Rational design of imine-linked three-dimensional mesoporous covalent organic frameworks with bor topology

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Abstract
Three-dimensional (3D) covalent organic frameworks (COFs) possess great potential applications in various fields. Constructing 3D COFs with large pore sizes is extremely challenging due to the interpenetration and collapse. Herein, we report a series of crystalline imine-linked 3D COFs (3D-bor-COF-1, 3D-bor-COF-2, 3D-bor-COF-3) with mesoporous channels through rationally designing the topology configuration. These 3D-bor-COFs display permanent porosity and Brunauer–Emmett–Teller (BET) surfaces of 3205.5, 1752.7, and 2077.3 m² g⁻¹ (S_Langmuir = 4277.7, 2480.3, and 2698.0 m² g⁻¹), respectively. The pore sizes of 3D-bor-COFs were confirmed by the lattice fringes from high-resolution transmission electron microscopy, as well as structural simulation and nitrogen adsorption isotherm analysis. 3D-bor-COFs display large pore sizes (3.8 nm for 3D-bor-COF-3), which is among the highest record of 3D COFs. Owing to the unstacked-aromatic pore environment and high specific surface area, 3D-bor-COFs display excellent adsorption capacity for benzene vapor (1203.9 mg g⁻¹ for 3D-bor-COF-3) under 298 K, which is three times higher than that of the best-reported 2D COF. This work not only provides inspiration for designing 3D mesoporous imine-COFs, but also demonstrates a strategy for constructing aromatics adsorption materials.

KEYWORDS
benzene vapor uptake, covalent organic framework, large pore size, lattice fringes, topology configuration

1 | INTRODUCTION

The emergence of covalent organic frameworks (COFs) provides a new direction for the development of porous materials.¹⁻³ COFs have the advantage of high specific surface area, crystallinity, and considerable chemical/thermal stability,⁴⁻⁷ which have great application prospects in photoelectricity,⁸ conduction,⁹,¹⁰ sensing,¹¹ catalysis,¹²,¹³ adsorption/separation,¹⁴⁻¹⁶ and so on. Narrow pores in the microporous COFs do not allow accommodating...
larger guests or anchoring functional groups, thus limiting mass-transport related applications, such as molecular capture/separation, catalysis, and drug delivery. Therefore, developing COFs with large pores is very essential and urgent.

Nevertheless, synthesizing mesoporous crystalline materials is difficult since larger pore tends to arise interpenetration and collapse; and the construction of mesoporous imine-linked 3D COFs is more challenging for the following reasons. First, the formation reaction of imine is less reversible than the early developed boroxine and boronate-ester linked COFs, since it hinders the error correction mechanism of COFs. Second, imine-linkage is a chain structure with three bonds, which not only leads to more spatial conformations compared with the ring structures of boroxine/boronate, but also creates challenges in getting precise reticular network, especially for 3D-imine-COFs.

The theoretical specific surface area of two-dimensional (2D) COFs is usually 2000–3000 m² g⁻¹, the theoretical limitation of 3D COFs could be as high as 7000–10 000 m² g⁻¹. However, the usually obtained surface area of 3D COFs was significantly lower than theoretical value, resulting from the widely observed crystallinity issue and interpenetration phenomena. Currently, methods to reduce the interpenetration are focused on: (1) shortening the length of the linkers, (2) increasing the steric hindrance, (3) controlling reaction conditions, and (4) increasing the repulsive effect of the linkers. Herein, we selected the topology that rarely occurs interpenetration phenomenon to prepare mesoporous imine-linked 3D COFs.

In 2007, Yaghi’s group reported two boronate-ester-linked COFs (COF-105 and COF-108) with ctu and tth topologies that have 1.8 and 2.96 nm pore sizes, respectively; notably, it was also the first report of 3D COFs. After that, McGrier’s group reported the second example of bor COFs, in which the boronate-ester-linked DBA-3D-COF 1 has a pore size of 2.8 nm. It is worth mentioning that these two bor topology boronate-ester-linked COFs also represent the high surface area in 3D COFs. Unfortunately, except for two cases, imine-linked COF with topology has not been reported so far.

In this work, we demonstrate a series of 3D imine-linked bor COFs (termed 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3) from the condensation reaction of [4 + 3] vertices. Remarkably, 3D-bor-COF-3 is a non-interpenetrated structure, so its pore size achieved 3.8 nm, which is among the highest record of 3D COFs (Figure 1 and Table S2). We also measured the pore sizes by high-resolution transmission electron microscopy (HRTEM), which is identical to the theoretical model (Figures 2(D), 2(H), and 2(I)).

