

Communication

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# The Construction of Covalent Organic Frameworks Bearing Three Different Kinds of Pores through Heterostructural Mixed Linker Strategy

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Supporting Information Placeholder

**ABSTRACT:** To create novel topologies and improve structural complexity for covalent organic frameworks (COFs) is very important because it might lead to unprecedented properties and applications. In spite of the progress achieved over the past decade, the structural diversity and complexity of COFs are quite limited. In this communication, we report the construction of COFs bearing three different kinds of pores through heterostructural mixed linker strategy, which has been realized by the condensation of a  $D_{2h}$  symmetric tetraamine and two  $C_2$  symmetric dialdehydes of different lengths. The complicated structures of the triple-pore COFs have been confirmed by PXRD studies and pore size distribution analyses.

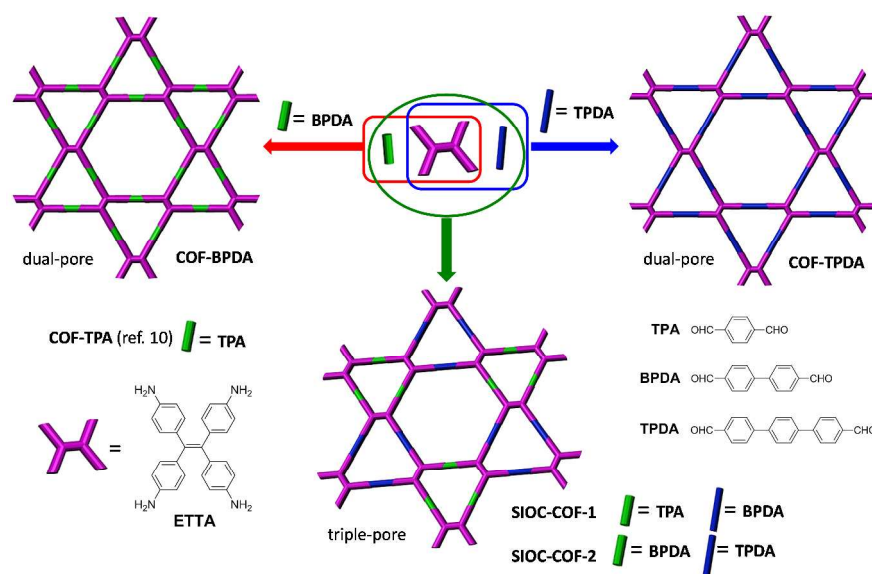
Covalent organic frameworks (COFs) have become a prominent field of research since its first discovery in 2005.<sup>1</sup> As an emerging class of crystalline porous materials, COFs exhibit great potential applications in various fields including gas storage,<sup>2</sup> separation,<sup>3</sup> catalysis,<sup>4</sup> energy storage<sup>5</sup> and photoelectric devices.<sup>6</sup> It is generally accepted that the topology of COFs has significant influence on their properties. Although a variety of COFs have been synthesized over the past decade,<sup>7</sup> compared to their analogs metal organic frameworks (MOFs),<sup>8</sup> topology and complexity of COFs are quite limited. The abundant and highly complicated topologies in MOFs can be attributed not only to the diverse building blocks but also to the flexible assembly approaches. Among those approaches, the use of mixing blocks with different structures, which is known as heterostructural mixed linker approach, enables the construction of MOFs with complicated structures from relatively simple building blocks.<sup>9</sup> We envisioned that this approach might also be a powerful tool to create novel topologies and improve structural complexity for COFs. However, to date whether heterostructural mixed linker approach can be applicable to the construction of COFs have never been demonstrated. In order to examine this possibility, in this work, a dual-pore (DP) COF which bears two different kinds of pores previously reported by us was chosen as a model system.<sup>10</sup> The DP-COF (denoted as COF-TPA) was prepared from the condensation of 4,4',4''-(ethene-1, 1,2,2-tetrayl)tetraaniline (ETTA) with terephthalaldehyde (TPA). To achieve mixing of linkers, two longer dialdehydes, [1,1'-biphenyl]-4,4'-dicarbaldehyde (BPDA) and

[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (TPDA) were selected. These two dialdehydes, together with TPA, constitute a linker pool, from which we can choose two of them to co-polymerize with ETTA. For the co-polymerization reaction, there will be several possibilities. First of all, it might yield amorphous polymers, as a result of the mutual interference of the different linkers; Secondly, two kinds of dual-pore COFs might be generated simultaneously through self-sorting of the linkers; Thirdly, if heterostructural mixed linker approach works for COFs, there will be no self-sorting but integrate both the two linkers to afford a new COF whose topology is totally different from the COFs prepared from the condensation of ETTA with either of the two dialdehydes. We herein report the construction of unprecedentedly complicated COFs which bear three different kinds of pores through the condensation of ETTA and two different dialdehydes. Moreover, two dual-pore COFs were also synthesized for comparison (Scheme 1). These results indicate that heterostructural mixed linker approach has a great potential to fabricate COFs with higher hierarchy and complexity.

