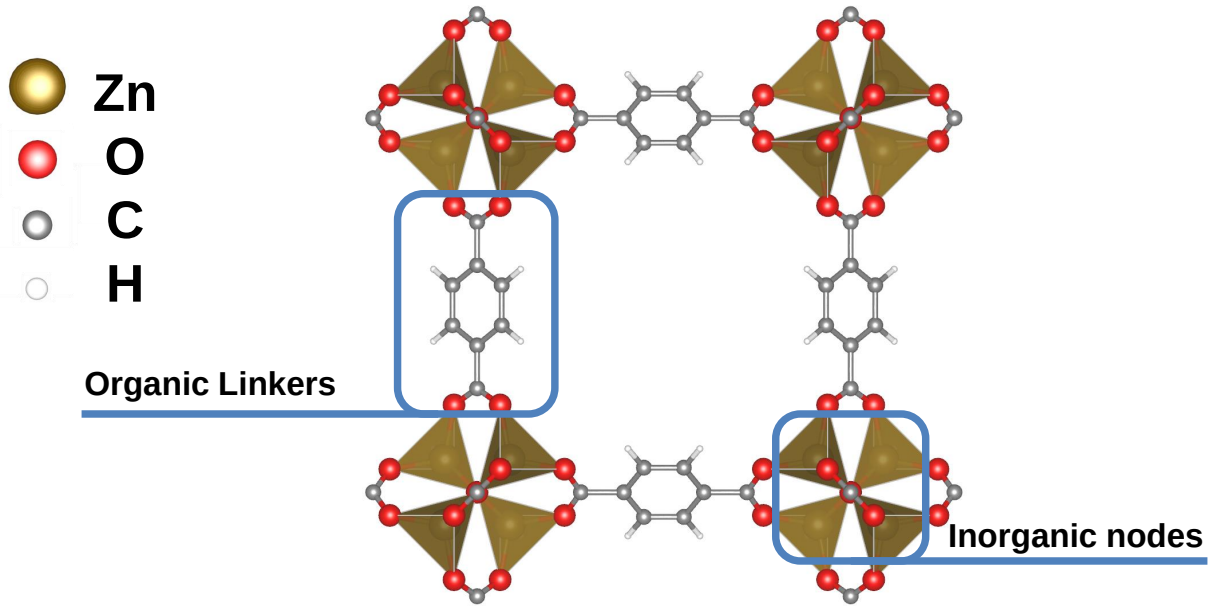
Application of atomistic force field potentials for the prediction of heat transport and phonon properties in metal-organic frameworks

Sandro Wieser
Institute of Solid-State Physics
DocDay of the Doctoral School Physics
02.02.2023

Special thanks to Egbert Zojer, Tomas Kamencek, Natalia Bedoya-Martínez (MCL Leoben), the Schmid group from the Ruhr Universität Bochum, and the Advanced Materials Modeling group at the Institute of Solid-State Physics

sandro.wieser@tugraz.at

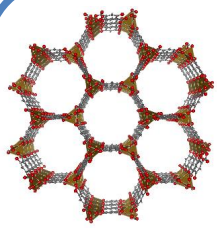
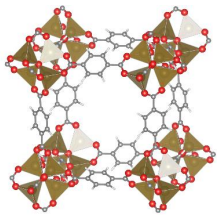
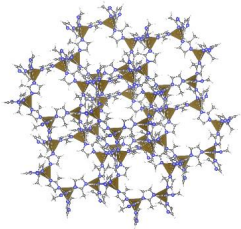
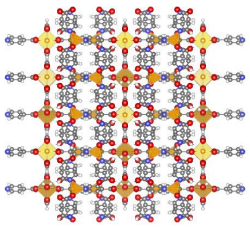
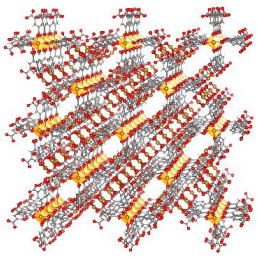
Metal-Organic Frameworks (MOFs)



Isoreticular MOF-1 (IRMOF-I)

sandro.wieser@tugraz.at

Why are we interested in phononic heat transport in MOFs?

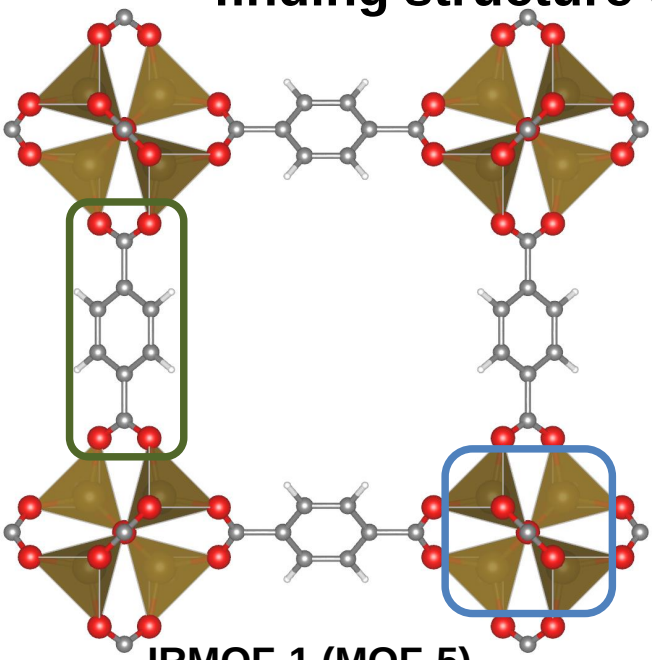
- Gas storage
- Devices
- Catalysis
- Gas separation
- Thermoelectric energy conversion
- Sensing
- Encapsulation

Many processes during applications generate heat
→ Heat dissipation often is a limiting factor!

Usually poor electrical conductors → Phononic heat transport

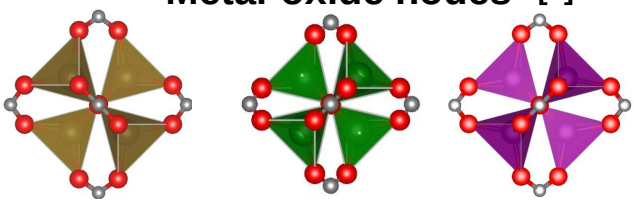
sandro.wieser@tugraz.at

Understanding heat transport: finding structure to property relationships



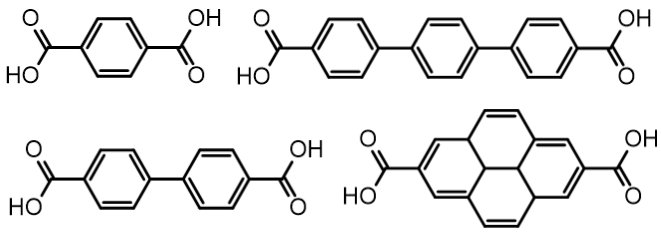
IRMOF-1 (MOF-5)

Metal-oxide nodes [1]



ZnO CaO MgO

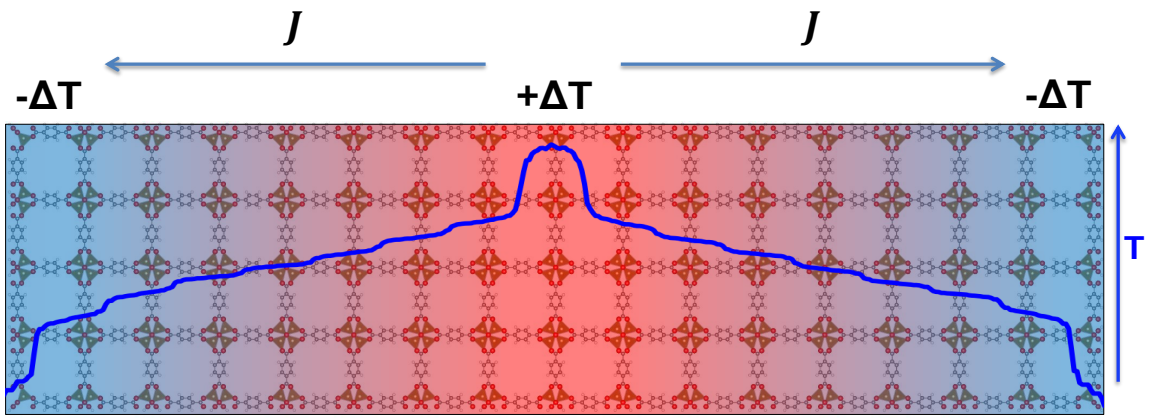
Organic linkers [2]



[1] S. Wieser et al., *Adv. Theory Simulations* **2020**, *2000211*.
[2] S. Wieser et al., *Nanomaterials* **2022**, *12*, 2142.

sandro.wieser@tugraz.at

Non-Equilibrium Molecular Dynamics (NEMD)



Fourier's Law

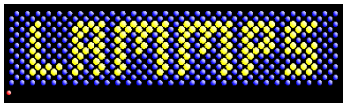
$$J = -\kappa \nabla T$$

Non-Equilibrium Molecular Dynamics (NEMD)

Require simulation times over several ns with fs timesteps involving thousands of atoms

→ System specific classical Force-fields:
MOF-FF[1] parameterized on ab-initio reference data

[2]



[1]: S. Bureekaew et al., *Phys. Status Solidi Basic Res.* **2013**, *250*, 1128.

