Molecular Assembly and Self-Assembly[a]

Molecular Nanoscience for Future Technologies

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ABSTRACT: In this review the emerging science of single molecules is discussed in the perspective of nanoscale molecular functions and devices. New methods for the controlled assembly of well-defined molecular nanostructures are presented: self assembly and single molecular positioning. The observation and selective modification of conformation, electronics, and molecular mechanics of individual molecules and molecular assemblies by scanning probes is demonstrated. To complement this scientific review, some of the possible consequences and visions for future developments are discussed, as far as they derive from the presented systems. The prospects of nanoscale science to stimulate technological evolution are exemplified.

KEYWORDS: molecular self-assembly; conformational switch; molecular adsorption; molecular nanotechnology from the bottom-up

NANOSCALE SCIENCE

With the emergence of the prefix *nano* in science and technology, many established fields were revisited and interdisciplinarily integrated to achieve new scientific and technologic goals. In this article, we first give a brief account of the evolution of molecular nanoscience from its roots in *biological systems*, man made *supramolecular chemistry*,[1–2] and *physical self-assembly and growth*. Then, in the main part of this review, we introduce two new principles of molecular self-assembly and layering: (1) conformational adaptive epitaxy, which is a consequence of the internal *conformal* flexibility of a molecule, and (2) a new mode of self-assembly that leads to so-called *self-intermixed monolayer phases* and derives from a delicate balance between electrostatic and Van der Waals interaction between static and fluctuating charge distributions of polar and polarizable molecules. In the final part of this article we discuss the scientific findings presented in terms of their technologic potential

and justify the high priority that has been given to molecular nanotechnology by governmental funding agencies and corporate research strategies.

Motivation

Functional devices, as they rule present day electronics, are mainly prepared by *top-down* methods starting from the bulk silicon single crystal and they involve only some *bottom-up* elements, such as material deposition and dopant implantation. Although the cost effective miniaturization of these devices remains the core target, hopes have evolved that *bottom-up* assembly of functional molecular elements and devices will allow for smaller functional elements with the possibility of reproducible integration. Among the milestones in this context are: the development of molecular electronics, the first imaging of atoms in real space by STM, and the first artificial written structure *IBM* by positioning Xe atoms on an ultracold metal substrate. Functional molecular electronics (e.g., organic light emitting diodes[3–4] and thin film transistors[5–6]) have been manifest for *thin films* many times thicker than one monolayer. This article now tries to account for the research that has been targeted at the behavior of single functional molecules at contacting interfaces. In our view, this is a major challenge in molecular science today since it evolved from distinctively different traditional fields: bioscience, supramolecular chemistry, and surface and interface science.

Molecular surface science was determined by the pioneering discoveries of Langmuir–Blodgett films,[7–9] self-assembled monolayers,[10–12] and the first studies of molecular epitaxy and layering in ultra high vacuum.[13] Molecular layer self-assembly has been the basis for new applications, such as micro contact printing.[14] A universal definition of self-assembly in the context of this introduction was coined by G.M. Whitesides:[15] "Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by non-covalent bonds. Molecular self-assembly is ubiquitous in biological systems and underlies the formation of a wide variety of complex biological structures."

