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Transformation of Metal-Organic Frameworks into Stable Organic Frameworks with Inherited Skeletons and Catalytic Properties

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Abstract: Metal-organic frameworks (MOFs) are an emerging class of porous materials with attractive properties; however, their practical applications are heavily hindered by the fragile nature. We report herein an effective strategy to transform fragile coordination bonds in MOFs into stable covalent organic bonds under mild annealing decarboxylative coupling reaction conditions, which results in highly stable organic framework materials. This strategy endows successfully inherit the intrinsic framework skeletons, porosity and properties of the parent MOFs in the daughter organic framework materials which exhibit excellent chemical stability under harsh catalytic conditions. Therefore, this work opens a new avenue to synthesize stable organic framework materials derived from MOFs for applications in different fields.

Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials constructed from metal ions/clusters and multidentate organic ligands that are connected by coordination bonds.¹ Different to traditional solid materials, the structures and properties of MOFs are systematically designable and tunable, which demonstrate great potential for applications in many fields, including gas storage and separation, chemical sensing and catalysis.² However, the practical applications of MOFs are heavily hindered by the fragile nature.³

It has been demonstrated that high temperature thermolysis of MOFs would result in stable nanoporous carbon (NPC) materials, consisting of in situ generated metal and/or metal oxide nanoparticles (NPs) in the pore space. Different to those supported in traditional porous carbon materials, the encapsulated nanoparticles in NPC materials pyrolyzed from MOFs are uniformly dispersed in the pore space, which exhibit attractive properties for applications as energy conversion and storage devices, and catalysts, etc.⁴ However, the extreme thermolytic conditions (up to 1000 °C) not only broke the coordination bonds but also wiped out most of the intrinsic properties of MOFs.

It has been known that thermal decomposition of transition metal benzoates or terephthalates (>300 °C) would produce volatile molecules, including benzene, benzophenone and biphenyl.⁵ The possible thermolysis mechanism evolves decarboxylation of aromatic carboxylates to form benzoyl or benzene radicals. Direct coupling of neighboring radicals would result in benzophenone, biphenyl and other products. As a result, the fragile coordination bonds between metal ions and carboxylates would be transformed into highly stable covalent organic bonds between decarboxylated carbon atoms. Therefore, we could deduce that the fragile MOFs, building from

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polydentate carboxylates and metal ions, would be transformed into stable organic framework materials under suitable thermal conditions. As expected, the metalloporphyrinic MOF CZJ-6, constructed from paddle-wheel [Cu₂(COO)₄] secondary building units (SBUs) and Cu^{II}-porphyrin ligands (Scheme S1), was successfully transformed into an organic framework material under mild annealing decarboxylative coupling reaction conditions, which presents high chemical stability under harsh catalytic conditions (Scheme 1).⁶ Different to NPC materials pyrolyzed from MOFs, the resultant organic framework material successfully inherited the structural skeleton, porosity and catalytic properties from the parent MOF CZJ-6.



Scheme 1. Schematic representation of the synthesis procedures for MOFderived organic framework material and NPC material.

The thermal behaviors of CZJ-6 were monitored by TG-MS plots under N₂ atmosphere. As shown in Figure 1A, a weight loss (16.0%) between room temperature and 150 °C is attributed to the release of encapsulated solvent molecules and water ligands in CZJ-6, which are consistent well with the release of water at 99 °C in the H₂O-MS plot. Another weight loss (16.0%) from 250 to 400 °C is very close to the calculated value (15.7 wt%) for the carboxylate groups in CZJ-6, indicating that Cu^{II}-porphyrin ligands were almost fully decarboxylated in this temperature range. There appear three peaks in both DTG and CO₂-MS plots, suggesting that the pyrolytic process consists of multiple steps for the destruction of [Cu₂(COO)₄] SBUs at elevated temperature. When the temperature is raised above 500 °C, continuous slight decay of TG curve occurs, which should be resulted from dehydrogenation and further carbonization of the organic residue. The residual mass at 800 °C (58.3 wt%) is much higher than the calculated values for pure metallic Cu (14.2 wt%) or Cu₂O (16.0 wt%) as the final products. Such a high residual mass indicates that the residue should consist of significant amount of nonvolatile organic matter.

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Figure 1. (A) TG-MS and DTG plots for CZJ-6. (B) SEM images (scale bar, 5 μ m), (C) FT-IR and (D) Raman spectra, and (E) PXRD patterns for CZJ-6 and the pyrolyzed samples of CZJ-6 at different temperatures.

