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Exploring the Complexity of Supramolecular Interactions for Patterning at the Liquid−Solid Interface

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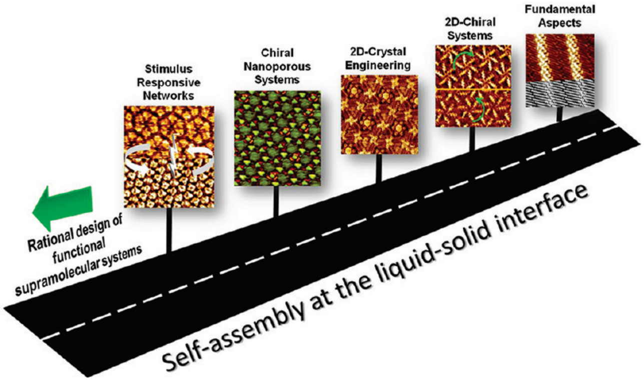

The use of self-assembly to fabricate surface-confined adsorbed layers (adlayers) from molecular components provides a simple means of producing complex functional surfaces. The molecular self-assembly process relies on supramolecular interactions sustained by noncovalent forces such as van der Waals, electrostatic, dipole−dipole, and hydrogen bonding interactions. Researchers have exploited these noncovalent bonding motifs to construct well-defined two-dimensional (2D) architectures at the liquid−solid interface. Despite myriad examples of 2D molecular assembly, most of these early findings were serendipitous because the intermolecular interactions involved in the process are often numerous, subtle, cooperative, and multifaceted. As a consequence, the ability to tailor supramolecular patterns has evolved slowly. Insight gained from various studies over the years has contributed significantly to the knowledge of supramolecular interactions, and the stage is now set to systematically engineer the 2D supramolecular networks in a "preprogrammed" fashion.

The control over 2D self-assembly of molecules has many important implications. Through appropriate manipulation of supramolecular interactions, one can "encode" the information at the molecular level via structural features such as functional groups, substitution patterns, and chiral centers which could then be retrieved, transferred, or amplified at the supramolecular level through well-defined molecular recognition processes. This ability allows for precise control over the nanoscale structure and function of patterned surfaces. A clearer understanding and effective use of these interactions could lead to the development of functional surfaces with potential applications in molecular electronics, chiral separations, sensors based on host−guest systems, and thin film materials for lubrication.

In this Account, we portray our various attempts to achieve rational design of self-assembled adlayers by exploiting the aforementioned complex interactions at the liquid−solid interface. The liquid−solid interface presents a unique medium to construct flawless networks of surface confined molecules. The presence of substrate and solvent provides an additional handle for steering the self-assembly of molecules. Scanning tunneling microscopy (STM) was used for probing these molecular layers, a technique that serves not only as a visualization tool but could also be employed for active manipulation of molecules. The supramolecular systems described here are only weakly adsorbed on a substrate, which is typically highly oriented pyrolytic graphite (HOPG). Starting with fundamental studies of substrate and solvent influence on molecular self-assembly, this Account describes progressively complex aspects such as multicomponent self-assembly via 2D crystal engineering, emergence, and induction of chirality and stimulus responsive supramolecular systems.

I. Introduction

Nature has been crafting complex supramolecular architectures for billions of years via the process of biorecognition and biomolecular organization which exploit noncovalent interactions. Learning from Mother Nature, chemists are now beginning to construct complex supramolecular

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systems in which individual components interact via noncovalent forces such as van der Waals interactions, hydrogen bonds, $\pi-\pi$ stacking electrostatic and dipole–dipole interactions. Described as the "chemistry beyond the molecules",[1] this field has already pervaded through most of chemistry and extended to the interfaces of chemistry with a diverse array of other disciplines including biology, physics, materials science, and engineering.

Although components of any size can self-assemble given a permissive environment, most of the concepts of self-assembly have historically come from studying molecular systems.[2] The motivation behind these studies lies not only in fundamental understanding of molecular recognition processes but also in the prospect of designing new class of materials with novel properties.[3] As a consequence, research on molecular self-assembly is being revived in the context of design and fabrication of molecular devices. It is in this context that the molecular self-assembly on surfaces has garnered considerable attention.

In contrast to their self-assembly in solution, ordering molecules on a solid surface imparts a high degree of coherence in their orientation and packing, leading to well-defined adlayers on substrates such as silicon, gold, copper, and HOPG which could then be integrated into devices. The liquid–solid interface provides a unique medium to construct flawless networks of surface confined molecules. Solvent provides a favorable environment for the dynamics of molecular components which imparts flexibility and "self-correction" ability to the process that is conducive for formation of highly ordered structures. The substrate, on the other hand, serves as a congregator of molecules which functions as a template by directing the self-assembly via favorable epitaxial interactions.

The self-assembly of numerous organic molecules has been investigated in detail by us and others for more than a decade by employing STM at the liquid–solid interface. Though limited to conductive substrates, the scanning tunneling microscope enables real-time and real-space imaging at high spatial resolution. Typical substrates include HOPG or Au(111) which provide atomically flat conductive surfaces ideal for probing molecular layers. A majority of initial studies were mainly aimed at high-resolution visualization of self-assembled patterns of molecules. This was the beginning of the "comprehension" phase which focused on understanding the nature of various molecular recognition phenomena. The "comprehension" phase continues to date, though the past decade has witnessed a paradigm shift in the approach toward the research on surface supported monolayers. Increasing importance is being given to "directed self-assembly" where the aim is to engineer particular functional groups on molecules to induce specific molecular networks on surface in a "preprogrammed" fashion. Almost overlapping with the "induction" phase described above, began the "manipulation" phase which involves nanoscale manipulation of surface confined molecules by using external stimuli such as light, electric field and temperature. Presently, an increasing number of studies are dedicated toward controlled and reversible manipulation of molecules on surfaces.

We among others have witnessed and contributed to the progress in the field of self-assembly at the liquid–solid interface. Although the ultimate task of design and fabrication of real-life functional supramolecular devices is still far from complete, enough has been explored that warrants an overview. The aim of this Account is to provide a retrospective view of the studies carried out in our laboratory to comprehend and explore the complexity of supramolecular interactions at the liquid–solid interface.

