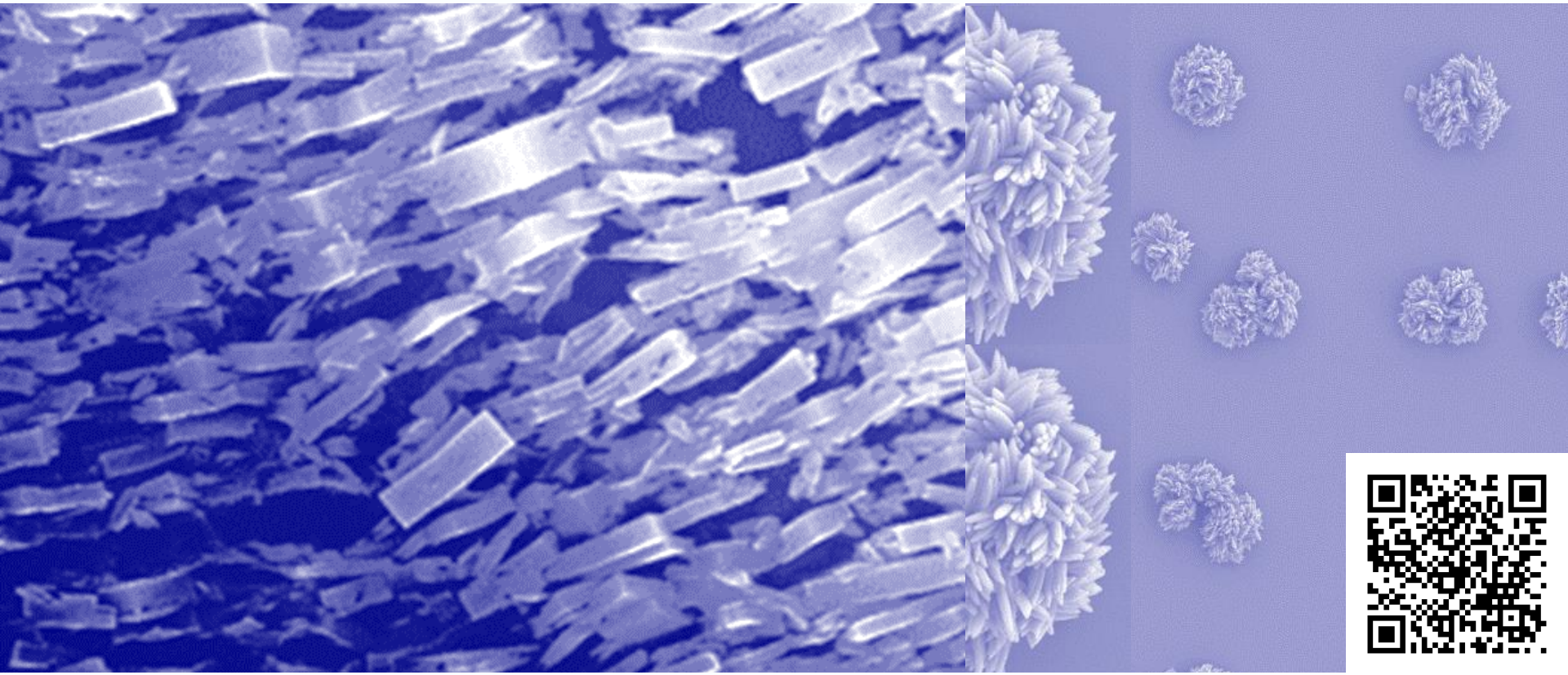


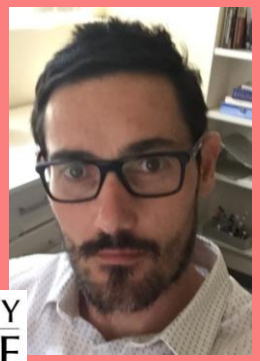
Engineering Metal-Organic Frameworks

Paolo Falcaro
Graz University of Technology

THE UNIVERSITY of ADELAIDE

Collaborators

THE UNIVERSITY of ADELAIDE



OPU

Leuven

CSIRO

Padova

ICN2

Canberra

Kyoto

CSIRO

Melbourne

Southampton

Dallas

TU-Graz

The funding organizations

Graz University of Technology

Lead Project LP-03

Porous Materials@Work

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme
(grant agreement No .771834)

Consolidator Grant POPCRYSTAL

European Research Council

Australian Government
Australian Research Council

JSPS

MOF platform

The TEAM

Chemist

Material Scientist

Physicist

Biotechnologist

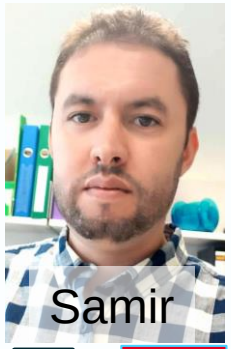
Engineer


Raffaele

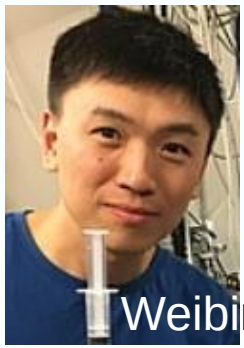

Mercedes


Francesco


Miriam


Samir


Marcello


Weibin


Efwita


Chiara


Tomas


Peter


Michael

Layout

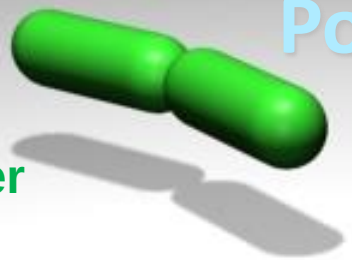
- MOFs…. and our vision
- Flavour of MOF bio-composites
- Device fabrication
- Ceramics and Composites
- Examples of progress in MOF-based device fabrication

Porous Coordination Polymers

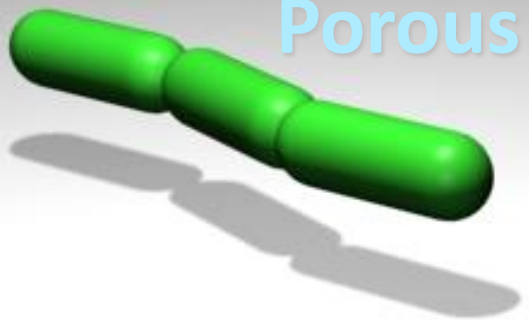
Monomer

Porous Coordination Polymers

Monomer



Porous Coordination Polymers



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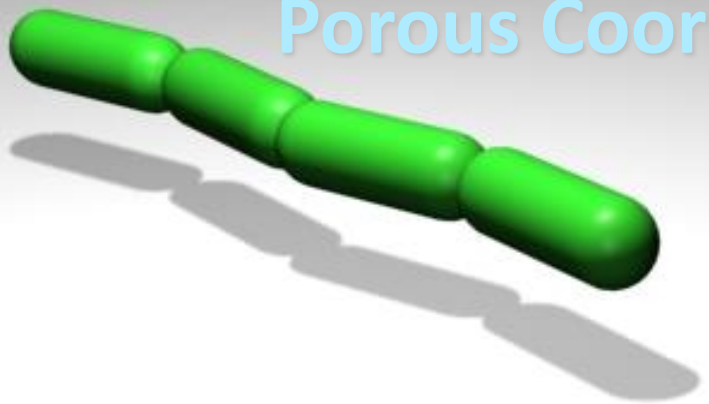
Porous Coordination Polymers



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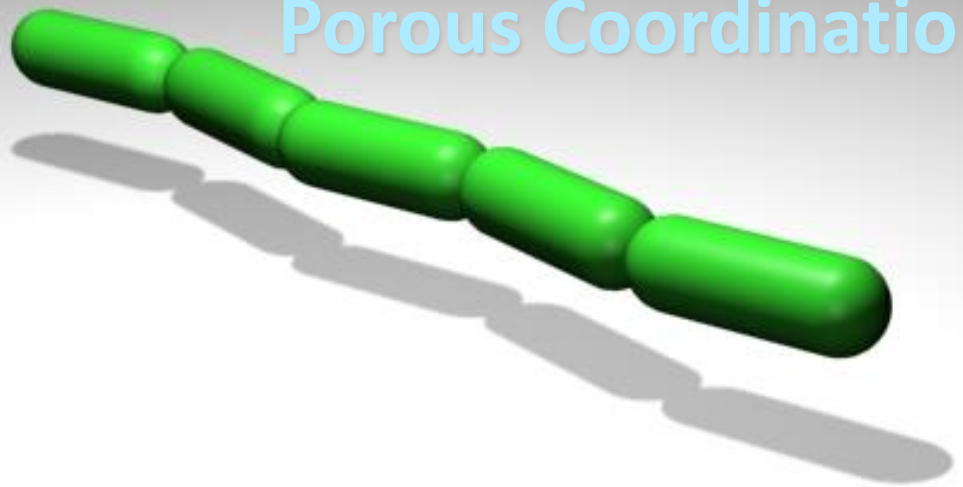
Porous Coordination Polymers



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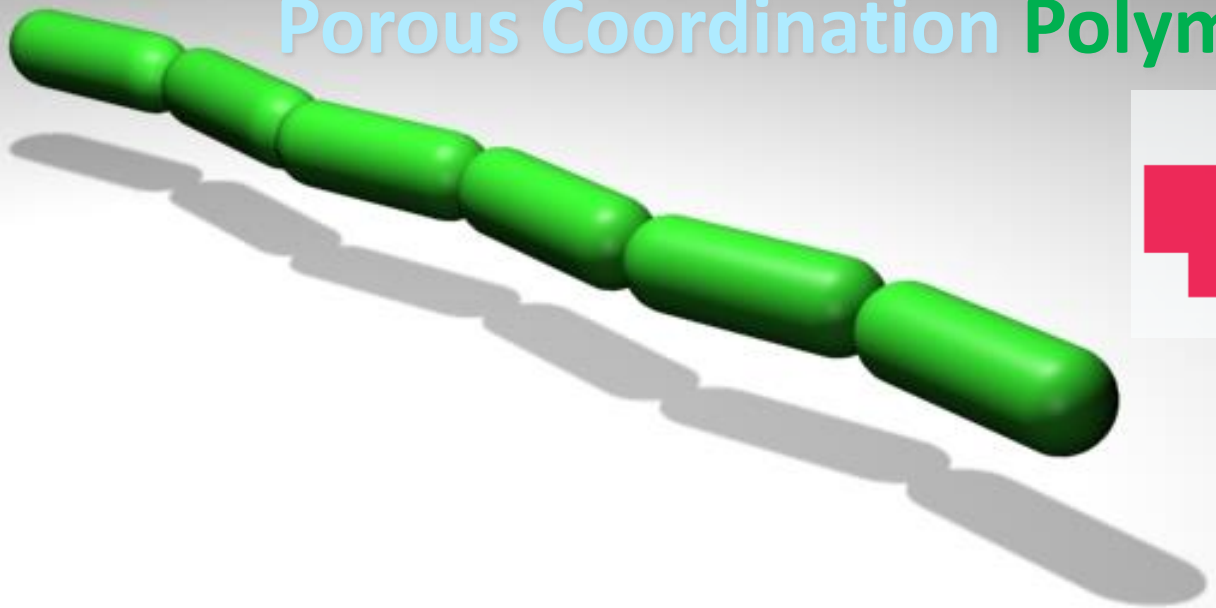
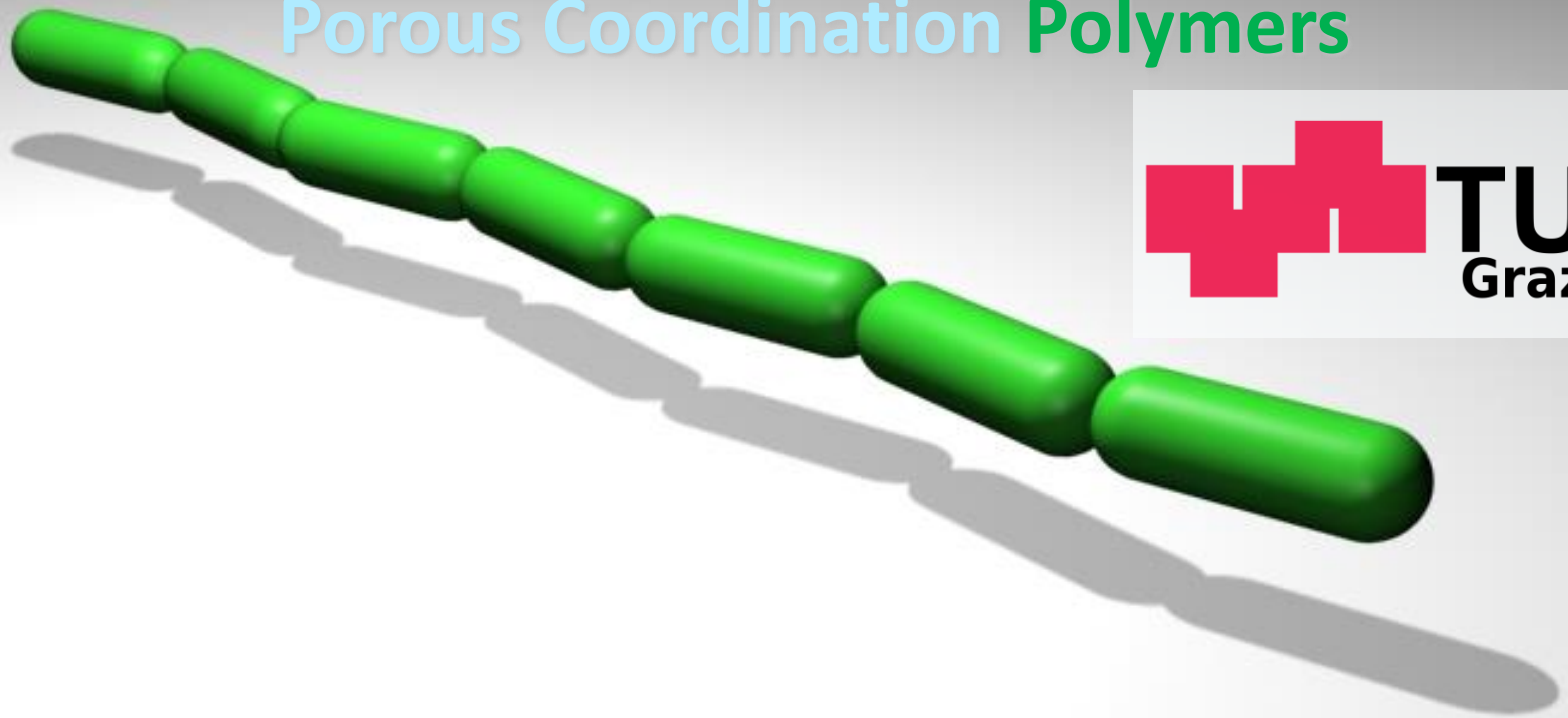
Porous Coordination Polymers

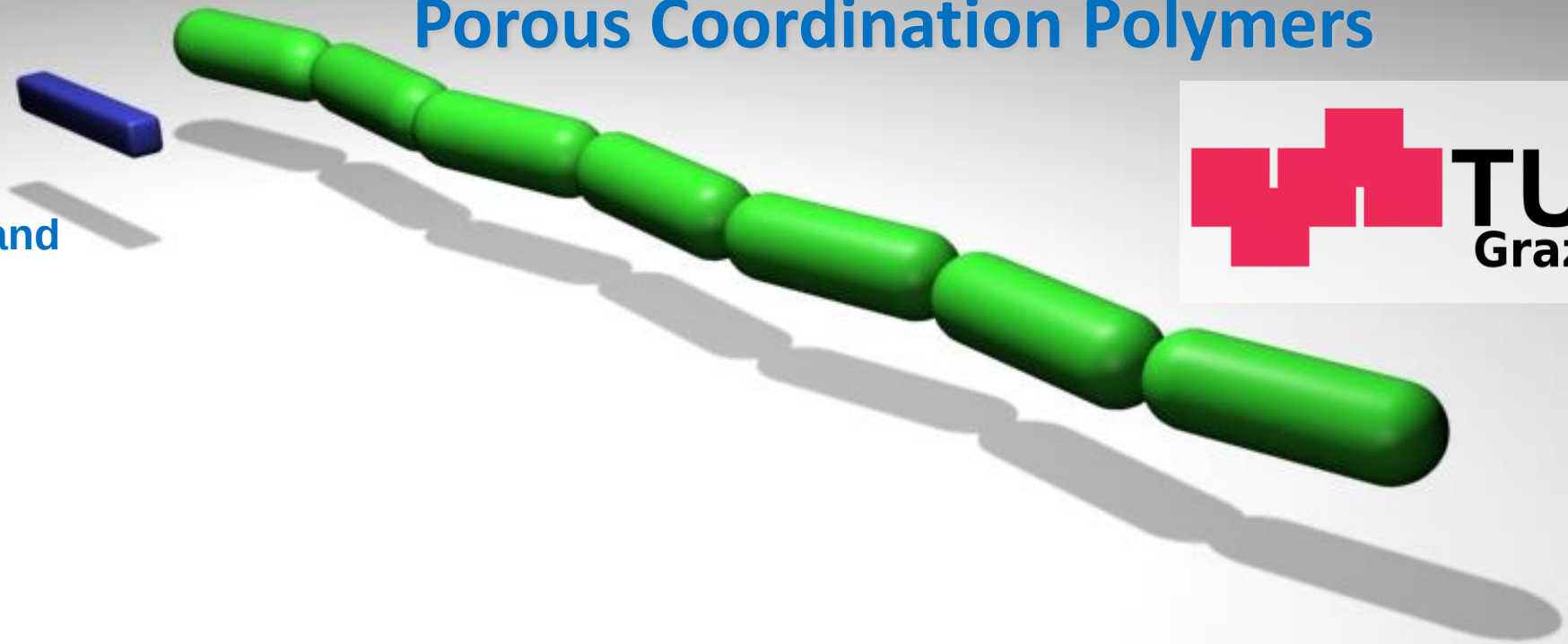


Porous Coordination Polymers

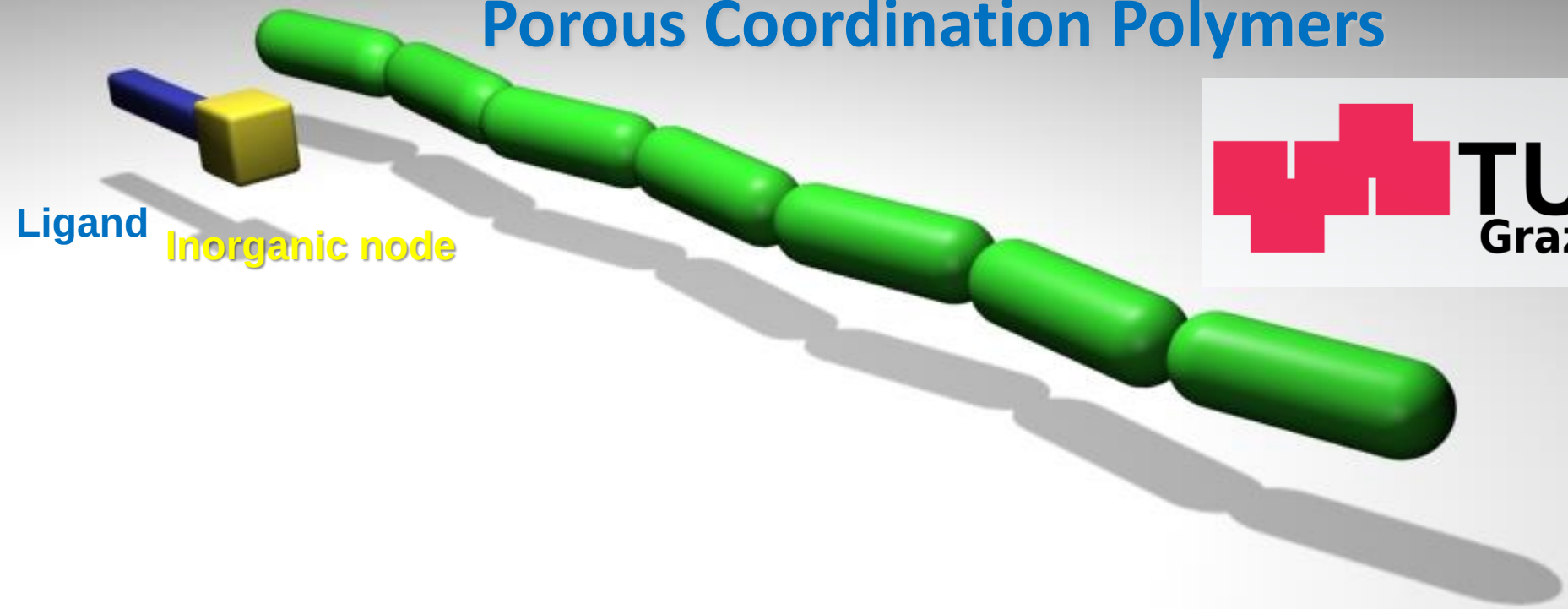


Porous Coordination Polymers

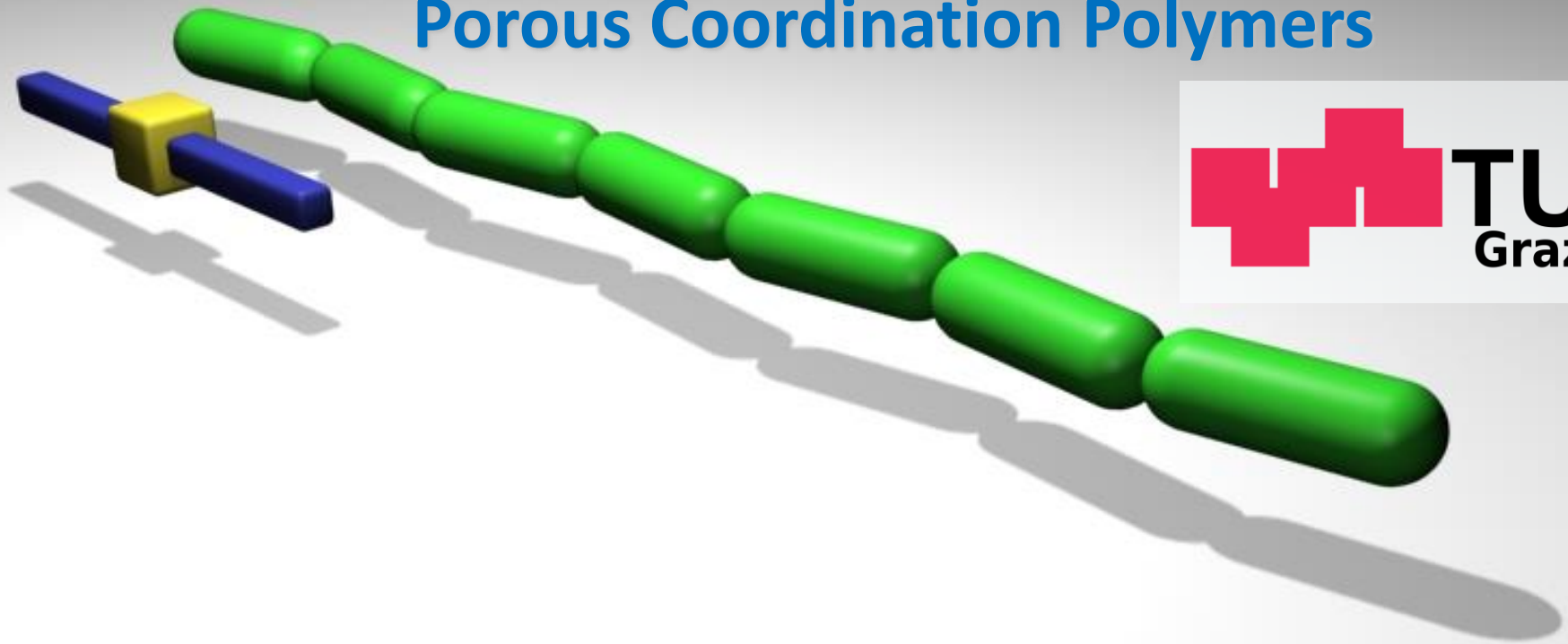
Ligand



Porous Coordination Polymers



Porous Coordination Polymers



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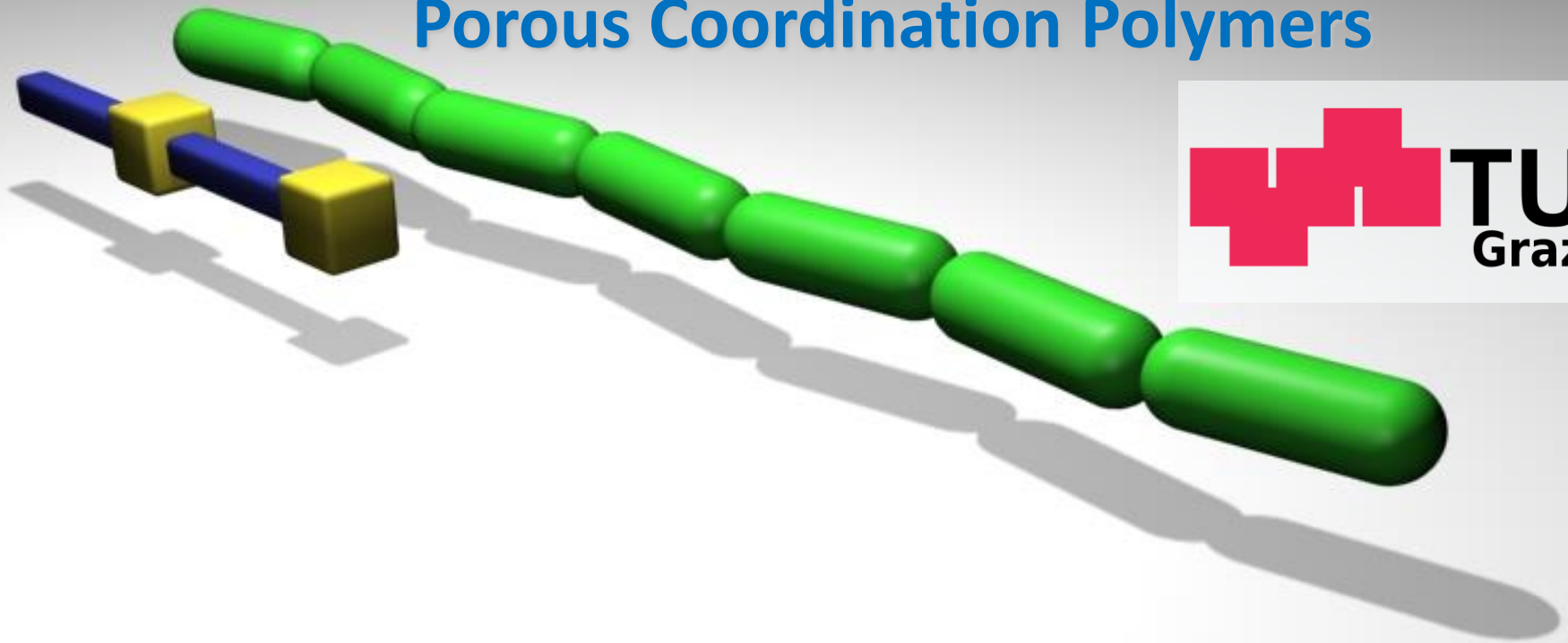
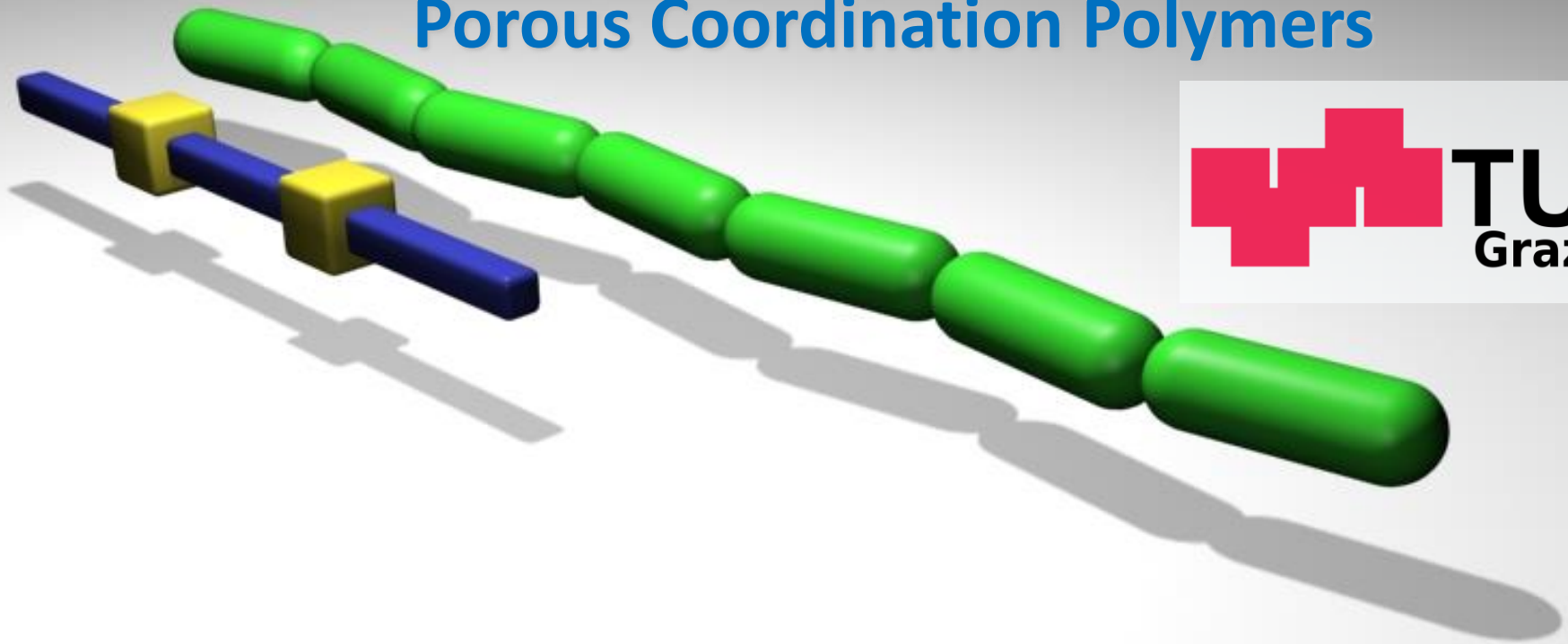
Porous Coordination Polymers



TU Graz

Porous Coordination Polymers



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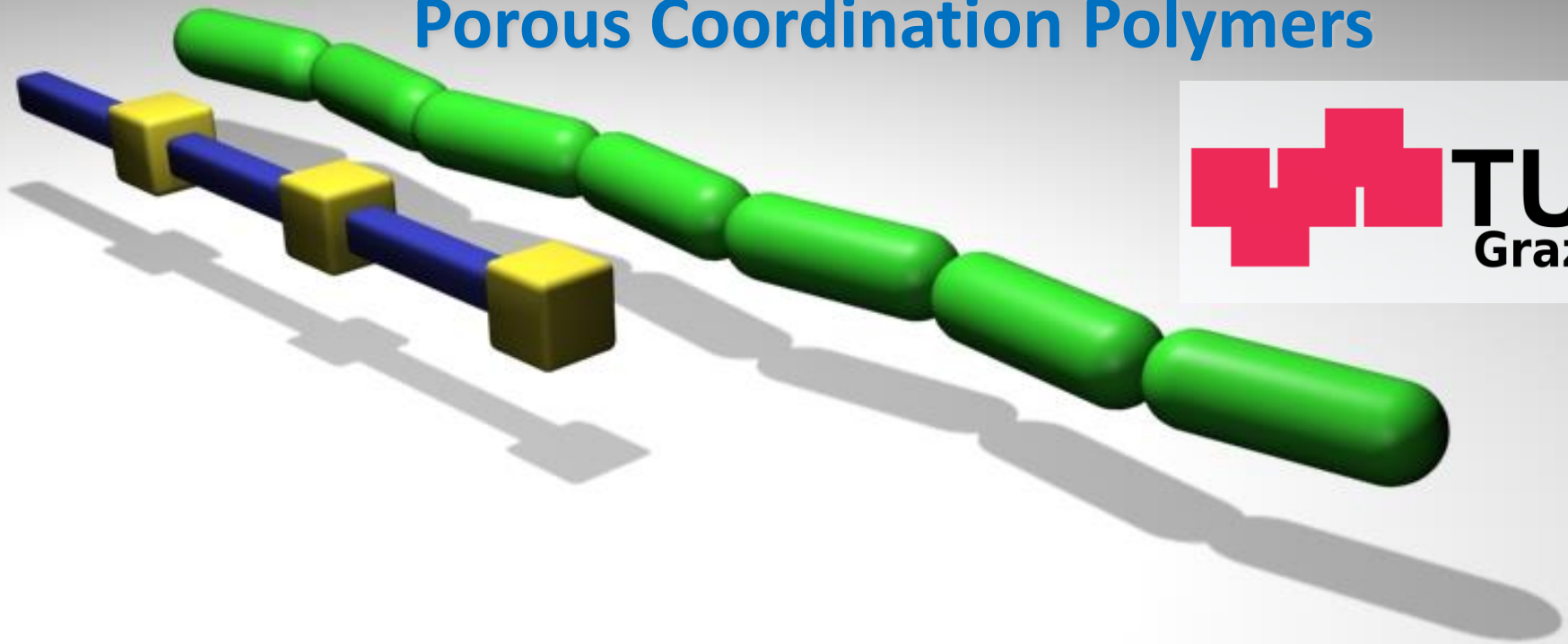
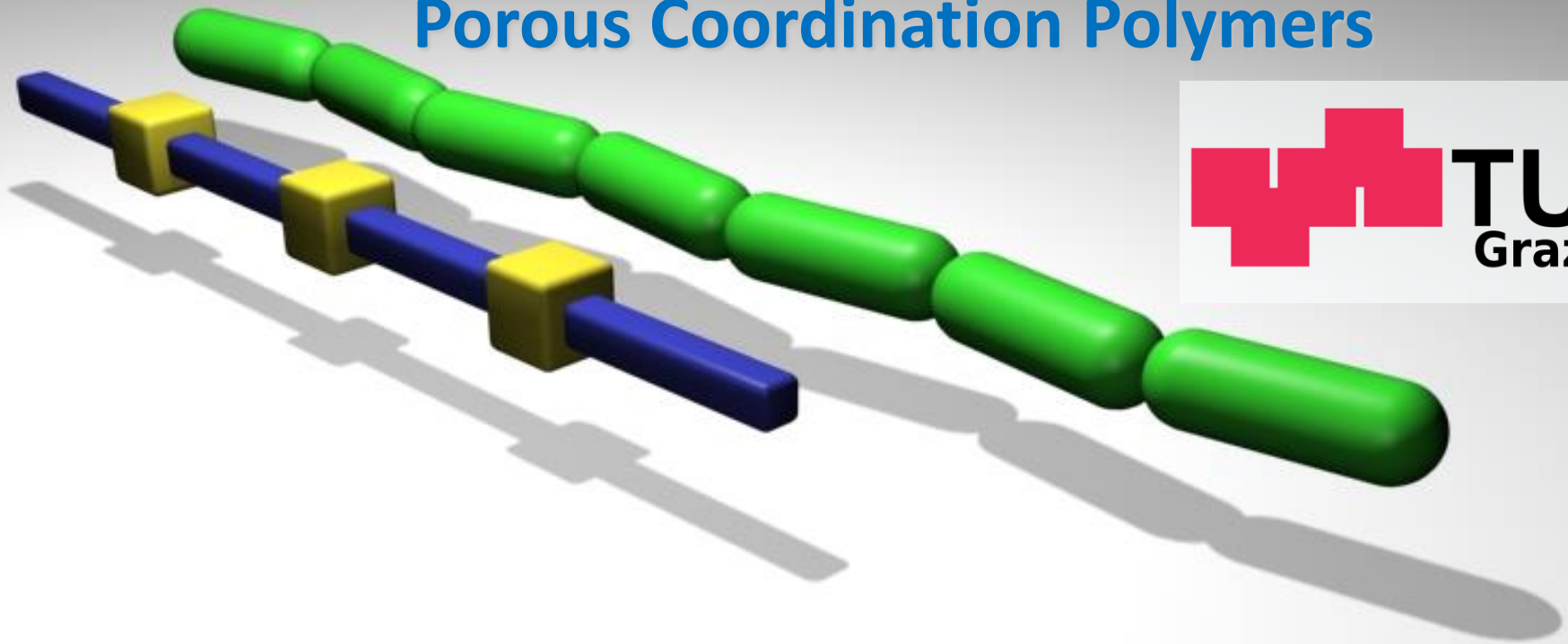


Porous Coordination Polymers



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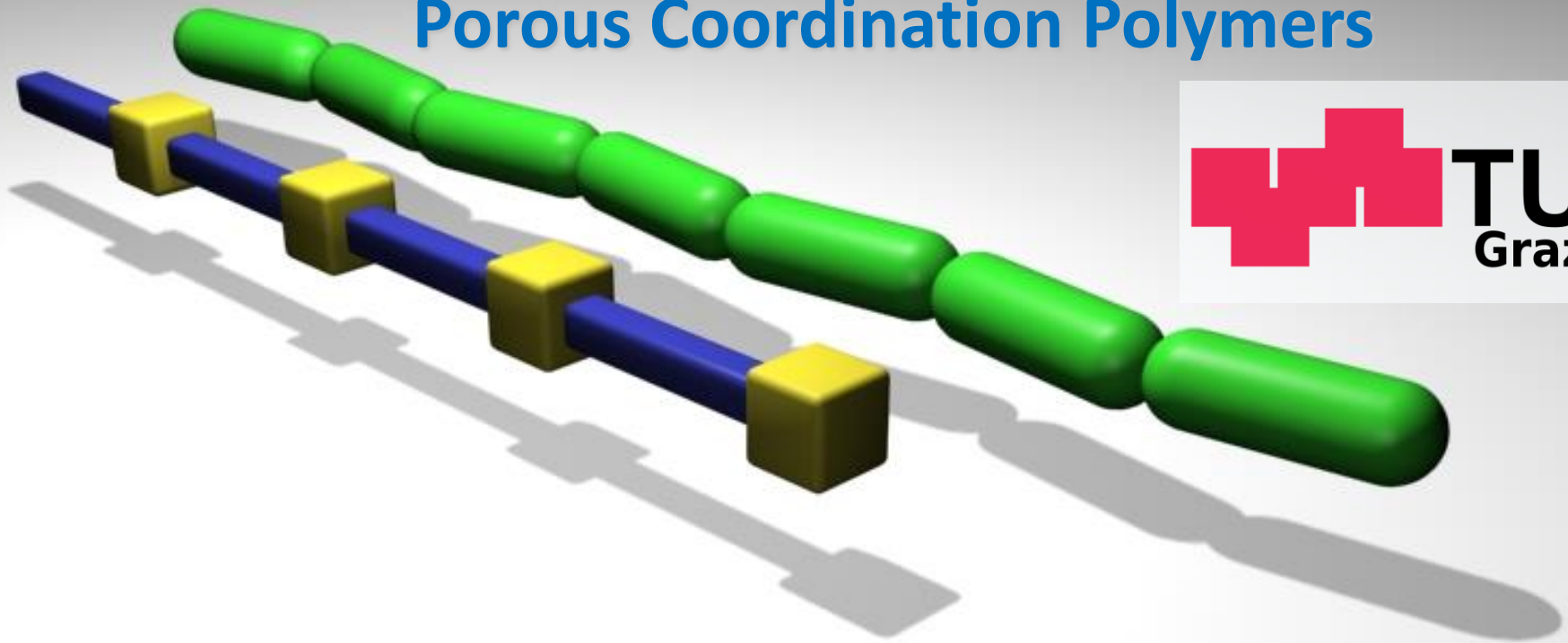
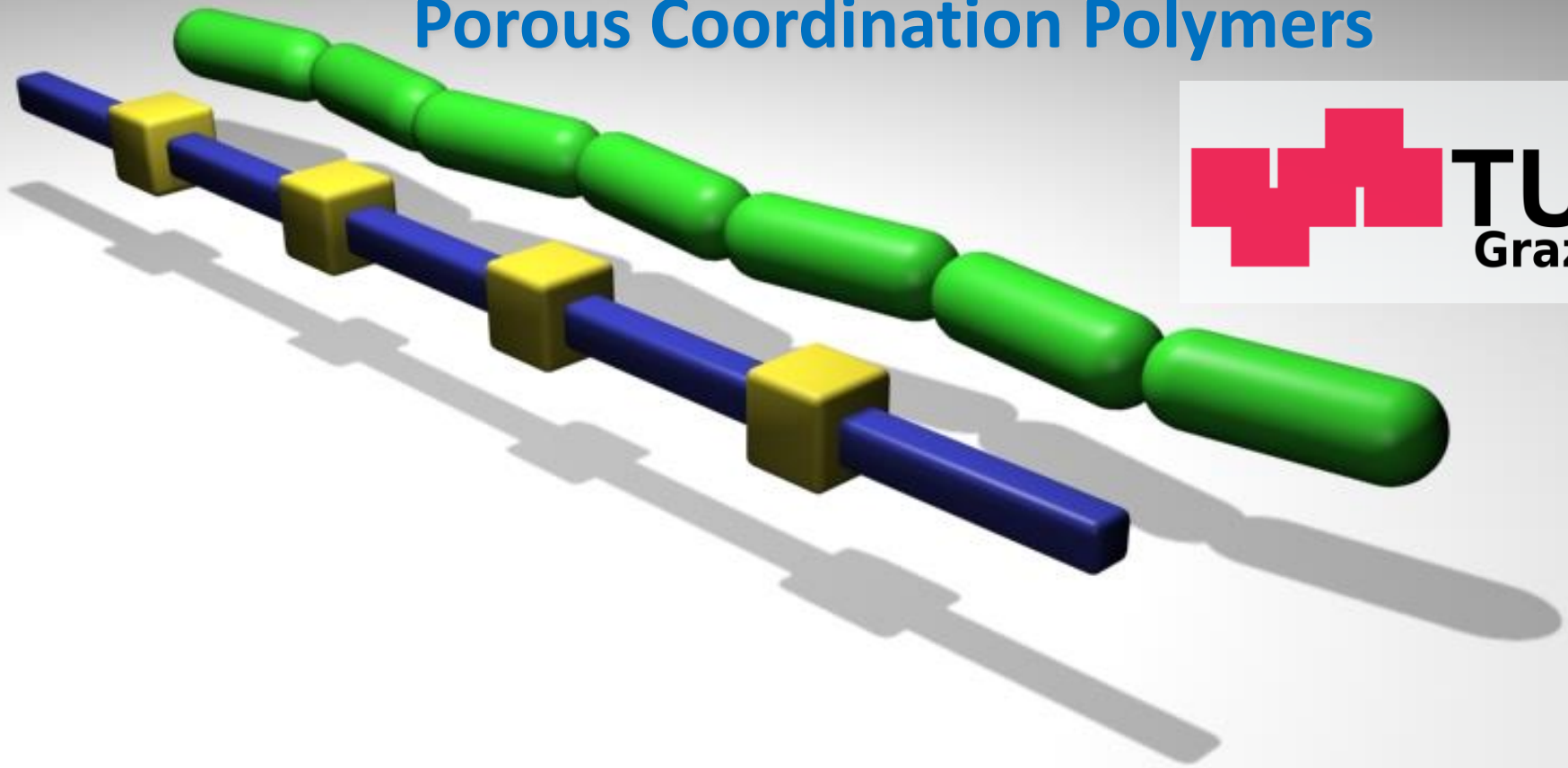
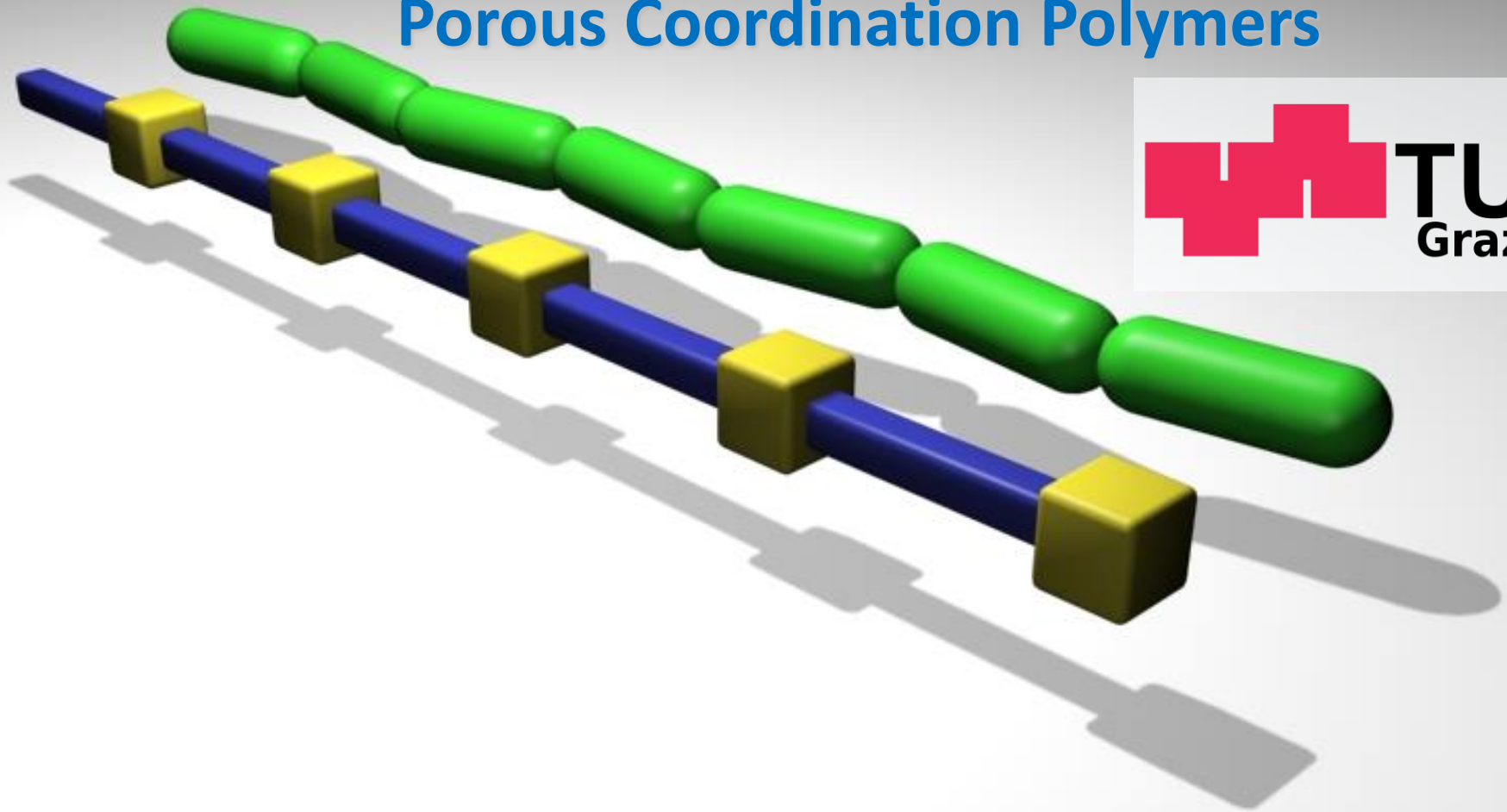
Porous Coordination Polymers



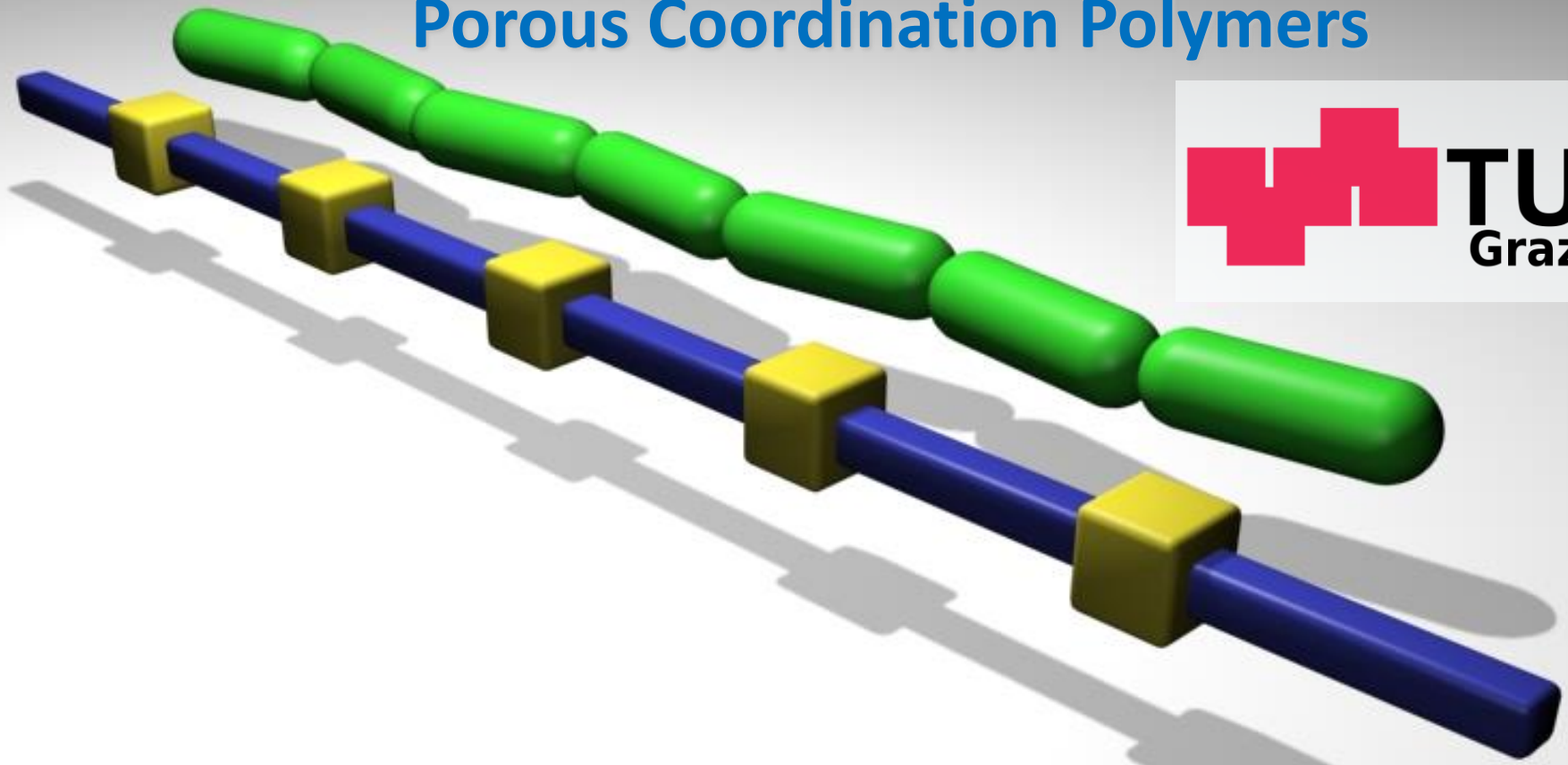
Porous Coordination Polymers



Porous Coordination Polymers

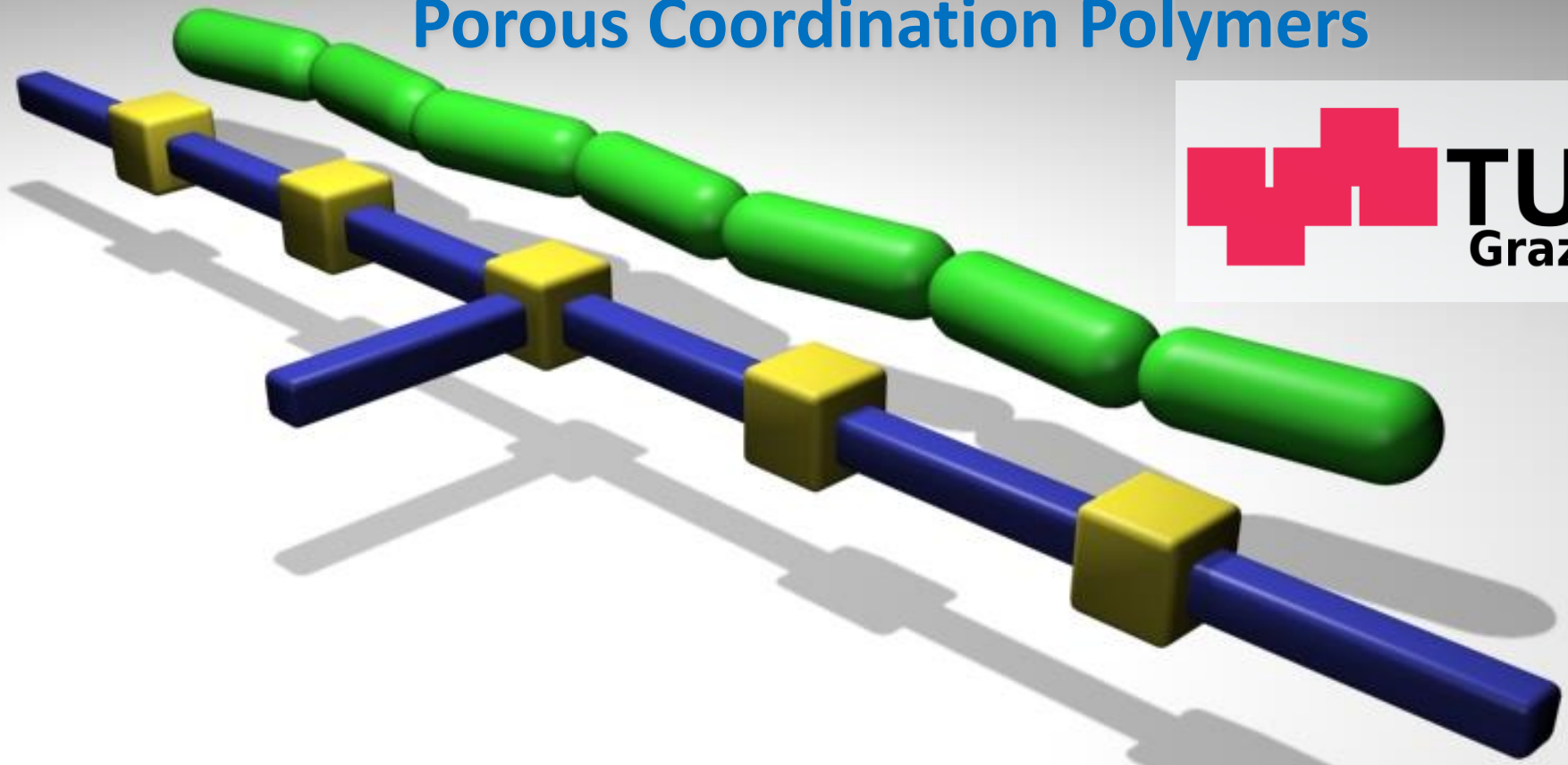


Porous Coordination Polymers



1D Coordination Polym

Porous Coordination Polymers



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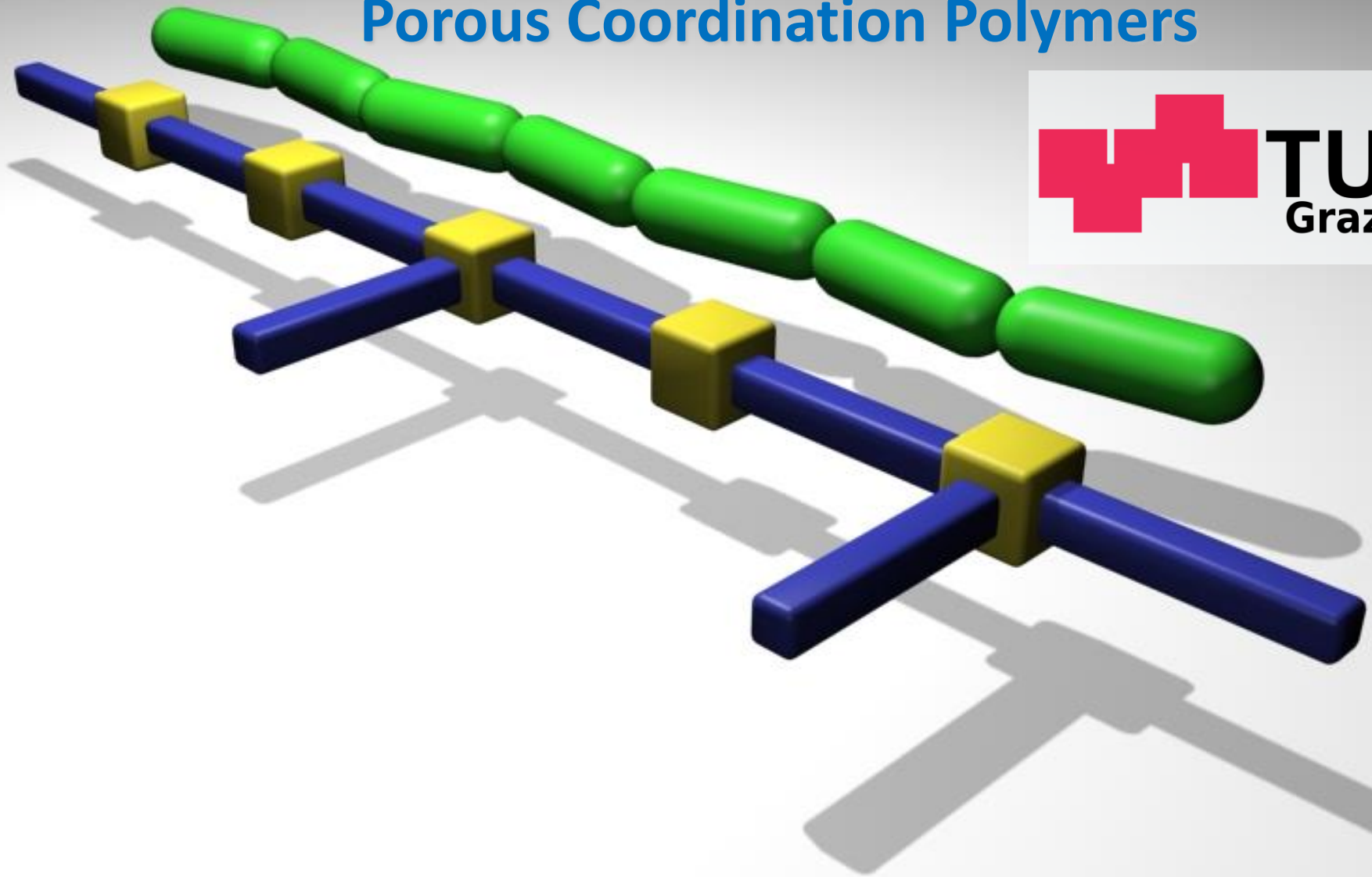
Porous Coordination Polymers



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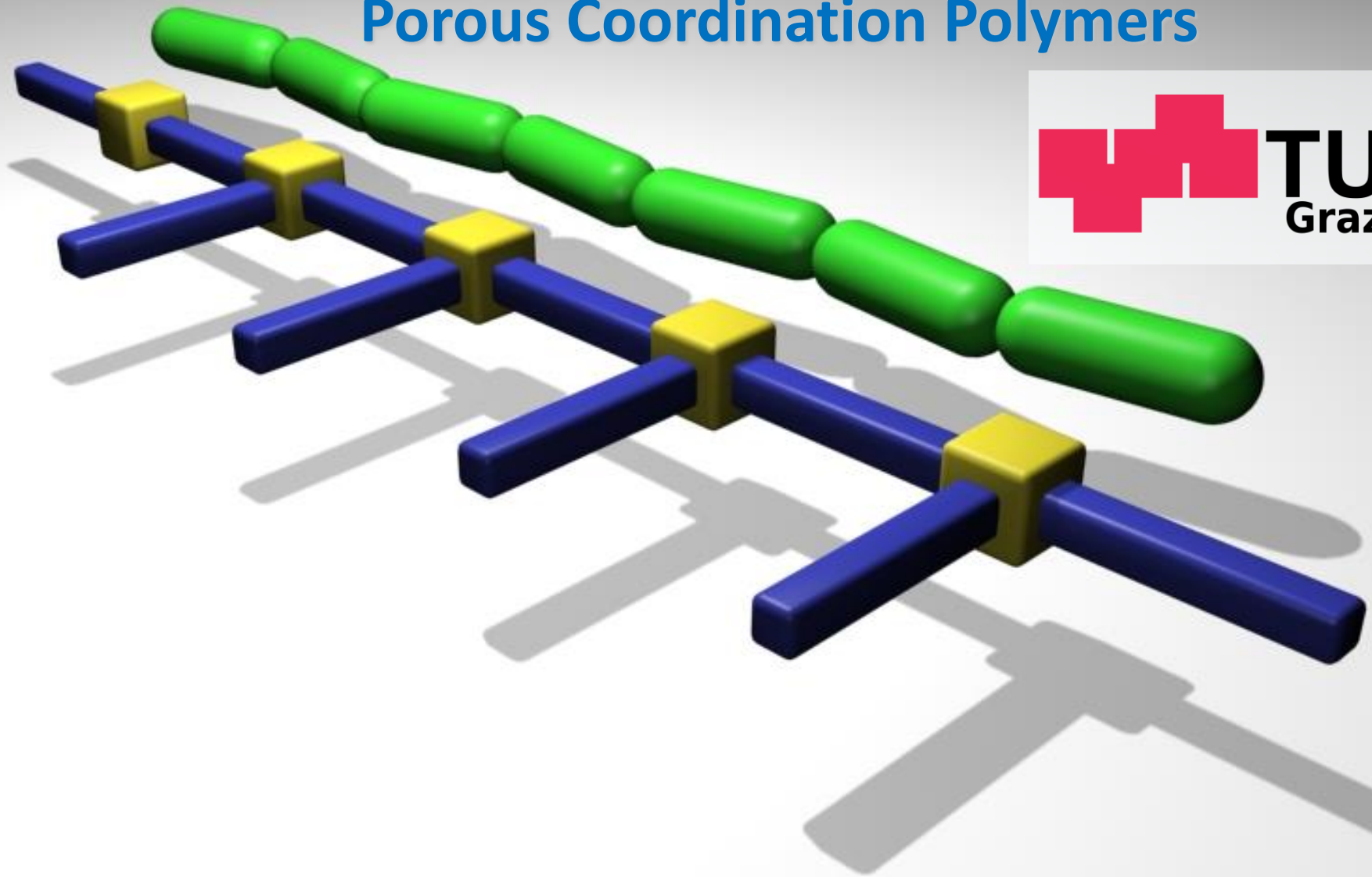

