

Transformation of Metal–Organic Framework to Polymer Gel by Cross-Linking the Organic Ligands Preorganized in Metal–Organic Framework

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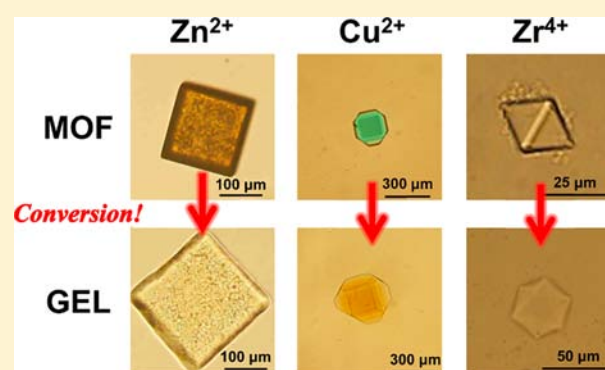
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Supporting Information

ABSTRACT: Until now, seamless fusion of metal–organic frameworks (MOFs) and covalently cross-linked polymer gels (PG) at molecular level has been extremely rare, since these two matters have been regarded as opposite, that is, hard versus soft. In this report, we demonstrate transformation of cubic MOF crystals to PG via inner cross-linking of the organic linkers in the void space of MOF, followed by decomposition of the metal coordination. The obtained PG behaved as a polyelectrolyte gel, indicating the high content of ionic groups inside. Metal ions were well adsorbed in the PG due to its densely packed carboxylate groups. A chimera-type hybrid material consisting of MOF and PG was obtained by partial hydrolysis of resulting cross-linked MOF. The shape of resulting PG network well reflected the crystal structure of MOF employed as a template. Our results will connect the two different network materials that have been ever studied in the two different fields to provide new soft and hard hybrid materials, and the unique copolymerization in the large void space of the MOF will open a new horizon toward “ideal network polymers” never prepared before now.



INTRODUCTION

Metal organic frameworks or porous coordination polymers are nanoporous crystalline materials constructed by metal ions and rigid organic linkers equipped with two or more ligation sites to form robust 3D network structures in the crystalline state. Their nanopores are stable in vacuum due to their robust 3D network structures, which enabled them to adsorb gaseous guest molecules. Recent extensive studies have been focused on molecular designs of the 3D network structures and their applications such as catalysis, storage, separation, and nanomaterials.^{1–9} On the other hand, polymer gels (PGs) are soft and wet materials prepared by covalently cross-linking of linear flexible polymers to form elastic 3D network structures. They are essentially insoluble in any media, and permeation of solvent molecules into the void between the network structures induces deformations of the 3D network structures, i.e., swelling or collapsing of PGs. The large deformation induced by the external stimuli is a key property to provide smart materials, and a number of studies have explored their applications in such as actuators,^{10–12} drug delivery systems^{13–15} and superabsorbent polymers.^{16,17} Recently, soft and wet interfaces of PGs have been found to show adhesion of PGs by supramolecular interactions.^{18–20}

However, seamless fusion of both three-dimension network structures at molecular level has been extremely rare, since these two matters have been regarded as opposite, i.e., hard vs soft. Although these two materials have the analogous network structures, they never overlap with each other, because they have been studied in the different fields, PG in polymer and material chemistry and metal–organic frameworks (MOFs) in inorganic and supramolecular chemistry. Most recently, we accomplished preparation of cubic gel particle by the transformation of cyclodextrin MOF (CD-MOF) to PG via cross-linking of CD by bifunctional epoxide to preserve the cubic shape.²¹ However, its applicability to other type of porous MOF crystal is still limited. Herein, we report the transformation of the rigid coordination networks of various MOF crystals to the flexible organic one of PG by internal cross-linking of the organic linkers via click reaction, followed by decomposition of the coordination network. Moreover, partial and directional decomposition provided the first example chimera-type hybrid materials of MOF and PG.

