Functional Inorganic Materials
Fall 2021

Tuesdays: 14.15 - 16.00
Thursdays: 12.15 - 14.00
Remote Zoom lectures

#	Date	Who	Topic
1	Tue 02.11.	Maarit	Introduction + Materials design
2	Thu 04.11.	Antti	Computational materials design
3	Tue 09.11.	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 11.11.	Maarit	Ionic conductivity (Oxygen): SOFC and Oxygen storage
5	Tue 16.11.	Maarit	Ionic conductivity (Lithium & Proton): Li-ion battery
6	Thu 18.11.	Antti	Thermal conductivity
7	Tue 23.11.	Antti	Thermoelectricity
8	**Thu 25.11.**	**Maarit**	**Hybrid materials**
9	Tue 30.11.	Maarit	Luminescence and optically active materials
10	Thu 02.12.	Antti	Piezoelectricity
11	Tue 07.12.	Antti	Pyroelectricity and ferroelectricity
12	Thu 09.12.	Antti	Magnetic and multiferroic oxides

LECTURE 8: Hybrid Materials

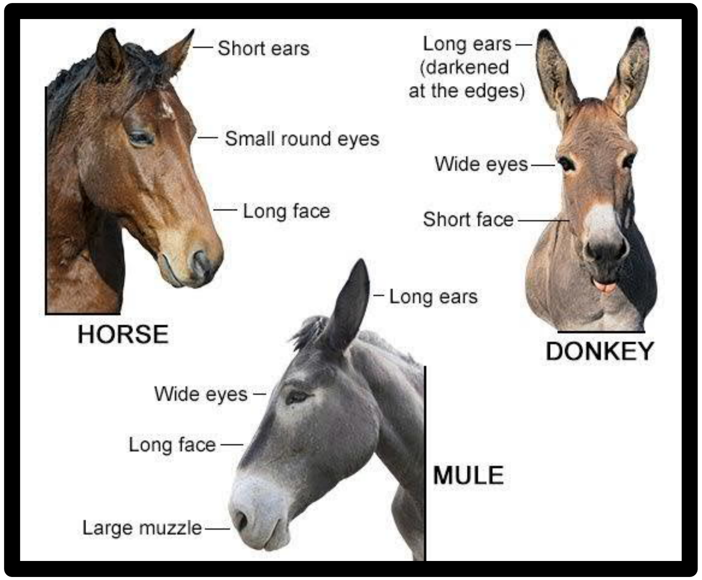
- ❖ **Inorganic-organic materials**
- ❖ **CPs & MOFs**
- ❖ **ALD/MLD**
- ❖ **Layer-engineering**
- ❖ **Superlattice**

LECTURE EXERCISE 8

1. What are the possible dimensionalities (0D, 1D, 2D or 3D) of the followings: (a) Metal complex ion, (b) Coordination polymer, (c) Metal-organic framework.
2. Are all CPs MOFs? Are all MOFs CPs? Please explain!
3. Explain why insertion of organic layers into inorganic matrix could be useful to enhance (a) mechanical, and (b) thermoelectric properties.
4. Give an example of an ALD/MLD synthesized material which is very difficult if not impossible to synthesize using conventional synthesis techniques. Explain the unique benefits of ALD/MLD in this synthesis with few sentences.
5. EXTRA QUESTION: The UV-activated photoisomerization reaction of the azobenzene moiety has been utilized to add a photoswitching effect on the magnetic properties of ε-Fe_2O_3:azobenzene superlattice thin films. Please propose some other application area where you could imagine that a similar switching effect could be useful/interesting.

Brought Together

SUM of BOTH PROPERTIES



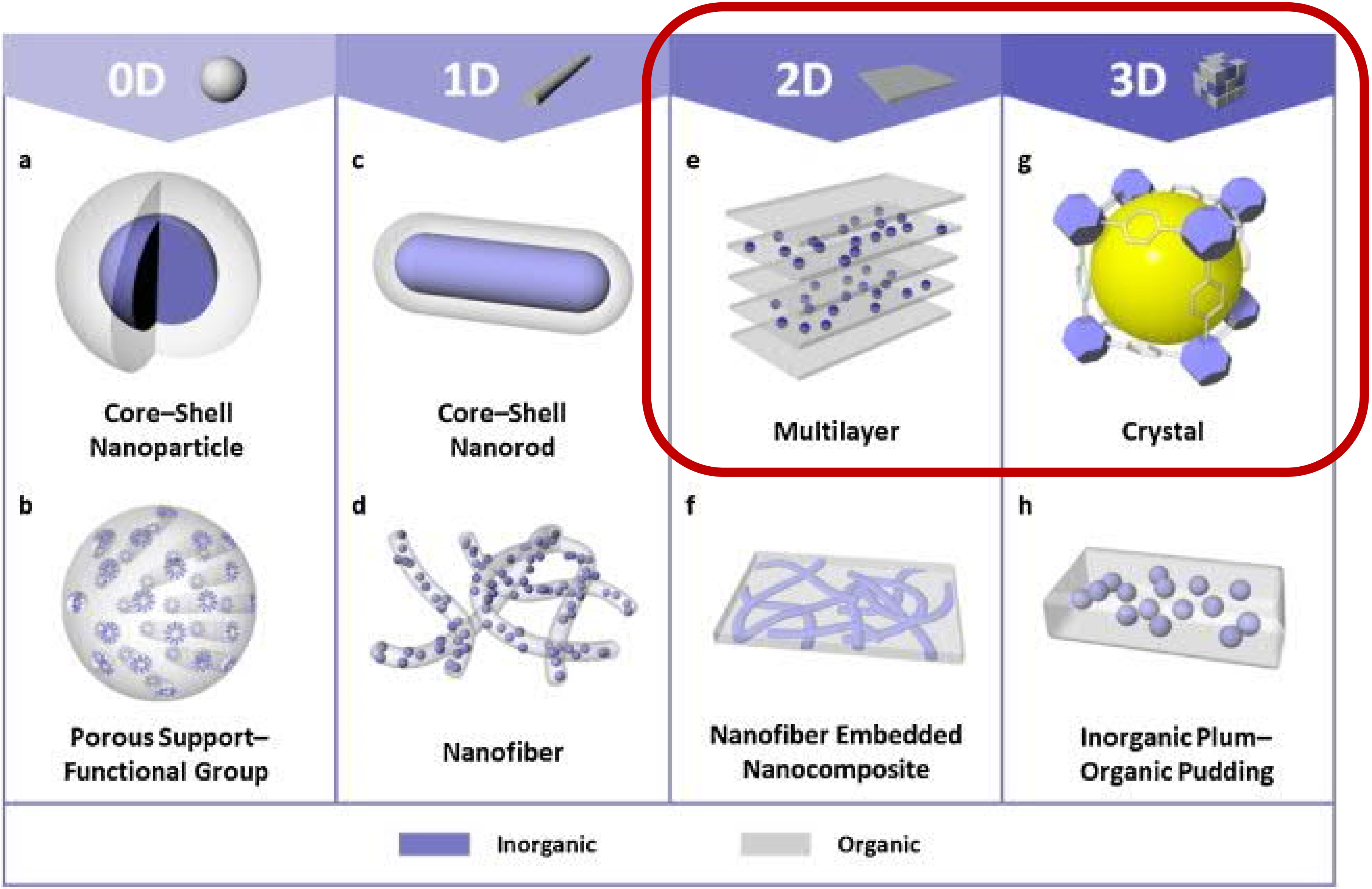
Fused Together

AVERAGE PROPERTIES

Intimately / Interactively Fused

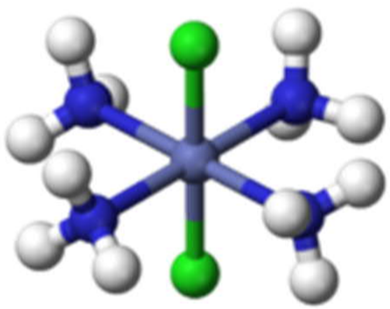
EXTRAORDINARY / MUTUALLY CONTRADICTORY PROPERTIES

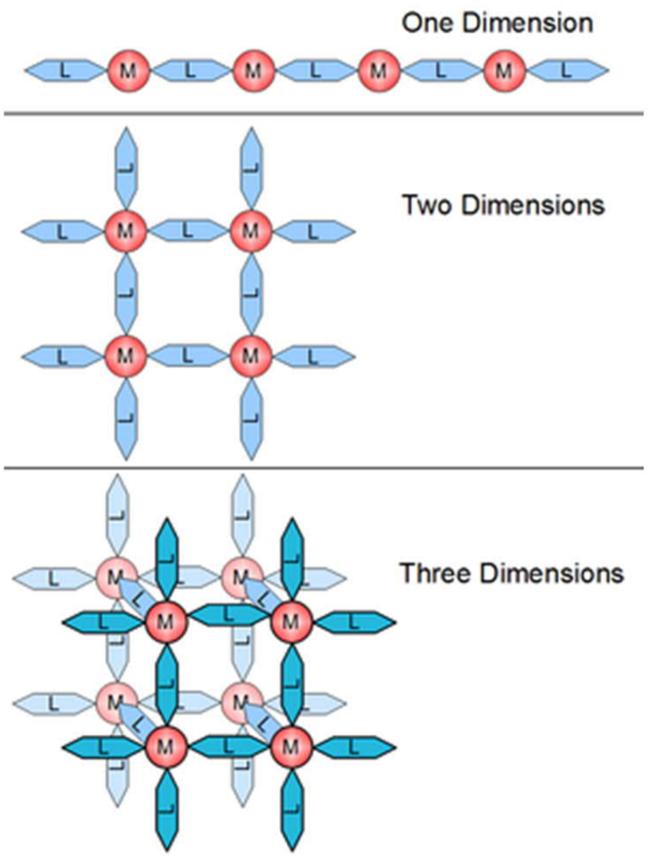
EXAMPLES of Inorganic-Organic Hybrid Materials

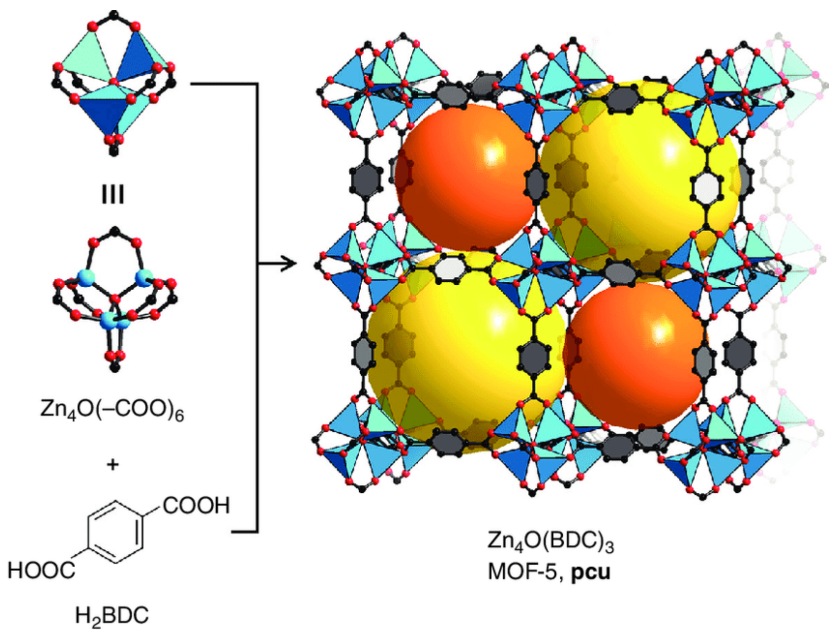


FOR CHEMISTS: Inorganic-Organic Material

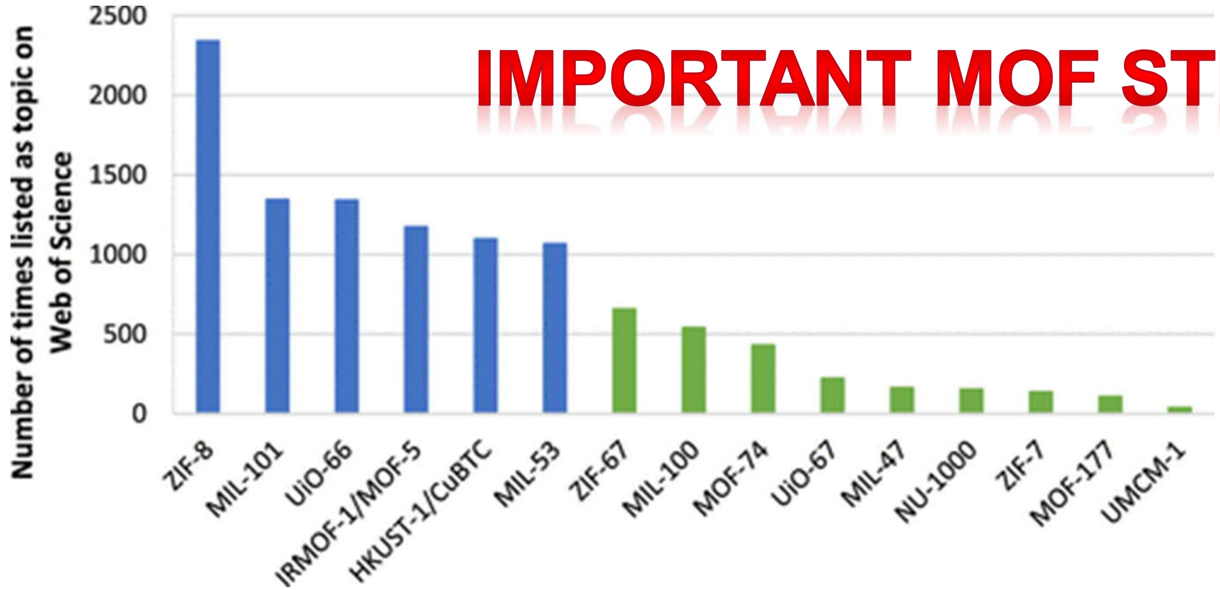
- **Single Compound (NOT Composite) with Chemical Bonds**
- **Coordination/Metal Complex: central metal ion + (organic) ligands**
- **Coordination Polymer (CP): ligands act as bridges**
- **Metal-Organic Framework (MOF): highly porous**

