# Giant molecular spoked wheels in giant voids: two-dimensional molecular self-assembly goes big†

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**We present here the formation of giant pores in surface-confined molecular networks of a triangular-shaped dehydrobenzo-[12]annulene derivative: the diameter of the pores reaches over 7 nm and the giant pores are used as templates to accommodate a giant molecular spoked wheel, which allows us to observe rotational and adsorption–desorption dynamics of single guest molecules.**

Engineering of nanometre-scale two-dimensional (2D) molecular architectures, so-called 2D molecular networks, by surface-confined self-assembly receives considerable attention due to its relevance in nanotechnology.[1] This approach turns out to be successful not only at the level of monolayer formation of the molecular building blocks themselves[2] but also by 2D host–guest chemistry *via* binding events between the supramolecular template layer and guest molecules.[3] In the latter case the guest molecules could be "isolated", therefore favoring single molecule studies.[4]

Despite these successes, it is challenging to control 2D molecular self-assembly with a targeted periodicity around 10 nm by using large molecular building blocks.[5–7] Non-balanced intermolecular and too strong molecule–substrate interactions may lead to disordered patterns,[8] or multilayer formation.[9] In addition, the formation of supramolecular networks with giant pores is thermodynamically unfavored because of the low surface coverage of the molecular networks. As a method to overcome this obstacle, we have shown that it was possible to form a porous molecular network with giant voids of diameter up to 5.4 nm based on the self-assembly of icosyloxy ($OC_{20}H_{41}$) substituted dehydrobenzo[12]annulene (DBA) **1** (Fig. 1a) by high dilution of the adsorbate concentration.[10c] However, the upper size limit of such voids, *i.e.* pores on the graphite surface, has not been explored yet. Moreover the giant pores can be used as a template to accommodate a rigid molecular spoked wheel based on phenylene–ethynylene subunits with a diameter of *ca.* 7 nm as a guest.[11]

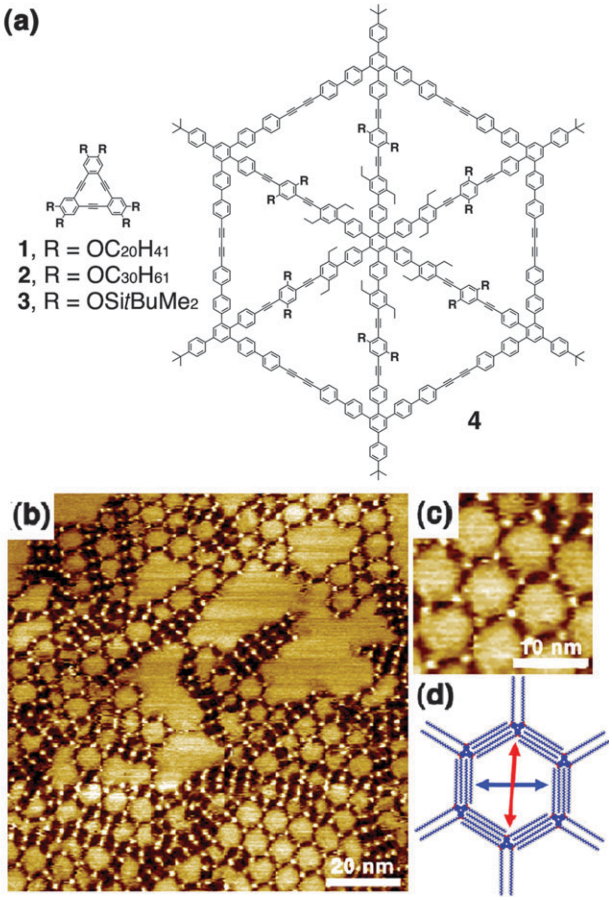

**Fig. 1** (a) Molecular structures of DBAs **1**, **2** and **3** and molecular spoked wheel **4** ($R = OC_{13}H_{33}$). (b, c) STM images of the self-assembly of **2** at the TCB–graphite interface ($I_{set}$ = 46 pA, $V_{bias}$ = −0.60 V). (d) Tentative network model of the honeycomb arrangement of **2**. The red and blue arrows indicate the corner to corner distance (7.5 nm) and edge to edge distance (7.0 nm), respectively.

