Functional Inorganic Materials
Fall 2023

Mondays: 10.15 - 12.00
Thursdays: 10.15 - 12.00

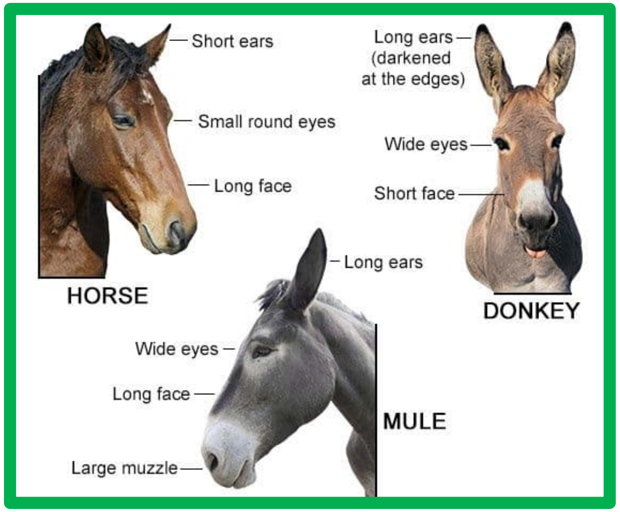
Lecture hall locations: U7 in Otakaari 1 / U-wing
Ke1 in Kemistintie 1 (CHEM building)

You can use https://usefulaaltomap.fi/ to see the exact location of U7.

#	Date	Place	Who	Topic
1	Mon 4.9.	U7 (U135a)	Maarit	Introduction + **Materials design (doping)**
2	Thu 7.9.	Ke1 (A305)	Antti	Introduction + Computational materials design
3	Mon 11.9.	U7 (U135a)	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 14.9.	Ke1 (A305)	Maarit	**Magnetic oxides**
5	Mon 18.9.	U7 (U135a)	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	Thu 21.9.	Ke1 (A305)	Maarit	Ionic conductivity (Lithium): **Li-ion battery**
7	Mon 25.9.	U7 (U135a)	Antti	Thermal conductivity
8	Thu 28.9.	Ke1 (A305)	Antti	**Thermoelectricity**
9	Mon 2.10.	U7 (U135a)	Antti	Piezoelectricity
10	Thu 5.10.	Ke1 (A305)	Antti	Pyroelectricity and ferroelectricity
11	Mon 9.10.	U7 (U135a)	Antti	**Luminescent** and optically active materials
12	**Thu 12.10.**	**Ke1 (A305)**	**Maarit**	**Hybrid materials**

LECTURE 12: Hybrid Materials

- Two or more different components
- Composite versus Single Compound
- Components: - brought together: sum of individual properties
  - fused together: intermediate properties
  - interactively fused: extraordinary properties
- Inorganic-organic materials
- CPs & MOFs
- ALD/MLD
- Layer-engineering & Superlattice



LECTURE EXERCISE 12

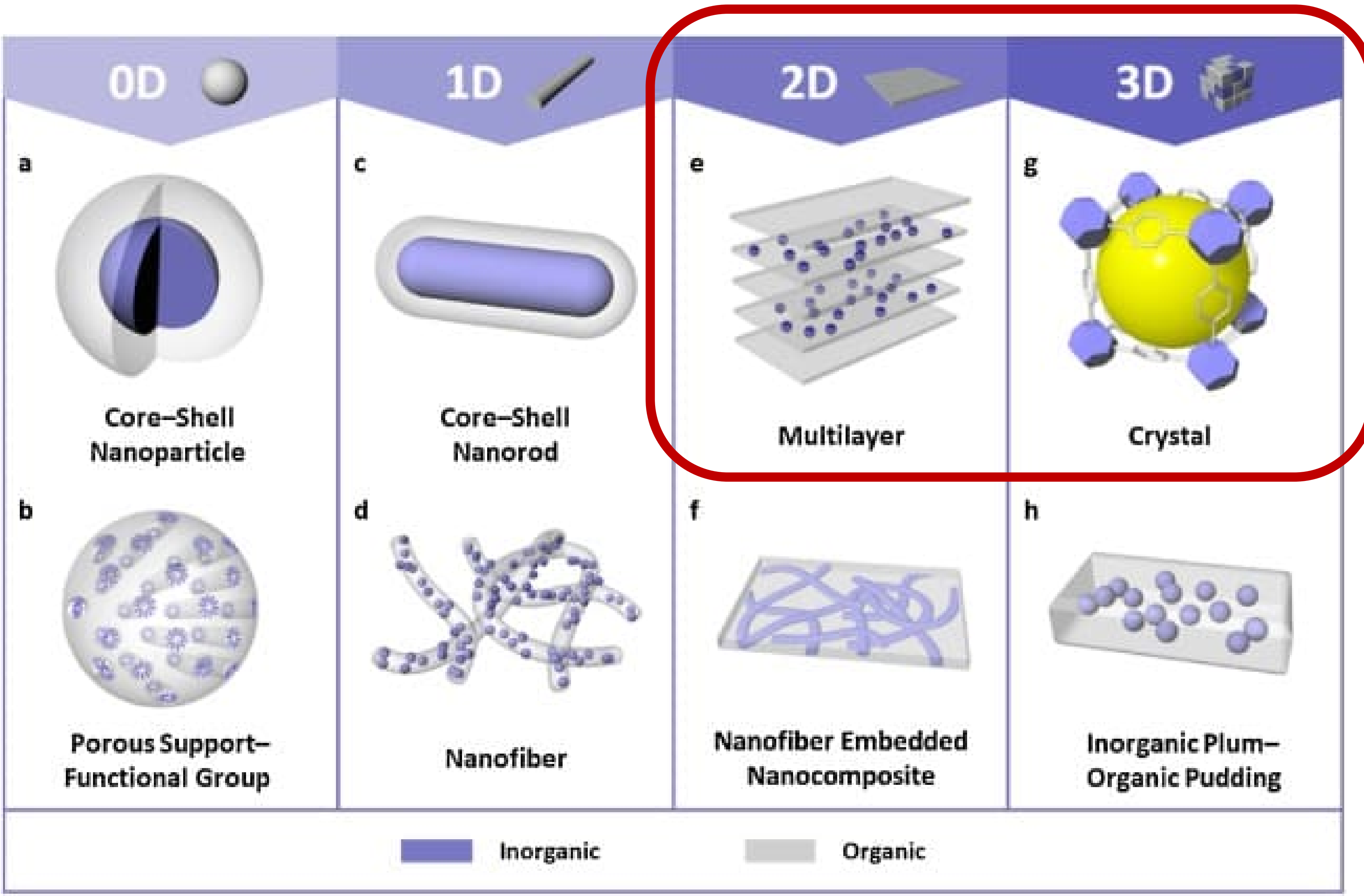
1. **What are the possible dimensionalities (0D, 1D, 2D or 3D) of the followings: (a) Metal-organic complex (coordination compound with organic ligands), (b) Coordination polymer, (c) Metal-organic framework.**

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).**

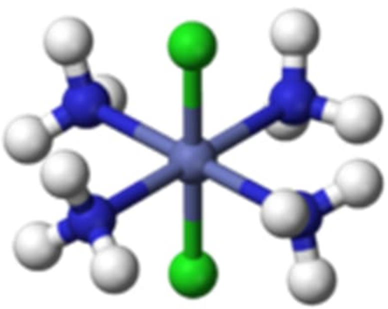
4. **Give examples of ALD/MLD fabricated materials which are difficult (if not impossible) to synthesize using conventional synthesis techniques. Explain the unique benefits of ALD/MLD in these selected cases with few sentences.**

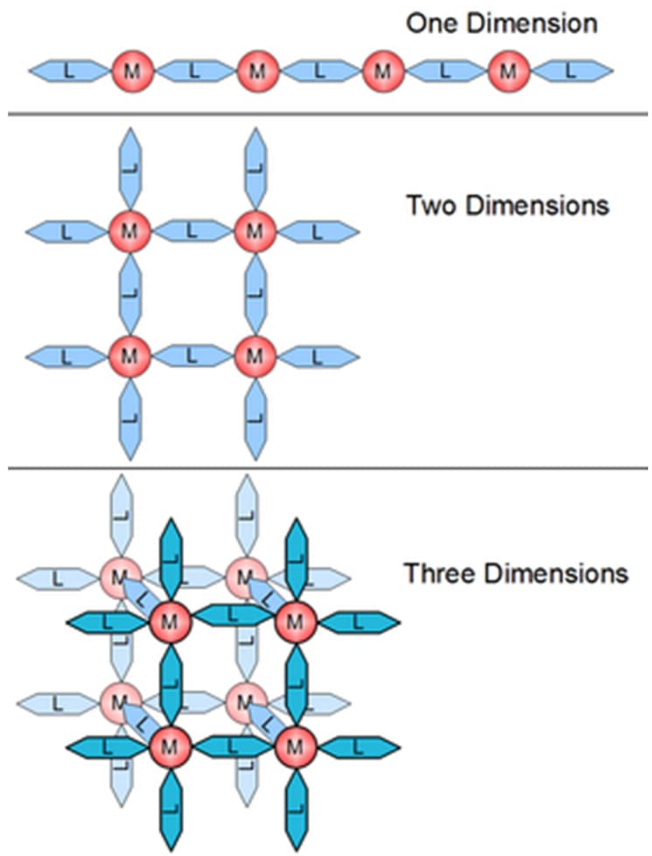
EXAMPLES of Inorganic-Organic Hybrid Materials

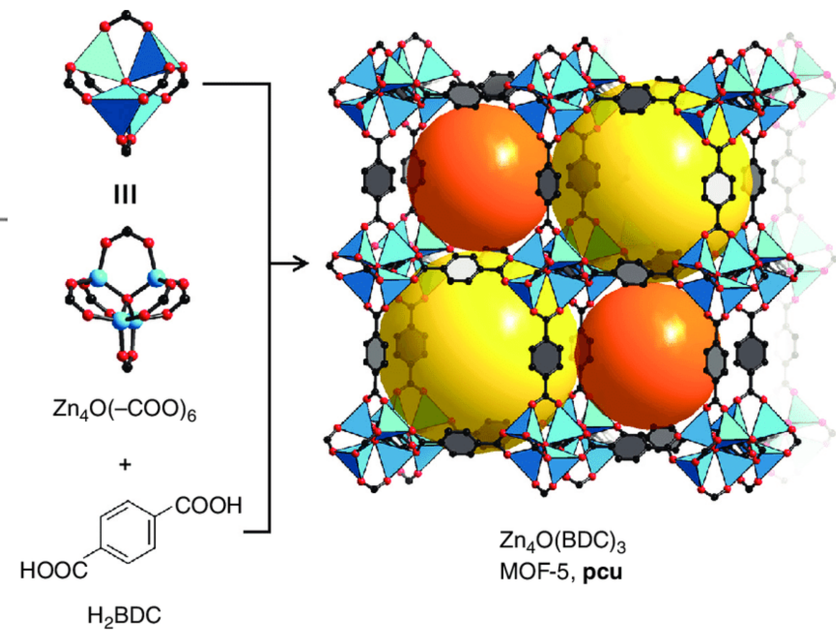


FOR CHEMISTS: Inorganic-Organic Material

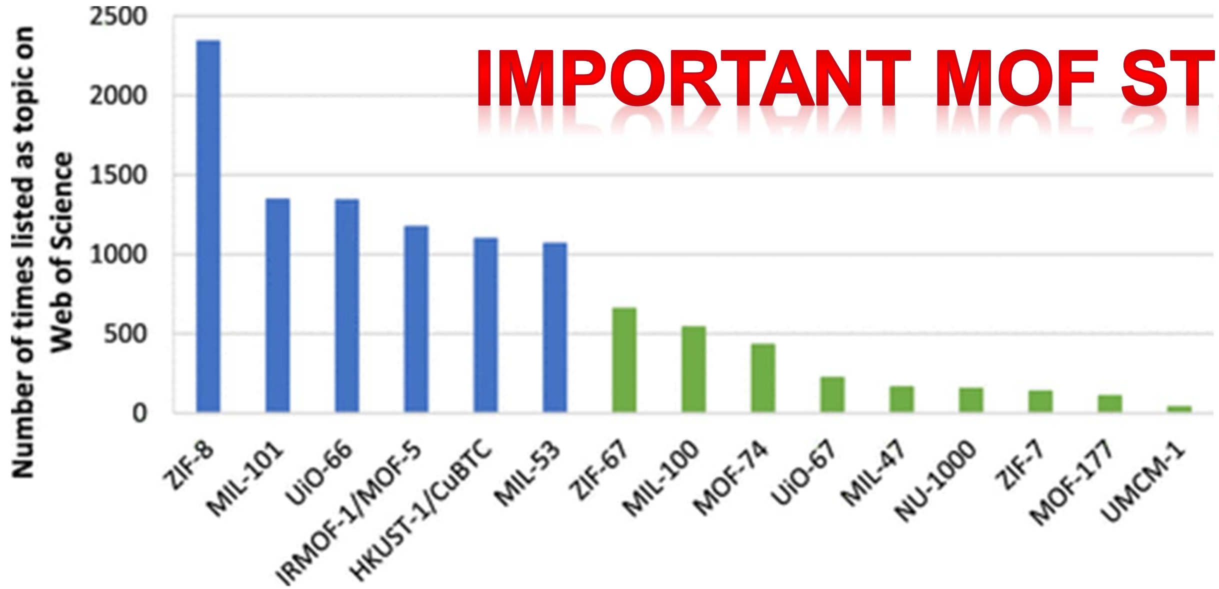
- **Single Compound (NOT Composite) with Chemical Bonds**
- **Coordination/Metal Complex: central metal ion + (organic) ligands**
- **Coordination Polymer (CP): ligands act as bridges**
- **Metal-Organic Framework (MOF): highly porous**

