LECTURE 4: Hybrid (inorganic-organic) materials

Functional Inorganic Materials
Fall 2020

Tuesdays: 10.15 - 12.00
Thursdays: 10.15 - 12.00
Remote Zoom lectures

#	Date	Who	Topic
1	Tue 27.10.	Maarit	Introduction + Superconductivity: High-T_c superconducting Cu oxides
2	Thu 29.10.	Maarit	Ionic conductivity (Oxygen): SOFC & Oxygen storage
3	Tue 03.11.	Maarit	Ionic conductivity (Lithium & Proton): Li-ion battery
4	**Thu 05.11.**	**Maarit**	**Hybrid (inorganic-organic) materials**
5	Tue 10.11.	Antti	Thermal conductivity
6	Thu 12.11.	Antti	Thermoelectricity
7	Tue 17.11.	Antti	Ferro-, pyro-, and piezoelectricity
8	Thu 19.11.	Antti	Magnetic and multiferroic oxides
9	Tue 24.11.	Mady	Metal-based energy-saving applications
10	Thu 26.11.	Mady	Metal-based energy-efficient windows and solar absorbers
11	Tue 01.12.	Mady	Metal oxides for energy-saving applications: Past and new trends
12	Thu 03.12.	Mady	Materials design and new perspectives

#	DATE	TOPIC & KEYWORDS
1	27.10.	**(High-T_c) Superconductivity** New-material design, Multi-layered crystal structure, Mixed-valency, Oxygen nonstoichiometry
2	29.11.	**Ionic conductivity: Oxygen** Oxygen vacancies, Redox-active cations, Mixed valency, Cation substitutions (isovalent/aliovalent), Crystal symmetry, Oxygen storage, SOFC
3	03.11.	**Ionic conductivity: Hydrogen & Lithium** Water absorption & Oxide/hydroxide, Li-ion battery, Solid-state electrolytes
4	05.11.	**Hybrid materials** Inorganic-organic materials, MOF, ALD/MLD, Layer-engineering, superlattice

LECTURE EXERCISE 4

1. Explain why insertion of organic layers into inorganic matrix could be useful to enhance (a) mechanical, and (b) thermoelectric properties.
2. Give an example of the ALD/MLD synthesis of new crystalline metal-organic material which is very difficult if not impossible to synthesize using conventional synthesis techniques. Explain the unique benefits of ALD/MLD with few sentences!
3. See the next page for this question, which is also related to Lecture 3.

EXERCISE 4.3

Read the relevant parts of the following articles on Li-ion thin-film micro-battery and answer (possibly with some illustrative figures from the articles) to the questions A-F; in the best case you can write a short overall story.

1. Notten et al., 3D integrated all-solid-state rechargeable batteries, *Appl. Mater.* 19, 4564 (2007).
2. Talin et al., Fabrication, testing and simulation of all-solid-state 3D Li-ion batteries, *ACS Appl. Mater. Interfaces* (2016).
3. Nisula et al, Atomic layer deposition of lithium phosphorous oxynitride, *Chem. Mater.* 27, 6987 (2015).
4. Nisula et al., In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery, *J. Mater. Chem. A* 6, 7027 (2018).
5. Heiska et al., Organic electrode materials with solid-state battery technology, *J. Mater. Chem. A* 7, 18735 (2019).

A. Readily integrable microbatteries are urgently needed as power sources for various autonomous devices. What is the main problem with the present planar thin-film microbatteries, and how the issue could be addressed (according to Ref. 1)?

B. In Ref. 2, sputtering is used as the thin-film deposition technique to fabricate 3D microbattery ($LiCoO_2$ cathode and LiPON electrolyte). What is the problem?

C. ALD could solve the problem, why?

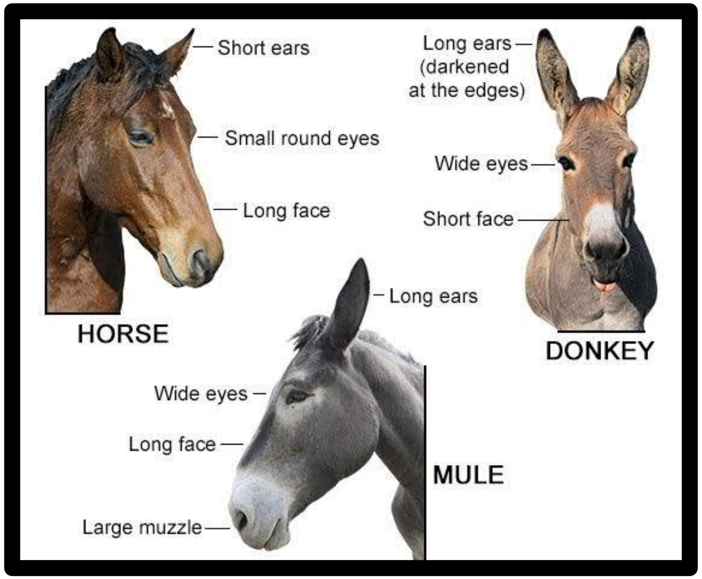
D. In Ref. 3, an ALD process is developed for the state-of-the-art thin-film electrolyte material, LiPON. What was the major challenge successfully addressed in the paper?

E. How about the conformality of the ALD-LiPON films?

F. In ref. 4, the ALD-LiPON process is combined with an ALD/MLD process for Li-organic anode material for an all-ALD-made microbattery. What are the unique advantages? You can also read Ref. 5 (page 18752) for further explanation.

Brought Together

SUM of BOTH PROPERTIES

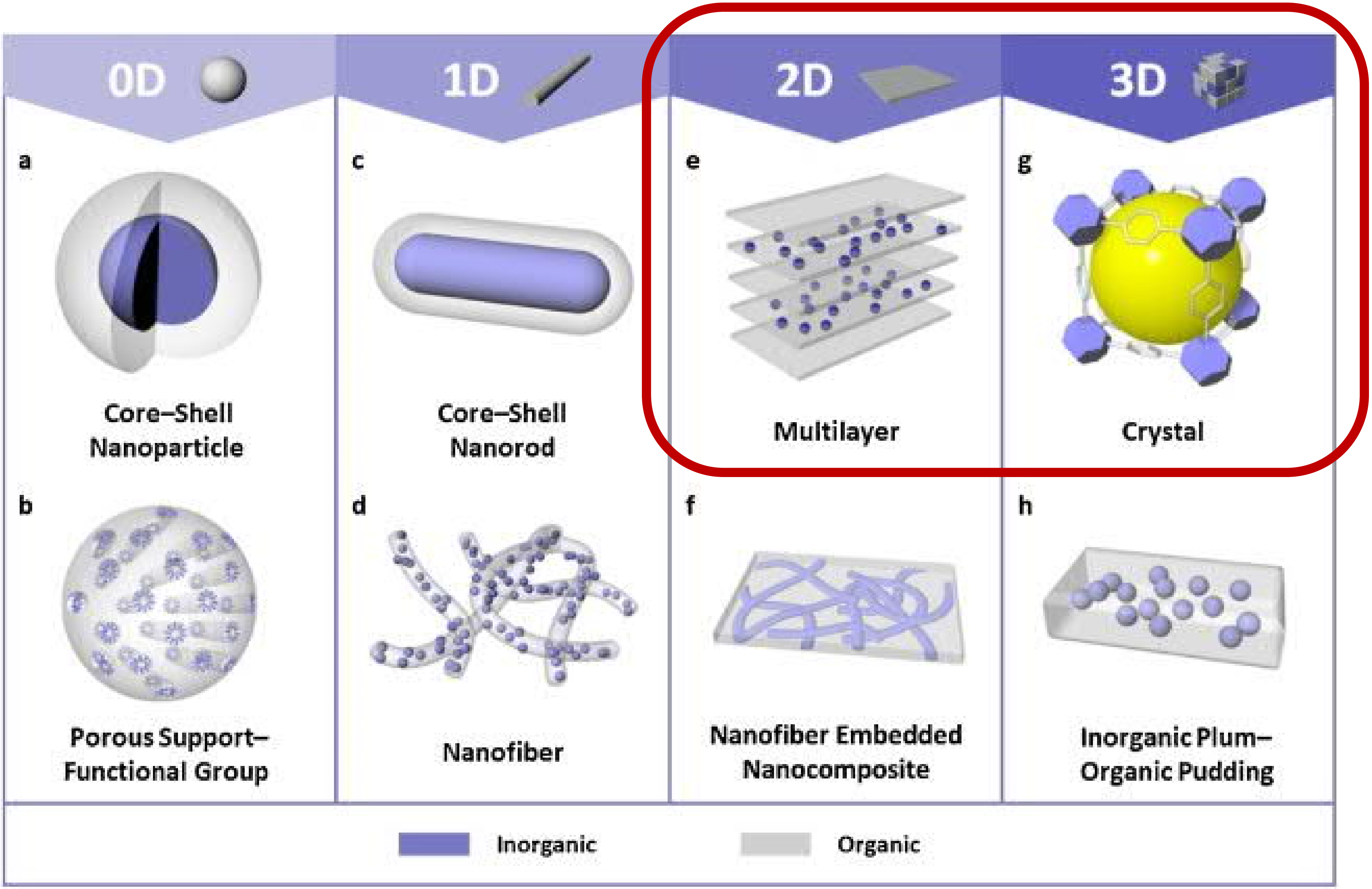


Intimately Fused

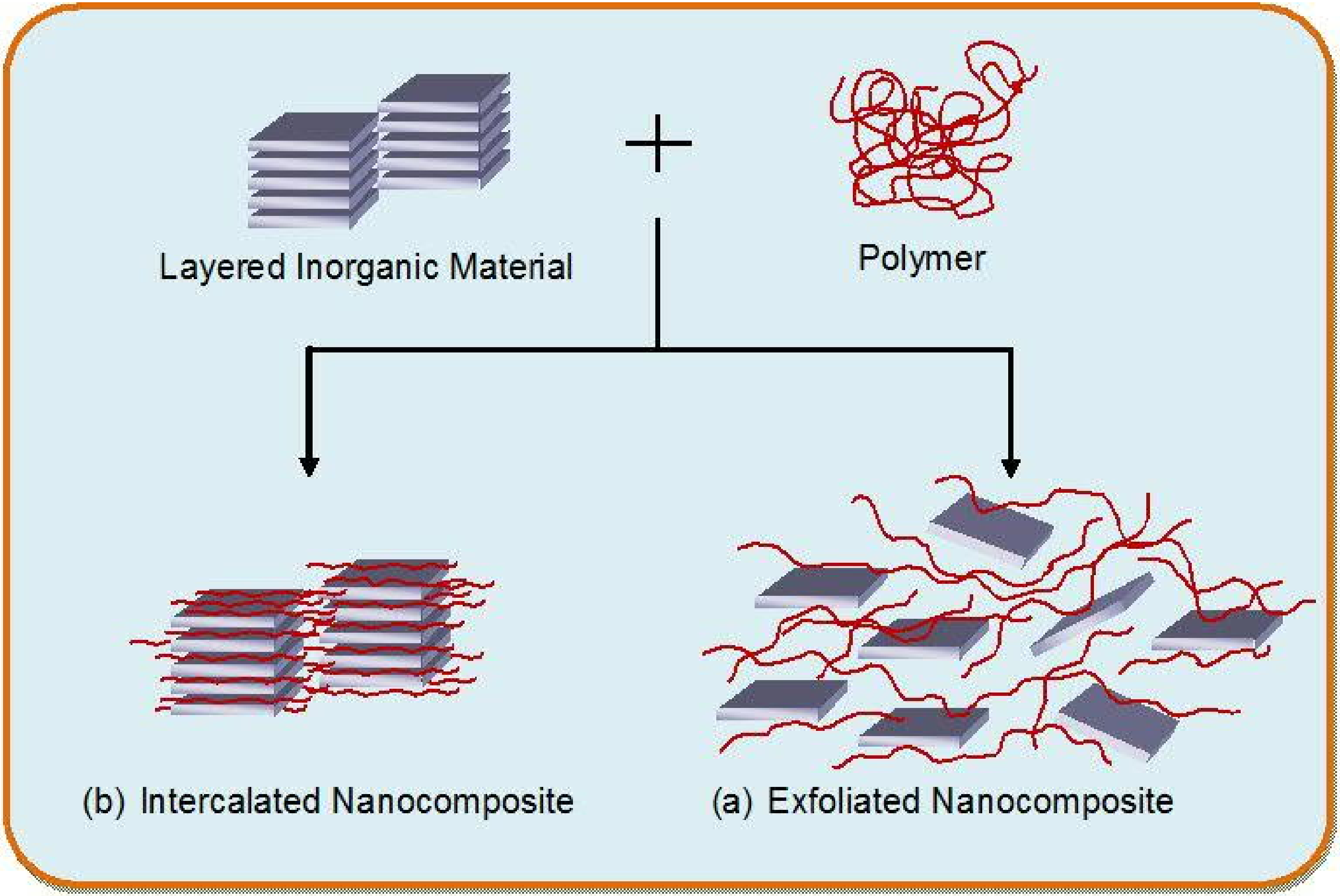
AVERAGE PROPERTIES

Intimately Fused

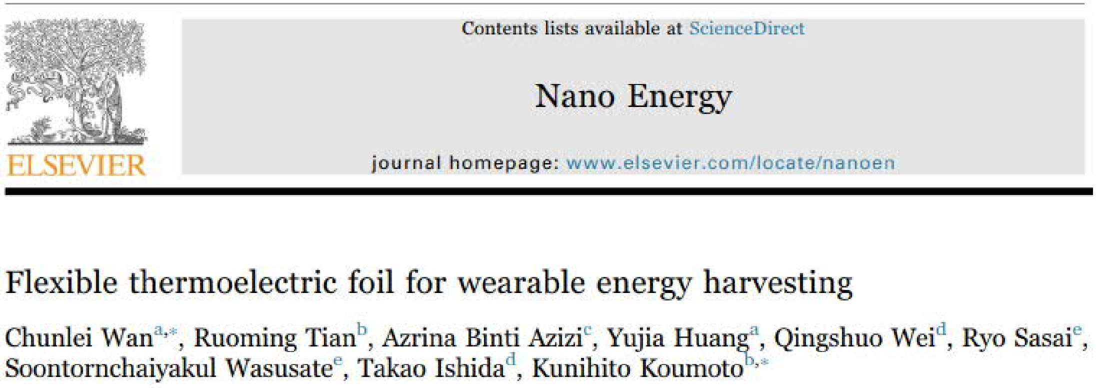
Unique/Unpredicted/Non-existing/Ground-breaking PROPERTIES


0D
1D
2D
3D
a
Core–Shell Nanoparticle
c
Core–Shell Nanorod
e
Multilayer
g
Crystal
b
Porous Support–Functional Group
d
Nanofiber
f
Nanofiber Embedded Nanocomposite
h
Inorganic Plum–Organic Pudding
Inorganic
Organic

Multilayered Inorganic-Organic Hybrids



Multilayered Inorganic-Organic Hybrids



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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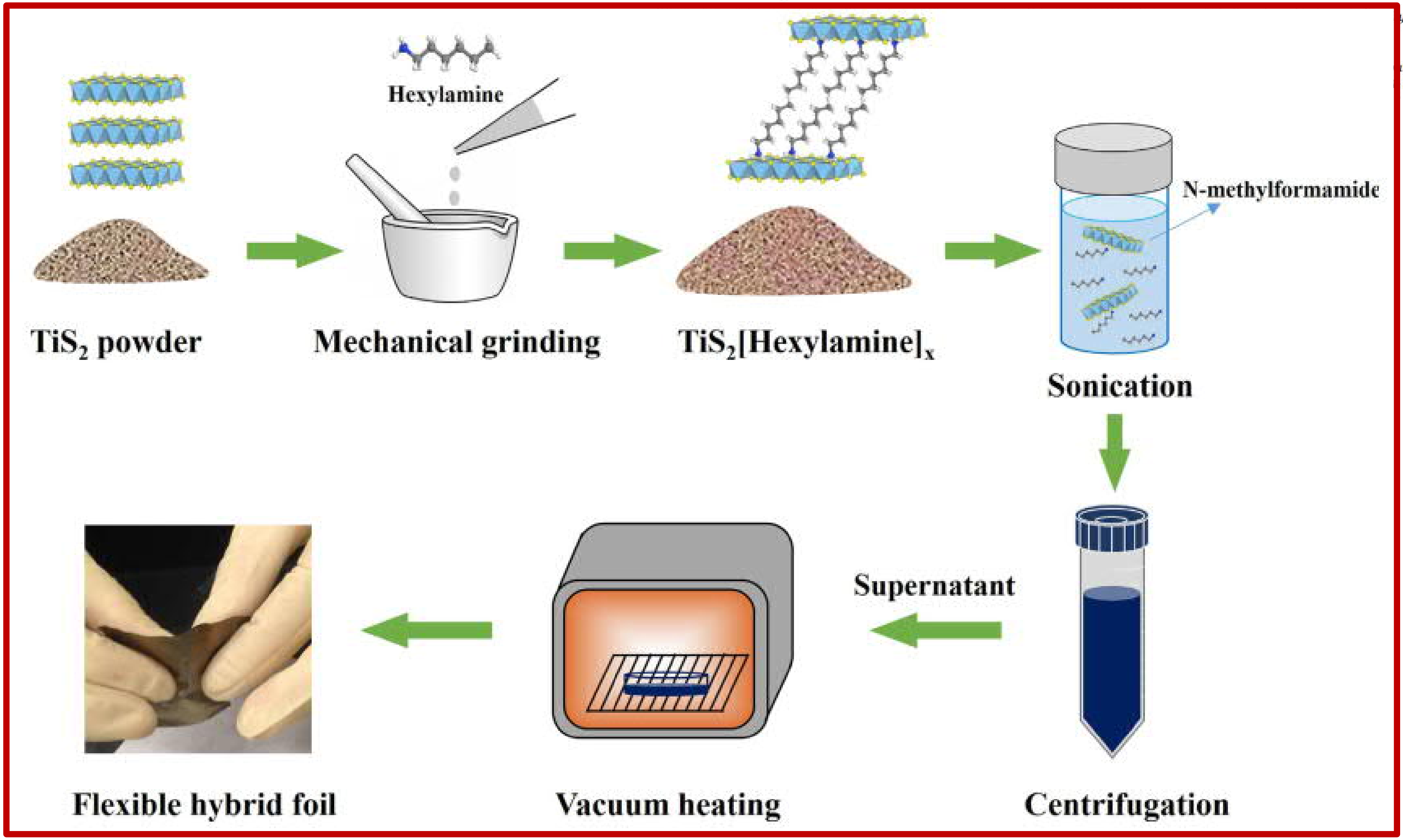
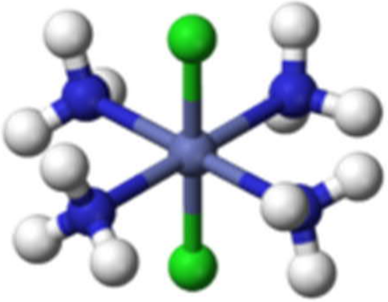
raki 305-8564, Japan

