

# Photon-induced reactions in hybrid molecular EUV photoresists

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ADVANCED RESEARCH CENTER FOR NANOLITHOGRAPHY

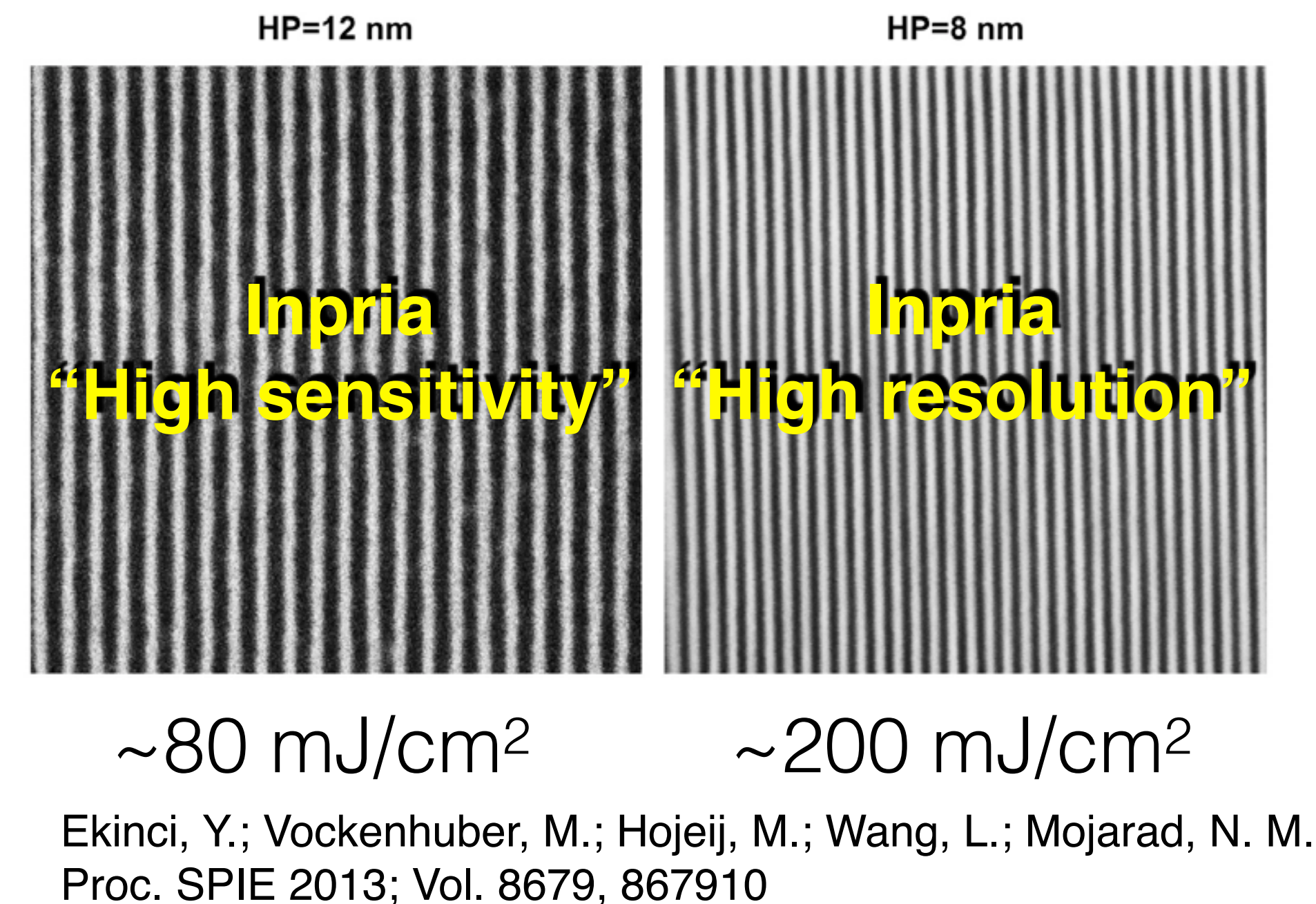
# main contributors

- dr. Sonia Castellanos (Group Leader EUV Photoresists)
- Lianjia Wu, Neha Thakur, dr. Ivan Beshpalov (EUV Photoresists)
- dr. Yu Zhang, dr. Jarich Haitjema (PhD students Nanophotochemistry)



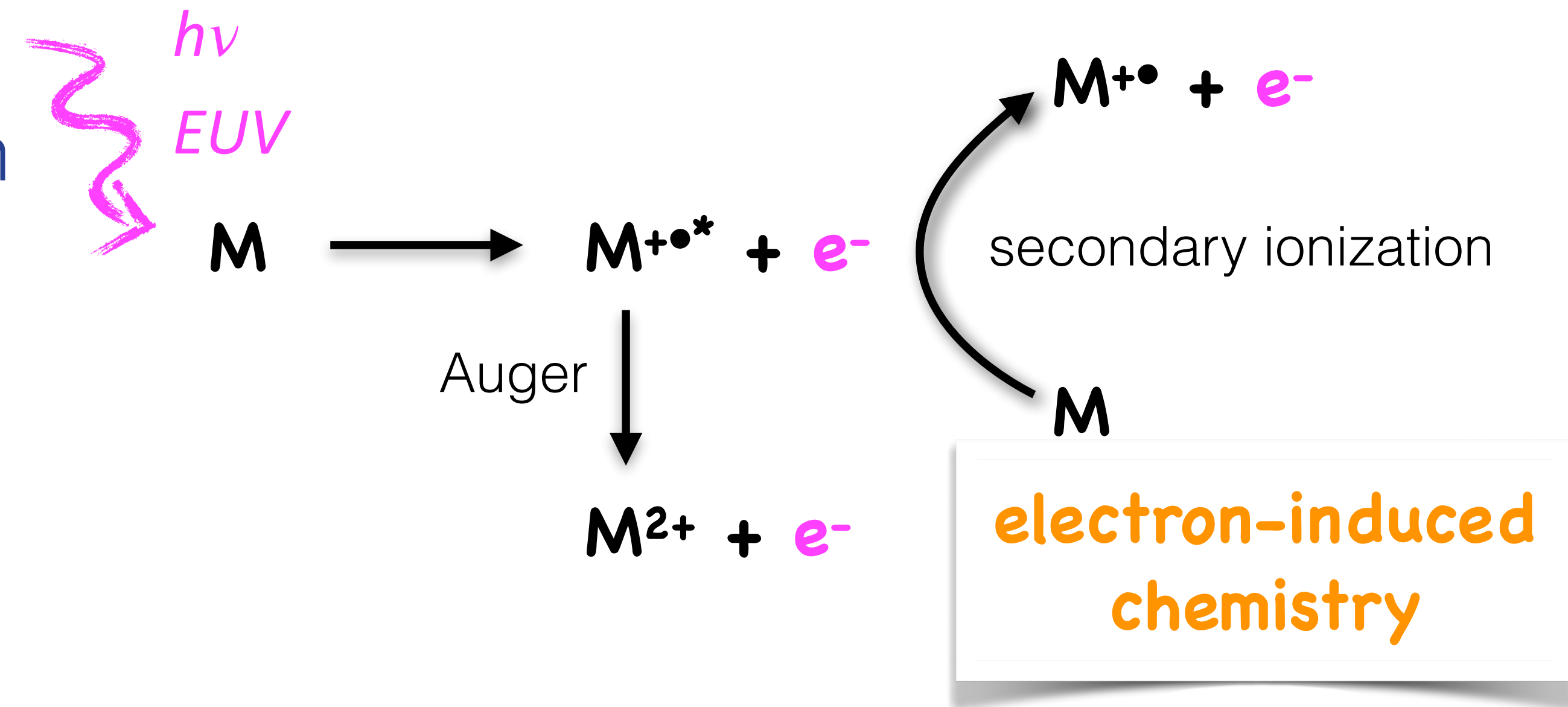
# EUV photo-resists

- *photoreactive* and *resistent* to etch
- requirements
  - sensitive
  - precise
    - small features ( $\sim 10$  nm)
    - accurate pattern ( $< 10\%$ )
- *understanding of chemistry and physics*



# EUV photoactivation

- 92 eV photons: ionizing radiation
- electrons kicked out of atomic and molecular orbitals
- secondary electrons
- two kinds of reactive species:
  - holes = ionized molecules
  - electrons = reduced molecules





# hybrid molecules

- combine organic and inorganic chemistry
  - organic: well established and understood reactivity
  - inorganic: absorption of high-energy photons, etch resistance
- molecular size  $\sim 1 \text{ nm}^3$ ; potential for suitable resolution

# periodic table of EUV absorption

- sensitivity requires sufficient absorption of 92 eV photon

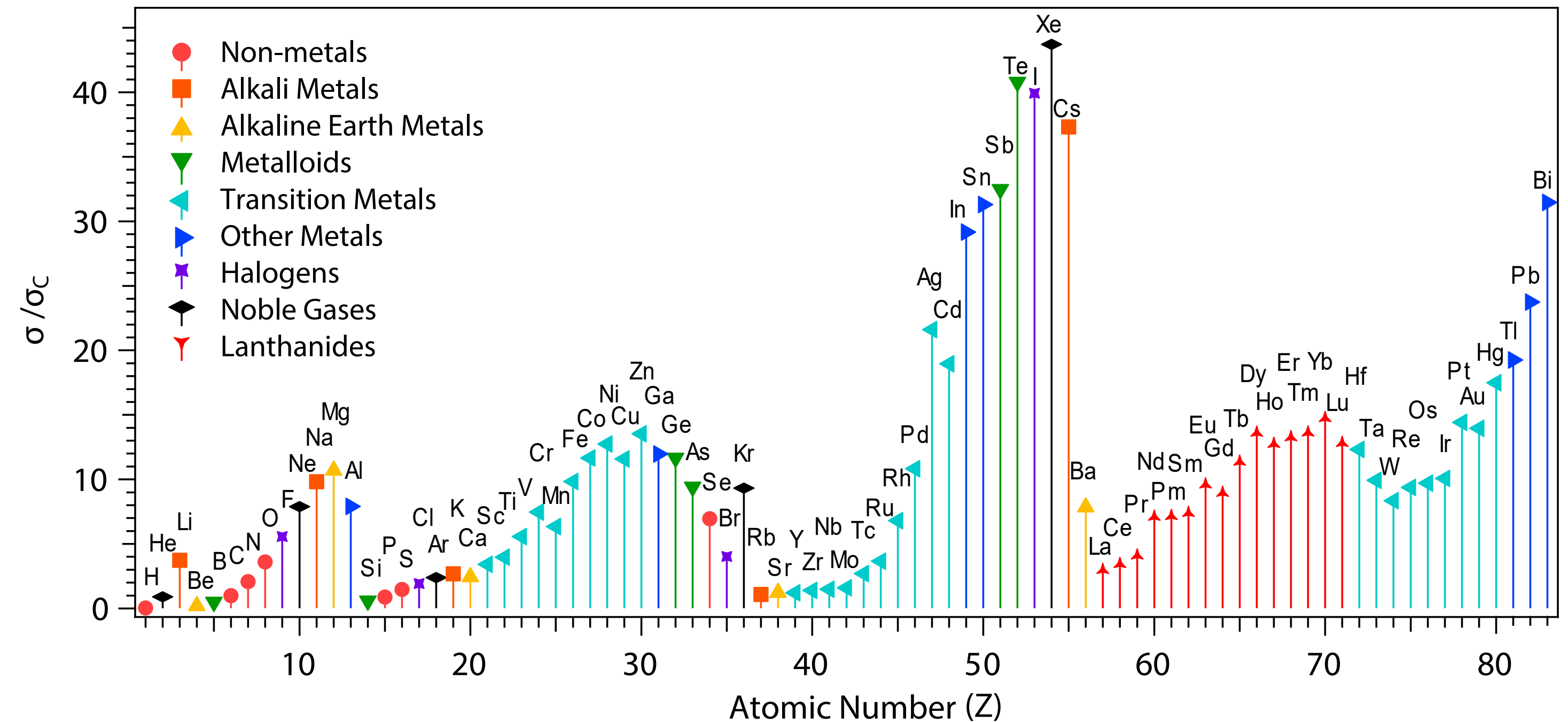


figure from Lianjia Wu

# periodic table of EUV absorption

- many metals absorb strongly

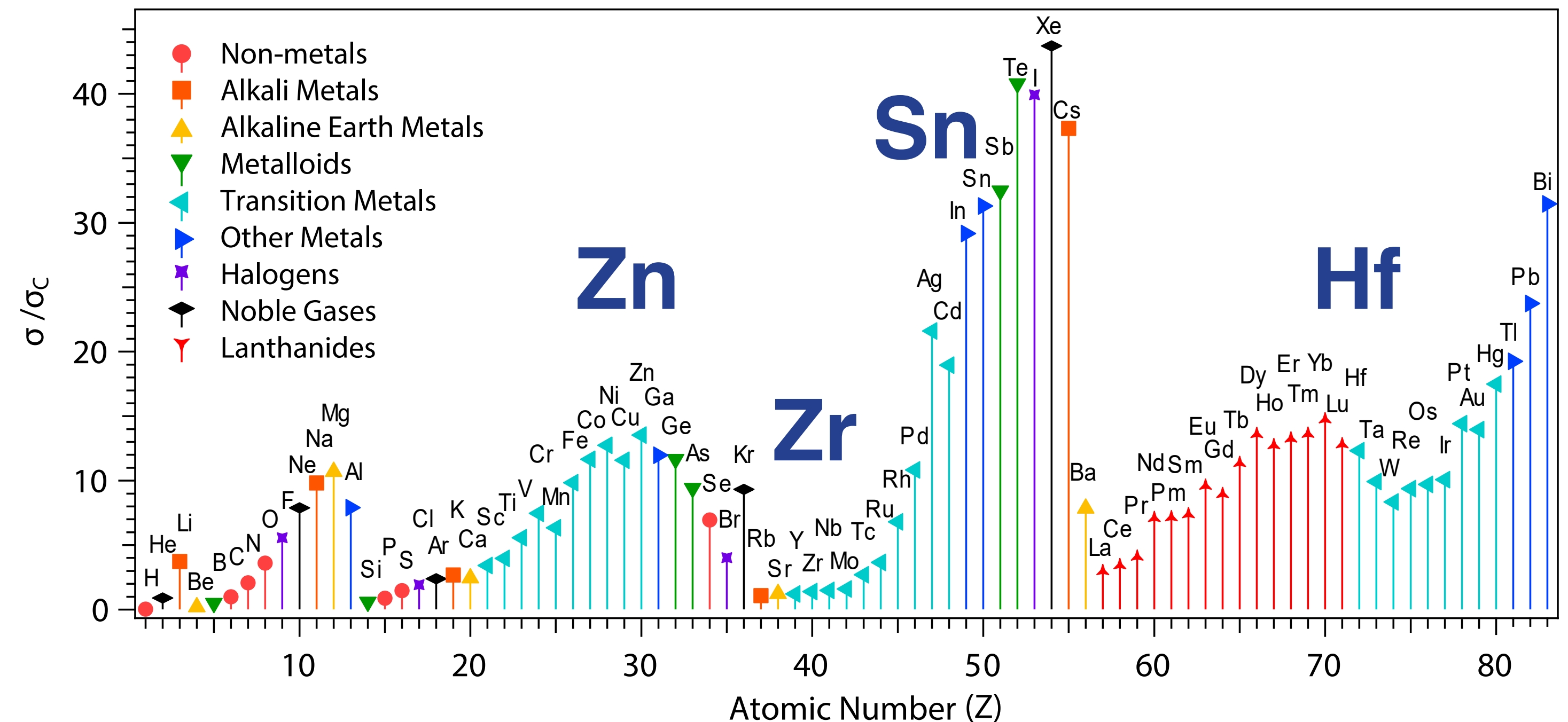
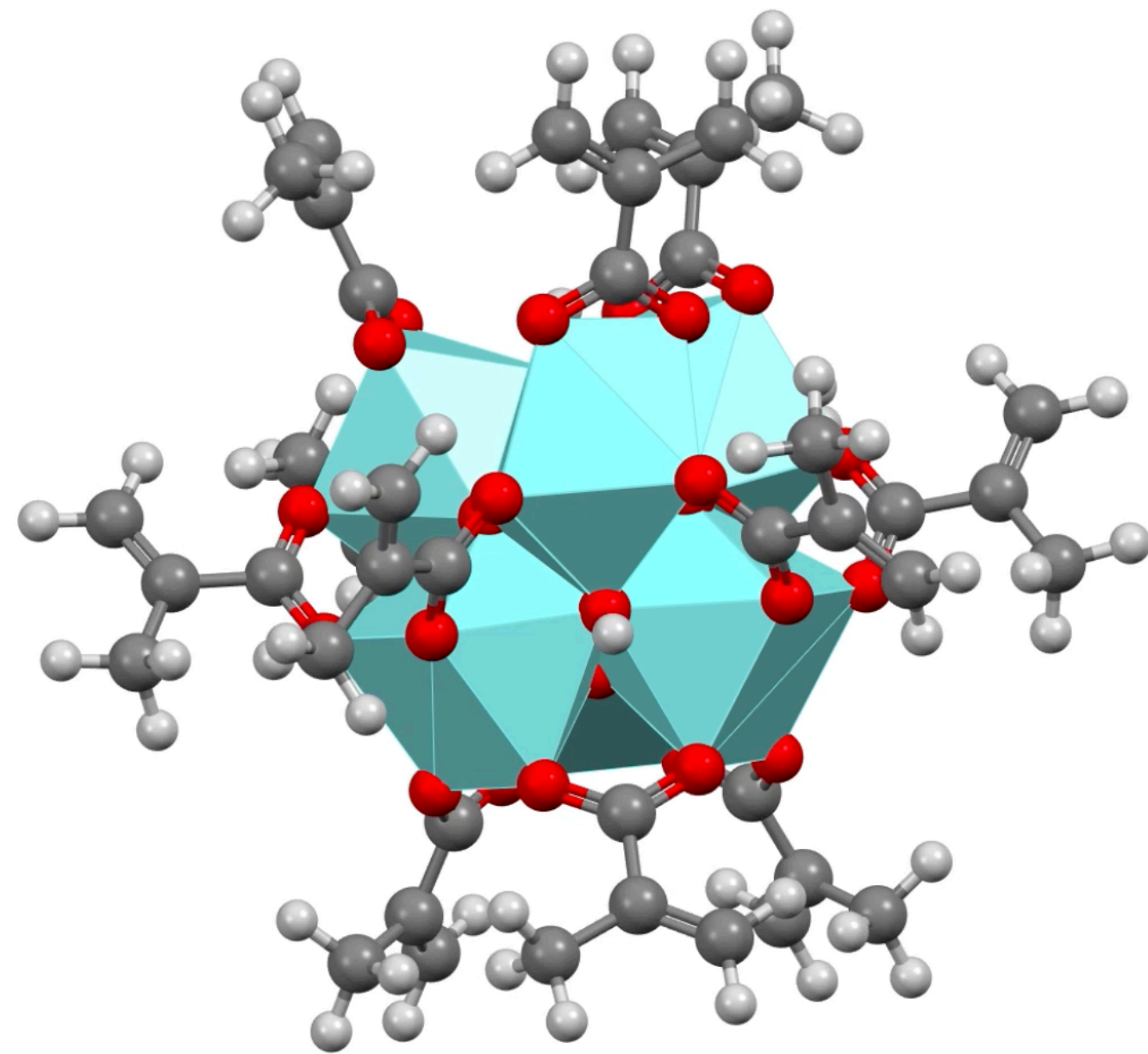
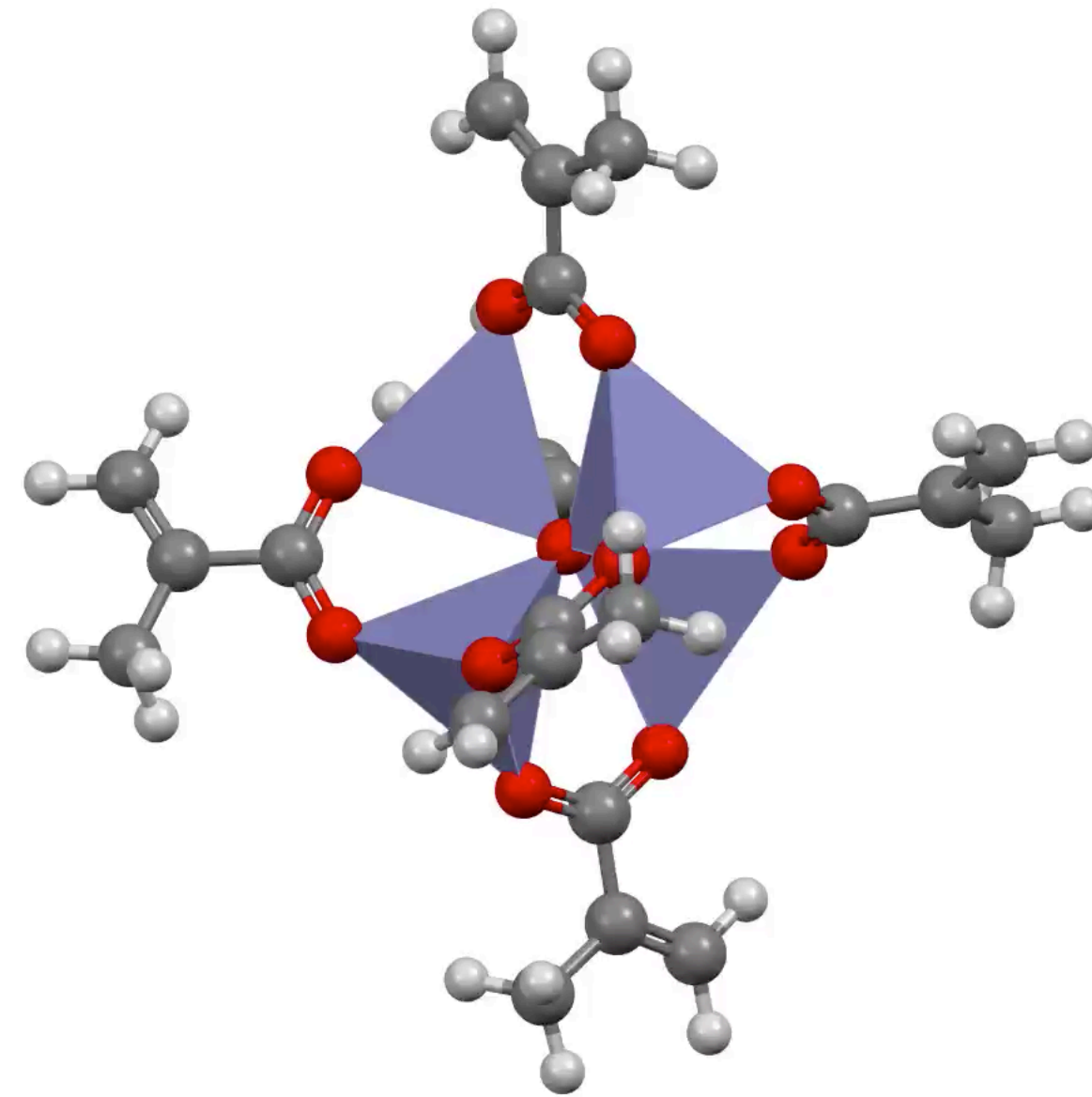


