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Communication

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Twist Building Blocks from Planar to Tetrahedral for the Synthesis of Covalent Organic Frameworks

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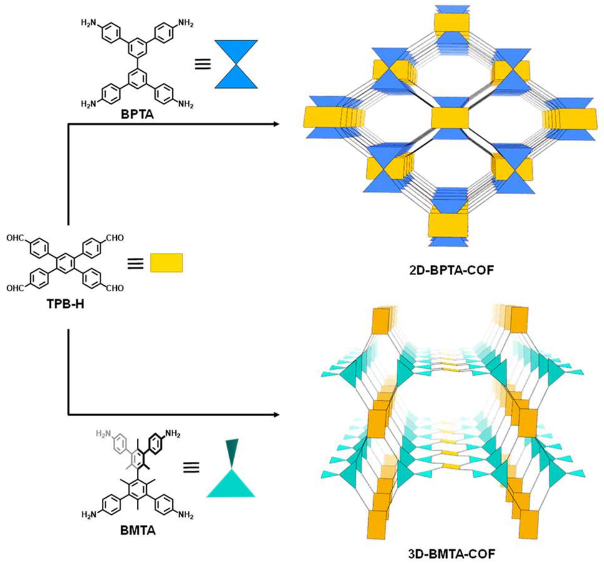
Supporting Information Placeholder

ABSTRACT: Rational construction of covalent organic frameworks (COFs) with novel structures still remains a challenge. Herein, we reported the designed synthesis of two COFs, 2D-BPTA-COF and 3D-BMTA-COF, starting from biphenyl-based precursors but with different groups on ortho positions. Both COFs exhibited high crystallinity and large surface area, and interestingly, 2D-BPTA-COF crystallizes into 2D sheets with AB stacking mode while 3D-BMTA-COF adopts a seven-fold interpenetrated structure with **pts** topology. This structural difference could be ascribed to the introduction of methyl groups in the building blocks, as the dihedral angle of biphenyl rings in 2D-BPTA-COF is ~0° while in 3D-BMTA-COF is ~60°. Therefore, it is possible to synthesize COFs with different structures by twisting building blocks from planar to tetrahedral with steric hindrance. We believe this result represents a general and straightforward way to expand the diversity of tetrahedral nodes for constructing 3D COFs in future, and moreover, a new tetrahedral node for constructing 3D COFs is now available.

Covalent organic frameworks (COFs) represent an emerging class of crystalline polymers with high porosity and structural tunability.[1] Since first announced by Yaghi in 2005,[2] COFs have gained intensive attention and shown great potentials in gas storage and separation,[3] heterogeneous catalysis,[4] optoelectronics devices,[5] sensors,[6] energy storage[7] and so on. According to the dimensionality of the covalent connectivity, COFs can be either categorized into two-dimensional (2D) layered structures or three-dimensional (3D) networks. Until now, most of the research efforts have focused on 2D structures, and a large number of 2D COFs have been reported.[8,9] In contrast, 3D COFs are much less studied (about only forty examples),[10-13] although their inherent characteristics (e.g. exceptionally high surface areas exceeding 5000 m^2/g) [10d] can make them as ideal candidate for excellent adsorption or catalysis. Fundamentally, such underdeveloped status can be attributed to the existing challenges in 3D COFs,[13] including synthetic difficulty, complicated structural determination, very few network topologies and limited building blocks. To our delight, some important progress in 3D COFs has been achieved over the past few years. For example, Wang, Sun and Yaghi developed a general strategy to grow large single crystal of 3D COFs,[11] and their structures were successfully determined by single-crystal X-ray diffraction. In another example, we demonstrated a new topology design to synthesize 3D COFs, starting from tetrahedral and quadrilateral building blocks connected through [4 + 4] condensation reactions.[3a,5a,12] However, it should be pointed out here, some challenges still need to be further explored, especially the limited availability of molecular building blocks.[13] In order to increase the structural diversity of 3D COFs, the exploration of novel building units is highly demanded.

Scheme 1. Schematic Representation of the Synthesis of 2D-BPTA-COF and 3D-BMTA-COF.



