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Integrating Reaction Chemistry into Molecular Electronic Devices

Qian Shen,^[a] Xuefeng Guo,^{*[a]} Michael L. Steigerwald,^[b] and Colin Nuckolls^{*[b]}

Dedicated to the 100th anniversary of the College of Chemistry, Peking University





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Abstract: This Focus Review provides an overview of the design and fabrication of new families of molecular electronic devices where reaction chemistry is an efficient means for covalently bridging the nanogaps between separated contacts. In each case ever-reducing top-down device fabrication existing in the silicon-based semiconductor industry is tailored to meet the requirements of ever-expanding length scales of bottom-up assembly. The

1. Introduction

The creation of efficient optoelectronic devices based on individual functional molecules, often termed "molecular electronics", is one of the ultimate goals in nanotechnology.^[1,2] Since the development of reliable techniques for producing conventional silicon-based devices with dimensions smaller than 15 nm is a formidable technological challenge, molecular electronics may fulfill technological roles that are complementary to silicon-based electronic devices.^[3-8] The attractive features of organic molecular devices, with the opportunities open to their wide-ranging functionalities, are the miniaturized dimensions and the high degree of control on molecular design possible through chemical synthesis. Thus far many molecules with desired rich properties, such as electromechanical, optical, thermoelectric, magnetic, and molecular recognition behaviors^[3-8] have been designed and synthesized; when sandwiched between molecular junctions

Beijing National Laboratory for Molecular Sciences (BNLMS) State Key Laboratory for Structural Chemistry of Unstable and Stable Species College of Chemistry and Molecular Engineering Peking University Beijing 100871 (P.R. China) Fax: (+86)10-62757789 E-mail: guoxf@pku.edu.cn [b] Dr. M. L. Steigerwald, Prof. C. Nuckolls Department of Chemistry and the Columbia University Center for Electronics of Molecular Nanostructures Columbia University New York, New York 10027 (USA) Fax: (+1)212-932-1289 E-mail: cn37@columbia.edu

combination of directed self-assembly and programmed chemical reactions with device fabrication allows us to modify the electrodes and then to complete electrical circuits by chemically connecting the electrodes.

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(Figure 1), these molecules might lead to novel devices that are not accessible by traditional materials or approaches.



Figure 1. Schematic diagrams of experimental configurations for molecular junctions (A) and covalent binding strategies for molecular junction formation (B). Electrodes in Figure 1B could be either metal or single-walled carbon nanotube (SWCNT) electrodes.

Figure 1A shows a general schematic diagram of metalmolecule-metal junctions that can be used to measure current transport through molecules. At present there exist several types of molecular junctions.^[3-6,8] Owing to the different geometries of the junctions, the different types of electrode materials employed, the different modes of molecule-electrode contact established, and the number of molecules tested,^[9] broad ranges of molecular conductance have been observed. In order to achieve consistent and reproducible results, one would prefer to wire a single molecule directly into an electrical circuit by chemically binding each end of the molecule directly to an electrode (Figure 1B). Although a vast store of flexible synthetic methodology exists, it is essentially untapped when it comes to incorporating molecules into electronic devices. Reaction chemistry can provide an efficient means to forge covalent connections between mole-

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[a] Q. Shen, Prof. X. Guo

cules and electrodes. Indeed, nanojunctions having different types of contact chemistry have been demonstrated.^[3-9] These flexible reaction chemistries give molecular materials an overwhelming amount of diversity and functionality. This could provide opportunities for nanoscale electronics to be synthesized rather than fabricated. We will be able to precisely control the contact geometry, chemistry, and physics down to the atomic scale and thereby measure the intrinsic properties of single molecules or prescribed collections of molecules between electrodes.

The most commonly used approach is to position molecules terminated with thiols between a pair of gold electrodes (Figure 2).^[10–25] This method has many advantages, but it also suffers from many shortcomings. Thiols react with air or oxygen, forming disulfides and oligomers through mild oxidation,^[26,27] or sulfinic and sulfonic acids upon further oxidation.^[28,29] It is very challenging to control the contact geometry precisely because of the high atomic mobility of gold and the large polarization field at the metal–molecule interface. Simply fabricating the gold electrodes is difficult,



Figure 2. Illustration of a single molecule attached to two point contacts formed from break gold electrodes. This graphic is reproduced from reference [7].



Xuefeng Guo received his PhD in 2004 from the Institute of Chemistry, Chinese Academy of Science, Beijing, with Daoben Zhu and Deqing Zhang. From 2004 to 2007, he was a postdoctoral scientist at Columbia University with Colin Nuckolls and Philip Kim. He joined the faculty at Peking University in 2008. His research focuses on functional nanometer/ molecular devices.



Colin Nuckolls completed his undergraduate studies at the University of Texas at Austin studying with Marye Anne Fox and then received his PhD in 1998 from Columbia University with Thomas Katz. He was an NIH postdoctoral fellow with Julius Rebek, Jr., at the Scripps Research Institute. He joined the faculty at Columbia University in 2000, and in 2006, he was promoted to the rank of Professor. and this leads to the formation of pitted gold electrodes and then uncertainty in the number of molecules that reside between the electrodes during a measurement. Given these difficulties, it is perhaps not surprising that broad ranges of molecular conductance have been observed in experimental charge-transport data using gold point junctions.^[30–33] Although the calculated conductance of alkanedithiol molecules agrees well for certain model electrode configurations with the experimental data,^[9,34] notable disagreement still exists between the experimental measurements and the theoretical calculations.^[30–33] In order to improve the measurements of molecular conductance and realize the intrinsic properties of molecular bridges, one should try to use chemi-contacts, contacts made by covalent bond formation, that are chemically as well-defined as possible.

This Focus Review describes the design, fabrication, and characterization of molecular electronic devices in two systems with different electrodes (metallic or single-walled carbon nanotube-based contacts) developed in the past decade. In each case reaction chemistry has been integrated into the design of the molecular device in order to circumvent the problems stated above. The combination of directed self-assembly and programmed chemical reactivity with sophisticated device fabrications allows us to construct complex, multicomponent molecular electronic devices. These two systems are the following: 1) Several sophisticated methods, including break junctions,[17,21,35-43] scanning probes,^[22,33,44–50] sandwich large-area molecular junctions,[51-53] liquid metal contacts,[54-57] self-aligned lithography,^[58-61] and on-wire lithography,^[62-65] have been developed to fabricate molecular-scale metal electrodes for the purpose of circumventing random attachment and oxidative oligomerization of dithiol molecules. 2) A reliable e-beam lithographic method has been developed to precisely cut 1-10 nm gaps in single-walled carbon nanotube (SWCNT) electrodes.^[7,66-71] We covalently rewire the gaps with conjugated molecules through amide linkages.^[7] This method is robust and general. A valuable aspect of this strategy is that one can include various and variable functionalities in the bridging molecular backbone. This allows diverse, yet distinct, external stimuli, such as protons, light, ions, and other chemical and electrostatic effects to modulate the conductance of the devices.^[7,66-71] However, molecular electronics is a diverse and rapidly growing field. Having limited space and references, we will only be able to cover some of the major contributions with the most general applicability and highlight the concept of integrating reaction chemistry into molecular devices, which was neglected in most previous reviews. Fortunately, there are a number of excellent previous review papers in the literature covering various aspects of molecular electronics, which can amend these deficiencies.[3,5,7-9,34]

2. Molecular-Scale Metal Electrodes

2.1. Break Junctions

In general, break junctions are formed from a single metal nanowire by one of two methods: mechanically controllable bending or electromigration. Each leaves a nanogap between the broken ends of the nanowire. Although neither of them can precisely control the exact geometry of the electrodes, the contact mode, and the number of molecules under investigation, these methods do provide some control on the size of the gaps and allow single-molecule conductance to be tested.

The first example of mechanically controllable break junctions (MCBJs) to make molecular junctions was done by Reed et al. in 1997.^[21] In this approach, a notched gold wire is glued onto a flexible substrate and is fractured by bending of the substrate, after which an adjustable tunneling gap can be established (Figure 3). A large reduction factor between



Figure 3. A) A schematic of a benzene-1,4-dithiolate SAM between proximal gold electrodes formed in an MCBJ. B) Typical I-V characteristics taken. Top illustrates a gap of 0.7 V, and the first conductance derivative, which shows a steplike structure. Middle shows three independent conductance measurements, offset for clarity, illustrating the reproducibility of the conductance values. Bottom represents the electrical measurement illustrating conductance values approximately twice the observed minimum conductance values. Resistances of ca. 14 megohm for the first step and 7.1 megohm (negative bias) and 5 megohm (positive bias) for the second step were measured. This graphic is reproduced from reference [21].

the piezo elongation and the electrode separation ensures an inherently stable contact or tunnel junction. The wire contacts are atomically sharp when broken. In the experiments, benzene-1,4-dithiol was simultaneously assembled from a tetrahydrofuran solution onto the two facing gold electrodes when the break junctions were broken in solution under an Ar atmosphere, resulting in formation of a self-assembled monolayer (SAM) on the gold electrodes that was nearly perpendicular to the surface. The THF solvent was allowed to evaporate in the ambient Ar atmosphere before the conductance measurements. Once the junctions were established, the conductance voltage curves were recorded (Figure 3). An apparent gap of ca. 0.7 V was observed in all cases. Each curve shows two steps in both bias directions. Figure 3B shows I(V) and G(V) measurements of one singular observation that gave resistances that were approximately half the value of the maximum resistances (ca. 22 megohm). This suggests a configuration of two noninteracting self-assembled molecules in parallel, substantiating the idea that the threshold resistance of a single molecule is about 22 megohm. This study provides a quantitative measure of the conductance of a junction containing a single molecule, which is a fundamental step in the emerging area of molecular-scale electronics.

