

Prototypical Single-Molecule Chemical-Field-Effect Transistor with Nanometer-Sized Gates

F. Jäckel,¹ M. D. Watson,^{2,*} K. Müllen,² and J. P. Rabe^{1,†}

¹*Department of Physics, Humboldt University Berlin, Newtonstraße 15, 12489 Berlin, Germany*

²*Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

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A prototypical single-molecule chemical-field-effect transistor is presented, in which the current through a hybrid-molecular diode is modified by nanometer-sized charge transfer complexes covalently linked to a molecule in an STM junction. The effect is attributed to an interface dipole which shifts the substrate work function by ~ 120 meV. It is induced by the complexes from electron acceptors covalently bound to the molecule in the gap and electron donors coming from the ambient fluid. This proof of principle is regarded as a major step towards monomolecular electronic devices.

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Electron transport through single molecules has attracted much interest due to remarkable experimental and theoretical advances in recent years [1,2]. Hybrid-molecular diodes [3] whose current-voltage characteristics are determined by a single molecule in a well controlled gap with dimensions on the order of 1 nm can be realized using a scanning tunneling microscope (STM) [4–6] or nanofabricated metal or break junctions [7,8]. Field effect transistors have been fabricated with carbon nanotubes [9,10] and single molecules [11,12]. The electrodes, however, were macro- or mesoscopic and not readily scalable to nanoscale dimensions. Scanning gate and scanning impedance microscopy have been used to detect single defects in carbon nanotube field effect transistors [13]. Under ultrahigh vacuum (UHV) conditions the coupling of adsorbed atoms to electronic surface states has been investigated [14]. Here we present a prototypical three-terminal device at the solid-liquid interface, in which the current through a hybrid-molecular diode is modified by nanometer-sized charge transfer complexes (“nanogates”) covalently linked to the molecule in the STM junction.

Large polycyclic aromatic hydrocarbons like the electron-rich graphene molecule hexa-*peri*-hexabenzocoronene (HBC) proved interesting for molecular electronics [4] and organic photovoltaic devices [15]. The key molecule for the present study (**1**, Fig. 1) is an HBC derivative with six strong electron acceptor substituents [anthraquinone (AQ)], which can form charge transfer complexes with an electron donor such as **6** [9,10-dimethoxyanthracene (DMA)]. Synthesis, optical properties, and self-assembly behavior of the compounds are described elsewhere [16]. Scanning tunneling microscopy and spectroscopy (STS) measurements at the graphite-liquid interface [17] were performed with a homebuilt STM interfaced with a commercial controller and software (Omicron). For STS the tip was positioned over the region of interest and a voltage ramp with 100 equidistant points between -1.5 and 1.5 V was run with the feedback loop switched off. The tip-substrate separation was deter-

mined by the tunneling parameters settings when switching off the feedback loop. Spectroscopic data were accepted only if imaging was stable with a typical contrast before and after measuring current-voltage (I - V) characteristics and if there was no lateral shift between images of forward and backward scan direction. Finally, tunneling spectra of a number of molecules were averaged, provided they met the setting of the feedback loop with acceptable accuracy ($\pm 10\%$).

Figure 2(a) displays an STM current image of **1** with submolecularly resolved features at a spatial resolution better than 1 nm, offering the possibility of tunneling spectroscopy with similar resolution. Within the rectangular unit cell one can identify the HBC cores at the corners as bright circular features with central spots corresponding to high tunneling currents [18,19], as well as four AQ moieties in between. Dark areas of the

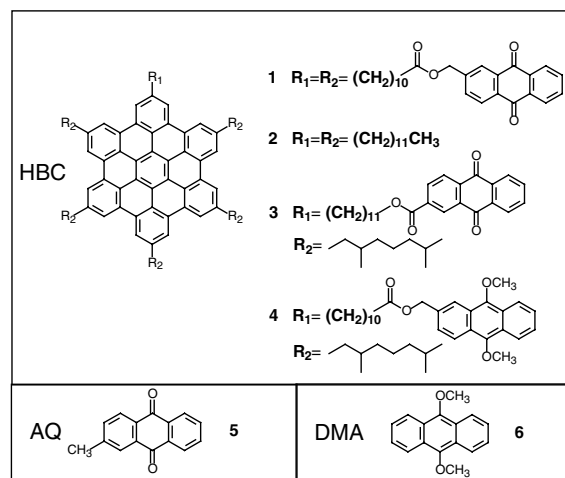


FIG. 1. Chemical formulas of the employed materials: hexa-*peri*-hexabenzocoronene (HBC) decorated with six anthraquinone (AQ) functions (**1**), hexaalkyl-HBC (**2**), HBC bearing either one AQ (**3**) or one 9,10-dimethoxyanthracene (DMA) function (**4**), methyl-AQ (**5**), and DMA (**6**).