INDIVIDUAL MOLECULES AND MOLECULAR LAYERS IN CONTACT

Single molecules or molecular assemblies with functional properties need to be supported and addressed by—presumably electronic—contacts. Although molecules in liquid or gas remain unidentifiable within their statistic entity, their deposition by sublimation or evaporation on a well prepared and atomically clean substrate (for an example, see Ref. 16) allows for individual identification and tracking. This is a prerequisite for the assembly and operation of molecules in single molecular devices, whatever function we envision. Self-organized nanostructures of an even higher complexity can be assembled by using substrates that are themselves produced by hetero epitaxial self-organization: periodic (vicinal) step edges provide a template for selective decoration of *nanowire patterns*. Material systems with mixed magnetic–nonmagnetic metal–insulator or semiconducting properties have been realized,[17] and chemically selective deposition of a molecular adsorbate has been demonstrated.[18] After immobilization of molecular submonolayers on such well
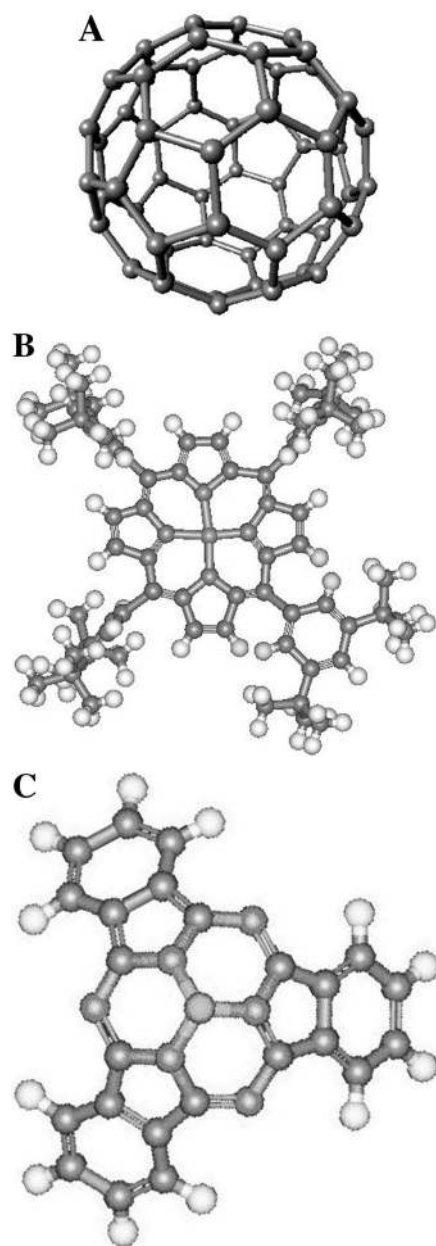
FIGURE 1. Chemical structure of **(A)** the Buckminster carbon-fullerene C_{60}, **(B)** of Cu-tetra-[3,5 di-*t*-butylphenyl]-porphyrin (Cu-TBPP), and **(C)** of chloro-[subphthalocyaninato]boron(III) (SubPc). The molecular diameters are 1 nm, 1.3 nm, and 1.5 nm, respectively, and all three molecules have large delocalized π-systems that are responsible for the Van der Waals attraction between the adsorbates and the substrates.

prepared and characterized substrates, scanning probe microscopy (SPM) provides the "eyes" and the "hands" for performing experiments with individual molecules and molecular assemblies. A large number of innovations, among them the above-mentioned thiol derived SAM and the LB systems, were discovered and demonstrated without the assistance of SPM. Here, however, SPM provided a more detailed picture of the mechanisms on the atomic or molecular level and helped to gain control of many parameters like defect densities.[19,20] Beyond imaging, SPM also allows the selective application of electric fields, currents, and a variety of forces to manipulate atomic or molecular objects. This review focuses on the self-organization of a well-known class of molecules, C_{60} Buckminster-Fullerenes (see FIGURE 1A), and porphyrins (FIG. 1B), as well as their close relatives, substituted phthalocyanines (FIG. 1C). All the layers shown were prepared by sublimation in ultra high vacuum, where the lack of a gas or solvent environment enables direct comparison of the experimental results with numerical simulations. Atomically clean substrates were prepared by using surface science techniques: sputter–anneal cleaning cycles followed by characterization using LEED, XPS, and STM.

