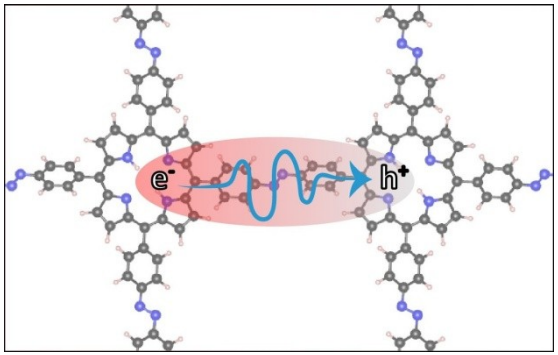
Charge Transport Mechanism in 2D COFs

2nd TAC Meeting

Elif Ünsal



Supervised by

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Dresden, August 30th 2022

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Motivation

Objectives and Challenges

Workflow

Results

- Porphyrin-based COFs
- DFTBephy: A DFTB-based Approach to Electron-Phonon Coupling (EPC)

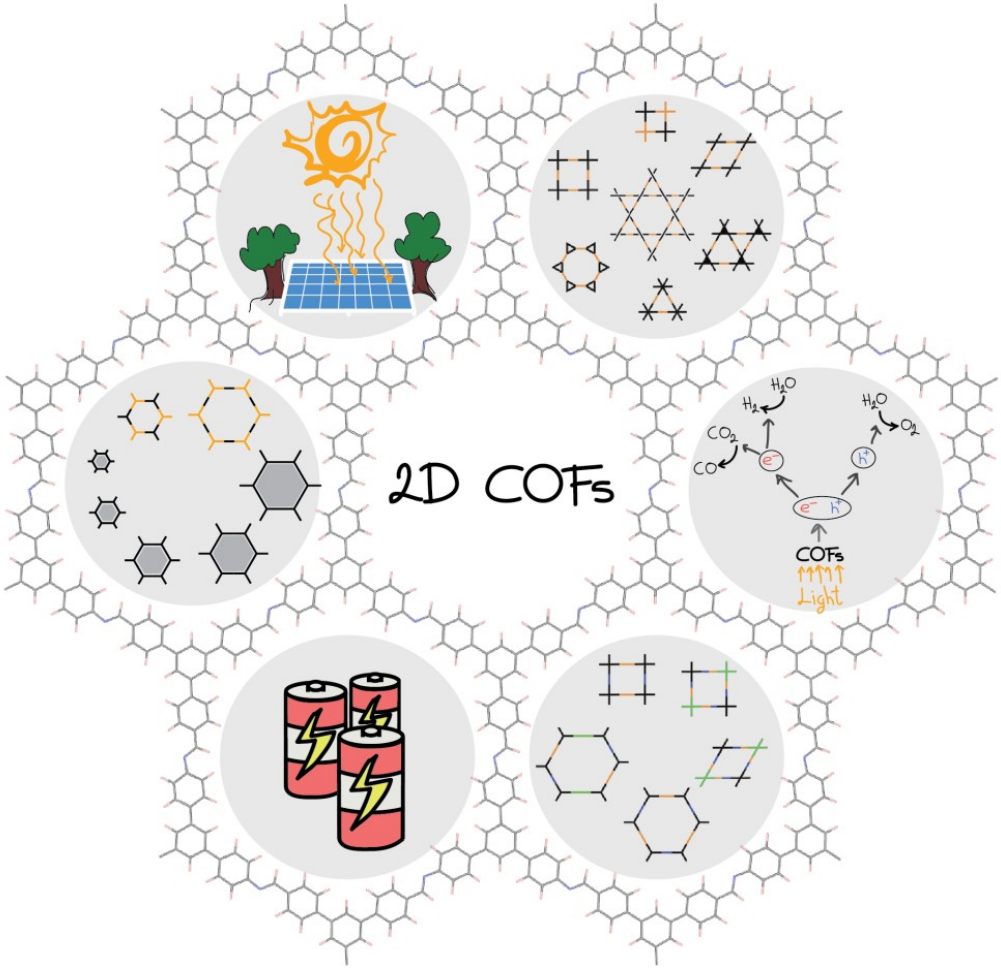
Ongoing Works & Collaborations

- COF Heterostructures (Organic-Inorganic)
- Stacking Types in COFs
- COF Heterostructures (Organic)

