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SUPPORTING INFORMATION

Solid-state isolation of a unique, small-molecule, supra-heterodimer of large hexameric assemblies of *C*-methylcalix[4]resorcinarene

Clive L. Oliver,* Nikoletta B. Báthori,* Graham E. Jackson, David Kuter and Dyanne L. Cruickshank

*Corresponding authors

Clive L. Oliver

Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

E-mail: clive.oliver@uct.ac.za

Fax: +27 21 6505195

Phone: +27 21 6503830

Nikoletta B. Báthori

Crystal Engineering Unit, Department of Chemistry, Faculty of Applied Sciences, Cape Town, 8000, South Africa.

E-mail: bathorin@cput.ac.za

Fax:+27 21 460 3854

Phone:+27 21 460 8354

Experimental:
A solution of 0.050 g of *C*-methylresorcinarene was dissolved 3 ml of 1-butanol with the solvent allowed to evaporate over two. Brown block-like crystals of **1** appeared after two weeks.

Single Crystal X-ray Diffraction Analysis and Structure Determination:
A suitable, single crystal of **1** 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 100 K. Data reduction and cell refinement were performed using SAINT-Plus.[1] The X-ray diffraction data were corrected for the Lorentz-polarization factor and scaled for absorption effects using SADABS.[1] Structure solution and refinement were performed using the crystallographic suite OLEX2.[2] The structure was solved by direct methods, implemented in SHELXS,[3] 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.[3] X-Seed[4] was used as interface to MSRoll[5] and POV-Ray[5] in order to calculate void spaces and generate graphics, respectively. Mercury[6] was also used to generate graphics and determine the hydrogen bond connectivity of the supra-heterodimer. CCDC 1430586 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www. ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

Table S1 Crystal data for **1**

Crystal Parameters	
Empirical formula	$C_{35.54}H_{40.21}O_{10.3}$
Formula weight	632.17
Temperature/K	100(2)
Crystal system	trigonal
Space group	R3c
a/Å	29.9017(19)
b/Å	29.9017(19)
c/Å	96.281(6)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	74553(11)
Z	72
ρ_{calc}g/cm^3	1.014
μ/mm^{-1}	0.074
F(000)	24181.0
Crystal size/mm^3	0.47 × 0.3 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.572 to 56.564
Index ranges	-39 < h < 17, -38 < k < 39, -128 < l < 122
Reflections collected	114453
Independent reflections	37710 [R_{int} = 0.0438, R_{sigma} = 0.0514]
Data/restraints/parameters	37710/1383/1748
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0577, wR_2 = 0.1501
Final R indexes [all data]	R_1 = 0.0846, wR_2 = 0.1653
Largest diff. peak/hole / e Å^{-3}	0.81/-0.33

Nuclear Magnetic Resonance (NMR) measurements:

NMR spectra were recorded using a BBO probe on a Bruker Advance 400 MHz spectrometer operating at 303 K. Selective 1D NOE spectra were recorded using the selnogp pulse sequence with a mixing time of 300 ms, a 3.98 s acquisition time and a 1 s relaxation delay.