II. Fundamental Aspects of Self-Assembly at the Liquid–Solid Interface

High resolution STM (HR-STM) imaging at the liquid–solid interface requires molecules to be laterally immobilized on the surface for the time it takes the STM tip to scan the area which varies from a few seconds to several minutes. At room temperature, under physisorption conditions, most low-molecular weight molecules are too mobile to be visualized at the liquid–solid interface, except if they are trapped in or being part of a 2D matrix. The successful formation of such 2D matrix necessitates a comprehensive understanding of various molecule–molecule, molecule–substrate, molecule–solvent, and solvent–substrate interactions which constitutes the "comprehension" phase.

A. Substrate Directed Molecular Self-Assembly. Though firmly established for inorganic systems,[4] the role of epitaxy in the formation of organic adlayers is less clearly understood because of the relatively weak and reversible interactions involved. The balance of these "soft" interactions makes organization of molecular films and mode of epitaxy rather unpredictable when compared to the behavior of bulk molecular crystals. One example of such peculiar behavior can be found in the 2D self-assembly of simple 4-alkoxybenzoic acids (4-ABAs).[5]

4-Icosyloxybenzoic acid (4-OC_{20}BA), when physisorbed at the 1-phenyloctane/HOPG interface, forms a relatively complex columnar network (Figure 1c) than what is expected

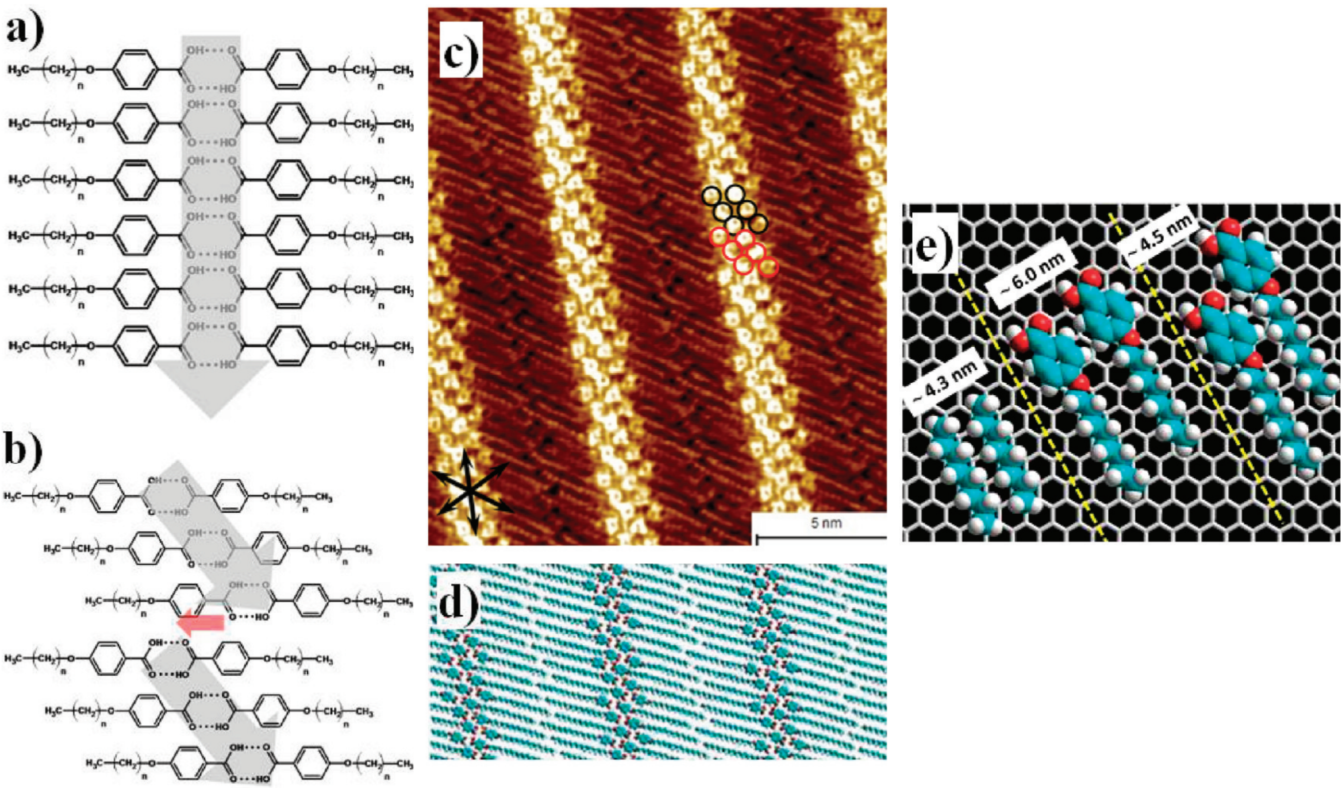

FIGURE 1. Schematic showing expected (a) and experimentally observed (b) supramolecular patterns of 4-ABAs. (c) HR-STM image of 4-OC$_{20}$BA at the 1-phenyloctane/HOPG interface. (d) Proposed model. (e) Molecular model showing the two possible arrangements of 4-ABAs on graphite lattice with corresponding distances between alkyl chains. Two molecules of simple alkane are also shown for comparison.

on the basis of its molecular structure (Figure 1a). The characteristic feature of these molecular columns is the presence of periodic kinks along the column which appear after every three dimers. This complex pattern of 4-OC$_{20}$BA could be explained by considering the influence of substrate lattice on molecular self-assembly. Despite their relatively weak nature, the molecule–substrate interactions have a strong bearing on the adsorption of molecules.[6]

The basal (0001) plane of graphite has a 3-fold symmetry and the zigzag orientation of carbon atoms along any C_3 axis matches with that of an all-*trans* alkyl chain. Moreover, the in-plane lattice constant of graphite (2.46 Å) is close to the distance between alternate methylene groups (2.58 Å) in an alkyl chain. This fortuitous match allows the methylene groups of an alkyl chain to rest over the voids of the hexagons in graphite lattice thereby providing an approximately commensurate packing. The lateral spacing between alkylated molecules is also dictated by the distance between every other carbon row along the $\langle 1\bar{1}00 \rangle$ directions of graphite (4.24 Å). Thus, graphite lattice provides epitaxial stabilization to alkylated molecules with stabilization energy of 64 meV per methylene group.[6]