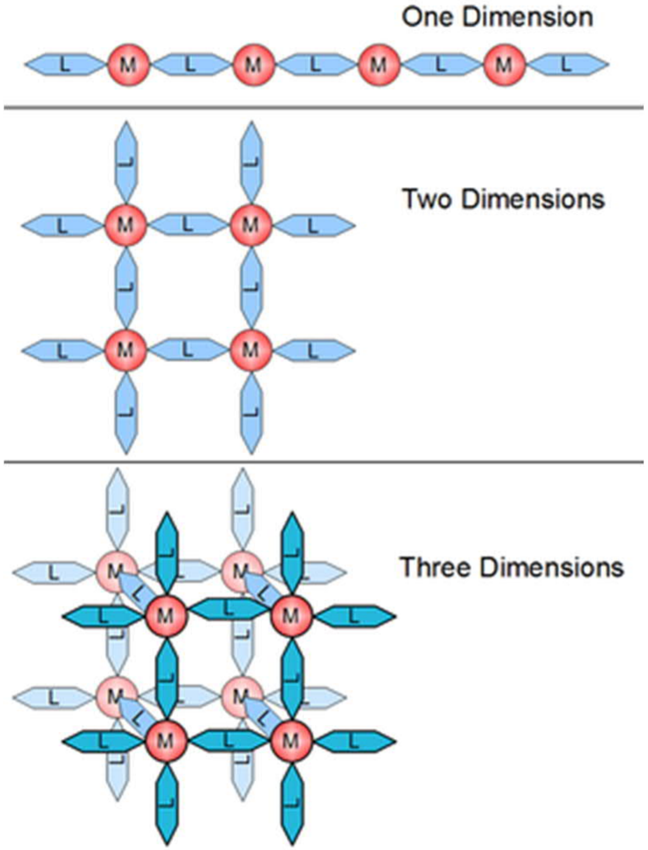
Japan

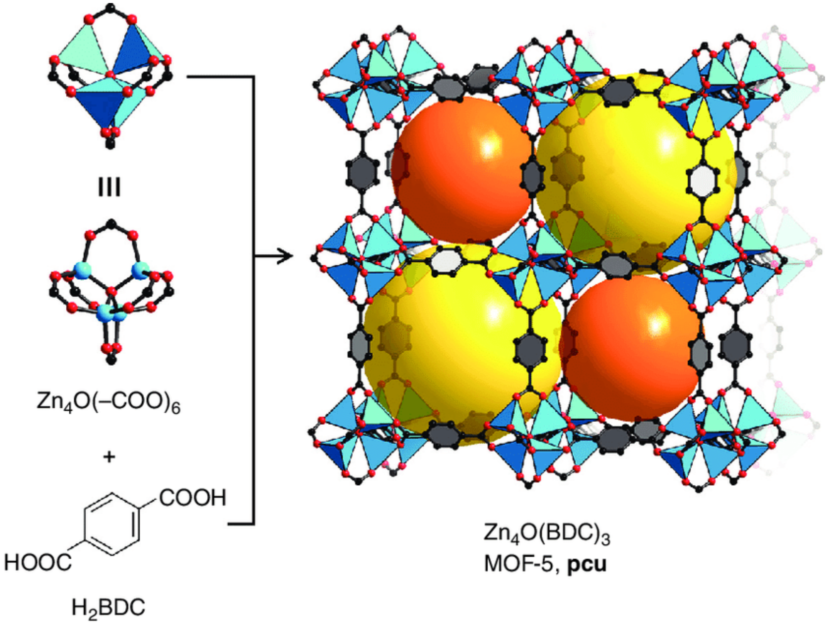


FOR CHEMISTS: Inorganic-Organic Material

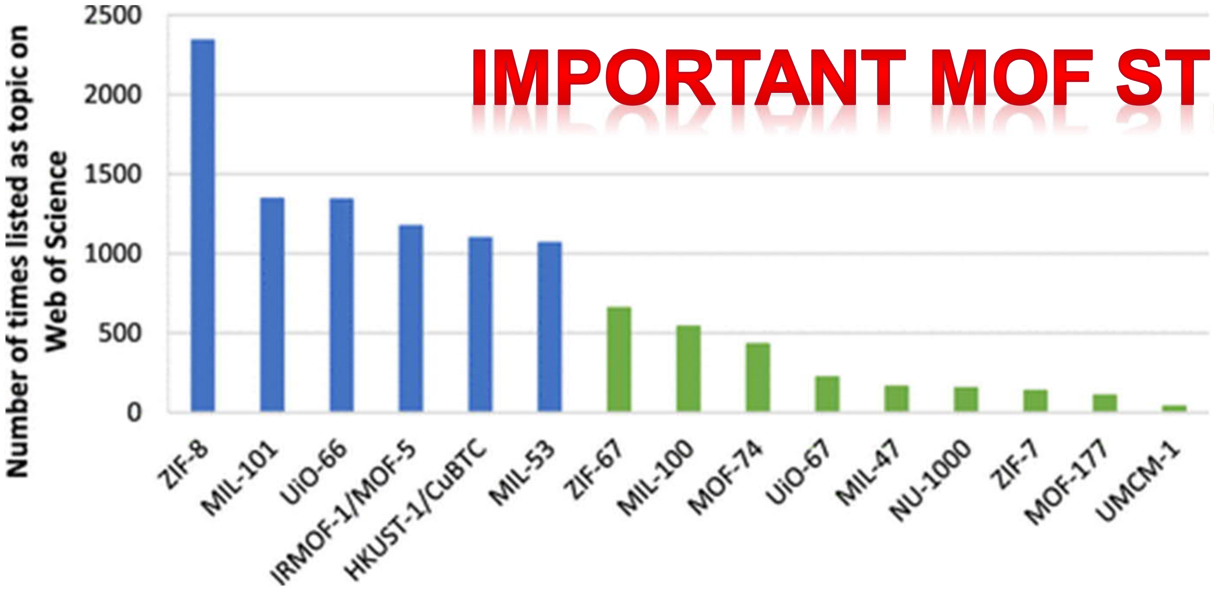
- Compound NOT Composite
- Coordination/Metal Complex: central metal ion + (organic) ligands
- Coordination Polymer/Network: ligands act as bridges
- Metal-Organic Framework (MOF): highly porous

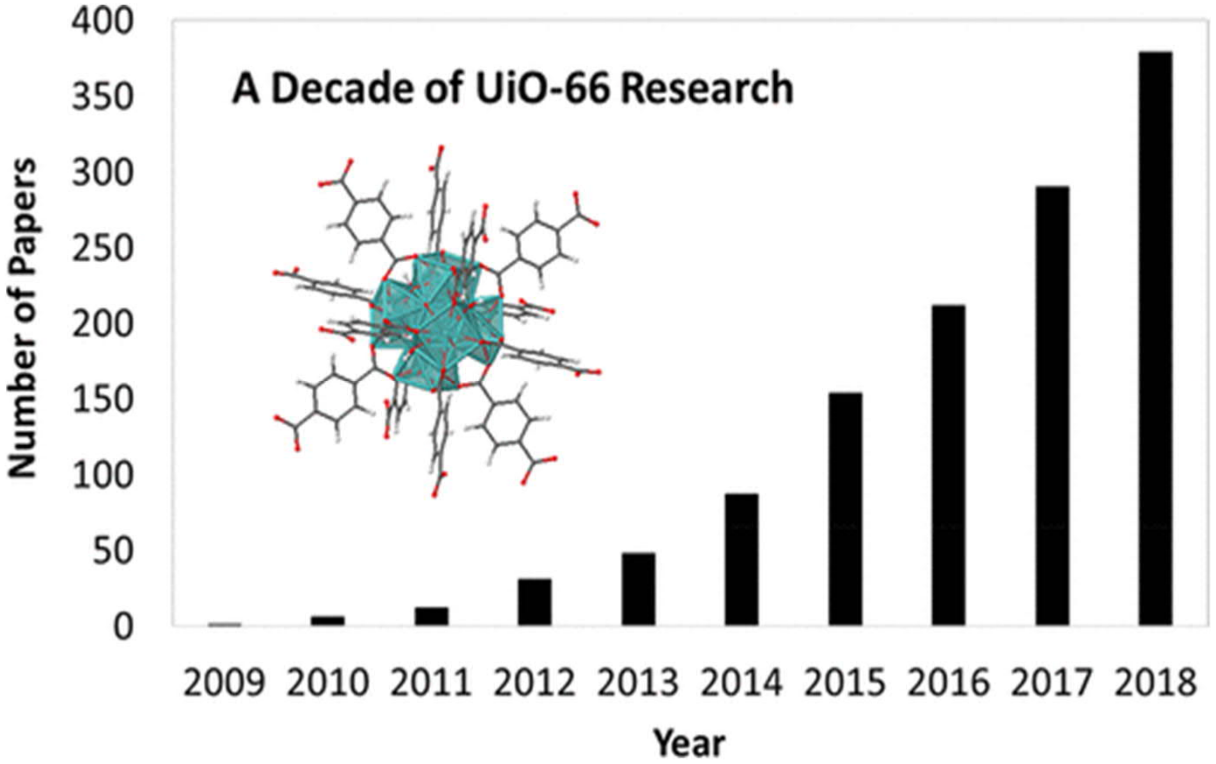




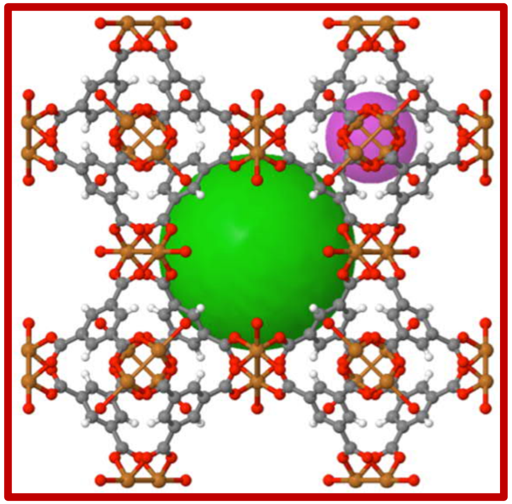


IMPORTANT MOF STRUCTURES

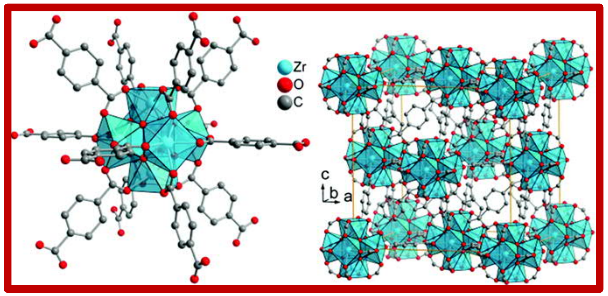


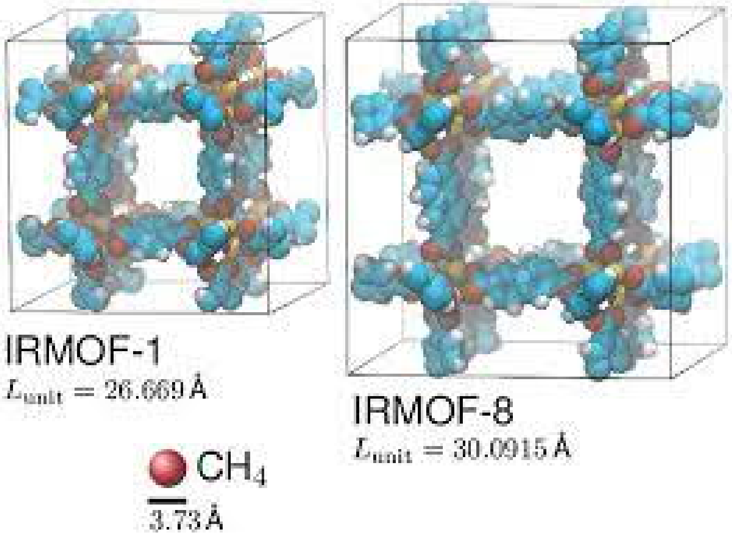


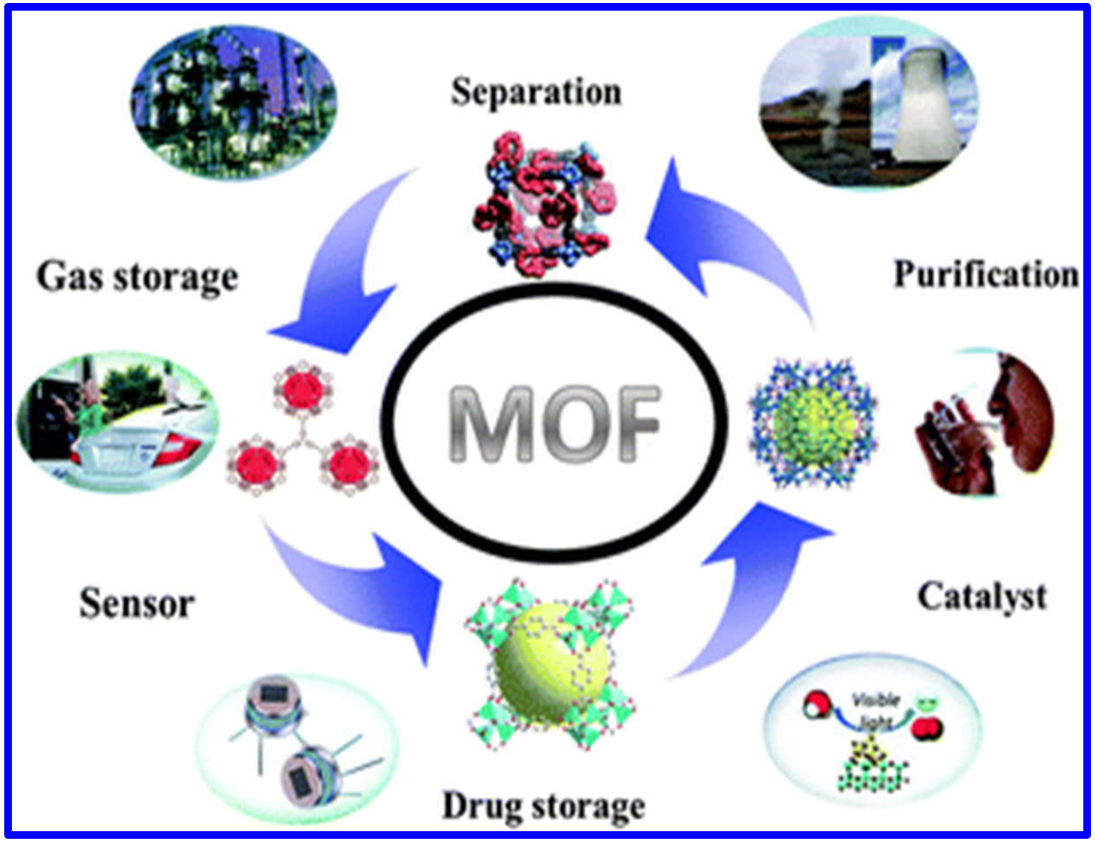
HKUST-1



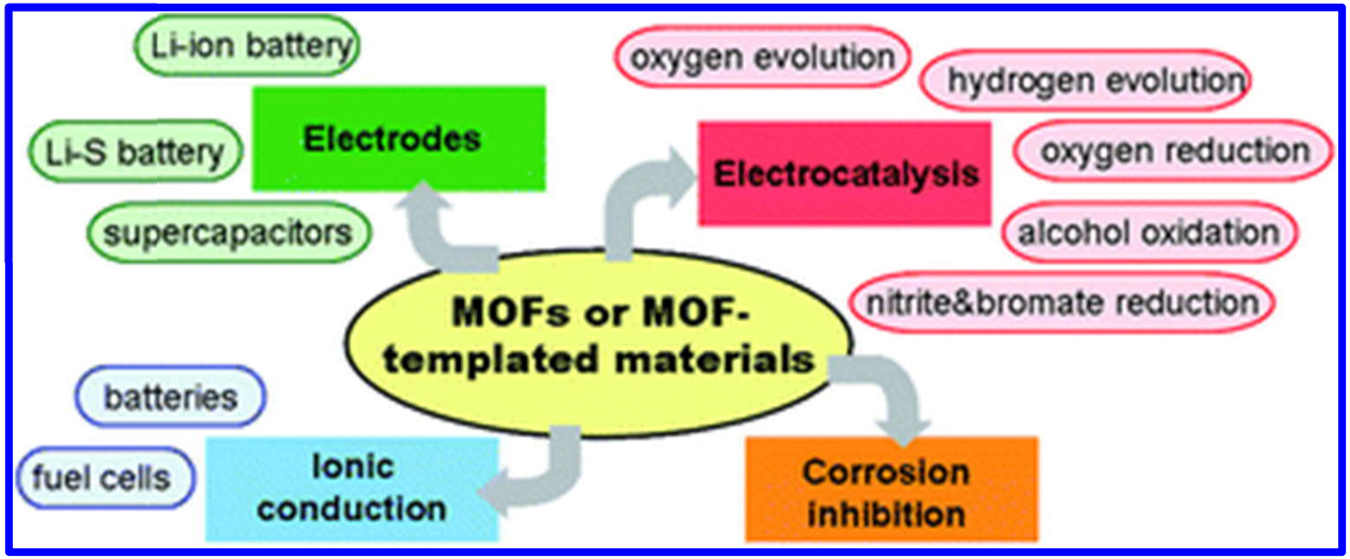
UiO-66





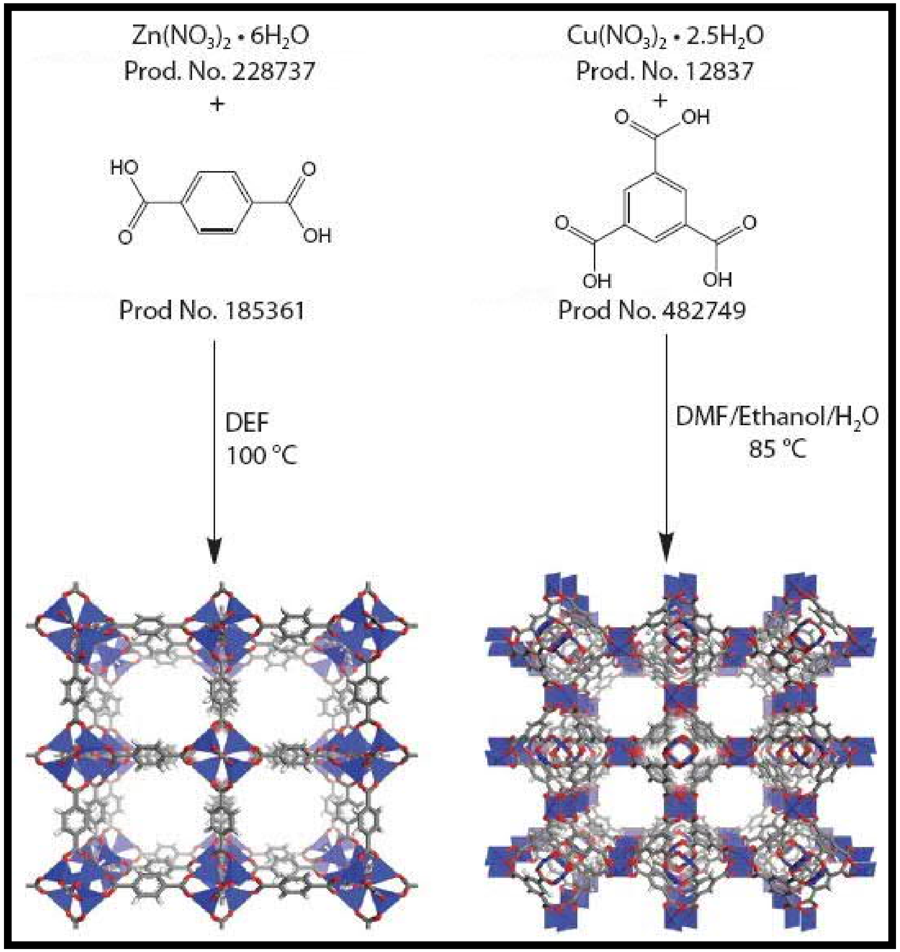


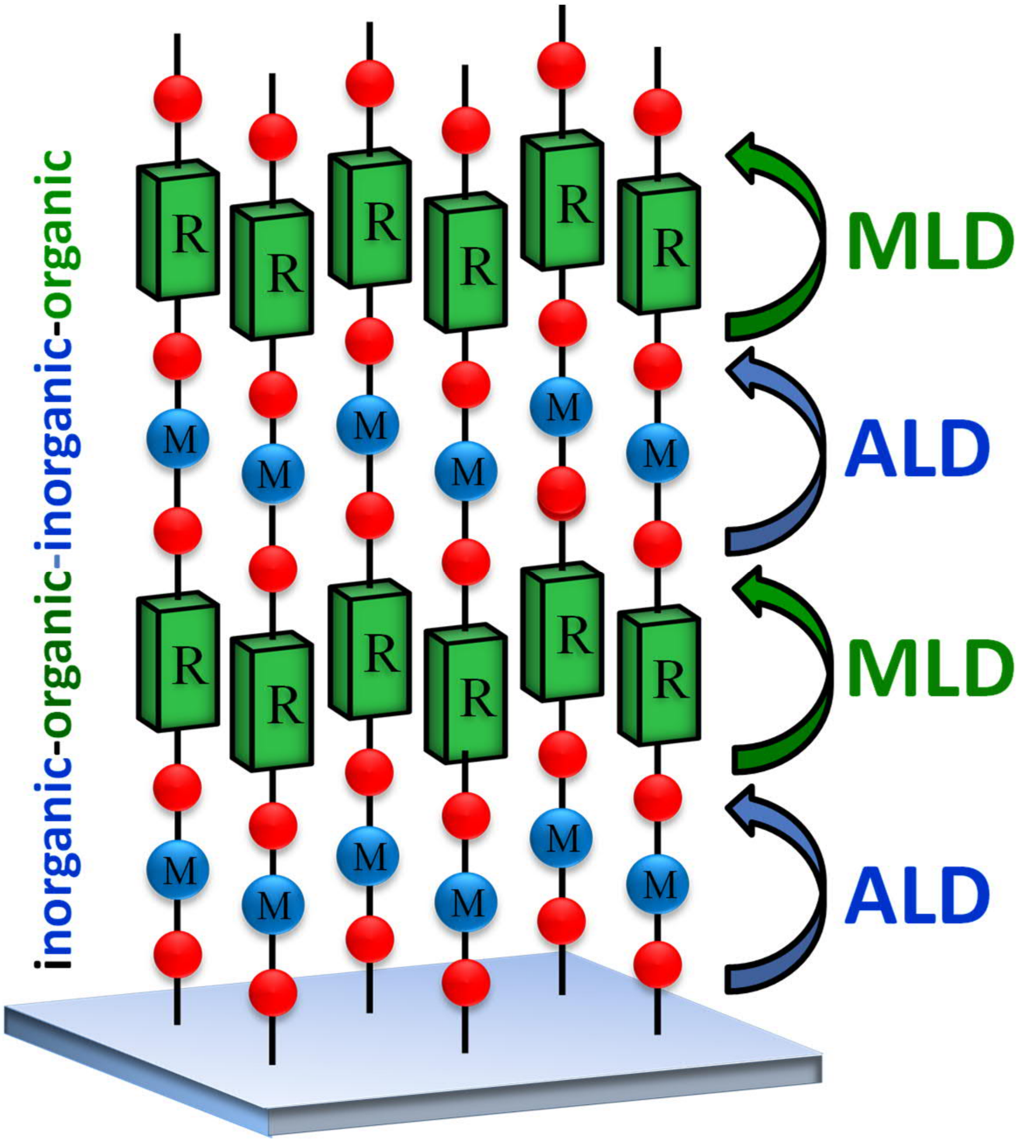
MOF THIN FILMS!



