Electronic Supplementary Material for CrystEngComm

Supplementary Material (ESI) for CrystEngComm

Highly symmetric columnar channels in metal-free cucurbit[n]uril hydrate crystals (n=6, 8).

David Bardelang, Konstantin A. Udachin, Donald M. Leek, John A. Ripmeester.

Experimental Section

Synthesis and characterization. All reactants were used as received without further purification. Glycouril, paraformaldehyde (95%) and formic acid (95-97%) were provided by Aldrich and glycerol (ACS Reagent) from ACP chemicals. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400.13 MHz and 100.60 MHz respectively on a Bruker DRX-400 spectrometer. ^{1}H NMR spectra were recorded with a 30 degree pulse, a 2 s acquisition time, a 4 s relaxation delay and a sweep width of 8200 Hz. ^{13}C NMR spectra were recorded with a 30 degree pulse, composite pulse ^{1}H decoupling, a 0.74 s acquisition time, a 0.26 s relaxation delay and a sweep width of 22000 Hz. 2D NMR spectra (HMQC and HMBC) were used to assist in the assignment.

Preparation of CB[n] macrocycles from a modified procedure from Day *and coll.*[i] and Kim *and coll.*[ii]:

Glycouril (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 found to be hard to dissolve in 37 % aqueous hydrochloric acid (160 mL) even under strong magnetic stirring. Gelation/solidification may

occur after partial dissolution and vigorous stirring should be maintained until all of the mixture sets as a gel. Alternatively, addition of solid paraformaldehyde to a prepared acidic glycouril solution greatly facilitated the procedure. After 30 minutes, the mixture was heated 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 around 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 in a formic/sulphuric acid solution that revealed to be CB[5] (around 2 g of centimetre-scale plates). CB[8] was recrystallized from fraction 1 and dissolved into a 37 % hydrochloric acid solution followed by slow solvent evaporation. Octahedral crystals (340 mg) were collected after two weeks from around 1 g of starting material. The process can be significantly accelerated by heating the solution on a hot plate (around 70-80°C) until the first crystals appear. Slow evaporation at room temperature afforded CB[8] crystals in approximate identical yield within one day. Single crystal X-ray analysis of the resulting octahedral crystals revealed that they belong to the $I_{41/a}$ space group as already reported.[ii]

Electronic Supplementary Material for CrystEngComm

Preparation of structure **1** crystals:

Procedure 1: Isolation of hexagonally based long prisms of CB[6] occurred from attempts to grow crystals of CB[6] in the process of fraction 3 purification. A hot aqueous sulphuric acid solution (around 1/1 vol. H_2SO_4/water) was added to the crude solid (around 5 g) until everything dissolved. The solution was then filtered before allowing acetone to slowly diffuse into the cucurbituril aqueous acid solution for around 10 days by which time the solution colour turned dark orange. Around 2.2 g of large hexagonal block crystals (centimetre scale) of CB[6] were then collected whose crystal structure was difficult to solve due to multiple twinning. The mother solution was then left for slow evaporation of the solvents, yielding a dark solid like layer on the surface and colourless hexagonal prism crystals in the dark solution (530 mg), experiments being reproducible. Starting from more concentrated acid solutions yields crystals with a higher amount of sulphate within the crystal structure that does not change significantly the cucurbituril positions.

Procedure 2: Isolation of hexagonal plates (that were shown to be of the same crystal structure) was also possible dissolving crude mixture 3 (1-2 g) in hot 37 % aqueous hydrochloric acid and water and letting the solution evaporate for several days. The mixture first showed some crystalline powder that was removed by filtration. Allowing the resulting solution to evaporate for a longer time afforded 441 mg of large hexagonal plate crystals that were used for single crystal X ray diffraction and were revealed to be of the same structure as the crystals obtained from procedure 1, except sulphate was replaced by chloride anions.

