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Watching the Gap Close

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The large current interest in molecular electronics has two complementary driving forces, namely the economic interest in cheaper and smaller devices and fundamental scientific curiosity. Molecules are the smallest building blocks that provide the structural diversity required to address different electronic functions. Should the integration of molecules become routinely accessible, various electronic tasks might be performed by tailor-made molecular structures.[1–6] While the enormous potential of molecules as engineered functional units in electronic circuits was hypothesized as early as the 1960s,[7,8] the current revival of the field is strongly driven by the increasing ability to handle nanoscale objects in a top-down approach assisted by the growing synthetic competence to assemble macromolecules of comparable dimensions from the bottom up.

A variety of experimental setups able to integrate small numbers of molecules into electronic circuits, ranging from a single molecule to laterally limited mono- and bilayer junctions, have been reported during the last decade.[9–11] For most of these experimental designs, the sizes of the junctions were adapted to the dimensions of the integrated molecular structures. From a scientific viewpoint, the contribution from these molecular junctions cannot be underestimated, as they represent the crucial experimental basis of structure–property relationships that allowed exploration of the potential of molecular building blocks. However, from an engineering viewpoint, the experimental designs did not usually allow the integration or even the designed interconnection of several junctions. Moreover, the dimensions of the integration and investigation setups were usually several orders of magnitude larger than the observed molecular junctions, and thus the small size of the junction cannot be effectively exploited.

Furthermore, in most cases either the conductance of a transient junction or the current–voltage characteristics of more stable junctions was the only information available. Unfortunately, at least an immobilization step (physisorption or chemisorption) is necessary between the chemical characterization of the molecule and the investigation of the molecular junction. In some experimental designs even additional intervening processing steps are required, for example the deposition of a top electrode or the wiring of the junction to macroscopic leads. During these processes molecules may be damaged, resulting in a considerable uncertainty regarding the final structure in the junction. Another important issue is the purity of the investigated compound. As transport currents are only observed through the junction of least resistance, even almost undetectable impurities (even single molecules) might dominate the transport features of the experimental setup. To date, these concerns were mainly dispelled either by investigating entire series of molecular structures in which particular structural features were altered and correlated with resulting trends in the transport features or by investigating a large number of comparable junctions and analyzing the results statistically.

Obviously, an additional analytical tool that would enable investigation of the molecules within the junction would be a marvelous supplement to such transport experiments. In first attempts, inelastic electron tunneling spectroscopy was used to further investigate the chemical structure of species immobilized in the junction.[12] However, the advantage of intrinsically higher sensitivity than optical spectroscopy will never compensate the experimental limitations, such as cryogenic temperatures. Surface-enhanced Raman scattering[13] and more recently even high-energy X-ray spectroscopy[14] were used to investigate molecular junctions.

Recently, a very elegant approach addressing several of these current challenges in molecular electronics was reported by an interdisciplinary team of experimentalists and theorists from Northwestern University.[15] The so-called "on-wire" lithography (OWL) that they developed allows an increase in both the number of available junctions and the dimensions of the nanoobject that must be contacted with top-down techniques. The OWL technique consists of the electrochemical growth of pillars consisting of multiple layers of at least two different metals in a porous alumina template (Figure 1 A). After the template has been removed, these pillars were coated from one side with a supporting insulator layer that provides the required stability. Subsequently, segments of the pillars consisting of less noble metals were dissolved, providing stable pillars comprising junctions with adjustable lengths (corresponding to the thickness of the

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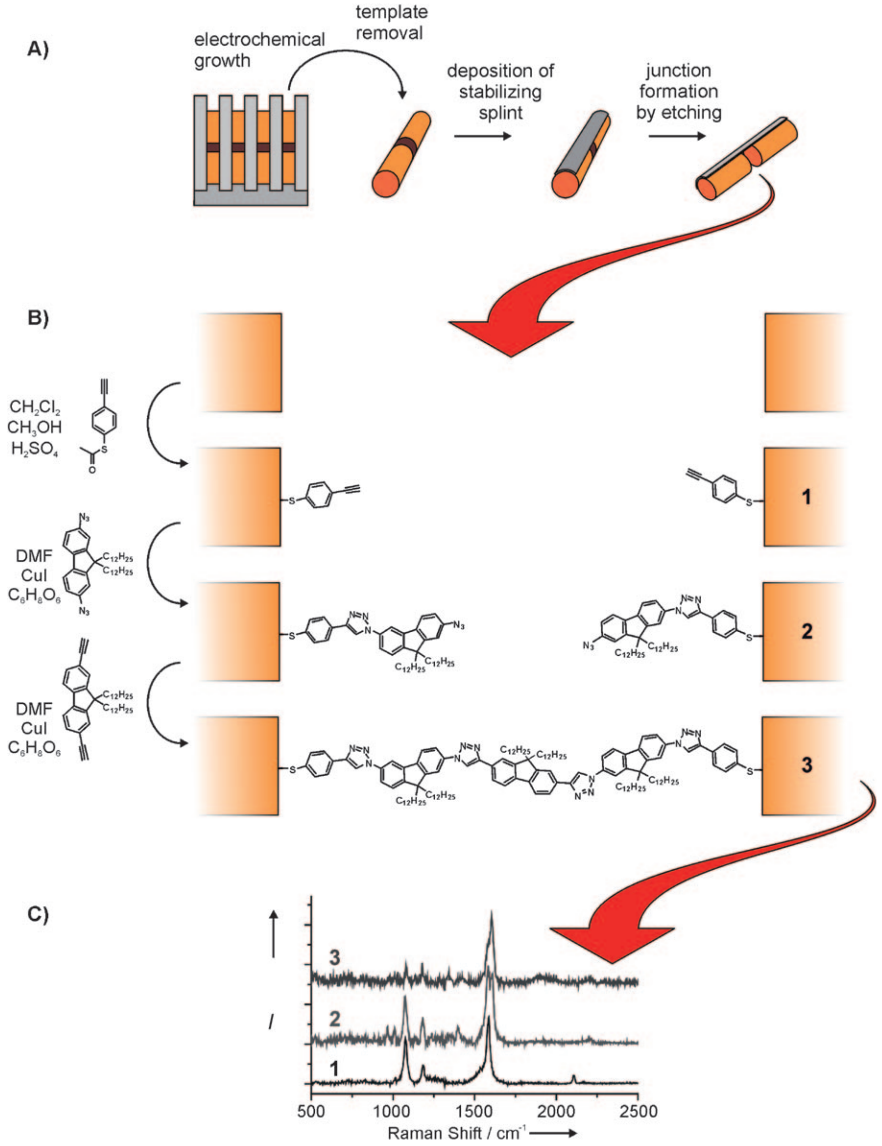

