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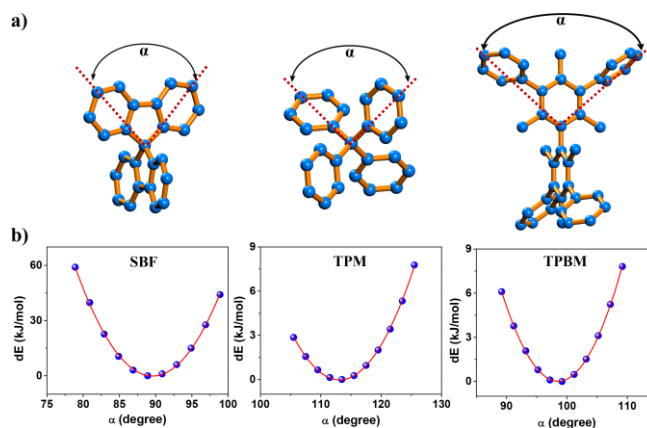
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Design and Synthesis of a Zeolitic Organic Framework

Yaozu Liu,[†] Pohua Chen,[†] Yujie Wang,^{*} Jinquan Suo, Jiehua Ding, Liangkui Zhu, Valentin Valtchev, Yushan Yan, Shilun Qiu, Junliang Sun,^{*} and Qianrong Fang^{*}

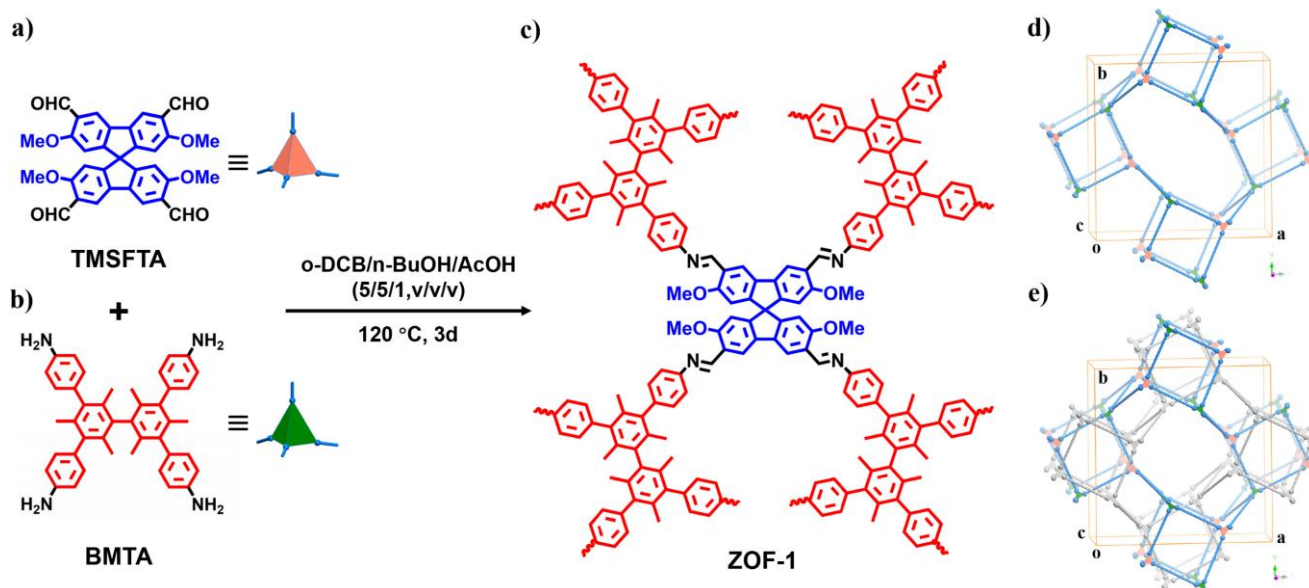
Abstract: The development of novel zeolite-like materials with large channel windows and high stability is of importance but remains a tremendous challenge. Herein, we report the first example of a 3D covalent organic framework with zeolitic network, namely the zeolitic organic framework (ZOF). By combining two kinds of tetrahedral building blocks with fixed or relatively free bond angles, ZOF-1 with the zeolitic **crb** net has been successfully synthesized. Its structure was determined by the single-crystal 3D electron diffraction technique. Remarkably, ZOF-1 shows high chemical stability, large pore size (up to 16 Å), and excellent specific surface area (~ 2785 m²/g), which is superior to its analogues with the same network, including traditional aluminosilicate zeolites and zeolitic imidazole frameworks. This study thus opens a new avenue to construct zeolite-like materials with pure organic frameworks and will promote their potential applications in adsorption and catalysis for macromolecules.