Our molecular design for conversion of the MOF to PG relies on the large reaction space of the 3D channels in MOF

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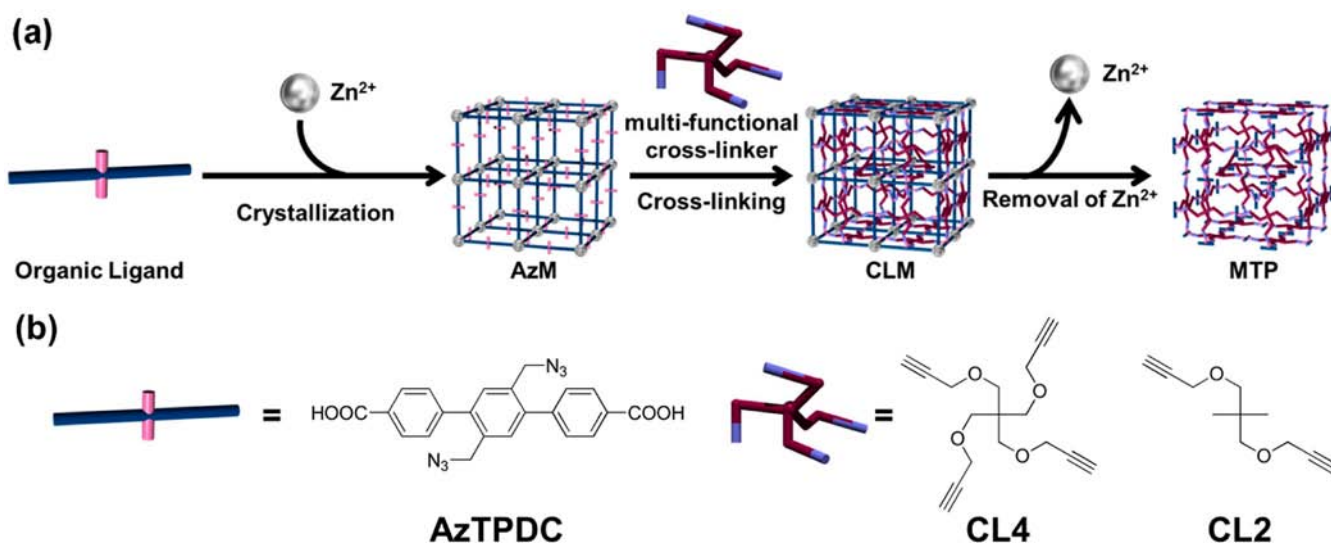


Figure 1. (a) Schematic illustration of cross-linking of the organic linkers in MOF (AzM) and subsequent decomposition to obtain polymer gel (PG). (b) Molecular structures of the organic ligand (AzTPDC) and the cross-linkers.

and postsynthetic reaction of MOF as shown in Figure 1. We previously reported preparation of the azide-tagged MOF (AzM) by introduction of two azide groups in the organic linker (AzTPDC) and in situ click reaction to various acetylenes as the guest substrates in the presence of Cu^+ , which provided the modification of MOF crystals directly without decomposition of the crystal structures.²² This prompted us to investigate cross-linking of the “clickable” organic linkers by in situ click reaction with multifunctional acetylene compounds in the nanopores of AzM after decomposition of the coordination network. Benzoic acid-type ligand such as AzTPDC is also known to possess coordination ability to various metal ions, indicative of a wide applicability to MOFs with diverse crystal systems, thus resulting PGs with diverse shapes.

EXPERIMENTAL SECTION

Materials and Instrumentation. Synthetic experiments for CL4 and CL2 were carried out under nitrogen atmosphere. All solvents and inorganic reagents were purchased from some commercial suppliers and were used without further purification. All experiments were carried out under ambient atmosphere. AzTPDC,²² AzBPDC,²³ and CL4²⁴ were synthesized according to the reported procedure.²⁴ ^1H NMR spectra were measured on a JEOL JNM-AL300 apparatus at 300 MHz. TMS (0.05%) is used as an internal standard at room temperature. FT ATR-IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Powder X-ray diffraction (XRD) patterns were obtained by RIGAKU Smart-Lab Diffractometer with $\text{Cu K}\alpha$ radiation source (40 kV, 30 mA). Thermogravimetric analysis were performed using a SEIKO instruments SSC/5200 TG/DTA 220 under 99.999% pure nitrogen (300 mL/min) gas stream, employing a heating rate of 5 $^\circ\text{C}/\text{min}$ from 30 to 500 $^\circ\text{C}$. Scanning electron microscope (SEM) images were acquired by using a JEOL JSM-7400F. Optical micrographs were recorded on an OLYMPUS BX51 microscope system. X-ray photoelectron spectroscopy was conducted with a JEOL JPS-9200 apparatus. ICP-AES analysis was carried out by a SHIMADZU ICPE-9000 instrument. SEM observation, XPS measurement, and ICP-AES analysis were conducted at the OPEN FACILITY, Hokkaido University Sousei Hall.

Preparation of AzM.²² AzTPDC (28 mg, 0.065 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (57 mg, 0.19 mmol) were dissolved in 5 mL of *N,N*-diethylformamide (DEF) in a screw top vial. The vial was kept

standing at 80 $^\circ\text{C}$ for 3 days. The solution was decanted, and yellow cubic crystals were repeatedly washed with DEF.