From the geometry perspective of constructing 3D COFs, it is essential to have at least one building unit that can be extended into three spatial directions. So far, tetrahedral nodes are the first direct choice for making such 3D networks and the reported tetrahedral linkers are exclusively based on tetraphenylmethane or adamantine derivatives. Consequently, this few options have seriously limited the number of attainable 3D COFs and the diversity of tetrahedral nodes needs to be further expanded. According to the principles of stereochemistry, it is possible to form tetrahedral geometry from planar molecules by increasing steric hindrance. For example, in biphenyl-based molecules, the size of ortho substituents can strongly affect the dihedral angle of two phenyl rings.[14] When four large groups are introduced onto the ortho positions, a rigid tetrahedral conformation can be obtained. Therefore, with proper design, building blocks with tetrahedral geometry can be achieved through the introduction of steric hindrance and consequent construction of 3D COFs with novel structure might become possible.

With these considerations in mind, we report herein the designed synthesis of two COFs (scheme 1), 2D-BPTA-COF and 3D-BMTA-COF, staring from biphenyl-based building blocks but with different groups on ortho positions. Both COFs exhibited high crystallinity and large surface area, and interestingly, 2D-BPTA-COF crystallizes into 2D sheets with AB stacking mode while 3D-BMTA-COF adopts a seven-fold interpenetrated structure with **pts** topology. Based on their crystal structures, the dihedral angle of biphenyl rings in 2D-BPTA-COF is ~0°. However, due to the existence of methyl groups, biphenyl rings in 3D-BMTA-COF have adopted a tetrahedral configuration with dihedral angle of ~60°. Consequently, introducing steric hindrance in ortho positions of biphenyl cores can change their geometry and thus provide a new tetrahedral node for constructing 3D COFs. To the best of our knowledge, this is the first time to investigate the effect of reinforced nonplanarity on the synthesis of COFs.

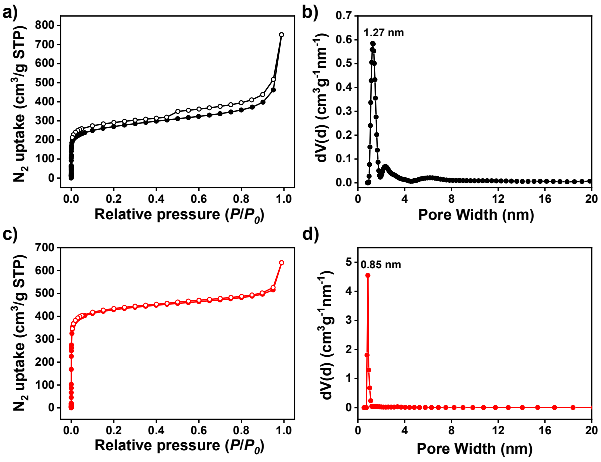


Figure 1. N_2 sorption isotherms of 2D-BPTA-COF (a) and 3D-BMTA-COF (c) at 77 K. Pore size distributions of 2D-BPTA-COF (b) and 3D-BMTA-COF (d).

In order to prove our idea, we decided to construct biphenyl-based COFs as discussed above. As shown in Scheme 1, we first designed and synthesized a linker, 3,3’,5,5’-tetra(*p*-aminophenyl)-biphenyl (BPTA) (Figure S1), which has hydrogen atoms at ortho positions. After condensation reaction of BPTA and 1,2,4,5-tetrakis-(4-formylphenyl)-benzene (TPB-H) in a mixture of *o*-dichlorobenzene, *n*-butanol and aqueous acetic acid for 7 days, 2D-BPTA-COF was obtained (Figure S3) as yellow powder insoluble in common organic solvents and water. The structure of 2D-BPTA-COF was then investigated by several techniques. From the Fourier transform infrared (FT-IR) spectrum, 2D-BPTA-COF exhibited a stretching vibration band at 1626 cm^{-1} (Figure S5), indicating the formation of imine bonds. According to the solid-state nuclear magnetic resonance (ssNMR) experiment (Figure S6), a new resonance at ~158 ppm was found, confirming again the presence of imine bonds. In addition, thermogravimetric analysis (TGA) showed 2D-BPTA-COF has a high thermal stability up to 530 °C under nitrogen (Figure S7), and scanning electron microscopy (SEM) revealed a flake-like morphology (Figure S8). Furthermore, we measured the nitrogen adsorption isotherms of 2D-BPTA-COF at 77 K. As can be seen in Figure 1a, 2D-BPTA-COF exhibited a type I sorption isotherm, indicating the existence of microporous structure. The Brunauer−Emmett−Teller (BET) surface area and the total pore volume were calculated to be 1000 m^2 g^{-1} and 1.16 cm^3 g^{-1}, respectively. By using quenched solid density functional theory (QSDFT), 2D-BPTA-COF showed a narrow pore size distribution centered at 1.27 nm (Figure 1b).