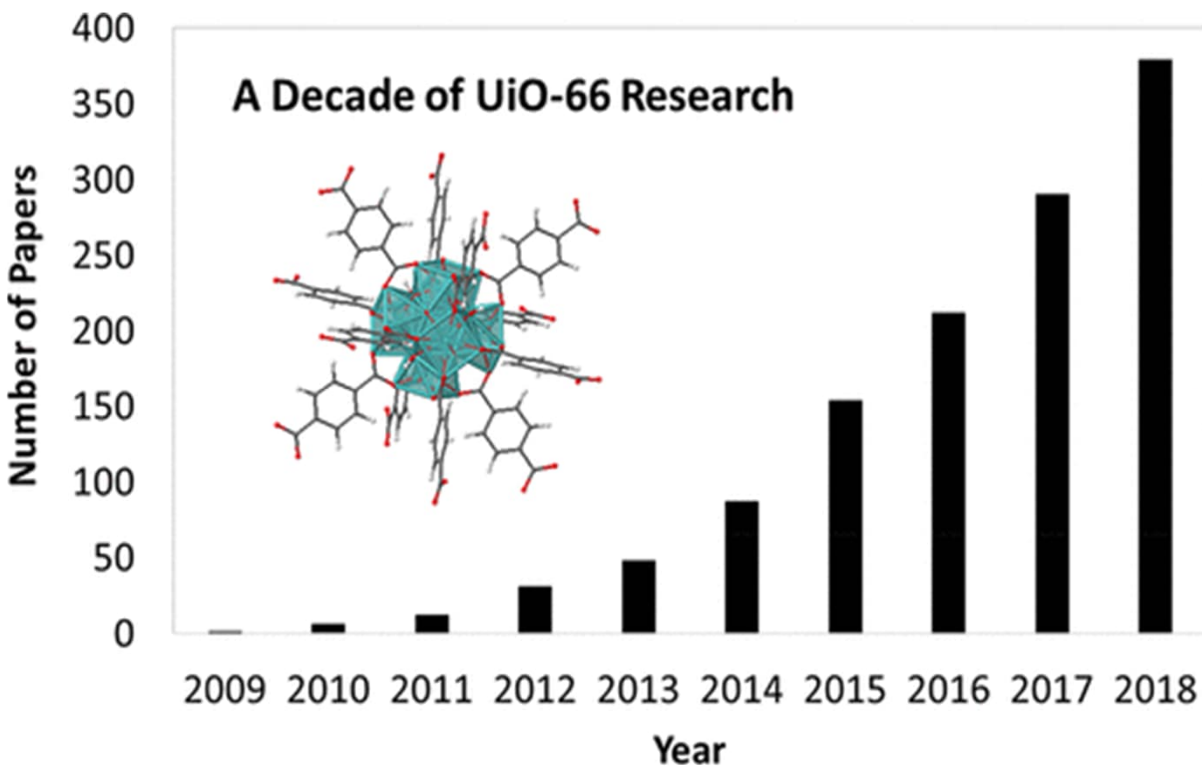




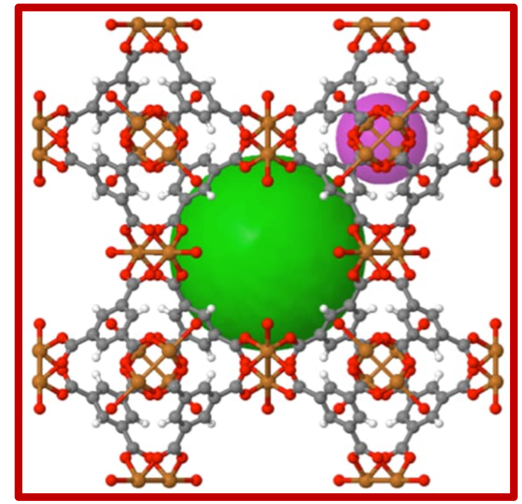


IMPORTANT MOF STRUCTURES

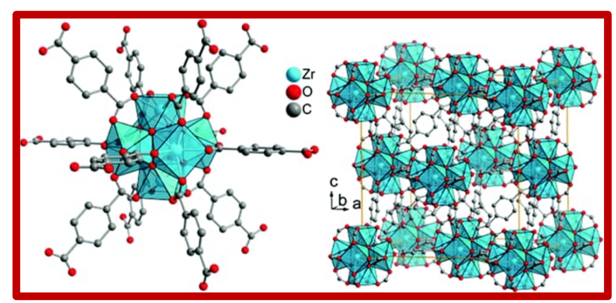


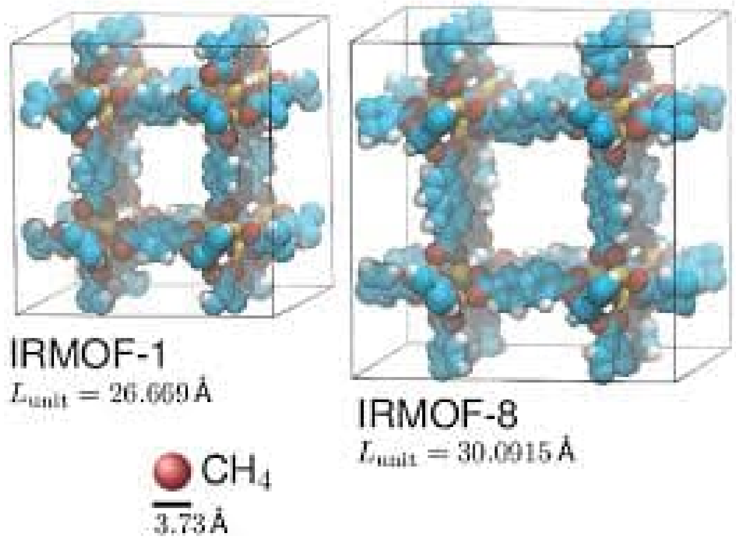


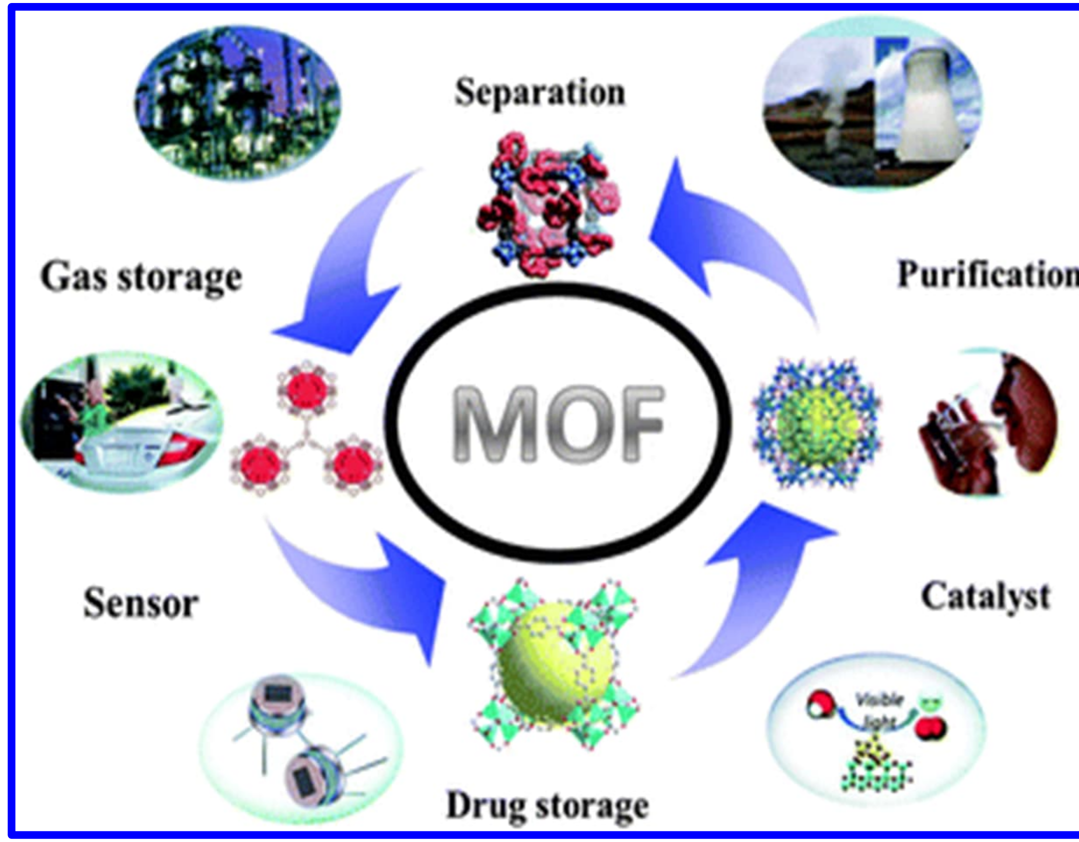
HKUST-1



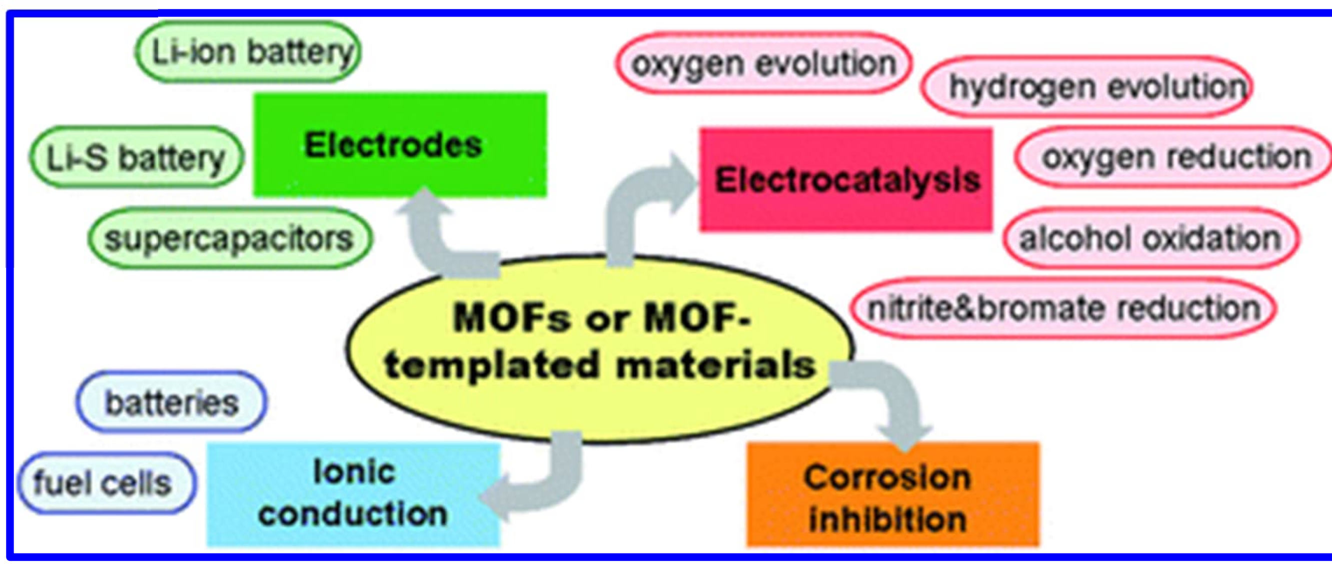
UiO-66





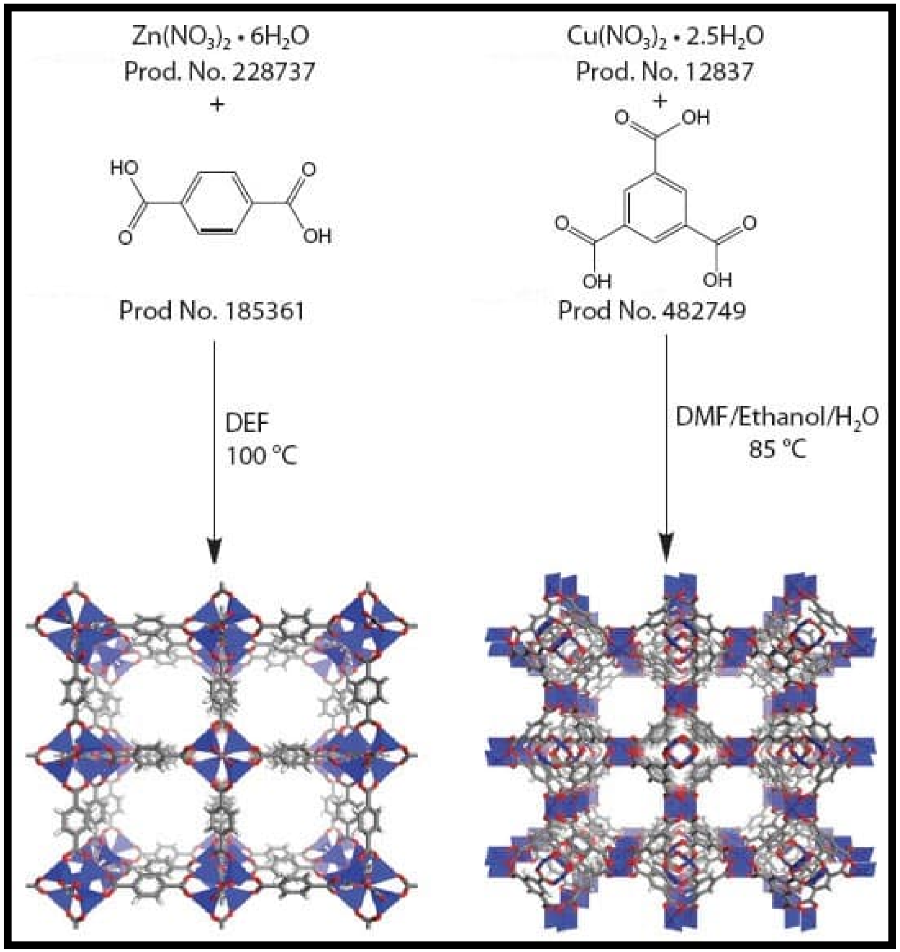


MOF THIN FILMS!



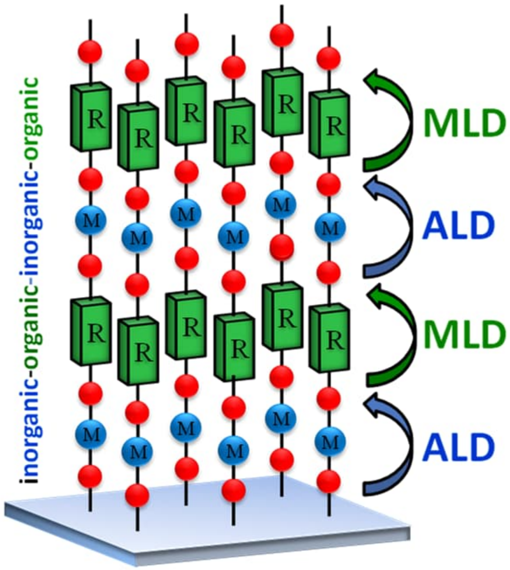
Synthesis of MOFs

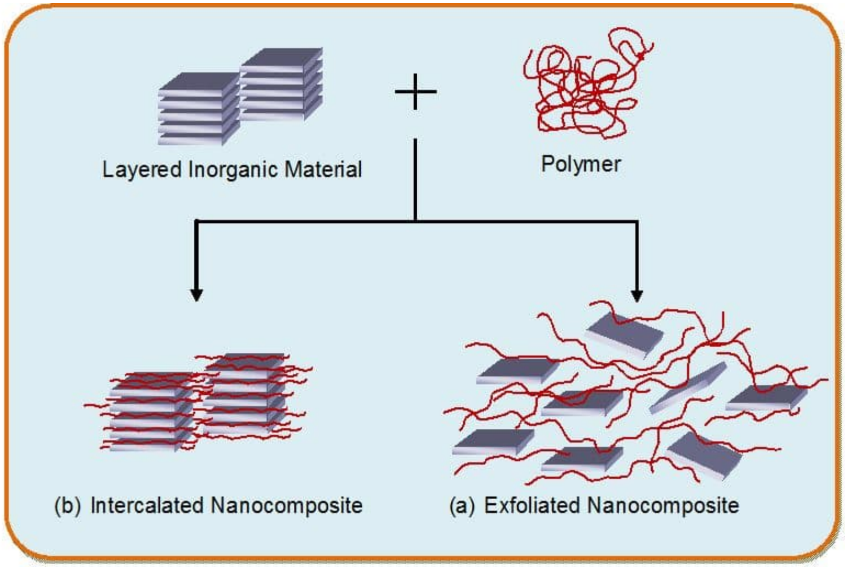
- **Synthesized most often in bulk form via solution techniques**
- **Porous structure → MOFs absorb readily/unintentionally solvent molecules**
- **Many prospective applications would require high-quality thin films**
- **No gas-phase deposition techniques (before ALD/MLD) !**

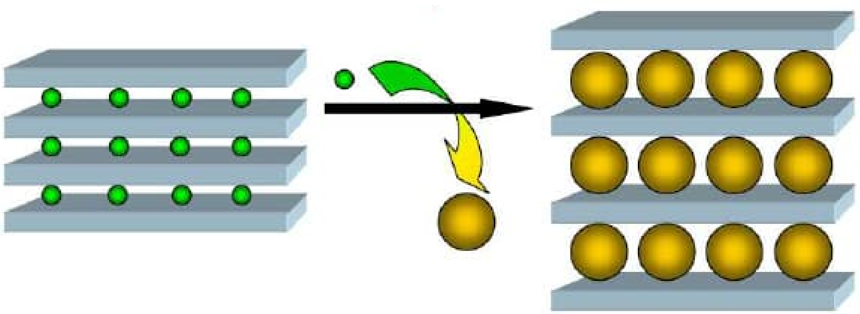


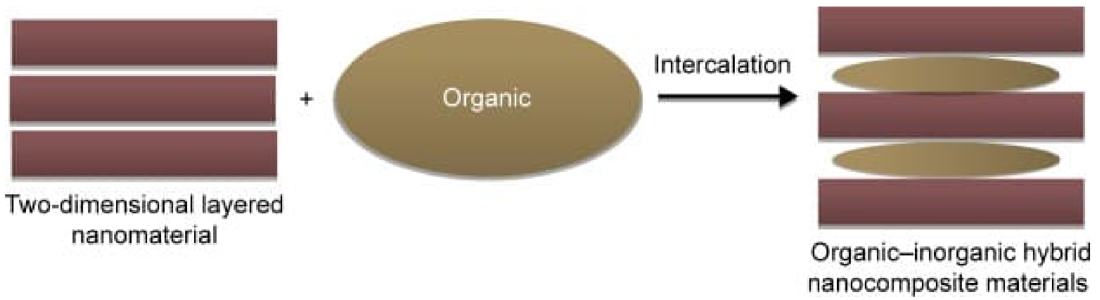
Layered Inorganic-Organic Materials

- **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
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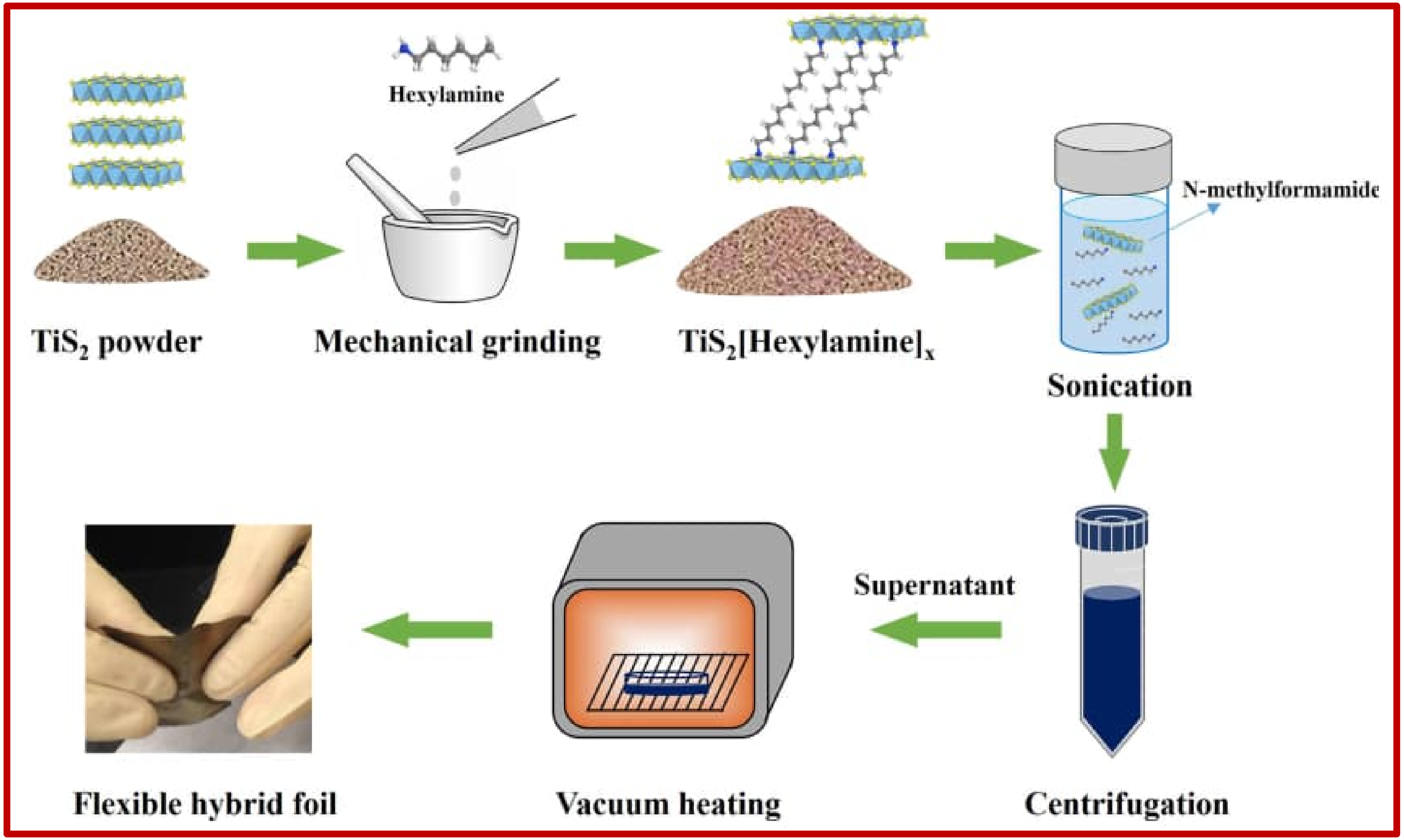
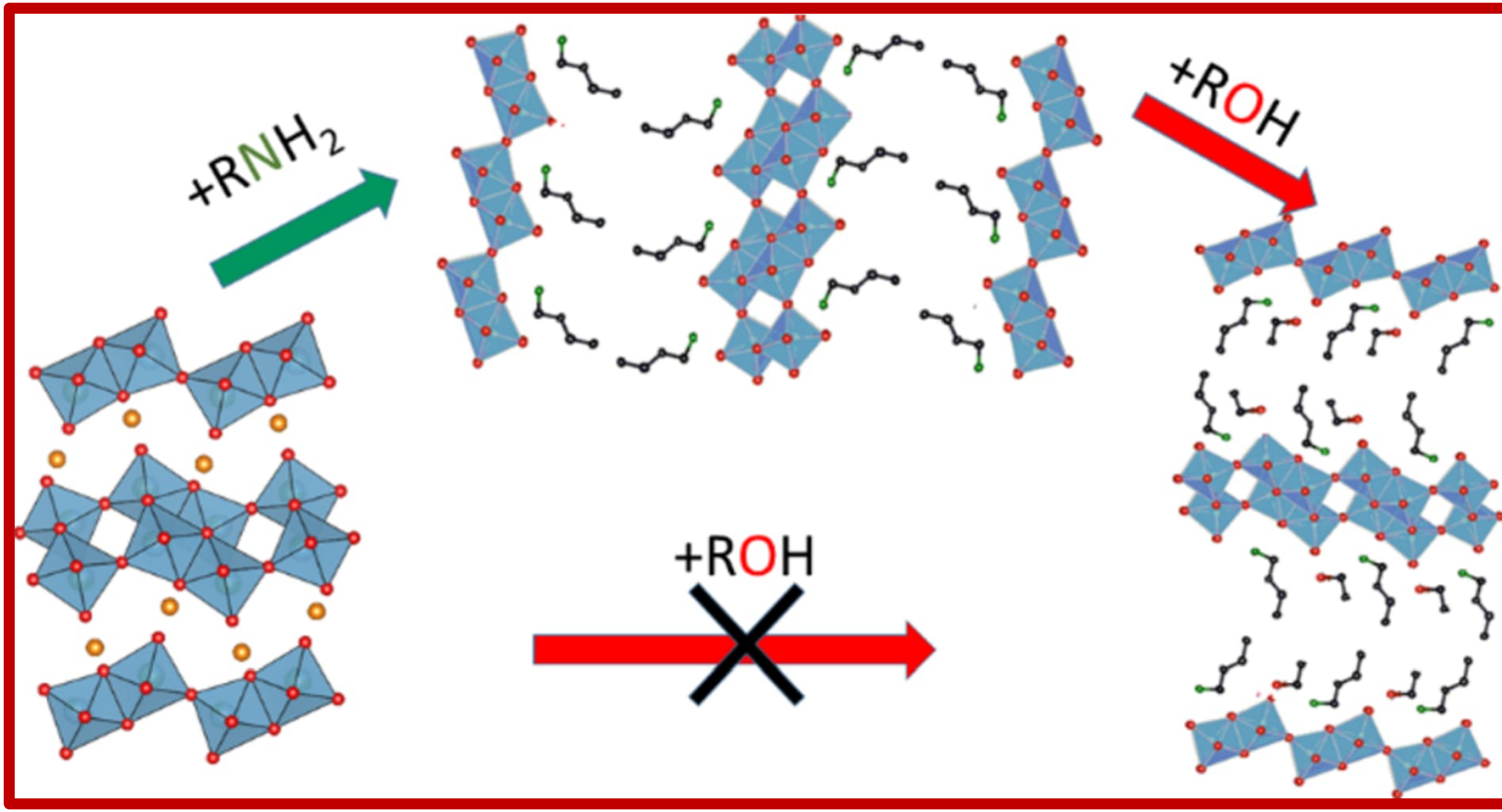
[d] Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan
[e] Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue 690-8504, Japan