figure from Lianjia Wu

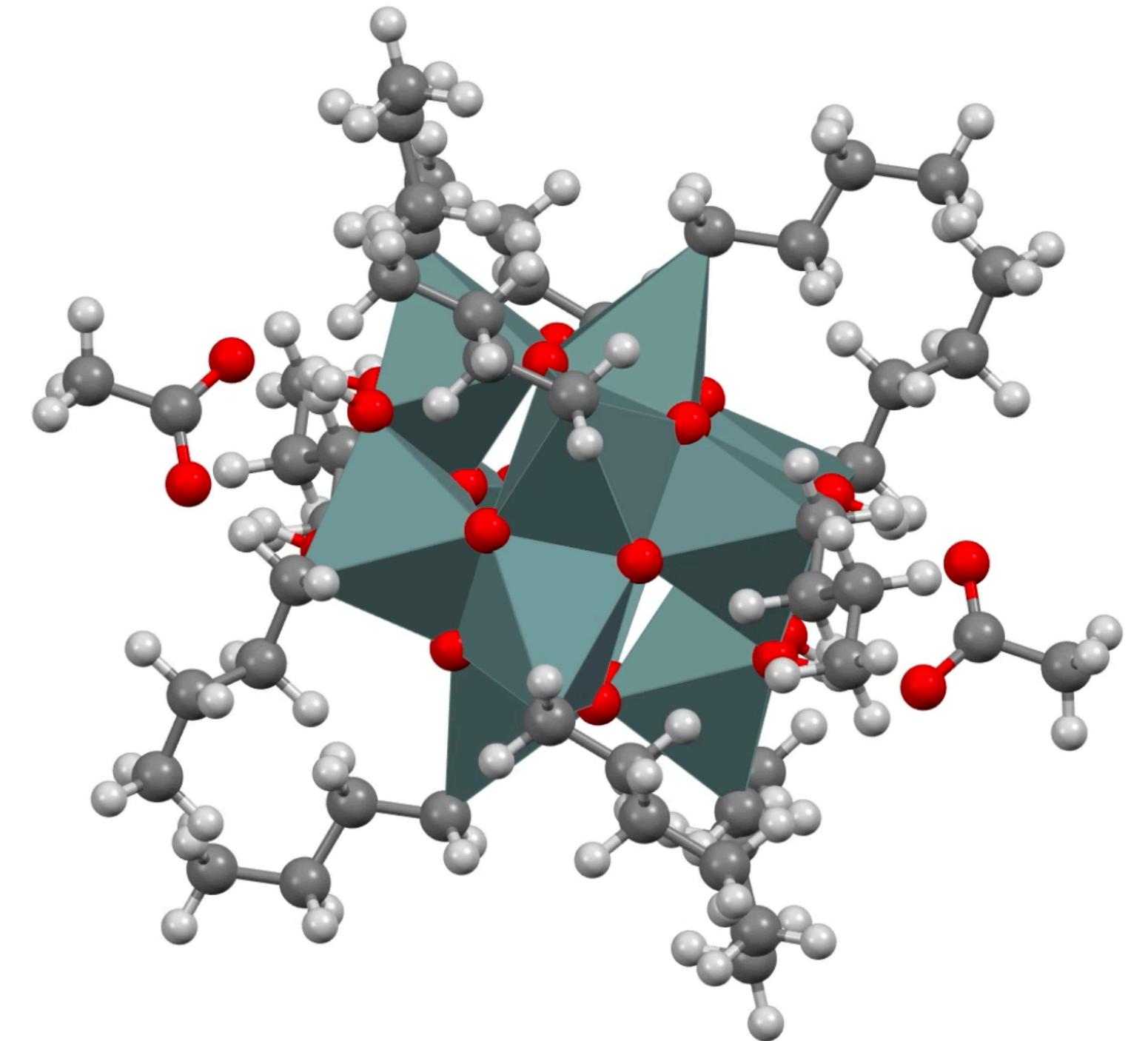
# materials & methods



$\text{Zr}_6$  oxo cluster



$\text{Zn}_4$  oxo cluster

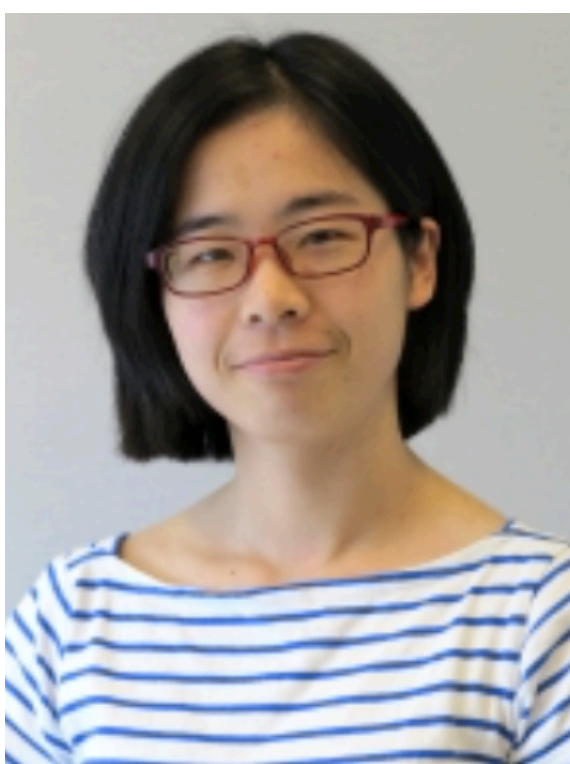


$(\text{nBu-Sn})_{12}$  oxo cage

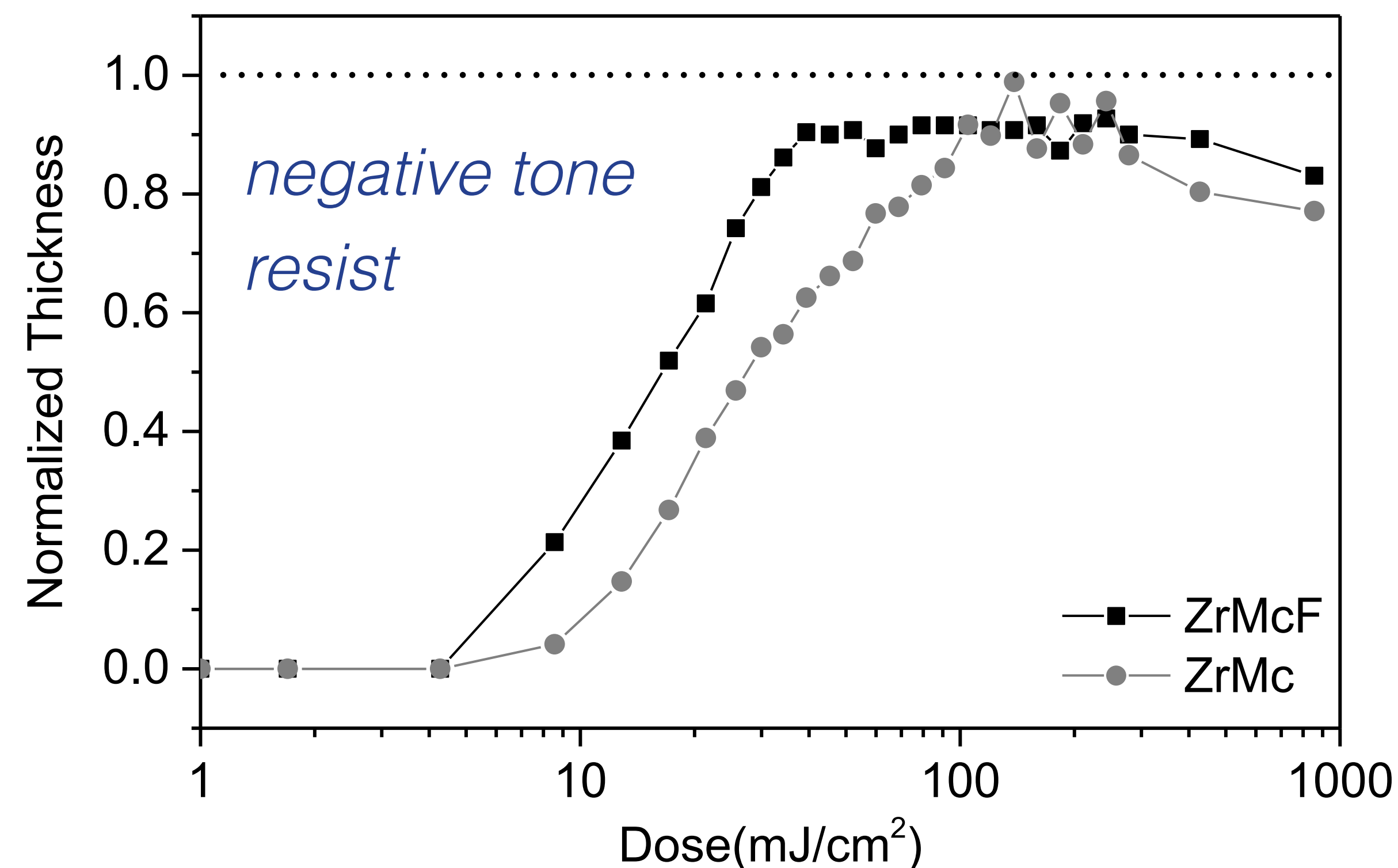
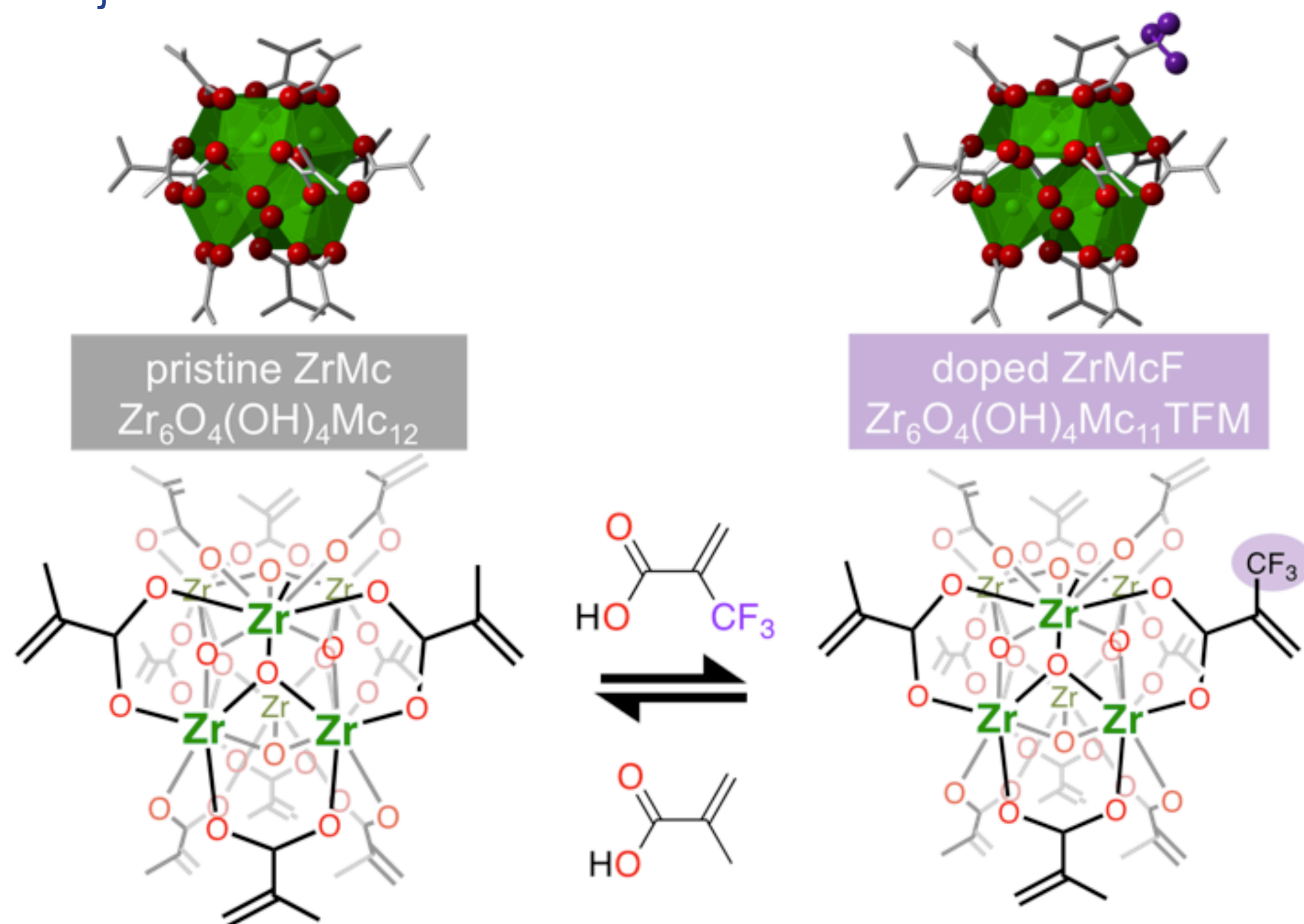
- design & synthesis — pattern formation — spectroscopy



# zirconium oxo clusters

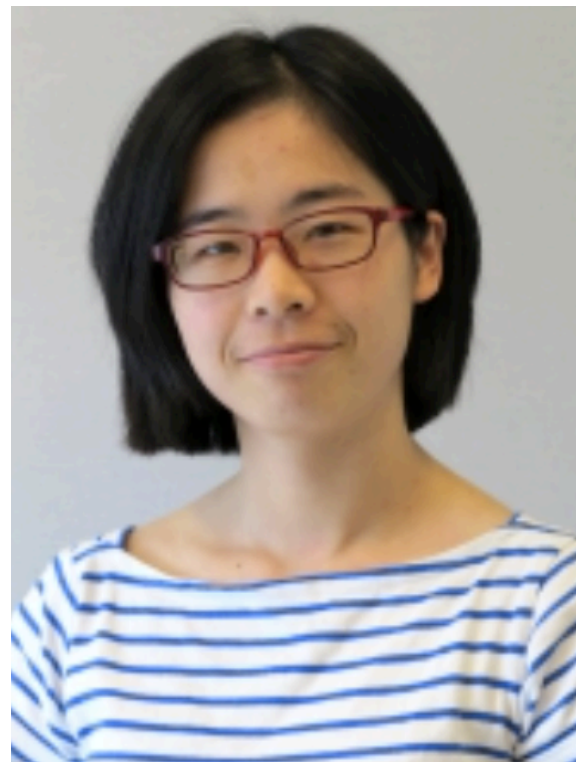


Lianjia Wu

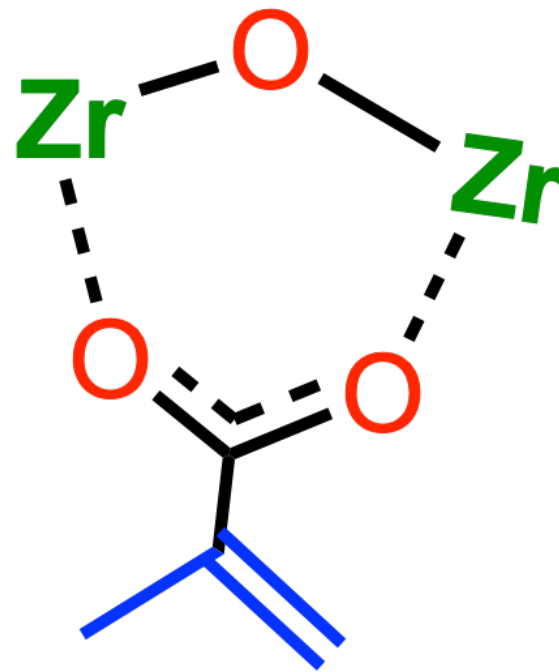


“Unravelling the effect of fluorinated ligands in hybrid Extreme Ultraviolet photoresists by X-ray spectroscopy”  
(J. Mater. Chem. C, doi:10.1039/d0tc03216f Hot Paper!)