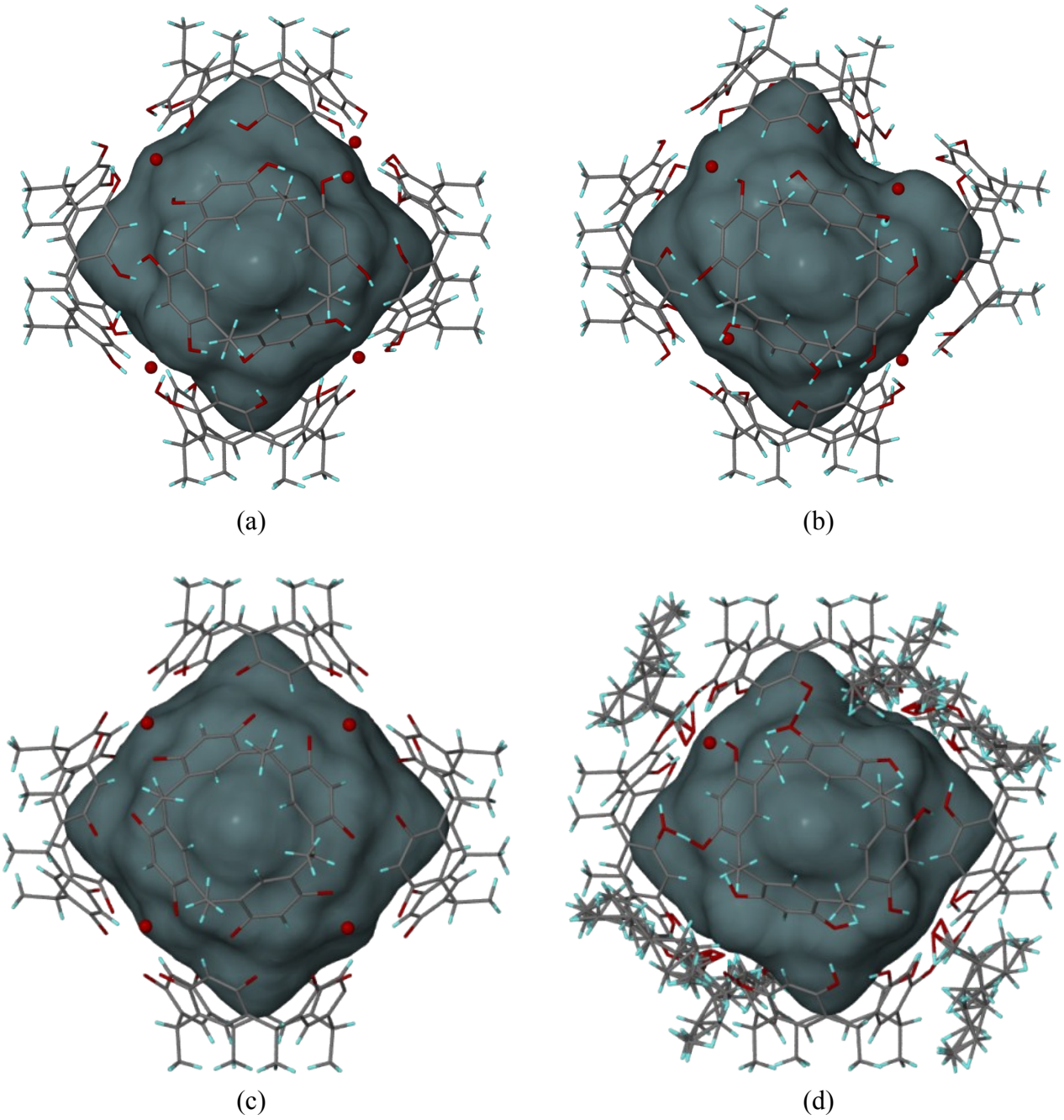
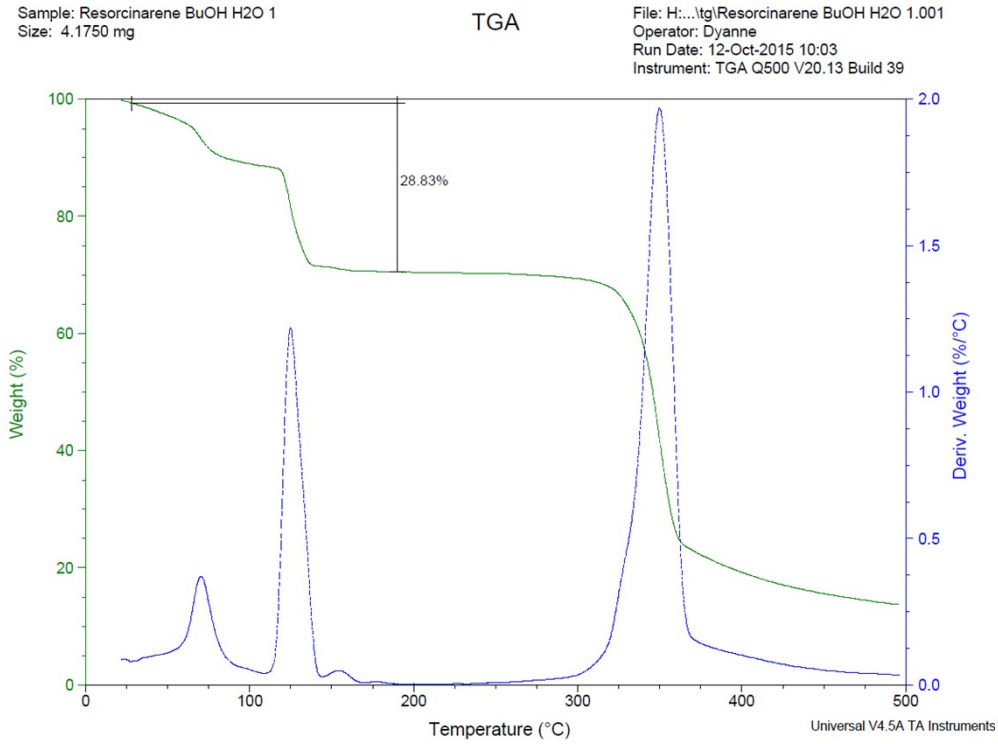