Figure 1. A) The OWL technique for the fabrication of pairs of electrodes. B) Closing of the junction by stepwise in-gap oligomer assembly. C) Monitoring of the in-gap synthesis by surface-enhanced Raman scattering.

dissolved segments) between two and several hundred nanometers.[15,16]

Instead of only making small gaps which might be bridged by individual molecules, they considered a more general chemical approach allowing interconnection of gaps of various dimensions. Specifically, they used a stepwise synthesis of the bridging structure inside the junction (Figure 1 B), a concept that was applied by Kagan and Lin using coordination oligomers to interlink lateral electrodes.[17] However, the Northwestern team pioneered interconnection by covalent bonding by using the copper-catalyzed version of the 1,3-dipolar cycloaddition to interlink fluorene subunits. This "click" reaction is ideally suited for several reasons: 1) mild reaction conditions, 2) the oligomer length is precisely controlled by the alternating exposure to two different building blocks, and 3) the expected bridging oligomers consist exclusively of π-conjugated subunits, namely triazole-interlinked fluorenes, thus optimizing the expected transport features of molecularly bridged junctions.

To demonstrate the potential of this concept of "knitting" the conducting compound in the junction, gold pillars with gaps of 2, 5, and 7 nm were fabricated. Subsequent molecular interconnection of the acetylene-functionalized electrodes was achieved by applying the required number of growth steps, providing oligomers of the length required to bridge the gap. Oligomers consisting of one, three, and five triazole-interconnected fluorenes were necessary for the 2, 5, and 7 nm gaps, respectively. Rather large variations in observed currents were attributed to different numbers of bridging oligomers.

While the course and completeness of the cycloaddition reaction with these building blocks on gold surfaces was demonstrated by X-ray photoelectron spectroscopy (XPS), considerable differences with respect to reagent transport into the spatially restricted junction draw the suitability of this comparison into question. However, as slightly larger OWL junctions have already been used as Raman hot spots with enhancement factors up to 10^8,[18] surface-enhanced Raman scattering (SERS) allowed monitoring of the oligomer growth within the junction (Figure 1 C). And indeed, characteristic signals of the involved functional groups appeared and disappeared, thus corroborating the growth of the bridging structure inside the junction. For technical reasons slightly different dimensions of junctions were used for the transport experiment and for the SERS investigation, such that the authors did not attempt in situ observation of the junction under voltage, as recently reported by Natelson and coworkers.[19] Finally, the electronic structure of the monomer bridging the 2 nm gap was calculated with density functional theory, and a single-level model[20] was applied to fit the current–voltage characteristics of the junction. Based on these calculations, hole transport through the molecule's highest occupied molecular orbital (HOMO) was postulated as the dominant transport process of the molecular junction. Good agreement between observed and calculated current–voltage traces further corroborates the suggested chemical structures bridging the junction.

In conclusion, a promising concept to functionalize prefabricated junctions with macromolecules synthesized in situ is presented. The modular nature of the assembly strategy even allows variation of the subunits of the bridging oligomer and thus the tailoring of the electronic properties of the resulting molecular junction. Furthermore, the OWL approach allows the chemical modification of numerous junctions in parallel and increases the dimensions of the nanoobject that has to be contacted from the top down. However, strategies to assemble numerous junctions in parallel remain to be developed. Once regular arrays of such junctions become available, another technology promoted by one of the authors, called dip-pen lithography,[21] will be the ideal tool for the deliberate variation of the molecular functionalization of each individual gap, thus providing a chemical approach to circuit programming.

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