

Reversible uptake of H₂O by imine based porous organic cage

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Electronic supplementary information:

Synthesis of **CC3-R**: Dichloromethane (100 ml) was layered slowly onto solid triformylbenzene (TFB, 5 g, 30.86 mmol) without stirring at room temperature. Trifluoroacetic acid (100 μ L) was added directly to this solution as a catalyst for the imine bond formation. Finally, a solution of (*R,R*)-1,2-diaminocyclohexane (5 g, 44.64 mmol) in dichloromethane (100 mL) was added to this, again without mixing. The reaction was covered and left to stand. The absence of stirring is important since it controls the dissolution rate of the TFB: similar results can be obtained by slow addition, for example with syringe pump, although the layering method is convenient, reproducible, and scalable to multigram quantities. Over 5 days, all of the solid triformylbenzene was used up and octahedral crystals of **CC3-R** grew on the sides of the glass reaction vessel. The crystalline product was removed by filtration and washed with 95 % ethanol / 5 % dichloromethane. Yield 6.5 g, 83 %. ¹H NMR (CDCl₃) δ 8.15 (s, CH=N, 12H), 7.89 (s, ArH, 12H), 3.33 (m, CHN, 12H), 1.9 – 1.4 (m, CH₂, 48H) ppm. ¹³C NMR (CDCl₃) δ 159.1, 136.7, 129.5, 74.7, 33.0, 24.4 ppm. IR (KBr pellet, ν) 2929 (s), 2858 (s), 1649 (s), 1601 (w), 1448 (m), 1372 (w), 1342 (w), 1306 (w), 1157 (m), 1092 (m), 1041 (w), 990 (w), 937 (w), 885 (w), 863 (w), 691 (m), 671 (m), 520 (w), 458 (w), 439 (w) cm⁻¹. MS (ES⁺) 1118 ([M+H]⁺). Accurate mass calculated for C₇₂H₈₅N₁₂: 1117.7020. Found: 1117.7065.

Water sorption procedure: Water adsorption isotherms, at 25 °C, were determined gravimetrically using a DVS Advantage 2 (*Surface Measurement Systems Ltd*). In order to ensure the sample was fully de-solvated before beginning analysis, the sample was heated to 100 °C in a flow of nitrogen until a constant weight was achieved. There was no further heating in between each cycle, as soon as one cycle completed, the next one started. During the isotherm determination, equilibrium was defined as a weight change of <0.002% / min, and it had to stay below that criterion for a period of 10 minutes before moving on to the next humidity. The experiment was performed at atmospheric pressure in a flow of nitrogen, with the humidity being generated / controlled by mass flow controllers / bubblers. The sample weight was ~34 mg.

