Functional Inorganic Materials
Fall 2022

Tuesdays: 12.15 - 14.00 (U8)
Thursdays: 10.15 - 12.00 (Ke1)

#	Date	Who	Topic
1	Mon 5.9.	Maarit	Introduction + Materials design consepts
2	Thu 8.9.	Antti	Introduction + Computational materials design
3	Tue 13.9.	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 15.9.	Maarit	Magnetic (oxide) materials
5	Tue 20.9.	Maarit	Ionic conductivity (Oxygen): SOFC & Oxygen storage
6	Thu 22.9.	Maarit	Ionic conductivity (Lithium & Proton): Li-ion battery
7	Tue 27.9.	Antti	Thermal conductivity
8	Thu 29.9.	Antti	Thermoelectricity
9	Tue 4.10.	Antti	Piezoelectricity
10	Thu 6.10.	Antti	Pyroelectricity and ferroelectricity
11	**Tue 11.10.**	**Maarit**	**Hybrid materials**
12	Thu 13.10.	Antti	Luminescent and optically active materials

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School of Chemical Technology

LECTURE 11: Hybrid Materials

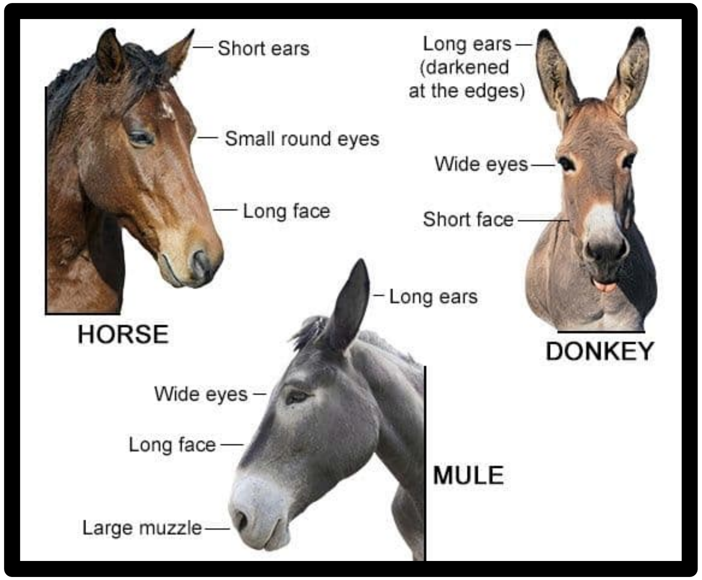
- Inorganic-organic materials
- CPs & MOFs
- ALD/MLD
- Layer-engineering
- Superlattice

LECTURE EXERCISE 11

1. **What are the possible dimensionalities (0D, 1D, 2D or 3D) of the followings: (a) Metal-organic complex (coordination compound with organic ligands), (b) Coordination polymer, (c) Metal-organic framework.**
2. **Are all CPs MOFs? Are all MOFs CPs? Please explain!**
3. **Give examples of properties which can be improved/controlled through insertion of organic layers into inorganic matrix (with short explanations).**
4. **Give examples of ALD/MLD fabricated materials which are difficult (if not impossible) to synthesize using conventional synthesis techniques. Explain the unique benefits of ALD/MLD in these selected cases with few sentences.**
5. **EXTRA QUESTION: The UV-activated photoisomerization reaction of azobenzene molecules has been utilized to add a photoswitching effect on the magnetic properties of ε-Fe_2O_3:azobenzene superlattice thin films. You could think/propose some other application area(s) where a similar switching effect could be useful/interesting.**

Brought Together

SUM of BOTH PROPERTIES



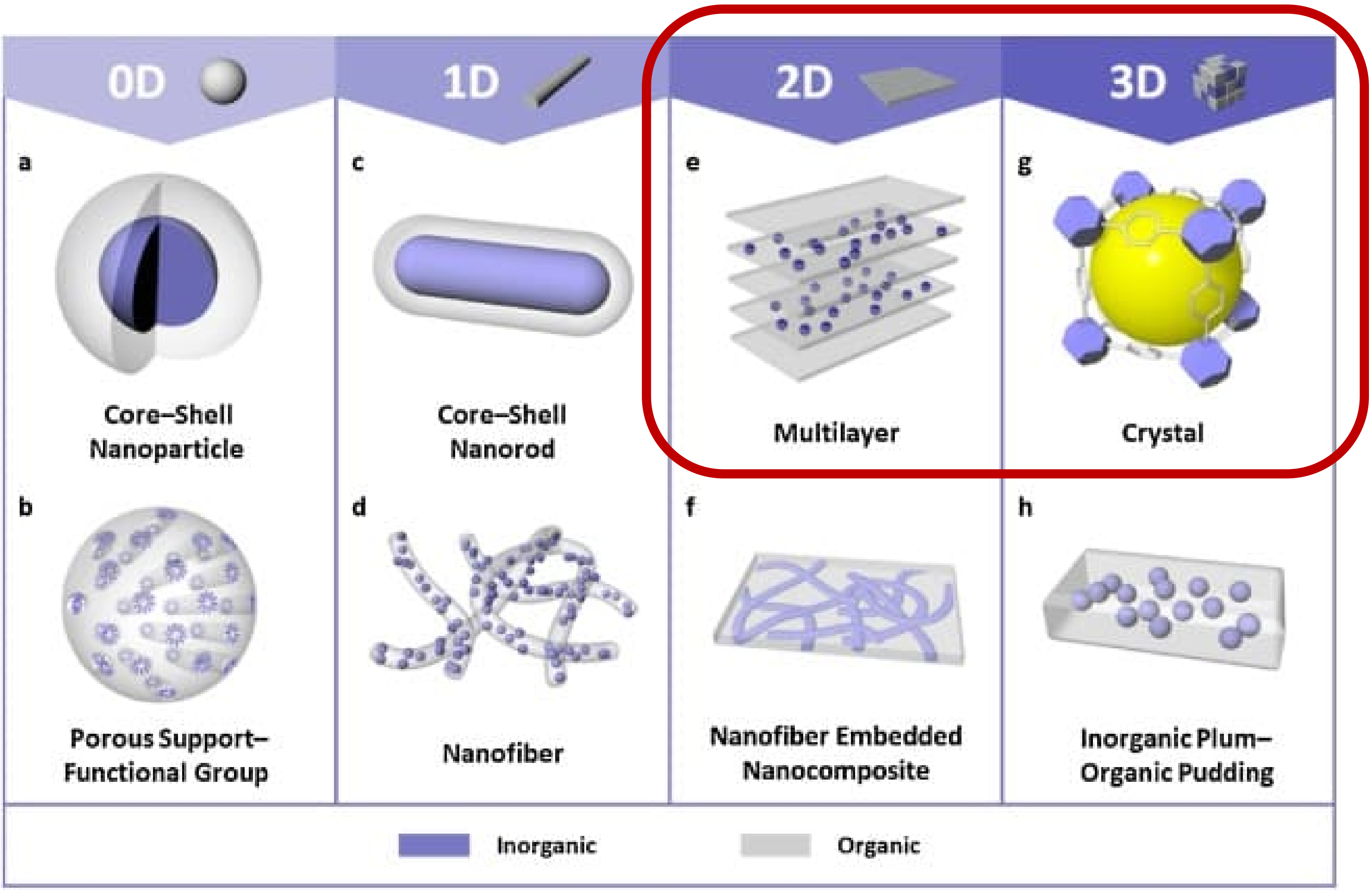
Fused Together

AVERAGE PROPERTIES

Intimately / Interactively Fused

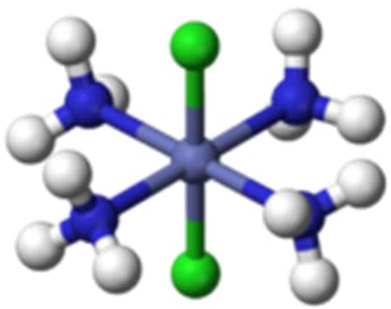
EXTRAORDINARY / MUTUALLY CONTRADICTORY PROPERTIES

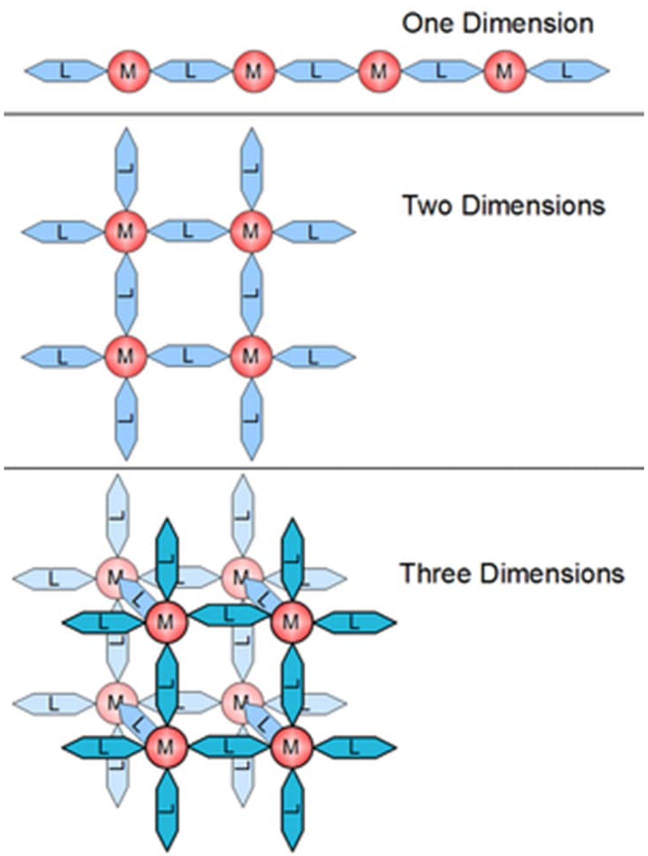
EXAMPLES of Inorganic-Organic Hybrid Materials

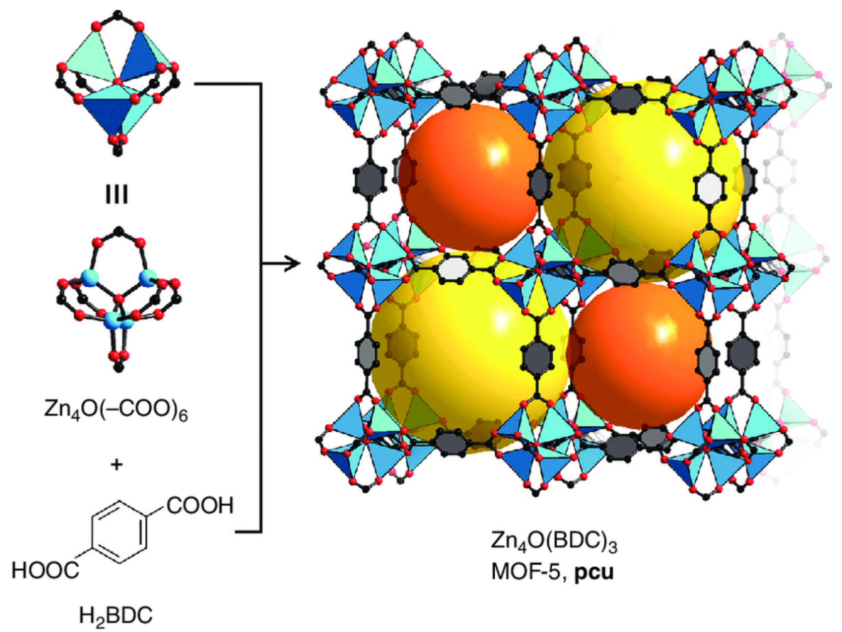


FOR CHEMISTS: Inorganic-Organic Material

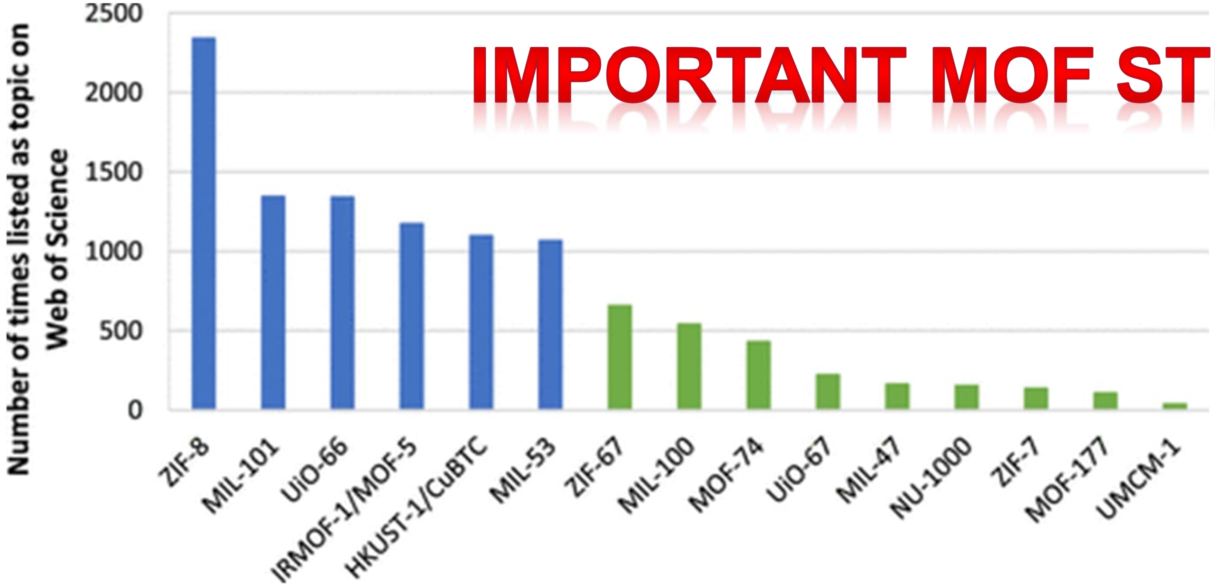
- Single Compound (NOT Composite) with Chemical Bonds
- Coordination/Metal Complex: central metal ion + (organic) ligands
- Coordination Polymer (CP): ligands act as bridges
- Metal-Organic Framework (MOF): highly porous