As a consequence of the aforementioned favorable epitaxial interactions, the registry of the alkyl chains with graphite lattice necessitates the chains to be placed close to 4.24 Å apart. This registry condition can be easily satisfied by unsubstituted alkanes however, forbidden in the present case due to presence of bulky phenyl "head-groups". Thus, there is a conflict between the restrictions imposed by the substrate lattice and the molecular parameters. Therefore, in order to satisfy the registry condition as well as to enforce requisite van der Waals contact, the phenyl rings are shifted such that the alkoxy chains are spaced 4.5 Å apart on the HOPG surface (Figure 1e). Considering the interchain distance and the offset between adjacent phenyl rings, alkoxy chains of only three molecules could be placed with an approximate registry in a given direction. The alkoxy chain of the fourth molecule, however, does not register correctly which results in accumulation of internal strain in rows of molecules, making it energetically unfavorable to pack more than three molecules in a straight row along one direction. Consequently, the fourth molecule is shifted which allows for correct registry with the substrate lattice.[5]

B. Solvent-Directed Molecular Self-Assembly. An extremely powerful and relatively less understood approach to control 2D pattern formation at the liquid–solid interface is

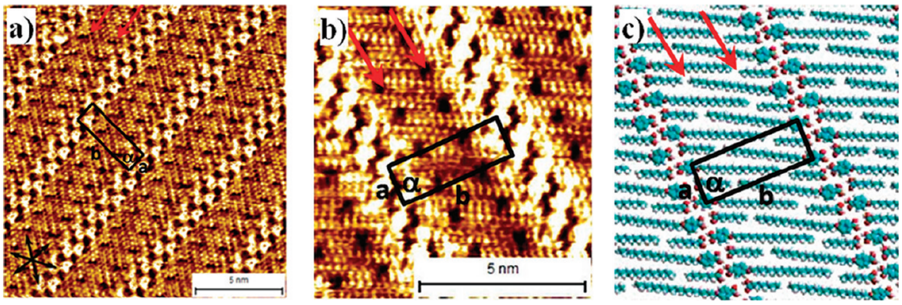

FIGURE 2. (a, b) HR-STM images of **4-OC$_{20}$BA** physisorbed at the 1-octanoic acid/HOPG interface. (c) Tentative molecular model. Red arrows indicate locations of terminal methyl groups.

"solvent-directed" self-assembly. Typical solvent properties such as viscosity and polarity have an impact on the self-assembly process. The solvent also enables adsorption–desorption dynamics, thereby affecting the mobility of molecules. Solvent-induced polymorphism, the effect of coadsorption, as well as solvent effects on chirality and electronic structure have been summarized recently.[7] In the most "active" mode of participation, solvent molecules undergo coadsorption with the adsorbate molecules to form a multicomponent monolayer[5,7] as described below.

Figure 2 shows the HR-STM image of **4-OC$_{20}$BA** physisorbed from a solution of 1-octanoic acid. In contrast to the characteristic fractured molecular arrangement observed at 1-phenyloctane/HOPG interface, **4-OC$_{20}$BA** molecules adopt a zigzag arrangement when adsorbed from 1-octanoic acid. The difference in the molecular packings observed in these two solvents is associated with the mode of interaction of the solvent with the solute molecules. A careful inspection of the high resolution image reveals that opposite every bright spot there is one striped feature. The length of these striped features corresponds to the length of 1-octanoic acid molecules (~1.1 nm), indicating the coadsorption of solvent. Thus, 1-octanoic acid hydrogen bonds with **4-OC$_{20}$BA** molecules and hence coadsorbs to form a two component monolayer. These experiments indicate that 1-phenyloctane acts as a neutral partner whereas 1-octanoic acid is actively involved in self-assembly via incorporation in the monolayer.

C. Concentration-Directed Molecular Self-Assembly. Solute concentration plays an important role in self-assembly at the liquid–solid interface, especially when two or more polymorphs are possible which differ in packing density or adsorption energy. One of the first examples of concentration dependent self-assembly[9] was discovered in case of alkoxylated dehydrobenzo[12]annulene (DBA) derivatives (Figure 3a). By using a meticulous concentration control strategy,[8] it is possible to obtain low-density nanoporous networks or a high-density linear packing. STM images displayed in Figure 3b and c clearly illustrate the concentration dependent surface coverage of the linear and porous honeycomb networks for a DBA-OC$_{16}$ derivative which is a general behavior for the DBA derivatives. A systematic examination of the concentration dependent self-assembly of DBAs with different alkoxy chain lengths, however, revealed that the concentration range where this transformation is observed depends on the alkyl chain length. The surface coverage of the honeycomb network follows a linear relation with concentration for DBAs with smaller alkoxy chains whereas for DBAs with longer alkoxy chains this relation is exponential. (Figure 3e)[8]

To further understand the mechanism of the concentration controlled structure selection of DBAs at the liquid–solid interface, a thermodynamic model[8] was proposed which reveals that the concentration dependence arises from different stabilities and molecular densities of the two patterns. A comparison between the adsorption energies per unit area of the linear and porous networks revealed that they are comparable for smaller DBAs and the difference increases with an increase in the chain length, favoring the close packed structure. This is consistent with the trend at high concentrations where the DBAs favor the linear structure. However, with decreasing concentration, the number of molecules adsorbed to cover the substrate surface decreases. Under such circumstances, DBAs favor the porous network in order to maximize the adsorption energy per molecule. By employing this "concentration-in-control" principle, it became feasible to construct porous supramolecular networks of DBA with pore diameter ranging from 3 nm to more than 7 nm. The controlled fabrication of such porous networks proved to be an important step in the development of a new field called "2D crystal engineering".[9]

III. 2D Crystal Engineering at the Liquid–Solid Interface

The construction of tailor-made, well-defined 2D supramolecular architectures via manipulation of supramolecular

