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Ambient Aqueous-Phase Synthesis of Covalent Organic Frameworks for Degradation of Organic Pollutants

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Supporting Information Placeholder

ABSTRACT: The development of a mild, low cost and green synthetic route for covalent organic frameworks (COFs) is highly desirable in order to open road for practical uses of this new family of crystalline porous solids. Herein, we report a general and facile strategy to prepare a series of microporous or mesoporous COFs in aqueous systems under ambient temperature and pressure . This synthesis route not only produces highly crystalline and porous COFs, but also can be carried out with a high reaction rate (only 30 mins), high yields (as high as 93%) and large-scale preparation (up to 5.0 g). Furthermore, a Fe(II)-doped COF shows an impressive performance in the oxidative degradation of organic pollutants in water. This research thus opens a promising pathway to large-scale green preparation of COFs and their potential application in environmental remediation.

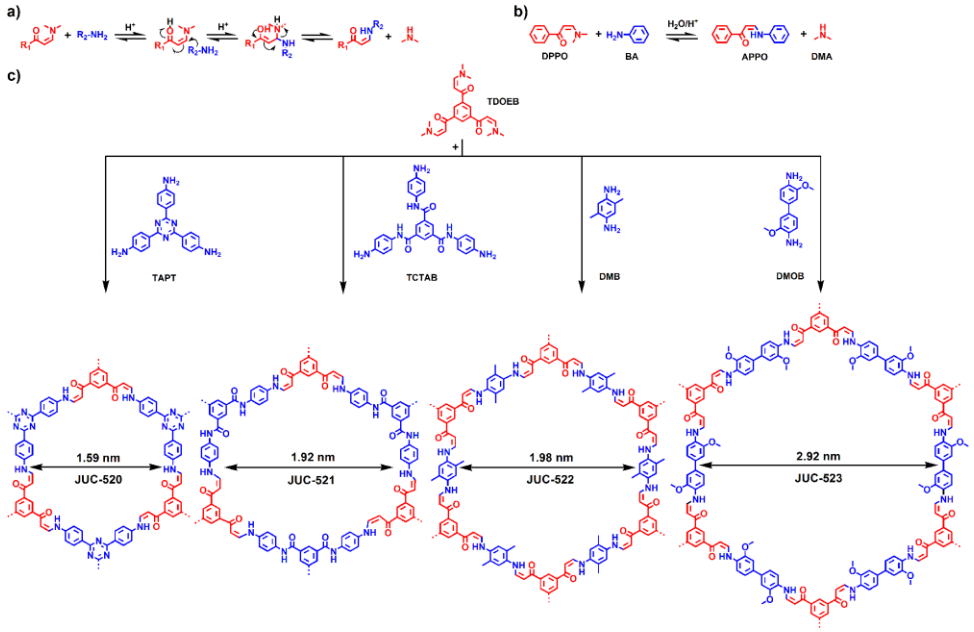
Covalent organic frameworks (COFs) as a new class of fascinating crystalline porous materials are composed of light elements, such as C, H, N, B and O, and connected by strong covalent bonds.[1-6] Due to their well-defined pore geometry, high surface area, and tunable framework composition, COFs hold great promise in a variety of potential applications, including gas adsorption and separation,[7-9] heterogeneous catalysis,[10-12] optoelectronic and electrical energy storage devices,[13-15] and several others.[16-23] Over the past decade, COFs have been obtained by some reversible chemical reactions, typically the formation of boroxine,[1] boronate-ester,[24] imine,[25] imide,[26] and alkene linkage.[27] However, almost all by-products of these chemical reactions are water molecules; thus, the classical synthesis of COFs so far is restricted to the solvothermal synthesis, which is implemented in sealed tubes with raising temperatures and pressures, and causes complicated operations, high energy expenditure, and releases volatile organic compounds (VOC). Recently, we exploited a fast, ambient temperature and pressure ionothermal synthesis of COFs;[28] however, due to the high cost of ionic liquid, this method will hinder its application for large-scale preparation of COFs. Therefore, the development of a simple, low cost and green synthetic strategy for COFs is still highly beneficial.