STM: THE EYE TO INVESTIGATE MOLECULAR EPITAXY AND LAYERING

A prerequisite for the formation of epitaxial layers is the diffusive mobility of the adsorbate during or after the deposition of molecular adlayers. On semiconductor substrates, the strong and directed covalent bonds between the adsorbate and the adsorbent atoms often inhibit the growth of periodic and defect free layers. There, molecules have been imaged and show interesting characteristics that, for example, allow the identification of molecular orientation and bonding.[21–23] In the case of metal substrates with lower reactivity, such as the noble metals Au and Ag, or Cu, the diffusiveness of the molecule on the substrate allows the observation and analysis of quite different phenomena: the molecules "feel" the corrugation of the substrate, and the lateral random-walk diffusion of a single adsorbate is determined by the corrugation of the potential energy surface (surface potential) of the adsorbate–substrate complex and by the kinetic energy available for hopping between stable adsorption sites. For Cu-TBPP adsorption on Ag(110) a complex adsorption behavior with fast diffusing precursor and slowly moving final adsorption states has been observed.[24] The diffusion of the adsorbed molecule is confined to discontinuous one-dimensional motion within atomic trenches formed by an adsorbate induced 6×1 reconstruction of the substrate, which is accompanied by conformational flexure of the molecule. This change of the diffusion pattern is caused by the different surface potential. Alternatively, Schunack et al.[25] demonstrated that two similar organic molecules, DC and HtBDC, on a Cu(110) surface exhibit distinctively different diffusion behavior. This is a consequence of the altered substrate–adsorbate interaction by the additional substituant of the HtBDC that is in contact with the adsorbate. Depending on temperature and intermolecular interaction, condensation of two-dimensional islands with lattice registry, or more diffusive gas phases can be identified. FIGURE 2A shows the condensation of a small molecular Cu-TBPP island in a chessboard-like overlayer structure. The opposite case is shown in FIGURE 2B, where we can identify a two-dimensional supramolecular island of SubPc that coexists with a two-dimensional

mobile gas phase. Notably, from the analysis of time-lapse imaging sequences, the hopping rate of the molecules was estimated to be of the order of $1/30\sec^{-1}$ at room temperature. A detailed account of two-dimensional mobile phases and of molecular diffusion on solid substrates is given in a recent paper by S. Berner.[26] Molecular *self-organization* generally leads to two-dimensional supra-structure islands with the lattice registry dictated by the substrate, quite different in spacing and symmetry from the bulk.

STM: THE HANDS TO MANIPULATE SINGLE MOLECULES

Beyond imaging and tracking of the individual diffusive adsorbates in thermodynamic equilibrium, SPM also allows molecular objects in non-equilibrium scenarios to be addressed. In FIGURE 2C we show the first successful supramolecular assembly by STM tip induced molecular repositioning made at room temperature. Here, the lateral diffusion barrier has been overcome by lateral thrusts of the STM tip in a *high proximity* mode at low gap voltages and high currents. By comparing numerical simulations and experimental data, it has been shown that the conformational flexibility of the Cu-TBPP molecules by torsion of the phenyl–porphyrin bond leads to a significant lowering of the diffusion barrier of this molecule on the Cu(100) substrate. The details of this technique can be found elsewhere.[27]

Very much like the examples listed in the introduction, molecular repositioning depends on a delicate balance of surface–molecular and intermolecular interaction forces. It is a prerequisite, that the forces exerted by the tip in modification conditions can override the barrier for lateral movement, but also that this barrier is high enough to resist room temperature diffusion. In addition to the repositioning of flexible prphyrins, other systems, mainly based on C_{60}, have also been found to meet these requirements.[28–29] Additional details of the repositioning mechanism have been resolved by recording the tunneling current during the manipulation in experiments at low temperatures[30] and at room temperature.

Both of the above findings, epitaxy and repositioning, were first observed for atoms at very low temperatures.[31] However, atoms are often too sticky to be played with and low temperature is a requirement for their stable repositioning.[b] Another manipulation technique for single molecules are optical tweezers (see the review Single Molecule Imaging and Manipulation by M. Hegner and A. Engel), where the objects are clamped with the aid of laser light.

CONFORMATIONAL SELF-ASSEMBLY AND DYNAMICS:
MOLECULAR MECHANICS

The special quality of a molecule is, however, that in its entity, it can be modified by synthetic chemists so that its interaction with both the tip and surface are specially designed and controlled, even at low temperature. Thus, weak bonds to the substrate can be maintained. Such synthetic molecules can also be used as building blocks for

