

Amino-Pyrylium molecular tectons for surface covalent networks

Andrés Lombana^{1,2}, Katharina Gratzner^{1,2}, Laurent Nony¹, Franck Bocquet¹, Franck Para¹, Christian Loppacher¹, Luca Giovanelli¹, Teodor S. Balaban², Frédéric Dumur³, Didier Gimes³, Olivier Chuzel², Jean-Luc Parrain², Sylvain Clair¹,

¹ Aix Marseille Univ, Univ Toulon, CNRS, IM2NP, Marseille, France

² Aix Marseille Univ, CNRS, Cent Marseille, ISM2, Marseille, France

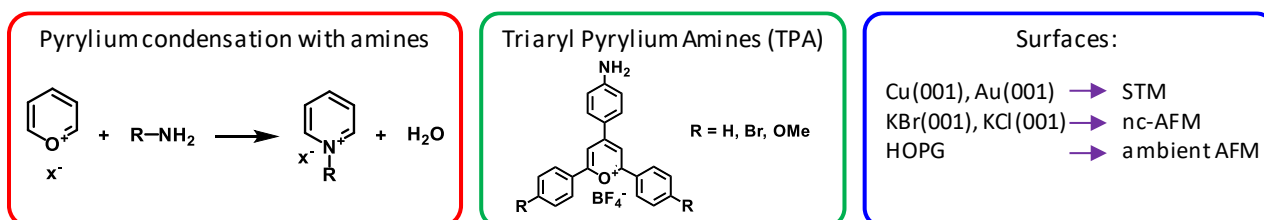
³ Aix Marseille Univ, CNRS, ICR, Marseille, France

andres.lombana@im2np.fr

In the field of advanced molecular nanotechnology, more and more complex structures are being elaborated on planar surfaces. [1] In this sense, practical applications require high stability and electronic communication between the molecules in surface networks. The formation of covalent bonds between molecular tectons has thus attracted recent focus, leading to the emergence of the on-surface synthesis field. Challenges in this field include the synthesis of molecules able to perform the desired reactions and finding convenient reaction approaches. [2] Here we explore the synthesis and surface reactivity of pyrylium salts bearing amine functions and designed to self-condensate and produce 1D poly-pyridinium chains. [3]

As a prototype molecule, a triaryl pyrylium amine (TPA) bearing two phenyl side-groups was first synthesized and its reactivity explored in the bulk powder. A thermogravimetric analysis (TGA) shows that a mass consistent with water is eliminated from the powder upon heating, hinting towards a thermally initiated condensation reaction. These observations are in agreement with the nanometric structures revealed by AFM after dropcast of the in-solution reaction products on a HOPG surface. Other synthesized TPA molecules feature additional side groups such as bromine atoms or methoxy moieties. TGA measurements show different reactivities in the corresponding powders, attributed to the different electron withdrawing or donating effects of the side-groups.

Deposition of the TAP molecules was then studied under UHV conditions on metal and insulating surfaces. Our first nc-AFM results show flat-lying supramolecular arrays of the brominated TPA on KBr(001), probably due to a match between the inter-bromine distance in the molecule and the lattice parameter of the surface. Moreover, the intermolecular distances on the obtained networks are characteristic for long-range repulsive interactions. After this study of deposition conditions, further analysis will explore surface temperature, surface coverage and geometry of adsorption as key parameters for the on-surface reaction.



References:

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