

STRUCTURE, DYNAMICS AND ELECTRONIC PROPERTIES OF MOLECULAR NANOSTRUCTURES OBSERVED BY STM

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ABSTRACT. A scanning tunneling microscope (STM) has been used to characterize molecular nanostructures at surfaces and solid-fluid interfaces on length and time scales of 10 pm and 10 μ s, respectively. We present the experimental set-up and describe imaging of solid surfaces under ambient conditions, including an organic conductor (difluoranthenyl-hexafluorophosphate), a layered semimetal (graphite) and a layered semiconductor (MoSe₂). We then discuss the determination of molecular structure and dynamics as well as electronic properties of molecular monolayers at solid-fluid interfaces. Finally, we give some perspectives for the modification of molecular nanostructures using an STM.

1. Introduction

Nanostructures based on molecular materials have attracted considerable interest [1]. Molecules can be viewed as extremely well defined quantum structures. They also may have some internal degrees of freedom, which could give rise to switching properties. Due to the richness of organic chemistry these building blocks can be largely varied, in order to exhibit a particular property profile. Provided they are not too complex, chemists can make them rather pure and in large quantities, and living organisms are able to make them even more complex. In order to obtain still more complex structures one may assemble the individual molecules into supermolecular structures, where, in general, the inter-molecular interactions are smaller than the intra-molecular ones. If designed properly such "self-assembled" molecular structures can be rather perfect. We report in the following on a number of relatively simple molecular nanostructures, and what one may learn about them using a STM.

2. Experimental

An analysis of the capabilities and limitations of STM for a quantitative characterization of molecular materials [2], as well as a review of the application of STM to molecular materials have been given recently [3]. The results reported below have been obtained with a home-built instrument, which was designed with an emphasis on *low currents* and *high scanning speeds*, since particular difficulties encountered with molecular materials include low electronic conductivities and high molecular mobility. Of interest is also the *temperature controlled* sample stage [4]. Between room temperature and up to 120°C the instrument allows atomic scale resolution with currents as low as 200 fA and scan speeds up to 1 ms per line. The images are recorded on video tape in real time and digitized later for digital image processing on a graphic workstation or for static image display.

All images have been recorded under ambient conditions using Pt/Ir or W tips, which were either electrochemically etched or mechanically formed. A schematic of the experimental set-up is displayed in Fig. 1. The images of the holes in graphite were obtained in the "constant current mode" (displayed is a height profile), whereas all other images have been recorded in the "constant height mode" (displayed is a current profile).

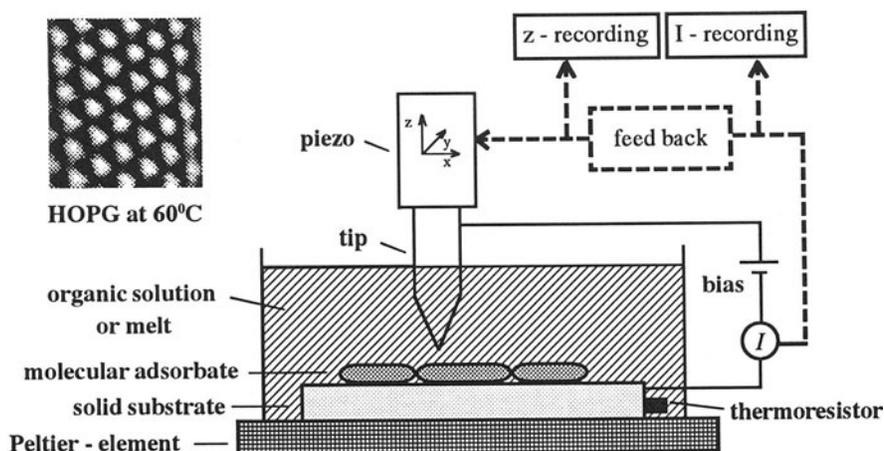


Fig. 1: Schematic of the experimental set-up [4].