Electronic Supplementary Material for CrystEngComm

Preparation of structure **2** crystals:

CB[8] (around 1 g) was simply dissolved in hot aqueous nitric acid before letting the solution evaporate for around 2 weeks. Large colourless hexagonal plate crystals were then collected (446 mg) prior to X ray crystal structure determination.

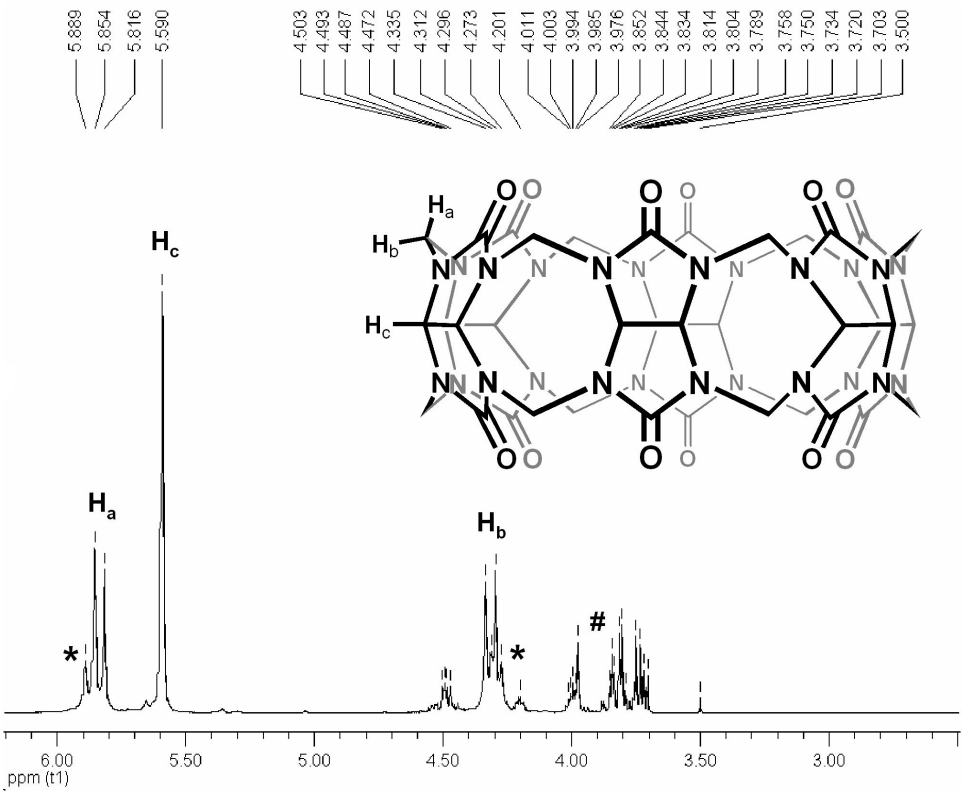

Figure S1. ^{1}H NMR spectrum of fraction 3 in $D_2O/CF_3CO_2D/D_2SO_4$ (1/1/0.15) that appeared to be mainly CB[6]. CB[7] is likely present in a small amount (*) as well as some additional signals that could come from uncyclized glycouril oligomers (#).