Overview

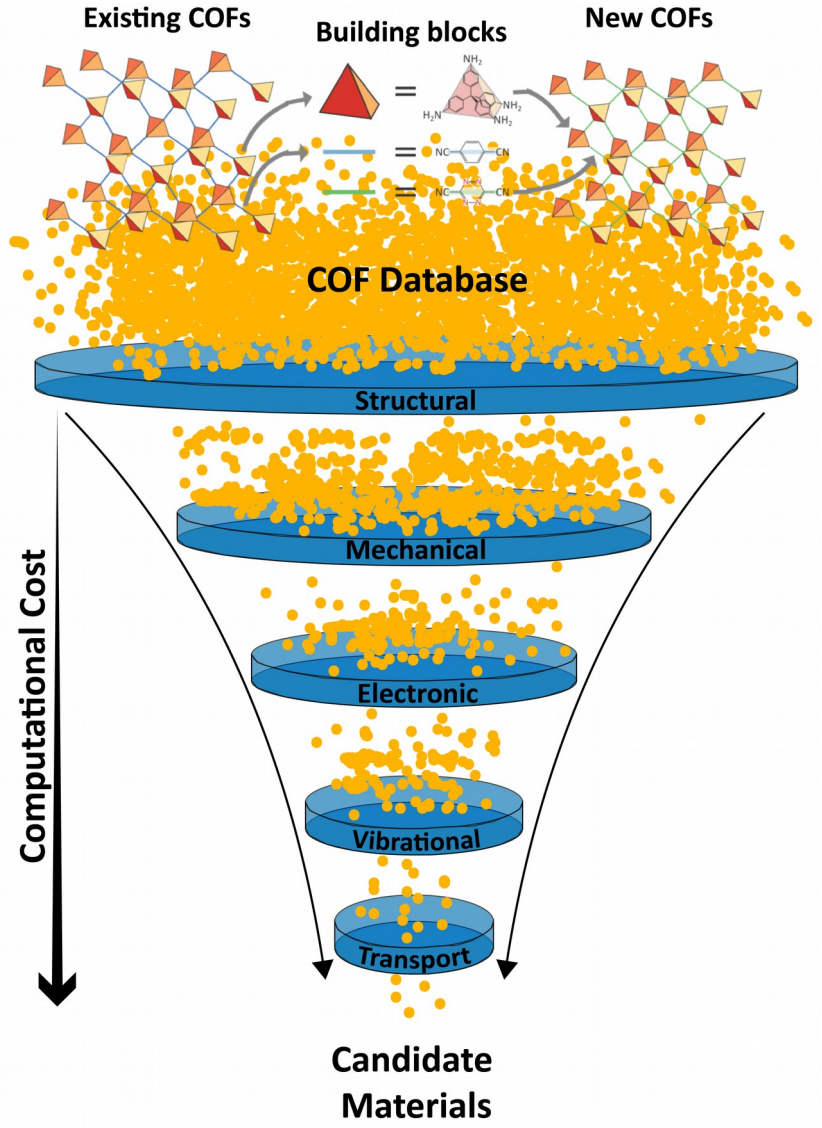
Motivation

- 2D COFs **attractive** for **wide range** of applications in:
  Photovoltaics, energy storage, catalysis etc.
- **Various types** of tailor-made 2D COFs
- **Feasibly tunable** physical properties!
- **Huge** variety of COFs **!!**
  Systematic investigation
  Predicting the promising materials
- **Charge transport** properties of most of 2D COFs are **still unknown**.