Preparation of CLM. AzM was immersed in 5 mL of 0.1 M CL4 solution (DEF) in a screw top vial, and 250 μL of saturated CuBr solution (DEF) was added to the mixture. The vial was kept standing at 80 $^\circ\text{C}$ for 1 week. The supernatant was decanted, and brown cubic crystals were repeatedly washed with DEF.

Preparation of MTP. CLM was immersed in a mixed solvent of concd HCl/DEF (1:5, v/v) in a screw top vial. The vial was kept standing at room temperature for 3 h. The supernatant was decanted, and brown cubic crystals were repeatedly washed with DEF.

Preparation of AzM-BP.²³ AzBPDC (26 mg, 0.074 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (57 mg, 0.19 mmol) were dissolved in 5 mL of DEF in a screw top vial. The vial was kept standing at 80 $^\circ\text{C}$ for 5 days. The solution was decanted, and yellow cubic crystals were repeatedly washed with DEF.

Preparation of CLM-BP. AzM-BP was immersed in 5 mL of 0.1 M CL4 solution (DEF) in a screw top vial, and 250 μL of saturated CuBr solution (DEF) was added to the mixture. The vial was kept standing at 80 $^\circ\text{C}$ for 2 weeks. The supernatant was decanted, and brown cubic crystals were repeatedly washed with DEF.

Preparation of MTP-BP. CLM-BP was immersed in a mixed solvent of concd HCl/DEF (1:5, v/v) in a screw top vial. The vial was kept standing at room temperature for 3 h. The supernatant was decanted, and brown cubic crystals were repeatedly washed with DEF.

Preparation of AzKUMOF. AzBPDC (25 mg, 0.071 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (25 mg, 0.10 mmol) were dissolved in 5 mL of DEF in a screw top vial, and 0.1 mL DMSO was added to the solution. The vial was kept standing at 80 $^\circ\text{C}$ for 3 days. The solution was decanted, and green truncated octahedral crystals were repeatedly washed with DEF.

Preparation of CLKUMOF. AzKUMOF was immersed in 5 mL of 0.1 M CL4 solution (DEF) in a screw top vial, and 250 μL of saturated CuBr solution (DEF) was added to the mixture. The vial was kept standing at 80 $^\circ\text{C}$ for 5 days. The supernatant was decanted, and moss green truncated octahedral crystals were repeatedly washed with DEF.

Preparation of KUMTP. CLKUMOF was immersed in a mixed solvent of concd HCl/DEF (1:5, v/v) in a screw top vial. The vial was kept standing at room temperature for 3 h. The supernatant was decanted, and brown cubic crystals were repeatedly washed with DEF.

Preparation of AzUiOMOF. ZrCl_4 (12 mg, 0.054 mmol) and benzoic acid (190 mg, 1.6 mmol) were dissolved in 2 mL of DMF in an autoclave. To that solution was added AzTPDC (22 mg, 0.065 mmol), and the sealed autoclave was kept standing at 120 $^\circ\text{C}$ for 24 h.

The solution was centrifuged (2000 rpm, 3 min), and the collected colorless crystals were repeatedly washed with DEF.

Preparation of CLUiOMOF. AzUiOMOF was immersed in 5 mL of 0.1 M CL4 solution (DEF) in a screw top vial, and 250 μL of saturated CuBr solution (DEF) was added to the mixture. The vial was kept standing at 80 $^{\circ}\text{C}$ for 5 days. The supernatant was decanted, and colorless crystals were repeatedly washed with DEF.

Preparation of UiOMTP. CLUiOMOF was immersed in a mixed solvent of concd HCl/DEF (1:5, v/v) in a screw top vial. The vial was kept standing at room temperature for 3 h. The supernatant was decanted, and colorless crystals were repeatedly washed with DEF.

