# EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

## Experiment Report Form

**ESRF**

| | **Experiment title:** Structural insight into benzene *vs*. cyclohexane adsorption by the covalent organic framework COF-300: the role of host-guest interactions and pore flexibility | **Experiment number**: CH-6220 |
|---|---|---|
| **Beamline:** ID22 | Keyword **Date of experiment**: from: March 8th 2022                    to: March 11th 2022 | **Date of report**: April 14th 2022 |
| **Shifts:** 9 | **Local contact(s):** Giorgia Confalonieri | *Received at ESRF:* |

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**Report:**

Experiment CH-6220, performed at the beamline ID22, was meant to get structural insight to unveil the role of pore flexibility and host-guest interactions in benzene (BEN) and cyclohexane (CH) adsorption by the known covalent organic framework [(TAM)(BDA)] (COF-300; TAM = tetrakis(4-aminophenyl)methane, BDA = terephthaldehyde) [1], taking advantage of *in situ* high-resolution X-ray powder diffraction (HR-PXRD). COF-300 is known to be flexible: it exists in narrow-pore (NP) and large-pore (LP) forms as a function of synthesis conditions or external stimuli. Previous to the experiment at the ESRF, in our laboratories we studied the NP form (evidence by PXRD and $N_2$ adsorption at 77 K, Fig. 1a) performing static and dynamic BEN and CH adsorption experiments. At 298 K, BEN is adsorbed in higher amount than CH (11.2 *vs*. 7.8 mmol/g, respectively, Fig. 1a) along step-like isotherms, typical of flexible materials; hysteresis loops are present along the desorption branches and they are larger for BEN, indicating stronger host-BEN interactions. Laboratory PXRD data acquisitions immediately after the adsorption experiments disclosed LP forms of different pore aperture for BEN and CH, fast converting back into the NP form when exposed to air (Fig. 1b). The NP-LP-NP conversion was also observed by PXRD upon wetting powdered COF-300 samples with BEN or CH. Single-component and BEN/CH mixture dynamic adsorption (*via* breakthrough experiments) in the 298-348 K range showed an initial co-adsorption of the two guests, but a higher retention time for BEN, reasonably due to stronger host-BEN interactions.

Though not reproducing the experimental conditions of the functional study just described, at ID22 we performed *in situ* HR-PXRD dosing BEN and CH on COF-300 at different vapour pressures.

At the Chemistry lab, we filled three different types of 1-mm kapton capillaries: $c_1$, filled only with COF-300; $c_2$, filled with COF-300 and BEN; $c_3$, filled with COF-300 and CH. In $c_2$ and $c_3$ (Fig. 1c), first of all we introduced the powdered sample; then, we introduced some cotton thread, so that the liquid did not immediately reach the powder and wet it; finally, we introduced a 0.5-mm kapton capillary, sealed at one end with UV-Vis glue, containing a few drops of BEN or CH.

Then, after sealing the capillaries with UV-Vis glue, those of type $c_2$ and $c_3$ were put in a freezer [m.p.$_{BEN}$ = 278.9 K; m.p.$_{CH}$ = 280 K], where they were left until HR-PXRD data acquisition, to avoid the diffusion of CH or BEN vapours into the COF.

At ID22, as a first part of the experiment we acquired HR-PXRD data on the capillary $c_1$ at the temperatures $T_C$ needed to obtain specific vapour



**Fig. 1.** (a) COF-300 $N_2$ adsorption at 77 K, BEN and CH adsorption at 298 K. The empty symbols characterize the desorption branch. (b) COF-300 PXRD patterns acquired before and after BEN or CH isotherms acquisition. (c) Schematic representation of a partitioned capillary.

pressures $p_V$ in the range 0.01-4 bar when in presence of BEN or CH ($T_C$ = 256-403 K, estimated with the Antoine equation). On the whole, we acquired data at 19 temperatures, taking advantage of the Oxford Cryosystems Cryostream cold-nitrogen-gas blower. These variable-temperature (VT) HR-PXRD data are needed as a zero-point to monitor the temperature-dependent crystal structure response at 0 bar of BEN or CH vapours. Indeed, we observed a progressive pore opening of the NP form as a function of the temperature. Then, with the $c_2$ and $c_3$ capillaries, we acquired data in isothermal conditions (Figure 2a) at 19 and 13 ($T_C$, $p_V$) couples, respectively, starting from the lowest temperature/vapour pressure. To equilibrate the powder/vapour system, after reaching a temperature value, we waited 15 minutes before acquiring the data. With both solvents, we observed the formation of different intermediate-pore (IP) forms as well as of the largest LP form reported in the literature. To verify if the pore opening is reversible, with both $c_2$ and $c_3$ capillaries, after reaching the highest vapour pressure we progressively lowered it, acquiring HR-PXRD data at some ($T_C$, $p_V$) couples.

