Molecularly precise electronic induction of on-surface tandem radical oligomerization

Gaolei Zhan[1], Younes Makoudi[1], Judicael Jeannoutot[1], Simon Lamare[1], Michel Féron[1], Frank Palmino[1], Marie-Laure Bocquet[2], Christophe M. Thomas[3,*] and Frédéric Chérioux[1,*]

[1] Institut FEMTO-ST, Univ. Bourgogne Franche-Comté, CNRS, 15B Avenue des Montboucons, F-25030 Besançon cedex, France

[2] Laboratoire PASTEUR, Département de chimie, Ecole normale supérieure de Paris, PSL Research University, Sorbonne Universités, UPMC Univ. Paris 06, CNRS, 75005 Paris, France

[3] Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France

Over the past decade, on-surface fabrication of organic nanostructures has been widely investigated for the development of molecular electronic devices, nanomachines, and new materials. Here, we introduce a new strategy to obtain alkyl oligomers in a controlled manner using on-surface radical tandem reactions that are triggered by the electrons between the sample surface and the tip of a scanning tunnelling microscope. This radical-mediated mechanism is substantiated by a detailed theoretical study, which highlights the adsorbat induced resonance state as a key-parameter of the initiation step. This single-electron transfer event allows access to reactive radical species under exceptionally mild conditions and can effectively 'switch on' a tandem sequence leading to formation of oligomers of defined size distribution due to the on-surface confinement of reactive species. Our approach enables new ways to initiate and control radical oligomerisations, leading to molecularly precise nanofabrication.