RESULTS AND DISCUSSION

AzM was prepared by the reported procedure,²² and afforded AzM was subjected to reaction with tetra-acetylene cross-linker (CL4) under the standard click reaction conditions at 80 $^{\circ}\text{C}$ in the presence of Cu^+ as a catalyst in DEF. After incubation for 1 week and washing by soaking in fresh DEF repeatedly, the product crystals were collected and dried on a filter paper to obtain a cross-linked MOF (CLM). Subsequently, the coordination of carboxylate anion to zinc(II) ion was decomposed by acidification with concd HCl in DEF (1/5, v/v), providing a MOF-templated polymer (MTP). Under microscopy observation, the MOFs gradually expanded their sizes, and the interface recognized by different contrast moved from the edge to the center of cubic MOF crystals due to penetration of external acid solution (Figure 2). In less than 10

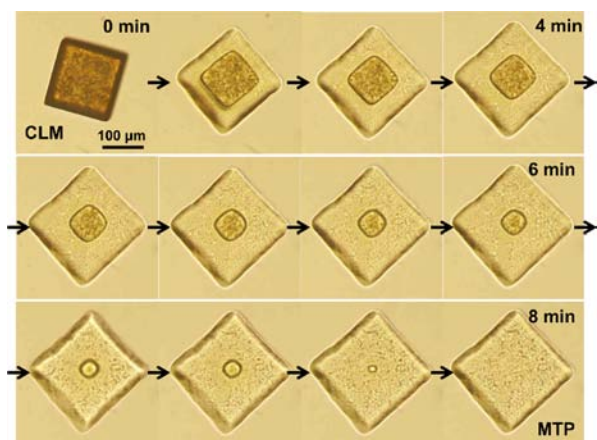


Figure 2. Optical microscopy images following the conversion of CLM to MTP upon acidification.

min, the cubic crystals of CLM with 300–500 μm in length became cubic gels. The cracks or scratches on the crystal surfaces were preserved on the gel surface even after the hydrolysis reaction. Decomposition of metal coordination network under other conditions such as 0.1 M HCl(aq), 1 M NaOH(aq), acetic acid, and pyridine also gave rise to similar phenomena. Under these conditions, AzM crystals before cross-linking were easily dissolved within a few minutes. Furthermore, AzM treated with diyne compound (CL2) instead of CL4 also rapidly dissolved in the same condition as shown in Figure S1. As a control experiment, we performed a simultaneous click reaction during the crystallization process of AzM, providing only amorphous powdery product (Figure S2). This result clearly indicates the importance of postsynthetic modification after formation of MOF crystal.

To obtain additional visual evidence, we observed AzM, CLM, and MTP using an optical microscope (OM) and a

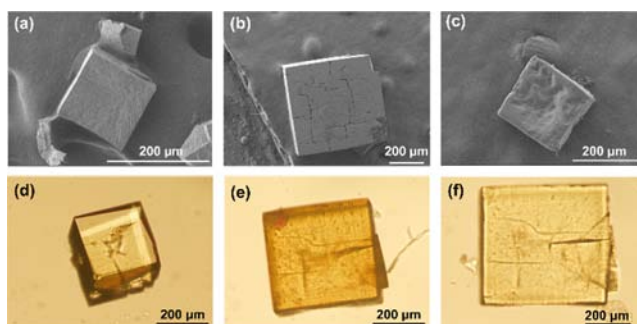


Figure 3. SEM images of (a) AzM, (b) CLM, and (c) MTP. Optical microscope images of (d) AzM, (e) CLM, and (f) MTP.

scanning electron microscope (SEM) as shown in Figure 3. The SEM observation of AzM and CLM revealed the smooth square surfaces of the CLM and AzM crystals (Figure 3a,b), and OM observation showed the preservation of the transparent cubic crystals with the sharp edges (Figure 3d,e). After decomposition of metal coordination network, MTP possesses rougher cubic shapes (Figure 3c,f) derived from MOF crystalline nature, while it contains no metal coordination network. These observations indicated that the cubic shape was retained after cross-linking reaction and decomposition of metal coordination.

We further characterized CLM and MTP by FT-IR, XRD, XPS, ICP-AES, and TGA after washing with DMF and dichloromethane repeatedly followed by drying in vacuo. The reaction process was monitored by FT-IR spectra as shown in Figure 4a. The disappearance of azide stretching band at 2094 cm^{-1} was observed upon the transformation of AzM to CLM. Judging from this IR spectral change, all azide groups on the organic linkers in the MOF crystals were consumed by the reaction with the acetylene moieties of the cross-linker. Other IR bands did not change, and in particular, the C=O symmetric vibration band (1397 cm^{-1}), assigned to carboxylate anion, remained unchanged after the click reaction, indicating that no changes occurred in the coordination bonds between zinc ions and the carboxylate anions of the linkers. After acidification to obtain MTP, the carbonyl symmetric vibration band for metal carboxylate at ca. 1397 cm^{-1} completely disappeared and a new band at 1704 cm^{-1} assigned as that of carboxylic acid appeared, indicating the transformation of the functional group on the organic ligands from carboxylate anion to carboxylic acid (Figure 4a). XPS analysis clearly illustrated the absence of the peaks assigned to Zn^{2+} (Figure S3), indicating complete removal of Zn^{2+} from the MOF crystals by the acidification. Additionally, ICP-AES analysis of the acidic decomposition solution indicated that more than 90% of Zn^{2+} ion was recovered in the solution.