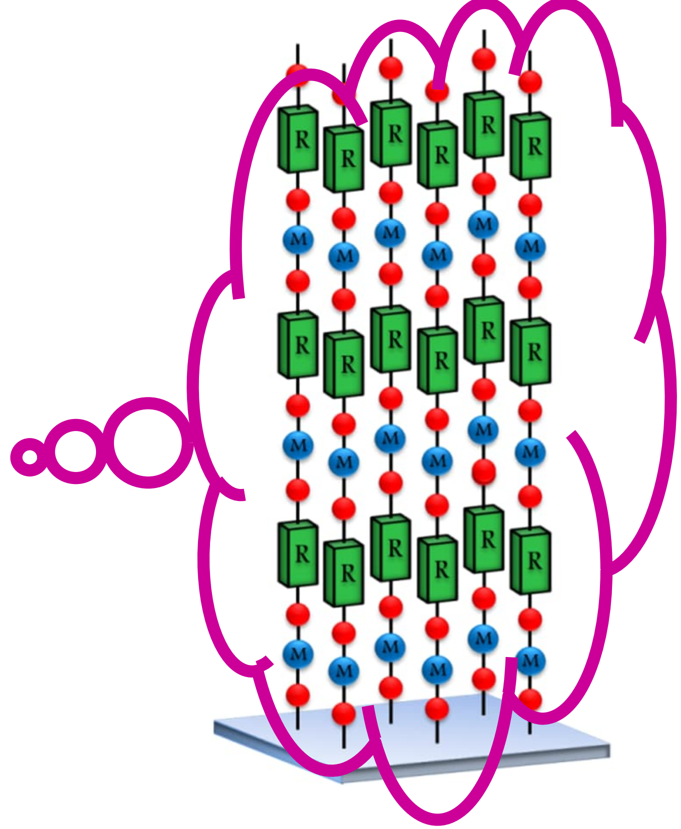
Inorganic Chemistry
Article
pubs.acs.org/IC

Intercalation of Primary Alcohols into Layered Titanoniobates

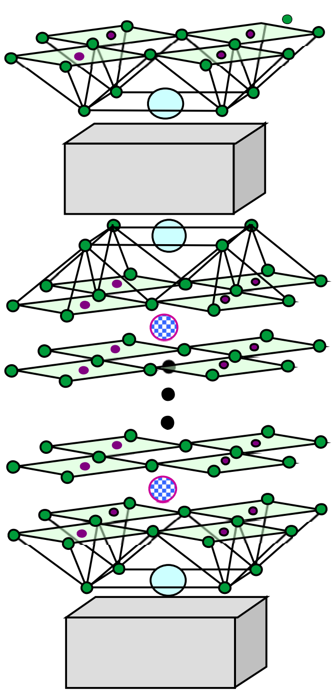
Chris I. Thomas* and Maarit Karppinen
Department of Chemistry and Materials Science, Aalto University, FI-00076 Espoo, Finland

MULTI-FUNCTIONAL MULTILAYERED MATERIALS

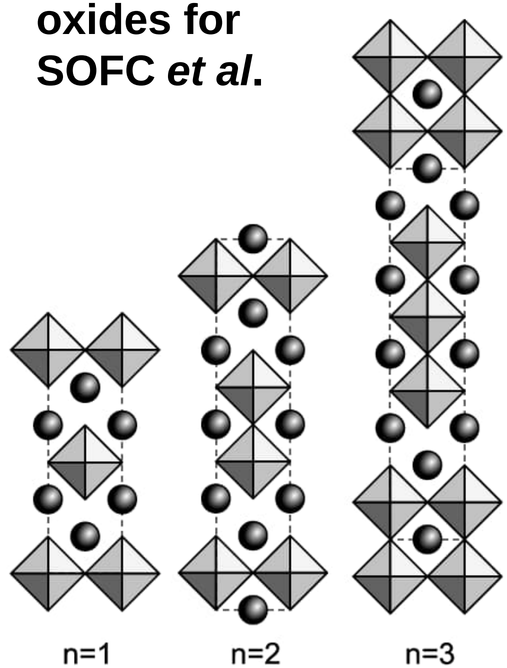
Layered inorganic-organic hybrid thin films



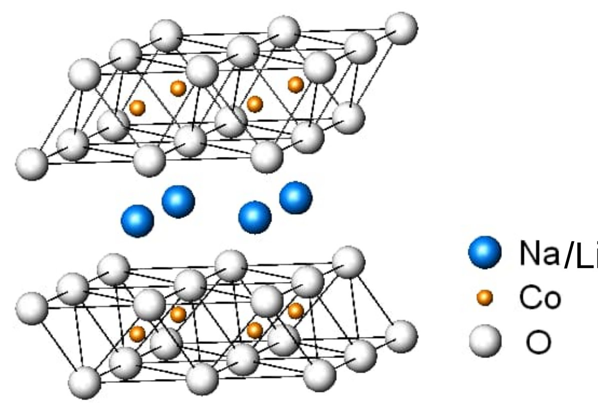
Multilayered Cu oxides for high-T_c superconductors

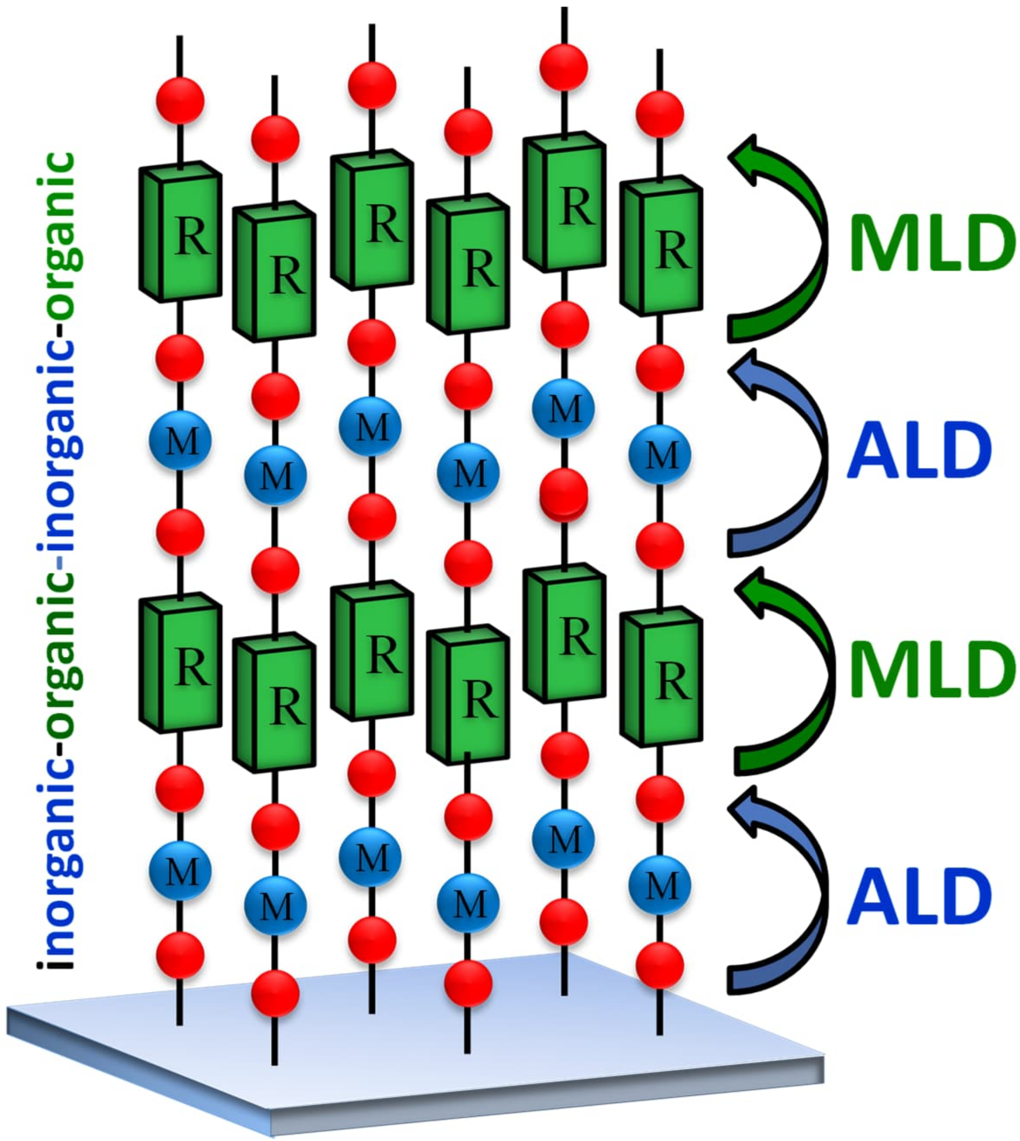


Ruddlesden-Popper oxides for SOFC *et al*.



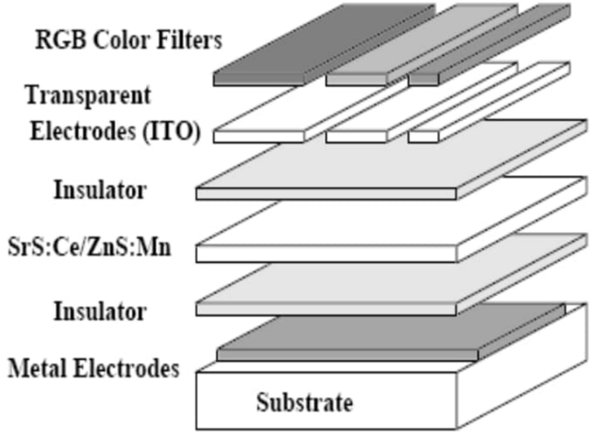
Layered Co oxides for Li-ion battery & thermoelectrics




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

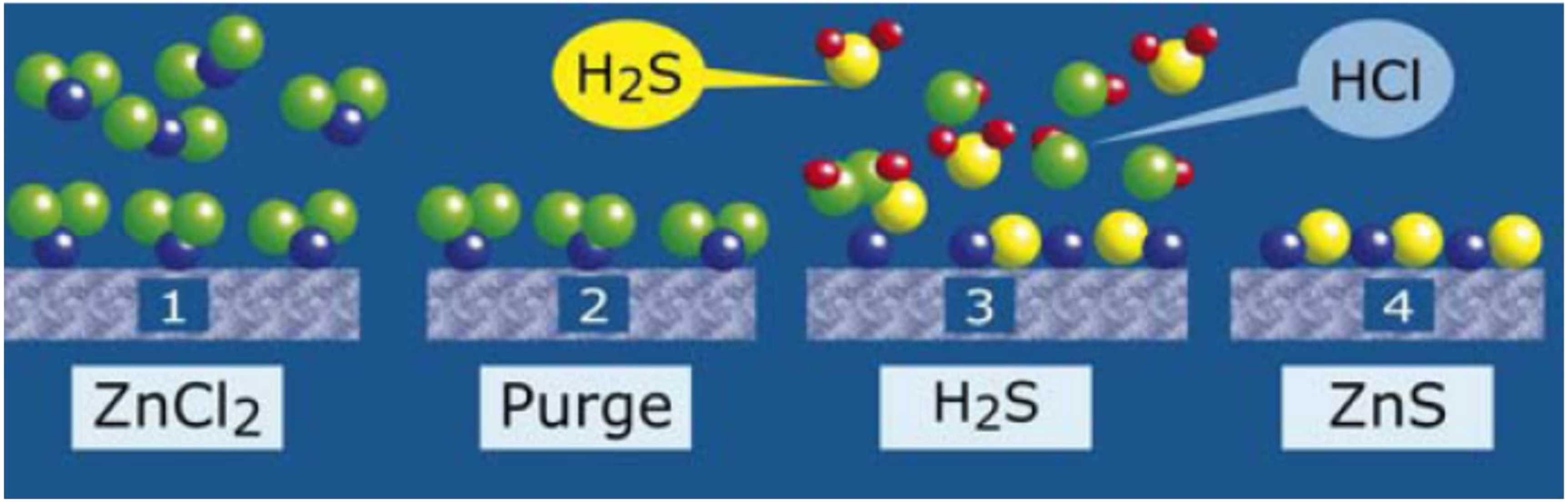
Atomic Layer Deposition (ALD) Thin-Film Technique

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



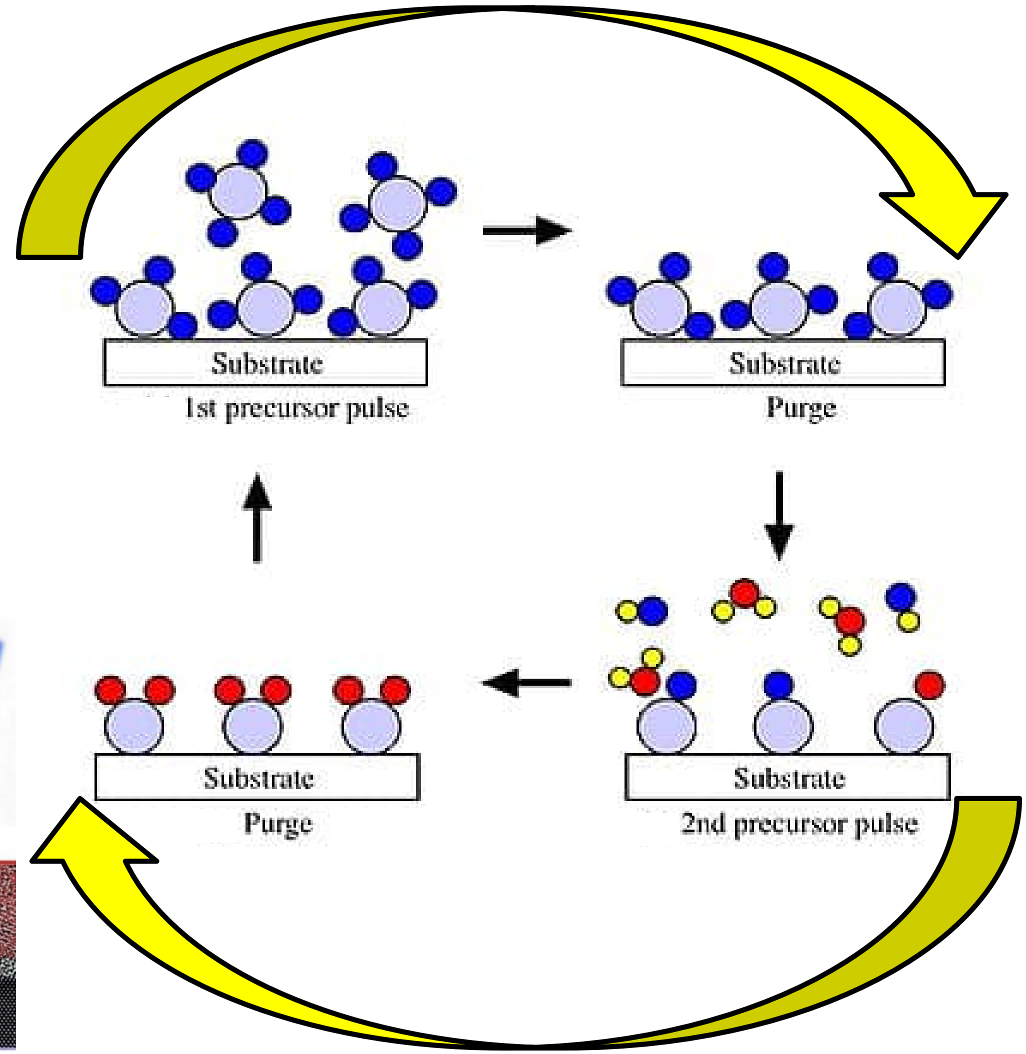
Electroluminescent display

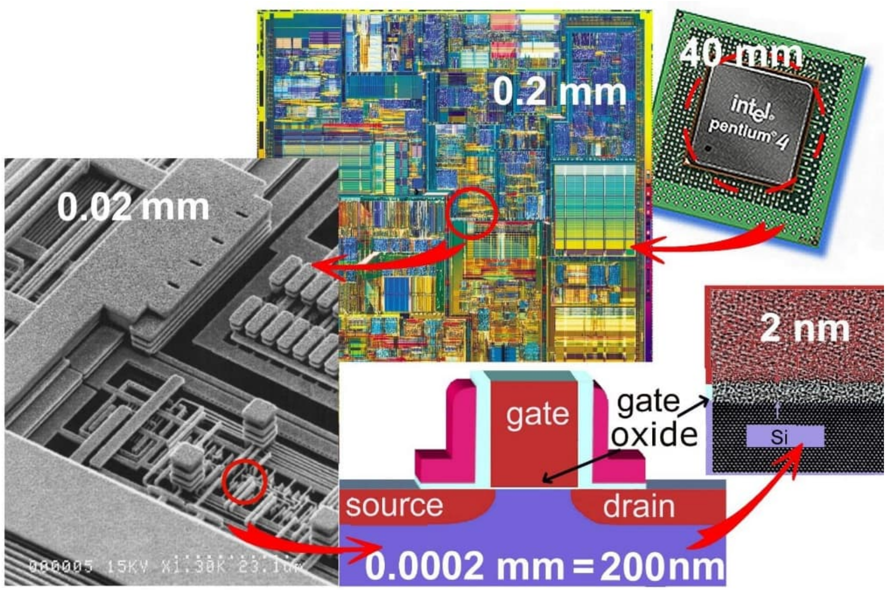
Instrumentarium / Finlux / Planar



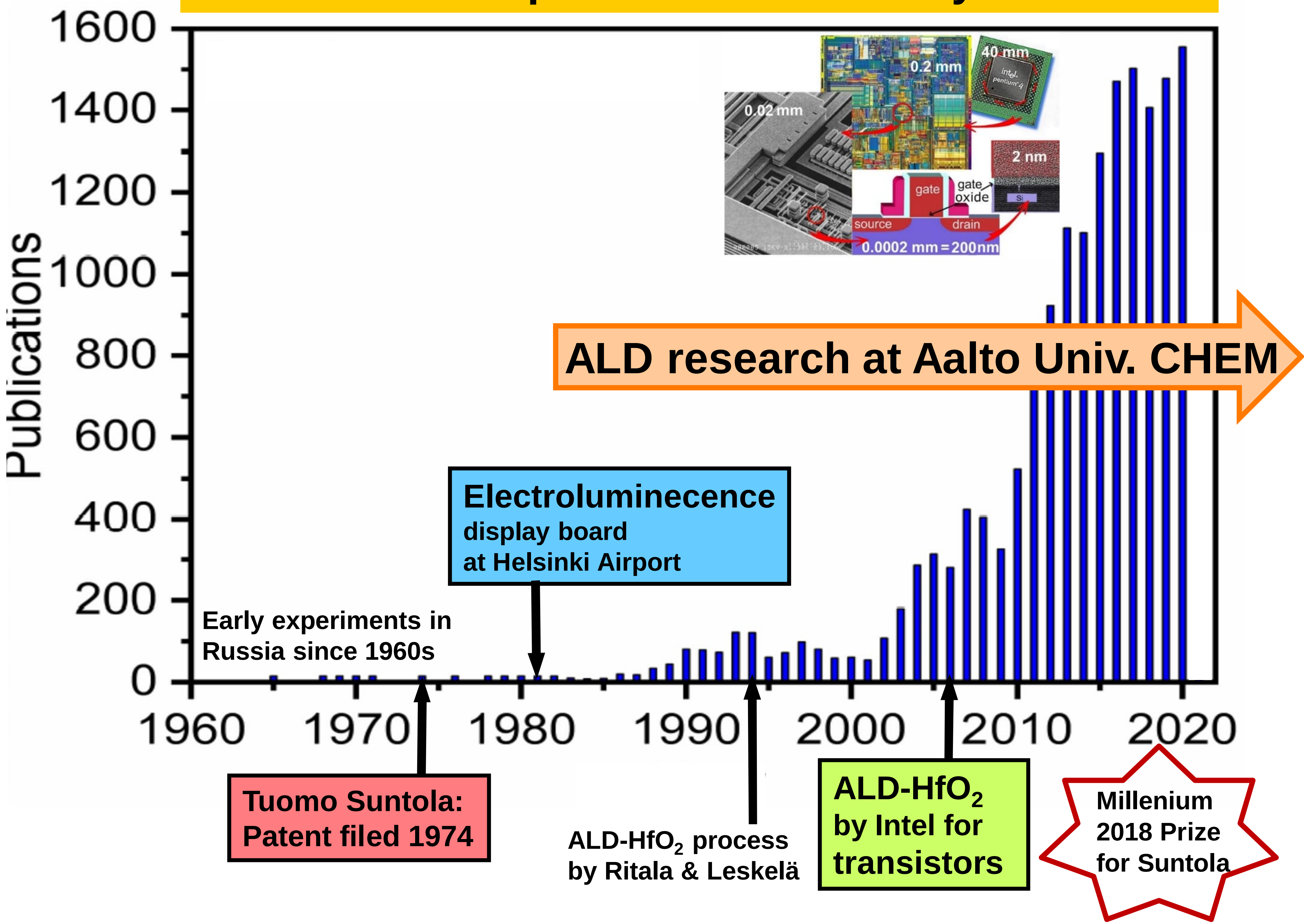
HfO_2-ALD
$HfCl_4 + H_2O$

ALD cycle





ALD publications annually



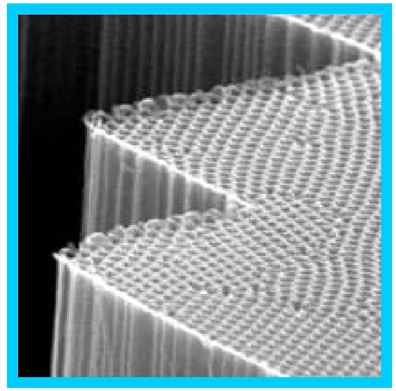
Advantages of ALD

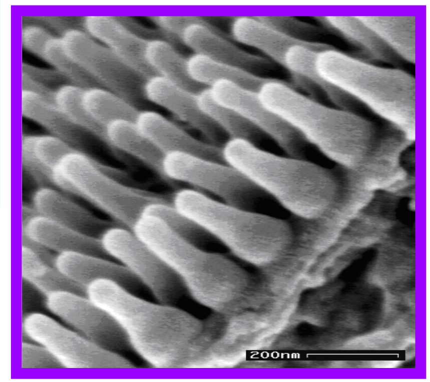
- Relatively inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Large area uniformity
- Easy doping

