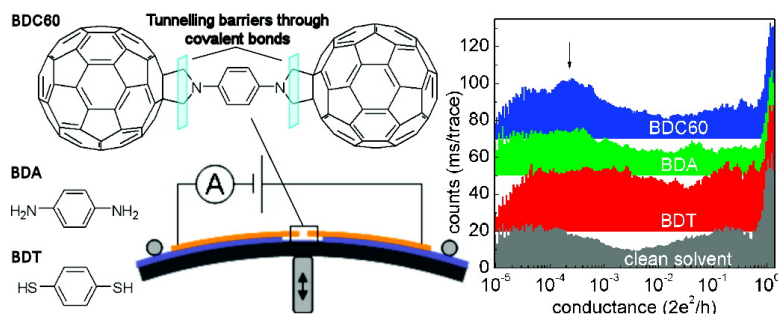


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Fullerene-Based Anchoring Groups for Molecular Electronics

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Self-assembly from solution with stable chemical anchoring is an important step in the robust formation of single-molecule junctions. To date, thiol moieties have been used extensively to attach single molecules to gold electrodes.¹ However, the thiol–gold bond exhibits variations and fluctuations that are reflected in the electronic properties of molecular junctions.² Only very recently, amino groups have successfully been applied in solution-based break junction experiments. Their binding motif reduced the conductance spread of single-molecule junctions significantly and allowed for more systematic studies of structure–property relationships.³ However, the signature of amines in mechanically controllable break junctions in vacuum was recently found to be small, probably due to the weak amine–gold bond.⁴

To attain larger junction stabilities and to minimize fluctuations due to atomic details at the anchoring site we have designed and synthesized a linear and rigid C₆₀-capped molecule. With their high symmetry and their affinity for noble metals, fullerenes are very interesting candidates for anchoring. Stable C₆₀ adlayers have been deposited from various solvents.⁵ Furthermore, C₆₀ is known to hybridize strongly with gold surfaces,⁶ leading to single-molecule conductances on the order of one tenth of the conductance quantum G₀ (1 G₀ = 2e²/h = 77 μS).⁷ As anchoring groups, C₆₀ moieties may lead to a significant increase in the contact area with the electrodes and to a shift of the limiting barriers for electronic conduction from the molecule–gold contact to the stable covalent bonds of the pyrrolidine moieties that connect the C₆₀ with the molecular backbone. This can also be advantageous for comparisons with theoretical models: In the extended molecule picture,⁸ the strong hybridization with the gold allows the fullerene anchors to be treated as effective electrodes, leading to well-defined charge injection into the molecular core.

To test the C₆₀ anchoring we have compared the electrical characteristics of 1,4-bis(fullero[c]pyrrolidin-1-yl)benzene (BDC60, Figure 1a) to those of 1,4-benzenediamine (BDA) and 1,4-benzenedithiol (BDT). Using lithographic mechanically controllable break junctions (MCBJs) we have studied low-bias conductances and junction stabilities. Figure 1b shows a schematic of the device architecture. Electron beam lithography was used to fabricate break junctions on polyimide-covered phosphor bronze substrates. The architecture allows for subangstrom control of the electrode displacement through a deflection of the substrate center. Prior to the electrical characterization we deposited the molecules of interest using self-assembly from solution. All measurements were carried out in a home-built setup in vacuum and at room temperature.

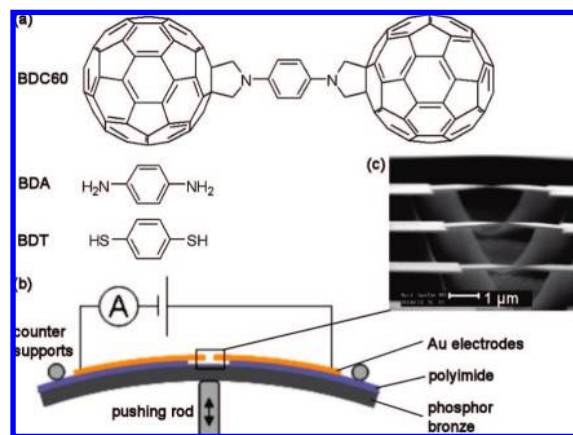


Figure 1. (a) Molecular structures of the studied benzene derivatives, (b) schematic of a mechanically controllable break junction, and (c) scanning electron micrograph of a device showing three of four independent junctions.

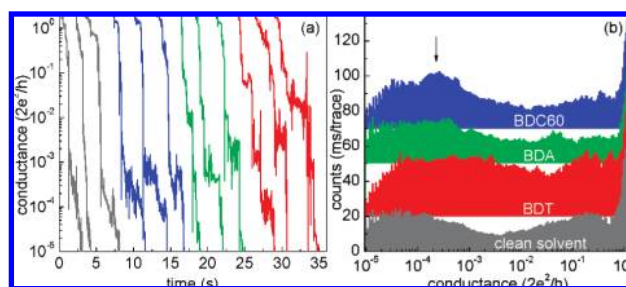


Figure 2. Breaking characteristics of junctions exposed to clean solvent and to solutions of the benzene derivatives at a DC bias of 50 mV and at room temperature. (a) Examples of conductance traces during breaking. (b) Conductance histograms on a semilog scale, constructed from 400 consecutive traces. The arrow marks the typical junction conductance of BDC60. All curves are offset for clarity. Colors in panel a correspond to those in panel b.