To evaluate the crystallinity of CLM and MTP, we examined XRD. As shown in Figure 4b, XRD patterns of the crystals before (AzM) and after (CLM) the click reaction showed identical peaks. Therefore, cross-linking by the click reaction did not affect the MOF network structure. On the other hand, no apparent diffraction peaks were observed after decomposition. This result clearly indicated that MTP had no crystallinity. MTP was practically insoluble in any solvents; however, imperfection of the cross-linking did not provide crystalline organic network polymer such as COF.^{25,26}

To evaluate the network structure with void space of the resulting CLM and MTP, we characterized them by TGA as

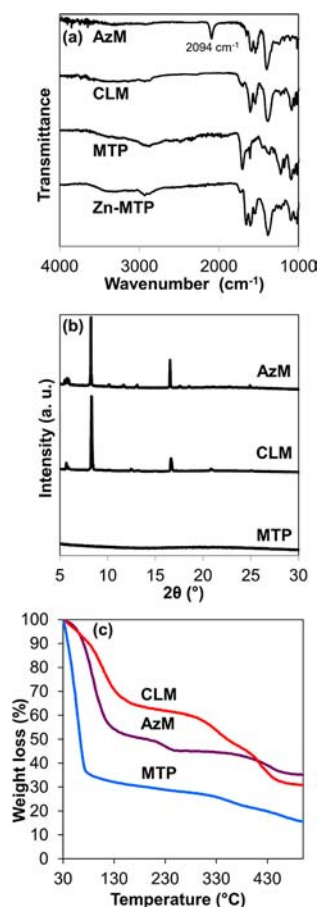


Figure 4. (a) FT-IR spectra of AzM, CLM, MTP, and Zn-MTP. (b) Powder X-ray diffraction patterns of AzM, CLM, and MTP. (c) Thermogravimetry chart of AzM, CLM, and MTP.

shown in Figure 4c. CLM soaked in DEF exhibited a similar thermal behavior to that of the starting AzM. The weight loss increased rapidly with increase of temperature, and saturated around 100 °C due to completion of release of the included DEF. Further heating induced the decomposition of MOF. The weight loss of AzM and CLM caused by the guest release below 200 °C was estimated at about 49% and 37%, which corresponded to 14 and 10 molecules of DEF as the guest molecule per the MOF unit structure, respectively. CLM exhibited similar inclusion ability for liquid guest molecules, and did not lose the inherent properties of MOF. The smaller number of the included guest molecules was attributed to a decrease of void space by chemical modification.^{27,28} The weight-loss of MTP was 66%, corresponding to 38 guest molecules per the ideally cross-linked unit structure on the basis of MOF unit structure. The large weight-loss of MTP compared to that of CLM originated from a decrease of the weight of the framework due to removal of heavy zinc ions in the unit structure and elastic expansion of the network of MTP in DEF. These results clearly suggest that decomposition of CLM converted a brittle nanoporous inorganic framework into an elastic organic framework.

To reveal the property as polymer gels (PGs), we further investigated the swelling behaviors of the resulting cubic materials by immersing in various solvents. The original cubic shapes as well as their defects or cracks were preserved in all cases during the swelling. The equilibrium swelling degrees (Q) of the cubic gels were defined by the following equation;

$$Q = (L_{\text{wet}}/L_{\text{dry}})^3$$

where L_{wet} and L_{dry} are average lengths of one side of MTP in wet and dried state, respectively. The lengths of several wet cubic gels were measured by microscope observation after immersing in the solution or solvents at room temperature for 48 h.

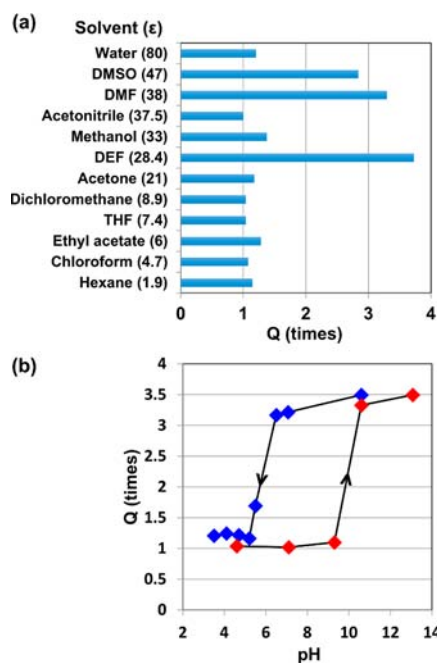


Figure 5. (a) Swelling behavior of MTP in various solvents. (b) pH-Dependent swelling behavior of MTP.