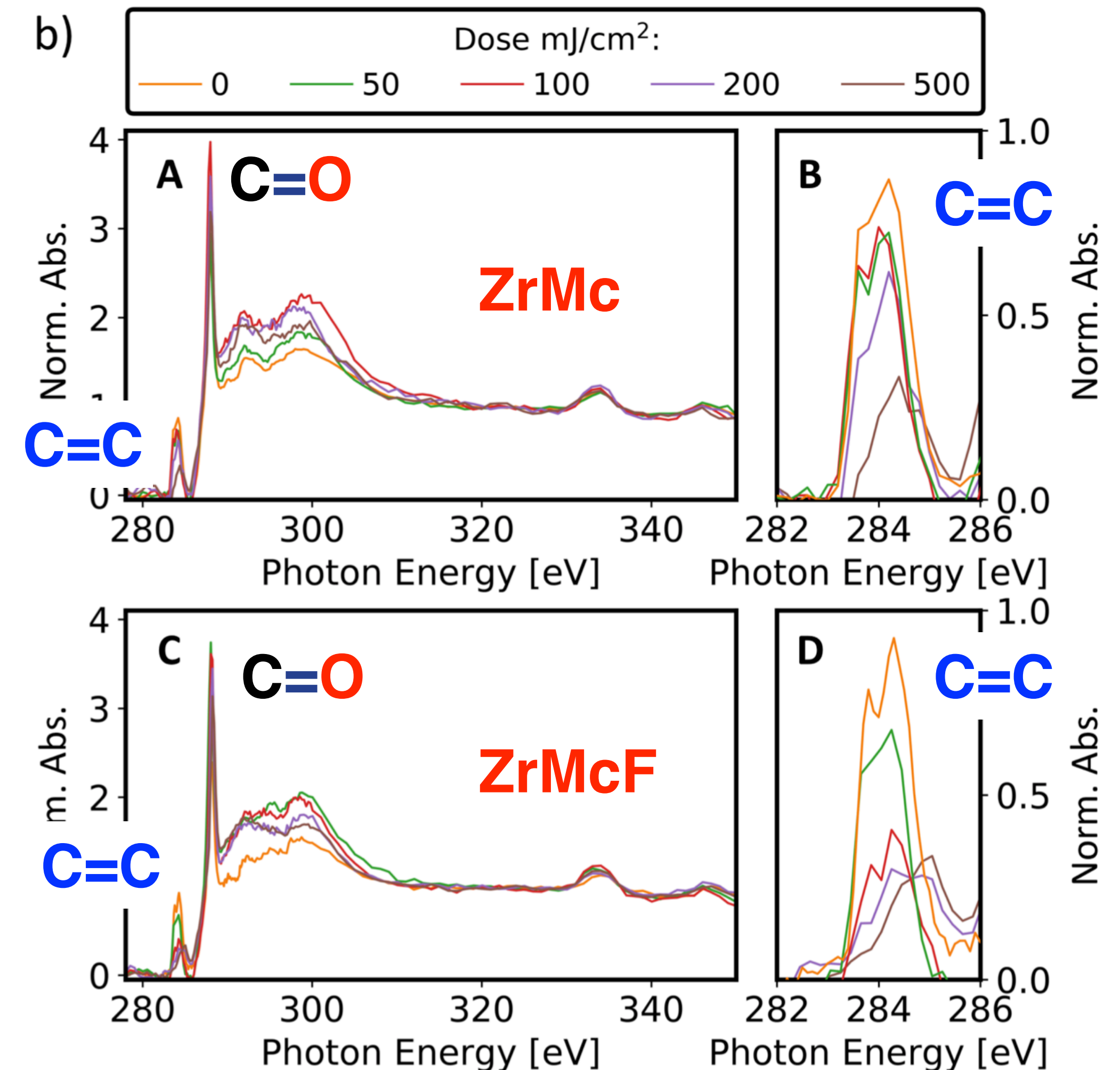
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Lianjia Wu

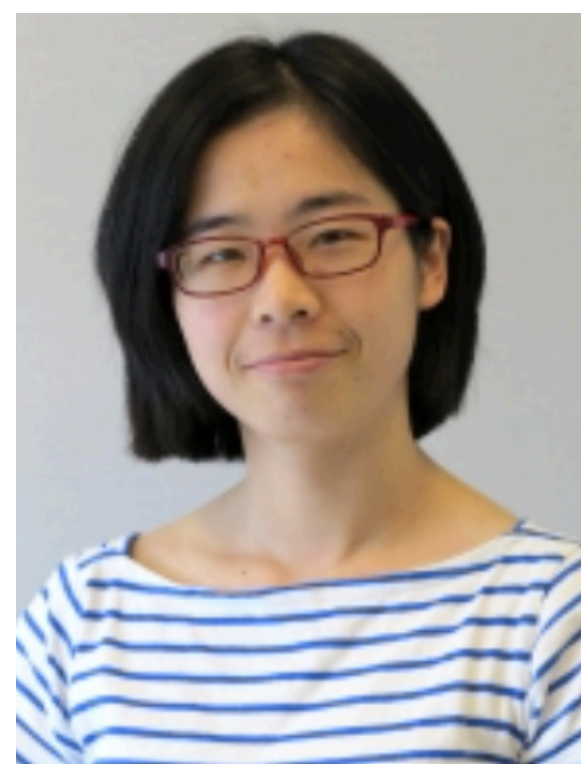


- X-ray absorption spectrum  
C1s  $\rightarrow$  vacant MO's
- Characteristic peaks  
for C=C ( $\sim 284$  eV) and  
for C=O ( $\sim 287$  eV)

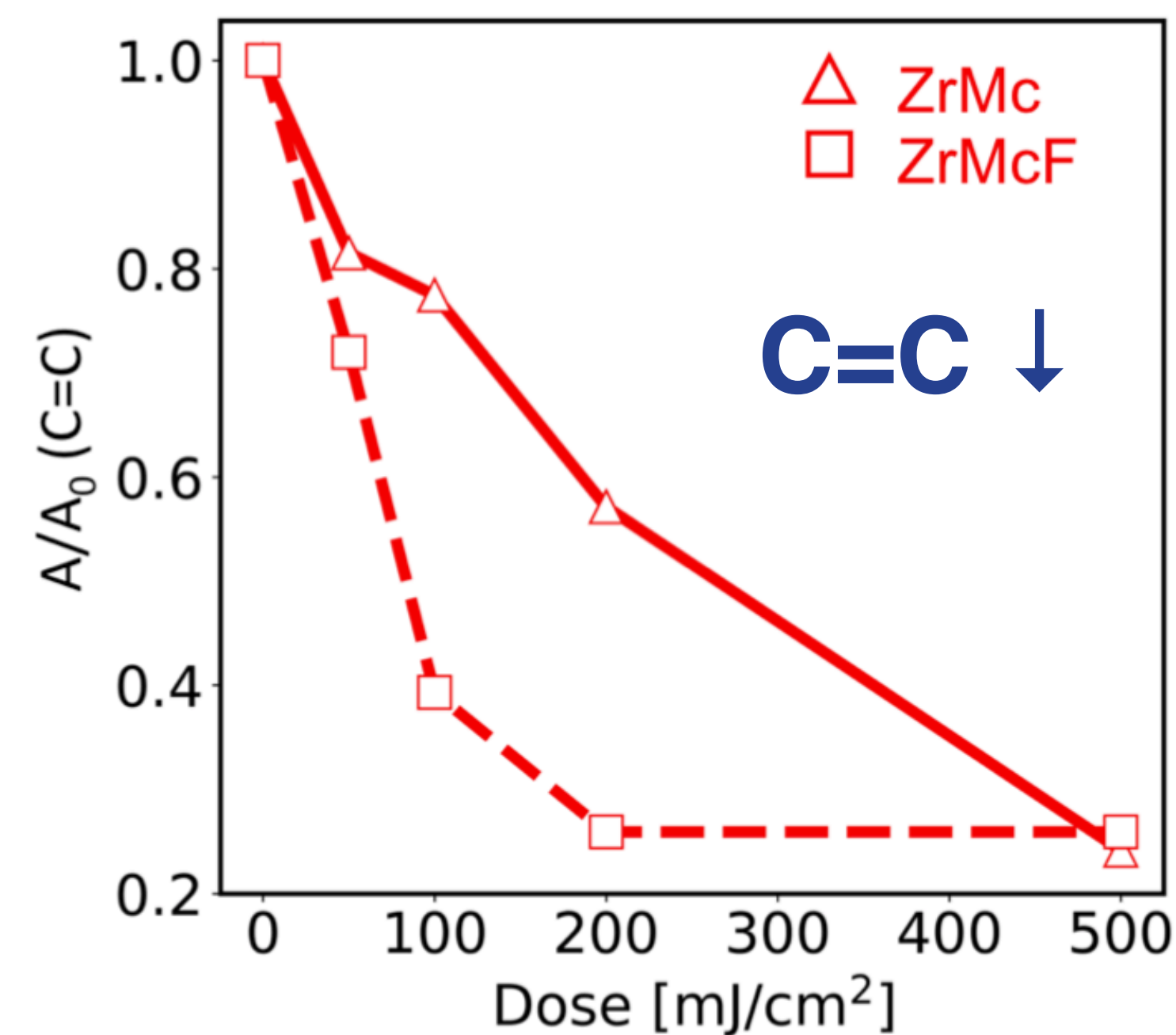
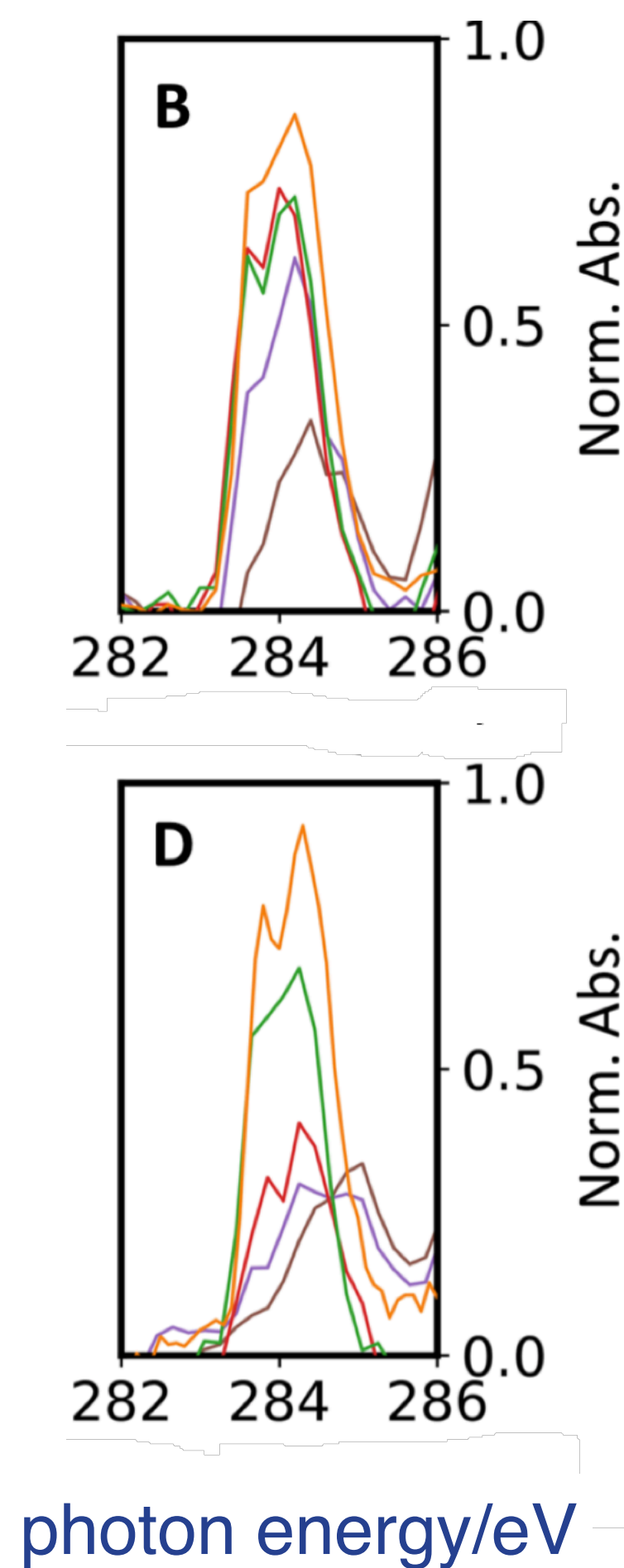




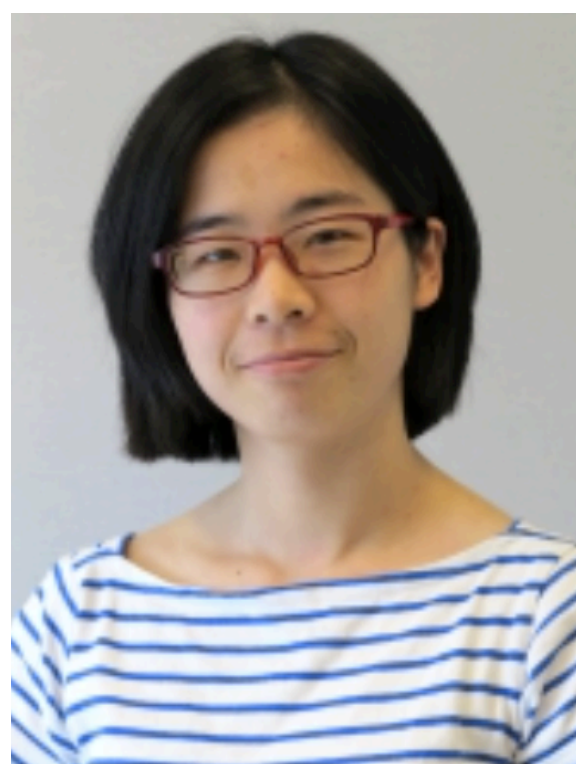
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Lianjia Wu

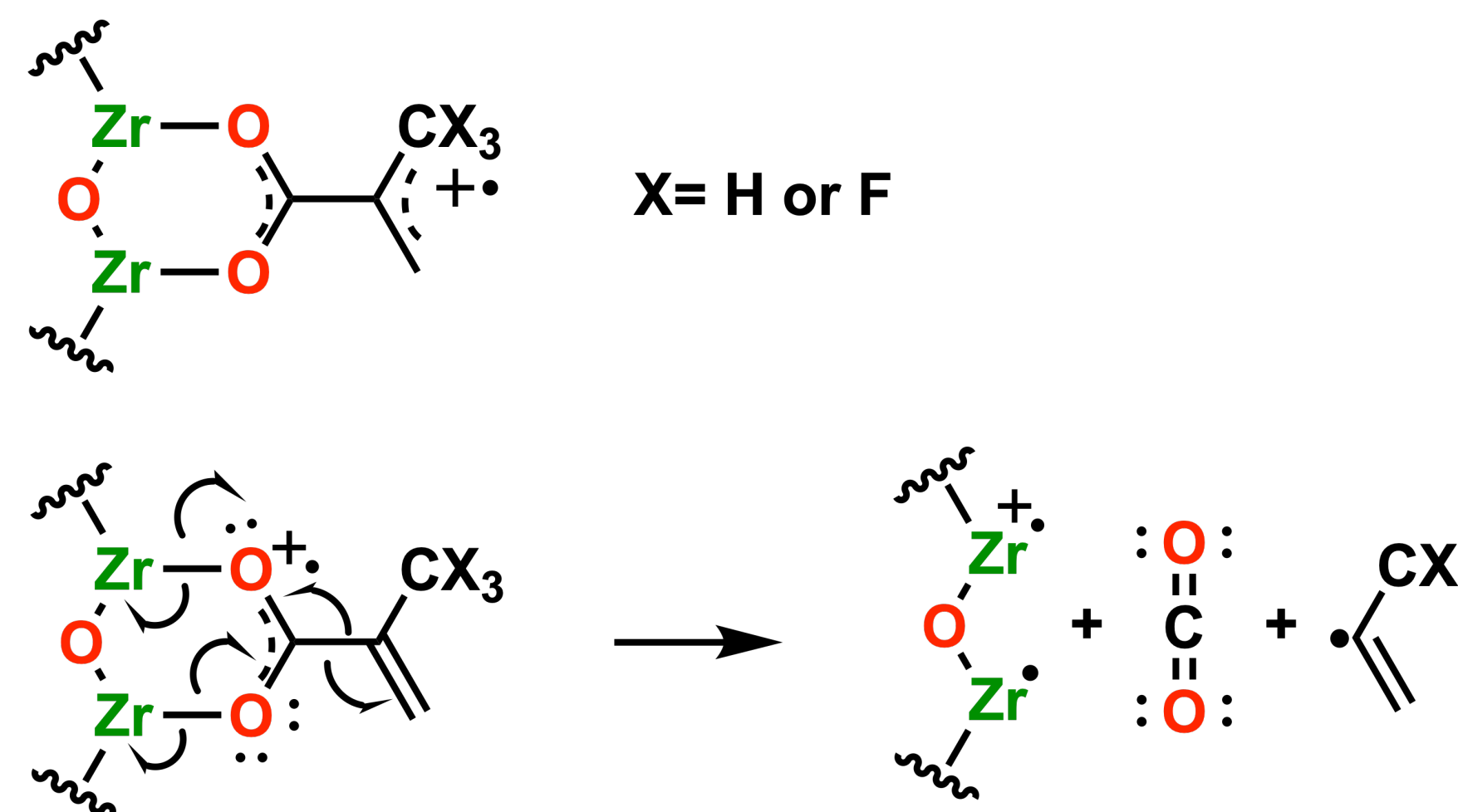


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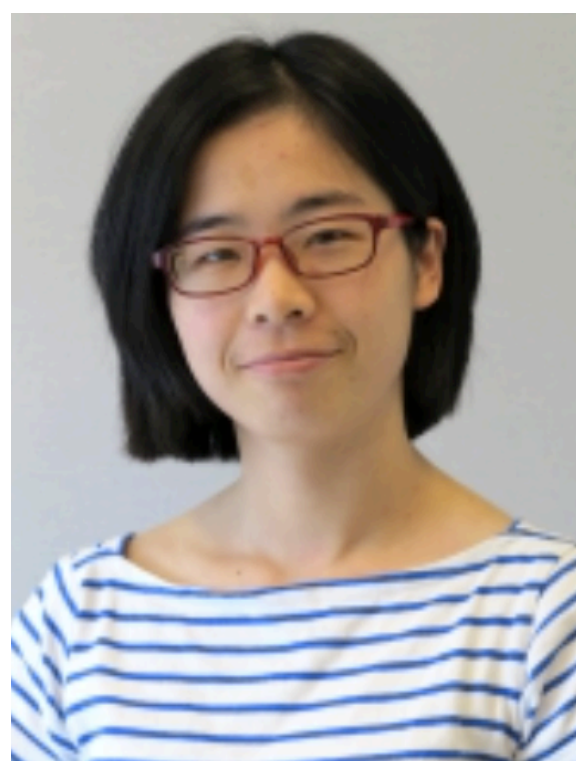
Lianjia Wu

