Supplementary Material (ESI) for Physical Chemistry and Chemical Physics
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Supplementary Material (ESI) for Physical Chemistry and Chemical Physics Supplementary Information:

Acetylene and Argon Adsorption in a Supramolecuar Organic Zeolite

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Synchrotron radiation HR-XRPD measurements

In-situ temperature-controlled synchrotron radiation X-ray powder diffraction experiments were performed at the high-resolution powder diffraction beam line ID31 at the ESRF, Grenoble (France).[1s] X-ray powder diffraction patterns were collected selecting X-rays, with wavelength 0.80314(4) Å for acetylene loaded sample and evacuated sample, and 0.79987(3) Å for Ar loaded sample, from an insertion device source with a double-crystal Si(111) monochromator.

Small amounts of calixarene were lightly ground with a pestle in an agate mortar and introduced into thin walled 1.0 mm diameter borosilicate glass capillaries. This operation was performed in a dry box in order to avoid adsorption of water molecules from the ambient atmosphere. Capillaries were then connected to the gas cell and further evacuated using a turbomolecular pump (10^{-6} mbar) during 1 hour for removing any possible extra water (or other guests) molecules.

Via a 3-ways valve the capillary was then loaded with the selected gas at a pressure of 0.5 atm for several hours. Gas loading was interrupted during data collection and a Swagelok quick-locks ensured the holding of the applied gas pressure.

The gas cell[2s] was mounted on a heavy-duty goniometer head mounted coaxial with the axis of the diffractometer and rocked during measurements in order to improve randomization of the orientations of the individual crystallites. Data were collected in a temperature range from room temperature down to 80 K using an Oxford Cryosystems Cryostream cold nitrogen gas blower mounted at about 45° with respect to the capillary.

Raw data were normalized against monitor counts and detector efficiencies and re-binned into steps of 0.005º 2θ. Numerous short 1minute scans were collected to investigate the occurrence of any radiation damage and - in case - avoid it by translating the capillary by ~2.1 mm in the beam.

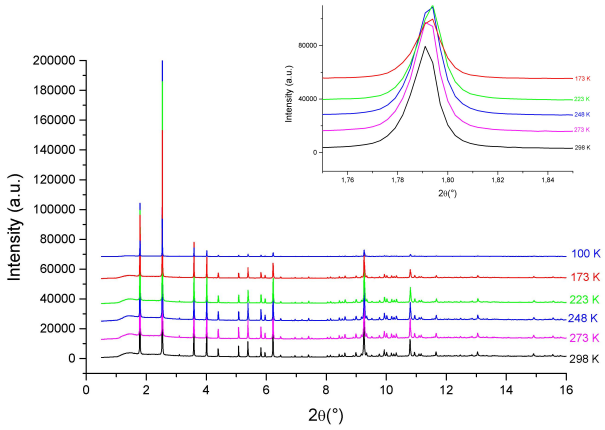

Fig. S1. X-ray diffraction patterns for an evacuated sample of **1**, in the inset the region showing the first peak, indexed as 110.

LeBail refinements

Le Bail refinements were accomplished with the program TOPAS.[3s] The peak profile was described by a Pearson VII function, in combination with a special function that accounts for the asymmetry due to axial divergence.[4s] No absorption correction was applied to the data. The atomic parameters were taken from the structure model obtained from the single-crystal X-ray diffraction data.

XRPD based simulated annealing

To confirm that the guest adsorption does not involve any change in the crystal system and in the space group, the HR-XRPD profiles were indexed from the positions of 2θ low-angle peaks using the program DICVOL.[5s] The resulting cells are cubic with values ranging from 36.2130(3) Å at 298 K to 36.2709(3) Å at 173 K in the case of acetylene loaded sample and from 36.2127(3) Å at 298 K to 36.231(1) Å at 80 K in the case of Ar loaded sample. Analysis of systematic absences in the HR-XRPD profiles confirmed the space group *Pn*3*n*.

Pattern decomposition by Le Bail method, localization of the gas molecules via simulated annealing and rigid body Rietveld refinement were accomplished using the program TOPAS.[3s]

Data in the range 1.5- 20.0° 2θ were included, which were modeled using the Pearson VII function with asymmetry corrected by a full axial model.

Two overall temperature factors (B) were refined, one for the atoms of the host molecule and the other for the atoms of the guest molecules, restraining the value between 1 and 60. The molecular geometry was restrained accordingly to the model obtained by single crystal X-ray diffraction. Bond and angle restraints were weighted by 0.05 Å and 5.00º, respectively. Hydrogen atoms were added to the model in their expected positions. The C-H distances were weighted by 0.001 Å.

6 overall parameters for the calixarene molecule (3 translations plus 3 rotations), 5 overall parameters for each acetylene molecules (3 translations plus 2 rotations), 2 isotropic temperature factors, the site occupancies of the acetylene carbon atoms, the profile and background parameters were refined. In the case of Ar loaded sample, for the guest atoms just the translations, the isotropic temperature factor and the sites occupancies were refined.

Simulation study

The Sorption Locate task available in Materials Studio 4.1 package6s has been used to find the preferential sites (lowest energy) for guest molecules inside the cubic framework. A Metropolis search of the configuration space of the sorbate-sorbent system is carried out while the temperature is slowly decreased. This process is repeated to ensure good coverage of the energy surface.

During the simulation, sorbate molecules within the framework are randomly rotated and translated. The configuration that results from one of these steps is accepted or rejected according to the selection rules of the Monte Carlo method being used for the simulation. The COMPASS26 force field has been used considering both the electrostatic and the van der Waals terms.

The final positions of the guest molecules as obtained by applying the simulated annealing process implemented in the TOPAS program and the Monte Carlo calculation are reported in Table S1 and S2, for acetylene and Ar loaded samples respectively.

Table S1. Comparison between the coordinates of the carbon atoms of acetylene molecules A and B by energy driven Monte Carlo search and diffraction based simulated annealing procedures.

		x	*y*	*z*
MS	C1(A)	0.0771	0.2783	0.7566
	C2(A)	0.0729	0.1758	0.7551
	C1(B)	0.7526	0.2640	0.7000
	C2(B)	0.7539	0.2893	0.6726
TOPAS	C1(A)	0.0824	0.2128	0.7421
	C2(A)	0.1101	0.1978	0.7333
	C1(B)	0.7049	0.3060	0.7100
	C2(B)	0.6915	0.2814	0.6930

Table S2. Comparison between the Ar atoms coordinates by energy driven Monte Carlo search and diffraction based simulated annealing procedures.

		x	*y*	*z*
MS	Ar (A)	0.52190	0.23531	0.77431
	Ar (B)	0.78726	0.45013	0.23566
TOPAS	Ar (A)	0.64887	0.26097	0.79471
TOPAS	Ar (B)	0.75000	0.43758	0.25000

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