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## A Case Study on the Influence of Substitutes on Interlayers Stacking of 2D Covalent Organic Frameworks

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**Abstract:** Interlayer stacking of 2D covalent organic frameworks (COFs) plays a crucial role in determining not only geometry of channels inside COFs but also mobility of carrier transport between COF layers. However, while topological structures of 2D COFs monolayers can be precisely predicted through the structures of building blocks, factors affecting their interlayer stacking remain poorly understood. In this work, a truxene-based building block on which six methyl groups are introduced was designed. The condensation of it with 1,4-diaminobenzene or benzidine afforded 2D COFs with the methyl groups extending out-of-plane of the layers. A significant influence of the methyl groups on interlayer stacking of the COFs was revealed by the adoption of inclined packing of monolayers, which has never been experimentally observed before. This unprecedented stacking manner was confirmed by PXRD study, pore size distribution analysis and TEM investigation.

Covalent Organic Frameworks (COFs) are a class of crystalline porous organic polymers whose organic units are covalently connected to form two-dimensional (2D) or three-dimensional (3D) periodic networks.<sup>[1]</sup> They have drawn a great deal of interest over the past decade due to their important applications in many aspects, including gas storage and separation,<sup>[2]</sup> catalysis,<sup>[3]</sup> sensing,<sup>[4]</sup> delivery,<sup>[5]</sup> energy storage,<sup>[6]</sup> and optoelectronics<sup>[7]</sup>. One distinct feature of COFs that is different from amorphous porous organic materials is their well-defined channels, which play a pivotal role in the realization of their versatile functions. For 3D COFs, the extending of building blocks in 3D space spontaneously results in the formation of permanent channels inside. In the case of 2D COFs, however, the building units just covalently extend in 2D space, which brings in periodical distribution of micro/meso-pores in 2D monolayers. It is the stacking of monolayers into 3D layered structures that leads to the generation of 1D channels orthogonal to the layers. In this context, the geometry of channels in a 2D COF is not only dictated by the original pore size and shape in monolayer, but also dependent on packing manner of the layers. On the other hand, the interlayer stacking also exerts a huge influence on the overlapping of conjugated skeletons of COFs, which defines interlayer electron or charge

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transport and thus has a profound effect on their optoelectronic properties.  $\ensuremath{^{[8]}}$ 

Over the past decade a variety of 2D COFs have been constructed. However, although the geometry and unit size of 2D network of a COF usually can be precisely predicted through the structures of the monomers used for polymerization, stacking manner of its layers still cannot be forecasted. Due to the lack of fundamental understanding, very little is known about how monomer structure exerts an influence on the stacking behavior of COF layers.<sup>[9]</sup> Some recent theoretical investigations suggested that notable differences might exist between experimental assignments and theoretical predictions for the interlayer stacking of 2D COFs.<sup>[10]</sup> However, so far this subject has hardly been experimentally studied. In this communication we demonstrate that substituents on building blocks can make a significant impact on the interlayer stacking of 2D COFs. A theoretically predicted stacking mode, that is, inclined stacking,<sup>[10a,b]</sup> has been experimentally observed for the first time

In this work we mainly focused on the influence of substituents on interlayer stacking of 2D COFs. While early COFs were mainly constructed from building blocks without substituents, more recently COFs with substituted skeletons have been fabricated to introduce specific functions through direct use of substituted building blocks<sup>[3c,11]</sup> or post-modification of COFs<sup>[3d,12]</sup> However, in most COFs the substituted groups are flexible and are almost in-plane of the 2D layers and thus make very little effect on the interlayer stacking. In a few cases bulky tert-butyl groups were introduced and they should be partly out-of-plane of the building blocks.<sup>[13]</sup> Although the *tert*-butyl groups can freely rotate to partly alleviate the steric hindrance, slipped-AA stacking was observed for the COF, which was attributed to the result of avoiding the clash of tert-butyl groups between neighbouring layers.<sup>[13a]</sup> In order to enhance the role of substituents in dictating interlayer stacking, in this work a building block was designed by incorporating methyl groups on a truxene core, which generates 3,8,11-tri(4-formylphenyl)-5,5,10,10,15,15-hexamethyltruxene (TFPHMT) (Scheme 1). Owing to the tetrahedral configuration of sp<sup>3</sup> carbon, the methyl groups locate out-of-plane of the truxene core. Using TFPHMT as a monomer, formation of 2D frameworks with hexagonal micropores can be predicted from condensations of it with 1,4diaminobenzene or benzidine. As a result of the rigid structure of TFPHMT, the methyl groups should also extend out-of-plane of the COF monolayers and thus are fixed at both sides of the layers, which leads to formation of the first COFs with inclined stacking.