The choice of alkylated DBA derivatives as building blocks for a host matrix is motivated by their proven performance in forming porous honeycomb networks with size-tunable hexagonal voids. Under proper concentration conditions the size of

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the voids is defined by the alkyl chain length.[10b,c] In this context, we designed DBA **2** with triacontyloxy chains ($OC_{30}H_{61}$, the alkyl chain length is 3.9 nm) in order to trap individual molecular wheel molecules **4**. Modeling studies predict that DBA **2** could form a honeycomb pattern with a periodicity of 8.4 nm and voids reaching a diameter of more than 7 nm. (7.5 nm corner-to-corner, 7.0 nm edge-to-edge, Fig. 1d). Such voids should be ideal to trap the molecular wheel **4**, given the size and shape complementarity. Our synthetic approach to DBA **2** is to introduce the substituents after the construction of the DBA π-core to avoid synthetic obstacles (See ESI†). For this purpose, *tert*-butyldimethylsilyl-protected hexahydroxy-DBA **3** was synthesized as a precursor of **2**. The six-fold alkylation reaction between anions generated *in situ* by treating CsF with **3**, and 1-bromotriacontane gave **2** in 48% yield.[12]‡

Scanning tunnelling microscopy (STM) observations of physisorbed self-assembled monolayers formed by DBA **2** at the 1,2,4-trichlorobenzene (TCB)–graphite interface show that non-porous structures are favored (Fig. S1 in ESI†) except for the lowest concentrations probed ($5.0 \times 10^{-6}$ mol $L^{-1}$), where DBA **2** shows a porous honeycomb network. The bright spots correspond to the conjugated core of the DBAs and the darker features connecting them are attributed to the interdigitated alkyl chains (Fig. 1b and c).[10,13] The featureless hexagonal bright regions with a size of about 7 nm correspond to the empty pores of the 2D network. In addition, broader dark stripes correspond to the densely packed linear structure of DBA **2**. Exclusive 2D porous network formation was not achieved, thereby revealing the size limit of the voids that can be constructed at the liquid–solid interface based on interdigitation of the alkoxy groups of DBAs.

In a next step, the 2D host–guest properties of this template layer *versus* the targeted molecular wheel guest **4** were investigated. Upon dropcasting a mixture of **2** and **4** in a 10 : 1 molar ratio in TCB on graphite, in some voids seven bright spots were observed (Fig. 2a and b: blue arrows). These bright spots are attributed to the phenylene parts in the molecular center and the six corners of the spoked wheel guest **4**, which is in line with its size and symmetry. The images of the wheel inside the voids correspond well with the images of the bare molecular wheel on graphite.[11] Note that the bright spots at the rim—the phenylene parts—appear to point to the corners of the pore. This agrees with the predictions of the molecular model (Fig. 2c) and is a result of the shape and size complementarity between the pore and the guest. In addition to empty voids, interestingly, some of the voids also appear bright though lacking any clear feature, as indicated by the red arrows in Fig. 2a and S2 (See ESI†). We attribute this particular (lack of) contrast to the (rotational) mobility of the spoked wheel **4** within these flexible voids.[10d,4] The 2D porous template clearly affects the corrugation of the surface. Only upon its formation, isolated molecular spoked wheels and also their rotational dynamics can be visualized. Despite its size, the interaction with the graphite substrate is weak and at the liquid–solid interface, isolated single molecules are mobile without the template. This is also confirmed by time-dependent experiments indicating desorption–adsorption events of the wheel molecules (Fig. S3 in ESI†). At present we attribute this to the fact that the molecular wheel contains also alkyl chains at its spokes which weaken the adsorption strength. Note that smaller guest molecules were not immobilized in the voids, nor was the spoked wheel **4** hosted in voids formed by DBA **1**.