Synthesis of MOFs

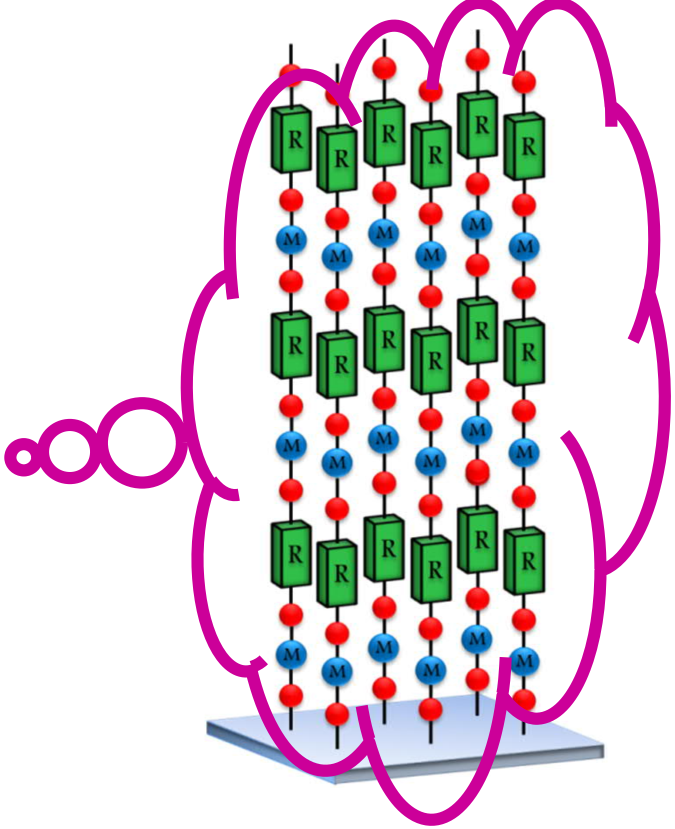
- **Synthesized most often in bulk form via solution techniques**
- **Porous structure →**
  MOFs absorb readily/unintentionally solvent molecules
- **Many prospective applications would require high-quality thin films**
- **No gas-phase deposition techniques (before ALD/MLD) !**



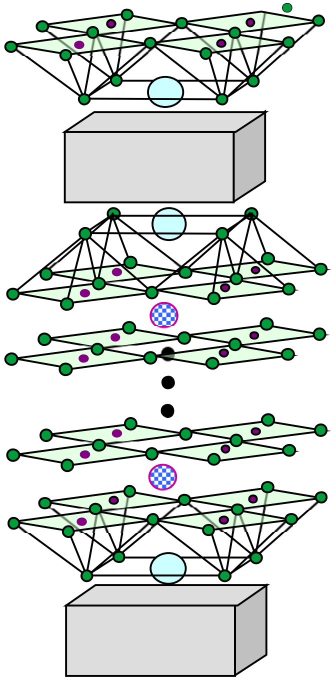

inorganic-organic-inorganic-organic
R
M
MLD
ALD
MLD
ALD

MULTI-FUNCTIONAL MULTILAYERED MATERIALS

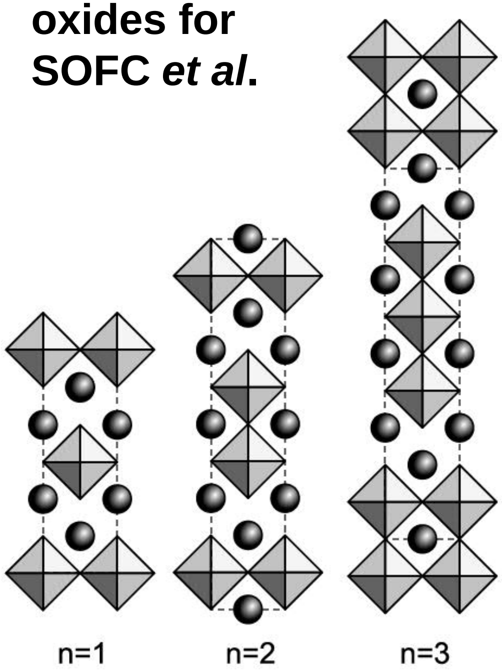
Layered inorganic-organic hybrid thin films



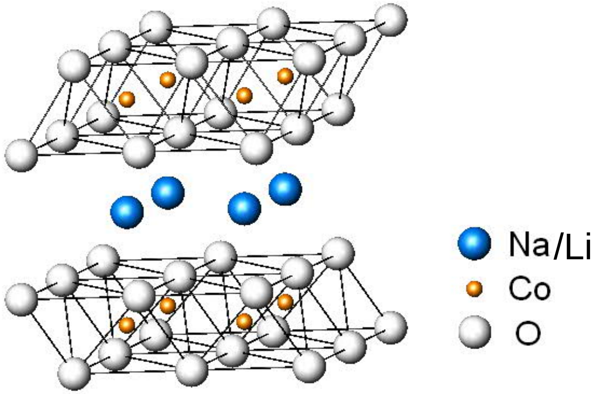
Multilayered Cu oxides for high-T_c superconductors



Ruddlesden-Popper oxides for SOFC *et al*.

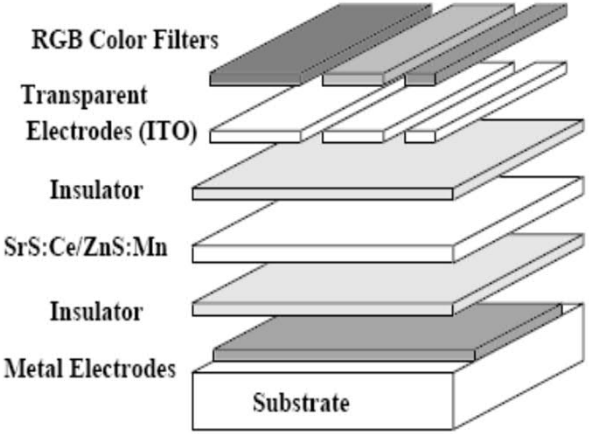


Layered Co oxides for Li-ion battery & thermoelectrics



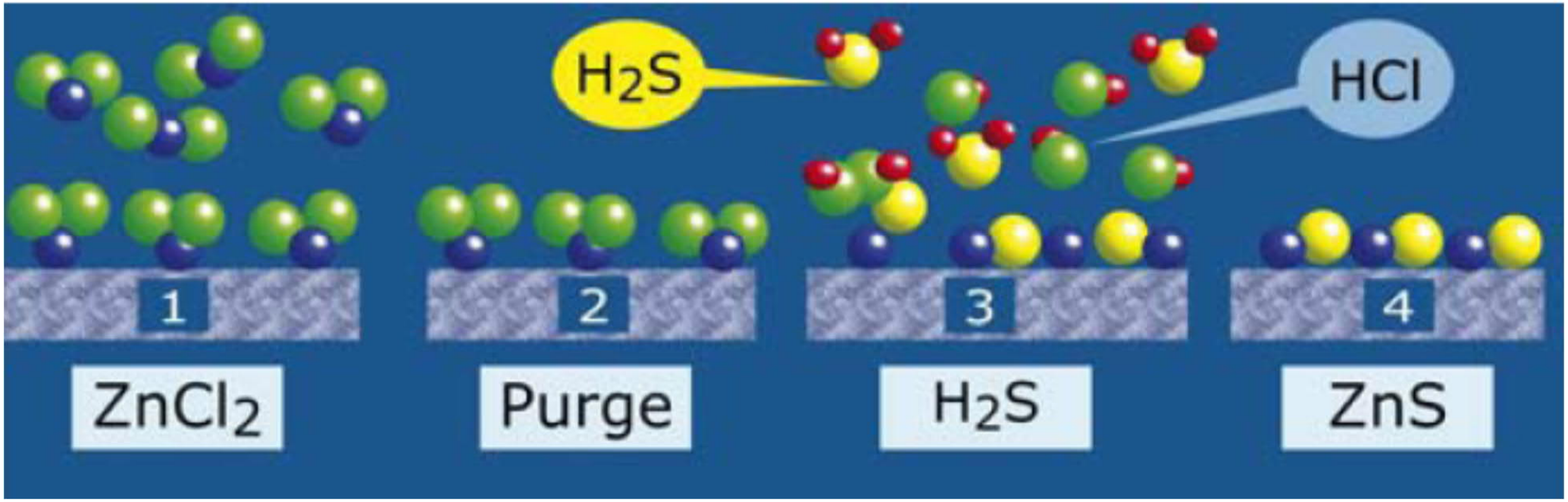
Atomic Layer Deposition (ALD) Thin-Film Technique

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



Electroluminescent display

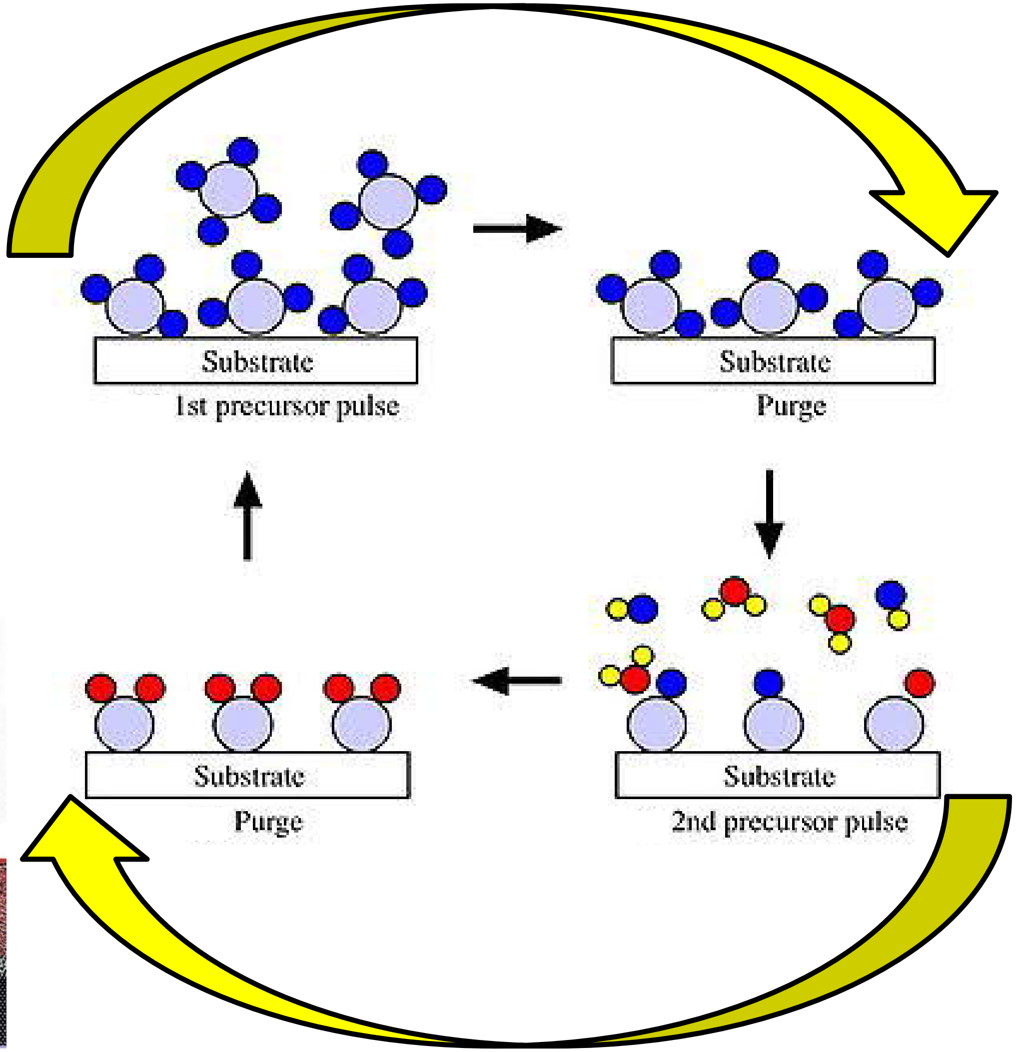
Instrumentarium / Finlux / Planar

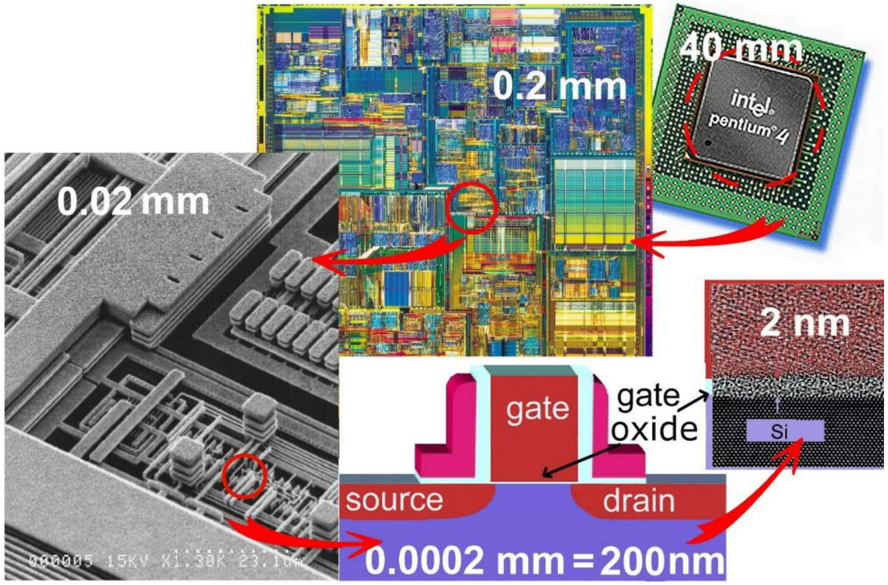


HfO$_2$-ALD

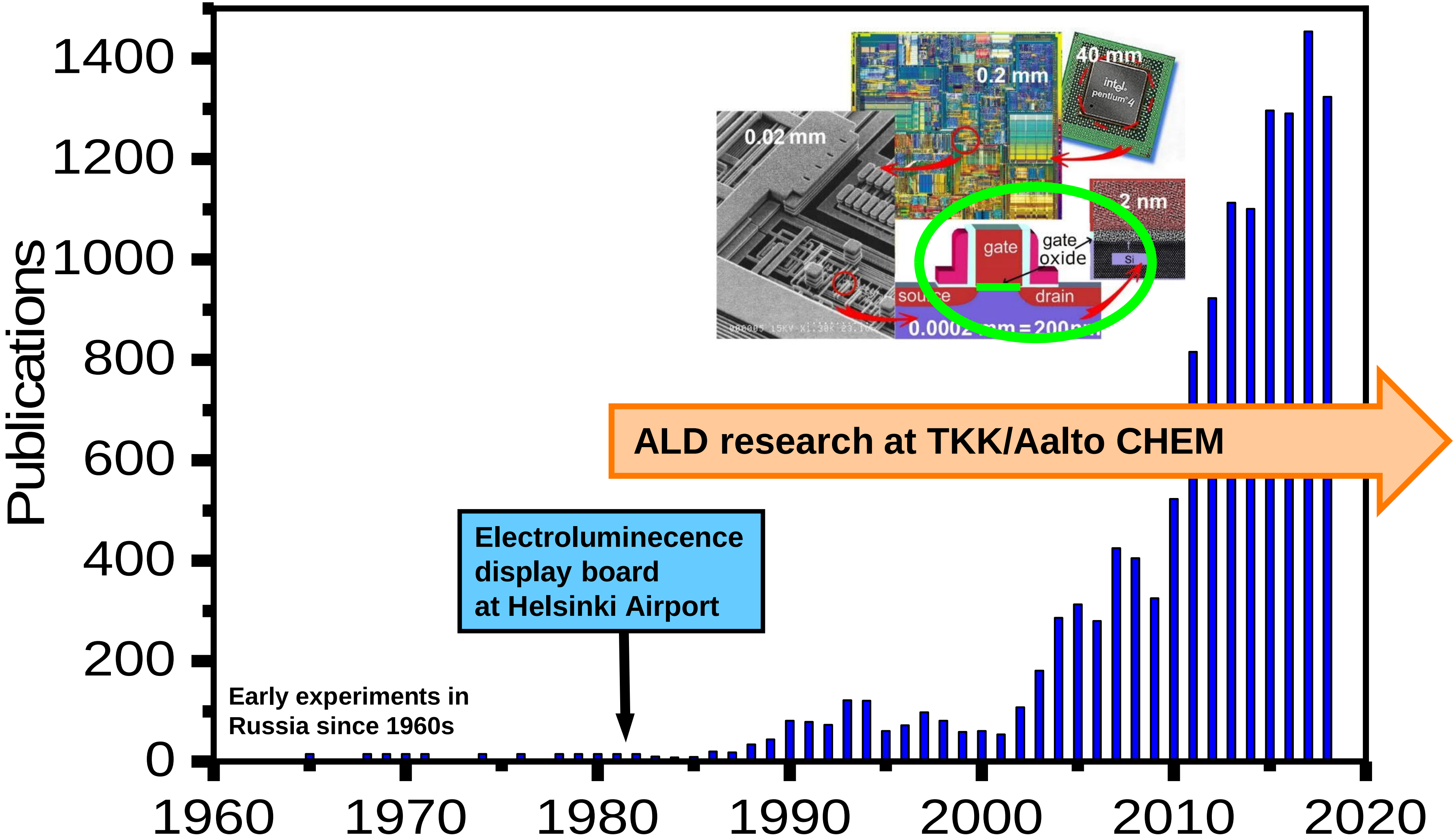
HfCl$_4$ + H$_2$O

ALD cycle





Atomic Layer Deposition (ALD)



