

ON-SURFACE PHOTOPOLYMERIZATION ON INSULATING IONIC CRYSTALS INVESTIGATED BY ncAFM UNDER UHV

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On-surface chemistry, which involves the covalent bonding of molecular building blocks adsorbed onto a surface, has grown significantly over the past two decades. To date, most nanostructures produced have been obtained under ultra-high vacuum (UHV) on the single-crystal surfaces of noble metals. The polymerization was induced by thermal annealing and was promoted by the catalytic role of surface adatoms. These materials, stemming from nano-engineering, are designed to have improved structural resistance, chemical sensitivity, conductivity, and overall properties. Unfortunately, the underlying metallic surface often alters the electronic properties of the molecules due, for example, to the hybridization of molecular states with the electronic bands of the metallic substrate.

To overcome this drawback, the use of insulating surfaces presents an interesting alternative that is increasingly developing [1]. However, the use of thermal annealing is no longer an effective way to initiate chemical reactions, as on these substrates, molecules often desorb at temperatures much lower than those required to trigger a reaction. Photons provide an alternative source of energy to induce the formation of covalent architectures, even though photochemistry is less common on surfaces than in solution [2]. In reality, the realization of light-induced reactions on inert surfaces seems very promising because this type of reaction does not necessarily require substrate electrons.

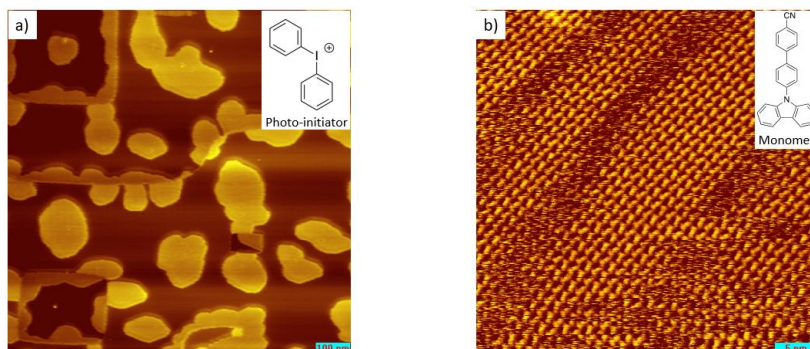


Fig. 1 Constant Δf nc-AFM images representing the self-assembly of: a) Photo-initiator ($1\mu\text{m} \times 1\mu\text{m}$) and b) Monomers ($50\text{ nm} \times 50\text{ nm}$) on the single-crystal surface of Rubidium Chloride RbCl.

One well-established and widespread strategy in solution is based on the use of a photo-initiator that strongly absorbs light and transforms into a trigger agent for a radical polymerization reaction of the monomers dispersed in solution [3]. Our work is inspired by this behavior in solution in an attempt to reproduce it on an insulating surface. We characterize the surface using a non-contact atomic force microscope (nc-AFM) under ultra-high vacuum (UHV) and at room temperature. Our first results in Fig. 1 show the assembly of the photo-initiator (a) and monomer (b) on the ionic single-crystal surface of Rubidium Chloride (RbCl). We will discuss the results of UV illumination on these structures.

References

- [1] E. Geagea, F. Palmino, F. Chérioux. *Chemistry*, 2022, **4**, 796.
- [2] F. Para, F. Bocket, L. Nony, C. Loppacher, M. Féron, F. Chérioux, D. Z. Gao, F. Federici Canova, M. B. Watkins. *Nature Chem*, 2018, **10**, 1112.
- [1] Y. Yagci, S. Jockusch, N. J. Turro. *Macromolecules*, 2010, **43**, 6245.