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Nanographenes as Active Components of Single-Molecule Electronics and How a Scanning Tunneling Microscope Puts Them To Work

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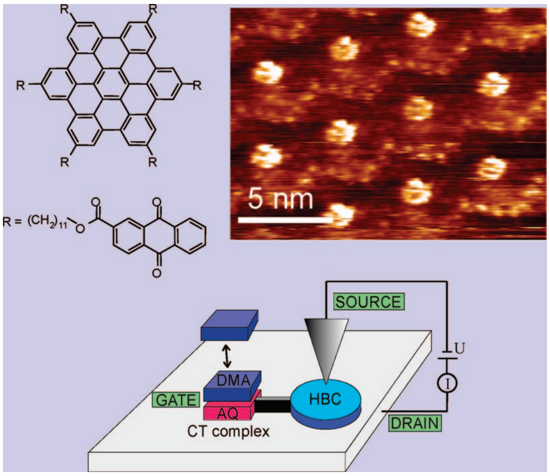

Single-molecule electronics, that is, realizing novel electronic functionalities from single (or very few) molecules, holds promise for application in various technologies, including signal processing and sensing. Nanographenes, which are extended polycyclic aromatic hydrocarbons (PAHs), are highly attractive subjects for studies of single-molecule electronics because the electronic properties of their flat conjugated systems can be varied dramatically through synthetic modification of their sizes and topologies. Single nanographenes provide high tunneling currents when adsorbed flat onto conducting substrates, such as graphite. Because of their chemical inertness, nanographenes interact only weakly with these substrates, thereby preventing the need for special epitaxial structure matching. Instead, self-assembly at the interface between a conducting solid, such as the basal plane of graphite, and a nanographene solution generally leads to highly ordered monolayers. Scanning tunneling spectroscopy (STS) allows the current−voltage characteristics to be measured through a single molecule positioned between two electrodes; the key to the success of STS is the ability to position the scanning tunneling microscopy (STM) tip freely with respect to the molecule in all dimensions, that is, both parallel and perpendicular to the surface.

In this Account, we report the properties of nanographenes having sizes ranging from 0.7 to 3.1 nm and exhibiting various symmetry, periphery, and substitution types. The size of the aromatic system and the nature of its perimeter are two essential features affecting its HOMO–LUMO gap and charge carrier mobility in the condensed phase. Moreover, the extended π area of larger substituted PAHs improves the degree of self-ordering, another key requirement for high-performance electronic devices. Self-assembly at the interface between an organic solution and the basal plane of graphite allows deposition of single molecules within the well-defined environment of a molecular monolayer. We have used STM and STS to investigate both the structures and electronic properties of these single molecules *in situ*. Indeed, we have observed key electronic functions, rectification and current control through single molecules, within a prototypical chemical field-effect transistor at ambient temperature.

The combination of nanographenes and STM/STS, with the PAHs self-assembled in oriented molecular mono- or bilayers at the interface between an organic solution and the basal plane of graphite and contacted by the STM tip, is a simple, reliable, and versatile system for developing the fundamental concepts of molecular electronics. Our future targets include fast reversible molecular switches and complex molecular electronic devices coupled together from several single-molecule systems.

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Introduction

Electronics based on electron transport through single molecules has attracted renewed interest due to the experimental and theoretical advances in recent years.[1] When Aviram and Ratner suggested in 1974 that a current could be rectified with a single molecule composed of a donor−bridge−acceptor structure fixed between two metal electrodes,[2] they envisaged an extended organic monolayer sandwiched between two metal electrodes. With the advent of the scanning tunneling microscope (STM) and its capability of addressing single molecules on conducting solid substrates, it became possible to measure current–voltage characteristics (scanning tunneling spectroscopy, STS) through a single molecule between two electrodes.[3] The fundamental difference between STS and the measurements on sandwich structures is the capability of positioning the STM tip, that is, one of the two electrodes, freely with respect to the molecule in all three dimensions, that is, both parallel and perpendicular to the surface. This also distinguishes the STM approach from mechanically controlled break junctions,[4,5] which allow precise distance control between the electrodes but lack any means of obtaining *in situ* information on the exact structure, that is, conformation and orientation of a molecule or a molecular aggregate within and with respect to the junction. We report here on the combination of scanning tunneling microscopy and spectroscopy (STM/STS) at solid−liquid interfaces, which provides *in situ* access to both structural information and electronic properties of single molecules and molecular complexes in a well-controlled junction between two electrodes.

