2D MATERIALS

Zipping up nanographenes

Although atomically precise nanographenes can be synthesized on metal single crystals, the synthesis of nanographenes on non-metallic surfaces has proved elusive. Now, reporting in *Science*, Marek Kolmer, Konstantin Amsharov and colleagues prepare nanographenes on metal oxide single crystals through intramolecular aryl–aryl coupling enabled by the presence of C–F bonds in a precursor. The multistep conversion of a precursor occurs with a high degree of regioselectivity, providing a route to the controlled synthesis of nanographenes on semiconducting surfaces.

“On-surface reactions of molecular precursors under ultrahigh vacuum enable the fabrication of target carbon nanostructures with atomic precision,” says Kolmer. However, the majority of these reactions are only effective on noble metal substrates, which catalyse the C–C coupling of the

precursors. This restriction limits the applicability of nanographenes in electronic devices, in which the nanographene should lie on an insulating or semiconducting substrate. The team overcome the substrate restriction by using reactive nanographene precursors that feature C–F groups, which facilitate intramolecular aryl–aryl coupling reactions on non-metallic surfaces. Moreover, the team show that judicious positioning of the C–F groups in the precursors enables the formation of specific target nanographene structures.

Hexabenzocoronene (HBC) was selected as a target molecule for synthesis on rutile TiO₂(011). The team start by preparing the precursor — a fluorinated oligophenylphene that is designed to give HBC in a challenging cyclization reaction involving five consecutive cyclodehydrofluorination steps and a final cyclodehydrogenation step. Following deposition of the precursor, the rutile substrate is heated to 670 K under ultrahigh vacuum, triggering the conversion of the precursor. Scanning tunnelling microscopy imaging of the rutile surface after thermal annealing confirms that only HBC and a single intermediate are present, indicating that the ‘zipping’ of the oligophenylphene chain occurs with a high degree of regioselectivity. The authors attribute this regioselectivity

to the selective activation of the C–F bonds. “Each cyclization step activates the next C–F bond,” explains Amsharov, “thus, the zipping process is controlled and exclusively gives the ‘preprogrammed’ carbon nanostructure.”

On a Au(111) surface, the team’s precursor does not undergo the series of cyclodehydrofluorination reactions to form HBC. Instead, the metallic surface catalyses competing cyclodehydrogenation reactions, indicating that the metal oxide has a key role in the cyclodehydrofluorinations. Indeed, chemical analyses in combination with theoretical calculations reveal both the elimination of HF from the rutile surface and the adsorption of HBC to surface hydroxyl groups.

A direct route to the formation of 2D carbon nanostructures on metal oxides is undoubtedly of technological interest. However, the team note that their approach also opens the door to the programmed design of diverse precursors and thus to a wide range of nanographenes. “We would like to apply our zipping approach to form functional molecules on metal oxide surfaces, and graphene nanoribbons are our next target,” says Kolmer.

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