Towards computational modeling of 2D Covalent Organic Frameworks

Investigating the electro-mechanical properties

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IMPRS

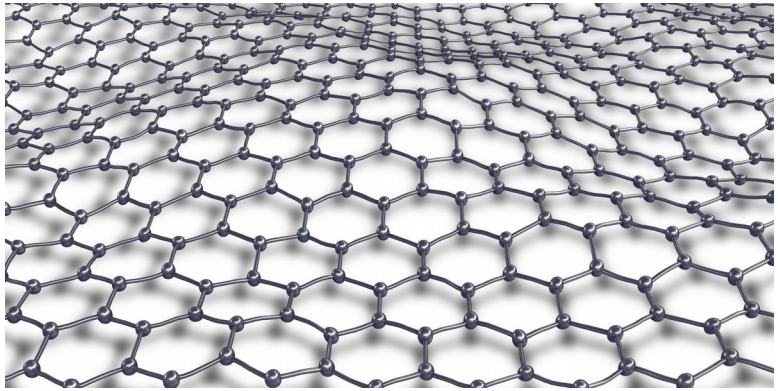
Chair of Materials Science and Nanotechnology

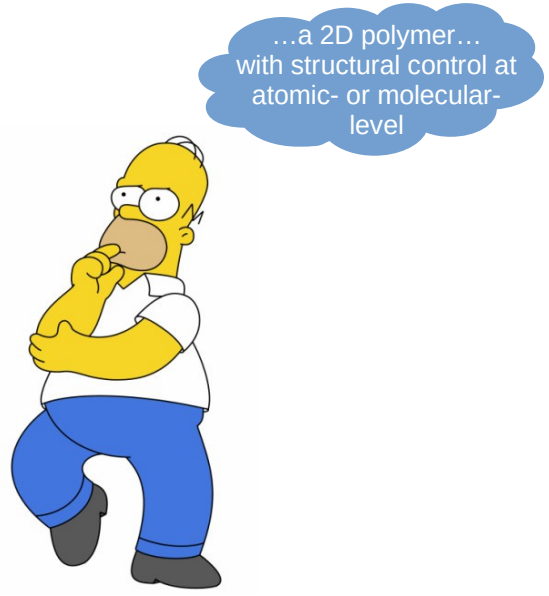
Dresden, July 21st 2021

Why 2-D COFs?

A theoretical view

- Beyond Graphene



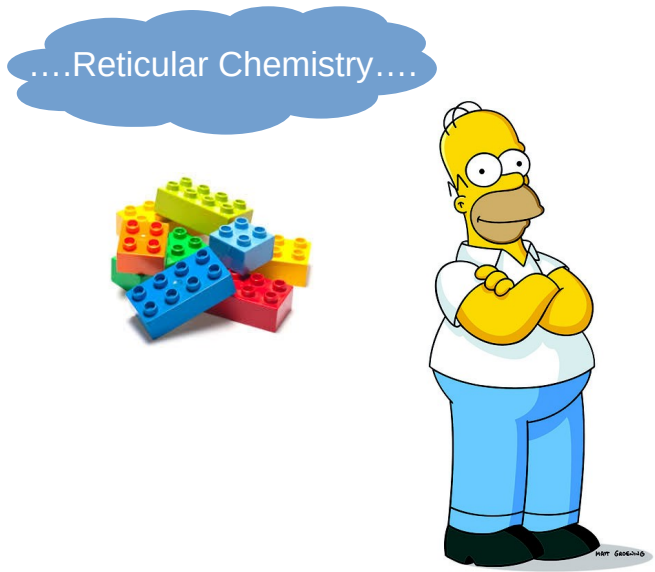


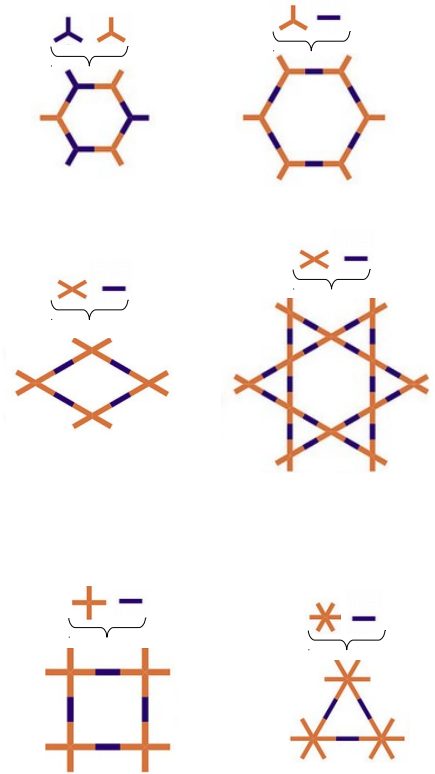
Why 2-D COFs?

A theoretical view

- Beyond Graphene
- 2D porous frameworks

  - various combinations of molecular building-blocks
  - different linkages
  - several lattice types





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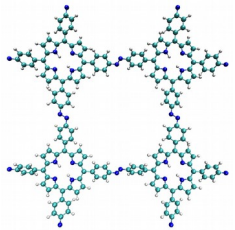

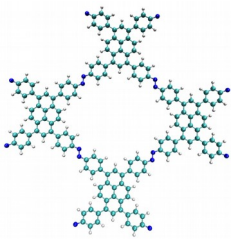

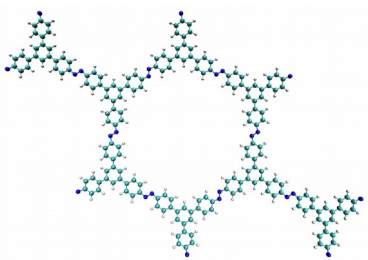

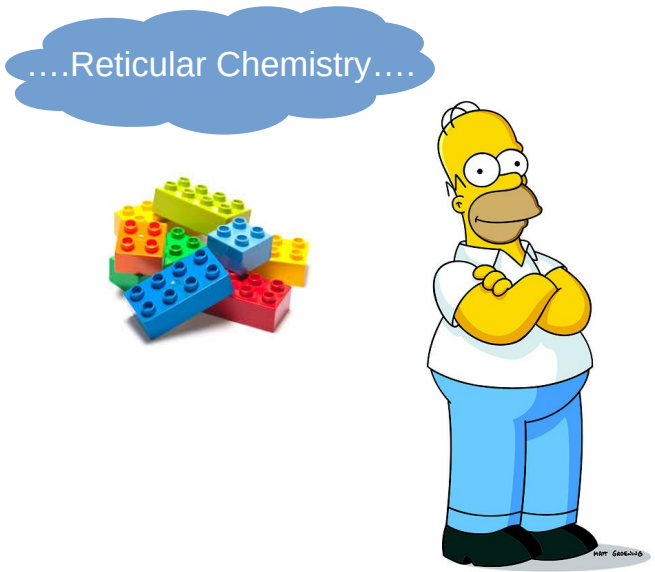

Why 2-D COFs?