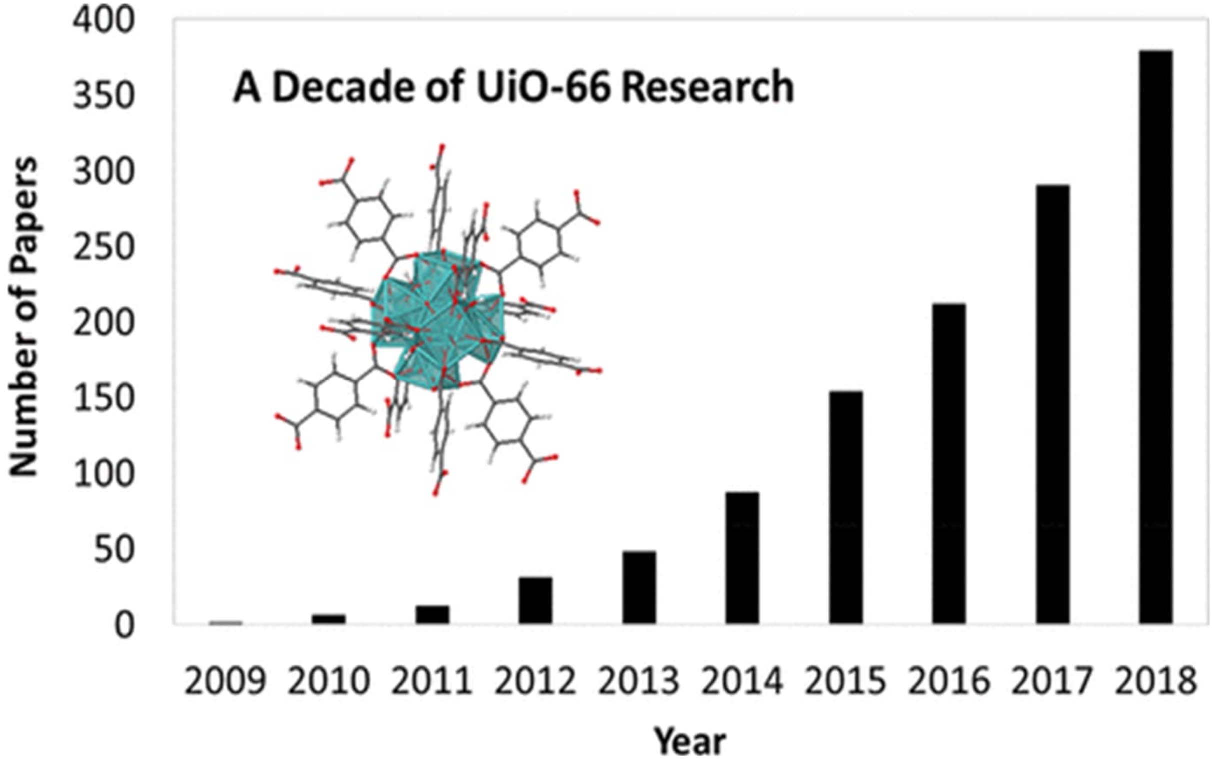




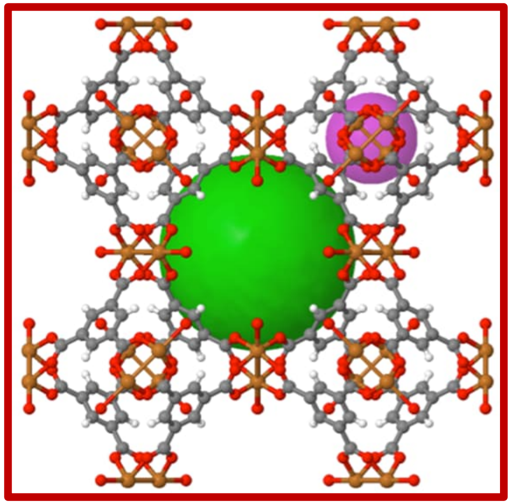


IMPORTANT MOF STRUCTURES

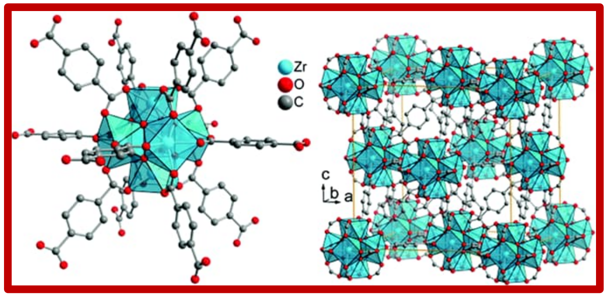


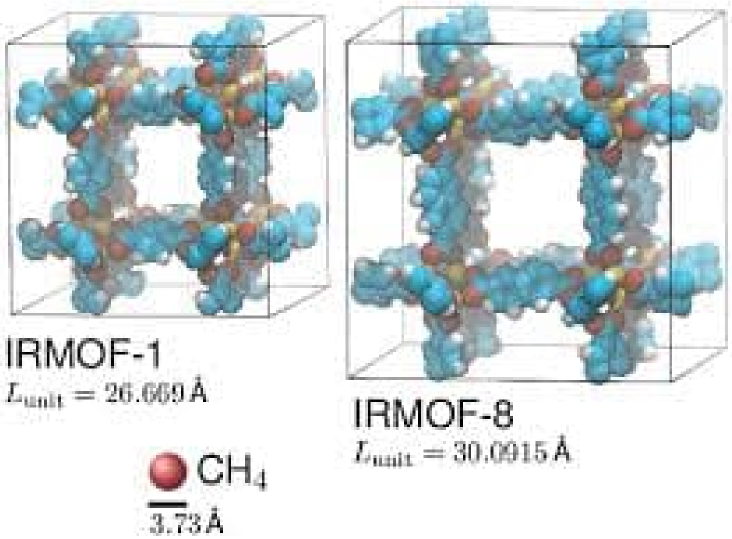


HKUST-1

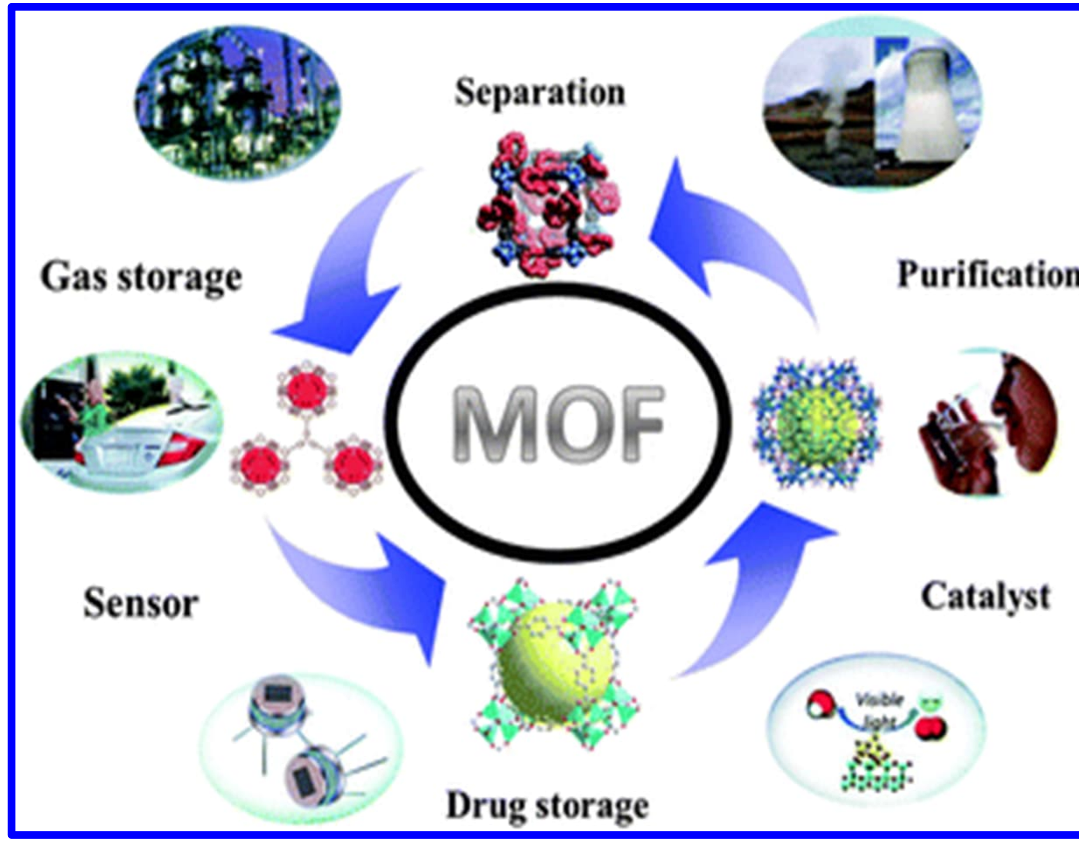


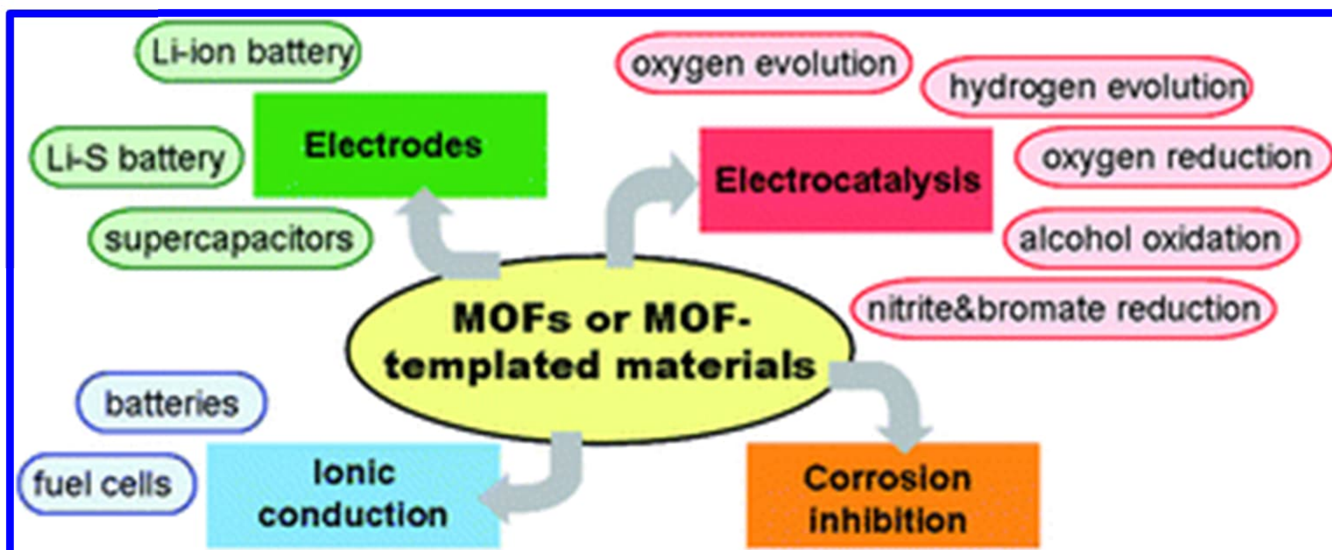
UiO-66





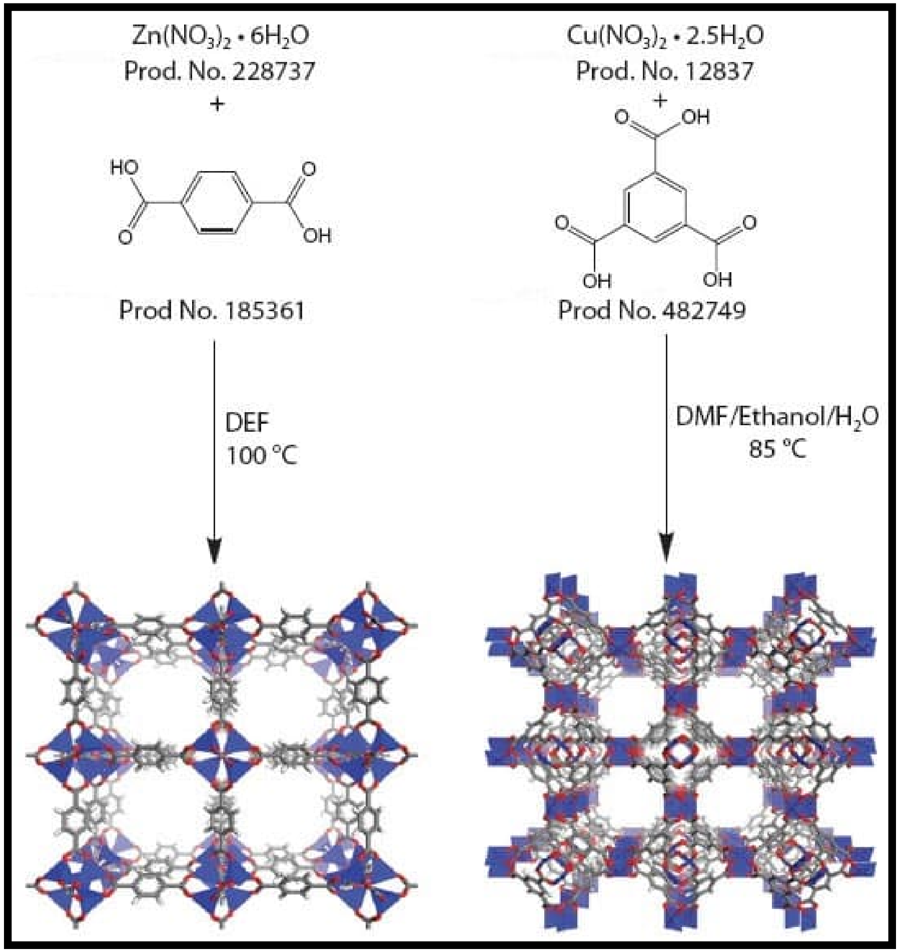
MOF THIN FILMS!





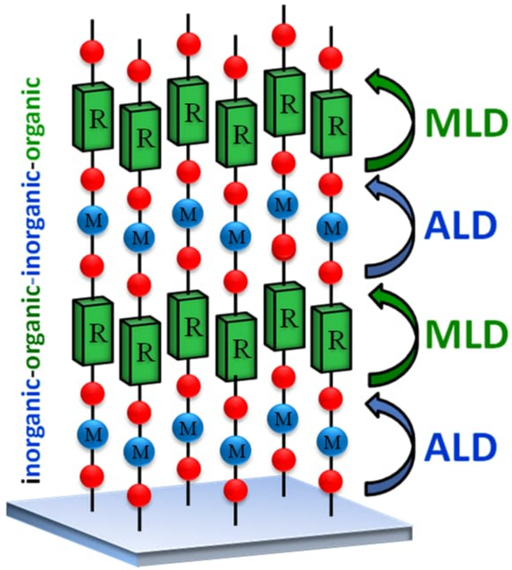
Synthesis of MOFs

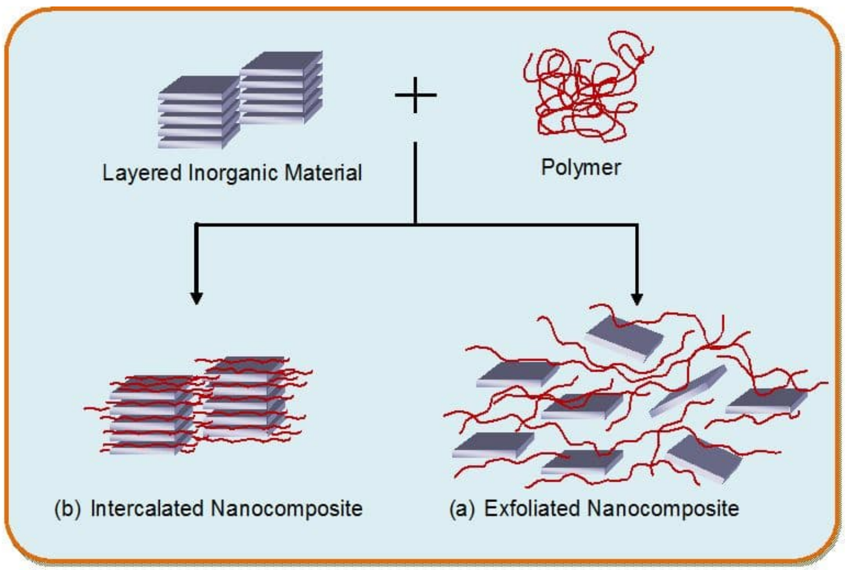
- Synthesized most often in bulk form via solution techniques
- Porous structure →
  MOFs absorb readily/unintentionally solvent molecules
- Many prospective applications would require high-quality thin films
- No gas-phase deposition techniques (before ALD/MLD) !

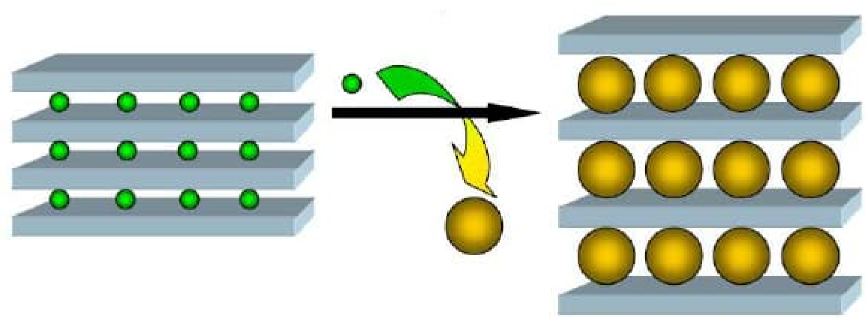


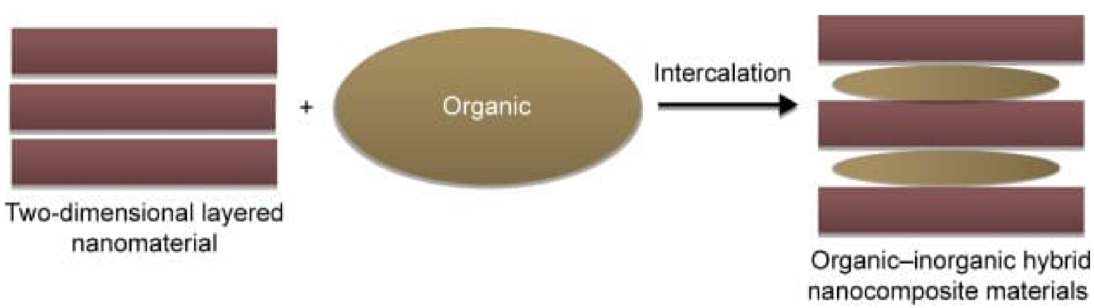
Layered Inorganic-Organic Materials

- **Exfoliation & mixing & precipitation** (solution)
- **Intercalation** (solution or solid state or gas/solid)
- (Ion/molecule) **Exchange** (= topotactic substitution)
- **Layer-by-layer piling** (liquid-to-solid or gas-to-solid)









Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Flexible thermoelectric foil for wearable energy harvesting

Chunlei Wan[a,*], Ruoming Tian[b], Azrina Binti Azizi[c], Yujia Huang[a], Qingshuo Wei[d], Ryo Sasai[e], Soontornchaiyakul Wasusate[e], Takao Ishida[d], Kunihito Koumoto[b,*]

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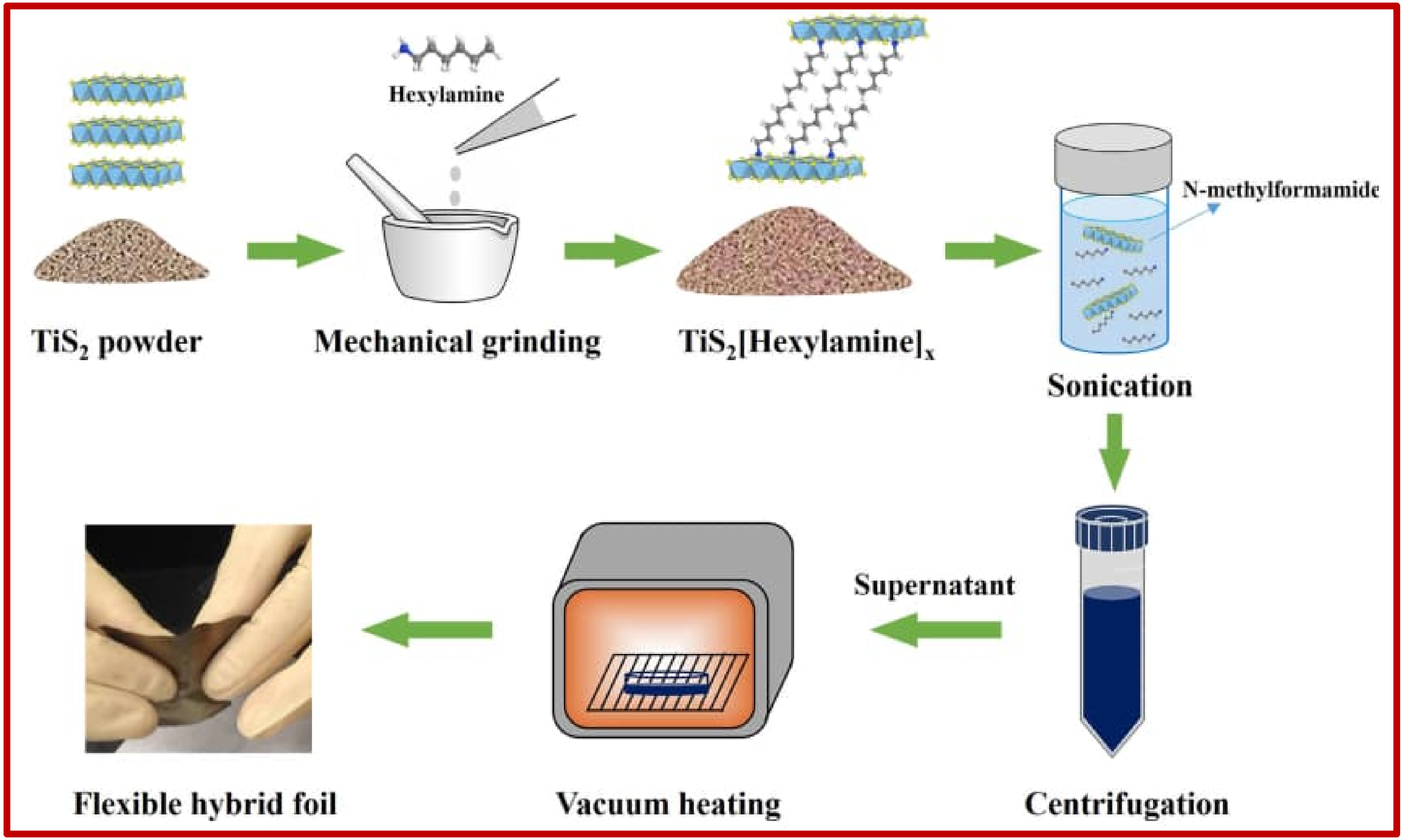
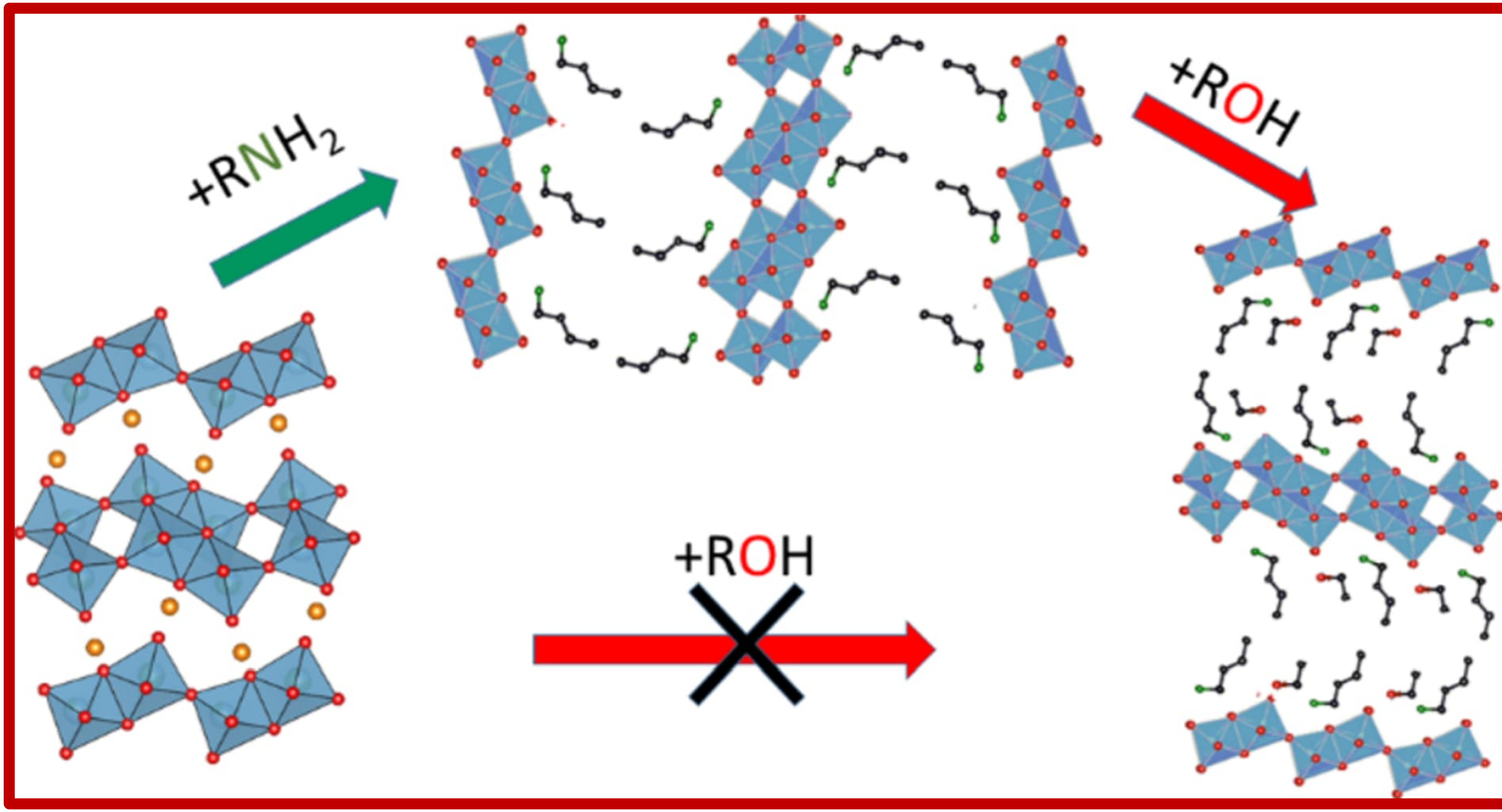
[e] Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue 690-8504, Japan