A molecular system that enables both the development of concepts for molecular electronics and the investigation of structure−function relationships of single-molecule devices should be simple, reliable, and versatile. We considered in particular two criteria: (i) any function should be easily detectable at ambient temperatures and pressures, and (ii) electronic functions should be controlled by the properties of single molecules and be varied systematically through the molecular structure. Since ambient temperatures call for large current densities and therefore short channels for the passing electron current, the molecules should be as thin as possible, ideally only a single atomic layer thick, and lie flat on the surface. Control over their electronic properties may then be achieved through their lateral structure, which can be widely varied via synthetic chemistry. The second criterion calls for molecules that interact only weakly with a solid substrate. While such molecules are difficult to immobilize individually, they can be held in place by their neighbors in a densely packed physisorbed monolayer. For this purpose, we used a method that we had developed to assemble highly ordered molecular monolayers at the interface between an organic solution or melt and a chemically inert and atomically flat solid substrate, such as the basal plane of highly oriented pyrolytic graphite (HOPG).[6,7]

We report here on flat-lying polycyclic aromatic hydrocarbons (PAHs) at the interface between an organic solution and HOPG. In this situation, individual PAHs can be addressed *in situ* by the STM tip within a two-dimensional crystal.[3] In the sections below, the molecular title systems and their self-assembly at the interface will be first described separately, followed by a discussion of molecular electronic functionalities as probed by STM and STS.

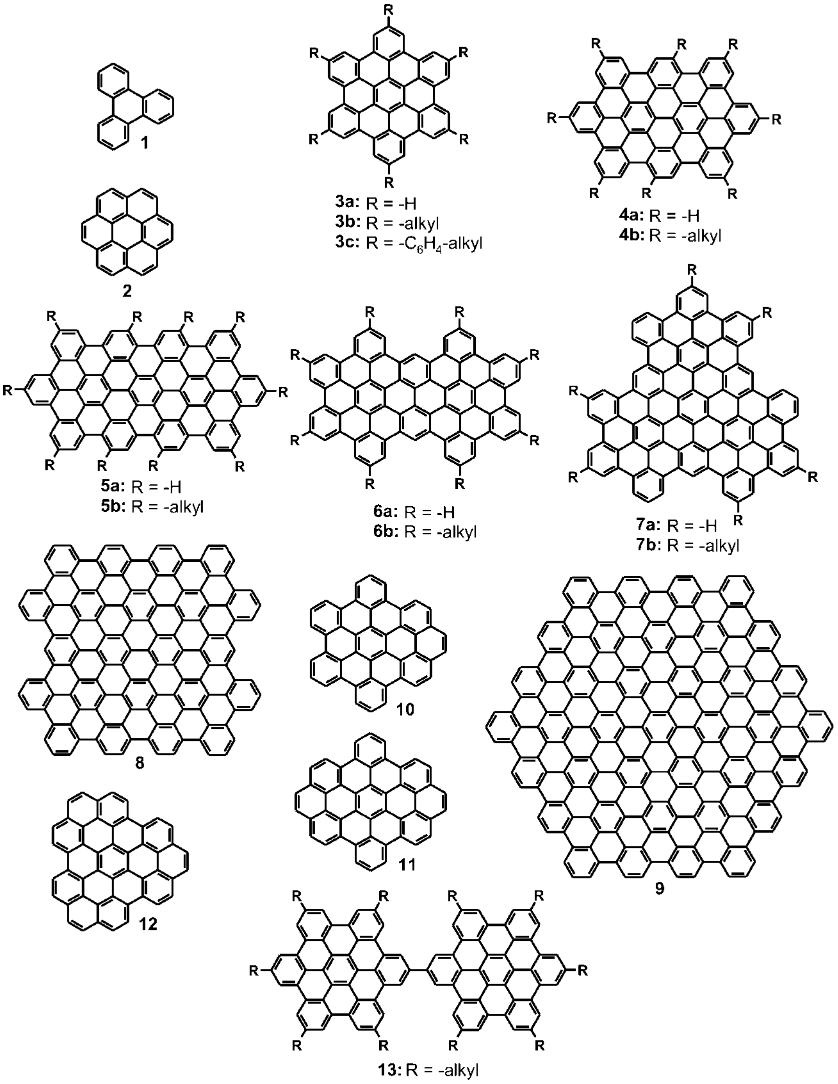
From Polycyclic Aromatic Hydrocarbons (PAHs) to Nanographenes

PAHs,[8−11] such as triphenylene (**1**) or coronene (**2**) (see Scheme 1), are classical examples of two-dimensional organic π-systems, which have served as important models for molecular orbital theory and spectroscopy. PAHs fulfill, in principle, the requirements of "thinness" and stability mentioned above, but before we could establish their role as active components of single-molecule electronics, crucial problems of design and synthesis had to be solved.

(i) Size. To lower the HOMO−LUMO gap and to control the assembly behavior in solution, in the melt, and at interfaces, we have extended PAHs in size toward true nanoobjects, that is, so-called nanographenes (see Scheme 1).[9,10] Several features are noteworthy:

- Hexa-*peri*-hexabenzocoronene (HBC, **3a**), the smallest member of our PAH series with 42 carbons (C42), is already three times larger than triphenylene (**1**).
- Compound **9** (C222), with hexagonal symmetry like **3a**−**c**, has a diameter of 3.1 nm.[9]
- Compounds **4a**,**b** (C60) and **5a**,**b** (C78) exhibit an increasing aspect ratio with a D_{2h}-symmetry of the core.[12,13]
- Due to their perimeter-type, **3a**−**c** (C42), **6a**,**b** (C72), and **7a**,**b** (C96) can be regarded as superbenzene, supernaphthalene, and superphenalene,[9] respectively, whereas **13** constitutes a superbiphenyl.[14]
- An increase in size can also be accomplished by going from the arm chair peripheries as in **3**−**9** to zigzag peripheries as in **10**−**12**.[15]
- Compound **8** (C132) is the largest insoluble PAH that could be deposited from a suspension into a crystalline monolayer.[16]