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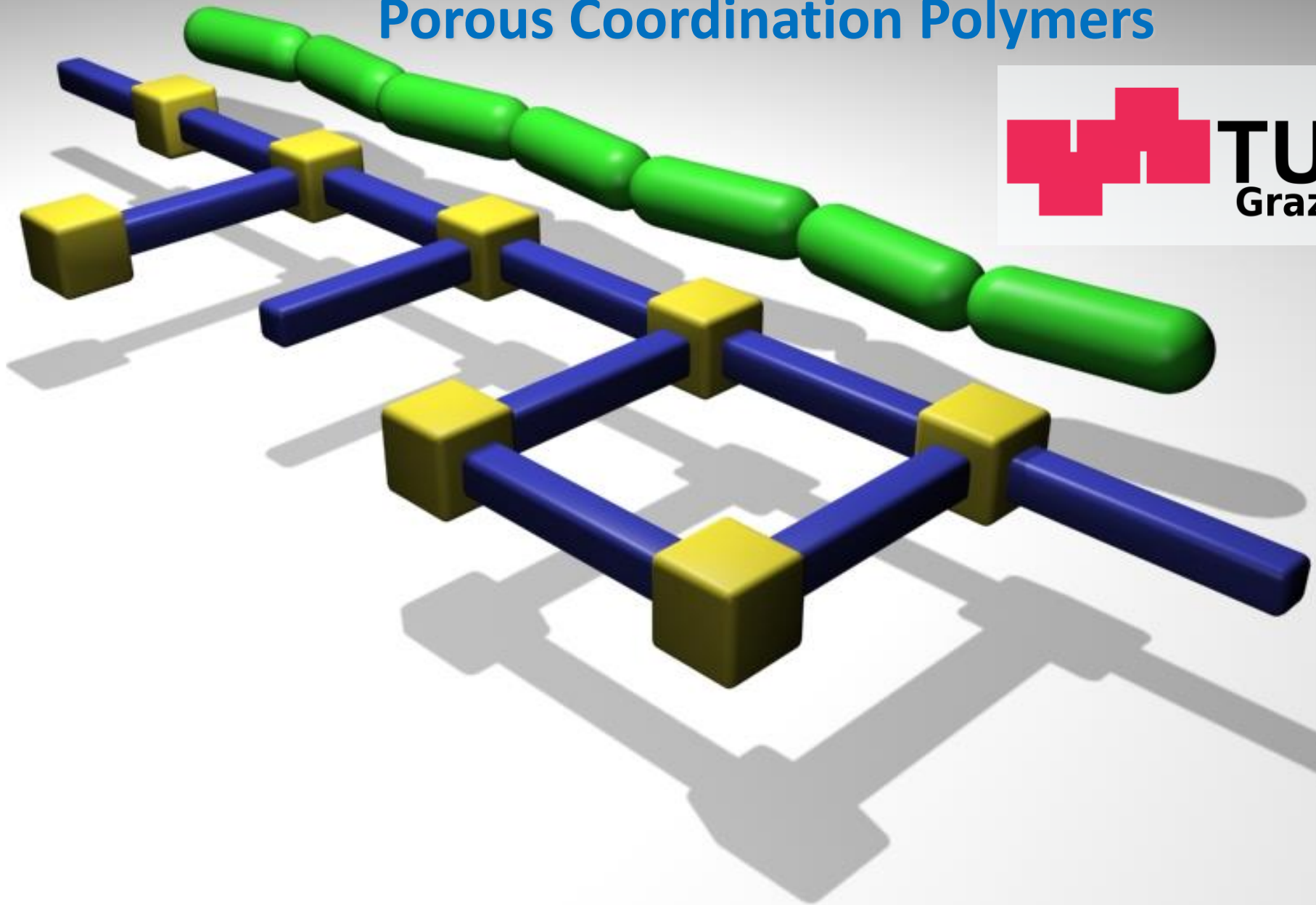

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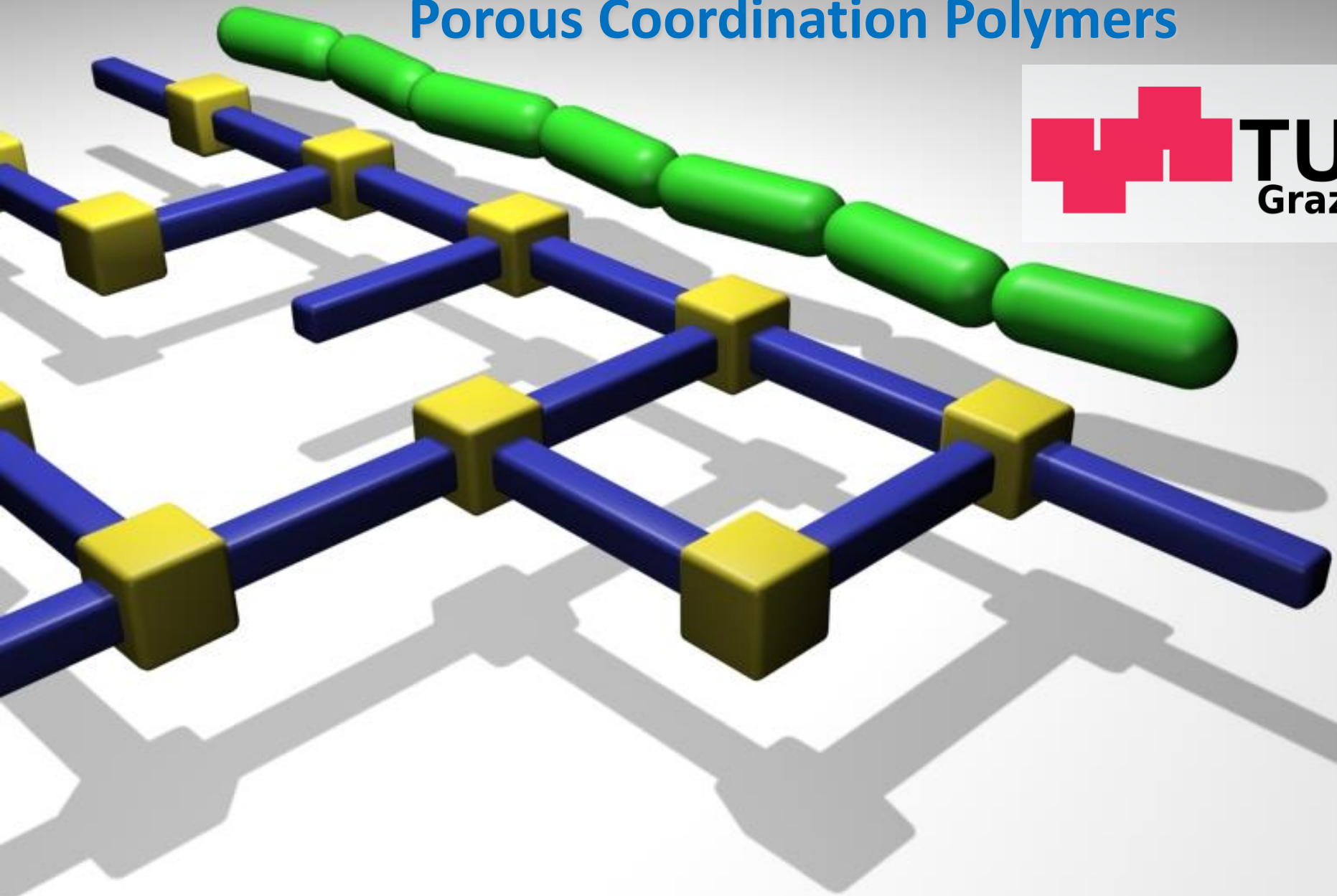

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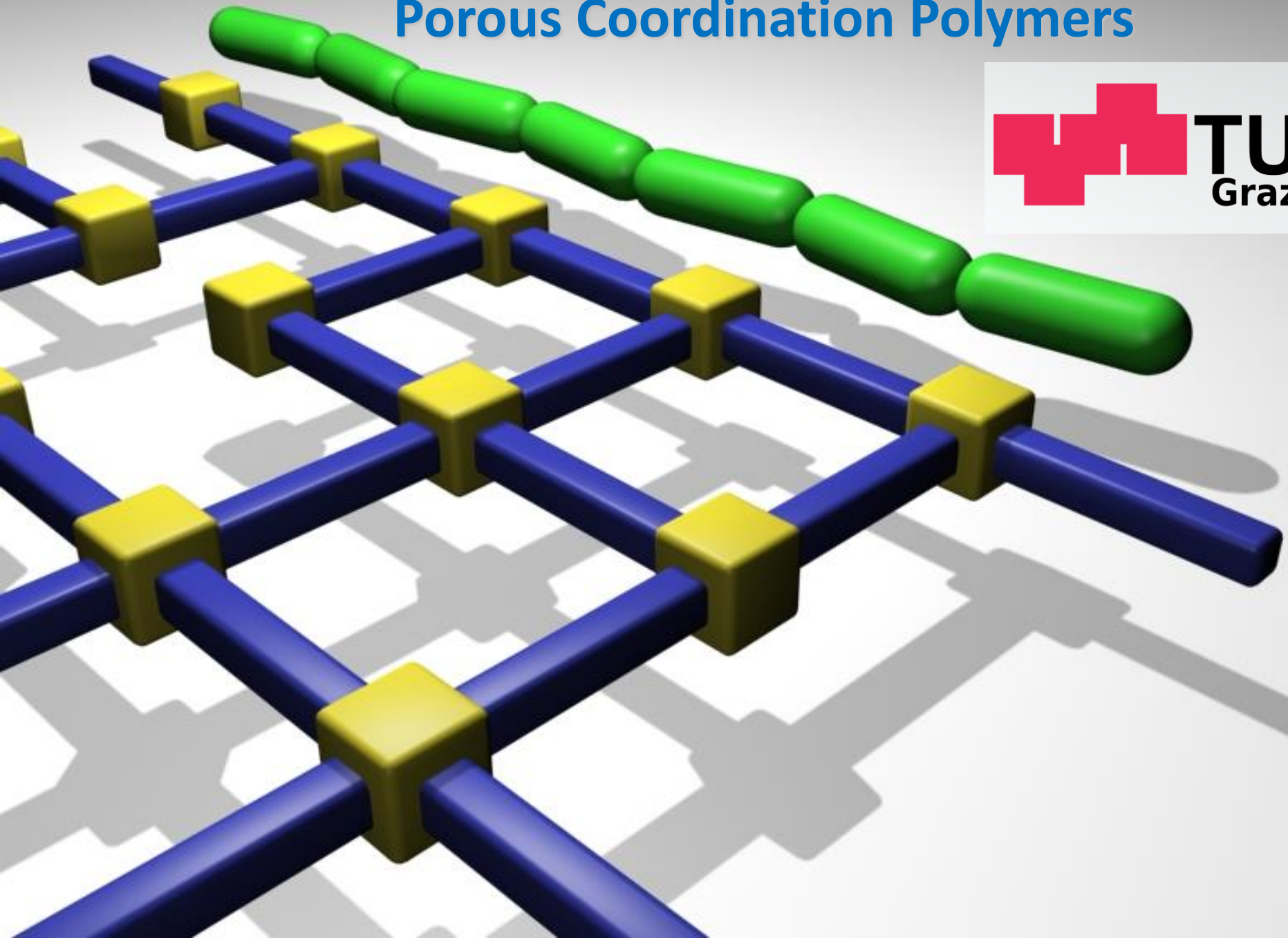
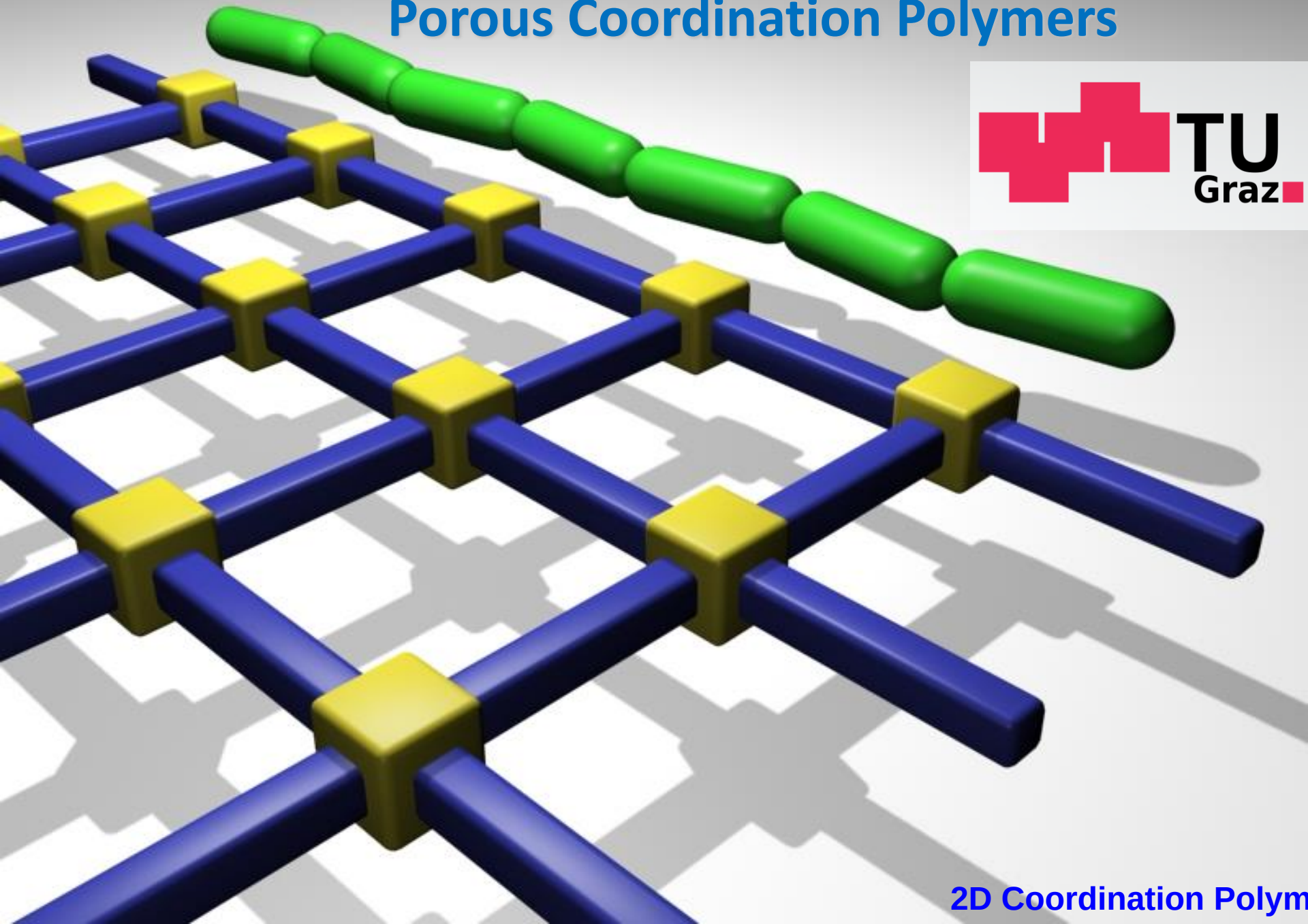
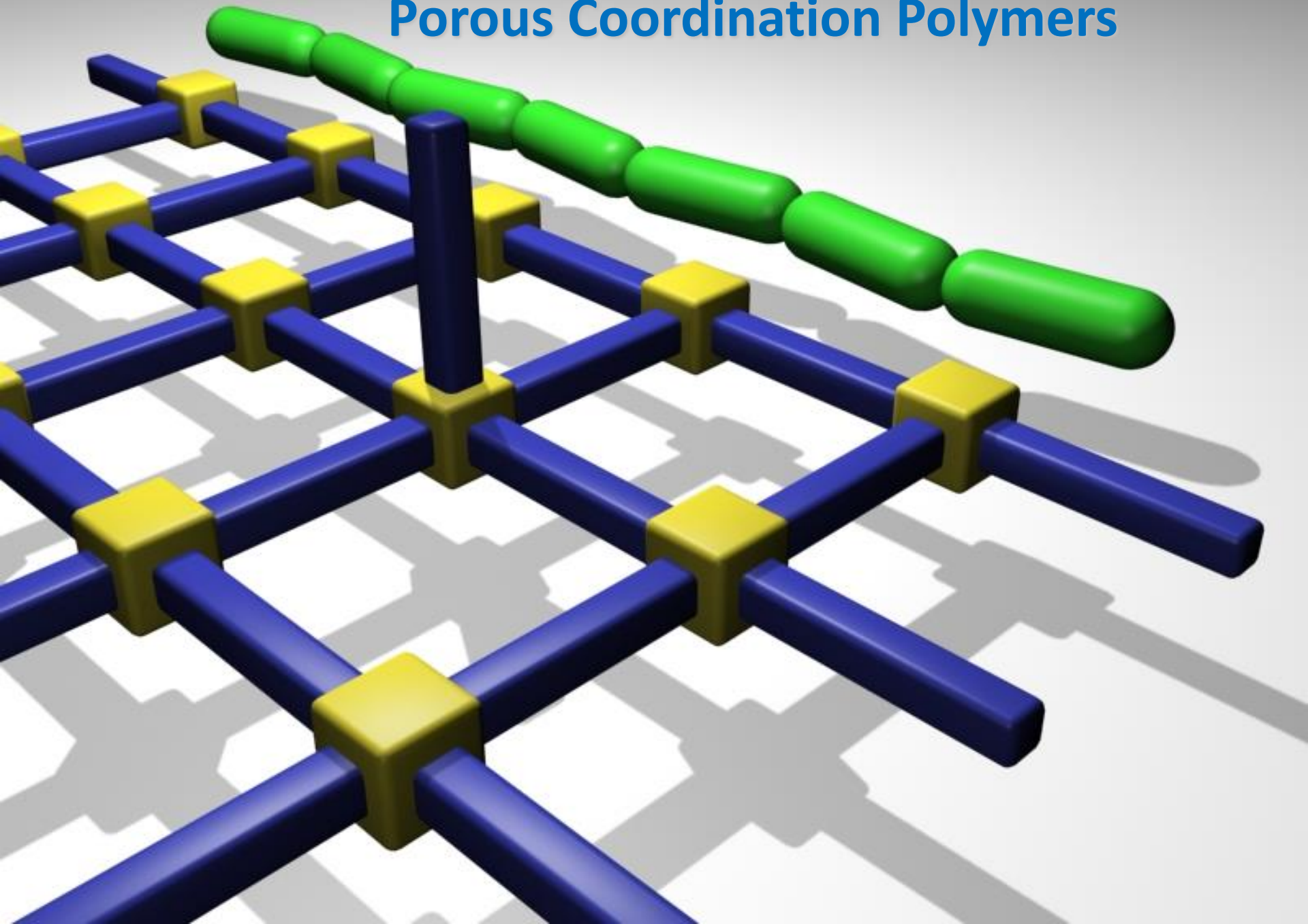


Porous Coordination Polymers

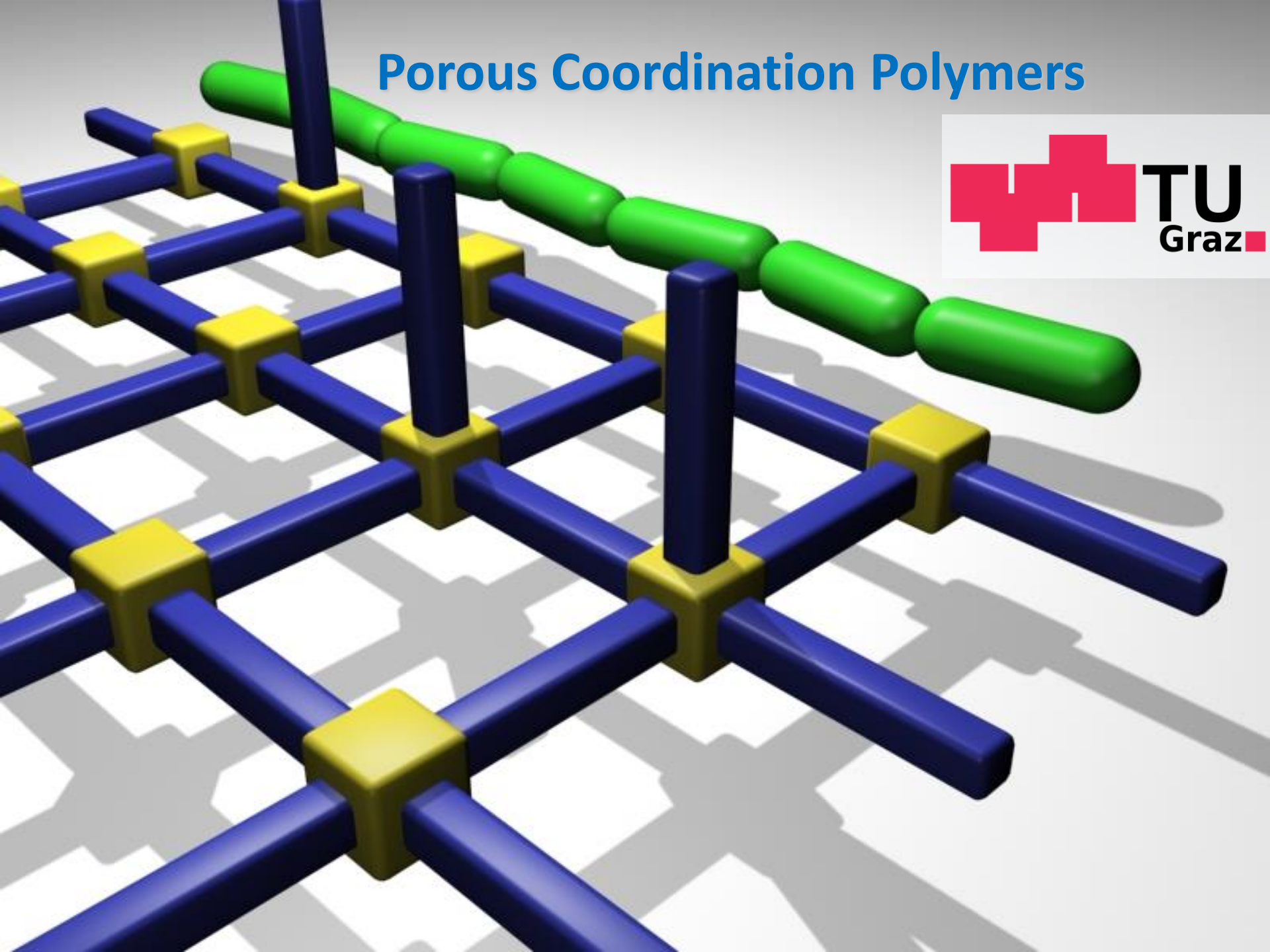


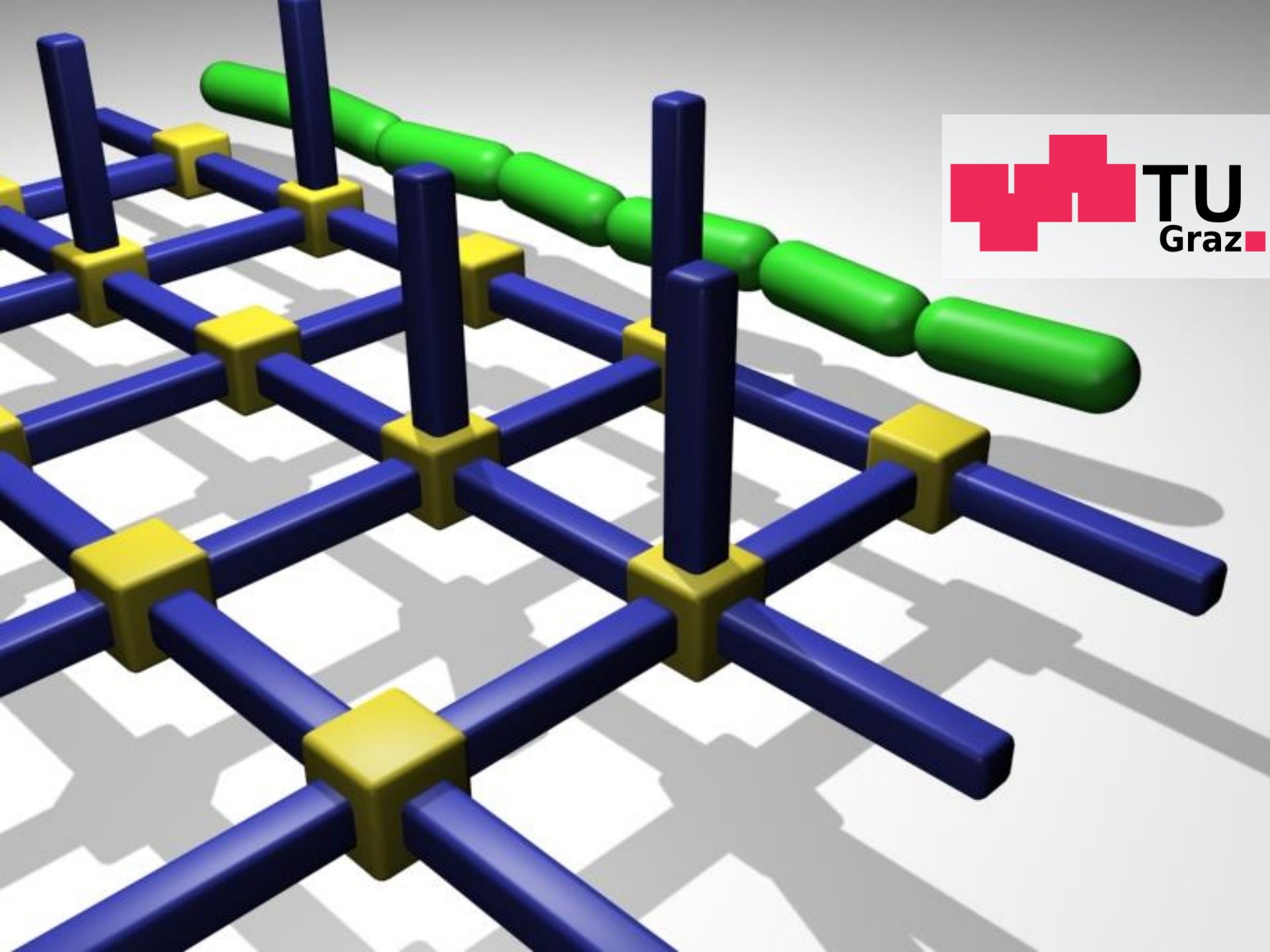
2D Coordination Polym

Porous Coordination Polymers



Porous Coordination Polymers

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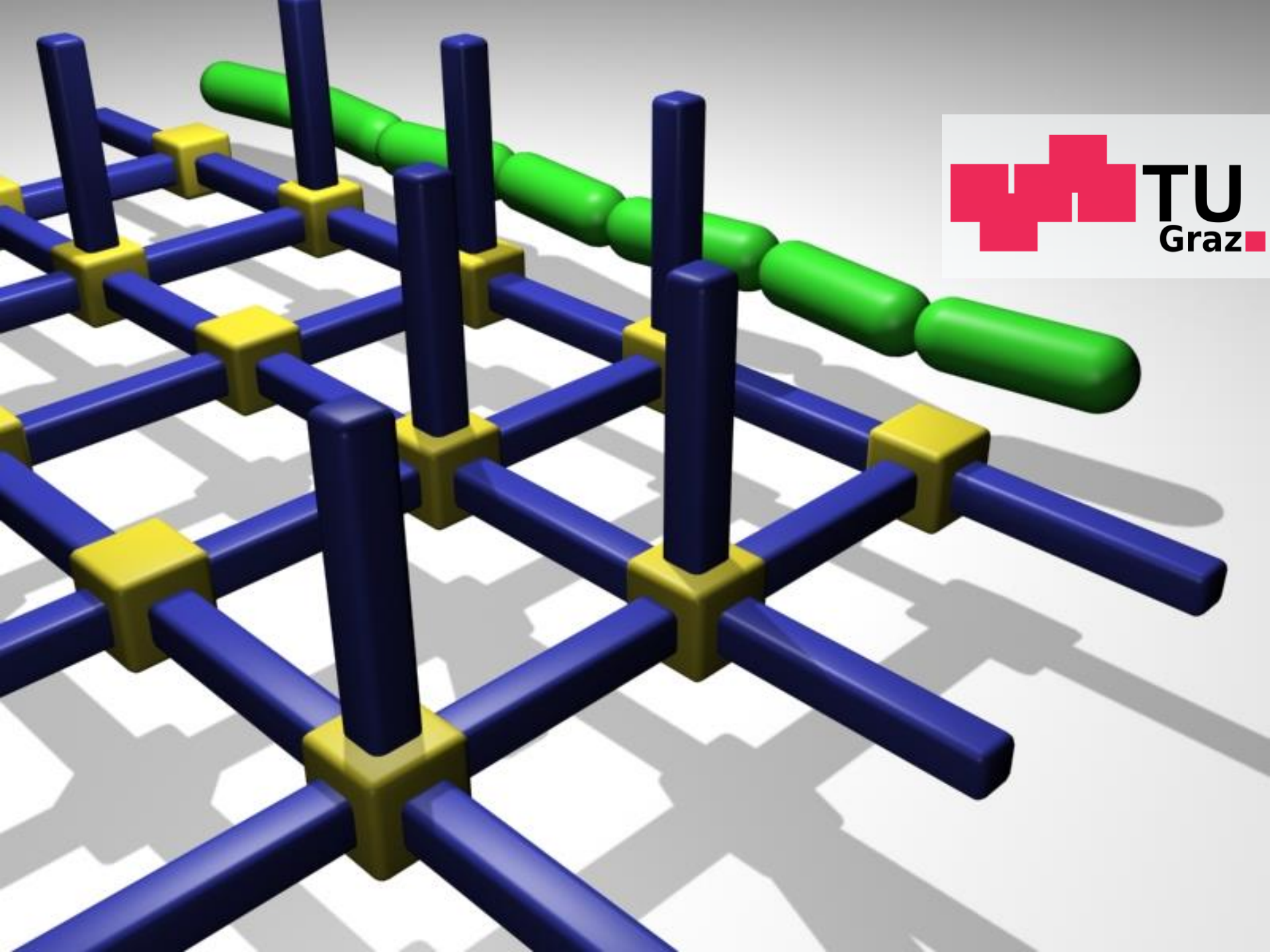
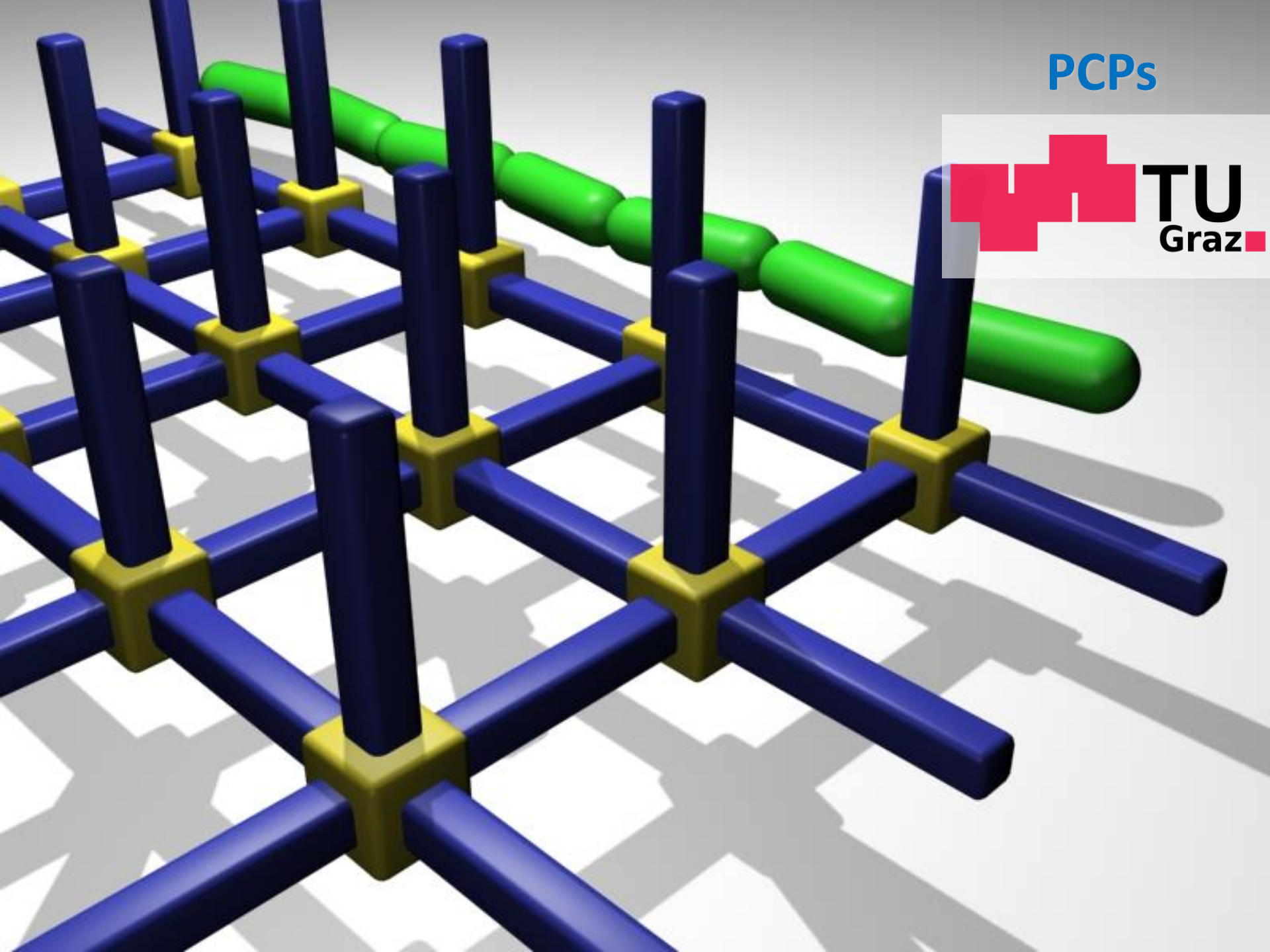

TU
Graz

PCPs



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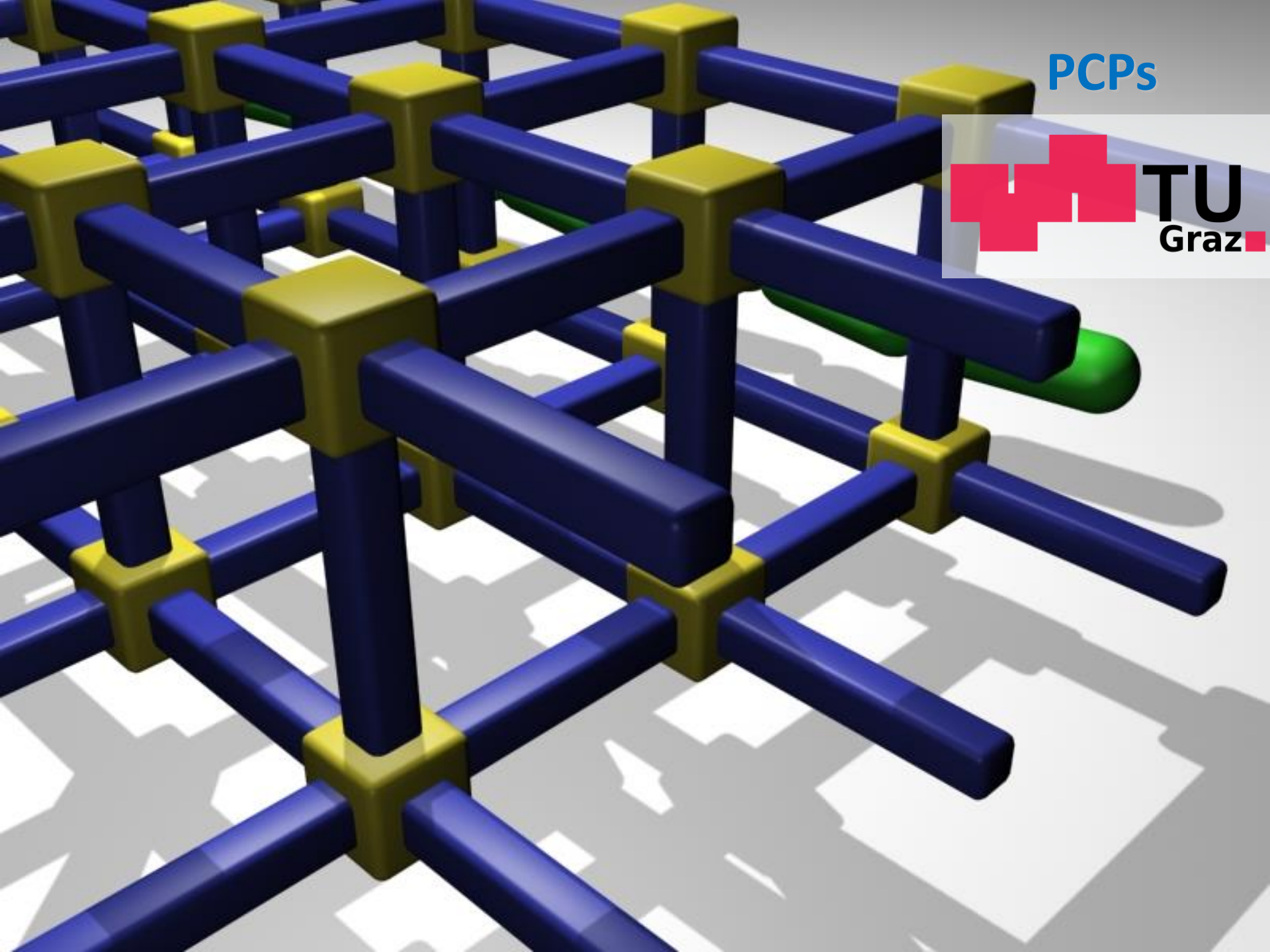

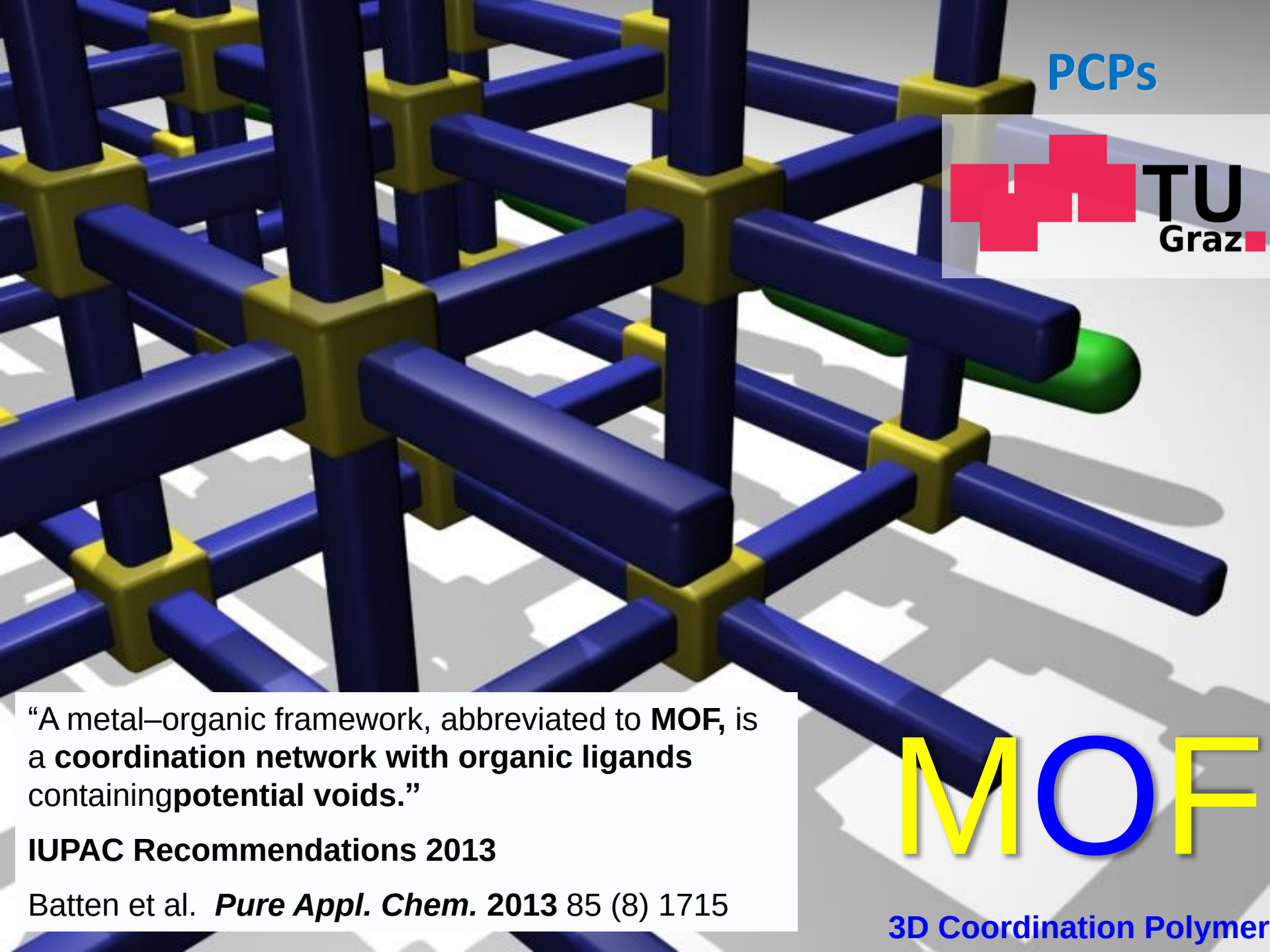

PCPs

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"A metal–organic framework, abbreviated to **MOF,** is a **coordination network with organic ligands** containing**potential voids."**

IUPAC Recommendations 2013

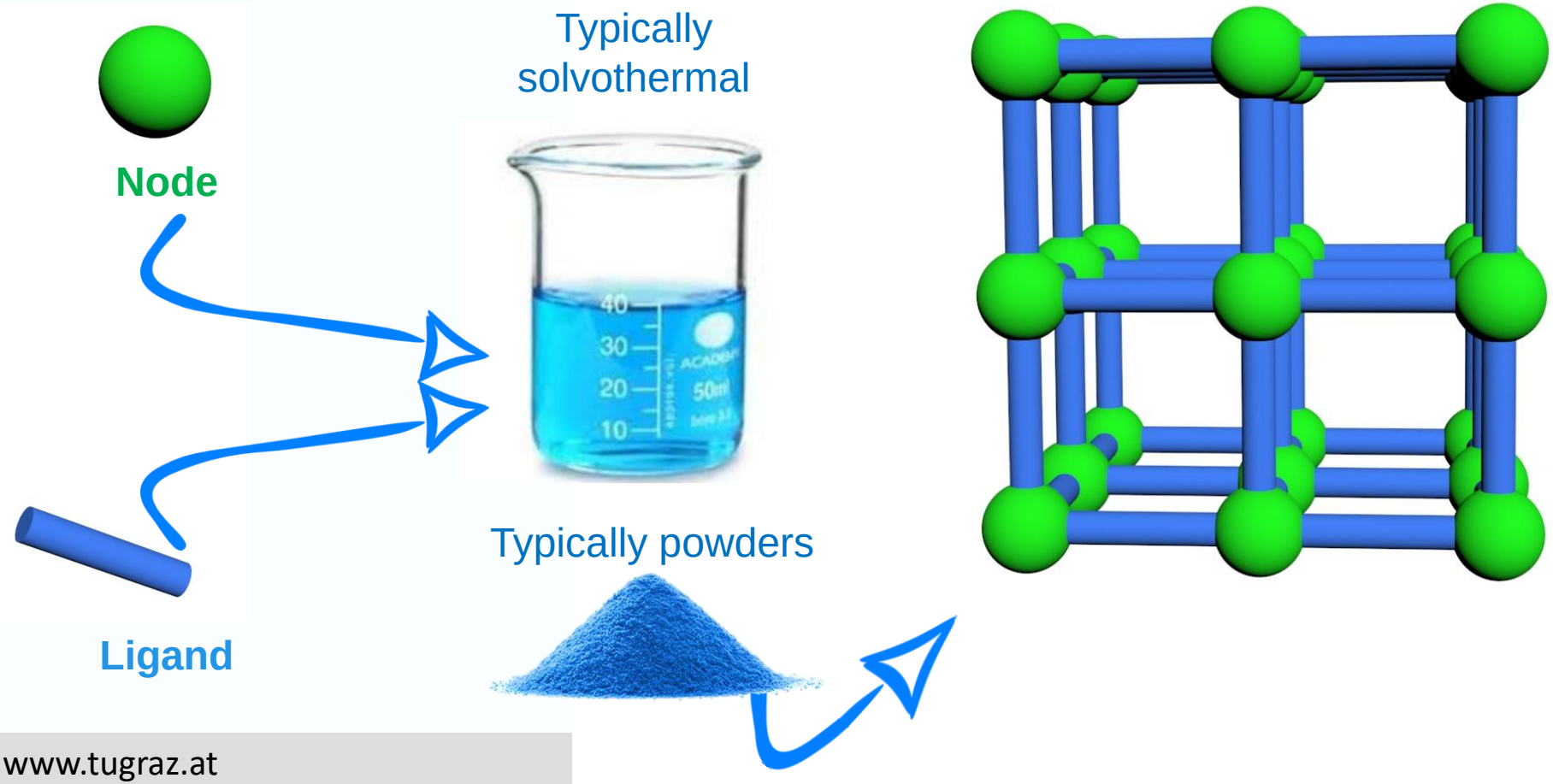
Batten et al. ***Pure Appl. Chem.*** **2013** 85 (8) 1715

MOF

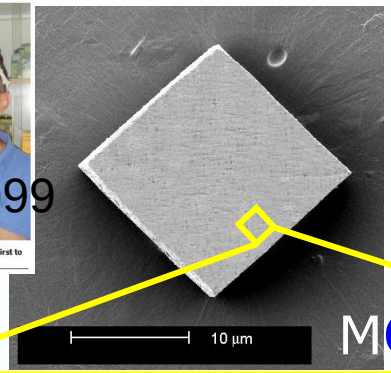
3D Coordination Polymer

Introduction:
Metal-Organic Frameworks (MOFs)

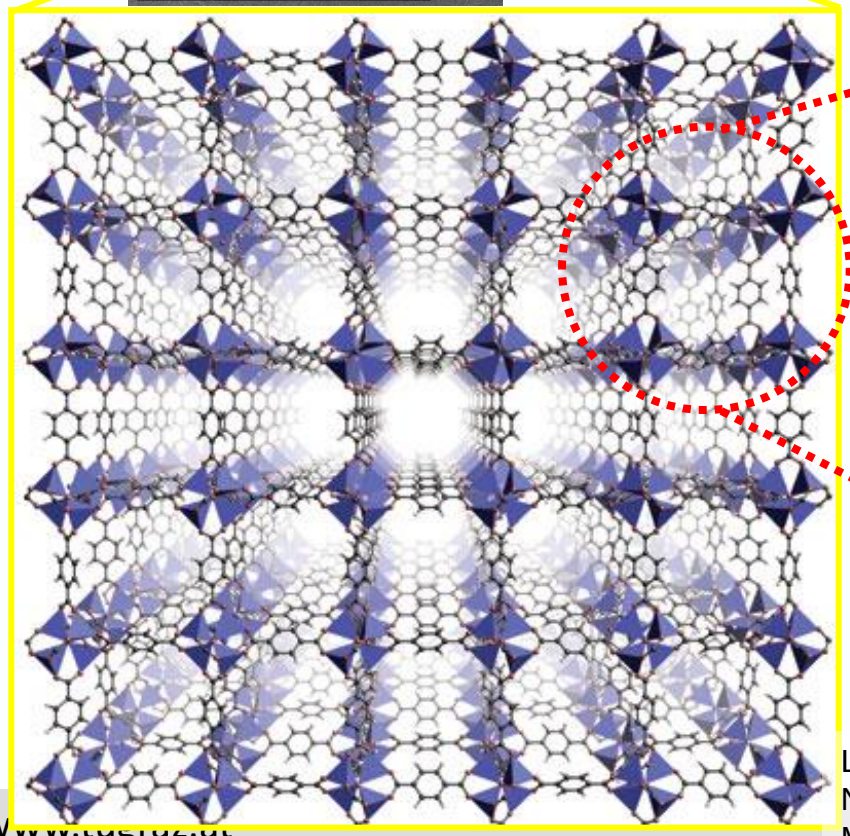
a recent class of Crystalline and Nano-Porous Materials



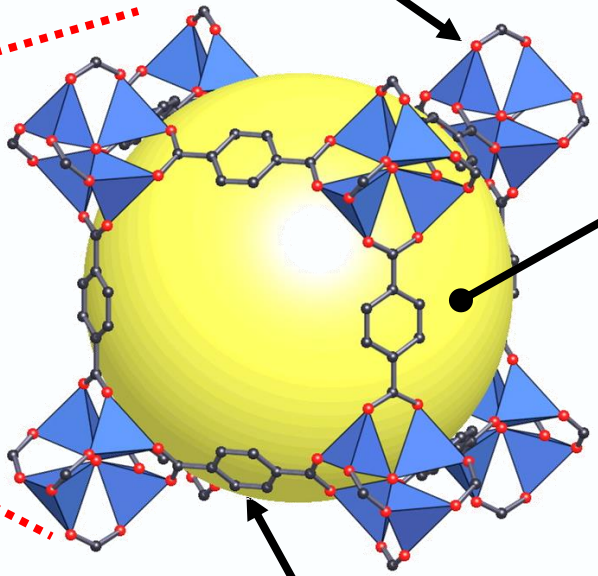
An example of an archetypal Zn (MOF)



MOF-5



Tetragonal Zinc Oxide arrangements



Open pore

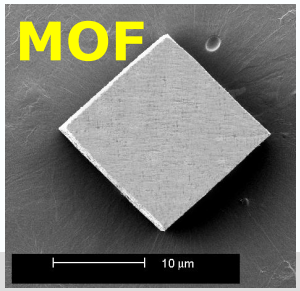
Aromatic linkers

Liu, Y. et al. **Microp. Mesop. Mater.**118, 296 (2009); Senderson K. Nature 448, 749 (2007); Li M. et al. **Nature** 402, 276 (1999); Eddaoudi M. et al. **Science** 469 (2002);

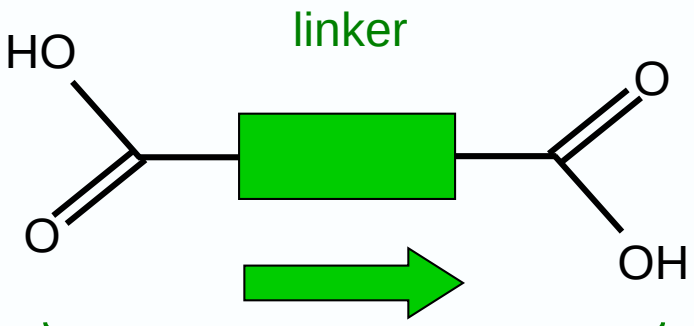
~ 7000 m^2g^{-1}

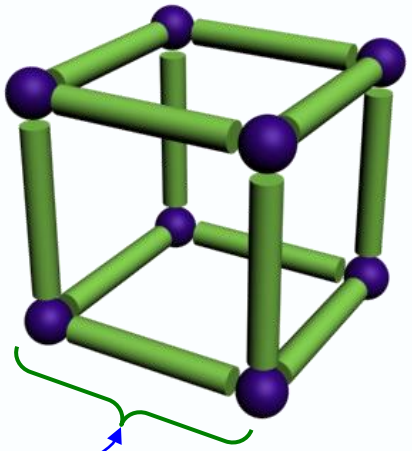
TU Graz

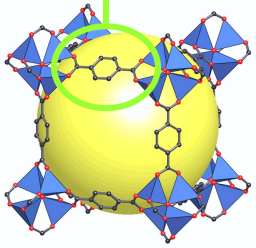
=



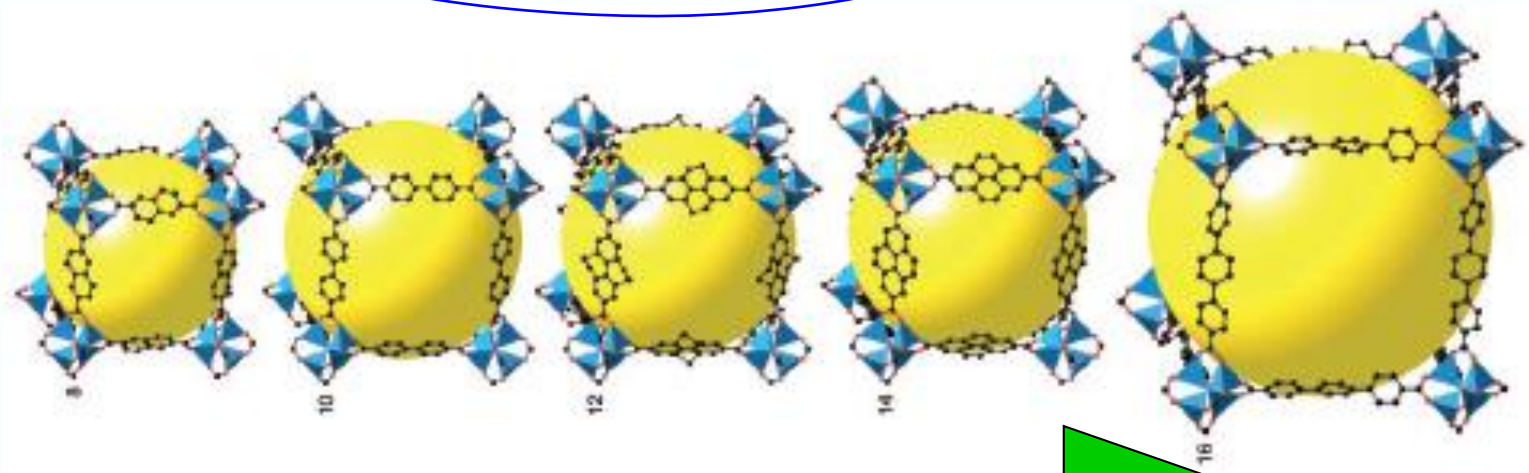
Pore size





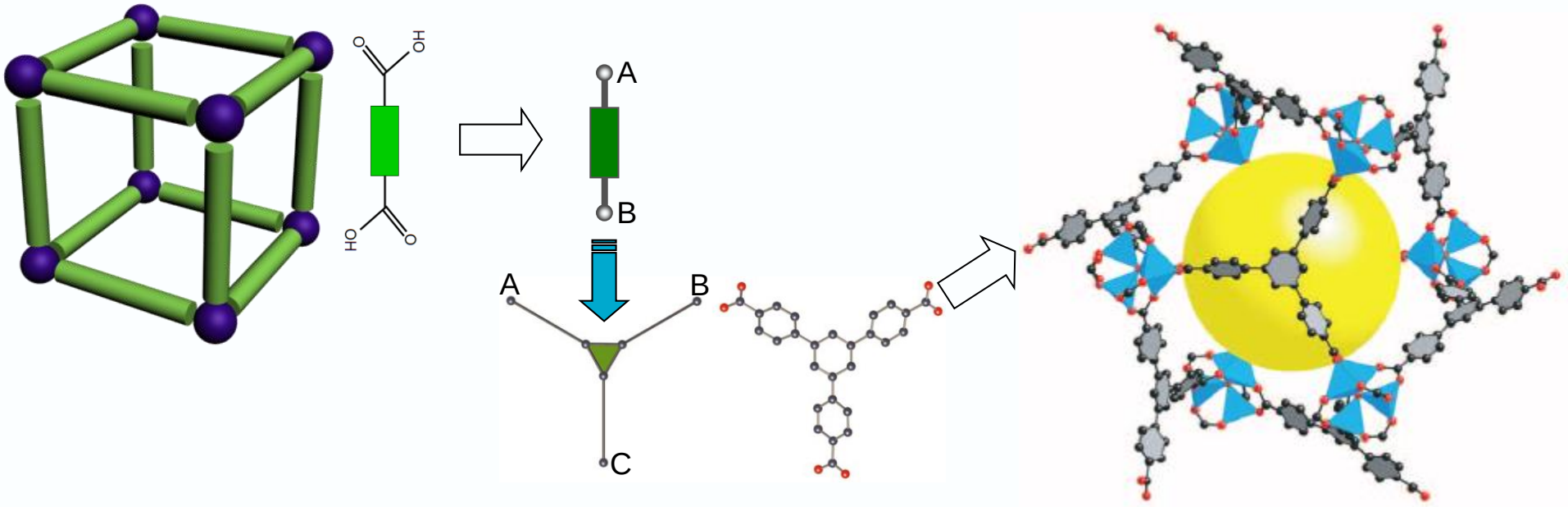


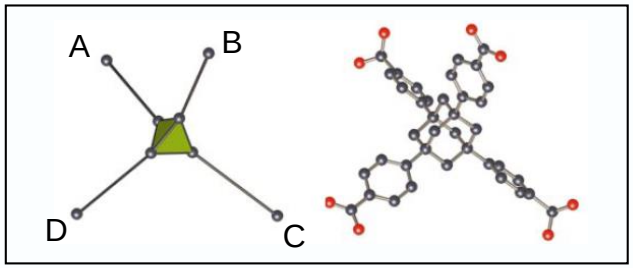
MOF-5

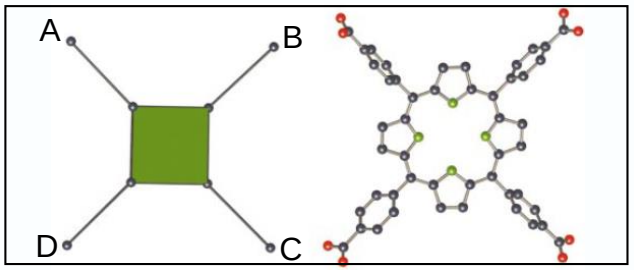


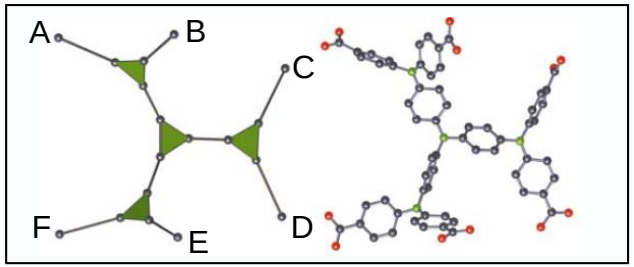
Eddaudi M. et al. *Science* 295(2002)

Architecture of the unit cell

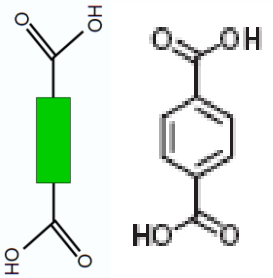


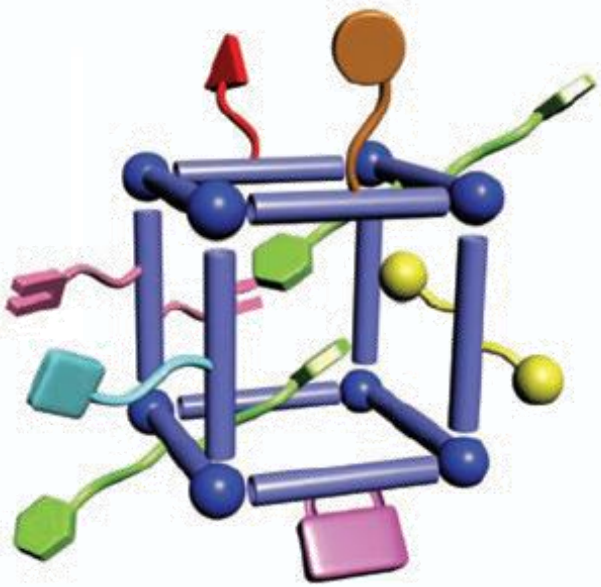




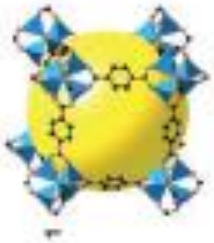


Functional groups



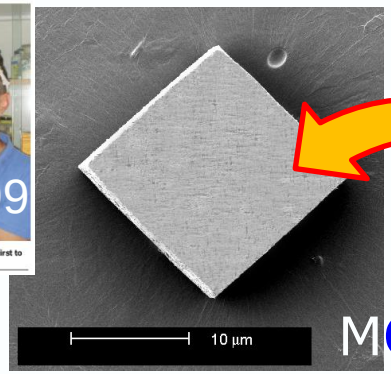


MTV-MOF-5 structure
with eight different functionalities



Deng M., Science 307, 2010

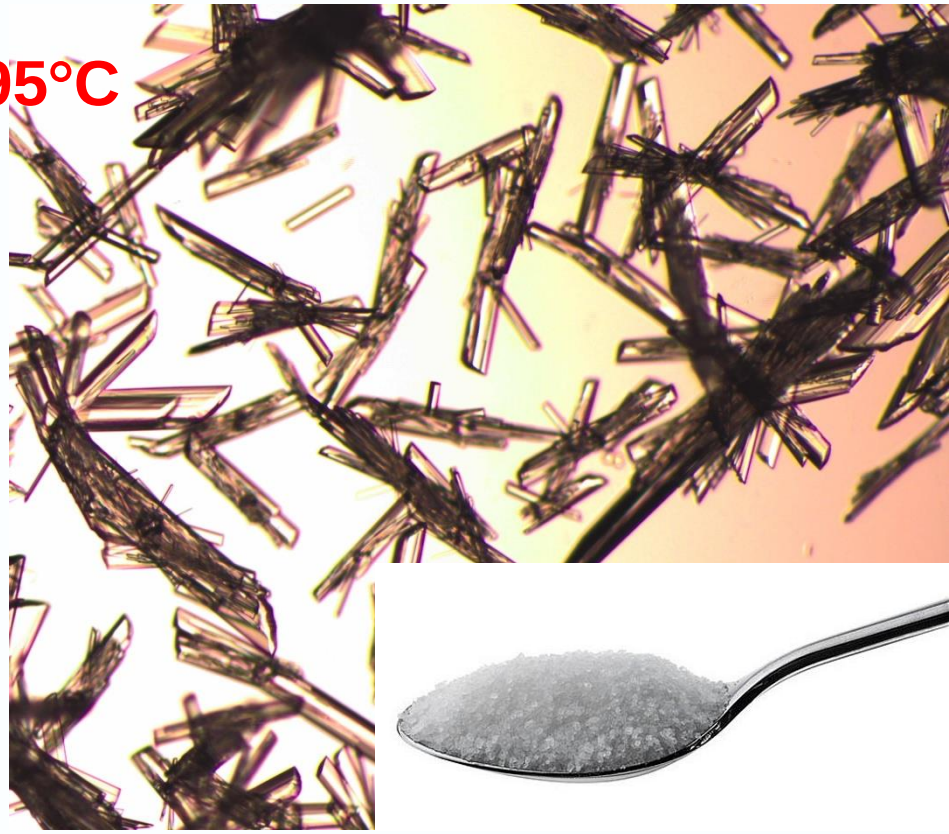
How do we make MOFs? The example of MOF-5



24 h @ 95°C

Zn precursor

Terephthalic acid

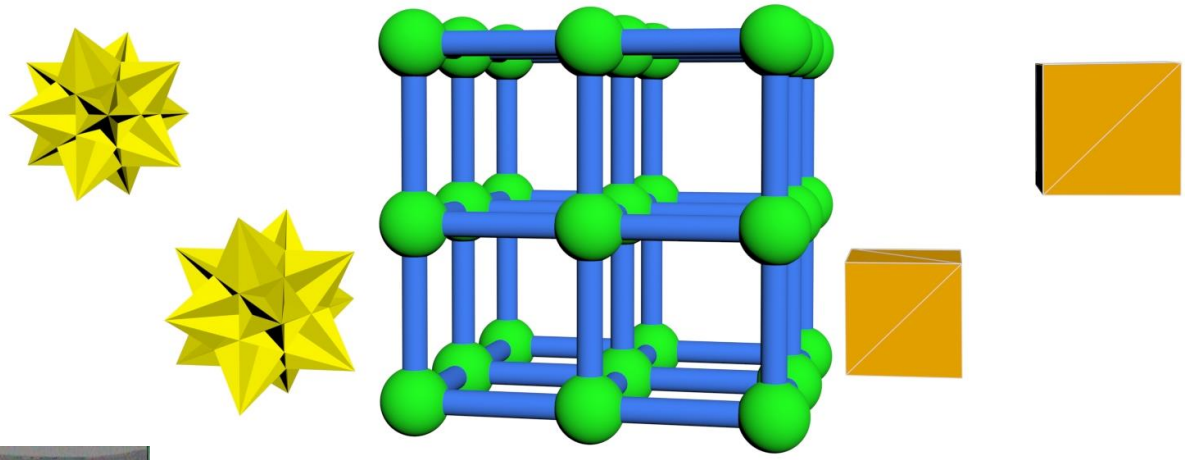


Self-assembly process, challenge to control the crystals growth

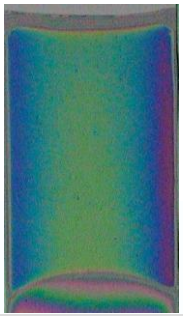
Liu, Y. et al. **Microp. Mesop. Mater.**118, 296 (2009); Senderson K. **Nature** 448, 749 (2007); Li M. et al. **Nature** 402, 276 (1999); Eddaoudi M. et al. **Science** 469 (2002);

Properties:
Metal-Organic Frameworks (MOFs)

1) Ultra-high accessible surface area
2) Uniform pore size
3) Tuneable pore size and chemical functionality



Separation,
Storage,
Catalysis,
Delivery.