Taking these considerations in mind, we herein report a general and and environmentally benign approach to construct microporous and mesoporous COFs ithe aqueous systems under ambient conditions. Based on this method, a series of highly crystalline COFs with pore sizes from 1.59 to 2.92 nm, denoted JUC-520 (JUC = Jilin University China), JUC-521, JUC-522 and JUC-523 were successfully prepared. Noteworthy, JUC-521 can be obtained in a short period of time (about 30 mins) with a high yield (> 93%) and large-scale for a COF material preparation (up to 5.0 g). Furthermore, a metal-doped COF, JUC-521-Fe, shows an impressive performance in the degradation of toxic organic pollutants in water. To the best of our knowledge, this study is the first case for fast and highly efficient synthesis of crystalline COF materials under ambient temperature and pressure aqueous-phase system.

Our stragety for green preparing COFs in the ambient aqueous system involves the Michael addition-elimination reaction of β-ketoenamines and aromatic amines. Scheme 1a shows the mechanistic pathway of this reaction. Different from previous chemical reactions, the by-products based on this reversible process are organic amines, and thus the preparation of COFs can be carried out in aqueous solution with high yields. Based on the strategy, the model reaction is implemented between 3-(dimethylamino)-1-phenyl-2-propen-1-one (DPPO) and benzenamine (BA) to form 3-anilino-1-phenyl-2-propen-1-one (APPO) and a by-product, dimethylamine (DMA, Scheme 1b). In the pursuit of COFs, 1,3,5-tris(3-dimethylamino-1-oxoprop-2-en-yl)benzene (TDOEB) is chosen as a C_3-symmetric β-ketoenamine-based node. Thus, the condensation of TDOEB and two other C_3-symmetric knots, 1,3,5-tris(4-aminophenyl) triazine (TAPT) and 1,3,5- tricarboxylic acid-tris(4-amino-phenyl-amide) benzene (TCTAB), or two C_2-symmetric linkers, 2,5-dimethyl-1,4-benzenediamine (DMB) and 3,3'-dimethoxybenzidine (DMOB), will give hexagonal microporous JUC-520 (1.59 nm), JUC-521 (1.92 nm) and JUC-522 (1.98 nm) as well as mesoporous JUC-523 (2.92 nm), respectively (Scheme 1c).

Typically, the syntheses were carried out by suspending TDOEB and TAPT, TCTAB, DMB or DMOB in aqueous solution with acetic acid as the catalyst, and followed by keeping at ambient temperature and pressure to produce highly crystalline solids. All COFs can be synthesized within 8 hrs, which is substantially shorter than those from the traditional solvothermal method (3-7 days). To further explore the ambient aqueous-phase synthesis of COFs, JUC-521 was selected

Scheme 1. Strategy for ambient aqueous-phase synthesis of COFs[a]



[a](a) Mechanistic pathway of Michael addition-elimination reaction of β-ketoenamines and aromatic amines. (b) Model reaction between DPPO and BA to form APPO and DMA. (c) Condensation of TDOEB and TAPT, TCTAB, DMB or DMOB to give JUC-520, JUC-521, JUC-522 or JUC-523 with different pores, respectively.

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as an example to study the influence of different reaction conditions, including temperature, the concentration of catalyst, and reaction time (Figures S1-3). Remarkably, highly crystalline JUC-521 can be obtained at room temperature in 6 M acetic acid aqueous solution for only 30 mins, accompanied by a high yield (93%). Moreover, scale-up synthesis of JUC-521 (5.0 gram) was also carried out under the same conditions, which exhibits a similar result (Figure S4). Thus, this simple, low cost and green scale-up process suggests that mass production of COFs can be reached based on this reaction strategy.