This proof-of-concept study was carried out by two steps. The first one is to assemble COFs from the condensation reactions of ETTA with BPDA or TPDA, respectively. The second step is to perform three-component condensation reactions using ETTA, TPA and BPDA or ETTA, BPDA and TPDA. All the reactions were carried out under solvothermal condition (see Supporting Information for details). The as-obtained yellow powders were denoted as COF-BPDA (from ETTA and BPDA), COF-TPDA (from ETTA and TPDA), SIOC-COF-1 (from ETTA, TPA and BPDA), SIOC-COF-2 (from ETTA, BPDA and TPDA), respectively.

Elemental analyses of these powders revealed that their C, H, and N contents were very close to the corresponding theoretical values calculated from the expected polymerization products (see Supporting Information for details). The carbon contents of these polymers increased along with the increasing number of benzene ring in the polymers, which was also consistent with the theoretical prediction. The Fourier transform infrared (FT-IR) spectra of the COFs show the stretching band of C=N at 1619.8  $\text{cm}^{-1}$ , confirming the formation of imine linkages in the polymers (Figure S1). The characteristic resonance peaks of imine carbons (around 157 ppm) were observed in solid-state  $^{13}\text{C}$  cross polarization/

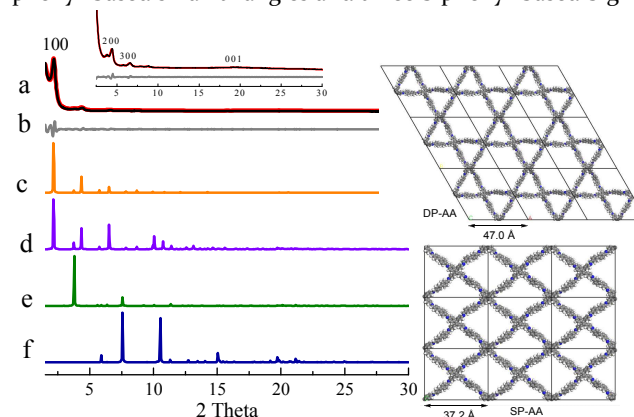
## Scheme 1. Cartoon Representation for the Synthesis of Dual-Pore and Triple-Pore COFs



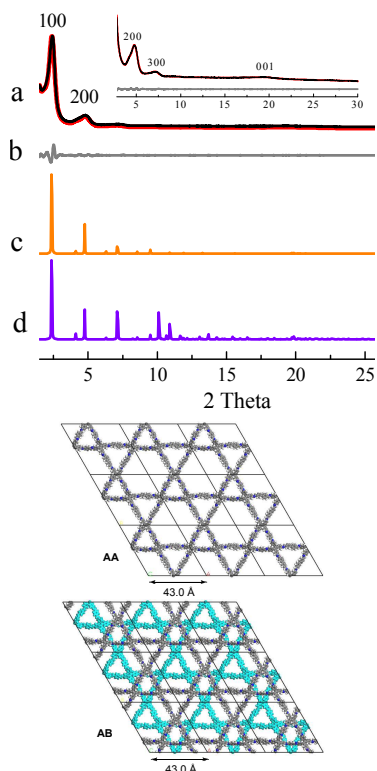
magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra of the COFs, again confirming the existence of imine linkages (Figures S2-5). Thermogravimetric analyses (TGA) indicated that the as-obtained polymers were highly thermostable. Less than 4% weight loss was observed for these materials when the temperature increased from 25 to 450 °C (Figure S6). Scanning electron microscopy (SEM) revealed that they all exhibited irregular morphology (Figure S7).