Figure 2a presents breaking traces of the lithographic MCBJs. As the electrodes are stretched their conductance decreases from several conductance quanta to a value below the noise floor of our setup. Nearly all breaking traces exhibit a plateau around 1 G₀, which corresponds to a single gold atom bridging the gap between the electrodes. Below 1 G₀, junctions that have been exposed to pure solvents⁹ display a jump out of contact followed by a roughly exponential decay upon stretching, typical of vacuum tunneling. The self-assembly of molecules on the junctions, in contrast, leads to pronounced plateaus in the sub-G₀ regime. These can be attributed to conduction through individual molecules bridging the gap between the gold electrodes.¹⁰

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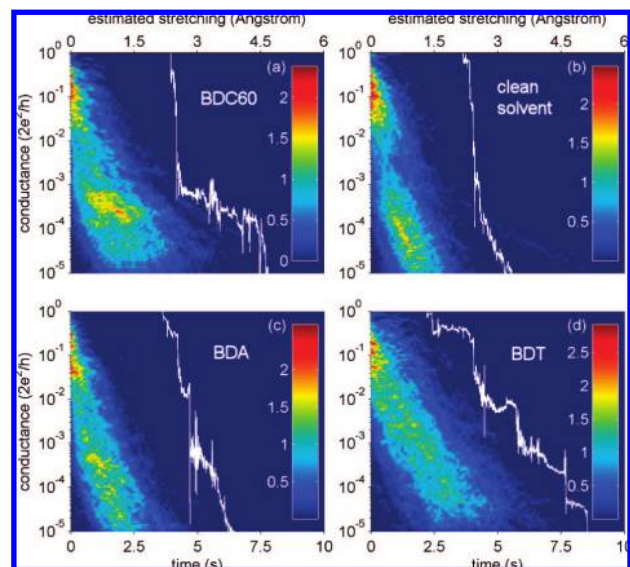


Figure 3. Trace histograms from 400 consecutive breaking traces. Histogram counts have been normalized to ms/trace and are color-encoded. Areas with highest counts represent the most typical breaking behavior of the individual junctions. In each histogram this is exemplified by one breaking trace (white). The stretching distance has been estimated from the displacement ratio of clean lithographic break junctions.

The statistical spread in plateau shapes and positions can be captured by constructing logarithmic conductance histograms from hundreds of breaking traces (see Figure 2b).¹¹ Histograms of junctions exposed to clean solvents typically exhibit a low and rather smooth background below $1 G_0$. Deviations from the expected flat signature of vacuum tunneling may be due to the slow breaking in vacuum.⁴ Histograms of BDC60, in contrast, display a peak around $3 \times 10^{-4} G_0$, which corresponds to junctions of the fullerene-anchored molecule. Its signature is more pronounced than that of both other benzene derivatives. For benzenediamine, faint features around $4 \times 10^{-4} G_0$ may be observed. Histograms of benzenedithiol do not show a clear structure but increased counts across the entire conductance range, indicating a large variation in junction conductance.

To investigate the stability of the new anchoring mode further we have compared the breaking dynamics of BDC60-junctions to those of the other benzene derivatives. Recently, histograms of plateau lengths have been used to characterize the stability of single-molecule junctions.¹² However, spontaneous conductance fluctuations during the slow breaking of lithographic MCBJs can render plateau detection in the sub- G_0 regime erroneous. We have applied a new statistical method that extracts the complete breaking dynamics below $1 G_0$. All data beyond the rupture of the last monatomic gold contact is evaluated statistically in both time, that is, stretching distance and conductance. In the resulting trace histograms, areas of high counts represent the most typical breaking behavior of the molecular junctions.

Figure 3a presents such a trace histogram for BDC60. Immediately after breaking it exhibits a narrow region of high counts around $0.1 G_0$. It is a sign of short-lived high-conductance states that are observed in all graphs in Figure 3. They may not be a characteristic feature of the molecular junctions and will hence be ignored in the discussion. After these initial states the trace histogram of BDC60 reflects a fast conductance decay and an extended region of high counts around $3 \times 10^{-4} G_0$ that is consistent with the histogram in Figure 2b. This region is due to individual breaking traces with plateaus at the same conductance,

similar to the white curve superimposed on Figure 3a. In trace histograms, flat plateaus below $1 G_0$ result in horizontal lines. Any variation in the molecular conductance causes a vertical blurring of these lines. Such a spread is indeed present in Figure 3a. Furthermore, the trace histogram indicates the presence of slightly sloped plateaus, which are also visible in the traces in Figure 2a. The horizontal spread of the accumulation region indicates that the fullerene-anchored junctions can be stable for more than 3 s.

Figure 3b presents the trace histogram of a junction that has been exposed to clean toluene. In contrast to molecular conductance plateaus, the exponential decay typical of vacuum tunneling results in a steeply sloped region of accumulation from about 10^{-3} to $10^{-5} G_0$. No accumulation regions of well-defined conductance can be observed. The trace histogram of BDA (Figure 3c) exhibits only a small region of enhanced counts around $4 \times 10^{-4} G_0$. Its width is smaller than for BDC60, supposedly due to the limited stability of the amine-gold bond.⁴ Note that this conductance value shows a deviation from recent results in solution^{3a} that remains to be explained. BDT junctions do not exhibit any preferred breaking behavior but a slow conductance decay with uniformly distributed counts (Figure 3d). The lack of a clear signature is consistent with the histogram in Figure 2b and can be attributed to the variability of the thiol-gold bond.^{2b}

In conclusion, we have demonstrated the suitability of fullerene-anchoring for single-molecule electronic measurements. Compared to thiols the fullerene-anchoring leads to a considerably lower spread in low-bias conductance. In addition, junctions of fullerene-anchored benzenes exhibit an increased stretching length before breaking. This finding opens up new opportunities for the formation of stable molecular junctions.

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Supporting Information Available: Synthesis, experimental details, and further data analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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