This work led to an explosion of both experimental and theoretical work, in addition to subsequent controversy. Using the same procedure, Reichert et al.^[35] performed the conduction measurements of different single organic molecules both at room temperature and 30 K. They observed that the conductance curves reflected the symmetry, or asymmetry, of the molecules. Dulic et al.^[36] investigated photochromic molecular switches that are self-assembled on gold pads formed by MCBJ technique. They observed oneway optoelectronic switching of the molecules from the conducting to the insulating state when illuminated with visible light ($\lambda = 546$ nm). The more recent improvements on MCBJs came from the work of the Ralph group,^[37,38] who was able to incorporate a gate electrode into the setup and place a single fullerene (C_{60}) between metal contacts. As a result, they can measure the transport properties of a single fullerene. They explored the Coulomb blockade and the Kondo effect of devices as a function of the electrode coupling. By tuning the electrode spacing, they measured the changes of a fullerene molecule in both the Kondo temperature and zero-bias conductance that were in good accord with theoretical expectations. This helps understand how the mechanical motion changes the relative coupling of the molecule to the electrodes.

Another type of break junctions is termed "electromigration" break junction. The initial work using this technique was reported by Hongkun Park et al. in 1999.^[41] In this paper, a simple yet highly reproducible method to fabricate metallic electrodes with nanometer separation was presented. By using electron-beam lithography and shadow evaporation, they prepared gold electrodes that were 10 nm thick and ca. 150 nm wide at the smallest region. When a voltage was applied across the wire, the large current flow caused the electromigration of gold atoms and the eventual breakage of the nanowire. The breaking process yielded two stable metallic electrodes separated by about 1 nm with high efficiency. They claimed that these electrodes were ideally suited for electron-transport studies of chemically synthesized nanostructures, and their utility was demonstrated by fabricating single-electron transistors based on colloidal cadmium selenide nanocrystals.

One of the major advantages of this technique is that electromigrated break junctions are fabricated to afford single-molecule transistors on silicon wafer substrates with a

native global back-gate electrode, which allows scientists to measure the charge transport properties as a function of the gate coupling. Following the initial demonstration with nanocrystals the same group in 2000^[42] fabricated singlemolecule transistors based on individual C₆₀ molecules connected to electromigrated break gold electrodes. Transport measurement results provided evidence for a coupling between the center-of-mass motion of the $C_{\!60}$ molecules and single-electron hopping. The coupling is manifest as quantized nanomechanical oscillations of the C₆₀ molecule against the gold surface, with a frequency of about 1.2 THz. This value is in good agreement with a simple theoretical estimate based on van der Waals and electrostatic interactions between C₆₀ molecules and gold electrodes. The next major achievements on quantum transport measurements using electromigrated break junctions were reported back-to-back by two excellent examples in Nature in 2002.^[17,43] Park et al.^[17] reported single-atom transistors formed from terpyridyl cobalt complexes where they could regulate the coupling of the electrode to the Co center using different alkyl chains and switch the system from one that displayed the Kondo effect to one that displayed Coulomb blockade. In the other report, Liang et al.^[43] employed an individual divanadium molecule to build single-molecule transistors in which the coupling was suitable for both the Kondo effect and Coulomb blockade to be present. They found that the Kondo resonance can be tuned reversibly using the gate voltage to alter the charge and spin state of the molecule (Figure 4). Recently, Strachan et al.^[40] used real-time TEM imaging to monitor the dynamics of nanogap formation by feedback-controlled electromigration (FCE) at the subnanometer scale and found that well-defined crystal facets appear as the nanogap forms, thus revealing that nanoscale electrodes formed by FCE are good for use as molecularscale contacts. The third type of break junctions based on scanning tunneling microscope (STM) will be discussed in detail below.

2.2. Scanning Probes

Scanning probe microscopes, such as STM and conductive probe atomic force microscopes

(CP-AFM), provide the powerful tools to make metal-molecule-metal junctions at the molecular level. These junctions can be made quickly using a gold tip and a gold substrate. In a typical STM break-junction experiment, an Au tip is driven into contact with an Au surface in a solution containing the sample molecules, and the junction conductance (G) is measured during subsequent retraction. Initially the measured conductivity decreases in a discrete



Figure 4. Demonstration of device structures of single-atom transistors using terpyridyl cobalt complexes (A) and single-molecule transistors incorporating individual divanadium molecules (B). The graphics are reproduced from reference [17] and [43], respectively.

manner as integer multiples of the conductance quantum. Eventually when the single chain of gold atoms breaks, the conductivity drops to zero. During the further pulling process the so-formed gaps can be bridged in situ where the breaking process is taking place, and a new sequence of steps in a lower conductance regime appears. This new behavior indicates the formation of a stable molecular junction with an integer number of trapped molecules. The main advantage of this method is its ability to repeatedly form thousands of molecular junctions in which molecules are directly connected to two electrodes and get good statistics. The first examples of this method were reported by Xu et al.^[33] where they applied the technique to two different sets of molecules (Figure 5). Following the initial work, the Tao group and others used similar methods to measure the conductance of single molecules with various chemical compositions.^[72] Venkataraman et al.^[31] have studied how internal properties of the junction molecules affect their conductance. For example, using α, ω -diamino-oligophenyls they have investigated the effect of the dihedral angle between two phenyl rings (in biphenyls) and the number of coplanar phenyl rings (in the family of oligophenyls) on the overall conductance (Figure 5). In a subsequent report they systematically studied the effects of the electronic energy levels on



Figure 5. A–F) Conductance data for 4–4'-bipyridine (A–D) using the STM-based break junction setup of the Tao group as the tip is pulled away from the substrate. G and H) Conductance measurements of 1,4-diaminobenzene and 2,7-diaminofluorene junctions using a similar setup in the Venkataraman group. Inset in (G) shows that a lorentzian line fits the sub- G_0 peak in the histogram of **1**. More details can be found in reference [31] and [33]. The graphics are reproduced from reference [31] and [33], respectively.

the transport by varying the chemical substituents on the benzene ring,^[73] and found excellent correlation between junction conductivities and electrochemical oxidation potentials, indicating that the HOMO levels are responsible for tunneling transport through these diamines.^[46] Recent work by the same group showed the rich contact chemistry of molecular conductance by using different link groups.^[47] They found that alkyl phosphines have extremely sharp conductance histograms and have the lowest contact resistance. These results augur well for the preparation of new types of linkages that go beyond ionic bonds to form electrically transparent contacts.

The use of CP-AFM can also simply form metal-molecule-metal junctions for performing molecular conductance measurements in addition to the force measurements, pioneered by the Frisbie group in Minnesota and the Lindsay group in Arizona. The first examples of CP-AFM junctions were developed by Kelley and Leatherman et al.^[44,50] One major advantage over STM is the ability of CP-AFM to control the formation of molecular junctions without relying on the parameter it seeks to measure, that is, conductance. This technique was successfully used to study organic crystals^[44] and self-assembled monolayers.^[50] The next major improvement of CP-AFM junctions was reported by the Lindsay group.^[13,22] In this approach, conducting molecules containing thiol groups at both ends were inserted in a preassembled monolaver of monoalkanethiols on an Au surface (Figure 6). The alkanethiolate layer served as an insulating matrix surrounding individual or small bundles of the more conducting dithiol molecules. The thiol groups exposed at the top of the film were derivatized with Au nanoparticles by incubating the monolayer in a nanoparticle-containing solution. Then an Au-coated conducting AFM probe was used to locate and contact individual particles bonded to the monolayer. Current-voltage measurement results can be quantized as integer multiples of one fundamental curve, an observation used to identify single-molecule contacts. The resistance of a single octanedithiol molecule was 900 ± 50 megohms, based on measurements on more than 1000 single molecules. In contrast, they also found that nonbonded con-



Figure 6. Schematic representation of the CP-AFM experiment. The sulfur atoms (dark gray dots) of octanethiols bind to a sheet of gold atoms (light gray dots), and the octyl chains (black dots) form a monolayer. The second sulfur atom of a 1,8-octanedithiol molecule inserted into the monolayer binds to a gold nanoparticle, which in turn is contacted by the gold tip of the conducting AFM. The graphic is reproduced from reference [22].

tacts to octanethiol monolayers were at least four orders of magnitude more resistive, less reproducible, and had a different voltage dependence, demonstrating that chemically bonded contacts play an important role in the measurement of intrinsic molecular properties.^[9]