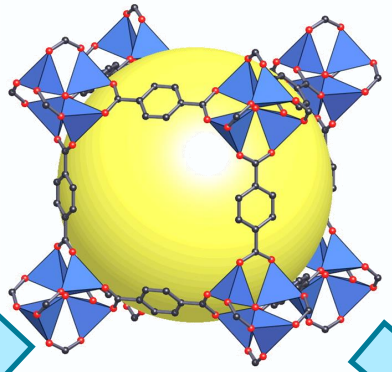


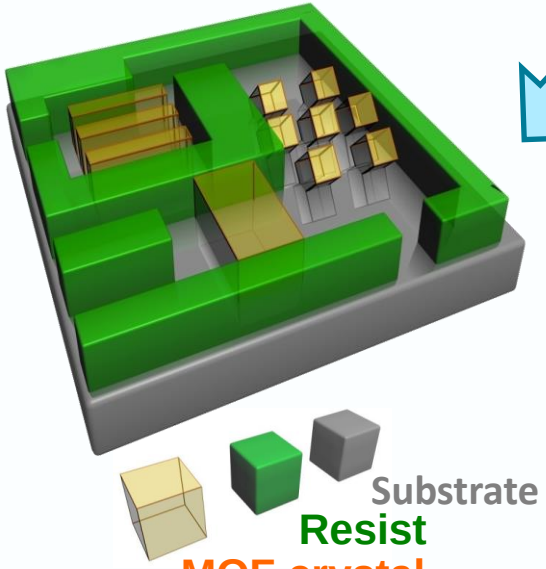
For device fabrication, films are required:

Membranes, Sensing, Dielectrics, Ion conductors, Optics, ...

What is our vision and contribution to the field?

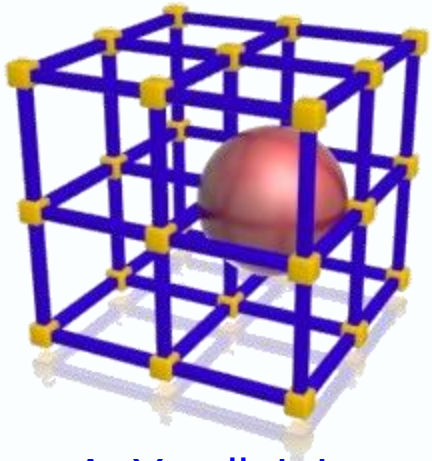
Device Fabrication





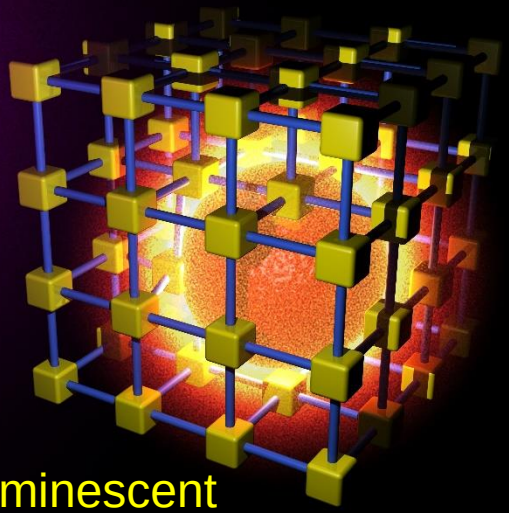
P. Falcaro, D. Buso, A. J. Hill, C. Doherty, ***Adv. Mater.*** 2012

Encapsulation

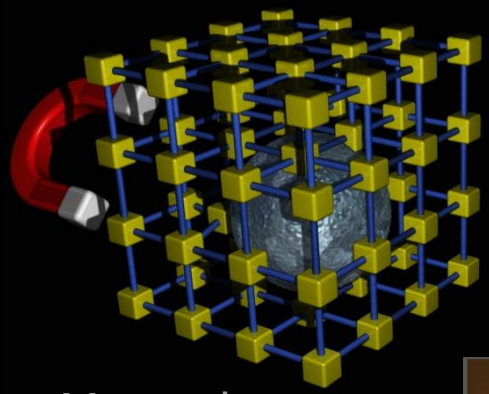


P. Falcaro, R. Ricco, A. Yazdi, I. Imaz, S. Furukawa, D. Maspoch, R. Ameloot, J. D. Evans, C. J. Doonan, ***Coord.Chem.Rev.*** 2015

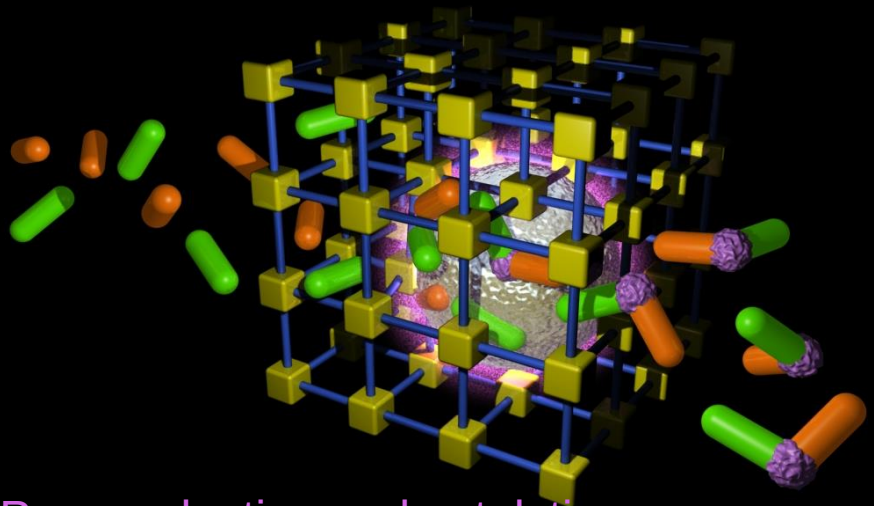
Functionalization with particles… and more…



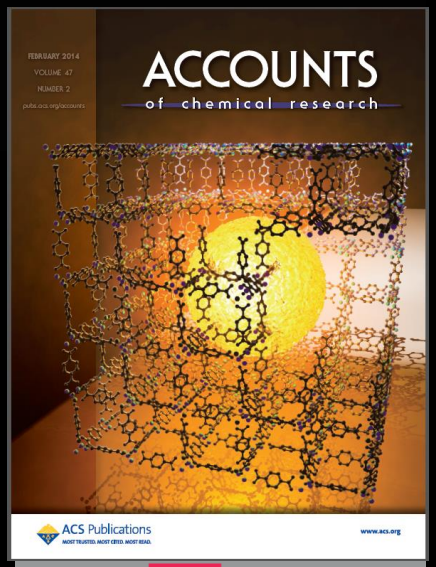
Luminescent



Magnetic

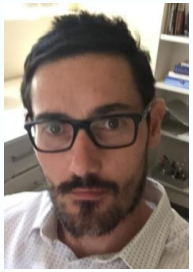


Perm-selective and catalytic

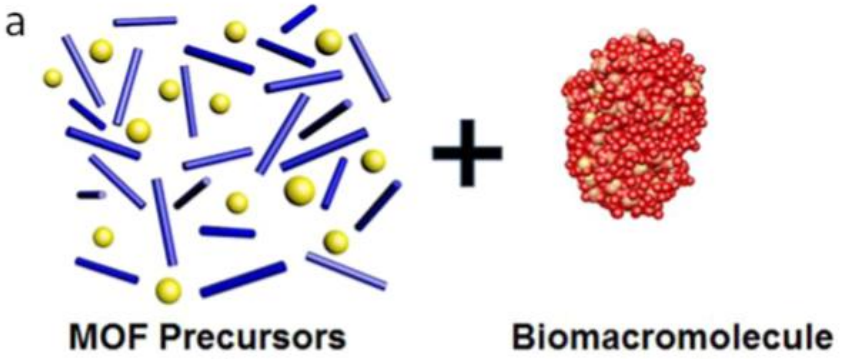


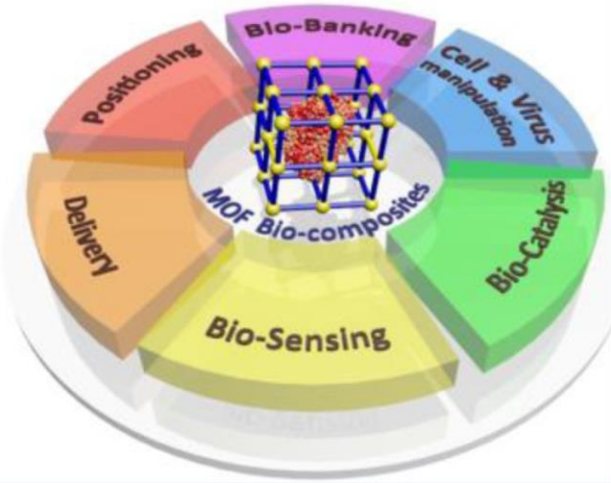
C.M. Doherty, D, Buso, A. J. Hill, S. Furukawa, S. Kitagawa, P. Falcaro, **Account of Chemical Research** 2014

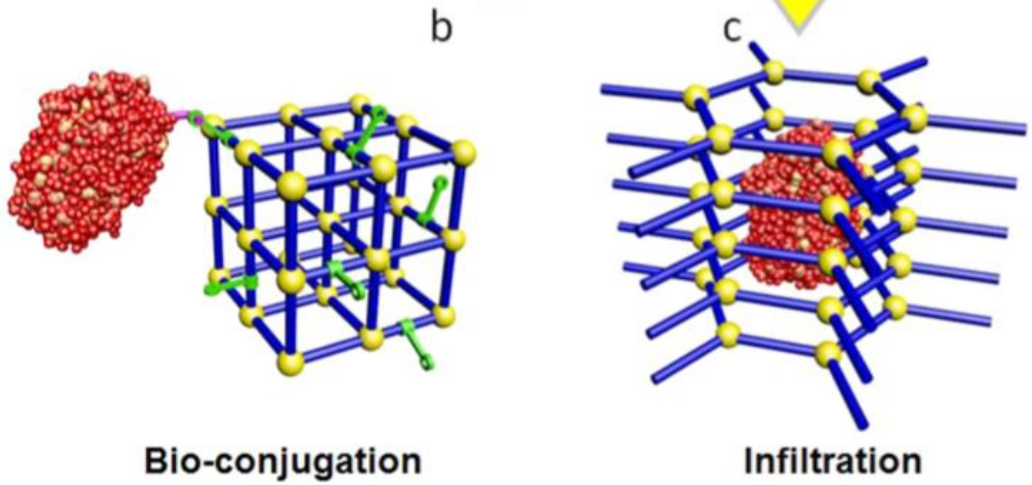
TU Graz



Use of biomacromolecules for the preparation of MOF-composites

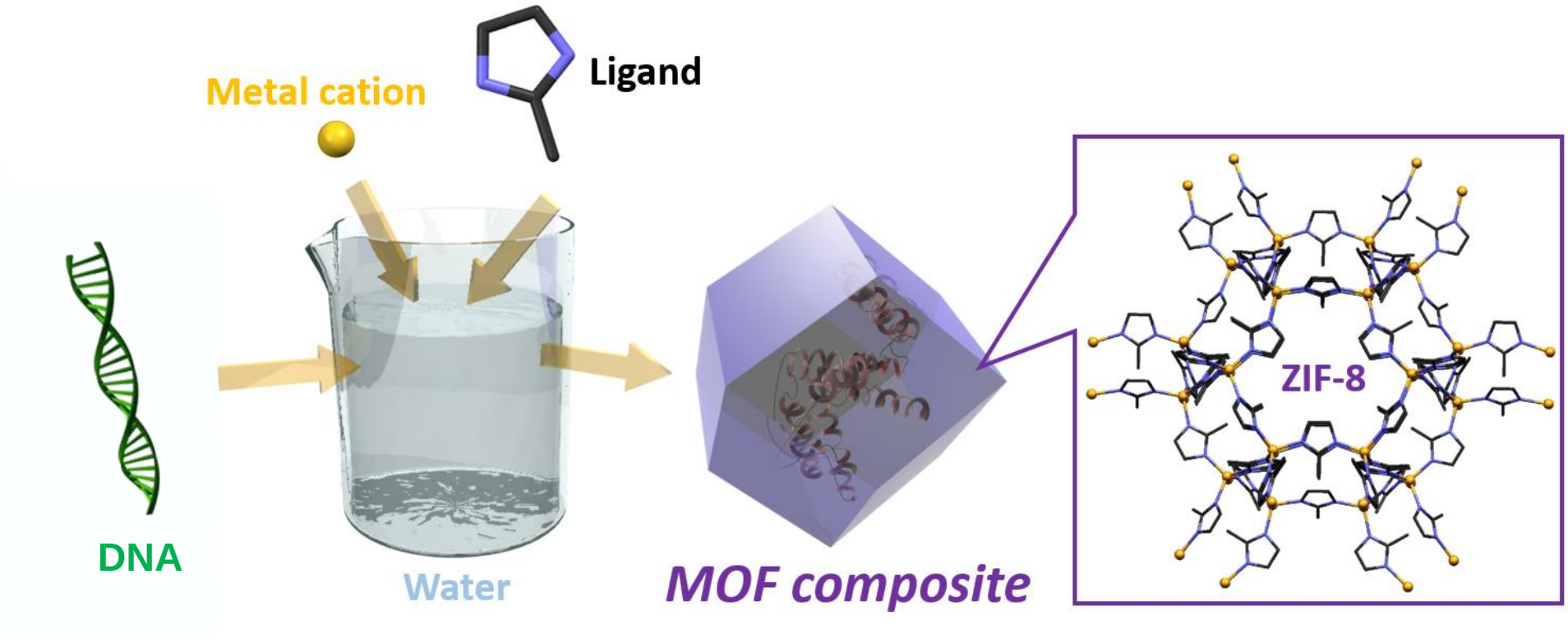






C. Doonan, R. Riccò, K. Liang, D. Bradshaw, P. Falcaro. *Metal–Organic Frameworks at the Biointerface: Synthetic Strategies and Applications.* **Acc Chem Res** 2017, 50(6), 1423–1432.

Use of biomacromolecules as seeds: Biomimetic Mineralization



Liang, Ricco, Doherty, Styles, Kirby, Mudie, Haylock, Hill, Doonan, Falcaro
Nature Communications, *2015*

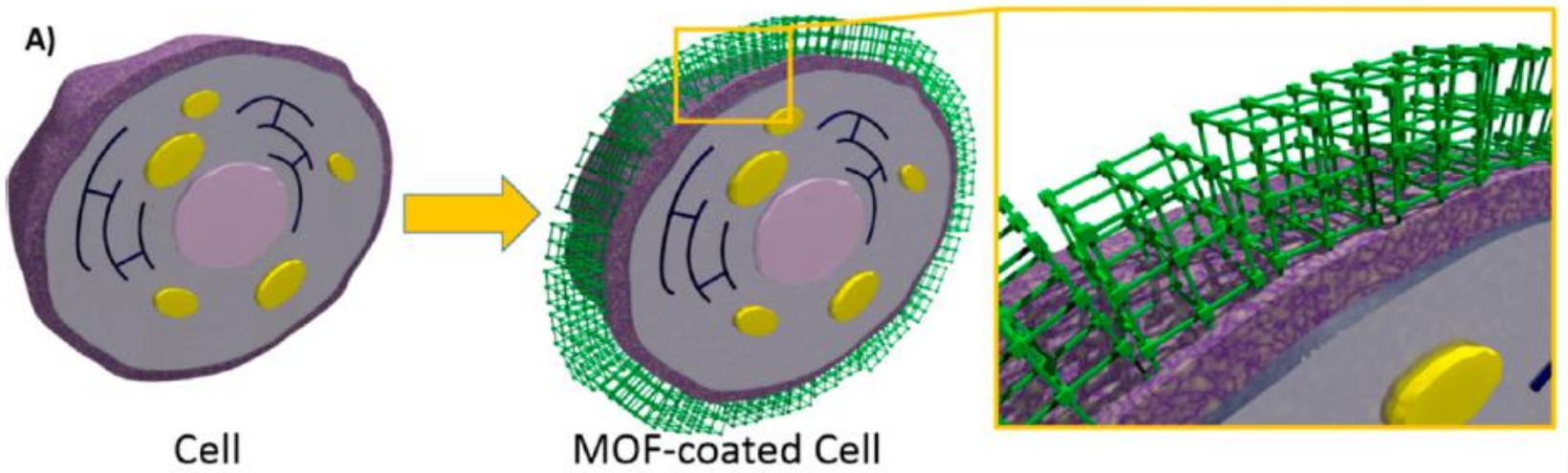
Ricco, Pfeiffer, Sumida, Sumby,Falcaro, Furukawa, Champness, Doonan,
CrystEngComm, 2016, 18, 6532-6542

MOF precursors

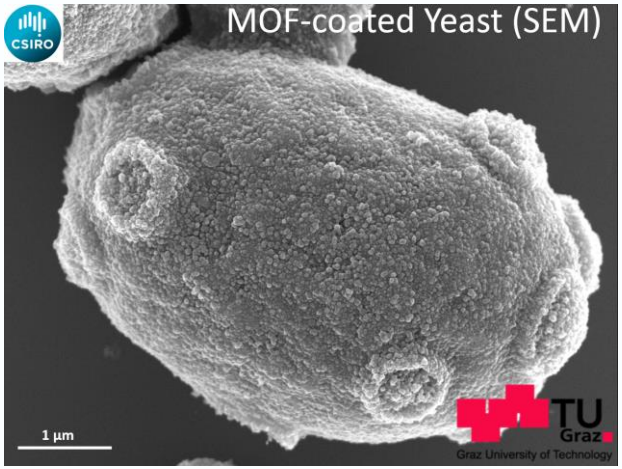
(2-methylimidazole, zinc acetate, water)

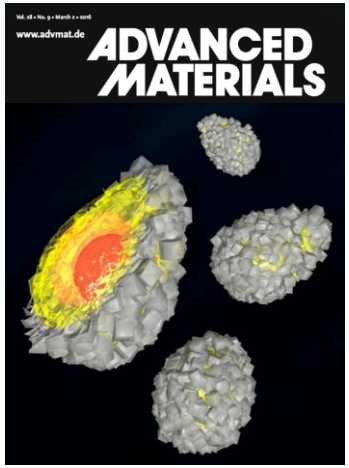
Bovine serum albumin (BSA)

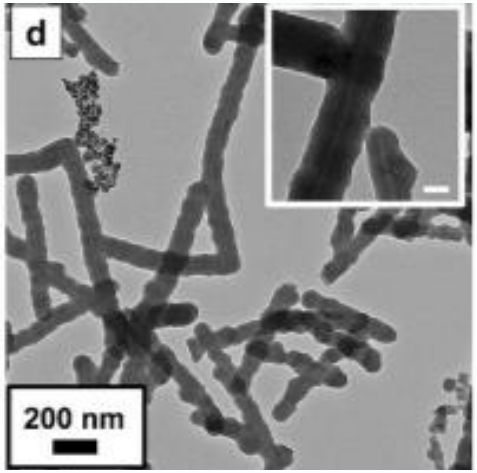
Biomimetic mineralization on Viruses and Cells



Riccò, Liang, Li, Gassensmith, Caruso, Doonan, Falcaro *Metal–Organic Frameworks for Cell and Virus Biology: A Perspective*. **ACS Nano 2018**, 12, 13–23





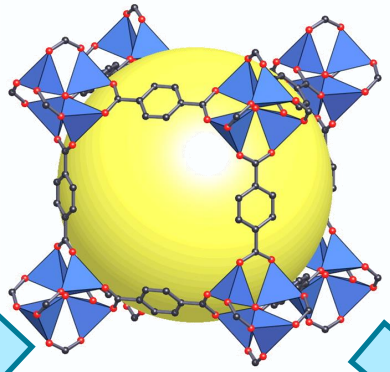


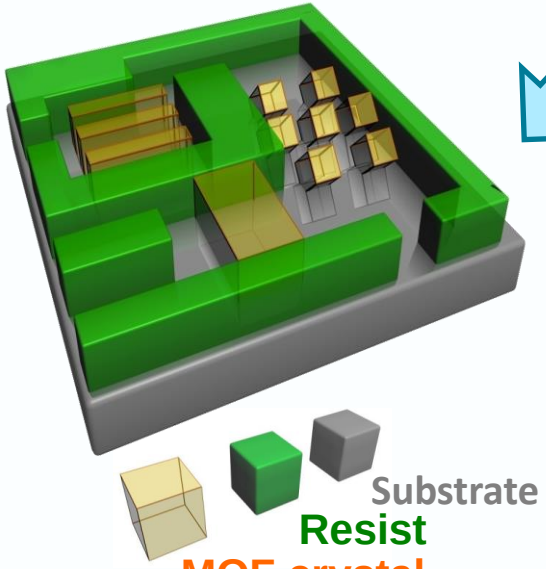
Advanced Materials 2016
Angew Chem Int Ed 2017

Gassensmith et al. **Angew Chem Int Ed**. 2016
Gassensmith et al. **ACS Appl. Mater. Interfaces** 2018

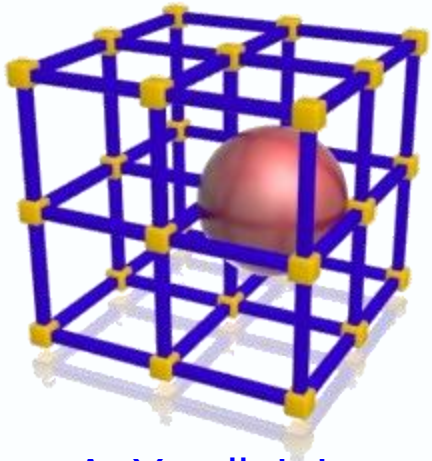
What is our vision and contribution to the field?

Device Fabrication



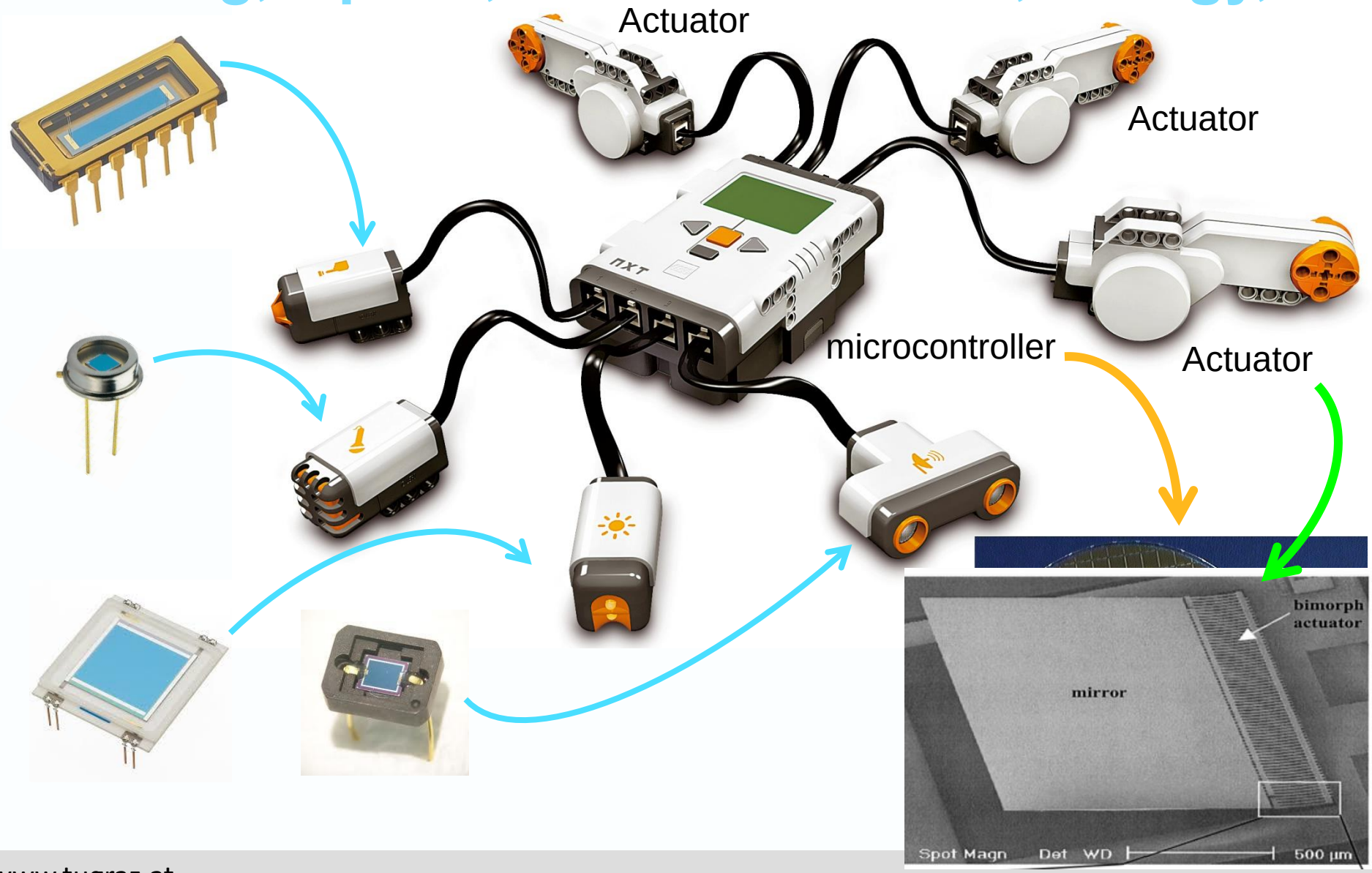


P. Falcaro, D. Buso, A. J. Hill, C. Doherty, ***Adv. Mater.*** 2012

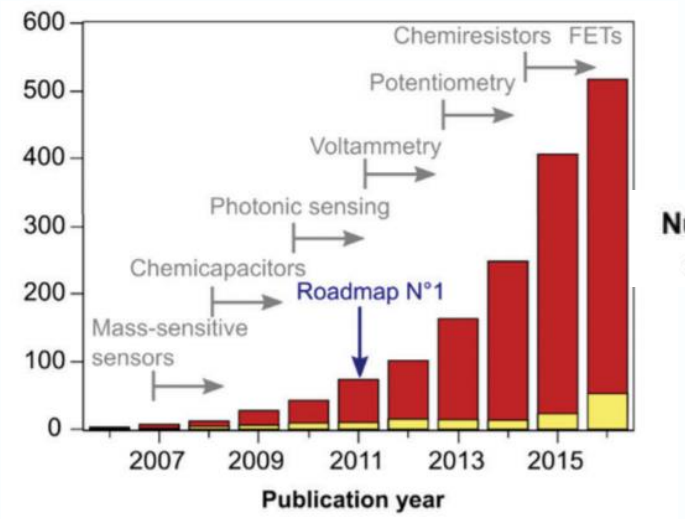


P. Falcaro, R. Ricco, A. Yazdi, I. Imaz, S. Furukawa, D. Maspoch, R. Ameloot, J. D. Evans, C. J. Doonan, ***Coord.Chem.Rev.*** 2015

Sensing, Optics, Microelectronics, Energy, …

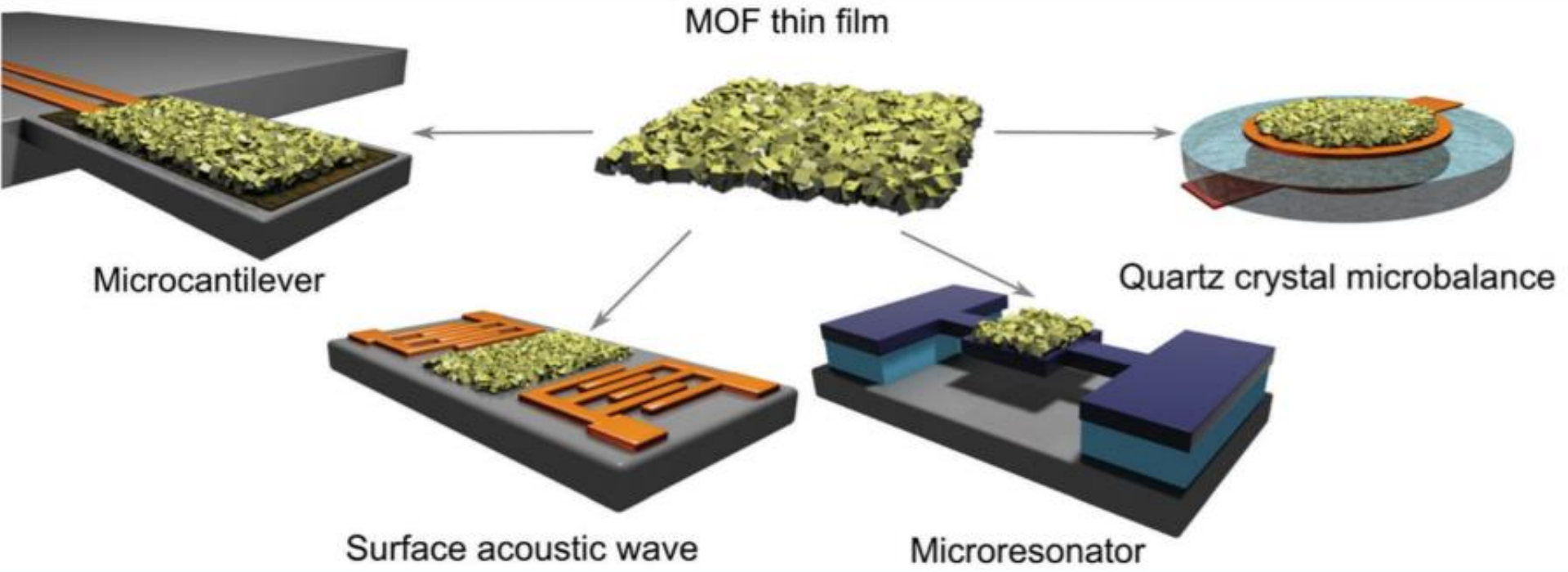


MOFs for sensing

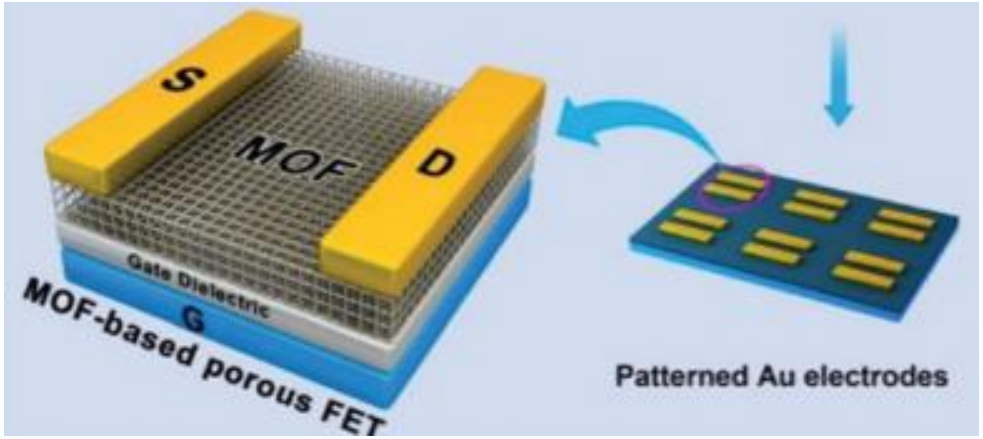


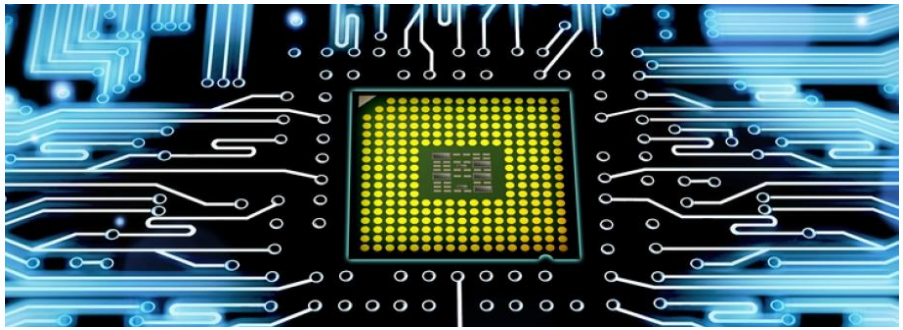
Number of publications:
<MOF> ∩ <sensor>

Journal articles
Patent applications

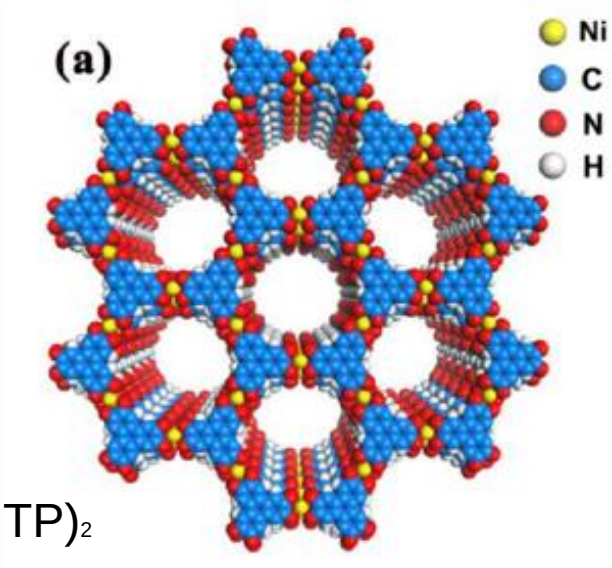


Stassen, Burtch, Talin, Falcaro, Allendorf, Ameloot, **Chem. Soc. Rev.**, 2017,46, 3185

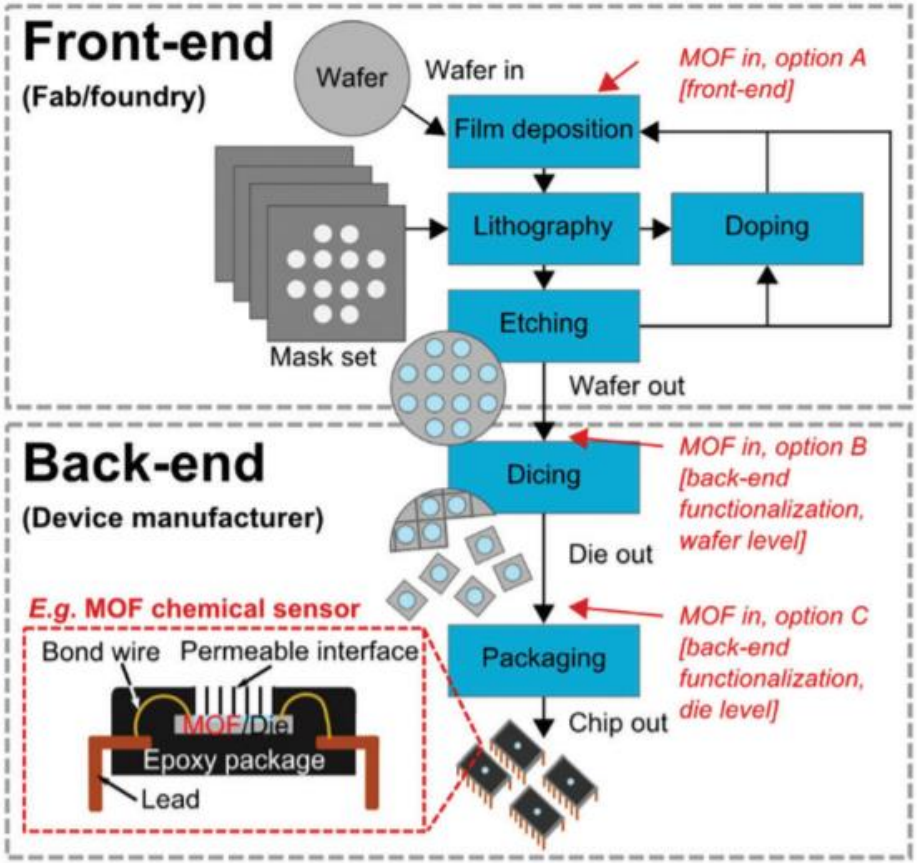




G. Wu, J. Huang, Y. Zang, J. He, G. Xu
JACS 2017.

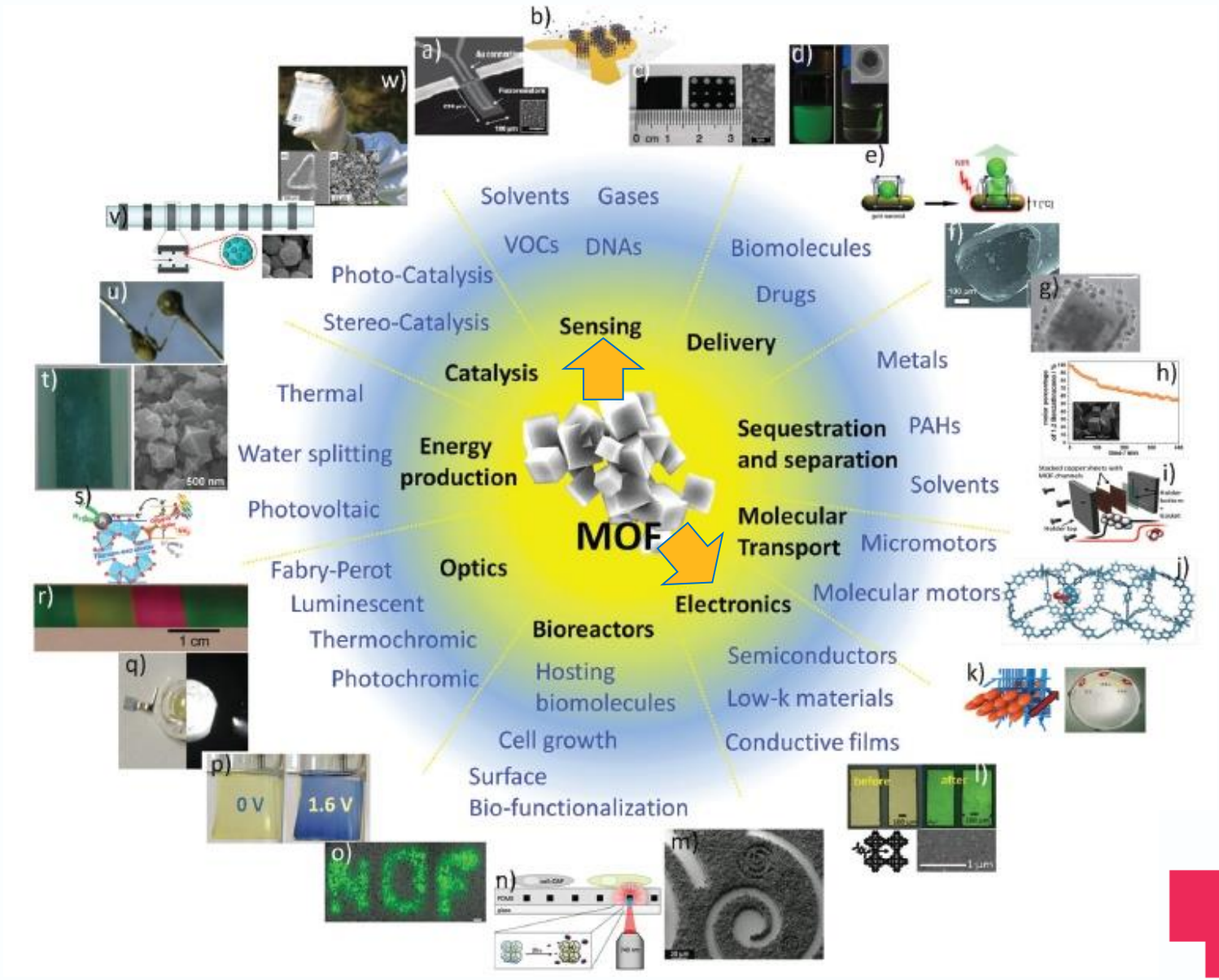


$Ni_3(HITP)_2$



Stassen, Burtch, Talin, Falcaro, Allendorf, Ameloot, **Chem. Soc. Rev.**, 2017,46, 3185

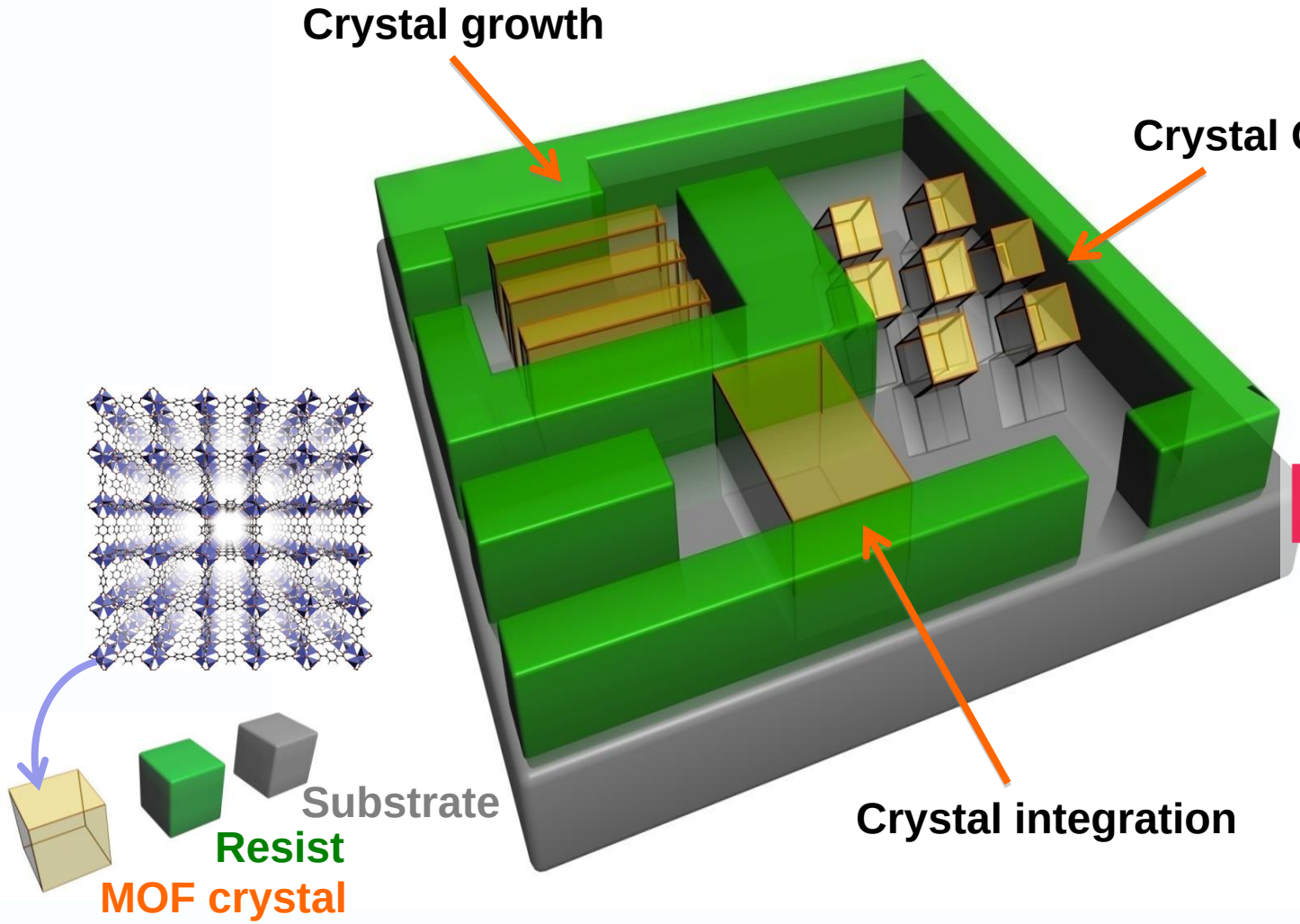
Increasing interest in **device fabrication** based on MOFs

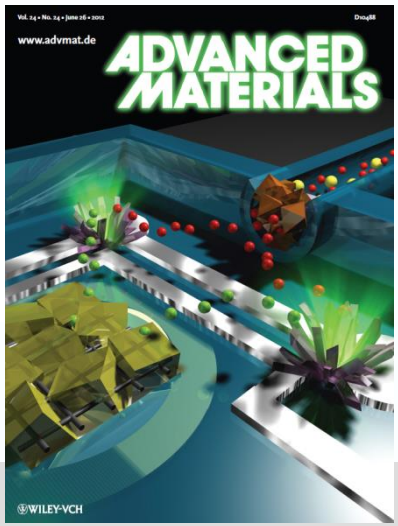


TU Graz

P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
"*MOF positioning technology and device fabrication*", ***Chem.Soc.Rev.*** 2014

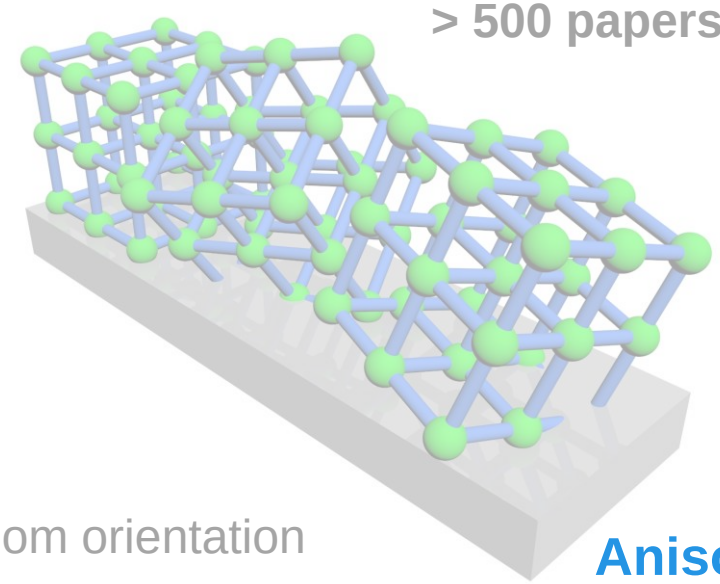
Device Fabrication …. Positioning MOFs





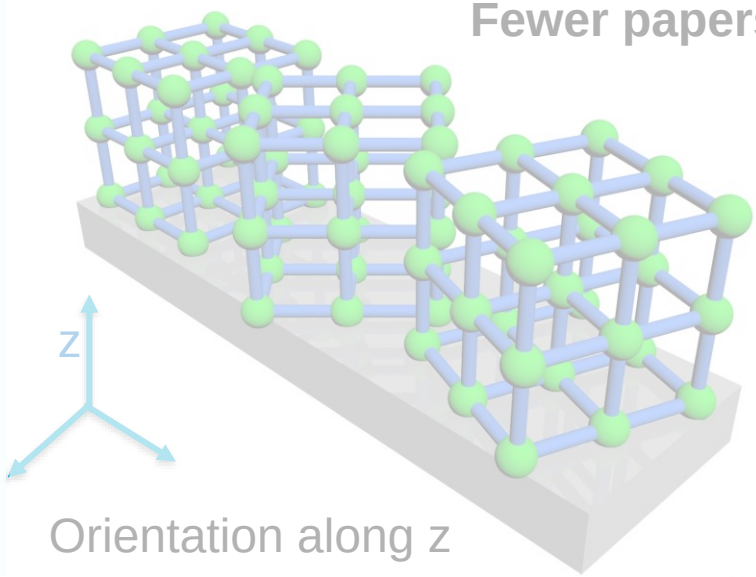
P. Falcaro, D. Buso, A. J. Hill, C. Doherty, ***Adv. Mater.*** 2012, *24*, 3153.

> 500 papers



Random orientation

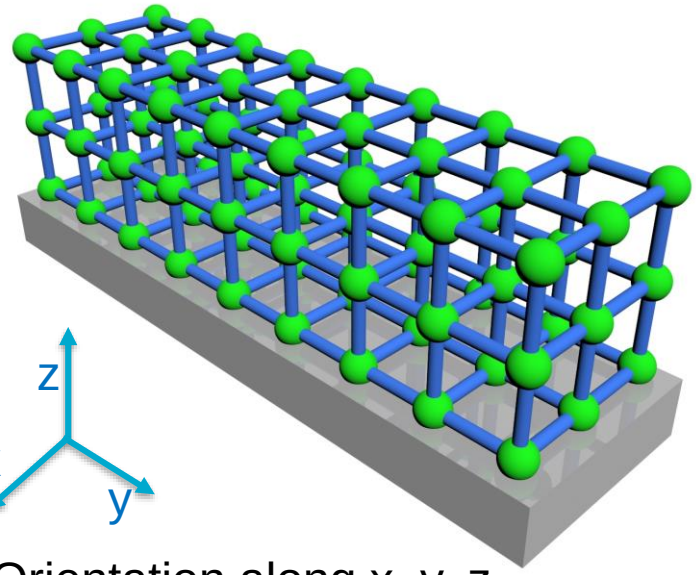
Fewer papers



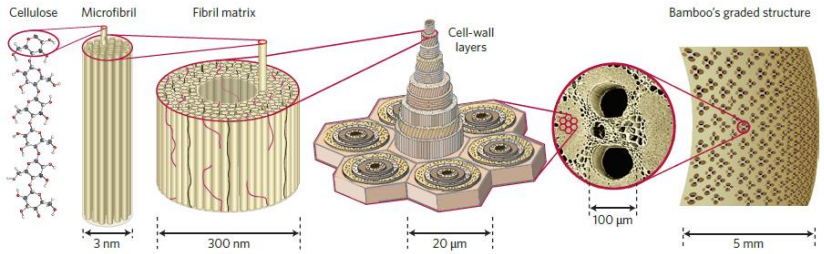
Orientation along z

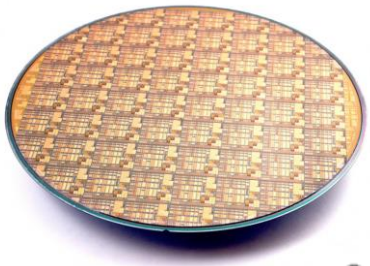
Anisotropic functional properties underpin technology

?

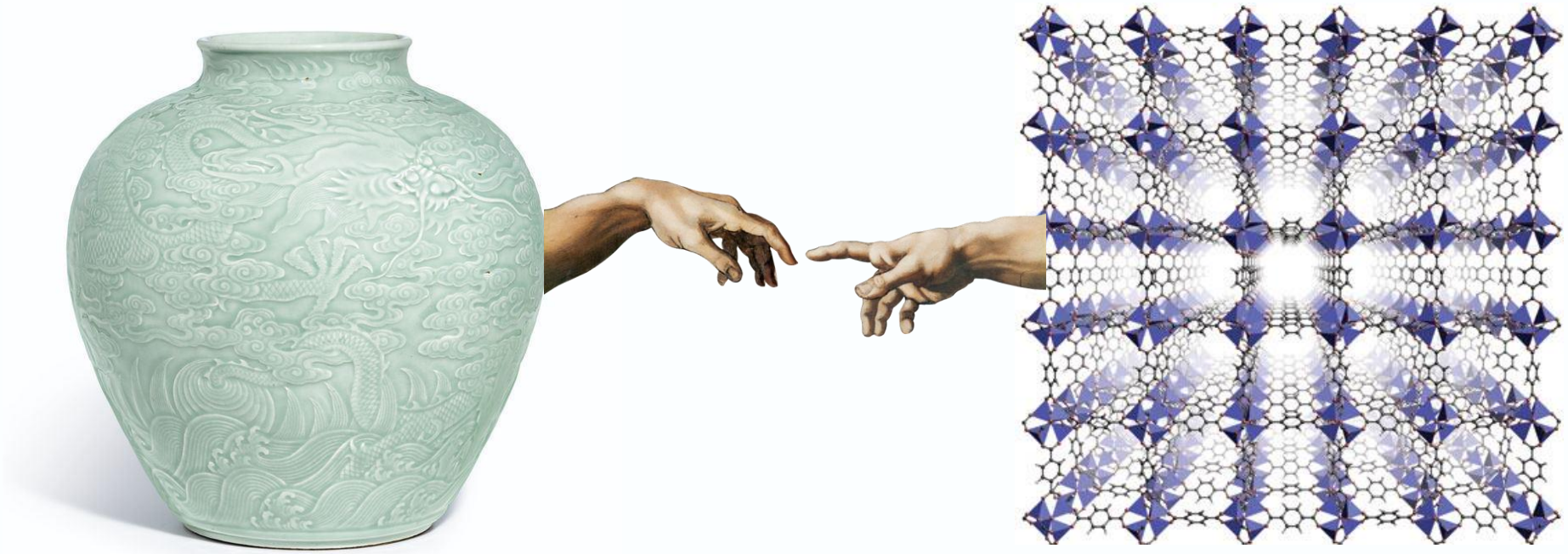


Orientation along x, y, z





….What is the connection with MOFs?



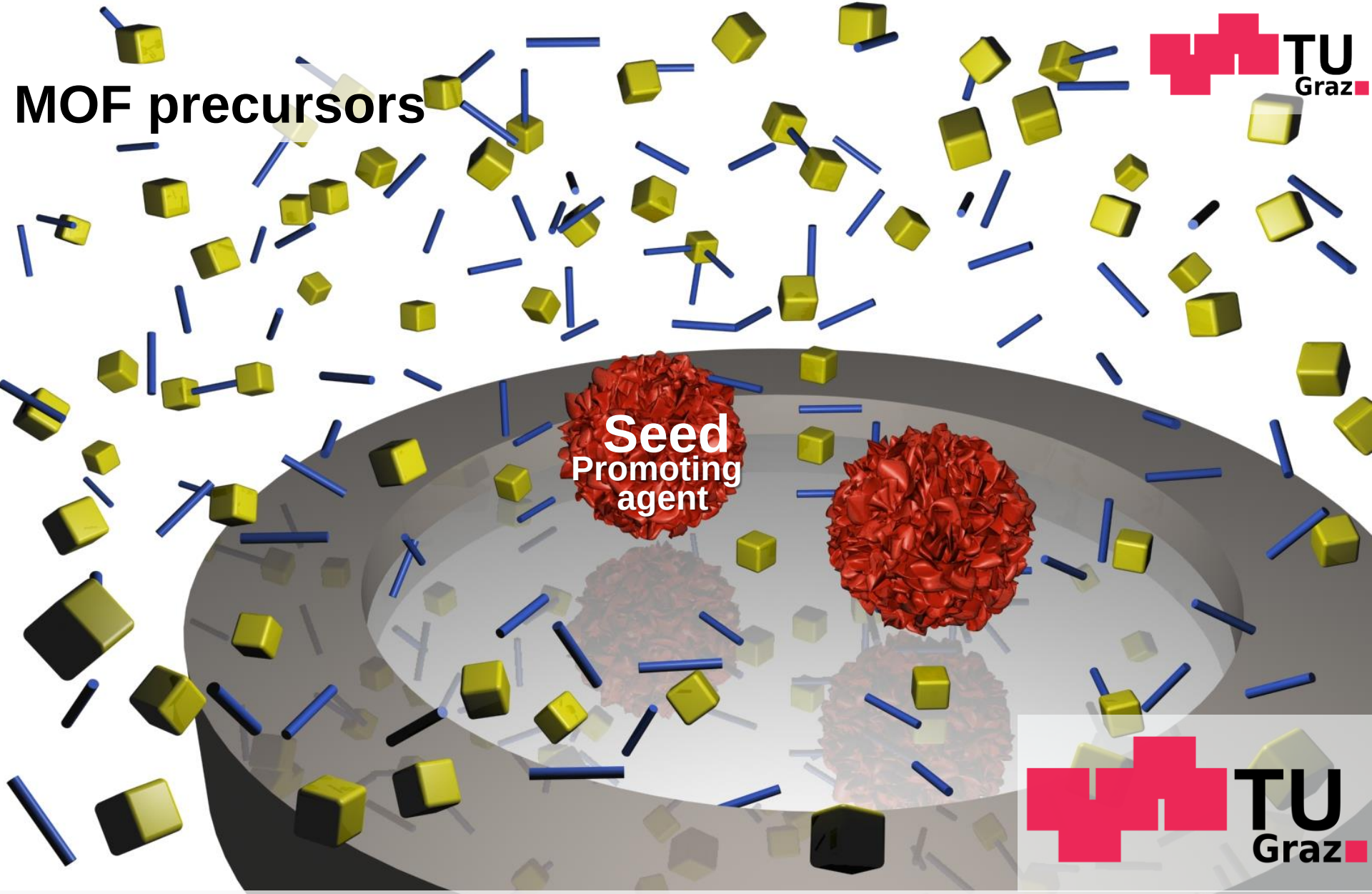
The Fonthill ‘Dragon’ Jar. (US$12,000,000),

MOF-5. (US$200/Kg),

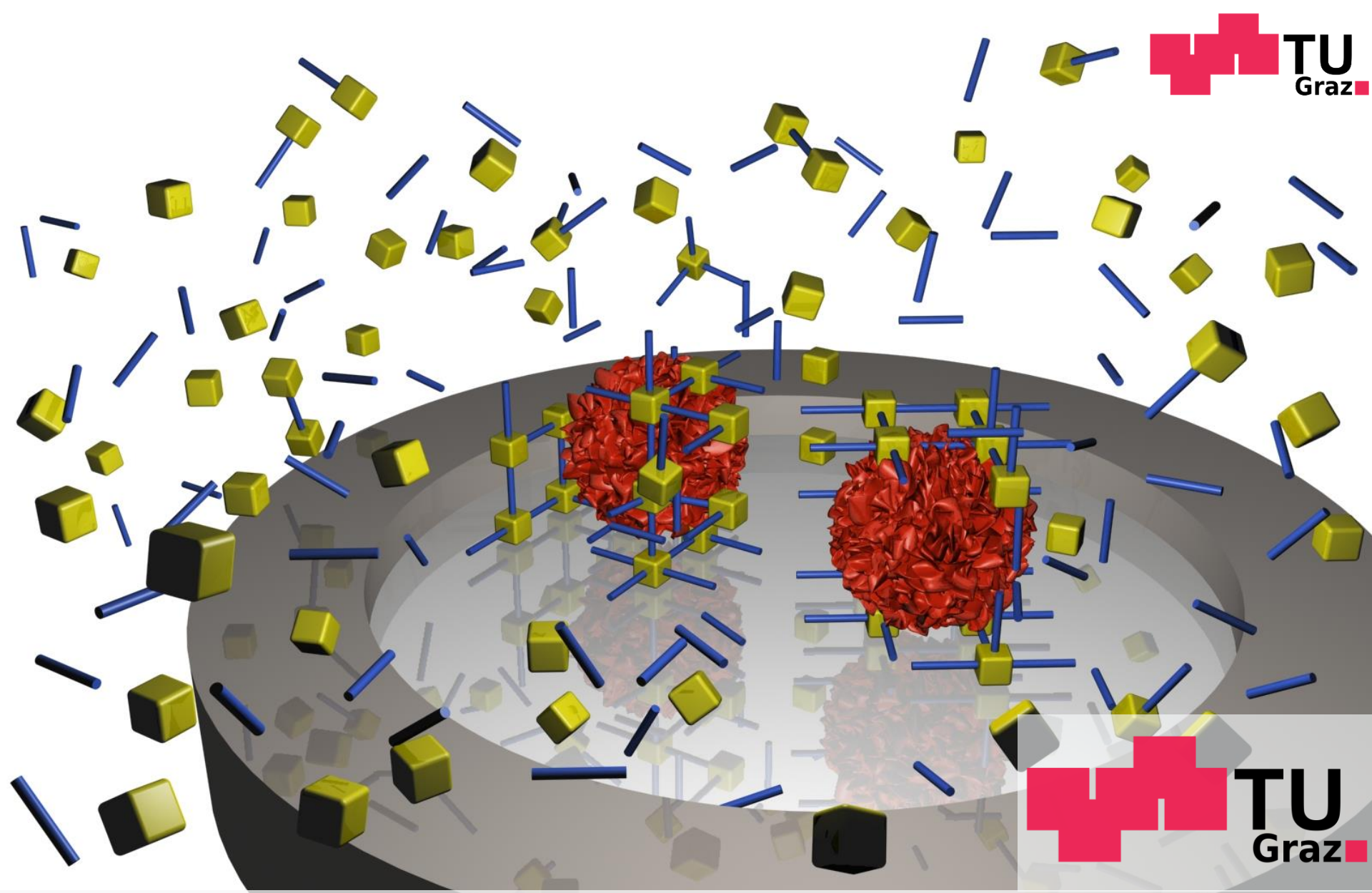
A few examples:

Al_2O_3	Reboul, Furukawa, Horike, Tsotsalas, Hirai, Uehara, Kondo, Louvain, Sakata, Kitagawa **Nat. Mater**. 2012, 11, 717
ZnO	Zanchetta, Malfatti, Ricco, Styles, Lisi,§, Coghlan, Doonan, Hill,Brusatin, Falcaro, **Chem.Mater.** 2015, 27, 690 Stassen, Styles, Grenci, Van Gorp, Vanderlinden, S. De Feyter, Falcaro, De Vos, Vereecken, Ameloot **Nature Materials** 2016
$Cu(OH)_2$	K. Okada, R. Ricco, Y. Tokudome, M.J. Styles, A.J. Hill, M. Takahashi, P. Falcaro **Adv Funct Mater** 2014, 24(14), 1969. Toyao, Ricco', Takahashi, Falcaro et.al. **Inorg. Chem. Front.** 2015, 2, 34. P. Falcaro, K. Okada, T. Hara, K. Ikigaki, Y. Tokudome, TA.W. Thornton, A.J. Hill, T. Williams, C. J. Doonan, M. Takahashi **Nat Mater** 2017, 16, 342.
$CaCO_3$	Sumida, Hu, Furukawa, Kitagawa **Inorg.Chem.** 2016, 55, 3700
$CuCO_3$	Ricco', Doonan, Falcaro et al. **Chem.Mater.** 2018

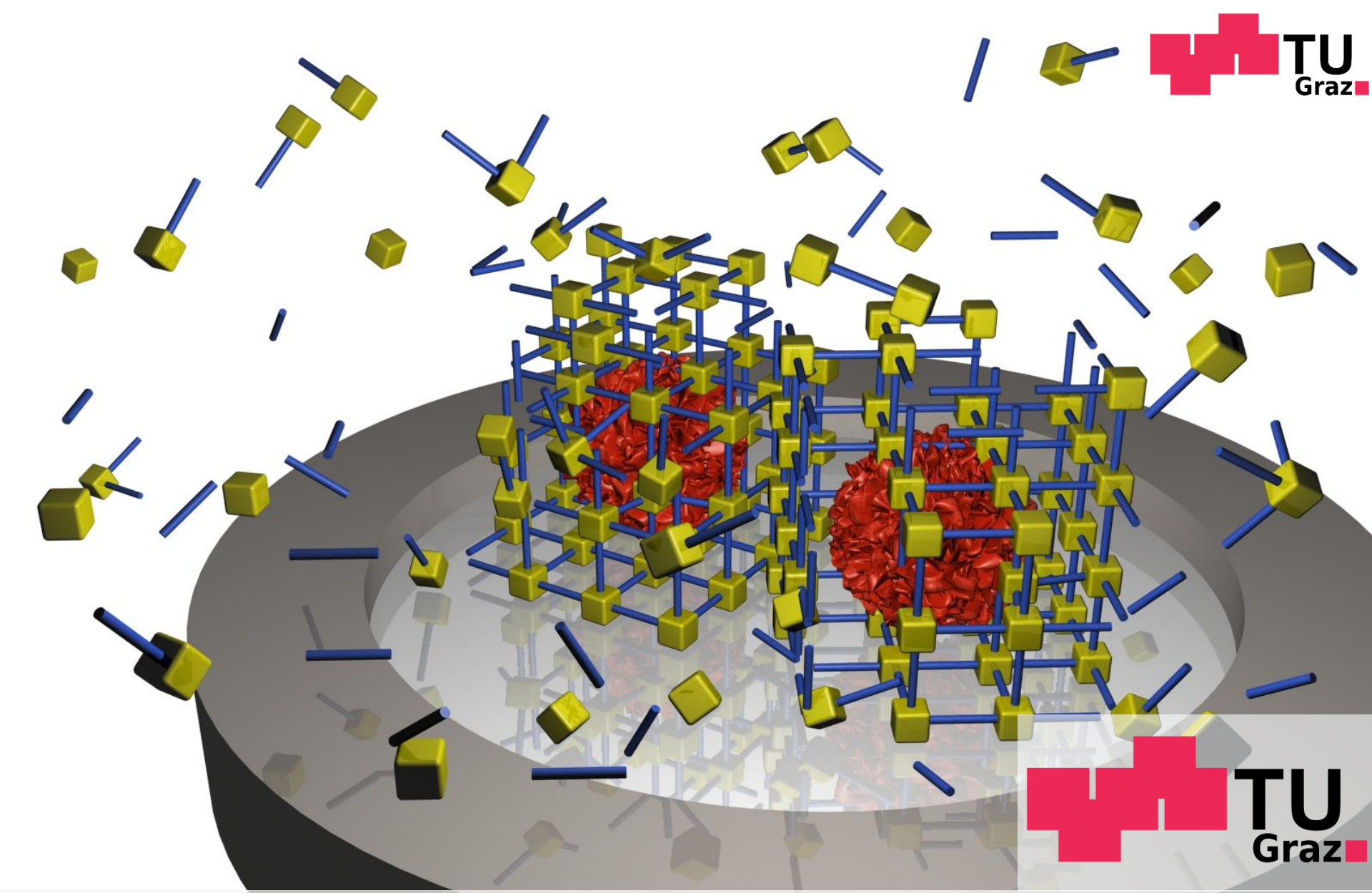
MOF precursors



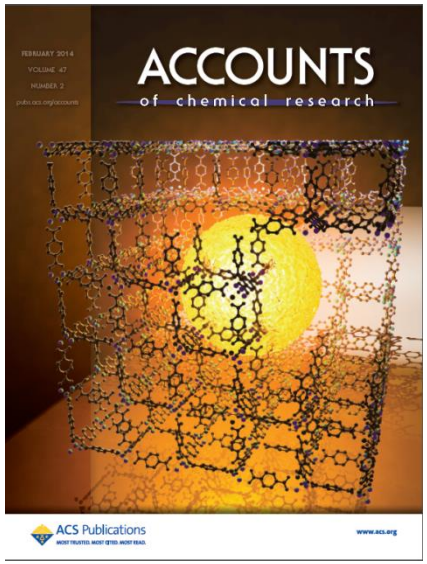
C.M. Doherty, Buso D., A.J. Hill, S. Furukawa, S. Kitagawa, P. Falcaro "*Using Functional Nano- and Micro-particles for the preparation of Metal Organic Framework Composites with novel properties*" **Account of Chemical Research** 2014, 47(2) 396-405.