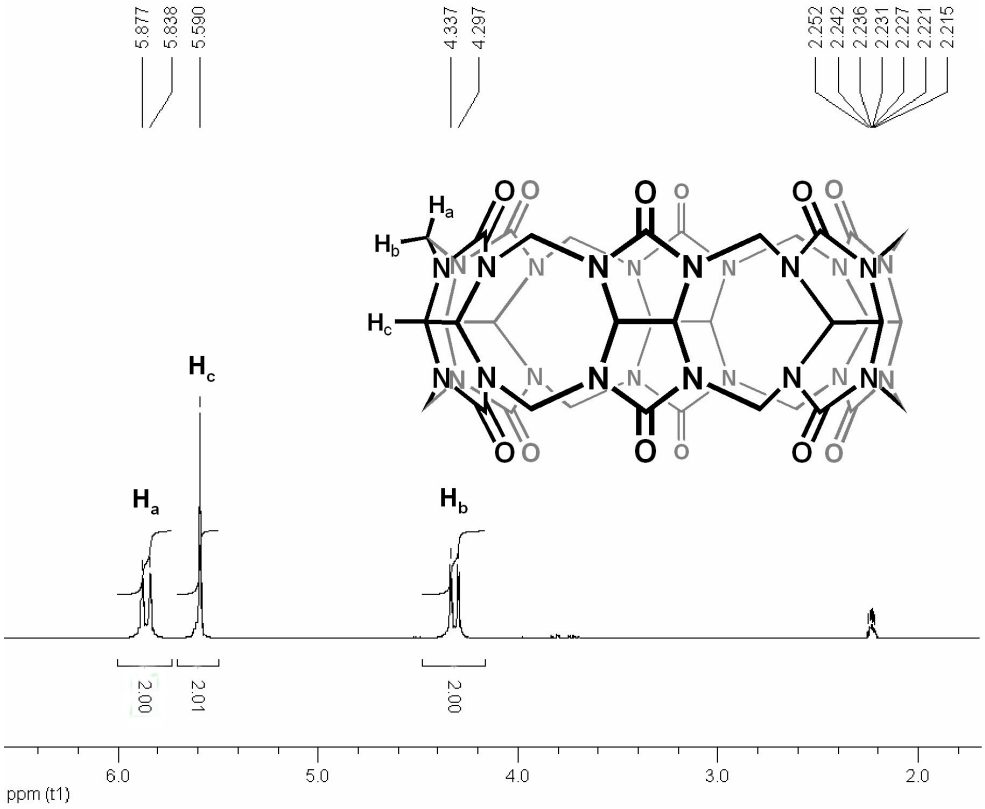

Figure S2. ^{1}H NMR spectrum of crystals of **1** (procedure 1) in $D_2O/CF_3CO_2D/D_2SO_4$ (1/1/0.15).

The small multiplet signal around 2.1 ppm does not match the expected singlet and chemical shift of acetone in this solvent and was attributed to an impurity (^{1}H NMR spectrum of acetone in the same acidic solvent mixture was performed giving a large singlet around 1.73 ppm). The ^{13}C NMR signal of methyl groups of acetone is found to be around 28 ppm in the $D_2O/CF_3COOD/D_2SO_4$ solvent and this signal is absent from the ^{13}C NMR spectrum of the prepared CB[6] crystals.

The ^{1}H NMR spectrum of the main large hexagonal block crystals (2.2 g) shown CB[6] only as for crystals of **1** (procedure 2).