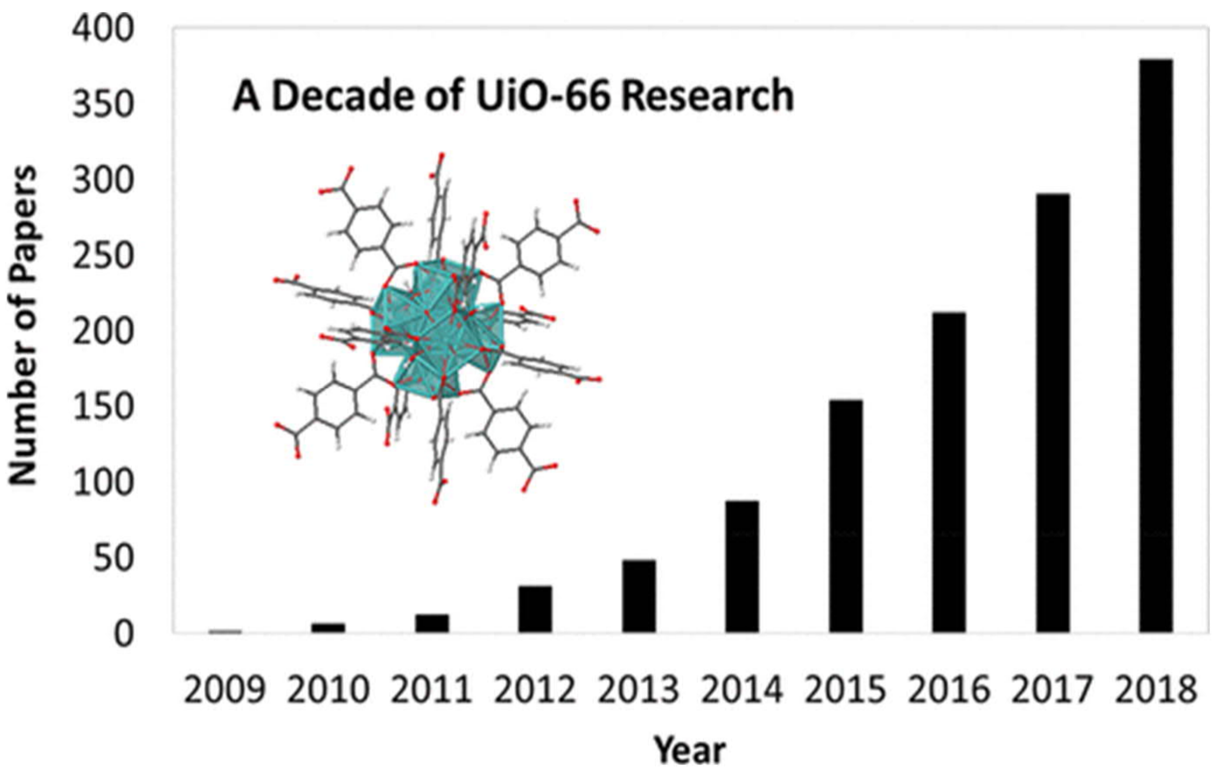




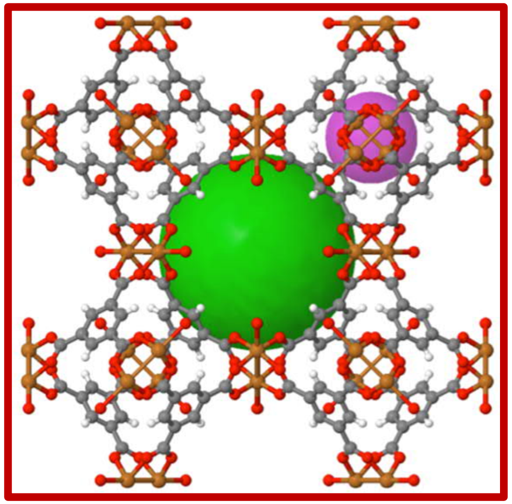


IMPORTANT MOF STRUCTURES

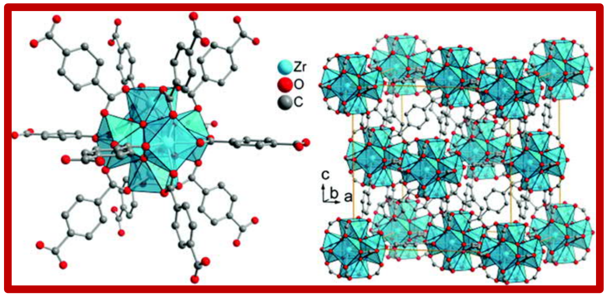


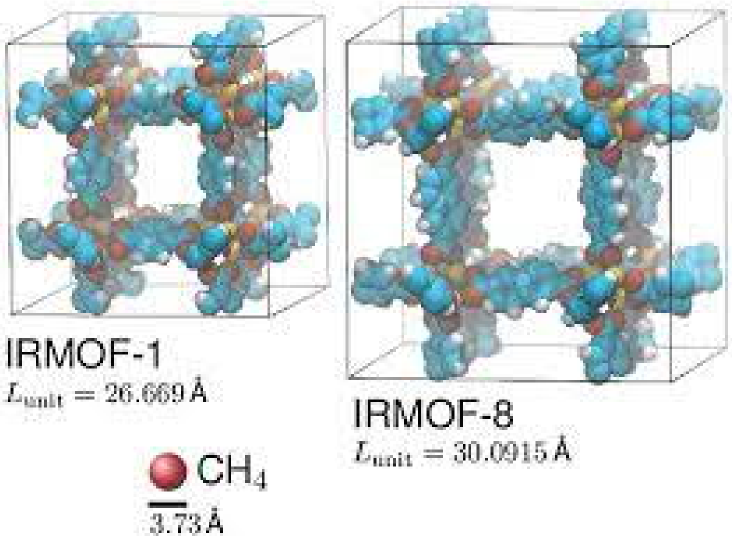


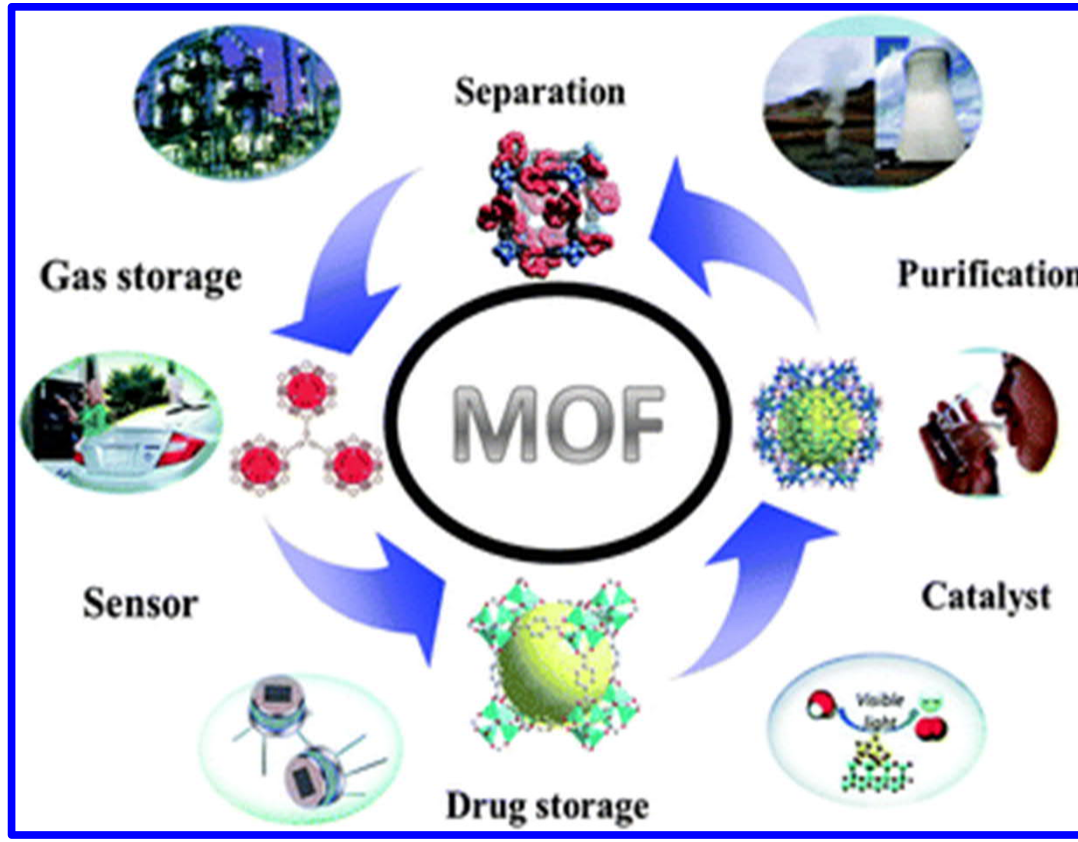
HKUST-1



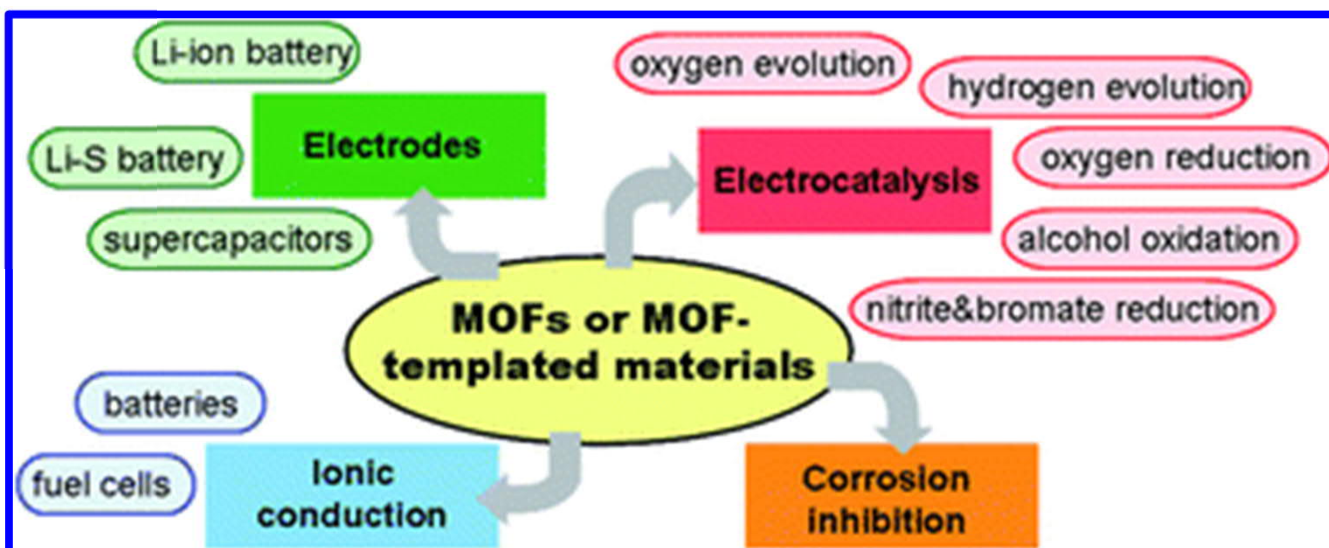
UiO-66





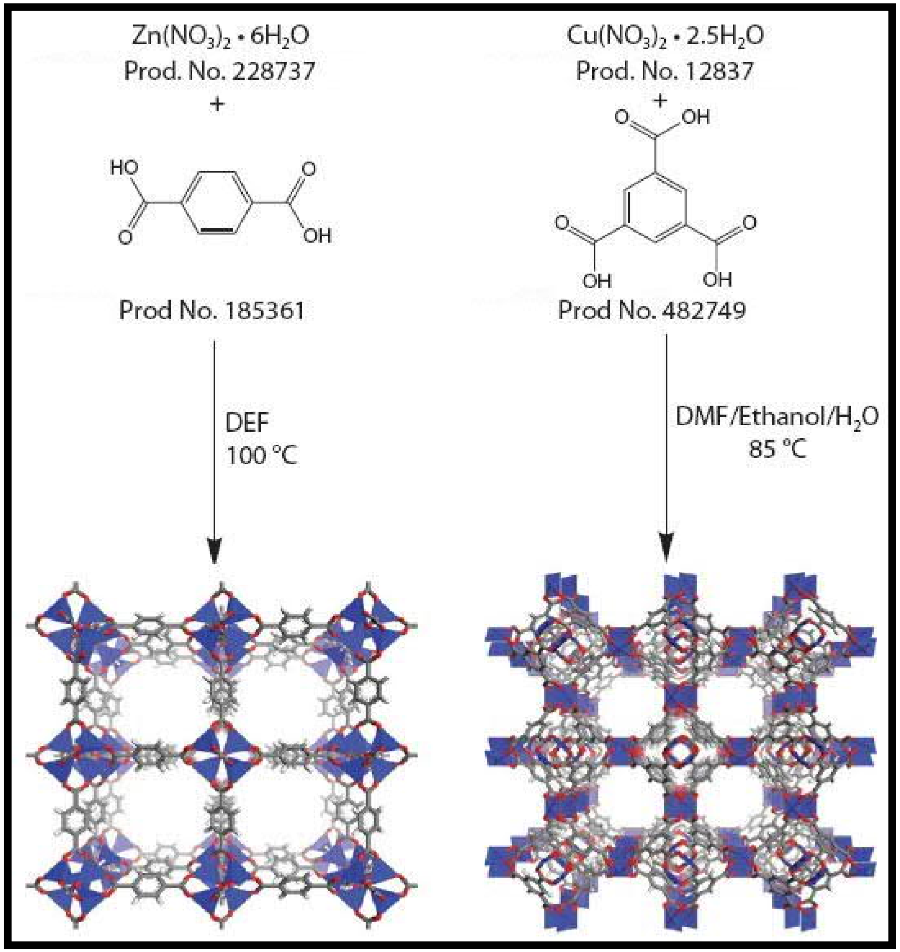


MOF THIN FILMS!



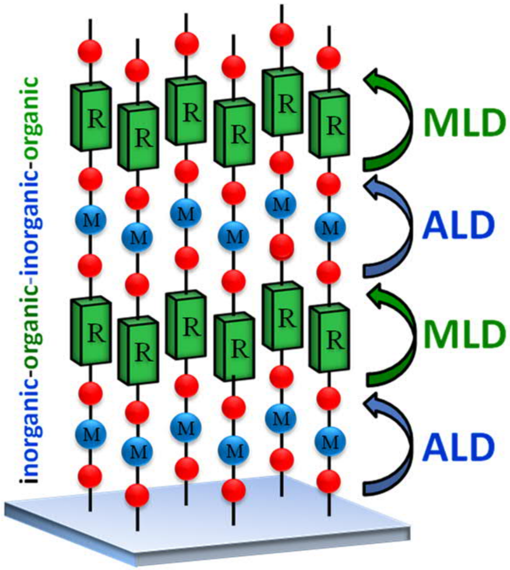
Synthesis of MOFs

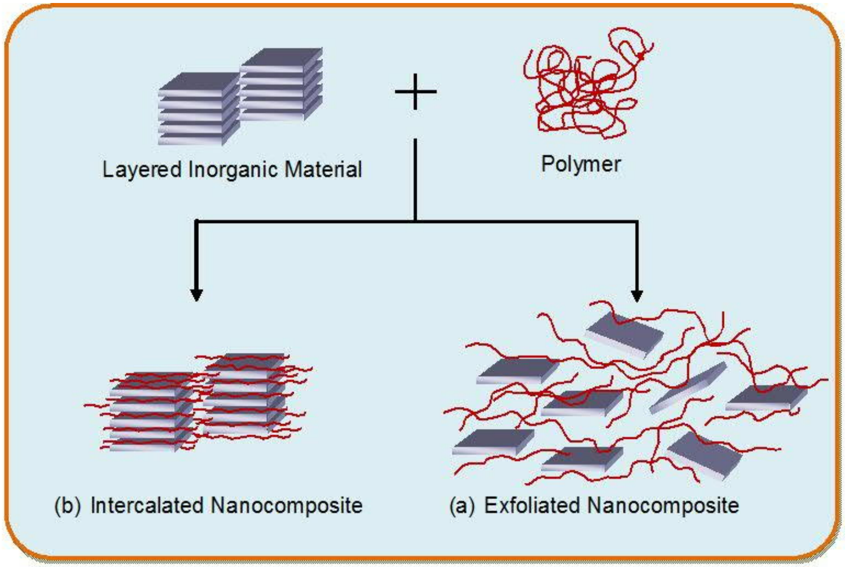
- **Synthesized most often in bulk form via solution techniques**
- **Porous structure → MOFs absorb readily/unintentionally solvent molecules**
- **Many prospective applications would require high-quality thin films**
- **No gas-phase deposition techniques (before ALD/MLD) !**

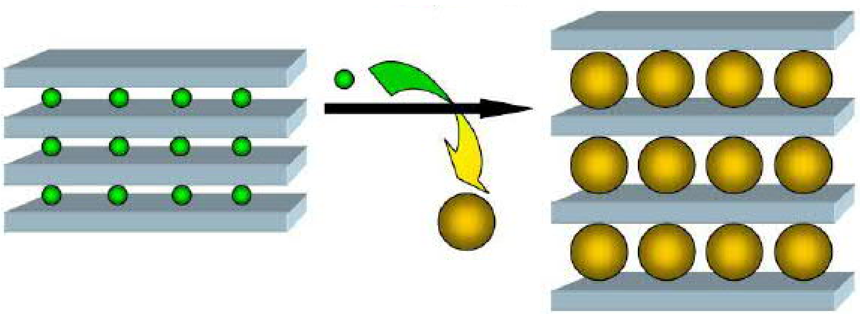


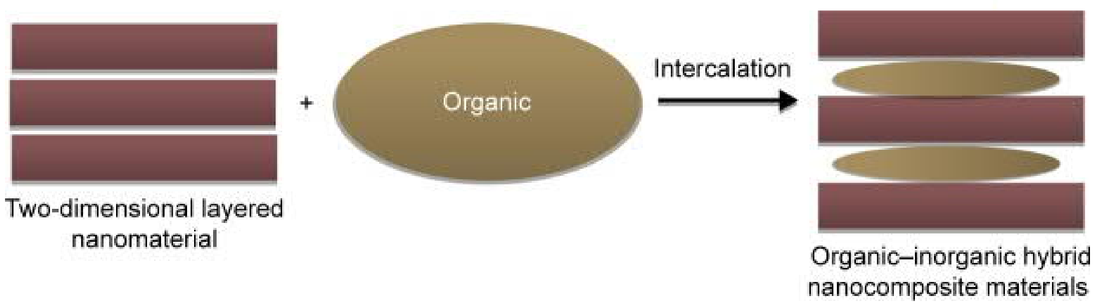
Layered Inorganic-Organic Materials

- **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

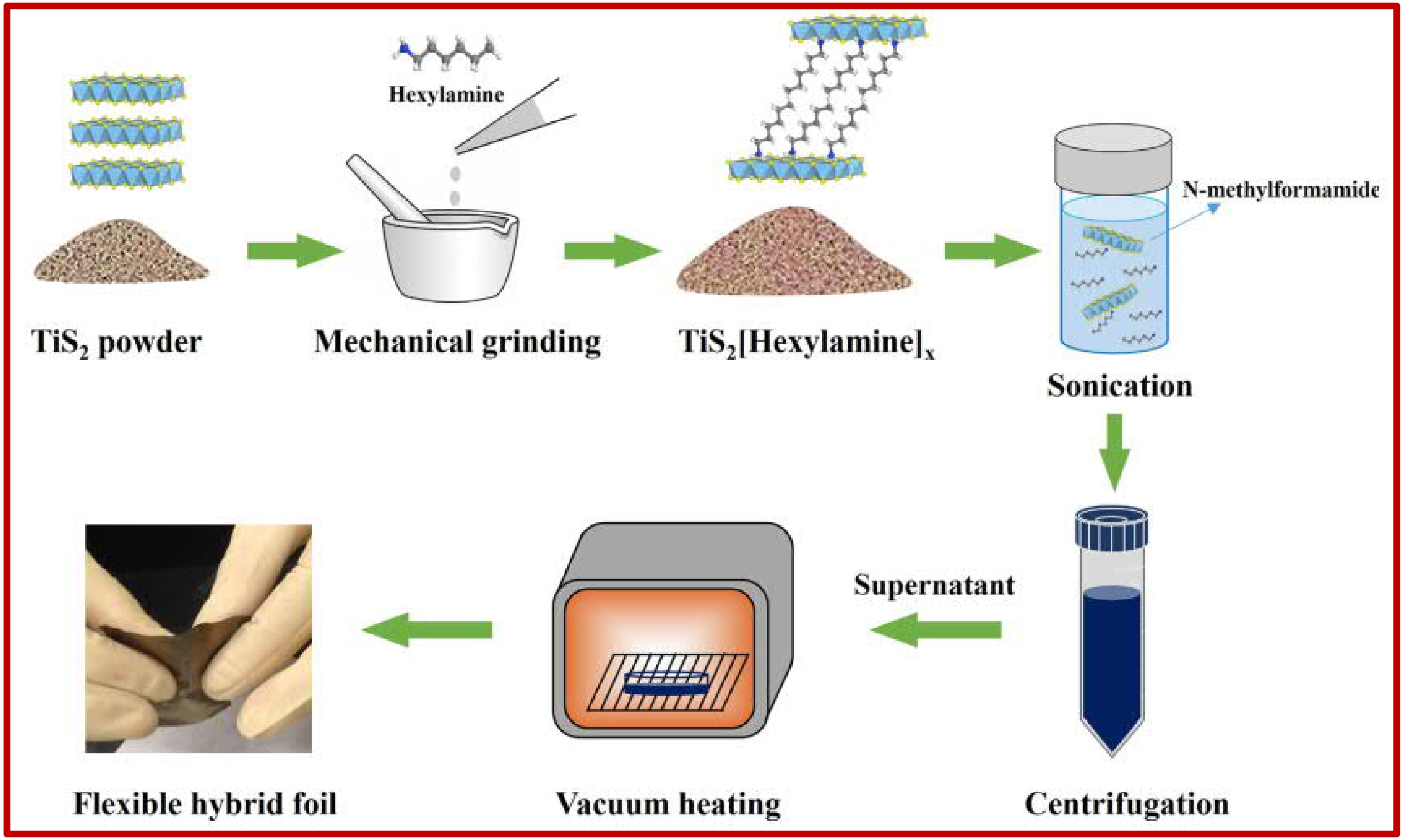
Nano Energy

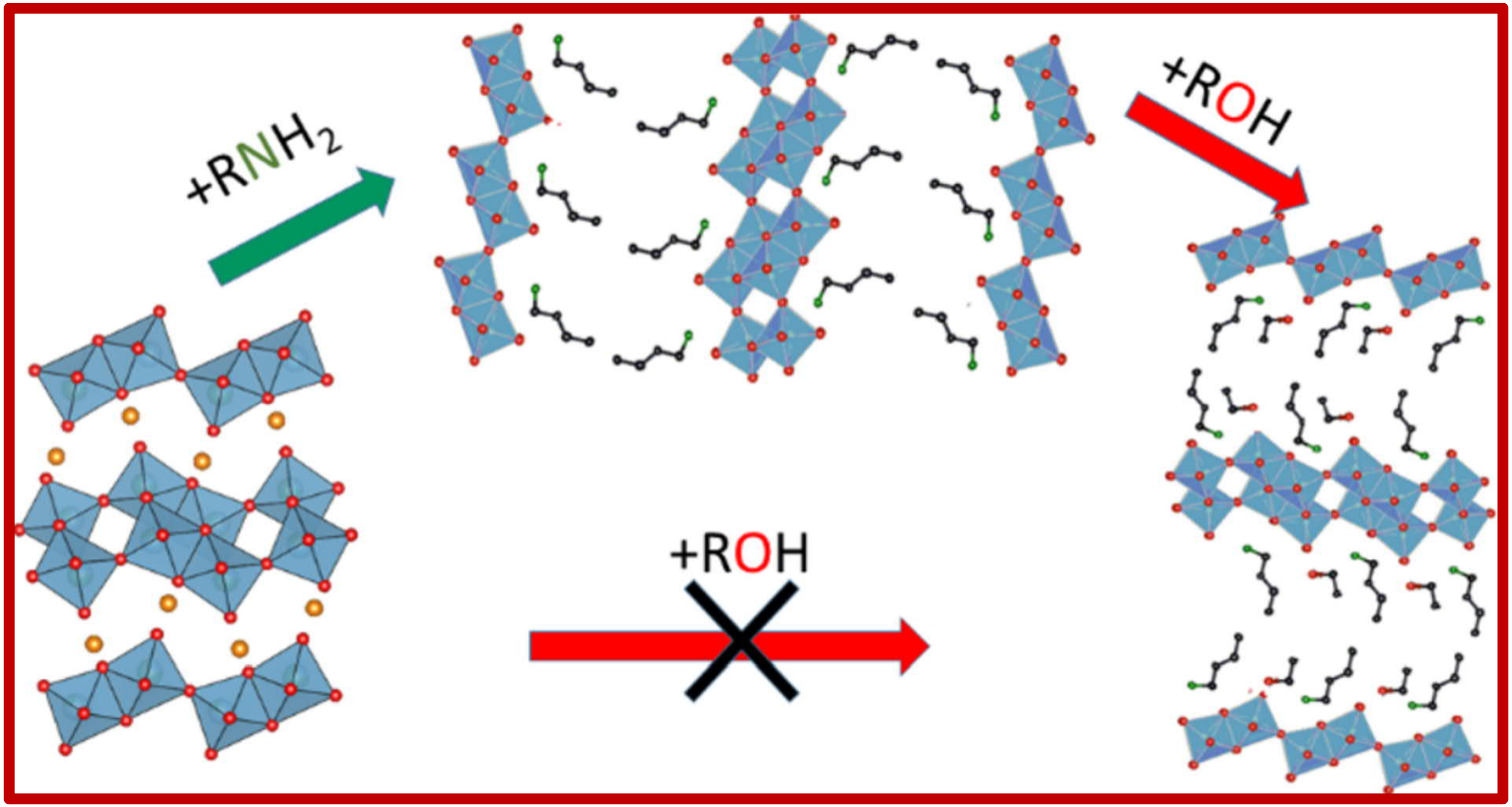
journal homepage: www.elsevier.com/locate/nanoen

