Ultrathin π-Conjugated Polymer Films for Simple Fabrication of Large-Area Molecular Junctions

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Molecules can be successfully employed as electronically active building blocks in the fabrication of electronic devices. The electronic properties of molecular architectures can be tailored by tuning the chemical unit's properties through functionalization and controlling their self-assembly on metallic electrodes. One of the major problems encountered in assembling metal–molecule–metal junctions is the chemical and mechanical fragility of the organic compounds, either as single molecules or organized in self-assembled monolayers (SAMs). In particular, contacting the molecules with metal electrodes is still a technical challenge, as both yields and reproducibility are often low. The nature of the contact seems to play an important role in determining the mechanism and the magnitude of the electron transfer rate.[1,2] Moreover, the high mobility of molecules chemisorbed on gold via a thiol linkage represents an additional limiting factor for the fabrication of molecular devices.[3]

In recent years, a large variety of different, often conceptually new metal–molecules–metal junctions have been designed and used for measurements of electron-transfer processes through molecules sandwiched between two metal surfaces. Each type of junction—break[4–7] and planar junctions,[2,8,9] those based on gold wires[10] or Hg electrodes[11–15]—incorporates specific advantages and disadvantages with respect to fabrication, reproducibility, and application. While a great effort was addressed to the measurement of current flowing through one or more molecules by using break junctions,[4–7] scanning tunneling microscopy[16–18] and modified atomic force microscopy,[19,20] only a few studies were focused on junctions incorporating large assemblies of molecules. Ultrathin layers or monolayers of organic molecules are better accessible systems than single molecules for application in organic electronics.

Junctions designed for incorporating a large number of molecules usually consist of a gold surface electrode supporting a SAM of organic molecules and a second electrode that is formed by deposition of evaporated gold onto the organic layer.[21] The fabrication of the second electrode on top of SAMs without damaging the fragile molecular layer and inducing electrical shorts between the two electrodes still represents a challenge. In an attempt to overcome this problem a number of different strategies, such as lift-off float-on Au pads[22] or deposition of cold gold[23] have been successfully employed. Although these approaches have produced laboratory test structures, it is difficult for them to be scaled up for the fabrication of circuits or molecular devices, because they are highly specialized and time consuming. A nanotransfer printing technique for gold electrodes has been introduced successfully for efficient fabrication of junctions based on semiconductors Ga/As–SAM–Au[24], and functionalized single-walled carbon nanotubes have been used as electrodes for assembling test-bed junctions.[25] A sophisticated approach which requires top-down nanofabrication has been used recently to develop gold electrodes on top of a layer of mixed polymers for measuring electron transfer through SAMs of aliphatic chains under vacuum.[26]

Herein we describe a new, simple approach for easy and inexpensive fabrication of large-area (about 1 mm^2) junctions in ambient atmosphere that allow for measurements of electron transfer rates through organic molecules organized in SAMs in air. The novel aspect of the junction consists of depositing an ultrathin, (80 nm thick) film of a commercial, undoped π-conjugated polymer on top of the organic monolayer. This film is expected to chemically insulate and mechanically protect the organic SAM, and therefore to prevent electrical shorts between the electrodes. Indeed, π-conjugated polymers[27] 1) offer a wide range of structures and charge mobilities (carrier mobility up to 1 cm^{2}V^{-1}s^{-1} and carrier lifetimes up to 5 ms),[28,29] 2) supply a versatile material for fabricating thin films and nanostructures,[29] 3) form a compliant, soft contact to the SAM, and 4) form films where the rigid structure of the aromatic backbone remains intact.[30,31] The latter feature is important in preventing the polymer from penetrating the defects of the SAMs. Among π-conjugated polymers, we have chosen a commercial yet undoped polyphenylenevinylene-type polymer, that is, poly[(m-phenylenevinylene)-co-(2,5-dioctoxy-p-phenylenevinylene)] (PmPV).[32]

The junction is schematized in the inset of Figure 1. It consists of 1) a gold surface electrode, 2) a SAM of organic molecules anchored to the gold surface by thiol groups, 3) a thin film of semiconducting polymer on top of the SAM, and 4) a second metal electrode, that is, a mercury drop, contacting the polymer film. This type of electrode has been chosen for an easy test of the performance of this new junction. The assembly of the junction is straightforward. A thin layer of gold with a nominal thickness of 25 nm was vacuum sublimed on mica films as reported in the Supporting Information. Alkylthiolate SAMs and terphenylthiolate SAMs were chemisorbed on the gold surface following the well-known protocol.[33] A layer of PmPV was spin-coated on top of the SAM. In order to control the thickness and homogeneity of the polymer film, we used solutions of PmPV of different concentrations ranging from 10^{-1} M to 10^{-4} M in different organic solvents. The thickness of the polymer films was routinely estimated with a profilometer.