ELECTRONICS

NANO

- Excellent conformality



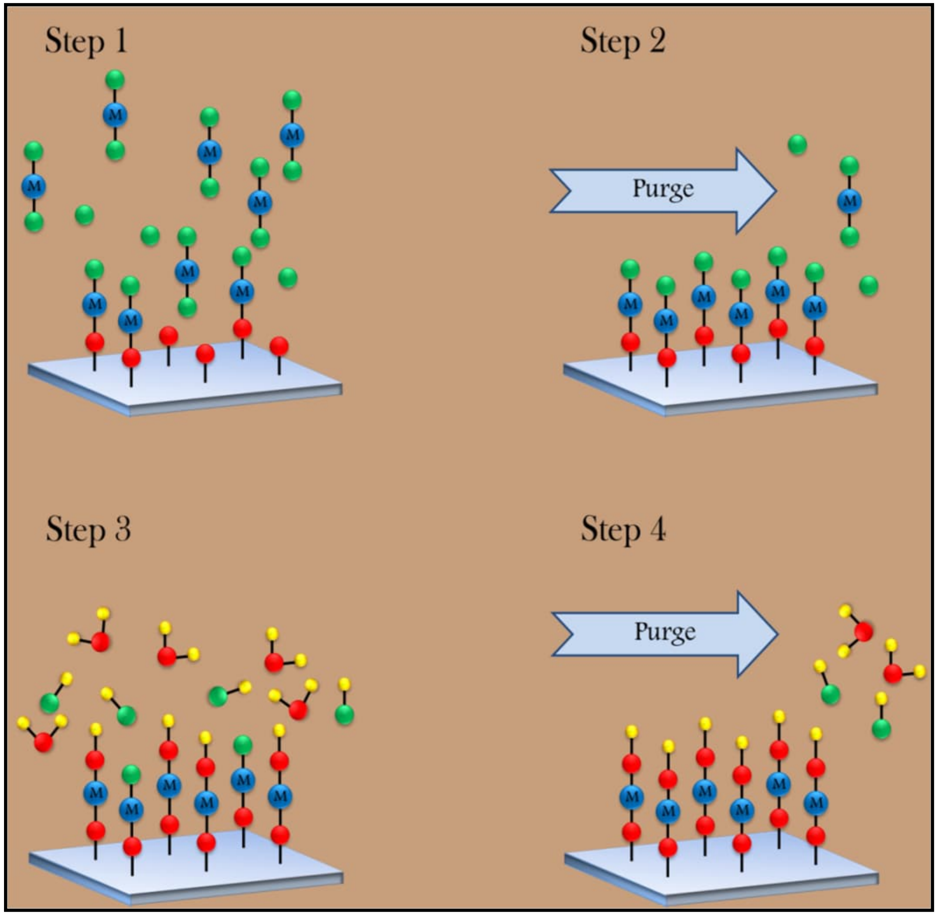


BIO

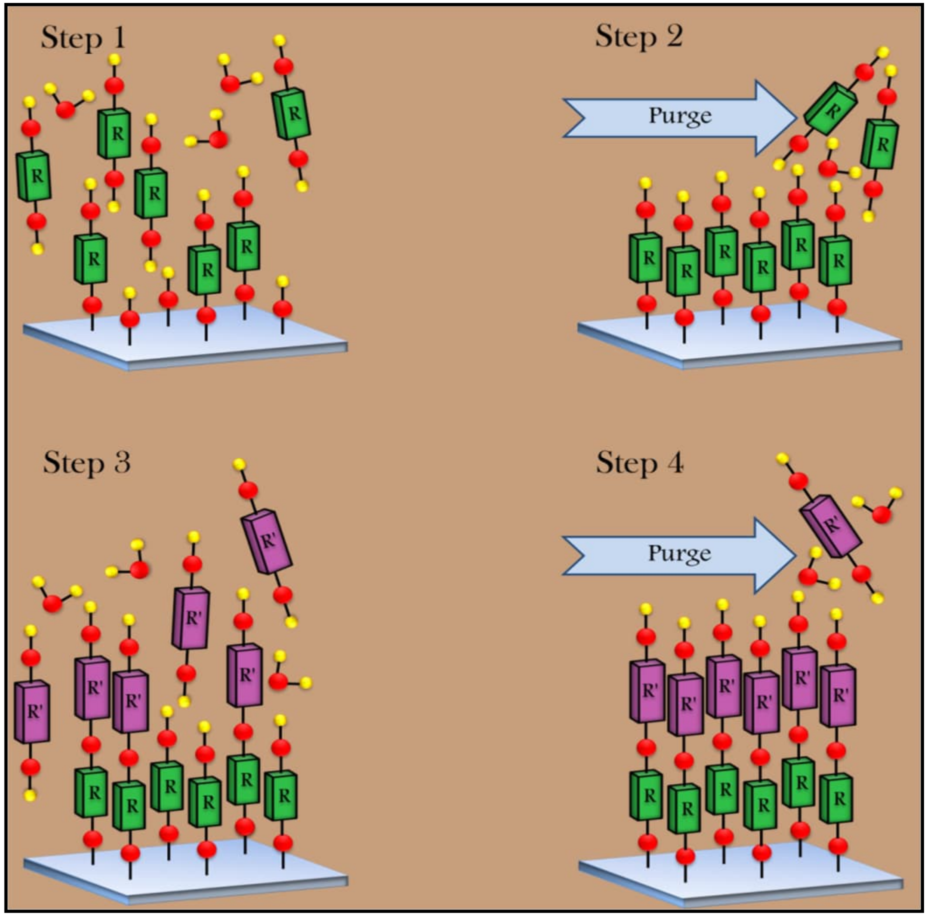
- Low deposition temperature
- Gentle deposition process

- Organic/polymer films
- Inorganic/organic hybrid materials

NEW



ALD (Atomic Layer Deposition)

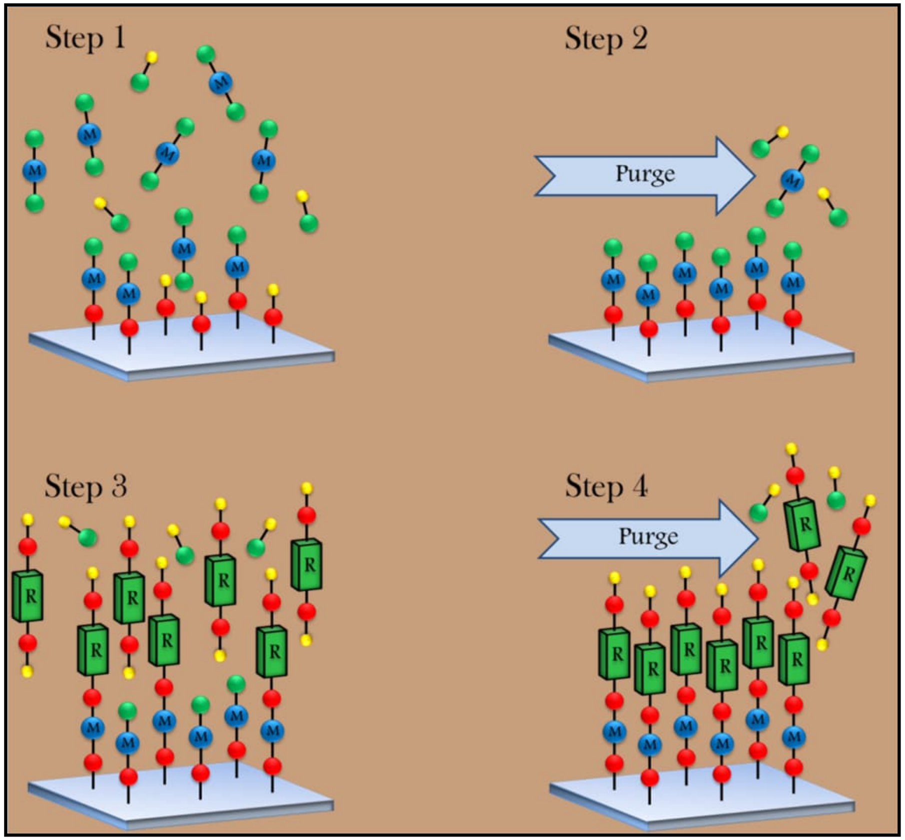


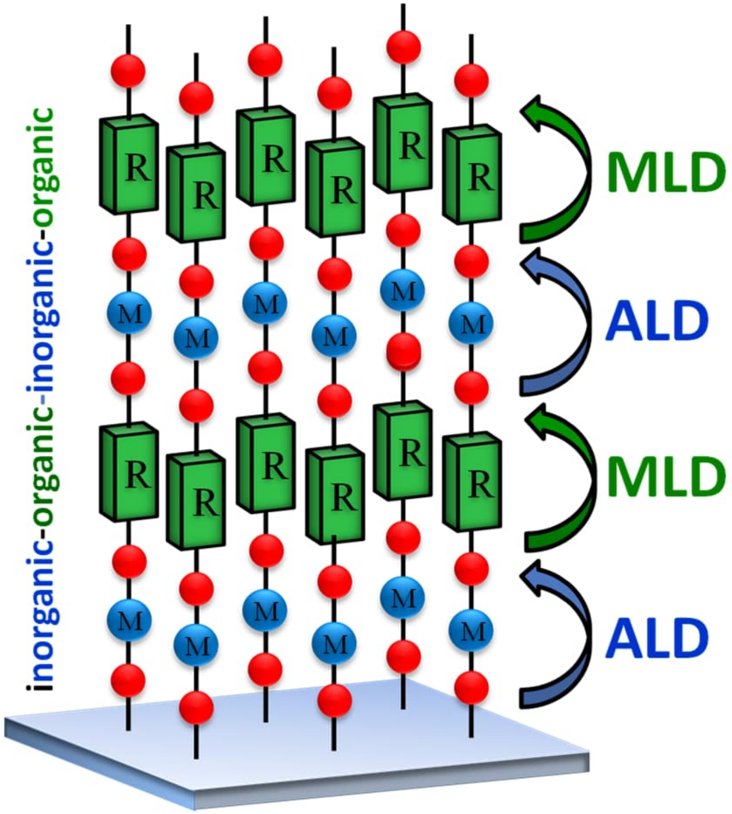
MLD (Molecular Layer Deposition)

High-quality
INORGANIC thin films
with atomic level control

ORGANICS !
(in 1990s)

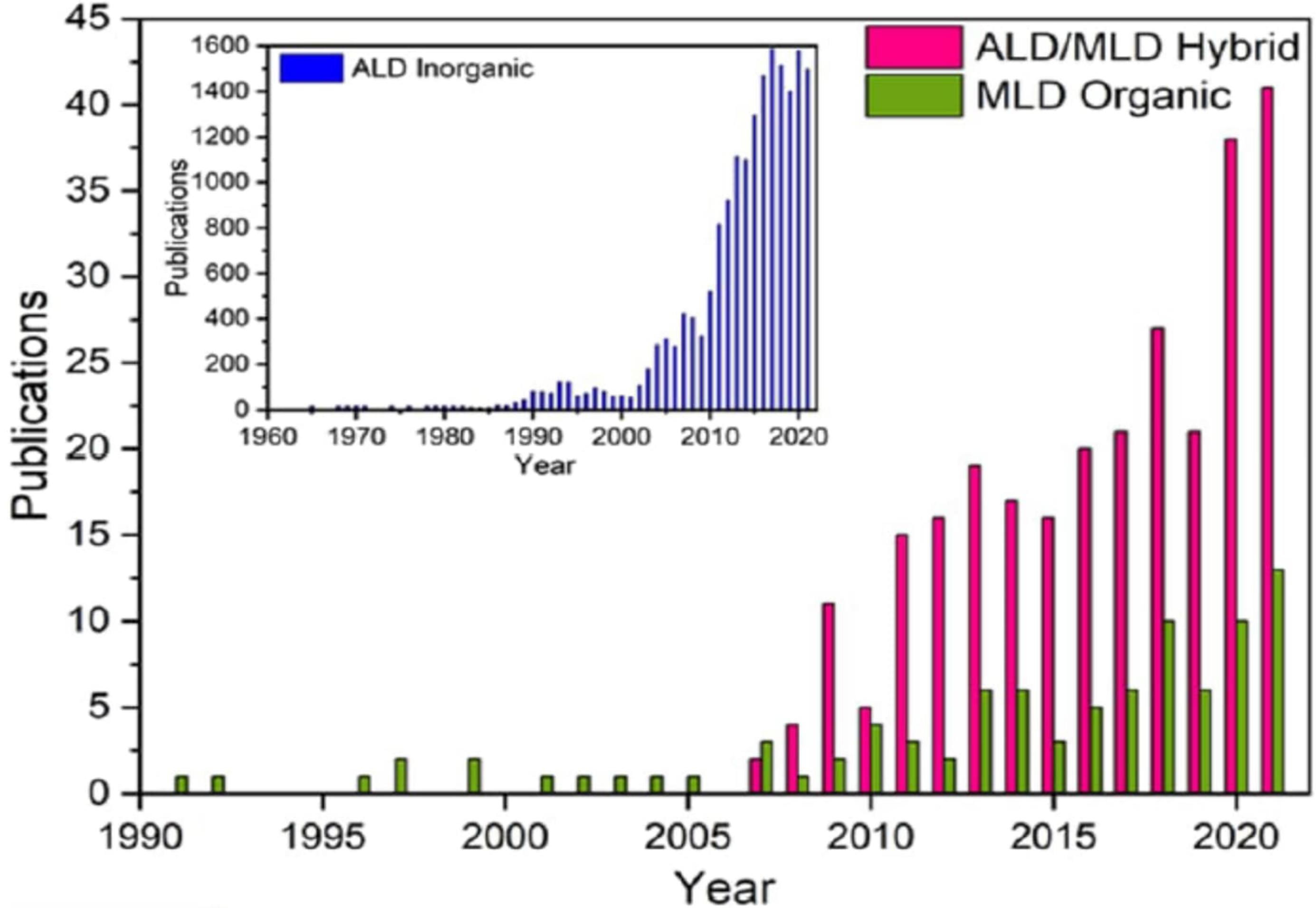
Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD





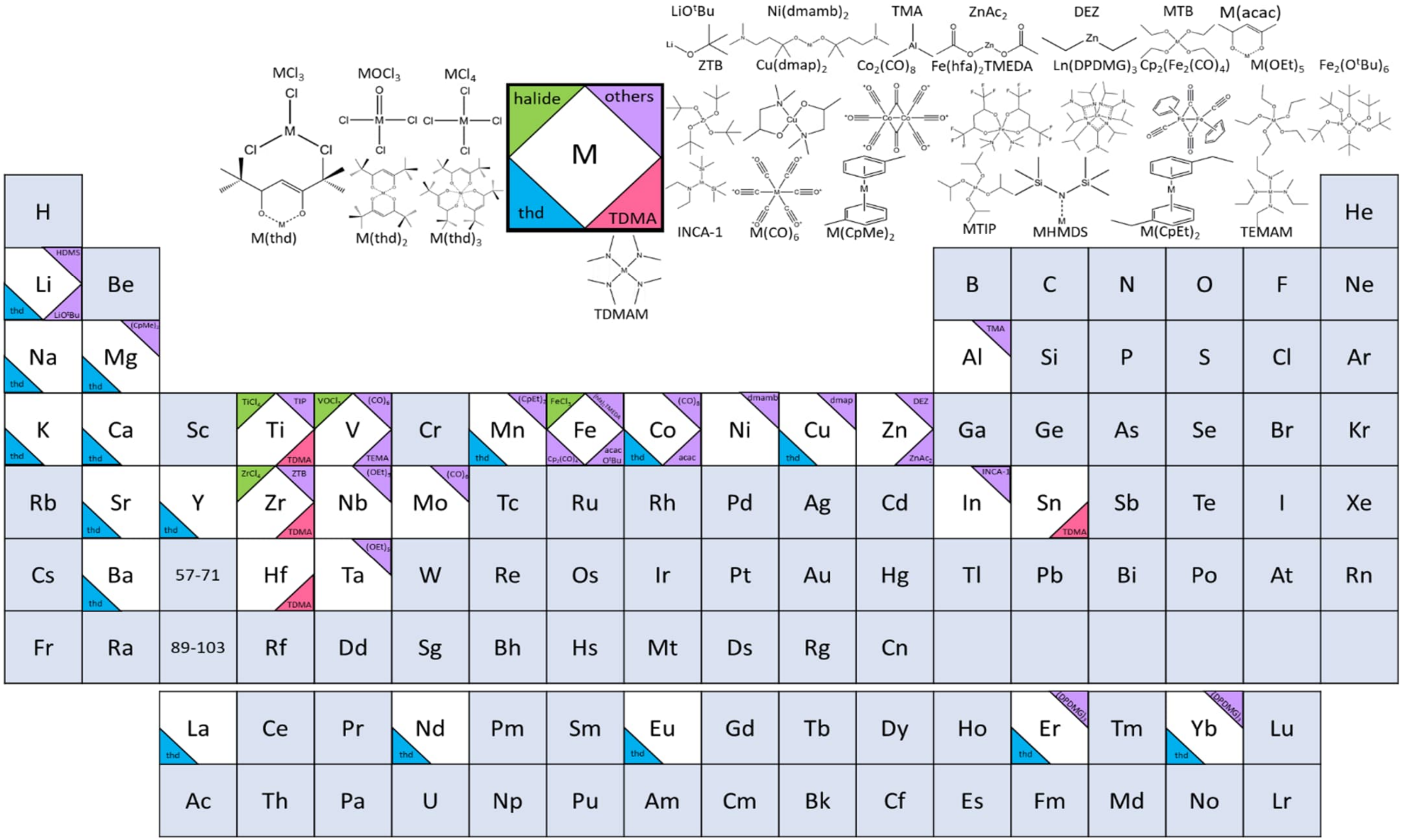
MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!