Figure 5a summarizes the swelling degrees in various organic solvents and aqueous solution with various pH. Among the organic solvents, MTP swelled in aprotic polar solvents such as DMF, DEF and DMSO due to suppression of hydrogen bonds among the carboxylic acid groups and good compatibility of phenyl rings of the organic linkers in MTP. In other solvents such as methanol, *n*-hexane, chloroform, THF, dichloromethane and water, MTP collapsed, and the swelling degrees were proved as 2 or less. The compatibility of these solvents with the polymer chain in MTP was not sufficient, resulting in poor swelling behavior of MTP. For pH dependence, in acidic solution the swelling degrees were nearly constant 1.2, due to poor compatibility of the networks and aggregation of many carboxylic acids, but at the higher pH (10.5), the swelling degrees increased to 3.2 because of the dissociation to carboxylate anions which induced the repulsive interaction between anionic groups and generation of osmotic pressure between interior and exterior of MTP. The phase transition in volume from the collapsed state at lower pH to swollen state at the higher pH was observed around pH = 10.0 and that from the swollen state to collapsed state was around pH = 5.5. This large hysteresis was attributed to difficulty of the penetration of water molecules into the polymer gel matrix due to poor compatibility of the polymer chains and strong hydrogen bonds between carboxylic acids. The transition at lower pH should reflect the deionization of the carboxylate groups. The loss of the charges in MTP induced its collapse. These swelling behaviors of MTP were quite similar to those of common polymer gels with carboxylic acid groups such as poly(acrylic

acid).²⁹ Therefore, the obtained MTP acts as polymer gels and swells in some solvents without changes of the shape, meaning that MTP possesses nanoporosity when swollen in DEF.

We further attempted regeneration of CLM by treatment of MTP with zinc nitrate in DEF. After the repeated washing with fresh DEF, the carbonyl stretching band for carboxylic acid at ca. 1697 cm^{-1} completely disappeared and a new band appeared at 1397 cm^{-1} assigned to carboxylate, in the IR spectrum of the resulting cubic mass (Zn-MTP, Figure 2a). This clearly indicated the regeneration of zinc carboxylate. Observation under microscope indicated that the cubic shape of MTP was retained during re-coordination of zinc ions to carboxylic acid. However, in the XRD as shown in Figure 2c, no apparent diffraction peaks were observed after re-coordination, indicating that no crystalline metal coordination network was recovered. This result clearly indicated that three-dimensional order of MOFs was already destroyed by decomposition of the coordination bonds, because coordination sites moved 10% in length during swelling in DEF. The preliminary extraction experiments provided its cation exchange capacity as 5.82, 5.19, and 3.68 mequiv/g for Na^+ , Zn^{2+} , and Eu^{3+} , respectively. These values were relatively high compared to those of the common ion-exchange resins. For a visible example, observation of MTP under UV irradiation (365 nm) revealed constant Eu^{3+} uptake of MTP immersed in 40 mM $\text{EuNO}_3 \cdot 6\text{H}_2\text{O}(\text{aq})$ as shown in Figure S4. Therefore, the obtained MTP exhibited the capacity as an ion-exchange resin due to a large number of well-organized carboxylic acid groups and their inherent void in the flexible network structures.

We performed directional and partial hydrolysis of a single piece of CLM crystal to seamlessly fused hybrid material between PG and MOF by contacting one crystal face of CLM on a wet membrane with 1 M $\text{NaOH}(\text{aq})$ for 5 min, followed by immersion in fresh DEF repeatedly to remove excess amount of the base. The cubic shape was remained under microscope observation as shown in Figure 6a. The XRD pattern of the whole crystal illustrated that it had the sharp diffraction peaks similar to those of the starting CLM, indicating that the crystalline MOF network was retained due

