

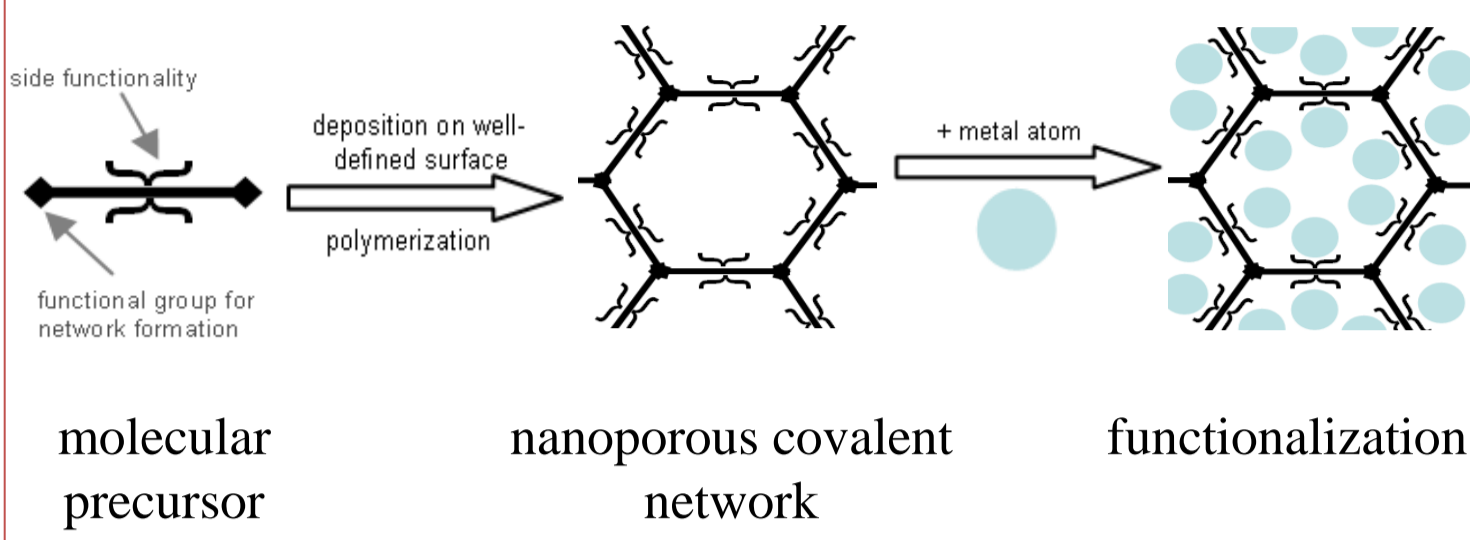
# COVANET: Réseaux 2D covalents fonctionnels pour l'immobilisation de métaux de transition

## Programme JCJC 2010



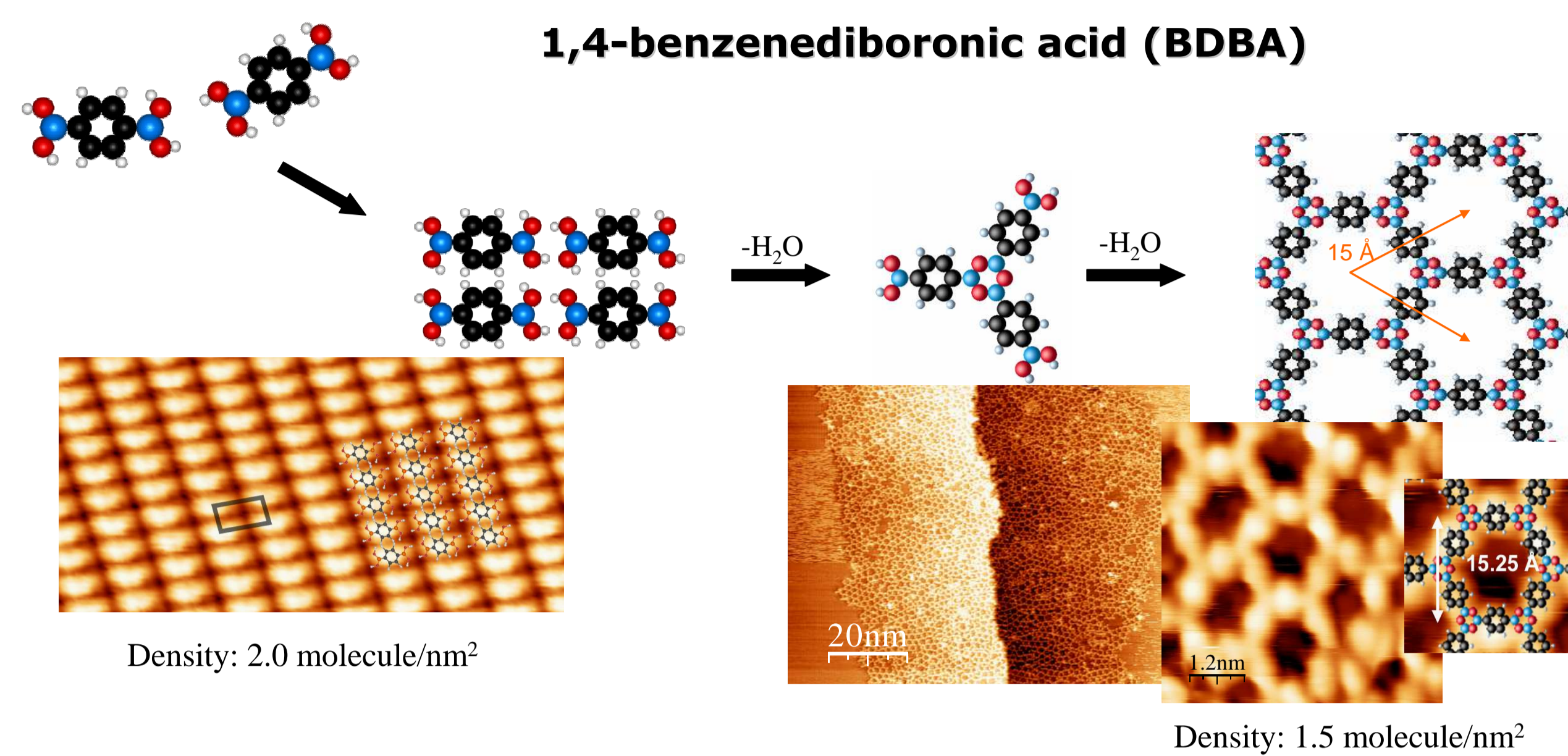
Sylvain Clair, Frédéric Dumur, Mathieu Abel, Thomas Faury, Mathieu Koudia, Didier Gigmes

