

## Oriented 2D Porous Organic Cage Crystals

Shan Jiang, Qilei Song,\* Alan Massey, Samantha Y. Chong, Linjiang Chen, Shijing Sun, Tom Hasell,\* Rasmita Raval, Easan Sivaniah, Anthony K. Cheetham, Andrew I. Cooper\*

**Abstract:** We report the formation of two-dimensional (2-D) oriented porous organic cage crystals on various substrates by solution-processing. Insight into the crystallinity, preferred orientation and cage crystal growth was obtained by experimental and computational techniques. For the first time, structural defects in porous molecular materials were observed directly and the defect concentration could be correlated with crystal growth rate. These oriented crystals suggest potential for future applications, such as solution-processable molecular crystalline 2-D membranes for molecular separations.

Porous molecular materials are attracting much interest because they can be rationally designed to achieve functions such as selectivity, processability, and stability.<sup>[1]</sup> For example, we have developed a series of porous organic cages (POCs), which can be used as synthetically-prefabricated 'molecular pores' for the construction of porous materials.<sup>[2]</sup> The synthetic versatility of POCs enables a wide range of functionality and tailored properties. The porosity of crystalline cage solids arises from both intrinsic pores within the molecules themselves and extrinsic pores between the cages. The packing of discrete cage molecules is dictated by weak van der Waals forces that give scope for dynamic motion, flexibility, and response to stimuli.<sup>[3]</sup> Also, unlike covalent organic frameworks (COFs), POCs are crystallized without any bond-forming reactions; hence, while single crystalline COFs are very rare,<sup>[4]</sup> it is relatively easy to grow high-quality single crystal POCs. POCs have been explored in various applications such as sensing,<sup>[5]</sup> gas storage,<sup>[2]</sup> molecular separations (e.g., xylene isomers,<sup>[6]</sup> noble gases<sup>[7]</sup> and chiral molecules<sup>[8]</sup>), and proton conductivity.<sup>[9]</sup> As discrete, soluble molecules, POCs can be processed in organic solvents in a way

that cannot be achieved with insoluble porous frameworks. For example, modular 'mix and match' assembly strategies have been used to form binary and ternary cocrystals,<sup>[10]</sup> and cage crystals can be incorporated into polymers to form composite membranes.<sup>[11]</sup>

The fabrication of functional materials into thin films, membranes, and oriented crystals on substrates is of importance for applications in sensors, catalysts, electronic devices, and electrodes for fuel cells.<sup>[12]</sup> Recently, amorphous cage thin films and membranes were fabricated on various substrates by spin coating.<sup>[13]</sup> Uniform and pinhole-free cage membranes were obtained and demonstrated molecular-sieving properties. However, it remains a significant challenge to control crystallinity, orientation, and surface nanostructures of cage thin films; for example, these amorphous spin-coated films showed dramatic ageing effects over time. As such, the preparation of crystalline POC films is a high-value target for applications such as gas separation. Various studies have been carried out on the assembly of well-organized 2D molecular systems, such as growth and alignment of organic semiconductor thin films.<sup>[14]</sup> Likewise, porous frameworks such as zeolites and metal organic frameworks (MOFs) have been fabricated into thin films and membranes.<sup>[15]</sup> However, there are fewer studies of crystalline *oriented* MOFs or zeolite films.<sup>[16]</sup> Most of the films are polycrystalline and well-controlled growth and orientation is challenging. Porous, thin film materials with high crystallinity and preferred orientation should present distinct adsorption, separation kinetics, and performance characteristics compared with bulk powders or amorphous films.

Orientation is not the only factor that affects guest diffusion in porous solids: defect engineering in porous frameworks has emerged as an active research field because defects can play a vital role in determining material performance such as sorption capacity, catalytic activity, stability, and mechanical strength.<sup>[17]</sup> However, our ability to characterize, understand, and control defects in porous solids is limited.<sup>[18]</sup> The presence of defects in MOFs may explain oft-noted discrepancies between properties derived from 'ideal' crystal structures and experimental measurements. POCs are interesting systems for investigating defects because, unlike MOFs and COFs, the synthesis and the crystallisation steps can be separated. The formation of defects such as point vacancies is thermodynamically unfavorable,<sup>[19]</sup> and it would be expected to be rare in molecular crystals. However, there is indirect evidence for the existence of defects in POCs;<sup>[20]</sup> for example, when cage molecules were crystallized both slowly and rapidly, the rapidly-crystallised sample exhibited substantially higher surface areas, despite both samples showing similar powder diffraction patterns.<sup>[21]</sup> Rapid crystallization would be expected to give crystals with more defects resulting in more extrinsic porosity and higher gas uptakes.<sup>[21a]</sup> It is challenging to characterize structural defects for bulk polycrystalline powders, and until now, defects have not been observed directly in POCs.

