This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ChemComm

COMMUNICATION

Covalent organic frameworks with spatially confined guest molecules in nanochannels and their impacts on crystalline structures

Jia Gao and Donglin Jiang*

We demonstrate profound effects of spatially confined guest molecules in one-dimensional nanochannels on X-ray diffraction behaviors of covalent organic frameworks. Our results give insights into the abnormal X-ray diffraction patterns and suggests a novel molecular dynamic strategy for resolving crystalline structures.

Covalent organic frameworks (COFs) is an emerging class of crystalline porous polymers in which organic building blocks are covalently linked to constitute extended structures with periodicities.[1-5] In two-dimensional (2D) COFs, vertices and edges are topologically linked in a 2D fashion to form monolayer. The 2D monolayers crystallise and stack via π-π interactions to yield lattice structures. Accordingly, the lattice symmetry of 2D-COFs can be divided into two levels in relation to their two structural hierarchies. The first level is the intrinsic symmetry of 2D polymer monolayer, which is determined by the structures of organic building blocks and the topological diagram. The secondary level is the spatial symmetry that is dependent on the stacking orders of 2D polymer layers. The differences of both two levels give rise to different global structural symmetry and yield different powder X-ray diffraction (PXRD) patterns. Although the PXRD pattern could provide essential data set for structural analysis and simulations, however, the absence of single crystals enhances the difficulty in identifying a suitable stacking structure for each member of COFs. Heine *et. al.* have reported the different stacking modes of a variety of COFs and provided insights into the structural effects on stacking energy and PXRD patterns.[5a,5b]

One-dimensional open channels are the structural bases for COFs to accommodate guest molecules. In this study, we focused on the host–guest interactions managed to elucidate the relationship between the guest confinement in the channels and the variation of PXRD patterns. To clarify the systems, we utilised a COF with the smallest pore, COF-1,[1b] and filled the channels with different contents of guest molecules, to show the effects of guest molecules on the PXRD patterns via molecular dynamic simulations (Supplementary Information).

The hexagonal texture of COF-1 gives rise to typical PXRD peaks that are assignable to 100, 110, and 200 facets. We focused on the relative intensities of the PXRD peaks of 100 and 110 facets because the peak of 200 facet is a second-order diffraction of the 100 facet. We rebuilt the structure of AA stacking mode without any external molecule in channels and shifted every second layer along zigzag vertices of the hexagonal channels to identify the changes of the PXRD pattern. Because this zigzag shift can change the overall intensity distribution of the PXRD patterns but it does not cause shift or split of the 100 and 110 peaks, we used the heights of X-ray diffraction peaks to quantitatively monitor their changes.

Figure 1 shows the dependency of the I_{110}/I_{100} value on the offset distance for COF-1 without guest molecules. In the case of the AA stacking mode (offset distance = 0), the I_{110}/I_{100} value is 0.04. By contrast, the staggered AB stacking mode gives rise to the highest I_{110}/I_{100} value of 0.15 (offset = 1*L* or 2*L*) among all of the stacking modes. On the other hand, the smallest I_{110}/I_{100} value was deduced to be 0.02 as the second layer has a medium offset (~ 0.5*L* or 2.5*L*) between the AA and AB stacking modes. All these theoretical values are however much less than the experimentally observed values ($I_{110}/I_{100} > 1$).

To clarify the reason of this large deviation, we considered the possibility of influence of guest molecules in the channels on the PXRD patterns. For this purpose, we built a crystalline structure by integration of mesitylene solvent molecules into the channels of COF-1 in both AA and AB stacking modes. Mesitylene was experimentally observed in the channels as the sole guest for COF-1.[1b,6]

a.Department of Materials Molecular Science, Institute for Molecular Science, National Institutes of Natural Sciences, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan; E-mail: jiang@ims.ac.jp

Figure 2 shows the calculated PXRD patterns of COF-1 with different stacking modes and guest conditions. Compared to the AA stacking mode without mesitylene (Fig. 2A; $P6/mmm$ space group), the presence of mesitylene in the channels yields an increased I_{110}/I_{100} value of 2.45 (Fig. 2C, one mesitylene per pore; Cc space group). Compared to the AB stacking mode without mesitylene (Fig. 2B; $P6_3/mmc$ space group), the existence of mesitylene resulted in a greatly enhanced I_{110}/I_{100} value of 13.8 (Fig. 2D, one mesitylene per pore; $P6_3mc$ space group).
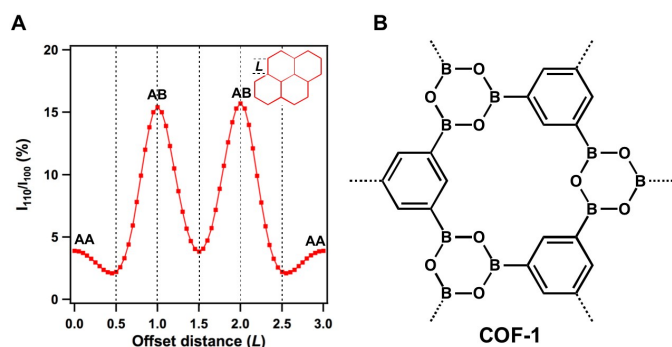