2.3. Sandwich Large-Area Molecular Junctions

For technological applications, molecular-scale junctions must be reliable, stable, and reproducible. Self-assembled monolayers (SAMs) may offer a promising route to the fabrication of reliable devices, and charge transport through SAMs of alkanethiols is well understood.^[5,9,34] Unfortunately, electrical shorts in SAMs are often formed upon vapor deposition of the top electrode, which limits the size of the devices to about 45 nm. Recently an impressive method to manufacture molecular junctions with diameters up to 100 μ m with high yields (>95%) was demonstrated in the de Boer group.^[51] This technique involves processing the molecular junctions in the holes of a lithographically patterned photoresist, and then inserting a conducting polymer interlayer between the SAM and the metal top electrode (Figure 7). A silicon wafer having predeposited gold bottom contacts is used as the substrate for the device. The photoresist was spin-coated and holes (diameter 10-100 µm) were cut through the photoresist. After self-assembly of alkane dithiolates on the gold bottom electrode by submerging the substrates in solution, a water-based suspension of poly(3,4ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid) (PEDOT:PSS) was spin-coated on top of the SAM, resulting in a layer thickness of about 90 nm. Next, the top gold electrode was vapor-deposited through a shadow mask. The top electrode acted as a self-aligned etching mask during the removal of the exposed PEDOT:PSS



Figure 7. Processing steps of a large-area molecular junction. A) Gold electrodes were vapor-deposited on a silicon wafer and a photoresist was spin-coated. B) Holes were photolithographically defined in the photoresist. C) An alkane dithiol SAM was sandwiched between a gold bottom electrode and the highly conductive polymer PEDOT:PSS as a top electrode. D) The junction is completed by vapor deposition of gold through a shadow mask, which acts as a self-aligned etching mask during reactive ion etching of the PEDOT:PSS. The dimensions for these large-area molecular diodes range from 10 to 100 mm in diameter. The graphic is reproduced from reference [51].

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using reactive ion etching. This simple approach is potentially low-cost and could pave the way for practical molecular electronics.

Following the initial work, the same group studied the tunneling current density versus voltage (J-V) characteristics of alkanethiols in large-area molecular junctions using the Simmons model.^[52] The Simmons model combined with the image potential gave a good description of the experimental data from tunneling current measurements in molecular junctions for the voltage range up to 1 V bias. Most recently the same group developed a remarkable technology by which they can simultaneously fabricate over 20000 molecular junctions using the same approach-each consisting of a gold bottom electrode, a self-assembled alkanethiol monolayer, a conducting polymer layer and a gold top electrode—on a single 150 mm wafer.^[53] The robustness of this technique is demonstrated in strings where up to 200 junctions are connected in series with a yield of unity. It should be mentioned, however, that the junction resistance and scaling with surface area depend on processing conditions such as the type of photoresist, chemical composition of the monolayer, the use of surfactants, and the drying conditions of the PEDOT:PSS.

2.4. Liquid–Metal Contacts

It is well-known that liquid mercury electrodes have been extensively used by electrochemists mostly owing to the ease of obtaining a clean, defect-free, metallic surface. For the purpose of measuring conductance across assemblies on electrode surfaces, mercury provides a convenient soft electrode besides the advantages listed above. Another advantage of liquid mercury electrodes is that mercury enables researchers to mechanically bring a metallic electrode that can conform to the bottom surface in contact with a molecular assembly. This provides the opportunity of using metallic electrodes for the second contact without the use of any further critical conditions (such as thermal and electron-beam evaporations). In order to survey this approach, we will focus on mercury–solid-metal junctions.

In the Whitesides group, bilayers of alkanethiols have been studies using a metal-insulator-metal junction based on self-assembled monolayers (SAMs).^[54] The junction consists of an SAM supported on a silver film (Ag-SAM(1)) in contact with a second SAM supported on the surface of a drop of mercury (Hg-SAM(2))—that is, a Ag-SAM(1)SAM(2)-Hg junction (Figure 8A). This system should be particularly valuable for physical organic studies for screening the electrical properties of a wide range of molecular structures for their ability to support electron transport. In another study,^[55] they described a simple experimental procedure to measure rates of electron transport across organic thin films having a range of structures, compared the data for several types of films, and outlined a theory appropriate for analyzing these rates. They examined a Ag-SAM(1)SAM(2)-Au junction with two sets of contact chemistry between two monolayers: In the first, the SAMs



Figure 8. A) Schematic illustration of a $J_{Ag-SAM(1)/(SAM(2)-Hg}$ junction. The photographic image is that of a $J_{Ag-C16//C16-Hg}$ junction. B) Current density versus potential for three different molecules in the Ag-molecule//molecule-Hg configuration. Left) The data with a relatively defect-free Ag electrode (obtained via the "template stripping" method). Right) The data with the defect-prone "as-deposited" Ag electrode. Notice the significance of the use of a defect-free substrate in enhancing the reproducibility in the experiments. The spread in the data decreased dramatically when the substrate was smooth. The averages (drawn as heavy black lines) also show a trend of decreasing current density with increasing chain length. The graphics are reproduced from reference [54] and [57], respectively.

contact through van der Waals interactions, and in the second, through covalent (amide CONH group), hydrogen, or ionic bonds (CO₂H…NH₂ pairs). They found that the current density measured at a particular value of applied voltage depended significantly on the structure of the interface. Based on the measurement results, they determined the orders of rates of tunneling transport: covalent> noncovalent bonds, and hydrogen bonds>van der Waals contacts, which is also supported by the work of Sek et al.^[56] In a further work by the same group,^[57] they compared the structural and electrical characteristics of SAMs of n-alkanethiolates on two types of silver substrates: one using silver films asdeposited (AS-DEP) by an electron-beam evaporator, and one using silver films prepared by the method of templatestripping, and detailed how the defects on the silver surface affect the conduction across such systems. They demonstrated that measurements of current density through Hg-drop junctions incorporating ultraflat silver, produced using the method of template stripping, are much more reliable than measurements through junctions incorporating AS-DEP silver (Figure 8B).

2.5. Self-Aligned Lithography

2.5.1. Primed Electrode Surfaces: In Situ Formation of Molecular "Lock-and-Key" Bridges

A recent important improvement of molecular-scale metal junctions is the integration of chemical reaction design into the formation of nanoscale electrical "sockets." This allows the insitu construction of three-component molecular wires.^[58] Previous work in molecular electronics, which has typically relied on ex situ synthesis of wire components such as using dithiols or other doubly functional groups followed by their subsequent insertion into devices,^[9-25] has been complicated by the tendency of dithiol molecules to oxidatively oligomerize. The oligomers can span gaps that are much larger than the original individual molecule. They can also randomly attach to arbitrary points on the electrodes, in some cases binding both of their surface-active groups to the same electrode.^[26-29] Our two-step reaction sequence mitigates these problems by exploiting reaction specificity. In the first step a monolayer of a bifunctional molecule is assembled on the electrode surface. We choose the bifunctional molecule such that only one end of the molecule reacts with the electrode; the second functional group has no affinity for the electrode. In the second step a second molecule is used to bridge the gap between the termini of the films (Figure 9A). The second molecule is chosen to



Figure 9. A) The strategy used to bridge electrode surfaces in a two-step sequence. B) Bridging gaps by first forming a thiol-terminated monolayer followed by the reaction with a diamine. The R group is a 4-dodecyloxy-substituted phenyl group added for solubility. C) Bridging by first forming a monolayer with the terpyridyl group and using cobalt ions to or chestrate wire formation. This graphic is reproduced from reference [58].

have a double affinity for the second functional group of the first molecule, but no affinity at all for the electrode surface. We use the first molecule to fashion a lock, and the second molecule is the key.

2.5.2. Self-Aligned Lithographic Approach for Production of Nanoscale Electrodes

To test these strategies within molecular electronic devices, a new technique, termed self-aligned lithography, has been created to fabricate molecular-scale electrical test beds. The paradigm is shown in Figure 10 A-D.^[58,74] The substrate for



Figure 10. A) A line of Al on Pt is deposited by electron beam lithography on a silicon wafer coated with ZrO_2 . B) Air in the ambient oxidizes aluminum to produce an overhanging aluminum oxide layer. C) Evaporation of the counter electrode produces platinum separated by the amount of aluminum oxide overhang. D) Dissolving the aluminum/aluminum oxide layer gives closely spaced platinum electrodes. E) SEM showing a 3 nm gap; the part in the gray rectangle is enlarged 200%. F) SEM showing a 5 nm gap. G) SEM showing a 10 nm gap. This graphic is reproduced from reference [58].

this process is a clean silicon wafer that has a surface of 20 nm thermal SiO_2 surmounted with a 5 nm layer of ZrO_2 . A 3-nm-thick Pt layer is deposited by electron-beam lithography, followed by 2.5-7 nm of Al (Figure 10A). The key to this process is that the thin native aluminum oxide layer forms an overhang structure over the Pt electrode after liftoff (Figure 10B). The second electrode is 2.5 nm Pt deposited by electron-beam evaporation overlapping with the first electrodes (Figure 10C). The portion of the second Pt deposit that overlaps with the alumina, along with the alumina and aluminum, are removed by wet etching. This exposes the nanogaps that were formed during the shadowed Pt deposition (Figure 10D). The size of the gap is determined by the thickness of the aluminum oxide layer, which scales with the aluminum film thickness for these ultrathin films. Figure 10E, F, and G show the nanogaps prepared by this method with ca. 3, 5, and 10 nm. This technique addresses one of the problems associated with extremely small electrode spacings: Defects and irregularities can plague the gap, thereby producing lower yields of devices and complicating the interpretation of the electrical measurements.