To construct the bor COF, we selected the stereoscopic building unit 3,3′,5,5′-tetakis (4-formylphenyl)bimesityl (TFBM) with a planar triangular building unit, 1,3,5-tri(4-aminophenyl)benzene (TAPB). The obtained frame structure is different from tth-defect, fcc, fjh, and tbo topologies, which linked by planar triangular and quadrangular building units. The as-synthesized COF displays a bor net with permanent porosity, a Brunauer–Emmett–Teller (BET) surface of 3205.5 m² g⁻¹, and the Langmuir surface area 4277.7 m² g⁻¹ for 3D-bor-COF-1, which is among the highest record of 3D COFs, especially in 3D-imine-COFs (Figure 1 and Table S2). Based on other triangular building units, 3D-bor-COF-2 and 3D-bor-COF-3 were also prepared, with BET surfaces of 1752.7 and 2077.3 m² g⁻¹, and the Langmuir surface areas of 2480.3 and 2698 m² g⁻¹, respectively.

Considering the high surface area, mesoporous feature, and the exposed aromatic pore environment of our 3D COFs, we explored their gas adsorption application. Unlike 2D COFs, the strong π–π stacking of planar precursors on 2D COFs is forced to be separated in 3D COFs, providing more efficient adsorption active sites. And surprisingly, we found the 3D-bor-COFs could serve as excellent capture materials for benzene vapor, with an adsorption capacity of 983.3 mg g⁻¹ for 3D-bor-COF-1, 953.5 mg g⁻¹ for 3D-bor-COF-2, and 1203.9 mg g⁻¹ for 3D-bor-COF-3.
FIGURE 2  $N_2$ sorption isotherms collected at 77 K and corresponding pore size distributions based on the nonlocal density functional theory (NLDFT) method of 3D-bor-COF-1 (A and B), 3D-bor-COF-2 (E and F), and 3D-bor-COF-3 (I and J). High-resolution transmission electron microscopy (HRTEM) images and lattice fringe distance measurements in red regions of 3D-bor-COF-1 (C and D), 3D-bor-COF-2 (G and H), and 3D-bor-COF-3 (K and L).

FIGURE 3  Benzene vapor adsorption–desorption isotherms at 298 K (Table S3)

under 298 K (Figure 3), respectively, which are among the highest record of porous materials, also the first attempt in the 3D COFs field. And 3D-bor-COFs demonstrates high hydrogen adsorption capacities of 172.05 cm$^3$ g$^{-1}$ for 3D-bor-COF-1, 128.67 cm$^3$ g$^{-1}$ for 3D-bor-COF-2, and 134.31 cm$^3$ g$^{-1}$ for 3D-bor-COF-3 under condition of 77 K and 1 atm (Figures S32–S37), respectively.

2  RESULTS AND DISCUSSION

2.1  Designed synthesis of 3D-bor-COFs and characterizations

Scheme 1 shows the strategy of constructing 3D-COFs with bor topology through the condensation reaction of a tetrahedral building unit (Figures S1 and S2), TFBM with C3-symmetric building units (Figures S3–S8), TAPB, N4,N4-bis(4′-amino-[1,1′-biphenyl]-4-yl)-[1,1′-biphenyl]-4,4′-diamine (TABPA), and 1,3,5-tri[4-amino(1,1-biphenyl-4-yl)]-benzene (TABPB). The synthesis of the imine-linked framework 3D-bor-COF-1 was carried out by solvothermalysis of a suspension of TFBM and TAPB with the molar ratio of 3:4 in a mixture of o-dichlorobenzene and 6 M acetic acid aqueous solution at 120°C for 4 days.