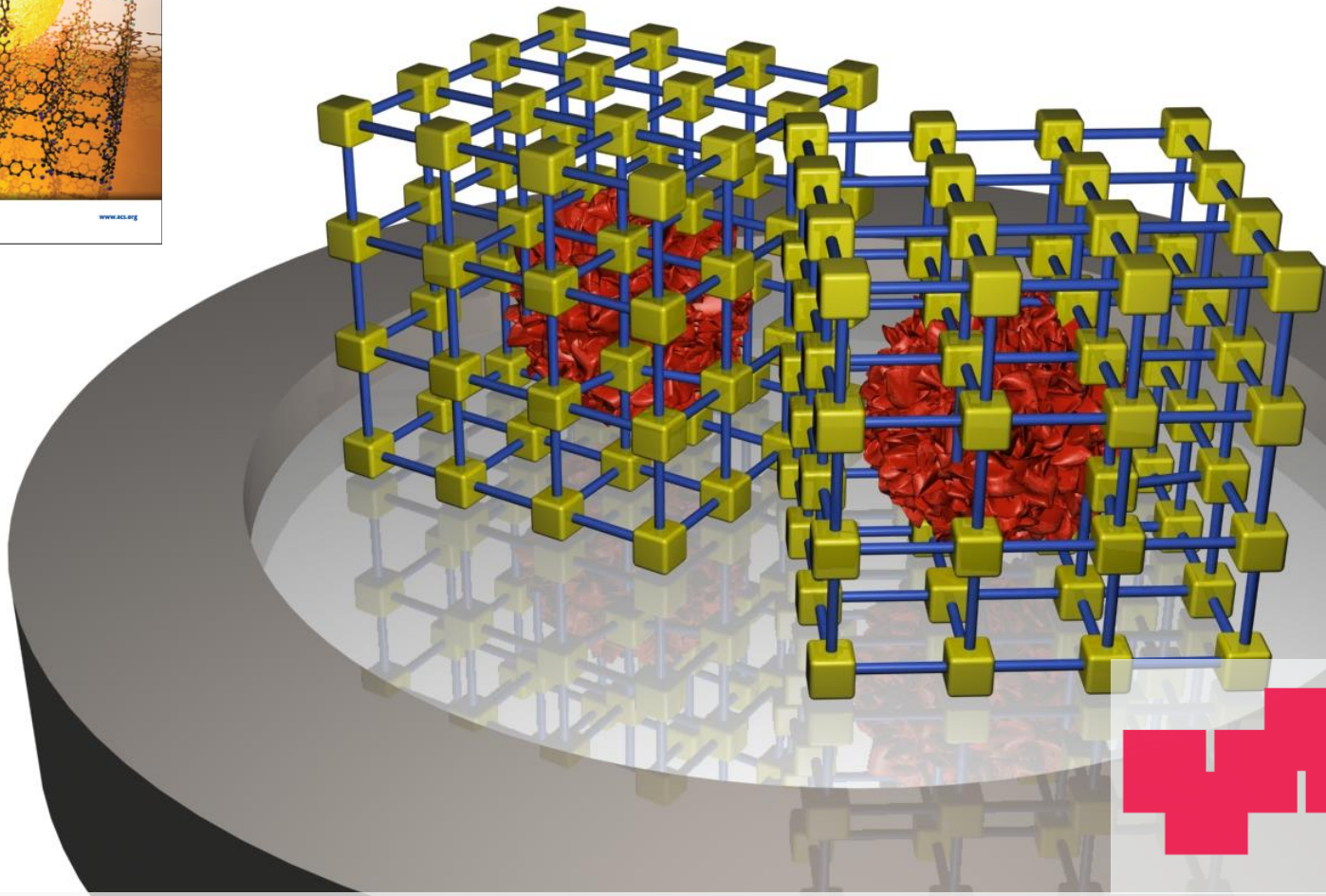
C.M. Doherty, Buso D., A.J. Hill, S. Furukawa, S. Kitagawa, P. Falcaro "*Using Functional Nano- and Micro-particles for the preparation of Metal Organic Framework Composites with novel properties*" **Account of Chemical Research** 2014, 47(2) 396-405.



C.M. Doherty, Buso D., A.J. Hill, S. Furukawa, S. Kitagawa, P. Falcaro "*Using Functional Nano- and Micro-particles for the preparation of Metal Organic Framework Composites with novel properties*" **Account of Chemical Research** 2014, 47(2) 396-405.



Ceramic nanoparticles



C.M. Doherty, Buso D., A.J. Hill, S. Furukawa, S. Kitagawa, P. Falcaro "*Using Functional Nano- and Micro-particles for the preparation of Metal Organic Framework Composites with novel properties*" **Account of Chemical Research** 2014, 47(2) 396-405.

Erika Zanchetta

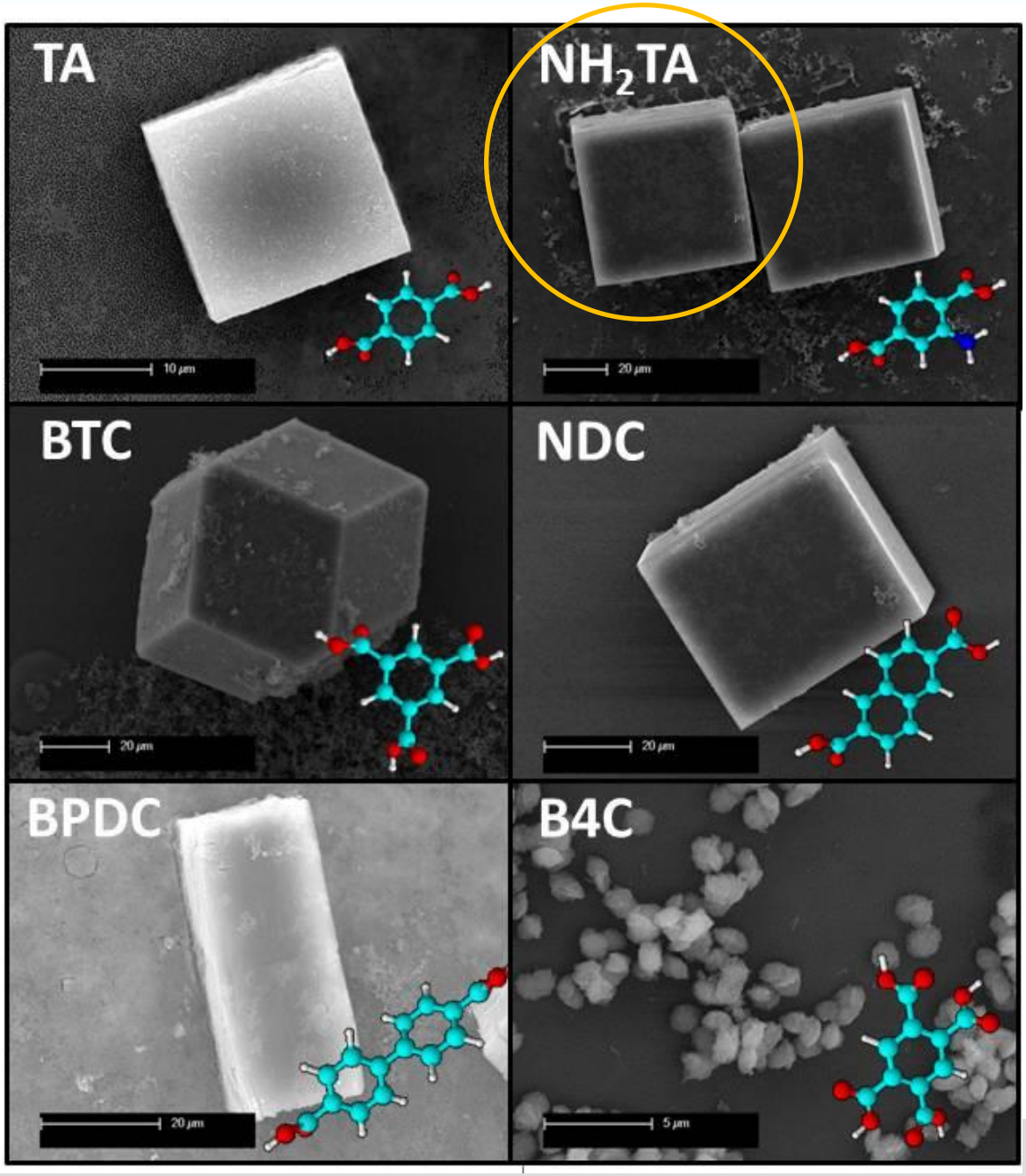
Prof. Giovanna Brusatin

ZnO

< 50 nm

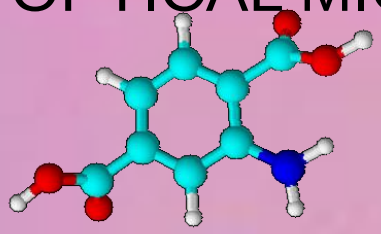
Zanchetta et al. ***Chem.Mater.*** *2015*

SEM - Solvothermal method, 1h@95°C




OPTICAL MICROSCOPE, following the reaction (time)
80 min
50 min
14 min
6 min
2 min
TU
Graz

OPTICAL MICROSCOPE, following the reaction (time)



80 min

50 min

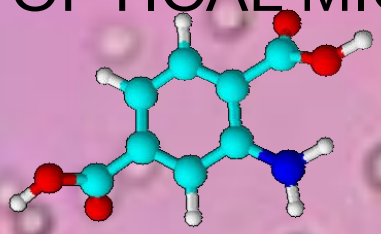
14 min

6 min

2 min

TU Graz

OPTICAL MICROSCOPE, following the reaction (time)



80 min

50 min

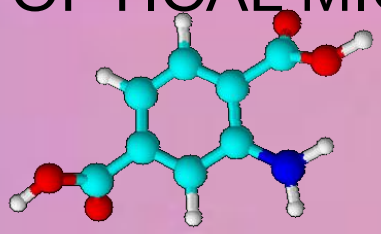
14 min

6 min

2 min

TU Graz

OPTICAL MICROSCOPE, following the reaction (time)



80 min

50 min

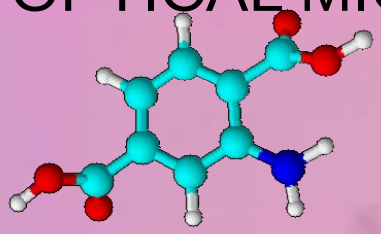
14 min

6 min

2 min

TU Graz

OPTICAL MICROSCOPE, following the reaction (time)



80 min

50 min

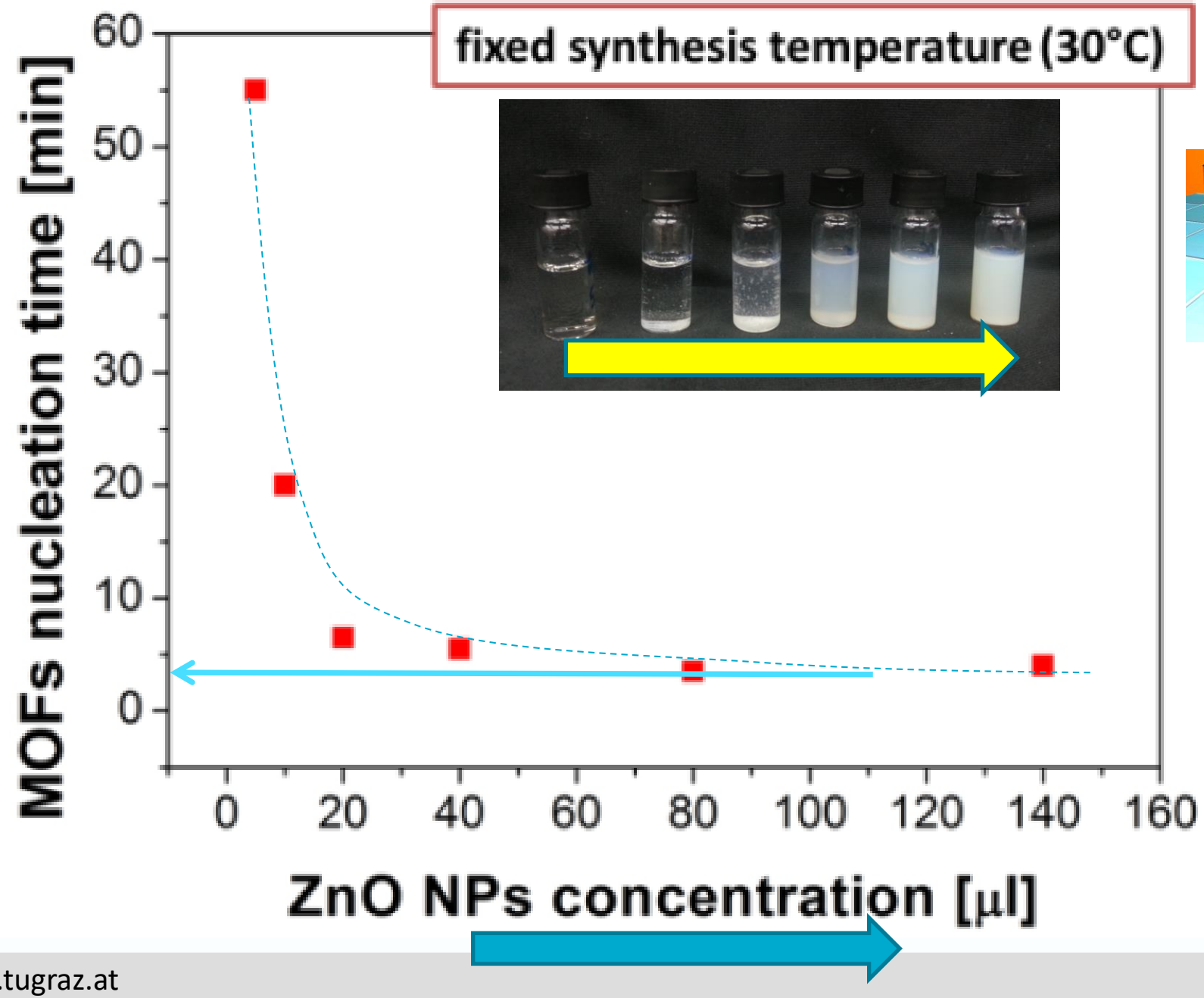
14 min

6 min

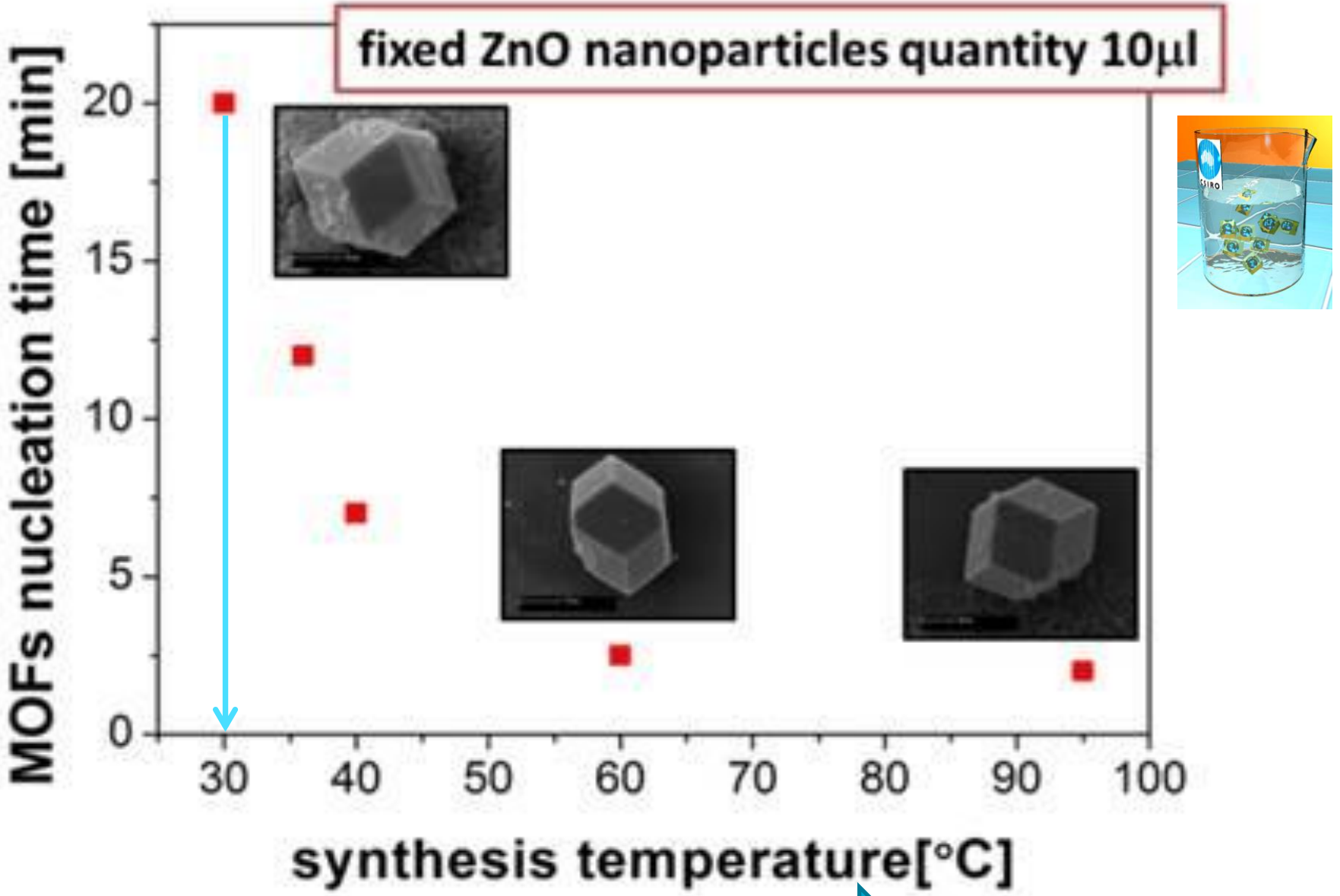
2 min

TU Graz

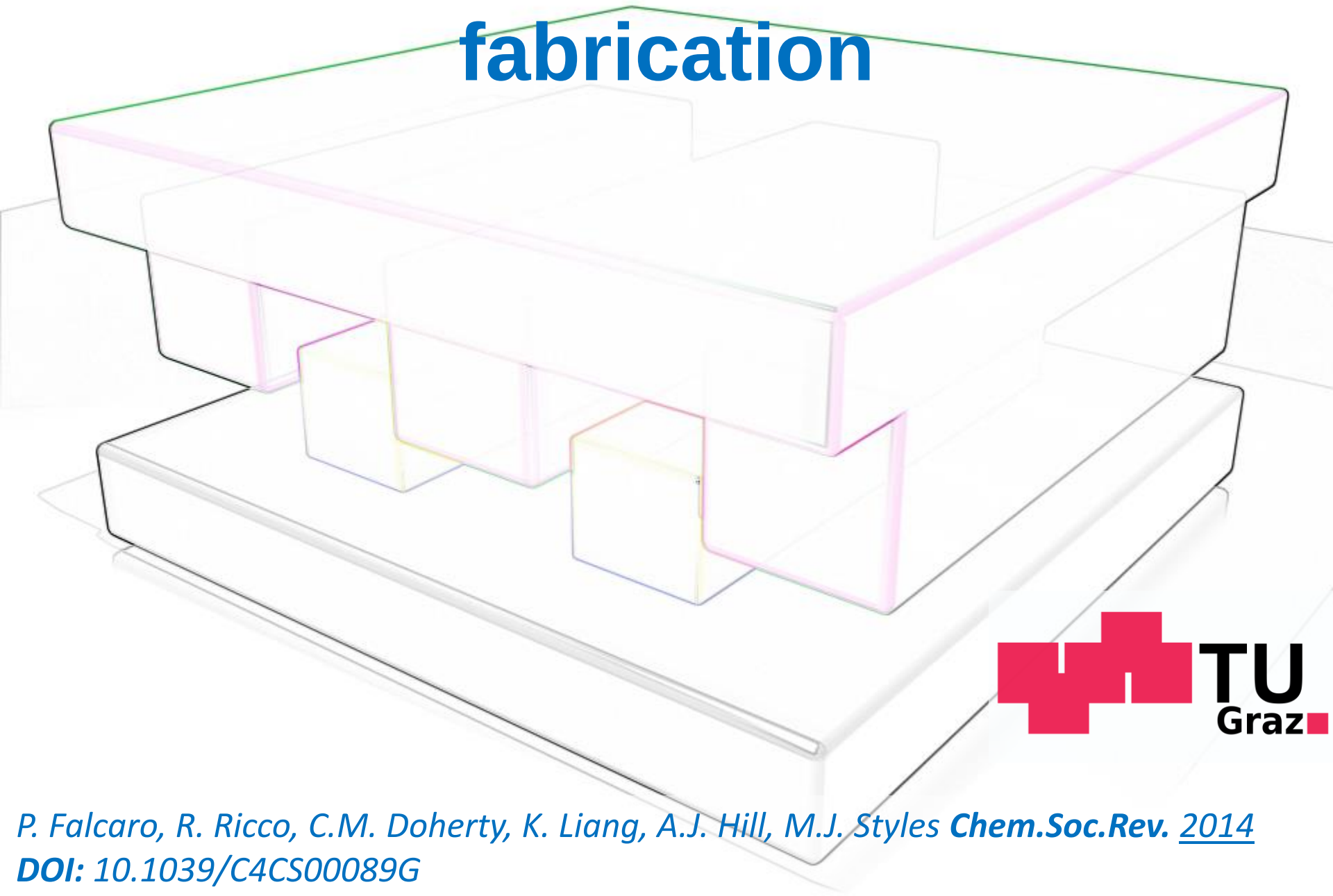
Dependence of the nucleation time with the concentration



Dependence of the nucleation time with the temperature



Micromolding for MOF pattern fabrication



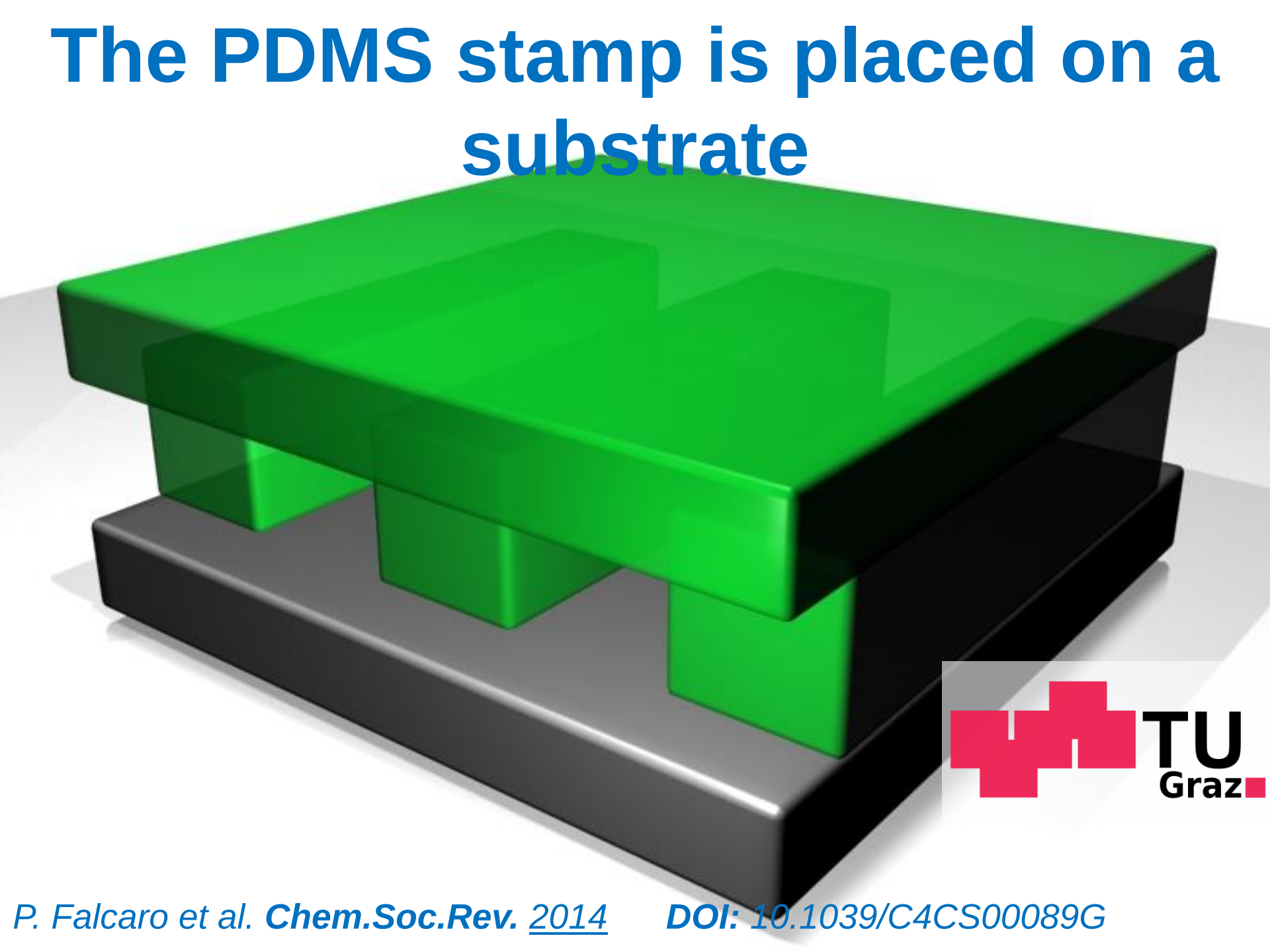
P. Falcaro, R. Ricco, C.M. Doherty, K. Liang, A.J. Hill, M.J. Styles ***Chem.Soc.Rev.*** *2014*
DOI: *10.1039/C4CS00089G*

PDMS stamp

TU Graz

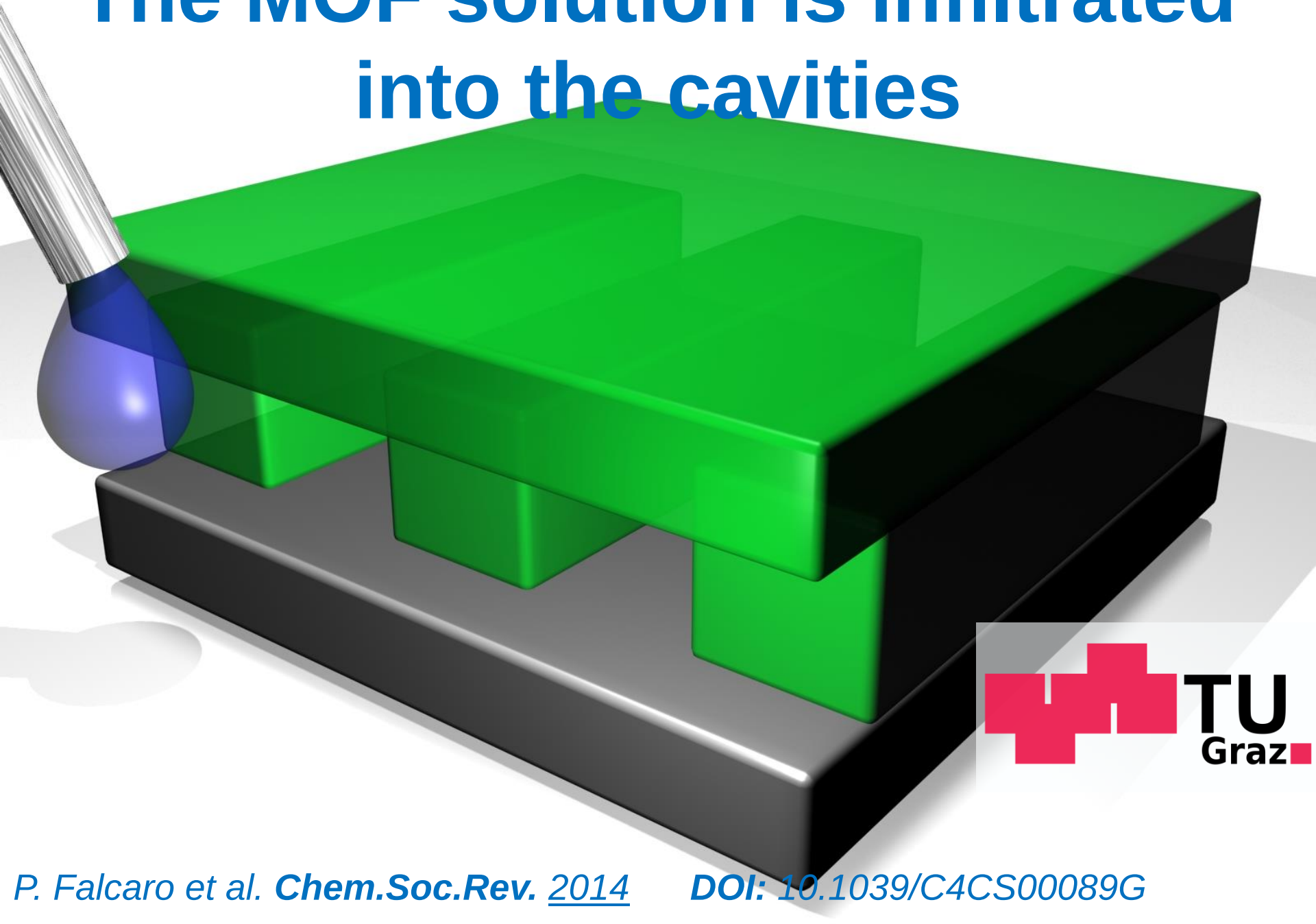
P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

The PDMS stamp is placed on a substrate



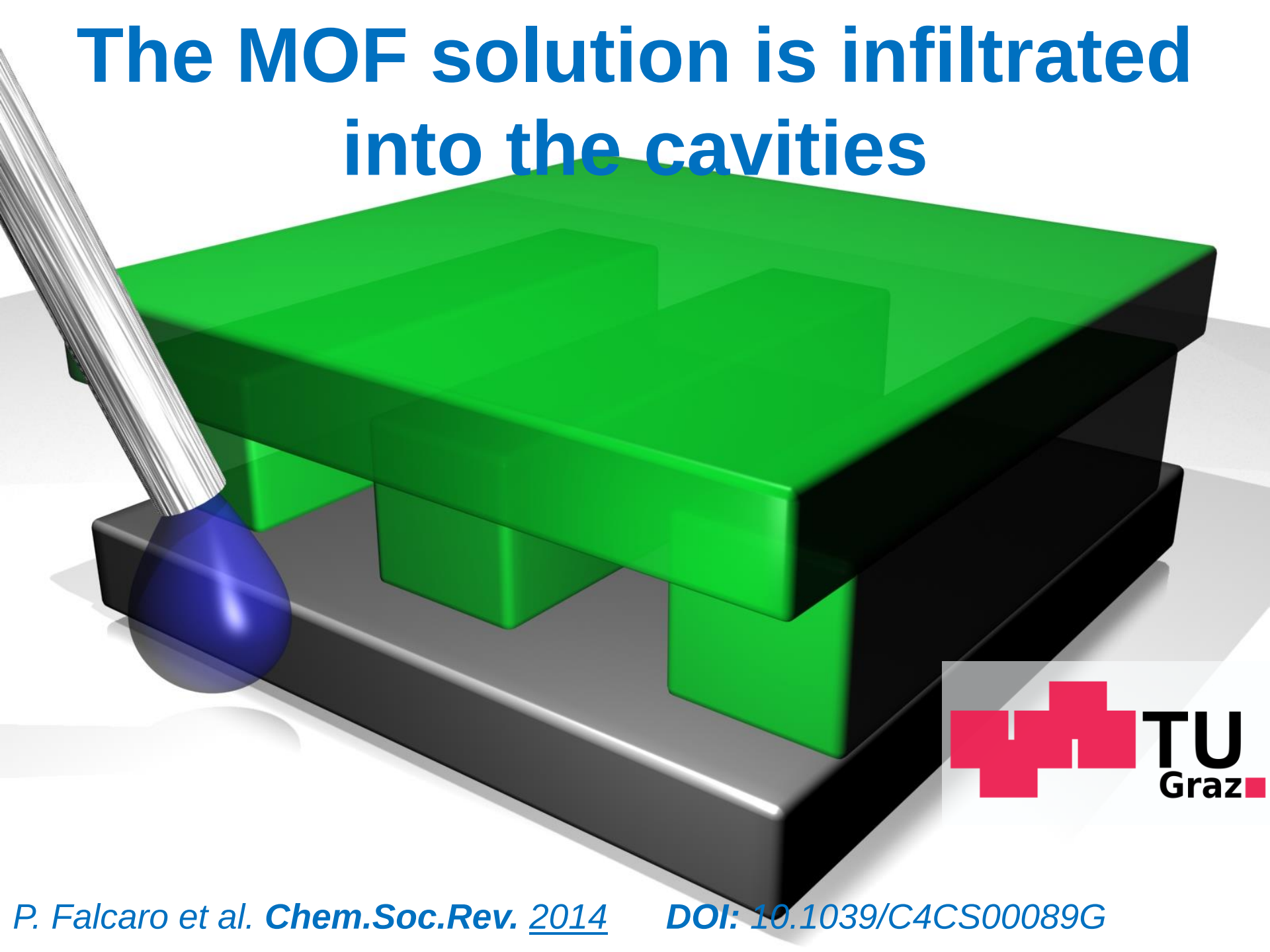
P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

The MOF solution is infiltrated into the cavities



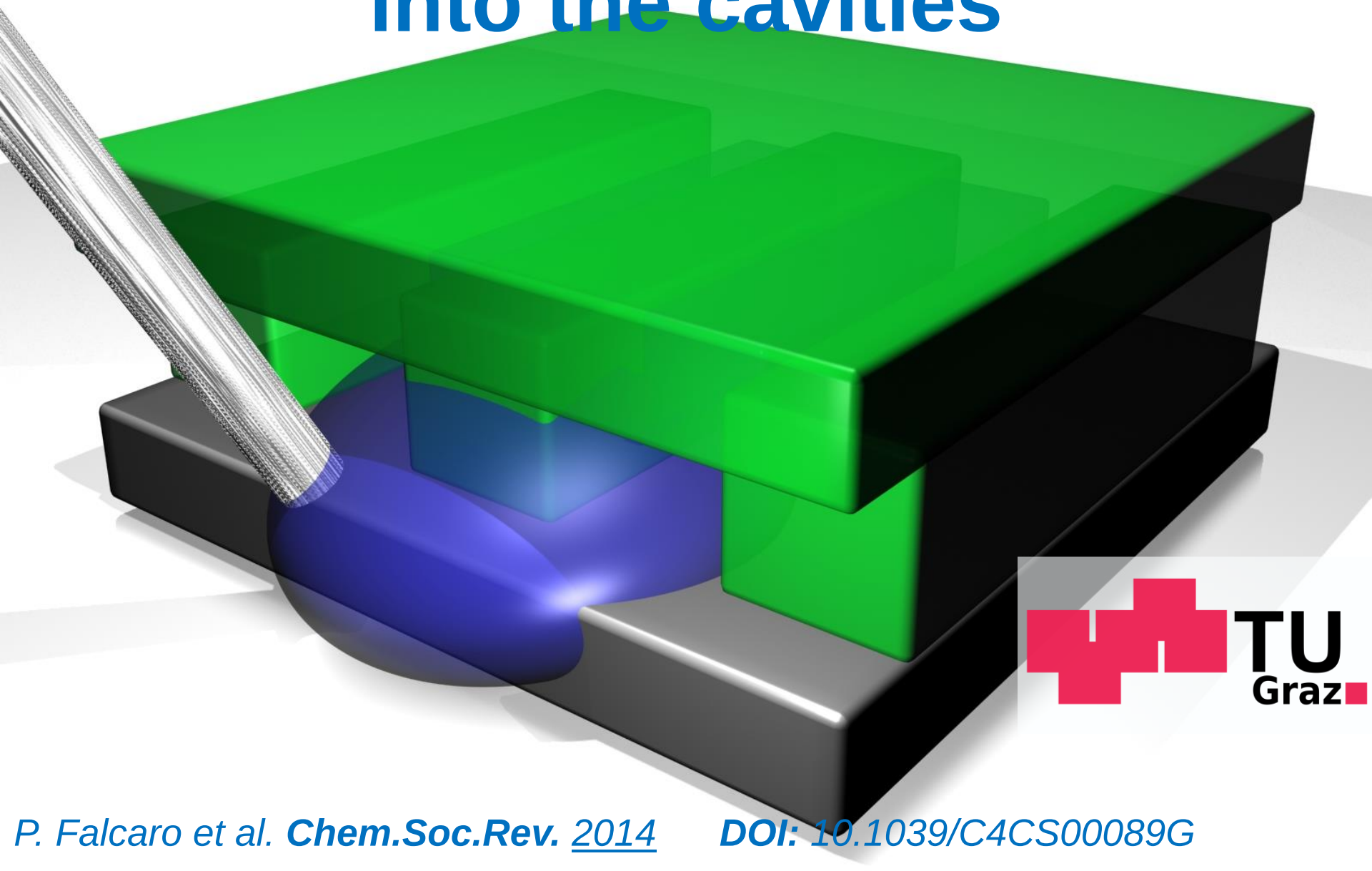
P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

The MOF solution is infiltrated into the cavities

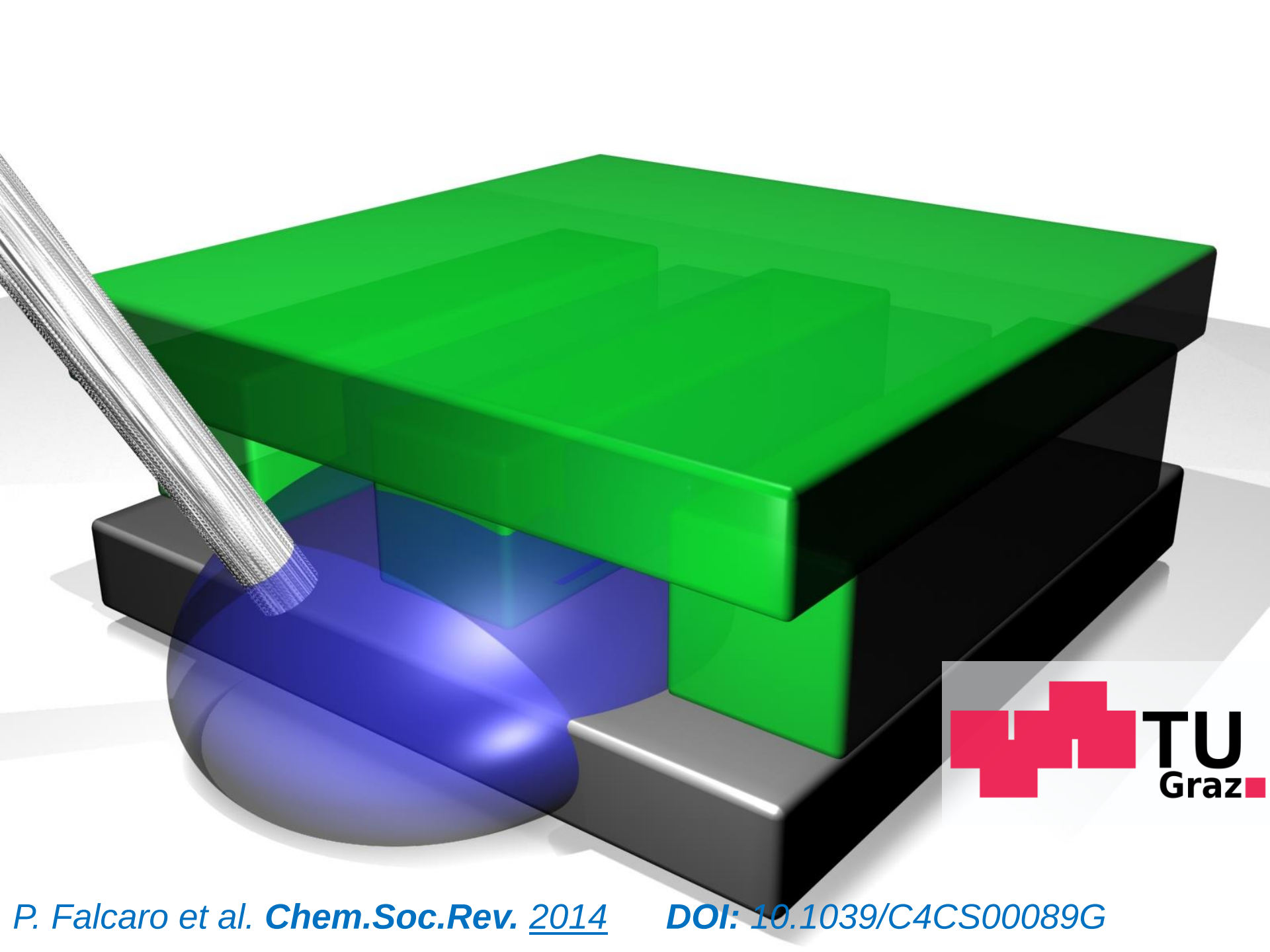


P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

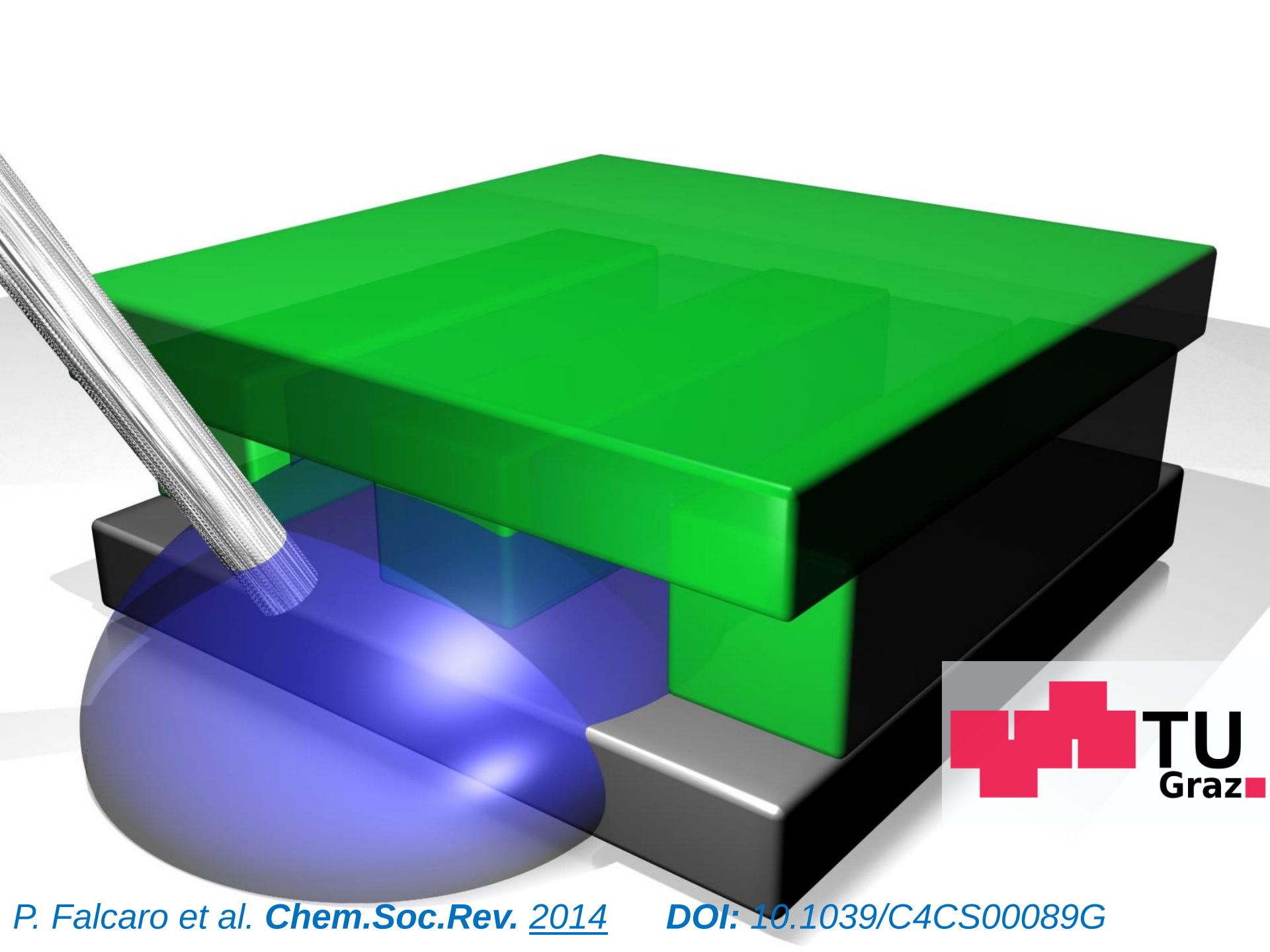
The MOF solution is infiltrated into the cavities



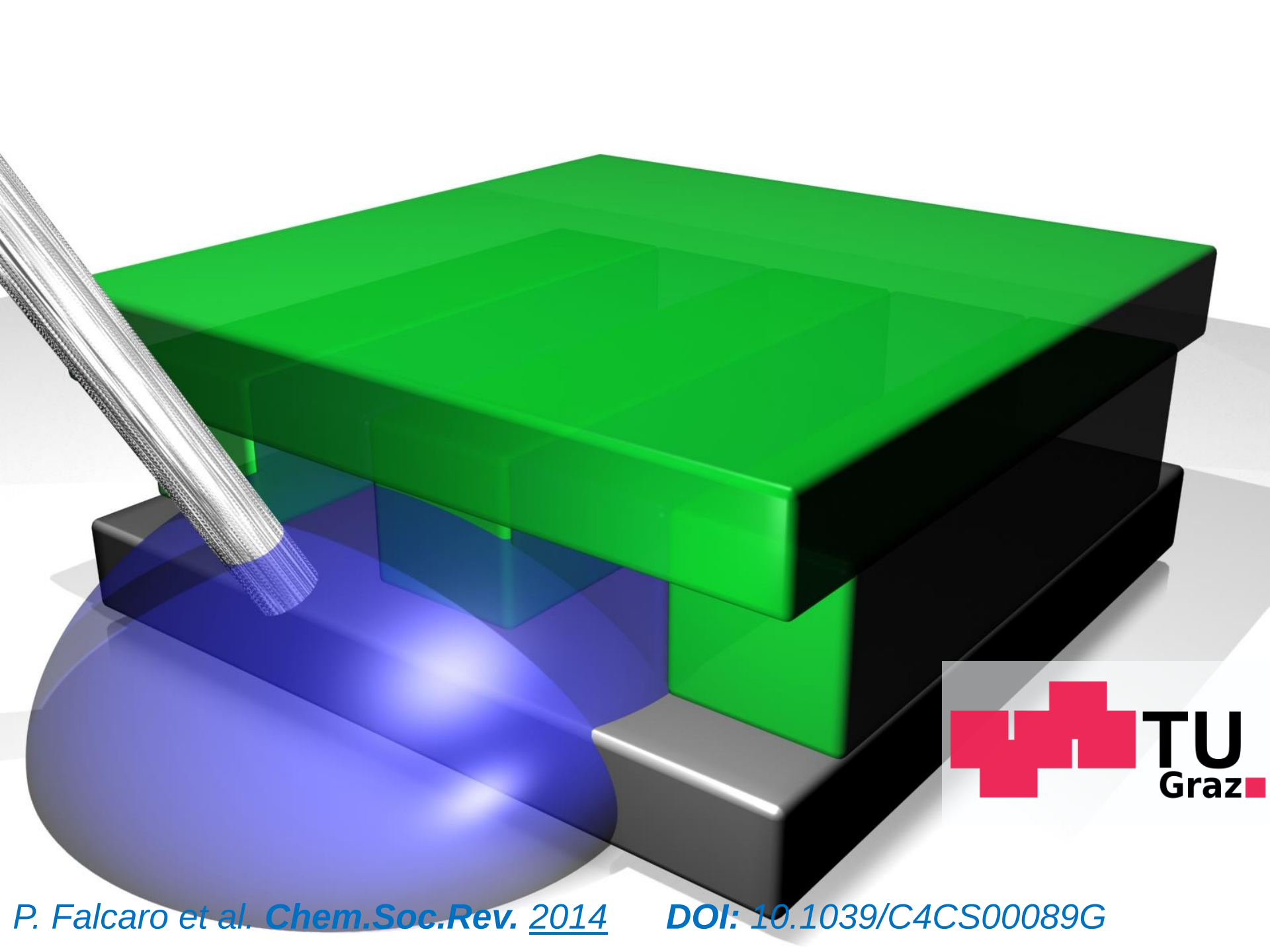
P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*



P. Falcaro et al. **Chem.Soc.Rev.** 2014 **DOI:** 10.1039/C4CS00089G



P. Falcaro et al. **Chem.Soc.Rev.** 2014 **DOI:** 10.1039/C4CS00089G



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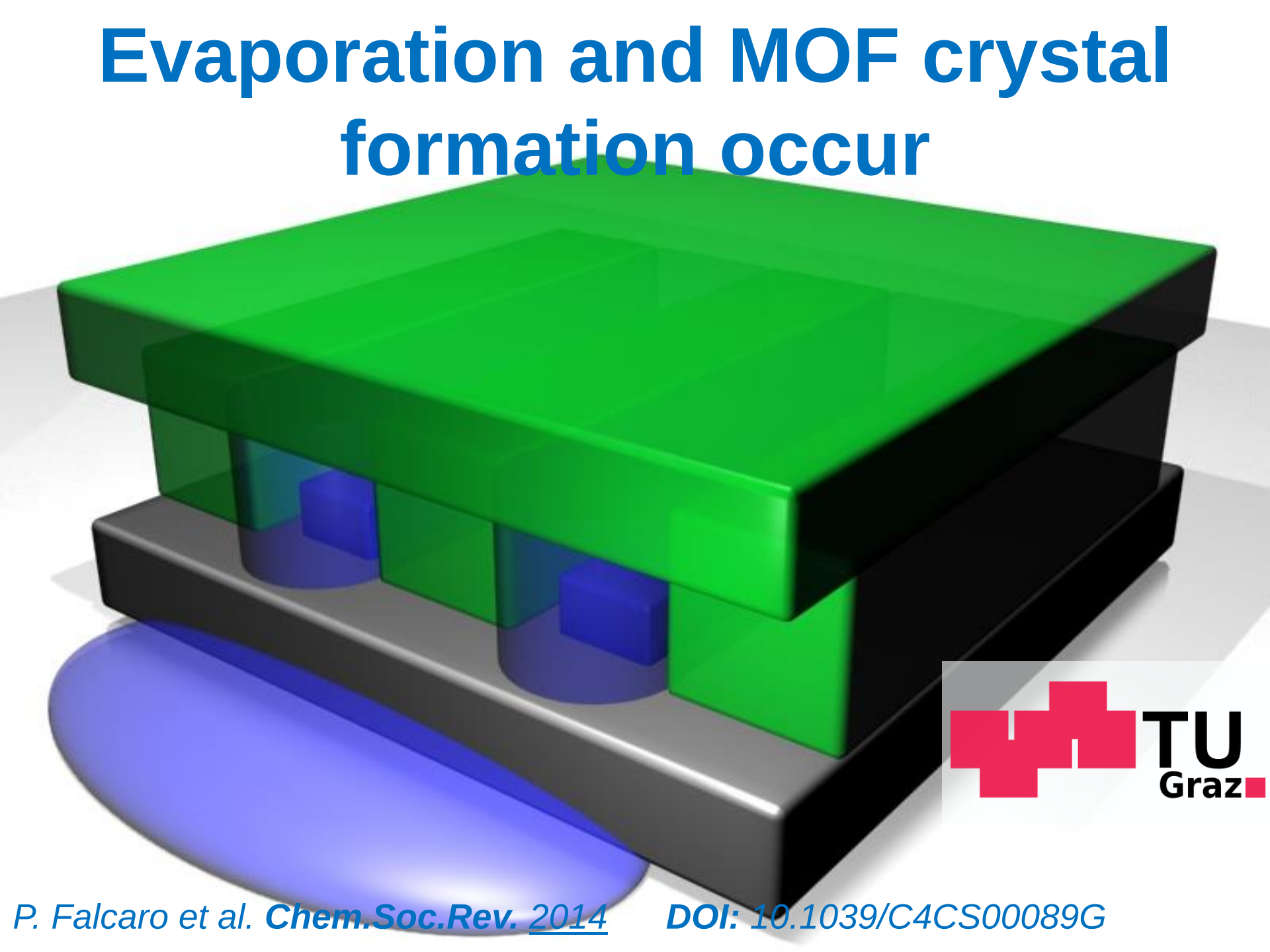
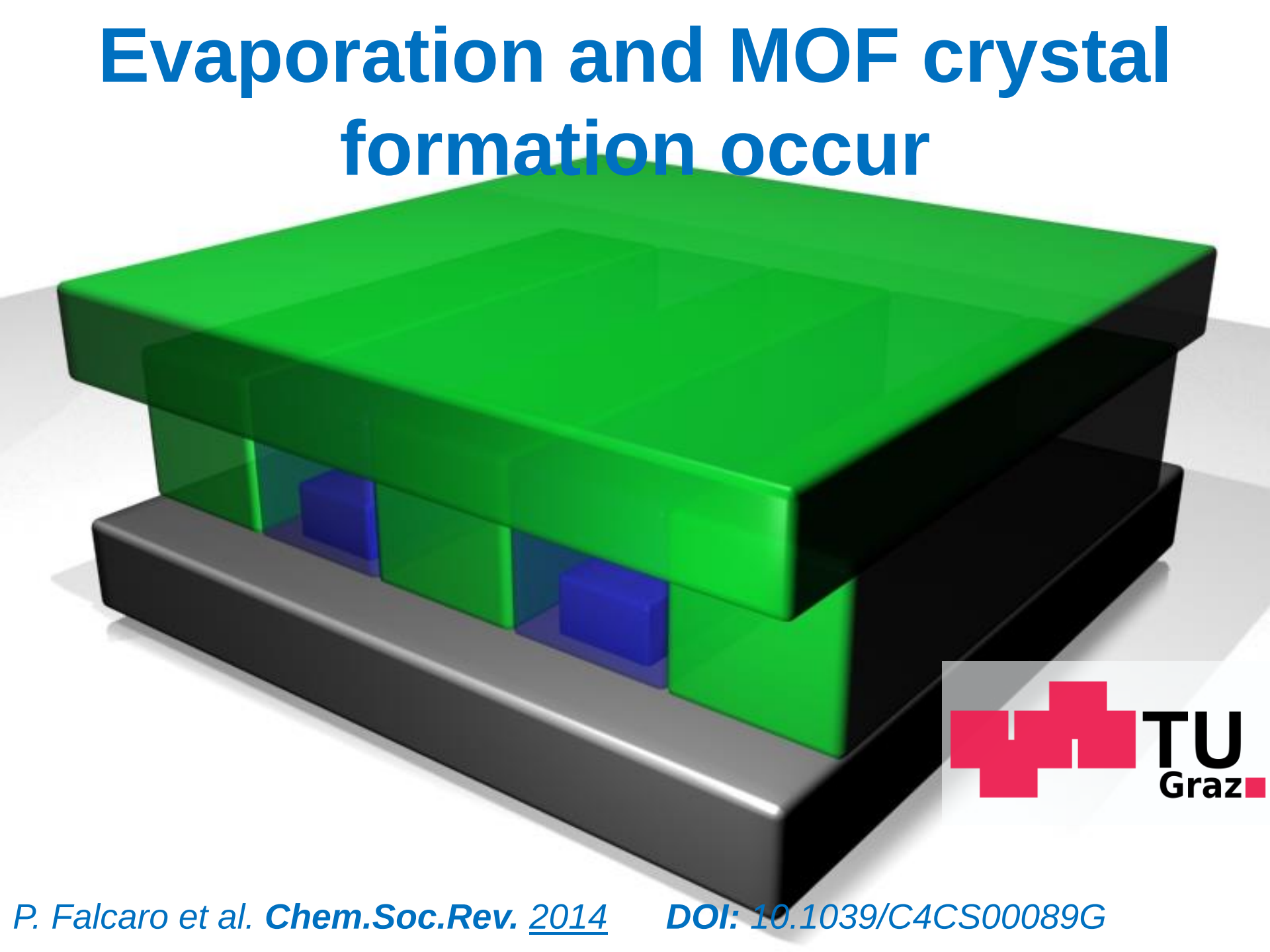
Evaporation and MOF crystal formation occur

