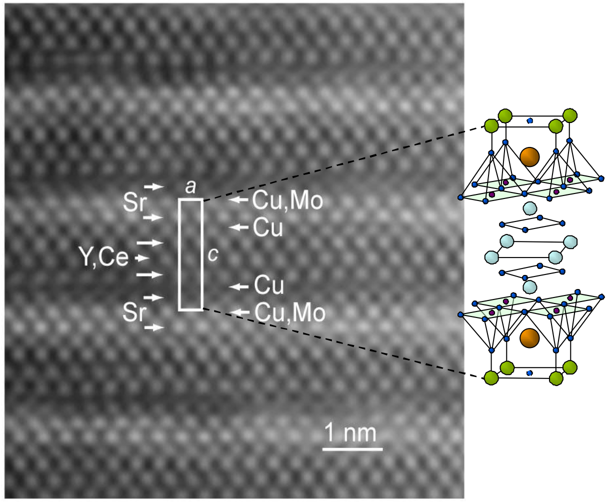
LECTURE SCHEDULE

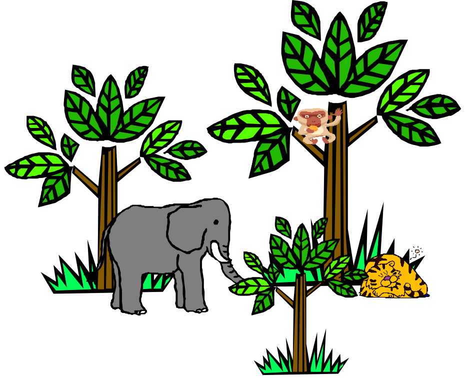
		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complex & POM, MOF, MLD
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Pt metals & Magnetism
12.	Wed	13.10.	Co, Ni, Cu & Superconductivity
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021 (in ZOOM) at 9.00 – 12.00



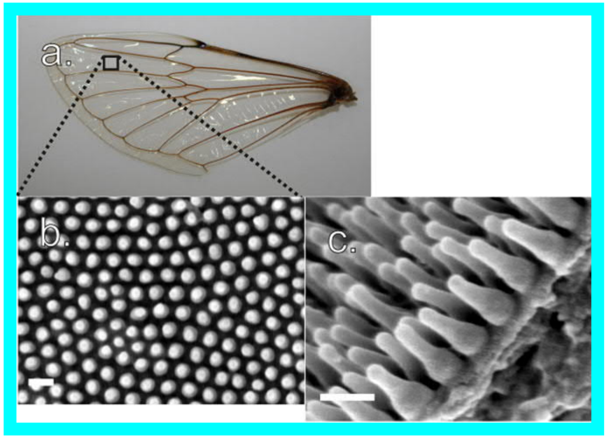
INORGANC CHEMISTRY

Aalto University
Department of Chemistry & Materials Science



Sustainable energy materials

- **Novel Functional (bulk) Oxide Materials**
  - **high-T_c superconductors**
  - **thermoelectric materials**
  - **exotic magnetic materials (halfmetals, ferroelectrics)**
  - **ionic conductors (fuel cell, battery, oxygen storage)**



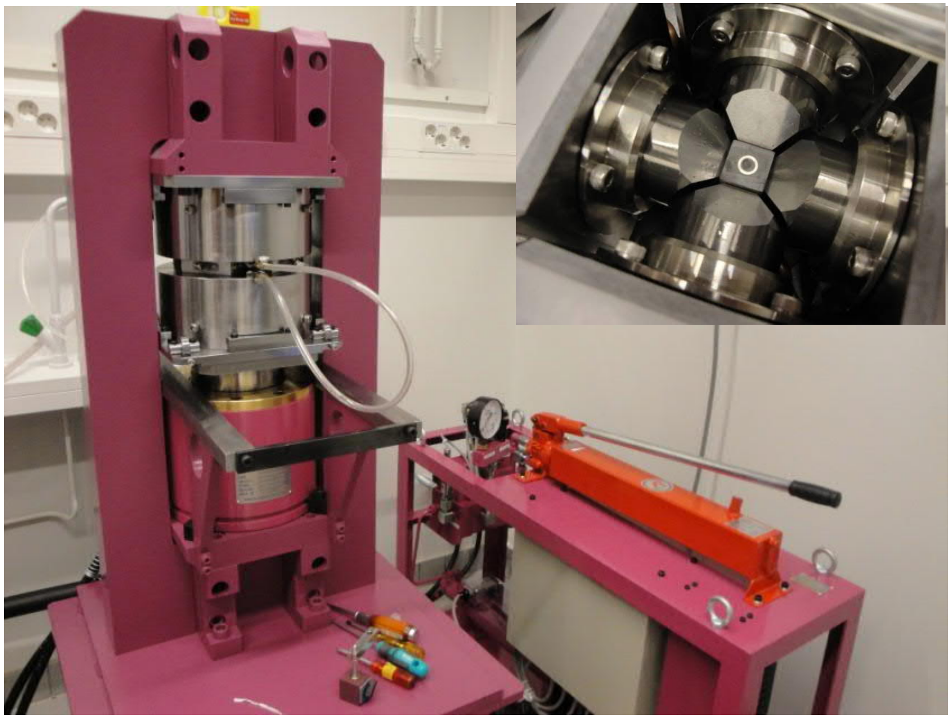
- **ALD (Atomic Layer Deposition) Thin Films**
  - **complex (ternary & quaternary) oxides**
  - **oxide coatings on novel/exciting surfaces (polymers, biomaterials, textiles, steel, etc.)**
  - **inorganic/organic hybrid materials**

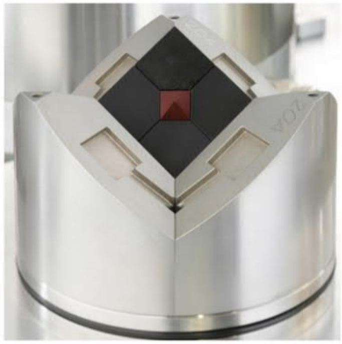
KEY CONCEPTS:

Layer-engineering & Oxygen-engineering & Nanostructuring

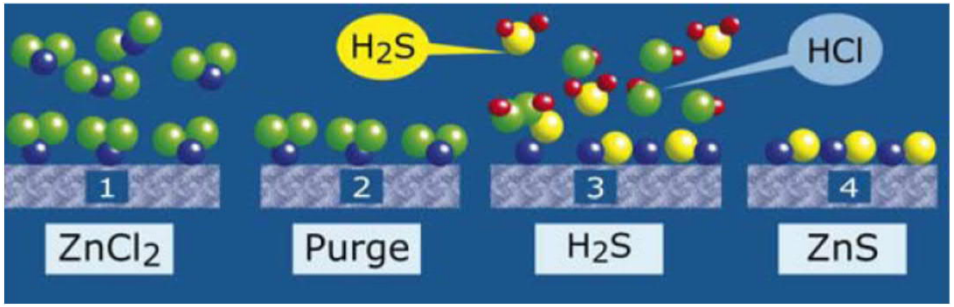
SYNTHESIS TECHNIQUES

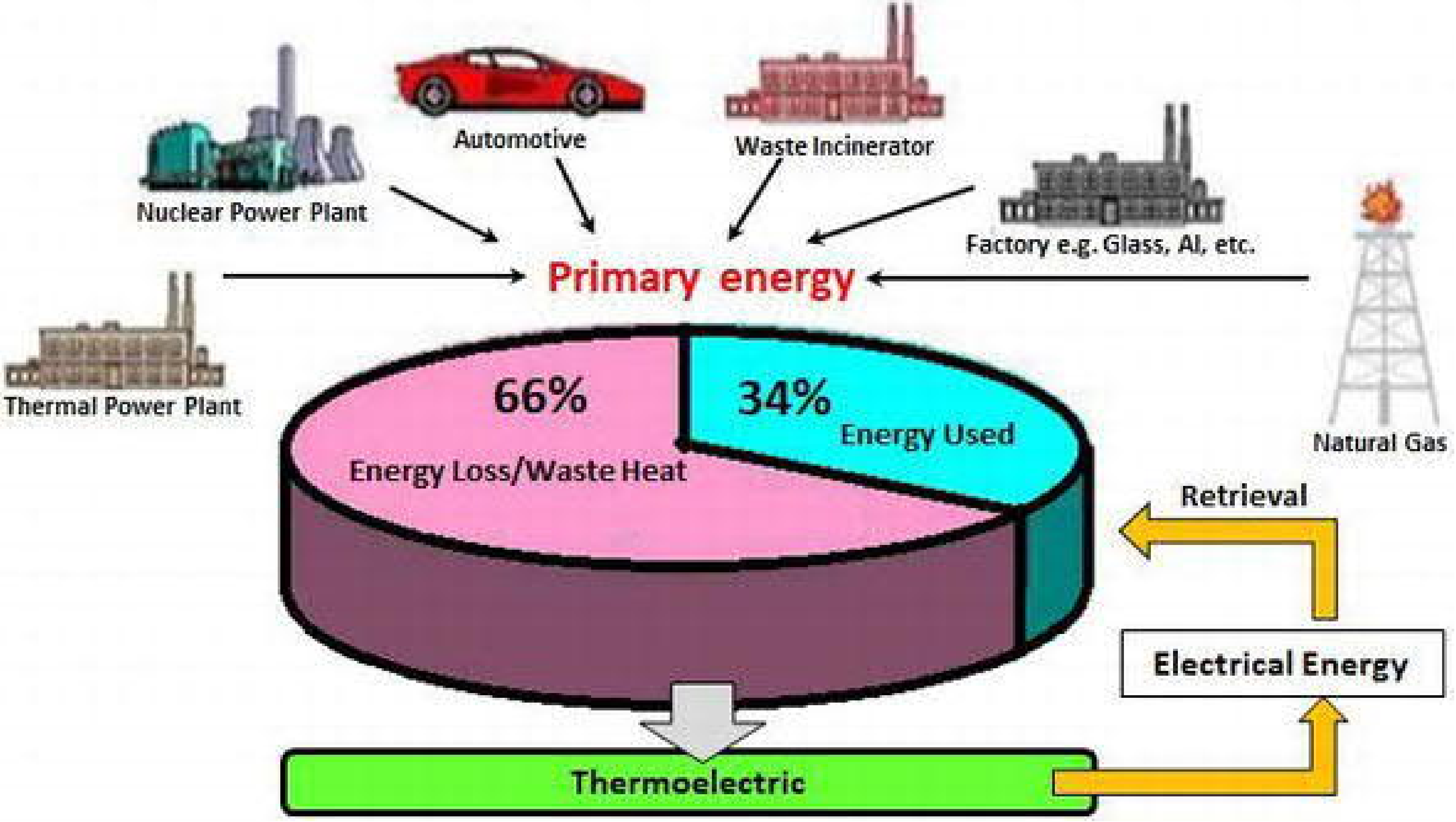
Ultra High-Pressure (HP) synthesis

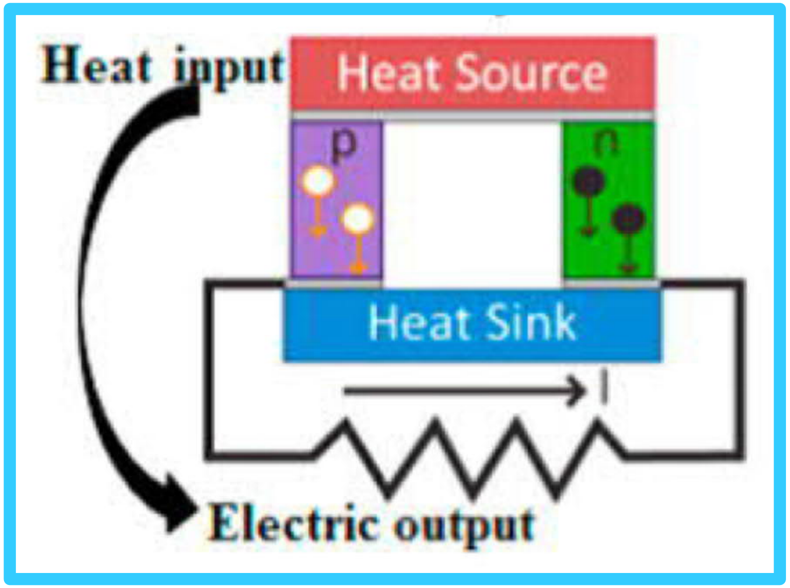


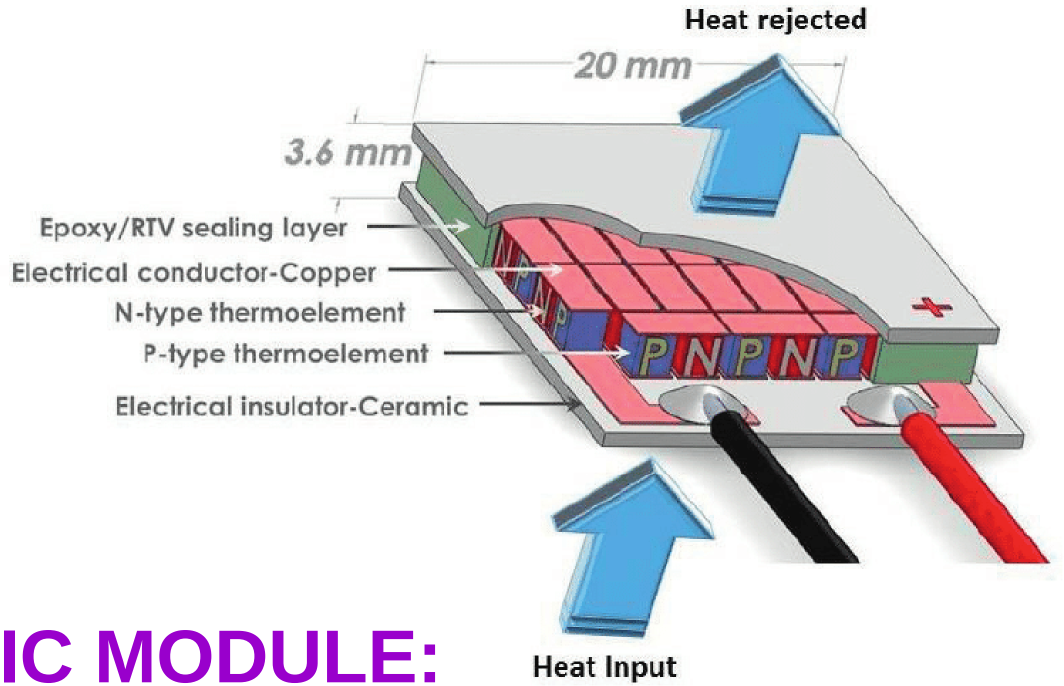


Atomic Layer Deposition (ALD) thin-film technology



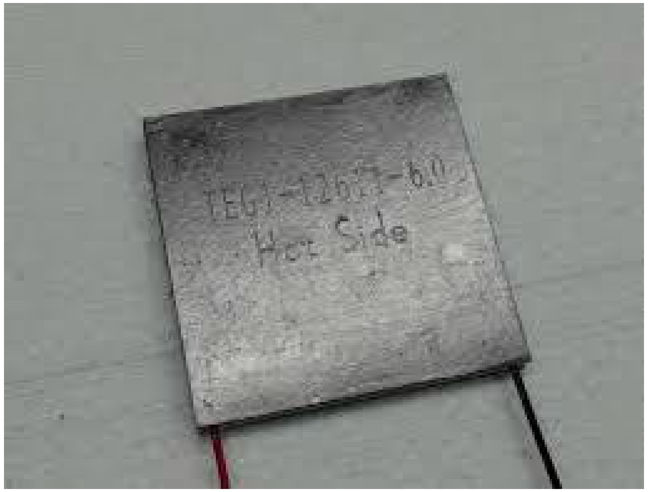

Nuclear Power Plant
Automotive
Waste Incinerator
Factory e.g. Glass, Al, etc.
Thermal Power Plant
Primary energy
Natural Gas
66%
Energy Loss/Waste Heat
34%
Energy Used
Retrieval
Electrical Energy
Thermoelectric





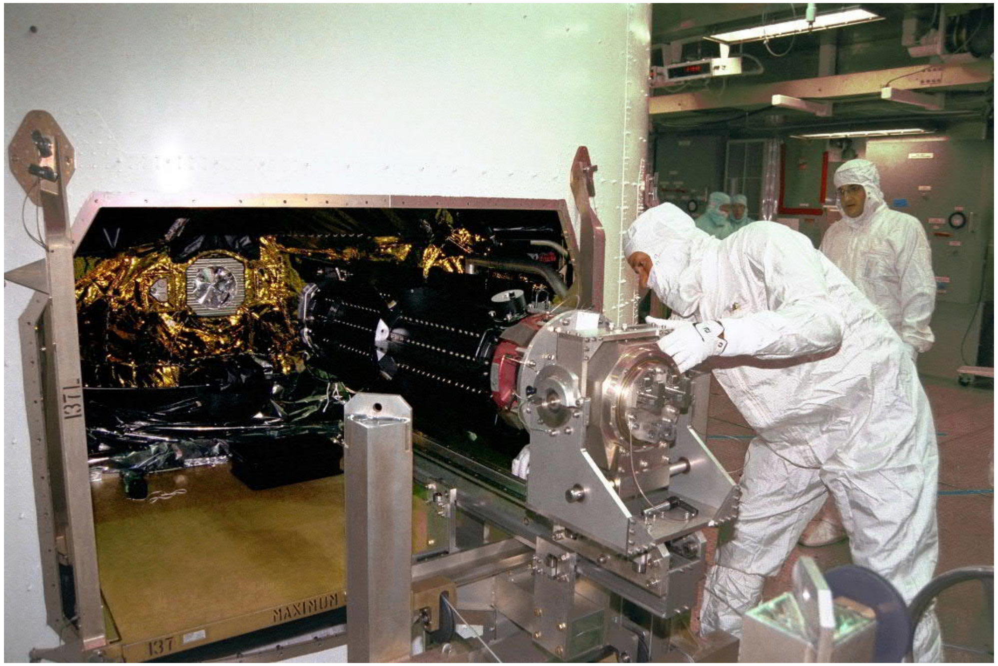
THERMOELECTRIC MODULE:

p- and n-type semiconductor legs

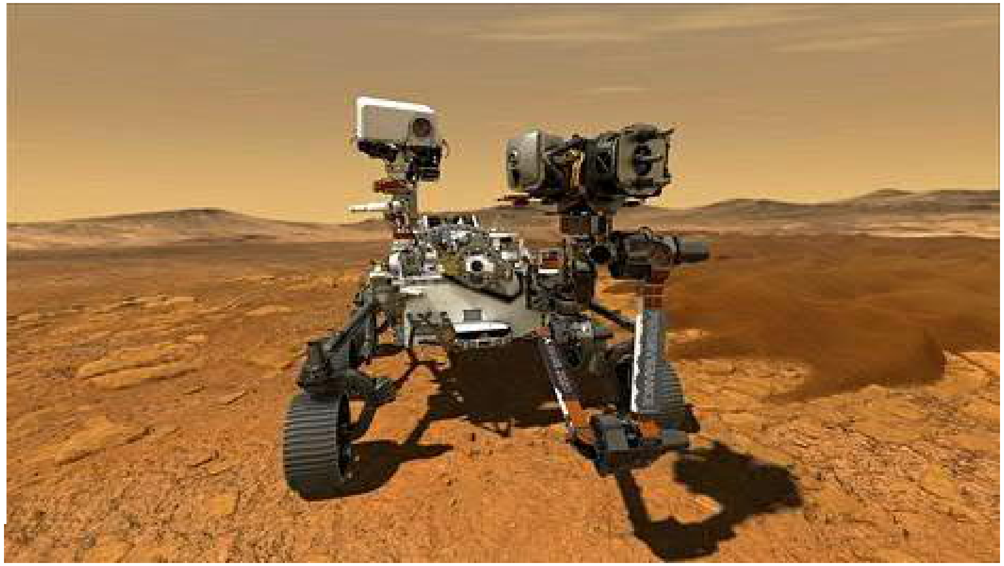


SPACE MISSIONS

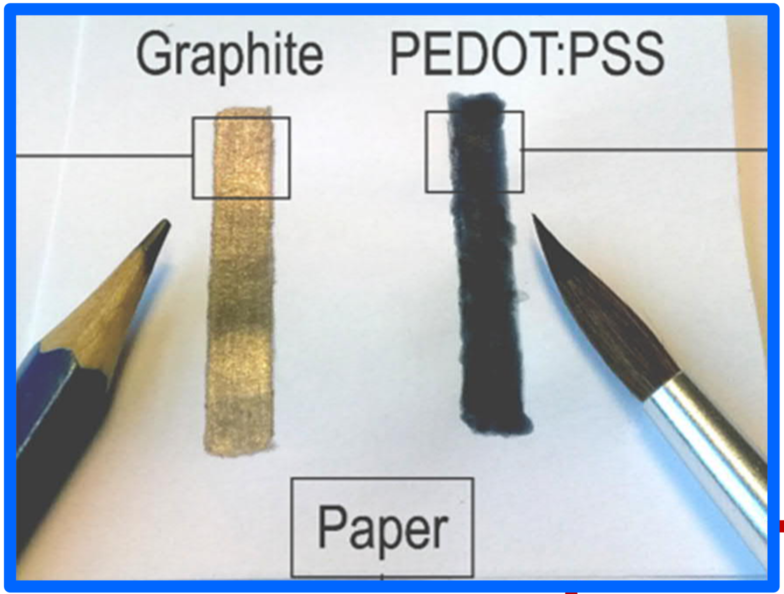
- Space exploration missions require: safe, reliable, long-lived power systems to provide electricity to the spacecraft itself and to its science instruments
- Uniquely capable power source: radioisotope thermoelectric generator (“nuclear battery”) that reliably converts heat into electricity
- ^{238}Plutonium radioactive decay provides reliable continuous heat source
- Radioisotope power has been used by NASA over the last four decades for tens of space missions up to Mars



One of the three radioisotope thermoelectric generators on Cassini



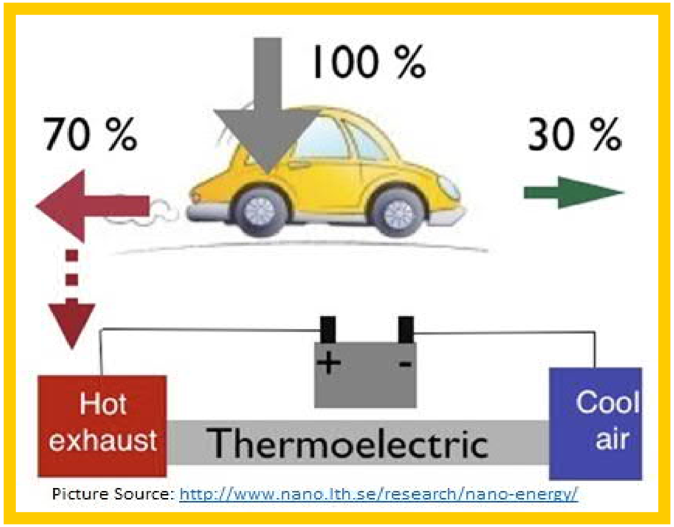
IT COULD BE AS SIMPLE AS THIS, TOO !



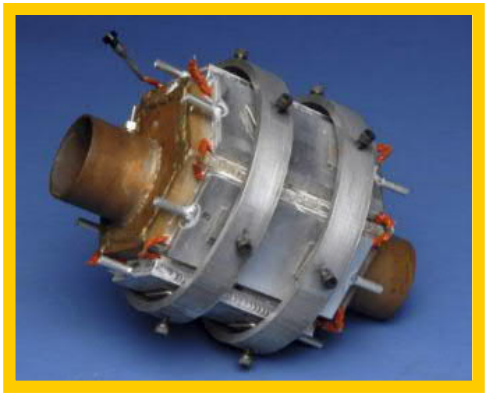
Paperiarkki, lyijykynä & sähkönjohtavaa muovia
Helmholtz Centre in Berlin

BioLite CampStove:
Akkua lataava risukeitin

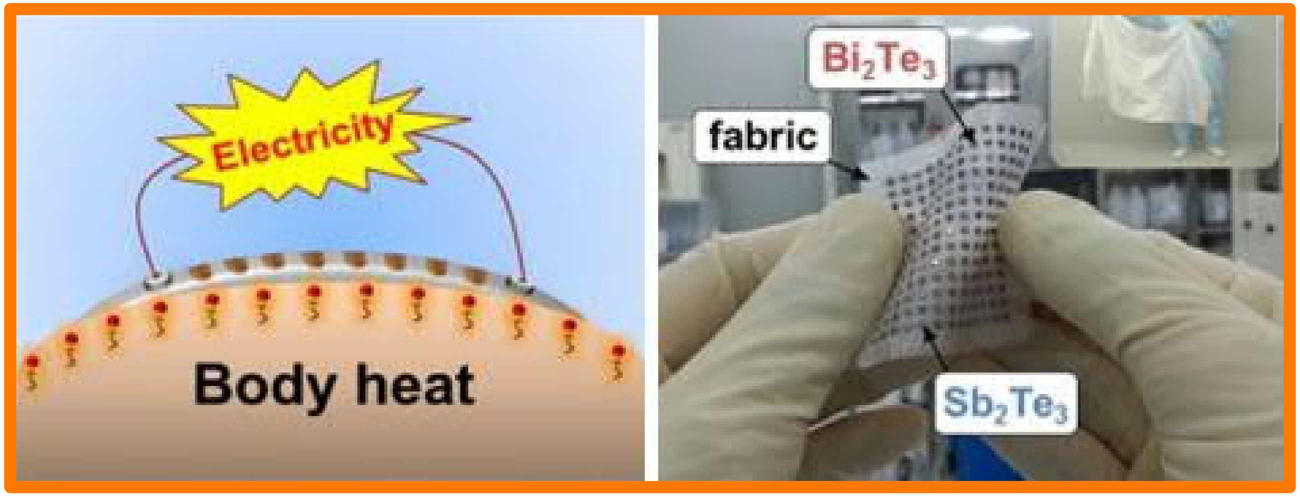
HawuPro sähkökamina



Picture Source: http://www.nano.lth.se/research/nano-energy/



THERMOELECTRICS: Examples of targeted applications

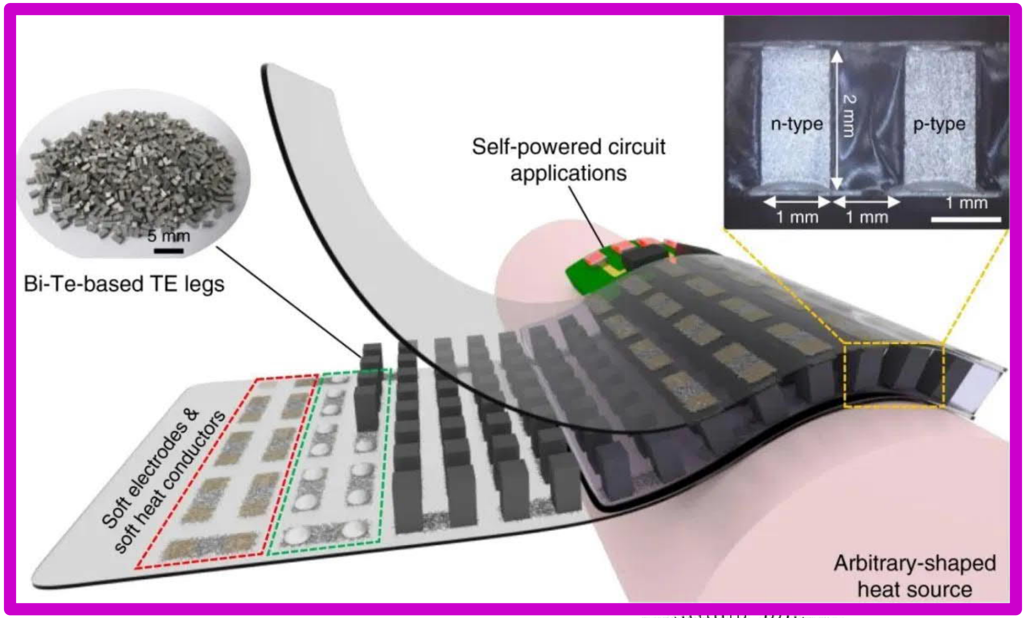


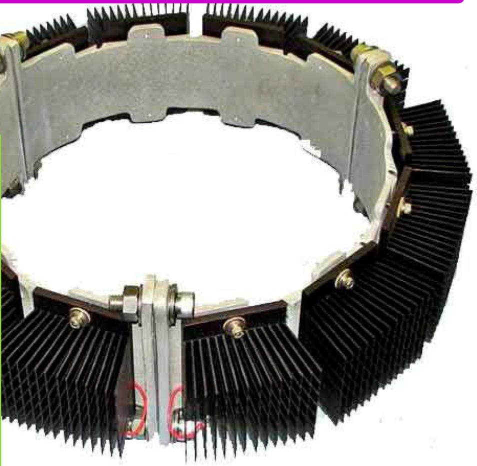
Aalto University
School of Chemical
Technology

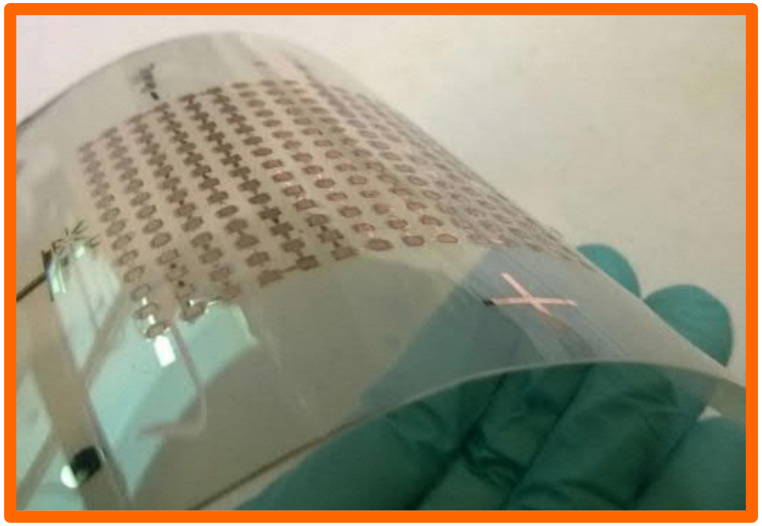
What kind of material requirements?

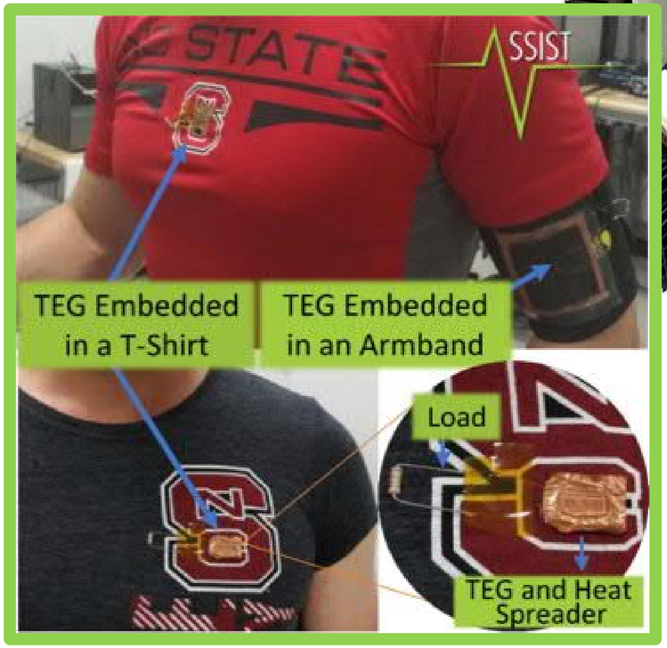
FLEXIBLE / WEARABLE THERMOELECTRICS

- Hot topic currently
- Flexibility needed for better contact with e.g. tubular heat sources
- Flexibility needed for wearable devices
- Micro-energy-harvesters in the power range of 10-1000 µW (for e.g. body-implanted pacemakers, sensors)







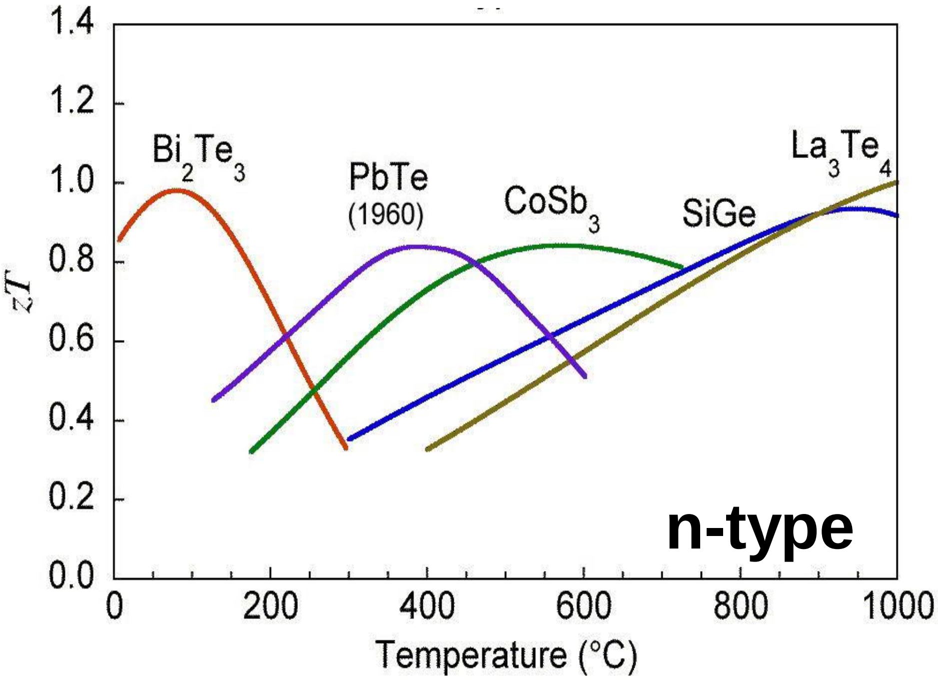


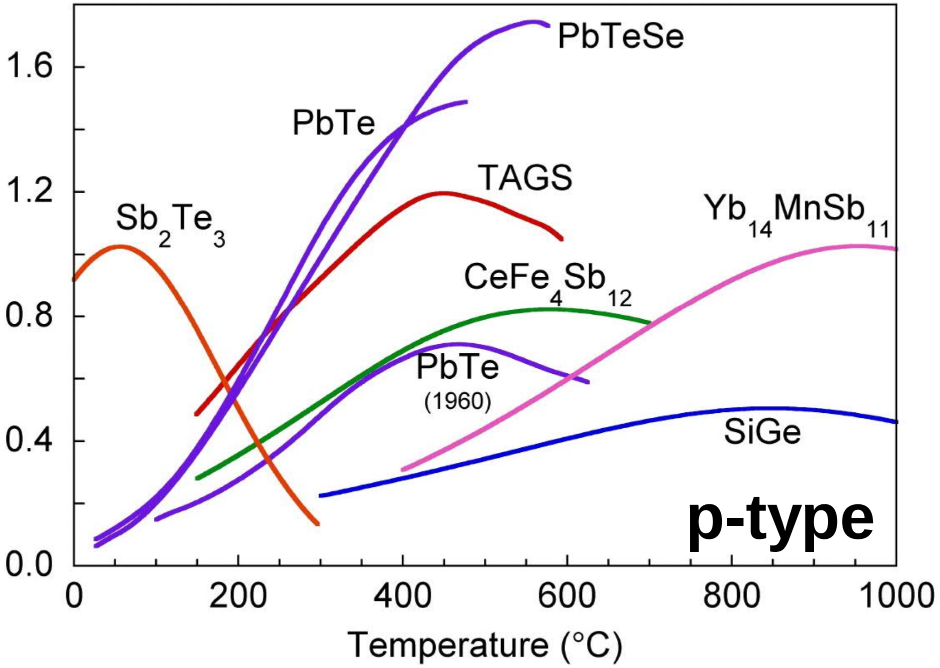
THERMOELECTRIC MATERIALS

- Figure-of-Merit (ZT)
- Heat-to-Electricity Conversion Efficiency (η)
- Conversion efficiency increases by increasing ZT
- ZT increases by increasing electrical conductivity (σ) & decreasing thermal conductivity (κ) → **DIFFICULTY**
- Two terms for κ: electronic (κ_e) and lattice (κ_L)
- More efficient for high-temperature application !

$$ZT = \frac{S^2\sigma}{\kappa}T, \ \kappa = \kappa_e + \kappa_L$$

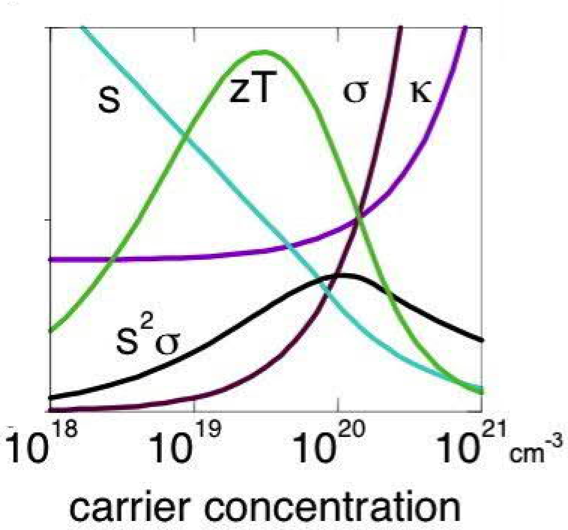
$$\eta = \frac{\Delta T}{T_h}\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_c/T_h}$$