Inorganic Chemistry
Article
pubs.acs.org/IC

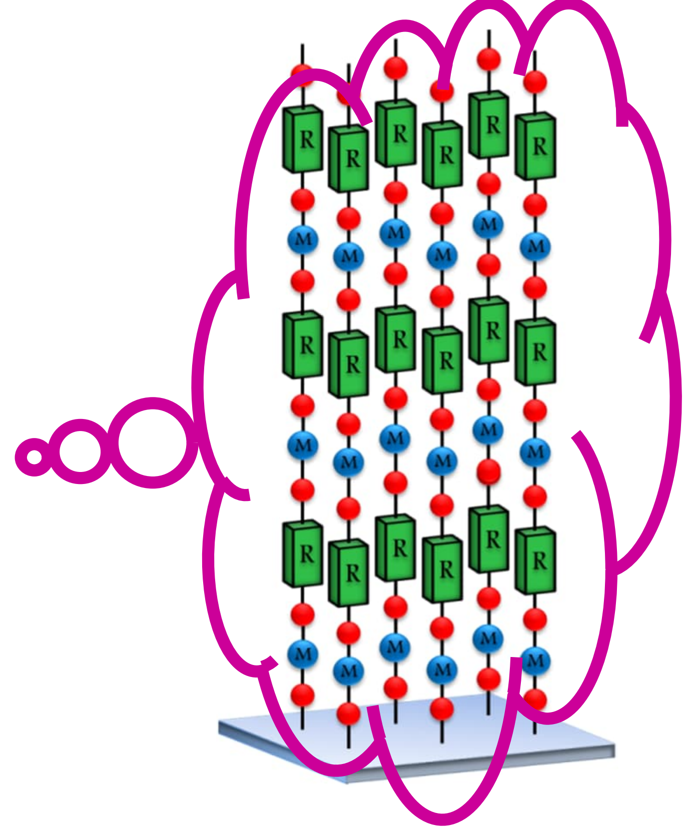
Intercalation of Primary Alcohols into Layered Titanoniobates

Chris I. Thomas* and Maarit Karppinen

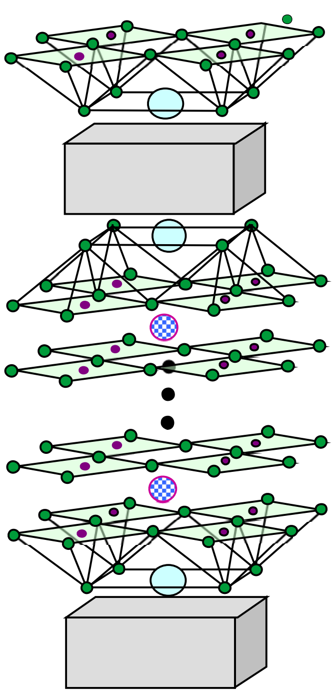
Department of Chemistry and Materials Science, Aalto University, FI-00076 Espoo, Finland

MULTI-FUNCTIONAL MULTILAYERED MATERIALS

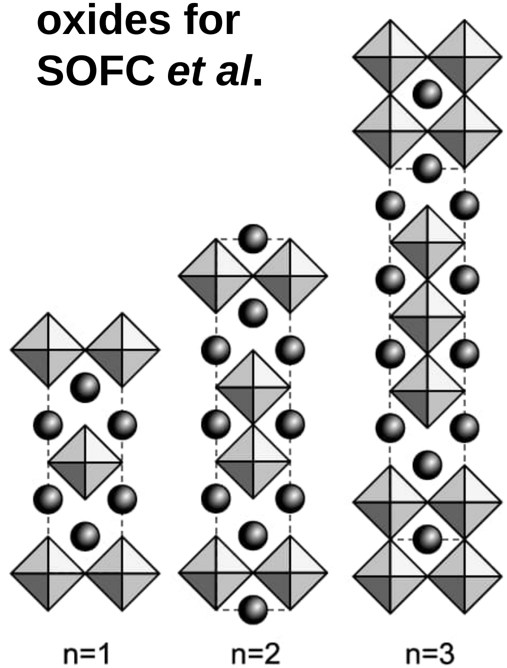
Layered inorganic-organic hybrid thin films



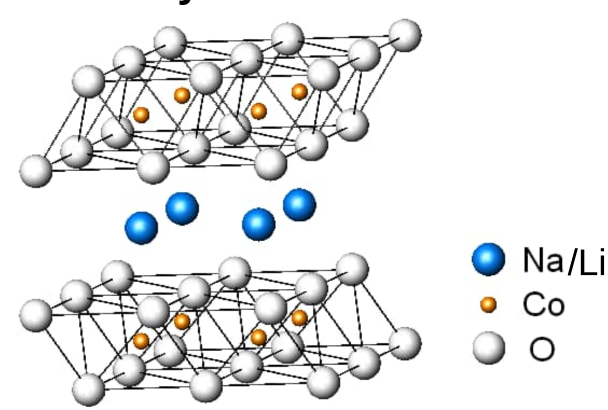
Multilayered Cu oxides for high-T_c superconductors

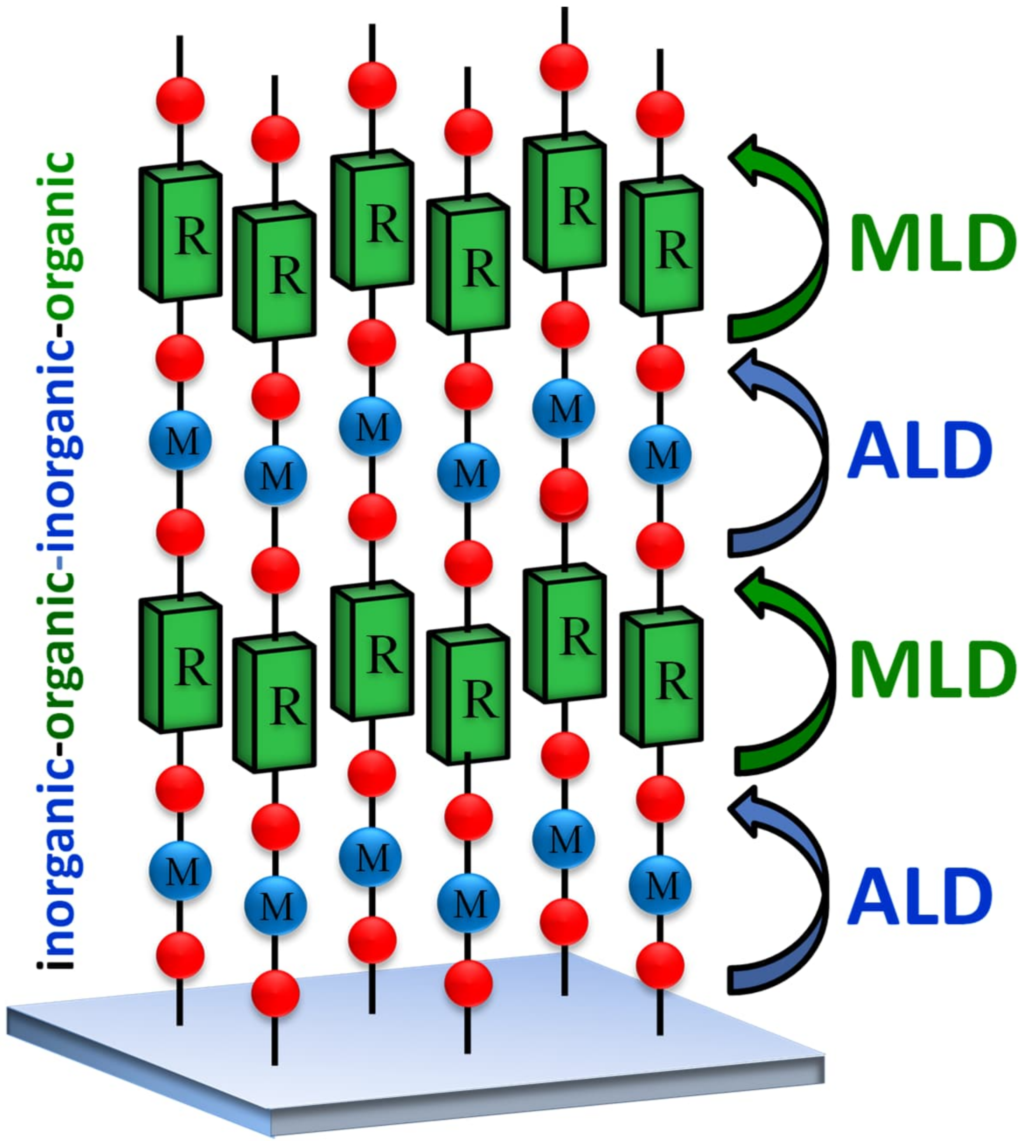


Ruddlesden-Popper oxides for SOFC *et al*.



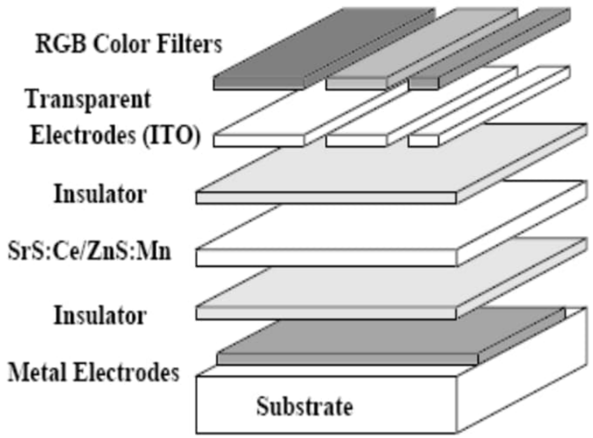
Layered Co oxides for Li-ion battery & thermoelectrics




inorganic-organic-inorganic-organic
R
M
MLD
ALD
MLD
ALD

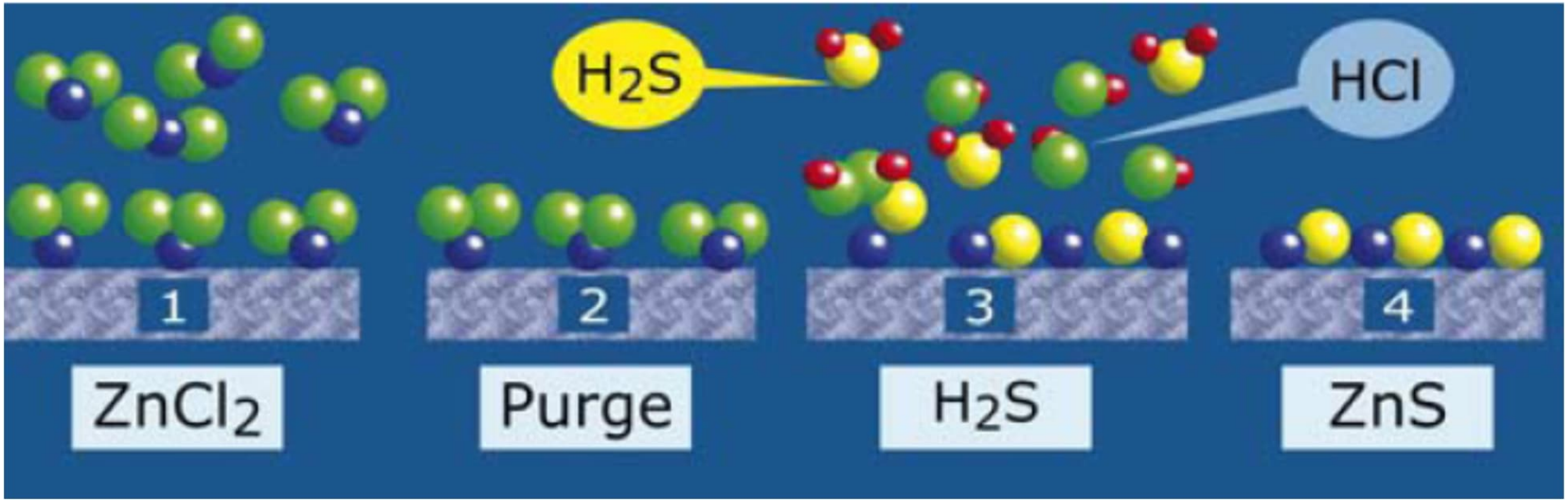
Atomic Layer Deposition (ALD) Thin-Film Technique

- **Gaseous precursors**
- **Self-limiting surface reactions**
- **Conformal, homogeneous thin films with atomic-layer accuracy**



Electroluminescent display

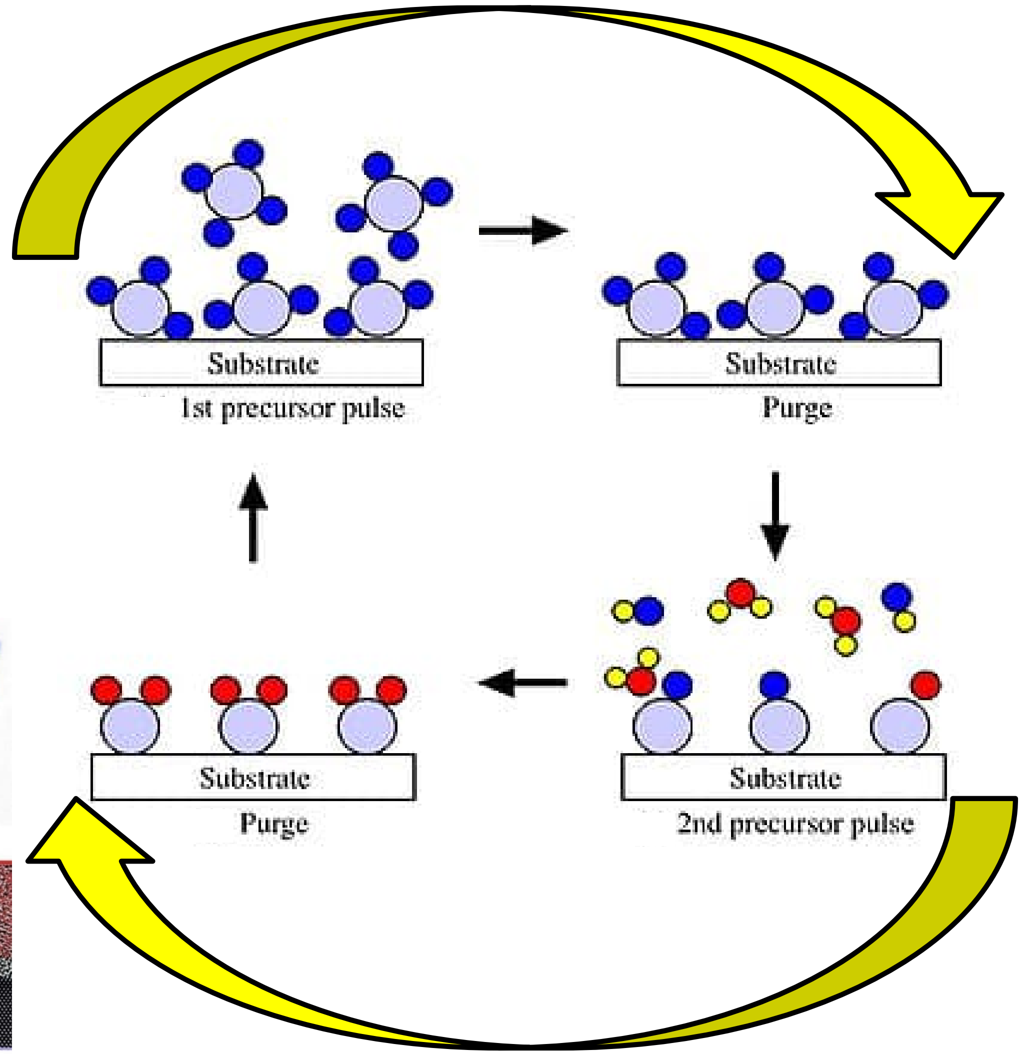
Instrumentarium / Finlux / Planar

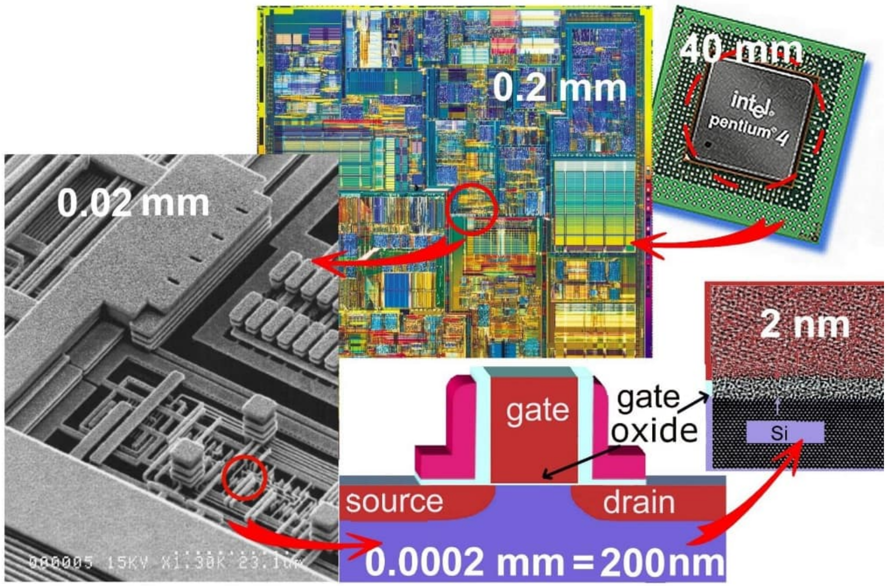


HfO_2-ALD

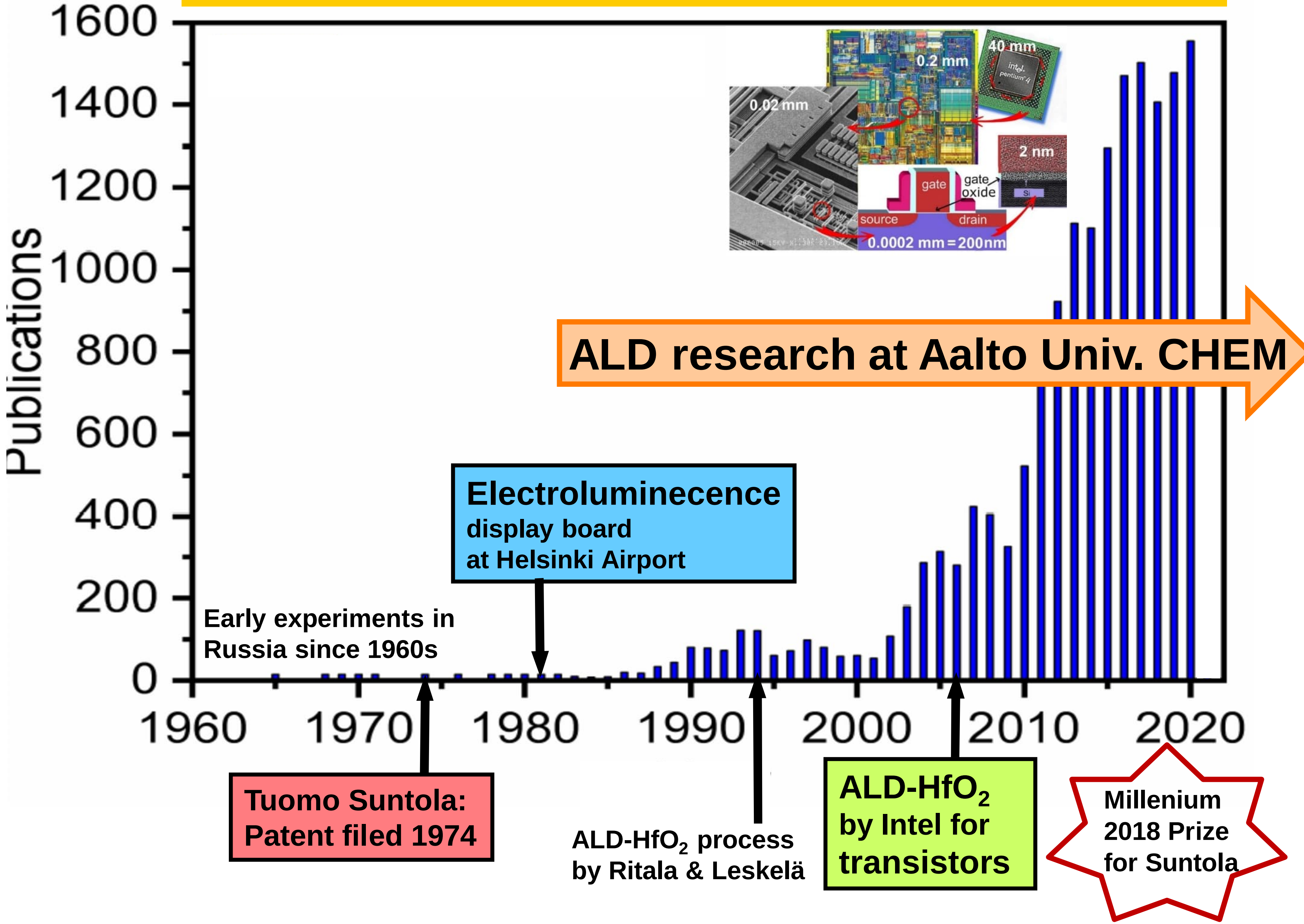
$HfCl_4 + H_2O$

ALD cycle



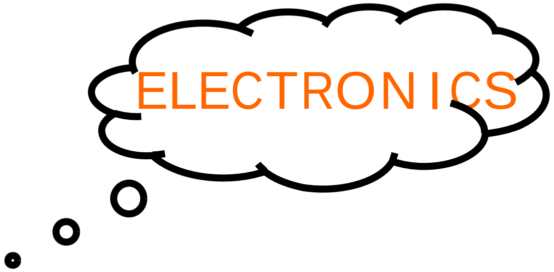


ALD publications annually

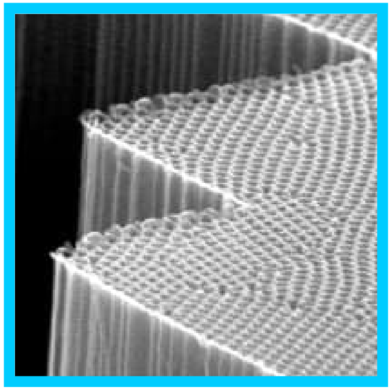


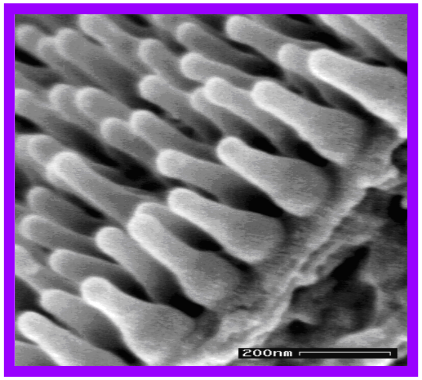
Advantages of ALD

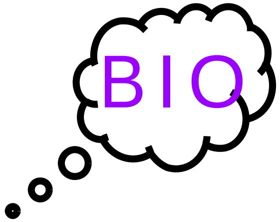
- Relatively inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Large area uniformity
- Easy doping



