Single-Molecule Junctions Based on Nitrile-Terminated Biphenyls

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The electronic transport through single - molecule junctions is known to be affected by the specific molecular conformation of the central unit [1]. This has triggered the hope that molecules can be incorporated into electronic devices as switches. Recently, the conductance dependence on the torsion angle between the two phenyl rings in biphenyl based molecules has been widely investigated. For cases in which the transport is HOMO dominated, the conductance has been found to decrease with increasing torsion angle [2,3]. In this work, we analyze this dependence in a case in which the transport occurs through the molecular LUMO. This was accomplished by contacting a family of biphenyl derivatives to gold electrodes via nitrile (CN) anchoring groups. As this group is electrowithdrawing, it shifts the molecular levels downwards, affecting in turn the nature of the transport mechanism. Furthermore, studying nitriles has given us the opportunity to explore a relatively "new" binding group in this discipline. The pursuit of the best anchoring group for the formation of stable and energetically well-aligned metal-molecule contacts represents one of the most important current issues in molecular electronics [4,5]. In this perspective, understanding how the conformational induced change in the conductance depends on the specific anchoring group is one of the points which needs to be clarified.

We studied the transport through the mentioned molecules both experimentally (by scanning tunneling microscope (STM) break-junction technique) and theoretically by ab initio calculations. We found [6] that the conductance of the molecular junctions is roughly proportional to the square of the cosine of the torsion angle between the two benzene rings of the biphenyl core, which demonstrates the robustness of this structure−conductance relationship.

The calculations revealed that only atop binding geometries of the nitrile-gold contact are stable. This result is due to the coordinative nature of the covalent N-Au bond, which is established via the nitrogen lone pair. In order to evaluate whether the temperature can affect the molecular structures and in turn the conductance values, we performed molecular dynamics simulations for the isolated molecules in both vacuum and a solvent environment. They revealed that the torsion angles fluctuate around the equilibrium values. We estimated the corresponding variations in the conductance and we found that they are smaller than those due to changes in the binding geometry.

References

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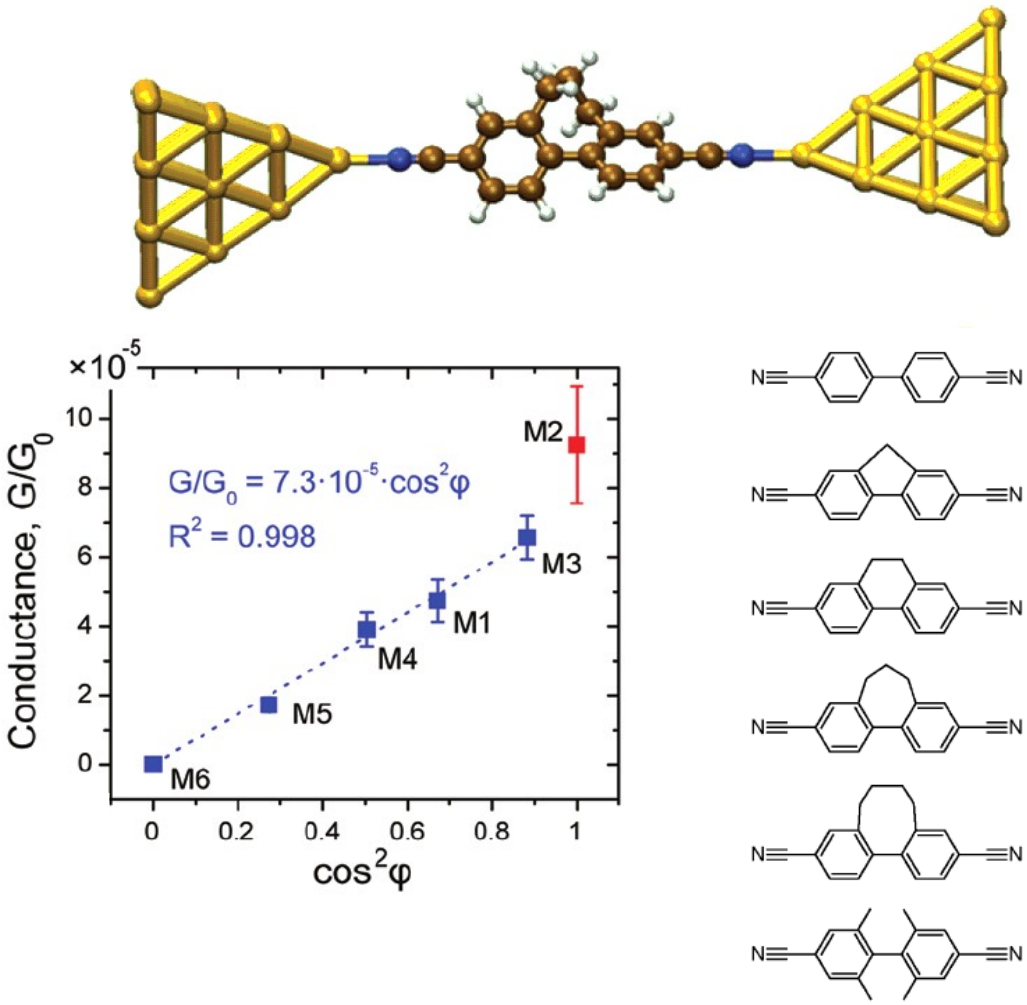
Figures



Top: Metal – molecule – metal junction for one of the studied molecules.
Lower left: Measured conductance vs cosine square of the torsion angle.
Lower right: Analyzed molecules