Stepwise method to fabricate conductive molecular wires characterized by scanning tunneling microscopy

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Abstract

Long, conductive molecular wires have attracted great interest due to their promising potential for single molecule devices.**[1]** Usually, long synthesized molecules are used as molecular wires but their syntheses are complicate and expensive.**[2]** Stepwise methods, based on self-assembly properties of molecules, can provide a simpler and reproducible solution to prepare supramolecular structures with molecular control. The scanning tunneling microscope (STM) is a versatile tool to fabricate and control the molecular assemblies at molecular scale. In particular, when it is operated at the solid/liquid interface, placing a solvent droplet between the STM tip and the substrate, it is possible to add molecules in order to create organized structures.**[3]**

We have been applying a stepwise method to built long molecular wires composed by zinc-octaethylporphyrins separated by 4,4'-bipyridines, as illustrated in Figure 1.**[4,5]** STM at solid/liquid interface was used to assembly the molecules on Highly Oriented Pyrolitc Graphite (HOPG). Each molecule is deposited individually, where each step is controlled in real time using molecular resolution images obtained by STM. Figure 2 shows a STM image of the 4th monolayer composed by bypiridines whit a darker region corresponding to the porphyrins of the previous monolayer. With this method, we fabricated wires composed by up to 25 individual molecules arranged in a well-defined sequence and assembled via bonding of the central metal of the porphyrin to the nitrogen atom of bipyridine. The final structure is a molecular wire with 14.29 nm in length (as determined by density functional theory using a SPARTAN software).

In addition, we have also measured the conductivity of each molecular wire using scanning tunneling spectroscopy (STS), where hundreds of I/V curves were recorded at each wire growth step. The length dependence of the molecular wires resistance was analyzed to assess the relative importance of tunneling and hopping processes. The results showed that these molecular wires are highly conductive with an ultralow attenuation factor (β) **[5]**. Similar low β values have been reported for other, though different, porphyrin-based systems.**[6]**

References

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Figures

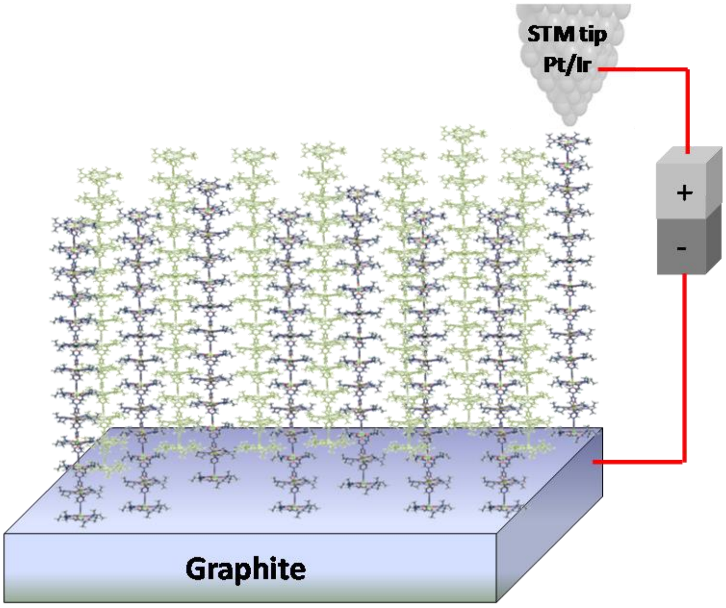

Figure 1. Scheme of a graphite substrate functionalized with molecular wires composed by alternating zinc octaetylporphyrins and 4,4' bypiridines

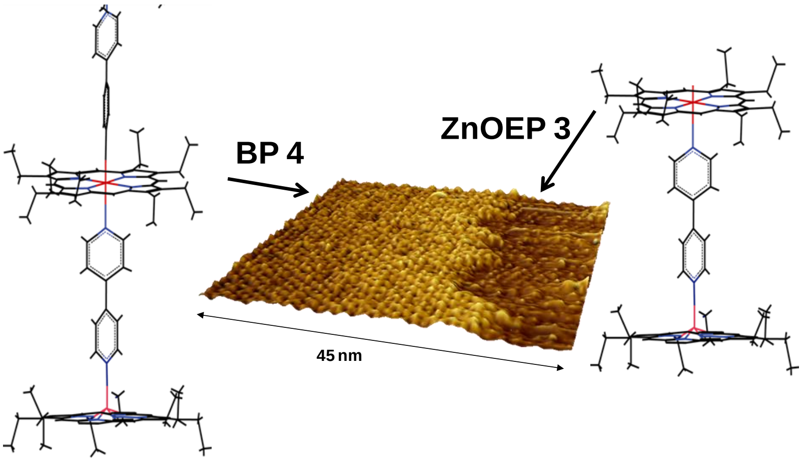

Figure 2. STM image ($45x45nm^2$) of the 4th monolayer composed by bypiridine molecules (BP4) where the darker region is composed by zinc octatethylporphyrin molecules from the previous monolayer (ZnOEP3)