- Excellent conformality

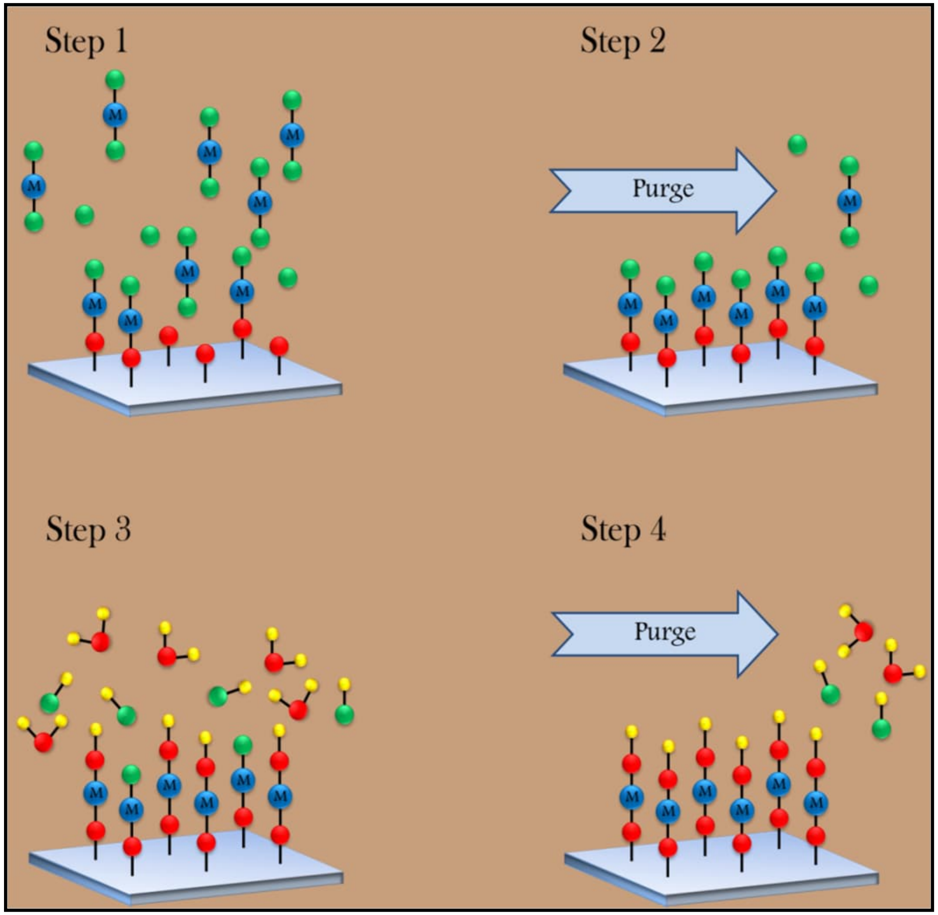




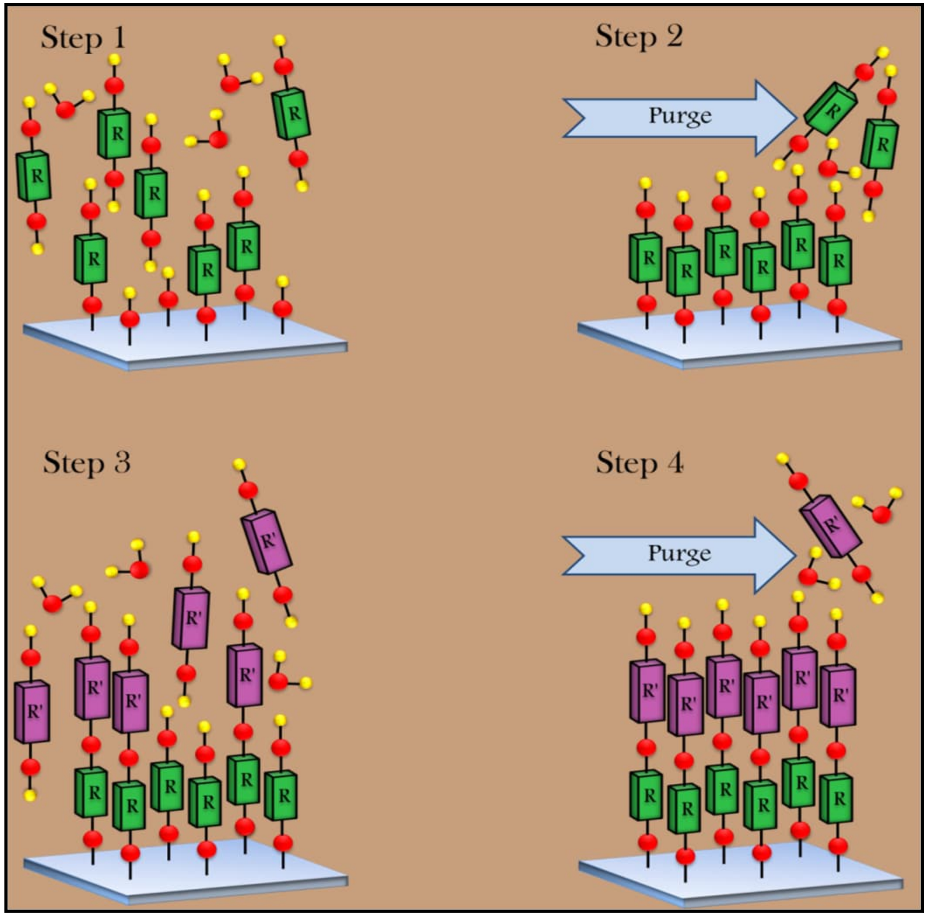


- Low deposition temperature
- Gentle deposition process

- Organic/polymer films
- Inorganic/organic hybrid materials



ALD **(Atomic Layer Deposition)**



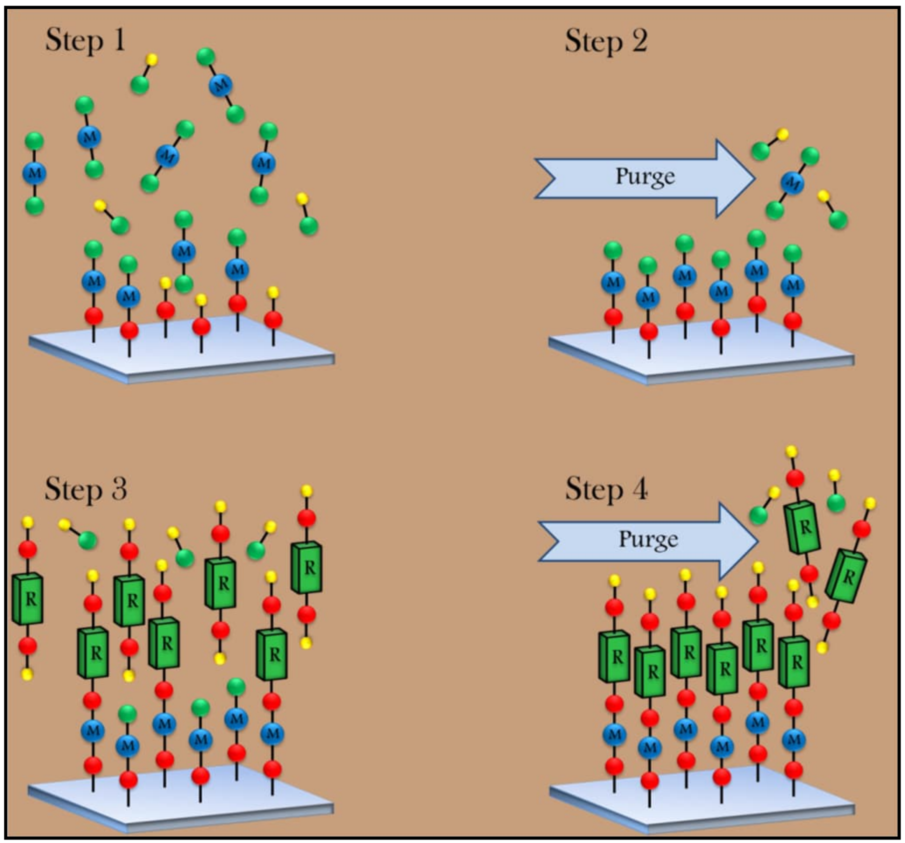
MLD **(Molecular Layer Deposition)**

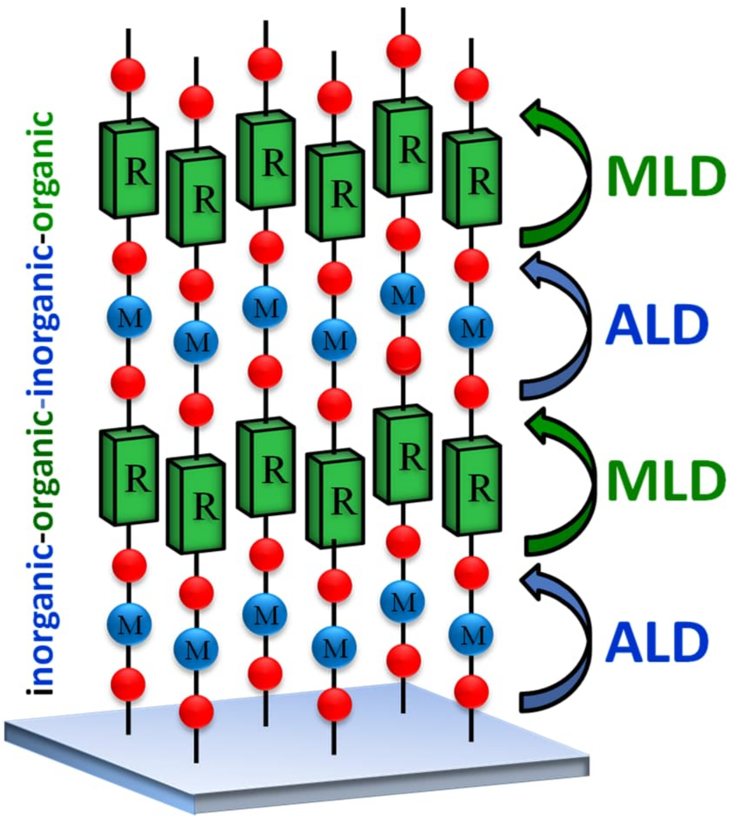
High-quality
INORGANIC thin films
with atomic level control

ORGANICS !

(in 1990s)

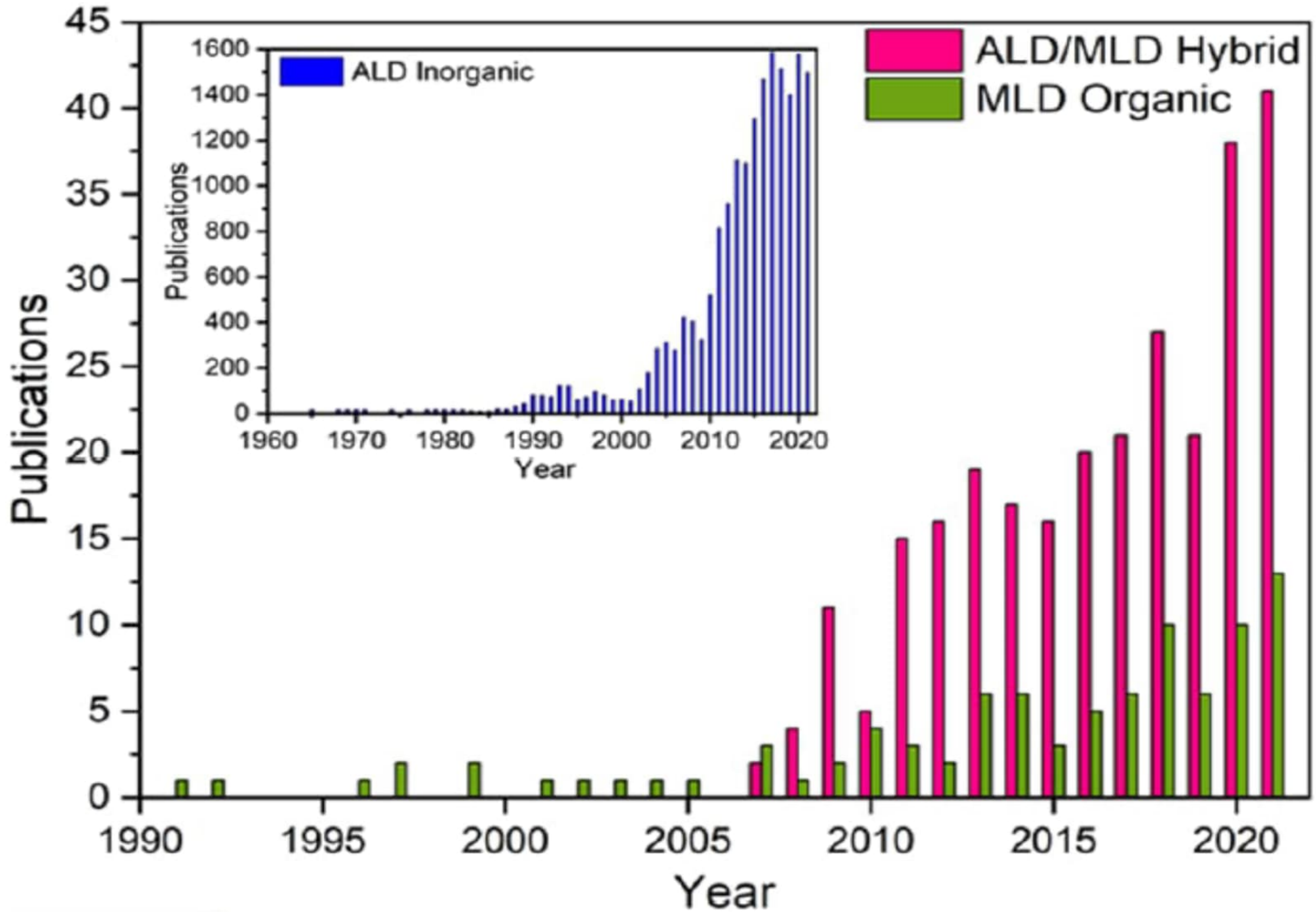
Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD





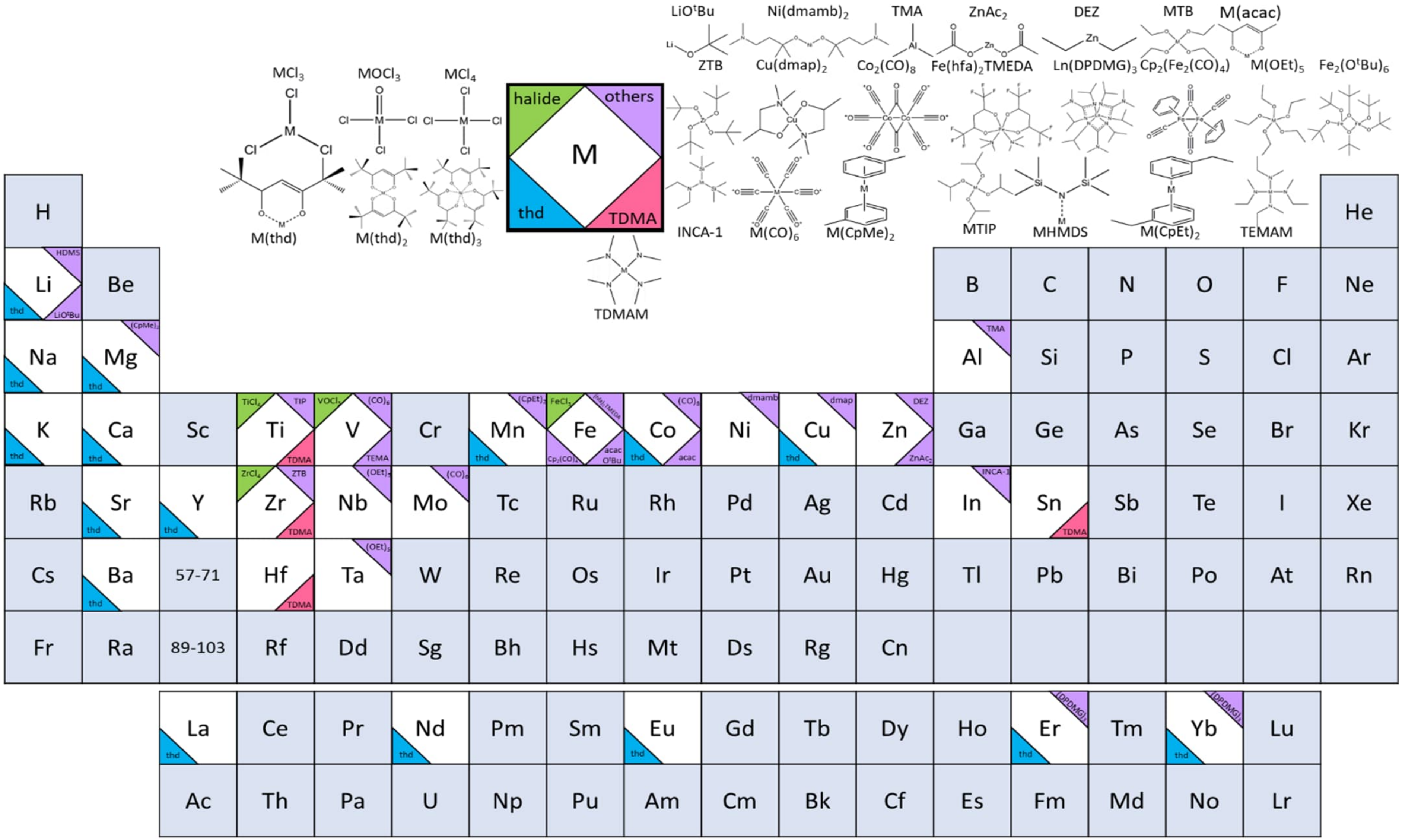
MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!