Annually published papers: MLD & ALD/MLD



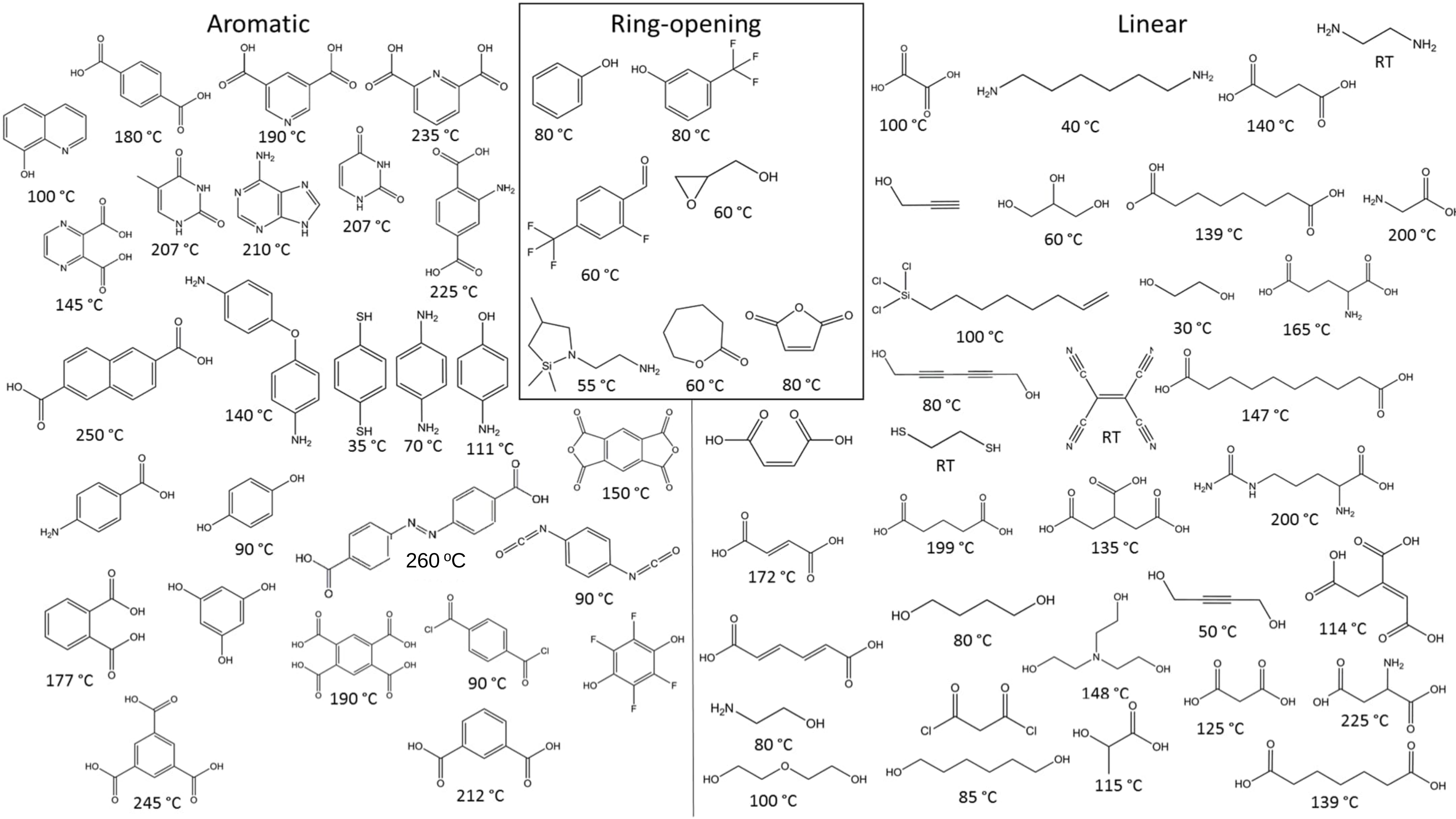
Yoshimura, Tatsuura & Sotoyama, *Appl. Phys. Lett.* **1991,** *59,* 482.
Yoshimura, Tatsuura, Sotoyama, Matsuura & Hayano, *Appl. Phys. Lett.* **1992,** *60,* 268.
Lee, Ryu, Choi, Lee, Im & Sung, *J. Am. Chem. Soc.* **2007,** *129,* 16034.
Smirnov, Zemtsova, Belikov, Zheldakov, Morozov, Polyachonok & 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.

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



ALD/MLD Processes: Metal Precursors

Aalto University
School of Chemical
Engineering

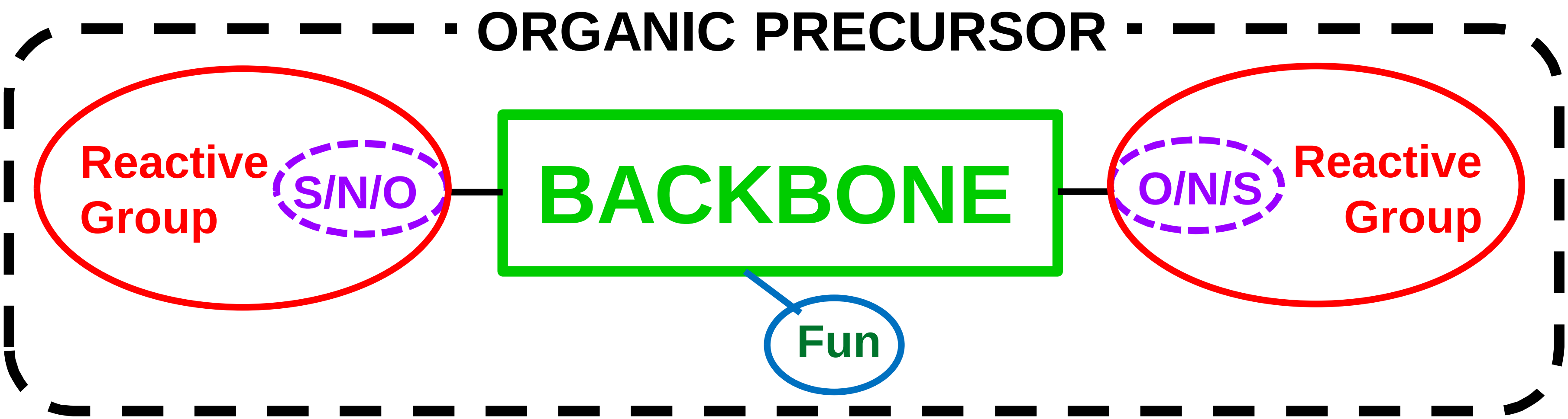


ALD/MLD Processes: Organic Precursors

(with temperatures used for evaporation)

Aalto University
School of Chemical
Engineering

Smart Tailoring of Innovative Organic Precursors



Reactive groups: e.g. –COOH, –OH

- → Selected so far mostly based on the reactivity towards the metal precursor
- → Control over bonding mode: monodentate (–OH) *versus* bidentate (–COOH)

Linker atom within the reactive group

- → Covalency of the bond towards the metal species (e.g. M–O, M–N or M–S)

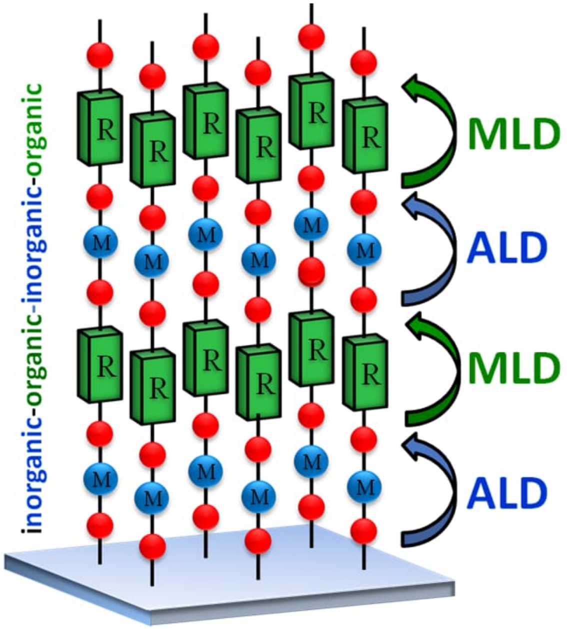
BACKBONE: very little challenged so far !!!

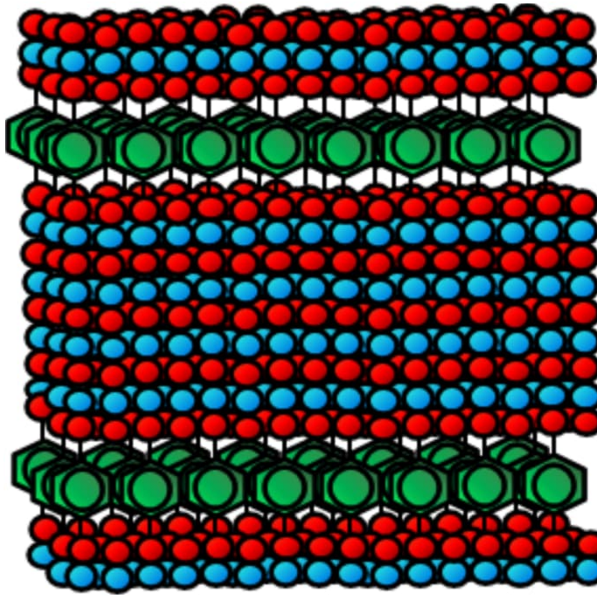
- → Main component in the resultant metal-organic thin film !!!
- → Size & mass (→ porosity), chemistry, functionality, etc.

Functional groups attached to the backbone: fine-tuning of the backbone

- → Steric hindrance, number of bonding sites, conjugation, etc.
- → Electron-donating (–NH_2) or electron-withdrawing (–OR) groups

Exciting ALD/MLD Approaches





SIMPLE **Metal-Organic** HYBRIDS

- **Amorphous**
- **Crystalline (2016) & Porous (2023)**

→ Unforeseen MOF thin films

Superstructures

- **Regular Superlattice (2013)**
- **Irregular Piling (2018)**

→ Layer-Engineering

→ Interface-Engineering

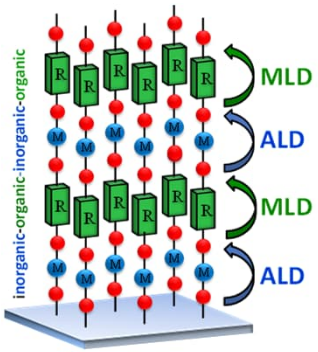
Aalto University School of Chemical Engineering

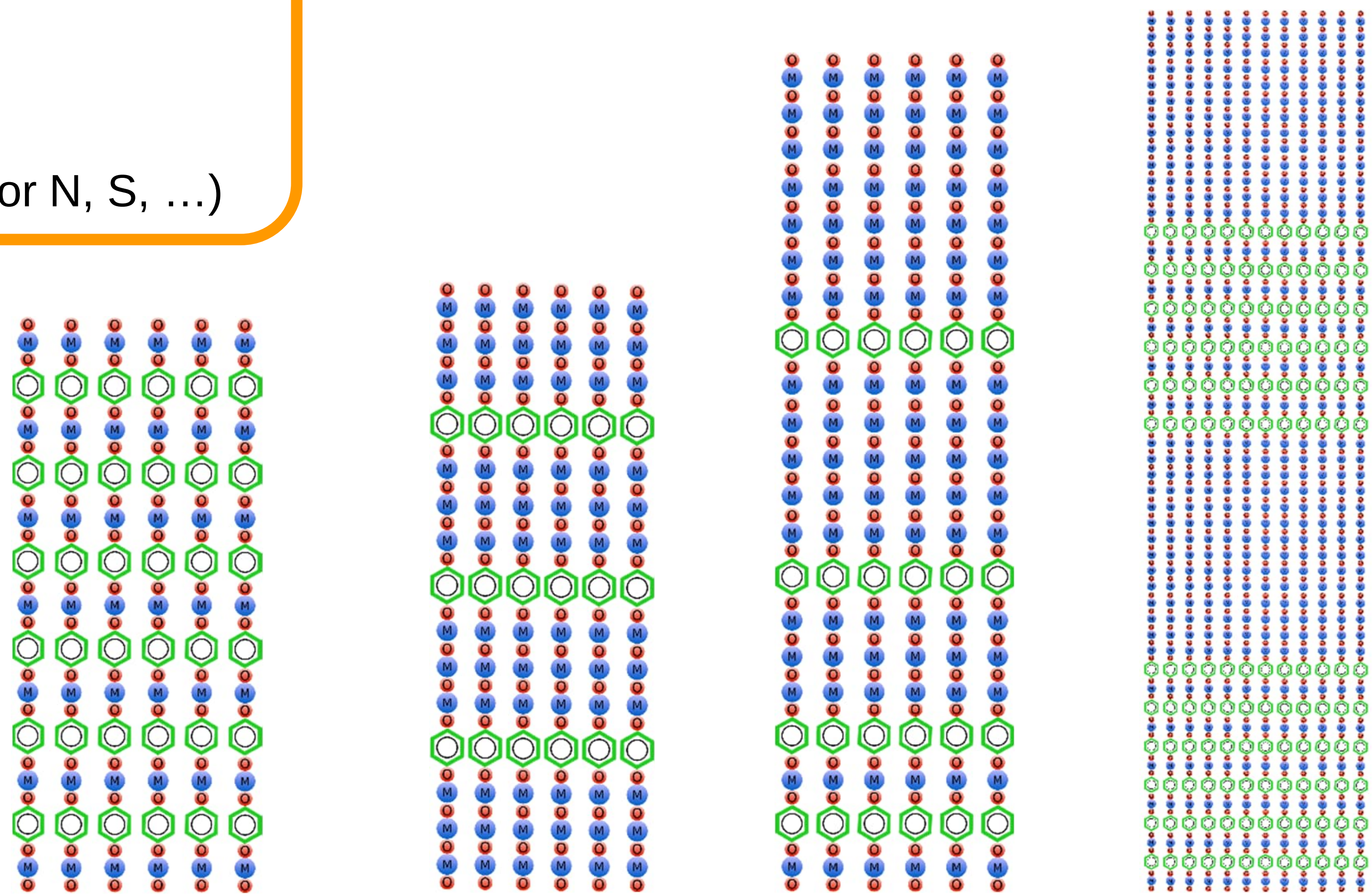
Multia, Kravchenko, Rubio-Giménez, Philip, Ameloot & Karppinen, **Nanoporous metal-organic framework** thin films prepared directly from gaseous precursors by atomic and molecular layer deposition: implications for microelectronics, ***ACS Appl. Nano Mater.* (2023).**

Organic (e.g. benzene)

Metal

Oxygen (or N, S, …)





Simple Metal-Organic Network (amorphous or crystalline)

Superlattice

Gradient hybrid

Nanolaminate

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Engineering

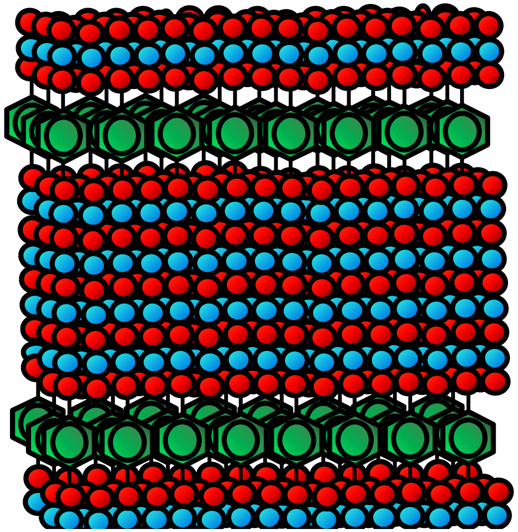
DIFFERENT LAYER SEQUENCES BY DESIGN

LAYER-ENGINEERED

INORGANIC-ORGANIC SUPERLATTICES

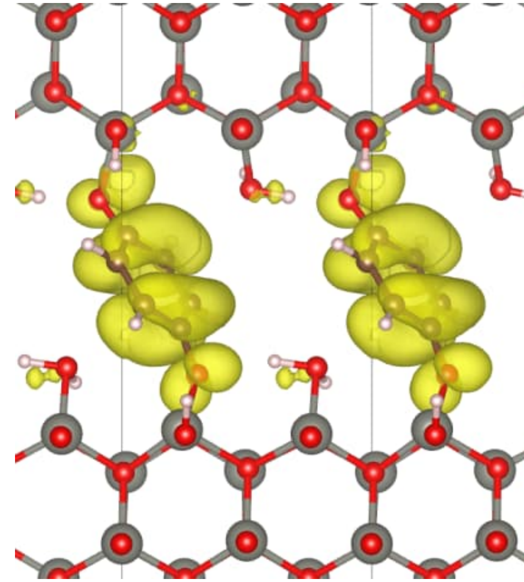
BY

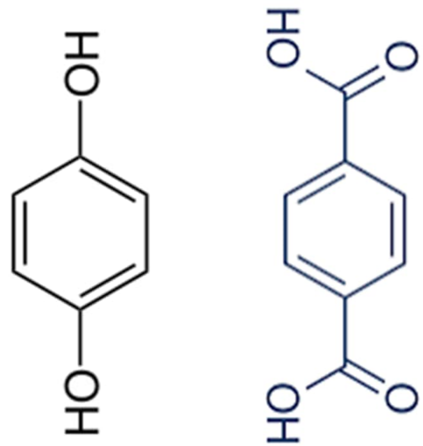
ALD/MLD

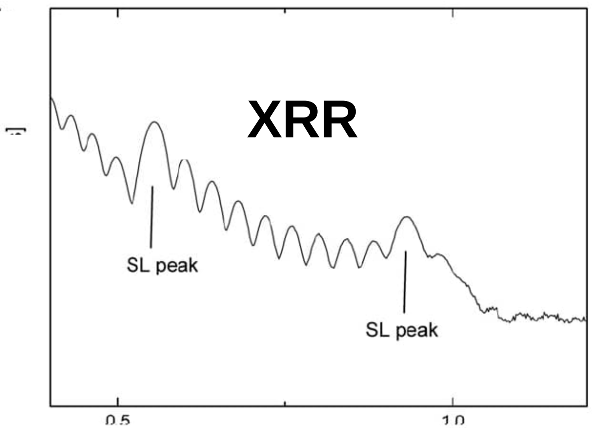


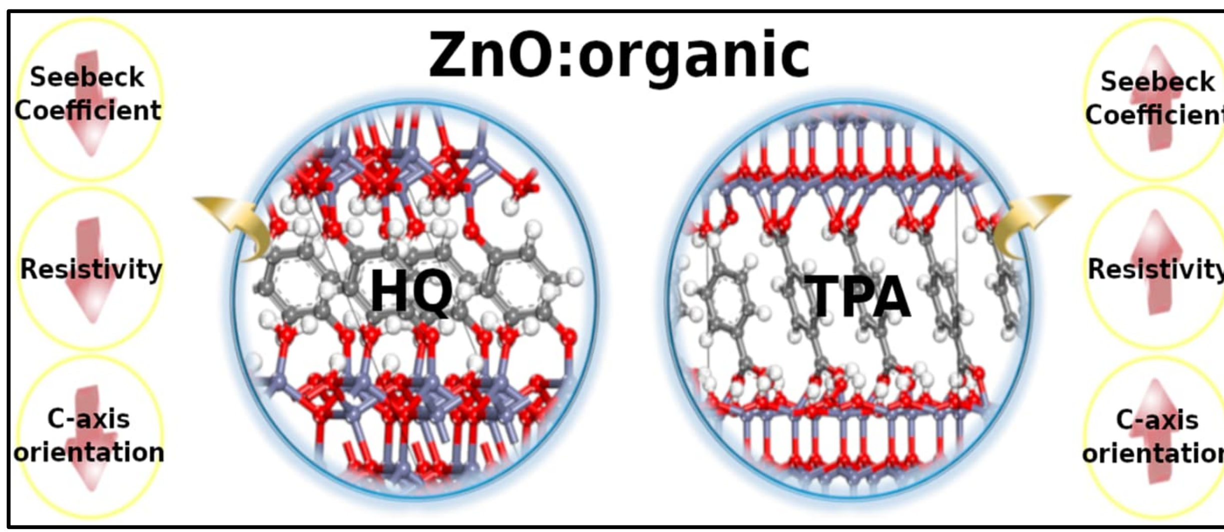
DFT Modelling

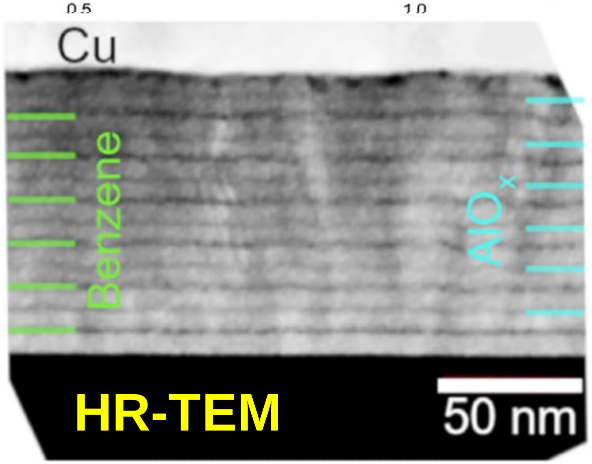
Karttunen, Tynell & Karppinen, *J. Phys. Chem. C* **119**, 13105 (2015).