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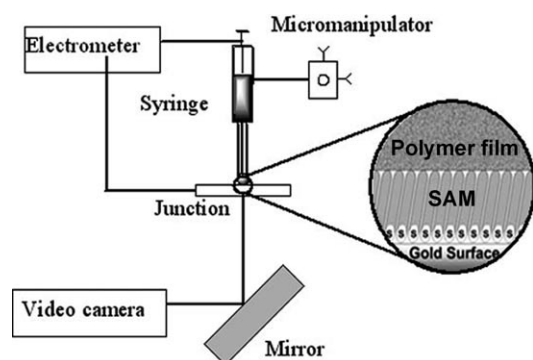
Figure 1. Schematic illustration of the junction: the micromanipulator brings the Hg electrode (syringe) in contact with the gold-SAM/polymer surface. The contact area is visible through the transparent gold surface. The image of the contact area is collected by a mirror and sent to a video camera.

The most homogeneous films were obtained by spin-coating 50 μL drops of solutions of PmPV (10^{-3} M in chloroform) on top of the gold surface covered by a SAM (see Supporting Information). To make an electrical contact, a small area of the gold electrode was left uncovered by the polymer and connected to the electrical circuit with a gold tip. A mercury-based electrode was brought into contact with the polymer film with a micromanipulator.

To explore the influence of the π-conjugated polymer film on the electron flow between the electrodes, we performed current–potential (I–V) measurements on a series of junctions that differed in 1) the thickness of the polymer and 2) contact area of the mercury electrode. The measurements revealed that 1) junctions incorporating polymer films of different thickness (from 80 to 300 nm) possess similar current values, and 2) junctions of different contact area (from 0.07 to 0.7 mm^2) are characterized by different current values and the same current densities (A cm^{-2}). Both these results suggest that the electrons flow only through the polymer in the area of the junction, and not along the polymer layer. This conclusion is very reasonable given that for these junctions the ratio between the thickness of the polymer film (i.e. 80 nm) and the diameter (which amounts to 10^5 nm) of the Hg/polymer contact area is ca. 1/1000.

To show that the currents measured using this junction correlate with the electronic structure of the molecules chosen to form the SAM, we recorded the current through junctions incorporating SAMs formed by alkanethiols of different lengths [CH$_3$(CH$_2$)$_{n-1}$SH, with n = 8, 10, 12, 14, 16] and SAMs formed by p-terphenylthiol. Using different type of junctions, we[12] and other authors[11, 20, 34] have demonstrated that current flowing through molecules is dominated by a through-bond tunneling mechanism, which can be properly described by the relation: $I = I_0 e^{-\beta d}$, where d is the length of the incorporated molecules, and β is an attenuation factor specific to the molecular structure. According to this relation, the current flowing through alkane chains of different length decays exponentially with the length of the thiolated molecule, and the current flowing through molecules possessing same length but different elec-

tronic structure can exhibit different values. The measured I–V curves are shown in Figure 2.

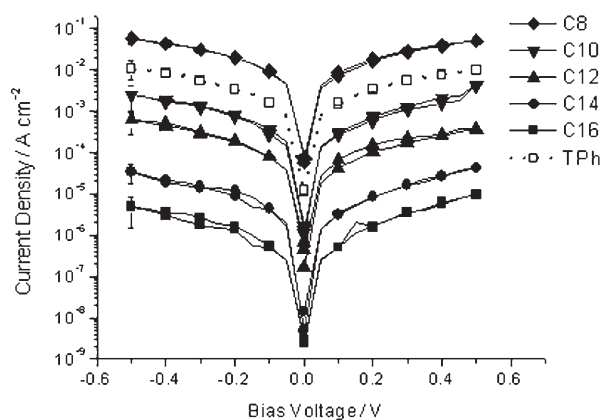The continuous lines in Figure 2 depict I–V curves of junctions incorporating SAMs of alkanethiols having different

Figure 2. Current–potential (I–V) curves measured through SAMs formed by alkanethiol chains of different length (——) and through SAMs formed by p-terphenylthiol (·····). The error bar on the measured current densities, being constant for each molecule type and independent of the bias voltage applied, is shown for each molecule only for the first data point on the left side.

lengths. They reveal a clear dependence of the current flow on the molecular length. Figure 3 shows the current density at a bias of 0.5 V on a logaritmic scale versus the length of the alka-
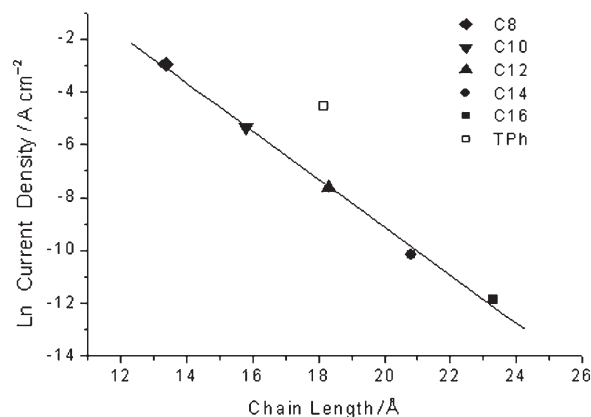