Annually published papers: MLD & ALD/MLD



Yoshimura, Tatsuura & Sotoyama, *Appl. Phys. Lett.* **1991,** *59,* 482.
Yoshimura, Tatsuura, Sotoyama, Matsuura & Hayano, *Appl. Phys. Lett.* **1992,** *60,* 268.
Lee, Ryu, Choi, Lee, Im & Sung, *J. Am. Chem. Soc.* **2007,** *129,* 16034.
Smirnov, Zemtsova, Belikov, Zheldakov, Morozov, Polyachonok & Aleskovskii, *Dokl. Phys. Chem.* **2007,** *413,* 95.
Nilsen, Klepper, Nielsen & Fjellvåg, *ECS Trans.* **2008,** *16,* 3.
Dameron, Seghete, Burton, Davidson, Cavanagh, Bertrand & George, *Chem. Mater.* **2008,** *20,* 3315.

J. Multia & M. Karppinen, Atomic/molecular layer deposition for designer's functional metal-organic materials, ***Applied Materials Interfaces*** 9, 202200210 (**2022**).



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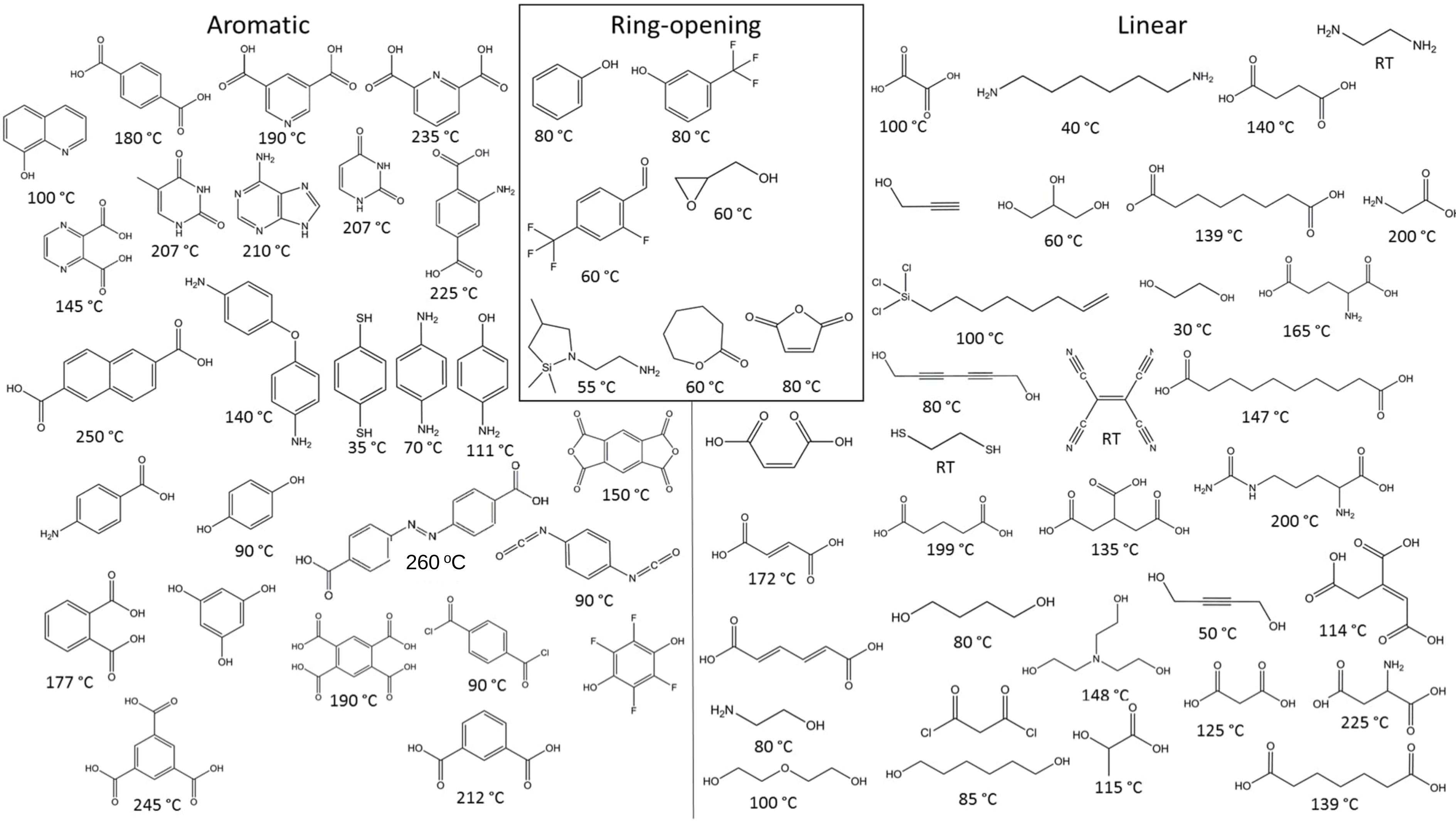
ALD/MLD Processes: Metal Precursors



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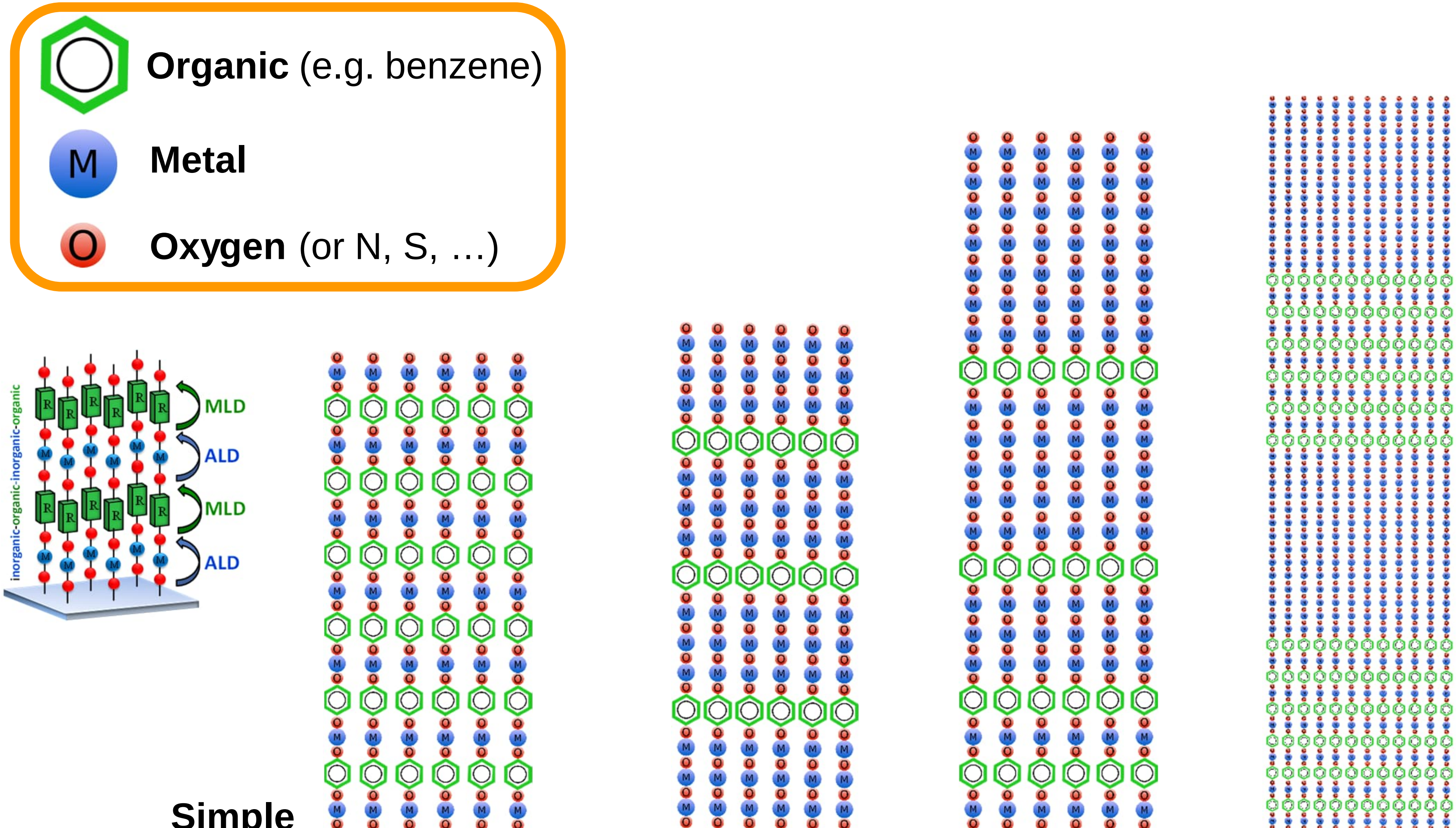
ALD/MLD Processes: Organic Precursors

(with temperatures used for evaporation)



Simple
Metal-Organic Network
(amorphous or crystalline)

Superlattice

Gradient hybrid

Nanolaminate

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DIFFERENT LAYER SEQUENCES BY DESIGN

LAYER-ENGINEERED

INORGANIC-ORGANIC SUPERLATTICES

BY

ALD/MLD

A!
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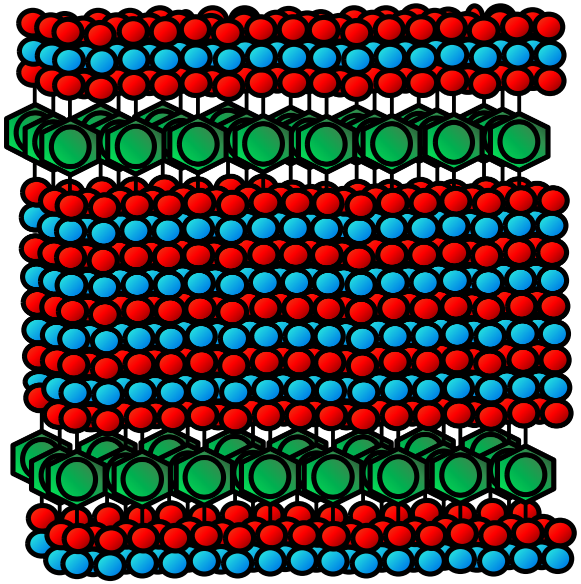
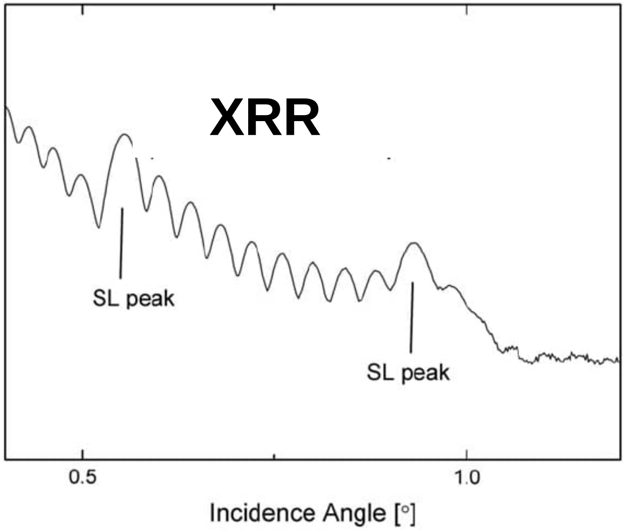
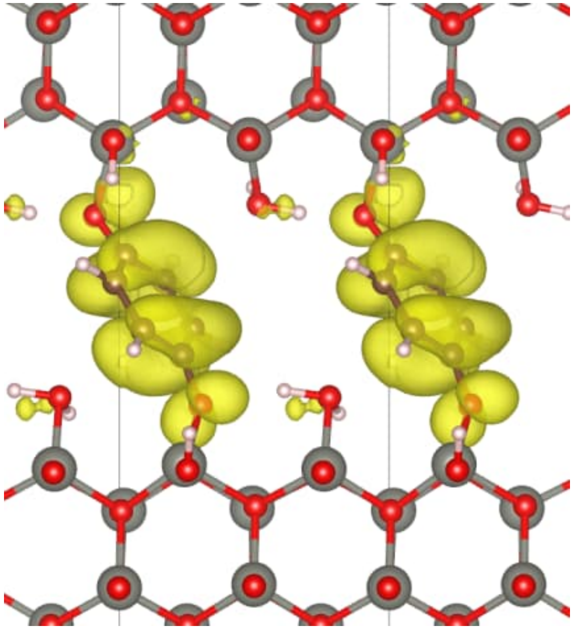
ZnO:benzene SUPERLATTICE



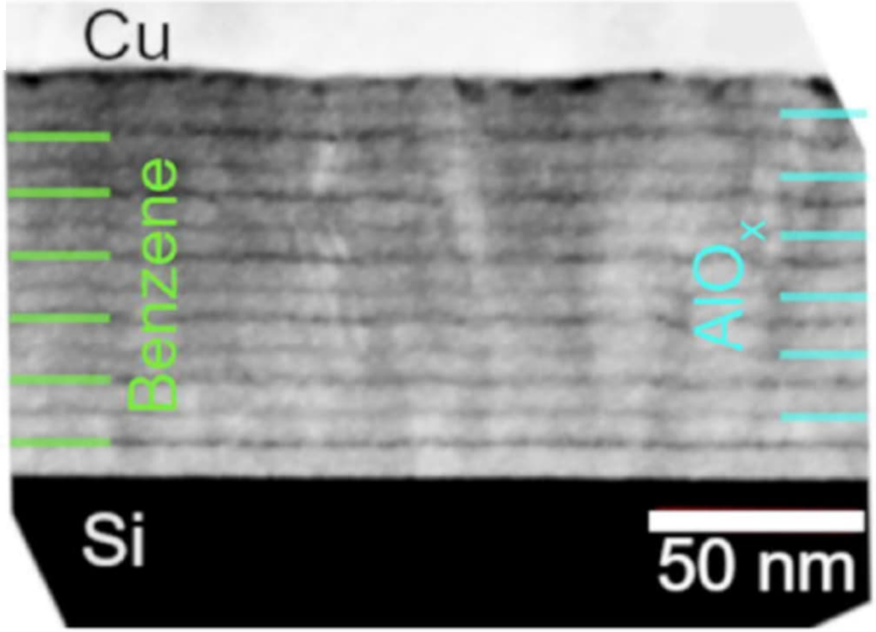


DFT Modelling

A.J. Karttunen, T. Tynell & M. Karppinen, *J. Phys. Chem. C* **119**, 13105 (2015).



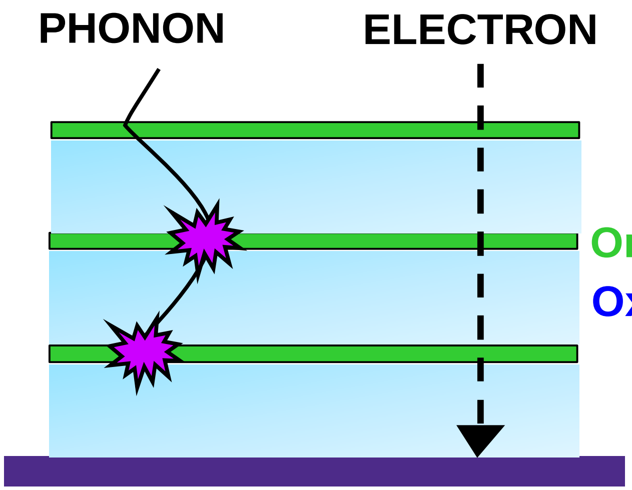
HR-TEM

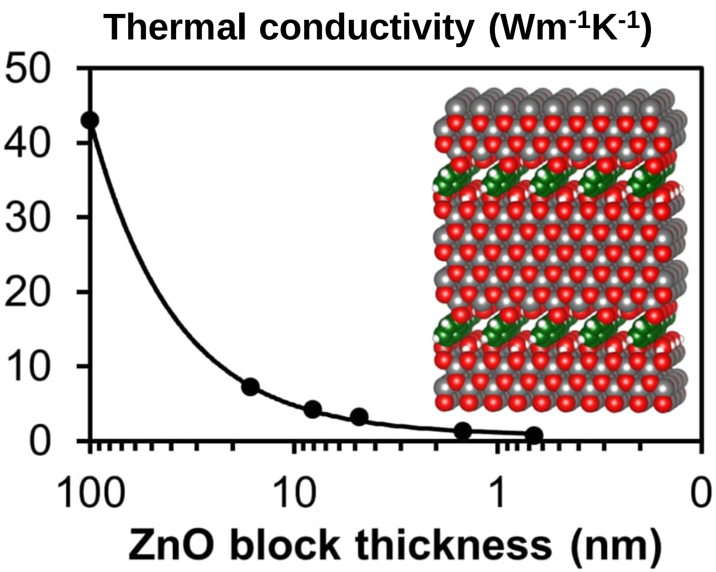


F. Krahl, Y. Ge & M. Karppinen, *Semicond. Sci. Technol.* **36**, 025012 (2020)

Mutually Contradictory Properties:
High electrical conductivity & Low thermal conductivity

- Thermal conductivity (κ) is important: thermal barriers, thermoelectrics, etc.
- Interfaces in the form of superlattice: metal oxide layers & organic layers
- Proof-of-concept data: ZnO:benzene in a scale of 1 ~ 20 nm for Zn
- Massive reduction in thermal conductivity: 43 → 0.7 W m^{-1} K^{-1}





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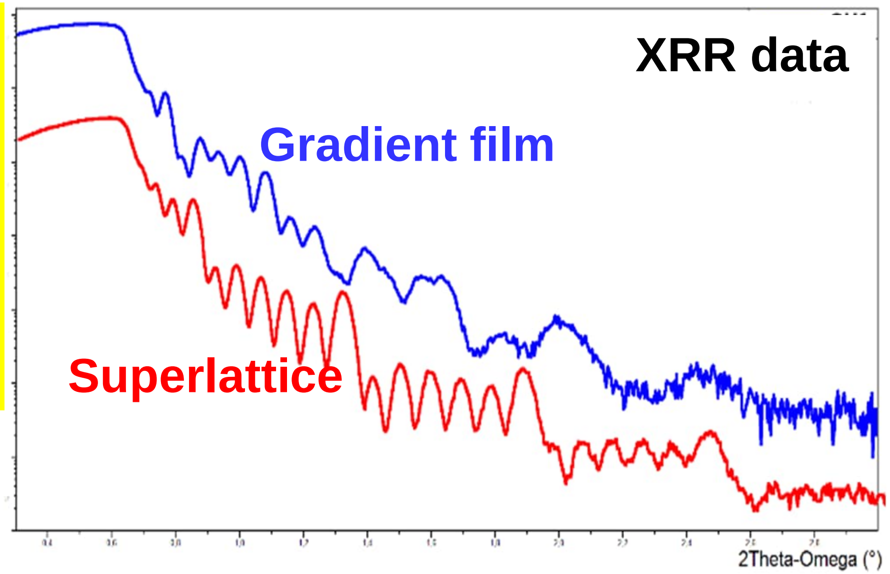
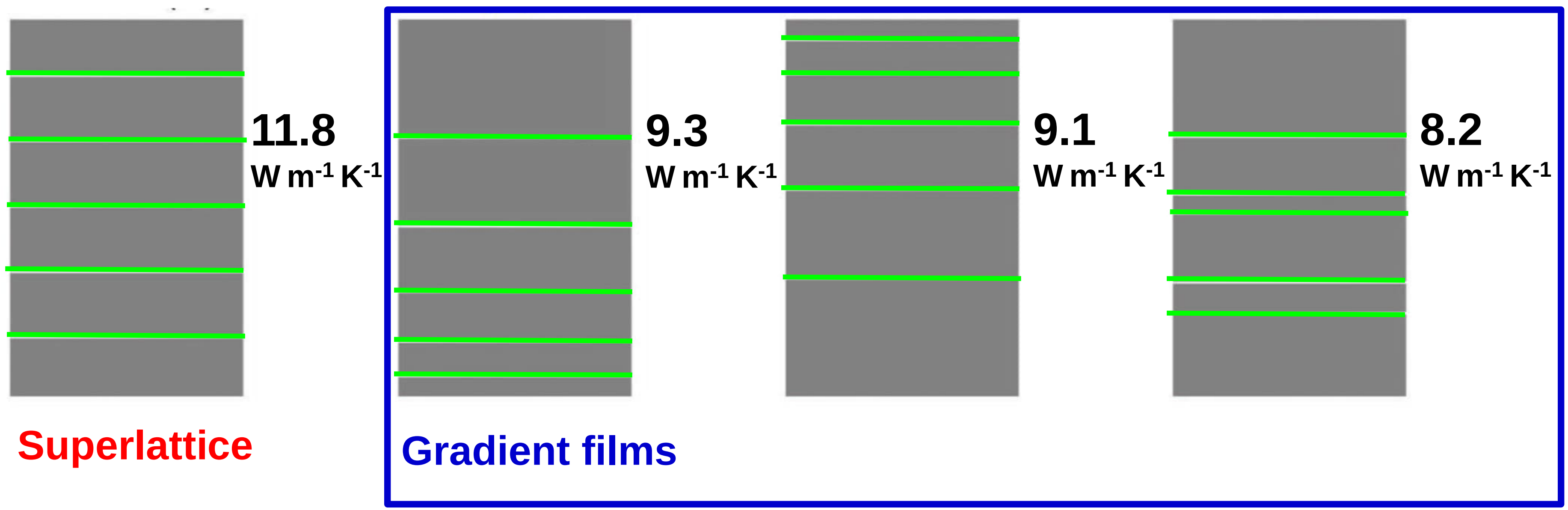
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, ***J. Mater. Chem. A* 2**, 12150 (2014).

