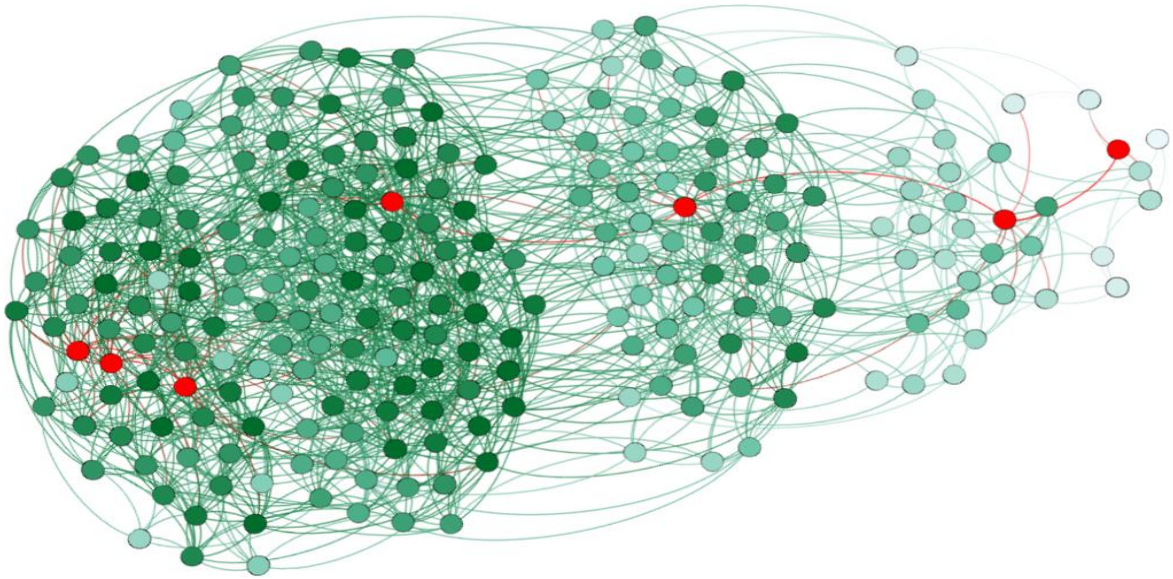
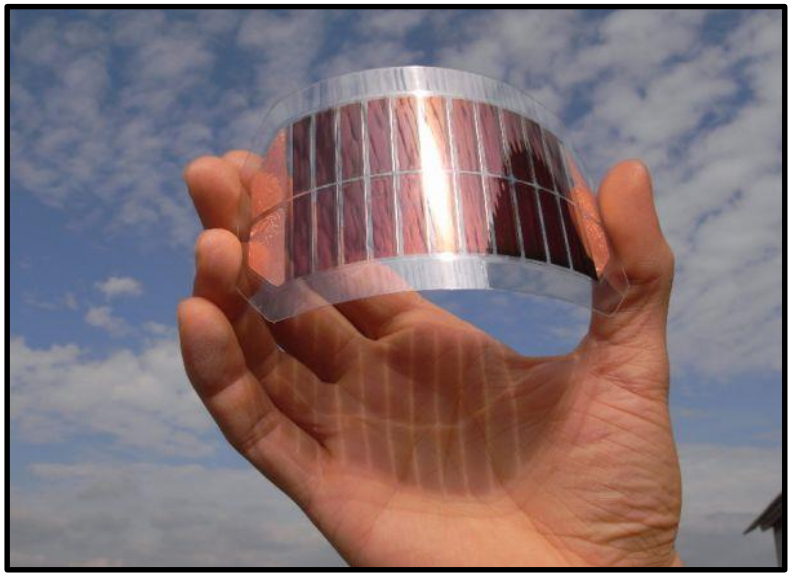
Rational Design of Hybrid Interfaces For Organic Electronics



Oliver T. Hofmann



Photovoltaic cells

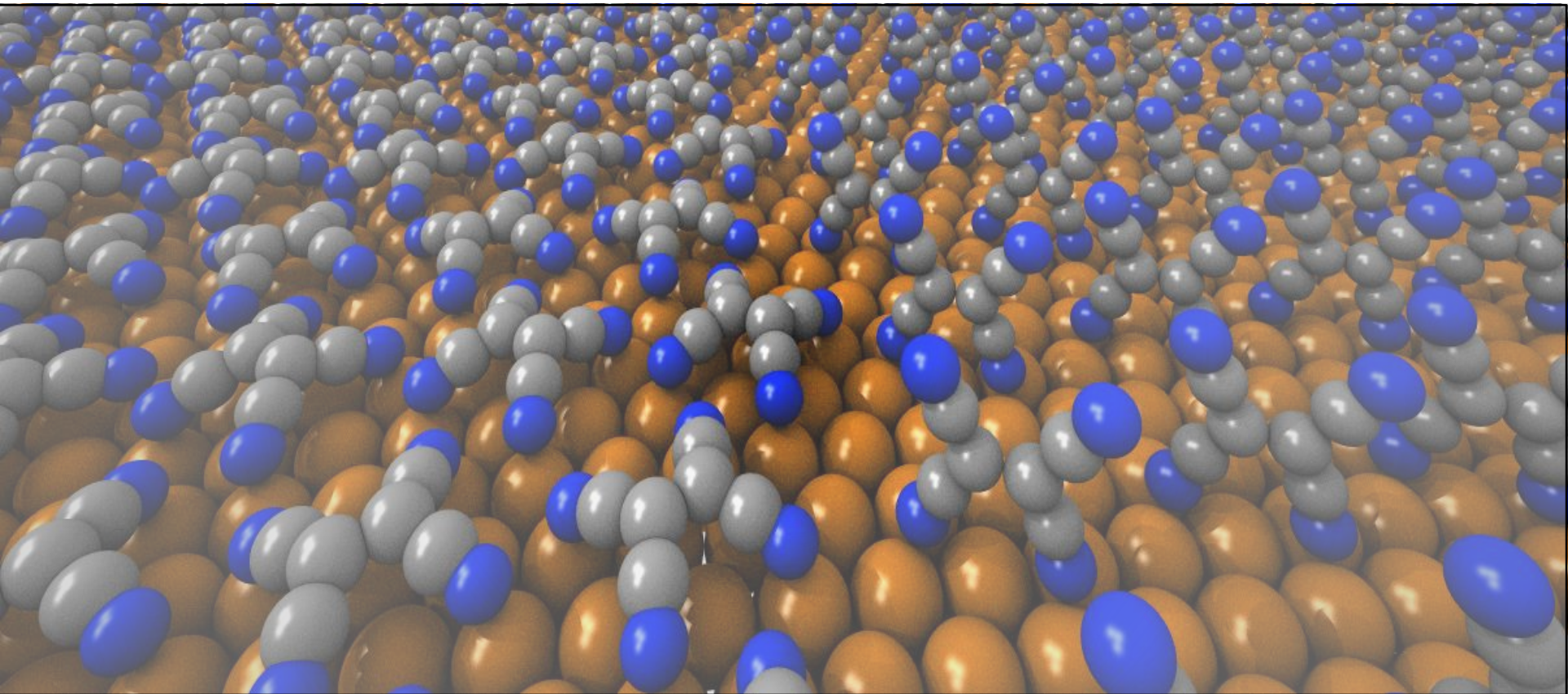
OLED displays

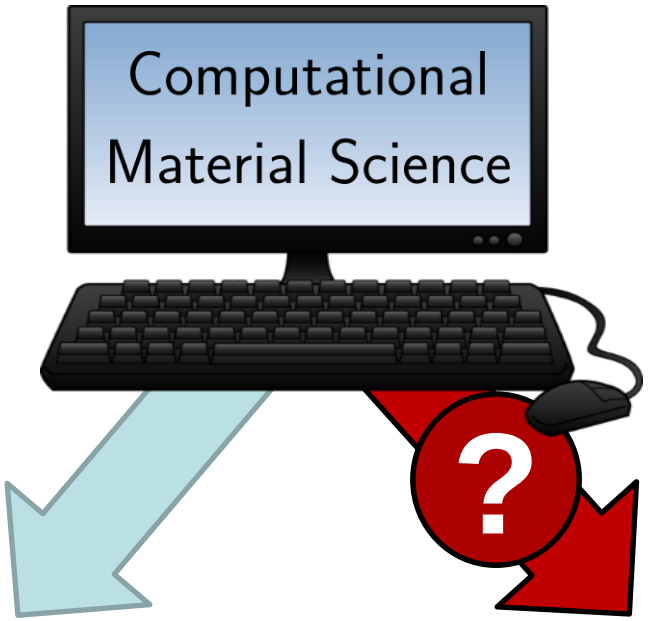
Improved materials drive innovation

Images from ecofriend.com/about-nano-structured-organic-photovoltaic-cells.html; *www.techhive.com/article/3154575/smart-tv/lgs-new-oled-tvs-are-real-wall-huggers.html; apps.pharmacy.wisc.edu/sopdir/lian_yu/*