[2]: A. P. Thompson et al., *Comput. Phys. Commun.* **2022**, *271*, 108171.

Non-Equilibrium Molecular Dynamics (NEMD)

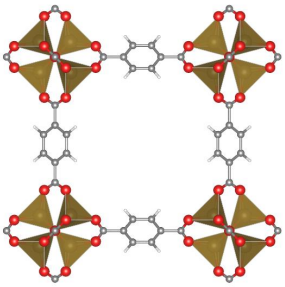
Require simulation times over several ns with fs timesteps involving thousands of atoms

LAMMPS [2]

→ System specific classical Force-fields:
MOF-FF[1] parameterized on ab-initio reference data

transferable force-fields often fail!

Method	finite size corrected thermal cond. / W/(mK)
experimental[3]	0.32
MOF-FF	0.29
Dreiding	1.10
UFF4MOF	0.85



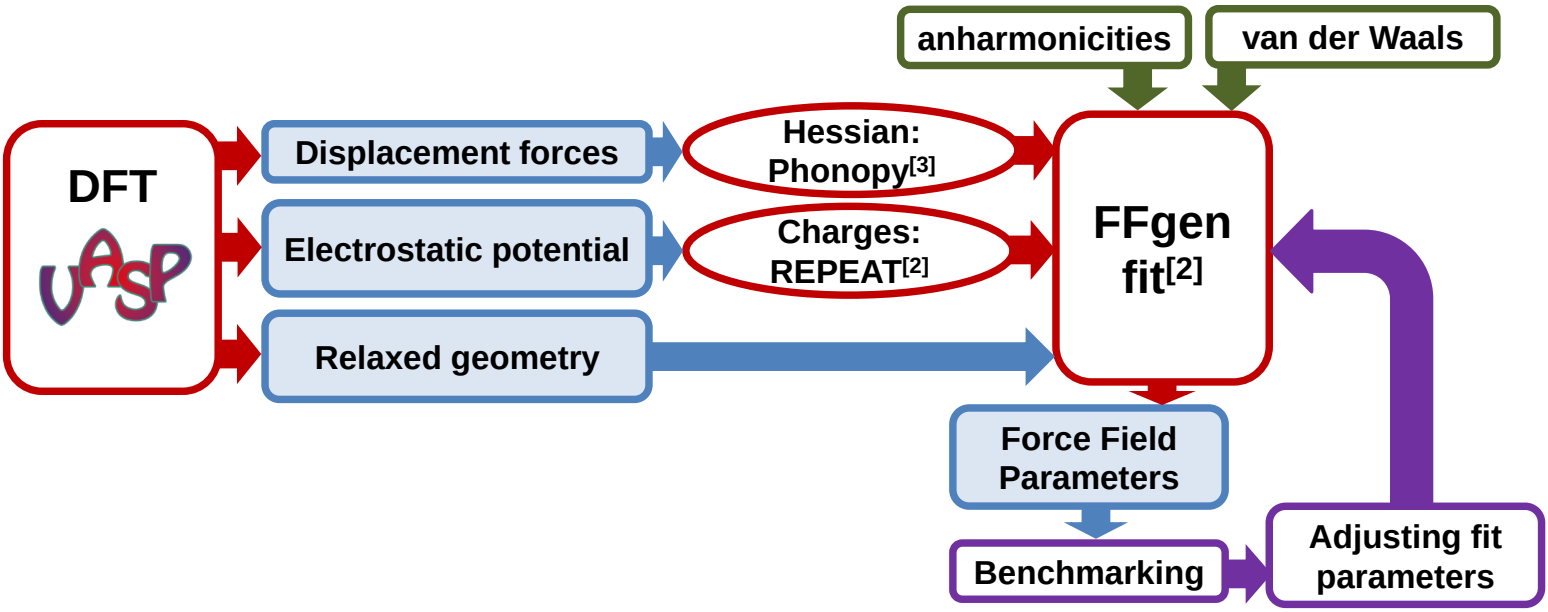
[3]: B.L. Huang et al. *Int. J. Heat Mass Transf.* **2007**, *50*, 405–411

[1]: S. Bureekaew et al., *Phys. Status Solidi Basic Res.* **2013**, *250*, 1128.

[2]: A. P. Thompson et al., *Comput. Phys. Commun.* **2022**, *271*, 108171.

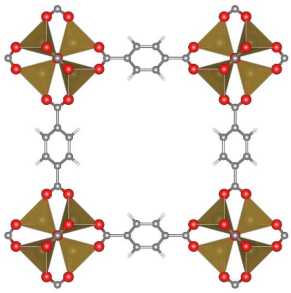
sandro.wieser@tugraz.at

Parameterization of MOF-FF potentials

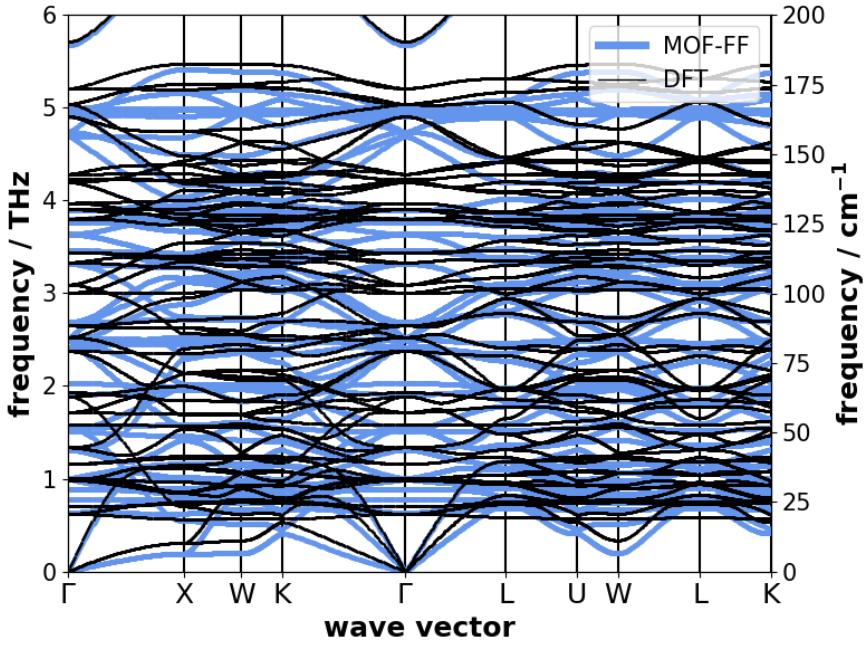


[1]: Bureekaew, S. et al. (2013). Physica Status Solidi (B), 250(6), 1128–1141; Dürholt, J. P. et al. (2019). JCTC, 15(4), 2420–2432.
[2]: Campañá, C. et al. *J. Chem. Theory Comput.* 2009, *5*, 2866–2878.
[3]: Togo, A. el al. *Scr. Mater.* 2015, *108*, 1–5.

Validation of the force field potential



Phonon band structure of IRMOF-1



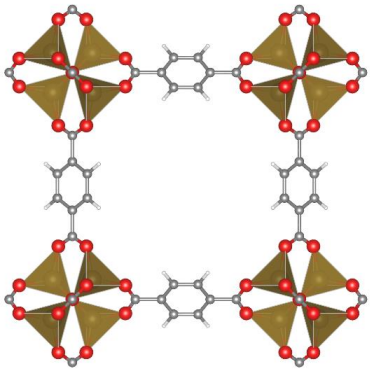
Also benchmarked:

- **forces**
- **geometry of structure**
- **thermal expansion**

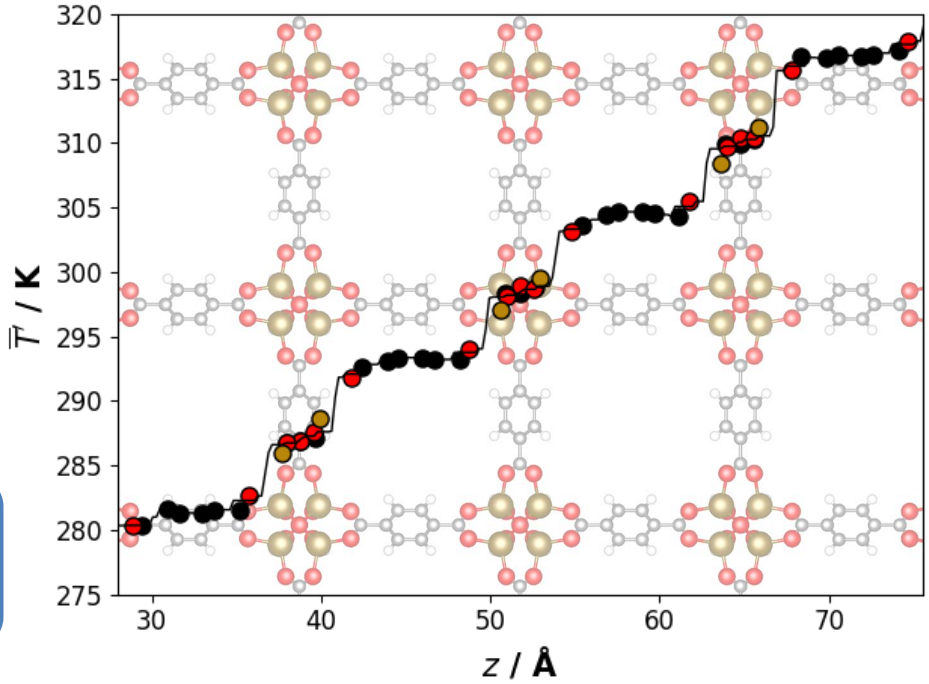
sandro.wieser@tugraz.at

Temperature profiles

IRMOF-1 (Zn)