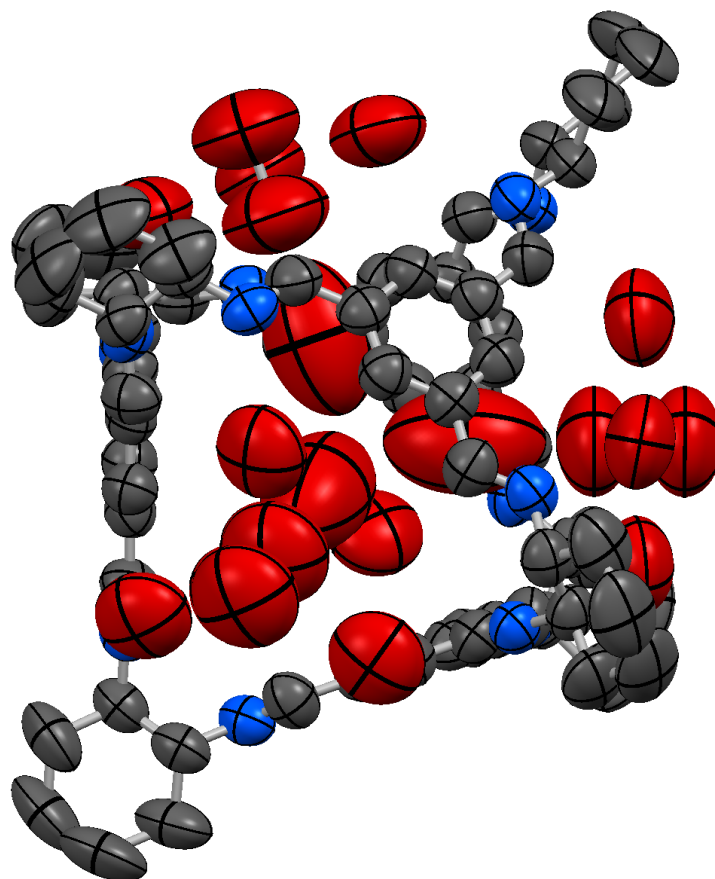


Figure S1. Single crystal X-ray structure of **H₂O@CC₃**. Ellipsoids at 50% probability level, H atoms omitted for clarity, C (grey), N (blue), O (red).