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,*]

[a] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] Toyota Physical and Chemical Research Institute, Nagakute 480-1192, Japan
[c] Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
[d] Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan
[e] Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue 690-8504, Japan





Inorganic Chemistry
Article
pubs.acs.org/IC

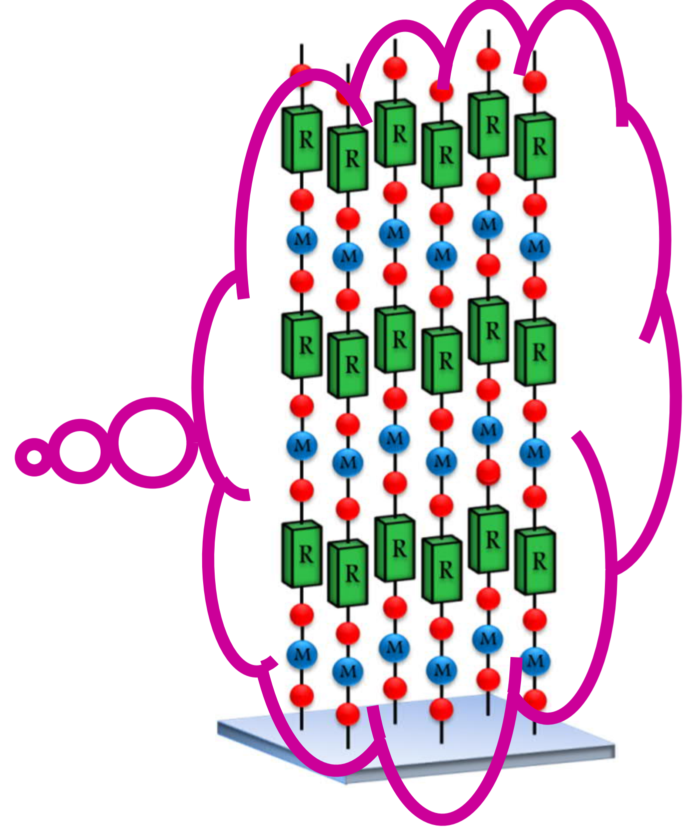
Intercalation of Primary Alcohols into Layered Titanoniobates

Chris I. Thomas* and Maarit Karppinen

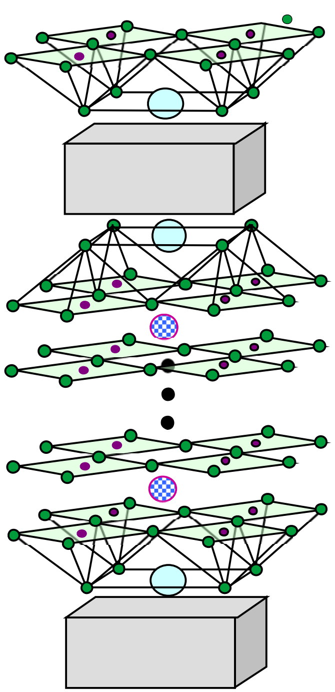
Department of Chemistry and Materials Science, Aalto University, FI-00076 Espoo, Finland

MULTI-FUNCTIONAL MULTILAYERED MATERIALS

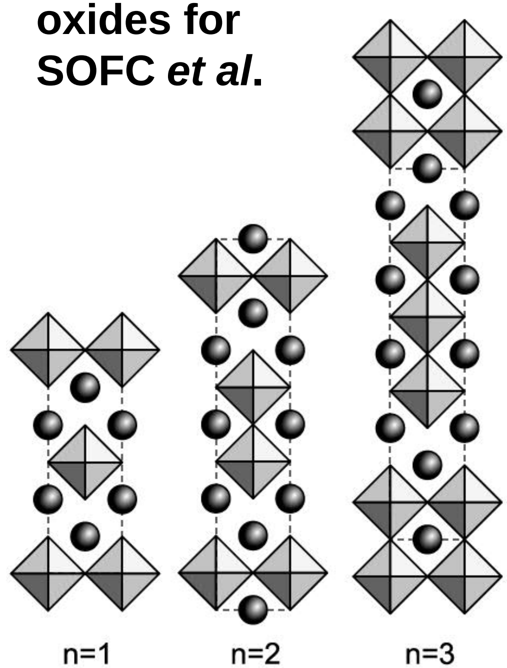
Layered inorganic-organic hybrid thin films



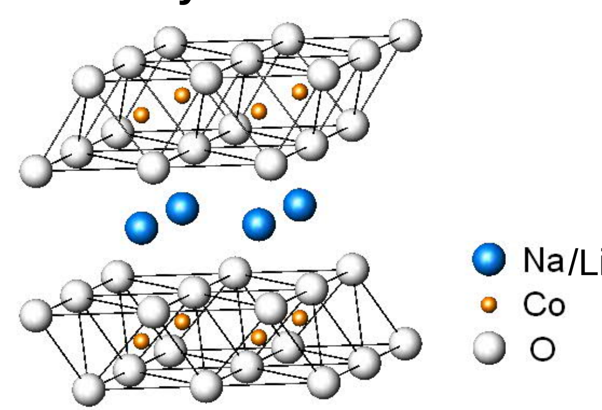
Multilayered Cu oxides for high-T_c superconductors

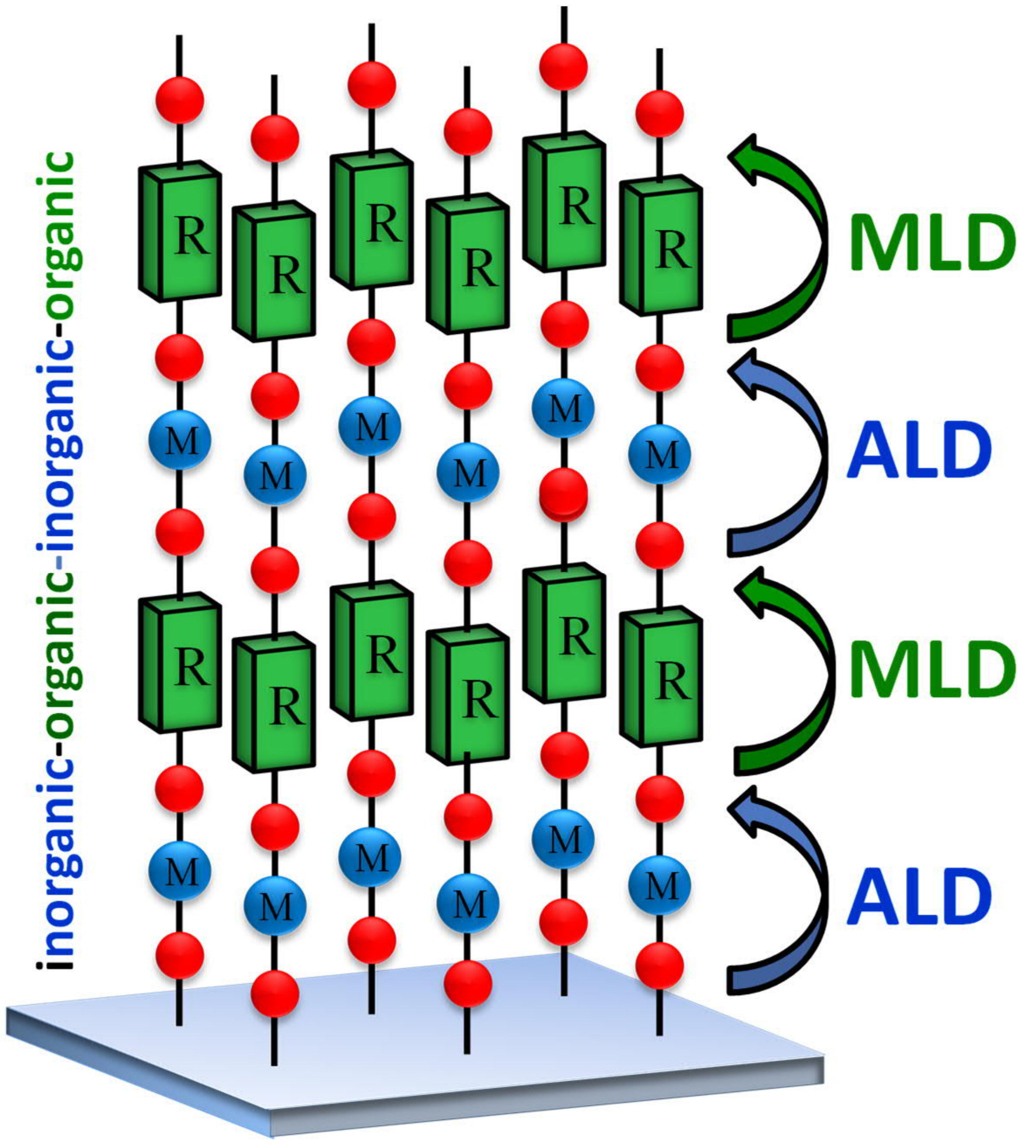


Ruddlesden-Popper oxides for SOFC *et al*.



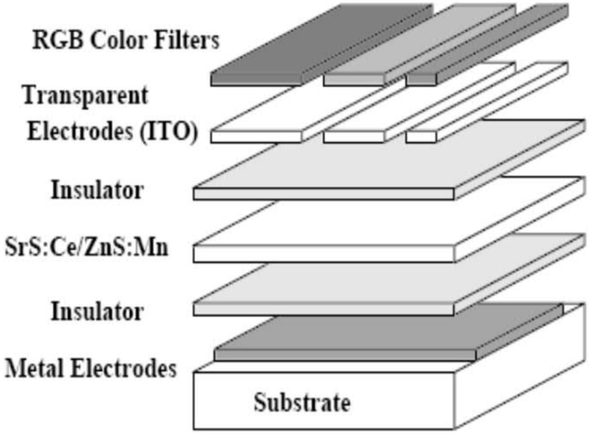
Layered Co oxides for Li-ion battery & thermoelectrics




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

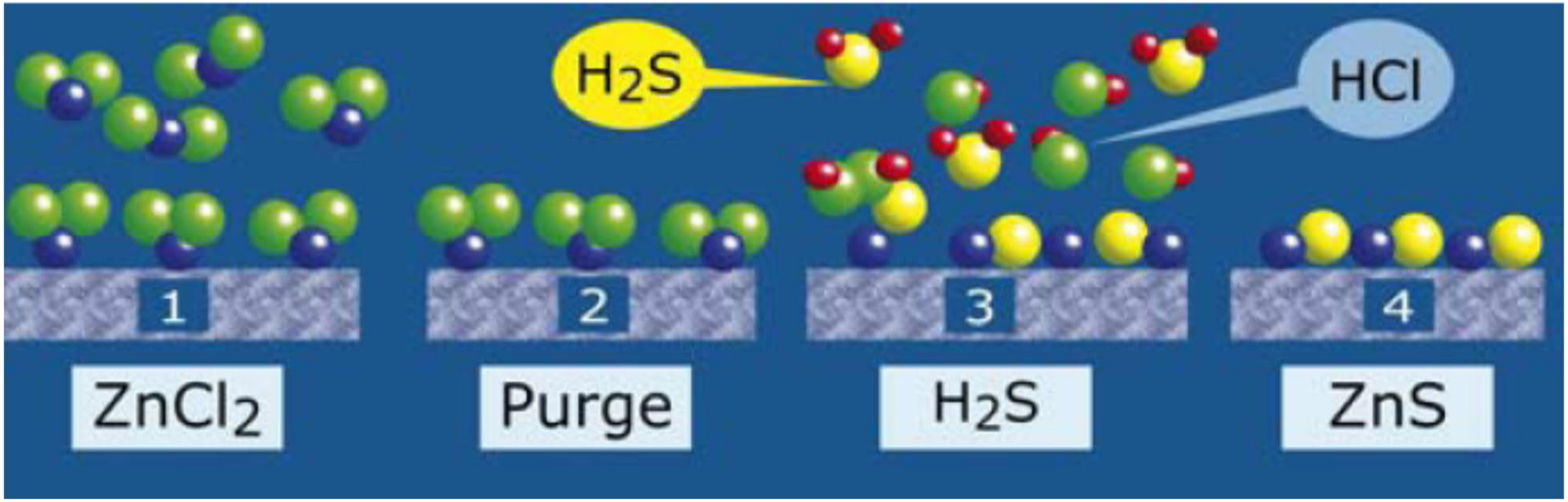
Atomic Layer Deposition (ALD) Thin-Film Technique

