Communication

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Three-Dimensional Mesoporous Covalent Organic Frameworks through Steric Hindrance Engineering

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Supporting Information Placeholder

ABSTRACT: The development of three-dimensional (3D) covalent organic frameworks (COFs) with large pores and high surface areas is of great importance for various applications. However, it remains a major challenge due to the frequent structural interpenetration and pore collapse after the removal of guest species situated in the pores. Herein, we report for the first time a series of 3D mesoporous COFs through a general method of steric hindrance engineering. By placing methoxy and methyl groups strategically on the monomers, we can obtain non-interpenetrated 3D COFs of diamondoid structures with permanent mesopores (up to 26.5 Å) and high surface areas (> 3000 m²/g), which are far superior to those of reported conventional COFs with the same topology. This work thus opens a new avenue to create 3D large-pore COFs for potential applications in adsorption and separation of large inorganic, organic, and biological molecules.

Covalent organic frameworks (COFs) are a class of crystalline porous polymers that are composed of light elements (typically H, B, C, N and O) linked by covalent bonds.1-4 They feature well-defined pores and high specific surface areas, and thus hold great promises in a variety of uses, such as adsorption and separation,5-7 organic electronics,8-12 heterogeneous catalysis,13-17 and some others.18-23 Over the past decade, most of COF materials, however, were exploited based on two-dimensional (2D) structures with characteristic eclipsed AA stacking. Three-dimensional (3D) COFs have recently attracted widespread attentions owing to their unique pores and excellent properties.24-32 Notably, the urgent issues emerging from the construction of 3D large-porous COFs include the frequent structural interpenetration, restricting the pore size, and pore shrinkage or collapse after the guest removal. For example, Wang and Zhang et al. have proven the reversible crystal-transformation and dynamic response in an interpenetrating 3D COF, LZU-301, which has pore size stretchable from 5.8 × 10.4 Å to 9.6 × 10.4 Å by the change of guests.33 Recently, by extending the linear linkers, we obtained the most interpenetrated framework for 3D COFs reported, 3D-IL-COF-3 with 11-fold interpenetrated net, exhibiting a small pore size of 12.4 Å and relatively low BET surface area of 870 m²/g.34 Thus, the expansion of 3D COFs with large pores and high surface areas is of importance but remains a tremendous challenge.

Herein, we report a series of 3D mesoporous COFs (3D-Meso-COFs) with unusual non-interpenetrated diamondoid (dia) topology based on the enhanced steric hindrance strategy. By employing methoxy-modified tetrahedral building unit and changing substituents (methyl groups) of linear building units, we can control these 3D-Meso-COFs successfully from pore shrinkage to partial and

Scheme 1. Strategy for preparing 3D mesoporous COFs

(a) Interpenetrated microporous framework constructed from undecorated edges. (b) Non-interpenetrated mesoporous framework built up from partially decorated edges, in which the pore shrinkage or collapse will happen after the guest removal. (c) Non-interpenetrated mesoporous framework created by highly decorated edges, in which the pores can be maintained entirely after the guest removal.
full pore maintenance. Remarkably, one of the obtained COF materials shows stable mesopore with a size of 26.5 Å and high BET surface area of 3023 m$^2$ g$^{-1}$, which are much higher than those of reported COFs with the same network. To the best of our knowledge, this study represents the first case of 3D mesoporous COF with non-interpenetrated dia topology.

Our strategy for the preparation of 3D-Meso-COFs is based on steric hindrance engineering of the monomers. Although the use of steric hindrance to control crystal structures of 2D COFs has been reported,\textsuperscript{35,36} there are significant differences in 3D frameworks, and three possible situations can occur: (a) interpenetrated microporous framework constructed from undecorated edges; (b) non-interpenetrated mesoporous framework built up from partially decorated edges, in which the pore shrinkage or collapse will happen after the guest removal; and (c) non-interpenetrated mesoporous framework created by highly decorated edges, in which the pores can be maintained entirely after the removal of guest species (Scheme 1). To implement this strategy, we firstly designed a novel methoxy-modified monomer, 2,2',7,7'-tetramethoxy-9,9'-spirobi[fluorene]-3,3',6,6'-tetracarbaldehyde (TMSFTA), as a tetrahedral building unit (Figure 1a). Further, we chose three linear linkers, 4,4'-diaminobiphenyl (DABP, Figure 1b) without any substituents, 4,4'-diamino-2,2'-dimethylbiphenyl (DADMBP, Figure 1c) with two methyl groups, and 4,4'-diamin-2,2',6,6'-tetramethylbiphenyl (DATMBP, Figure 1d) with four methyl groups. The condensation of TMSFTA and DABP, DADMBP or DATMBP produced a series of 3D COFs, termed JUC-550, JUC-551 and JUC-552 respectively (JUC = Jilin University China, Figure 1e-g). In light of the linking of tetrahedral and linear building units and their steric hindrance, these structures are expected to be the non-interpenetrated dia nets (Figure 1h and 1i).\textsuperscript{37}

Typically, the syntheses were carried out by suspending TMSFTA with DABP, DADMBP or DATMBP into the solvent of dioxane or mesitylene in the presence of acetic acid, followed by heating at 120 °C for 3 days to give crystalline solids at high yields of 85% for JUC-550, 83% for JUC-551, and 87% for JUC-552, respectively. These products were stable in various organic solvents, such as acetone, hexanes, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO).

