of the parent MOF.[27] SEM observation revealed the production of spherical particles with a size of several microns that were aggregates of submicron cubic particles. NMR and SEC measurements after digestion of the particles with acid suggested the presence of the original polymeric ligand, which means that the crystalline powder contained the polymeric ligand, not a low molecular weight fraction. The polyMOF exhibited excellent film-forming properties, and the sample prepared at 80 °C formed a crystalline film with a thickness of 20 µm. The contact angle of the film increased to 102° on increasing
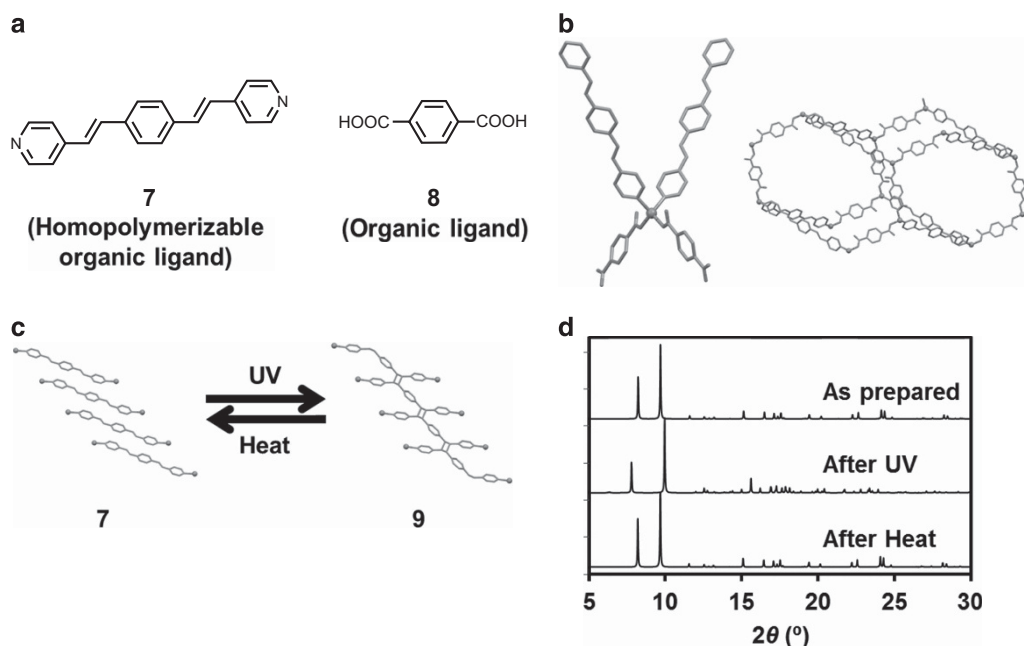
Figure 5 (a) Chemical structures of organic ligands **7** and **8**. (b) Crystal structure of the MOF formed from these ligands and Zn(II). (c) Crystal transformation on UV irradiation and heat treatment. (d) XRD patterns at each stage. A full color version of this figure is available at the *Polymer Journal* journal online.

the alkyl chain length; this improved the durability of the polyMOF toward ambient atmosphere or water treatment. Additionally, the incorporation of alkyl chains improved the selectivity of the MOF for carbon dioxide ($N_2$: $856\ cm^3\ g^{-1}$, $CO_2$: $41\ cm^3\ g^{-1}$) compared with that of the parent MOF ($N_2$: $2963\ cm^3\ g^{-1}$, $CO_2$: $30\ cm^3\ g^{-1}$).

Carbon dioxide selectivity was further improved by using nitrogen-containing pillar co-ligands, such as **11**, 4,4′-bipyridine (**12**) or 1,2-(4′,4″-bipyridyl)ethane (**13**) (Figure 6a).[53] **10** ($x = 5-12$) was employed as the polymeric ligand. Mixing these ligands with Zn(II) ions provided crystalline powders that exhibited identical XRD patterns to the parent MOF (Figure 6b).[54,55] The MOF obtained from **10** and **12** showed a type II $N_2$ adsorption isotherm, which is indicative of nonporous or macroporous absorbents, and the MOF obtained from **10** and **13** showed no detectable adsorption. However both MOFs showed high performance in the adsorption of $CO_2$, with adsorptions of 97 and $140\ cm^3\ g^{-1}$ for the MOF from **10** and **12** and the MOF from **10** and **13**, respectively (Figure 6c). The selective adsorption of these polyMOFs is attributed to a kinetic sieving effect, in which small windows in the structure restrain the diffusion of the larger $N_2$ molecules (3.64 Å), whereas the smaller $CO_2$ molecules (3.30 Å) can penetrate into the micropores.[55] Even after water treatment, these polyMOFs exhibited high $CO_2$ adsorption, which would be an advantage for their practical usage.

