Long-range Ordered Cycloaddition with Graphene Reversibly Switched by UV Irradiation

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Due to the unique electronic structure at the Dirac point, graphene is capable of serving as both donor and acceptor in cycloaddition reactions, *e.g.* the Diels-Alder (D-A) reaction. Cycloaddition has been demonstrated to be an effective path to introduce sp^3 hybridization hence functionalize graphene, yet still presenting considerable challenges. Albeit the diverse methods to enable the reactions, such as heating, long soaking in solution, electric pulse, or tip press, photocycloaddition of graphene has been fairly scarce; nevertheless, its potential merits, such as simplicity, remote controllability, and compatibility with other photo-related techniques, would be desirable for practical applications. As widely demonstrated by theoretical results and experimental observations, cycloaddition favors graphene defects and edges, and has a low probability of occurring on defect-free pristine graphene. Even if the reactions were induced, based on the samples prepared in solution and the globally averaging measurements, it is rather challenging to determine the local reaction sites, or ascertain whether the reaction occurred with the target molecules or impurities. Scanning probe microscopy (SPM) under ultrahigh vacuum (UHV) conditions is more appropriate to addressing these challenges. However, only one successful demonstration of cycloaddition in UHV has been reported, where the reaction was accomplished exclusively on isolated molecules at liquid helium temperature. So far, it has not been possible to realize chemical reactions of graphene with molecular networks nor achieve two-dimensional (2D) order of reaction sites at atomic/molecular scale.

Here, we report a reversible *in situ* D-A reaction of an extended molecular network placed on a single-layer defect-free pristine graphene sheet, directly visualized by high-resolution scanning tunnelling microscopy and confirmed by *ab initio* density functional theory calculations and Raman spectroscopy. The reaction is triggered by ultraviolet irradiation at room temperature, with the reaction sites being spatially selective and in a 2D long-range order. As the first example for reaction of graphene with molecular network, this work opens up an efficient and convenient route to fabricate highly precise and long-range ordered electronic matrix of graphene, and may spark considerable enthusiasm to develop diverse fascinating electronic matrixes by the facile chemical reactions of supramolecular networks with graphene for designing and engineering graphene-based optoelectronics devices and microelectronic techniques.