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Collective radical oligomerisation induced by an STM tip on a silicon surface

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Abstract:

Over the two past decades, on-surface covalent synthesis of organic nanostructures, has been widely investigated in the aim of fabrication of molecular electronic components and functional nanomaterials, owning to the Scanning Tunneling Microscopy monitoring which enhanced the synthesis comprehension at the atomic-scale size precision.[1] Here, we introduce a new strategy to obtain alkyl oligomers in a controlled manner using on-surface radical oligomerisations that are triggered by electrons between the tip of a scanning tunnelling microscope and the Si(111)-B surface (Figure).[2] This electron transfer event only occurs when the bias voltage is below -4.5 V and allows access to reactive radical species under exceptionally mild conditions. This transfer can effectively 'switch on' a sequence leading to the formation of oligomers of defined size distribution due to on-surface confinement of the reactive species. Our approach enables new way to initiate and control radical oligomerisations with tunnelling electrons, leading to molecularly precise nanofabrication.

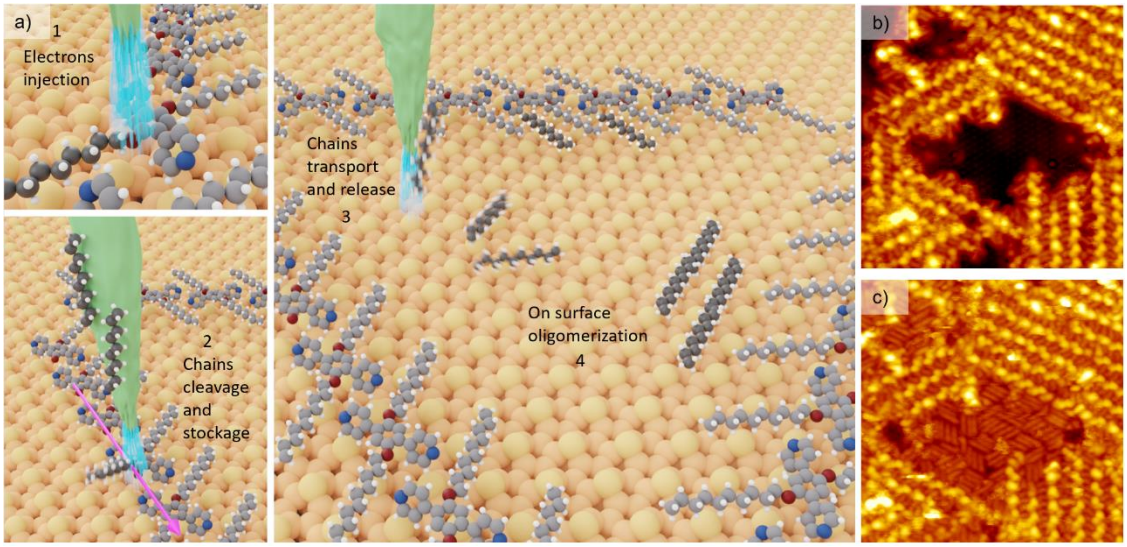

Figure: a) Representative schemes of the new strategy showing the subsequent steps of stm tip induced olygomerisations on Si(111)-B surface. b) STM image (25x25 nm2, Vs = -1.3 V, It = 7 pA, T = 110 K) representing an nano-pore inside the supramolecular network. c) The same nano-pore fully filled with rod-like structure released by STM tip during scanning.

References:

[1] Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M. V.; Hecht, S. Nat. Nanotech. 2007, 2, 687

[2] Geagea, E.; Jannoutot, J.; Feron, M.; Palmino, F.; Rochefort, A.; Thomas, C. M.; Chérioux, F. Nanoscale 2021, 13, 349