According to the TG-MS results, CZJ-6 was heated at different elevated temperatures under N₂ atmosphere (denoted as CZJ-6-T; T = temperature) (Figure S1). After heating at 250 °C for 4 hours, brown solid sample of CZJ-6 was transformed into dark brown solid, which should be ascribed to the loss of water ligands and the partial reduction of copper(II) nodes. When the temperature was raised from 300 to 450 °C, the color of the solid sample was gradually changed from light violet to dark purple. Above 500 °C, the metalloporphyrin moieties began dehydrogenation and further carbonization, which was almost fully carbonized at 800 °C. These results are consistent well with the TG-MS results. SEM and TEM images showed that the octahedral morphology of CZJ-6 was well reserved under different thermal conditions (Figures 1B and S2).

UV-visible diffuse reflectance spectrum of CZJ-6 showed that the characteristic Soret band of porphyrin is located at 425 nm with two Q bands centered at 553 and 593 nm (Figure S3). The porphyrin moieties in the annealed sample remain intact under thermal treatment at 450 °C. Additionally, the broad band assigned to the aromatic moieties on Cu^{II}-porphyrin gradually shifted from 272 to 258 nm in the near-UV region upon raising the annealing temperature, which should be resulted from the loss of the carboxylate groups on benzene rings.

FT-IR spectroscopy was used to monitor the organic residual moieties in the annealed products of CZJ-6 (Figure 1C). Broad bands at 1535 and 1398 cm⁻¹ are ascribed to the asymmetric and symmetric stretching vibrations of carboxylate groups, and the peak centered at 1003 cm⁻¹ is corresponding to the characteristic Cu-N vibration band for Cu^{II}-porphyrin.⁷ No obvious change of the absorption peaks in the FT-IR spectrum

of CZJ-6-250 suggests that the structure of Cull-porphyrin and Cu-O bonds remain intact. When the annealing temperature was raised to 300 °C, the stretching vibration intensities for carboxylate groups are significantly weakened, indicating that decarboxylation reaction occurred. It is worth noting that the typical C=C stretching vibration bands at 1590 cm⁻¹ for phenyl moieties and at 1493 cm⁻¹ for Cu^{II}-porphyrin are almost intact. Upon raising the annealing temperature to 350 °C, the vibration bands for carboxylate groups almost disappeared, while Cullporphyrin remained intact when the temperature was raised to 400 °C. Additionally, the characteristic out-of-plane bending vibration bands of substituted phenyl groups at 760 and 696 cm⁻ became predominant, which further confirmed the occurrence of decarboxylation reaction. There is almost no valuable peak in the FT-IR spectrum of CZJ-6-800, which should be a result of complete carbonization of the organic moieties. In the Raman spectra, all thermally treated samples, except for CZJ-6-800, exhibit similar vibration peaks at 1580, 1386 and 402 cm⁻¹, which are assigned to the phenyl ring vibration, pyrrolic C-N symmetric stretching vibration and Cu-N stretching vibration, respectively (Figure 1D).⁸ In contrast, the presence of D and G bands centered at 1345 and 1596 cm⁻¹ indicates that CZJ-6-800 was highly graphitized.9

The thermal decarboxylation process was further monitored by PXRD patterns. When a sample of CZJ-6 was thermally treated at 250 °C for 4 h, the diffraction peaks are significantly weakened. When the annealing temperature was raised to 300 °C, the low-angle diffraction peaks almost disappeared, indicating that the long-range order of the structure of CZJ-6 did not retain. Meanwhile, there appear the characteristic diffraction peaks for Cu₂O (JCPDS, Card No. 05-0667, 36.4, 42.3 and 61.4°) and metallic Cu (JCPDS, Card No. 04-0836, 43.2 and 50.5°) in the PXRD pattern. When the temperature was raised to 800 °C, there appears a broad peak centered at 24° for the (002) planes of graphite carbon, indicating that Cu^{ll}-porphyrin moieties were carbonized.¹⁰ Induced by the uniform distribution of [Cu₂(COO)₄] SBUs in CZJ-6, the cupreous particles are homogeneously dispersed in the annealed samples with diameters of 10-20 nm as revealed by TEM images, except for CZJ-6-800 (Figure S2).

To identify the composition of the organic residues in the annealed products, the annealed samples were eluted with CHCl₃. Brown eluates were obtained from the samples of CZJ-6-300, 350, 400 and 450, and no colored product was extracted from the samples of CZJ-6-250, 500 and 800 (Figure S4). UVvis absorption spectroscopy analysis revealed that the absorption peaks of the brown eluates are identical to the characteristic absorption peaks of copper(II)-5,10,15,20tetrakis[(3,5-diphenyl)phenyl]-porphyrin (Cu-TDPPP), the decarboxylated analog of Cu^{ll}-porphyrin ligand (Scheme S2 and Figure S5). The concentration of Cu^{II}-porphyrin in the eluates gradually decreased upon raising the annealing temperature. These results indicate that decarboxylation reaction occurred at low temperature (300 °C) but decarboxylative coupling reaction requires higher temperature. Upon raising the annealing temperature, Cu^{II}-porphyrin concentration in the eluate gradually decreased. In contrast, there are intense peaks for porphyrins in the FT-IR, UV-vis and Raman spectra of the CHCl₃-eluted samples of CZJ-6-350, 400 and 450 (denoted as CZJ-6-TA) (Figures S6-S8). These results indicate that annealing treatment of CZJ-6 resulted in organic polymers, and the polymerization degree is highly dependent on the annealing temperature.