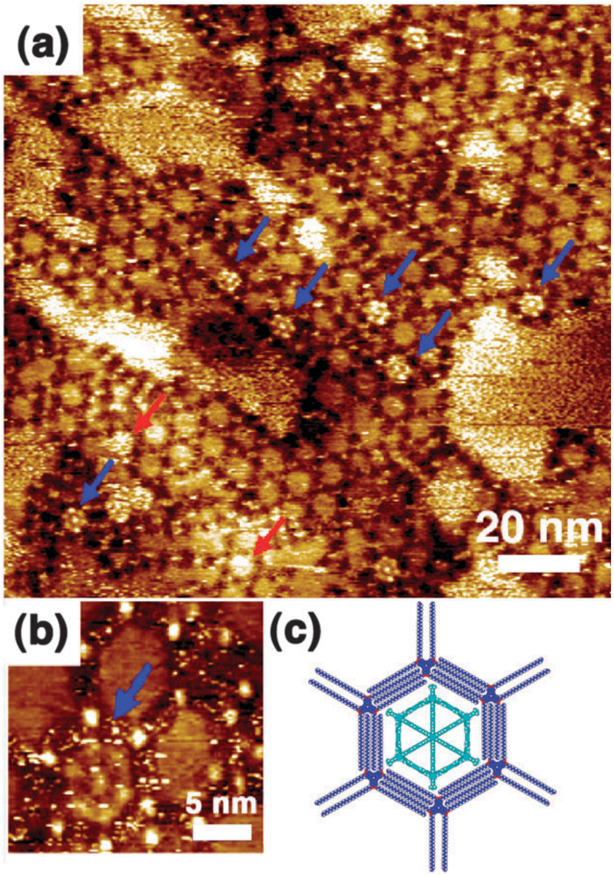

**Fig. 2** (a, b) STM images of the assembly of a mixture of DBA **2** and molecular spoked wheel **4** at the TCB–graphite interface ($I_{set}$ = 48 pA. $V_{bias}$ = −0.42 V for (a) and $I_{set}$ = 46 pA. $V_{bias}$ = −0.50 V for (b)). (c) Network model of 2D host–guest architecture composed of DBA **2** (blue) and molecular spoked wheel **4** (turquoise). The blue arrows indicate the location of immobilized spoked wheel **4** and the red arrows point to pores with featureless bright spots.

As targeted, we demonstrated the formation of 2D molecular patterns with huge voids, the diameter of which reaches over 7 nm, at the liquid–solid interface. This pore size seems also to be the practical limit of concentration controlled polymorph selection for this kind of alkylated DBA derivatives,[10c] as far as the formation of extended porous 2D networks on graphite is concerned. As the structural properties of the host network were tuned to the symmetry and size of the molecular wheel guest, individual guest molecules could be trapped and their dynamics revealed. The size-tunability of the voids, based upon the proper selection of the alkyl chain length, is a powerful approach to isolate guests, reaching the 10 nm scale. As these networks are fragile, efforts to stabilize them are in progress.

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## Notes and references

‡ *General comments* on the synthesis of **2**. Reaction was performed in an inert gas (argon) atmosphere. All solvents were distilled before use. All commercially available reagents were used as received. Synthesis of DBA **3** is described in the ESI.† 1-Bromotriacontane was synthesized from commercially available 1-triacontanoic acid following the same procedure described in a previous paper.[14]

*Synthesis of* **2**. Under a nitrogen atmosphere, **3** (20.0 mg, 18.5 μmol), CsF (41.4 mg, 273 μmol), and 1-bromotriacontane (137 mg, 273 μmol) were placed in a Schlenk tube. Freshly distilled DMF (1.0 mL) and THF (1.0 mL) were added to the mixture *via* syringes. After stirring at 100 °C for 2 h, the reaction mixture was poured into water. The products were extracted with hot CHCl$_3$ (50 mL), and the extract was washed with water and brine, dried over MgSO$_4$ and evaporated. Recrystallization from CHCl$_3$ gave hexakis(triacontyloxy)hexadehydrotribenzo[12]annulene **2** (26 mg, 48%) as a yellow solid. Mp 88.0–89.2 °C; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) $\delta$ 6.72 (s, 6H), 3.96 (t, $J$ = 6.4 Hz, 12H), 1.80 (tt, $J$ = 7.2, 6.4 Hz, 12H), 1.50–1.20 (m, 324H), 0.90 ppm (t, $J_{\mathrm{H-H}}$ = 7.2 Hz, 18H); $^{13}$C NMR (67.5 MHz, CDCl$_3$, 50 °C) $\delta$ 149.3, 120.0, 116.4, 91.9, 69.4, 32.0, 29.77, 29.72, 29.5, 29.42, 29.35, 26.13, 22.7, 14.1 ppm; IR (KBr) 2918, 2850, 1594, 1509, 1470, 1349, 1227, 1072, 1014, 859, 720 cm$^{-1}$; MS (MALDI-TOF): *m*/*z* 2919 (M$^+$).

*Details of STM investigations*. All experiments were performed at 20–24 °C. Experiments were performed using a PicoSPM (Agilent). Tips were mechanically cut Pt–Ir wire (80% : 20%, diameter 0.2 mm).

Prior to imaging, DBA **2** and wheel **4** were dissolved in 1,2,4-trichlorobenzene and a drop of this solution was applied on a freshly cleaved surface of graphite (grade ZYB, Advanced Ceramics Inc., Cleveland, OH). The STM investigations were then performed at the liquid–solid interface within 1.5 h from dropping the solution.

The network models are constructed by the following procedure. First, a molecular model was optimized with PM3 method under $D_{3\mathrm{h}}$ symmetry. Then, the orientation of alkyl chains was changed for alkyl chain interdigitation under $D_{3\mathrm{h}}$ symmetry.

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