Modelling dynamic effects to determine transport properties in semiconducting MOFs containing 1D pentacene stacks

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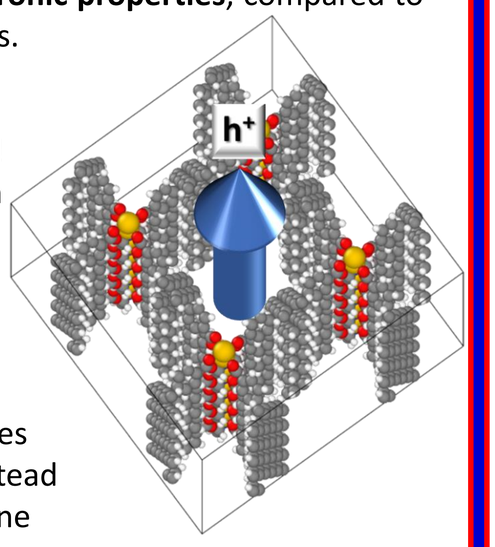
Semiconducting MOFs?

Metal-Organic Frameworks can be used to **extrinsically control** the arrangement of molecules with respect to each other. In this way, **π-conjugated units** can be positioned to create materials with **favourable electronic properties**, compared to their traditional organic semiconducting counterparts.

What does that look like?

Exemplary case: a system of **1D stacks of molecules**! This can e.g. be done with pentacene [1] and with tetrathiafulvalene (TTF) [2] linkers.



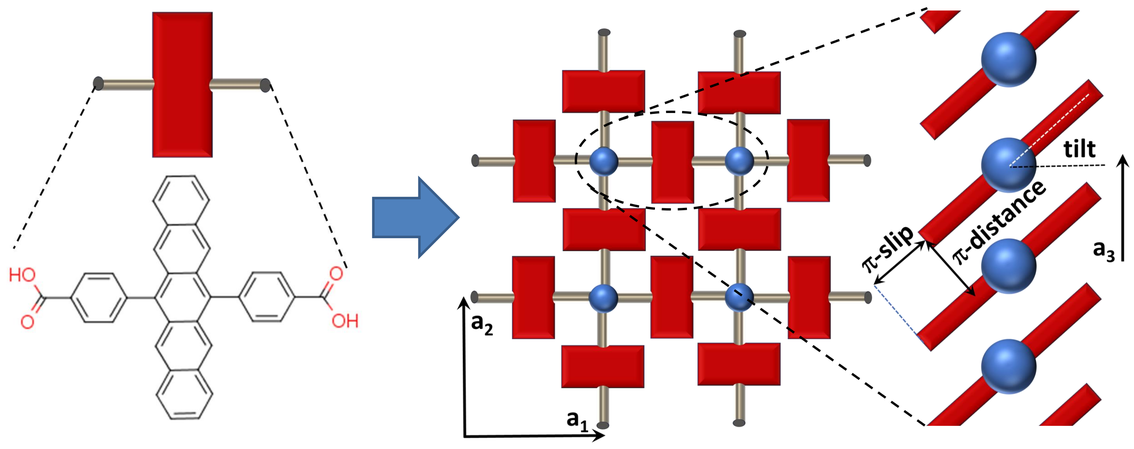
Complications

- **Stacking Motif**: causes unfavourable shift of neighboring pentacene [3] or TTF [4] units.
- **Distorted Structures**: most orthorhombic structures are unstable, heavily distorted structures form instead
- **Dynamic disorder**: torsional vibrations of pentacene linkers hinder transport [1]