SCHEME 1. Polycyclic Aromatic Hydrocarbons

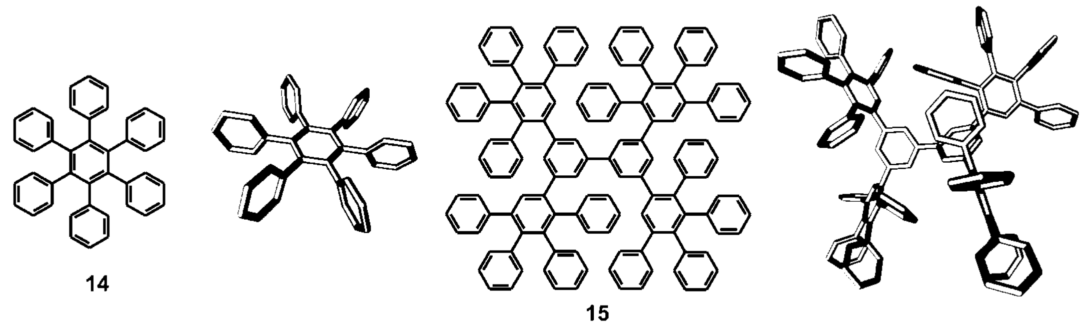


(ii) Precursor Synthesis. Since the synthesis of the nanographenes is not feasible via the direct fusion of smaller PAH-building blocks, we had to develop a precursor route in which branched (three-dimensional) polyphenylenes are planarized to the disk-type target molecules by an intramolecular cyclo-dehydrogenation.[9,10] The oxidative removal of the benzene hydrogens can thereby be accomplished both chemically and electrochemically. The critical design issue is the topology of the precursor molecules: toward defect-free nanographene sheets, all benzene rings of the precursor must "fit" as suggested by their 2D formulas. Thus, **3a** and **8** are formed from the readily available propeller-shaped hexaphenylbenzene **14** and the dendrimer **15**, respectively (see Scheme 2).[9,10]

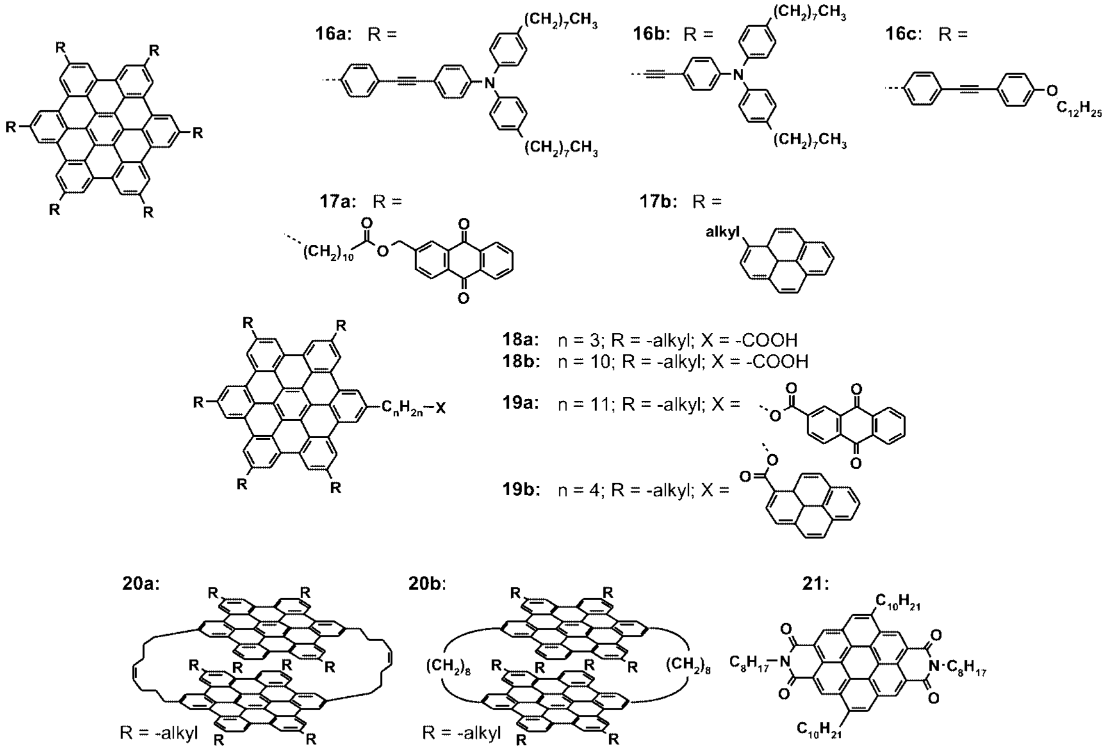
(iii) Chemical Substitution. The low solubility of the parent nanographenes with R = H (e.g., designated as **3a**, **4a**, and **6a**) renders chemical purification, spectroscopic structure proof, and deposition from solution difficult. It is therefore important that the above synthesis can also furnish alkyl-substituted derivatives such as **3b** and **7b** or *p*-alkylphenyl-substituted analogues such as **3c**. The high affinity of the alkyl chains to the basal plane of graphite also helps to orient the attached aromatic discs parallel to the substrate,[3] rather than in columns of edge-on discs.[17] Moreover, the alkyl chains themselves can serve as a reference system for the scanning tunneling spectroscopy of the PAHs.[3]

