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# Passing the framework skeleton and properties of coordination material on to organic framework material

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A practically applicable strategy for transforming fragile metalorganic frameworks (MOFs) into highly stable and ordered organic framework materials (OFMs) is deveoped by replacing the labile coordination bonds in MOFs with stable covalent bonds in OFMs, which exhibit hypothetically approximated topology, porosity and properties of the parent MOFs by merging the advantages of MOFs and porous organic materials, thus providing a general pathway for the synthesis of highly ordered OFMs with merged advantages of MOFs and organic polymers.

Metal-organic frameworks (MOFs) are a class of long-range ordered porous crystalline materials, constructed from coordination bond connections between metal nodes and multidentate organic ligands.<sup>1</sup> The systematically tunable nature of MOFs offers unique advantages over traditional porous materials in that numerous functional moieties are readily incorporated into the frameworks for potential applications by either ligand design or postsynthetic modification.<sup>2,3</sup> However, this promise has not been fulfilled in practical applications, mainly because the coordination bonds in most MOFs are chemically susceptible, even under ambient environment.<sup>4</sup>

Porous organic polymers (POPs), connected by robust covalent bonds, are a new type of porous materials for applications in different fields, which offer superior stability, even under harsh environments.<sup>5,6</sup> However, the irreversible nature of most covalent organic bonds generally resulted in highly disordered connections of the building synthons in POPs, except for the dynamic covalent bond-connected covalent organic frameworks (COFs).<sup>5a-c</sup>

It has been demonstrated that MOFs could be transformed into POPs under stuitible conditions; however, the framework skeletons and properties of MOFs could not be well inherited by the daughter POPs.<sup>6d,6e</sup> We report herin an effective strategy for the synthesis of highly ordered organic framework materials (OFMs) by replacing the dynamically formed coordination moieties in MOFs with covalent bond-connected organic synthons that have the same symmetry, which could full take the advances of reversible coordination bonds and irreversible organic covalent bonds.



Scheme 1 (A) Model reaction between copper benzoate and TBMB. (B) Schematic illustration of the transformation from fragile MOF material CZJ-6 into stable organic framework material OFM-1.

Inspired by the reaction between benzyl bromide and carboxylic acids which has been widely used to protect the carboxyl groups by forming benzyl esters in organic synthesis, we conducted the reaction between coordination compound copper benzoate and 1,2,4,5-tetrakis(bromomethyl)benzene (TBMB), which also resulted the corresponding ester under the identical base-catalyzed nucleophilic reaction conditions (Scheme 1). Since copper benzoate coordination moiety is one of the very important SBUs in MOFs, the fragile copper benzoate coordination moieties in MOFs should be also easily transformed into stable ester covalent bonds under similar reaction conditions, which would generate stable OFMs with inherited framework structures and properties from the parent MOFs. As a proof of this concept, we reacted the MOF CZJ-6,<sup>7</sup>

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building from four-connected paddle-wheel  $[Cu_2(COO)_4(H_2O)_2]$ (abbreviated as  $\{Cu_2\}$ ) secondary building units (SBUs) and eight branched metalloporphyrin ligands Cu-L ( $H_{10}L$  = tetrakis-3,5bis((4-hydroxycarbonyl)-phenyl)phenylporphine), with tetrabranched TBMB by equivalent symmetry substitution of fourconnected coordination moieties with tetra-branched organic synthons under solvothermal reaction conditions, and successfully targeted a highly stable organic material, named as OFM-1.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the regular octahedral morphology of CZJ-6 was well reserved by OFM-1, indicating that the substituent reaction could retain the apparent morphology of the parent MOF (Fig. 1 and S1<sup>+</sup>). This result should be ascribed to the large pore space of CZJ-6 with pore cages of 1.4 and 2.3 nm in dimensions, which could endow the substituent reaction occur inside the pores.



Fig. 1 (A) SEM images of CZJ-6. (B) SEM images of OFM-1. (C) FT-IR spectra of porphyrin ligand ( $H_{10}L$ ), CZJ-6, CZJ-6(t) and TBPP.