Very recently, the transformation of a 1D coordination polymer into a MOF was reported by Choi *et al.*[56] An organic ligand derived from terephthalic acid with a (4-nitrophenyl)pyrrolidine side chain (**NPP**) with a high dipole moment (7D) was used in this study. Mixing the ligand with Zn(II) in DMF at 100 °C for 120 h provided 1D coordination polymer **ZnNPP(A)** in solution, precipitation with methanol then gave **ZnNPP(B)** by removal of solvated DMF owing to the strong dipole–dipole interaction between the **NPP** side chains and the dipole–static charge interaction between **NPP** and the SBU. When **ZnNPP(B)** powder was kept under ambient atmosphere it was transformed into porous solid **ZnNPP(C)** by removal of coordinated DMF, and additional heat treatment at 120 °C for 12 h provided

MOF-like 3D coordination polymer **ZnNPP(D)**. XRD measurement showed the appearance of new peaks on transformation from **ZnNPP(B)** to **ZnNPP(C)** and **ZnNPP(D)**, which were derived from the structure of MOF-5.[26] SEM observation indicated aggregated sub-micron cubic particles of **ZnNPP(D)**, which is consistent with the XRD measurement. The 1D coordination polymer **ZnNPP(A)** exhibited good film-forming properties in DMF solution, and the film showed a sharp XRD pattern.

## MOF-TEMPLATED SYNTHESIS OF POLYMER PARTICLES AND LINEAR POLYMERS

Even though not a network polymer from organic polymer and MOF, preparation of polymer particle by using non-functionalized MOF as a structure directing agent has been reported by several research groups. Uemura, Kitagawa and coworkers reported the production of 2D polypyrrole sheet-stacking particle, oxidatively polymerized by Fe(III) ion included in 2D coordination sheet.[57] They also reported the synthesis of 3D polypyrrole particle in a MOF with 3D nanochannel, which was polymerized in an oxygen atmosphere and gave a replicated structure reflecting the shape of original MOF.[58] Zhang and colleague[59] subsequently reported the preparation of 1D polypyrrole particle polymerized in MOF with 1D nanochannel. For other organic polymers, poly(vinylcarbazole) particle was synthesized by Uemura *et al.*,[60] providing an excellent photoconductivity derived from the face-to-face stacking of carbazole moiety. The same group likewise investigated the preparation of polystyrene particle polymerized in MOF with 1D nanochannel, and the shape of obtained particle was controllable by that of the original MOF.[61]

In linear polymer synthesis in nanochannel of MOF, the primary structure, such as molecular weight or monomer sequence, is also controllable, as ascertained by Uemura, Kitagawa and coworkers. For examples, a radical polymerization of styrene in MOF nanochannel resulted in a production of polystyrene with lower molecular weight distribution compared with free radical polymerization.[62] When a divinylbenzene was polymerized in 1D channel of MOF, only one
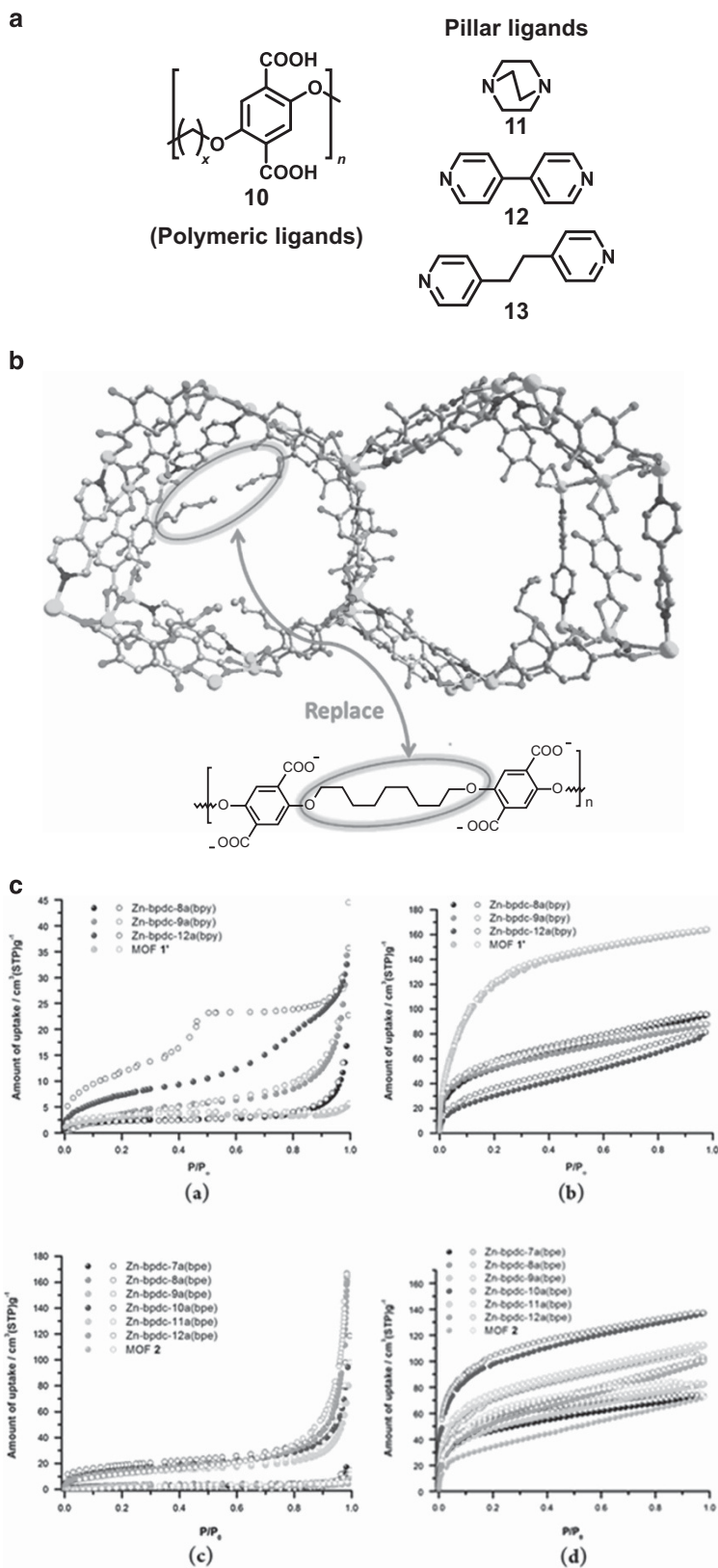
**a**