ALD research at TKK/Aalto CHEM

Electroluminecence display board at Helsinki Airport

Early experiments in Russia since 1960s

Tuomo Suntola: Patent filed 1974

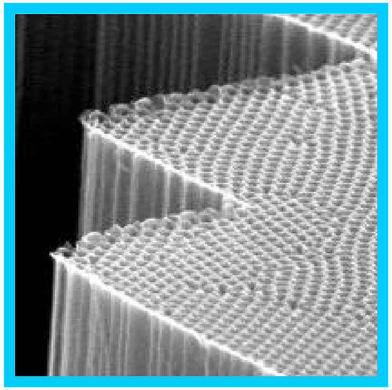
ALD-HfO_2 by Intel for transistors

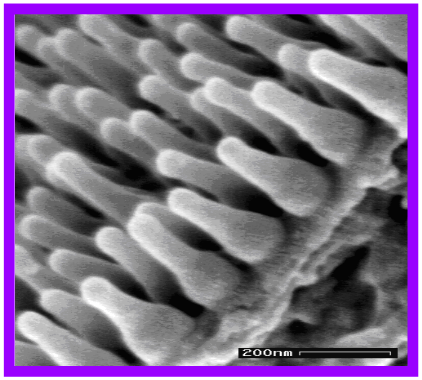
Millenium 2018 Prize for Suntola

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

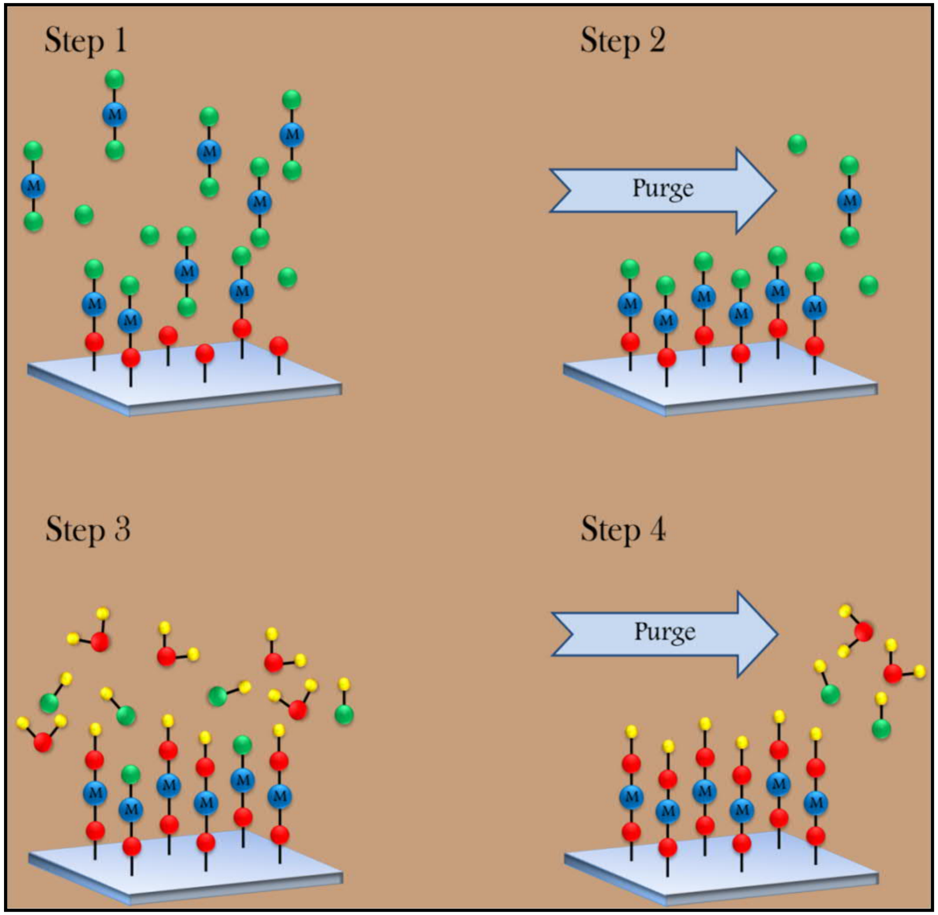
- Organic/polymer films
- Inorganic/organic hybrid materials

ELECTRONICS

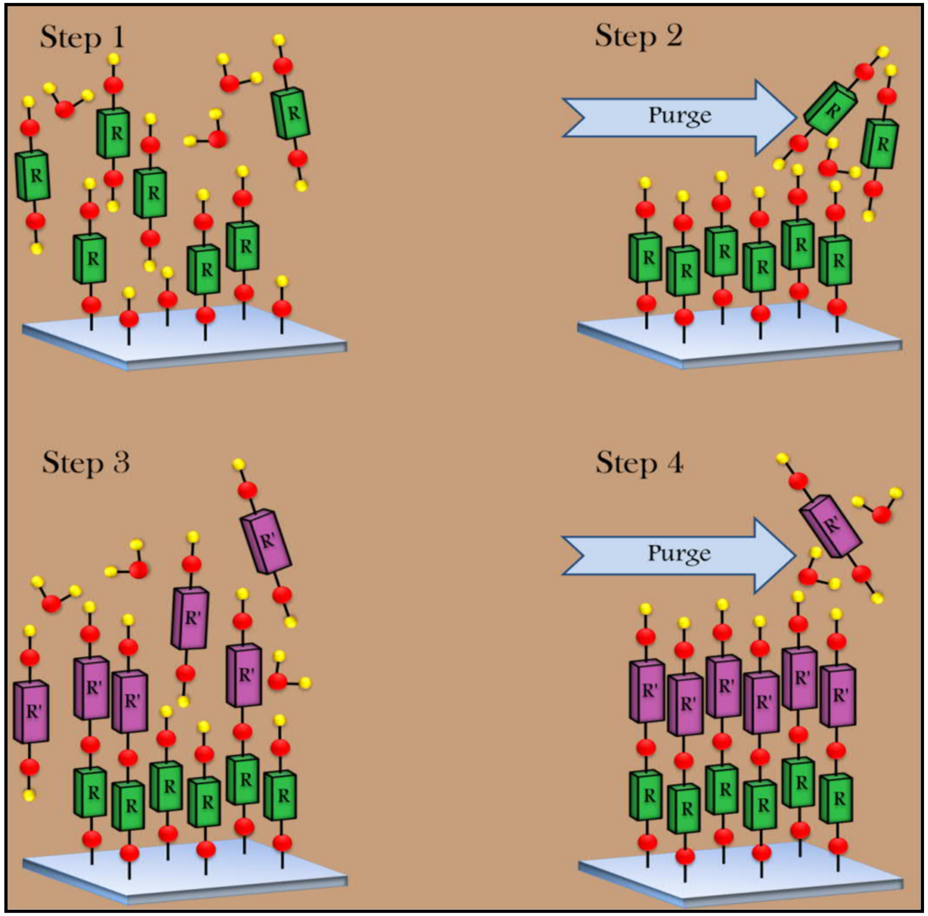
NANO

BIO

NEW



ALD **(Atomic Layer Deposition)**

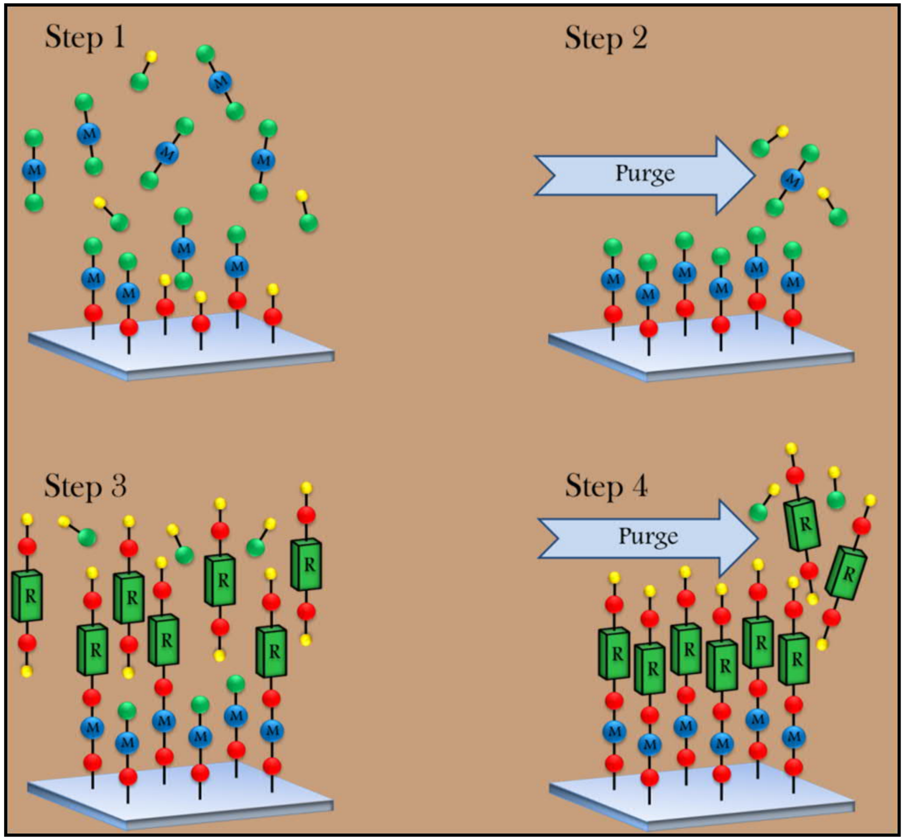


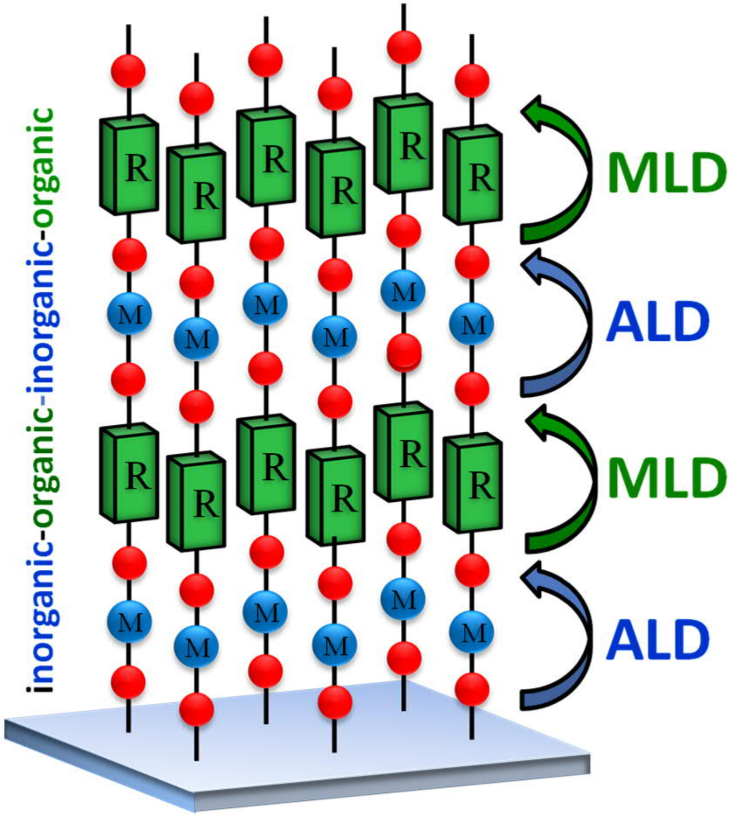
MLD **(Molecular Layer Deposition)**

High-quality
INORGANIC thin films
with atomic level control

ORGANICS !
(in 1990s)

Inorganic-Organic Hybrid Thin Films by Combined ALD/MLD

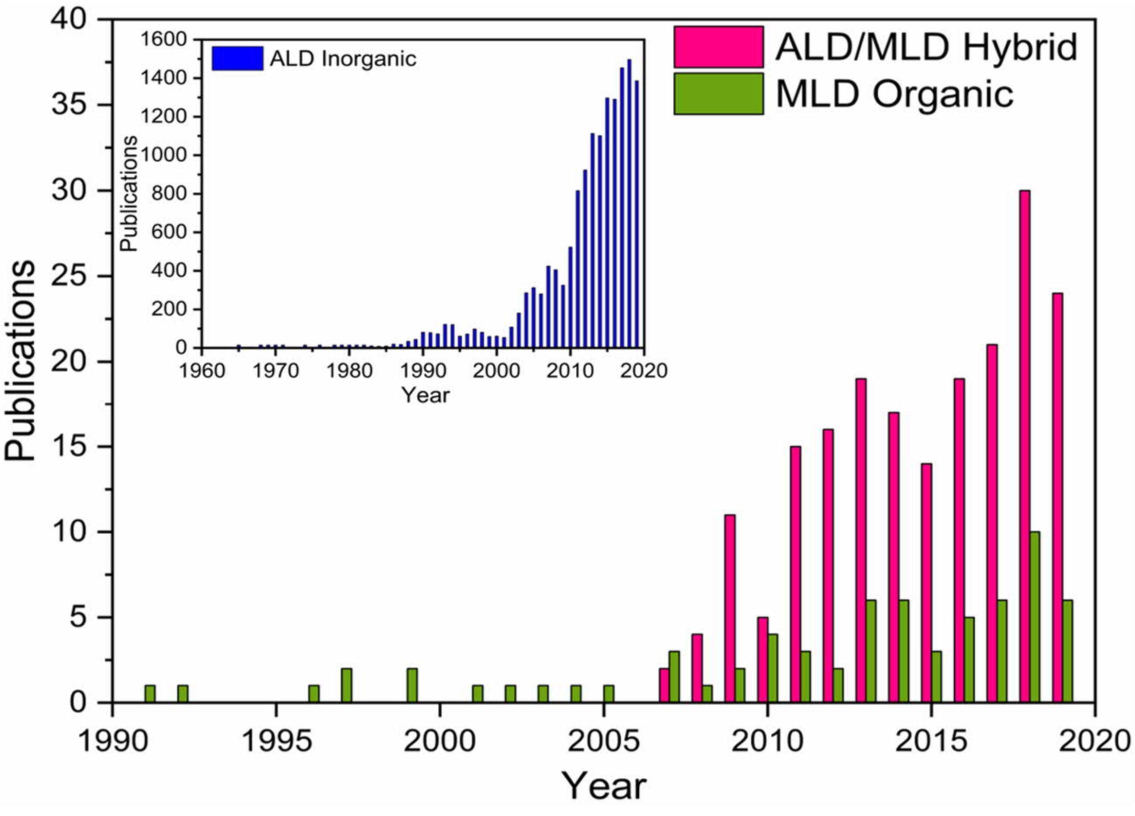




MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!

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.

Kubono, Yuasa, Shao, Umemoto & Okui, *Thin Solid Films* **1996,** *289,* 107.

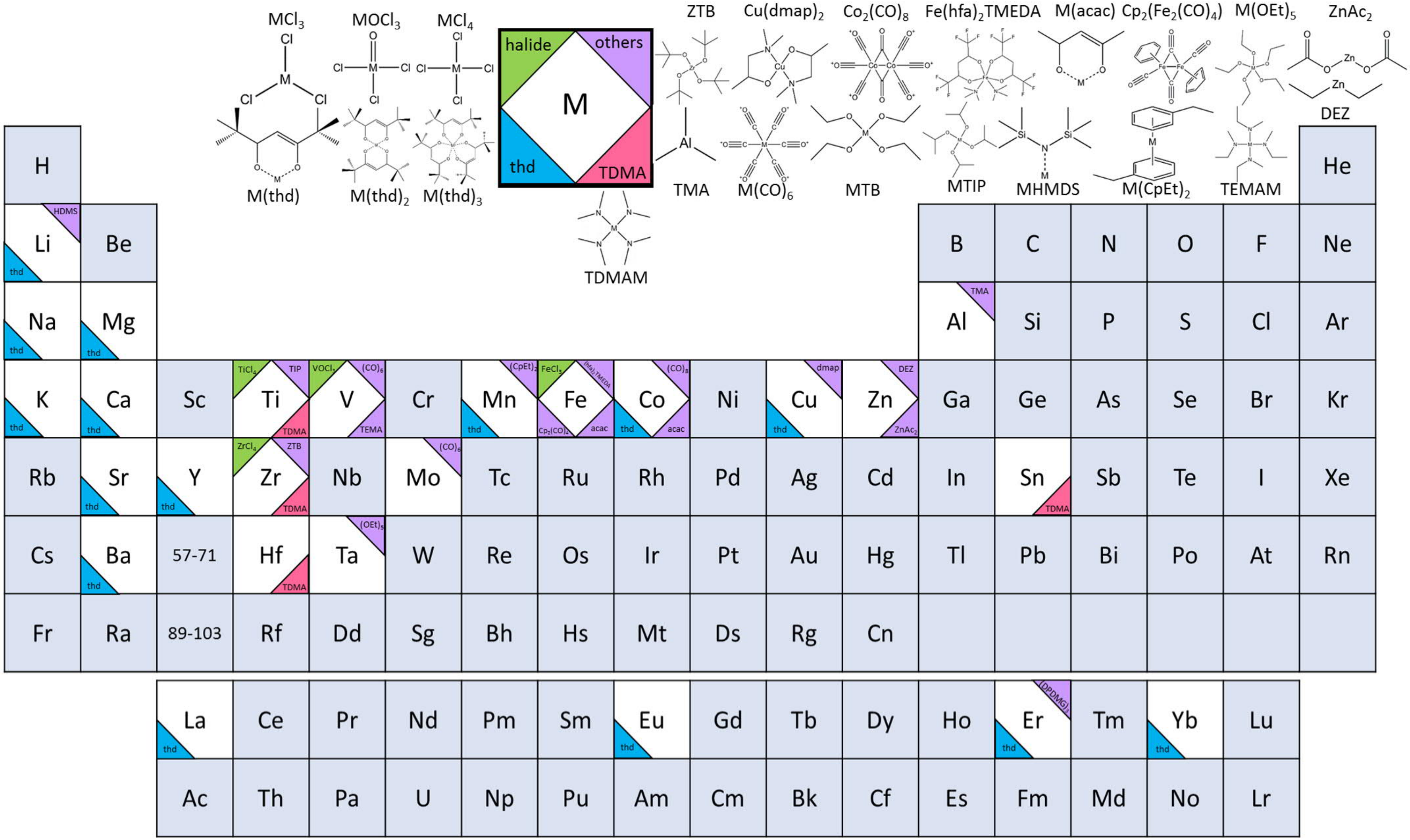
Shao, Umemoto, Kikutani & Okui, *Polymer* **1997,** *38,* 459.

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.

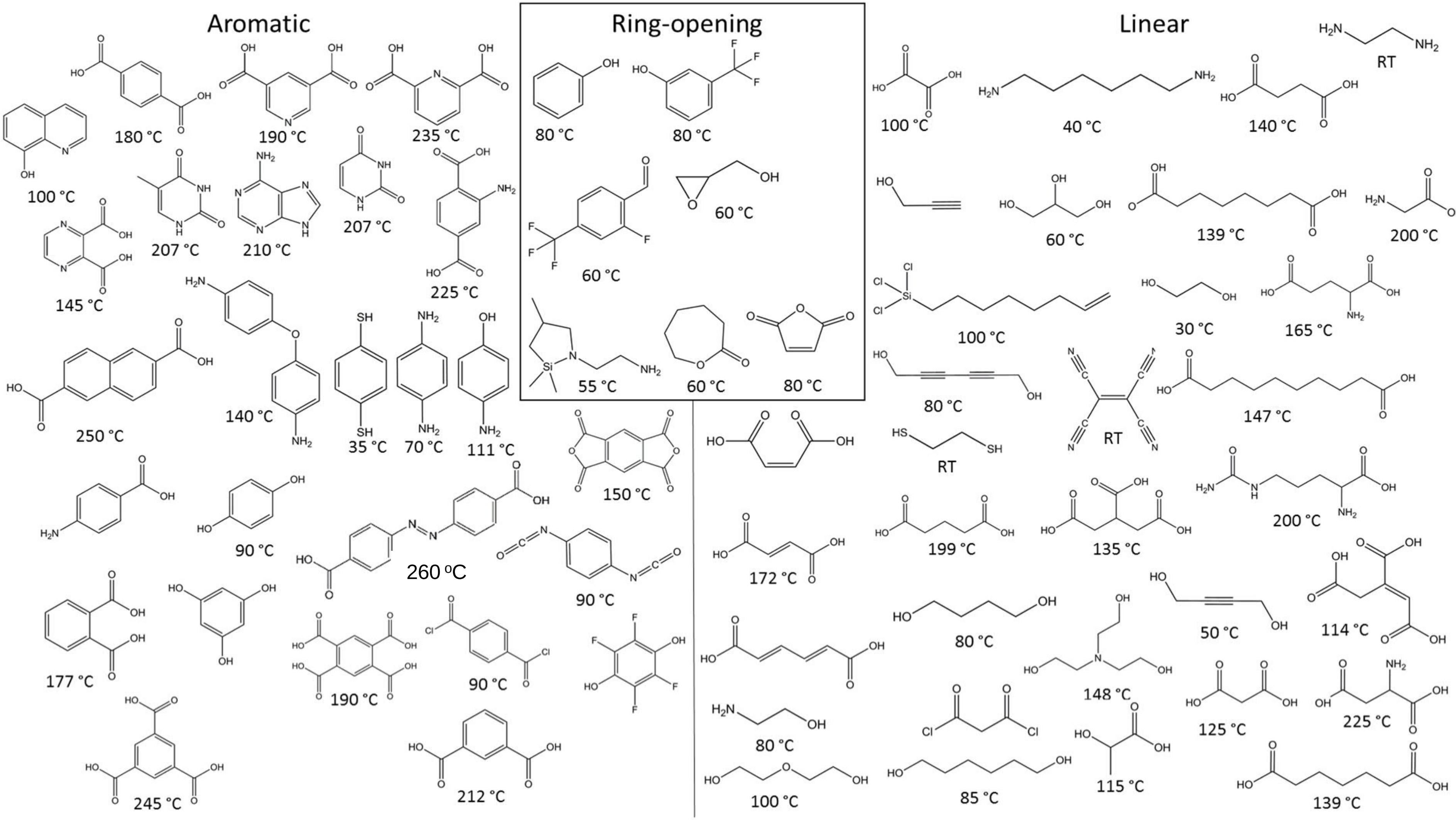
Nilsen, Klepper, Nielsen & Fjellvåg, *ECS Trans.* **2008,** *16,* 3.