### General strategy

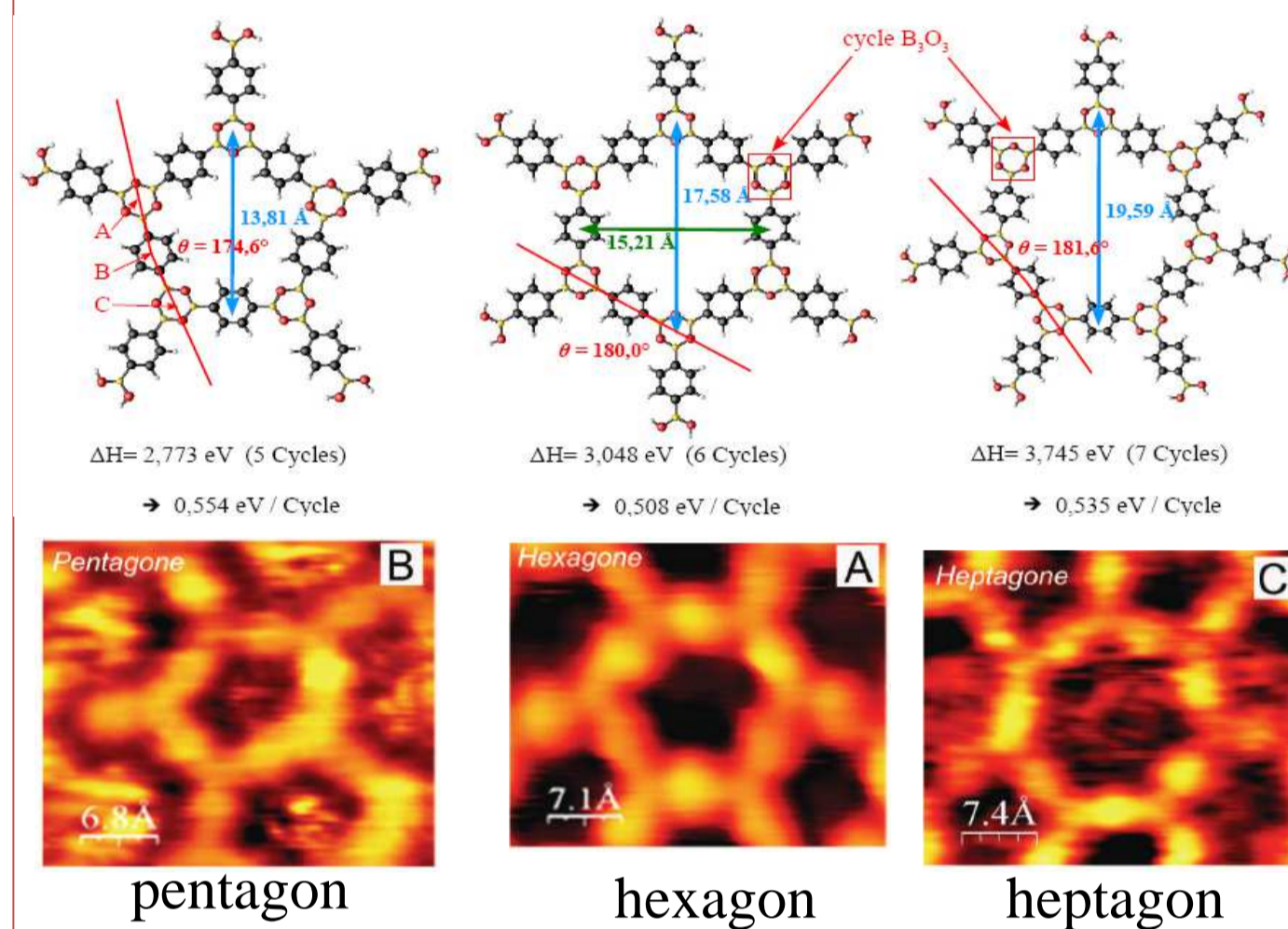


Supramolecular self-assembly at surfaces constitutes a very efficient way to create atomically-controlled organic nanostructures. The possibility of extending its concepts to the formation of covalent bonds between molecular tectons has attracted recent focus, and the demonstrations of covalent polymerization performed directly at surfaces have opened promising perspectives. The objective of the present project is to gain better understanding of the complex mechanisms governing the self-organization and polymerization of boronic acids on metal surfaces and to improve the functionality of the network by use of new boronic acids bearing secondary functionalities favorable to chelate metal atoms.