Fig S1 MSRoll mapping of the interior space of (a) assembly A and (b) assembly B. A probe radius of 1.5 Å was used with "contact surface" type of mapping. The 1-butanol molecule modelled in assembly A was deleted in order to map the interior space. Assembly A has an internal volume of 1306 $Å^3$, whilst assembly B has an interior space of 1186 $Å^3$. Both are smaller than the (c) Atwood et al. and (d) Holman et al. interior spaces of 1411 and 1337 $Å^3$, respectively. Note the Atwood and Holman interior cavities differ from those reported by the authors (1375 and 1290$Å^3$) which is probably due to using different probe radii and software programs.



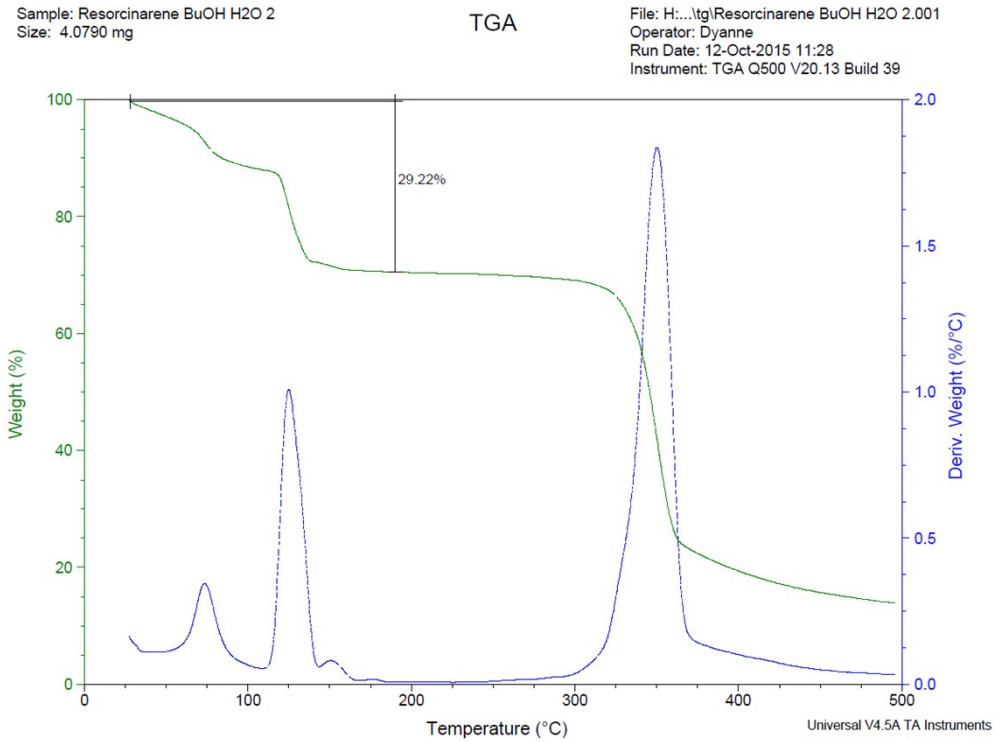


Figure S2. Duplicate TGA graphs of weight % vs temperature (in green) and the first derivative of weight % with respect to temperature (in blue) of the supraheterodimer**.** The mass loss was determined from 28-190°C (the upper temperature limit was taken after the fourth peak in the derivative of weight % with respect to temperature graph).

