Metal Organopolymeric Framework

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Metal–Organic Organopolymeric Hybrid Framework by Reversible [2+2] Cycloaddition Reaction**

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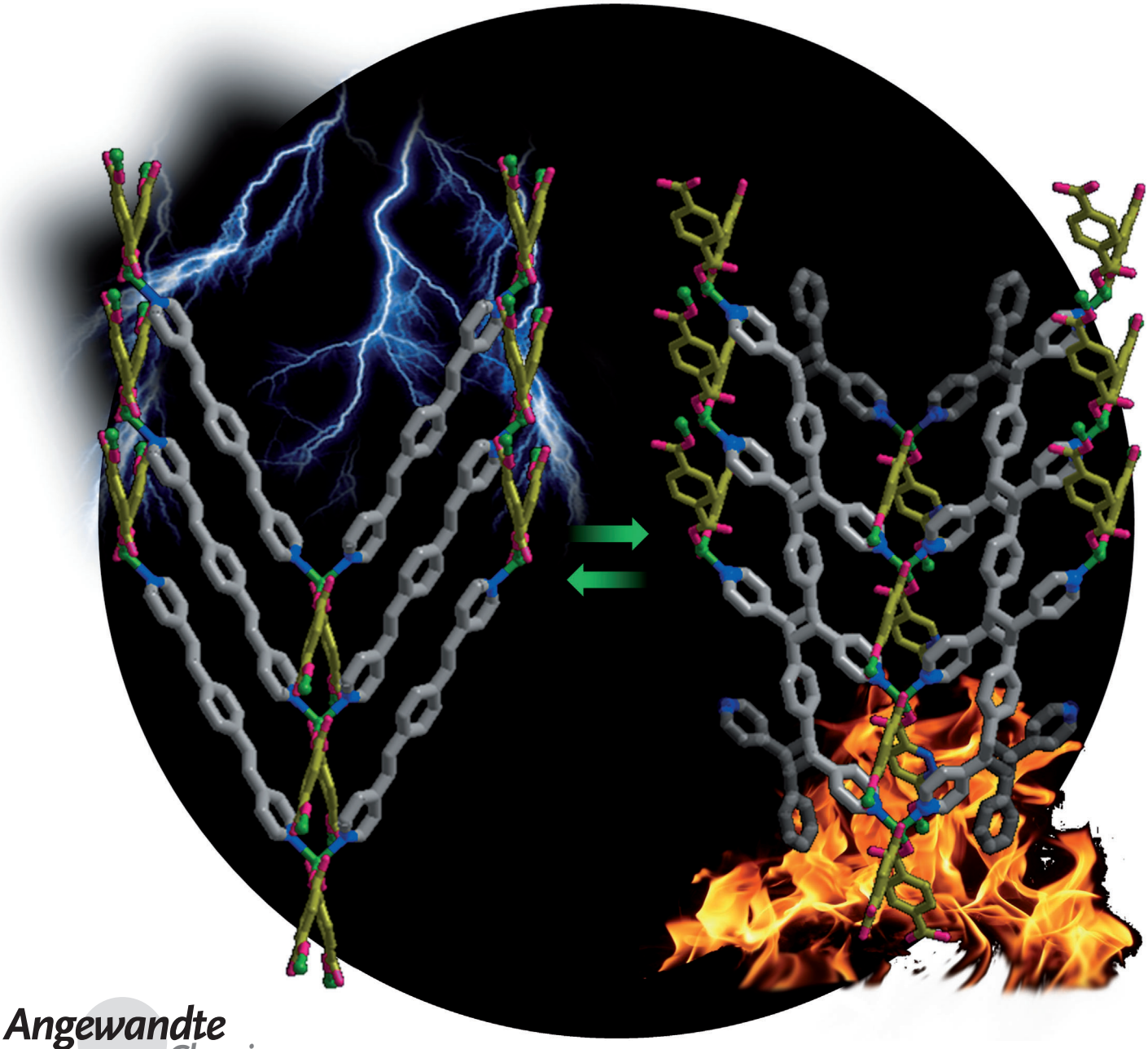