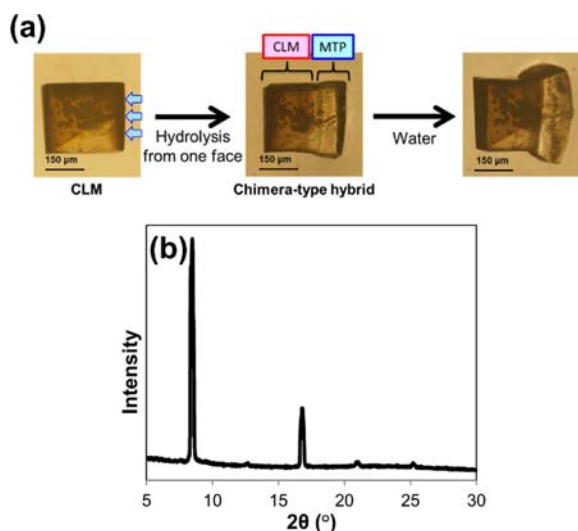


Figure 6. (a) Optical microscopy images before and after the partial hydrolysis of CLM to chimera-type hybrid, and subsequent immersion in water. (b) Powder X-ray diffraction pattern of a single piece of whole chimera-type hybrid.

to controlled diffusion of alkaline solution. Then, in order to confirm the decomposition of metal coordination, we immersed it in neutral water. Within a few minutes, the portion of the crystal exposed to the alkaline solution expanded and the cubic shape was largely deformed. This observation manifests that the alkaline hydrolysis prompted decomposition of zinc coordination and replacement of counter cation of carboxylate from zinc to sodium ion in the network structure. They swelled largely in water because of electrostatic repulsion between anion charges and generation of osmotic pressure in the network. The other half portion remained unchanged cubic shape with sharp edges due to the robust dual networks of zinc coordination network and cross-linked polymer network. This result clearly illustrates the formation of the chimera-type hybrid of PG and MOF.

To generalize cross-linking of organic ligands in the MOF crystals to form PG, we further investigated cross-linking of other MOFs that consisted of biphenyl-type organic linkers with two azide groups (AzBPDC) and some other metal ions. Cross-linking and transformation to PG were summarized in Figure 7. Starting from AzBPDC as another reactive organic linker,²³ treatment of Zn^{2+} and Cu^{2+} provided colorless cubic and green truncated octahedral MOF crystal under the standard solvothermal synthesis in DEF and DEF-DMSO, respectively. Moreover, solvothermal synthesis from AzTPDC and Zr^{4+} in DMF at 120 °C provided colorless octahedral crystal. XRD patterns and IR spectra of these MOF crystals revealed that they had the same crystal structures as their parents without azide groups (Figures S5, S6, and S7 for AzMBP, AzKUMOF, and AzUiOMOF, respectively). In addition, they were further employed for cross-linking in the MOF crystals by click reaction and followed by decomposition of metal coordination in HCl-DEF or $\text{H}_2\text{SO}_4\text{-DMSO}$. After the acid treatment, all the crystals became insoluble and were successfully converted to PG. In all cases, their sizes became slightly larger due to swelling of PG, and their shapes were very similar to those of the starting MOFs. These results were essentially the same as those of CDMOF to CPG²¹ and the MOF crystals from AzTPDC with Zn^{2+} , i.e., AzM and related PG. Therefore, the cross-linking reaction between the organic linkers in MOF crystals should be a general and valid method for preparation of PG that possesses well-defined shape and size. A wide variety of MOF crystals from metal ions and organic linkers should provide PG with various polyhedral shapes.

CONCLUSION

In summary, we demonstrated transformation of PG from MOF by the cross-linking of organic ligand in MOF and following hydrolysis. The obtained PG showed typical behavior of polyelectrolyte gel, indicative of high contents of ionic groups inside. The densely packed carboxylate groups in PG adsorbed metal ions such as Zn^{2+} , Eu^{3+} , and Na^+ . Partial hydrolysis of resulting cross-linked MOF yielded their chimera-type seamless hybrid material, thus MOF and PG, presumably possessing gradient pore structure of both porous materials. The use of various MOFs as templates allowed us to prepare PGs with various shapes reflecting the crystal structure of the MOFs. On the basis of these findings, we believe that our transformation reactions from well-defined three-dimensional nanoporous network of MOFs, which act as templates, to other network material, will be one of the most promising routes for creation of the polymer networks with well-defined repeating