2.5.3. Bridging Gaps Using Imine Chemistry

When we prime the surface with the molecules that are terminated with aldehydes (Figure 9B), there is essentially no change in the electrical properties of the devices (Figure 11A). Reactions of these primed electrode surfaces with the bridging diamines gives devices in the ON state (Fig-

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Figure 11. A) Reaction sequence showing the current–voltage curves for the unreacted devices (solid dark gray trace); devices after monolayer formation with the aldehyde terminated thiol (dashed trace); and reaction with the diamine bridge (solid light gray trace). B) Reaction sequence showing the current–voltage curves for the unreacted devices (solid dark gray trace); devices after monolayer formation with the terpyridyl terminated thiol (dashed trace); and reaction with cobalt diacetate (solid light gray trace). This graphic is reproduced from reference [58].

ure 11 A). The yield of working devices is ca. 13% (8 out of 60 electrode pairs). We can estimate upper and lower limits on the conductance of an individual molecular wire (assuming the self-assembled monolayers of both the aldehyde-terminated films have high coverage and are upright). Based on the area of the electrode surface (ca. 60 nm²), in the case of the aldehyde-terminated monolayers between 1 and 23 molecules would cover the entire lateral edge of the electrode, then the conductance for each metal–wire–metal junction would range between 1×10^{-3} to $5 \times 10^{-5} e^2 h$.

2.5.4. Terpyridyl-Metal Interactions as a Bridging Strategy

We can similarly prime the surface with molecules that are terminated with terpyridyls (Figure 9C). Once the monolayers are in place, we insert additional cobalt ions to turn on the devices (Figure 11 B). The yield of working devices is 27% for this reaction of cobalt acetate with the electrodes primed with the terpyridyl groups (32 out of 120 electrode pairs). The higher yield for the junctions formed through coordination chemistry may reflect a greater degree of reversibility and less restrictive bonding angles relative to the imine bridges. Using an analysis similar to that used above, we estimate the conductance of each cobalt/terpyridyl wire to be between 1.3×10^{-4} to $1.6 \times 10^{-6} e^2 h$.

The coordination complexes offer the chance to study the reversibility of the circuit-completing reactions (Figure 12 A). Figure 12 B shows a cycle of decomplexation and reconnection with cobalt ions. This is the same device shown in Figure 11 B. After the connected device is immersed in a solution of EDTA, the Co is removed, and the device becomes an open circuit. When $Co(OAc)_2$ is reintroduced, the device returns to the closed-circuit, ON, state. We can repeat the sequence, switching the device to the OFF state by treatment with EDTA again.

This "lock-and-key" approach is useful because it not only avoids the assembly and reactivity problems associated with dithiols, but it also offers a process by which complex materials can be made and measured. The method provides a clear path to multifunctional molecular electronic devices.



Figure 12. A) Strategy applied to disconnect and reconnect the devices. B) Device from Figure 5B after reaction with EDTA to strip out the metal bridge, reinsertion of the metal ion, and again removal of the metal ion. C) SEM of the device used in (B) after the reaction sequence. This graphic is reproduced from reference [58].

For example, Taniguchi et al.^[59] used the interconnect method to program three kinds of component molecules with their own functions for building light-controllable conductance switches.^[60,61,65,69,75]

2.6. On-Wire Lithography

2.6.1. Template-Directed Synthesis of Nanowires with Nanogaps

Another area that deserves mention is the area of on-wire lithographic methodology (OWL) pioneered by the Mirkin group at Northwestern.^[62,63] The basic idea of OWL is that one can make segmented nanowires consisting of at least two types of materials, one that is susceptible and one that is resistant to wet chemical etching. The materials they used are Au-Ag and Au-Ni. They first grew Au-Ni or Au-Ag nanowires through electrodeposition into porous alumina templates in a controlled fashion from suitable plating solutions through well-established methods (Figure 13). The length of each segment can be tailored by controlling the charge passed during the electrodeposition process. After removing the template, the nanowires were released in solution. Then, the nanowire aqueous suspension was spincoated on a glass microscope slide, pretreated with piranha solution to make it hydrophilic, and dried in a dessicator. After deposition of a silica layer (50 nm) for Ni and an Au/ Ti bilayer (40 nm/10 nm) for Ag, the substrate was immersed in ethanol and sonicated for releasing the wires. The final step of the OWL process involves the selective wet chemical etching of the sacrificial segments (Ni or Ag). The Ni can be removed from the wires by treating them with concentrated HNO3 for one hour to generate nanowire

1. Removal of templates 2. Dispersion of wires Sonication

Figure 13. Demonstration of OWL methodology for making nanowire with nanogaps. This graphic is reproduced from reference [63].

structures with gaps precisely controlled by the length of the original Ni segments. The Ag was removed by treating the wires with an etching solution consisting of methanol, 30% ammonium hydroxide, and 30% hydrogen peroxide (4:1:1, v/v/v) for one hour. Using the controllable OWL procedure, they prepared nanowires with designed gaps of 5, 25, 40, 50, 70, 100, 140, and 210 nm. As proof of concept, they used the nanowires with 13 nm gaps to study the transport properties of conducting polymers deposited within by dip-pen nanolithography.

2.6.2. Bridging the Gaps with Molecular Wires

OWL relies on the template-directed synthesis of nanowires in an anodized aluminum oxide membrane (pore diameter ca. 360 nm) by the electrochemical deposition of desired materials.^[63] By selectively introducing a thin sacrificial layer of Ni, one can subsequently create a gap of well-defined thickness by selective wet chemical etching. The gap size is controlled by the number of coulombs passed in the electrochemical synthesis of the Ni layer. For example, 3 nm Ni segments are obtained when 30 mC of charge is applied during electrochemical deposition, while 2-nm-thick segments result from 20 mC of passed charge. The structure is held together by a thin coat of silica on one face of the wire, which is introduced prior to the etching step. From a molecular electronics point of view, OWL-fabricated structures could offer a transport test bed of remarkable simplicity, stability, and scalability. Indeed, a recent work from the same group^[64] demonstrated that OWL-fabricated nanogaps can serve as a new test bed to construct molecular transport junctions (MTJs) through the assembly of thiolated molecular wires across a gap formed between two Au electrodes. They used two molecular wires of different dimensions to treat the fresh nanogap devices. They observed the significant current-voltage responses after immersing the devices in the solutions of molecular wires, suggesting the assembly of the molecules across the gap with chemical connectivity to each of the gold electrodes.

As discussed above, most of the previous work in MTJ fabrication relies primarily on *ex situ* syntheses of molecular wires (e.g., dithiolated molecules) followed by subsequent insertion of the molecules into the gap devices. To circumvent the problems associated with this approach, a modular

face-enhanced Raman scattering (SERS) to characterize the assembly processes within the gaps. The general scheme for bridging the nanogaps by using click chemistry for MTJ fabrication is shown in Figure 14. In a typical experiment, 4-



Figure 14. A) Schematic illustration of click chemistry within the nanogaps. B) Molecules used in this study. C) The alkyne–azide click reaction. This graphic is reproduced from reference [65].

ethynyl-1-thioacetylbenzene (TB) is first assembled into a monolayer on the surfaces of the electrodes, which are located at opposite ends of an OWL-fabricated nanogap, by immersing the entire device in a solution of the molecule. After treatment with concentrated sulfuric acid to deprotect the thiol groups, the device is rinsed with solvents, and then immersed in a solution of 2,7-di-azido-fluorene (AF) in DMF containing a solution of copper sulfate and ascorbic acid. One of the azide groups in AF reacts with the alkyne group on electrode-immobilized **TB** to form a 1,2,3-triazole unit at one end, while the azide group at the other end is left unchanged. This structure can be further extended by reaction with 2,7-diethynyl-fluorene (DF), which in turn can be reacted again with AF. Following the appropriate number of reaction cycles, the molecular wires that grow from the opposing electrodes combine and bridge the nanogap. The point at which the bridge is formed can be determined from the I-V characteristics of the device, and the number of reaction steps required to form a bridge depends on the size of the gap.

