# Guest induced structural changes of a supramolecular organic zeolite by time resolved single crystal X-ray diffraction

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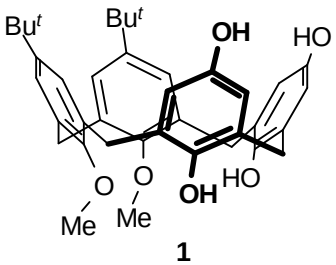
Experiment # CH-2833

Beamline: ID11

## Introduction

At the Dept. of Chemistry of the University of Salerno we have prepared and characterized a new crystalline solid based on *p*-Bu$^t$-calix[4]dihydroquinone **1** revealing the simultaneous existence of water channels and very large hydrophobic cavities (~1000 Å$^3$).[1]




**1**

Single crystal X-ray diffraction studies have been carried out on these compounds using synchrotron radiation, since the crystals are small (ca. 0.1 mm size) and intrinsically weakly diffracting. The compound has a cubic structure ($a$ = 36.412(4) Å) with 48 calixarene molecules and 155 water molecules in the unit cell.[1]

The simultaneous presence of networked channels, filled with easily removable water, and isolated hydrophobic cavities implies potential applications of nanotechnological interest.[2] Interestingly, solvent-induced polymorphism can be observed. By exposing a capillary containing the crystalline cubic phase powder to vapours of acetonitrile, single crystals had formed in the capillary. The resulting rather small and twinned crystals were analyzed by X-ray diffraction at the SNBL at the ESRF, showing the presence of monoclinic co-crystals of **1** with water and acetonitrile.[3]

This proposal aims to characterize the guest uptake properties of this new material by exposing single crystals to several volatile compounds and to locate the guest molecules inside the channels of the cubic crystalline form. Moreover it has also been investigated the role of guest molecules in promoting the formation of new crystalline forms.

## Experimental details

Single crystal X-ray diffraction experiments have been performed at ID11 beam line at low temperatures (using a liquid nitrogen cryostream) and for one sample also at room temperature, using a wavelength of 0.32887 Å and a distance between the sample and the detector of 130 mm. Different exposure times have been used to obtain good quality data both at high and at low angle.

Crystallization procedures did not produced single crystals of **1**, the selected samples were always constituted by one large crystal surrounded by one or more smaller crystals .

Crystalline samples were sealed into Lindemann capillaries previously filled with a drop of organic volatile compound, $CHCl_3$, $CCl_4$, EtOH, $CH_3OH$ and $CH_3CN$ were used.

In one case a different approach has been followed: a crystalline sample was soaked in a drop of toluene and then mounted in a cryo-loop.

Moreover cubic crystalline powders of **1** were exposed to acetonitrile vapours for 72 hours obtaining very small single crystals, which were fully characterized.

## Results

A total of 15 samples have been analysed, obtaining 6 crystal structures. The data collected exposing the crystals to vapours of EtOH, $CH_3CN$ and $CHCl_3$ do not allow to give final results.

1. The first sample was a crystal of **1** as obtained from chloroform and ethyl acetate. Data were collected at 120K.

Crystal data for **1**: Formula: $(C_{38}H_{44}O_6) \cdot 0.33\ H_2O \cdot 4\ H_2O$, FW = 667.53, cubic, space group $Pn\bar{3}n$ (no. 222), Z = 48, $a$ = 35.949(8) Å, $V$ = 46458(18) Å$^3$, $D_x$ = 1.145 g cm$^{-3}$, $\mu_{calc}$ = 0.010 mm$^{-1}$.

The data were processed using the Bruker package (SMART, Saint and SADABS).
The overall completeness of the data is 98.2% in the resolution shell 16.08 – 0.90 Å. The overall Rmerge is 0.069, whereas the redundancy is as high as 21. The structure has been solved by direct method using the program SHELXS. The structure obtained has been refined using SHELXL97. The contribution of diffuse solvent regions has been modelled using Babinet's principle. Anisotropic thermal factors were used only for all non-hydrogen atoms of the calixarene molecule. A total of 434 refinable parameters were finally considered.
Final disagreement indices considering all the 3445 independent reflections are R1 = 0.11, wR2 = 0.36.

2. The second sample has been obtained exposing the crystal to $CCl_4$ vapours and data have been collected a 120 K.

Crystal data for **2**: Formula: $(C_{38}H_{44}O_6) \cdot 0.33\ H_2O \cdot 0.31\ H_2O \cdot CCl_4$, FW = 706.25, cubic, space group $Pn\bar{3}n$ (no. 222), $Z$ = 48, $a$ = 36.124(7) Å, $V$ = 47141(35) Å$^3$, $D_x$ = 1.218 g cm$^{-3}$, $\mu_{calc}$ = 0.018 mm$^{-1}$.
The data were processed using the Bruker package (SMART, Saint and SADABS).
The overall completeness of the data is 98.1% in the resolution shell 16.16 – 0.90 Å. The overall Rmerge is 0.09, whereas the redundancy is as high as 24. The structure has been solved by direct method using the program SHELXS. The structure obtained has been refined using SHELXL97. The contribution of diffuse solvent regions has been modelled using Babinet's principle. Anisotropic thermal factors were used for all non-hydrogen atoms. A total of 510 refinable parameters were finally considered.
Final disagreement indices considering all the 7920 independent reflections are R1 = 0.14, wR2 = 0.39.

3. The third sample has been obtained exposing the crystal to $CCl_4$ vapours and data have been collected at room temperature.