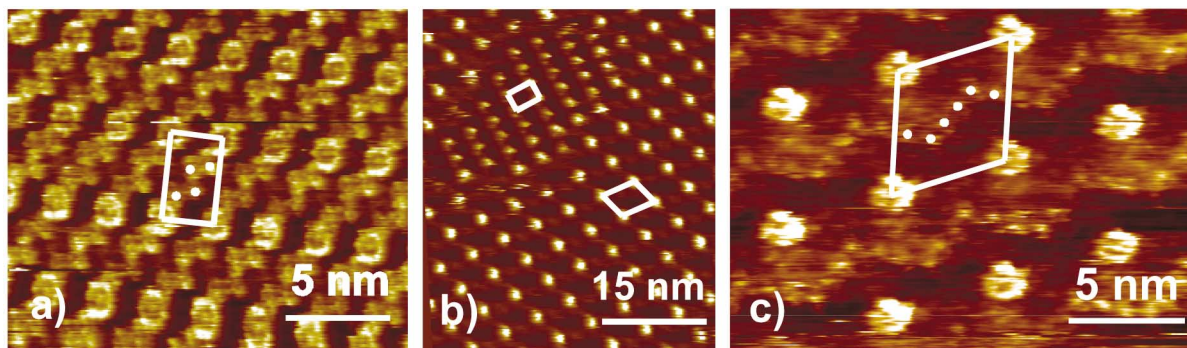


FIG. 2 (color). STM current images of highly ordered monolayers on highly oriented pyrolytic graphite of (a) **1** ($U_s = 1.4$ V, $I_t = 300$ pA), (b) **1+6** ($U_s = -1.4$ V, $I_t = 108$ pA), (c) **1+6** ($U_s = -1.2$ V, $I_t = 270$ pA). Unit cells, Aqs in (a) and charge transfer complexes in (c) are indicated.

images are attributed to the only partially ordered alkyl chains.

Figure 3(a) displays I - V 's recorded through HBC cores and alkyl chain regions, respectively, in monolayers of **1**. The almost symmetric I - V 's through alkyl chains reflect the intrinsic asymmetry of the tunneling junction caused by different electrodes since due to the large gap between their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [18] no resonant contribution to the tunneling current is expected [20]. In contrast, I - V 's through HBC cores exhibit a rectifying behavior with larger currents at *negative* sample bias. Assuming the molecules are closer to the substrate than to the tip (otherwise no stable imaging of the monolayer can be expected), and the Fermi level lying energetically in between the HOMO and the LUMO of the molecule, we attribute the increased tunneling probability at negative sample bias to resonant contributions caused by the HOMO. Remarkably enough, I - V 's recorded through Aqs in monolayers of **1** (not shown here) reveal rectifying behavior with enhanced tunneling probability at *positive* sample bias which is opposite to the I - V 's through HBC cores, and can be explained by resonant contributions due to the LUMO of AQ [21].

Figures 2(b) and 2(c) display STM current images of monolayers obtained from mixed solutions of **1** and the donor DMA **6** with a tenfold molar excess of **6** (further referred to as **1+6**). A new, much larger unit cell with parameters $a = (4.2 \pm 0.2)$ nm, $b = (5.1 \pm 0.2)$ nm, and $\alpha = (66 \pm 3)^\circ$ is observed. The high resolution image clearly resolves six additional bright spots per unit cell arranged in a zigzag row between the HBC cores. AQ and DMA are known to form charge transfer (CT) complexes in the solid state [22], and we attribute these spots to DMA-AQ-CT complexes coadsorbed in this arrangement. The new arrangement coexists with the unit cell known of neat **1** where no DMA is coadsorbed [Fig. 2(b)]. The key result is presented in Fig. 3(b), which displays I - V 's through HBC cores in monolayers of **1+6** measured in the two different unit cells. While the I - V 's measured in the unit cell in which no DMA is coadsorbed are virtually

identical to those obtained from neat **1** [Fig. 3(c)], a much more symmetric I - V is observed through HBCs where DMA-AQ-CT complexes are coadsorbed in the unit cell. The two I - V types were observed in the respective domains both within the same and in repeated experiments. Upon shifting the latter I - V by 0.12 V to larger sample bias and normalizing [inset of Fig. 3(b)] one obtains the first type of I - V , a fact that will be discussed further below.