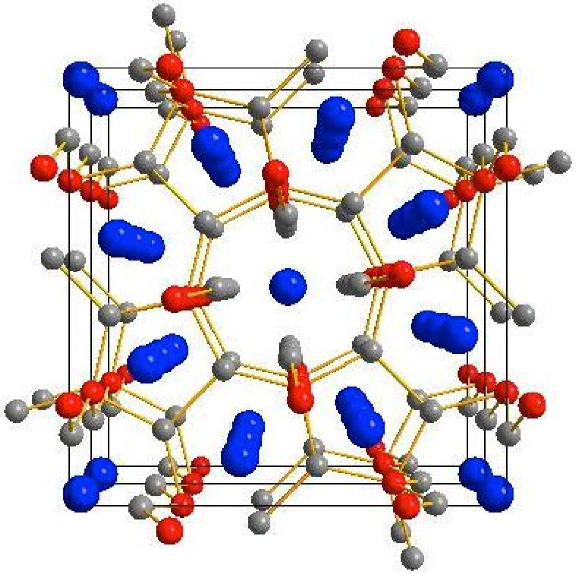
http://thermoelectrics.matsci.northwestern.edu/graphics/thermoelectrics/n-zT.jpg

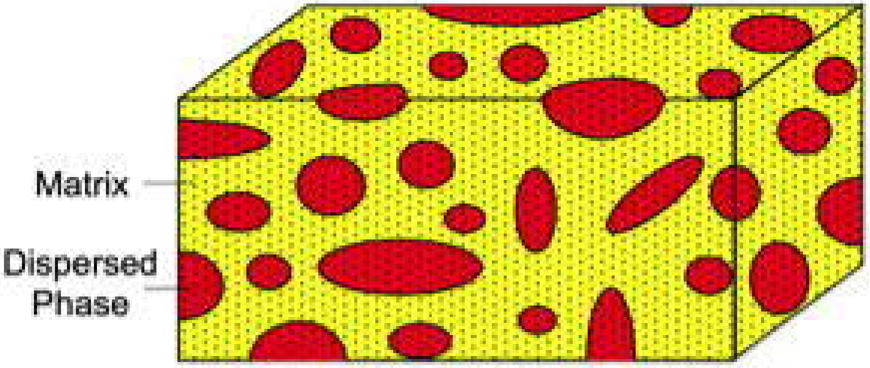
$$ZT = \frac{S^2\sigma}{\kappa}T, \ \kappa = \kappa_e + \kappa_L$$



WELL-KNOWN WAYS TO ENHANCE ZT

- Carrier concentration tuning:
  - In particular for optimized combination σ and S (Seebeck coefficient)
- For reducing thermal conductivity (lattice κ_L):
  - Heavy elements (often the rarest !)
  - Complex crystal structures
  - Defect engineering (phonon scattering)
  - Nanostructuring





THERMOELECTRICS SUMMARY

- **Over 65% of all energy produced is lost as waste heat**
- Thermoelectric power generators, which are semiconductor-based electronic devices, can turn this heat into electricity via the **Seebeck effect**
- These devices are **simple** to construct (just two different solid materials), easy to **scale-up** & long-term **reliable**
- However, we need **MATERIALS** that are **good electrical conductors** but have **extremely low thermal conductivity** → This is a very **tricky combination** to achieve (but a materials chemists dream research topic)
- Moreover, the devices should stand heat sources **as hot as 500 °C**
- Also, **mechanical flexibility** desired
- True commercialization of thermoelectric technology has been seriously limited by the low ZT values and the presence of toxic elements (e.g. Pb) or **rare elements** (e.g. Te)
- **Minimum criterion: ZT > 1**
  Long desired: ZT > 2
  Dream-of-the-Dream: ZT > 4

SnSe

Single crystal SnSe

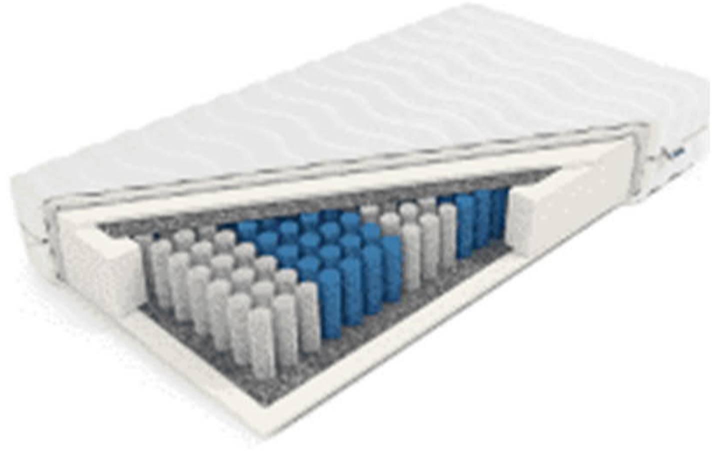
- Record low thermal conductivity among crystalline (electrically conducting) materials
- Heat (lattice vibrations or phonons) does not travel through this material because of its soft but “posture-pedic mattress” like layered crystal structure
- SnSe can stay hot on one side while remaining cool on the other side

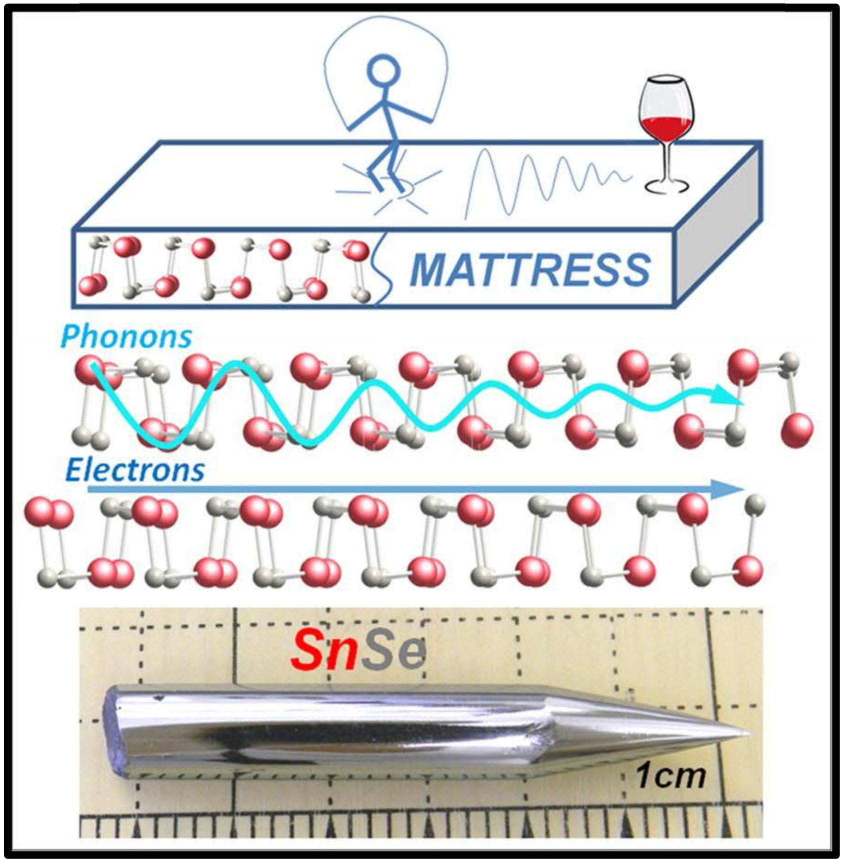
Mercouri Kanatzidis Group: Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals, *Nature* (2014).

Polycrystalline SnSe

- Heat-to-Elec conversion efficiency: ca. 20%
- ZT = 3.1 at 783 K
- SnSe is p-type semiconductor; next goal is to find its matching n-type counterpart

Mercouri Kanatzidis Group: Polycrystalline SnSe with a thermoelectric figure of merit greater than the single crystal. *Nature Materials* (2021).

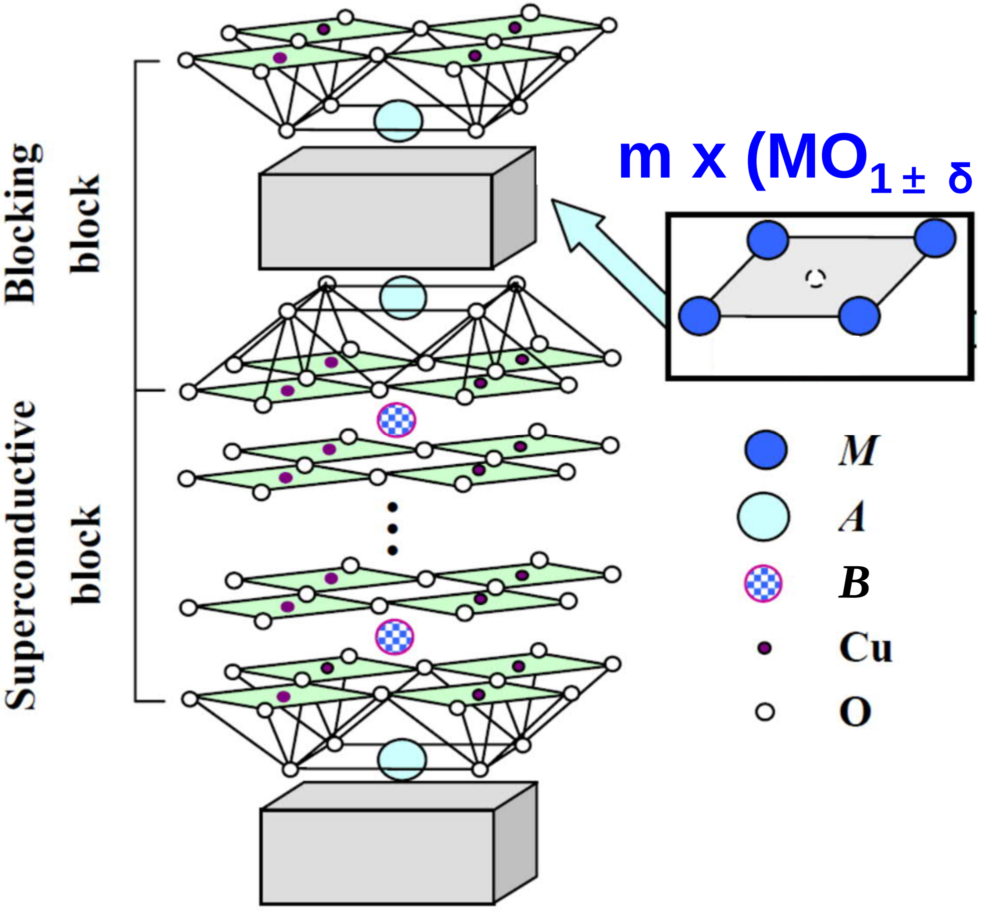




https://chemgroups.northwestern.edu/kanatzidis/research.html

GENERAL FORMULA of High-T_c Superconductors

- $M_mA_2B_{n-1}Cu_nO_{m+2+2n\pm\delta}$
- M-m2(n-1)n
- HOMOLOGOUS SERIES: M, m, A and B fixed, n varies



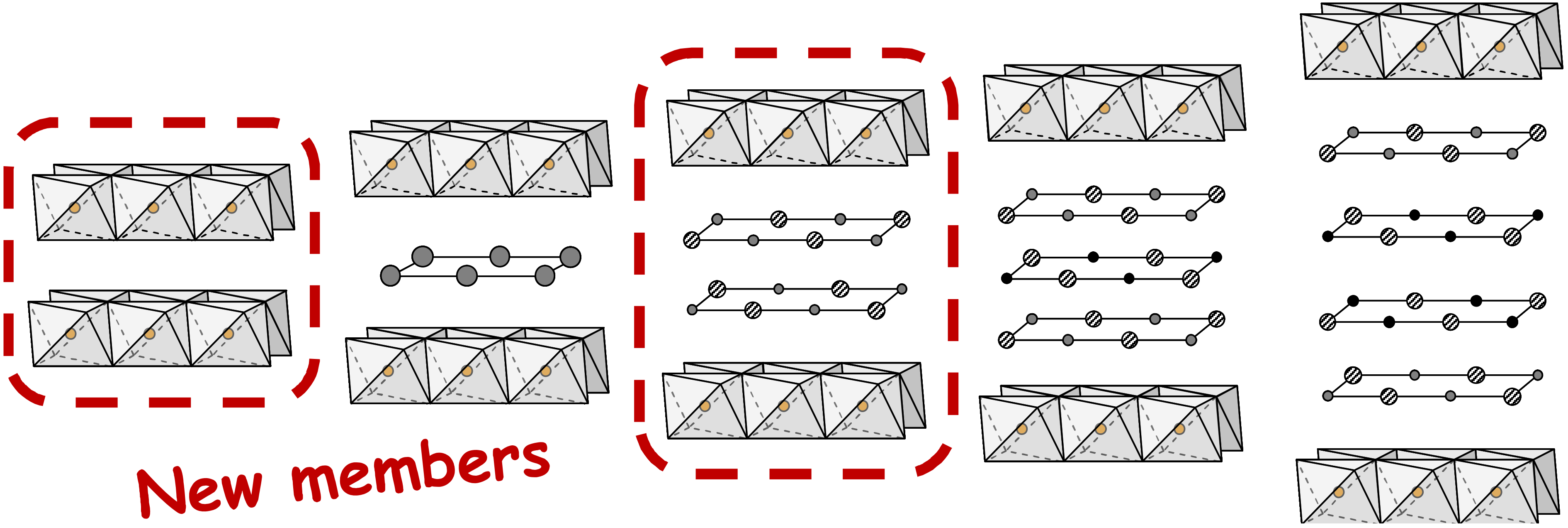
m x ($MO_{1\pm\delta}$ layers)

M. Karppinen & H. Yamauchi,
Control of the charge inhomogeneity and high-*Tc* superconducting properties in homologous series of multi-layered copper oxides, *Mater. Sci. Eng. R* **26**, 51-96 (1999).

HOMOLOGOUS SERIES of Thermoelectric Misfit Oxides

$[(MO)_m(AO)_k]_qCoO_2$

- Thermoelectric material: high electrical conductivity & ultralow thermal conductivity
- First oxide thermoelectric material: Na_xCoO_2 (viz. Li_xCoO_2 battery cathode)
- Thermoelectric $[CoCa_2O_3]_qCoO_2$ and $[Bi_2Sr_2O_4]_qCoO_2$ CoO_2 were discovered later
- CoO_2 layers with mixed-valent cobalt → electrical conductivity (viz. HTSCs)
- ”Misfitting” metal oxide layers → structural complexity → low thermal conductivity
- Homologous series: understanding the general trends in the properties