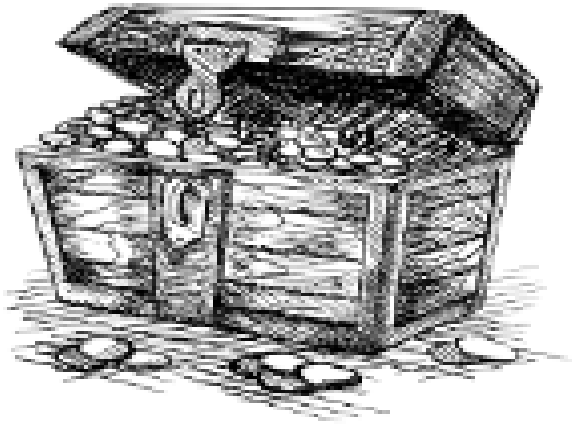
Organic Nanotechnology

- Flexibility of organic chemistry
- Emergent properties of interfaces



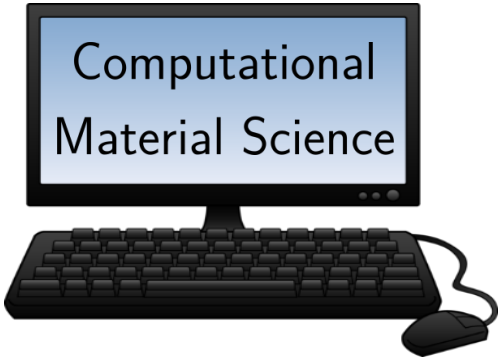


Find „hidden treasure“

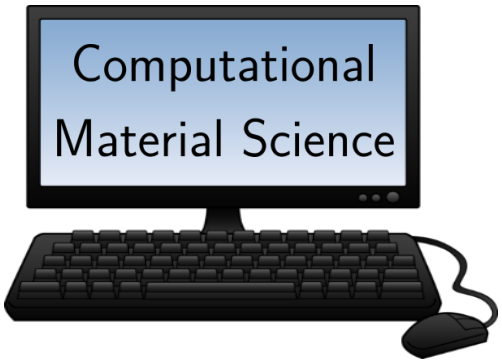


… and how to get there

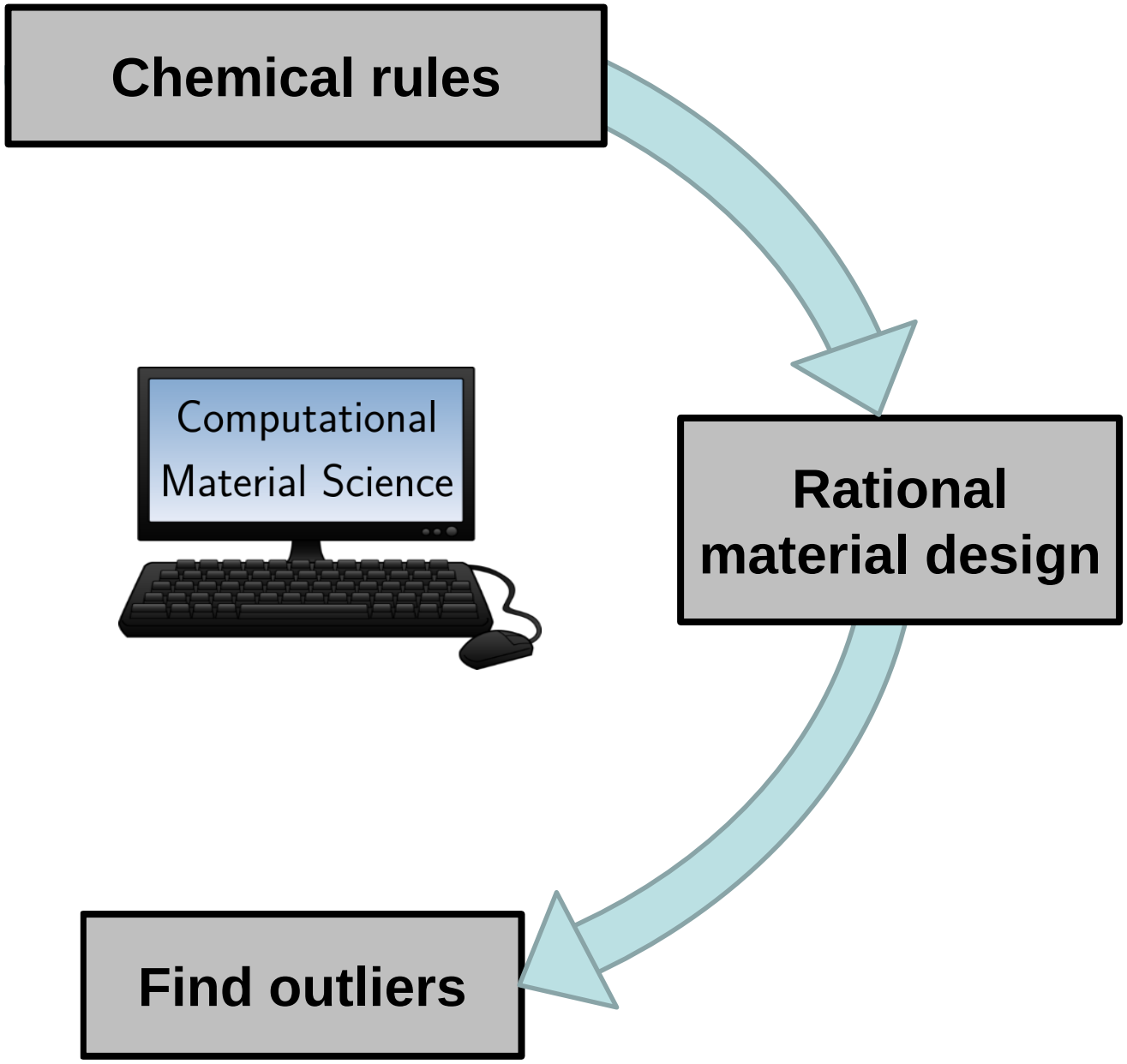
Chemical rules

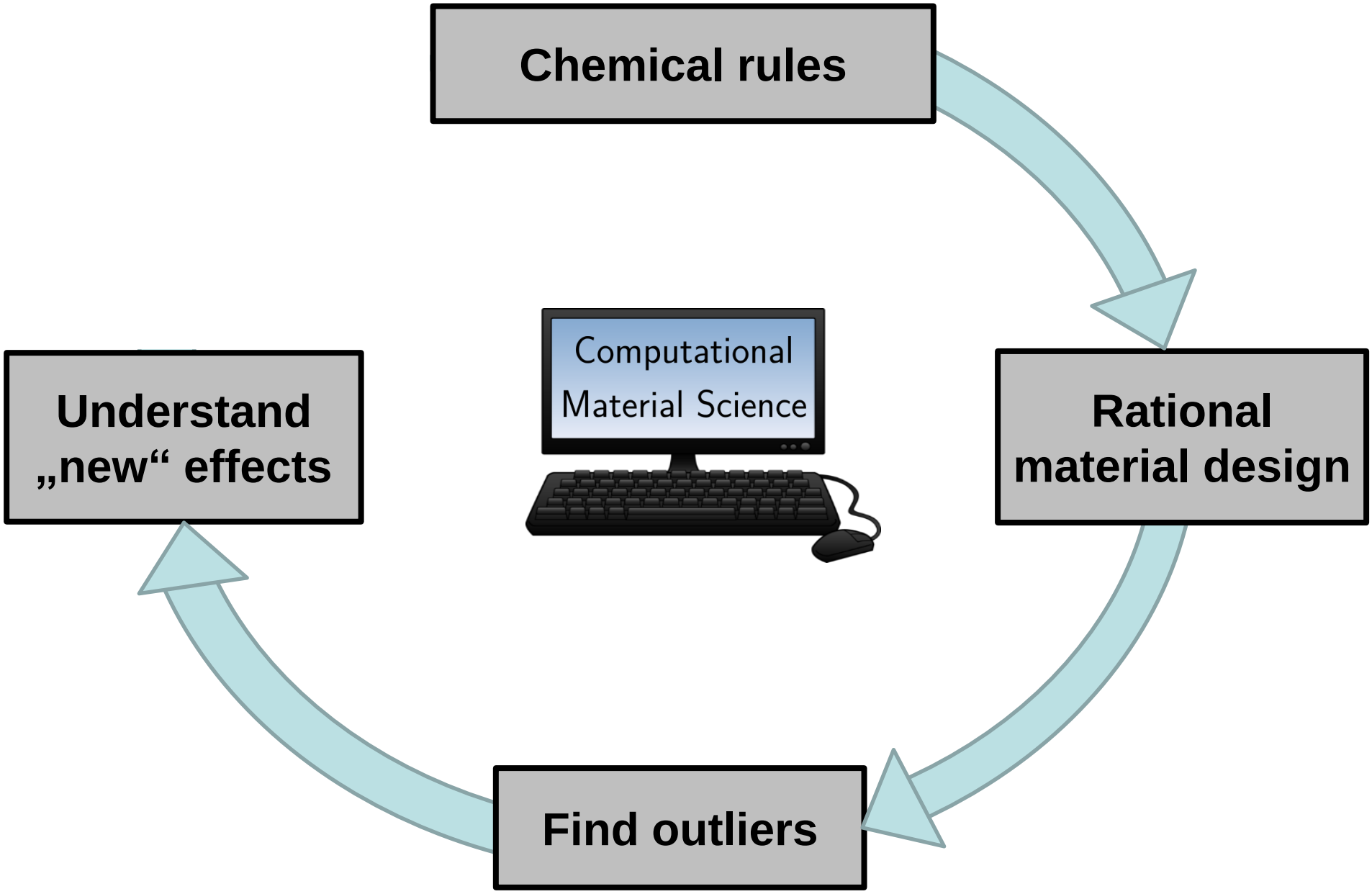


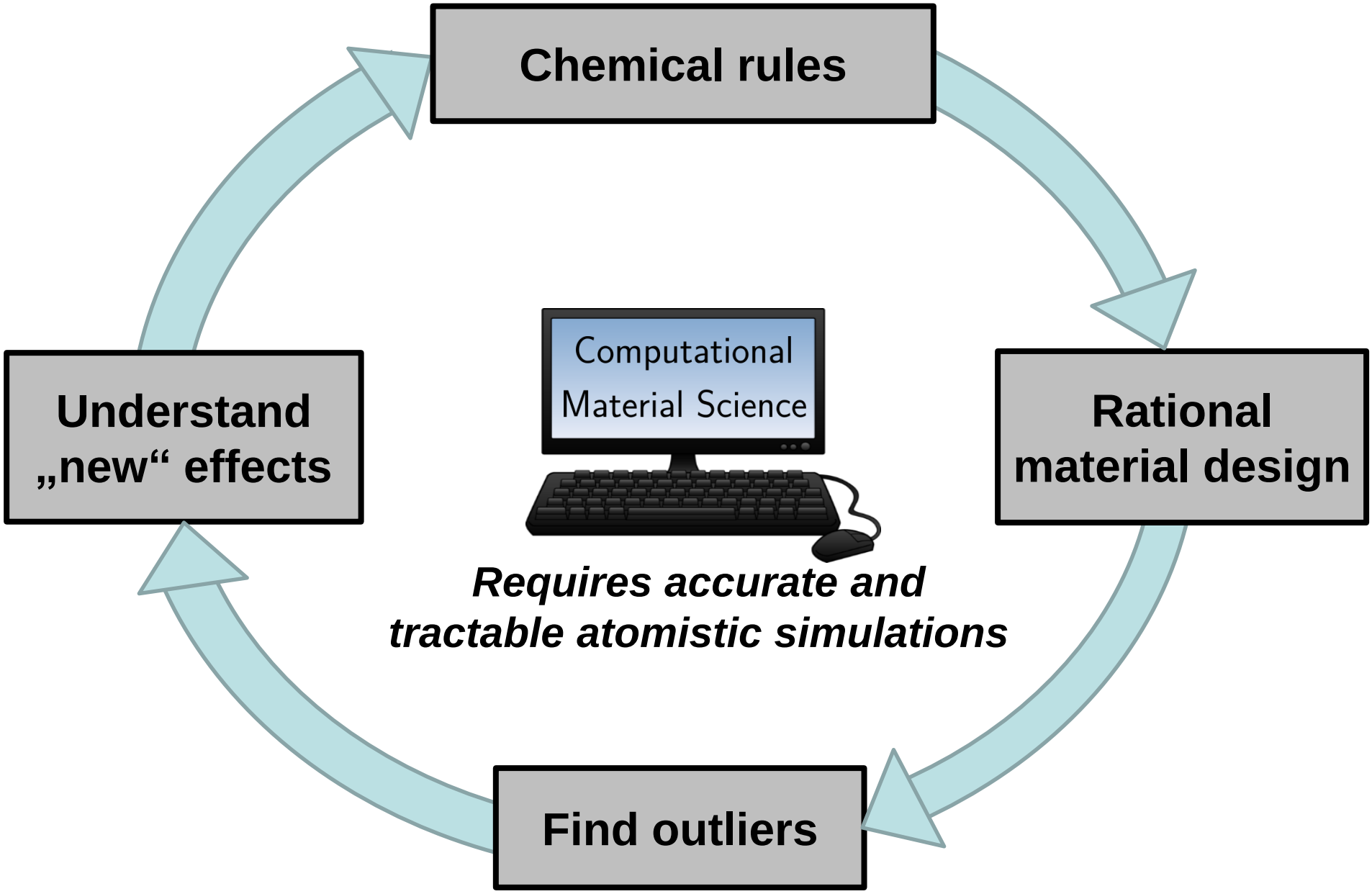
Chemical rules



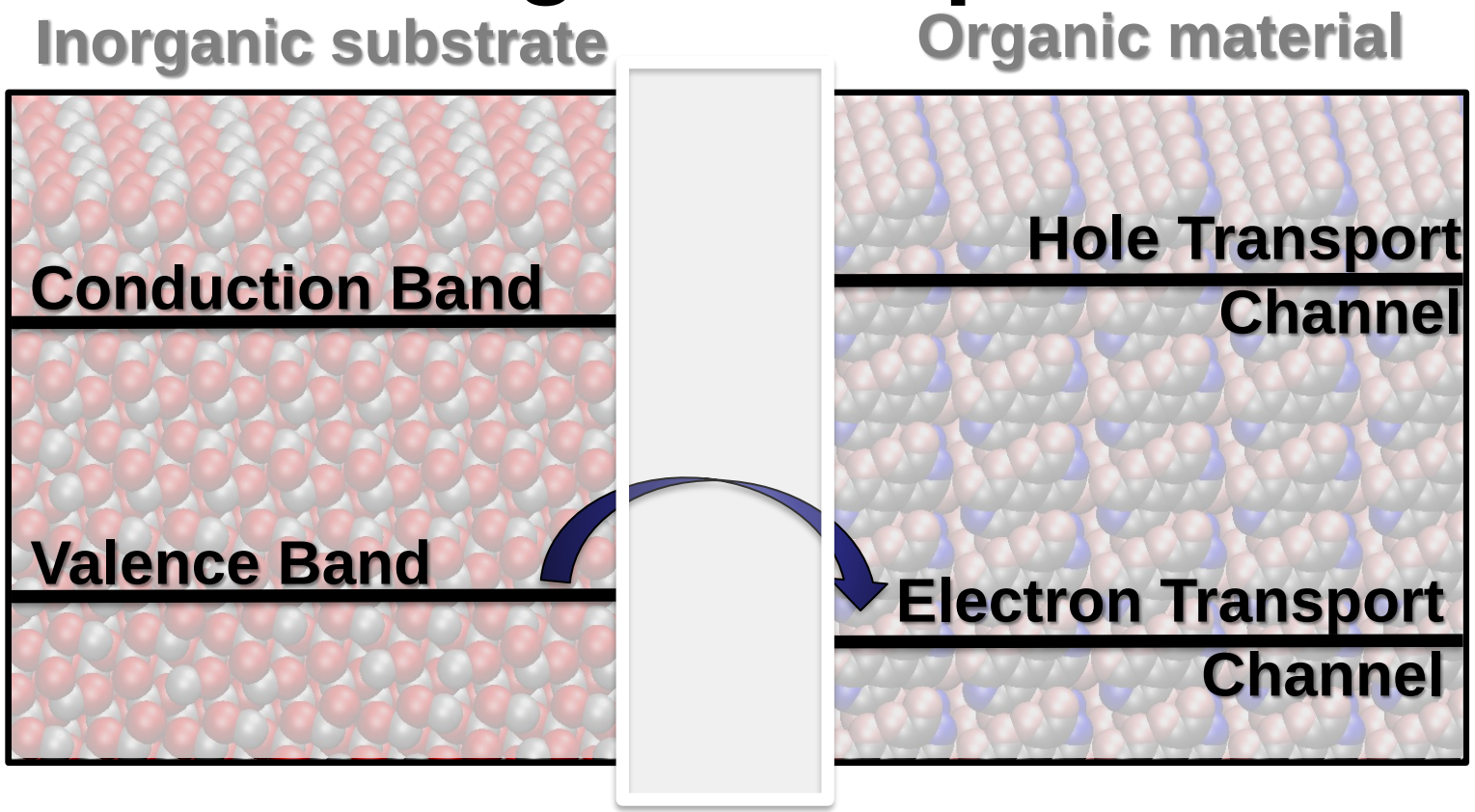
Rational material design


Chemical rules
Computational
Material Science
Rational
material design
Find outliers


Chemical rules
Rational material design
Find outliers
Understand „new“ effects
Computational Material Science

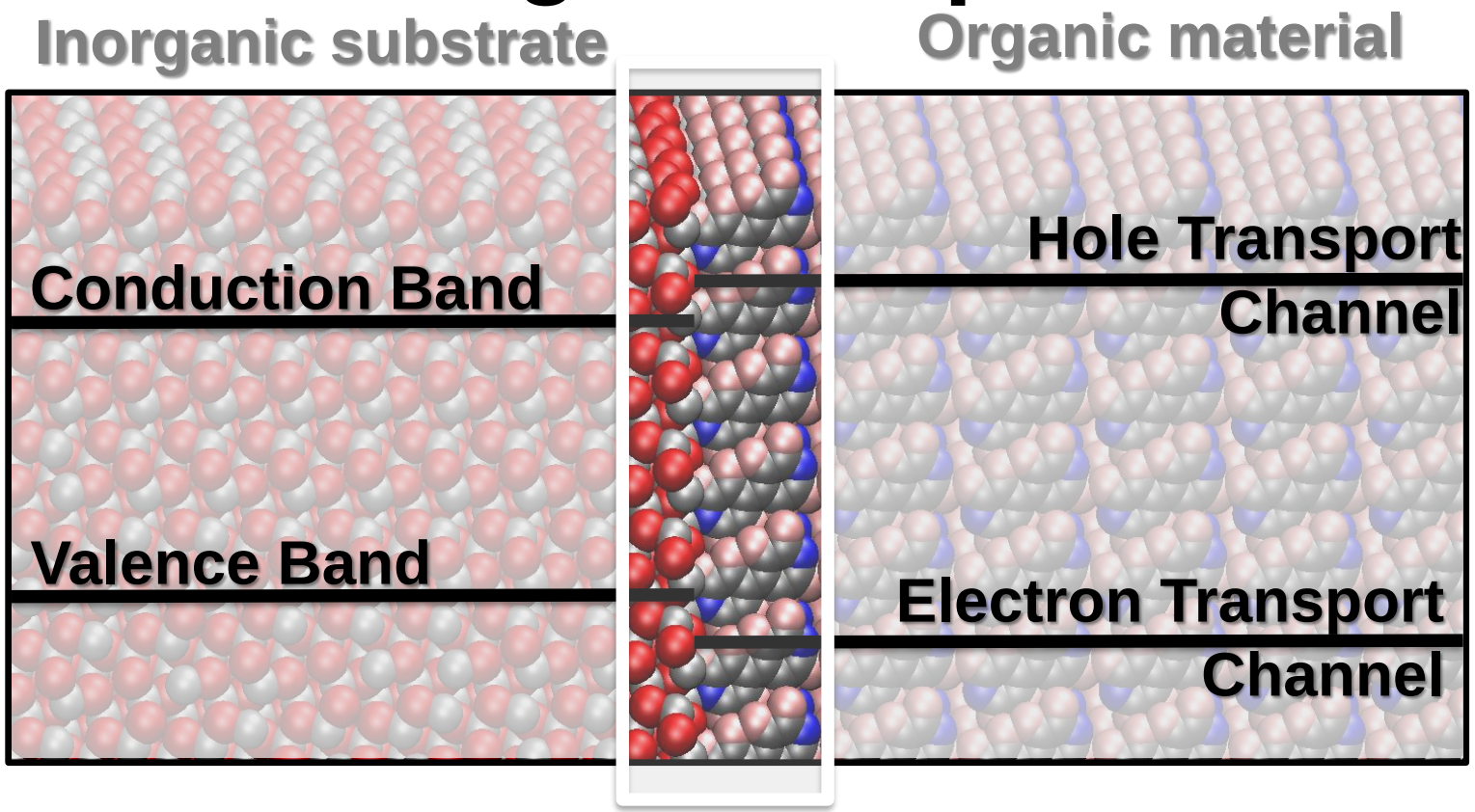

Chemical rules
Rational material design
Find outliers
Understand „new“ effects
Computational Material Science
Requires accurate and tractable atomistic simulations

Material Design Example



governs charge- and energy transfer

Material Design Example



Formation of interface dipole

Material Design Example

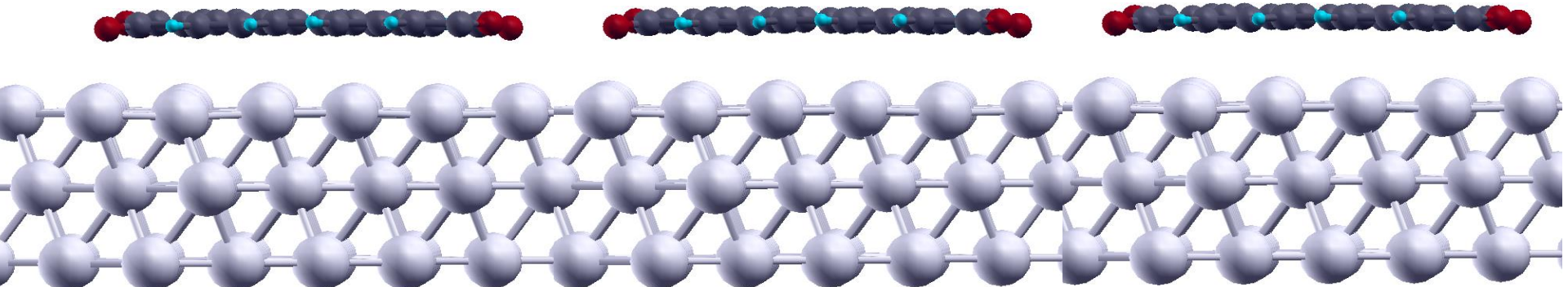
Design target:

Optimize injection barriers →

Tuning of the work function Φ

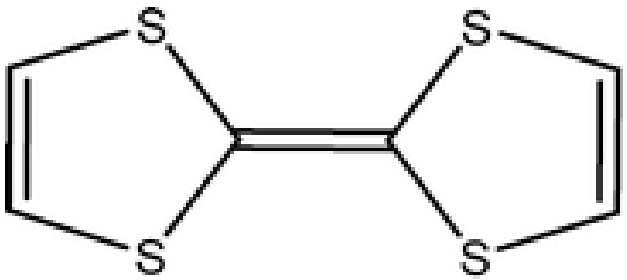
Design hypothesis:

Adsorption of electron donors / acceptors



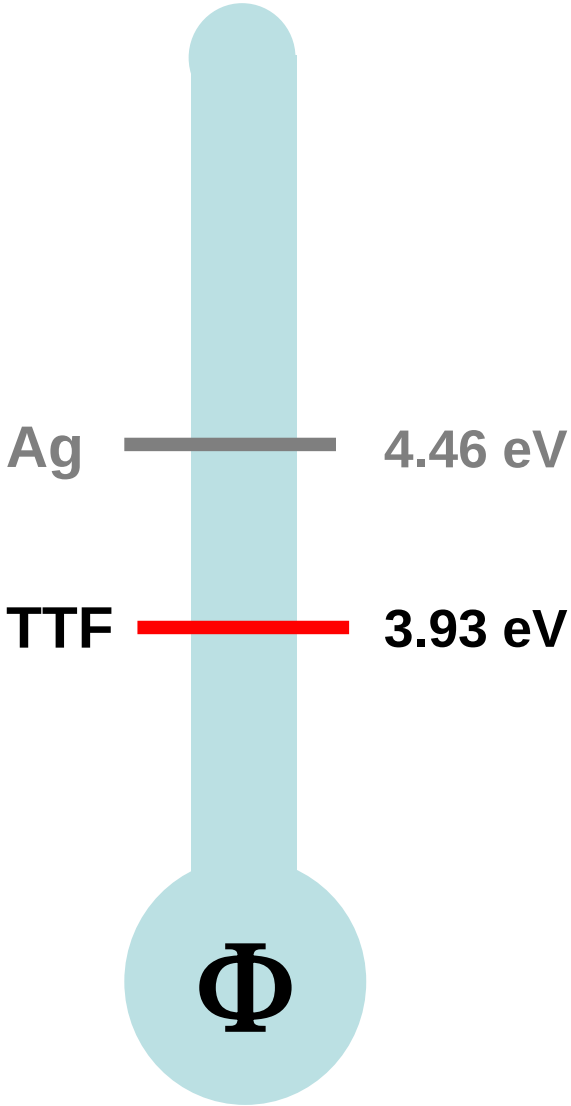
Example: Tune the work function Φ

Electron donors on Ag(111)



TTF

Molecule	IE [eV]
TTF	6.34



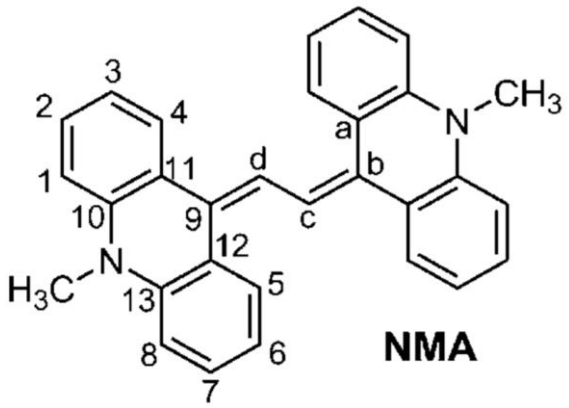
OTH, G. Rangger, E. Zojer, *J. Phys. Chem. C*, 2008

B. Bröker, R.-P. Blum, L. Beverina, OTH, et al., ChemPhysChem, 2009

B. Bröker, R.-P. Blum, J. Frisch, A. Vollmer, OTH, et al., Appl. Phys. Lett. 2008

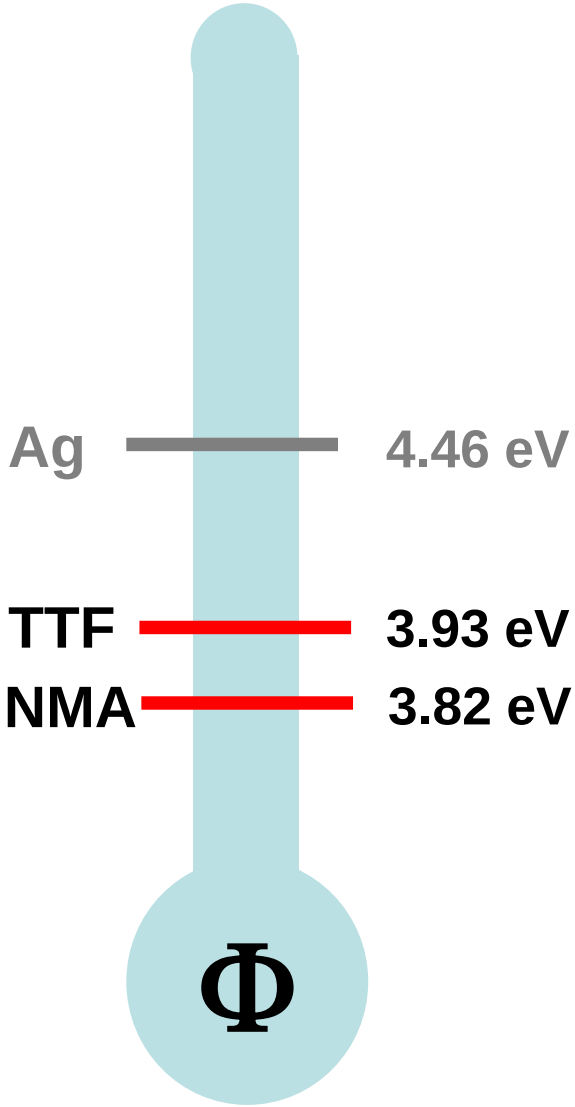
Example: Tune the work function Φ

Electron donors on Ag(111)



NMA

Molecule	IE [eV]
TTF	6.34
NMA	5.54



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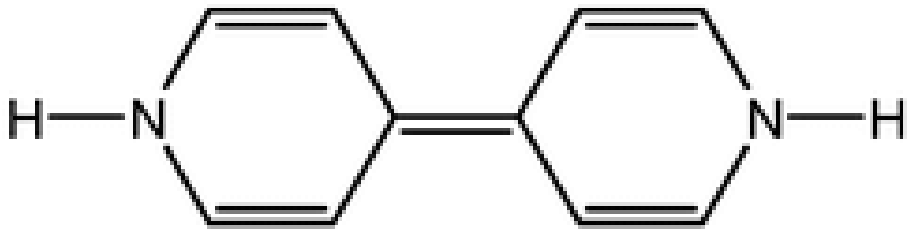
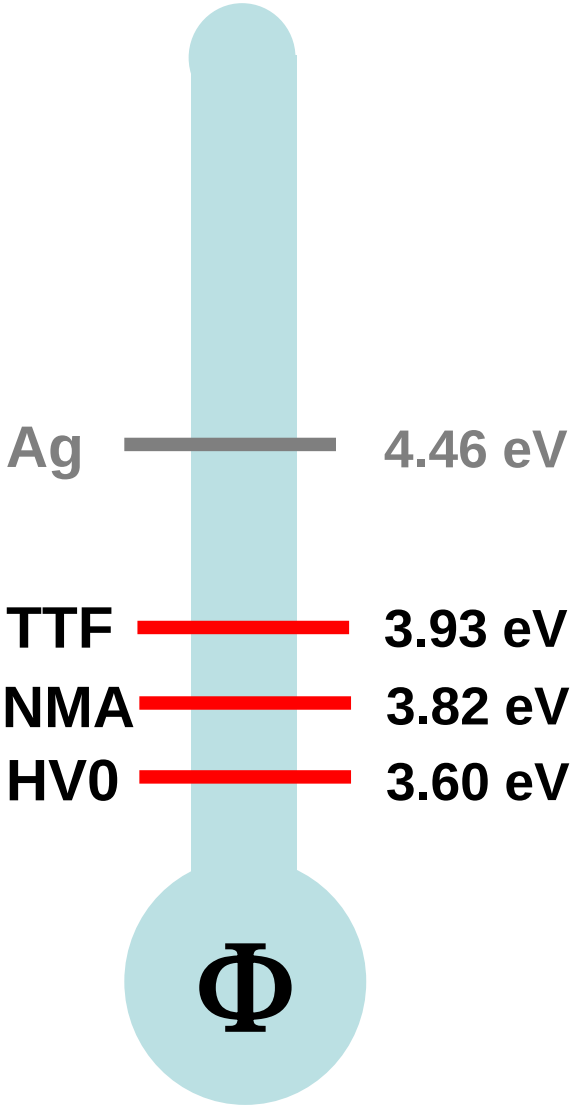
Example: Tune the work function Φ

Electron donors on Ag(111)



Viologen

Molecule	IE [eV]
TTF	6.34
NMA	5.54
Viologen	4.85



OTH, G. Rangger, E. Zojer, *J. Phys. Chem. C*, 2008

B. Bröker, R.-P. Blum, L. Beverina, OTH, et al., ChemPhysChem, 2009

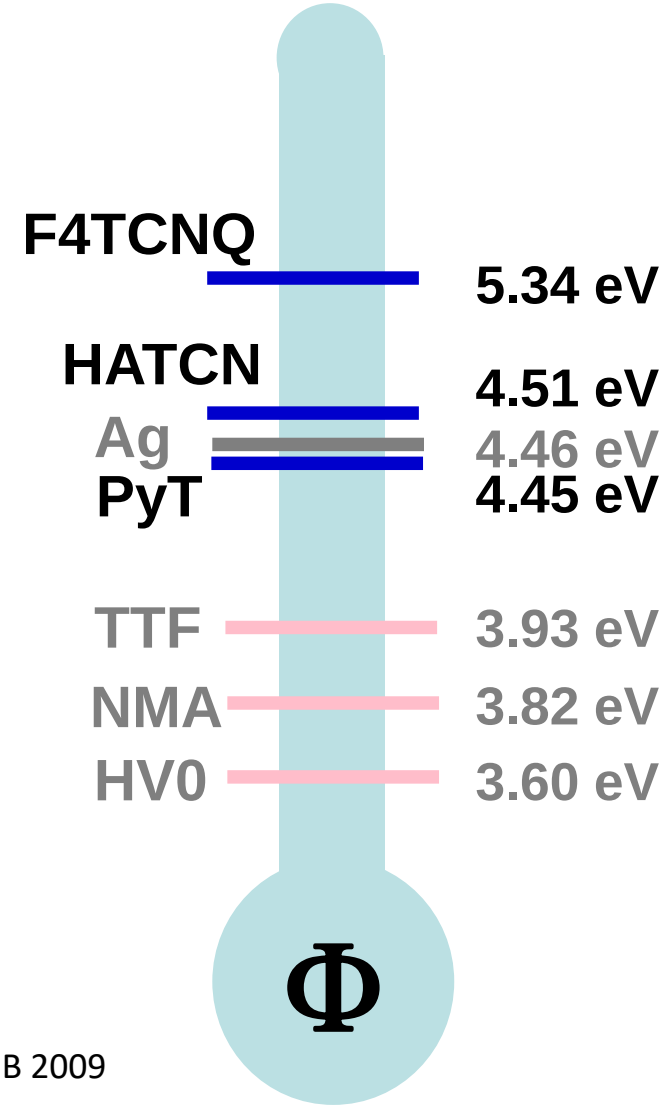
B. Bröker, R.-P. Blum, J. Frisch, A. Vollmer, OTH, et al., Appl. Phys. Lett. 2008