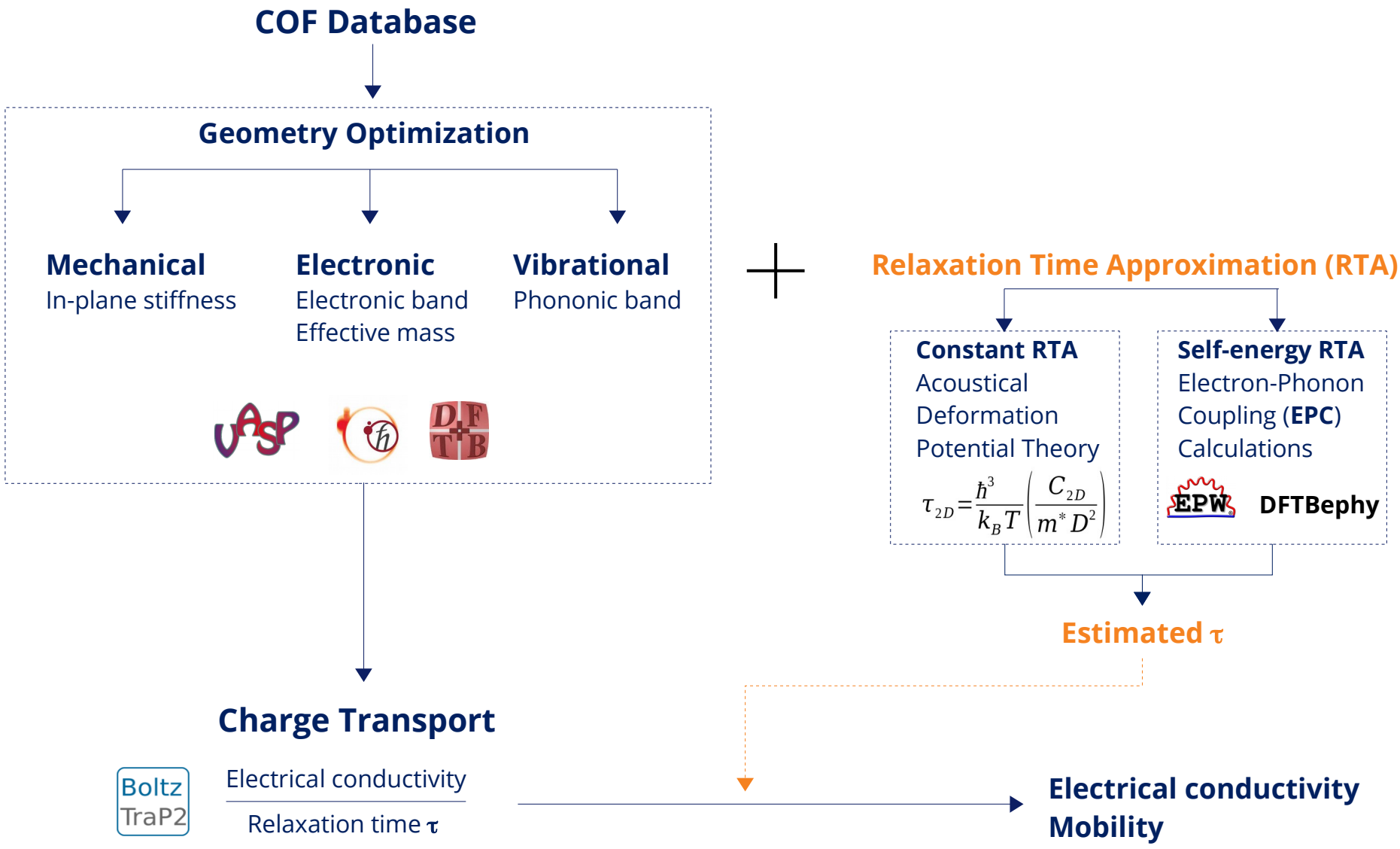
[1] Diercks and Yaghi, Science, 355, eaal 1585 (2017).
[2] Dong and Feng, Chem. Rev., 118(13), 6189-6235 (2018).
[3] Feng *et al.* Chem. Soc. Rev., 41, 6010-6022 (2012)

Objectives and Challenges



- To **understand** **the charge transport** mechanism in 2D COFs using **first-principles approaches**
- To **design** novel 2D COFs with **functional transport properties**
- To **screen** wide range of COFs
- Most of the COFs contains **large amounts of atoms** in their unit cells.
- Even for the geometry optimization with **standard DFT method**, **material screening** is **challenging**.

Workflow


COF Database
Geometry Optimization
Mechanical
In-plane stiffness
Electronic
Electronic band
Effective mass
Vibrational
Phononic band
Relaxation Time Approximation (RTA)
Constant RTA
Acoustical
Deformation
Potential Theory
$\tau_{2D} = \frac{\hbar^3}{k_B T}\left(\frac{C_{2D}}{m^* D^2}\right)$
Self-energy RTA
Electron-Phonon
Coupling (EPC)
Calculations
EPW
DFTBephy
Estimated τ
Charge Transport
Boltz
TraP2
Electrical conductivity
Relaxation time τ
Electrical conductivity
Mobility

Results: Porphyrin-based COFs

Why porphyrin-based COFs?