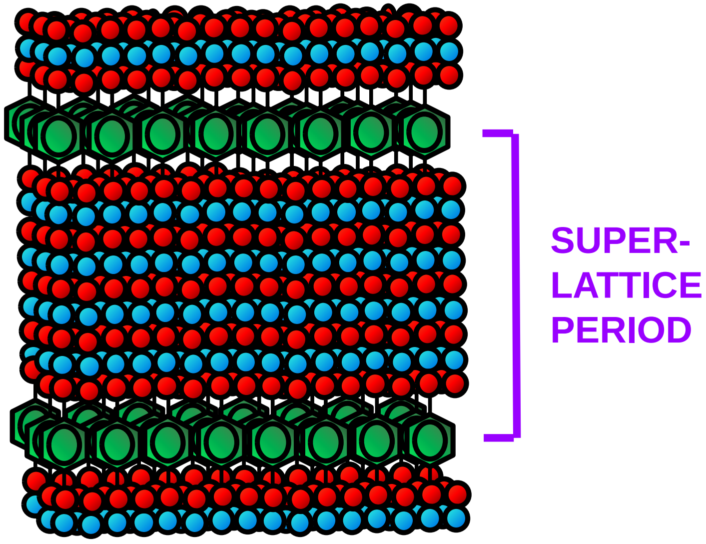




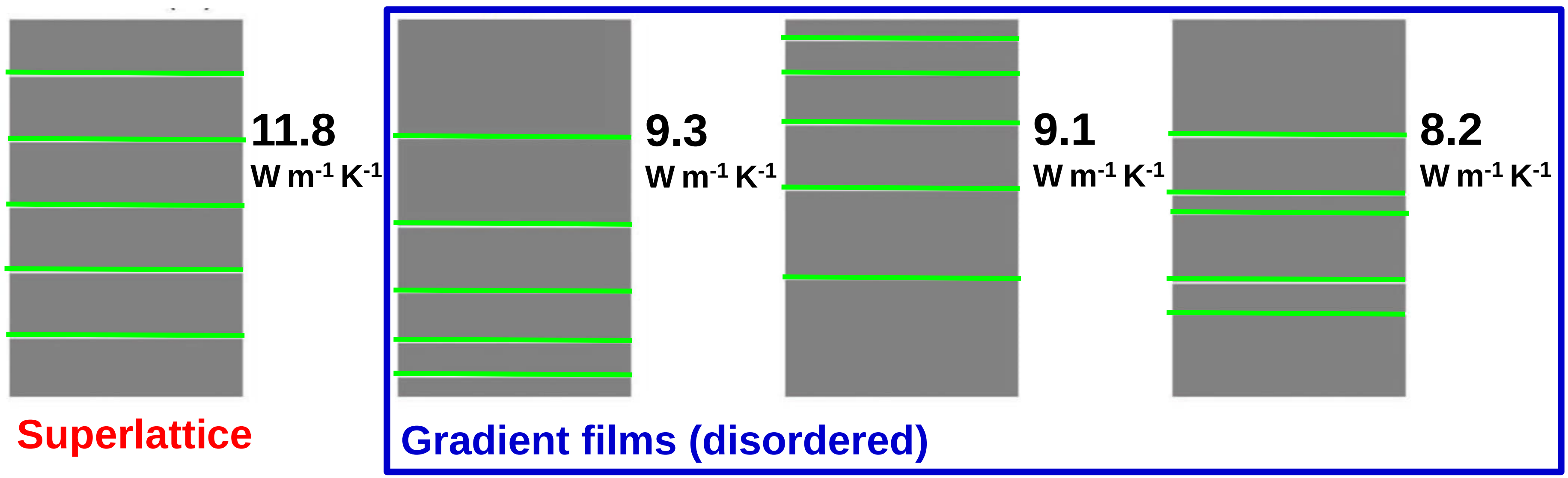




Ghiyasi, Tewari & Karppinen, Organic-component dependent crystal orientation and electrical transport properties in ALD/MLD grown ZnO-organic superlattices, *J. Phys. Chem. C* **124**, 13765 (2020).

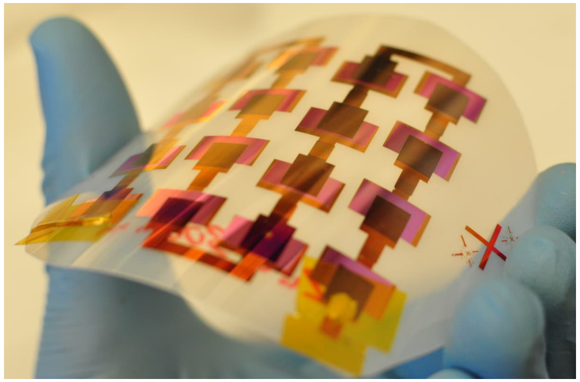


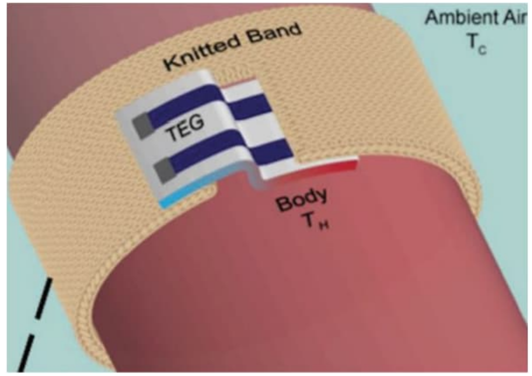
Thermal conductivity [W m^{-1} K^{-1}]	
ZnO (~100 nm)	~43
5 org. layers	11.8
6 org. layers	7.1
12 org. layers	4.1
20 org. layers	3.1
40 org. layers	1.3
80 org. layers	0.7

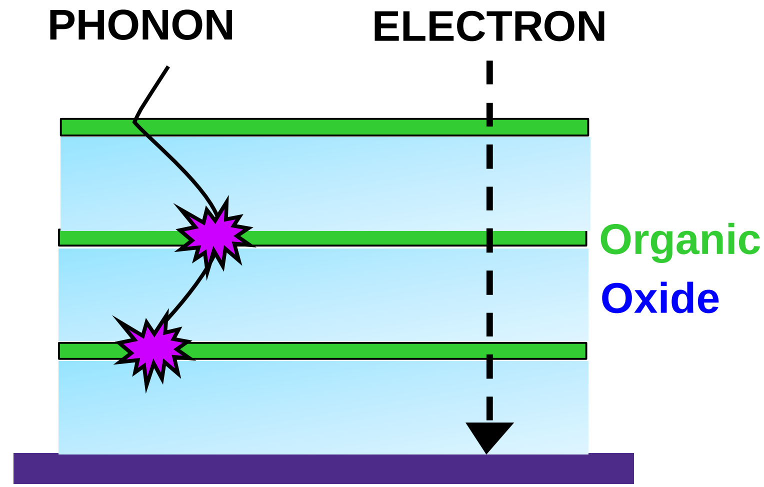


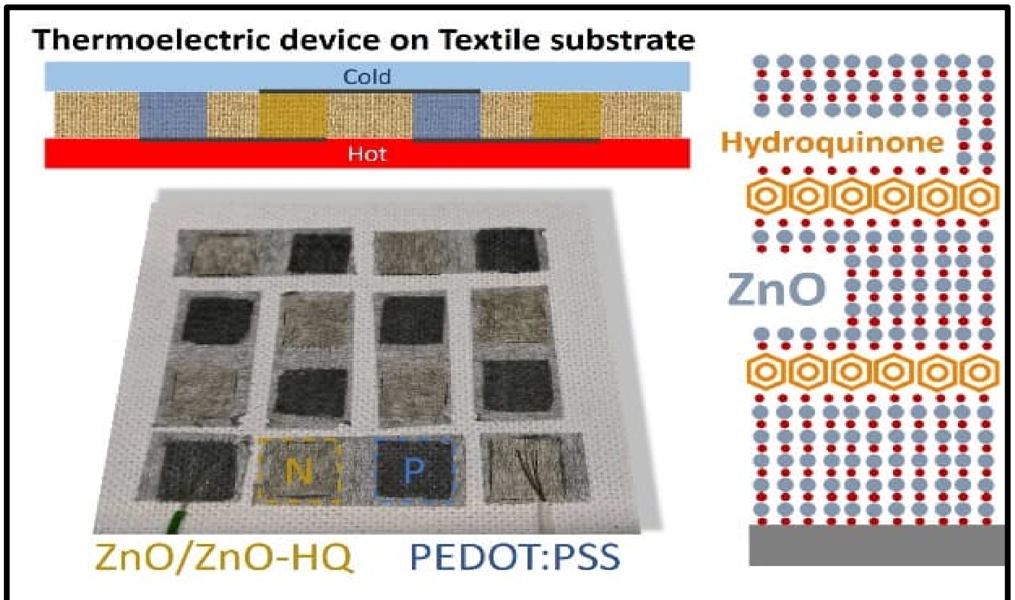
F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen, Thermal conductivity reduction at inorganic-organic interfaces: from regular superlattices to irregular gradient layer sequences ***Advanced Materials Interfaces*** 5, 1701692 (**2018**).

Textile-integrated thermoelectrics









Organic layers in ZnO:org superlattices reduce thermal conductivity (into 1 / 50) without lowering electrical conductivity.

Another unique feature is that the film grows in a conformal manner on textile fibers so that the entire textile piece becomes an active part of the device.

G. Marin, R. Funahashi & M. Karppinen, *Adv. Eng. Mater.* 22, 2000535 (2020).

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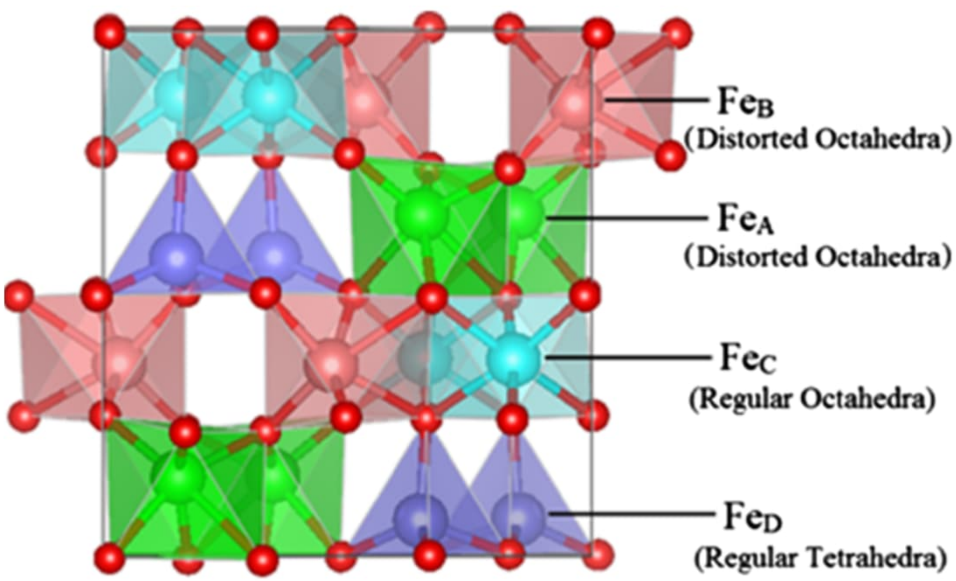
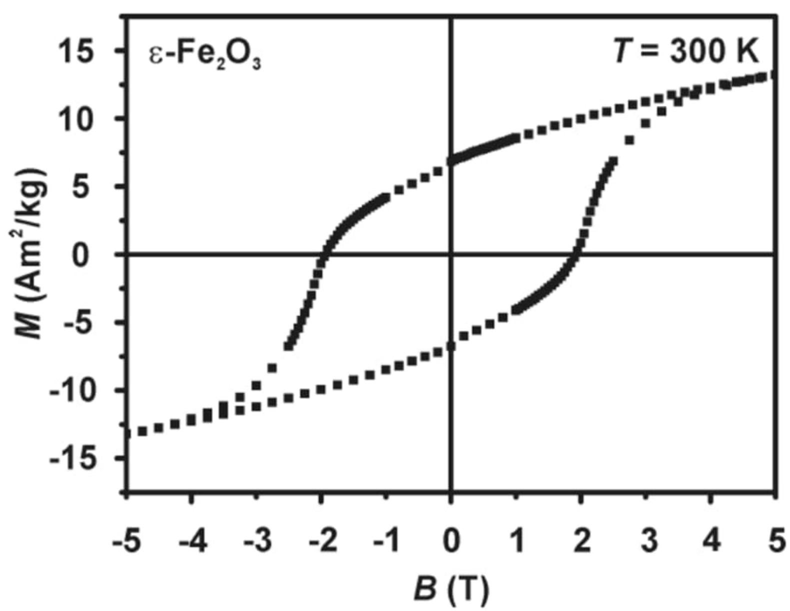
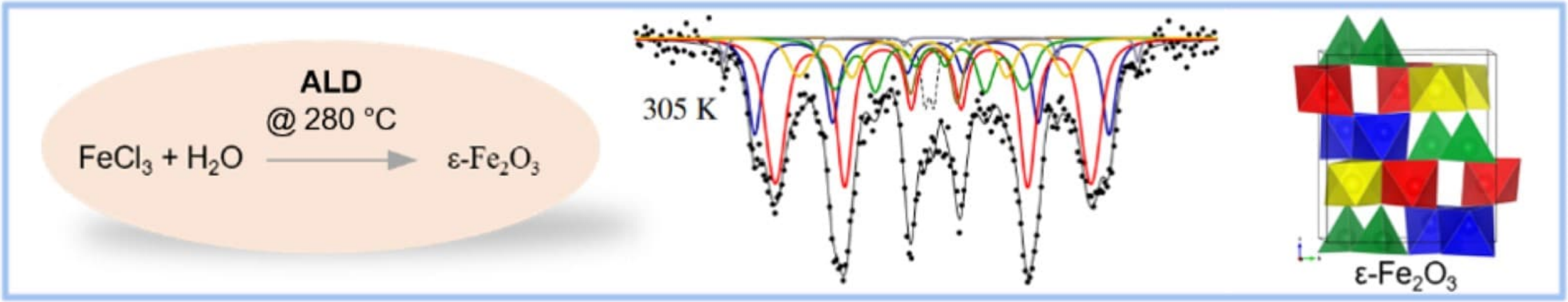
NEXT:
ZnO is n-type semiconductor. For a full thermoelectric device, we will next need a p-type counterpart: e.g. SnO, CuO

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

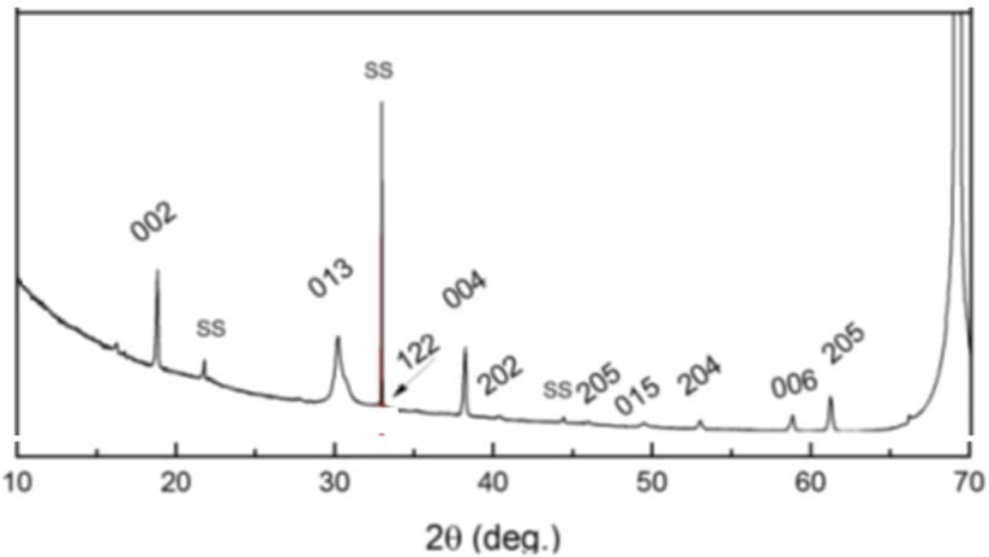
- ε-Fe_2O_3 is the rarest of the iron(III) oxide polymorfs
- Critical-raw-material-free
- RT ferrimagnet ($T_C \approx 490$ K)
- Colossal coercive field
- Magnetoelectric
- PROBLEM: stabilized/synthesized in nano-scale amounts only





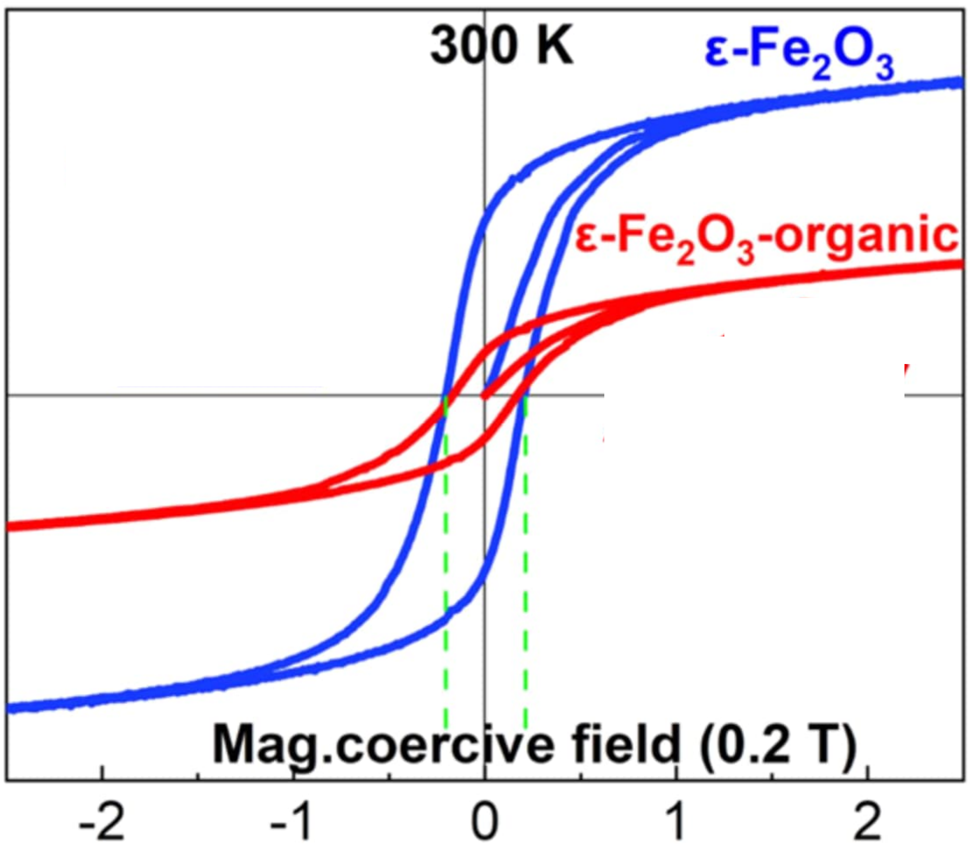


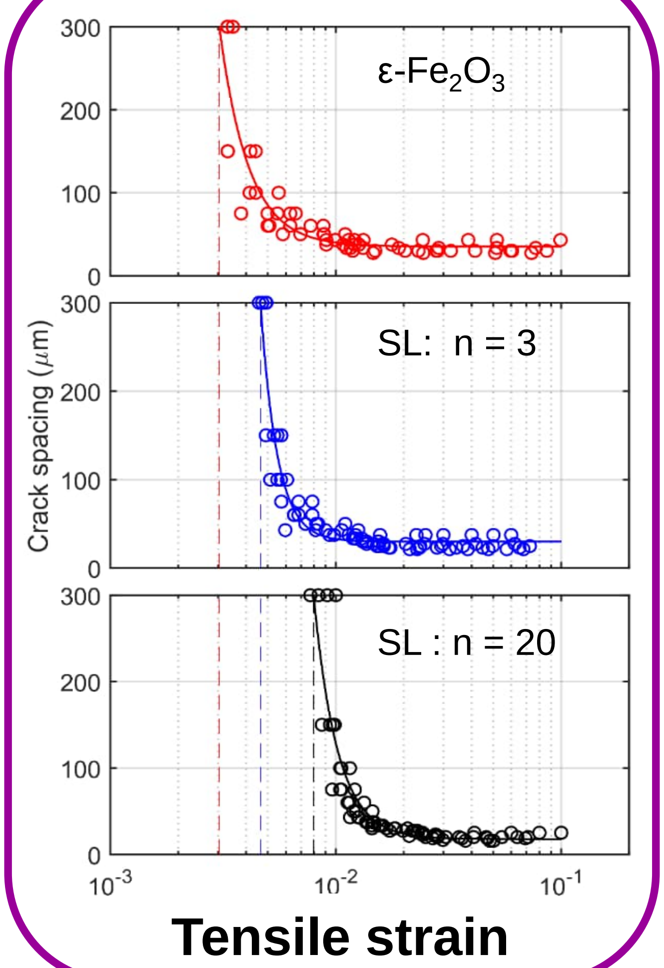
- **Substrate: silicon, flexible glass, Kapton, polyimide, etc.**
- **Large-area homogeneity & Conformality over large-surface-area templates → "MASS production"**



- Tanskanen, Mustonen & Karppinen, Simple ALD process for ε-Fe_2O_3 thin films, *APL Mater.* 5, 056104 (2017).
- Philip, Niemelä, Tewari, Putz, Edwards, Itoh, Utke & Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).
- T. Jussila, A. Philip, J. Linden & M. Karppinen, High-quality magnetically hard ε-Fe_2O_3 thin films through ALD for room-temperature applications, *Adv. Eng. Mater.* 25, 2201262 (2023).