Fig. 1 (A) Dependency of the I_{110}/I_{100} value of COF-1 (free of guest molecules) on the offset distance (L) in zigzag direction. (B) One-pore structure of COF-1.

We conducted molecular dynamics (MD) simulations on the AA stacking mode of COF-1 without guest molecules in the channels (Figures S1-S4). We utilised 3 x 3 supercells and 10 layers of COF-1 and simulated the structural deformations. From the stable structure, COF-1 tends to adopt slipped AA arrangements between layers but with irregular stacking orientations; which also agrees well with the total energy calculations previously.[5b,5d,5e] Based on this result, a stable structure was chose to integrate mesitylene molecules into the channels with an aim to show their impacts on the X-ray diffraction behaviours. Figure 3A depicts the change of simulated PXRD patterns as the apparent density of mesitylene in the channels was increased from 0.1 to 0.9 g cm^{-3}. Clearly, a strong correlation between the I_{110}/I_{100} value and the density of mesitylene was observed. At low guest contents, the PXRD patterns (Fig. 3, red, green, magenta and blue curves) are close to the experimentally observed PXRD pattern for COF-1 without guests. As the loading density was increased, the I_{110}/I_{100} value increased (sky blue, green and yellow curves). As the loading of mesitylene reach the maximum density (0.9 g cm^{-3}), the PXRD pattern (black curve) becomes to match perfectly with the experimentally observed PXRD profile of as-synthesised COF-1 with mesitylene in the channels. As shown in Figure 3B and 3C, MD simulations suggest that the guest mesitylene molecules in the channels, irrespective of their densities, are randomly distributed in the nanochannels (Figure S4).

For a crystalline solid, the incident X-ray is scattered from lattice planes and the reflected X-rays interfere with each other to form diffraction patterns. The channel size of COF-1 is only 11 Å, which is a confined space for guest molecules such as mesitylene. Therefore, in the channels of COF-1, mesitylene molecules are spatially confined. From the density and structural matching, each hexagonal pore can load one mesitylene molecule per layer. This spatial confinement of mesitylene in the central parts of the channels causes considerable effects on the X-ray diffractions; samples with and without mesitylene are totally different from each other. The mesitylene guests in the channels offer a 'pseudo structure phase' that affects both the calculated and experimental PXRD patterns of the samples. Such a spatially confined phase changes the symmetry of the lattice and varies the PXRD patterns dramatically.
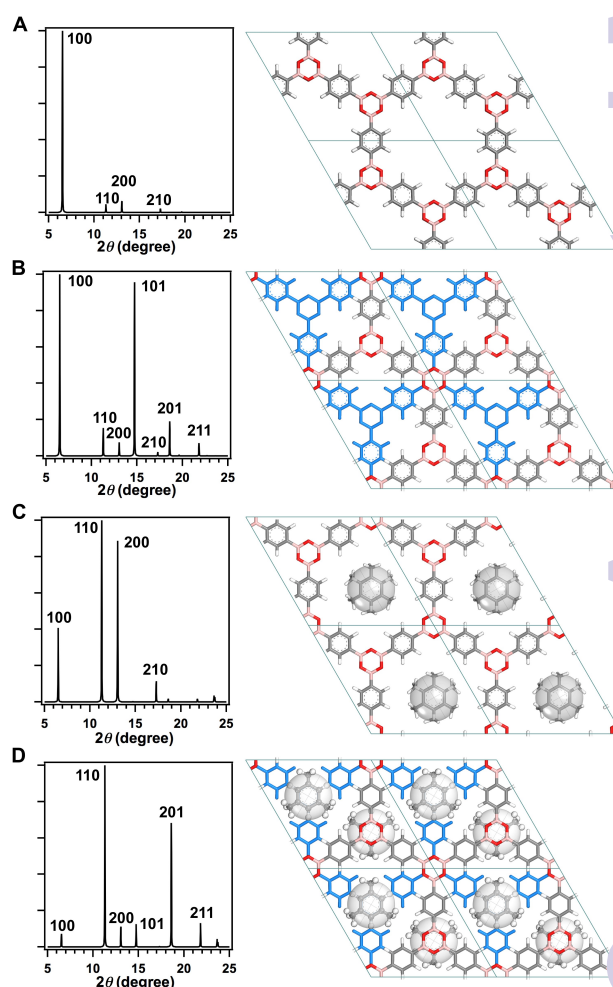

