Understanding of the structure of molecular layers on surfaces is of a great importance because its atomic arrangement determines the mechanical properties, electronic behaviour and reactivity of surfaces. Peptide nucleic acid (PNA) is an achiral and uncharged DNA mimic of high biological and chemical stability that could have preceded RNA at the first stages of molecular evolution. Previous studies have reported the unique properties of ssPNA oligomers for self-assembly on gold surfaces as well as their capability for recognizing complementary DNA in solution. Therefore, we have investigated the interaction between single stranded PNA oligomers on surfaces, as a first approach for understanding the role played by surfaces in the origin and evolution of life.

Here we report on the structural characterization of the ssPNA adlayers immobilized on natural pyrite surfaces through a comparison with the gold case. We have investigated the chemical interactions of ssPNA at different molecular coverage, and the role played by the surface has been analyzed in detail. These results were obtained by the combined use of surface characterization techniques: X-ray photoemission spectroscopy (XPS), X-ray absorption near-edge spectroscopy (XANES), Reflection Absorption Infrared Spectroscopy (RAIRS) and Atomic Force Microscopy (AFM). We have shown that whereas single stranded PNA forms partially-ordered self-assembled monolayers (SAMs) on gold surfaces, no preferential orientation of thiolated ssPNA is observed upon adsorption on natural pyrite (FeS$_2$) surfaces. ssPNA interacts strongly with the Fe from the pyrite surface, and adsorbs without forming an unique covalent bonding to the surface through the S atom.