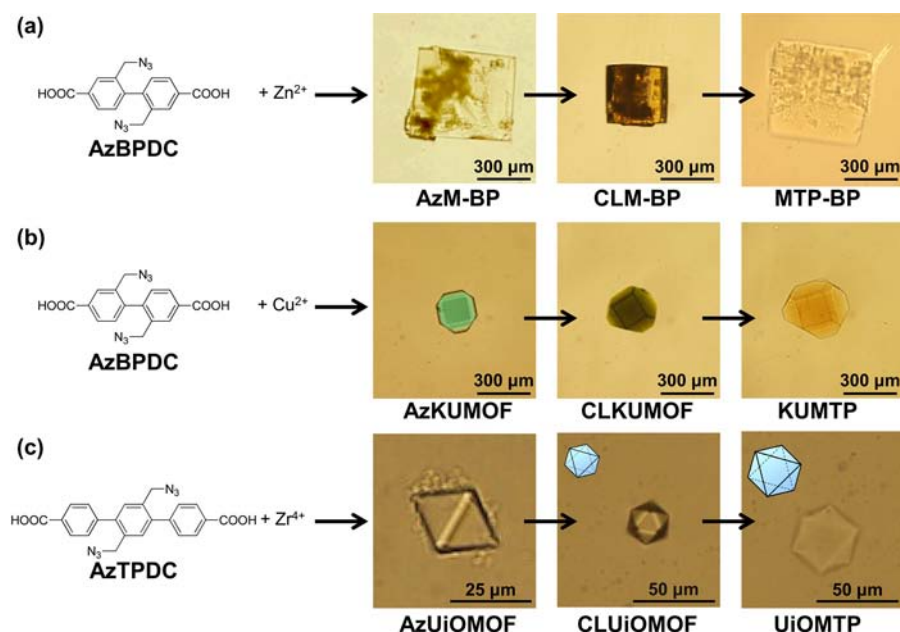


Figure 7. (a) Optical microscopy images of (a) AzM-BP, (b) AzKUMOF, and (c) AzUiOMOF, and subsequent cross-linking and transformation of them, respectively.

units in the network structure, i.e., “ideal network polymers”, which have never been prepared until now.³⁰

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, results of XPS, FTIR spectroscopies, XRPD, analysis, and optical photographs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Czaja, A. U.; Trukhan, N.; Mueller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284.
- (2) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.
- (3) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294.
- (4) Yanai, N.; Kitayama, K.; Hijikata, Y.; Sato, H.; Matsuda, R.; Kubota, Y.; Takata, M.; Mizuno, M.; Uemura, T.; Kitagawa, S. *Nat. Mater.* **2011**, *10*, 787.
- (5) Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563.
- (6) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450.
- (7) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

- (8) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.
- (9) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.
- (10) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
- (11) Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Nature* **1995**, *374*, 240.
- (12) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621.
- (13) Langer, R.; Tirrell, D. A. *Nature* **2004**, *428*, 487.
- (14) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297*, 967.
- (15) Urich, K. E.; Cannizzaro, S. M.; Langer, R. S.; Shakesheff, K. M. *Chem. Rev.* **1999**, *99*, 3181.
- (16) Chen, J.; Park, H.; Park, K. *J. Biomed. Mater. Res.* **1999**, *44*, 53.
- (17) Lin, J. M.; Wu, J. H.; Yang, Z. F.; Pu, M. L. *Macromol. Rapid Commun.* **2001**, *22*, 422.
- (18) Harada, A.; Kobayashi, R.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H. *Nat. Chem.* **2011**, *3*, 34.
- (19) Nakahata, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Nat. Commun.* **2011**, *2*, 511.
- (20) Yamaguchi, H.; Kobayashi, Y.; Kobayashi, R.; Takashima, Y.; Hashidzume, A.; Harada, A. *Nat. Commun.* **2012**, *3*, 603.
- (21) Furukawa, Y.; Ishiwata, T.; Sugikawa, K.; Kokado, K.; Sada, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 10566.
- (22) Goto, Y.; Sato, H.; Shinkai, S.; Sada, K. *J. Am. Chem. Soc.* **2008**, *130*, 14354.
- (23) Nagata, S.; Sato, H.; Sugikawa, K.; Kokado, K.; Sada, K. *CrystEngComm* **2012**, *14*, 4137.
- (24) Papp, I.; Dervedde, J.; Enders, S.; Haag, R. *Chem. Commun.* **2008**, 5851.
- (25) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166.
- (26) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortes, J. L.; Cote, A. P.; Taylor, R. E.; O’Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316*, 268.
- (27) Tanabe, K. K.; Cohen, S. M. *Chem. Soc. Rev.* **2011**, *40*, 498.
- (28) Wang, Z.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315.
- (29) Ricka, J.; Tanaka, T. *Macromolecules* **1984**, *17*, 2916.
- (30) Kissel, P.; Erni, R.; Schweizer, W. B.; Rossell, M. D.; King, B. T.; Bauer, T.; Goetzinger, S.; Schlueter, A. D.; Sakamoto, J. *Nat. Chem.* **2012**, *4*, 287.