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[b]Note added in proof: Very recently R. Bennewitz *et al.* achieved reliable atomic repositioning at room temperatures; see R. Bennewitz, J.N. Crain, A. Kirakosian, *et al.* Atomic scale memory at a silicon surface. *Nanotechnology,* **13**(4): 499–502 (2003).
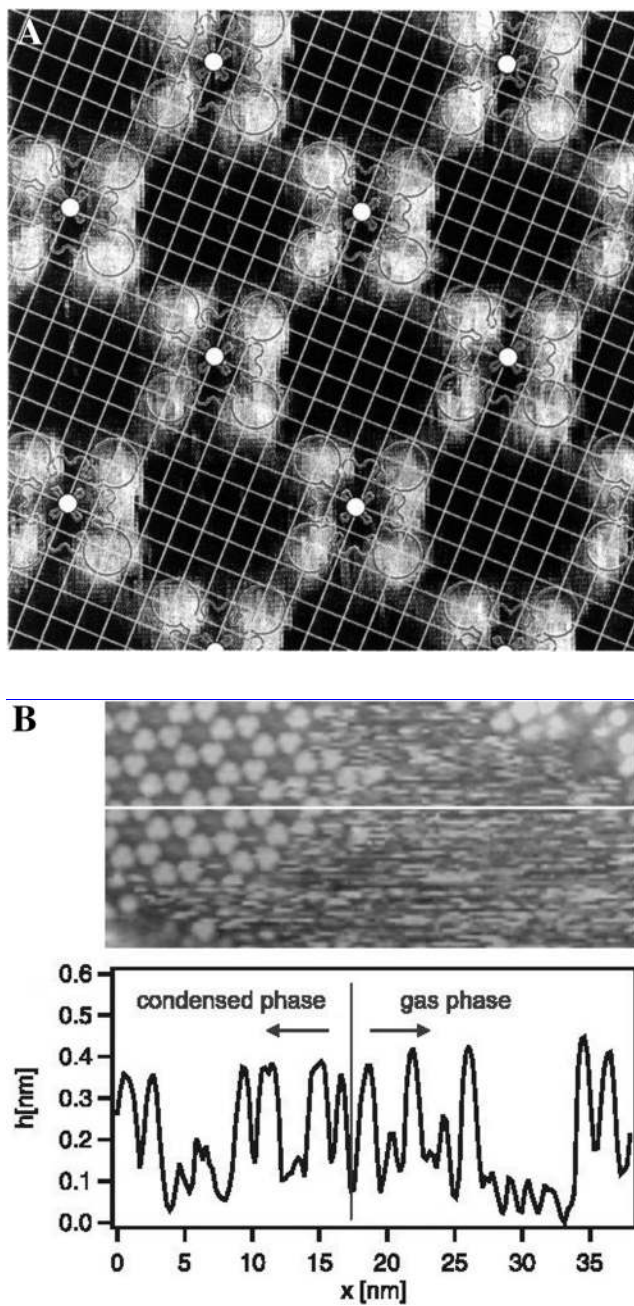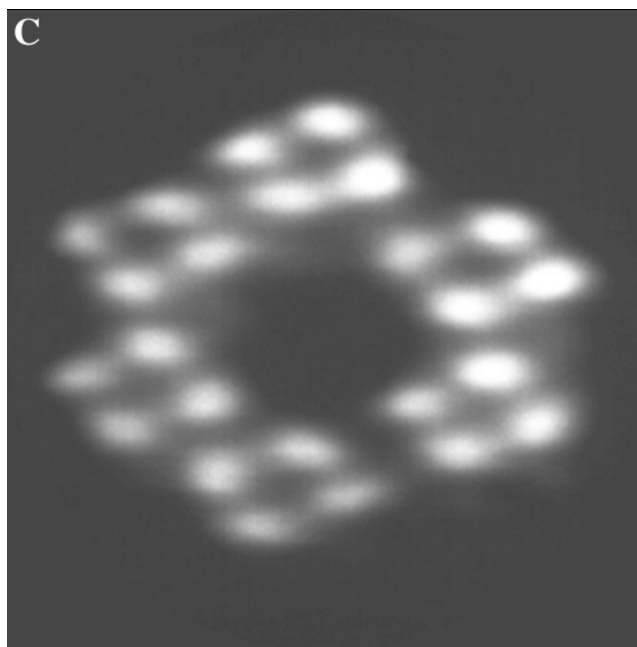
FIGURE 2. Continued on opposite page.

