

Unravelling the localization of counter-ions in ionic self-assemblies on a HOPG surface

Jean Joseph,^a Frank Palmino,^b Judicaël Jeannoutot,^b Jésus Raya,^a Mathilde Berville,^a Jean Weiss,^a Jennifer A. Wytko^a, and Frédéric Chérioux^{*b}

^aInstitut de Chimie, UMR 7177 CNRS-Université de Strasbourg, 4 rue Blaise Pascal, 67008 Strasbourg, France.

^bUniversité Franche-Comté, CNRS, FEMTO-ST, 25000 Besançon FRANCE. E-mail: frederic.cheriu@femto-st.fr

Abstract:

Adsorption of supramolecular networks is considered a useful technique to tune the electronic properties of the underlying surfaces. Organic molecules with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) at suitable positions with respect to the Fermi level of underlying surfaces can be used to dope surfaces. The degree of doping is strongly driven by the on-surface organization of adsorbed molecules. Among all π -conjugated molecules, redox-active viologens (or 4,4'-bipyridiniums) with low-lying LUMOs have emerged as promising candidates to address this major challenge.

Atomic force microscopy (AFM) is a commonly used method to investigate the self-organization of molecules on surfaces under ambient conditions at the sub-molecular level. However, in the case of organic salts, such as viologens, the position of the organic cations is well determined whereas the position of the corresponding anions has been less investigated mainly because these anions are often smaller than organic cations. The role of electrostatic interactions between anions and cations is essential to the understanding of on-surface organization. These electrostatic interactions strongly depend on the relative positions of the charged species and require the precise determination of the positions of both the cations and the anions. Whereas attempts to combine solid state NMR (ssNMR) with optical microscopy have been successfully reported for liquid crystalline viologen derivatives, the complementarity of ssNMR and AFM was neither established nor reported. This work describes an original strategy, based on a combination of AFM images and ssNMR, to unravel the position of anions and cations in organic salts deposited on a highly-oriented pyrolytic graphite (HOPG) surface. This simple strategy shows that ssNMR can quickly indicate the tendency of building blocks to organize efficiently prior to AFM studies.

We have combined ss-NMR spectroscopy and AFM topography images to obtain a complete picture of the supramolecular self-assemblies of organic salts on an HOPG surface. This original, simple and efficient method paves the way to the construction of supramolecular self-assembled nanostructures with promising electronic properties.