

# Europium



Aalto University  
School of Chemical  
Engineering

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# What and where?

Periodic Table of the Elements

The periodic table displays elements from Hydrogen (1) to Oganesson (118). The lanthanide series (La to Lu) and actinide series (Ac to Lr) are shown below the main table. The element Europium (Eu) is highlighted with a red box.

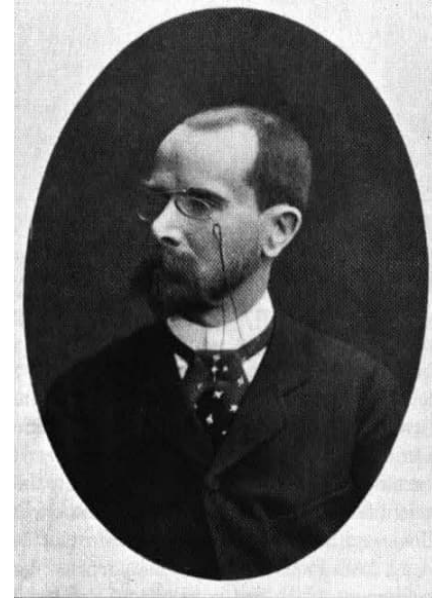
* 138.91 57 La Lanthanum (Std. At. Wt.)	140.12 58 Ce Cerium (Std. At. Wt.)	140.91 59 Pr Praseodymium (Std. At. Wt.)	144.24 60 Nd Neodymium (Std. At. Wt.)	(145) 61 Pm Promethium (Std. At. Wt.)	150.36 62 Sm Samarium (Std. At. Wt.)	<b>151.96 63 Eu Europium (Std. At. Wt.)</b>	157.25 64 Gd Gadolinium (Std. At. Wt.)	158.93 65 Tb Terbium (Std. At. Wt.)	162.50 66 Dy Dysprosium (Std. At. Wt.)	164.93 67 Ho Holmium (Std. At. Wt.)	167.25 68 Er Erbium (Std. At. Wt.)	168.93 69 Tm Thulium (Std. At. Wt.)	173.05 70 Yb Ytterbium (Std. At. Wt.)
* 227.10 89 Ac Actinium (Std. At. Wt.)	232.04 90 Th Thorium (Std. At. Wt.)	231.04 91 Pa Protactinium (Std. At. Wt.)	238.03 92 U Uranium (Std. At. Wt.)	237.05 93 Np Neptunium (Std. At. Wt.)	244.08 94 Pu Plutonium (Std. At. Wt.)	247.07 95 Am Americium (Std. At. Wt.)	251.10 96 Cm Curium (Std. At. Wt.)	261.10 97 Bk Berkelium (Std. At. Wt.)	267.10 98 Cf Californium (Std. At. Wt.)	288.10 99 Es Einsteinium (Std. At. Wt.)	287.10 100 Fm Fermium (Std. At. Wt.)	289.10 101 Md Mendelevium (Std. At. Wt.)	289.10 102 No Nobelium (Std. At. Wt.)

# History of Europium

**Discovered 1901 by E.A. Demarcay in France** [1]

- Not your ordinary scientist:
  - Abandoned his academic career to travel the world
  - Only short bibliography left of his work

**Origin of the name: Europe** [2]



# How was Europium discovered?

**Demarcay proposed in 1896 that an element lay between Samarium and Gadolinium.**

**A spark spectrum instrument built by E.A. Demarcay**

- Used to follow the separation of rare earth elements

**New separation technique developed by E.A. Demarcay**

- Involved crystallization of double magnesium nitrate salts.

**-> Separation and announcement of new element 1901. [1]**

# Abundance & world production

One of the rare earth elements

In earth crust: 2-2.2 ppm <sup>[2]</sup>

Does not occur on its own

Mined together with other rare earth elements.

600 tons produced in 2010. <sup>[3]</sup>



# Europium in general

Pale yellow tint

Density 5.234 g/cm<sup>3</sup>

Melting point 822 °C

Boiling point 1429 °C

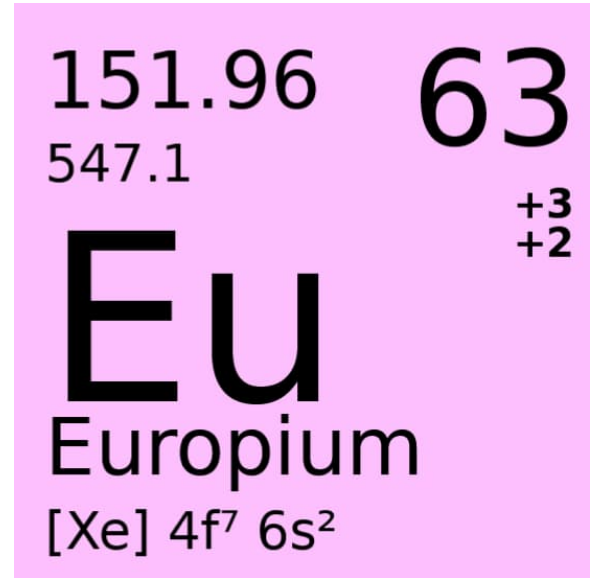
Electrical resistivity 90 μΩcm

Naturally occurring isotopes: <sup>151</sup>Eu & <sup>153</sup>Eu

<sup>151</sup>Eu half-life 5x10<sup>18</sup>

<sup>153</sup>Eu stable

[2]



