Exploring the phase stability in interpenetrated diamondoid covalent organic frameworks

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Responsive nanoporous materials undergo structural phase transitions between different metastable phases under external stimuli such as temperature, pressure, or adsorption.[1] As these phase transitions impact their internal pore architecture, these soft porous crystals (SPCs) are highly sought-after for applications including gas and fluid capture, nanosensing, and shock absorption. Generally, the topology of these materials endows them with a potential for flexible behavior, whereas the specific building units that decorate the topology dictate whether this flexibility comes to expression. While several studies have sought to investigate the effect of the latter (altering the linker or metal ion in MOFs[2–4]), the role of interpenetration, *i.e.*, the occurrence of two

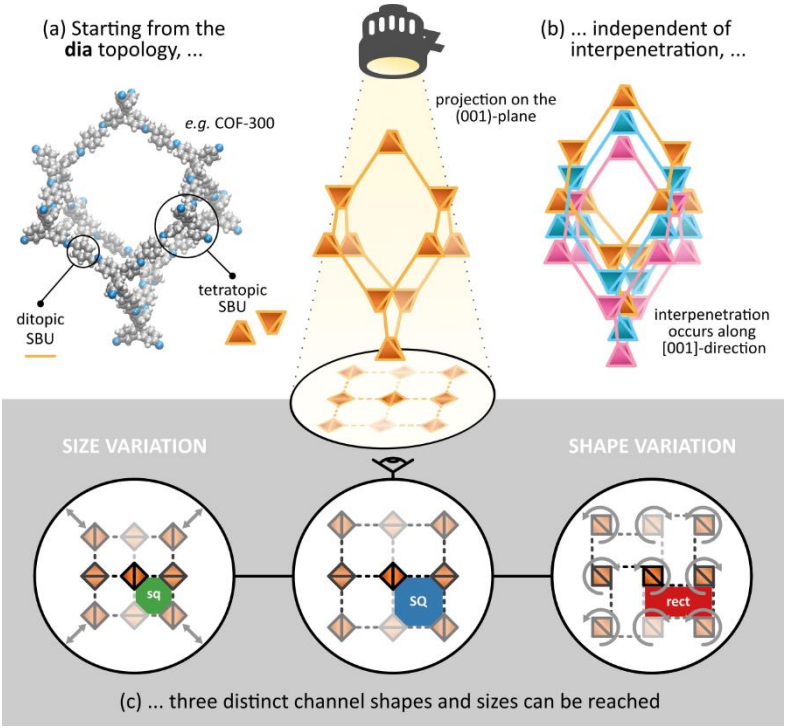

***Figure 1**: Flexibility of the (interpenetrated) **dia** topology, as characterized by the relative orientation and distance between adjacent tetratopic building units.*

or more individual networks catenated with each other,[5] on the relative phase stability in SPCs remains ill-understood despite the vast amount of interpenetrated framework structures. To this end, we here propose a protocol to explore the phase stability of COFs exhibiting the flexible **dia** topology, which is the most prevalent topology to date for 3D COFs that almost exclusively occurs with some degree of interpenetration, and verify its general applicability by determining the free energy landscapes of four **dia** COFs as a function of the degree of interpenetration.

Free energy landscape as a function of interpenetration

As a case study, Figure 2 demonstrates that our protocol successfully describes the observed flexibility in COF-300, using an umbrella sampling protocol relying on judiciously chosen collective variables that describe the transitions illustrated in Figure 1. Evidently, with increasing interpenetration, the accessible phase space decreases owing to the steric repulsion that accompanies the density increase. However, the dispersive interactions between the individual networks counteract this and favor smaller pores, stabilizing rectangular channel phases for intermediate degrees of interpenetration. Our work thus shows that the compliance of the 1D channel shape in the **dia** topology can be controlled by adjusting the degree of interpenetration.

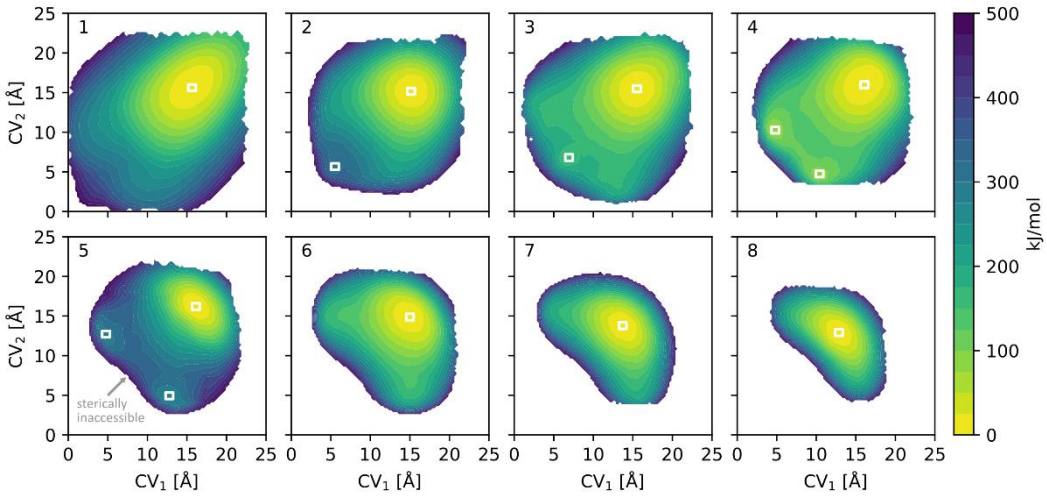

***Figure 2**: Free energy landscape for COF-300, at 300 K, as a function of interpenetration. The different (meta)stable phases are indicated by a white rectangle.*

References

[1] S. Horike, *Nat Chem*, 1, 695, **2009** [2] A. Schneemann, *Chem. Soc. Rev.*, 43, 6026, **2014** [3] G. Fraux, *Chem. Commun.*, 53, 7211, **2017** [4] S. M. J. Rogge, *Nat. Commun.*, 10, 4842, **2019**, [5] K. Barthelet, *Angew. Chem. Int. Ed.*, 41, 281, **2002**.