It must be mentioned that alkyl substitution can also allow the nanographenes to melt into discotic mesophases with columnar superstructures as a result of nanophase separation between the aromatic and the alkyl region.[18] Due to their high charge carrier mobilities, they constitute very attractive semiconductor components for organic electronic and optoelectronic devices.[19,20] Depending on the desired application, the stacks must be oriented either "face-on" relative to the sur-

SCHEME 2. Precursor Molecules **14** and **15** for the Synthesis of the PAHs **3a** and **8**



SCHEME 3. Polycyclic Aromatic Hydrocarbon Derivatives



face as for solar cells or "edge-on" as for organic field-effect transistors (OFETs).[17]

Although the above cyclodehydrogenation does not tolerate all heteroatoms, introduction of chemically different polar substituents at the cores or at the alkyl chains is possible.[21] Thereby, not only can the electron density of the π-system be modified but also the mode of deposition from solution (edge-on vs face-on, mono- vs multilayer) can be controlled.[17,18,21] Other chemical modifications such as ethinylation of the aromatic core give rise to the formation of the star-type architecture present in **16a**,**b**.[22] Hydroxy or carboxy functions at the ends of the alkyl chains allow for the covalent coupling of nanographenes with other π-systems such as pyrene or the electron-poor anthraquinone to yield complex dyad systems such as **17a**,**b**.[24] A particularly important feature for the assembly of the discs in different phases is chemical desymmetrization of the aromatic core, as in nanoamphiphiles **18a**,**b**[25] or dyads like **19a**,**b**[24,23] (see Scheme 3).

Molecular Self-Assembly at Chemically Inert Solid–Liquid Interfaces

Single molecules may be immobilized through chemical bonds to solid substrate surfaces; however, immobilization often alters strongly the electronic structures of both the molecule and the substrate surface. If a particular binding group is introduced to decouple the binding from the electronic function, this will require larger and more complex molecules. In our approach, we use interfacial forces between an organic solution and a chemically inert, single- crystalline solid substrate.[6,7,26] Together with interatomic repulsions, they very generally allow the immobilization of single unfunctionalized molecules in highly ordered *physisorbed* monolayers at solid–liquid interfaces. Here the ordered monolayer serves two purposes: (i) it immobilizes a molecule at a temperature at which, in isolation, it would diffuse quickly across the surface, and (ii) together with the solid substrate and the STM tip, it defines precisely the environment of the molecule.

In our method, a concentrated, but not saturated, organic solution of the molecules is applied to an atomically flat and inert solid substrate surface such as the basal plane of highly oriented pyrolytic graphite (HOPG). Both solute and solvent molecules experience an attractive force at the interface, which at least in part is due to the large difference in the dielectric function of the organic liquid and the conducting substrate. It decays over about a nanometer and depends in detail on the specific molecule.[27] Typically one obtains a molecular monolayer at the interface, which is attributed to a larger gain in free energy upon the formation of a monolayer of the large and rigid PAH molecules as compared with a layer of the much smaller solvent molecules.[27] The monolayer adsorbate is often crystalline, which is attributed to the fact that a crystal is usually the most dense phase that minimizes the free energy. Moreover, the layer is oriented with respect to the substrate lattice. However, according to the 3-fold symmetry of the HOPG lattice, the homogeneously nucleating adsorbate layer is polycrystalline and undergoes Ostwald ripening with time.[28] Despite the crystallinity and the orientation, the system is generally not simply commensurate, since for a weakly interacting substrate the gain in energy for a commensurate adsorbate layer is small compared with the *intermolecular* energy contributions for variable two-dimensional molecular densities.[6] Accordingly, there is no need for lattice matching between adsorbate and substrate structure, which renders the method very versatile. It implies, for instance, that the electrode material is not limited to HOPG, but may be any other chemically inert, atomically flat conductor such as the cleavage plane of a transition metal dichalcogenide.[29]

Molecular self-assembly at solid–liquid interfaces shows both similarities and differences when compared with deposition through vacuum sublimation. HBC (**3**) is a molecule that has been deposited as a close-packed epitaxial monolayer on the basal plane of HOPG using both methods.[16,30] The unit cell of the 2D crystal and its orientation relative to the substrate lattice are identical,[16,30] indicating that preparation and imaging in ultrahigh vacuum and at solid–liquid interfaces can provide identical results.