Fig. 2 PXRD patterns of (A) AA stacking without mesitylene, (B) AB stacking without mesitylene, (C) AA stacking with mesitylene in pores and (D) AB stacking with mesitylene in pores. Right side of each PXRD pattern shows the corresponding unit cell structure of COF-1.

COFs are designable in both skeletons and channels; the high flexibility in structural design leads to the

generation of a variety of COFs with different building blocks and channel sizes. COF-1 represents the simplest COF member and offers the smallest pore among unmodified COFs, whereas many other COF members can be engineered to create similar small channels.[3b,3c] We emphasise that the present approach is not limited to COF-1. Any COFs with a channel size that matches with the guest molecules aligned in the channels may lead to abnormal X-ray diffraction behaviours as observed for COF-1, irrespective of their topologies and linkages.

The present results unambiguously demonstrate that the layered structure of COFs is highly dependent on the skeletons that directly provide the π-π forces in directing the framework formation, whereas solvents and/or guest molecules are fully involved in the crystallisation process. Not only the stacking mode but also the PXRD pattern of the resulting COF samples is highly dependent on the solvent or guest molecules involved. The molecular dynamic strategy provides a new tool to resolve the lattice structures of COFs. Our results also imply that the integration of 'designed guest' with suitable size to fill the channel space may help to form well-defined crystals of COFs and leads to unambiguous resolution of crystal structures of COF materials.
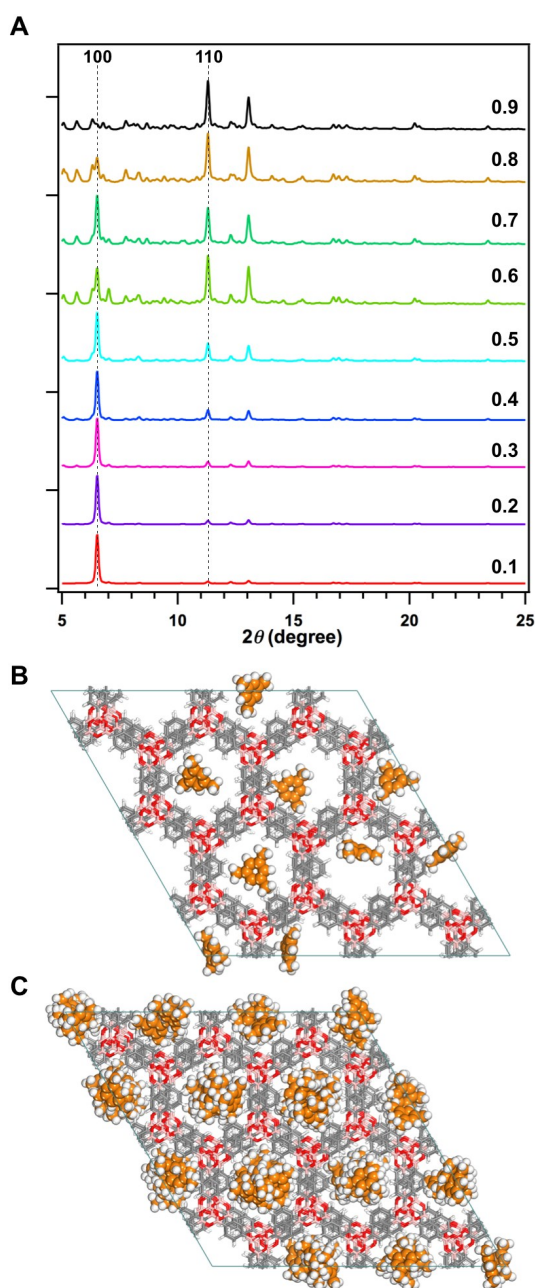

Fig. 3 (A) Dependency of simulated PXRD patterns of COF-1 (3 x 3; 10 layers) on the density of mesitylene in pores (Values on curves are density in g cm^{-3}). Snapshot structures of COF-1 with mesitylene in the channels at density of (B) 0.1 and (c) 0.9 g cm^{-3}.

