



INTRODUCTION

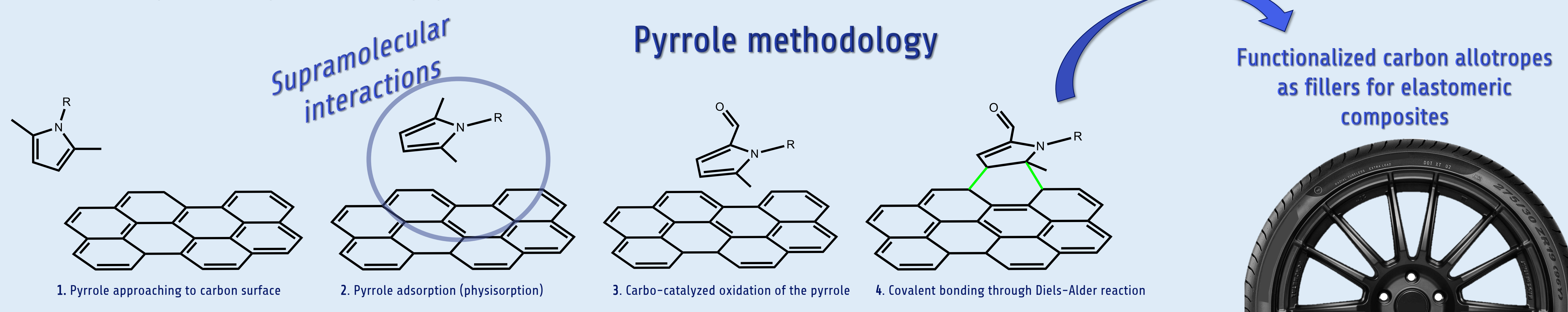
Surface modification of fillers for high-level technological applications such as polymer composites for tire industry has seen a considerable increase in interest since it can boost the properties of the final material. Nano-sized carbon allotropes such as graphene and carbon nanotubes are a suitable class of compounds for these purposes: high thermal and electrical conductivity along with considerable mechanical reinforcement are the main enhancements that these fillers bring to the composite and their elevated surface area allows to reduce the filler volume ratio compared to more common alternatives.

An efficient and reliable procedure to tweak the surface of these nano-fillers is the so-called **pyrrole methodology**, [1] a mild procedure that involves bio-sourced reagents to introduce functional groups on the graphitic planes and that has been recently employed in the fabrication of elastomeric composites with improved mechanical properties [2].

In order to understand the mechanism beneath the interaction between the pyrrole and the substrate and thus the behavior of the functionalized filler, a more in-depth analysis is requested. A theoretical work based on **molecular dynamics simulations** and a DFT study were performed to investigate:

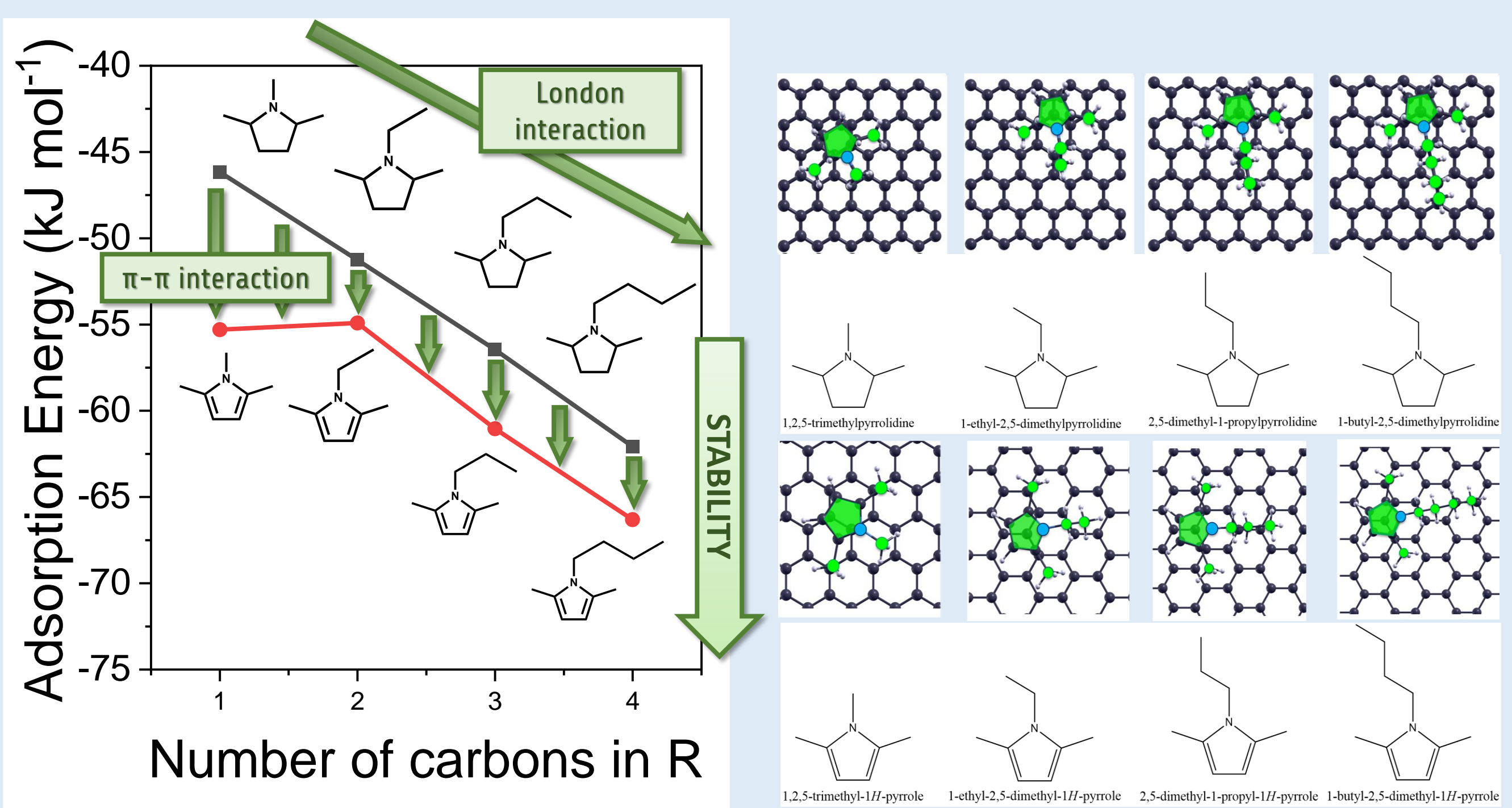
- The magnitude of the interaction between the adsorbate and the sp^2 carbon surface
- The mobility of N-substituted pyrrole molecules adsorbed on the graphene planes.
- The effect of temperature and surface coverage on the adsorption

This theoretical study at atomistic level can help design a new class of high-performance fillers by better understanding the interaction mechanism [3] given the important role of **supramolecular interactions**.



Density Functional Theory

For the initial geometry of the adsorption systems, optimized pyrroles and pyrrolidines were placed in a planar configuration at 5 Å from the graphene sheet. **Adsorption energy**, which gives an estimation of the stability of the system, was calculated for every molecule-graphene configuration.