2.2  Characterization of 3D-bor-COFs

To demonstrate the generality of this bor COF construction strategy, we extended the triangular structure unit to two benzene rings and prepared other two new COFs (3D-bor-COF-2 and 3D-bor-COF-3). Fourier-transform infrared spectroscopy (FT-IR) displayed the
C=N characteristic stretching signal with 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 (ν_{C=N} = 1600, 1602, and 1594 cm⁻¹; Figures S14–S16), indicating the formation of imine bonds. With the¹³C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra (Figures S11–S13), the presence of carbon (C=N) at 157.8, 158.0, and 158.4 ppm and the weakening of the aldehyde carbon at 189.4, 190.8, and 191.4 ppm also confirmed the formation of the imine bonds. Enormous difference from the powder X-ray diffraction (PXRD) patterns of the target products and the precursors also confirmed the Schiff-base reaction (Figures S23–S25). According to elemental analysis (EA) (Table S1), the atomic composition of 3D-bor-COF-1 can be confirmed (3D-bor-COF-1): Calcd for C\textsubscript{234}H\textsubscript{120}N\textsubscript{12}, corresponding to (TFBM)\textsubscript{3}(TAPB)\textsubscript{4}imine; C, 90.67; H, 3.90; N, 5.42%. Found: C, 83.10; H, 5.80; N, 4.69%. 3D-bor-COF-2: Calcd for C\textsubscript{382}H\textsubscript{186}N\textsubscript{16}, corresponding to [(TFBM)\textsubscript{3}(TABPA)\textsubscript{4}]imine; C, 89.87; H, 4.17; N, 5.95%. Found: C, 84.40; H, 5.96; N, 4.79%. 3D-bor-COF-3: Calcd for C\textsubscript{306}H\textsubscript{168}N\textsubscript{12}, corresponding to [(TFBM)\textsubscript{3}(TAPBP)\textsubscript{4}]imine; C, 91.58; H, 4.22; N, 4.19%. Found: C, 83.30; H, 5.74; N, 3.39%. The thermogravimetric analysis (TGA) (Figures S17–S19) indicates that 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 start to decompose at around 500°C, where a weight loss was ~5% under nitrogen atmosphere.

Moreover, to test the chemical stability of 3D-bor-COFs, 20 mg samples were exposed to common organic solvents (including acetone, tetrahydrofuran, hexane, acetonitrile, dichloromethane, chloroform, DMF, DMAc, and DMSO) and water (pH = 1, 7, 14) for 24 h at room temperature. 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 maintain their crystallinity well after treatment under above conditions, which were demonstrated by the PXRD patterns (Figures S20–S22). The stability of COFs depends largely on the bond type, vinylene-linked and sp² carbon-conjugated COFs is more stable than the all-imine-linked COFs reported because of its low reversibility. However, for the above two examples, their crystallinity and BET surface area are worse than our 3D-bor-COFs. In fact, it is not easy for imine-linked COFs to have high crystallinity, high specific surface area, and high stability at the same time.

The crystalline structures were evaluated by PXRD. 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 matched coincide with the simulated patterns obtained from bor network.

As shown in Figure 4(A), 3D-bor-COF-1 had peaks at 2.13°, 3.14°, and 6.14° corresponding to (1 0 0), (2 0 0), and (2 2 0) facets, respectively (Figure 4(A), black line). And the Pawley refinement yielded a pattern (Figure 4(A), red line), that is consistent with the experimentally observed pattern, with a negligible difference (Figure 4(A), blue line). The refinement led to a space group of P-43m with a = b = c = 43.9395 Å, α = β = γ = 90°, which is similar to the calculated structure based on bor model, and Rwp and Rp values of 7.60% and 3.82%, respectively. As shown in Figure 4(C), 3D-bor-COF-2 had peaks at 1.99°, 3.29°, and 5.36° corresponding to (1 0 0), (2 0 0), and (2 2 0) facets, respectively (Figure 4(C), black line). 3D-bor-COF-3 had peaks at 1.74°, 3.59°, and 4.93°, corresponding to (1 0 0), (2 0 0), and (2 2 0) facets, respectively (Figure 4(E), black line). The Pawley refinement further confirmed the consistency of calculated crystalline structures with experimentally observed PXRD patterns, with Rwp and Rp values of 3.86% and 2.08% for 3D-bor-COF-2, and 2.22% and 1.65% for 3D-bor-COF-3. Both of them led to a space group of P-43m with a = b = c = 47.5436 Å and a = b = c = 50.5534 Å, α = β = γ = 90°. According to Reticular Chemistry Structure Resource,⁶⁶ we compared it with other two possible topologies, ctn and oP (Figure 5 and Tables S4–S12). However, the calculated patterns did not match with the experimental PXRD patterns. Therefore, we identify 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 as bor network. It is worth noting that the peak at 3.88° disappeared in the XRD obtained from the experiment, which may be due to
the influence of crystal defects or trapped molecules in the materials.

2.3 | N2 adsorption, SEM, and HRTEM tests

The porosity of 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 was evaluated by nitrogen adsorption isotherm measurement at 77 K. As shown in Figures 2(A), 3(E), and 3(I), a sharp uptake exhibited type IV isotherm under low relative pressures region (below \( P/P_0 = 0.05 \)), followed by a second step, indicating a characteristic of mesoporous materials. The specific surface areas calculated by the BET method (Figures S26–S28) were 3205.5, 1752.7, and 2077.3 m² g⁻¹ and by the Langmuir method (Figures S29–S31) were 4277.7, 2480.3, and 2698 m² g⁻¹, respectively. The nonlocal density functional theory (NLDFT)-simulated pore sizes of 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 revealed a major peak centered at 3.1, 3.6, and 3.8 nm (Figures 2(B), 3(F), and 3(J)). Preparation of mesoporous imine-COFs yet with a high surface area is rather challenging (Figure 1 and Table S2), since the formation reaction of imine-COF is less reversible²²,²³ and the generated large 3D pores have a higher tendency to be collapsed.²¹ The scanning electron microscopy (SEM) and
FIGURE 5  [4+3] connected 3D network with three different possible topologies: (A) bor, (B) ctn, and (C) ofp