To determine the crystal structures of the as-obtained polymers, theoretical simulations and powder X-ray diffraction (PXRD) experiments were conducted. The simulations were carried out by using Materials Studio version 7.0. Similar to the dual-pore COF reported before,<sup>10</sup> two types of possible 2D structures were generated for COF-BPDA and COF-TPDA, that is, dual-pore structures and single-pore (SP) structures. For each type of the structures, eclipsed stacking (AA) and staggered stacking (AB) were constructed (Table S1-2). In the experimental PXRD profile of COF-BPDA (Figure 1a, black curve), a strong peak at 2.19° together with some relatively weaker peaks at 3.82°, 4.41°, 6.65° and ca. 19.4° were observed, which were assigned to (100), (110), (200), (300) and (001) diffractions. This PXRD pattern was in good agreement with the simulated PXRD pattern of BPDA-based DP-AA structure (Figures 1c and S8), which strongly suggests that COF-BPDA holds a dual-pore structure with AA stacking model. Subsequently, Pawley refinements yielded unit cell parameters of  $a = b = 46.83 \text{ \AA}$ ,  $c = 4.50 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  with factors of  $R_p = 2.96 \%$  and  $R_{wp} = 3.67 \%$ . The refined PXRD pattern well reproduced the experimental PXRD pattern, as revealed by the difference plot (Figure 1b). In the case of COF-TPDA, diffraction peaks corresponding to the reflections from (100), (110), (200), (210), (300), (220), (400) and (001) planes were observed at 1.86°, 3.27°, 3.75°, 4.99°, 5.62°, 6.68°, 7.50° and ca. 19.7°, respectively (Figure S9), on the basis of which a dual-pore structure with AA packing was assigned for it, after the comparison with the simulated PXRD pattern. Pawley refinements yielded unit cell parameters of  $a = b = 55.29 \text{ \AA}$ ,  $c = 4.50 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  with factors of  $R_p = 3.58 \%$  and  $R_{wp} = 5.34 \%$ , which matched with the experimental data quite well.

After the structures of the two dual-pore COFs were established, the validity of constructing COFs through heterostructural linker strategy was examined. The as-prepared powders SIOC-COF-1 and SIOC-COF-2 were also subjected to PXRD analyses. In the case of SIOC-COF-1, a strong peak at 2.42° (100) was observed (Figures 2 and S10). This peak neither belonged to the (100) diffraction of COF-BPDA (2.19°), nor corresponded to the (100) diffraction of COF-TPDA (2.78°), as clearly revealed by the comparison of the positions of the peaks (Figure S11). This result indicated the formation of a COF with new structure. In addition to the peak at 2.42°, a set of diffraction peaks which were assigned to (200), (300) and (001) planes were also observed at 4.81°, 7.15° and ca. 19.4°, respectively. Since SIOC-COF-1 was obtained by the condensation of ETTA, TPA and BPDA in a molar ratio of 1:1:1, a triple-pore (TP) COF in which half of the phenyl linkers in the dual-pore COF COF-TPA were replaced by biphenyl linkers was proposed and constructed. It generated a COF whose unit consists of an inequilateral hexagon, three phenyl-based small triangles and three biphenyl-based big



**Figure 1.** (a) Experimental (black) and refined (red) PXRD patterns of COF-BPDA, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of BPDA-based (c) DP-AA, (d) DP-AB, (e) SP-AA, and (f) SP-AB structures.



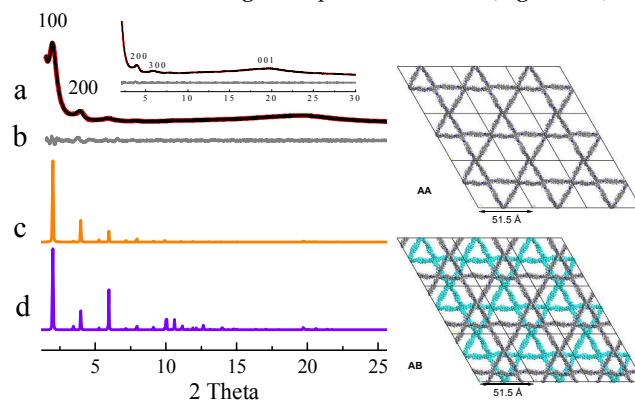
**Figure 2.** (a) Experimental (black) and refined (red) PXRD patterns of **SIOC-COF-1**, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of triple-pore COF with (c) AA and (d) AB stacking.

triangles (see Scheme 1 for its structure). Theoretical simulation was performed for this triple-pore COF, which generated unit cell parameters of  $a = b = 43.0 \text{ \AA}$ ,  $c = 4.5 \text{ \AA}$  (AA stacking) or  $9.0 \text{ \AA}$  (AB stacking),  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  (Table S3). The simulated PXRD pattern generated from triple-pore structure with AA stacking was in good agreement with the experimentally observed PXRD pattern of **SIOC-COF-1**, suggesting it holds a structure with three different kinds of pores and AA stacking model. Pawley refinements reproduced the experimental PXRD pattern quite well and yielded unit cell parameters of  $a = b = 42.63 \text{ \AA}$ ,  $c = 4.50 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$ , with factors of  $R_p = 2.59 \%$  and  $R_{wp} = 3.31 \%$ .

