

Nanopatterning by Molecular Self-assembly on Surfaces

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Abstract: The ability to pattern surfaces down to the nanoscale is of increasing importance in nanoscience research. The use of supramolecular chemistry to drive the formation of self-assembled networks allows for a bottom-up approach to achieve nanopatterned surfaces. This short review highlights some of the recent breakthroughs in achieving long-range order in such molecular based systems, complemented with examples from our own work. The tuning of molecular architectures can exert control on the emergent properties and function of molecules at interfaces. In particular the formation of porous honeycomb networks allows the rational design of highly ordered patterned surface domains and the investigation of molecular dynamics, chirality and templating effects on surfaces.

Keywords: H-bonding · Self-Assembly · STM · Supramolecular chemistry · Surfaces

1. Introduction

Synthetic organic chemistry is most commonly conducted in solution for ease of processability, however natural living systems perform much of their magic at interfaces through the exclusion of solvent. In cells proteins create folded surfaces to obtain regio- and stereo-selective reaction control.^[1] Physical processes involving electron transfer such as photosynthesis^[2] or the transport of charges across membranes to generate local electric fields and propagate neural signals^[3] all occur at well-defined interfaces.

For many promising developments in nanoscience and technology in the areas of molecular electronics,^[4] optoelectronic metamaterials,^[5] photonic crystals,^[6] DNA

sequencing^[7] and organic photovoltaics^[8] the precise design of interfaces is essential, however, we are currently limited by our ability to control interfacial structures both on an extended length scale and down to the bottom of the nanoscale.

Using nature as our guide, crystal growth is a nice example of how this control can be achieved. The process of crystallization can be characterized by two primary factors, symmetry and branching.^[9] The intrinsic property of molecular structure controls the symmetry of the system under enthalpic control. The extrinsic environment including temperature, pressure and concentration affects the branching under entropic control.

The simple molecule H₂O crystallizes into a hexagonal lattice whose symmetry is determined by its three coordination sites available to form four H-bonds. But the localized crystalline domains quickly diverge in a random fashion in the formation of a snow flake.^[10] This branching effect is due to the external conditions at the site of crystal growth. It is commonly said that ‘no two snow flakes are the same’, however they all have hexagonal symmetry. These emergent properties arise from the interplay of the intrinsic molecular structure with the localized external environment, so that even starting from the same initial conditions highly divergent outcomes are achieved.

Intermolecular, non-covalent interactions can increase the enthalpy term, thereby reducing the effect of the entropy term on the system.^[11] By tuning the molecular

structure we can exert control on the emergent properties and function of molecules, allowing for the rational design of highly ordered, patterned surfaces.^[12]

2. Supramolecular Chemistry in Solution

Supramolecular chemistry is a maturing field in the synthesis of organic molecules and offers a way to overcome the entropic barriers of the free energy of association to achieve self-ordered systems.^[13] There are many possible non-covalent intermolecular interactions that can be used to drive self-assembly. Most well known is H-bonding,^[14] and its related halogen bonding,^[15] not forgetting van der Waals interactions,^[16] metal coordination,^[17] π - π ,^[18] cation- π ^[19] and even anion- π interactions.^[20] Supramolecular approaches have recently resulted in the first functional artificial synthetic machine, mimicking the function of a ribosome.^[21] Dynamic covalent chemistry has greatly increased our understanding of biological and chemical systems.^[22] The group of Samuel Stupp have pioneered the application of supramolecular interactions in polymeric systems which mimic analogues of human tissues.^[23] The Mayor group recently reported the synthesis and self-aggregation of molecular daisy chains in solution.^[24] These solution based, non-covalent aggregates are held together by mechanically interlocked supramolecular binding concepts.^[25]

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The focus of this work is to illustrate approaches and advantages of applying these solution-based concepts to surfaces.