A limitation of STS at solid–liquid interfaces arises from electrochemical reactions of the solvent or any contamination at the solid–liquid interface, which cause an extra current beyond tunneling and thereby limit the accessible bias voltage range for STS to a window below the oxidation and reduction potentials of the liquid. This range is often determined by traces of water, which are impossible to remove completely from organic solvents. On the other hand, at the interface between an electrolyte and a solid substrate, the electrochemical control of the substrate potential independent of the tunneling bias provides an extra degree of freedom to control the molecular structures at solid–liquid interfaces.[31]

An obvious advantage of the self-assembly at solid–liquid interfaces is that very large molecules can be processed, which cannot be sublimed nondestructively.[32] This is because even minute amounts of solute in a saturated solution can be sufficient to deposit a molecular monolayer.[16] Another advantage is the fact that the weak forces at the interface between an organic solution and a chemically inert substrate cause substantial molecular dynamics at the solid–liquid interface.[6,7,33] This is a prerequisite for fractionation[26] as well as Ostwald ripening,[28] which together allow for the fabrication of virtually flawless large area molecular layers, where each individual molecule is weakly interacting with its environment. Since the thermodynamic driving force for the ordering is due to interfacial forces rather than very specific intermolecular forces, this a powerful approach toward ordered molecular layers.

Self-assembly at solid–liquid interfaces has been widely applied to assemble molecular layers of a large variety of molecular systems exhibiting a broad range of architectures.[34–36] One structural class is linear molecules such as alkylated oligothiophenes[37,38] or phenyleneethynylenes,[26,39] which self-assemble with both the rod and the alkyl side chains parallel to the substrate surface. The resulting molecular patterns exhibit a nanophase separation between conjugated molecular segments and alkyl side chains, reflecting the favorable interaction of both the aromatic and the aliphatic molecular parts with the HOPG surface.

Similarly, alkyl-substituted disk-like molecules such as nanographenes form self-assembled patterns with the discs parallel to the surface. While the aromatic ring in substituted benzenes is tilted with respect to the graphite plane,[6,7] PAHs such as alk(ox)ylated triphenylenes[40–42] have been shown to lie flat on the surface. The same holds for the larger PAHs such as **4b**[12] and **13**[14] with 60 and 84 carbons in the aromatic core, respectively.

The alkyl side chains of the nanographenes serve several purposes. First, they improve solubility.[43] Second, the high affinity of the alkyl chains to the basal plane of graphite[27] drives the chains to orient parallel to the surface, which in turn forces the attached nanographenes into a face-on arrangement onto the substrate. Third, the flexibility of the alkyl chains helps to form a very close packed monolayer of the neat system, which, due to the attraction between the solute and the solid substrate, is thermodynamically strongly favored.[26] By comparison, the rigid nanographenes, if not highly symmetric, will generally leave voids within the monolayer. The exact nature of the side chains will influence the packing in two dimensions. For instance, molecule **3c** with alkyl chains containing stereogenic carbon centers attached via a phenylene spacer to the aromatic core result in a molecular lattice with a hexagonal superstructure.[43]

The close-packed systems described above provide no space to incorporate any solvent molecules. The rigid star-shaped molecule **16c**, on the other hand, exhibits voids between its arms, which can incorporate small solvent molecules in order to self-assemble in a dense layer.[44] Moreover, the molecule self-assembles with two distinctly different packings within the first and a second ordered monolayer on top, and both layers can be independently visualized by STM. The self-assembly of such double layers provides an additional degree of freedom for the design of functional nanostructures for molecular electronics.

The mechanism described above leaves directional intermolecular forces to be used specifically to control supramolecular structure formation at interfaces. Typical examples are hydrogen-bonded dimers of long chain alkanols and fatty acids.[6,45] With the introduction of carboxylic acid functions to the core of **3** via an alkyl tether of variable length (**18a**,**b**) (see Scheme 3), hydrogen bonding has also been employed to influence the supramolecular organization of PAHs both in bulk and at solid–liquid interfaces.[25] It has further been used to direct the self-assembly of two-component systems. In a first example, 5-alkoxy isophthalic acids were shown to form monolayers of 2:1 stoichiometric donor–acceptor complexes with the bifunctional bases pyrazine and 2,5-dimethylpyrazine.[46]

π-Stacking is another interaction that has been capitalized on to form crystalline PAH double layers, either in alkyl-substituted cyclophanes of HBC, **20a**,**b** (see Scheme 3),[47] or in neat HBC double layers.[48] The stacks may be considered as building blocks of quasi-one-dimensional π-stacked columns and ribbons at surfaces.[49] The orientation of the stacks relative to the substrate surface can be influenced by the solid substrate and its surface, the alkyl side chains around the PAH, and the deposition conditions.