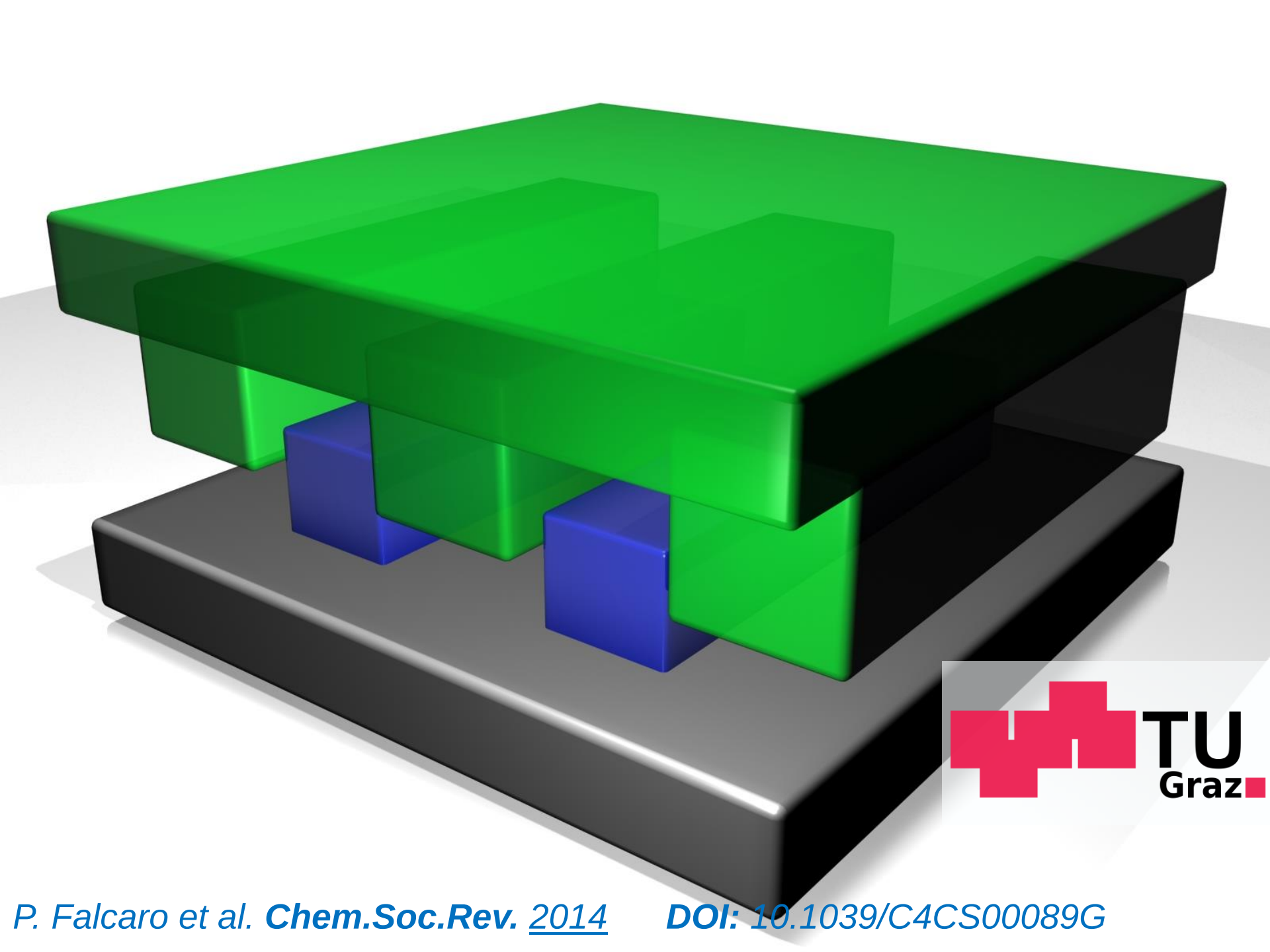


P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

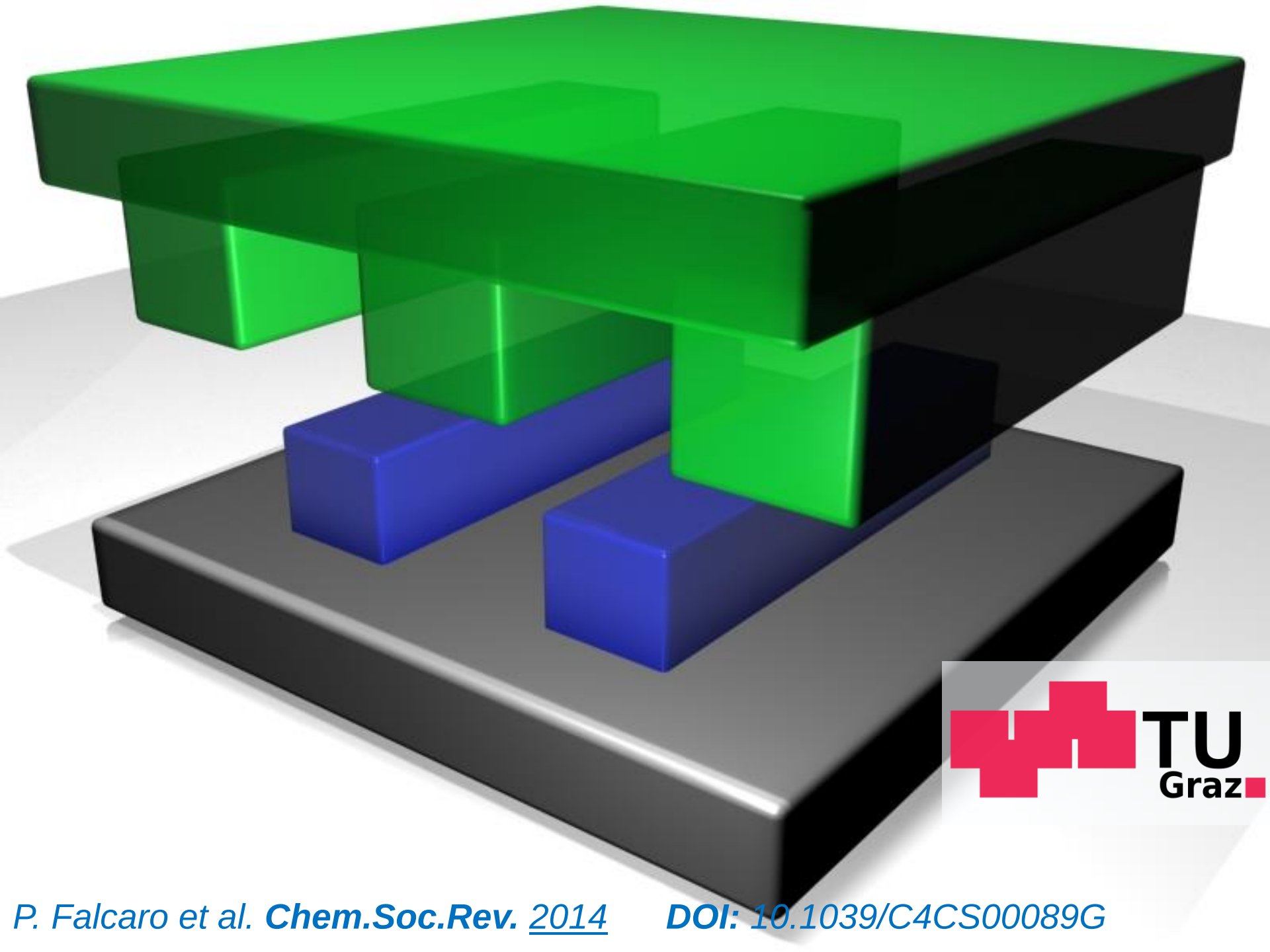
Evaporation and MOF crystal formation occur



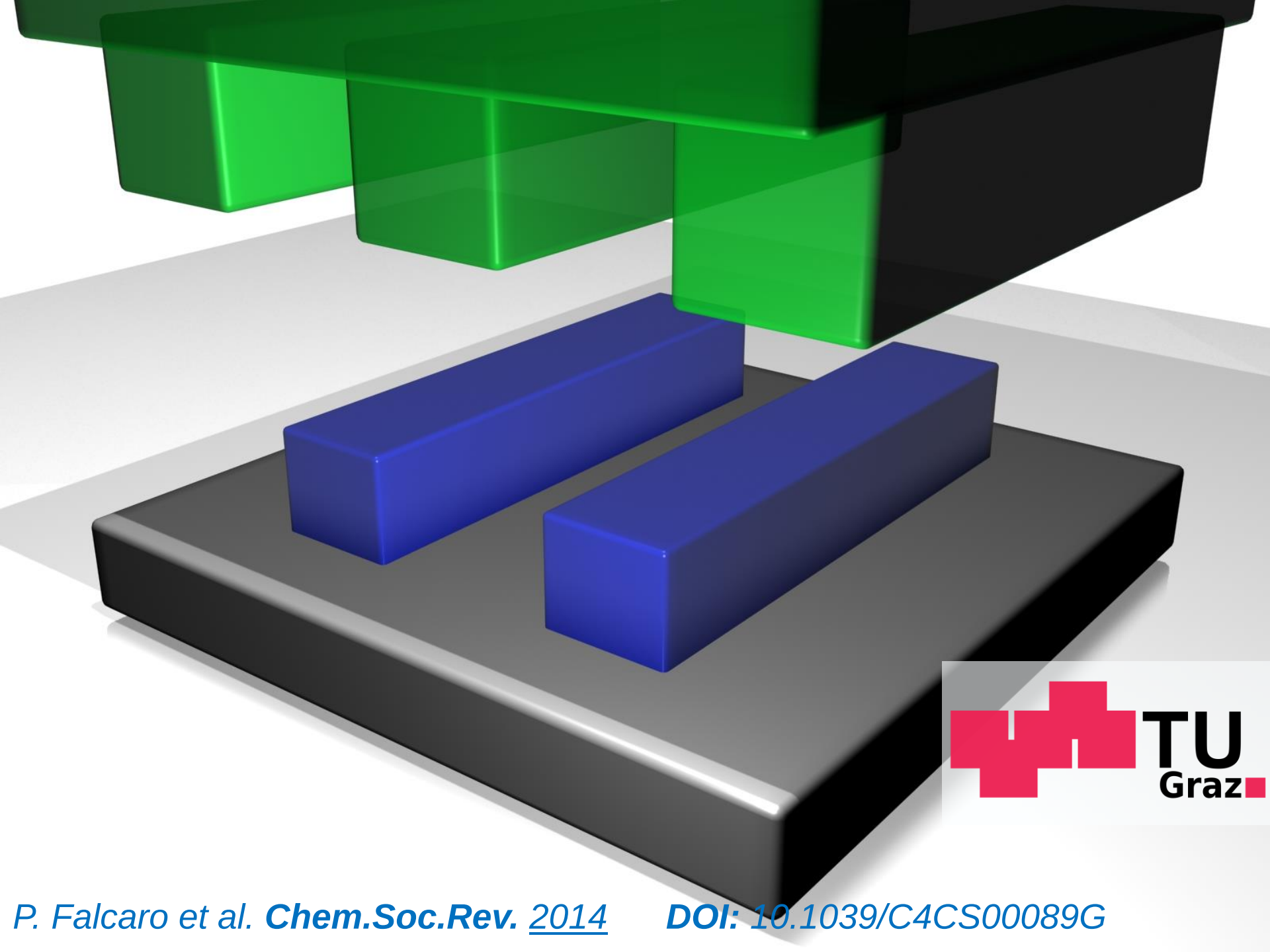
P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*



P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

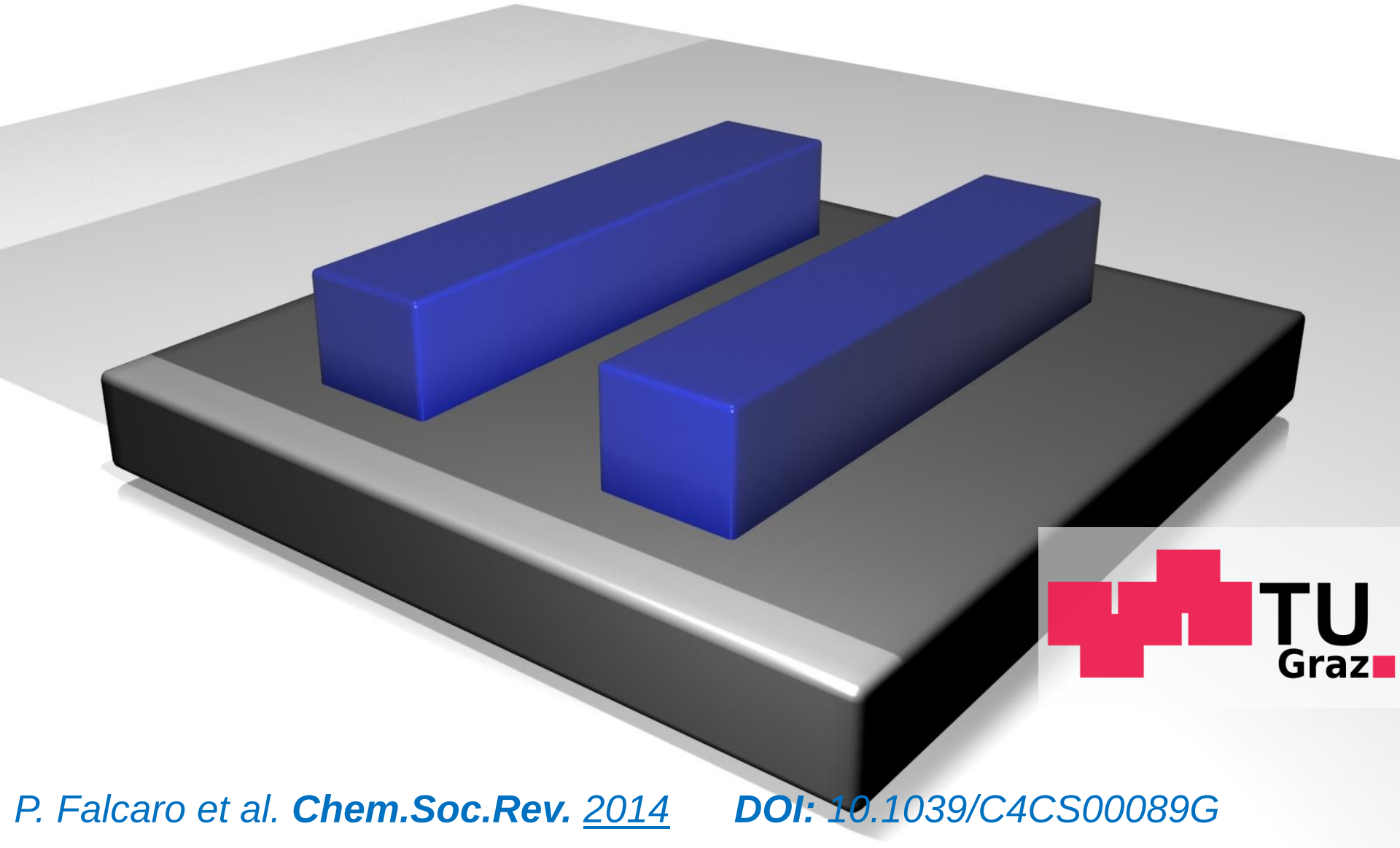


P. Falcaro et al. **Chem.Soc.Rev.** 2014 **DOI:** 10.1039/C4CS00089G



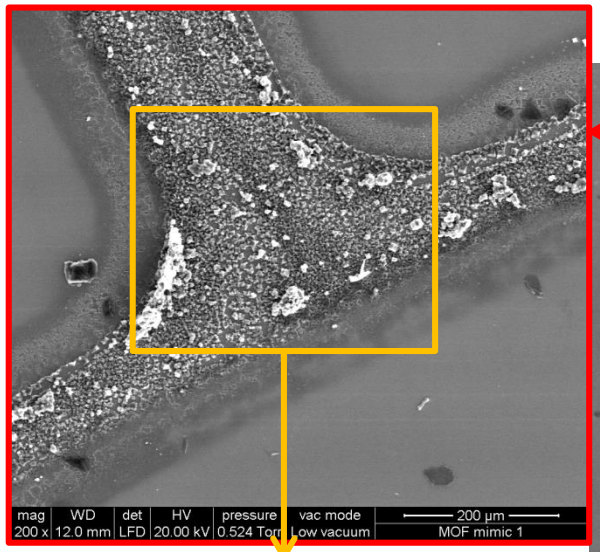
P. Falcaro et al. **Chem.Soc.Rev.** 2014 **DOI:** 10.1039/C4CS00089G

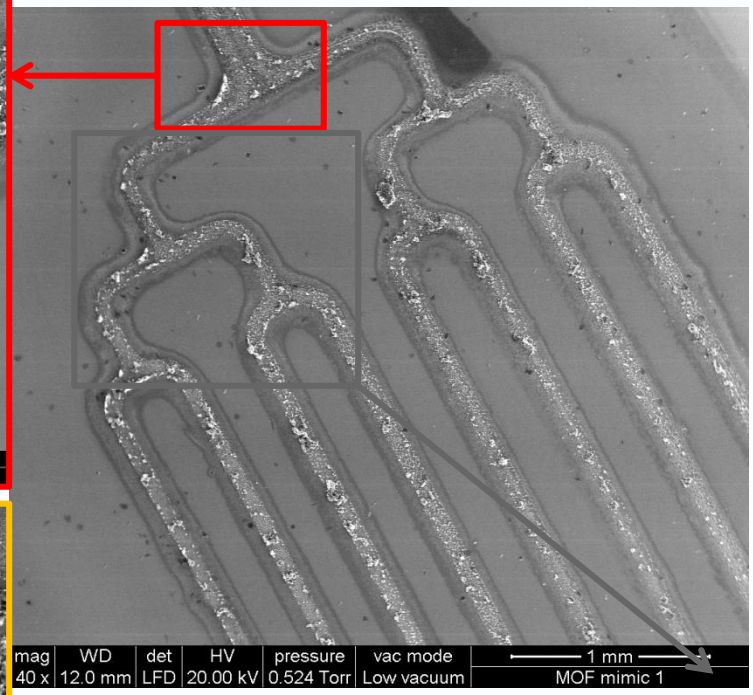
MOF Pattern formation

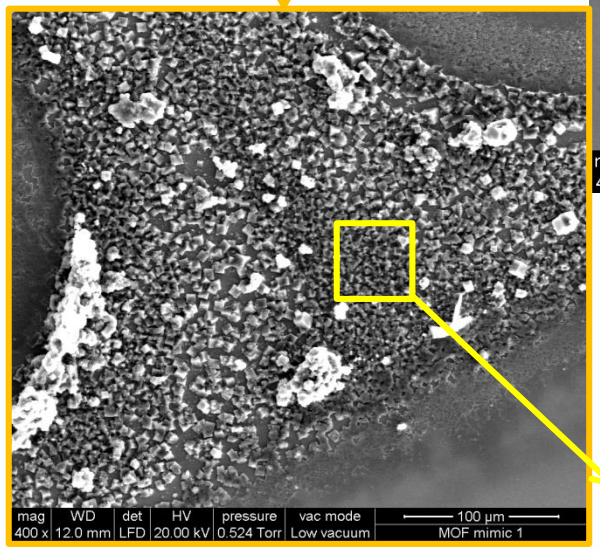


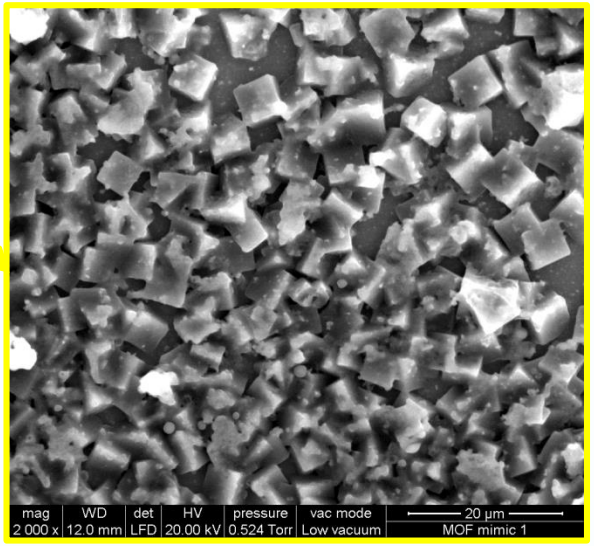
P. Falcaro et al. ***Chem.Soc.Rev.*** *2014* ***DOI:*** *10.1039/C4CS00089G*

Pattern MIMIC - controlled growth in the channels

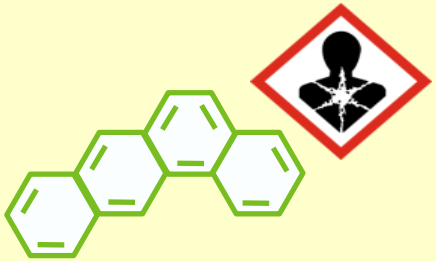


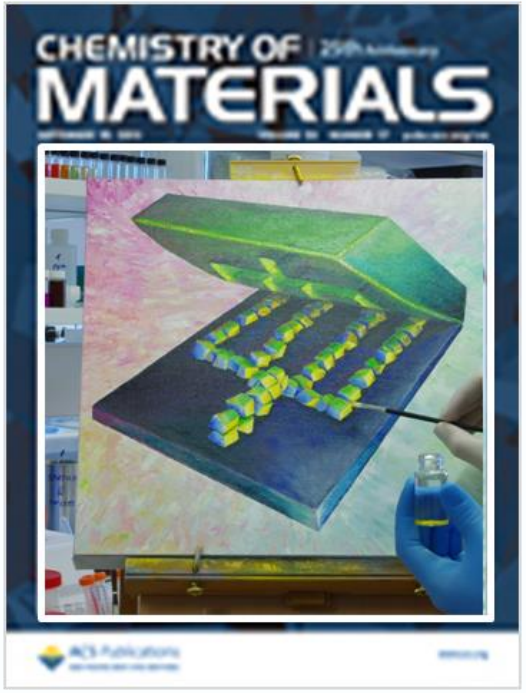






Application:
Fast sequestration of





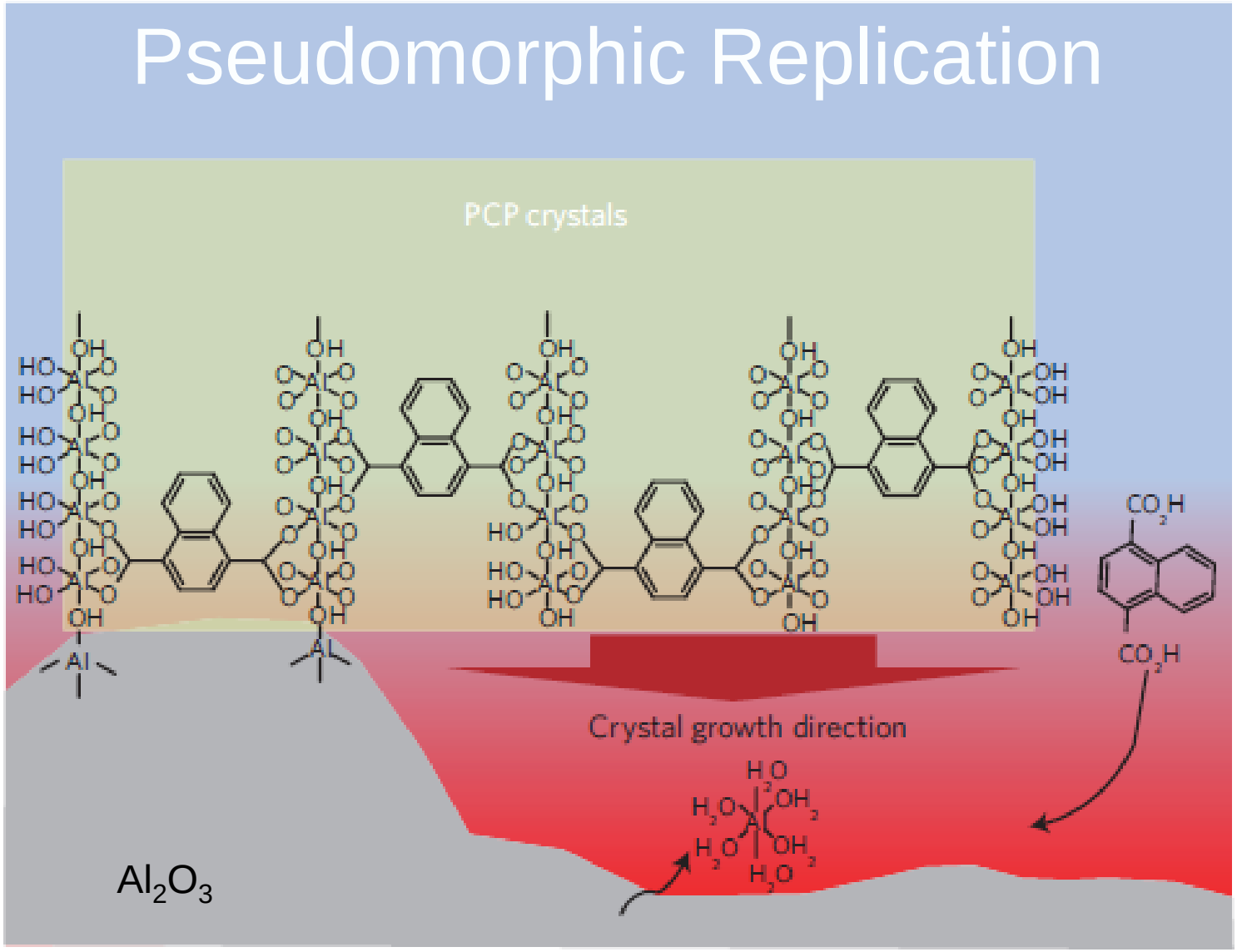
***Chem.Mater.* 2015**

Structuralization

MOFs

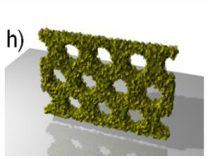
Kenji Sumida, Kang Liang, Julien Reboul, Ilich A. Ibarra, Shuhei Furukawa, Paolo Falcaro *Sol–Gel Processing of Metal–Organic Frameworks* **CHEM.MATER**. (2017), Accepted

Pseudomorphic Replication



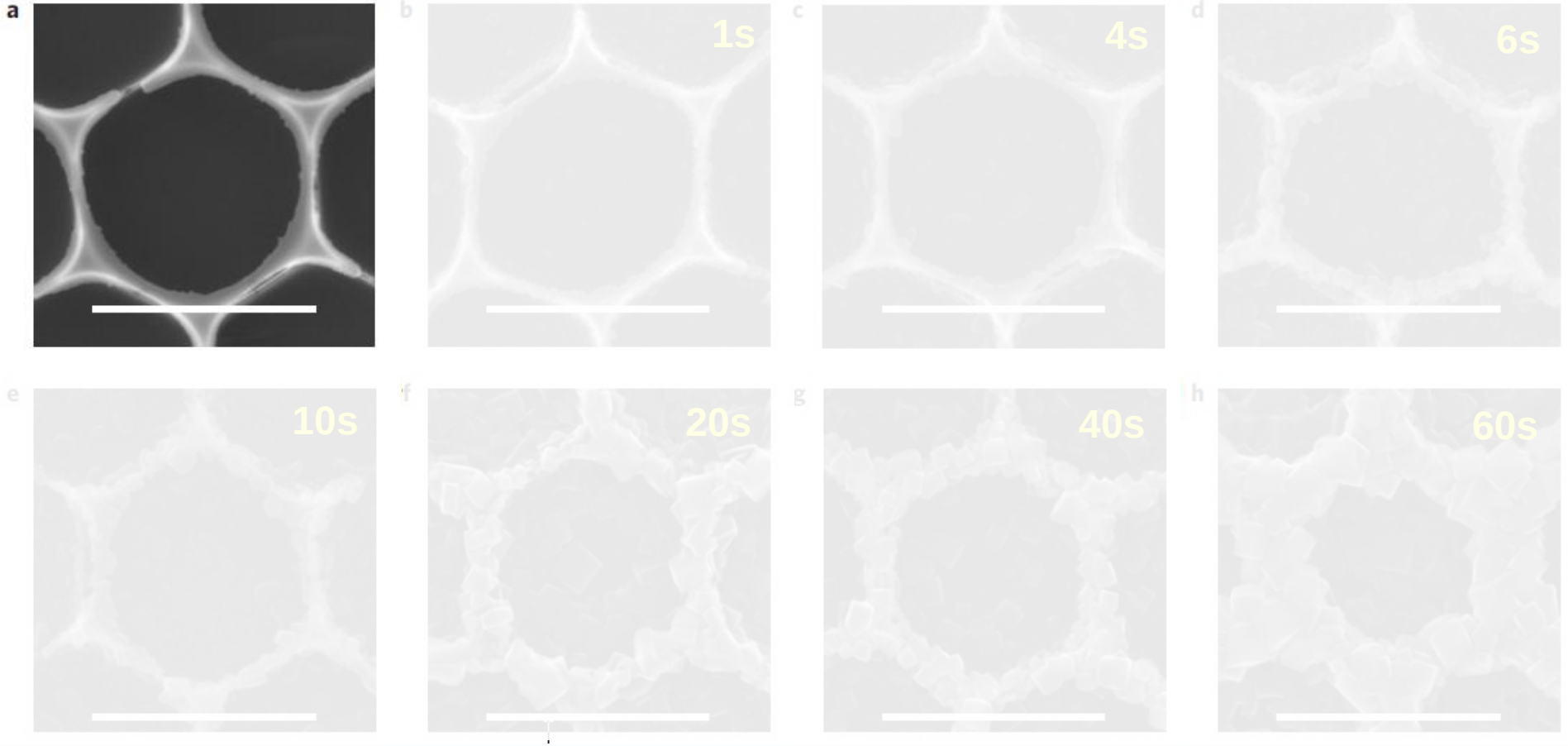
Julien Reboul, Shuhei Furukawa, Nao Horike, Manuel Tsotsalas, Kenji Hirai, Hiromitsu Uehara, Mio Kondo, Nicolas Louvain, Osami Sakata & Susumu Kitagawa

nature materials
11, 717–723 (2012) | doi:10.1038/nmat3359



Separation Water/Ethanol

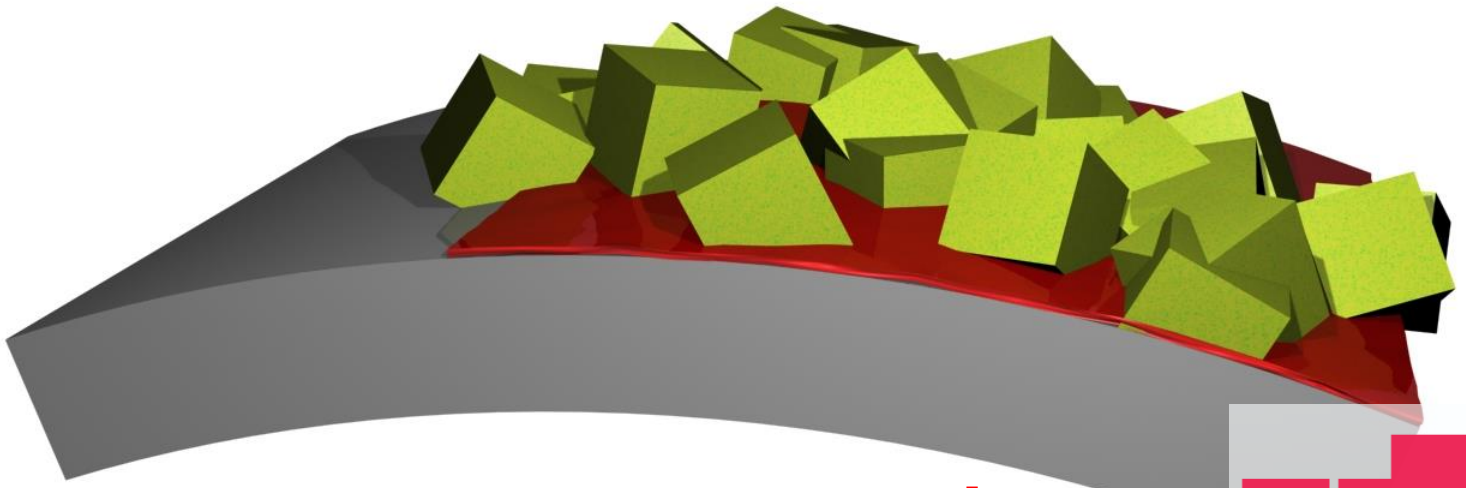
Microwaves assisted, T = 140°C



Julien Reboul, Shuhei Furukawa, Nao Horike, Manuel Tsotsalas, Kenji Hirai, Hiromitsu Uehara, Mio Kondo, Nicolas Louvain, Osami Sakata & Susumu Kitagawa

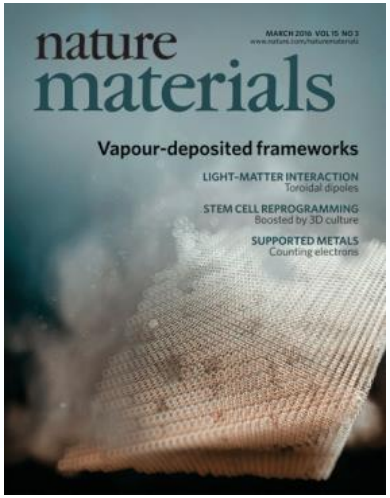
nature materials
11, 717–723 (2012) | doi:10.1038/nmat3359

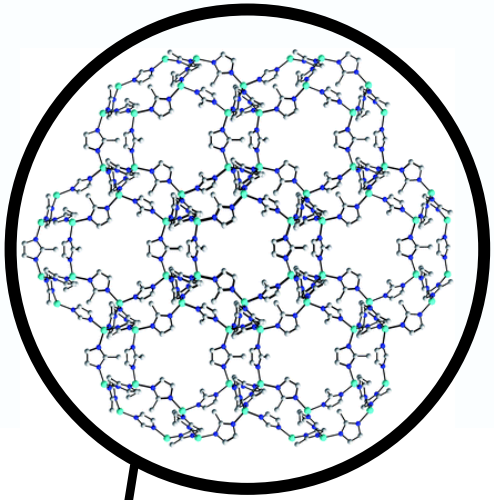
Positioning



Kenji Sumida, Kang Liang, Julien Reboul, Ilich A. Ibarra, Shuhei Furukawa, Paolo Falcaro *Sol–Gel Processing of Metal–Organic Frameworks* **CHEM.MATER**. (2017), Accepted

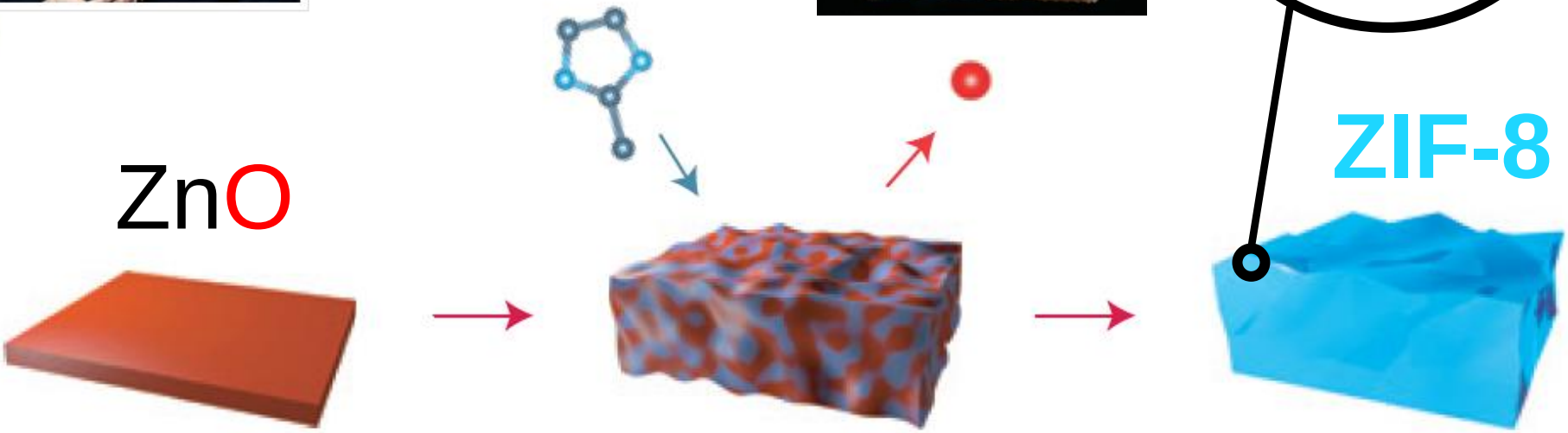
MOFs Via CVD





a

ZnO



ZIF-8

$$ZnO + 2\,HmIM \rightarrow H_2O + ZIF\text{-}8$$

I. Stassen, M.J. Styles, G. Grenci, H. Van Gorp, W. Vanderlinden, S. De Feyter, P. Falcaro, D. De Vos, P. Philippe Vereecken **R. Ameloot Nature Materials** 2016

(1)

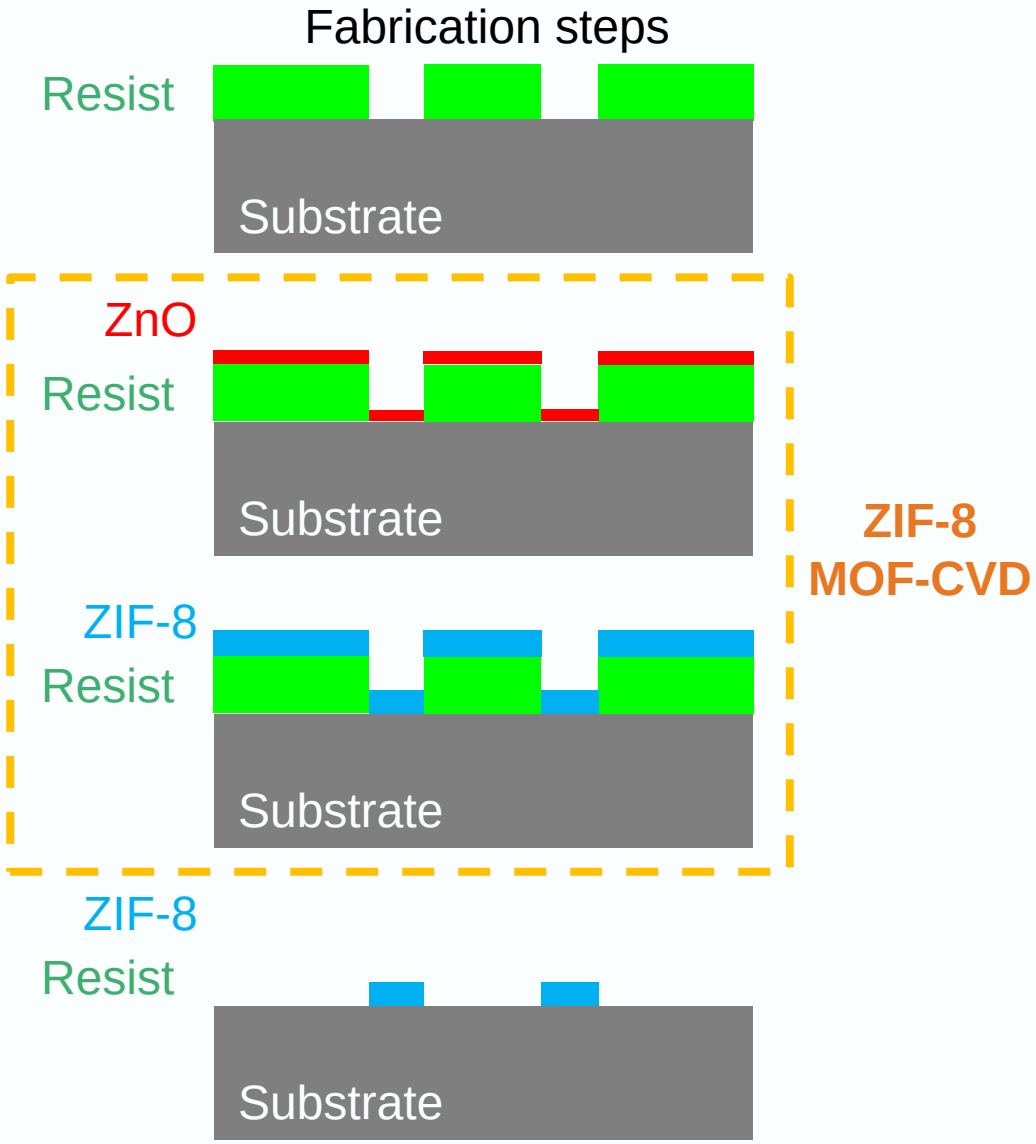
Atomic Layer deposition of ZnO

(2)

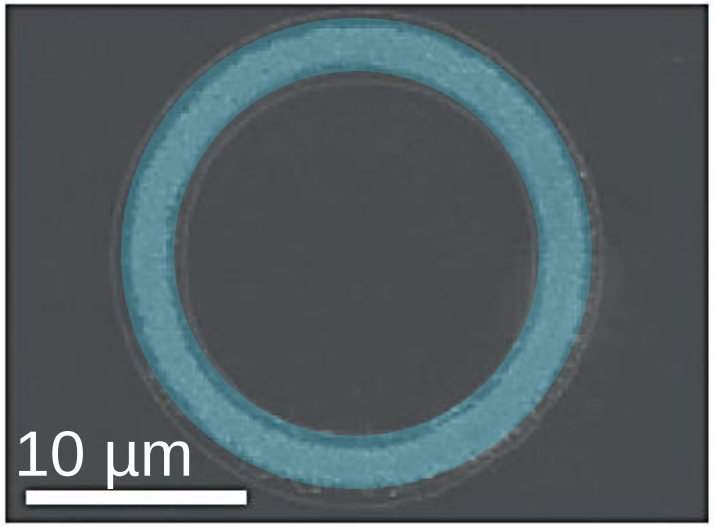
Vapours of the ligand

I. Stassen, M.J. Styles, G. Grenci, H. Van Gorp, W. Vanderlinden, S. De Feyter, P. Falcaro, D. De Vos, P. Philippe Vereecken R. Ameloot **Nature Materials** 2016

Compatible with the current lithographic protocols (lift-off)



ZIF-8
MOF-CVD

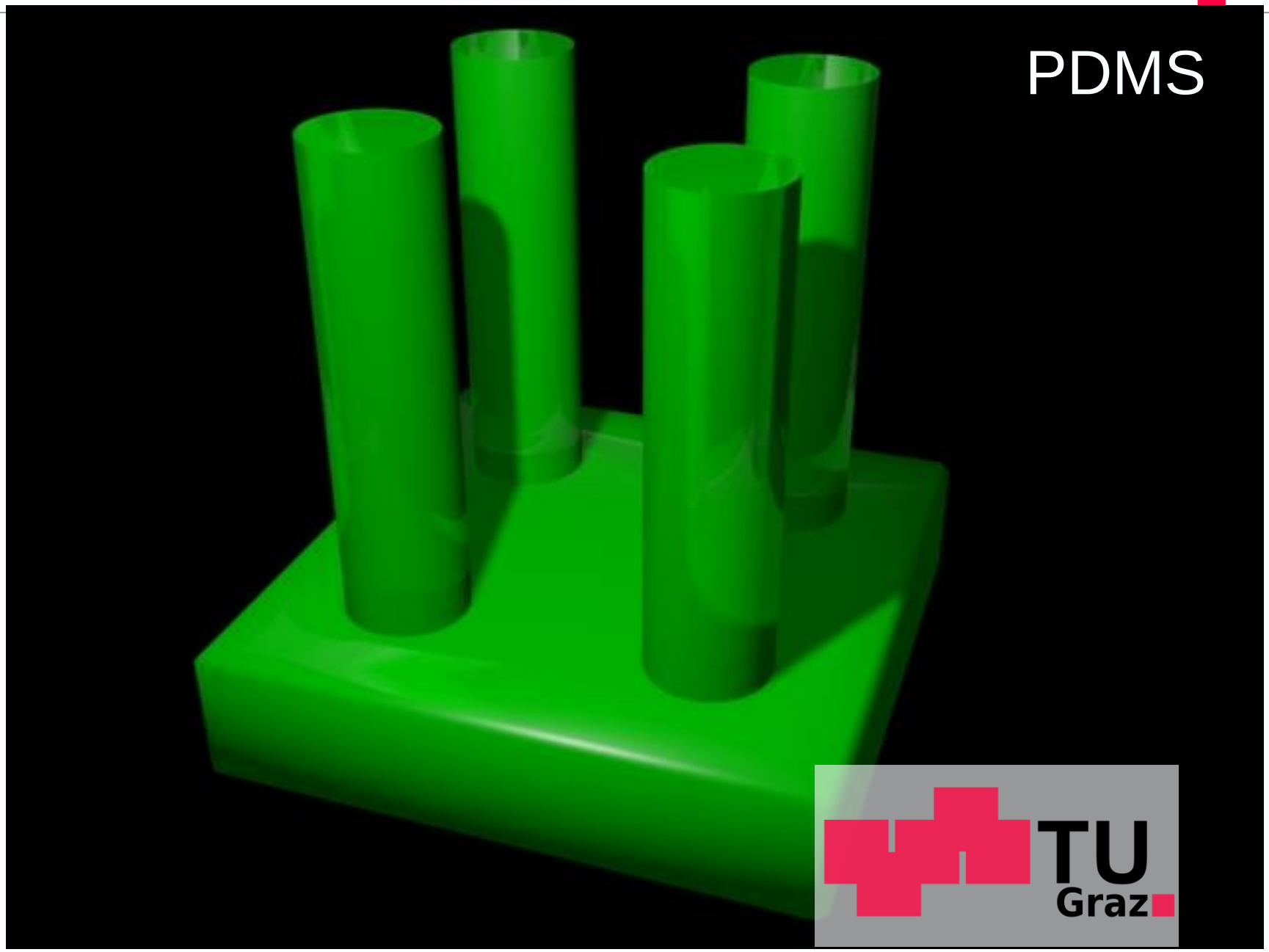


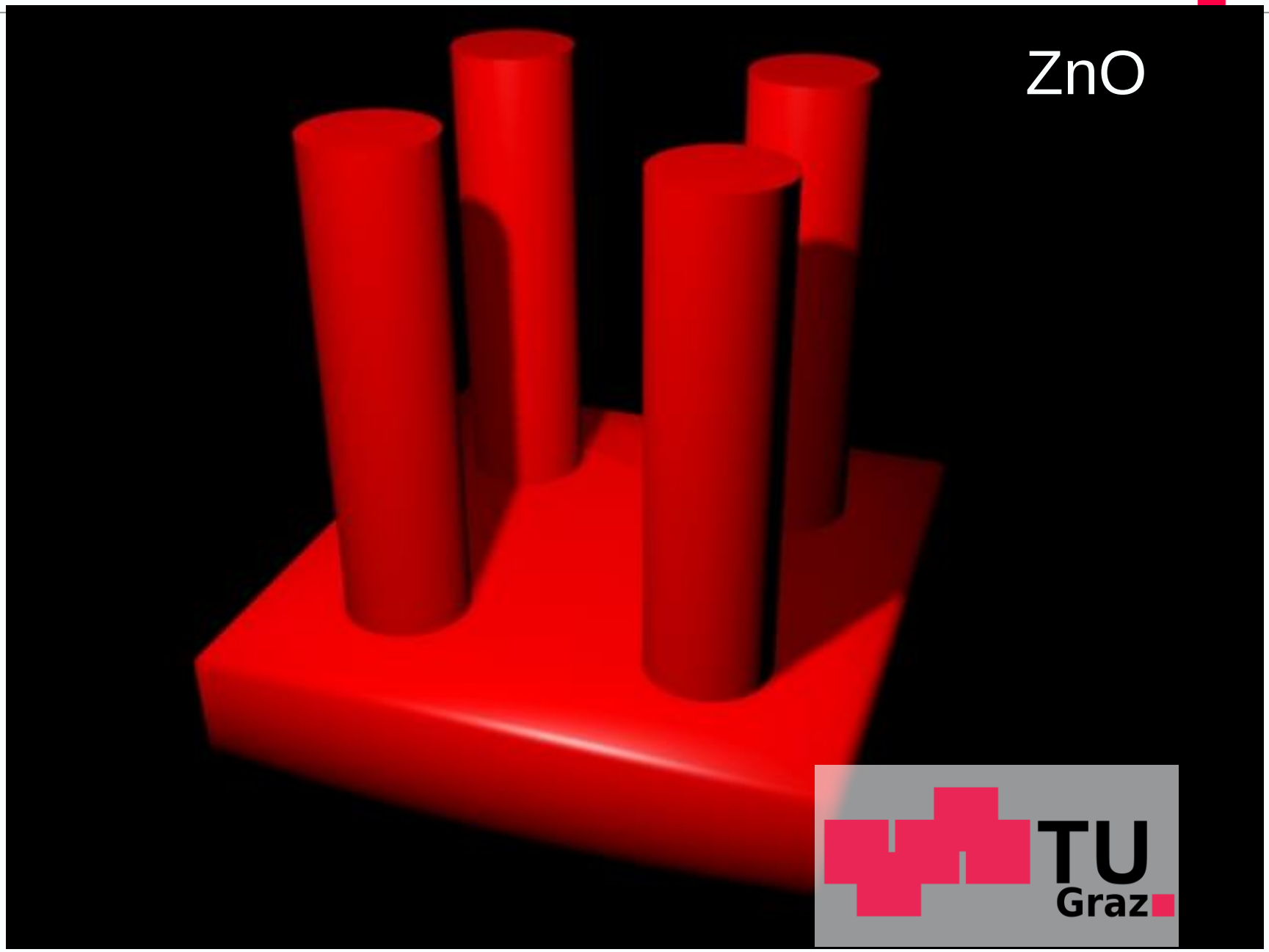
I. Stassen, M.J. Styles, G. Grenci, H. Van Gorp, W. Vanderlinden, S. De Feyter, P. Falcaro, D. De Vos, P. Philippe Vereecken R. Ameloot **Nature Materials** 2016