Example: Tune the work function Φ

Electron acceptors on Ag(111)

Molecule	EA [eV]
PyT	2.21
HATCN	2.50
F4TCNQ	3.52

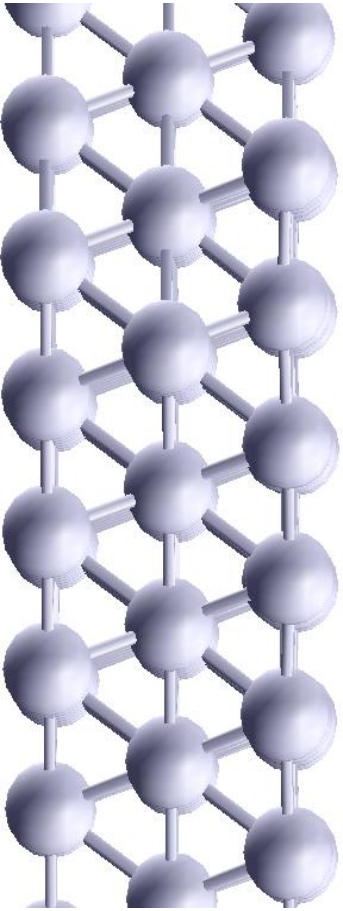
Molecule	IE [eV]
TTF	6.34
NMA	5.54
Viologen	4.85

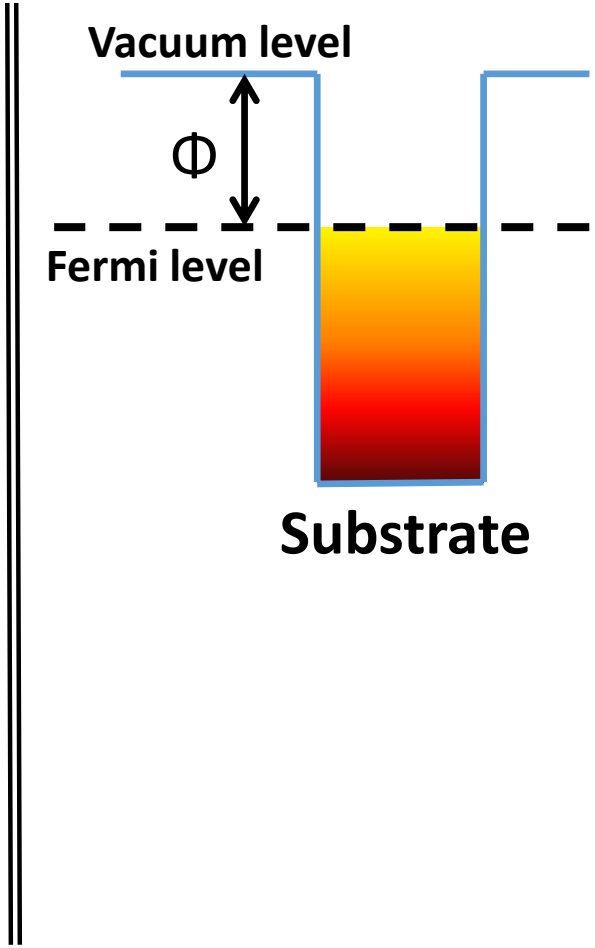


OTH, V. Atalla, P. Rinke, M. Scheffler, New Journal of Physics, 2013

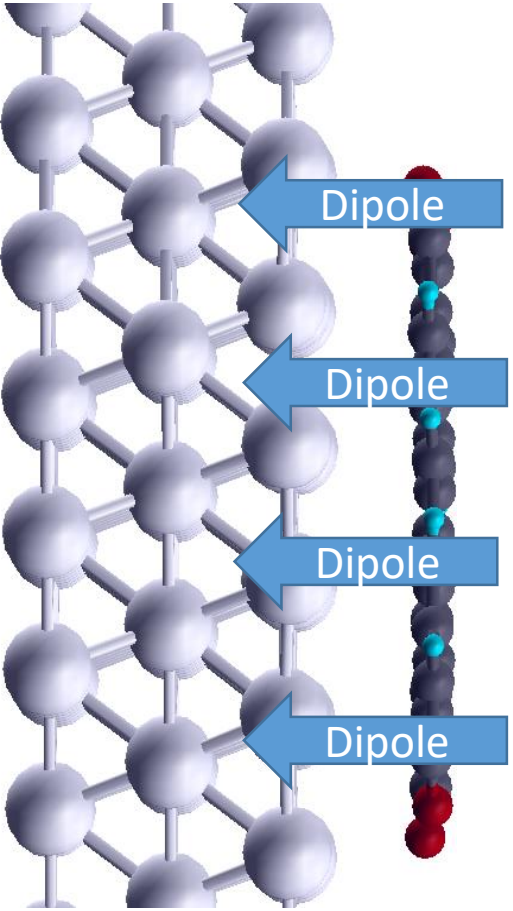
H. Glowatzki, B. Bröker, R.-P.-Blum, OTH et al., Nano Lett., 2008

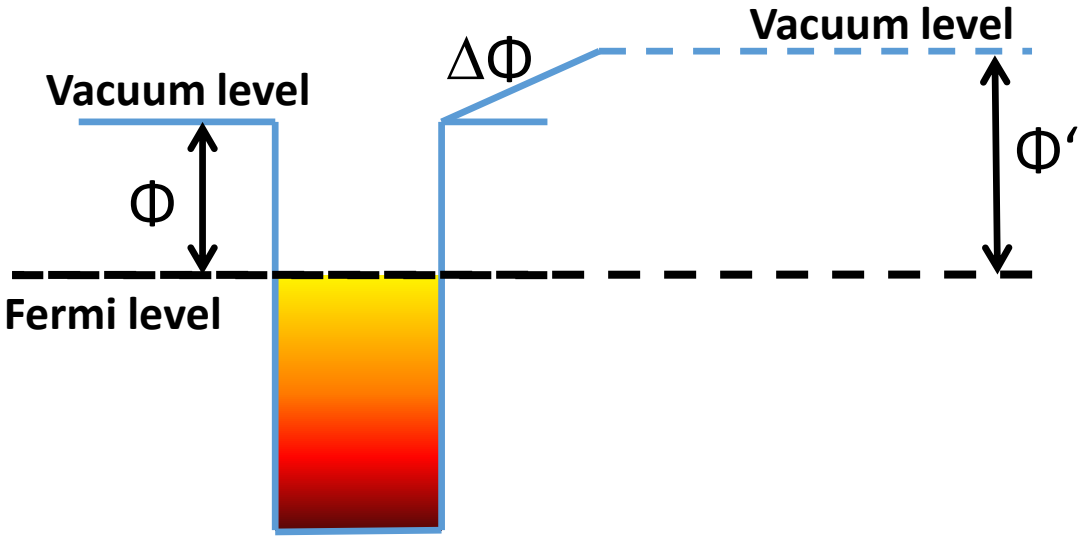
G. Rangger, OTH, L. Romaner, G. Heimel, B. Bröker, et al., PHYSICAL REVIEW B 2009





Modified from: O.T. Hofmann, V. Atalla, N. Moll, P. Rinke, M. Scheffler, New Journal of Physics, 15, 123028 (2013)





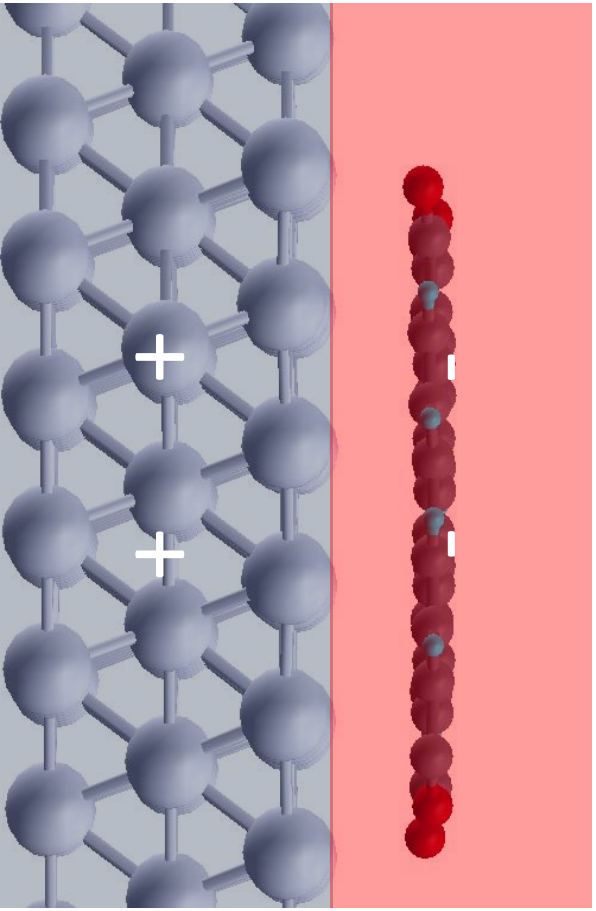
Substrate

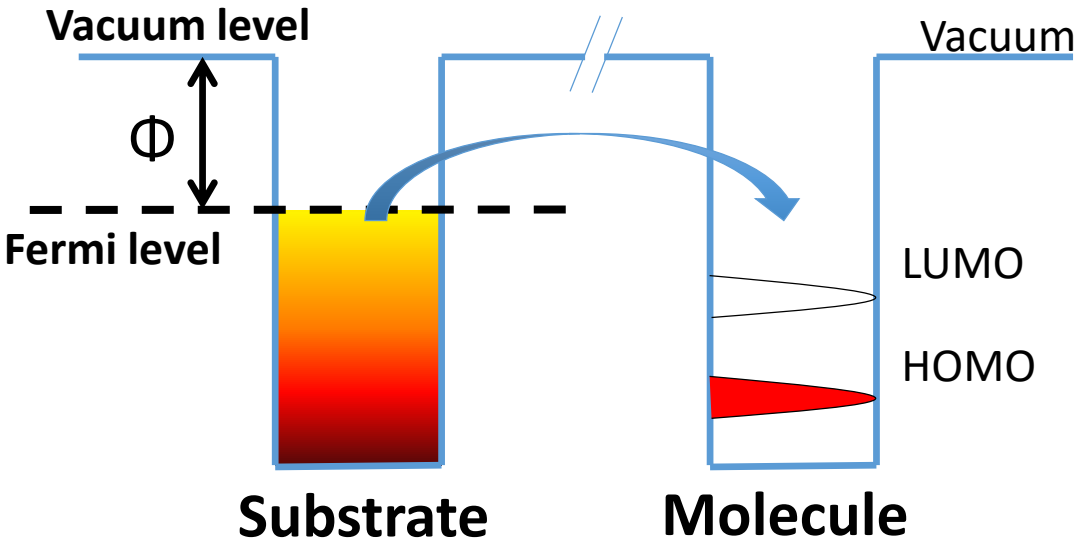
$$\Delta\Phi \propto \frac{\mu}{A}$$

Work function change depends on dipole density

Dipole sources can be
Molecular dipoles, charge transfer, etc…

Modified from: O.T. Hofmann, V. Atalla, N. Moll, P. Rinke, M. Scheffler, New Journal of Physics, 15, 123028 (2013)





If the LUMO is below E_F, charge transfer ensues

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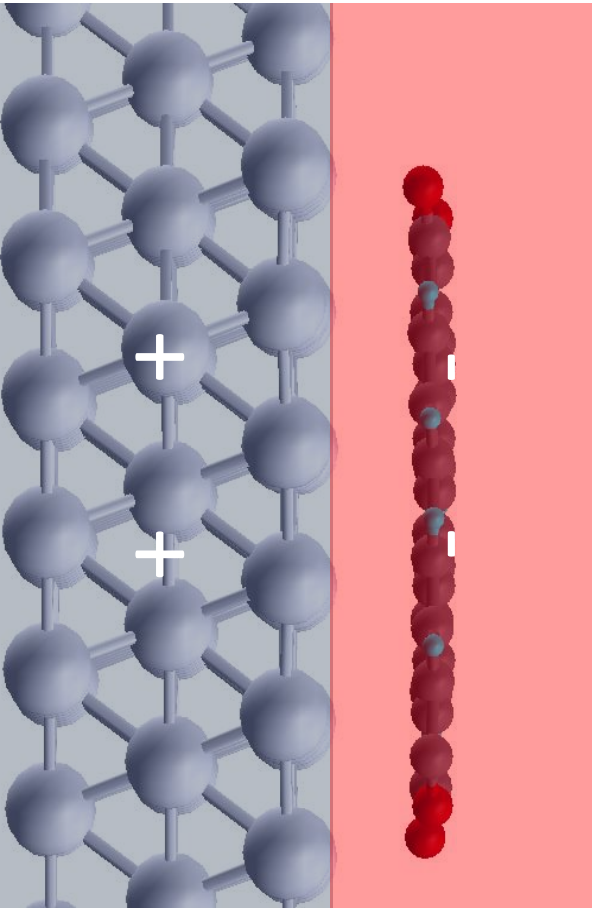

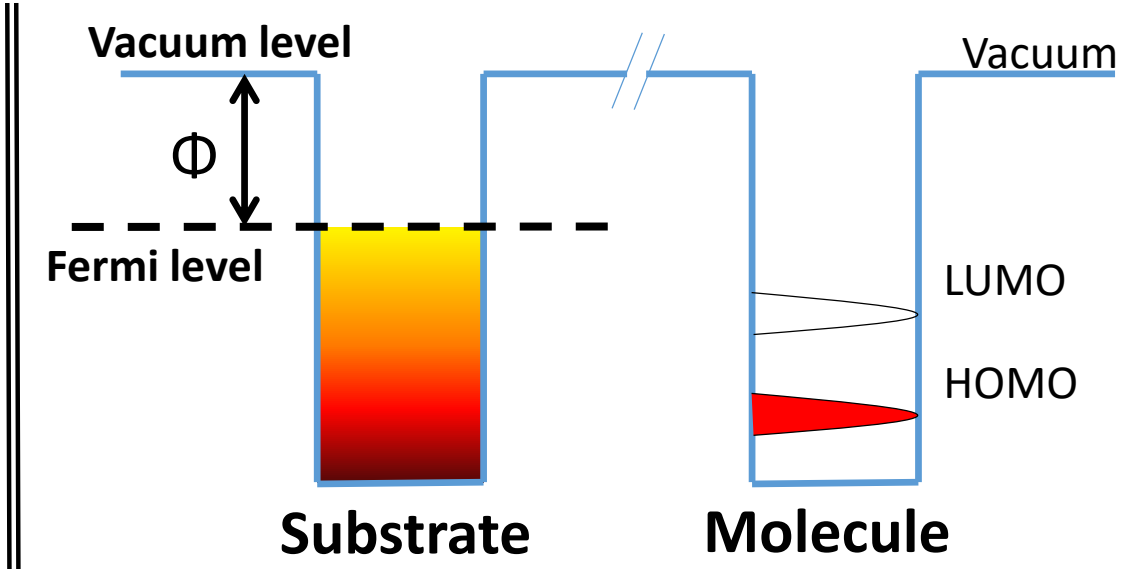

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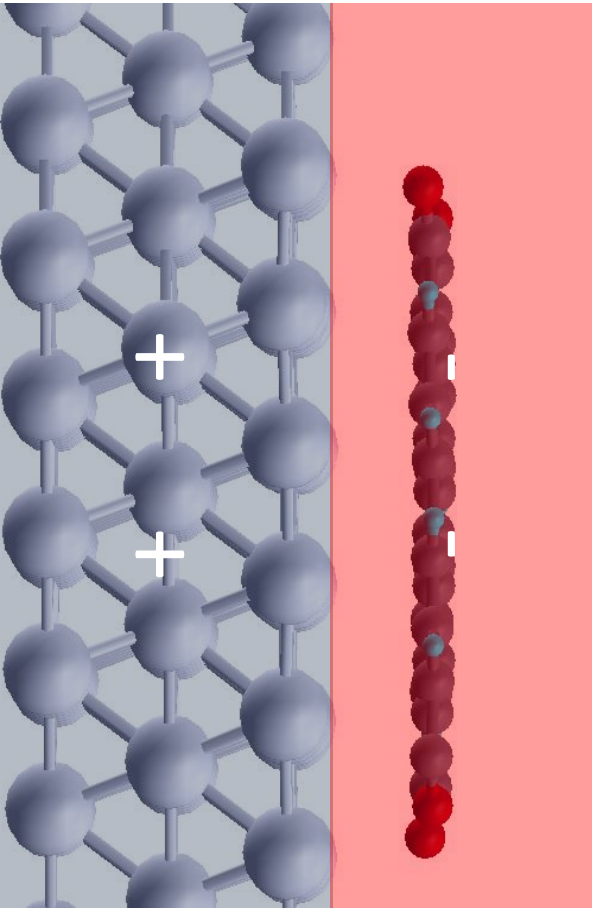

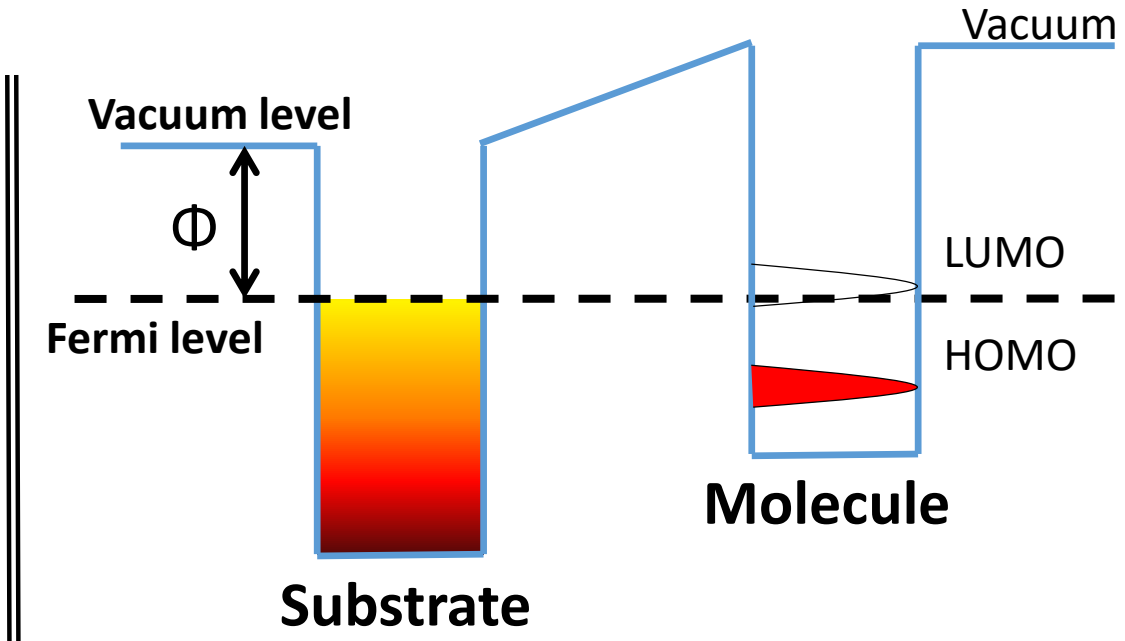

If the LUMO is below E_F, charge transfer ensues,
Until the LUMO is in resonance with E_F

