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SUPPORTING INFORMATION

A propanol-seamed *C*-methylcalix[4]resorcinarene hexamer accessible via solution crystallization, liquid-assisted grinding and vapour sorption

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Experimental

C-methylcalix[4]resorcinarene **1** was purchased from Sigma Aldrich and used as received. 100 mg of **1** was dissolved in 2 mL of 1-propanol (**1-PrOH**) with swirling. The vial was left to stand uncapped at room temperature. Slow evaporation of the solvent led to the appearance of crystals of $\mathbf{1}_6 \cdot (H_2O)_4 \cdot (\mathbf{1\text{-}PrOH})_{18}$, **5**, after approximately 3 days. **5** could also be prepared by liquid-assisted grinding of **1** with 1-propanol for 10 minutes, as well as exposing desolvated **5** (**5'**), which is very closely related to **1**, to 1-propanol vapour for 4 hours.

Thermogravimetric analysis (TGA) was performed using a TGA Q500 instrument. The samples (~8 mg) were weighed directly into open aluminium crucibles. During the experiments the sample holder was continuously purged with a dry nitrogen flow of 60 mL/min. Measurements in the TGA were done using a heating rate of 10 °C/min.

Vapour sorption on 60 mg **5'** was performed on a Micromeritics 3Flex Surface Area Analyzer. The sample was prepared by heating **5** under vacuum for 4 hours at 125°C.

X-ray powder data were collected on a Bruker D8 Advance X-ray diffractometer with copper radiation (Cu Kα, λ = 1.5406 Å). In the variable-temperature powder X-ray experiment (VT-PXRD) the X-rays were generated at 40 kV and 40 mA, whilst the sample (**5**) was scanned between 4 and 40° 2θ (step size of 0.020°) in the temperature range 25-150 °C. In the *in situ* 1-propanol vapour sorption experiment the X-rays were generated at 40 kV and 30 mA, whilst the sample was scanned between 4 and 40° 2θ (step size of 0.014°). The sample was placed in a modified sample stage which had wells next to the sample (**5'** – prepared by heating **5** at 175 °C with no vacuum for 3 hours) containing the solvent, whilst the whole stage was covered with Mylar film.[1] MERCURY[16] was used to calculate predicted PXRD patterns from single crystal data for comparison with experimentally obtained patterns.

A suitable, single crystal of **5** was mounted on a cryoloop using Paratone N oil. Data collection was carried out on a Bruker DUO APEX II CCD diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) using an Oxford Cryostream-700 to maintain the temperature at 173 K. Data reduction and cell refinement were performed using SAINT-Plus.[2] The X-ray diffraction data were corrected for the Lorentz-polarization factor and scaled for absorption effects using SADABS.[2] Structure solution and refinement were performed using the crystallographic suite OLEX2.[3] The structure was solved by direct methods, implemented in SHELXS,[4] with refinement proceeding using the full-matrix least-squares method, based on F^2 values against all reflections, including anisotropic displacement parameters for all non-H atoms, as implemented in SHELXL-2014/7.[4] X-Seed[5] was used as interface to MSRoll[6] and POV-Ray[6] in order to calculate void spaces and generate graphics, respectively. Mercury[7] was also used to generate graphics and determine the hydrogen bond connectivity. The crystallographic information file (CIF) CCDC 1590340 contains the supplementary crystallographic data for this paper and can be obtained free of charge via the Cambridge Crystallographic Data Centre (CCDC) from the website https://www.ccdc.cam.ac.uk/structures/.

Table S1 Crystal data for **5**

Crystal Parameters	
Empirical formula	$C_{41}H_{59.33}O_{12.67}$
Formula weight	754.88
Temperature/K	173.15
Crystal system	trigonal
Space group	R-3
a / Å	33.6175(18)
b / Å	33.6175(18)
c / Å	20.9185(13)
α / °	90
β / °	90
γ / °	120
Volume / Å^3	20473(3)
Z	18
ρ_{calc} g/cm^3	1.102
μ / mm^{-1}	0.081
F(000)	7320.0
Crystal size / mm^3	0.58 × 0.53 × 0.5
Radiation	MoKα (λ = 0.71073)
2θ range for data collection / °	2.398 to 61.248
Index ranges	-44 ≤ h ≤ 20, -31 ≤ k ≤ 47, -29 ≤ l ≤ 29
Reflections collected	34346
Independent reflections	13326 [R_{int} = 0.0553, R_{sigma} = 0.0870]
Data/restraints/parameters	13326/195/533
Goodness-of-fit on F^2	1.165
Final R indexes [I>=2σ (I)]	R_1 = 0.1158, wR_2 = 0.3286
Final R indexes [all data]	R_1 = 0.2085, wR_2 = 0.3975
Largest diff. peak/hole / e Å^{-3}	0.80/-0.61