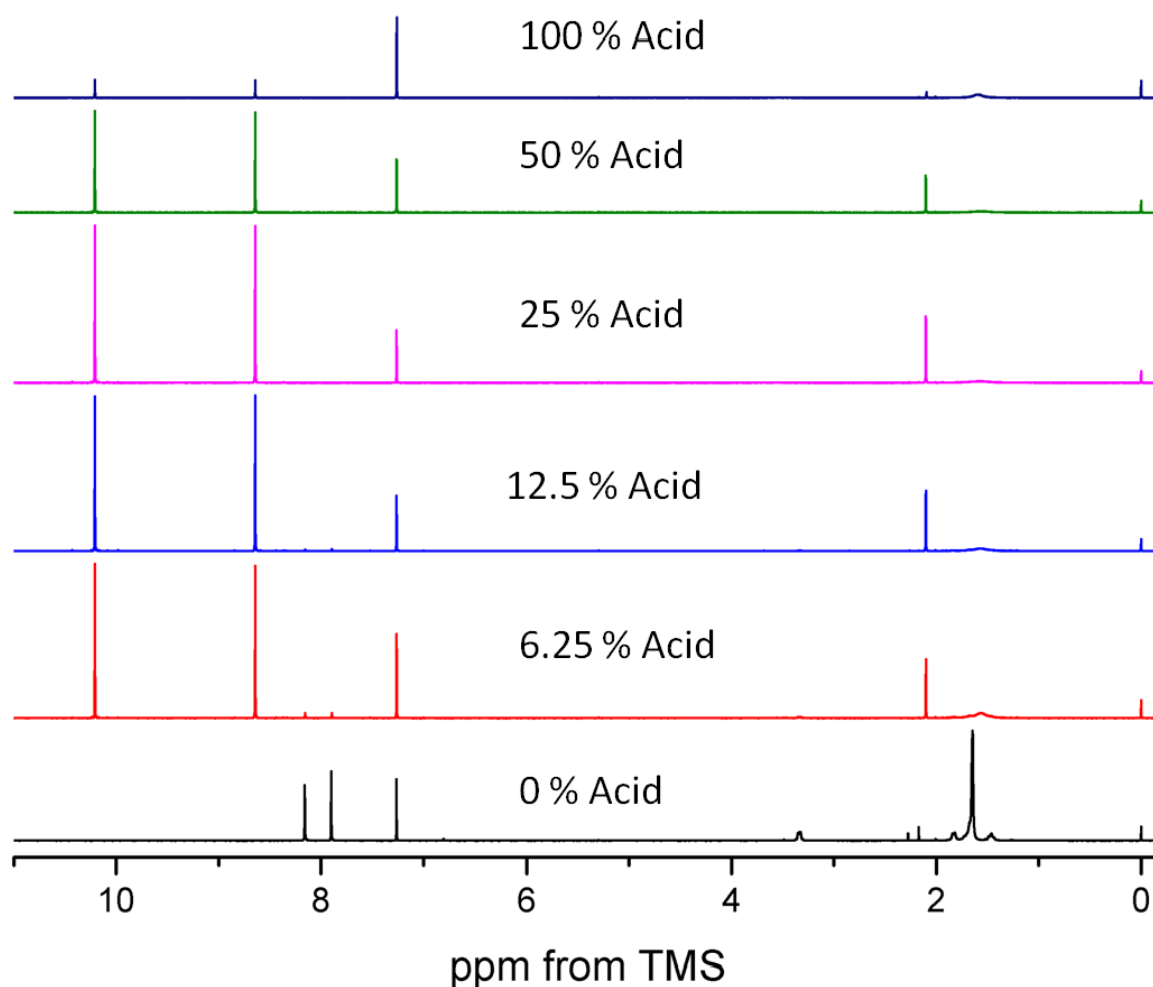


Figure S2. ^1H NMR in CDCl_3 - samples of **CC3** that have been immersed in aqueous solution for 4 days, with various proportions of acetic acid. In pure water (bottom) only **CC3** is detected in the spectrum. After the addition of acetic acid (2.1 ppm), the **CC3** is broken down to the precursor, triformyl benzene (10.2 and 8.6 ppm). Some **CC3** signal is still detectable at 6.25 % and 12.5 % acid, but by 25 % acid there is no longer any detectable signal for **CC3**.