[a] Dr. S. Jiang, Dr. S. Y. Chong, Dr. L. Chen, Dr. T. Hasell, Prof. A. I. Cooper  
Department of Chemistry, Materials Innovation Factory  
University of Liverpool, Liverpool L69 7ZD, UK  
Email: T.Hasell@liverpool.ac.uk, aicooper@liverpool.ac.uk

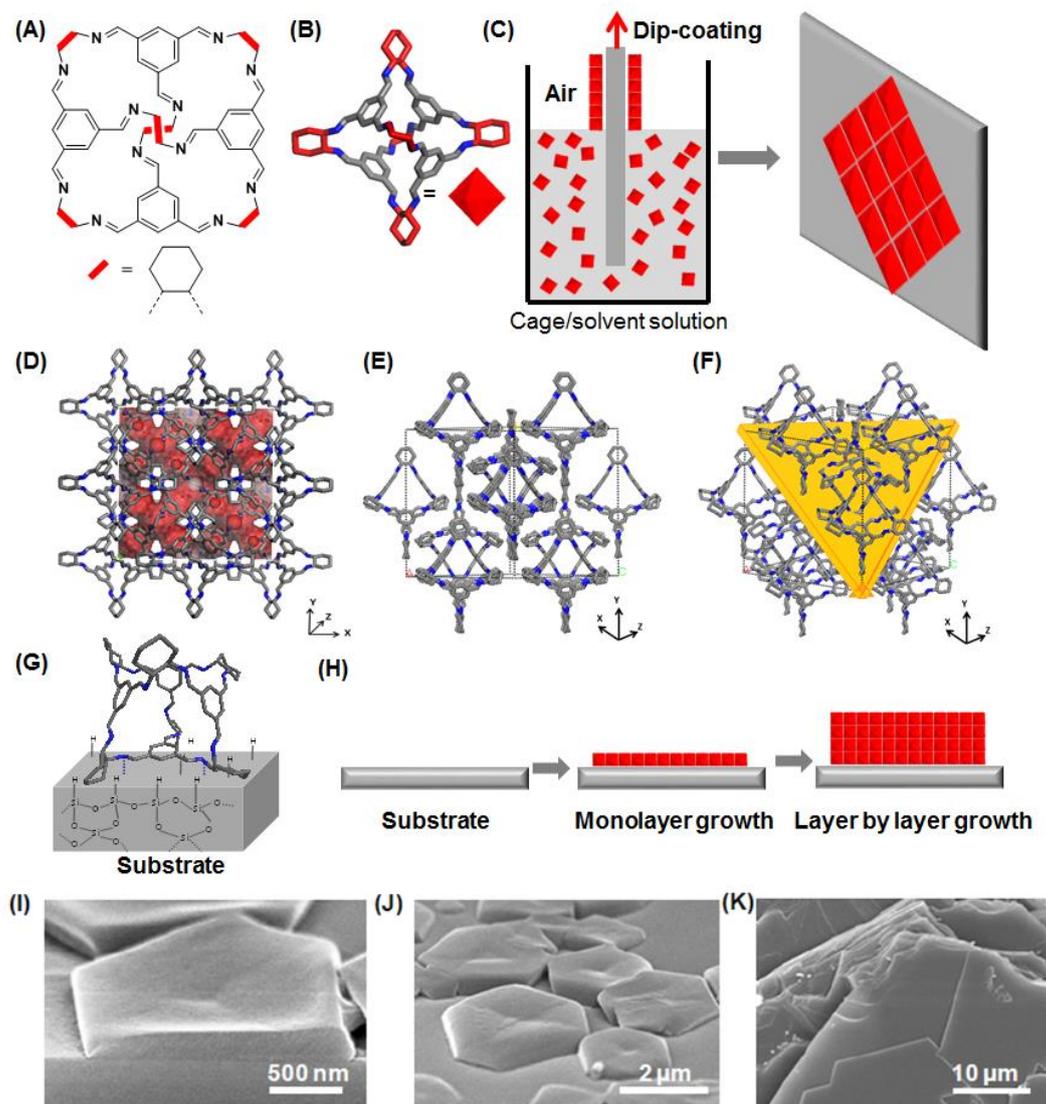
Dr. Q. Song  
Barrer Centre, Department of Chemical Engineering, Imperial  
College London, London SW7 2AZ, UK.  
Email: q.song@imperial.ac.uk

Dr. A. Massey, Prof. R. Raval  
Surface Science Research Centre, Department of Chemistry,  
University of Liverpool, L69 3BX, Liverpool, U.K.