# Chemistry of Europium

Crystal structure: bcc

Oxidation states +2 and +3 possible

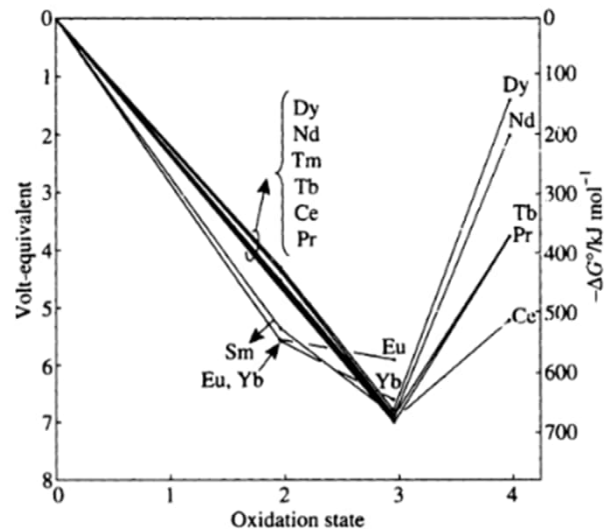
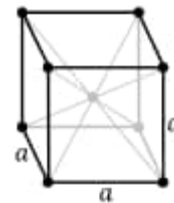
Metal radius (CN6) 2,084 Å

Ionic radius (CN6):

+2: 1,17 Å

+3: 0,947 Å

- Most reactive



[2]

# Compounds and applications

**A''**

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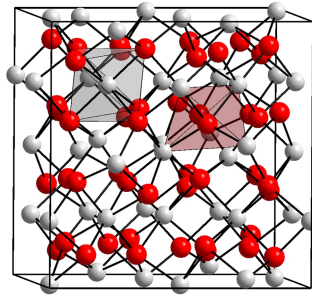
Alchemy 2019. GRAPHIC BY: Julie Ho. TWITTER, FACEBOOK: @alchemyviz



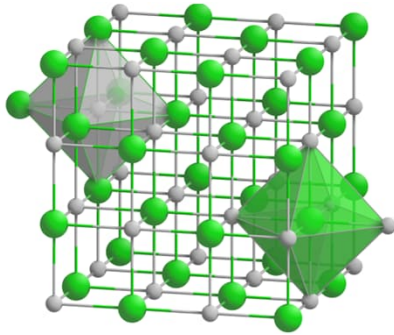
# Oxides



non-magnetic  
luminescent



magnetic  
semiconductor



Under  
UV light

Phosphor powder



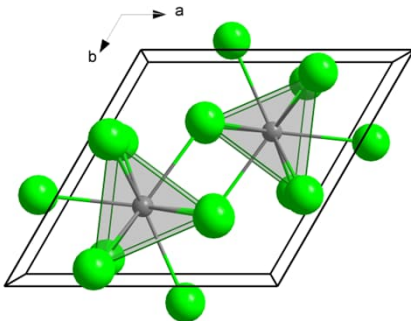
**A?**

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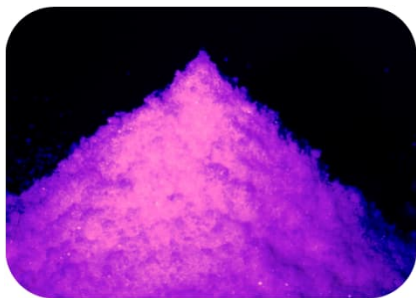
# Halides and sulfide

Eu can form **divalent** or **trivalent** compounds with all halogen elements

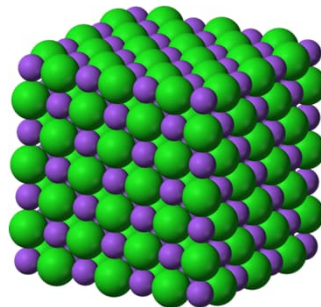
Eu(III)  
chloride



EuCl<sub>3</sub>·6H<sub>2</sub>O



Europium(II) sulfide



Eu-S bond lengths: 2.41 Å

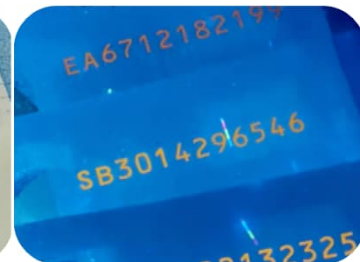
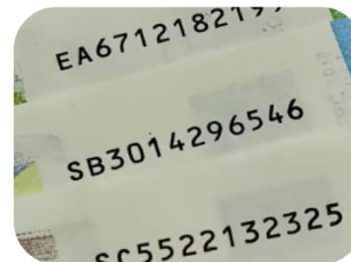
melting point: 2250°C