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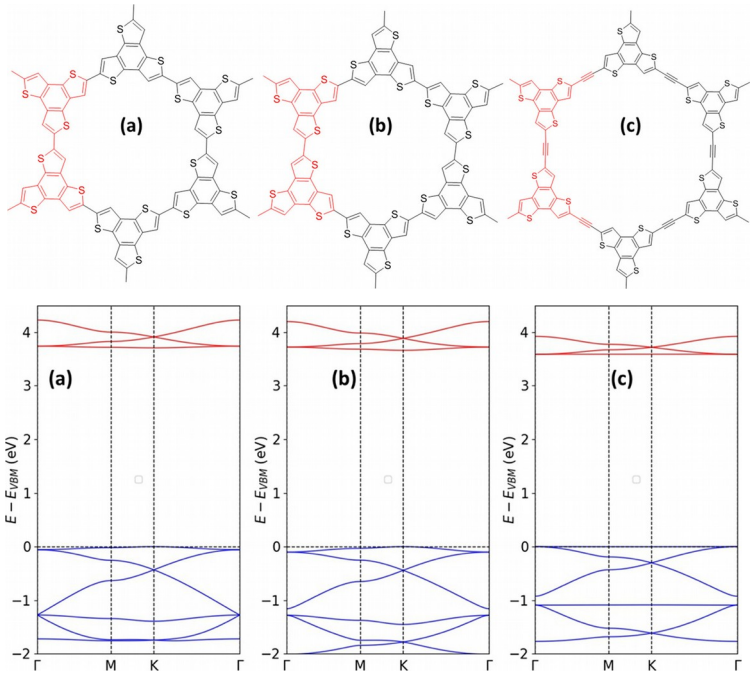
  - *several lattice types*
- *Computational modeling*
  - *methods (DFT / MD)*



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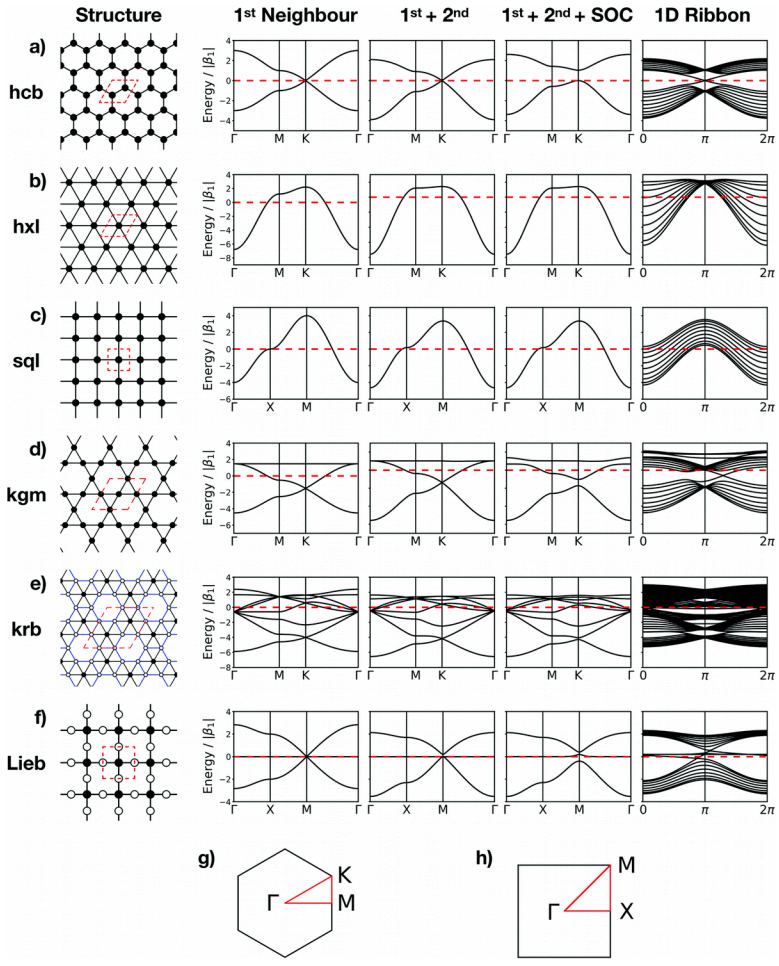

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Contents

More than 500 COFs

Combining calculations with theory

- *Predicting the bulk modulus from the elasticity of the monomers via analytical models*

- *Manipulation of the electro-mechanical properties*

- *Predicting the electronic band gap from 1D-polymer or organic monomers using multiple linear regression techniques*

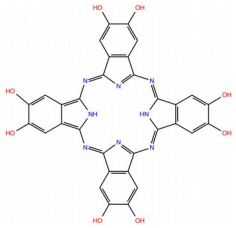
Mechanical Properties

Predicting the 2D bulk modulus from the elasticity of the monomeric units

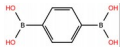
Mechanical properties – COFs with square lattice type

Pc-PBBA COF

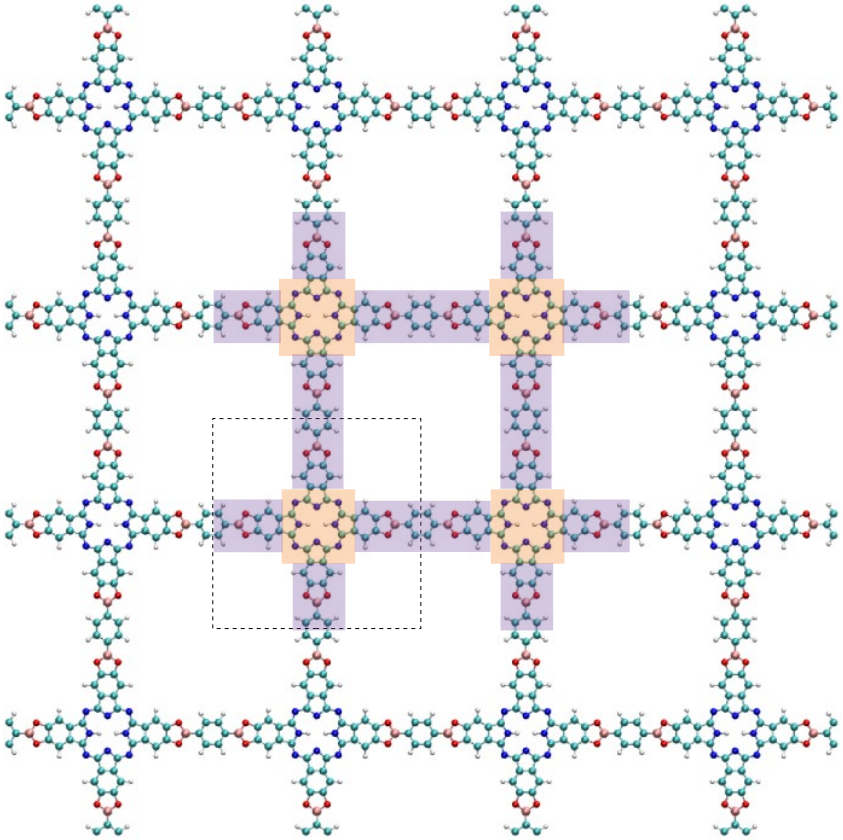
Phthalocyanine

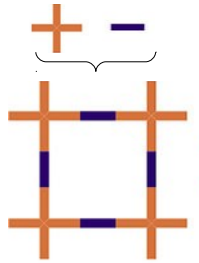


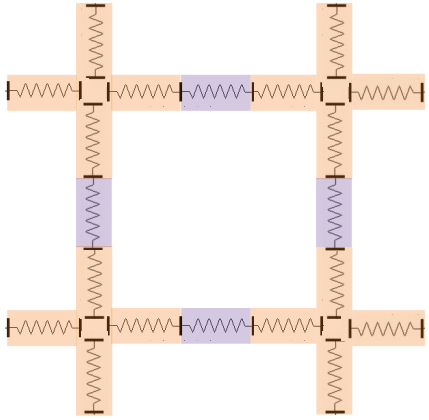
phenylenebis(boronic acid)



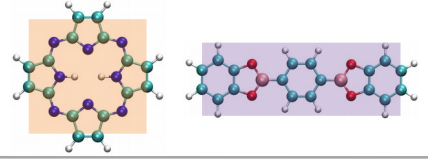
(Experimentally)
Molecular building-blocks