The condensation reactions were carried out under solvothermal conditions, which afforded **SIOC-COF-8** and **SIOC-COF-9** as yellow powders (see supporting information for the detailed procedures). IR spectra of the powder showed that the peak corresponding to  $-NH_2$  groups almost disappeared and peaks around 1618 cm<sup>-1</sup> appeared, suggesting a high degree of

polymerization and the formation of C=N linkages (Figure S1-2). Moreover, peaks corresponding to the vibration of -CH<sub>3</sub> groups were also observed around 3000 cm<sup>-1</sup>, indicating existence of methyl units in the two COFs. The formation of polyimine from the condensation of the starting materials was also supported by the appearance of C=N signals (156 ppm) in their solid-state <sup>13</sup>C CP-MAS NMR spectra (Figures S3-4). Furthermore, peaks corresponding to methyl groups were also observed at 21 ppm in the spectra, again indicating that methyl groups were retained in the COFs. Thermogravimetric analysis (TGA) indicated that 5% weight loss occurred at 470 and 364 °C for SIOC-COF-8 and SIOC-COF-9, respectively (Figures S5), demonstrating that they have high thermal stabilities. Scanning electron microscopy (SEM) and atomic force microscopy (ATM) investigations revealed that the COFs displayed irregular morphology (Figures S6).



Scheme 1. Synthesis and structures of SIOC-COF-8 and SIOC-COF-9. Note: only one pore unit and single layer are presented for clarity.

Powder X-ray diffraction (PXRD) profiles of the as-prepared powders were recorded. Both of them exhibited diffraction peaks with high intensities (Figure 1), suggesting a high crystallinity. In

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Figure 1. Experimental, refined and simulated PXRD patterns of (a) SIOC-COF-8 and (b) SIOC-COF-9 with different stacking manners. And (c) views of SIOC-COF-8 with inclined stacking generally along the z (left) and x (right) axes, respectively. Methyl groups were highlighted in red. SIOC-COF-9 exhibits the similar stacking (Figure S9).

order to determine their crystal structures, theoretical simulations were carried out by using Accelrys Materials Studio 7.0 software package. In the simulations, infinite 2D networks possessing hexagonal pores, as illustrated in Scheme 1, were constructed. Since in literature nearly all the 2D COFs have been experimentally reported to adopt eclipsed (AA) stacking, PXRD patterns of the COFs with AA stacking of monolayers were firstly simulated and compared with the experimentally observed PXRD patterns. It should be noted that the common interlayer distance range of 3.5-4.5 Å in 2D COFs could not be set for SIOC-COF-8 and SIOC-COF-9, because in AA stacking steric repulsions between the methyl groups would arise if the layers maintain a close distance. Therefore, the interlayer distance was enlarged to 6.0 Å, a value at which the methyl groups between the layers of eclipsed packing just separate from each other and make no contact. The comparisons indicated that their experimental PXRD patterns show dramatic differences from the simulated PXRD patterns of AA stacking in the positions of the diffraction peaks, which strongly suggests that SIOC-COF-8 and SIOC-COF-9 do not adopt AA stacking manner. Next, PXRD patterns of staggered (AB) stacking were simulated, which, however, were not consistent with the experimental PXRD data, either. Since both the two classic stacking models are inconsistent with the experimental results, a third stacking manner, that is, slipped-AA stacking (serrated stacking) was simulated.<sup>[10]</sup> In this model, four horizontal offsets by 5, 10, 15 and 20 Å were used. The resulted theoretical PXRD patterns were compared with the experimental PXRD patterns again and it turned out that large discrepancies still existed between them (Figure S7-8).