insulating ferromagnets

ferromagnetic semiconductors

# banknote

Eu(III) complex

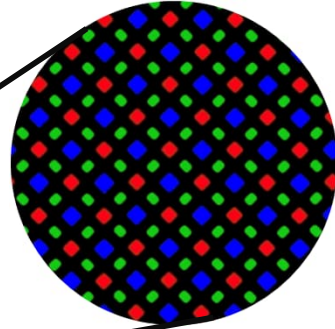
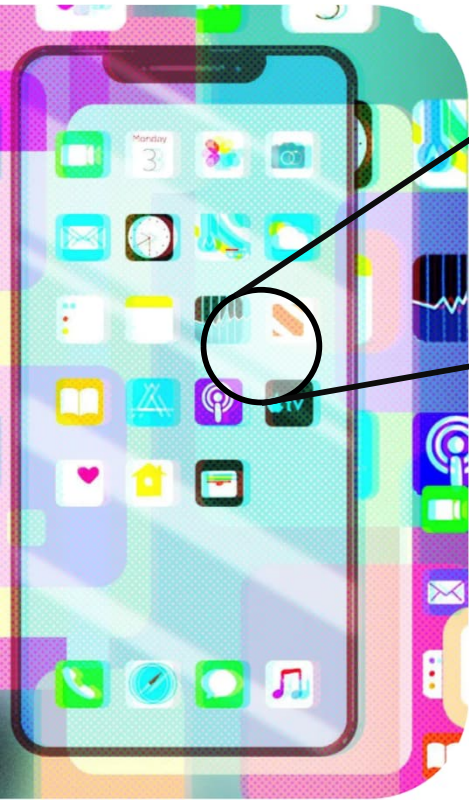


Eu(III) complex



Eu(III) complex

# OLED



Which color  
is Europium  
mostly  
contributed to?

OLED



LCD



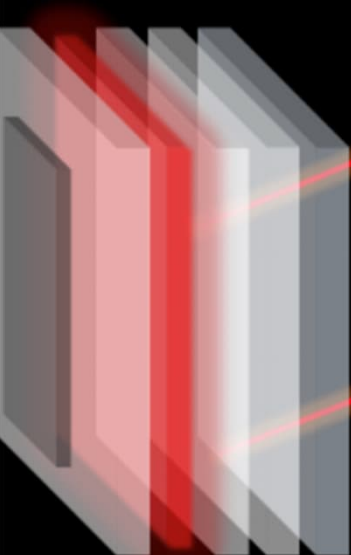
Thinner and lighter

Better viewing angles

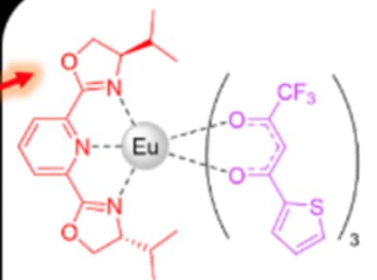
Better contrast ratios

# OLED

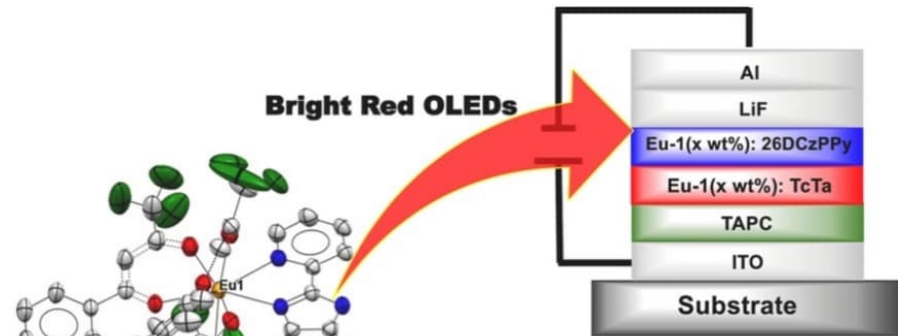
OLED  
electroluminescence



$\text{Eu}(\text{TTA})_3\text{Phen}$



$\text{Eu}(\text{TTA})_3\text{PrPyBox}$



[5]

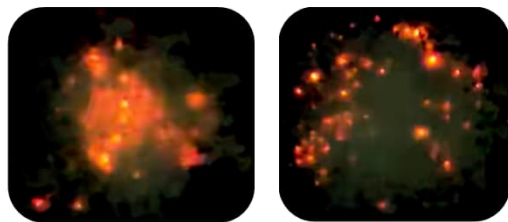
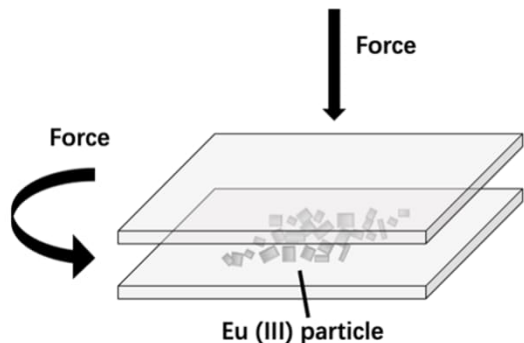
Eu(III)

[4]