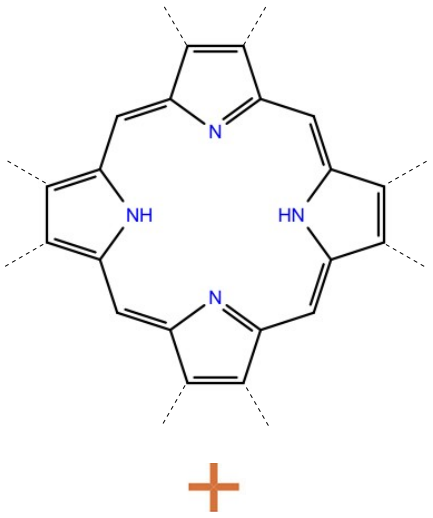


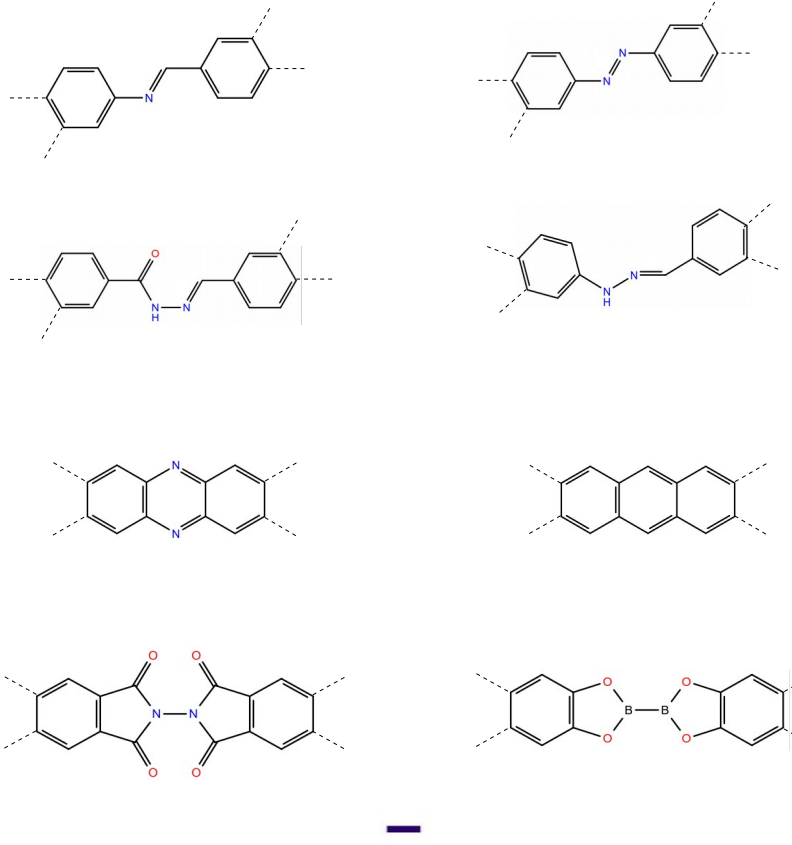


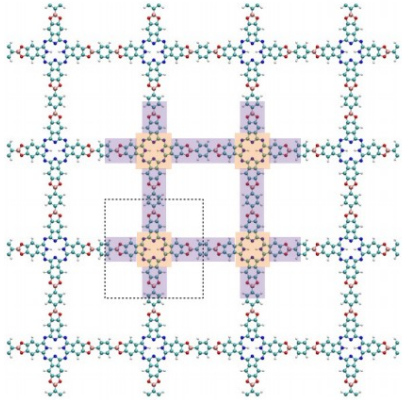
(Theoretical approach)
Monomeric units

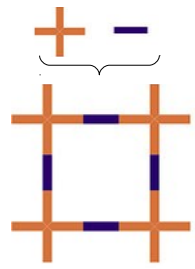


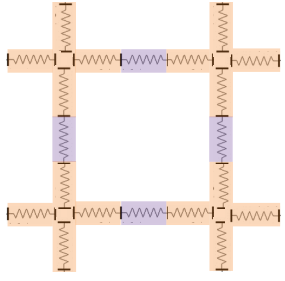
Mechanical properties – COFs with square lattice type