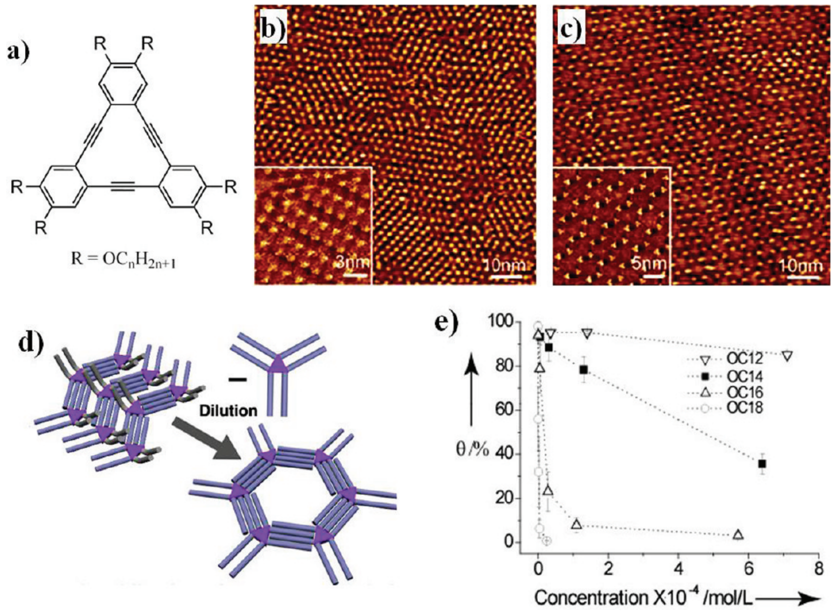

FIGURE 3. (a) Molecular structure of triangular DBA. (b, c) DBA-OC$_{16}$ monolayer at high (b, 1.1×10^{-4} mol L^{-1}) and low (c, 5.7×10^{-6} mol L^{-1}) concentrations obtained from 1,2,4-trichlorobenzene (TCB) solutions. (d) Schematic illustration of the linear to porous transition. (e) Dependence of the surface coverage of honeycomb pattern (θ) on the DBA concentration for different DBA derivatives.

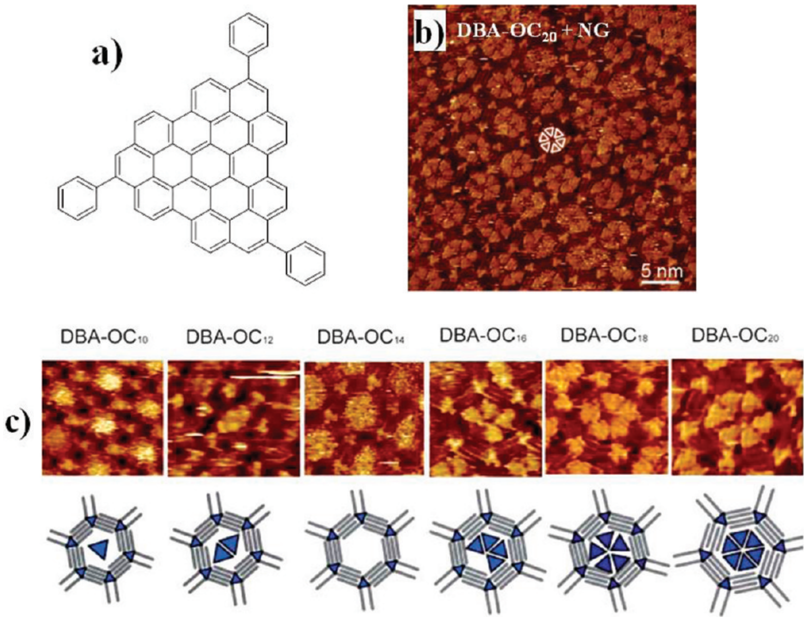

FIGURE 4. (a) Molecular structure of Nanographene. (b, c) STM images of DBA derivatives with NG clusters inside the voids.

interactions could be called 2D-crystal engineering. This aspect mainly constitutes the "induction" phase wherein fundamental knowledge of supramolecular interactions is used to design and fabricate surface-confined molecular modules in a preprogrammed fashion. Various interactions such as hydrogen bonding, metal−ligand coordination, and ionic interactions could be exploited for this purpose; however, here we will highlight the van der Waals interactions based self-assembly of DBA derivatives. The unique self-assembly behavior of the DBA building blocks could be used to create complex multicomponent supramolecular structures[9] as described below.

In addition to the relative proportions of molecules in solution and on surface, coadsorption of solvent molecules (e.g., TCB) also contributes to the stability of the pores. However, for higher pore sizes, the solvent coadsorption alone cannot compensate for the energy loss caused by increasing the void area. By replacing the solvent molecules by larger guest molecules which have higher affinity for the surface, it is possible to stabilize relatively large porous networks.[9] For example, a polyaromatic hydrocarbon, Nanographene (NG, Figure 4a), can template and stabilize the voids of DBAs with longer chains.[9b] Depending on the pore size, one up to six NG molecules can be accommodated inside the DBA pores. Apart from DBA-OC_{10} and DBA-OC_{14}, the NG molecules are well-immobilized inside the pores and could be visualized with molecular resolution. For a particular alkyl chain length, a specific number of NG molecules forms a cluster (Figure 4c) in the majority of the pores. Moreover, the appearance of a number of distorted pores indicates that the host matrix can change its structure to accommodate higher guest clusters. This flexibility arises from the weak van der Waals interactions between interdigitating alkoxy chains holding the honeycomb structure together.[9b]

A very interesting aspect is the structural transformation of the otherwise high-density linear structure into a low-density porous structure upon addition of guest molecules. Such transformation is driven by a gain in energy resulting from template–substrate interactions, increased host–substrate interactions (six alkoxy chains adsorbed instead of four), and host–template interactions which overcome the loss of stability inherent to the formation of low-density host matrices. These results inspired the quest for more advanced host–guest systems. In contrast to the widely reported[9c] bicomponent 2D crystalline lattices, multicomponent architectures containing more than two molecular building blocks are rare due to the complexity of interactions involved.[9f] However, by using a combination of van der Waals and hydrogen bonding interactions, a three-component architecture could be successfully fabricated as described below.

At the 1-octanoic acid/HOPG interface, isophthalic acid (ISA) self-assembles into a close-packed zigzag arrangement. However, upon addition of coronene (COR), a well-defined heterocluster emerges, wherein six hydrogen-bonded ISA molecules capture one COR molecule (COR_1-ISA_6, Figure 5a).

This heterocluster can be hosted inside a DBA-OC_{10} honeycomb network to form a three-component supramolecular architecture as displayed in Figure 5b.[10d] Moreover, as DBA-OC_{10} does not form a stable honeycomb network in 1-octanoic acid, the heterocluster acts as a template and induces the structural transformation from linear to porous network. The final architecture can be obtained both by premixing the three components in solution or by addition of an ISA/COR solution to an existing monolayer of DBA.[9d]

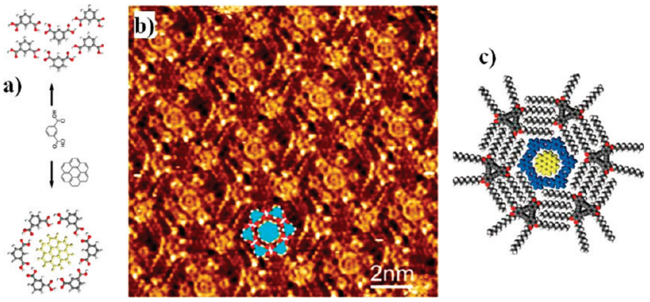

FIGURE 5. (a) Schematic showing the structural transformation in the packing of ISA molecules upon addition of COR. (b) Three component supramolecular architecture built from COR_1-ISA_6 cluster trapped in the porous network of DBA-OC_{10} (c) Proposed molecular model.