S. Sun, Prof. A.K. Cheetham  
Department of Materials Science and Metallurgy, University of  
Cambridge, Cambridge, CB3 0FS, UK.

Prof. E. Sivaniah  
Institute for Integrated Cell-Material Sciences (iCeMS) Kyoto  
University Kyoto 606-8501, Japan

Supporting information for this article is given via a link at the end of the document.



**Figure 1.** (a) Molecular structure of **CC3**. (b) 3D structure of **CC3** showing tetrahedral symmetry. (c) Scheme illustrating controlled dip coating of **CC3** on a substrate to form oriented layers. (d) Crystal structure of **CC3** with a Connolly surface in red viewed along the Y axis. (e) Crystal structure of **CC3** along XZ orientation. (f) (111) plane in **CC3** crystal structure, displayed in yellow. (g) Noncovalent intermolecular interaction between the cage molecule and silicon wafer substrate. (h) Scheme showing layer by layer growth of cage molecules on substrate. (i) Cross-sectional SEM view of one oriented cage **CC3** crystal on silicon wafer substrate. (j) SEM image for oriented **CC3** crystals grown on a silicon wafer. (k) Cross-sectional SEM image of a bulk oriented **CC3** crystal showing multiple layers of molecular cage sheets.

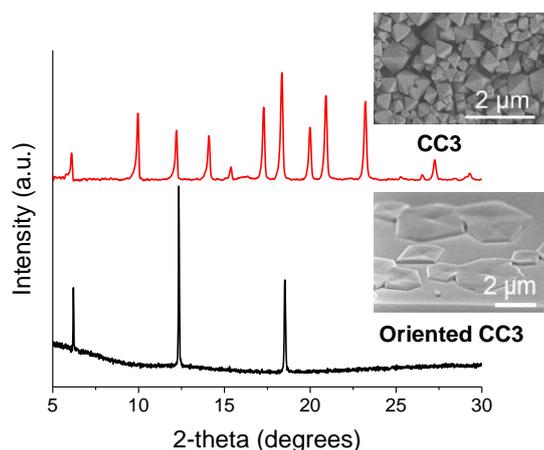
In this study, we report the oriented assembly of POC crystals on surfaces such as silicon wafers and glass substrates. Cage crystals were grown as 2D hexagonal layers, aligned in parallel with the substrate. This new morphology was fabricated by the simple technique of dip coating. Local point defects were directly observed, for the first time, using atomic-force microscopy (AFM). A 'perfect' aligned cage crystal was obtained using a slow crystallization process, while molecular vacancies were formed by rapid removal of the solvents. The concentration of defects was also found to be related to the crystal growth rate.

**CC3** was synthesized as described previously.<sup>[2]</sup> This cage molecule has tetrahedral symmetry with an internal void and four open triangular windows (Figure 1a-b). The crystal structure, **CC3 $\alpha$** , shows a window-to-window packing motif, leading to an

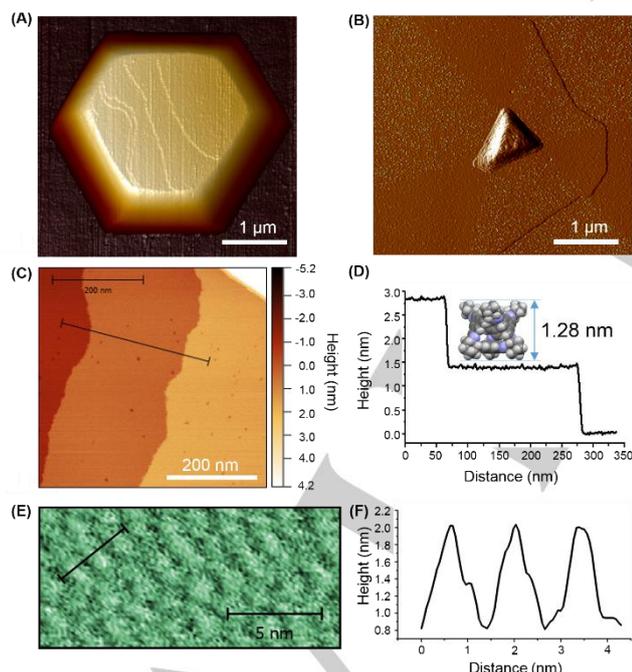
interconnected 3-dimensional (3D) pore channel, as shown in Figure 1d-f.<sup>[22]</sup> The Brunauer-Emmett-Teller (BET) surface area of **CC3 $\alpha$**  is 409 m<sup>2</sup> g<sup>-1</sup> when formed as a highly crystalline solid.<sup>[21a]</sup>