The structural characteristics of new COFs were determined by a series of complementary methods. The crystal morphology was observed by scanning electron microscopy (SEM), which shows isometric crystals (Figures S1-3). Fourier transform infrared (FT-IR) spectra exhibited new peaks around 1617 cm$^{-1}$ for JUC-550, 1612 cm$^{-1}$ for JUC-551 and 1617 cm$^{-1}$ for JUC-552, corresponding to typical

![Figure 1](image1.png)

**Figure 1.** (a-d) Molecular structures of TMSFTA (a) as a tetrahedral building unit and DABP (b), DADMBP (c) and DATMBP (d) as a linear building unit, respectively. (e-g) 3D mesoporous COFs, denoted as JUC-550 to -552, constructed by the condensation reaction of TMSFTA and DABP, DADMBP or DATMBP. (h and i) Single dia network and 3D non-interpenetrated dia structure with decorated edges in these obtained COFs.

![Figure 2](image2.png)

**Figure 2.** PXRD patterns of the acetone-solvated samples for JUC-550 (a), JUC-551 (b) and JUC-552 (c).
C=N stretching vibrations (Figures S4-6). Furthermore, the solid state $^{13}$C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra confirmed the presence of carbon from the C=N bond at 158 ppm for JUC-550, 161 ppm for JUC-551, and 159 ppm for JUC-552, respectively (Figures S7-9). According to the thermogravimetric analysis (TGA), these COFs were thermally stable up to 350 °C under nitrogen (Figures S10-12).

Figure 3. Structural representations of JUC-550 (a), JUC-551 (b) and JUC-552 (c). C, blue; H, gray; N, green; O, pink. The spheres with different colors represent the pores in 3D-Meso-COFs.

The structures of 3D-Meso-COFs were resolved by powder X-ray diffraction (PXRD) combined with structural simulations (Figure 2). After a geometrical energy minimization by using the Materials Studio software package based on the non-interpenetrated dia net, the unit cell parameters were obtained ($a = b = 27.5727$ Å, $c = 74.5020$ Å and $\alpha = \beta = \gamma = 90^{\circ}$ for JUC-550; $a = b = 27.8446$ Å, $c = 74.6490$ Å and $\alpha = \beta = \gamma = 90^{\circ}$ for JUC-551; and $a = b = 27.8435$ Å, $c = 74.6423$ Å and $\alpha = \beta = \gamma = 90^{\circ}$ for JUC-552). The simulated PXRD patterns were in good agreement with the experimental results. Full profile pattern matching (Pawley) refinements were carried out on the experimental data from solvated samples. Peaks at 3.35, 4.98, 6.74, 7.53, 10.07, 11.96 and 13.65° for JUC-550 correspond to the (101), (112), (200), (202), (301), (224), (314) and (402) Bragg peaks of the same space group, respectively. The refinement results yielded unit cell parameters nearly equivalent to the predictions with good agreement factors ($R_p = 2.58\%$ and $\omega R_p = 3.77\%$ for JUC-550; $R_p = 3.98\%$ and $\omega R_p = 5.06\%$ for JUC-551; and $R_p = 2.59\%$ and $\omega R_p = 3.81\%$ for JUC-552). Some alternative structures, such as 2- and 3-fold interpenetrated dia nets, were also set up; however, their simulated PXRDs did not match to the experimental ones (Figures S13-24). Thus, the obtained COFs were proposed to have the expected mesoporous frameworks with non-interpenetrated dia topology (Figure 3). Notably, a similar tetrahedral knot, 3,3',6,6'-tetramine-9,9'-spirobifluorene, has been employed to construct another 3D COFs, SP-3D-COFs with dia nets; however, these COFs were highly interpenetrated microporous frameworks due to the absence of methoxy groups.39

Figure 4. $N_2$ adsorption-desorption isotherms for JUC-550 (a), JUC-551 (b) and JUC-552 (c).