$$\Phi^{max} \approx \epsilon(LUMO)$$

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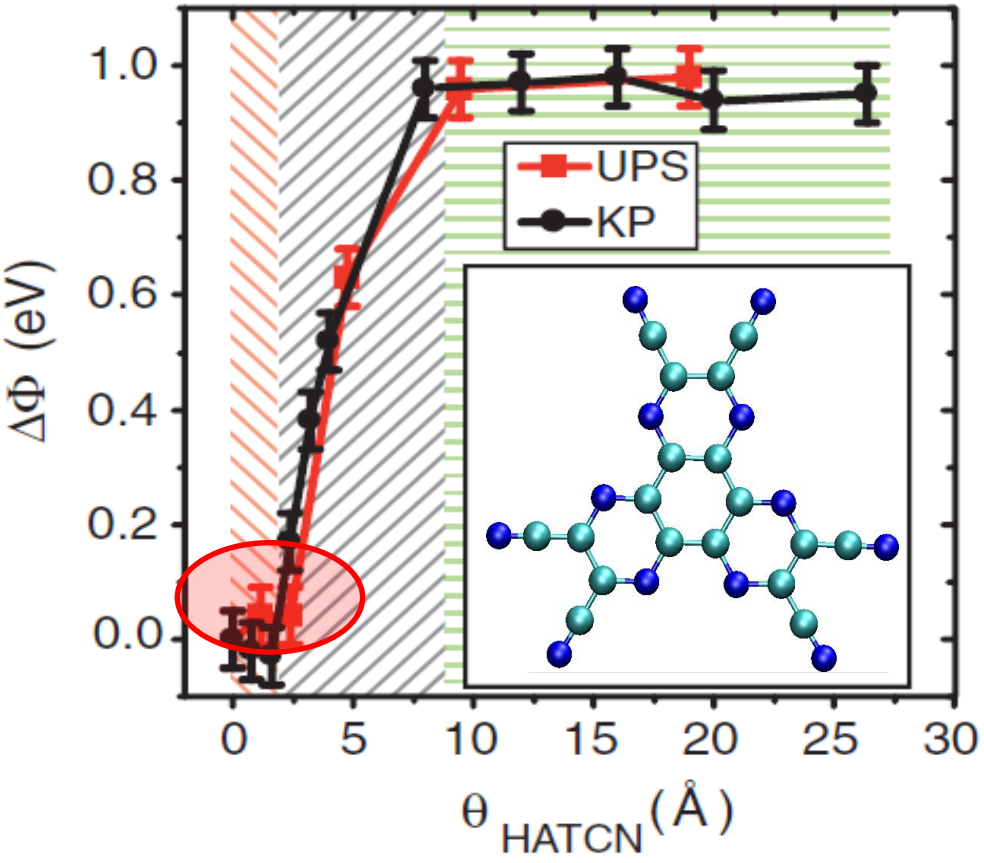
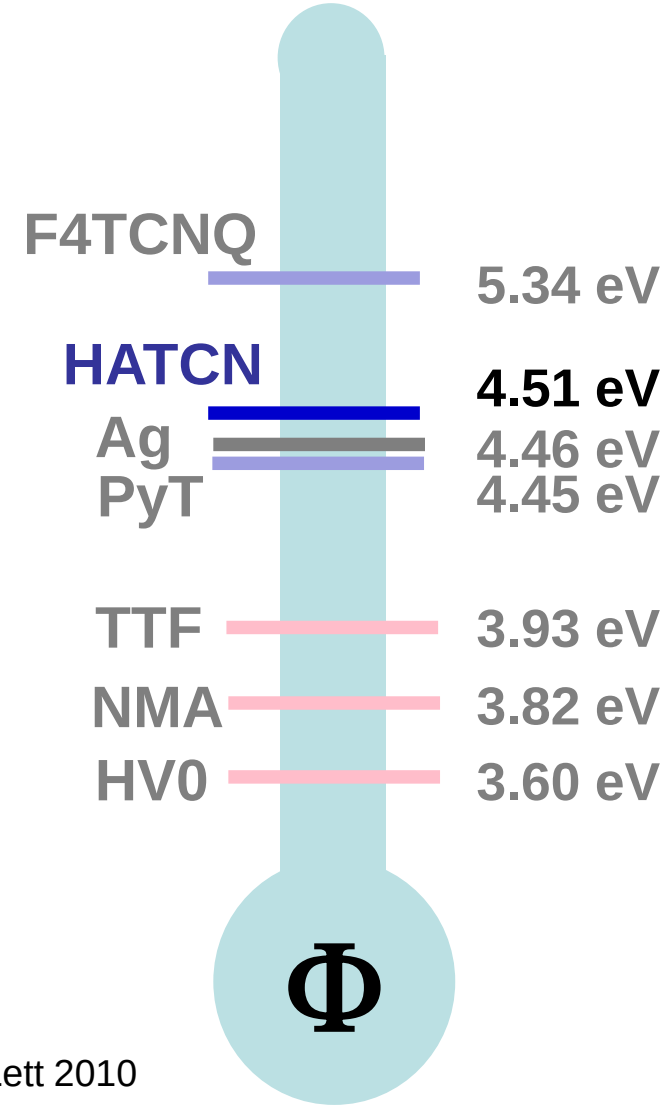
Example: Tune the work function Φ

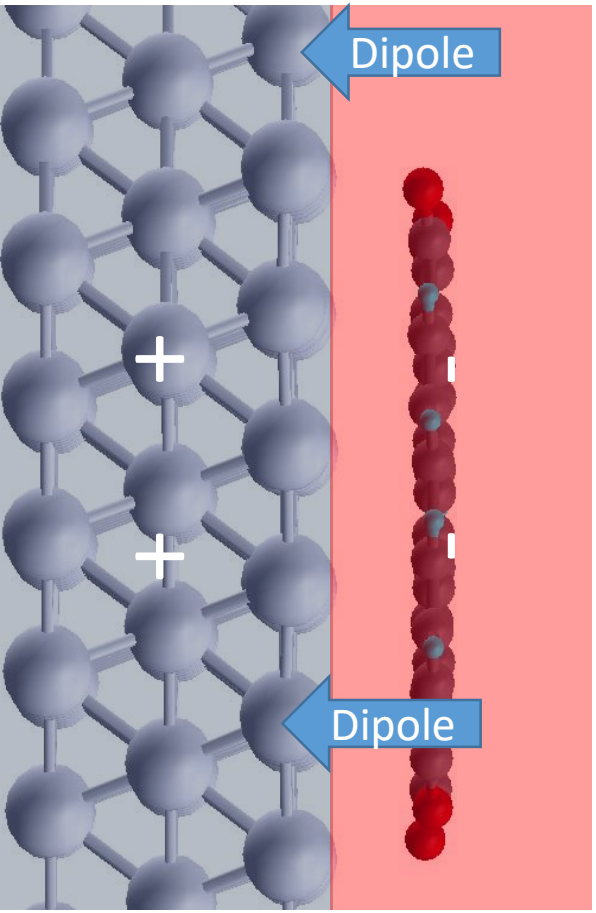
The outlier: HATCN

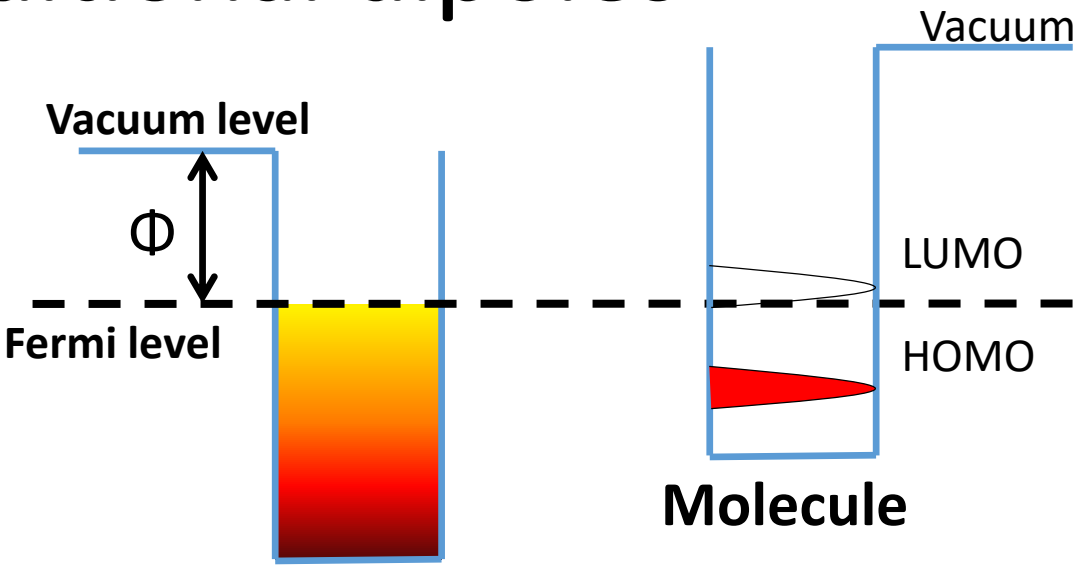




B. Bröker, OTH, G. Rangger, P. Frank, R.-P. Blum, et al., Phys. Rev. Lett 2010

Impact of additional dipoles





If the LUMO is below E_F, charge transfer ensues,
Until the LUMO is in resonance with E_F

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O.T. Hofmann, D.A. Egger, E. Zojer, Nano Lett. 10, 4369 (2010)

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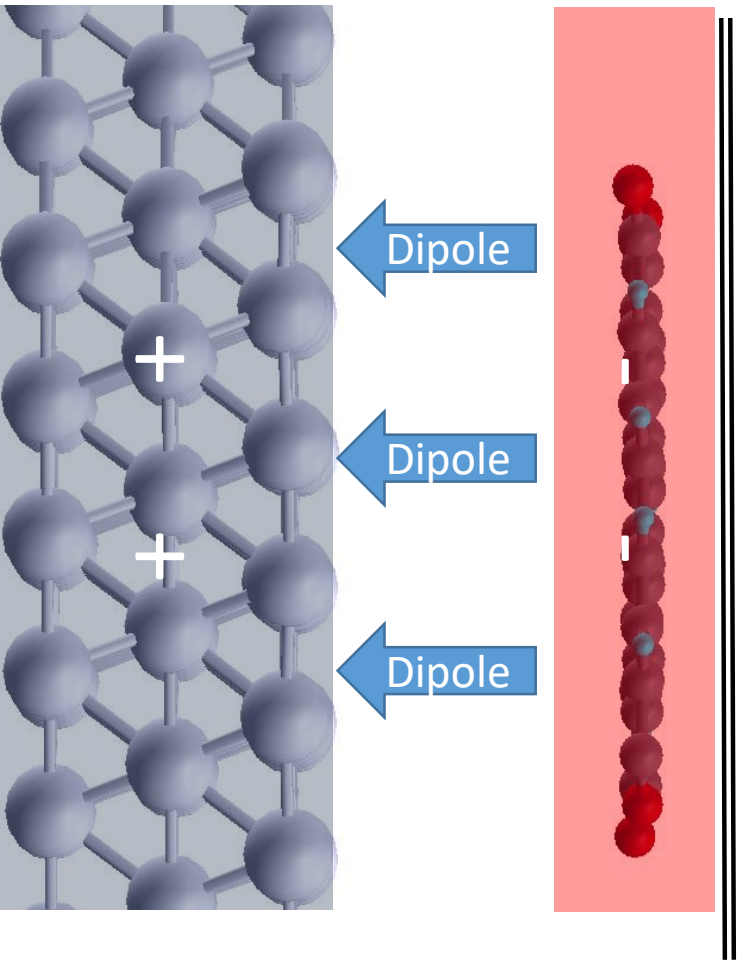
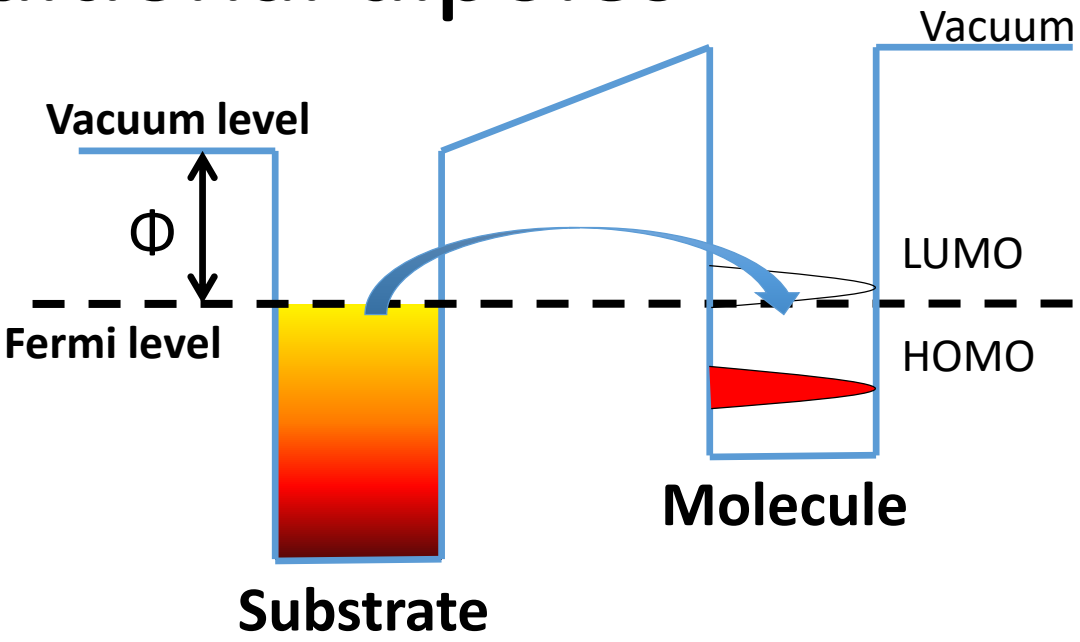


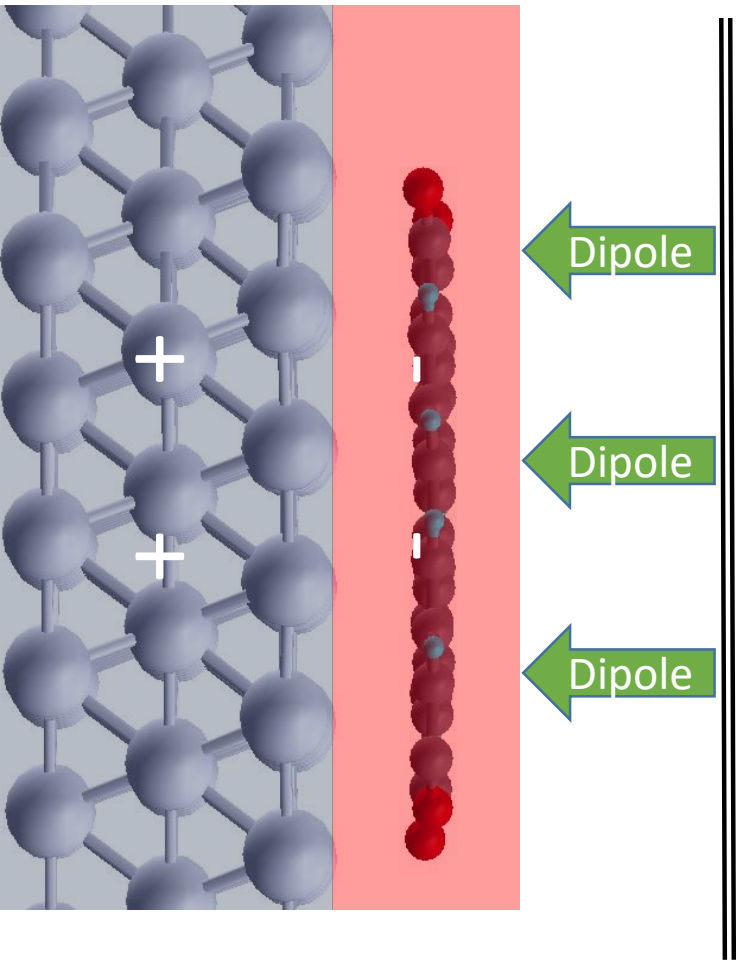


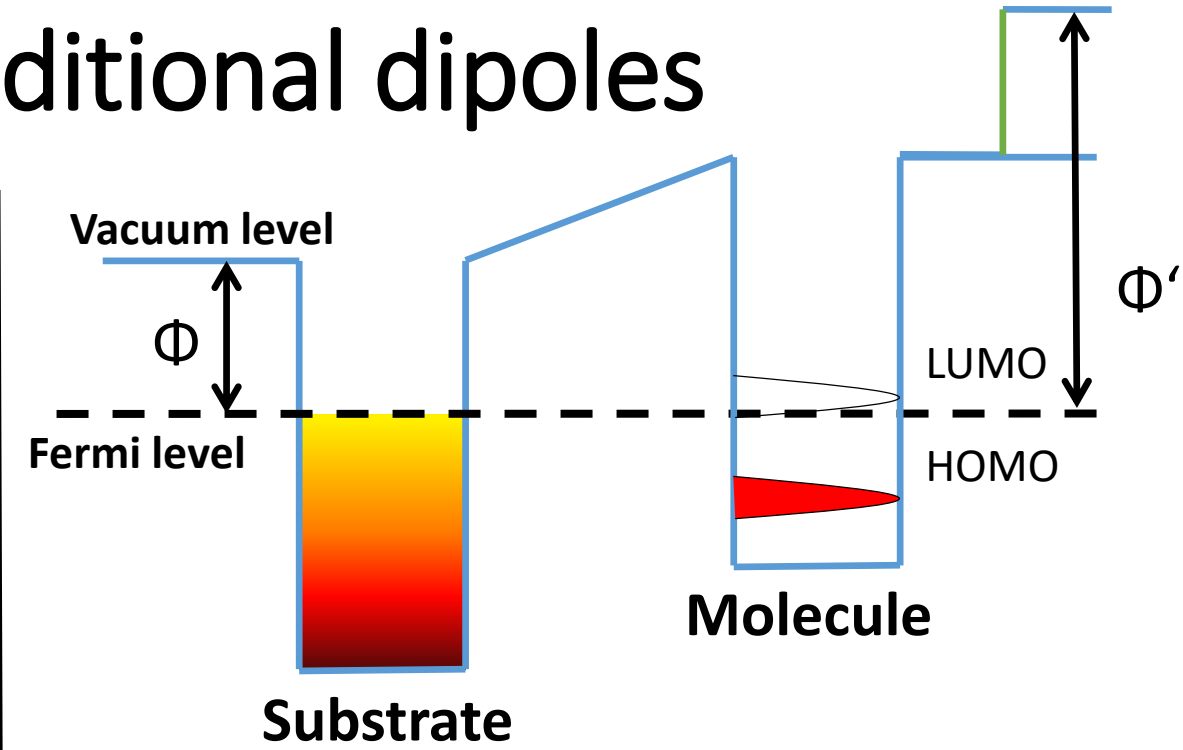
Dipoles between molecule and substrate:
Increased charge transfer cancels dipole

$$\Phi^{max} \approx \epsilon(LUMO)$$

O.T. Hofmann, D.A. Egger, E. Zojer, Nano Lett. 10, 4369 (2010)

Impact of additional dipoles





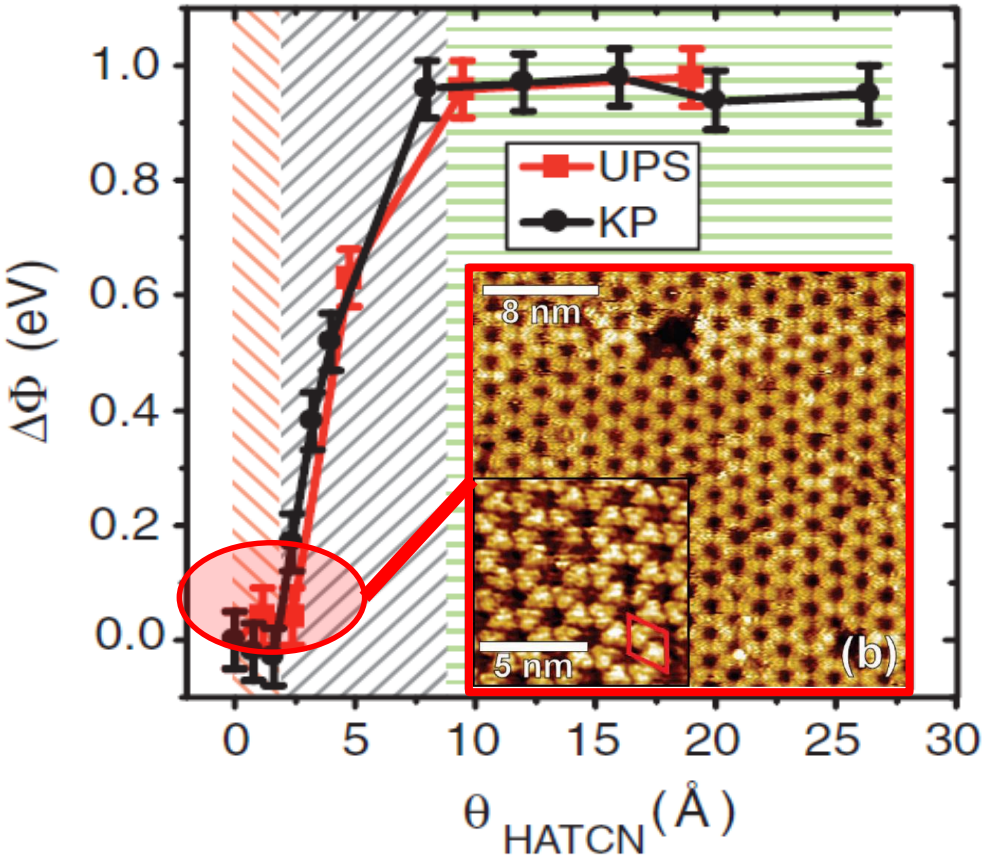
Dipoles outside molecule and substrate:
Change of LUMO energy w.r.t. vacuum