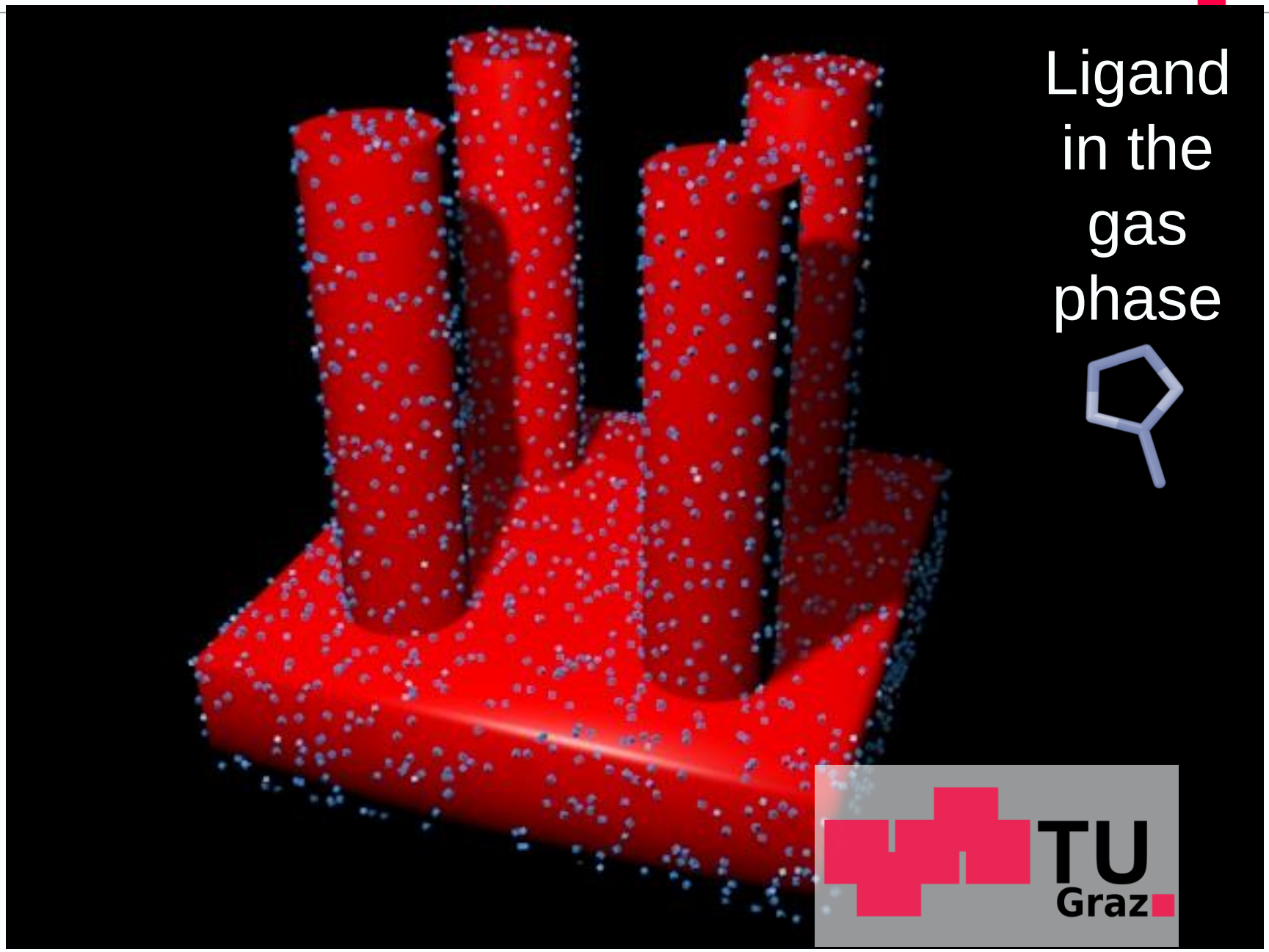

PDMS
Replica
Mould

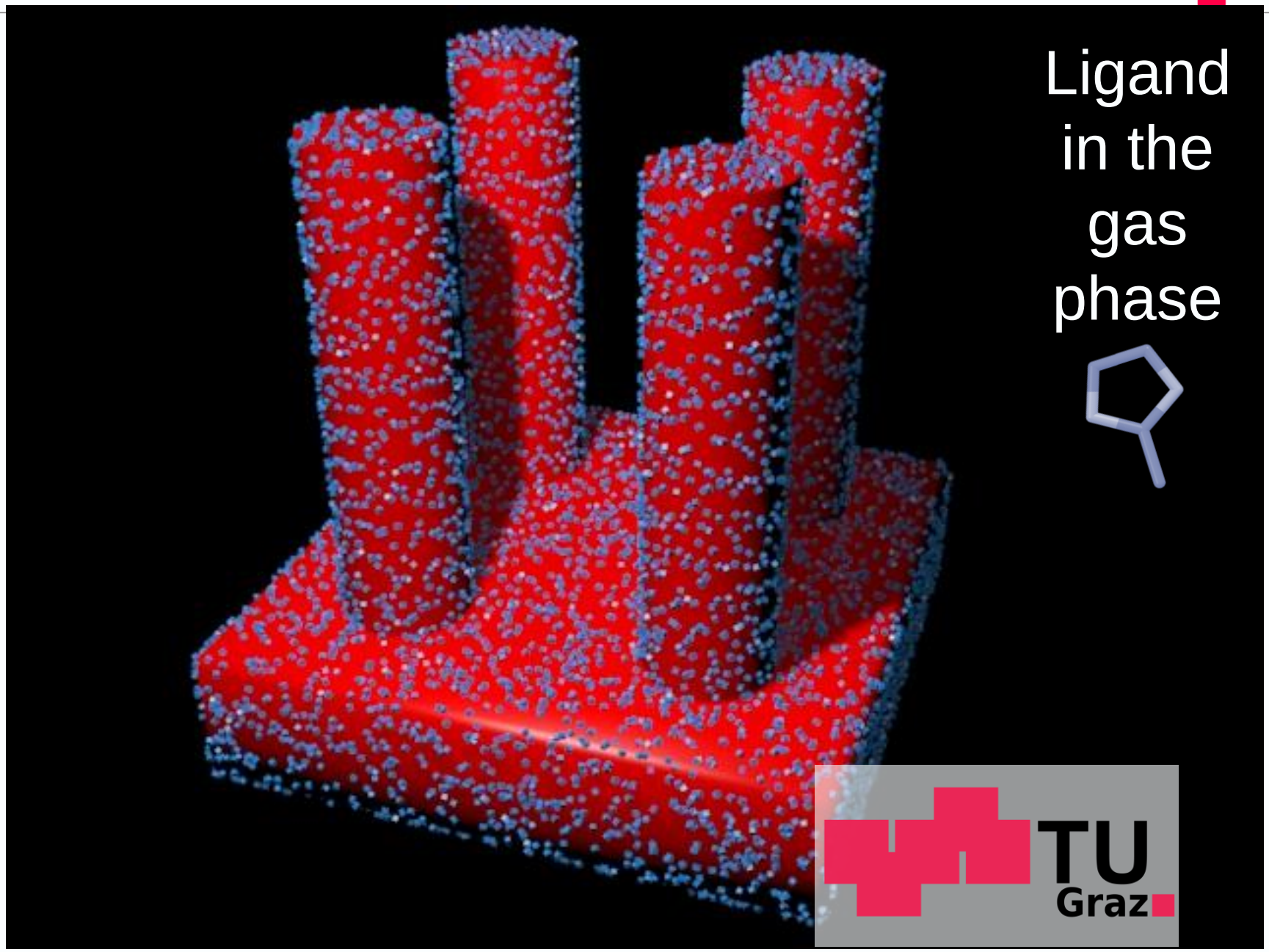
Replica

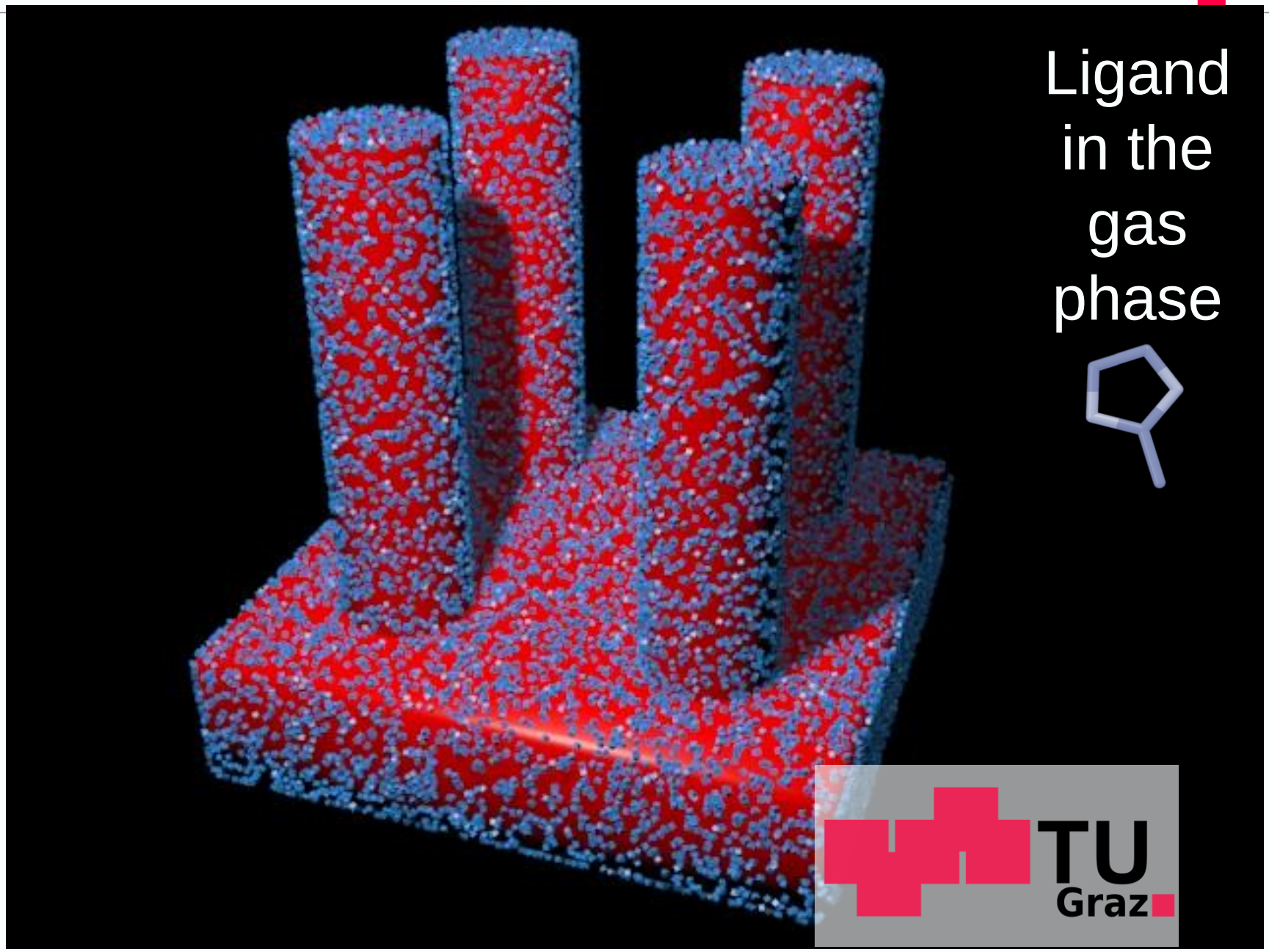
Mould

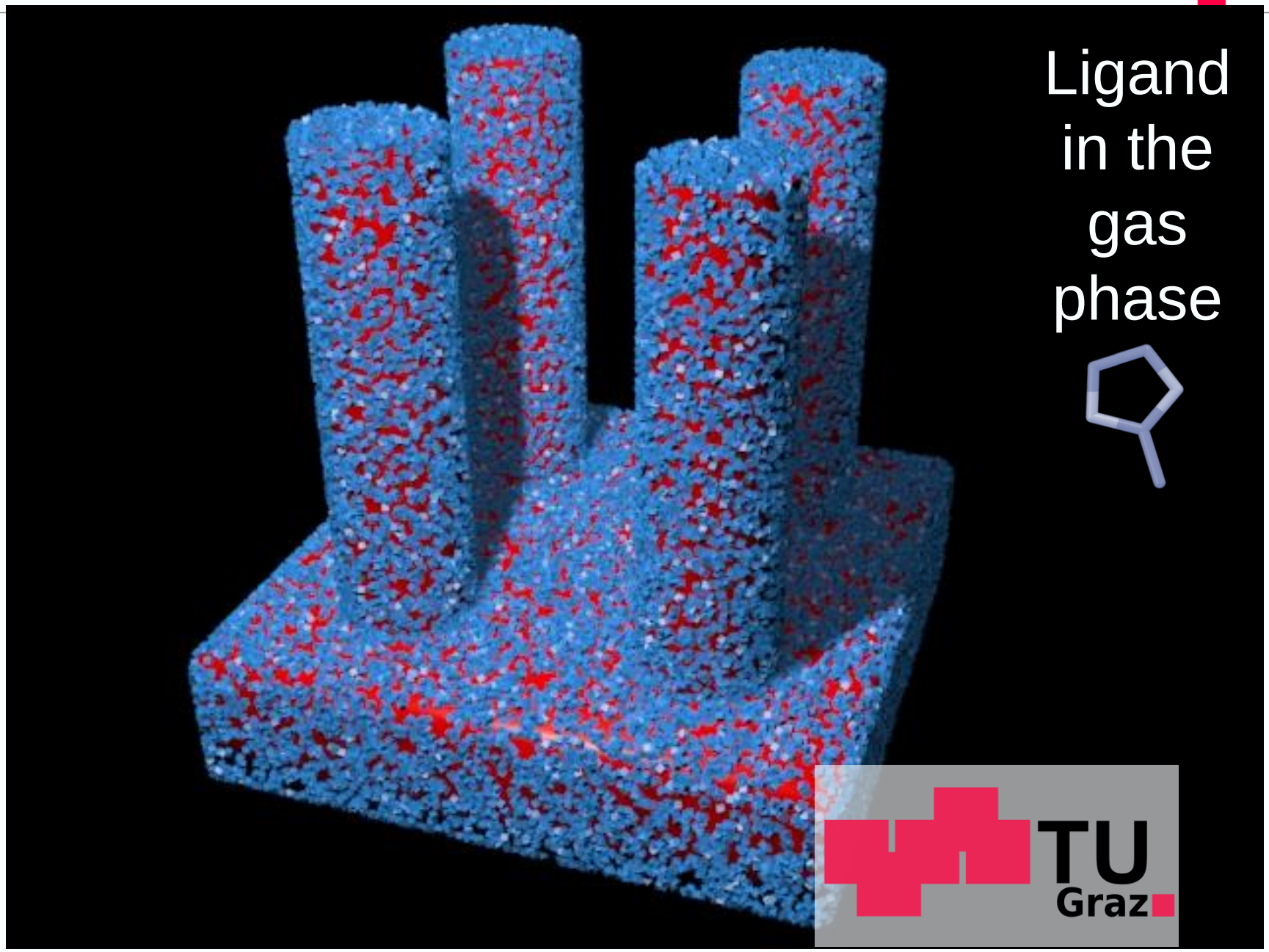

PDMS

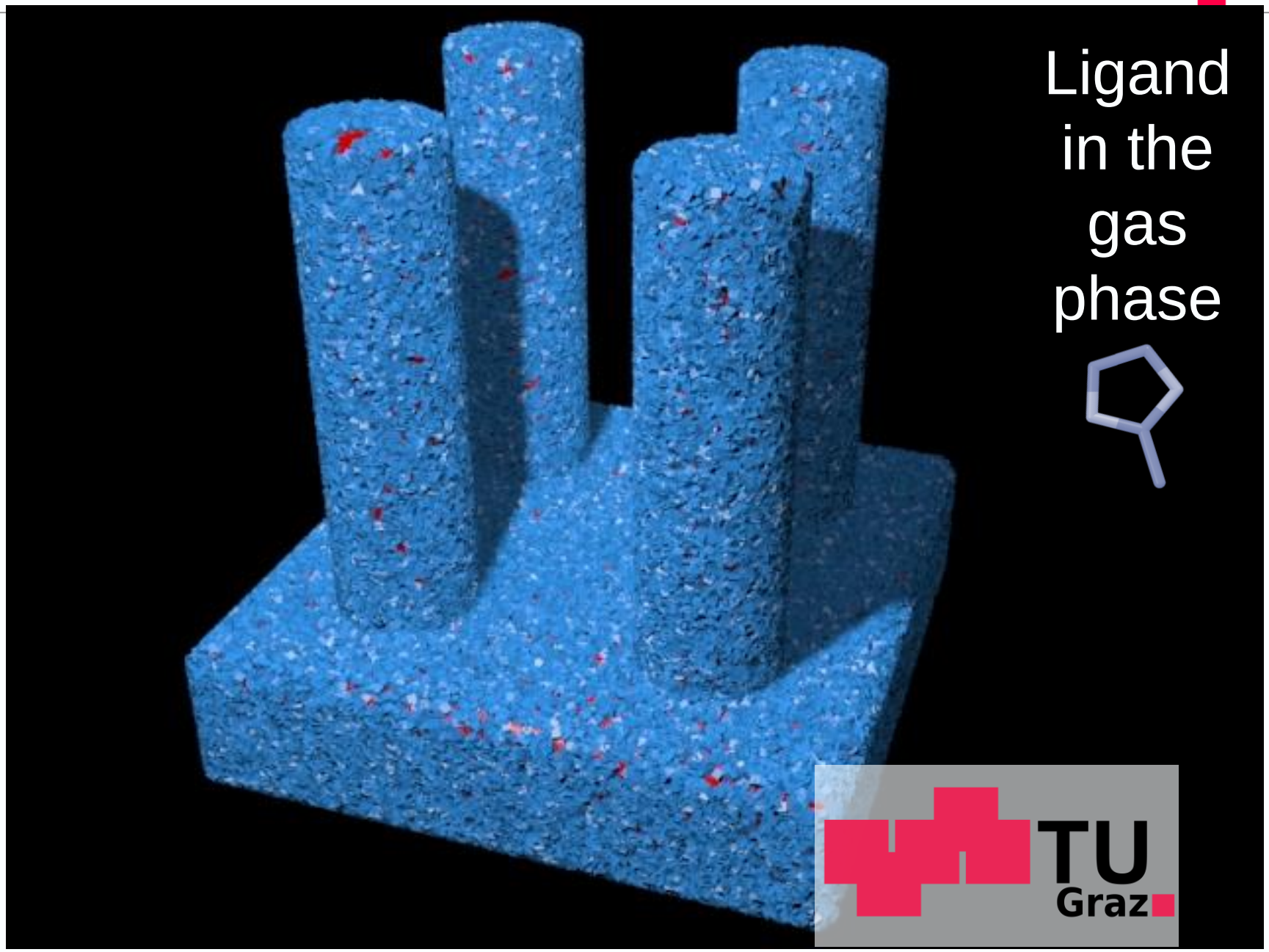

ZnO


Ligand
in the
gas
phase

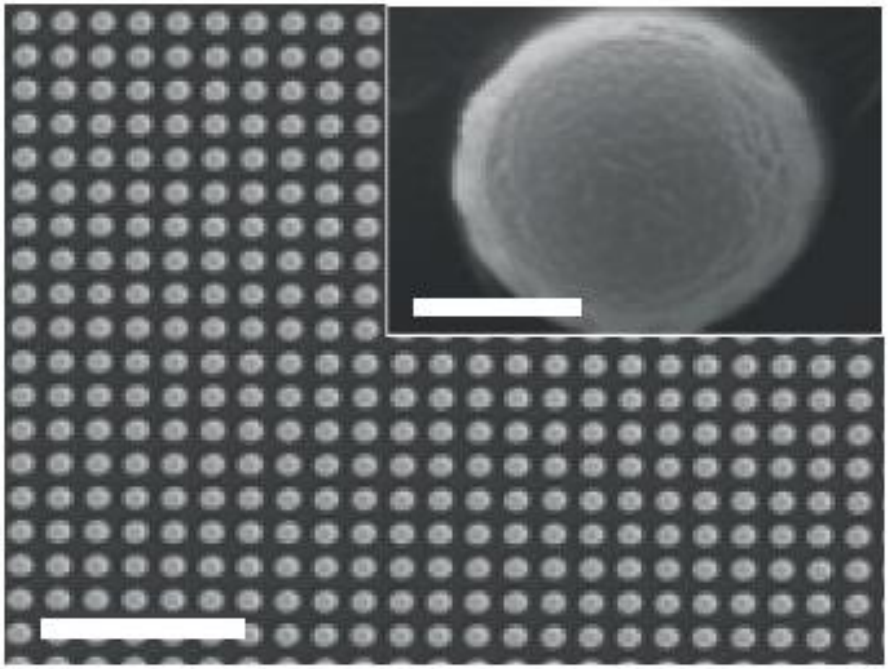

Ligand
in the
gas
phase
TU
Graz


Ligand
in the
gas
phase
TU
Graz

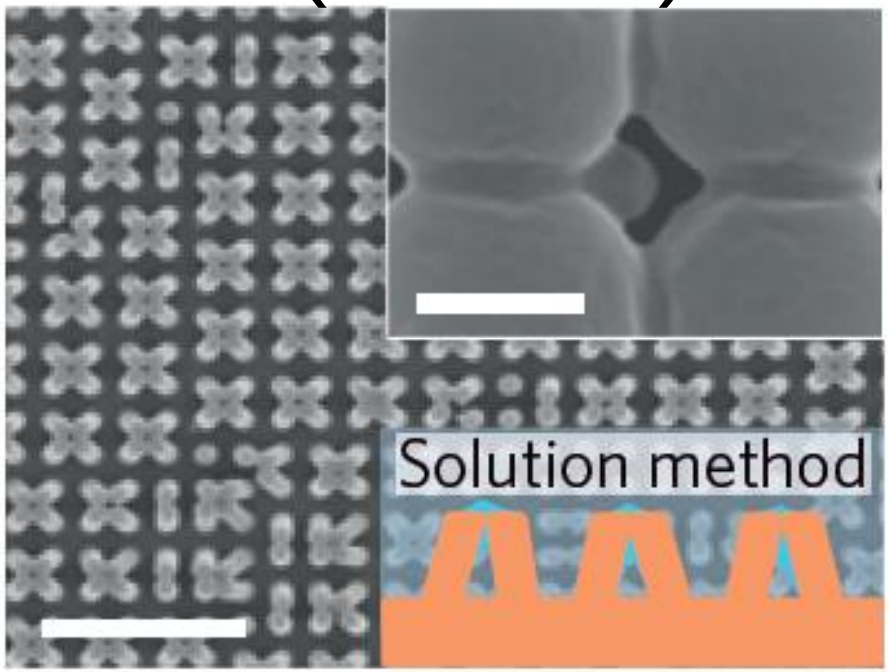

Ligand
in the
gas
phase
TU
Graz


Ligand
in the
gas
phase
TU
Graz

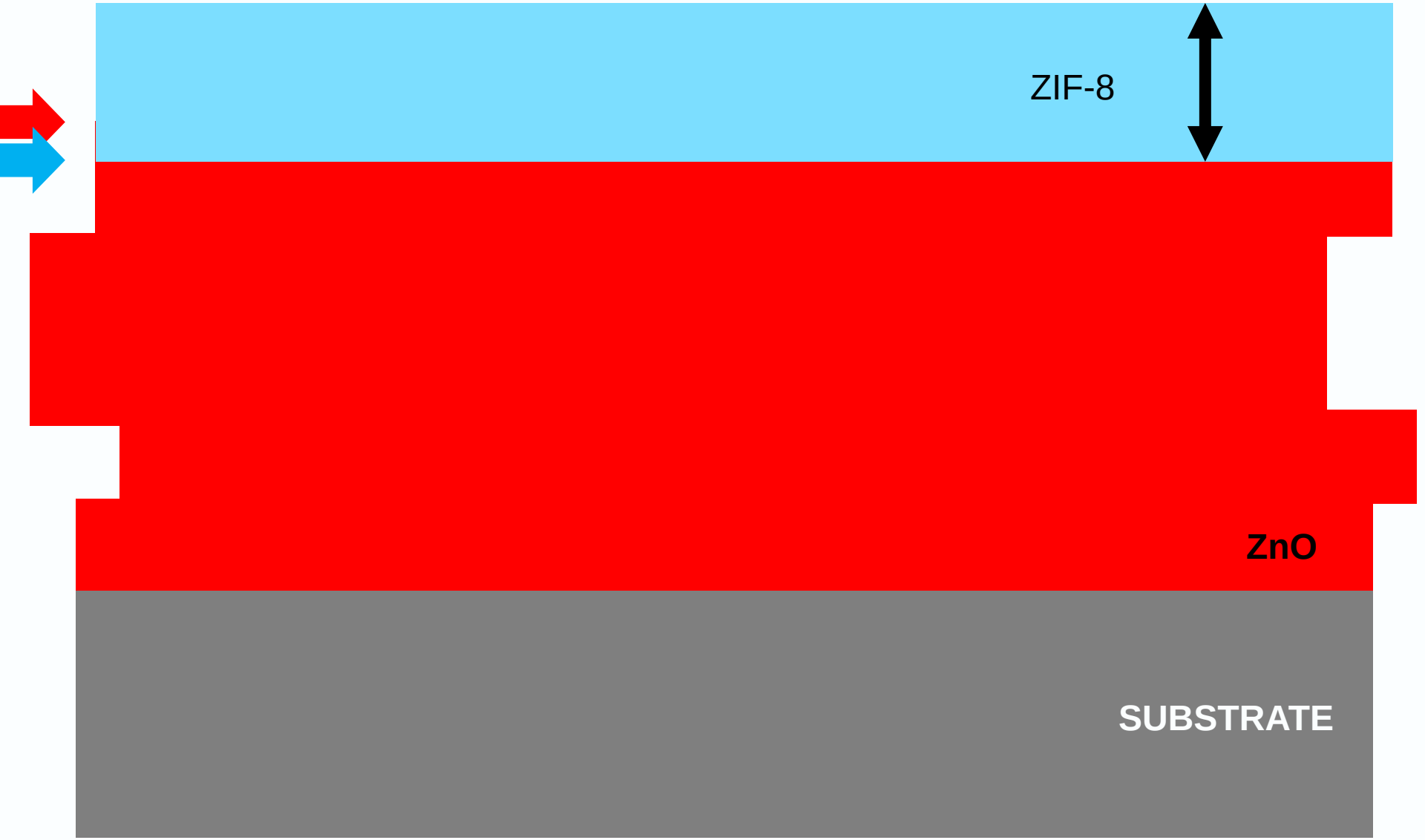
MOFs via CVD (gas)



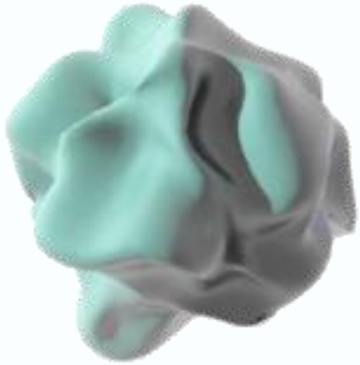
MOFs via solvothermal (solution)

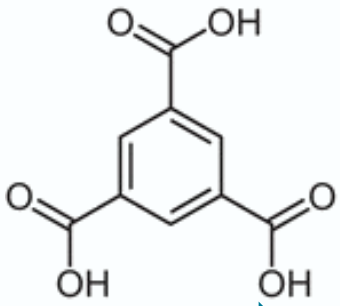


I. Stassen, M.J. Styles, G. Grenci, H. Van Gorp, W. Vanderlinden, S. De Feyter, P. Falcaro, D. De Vos, P. Philippe Vereecken R. Ameloot **Nature Materials** 2016

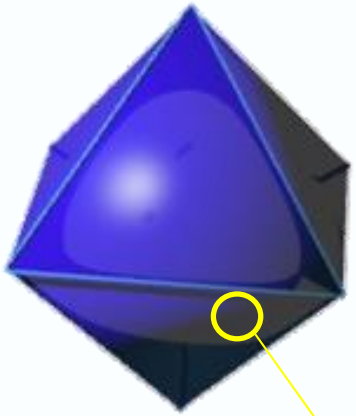

ZIF-8
ZnO
SUBSTRATE

Other Conversions from Ceramics



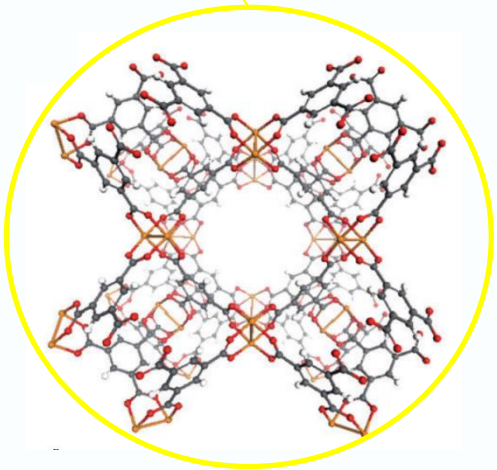


Ethanol/water (10 min)



$Cu(OH)_2$

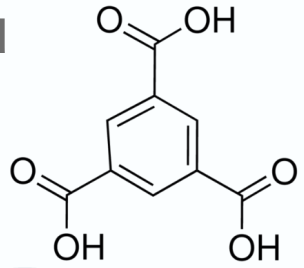
HKUST-1



Majano et al. ***Adv.Mater.*** *2013*, 25, 1052

How can we use it for device fabrication?

Benzene-1,3,5-TriCarboxylic acid



Step 1 ceramic

Step 2 MOF

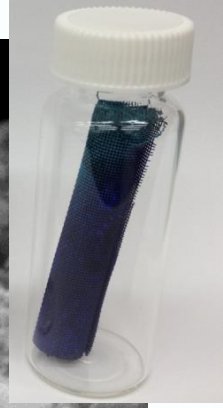
Metal

500 µm

Adv. Funct. Mater. 2014, 24, 1969–1977

100 µm

Adv. Funct. Mater. 2014, 24, 1969–1977

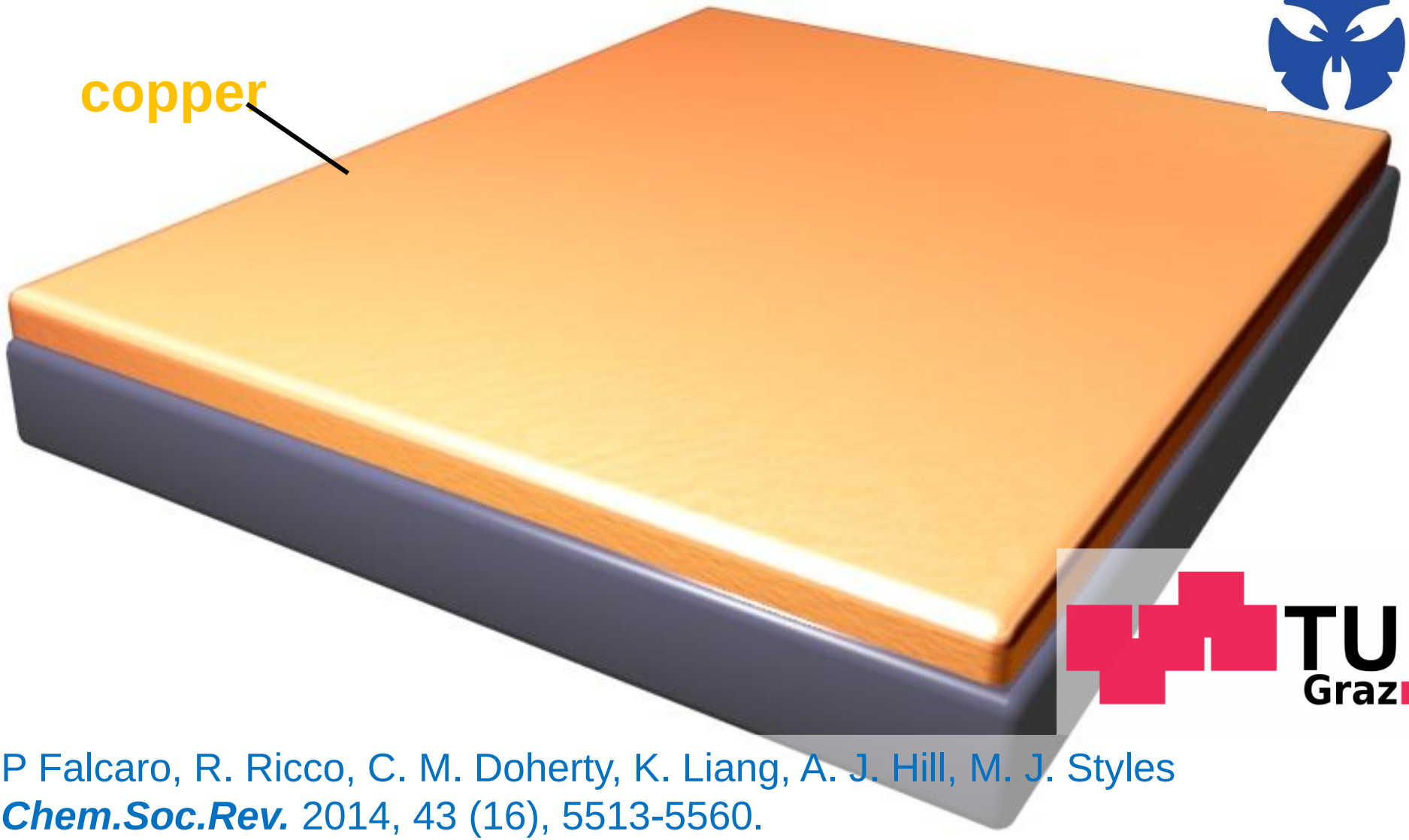


10 µm

Adv. Funct. Mater. 2014, 24, 1969–1977

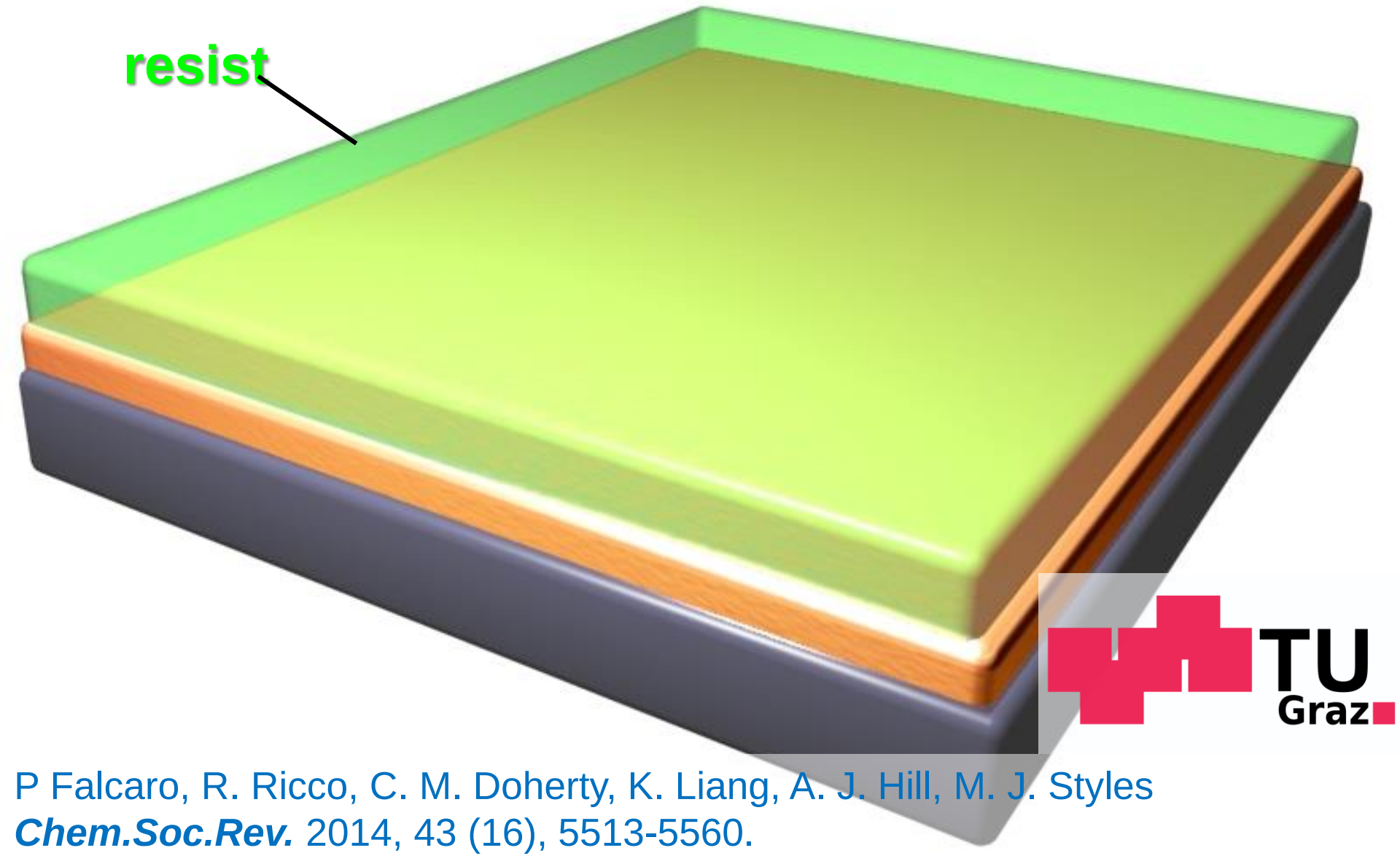
Supported copper substrat

Kenji Okada
Prof. Masahide Takahashi



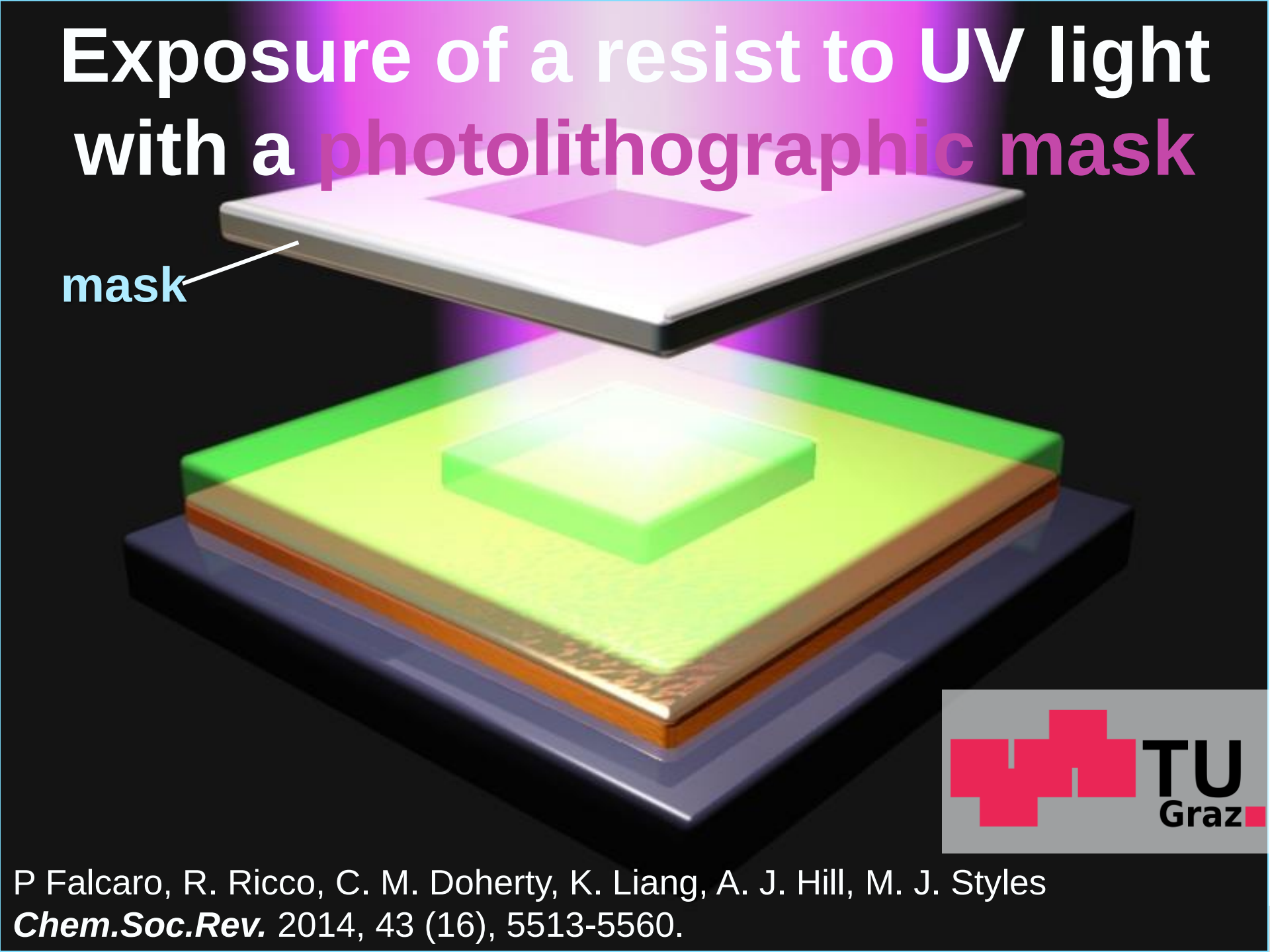
P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Photoresist deposited on copper



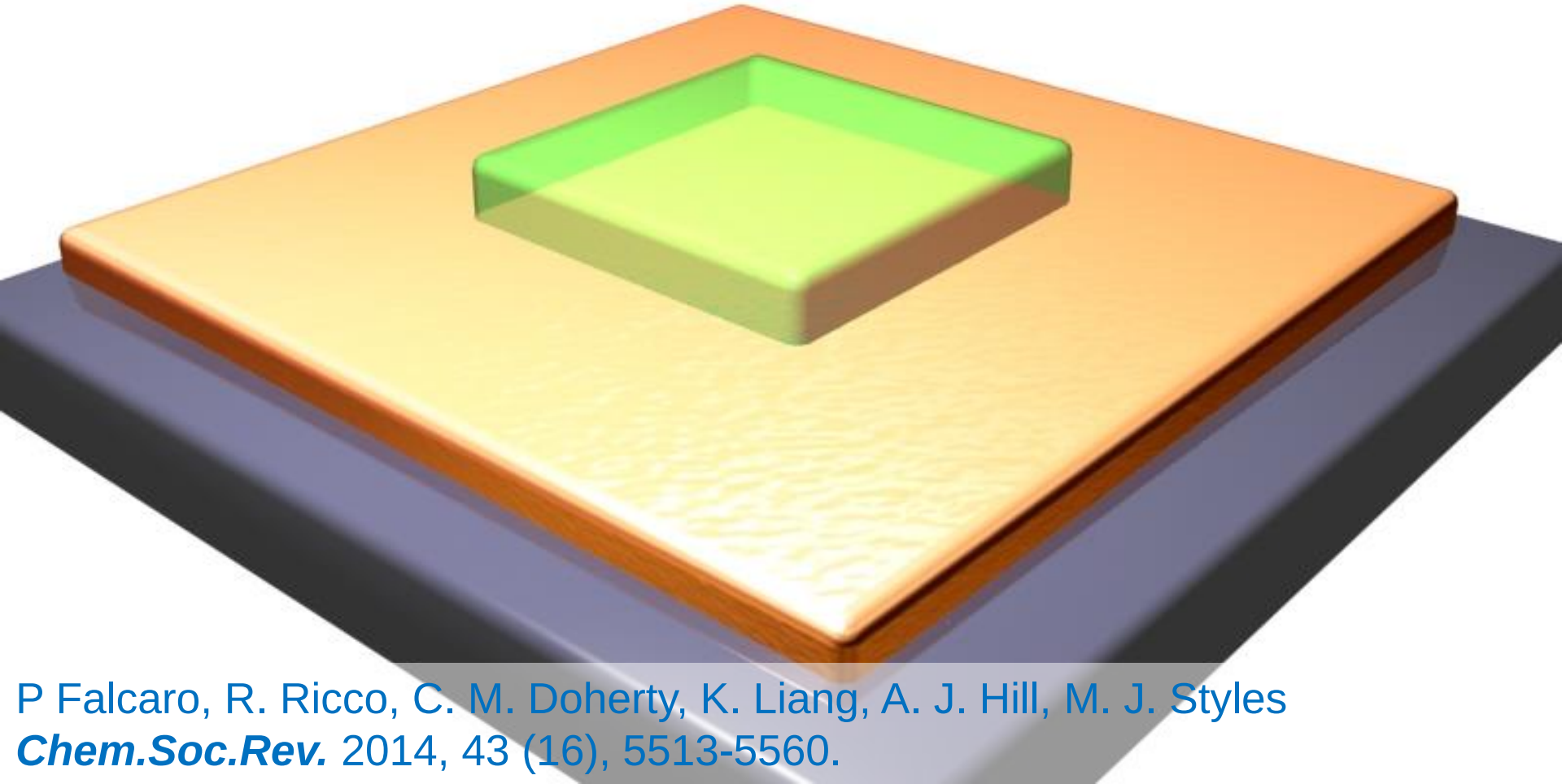
P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Exposure of a resist to UV light with a photolithographic mask



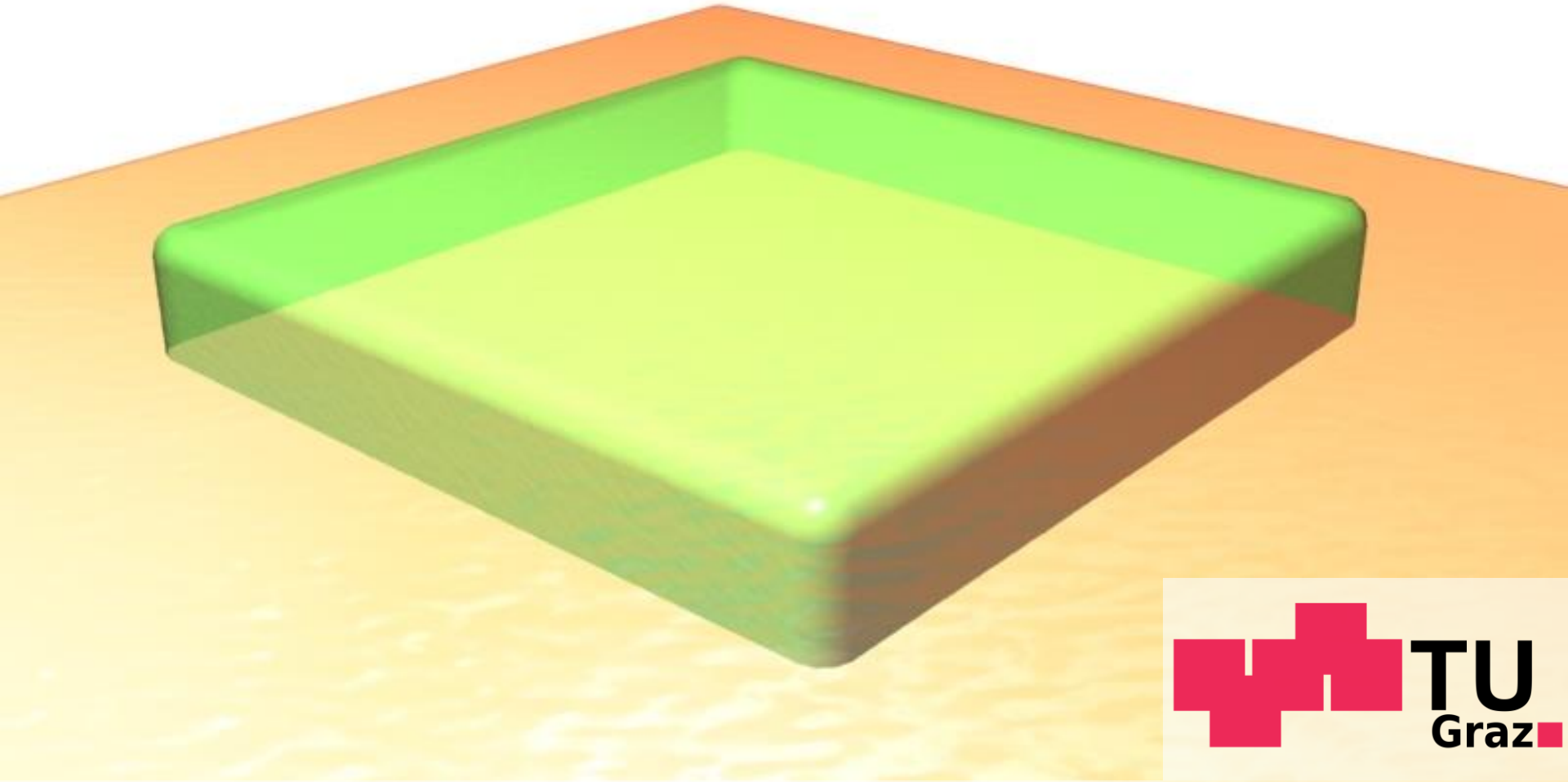
P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Etching of the masked (unexposed) regions



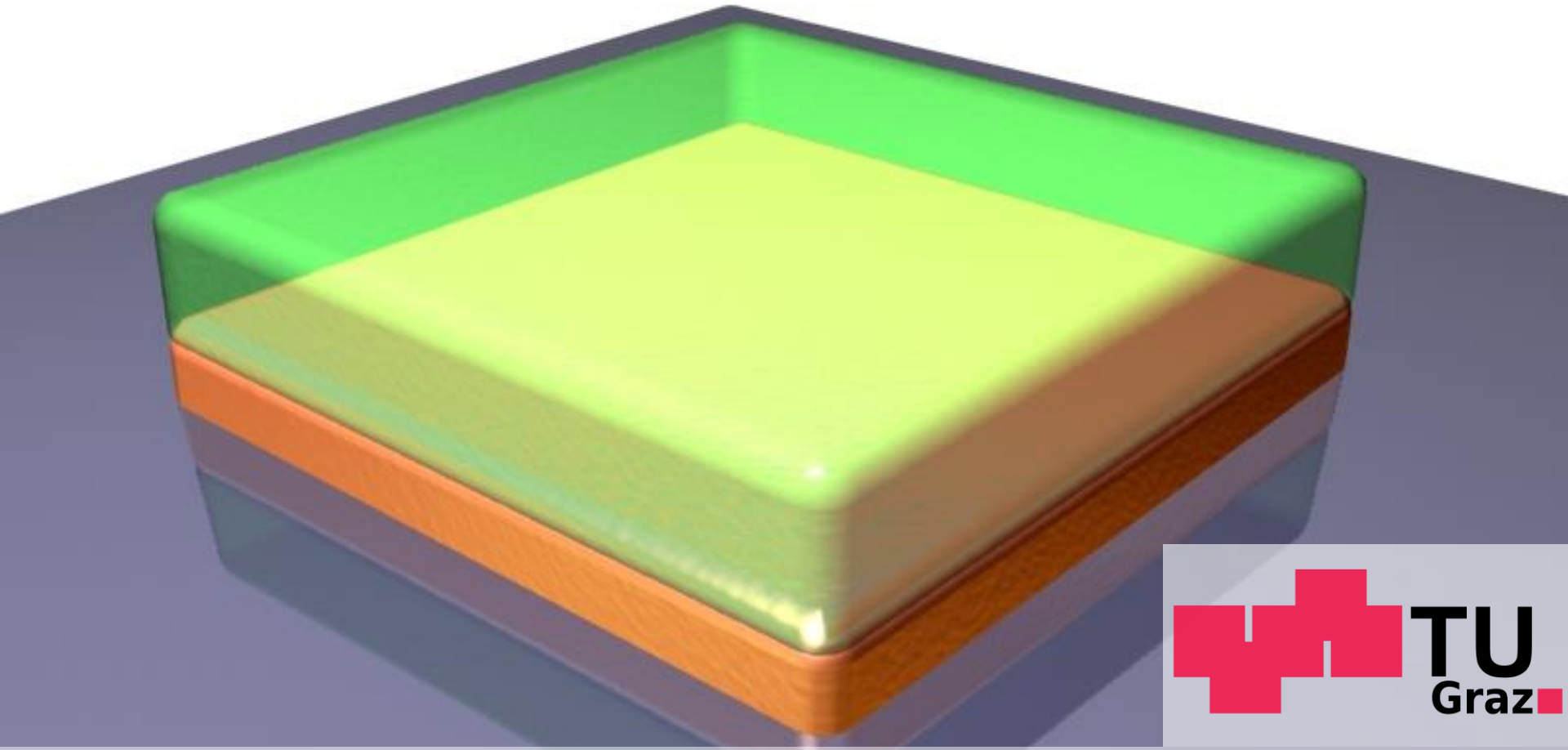
P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Zoom on the developed resist



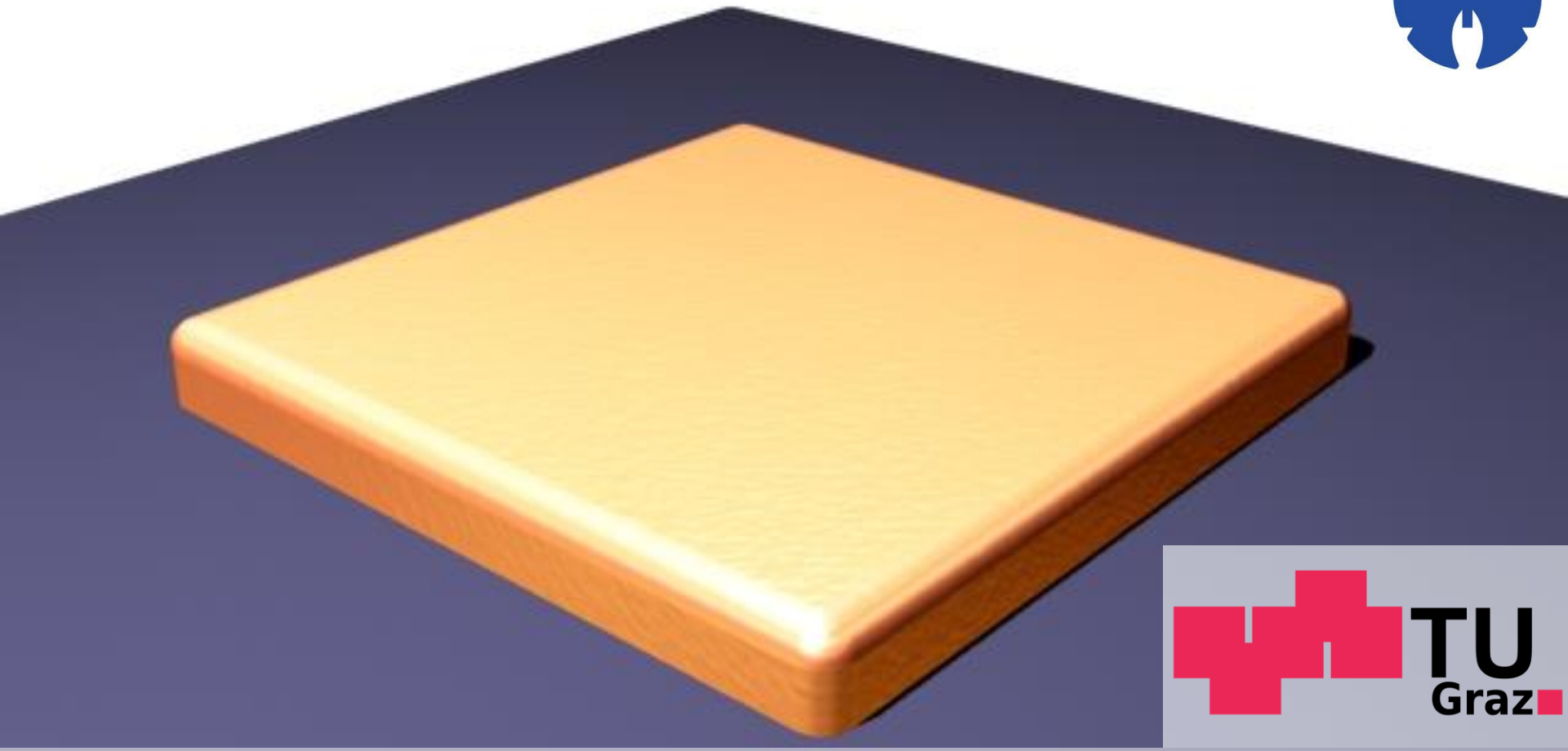
P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Etching of the exposed copper

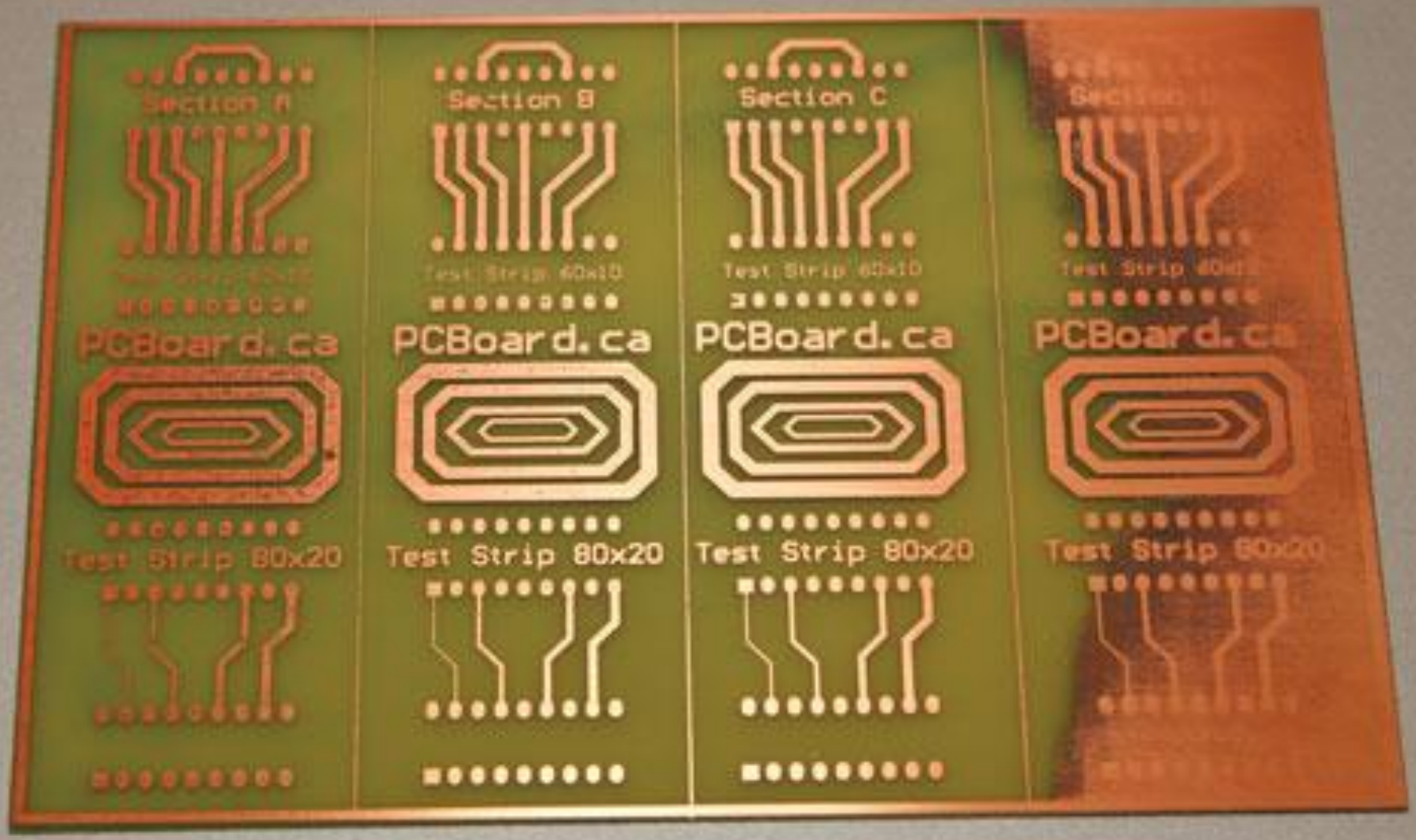


P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Removal of the protective photoresist

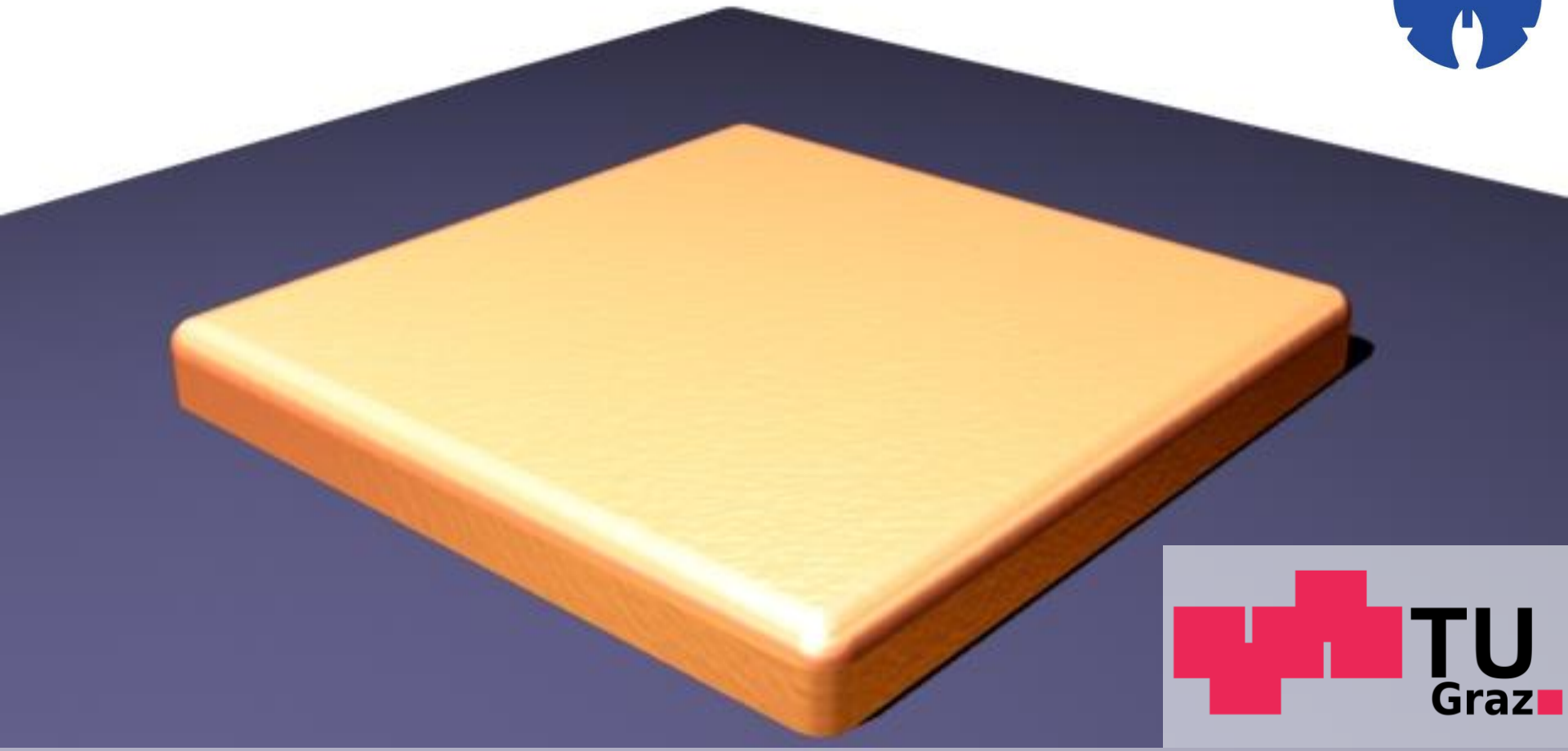


P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.



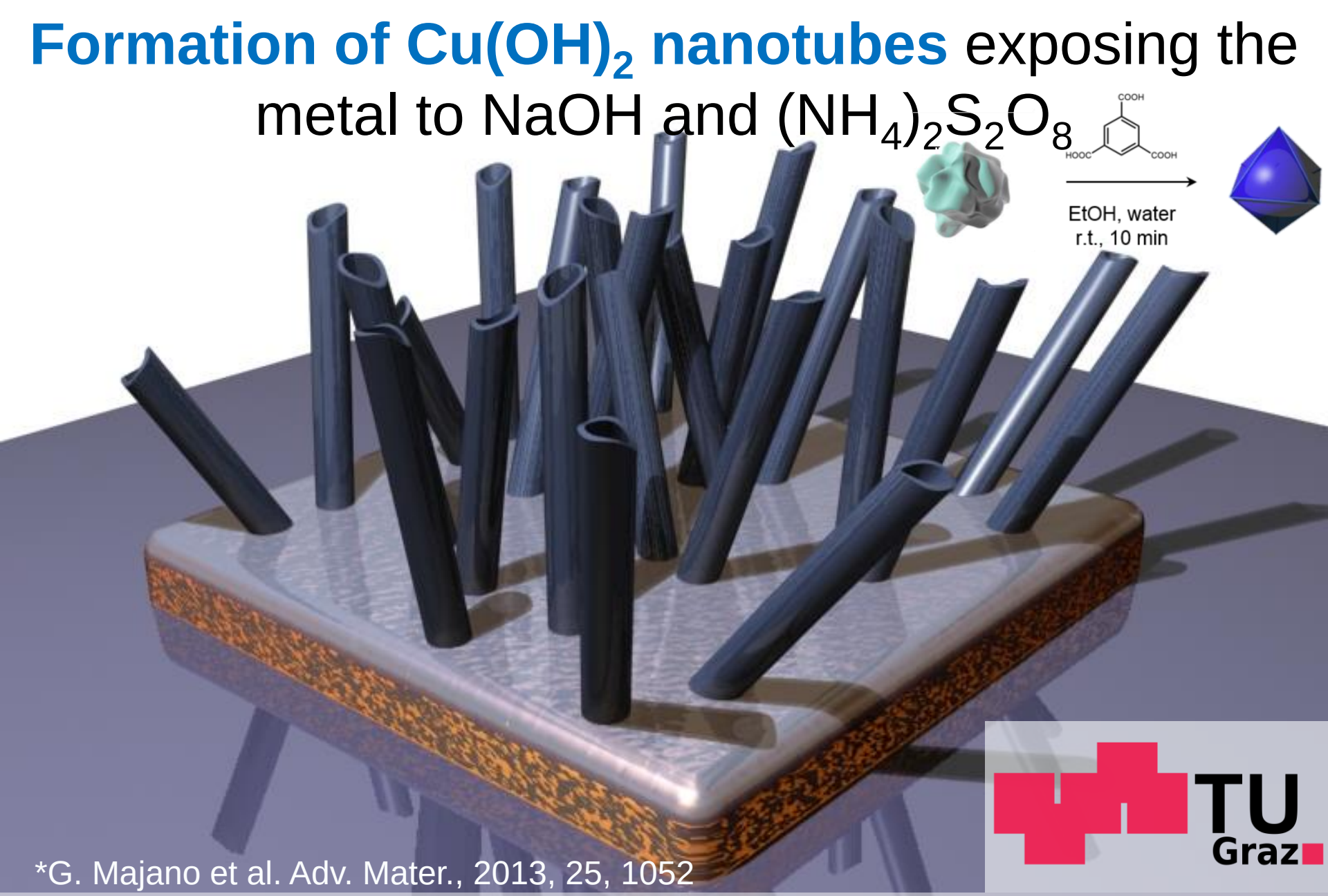
https://info.pcboard.ca/uv-led-pcb-exposure-build/

Removal of the protective photoresist



P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

Formation of $Cu(OH)_2$ nanotubes exposing the metal to NaOH and $(NH_4)_2S_2O_8$

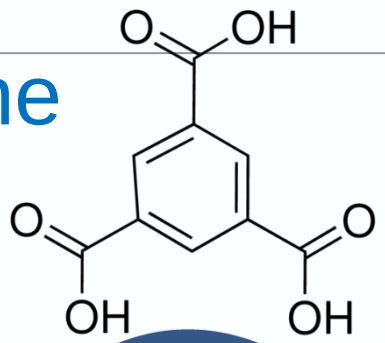


*G. Majano et al. Adv. Mater., 2013, 25, 1052

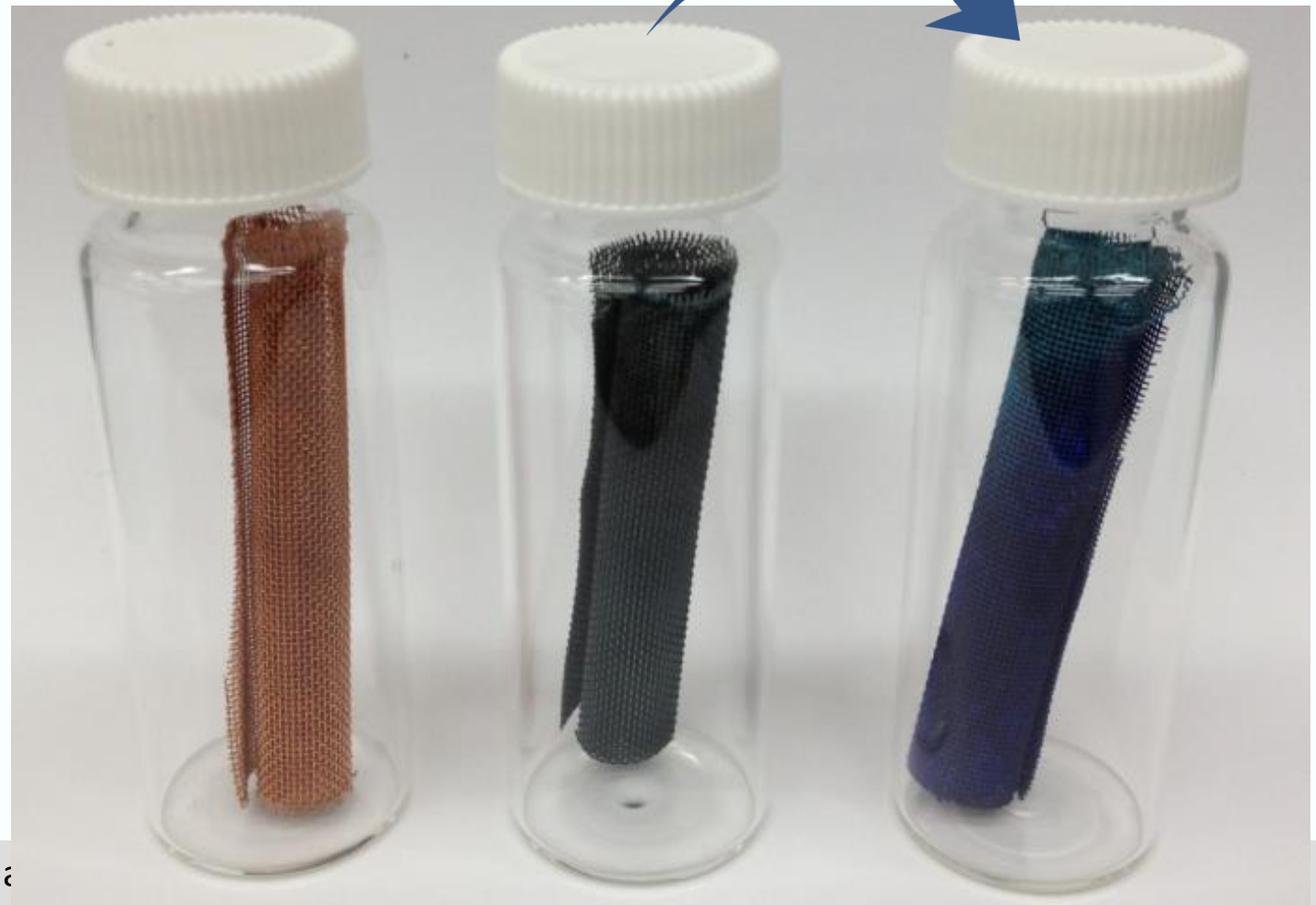
TU Graz

P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

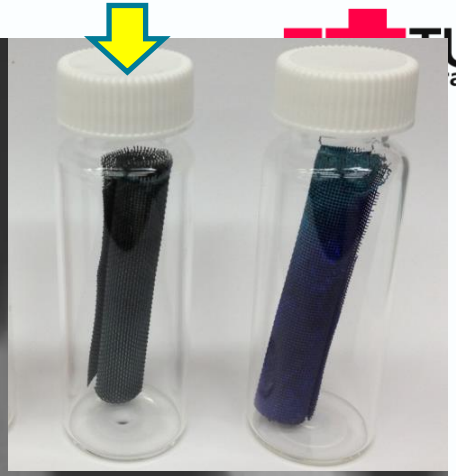
In our case, how does the conversion occur?