Figure 3. Natural log (Ln) of current densities measured at 0.5 V versus molecular length for junctions incorporating alkanethiols [CH$_3$(CH$_2$)$_{n-1}$SH, n = 8, 10, 12, 14, 16] and terphenylthiol SAMs.

nethiolates forming the SAM. These results are consistent with a simple tunneling mechanism: at a very long distance (24 Å) the current density shows very low values.

From this plot, we calculate a decay factor for alkyl chains of $\beta = 0.90 \pm 0.03$ Å^{-1}. This value fits well with the electrical measurements of identical chemical systems performed employing different type of junctions.[10, 11, 12, 20]

The dotted line in Figure 2 represents the *I–V* curve measured in junctions incorporating a *p*-terphenylthiol SAM. Significantly, we observe that molecules of the same length but with a different electronic structure, such as *p*-terphenylthiol[35] and dodecanethiol,[36] show a large difference in their electrical characteristics: the current for *p*-terphenylthiol is higher by two orders of magnitude than that for dodecanthiolate. This difference is in agreement with literature data and suggests a decay factor of 0.6 Å^{-1}.[13,20] This value is confirmed by the following estimation: junctions incorporating aliphatic and oligophenyl chains exhibit, as expected, similar values of current density across the metal–S–C interface, that is, at distance $d = 3.47$ Å.[13,37,38] In our case, the data for aliphatic chains were extrapolated to $d = 3.47$ Å; this value together with that measured for the *p*-terphenylthiol allows us to estimate a decay factor for the *p*-phenylene oligomer of $\beta = 0.61 \pm 0.03$ Å^{-1}. It is also noteworthy that the values of β for phenyl chains calculated from the data obtained with the present junction are in line with those reported by several authors by using different junctions.[12,21]

These data provide unambiguous evidence that the current measured through this junction reflects the electrical characteristics of the incorporated organic molecules, and that the polymer film represents a constant barrier to the electron transport process. Likewise, the effect of the PmPV–Hg interface, whether Ohmic or Schottky type, can be regarded as a constant factor. We do not observe rectification in the *I–V* curves (Figure 2) typical for Schottky barriers; however, this effect may be weak.

We have evaluated the contribution of the undoped polymer film to the overall "resistivity" of the system by comparing the current flowing through the present junction incorporating the polymer film, Au–SAM/PmPV–Hg, with a Au–SAM/SAM–Hg junction, which was prepared as described previously[12] (SAM = dodecanethiolate). The current density measured for the two junctions at 0.5 V amounts to 4.8×10^{-4} A cm^{-2} for Au–SAM/PmPV–Hg and 3.2×10^{-5} A cm^{-2} for Au–SAM/SAM–Hg. These values unequivocally indicate that a 80 nm thick PmPV layer is more transparent to electrons than the 1.2 nm-thick monolayer of dodecanethiolate.[11,12]

It is well known that PmPV layers exposed to oxygenated atmosphere and/or irradiation undergo slow degradation processes.[30] Noteworthily, we found that the junctions give reproducible results for a few days when kept in air, and for several weeks when kept in deoxygenated atmosphere. This is an advantage that can be obtained only for undoped polymeric films and represents a step forward from the recent report by de Boer and co-workers.[26]

In conclusion, we have described the fabrication and electrical characteristics of a highly stable junction suitable for measuring in air and for comparing electron transfer rates through SAMs of organic molecules. The chemical, mechanical and electrical stability is achieved by depositing a thin layer of an undoped semiconducting polymer on the SAMs. The *I–V* measurements revealed a correlation of the current with the length and the electronic structure of the molecules, and indicate that the junction reflects the electrical properties of the incorporated molecules. Significantly, a comparison of the "resistivity" of the PmPV film with that of alkanethiolate SAMs indicates that an 80 nm thick polymer film is more transparent to electrons than a 1.2 nm thick aliphatic or aromatic SAM. This system offers several advantages with respect to other types of junctions: 1) it allows for fabrication of functional devices in high yields (75%), 2) it is easy and inexpensive to assemble, 3) it is based on a commercially available material (i.e. PmPV), 4) it sustains high applied voltages, and v) it should inhibit the mobility of the thiolate molecules across the metal surface. The unique combination of these characteristics makes this system a potential candidate for applications in molecular-scale electronics. Ongoing work in our laboratories is focused on the fabrication of solid metal electrodes on top of various semiconducting polymer films on SAMs formed by different organic molecules.

Acknowledgements

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