3. Solid surfaces under ambient conditions

Surfaces of conducting solids may be investigated under ambient conditions, provided they are sufficiently inert. Examples include thin films of gold or silver, which, if evaporated onto mica at some elevated temperatures, exhibit (111) surfaces [5]. Since STM, per se, does not require any order it allows also to study non-crystalline materials. Interesting examples include conductive polymers, like, e.g., iodine doped polydiacetylene, whose fibrillar structure has been visualized by STM [6]. However, for use as substrates for ultrathin organic layers single crystalline materials have the advantage that their local atomic structure is precisely defined.

3.1. Organic Conductors

A class of molecular materials, whose surfaces can be directly investigated by STM are organic conductors. An example is given in Fig. 2, displaying an STM image and the corresponding model of the bc-surface of a single crystal of difluoranthenyl-hexafluorophosphate [7]. Even though no atomic resolution is achieved, the molecular columns are well resolved. Similarly, other single crystals of organic materials have been imaged before, including, e.g., tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) [8] or β -(BEDT-TTF)₂I₃ [9]. A common problem is the fact that the limited chemical and/or mechanical stability of these materials, since it is observed that the outer layers may be altered during prolonged scanning.

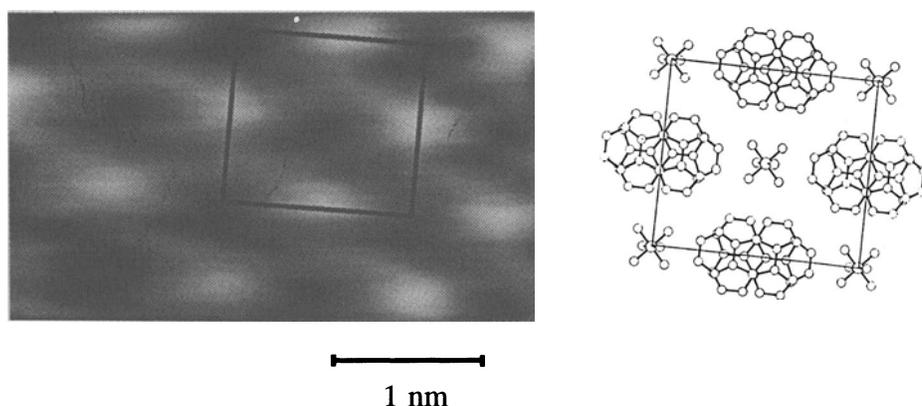


Fig. 2: STM image and model of difluoranthenyl-hexafluorophosphate [7].

4. Molecular Monolayers at Solid-Fluid Interfaces

A class of molecular nanostructures, which have been investigated quite systematically by STM, are monolayers of alkanes and alkyl-derivatives, self-assembled at the interface between the basal plane of HOPG and a melt or an organic solution [4,7,13-18]. Fig. 4 displays the structure of a monolayer of a simple alkane, adsorbed from phenyloctane solution and imaged in-situ by STM. It reveals a highly ordered monolayer with lamellae, in which the main axes of the flat lying molecules are oriented perpendicular to the lamella boundaries [14]. Upon closer inspection one notices a change in contrast along an individual molecule, while across the image each molecule appears identical. The contrast change along a molecule has been attributed to a moiré pattern caused by the linear carbon chains in the graphite and the alkane, respectively, reflecting the incommensurability of the two linear lattices [14]. On the other hand, the identical appearance of all molecules within the two-dimensional molecular pattern reflects the commensurability of the molecular adsorbate lattice with the substrate [7,13,14].