New members

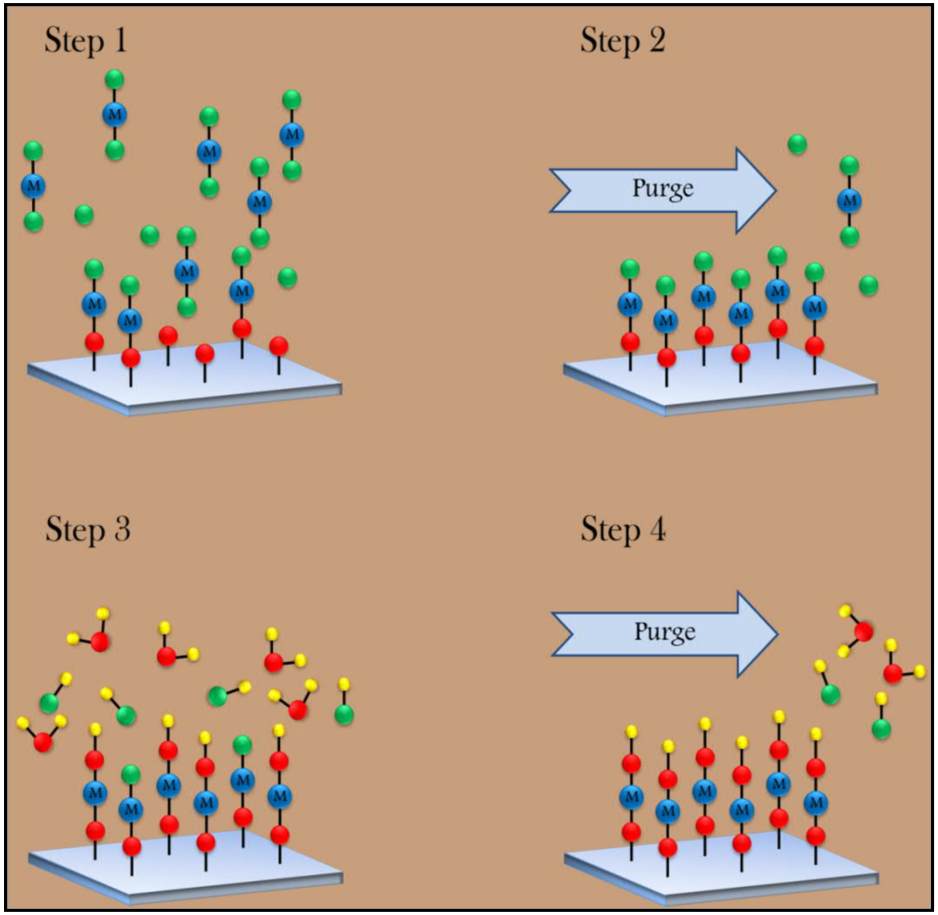
CoO_2
k=0, m=0

Na_xCoO_2
k=1, m=0

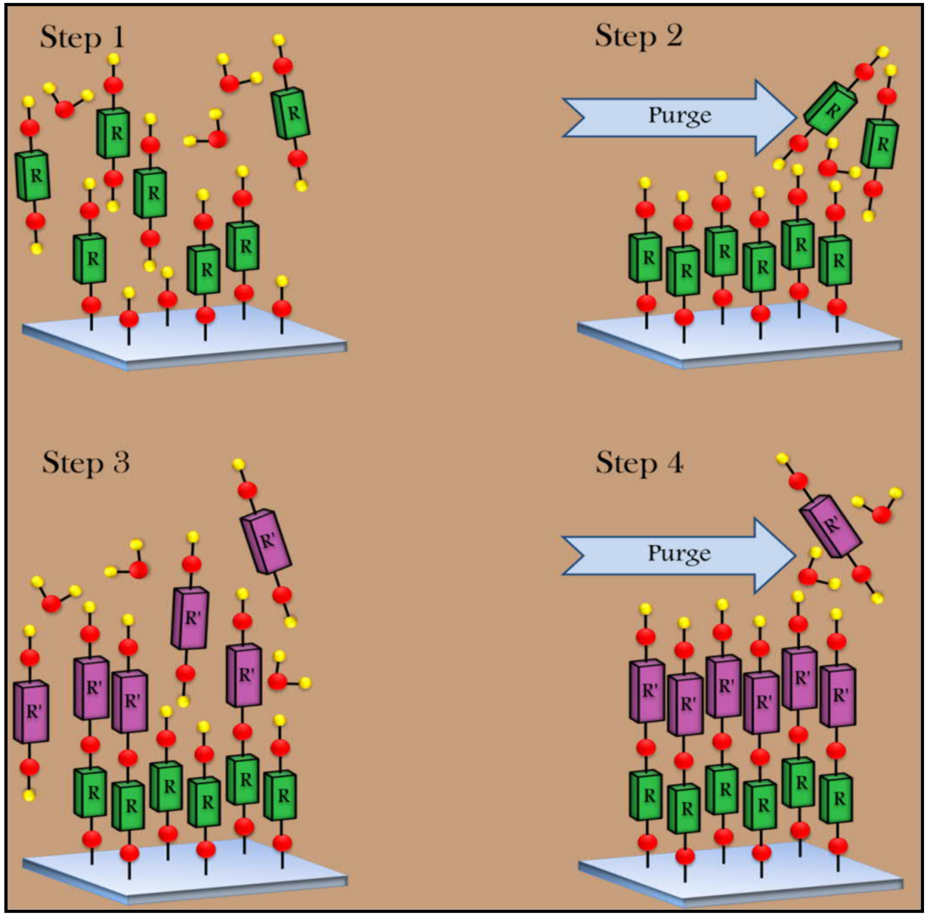
$[Sr_2O_2]_{0.5}CoO_2$
k=2, m=0

$[CoCa_2O_3]_qCoO_2$
k=2, m=1

$[Bi_2Sr_2O_4]_qCoO_2$
k=2, m=2



ALD **(Atomic Layer Deposition)**



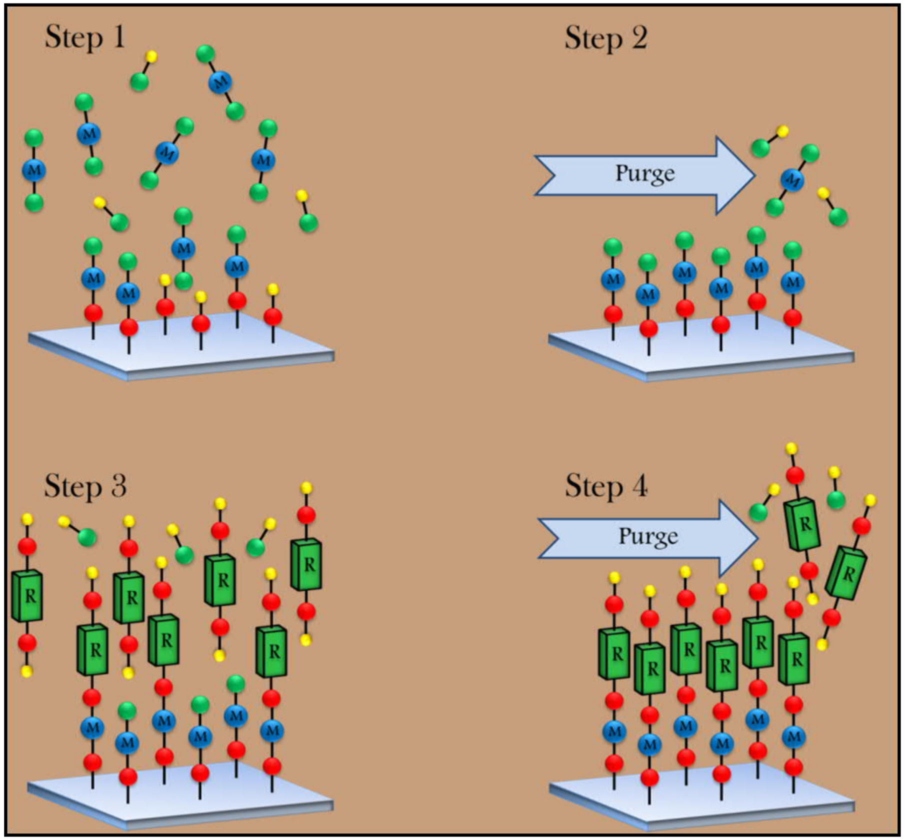
MLD **(Molecular Layer Deposition)**

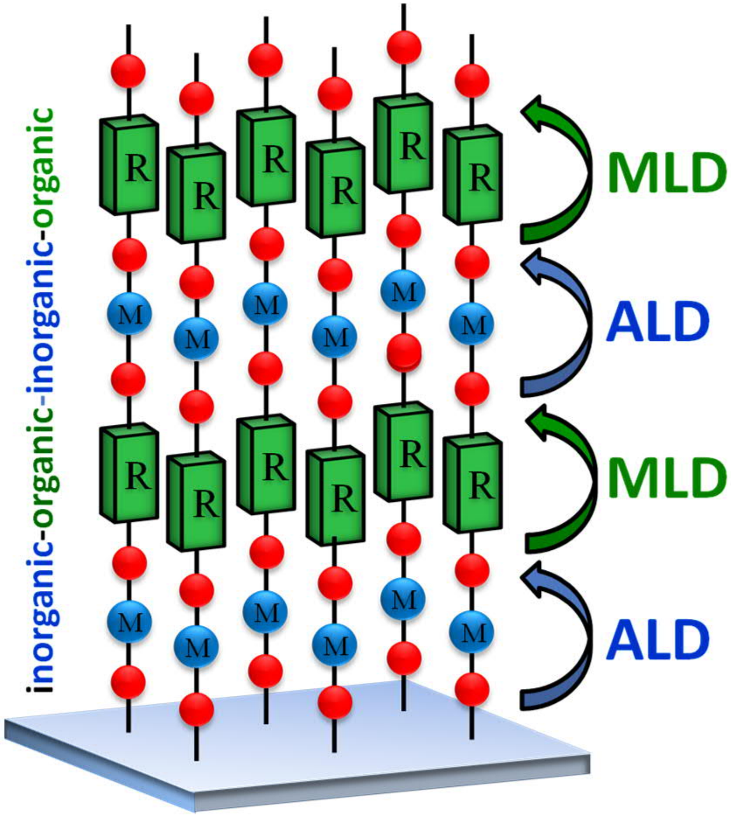
High-quality INORGANIC thin films
with atomic level control
for microelectronics and beyond

ORGANICS !

T. Yoshimura, S. Tatsuura & W. Sotoyama,
Polymer films formed with monolayer growth steps by molecular layer deposition,
Appl. Phys. Lett. 59, 482 (1991).

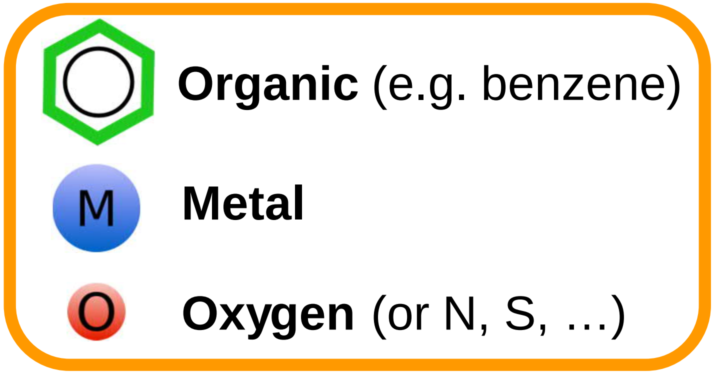
Inorganic-Organic (Metal-Organic) Thin Films
by Combined ALD/MLD





NOVEL FLEXIBLE MULTIFUNCTIONAL HYBRID MATERIALS

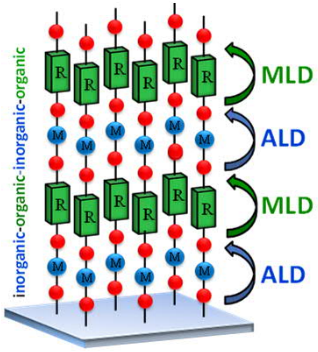
DIFFERENT LAYER SEQUENCES BY DESIGN

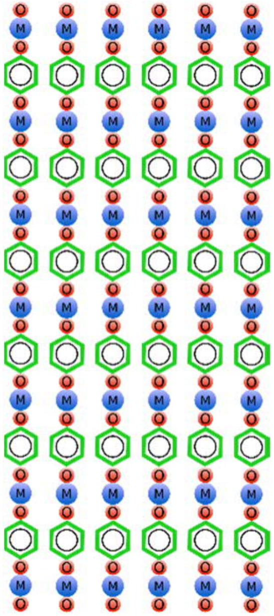


Organic (e.g. benzene)

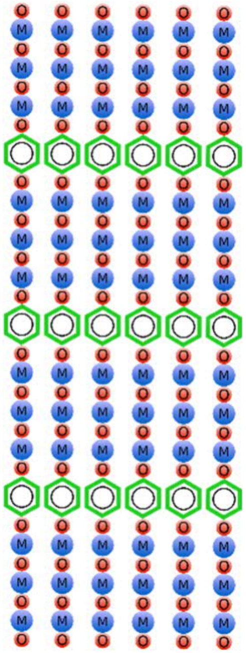
Metal

Oxygen (or N, S, …)

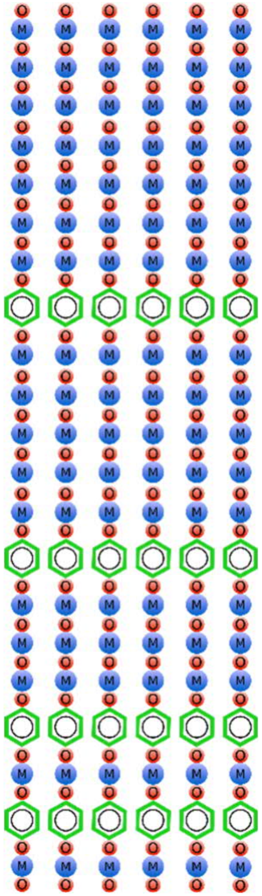




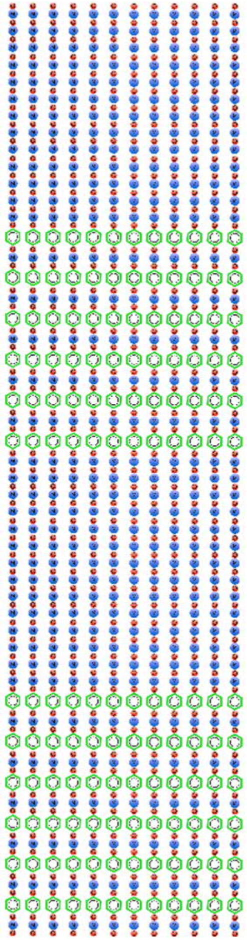
Simple
Metal-Organic Network
(amorphous or crystalline)



Superlattice

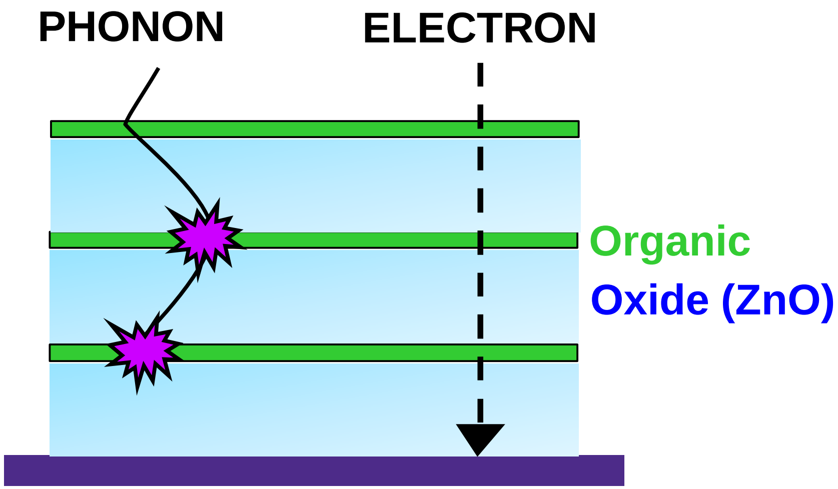


Gradient



Nanolaminate

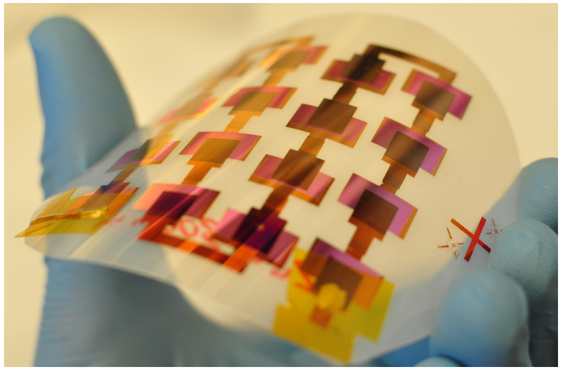
TEXTILE THERMOELECTRICS: ALD/MLD ZnO:organic



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

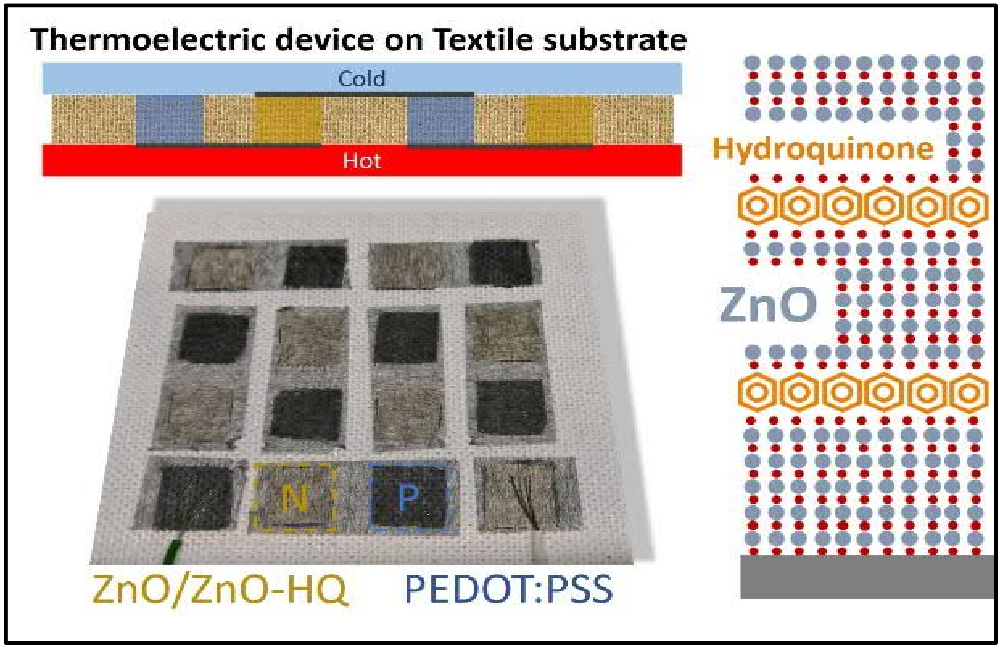
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, *J. Mater. Chem. A* 2, 12150 (2014).

Flexible TE "device" on plastics

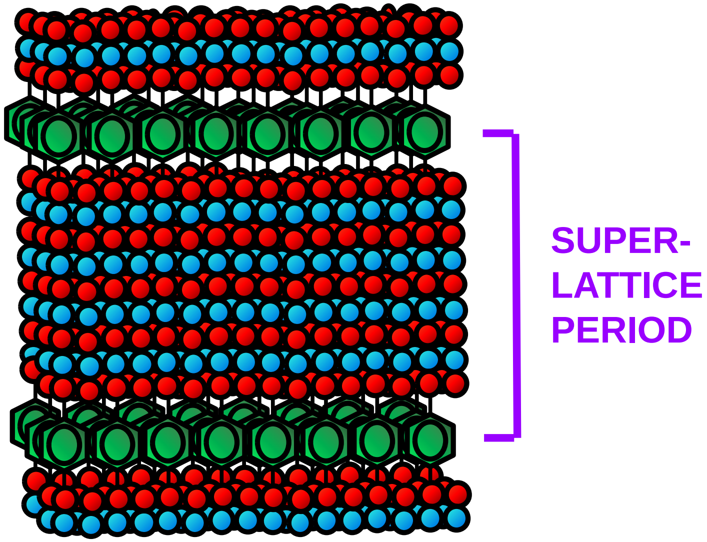


Textile-integrated thermoelectrics

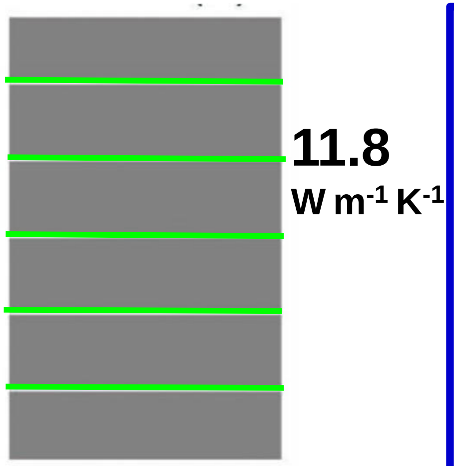
ZnO:org film grows in a conformal manner on textile fibers so that the entire textile piece becomes an active part of the device



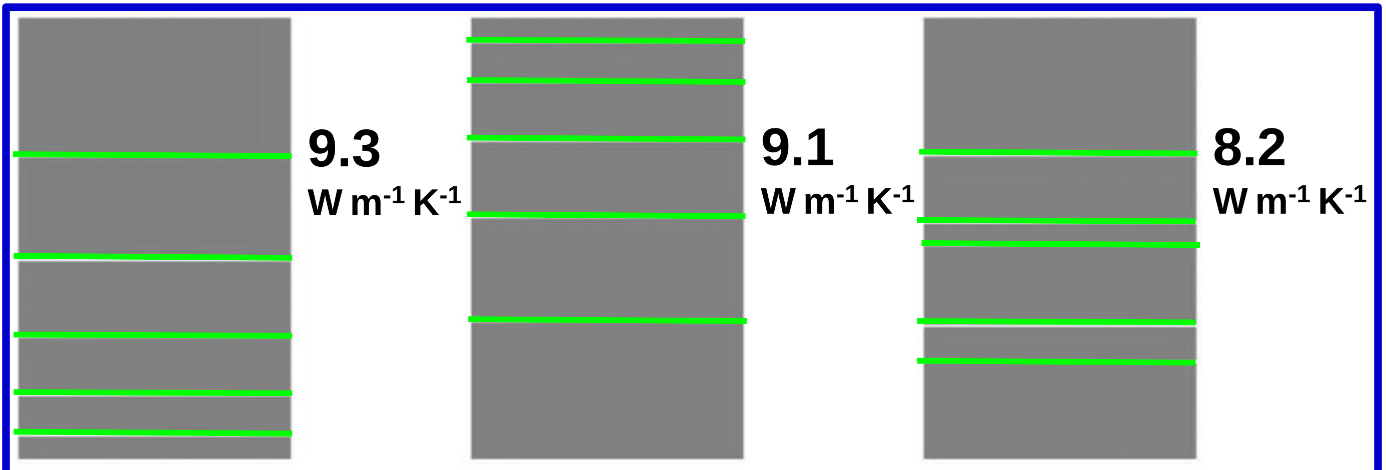
G. Marin, R. Funahashi & M. Karppinen, *Adv. Eng. Mater.* **22**, 2000535 (2020).