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



Electroluminescent display

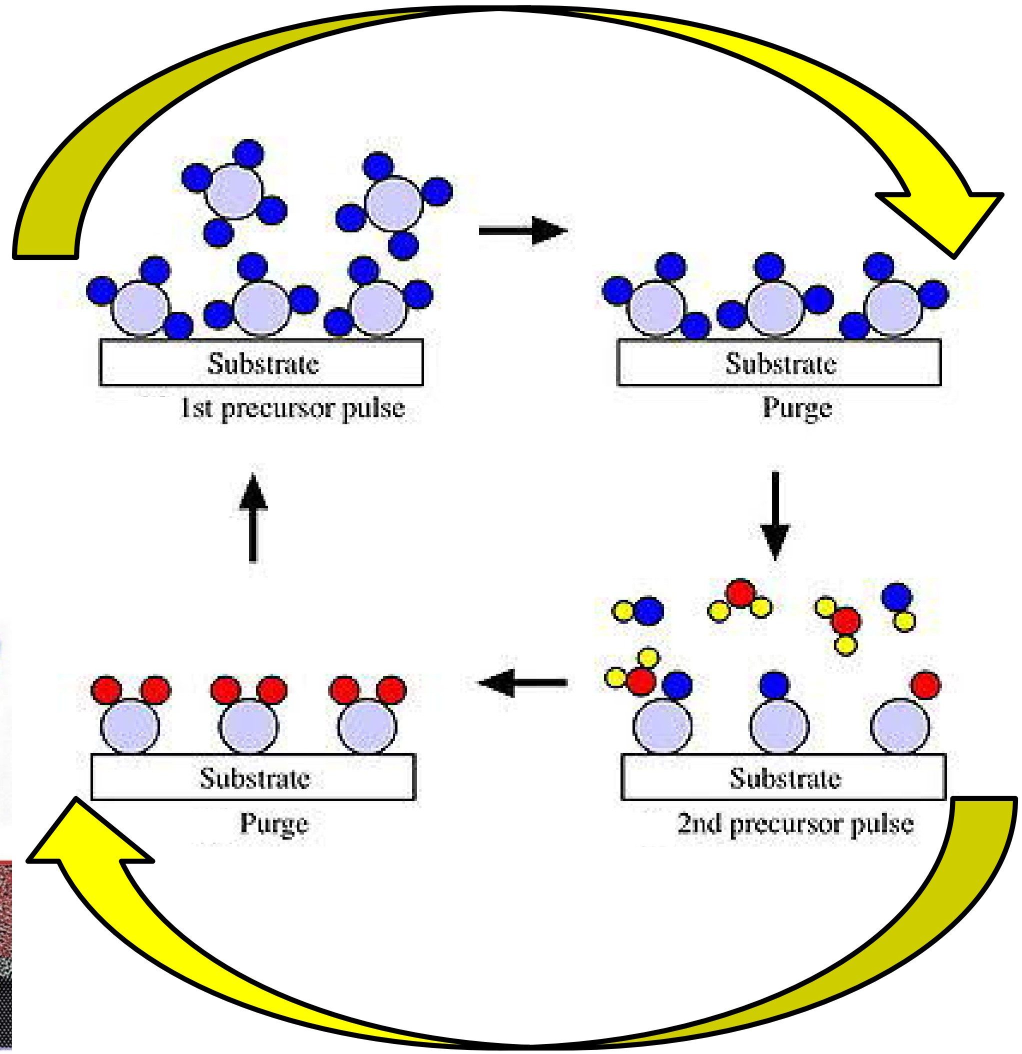
Instrumentarium / Finlux / Planar

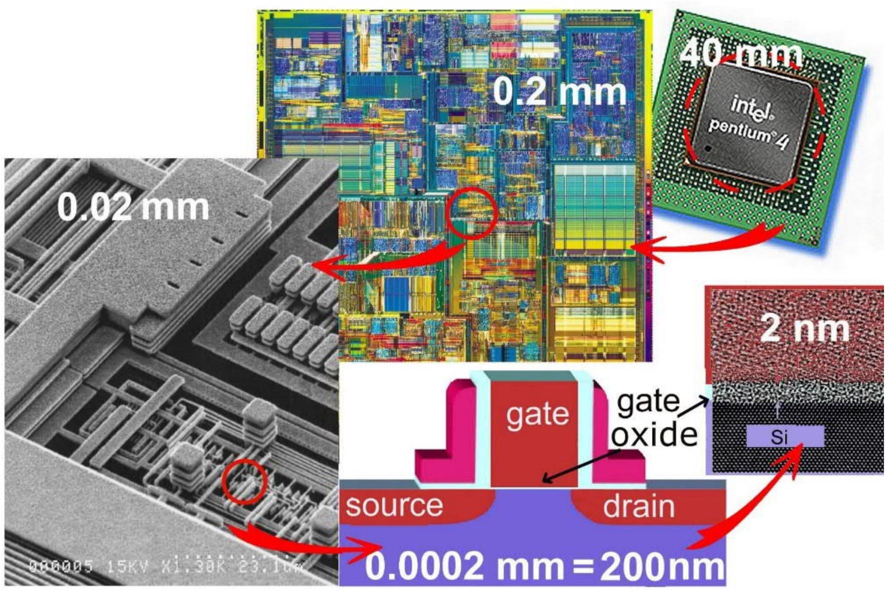


HfO_2-ALD

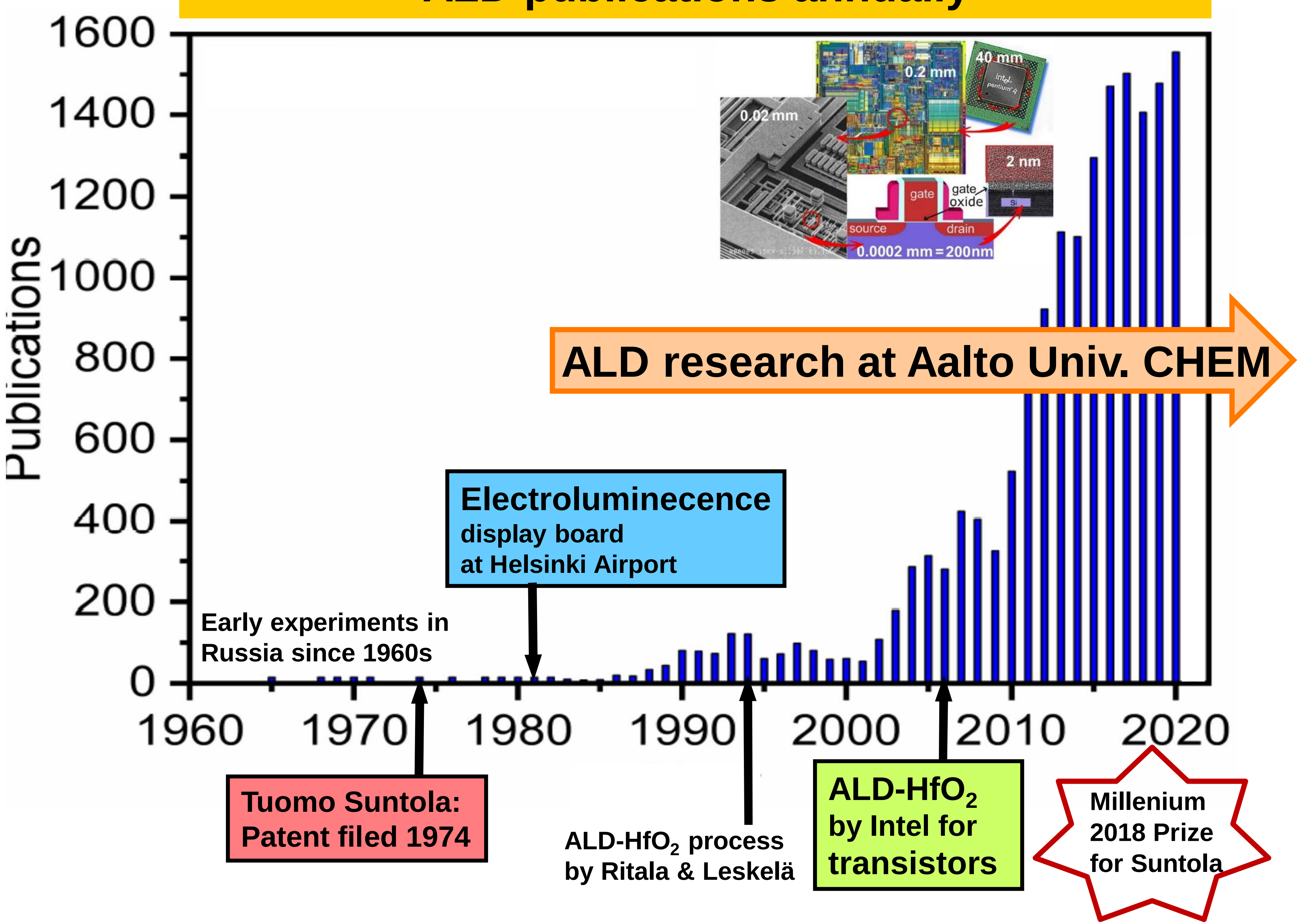
$HfCl_4 + H_2O$

ALD cycle





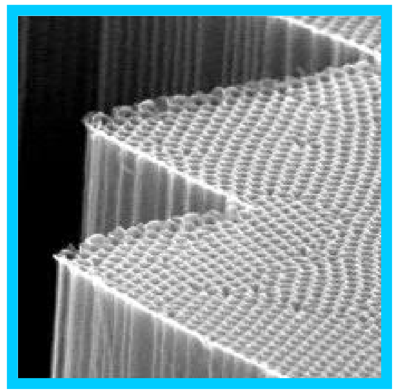
ALD publications annually



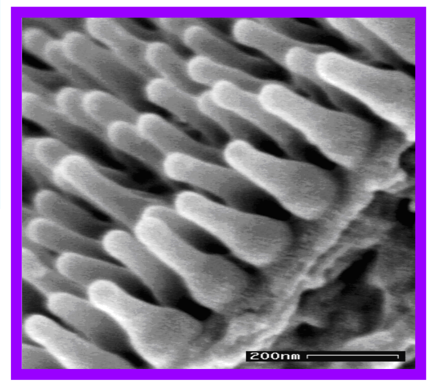
Advantages of ALD

- 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



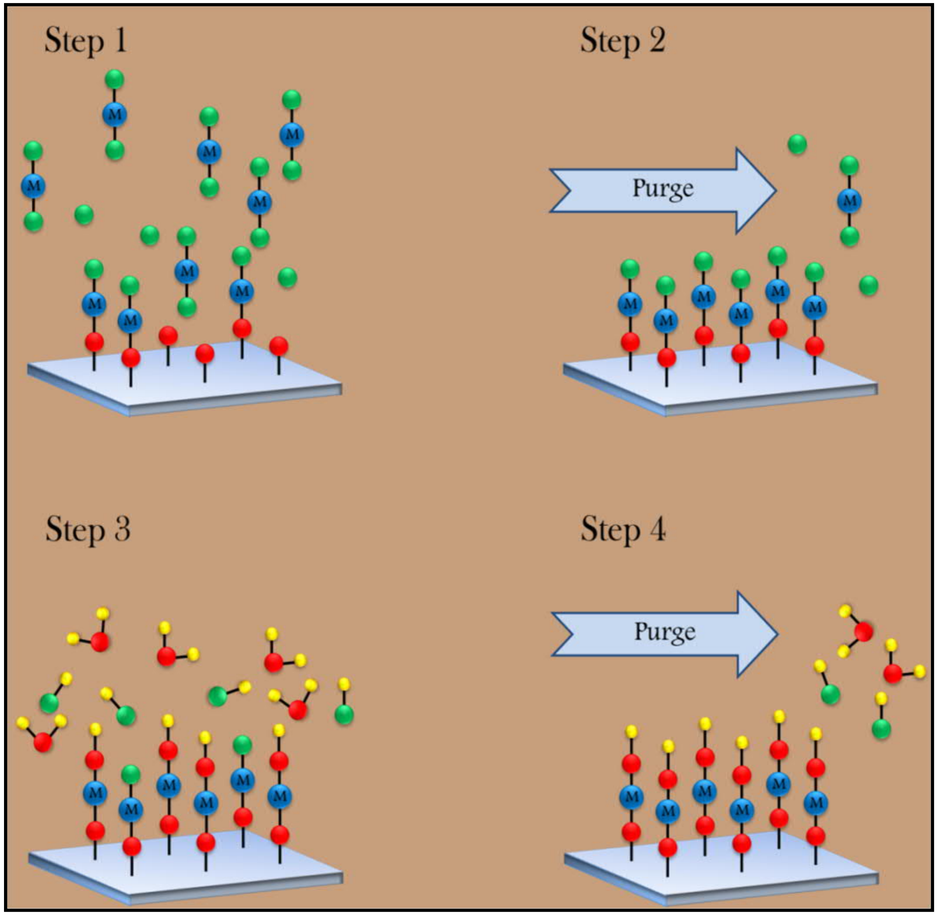
- Organic/polymer films
- Inorganic/organic hybrid materials

ELECTRONICS

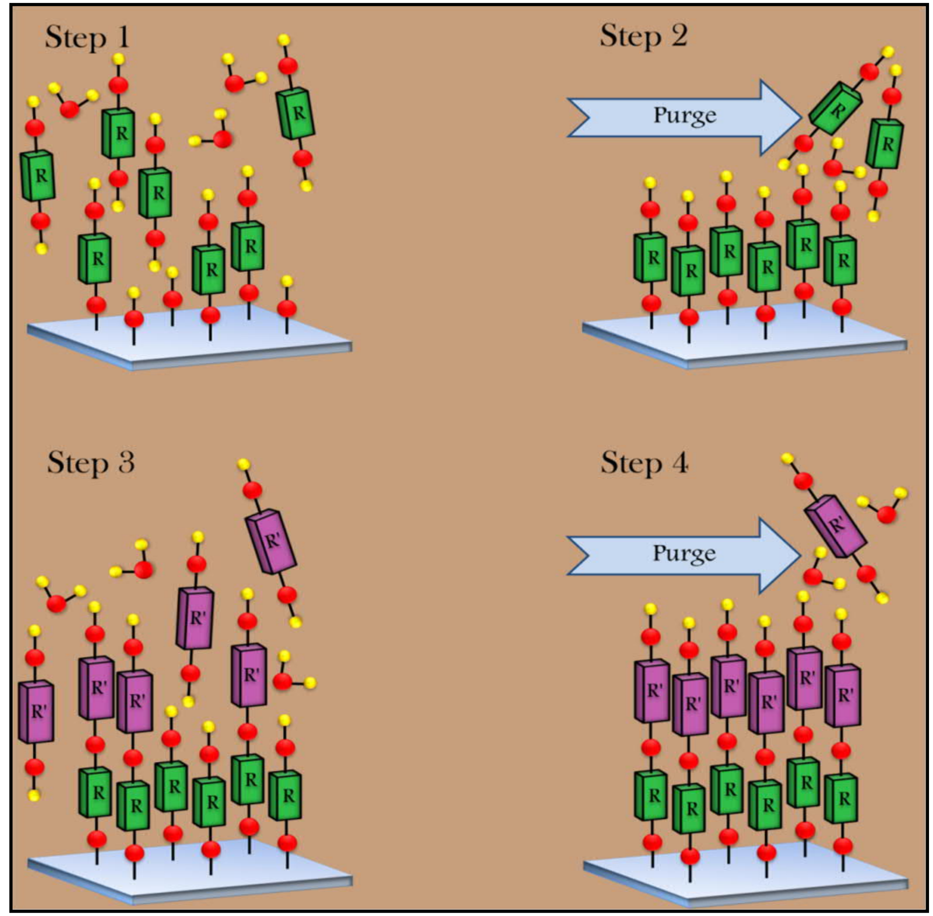
NANO

BIO

NEW



ALD (Atomic Layer Deposition)



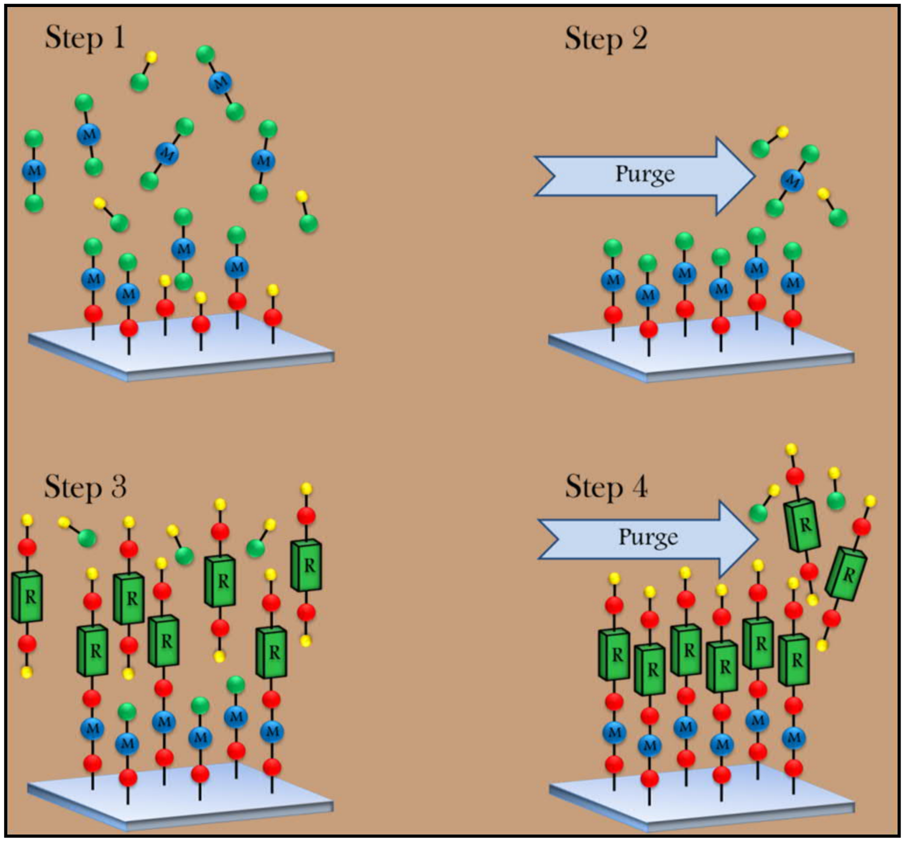
MLD (Molecular Layer Deposition)

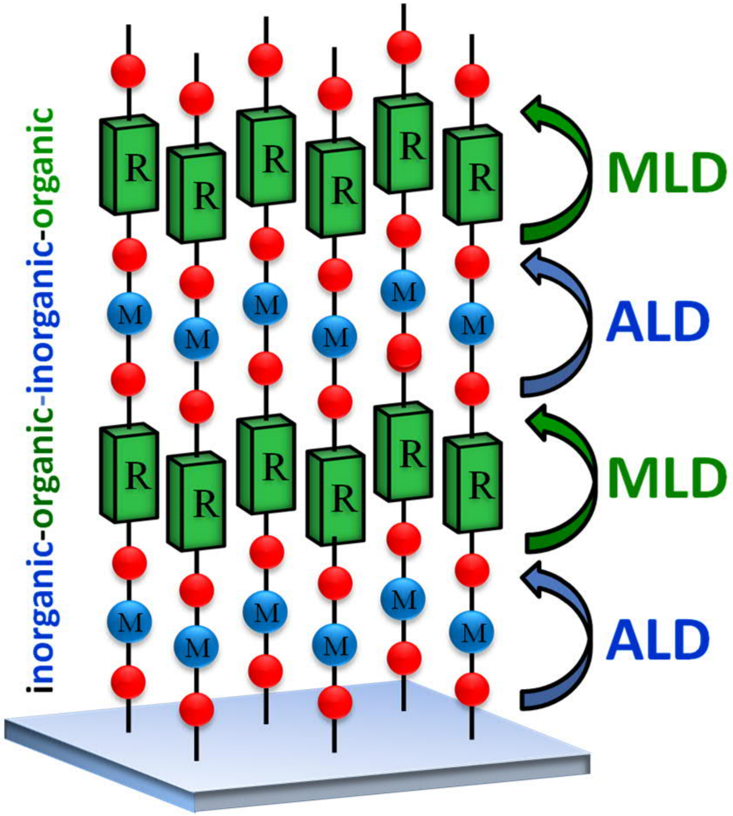
High-quality INORGANIC thin films with atomic level control

ORGANICS !

(in 1990s)

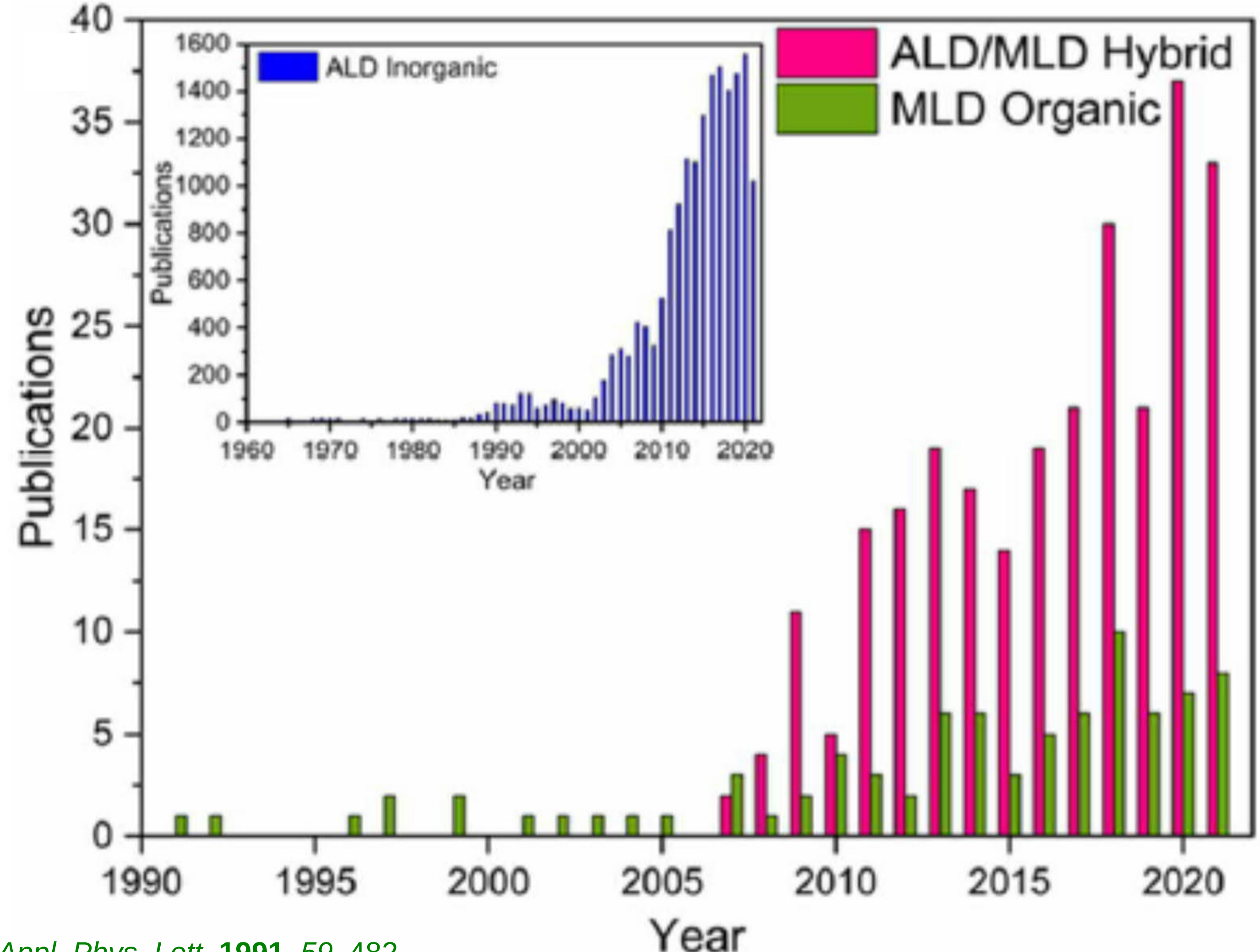
Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD



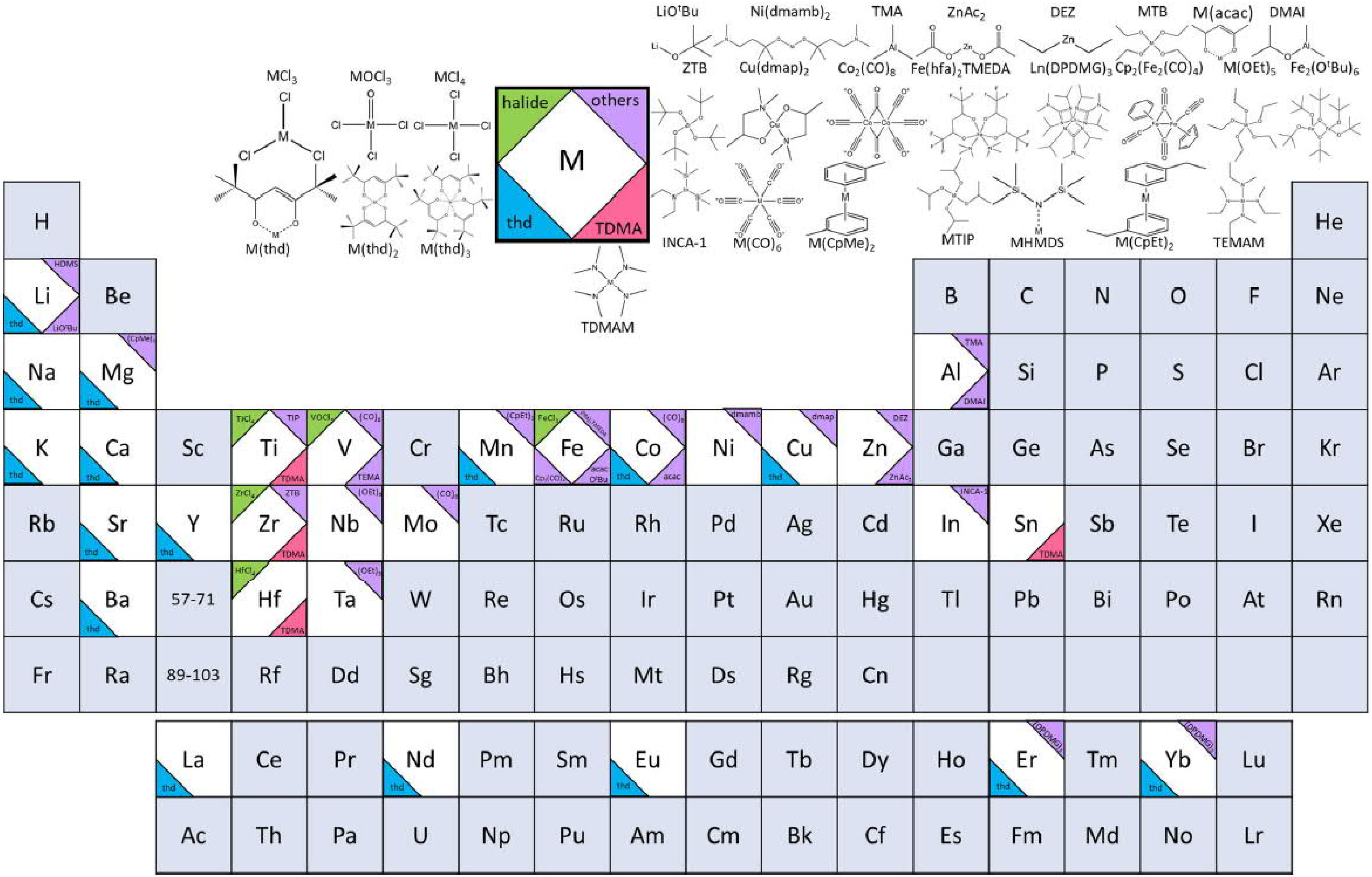


MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!