Aluminosilicate zeolite is a class of crystalline microporous inorganic materials that has been employed in a wide variety of practical applications across chemical industries.^[1,2] However, the windows and pores of these materials are usually tiny because their frameworks are built from corner-sharing, tetrahedrally coordinated TO₄ principal units (where T is a tetrahedral atom, such as Si and Al), which extremely limits their uses in adsorption and catalysis for macromolecules. Subsequently, an inorganic-organic hybrid zeolite-like material, termed zeolitic imidazolate framework (ZIF), was widely reported, in which transition metals (Zn or Co) substitute



Scheme 1. Energy scans analysis of tetrahedral building units as a function of bond angle. (a) Structures of SBF (left) with fixed bond angles as well as TPM (middle) and TPBM (right) with relatively free bond angles. (b) Potential energy scans of different tetrahedral building units based on variable bond angles.

tetrahedrally coordinated atoms (for example, Si), and imidazolate linkers replace bridged oxygen atoms.^[3,4] Although the pores of ZIFs have been greatly improved, their channel windows are still small, and especially chemical stability of ZIFs is a major issue due to the nature of coordination bonds. Therefore, developing new crystalline zeolite-like materials with large channels and high stability is of importance but remains a great challenge.



Scheme 2. A strategy for constructing ZOF-1 with **crb** net. Molecular structures of TMSFTA (a) as a tetrahedral building unit with fixed bond angles and BMTA (b) as a tetrahedral building unit with relatively free bond angles. (c) A novel 3D COF with zeolitic **crb** net, ZOF-1, constructed from the condensation reaction of TMSFTA and BMTA. (d) Non-interpenetrated **crb** net and (e) twofold interpenetrated **crb** net.

Covalent organic frameworks (COFs)^[5,6] are an emerging class of crystalline porous polymers that are assembled from organic building blocks linked by covalent bonds. Since the initiated work of Yaghi in 2005, these materials have attracted extensive attention in different fields, such as energy storage, gas separation, heterogeneous catalysis, optoelectronics, and many others.^[7-16] Recently, developing three-dimensional (3D) COF materials has been considered indispensable because of their promising advantages in interconnected pores and higher specific surface areas than two-dimensional (2D) counterparts.^[17-19] Up to now, the building units in 3D architectures are

mostly on the basis of the tetrahedral (4-connected, T_d) geometry, such as the derivatives of tetraphenylmethane, tetraphenylsilane, and adamantane.^[20-23] A few successful examples with higher numbers of connections (> 4 points of extension) have been reported, e.g., a 3D cage-based COF with a twofold interpenetrated **acs** net^[24] and polycubane COFs with the **bcu** net based on cubic (8-connected) units.^[25] By applying triangular prism (6-connected, D_{3h}) triptycene linkers as node centers, we also designed a series of 3D COFs with various networks, such as JUC-564 with **stp** net,^[26] JUC-568 and JUC-569 with **ceq** or **acs** net,^[27] as well as JUC-596 and JUC-597 with **hea** net.^[28] However, it is still a challenge to obtain building units with a high extension due to the difficulties in the synthesis and purification. It should be noted that aluminosilicate zeolites as a widely-used crystalline porous material could be constructed to obtain more than 250 topologies by simple tetrahedral geometry (SiO_4 or AlO_4).^[29] In principle, more novel frameworks in 3D COFs, such as zeolite-like networks, could be also created by tetrahedral moieties as interlinked centers rather than just a limited number of topologies, e.g., **dia**, **ctn**, **bor**, and **pts**.^[30-37] However, this avenue has not yet been explored.

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Herein, we report a 3D COF with the zeolitic net, namely zeolitic organic framework (ZOF). By employing two kinds of tetrahedral building units with fixed or relatively free bond angles, we successfully design and synthesize a crystalline porous ZOF with zeolitic **crb** net (namely zeolite **BCT**),^[38] termed ZOF-1, which has been determined its structure by the single-crystal 3D electron diffraction (ED) technique. Notably, ZOF-1 displays excellent chemical stability, large pore size (~ 16 Å), and specific surface area (~ 2785 m²/g), which is much higher than its analogues with the same net, such as traditional aluminosilicate zeolites and zeolitic imidazole frameworks (ZIFs). To the best of our knowledge, this study represents the first case of zeolite-like crystalline porous organic materials.