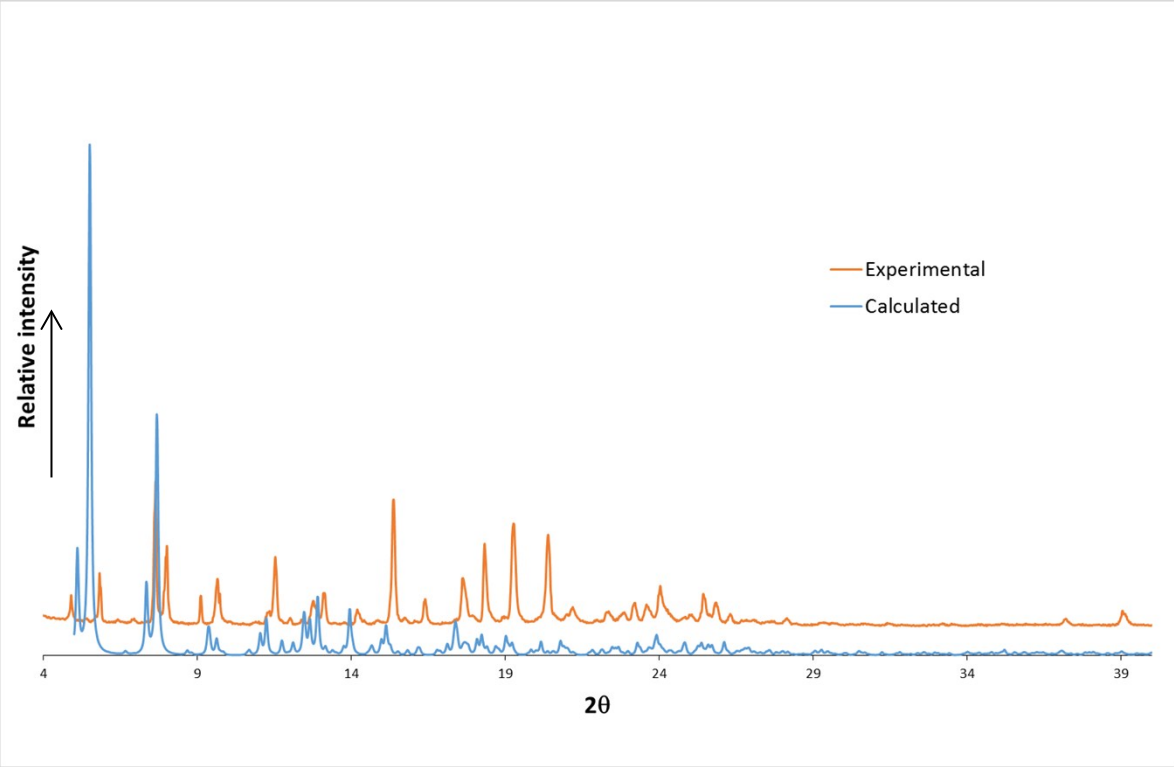


Figure S3. Calculated powder X-ray diffraction pattern of the supra-heterodimer from the single crystal structure (at 100 K) agrees well with the experimental powder X-ray diffraction pattern (298 K), except for a shift in 2θ attributed to the different temperatures of analyses.

Supporting information references

[1] Bruker(2007), **Bruker AXS Inc., Madison, Wisconsin USA**, *1*, 2007.

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[3] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

[4] L. J. Barbour, *Journal of Supramolecular Chemistry* **2001**, *1*, 189 <last_page> 191.

[5] *Persistence of Vision Raytracer Pty. Ltd.* **2004**, *3.6*.

[6] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *Journal of Applied Crystallography* **2008**, *41*, 466-470.