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method for the in situ synthesis of molecular wires to bridge merits nanogaps development.^[58] In a further report, they reported a method for the fabrication of MTJs by using the alkyne-azide "click reaction" within nanogaps fabricated by on-wire lithography (OWL).^[65] Another remarkable result of this approach is that they succeeded in using surface-enhanced Raman scattering (SERS) to characterize the

As a proof of concept, they first attempted a one-step click reaction with **TB** and **AF** to bridge a 2 nm OWL-fabricated gap and form MTJs. The calculated S–S distance of the target-bridging molecule is 2.6 nm, which is long enough to span the gap. Figure 15 A and B show a typical wire struc-



Figure 15. A) SEM image of a 2 nm OWL-fabricated nanogap. B) An SEM image of 2 nm nanogap-MTJ device. C) Representative I-V response for 2 nm OWL-fabricated gaps before (\blacksquare), after (Δ) modification with **TB**, and the bridging click reaction of **AF** with **TB** (\bigtriangledown). The plain gray line shows the theoretical fitting of the I-V curve. This graphic is reproduced from reference [65].

ture with 2 nm nanogaps and the device structure used. Figure 15C shows the two-terminal I-V characteristics of the gap devices measured at room temperature before and after click reactions. The empty nanogaps, or nanogaps modified with a monolayer consisting only of TB, exhibit no conductance within the noise limit of the measurement (< 2 pA). However, following the click reaction of TB and AF within the gap, the I-V characteristics show a clear molecular response in the mA range, which indicates the realization of a conjugated molecular bridge within the nanogap formed as a result of the click reaction. The yield for working devices is 41 % (12 out of 29 devices with I > 0.1 nA at 1 V bias). In control experiments, they used the dithiol from TB and AF to bridge the nanogaps ex situ. However, the yield of working devices is lower (ca. 10%, 3 out of 31) than that of MTJ devices assembled in situ. This observation is likely to result from the slow diffusion of the large molecule into the nanogap. In addition to the electrical characterization, other spectroscopic methods, such as X-ray photoelectron spectroscopy and surface-enhanced Raman scattering spectroscopy, were also used to characterize the molecular assembly process within the gaps (more details please see reference [65]).

Multistep reactions can also be carried out within the nanogaps in a stepwise approach that is analogous to solidphase synthesis. When **DF** is reacted with the available azide from **AF** on the Au electrode under click reaction conditions, the oligomeric fluorene chain is extended, which either bridges the gap or leaves an azide group available for further reaction (Figure 16). The number of **DF** units in the



Figure 16. Representative I-V response curves for the multistep click reactions within OWL-fabricated gaps before and after the final click reaction step. A) 5 nm OWL-fabricated gap, two-step click reaction and B) 7 nm OWL-fabricated gap, three-step click reaction. This graphic is reproduced from reference [65].

oligomeric chain is controlled precisely by the number of reaction steps and the gap size. For example, in the case of the 5 nm gap, no current is seen until two reactions have been carried out (Figure 16A), and, in the case of the 7 nm gap, no current is seen until three reactions have been carried out (Figure 16B). These experiments demonstrate the ability to carry out multiple reaction steps within the gap.

Click chemistry is useful because it forms MTJs in high yields and can be used to test different molecules. Its ability to extend and vary the chemical structure within MTJs in situ allows the construction of nanoelectronic devices with diverse functions and applications in a high-throughput, combinatorial fashion. We anticipate that both MTJ lithographic methods, self-aligned lithography and on-wire lithography, will dramatically boost the development of molecular electronics. However, for asymmetric molecular devices, such as molecular diodes, ex situ synthesis appears to be more suitable than in situ formation of molecular components for introducing spatial asymmetry into a junction to achieve interesting functions in a controlled fashion.

3. Single-Molecule Circuits

3.1. Holistic Construction: Synthesizing Devices

Current research in single-molecule electronics still has many great challenges. One of the greatest challenges is the ill-defined bonding at the molecule–metal contact interface, even for the most well-studied thiol–gold contacts.^[9–19] Moreover, even if more conductive contact structures are built (such as alkylidenes on transition metals and on metal carbides),^[76–78] molecular-scale metal electrodes are extremely difficult to fabricate and lack specific chemistry for molecular attachment at their interfacial ends. To achieve consistent and reproducible results, one should try as best as possible to consider the electrode fabrication process as a holistic one. The electrode materials, contact chemistry, and the number of molecules within a given junction are so closely interrelated that they cannot be optimized independently. An improved strategy would create a well-defined contact between the electrode and the molecule of interest, would have a limited number of binding sites, and would be intrinsically molecular in scale. We detail such a system below. Amide linkages are used to covalently connect cut single-walled carbon nanotubes (SWNTs), acting as nanoscale electrodes to molecules that conduct electrical current.^[7,79,80] All of the elements in the resulting molecular circuits are naturally at small dimensions because the SWNTs are one-dimensional (1D) ballistic conductors or semiconductors that are the same size in diameter as the dimensions of the molecules being probed. Based on this reliable strategy, we have tested a number of different types of molecules and installed functionalities on single-molecule-bridged nanodevices that allow external stimuli, such as proton, light, ion, and other chemical and electrostatic effects to modulate the molecular conductance.^[7,66-71,79-81]

3.2. SWNTs: Ideal Ballistic Electrodes

Since their discovery in 1991 by Ijima,^[82] carbon nanotubes have been regarded as one of the best nanostructural materials derived from bottom-up chemical synthesis approaches.^[1-2] Carbon nanotubes have the simplest chemical composition and atomic bonding configuration but exhibit perhaps the most extreme diversity and richness among nanomaterials in structures and structure–property relations.^[83–85] SWNTs are one-dimensional (1D) ballistically conducting nanowires that are intrinsically the same size in diameter as the dimensions of the molecules. They are easy to process for nanofabrication. The structure of SWNTs can be appreciated by folding up a graphene sheet into a cylinder along a certain lattice vector. This hints at useful conduction via the π -bonding network. Moreover, depending on the way the graphene is rolled, different chiralities are possible which are commonly distinguished by their chiral vector (*n.m*). Based on the chirality and diameter, SWNTs can be either metallic (n-m=3q, where q is an integer) or semiconducting. This suggests different energy band alignment scenarios between SWNTs and molecules. These can be expected to yield a useful variety of device properties. Ultimately, SWNTs are molecular chemicals, and therefore we can, to an extent, tailor their chemical reactivity. As a result of all of these features, SWNTs should be ideal point contacts for single-molecule devices.

3.3. Cutting SWNT Electrodes

We form SWNT electrodes by cutting them by precise local oxidation through a polymethylmethacrylate (PMMA) mask. The mask is created by a well-defined e-beam lithographic method. This process leaves two ends that are separated by a gap of <10 nm (Figure 17A,B).^[68] This method differs from the formation of SWNT electrodes by electrical breakdown, which has been used recently to realize pentacene nanotransistors by Qi and Tsukagoshi et al.[86,87] In both cases, applying a high current through the channel disconnected each single-walled or multiwalled carbon nanotube that bridged the two metal leads. Organic materials were then thermally evaporated to bridge the gap. This formed ultrasmall OFETs having nanoscale channel lengths. These two studies have proven that carbon nanotubes can be novel electrodes for a variety of organic optoelectronic devices.^[80] However, because electrical breakdown produces carbon nanotube electrodes that are incompletely functionalized by carboxylic acids and lacks precise control of the gap size, these electrodes are unsuitable for chemically connecting molecular wires.



Figure 17. A) Very fine cutting of SWNT with oxygen plasma introduced through an opening in a window of PMMA defined with e-beam lithography. B) The results of oxidative opening of the tubes are point contacts that are functionalized on their ends and separated by as little as ca. 2 nm. C) Scanning electron micrograph of a SWCNT with Au on Cr leads that had been cut using e-beam lithography and an oxygen plasma. D) AFM image of the gap cut into the SWNT. Inset: height profile of the isolated tubes. This graphic is reproduced from reference [68].

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To fabricate the SWNT electrodes we start by preparing an array of SWNT transistors and spin-coating this array with a blanket layer of PMMA. Then we open a window (<10 nm) on top of individual SWNT transistors using ultra-high-resolution electron-beam lithography. We then cut the nanotubes through the window via oxygen plasma ion etching. Given the strongly oxidizing conditions of this method, we expect the cut ends of these half-tubes to be capped predominately with carboxylic acids. We control the degree of cutting, and therefore the gap size, by varying the time of the exposure to the oxidant. Longer etch times give higher yields of the cutting, but lower yields of the subsequent chemical connection reactions. Figure 17D shows an AFM image of one nanogap. Given the imaging convolution of the AFM tip size, an upper bound on the size of a typical gap in these micrographs is ca. 10 nm. Under optimized conditions, about 20-25% of the tubes were completely cut, showing the conductance down to the noise limit of the measurement (\leq ca. 2.0 pA).

3.4. Connecting SWNT Devices with Conductive Molecules: Covalent Link Chemistry

The cutting process creates carboxylic acid end groups on the half-tubes. We exploit these functional groups in the subsequent connection chemistry. We covalently wire the different conjugated molecular wires having the requisite amine functionality (1-3) into precisely cut SWNT nanogaps using a pyridine solution containing the well-known carbodiimide dehydrating/activating agent EDCI (Figur-

e 18A, B).^[88] Electrical measurements on devices before cutting, when cut, and after connection with 1 are shown in Figure 18C. The black curve shows the source-drain current (I)plotted against the gate voltage (V_g) at constant S-D bias voltage $(V_{SD} = 50 \text{ mV})$ for a metallic device before cutting. The bottom trace, taken after cutting, shows no conductance down to the noise limit of the (< ca. 2.0 pA). measurement The gray trace shows the devices after molecular reconnection of the SWNT leads. In all cases, the reconnected devices recovered their original (either metallic or semiconducting) behavior. The magnitude of the current is reduced, however; this indicates that the gate modulates the conductance of the nanotube more strongly than that of the molecules. We can estimate the resistance, and thus the molecular conductance, from the drop in current after molecular connection. For example, the molecular conductance of 1 in the metallic device shown in Figure 18C is calculated to be $6.4 \times 10^{-3} e^2 h$. The conductance can be greater than $10^{-2} e^2 h$ for some devices rejoined by 3. One factor that hampers our ability to extract more quantitative information is that the measured values vary for any given molecule. Variations in the conformation of the molecules bridging the SWNT gaps, the possibility of an additional molecular bridge in the same gap, the lack of atomic-level precision in the cutting procedure, and the lack of synthesis of SWNTs with uniform diameter and chirality are challenges for future studies to overcome.^[7,89,90] Another challenge is that the small junction sizes (normally only a few nanometers wide) usually prohibits the use of routine spectroscopic tools to identify the accurate contents of molecular junctions.