In order to construct a novel COF with the zeolitic net, our strategy is based on the reasonable regulation of tetrahedral building units by reticular chemistry.^[39] As shown in Scheme 1, we performed potential energy scans of three tetrahedral building units, 9,9'-spirobifluorene (SBF), tetraphenylmethane (TPM) and 3,3',5,5'-tetraphenyl-bimesitylene (TPBM), as the bond angles changed between $\pm 10^\circ$ by using Gaussian 09 software package.^[40] Obviously, the relatively free TPM and TPBM showed small energy changes (~ 8 kJ/mol), demonstrating that such building blocks are apt to form a traditional structure with **dia** net, an optimal conformation based on the lowest energy, by altering their bond angles.^[19] Different with flexible TPM and TPBM, SBF as a highly fixed linker exhibited major changes of the energy (~ 60 kJ/mol),

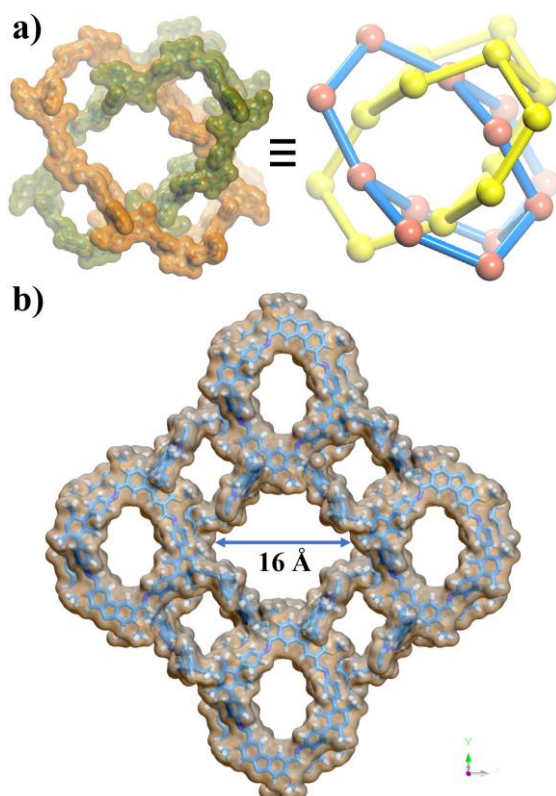


Figure 2. (a) Twofold interpenetrated cage in ZOF-1. (b) Extended porous framework of ZOF-1 viewed along the *c* axis. C, sky blue; H, gray; N, blue; O, yellow.

which indicates that it will probably tend to set up new architectures instead of the traditional optimal **dia** network

due to the hard-to-change bond angles. Based on this strategy, we synthesized a derivative of SBF containing aldehyde groups, 2,2',7,7'-tetramethoxy-9,9'-spirobifluorene-3,3',6,6'-tetracarbaldehyde (TMSFTA, Scheme 2a). By the condensation of TMSFTA and a building unit containing amino groups, 3,3',5,5'-tetra(*p*-aminophenyl)-bimesitylene (BMTA, Scheme 2b), we successfully developed the first 3D COF with the zeolitic net, ZOF-1 (Scheme 2c).

Typically, the synthesis of ZOF-1 was carried out by suspending TMSFTA and BMTA in a mixed solution of *n*-butyl alcohol and 1,2-dichlorobenzene with the presence of 9 M acetic acid aqueous solution, followed by heating at 120 °C for 3 days. Complementary methods were employed for precise structural determination and characterization. Scanning electron microscopy (SEM) and image revealed that ZOF-1 exhibited approximate rectangular crystals (Figure S1). The Fourier transform infrared (FT-IR) spectra demonstrated the formation of ZOF-1 by a newly appeared C=N stretching peak at 1615 cm⁻¹ and the disappearance of N-H stretching band at 3310~3400