Charge-transfer interactions are particularly interesting for applications in molecular electronics. They have been used to promote the solubility of PAHs, as well as to assemble mixed double layer crystals of donors and acceptors.[16] Monolayers of ordered arrays of donors and acceptors have been fabricated from alkyl-substituted hexa-*peri*-hexabenzocoronene **3b**derivatized with covalently tethered PAHs such as anthraquinone (**17a**, **19a**)[50,51] or pyrene (**17b**, **19b**) (see Scheme 3).[23] Within such arrays, single donors and acceptors can be addressed individually with an STM tip.

Probing Molecular Electronic Functions by STM and STS

A key molecular electronic function is rectification. Within an STM junction a molecular rectifyer can be realized with a single symmetrical molecule,[3] which is even simpler than within the concept of Aviram and Ratner.[2] The reason for this is the free positioning of the STM tip in the direction normal to the surface, which allows the symmetry of the whole system to be broken. This is the case even for a single-molecular system between two identical electrodes, because for sufficiently large gaps between the electrodes, there will be a double well potential with the molecule in one of the wells (Figure 1a). Large flat molecules will reside most likely in the well close to the flat solid substrate. In this geometry, within a resonant tunneling model,[52,53] (Figure 1b) the forward-bias direction will depend on the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with respect to the Fermi energy. For an electron acceptor at sufficiently large positive sample bias, resonant tunneling through the LUMO becomes possible, while at the same opposite bias, no resonant contribution occurs. The situation is reversed for an electron donor.[50] This prediction has been tested with the molecular dyad **17a**, which adsorbs onto HOPG such that it presents the electron donor part (hexa-*peri*-hexabenzocoronene, HBC), the electron acceptor (anthraquinone, AQ), and the insulating alkyl chain flat on the substrate (Figure 2). Current–voltage ($I-V$) characteristics have then been recorded through both parts with the same STM tip one after the other (Figure 3), revealing the rectification through both donors and acceptors and a reversal of the forward bias direction in agreement with the resonant tunneling model.[50] Moreover, in accordance with the model, the rectification improves as the HOMO energies increase in the series **3b**, **4b**, and **5b**.[13]

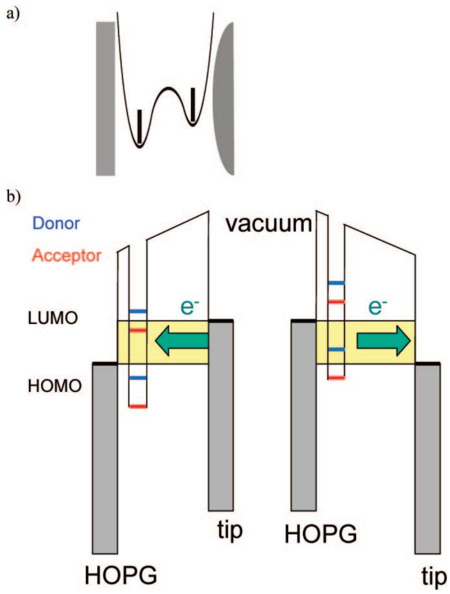


FIGURE 1. (a) Molecule located asymmetrically within the tunneling junction and (b) energy diagrams for a donor (blue) and an acceptor (red) placed closer to the substrate than to the tip. Within the resonant tunneling model,[50,52,53] for the electron acceptor at sufficiently large positive sample bias, resonant tunneling through the LUMO becomes possible, while at the same opposite bias, no resonant contribution occurs. The situation is reversed for an electron donor.

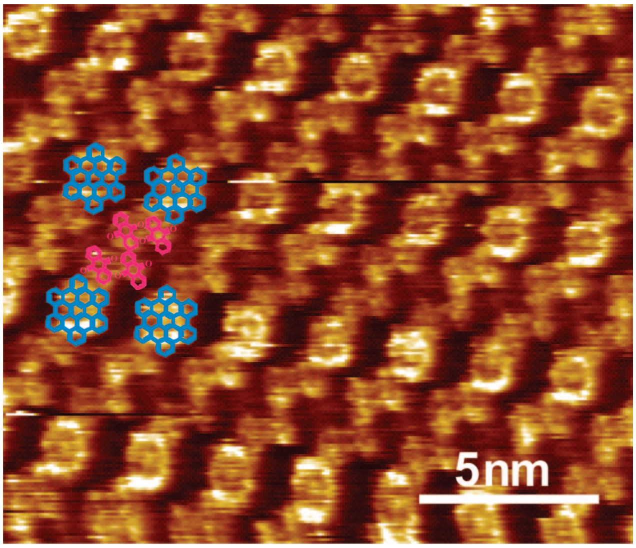


FIGURE 2. STM image of dyads **17a** with the donor (HBC, blue) and acceptor (AQ, purple) parts adsorbed parallel to the substrate and next to each other.[50]