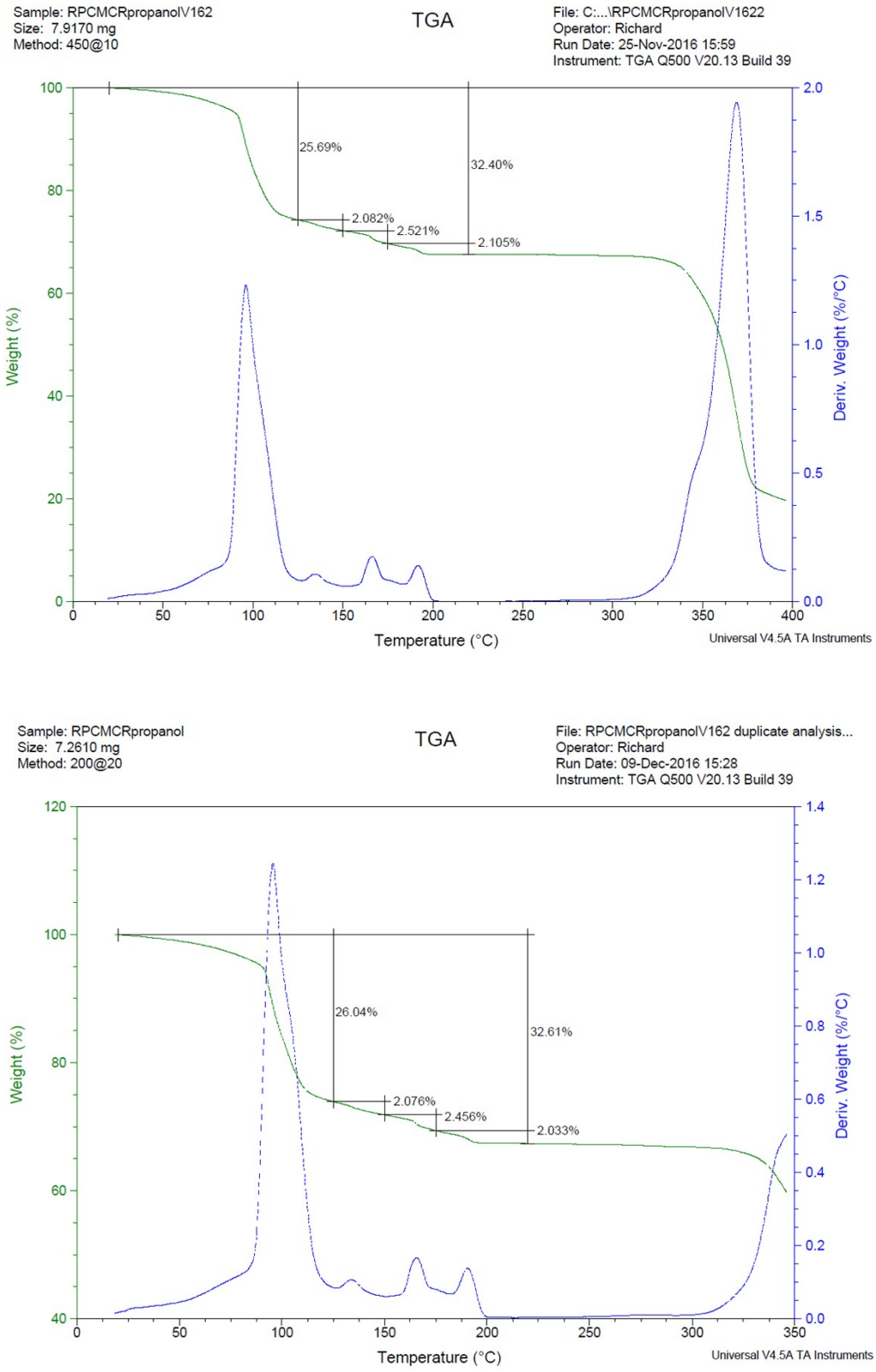

Figure S1. Duplicate TGA graphs of weight % vs temperature (in green) and the first derivative of weight % with respect to temperature (in blue) for **5** in the range 20-220°C. Values reported in the main paper are averages of the duplicate analyses.