Crystal data for **3**: Formula: $(C_{38}H_{44}O_6) \cdot 0.33H_2O \cdot H_2O \cdot 0.5\ CCl_4$, FW = 706.47, cubic, space group $Pn\bar{3}n$ (no. 222), $Z$ = 48, $a$ = 36.510(8) Å, $V$ = 48666(11) Å$^3$, $D_x$ = 1.229 g cm$^{-3}$, $\mu_{calc}$ = 0.177 mm$^{-1}$.
The data were processed using the Bruker package (SMART, Saint and SADABS).
The overall completeness of the data is 97.4% in the resolution shell 16.33 – 0.90 Å. The overall Rmerge is 0.10, whereas the redundancy is as high as 24. The structure has been solved by direct method using the program SHELXS. The structure obtained has been refined using SHELXL97. The contribution of diffuse solvent regions has been modelled using Babinet's principle. Anisotropic thermal factors were used for all non-hydrogen atoms. A total of 466 refinable parameters were finally considered.
Final disagreement indices considering all the 8100 independent reflections are R1 = 0.15, wR2 = 0.47.

4. The fourth sample was obtained exposing the crystal to MeOH vapours and data have been collected at 120 K.

Crystal data for **4**: Formula: $(C_{38}H_{44}O_6) \cdot 1.25\ H_2O \cdot 0.83\ CH_3OH$, FW = 642.51, cubic, space group $Pn\bar{3}n$ (no. 222), $Z$ = 48, $a$ = 36.0101(5) Å, $V$ = 46695(1) Å$^3$, $D_x$ = 1.019 g cm$^{-3}$, $\mu_{calc}$ = 0.043 mm$^{-1}$.
The data were processed using the Bruker package (SMART, Saint and SADABS). Two dataset have been merged: one collected with an exposure time of 1 s and the other with an exposure time of 10 s, combined the advantages coming from the two exposures.
The overall completeness of the data is 98.7% in the resolution shell 16.11 – 0.90 Å. The overall Rmerge is 0.08, whereas the redundancy is as high as 15. The structure has been solved by direct method using the program SHELXS. The structure obtained has been refined using SHELXL97. The contribution of diffuse solvent regions has been modelled using Babinet's principle. Anisotropic thermal factors were used for all non-hydrogen atoms. A total of 417 refinable parameters were finally considered.
Final disagreement indices considering all the 8100 independent reflections are R1 = 0.14, wR2 = 0.43.

5. The fifth sample was obtained by soaking in toluene and mounting the crystal in a cryo-loop. Data were collected at 120 K.

Crystal data for **5**: Formula: $(C_{38}H_{44}O_6) \cdot 0.33H_2O \cdot 0.5C_7H_8 \cdot 0.25H_2O$, FW = 653.27, cubic, space group $Pn\bar{3}n$ (no. 222), $Z$ = 48, $a$ = 35.778(8) Å, $V$ = 45798(2) Å$^3$, $D_x$ = 1.039 g cm$^{-3}$, $\mu_{calc}$ = 0.044 mm$^{-1}$.
The data were processed using the Bruker package (SMART, Saint and SADABS). The overall completeness of the data is 99% in the resolution shell 16.00 – 0.90 Å. The overall Rmerge is 0.11, whereas the redundancy is as high as 16. The structure has been solved by direct method using the program SHELXS. The structure obtained has been refined using SHELXL97. The contribution of diffuse solvent regions has been modelled using Babinet's principle. Anisotropic thermal factors were used for all non-hydrogen atoms. A total of 457 refinable parameters were finally considered.
Final disagreement indices considering all the 3989 independent reflections are R1 = 0.12, wR2 = 0.36.

6. The sixth sample has been obtained by re-crystallization of the cubic powder from acetonitrile vapours; the crystal was in a cryo-loop and data have been collected at 120 K.

Crystal data for **6**: Formula: $2(C_{38}H_{44}O_6) \cdot 3CH_3CN \cdot H_2O$, FW = 1324.56, triclinic, space group $P\bar{1}$ (no. 2), $Z$ = 2, $a$ = 10.418(7) Å, $b$ = 17.928(11) Å, $c$ = 19.807(13) Å, α = 83.389(6)°, β = 85.269(6)°, γ = 88.449(6)°, $V$ = 3661(2) Å$^3$, $D_x$ = 1.201 g cm$^{-3}$, $\mu_{calc}$ = 0.010 mm$^{-1}$.

The data were processed using the Bruker package (SMART, Saint and SADABS). The overall completeness of the data is 88.2% in the resolution shell 9.49 – 0.80 Å. The overall Rmerge is 0.04, whereas the redundancy is as high as 1.6. The structure has been solved by direct method using the program SHELXS. The structure obtained has been refined using SHELXL97. Anisotropic thermal factors were used for all non-hydrogen atoms. A total of 883 refinable parameters were finally considered.

Final disagreement indices considering all the 13213 independent reflections are R1 = 0.07, wR2 = 0.29.

## Conclusions

The above experiments allowed us to elucidate the structural changes upon guest adsorption and to characterize the host-guest interactions. It was possible to evaluate the effect of size and affinity upon guest inclusion.

The cubic nanoporous structure is always retained except for the case of acetonitrile for which a new triclinic phase has been obtained, as an example of guest induced pseudopolymorphism.

## References

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

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[3] C.Tedesco, L. Erra, I .Immediata, C. Gaeta , M. Brunelli, M. Merlini, C. Meneghini, P. Pattison, P. Neri, *Cryst. Growth & Des.* 2010, in press.