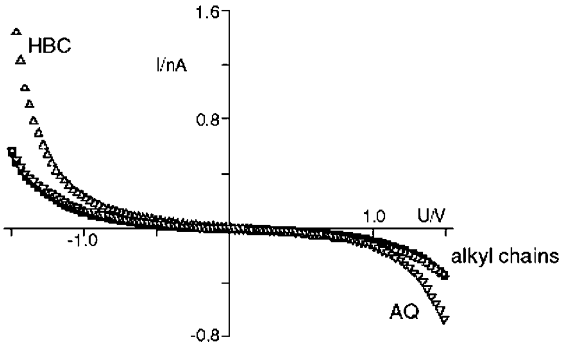


FIGURE 3. Current–voltage characteristics through donor, acceptor, and alkyl parts of **17a**,[50] displayed as normalized *I*–*V* curves for HBC (△), AQ (▽), and alkyl regions (■) (see also Figure 2). *I*–*V* curves were normalized to the tunneling impedance of the alkyl chain region *I*–*V* curves at positive and negative sample bias for HBC and AQ regions, respectively, since there is no resonant contribution to be expected. With one normalizing factor for each molecule, the *I*–*V* curves through the alkyl parts are identical to those of the donor in the positive bias range and to the acceptor in the negative bias range, which is consistent with the model.

Since the PAHs are only about 350 pm thick, tunneling currents through double layers are sufficiently large to allow both STM and STS. The simplest case is tunneling through alkyl-substituted HBC cyclophanes **20a**,**b**,[47] which exhibit qualitatively the same *I*–*V* characteristics as the single HBC **3b**. Interestingly, double layers of unsubstituted HBC exhibit a very close hexagonal packing in the first layer and a less compact second layer.[48] This causes two crystallographically inequivalent double stacks, which also exhibit very different *I*–*V* characteristics: one has the same forward bias as a single alkyl-substituted HBC **3b** or the corresponding cyclophanes **20a**,**b**, and the other has the opposite, highlighting the significance of the packing in the molecular stack.[48]

Self-assembled double stacks of donors and acceptors can also be used to fabricate molecular junctions of the Aviram–Ratner type. The first reported example is a self-assembled double layer on HOPG consisting of a close-packed monolayer of HBC and a mixed monolayer of HBC and the substituted coronenediimide **21**.[16] This structure provides the opportunity to measure *I*–*V* characteristics through an oriented donor–acceptor stack, where the "bridge" between the two moieties is the tunneling barrier between the molecules. The forward bias direction is in agreement with the Aviram–Ratner model;[2] that is, with the acceptor on top of the donor, the current is larger if the top electrode is negative. The complementary orientation of a acceptor–donor stack has been realized using an HBC with one extra double bond at a bay of the periphery (**10**) ("zigzag HBC")[15] and the previously mentioned coronenediimide **21**. In this case, the forward bias is reversed, again in agreement with the model. It should be noted that this donor–acceptor stack on the basal plane of graphite within an STM junction is probably the best defined system of the Aviram–Ratner-type described so far. Compared with, for example, a metal surface with reactive, partially flexible adsorbates in self-assembled monolayers, both the graphite substrate and the PAHs are extremely stable and rigid.

While the STM geometry readily lends itself to the investigation of two-terminal devices such as molecular diodes, three-terminal molecular devices such as a transistor have been investigated between two lithographically fabricated electrodes on an insulating substrate with a back electrode.[54] However, such devices cannot be readily scaled down to the molecular scale, since the three electrodes define the size of the device. In an attempt to further miniaturize a single-molecule transistor, we used the dipole moment provided by molecular charge transfer complexes to modify the diode-like $I-V$ characteristics through a single molecule in an STM junction. For that purpose, dyad **17a** was assembled at a solid–liquid interface, and the $I-V$ through the HBC was measured (see Figures 2 and 3). Upon addition of an electron donor, 9,10-dimethoxyanthracene, to the solution, a new molecular packing was observed (Figure 4a), which is due to the formation of charge-transfer complexes between the anthraquinone units and dimethoxyanthracene.[51] Figure 4b displays the $I-V$ curves though the HBC before and after the formation of the complexes. The significant change has been attributed to the dipole moment of the charge transfer complexes causing an interface dipole, which shifts the $I-V$ curve by about 120 mV.[51] This number is consistent with the calculated dipole moments of the charge transfer complexes and their two-dimensional density at the interface. Since the corresponding energy is about three times k_BT at room temperature, the effect can be readily observed. Notabene dipole moments parallel to the surface have no effect.[55] The shift of the $I-V$ curve indicates that charge -transfer complexes can act as nanosized gates in a single-molecule chemical field-effect transistor (Figure 4c[51]).

