

## Self-Assembly and Self-Esterification of Plant Lipids on Mica Surface

*J.A. Heredia-Guerrero<sup>1</sup>, M.A. San-Miguel<sup>2</sup>, M.P. Sansom<sup>2</sup>, A. Heredia<sup>3</sup> and J.J. Benítez<sup>1</sup>.*

*<sup>1</sup>Instituto de Ciencias de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, Avda. Americo Vespuccio 49, 41092 Sevilla, Spain.*

*<sup>2</sup>Department of Biochemistry, University of Oxford, South Parks Roads, Oxford OXI 3QU, England.*

*<sup>3</sup>Departamento de Biología Molecular y Bioquímica, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain.*

*[alejandrohg@cartuja.csic.es](mailto:alejandrohg@cartuja.csic.es)*

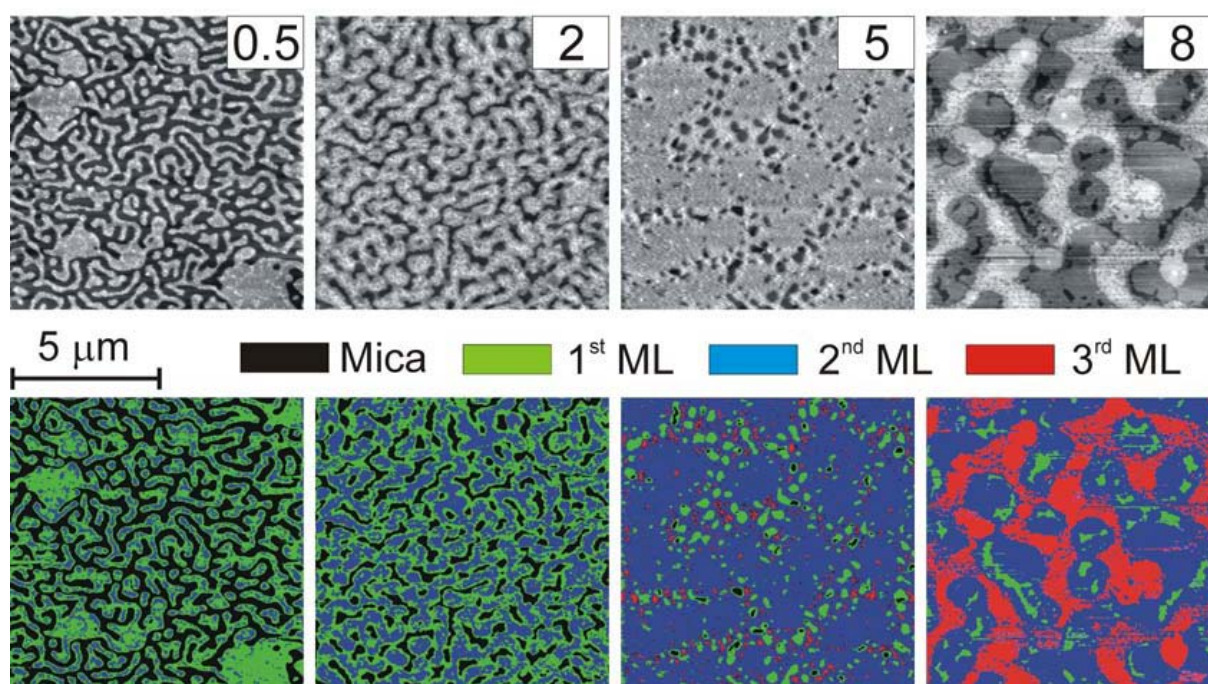
Ultimate knowledge of the reaction mechanism between single molecules requests a precise recognition of their intermolecular interactions at the sub-nanometer scale. Several analysis techniques to carry out this task are currently available to researchers. Among them, scanning probe microscopies have proven to be very useful. Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM), for instance, can resolve the packing structure of self-assembled layers (SAMs) of functionalized long chain alkyl molecules on a flat substrate [1,2]