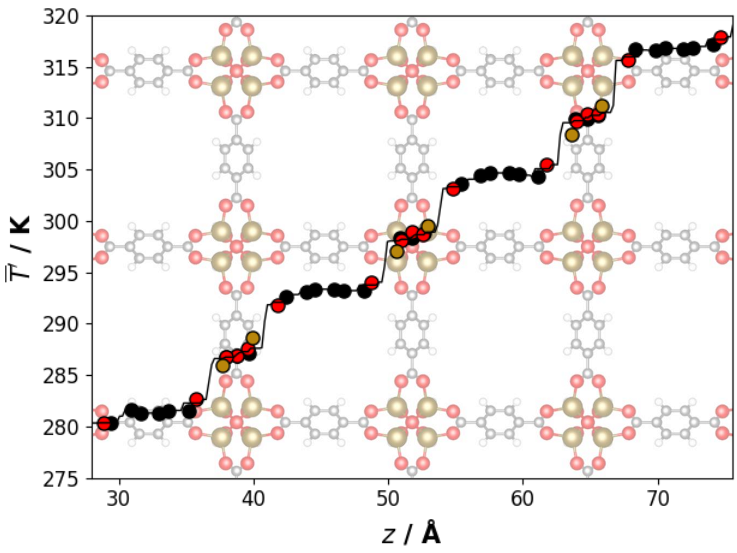
Linker/Node interface: heat transport bottleneck



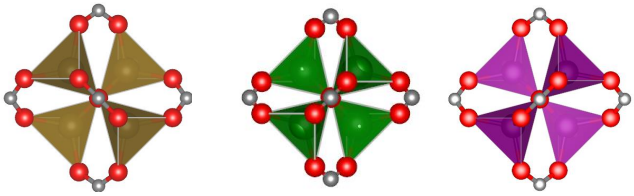
S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

sandro.wieser@tugraz.at

The impact of the node metal

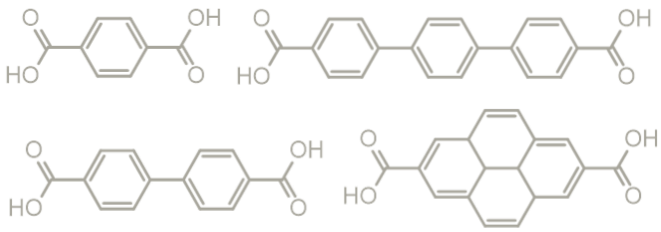


Metal-oxide nodes [1]



ZnO CaO MgO

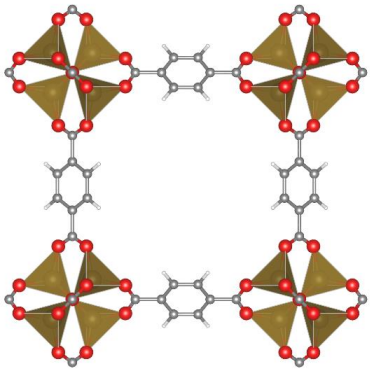
Organic linkers [2]

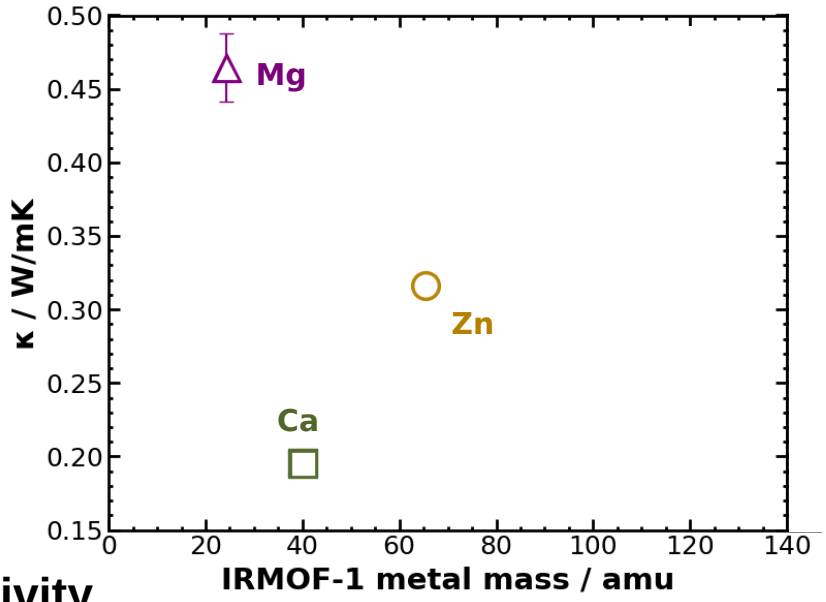


[1] S. Wieser et al., *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.
[2] S. Wieser et al., *Nanomaterials* **2022**, *12*, 2142.

sandro.wieser@tugraz.at

Thermal conductivities for investigated MOFs at 300K





Expectation:
lower metal mass:
→ higher thermal conductivity

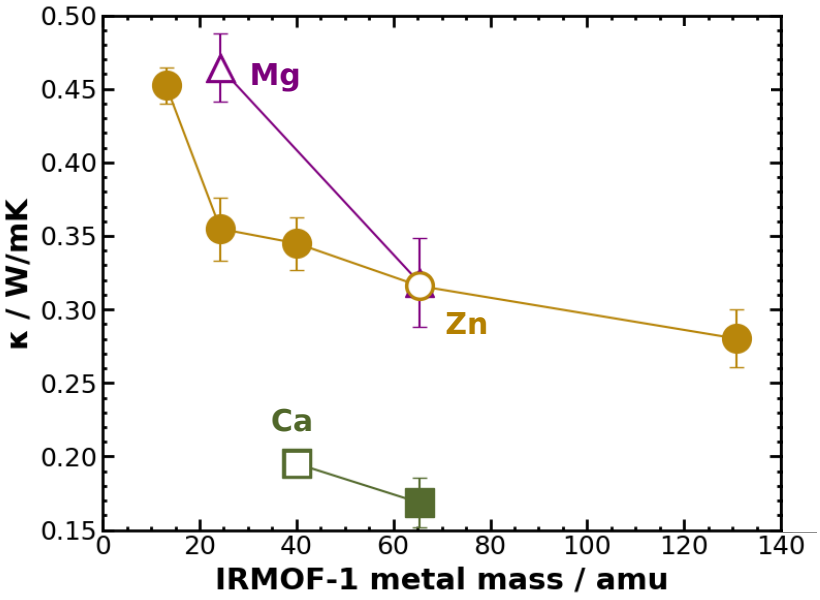
S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

sandro.wieser@tugraz.at

Thermal conductivities for investigated MOFs at 300K

Scaling of metal masses:
- **Hypothetical systems**
- **Real systems**

→ The difference in mass does not explain the low thermal conductivity for Ca

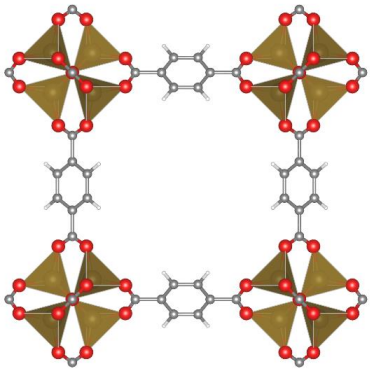


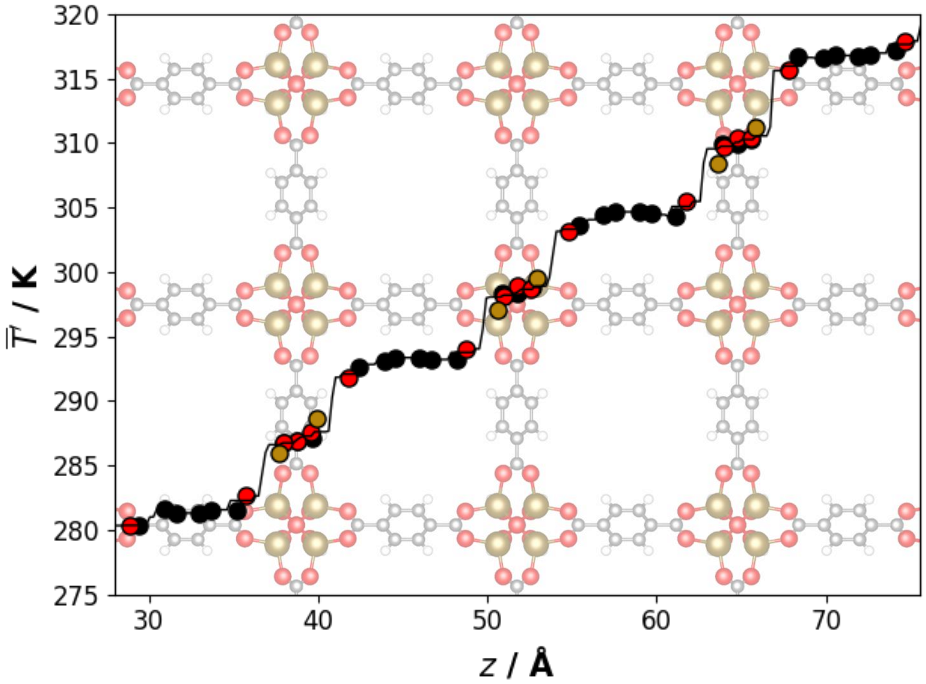
S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

sandro.wieser@tugraz.at

Temperature profiles

IRMOF-1 (Zn)





