Single-Molecule Wires Get a Lift**

Jeffrey M. Mativetsky and Paolo Samorì

Single-molecule wires, resistors, transistors, and logic elements represent the ultimate end-point of miniaturization in electronics, and the principal goal of molecular electronics.[1,2] Technologically speaking, consumer electronics based on single-molecule components is still a long way off due to enormous barriers in nanofabrication and integration; nonetheless, pioneering fundamental studies on small numbers of molecules, and even single molecules, are starting to show a range of electrical function including single-electron transistor properties,[3,4] rectification,[5–7] and switching.[8–11] In addition, electrical devices, such as transistors, light-emitting diodes, and solar cells built from thin films of organic materials are already entering the commercialization stage.[12–14] A fundamental understanding of the intrinsic intramolecular transport properties of molecules is therefore of great interest for the further advancement of large-area organic electronics, and increasingly for the potential emergence of organic nanoelectronics.

The greatest problems in single-molecule electronics have always been: 1) How do you reproducibly electrically contact a single molecule? 2) How can you gain a direct picture of the structure of the junction/device? 3) How do you systematically tune the device properties? Many inventive methods have been devised that answer one or two of these questions at a time; however, experiments where single-molecule devices are assembled, structurally characterized, and modulated have been elusive. Very recently, Lafferentz et al. have developed an elegant approach that combines scanning tunneling microscopy

(STM) imaging, nanomanipulation, and electrical measurement in order to controllably probe electrical conductance in a highly defined system.[15] In addition, this work enables the unprecedented measurement of single-molecule conductance as a function of length along the molecule, so far at lengths up to 20 nm.

Reproducible electrical characterization of single or small groups of molecules can be done ''blindly'', that is, without providing direct structural information, by various techniques such as mechanical break junctions,[5,6,16] nanopore junctions,[17] crossed nanowires,[18] nanoparticle bridges,[19,20] and electromigration-induced junctions.[3,4] Complementary to these methods, scanning probe microscopy (SPM) approaches have been among the most successful for measuring the electrical properties of nanometer-scale molecular junctions but with the additional bonus of offering structural characterization with resolution even down to the subnanometer scale.[21] STM imaging and scanning tunneling spectroscopy (STS) provide spatially resolved information about the local density of electronic states of molecules immobilized between an atomically sharp metallic tip and a conducting substrate, allowing the elucidation of single-molecule behavior, such as switching, for example.[10] Measurements have also been performed over specific regions of flat-lying molecules, electron-donating or -accepting parts, revealing highly localized characteristics such as differences in the rectification behavior.[7] Nevertheless, in this type of measurement there is normally some ambiguity about the distance between the tip and molecule since the tip–sample distance is regulated by the tunneling current through the junction, and the molecule is generally not in physical contact. Conducting atomic force microscopy (C-AFM) addresses this issue by using an AFM tip with a conducting coating as a movable probe, which can contact a sample with a regulated force, although, due to the size of the tip in the tens-of-nanometers range, multiple molecules are usually contacted at a time, depending on the system under investigation.[22,23] Furthermore, although this method offers the possibility of imaging the sample prior and after electrical characterization, to date these studies are often performed blindly. In an important recent study, this approach was used by

[*] Prof. P. Samorì, Dr. J. M. Mativetsky
Institut de Science et d'Ingénierie Supramoléculaires (ISIS)
CNRS 7006
Université de Strasbourg
8 allée Gaspard Monge, 67000 Strasbourg (France)
E-mail: samori@isis-ulp.org

Frisbie and co-workers to systematically probe conductance as a function of molecular length in nanoscale junctions with molecules up to 7 nm long, revealing a transition between tunneling and hopping regimes.[23]

A relatively new approach to measuring single-molecule conductance is the SPM-based break junction. This method has opened up the possibility of electrically probing single molecules by tethering a conducting tip to molecules chemisorbed on an Au (111) surface by simply approaching the tip to the surface; this is followed by the pulling of the tip out of contact while monitoring the conductance.[24] The conductance was found to decrease in a stepwise manner as individual bonds between the tip and the molecules are broken. Histograms, obtained from hundreds of curves, exhibit highly reproducible conductance peaks with integer multiples of a fundamental peak, attributed to single-molecule conductance. In break junctions based on C-AFM, forces and currents can be monitored simultaneously, providing information about the molecular conductance and the molecule–electrode bonding forces.[25] Over just a short time, break-junction SPM methods have been highly successful in yielding single-molecule conductance measurements for molecules with different lengths and end groups, thus providing parameters such as the tunneling damping factor, and contact resistance.[26,27] Unfortunately such an approach does not provide structural information about the junction.