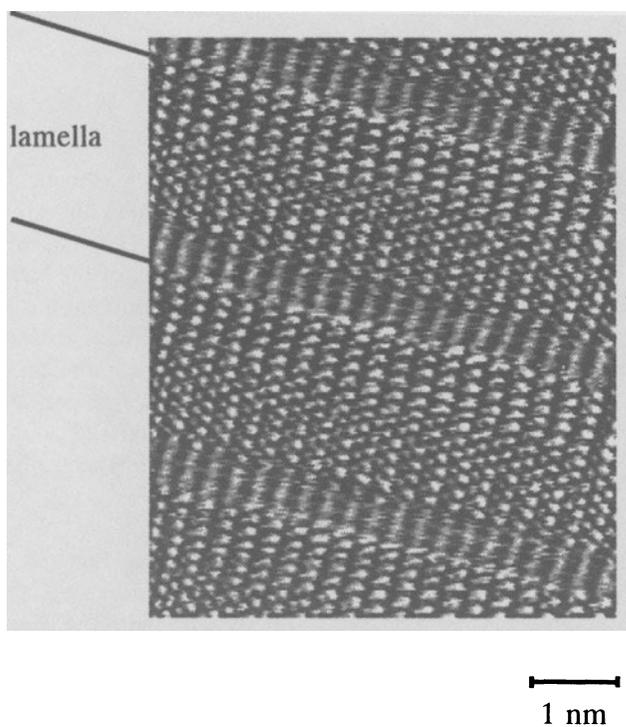


Fig. 4: STM image of a $C_{27}H_{56}$ monolayer on HOPG [7].

Similarly, highly ordered monolayers form at the interface between alkane solutions and MoSe₂ surfaces (Fig. 5). Interestingly, however, the molecular structure is different: While on HOPG the alkane chains pack with their long axis perpendicular to the lamella boundaries, on MoSe₂ this angle is 60° [11].

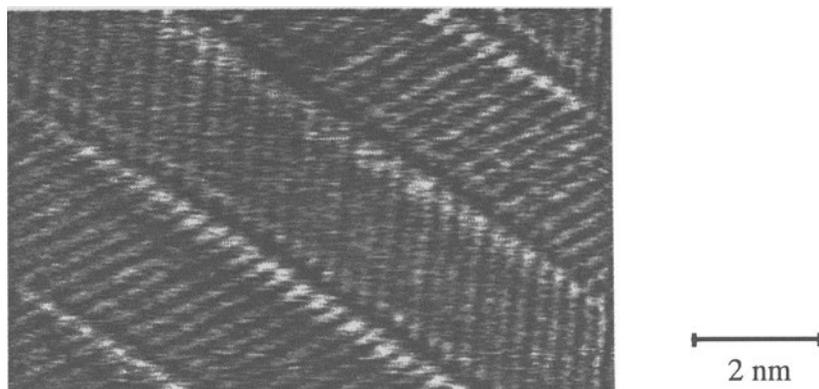


Fig. 5: STM image of a C₃₂H₆₆ monolayer on MoSe₂ [11].

Many other long chain alkyl-derivatives have also been shown to form two-dimensional molecular patterns at the interface between HOPG and organic solutions. Particularly interesting are the images of the fatty acids [14], because they exhibit a superstructure along the lamellae. Since the lattice constants of the substrate are very well known, the superstructure allows a very accurate determination of the molecular distances within the adsorbate layer. In the case of the fatty acids the interchain distance is about 50 pm larger than in the case of the alkanes and alkanols. The reason is that the alkyl carbon skeleton planes are oriented parallel or perpendicular to the graphite plane, respectively [14,15]. Moreover, domain boundaries could be imaged at sub-molecular resolution [14,16,17], and different mixed monolayer phases have been observed [17,18].

So far the images have been interpreted as static, assuming that the time scales of molecular dynamics and image recording are sufficiently different. However, it is also possible to observe molecular reorientations directly with the STM. Examples include the motion of domain walls in a dialkylated benzene [16], as well as cooperative tilt flips within alkanol [14] and alkane lamellae [15]. Fig. 6 shows the progressive roughening of alkane lamellae at the interface between HOPG and an organic solution upon raising the temperature. The data indicate a continuous increase in the amplitude of a motion along the long molecular axis until the lamellar order disappears [4].