Importantly, the cruciform π systems **1** and the longer oligothiophenylenes **2** have side chains that not only make them highly soluble, but also provide considerable width to these molecules. Given the volume that **1**, **2**, and **3** occupy, it is difficult to bridge the gaps with more than one molecule and certainly no more than two (Figure 18), thus forming the true single-molecule transistors. The amidation also allows us to calibrate the etch process itself because the different species can be used as molecular rulers. Under identical conditions, for example, the yield for connection of **1** is about 10% while the longer molecules (**2** and **3**) give lower yields in their connection reactions (ca. 5%). We believe, therefore, that the chemically effective gap is closer to 2 nm.



Figure 18. A) Covalent link chemistry used for reconnection. B) Molecular structures for 1–3. C) and D) Device characteristics of two SWNT electrodes connected with 1. This graphic is reproduced from reference [68].

3.5. Installing Functionalities on Rejoined Devices

The chemical contacts provided by amide-linked molecular bridges are robust and can tolerate broad changes in environment. This provides us with the opportunity to install capabilities into the electrical devices that are inherent to the synthetic molecular backbones. Functionality can be installed in the molecular backbone that allows the creation of pH-, redox-, and photo-gated switches, as well as metal ion recognition devices. Furthermore, this method allows for the assembly of multicomponent structures, which offers devices that are sensitive to protein/substrate binding and DNA hybridization.^[7,66-71,79-81]

3.5.1. In-Line Molecular Bridge: Photogated Switching

We explored how SWNT-based devices might respond to changes in pH by incorporating oligoaniline into the bridge. The molecular structure and the response to changes in pH for the oligoaniline-based device are shown in Figure 19. The electrical characteristics for this device before cutting, after cutting, and after rejoining with the oligoaniline diamine are similar to those in Figure 18. Cutting the SWNT gives an open circuit, and rejoining the tube returns the device to its original state, albeit at a lower conductance. We expect the oligoaniline to be oxidized to the emeraldine form during the reaction and become pH-sensitive, the protonated form being more conductive. We performed a series of protonations (pH 3) and deprotonations (pH 11) while monitoring the current changes at saturation for devices that were rinsed, dried, and tested. The molecular conductance changes by nearly an order of magnitude, from

ca. $5.2 \times 10^{-4} e^2 h$ at low pH to ca. $5.0 \times 10^{-5} e^2 h$ at high pH. This behavior persists over many switching cycles. When the same experiment is performed on devices connected with 2, which lacks basic nitrogen atoms and thus should not switch with pH, only slight pH dependence is observed. It is noteworthy that the change is in the opposite direction from the device connected with the pH- and redox-active oligoaniline 4. This nanodevice, using at most a few molecules, provides a reliable local probe for monitoring pH.

We also rejoined the cut SWNTs with photochromic molecules in order to assay their ability to reversibly toggle between two distinct conductive states in response to external triggers.^[66] Diarylethenes switch between open (nonconjugated)



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Figure 19. A) The molecular structure of oligoaniline 4. B) Oligoaniline 4 provides a redox- and pH-sensitive molecular bridge. Protonation and deprotonation give rise to high- (5) and low-conductance (6) forms. C) Green circles show the ON-state resistance for 4 when alternately immersed in solutions of low and high pH. The triangles show small changes in ON-state resistance for 2 when alternately immersed in solutions of low and high pH. This graphic is reproduced from reference [68].

and closed (conjugated) states and have been installed into single-molecular devices with gold contacts.^[36,91] We used two kinds of photochromic diarylethenes, **7** and **8** in Figure 20 A. In each of these molecules the reversible interconversion between the two states causes the rearrangement of the covalent bonds such that π -bond conjugation (and therefore the electrical conductivity) through the molecule can be switched on and off (Figure 20B). As expected, we find that both semiconducting and metallic devices bridged with **7** show one-way switching of the associated molecule from the lower conductance state to the higher conductance state upon exposure to UV light (365 nm) owing to large exten-



Figure 20. A) Molecular bridges between the ends of individual SWNT electrodes. B) Switching between nonconjugated and conjugated molecular structures. C) Individual semiconducting SWNT device bridged by **open-**8 before UV irradiation. D) The same device after UV irradiation to form **closed-8**. E) Steps in the conductance for a device reconnected with 8 when the UV light is pulsed. This graphic is reproduced from reference [66].

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sion of π conjugation in the molecular backbone. When the light is extinguished, the current through the device remains at the higher level for several weeks. **Closed-7** is unable to revert back to the open state photochemically. Interestingly, the opposite phenomenon occurs in the devices made with dithiolated molecules within gold-electrode break junctions. The molecules switch from a closed to the open state and do not revert.^[36]

To achieve reversible switching, we intended to use pyrrole-based molecule 8, which shows the thermal back-conversion (Figure 20B), to rejoin the devices. When a cut SWNT is reconnected with open-8 diamine, the source-drain current through the device is very low (Figure 20C). With UV irradiation the bridge cyclizes, and the current increases by more than five orders of magnitude (Figure 20D). The low-conductance state is restored when the device is aged at room temperature overnight, and the on/off cycle can be toggled many times. The high conductance of closed-8 may be a consequence of multiple bridges in the SWNT gap, as the diameter of the tube (ca. 2.4 nm) can accommodate as many as eight molecular bridges. UV-pulse experiments support the notion of there being several molecular bridges across the same gap; there is an observed increase in conductance after each pulse (Figure 20E). This design concept, which significantly extends the stark example of thermally reversible photoswitching of single-molecule devices, provides a deeper understanding of the interplay between molecular structure, electrode materials, and emergent functions at the nanoscale level, promising the potential of applications in future nanodevices.

3.5.2. Side-Arm DNA Bridges: Conductivity and Sensing of a Single DNA Duplex

We are developing bioassay techniques by using bridge molecules with functional side groups capable of subsequent biocompatible assembly. We have been able to form complex multicomponent nanostructures from single-molecule SWNT-based devices by combining programmed chemical reactivity and directed self-assembly.^[67,71] We bridge a SWNT with a molecule that can react with a biochemical probe molecule. The probe then binds to a complementary molecule to form a noncovalent assembly. We electrically monitor each step of the process at the single-event level. We have tested this approach in biological systems, including DNA hybridization and biotin/streptavidin binding. We have used a similar method to probe isolated metal nanoparticles. One key advantage of this approach to biosensing is the ability to form a well-defined chemical linkage between a molecular wire and a probe molecule. Furthermore, because it is constructed from a single molecule, each device can monitor individual binding events. This methodology demonstrates a connection between electrical conduction and biology that offers a glimpse into the future of integrated multifunctional sensors and devices.^[7,92-95]

For example, we have used the method of creating multicomponent electronic devices to measure the conductivity of a single DNA duplex, which is an area of substantial interest.^[71] To date, numerous charge transfer measurements on DNA strands bridging two electrodes have been carried out in an effort to establish the conductivity of DNA,^[96-98] and these have yielded a remarkably wide range of resistance values (1–10⁷ M Ω). However, in all of the conductivity measurements carried out so far, either the integrity of the DNA was not well established, the connections to the duplex were not well defined, or the measurement was not definitively of a single DNA duplex. Therefore, the integration of DNA strands into SWNT electrodes allows the first measurements of electrical properties of a single DNA duplex in its native conformation.

In order to make these measurements, DNA sequences having amines on their termini are coupled to the SWNT electrodes through the now-familiar amide linkages in a two-step strategy: acid activation and amide formation. Two different device connectivities are explored. In one case, both of the 5' ends of a DNA duplex are modified with amines, which are used to bridge each end of the half-tubes. In another case, both the 3' and 5' ends of a single strand are amine-functionalized and linked to the SWNT gap, allowing the measurement of electrical properties of complementary and mismatched strands. In both cases the reconnected carbon nanotube devices recovered their original electrical characteristics (p-type semiconducting or metallic). These measurements place the resistance of well-matched DNA duplexes with ca. 6 nm length in the range of 0.1-5 M Ω . For comparison, the conductivity of a piece of highly oriented pyrolytic graphite (HOPG) of similar dimensions should also be about $1 M\Omega^{[71]}$ Interestingly, a single GT or CA mismatch in a DNA 15-mer for the second connection scheme increased the resistance of the duplex ca. 300-fold relative to a well-matched one owing to the perturbations in stacking of aromatic base pairs in the core.^[99] Importantly, one DNA sequence oriented within this gap was also a substrate for Alu I, a blunt end restriction enzyme, which cuts the DNA, eliminating the conductive path (Figure 21). Thus the well-matched DNA assembled between SWNT electrodes maintains its native conformation when bridging the



Figure 21. Source-drain current versus gate voltage at a constant sourcedrain voltage (50 mV) for a metallic SWNT device after cutting and reconnection with the DNA sequence shown before (light gray curve: 1) and after reaction with Alu 1 (dark gray curve: 2) These graphics are reproduced from reference [71].

ends of the SWNTs. These results suggest that DNA molecules bridging nanodevices can serve as uniquely powerful reporters to transduce biochemical events into electrical signals at the single-molecule level.