Building on this, Lafferentz et al. extend the break-junction approach further. Instead of having a tightly packed array of upright molecules in a self-assembled monolayer, long chain-like polymers are grown on a metallic surface. This makes it possible to investigate long molecules that are too flexible to form chemisorbed layers. Instead of forming junctions at a random position on the surface and using a statistical approach, prior to performing electrical measurements, the sample is visualized by STM, and the submolecular structure of the chain is resolved. Then, after a particular chain is selected, one extremity is approached by the STM tip, leading to the non-specific attachment of the molecule to the tip. While vertically retracting the tip from the surface, thus stretching the molecule, electrical properties of the junction are measured as a function of the length of the molecular wire incorporated between the tip and substrate. Using this approach, exceptional control over the junction structure and dimensions are achieved. Through the investigation of individual isolated molecules having a well-characterized structure, important insight into the connection between structure and function is gained, giving access to the particular behavior associated with a specific nano-object, which may be smoothed out or lost in measurements on ensembles.

To have a well-defined, clean, and mechanically stable system, ultrahigh-vacuum and low-temperature (10 K) conditions are used. The basic process of the experiment is illustrated in Figure 1. First, dibromoterfluorene (DBTF) monomers are thermally evaporated onto a Au(111) surface, followed by a heating step, which promotes the diffusion and on-surface polymerization of DBTF conjugated polymers.[28] Then, after imaging the surface by STM, the STM tip is approached in close proximity to the end of a DBTF chain, and slowly retracted. During the approach and retraction, a constant voltage is held between the tip and the gold substrate and the current is recorded, providing an electrical fingerprint corresponding to the manipulation process. Upon successful lifting of the molecule from the surface, the current during the retraction becomes significantly larger than during the approach (up to two orders of magnitude after a few angstroms), confirming the attachment of the molecular chain to the tip, and the transport of charge through the molecule, rather than though vacuum (Figure 1b). A successful measurement is also accompanied by a change in the polymer shape after the lifting event, as a result of the chain relaxing back onto the surface in a new conformation. Finally, STM imaging provides unambiguous evidence that the chain is not damaged by the manipulation or the electrical measurement.

Using this vertical manipulation procedure, controlled measurements of conductance versus length (Figure 2a) and current versus voltage at specific lengths (Figure 2b) could be performed. Over a distance of 4 nm, the conductance $G(z)$ exhibits an exponential dependence on the extension of the piezo along the z axis, together with a conductance modulation having a period of about 1 nm. The exponential decay was fit to
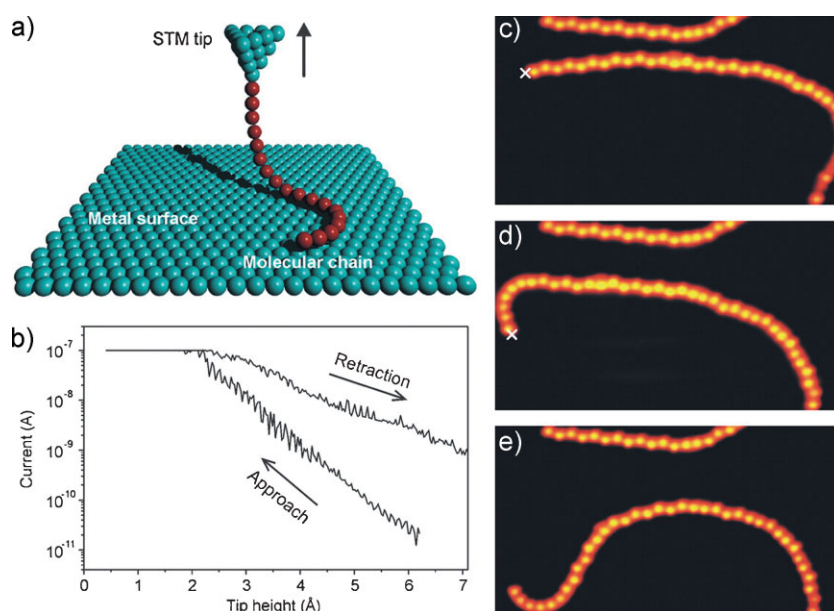