In 2010 Heine and co-workers theoretically proposed four possible interlayer stacking forms, that is, eclipsed (AA), staggered (AB), serrated and inclined stackings, for 2D COFs on the basis of DFT calculations.<sup>[10a,10b]</sup> While the former three have already been experimentally observed, the last one has never been found in the COFs previously reported. Since the

experimental PXRD patterns of SIOC-COF-8 and SIOC-COF-9 did not coincide with those of the three former stacking models, layered structures with inclined stacking were built for the two COFs and their theoretical PXRD patterns were simulated (Figure 1). To our delight, the simulated PXRD patterns of the COFs with an inclined stacking model (adjacent two monolayers offsetting by 8.2 Å) well reproduced the experimental data. This result strongly suggests that the layers in the two COFs adopt inclined stacking. On the basis of the simulations, the diffraction peaks of SIOC-COF-8 observed at 2.69°, 3.42°, 4.10°, 5.43°, 6.48°, 6.85°, 8.97°, 10.29° and 19.30° 20 could be attributed to (1 0 0), (1 -1 0), (1 1 0), (2 0 0), (2 1 0), (2 -2 0), (3 1 0), (3 -3 0), (0 0 1) facets, respectively. In the case of SIOC-COF-9, the peaks at 20 = 2.35°, 2.99°, 4.69°, 5.99°, 9.00° and 19.39° are assignable to (1 0 0), (1 -1 0), (2 0 0), (2 -2 0), (3 -3 0) and (0 0 1) reflections, respectively. The (0 0 1) peaks indicate interlayer distances of 4.53 Å and 4.50 Å for SIOC-COF-8 and SIOC-COF-9, respectively, which are larger than those of the COFs reported in literature. Pawley refinement gave rise to unit cell parameters of a = b = 51.52 Å, c = 9.60 Å,  $\alpha = 40.41^{\circ}$ ,  $\beta =$ 40.45°,  $\gamma = 60.00^{\circ}$  (residuals:  $R_p = 4.55$  % and  $R_{wp} = 6.07$  %) for SIOC-COF-8. In the case of SIOC-COF-9, unit cell parameters of a = b = 59.00 Å, c = 9.30 Å,  $\alpha = 40.82^{\circ}$ ,  $\beta =$ 40.91°,  $\gamma$  = 60.00° (residuals:  $R_{p}$  = 4.18% and  $R_{wp}$  = 5.53%) were produced by Pawley refinement. The difference plots indicate that their experimental PXRD patterns match with the refined ones quite well.

Another key evidence for the inclined stacking of the layers in the two COFs was provided by pore size distribution (PSD) analysis. Nitrogen adsorption-desorption experiments were carried out for SIOC-COF-8 and SIOC-COF-9 at 77 K. Both the COFs exhibited the type IV absorption isotherm.<sup>[14]</sup> Curves of sharp uptake under low relative pressures at P/P<sub>0</sub> <0.01 followed by a second step in the range of  $0.05 < P/P_0 < 0.2$  were observed, which is indicative of mesoporous materials (Figure 2). Brunauer-Emmett-Teller (BET) model was applied to the isotherms in the range of P/P<sub>0</sub> between 0.05 and 0.2, which gave BET surface areas of 825.17 and 1676.47 m<sup>2</sup> g<sup>-1</sup> for SIOC-COF-8 and SIOC-COF-9, respectively (Figures S10-11). Their pore size distributions were estimated using nonlocal density functional theory (NLDFT), which showed narrow pore size distributions around 25.6 Å for SIOC-COF-8 and 30.2 Å for SIOC-COF-9 (Figures 2b and 2d). The values are fully consistent with theoretical diameters of the channels predicted for the COFs with inclined stacking, which are 24.5 Å (SIOC- $\mbox{COF-8}\)$  and 28.6 Å (SIOC-COF-9) (Figures S12-13). If the COFs should adopt AA stacking, pore size distributions would be observed around 51.5 Å for SIOC-COF-8 and 59.0 Å for SIOC-COF-9 (Figures S14-15). On the other hand, AB stacking of the layers would give rise to pore size distributions at 20.2 and 25.6 Å for SIOC-COF-8 and SIOC-COF-9, respectively (Figures S16-17). For serrated stacking, the pore sizes should be close to that of AA stacking or AB stacking, or exhibit multiple distributions, depending on the value of the offset (Figures S18-19). The PSD results corroborate again that SIOC-COF-8 and SIOC-COF-9 adopt inclined stacking. Furthermore, the results also clearly demonstrate that the size of channels in 2D COFs changes with the alteration of interlayer stacking. The theoretical maximum BET surface areas of the COFs experimentally obtained

