Electronic Supplementary Information

Exploring cooperative porosity in organic cage crystals using *in situ* diffraction and molecular simulations

Linjiang Chen,[a,b] Yu Che,[a,b] Andrew I. Cooper,[a,b] and Samantha Y. Chong*[a]

* Corresponding author
[a] Materials Innovation Factory and Department of Chemistry, University of Liverpool, 51 Oxford Street, Liverpool, L7 3NY, UK. E-mail: s.chong@liverpool.ac.uk
[b] Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory and Department of Chemistry, University of Liverpool, 51 Oxford Street, Liverpool, L7 3NY, UK.

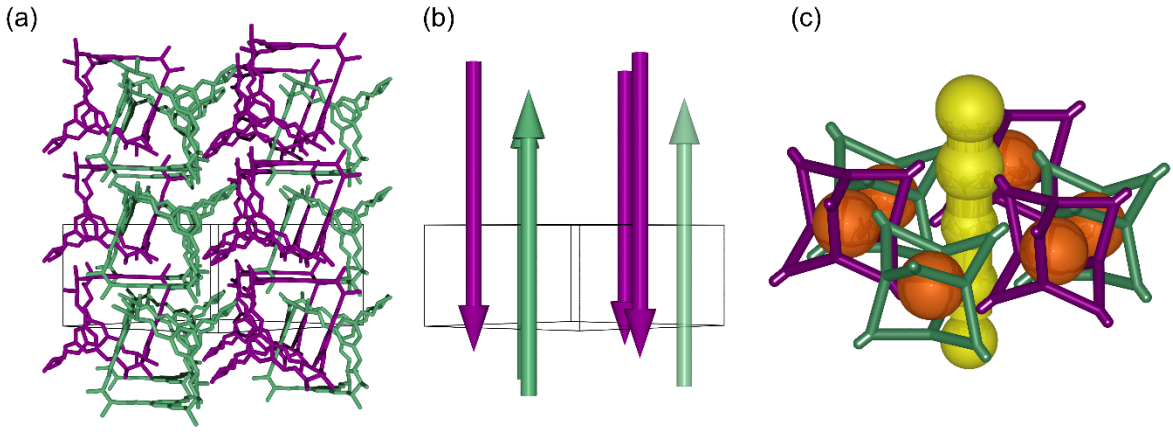

Figure S1. (a) Crystal structure of **α-CC2** viewed parallel to [110] (hydrogen atoms omitted for clarity). Cage molecules form stacks in which the cages are arranged window-to-arene. (b) The stacks form a hexagonal array in which adjacent stacks are offset and have the opposing orientation. (c) A 1-dimensional channel runs through the extrinsic space formed between the stacks of molecules. Methyl group protrude into the channel to form narrow 'necks', and the intrinsic cage pores are formally disconnected, based on a static crystal structure.

Table S1. Unit cell parameters and agreement factors for Le Bail refinement of the powder X-ray diffraction data collected under SF_6 atmosphere.

	SF_6 gas pressure / bar			
	Dynamic vacuum	**0.2**	**1.1**	**2.7**
***a*, *b*, *c* / Å**	18.8302(2), 19.0295(4), 10.9121(2)	18.8144(2), 19.0306(4), 10.9254(1)	18.8448(2), 19.0581(4), 10.9223(1)	18.9114(2), 19.1143(4), 10.9196(1)
***α*, *β*, *γ* / °**	90.222(2), 89.914(2), 119.952(1)	90.325(2) 89.830(2) 119.975(1)	90.255(1), 89.928(1), 119.935(1)	90.137(2), 89.996(1), 119.878(1)
***V* / Å^3**	3387.9(1)	3388.5(1)	3399.3(1)	3422.6(1)
R_{wp}, R_p / %	1.80, 1.19	1.11, 1.08	1.28, 1.10	1.16, 1.02
χ^2	3.74	6.12	3.09	2.61