4. Summary and Outlook

This Focus Review has described a new direction in molecular electronics: integrating powerful reaction chemistry with the current sophisticated device fabrication methods. We have outlined two types of molecular electronic device systems. The common theme is the combination of directed self-assembly and programmed chemical reactivity to modify the electrode interface, wire the electrodes, and construct multicomponent and multifunctional molecular electronic devices. First, we highlighted several sophisticated methods developed recently, including break junctions, scanning probes, sandwich large-area molecular junctions, liquid-metal contacts, self-aligned lithography, and on-wire lithography, to fabricate molecular-scale metal electrodes for the purpose of circumventing random attachment and oxidative oligomerization of dithiol molecules. Second, consideration of all the parameters in molecule-scaled devices, such as the electrode fabrication process, the choice of electrode materials, contact chemistry, and the number of molecules to be tested, produces an improved strategy for creating a well-defined covalent bond between the electrode and the molecule with a limited number of molecular bonding sites at the single-molecular level. Precisely cut singlewalled carbon nanotube electrodes, separated by a few nanometers, can be covalently wired by different single conjugated molecules through robust amide linkages. This strategy is reliable and allows a wide variety of single molecules, or small collections of molecules, to be tested electrically. Installation of functionalities in electrical devices can be achieved by employing a diversity of molecules with either in-line or side-arm functional groups. This gives single-molecule devices whose conductance can switch in response to external stimuli, such as change in pH, light, ionic or other chemical or electrostatic environments. Basic research on constructing the functional devices with controllable optoelectronic properties is just starting, and further detailed investigations in this field are expected.

Although much has been learned about the fundamental properties of molecules at the nanometer scale, and the research in this area is expanding swiftly, molecular electronics is still in its infancy and many of the remaining challenges are large. Scientists and engineers from diverse backgrounds need to come together to explore and develop these new systems where the electrode can function as a chemical reagent and serve as a platform for chemistry. Another formidable issue in molecular electronics is a great shortage of efficient integration strategies.^[100–106] Predictably, the next generation of devices would be a network of interface where the molecules function as pivotal elements to control the interface.^[93–95] More research is necessary to bridge hard elec-

tronics with the vast store of the soft-molecular world. It is not the wire, it is the wiring.

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- [1] J. Robertson, Mater. Today 2007, 10, 36.
- [2] S. E. Thompson, S. Parthasarathy, Mater. Today 2006, 9, 20.
- [3] Y. Selzer, D. L. Allara, Annu. Rev. Phys. Chem. 2006, 57, 593.
- [4] G. Cuniberti, G. Fagas, K. Richter, Lect. Notes Phys. 2005, 680, 1.
- [5] N. J. Tao, Nat. Nanotechnol. 2006, 1, 173.
- [6] C. Joachim, M. A. Ratner, Proc. Natl. Acad. Sci. USA 2005, 102, 8801.
- [7] A. K. Feldman, M. L. Steigerwald, X. Guo, C. Nuckolls, Acc. Chem. Res. 2008, 41, 1731.
- [8] B. Ulgut, H. D. Abruna, Chem. Rev. 2008, 108, 2721.
- [9] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, *15*, 1881.
- [10] M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Haenisch, D. Beckmann, M. Fischer, *Angew. Chem.* **2003**, *115*, 6014; *Angew. Chem. Int. Ed.* **2003**, *42*, 5834.
- [11] K. V. Mikkelsen, M. A. Ratner, Chem. Rev. 1987, 87, 113.
- [12] R. McCreery, J. Dieringer, A. O. Solak, B. Snyder, A. M. Nowak, W. R. McGovern, S. DuVall, J. Am. Chem. Soc. 2003, 125, 10748.
- [13] X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, L. A. Nagahara, S. M. Lindsay, J. Phys. Chem. B 2002, 106, 8609.
- [14] C. L. McGuiness, A. Shaporenko, C. K. Mars, S. Uppili, M. Zharnikov, D. L. Allara, J. Am. Chem. Soc. 2006, 128, 5231.
- [15] M. P. Stewart, F. Maya, D. V. Kosynkin, S. M. Dirk, J. J. Stapleton, C. L. McGuiness, D. L. Allara, J. M. Tour, *J. Am. Chem. Soc.* 2004, *126*, 370.
- [16] H. Basch, R. Cohen, M. A. Ratner, Nano Lett. 2005, 5, 1668.
- [17] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, D. C. Ralph, *Nature* **2002**, *417*, 722.
- [18] N. B. Zhitenev, A. Erbe, Z. Bao, Phys. Rev. Lett. 2004, 92, 186805/ 1.
- [19] N. B. Zhitenev, H. Meng, Z. Bao, Phys. Rev. Lett. 2002, 88, 226801/
 1.
- [20] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, Science 1999, 286, 1550.
- [21] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* 1997, 278, 252.
- [22] X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, S. M. Lindsay, *Science* 2001, 294, 571.
- [23] A. Nitzan, M. A. Ratner, Science 2003, 300, 1384.
- [24] G. K. Ramachandran, T. J. Hopson, A. M. Rawlett, L. A. Nagahara, A. Primak, S. M. Lindsay, *Science* 2003, 300, 1413.
- [25] M. Mayor, H. B. Weber, Angew. Chem. 2004, 116, 2942; Angew. Chem. Int. Ed. 2004, 43, 2882.
- [26] J. M. Tour, L. Jones, II, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh, S. Atre, *J. Am. Chem. Soc.* **1995**, *117*, 9529.
- [27] C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, J. Am. Chem. Soc. 1989, 111, 321.

- [28] E. J. Corey, K. A. Cimprich, Tetrahedron Lett. 1992, 33, 4099.
- [29] T. Takata, Y. H. Kim, S. Oae, Tetrahedron Lett. 1979, 20, 821.
- [30] L. Venkataraman, J. E. Klare, I. W. Tam, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* 2006, 6, 458.
- [31] L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nature* 2006, 442, 904.
- [32] L. Venkataraman, Y. S. Park, A. C. Whalley, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* 2007, 7, 502.
- [33] B. Xu, N. Tao, Science 2003, 301, 1221.
- [34] S. M. Lindsay, M. A. Ratner, Adv. Mater. 2007, 19, 23.
- [35] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Lohneysen, *Phys. Rev. Lett.* 2002, 88, 176804/1.
- [36] D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402/1.
- [37] A. R. Champagne, A. N. Pasupathy, D. C. Ralph, Nano Lett. 2005, 5, 305.
- [38] J. J. Parks, A. R. Champagne, G. R. Hutchison, S. Flores-Torres, H. D. Abruna, D. C. Ralph, *Phys. Rev. Lett.* **2007**, *99*, 026601.
- [39] 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.
- [40] D. R. Strachan, D. E. Johnston, B. S. Guiton, S. S. Datta, P. K. Davies, D. A. Bonnell, A. T. C. Johnson, *Phys. Rev. Lett.* 2008, 100, 058805/1.
- [41] H. Park, A. K. L. Lim, A. P. Alivisatos, J. Park, P. L. McEuen, *Appl. Phys. Lett.* **1999**, 75, 301.
- [42] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, P. L. McEuen, *Nature* 2000, 407, 58.
- [43] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* 2002, 417, 725.
- [44] T. W. Kelley, E. L. Granstrom, C. D. Frisbie, Adv. Mater. 1999, 11, 261.
- [45] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, II, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **1996**, *271*, 1705.
- [46] J. R. Quinn, F. W. Foss Jr., L. Venkataraman, R. Breslow, J. Am. Chem. Soc. 2007, 129, 12376.
- [47] Y. S. Park, A. C. Whalley, M. Kamenetska, M. L. Steigerwald, M. S. Hybertsen, C. Nuckolls, L. Venkataraman, J. Am. Chem. Soc. 2007, 129, 15768.
- [48] J. M. Mativetsky, G. Pace, M. Elbing, M. A. Rampi, M. Mayor, P. Samori, J. Am. Chem. Soc. 2008, 130, 9192.
- [49] M. Del Valle, R. Gutierrez, C. Tejedor, G. Cuniberti, Nat. Nanotechnol. 2007, 2, 176.
- [50] G. Leatherman, E. N. Durantini, D. Gust, T. A. Moore, A. L. Moore, S. Stone, Z. Zhou, P. Rez, Y. Z. Liu, S. M. Lindsay, *J. Phys. Chem. B* **1999**, *103*, 4006.
- [51] H. B. Akkerman, P. W. M. Blom, D. M. D. Leeuw, B. de Boer, *Nature* 2006, 441, 69.
- [52] H. B. Akkerman, R. C. G. Naber, B. Jongbloed, P. A. V. Halt, P. W. M. Blom, D. M. D. Leeuw, B. de Boer, *Proc. Natl. Acad. Sci.* USA 2007, 104, 11161.
- [53] P. A. V. Hal, E. C. P. Smits, T. C. T. Geuns, H. B. Akkerman, B. C. D. Brito, S. Perissinotto, G. Lanzani, A. J. Kronemeijer, V. Geskin, J. Cornil, P. W. M. Blom, B. de Boer, D. M. D. Leeuw, *Nat. Nanotechnol.* 2008, *3*, 749.
- [54] R. E. Holmlin, R. Haag, M. L. Chabinyc, R. F. Ismagilov, A. E. Cohen, A. Terfort, M. A. Rampi, G. M. Whitesides, J. Am. Chem. Soc. 2001, 123, 5075.
- [55] R. E. Holmlin, R. F. Ismagilov, R. Haag, V. Mujica, M. A. Ratner, M. A. Rampi, G. M. Whitesides, *Angew. Chem.* **2001**, *113*, 2378; *Angew. Chem. Int. Ed.* **2001**, *40*, 2316.
- [56] S. Sek, R. Bilewicz, K. Slowinski, Chem. Commun. 2004, 404.
- [57] E. A. Weiss, R. C. Chiechi, G. K. Kaufman, J. K. Kriebel, Z. Li, M. Duati, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* 2007, 129, 4336.
- [58] J. Tang, Y. Wang, J. E. Klare, G. S. Tulevski, S. J. Wind, C. Nuckolls, Angew. Chem. 2007, 119, 3966; Angew. Chem. Int. Ed. 2007, 46, 3892.