Abstract: *Organic polymers are usually amorphous or possess very low crystallinity. The metal complexes of organic polymeric ligands are also difficult to crystallize by traditional methods because of their poor solubilities and their 3D structures can not be determined by single-crystal X-ray crystallography owing to a lack of single crystals. Herein, we report the crystal structure of a 1D Zn^{II} coordination polymer fused with an organic polymer ligand made in situ by a [2+2] cycloaddition reaction of a six-fold interpenetrated metal–organic framework. It is also shown that this organic polymer ligand can be depolymerized in a single-crystal-to-single-crystal (SCSC) fashion by heating. This strategy could potentially be extended to make a range of monocrystalline metal organopolymeric complexes and metal–organic organopolymeric hybrid materials. Such monocrystalline metal complexes of organic polymers have hitherto been inaccessible for materials researchers.*

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are made up of metal ions and organic linkers and are highly organized crystalline materials known for their large surface areas and their tunable pore size and internal surface area. The modular nature of these extended networks makes them attractive for a wide variety of applications.[1] In recent years, covalent organic frameworks (COFs) assembled entirely from organic building units through strong covalent bonds have also attracted attention for similar reasons.[2] Blending the organic polymers into the MOFs may combine the structural regularity of the metal-containing MOFs and the unique properties of the organic polymers to produce new and better functional hybrid materials. Since the direct incorporation of organic polymers into MOFs is clearly a challenge, it might be achieved indirectly in the solid state. Recently Sada et al. have transformed MOF crystals into flexible organic polymer gels through internal crosslinking of the organic linkers by using click reactions followed by decomposition of the coordination network.[3] Furthermore, a number of ethylene-containing molecules have been polymerized inside the channels of PCPs by Kitagawa and co-workers by crosslinking the ethylene bonds at the backbone with the spacer ligands.[4]

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Solid-state reactions offer products that cannot be achieved by solution synthesis. For example, highly crystalline organic polymers have been generated both thermally and photochemically in the solid state for diacetylenes,[2b,5] diolefins,[6] a triacetylene,[6c,7] a triene,[8] and quinodimethanes.[9] Recently Wuest et al. reported monocrystalline COF compounds.[10] In this respect, polycyclobutanes generated by the solid-state [2+2] cycloaddition of conjugated diolefins, for example 2,5-distyrylpyrazine, are an interesting class of crystalline organic polymers.[11] Such an organic polymer that contains cyclobutane rings can be introduced into a MOF if the conjugated C=C bonds are infinitely aligned closely in a slip-stacked manner such that one C=C bond pair is aligned between any two adjacent spacer ligands in the MOF. In the two MOFs reported, the conjugated diene spacer ligand, 1,4-bis[2-(4′-pyridyl)ethenyl] benzene (bpeb), has been found to align in a face-to-face or out-of-phase manner to undergo double cycloaddition and single cycloaddition, respectively, in a single-crystal-to-single-crystal (SCSC) manner[12] but not the expected slip-stacked packing.

Herein, we describe how the infinite slip-stacked assembly of the two C=C bonds in bpeb ligands in an overall six-fold interpenetrated MOF with diamondoid (**dia**) topology undergoes a double [2+2] cycloaddition reaction to yield a true organic polymer fused in the MOF. The polymer comprises cyclobutane rings separated by phenylene rings with 2,4-pyridyl pendants as shown in Figure 1. The cycloaddition

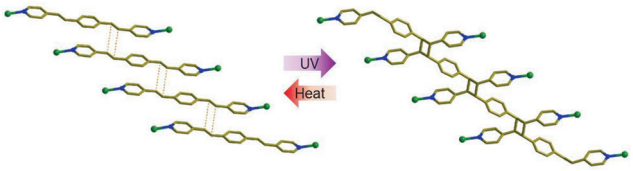

Figure 1. Reversible polymerization by [2+2] photo-cycloaddition of slip-stacked bpeb ligands in a MOF and depolymerization of the resultant polycyclobutanes. Both processes occur through SCSC transformations.

reaction thus furnished the expected metal–organic organopolymeric hybrid structure. Furthermore, the cyclobutane ring was successfully cleaved to achieve the depolymerization process when single crystals of this hybrid framework compound were heated at 250 °C for 3 h, and the structure reverted back to the original MOF structure through SCSC transformation.

