

## Guest inclusion properties of a novel calix[4]hydroquinone compound

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### Introduction

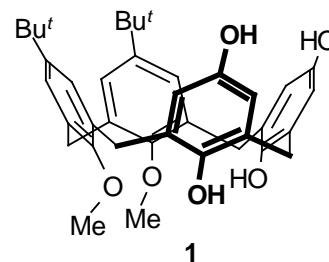
At the Dept. of Chemistry of the University of Salerno we prepared and characterized a new crystalline solid based on *p*-Bu<sup>t</sup>-calix[4]dihydroquinone **1** revealing the simultaneous existence of water channels and very large hydrophobic cavities (988 Å<sup>3</sup>). The compound has a cubic structure ( $a=36.412(4)$  Å) with 48 calixarene molecules and 155 water molecules in the unit cell.

Interestingly the supramolecular framework is preserved also after the removal of channel water molecules, as demonstrated by X-ray powder diffraction (XRPD) measurements.<sup>1</sup>

The simultaneous presence of networked channels, filled with easily removable water, and isolated hydrophobic cavities may prelude to potential applications of nanotechnological interest.

This proposal aims to fully explore the guest uptake and release properties of the new material using several solvents and gases under different temperature conditions.

The translating imaging plate set-up available on GILDA beamline allows to monitor *in situ* the transformation induced by the guest uptake and release also as a function of the temperature. It enables continuous recording of the diffracted intensities with a good counting statistics and minute time resolution.



### Experiment

Time resolved x-ray powder diffraction have been performed at GILDA (BM08) beamline using the translating image plate (TIP) system, a hot gas blower. 1.0 mm glass capillaries have been filled with powder sample and mounted on a goniometer head specifically designed for the recovery of the fluxed gases or solvent vapours.

Gases have been be fluxed directly through the capillary, solvent vapours were carried by a nitrogen flow into the capillary and then recovered in a liquid nitrogen trap.

For each solvent or gas a temperature scan has been performed in the range 25-140°C or 25-50°C.

9 shifts were allocated out of the required 12: the first shift was used to perform instrument calibration, to select appropriate wavelength ( $\lambda = 0.68895$  Å), sample to detector distance ( $d=277.032$  mm), IP slit apertures and IP translation speed. 5 shifts were used to perform time resolved experiments with a gas flow in the temperature range 25-140°C, 3 shifts were used to perform time resolved experiments with solvent vapours in the temperature range 25-140°C. In particular nitrogen, methane, argon, carbon monoxide were used as gases, vapors of water, chloroform and acetonitrile as solvents.

There was not enough time to perform time resolved experiments with methanol and CCl<sub>4</sub> as solvents and also low temperature measurements as described in the proposal. A problem in the tunnel beyond BM08 front end caused a delay of 3 hrs.

### Results

Initial experiments were performed under nitrogen flow increasing the temperature from 25 to 140°C and then decreasing again to 25 °C. The observed changes are related to the low  $2\theta$  values of the diffraction pattern, while the higher angle part remains quite unaltered (see Fig 1). The ratio between the 110 and the 200 peaks changes as soon as nitrogen flows through the capillary, the 200 peak increases until 95°C, then it starts decreasing, at 140 °C the 110 and 200 peaks have the same height and this is until 25°C. There is also a peak at  $2\theta = 4.30^\circ$ , whose intensities varies reversibly with the temperature.

At 50°C a small peak at  $2\theta = 3.75^\circ$  becomes visible and its intensity remains constant throughout the experiment, this peak could not be indexed within a cubic cell.

Noteworthy, the diffraction patterns of two samples from the same batch measured at ambient conditions at different times showed a remarkable difference in the ratio between the peaks 110 and 200, an hypothesis is that the observed behaviour has to be related to the water content of the material with respect to ambient humidity.

To prove this hypothesis the nitrogen flow was kept passing in a flask containing distilled water before flowing in the capillary containing the calixarene sample. As shown in Fig. 2 the intensities of peaks 110 and 200 are directly related to the water content of the material and this is influenced by ambient humidity.

Measurements with CO, CH<sub>4</sub> and Ar flow do not show any significant difference from what observed with N<sub>2</sub> flow. On the contrary completely different behaviour has been observed when a nitrogen flow was allowed to pass in a flask containing chloroform (or acetonitrile) so that solvent vapours were carried by the nitrogen flow in the capillary containing the calixarene sample. To avoid the transformation detected above 50°C, all measurements were made below this temperature.

Figure 3 shows the sample transformation under chloroform vapours: the most notable change is the progressive disappearance of the 200 peak. Peak positions do not show any significant variation and it is possible to index the final diffraction pattern assuming a cubic cell with  $a = 36.616(10)$  Å. We can conclude that chloroform molecules are able to enter the channels, while the calixarene while preserving the cubic structure.

Figure 4 shows sample transformations under acetonitrile vapours: the 200 peak is almost immediately affected by the acetonitrile flow. Peak positions do not show any significant variation and it is possible to index the final diffraction pattern assuming a cubic cell with  $a = 36.437(14)$  Å. We can conclude that also acetonitrile molecules are able to enter the channels while the calixarene cubic structure remains preserved.