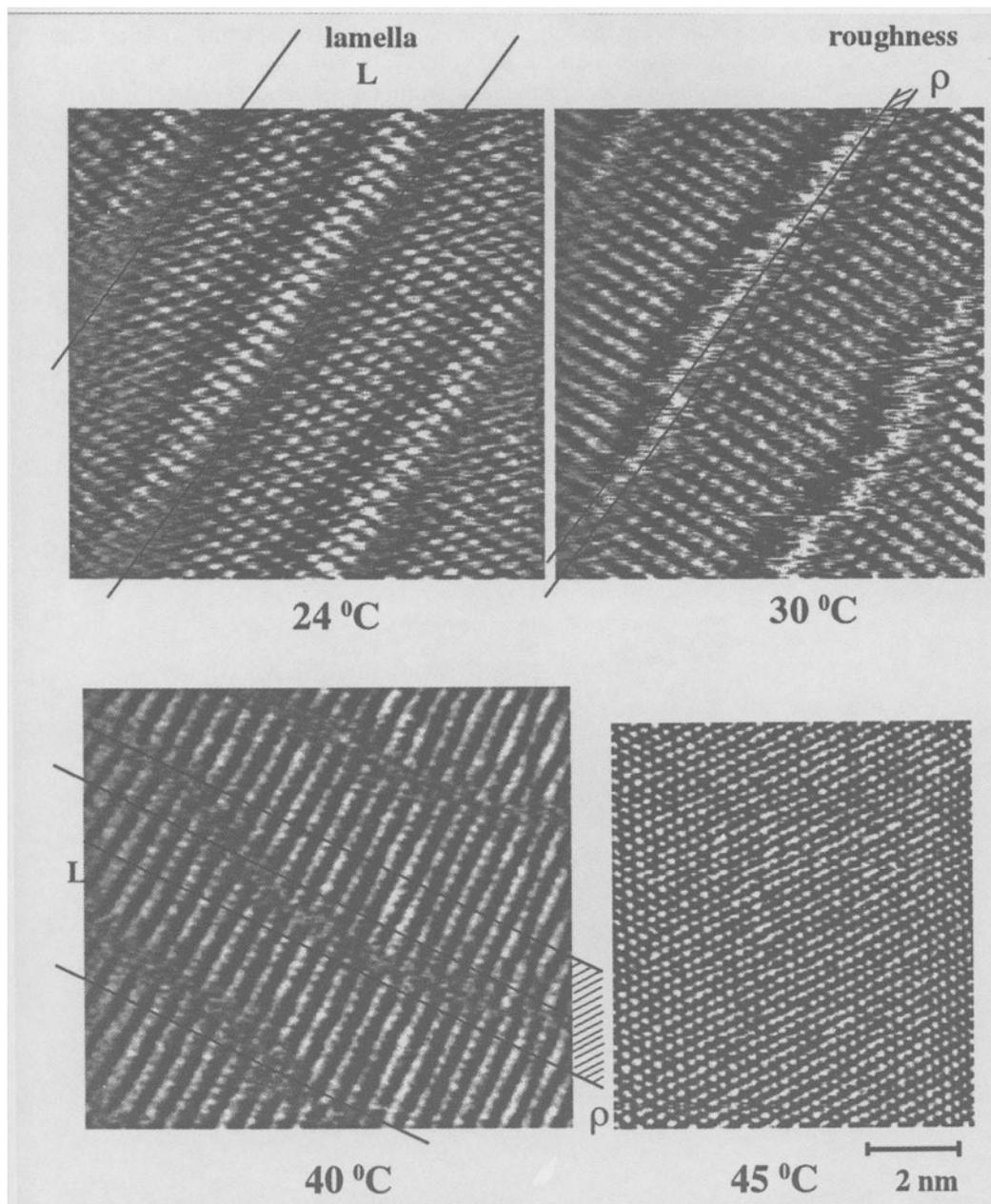


Fig. 6: Temperature induced roughening of adsorbed alkane lamellae [4].

STM imaging is also possible at the interface between a rigid conducting substrate and a "soft" and insulating organic solid on top [19,20]. In this case the STM tip may penetrate through the soft solid, and image just the first monolayer in contact with the rigid substrate. Provided the organic film is not too thick the forces exerted by the organic layer can be small enough to allow reproducible scanning.

The interpretation of the images in terms of structure and dynamics has been based to a large extent on symmetry and dimensions. Given the structure one may then use the contrast to learn something about the electronic properties of the molecules in their particular environments. Since the tunneling current will depend on the initial and final electronic states as well as on the barrier between them, it will contain information on tip, substrate and molecular adsorbate. For instance, in the case of xenon on nickel under ultrahigh vacuum conditions it has been argued that adsorbate states, which are electronically far away from the Fermi level, may contribute sufficiently to the electronic density of states at the Fermi level, in order to explain the contrast [21]. An interesting molecular example is given in Fig. 7. It displays a small