For **SIOC-COF-2** which was prepared from the condensation of **ETTA**, **BPDA** and **TPDA**, a set of diffraction peaks at  $1.96^\circ$ ,  $3.88^\circ$ ,  $5.84^\circ$  and ca.  $19.7^\circ$  assignable to (100), (200), (300) and (001) planes were observed in its experimental PXRD pattern (Figures 3 and S12). This set of peaks was totally different from that of **COF-BPDA** and **COF-TPDA** (see Figure S13 for the comparison), indicating a new COF was obtained. A triple-pore structure similar to **SIOC-COF-1** was theoretically constructed and the simulation gave unit cell parameters of  $a = b = 51.5 \text{ \AA}$ ,  $c = 4.5 \text{ \AA}$  (AA stacking) or  $9.0 \text{ \AA}$  (AB stacking),  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$ . The simulated PXRD pattern of a triple-pore COF with AA stacking well matched with the experimentally observed PXRD pattern of **SIOC-COF-2**. Pawley refinements produced unit cell parameters of  $a = b = 51.42 \text{ \AA}$ ,  $c = 4.49 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  with factors of  $R_p = 1.53 \%$  and  $R_{wp} = 2.04 \%$ . This result confirmed again that triple-pore COF could be produced from the

three-component condensation. It should be noted that COFs which bear only one kind of pores may also be expected from the three-component condensation of the monomers used above. However, the formation of such structures was ruled out by the comparisons of the experimental PXRD patterns of the as-prepared materials with the simulated PXRD patterns of single-pore COFs (Figure S14-15).

To further corroborate the assigned crystal structures of the as-prepared COFs, nitrogen sorption measurements were carried out to assess their porosities and to analyze their pore size distributions (Figure 4). **COF-BPDA** and **COF-TPDA** exhibited similar nitrogen sorption isotherms (Figure S16).



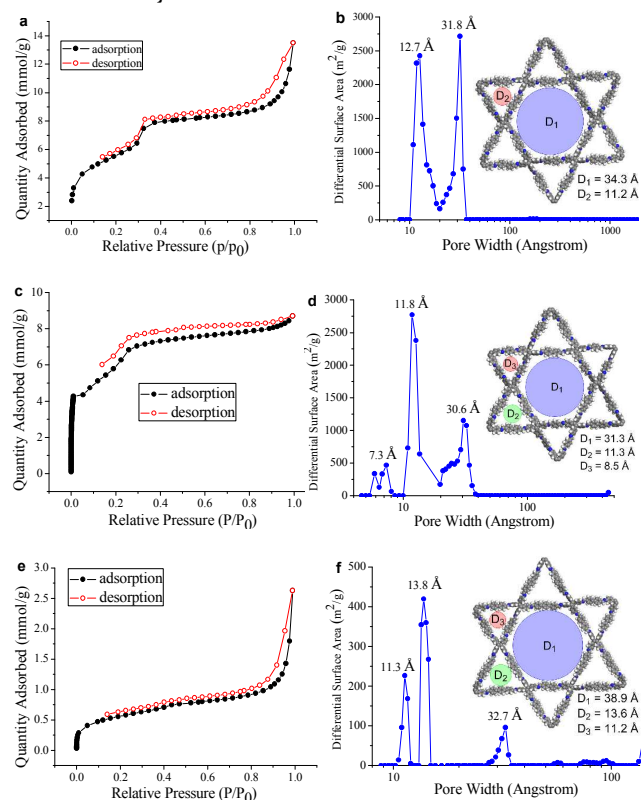
**Figure 3.** (a) Experimental (black) and refined (red) PXRD patterns of **SIOC-COF-2**, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of triple-pore COF with (c) AA and (d) AB stacking.