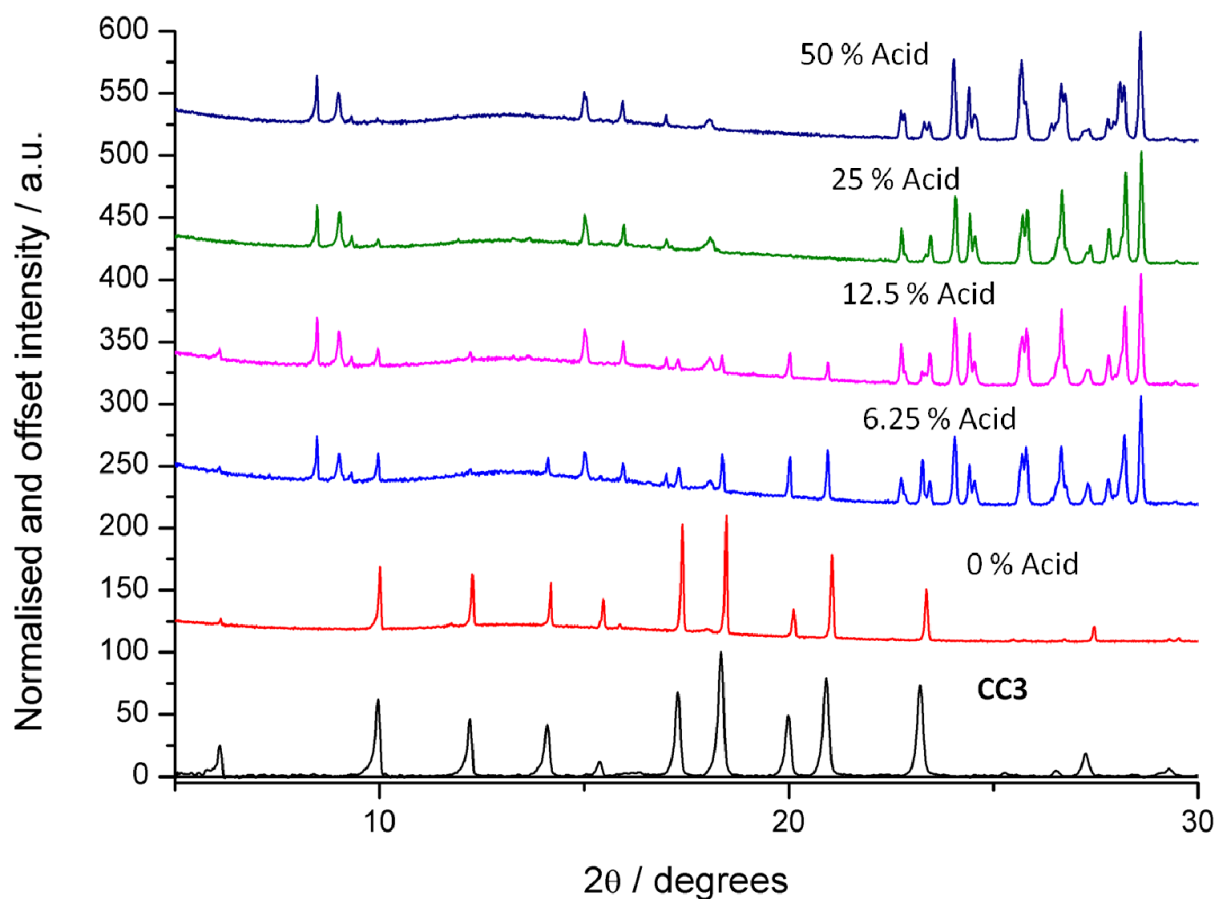


Figure S3. Powder X-ray diffraction patterns of samples of **CC3** that have been immersed in aqueous solution for 4 days, with various proportions of acetic acid, and in comparison to as made **CC3**. After exposure to pure water, only the diffraction pattern associated with **CC3** is detected. However, after exposure to acetic acid, additional peaks are detected corresponding to crystalline triformyl benzene. Some peaks for **CC3** are still detected up to 12.5 % acid. The sample exposed to 100 % acetic acid (not shown) became amorphous.

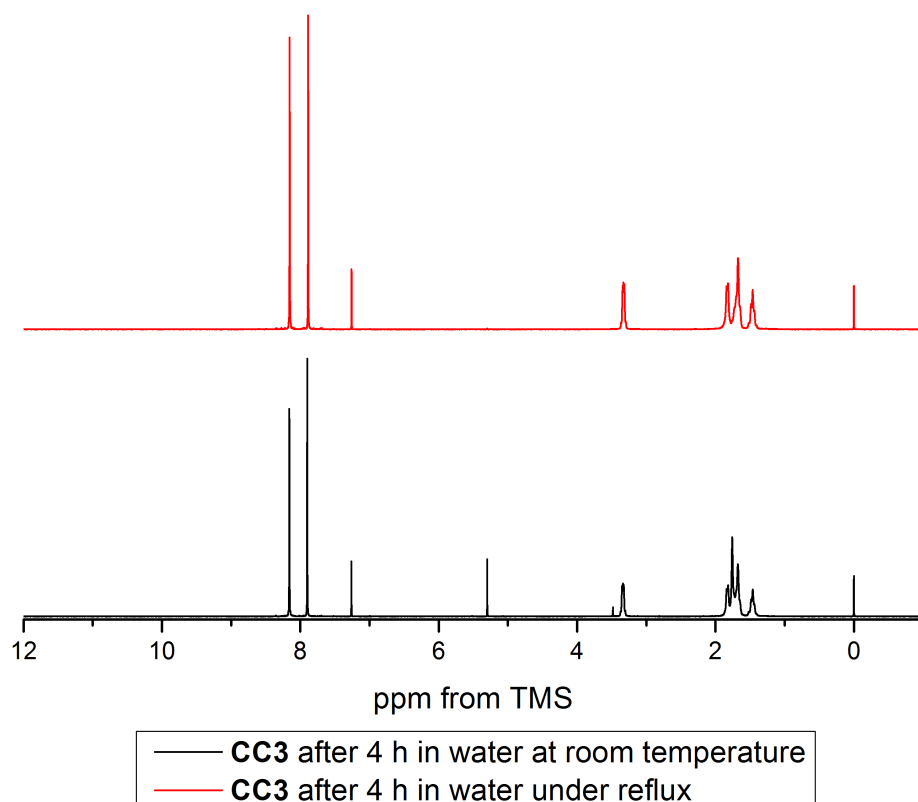


Figure S4. ^1H NMR in CDCl_3 - samples of CC3 that have been immersed in aqueous solution for 4 hours, either at room temperature or under reflux conditions. No change in the cage structure is detected.