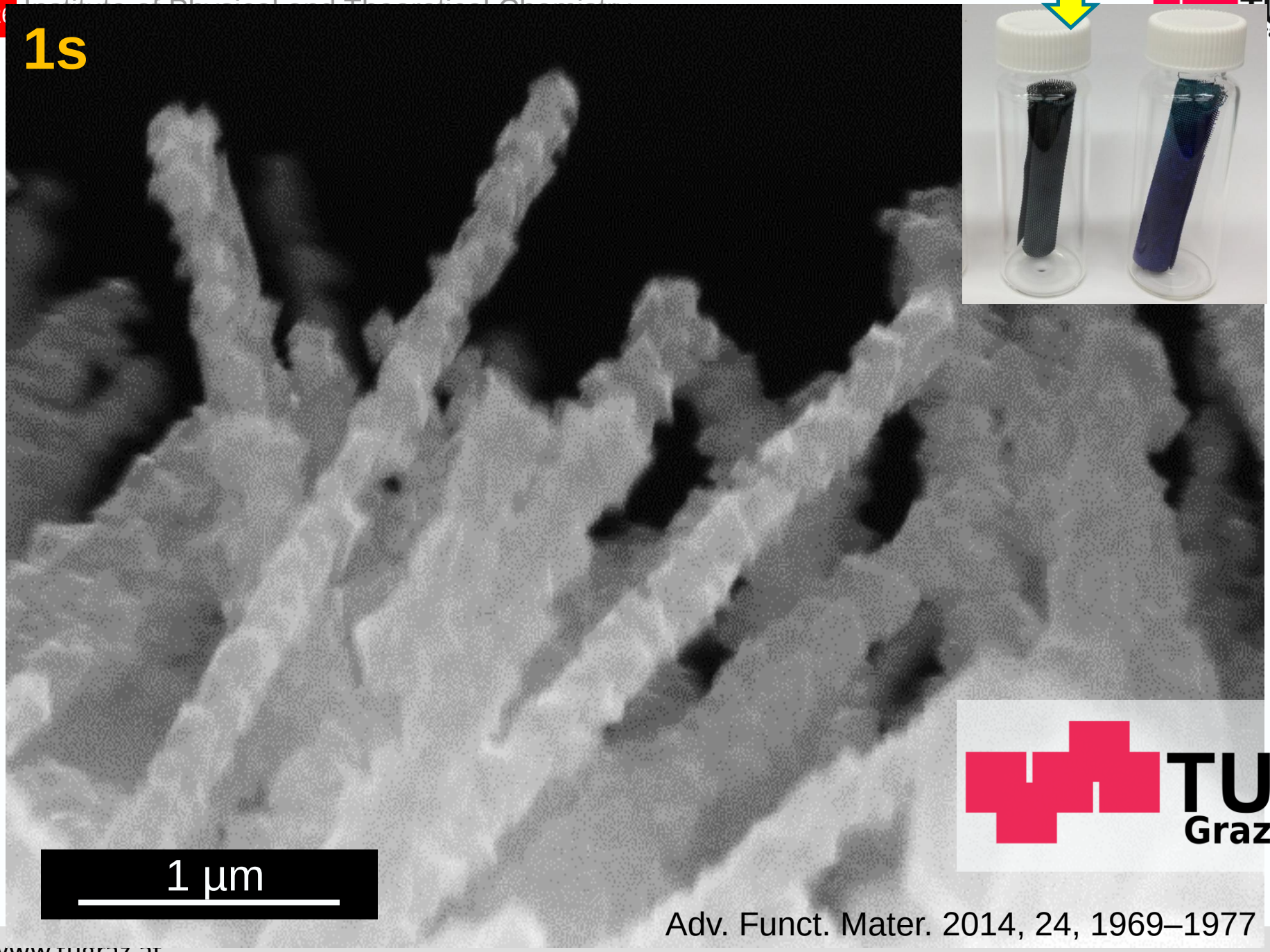
Chemical process



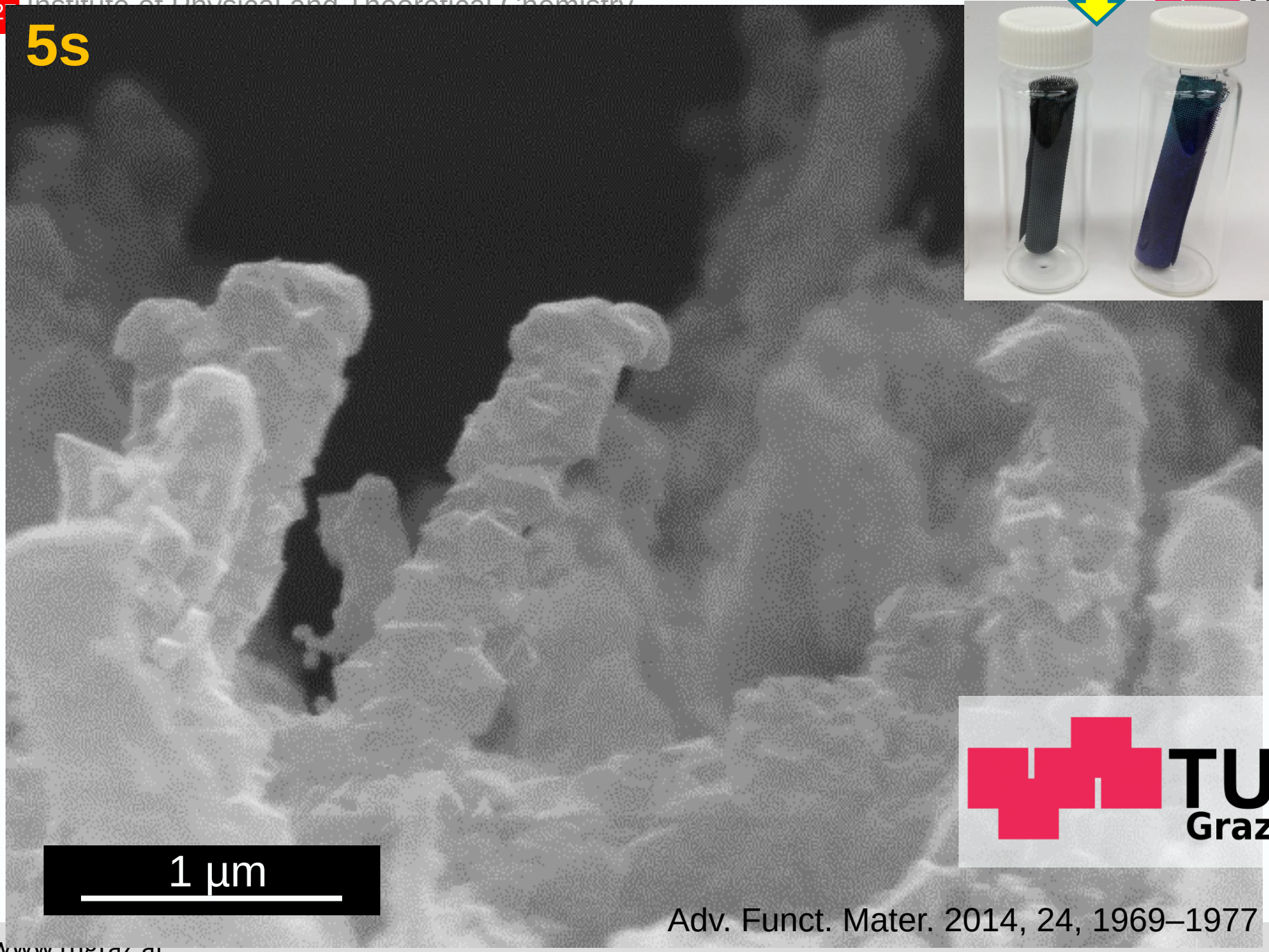
$Cu(OH)_2$ NTs / Time evolution



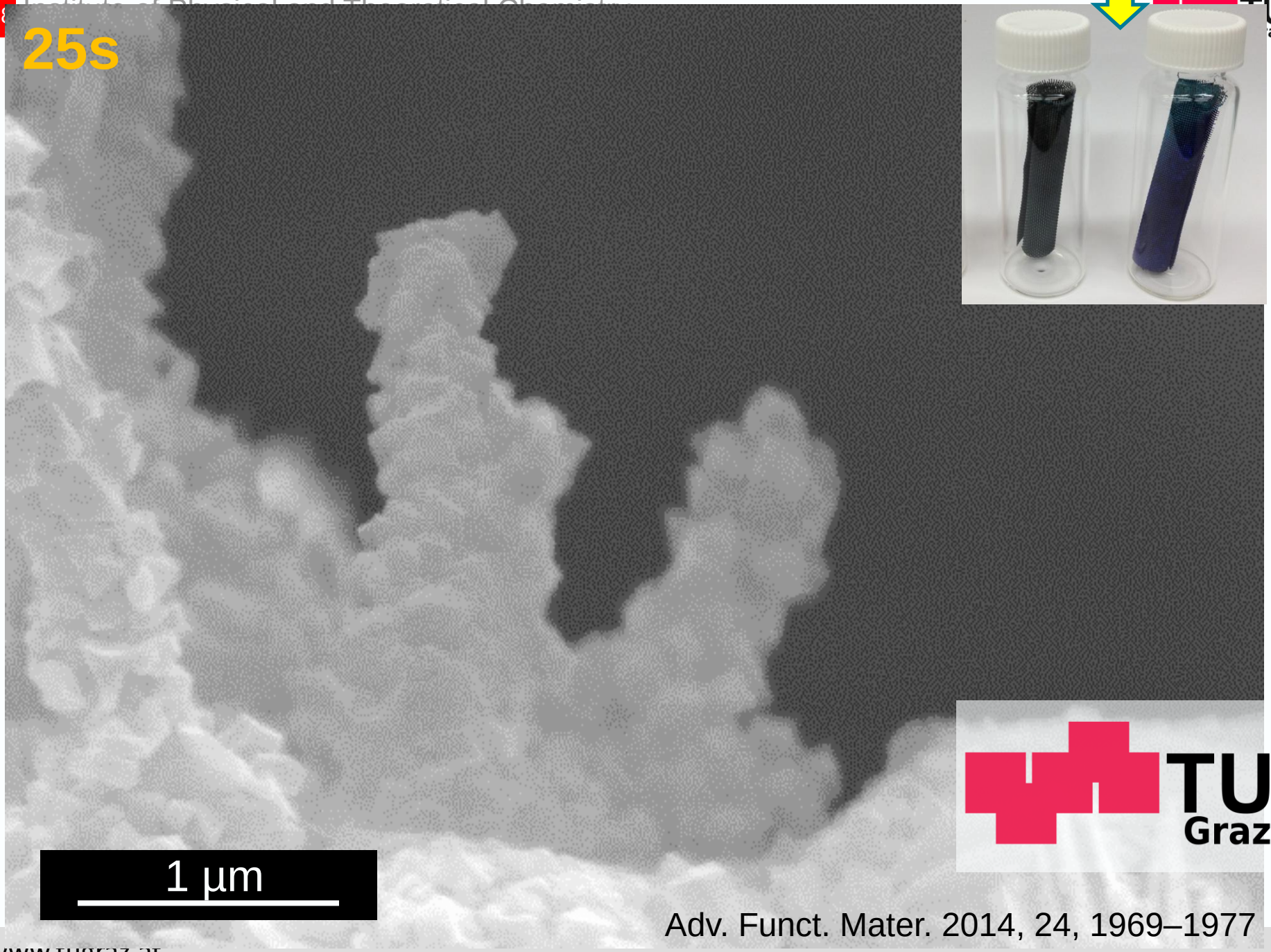
1 µm



Adv. Funct. Mater. 2014, 24, 1969–1977



Adv. Funct. Mater. 2014, 24, 1969–1977

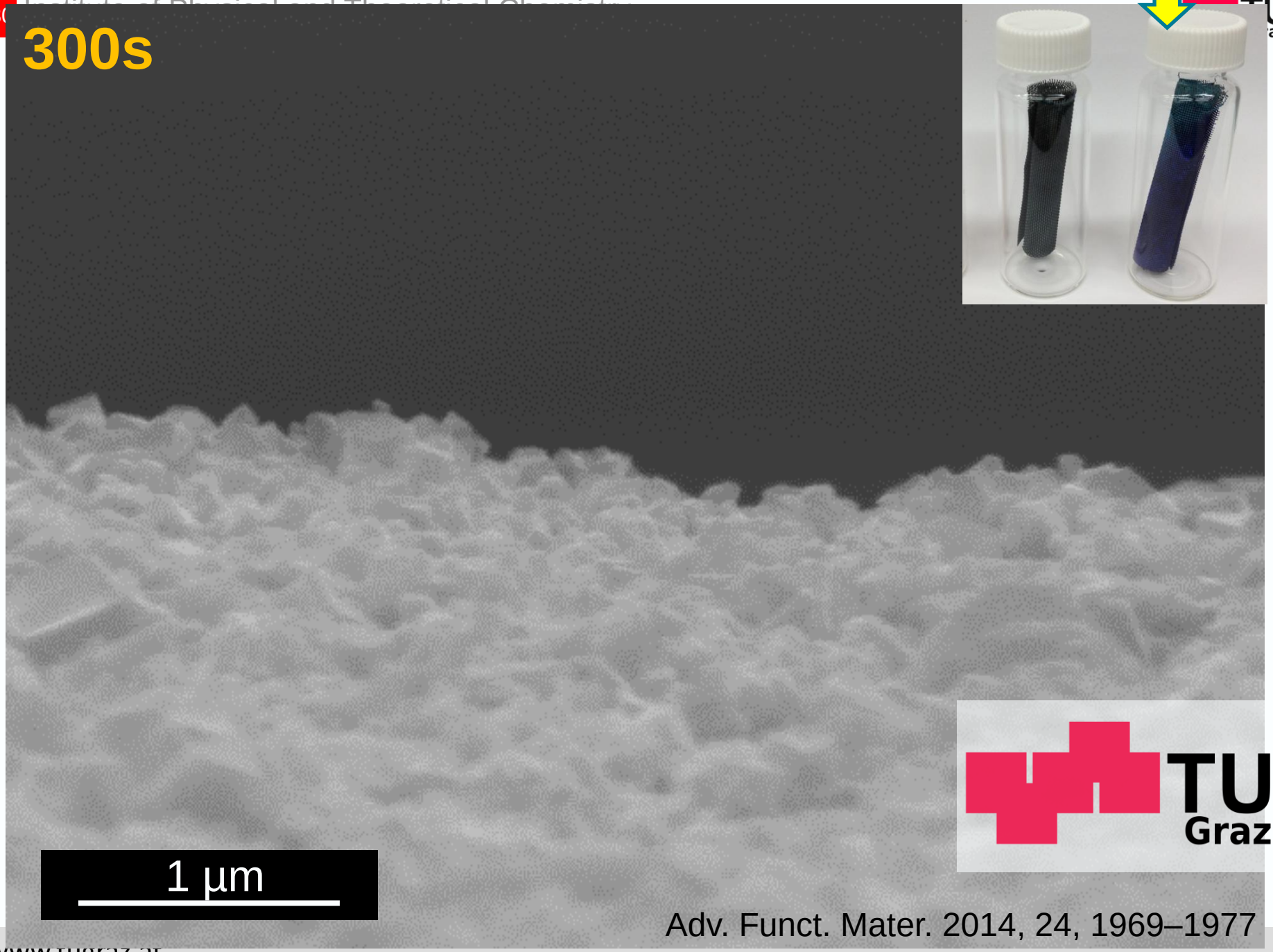


Adv. Funct. Mater. 2014, 24, 1969–1977

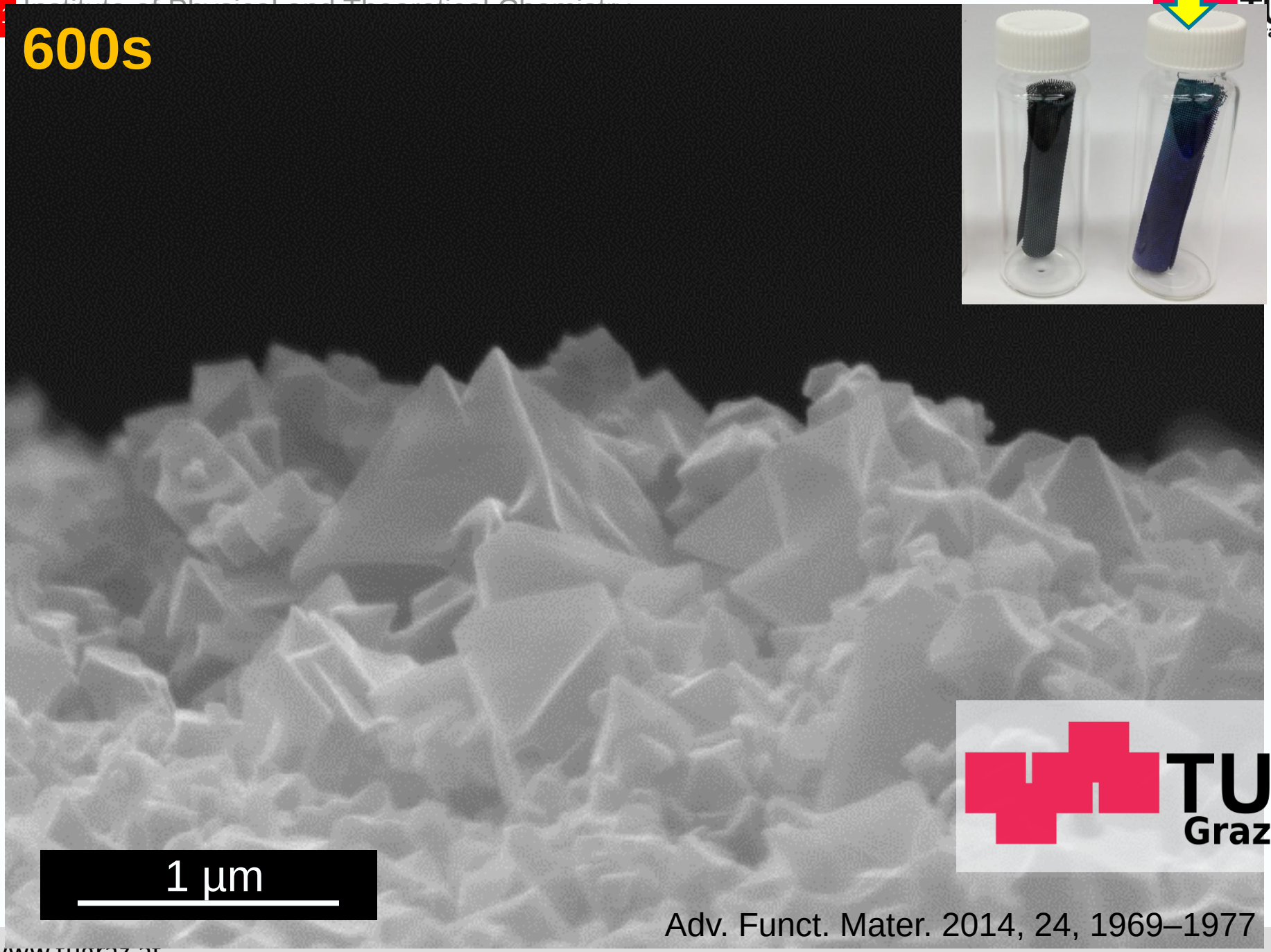
60s

1 µm

Adv. Funct. Mater. 2014, 24, 1969–1977

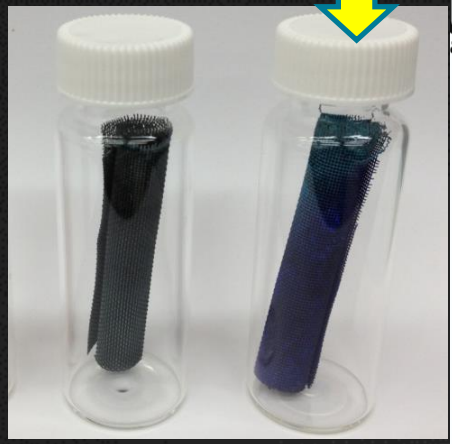


Adv. Funct. Mater. 2014, 24, 1969–1977



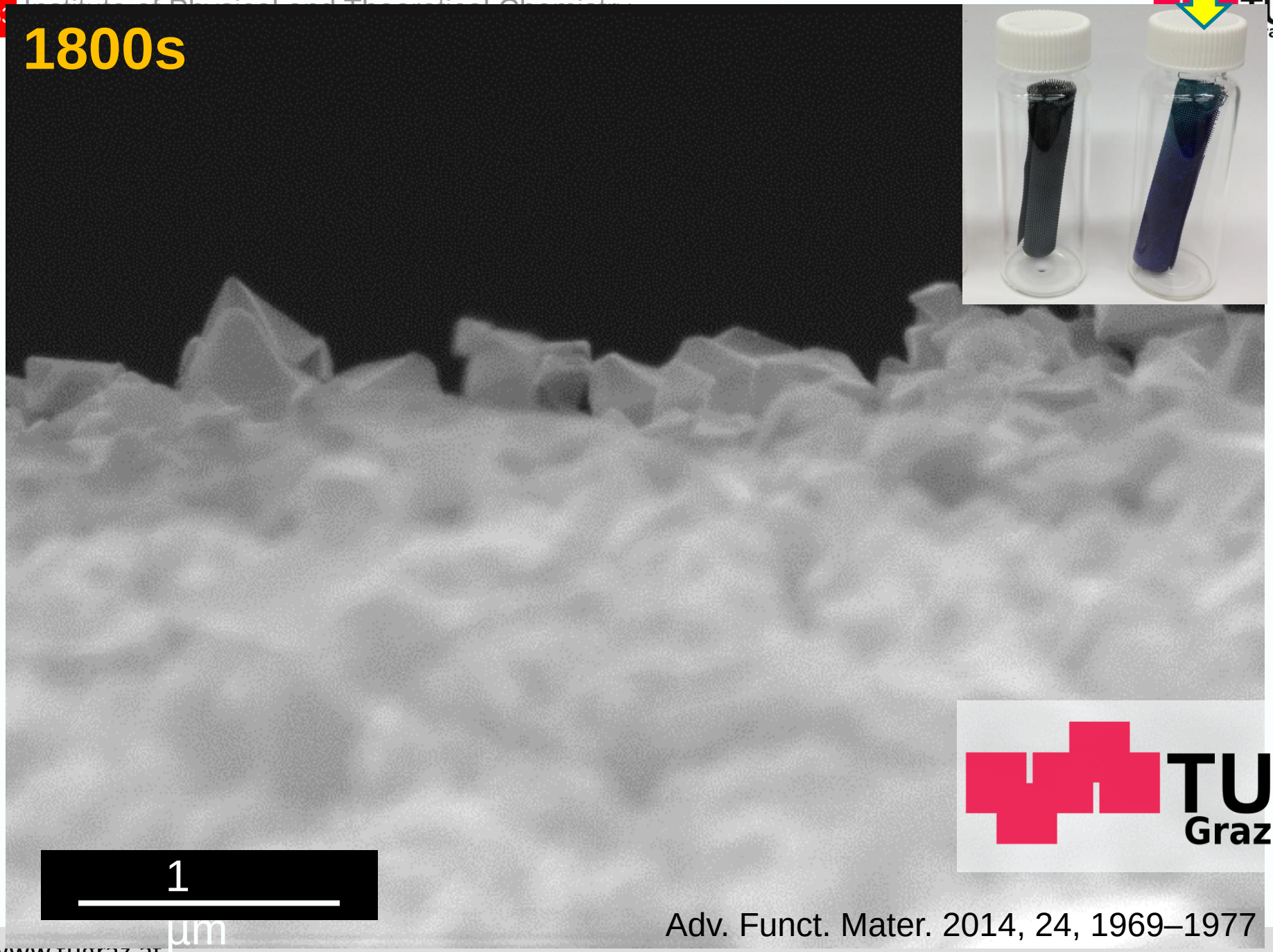
Adv. Funct. Mater. 2014, 24, 1969–1977

1200s



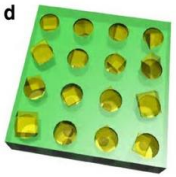
1 µm

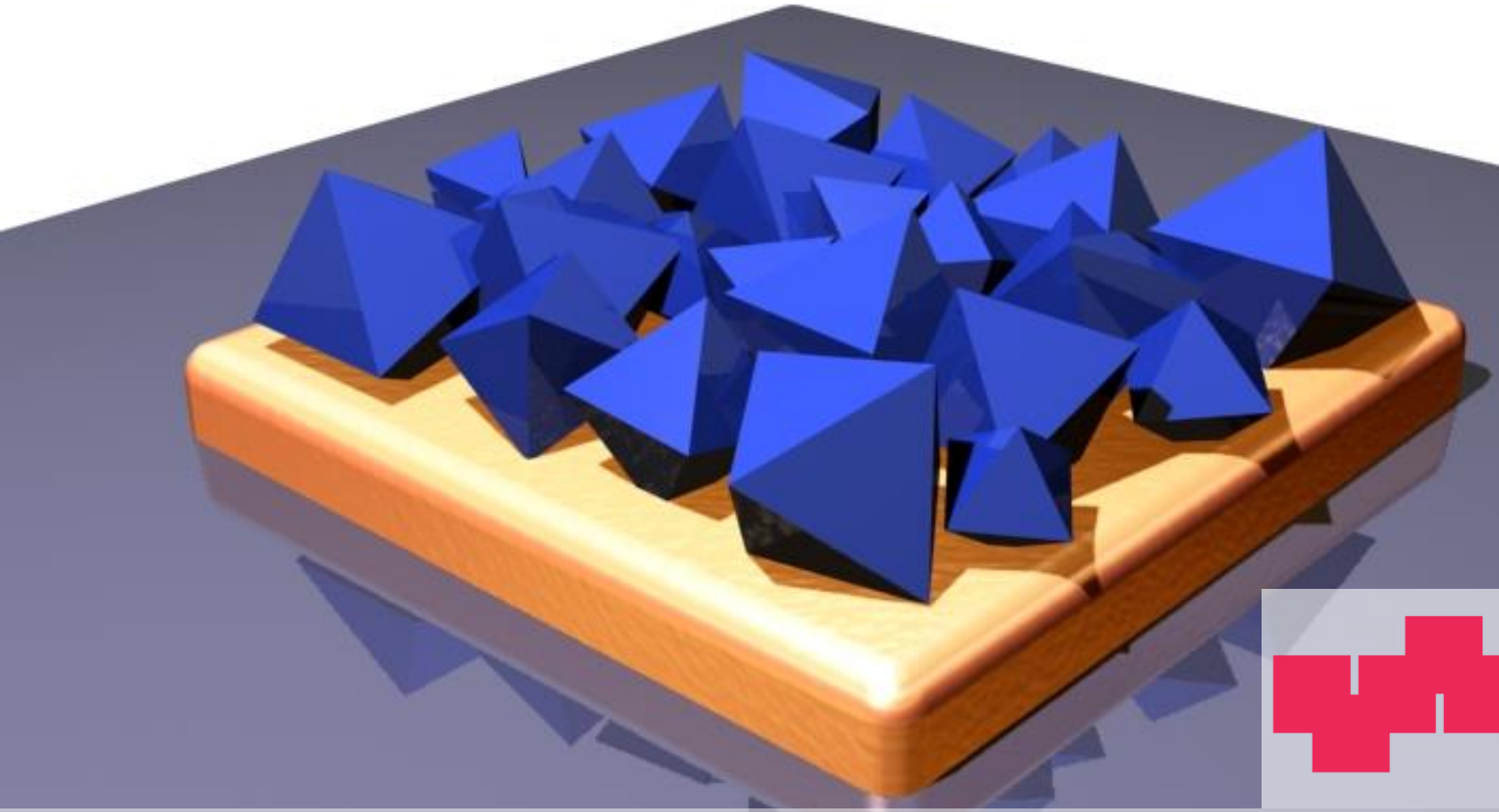
Adv. Funct. Mater. 2014, 24, 1969–1977



Adv. Funct. Mater. 2014, 24, 1969–1977

Conversion of the nanotubes into MOFs (HKUST-1)*





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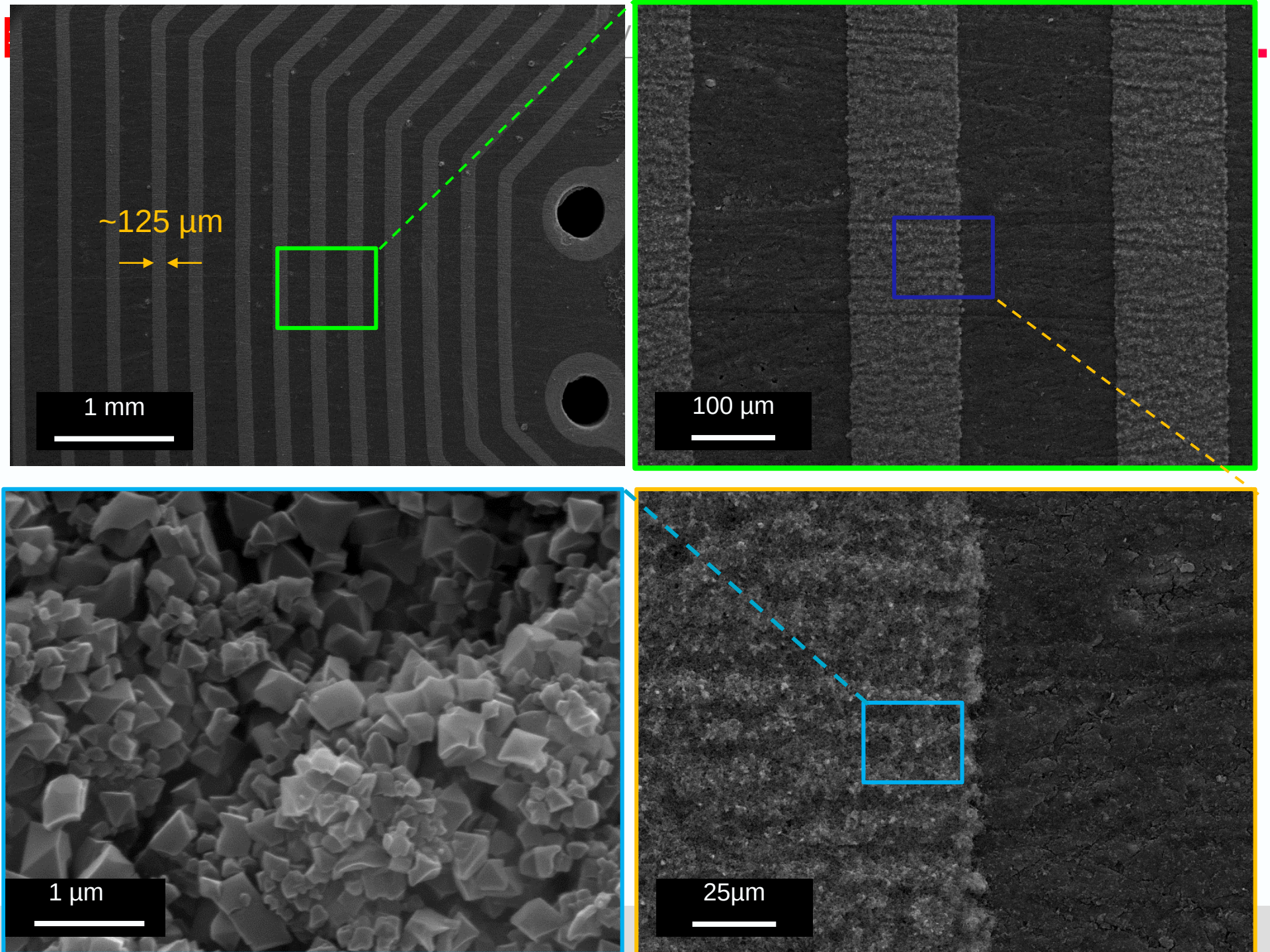
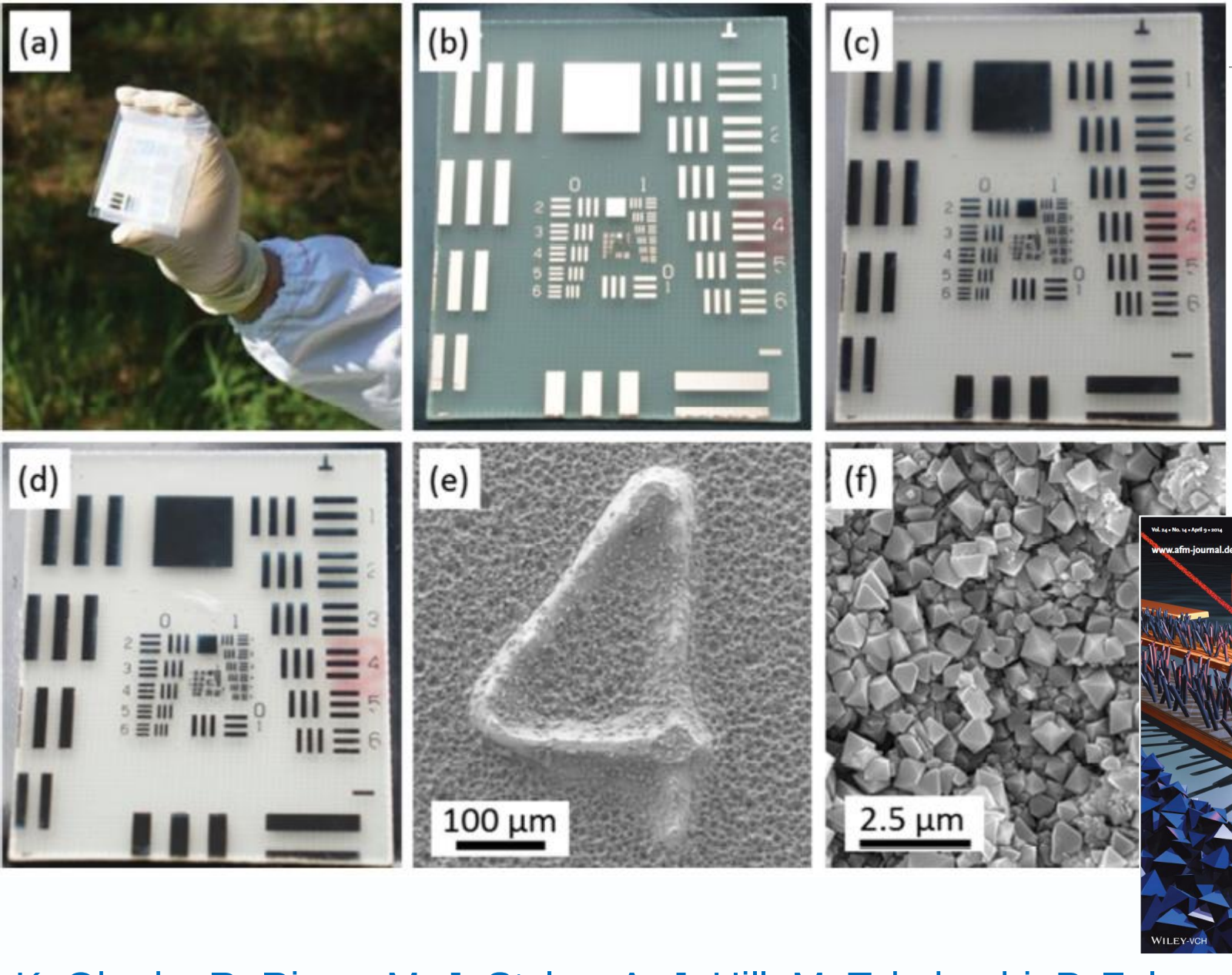
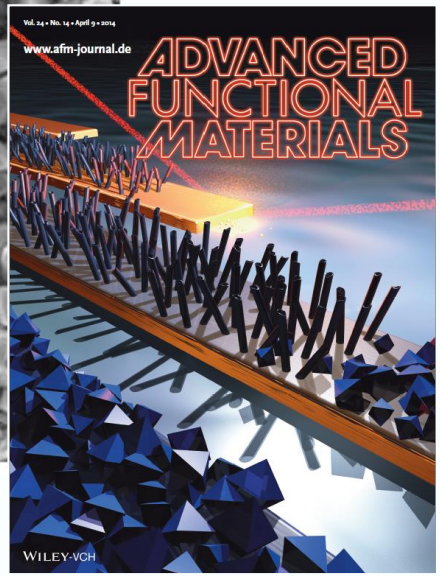
P Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles
Chem.Soc.Rev. 2014, 43 (16), 5513-5560.

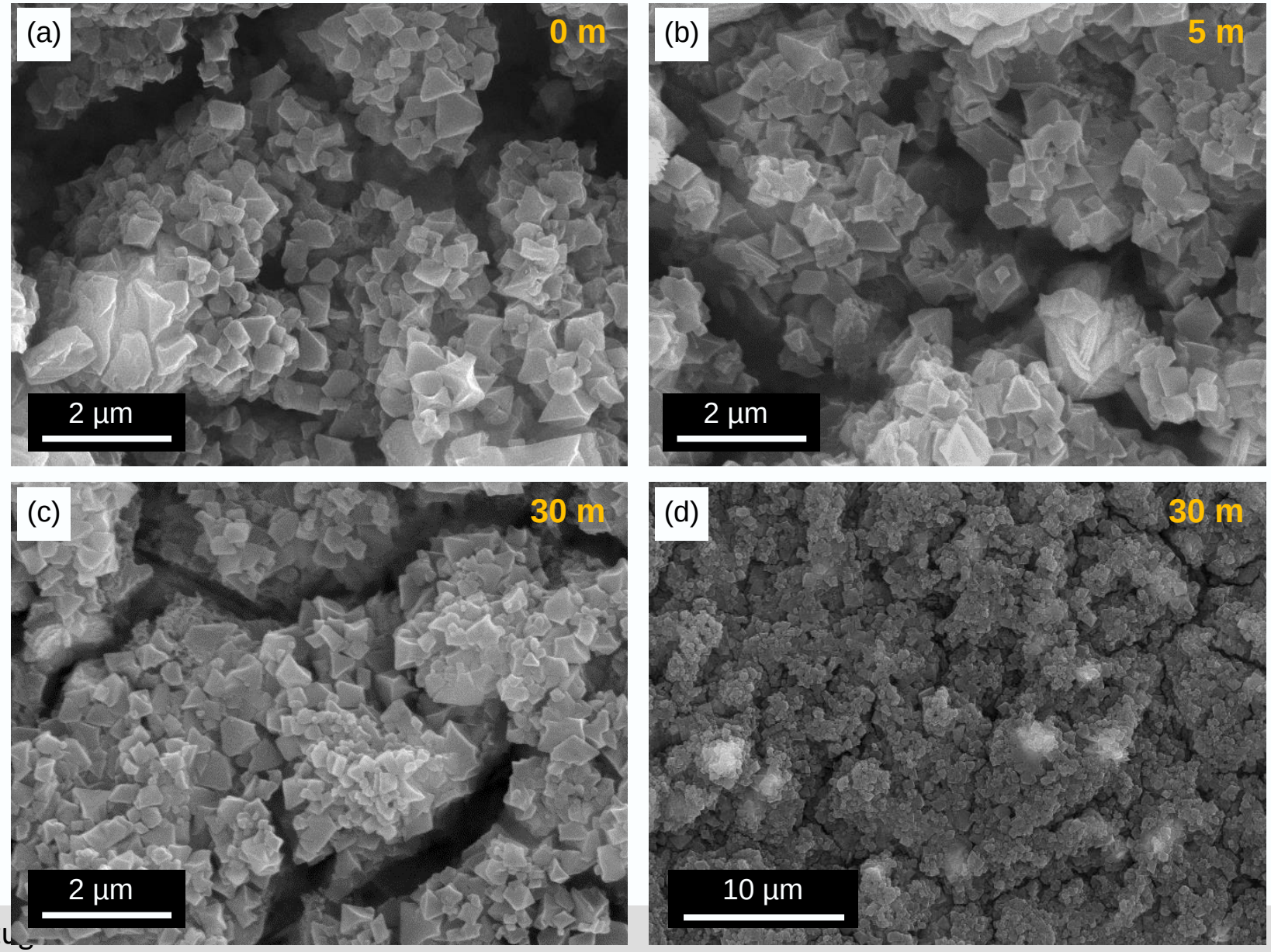

~125 µm
1 mm
100 µm
1 µm
25µm

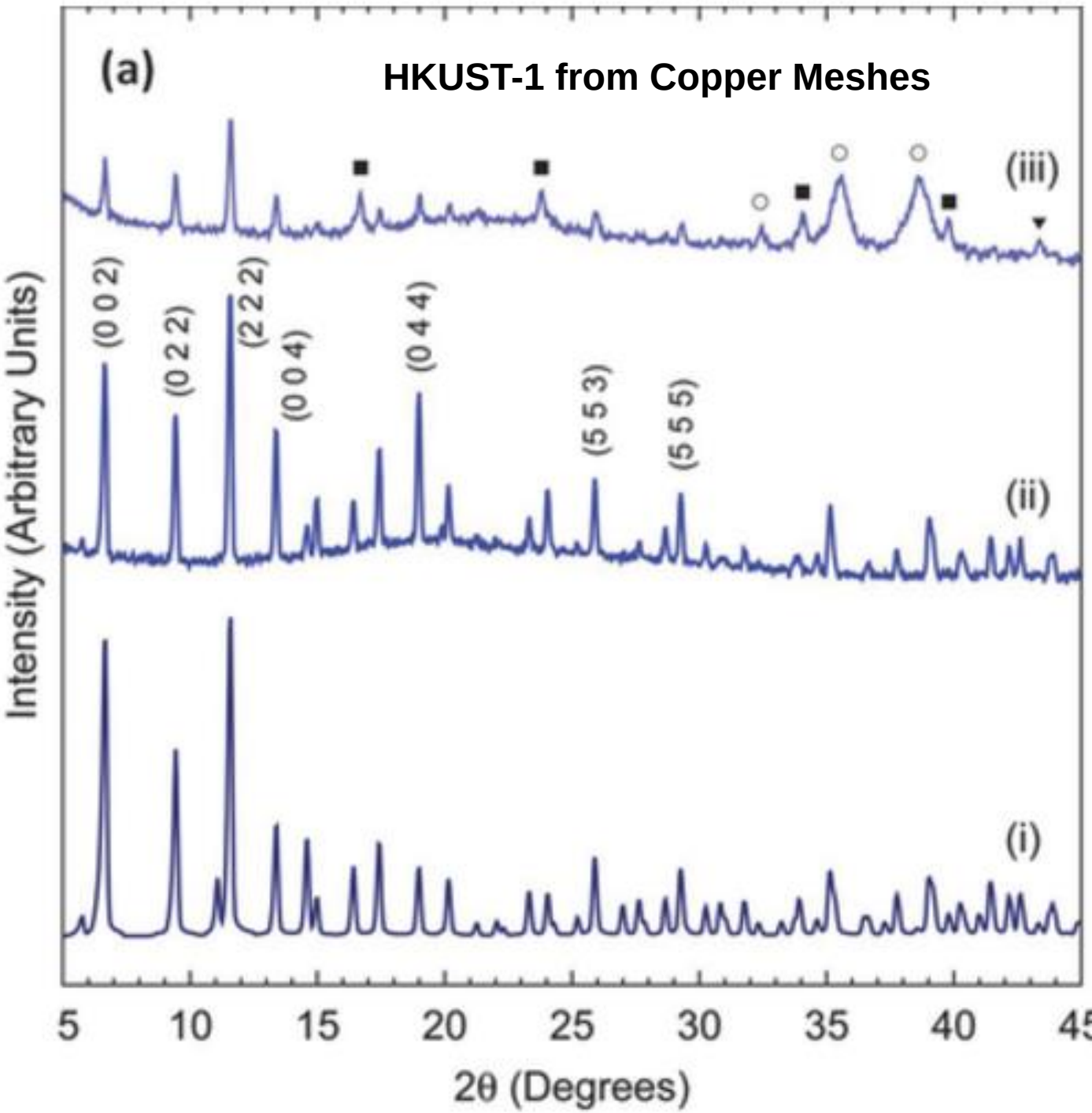




K. Okada, R. Ricco, M. J. Styles, A. J. Hill, M. Takahashi, P. Falcaro ***Advanced Functional Materials*** 2014, 24(14), 1969–1977

Crystals after sonication





■ CuO
○ $Cu(OH)_2$
▼ Cu(metal)

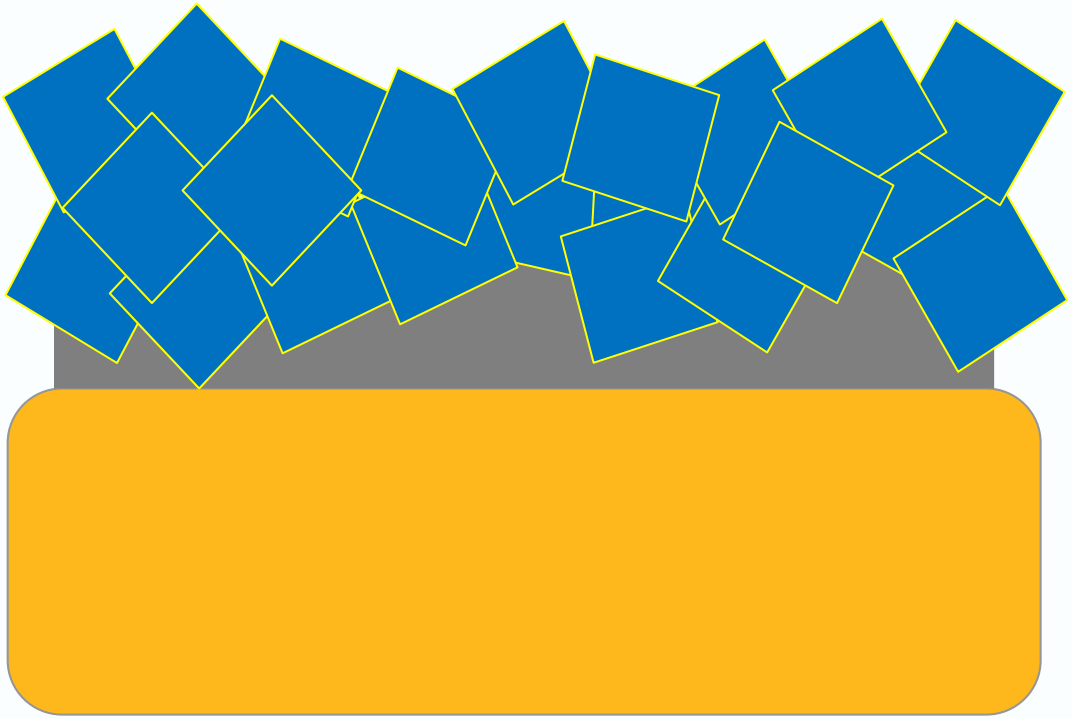
Standard HKUST-1

Simulated HKUST-1

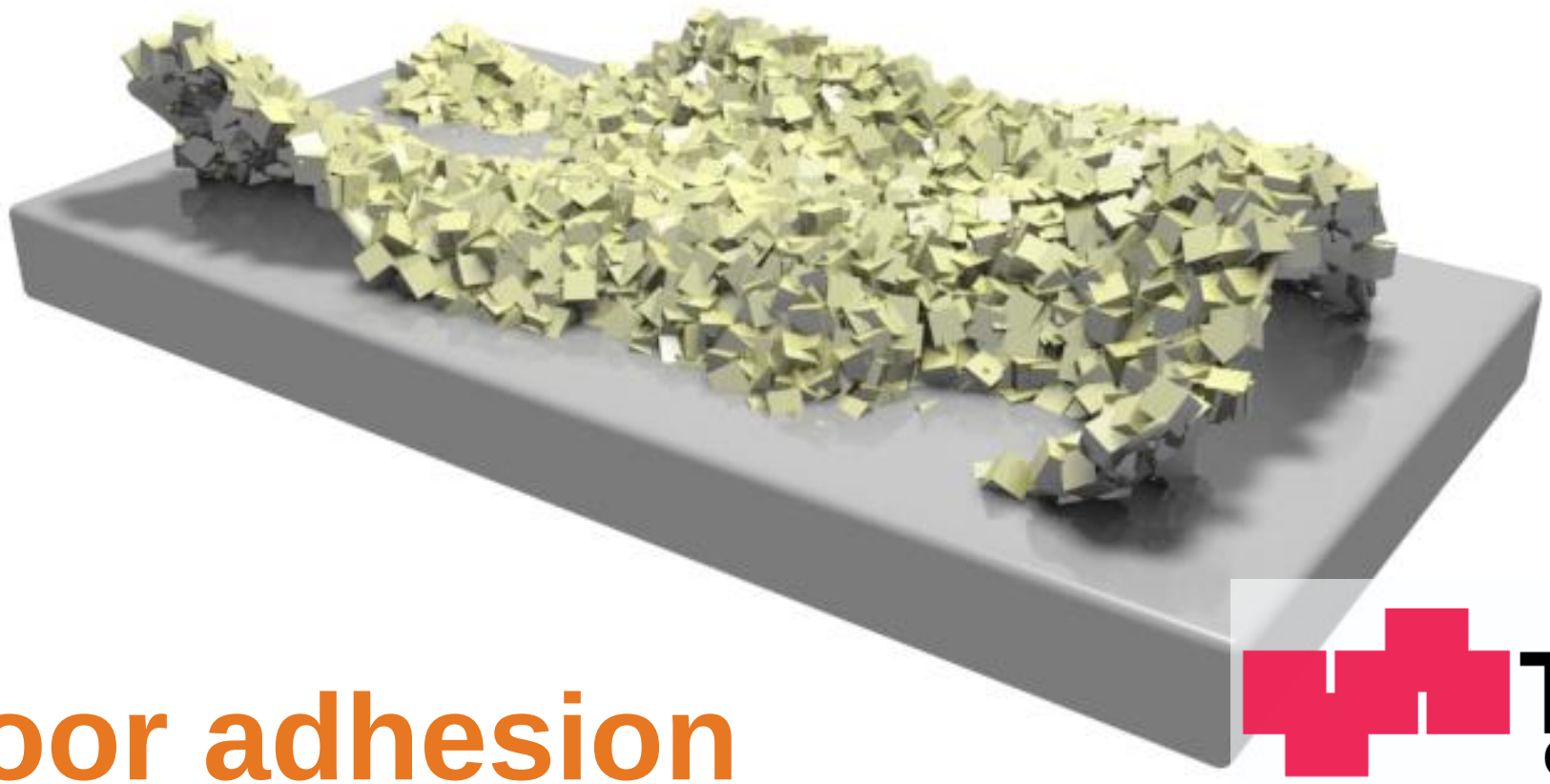
HKUST-1

$Cu(OH)_2$

Copper



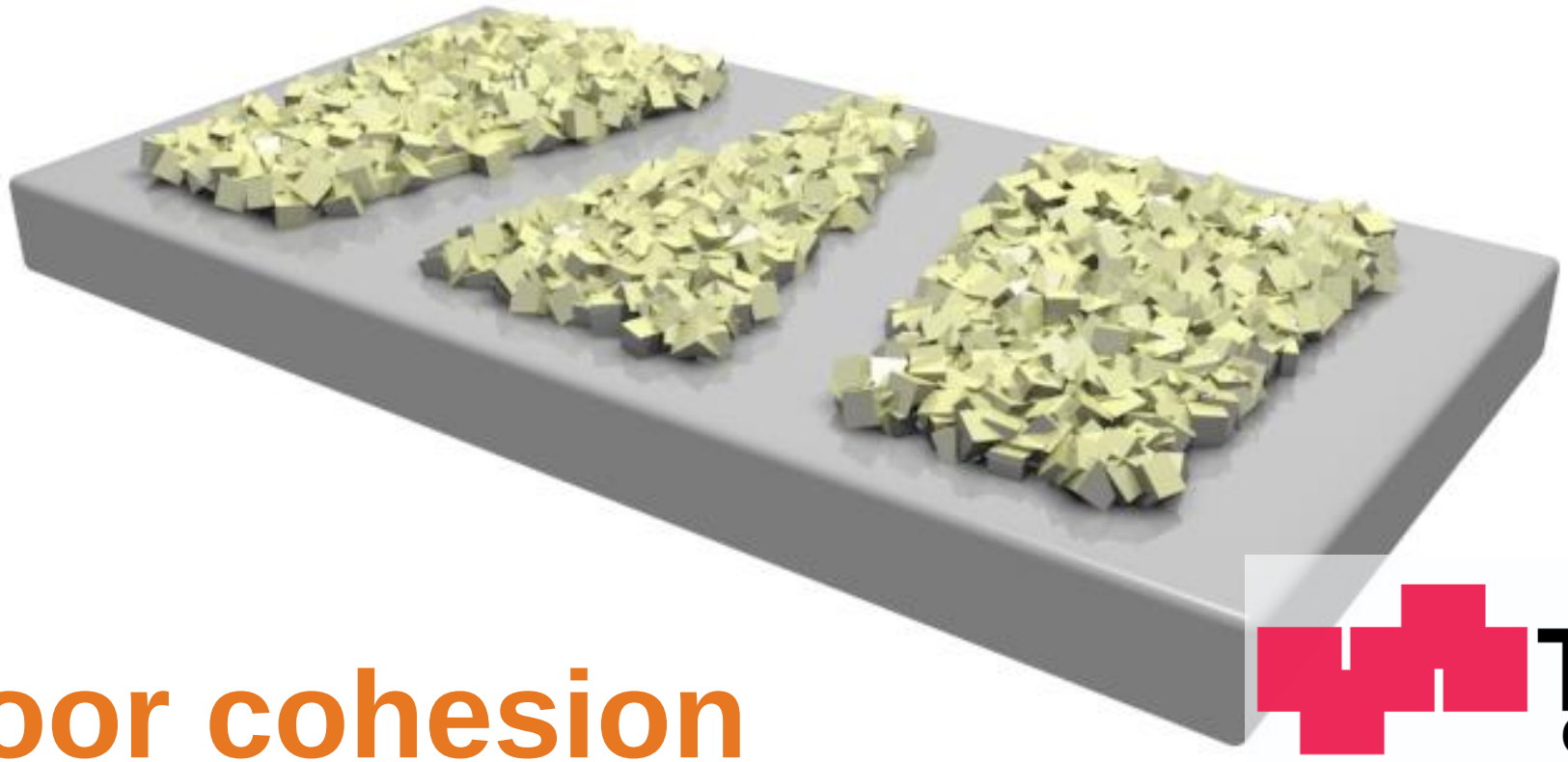
MOF film, case 1



Poor adhesion

I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf, R. Ameloot, **Chem. Soc. Rev.,** 2017,46, 3185-3241

MOF film, case 2

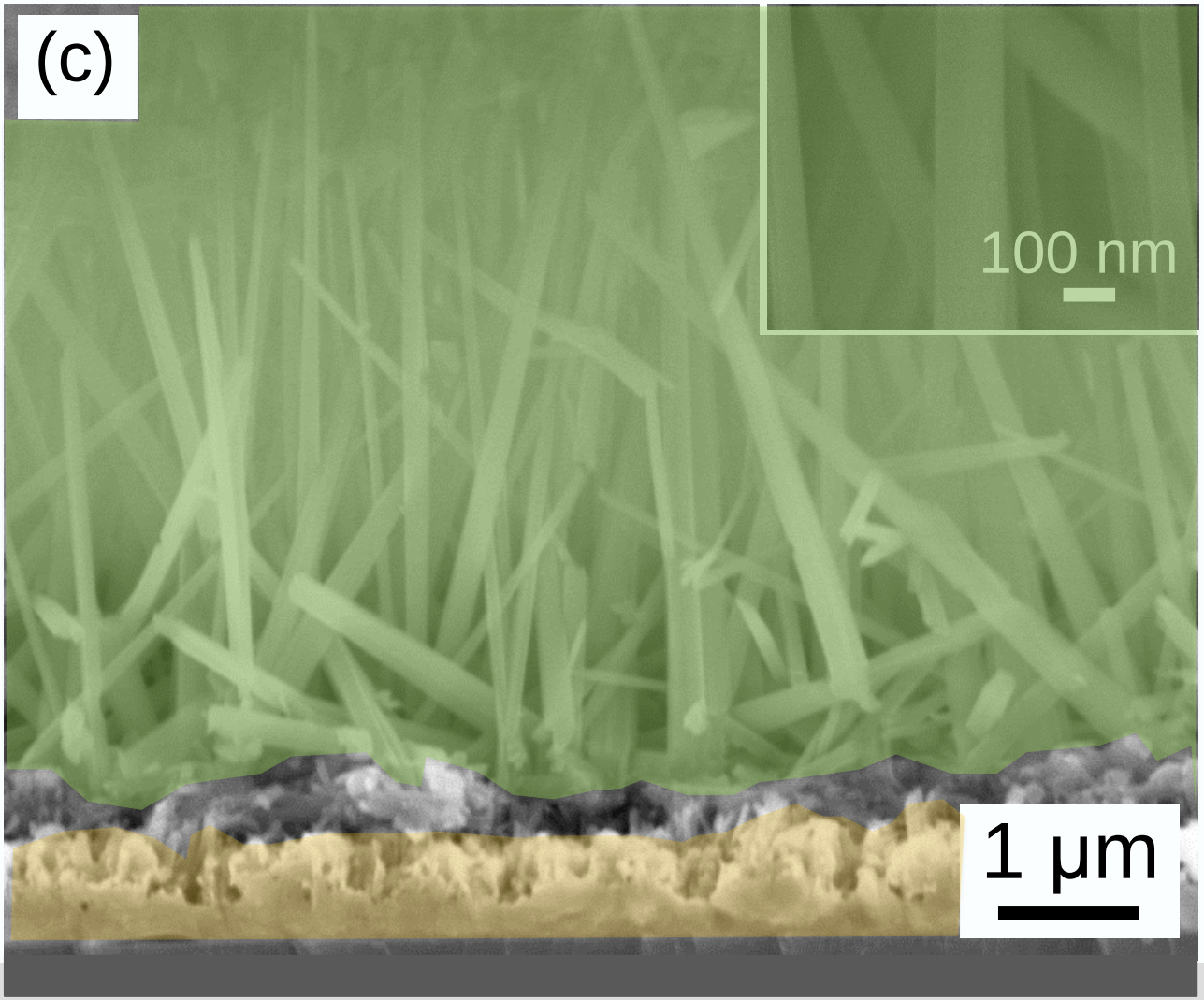


Poor cohesion

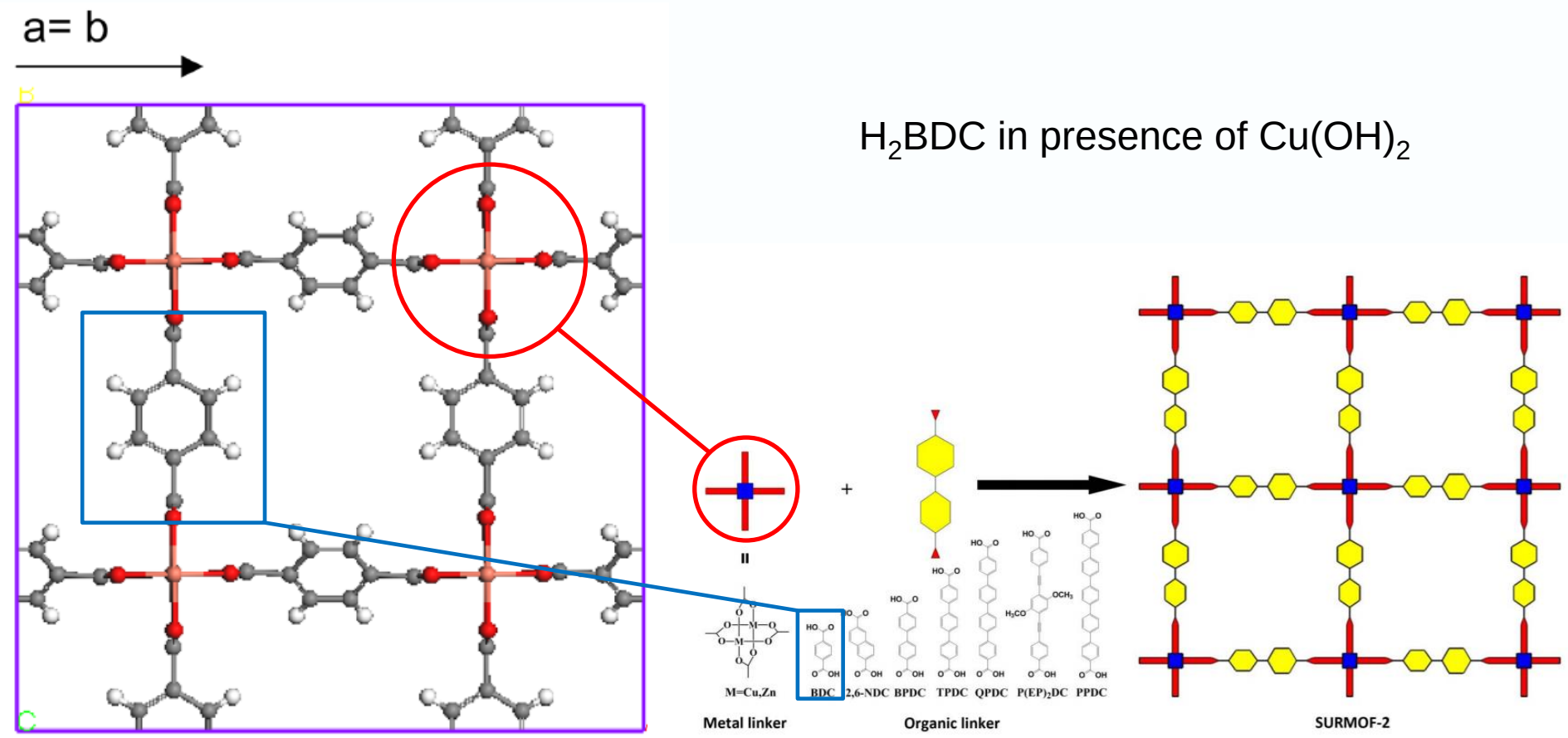
I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf, R. Ameloot, **Chem. Soc. Rev.,** 2017,46, 3185-3241

$Cu(OH)_2$ nanotubes, on Cu(m) on a silicon wafer

$Cu(OH)_2$



Ethanolic solution



Cu-BDC SURMOF-2 with
a=b=10.803A;
c=5.60A ° .