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



Superlattice



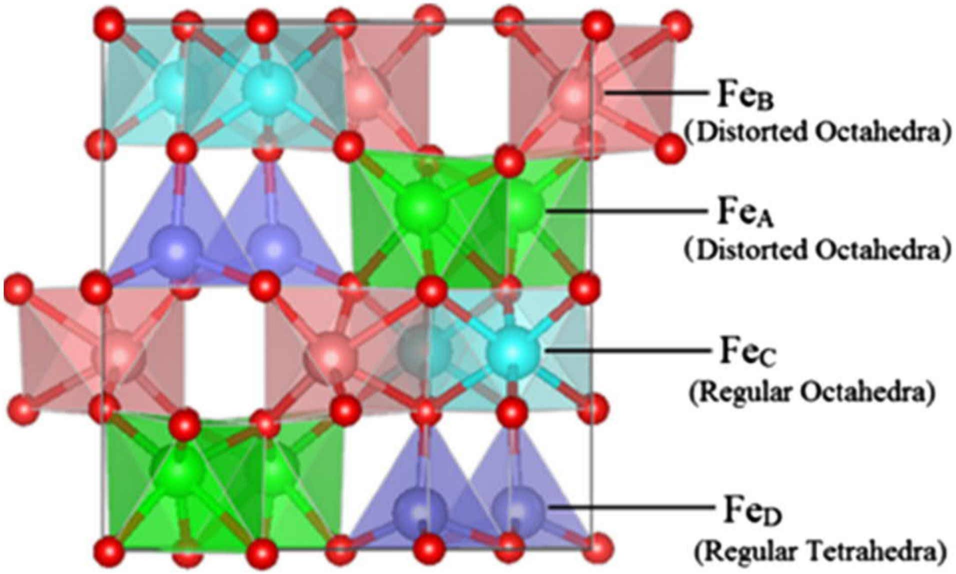
Gradient films (disordered)

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).

OTHER ALD/MLD RESEARCH EXAMPLES

ε-Fe_2O_3

- **Simple & critical-raw-material-free**
- **Rarest of the Fe_2O_3 polymorfs**
- **RT ferrimagnet ($T_C \approx 490$ K)**
- **Colossal coercivity**
- **Magnetoelectric**



1934: First observed by Forestier and Guiot-Guillain

1963: Named by Schrader and Buttner

2004: Synthesis of pure ε-Fe_2O_3 with giant coercive field values (up to 2 T)
- J. Jin, S.I. Ohkoshi & K. Hashimoto, Adv. Mater. 16, 48 (2004)

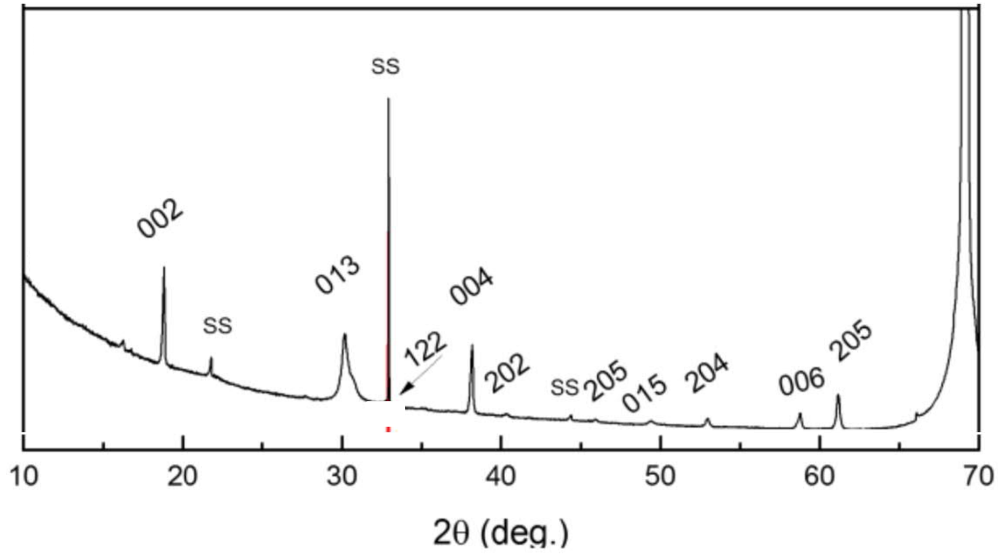
State-of-the-art: Synthesized in nano-scale/trace amounts only
- J. Tuček, R. Zbořil, A. Namai & S.I. Ohkoshi, Chem. Mater. 22, 6483 (2010)

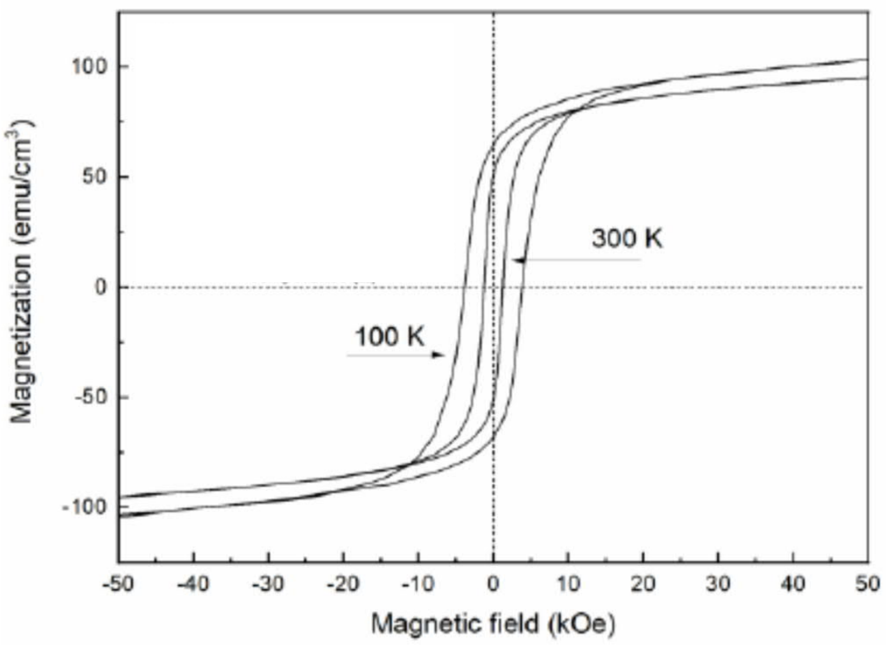
2017: ALD of ε-Fe_2O_3 thin films
- A. Tanskanen, O. Mustonen & M. Karppinen, APL Mater. 5, 056104 (2017)

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"

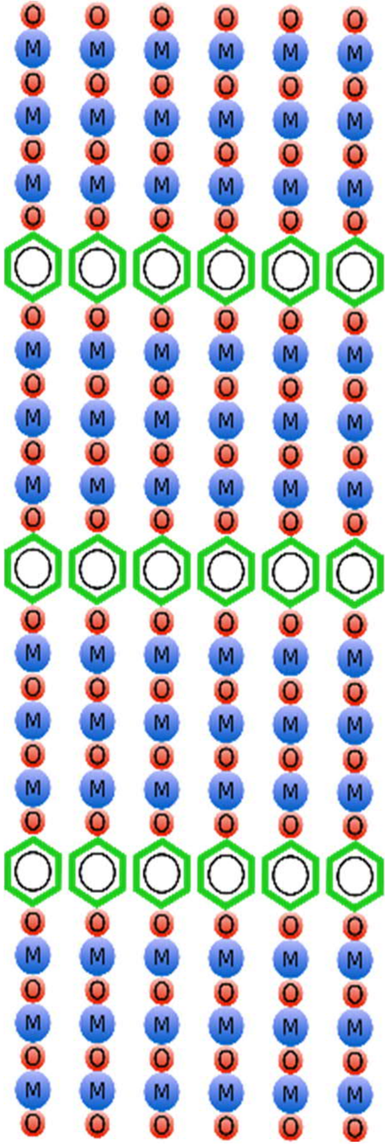




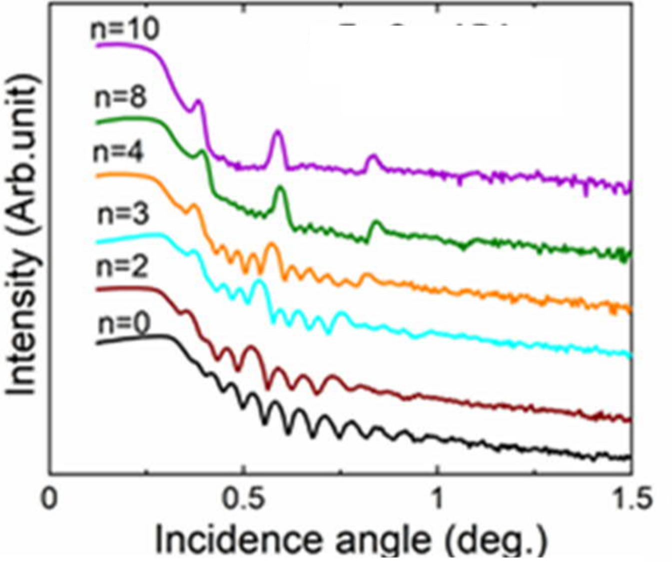
A. Tanskanen, O. Mustonen & M. Karppinen, Simple ALD process for ε-Fe_2O_3 thin films, *APL Materials* **5**, 056104 (2017).

ε-Fe$_2$O$_3$:Organic Superlattices (SL) by ALD/MLD

ORGANICS: terephthalic acid (TPA) or azobenzene (AZO)

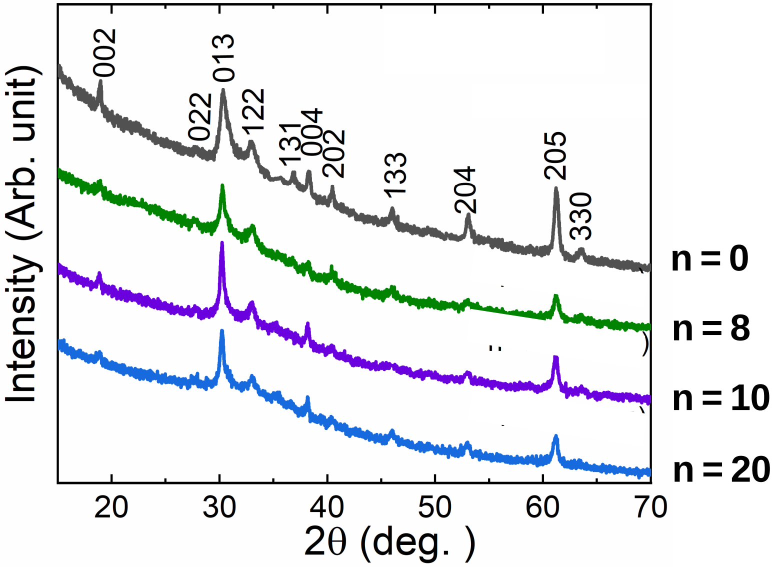


XRR: X-ray reflection

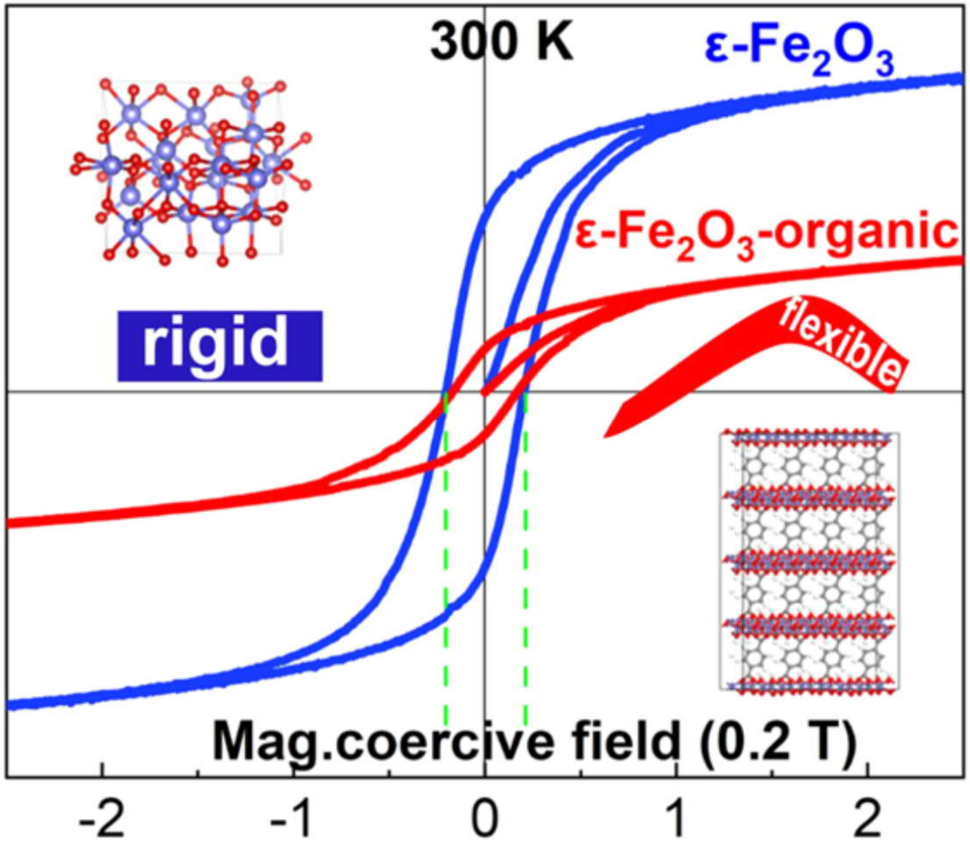


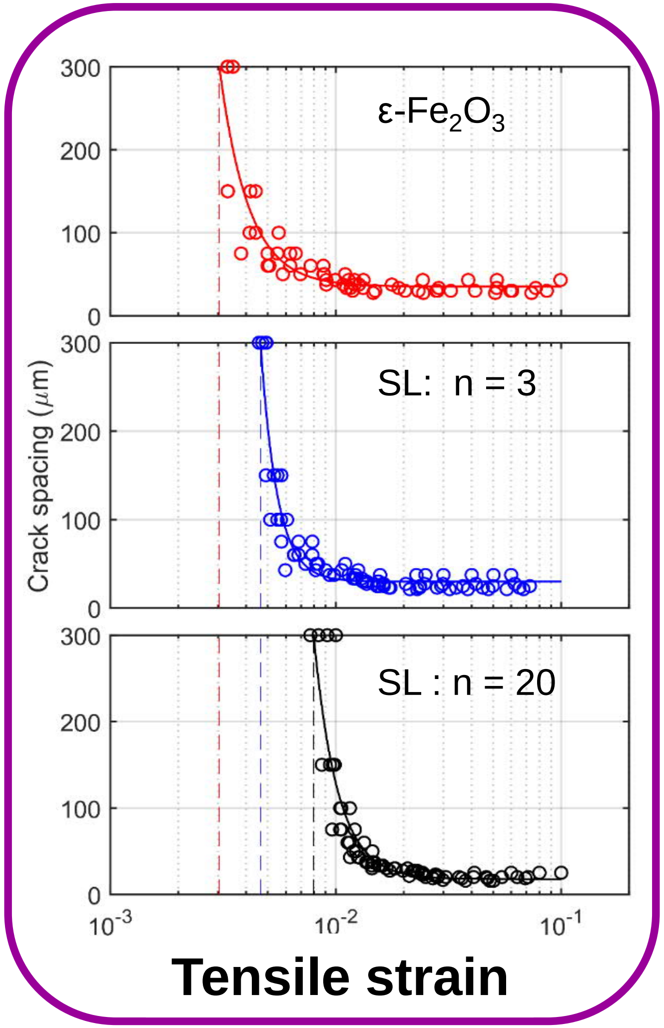
n: number of organic layers

GI-XRD



MECHANICALLY FLEXIBLE: ε-Fe_2O_3:TPA

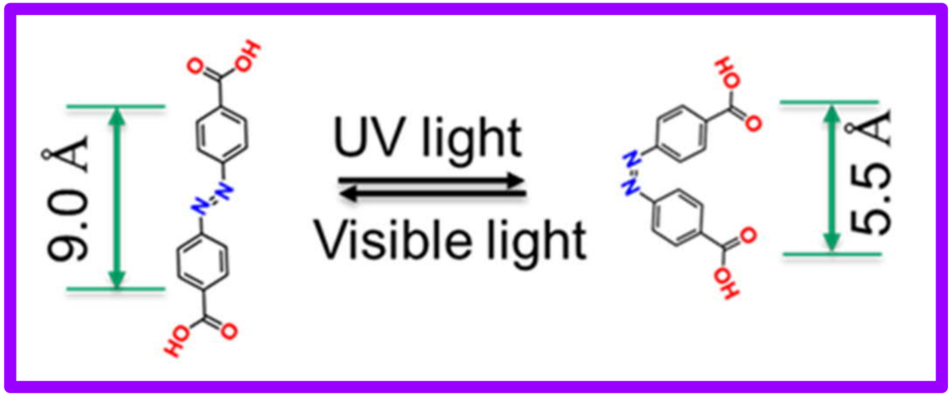


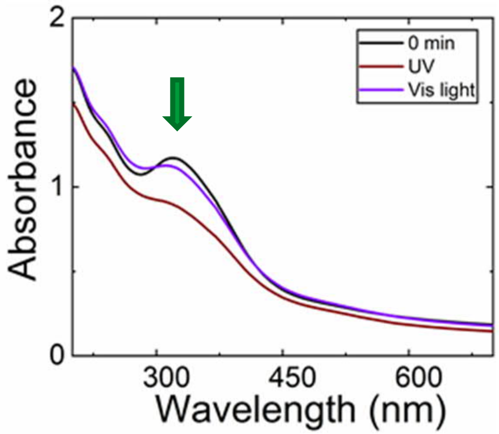


A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

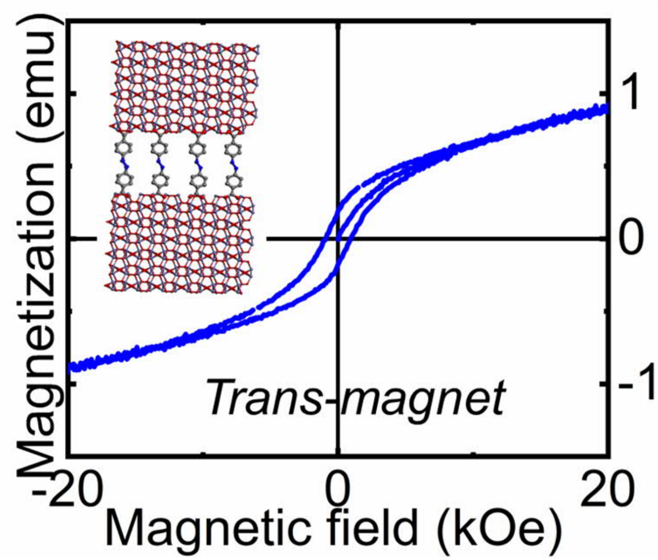
PHOTOSWITCHABLE: ε-Fe$_2$O$_3$:AZO

Trans **Cis**

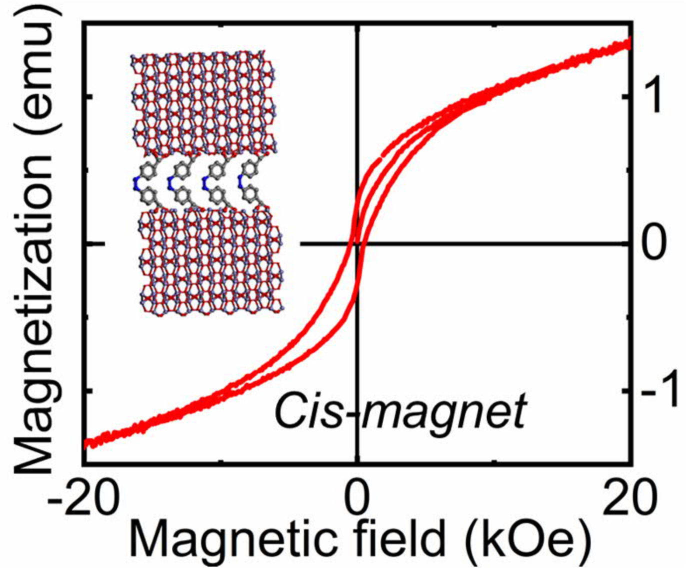




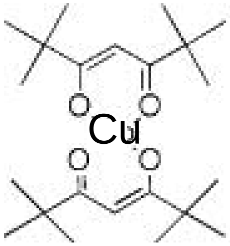
UV absorption: trans-cis transition is reversible