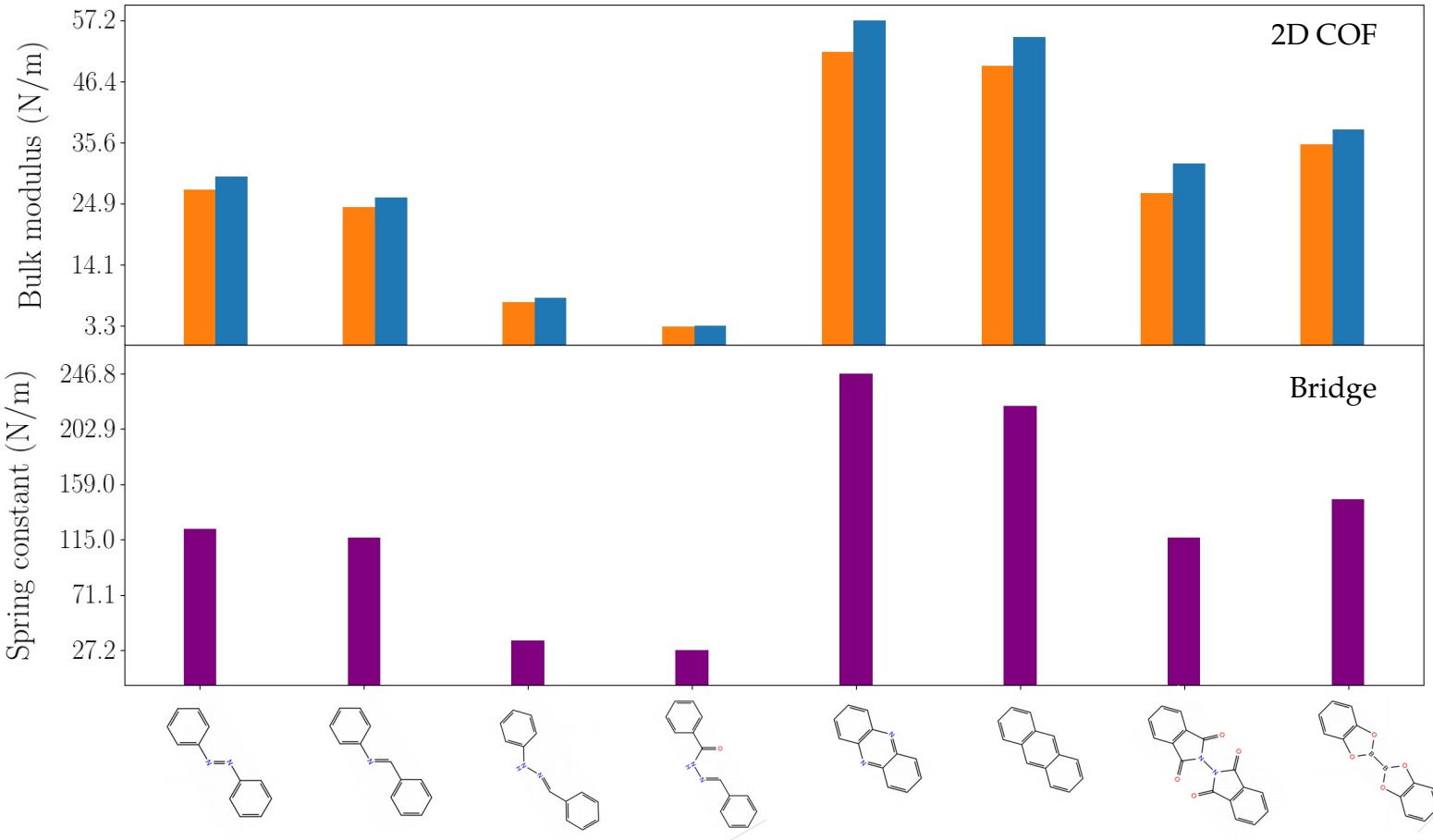




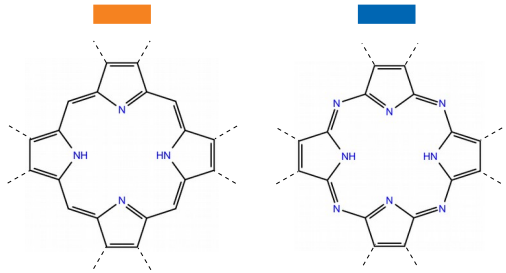




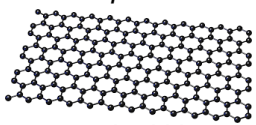
Mechanical properties – COFs with square lattice type



Change of the molecular core

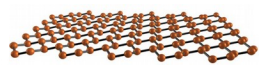


Graphene



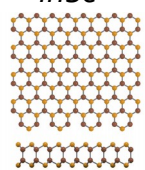
~ 210 N/m

Silecene



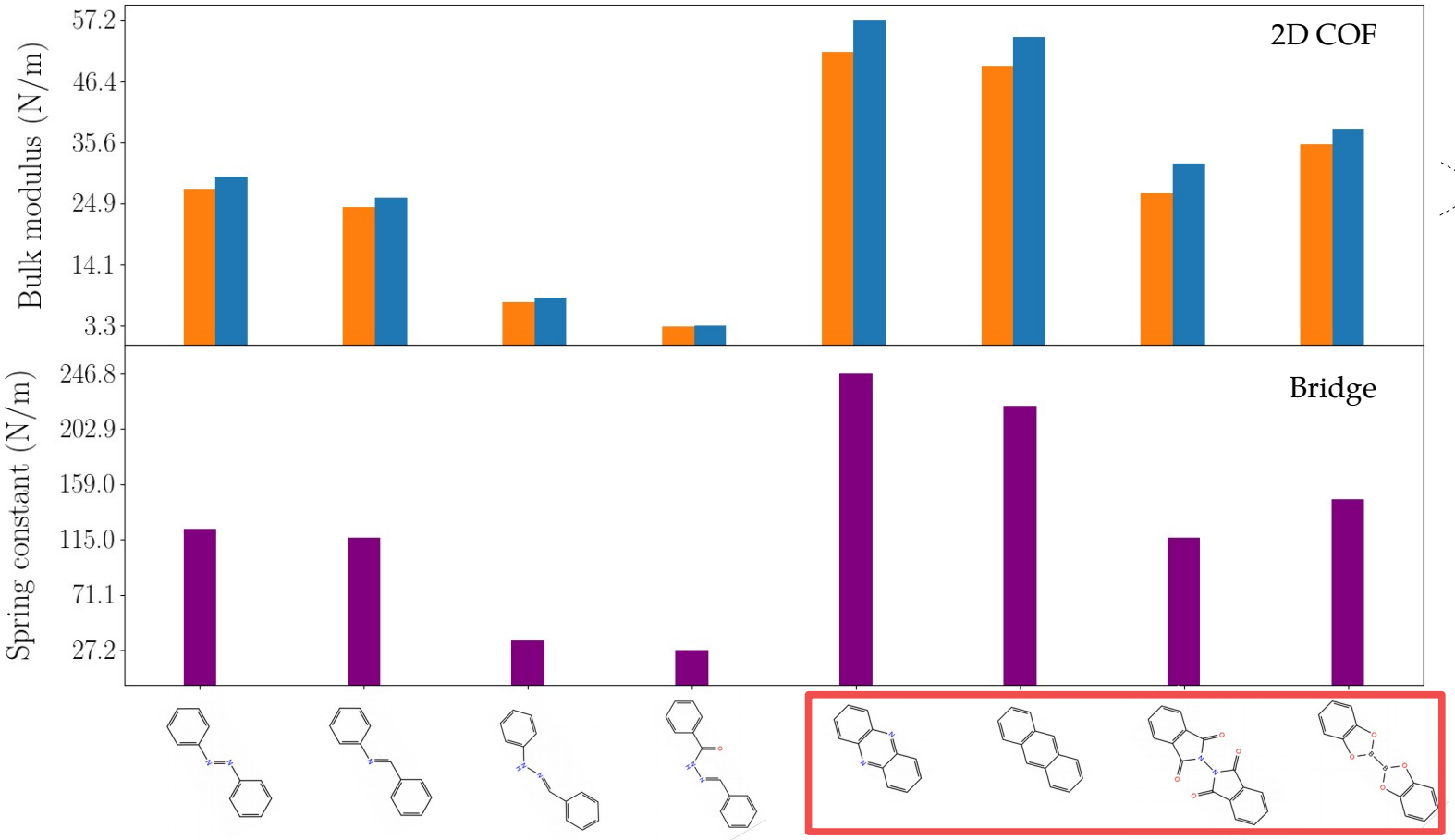
~ 45 N/m

InSe



~ 35 N/m

Mechanical properties – COFs with square lattice type



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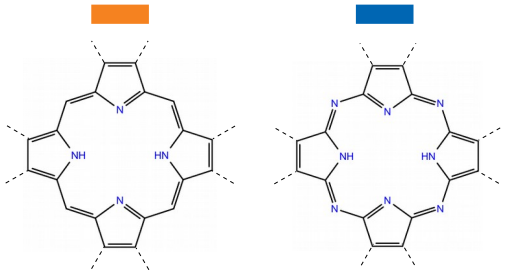
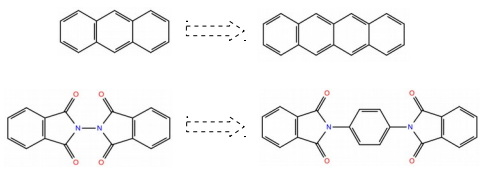
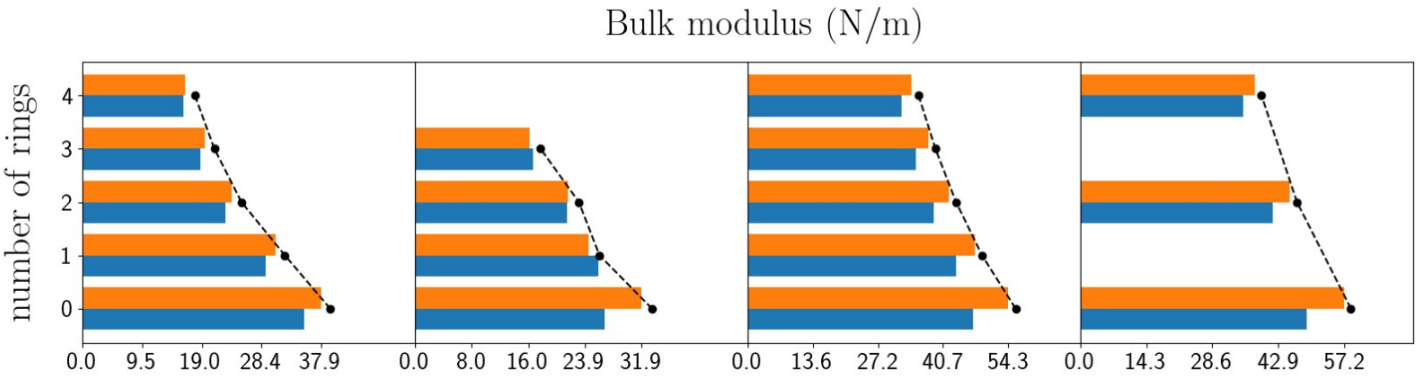
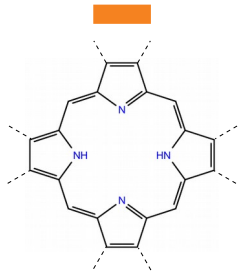