### Growth of Surface Covalent Organic Frameworks

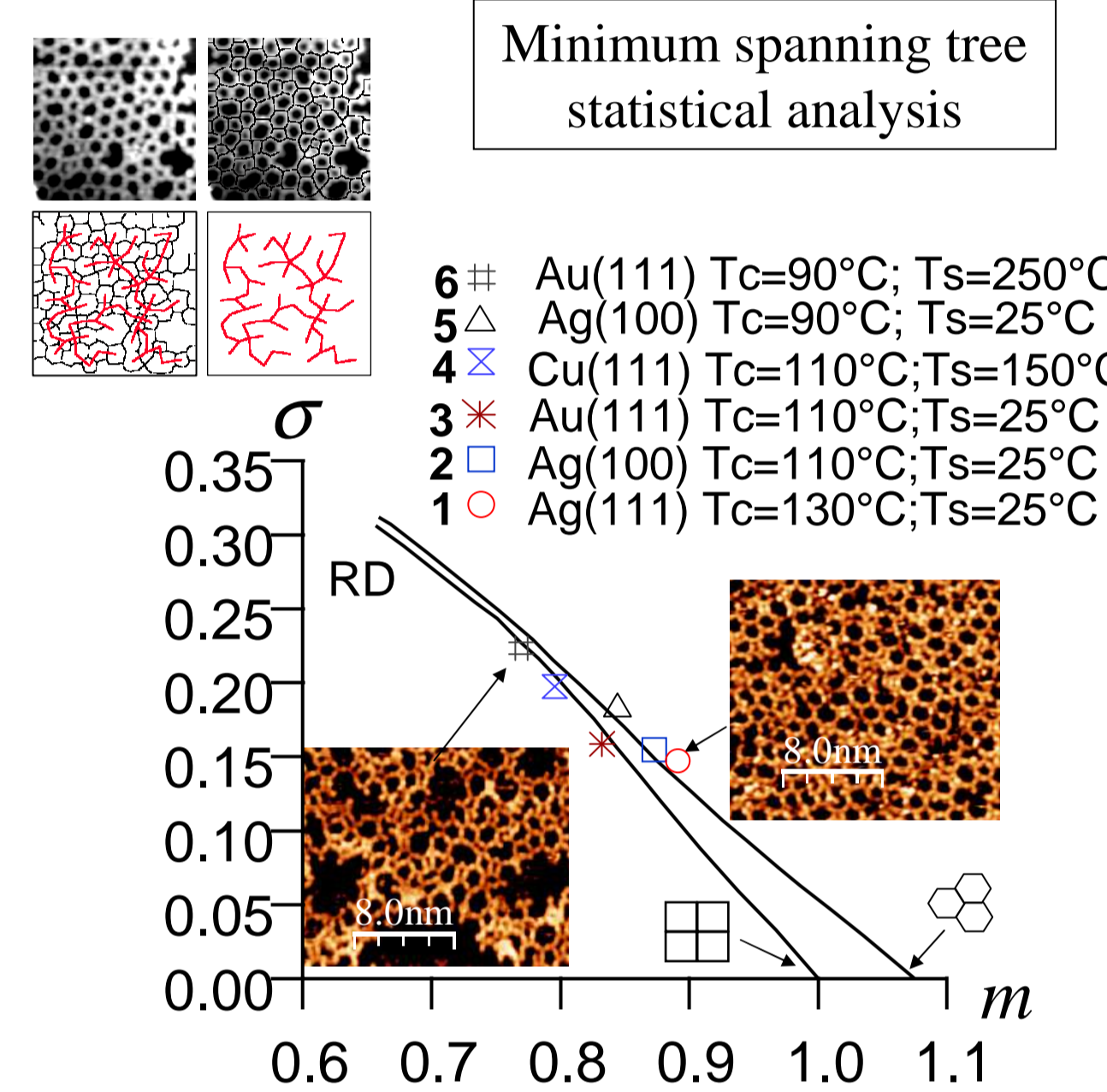


DFT calculation of the polygonal pore formation enthalpy



The formation enthalpy is almost independent of the pore geometry

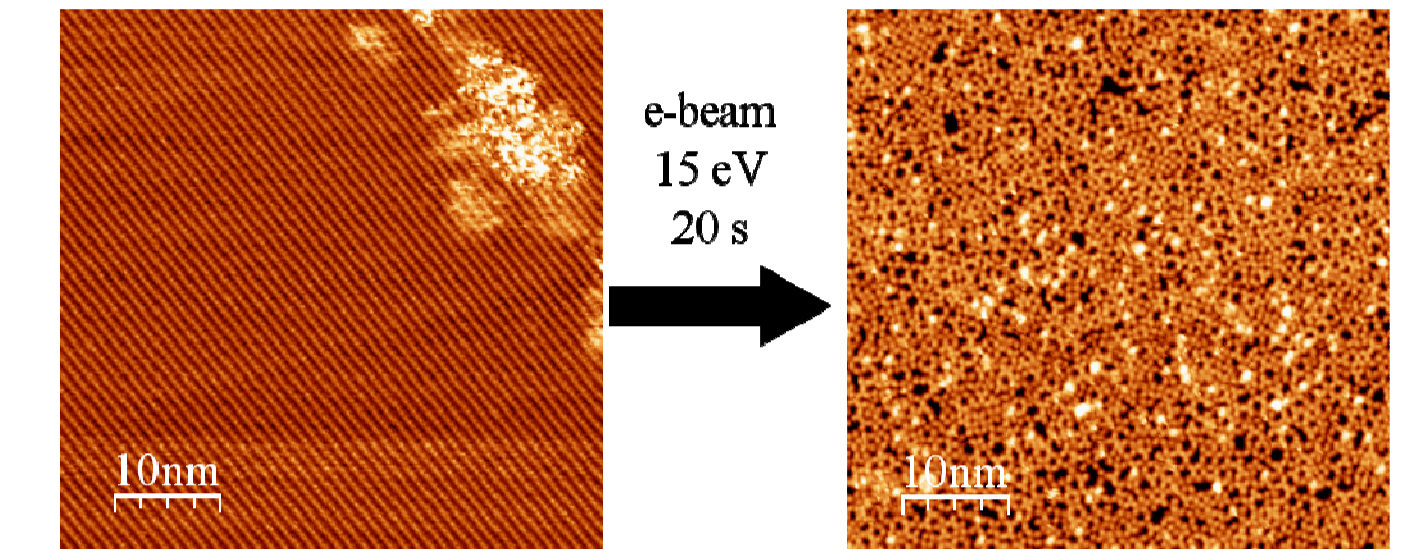
Minimum spanning tree statistical analysis