Hole mobilities ***up to 8.1*** $cm^2V^{-1}s^{-1}$

Chem. Mater., 2011, 23, 18 4094-4097.

- Method: DFT- PBE
- Quadratic unit cell
- In-plane stiffness C_{2D}:

  $C_{2D,azo} > C_{2D,imine} > C_{2D,ethene}$

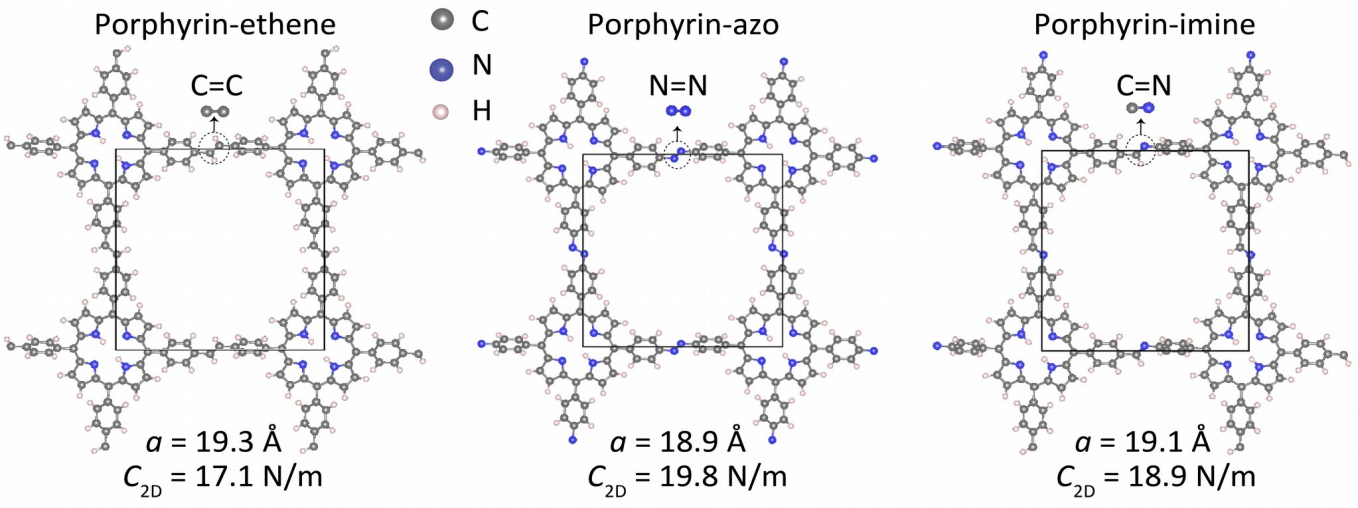
- Direct band gap

  $E_{G,imine} > E_{G,ethene} > E_{G,azo}$

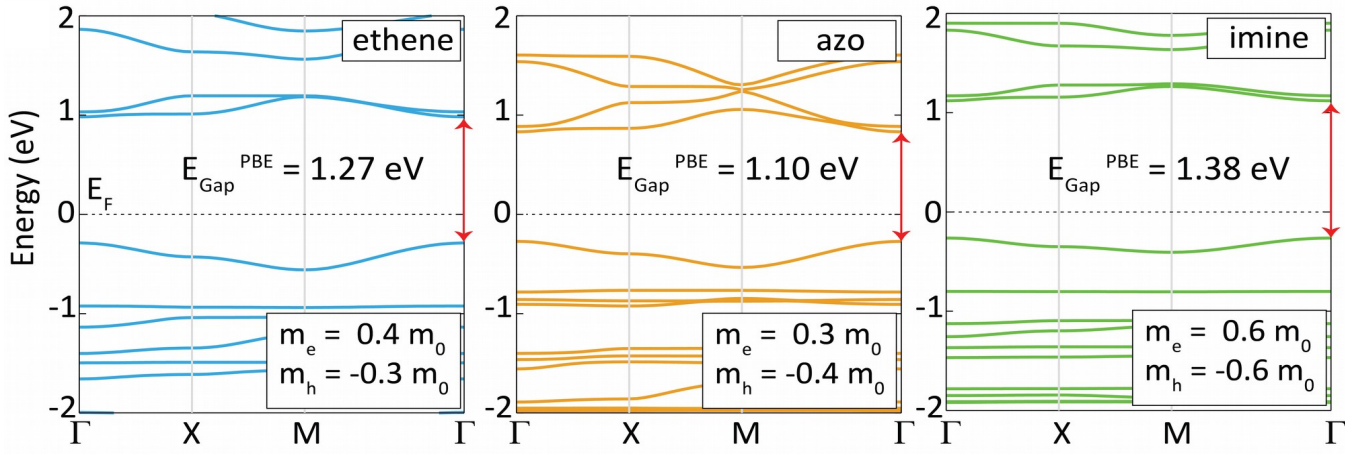
- Deformation potential constant

	$D_{electron}$	D_{hole}
ethene	-1.07	-2.96
azo	-1.34	-2.57
imine	-1.17	-2.50

Structural and Mechanical Properties



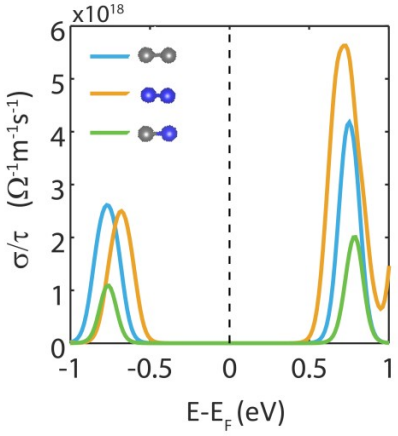
Electronic Properties



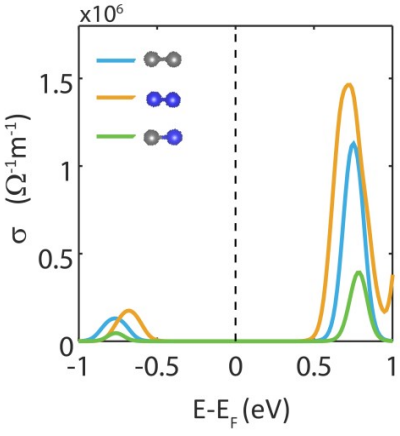
Results: Porphyrin-based COFs