The curves displayed a combination of type I and type IV nitrogen sorption isotherms,<sup>11</sup> suggesting that micropores and mesopores coexist in these two COFs. The BET surface areas calculated from the isotherms of **COF-BPDA** and **COF-TPDA** in the range of  $P/P_0$  between 0.05 and 0.2 were  $447.76 \text{ m}^2/\text{g}$  and  $83.77 \text{ m}^2/\text{g}$  for **COF-BPDA** and **COF-TPDA**, respectively (Figures S17-18). The total pore volumes (evaluated at  $P/P_0 = 0.99$ ) of **COF-BPDA** and **COF-TPDA** were estimated to be  $0.47 \text{ cm}^3/\text{g}$  and  $0.10 \text{ cm}^3/\text{g}$ , respectively. The pore size distribution of **COF-BPDA** was generated by using nonlocal density functional theory (NLDFT), which revealed two main distributions at  $12.7$  and  $31.8 \text{ \AA}$  (Figure 4b), indicating the existence of two kinds of pores of different sizes in the COF. The experimental pore size distributions are close to the theoretical pore sizes of **COF-BPDA** ( $11.2$  and  $34.3 \text{ \AA}$  as estimated by  $\text{PM}_3$  calculations), confirming again that **COF-BPDA** holds a dual-pore structure. Similarly, the pore size distribution analysis of **COF-TPDA** exhibits two main distributions at  $14.8$  and  $37.0 \text{ \AA}$ , which is close to its theoretical pore sizes ( $14.0$  and  $42.1 \text{ \AA}$ ), indicating that **COF-TPDA** also possesses a dual-pore structure.

**SIOC-COF-1** displayed a  $\text{N}_2$  sorption isotherm similar to the above dual-pore COFs (Figure 4c). On the basis of its  $\text{N}_2$  sorption data, BET surface area of **SIOC-COF-1** was calculated to be  $478.41 \text{ m}^2/\text{g}$  (Figure S19) and its total pore volume (evaluated at  $P/P_0 = 0.99$ ) was estimated to be  $0.30 \text{ cm}^3/\text{g}$ . Pore size distribution analysis was performed for **SIOC-COF-1**. Three major pores around  $7.3$ ,  $11.8$  and  $30.6 \text{ \AA}$  were observed (Figure 4d), which well matched with the theoretical pore sizes of the proposed triple-pore COF ( $8.5$ ,  $11.3$  and  $31.3$



Å, as estimated by PM<sub>3</sub> calculations). For SIOC-COF-2, BET surface area of 46.13 m<sup>2</sup>/g (Figure S20) and total pore volume (evaluated at P/P<sub>0</sub> = 0.99) of 0.09 cm<sup>3</sup>/g were obtained from its nitrogen sorption isotherm. Pore size distribution analysis revealed three main distributions around 11.3, 13.8 and 32.7 Å (Figure 4f). These values are consistent with the simulated pore distributions which were predicted to be 11.2, 13.6 and 38.9 Å. The results from pore size distribution analyses, together with the PXRD investigation, corroborated the obtention of triple-pore COFs from the three-component copolymerization. It should be noted that BET surface areas of TPDA-based COFs are quite low and the reason is currently unclear. However, it detracts nothing from the determinations of the crystal structures of the COFs.



**Figure 4.** N<sub>2</sub> adsorption-desorption isotherms (77 K) of (a) COF-BPDA, (c) SIOC-COF-1 and (e) SIOC-COF-2, and pore size distribution profiles of (b) COF-BPDA, (d) SIOC-COF-1 and (f) SIOC-COF-2.

In conclusion, COFs which bear three different kinds of ordered pores with controllable sizes have been constructed through heterostructural mixed linker strategy. While the condensation of a D<sub>2h</sub> symmetric tetraamine and a C<sub>2</sub> symmetric dialdehyde gave rise to a dual-pore COF containing two different kinds of pores (triangular micropores and hexagonal mesopores), the copolymerization of a D<sub>2h</sub> symmetric tetraamine and two C<sub>2</sub> symmetric dialdehydes of different lengths produced a triple-pore COF in the unit of which an inequilateral hexagonal mesopore is alternatingly surrounded by three small triangular micropores and three big triangular micropores. These COFs represent a new topology with unprecedented hierarchy and structural complexity. This work for the first time demonstrates that heterostructural mixed linker strategy can also be applicable to construction of COFs. It may open up a new way to fabricate COFs with

sophisticated topologies from relatively simple building blocks. Its potential to construct more complicated COFs is currently under investigation in our laboratory.

## ASSOCIATED CONTENT

### Supporting Information

Procedure for the preparation of the polymers, FT-IR spectra, solid-state <sup>13</sup>C CP-MAS NMR spectra, BET plots, TGA traces, and SEM images. 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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