When the reaction was proceeded for a certain time, the reaction was intentionally interrupted by cooling to room temperature, and the solid reaction intermediates, denoted as CZJ-6(t) (t represents the reaction time), were recovered by centrifugation. UV-Vis absorption spectral of the Supermarks show that the maximum absorption peak of TBMB decreases gradually when prolonging the reaction time, indicating that there might occur gradual substitution reaction between  $\{Cu_2\}$  SBUs and TBMB (Fig. S2<sup>+</sup>).

FT-IR spectrum of the porphyrin ligand shows a strong C=O bond stretching vibration band appeared at 1701 cm<sup>-1</sup> (Fig. 1C). The peak almost disappeared in the FT-IR spectrum of CZJ-6, and there emerged two new peaks at 1538 and 1401 cm<sup>-1</sup>, ascribed to the asymmetric and symmetric stretching vibrations of coordinated carboxylate groups, respectively.<sup>8</sup> The vibration peaks of CZJ-6(3h) are similar to those of CZJ-6, indicating that most of the Cu-carboxylate coordination bonds remained intact. When the reaction time was extended to 6 h, the asymmetric stretching vibration at 1538 cm<sup>-1</sup> for the coordinated carboxylate groups almost disappeared, and the symmetric stretching vibration at 1401 cm<sup>-1</sup> was red-shift, indicating that most of the Cu-carboxylate coordination bonds were destroyed. Additionally, the C=O stretching vibration bands at 1701 and 1720 cm<sup>-1</sup> are highly enhanced, and there appeared two new peaks at 1268 and 1102 cm<sup>-1</sup>, suggesting the formation of ester moieties. When further extending the reaction time, these absorption bands were enhanced, which are almost identical to those of the porphyrin molecular analog 5,10,15,20-tetrakis-3,5-bis((4-

benzyloxycarbonyl)phenyl)phenylporphine (TBPP). These results indicate that most of the Cu-carboxylate moieties were replaced by the ester moieties to result an organic framework material OFM-1.

Powder X-ray diffraction (PXRD) pattern of OFM-1 shows that there is no sharp diffraction peak, indicating that the building synthons are distortedly connected in the structure (Fig. S3<sup>+</sup>). In the Raman spectrum, OFM-1 exhibits two broad peaks at 1345 and 1580 cm<sup>-1</sup>, which are ascribed to the out-of-phase coupled stretch and asymmetric stretch vibrations of porphyrin rings, respectively (Fig. S4<sup>+</sup>).<sup>9</sup> UV-Vis diffuse reflectance spectrum of OFM-1 shows that the characteristic Soret band of porphyrin locats at 434 nm with two Q bands centered at 557 and 590 nm, which are similar to those of CZJ-6 (Fig. S5<sup>+</sup>).

The solid intermediate samples of CZJ-6(t) could be partially decomposed by hydrochloric acid aqueous solution (pH = 1) to release the unreacted and low-polymerized moieties, which were thoroughly extracted by THF solvent. The obtained supernates, denoted as CZJ-6(t)-MS, were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). As shown in Fig. 2, a strong peak at m/z 1637.3 is very close to the molecular mass of  $Cu-H_8L$ (exact mass = 1635.3) for CZJ-6-MS, and a new peak at m/z 1629.3 is ascribed to Cu-L for CZJ-6(3h)-MS. There also appears a weak peak at m/z 3442.8, which is different to the peak at m/z 3337.8 in CZJ-6-MS, indicating that there occurred the reaction between {Cu<sub>2</sub>} SBU and TBMB. When the reaction time was prolonged to 6 h, a series of weak peaks appeared at m/z 5335, 7126 and 8837 for CZJ-6(6h)-MS, indicating that the Cu-O coordination moieties were gradually reacted with TBMB.

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Further prolonging the reaction time, the released Cu<sup>II</sup>porphyrin is undetectable, suggesting that the transformation reaction should be completed, which is in agreement with the UV-Vis and FT-IR spectroscopy analysis results.