We developed a simple and efficient method to create oriented **CC3** structures on substrates by dip coating. As illustrated in Figure 1c and Figure S1, the substrate was immersed into a solution of **CC3** in chloroform or dichloromethane for an appropriate period of time to grow oriented seed crystals. By pulling the substrate upward at a constant speed, oriented cage crystals were formed on the substrate upon solvent evaporation. The cage molecules preferentially nucleate and adhere to the surface of the substrate via van der Waals interactions, and are subsequently assembled into aligned crystalline layers or films (Figure 1g and h).

Scanning electron microscopy (SEM) images revealed that cage molecules formed hexagonal shaped crystals on the surface of silicon wafer (Figure 1i and j), in contrast to the octahedral morphology of bulk **CC3** crystals (Figure 2, insets; Figure S2). The diameter of the hexagonal shaped crystals was 3–5  $\mu\text{m}$  with an average thickness of  $\sim 200$  nm, and these microcrystals were formed discontinuously on the substrate (that is, the substrate was not fully covered; Figure S3). These hexagonal cage crystals could also be fabricated on other substrates such as glass and carbon TEM grids (Figure S4-5).



**Figure 2.** PXRD patterns of bulk 3D **CC3** crystals (upper) and oriented 2D **CC3** crystals grown on silicon wafer (lower). SEM images show octahedral crystals for bulk **CC3** and hexagonal shaped crystals of oriented **CC3**.



**Figure 3.** AFM analyses of surfaces of oriented cage crystals. (a) AFM image of defect-free oriented cage crystal on silicon wafer. (b) AFM PeakForce error image of a quickly-grown oriented **CC3** crystal showing the segments of the hexagonal crystal (c-d) Line scan of individual terrace steps (from Figure 3b) on top of the crystals showing a step height of  $1.41 \pm 0.18$  nm, space-filling model of **CC3** shown to scale of the Y-axis. (e) AFM topographic images of well-grown oriented cage **CC3** crystal (f) Height profile along the pathway as shown in the image of (e).

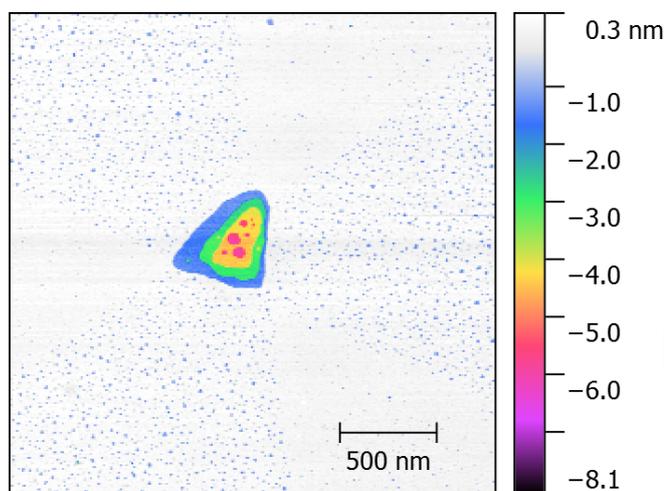
The crystallinity and preferred orientation of these aligned **CC3** crystals were further characterized by powder X-ray diffraction (PXRD). The PXRD patterns of oriented **CC3** crystals fabricated on the surface of silicon wafer show that they possess cubic  $F4_32$  symmetry with  $a = 25.4$   $\text{\AA}$ , in good agreement with bulk **CC3** crystals (Figure 2, S7). Only three diffraction peaks are observed for the surface deposited **CC3** crystals, indicating the oriented nature of the materials. The peaks can be indexed as (111), (222) and (333). Therefore, **CC3** cage molecules were grown in the (111) direction on silicon wafer surface. The cage packing along (111) orientation is illustrated in Figure S8. AFM was also used to characterize these oriented crystals. Figure 3a shows the AFM image of an entire hexagonal shape cage crystal grown on a silicon wafer substrate. Figure 3c and d shows the individual terraces on top of the cage crystals. The height of these terraces is measured as  $1.41 \pm 0.18$  nm, which agrees well with the size of cage molecule as measured from the single crystal structure. A topographic study of oriented **CC3** crystals is shown in Figure 3e showing the cage packing structure on the crystal surface. The height profile showed that the cage molecules have an intermolecular spacing of  $1.41 \pm 0.18$  nm (Figure 3f). Both PXRD analysis and AFM images suggest that the cage molecules are assembled by a layer-by-layer growth mechanism with preferential (111) orientation.