3. Supramolecular Chemistry on Surfaces

Currently, patterned surfaces are usually formed by the top-down approach using lithographic techniques. However, in order to enter the sub-5 nm regime and achieve single-molecule resolution bottom-up approaches based on self-organised molecular scale architectures are required.^[26] This length scale also defines the requirements for imaging techniques, of which scanning tunneling microscopy (STM), among others,^[27] is a very powerful method to investigate molecules at surfaces. Typically higher-resolution STM images are obtained at reduced temperatures under ultra high vacuum (UHV) conditions.^[28] The compound of interest is either sublimed or sputtered onto a substrate, and consequently the molecules used must also be well matched to these harsh deposition conditions.^[29] The alternative of measurements at the solid-liquid interface typically implies a limited temperature range and typically lower resolution. Furthermore, structures can be sensitively dependent on the experimental conditions.^[30] These limitations can be somewhat overcome by first preparing the sample at the liquid-solid interface and then measuring *ex situ* under ambient conditions.^[31]

Patterns of molecules can be achieved with control dictated by either the substrate or by the molecular structure, often adapting ideas borrowed from crystal engineering applied to 2D networks.^[32–34] When porous networks are formed, further functionalization of the surface becomes possible.^[35] Chemical reactions can be induced by manipulation from the STM tip^[36] leading to the exciting prospect of growing 2D covalent sheets that form graphene nanoribbons.^[37] Light-activated functional surfaces can even release drug targets on demand.^[38]

The Mayor group have investigated acetylene based π -oligomers on surfaces,^[39] however the most ordered pattern domains were obtained from a series of investigations applying halogen- π interactions. Electron-rich acetylenes are a unique moiety for H-bonding motifs on surfaces because the terminal acetylene can act as an H-donor and their high π -density can act as a proton acceptor.^[40] In our case molecular rods of pentafluorophenyl subunits **1** and **2** linked by a diacetylene, self-assembled into ordered domains of interlocked parallel lines^[41,42] (Fig. 1a,b). A bent rod and star structure **3** with acetylene linkers assembled into interdigitated 2D chiral po-

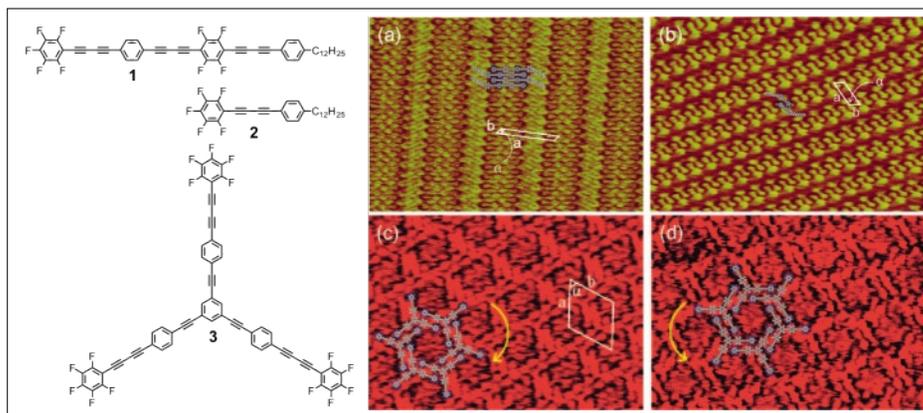


Fig. 1. Pentafluorophenyl OPE rods **1**, **2** and star **3** were deposited on HOPG surfaces and imaged by STM in constant current mode. a) Overlaid modeling of OPE **1** on STM, $V_{\text{bias}} = -0.95$ V, $I_{\text{set}} = 0.6$ nA. b) Overlaid modeling of OPE **2** on STM, $V_{\text{bias}} = -0.90$ V, $I_{\text{set}} = 0.6$ nA. c and d) High-resolution STM images $V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 1.43$ nA. d) a mirrored arrangement of the domain in c) demonstrating change in chiral domain. Both are overlaid with modeling of OPE star **3**. (Images a and b reprinted with permission from ref. [41]. Copyright 2011, Langmuir. Images c and d reprinted with permission from ref. [43]. Copyright 2008, American Chemical Society.)

rous networks driven by Aryl-H \cdots F bonding^[43] (Fig. 1c,d). It was also possible to design and synthesize halide end-capped oligo-phenyl-ethynylene (OPE) rods and compare their 3D crystal structure to their 2D arrangement on surfaces.^[44] Currently we are working to combine such phenyl-acetylene architectures with a porous network to investigate template effects and even the dynamics of molecular motion at the interface.