COOH

[structure of polymeric ligand 10]

**10**

**(Polymeric ligands)**

**Pillar ligands**

**11**

**12**

**13**

**b**



Replace

**c**



**Figure 6** (**a**) Chemical structures of **10** ($x = 5–12$) and pillar ligands **11**, **12** and **13**. (**b**) Crystal structure of the parent MOF from **10** and **12**. (**c**) $N_2$ (left) and $CO_2$ (right) adsorption isotherms of MOF from **10** and **12** (top), and from **10** and **13** (bottom). Adapted with permission from ref. 53. Copyright 2016 American Chemical Society. A full color version of this figure is available at the *Polymer Journal* journal online.

vinyl group was consumed in the radical polymerization, and a linear poly(vinylstyrene) was obtained.[63] By using an unsaturated metal site in MOF for monomer fixation, the control of monomer proportion was achieved, thus it was also tuned by changing the polymerization temperature.[64] Even a monomer with low rate constant for propagation ($k_p$), such as 2,3-dimethyl-1,3-butadiene, could be polymerizable in 1D nanochannel of MOF by avoiding unfavorable termination reaction.[65] In the case of a saccharide monomer, less branched polyglucose was produced as a result of ring-opening polymerization in 1D nanochannel of MOF.[66] These features of polymerization in MOF micropore can be regarded as a kind of polymerization in a confined space, as overviewed by Miyata and Sada, in which the relationship between the size of monomer and the reaction space governs the structure of obtained polymers.[67,68]

## CONCLUSION

This review article summarizes three approaches for the hybridization of flexible organic polymers and rigid MOFs. The first approach, the CC method, gives network polymers with controlled shapes and could be used to form uniform gel films. Although the network structure is still amorphous and lacking in structure, the wide range of applicable crosslinkers is highly advantageous, and allows the selection of crosslinkers with the proper size for adsorption in the micropores of the MOF. The second approach involves a reversible single-crystal-to-single-crystal phase transition from a MOF to a hybrid network polymer and *vice versa*. The network polymer resulting from this approach has the highest molecular orientation among the three approaches introduced in this review, but presents difficulties in molecular design and finding suitable MOFs. Finally, surprising crystallization behavior was observed in the third approach, which employs polymeric organic ligands for MOF fabrication. These examples clearly indicate the unanticipated proximity of the network polymer field to that of MOFs. Even though the intrinsic problem of crystals for scalability should be solved through quantity synthesis or use of a substrate, these techniques will thus enable the as-yet unexplored precise structural control of network polymers on the molecular to macroscale in the immediate future, which would lead to a unique electronic or mechanical characteristics.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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