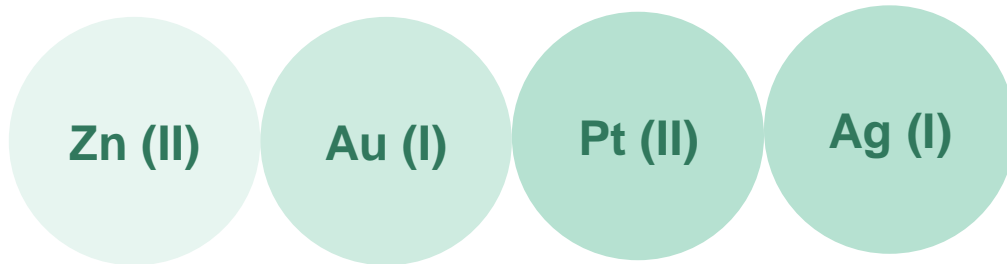
Eu (II)

# Mechanochromic luminescence

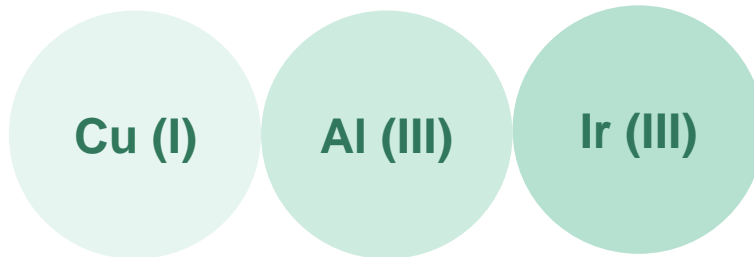
changes **emission color** by applying **mechanical stimuli** such as grinding, shearing, smashing, or rubbing



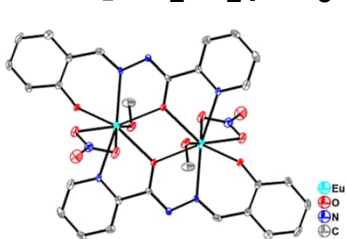
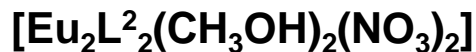
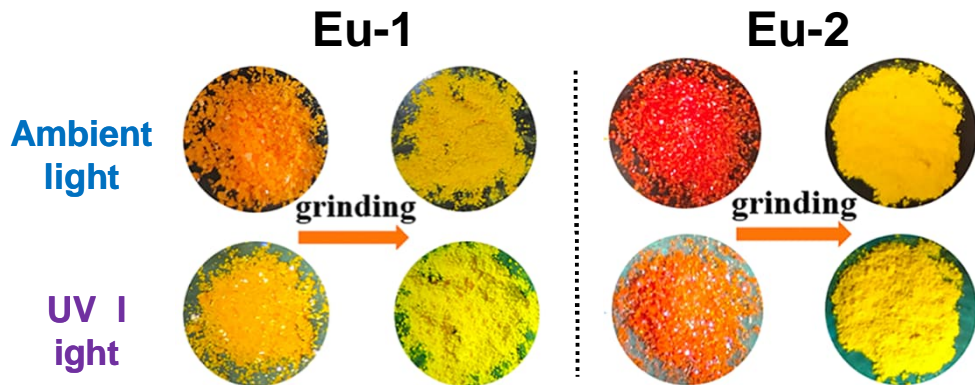
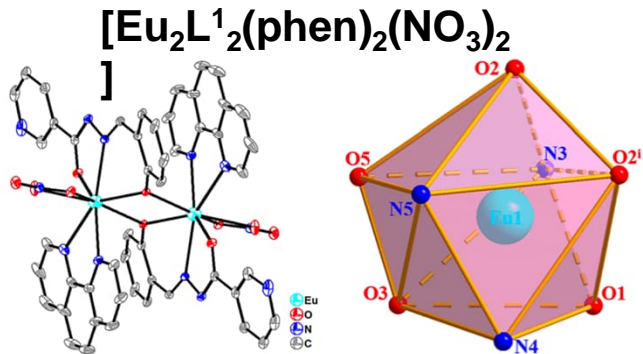
Tetra(1,3-diphenyl-1,3-propanedionato) europium(III) triethanolamine



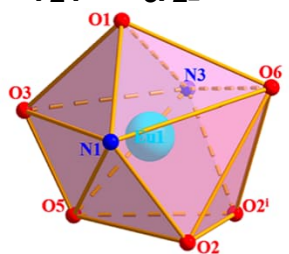
metal complex systems



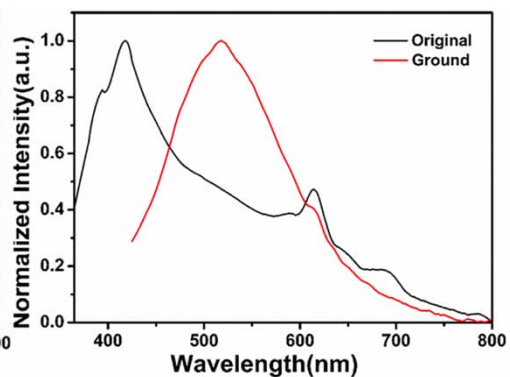
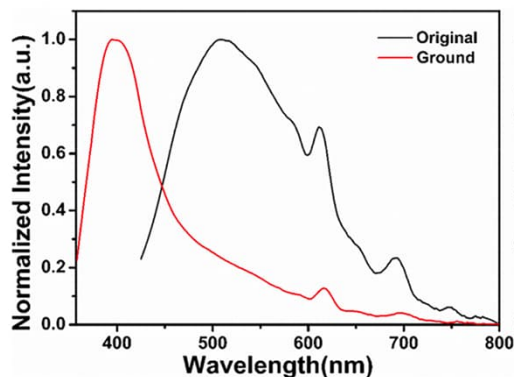
# Mechanochromic Luminescence