It should be noted that some peaks after $2\theta > 15^{\circ}$ in JUC-550 were violent, while those of JUC-551 showed low intensity. On the contrary, the corresponding peaks of JUC-552 were very weak, revealing the impact of different substituents on the crystalline frameworks. Furthermore, after activation under vacuum at 100 °C for 12 h, the first peak disappeared in JUC-550, while showed a slight variation in...
JUC-551. However, JUC-552 exhibited highly enhanced intensity for its first peak (2θ = 3.34°), which means its mesopores have been well retained. Notably, this process can be recovered after immersing these samples into organic solvents, such as acetone (Figures S25–27). These results demonstrated clearly that a guest-induced reversible crystal-structure transformation took place in JUC-550, however, the linker with high substituents, DATMPB, gives rise to JUC-552 with increased structural rigidity due to the strong steric hindrance, and thus can effectively eliminate the dynamic behavior of frameworks.\(^{40}\)

The influence of steric hindrance in activated 3D-Meso-COFs was further proved by nitrogen (N\(_2\)) adsorption-desorption isotherms at 77 K. As can be seen in Figure 4a, a rapid uptake at low relative pressure as a characteristic of micropore material was observed for JUC-550, which reveals a pore shrinkage. JUC-551 showed a sharp uptake at a low pressure of \(P/P_0 < 0.05\), followed by two other steps at \(P/P_0 = 0.1\) and 0.4, which means its partial pore shrinkage and the presence of different pores. On the contrary, JUC-552 had a high adsorption at a low pressure of \(P/P_0 < 0.05\), along with a second step at \(P/P_0 = 0.3\), which is a typical characteristic of mesoporous materials. All curves of 3D-Meso-COFs showed desorption hysteresis, which can be attributed to the effect of substituents and textural mesopores from the agglomeration of COF microcrystals.\(^{41}\) The Brunauer-Emmett-Teller (BET) equation was carried out, and JUC-552 had a much higher surface area (846 \(m^2g^{-1}\)) for JUC-550, 1728 \(m^2g^{-1}\) for JUC-551, and 3023 \(m^2g^{-1}\) for JUC-552). Furthermore, their pore-size distributions calculated by nonlocal density functional theory (NLDFT) demonstrated the micropores with the size of 10.6 Å for JUC-550 and two kinds of pores with the sizes of 14.0 Å and 22.0 Å for JUC-551. Notably, JUC-552 showed the mesopores with the dominant size of 26.5 Å, which is in good agreement with that of the proposed model (26.0 Å), indicating that the pores can be maintained after the guest removal.

As a comparison, we summarized the BET surface areas and pore sizes of current reported COFs with \textbf{dia} topology in Figure 5 and Table S1.\(^{31,42-44}\) Remarkably, the pore size of JUC-552 (26.5 Å) is far superior to those of reported materials, such as 4.0 Å for COF-300-C7,\(^{42}\) 12.0 Å for COF-320,\(^{43}\) 13.0 Å for JUC-508,\(^{32}\) and 13.5 Å for 3D-IL-COF.\(^{31}\) The BET surface area of JUC-552 (3023 \(m^2g^{-1}\)) is also much higher than those of reported COFs, such as 517 \(m^2g^{-1}\) for 3D-IL-COF-1,\(^{32}\) 864 \(m^2g^{-1}\) for 3D-HNU-5,\(^{44}\) 1762 \(m^2g^{-1}\) for COF-DL229,\(^{45}\) and 2403 \(m^2g^{-1}\) for PI-COF-4.\(^{41}\) These data revealed that the enhanced steric hindrance is a promising strategy for the construction of COF materials with large pores and high specific surface areas.

To further demonstrate the adaptability of the mesopores in 3D-Meso-COFs, we explored the inclusion of a large dye molecule, Rh6G with the kinetic diameter of 14.5 \(\times 16.0\) Å. Typically, the samples of 3D-Meso-COFs were immersed in an aqueous solution of Rh6G (0.1 mM). The amount of Rh6G in the supernatant was monitored through UV-Vis spectrophotometry, and the characteristic absorbance at 526 nm was measured over a period of 60 mins. As showed in Figures S35 and S36, the results displayed a continuous decrease of the amount of Rh6G in solvated 3D-Meso-COFs due to their maintained mesopores. As a control, a similar experiment was carried out with COF-320, whose pore size (12.0 Å) is smaller than Rh6G. Obviously, no obvious reduction in absorbance was found (Figures S35 and S36), confirming the absence of Rh6G adsorbed in COF-320.

In conclusion, we designed and synthesized a series of 3D mesoporous COFs by a simple and effective strategy of enhanced steric hindrance. By utilizing methoxy-modified tetrahedral building unit, 3D-Meso-COFs can be prepared as non-interpenetrated \textbf{dia} structures, and by tuning the amount of substituents in the linear building units, 3D-Meso-COFs showed stable mesopores (~26.5 Å) and outstanding specific surface areas (up to 3023 \(m^2g^{-1}\)), which are much higher than those of reported COFs with the same topology. This research starts a new avenue to construct 3D large-pore COFs for various applications, such as adsorption and separation of biological, inorganic, and organic molecules with large sizes.

**ASSOCIATED CONTENT**

**Supporting Information**

Synthetic procedures, SEM, FTIR, solid state \(^{13}C\) NMR, TGA, BET plots, and pore size distribution. 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 interests.

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