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.



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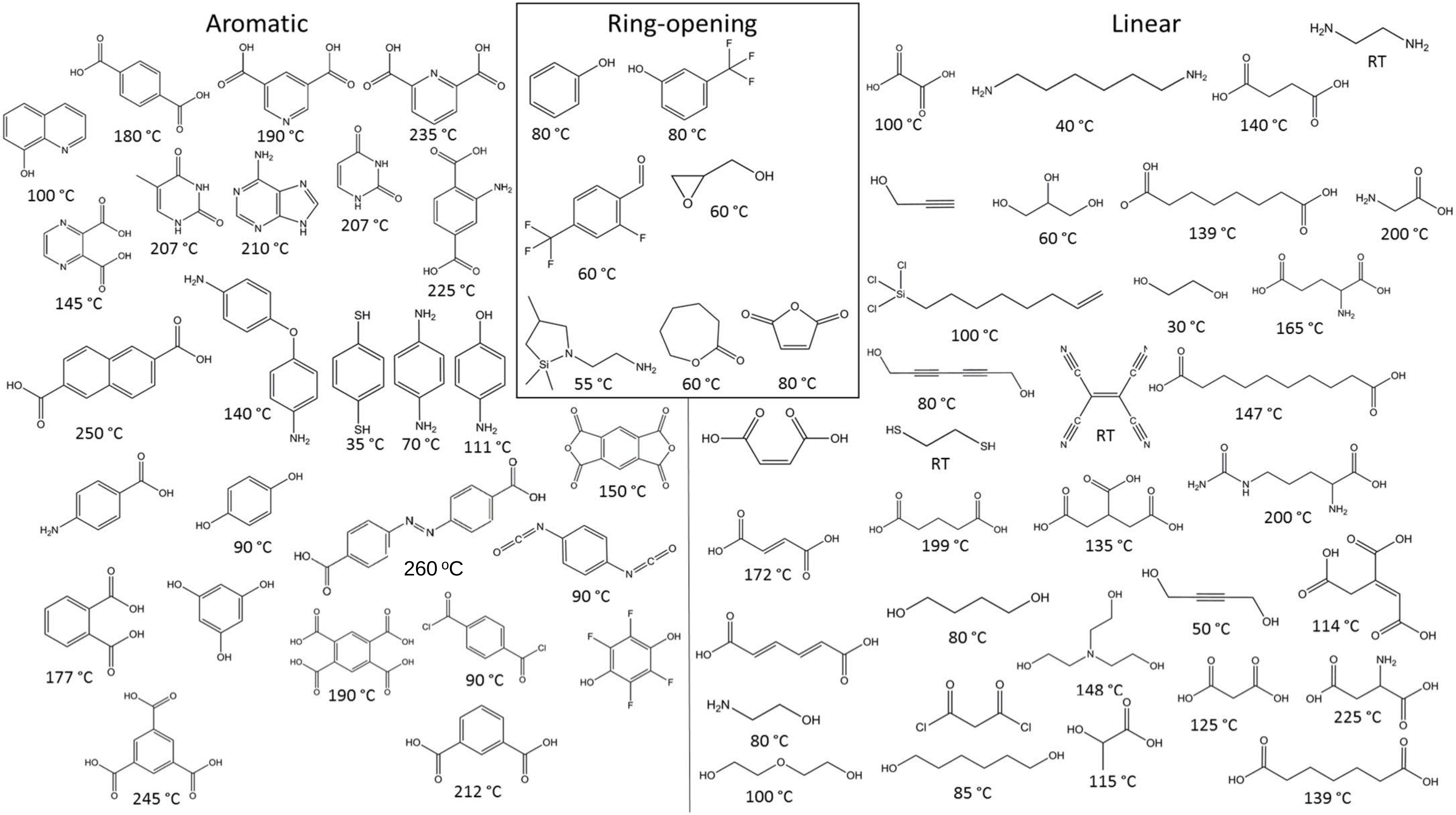
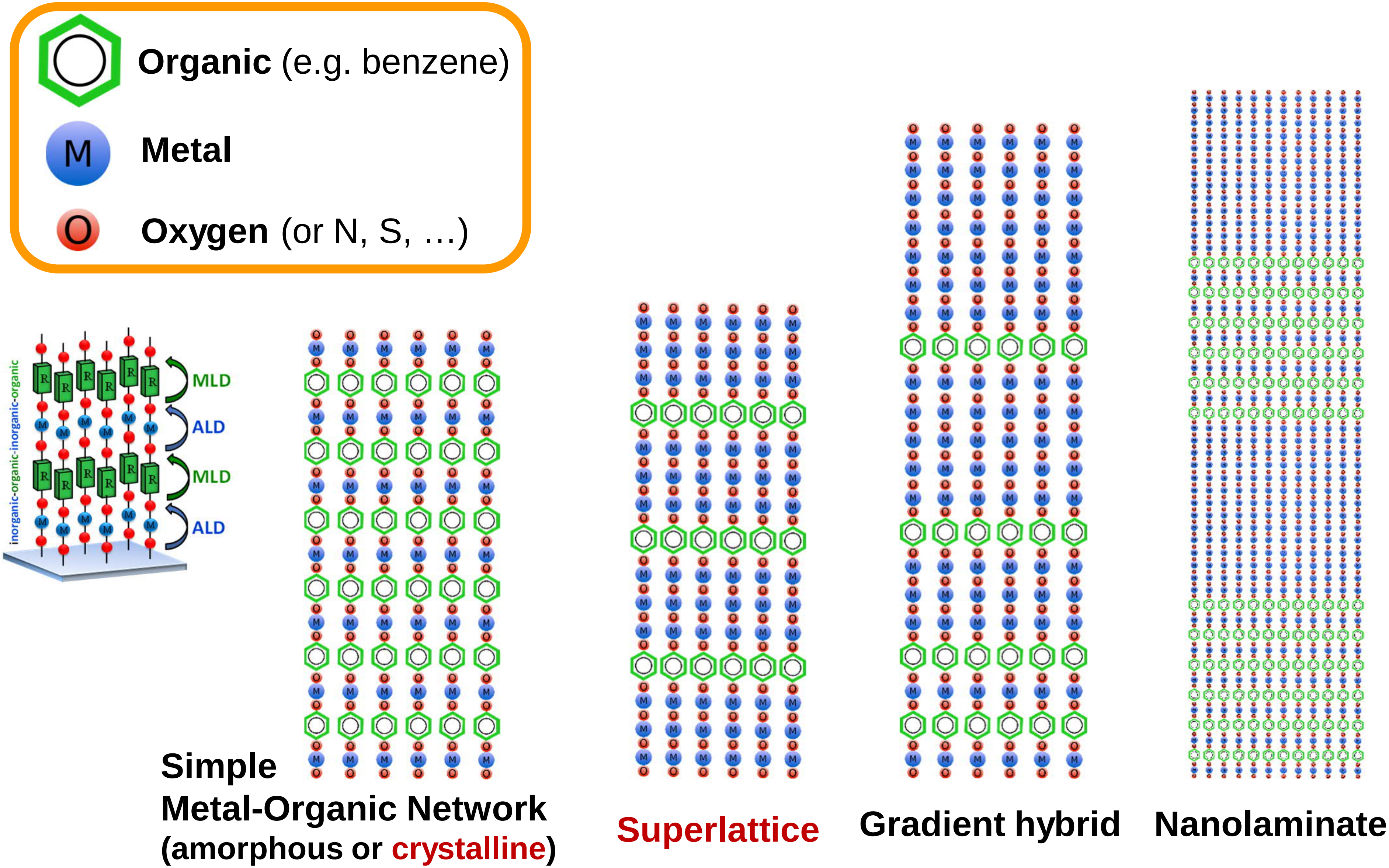
School of Chemical
Engineering

ALD/MLD Processes: Metal Precursors



ALD/MLD Processes: Organic Precursors

(sublimation temperatures !)



DIFFERENT LAYER SEQUENCES BY DESIGN

LAYER-ENGINEERED

INORGANIC-ORGANIC SUPERLATTICES

BY

ALD/MLD

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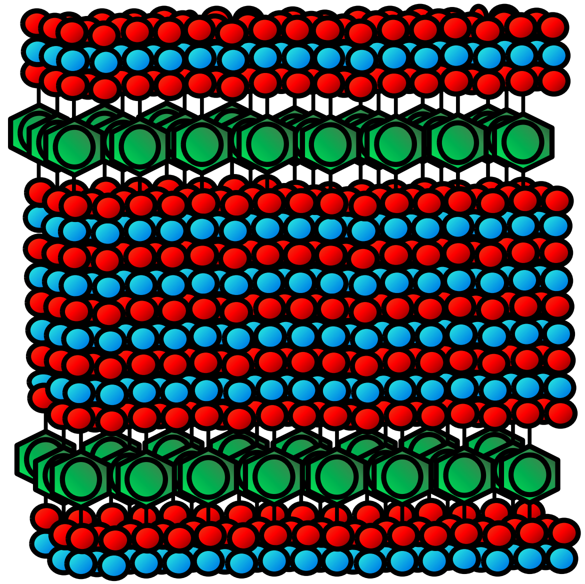
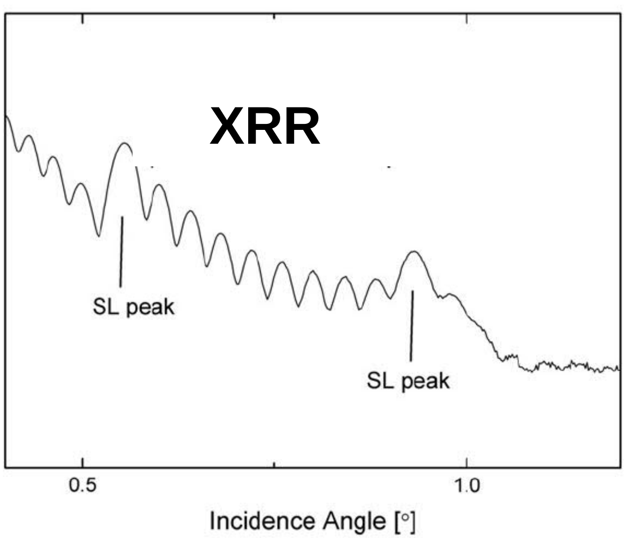
School of Chemical
Engineering

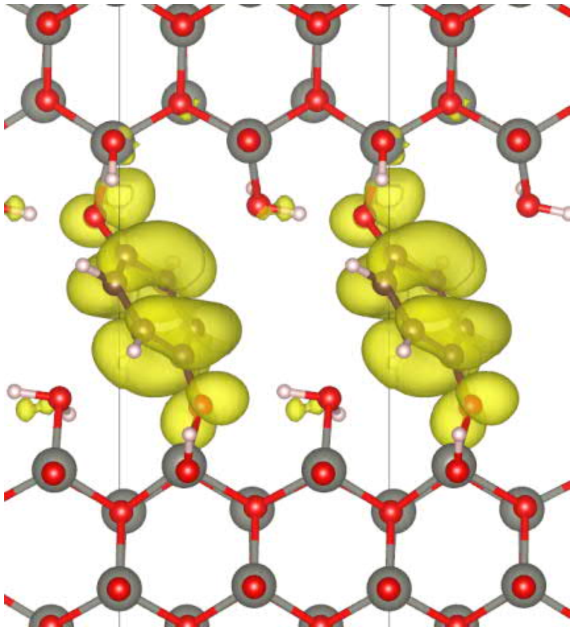
ZnO:benzene SUPERLATTICE



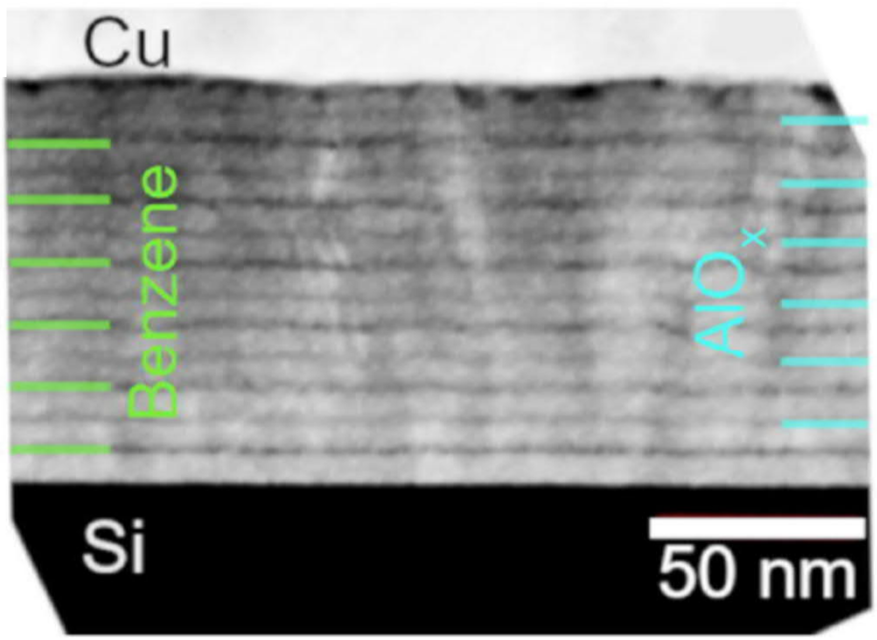


DFT Modelling

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



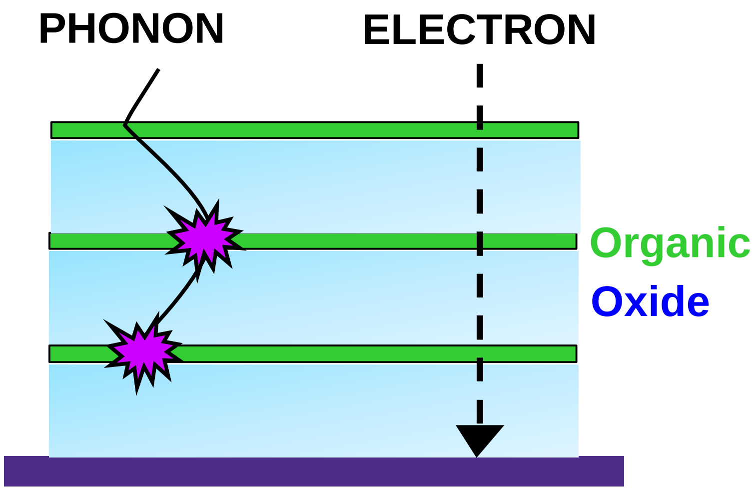
HR-TEM

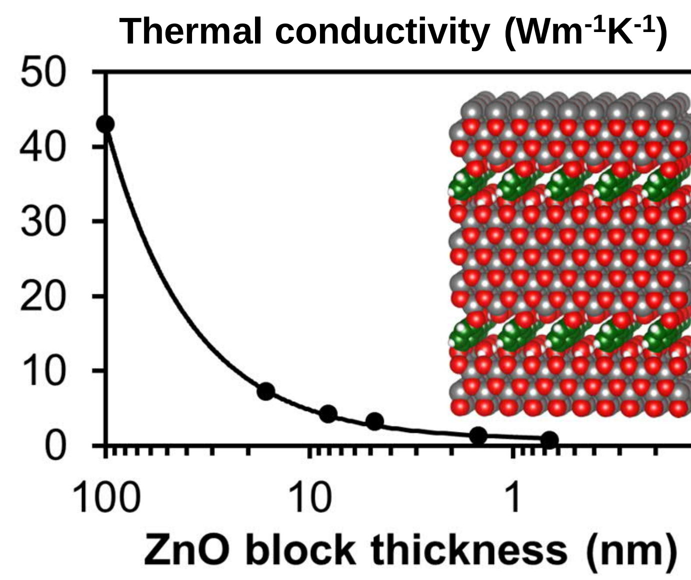


F. Krahl, Y. Ge & M. Karppinen, *Semicond. Sci. Technol.* **36**, 025012 (2020)

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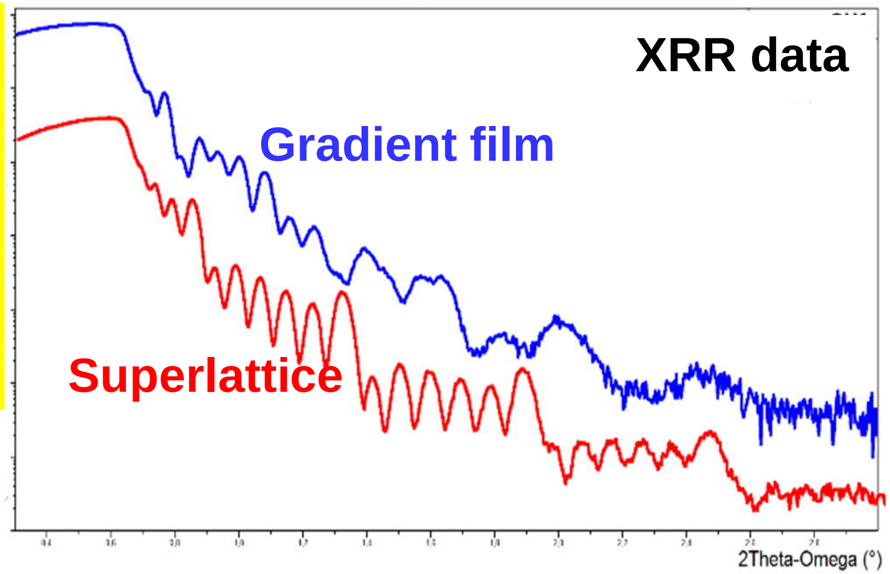
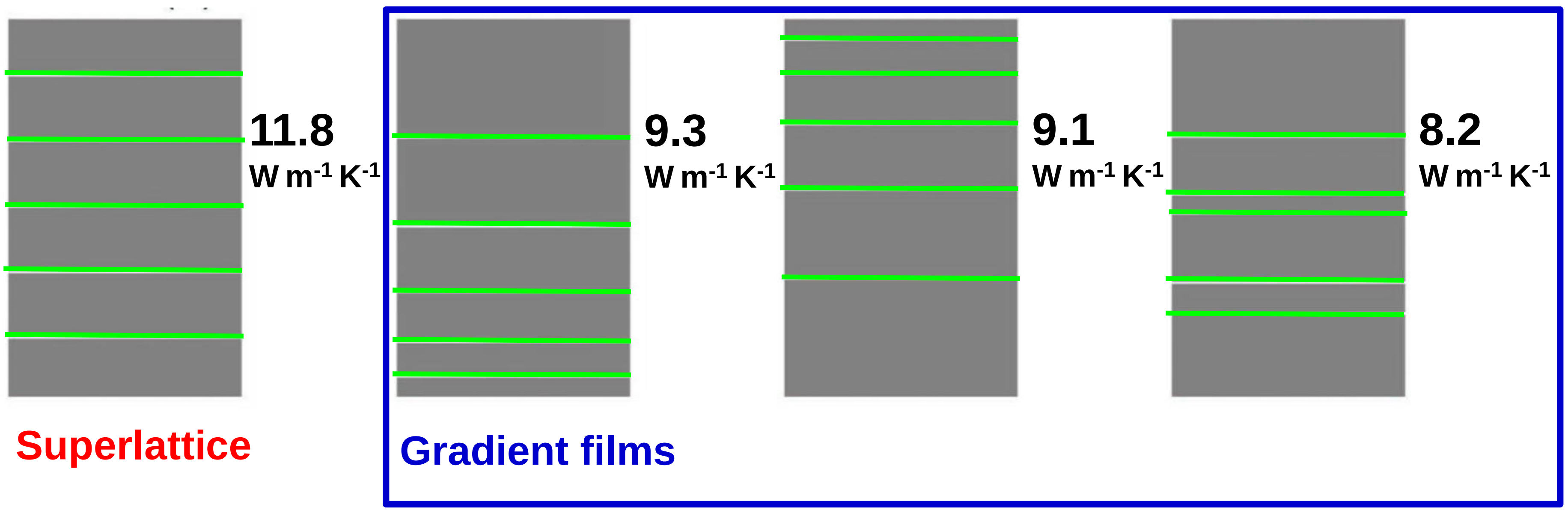
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, ***J. Mater. Chem. A* 2**, 12150 (2014).