Notes and references

1   (a) X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.,* 2012, **41**, 6010. (b) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O' Keeffe, A. J. Matzger and O. M. Yaghi, *Science,* 2005, **310**, 1166. (c) X. Chen, M. Addicoat, E. Jin, L. Zhai, H. Xu, N. Huang, Z. Guo, L. Liu, S. Irle and D. Jiang, *J. Am. Chem. Soc.,* 2015, **137**, 3241. (d) C. R. DeBlase, K. E. Silberstein, T. -T. Truong, H. D. Abruña and W. R. Dichtel, *J. Am. Chem. Soc.,* 2013, **135**, 16821. (e) S.-Y. Ding, W. Wang, *Chem. Soc. Rev.,* 2013, **42**, 548. (f) H.-S. Cho. H. Deng, K. Miyazaki, Z. Dong, M. Cho, A. V. Neimark, J. Ku, O. M. Yaghi, O. Terasaki, *Nature*, 2015, DOI: 10.1038/nature15734.
2   (a) Y. Zeng, R. Zou, Z. Luo, H. Zhang, X. Yao, X. Ma, R. Zou and Y. Zhao, *J. Am. Chem. Soc.,* 2015, **137**, 1020. (b) D. D. Medina, J. M. Rotter, Y. Hu, M. Dogru, V. Werner, F. Auras, J. T. Markiewicz, P. Knochel and T. Bein, *J. Am. Chem. Soc.,* 2015, **137**, 1016. (c) T. Zhou, S. Xu, Q. Wen, Z. Pang and X. Zhao, *J. Am. Chem. Soc.,* 2014, **136**, 15885. (d) S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine and R. Banerjee, *Angew. Chem., Int. Ed.,* 2013, **52**, 13052. (e) L. M. Lanni, R. W. Tilford, M. Bharathy and J. J. Lavigne, *J. Am. Chem. Soc.,* 2011, **133**, 13975. (f) P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.,* 2008, **47**, 3450. (g) Z. Li, X. Feng, Y. Zou, Y. Zhang, H. Xia, X. Liu and Y. Mu, *Chem. Commun*., 2014, **50**, 13825. (h) X. Ding, Y. Li, H. Hu, Y. Sun, J. Wang, C. Wang, C. Wang, G. Zhang, B. Wang, D.-Q. Zhang, *Chem. Eur. J.* 2014, **20**, 14614.
3   (a) X. Liu, C. Guan, S. Ding, W. Wang, H. Yan, D. Wang and L. Wan, *J. Am. Chem. Soc.,* 2013, **135**, 10470. (b) N. Huang, X. Chen, R. Krishna and D. Jiang, *Angew. Chem., Int. Ed.,* 2015, **54**, 2986. (c) H. Xu, X. Chen, J. Gao, J. Lin, M. Addicoat, S. Irle and D. Jiang, *Chem. Commun.,* 2014, **50**, 1292. (d) D. B. Shinde, S. Kandambeth, P. Pachfule, R. R. Kumar and R. Banerjee, *Chem. Commun.,* 2015, **51**, 310. (e) P. Pachfule, M. K. Panda, S. Kandambeth, S. M. Shivaprasad, D. Díaz Díaz and R. Banerjee, *J. Mater. Chem.* A, 2014, **2**, 7944.
4   (a) Q. Fang, Z. Zhuang, S. Gu, R. B. Kaspar, J. Zheng, J. Wang, S. Qiu and Y. Yan, *Nat. Commun.,* 2014, **5**, 4503. (b) S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. Song, C. Su and W. Wang, *J. Am. Chem. Soc.,* 2011, **133**, 19816.
5   (a) B. Lukose, A. Kuc and T. Heine, *Chem. - Eur. J.,* 2011, **17**, 2388. (b) B. Lukose, A. Kuc, J. Frenzel and T. Heine, *Beilstein J. Nanotech.,* 2010, **1**, 60. (c) Y. Du, D. Calabro, B. Wooler, Q. Li, S. Cundy, P. Kamakoti, D.

Colmyer, K. Mao and P. Ravikovitch, *J. Phys. Chem. C*, 2014, **118**, 399. (d) W. Zhou, H. Wu and T. Yildirim, *Chem. Phys. Lett.*, 2010, **499**, 103-107. (e) 7B. T. Koo, W. R. Dichtel and P. Clancy, *J. Mater. Chem.*, 2012, **22**, 17460.