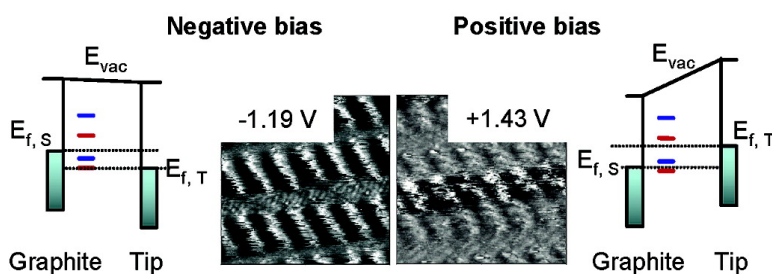


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Bias-Dependent Visualization of Electron Donor (D) and Electron Acceptor (A) Moieties in a Chiral DAD Triad Molecule

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The performance of conjugated oligomeric and polymeric semiconductors¹ depends critically on the mesoscopic ordering of these π -conjugated moieties. A number of liquid-crystalline materials with high-charge-carrier mobilities as a result of the high order has been developed in recent years.² Covalent linkage between electron donor (D) and acceptor (A) molecular fragments provides an excellent approach to achieve dimensional control over phase separation in D–A networks³ and are of interest in the field of molecular electronics.⁴

Scanning tunneling microscopy (STM) is a unique technique to study the ordering of molecules on conductive surfaces, often with submolecular resolution.^{5,6} In addition, STM is sensitive to the electronic properties of the adsorbates under investigation.⁷ It was soon noticed that STM shows chemical sensitivity; certain functional groups (e.g., aromatic moieties, amines, sulfides) are more conductive than others (e.g., alkyl chains). The latter are in turn more “transmissive” for the tunneling current than perfluorinated alkyl chains.^{5ab,8} Several theoretical approaches have been developed to explain the contrast of organic adsorbates in STM.⁹ Bias- and potential-dependent imaging have been used before to probe the electronic levels involved in the tunneling process,^{8g,10} but the system under investigation is unique for the following reasons: (1) it combines an electron donor and electron acceptor part covalently linked to each other and (2) the donor and acceptor parts are relatively large and well-separated in space, allowing them to be addressed individually.

In this contribution, we present an STM study of the ordering and bias-dependent contrast of a unique symmetric D–A–D system, composed of two oligo *p*-phenylene vinylene (OPV) D-units and a central perylenediimide (PDI) A-core, of which the chemical structure is shown in Figure 1a. The compound forms well-ordered two-dimensional patterns when physisorbed from 1-phenyloctane on graphite (HOPG) at the solid–liquid interface, as measured by STM in the constant-height mode. Figure 1b is a large-scale STM image showing rows of stacked bright rods, which are ordered in domains. The relative orientation of the domains reflects the 3-fold symmetry of the graphite substrate underneath. The length of such a rod (6.00 ± 0.07 nm) corresponds to the distance between the outermost phenyl groups of the DAD molecule. Hence, the molecule is not standing upright but is lying with its molecular axes parallel to the graphite plane. As a result, the tunnel path through the aromatic core is tip–D–graphite or tip–A–graphite and not tip–D–A–D–graphite. Of course, the tunneling direction (tip–graphite or graphite–tip) depends on the bias polarity. Alkyl chains occupy the

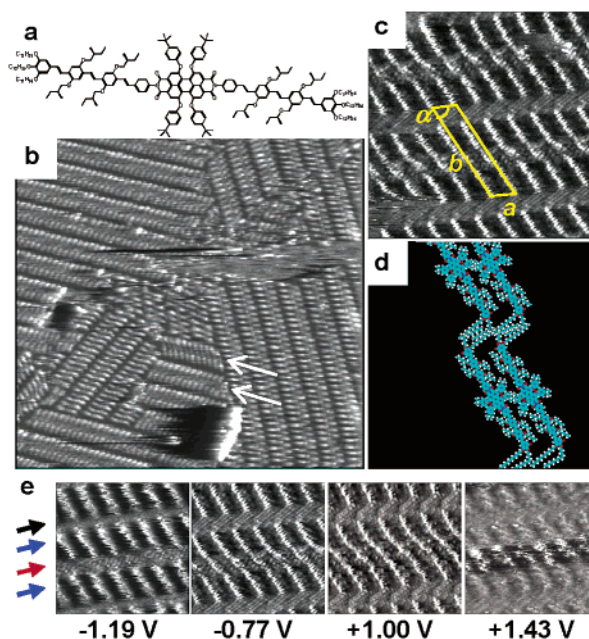


Figure 1. (a) Chemical structure of donor–acceptor–donor triad, OPV₄–PDI–OPV₄. (b) STM image of OPV₄–PDI–OPV₄ monolayer formed by physisorption at the 1-phenyloctane–graphite interface. The different sets of arrows indicate examples of mirror image-type packings. Image size is 70.2×70.2 nm². $I_{\text{set}} = 0.15$ nA. $V_{\text{bias}} = -0.96$ V. (c) High-resolution STM image of an OPV₄–PDI–OPV₄ monolayer. $I_{\text{set}} = 0.40$ nA, $V_{\text{bias}} = -0.70$ V, image size is 15.5×15.5 nm². Unit cell parameters are $a = 1.71 \pm 0.02$ nm, $b = 7.41 \pm 0.10$ nm, $\alpha = 62 \pm 1^\circ$. (d) Tentative molecular model reflecting the ordering in c. (e) Bias-dependent imaging of OPV₄–PDI–OPV₄. The applied sample bias is indicated below each image. Image size is 10.1×10.1 nm². $I_{\text{set}} = 0.40$ nA. Arrows outside the images refer to alkyl chains (black), OPV (blue), and PDI moieties (red).