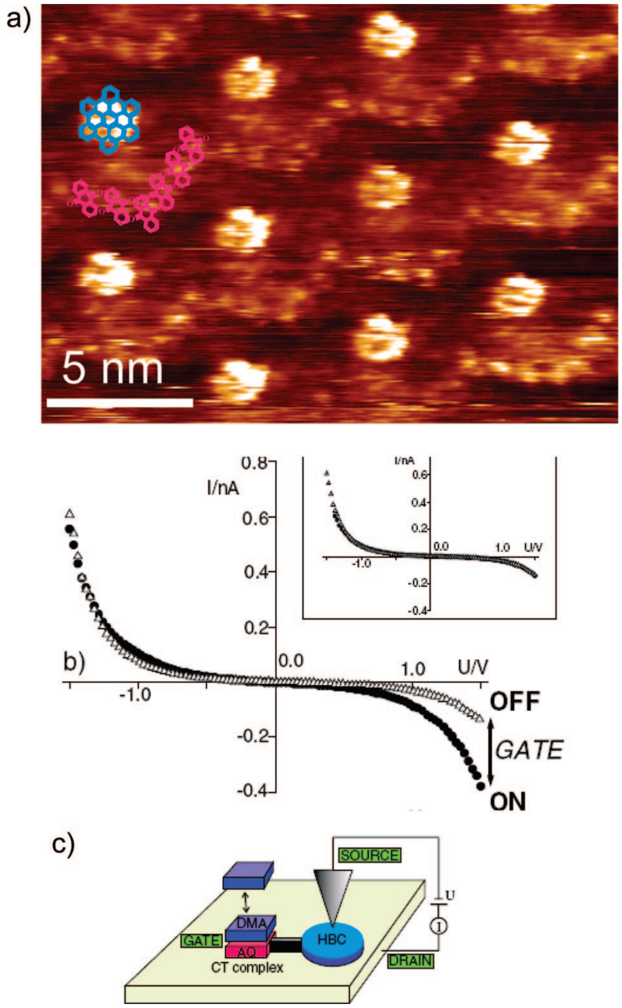


FIGURE 4. Single-molecule transistor:[51] (a) STM current image of a monolayer of **19a**, where the anthraquinones (purple) formed charge-transfer complexes with dimethoxyanthracene added to the solution; (b) $I-V$ curves through the HBC cores before ("OFF") and after ("ON") the formation of the charge-transfer complexes; inset: normalized data (c) scheme of the resulting single-molecule chemical field-effect transistor.

Conclusions and Outlook

Nanographenes self-assembled in oriented molecular mono- or bilayers at the interface between an organic solution and the basal plane of graphite and contacted by an STM tip provide a simple, reliable, and versatile system that allows concepts for molecular electronics to be developed and structure–function relationships of prototypical single-molecule electronic devices to be investigated. Polycyclic aromatic hydrocarbons or nanographenes have been synthesized with various symmetries and peripheries and with sizes from 0.7 nm (**1**) up to 3.1 nm (**9**). The increase in size of the aromatic systems and a variation of the perimeter type are essential with regard to the reduction of the HOMO–LUMO gap and the improvement of the charge carrier mobilities. Moreover, larger substituted PAHs exhibit an improved self-ordering due to the extended π-area, which is another key feature to yield high performances in electronic devices.

PAHs self-assemble in precisely defined molecular mono- and bilayers at the interface between an organic solution and an atomically flat and chemically inert solid substrate such as the basal plane of graphite. STM and STS at such solid–liquid interfaces allow current–voltage characteristics of a system to be measured, where the electrodes and their relative positions with respect to the molecule within the gap are precisely defined. Besides molecular rectifyers, a concept for a single-molecule chemical field-effect transistor has also been developed. The properties of prototypical single-molecule devices can be systematically tuned with the exact structure of the nanographenes. Challenges for the future include the controlled triggering of the transistor, which may be achieved by optically switching a molecular dipole moment. Another issue is to couple two or more of such single-molecule devices. For that purpose, a dipole moment switched on parallel to the surface may be employed, and an electronically active substrate will facilitate this process. Conjugated molecular bridges between two nanographenes may be also used to control the electronic coupling between them, which is a prerequisite to fabricate any electronic circuit from single-molecule devices.

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BIOGRAPHICAL INFORMATION

Klaus Müllen studied chemistry at the University of Cologne and then earned his doctorate in the group of Prof. F. Gerson at the University of Basel. Following postdoctoral work and habilitation with Prof. J. F. M. Oth at ETH Zürich, he accepted a professorship at the University of Cologne. He subsequently moved to the University of Mainz and then assumed his current position as the Director of the Max Planck Institute for Polymer Research in Mainz. His many research interests include new polymer-forming reactions, multidimensional polymers with complex, shape-persistent architectures, functional polymeric networks, dyes and laser writing in polymers, chemistry and physics of single molecules, molecular materials with liquid crystalline properties for electronic and optoelectronic devices, materials for lithium or hydrogen storage, biosynthetic hybrids, and nanocomposites.

Jürgen P. Rabe studied physics and mathematics at RWTH Aachen, and received his Dr. rer. nat. from TU Munich for work on interfacial optics of lipid layers. After postdoctoral research at the IBM Research Center in San Jose, CA, on the first STM experiments on ultrathin organic layers, he joined the Max Planck Institute for Polymer Research in Mainz, obtained his habilitation in physical chemistry, and became professor at the University of Mainz. Presently he is professor for experimental physics at the Humboldt University Berlin and an external member of the Max Planck Institute for Colloids and Interfaces at Potsdam. His current research interests include molecular self-assembly, structure–property relationships of single macromolecules, molecular electronics, interfaces, and scanning probe microscopies.

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