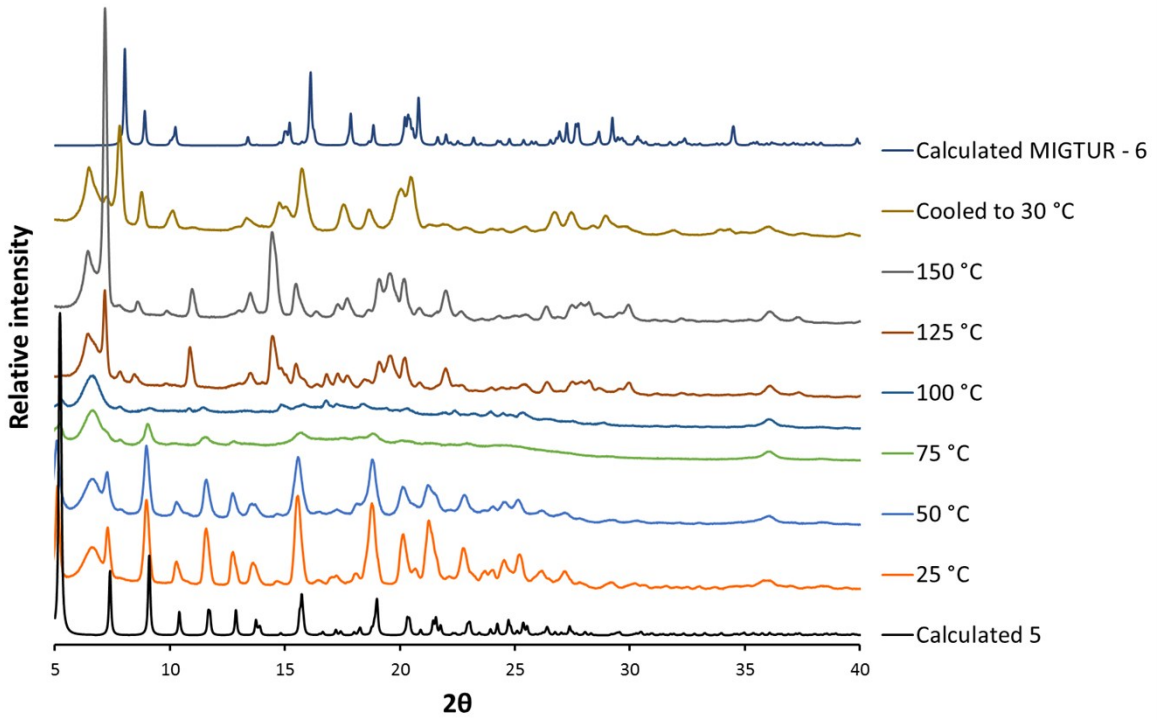

Figure S2. Variable-temperature PXRD patterns of **5** heated from 25-150 °C and subsequently cooled to 30 °C compared with PXRD patterns calculated from single crystal structures of hexamer **5** and a bilayer, monohydrate of **1** (CSD code MIGTUR; **6**). Broad peaks at 6.5° 2θ are due to the sample holder.