binuclear molecule



coordination polyhedron around  $\text{Eu}^{3+}$

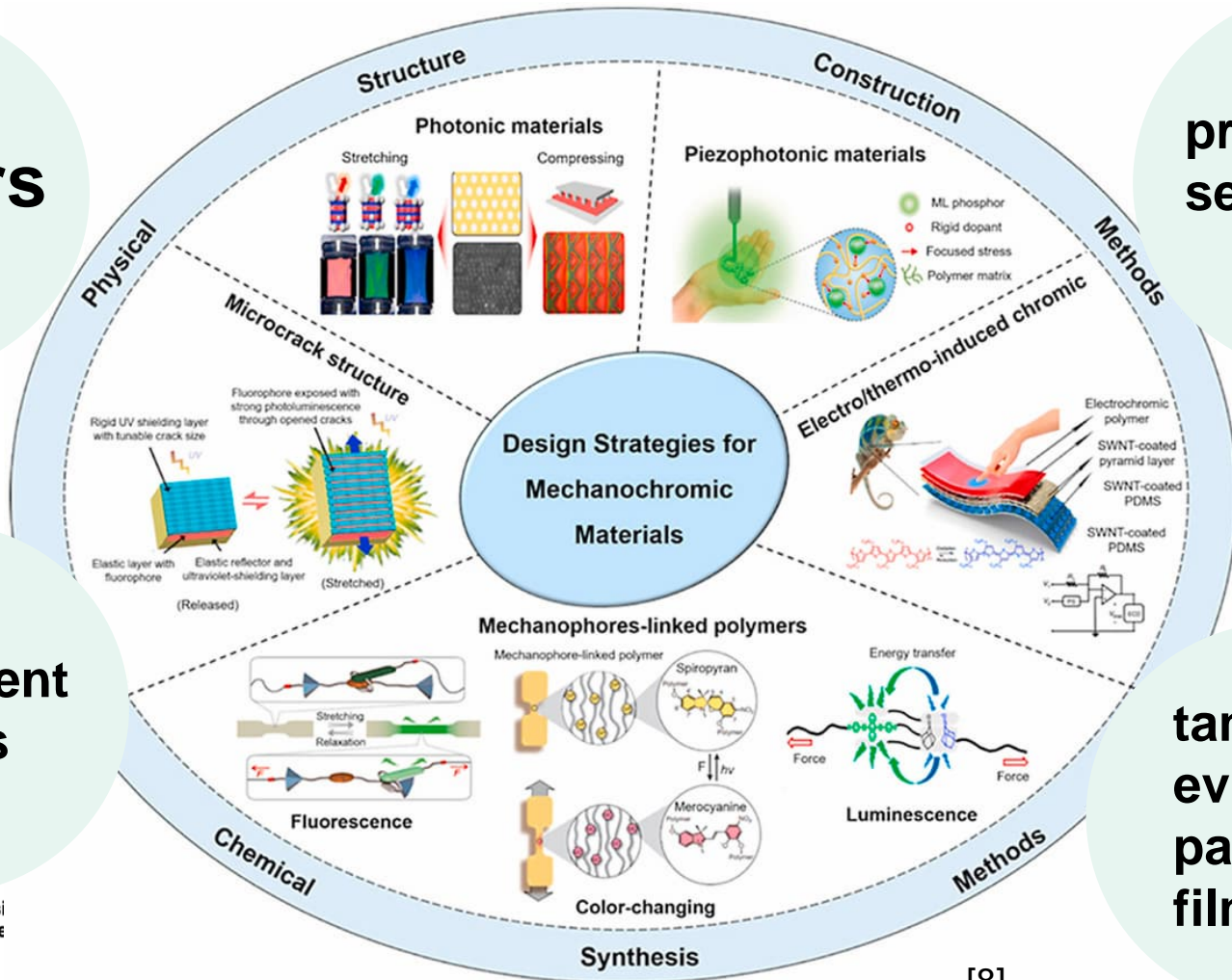


sensors

pressure-sensing films

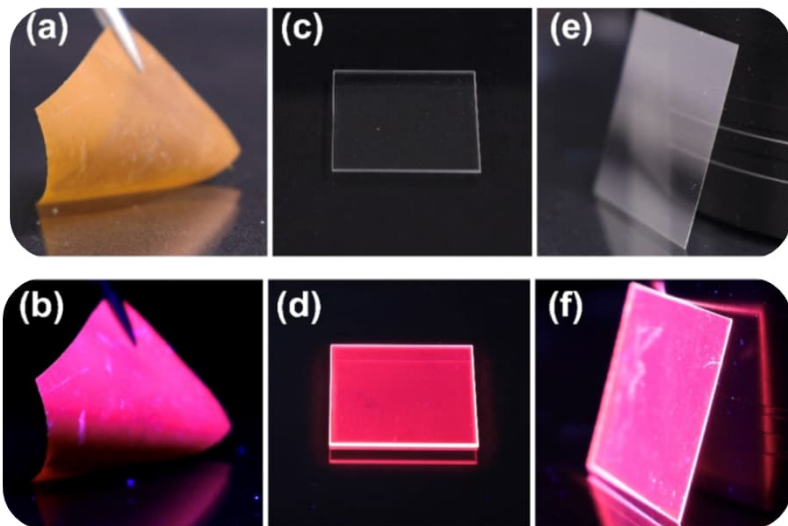
fluorescent switches

tamper-evidencing packaging films



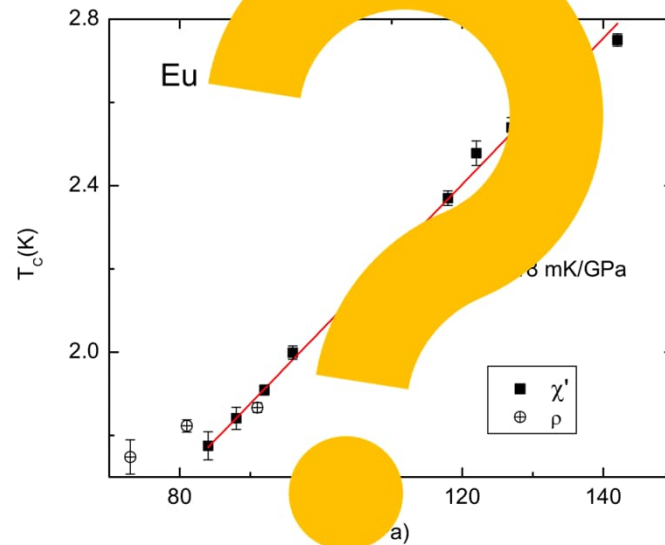