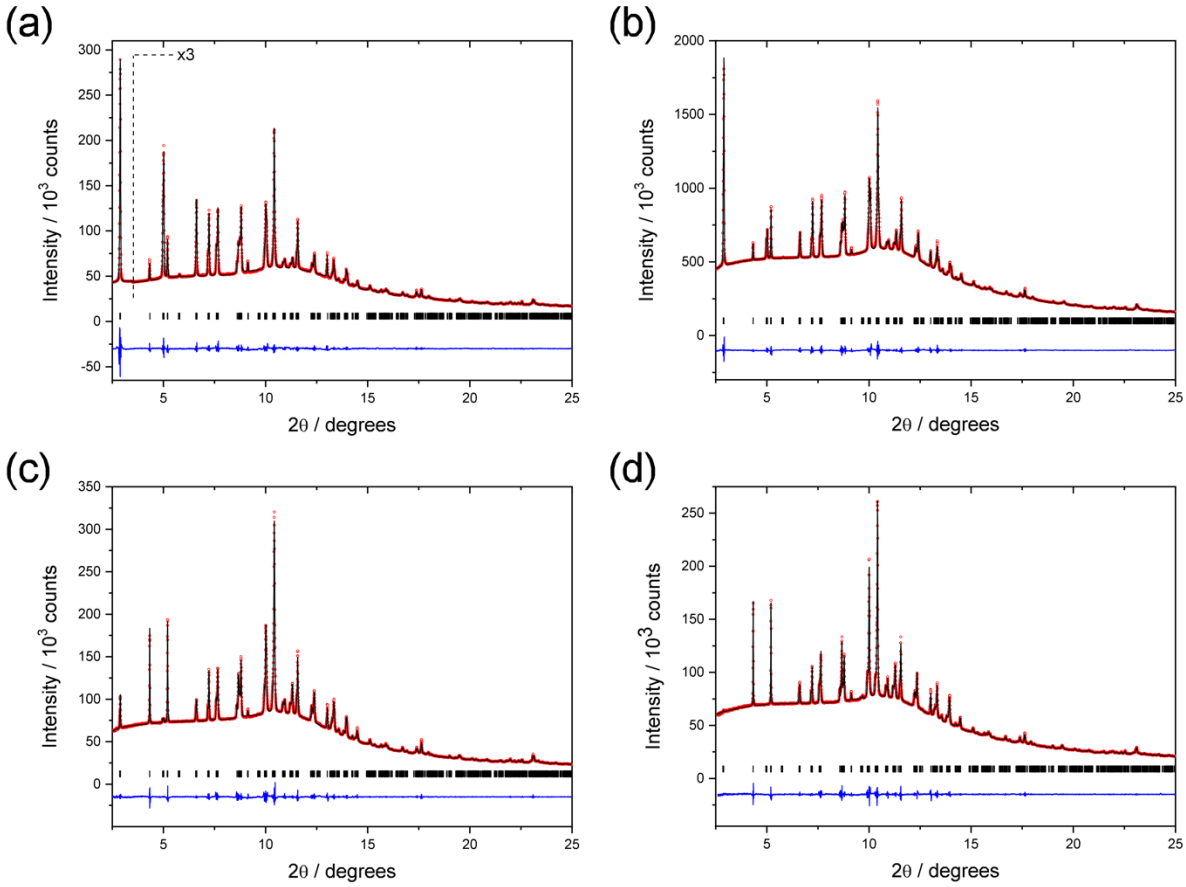

Figure S2. Final observed (red points), calculated (black line) and difference (blue line) profiles for Le Bail refinement of PXRD data collected in situ under (a) dynamic vacuum, (b) 0.2 bar, (c) 1.1 bar and (c) 2.7 bar SF_6 atmosphere. Reflections positions are marked below.

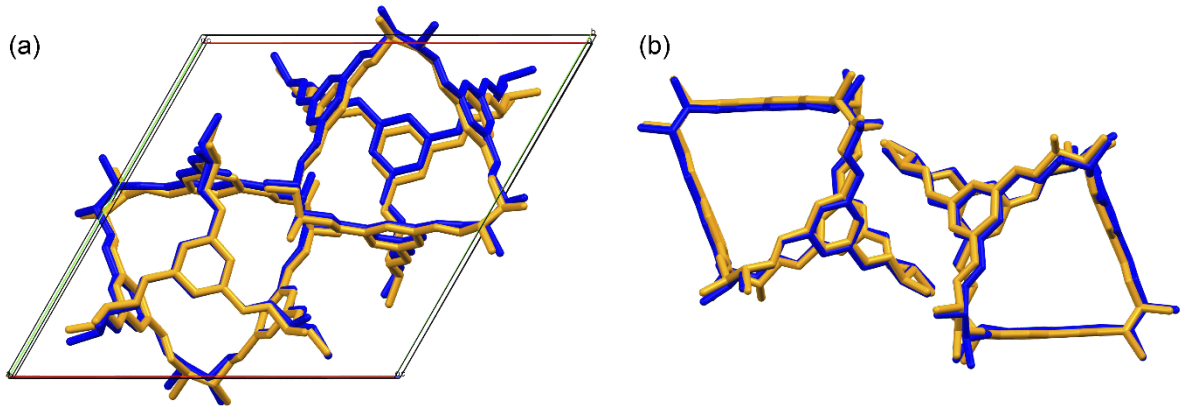

Figure S3. Comparison of the structure of **α-CC2** (orange) and the host cage framework in **CC2•**$(SF_6)_{1.93}$ (hydrogen atoms and SF_6 omitted for clarity) (a) viewed parallel to the [001] and (b) [110] directions.