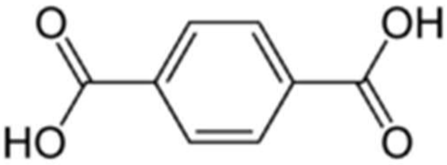
UV (365 nm)



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



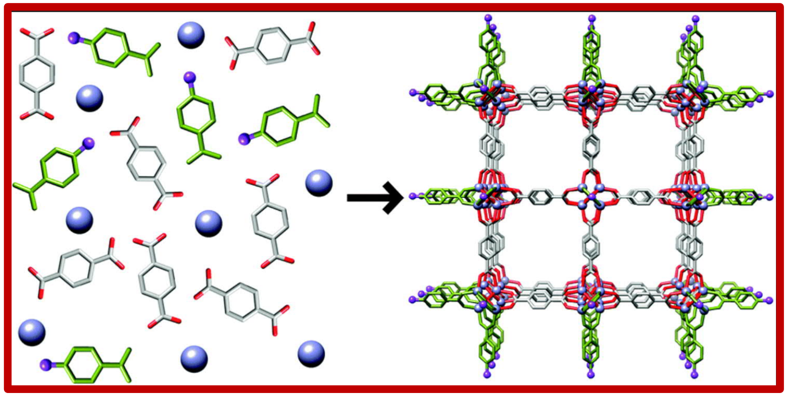
$Cu(thd)_2$

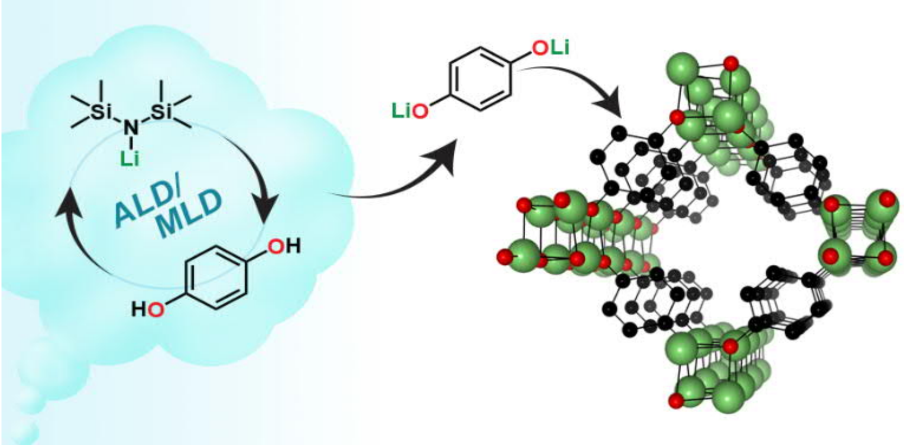


Terephthalic acid (TPA)

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

Known
MOF-2
structure

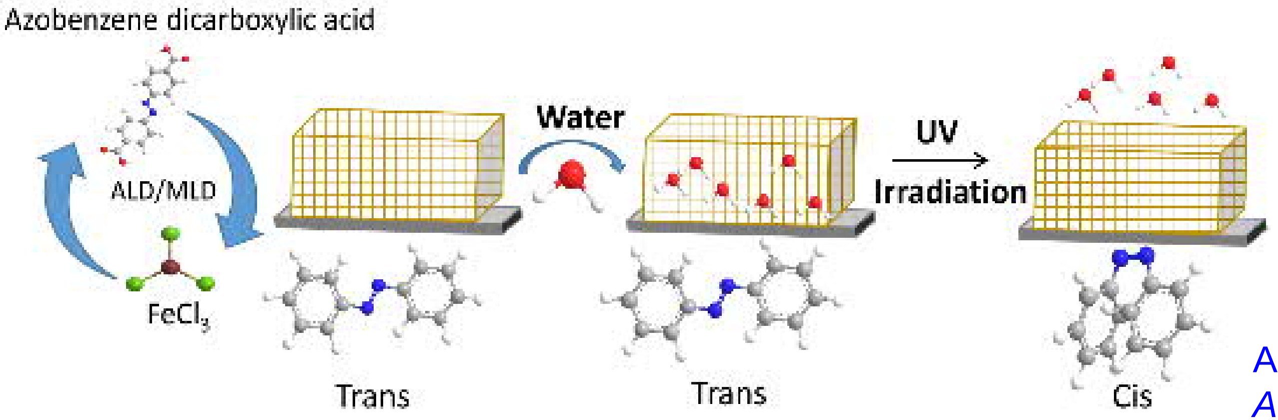




Lithium-benzoquinone

- 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).



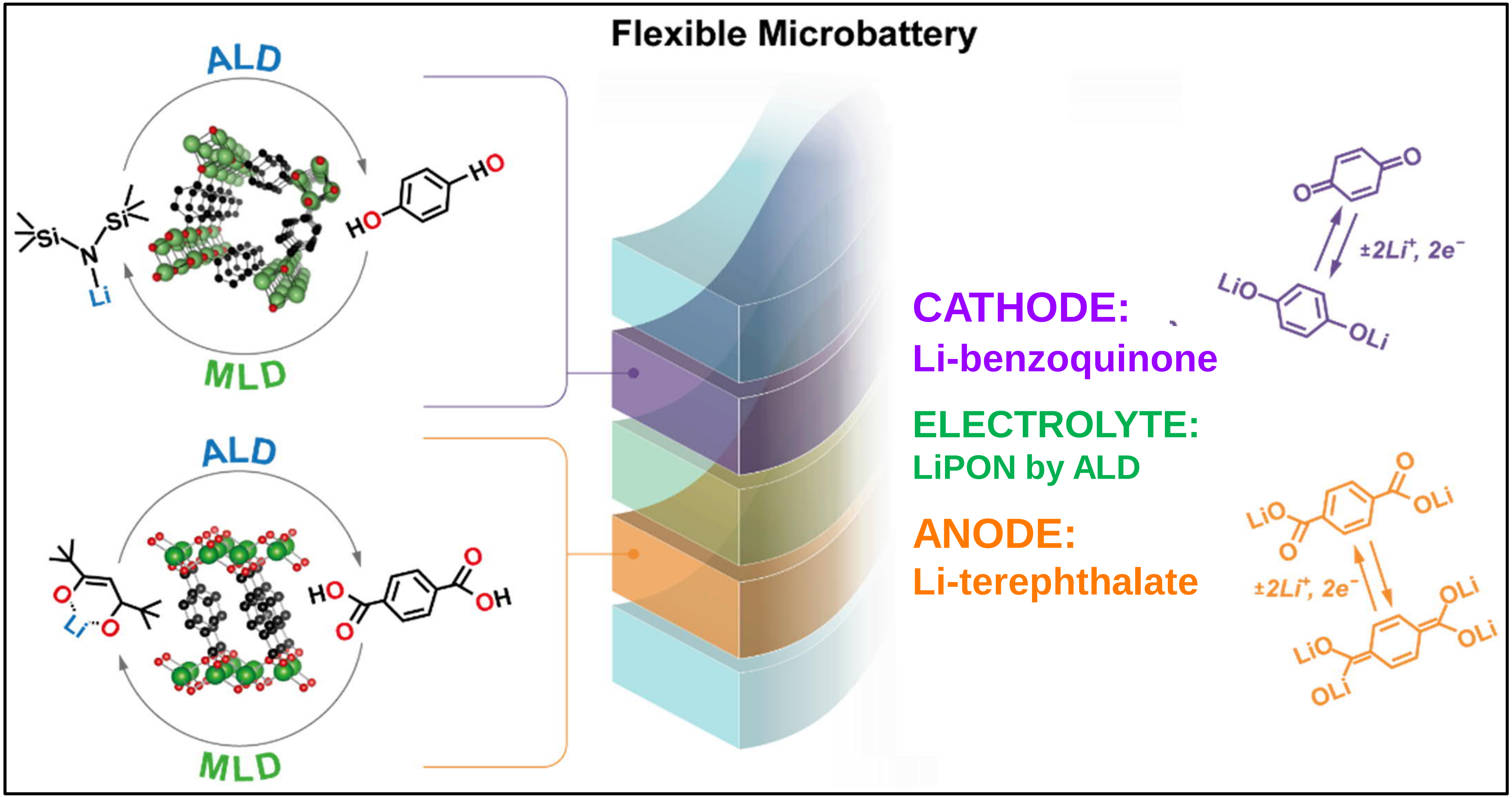
Iron-azobenzoate

- 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

MATERIAL FUNCTION HIGHLIGHTS: Li-ion microbattery



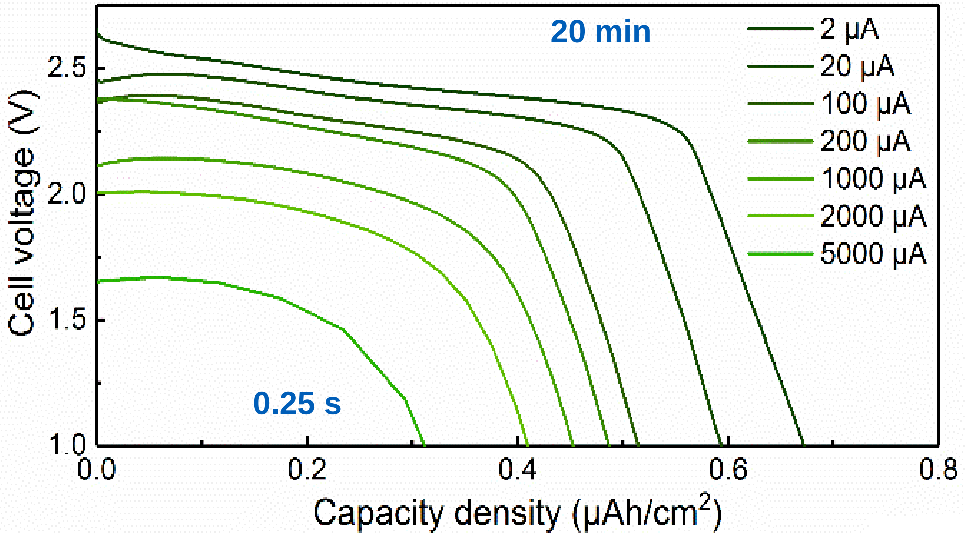
CATHODE:
Li-benzoquinone

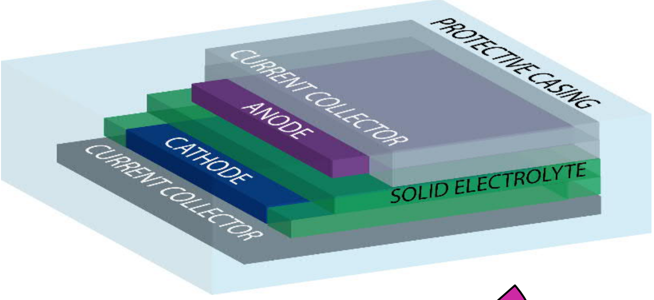
ELECTROLYTE:
LiPON by ALD

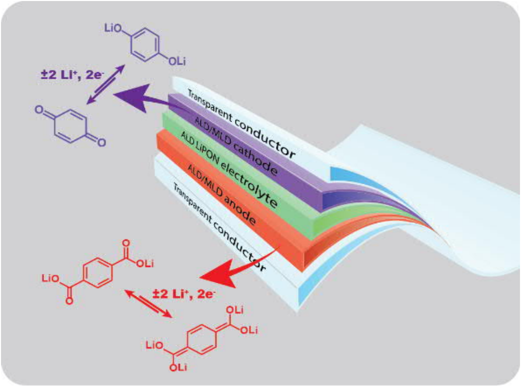
ANODE:
Li-terephthalate

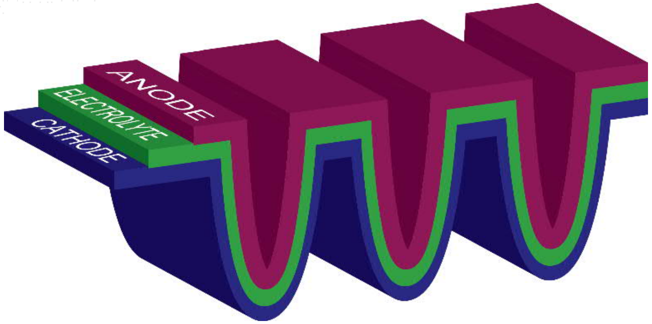
M. Nisula & M. Karppinen, In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery, *Journal of Materials Chemistry A* 6, 7027 (2018).