Yellow block crystals of $[Zn(bpeb)(bdc)]\cdot H_2O\cdot 0.1\,DMA$ ($\mathbf{1}\cdot H_2O\cdot 0.1\,DMA$) suitable for single-crystal X-ray diffraction were obtained under solvothermal conditions from $Zn(NO_3)_2\cdot 4H_2O$, 1,4-benzenedicarboxylicacid (H_2bdc), and bpeb in a mixture of dimethylacetamide (DMA), dimethylsulfoxide (DMSO), and water at 100 °C, followed by slow cooling. The purity of the bulk product was confirmed by comparing the simulated powder X-ray diffraction pattern from the single-crystal data with that of the bulk sample (Figure S1 in the Supporting Information). X-ray crystallographic experiments carried out at −100 °C revealed that **1** crystallizes in the monoclinic space group $P2/n$ with $Z = 2$.

The asymmetric unit contains half the formula unit, in which Zn1 sits on the crystallographic two-fold axis. Zn1 is coordinated with a highly distorted tetrahedral geometry [93.2(2)–122.9(1)°] to two nitrogen atoms from the bpeb spacer ligands and two oxygen atoms from the bdc ligands (Figure 2a). The Zn1···O2 distance of 2.94 Å indicates that

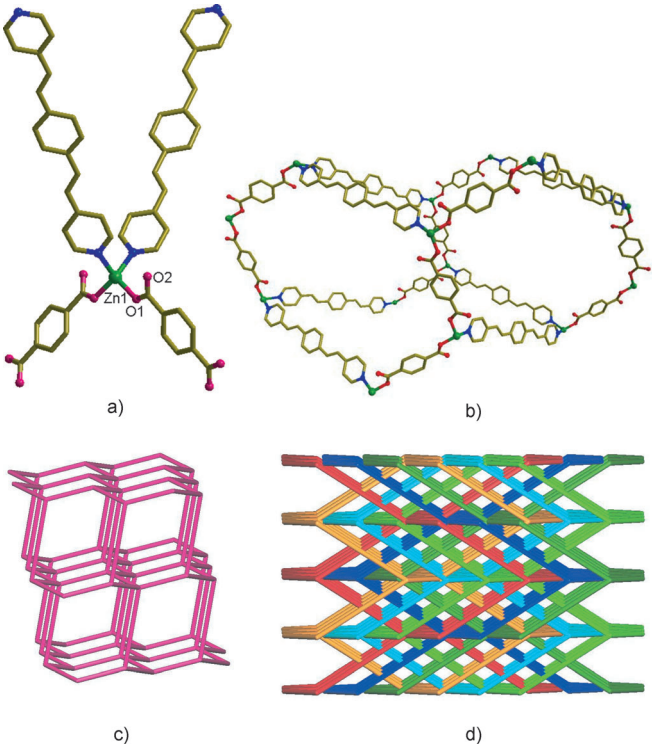

Figure 2. a) A perspective view showing the coordination sphere of Zn1 in **1**. b) The connectivity showing a single diamondoid network. Zn (green), O (red), N (blue), and C (gold). c) The **dia** topology in **1**. d) The six-fold interpenetration, with channels along the *c*-axis.

this carbonyl oxygen atom is not bonded. The crystallographic inversion symmetry present in the middle of each spacer ligand generates a 3D coordination polymer with **dia** topology as shown in Figure 2b, c. The large void produced in this connectivity is filled by six-fold interpenetration (Figure 2d). Despite six-fold interpenetration, **1** has porous channels parallel to the *b*-axis with a calculated solvent accessible void of 30.8% (Figure 2c).[13] The solvent molecules in these channels were found to be severely disordered water and a small fraction of DMA molecules.