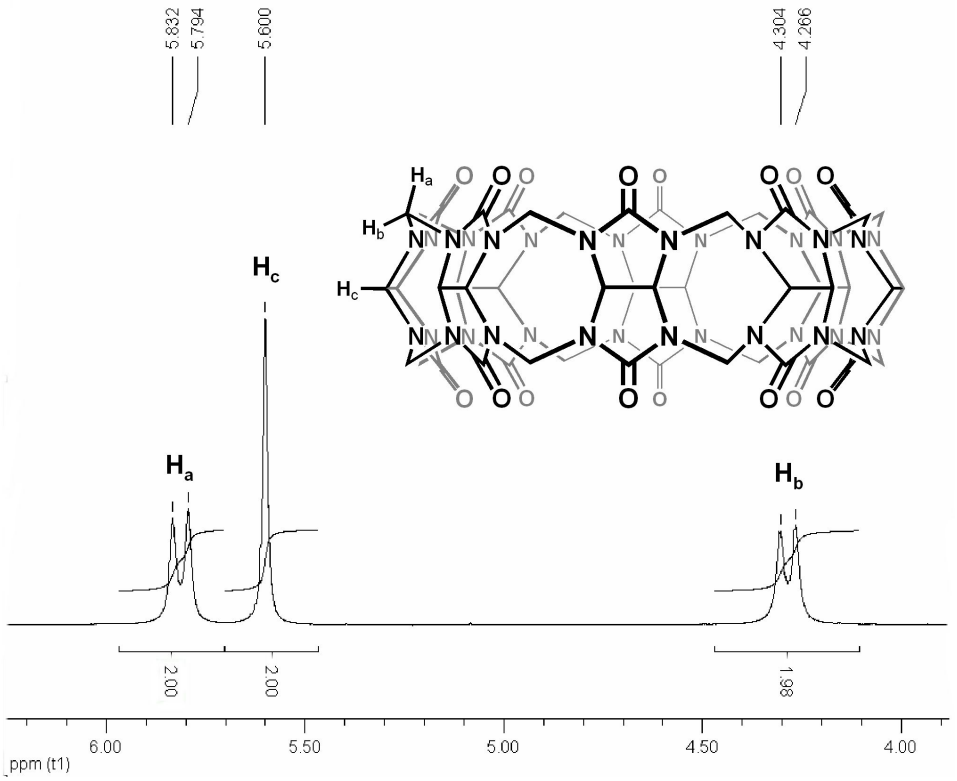

Figure S3. ^{1}H NMR spectrum of crude CB[8] in $D_2O/CF_3CO_2D/D_2SO_4$ (1/1/0.15) that appeared to be CB[8] only.

TGA experiments were performed on a TA 2050 analyzer under nitrogen flows of 50 and 20 $mL.min^{-1}$ for around 6 mg of structure **2** crystals. Special care has been taken to proceed as fast as possible once the crystals were out of the mother solution due to the rapid solvent loss under ambient conditions.

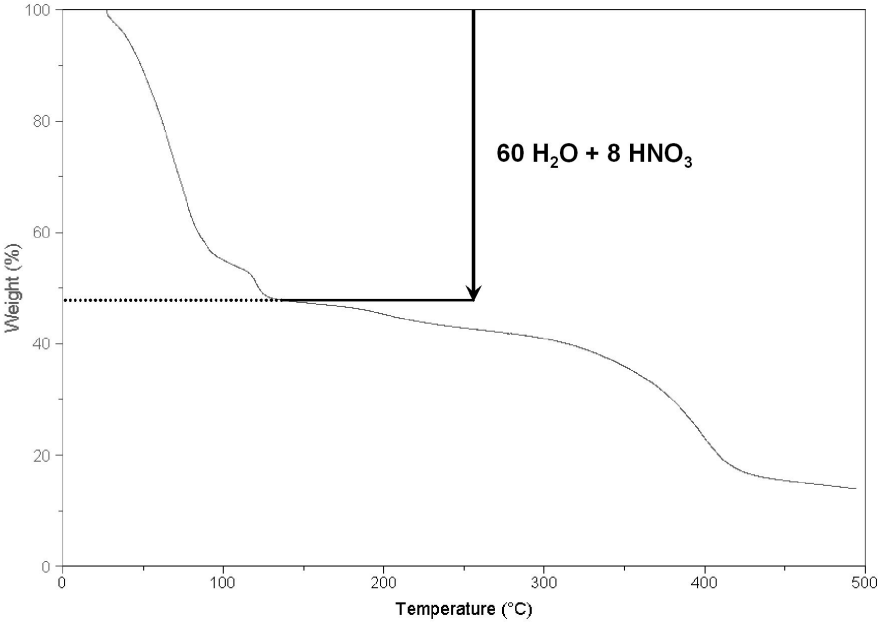

Figure S4. TGA analysis of CB[8] based crystals of structure **2**.

A rapid mass loss is observed from room temperature to around 120°C likely due to water and nitric acid removal. After a small plateau is reached, CB[8] may start to slightly decompose before clear macrocycle destruction after 300°C.

[i] A. Day, A. P. Arnold, R. J. Blanch, B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094-8100. This article is also advised to be read: A. I. Day, R. J. Blanch, A. Coe, A. P. Arnold, *J. Incl. Phenom. Macrocyclic. Chem.*, 2002, **43**, 247-250.

[ii] 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.