Detecting Mechanochemical Atropisomerization within an STM Breakjunction using Porphyrins

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Abstract

The study of porphyrin molecular wires is a fruitful area within the field of molecular electronics [1, 2, 3]. We have employed the scanning tunneling microscope break-junction technique to investigate the single-molecule conductance of a family of 5,15-diaryl porphyrins bearing thioacetyl (SAc) or methylsulfide (SMe) binding groups at the *ortho* position of the phenyl rings [1]. These *ortho* substituents lead to two atropisomers, *cis* and *trans*, for each compound, which do not interconvert in solution under ambient conditions; even at 140 °C, isomerization takes several hours ($\Delta H^{\ddagger}$ = 63 kJ mol^{-1}; $\Delta S^{\ddagger}$ = –200 J mol^{-1} K^{-1} for SAc in $C_2Cl_4D_2$). They can be separated quite easily allowing us to study the single molecule conductance behaviour of *cis* and *trans* isomers independently. During elongation of single molecule junctions at room temperature, isomerization does in fact take place when the binding group is SAc, but not SMe, due to the strength of the Au-S bond. When the binding group is SMe, the difference in junction length distributions between *cis* and *trans* isomers reflects the difference in S-S distance (0.3 nm) between the two. In the case of SAc, we find no discernible differences between the plateau length histograms of the two isomers, and both show maximal stretching distances well exceeding their calculated junction lengths. Contact deformation accounts for part of the extra length, but the results strongly suggest that *cis*-to-*trans* conversion takes place in the junction for the *cis* isomer. The barrier to atropisomerization is lower than the strength of the thiolate Au-S and Au-Au bonds, but higher than that of the Au-SMe bond, which explains why the strain in the junction only induces isomerization in the SAc compound. This implies that the porphyrin ring adopts significantly non-planar conformations within the junction.

References

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Figures

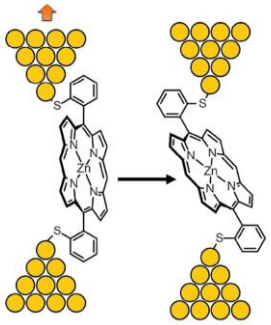

Figure 1: Mechanically-induced atropisomerization in a single porphyrin molecular junction.