Structural features of new COFs were determined by complementary methods. The crystal morphology was observed by scanning electron microscopy (SEM). Relatively small ca. 0.2 μm building complex aggregates are charaaacccteriiistic for all samples (Figures S5-8). Fourier transform infrared (FT-IR) spectra displayed the disappearance of characteristic N–H stretching of the primary amines (~ 3450 cm^{-1}) and N–CH_3 stretching of TDOEB (1438 cm^{-1}), which confirms that the reaction has taken place (Figures S9-13). The solid state ^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra further demonstrated that all COFs showed a characteristic signal at ~145 ppm, corresponding to the carbon of secondary amine bonds (Figures S14-17). According to the thermogravimetric analysis (TGA, Figures S18-21), these

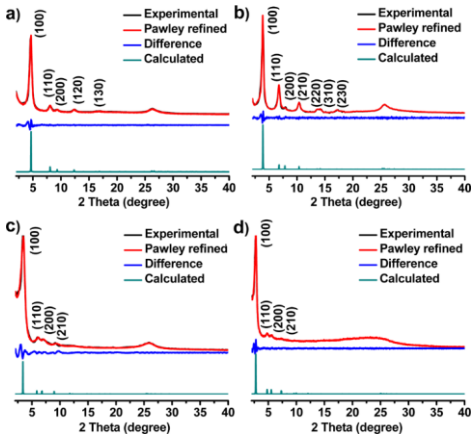


Figure 1. PXRD patterns of JUC-520 (a), JUC-521 (b), JUC-522 (c) and JUC-523 (d).

COFs are thermally stable up to 350 °C. Furthermore, their crystalline structures can be preserved in a variety of organic solvents as well as acid (1.0 M HCl) and base (1.0 M NaOH) aqueous solutions (Figures S22-25).

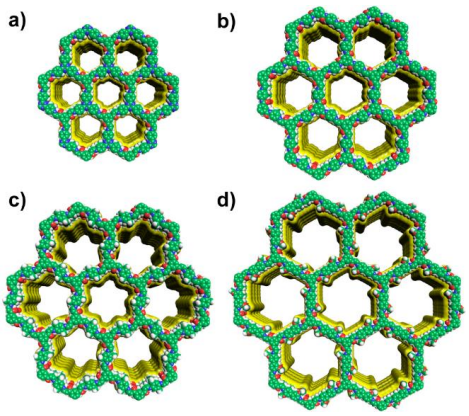


Figure 2. Structural representations of JUC-520 (a), JUC-521 (b), JUC-522 (c), and JUC-523 (d). C, green; H, gray; N, blue; O, red.

The unit cell parameters of COFs were resolved by the powder X-ray diffraction (PXRD) patterns combined with structural simulations. After a geometrical energy minimization by using the Materials Studio software package,[29] their unit cell parameters based on the AA stacking boron nitride net (**bnn**) were obtained ($a = b = 22.4795$ Å, $c = 3.5114$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ for JUC-520; $a = b = 26.4476$ Å, $c = 3.5064$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ for JUC-521; $a = b = 30.0949$ Å, $c = 3.5075$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ for JUC-522; and $a = b = 36.9035$ Å, $c = 3.5605$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ for JUC-523, respectively). The experimental PXRD peaks were in good agreement with the simulated ones (Figure 1). Furthermore, full profile pattern matching (Pawley) refinements were applied. Peaks at 4.66, 8.07, 9.31, 12.38 and 16.64° 2θ for JUC-520 correspond to the (100), (110), (200), (120) and (130) Bragg peaks of space group *P*-6 (No. 174); peaks at 3.87, 6.76, 7.89, 10.36, 13.56, 14.19 and 17.21° 2θ for JUC-521 correspond to the (100), (110), (200), (210), (220), (310) and (230) Bragg peaks of space group *P*-6 (No. 174); peaks at 3.41, 6.07, 7.05 and 9.21° 2θ for JUC-522 correspond to the (100), (110), (200) and (210) Bragg peaks of space group *P*6 (No. 168); and peaks at 2.77, 4.79, 5.57 and 7.31° 2θ for JUC-523 correspond to the (100), (110), (200) and (210) Bragg peaks of space group *P*6 (No. 168), respectively. The refinement results show unit cell parameters very close to the predictions with ideal agreement factors (ωRp = 3.63% and Rp = 2.52% for JUC-520; ωRp = 5.34% and Rp = 3.92% for JUC-521; ωRp = 3.77% and Rp = 2.45% for JUC-522; and ωRp = 3.91% and Rp = 2.55% for JUC-523, respectively). In contrast, the alternative staggered 2D arrangements (AB stacking) and simulated PXRD data showed significant deviations compared with the experimental ones (Figures S26-37). On the basis of these results, the obtained COFs were proposed to have the expected frameworks with hexagonal micropore for JUC-520, JUC-521 and JUC-522 as well as mesopore for JUC-523 (Figure 2).