Total film thickness: ~105 nm
Number of organic layers: 5
Average ZnO layer thickness: ~17 nm

Superlattice: all ZnO layers ~17 nm
Gradient film: ZnO layers 9 ~ 28 nm





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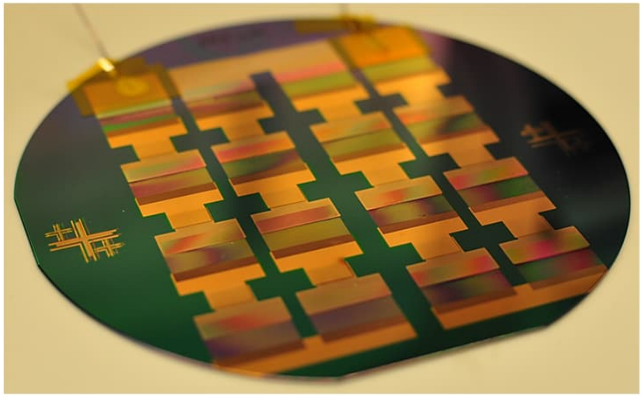
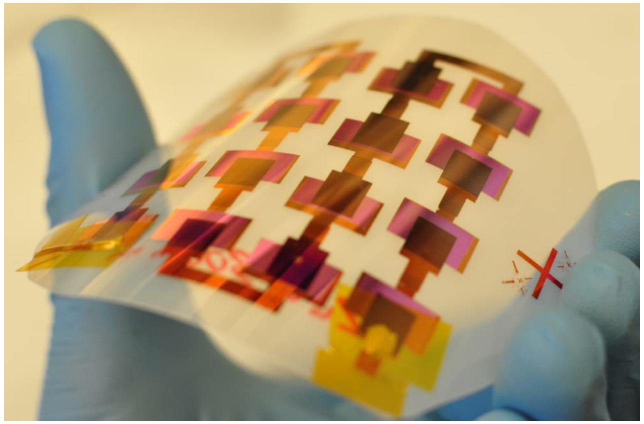
F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen,
Thermal conductivity reduction at inorganic-organic interfaces:
from regular superlattices to irregular gradient layer sequences,
Adv. Mater. Interfaces **5**, 1701692 (2018).

THERMOELECTRIC MODULE

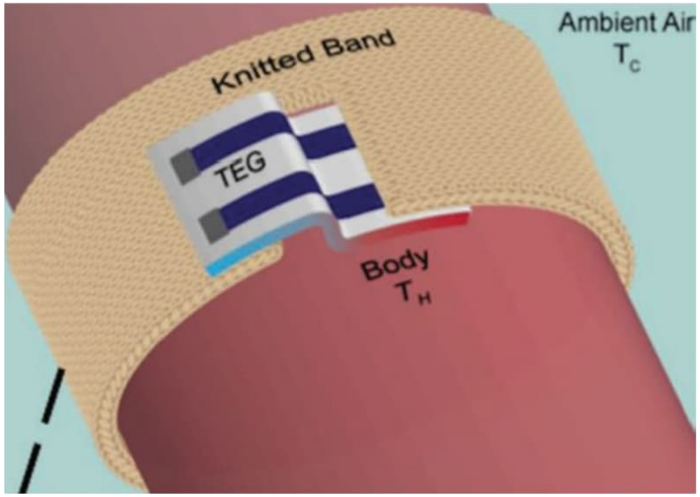
Silicon

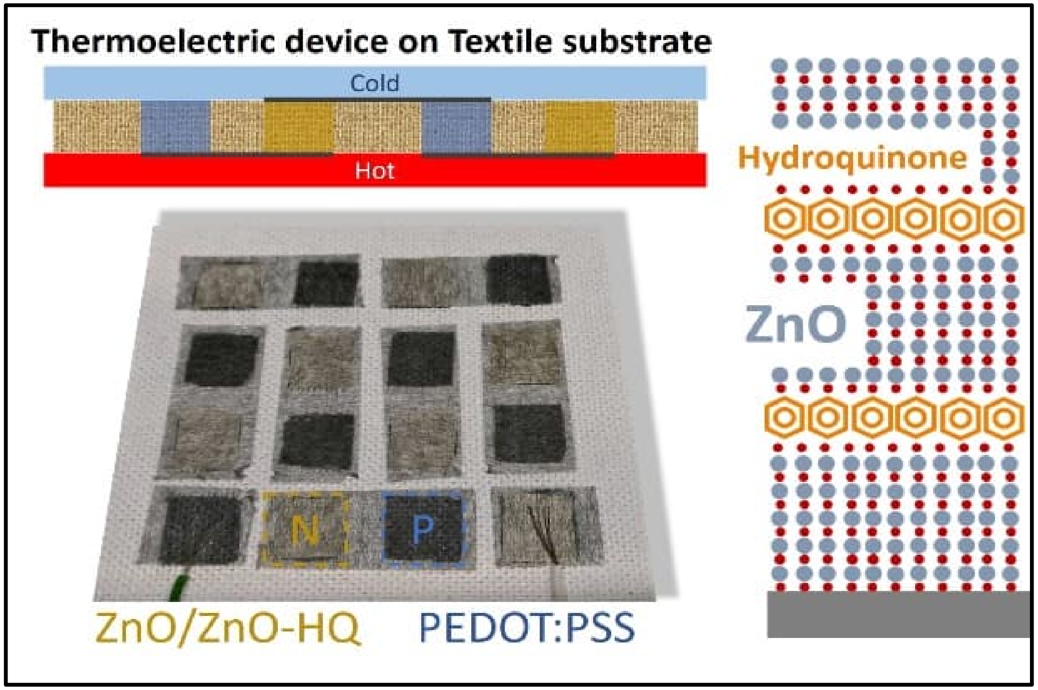


Plastics



Textile





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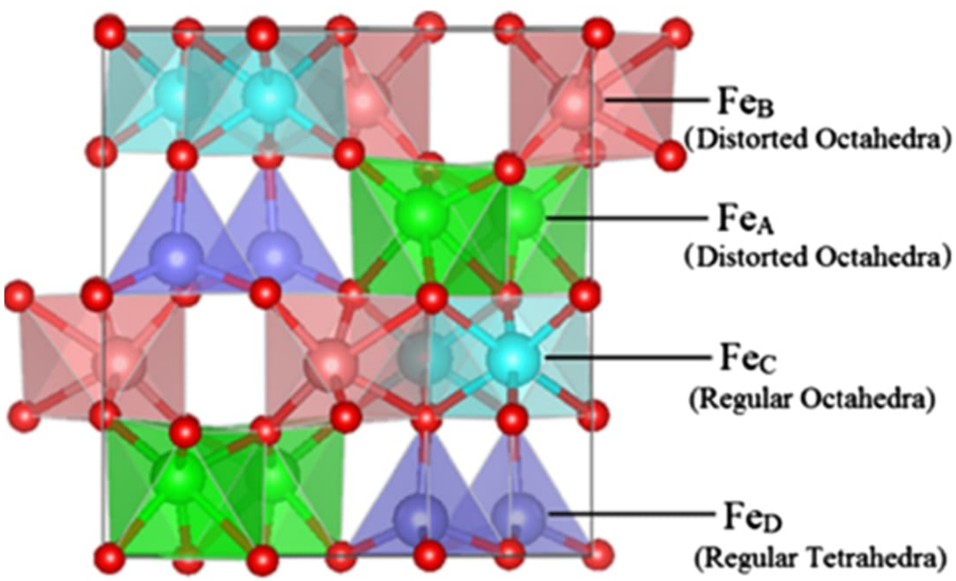
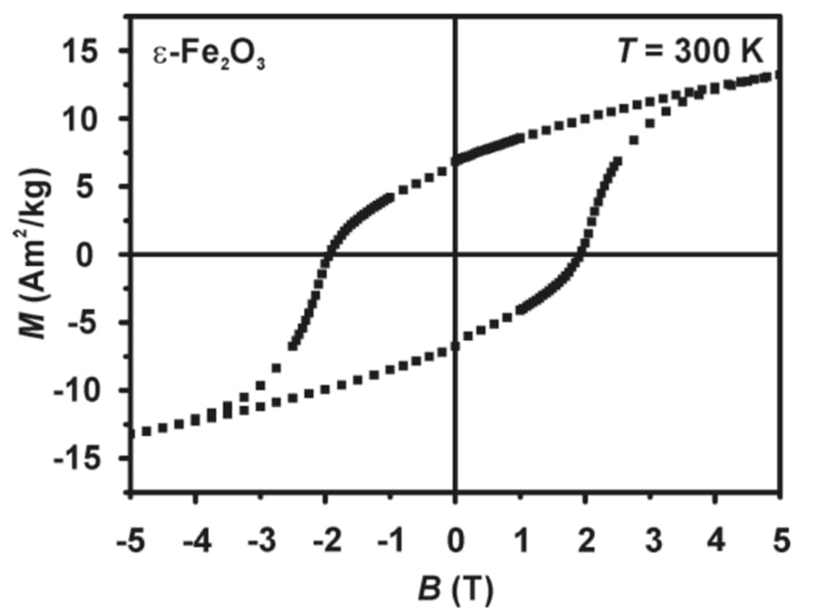
G. Marin, R. Funahashi & M. Karppinen,
Textile-integrated ZnO-based thermoelectric device using atomic layer deposition, *Advanced Engineering Materials* **22**, 2000535 (2020).

Extraordinary Property Combination: Mechanically flexible hard magnet ε-Fe_2O_3:organics

- ε-Fe_2O_3 is the rarest of the iron(III) oxide polymorfs
- Critical-raw-material-free
- RT ferrimagnet ($T_C \approx 490$ K)
- Colossal coercive field
- Magnetoelectric
- PROBLEM: stabilized/synthesized in nano-scale amounts only

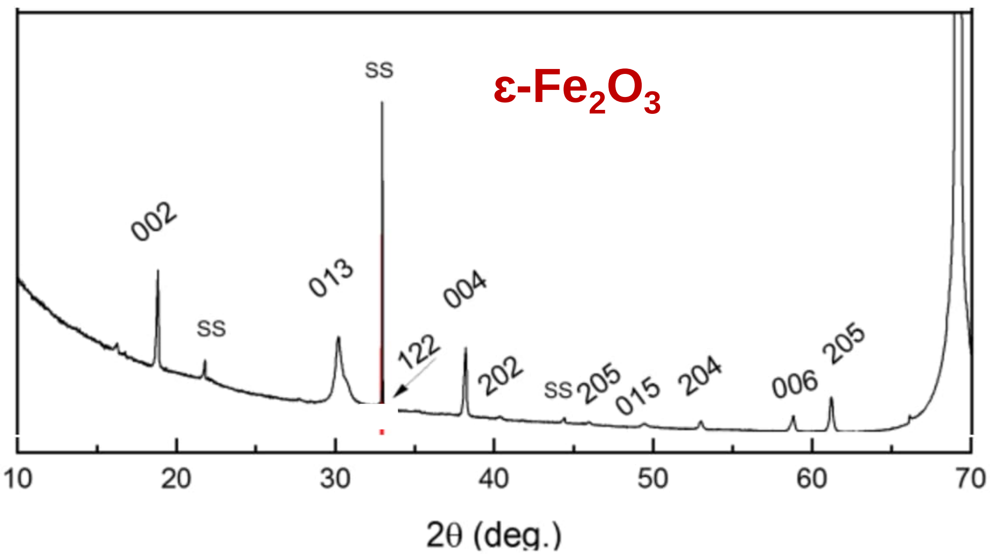


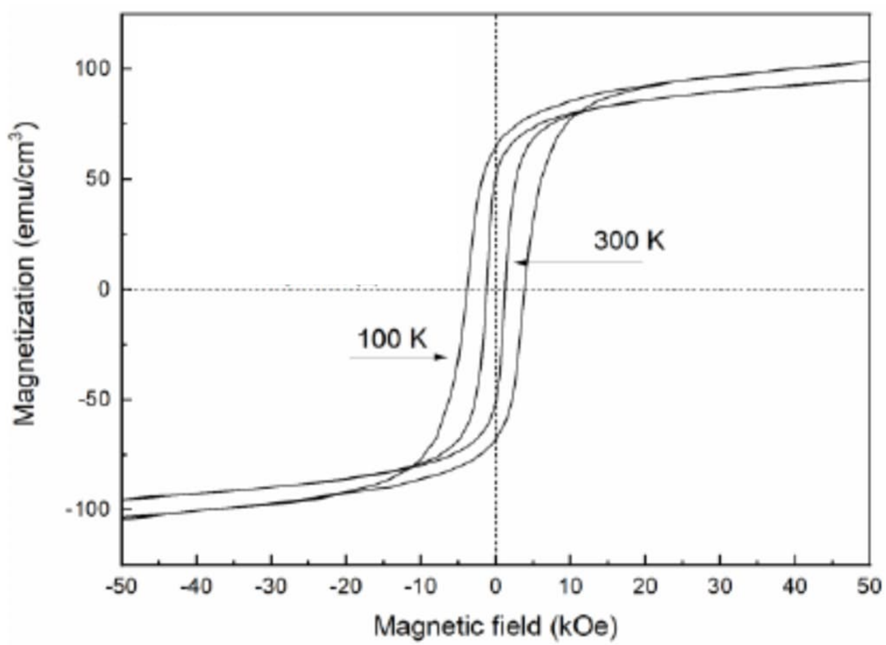


Facile ALD process for stable ε-Fe_2O_3 thin films

- **Just "most common" precursors: $FeCl_3$ & H_2O**
- **Deposition temperature: 280 ºC**
- **Substrate: silicon, flexible glass, Kapton, polyimide, etc.**

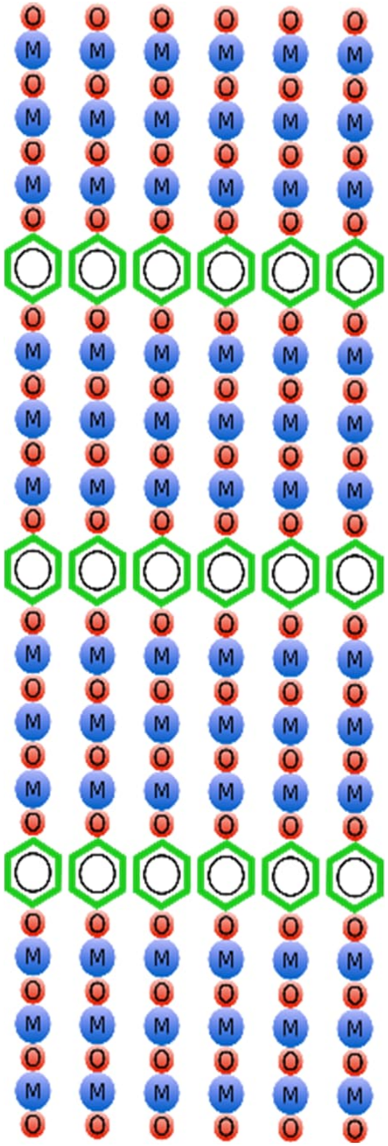
ALD: large-area homogeneity & conformality over porous templates → "MASS production"



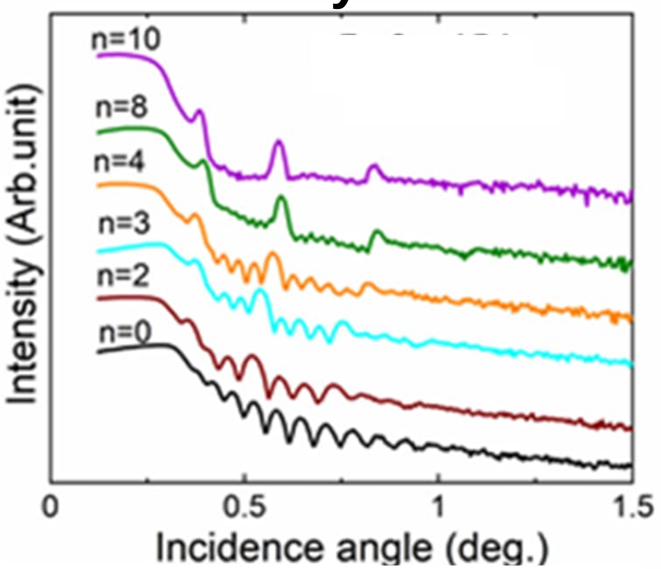


A. Tanskanen, O. Mustonen & M. Karppinen, Simple ALD process for ε-Fe_2O_3 thin films, *APL Materials* **5**, 056104 (2017).

ε-Fe_2O_3:TPA Superlattices (TPA: terephthalic acid)