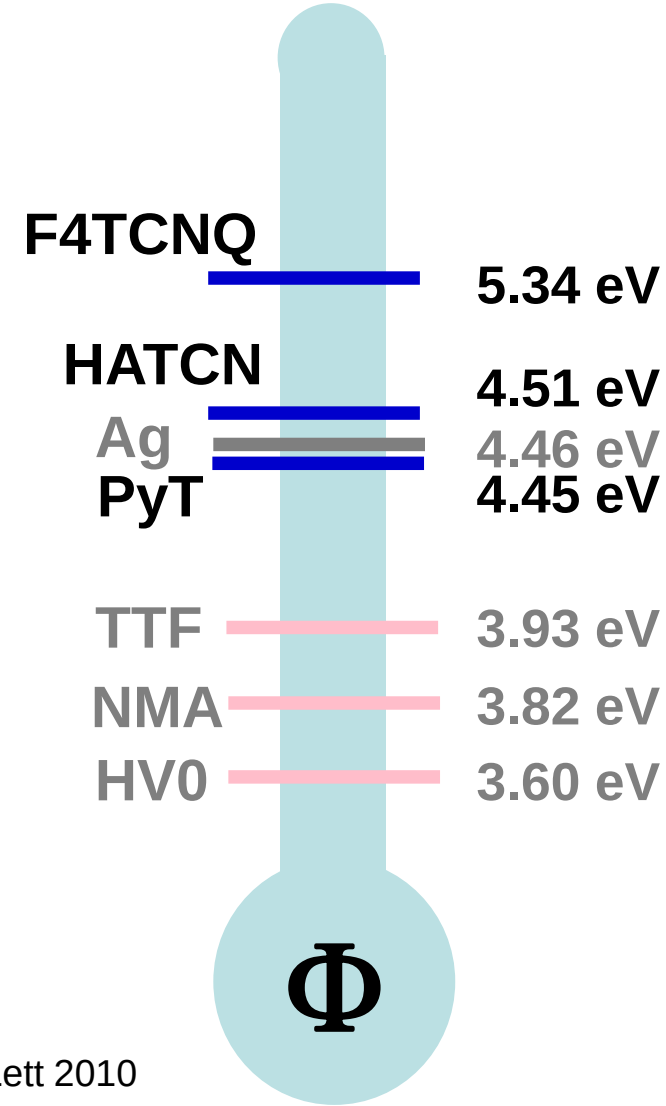
$$\Phi^{max} \approx \epsilon(LUMO)$$

O.T. Hofmann, D.A. Egger, E. Zojer, Nano Lett. 10, 4369 (2010)

Example: Tune the work function Φ

Theory and experiment agree well except for HATCN





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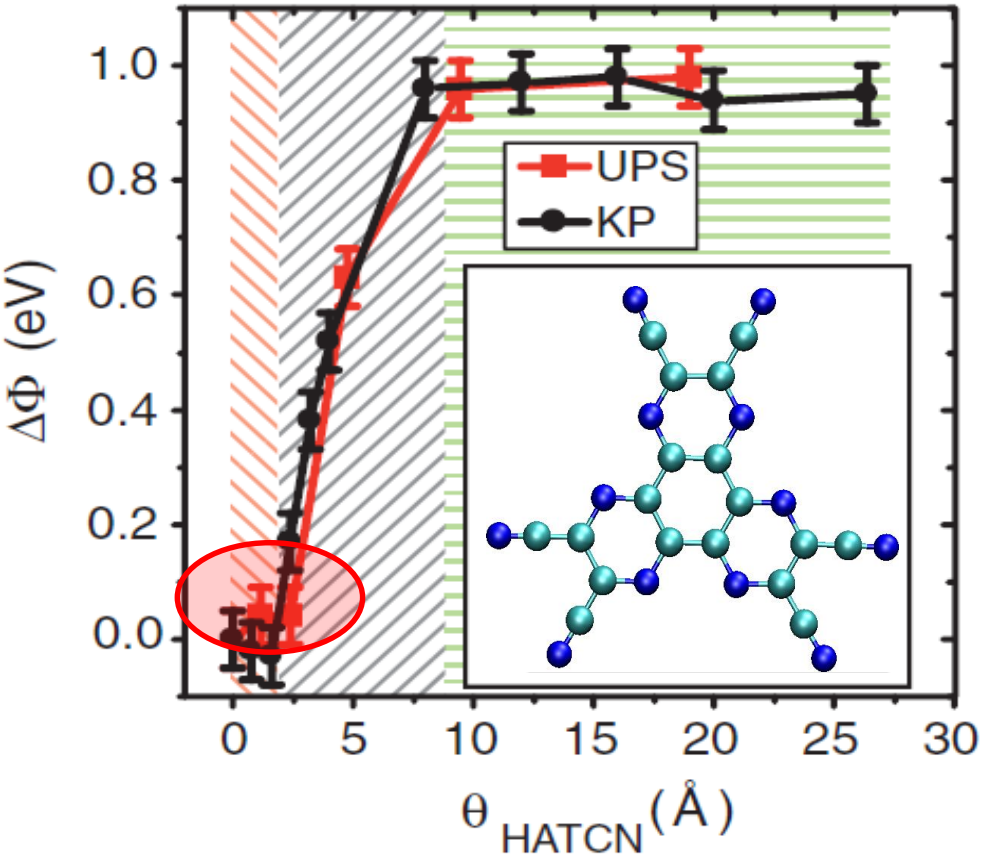
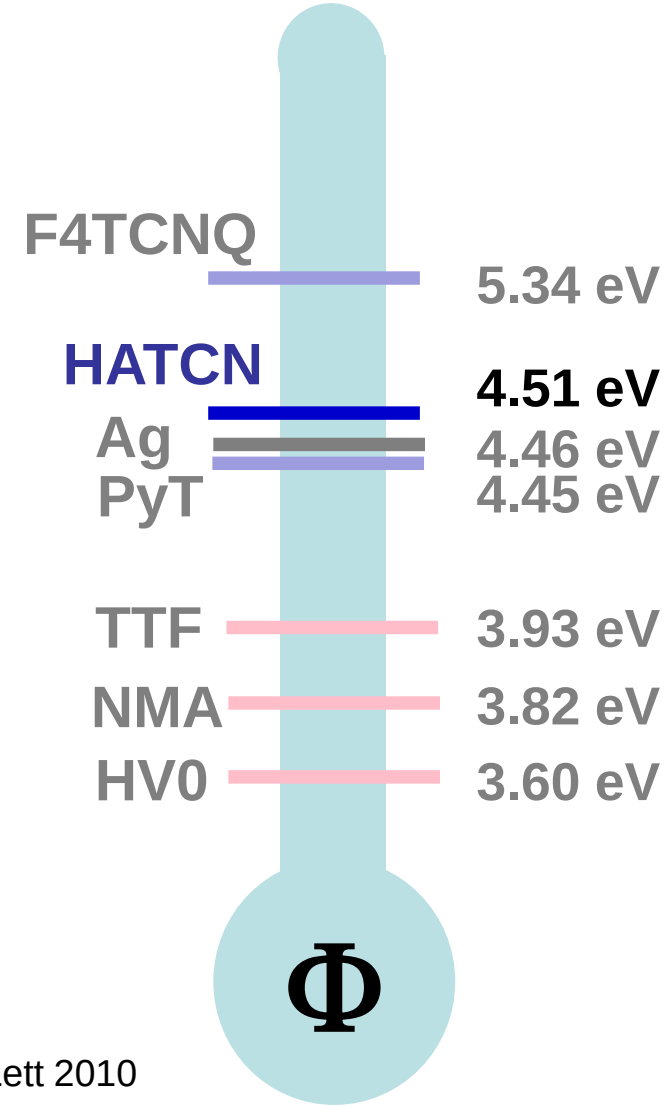
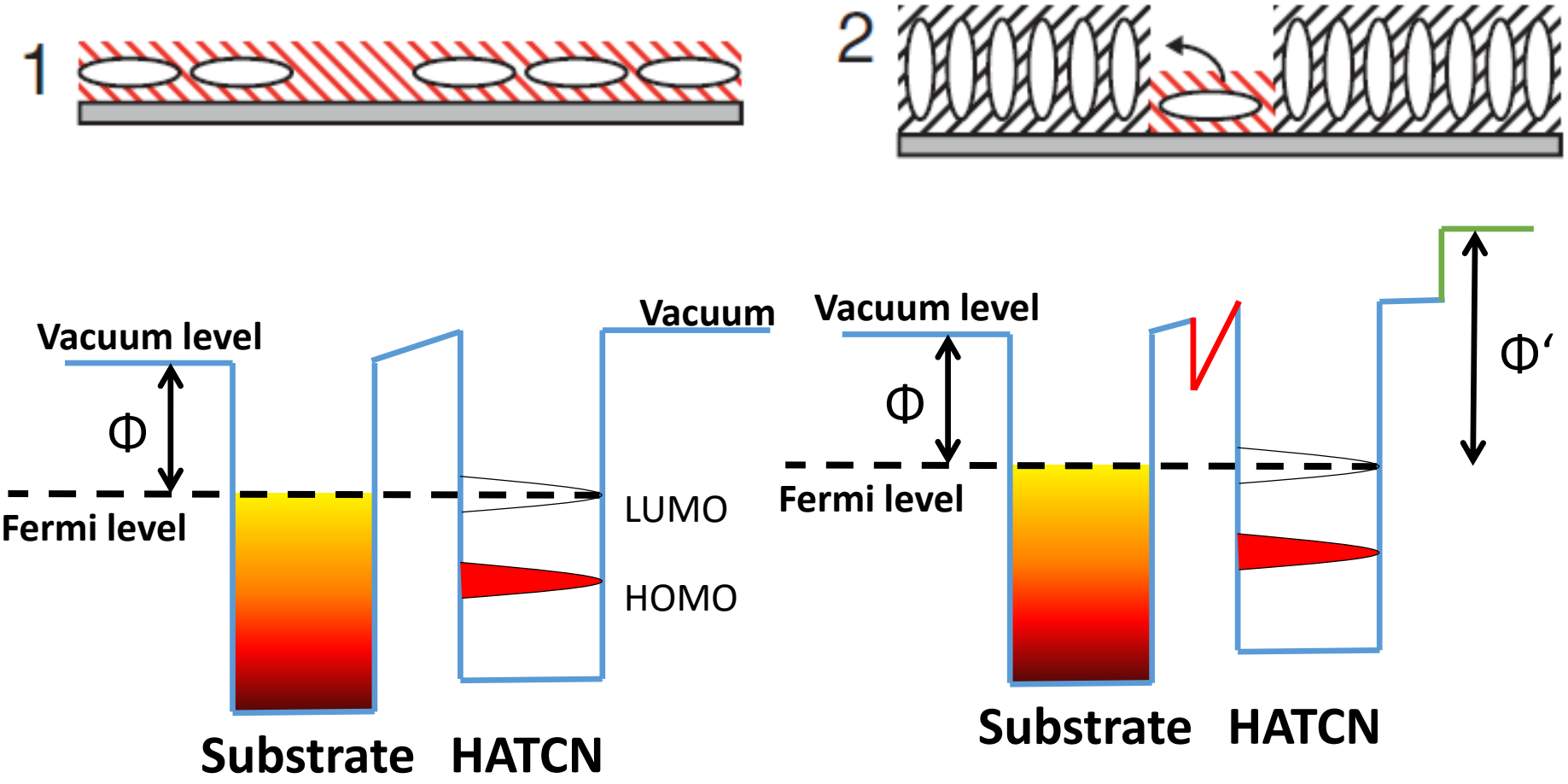




B. Bröker, OTH, G. Rangger, P. Frank, R.-P. Blum, et al., Phys. Rev. Lett 2010

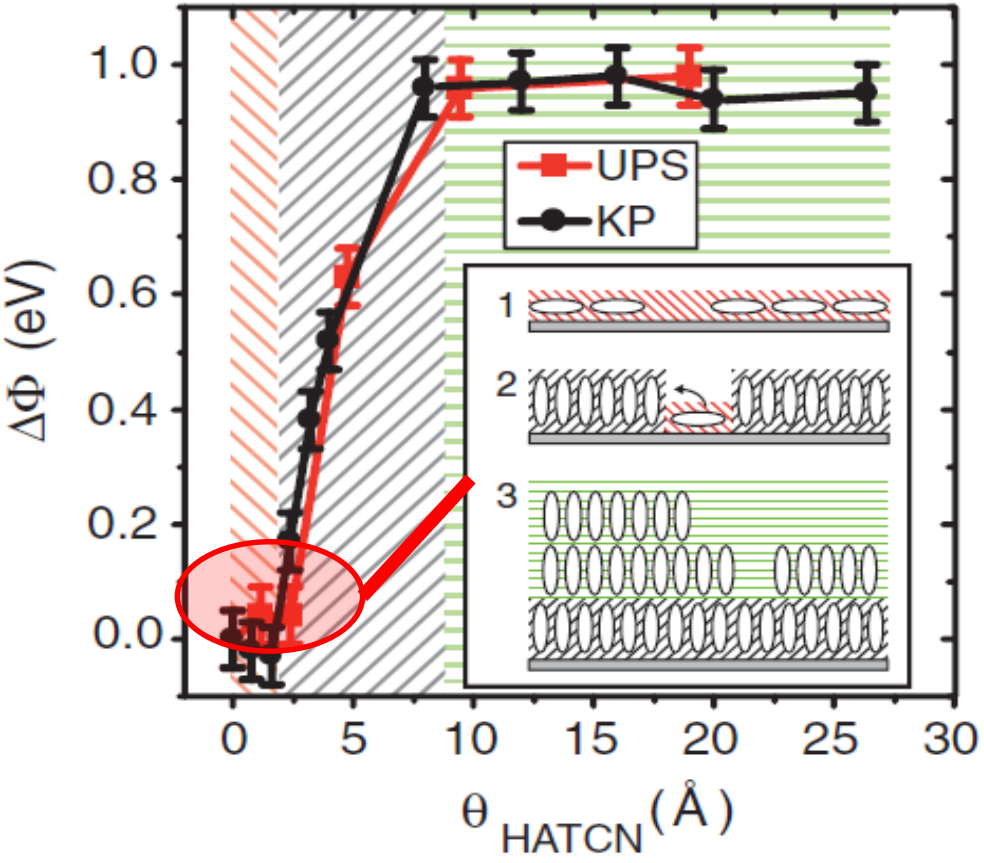
Is a phase transition responsible?

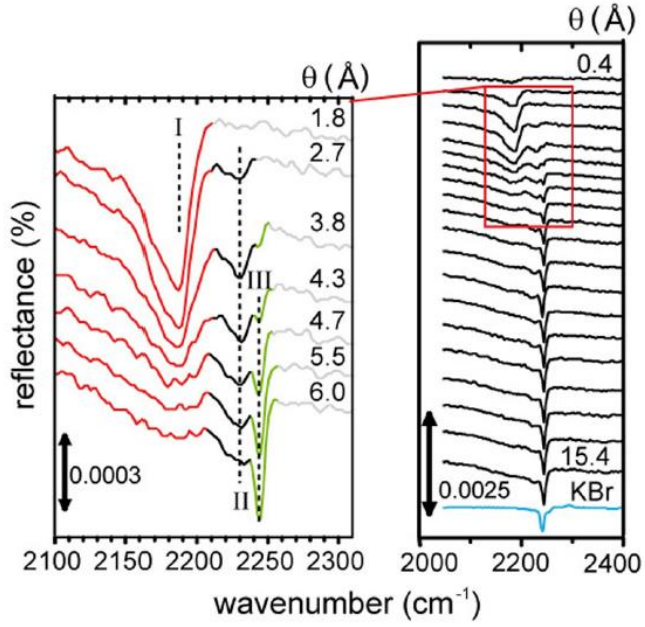


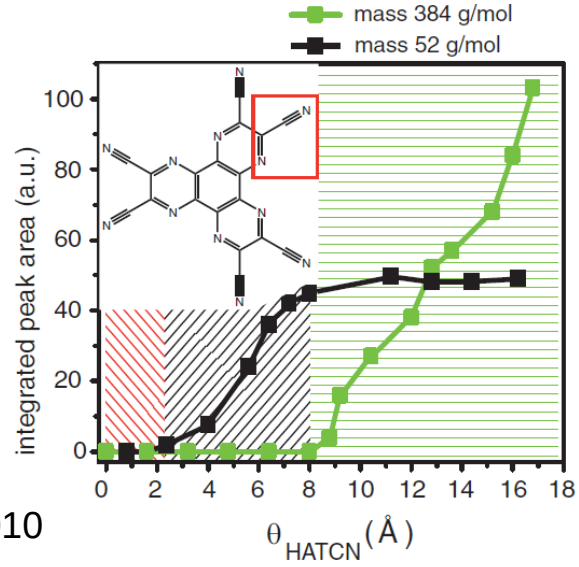
B. Bröker, O.T. Hofmann, G. M. Rangger, P. Frank, R.-P. Bum, R. Rieger, L. Venema, A. Vollmer, K. Müllen, J.-P. Raube, A. Winkler, P. Rudolf, E. Zojer, and N. Koch, Phys. Rev. Lett 2010, 104: 246805

Example: Tune the work function Φ

Theory and experiment agree well except for HATCN







B. Bröker, OTH, G. Rangger, P. Frank, R.-P. Blum, et al., Phys. Rev. Lett 2010

What did we learn?

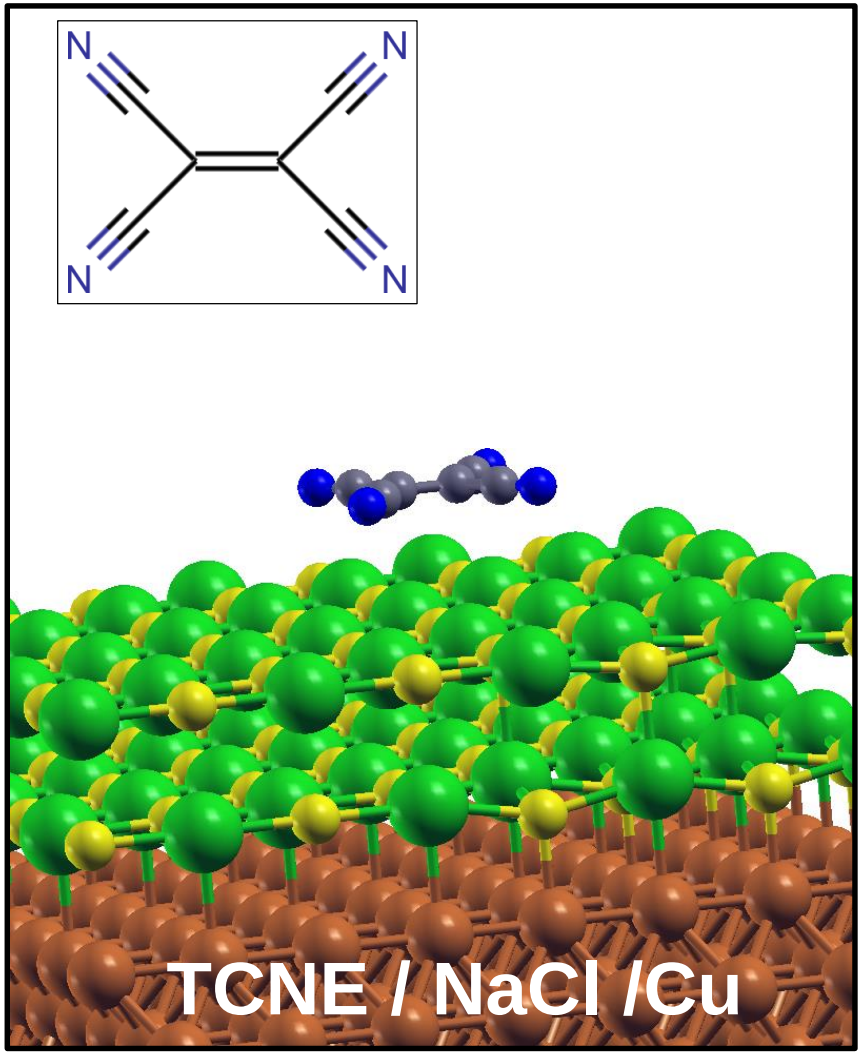
- **Coupling between charge-transfer and molecular dipoles**
- **Relevance of local dipoles in non-dipolar molecules**
- **Position of dipoles matters**