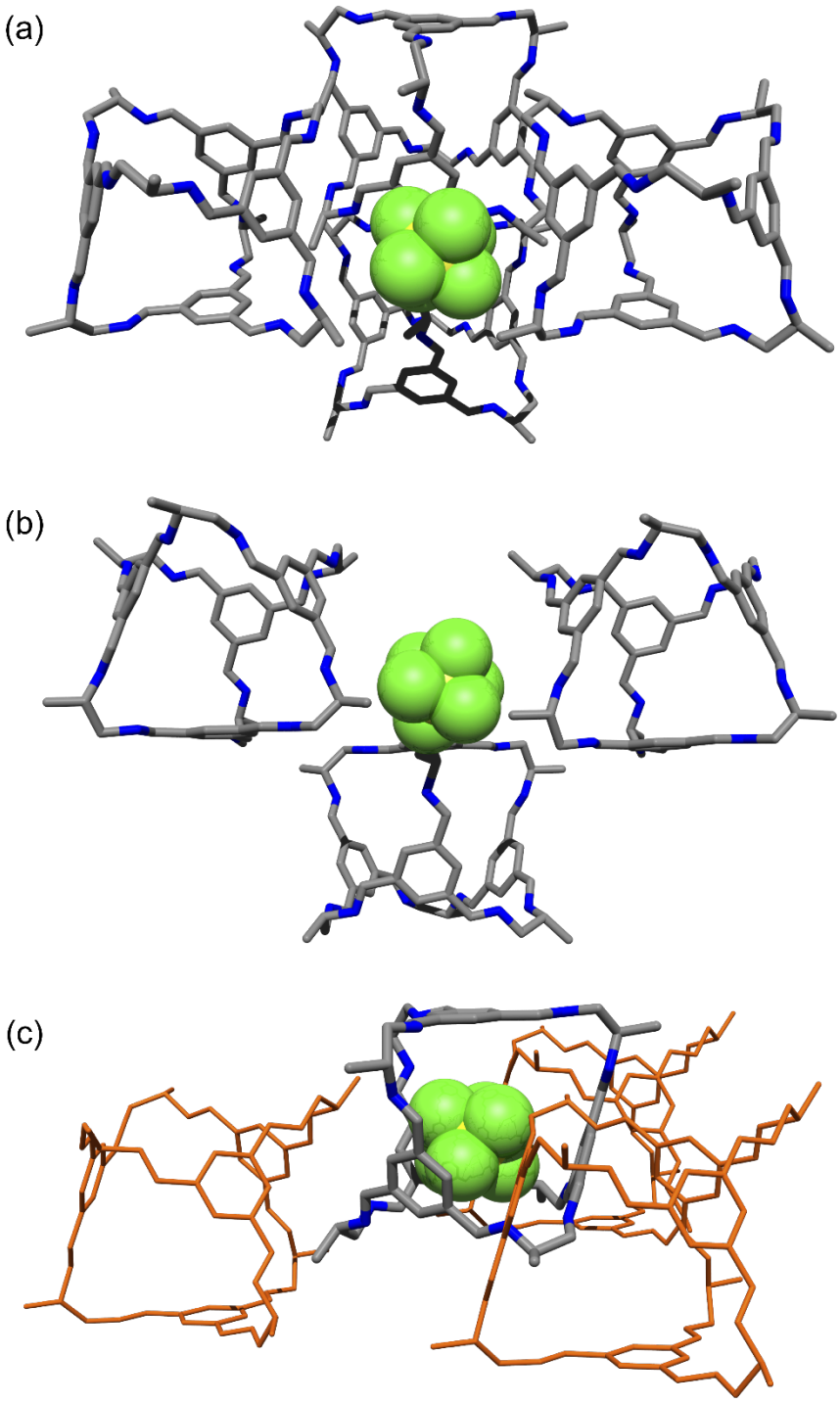

Figure S4. Refined positions of SF_6 guest in the **CC2**•$(SF_6)_{1.93}$ structure. Two sites in the connected pore channel are occupied; (a) the more highly occupied site (85(2) % occupancy) resides in the wider sections of the channel, whereas (b) the second channel (56(3) %) site is closer to the 'neck' formed by the presence of methyl groups. (c) Position of the SF6 molecule in the cage pore is located away from the centre due to the vertex groups of neighbouring cages entering the central cage window.