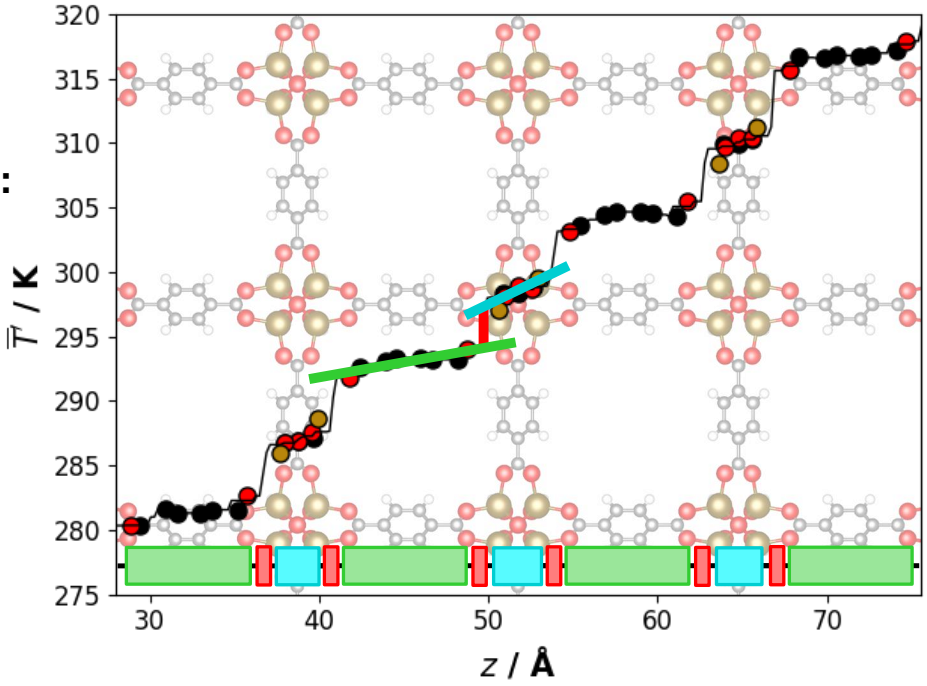
S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

sandro.wieser@tugraz.at

Temperature profiles

Model for thermal resistance contributions:

$$r_{A,unit} = r_{A,node} + r_{A,linker} + 2 \cdot r_{A,interface}$$



S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

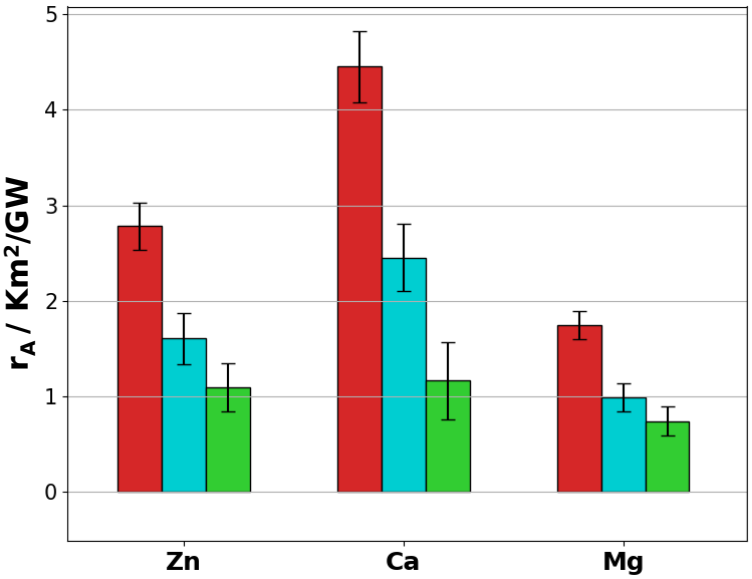
sandro.wieser@tugraz.at

Contributions toward the thermal resistance

$r_{A,interface}$

$r_{A,node}$

$r_{A,linker}$



→ The interface shows the largest thermal resistance contribution

S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

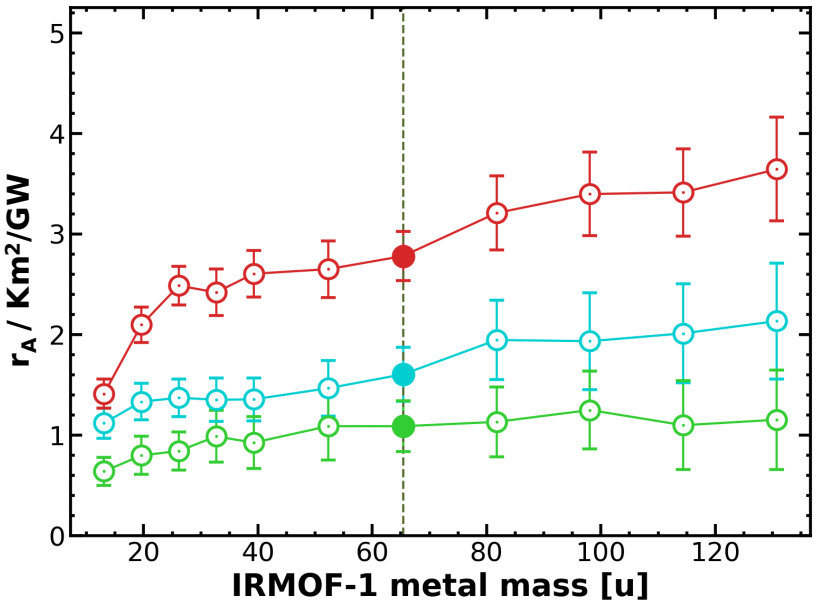
sandro.wieser@tugraz.at

Effect of the metal mass: IRMOF-I (Zn)

Scaling of metal masses:

- ⊙ **Hypothetical systems**
- ● **Real systems**

- ⊙ $r_{A,interface}$
- ⊙ $r_{A,node}$
- ⊙ $r_{A,linker}$



→ **Lower metal mass reduces interface resistance**

S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

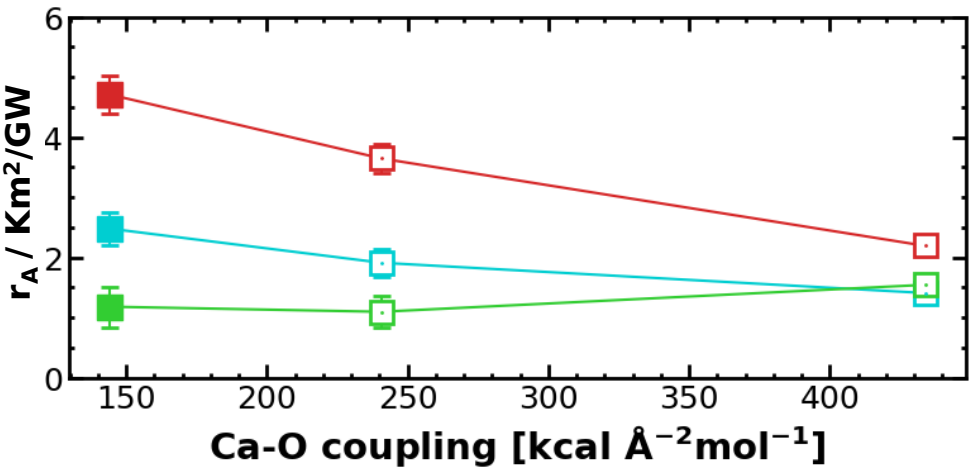
sandro.wieser@tugraz.at

Effect of node-linker interaction strength: IRMOF-I (Ca)

Scaling of metal masses:

- Hypothetical systems
- Real systems

- $r_{A,interface}$
- $r_{A,node}$
- $r_{A,linker}$

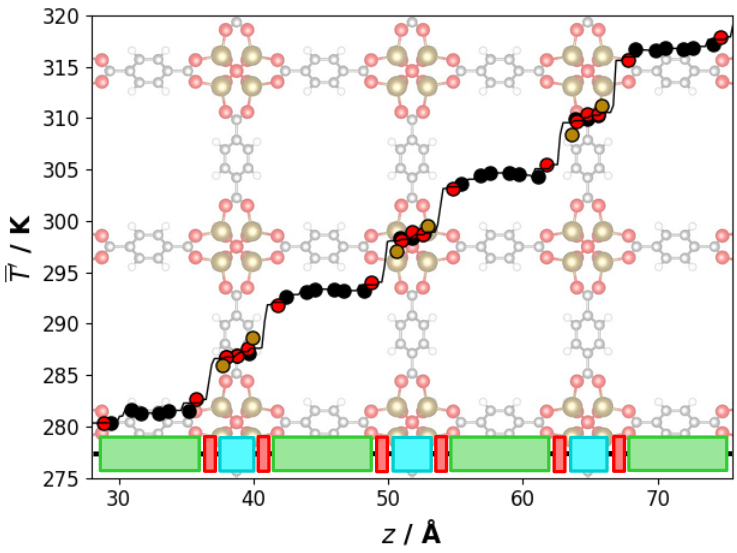


→ **Higher coupling strength reduces interface resistance**

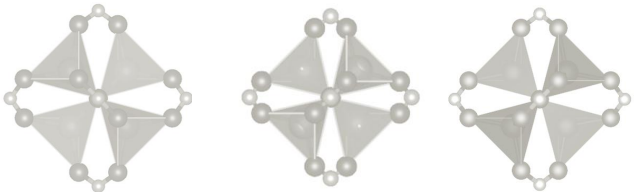
S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer, *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.

sandro.wieser@tugraz.at

The impact of the organic linker

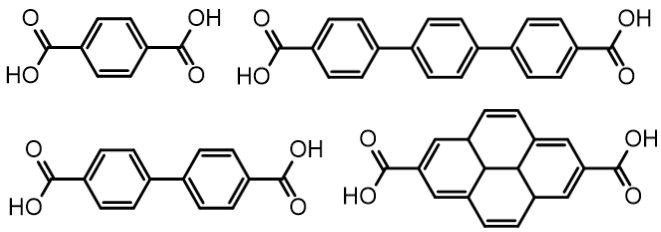


Metal-oxide nodes [1]



ZnO CaO MgO

Organic linkers [2]



[1] S. Wieser et al., *Adv. Theory Simulations* **2020**, *2000211*, DOI 10.1002/adts.202000211.
[2] S. Wieser et al., *Nanomaterials* **2022**, *12*, 2142.

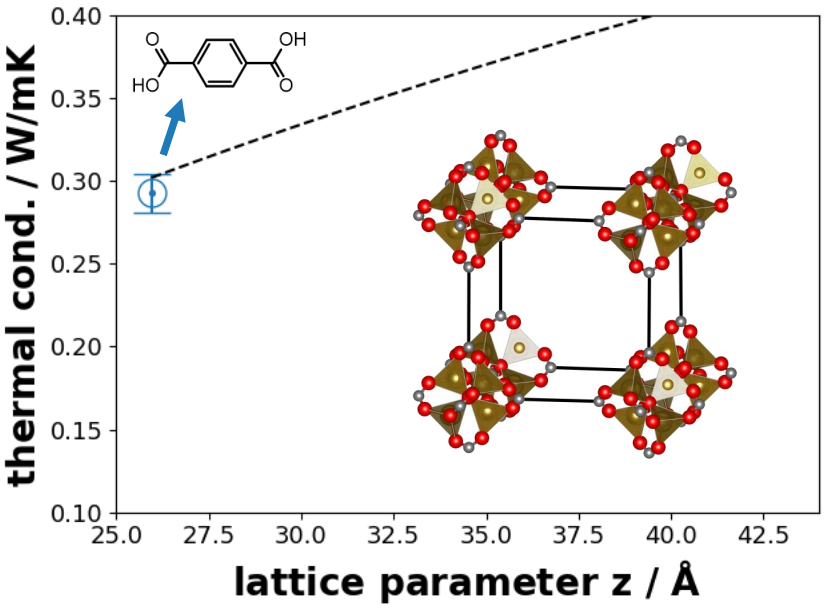
sandro.wieser@tugraz.at

Effect of linker length

Model for thermal resistance contributions:

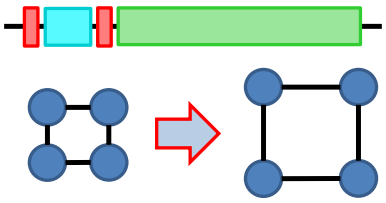
$$r_{A,unit} = r_{A,node} + r_{A,linker} + 2 \cdot r_{A,interface}$$

Assumptions:
----- reduce interface density



Effect of linker length

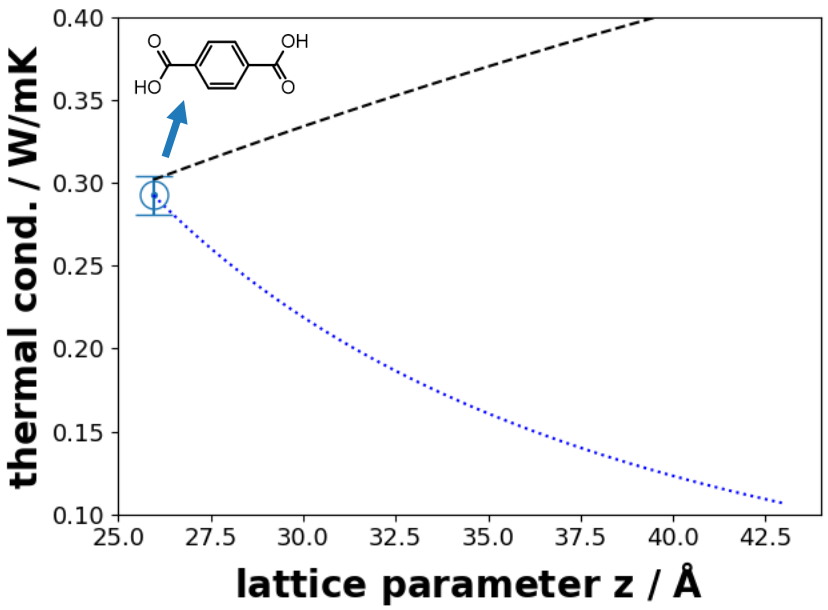
Model for thermal resistance contributions:



Assumptions:

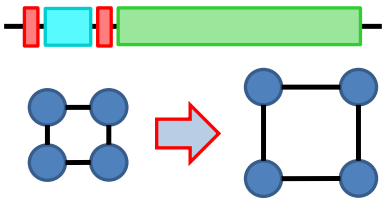
----- **reduce interface density**

····· **heat transport ~ $1/A_{cross}$**



Effect of linker length

Model for thermal resistance contributions:

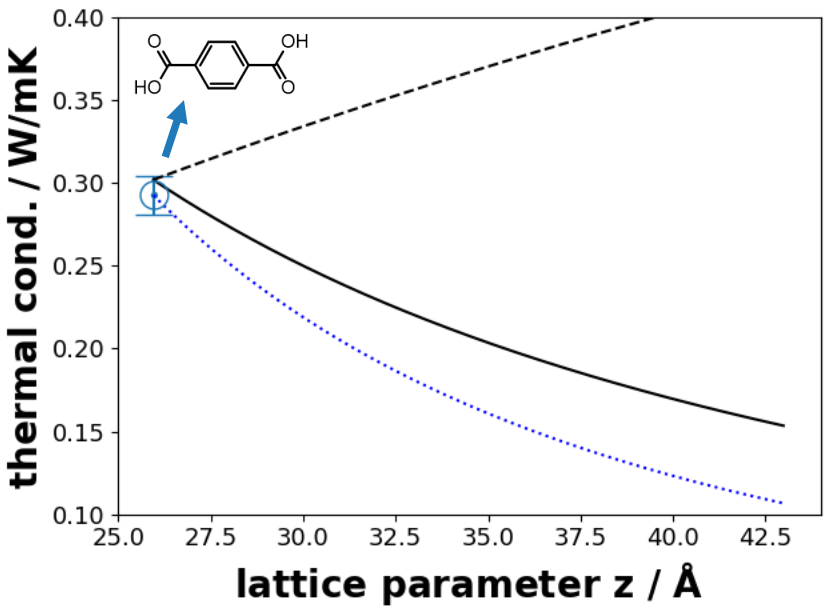


Assumptions:

----- reduce interface density

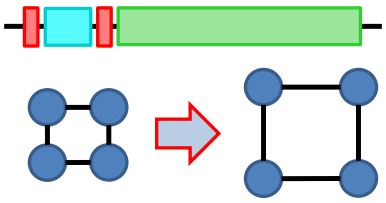
····· heat transport ~ $1/A_{cross}$

—— combined effect



Effect of linker length

Model for thermal resistance contributions:

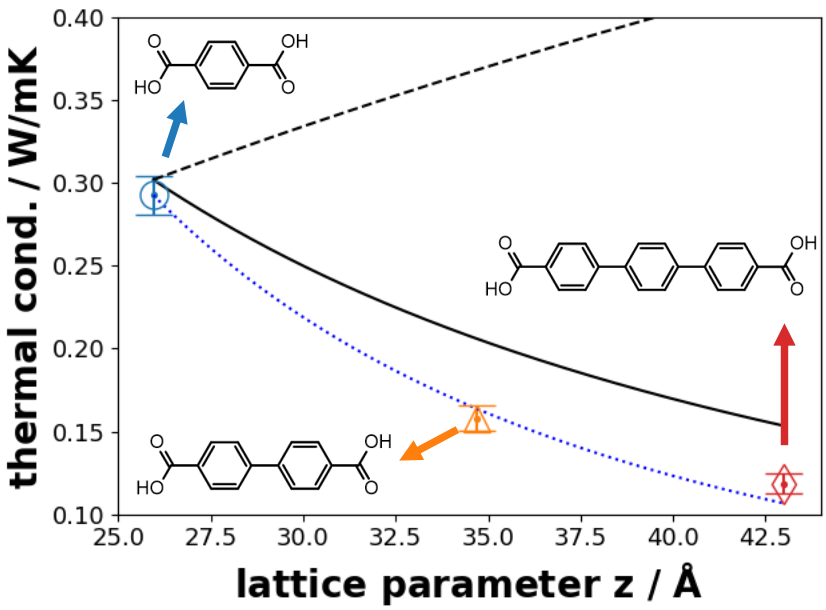


Assumptions:

----- reduce interface density

····· heat transport ~ $1/A_{cross}$

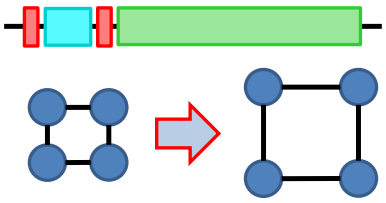
—— combined effect



sandro.wieser@tugraz.at

Effect of linker length

Model for thermal resistance contributions:

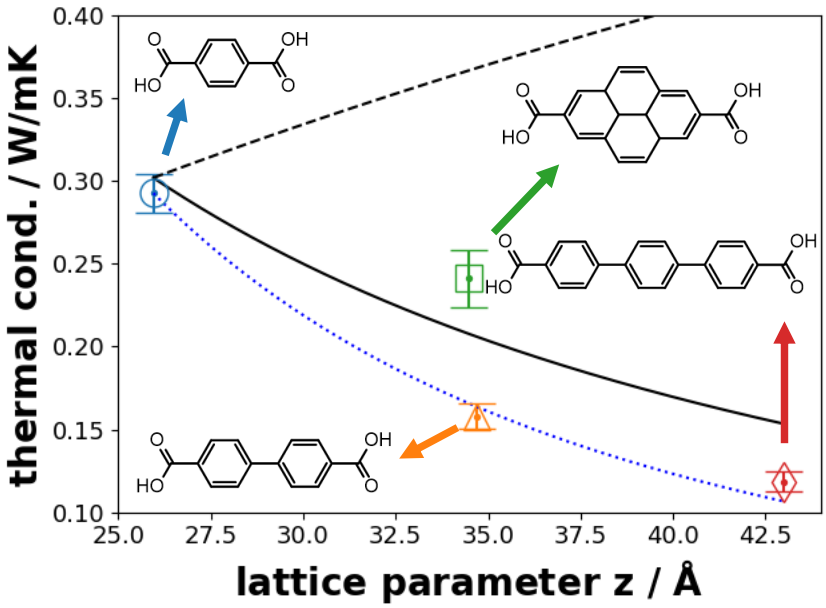


Assumptions:

----- reduce interface density

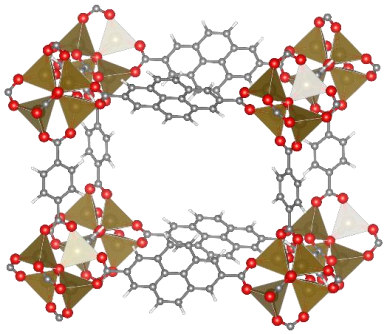
····· heat transport ~ $1/A_{cross}$

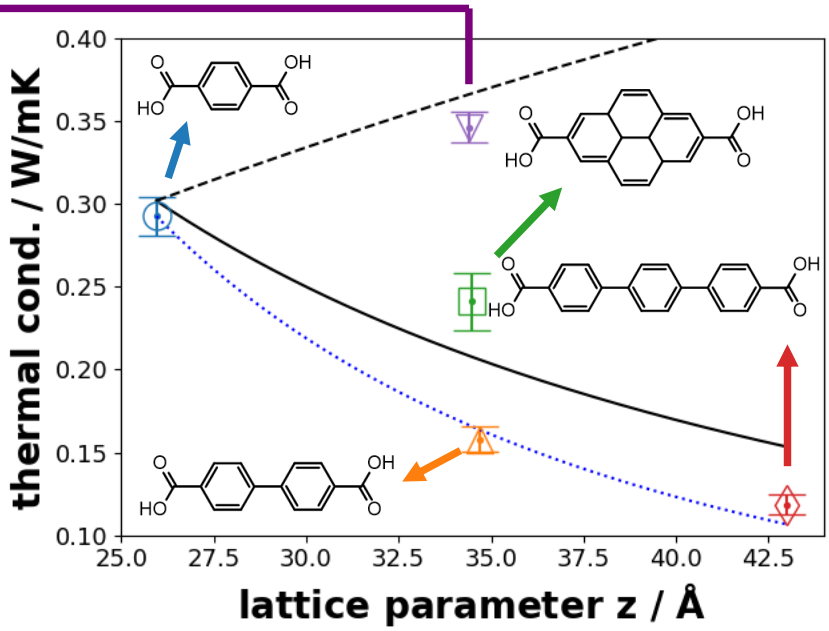
—— combined effect



sandro.wieser@tugraz.at

Effect of linker length





Assumptions:

----- reduce interface density

····· heat transport ~ $1/A_{cross}$

—— combined effect

sandro.wieser@tugraz.at

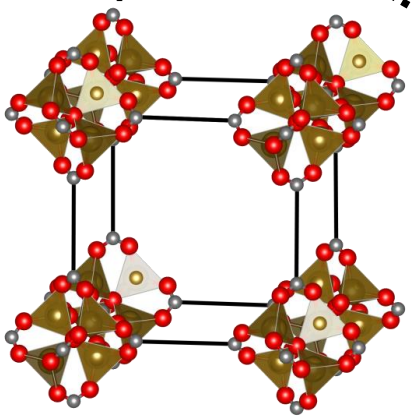
Thermal resistance contributions

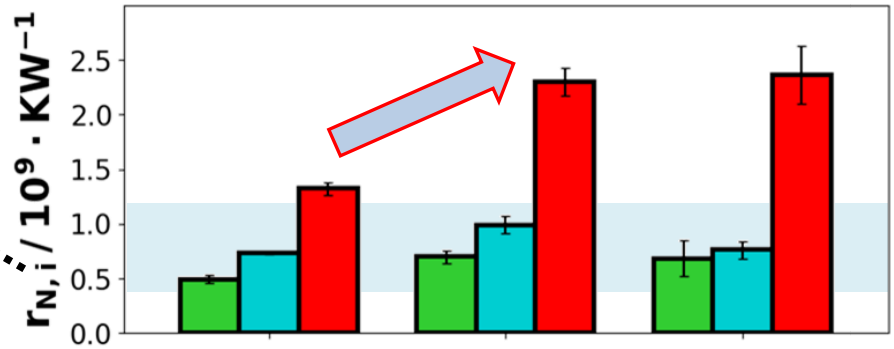
interface

node

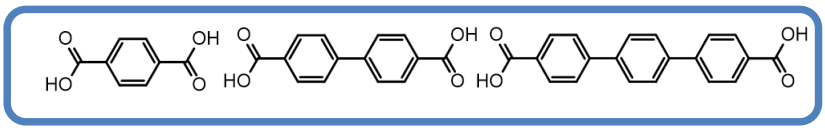
linker

for each heat transport channel





+



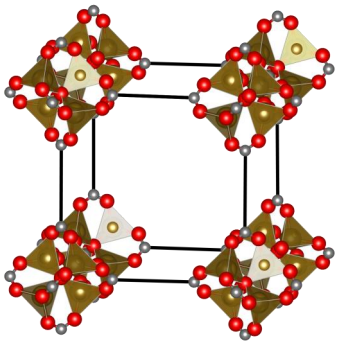
→ **Longer linkers lead to higher interface resistance**

