

First Direct Observation of Diels-Alder Reactions on Graphene without Defects

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Although graphene has fascinating properties and a large potential for applications, functionalization of this highly non-reactive semiconductor with zero-bandgap remains an important challenge. Diels-Alder (DA) cycloaddition reactions represent a promising approach towards covalently attaching molecules to graphene. Using exfoliated graphene, the team of Robert C. Haddon has demonstrated that the D-A reaction works and is reversible [1]. They followed the reaction by Raman spectroscopy, determining the ratio of the G to D bands, which ascertained that graphene has been modified. However, this globally averaging measurement was not able to identify the locations where graphene was actually functionalized. Their seminal work raised the question if pre-existing defects (step-edges, holes,...) were necessary for enabling the DA reaction. Later, the same team published theoretical studies suggesting that only graphene edges (or holes) might be functionalized by a cycloaddition reaction but that no interior region of graphene could be modified [2]. Here, based on a LT-STM study, we present a direct visualization of DA reactions performed for some specific molecules deposited on graphene. These studies showed that the DA cycloaddition reactions can be carried out on the basal plane of graphene, even when it is free of any pre-existing defects. In the course of covalently grafting molecules to graphene, the sp² conjugation of carbon atoms is broken up and two local sp³ bonds are created. The grafted molecules perturb the graphene lattice, generating a standing wave pattern associated to a 1,4 cycloaddition. Globally averaging spectroscopic techniques, XPS and ARPES, were used to determine the modification in the elemental composition of the samples after the reaction and to search for a possible opening of electronic bandgap of graphene.

[1] Sarkar, S. ; Bekyarova, E. ; Niyogi, S. ; Haddon, R. C. Diels-Alder Chemistry of Graphite and Graphene : Graphene as Diene and Dienophile. *J. Am. Chem. Soc.* 2011, 133, 3324–3327.

[2] Yang Cao, Sílvia Osuna, Yong Liang, Robert C. Haddon, and K. N. Houk. Diels–Alder Reactions of Graphene: Computational Predictions of Products and Sites of Reaction *J. Am. Chem. Soc.* **2013** 135 (46), 17643-17649