4. Templatation and Molecular Dynamics on Surfaces

The use of templating and host-guest interactions allows organization of molecules on a surface that would not otherwise self-assemble in a given pattern. The group of Dieter Schlüter have been able to form 2D polymer sheets at the water/air interface, which can coordinate Fe^{2+} metal centres.^[45] Jay Siegel and coworkers^[46] used corannulene buckybowls as hosts for C_{60} . These templating concepts are analogous to those seen in solution, however an interface is also a pro-chiral environment dictated by the facial selectivity of an adsorbed molecule and the generation of surface confined networks, which can both lead to chiral recognition.^[47]

Identification of different conformational geometries of a molecule on a surface was first reported by Jung *et al.*^[48] for a tetra-substituted porphyrin determined by STM. They were able to assign the different 'landing geometries' of the porphyrin and investigate conformational changes governed by the interaction of the molecule with the surface. Schramm *et al.*^[49] experienced first hand the difficulties that arise when a desired 'landing geometry' is disfavoured.

Thermally induced motion was used by Gimzewski *et al.*^[50] to investigate the mechanics of a single molecule, supramolecular bearing. Directionally controlled, concerted molecular motion was recently achieved by Ben Feringa and co-workers^[51] by manipulation of an STM tip on a nanocar. Careful design and synthesis of the 'wheels' of the car was required to ensure that the axels were of opposite handed-ness, however they too had to first search for molecules that had the correct 'landing geometry'. It may be possible to obtain directional motion of single molecules by confinement within a cavity to overcome this limitation, so long as there is still sufficient space to allow for molecular rotations. Below we discuss the approaches towards such surfaced confined rotors.

5. Porous Honeycomb Networks

Ludwig Bartels and co-workers found an anthraquinone-based H-bonded network on a Cu(111) surface that arranged spontaneously at low surface coverage and low temperatures (between 10–200 K) into a honeycomb network with long range ordering^[52] (Fig. 2a). This network formation was notable for two key features. The H-bonding that drove the self-assembly was mediated between a carbonyl group and an aromatic proton (Fig. 2b). Secondly, the cavity that was formed was roughly 50 Å, more than five times the space filling of the individual anthraquinone units, seemingly driven by the delicate interplay of weakly attractive H-bonding and substrate mediated adsorbate-adsorbate repulsion. At higher anthraquinone densities islands of closed packed molecules were preferred, indicative of a shift to another polymorphic state.

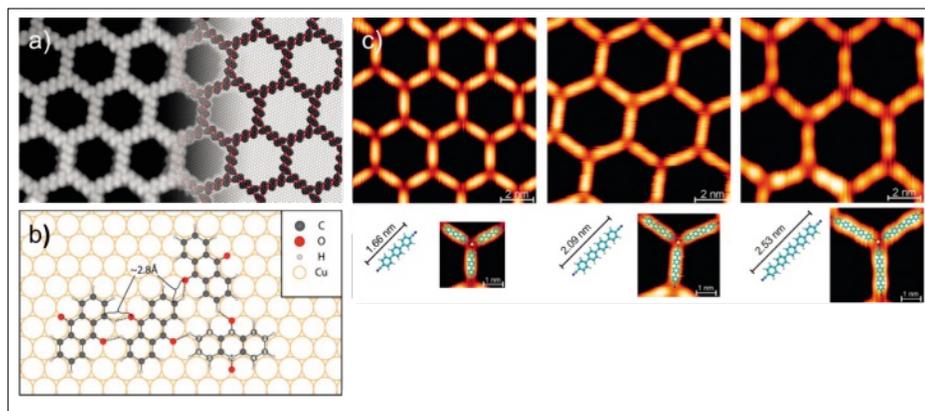


Fig. 2. a) Anthraquinone molecules form a honeycomb network on a Cu(111) surface with pores of 150 Å by 260 Å, right) unit cell model overlaid. b) Schematic of anthraquinone molecules forming H-bonding. C-H-O distances are indicated. (Image reprinted with permission from ref. [52]. Copyright 2006, Science.) c) Tuning of the pore size by increasing the length of oligo-phenyl linkers by co-directed self-assembly. below) modeling of oligo-phenyl linkers overlaid on a structural motif from the STM. (Images reprinted with permission from ref. [53]. Copyright 2007, Nano Letters.)