FIGURE 2. A. STM image of a condensed Cu-TBPP-island on Cu(100) after anneal-ing at 250°C. Each of the molecules is resolved as four bright lobes with square symmetry. The positions of the molecular units in the two-dimensional overlayer is outlined (repro-duced from Ref. 39). **B.** Condensed subPc-island on Ag(111) surrounded by a two-dimen-sional gas-phase. The *white line* shows the location of the cross section, which is parallel to the fast scanning direction: single molecules are also clearly visible in the noisy pattern of the gas-phase. This strongly suggests that the molecules can hop to adjacent adsorption sites, but that the residence time on a particular adsorption site is comparable to the time required by the scanning tip to pass over a single molecule. Scan range, $38.4\,nm \times 18.9\,nm$; sample bias, $U = 0.85\,V$; tunneling current, $I = 12\,pA$. **C.** Image of an artificially created supramolecular structure, assembled by an STM tip. To move individual molecules the tip is placed near one molecule and the tunneling parameters are changed to manipulation. Then the tip is moved to the desired direction across the position of the previously imaged molecule. After switching back to imaging mode, the scan reveals a displacement of the molecule. The positions of all other molecules remain unaffected. After moving all mole-cules to the chosen places, the artificial hexameric ring is constructed.

artificial supramolecular structures, as has been exemplified.[32] One main difference between molecules and atoms, besides the aforementioned functionalization and stickiness, is their more complex shape, which essentially enables excitation of inter-nal conformational degrees of freedom. Molecular conformation has been one of the keys in bio- and life-sciences, where analytical methods like XRD[33] and NMR[34] have enabled the visualization and understanding of complex proteins, their struc-ture, function, and dynamics. Together with other experimental techniques, these studies raised the issue of molecular conformation and three-dimensional molecular

assembly in biomolecular aggregates and enzyme assemblies. For single molecular objects and small numbers of molecular assemblies, however, all these averaging techniques fail for lack of single molecule sensitivity. Other techniques, such as FIM, TEM, and HREELS, require a self-selective sample preparation that allows experiments restricted to very special preparation conditions.
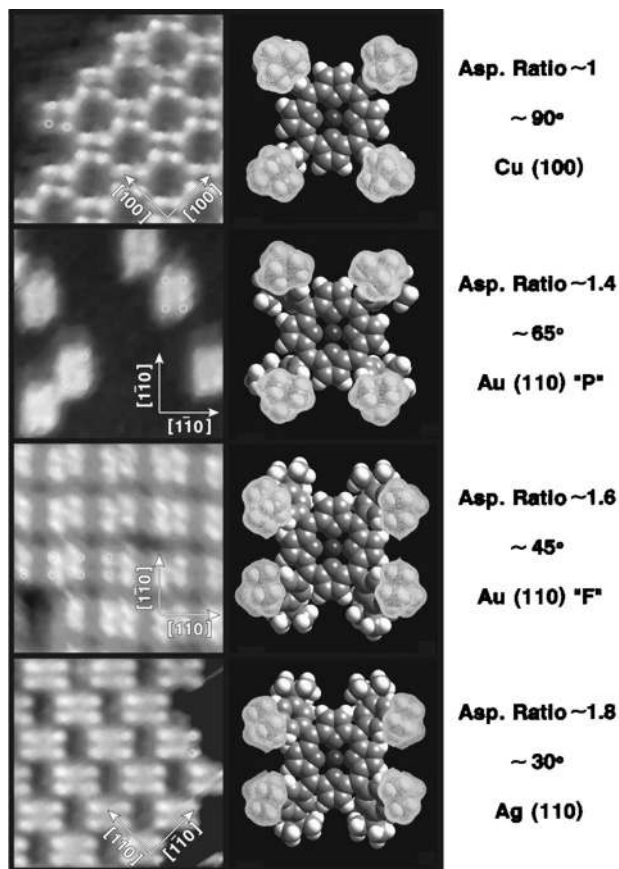

FIGURE 3. Molecular *epitaxial self-assembly* on a selection of metallic substrates. The overlayer symmetry and the orientation of each supramolecular adlayer island can be identified from the high (sub-molecular) resolution STM data. The four-lobed quadrilateral forms with varying substrate-dependent aspect ratio are clearly visible in the STM data (*left column*). The lobes can be identified as the uppermost *t*-butyl groups of each of the four large (about 1 nm) substituents. In the models shown in the *center column*, the four bond angles of the phenyl-porphyrin bonds of each molecule have been determined so that the conformation of the model corresponds to STM data. The experimentally determined aspect ratio and the resulting bond angles are listed in the *right column*, together with the substrate type and orientation. This contrast change reflects shifts of the electronic states of the porphyrin groups and their coupling to the substrate.

