

Electronic Supplementary Information (ESI)

**Single-crystal to single-crystal phase transition of cucurbit[5]uril
hydrochloride hydrates: large water-filled channels transforming to layers of
unusual stability.**

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- Figure S1.** Carbonyl-carbonyl oxygen distances within each rim of CB[5] as deduced from single crystal X ray diffraction structures highlighting the slight distortion compared to D_{5h} symmetry for form **I** crystals.
- Figure S2.** Carbonyl-carbonyl oxygen distances within each rim of CB[5] as deduced from the single crystal X ray diffraction structure highlighting the slight distortion compared to D_{5h} symmetry for form **II** crystals.
- Figure S3.** Structural features of the channels as depicted by the separation between the centres of each six-unit centroid within the two (a and b) alternating CB[5] planes perpendicular to the channel axes in Form **I** CB[5] crystals.
- Figure S4.** Channel shape of form **I** CB[5] hydrate crystals as defined by allowing a sphere of diameter 2.0 Å to roll over the surface of the ordered network (guests have been removed).
- Figure S5.** Powder X ray diffractograms of form **II** CB[5] crystals.

Preparation of CB[5] and crystal growth.

The preparation of CB[5] and its isolation as large single crystals has been published previouslyⁱ but the relevant part is recalled here:

Preparation of CB[n] by a modified procedure from Day *and coll.*ⁱⁱ and Kim *and coll.*ⁱⁱⁱ

Glycoluril (100 g, 0.7 mol) and paraformaldehyde (42.2 g, 1.4 mol) were weighed together in a 500 mL round bottom flask. The compounds were difficult to dissolve in 37 % aqueous hydrochloric acid (160 mL) even under strong magnetic stirring. Alternatively, addition of solid paraformaldehyde to an aqueous acid glycoluril solution greatly facilitated dissolution. After 30 minutes, the mixture was heated for one hour at 100°C and then the temperature was allowed to rise to 110°C for 17 hours more. The white precipitate (55 g) was collected by filtration. The solid was then stirred in a 60 % aqueous formic acid solution (100 mL) before filtration, and this was repeated three times to afford about 9 g of a white powder (CB[8]) as fraction 1. The formic acid fractions were then collected together with the first filtrate prior to solvent removal under reduced pressure. The resulting solid was then treated with hot 20 % aqueous glycerol (to solubilize CB[7] and CB[5]) and filtered with a glass frit under high vacuum. Methanol (500 mL) was then added to precipitate CB[7] from the glycerol solution. Fraction 2 (3 g) was then collected by filtration on filter paper without vacuum and rinsed three times with methanol. Around 100 g of CB[6] together with a small amount of CB[7] remained (fraction 3) from which pure CB[6] crystals could be isolated by slow diffusion of acetone into sulphuric acid or hydrochloric acid solutions. Crystals later grown from the remaining filtrate that were collected and recrystallized by slow diffusion of THF/acetone into a formic/hydrochloric acid solution proved to be CB[5] (around 2 g of centimetre-scale plates).