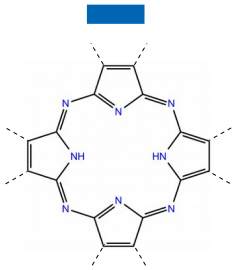


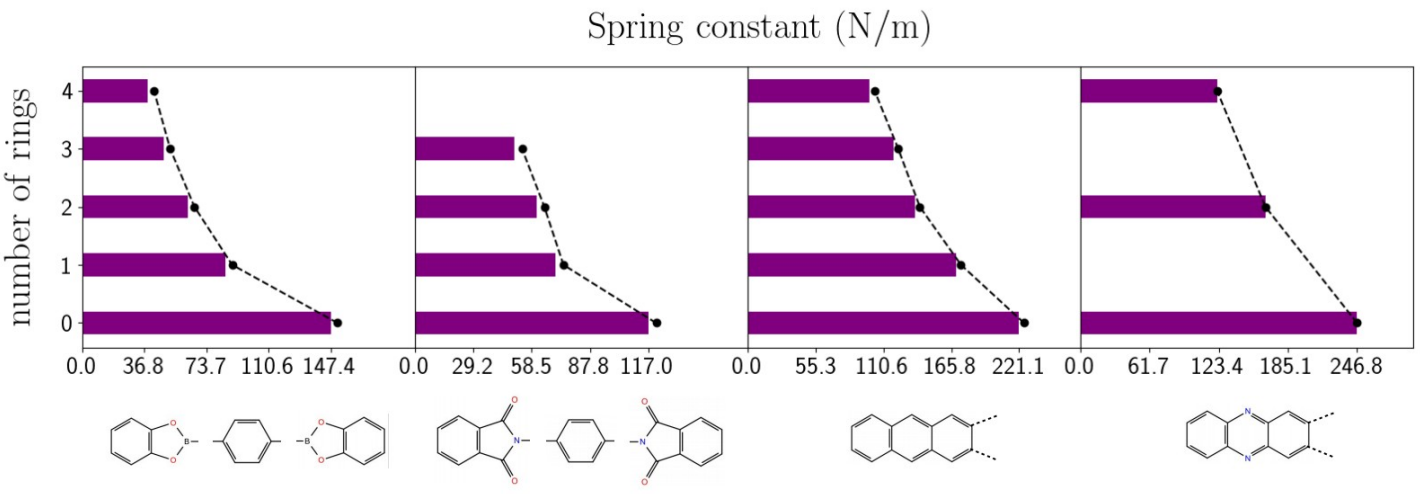
Adding polycyclic compound in the bridge

Mechanical properties – COFs with square lattice type

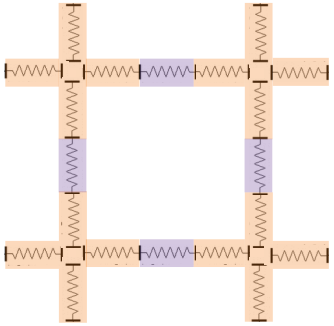




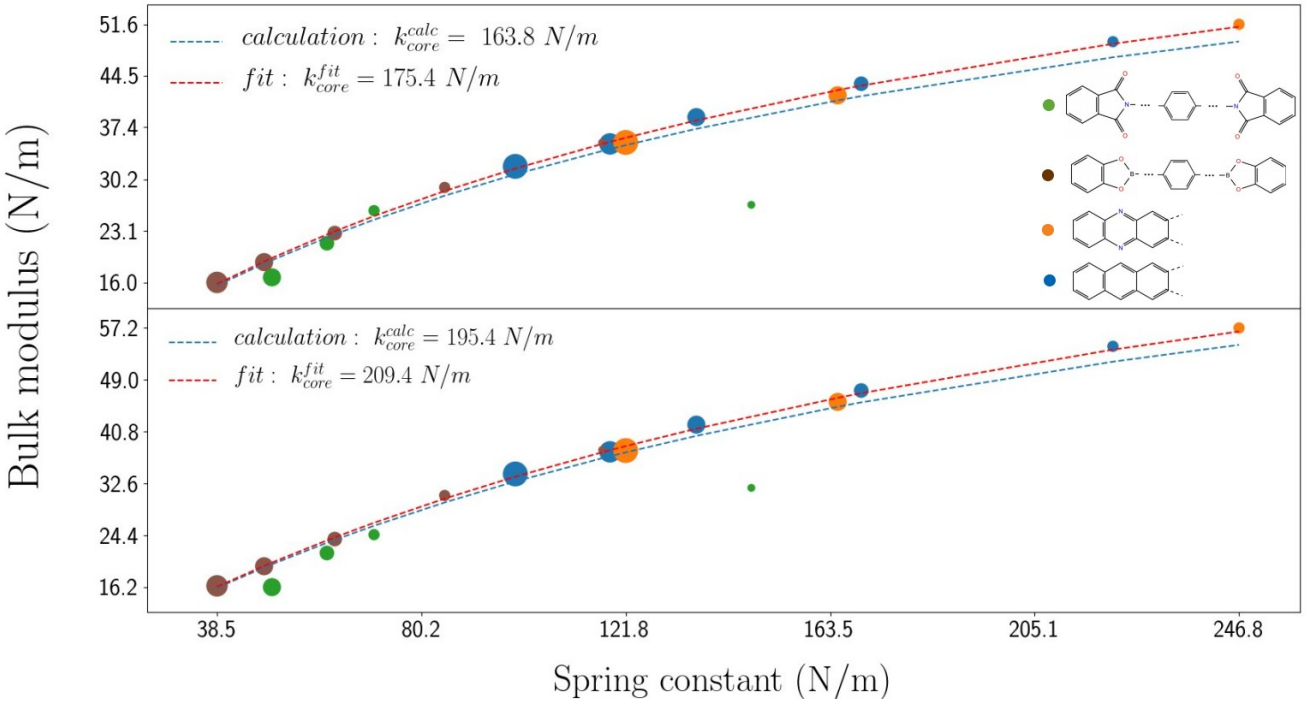


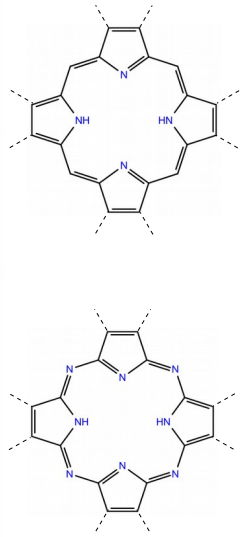


Mechanical properties – COFs with square lattice type



$$B_{2D} = \frac{1}{2} \cdot \frac{k_{core} \cdot k_{bridge}}{k_{core} + k_{bridge}}$$