Precise control of the dip-coating method (see ESI) allowed us to adjust the nanostructure of the crystals to produce either near-perfect crystals with very few defects or crystals with a high number of vacancy-defects. AFM showed that the local morphology was affected by the growth conditions. High resolution AFM deflection imaging of a slowly-crystallized sample showed a flat, hexagonal shape and defect free crystal surfaces (Figure 3a and Figure S9). We also prepared quickly grown oriented **CC3** crystals. AFM images revealed a hexagonal crystal with a triangular nucleation point in the center (Figure 3b and Figure S10) surrounded by six segments relating to the hexagonal packing of cages in the crystal structure. Molecular vacancies were observed on the surface of the crystal, as shown in Figure 3b and Figure 4. The defects on the crystal surface are localized within three of the six segments (Figure 3b, and Figure 4), producing an alternating pattern of high and low defect concentration. More AFM images of other quickly grown **CC3** crystals also show a similar pattern and a large number of vacancy-defects (Figure S11-12). This pattern is related to the growth of the segments and the crystallographic directions (Figure S13). The segments of the crystal formed at the apex of the central triangular defect have 2% surface vacancies while the segments formed at the edges of the triangle have 10–12% surface vacancies. Initial formation of a triangular {111} face by growth of the crystal parallel to the surface, followed by propagation from the vertices (parallel to  $\langle 100 \rangle$ ) and edges (along  $\langle 110 \rangle$ ) would account for the observed crystal shape. Differences in vacancies i.e. 'missing cages', and void defect concentrations between the sectors can be related to edge vs. point growth, with the probability of imperfections higher for growth from the edge, due to the larger area of the growth front and potential differences in the both the intermolecular interactions presented by the cages in this direction. The size of the defects ranges from individual molecular vacancies up to 27.5

## COMMUNICATION

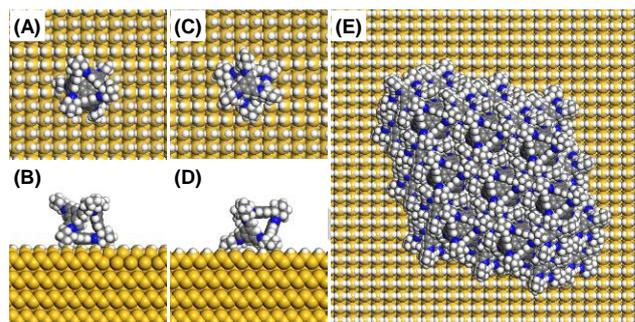
nm multiple vacancy pores, which indicates that multiple cage molecules are absent during the rapid crystal growth. In addition, Figs. 3b and S10 show that the defects are not just present at the surface. The formation of a new layer of cage molecules growing on top of the crystal surface with defects beneath it suggests that additional pore-volume due to defects is retained in the subsurface crystal structure. This is the first direct evidence for the existence of vacancy-defects, which have been invoked previously to explain the properties of porous molecular materials.<sup>[20-21]</sup> This explains our observation, for example, that rapidly crystallized bulk **CC3** has significantly higher surface area than slowly crystallized **CC3**.

The ability to control and to quantify vacancies as a direct function of crystallization rate demonstrates a viable 'defect engineering' strategy for POCs via controlled solution processing.



**Figure 4.** An AFM image showing the central triangular defect of a cage crystal which was grown with defects (2.5 x 2.5 micron scan). The individual layers of the crystal can be seen, the top layer is white, 2<sup>nd</sup> Blue, 3<sup>rd</sup> green 4<sup>th</sup> yellow and the bottom layer is magenta. The 3 hyperporous areas show an increase in blue speckled areas corresponding to molecule vacancies in the top surface layer.