The porosity and the textural characteristics of the synthesized series of COFs were determined by nitrogen (N_2) adsorption-desorption isotherms at 77 K. As shown in Figure 3a-c, a sharp gas uptake can be observed at low pressure (below 0.05 P/P_o) for JUC-520, JUC-521 and JUC-522 respectively, which reveals their microporous nature. On the contrary, JUC-523 showed a rapid uptake at a low pressure of $P/P_o < 0.05$, followed by a second step between $P/P_o = 0.1$ and 0.2 (Figure 3d), which is the characteristic of mesoporous materials. The Brunauer-Emmett-Teller (BET) surface areas of these COFs are 976 $m^2 g^{-1}$ for JUC-520, 1127 $m^2 g^{-1}$ for JUC-521, 1182 $m^2 g^{-1}$ for JUC-522, and 1435 $m^2 g^{-1}$ for JUC-523, respectively (Figures S38-41), which are much higher than those of previous COFs obtained via Michael addition-elimination of β-ketoenols with amines (~ 500 $m^2 g^{-1}$).[30] The total pore volume was calculated at $P/P_o = 0.9$ to be 0.56 $cm^3 g^{-1}$ for JUC-520, 0.67 $cm^3 g^{-1}$ for JUC-521, 0.69 $cm^3 g^{-1}$ for JUC-522, and 0.88 $cm^3 g^{-1}$ for JUC-523. Their pore-size distributions were estimated by nonlocal density functional theory (NLDFT), and showed the narrow pore width (1.53 nm for JUC-520, 1.87 nm for JUC-521, 1.95 nm for JUC-522, and 2.88 nm for JUC-523, Figures S42-45), which is in a good match with those from their crystal structures.

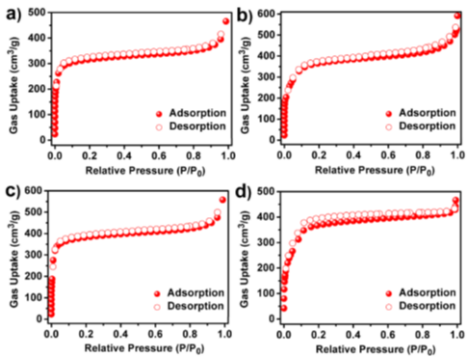


Figure 3. N_2 adsorption-desorption isotherms of JUC-520 (a), JUC-521 (b), JUC-522 (c), and JUC-523 (d).

Encouraged by the high surface area and abundant β-ketoenamine units, Fe(II)-loaded JUC-521 (JUC-521-Fe) was subsequently acquired by immersing the pristine material in a methanol solution of $FeSO_4$. The ferrous complexation of JUC-521 could be easily observed by the color change (Figure S46). Furthermore, energy dispersive X-ray spectra (EDS) mapping image showed the uniform distribution of Fe species in the crystals (Figure S47). FT-IR spectroscopy revealed the strong chelation interaction between β-ketoenamine units and Fe(II) ions based on the shift of the IR bands for the carbonyl groups from 1662 to 1653 cm^{-1} and secondary amine bond from 1221 to 1212 cm^{-1} (Figure S48). The ICP analysis of JUC-521-Fe displayed that most of the β-

ketoenamine units have been coordinated by metal ions (see Section S1 in SI). The porosity of JUC-521-Fe was also evaluated by N_2 adsorption analysis, which pointed out the adsorption capacity slightly lower than that of the parent material (Figure S49). In addition, the PXRD pattern of JUC-521-Fe indicated that the pristine framework was preserved after the metal incorporation (Figure S50).

