## STM-tip induced C-C and C-O cleavage towards the formation of alkane oligomers

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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<sup>[1]</sup>. 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<sup>[2]</sup>. 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.



**Figure 1:** Results of application of Vs=-3 V to CDB-OC10 on Cu(111). a) STM image of the obtained supramolecular network after the deposition of CDB-OC10 on a Cu(111) surface. Then, the STM tip was moved step by step, along the dash red arrow, at Vs=-3 V. b) STM image of the same area. All bright rods extending out of the supramolecular network have been broken. c) STM image showing two C10 alkane chains (white arrow) confined between intact CDB-OC10 molecules. Imaging conditions Vs= -1.4 V, I= 1.00 nA, 110 K, scale bar 2 nm.

## References

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