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

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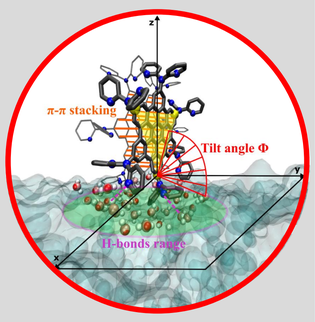
Computational Protocol

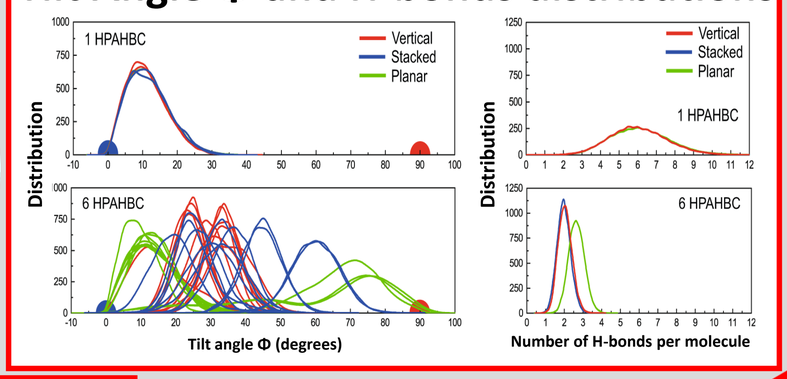
DFT Geom. Opt. (B3LYP-D3) → Parameterization OPLS-AA Force Field → Molecular Dynamics (MD) simulations → Processing and Analysis → Results

Experimental preparation of atomically thin nanoporous carbon membranes in Langmuir-Blodgett device

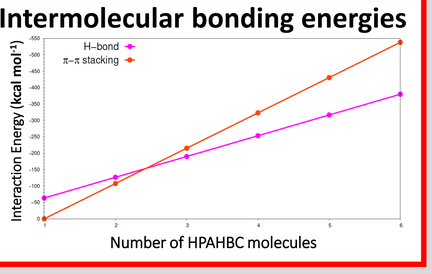
PAHs → CHCl3 → Cu substrate → Langmuir-Schäfer transfer



Tilt Angle Φ and H-bonds distributions



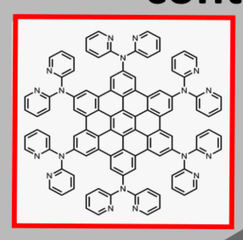
Intermolecular bonding energies



BLYP-D3 (TZP) Geom.Opt.	Energy (kcal mol^{-1})
E_{1water}	-315.52
$E_{monomer}$	-28038.61
$E_{monomer+1water}$	-28364.68
E_{dimer}	-56184.83
H-bond	-10.55
π-π stacking	-107.61

HPAHBC[1]

Cooperative ππ-stacking interaction drives the vertical aggregation dominating the H-bond contribution



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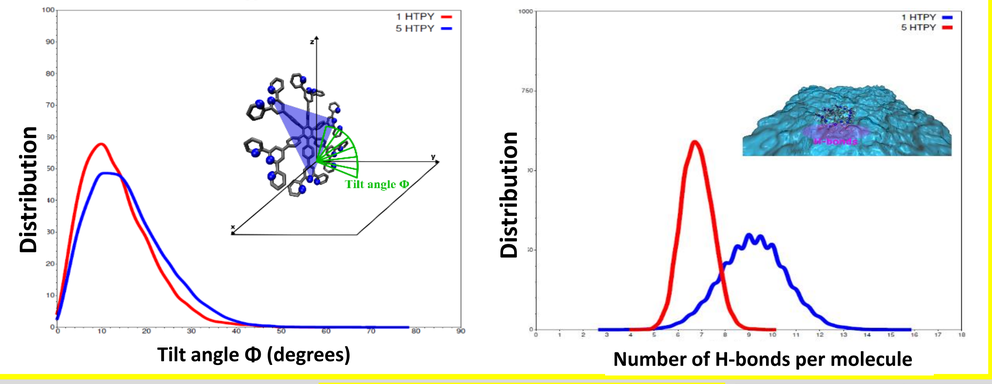
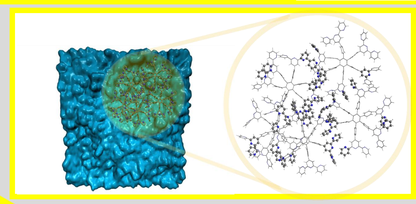
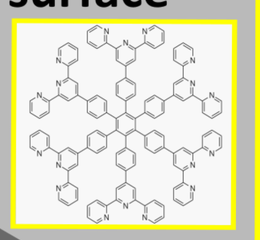