Dameron, Seghete, Burton, Davidson, Cavanagh, Bertrand & George, *Chem. Mater.* **2008,** *20,* 3315.



Aalto University
School of Chemical Technology

ALD/MLD Processes: Metal Precursors



Aalto University
School of Chemical Technology

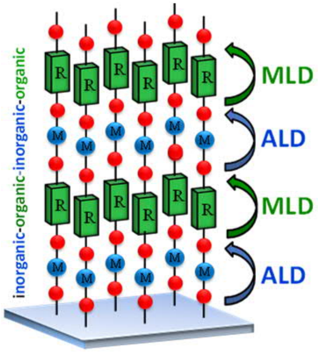
ALD/MLD Processes: Organic Precursors

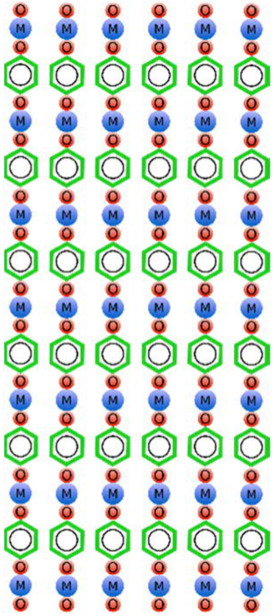
(sublimation temperatures !)

⬡ **Organic** (e.g. benzene)

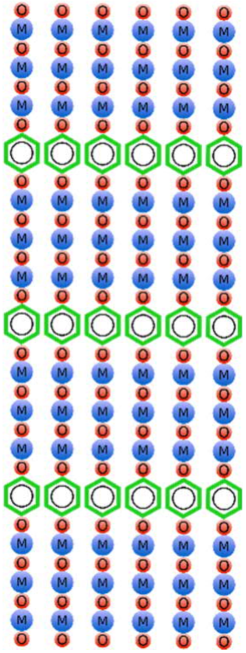
M **Metal**

O **Oxygen** (or N, S, …)

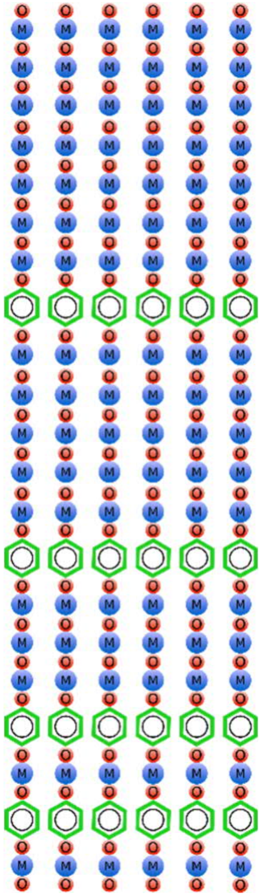




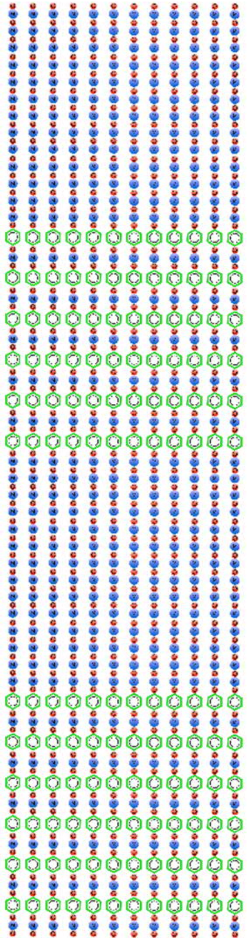
Simple
Metal-Organic Network
(amorphous or crystalline)



Superlattice



Gradient hybrid



Nanolaminate

DIFFERENT LAYER SEQUENCES BY DESIGN

LAYER-ENGINEERED

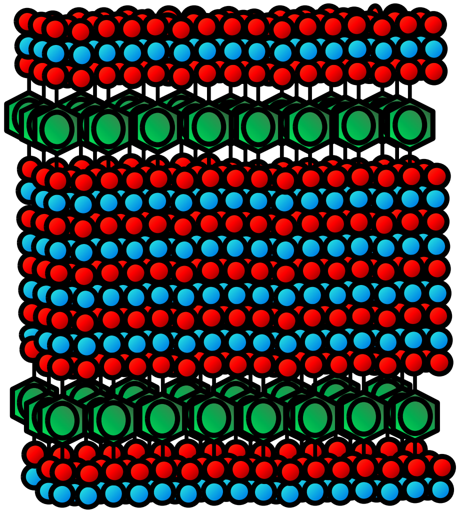
INORGANIC-ORGANIC SUPERLATTICES

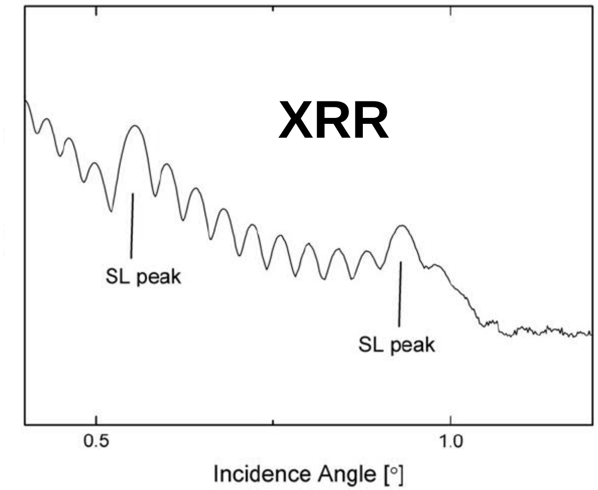
BY

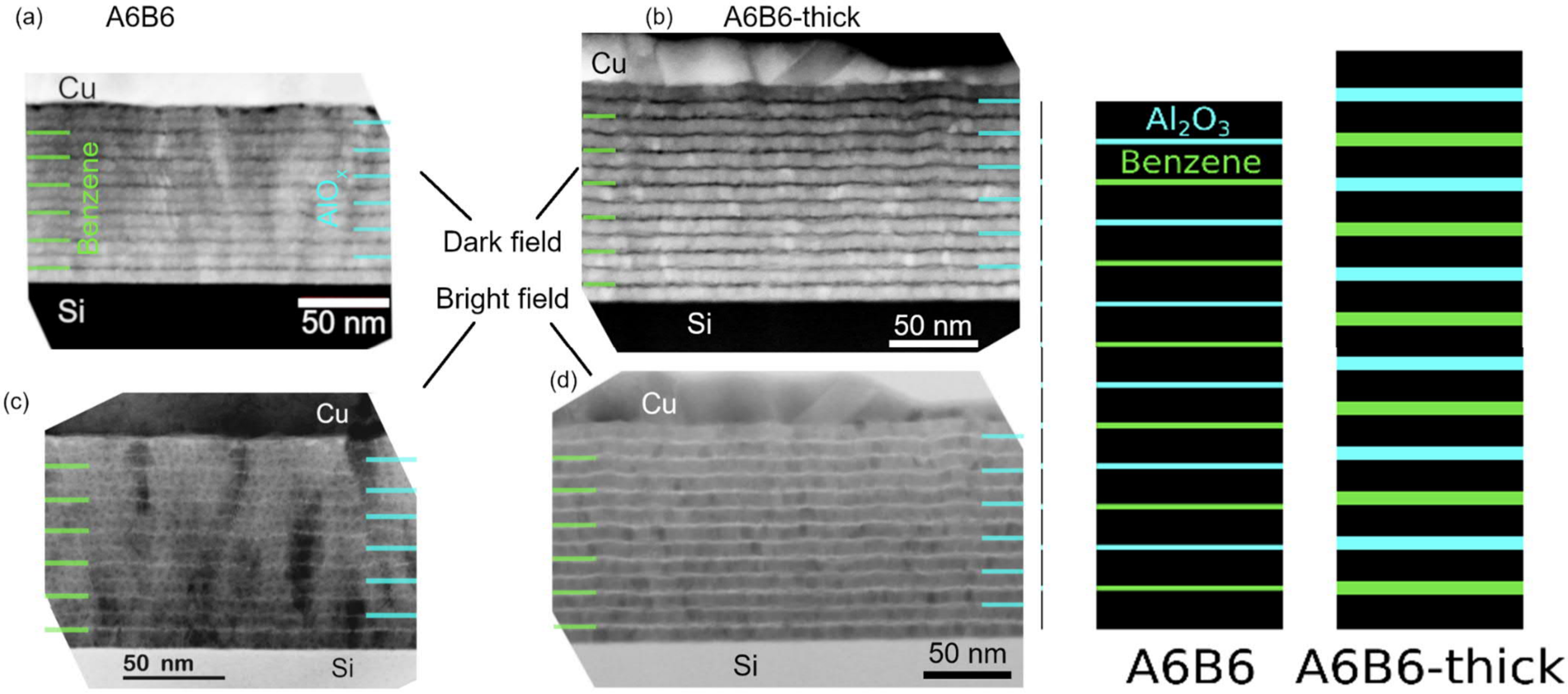
ALD/MLD

Aalto University
School of Chemical
Technology

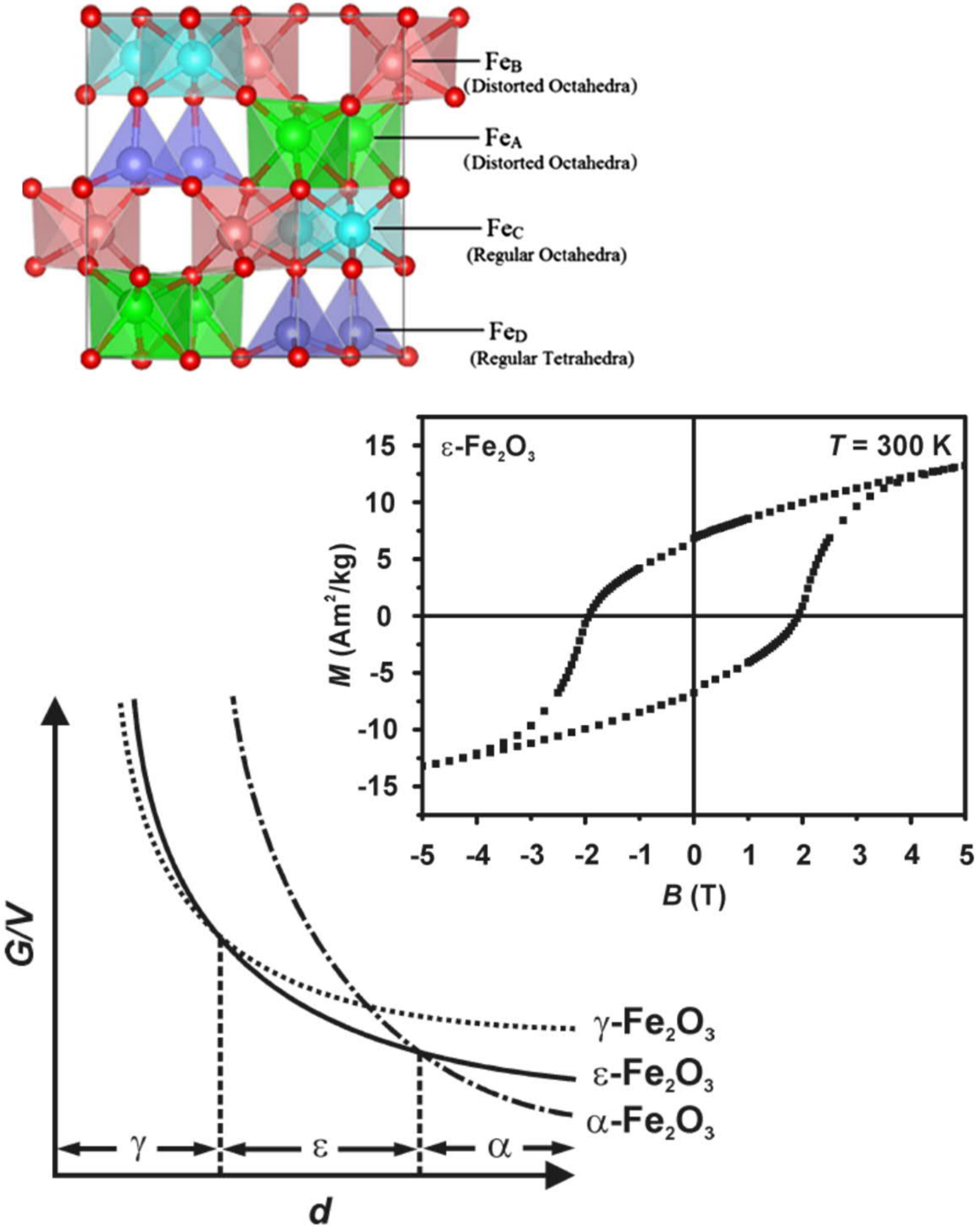
ZnO:benzene SUPERLATTICE

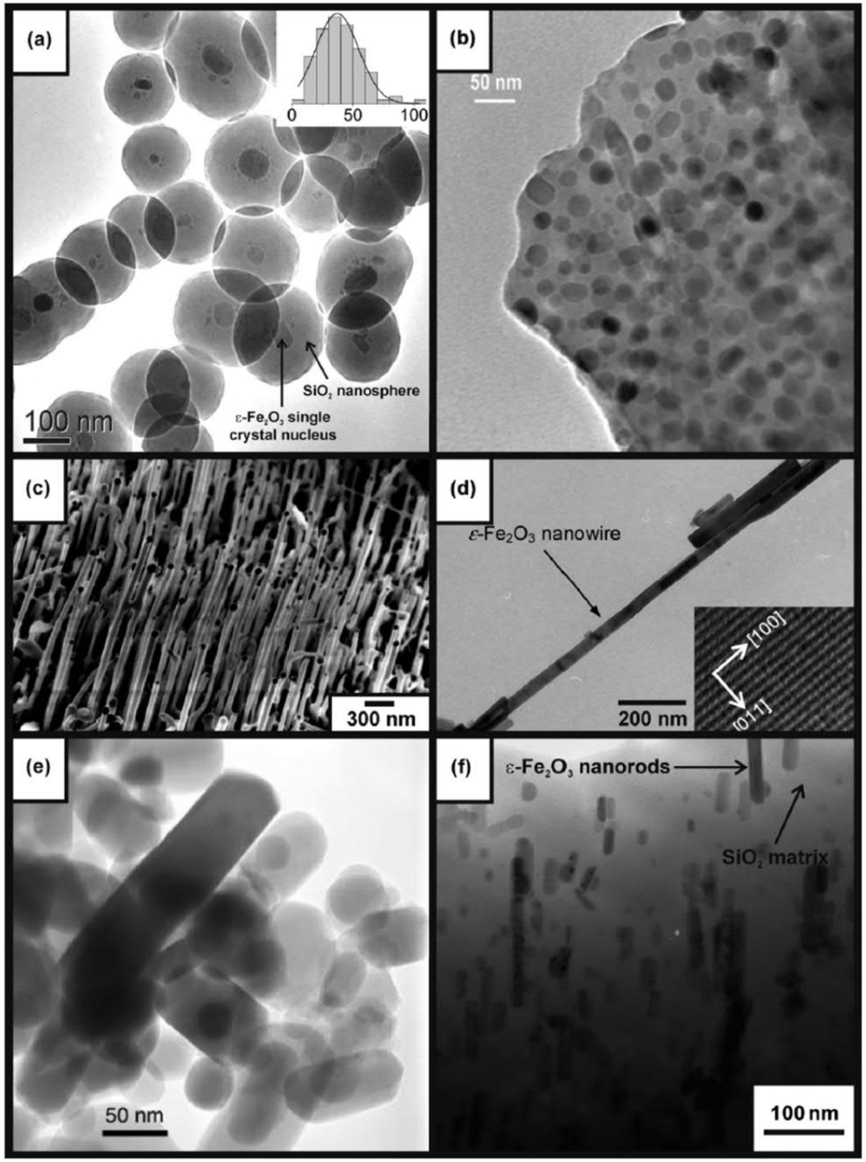






Maghemite (γ) – ε-Fe_2O_3 – Hematite (α)

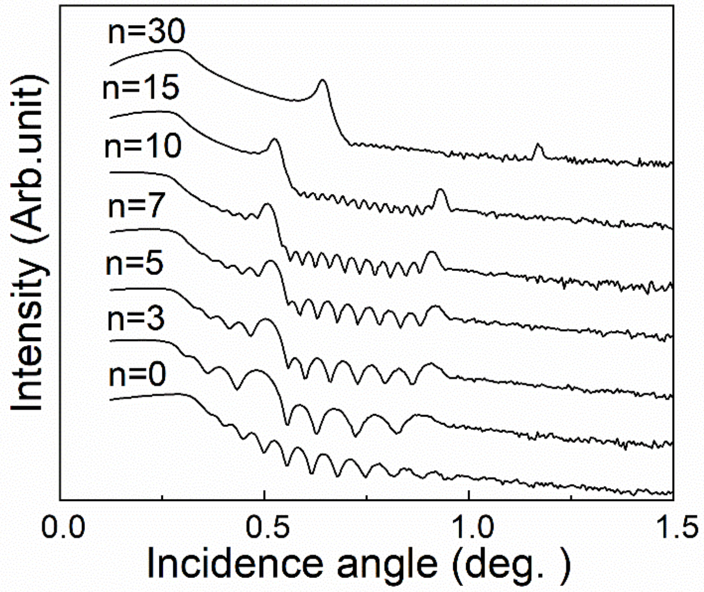


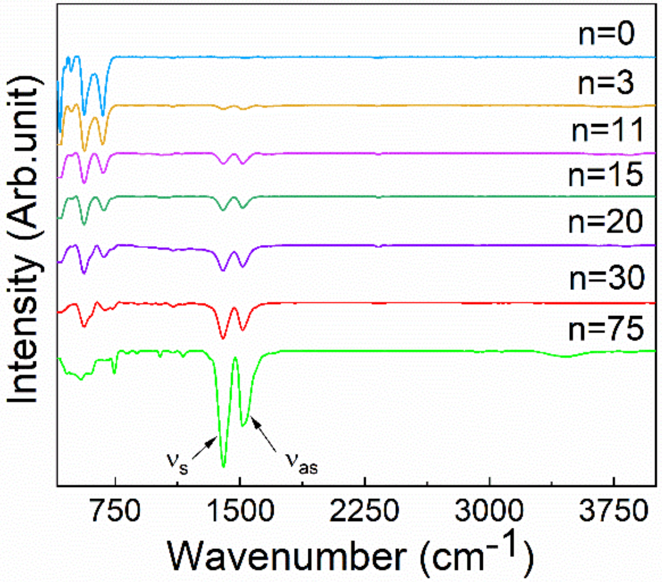


J. Tucek, R. Zboril, A. Namai & S. Ohkoshi, ε-Fe_2O_3: an advanced nanomaterial exhibiting **giant coercive field**, millimeter-wave ferromagnetic resonance and magnetoelectric coupling, *Chemistry of Materials* **22**, 6483 (2010).