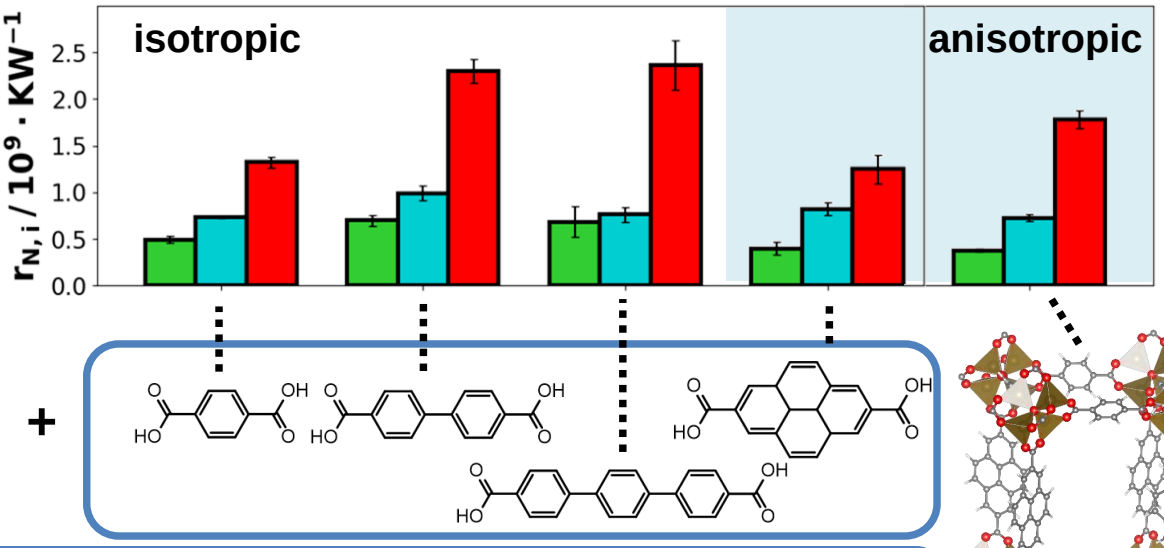
Thermal resistance contributions

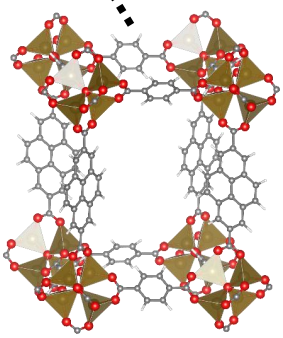
interface

node

linker





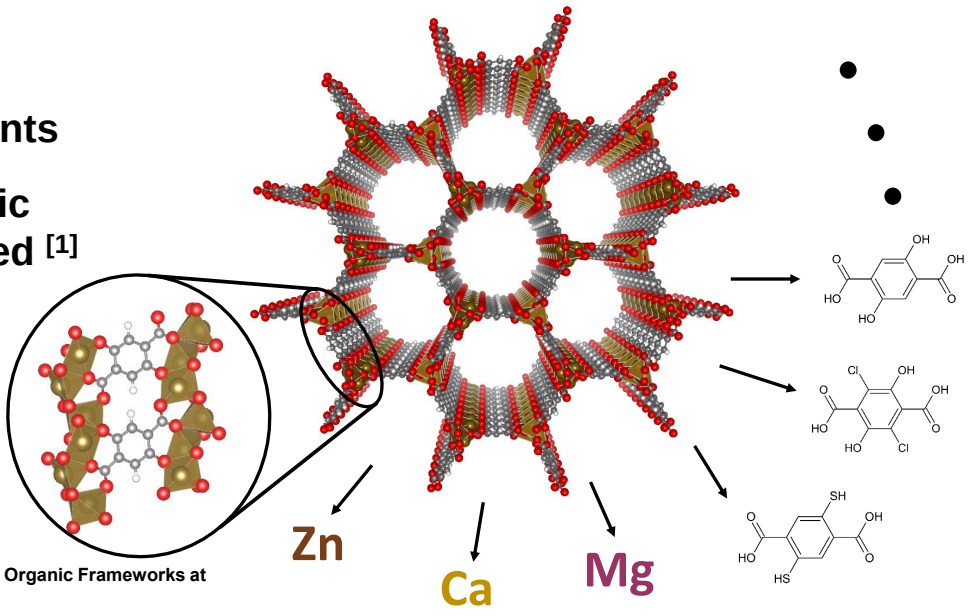


→ Longer linkers lead to higher interface resistance
→ Pyrene linkers do not show this increase

Investigating different materials: Example of MOF-74

Structure dependent heat transport in MOF-74 variants

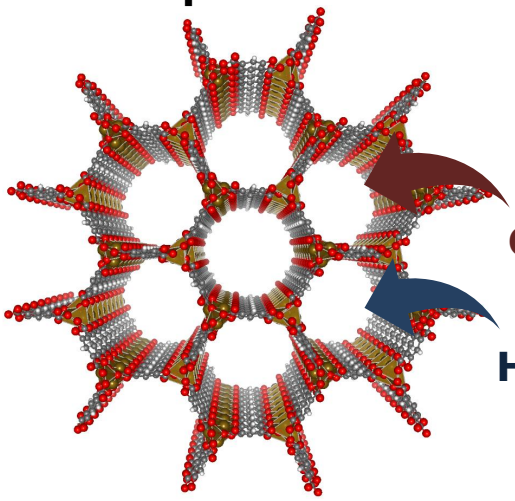
Large differences in elastic properties already reported [1]



[1] Kamencek, T.; Zojer, E.
Understanding the Anisotropic Elastic Properties of Metal − Organic Frameworks at the Nanoscale : The Instructive Example of MOF-74.
Journal of Physical Chemistry, **2021**

The problems with the force field creation approach: The example of MOF-74

- complex MOFs



MOF-74 (Zn)

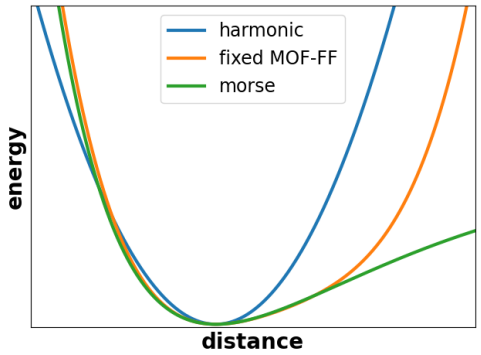
CO_2

H_2O

- adding guests

- human resource intensive

- Anharmonic contributions



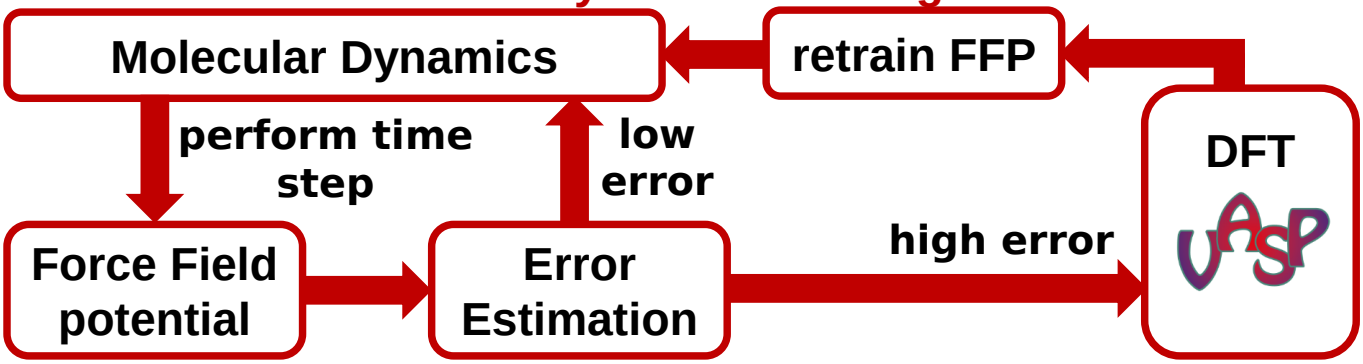
SOLUTION: machine learning potentials

Machine learned potentials

- **requires little human input**
- **capable of interpolating well within the reference data set**

How to properly obtain representative reference data sets?