In **1,** Zn(bdc) and Zn(bpeb) zigzag chains are disposed normal to each other at the tetrahedrally coordinated Zn^{II} atoms. The Zn(bdc) chains are packed one below the other to form a sheet in the $(10\bar{1})$ plane, while the Zn(bpeb) chains propagate parallel to the [101] direction and stack in the (101) plane along the *b*-axis. As a result of this zigzag packing, the bpeb ligands are slip-stacked (or "out-of-phase") relative to each other in such a way that each phenylene ring in the middle of bpeb is closer to a neighboring pyridyl group (centroid to centroid distance 3.617 Å). This indicates the presence of a strong face-to-face π–π interaction (Figure 3).

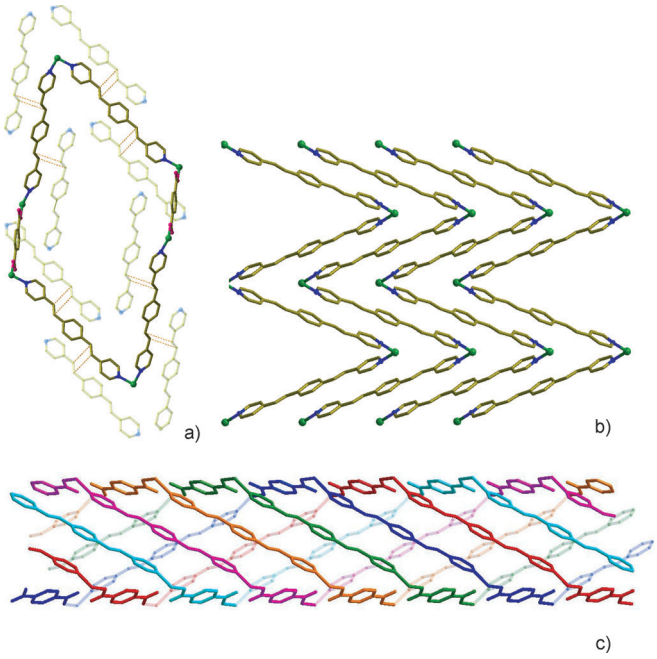

Figure 3. a) A perspective view of the packing showing the alignment of C=C bonds. b) and c) The "slip-stacked" alignment of the bpeb spacers in **1**.

Furthermore, the distance between the centers of the adjacent C=C bonds of 3.68(1) Å and the slip-stacked intermolecular bpeb spacer ligands point toward the feasibility of a photochemical reaction. It is evident from Figure 2 that if such a [2+2] cycloaddition reaction were to occur, it would lead to the formation of a cyclobutane organic polymer within this MOF structure. Furthermore, the interpenetration observed in **1** would disappear as a result of cyclobutane ring formation across the interpenetrated frames in the **dia** net.

Irradiating the yellow crystals of **1** under a xenon lamp at wavelength 365 nm for 2 h resulted in pale yellow crystals of [Zn(*poly*-bppcb)(bdc)]·H_2O·0.1 DMA (**2**·H_2O·0.1 DMA) (where *poly*-bppcb is 1,3-(4,4′-bipyridyl)-2-phenylcyclobutane polymer, Figure S10) suitable for single-crystal X-ray crystallographic analysis. Further characterization by solution ^{1}H NMR spectroscopy was hampered by the insolubility of **2** even in strong acids, thus indirectly indicating the formation of the organic polymer. Hence ^{13}C CP–MAS solid-state NMR spectroscopy was used to characterize both the bulk product **2** and *poly*-bppcb separated from **2** (Figures S20–S23).

The X-ray crystallographic analysis revealed that a quantitative photopolymerization reaction had occurred accompanied by the SCSC transformation.