The PXRD pattern of 2D-BPTA-COF exhibited a intense peak at 5.76˚ and two small ones at 9.46˚ and 11.64˚ (Figure 2a), indicating the long-range ordering. We then used a 3D electron diffraction (ED) technique, continuous rotation electron diffraction (cRED),[15] to elucidate the unit cell and crystal structure. Based on the collected cRED data (Figure 2b), the 3D reciprocal lattice was reconstructed, which contains a serial of streaks along the c* axis and forms orthogonal pattern in the a*-b* plane. Accordingly, 2D-BPTA-COF may have a layered structure (a = 18.5 Å, b = 26.1 Å and γ = 90°) and the streaks could be induced by stacking faults along the c-axis. From this unit cell information, possible 2D structure models for 2D-BPTA-COF were built by using Materials Studio software package (Figure 3 and Figure S12), and the simulated PXRD pattern with AB stacking mode shows excellent agreement with the experimental pattern in peak positions and relative intensities (Figure 2a). Finally, a more accurate structure model of 2D-BPTA-COF with AB stacking mode (unit cell parameters: a =18.500(0) Å, b = 26.330(9) Å, c = 7.801(4) Å, $\alpha = \gamma$ = 90°, and β = 96.088(9)°; space group: $C2/m$) was obtained by the Rietveld refinement with acceptable low residuals R_p = 6.03% and R_{wp} = 7.50% (see Tables S1 and S2 for details).

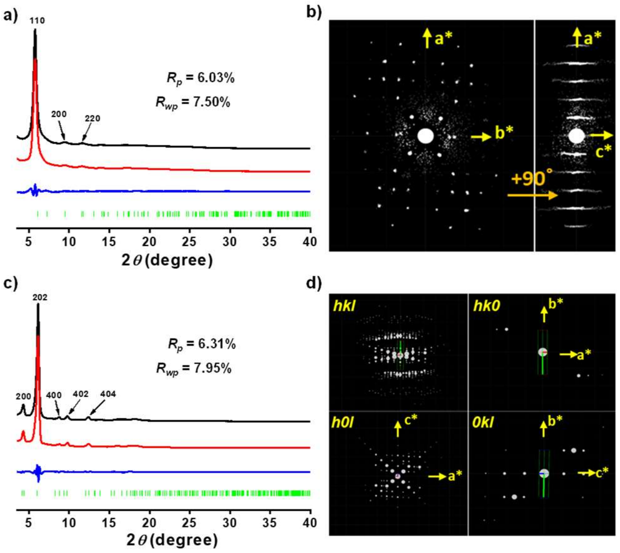


Figure 2. Powder X-ray diffraction patterns of 2D-BPTA-COF (a) and 3D-BMTA-COF (c). The experimental XRD patterns are shown in black, the refined patterns in red, the difference between the observed and refined profiles in blue, Bragg position from crystal structures in green. 3D reciprocal lattice of 2D-BPTA-COF (b) and 3D-BMTA-COF (d).