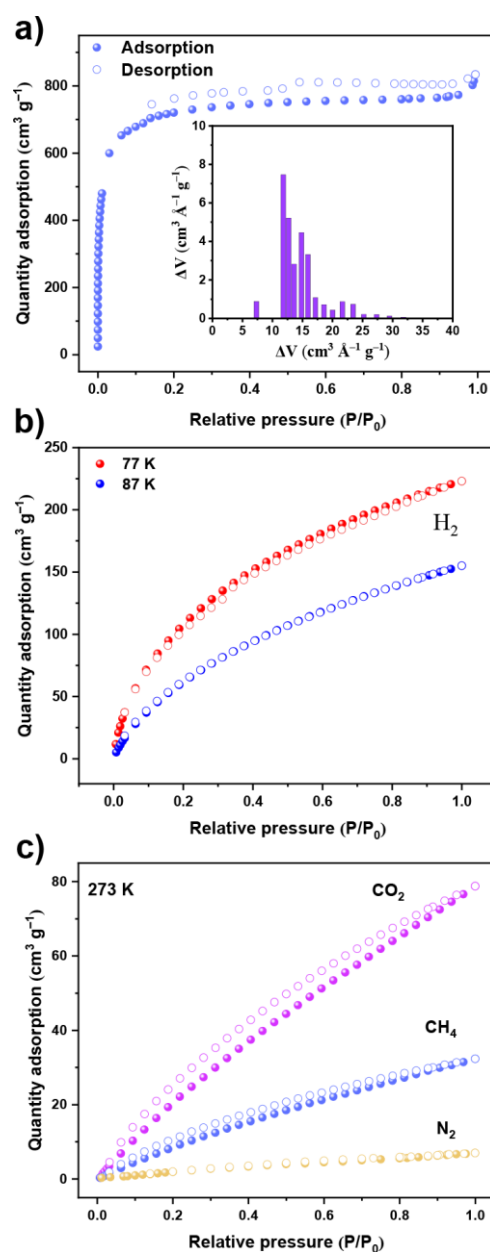


Figure 3. (a) N₂ adsorption-desorption isotherm of ZOF-1 at 77 K. (b) H₂ adsorption of ZOF-1 at 77 K and 87 K. (c) Uptakes of CO₂, CH₄ and N₂ of ZOF-1 at 273 K. Inset: pore-size distribution of ZOF-1.

cm⁻¹ and C=O stretching band at 1696 cm⁻¹, manifesting the completed conversion of Schiff-base polymerization (Figure S2). Solid-state ¹³C cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy of ZOF-1 further verified the presence of a new C=N bond by the peak at 162 ppm (Figure S3). In addition, ZOF-1 showed high thermal stability (up to 300 °C) according to the thermogravimetric analysis (TGA) under nitrogen gas, and excellent chemical stability for the stable existence in different organic solvents and aqueous solutions for 24 h, such as strong acid (HCl with pH = 1) and strong base (NaOH with pH = 14, Figures S4-9).

The unit cell and crystal structure of ZOF-1 were resolved by a 3D ED technique continuous rotation electron diffraction (cRED, Figures 1b and S10). The cRED data were collected on a JEOL 2100-plus TEM equipped with MerlinEM direct electron detector under 200 kV acceleration voltage at 100 K. The data were visualized with program RED^[41] and processed using XDS^[42] with the aid of Instamatic^[43] for batch processing. These data were recorded with the tilting angle from -51.12° to 63.86°. Each frame was collected with an exposure time of 1 s, resulting in a 0.75° wedge per frame. The resolution cutoff was set to 2.0 Å according to the criteria of $1/\sigma > 1$. The diffraction can be indexed with the cell parameter of $a = 30.37$ Å, $b = 30.00$ Å, $c = 18.71$ Å, $\alpha = 89.79^\circ$, $\beta = 89.78^\circ$, and $\gamma = 90.09^\circ$. Pointless^[44] analysis indicated that the diffraction belongs to *Cmmm* Laue group and not to a tetragonal lattice. Thus, the unit cell was converted to an orthorhombic *C*-lattice with the cell parameters of $a = 42.62$ Å, $b = 42.76$ Å, $c = 18.73$ Å. Due to the low resolution (2.0 Å), we turned to the molecular replacement method (Phaser).^[45] The initial positions of two monomers were found using this method, and they were then adjusted manually to form a continuous network. Finally, the model was optimized by Forcite module in the Materials Studio with COMPASS II force field (Table S1).^[46] In light of these results, ZOF-1 was defined as a 3D framework with twofold interpenetrated **crb** net and interconnected channels (up to 16 Å, Scheme 2d, 2e, and Figures 2, S14, S15).

The structure of ZOF-1 was also studied via PXRD combined with the structural simulation. The experimental PXRD pattern of ZOF-1 was in good agreement with the calculated one from the cRED model (Figure S11). Full profile pattern matching (Pawley) refinement was carried out. As shown in Figure 1a, peaks at 2.92°, 4.13°, 5.55°, 6.29°, and 7.54° could be attributed to the (110), (200), (111), (201), and (131) Bragg peaks. The refinement results yielded similar unit cell parameters with good agreement factors ($R_p = 5.91\%$ and $\omega R_p = 6.78\%$). An alternative structure, a non-interpenetrated **crb** net, was also set up; however, its simulated PXRD did not match the experimental one (Figure S12).