# ALD and superconductor



ALD/MLD thin film phosphors on various kinds of substrate materials [9]

2009 Debess, ... ka, et.al



[10]

2021 J.E. Hirsch:  
**Is that true?** [11]

# Thank you for your attention



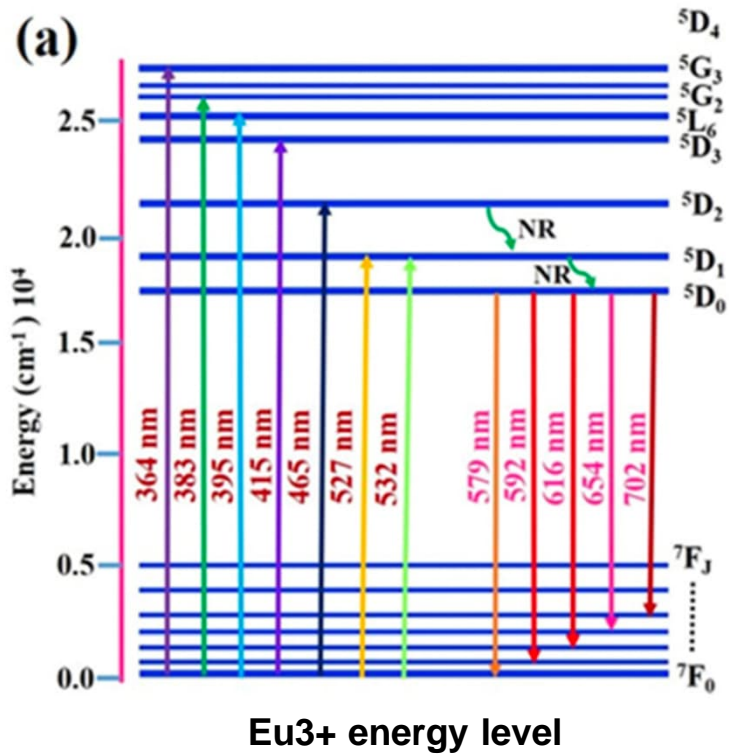
[aalto.fi](http://aalto.fi)