According to the structure of 2D-BPTA-COF, the biphenyl rings exhibited a planar conformation with a D_{2h} symmetry and have a dihedral angle of ~0°. Since the introduction of steric hindrance at the ortho positions can render the two rings orthogonal with a tetrahedral symmetry, we predicted the resulting building units may be suitable for constructing 3D COFs. To assess this concept, force-field simulation was then applied to calculate the framework energy for possible 2D structure models (Figure S15) after incorporation of methyl groups into the biphenyl core as steric hindrance. In addition, as it is reasonable to construct 3D COFs starting from tetrahedral and quadrilateral precursors through [4 + 4] connection,[3a,5a,12] we also built a 3D structure with non-interpenetrated **pts** topology (Figure S16). After geometry optimization, the energy of 2D framework with methyl groups (949.02 Kcal/mol for AA stacking and 930.27 Kcal/mol for AB stacking) was found to be much higher than that of the 3D structure with non-interpenetrated **pts** topology (859.72 Kcal/mol). The detail calculated information can be found in section S6. Therefore, a 3D framework can be expected after introducing methyl groups as steric hindrance to BPTA.

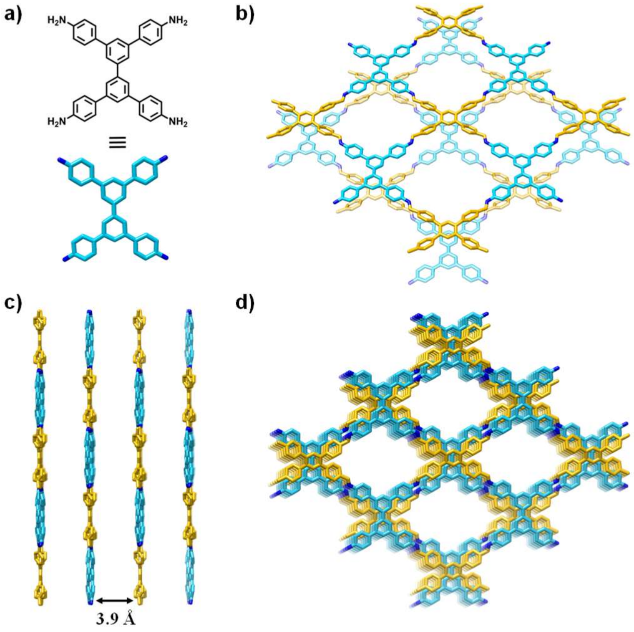


Figure 3. Structural representations of 2D-BPTA-COF. (a) Conformation of BPTA unit in 2D-BPTA-COF, (b) the structure of adjacent two-layer, (c) side view, (d) top view.

We then designed and synthesized a new linker 3,3',5,5'-tetra(*p*-aminophenyl)-bimesitylene (BMTA) (Scheme 1 and Figure S2), by introducing the methyl groups in BPTA. After condensation with TPB-H, 3D-BMTA-COF was finally isolated (Figure S4) as gray powder insoluble in common organic solvents and water. Same as before, FT-IR spectra (Figure S5) and ssNMR spectra (Figure S6) of 3D-BMTA-COF provided solid evidence for the formation of imine bonds, and TGA plot exhibited high thermal stability of ~510 °C (Figure S7). However, unlike 2D-BPTA-COF, the SEM images of 3D-BMTA-COF exhibited granular morphology (Figure S8). Moreover, from the nitrogen sorption measurement (Figure 1c), 3D-BMTA-COF showed a higher BET surface area (1650 m^2 g^{-1}) and smaller pore size (0.85 nm, Figure 1d) compared to 2D-BPTA-COF.