9(10), 16- Dihydroxypalmitic acid (diHPA) is a particularly interesting plant poly hydroxylated fatty acid. First, because it is the main monomer of cutin, the most abundant biopolyester in nature. Secondly because the presence of a terminal and a secondary hydroxyl group in mid-chain positions provides an excellent model to study their respective intermolecular interactions in a confined phase such as self-assembled layers [3]. In this study we have combined AFM, XPS, ATR-FT-IR as well as MD simulations to conclude that the self-assembling of diHPA molecules on mica is a layer by layer process following a BET type isotherm and with the first layer growing much faster than the rest. Secondary to secondary hydroxyl interactions reinforces the cohesive energy of the monolayers while the presence of the terminal hydroxyl group is necessary to trigger the multilayered growth. Besides, XPS and ATR-FT-IR spectroscopies clearly indicate that spontaneous self-esterification occurs upon self-assembling. The esterification reaction is a pre-requisite to propose a self-assembly route for the biosynthesis of cutin in nature. Molecular dynamics simulations have shown that internal molecular reorganization within the self-assembled layers provides the right molecule to molecule orientation to facilitate the nucleophilic attack and the release of a water molecule requested by the esterification reaction.

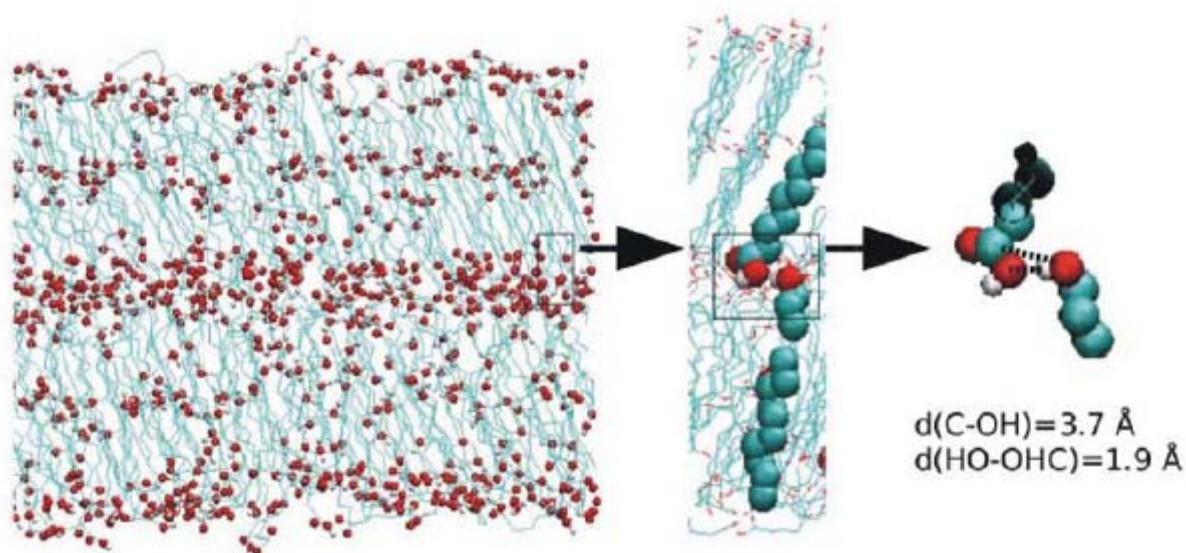
### References:

- [1] Alves, C. A.; Smith, E. L.; Porter, M. D., *J. Am. Chem. Soc.*, **114** (1992) 1222.
- [2] Liu, G.; Salmeron, M. B., *Langmuir*, **10** (1994) 367.
- [3] Benítez, J. J.; Heredia-Guerrero, J. A.; Serrano, F. M.; Heredia, A., *J. Phys. Chem. C* **112** (2008) 16968.

## Figures:



**Figure 1.**  $10 \times 10 \mu\text{m}^2$  topographic AFM images showing the evolution of diHPA self-assembled layers on mica after preparation from 0.5, 2, 5 and 8 mM solutions. The colour coded image below is added to better distinguish mica support and 1<sup>st</sup> to 3<sup>rd</sup> diHPA monolayer regions.



**Figure 2.** Molecular dynamics simulation results showing the packing structure of a bilayer of diHPA supported on mica. As seen on the magnified drawing of the first-second monolayer boundary, diHPA molecules adopt the right relative orientation to generate an esterification reaction.