The group of Johannes Barth, building on the unprecedented size of Bartel's pores^[52] targeted a self-assembled network that would afford a similarly large cavity, but with greater stability. In order to achieve this they focused on forming 2D arrays of metal-organic frameworks, as the coordination should be stronger than H-bonding. Initially they investigated oligo-phenyl rods of varying length^[53] (Fig. 2c) based on a tri-dentate binding motif of Co-carbonitrile which formed hexagonally symmetric networks over a μm^2 domain on Ag(111) surfaces. The largest pore size of 5.7 nm of the honeycomb network allowed for isolated cases of cavity filling. The deposited rods, caged in by the cavity walls could be switched by manipulation from the STM tip by changing the scan direction or applied bias voltage.

In an attempt to create even larger cavities they synthesized a *para*-hexaphenyl-dicarbonitrile rod **4** (Fig. 3) by Suzuki coupling^[55] which when deposited with cobalt atoms lead to the formation of a 67 Å long pore.^[56] The honeycomb network was further stabilised by the epitaxial fit of the coordination sites with the underlying Ag(111) substrate which was imaged by STM with atomic resolution. After further investigations in the 70–300 K temperature range, the network was found to still be stable without degradation at room temperature, however any uncoordinated rods became highly mobile.

In order to functionalise the surface further and investigate constitutional dynamics of these uncoordinated rods trapped in the pores Kühne *et al.*^[54] played with the deposition conditions. The ideal stoichiometry of this nanomesh is 3:2 of rod:cobalt. If more rods are present they begin to deposit in the network cavities. At a 10% excess of *para*-hexaphenyl-di-

carbonitrile monomers to this ratio, trimers are formed (Fig. 3c). These rods are themselves epitaxial with the Ag(111) surface with the nitrogen of the terminal nitriles located at hollow sites on the Ag surface. These trimer guests are found in two enantiomorphous forms which are distinguishable at low temperatures. They performed a series of STM measurements with increasing temperature to investigate the possibility of a dynamer^[57] response. They were able to resolve concerted rotational motion of the trimers while maintaining their chirality (Fig. 3d). Above 70 K in-

terconversion between the two dynameric enantiomers occurs, removing any chiral signature, demonstrating a rare example of constitutional dynamics inside the nanopores of this self-assembled system.

These examples of progressively more functional cavities raises the prospect of designing such a porous network that allows for even greater control over the rotations of the guest, with the possibility of directionality and addressability by external stimuli, *i.e.* not limited to thermally induced random rotational motions in a nanopore.

6. Melamine-PTCDI Honeycomb Networks

In a multi-component system there is greater scope for rational design of the surface architecture to encourage formation of porous sites. Theobald *et al.*^[58] explored the formation of a two-component assembly using the strong H-bonding formed between perylene tetra-carboxylic di-imide (PTCDI) and melamine (Fig. 4). The conditions of formation must be carefully controlled, otherwise a wide variety of polymorphic domains of the melamine-PTCDI are accessible, with a particular dependence on the annealing temperature.^[59] The three-fold symmetry of the melamine allows the formation of a honeycomb network by annealing at 100 °C after a step-wise deposition of the two components, where the network remains commensurate

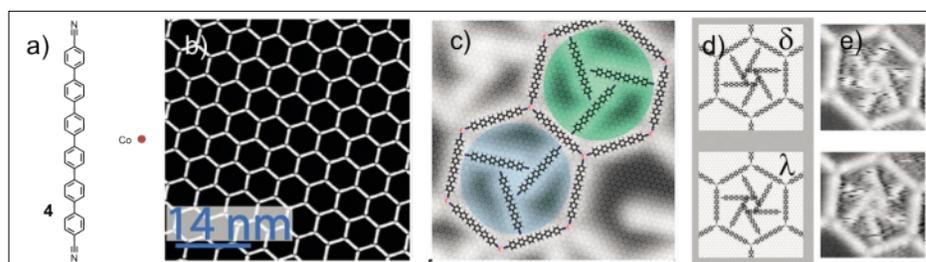


Fig. 3. a) *para*-Sexiphenyl-dicarbonitrile **4** and cobalt generate b) well defined 2D coordination honeycomb network on a Ag(111) surface with a cavity of van der Waals radius of 24 nm². c) Structure model overlaid on STM images showing two chiral arrangements of trimers. d) The chiral configurations ($\delta + \gamma$) can be interconverted at 146 K and gives rise to e) rotations seen by STM in the pore. Images reprinted with permission from ref. [54]. Copyright 2010, PNAS.