We also tried to grow oriented cage films on glass substrates. Microscopy showed large hexagonal crystals grown continuously on the glass surface (Figure S14), suggesting potential for forming conformal porous crystalline coatings. The key to successful growth of these uniformly oriented large crystals was appropriate solvent evaporation conditions. The resultant bulk oriented crystals exhibited multiple cage layers (Figure 1k and S14). PXRD shows three main peaks at  $2\theta = 6.2^\circ$  (111),  $12.4^\circ$  (222) and  $18.6^\circ$  (333) (Figure S15), indicating that oriented growth on glass occurs parallel to the (111) crystal planes, as for the silicon surface. After the oriented crystals were ground to fine powders, the PXRD was fully consistent with the known **CC3** crystal structure<sup>[2]</sup> (Figure S16). Hence, the oriented **CC3** crystals pack window-to-window, but grow in a preferentially oriented manner. In addition, a multiple dip-coating process was carried out to promote secondary growth of oriented cage crystals. After more than 100 cycles of dip coating, the substrate was densely covered by discrete hexagonal crystals with a surface coverage of up to 85%, although the orientation was lost on the uppermost layers (Figure S17).



**Figure 5.** Atomistic models of cage molecules on the surface of silicon (100) wafer. A single cage molecule can sit on the silicon surface with a cage arene face (a, b; two viewing directions) or a cage window (c, d) attached to the surface. (e) Structural model of oriented cage crystals. The cage molecules are assembled in a window to window packing arrangement with a preferred orientation as refined from PXRD.

Simulations were used to generate representative structural models of the interactions between **CC3** and the silicon surface. There are two possible geometries for the growth of oriented cage crystals on silicon, with either the cage window or cage arene face attached to the surface. The atomistic model for each of these cases (Figure 5 a-d) was geometry-optimized at the PBE-D3 level of theory, using the CP2K package.<sup>[23]</sup> Surface binding energies derived from these models showed that the cage arene interacts with the silicon wafer more strongly by  $16.1 \text{ kJ mol}^{-1}$ . The structural model of oriented cage crystals (Figure 5e) was constructed from a starting model based on the reported crystal structure of **CC3a**, with 2D layers of cage molecules grown in the (111) direction.

In summary, this study demonstrates the controlled surface growth of aligned cage crystals for the first time. Cage molecules can be grown in a preferentially oriented manner on several substrates. A structural model was generated to represent the cage packing motifs on a silicon substrate. The dip coating approach is a simple and efficient way to fabricate porous molecular materials into thin films with control over defect concentration. This is the first time that defects have been observed directly in crystalline POCs, and the defect concentration can be correlated with the crystallization rate. These results suggest new opportunities for these molecular cage materials; for example, large coherent crystalline POCs thin films might be useful for molecular-sieving, allowing the excellent potential that has been demonstrated for bulk POCs,<sup>[7, 24]</sup> to be transferred into more practicable and scalable membrane technologies.

## Experimental Section

**CC3 synthesis:** 100 ml dichloromethane (DCM) was added into 1, 3, 5-triformylbenzene (1.0 g, 6.2 mmol). A solution of (1R, 2R)-1, 2-diaminocyclohexane (1.1 g, 9.3 mmol) in 100 ml DCM was added. The mixed solution was covered and left at the room temperature for 5 days. The crystalline product was obtained by solvent evaporation and washed with 95% MeOH/5% DCM. Yield: 85%.

**Fabrication of oriented cage crystals by dip coating:** CC3 was dissolved in chloroform (CHCl<sub>3</sub>) with a concentration of 5 mg/ml. Dip coating was performed on silicon wafer (100) substrate. A program has been set up as follows to prepare perfect 2D aligned cage crystals: the substrate (approximately 1 cm x 3 cm) was immersed into the cage solution at a constant dipping speed of 2 mm/min followed by a dwell time of 15 min. The substrate was then pulled upward at a constant withdrawal speed of 2 mm/min followed by a drying time of 15 min in air. The travel distance when pulling up or down was 25 mm. 20 dip-coating cycles were carried out for this sample in order to achieve good surface coverage.

For the 2D aligned cage crystals with defects: the substrate (approximately 1 cm x 3 cm) was immersed into the cage solution at a constant dipping speed of 100 mm/min followed by a dwell time of 15 min. The substrate was then pulled upward at a constant withdrawal speed of 100 mm/min followed by a drying time of 15 min in air. The travel distance when pulling up or down was 25 mm. The substrate was dipped with 20 cycles.

**Growth of large oriented cage crystals:** 60 mg CC3 was dissolved in co-solvent of 2 ml DCM and 0.1 ml MeOH. The cage solution was kept in the glass vial and left for a slow solvent evaporation. Hexagonal shaped crystals were grown on the internal surface of glass vial after 30 days as shown in Figure S14 (a-b).