Transport Properties within Constant RTA

Electrical Conductivity at 300K



$$\tau_{2D} = \frac{\hbar^3}{k_B T}\left(\frac{C_{2D}}{m^* D^2}\right)$$



- Stiffest
- Lighter effective mass
- Almost robust band edge against strain

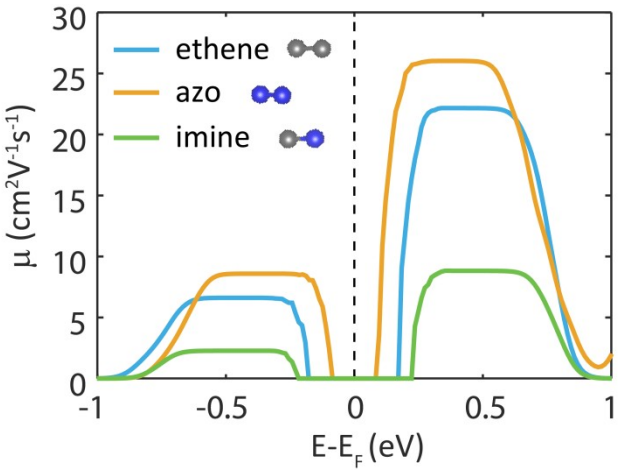
→ *High conductivity*

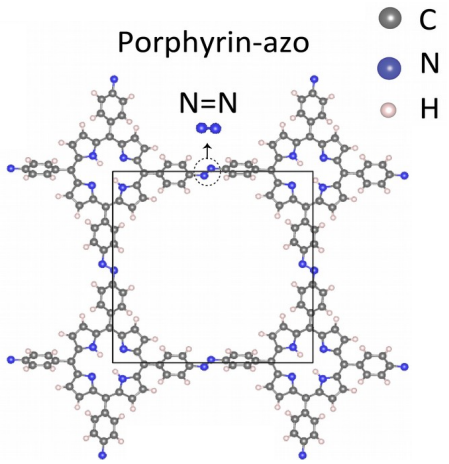
Mobility at 300K

$$\mu_{d_{\alpha\beta}}(T;\mu) = \frac{\sigma_{\alpha\beta}(T;\mu)}{e} \times \frac{1}{n(T;\mu)}$$

$\mu_{d\alpha\beta}$: the charge carrier mobility
$\sigma_{\alpha\beta}$: the electrical conductivity
e : the electron charge
n : the charge carrier concentration

Gibbs *et al.* npj Comput Mater 3, 8 (2017).