In order to determine the crystal structure of 3D-BMTA-COF, PXRD and cRED techniques were applied. The PXRD pattern (Figure 2c) clearly demonstrated the crystalline nature of 3D-BMTA-COF, but due to the low intensity of the high angle peaks, it was very difficult to resolve the structure directly. As the crystal size of 3D-BMTA-COF is too small to collect 3D ED data, we were not able to solve the crystal structure, even for the unit cell. After many synthesis trials, 3D-BMTA-COF with bigger crystal size was successfully obtained for cRED studies (Figure 2d) by adding aniline as a modulator under optimized conditions (Section S4). Although the resolution of 3D ED dataset was only 2 Å, the central carbon atoms of tetrahedral and quadrilateral building blocks can be located by *SHELXT*[16]. Based on the atom coordinates determined from cRED data, we successfully built a structure model with a seven-fold interpenetrated **pts** topology (Figure 4). As expected, due to the existence of methyl groups, the dihedral angle of biphenyl rings was found to be ~60°, which resulted in a tetrahedral conformation with D_2 symmetry. Finally, the structure of 3D-BMTA-COF (unit cell parameters: a = 41.216(3) Å, b = 4.927(2) Å, c = 40.237(4) Å, and β = 89.943(3)°; space group: $C2/c$) was obtained by the Rietveld refinement with acceptable low residuals R_p = 6.31% and R_{wp} = 7.95% (see Tables S3 and S4 for details). We should mention here, due to the presence of sp^2 hybridised bridge carbon atoms in biphenyl nodes, 3D-BMTA-COF is a conjugated 3D COF. Based on these results, it is possible to synthesize COFs with different structures through steric-reinforced nonplanarity.

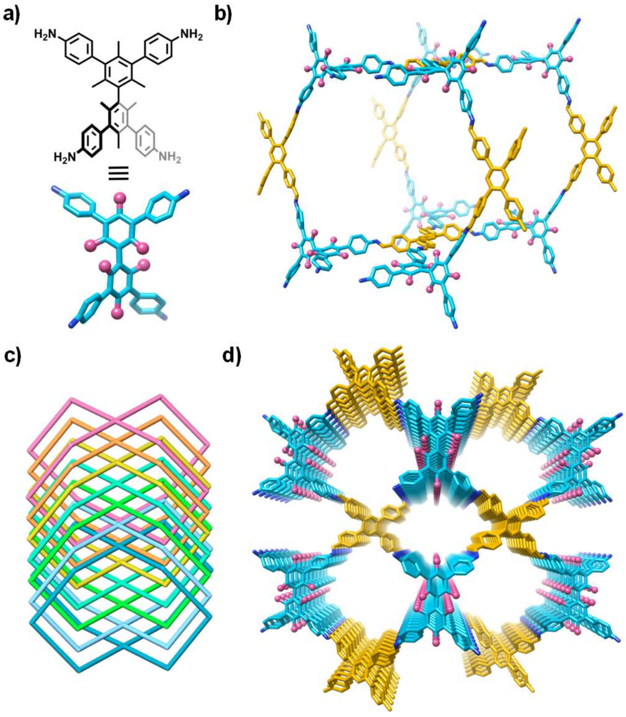


Figure 4. Structural representations of 3D-BMTA-COF. (a) Conformation of BMTA unit in COF, (b) single **pts** network of 3D-BMTA-COF, (c) seven-fold interpenetrated **pts** topology, (d) the porous structure of 3D-BMTA-COF.

In summary, we have described the designed synthesis of two biphenyl-based COFs with high crystallinity and large surface area. By combining PXRD and cRED techniques, 2D-BPTA-COF was determined to adopt a 2D layered structure with AB stacking mode, while 3D-BMTA-COF showed a seven-fold interpenetrated structure with **pts** topology. From the crystal structure, the dihedral angle of biphenyl rings in 2D-BPTA-COF is ~0° while in 3D-BMTA-COF is ~60°. Therefore, their framework difference can be explained by this different conformation of biphenyl cores, which should be ascribed to the introduction of steric hindrance with methyl groups. Consequently, by twisting building blocks from planar to tetrahedral with steric hindrance, COFs with different structures can be obtained. We believe this result represents a general and straightforward way to expand the diversity of tetrahedral nodes, and moreover, a new tetrahedral node for constructing 3D COFs is now available. Considering the sp^2 hybridised bridge carbon atoms in biphenyl nodes, more conjugated 3D COFs with interesting applications can be imagined.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, FT-IR, solid state ^{13}C NMR, TGA, SEM, TGA, N$_2$ sorption isotherms, crystal structure analysis can be found in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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†C.G. and J. L. contributed equally.

Notes

The authors declare no competing financial interests.

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