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SUPRAMOLECULAR AGGREGATION OF POLYCYCLIC AROMATIC HYDROCARBONS ON THE WATER SURFACE: DFT AND MOLECULAR DYNAMICS

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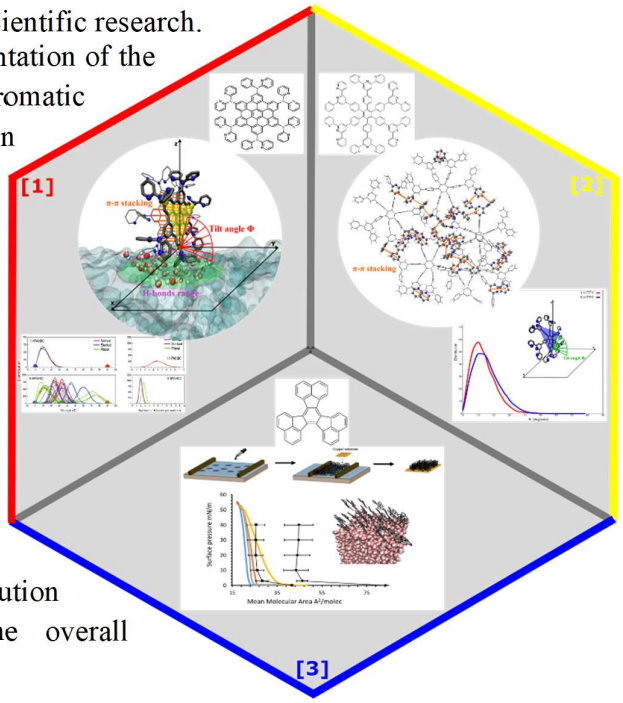
Simulations are always the other face of the Moon in the scientific research. In this context, the structure, the aggregation, and the orientation of the core-rim amphiphilic and propellerenes polycyclic aromatic hydrocarbons (PAHs) on the water surface have been explored by DFT calculations and molecular dynamics (MD) simulations. We find that the supramolecular arrangements of PAHs on the water slab depend on the balance between competitive π-π stacking of PAHs and possibly hydrogen bond interactions between water and functional groups of PAHs.



An investigated core-rim structured PAHs with a conjugated planar core (hexabenzocoronene core) presents an evident change in the aggregation properties by increasing the number of interacting monomers on the water slab: the π-π stacking becomes the dominant contribution compared to the hydrogen-bond in determining the overall arrangement. [1]

On the other hand, a core-rim PAHs with a less-conjugated non-planar core (hexaphenyl benzene) shows a significant role of hydrogen-bonds guiding the arrangement on the water surface. In this case, the π-π stacking interaction between edges moieties is also observed, which is consistent with results from the single-crystal structure. [2]

Finally, the decacyclene propeller shows to form thin films without requiring any covalent crosslinking. Thin films were found mechanically stable enough to be free-standing over micrometer distances, held together solely by non-covalent interactions. We got a molecular picture of the packing of decacyclene at the air-water interface and we simulate the Lagmuir-Blodgett compression extracting a computational isotherm in agreement with the experimental one. [3]

References:

[1] Liu, X., He, M., Calvani, D. *et al.* Power generation by reverse electrodialysis in a single-layer nanoporous membrane made from core–rim polycyclic aromatic hydrocarbons. *Nat. Nanotechnol.* 15, 307–312 (2020). https://doi.org/10.1038/s41565-020-0641-5

[2] Liu, X., Qi, H., Calvani, D. *et al.* Monolayer free-standing amorphous carbon synthesized from pyrolyzing Langmuir monolayers of polyaromatic hydrocarbon. (to be submitted)

[3] van der Ham, A., Liu X., Calvani D. *et al.* Freestanding Non-covalent Thin Films of the Propeller-shaped Polycyclic Aromatic Hydrocarbon Decacyclene. (manuscript submitted)