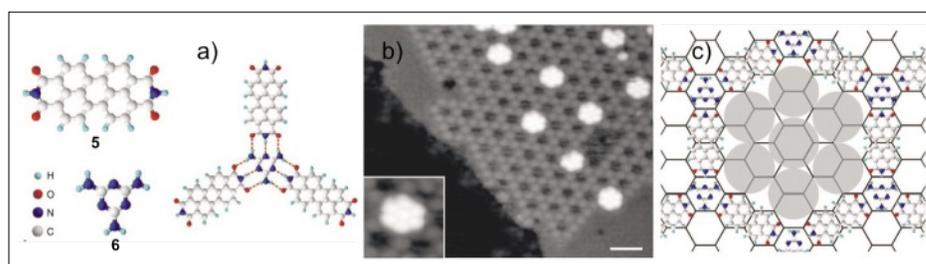


Fig. 4. Perylene tetra-carboxylic di-imide (PTCDI) **5** and melamine **6** can a) H-bond to form three coordinate 2D networks. b) STM image of heptamers of C₆₀ filling the cavities of melamine-PTCDI honeycomb network. c) Schematic modeling of the surface network. Image reprinted with permission from ref. [58]. Copyright 2003, Nature.

with the underlying Ag/Si(111) surface. Uniquely they were then able to sublime a third molecular component, filling the cavities with heptamers of C_{60} .

The Buck group have looked to combine this supramolecular approach to patterning surfaces with the more traditional concept of self-assembled monolayers (SAMs).^[60] In the examples above (Figs 2–4), all STM investigations were performed under UHV conditions, which is restricted to molecules which can be easily sublimed. Madueno *et al.*^[31] moved to a solution-based fabrication which additionally allows for the formation of SAMs. They first formed the same melamine-PTCDI network on a Au(111) surface from a solution of DMF which gave higher surface coverage than under UHV conditions (see discussion above^[58]). By working on a gold surface they were then able to form SAMs of alkane thiols corralled in the honeycomb cavity (Fig. 5a,b). Due to the template control of where the SAMs were formed and the stability of this network, it was even possible to further process the surface. Cu was selectively inserted at the SAM–substrate interface by underpotential deposition^[61] (UPD, Fig. 5c), thus rendering the thiol–substrate bond even more stable.^[62] Notably, the Cu-UPD occurred more readily in this hybrid system than for densely packed uniform SAMs. In later studies it was shown that the melamine-PTCDI hydrogen-bonded network acts as a diffusion barrier to the deposited Cu adatoms, limiting their presence on the surface to the 3.5 nm pore.^[63]

The role of the melamine-PTCDI honeycomb is not just limited to a template. It can also be used as a sacrificial mask to generate binary self-assembled monolayers^[64] (Fig. 6). After formation of the network (Fig. 6a) and templated SAM formation using an aromatic thiol (Fig. 6b), the stability of the SAM islands was increased by Cu-UPD (Fig. 6c). This allowed for a subsequent substitution of the network backbone with a second thiol, in this case adamantane-thiol (Fig. 6d). This high level of processing relies on the stability of the SAM nanoislands in relation to further displacement or lateral diffusion by the second thiol, intimately controlled by the kinetics and thermodynamics of the binary SAM.

Chemical modification of the PTCDI monomers by substitution at the perylene core with adamantane thioether groups^[65] results in two enantiomers when adsorbed on the surface.^[66] Their statistical arrangement in the bimolecular honeycomb network gives rise to different pore geometries which yields pronouncedly different arrangements of C_{60} molecules deposited in the cavities. These studies demonstrate the robustness of the triple-hydrogen bonded