Figure 1. a) Schematic diagram of the experimental setup: an STM tip is used to lift the end of a molecular chain. b) During this vertical manipulation, the current between the metallic tip and substrate is monitored at a constant voltage. The current during the retraction is significantly higher than during the approach, due to the attachment of the conducting molecule. c–e) STM images (25.4 nm × 13.7 nm) of DBTF chains between manipulations. The cross marks the position of the tip during the lifting event. The chain changes shape as it relaxes back on the surface following the manipulation. Reprinted with permission from Reference [15]. Copyright 2009, American Association for the Advancement of Science.
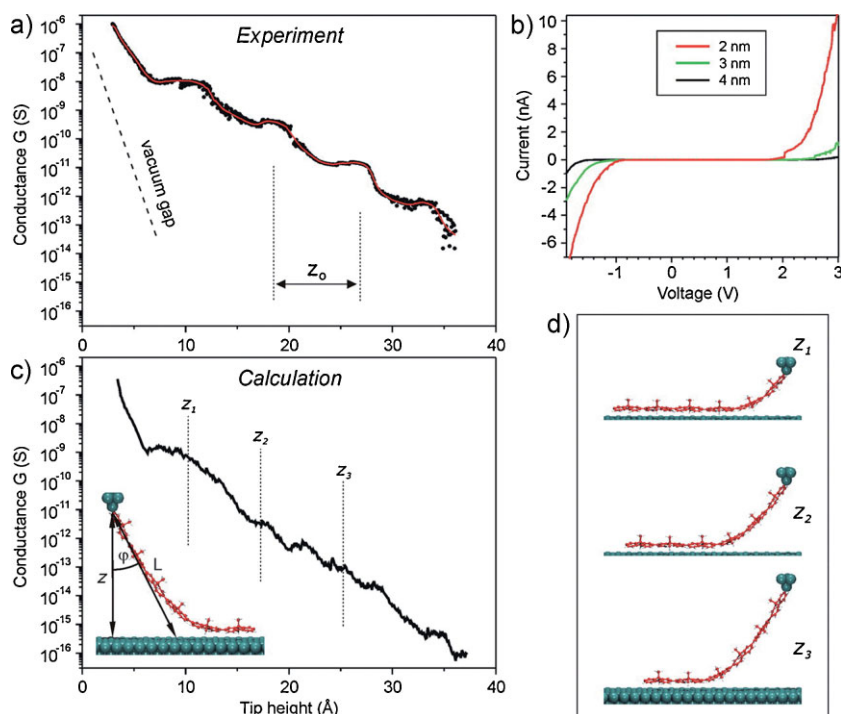
Figure 2. Conductance measured as a DBTF chain is lifted from the surface. The experimental (a) and calculated (c) conductance curves both follow an exponential decay with characteristic oscillations. The inset in (c) shows a diagram of the expected shape of the molecular wire during the pulling process. b) Current–voltage traces recorded at three fixed tip–sample distances. d) Schematic image of the molecular conformation at three tip–sample distances marked in (c). Reprinted with permission from Reference [15]. Copyright 2009, American Association for the Advancement of Science.

$G(z) = G_0\ e^{-\beta z}$, yielding a damping factor of $\beta = 0.38 \pm 0.09\,\text{Å}^{-1}$, which is in good agreement with a calculated value of $0.36\,\text{Å}^{-1}$ (Figure 2c), and previous measurements on conjugated molecules.[22] Taking into the account the curvature of the molecular chain during the lifting event (Figure 2c inset), a slightly reduced damping factor of $\beta = 0.3\,\text{Å}^{-1}$ was obtained. Through comparisons with theoretical modeling, the conductance oscillations were linked to the successive detachment of each monomer unit, with conductance maxima taking place just before monomer detachment. Current–voltage measurements at fixed lengths exhibited some asymmetry, which was attributed to a molecular highest occupied molecular orbital (HOMO) level, which is closer to the Fermi energy of the electrodes than the lowest unoccupied molecular orbital (LUMO). In addition, manipulation experiments were successfully performed with chain lengths up to 20 nm, in some cases with the entire molecular wire being lifted from the surface.