In similar mixtures of **2** (HBC without acceptor) and the donor **6**, no changes in structural arrangement (images not shown) or I - V 's [Fig. 3(d)] in comparison to monolayers of neat **2** were observed, which rules out that the changes in the I - V 's are due to a complex formation of the two donors HBC and DMA. Furthermore, mixtures of **3** (HBC with one acceptor) and the donor **6** and of **4** (HBC with one donor) and the acceptor **5** (molar excess of **5** and **6**, respectively) did not lead to any new structure or electronic behavior when compared to the neat compounds **3** and **4** (images and I - V 's not shown). Since for **3** and **4** most substituents are not packed on the graphite surface we conclude that the changes in I - V 's are not due to any potential AQ-DMA complex solvated in the supernatant solution. Also, the presence of DMA in the supernatant solution cannot cause the changes in the I - V 's since in monolayers of **1+6** both I - V types are observed within different domains but with the same solution above. All this leads to the conclusion that the changes in I - V 's of HBC cores in **1** compared to **1+6** must be attributed to the properties of the coadsorbed CT complexes.

Two effects shall be discussed that can be caused by the dipoles of the CT complexes, namely, a potential step due to an interface dipole and a molecular Stark effect. When crossing through a layer of dipoles with strength μ and density N the change in potential is given by the Helmholtz equation

$$\Delta\phi = \frac{eN\mu}{\epsilon_0\epsilon_r}. \quad (1)$$

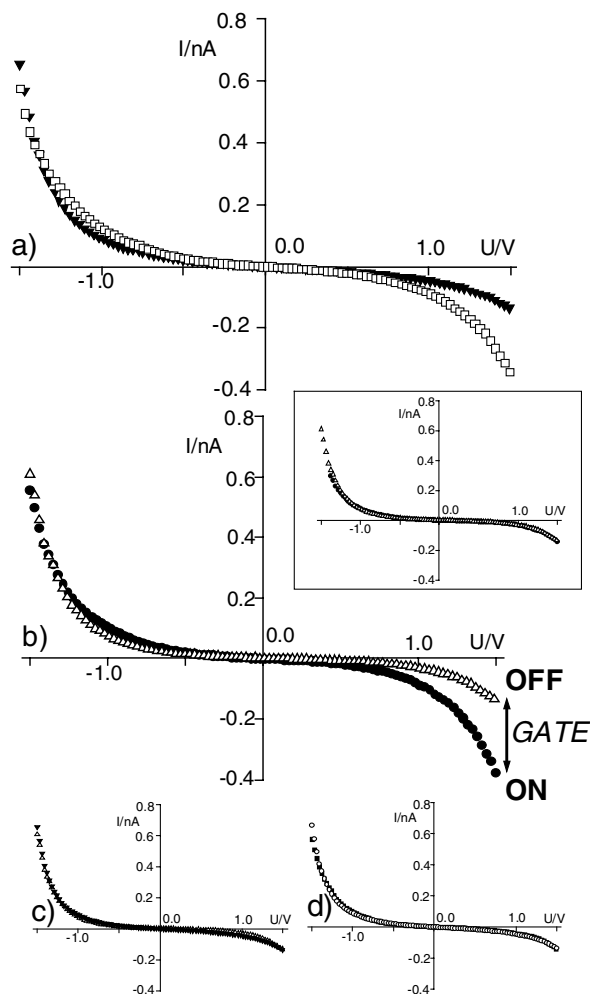


FIG. 3. I - V 's (raw data) through (a) HBC cores (solid triangles) and alkyl chains (open squares) in monolayers of **1**. (b) HBC cores in domains of **1+6** where CT complexes are adsorbed (solid circles) or not adsorbed (open triangles). Inset: shifted and normalized data; see text. (c) HBC cores in monolayers of **1+6** where no CT complexes are present (open triangles) and in monolayers of **1** (solid triangles). (d) HBC cores in monolayers of **2+6** (solid squares) and **2** (open circles). The size of the symbols reflects the experimental error.