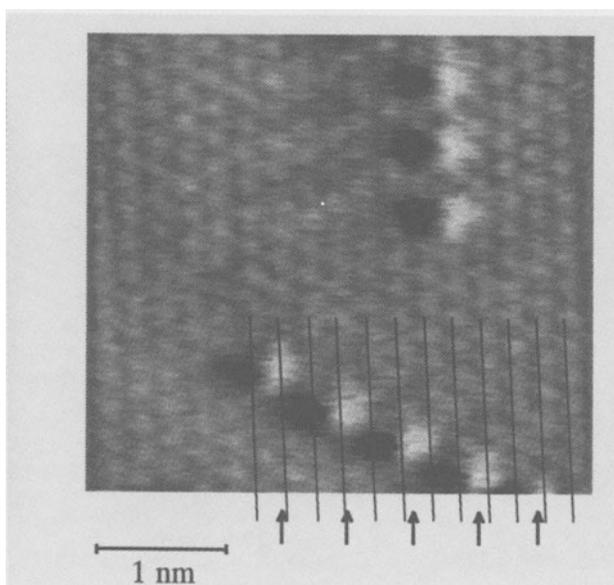


Fig. 7: STM image at a domain boundary in a didodecylbenzene monolayer on HOPG. Under the given tunneling conditions the image is dominated by the underlying graphite lattice (vertical lines) and the bright benzenes on top (arrows) [3,22].

area within a didodecylbenzene monolayer on HOPG, recorded under imaging conditions, where the alkyl chains hardly contribute anything to the contrast, while the current through the benzene rings is particularly large [3,16]. Similarly, a considerable number of other alkylated molecular segments have been investigated [22]. It seems that, to a first approximation, the tunneling current increases as the energy difference between the molecular states and the Fermi level decreases. Quantum chemical ab-initio calculations of the electronic states of van der Waals complexes may be useful to quantify this [23].

5. Perspectives for Modification of Molecular Materials

The STM allows not only the characterization but also the modification at interfaces. A comprehensive review has been given recently [24]. Several mechanisms may be invoked. So far, systematic work has been carried out primarily on surfaces of inorganic materials, but the underlying physics does not prevent the application to organic materials in the future. In order to use such processes for high density information storage purposes they need to fulfil some requirements: For instance, both writing and reading should be *fast*, the initial as well as the final structures should be sufficiently *stable*, the local change should *not perturb the molecular environment* much, and the change should be *clearly detectable* by STM. In the following we discuss some cases, which demonstrate that these requirements may be met in principle, even though the different requirements are not met equally well in all cases.

A fundamentally important process is field evaporation, which may be used to create holes and deposits on gold and silver [25,26]. Holes on Ag(111) have been fabricated, for instance, using bias pulses of about 5 V and as short as 10 nanoseconds at a base line current of 2 pA [26]. This may be attractive for high density data storage: On the hand, the primary writing process occurs at least on the 10 nanosecond time scale, and, on the other hand, depressions may be read out fast, since the height of the flying tip needs not to be adjusted.

Another interesting example is the local chemical modification of graphite under ambient conditions or at the interface with undried solvents. Metastable surface modifications of less than 1 nm diameter can be produced at a moderate bias of about 2 V [6,27], while long-term stable holes of a few nanometers in diameter could be etched with bias pulses of the order of 1 ms and 5 V [27-29]. The processes have been explained in terms of an anodic oxidation of graphite [29]. Moreover, holes typically one monolayer deep and between 5 nm and a few 100 nm in diameter have been made by gasification in air at temperatures around 650°C [30,31] (see also Fig. 8).

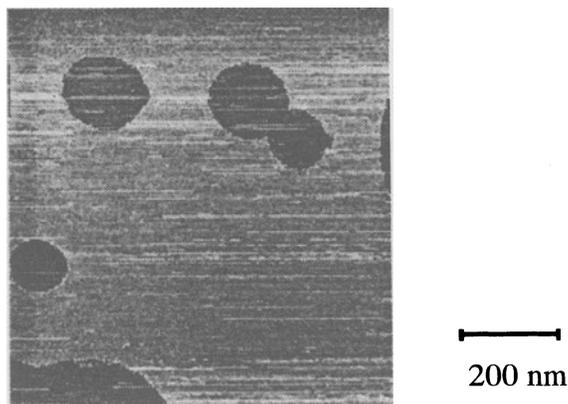


Fig. 8: STM image of thermally etched holes in HOPG, which are typically circular and one monolayer deep [31].