the HRTEM revealed that 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3 have a spherical-like morphology (Figures S9 and S10). It is interesting to note that we rarely verified the pore sizes of 3D-bor-COFs through the lattice fringes of HRTEM (Figures 2(C), 3(D), 3(G), 3(H), 3(K), and 3(L)). HRTEM techniques are often used to analyze pore structures in 2D COFs, but difficult for complex 3D COFs.47,48

2.4 Benzene vapor adsorption tests

Aromatic molecules are commonly used solvents and important synthetic reactants in the laboratory and industry. However, most of them are volatile molecules, and thus cause serious environmental problems, especially threat to the health of humans and various organisms. In recent years, significant efforts have been put into developing effective methods to reduce aromatics emissions. In the past decade, a lot of exploration have been made on the adsorption of benzene by metal-organic frameworks.45 Considering 3D-bor-COFs possess unstacked-aromatic pore environment, high specific surface area, and mesoporous properties, we believed that the material has excellent adsorption properties for large volatile molecules such as aromatic hydrocarbon. 3D-bor-COFs showed high benzene capacities under 298 K (983.3 mg g$^{-1}$ for 3D-bor-COF-1, 953.5 mg g$^{-1}$ for 3D-bor-COF-2, and 1203.9 mg g$^{-1}$ for 3D-bor-COF-3). 3D-bor-COF-3 is around the three times of the reported 2D COF materials, TTPE-COF (452.4 mg g$^{-1}$).30 And it is also comparable with the best results of the porous frameworks (Table S3) PAF-1 (1306.0 mg g$^{-1}$, $S_{\text{BET}}$ = 5600 m$^2$ g$^{-1}$),51 MIL-101 (1302.6 mg g$^{-1}$, $S_{\text{BET}}$ = 3900 m$^2$ g$^{-1}$).52 Notably, we found that 3D-bor-COF-2 has an adsorption capacity of up to 711.28 mg g$^{-1}$ in the low-pressure zone ($P/P_0 = 0.1$), which suggests it can effectively adsorb benzene vapor under ultra-low pressure (Figure 3). We think that high specific surface area, central nitrogen atom, and large pore size are conducive to aromatic hydrocarbon adsorption.

In order to better understand the trend of benzene vapor adsorption, we calculated the distribution density of benzene in 3D-bor-COFs using Metropolis Monte Carlo method. As shown in Figures S38–S40, exposed $\pi$-plane and central nitrogen atoms provide a great influence on benzene vapor adsorption. To further study the enhanced benzene vapor adsorption capacities of 3D-bor-COFs, we investigated the intermolecular interactions between the building units and benzene vapor using density-functional theory calculation. We built a model (Figures S41–S44) for TAPB, TABPA, TABPB, and TFBM. As shown in Figure S41, exposed $\pi$-plane of central phenyl-, phenyl-, and imine bond of the unstacked TAPB showed adsorption energy of $-27.47$, $-24.04$, and $-25.07$ kJ mol$^{-1}$, respectively. Further, as for the aromatic ring-based adsorption sites, the position of central nitrogen for TABPA showed adsorption energy of $-29.48$ kJ mol$^{-1}$; this result suggests that nitrogen atom provides different charge environments resulting in higher adsorption heat than exposed $\pi$-plane of phenyl- ($-28.24$ kJ mol$^{-1}$) and imine group ($-26.26$ kJ mol$^{-1}$; Figure S42). TABPB central phenyl-, exposed $\pi$-plane of phenyl-, and imine bond showed adsorption energy of $-27.54$, $-24.37$, and $-25.07$ kJ mol$^{-1}$, respectively (Figure S43); the biphenyl- position of TFBM unit showed much stronger interaction with benzene vapor, with an adsorption energy of $-35.36$ and $-27.82$ kJ mol$^{-1}$, imine bond showed $-26.85$ kJ mol$^{-1}$ (Figure S44). This result suggests the exposed aromatic rings in 3D-COFs would have a stronger interaction with benzene vapor, and the unique structure of TFBM make it a preferred adsorption site for benzene vapor.