## Acknowledgements

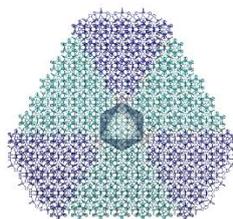
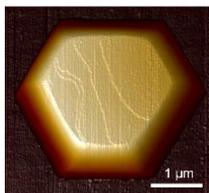
We acknowledge EPSRC (grants EP/N004884/1, and EP/M01486X/1) for funding. This work made use of the facilities of N8 HPC Centre of Excellence, provided and funded by the N8 consortium, and the ARCHER UK National Supercomputing Service via an EPSRC Programme Grant (EP/N004884). Q.S. acknowledges the financial support from Department of Chemical Engineering at Imperial College London. Tom Hasell holds a Royal Society URF.

**Keywords:** Porous organic cages • oriented molecular crystals • crystal defects

- [1] (a) A. G. Slater, A. I. Cooper, *Science* **2015**, *348*; (b) N. B. McKeown, *J. Mater. Chem.* **2010**, *20*, 10588-10597; (c) G. Zhang, M. Mastalerz, *Chem. Soc. Rev.* **2014**, *43*, 1934-1947.
- [2] T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacska, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973-978.
- [3] D. Holden, S. Y. Chong, L. Chen, K. E. Jelfs, T. Hasell, A. I. Cooper, *Chem. Sci.* **2016**, *7*, 4875-4879.
- [4] (a) Y.-B. Zhang, J. Su, H. Furukawa, Y. Yun, F. Gándara, A. Duong, X. Zou, O. M. Yaghi, *J. Am. Chem. Soc.* **2013**, *135*, 16336-16339; (b) D. Beaudoin, T. Maris, J. D. Wuest, *Nat. Chem.* **2013**, *5*, 830-834.
- [5] M. Brutschy, M. W. Schneider, M. Mastalerz, S. R. Waldvogel, *Adv. Mater.* **2012**, *24*, 6049-6052.
- [6] T. Mitra, K. E. Jelfs, M. Schmidtman, A. Ahmed, S. Y. Chong, D. J. Adams, A. I. Cooper, *Nat. Chem.* **2013**, *5*, 276-281.
- [7] L. Chen, P. S. Reiss, S. Y. Chong, D. Holden, K. E. Jelfs, T. Hasell, M. A. Little, A. Kewley, M. E. Briggs, A. Stephenson, K. M. Thomas, J. A. Armstrong, J. Bell, J. Busto, R. Noel, J. Liu, D. M. Strachan, P. K. Thallapally, A. I. Cooper, *Nat. Mater.* **2014**, *13*, 954-960.
- [8] J.-H. Zhang, S.-M. Xie, L. Chen, B.-J. Wang, P.-G. He, L.-M. Yuan, *Anal. Chem.* **2015**, *87*, 7817-7824.
- [9] M. Liu, L. Chen, S. Lewis, S. Y. Chong, M. A. Little, T. Hasell, I. M. Aldous, C. M. Brown, M. W. Smith, C. A. Morrison, L. J. Hardwick, A. I. Cooper, *Nat. Commun.* **2016**, *7*, 12750.
- [10] T. Hasell, S. Y. Chong, M. Schmidtman, D. J. Adams, A. I. Cooper, *Angew. Chem. Int. Ed.* **2012**, *51*, 7154-7157.
- [11] (a) A. F. Bushell, P. M. Budd, M. P. Atfield, J. T. A. Jones, T. Hasell, A. I. Cooper, P. Bernardo, F. Bazzarelli, G. Clarizia, J. C. Jansen, *Angew. Chem. Int. Ed.* **2013**, *52*, 1253-1256; (b) J. D. Evans, D. M. Huang, M. R. Hill, C. J. Sumby, A. W. Thornton, C. J. Doonan, *J. Phys. Chem. C* **2014**, *118*, 1523-1529.
- [12] O. Shekha, J. Liu, R. A. Fischer, C. Woll, *Chem. Soc. Rev.* **2011**, *40*, 1081-1106.
- [13] Q. Song, S. Jiang, T. Hasell, M. Liu, S. Sun, A. K. Cheetham, E. Sivaniah, A. I. Cooper, *Adv. Mater.* **2016**, *28*, 2629-2637.
- [14] A. A. Virkar, S. Mannsfeld, Z. Bao, N. Stingelin, *Adv. Mater.* **2010**, *22*, 3857-3875.
- [15] (a) J.-L. Zhuang, A. Terfort, C. Wöll, *Coord. Chem. Rev.* **2016**, *307*, 391-424; (b) D. Zacher, A. Baunemann, S. Hermes, R. A. Fischer, *J. Mater. Chem.* **2007**, *17*, 2785-2792.