During this process, the space group had changed from $P2/n$ in **1** to $P\bar{1}$ in **2** with $Z = 2$, with the full repeating unit in the asymmetric unit owing to reduced symmetry. The distorted tetrahedral geometry is maintained at Zn1 as in **1** but with variations owing to photopolymerization of the bpeb ligands (Figure 4a). The crystallographic center of inversion in the middle of the bdc ligand and the cyclobutane rings of the new polymer ligand *poly*-bppcb (Figure 4b) generate the 3D structure (Figure 4c). The six-fold interpenetrated net has transformed into a single net as a result of

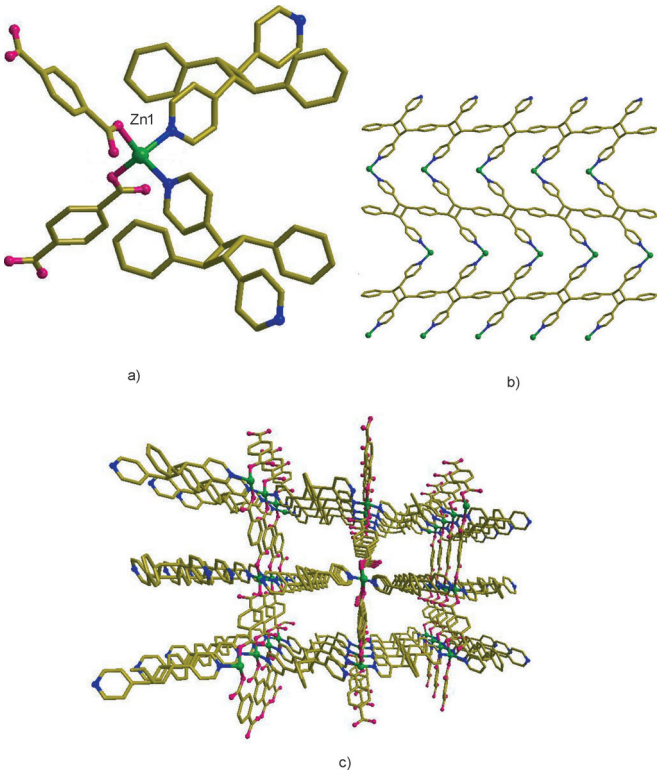

Figure 4. a) A perspective view of the coordination environment of Zn1 in **2**. b) The 2D sheets formed by the *poly*-bppcb with Zn^{II} atoms. c) A portion of the 3D network structure of **2** showing the channels. Zn (green), O (red), N (blue), and C (gold).

the formation of cyclobutane rings, which unite the interpenetrated **dia** nets. However, the channels along the *a*-axis (Figure 4c) remain with a small reduction in the calculated solvent accessible void to 28.3% in comparison to **1**.[13] The solvent molecules in these channels were found to be highly disordered as in **1**.

The single net formed in **2** as a result of a 2D herringbone net (Figure 4b) assembled from Zn^{II} atoms and the polymer ligand *poly*-bppcb is extended into a 3D structure by the bdc spacers (Figure 4c). This unusual binodal net is made up of tetrahedral nodes of Zn^{II} atoms and square planar nodes created by the cyclobutane rings of the *poly*-bppcb ligand. It is this infinite extension of the ligand which results in a new (4,4)-connected net, which we call **jjv1** (Figure 5), with point symbol $\{6.8^5\}\{6^4.8^2\}$ and vertex symbol $[6^2.8^2.8^5.8^5.8^5.8^5]$ $[6.6.6.6.8^2.10^{12}]$. There are two reports that discuss the solid-state polymerization of metal–organic polymers by γ-irradiation[14] and by a thermal method;[15] nevetheless, the nature of the resulting structures remains unknown. Recently, [2+2] cycloaddition reactions of metal complexes have been shown to lead to 1D coordination polymers.[16] However, **2** appears to be the first metal complex of an organic polymer for which the 3D crystal structure has been determined unequivocally from the single-crystal data. Since the work of Schmidt and co-workers on the photodimerization of cinnamic acid,[17] solid-state reactions offer pure regio- and stereo-isomers and complicated metal-coordination polymers[18] that cannot be synthesized by the usual solution methods. Compound **2** is