Using the dipole density as determined from the STM results on monolayers of **1+6** together with a reasonable assumption for the separation between AQ and DMA in the CT complex of 0.35 nm, one obtains a change in work function of the substrate due to this interface dipole, which is equal to the relative shift between the adsorbate's molecular orbitals and the Fermi level of the substrate, of

$$\Delta\phi = \frac{f_{CT}}{\epsilon_r} 2 \text{ eV}, \quad (2)$$

where f_{CT} describes the extent of charge transfer. For typical dielectric constants of about 3 for organic materials and only partial charge transfer, changes in the work function of some 10 to 100 meV are possible. From the I - V normalization displayed in Fig. 3(b) (inset), a change in work function of about 120 meV can be concluded.

Indeed, with an estimated dipole strength of up to 3 D and a dielectric constant of 3, a change in work function of about 130 meV is obtained. However, the HBC experiences only the local interface dipole [23] and the relative orientation of the dipole with respect to the surface normal and the extent of charge transfer are not known. Furthermore, the HBC is likely to be located within the interface dipole. Since for normalization according to this model the I - V had to be shifted to more positive sample bias, we conclude that the normal component of the interface dipole points away from the substrate which implies that the donor (DMA) is positioned above the acceptor (AQ).

In addition, one may consider the change of the I - V by increased resonant tunneling currents originating from a shift of the LUMO due to the Stark effect. Evaluating the strength of the field of a single dipole (same assumptions as above) 2 nm apart from its center perpendicular to the dipole direction, one obtains a field strength of

$$\frac{f_{CT}}{\epsilon_r} 6 \times 10^7 \frac{\text{V}}{\text{m}}. \quad (3)$$

Since even for complete charge transfer this field strength is 2 orders of magnitude lower than the fields usually applied in STM experiments ($\sim 10^9$ V/m), we rule out that the Stark effect plays a major role.

The temperature dependence of the phenomena reported here can only be studied in a very limited temperature range, which is given at the lower end by the melting point of the solvent used, and at the higher end by the stability of the quasi-2D crystal at the solid-liquid interface. In the range of 18 to 33 °C we did not detect any temperature dependence. At temperatures well below 100 K new phenomena originating from bridge charging and vibronic levels have been reported in the literature [24,25]. We have not observed such phenomena in the temperature range accessible for our chemical-field-effect transistor (CFET).

In conclusion, we demonstrated the modification of current-voltage characteristics through a single molecule in an STM junction by nanometer-sized charge transfer complexes covalently linked to this molecule. The effect observed can be explained by a relative shift between the

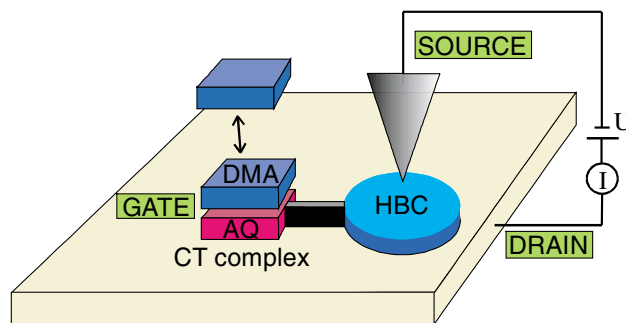


FIG. 4 (color). Schematic of a prototypical single-molecule CFET.

Fermi level of the substrate and the adsorbate's molecular orbitals due to the formation of a dipole at the interface. This setup can be viewed as a CFET based on a single molecule with an integrated nanometer-sized gate (Fig. 4), since the charge transfer complexes, responsible for the change in the I - V 's, are formed between an acceptor covalently bound to the molecule in the tunneling junction and a donor coming from the ambient solution. This proof of principle is a major step towards monomolecular electronics [1] and highly sensitive electronic molecular probes.

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*Present address: Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, USA.

†Corresponding author.

Email address: rabe@physik.hu-berlin.de

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