In the following paragraph, molecular conformation of surface adsorbates is discussed, its recognition by scanning probe microscopy, as well as its adaptation, dynamics, and switching. In FIGURE 3, the conformational flexure and identification of Cu-TBPP as it is deposited on a selection of metallic substrates is shown. For this molecule, the primary conformational degree of freedom consists of the rotation around the four phenyl–porphyrin dihedral angles. This rotation brings the π-systems
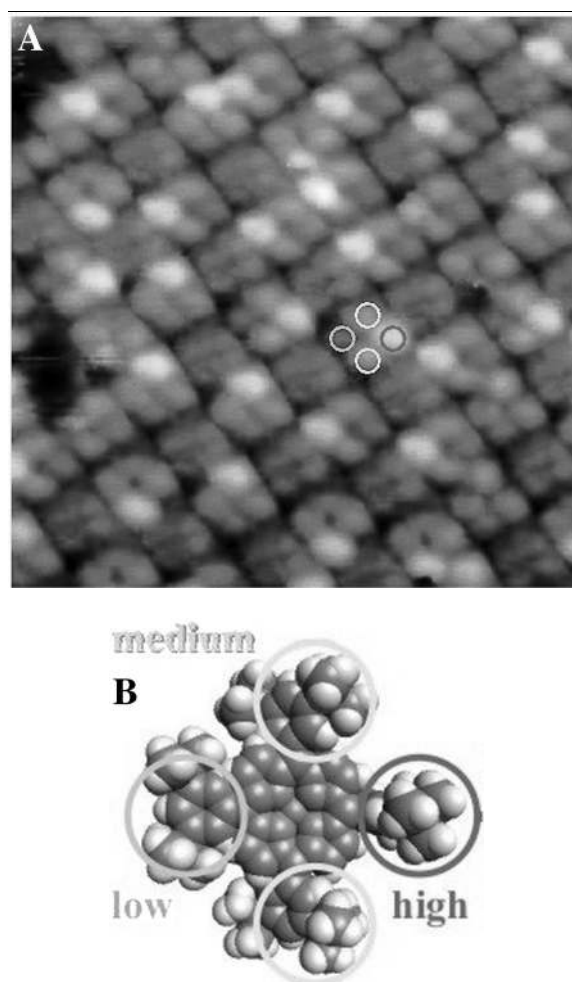

FIGURE 4. A. STM image of a condensed Cu-TBPP-island on Ag(100). The molecules are adsorbed with asymmetric conformation. Individual ligands are turned with different angles and, therefore, appear with specific brightness in the STM images (The three observed heights are marked with *circles*). Image size, $12 \times 12 \, nm^2$; sample bias, $U = 1 \, V$; tunneling current, $I = 40 \, pA$. **B.** Model of the deformed molecule, adapted to the Ag(100) surface, shows the rotation of the TBP groups around the σ-bonds.

of the ligands closer to overlap with the π-systems of the porphyrin-core. The full rotation is sterically hindered by the overlap of the porphyrin and ligand hydrogen atoms (FIG. 1 B). This conformational change can be observed when the ligands turn out and the porphyrin π-system gets closer to the metallic substrates, so that the square symmetry of the molecule is broken. The aspect ratio of the rectangular shape of one molecule can be used to estimate the bond angle of each molecule.[35]

Experimental sequences reveal that other molecular properties change in conjunction with conformational flexure: the overlap of the π-electronic states with metallic states and the diffusibility of the molecules are the most prominent examples. FIGURE 4 A demonstrates that conformational flexure can go beyond a static phenomenon. The asymmetric conformation of Cu-TBPP within a monolayer as deposited on Ag(100) changes repeatedly within a time-lapsed sequence of images. We speculate that the overall strain in the monolayer, which is a consequence of the strong molecule–substrate interaction, leads to an asymmetric conformation (FIG. 4 B) because the substituents can more closely pack in this conformation. This view is supported by the observation that neighboring molecules show correlated shape changes: the high substituent hardly exists in the nearest neighbor positions. These results give clear evidence about the flexure and dynamics of the conformation of a molecule. In our ongoing studies, we have also reproducibly observed the repeated pinning and depinning of Cu-TBPP molecules by STM.[36] Two other groups have further refined this picture of the underlying process by performing these experiments at ultralow temperatures[37] and by using an atomic force microscope (AFM) to measure the forces.[38] With an AFM, the force to bend down a single leg by the pushing tip can directly be measured.