To identify the pyrolyzed fragments, we analyzed the eluates by MALDI-TOF MS (Figure 2). The m/z signals centered at 1283, 2568 and 3852 are very close to the molecular mass of mono-, di- and trimer of the decarboxylated analog Cu-TDPPP (Mw = 1283.4) for CZJ-6-300. These results provided solid evidences to prove that decarboxylative coupling reaction took place between Cu^{II}-porphyrin moieties in CZJ-6 at 300 °C. Upon raising the annealing temperature, the peak areas for highly polymerized oligomers gradually increased (Figure S9). These results suggest that the decarboxylative coupling reaction between metalloporphyrins is depending on the annealing temperature. However, excessively higher temperature resulted in partial bond breaking between the aromatic substituents and porphyrin cores. This conclusion was proved by monitoring the shoulder peaks with difference of m/z 229, which were derived from the loss of the aromatic substituents on Cu^{II}-porphyrin. The shoulder peaks become stronger in the MALDI-TOF MS for CZJ-6-450, indicating that there occurred severe cracking of the metalloporphyrin residues at higher temperature. These results proved that Cu^{II}-porphyrin ligands in CZJ-6 underwent decarboxylative coupling reaction to form cross-linked organic polymers under annealing treatment conditions, and the optimized temperature should be 400 °C for CZJ-6.



Figure 2. MALDI-TOF MS spectra of the eluates extracted from the annealed samples of CZJ-6 at different temperatures.

To get detailed information of the metalloporphyrin residues in the annealed samples of CZJ-6, the encapsulated metallic Cu and Cu₂O NPs were etched with FeCl₃/HCl solution, which resulted in mesopores in the etched samples (denoted as CZJ-6-TB; Figures S10 and 11). The surface chemical compositions of the etched samples were characterized by monitoring the electronic states of Cu, N and C in XPS spectra (Figure 3). The calculated atomic ratios of N/Cu in CZJ-6-350B and 400B are very close to 4:1, which are consistent well with the value in Cullporphyrin (Table S1). The N/Cu ratio increased under higher temperature due to partial decomposition of Cu^{II}-porphyrin. In the high-resolution Cu2p XPS spectra, the absence of Cu2p_{3/2} peaks for metallic Cu (932.7 eV) and Cu₂O (932.5 eV) further proved sufficient etching of the metallic Cu and Cu₂O species.¹¹ Additionally, except for CZJ-6-800B, all samples exhibit a dominant peak at 935.2 eV for Cu2p_{3/2}, associating with a broad satellite peak centered at ~943 eV, which match well with those signals for Cu^{II}-porphyrin.¹² The missing of the Cu2p_{3/2} peak at 935.2 eV in the XPS of CZJ-6-800B indicates that Cu^{II}-porphyrin was completely carbonated at 800 °C. In the N1s XPS spectra, two peaks centered at 398.7 and 399.9 eV are corresponding to Cu-N₄ and pyrrolic nitrogen species, respectively.¹³ As expected, the pyrrolic nitrogen became the predominant species at 800 °C. along with a new peak at 398.4 eV that belongs to the pyridinic nitrogen. The C1s deconvoluted scan showed two representative domains with binding energies at 284.8 and 286.7 eV, which attribute to the C-C and C-N bonds in Cullporphyrin, respectively.¹⁴ The shift of the binding energy of C-C bonds to 284.6 eV implies the formation of carbonized material at 800 °C. These conclusions were further proved by FT-IR, UVvis and Raman spectroscopy (Figures S12-S14).



Figure 3. (A) XPS survey spectra, high-resolution (B) Cu2p, (C) N1s and (D) C1s XPS spectra of CZJ-6-TB.