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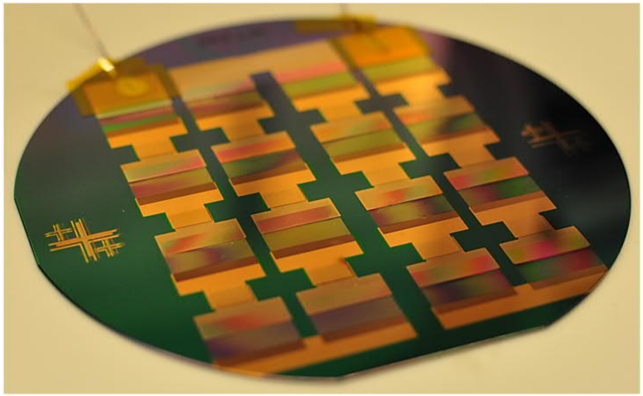
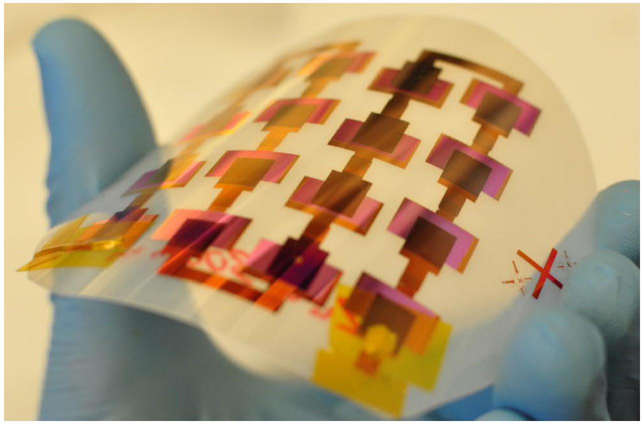
F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen,
Thermal conductivity reduction at inorganic-organic interfaces:
from regular superlattices to irregular gradient layer sequences,
Adv. Mater. Interfaces **5**, 1701692 (2018).

THERMOELECTRIC MODULE

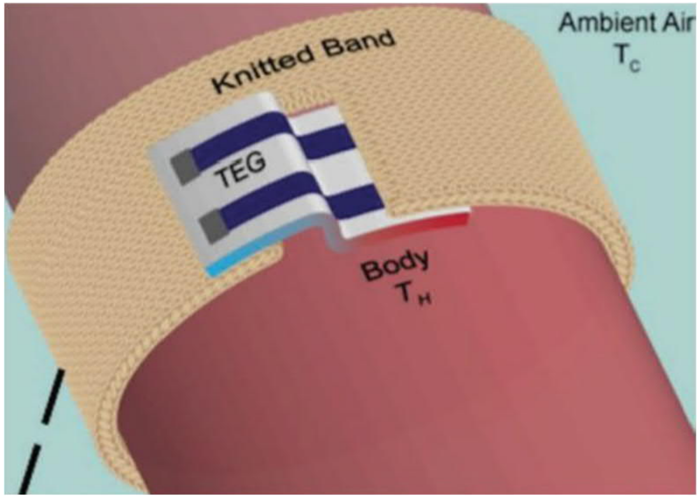
Silicon

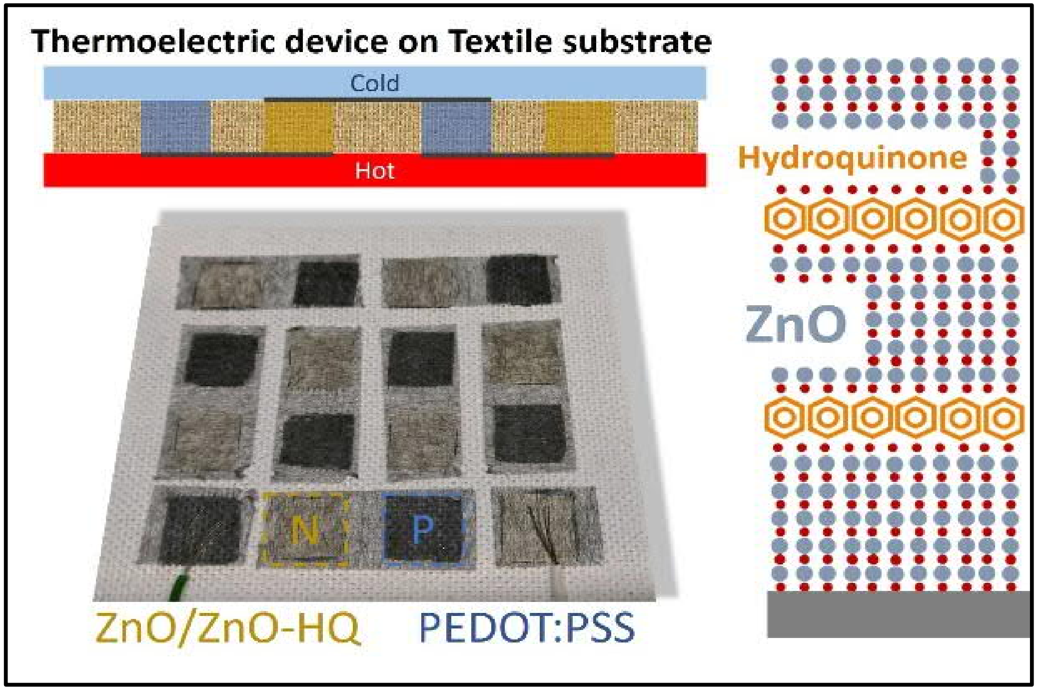


Plastics



Textile



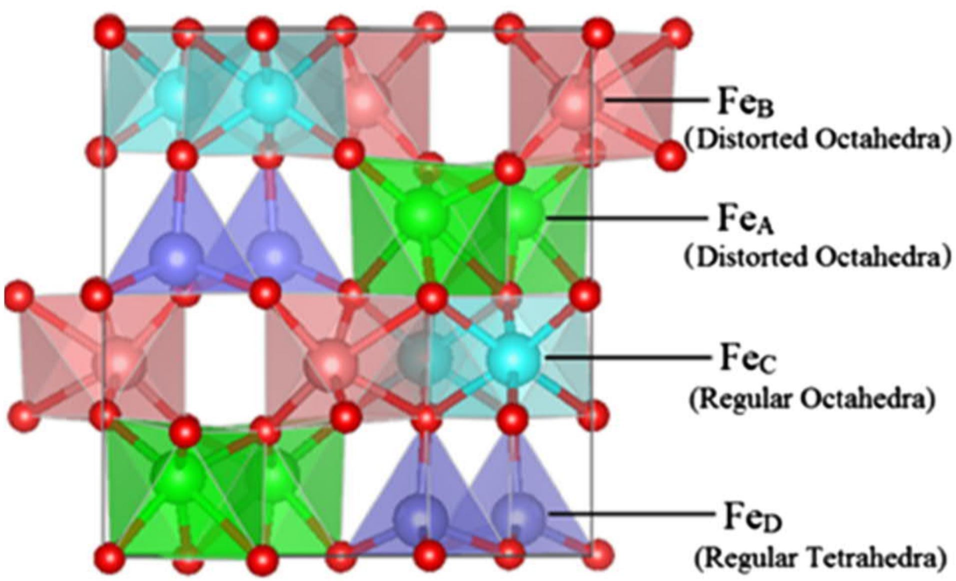


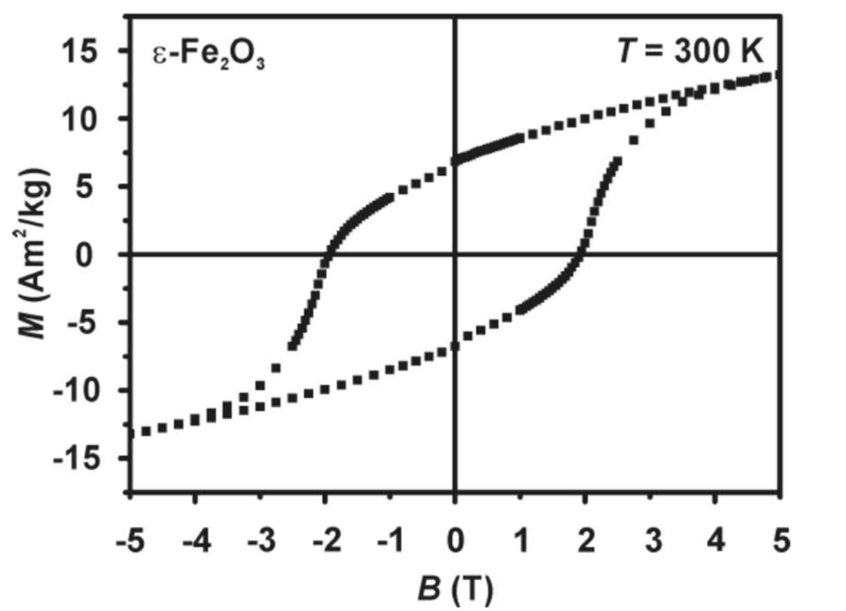
Aalto University
School of Engineering

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

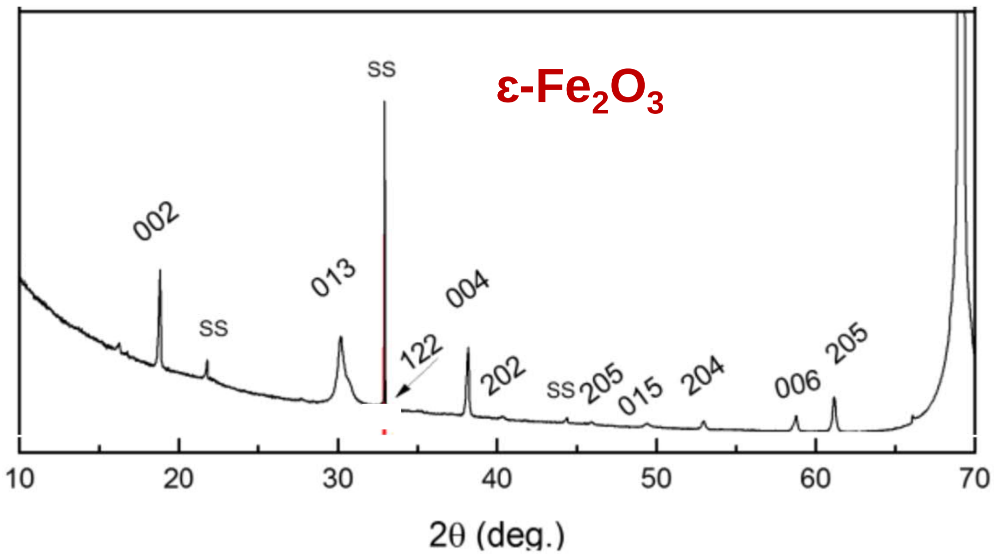


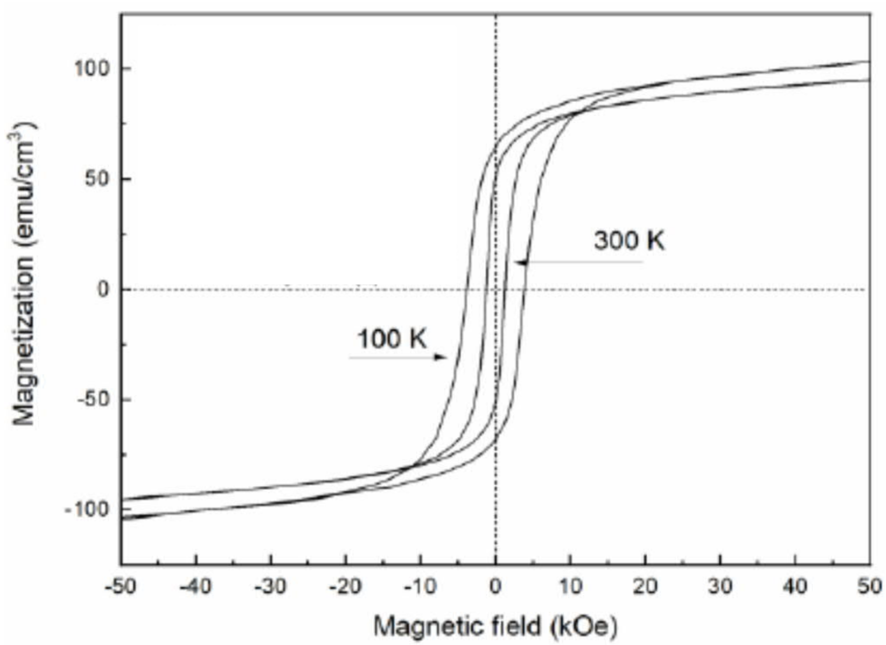


Facile ALD process for stable ε-Fe_2O_3 thin films

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

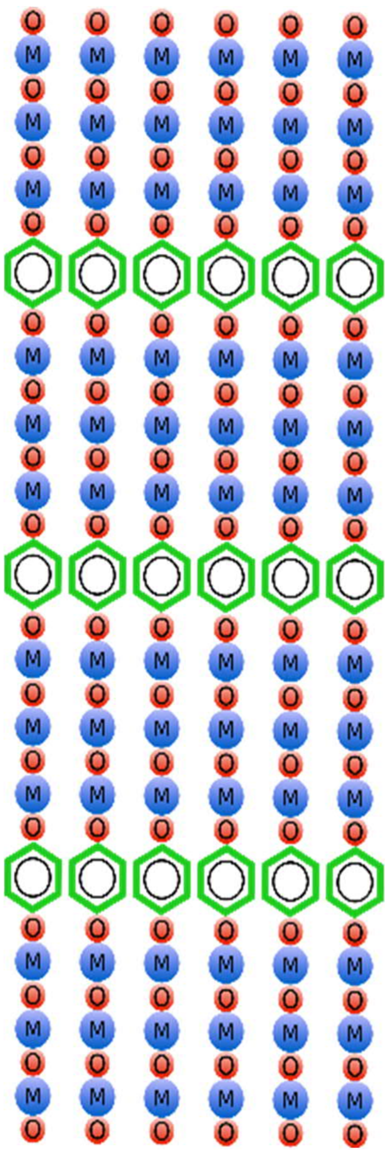
ALD: large-area homogeneity & conformality over porous templates → "MASS production"



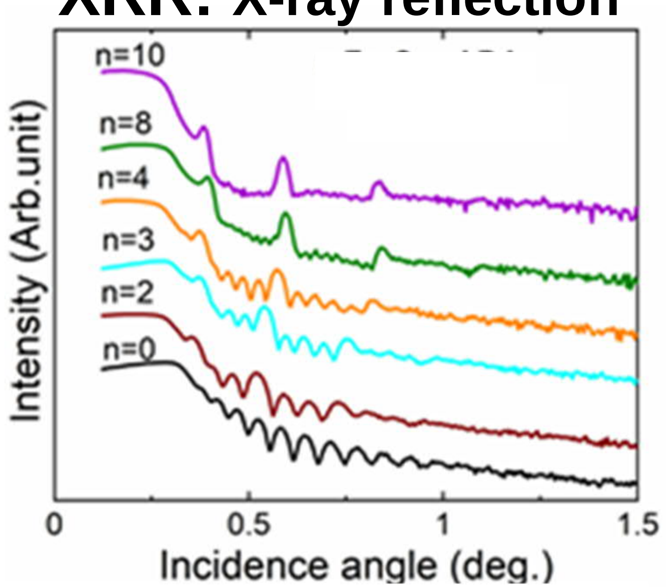


A. Tanskanen, O. Mustonen & M. Karppinen, Simple ALD process for ε-Fe_2O_3 thin films, *APL Materials* **5**, 056104 (2017).