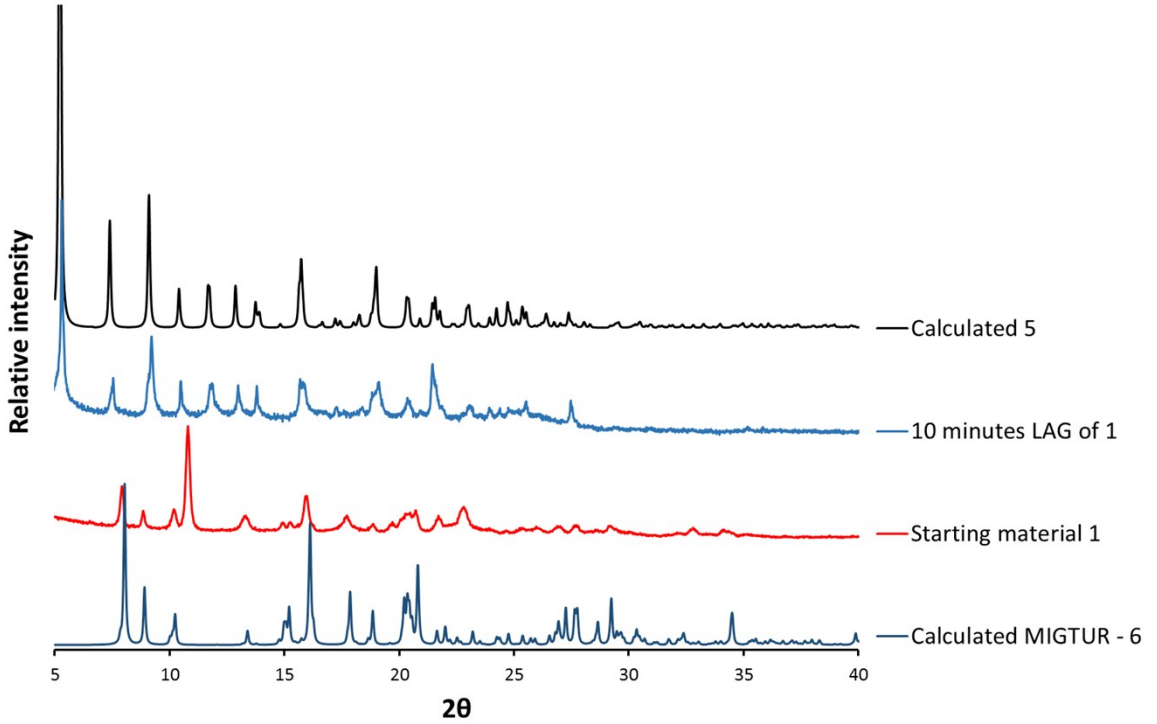

Figure S3. PXRD patterns of starting material of **1**; calculated from single crystal structure of bilayer, monohydrate of **1** (CSD code MIGTUR; **6**); 10 minutes liquid-assisted grinding (LAG) of **1** with 1-propanol and calculated from single crystal structure of hexamer **5**.

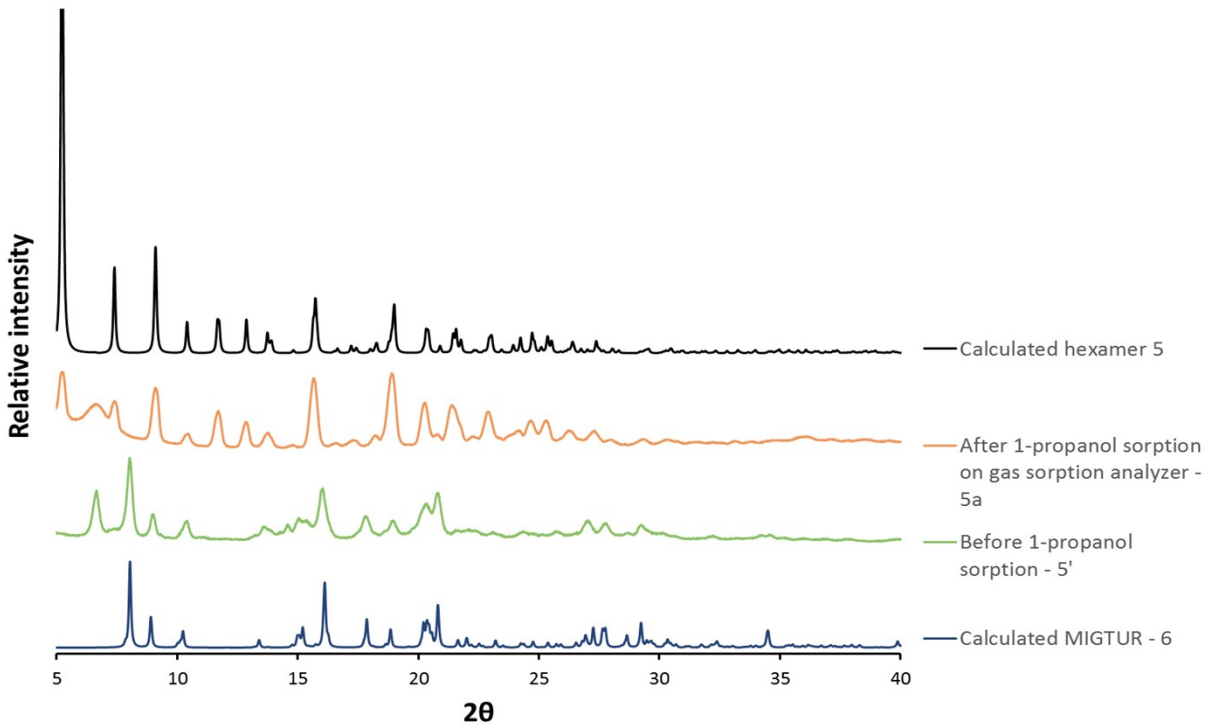

Figure S4. PXRD patterns before and after 1-propanol vapour sorption on 3Flex gas sorption analyzer. PXRD pattern of desolvated **5** (**5'**) agrees closely with calculated pattern of bilayer, monohydrate structure of **1** (CSD code MIGTUR - **6**), and subsequently, after 1-propanol vapour sorption, **5a** agrees closely with calculated PXRD pattern of the original hexamer **5**.

Supporting information references

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Figure S4. *In situ* PXRD vapour sorption experiment shows that the sample starts off with a structure that is close to that of the bilayered structure of **1** (CSD code: MIGTUR) and transforms after ~4 hours to the hexamer **5**.