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





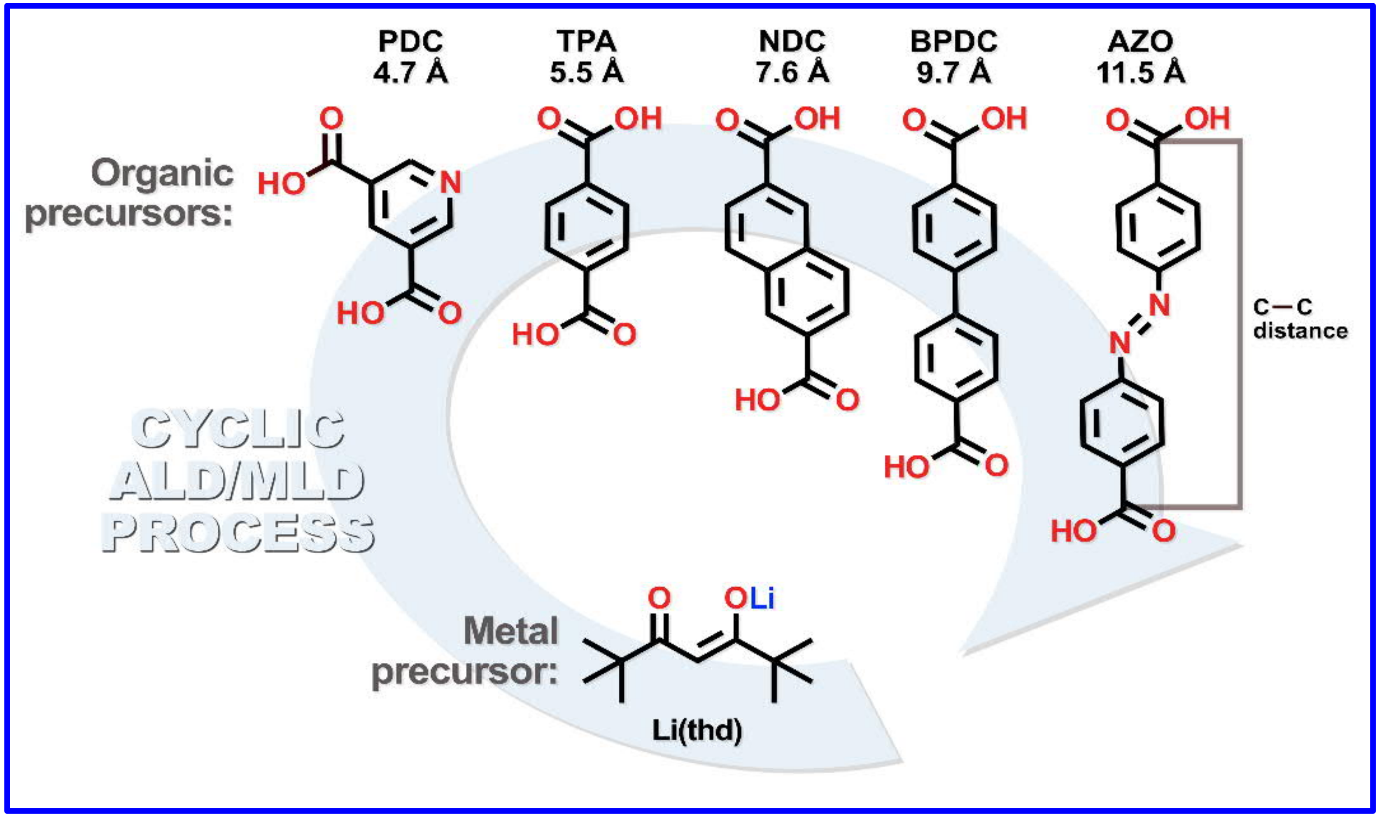


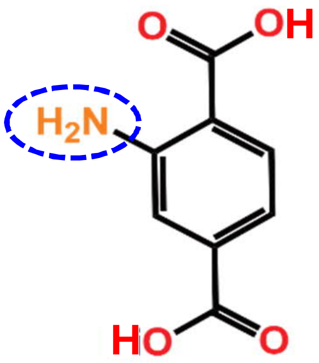


3D

HIGH POWER & ENERGY DENSITY

- 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).**

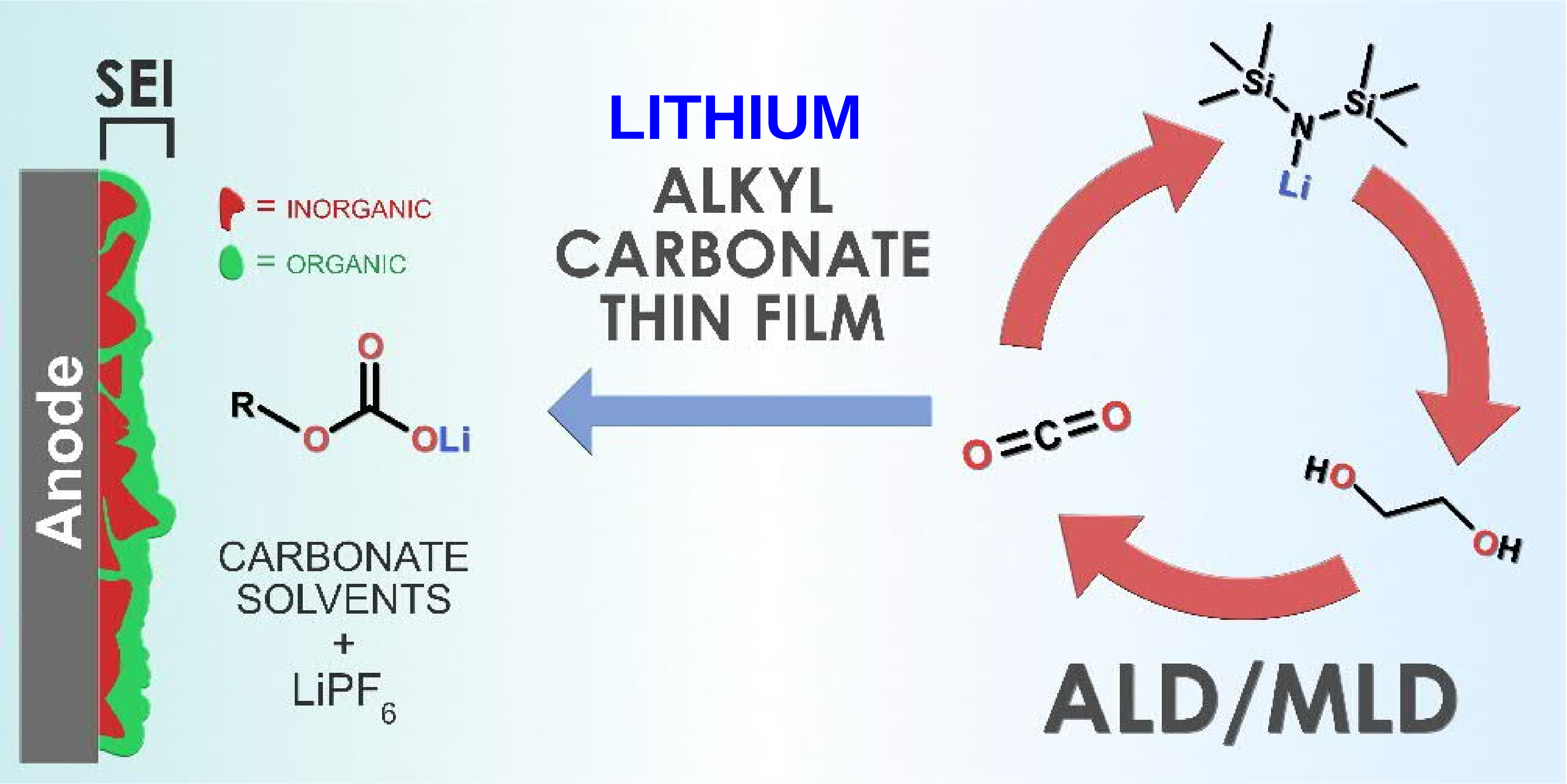




Electron-withdrawing amino group → Redox potential increases

- 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).

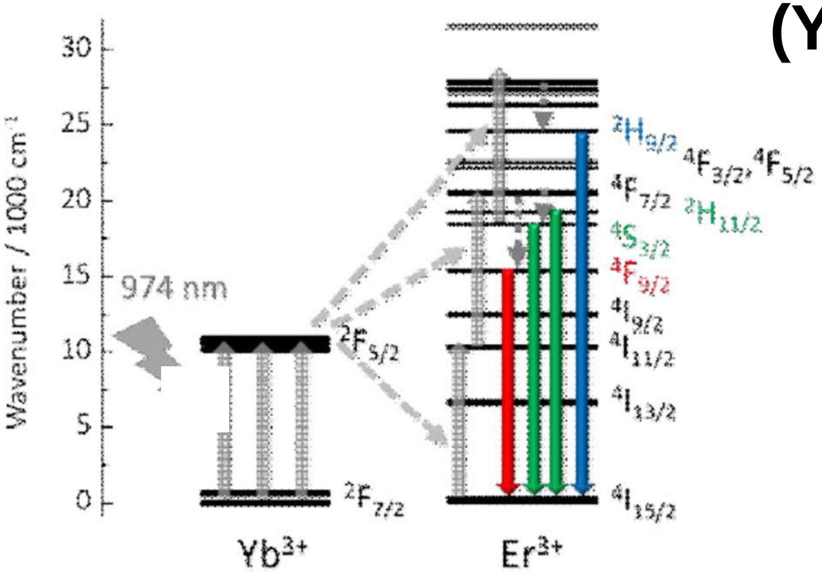
MATERIAL FUNCTION HIGHLIGHTS: Artificial SEI-barrier



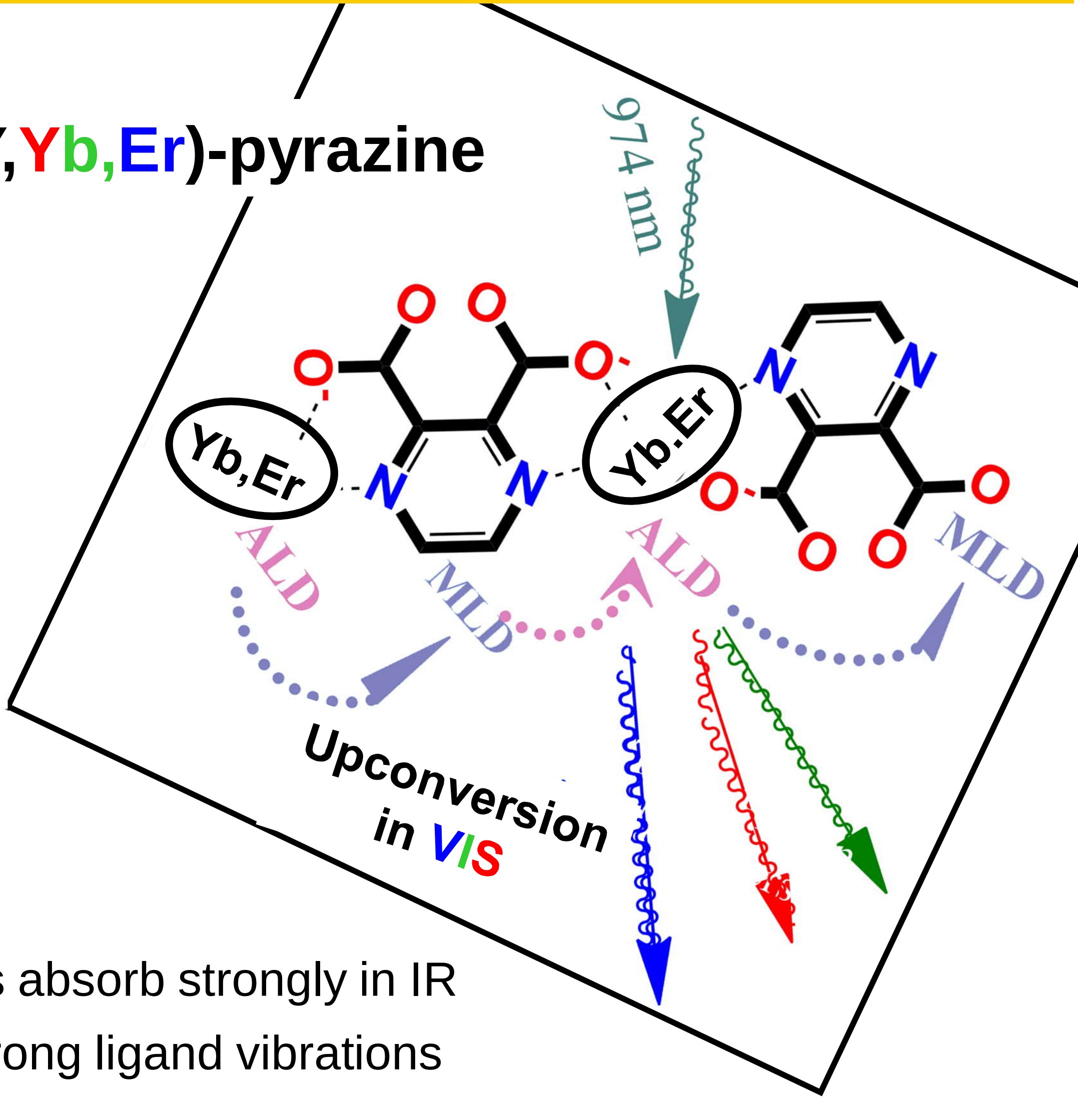
SEI: Solid Electrolyte Interphase (forms naturally in Li-ion battery)

J. Heiska, M. Madadi & M. Karppinen, CO_2-based atomic/molecular layer deposition of **lithium ethylene carbonate** thin films, *Nanoscale Advances* 2, 2441 (2020).

MATERIAL FUNCTION HIGHLIGHTS: Upconversion for PV

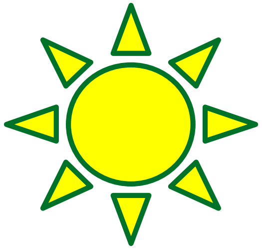


UPCONVERSION:
Near-IR → VIS light



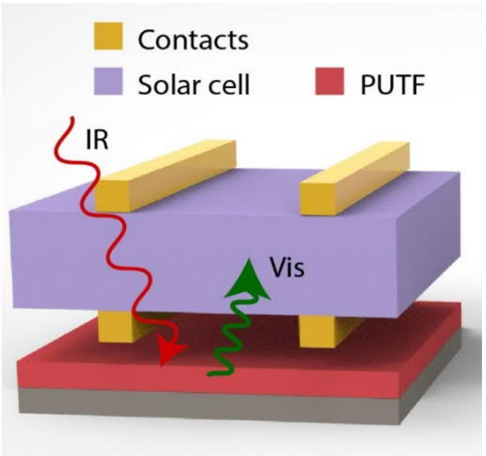
- **Metal-Organic COMPLEX:** organics absorb strongly in IR
- **PROBLEM:** energy losses due to strong ligand vibrations
- **ALD/MLD Ln-ORGANIC FILMS: organics more tightly bound → losses avoided**

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

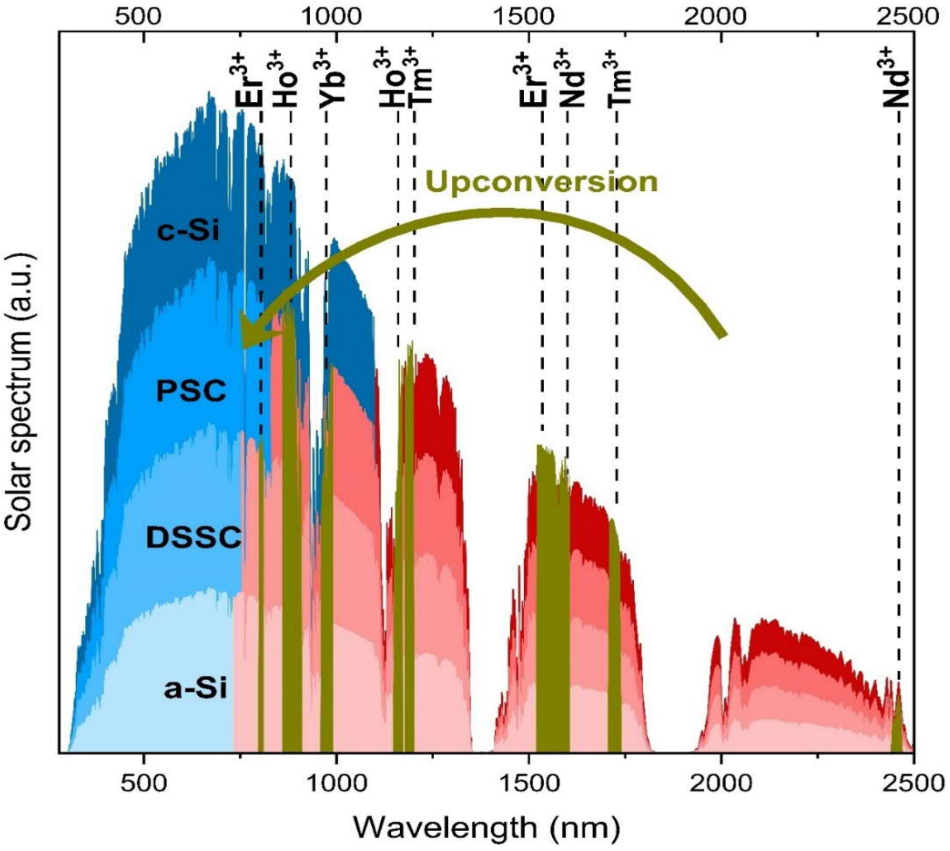


SOLAR CELLS

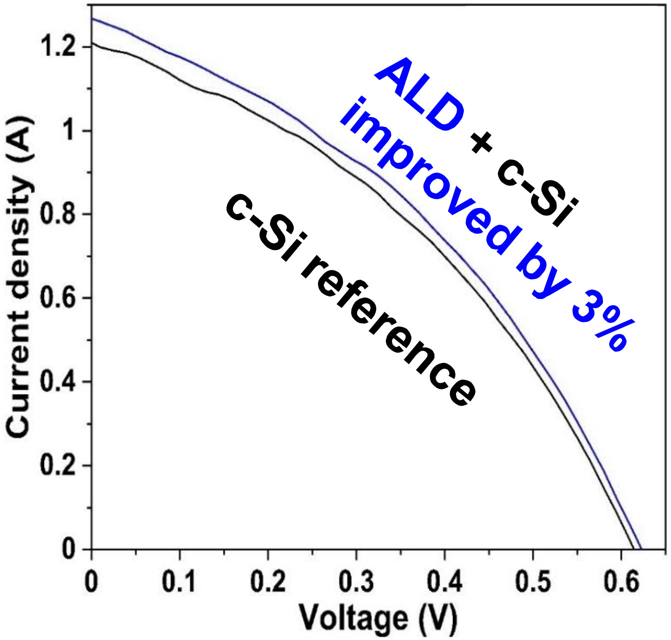
- Solar spectrum: UV + VIS + IR
- Solar cells utilize mostly VIS light
- Photon Upconverting Thin Film (PUTF)