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

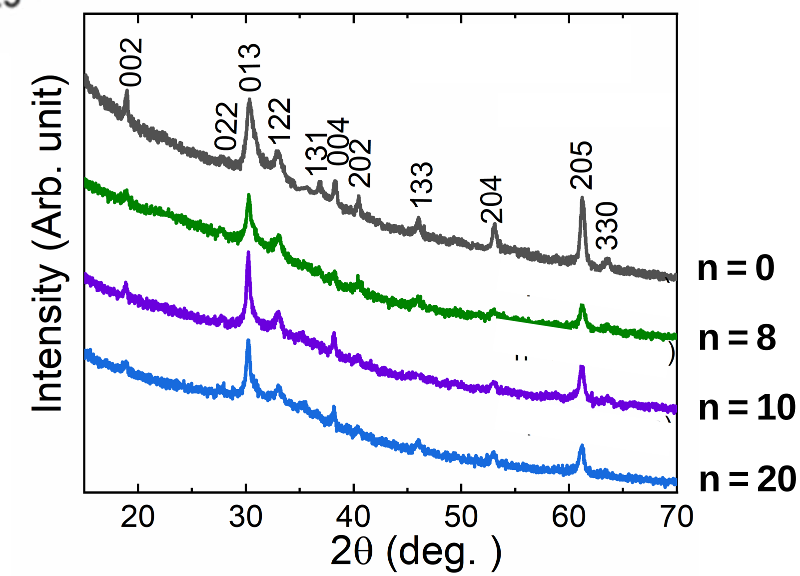


XRR: X-ray reflection

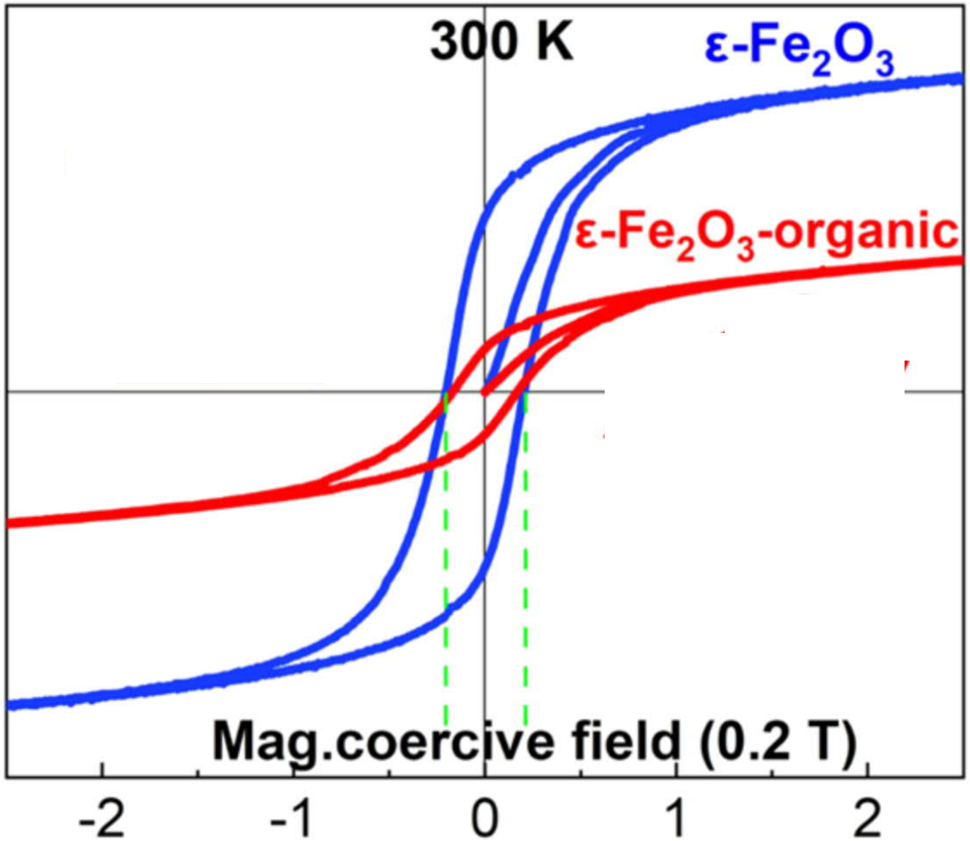


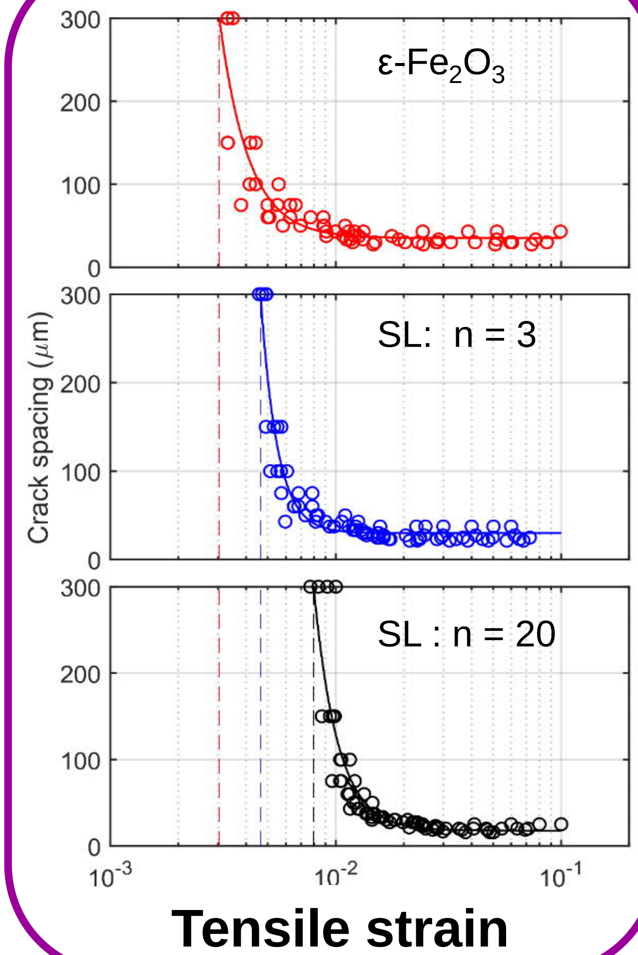
n: number of organic layers

GI-XRD



Mechanical property testing: ε-Fe_2O_3:TPA





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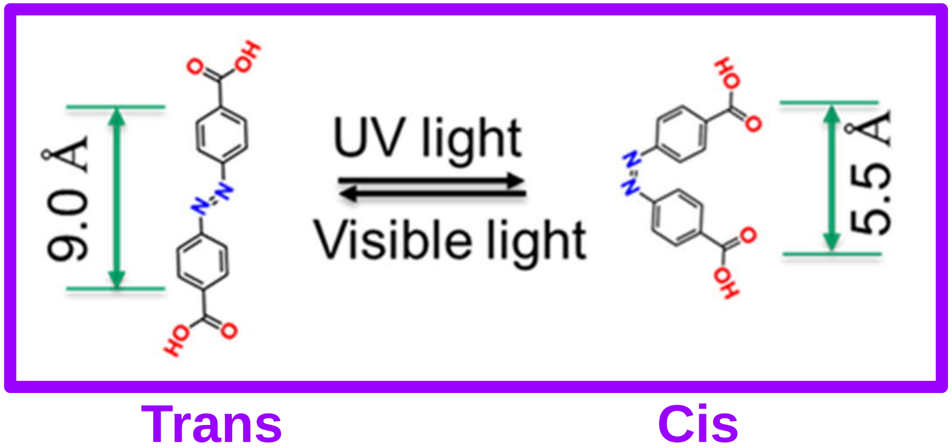
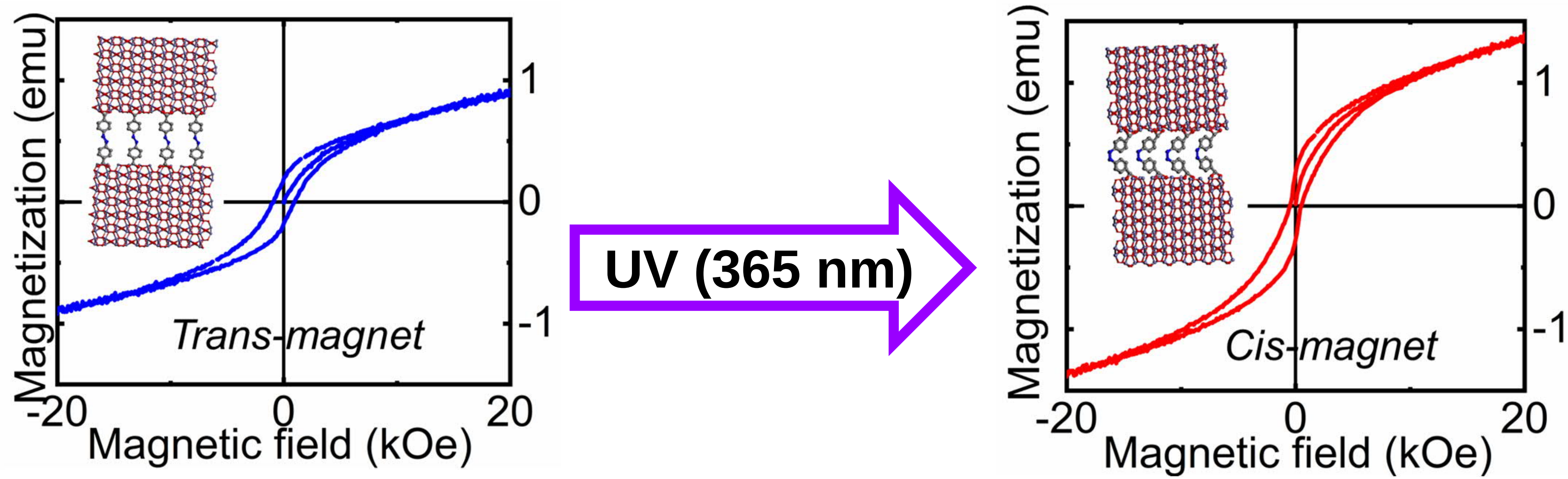
A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

Extraordinary Functionality:

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





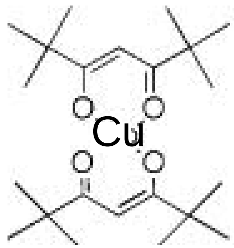
- **Magnetization (remanent and saturation) increased (doubled)**
- **Coercivity decreased (into half)**

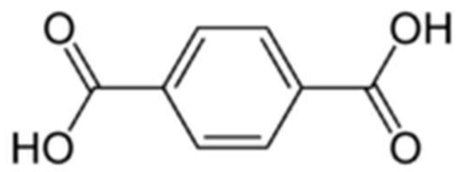
MOFs

METAL-ORGANIC FRAMEWORKS

BY

ALD/MLD

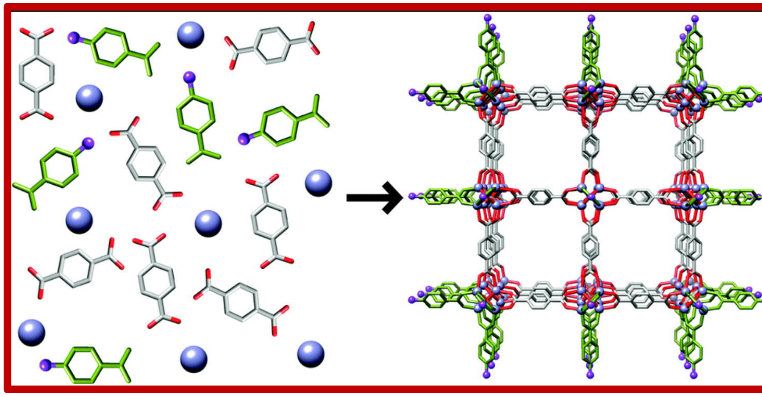


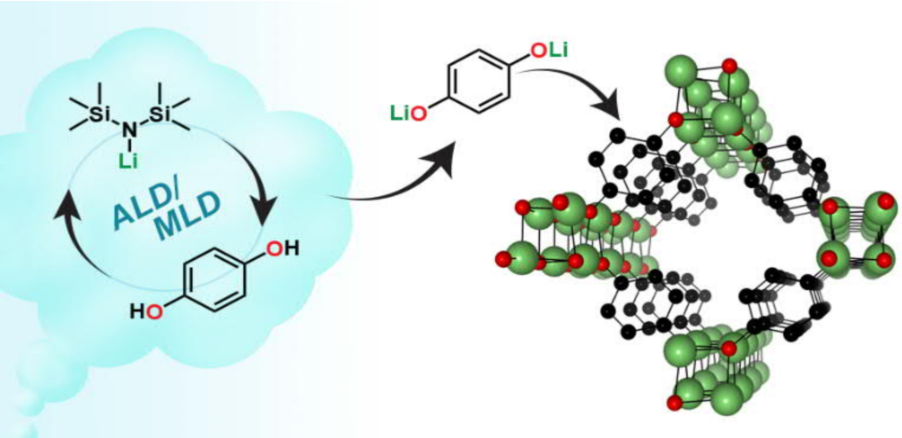


$Cu(thd)_2$ **Terephthalic acid (TPA)**

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

Known MOF-2 structure

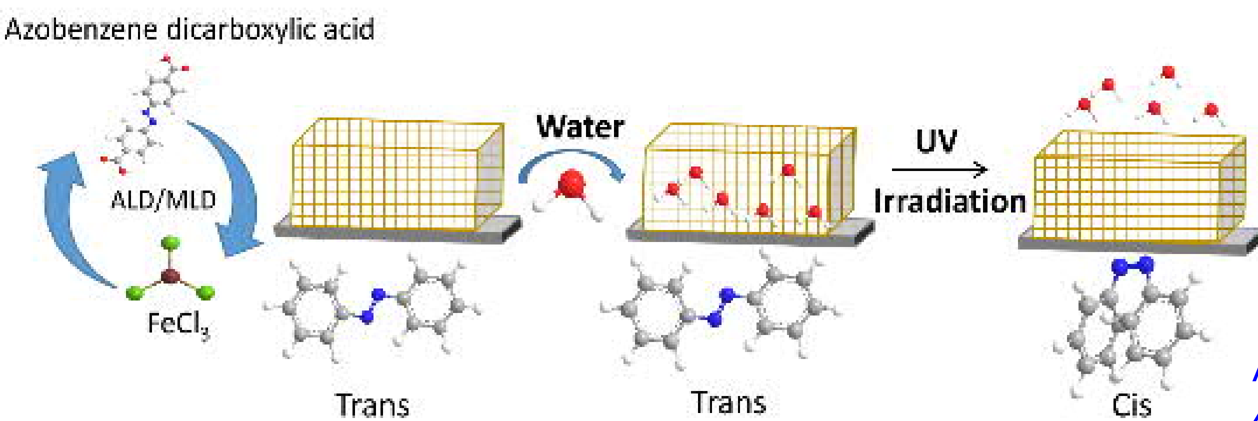




Lithium-benzoquinone

- 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).

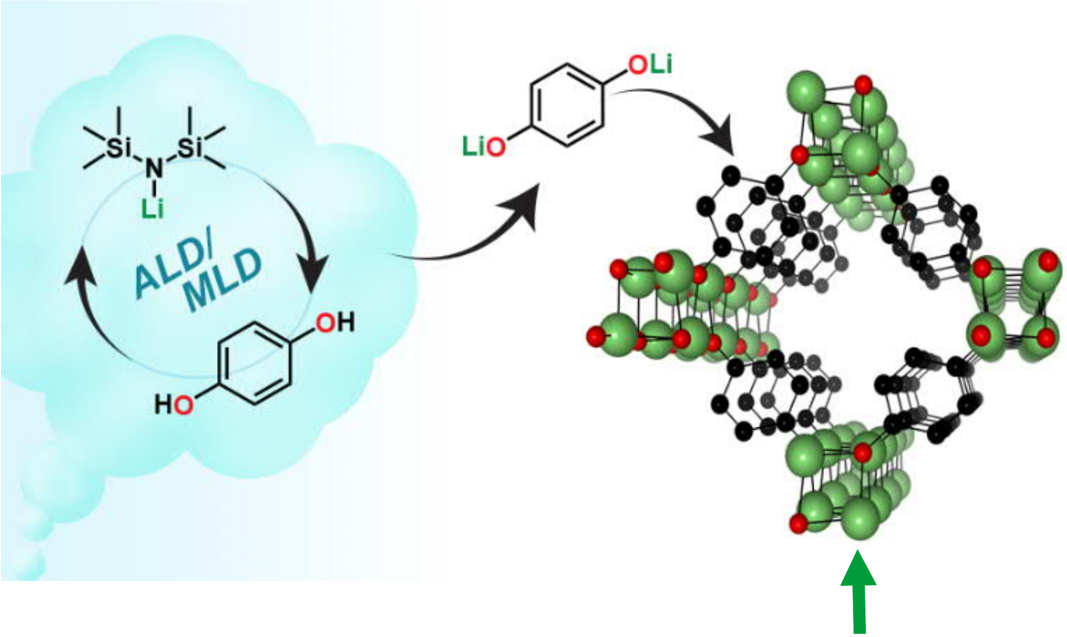


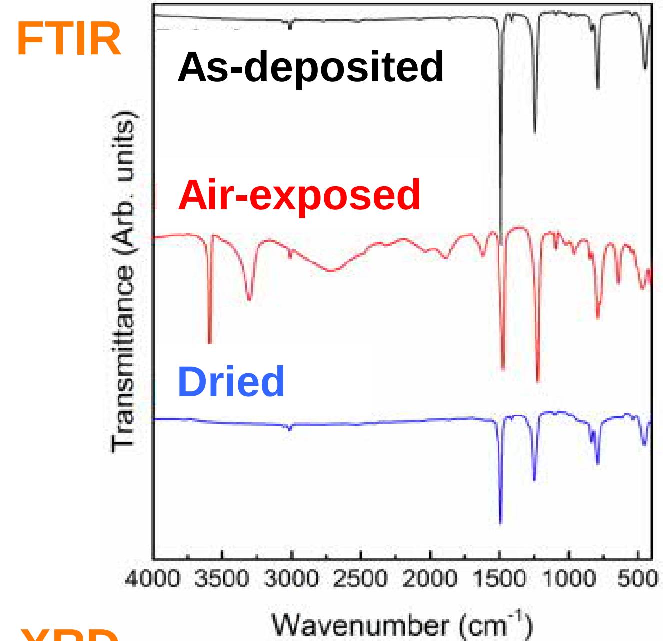
Iron-azobenzoate

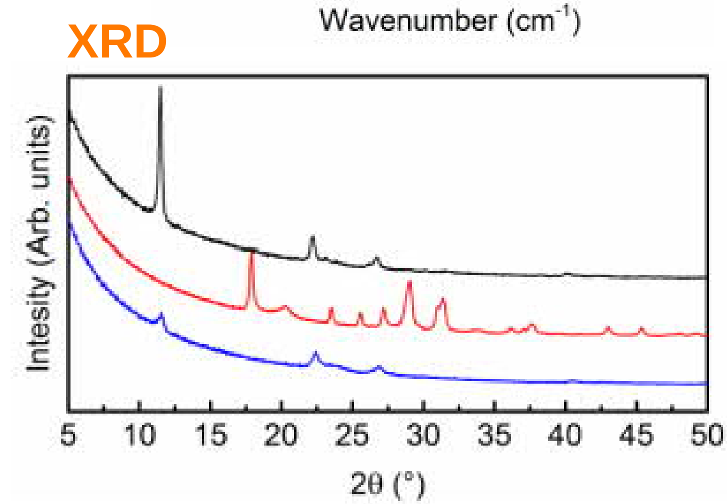
- New material
- Structure not yet known
- UV-switchable (cis-trans)