(inclined stacking with offsetting by 8.2 Å) was calculated by using Monte Carlo Metropolis method in Materials Studio,<sup>[15]</sup> which yielded a theoretical surface areas of 3533.3 and 3900.2 m<sup>2</sup> g<sup>-1</sup> for **SIOC-COF-8** and **SIOC-COF-9**, respectively (Figures S20-23). Moreover, theoretical BET surface areas for the COFs with inclined stacking at different offsets of adjacent two monolayers were also calculated for comparison. For **SIOC-COF-8**, theoretical surface areas of 2296.9 and 3219.5 m<sup>2</sup> g<sup>-1</sup> were obtained for offset values of 3.1 and 5.5 Å, respectively. In the case of **SIOC-COF-9**, the simulations gave rise to 2546.9 and 3294.7 m<sup>2</sup> g<sup>-1</sup> for the models at offsets of 3.3 and 5.5 Å, respectively (Figures S20-23).



Figure 2. N<sub>2</sub> adsorption-desorption isotherms (77 K) of (a) SIOC-COF-8, and (c) SIOC-COF-9, and pore size distribution profiles of (b) SIOC-COF-8, and (d) SIOC-COF-9.



Figure 3. HRTEM images and fast Fourier transform patterns (top right inset) of (a) SIOC-COF-8 and (b) SIOC-COF-9. And (c) illustrations for the projections of the channels in SIOC-COF-8 (left) and SIOC-COF-9 (right) along (100) facet.

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Transmission electron microscopy (TEM) investigation provided the third evidence for the inclined stacking of the layers in SIOC-COF-8 and SIOC-COF-9. The stacked layers resulted in the formation of 1D channels through the overlapping of pores in monolayers of the COFs, which were clearly observed in theirTEM images, as revealed by the highly ordered straight black-and-white stripes (Figure 3a and 3b). Fast Fourier transform of the marked areas (enclosed in the red squares) in the TEM images gave rise to ordered diffraction spots (insets of Figure 3a and 3b), suggesting extremely high crystallinity of the COFs. The spacings of the straight stripes can be acquired through direct measurement in the TEM images, or more accurately, from the spacings of the diffraction spots in the fast Fourier transform patterns, which gave the spacings of the stripes to be 3.02 nm for SIOC-COF-8 and 3.56 nm for SIOC-COF-9. On the basis of the comparison of the values with the PXRD data (Table S1-2), they are identified to be the projections of the channels along (1 0 0) plane, as illustrated in Figure 3c.

In summary, we have demonstrated that substituents can have a significant influence on interlayer stacking of 2D COFs. Through introducing steric substituents between the layers of 2D COFs, inclined stacking of the layers, which was theoretically proposed several years ago, has been experimentally realized for the first time. While currently most studies have mainly focused on constructing COFs with novel structures and exploiting their applications, fundamental principles of COFs, such as the formation mechanism of COF networks and interlayer stacking, are less understood. Better understanding of these principles is undoubtedly very important for the design of COFs and development of COF-based materials. We believe this study should be helpful in analyzing 3D layered lattices of 2D COFs. Moreover, this work also suggests that the stacking of COF layers can be manipulated by reasonably introducing substituents at suitable positions of COF skeletons. Since the interlayer stacking not only defines the geometry of channels in COFs but also affects carrier transport between layers, endowing COFs with novel properties and functions through tuning their stacking model can be expected, which may provide new guidance to the design of COF-based functional materials in future.

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**Inclined stacking** of covalent organic framework monolayers has been experimentally confirmed for the first time. The unprecedented stacking manner was realized through the condensation of 1,4-diaminobenzene or benzidine with a truxene-based building block in which six methyl groups were fixed out-of-plane of the truxene core. Yu Fan, Qiang Wen, Tian-Guang Zhan, Qian-Yan Qi, Jia-Qiang Xu, Xin Zhao\*

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