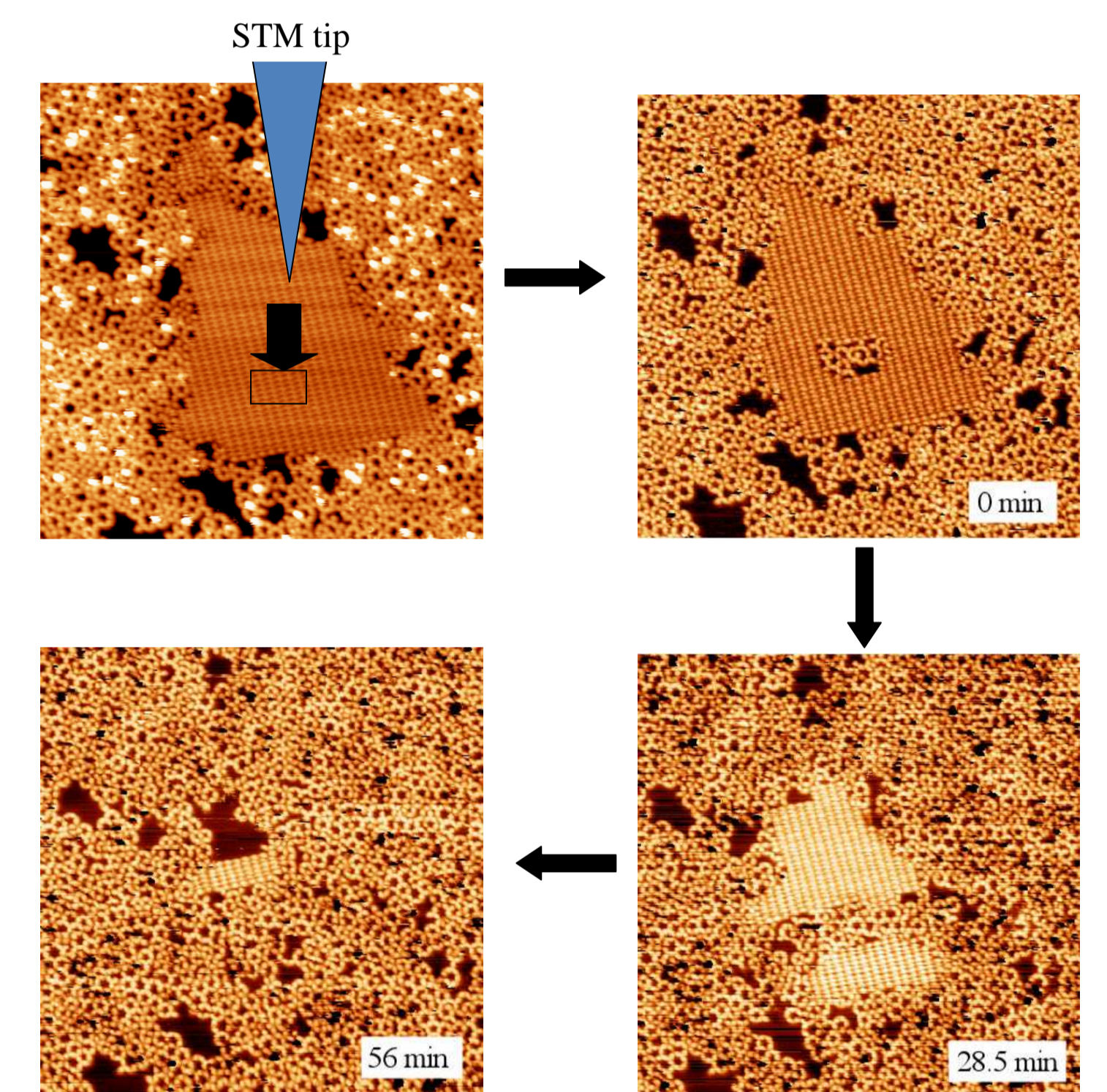
Quantification of the polymer quality for different substrates and deposition conditions