ε-Fe_2O_3-benzene SUPERLATTICES

- **Benzene-ring layers embedded in ε-Fe_2O_3 matrix**
- **Terephthalic acid (TPA) as organic precursor**
- **$[(FeCl_3+H_2O)_m+(FeCl_3+TPA)]_n + (FeCl_3+H_2O)_m$**
- **Number of benzene-ring layers: n**
- **Deposited on: silicon, flexible glass, polymer film, etc.**

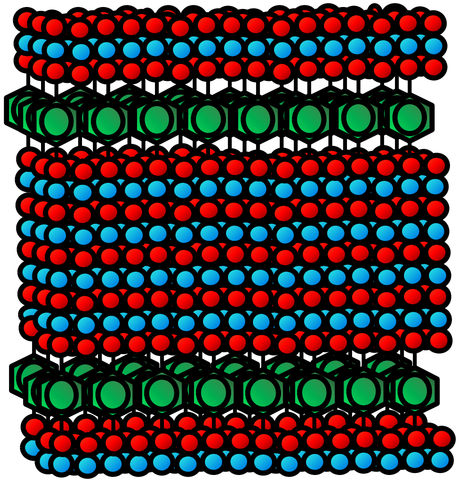


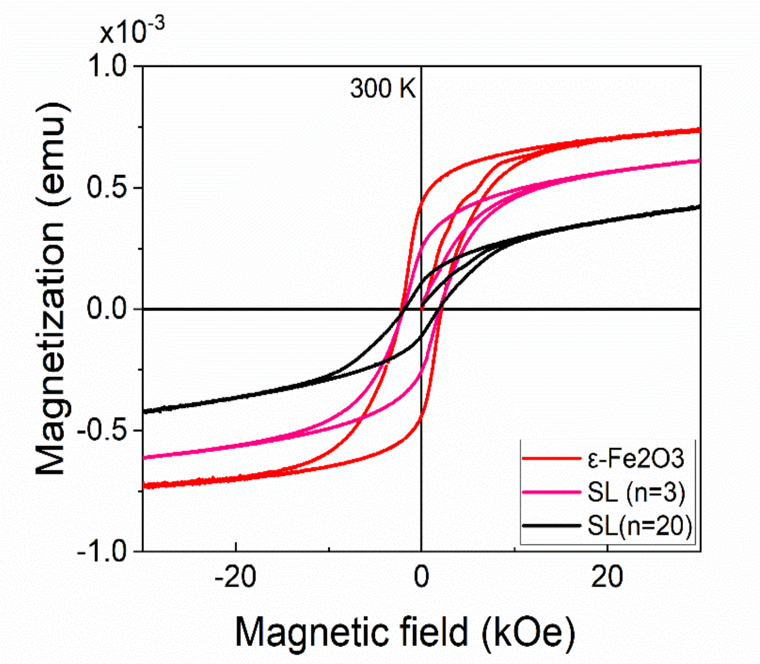


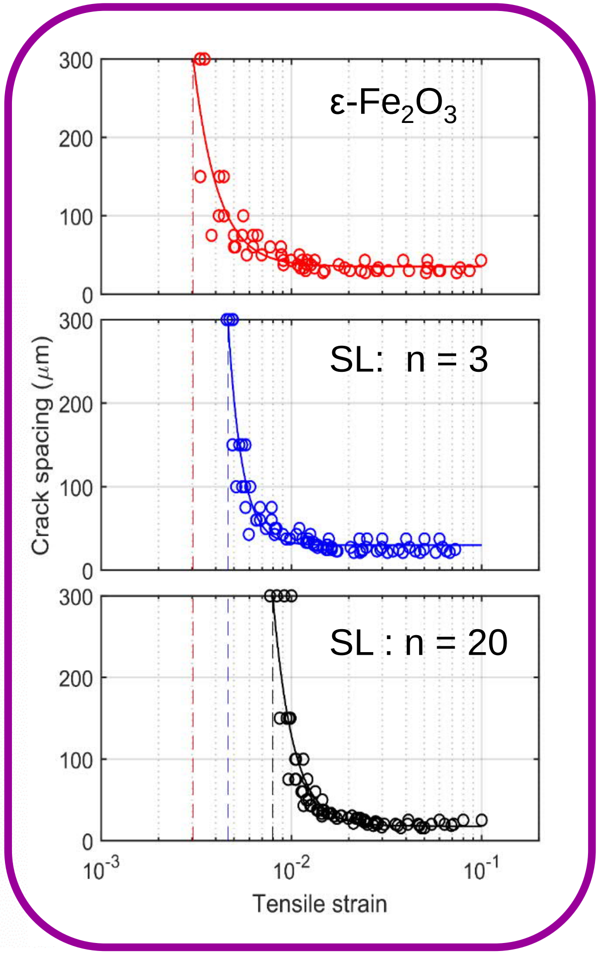
A. Tanskanen & M. Karppinen, Tailoring of optoelectronic properties of ε-Fe_2O_3 thin films through insertion of organic interlayers, *Physica Status Solidi – Rapid Research Letters*, 1800390 (2018).

Flexible Hard-Magnet Superlattice Thin Films:

- ε-Fe_2O_3 + n benzene layers (deposited on flexible substrate):
- Critical strain magnitudes larger for the ε-Fe_2O_3:benzene SLs





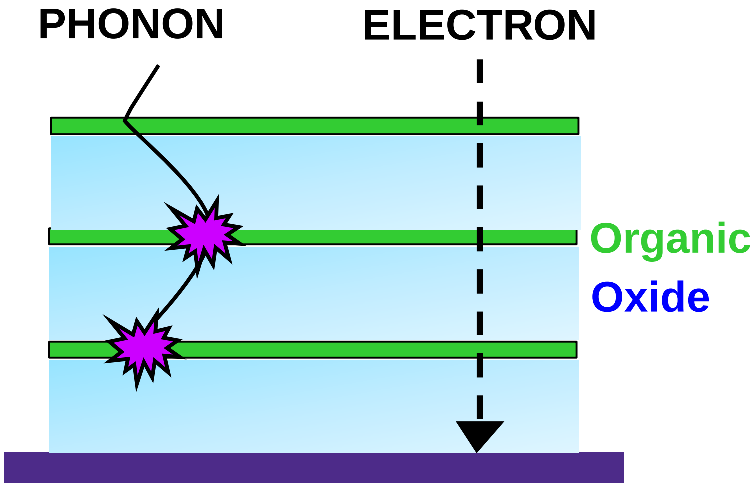


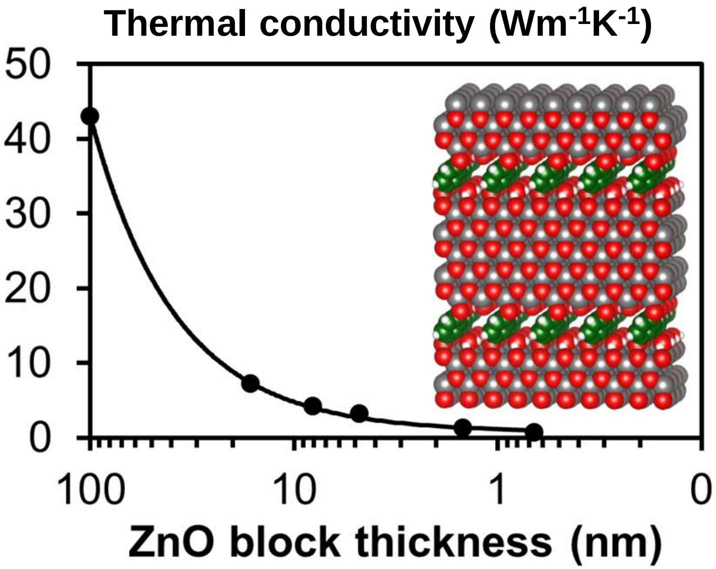
A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen,
Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD,
ACS Applied Materials & Interfaces **12**, 21912 (2020).

Inorganic-Organic INTERFACES:

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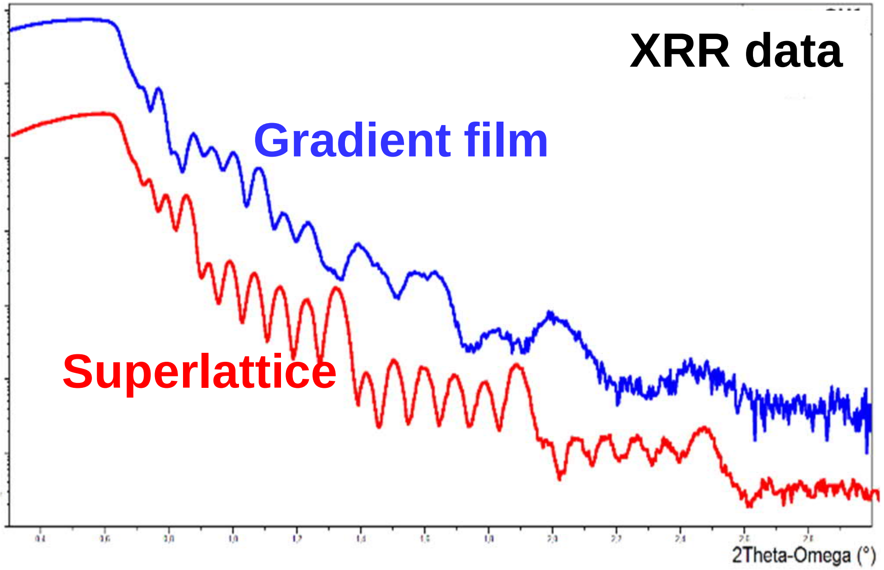
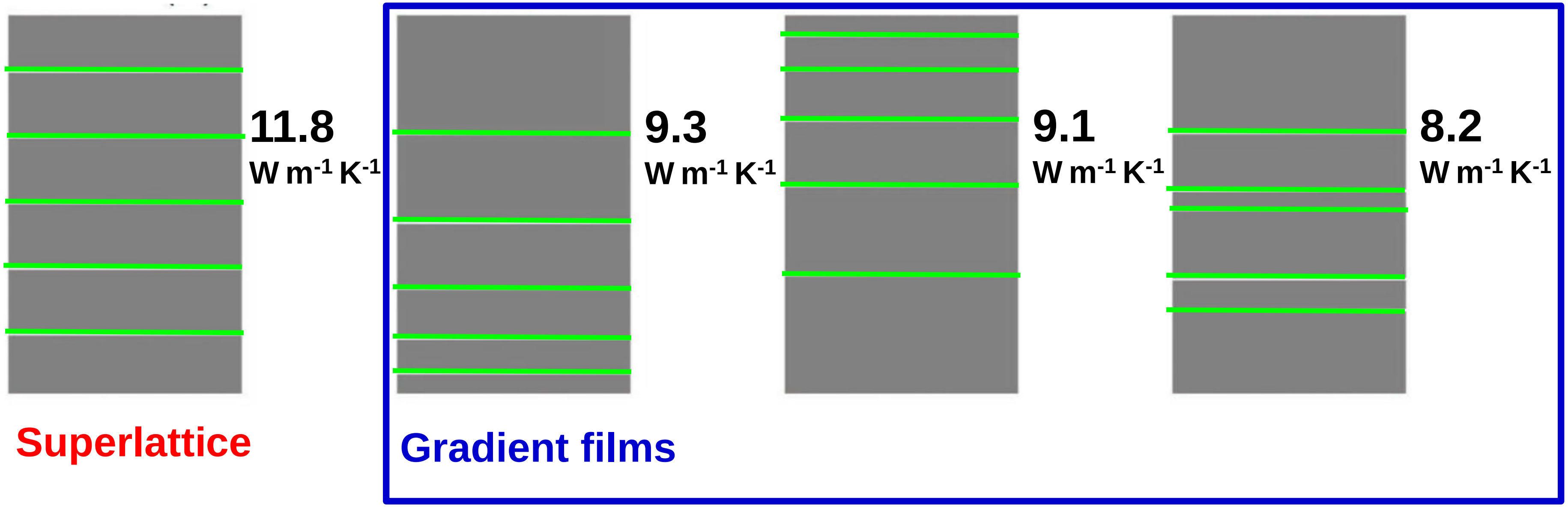
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, ***J. Mater. Chem. A* 2**, 12150 (2014).

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





Superlattice

Gradient films

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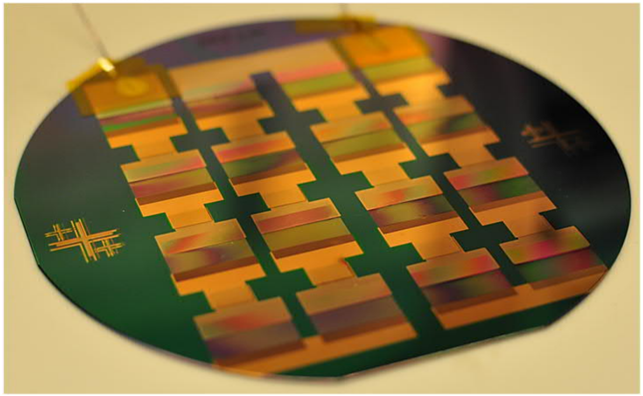
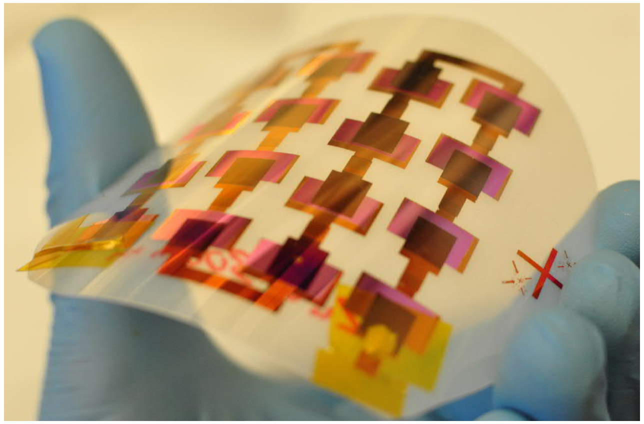
F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen,
Thermal conductivity reduction at inorganic-organic interfaces:
from regular superlattices to irregular gradient layer sequences,
Adv. Mater. Interfaces **5**, 1701692 (2018).

THERMOELECTRIC MODULE

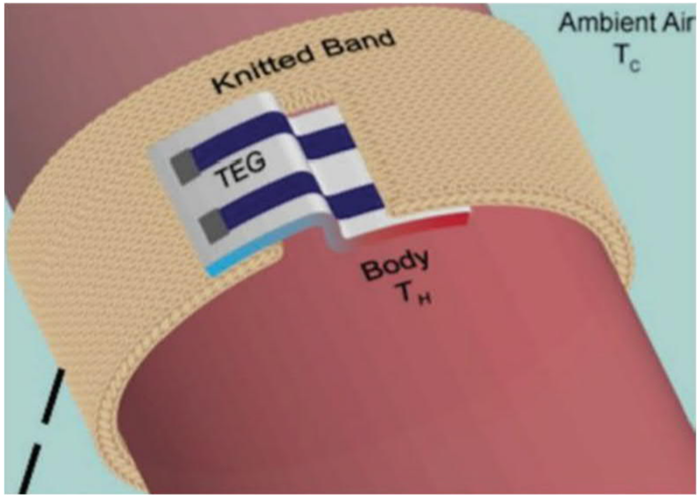
Silicon

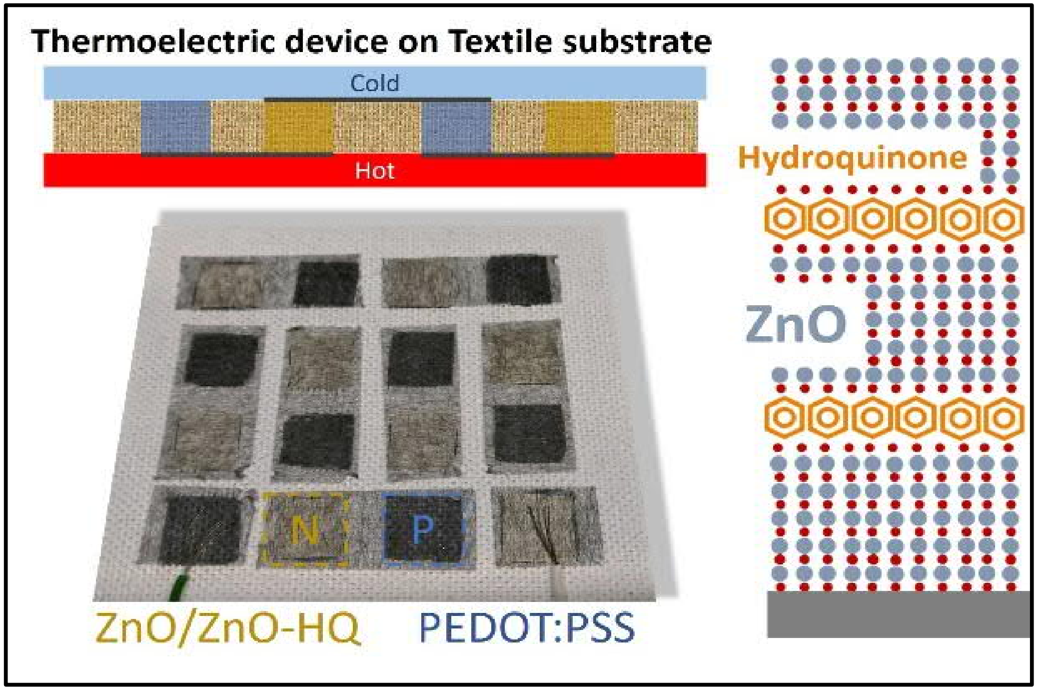


Plastics



Textile





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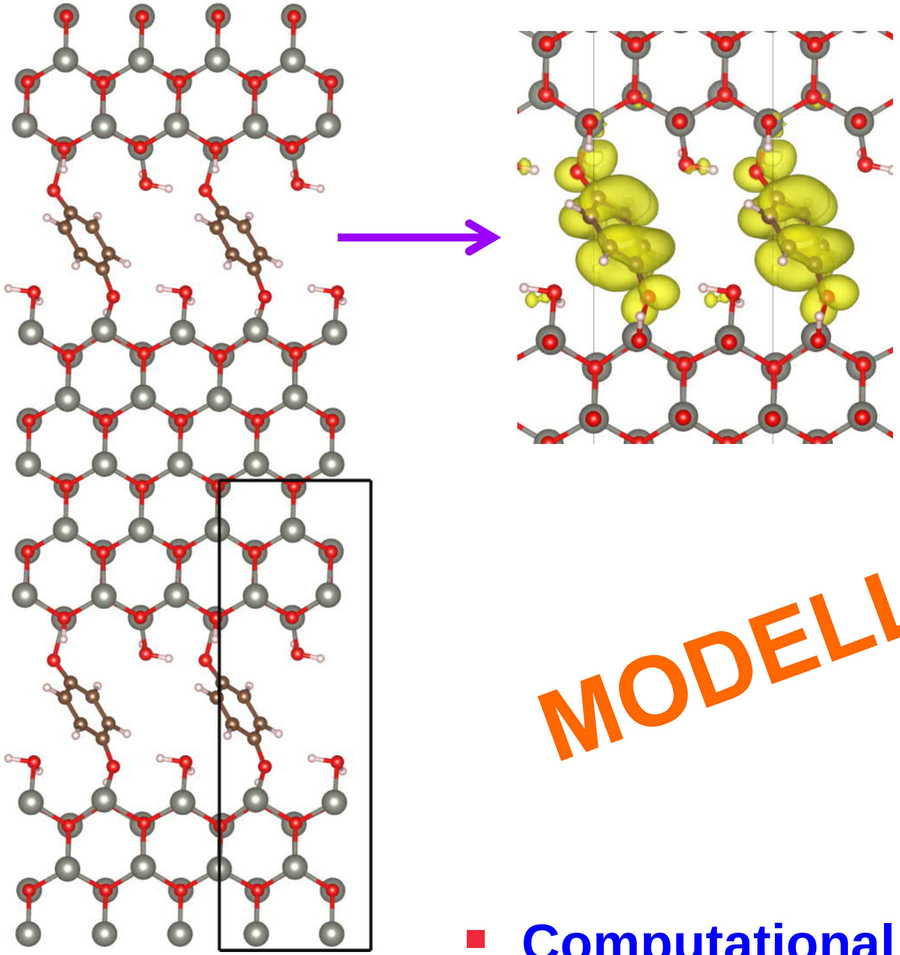
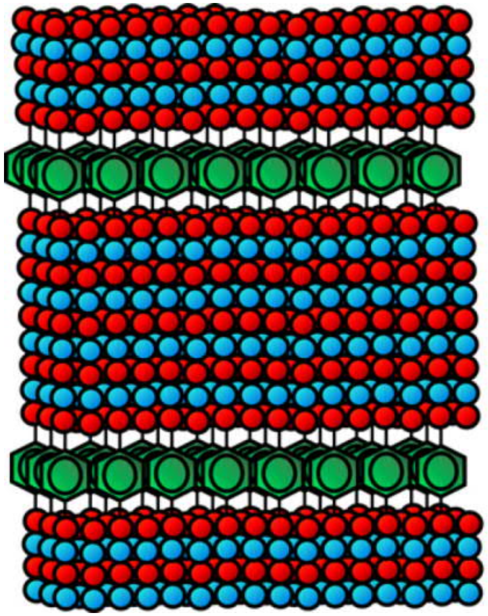
School of Engineering

