

Molecularly precise electronic induction of on-surface tandem radical oligomerization

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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. The resulting radical-mediated mechanism is substantiated by a detailed theoretical study. 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 with tunnelling electrons, leading to molecularly precise nanofabrication.

