Poster

Unveiling the crystallochemistry of a soft covalent organic framework during benzene and cyclohexane adsorption by *in situ* powder X-ray diffraction

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The so-called hydrogen economy [1] refers to the use of molecular hydrogen as a clean energy vector. This issue has recently returned to the scene, urged by the need of ensuring access to clean and affordable energy to all, as stated, *e.g.*, by Goal 7 of the 17 Sustainable Development Goals promoted by the United Nations [2]. Two of the challenges of the hydrogen economy are the safe storage and transportation of this chemical. Chemisorption, as in liquid organic hydrogen carriers (LOHCs), is a promising alternative to physical storage, which is energy demanding and poses safety concerns. Benzene and cyclohexane are a potential couple of LOHCs, but their separation after hydrogenation/dehydrogenation cycles would be demanding, due to the very similar boiling points. An attractive approach to ease their separation is the selective physisorption, triggered by preferential host-guest interactions, of one of the two molecules on tailored porous materials.

In this context, we studied the narrow-pore form of the three-dimensional, 7-fold interpenetrated covalent organic framework (COF) [(TAM)(BDA)$_2$] [3] [COF-300; TAM = tetrakis-(4-aminophenyl)-methane; BDA = terephthaldehyde] as adsorbent of benzene and cyclohexane in static and dynamic conditions [4], revealing its higher affinity for the former. To shed light onto COF-300 structural evolution during the adsorption of the two chemicals, we recurred to high-resolution powder X-ray diffraction (PXRD) [5], *in situ* dosing their vapours in the pressure range 0.01–4.74 bar. The extensive data treatment revealed the progressive appearance of intermediate- and large-pore forms (Fig. 1), confirming the flexibility of COF-300 also in this applicative context. More importantly, we retrieved key, otherwise inaccessible crystallochemical details – structural-feature changes, in addition to pore widening, favouring adsorption; primary adsorption sites; host-guest interactions - collectively rationalising the observed functional behaviour.

Overall, this work highlighted the role of framework softness and structural-feature modifications in the adsorption of benzene and cyclohexane enriching, with relevant information, both this case of study and the design of new-generation materials intended for the same purpose. Finally, this first *in situ* PXRD investigation of the adsorption of the two chemicals on a COF contributes to emphasize the relevance and versatility of this approach for the solid-state characterization of advanced materials.

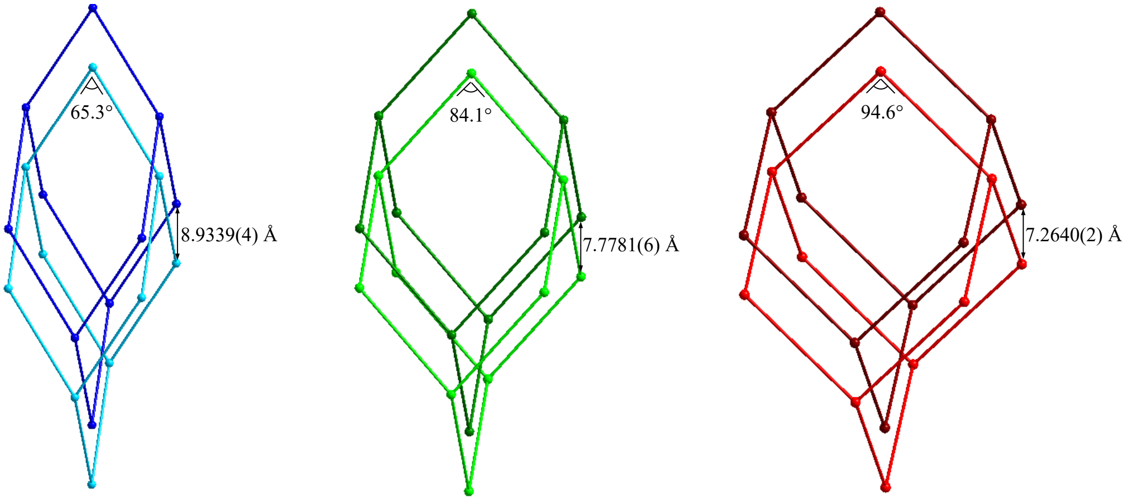

Figure 1. From the left: evolution of COF-300 framework from the narrow- to the intermediate- and large-pore form during benzene dosage.

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