In a more general sense, the observation of conformational effects for single molecules is an astounding achievement in experimental molecular science and may give us even deeper insight into processes that occur at surfaces and play a fundamental role in catalysis, molecular electronics, optoelectronics, and tribology. For the nanoscale sciences, most importantly, the relation between chemical structure and property or function has to be studied for these molecules. This is in close analogy to one of the paradigms of molecular biology, with one additional complication: molecular nanostructures for electronic, optoelectronic, and mechanic operation need to be supported and contacted. The findings presented in this paper suggest that either property of a nanoscale molecular device emerges from the molecule and its interaction with the substrate; for example, conformal self-assembly, chemical bonding, and charge transfer.

SELF-INTERMIXED MONOLAYER PHASES

Although there is powerful means to reposition atoms and molecules at surfaces from the bottom up, it remains a challenge to handle a large number of atoms and organize them into structures with a high level of complexity. Despite powerful developments in SPM parallelization like the IBM Millipede© device, the piece-by-piece assembly and integration of functional nanostructures and devices is not a currently promising approach for the assembly of integrated molecular structures. In a technologic sense the bottle-neck is the speed or bandwidth (order of kHz) of our

current tools, the scanning probe microscopes, that serve as the major instrumental links between the nano and the human world. Construction of a device with 10^6 elements in a Gedankenexperiment (for example Cu-TBPP porphyrins as conformally bistable storage elements) through molecular requires about one million strokes. Each of these strokes would require a molecular drag and drop procedure, which at the moment can be achieved in just under one minute for each molecule that leaves our Gedankenexperiment to be achieved on the timescale of 700 days when using current sequential nanotechnology. This is undoubtedly not an adequate method to construct a complex device with millions of elements (a state of the art Pentium 4 consists of 42 million transistors [MOSFETS] that work at 2.2 GHz). This is the flip side of the visionary statement: "There is plenty of room at the bottom" made by R.P. Feynman in the 1960s and which we would translate to: "There are plenty of atoms in the wiring for submicrometer technology." Although we have reached "the bottom" in our current research, it remains difficult to make both ends meet and communicate from the level of bistable molecules up to the level of integrated electronic structures and macroscopic wires.

A promising way to overcome this obstacle is the self-assembly of mesoscopic structures. A completely new scheme for the self-organization of molecular patterns at the solid vacuum interface has been recently discovered.[39] Unlike all other modes of molecular self-assembly, the molecules here form two-dimensional periodic superstructures with an exceptionally high fraction of vacant adsorption sites. This is achieved by co-sublimation of two different molecules, one polar, the other highly polarizable, on a relatively inert metallic substrate in UHV. The two component, chloro-[subphthalocyaninato]boron(III) (SubPc) (see FIG. 1 C) and carbon fullerene (C_{60}) (see FIG. 1 A), co-deposited onto Ag(111) show a spectacular growth behavior. The growth and self-organization of this mixed monolayer is completely different from the pure monolayer islands of either component sublimed onto the
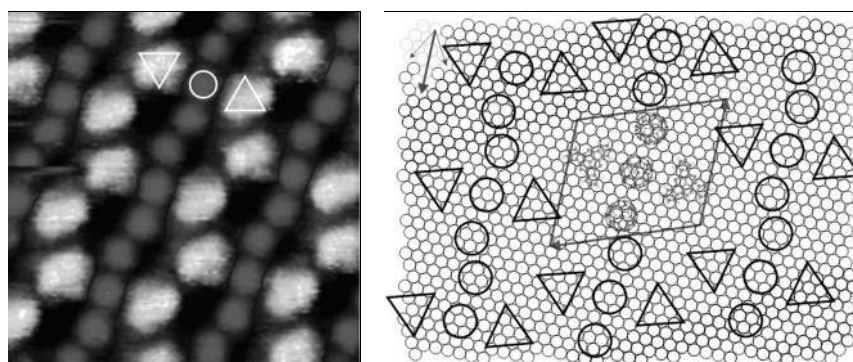