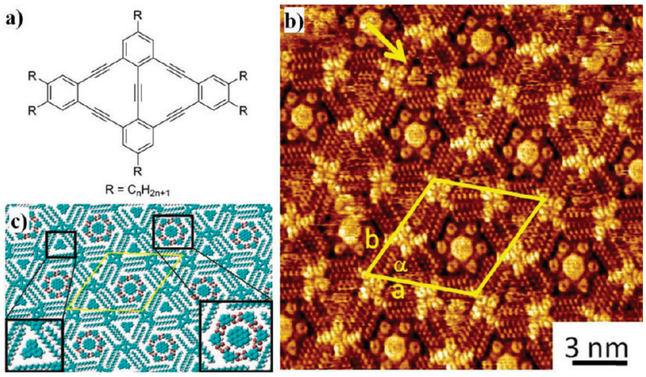

FIGURE 6. (a) Molecular structure of bisDBA. (b) HR-STM image of a four-component supramolecular architecture. (c) Proposed molecular model.

A modified approach in 2D crystal engineering of DBAs yields an even more complex four-component architecture. Structurally different bisDBA derivatives (Figure 6a) readily form a Kagomé network which offers spatially well-ordered hexagonal and triangular voids. However, bisDBA-C_{12} (chosen due to the similar size of the hexagonal voids) does not form a Kagomé network at the 1-octanoic acid/HOPG interface. Only when the COR and ISA are added, a stable three-component network is obtained, with the hexagonal cavity filled with a COR_1-ISA_6 cluster. By adding a triangular guest molecule such as triphenylene (TRI) a four-component 2D crystal is successfully fabricated, with the triangular cavities filled with TRI as depicted in Figure 6b. An important finding is that, upon proper concentration control, this four-component pattern spontaneously emerges at the solvent–graphite interface upon simply depositing a drop of the solution containing the mixture.[9e]

IV. Emergence and Induction of Chirality at the Liquid–Solid Interface

The presence or absence of chiral centers strongly affects the supramolecular recognition processes. This facet can be exploited by encoding the chiral information at the level of the single molecule and then transmitting it to the supramolecular level to produce enantiomorphous monolayers. Chirality is an immensely important aspect in pharmaceutical sciences where separation of enantiomers is a major concern and the study of chirality on surfaces could be of great potential.

In contrast to its expression in solution or in crystals, chirality is easily achieved in 2D due to the loss of symmetry elements. This is because an interface does not have a center of symmetry and reflection planes can only be maintained normal to the surface. This implies that a prochiral molecule can become chiral when confined at an interface.[10] In monolayers formed by achiral molecules, an equal amount of both 2D enantiomers is observed which adsorbs in different domains related by mirror-image symmetry. Enantiopure molecules give rise to homochiral monolayers. Finally, self-assembly of molecules from a racemic mixture leads to different possibilities of formation of a conglomerate, a racemic compound, or a solid solution, analogous to crystallization in 3D. Chiral induction experiments[11] are aimed at inducing homochirality in achiral monolayers by employing a chiral solvent,[11a] by exposing the monolayers to external magnetic fields,[11b] or by addition of chiral modifiers.[11c] In the following, we describe the different approaches adopted in our lab to induce chirality in monolayers formed by achiral molecules.

In addition to its role as a dispersing medium which may or may not be actively involved in the self-assembly process, one can also store chiral information in the solvent and transfer it to the self-assembled network of achiral molecules adsorbed from it. When adsorbed from achiral solvents, achiral diaminotriazine oligo-*p*-phenylene vinylene (OPV) derivatives (A-OPV4T, Figure 7a) self-assemble in the form of cyclic hexamers (rosettes) which could be oriented either clockwise (CW) or counter-clockwise (CCW) and there is no bias toward either CW or CCW rosettes. However, when adsorbed from enantiomerically pure 1-phenyl-1-octanol, a clear bias toward either CW or CCW rosettes could be induced depending on the chirality of the solvent.[11a] Figure 7b and c show HR-STM images of A-OPV4T adsorbed from solutions of enantiopure (*R*)-1-phenyl-1-octanol and (*S*)-1-phenyl-1-octanol, respectively. These STM images reveals that the rosettes formed from enantiopure solvents are chiral and analysis of a number of large scale images reveals a clear bias toward formation of CCW rosettes in (*R*)-1-phenyl-1-octanol and CW rosettes in (*S*)-1-phenyl-1-octanol.[11a]

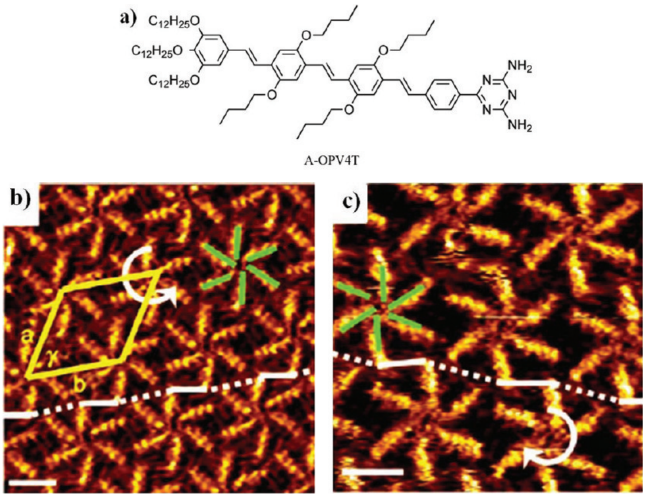

FIGURE 7. (a) Molecular structure of A-OPV4T. (b) A-OPV4T at the (*R*)-1-phenyl-1-octanol/HOPG interface. (c) A-OPV4T at the (*S*)-1-phenyl-1-octanol/HOPG interface.