Next Step: Calculating their transport properties within self-energy RTA

Results: DFTBephy

EPC calculations from ab-initio are computationally too expensive! → Roughly takes weeks for 12-atom unit cell

Especially for the systems with large number of atoms → COFs

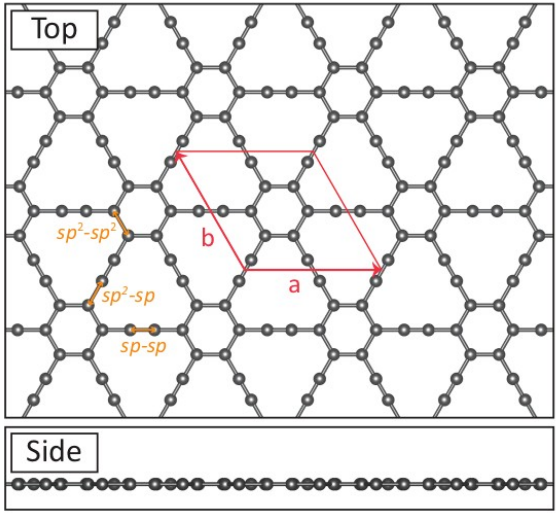
DFTBephy: A DFTB-based Approach for El-Ph Coupling Calculations

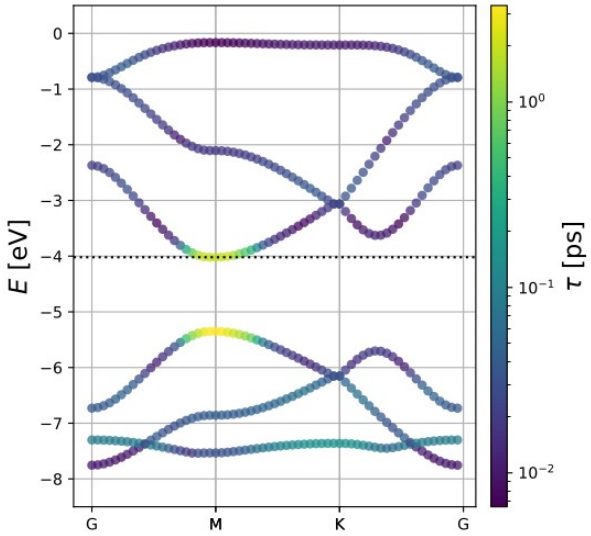
Collaboration with A. Pecchia and A. Croy

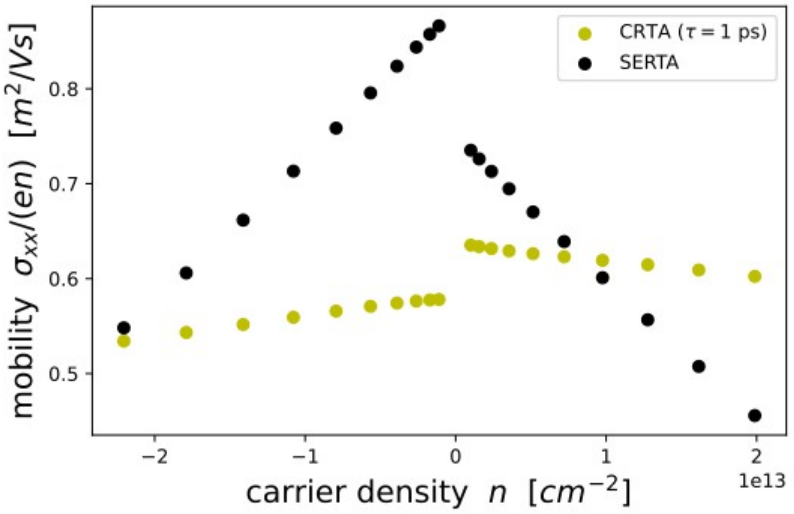
- Charge carrier relaxation times within self-energy RTA [Ponce et al. Rep. Prog. Phys. 83,2020]

Phonopy

Preliminary results for γ-graphyne:







Duration → 4-5 hours → ***A chance for COF screening***

Next Step: Our results will be benchmarked against EPW calculations

Ongoing Works & Collaborations

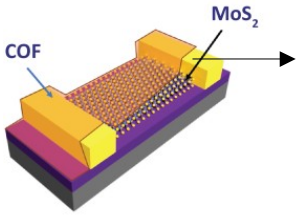
Nanochemistry Lab. (Paolo Samori) , I.S.I.S.