Mechanical property testing: ε-Fe_2O_3:TPA





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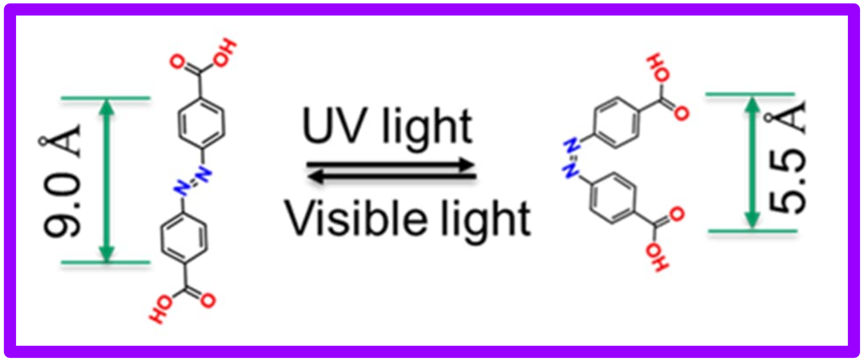
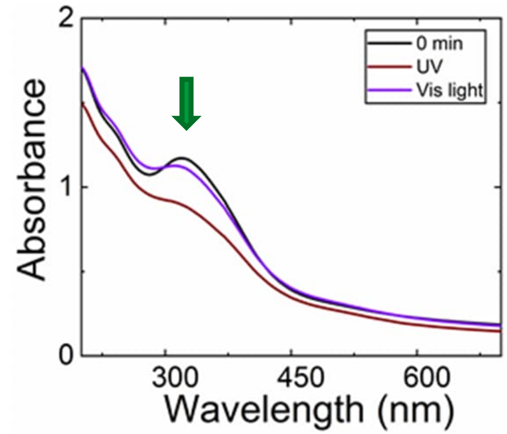
A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

PHOTO-SWITCHABILITY: ε-Fe_2O_3:AZO





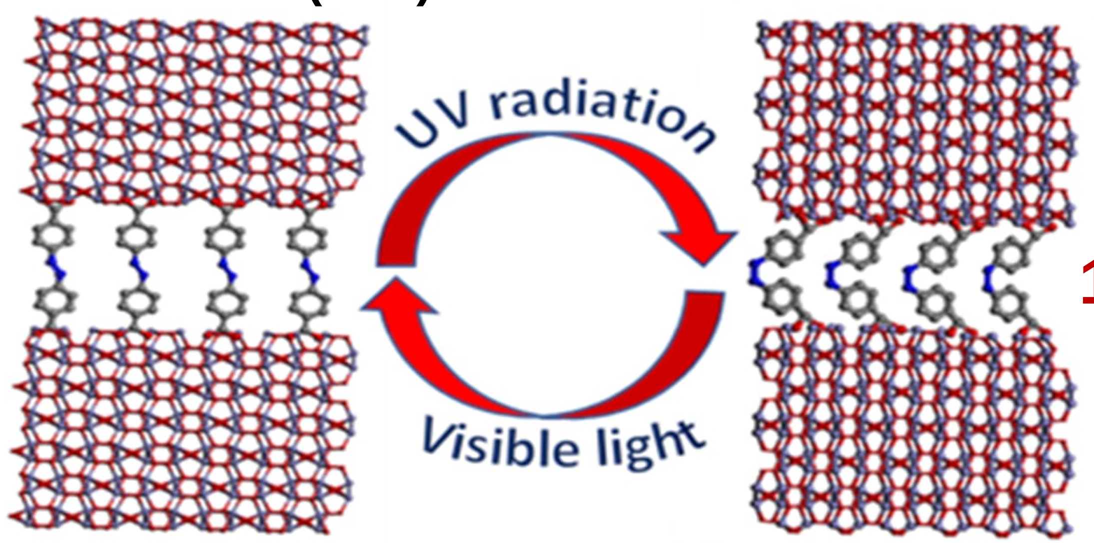
<u>UV absorption</u>

trans-cis-trans transition is REVERSIBLE

970 **(1.88)**

Coer. [Oe]

(Remn. Magn.)



1060 **(1.94)**

990 **(1.86)**

A. Philip, Y. Zhou, G.C. Tewari, S. van Dijken & M. Karppinen, Optically controlled large-coercivity room-temperature thin-film magnets, *J. Mater. Chem. C* 10, 294 (2022).

MOFs

METAL-ORGANIC FRAMEWORKS

BY

ALD/MLD

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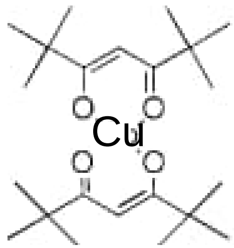
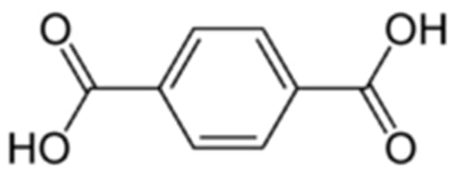
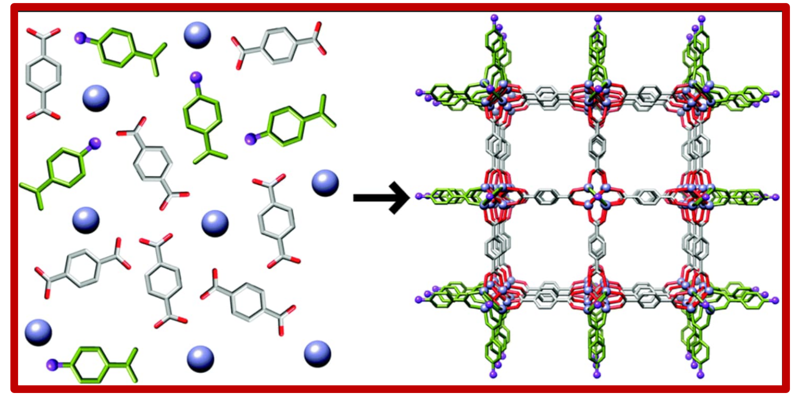


$Cu(thd)_2$

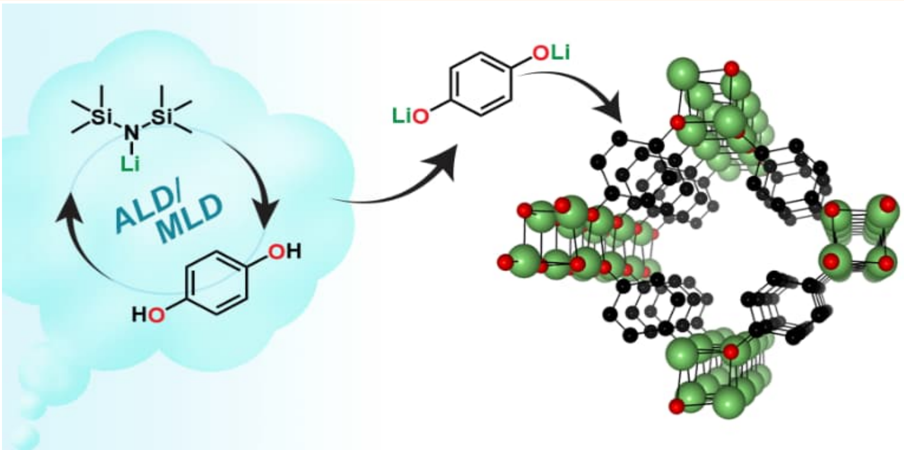


Terephthalic acid (TPA)

Known MOF-2 structure



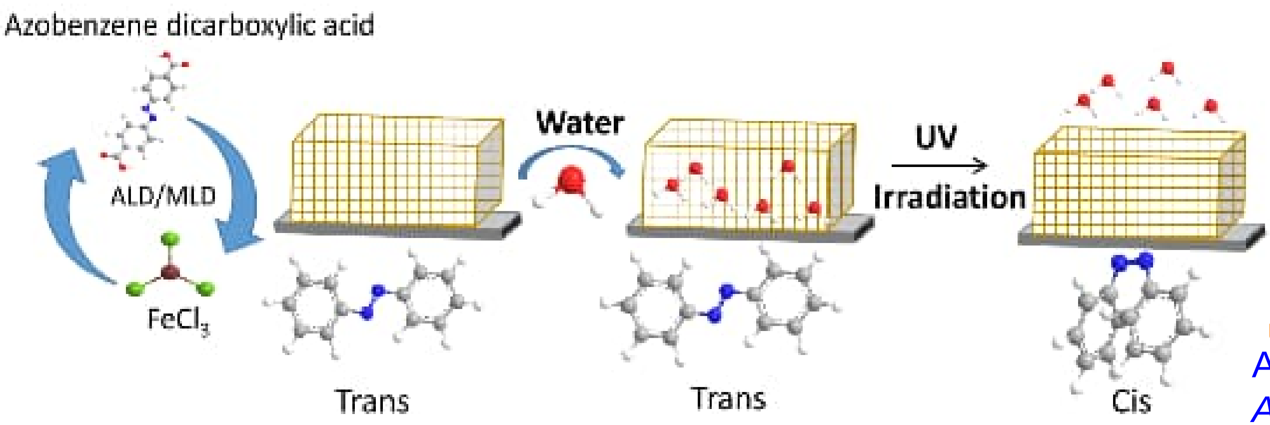
E. Ahvenniemi & M. Karppinen, Chem. Commun. **52**, 1139 (2016).



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).

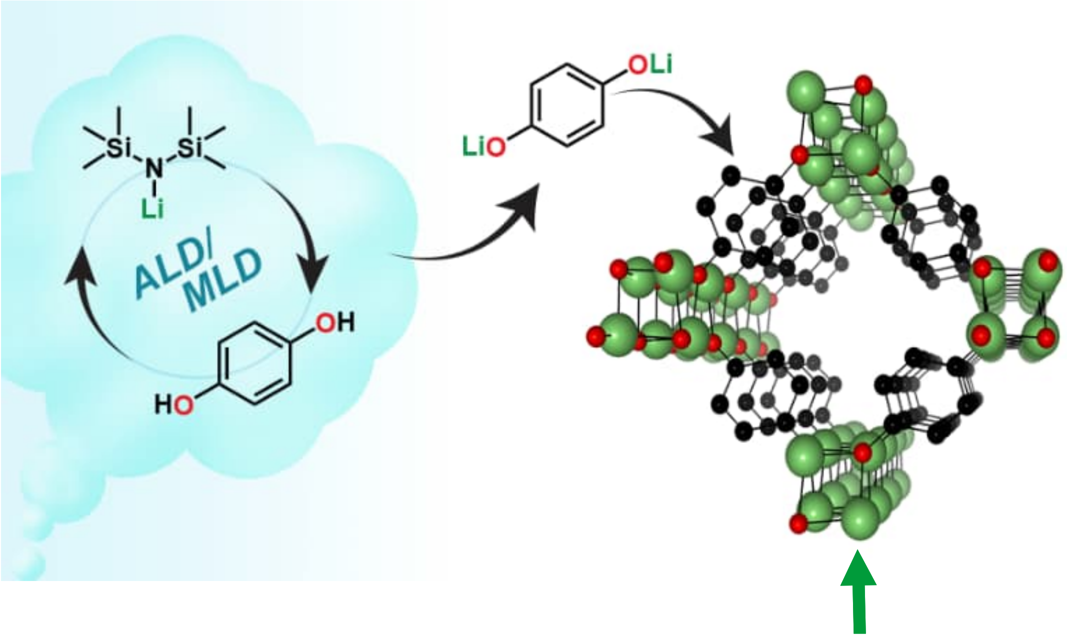


Iron-azobenzoate

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

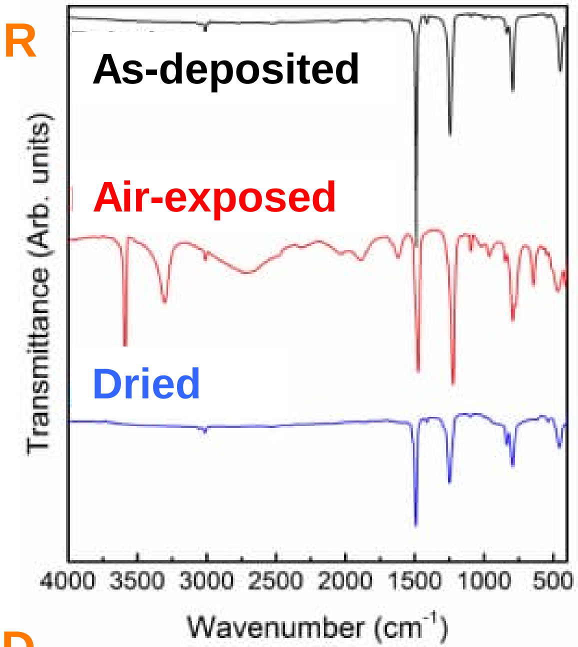
A. Khayyami, A. Philip & M. Karppinen, *Angew. Chem.* **58**, 13400 (2019).

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

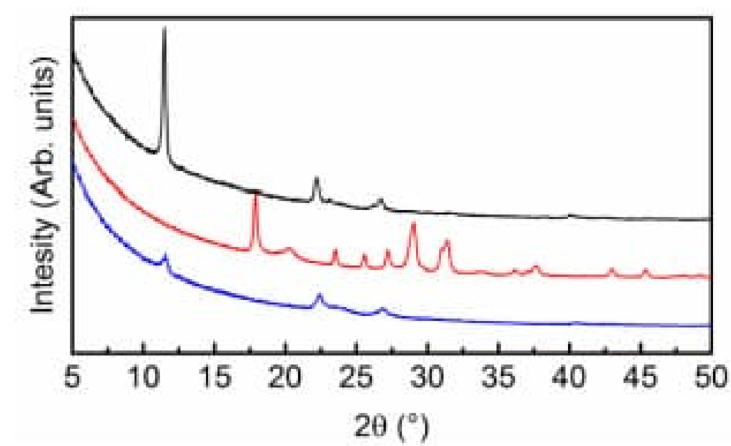


3-coord.
Li-site

FTIR



XRD



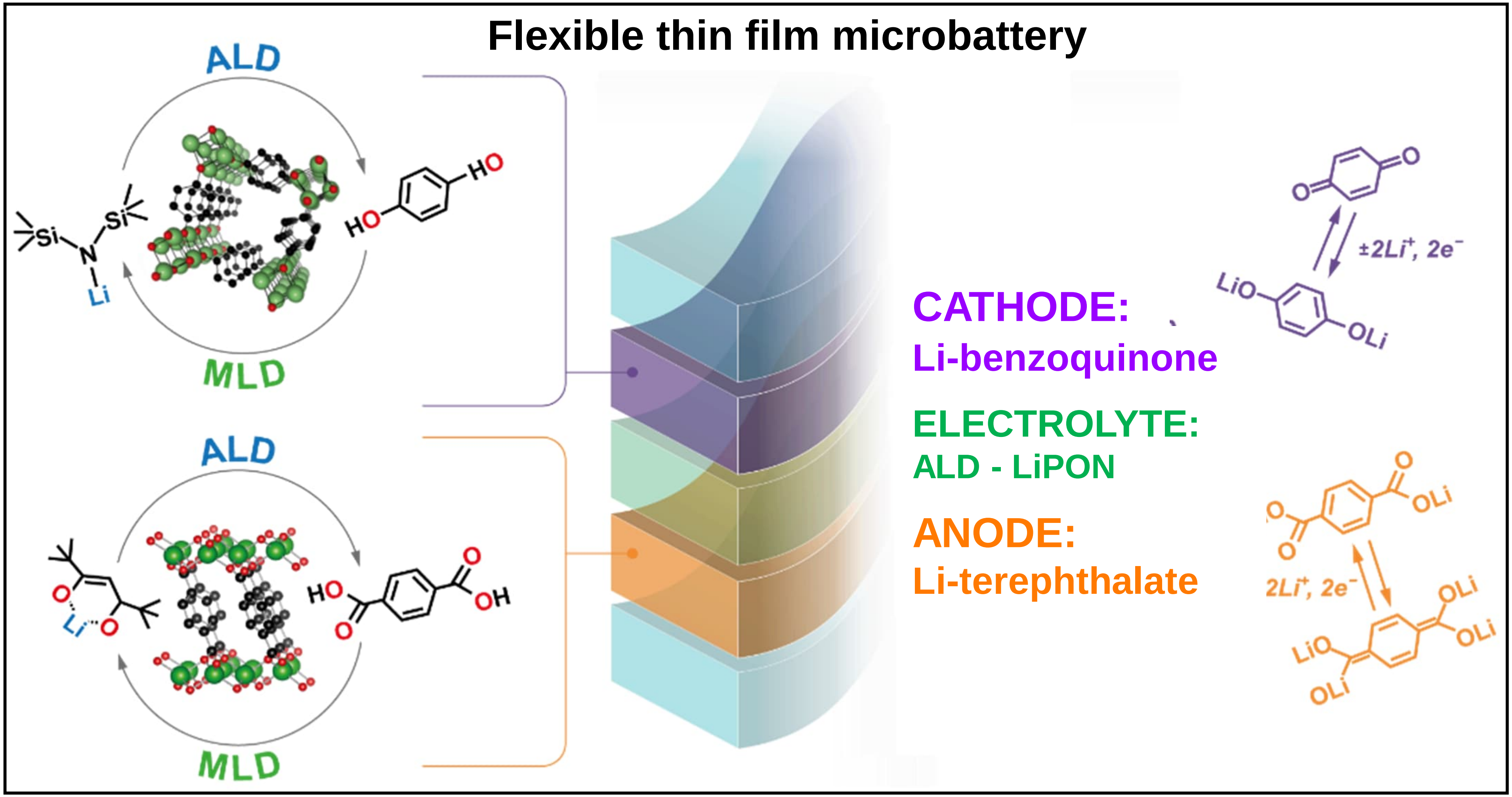
Li + Hydroquinone

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

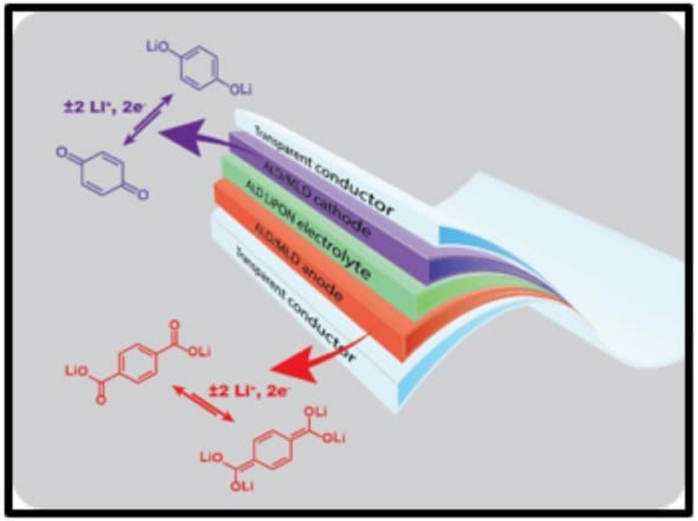
Structure predicted by DFT

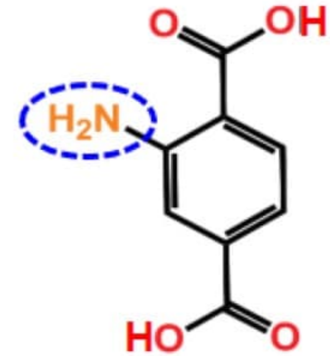
M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chemistry – A European Journal* **23**, 2988 (2017).