These measurements are reminiscent of single-molecule pulling experiments performed by AFM-based force spectroscopy, primarily on biomolecules; individual molecules are lifted at random from a surface, and upon vertical stretching details about their mechanical properties are obtained.[29,30] A promising direction for future work is to combine both approaches, that is, to employ C-AFM whereby a conducting probe is used to pick up a linear macromolecule while the force and current are simultaneously recorded. This will provide direct insight into the correlation between conformation and electrical characteristics of single molecular wires during

the manipulation experiment. Further advances can also be foreseen by using SPM imaging to determine the polymer persistence length, which quantifies mechanical stiffness of the chain.[31] Together these approaches promise new levels of understanding of the electromechanical properties of single molecules, laying the foundations for monomolecular electroactive devices.

[1] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
[2] N. J. Tao, *Nat. Nanotechnol.* **2006**, *1*, 173.
[3] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, P. L. McEuen, *Nature* **2000**, *407*, 57.
[4] W. J. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **2002**, *417*, 725.
[5] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Lohneysen, *Phys. Rev. Lett.* **2002**, *88*, 176804.
[6] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hanisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 8815.
[7] K. Müllen, J. P. Rabe, *Acc. Chem. Res.* **2008**, *41*, 511.
[8] A. S. Blum, J. G. Kushmerick, D. P. Long, C. H. Patterson, J. C. Yang, J. C. Henderson, Y. X. Yao, J. M. Tour, R. Shashidhar, B. R. Ratna, *Nat. Mater.* **2005**, *4*, 167.
[9] J. M. Mativetsky, G. Pace, M. Elbing, M. A. Rampi, M. Mayor, P. Samorì, *J. Am. Chem. Soc.* **2008**, *130*, 9192.
[10] C. Silien, N. Liu, W. Ho, J. B. Maddox, S. Mukamel, B. Liu, G. C. Bazan, *Nano Lett.* **2008**, *8*, 208.
[11] G. Pace, V. Ferri, C. Grave, M. Elbing, C. von Hanisch, M. Zharnikov, M. Mayor, M. A. Rampi, P. Samorì, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 9937.
[12] S. R. Forrest, *Nature* **2004**, *428*, 911.
[13] D. J. Gundlach, *Nat. Mater.* **2007**, *6*, 173.
[14] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
[15] L. Lafferentz, F. Ample, H. Yu, S. Hecht, C. Joachim, L. Grill, *Science* **2009**, *323*, 1193.
[16] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252.
[17] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, *286*, 1550.
[18] J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, J. C. Yang, T. L. Schull, J. Naciri, M. H. Moore, R. Shashidhar, *J. Am. Chem. Soc.* **2002**, *124*, 10654.
[19] T. Dadosh, Y. Gordin, R. Krahne, I. Khivrich, D. Mahalu, V. Frydman, J. Sperling, A. Yacoby, I. Bar-Joseph, *Nature* **2005**, *436*, 677.
[20] C. Chu, J.-S. Na, G. N. Parsons, *J. Am. Chem. Soc.* **2007**, *129*, 2287.
[21] P. Samorì, *J. Mater. Chem.* **2004**, *14*, 1353.
[22] J. M. Mativetsky, M. Palma, P. Samorì, *Top. Curr. Chem.* **2008**, *285*, 157.
[23] S. H. Choi, B. Kim, C. D. Frisbie, *Science* **2008**, *320*, 1482.
[24] B. Q. Xu, N. J. J. Tao, *Science* **2003**, *301*, 1221.
[25] B. Q. Xu, X. Y. Xiao, N. J. Tao, *J. Am. Chem. Soc.* **2003**, *125*, 16164.
[26] F. Chen, X. L. Li, J. Hihath, Z. F. Huang, N. J. Tao, *J. Am. Chem. Soc.* **2006**, *128*, 15874.

[27] G. Sedghi, K. Sawada, L. J. Esdaile, M. Hoffmann, H. L. Anderson, D. Bethell, W. Haiss, S. J. Higgins, R. J. Nichols, *J. Am. Chem. Soc.* **2008**, *130*, 8582.

[28] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, *2*, 687.

[29] M. Rief, H. Clausen-Schaumann, H. E. Gaub, *Nat. Struct. Biol.* **1999**, *6*, 346.

[30] C. Bustamante, J. C. Macosko, G. J. L. Wuite, *Nat. Rev. Mol. Cell Biol.* **2000**, *1*, 130.

[31] P. Samorì, C. Ecker, I. Gössl, P. A. J. de Witte, J. J. L. M. Cornelissen, G. A. Metselaar, M. B. J. Otten, A. E. Rowan, R. J. M. Nolte, J. P. Rabe, *Macromolecules* **2002**, *35*, 5290.