### Control on the reaction kinetics and localization

Full reaction observed after low-energy electron irradiation

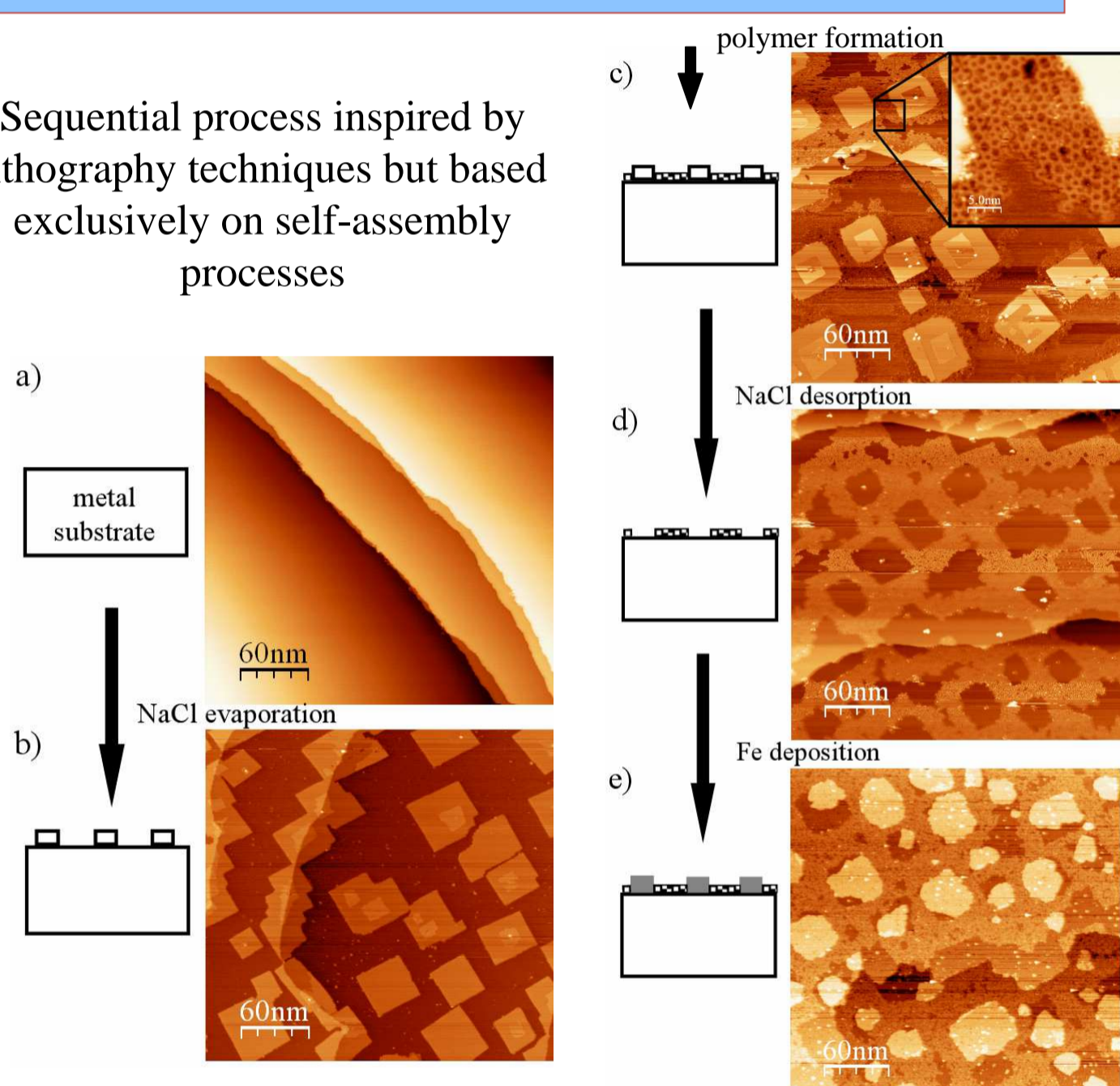


Manipulation with the STM tip to initiate locally the reaction