- some loss of C=O groups
- more loss of C=C



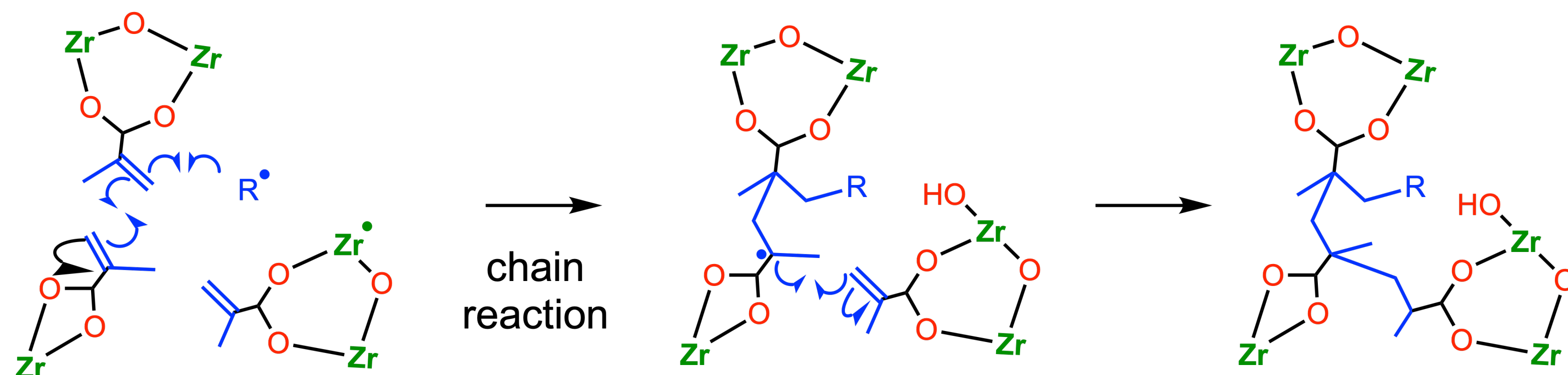
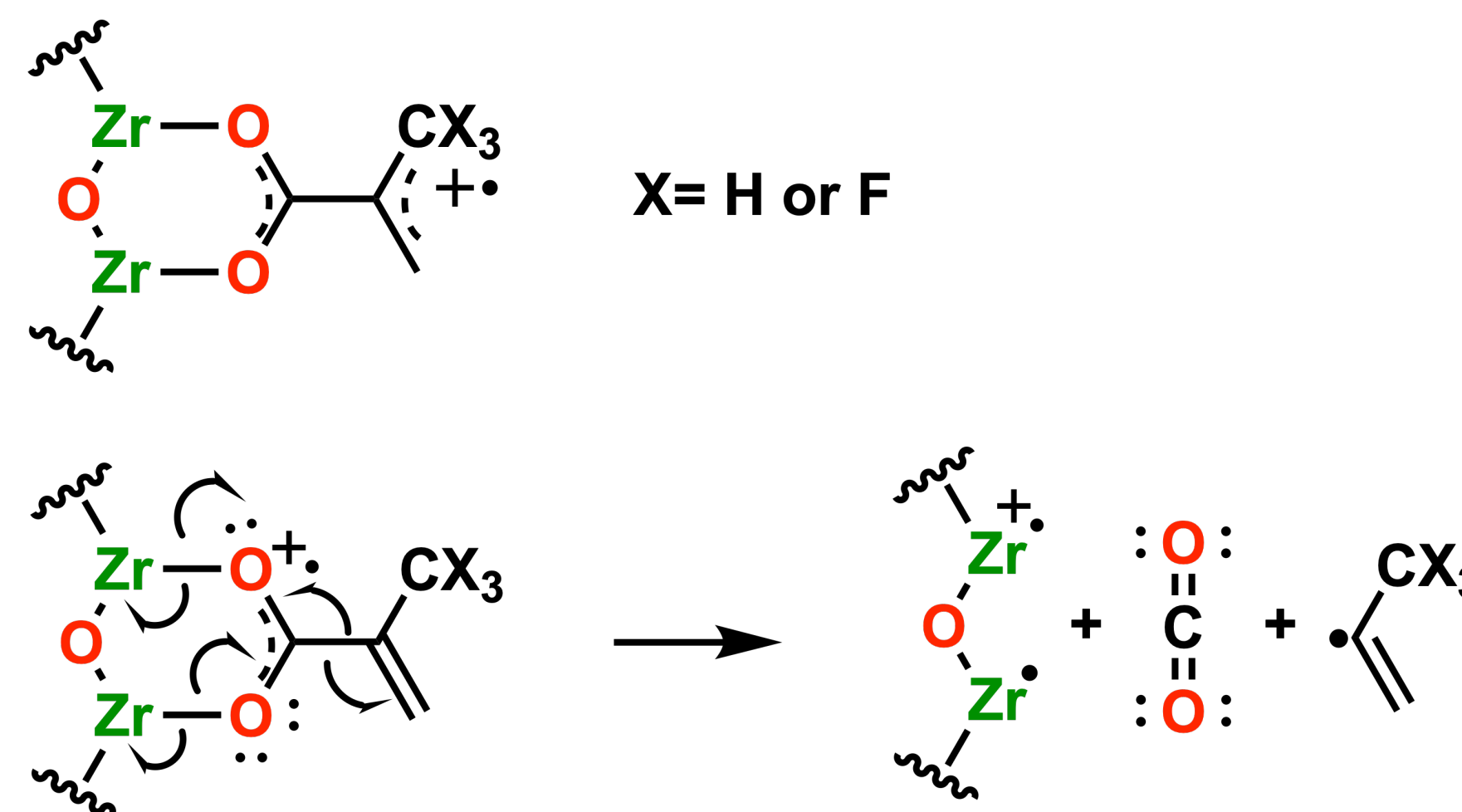


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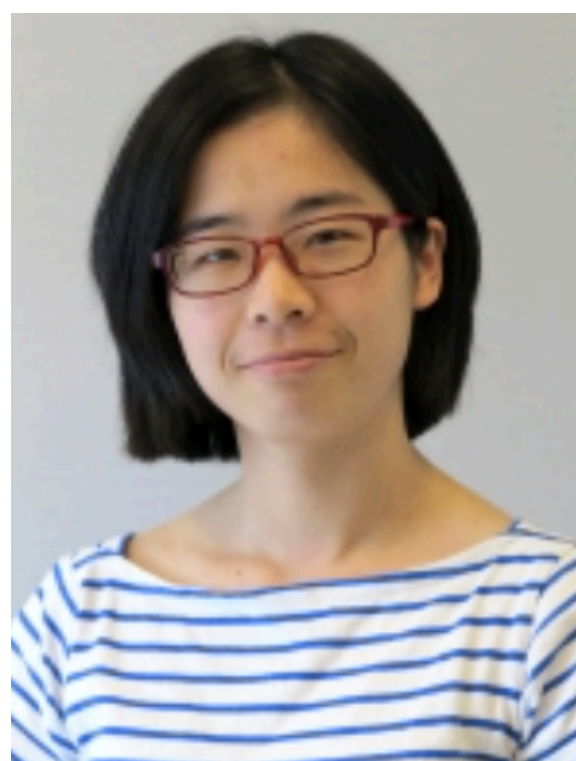


Lianjia Wu

- some loss of C=O groups
- more loss of C=C
- polymerization
- little outgassing

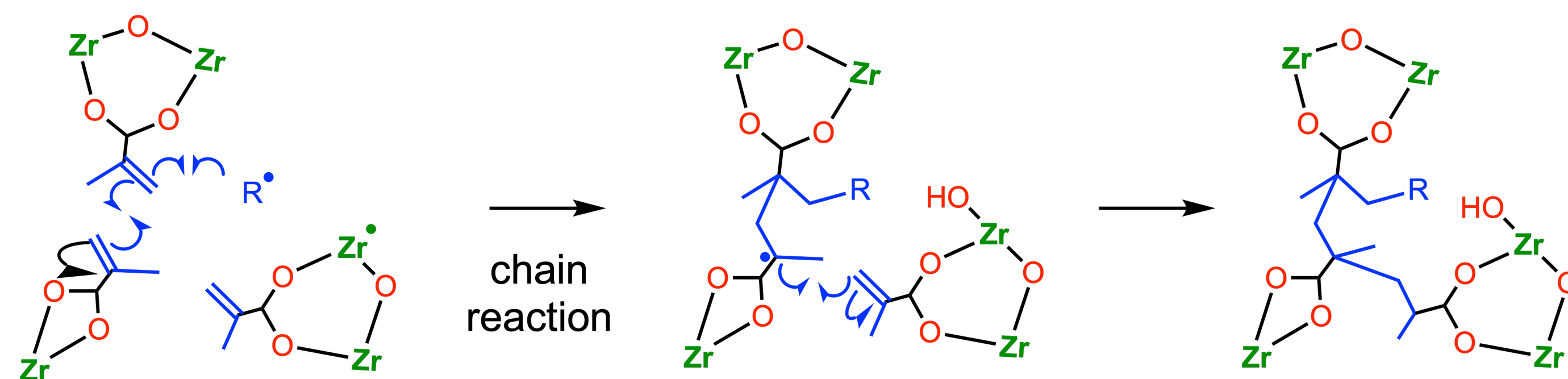


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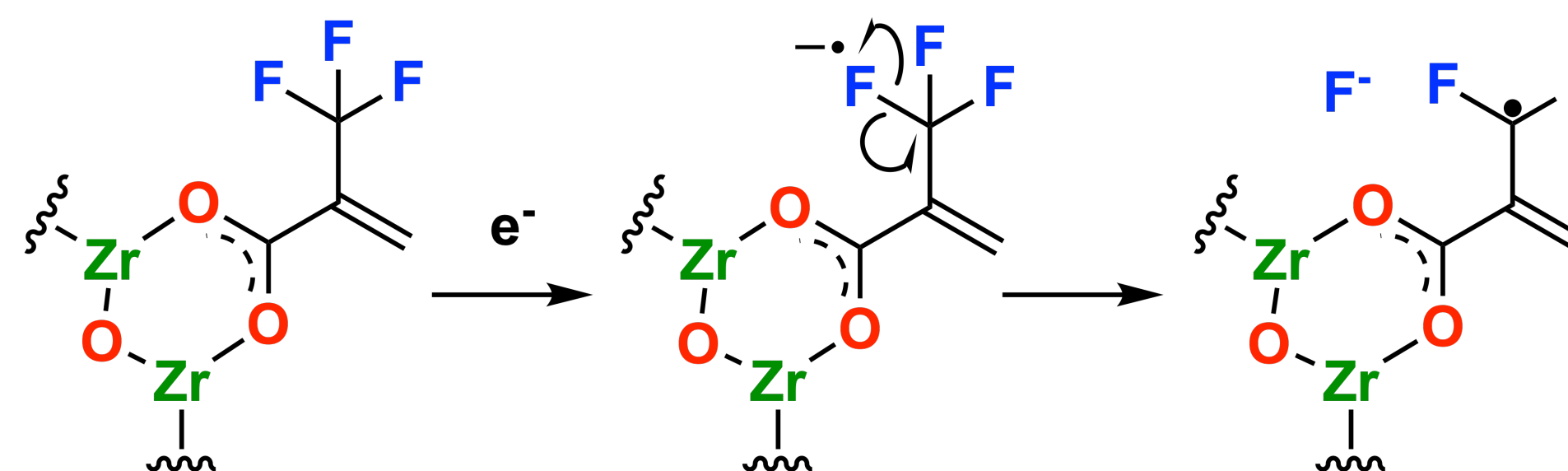


Lianjia Wu

- some loss of C=O groups
- more loss of C=C
- polymerization
- little outgassing



- fluorine opens *extra channels* for reaction



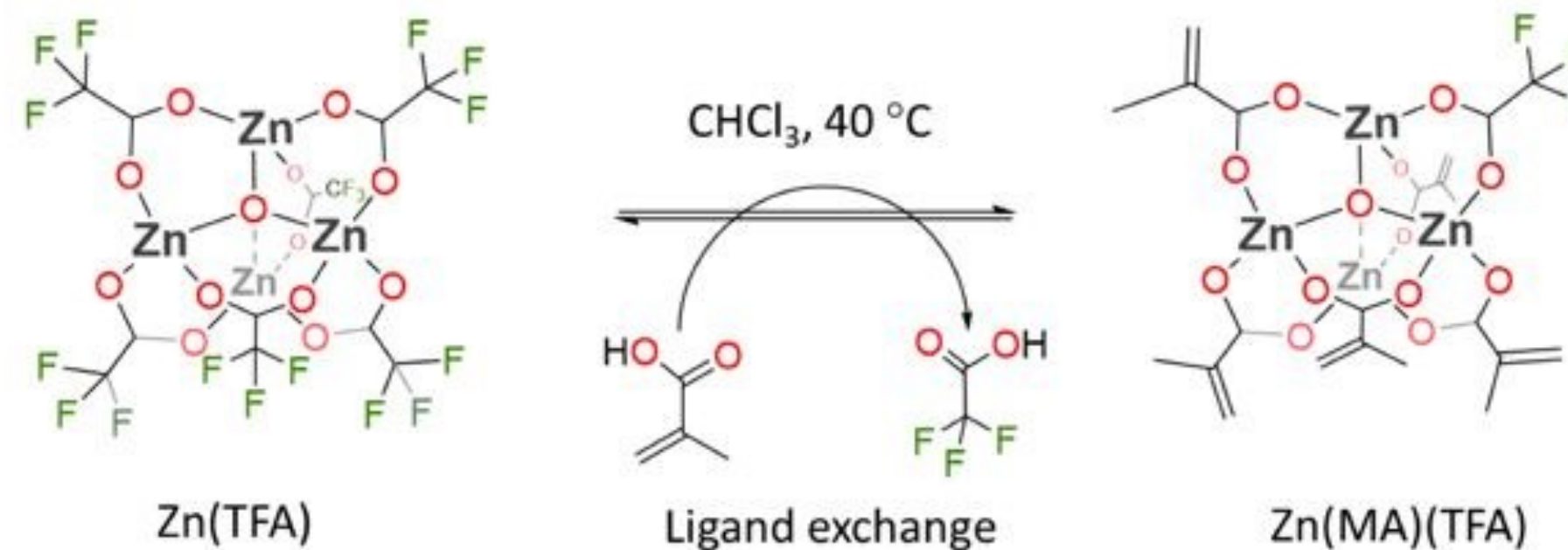




Neha Thakur

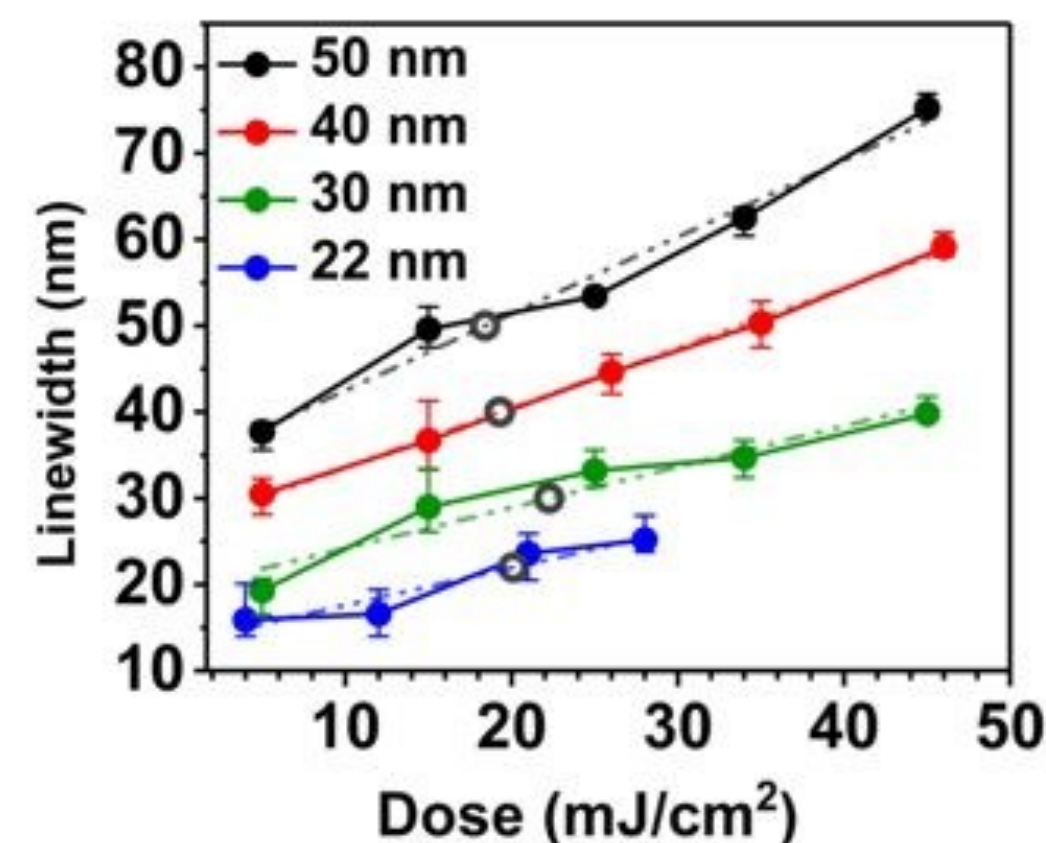
# zinc oxo clusters

(a)

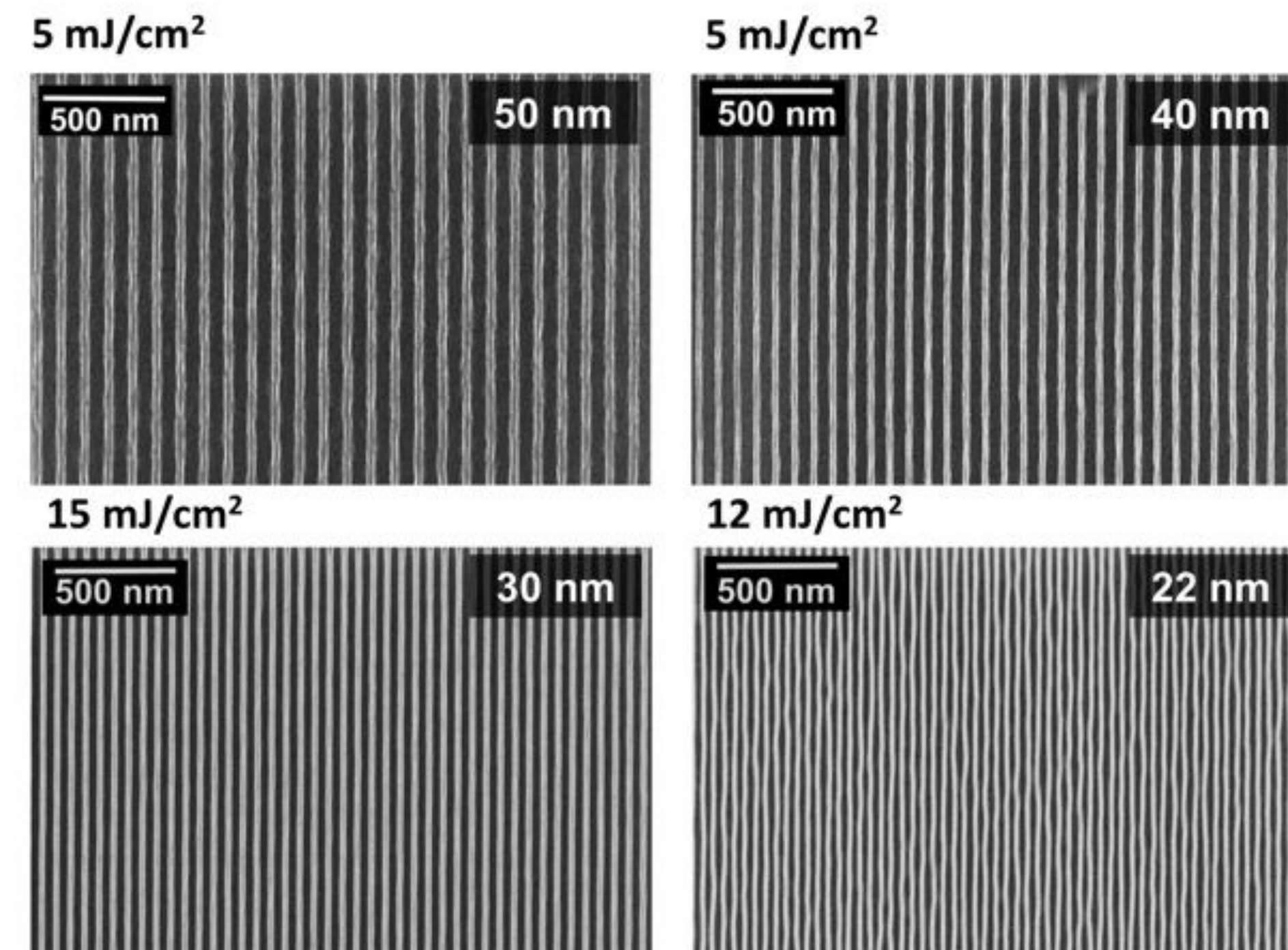


*negative tone  
resist*

(b)