We further explored the application of JUC-521-Fe in the degradation of organic pollutants in aqueous medium based on Fenton reaction. It is well-known that Fenton reaction, one of the most popular advanced oxidation processes (AOP), involves an in-situ generation of hydroxyl radicals (•OH or HO_2•) from hydrogen peroxide (H_2O_2) activated by ferrous ions, to degrade hazardous organic compounds.[31-33] However, the traditional Fenton reaction was carried out with homogeneous catalysts, which is strongly limited because of poor recyclability and high energy consumption. Herein, the JUC-521-Fe was studied as a heterogeneous Fenton catalyst for effective degradation of organic pollutants due to their high surface area, chemical stability, and abudent catalytic sites. Typically, rhodamine 6G (Rh6G), a famous toxic dyestuff, was used as a model substrate. As shown in Figure 4a, nearly all of Rh6G was degraded in 1.5 hrs in the presence of JUC-521-Fe and H_2O_2. As a comparison, H_2O_2, metal-free pristine material (JUC-521/H_2O_2) and $FeSO_4/H_2O_2$ were also tested under the same conditions, respectively. Much lower degradation abilities for Rh6G were observed (Figure 4b-e), such as only 4% for H_2O_2, 19% for JUC-521/H_2O_2 and 21% for $FeSO_4/H_2O_2$ within 1.5 hrs, which further demonstrated the high performance of JUC-521-Fe in the degradation of organic pollutants. PXRD patterns confirmed the retained crystallinity of JUC-521-Fe after the catalytic reaction (Figure S51). Furthermore, ICP analysis revealed that almost no ferrous ions leached during the degradation (see Section 1 in SI). Thus, as a heterogeneous catalyst, JUC-521-Fe can be reused for at least three times almost without loss of activity (Figure 4f).

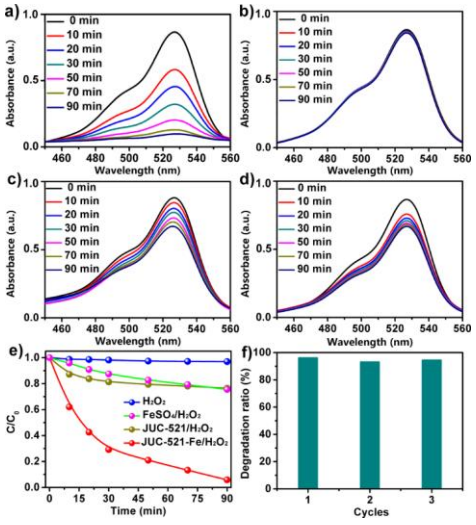


Figure 4. UV-vis spectra of Rh6G aqueous solution in the presence of JUC-521-Fe/H_2O_2 (a), H_2O_2 (b), $FeSO_4/H_2O_2$ (c) and JUC-521/H_2O_2 (d), respectively. (e) Comparison of the degradation abilities of Rh6G for different materials. (f) Recyclability study of JUC-521-Fe.

In conclusion, we have for the first time achieved a mild, low cost and green process to prepare a number of microporous or mesoporous COFs under ambient synthesis condition employing aqueous systems. This strategy not only yields highly crystalline and porous COFs, but also offers the advantage of a high reaction rate (30 mins), impressive yield (93%) and scalability potential (5.0 g). Moreover, the metal-doped COF, JUC-521-Fe, shows great performance and reusability in the degradation of toxic organic pollutants in water. This research thus provides a promising synthetic strategy to large-scale production of COFs, and expands their potential application in the environmental remediation.

ASSOCIATED CONTENT

Supporting Information

Methods and synthetic procedures, SEM, FTIR, solid state ^{13}C NMR, TGA, BET plots, pore size distribution, characterization of JUC-521-Fe, and unit cell parameters. This material is available free of charge via the internet at http://pubs.acs.org.

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Author Contributions

§These authors contributed equally.

Notes

The authors declare no competing financial interests.

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