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

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







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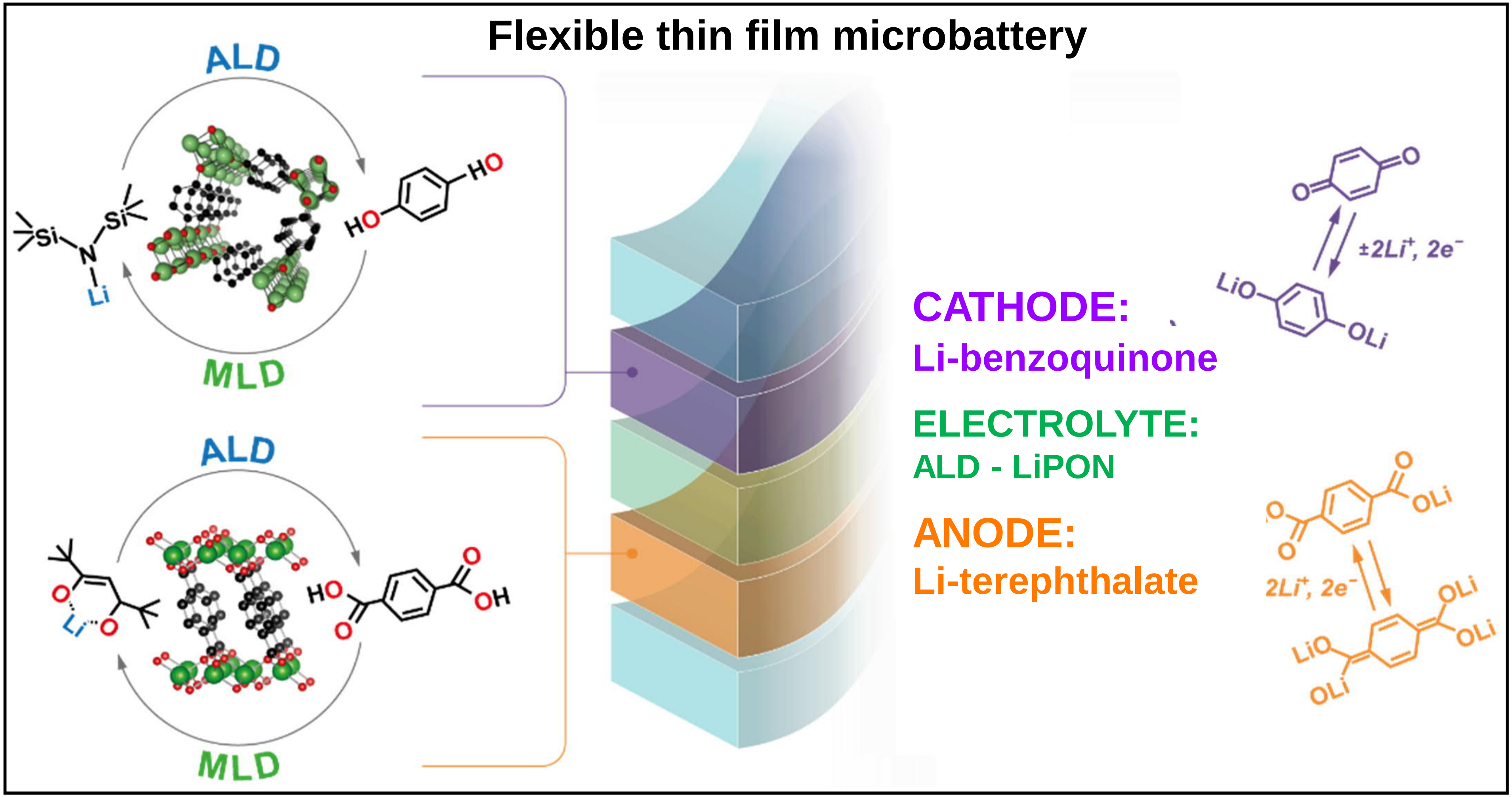
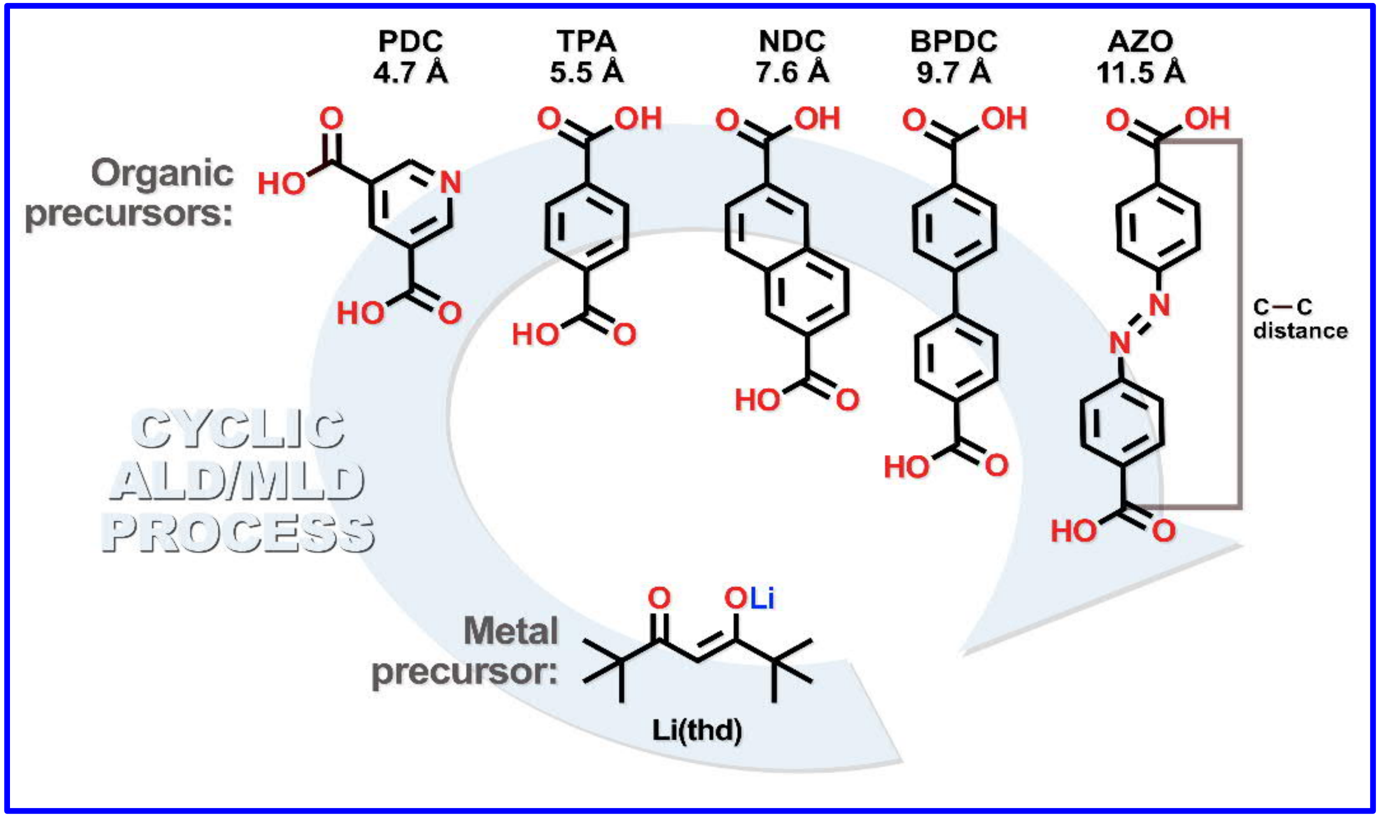
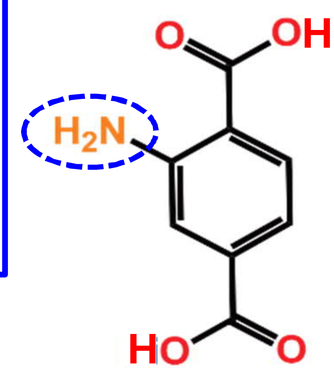
M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chemistry – A European Journal* **23**, 2988 (2017).

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.

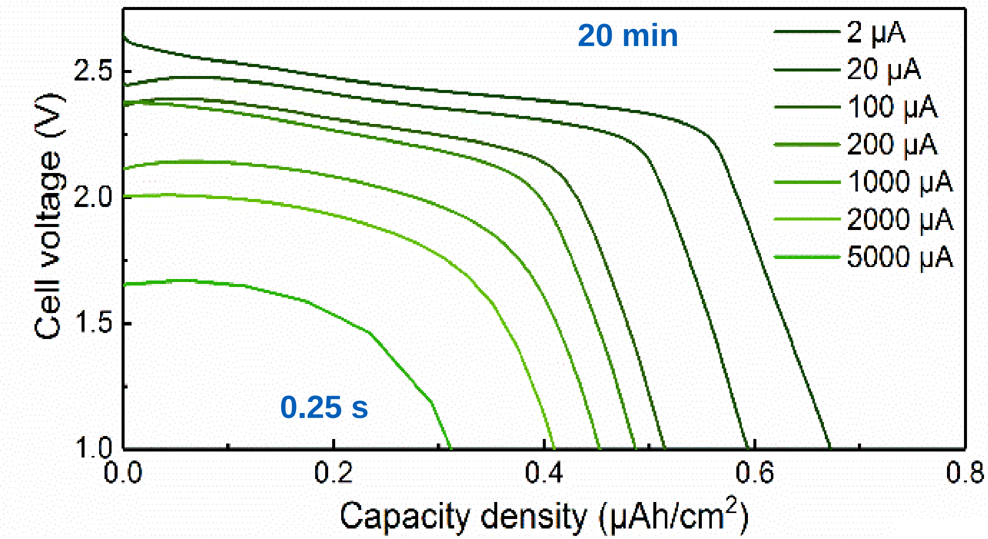


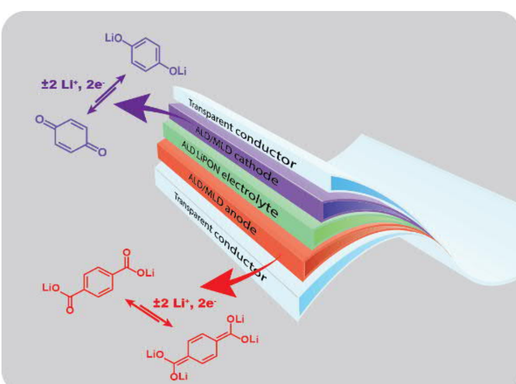


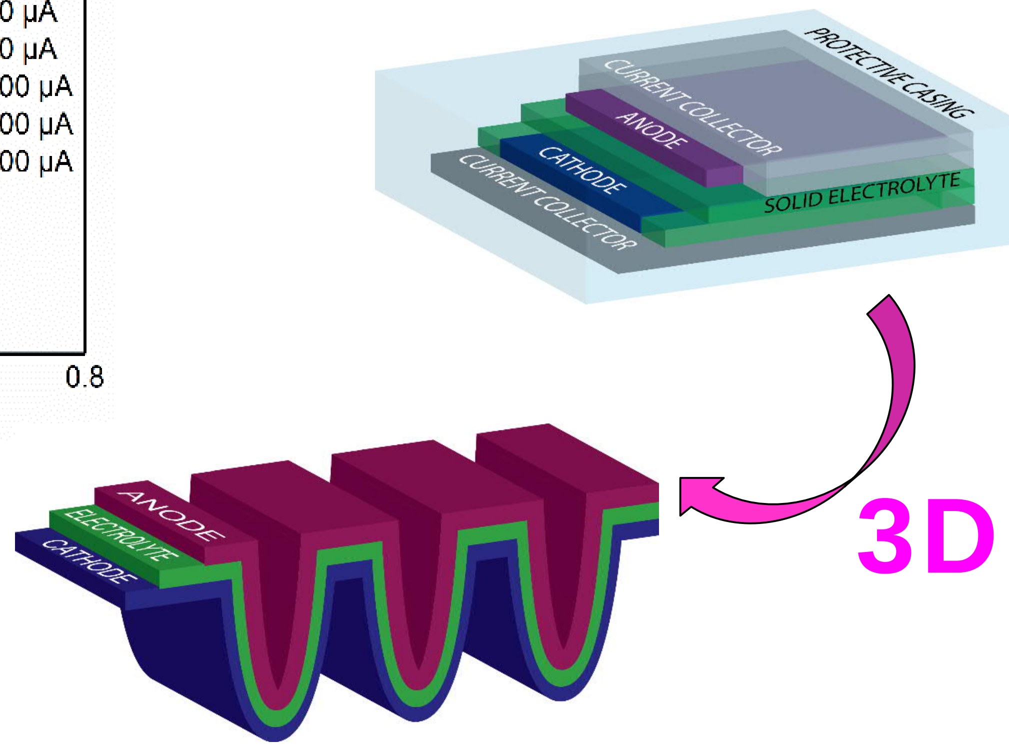
Electron-withdrawing amino group → Redox potential increases

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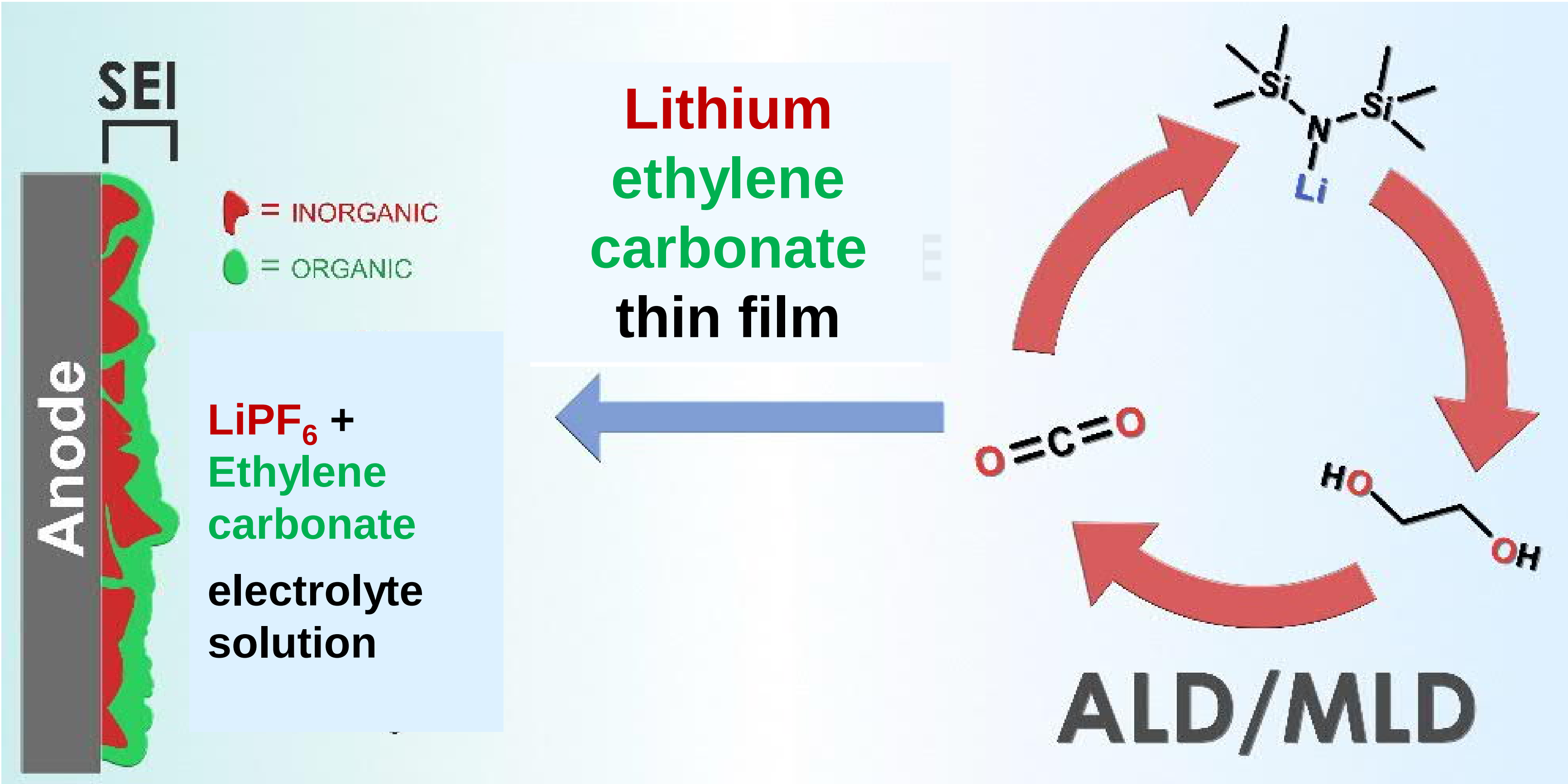
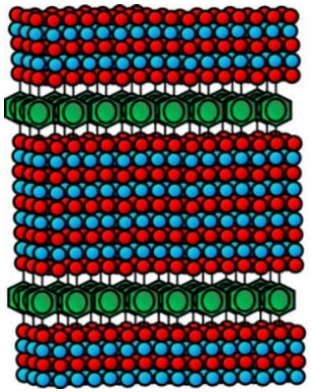
- M. Nisula, Y. Shindo, H. Koga & M. Karppinen, ***Chem. Mater.*** 27, 6987 **(2015)**.
- M. Nisula & M. Karppinen, ***Nano Lett.*** 16, 1276 **(2016).**
- M. Nisula & M. Karppinen, ***J. Mater. Chem. A*** 6, 7027 **(2018)**.
- J. Heiska, M. Nisula & M. Karppinen, ***J. Mater. Chem. A*** 7, 18735 **(2019).**

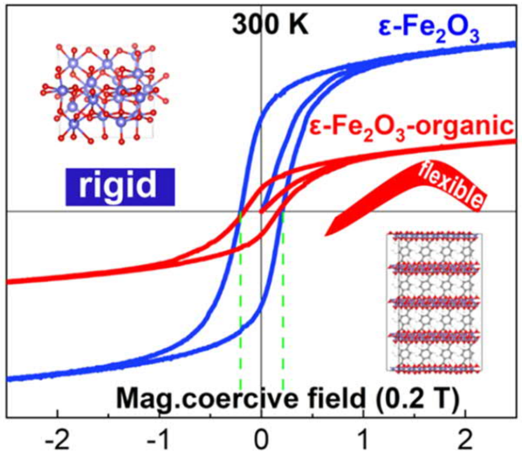
ALD + MLD: Artificial SEI-layer for Li-ion battery

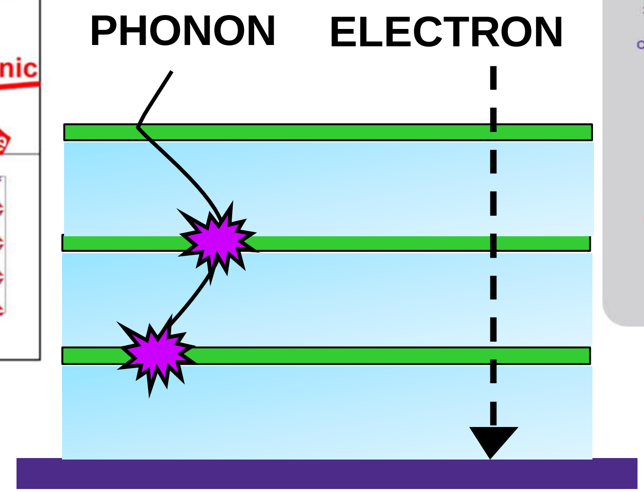


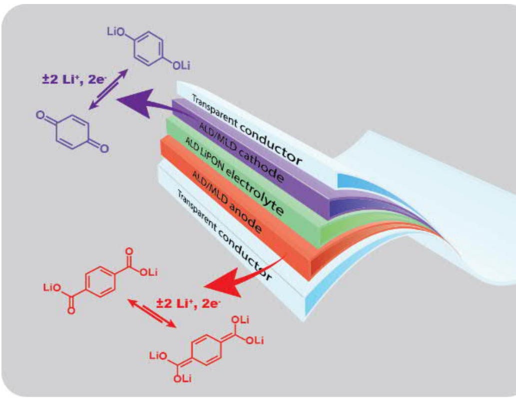
SEI (Solid Electrolyte Interphase)

- 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

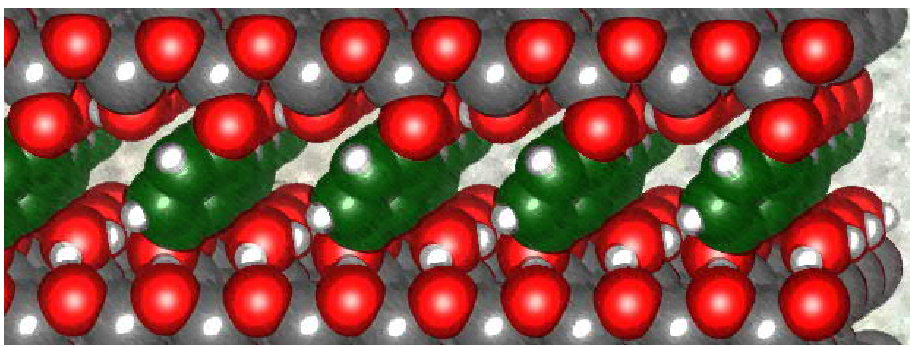


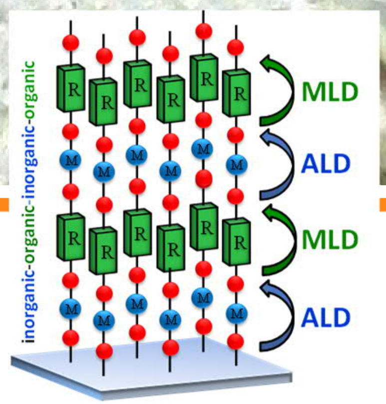






- **ALD/MLD can yield various new types of hybrid materials: new MOFs & layer-engineered superlattice and gradient materials**
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties have been discovered and much more expected !!!**





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