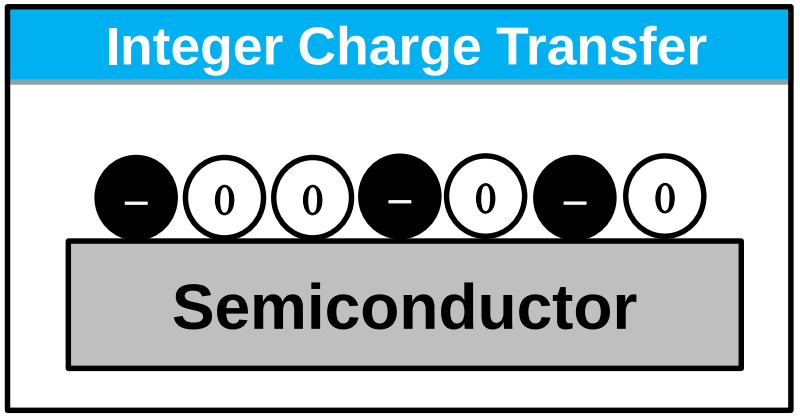
New Design Principles

OTH, D. Egger, E. Zojer, Nano Letters, 2010

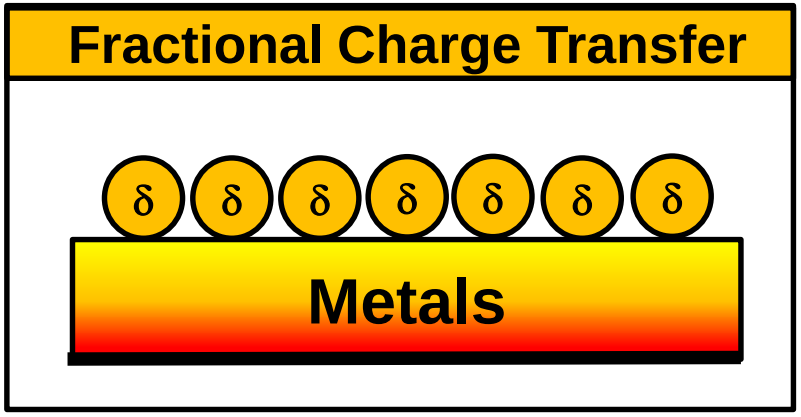
Importance of the atomistic structure

Other examples for structural relevance





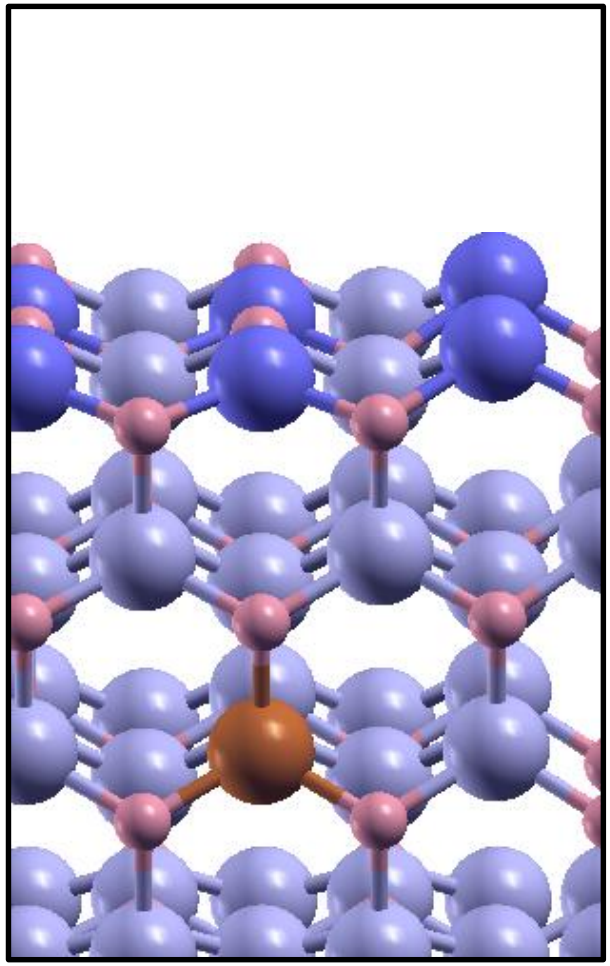
OR



OTH, P. Rinke, M. Scheffler, G. Heimel, ACS Nano, **2015**

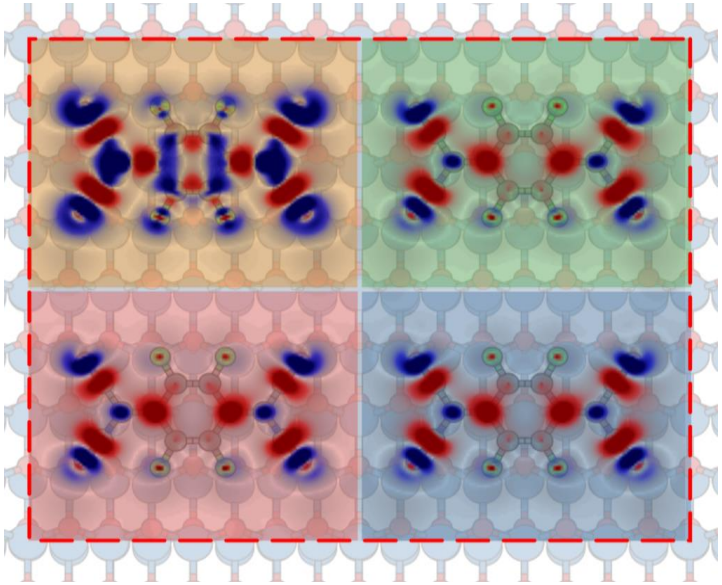
Other examples for structural relevance

Doping and surface reconstructions in semiconductors



O. Sinai, OTH, P. Rinke, M. Scheffler, et al., Phys. Rev. B., 2015
S. Erker, N. Moll, P. Rinke, OTH New J. Phys., 2017

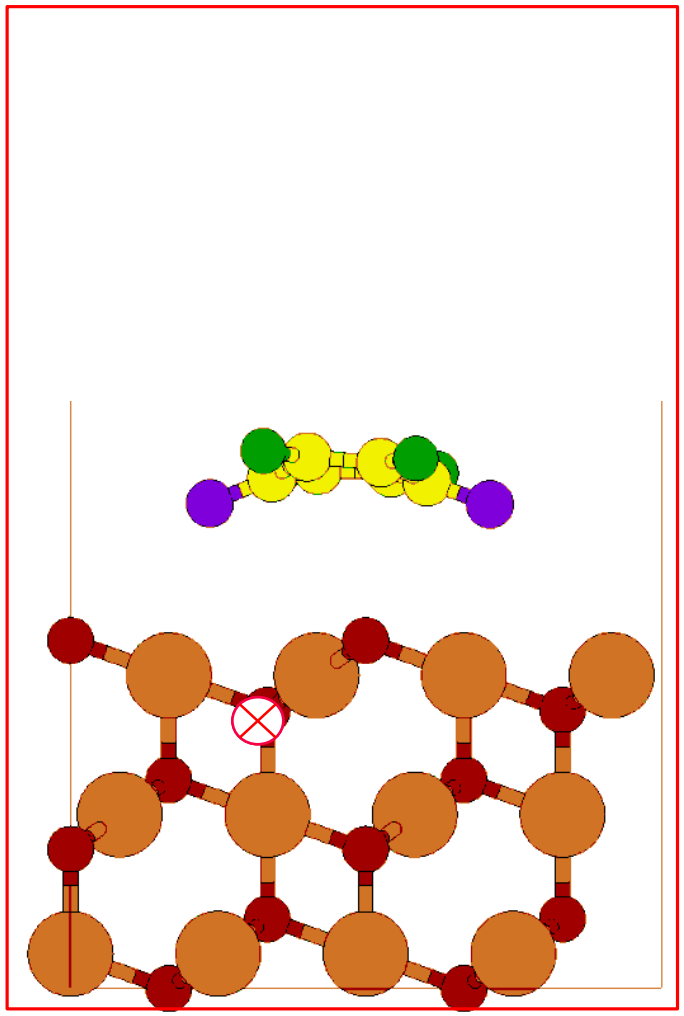
Amount and distribution of charge

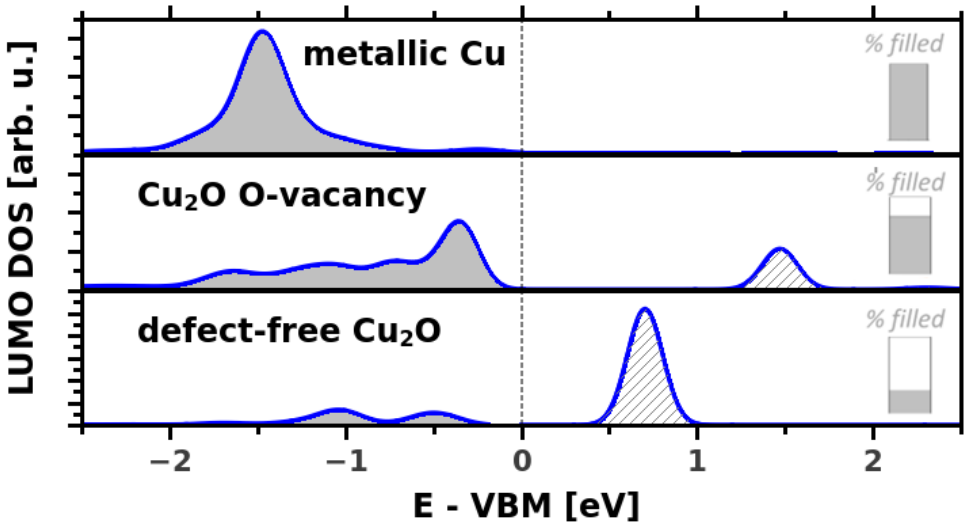


S. Erker and OTH, J. Phys. Chem. Lett. **10**, 848 (2019)

Y. Xu, OTH, R. Schlesinger, S. Winkler, et al., Phys. Rev. Lett. 2013

Defects in semiconductors

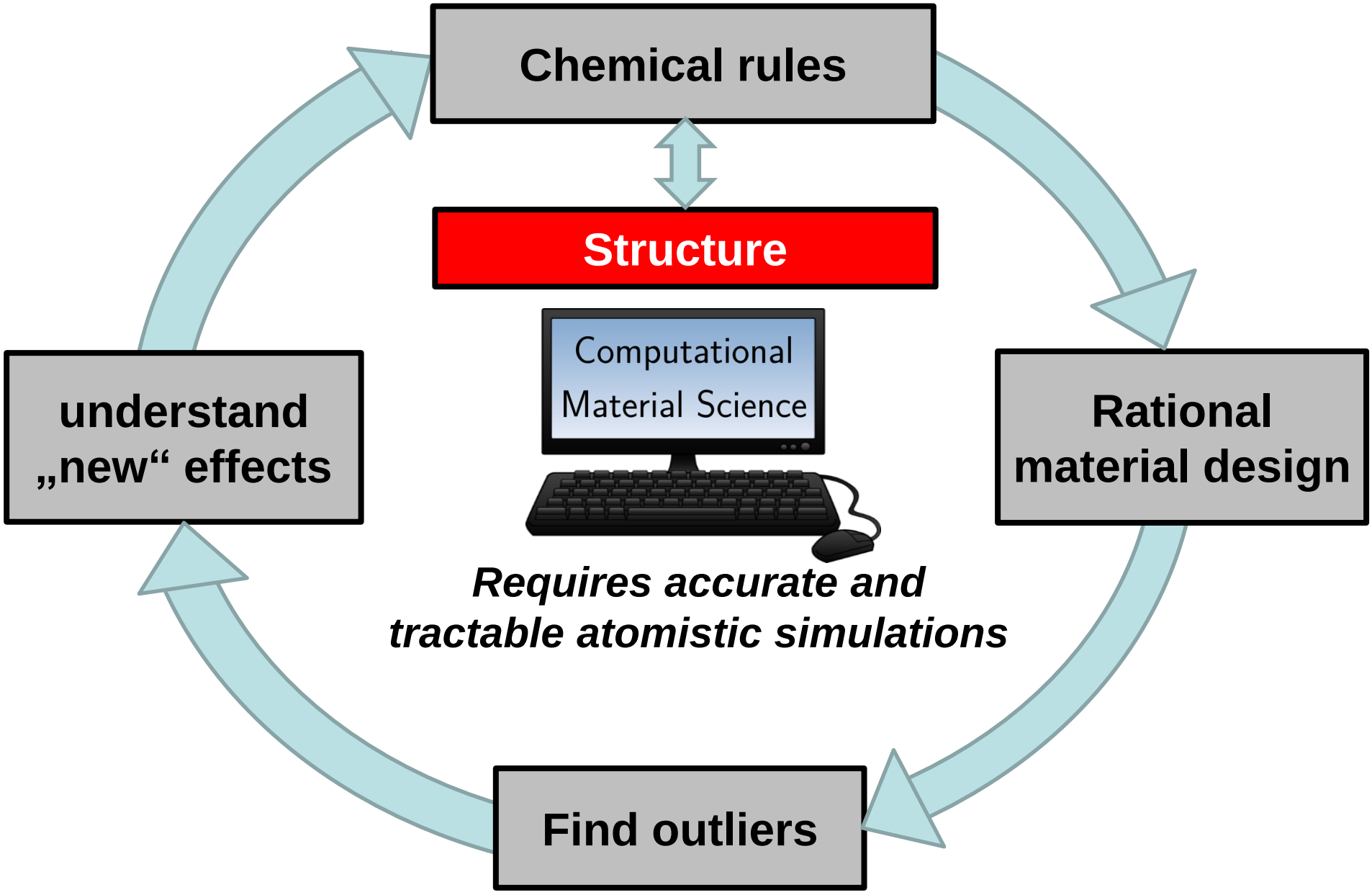




Surface defects mediate strong interaction

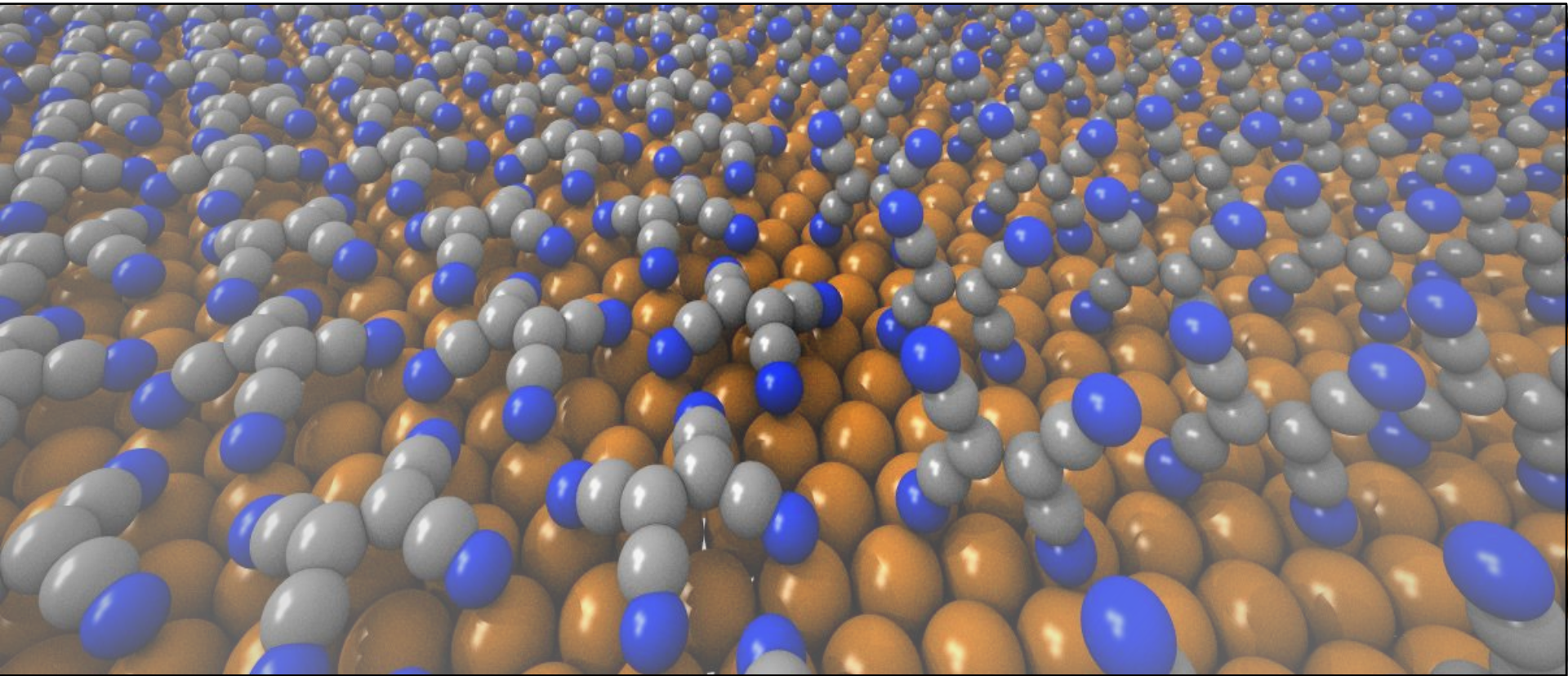
Charge transfer where conventional models predict none

E. Wruss, L. Hörmann and OTH, *JPCC, 2019*


Chemical rules
Structure
Computational
Material Science
Rational
material design
Find outliers
understand
„new“ effects
Requires accurate and
tractable atomistic simulations

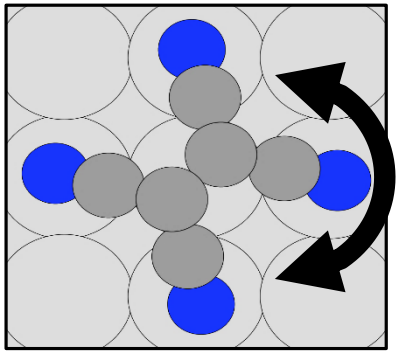
First principles structure determination

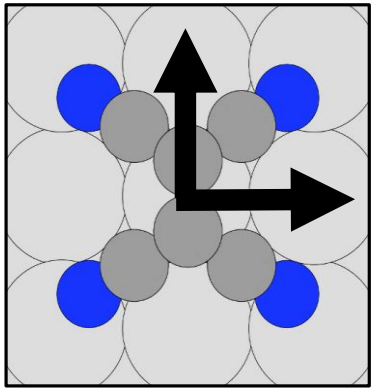
- is indispensable for material design
- allows tackling new scientific questions
- used to be impossible (at interfaces)



Structure Search at Interfaes

- Accuracy and computational cost
- Search strategies optimized for single molecules
- Stochastic
- Configuration êxplosion





For each molecule:

Translation x: $\sim$ **10 steps**
Translation y: $\sim$ **10 steps**
Rotation: $\sim$ **10 steps**
3 mol.: $(10 \times 10 \times 10)^3 = 1$ **billion**

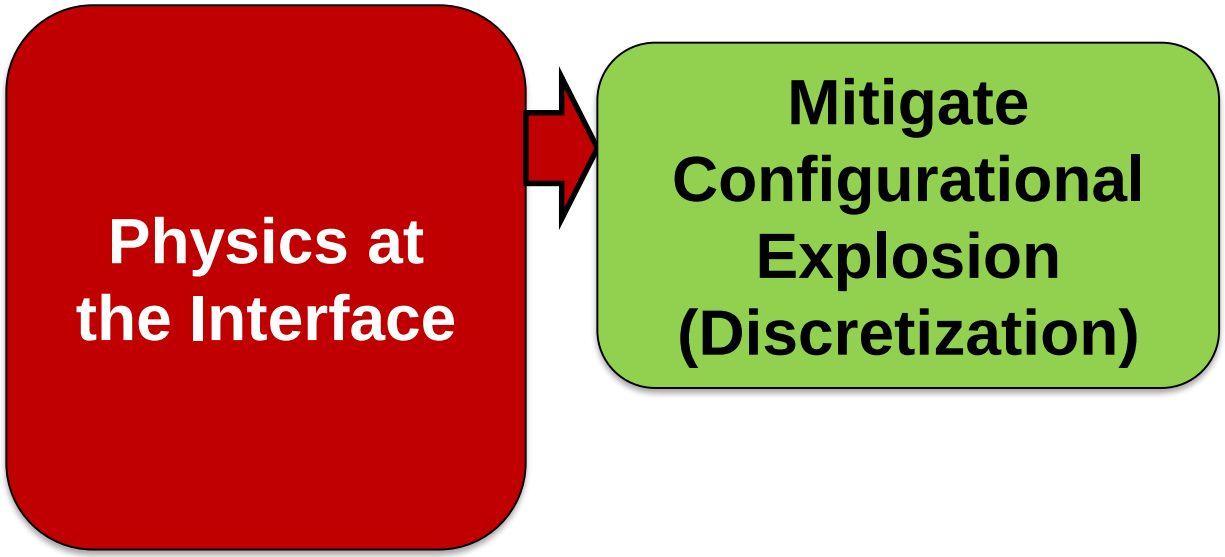
Different size and shape of unit cells compliate the problem further

Structure Search at Interfaes

- Accuracy and computational cost
- Search strategies optimized for single molecules
- Stochastic
- Configuration explosion

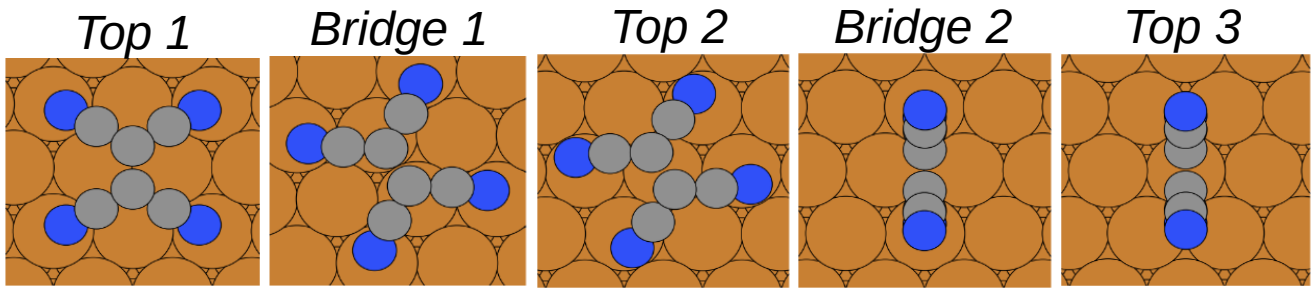
Solution: **Exploit physics at the interface**