FIGURE 5. Self-intermixed monolayer phase, C_{60} and SubPc (see FIG. 1 A and C) codeposited on Ag(111), intermix and form a strongly anisotropic pattern. The C_{60}s are adsorbed in a quasilinear arrangement, and the SubPcs act as spacers between these C_{60} lines. Image size, 9.7×9.7 nm^2; sample bias, $U = 1.9$ V; tunneling current, $I = 20$ pA. On the *right*, the proposed model of the registry on Ag(111) is shown. The positions of the C_{60} and SubPc molecules and the orientations of the latter are depicted inside the unit cell.

same substrate.[26] In typical room-temperature STM images (see FIGURE 5 left), individual molecules can be clearly identified by their size and characteristic triangular or spherical shapes that agree with STM studies of the single-component monolayers. In the proposed model (FIG. 5 right), the positions, orientations and shapes of the molecules can be seen. Due to attractive intermolecular interactions, the two kinds of molecules are periodically intermixed and not segregated into two separate phases: the C_{60} molecules are arranged in quasilinear rows, whereas the SubPc molecules form a zigzag spacer row. The self-intermixed assembly observed here relies crucially on sufficient mobility of each component at the deposition temperature. Remarkably, a significant fraction of the surface remains uncovered between the SubPc molecules (the underlying Ag substrate appears black), leading to a loosely packed superstructure. The feasibility of manipulating molecules within these spacings opens the possibility to store data by modification of specific self-assembed molecular patterns.

NANOTECHNOLOGY: OPPORTUNITIES AND VISIONS ON SCIENTIFIC GROUNDS

To conclude, there are ample possibilities to organize and observe single, identifiable molecular objects when they are organized at surfaces. Using SPM as eyes and hands, molecular organization and diffusion can be observed, molecules can be locally organized and probed in their electronic, mechanic, and optic interaction with the environment. In particular, the observed time lapse imaging sequences provide visual information about diffusion and conformation dynamics that would not have been imagined before the invention of SPM, and are only believed after many years of experimental consolidation. The rapid evolution and the confluence of scientists from many disciplines into nanotechnology has triggered many hopes. To produce ultrasmall structures that provide functionality to our decimeter world, two key problems need to be addressed: first, ultrasmall devices need to be manufactured, and second, they need to be interconnected and wired at least to the micrometer level that is accessible by state-of-the-art technology.

Molecular Level Data Storage

In a visionary context and on the basis of the key inventions described above, it seems plausible that there may be technologic implementations of single molecule storage on materials, as suggested by the SIMP material described above. The assignment of bits and bytes to the zig-zag rows is straightforward, whereas the read/write rates are further away from competitive technology.

Molecular Optoelectronics

For fundamental and applied reasons, the molecular bistability and conformational and positional switching, as shown in this review, is of high scientific and technologic interest. The reason is that, on a molecular level, molecular mechanics and electronics share the same origin. Redistribution of electrons in a molecule upon bonds formation and physical interaction with the substrate simultaneously affects

chemical reactivity, optics, and electronics, as well as the adsorbate structure. This is one of the most important results of the research discussed: the positional and conformational bistability of all systems presented above is not a consequence of a synthesized molecular switch, but of a complex behavior of a molecule when adsorbed in the surface potential of the substrate. Future experimental and theoretical efforts towards nanoscale devices need to investigate these complex interactions in more detail, in order to be able to predict functions for new "to be synthesized" systems.

To conclude, this article has given an account of our current scientific knowledge about single molecule behavior when adsorbed on a solid substrate. Mechanic, electronic, and optic properties of ad-molecules all depend on the collective electronic behavior of the substrate–adsorbate system. Methodologically, it seems worth noting that SPM-based techniques are the *only* techniques that allow us to observe the conformation, electronics, and mechanics of single molecules. To complement this scientific account, we have discussed some potential applications of nanotechnology. Most importantly, there is a huge potential for research and discovery, and this has motivated national and international research programs to collaborate with multinational corporations in one or the other domain of nono-science.

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