Owing to its flexible structure with microporous blocking effect at very low temperature, OFM-1 could not take up N<sub>2</sub> at 77 K.<sup>10</sup> The permanent porosity of OFM-1 was examined by CO<sub>2</sub> gas adsorption measurement at 195 K (Fig. S6<sup>+</sup>). The activated sample of OFM-1 takes up 109.7 cm<sup>3</sup> g<sup>-1</sup> CO<sub>2</sub> at 195 K and 780 mmHg, resulting a Brunauer-Emmett-Teller (BET) surface area of 316.9 m<sup>2</sup> g<sup>-1</sup> and a dominated pore size of about 1.8 nm, calculated from the CO<sub>2</sub> adsorption profile of OFM-1. The above results are very close to the BET surface of 336.0 m<sup>2</sup> g<sup>-1</sup> and dominated pore size of about 1.8 nm for CZJ-6, respectively, indicating that OFM-1 successfully inherited the porosity of CZJ-6. TG-MS curves show that the maximum degradation rate of CZJ-6 was found at 324 °C with an increased intensity of MS signal at m/z = 44 for CO<sub>2</sub>, the decarboxylated product of metalloporphyrin ligands (Fig. S8<sup>+</sup>). Compared with CZJ-6, the maximum degradation rate of OFM-1 increased to 435 °C, indicating that transformation of CZJ-6 into OFM-1 would improve the thermal stability. The copper content was decreased from 14.6 wt% in CZJ-6 to 3.7 wt% in OFM-1, which is very close to the calculated value (3.5 wt%) for the Cu<sup>II</sup>porphyrin moieties in OFM-1, indicating that the {Cu<sub>2</sub>} coordination SBUs in CZJ-6 were almost fully substituted by covalently bonded organic moieties in OFM-1.

X-ray photoelectron spectroscopy (XPS) was also used to monitor the transformation of CZJ-6 into OFM-1 (Fig. 3). Compared with that of CZJ-6, the Cu 2p XPS intensity of OFM-1

is markedly decreased in the XPS survey spectrum, due to removal of the {Cu<sub>2</sub>} SBUs (Fig. S9<sup>+</sup>). In the ክያክንድ አባቢቲ በሪጉ የሮ 2p XPS spectrum of CZJ-6, each Cu 2p peak can be divided into 934.7 and 935.2 eV for Cu 2p<sub>3/2</sub>, and 954.6 and 955.1 eV for Cu  $2p_{1/2}$  with a broad satellite band, ascribed to the porphyrin Cu<sup>II</sup> and carboxylate-coordinated {Cu<sub>2</sub>} moieties, respectively (Fig. 3A).<sup>11</sup> In contrast, there are only two XPS signals at 934.7 and 954.6 eV ascribed to the porphyrin Cull in OFM-1, indicating that the {Cu<sub>2</sub>} SBUs had been successfully substituted and removed. In the C 1s XPS spectrum of CZJ-6, the peak at 284.8 eV is ascribed to the porphyrin and benzoic rings, and the peaks at 288.7 and 292.5 eV are attributed to the uncoordinated carboxyl groups on the surface of CZJ-6 and coordinated carboxyl groups in {Cu<sub>2</sub>} SBUs, respectively (Fig. 3B).<sup>12</sup> Compared with CZJ-6, the peak at 292.5 eV disappeared in the C 1s spectrum of OFM-1, and there appeared a new peak at 286.5 eV, ascribed to the newly formed C-O moieties. In the N 1s XPS spectra, the peaks at 398.5 and 400.4 eV are ascribed to the Cu-N<sub>4</sub> and pyrrolic nitrogen species, respectively, indicating that the Cu<sup>II</sup>-porphyrin moieties remain intact (Fig. 3C).<sup>11</sup> In the high-resolution O 1s XPS spectrum of CZJ-6, the peak at 532.0 eV is corresponding to the Cu-O moieties, whereas the peak at 533.9 eV is ascribed to the coordinated water (Fig. 3D).13 Different to that of CZJ-6, the O 1s XPS signal of OFM-1 can be divided into two peaks at 531.7 and 533.1 eV, assigned to the C=O and C-O-C moieties in ester groups, respectively.<sup>12</sup> These characterization results indicate that MOF CZJ-6 was successfully transformed into stable OFM-1. In contrast, direct reaction between H<sub>10</sub>L and TBMB resulted a highly distorted organic polymer under the identical reaction conditions, in which only part carboxylate groups were participated in the polymerization process (Fig. S10-S13<sup>+</sup>).



