Observing the formation of 2D Dynamic Covalent Polymers in Real Time

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Synthetic 2D, atom-thin, porous polymers are a fast growing field with a potential interest in many areas from heterogeneous catalysis to electronics. Yet, to this date, how these polymers grow has been only hypothesised. We have now been able to directly observe all the events leading to the formation of these polymers with the help of electronic, scanning tunnelling, microscopy [1]. This technique is able to yield one image per minute of the growing polymer, which matches the growing rate of 2D boroxine on graphite, thus yielding a sequential movie of the polymerization process, from the starting monomers until a full 2D boroxine polymer is obtained, Figure 1.

The microscope images unveil a highly dynamic process which was thought to happen from indirect observations. First, isolated monomers of pyrene-2,7-diboronic acid were observed on the surface. Later, dimers and oligomers appear, and are observed in successive images to shrink and enlarge until a certain size is reached jumpstarting the final polymerization process which ends up covering the surface. From these observations, we perform computer simulations to understand the thermodynamics of the different mechanisms at play to rationalise the observations, Figure 2.

This research was the fruit of a multidisciplinary collaboration led by KU Leuven (Belgium), that performed the microscopy, with POLYMAT (Spain) that tuned the chemical synthesis, and the University of Aveiro where the modelling took place.

These polymers are the basic building blocks of covalent organic frameworks which rely on error-correction and self-healing mechanisms which had not been directly observed before. The novel and detailed understanding of the process will pave the way towards improved, less defective, materials and may yield new methods to provide novel layered heteromaterials with large potential in several areas from electronics to catalysis.

Reference

[1] Nature 603, 7903, 835, 2022

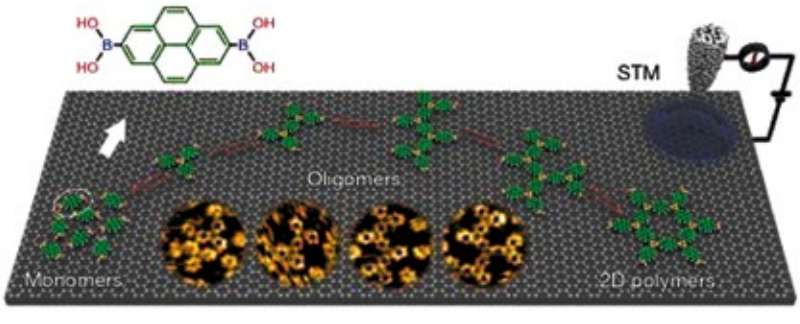

FIGURE 1
Scheme of the experiment.

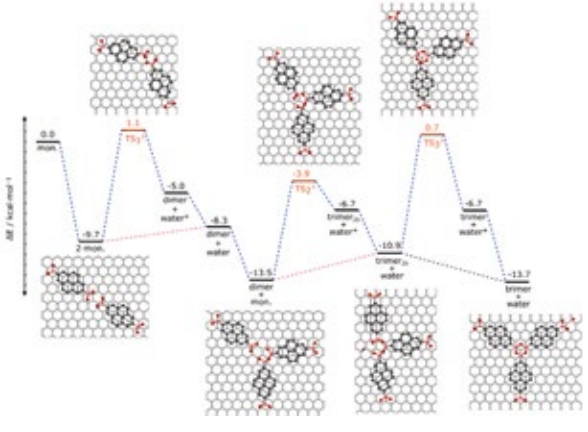

FIGURE 2
Computer models of the fundamental polymerization steps with relative energies in kcal/mol.