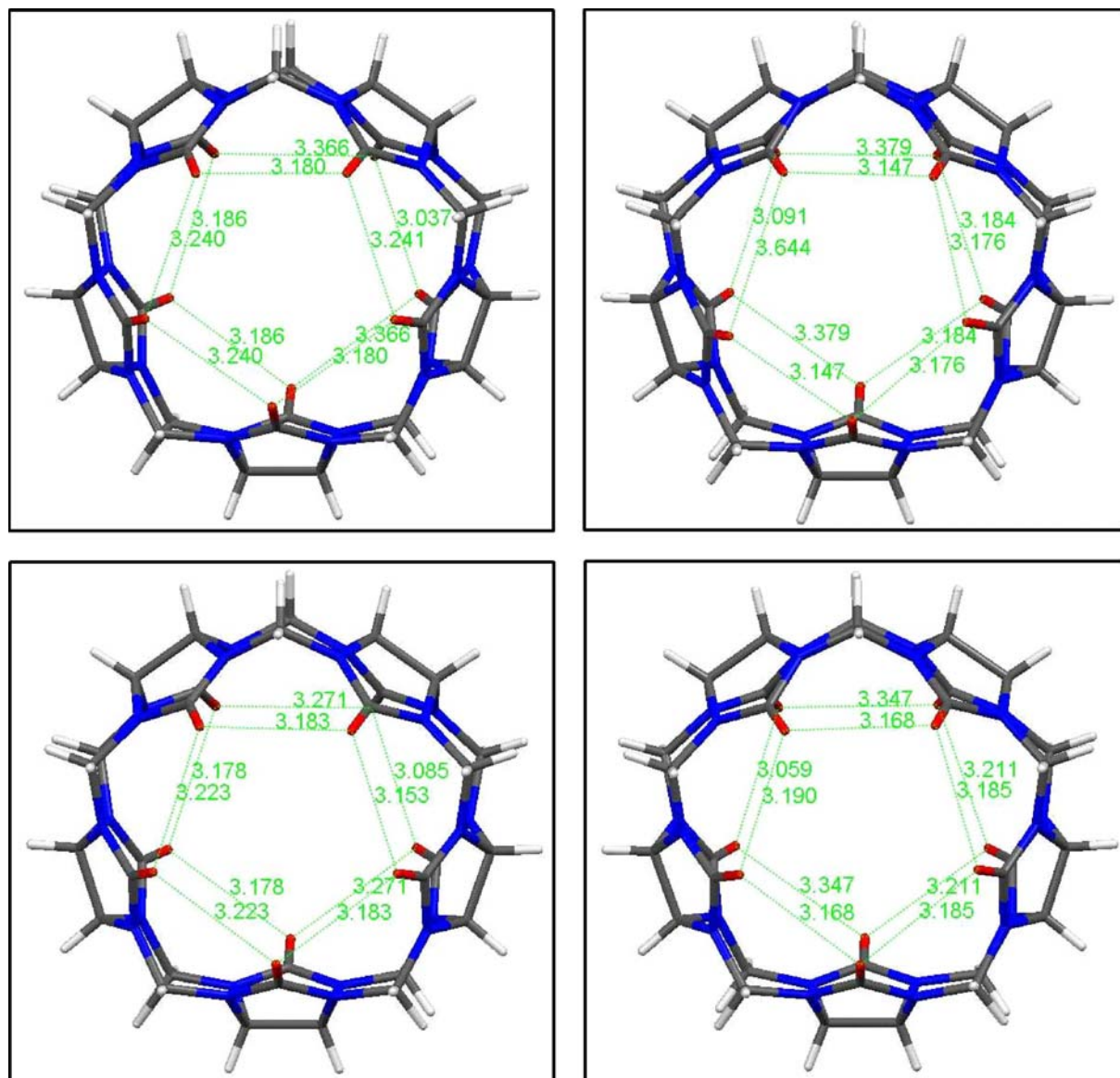


Figure S1. Carbonyl-carbonyl oxygen distances within each rim of CB[5] as deduced from single crystal X ray diffraction structures highlighting the slight distortion compared to D_{5h} symmetry for form **I** crystals.

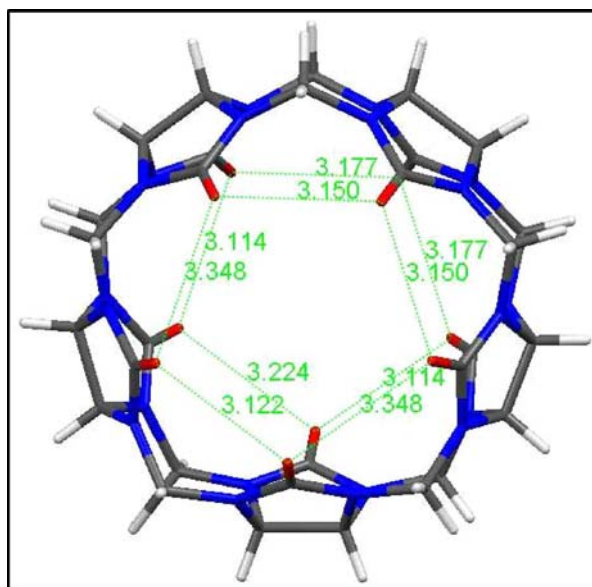


Figure S2. Carbonyl-carbonyl oxygen distances within each rim of CB[5] as deduced from the single crystal X ray diffraction structure highlighting the slight distortion compared to D_{5h} symmetry for form **II** crystals.