Fig. 3 XPS spectra of CZJ-6 and OFM-1 referenced to (A) Cu 2p, (B) C 1s, (C) N 1s and (D) O 1s.

Transformation of MOFs into OFMs should be able to tune the hydrophobic/hydrophilic properties, which was confirmed by water contact angle measurements. Compared with the pristine MOF CZJ-6 with a hydrophilic water contact angle of

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15°, OFM-1 generates a water contact angle of 136°, indicating its hydrophobic nature (Fig. S14<sup>+</sup>). Solvent test results revealed that OFM-1 is very stable in water and common organic solvents, even in 6 M hydrochloric acid (Fig. S15-S17<sup>+</sup>).

The catalytic properties of CZJ-6 were also successfully inherited by OFM-1. OFM-1 could smoothly prompt aerobic oxidation of ethylbenzene with 51% acetophenone yield, which is higher than the literature result of 45% yield under the identical catalytic conditions.<sup>7</sup> Since OFM-1 is hydrophobic and highly stable, we evaluated its catalytic properties in those reactions that cannot be catalyzed by fragile MOFs under extreme conditions, such as using water as solvent in the presence of strong Lewis acid. This consideration prompted us synthesize a composite catalyst, Pd@OFM-1, by simple posttreatment of OFM-1 with palladium acetate and followed by hydrogen reduction (Fig. S18-S22<sup>+</sup>). Pd@CZJ-6 was also prepared as a reference catalyst.

Cyclohexanol and cyclohexanone, known as K-A oil, are readily oxidized into adipic acid, an important intermediate in the manufacture of condensation polymers, such as Nylon-6 and Nylon-66.14 To evaluate the catalytic properties and stability of Pd@OFM-1 in harsh environment, catalytic phenol hydrogenation was performed in aqueous phase. Pd@OFM-1 smoothly prompted the hydrogenation reaction in the presence of AlCl<sub>3</sub> co-catalyst at 90 °C in water, which generated a high yield of 97.5% for the K-A oil products (Fig. S23<sup>+</sup>). In contrast, when Pd@CZJ-6 was used instead of Pd@OFM-1 to catalyze the reaction, the yield of K-A oil is of 81.2%, and Pd@CZJ-6 was completely decomposed during catalysis, indicating that Pd@CZJ-6 cannot tolerate the harsh catalytic conditions. No obvious leaching of the metalloporphyrin and Pd residues was observed in the reaction mixture for Pd@OFM-1 after catalysis, as confirmed by UV-Vis absorption spectroscopy and ICP-OES analysis (Fig. S24<sup>+</sup>).

Pd@OFM-1 can be simply recovered by centrifugation, and reused in the successive run with almost retained high catalytic properties. ICP-OES analysis results revealed that the Pd content in the recovered Pd@OFM-1 is identical to that in the pristine one. HRTEM image and PXRD pattern indicate no obvious aggregation of the Pd nanoparticles in the recovered catalyst (Fig. S18 and S25<sup>+</sup>). FT-IR spectrum shows that the ester groups in Pd@OFM-1 remain intact; SEM image shows that the morphology was retained; and CO<sub>2</sub> adsorption experiments indicate that the porous structure was remained after catalysis (Fig. S26-S28<sup>+</sup>). These results demonstrate that transformation of MOFs into OFMs could highly improve the stability under harsh catalytic conditions.

In summary, we developed a strategy to address the most concerned fragile issue of MOFs by substituting the labile coordination moieties with stable covalent bond-connected organic synthons, which endowed us successfully transform fragile MOF CZJ-6 into stable OFM-1. OFM-1 not only inherited the regular morphology, porosity and catalytic properties from the parent MOF CZJ-6, but also exhibits excellent stability under harsh catalytic conditions. Since there have been numerous functional MOFs that could be readily transformed into OFMs in the literature, this work should open a new avenue to develop highly stable and ordered organic materials with inherited properties from the parent OMOF<sup>10</sup>7Adderary practical applications.

#### **Conflicts of interest**

There are no conflicts to declare.

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