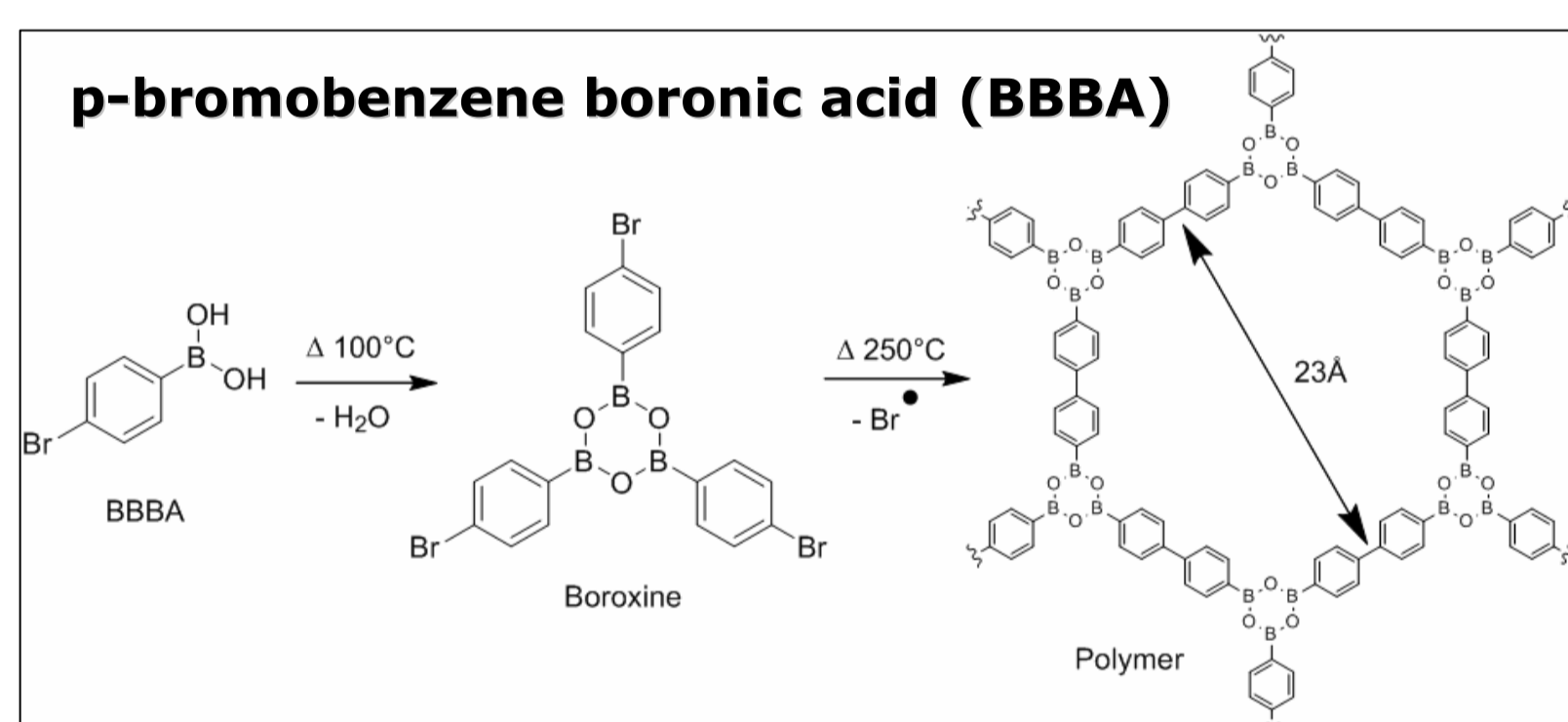


### Nanolithography

Sequential process inspired by lithography techniques but based exclusively on self-assembly processes