Although 100% chiral induction is never observed, the measured enantiomeric ratios clearly indicate that solvent with a particular chirality clearly favors rosettes with either CW or CCW orientation. The lack of chiral induction in enantiopure 1-phenyl-1-octyl acetate indicates that the hydrogen bonding interactions between enantiopure 1-phenyl-1-octanol and A-OPV4T play a vital role in the induction process. The process of chiral induction probably involves interactions between the solvent and the rosettes, chiral desolvation processes, steric restrictions favoring order, or most probably a complex interplay of all these effects. A more probable justification is that the use of a chiral solvent favors the formation of transient solute–solvent complexes with a particular handedness on the surface.[11a]

The chiral modifier approach consists of employing an additional chiral solute to steer the (chiral) self-assembly: for instance, nucleoside-assisted self-assembly of achiral OPVs.[11c] A-OPV3T (Figure 8a) self-assembles into chiral cyclic hexamers and forms a racemic conglomerate at the 1-octanol/HOPG interface. In the absence of any chiral influence, an equal amount of CW and CCW rosettes is formed. The self-assembling pattern of A-OPV3T changes drastically in the presence of a nucleoside, D-thymidine. Figure 8b–e shows STM images obtained from mixtures of D-thymidine and A-OPV3T with varying mole ratios (molar ratio $R = [\text{D-thymidine}]/[\text{A-OPV3T}]$). A dynamic transformation from hexameric rosettes to dimers is observed. The surface coverage of rosettes decreases with time with a concomitant increase in the surface coverage of dimers. Furthermore, a strong dependence on the value of R is observed (Figure 8f)

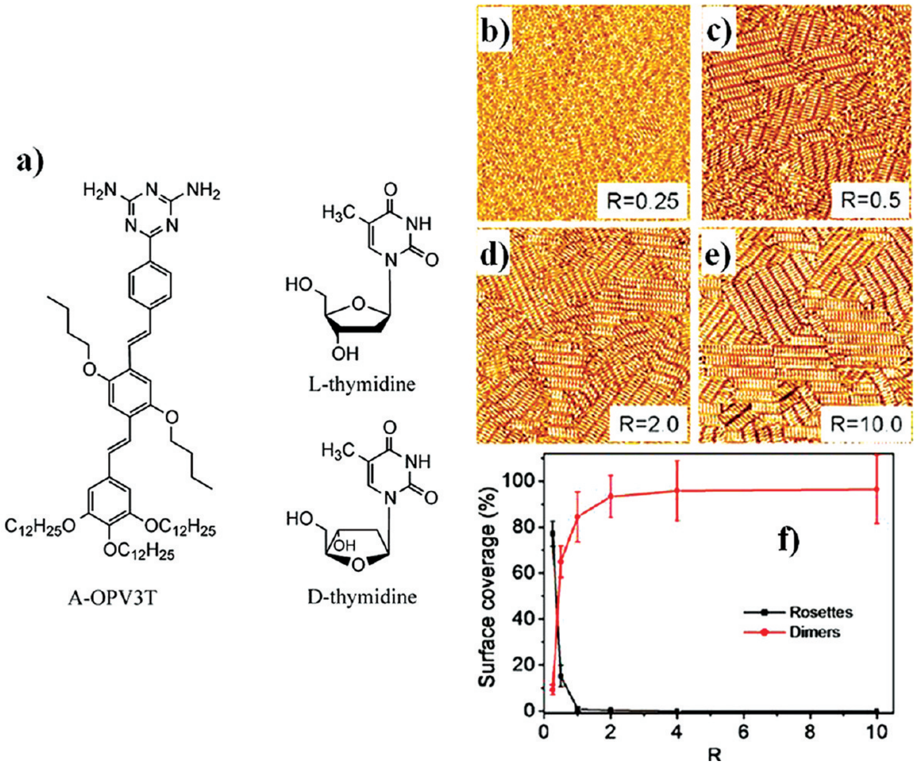

FIGURE 8. (a) Molecular structures of A-OPV3T, L-thymidine and D-thymidine. (b–e) Mole ratio dependent transformation of A-OPV3T at the 1-octanol/HOPG interface with increasing proportion of D-thymidine. Image size 80 × 80 nm. (f) Surface coverage of rosettes and dimers as a function of *R*.

with the rosettes completely disappearing at the cost of the dimers at $R = 10$. All the dimers are oriented CCW, defined as the direction of dimers against the normal of the row axis.

Most importantly, the orientation of the dimers formed from a combination of A-OPV3T with L-thymidine is CW indicating the influence of opposite handedness of the chiral handle on the self-assembly. Moreover, comparison of the unit cell parameters at different values of *R* indicated that thymidine molecules are incorporated in the monolayer. These results clearly indicate that thymidines are able to interact with A-OPV3T and in addition to the structural transformation from rosettes to dimers they also transfer their chirality to the otherwise achiral monolayer by incorporating themselves in the monolayer.[11c]

The chiral induction for A-OPV3T involved the use of stoichiometric amounts of chiral auxiliary. However, chirality can also be transferred via the so-called "sergeant-soldiers" approach wherein a small amount of chiral molecules transfer their chirality to a majority of achiral molecules turning the entire system chiral. The sergeant-soldiers principle has been successfully applied to induce and transfer chirality in solution[12] and on surfaces.[13] Recently, we adapted the concept of 2D chirality for the nanoporous networks formed by DBAs.[14]

Chirality in the hexagonal pores of DBA network is realized by considering the relative alignment (– or + type interdigitation, Figure 9b,c) of the four interdigitated alkyl chains per pair of DBA molecules. A virtual CW or CCW nanopore is formed by combining six – or + type interdigitation patterns, respectively, as shown in Figure 9c. The labels CW and CCW refer to the sense of rotation of the six alkyl chains making up the rim of the nanopore. Achiral DBA molecules self-assemble into mirror image chiral structures. Homochirality could be induced in such nanoporous networks either by self-assembly of homochiral building blocks via synthesis of chiral DBAs (cDBAs) or by self-assembly of achiral DBAs in presence of a cDBA via a hierarchical supramolecular chiral recognition process.[14]

The adsorption of enantiopure cDBAs at the 1-phenyloctane/HOPG interface indeed leads to the formation of homochiral porous monolayers as shown in Figure 9d, e. Thus, monolayers of cDBA-OC_{12}-(S) exhibit – type interdigitation pattern, exclusively giving rise to CW nanopores whereas those of cDBA-OC_{13}-(*R*) show only + type interdigitation thus forming CCW pores., The possibility of chiral induction by employing "sergeant-soldiers" approach was evaluated by employing the chiral DBA, cDBA-OC_{12}-(S)-OC_{13}-(*R*) (Figure 9a) bearing alternating (*S*)-OC_{12} and (*R*)-OC_{13} chains with opposite absolute