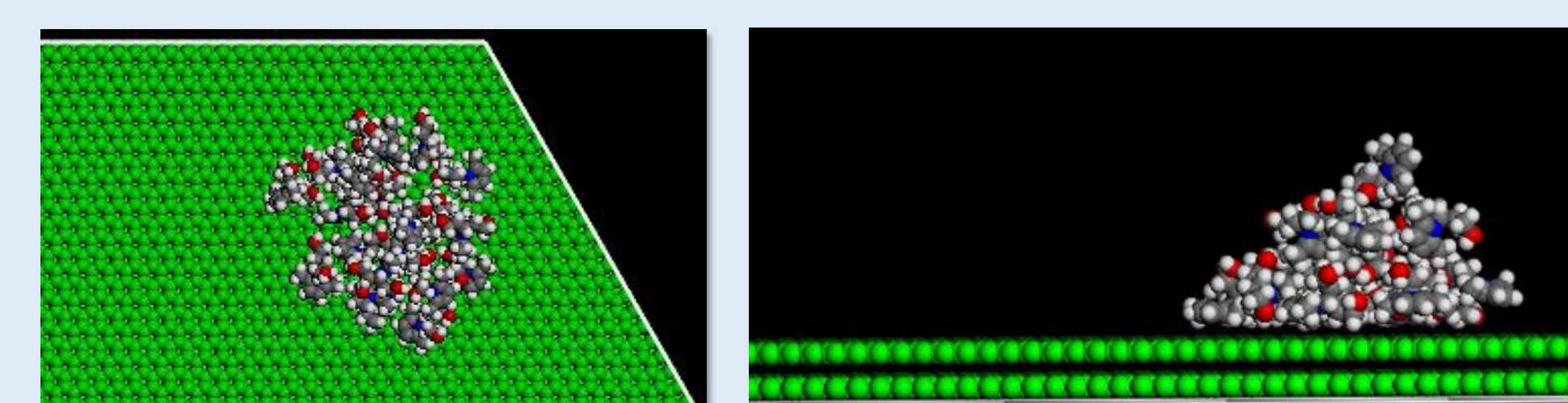
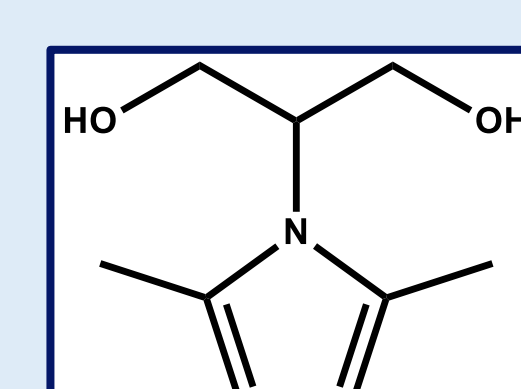
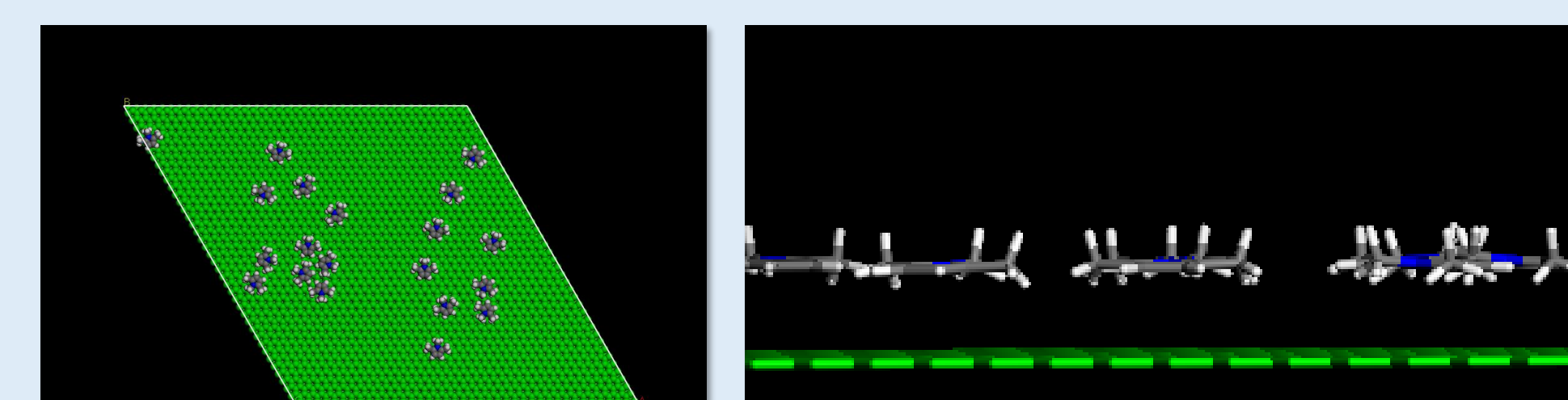
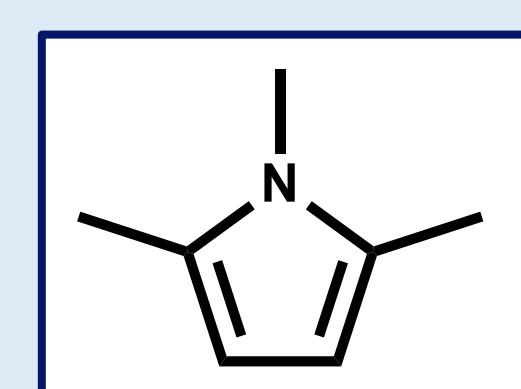
Two main factors were found to be important:

- Enhanced London dispersion interactions at increasing carbon atoms in alkyl nitrogen substituent
- Pyrroles are more stable than pyrrolidines because of the additional $\pi-\pi$ interaction

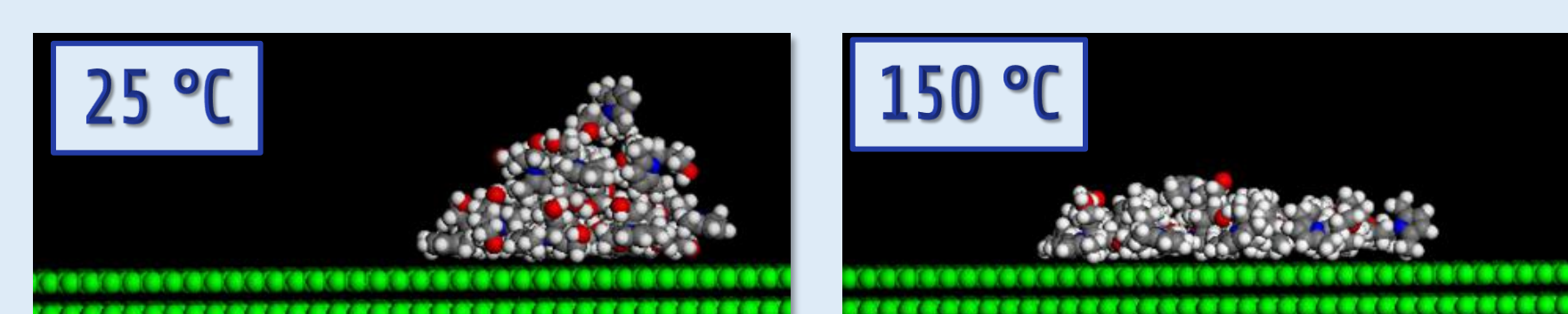
RESULTS

Molecular Dynamics

20 molecules of pyrroles with two different nitrogen substituent, one lipophilic (TMP) and the other hydrophilic (SP), were adsorbed at 25 °C on a two-layer graphene sheet.



At 25 °C, the nature of the nitrogen substituent of the pyrrole strongly influences the spreading of the molecule on the carbon surface. Molecule-molecule interaction is much stronger with serinol-pyrrole because of hydrogen bonding between the hydroxyl groups, as it can be seen from the agglomeration of the adsorbates. At 25 °C TMP forms a monolayer.



For serinol-pyrrole, increasing the temperature from 25 to 150 °C results in the spreading of the molecules and the consequent expansion of the mono-layer, as the hydrogen bonding between the pyrroles is weakened.

CONCLUSIONS

N-substituted pyrroles and pyrrolidines with increasing carbon atoms in the substituent alkyl chain were adsorbed on a pristine graphene surface.

Two main stabilizing effects were found to be relevant:

- Pyrrole sp^2 configuration allowed $\pi-\pi$ bonding with the graphene surface
- Longer alkyl chains promoted London dispersion interactions.

Molecular dynamics was then used to study the behavior of 20 molecules of different pyrroles. Polarity of the nitrogen substituent and temperature were found to be central for the spreading of the substances on the graphene surface.

REFERENCES

- [1] V. Barbera, L. Brambilla, A. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, *Nanomaterials*, 2019, 9, 44.
- [2] G. Raffaini, A. Citterio, M. Galimberti, M. Catauro, *Macromol. Symp.* 2021, 295, 2000198.
- [3] G. Raffaini, F. Ganazzoli, *Langmuir*, 2013, 29, 4883-4893.