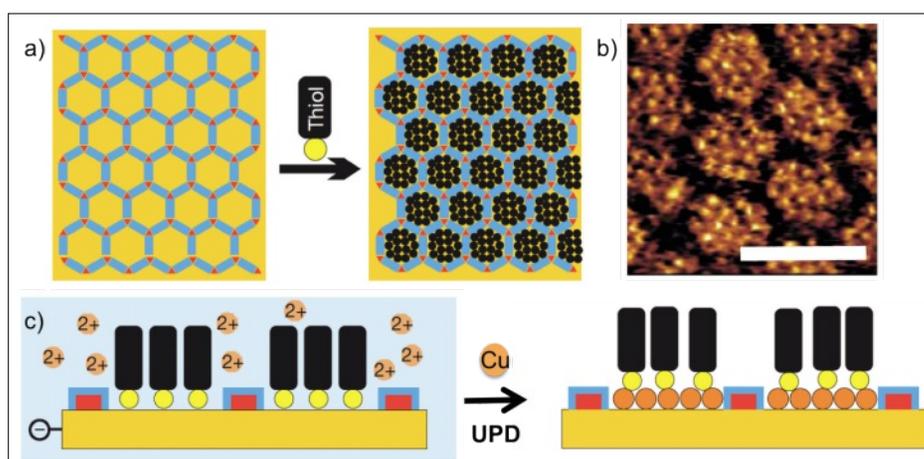


Fig. 5. a) Schematic of SAM formation in the pores of a melamine-PTCDI network on Au. b) High-resolution STM image of a C12SH alkyl thiol SAM framed by the honeycomb network, scale bar 5 nm. c) Illustration of UPD electrochemical Cu deposition in the porous network at the alkane thiol/Au interface. Image reprinted with permission from ref. [31]. Copyright 2008, Nature.

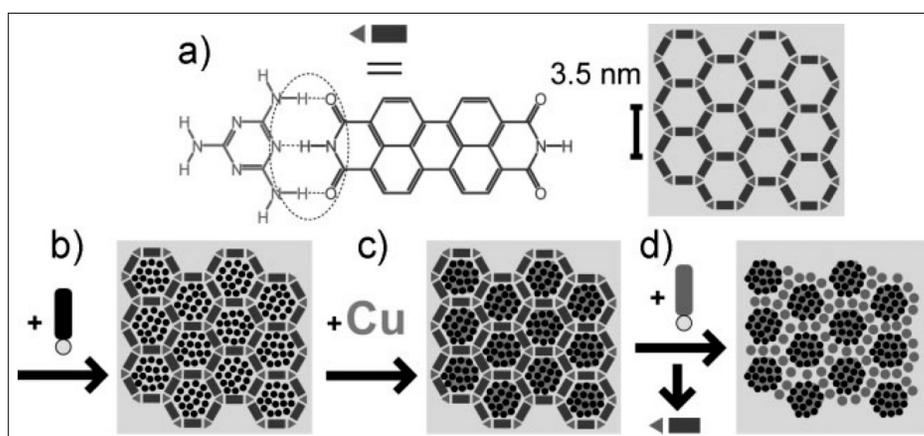


Fig. 6. a) Three-fold H-bonding of melamine-PTCDI generates a regular hexagonal porous network on Au(111). b) Templated SAM formation of an aromatic-thiol. c) Cu UPD insertion d) addition of a second thiol substitutes the melamine-PTCDI sacrificial network. Image reprinted with permission from ref. [64]. Copyright 2010, Small.

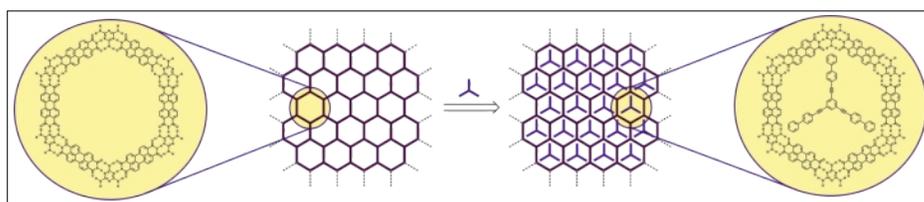


Fig. 7. Schematic of a melamine-PTCDI honeycomb network with the pores filled with OPE star molecules. Zooms show the proposed molecular arrangement on an Au(111) surface with idealized geometry.

system and that bulky 3D substituents can both be deposited and resolved by STM in the honeycomb network.

7. Outlook

Using advanced techniques in phenylacetylene synthesis^[67] we are currently investigating a series of star-shaped guests for deposition into a melamine-PTCDI honeycomb network (Fig. 7). We hope to see rotation of the stars inside the cavities, and even to use the secondary pores

formed to host another guest, achieving an unprecedented level of surface patterning and molecular control. By adding H-bonding moieties to the periphery of the star, these guests should influence the relative rate of molecular motion mediated through non-bonding interactions with the honeycomb network.

The selected examples described above highlight some of the latest developments in supramolecular surface science in the past half-decade. They demonstrate the amazing degree of control and precision hierarchical molecular systems have for

tailoring the emergent properties of a surface. We look forward with great anticipation to further developments in the field and to new self-assembled functional surface systems.

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