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





MODELLING

- **Computational** first-principles calculations
- **Atomic-level bonding models**
- **Band structures**
- **Prediction of physical properties**

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

MOFs

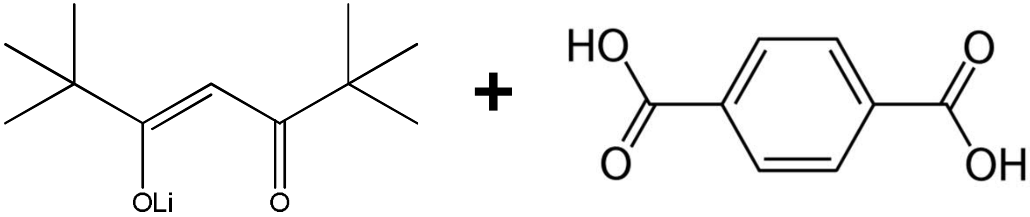
METAL-ORGANIC FRAMEWORKS

BY

ALD/MLD

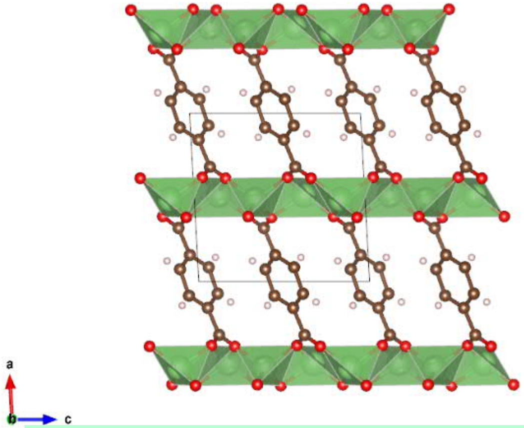
ANODE
Li-terephthalate

ALD/MLD:
Li-thd + TPA

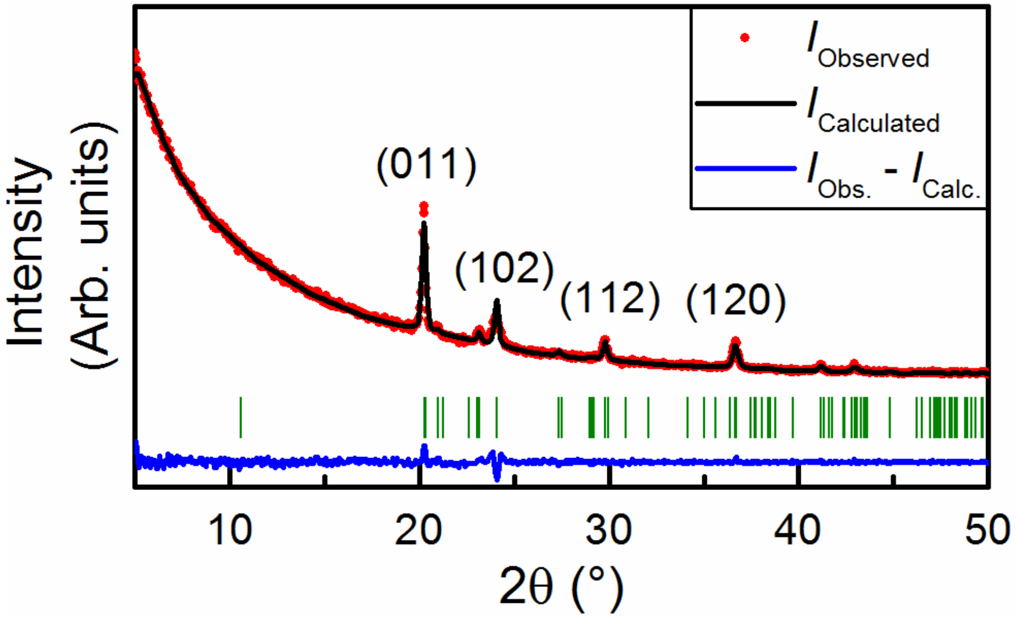


Li-thd

Terephthalic acid



Layered structure with alternating layers of LiO_4 tetrahedra & benzene-rings



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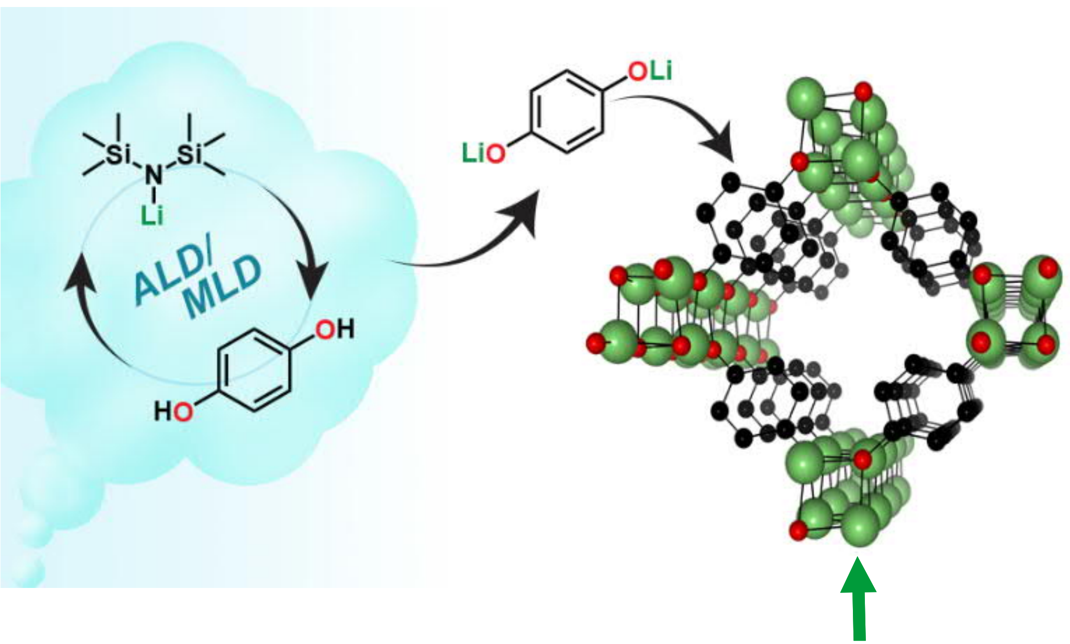
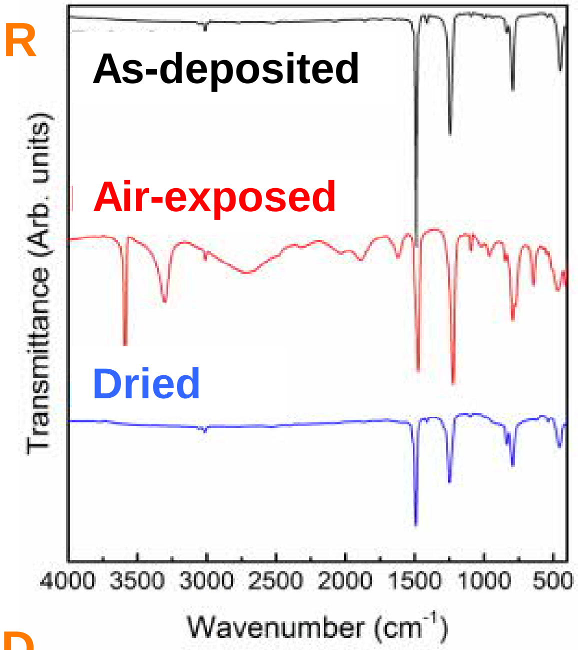
M. Nisula & M. Karppinen, Atomic/molecular layer deposition of lithium terephthalate thin films as high rate capability Li-ion battery anodes, *Nano Lett.* **16**, 1276 (2016).

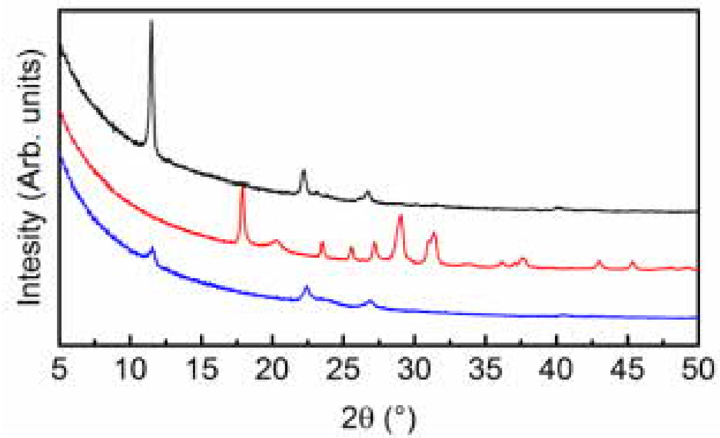


3-coord.
Li-site

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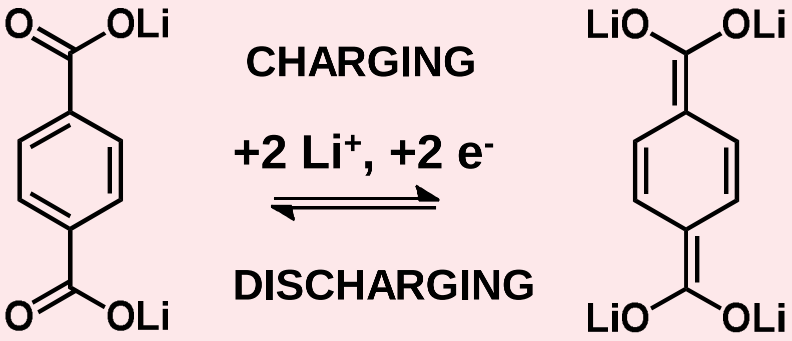
M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chemistry – A European Journal* **23**, 2988 (2017).

ORGANIC ELECTRODE MATERIALS

- **Sustainable in terms of elemental composition → Long-term dream**
- **Light elements only & Multiple electron transfer reactions → High specific capacities**
- **For example: Tarascon *et al.*, *Nature Mater*. 8, 120 (2009)**

Lithium terephthalate Li-TP

- Redox potential: 0.8 V vs. Li
- Specific capacity: 300 mAh/g
- Volume change: small (6%)



- **MAJOR PROBLEMS (in a conventional bulk wet-cell)**

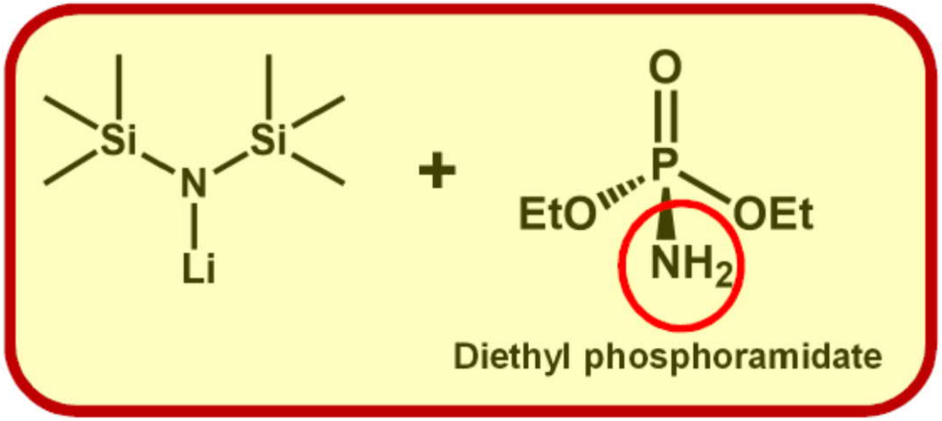
- Dissolution in conventional liquid electrolytes → Solid electrolyte

- Intrinsically extremely low electronic conductivity → Ultrathin film

→ THIN-FILM MICROBATTERY

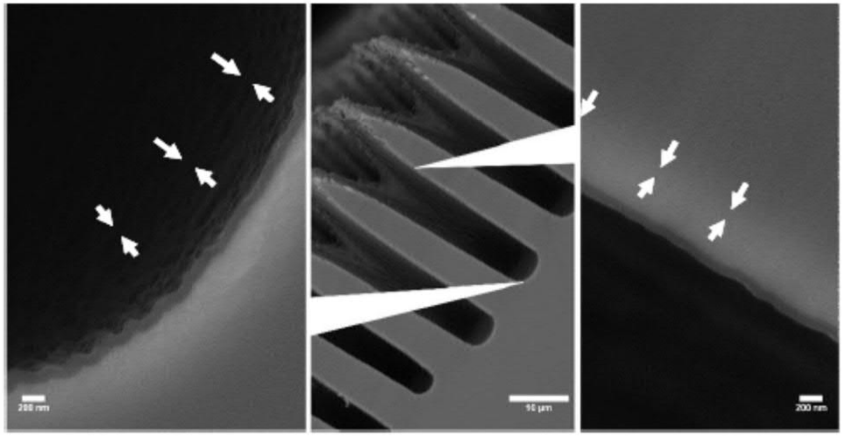
LiPON BY ALD WITH TOYOTA

- Lithium phosphorous oxynitride $Li_xPO_yN_z$
- A promising solid-state electrolyte for thin-film Li-ion microbattery



Diethyl phosphoramidate

RBS-NRA	Ionic cond.
$Li_{0.94}PO_{3.00}N_{0.60}$	7×10^{-7} S cm^{-1}

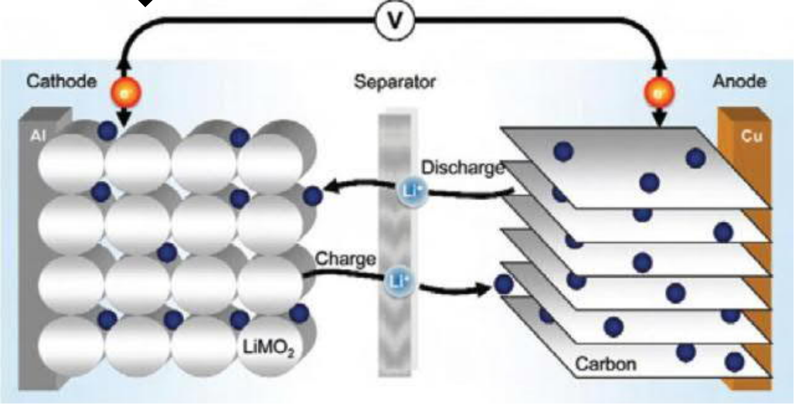


M. Nisula, Y. Shindo, H. Koga & M. Karppinen, *Chem. Mater.* **27**, 6987 (2015).

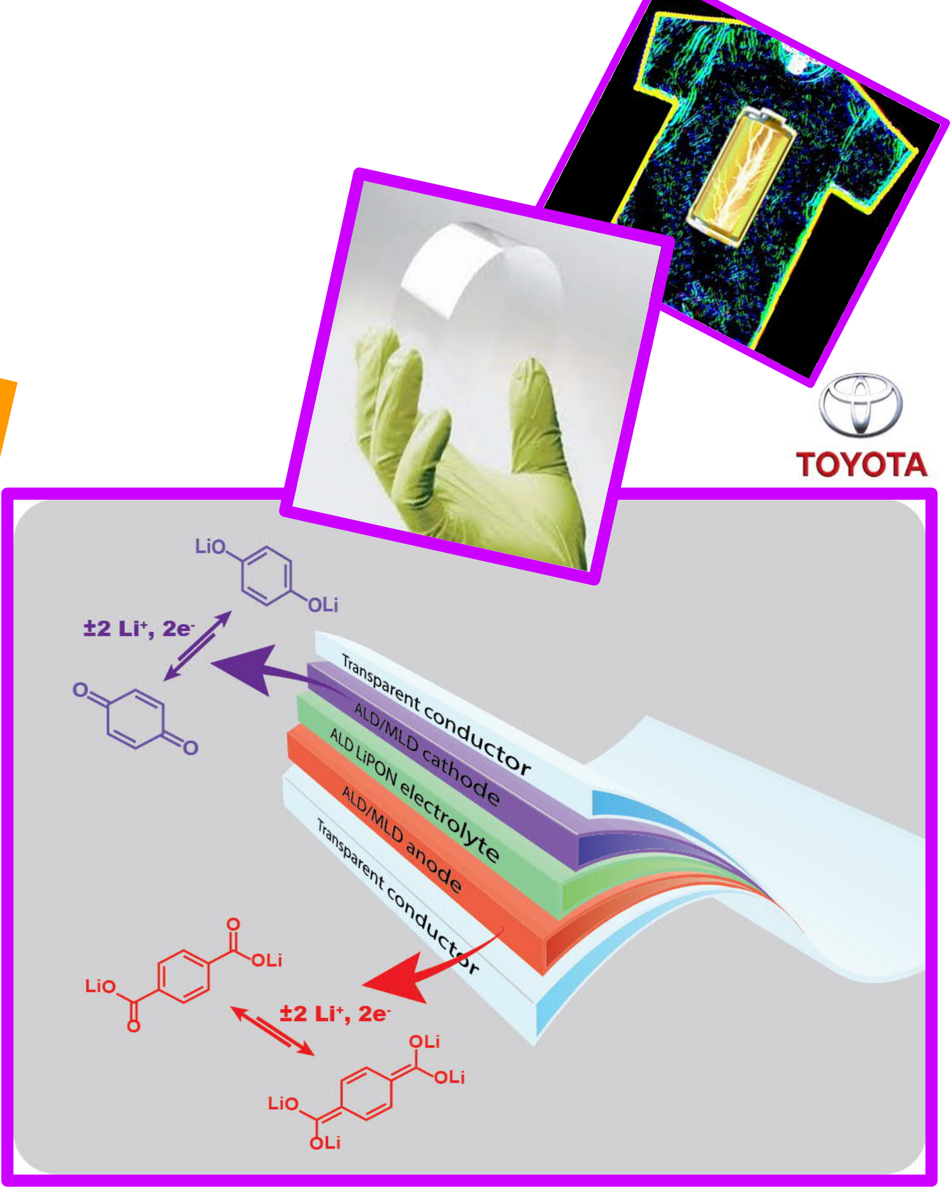
Goodenough, Whittingham & Yoshino

1991
Li-ion battery
(Sony)

1980
Li_xCoO_2 cathode
(Goodenough)



Current Li-ion Battery Technology



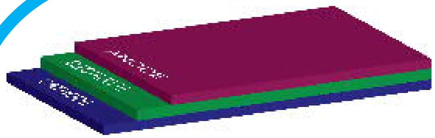
ALD/MLD made metal-sparing flexible Li-organic thin-film battery