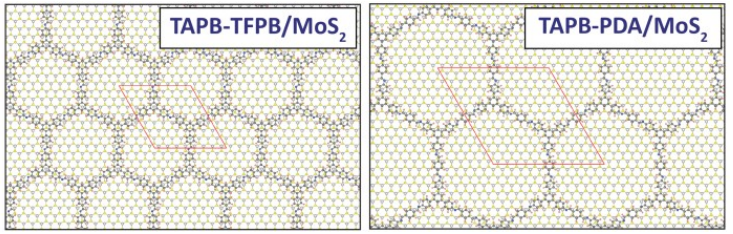
◆ Charge transfer in COF/MoS_2 Heterostructures

1) Electron transfer: COF → MoS_2

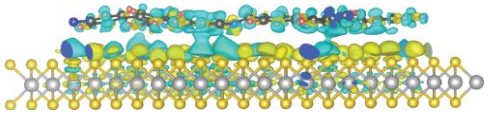
2) Larger doping level for "smaller" COF

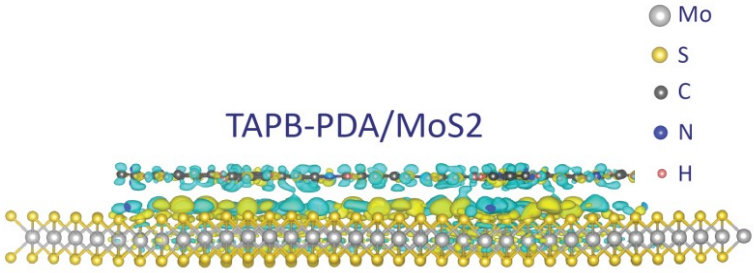
3) Interfacial charges mostly localized around N atoms



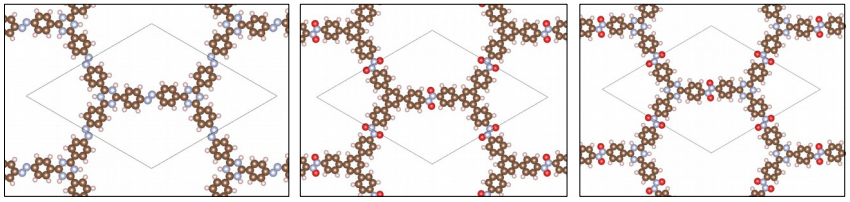


Charge Transfer per Area [e/cm³]	TFPB MoS_2		PDA MoS_2
Calculated	8.8×10^{11}	>	8.0×10^{11}
Experimental	21.8×10^{11}	>	14.6×10^{11}