- [59] M. Taniguchi, Y. Nojima, K. Yokota, J. Terao, K. Sato, N. Kambe, T. Kawai, J. Am. Chem. Soc. 2006, 128, 15062.
- [60] K. Matsuda, H. Yamaguchi, T. Sakano, M. Ikeda, N. Tanifuji, M. Irie, J. Phys. Chem. C 2008, 112, 17005.
- [61] S. J. van der Molen, J. Liao, T. Kudernac, J. S. Agustsson, L. Bernard, M. Calame, B. J. van Wees, B. L. Feringa, C. Schonenberger, *Nano Lett.* 2009, 9, 76.
- [62] J. K. N. Mbindyo, T. E. Mallouk, J. B. Mattzela, I. Kratochvilova, B. Razavi, T. N. Jackson, T. S. Mayer, J. Am. Chem. Soc. 2002, 124, 4020.
- [63] L. Qin, S. Park, L. Huang, C. A. Mirkin, Science 2005, 309, 113.
- [64] X. Chen, Y.-M. Jeon, J.-W. Jang, L. Qin, F. Huo, W. Wei, C. A. Mirkin, J. Am. Chem. Soc. 2008, 130, 8166.
- [65] X. Chen, A. B. Braunschweig, M. J. Wiester, S. Yeganech, M. A. Ratner, C. A. Mirkin, Angew. Chem. 2009, 121, 5280; Angew. Chem. Int. Ed. 2009, 48, 5178.
- [66] A. C. Whalley, M. L. Steigerwald, X. Guo, C. Nuckolls, J. Am. Chem. Soc. 2007, 129, 12590.
- [67] X. Guo, A. Whalley, J. E. Klare, L. Huang, S. O'Brien, M. L. Steigerwald, C. Nuckolls, *Nano Lett.* 2007, 7, 1119.
- [68] X. Guo, J. P. Small, J. E. Klare, Y. Wang, M. S. Purewal, I. W. Tam, B. H. Hong, R. Caldwell, L. Huang, S. O'Brien, J. Yan, R. Breslow, S. J. Wind, J. Hone, P. Kim, C. Nuckolls, *Science* **2006**, *311*, 356.
- [69] X. Guo, M. Myers, S. Xiao, M. Lefenfeld, R. Steiner, G. S. Tulevski, J. Tang, J. Baumert, F. Leibfarth, J. T. Yardley, M. L. Steigerwald, P. Kim, C. Nuckolls, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 11452.
- [70] X. Guo, L. Huang, S. O'Brien, P. Kim, C. Nuckolls, J. Am. Chem. Soc. 2005, 127, 15045.
- [71] X. Guo, A. A. Gorodetsky, J. Hone, J. K. Barton, C. Nuckolls, *Nat. Nanotechnol.* 2008, *3*, 163.
- [72] N. Tao, J. Mater. Chem. 2005, 15, 3260.
- [73] L. Venkataraman, Y. S. Park, A. C. Whalley, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* 2007, 7, 502.
- [74] J. Tang, E. P. De Poortere, J. E. Klare, C. Nuckolls, S. J. Wind, *Microelectron. Eng.* 2006, 83, 1706.
- [75] B.-Y. Choi, S.-J. Kahng, S. Kim, H. Kim, H. W. Kim, Y. J. Song, J. Ihm, Y. Kuk, *Phys. Rev. Lett.* **2006**, *96*, 156106/1.
- [76] M. Siaj, P. H. McBreen, Science 2005, 309, 588.
- [77] G. S. Tulevski, M. B. Myers, M. S. Hybertsen, M. L. Steigerwald, C. Nuckolls, *Science* 2005, 309, 591.
- [78] F. Ren, A. K. Feldman, M. Carnes, M. L. Steigerwald, C. Nuckolls, *Macromolecules* 2007, 40, 8151.
- [79] X. Guo, C. Nuckolls, J. Mater. Chem. 2009, 19, 5470.
- [80] Y. Cao, M. L. Steigerwald, C. Nuckolls, X. Guo, Adv. Mater. 2009, DIO: 10.1002/adma.200900504.
- [81] X. Guo, S. Xiao, M. Myers, Q. Miao, M. L. Steigerwald, C. Nuckolls, Proc. Natl. Acad. Sci. USA 2009, 106, 691.
- [82] S. Iijima, Nature 1991, 354, 56.
- [83] P. Avouris, Acc. Chem. Res. 2002, 35, 1026.
- [84] H. Dai, Acc. Chem. Res. 2002, 35, 1035.
- [85] S. J. Tans, A. R. M. Verschueren, C. Dekker, Nature 1998, 393, 49.
- [86] P. Qi, A. Javey, M. Rolandi, Q. Wang, E. Yenilmez, H. Dai, J. Am. Chem. Soc. 2004, 126, 11774.
- [87] K. Tsukagoshi, I. Yagi, Y. Aoyagi, Appl. Phys. Lett. 2004, 85, 1021.
- [88] A. Williams, I. T. Ibrahim, Chem. Rev. 1981, 81, 589.
- [89] W. Ren, J. R. Reimers, N. S. Hush, Y. Zhu, J. Wang, H. Guo, J. Phys. Chem. C 2007, 111, 3700.
- [90] Z. Qian, S. Hou, J. Ning, R. Li, Z. Shen, X. Zhao, Z. Xue, J. Chem. Phys. 2007, 126, 084705/1.
- [91] J. He, F. Chen, P. A. Liddell, J. Andreasson, S. D. Straight, D. Gust, T. A. Moore, A. L. Moore, J. Li, O. F. Sankey, S. M. Lindsay, *Nano*technology **2005**, *16*, 695.
- [92] Y. Cui, Q. Wei, H. Park, C. M. Lieber, Science 2001, 293, 1289.
- [93] F. Patolsky, B. P. Timko, G. Yu, Y. Fang, A. B. Greytak, G. Zheng, C. M. Lieber, *Science* **2006**, *313*, 1100.
- [94] G. Zheng, F. Patolsky, Y. Cui, W. U. Wang, C. M. Lieber, *Nat. Bio*technol. 2005, 23, 1294.
- [95] F. Patolsky, G. Zheng, O. Hayden, M. Lakadamyali, X. Zhuang, C. M. Lieber, Proc. Natl. Acad. Sci. USA 2004, 101, 14017.

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- [96] H. W. Fink, C. Schonenberger, Nature 1999, 398, 407.
- [97] J. Hihath, B. Xu, P. Zhang, N. Tao, Proc. Natl. Acad. Sci. USA 2005, 102, 16979.
- [98] D. Porath, A. Bezryadin, S. de Vries, C. Dekker, *Nature* 2000, 403, 635.
- [99] S. O. Kelley, J. K. Barton, Science 1999, 283, 375.
- [100] J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. DeIonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* 2007, 445, 414.
- [101] A. M. Fennimore, T. D. Yuzvinsky, W.-Q. Han, M. S. Fuhrer, J. Cumings, A. Zettl, *Nature* 2003, 424, 408.
- [102] S. Liu, Q. Shen, Y. Cao, L. Gan, Z. Wang, M. L. Stergerwald, X. Guo, *Coord. Chem. Rev.* 2009, DOI: 10.1016/j.ccr.2009.11.007.

- [103] T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C.-L. Cheung, C. M. Lieber, *Science* 2000, 289, 94.
- [104] E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, Nature 1998, 391, 775.
- [105] Z. Chen, J. Appenzeller, Y.-M. Lin, J. Sippel-Oakley, A. G. Rinzler, J. Tang, S. J. Wind, P. M. Solomon, P. Avouris, *Science* 2006, 311, 1735.
- [106] Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K.-H. Kim, C. M. Lieber, *Science* 2001, 294, 1313.

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