Metal-saving Li-organic microbattery

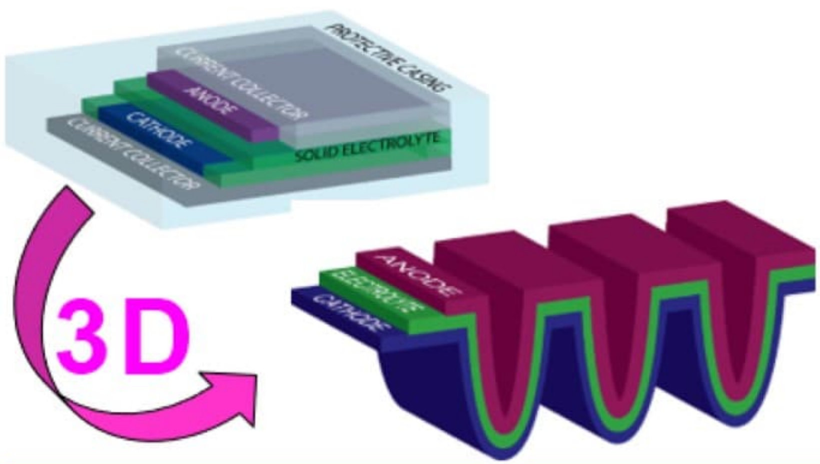


ALD/MLD-made Li-organic microbattery is cobalt-free. Whole battery structure can be deposited active-layer by active-layer in a same reactor, without additives. It is ultrafast to charge, but the problem is the low energy capacity.



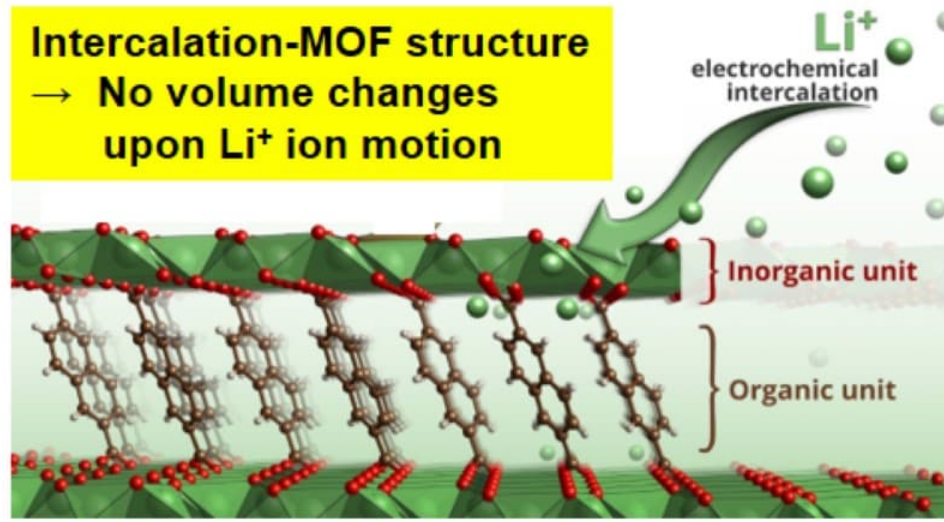


Electron-donating/electron-withdrawing groups
→ Redox potential control



From planar to 3D substrate
→ Energy density increases without compromising power density

Intercalation-MOF structure
→ No volume changes upon Li^+ ion motion



- 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).

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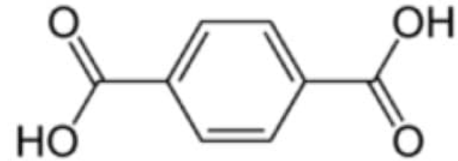
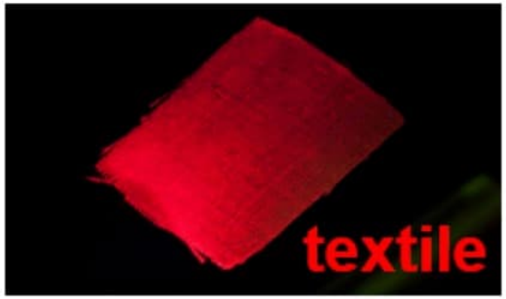
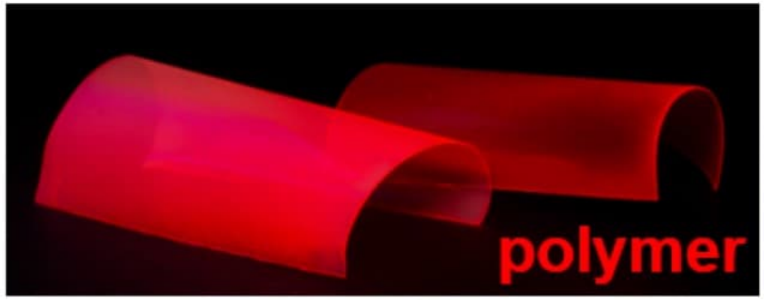
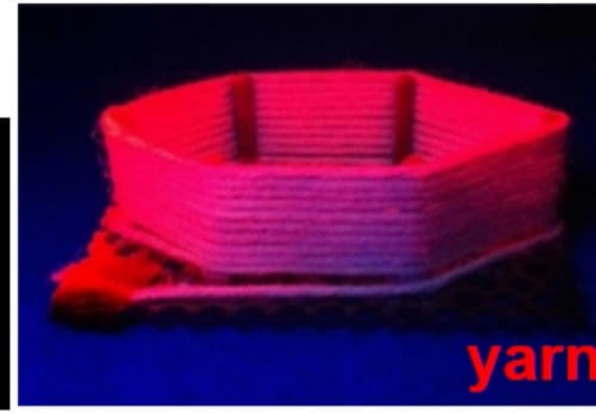
Flexible Lanthanide-Organic Phosphors

PRECURSORS:
$Eu(thd)_3$ + terephthalic acid

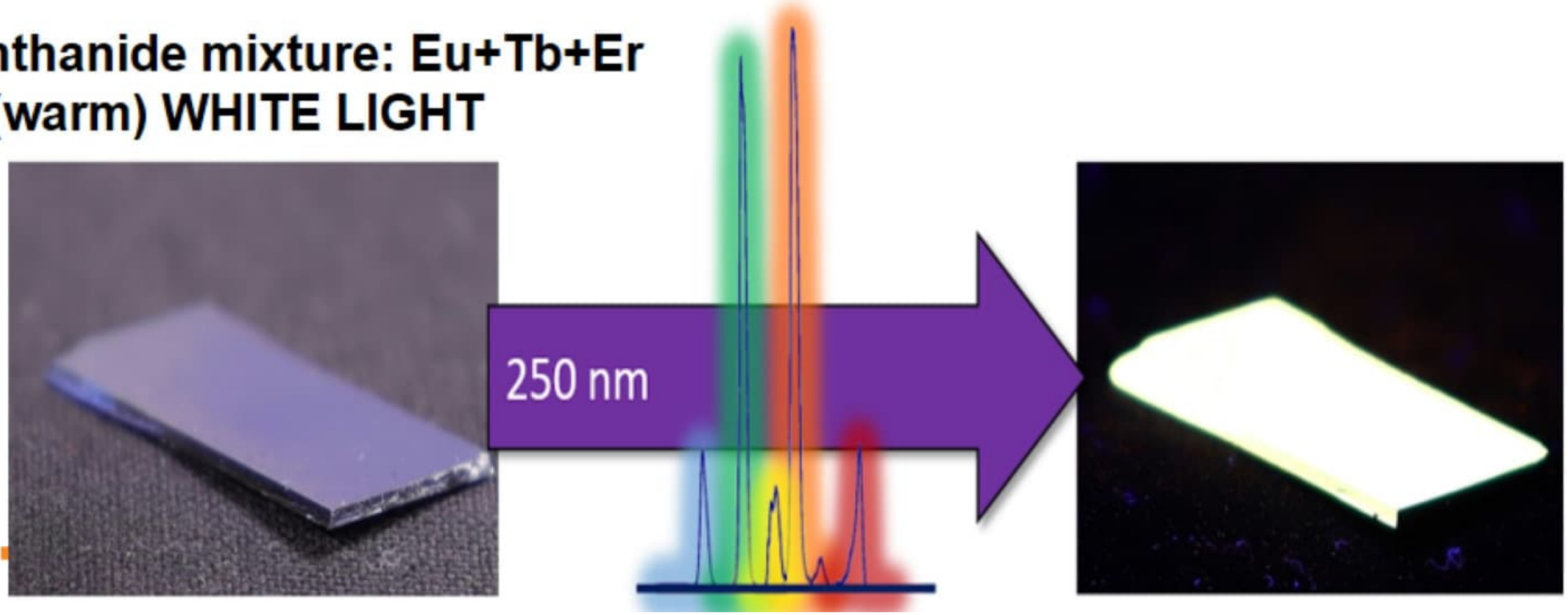






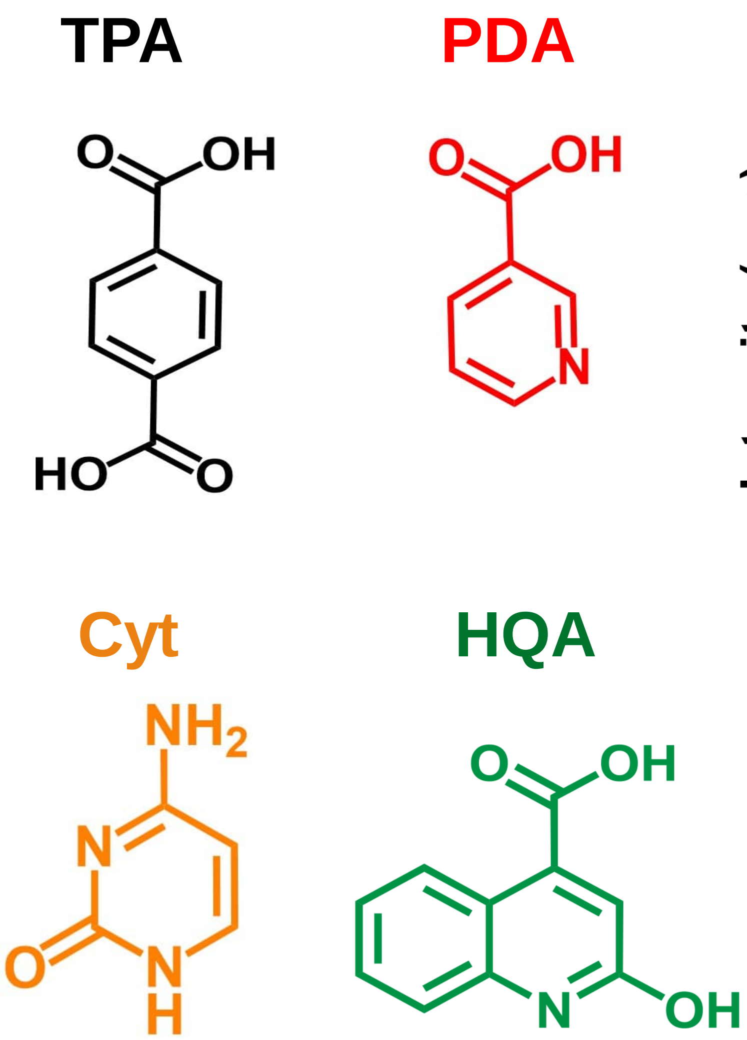


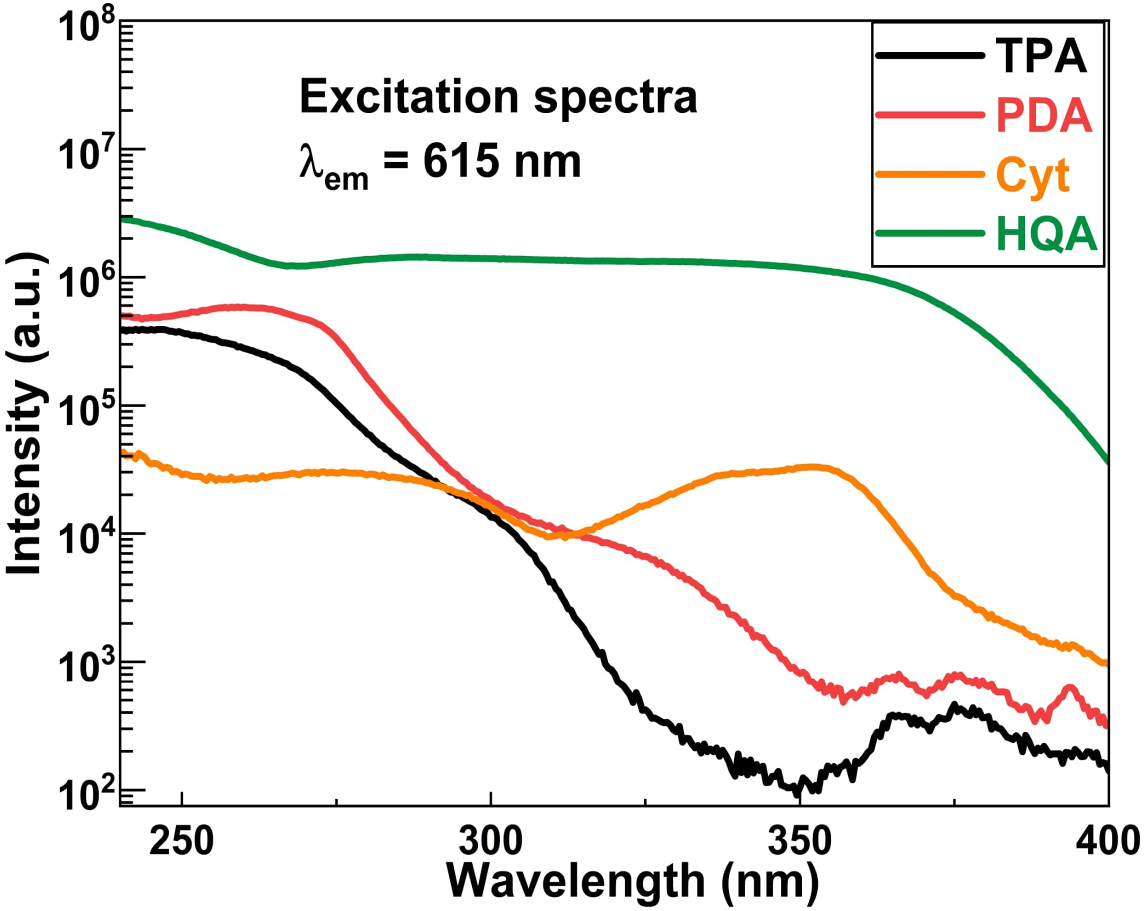
Lanthanide mixture: Eu+Tb+Er
→ (warm) WHITE LIGHT



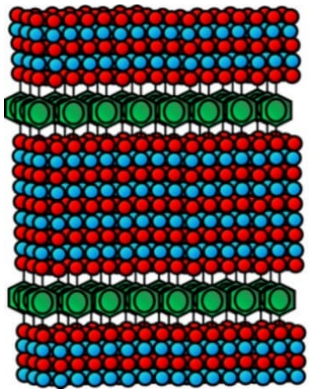
A. Ghazy, M. Lastusaari & M. Karppinen, White-light emitting multi-lanthanide terephthalate thin films by atomic/molecular layer deposition, *Journal of Materials Chemistry C* **11**, 5331 (2023).

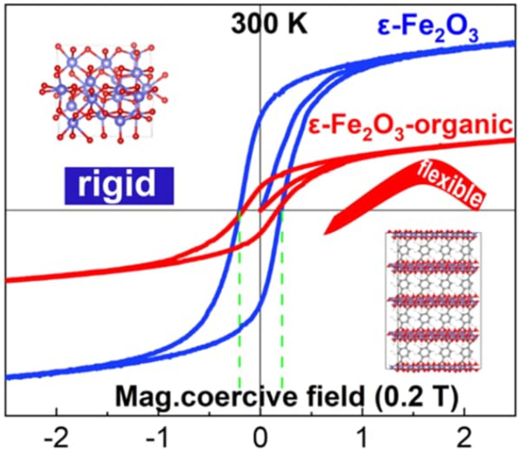
Excitation-Wavelength Engineering:
- Choice of the organic component

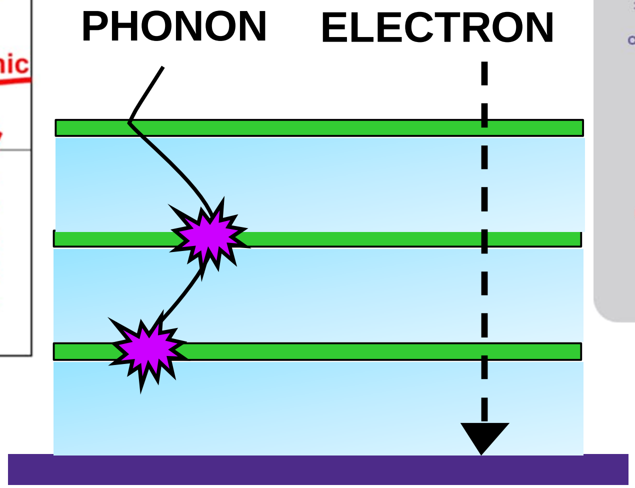


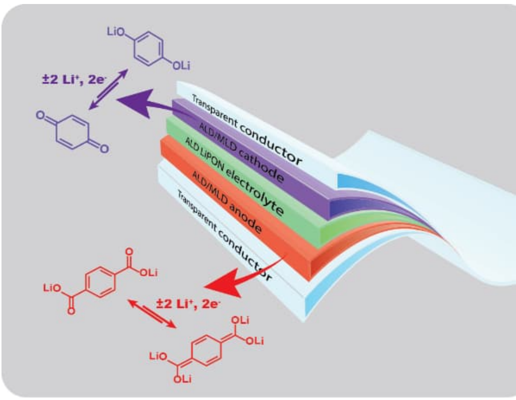


Ghazy, Lastusaari & Karppinen, Excitation wavelength engineering through organic linker choice in luminescent atomic/molecular layer deposited lanthanide-organic thin films, *Chemistry of Materials* **35**, 5988 (2023).

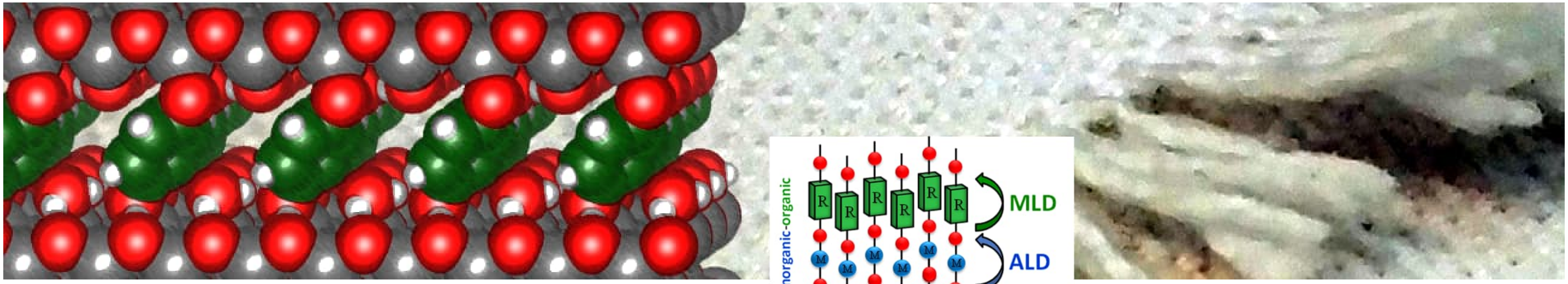


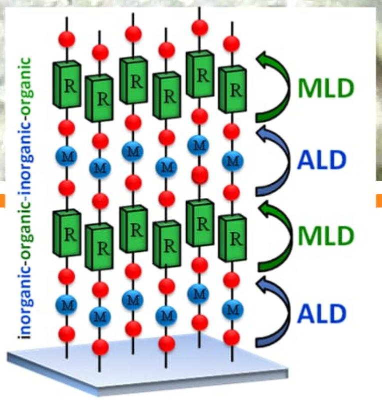






- **ALD/MLD can yield various new types of hybrid materials: new MOFs & layer-engineered superlattice and gradient materials**
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties have been discovered and much more expected !!!**





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