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A statistical model for representing stacking disorder of 2D covalent organic frameworks

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Since rise of the two-dimensional covalent organic framework (2D COF) field, there is a systematic discrepancy between predicted theoretical and experimental structures. [1] It is attributed to that the experimental materials do not have ideal structure, but contain diverse stackings, or even some extent of disorder. [2] The structure models commonly used in theoretical calculations are too idealistic, and cannot represent this configurational entropy in the materials, which is also existed in experimental interpretation. We have therefore built statistical models correctly describing both local structure and the long-range disorder in 2D COFs and 2D polymers in general. We studied honeycomb lattice as found in COF-1, COF-5 and square lattice in ZnPc-pz COF as examples, and were able to create realistic models with PXRD patterns consistent with the experimental results for those materials, for the first time. Our statistical model takes different slip directions into account, which contain broader peaks at correct positions and lacking the typical small peaks known from theoretical predictions. We have also demonstrated that the experimental samples exhibit stacking disorder combining different configurations, such as a mixture AA and ABC stacking. This has large implication on the properties of the material, especially on electronics, as it means that most lot of currently used models inherently lack important features present in the real materials.

References

[1] Lukose, B., Kuc, A., Heine, T., Chem. Eur. J., 8 (2011) 2388-2392.
[2] Pütz, A. M., Terban, M. W., Bette, S., Lotsch, B. V., et. al., Chem. Sci., 47 (2020) 12647-12654.

Figures

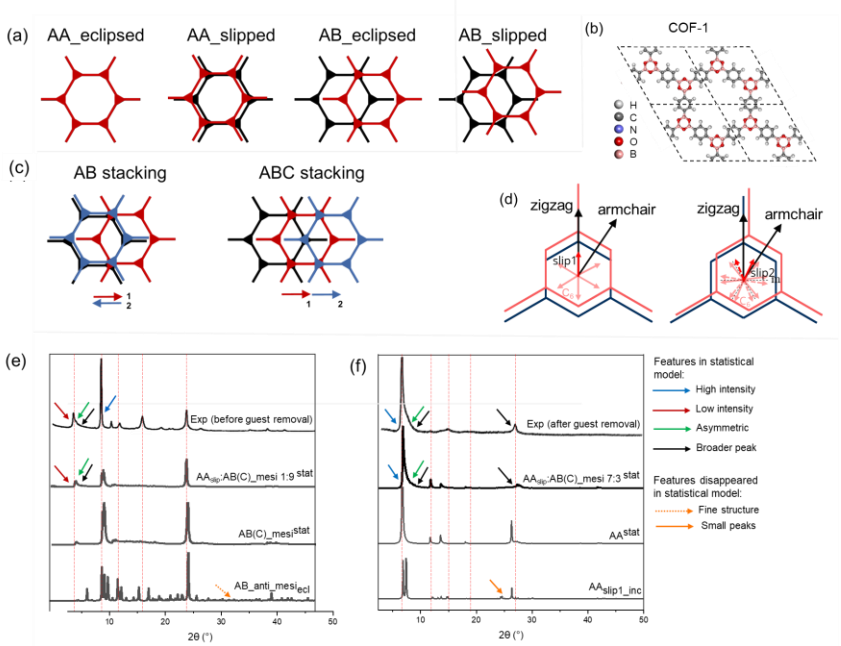

Figure 1: (a) AA and AB stacking configurations of honeycomb lattice with (*_slipped) or without (*_eclipsed) lateral interlayer slip. (b) Top view of COF-1. (c) Representation of main possible AB and ABC configurations. Successive layers depicted in black, red and blue. (d) Depictions of the slip vectors in COF-1 as models of planar COFs with honeycomb lattice. The calculated XRD of the best fitting statistically built structures, and the most stable small-UC bulk models configurations of (a) $AB(C)^{stat}$, (f) AA^{stat} stacking for COF-1.