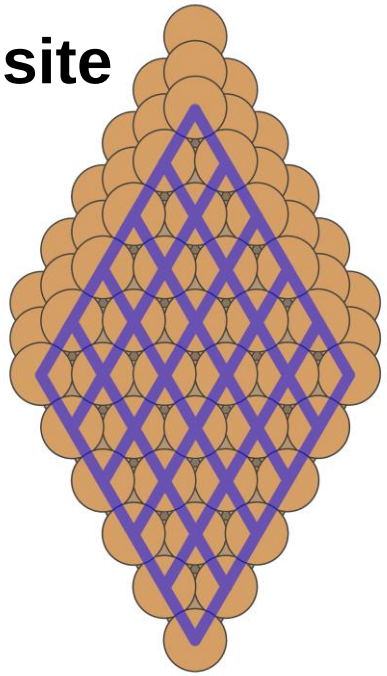
arXiv:1811.11702


Physics at the Interface
Mitigate Configurational Explosion (Discretization)

Physically motivated coarse-graining

- **Each molecule sits in dedicated adsorption site**



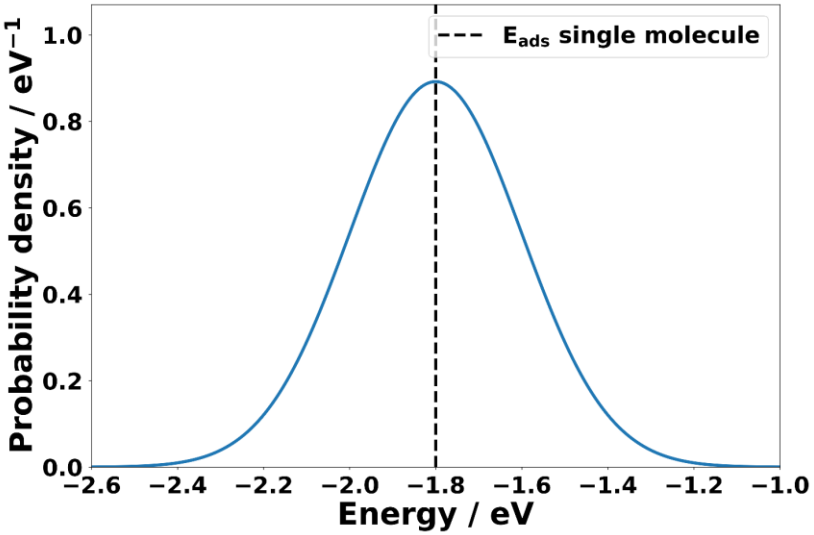


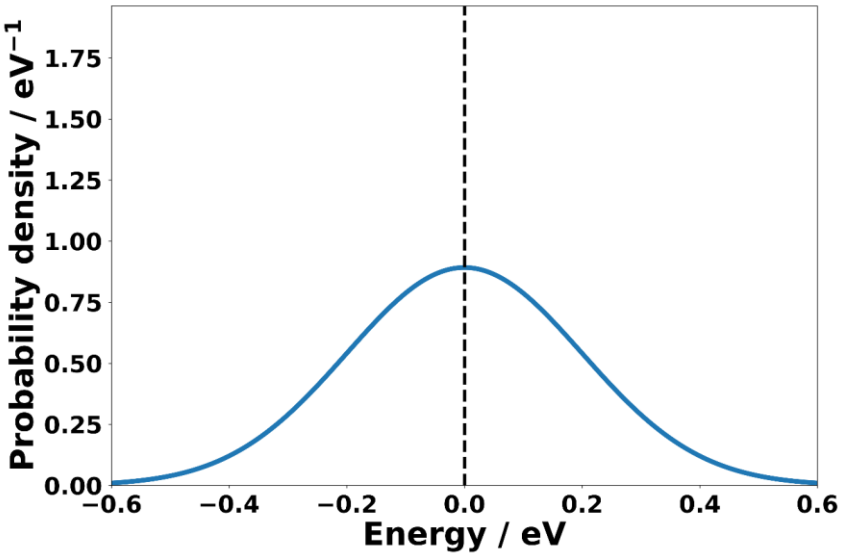
- **Place molecules onto grid**

Result:

List of Polymorph Candidates (typically a few 100.000)

Too many for DFT → **Machine Learning**

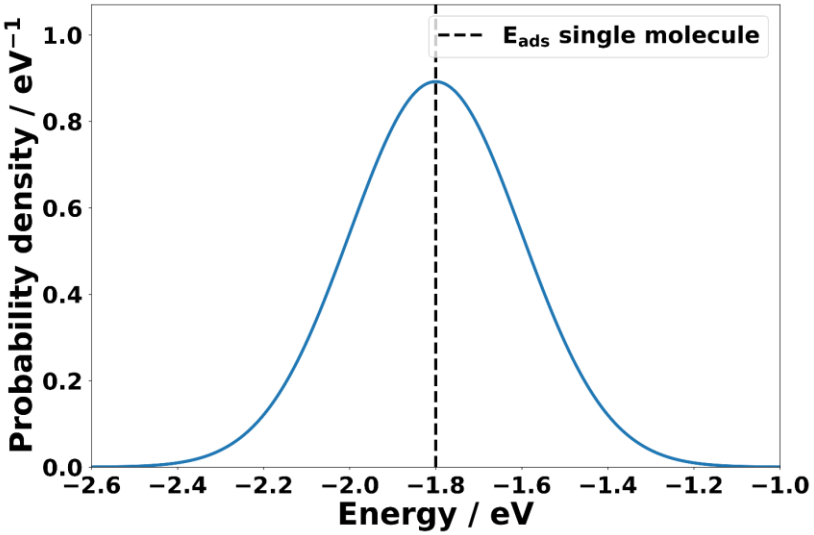


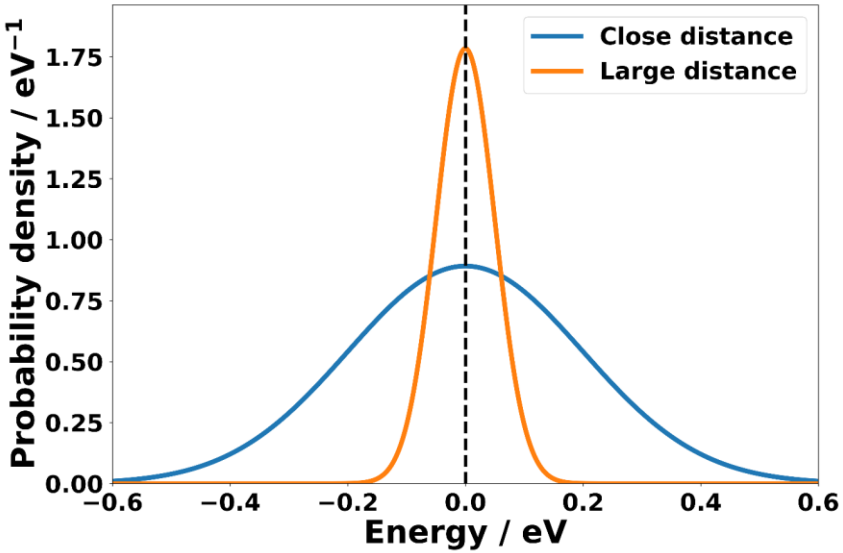


$$\mathbf{E} = \sum_{\mathbf{i}} \mathbf{n_i U_i} + \sum_{\mathbf{p}} \mathbf{n_p V_p}$$

Similar to isolated molecule

Individual terms are small





$$\mathbf{E} = \sum_{i} \mathbf{n_i U_i} + \sum_{p} \mathbf{n_p V_p}$$

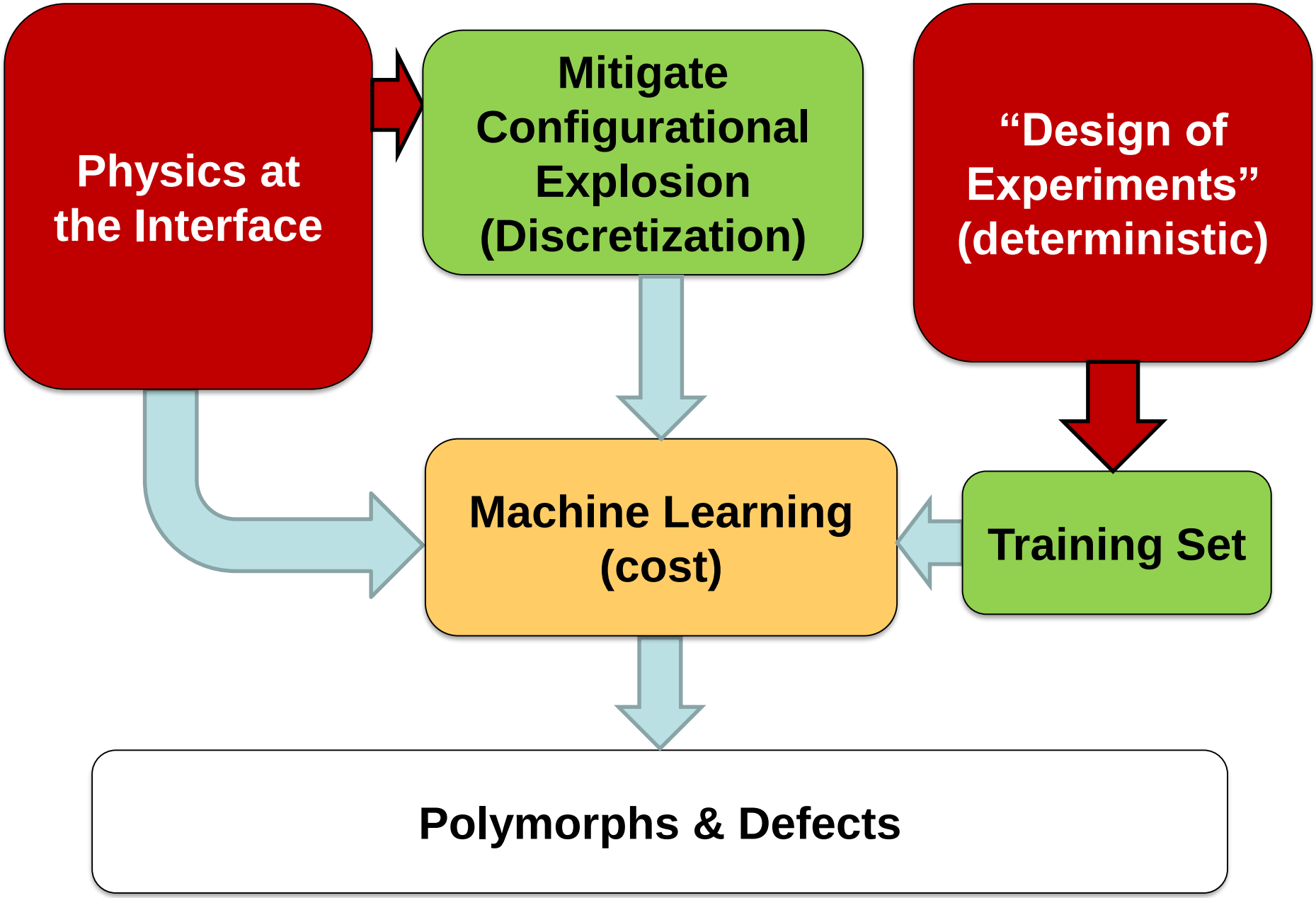
Similar to isolated molecule

Individual terms are small

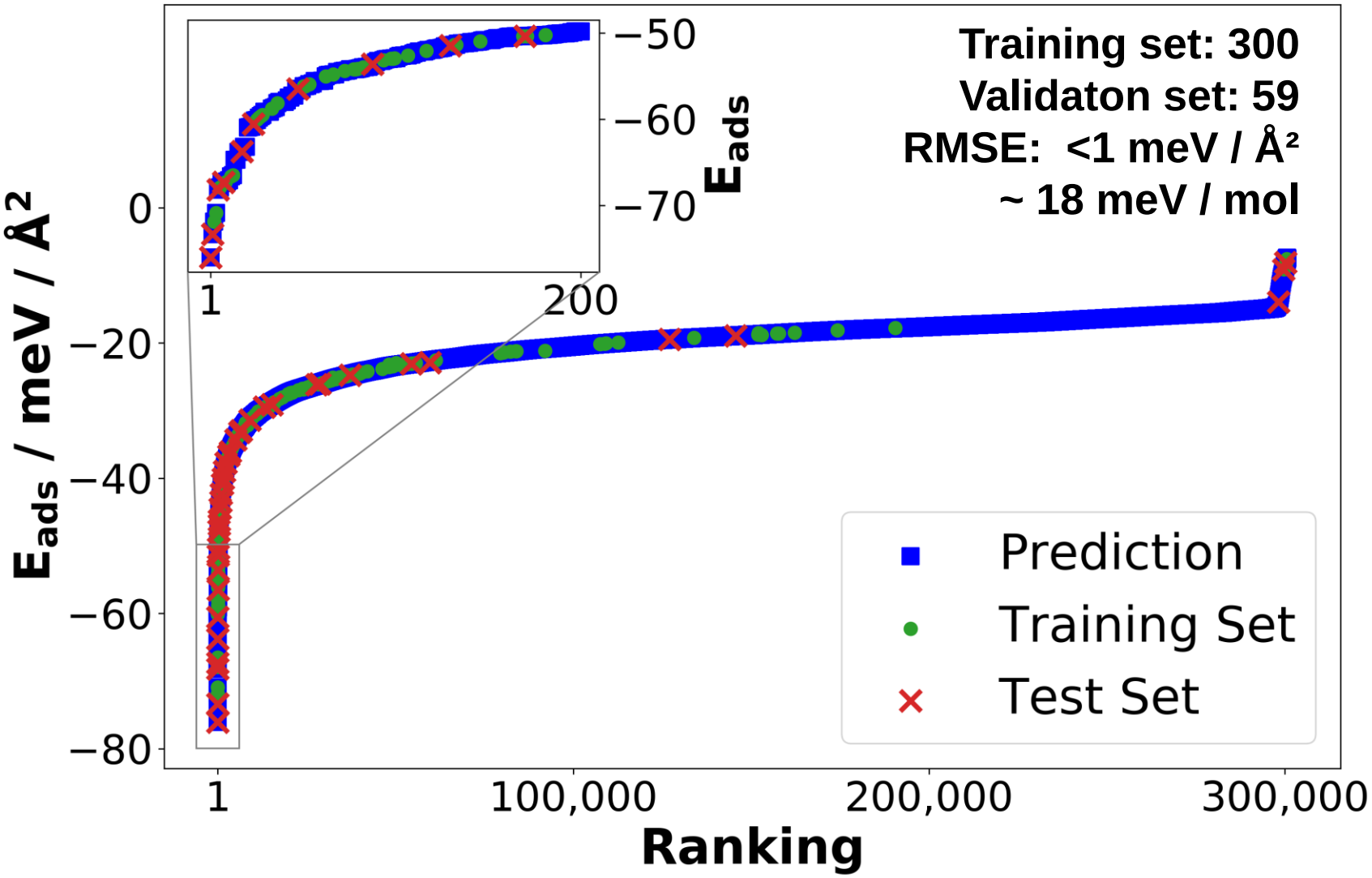
Larger distance → less interaction

Similar structures → similar interaction

SAMPLE

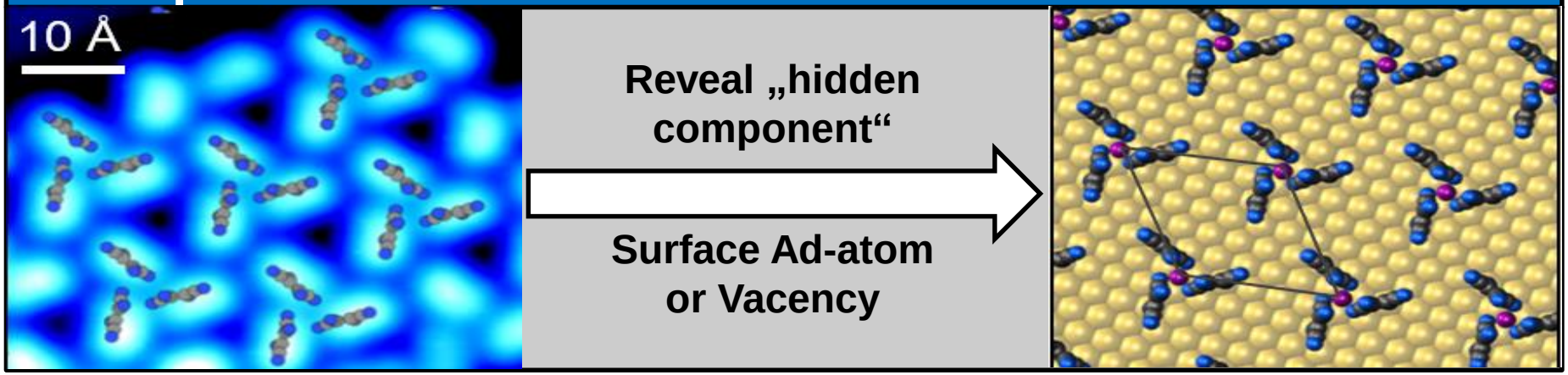

Physics at the Interface
Mitigate Configurational Explosion (Discretization)
“Design of Experiments” (deterministic)
Machine Learning (cost)
Training Set
Polymorphs & Defects

Machine Learning Performance



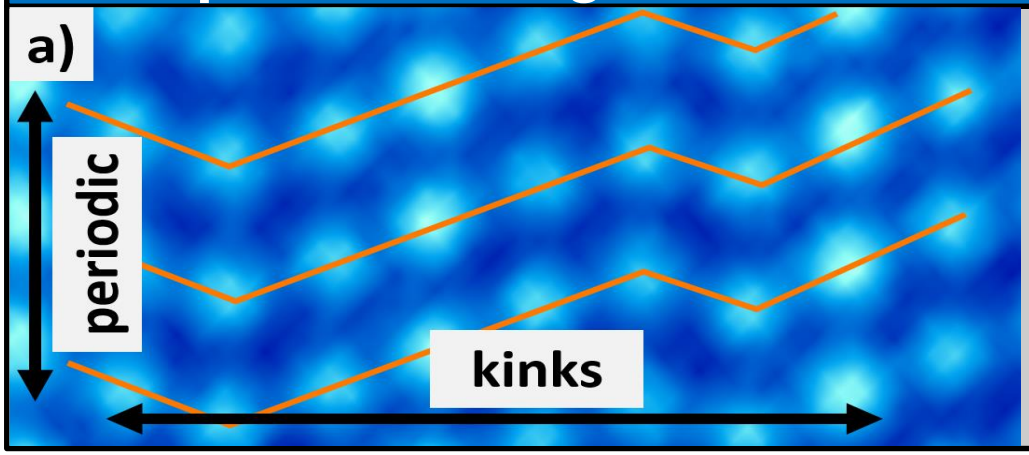
Sucessful Applications

Example: TCNE/Au



V. Obersteiner, M. Scherbela, L. Hörmann, D. Wegner, OTH, *Nano Lett.*, 2017

Example: TCNE/Ag



Explain interplay of

- **Molecule-substrate interaction**
- **Molecule-molecule interaction**
- **Close packing**
- **Symmetry**

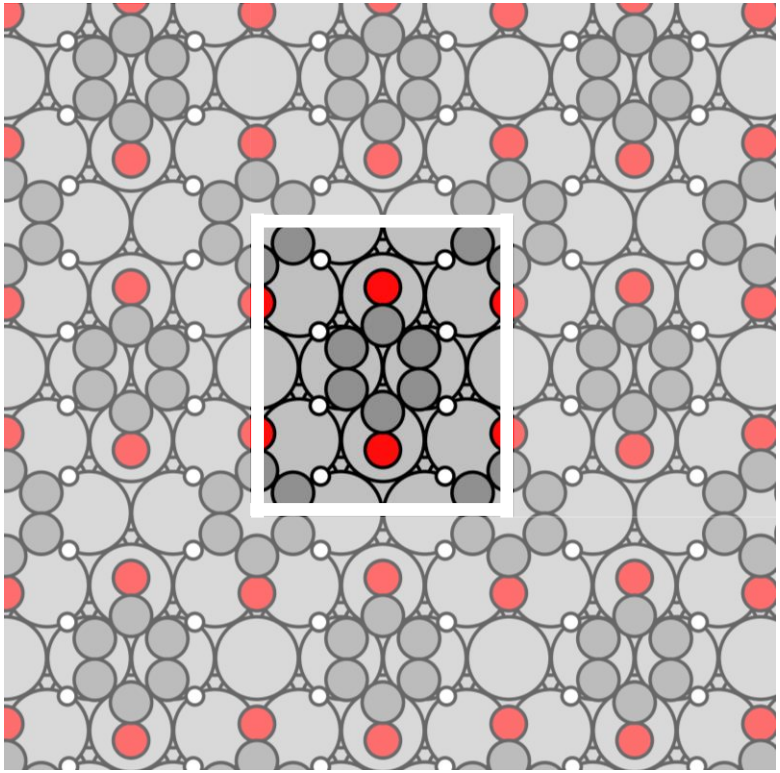
M. Scherbela, L. Hörmann, A. Jeindl, V. Obersteiner, OTH, Phys. Rev. Materials, 2018