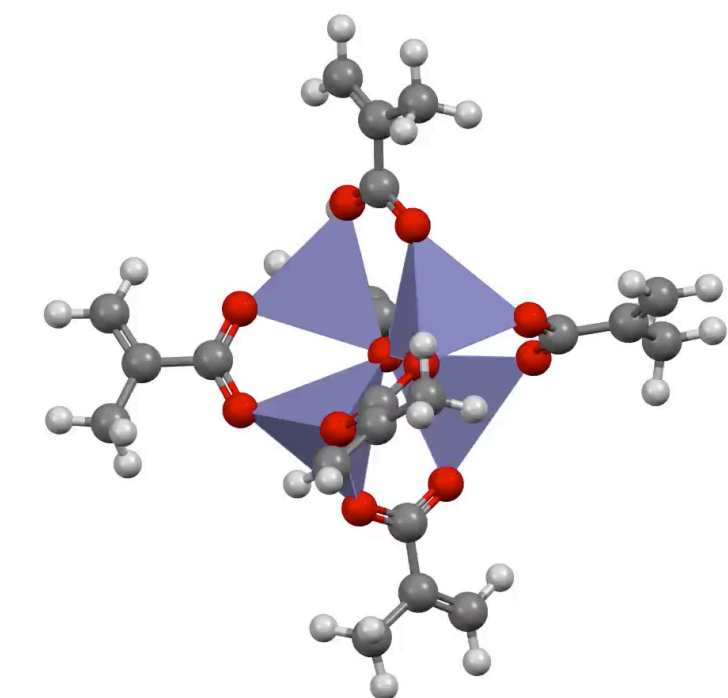
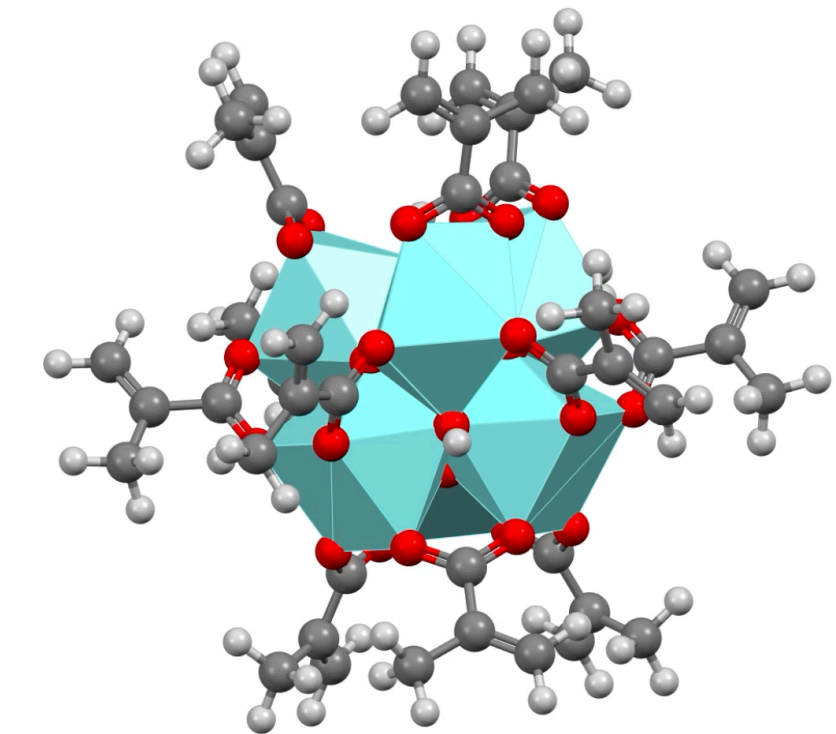
(c)



“Mixed-ligand zinc-oxoclusters: efficient chemistry for high resolution nanolithography”  
(J. Mater. Chem. C, doi:10.1039/d0tc03597a)

# metal oxo clusters

- flexible synthesis via ligand exchange
- activation via electron transfer
- radicals formed
- acrylate cross-linking
- *negative tone photoresists*
- advantage: little outgassing (only some CO<sub>2</sub>)



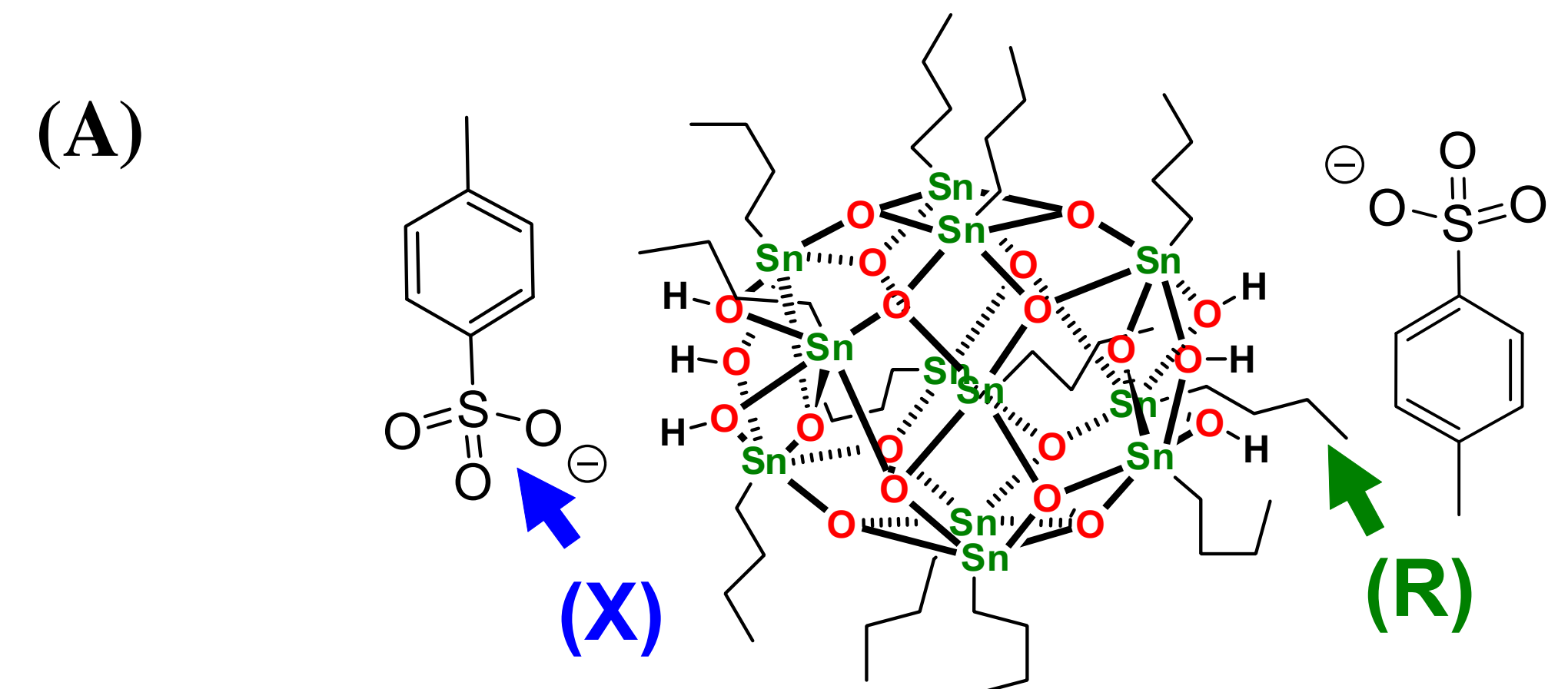


# organotin oxo cages

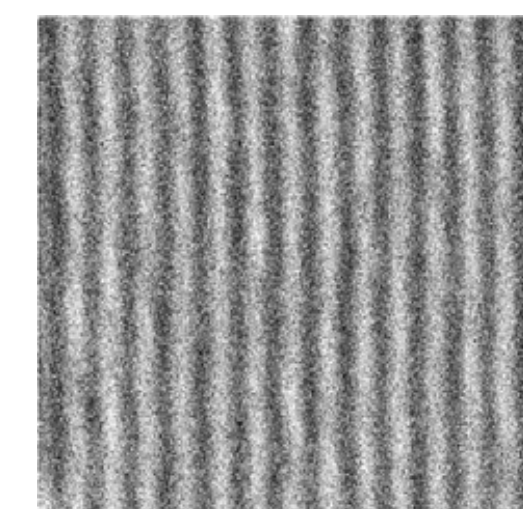
Photolithographic properties of tin-oxo clusters using extreme ultraviolet light (13.5 nm)

Brian Cardineau<sup>a</sup>, Ryan Del Re<sup>a</sup>, Miles Marnell<sup>b</sup>, Hashim Al-Mashat<sup>b</sup>, Michaela Vockenhuber<sup>c</sup>, Yasin Ekinici<sup>c</sup>, Chandra Sarma<sup>d</sup>, Daniel A. Freedman<sup>b</sup>, Robert L. Brainard<sup>a,\*</sup>

- introduced in EUV photoresist field by Brainard
- large EUV absorption
- easy to synthesize
- chemical reactivity virtually unexplored



(B)



$[(\text{PhSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2$

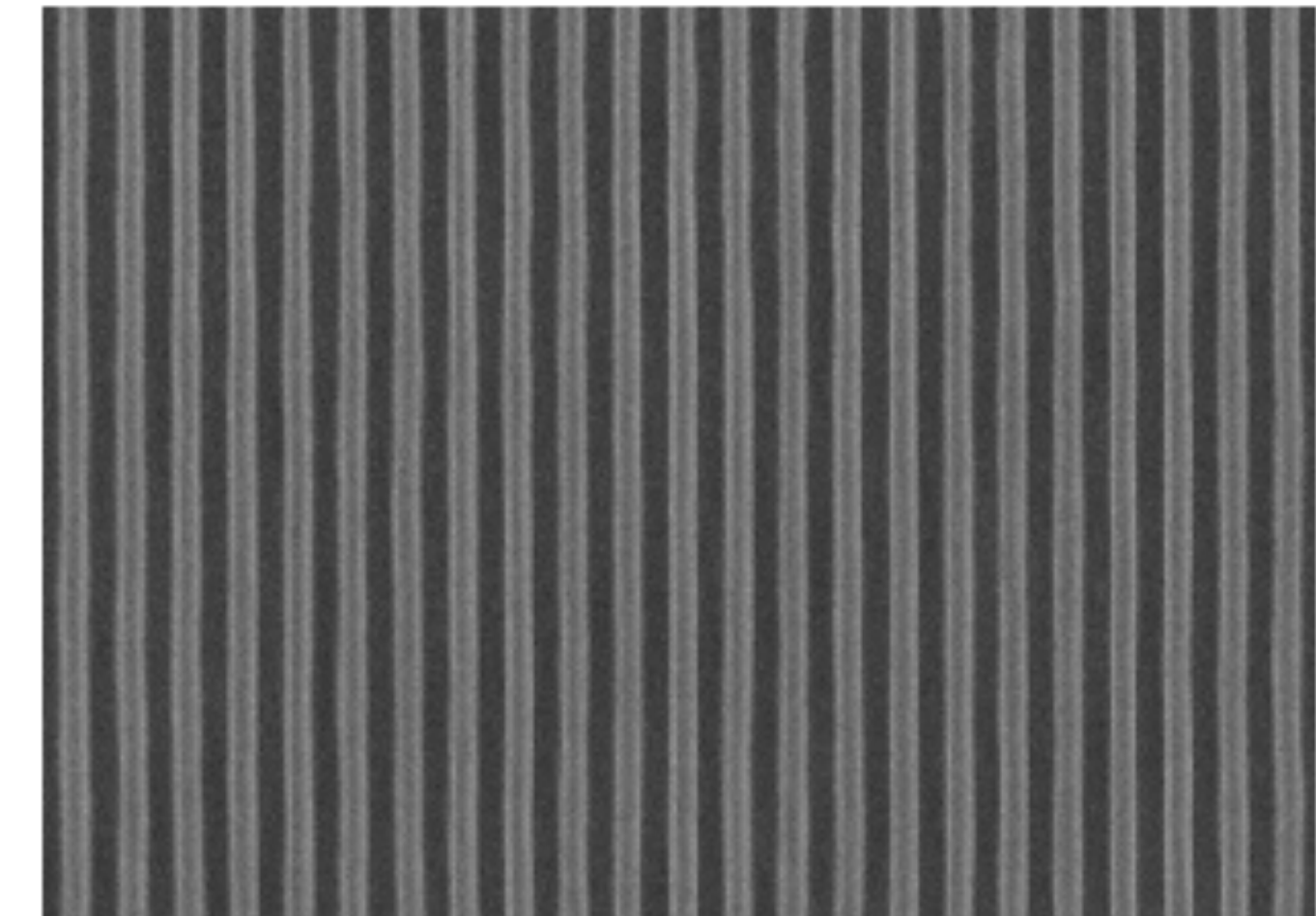
Dose: 350 mJ/cm<sup>2</sup>

Resolution: 18 mJ/cm<sup>2</sup>

# patterning tin cages



40 nm HP lines, 74 mJ/cm<sup>2</sup>

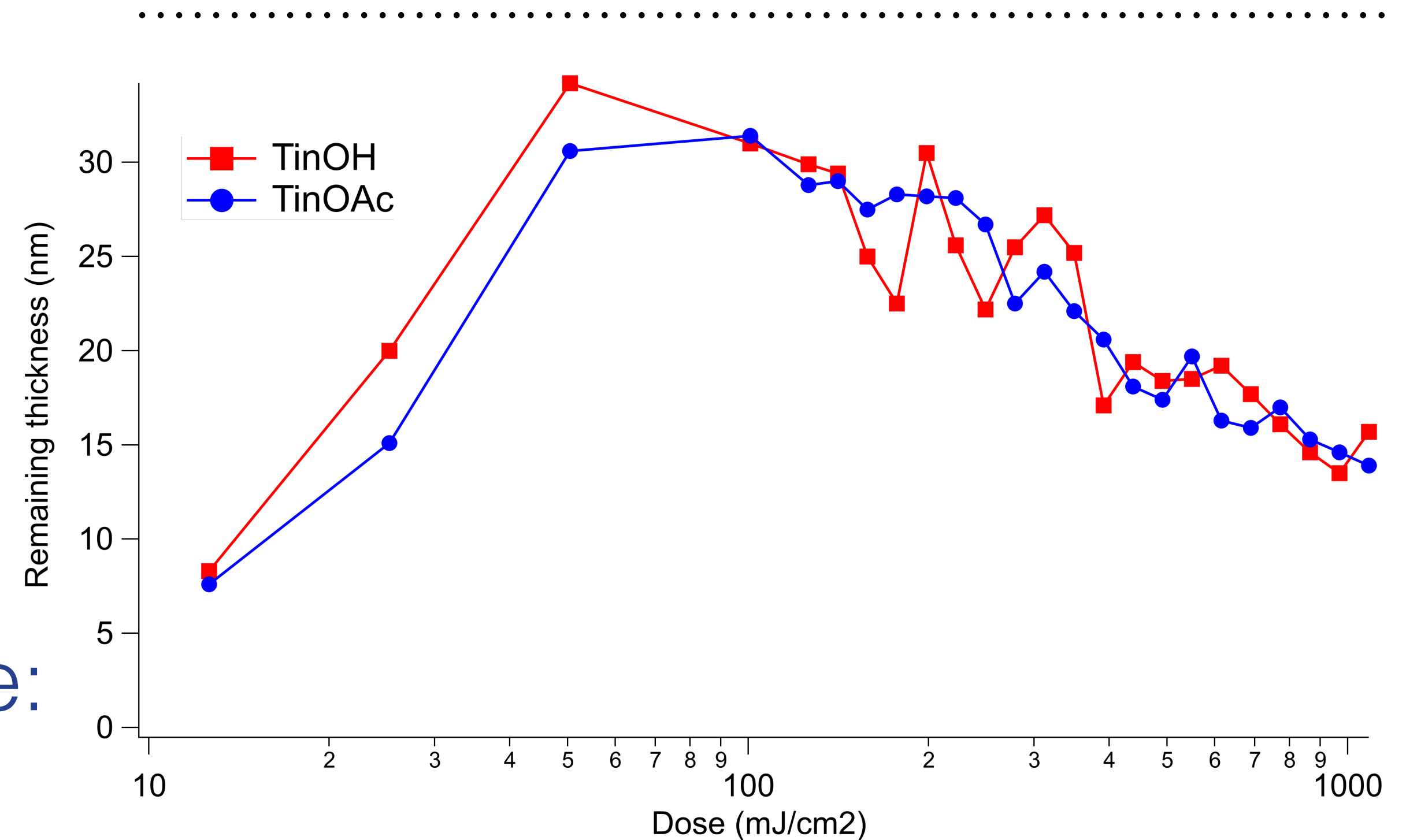


- EUV exposure and interference litho at PSI
- higher sensitivity than published by Brainard group



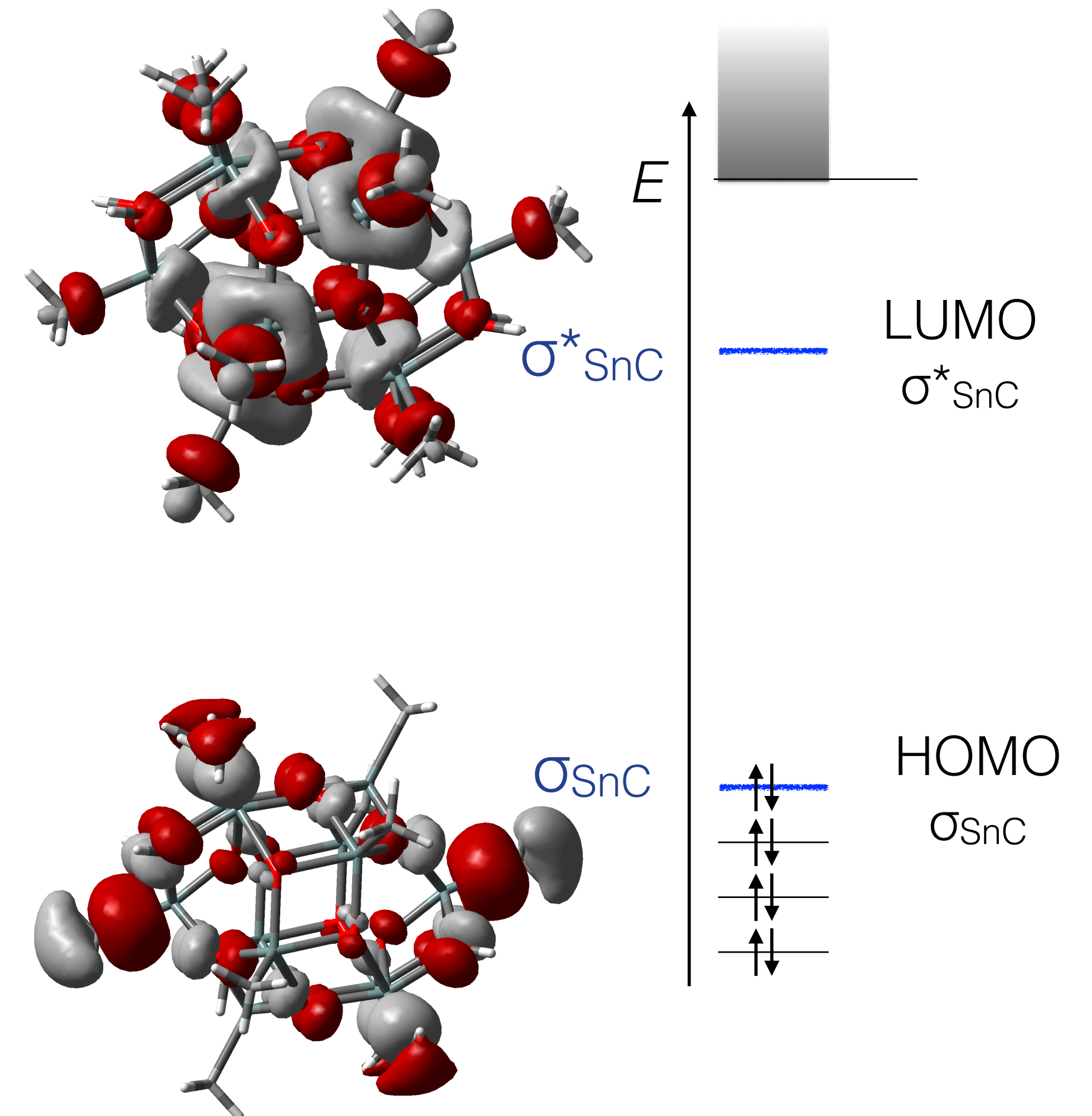
# “contrast curve”