Methods

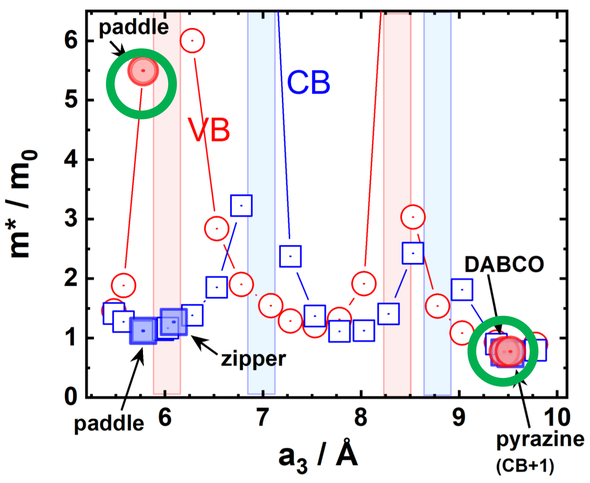
Software:	VASP version 6.3.0
DFT functional:	PBE [5]
VdW correction:	DFT-D3 (BJ) [6]
Molecular dynamics:	NPT run performed with force fields created using VASP's on-the-fly machine learning. [7] Learned at T = 330 K, used at T = 300 K.

Impact of the stacking motif [3]

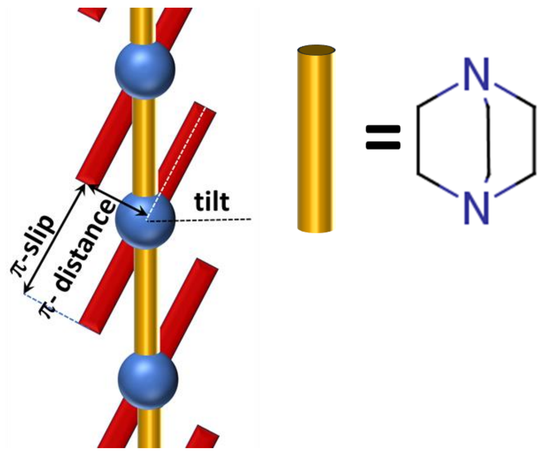


Schematic structure of the idealized orthorhombic pentacene MOF [3]

- **Stacking distance determines π-slip**, as the π-distance changes only marginally
- **Electronic coupling can vanish** for a certain π-slip (due to orbital symmetry) [8]
- **Hole transport: hindered** due to unfavourable stacking of bare Zn paddlewheel nodes



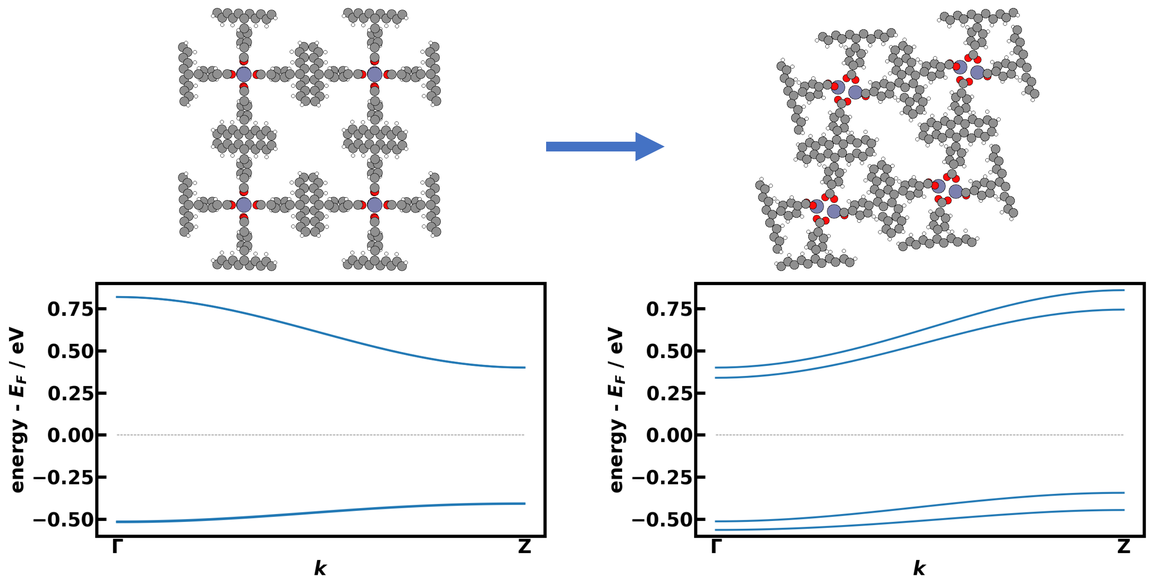
Effective mass as a function of the stacking distance between Zn paddlewheels