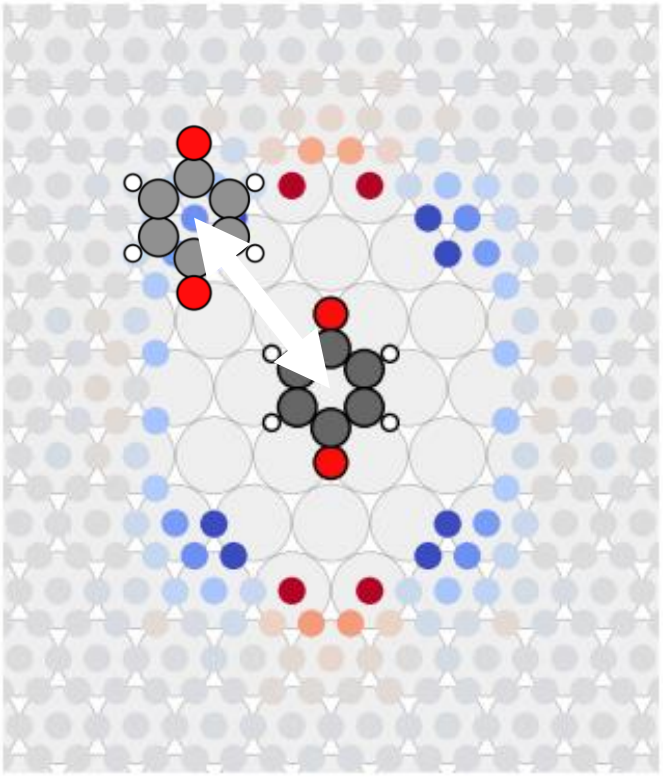
First principles structure determination

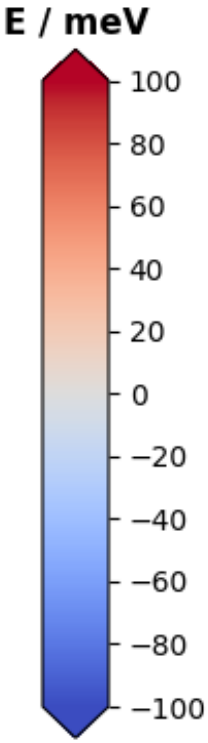
- is indispensable for material design
- allows tackling new scientific questions
- ~~used to be impossible (at interfaces)~~

- Obtain physical insight
- Obtain control over structure

Intermolecular interactions

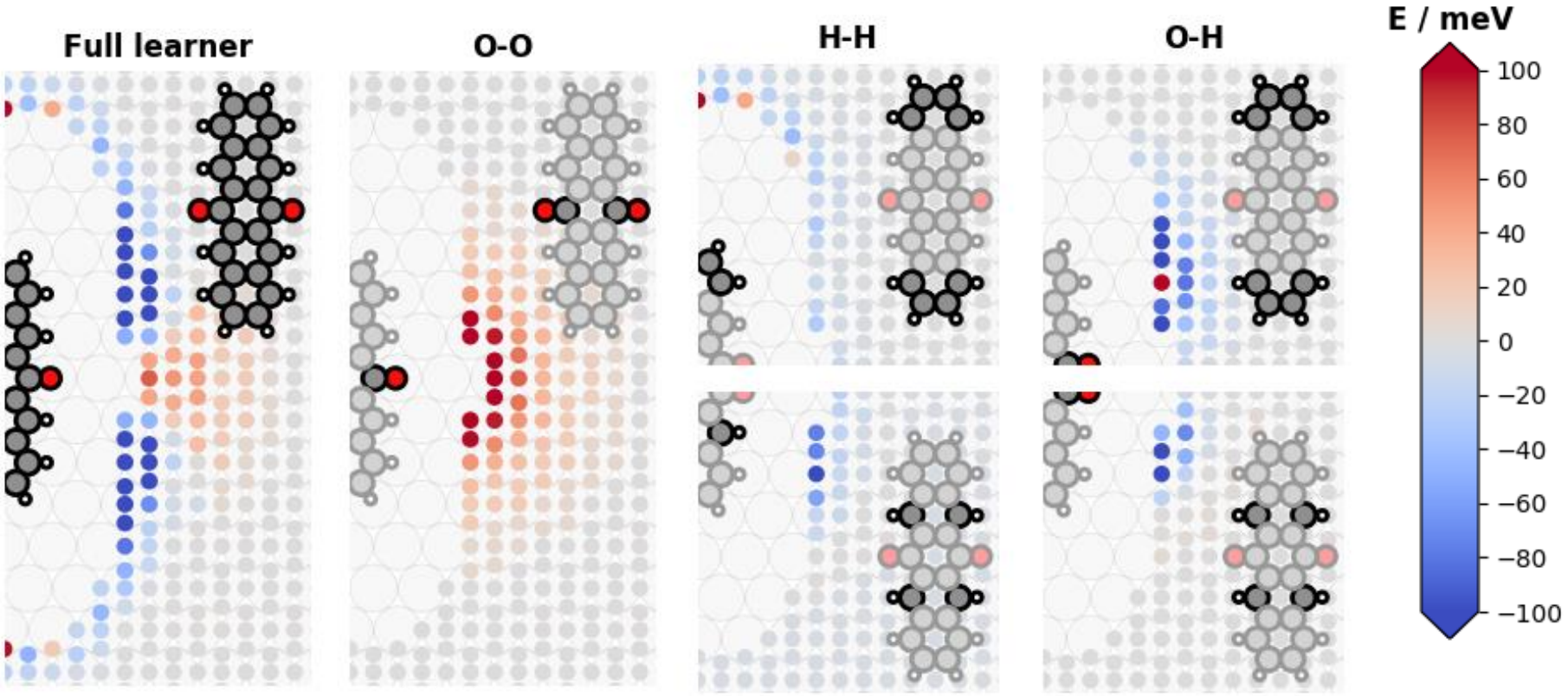






A. Jeindl et al., in preparation

Mapping on Molecule Parts



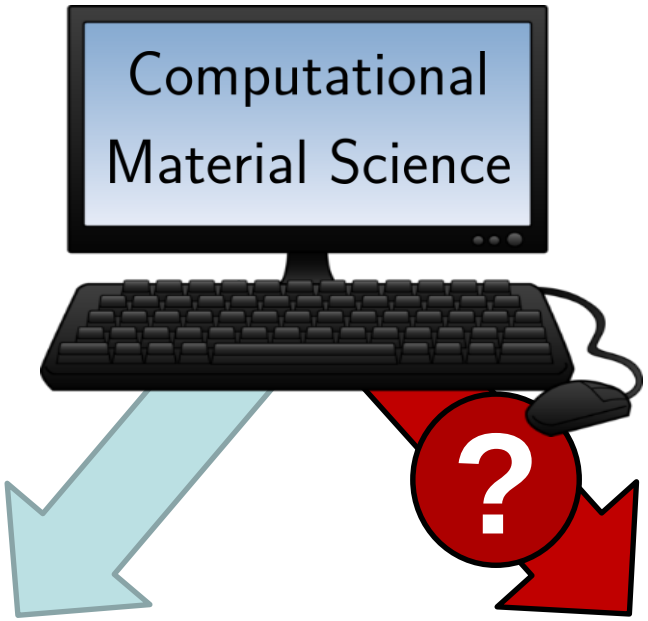
<u>Target</u>:

Obtain a library of interactions

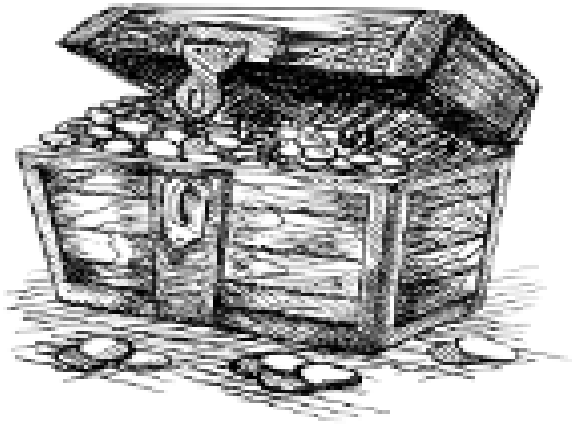
Combine molecular fragements

Design potential energy surface / polymorphs

A. Jeindl et al., in preparation



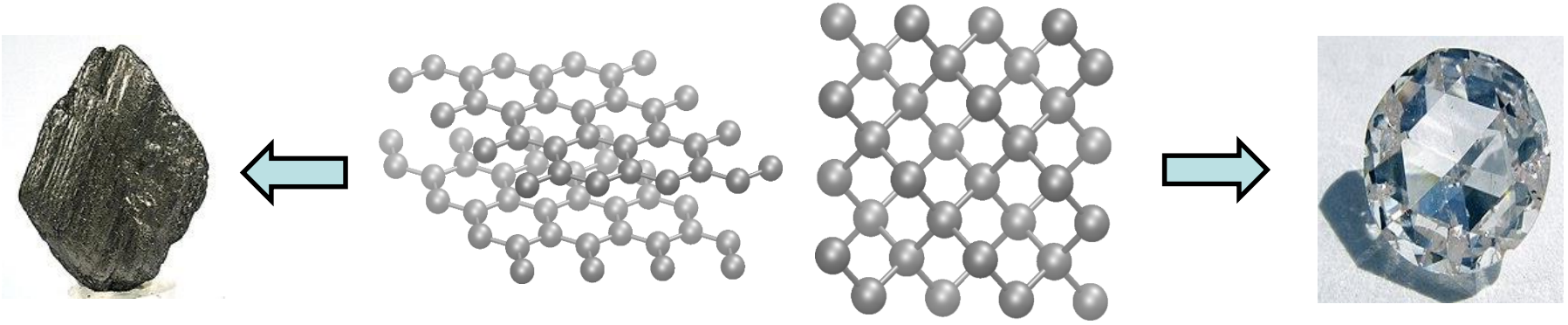
Find „hidden treasure“



… and how to get there

The chemical route: Change composition

The physical route: Change atomistic arrangement (polymorphism)

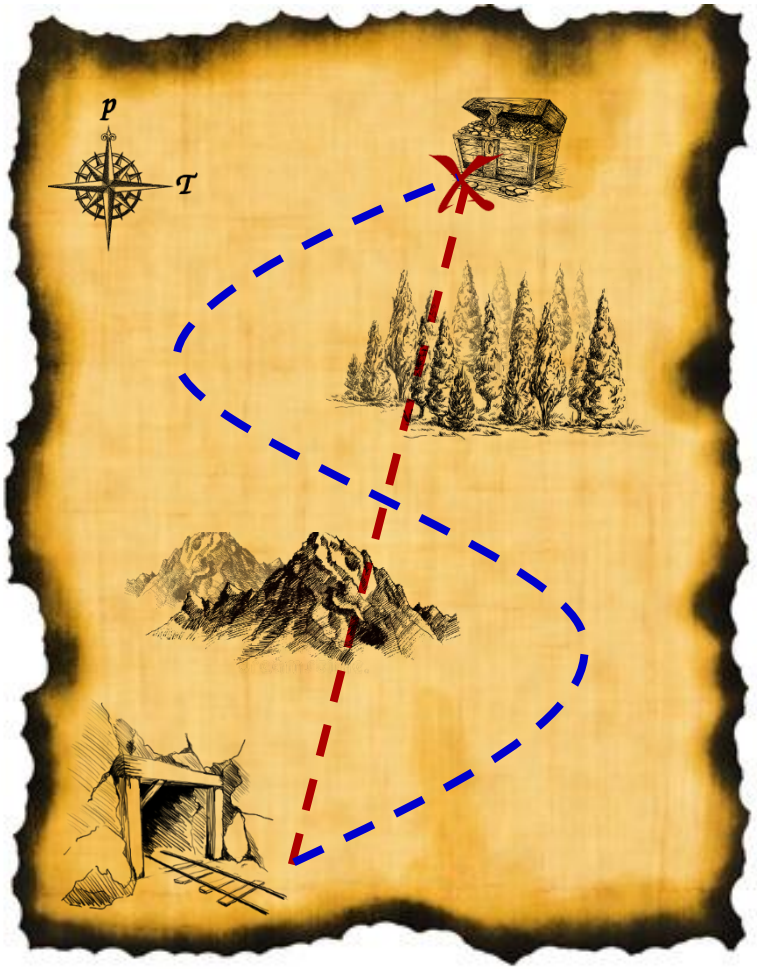


Metastable materials often superior!

How can they be made experimentally?

Approach – The Map Analogy

To create a map, we need

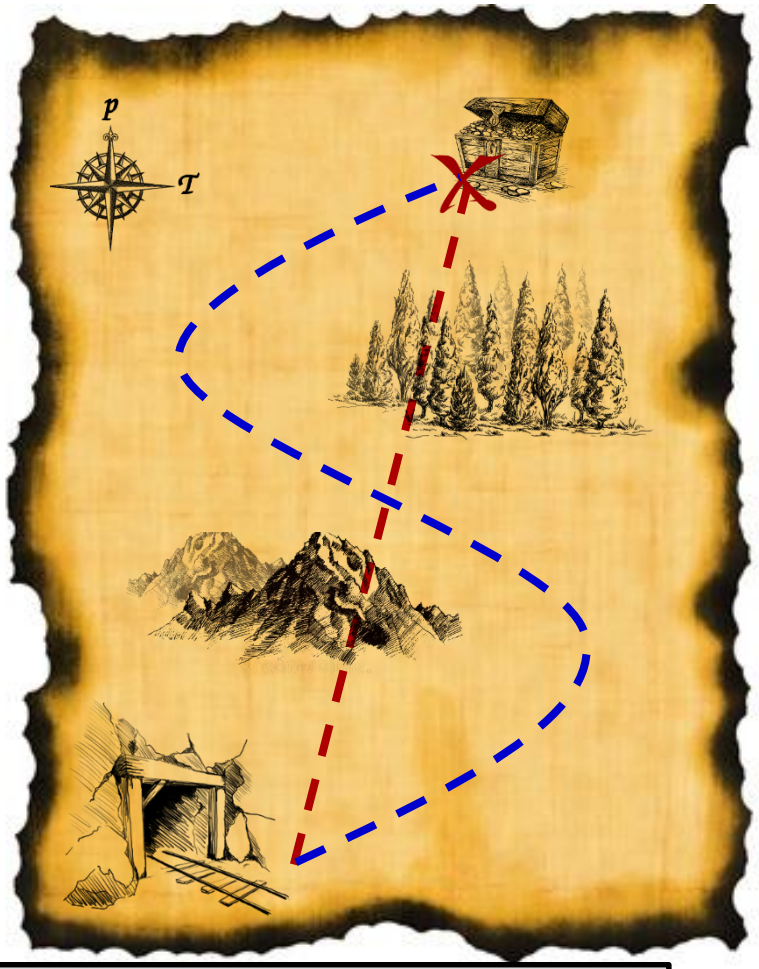


- the destination
  - excels at desired property
  - sufficient lifetime (metastable)
  - experimentally attainable
- a route
  - robust, reproducible start
  - directions (substrate, temperature, solvent, pressure, ...)
  - avoid barriers and unwanted transitions
  - minimize effort / maximize gain

Approach – The Map Analogy

The Challenge

need for



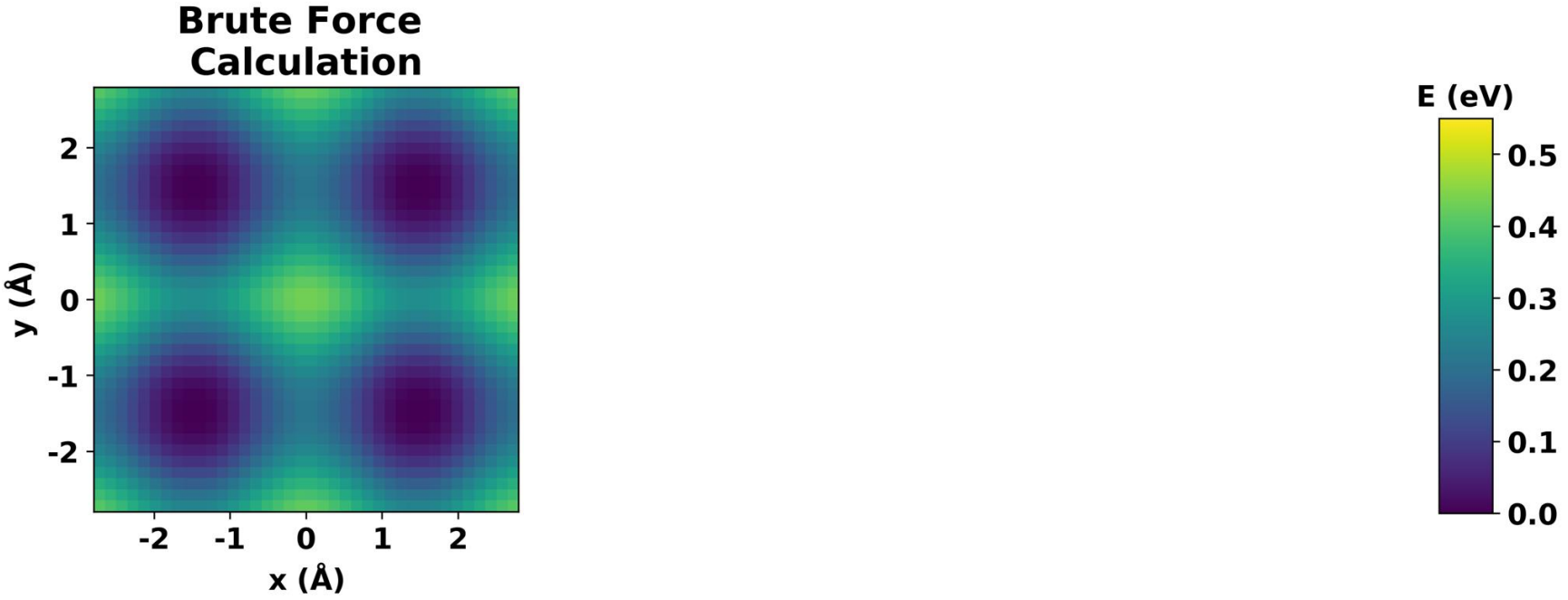
Large amount of highly accurate data!

- Comprehensive overview over polymorphs
- Good estimates of transition barriers

Find the Routes: Overview of Barriers

Challenge: Eliminate irrelevant pathways
Solution: Approximate model for upper/lower limit from vibrations (free)

Challenge: Identify effective reaction pathways and rates
Solution: Refine model with machine learning: Gaussian Process Regression



Conclusion

- **Interface dipoles well understood, provide design principles**
- **Molecular properties qualitative indicators, quantitativey determined by monolayer**
- **To predict new materials, we must know (or predict) the interface geometry**

arXiv:1811.11702

Internat. Collaborations (Exp.)

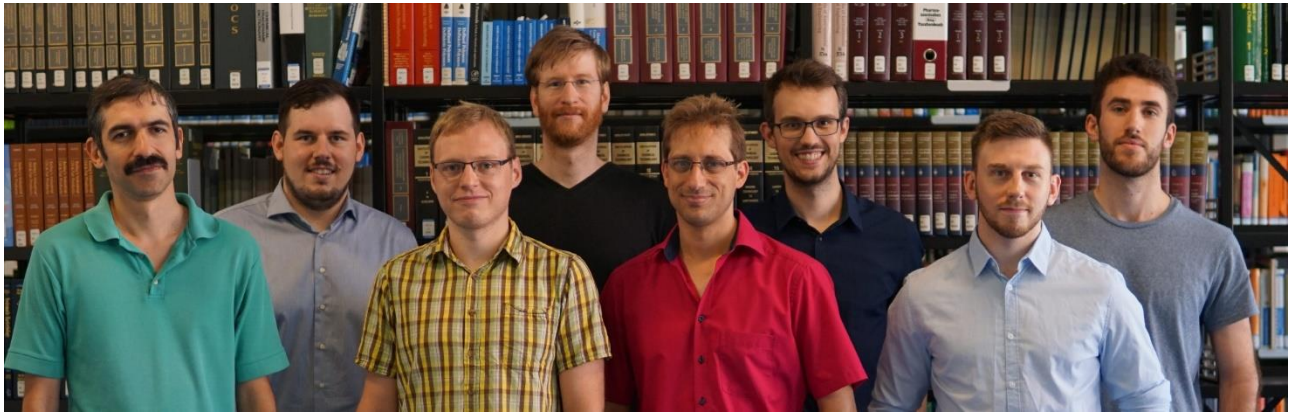
Julia Stähler (FHI Berlin)
Reinhard J. Maurer (Warwick)
Petra Tegeder (U Heidelberg)
Daniel Wegner (Nijmegen)
Christof Wöll (KIT)
Norbert Koch (HU Berlin)
Emil List (HU Berlin)
Frank Schreiber (Tübingen)
Torsten Fritz (FSU Jena)

Internat. Collaborations (Theory)

Matthias Scheffler (FHI Berlin)
Patrick Rinke (Aalto)
Volker Blum (Duke)
Noa Marom (CMU)
Reinhard Maurer (Warwick)
Karsten Reuter (TU Munich)

Local Collaborations

Egbert Zojer
Roland Resel
Robert Schennach
Chrstian Slugovc
Gregor Trimmel



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