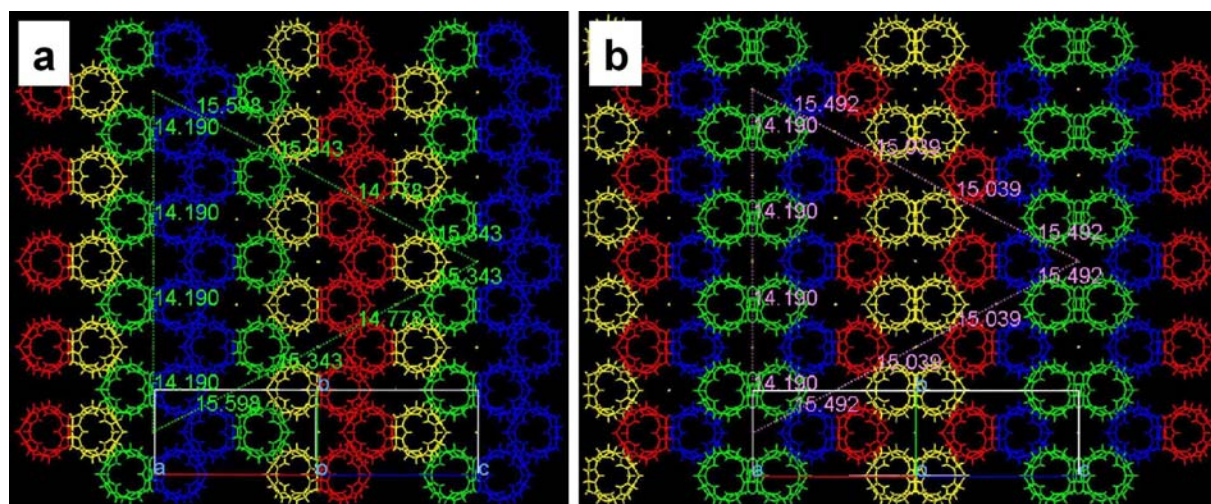


Figure S3. Structural features of the channels as depicted by the separation between the centres of each six-unit centroid within the two (a and b) alternating CB[5] planes perpendicular to the channel axes in Form **I** CB[5] crystals.

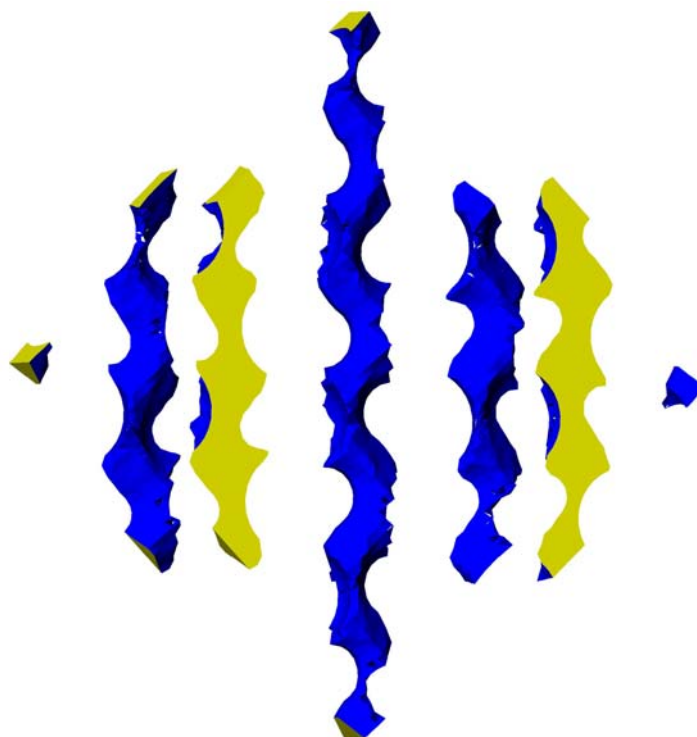


Figure S4. Channel shape of form **I** CB[5] hydrate crystals as defined by allowing a sphere of diameter 2.0 Å to roll over the surface of the ordered network (guests have been removed).

The periodically constricted channels of the form **I** crystals were constructed using ATOMS^{iv} and the disordered water molecules found inside the channels were artificially removed. This process serves to better emphasize the periodic wave-like nature of the channels. In order to evaluate the space in the channels, a sphere of given diameter was allowed to slide along the channels (settings: grid spacing, 0.2 Å, unit cell values of 1, 1, 1 along *a*, *b* and *c*). A progressive increase of the sphere diameter was performed until movement became restricted at the size of 7.4 Å; thus giving the smallest diameter of the channels (based on contact between the sphere and cucurbituril atoms without overlap considering van der Waals radii).^v To determine the maximum size of the broader regions of the channel, the diameter of the sphere was varied until it became too large to be accommodated anywhere inside the channel, at a value of ~ 9.4 Å.