- [16] (a) R. Makiura, S. Motoyama, Y. Umemura, H. Yamanaka, O. Sakata, H. Kitagawa, *Nat. Mater.* **2010**, *9*, 565-571; (b) T. C. T. Pham, H. S. Kim, K. B. Yoon, *Science* **2011**, *334*, 1533-1538; (c) Z. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis, D. G. Vlachos, *Science* **2003**, *300*, 456-460; (d) J. Choi, S. Ghosh, Z. Lai, M. Tsapatsis, *Angew. Chem. Int. Ed.* **2006**, *45*, 1154-1158; (e) P. Falcaro, K. Okada, T. Hara, K. Ikigaki, Y. Tokudome, A. W. Thornton, A. J. Hill, T. Williams, C. Doonan, M. Takahashi, *Nat. Mater.* **2017**, *16*, 342-348.
- [17] (a) D. S. Sholl, R. P. Lively, *J. Phys. Chem. Lett.* **2015**, *6*, 3437-3444; (b) Z. Fang, B. Bueken, D. E. De Vos, R. A. Fischer, *Angew. Chem. Int. Ed.* **2015**, *54*, 7234-7254; (c) A. K. Cheetham, T. D. Bennett, F.-X. Coudert, A. L. Goodwin, *Dalton Trans.* **2016**, *45*, 4113-4126; (d) H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim, W. Zhou, *J. Am. Chem. Soc.* **2013**, *135*, 10525-10532; (e) T. D. Bennett, A. K. Cheetham, A. H. Fuchs, F.-X. Coudert, *Nat. Chem.* **2017**, *9*, 11-16.
- [18] M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert, A. L. Goodwin, *Nat. Commun.* **2014**, *5*, 4176.
- [19] J. D. Wright, *Molecular Crystals*, Cambridge University Press, Cambridge, 1995.
- [20] T. P. Money Penny, N. P. Walter, Z. Cai, Y.-R. Miao, D. L. Gray, J. J. Hinman, S. Lee, Y. Zhang, J. S. Moore, *J. Am. Chem. Soc.* **2017**, *139*, 3259-3264.
- [21] (a) T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* **2012**, *134*, 588-598; (b) T. Hasell, J. L. Culshaw, S. Y. Chong, M. Schmidtman, M. A. Little, K. E. Jelfs, E. O. Pyzer-Knapp, H. Shepherd, D. J. Adams, G. M. Day, A. I. Cooper, *J. Am. Chem. Soc.* **2014**, *136*, 1438-1448.
- [22] J. T. A. Jones, T. Hasell, X. Wu, J. Bacska, K. E. Jelfs, M. Schmidtman, S. Y. Chong, D. J. Adams, A. Trewin, F. Schiffman, F. Cora, B. Slater, A. Steiner, G. M. Day, A. I. Cooper, *Nature* **2011**, *474*, 367-371.
- [23] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comput. Phys. Commun.* **2005**, *167*, 103-128.
- [24] (a) M. Mastalerz, M. W. Schneider, I. M. Opper, O. Presly, *Angew. Chem. Int. Ed.* **2011**, *50*, 1046-1051; (b) H. Ding, Y. Yang, B. Li, F. Pan, G. Zhu, M. Zeller, D. Yuan, C. Wang, *Chem. Commun.* **2015**, *51*, 1976-1979; (c) Y. Jin, B. A. Voss, A. Jin, H. Long, R. D. Noble, W. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 6650-6658; (d) T. Hasell, M. Miklitz, A. Stephenson, M. A. Little, S. Y. Chong, R. Clowes, L. Chen, D. Holden, G. A. Tribello, K. E. Jelfs, A. I. Cooper, *J. Am. Chem. Soc.* **2016**, *138*, 1653-1659.

## COMMUNICATION

Oriented 2D porous organic cage crystals have been fabricated on various substrates with a new hexagonal shaped morphology. The controlled cage crystal growth, alignment, and molecular defects have been discovered and investigated for the first time.



*Shan Jiang, Qilei Song,\* Alan Massey, Samantha Y. Chong, Linjiang Chen, Shijing Sun, Tom Hasell,\* Rasmita Raval, Easan Sivaniah, Anthony K. Cheetham, Andrew I. Cooper\**

**Oriented 2D Porous Organic Cage Crystals**

WILEY-VCH