At present, we have already treated the VT-HR-PXRD data that we need as a blank, performing whole powder pattern refinements. As a result, we retrieved the behaviour of the unit cell parameters due to temperature variation (Figure 2b), which will be substracted when dealing with the data acquired in the presence of BEN or CH. As for the latter data, after treating all of them with whole powder pattern refinements, for selected data, representative of the NP, IP and LP forms,



**Fig. 2.** a) PXRD data acquired on capillary $c_2$, containing benzene, at different temperatures in isothermal conditions: NP form, red; IP forms, green and blue; LP form, orange. b) Percentage relative variation of the unit cell parameters of the NP form as retrieved from VT-HR-PXRD experiment.

we will locate the solvent molecules within the pores with a direct-space approach followed by Rietveld refinements. This will enable us to *i*) identify the primary adsorption sites and the main host-guest interactions; *ii*) quantify the solvent molecules entered into the pores, so to build an adsorption isotherm.

The results of this work will help rationalizing the role of pore flexibility and host-guest interactions in BEN and CH adsorption not only for COF-300, but also for and new-generation covalent organic frameworks.
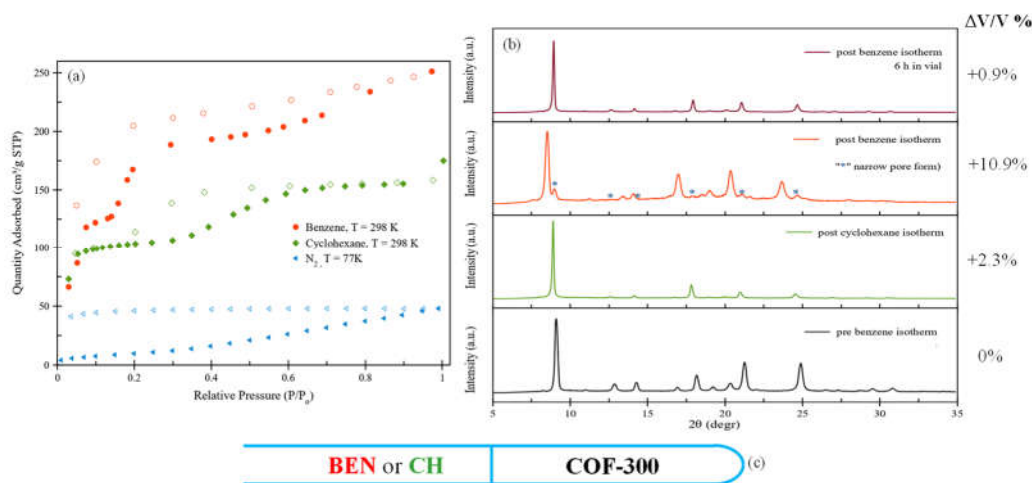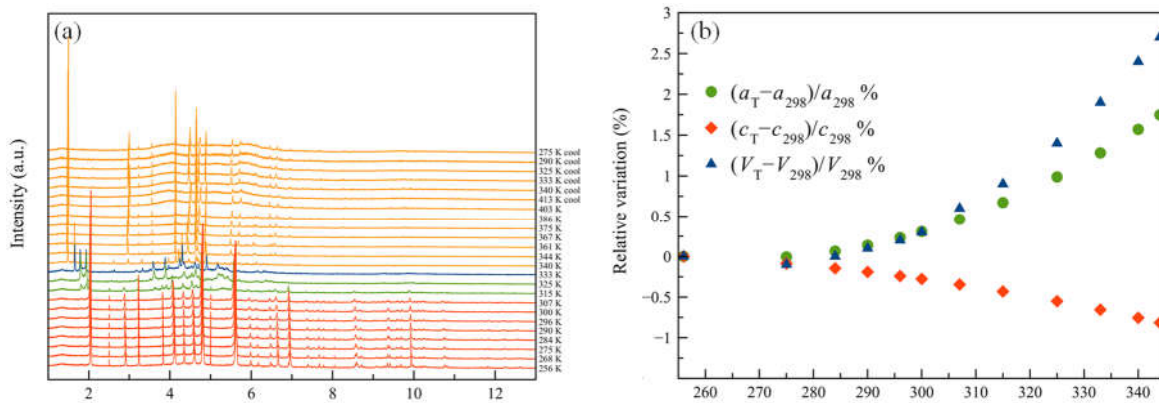
References:
[1] *J. Am. Chem. Soc.* 2009, *131*, 4570.
[2] *Nat. Commun.* 2020, *11*, 6128.