M. Nisula & M. Karppinen,
Journal of Materials Chemistry A **6**, 7027 (2018).

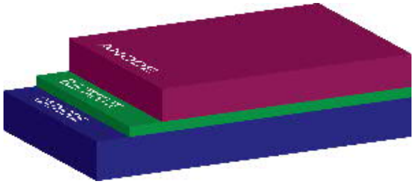
THIN-FLIM MICROBATTERY

- **Trade-off: Energy density – *versus* – Power density**
- **SOLUTION: Planar → 3D structure**

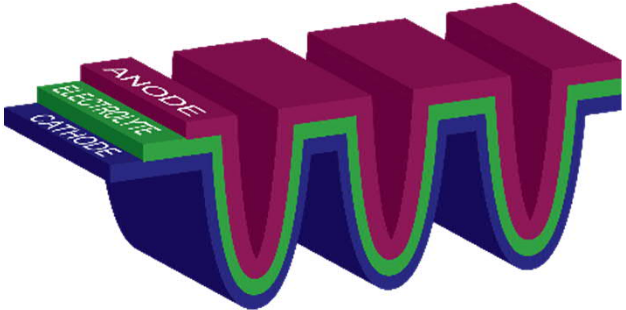
Concept of 3D Thin-Film Battery



High POWER



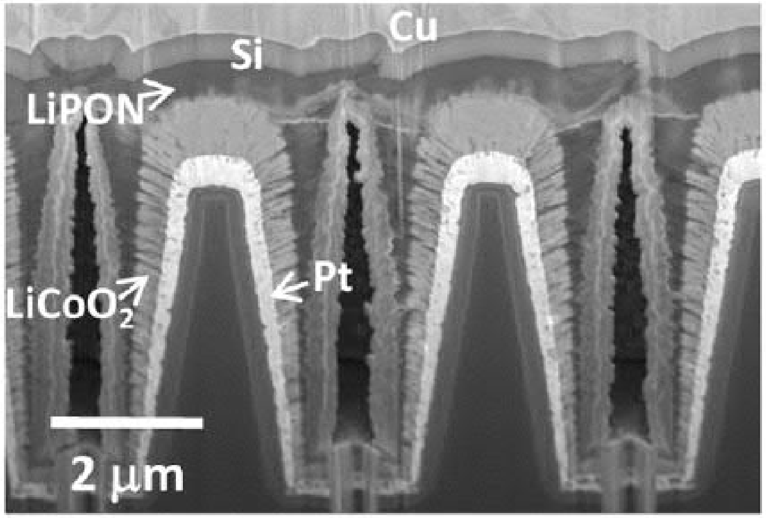
High ENERGY



Notten *et al*.,
3D integrated all-solid-state
rechargeable batteries,
***Appl. Mater.* (2007)**

Sputtering → Low Performance

Talin et al.,
Fabrication, testing and simulation of
all-solid-state 3D Li-ion batteries,
***ACS Appl. Mater. Interfaces* (2016)**



Acting

Sensing

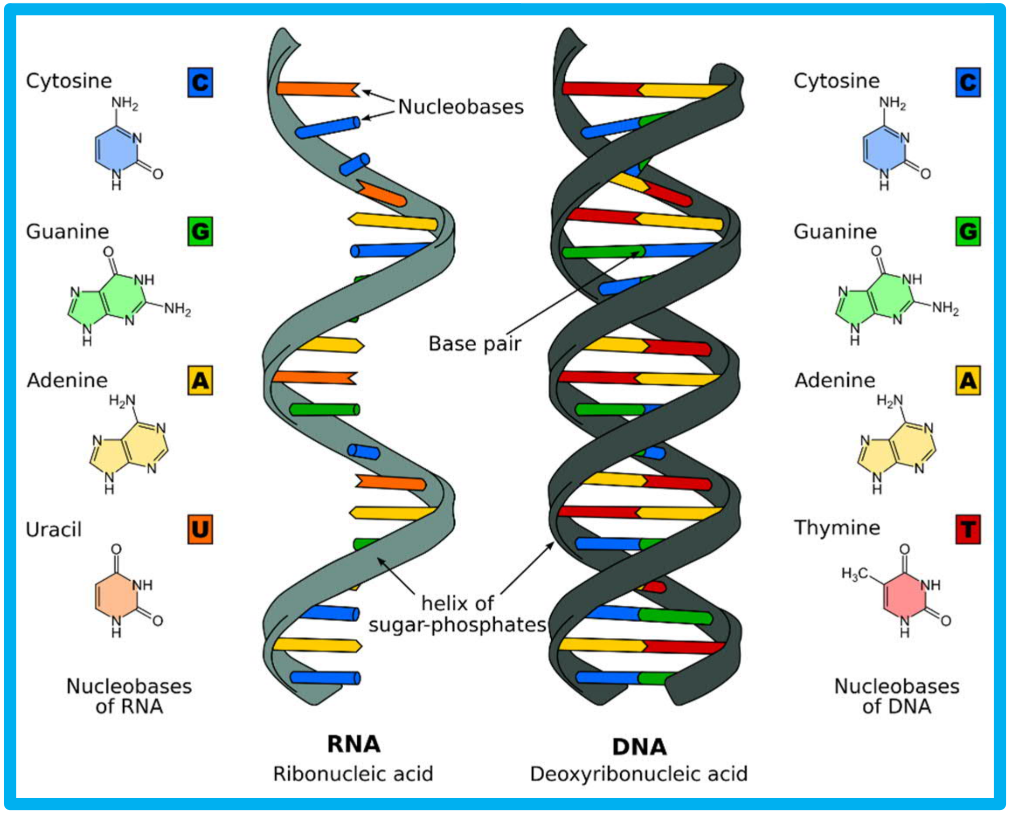
Responding

Connecting

THERMOELECTRICS: electricity locally from waste heat

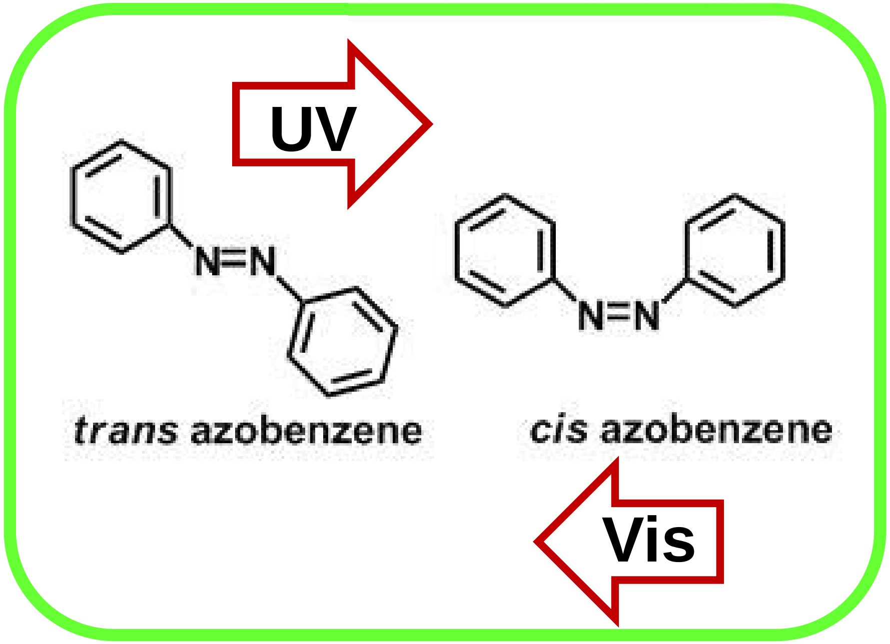
MICROBATTERY: local electric energy storage

NUCLEOBASES FROM NATURE



Z. Giedraityte, O. Lopez-Acevedo, L.A. Espinosa Leal,
V. Pale, J. Sainio, T.S. Tripathi & M. Karppinen,
J. Phys. Chem. C **120**, 26342 (2016).

PHOTORESPONSIVE AZOBENZENE



A. Khayyami & M. Karppinen, *Chem. Mater.* 30, 5904 (2018).

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

A!
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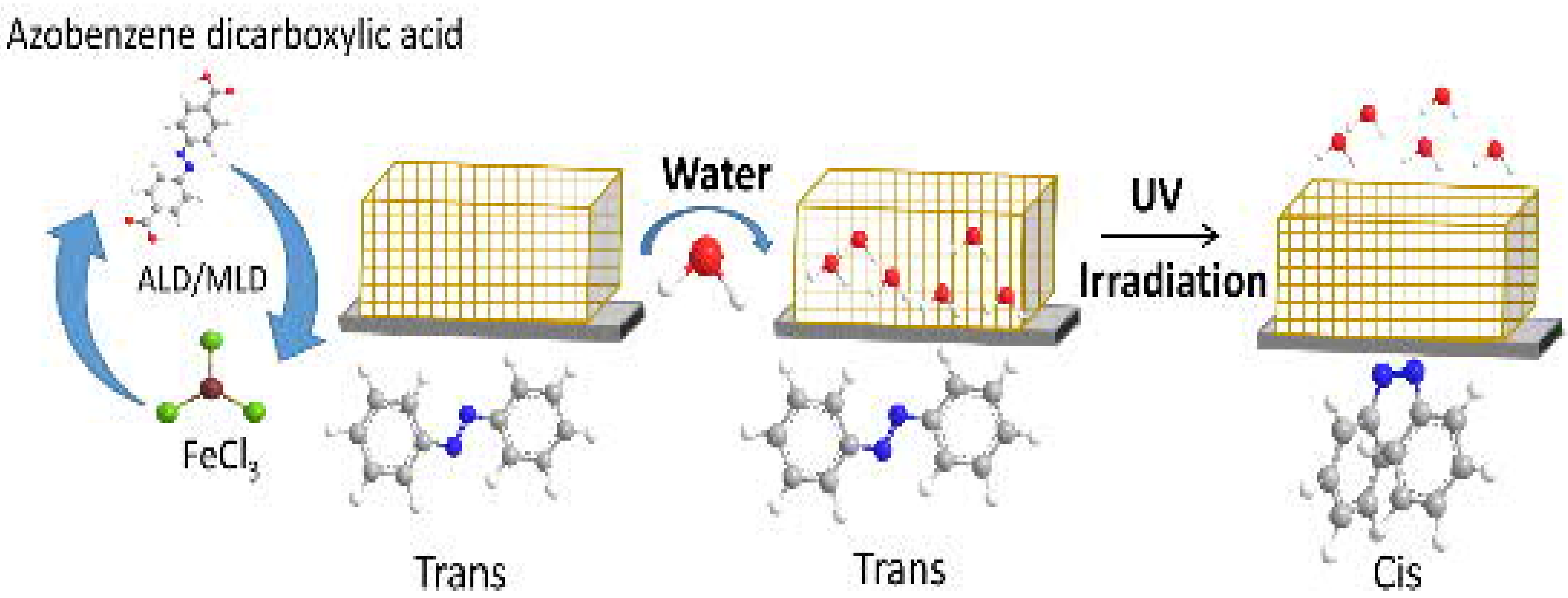
School of Chemical
Engineering

NEW EXCITING ORGANIC COMPONENTS

Iron-Azobenzene MOFs

- $FeCl_3$ + azobenzene dicarboxylic acid
- Crystalline (unknown structure) films
- Trans-to-cis transition upon UV irradiation
- Reversible water absorption (trans, 75% RH) / release (UV, cis)



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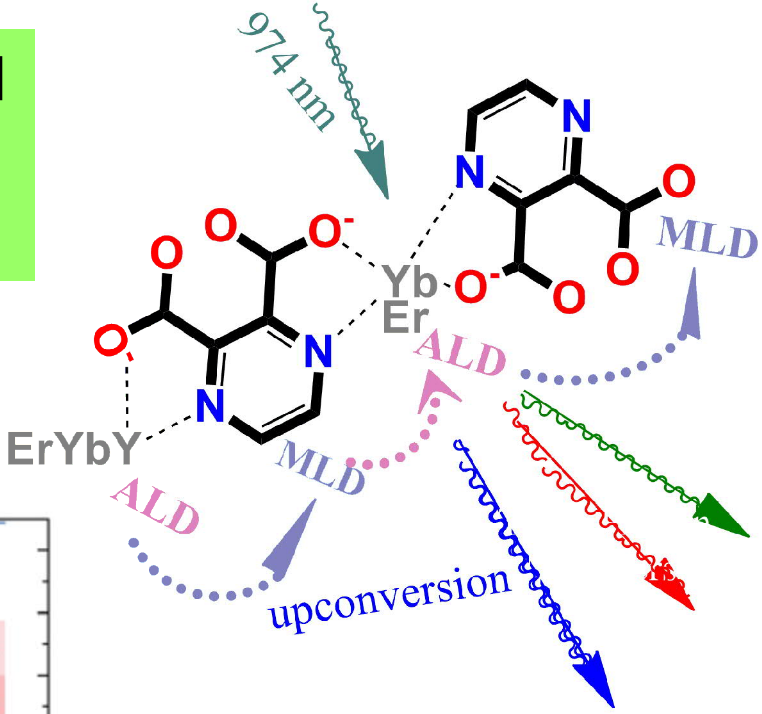
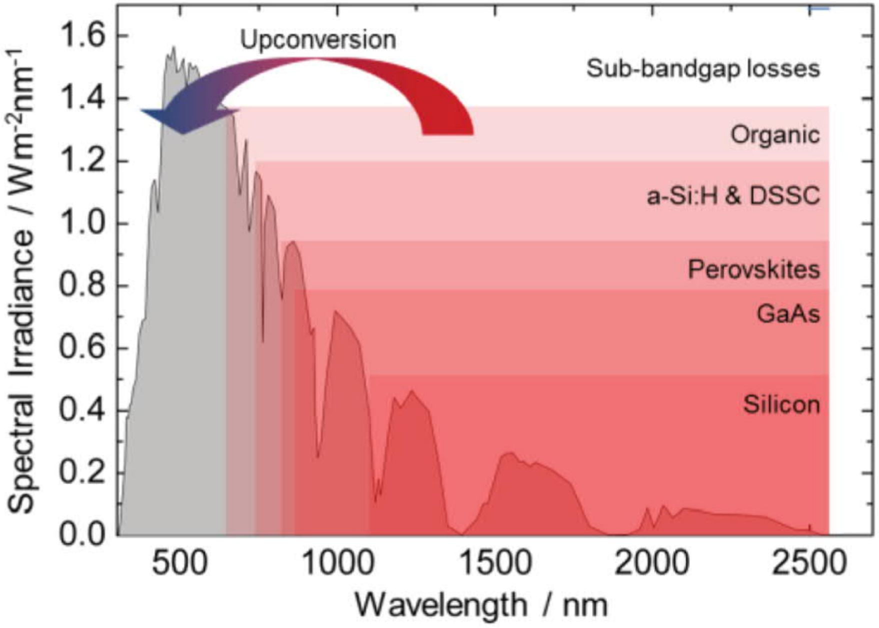
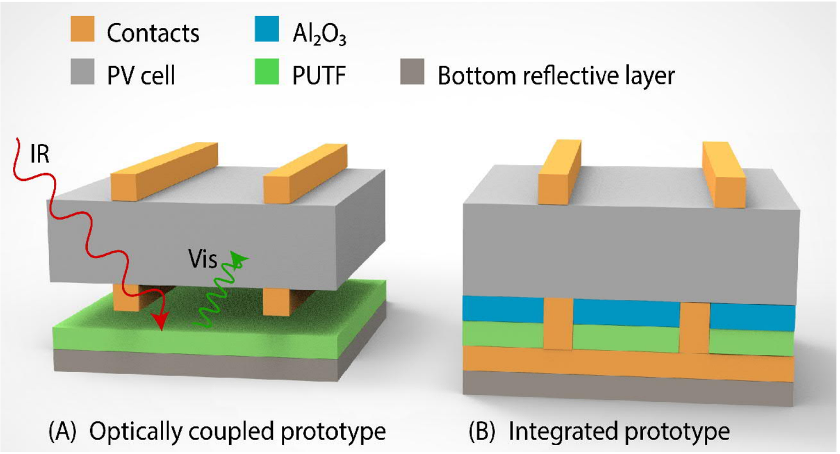
A. Khayyami, A. Philip & M. Karppinen, Atomic/molecular layer deposited iron-azobenzene framework thin films for stimuli-induced gas molecule capture/ release, ***Angewandte Chemie International Edition* 58**, 13400 (2019).

PHOTON-UPCONVERSION THIN FILM (PUTF): IR-absorbing organics



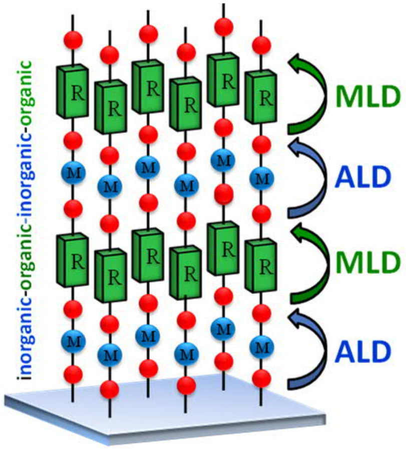


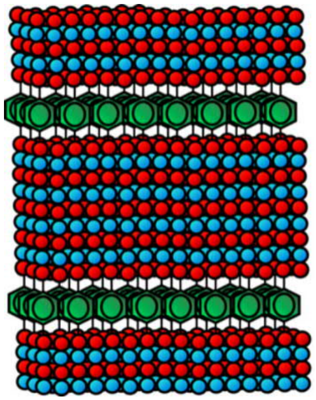


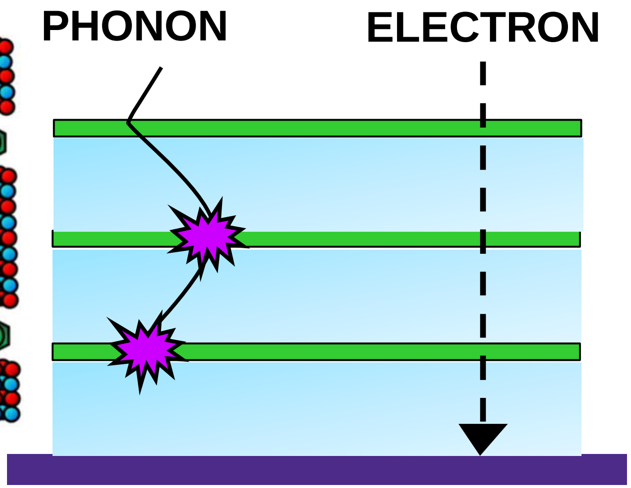
(A) Optically coupled prototype (B) Integrated prototype

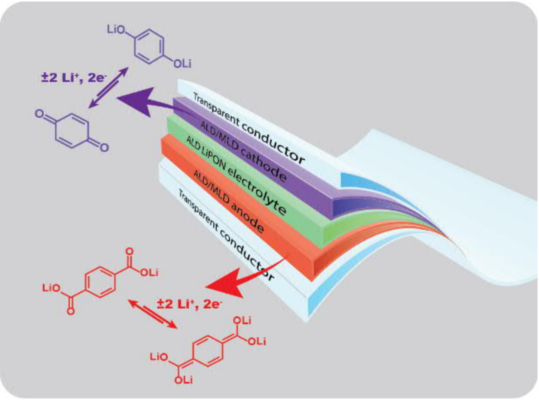
- Z. Giedraityte, M. Tuomisto, M. Lastusaari & M. Karppinen, Three- and two-photon NIR-to-vis (Yb,Er) up-conversion from ALD/MLD fabricated molecular hybrid thin films, ***ACS Appl. Mater. Interfaces*** **10**, 8845 (2018).

- A. Ghazy, M. Safdar, M. Lastusaari, A. Aho, A. Tukiainen, H. Savin, M. Guina & M. Karppinen, Luminescent $(Er,Ho)_2O_3$ thin films by ALD to enhance the performance of silicon solar cells, *Solar Energy Materials & Solar Cells* **219**, 110787 (2021).









- **ALD/MLD can yield various new types of hybrid materials, such as MOF-structured materials and layer-engineered superlattice and gradient materials**
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties discovered and much more expected !!!**
- **Fabricated with industry-feasible state-of-the-art ”Finnish” technology**
- **Flexible coatings which could be integrated with e.g. textiles**