3 CONCLUSION

We here developed the first example of imine-linked three-dimensional COFs with bor topology. The mesoporous 3D-bor-COF-3 possesses a pore size of 3.8 nm, while 3D-bor-COF-1 owns a BET surface area of 3205 m$^2$ g$^{-1}$ and a Langmuir surface area of 4277.7 m$^2$ g$^{-1}$, which are among the best results of 3D imine COFs. We demonstrate a new method to measure the pore size by HRTEM. Moreover, 3D-bor-COFs with the plane of exposed aromatic rings, high specific surface area, and large pore size displayed excellent adsorption capacity for benzene vapor. This work not only enriches the family of 3D COFs, but also provides inspiration for the design of mesoporous 3D COFs. Meanwhile, it also opens up a possibility for
the application of 3D COFs in the capture of aromatic hydrocarbon.

4 | EXPERIMENTAL PROCEDURES

4.1 | Materials

All starting materials and solvents, unless otherwise noted, were obtained from J&K scientific LTD. and used without purification. All products were isolated and handled under nitrogen using either glovebox or Schlenk line techniques.

4.2 | General method for synthesis of 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3

A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm² was charged with TFBM (19.62 mg and 0.03 mmol) and TAPB (14.04 mg and 0.4 mmol) in a mixed solution of o-dichlorobenzene (1.5 ml) and 6.0 M acetic acid (0.15 ml). The tube was flash frozen at 77 K (LN₂ bath), evacuated to an internal pressure of ~0.1 MPa and flame sealed. The reaction mixture was heated at 120°C for 4 days to obtain a light-yellow precipitate, which was isolated by filtration over a medium glass frit and washed with anhydrous acetone (40.0 ml). The product was immersed in anhydrous acetone (40.0 ml) for 24 h. During this period, the activation solvent was decanted and freshly replenished several times. The 3D-bor-COF-1 was obtained by removing solvent in vacuum at 80°C, which was a light yellow crystalline solid. Under the same conditions, replacing TAPB with TABPA (20.72 mg and 0.4 mmol) and TABPB (23.20 mg and 0.4 mmol) respectively will obtain dark red and dark brown precipitates named 3D-bor-COF-2 and 3D-bor-COF-3.

4.3 | Characterizations

¹H NMR spectra were recorded on a JEOL JNM-ECA600 NMR spectrometer. ¹³C NMR spectra were recorded on a JEOL JNM-EZ600R 600 MHz solid-state NMR spectrometer. The FT-IR spectra was obtained by using a Bruker VERTEX 70 Fourier transform infrared spectrophotometer. TGA was carried out under nitrogen on a METTLER TOLEDO 1600LF thermal analyzer, measured over the temperature from 50 to 750°C with a heating rate of 10°C min⁻¹ and a N₂ flow rate of 30 ml min⁻¹. Samples for TGA were dried under vacuum at RT for 4 h, and then 80°C for 6 h. EAs were performed by using a Thermo Scientific FlashSmart elemental analyzer. PXRD data were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5418 Å) over the range of 2θ = 1.0–40.0° with a step size of 0.02° and 2 s per step. The sorption isotherm for N₂ was measured by using a BEL sorp-max II analyzer with ultra-high-purity gas (99.999% purity). To estimate pore size distributions for 3D-bor-COF-1, 3D-bor-COF-2, and 3D-bor-COF-3, NLDFT was applied to analyze the N₂ isotherm on the basis of the model of N₂ at 77 K on carbon with slit pores and the method of non-negative regularization. The sorption isotherm for benzene was measured by using a BSD-VVS Vacuum Vapor/Gas Sorption Analyzer. The SEM images were obtained by Zeiss Gemini scanning electron microscope. The TEM images were obtained by JEOL JEM-2100PLUS Transmission electron microscope.

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AUTHOR CONTRIBUTIONS
Z. L., C. H., Y. Y., H. X., and X. H. conceived and designed the research. C. H., Z. T., and J. C. synthesized the organic linkers and COFs. H. G. and M. L. carried out the structural characterization of all the COFs. X. W. took the high-resolution TEM images of COFs and H. C. took the SEM images of all the samples. D. R. operated the TGA experiments. C. H., Z. T., and H. C. performed EA, FT-IR, ¹H NMR, ¹³C NMR, and ssNMR. Z. L. operated the chemical stability experiments. C. H. operated gas and benzene vapor adsorption experiments. Z. L., C. H., and H. X. prepared the manuscript, and all authors participated in drafting the paper, and gave approval to the final version of the manuscript.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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**SUPPORTING INFORMATION**

Additional supporting information may be found in the online version of the article at the publisher’s website.

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