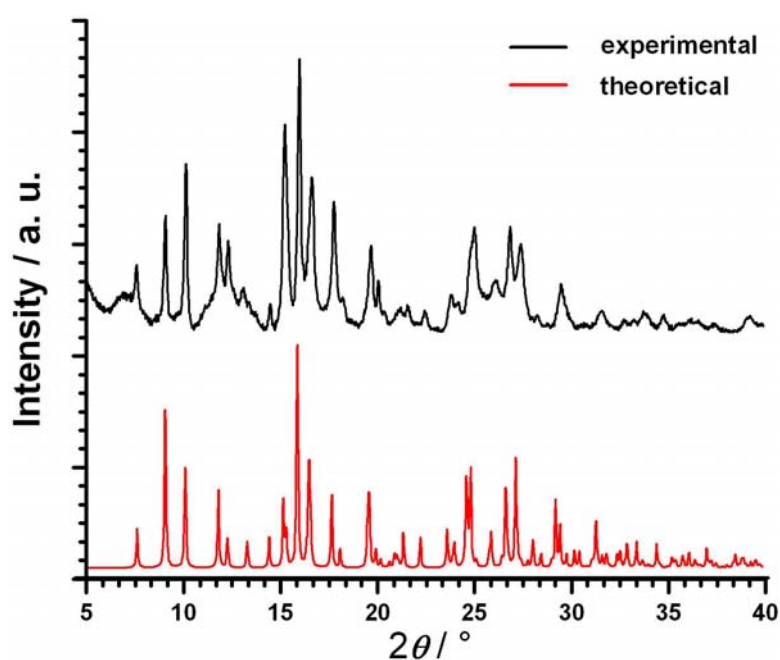


Figure S5. Powder X ray diffractograms of form **II** CB[5] crystals.

Powder X-ray diffraction.

Diffractograms were recorded on a Bruker D8 Advance diffractometer using a $\text{Cu}_{K\alpha}$ radiation at $\lambda = 1.54053 \text{ \AA}$. Reflexions were collected from 5 to 60° with a step width of 0.03° and a step time of 189 s at 17°C .

Solid state ^{129}Xe NMR.

Powdered samples were prepared by grinding form **II** CB[5] single crystals. Before the hyperpolarized NMR experiment, the samples were purged with a continuous flow of the Xe-N₂-He gas mixture (BOC, Canada, volume composition Xe:N₂:He = 1%:3%:96%) at room temperature for 10-15 minutes in the NMR probe. Hyperpolarized ^{129}Xe NMR spectra were obtained on a Bruker AMX300 spectrometer operating at 83.013 MHz (magnetic field 7.05 T) using a customized probe from Morris Instruments. These experiments were performed using a continuous flow of hyperpolarized Xe gas, as described previously.^{vi} The continuous flow of hyperpolarized (CF HP) Xe was delivered to the NMR coil through 2 mm plastic tubing. The temperature in the probe was controlled using a Bruker BT1000 temperature controller with an accuracy of 0.1 K. A Bloch decay one-pulse sequence was used with 90° pulse length of 3 μs and a recycle time of 1 s.

Static and MAS ^{129}Xe NMR spectra of thermally polarized xenon were collected on Bruker DSX200 and DSX400 instruments (magnetic field of 4.7 and 9.4 T, respectively) on CB[5] powders pressurized with *ca.* 10 atm of xenon gas enriched in ^{129}Xe (98.5%) and sealed in 5mm glass tubes. MAS ^{129}Xe NMR measurements were performed at spinning rates of 2500 Hz for a total of 8000 scans using a cross-polarization pulse acquisition sequence with a contact time of 10 ms and relaxation delay of 3 s.

ⁱ D. Bardelang, K. A. Udachin, D. M. Leek, J. A. Ripmeester, *CrystEngComm*, 2007, **9**, 973-975.

ⁱⁱ a) A. Day, A. P. Arnold, R. J. Blanch, B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094-8100; b) A. I. Day, R. J. Blanch, A. Coe, A. P. Arnold, *J. Incl. Phenom. Macrocyclic. Chem.*, 2002, **43**, 247-250.

ⁱⁱⁱ J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540-541.

^{iv} E. Dowty, ATOMS, Ver. 5.0.6. Complete Program for Displaying Crystal Structures; Kingsport, TN, 1999.

^v A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.

^{vi} I. L. Moudrakovski, A. Nossov, S. Lang, S. R. Breeze, C. I. Ratcliffe, B. Simard, G. Santyr, J. A. Ripmeester, *Chem. Mater.*, 2000, **12**, 1181-1183.