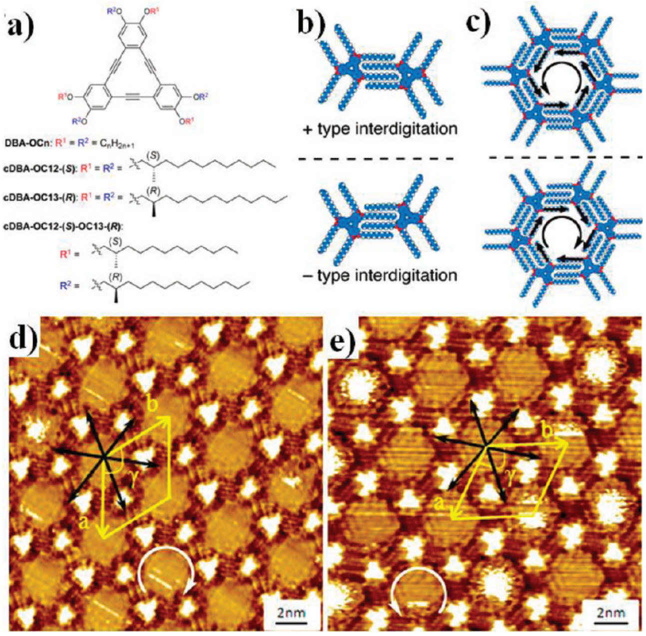

FIGURE 9. (a) Molecular structures of achiral and chiral DBAs. (b) Molecular models for the + (upper) and − (lower) interdigitation motifs. (c) CW or CCW rotation of a nanopore. (d, e) HR-STM images of monolayers formed by (d) cDBA-OC_{12}-(*S*) and (e) cDBA-OC_{13}-(*R*).

configurations as a sergeant . This structural design ensures that all the methyl groups attached to stereogenic centers are oriented in the same direction with respect to the molecular plane. Considering that the adsorption geometry with all the methyl groups facing down is unfavorable, the adsorption face of this cDBA could be uniquely controlled.[14]

Chiral induction experiments carried out by premixing cDBA-OC_{12}-(S)-OC_{13}-(*R*) and achiral DBA-OC_{12} (molar ratio of 1:10) indicate exclusive formation of CW honeycombs as shown in the STM image in Figure 10c. Perfect chiral induction was achieved by using 9 mol % of the chiral auxiliary. The cDBA molecules could be identified in the monolayer by their peculiar appearance as shown in the inset of Figure 10c. Increase in the mole percent of cDBA-OC_{12}-(S)-OC_{13}-(*R*) in solution, on the other hand, leads to an increase in the fraction of distorted hexagonal structures (Figure 10d) which is consistent with the observation that pure cDBA-OC_{12}-(S)-OC_{13}-(*R*) itself forms distorted hexagonal structures.[14]

The remarkable success of the sergeant-soldiers approach in this case could be explained by invoking a hierarchical chiral induction mechanism. A CW honeycomb structure composed of five DBA-OC_{12} molecules and one cDBA-OC_{12}-(S)-OC_{13}-(*R*) shows perfect interdigitation at all sites. On the other hand, the CCW honeycomb structure suffers from an energy penalty of 6.32 kcal mol^{-1} relative to

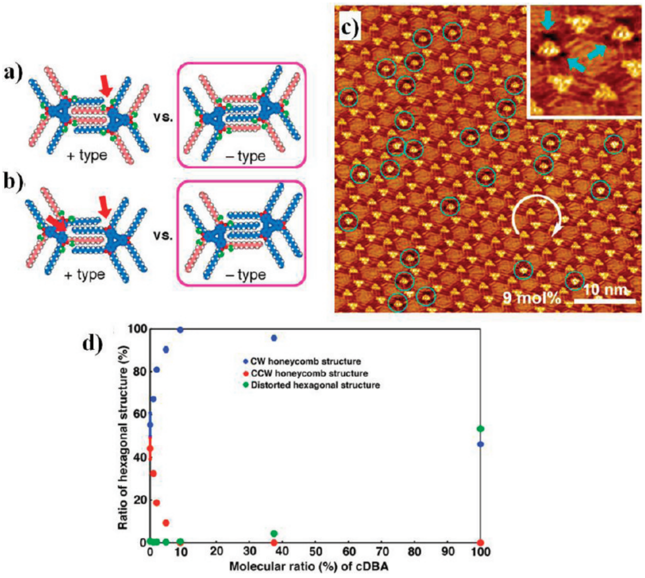

FIGURE 10. (a, b) Schematic of + and − type interdigitation patterns formed by (a) two cDBA molecules and (b) heterodimer of cDBA with achiral DBA-OC_{12}. Higher van der Waals contact favors the − type. (c) Monolayer obtained from cDBA-OC_{12}-(*S*)-OC_{13}-(*R*) and DBA-OC_{12} at 1:10 mixing ratios (9 mol % cDBA). Turquoise circles represent the cDBA molecules. Inset: Enlarged area of (c) with turquoise arrows pointing to the black contours surrounding the cDBA molecules. (d) Plot showing the induction of 2D chirality.

the CW structure due to a mismatch in alkyl chain interdigitation because of different chain lengths. The strength of the chiral modifier thus lies in the mismatch of the interdigitation pattern upon formation of CCW hexagonal structures, and thus, the presence of a single cDBA-OC_{12}-(S)-OC_{13}(*R*) molecule forces the remaining achiral molecules to form a CW honeycomb network.[14] These findings reveal the importance of long-range supramolecular recognition processes for successful chiral induction in a wide variety of 2D systems.