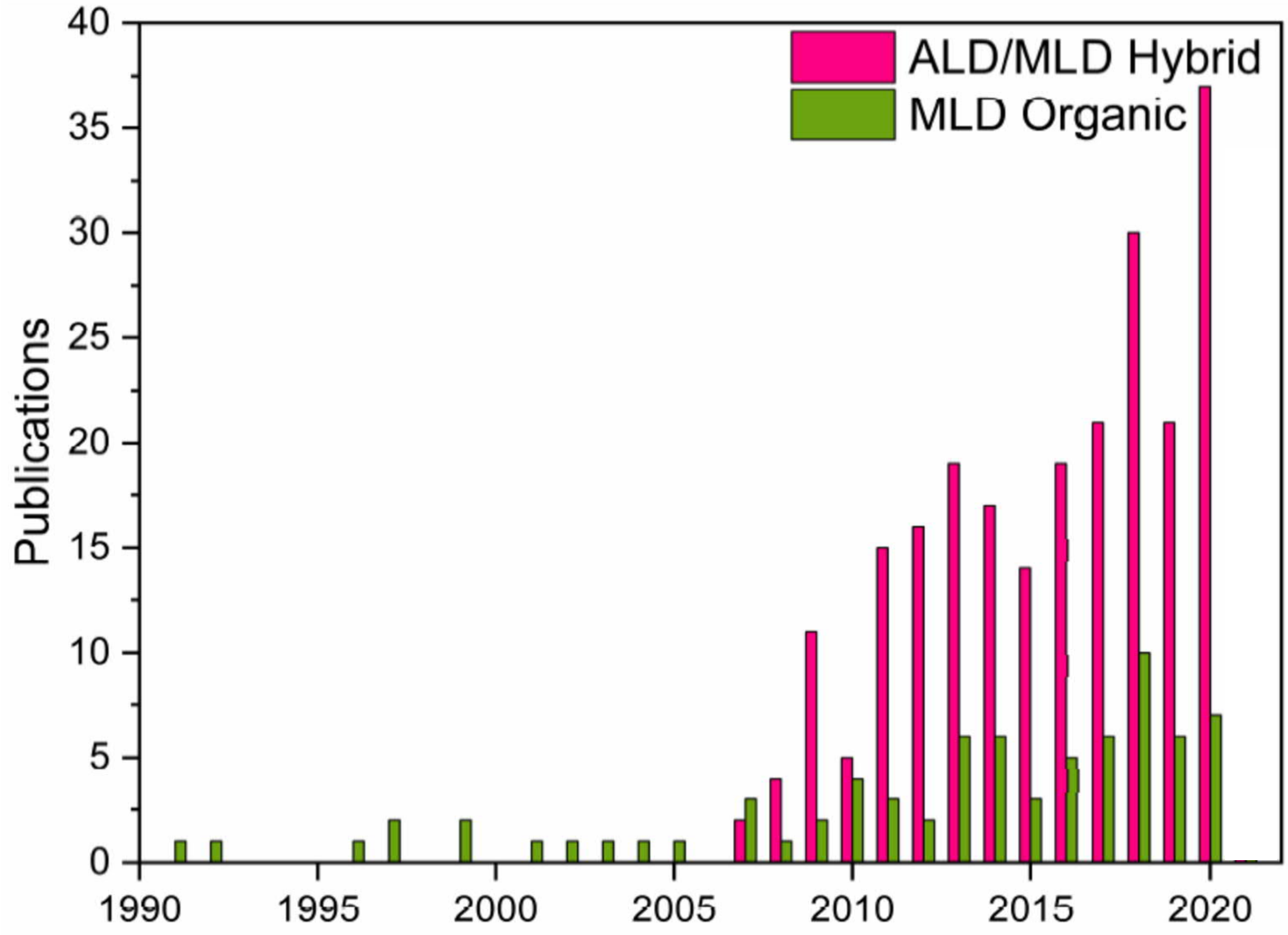
← UV VIS IR →



c-Si PV + ALD $(Er,Ho)_2O_3$ PUTF

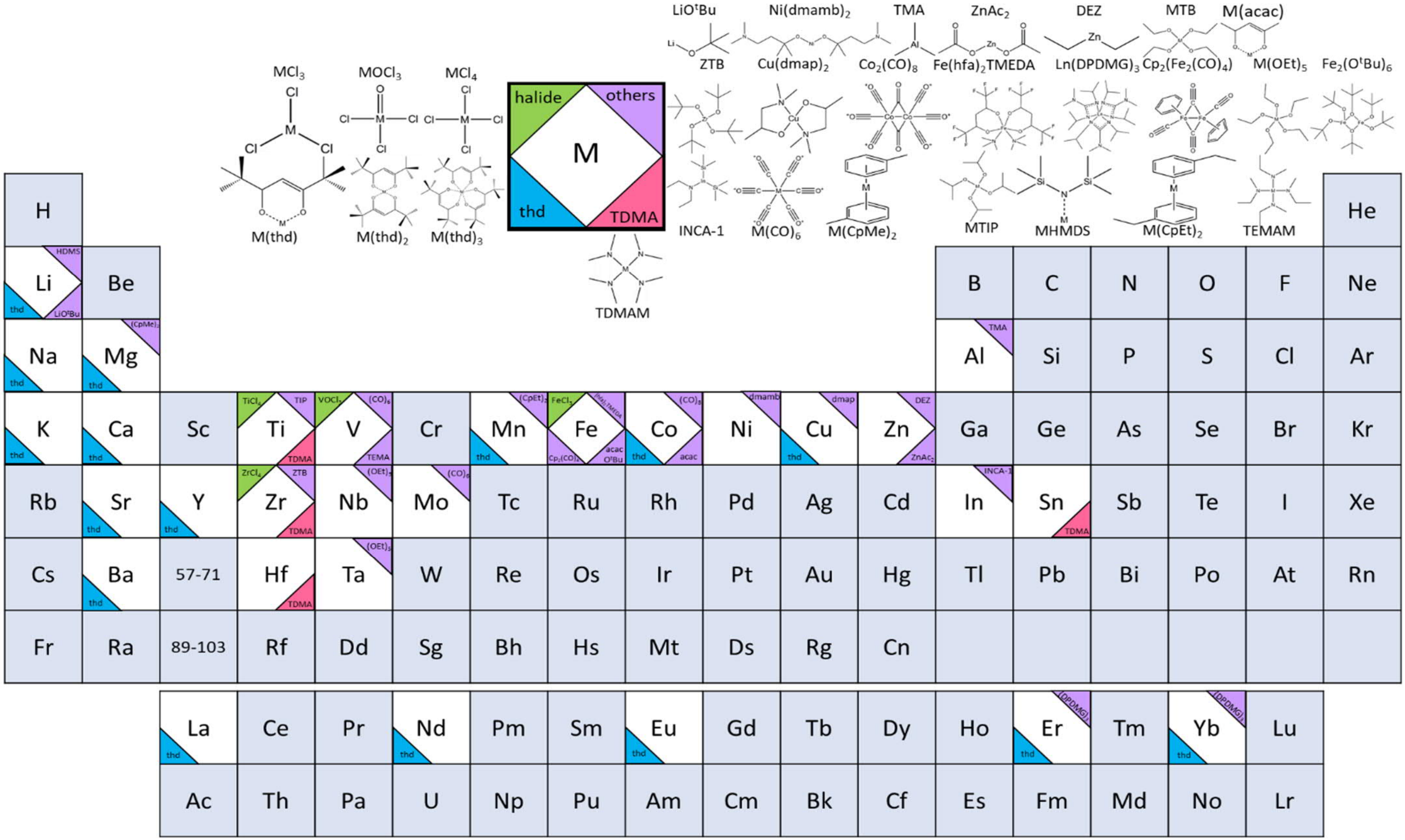


A. Ghazy, M. Safdar, M. Lastusaari, A. Aho, A. Tukiainen, H. Savin, M. Guina & M. Karppinen, Luminescent $(Er,Ho)_2O_3$ thin films by ALD to enhance the performance of silicon solar cells, *Solar Energy Materials & Solar Cells* 219, 110787 (2021).

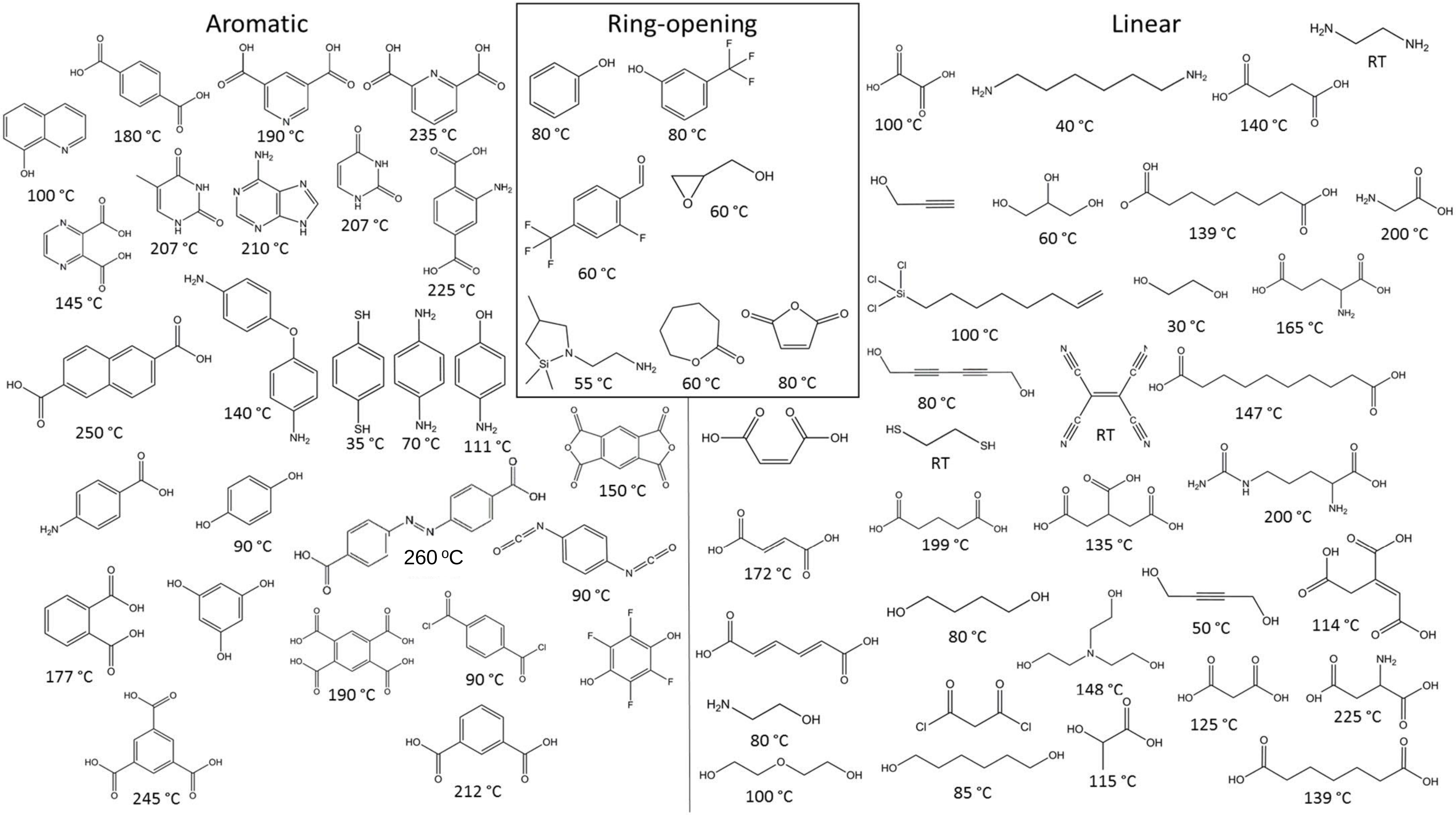


- Yoshimura, Tatsuura & Sotoyama, *Appl. Phys. Lett.* **1991,** *59,* 482.
- Yoshimura, Tatsuura, Sotoyama, Matsuura & Hayano, *Appl. Phys. Lett.* **1992,** *60,* 268.
- Kubono, Yuasa, Shao, Umemoto & Okui, *Thin Solid Films* **1996,** *289,* 107.

- 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.



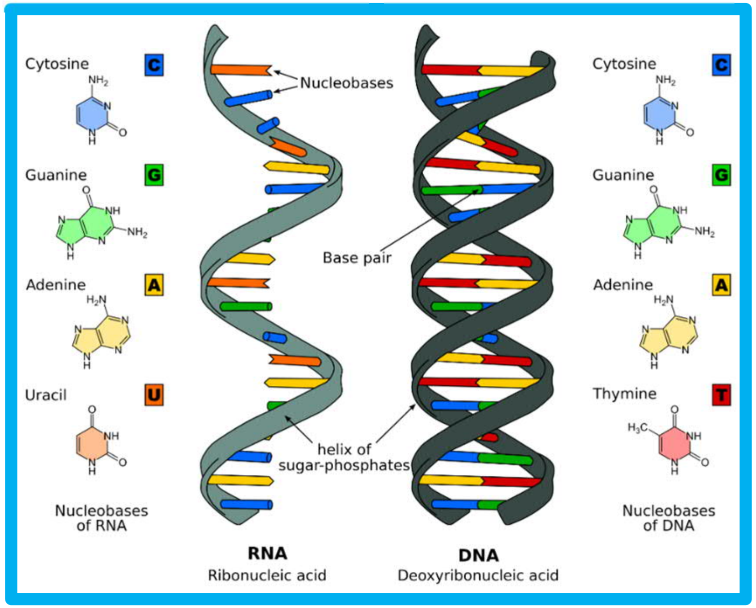
ALD/MLD Processes: Metal Precursors



ALD/MLD Processes: Organic Precursors

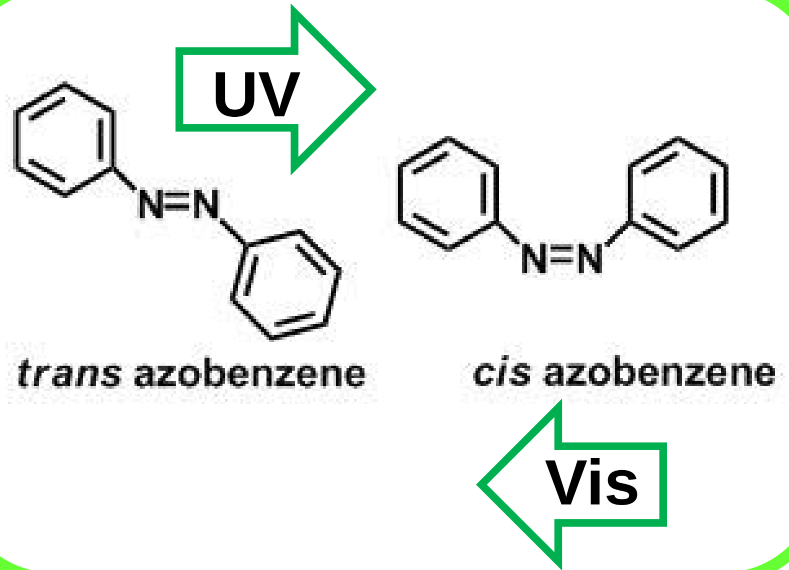
(with temperatures used for evaporation)

NUCLEOBASES FROM NATURE



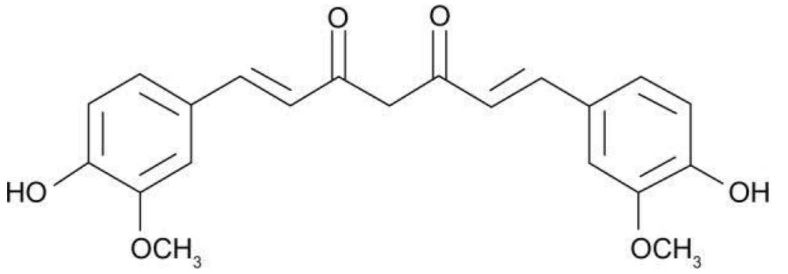
Z. Giedraityte, O. Lopez-Acevedo, L.A.E. Leal, V. Pale, J. Sainio, T.S. Tripathi & M. Karppinen, *J. Phys. Chem. C* **120**, 26342 (2016).

PHOTORESPONSIVE AZOBENZENE



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

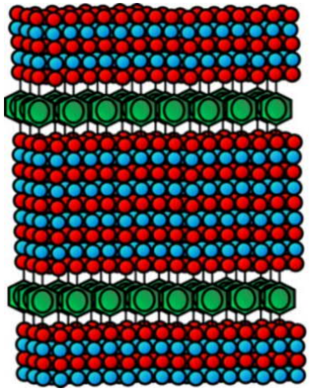
ANTIVIRAL CURCUMIN

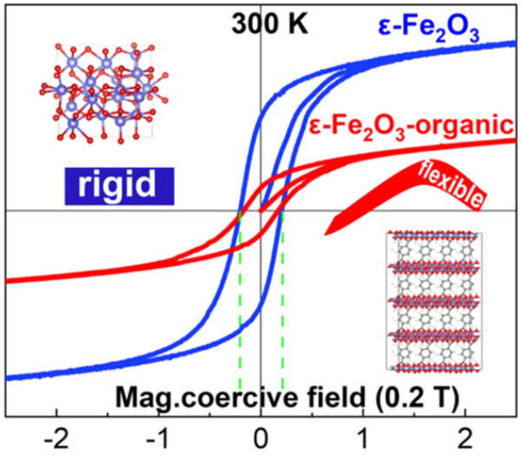


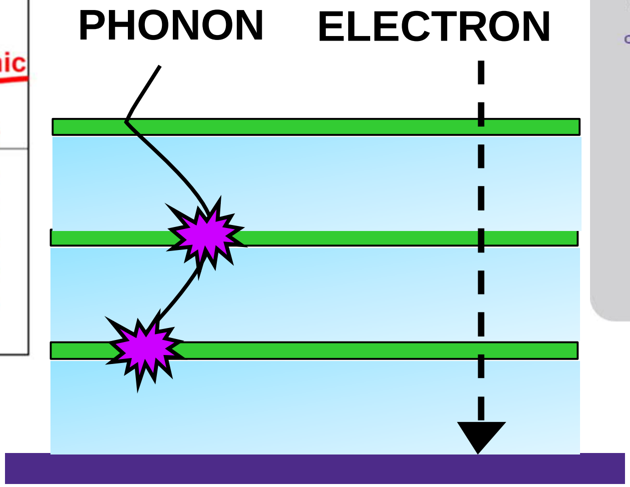
A. Philip, R. Ghiyasi & M. Karppinen, *ChemNanoMat* 7, 253 (2021).

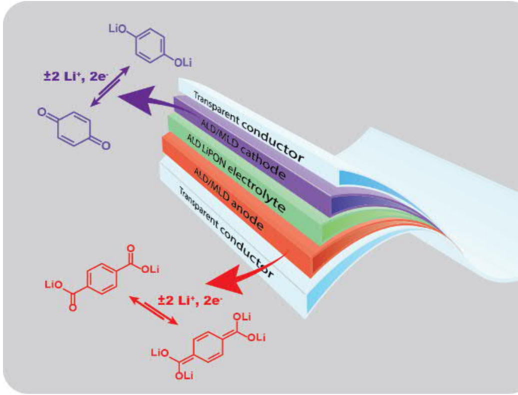
A!
Aalto University
School of Chemical
Engineering

NEW EXCITING ORGANIC COMPONENTS

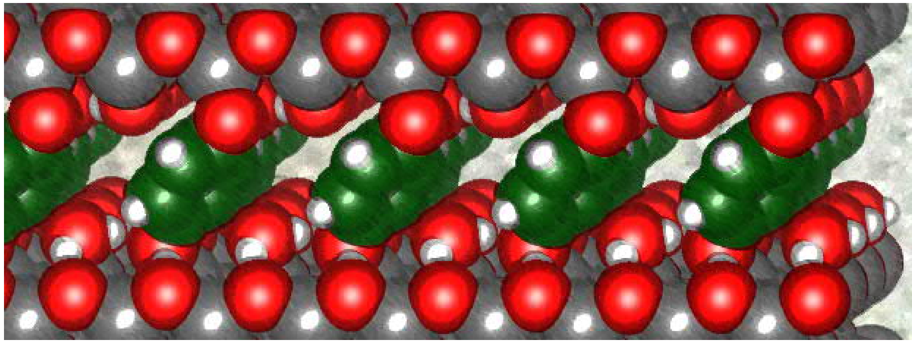


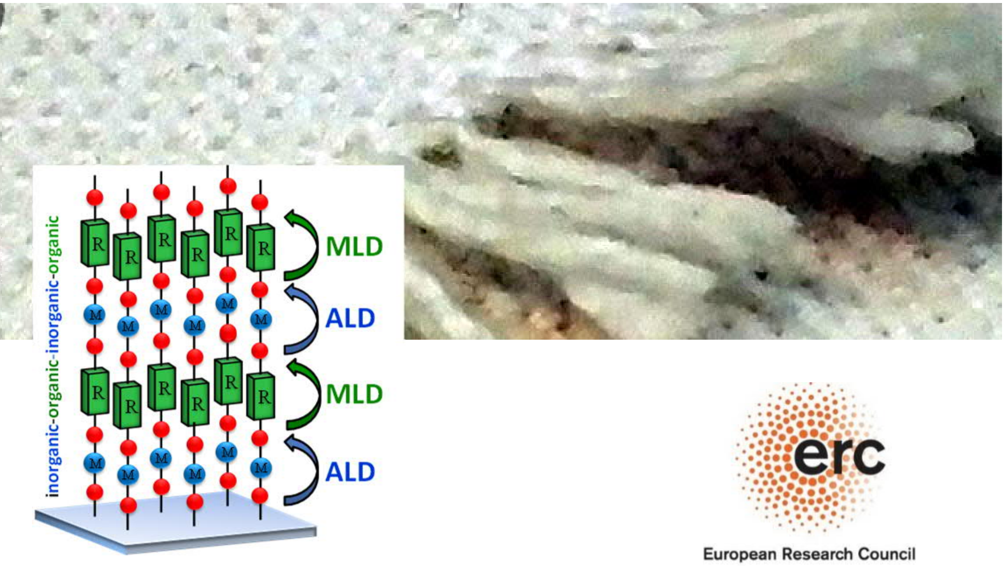






- **ALD/MLD can yield various new types of hybrid materials: new MOFs & layer-engineered superlattice and gradient materials**
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties have been discovered and much more expected !!!**





European Research Council