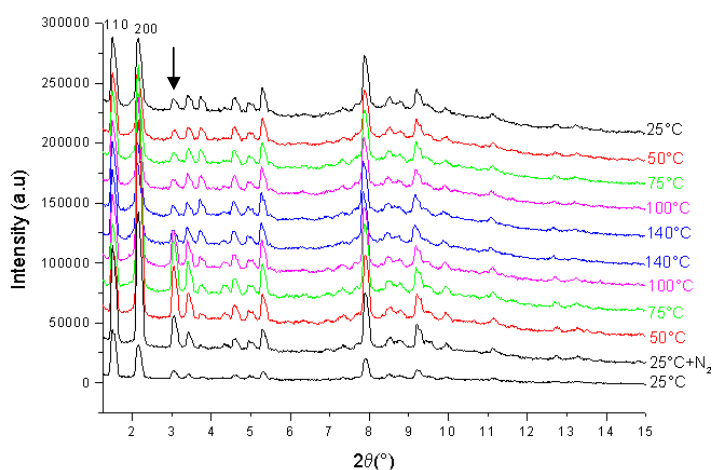


Fig. 1. Variable temperature XRPD patterns under nitrogen flow.

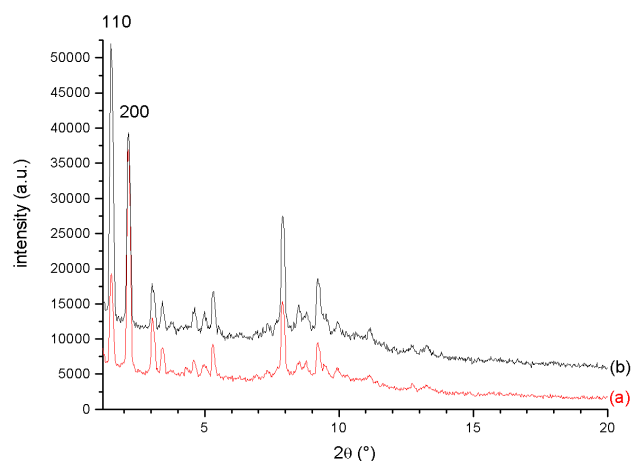


Fig. 2. (a) XRPD pattern as obtained in ambient conditions, (b) XRPD pattern after 15 minutes exposure to water

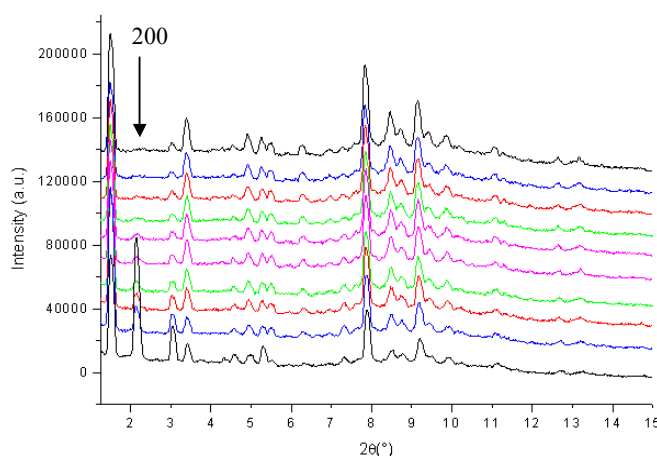
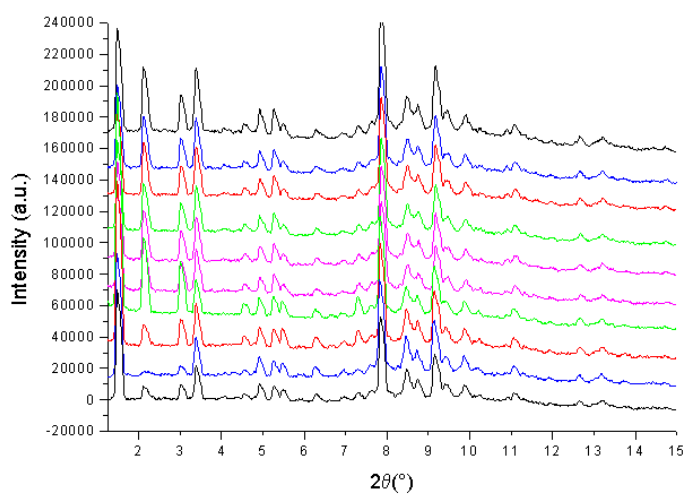


Fig. 3: XRPD patterns under chloroform vapours.

The performed experiments demonstrate that the host cubic framework is surprisingly robust and the material behaves as a purely organic supramolecular zeolite.



**Fig. 4:** XRPD patterns under acetonitrile vapours.

#### References

[1] C. Tedesco, I. Immediata, L. Gregoli, L. Vitagliano, A. Immirzi, P. Neri, *CrystEngComm* 2005, 7, 449-453.

#### Publications

C. Tedesco, L. Erra, I. Immediata, M. Merlini, C. Meneghini, A. Immirzi, P. Neri, in preparation.

**Experiment n. 08-02-617**