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# References

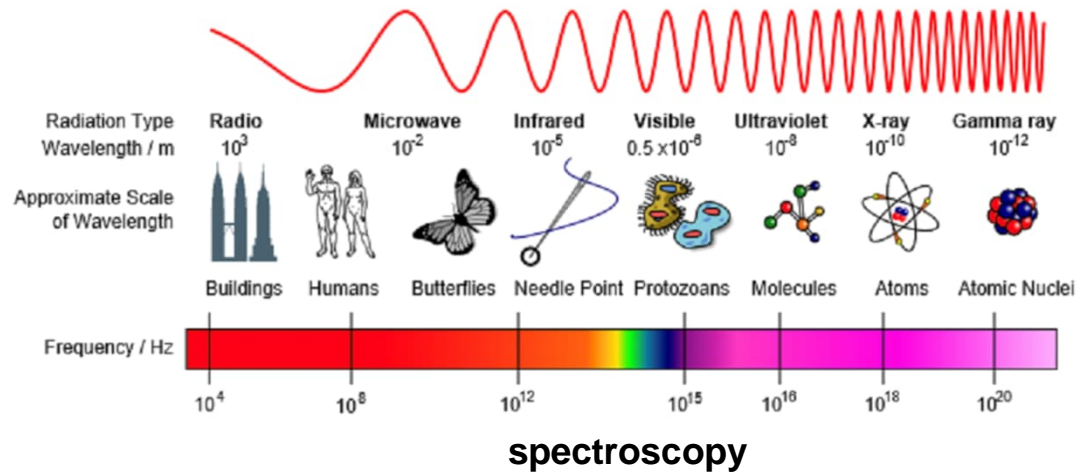
- [1] J. L. Marshall and V. R. Marshall, "Rediscovery of the Elements: Europium-Eugene Demarcay," *THE HEXAGON*, (2003): 19–21.
- [2] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed. Oxford: Elsevier Butterworth-Heinemann, 1997.
- [3] Anonymous, "Europium, Eu, ordinal 63 ." Accessed: Oct. 01, 2023. [Online]. Available: <https://en.institut-seltene-erden.de/seltene-erden-und-metalle/seltene-erden/Europium/#:~:text=Extraction%20of%20europium,to%20the%20metal%20and%20sublimated>
- [4] Zinna, Francesco, et al. "Impact of chiral ligands on photophysical and electro-optical properties of  $\beta$ -diketonate europium complexes in circularly polarized OLEDs." *Chirality*, 35.5 (2023): 270-280.
- [5] Ilmi, Rashid, et al. "A tris  $\beta$ -diketonate europium (III) complex based OLED fabricated by thermal evaporation method displaying efficient bright red emission." *Organic Electronics* 96 (2021): 106216.
- [6] Zhang, Xiqi, et al. "Recent advances in mechanochromic luminescent metal complexes." *Journal of Materials Chemistry C* 1.21 (2013): 3376-3390.
- [7] Xiao, Tong, et al. "Hydrazone-Based Europium (III) Complexes: Mechanochromic Luminescence and Turn-On Fluorescence Detection of Quinolone Antibiotics in Human Urine." *Crystal Growth & Design* 23.8 (2023): 5957-5964.
- [8] Guo, Quanquan, and Xinxing Zhang. "A review of mechanochromic polymers and composites: From material design strategy to advanced electronics application." *Composites Part B: Engineering* 227 (2021): 109434
- [9] Ghazy, Amr, Mika Lastusaari, and Maarit Karppinen. "Excitation Wavelength Engineering through Organic Linker Choice in Luminescent Atomic/Molecular Layer Deposited Lanthanide–Organic Thin Films." *Chemistry of Materials* 35.15 (2023): 5988-5995.
- [10] M. Debossai, T. Matsuoka, J. J. Hamlin, J. S. Schilling, K. Shimizu, Pressure-induced superconducting state of europium metal at low temperatures, *PRL* 102 (2009) 197002.
- [11] Hirsch, J. E. "About the pressure-induced superconducting state of europium metal at low temperatures." *Physica C: Superconductivity and its Applications* 583 (2021): 1353805.

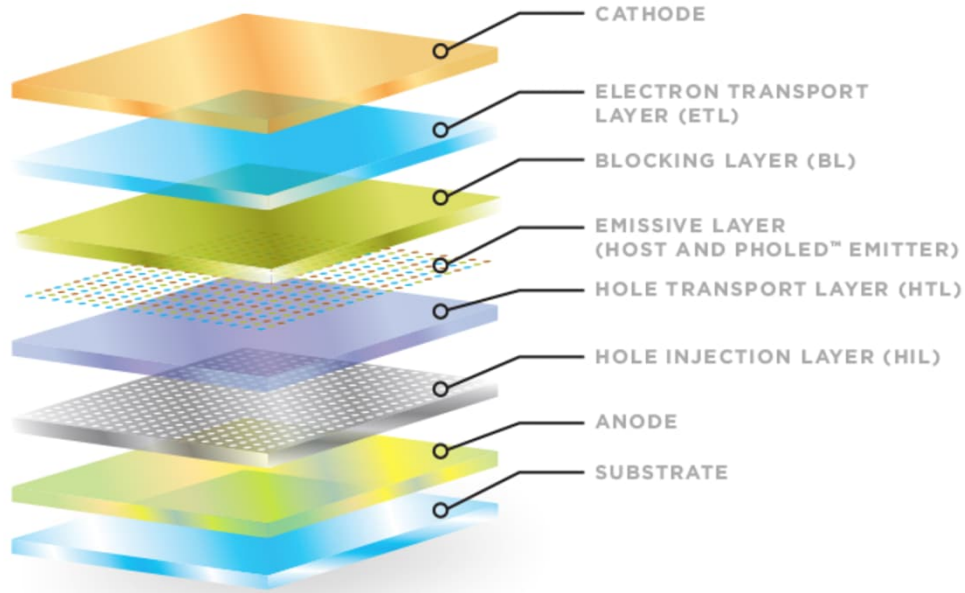


Eu<sup>3+</sup> energy level

Schematic representation of the **Eu<sup>3+</sup> energy level** showing the pertinent electronic transitions

europium ( $\text{Eu}^{2+}, \text{Eu}^{3+}$ )  
 praseodymium ( $\text{Pr}^{3+}$ )  
 samarium ( $\text{Sm}^{3+}$ )





structure of OLED  
(Organic light-emitting diodes)