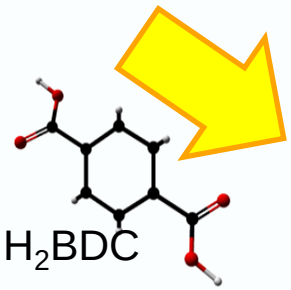
Engelbert Redel, Zhengbang Wang, Stefan Walheim, Jinxuan Liu, Hartmut Gliemann, and Christof Wöll
APPLIED PHYSICS LETTERS **103**, 091903 (2013)

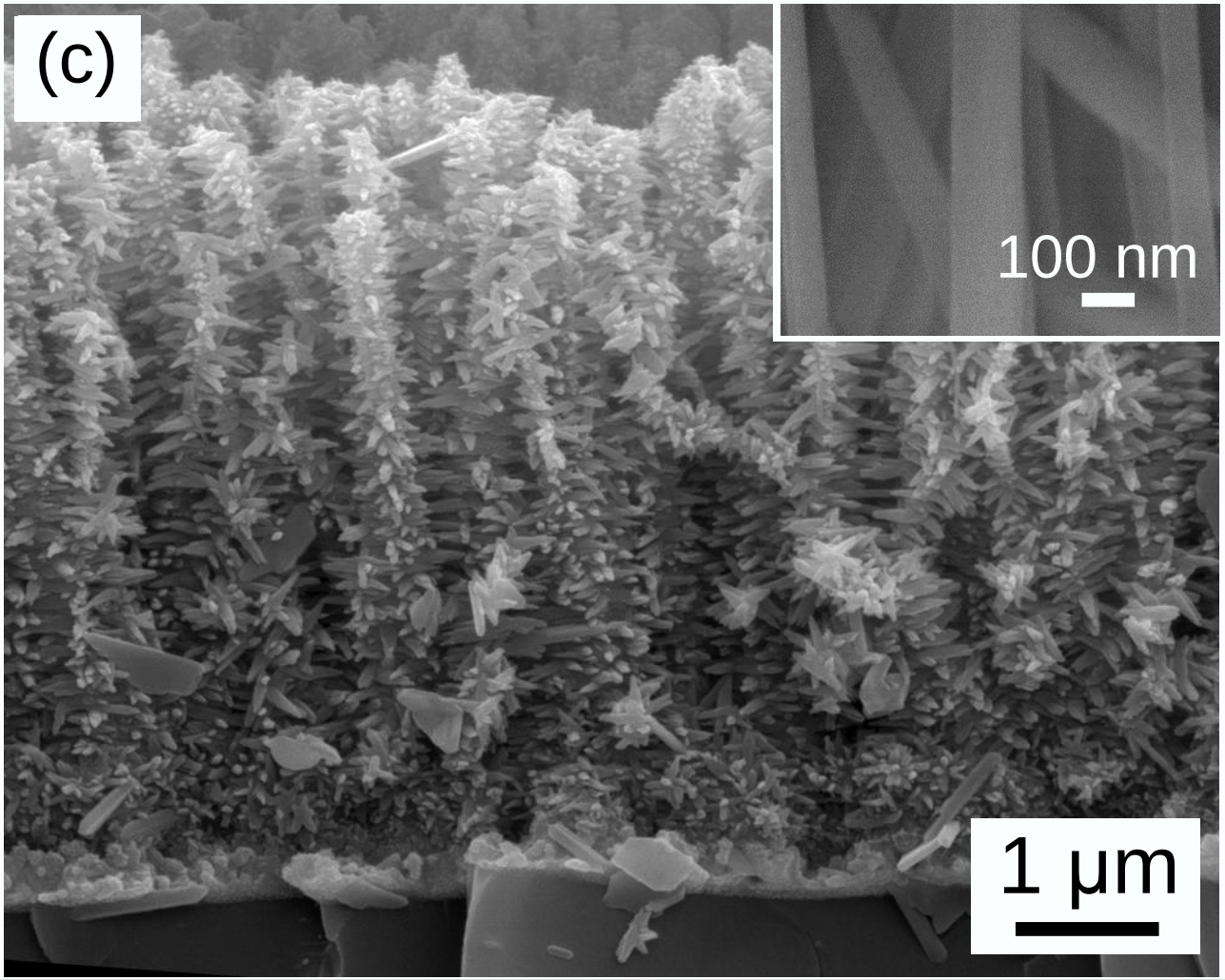
Jinxuan Liu[1], Binit Lukose[2], Osama Shekhah[1,3], Hasan Kemal Arslan[1], Peter Weidler[1], Hartmut Gliemann[1], Stefan Bräse[4,5], Sylvain Grosjean[4,5], Adelheid Godt[6], Xinliang Feng[7], Klaus Müllen[7], Ioan-Bogdan Magdau[1,2], Thomas Heine[2] & Christof Wöll[1]

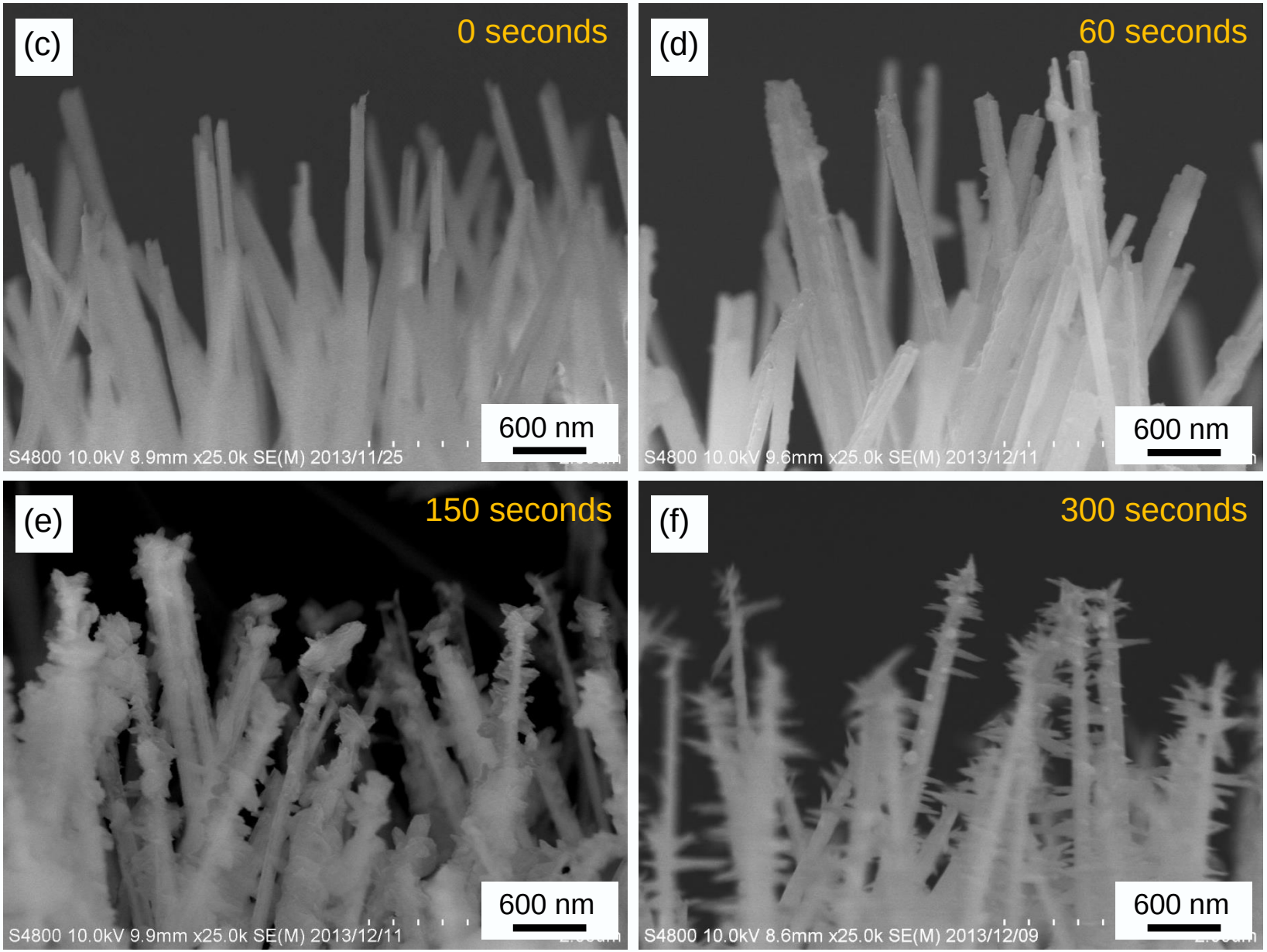
SCIENTIFIC REPORTS 2 : 921 | DOI: 10.1038/srep00921

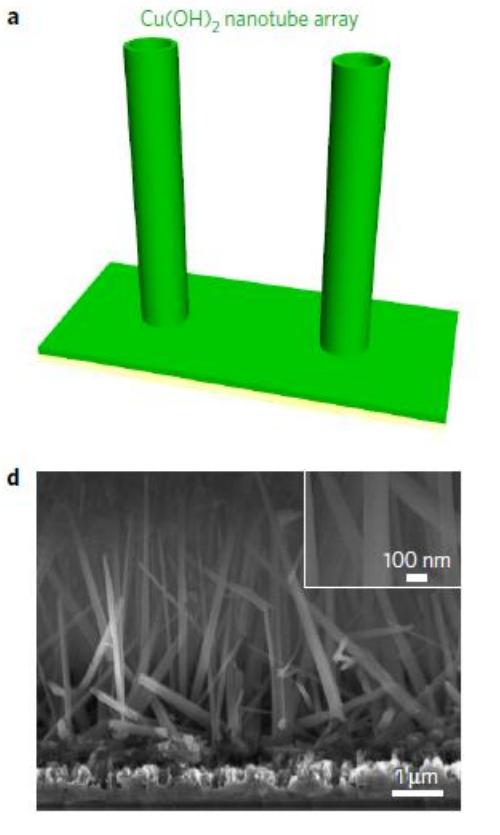
$Cu(OH)_2$ nanotubes, on Cu(m) on a silicon wafer

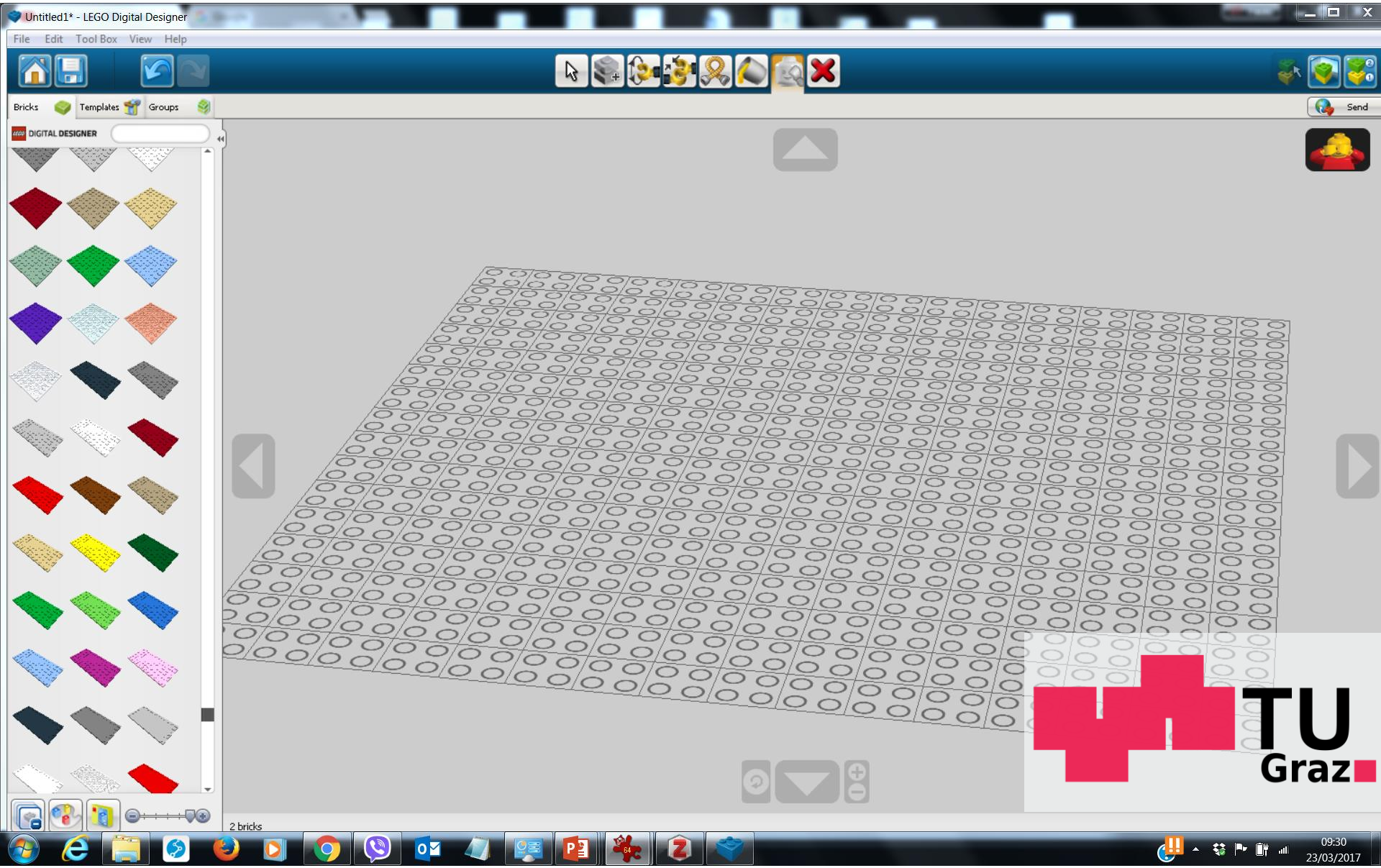
Ethanolic solution

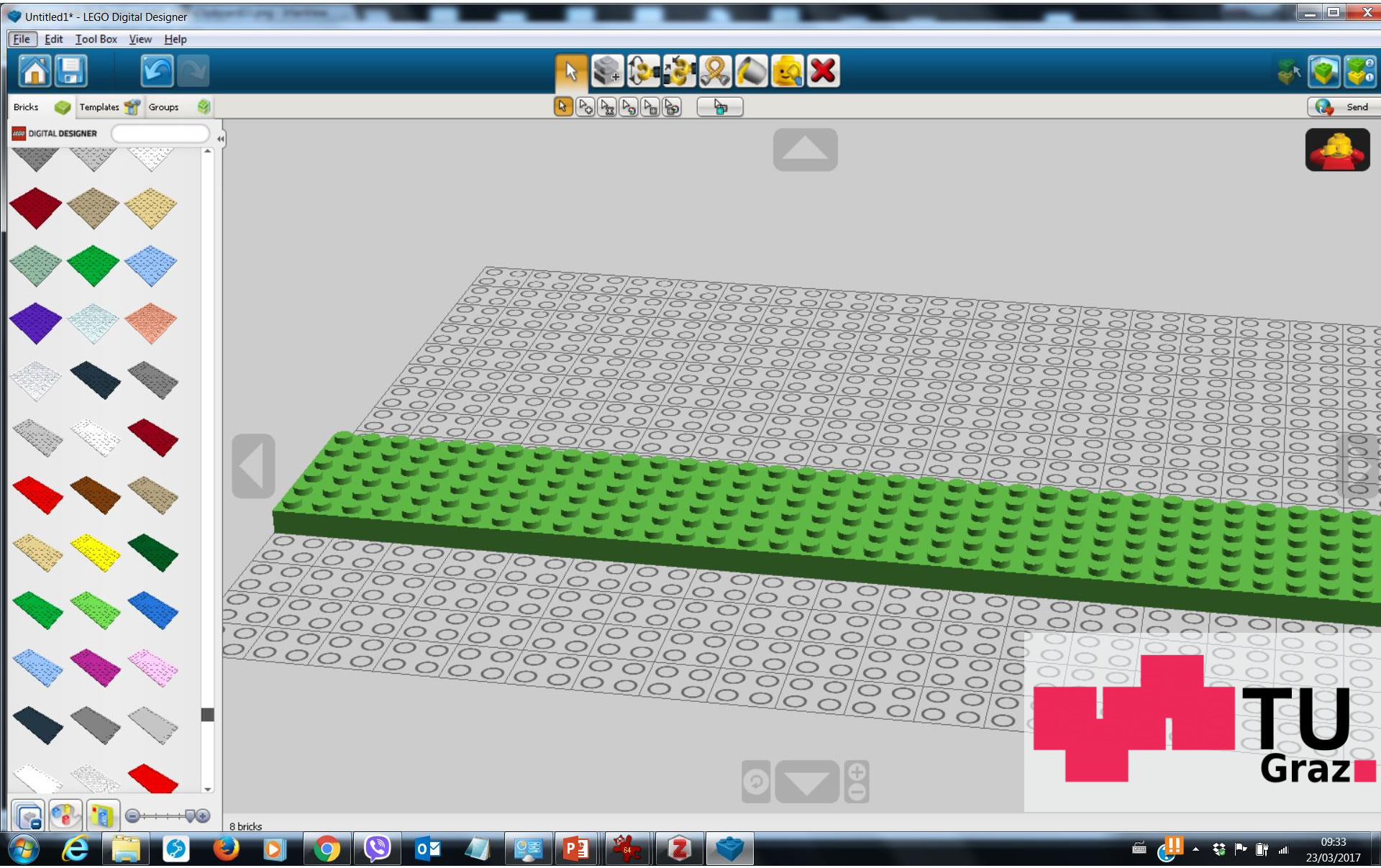





(c)
0 seconds
600 nm
S4800 10.0kV 8.9mm x25.0k SE(M) 2013/11/25
(d)
60 seconds
600 nm
S4800 10.0kV 9.6mm x25.0k SE(M) 2013/12/11
(e)
150 seconds
600 nm
S4800 10.0kV 9.9mm x25.0k SE(M) 2013/12/11
(f)
300 seconds
600 nm
S4800 10.0kV 8.6mm x25.0k SE(M) 2013/12/09


a
Cu(OH)2 nanotube array
d
100 nm
1 µm


Untitled1* - LEGO Digital Designer
File Edit Tool Box View Help
Bricks Templates Groups
DIGITAL DESIGNER
Send
2 bricks
09:30
23/03/2017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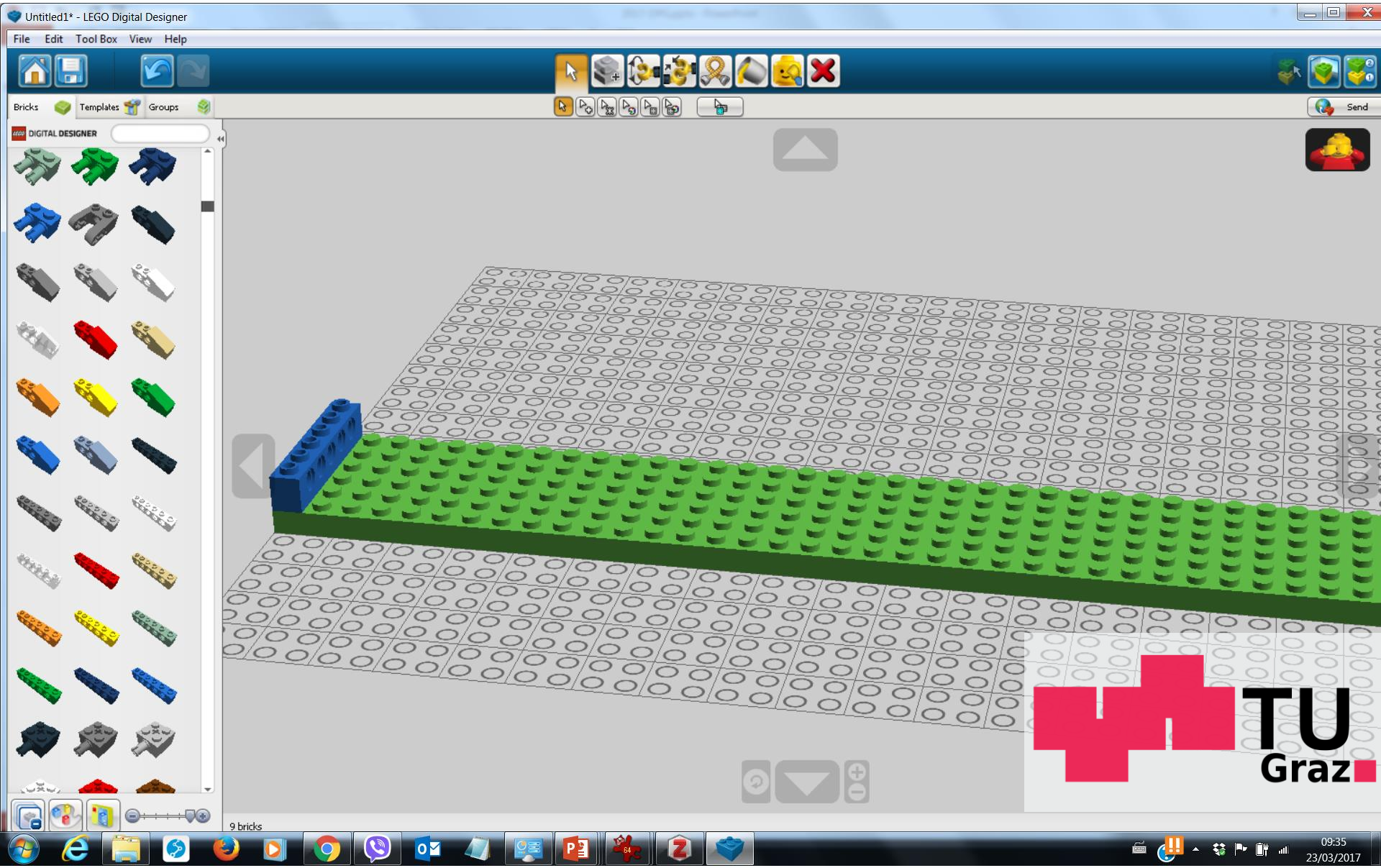
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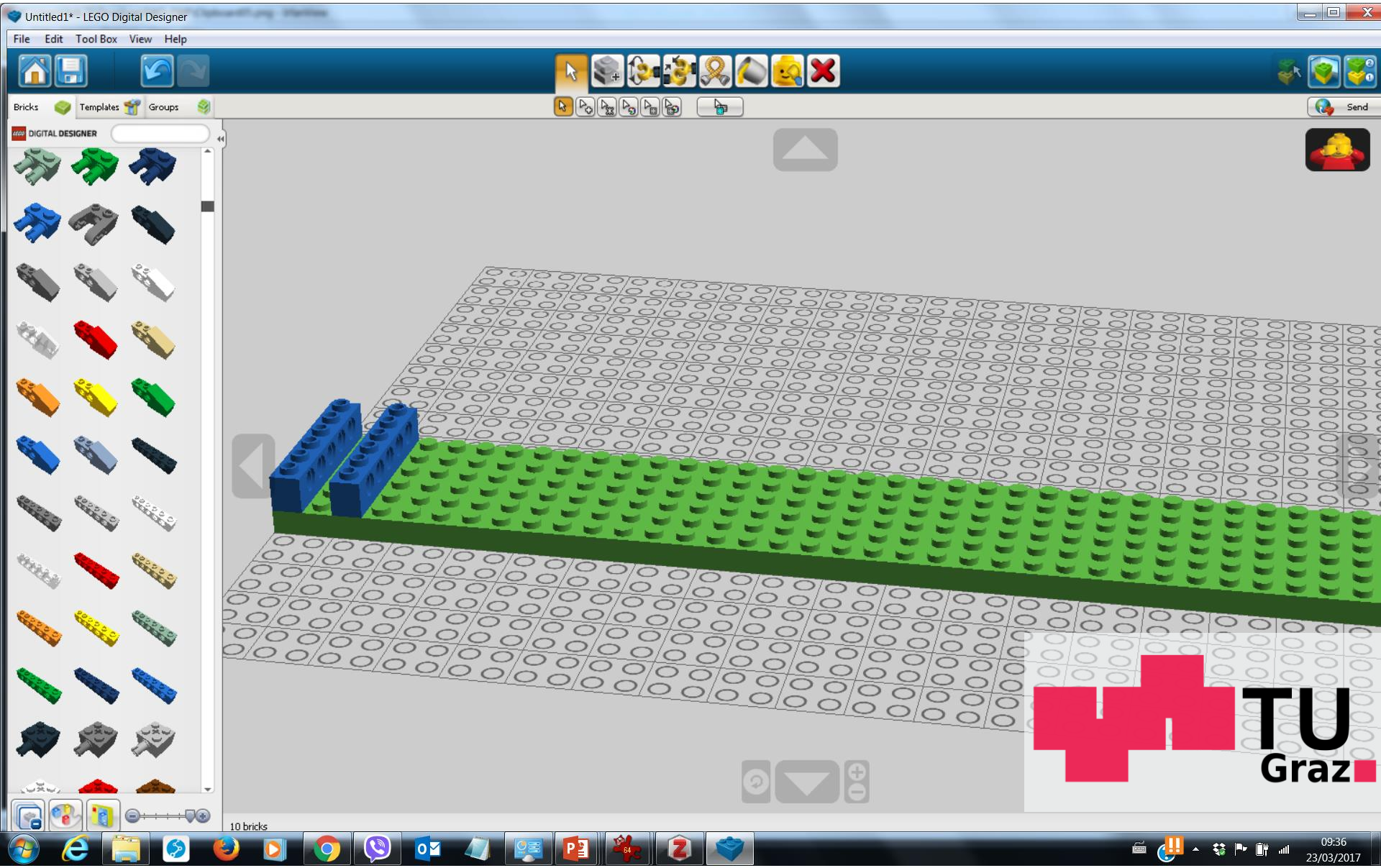
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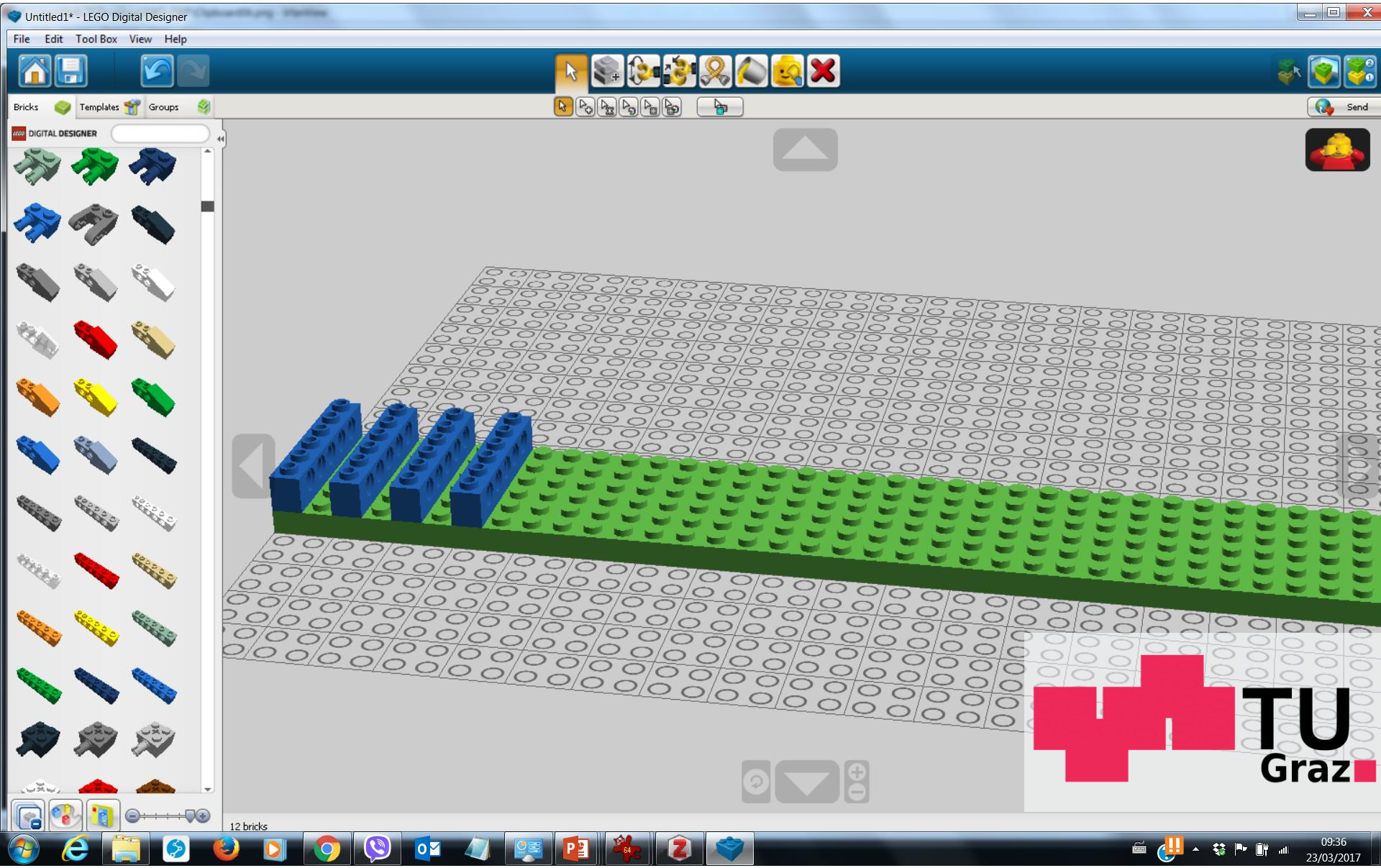
23/03/2017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File Edit Tool Box View Help
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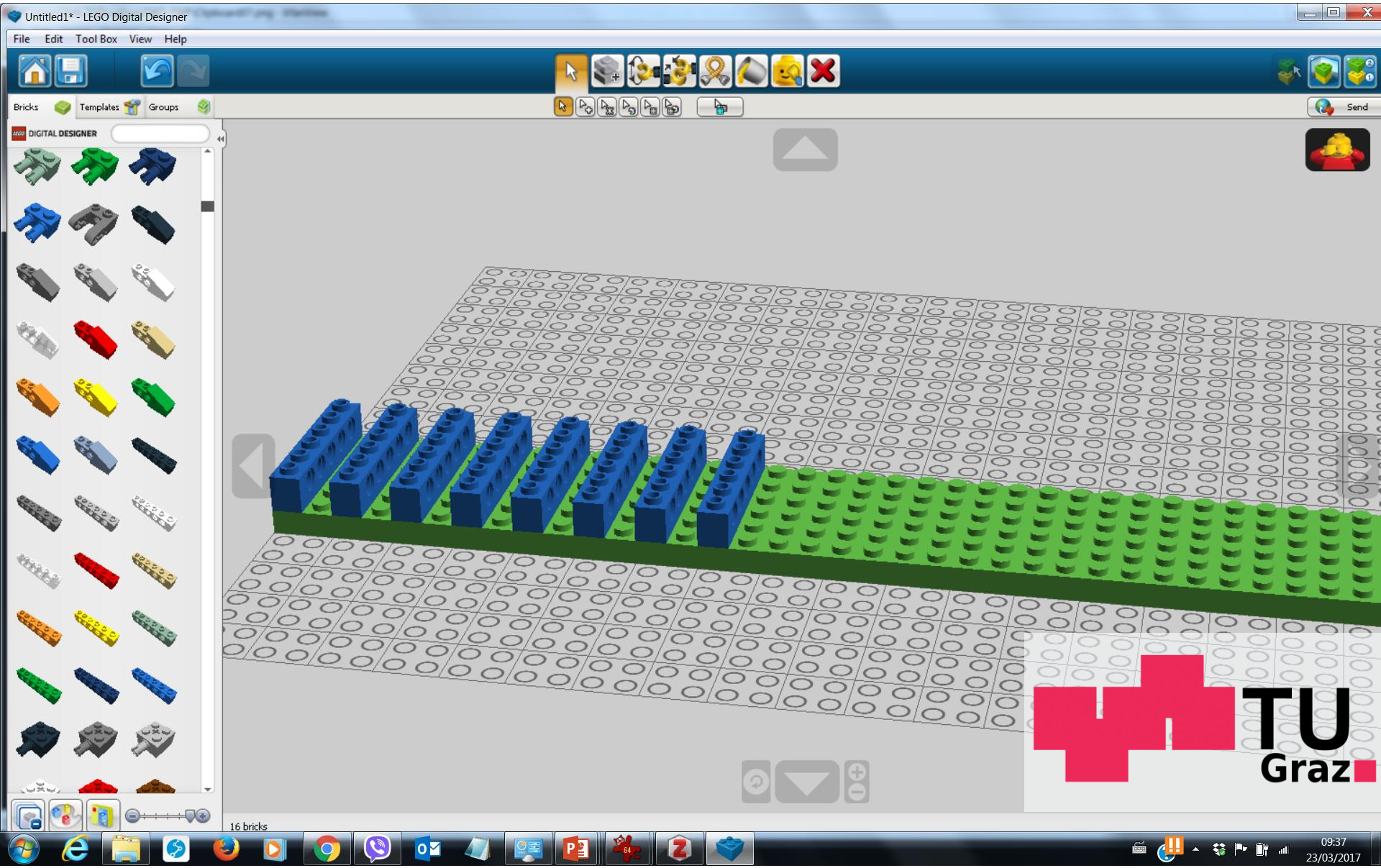
23/03/2017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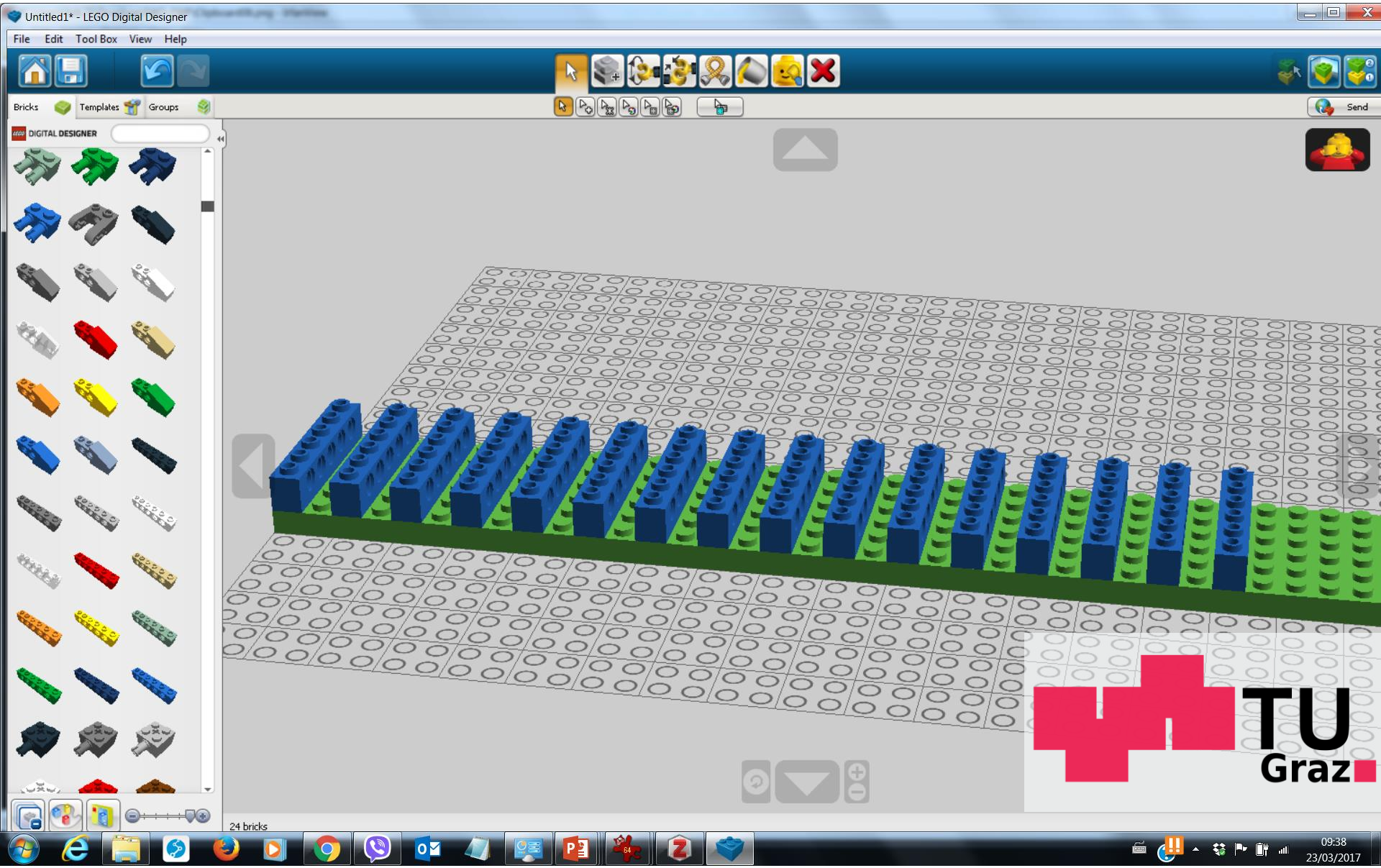
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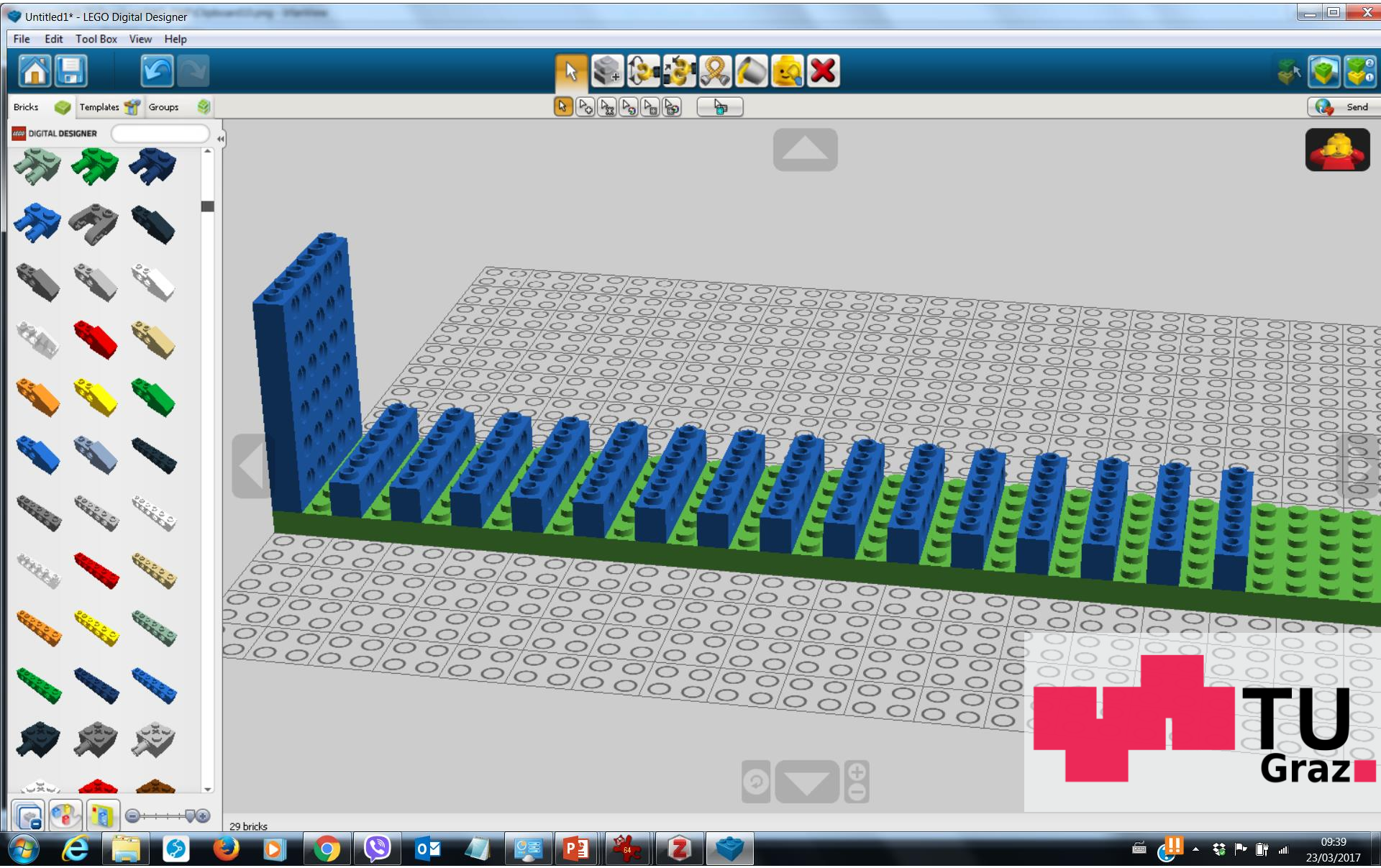
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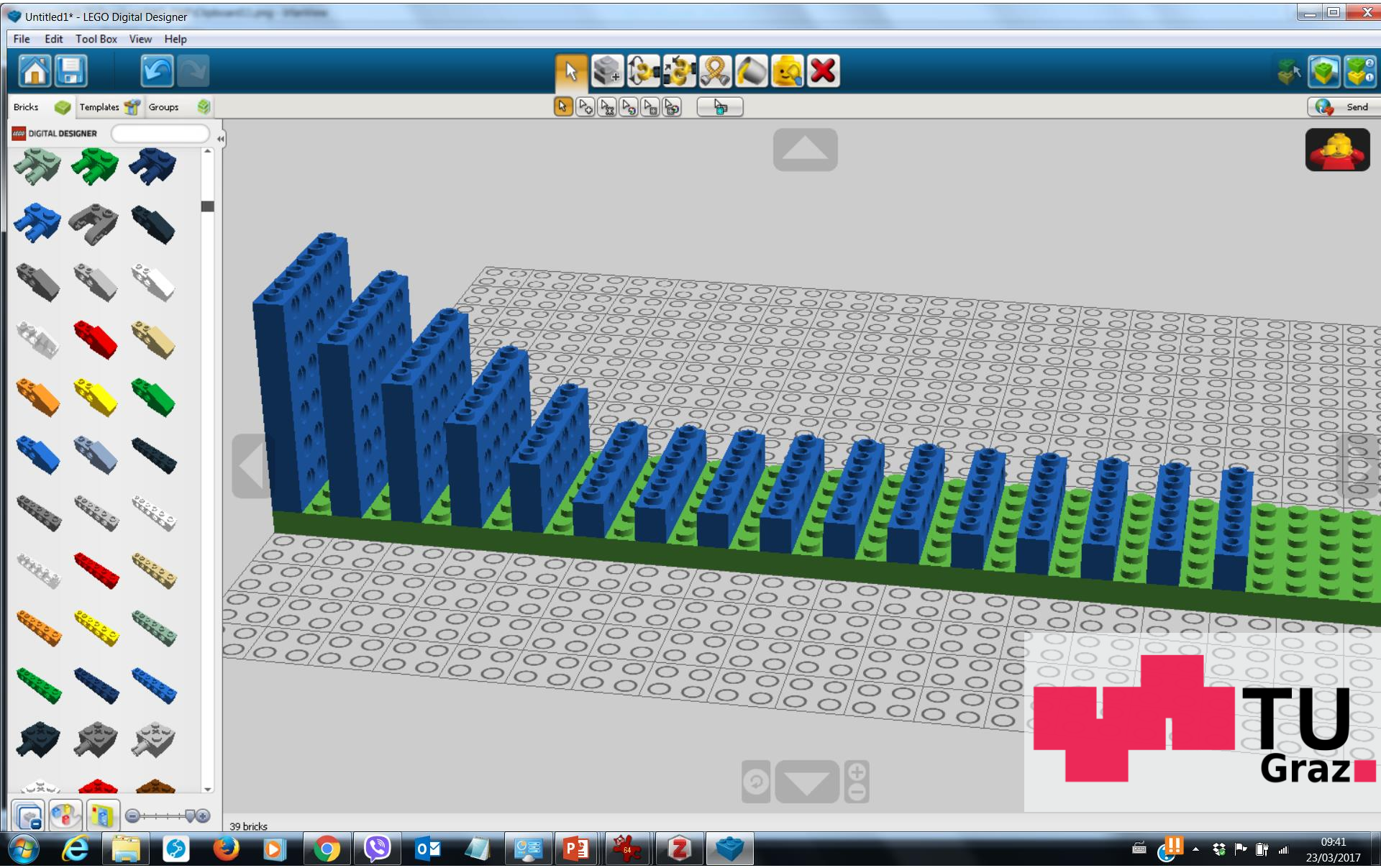
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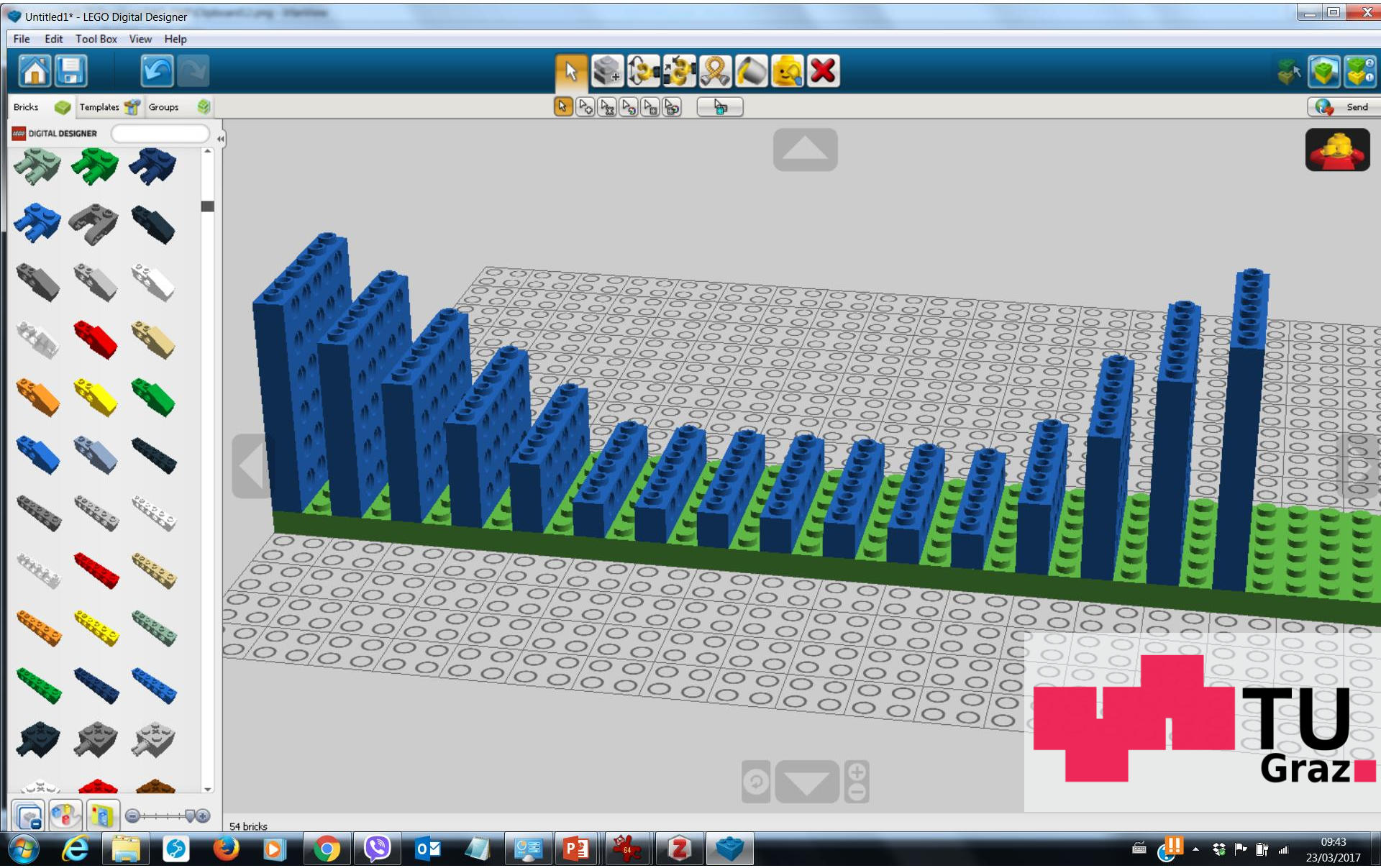
23/03/2017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File Edit Tool Box View Help
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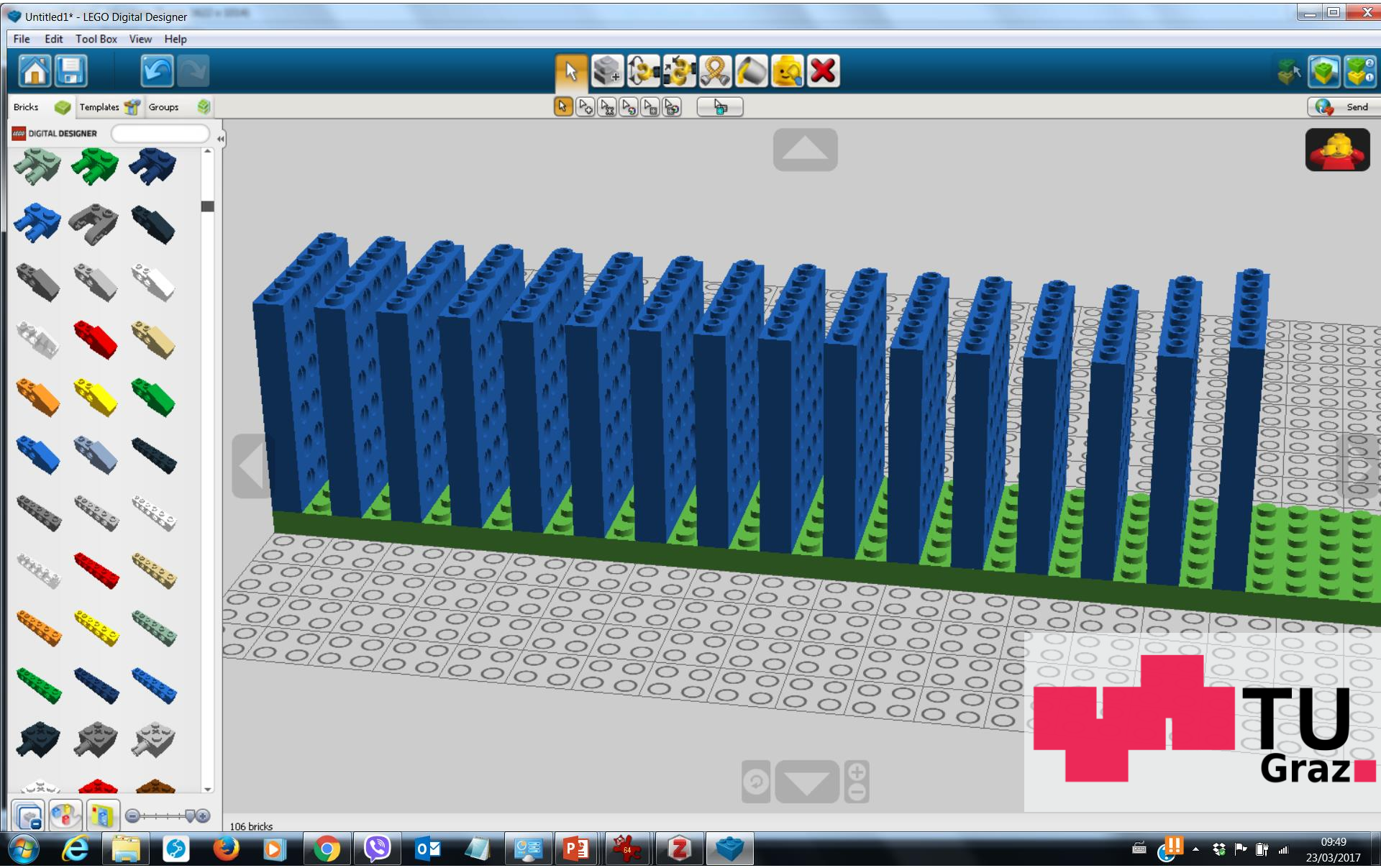
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File Edit Tool Box View Help
Bricks Templates Groups
DIGITAL DESIGNER
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106 bricks
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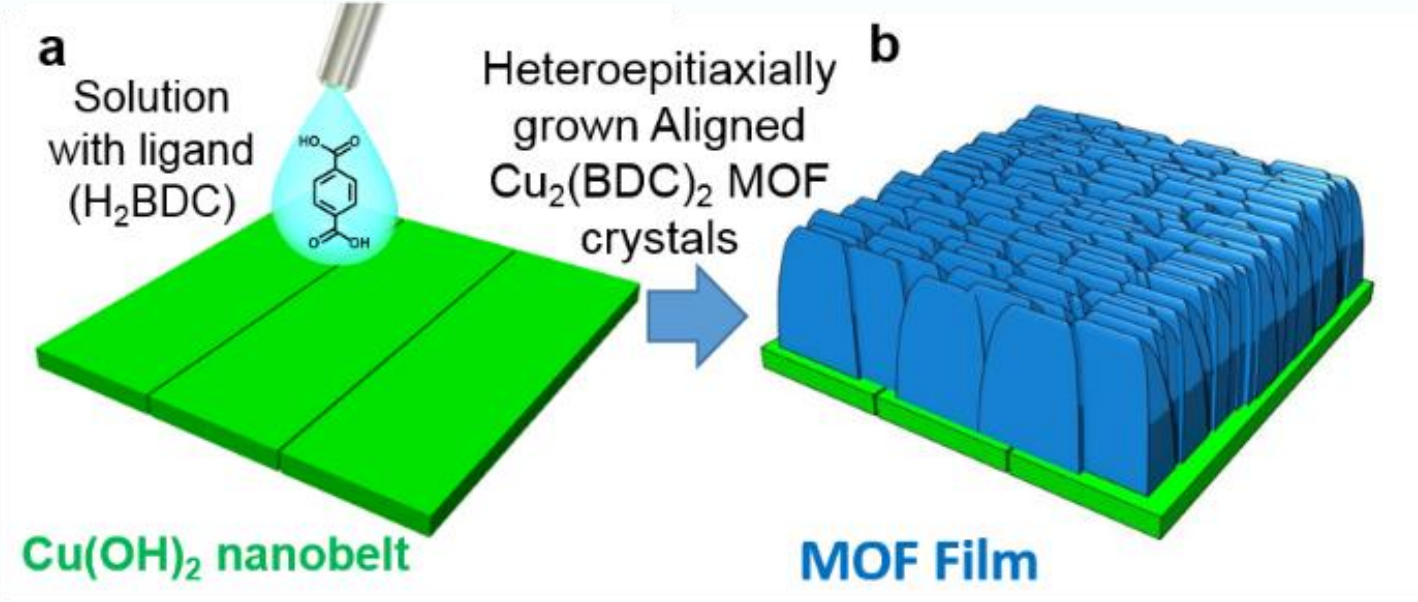
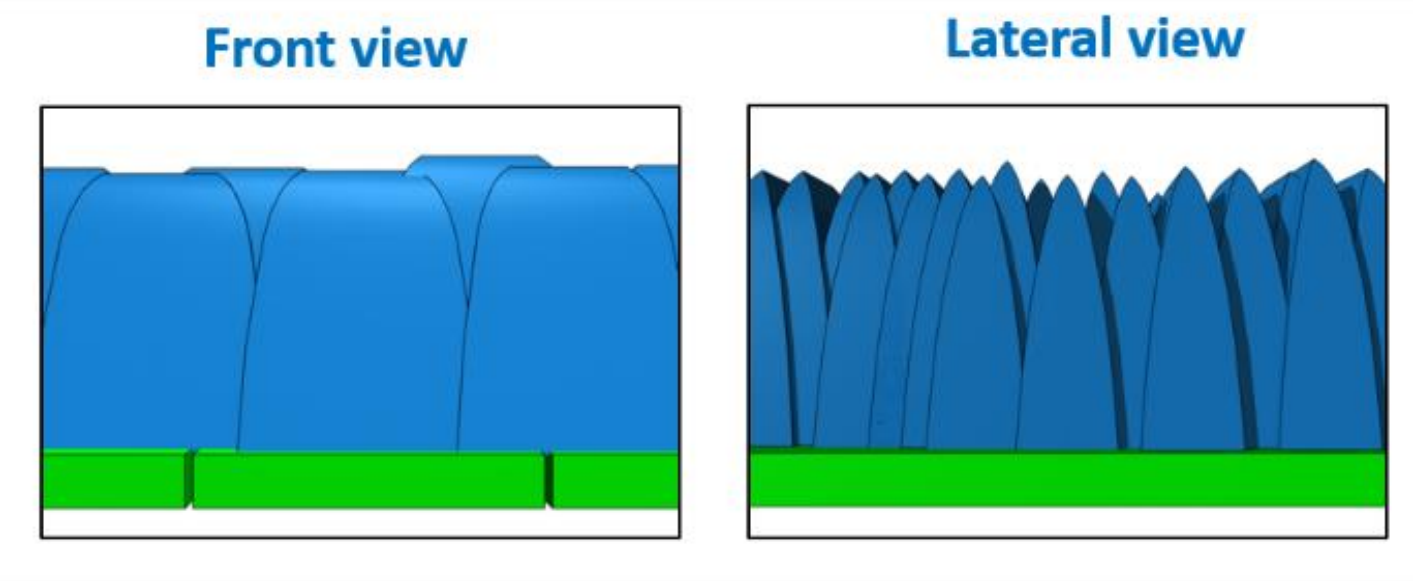
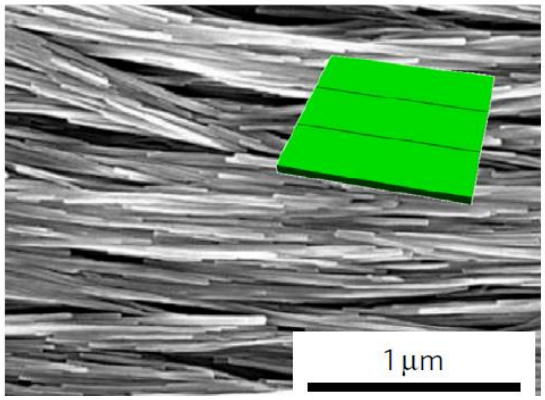
23/03/2017


MOF-htero1.lxf* - LEGO Digital Designer
File Edit Tool Box View Help
Bricks Templates Groups
DIGITAL DESIGNER
Send
We could align pores!
106 bricks
09:55
23/03/2017

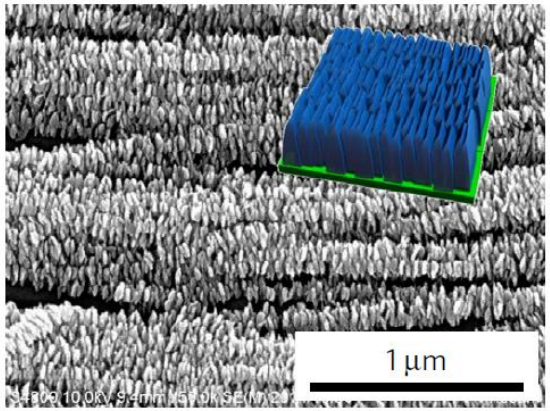

a
Solution with ligand (H_2BDC)
Heteroepitiaxially grown Aligned $Cu_2(BDC)_2$ MOF crystals
b
$Cu(OH)_2$ nanobelt
MOF Film


Front view
Lateral view

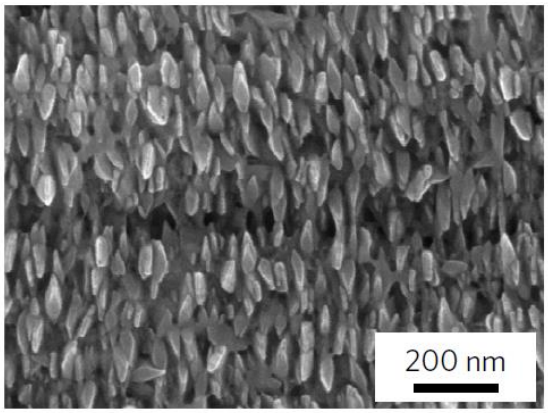
$Cu(OH)_2$



b



c



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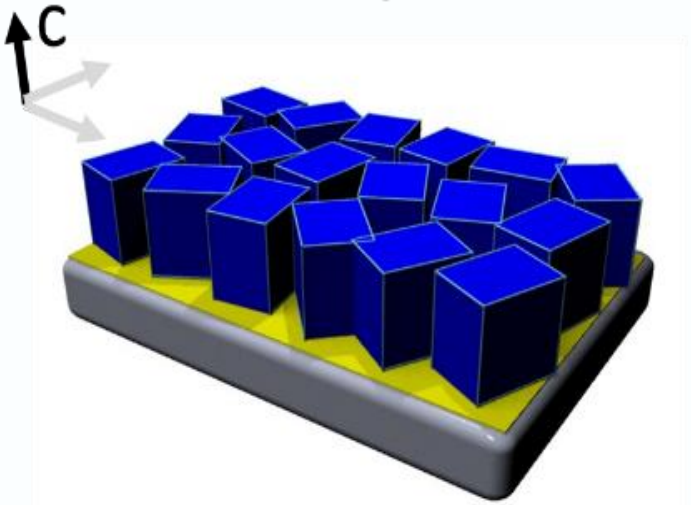
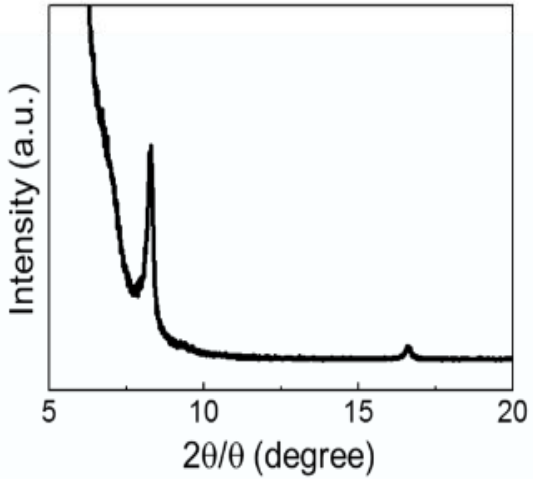
Out-of-plane investigation

Order along the c axis

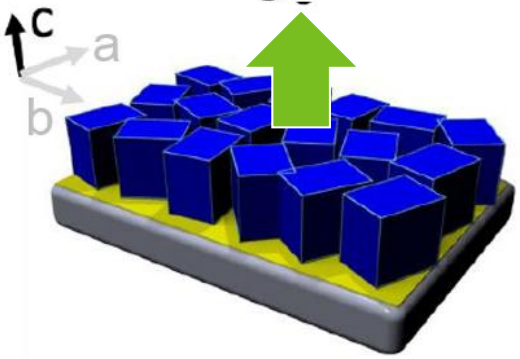


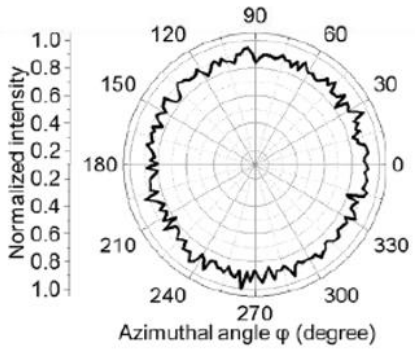


Azimuthal angle dependence investigation

Prof Takahashi Group

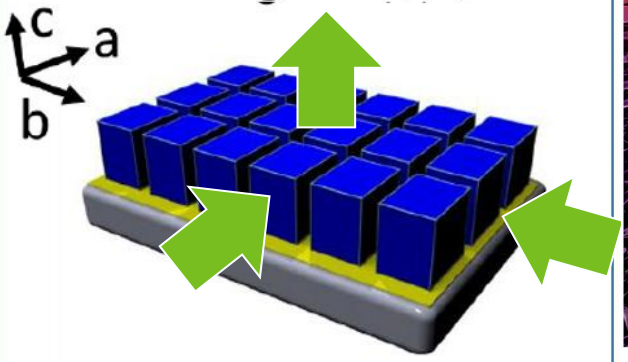
Order along the c axis

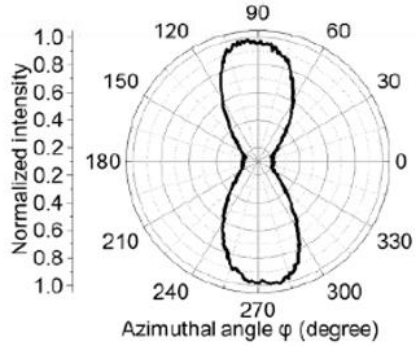




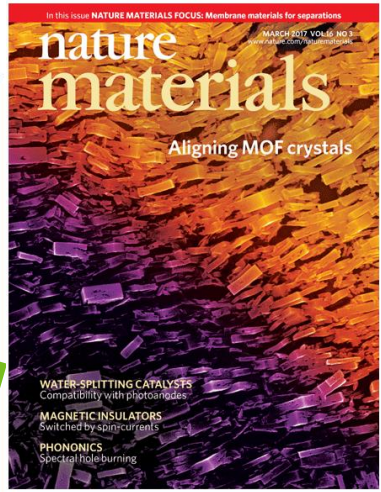
Other methods for the MOF growth

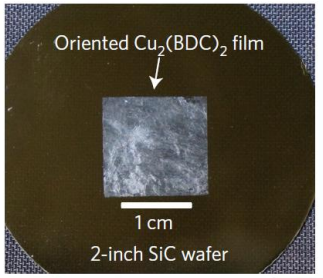
Order along the a, b, c axes

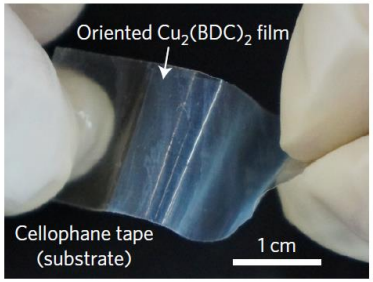


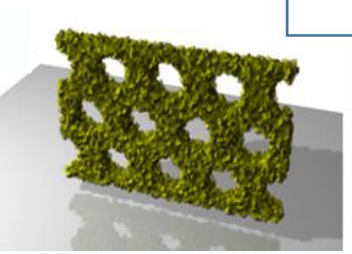


Heteroepitaxially grown MOFs









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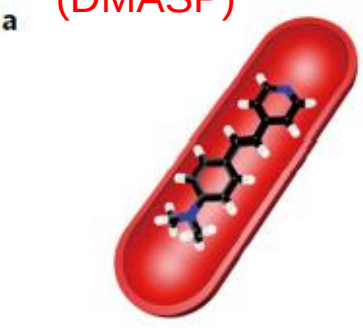
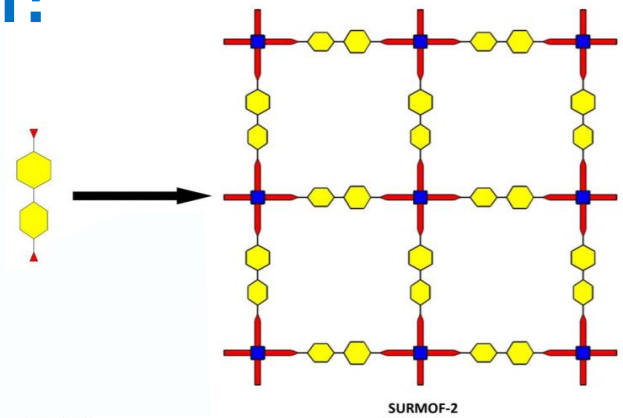
Paolo Falcaro[1,2,3,4]*, Kenji Okada[5,6], Takaaki Hara[5], Ken Ikigaki[5], Yasuaki Tokudome[3,5], Aaron W. Thornton[2], Anita J. Hill[2], Timothy Williams[7], Christian Doonan[4] and Masahide Takahashi[3,5]*

Application!

Fluorescent dye 4-[4-(dimethylamino)-styryl]pyridine (DMASP)



$Cu_2(BPDC)_2$



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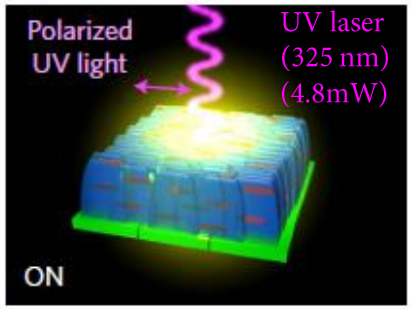
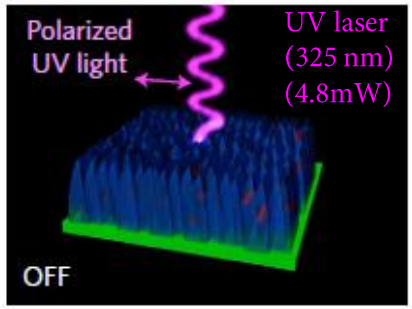
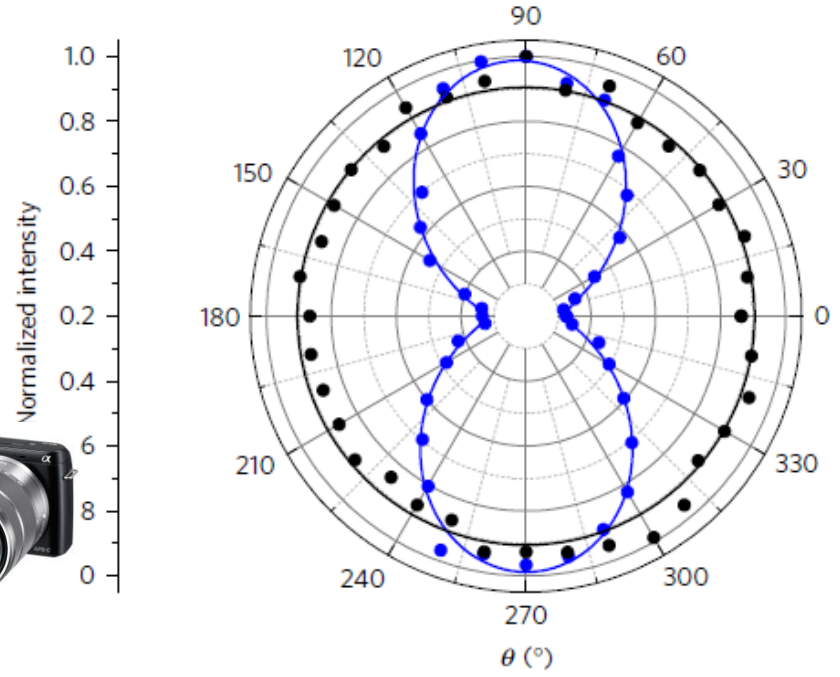
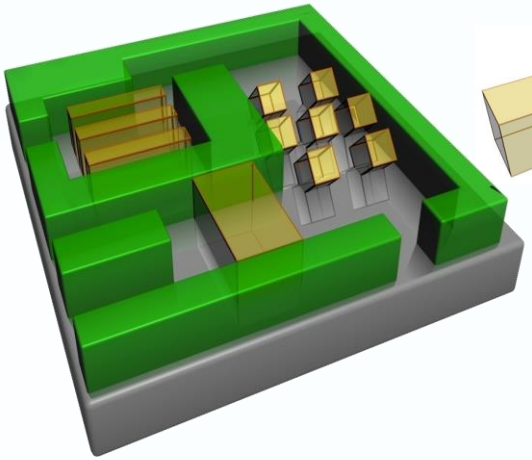






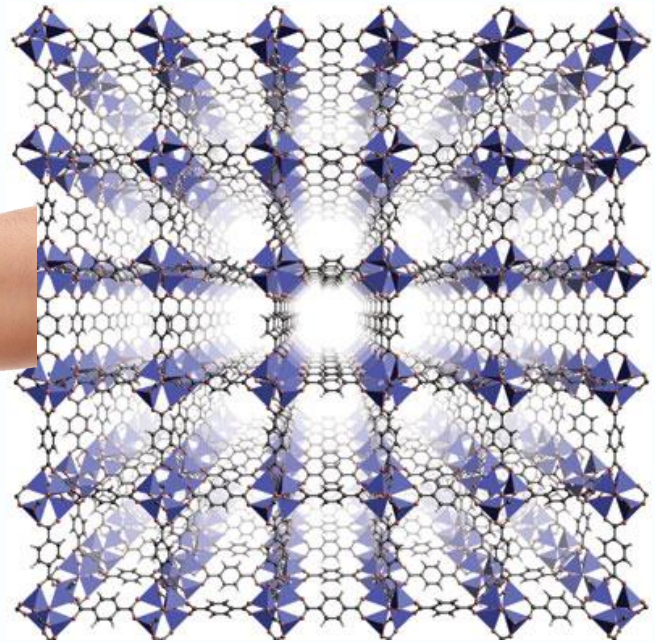
Summary!



Ceramics

The Fonthill 'Dragon' Jar. (US$12,000,000),

MOFs



MOF-5. (US$200/Kg),

Thank you!

Paolo.Falcaro@tugraz.at

3nd International Conference on Metal Organic Frameworks and Porous Polymers

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