On-the-fly Active learning[1]



[1] R. Jinnouchi, F. Karsai, G. Kresse, *Phys. Rev. B* **2019**

Moment Tensor Potentials

- **VASP potential can be learned fast, but: too slow for NEMD**

- **Solution: Moment tensor potentials (MTPs)[1] trained on the VASP sampled reference data**

$$E(\mathrm{cfg}) = \sum V_{atom,i}(\mathrm{neighborhood})$$

VASP
dynamic basis set based on local configurations

MTP
fixed basis set based on physically motivated interactions

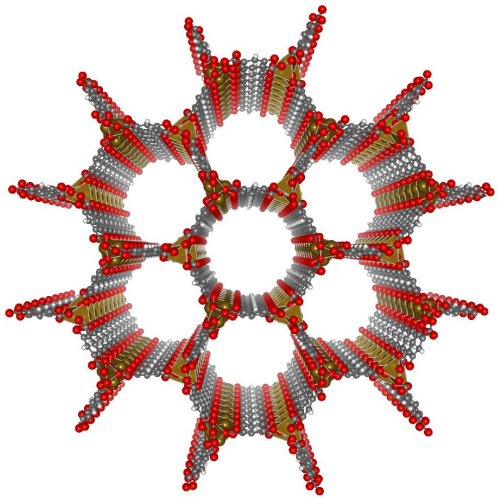
Advantages:

- **faster**
- **easy precision/speed adjustment**
- **increased accuracy**

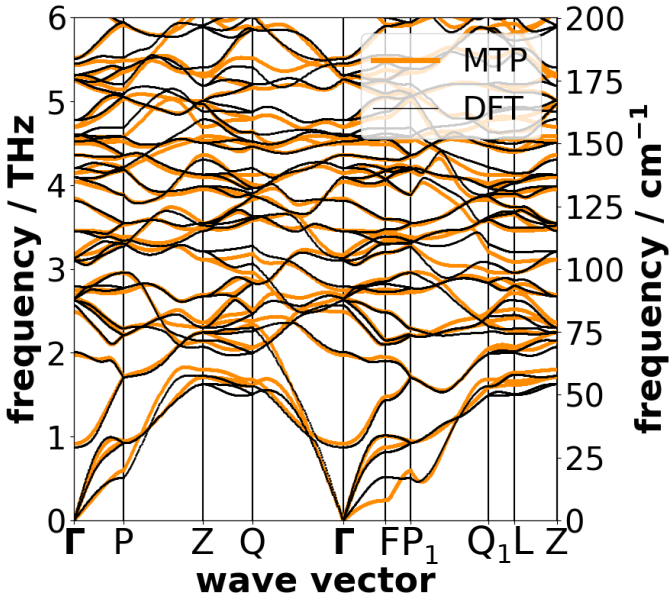
[1] A. V Shapeev, *Multiscale Model. Simul.* **2016**, *14*, 1153.

sandro.wieser@tugraz.at

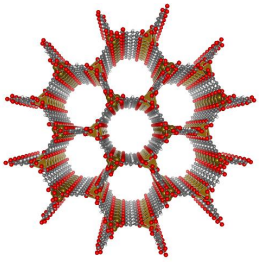
Agreement of phonon frequencies



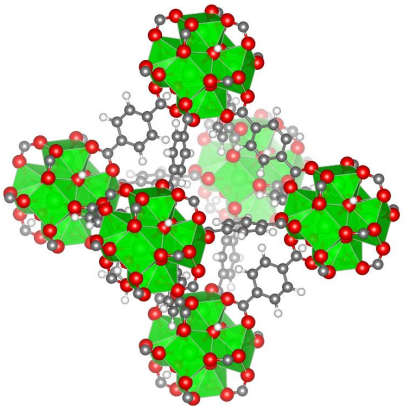
MOF-74 (Zn)



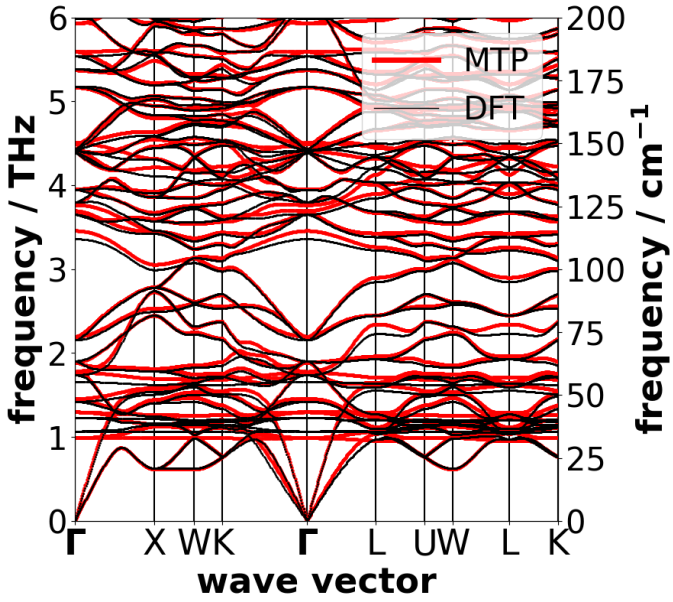
Agreement of phonon properties



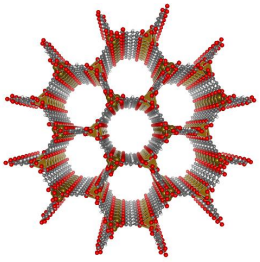
MOF-74 (Zn)



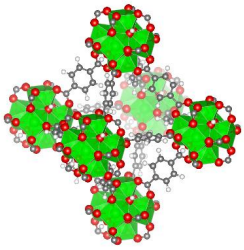
UiO-66 (Zr)



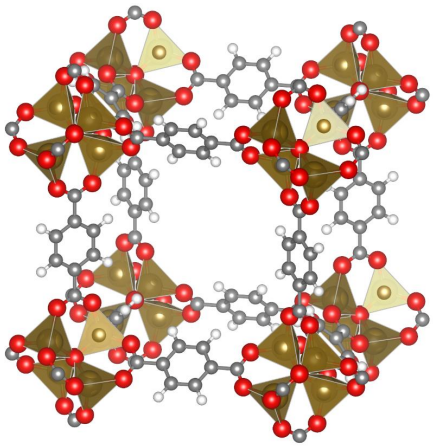
Agreement of phonon properties



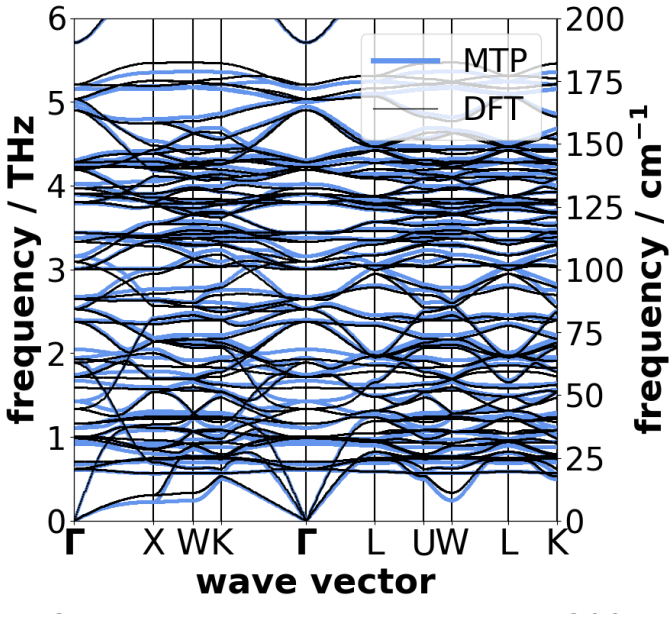
MOF-74 (Zn)



UiO-66 (Zr)

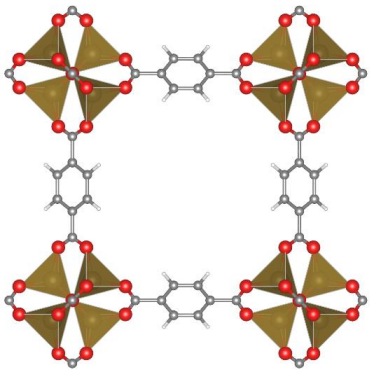


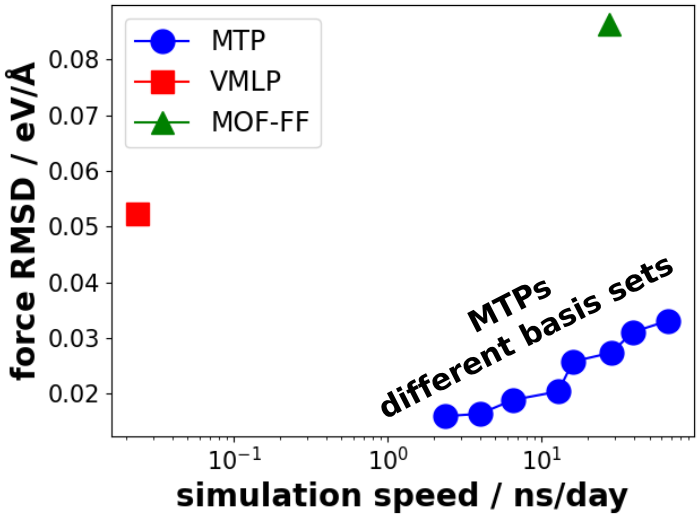
IRMOF-1 (Zn)



Comparison of computational speed and accuracy

IRMOF-1 (Zn)





➢ **Computation of the thermal conductivity feasible**

Result at 300 K: 0.33 W/mK compared to experiment[1]: 0.32 W/mK

[1]: B.L. Huang et al. *Int. J. Heat Mass Transf.* **2007**, *50*, 405–411

sandro.wieser@tugraz.at

Conclusion

- → Node-Linker interface represents the most significant barrier for heat transport
- → Lower metal masses and stronger metal-oxygen interaction strengths increase the thermal conductivity.
- → Longer linker length reduces the thermal conductivity primarily due to pore size but also due to an increase in interface resistance
- → Emerging Machine learning potential approaches offer an excellent tool to accurately describe phonon properties even in complex materials such as MOFs

Grant No. 26163

Lead Project (LP-03):
Porous Materials@Work