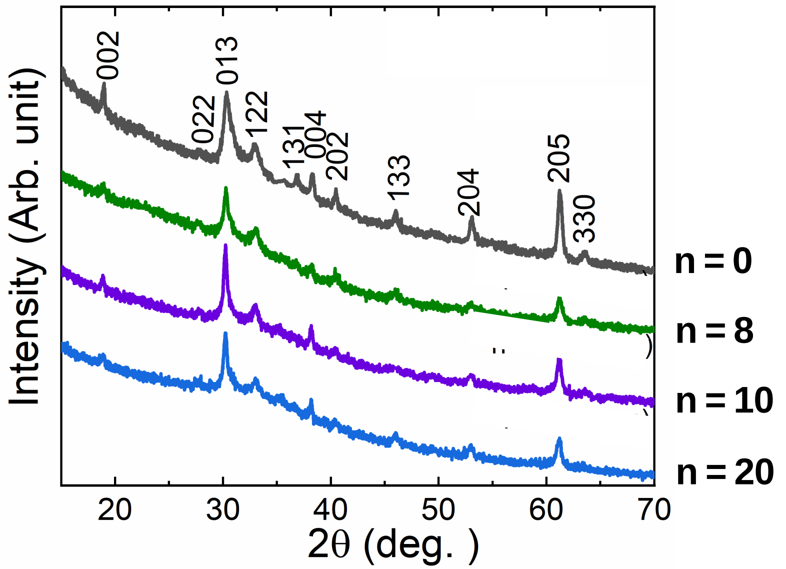


XRR: X-ray reflection

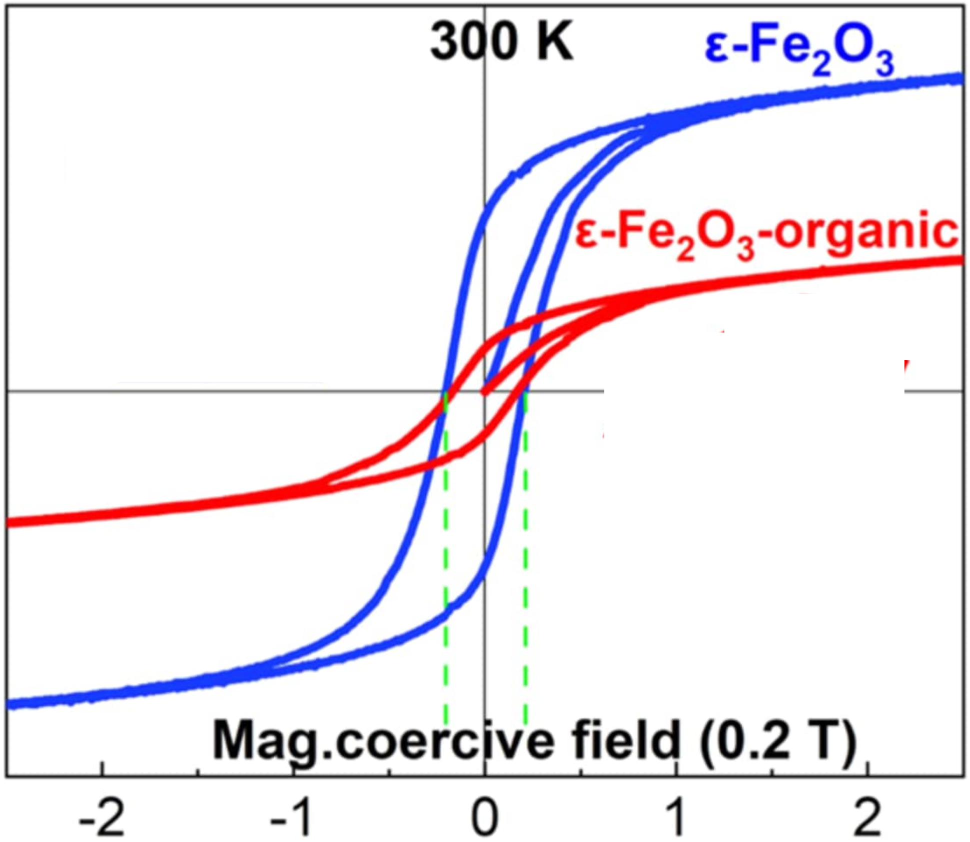


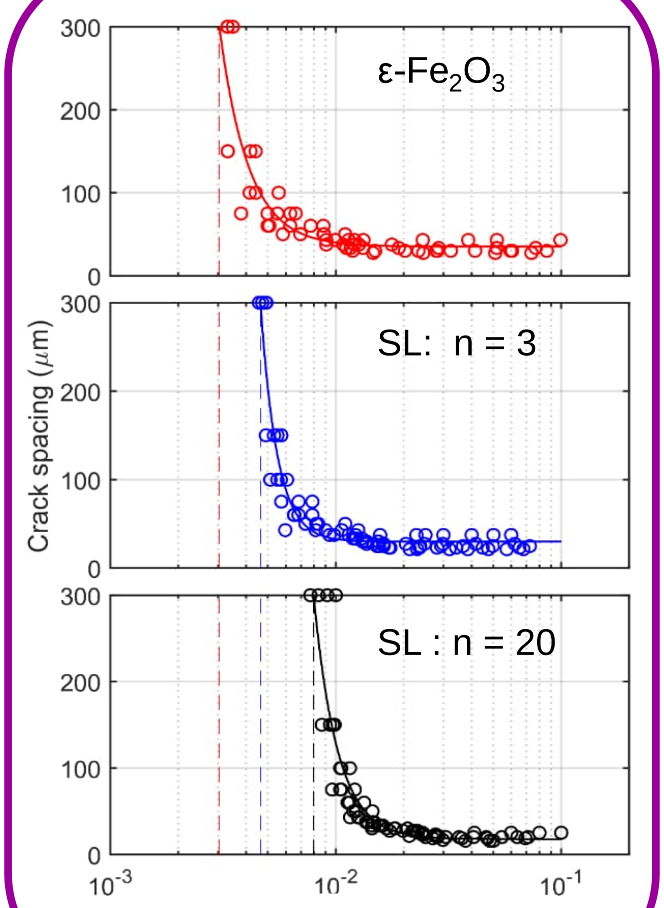
n: number of organic layers

GI-XRD



Mechanical property testing: ε-Fe_2O_3:TPA





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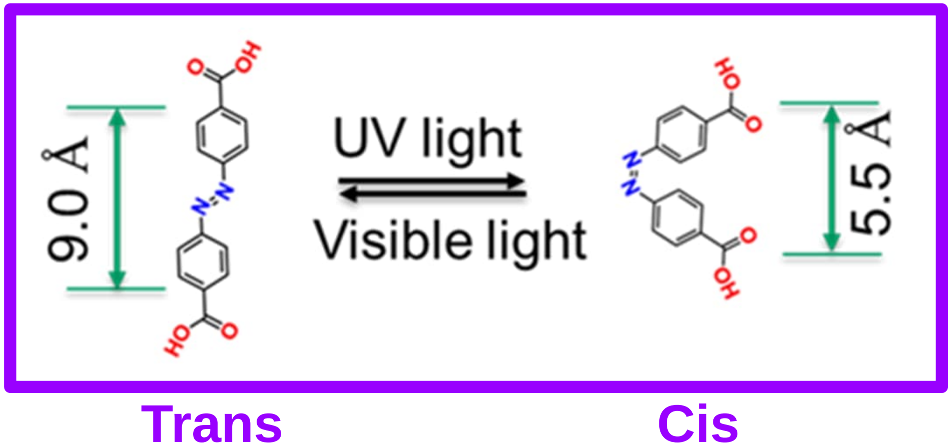
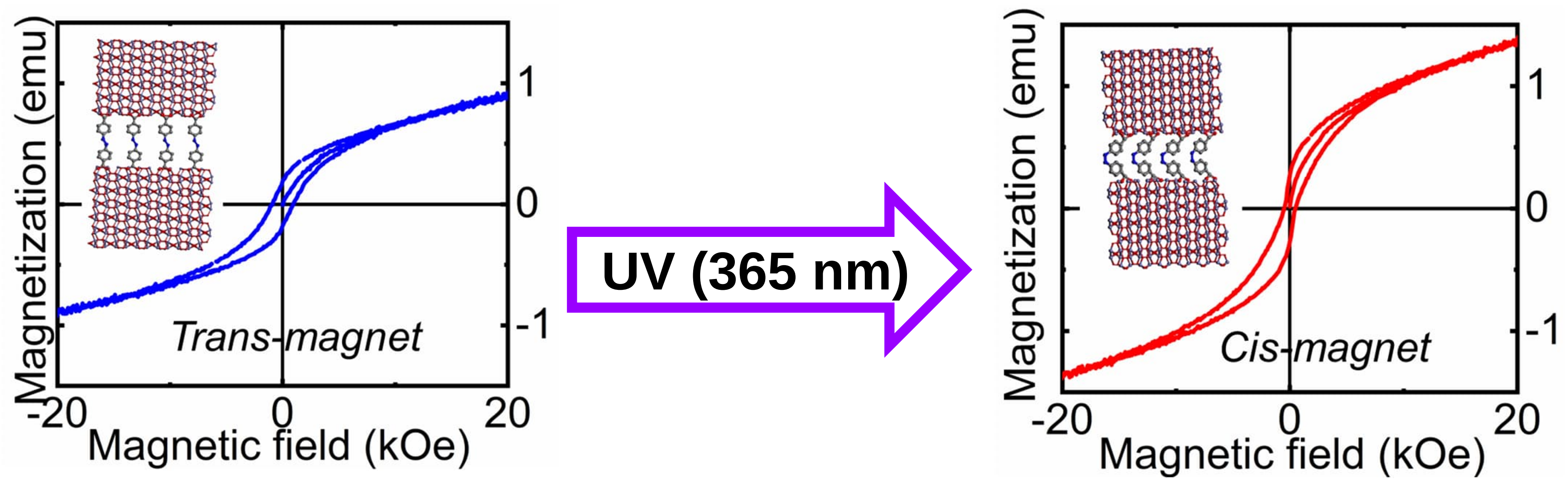
A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

Extraordinary Functionality:

Photoswiched magnetism ε-Fe_2O_3:AZO (AZO = azobenzene)





- **Magnetization (remanent and saturation) increased (doubled)**
- **Coercivity decreased (into half)**

MOFs

METAL-ORGANIC FRAMEWORKS

BY

ALD/MLD

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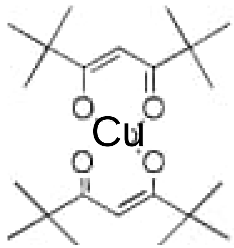
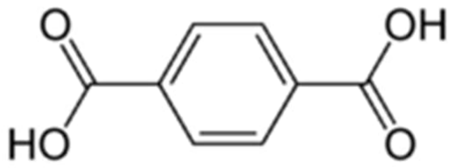
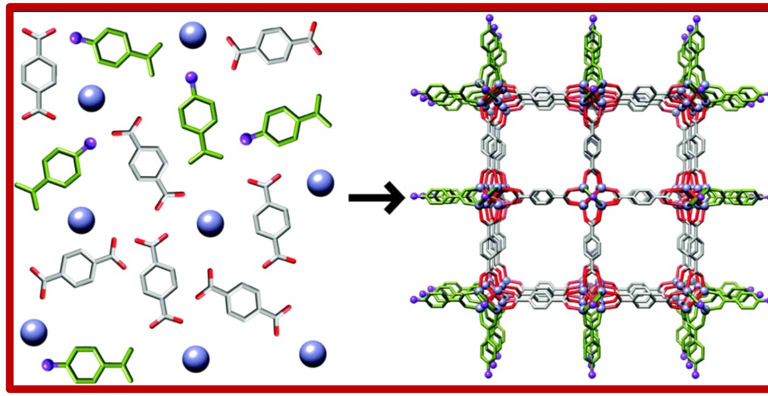


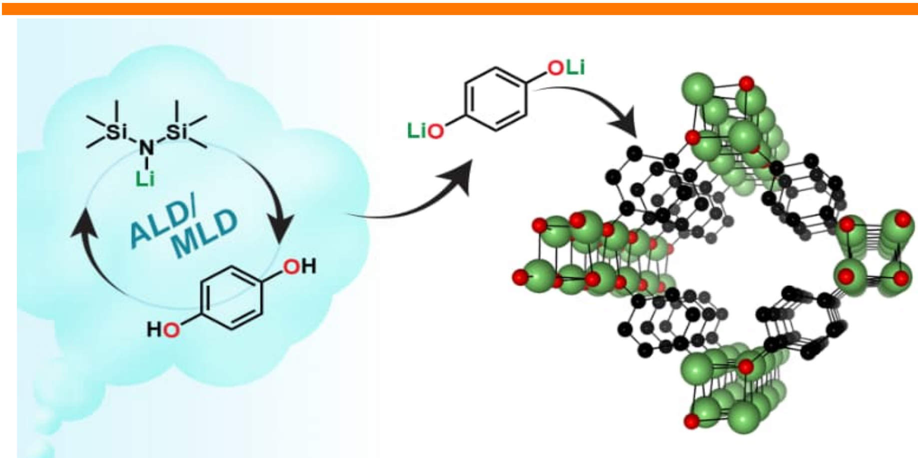


$Cu(thd)_2$ **Terephthalic acid (TPA)**

E. Ahvenniemi & M. Karppinen, Chem. Commun. **52**, 1139 (2016).

Known MOF-2 structure

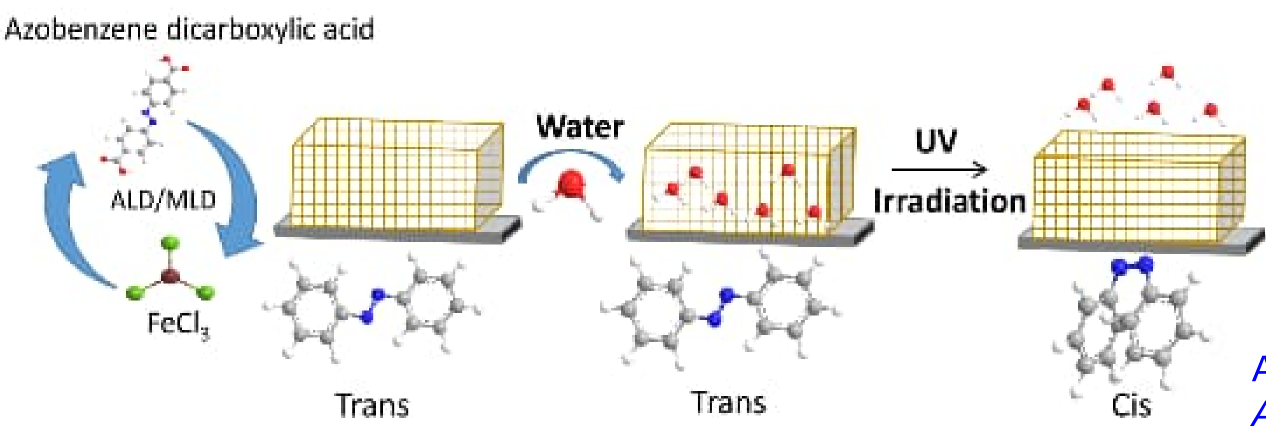




Lithium-benzoquinone

- Previously non-existing material
- Structure predicted by DFT
- Under-coordinated lithium (3-coord.)

M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, *Chem. – Eur. Journal* **23**, 2988 (2017).

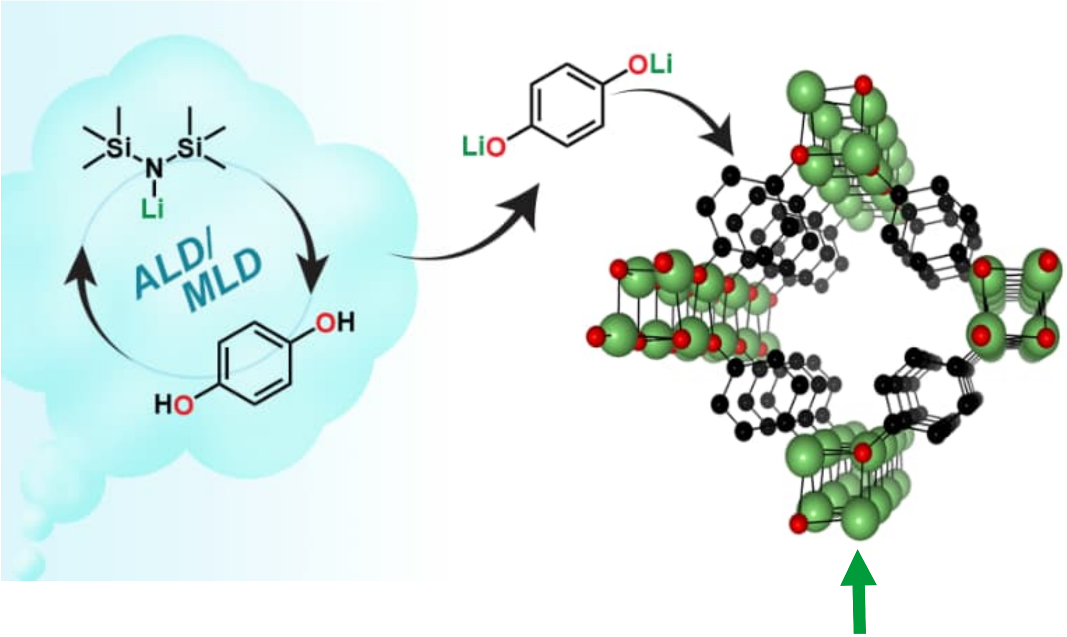


Iron-azobenzoate

- New material
- Structure not yet known
- UV-switchable (cis-trans)

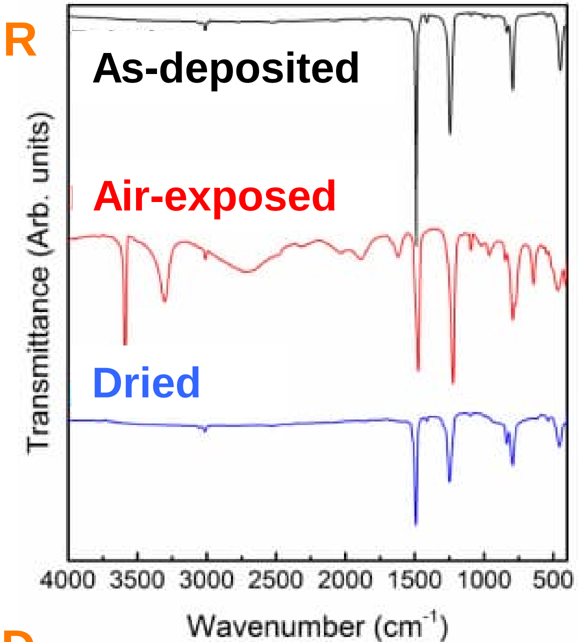
A. Khayyami, A. Philip & M. Karppinen, *Angew. Chem.* **58**, 13400 (2019).

EXAMPLES: In-Situ CRYSTALLINE Metal-Organic films via ALD/MLD

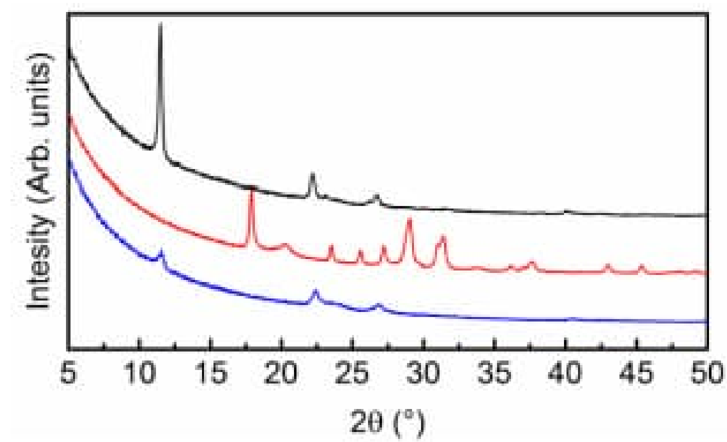


3-coord.
Li-site

FTIR



XRD



Li + Hydroquinone

- **Crystalline films**
- **NOT synthesized by any other technique**
- **Under-coordinated Li-site**
- **Reversible water absorption (gas absorption)**
- **Potential application: Li-ion battery cathode**