- dose-to-gel  $\sim 50 \text{ mJ cm}^{-2}$
- not much material lost at maximum remaining thickness
- shrinkage upon over-exposure: loss of organic groups



# reactivity

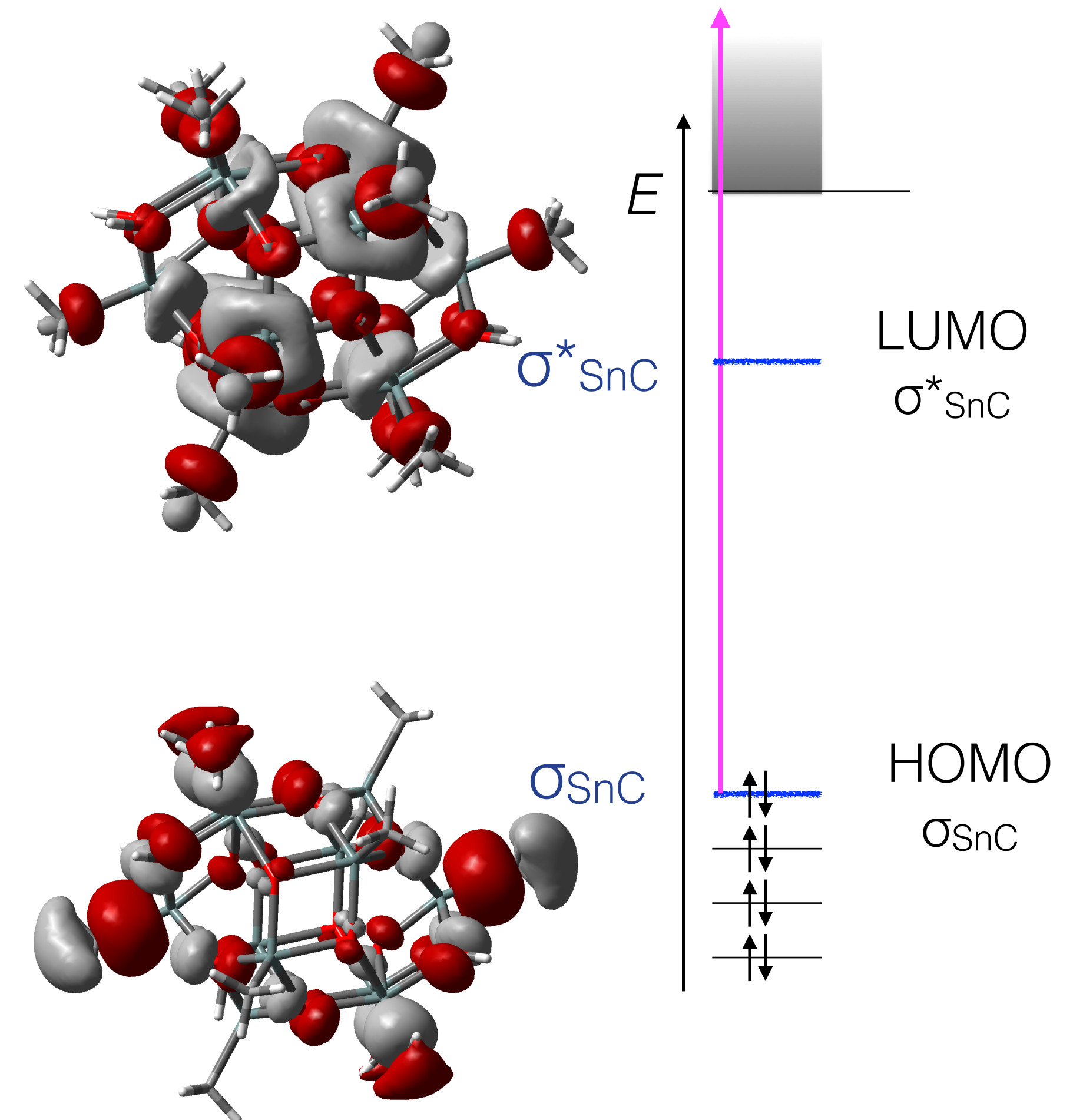
- Sn-C bonds are the weak spot
- $E_{\text{bond}} \approx 2.5 \text{ eV}$
- Molecular Quantum Chemistry  
Density Functional Theory





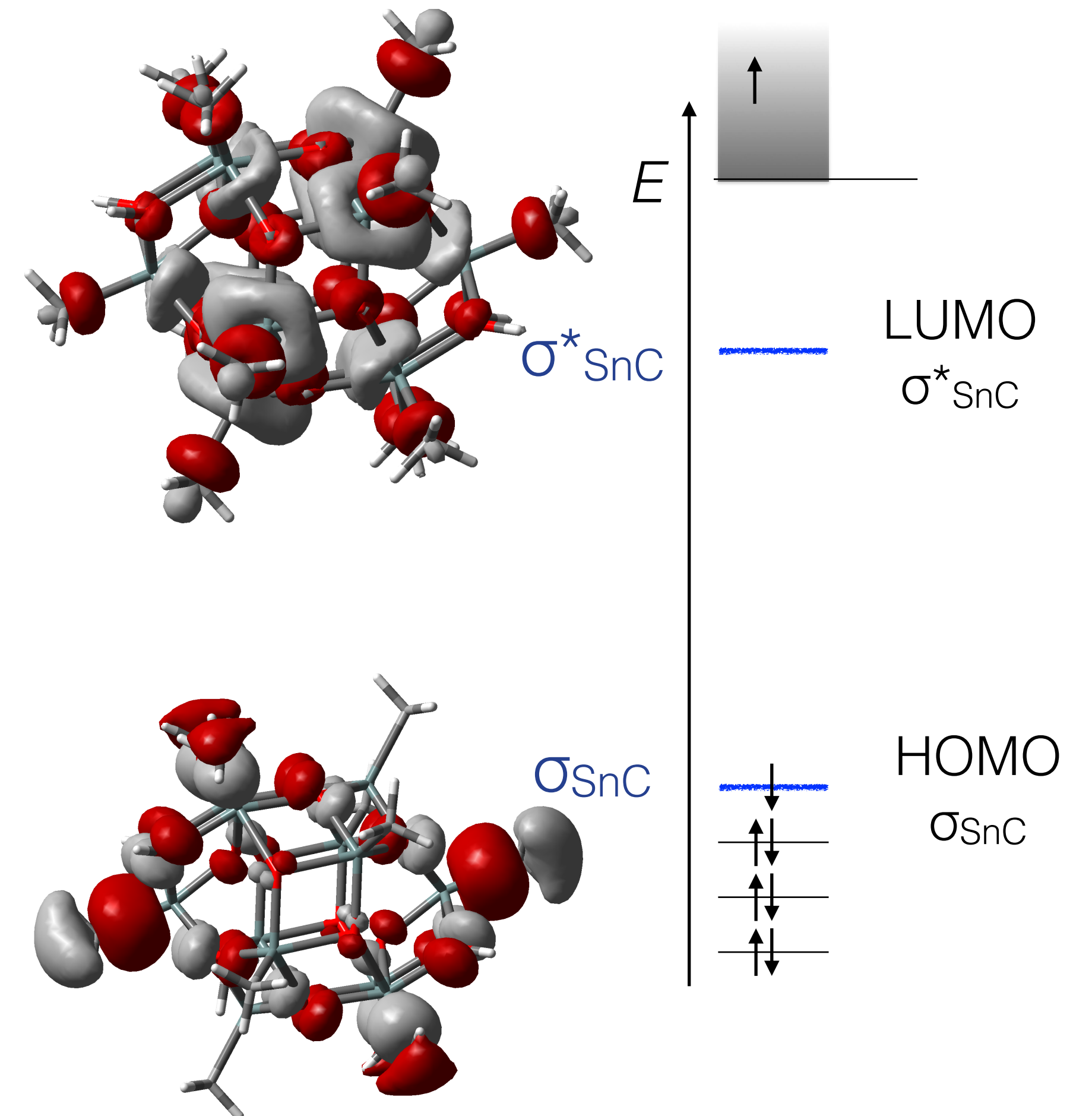
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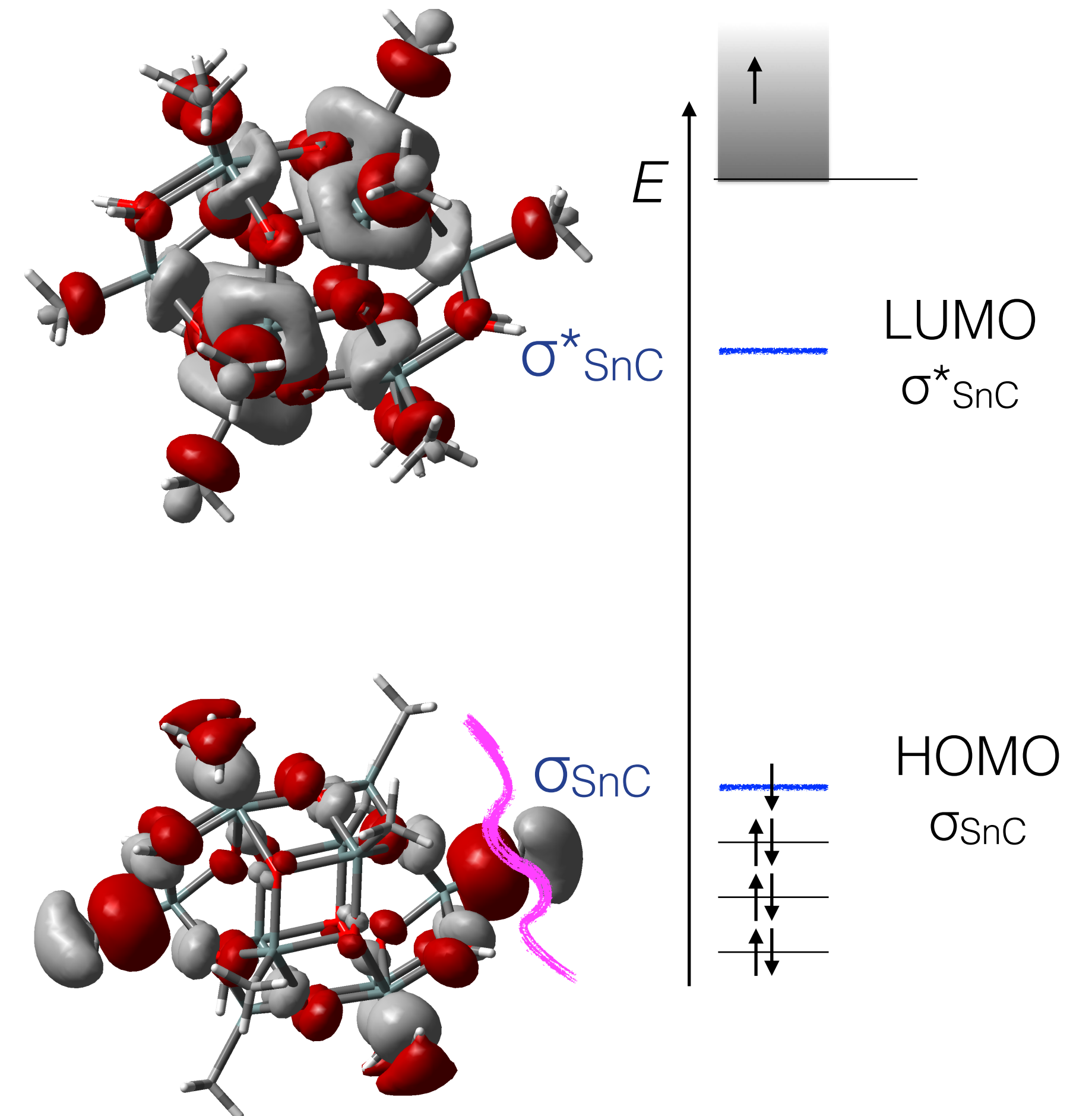
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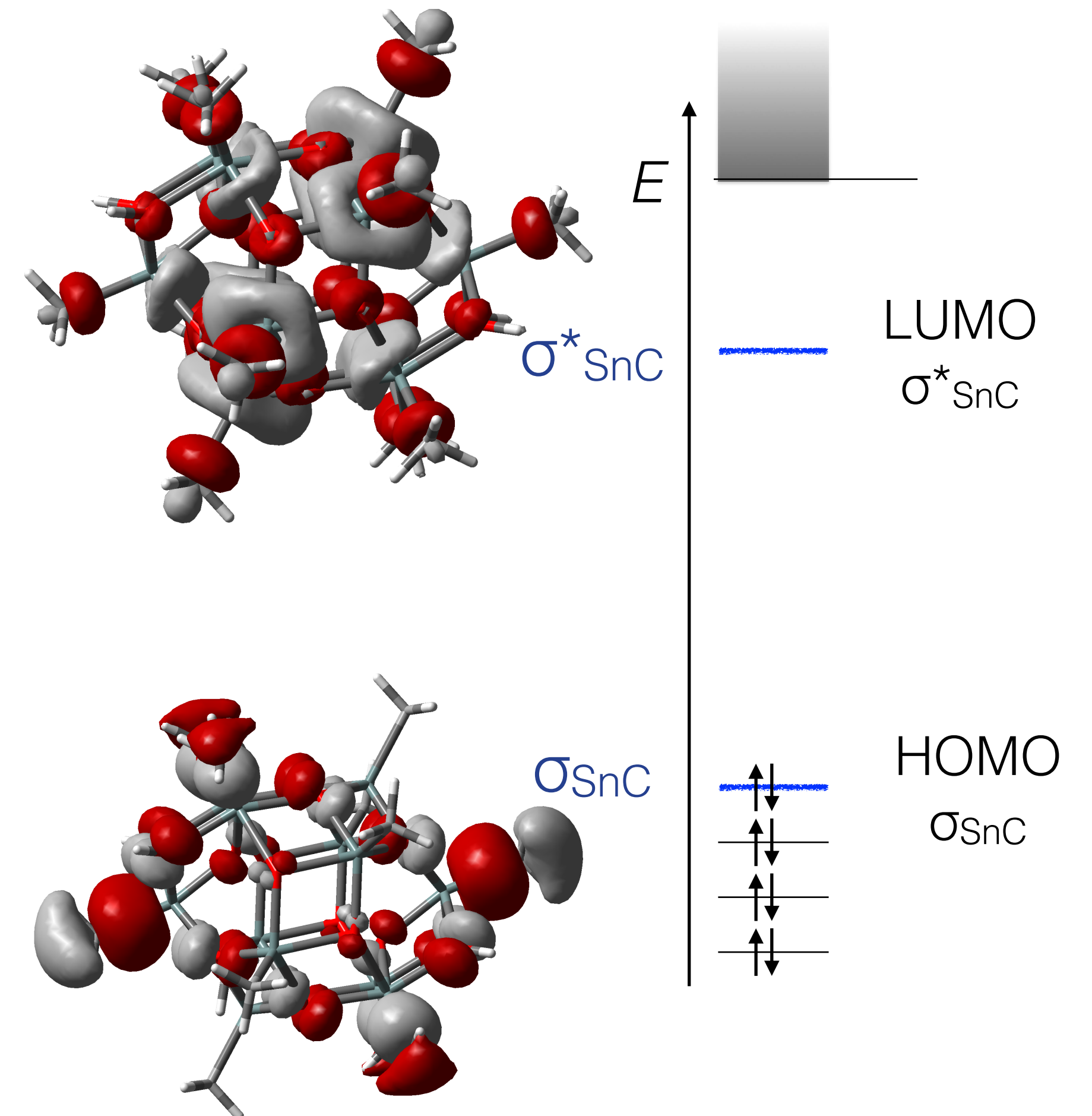
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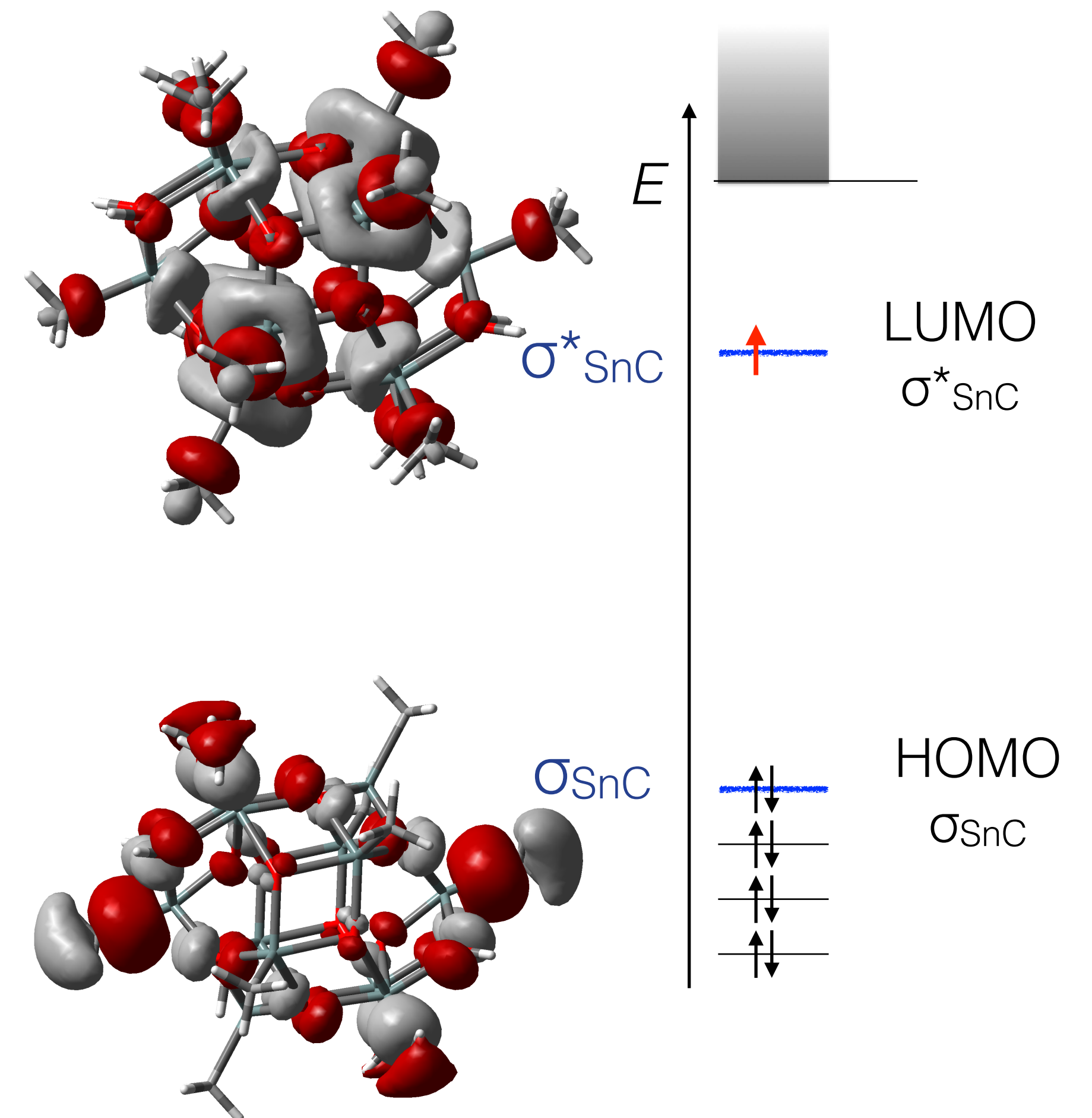
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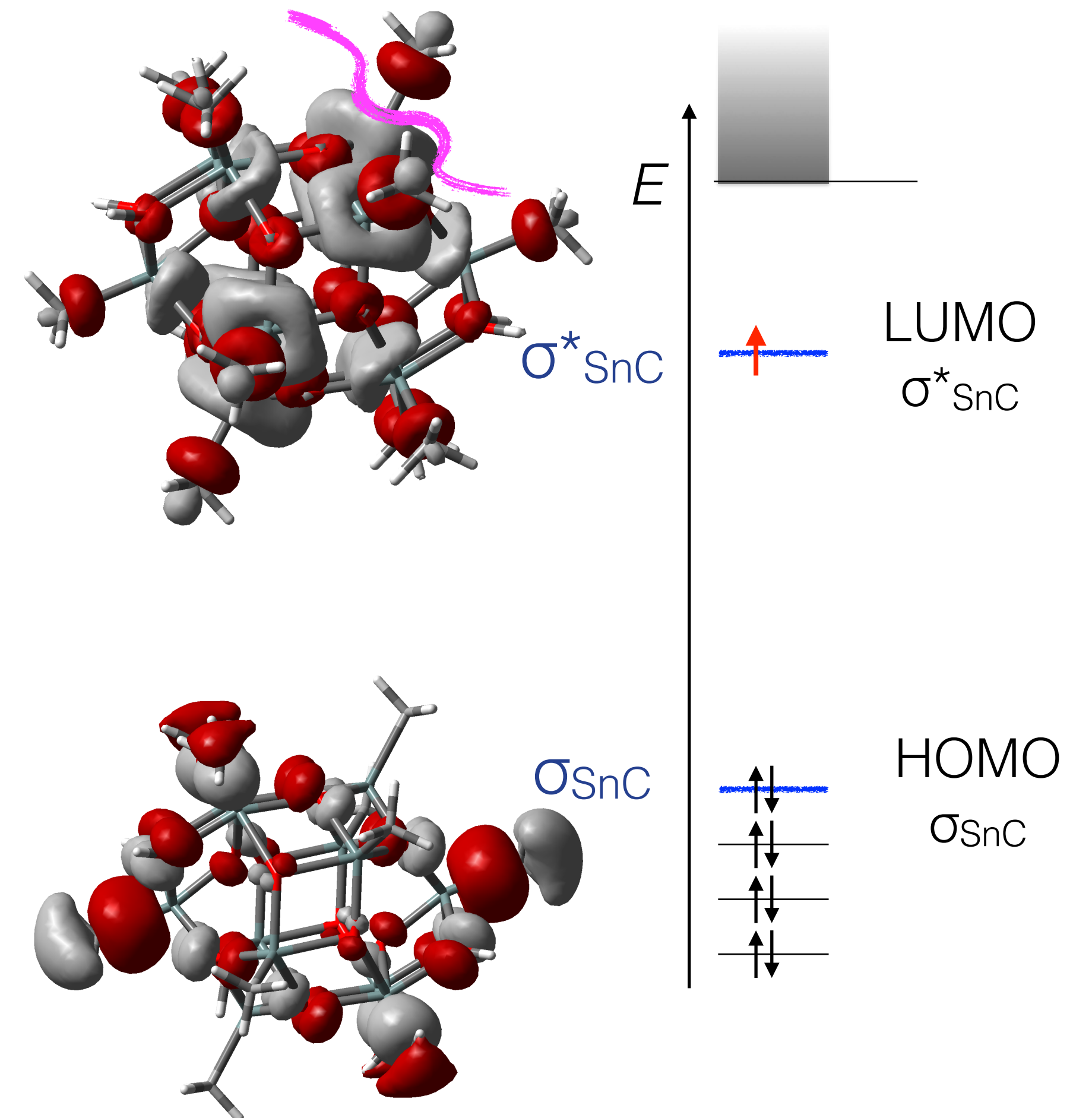
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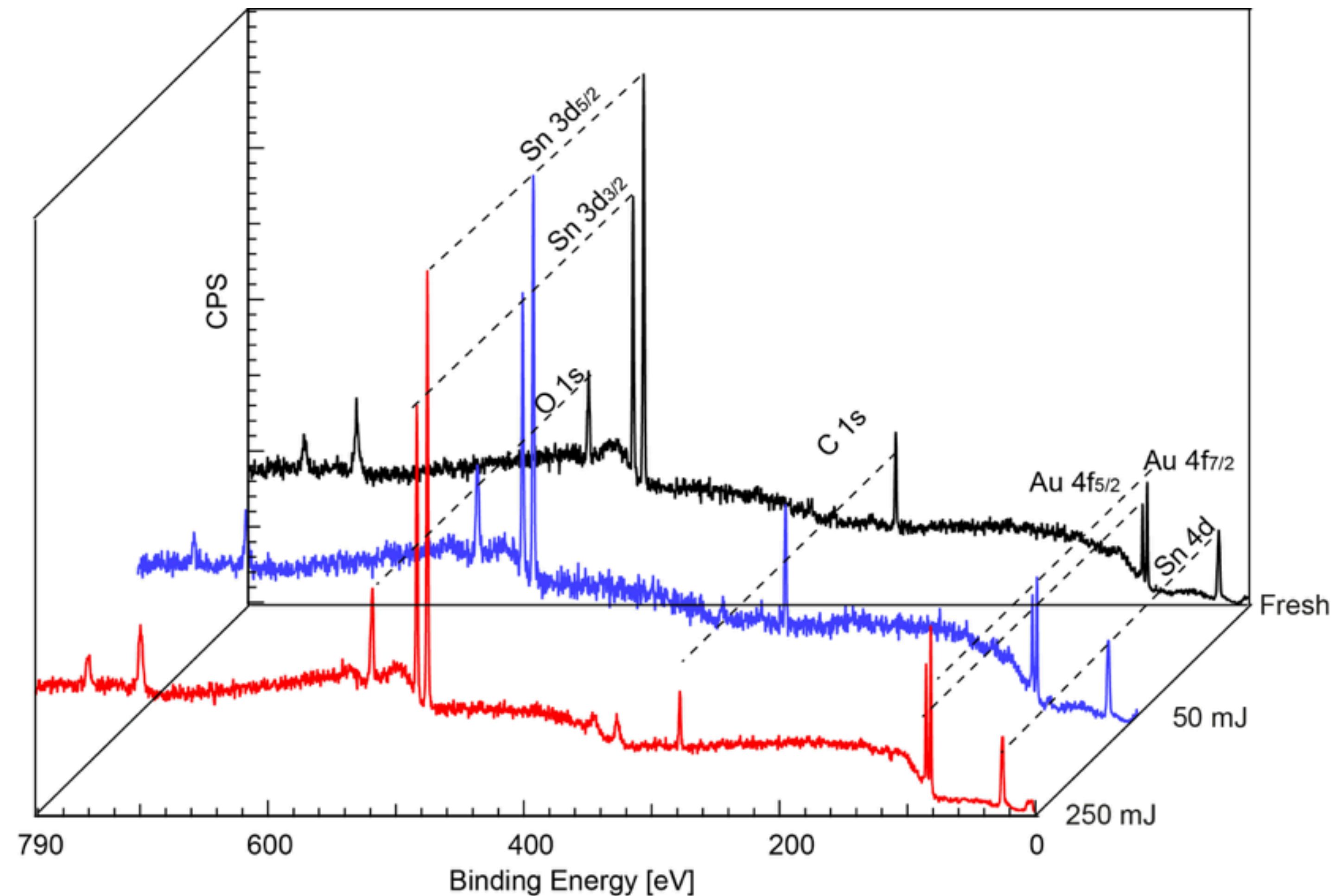
# experiments

