

# New approaches towards surface-supported two-dimensional covalent organic frameworks.

Nerea Bilbao<sup>a</sup>

Oleksandr Ivasenko,<sup>a</sup> Kunal S. Mali,<sup>a</sup> Marta Martínez-Abadía,<sup>b</sup> Aurelio Mateo-Alonso,<sup>b</sup> Steven De Feyter.<sup>a</sup>

<sup>a</sup>KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.

<sup>b</sup>POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, 20018 San Sebastian, Spain.

[nerea.bilbao@kuleuven.be](mailto:nerea.bilbao@kuleuven.be)

**Dynamic covalent chemistry** (DCC) has a central role in organic synthesis due to its ability to form products which are otherwise not easily accessible through classic synthetic routes. DCC is a versatile approach that allows harvesting one desired product out of a combinatorial library through selection of well-defined and controlled equilibrium conditions. **Dynamic polymers** have the ability to break and reform their linkages and thus, to adapt their structures and constitutions by reorganization of their building blocks under thermodynamic conditions.<sup>[1]</sup> As a consequence, they have opened the possibility to design responsive materials by combining DCC and polymer science. The formation of imine bonds and the condensation of boronic acids are simple yet efficient DCC reactions, which are extensively used in the synthesis of **two-dimensional covalent organic frameworks (2D-COFs)**, an appealing new family of materials marked by crystalline extended organic architectures in which the building blocks are linked together by strong covalent bonds. Under optimal conditions, these reactions yield at the interface between a liquid and a solid substrate and under ambient conditions extended porous networks that compete with supramolecular systems, both in terms of domain size and structural quality.<sup>[2]</sup> By associating molecules of appropriate structure and functionality in a covalent manner, robust sheets of

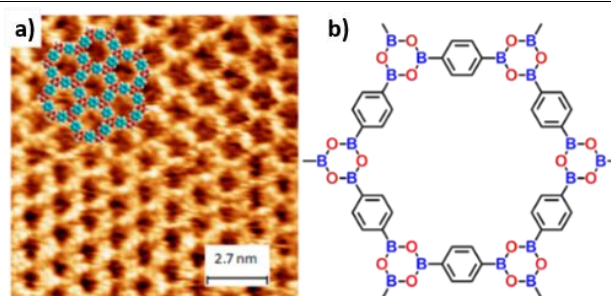
material with a well-defined composition and porosity are created.

In this work, atomically-flat conductive substrates, such as highly oriented pyrolytic graphite (HOPG), serve as support for the adsorption and self-assembly of the molecules, as well as prevent the stacking of the layers; and scanning probe microscopies (SPM), such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), are used to visualize the adsorbates. It will be shown how this methodology allows for a close monitoring of the *in situ* reaction with (sub)molecular resolution, which in turn grants precise control over the synthetic process. It will be exemplified how SPM techniques are a great asset to the design and investigation of 2D materials.<sup>[3]</sup>

## References

- [1] N. Roy, B. Bruchmann, J.-M. Lehn, *Chem. Soc. Rev.*, 44 (2015) 3786.
- [2] J. Plas, O. Ivasenko, N. Martsinovich, M. Lackinger, S. De Feyter, *Chem. Commun.*, 52 (2016) 68.
- [3] N. Bilbao, K.S. Mali, S. De Feyter, *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry* (Ed.: A. Douhal), Elsevier Inc. (2017). DOI: 10.1016/B978-0-12-409547-2.13631-5.

## Figures



(a) STM image of a 2D-COF on graphite synthesized from 1,4-phenyldiboronic acid with superimposed molecular model; and (b) chemical structure of the cyclic unit.