Structure predicted by DFT

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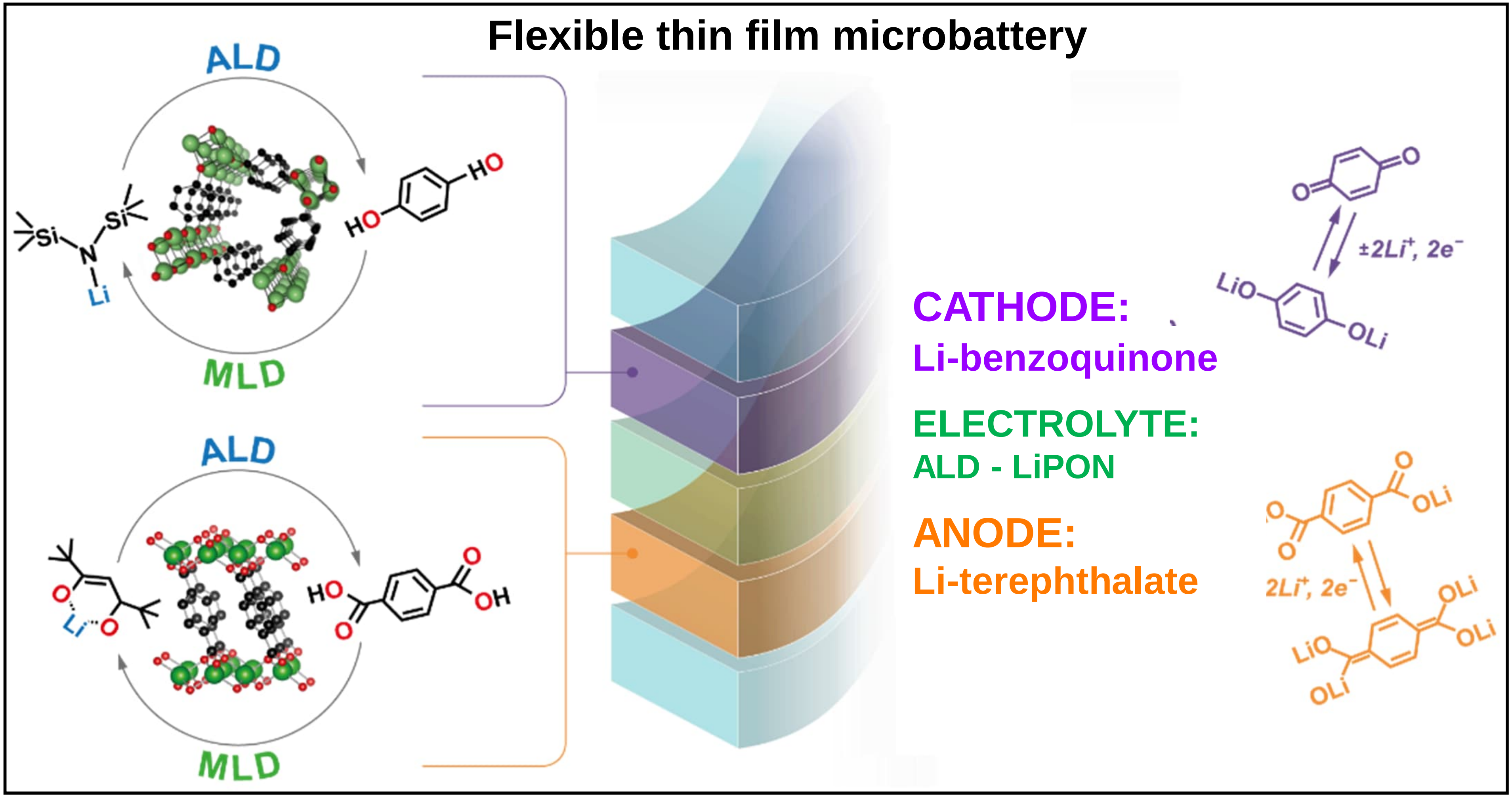
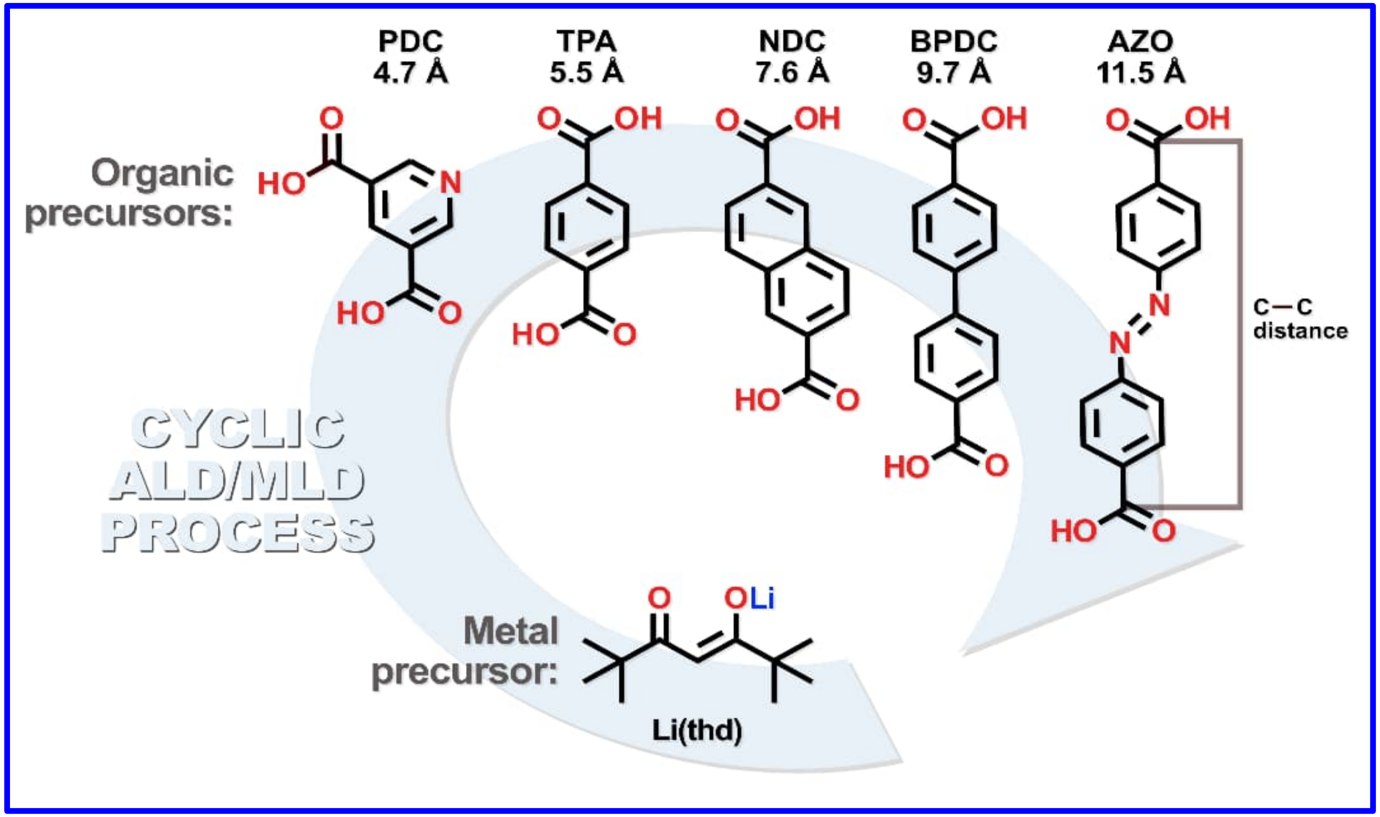
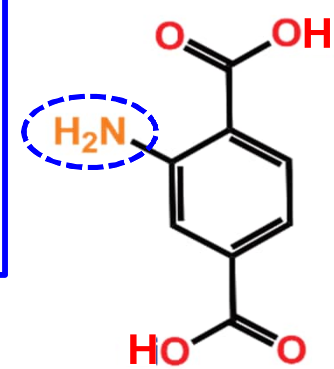
M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chemistry – A European Journal* **23**, 2988 (2017).

ALD + MLD: Metal-saving Li-organic microbattery



ALD/MLD-made Li-organic microbattery is flexible and cobalt-free. It is ultrafast to charge, but the problem is the low energy capacity. Whole battery structure can be deposited active-layer by active-layer in a same reactor, without additives.

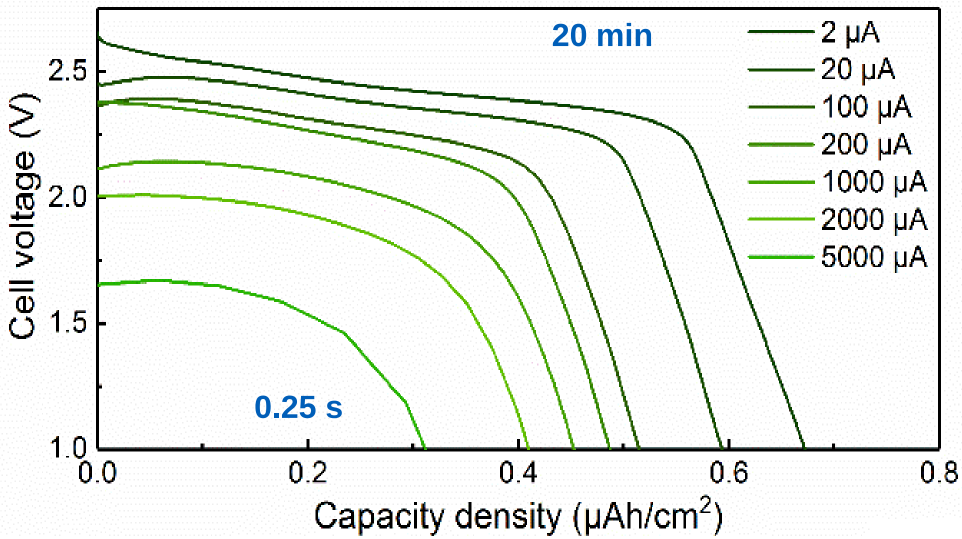


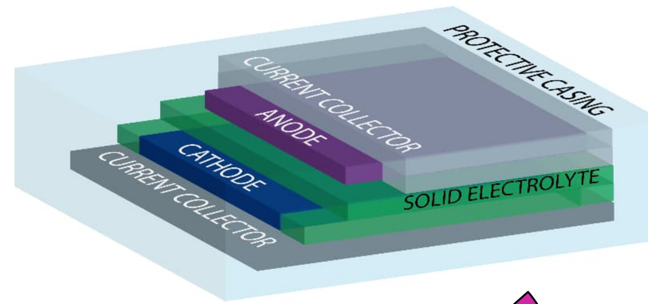


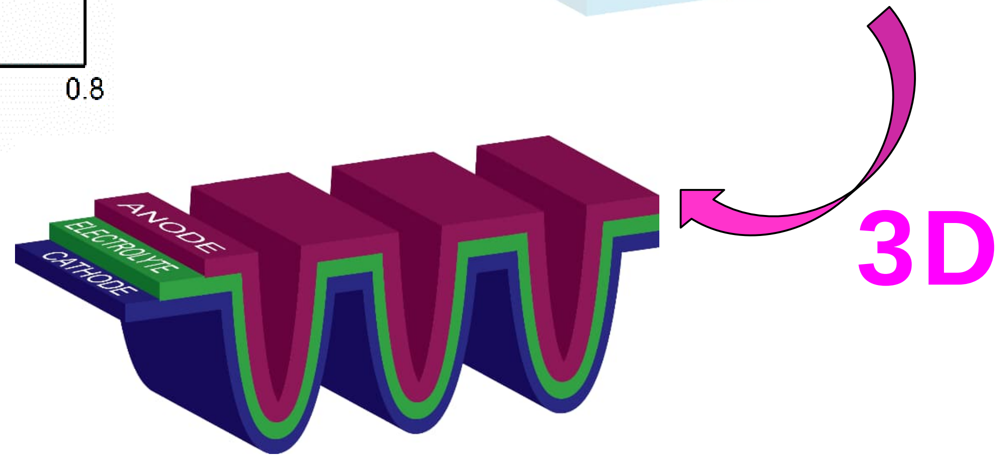
Electron-withdrawing amino group → Redox potential increases

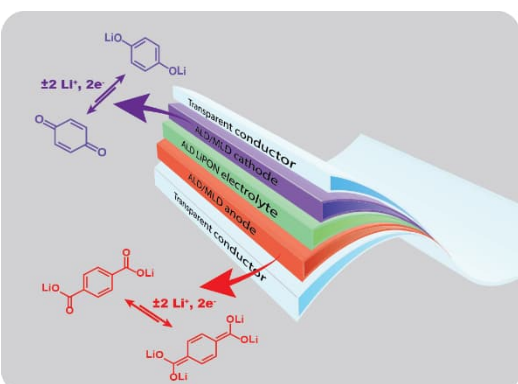
- J. Heiska, M. Nisula, E.-L. Rautama, A.J. Karttunen & M. Karppinen, Atomic/molecular layer deposition and electrochemical performance of dilithium 2-aminoterephthalate, *Dalton Transactions* 49, 1591 (2020).
- J. Multia, J. Heiska, A. Khayyami & M. Karppinen, Electrochemically active in-situ crystalline lithium-organic thin films by ALD/MLD, *ACS Applied Materials & Interfaces* 12, 41557 (2020).

- Charging/discharging: extremely fast
- Power density: ~500 W/cm^3
- Energy density: ~100 mWh/cm^3









HIGH POWER & ENERGY DENSITY

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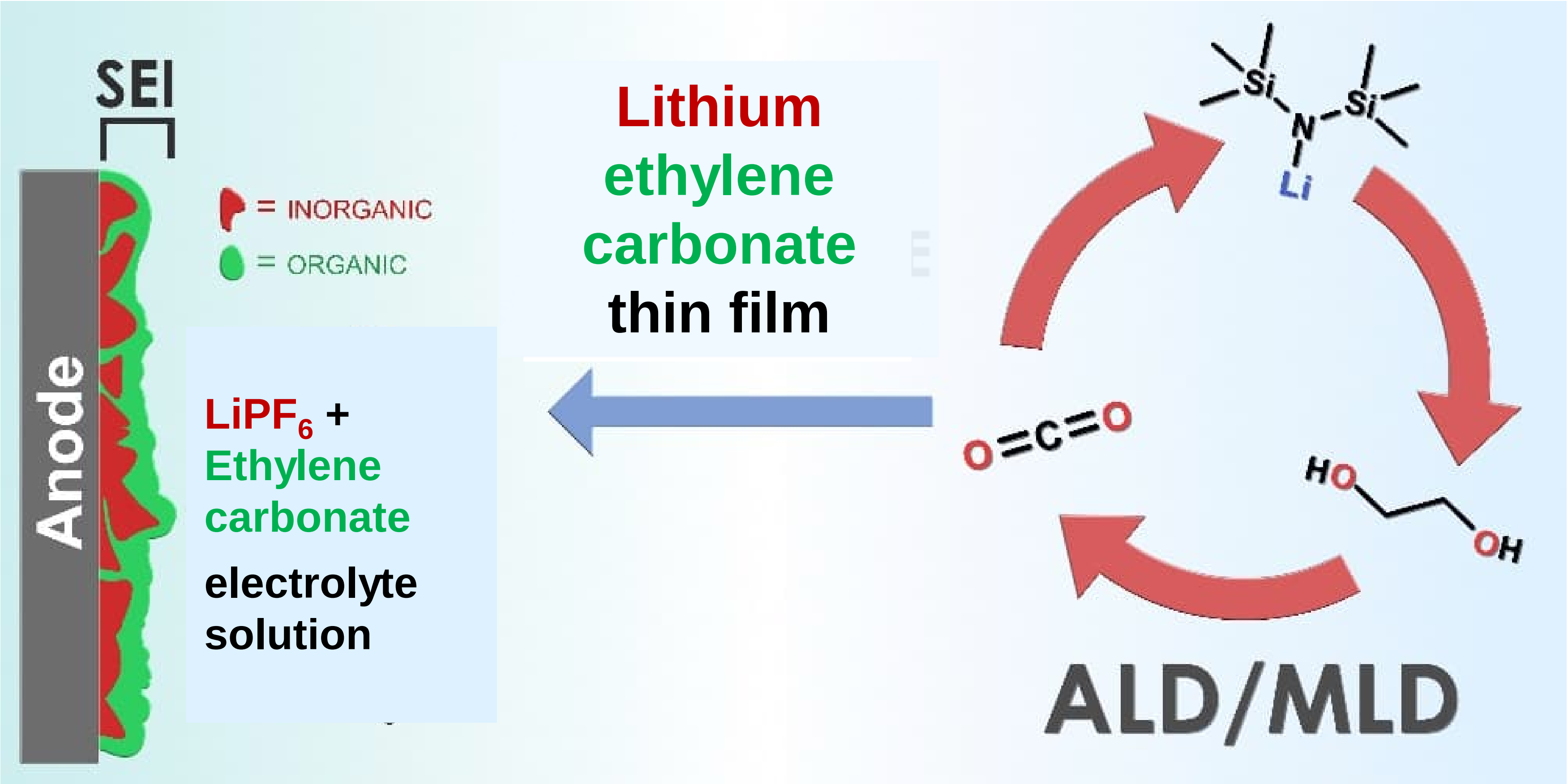
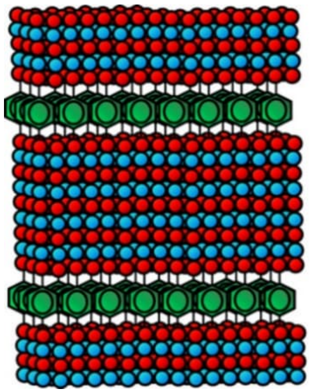
- M. Nisula, Y. Shindo, H. Koga & M. Karppinen, ***Chem. Mater.*** 27, 6987 **(2015)**.
- M. Nisula & M. Karppinen, ***Nano Lett.*** 16, 1276 **(2016).**
- M. Nisula & M. Karppinen, ***J. Mater. Chem. A*** 6, 7027 **(2018)**.
- J. Heiska, M. Nisula & M. Karppinen, ***J. Mater. Chem. A*** 7, 18735 **(2019).**

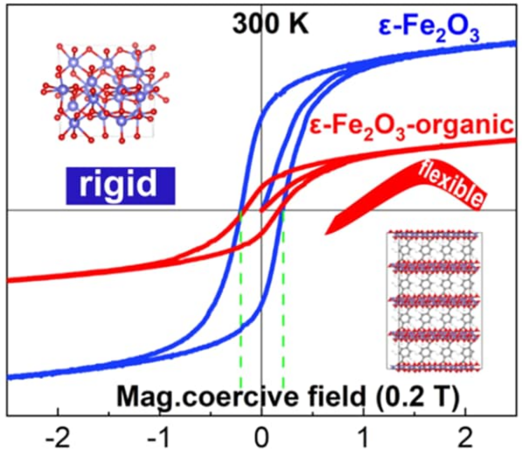
ALD + MLD: Artificial SEI-layer for Li-ion battery

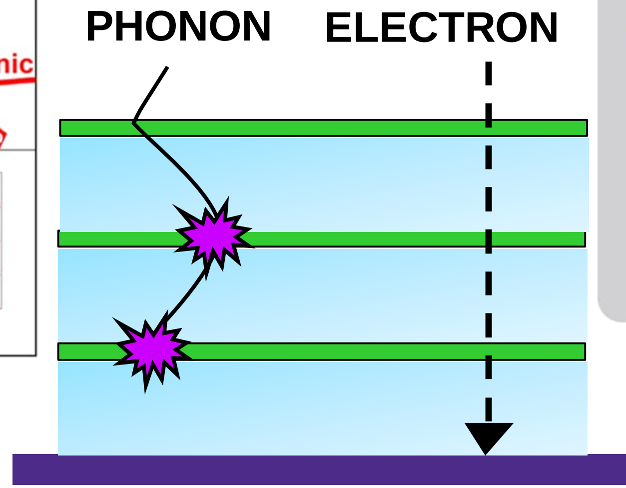


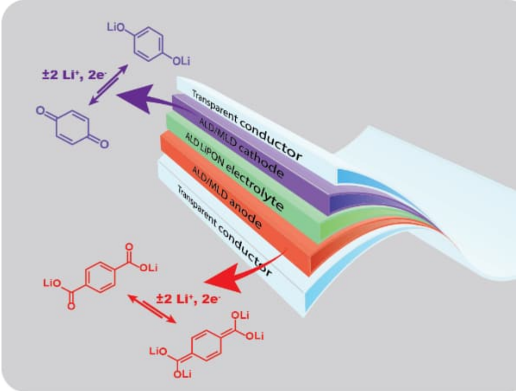
SEI (Solid Electrolyte Interphase)

- SEI-layer forms naturally/unavoidably upon charging/discharging on top of the anode surface due to the unwanted reactions between anode and liquid electrolyte
- SEI protects the anode from further reactions (requirement: homogeneous and pinhole-free), but it consumes Li-ions when it forms
- ALD/MLD: high-quality artificial barrier coating which esembles the natural SEI layer

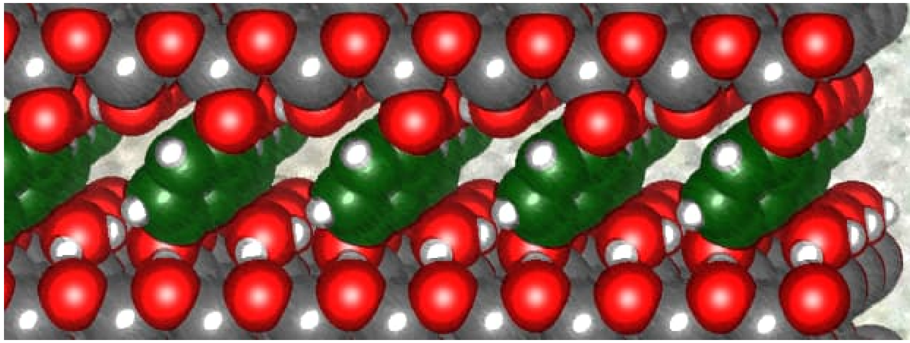


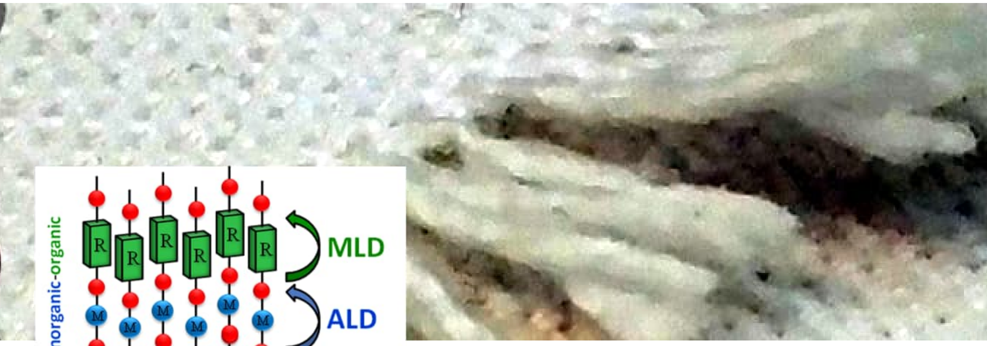


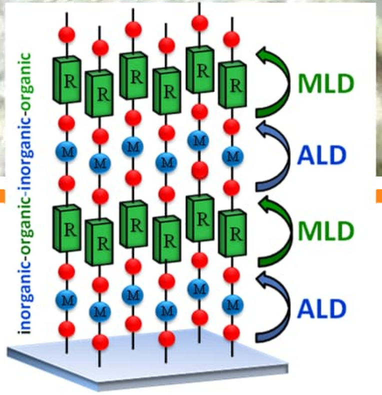




- **ALD/MLD can yield various new types of hybrid materials: new MOFs & layer-engineered superlattice and gradient materials**
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties have been discovered and much more expected !!!**







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