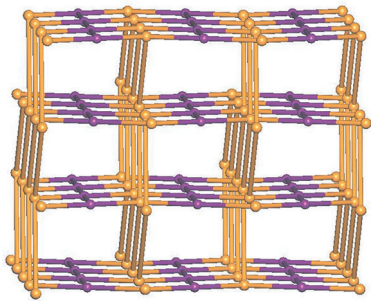

Figure 5. A perspective view of the non interpenetrated net **jjv1** viewed along the *a*-axis. A topological representation of the 3D framework created from herringbone style 2D sheets formed from tetrahedral Zn1 nodes (golden yellow) and *poly*-bppcb nodes (violet) through the linear bdc spacer.

another polymeric hybrid material that illustrates the advantages of the solid-state reactions that can be accomplished by crystal engineering. The infinitely slip-stacked arrangement of the conjugated diene ligands in a plane appears to be key for the photopolymerization reaction that has been obtained as a result of having metal ions with a tetrahedral coordination geometry.

It has recently been shown that the cyclobutane rings in coordination polymers can be thermally cleaved.[19] To investigate whether this is true for **2**, single crystals were heated to 250 °C for 3 h in a hot-air oven, and the pale yellow crystals of **2** turned into light brown crystals (termed **1′**) with some cracks. These crystals were cut later and used for single-crystal X-ray diffraction. Structure determination of the heated sample (**1′**) revealed that the space group and 3D structure of **1** were retained. Whereas crystals of **2** were insoluble in acid owing to the presence of organic polymers and thus could not be characterized by ^{1}H NMR spectroscopy, **1′** was found to be completely soluble under these conditions and gave a clear yellow solution. The ^{1}H NMR spectrum shows the presence of monomer bpeb signals (Figure S5). The variable-temperature powder X-ray diffraction (VT-PXRD) patterns of **2** recorded from room temperature to 295 °C show a gradual change in the diffraction patterns above 230 °C (Figure S11). The PXRD pattern recorded after subsequent cooling to room temperature matched well with that of **1**, a result that provides direct evidence for the phase change from triclinic $P\bar{1}$ (**2**) to monoclinic $P2/n$ (**1**; Figure S12). Although reversible cleavage of cyclobutane rings is known in organic systems[20], to date such reversible structural transformations that occur in an SCSC fashion are unknown in MOFs or organic polymers.

Compounds **1** and **2** show no weight loss up to 320 °C after the solvent was removed in the temperature range 40–120 °C (see thermogravimetry (TG) results, Figures S3 and S4). PXRD studies showed that the framework structures were retained after desolvation (Figures S1 and S2). Although TG indicated a very small weight loss of 4.9%, gas sorption experiments were carried out to test the properties of these compounds (Figure S13–S19). Both **1** and **2** can adsorb a small amount of CO_2. Furthermore, **1** can adsorb more CO_2 than **2** (14 vs. 8 cc/g) at −78 °C and 1 bar. Efforts are underway to

increase the surface area and pore size by reducing the interpenetration in the precursor compound **1**.

In this work, a photochemical [2+2] cycloaddition reaction was used to carry out the polymerization of the conjugated diene ligand bpeb. The photopolymerization occurs in a MOF and is assisted by tetrahedrally coordinated Zn^{II} atoms, which align all the bpeb ligands to pack slip-stacked infinitely in a plane. The structural transformation takes place under UV light, starting from the six-fold interpenetrated diamondoid network structure **1**, and giving rise to the non-interpenetrated structure **2** in an SCSC manner as a result of the formation of cyclobutane rings between the neighboring double bonds. The resultant structure has the new topology **jjv1**. This photopolymerized structure has an unusual organic polymer ligand fused with a 1D coordination polymer [Zn(bdc)]. This monocrystalline hybrid structure is unlikely to be synthesized by other means and differs from those reported by Sada[3] and Kitagawa[4]. It is notable that the microporosity of these materials was retained upon photopolymerization, thus demonstrating the potential for applications similar to those of MOFs. Furthermore, the cyclobutane rings in **2** were cleaved successfully by heating to regenerate **1** in an SCSC manner. Such reversible polymerization and depolymerization reactions appear to be unprecedented.