Interestingly, there are a number of modification mechanisms, which are particular to molecular materials. An example may be the reorientation of molecules within a molecular pattern. In two-dimensional patterns of long chain molecules several of the prerequisites for information storage schemes described above can be fulfilled. Fig. 9 shows the image of a monolayer of long chain alkanes with a single square of molecules, which are rotated by 90° with respect to the other molecules within this domain. Obviously, the situation is metastable enough to be imaged, the rest of the molecular pattern is not perturbed, and the square is easily detectable. While it is not obvious, how to rotate the molecules in this square on purpose, one may imagine related molecules, which should allow this process.

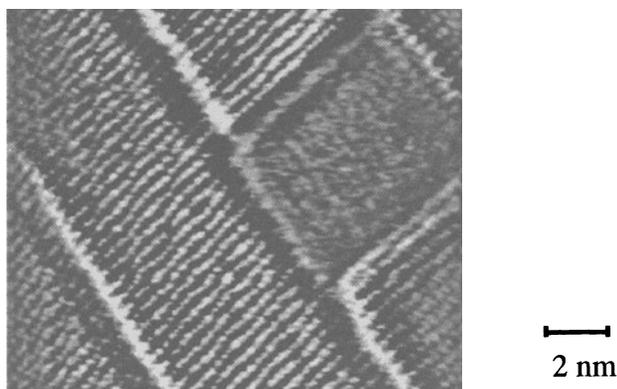


Fig. 9: STM image of a metastable square of alkane ($C_{44}H_{90}$) molecules rotated by 90° with respect to the other molecules within this domain.

Another molecular property, which may be modified, is the conformation of a molecule. Azobenzenes, for instance, exhibit a stable *trans*- and a metastable *cis*-conformation. In bulk materials their conformation can be switched back and forth via the appropriate visible light. Fig. 10 shows that monolayers may be formed from an azobenzene derivative in its *trans*-conformation. Upon illuminating these patterns with light, which switches the molecules into their *cis*-conformation, the pattern can be destroyed [32]. A proper molecular design may allow that the *cis*-forms can also order well.

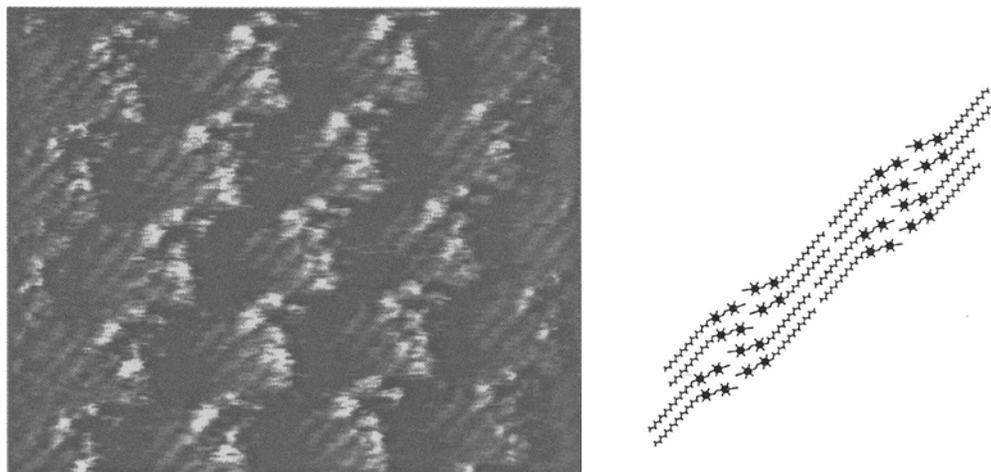


Fig. 10: STM image (12.7 nm x 10.2 nm) and model of a hexadecyl-cyanoazobenzene monolayer on HOPG [32].

Finally, chemical reactions, including complexations, dimerizations or polymerizations may be employed. While potentially reactive molecules (e.g., diacetylenes [22]) have been organized within molecular patterns, in which they may react, the demonstration of a controlled intermolecular reaction remains a challenge for the future.

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7. References

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