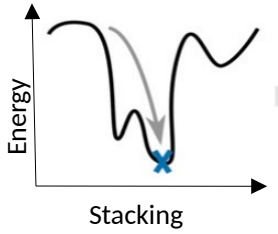


◆ Stacking Analysis in Triazine-Based COFs



Energy landscape

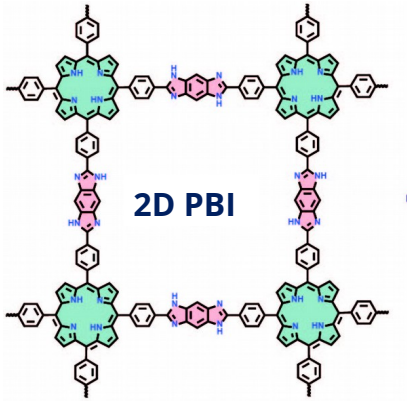
with static approach

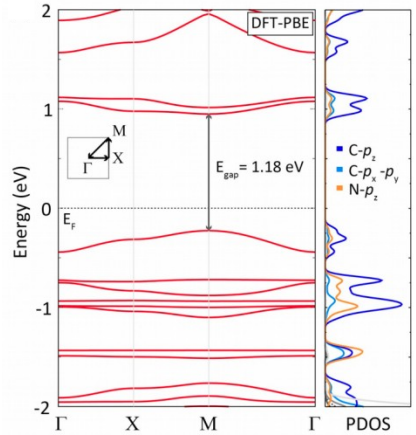


Ongoing Works & Collaborations

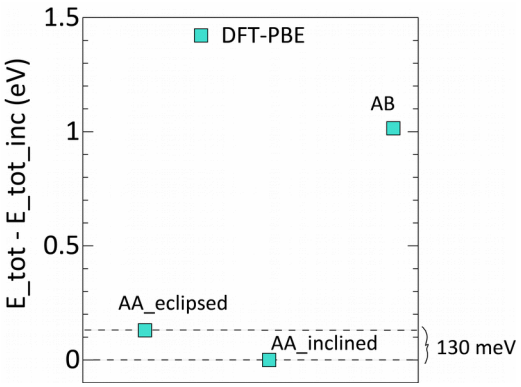
Anupam Prasoon, Renhao Dong, Xinliang Feng, TU Dresden

- **Stacking in Few-Layer Polybenzimidazole (PBI) COF**



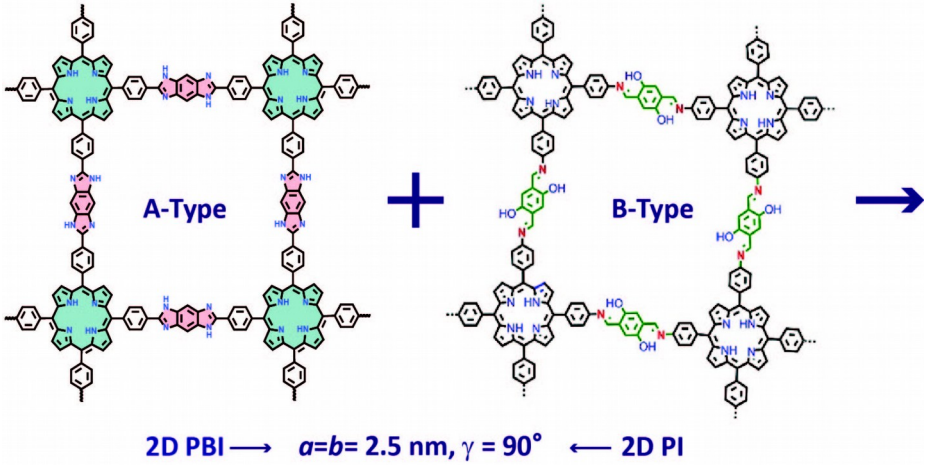


Stacking in bulk counterpart



Next step: Electronic properties of few-layer PBI

- **Charge Transport in 2D PBI-Polyimine (PI) Heterostructure**



No lattice mismatch!

Synthesized:
- AB-Type
- BA-Type

Charge transfer between the layers

In-plane mobility of the heterostructure
- Computational
- Experimental

Overview

Workshops and Conferences :

Poster Presentations:

- Chem2DMat, online (August 31-September 3, 2021)
- IWOM2021-TYC workshop on Charge Transport in Organic Materials (June 21-25, 2021)
- Daresbury DFTB+ School, Daresbury, UK (June 6-10, 2022)
- CRC1415 Retreat 2022, Niederwiesa, DE (June 15-17, 2022)
- Quantum Transport Methods and Algorithms, Zurich, CH (June 6-8,2022)

Talk:

- CRC 1415 MGK Seminar, Dresden, DE (August 16, 2022)

Publications:

- DFTBephy: A DFTB-based Approach for El-Ph Coupling Calculations (in preparation)
- Modulating the electronic properties of TMDs with 2D covalent organic networks (in preparation)
- Few layer PBI (in preparation)

Overview

Anticipated Workshops and Conferences :

Talk:

- DPG-Tagung, Regensburg, DE (September 4-9, 2022)

ULTIMATE related:

- 5th Progress Meeting, Genova, IT (November 2022)
- Entrepreneurship and career planning (IBM, ULTIMATE) (April 2023)

ULTIMATE Secondements:

- @UNISTRA (February 14-March 27 2022) ✓
- @DWI – Leibniz Institute for Interactive Materials (4 Weeks)
- @IBM (2 Weeks)

Courses:

Winter term 2022/2023

- Computational Materials Science: Molekulardynamik
- Werkstoffe der Energietechnik

Rigorosum:

Summer term 2022/2023

- Nanostructured Materials
- Many-Body Theory in Condensed Matter