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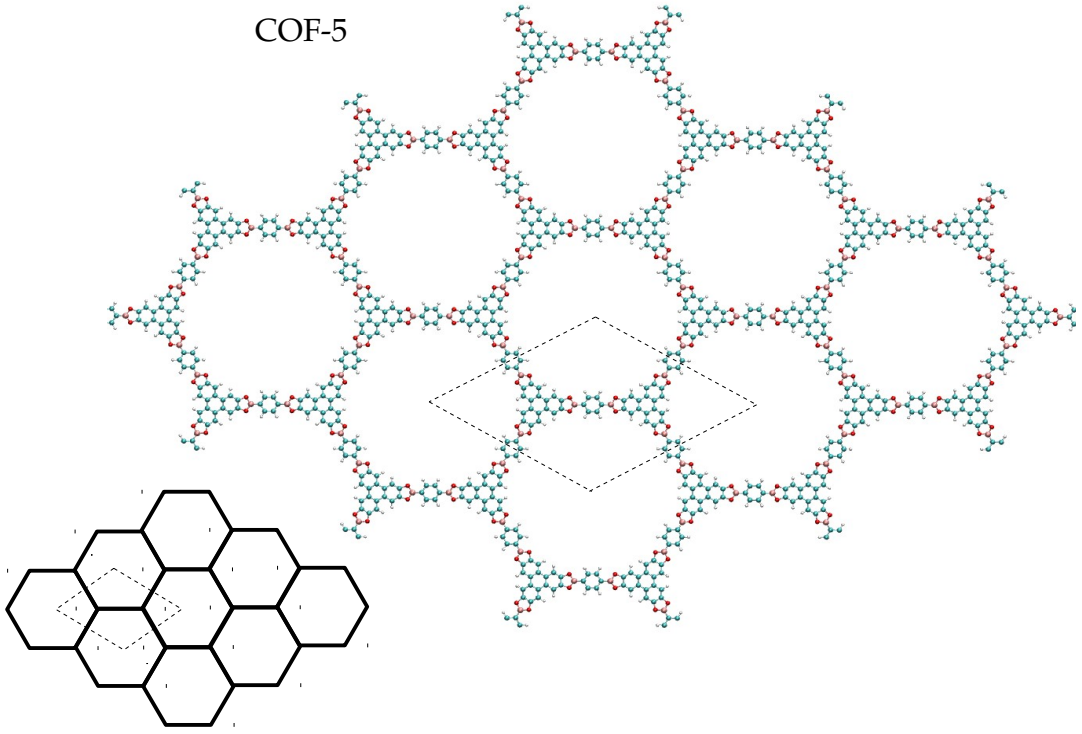
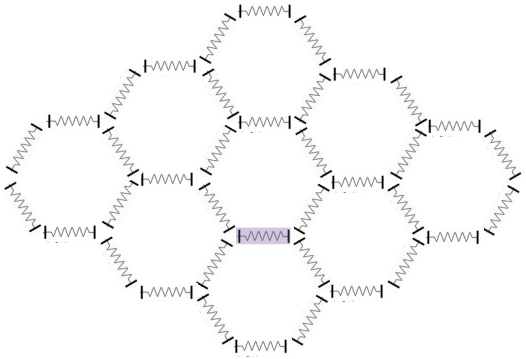
Mechanical properties – COFs with hexagonal lattice type

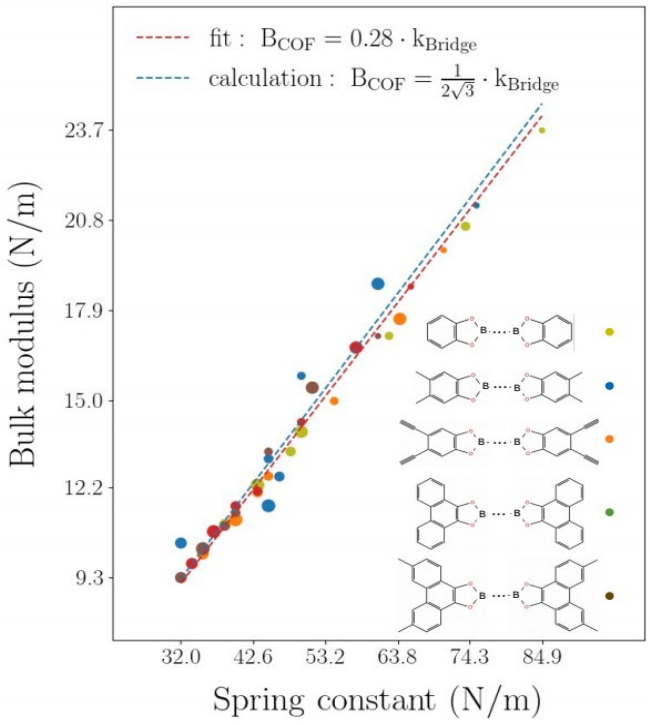


Mechanical properties – COFs with hexagonal lattice type

Spring network



$$B_{2D} = \frac{1}{2 \cdot \sqrt{3}} \cdot k_{bridge}$$



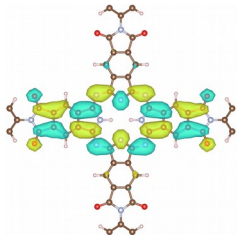
Electronic Properties

2D π-conjugated COFs

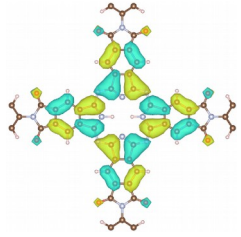
Electronic properties – 2D π-conjugated COFs