- analysis of thin photoresist films
  - X-ray Photoelectron Spectroscopy
  - Scanning Transmission X-ray Microscopy
- gas phase photofragmentation
- Low Energy Electron exposure
- *main change: loss of carbon after Sn-C bond broken*



# XPS after EUV exposure

- dose-to-gel  $\sim 50 \text{ mJ cm}^{-2}$
- little carbon lost at this point
- XPS is surface sensitive



# Key Role of Very Low Energy Electrons in Tin-Based Molecular Resists for Extreme Ultraviolet Nanolithography

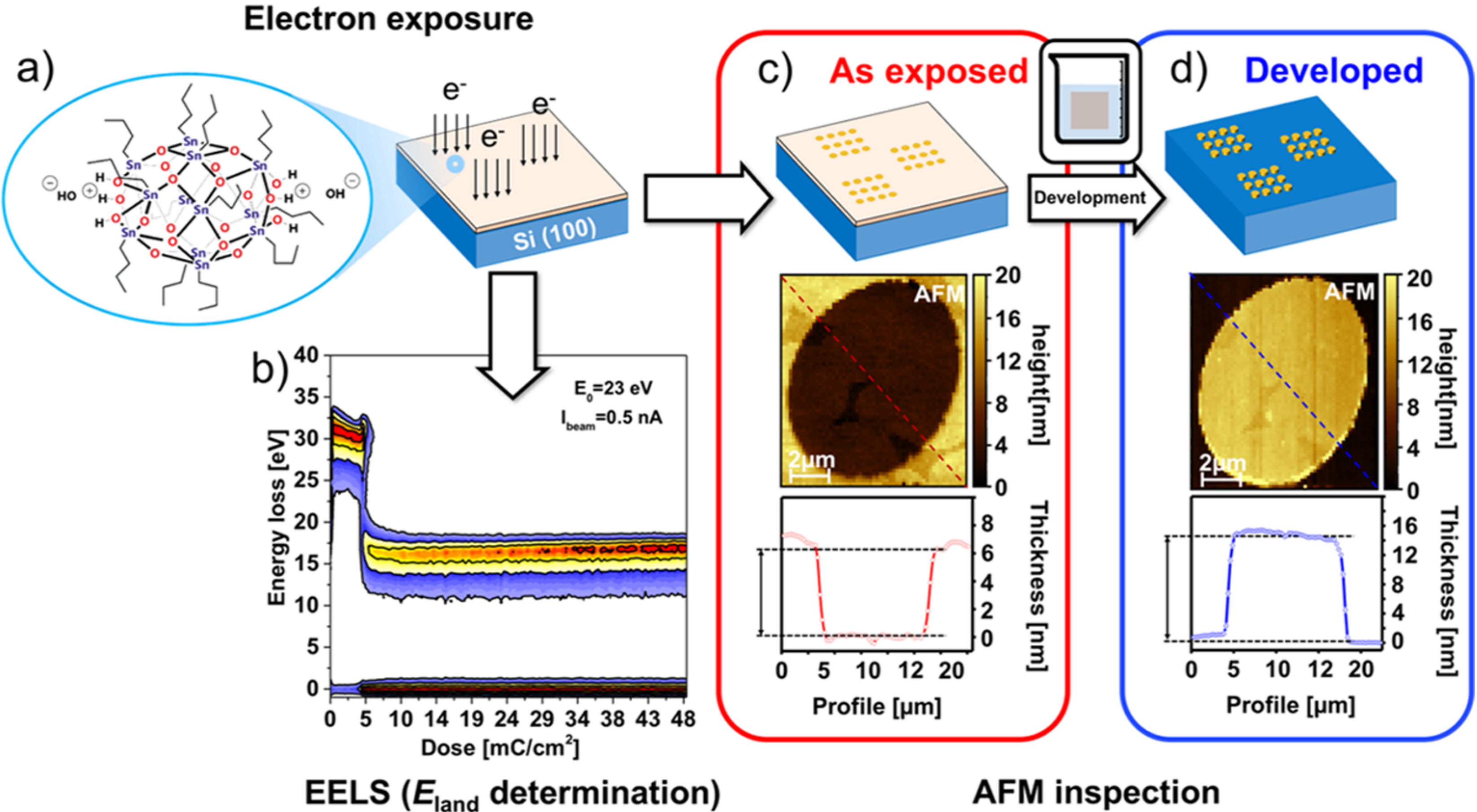
Ivan Bespalov,<sup>\*</sup> Yu Zhang, Jarich Haitjema, Rudolf M. Tromp, Sense Jan van der Molen, Albert M. Brouwer, Johannes Jobst,<sup>\*</sup> and Sonia Castellanos<sup>\*</sup>



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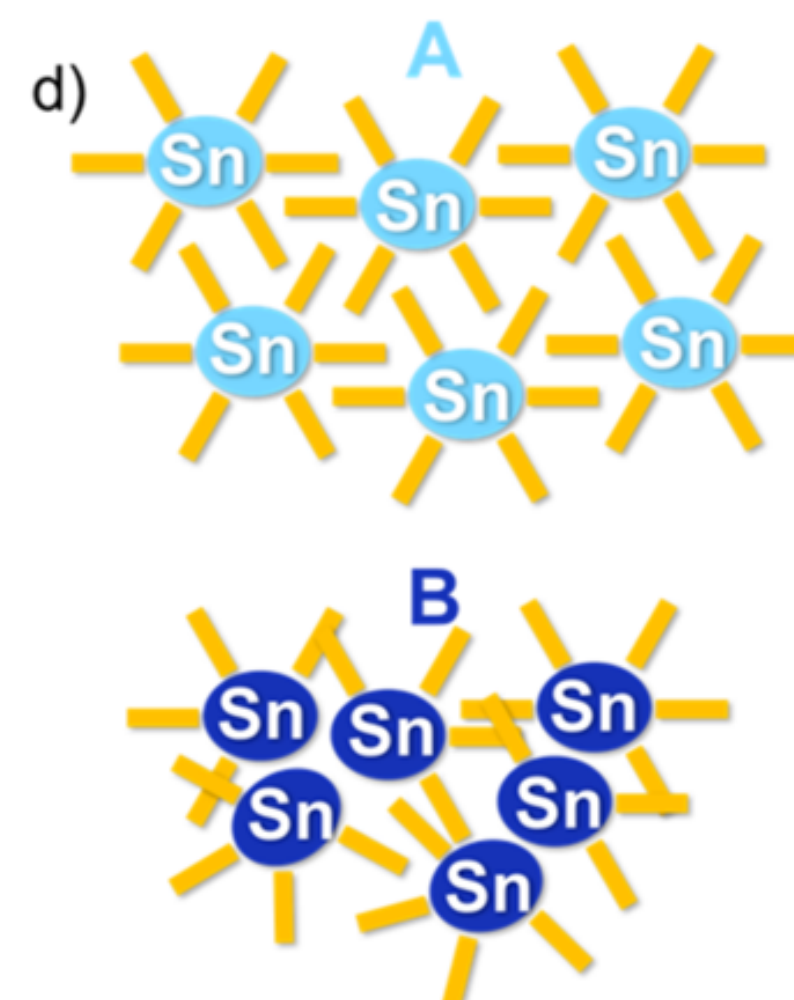
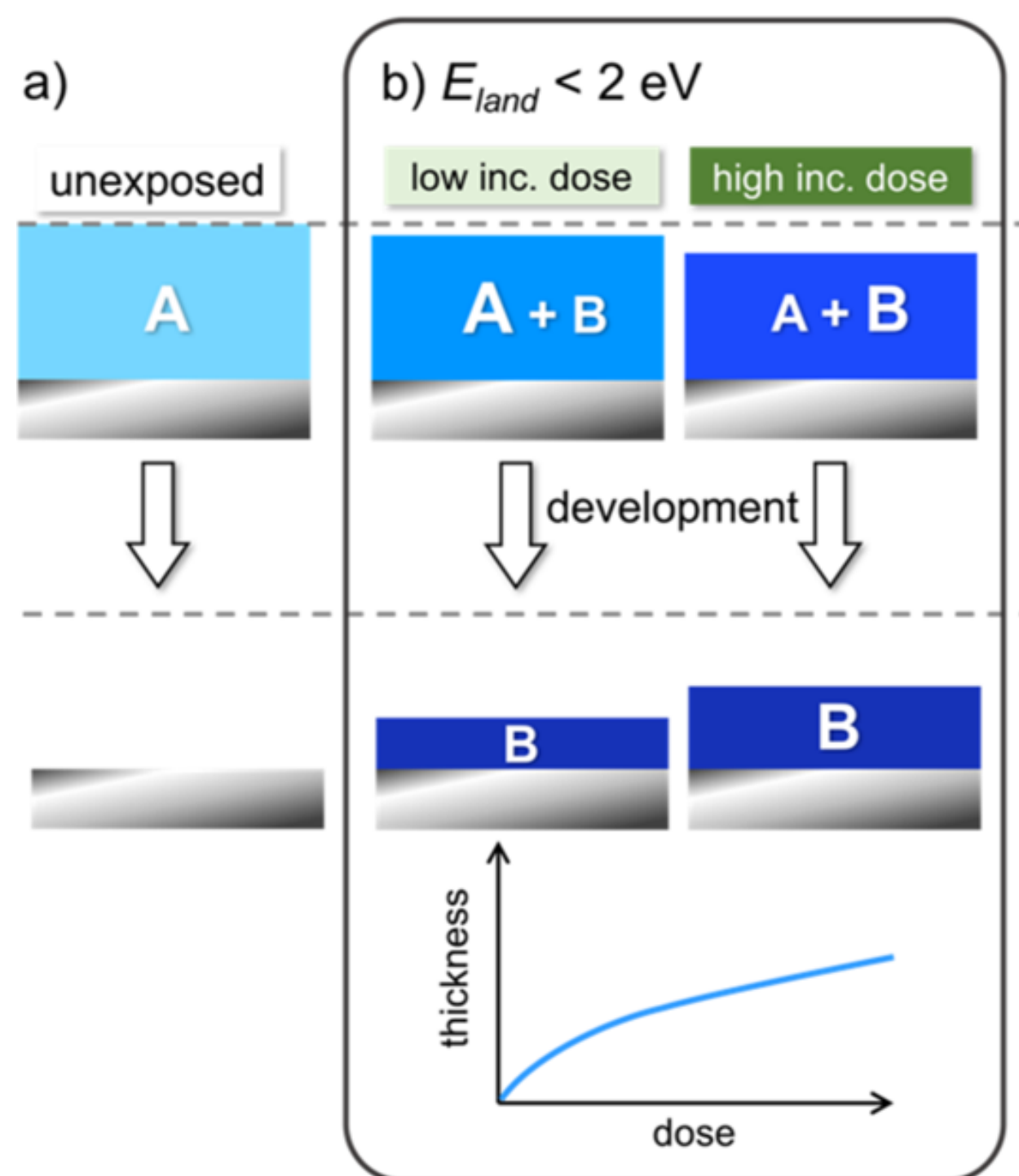
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- low energy electrons:
- $\text{Sn}_{12}\text{Bu}_{12} + e^- \rightarrow [\text{Sn}_{12}\text{Bu}_{12}^-] \rightarrow \text{Sn}_{12}\text{Bu}_{11}^- + \text{Bu}$