DFTB-D3BJ Single Point	Energy (kcal mol^{-1})
1HTPY	-945771.78
5HTPY cluster	-945598.19
Total pyridine π-π stacking interaction	-173.6
Pyridine π-π stacking interaction for interacting pyridines	-4.13

HTPY[2]

Pyridine ππ-stacking and H-bond intercations balance for a planar aggregation on the water surface



Decacyclene[3]

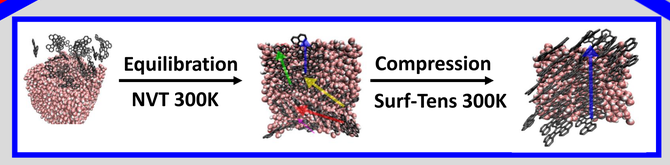
ππ-stacking interaction is the only driving force for the free-standing aggregation in the stable membrane

CONCLUSIONS

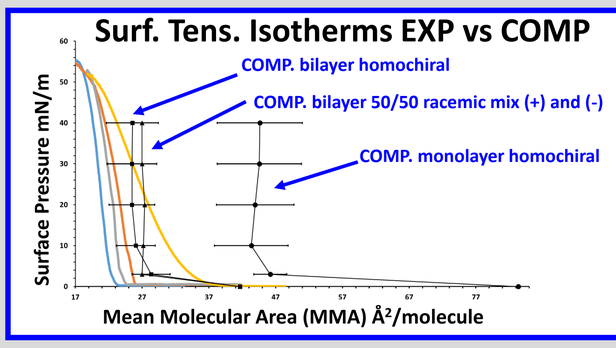
- **Single HPAHBC** molecule maximize the number of hydrogen bonds[4] (on average 6). The HBC core essentially **parallel** (tilt angle ~10°) to the water surface.
- **Increasing HPAHBC molecules** on the water surface, the **cooperative π- π stacking interaction**[5] becomes the dominant contribution in determining the overall arrangement. The molecules adopt a parallel-displaced stacking with the HBC core plane forming **a tilt angle** of around ~35° with the water-surface (on average 2 hydrogen bonds).
- From the trend observed in the MD simulations we expect that the tilt angle will approach a **vertical orientation** (90°) by increasing the concentration of molecules on the surface, approaching the experimental result.

Would you like know more about this?

SCAN ME!



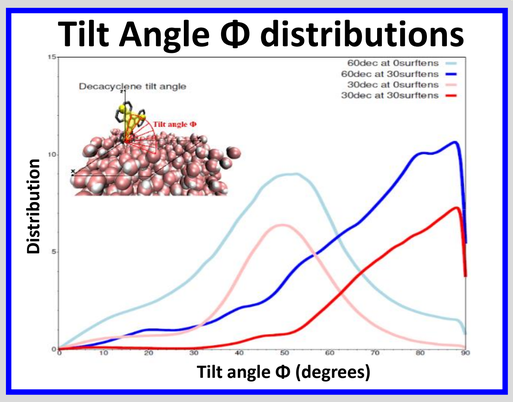
Surf. Tens. Isotherms EXP vs COMP



CONCLUSIONS

- Both amount, 60 and 30 molecules, on the water surface the tilt angle average changes from ~50° to ~90°, for 0 and 30 mN/m Surf.Tens. respectively, in accord with the experimental expected **vertical orientation**.
- **Evident domains ordering** after the compression, from 0 to 30 mN/m Surf.Tens. .
- **Impressive matching** between **the computational bilayer isotherm** (MMA ~26 Å²/molecule) and **experimental isotherms**, confirming the experimental bimolecular layer thickness of ~24 Å².

Tilt Angle Φ distributions



CONCLUSIONS

- **Single HTPY** molecule **maximize the number of hydrogen bonds**[3] (on average 9). The molecule is essentially **flat** (tilt angle ~13°) on the water surface.
- With **five HTPY** molecules on the water surface, the **π- π stacking interaction** between pyridines and the **hydrogen bond** with water (on average 7 hydrogen bonds) are **equally crucial** in determining the **planar** arrangement with tilt angle of around ~15.5°.
- Flagrant **planar clustering of 5 molecules** with intermolecular π-π stacking interactions between **pyridine moieties**. DFTB energy estimation of π- π stacking in the X-shape interacting site is in good agreement with literature. [6]

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