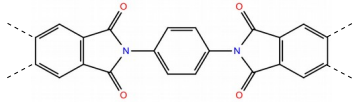
nonconjugated COFs

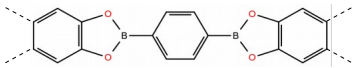
LUMO

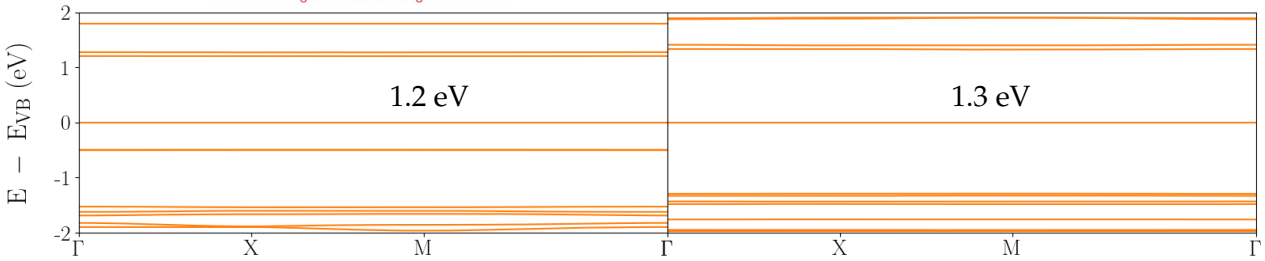


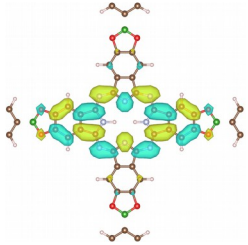
HOMO

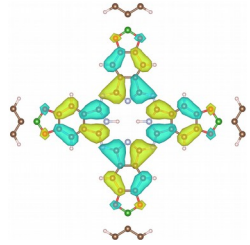








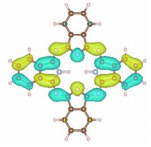


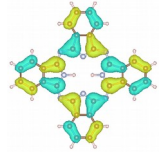


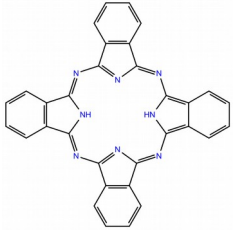
LUMO

1.5 eV

HOMO

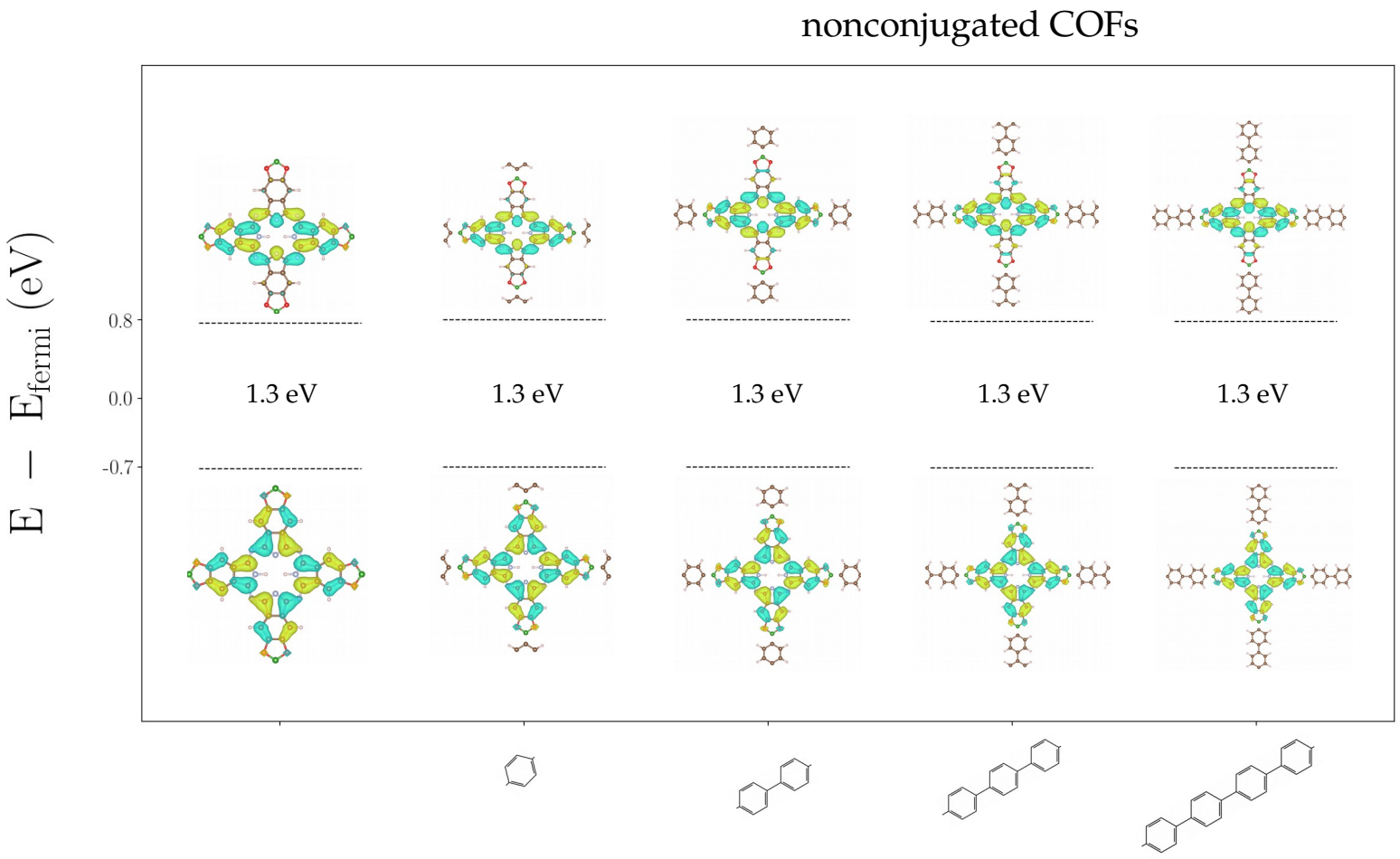






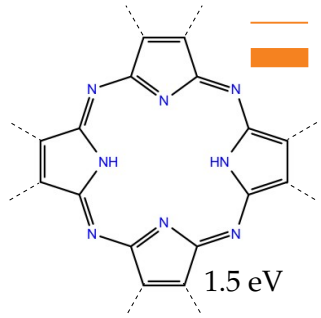
Phthalocyanine

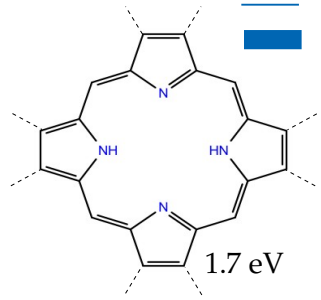
Electronic properties – 2D π-conjugated COFs

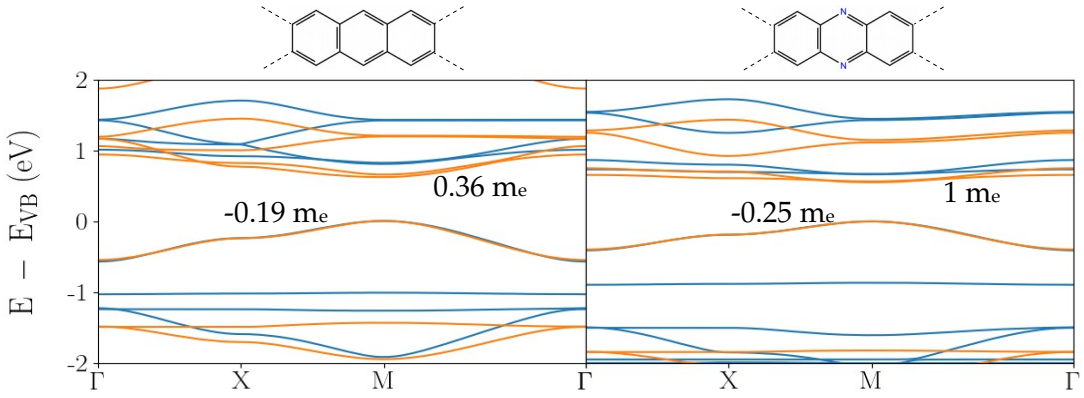


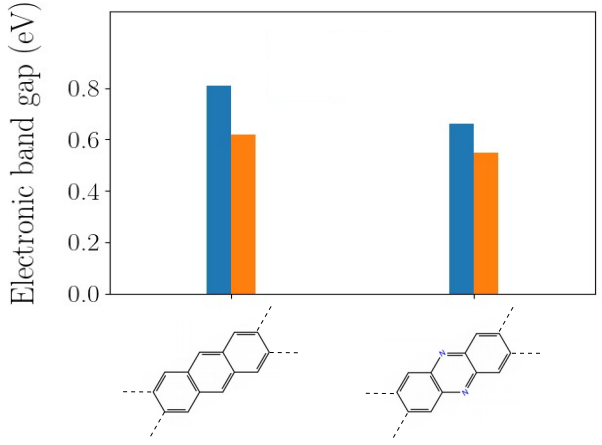
Electronic properties – 2D π-conjugated COFs

fully π-conjugated COFs





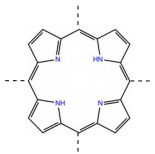


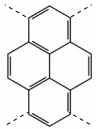


Electronic properties – Predicting the electronic band gap

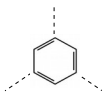
~ 330 COFs

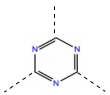
4-arm cores

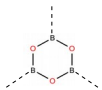


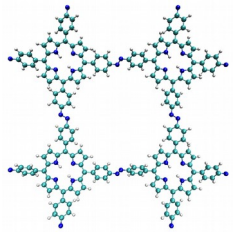


3-arm cores









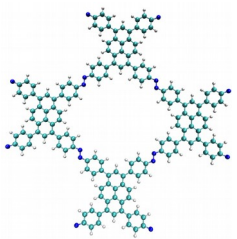
Calculation

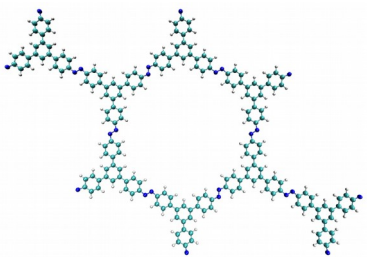
COF

Electronic band structure

Monomers
(cores and bridges)

