Reversible C-C bond formation in a surface reaction catalysed by graphene on Ru(0001)

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When working on transition metals, graphitic carbon structures usually are a major obstacle for catalytic processes: Carbon deposits physically block the surface active sites, poisoning the catalytic reaction due to its chemical inertness. However, we demonstrated in a previous work that nanostructured graphene on Ru(0001) can be covalently functionalized employing $CH_2CN^{\bullet}$ radicals, resulting in an extremely high yield and site-selectivity [1][2].

On the other hand, TCNQ molecules become radicals upon adsorption on gr/Ru(0001) due to a charge transfer process [3]. Now, we found that TCNQ molecules react with the previously attached -CH_2CN groups forming a new C-C bond promoted by graphene, as demonstrated by means of scanning tunnelling microscopy (STM) and density functional theory (DFT). Furthermore, this newly formed C-C bond can be reversed using STM manipulation techniques, recovering the bond between the -CH_2CN group and graphene, while the TCNQ moiety remains pristine.

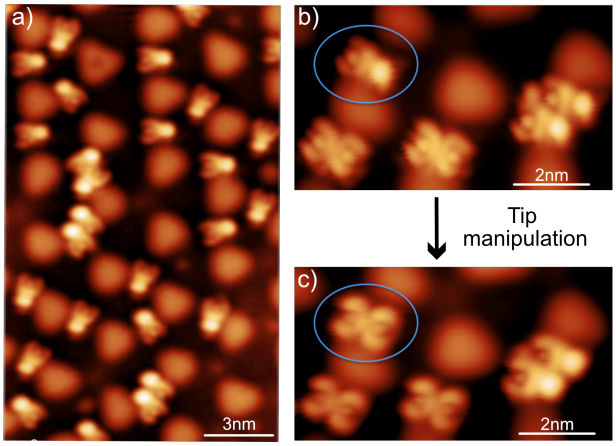

Fig 1. a) STM image (-1.5 V, 5 pA) showing the product molecules, resulting from the C-C bond formation between -CH_2CN and TCNQ, adsorbed on gr/Ru(0001). b) and c) STM images (-2 V, 20 pA) taken on a certain area before and after tip manipulation on the encircled molecule.

References:

[1] J.J. Navarro, S. Leret, F. Calleja, D. Stradi, A. Black, R. Bernardo-Gavito, M. Garnica, D. Granados, A.L. Vázquez de Parga, E.M. Pérez and R. Miranda. Nano Lett. **16**, 355-361 (2016)

[2] J.J. Navarro, F. Calleja, R. Miranda, E.M. Pérez and A.L. Vázquez de Parga. Chem. Commun. **53**, 1041-10452 (2017)

[3] M. Garnica, D. Stradi, S. Barja, F. Calleja, C. Díaz, M. Alcamí, N. Martín, A.L. Vázquez de Parga, F. Martín and R. Miranda. Nat. Phys. **9**, 368 (2013)