The permanent porosity and specific surface area of ZOF-1 were obtained by N₂ adsorption analysis at 77 K. As shown in Figure 3a, a sharp increase was observed at low pressure (below 0.1 P/P₀), which reveals a microporous nature. The slight desorption hysteresis and inclination above 0.9 P/P₀ can be attributed to textural mesopores from the agglomeration of crystals.^[47] According to its N₂ adsorption isotherm, the Brunauer–Emmett–Teller (BET) specific surface area of ZOF-1 was as high as 2785 m²/g (Figure S13). Furthermore, the pore-size distribution was calculated by nonlocal density functional

theory (NLDFT), which is in good agreement with those of the crystal structure (Figure 3a, inset). Remarkably, ZOF-1 displayed an impressive BET surface area (2785 m²/g) and pore size (up to 16 Å) compared to other zeolite-like materials with the same **crb** net, including traditional aluminosilicate zeolites and ZIFs, such as BTC zeolite (3 Å),^[48] ZIF-1 (3 Å),^[49] ZIF-2 (6 Å),^[49] and ZIF-64 (6 Å),^[50] which demonstrates that such pure organic frameworks have fascinating potential due to their high surface areas and large pores (Table S2).

We further investigated the H₂ adsorption performance of ZOF-1. As shown in Figures 3b, ZOF-1 showed a high capacity in H₂ uptake up to 223 cm³/g (1.99 wt%) at 77 K and 154 cm³/g (1.38 wt%) at 87 K at 1 bar, which is comparable with best performing porous materials, such as CTC-COF (125 cm³/g or 1.12 wt%),^[51] MOF-177 (139 cm³/g or 1.25 wt%),^[52] PAF-1 (179 cm³/g or 1.60 wt%).^[53] Furthermore, the isosteric heat of adsorption (Q_{st}) of ZOF-1 for H₂ was calculated to be 6.37 kJ/mol (Figure S16). In addition, we studied the potential application of ZOF-1 for CO₂ adsorption and separation. The adsorption isotherms of CO₂, N₂, and CH₄ were measured at 273 K (Figure 3c). Notably, the sorption amount of ZOF-1 for CO₂ was as high as 78.78 cm³/g, which is much higher than the other two gases, CH₄ (32.34 cm³/g) and N₂ (7.01 cm³/g). The ideal adsorption selectivity of ZOF-1 was calculated from the ratio of the initial slopes based on the Henry region of the isotherms (Figure S17), and good selectivity of CO₂/N₂ (6.7) or CO₂/CH₄ (19.1) was observed (Table S3).

In summary, we successfully designed and synthesized a zeolite-like crystalline porous organic material, ZOF-1 with the zeolitic **crb** net, by using two kinds of tetrahedral building blocks with fixed or relatively free bond angles, TMSFTA and BMTA. The crystal structure of ZOF-1 was well determined by a cRED technique as well as PXRD patterns combined with the structural simulation. Furthermore, ZOF-1 showed high chemical stability, large pore size (~ 16 Å), and exceptional specific surface area (~ 2785 m²/g), which exceeds its analogues with the same framework involving traditional aluminosilicate zeolites and ZIFs. Therefore, this work expands a new avenue to create crystalline zeolite-like materials constructed from organic building units and will facilitate their promising potentials for adsorption and catalysis of large molecules.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

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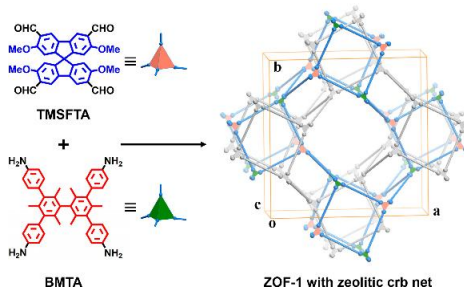
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Zeolitic Organic Framework

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Design and Synthesis of a Zeolitic Organic Framework



Herein, we report the first case of zeolite-like crystalline porous organic materials, ZOF-1 with high chemical stability, large pore size (up to 16 Å), and excellent specific surface area (~2785 m²/g), which is superior to its analogues with the same network, including traditional aluminosilicate zeolites and zeolitic imidazole frameworks.