Transformation of MOFs into organic framework materials would result in tuning the hydrophilic/hydrophobic nature. The contact angle of a water droplet on pristine CZJ-6 was estimated to be 17°, which was dramatically increased to 102° for CZJ-6-400B, indicating that the annealing treatment overturned the surface properties from hydrophilic CZJ-6 to hydrophobic

organic framework material CZJ-6-400B (Figure S15). The hydrophobic nature is important in catalysis, which would protect the active sites from toxic hydrophilic species.¹⁵

N₂ sorption measurements were carried out to study the textual characters of MOF CZJ-6, organic framework material CZJ-6-400B and NPC material CZJ-6-800B (Figure S16). CZJ-6, CZJ-6-400B and CZJ-6-800B take up 530, 103 and 134 cm³ g⁻¹ N₂ at 77 K and 1 bar, resulting microporous BET surface areas of 394, 145 and 415 m²/g, respectively. Pore size distribution analysis showed that there are two kinds of micropores for CZJ-6-400B (1.15 and 1.30 nm) and CZJ-6-800B (1.05 and 1.25 nm) (Figure S17). These values are very close to those of MOF CZJ-6 (1.20 and 1.35 nm), which suggest that the pore characters of CZJ-6 were successfully inherited in the daughter materials CZJ-6-400 and CZJ-6-800. The slight shrinkage of pore sizes should be resulted from decarboxylation of metalloporphyrin ligands and further carbonization at elevated temperature. CO₂ adsorption isotherms showed that CZJ-6, CZJ-6-400B and CZJ-6-800B take up 51.9, 68.3 and 110.2 mg/g CO₂ at 273K, respectively (Figure S18). To get better understanding of the adsorption behaviors, isosteric heats of CO₂ adsorption (Q_{st}) for these materials were calculated based on Clausius-Clapeyron equation from CO₂ adsorption isotherms at 273 and 298 K.¹⁶ At the initial stage, the Q_{st} value for CZJ-6-400B (26.4 KJ/mol) is higher than those for CZJ-6 (21.5 KJ/mol) and CZJ-6-800B (22.9 KJ/mol). These results indicate that there are stronger interactions between the pore surfaces of CZJ-6-400B and CO₂ molecules at low pressure, which might be ascribed to the hydrophobic pore nature and the binding affinity of CO₂ for the open porphyrin copper(II) sites.¹²

To evaluate the stability and the accessibility of Cullporphyrin sites in the organic framework materials, we examined the catalytic properties of CZJ-6-TB in cross dehydrogenative coupling (CDC) esterification reaction between C(sp³)-H and carboxylic acid.¹⁷ As shown in Table S2, molecular Cu-TDPPP catalyzed the CDC esterification reaction between benzoic acid and 1,4-dioxane to afford ester product with 75% yield. However, Cu-TDPPP almost degraded after catalysis, because of selfoxidative reaction.^{2g} When MOF CZJ-6 was used as a catalyst, after catalysis. solid was completely dissolved the accompanying degradation of Cu^{II}-porphyrin. In contrast, the organic framework materials CZJ-6-TB exhibited high stability in catalyzing the CDC reaction. The catalytic activity of CZJ-6-400B (92% ester yield) is also much higher than that of MOF catalyst CZJ-6 (73% yield). Because low annealing temperature would result in low-degree polymerization, CZJ-6-350B was partially decomposed when catalyzing the CDC reaction, leading to low ester yield (44%). However, excessively higher temperature let Cu^{II}-porphyrin suffer from severe decomposition, resulting in decreased ester yields (46-62%), while the carbonized material CZJ-6-800 only resulted in 8% ester yield. No obvious leaching of Cu^{II}-porphyrin was observed in the supernatants for CZJ-6-TB (T \ge 400 °C) after catalysis as confirmed by UV-vis spectra and ICP-OES (Figures S19 and S20). FT-IR spectrum showed that Cu^{II}-porphyrin in CZJ-6-400B remained intact after catalysis (Figure S21). The above results revealed that the chemical stability of organic framework material CZJ-6-400B is much higher than that of the parent MOF

and the catalytic properties are much superior to those of the carbonized material.

In summary, we developed an effective strategy to transform instable MOFs into stable organic framework materials under decarboxylative coupling reaction conditions. As an illustrated example of CZJ-6, the fragile coordination bonds were replaced with stable covalent C-C bonds under mild annealing conditions, which resulted in a highly stable organic framework material with inherited framework skeleton, porosity and catalytic properties from the parent MOF. Enlightened by the results of this work, we expect that numerous highly stable organic framework materials with inherited properties from the parent MOFs will be created for applications in various fields.

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Keywords: Metal-organic frameworks • Organic framework materials • Decarboxylative coupling reaction • Coordination bonds • Covalent bonds

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An effective strategy is developed to transform fragile coordination bonds in metal-organic frameworks (MOFs) into stable covalent organic bonds under mild annealing decarboxylative coupling reaction conditions, which results in highly stable organic framework materials with inherited framework skeletons, porosity and properties from the parent MOFs for catalytic applications under harsh conditions.



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