dark regions between the rows of bright rods. In most of the rows, the long rod axis is rotated counterclockwise with respect to the normal on the long rod axis, although a nonnegligible number of rods are oriented clockwise within the rows. Enantiopure molecules normally do not form both possible mirror-image patterns, but only one of them.¹¹ Apparently, the presence of the rather bulky acceptor core weakens the interaction of the stereogenic centers with the graphite substrate, and the core might not be completely planar.¹² From the high-resolution image in Figure 1c, it is clear that the bright rods consist of three parts: the central part is attributed to the location of the PDI part and the outermost parts correspond to the OPV moieties. Measured along the propagation direction of the lamella, the distance between the aromatic cores is determined to be $(a) 1.71 \pm 0.02$ nm. This distance allows the OPV parts of the molecules to lie flat on the substrate. The acceptor part cannot

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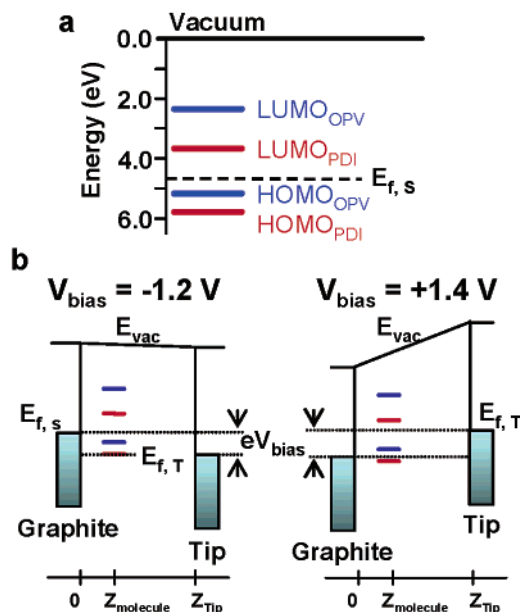


Figure 2. (a) Scheme of the frontier orbitals (HOMO and LUMO) of OPV (blue) and PDI (red) relative to the vacuum level and Fermi level of graphite. (b) Tentative energy level diagrams illustrating the relative position of the HOMO and LUMO levels of OPV (blue) and PDI (red) with respect to the graphite and Pt/Ir tip Fermi levels upon applying a bias on the sample. Left: negative sample bias. Right: positive sample bias. Fermi levels of graphite ($E_{f,s}$) and STM tip ($E_{f,T}$) are indicated with dotted lines. The energy levels of PDI and OPV were estimated from CV measurements and the absorption spectra. The slope of the vacuum level is determined by the difference in work function between substrate and tip and the applied bias voltage.

lie completely flat on the substrate due to the presence of the *tert*-butylphenoxy groups, which must be partly rotated away from the substrate. The slight curvature (S-shape) of the rods suggests only a limited tilt angle between the OPV and PDI planes. The distance between adjacent rows (b) measures 7.4 ± 0.1 nm and α measures $62 \pm 1^\circ$. Two out of three dodecyloxy chains are nicely resolved in several images. These chains are oriented along one of the main symmetry axes of the graphite substrate. The exact location of the third chain cannot be determined. Figure 1d is a molecular model reflecting the ordering as proposed.

Figure 1e shows a sequence of images recorded at different sample bias (from negative to positive). At high negative voltages (-1.19 to -1.06 V), the OPV parts appear brighter compared to the central PDI moiety. By changing the bias voltage from negative to positive, the PDI part gradually becomes brighter (from -0.77 to $+0.80$ V). Upon further increasing the positive bias voltage, we found that the PDI parts become brighter than the OPV units. These experiments have been repeated several times, using different tips, different set-point currents, and different scan directions, all showing qualitatively the same result.

The bias-dependent contrast changes can be explained by the schematic energy diagrams proposed in Figure 2, which are based upon a number of assumptions: (1) The tunneling junction is asymmetric with the molecules closer to the substrate than to the tip. (2) The interaction between the molecules and the substrate is weak; physisorption does not significantly affect the energy levels of HOMO and LUMO. (3) The molecular orbital that is closer in energy to the Fermi level of the negatively biased electrode (the electron source) affects the tunneling process more strongly. (4) OPV and PDI moieties are electronically decoupled or only weakly coupled as indicated by the absorption spectrum. As depicted in the left scheme, at negative sample bias, the HOMO_{OPV} level is located close to the Fermi level of graphite. Therefore, electrons

tunneling from graphite to the tip couple more strongly to the HOMO_{OPV} level than to the other energy levels. At high positive bias voltages (right scheme), the LUMO_{PDI} level is closer to the Fermi level of the tip than other states and, accordingly, is expected to affect the tunneling process, from tip to substrate, to a greater extent. This simplified model is in line with experimental observations: OPV moieties appear brighter at negative sample bias while the PDI moiety appears brighter at high positive sample bias.

In conclusion, we have presented the two-dimensional ordering of a unique electron donor–acceptor–donor triad molecule. By bias-dependent scanning tunneling microscopy imaging, the donor and acceptor parts of the molecule were distinguished. The bias-dependent contrast reflects the different electronic states involved in the tunneling process.

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Supporting Information Available: Absorption spectrum, CV curve, and determination energy diagrams (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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