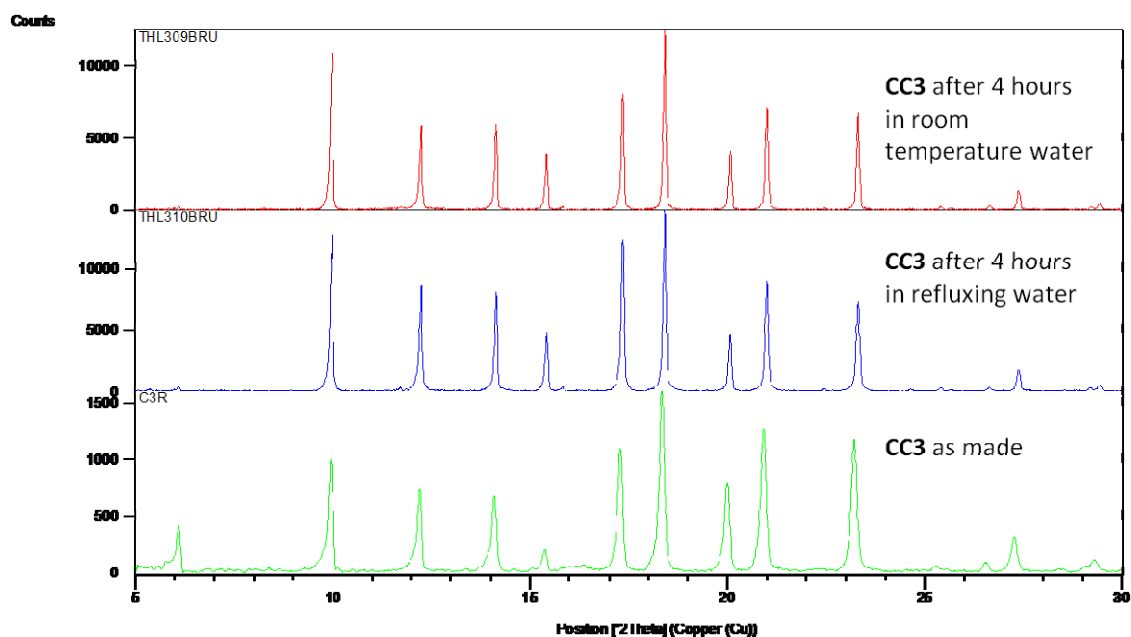


Figure S5. Powder X-ray diffraction patterns of samples of CC3 that have been immersed in aqueous solution for 4 hours, either at room temperature or under reflux conditions. No change in the cage structure is detected.

Porosity:

The porosity of the cage is maintained after exposure to moisture. The apparent BET surface areas were measured at 360 m²g⁻¹ for **CC3** left in room temperature water for 4 hours, and 352 for **CC3** refluxed in water for 4 hours. Nitrogen isotherms were measured at 77 K using a Quantachrome Nova surface area analyser.

Single crystal X-ray data:

Single crystal X-ray data of C₇₂H₈₄N₁₂ · 12 H₂O were measured on a Rigaku MicroMax-007 HF rotating anode diffractometer (Mo-K α radiation, λ = 0.71073 Å, Kappa 4 circle goniometer, Rigaku Saturn724+ detector). An empirical absorption corrections using equivalent reflections was performed with the program SADABS¹ the structure was solved with the program SHELXD and refined using SHELXL.² All non H atoms were refined anisotropically and H atoms were fixed to geometric positions using the riding model, for the water molecules no H positions could be located. Formula C₇₂H₁₀₈N₁₂O₁₂, M = 1333.70 g·mol⁻¹, cubic space group $F4_132$, a = 25.1381(7) Å, V = 15885.4(8) Å³, Z = 8, ρ = 1.115 g·cm⁻³, μ = 0.077 mm⁻¹, $F(000)$ = 5760, crystal size = 0.22 x 0.20 x 0.18 mm³, T = 295 K. 73441 reflections ($2.29 < \theta < 23.25^\circ$) measured, 975 unique ($R_{\text{int}} = 0.0557$), 914 observed ($I > 2 \sigma(I)$), $R_1 = 0.0881$ for the observed and $R_1 = 0.0902$ for all reflections, max/min residual electron density 0.209 and -0.206 e·Å⁻³, data / restraints / parameters = 975 / 0 / 75, GOF = 1.278.

1. G. M. Sheldrick, University of Göttingen, Germany, 2008.
2. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.