The above synthetic methodology could potentially be extended to the design and synthesis of a range of new metal–organic organopolymeric hybrid materials, as well as metal organopolymeric structures, by employing photopolymerization. The properties of these new compounds are potentially interesting, but these are yet to be explored.

Experimental Section

[Zn(bpeb)(bdc)]·H_2O·0.1 DMA (**1**·H_2O·0.1 DMA): A mixture of bpeb (20.2 mg, 0.071 mmol), H_2bdc (11.7 mg, 0.071 mmol), and $Zn(NO_3)_2{\cdot}4H_2O$ (18.6 mg, 0.071 mmol) dissolved in DMA (3 mL), H_2O (1 mL), and DMSO (0.5 mL) were placed in a 10 mL glass tube, and 3–4 drops of 0.1M NaOH were added. The tube was sealed and kept at 100 °C for 12 h, followed by cooling to room temperature over 8 h. Yellow block-shaped crystals of **1** suitable for X-ray analysis were obtained. Yield: 63 %

[Zn(*poly*-bppcb)(bdc)]·H_2O·0.1 DMA (**2**·H_2O·0.1 DMA): Single crystals of **2** were obtained by UV irradiation of single crystals of **1** for 2 h.

[Zn(bpeb)(bdc)] (**1′**): Single crystals of **2** were heated to 250 °C in a hot-air oven. After 3 h, light brown crystals of **1′** suitable for X-ray analysis were obtained.

Crystal data for **1**: $C_{28}H_{20}N_2O_8Zn$, fw = 513.83, Monoclinic, $P2/n$, $a = 13.9159(4)$, $b = 7.6229(2)$, $c = 14.2827(5)$ Å, $\beta = 99.271(2)°$, $V = 1495.31(7)$ Å^3, $Z = 2$, $D_x = 1.301$ g cm^{-3}, $\mu = 0.851$ mm^{-1}, $R_{int} = 0.0489$, GOF = 1.028, $R_1 = 0.0588$, $wR_2 = 0.1733$ for 2134 data $I > 2\sigma(I)$.

Crystal data for **2**: $C_{28}H_{20}N_2O4Zn$, fw = 513.83, triclinic, $P\bar{1}$, $a = 7.3936(8)$, $b = 14.3076(16)$, $c = 14.5432(16)$ Å, $\alpha = 103.721(8)$, $\beta = 92.319(8)$, $\gamma = 93.281(8)°$, $V = 1489.8(3)$ Å^3, $Z = 2$, $D_x = 1.145$ g cm^{-3}, $\mu = 0.854$ mm^{-1}, $R_{int} = 0.0926$, GOF = 1.008, $R_1 = 0.0626$, $wR_2 = 0.1385$ for 3200 data $I > 2\sigma(I)$.

Crystal data for **1′**: $C_{28}H_{20}N_2O_4Zn$, fw = 513.83, triclinic, $P2/n$, $a = 13.9519(9)$, $b = 7.6512(5)$, $c = 14.2991(10)$ Å, $\beta = 99.359(5)°$, $V = 1506.1(2)$ Å^3, $Z = 2$, $D_x = 1.321$ g cm^{-3}, $\mu = 0.867$ mm^{-1}, $R_{int} = 0.1135$, GOF = 1.043, $R_1 = 0.0830$, $wR_2 = 0.2370$ for 1665 data $I > 2\sigma(I)$.

CCDC 924307 (**1**), 924308 (**2**) and 926445 (**1′**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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