## Emissive Layer

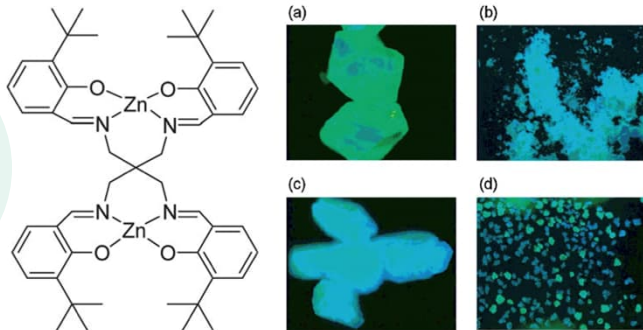
**Heart** of the device and where light is made

The emissive layer consists of a color-defining emitter doped into a host

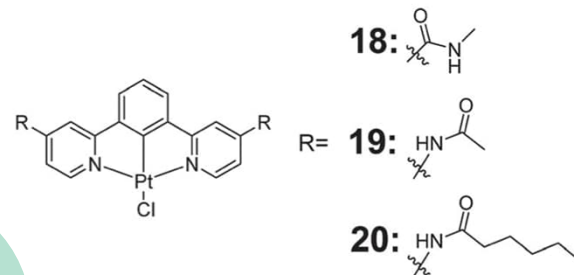
Where the **electrical energy** is directly converted **into light**.

# Mechanochromic luminescence

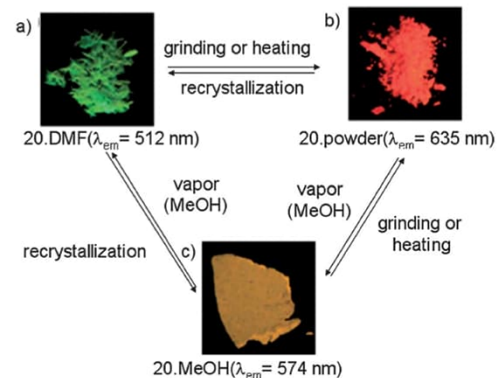
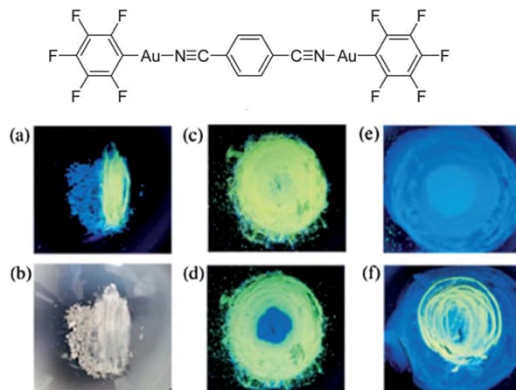
Zn (II)



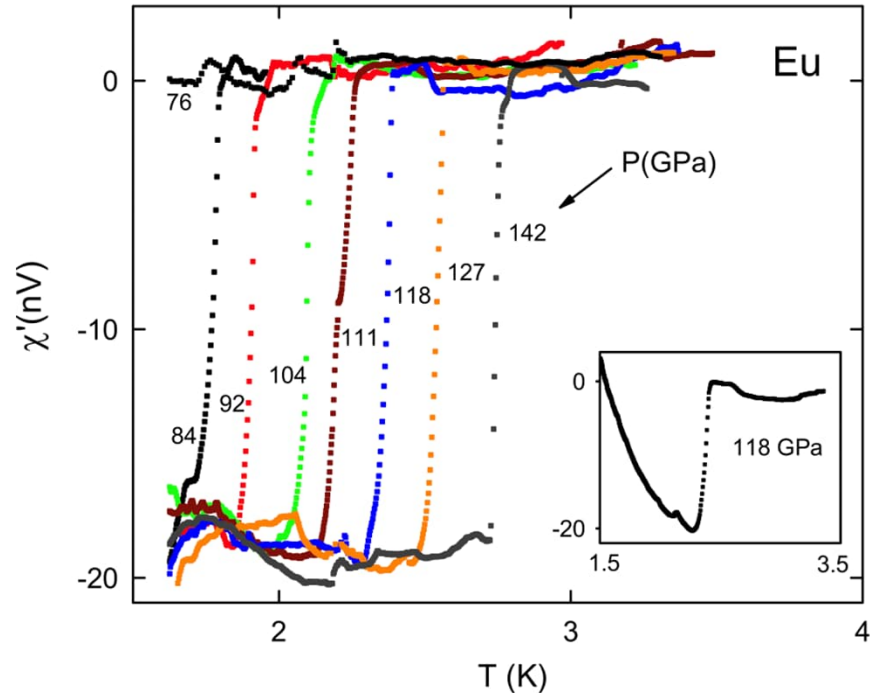
Pt (II)



Au (I)



# superconductor



The superconducting transition appears at 84 GPa and shifts slowly under pressure to higher temperatures.

## J.E. Hirsch:

"it was reported that the element Eu becomes superconducting in the pressure and temperature range [84–142 GPa], [1.8–2.75 K]. The claim was largely based on AC susceptibility measurements. Here I point out that recently reported ac susceptibility measurements on a hydride compound under pressure that appears to become superconducting near room temperature (Nature 586 (2020) 373) cast serious doubt on the validity of the results for Eu as well as for the hydride."