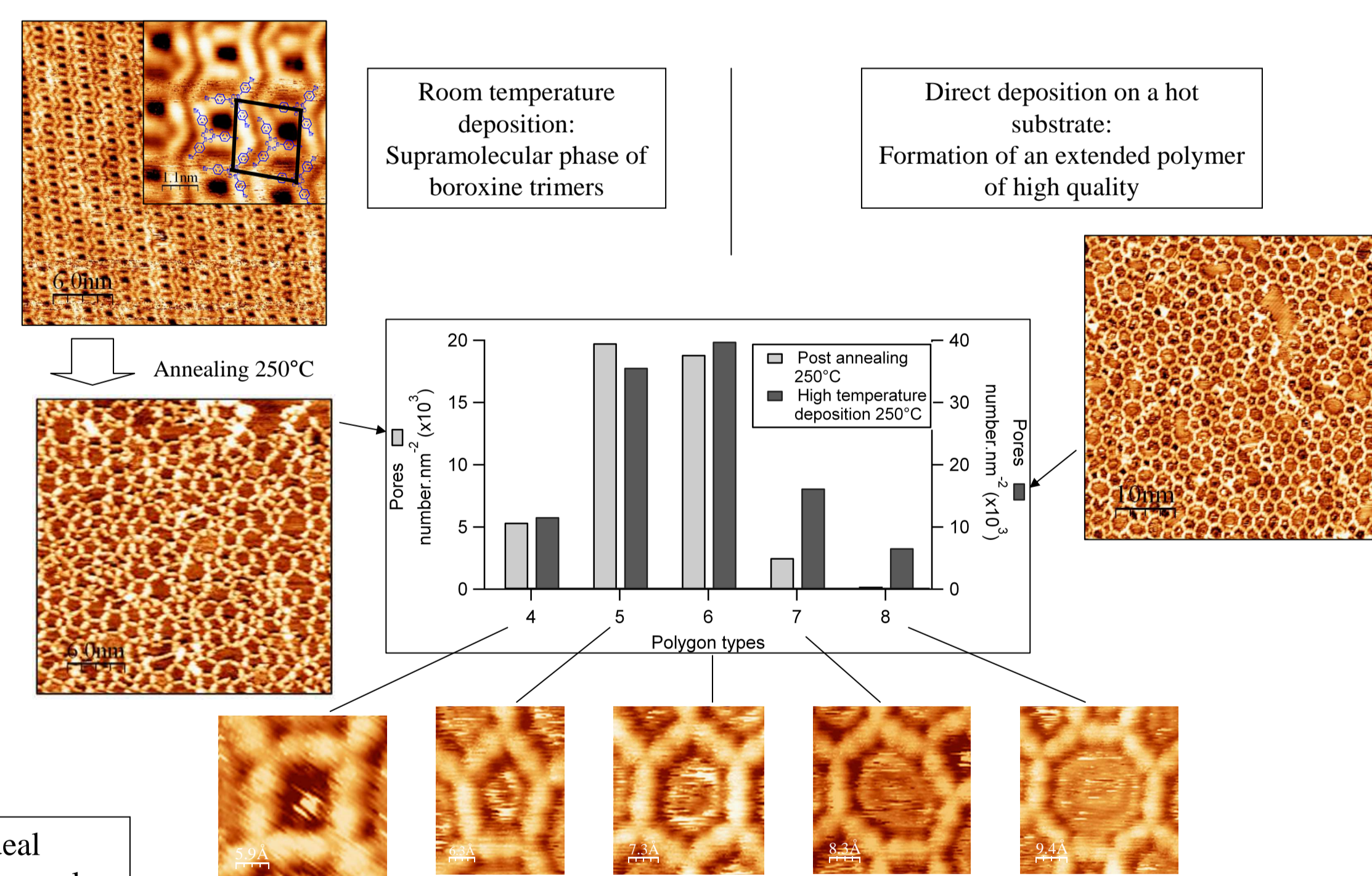


### Sequential linking

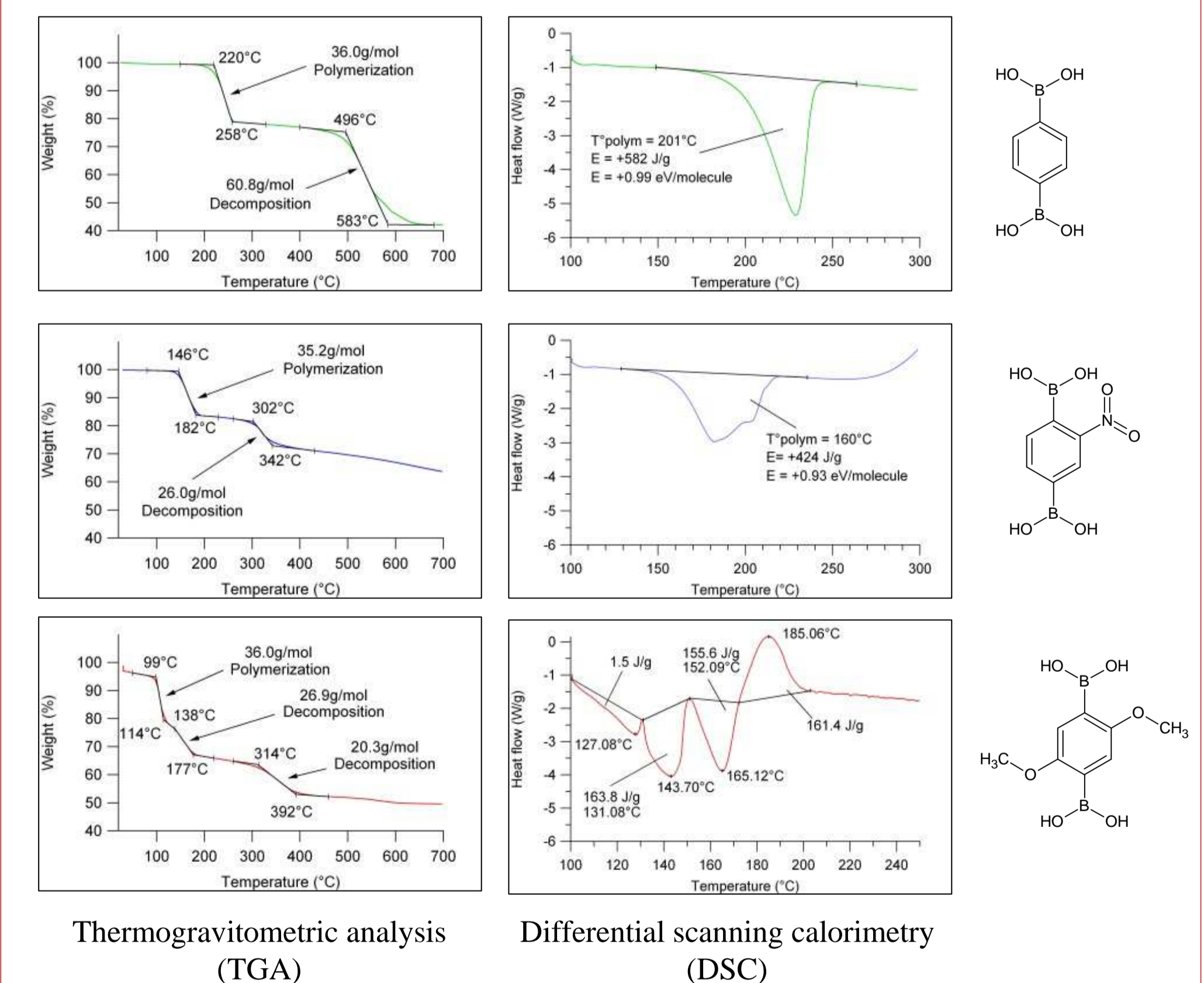


In a first step the boronic acid moieties react to form trimers linked by covalent boroxine rings. In a second step, an Ullmann coupling reaction is thermally activated to form C-C bonds between the trimers leading to the final polymeric network. By this procedure the growth mechanism can be optimized and the polymerization reaction yield approaches 100%.

A well-extended network is obtained, differing from the ideal honeycomb-like network by a substantial number of non-hexagonal pores, which are intrinsic defects to the polymer structure.



### Organic synthesis



### Production scientifique

#### Tip- and electron beam-induced surface polymerization

S. Clair, O. Ourdjini, M. Abel, L. Porte, *Chemical Communication* 47, 8028 (2011)

#### Substrate-mediated ordering of surface covalent organic framework

O. Ourdjini, R. Pawlak, M. Abel, S. Clair, et al., L. Porte, *Physical Review B* 84, 125421 (2011)

#### Two-dimensional polymer as a mask for surface nanopatterning

S. Clair, O. Ourdjini, M. Abel, L. Porte, *Advanced Materials* 24, 1252 (2012)

#### Sequential linking to control the growth of a surface covalent organic framework

T. Faury, S. Clair, M. Abel, F. Dumur, D. Gigmes, L. Porte, *Journal of Physical Chemistry C* 116, 4819 (2012)

#### Side Functionalization of Diboronic Acid Precursors for Covalent Organic Frameworks

T. Faury, F. Dumur, S. Clair, M. Abel, D. Gigmes, L. Porte, *CristEngComm*, submitted (2012)

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