V. Stimulus Responsive Supramolecular Systems

The weak and reversible nature of supramolecular interactions inherently warrants stimulus responsive properties. Since controlled and reversible molecular manipulation is a key step in realizing future generation molecule based devices, a number of studies have focused on extracting reversible response from adsorbed molecules.[15] Different stimuli such as STM tip induced manipulation,[15a] optical excitation,[15b] temperature,[15c] and electric field[15d,e] have been used to induce controlled and reversible changes in the molecular patterns adsorbed at the liquid–solid interface. Recently, we exploited the delicate balance between long-range electrostatic (repulsive) intermolecular interactions and short-range molecule–substrate van der Waals

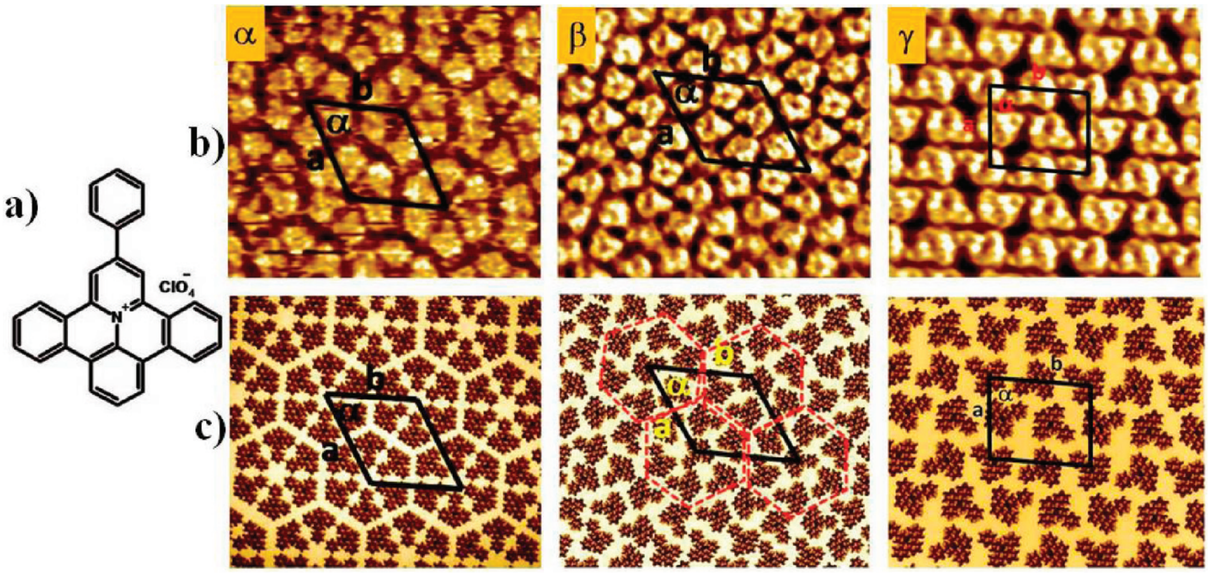

FIGURE 11. (a) Molecular structure of $PQPClO_4$. (b) STM images showing different supramolecular patterns (α, β, and γ) formed by $PQPClO_4$ at the 1-octanoic acid/HOPG interface. α and β phases can be reversible interconverted by supplying electric stimulus whereas γ phase is metastable and gets transformed into β phase in a time dependent fashion. (c) Proposed molecular models for α, β, and γ phases.

(attractive) interactions to realize reversible switching in the monolayers of a charged discotic polycyclic aromatic hydrocarbon (PAH), $PQPClO_4$ (Figure 11a) at the liquid–solid interface.[15e]

The supramolecular scaffolds of $PQPClO_4$ could be reversibly switched between dissimilar polymorphs of different molecular densities (α and β) as shown in Figure 11b. This reversible interconversion which occurs almost instantaneously (few seconds) could be effected by either changing the substrate bias by large values ($\geq$300 mV) or by applying voltage pulses to the STM tip. In both instances, a sudden large change in the electric field surrounding adsorbed ions acts as a "trigger" to induce the transformation. Besides these two phases, a third phase (γ) could also be observed as a metastable phase indicating rich self-assembling properties of these charged molecules. The metastable nature of the γ phase coupled with its slow time-dependent transformation (several seconds to few minutes) into β phase further gives indirect evidence for 2D dynamics which is a desirable property for potential applications. Considering the prevalence of substantial surface dynamics in this system, once the transformation is induced locally, it is probably transmitted via cooperative mechanism similar to what has been observed in numerous ionic self-assembly processes. These results highlight the utility of STM not only as a visualization technique but also as an active manipulation tool at the nanoscale.[15e]

The electrical stimulus supplied to the PQP monolayers induced molecular rearrangement in a reversible fashion. However, the energy provided by such external stimulus could also be used to carry out chemical changes in the adlayers to produce 1D or 2D polymers which can be monitored in situ using STM. In particular, the supramolecular self-assembly approach is useful since by using various interactions one can place reactive functional groups in close proximity thereby providing favorable conditions for a reaction. The research on surface reactivity and catalysis has already garnered considerable attention, and a few contributions have already demonstrated the viability of inducing and/or studying various reactions on surfaces in an STM setup.[16]

VI. Summary and Outlook

The research on molecular self-assembly at the liquid–solid interface has witnessed a paradigm shift from mere serendipitous observations of self-assembled networks to meticulous induction of well-defined patterns. Although a lot more needs to be unravelled so far as the basics of surface supramolecular self-assembly are concerned, attempts have already begun to implement the acquired knowledge to construct highly complex supramolecular architectures. By specifically engineering functional group via covalent approach, it is now possible to control the noncovalent interactions and thus the supramolecular patterns. This has important implications in the construction of multicomponent architectures and induction of 2D supramolecular chirality. With the ability to precisely position the functional groups in a predesigned fashion, we are now tantalizingly close to realizing 2D covalent polymers, the growth of which could be induced and monitored in situ by employing STM.

After a little over a decade of its inception, the molecular self-assembly approach at the liquid−solid interface is expected to deliver on various fronts. This approach has already provided a myriad of surface-confined self-assembled modules which contribute significantly to the bottom-up nanofabrication process. The sustainability and future of this research will largely depend on whether or not these 2D architectures could be integrated into real-life functional nanosystems. Robustness of the supramolecular networks poses a main challenge in using such weakly adsorbed molecular modules for real-life applications. Covalent binding within the surface-confined molecules and the grafting of such 2D polymers on the surface appear to be promising avenues for pursuing applications such as templated synthesis, molecule-based separations, and sensors. Second, although the controlled and reversible manipulation in molecular adlayers has paved the way for molecule-based storage devices and switches, connecting this molecular circuitry to the outside world and amplification of the nanoscale response remain challenging aspects. Finally, in a broader context, there is need to integrate this approach with material science and physics in general which will facilitate the fabrication of surface-based composite materials and their integration into molecular devices. It is our hope that the insights gained from the work carried out to date will one day lead to real-life functional supramolecular systems.

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FOOTNOTES

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