Solution: maximize hole transport by using DABCO as apical linker

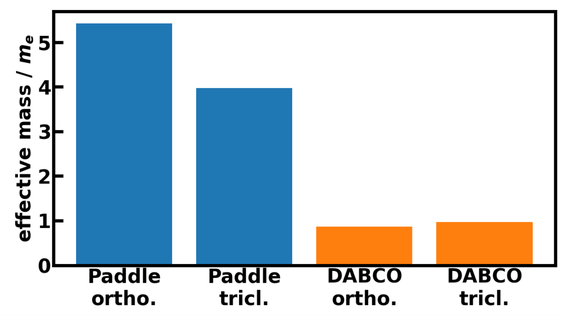
Impact of the distortions of the unit cell

- Upon full relaxation, the Zn paddlewheel structures adopts a reduced symmetry conformation resulting in a **massively distorted structure.**
- The structure containing **DABCO remains close to orthorhombic**
- This influences the band structure, and, thus, the **effective mass**



PBE-calculated frontier bands for the idealized orthorhombic structure (left) and the fully relaxed triclinic structure (right)

- the distortion **decreases m* for the paddle system**
- it slightly **increases m* for the DABCO system**

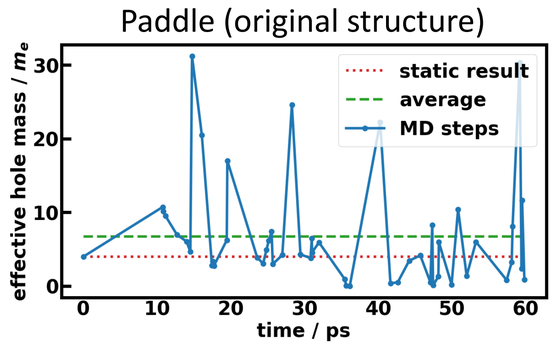


Dynamic disorder (preliminary)

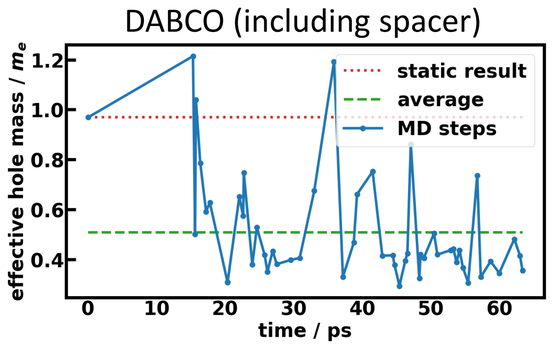
- A molecular dynamic simulation is performed at 300K; the effective mass is sampled throughout the trajectory.
- For now: consider primitive UC → consider only Γ-point vibrations
- At 300K, the symmetry of the **DABCO is also reduced**

- m* of paddle is on average almost **twice the static result**!
- m* of DABCO is on average almost **half the static result**! Mainly due to the shift to a triclinic system.

Paddle (original structure)



DABCO (including spacer)



Conclusions

- Effective mass highly dependent on both static structure, and dynamic disorder
- Spacers expected to boost the carrier mobility in the studied system
- **Average m* can be increased or decreased** in the dynamic picture, depending on the structure

Outlook

- Consider quantities potentially more suitable for describing disordered structures (like **transfer integrals**, hopping mobility, etc)
- Describe the actual carrier dynamics via Monte-Carlo type approaches
- Go **beyond Γ-point vibrations** by studying supercells
- Analyze specific **structures with extremely high/low effective masses**
- Study impact of metal ions (e.g. Cu) on distortions
- Potentially design linkers resulting in a suppressed dynamic disorder

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References

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