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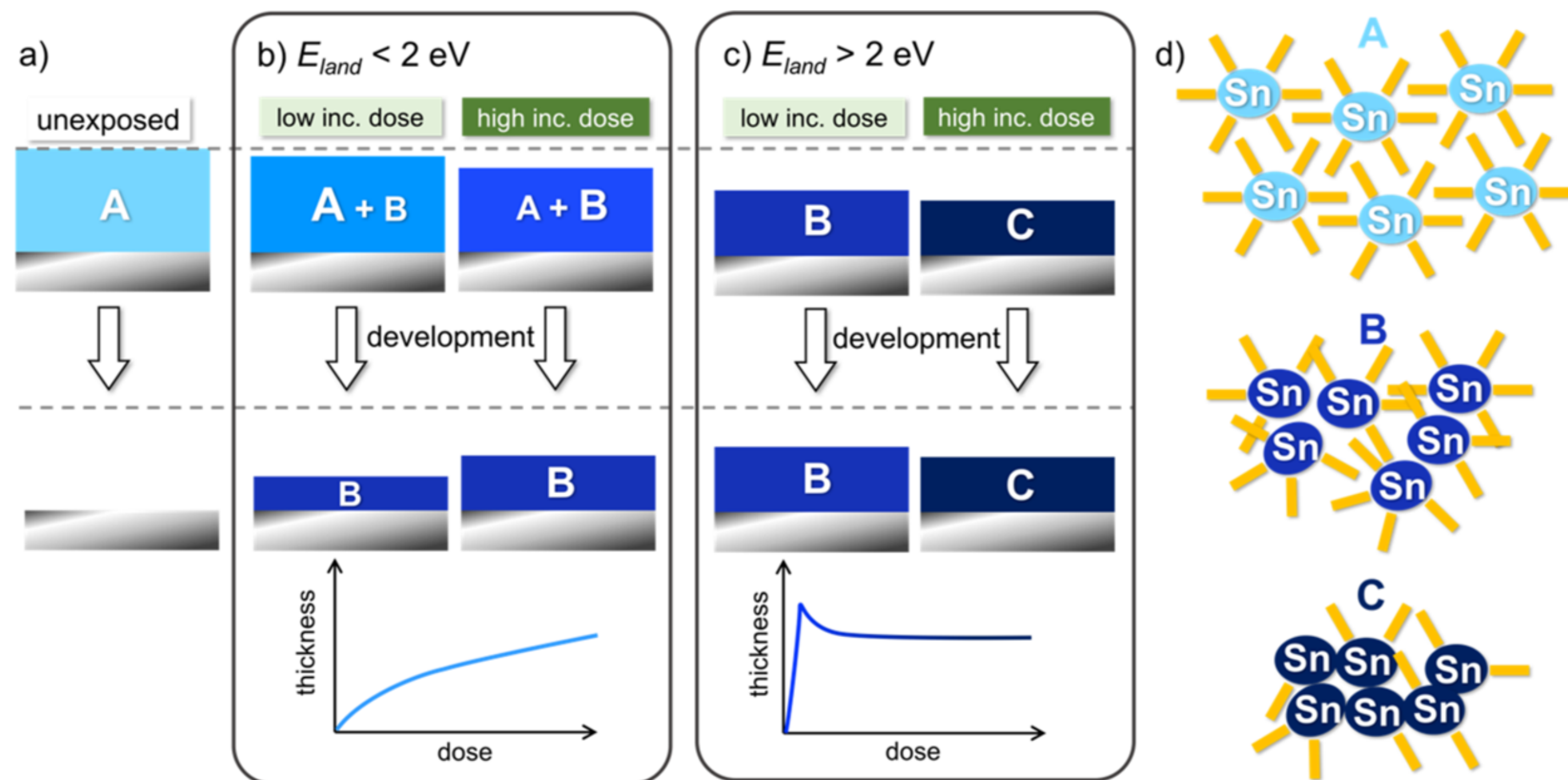
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- low energy electrons:
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- higher energy electrons:
  - $\text{Sn}_{12}\text{Bu}_{12} + e^- \rightarrow [\text{Sn}_{12}\text{Bu}_{12}^+] + 2e^- \rightarrow \text{Sn}_{12}\text{Bu}_{11}^+ + \text{Bu} + 2 [\text{Sn}_{12}\text{Bu}_{12}^-] \rightarrow \text{Sn}_{12}\text{Bu}_{11}^+ + 2 \text{Sn}_{12}\text{Bu}_{11}^- + 3\text{Bu}$

# Key Role of Very Low Energy Electrons in Tin-Based Molecular Resists for Extreme Ultraviolet Nanolithography

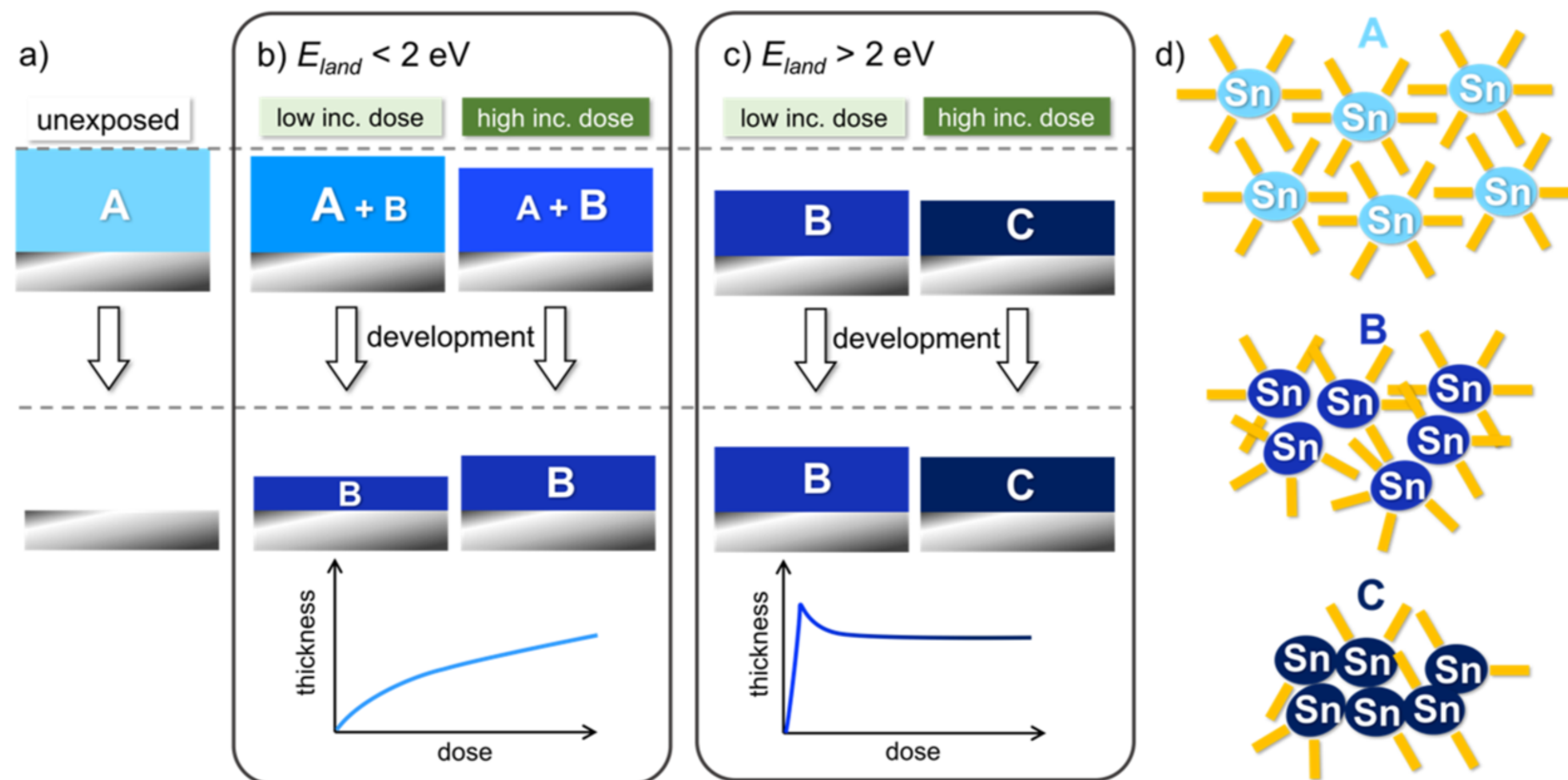
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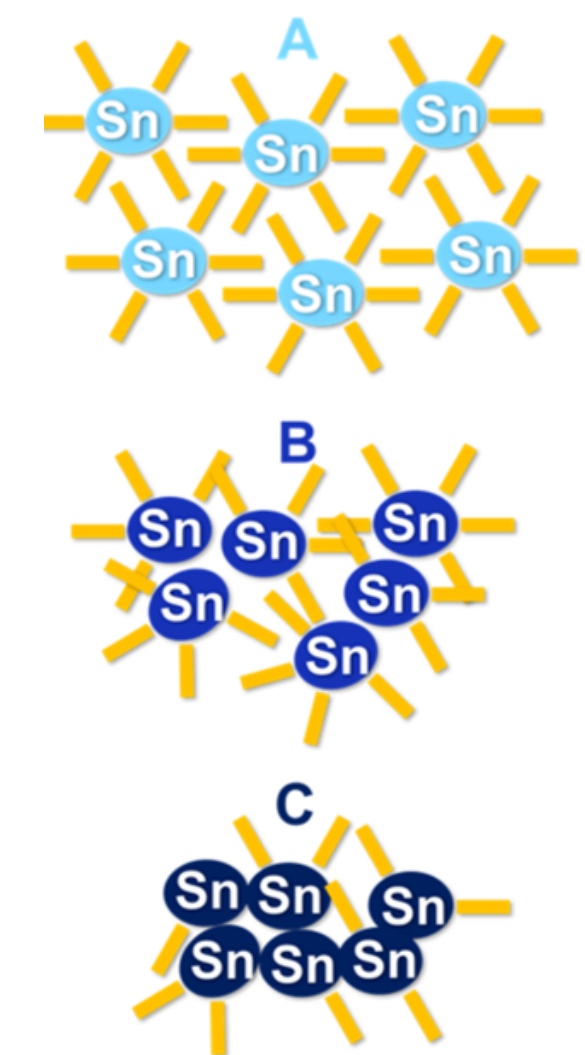
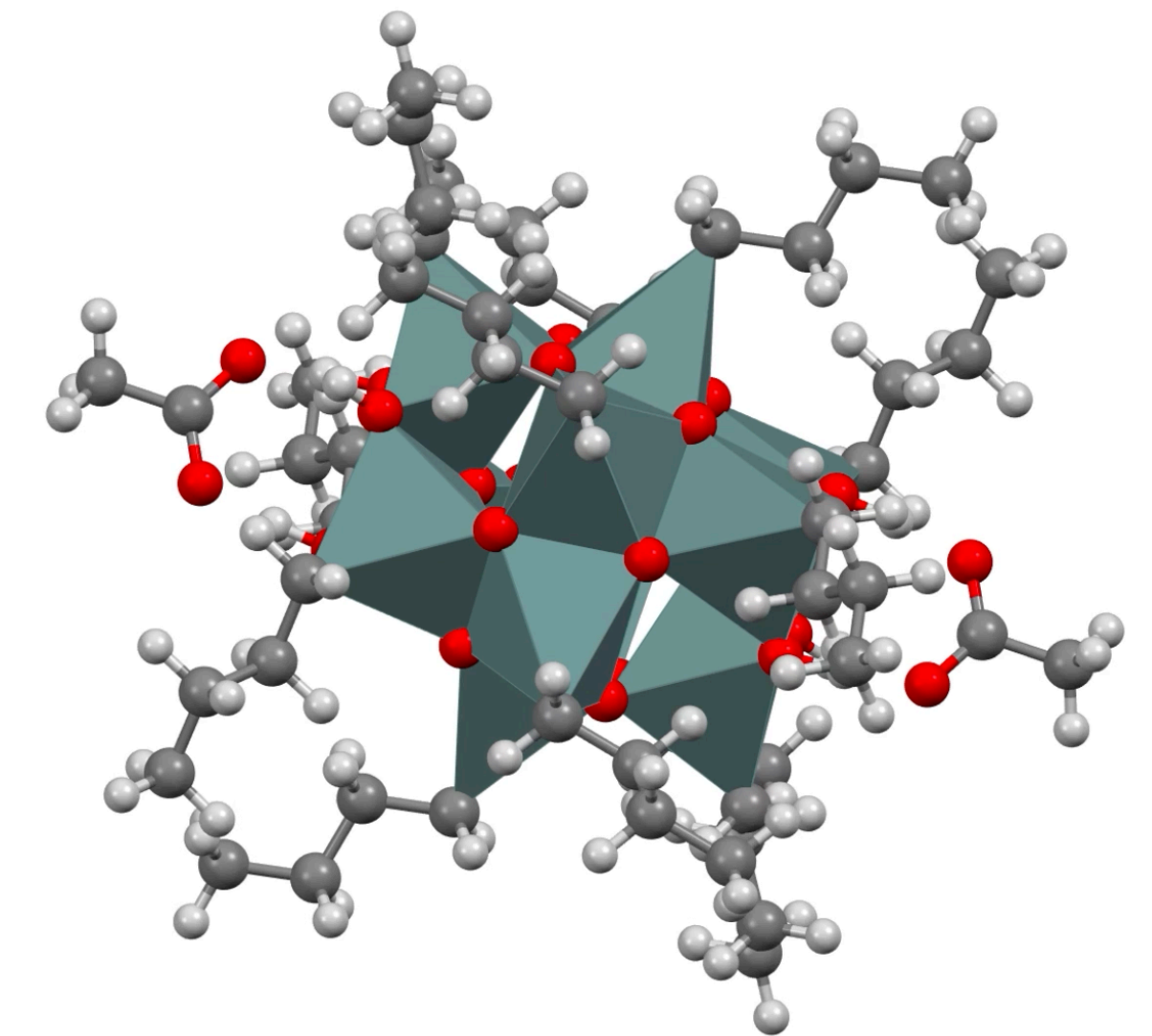


- low energy electrons:
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- higher energy electrons:
  - $\text{Sn}_{12}\text{Bu}_{12} + e^- \rightarrow [\text{Sn}_{12}\text{Bu}_{12}^+] + 2e^- \rightarrow \text{Sn}_{12}\text{Bu}_{11}^+ + 2 \text{Sn}_{12}\text{Bu}_{11}^- + 3\text{Bu}$
- conversion efficiency  $A \rightarrow B \approx 0.1$



# tin oxo cages

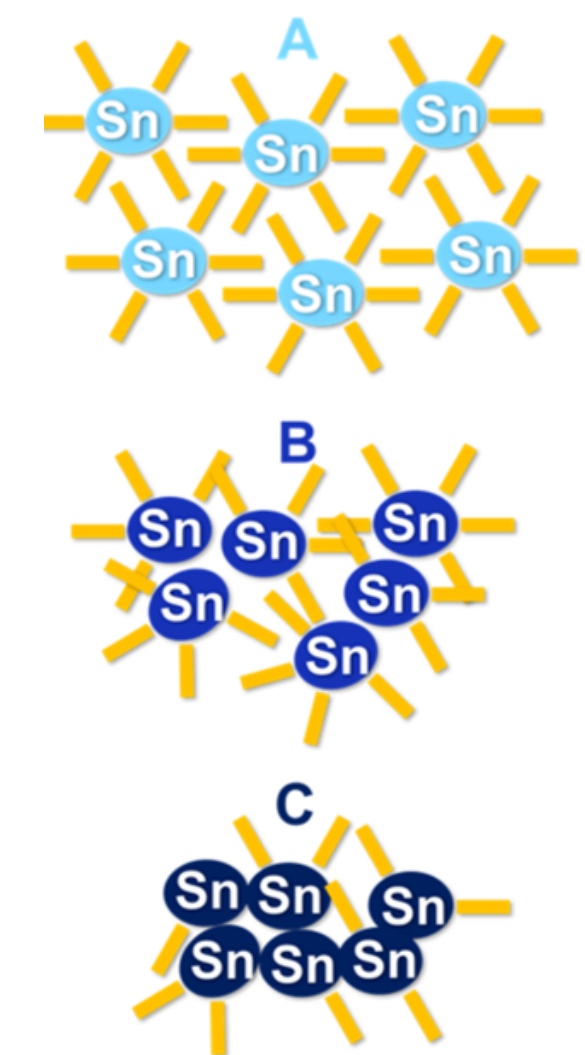
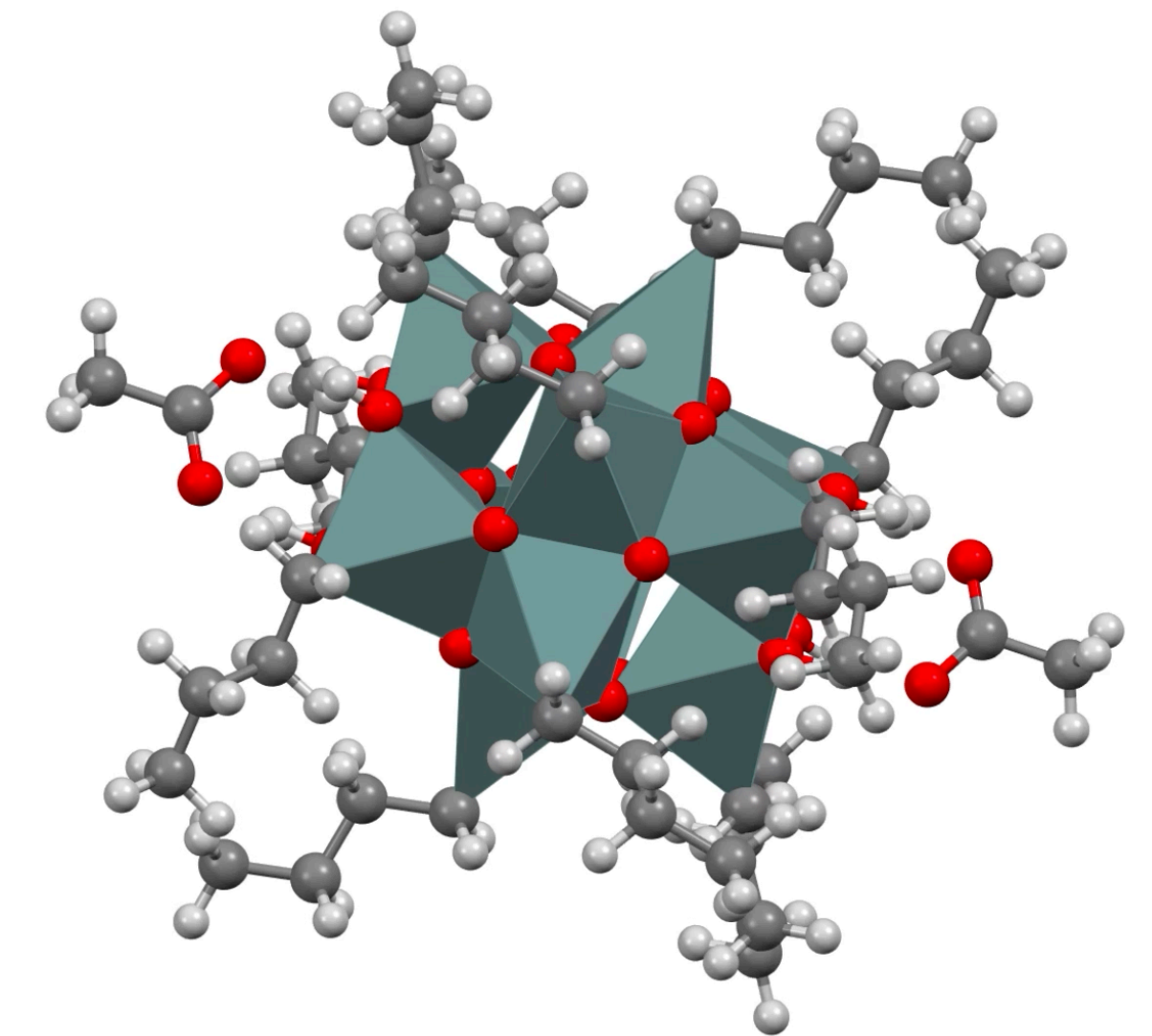
- *negative tone photoresists*
- activation via Sn-C bond breaking
  - outgassing of carbon-containing molecules
  - shrinkage upon EUV exposure
- cross-linking mechanism as yet unknown





# tin oxo cages

- *negative tone photoresists*
- activation via Sn-C bond breaking
  - outgassing of carbon-containing molecules
  - shrinkage upon EUV exposure
- cross-linking mechanism as yet unknown



# conclusions

- hybrid inorganic/organic EUV photoresists hold promise but need further development
- tuning physical properties (solubility, adhesion, etc.)
- understanding chemical mechanisms
  - rational design of improved materials

# many open questions

- EUV photons cause ionization, but ....
  - role of secondary electron generation?
  - do electron energies matter?
  - what are the structures of the insoluble materials?
  - how many bonds to break/make to switch solubility?
  - blurring due to diffusion of electrons?
  - resolution limits?



# external collaborators

- Paul Scherrer Institute
  - Yasin Ekinici
  - Michaela Vockenhuber
  - Dimitris Kazazis
  - Roberto Fallica
  - Benjamin Watts
  - Katharina Witte
- Leiden University
  - Sense Jan van der Molen
  - Ruud Tromp
  - Johannes Jobst