HOMO-LUMO levels
Fermi level

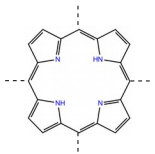


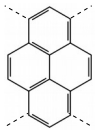


Electronic properties – Predicting the electronic band gap

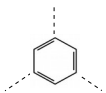
~ 330 COFs

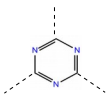
4-arm cores

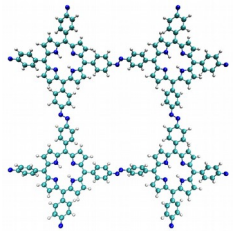




3-arm cores





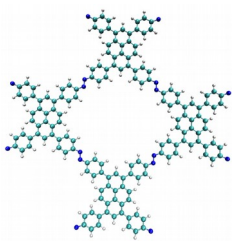


Calculation

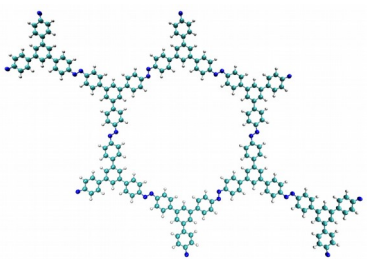
COF — Electronic band structure

4-arm cores

Monomers (cores and bridges) — HOMO-LUMO levels, Fermi level



1D-polymer — Electronic band structure
- Electronic gap
- bandwidth of conduction/valence bands



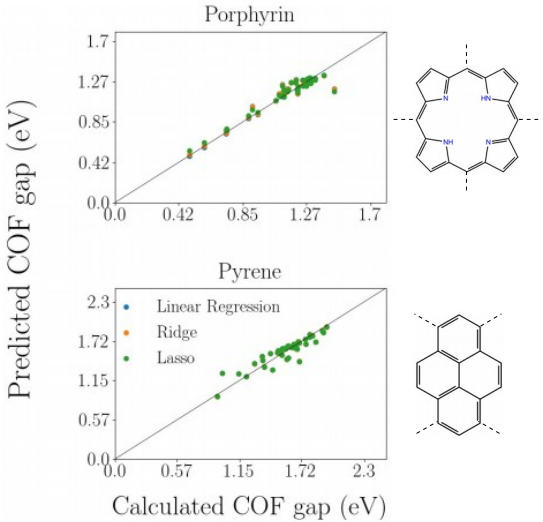
Could someone predict the gap of a COF from the monomers?

Electronic properties – Predicting the electronic band gap

Variables

From the 1D-polymer's electronic band structure:

- gap
- bandwidths

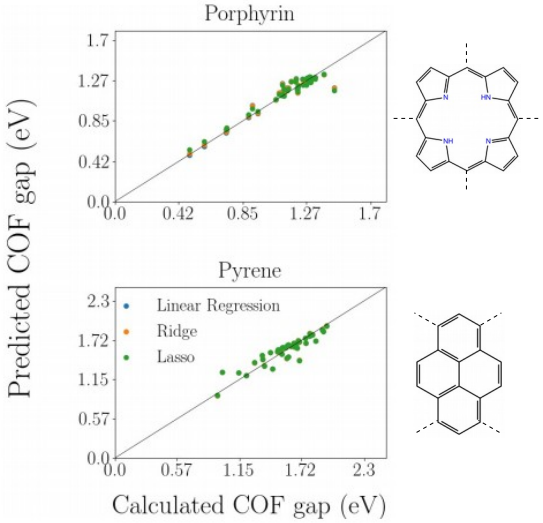


Electronic properties – Predicting the electronic band gap

Variables

From the 1D-polymer's electronic band structure:

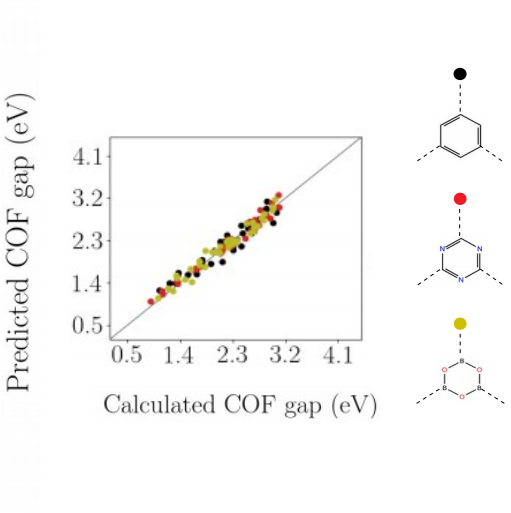
- gap
- bandwidths



Variables

From the monomers (core and bridge)

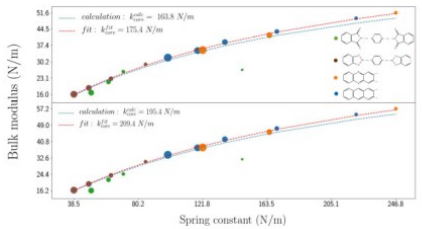
- HOMO and LUMO levels
- Fermi level

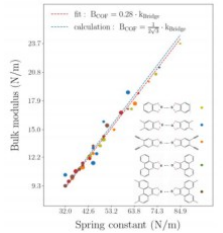


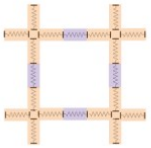
Concluding…

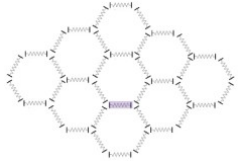
- *Prediction of Bulk modulus via analytical models*

  - *Square lattice type*
  - *Hexagonal lattice type*

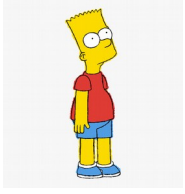






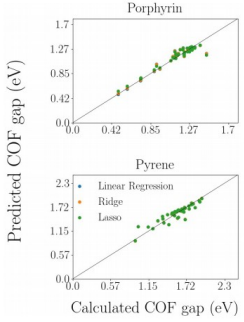


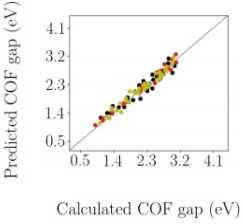
- *Predicting the electronic band gap from 1D-polymer or organic monomers using multiple linear regression techniques*



Future work

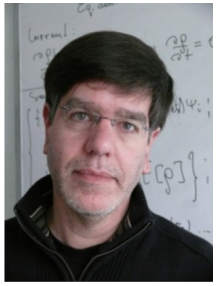
- *Faster optimization methods (FF)*
- *Export materials properties from the molecular building-blocks using a single descriptor (ML)*





Acknowledgements

Dr. Alexander Croy



Dr. Rafael Gutierrez

Dr. Arezoo Dianat

Prof. Dr. Gianaurelio Cuniberti


THANK
YOU
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BÏYAN
SHUKRIA
TASHAKKUR ATU
YAQHANYELAY
TINGKI
SUKSAMA
EKHMET
MEHRBANI
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