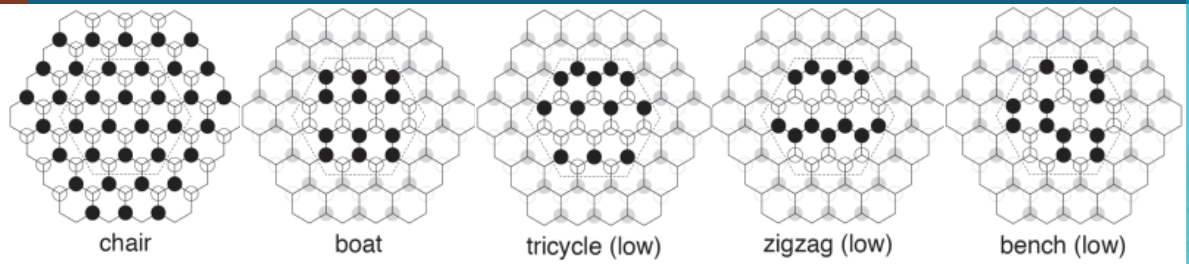
SAND2021-9481PE

Investigating the Energy-Disorder Relationship in CF_x Structures



Kelly Nieto

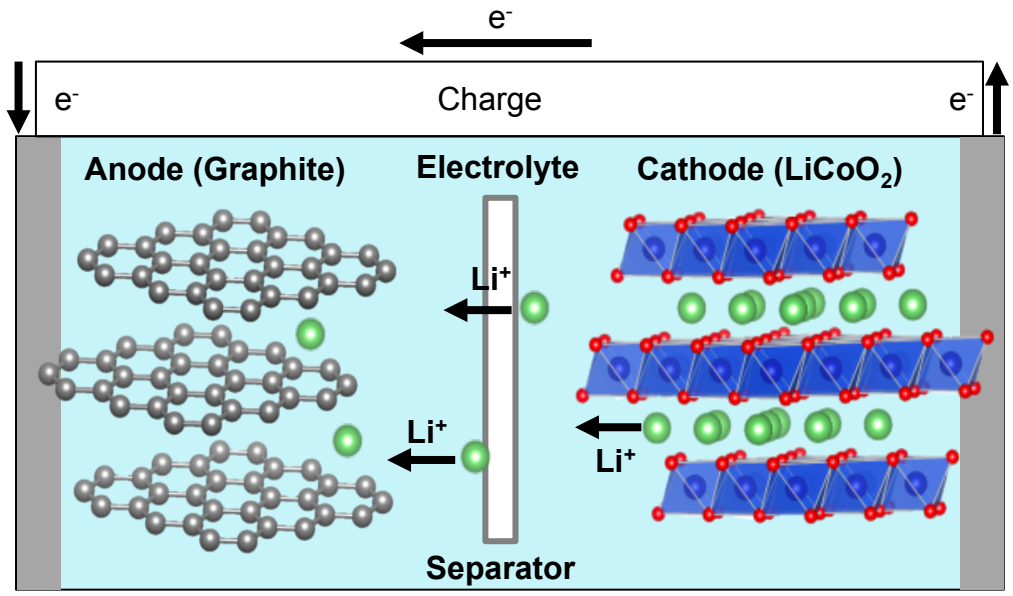
Advisor: Dr. Todd Alam

August 4th, 2021

EERE AMO Internship 2021 Summer Presentation

Understanding Battery Chemistry is Crucial for Optimization

Commercial Li-ion Battery



Chemistry	Representative Reaction
Li-ion	$LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$
Li-primary	$nLi + (CF)_n \rightarrow nLiF + (C)n$

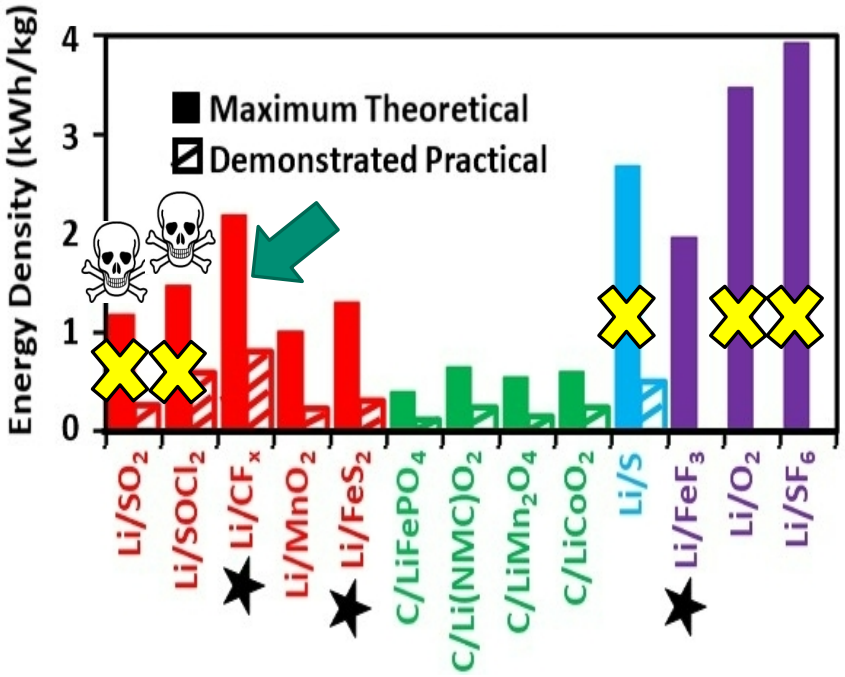
What would we like to improve

- How long the battery lasts on a single charge (Energy Density)
- How fast the battery can charge/discharge (Power Density)
- Lifetime of the battery (Cycle Life)
- Cost and safety

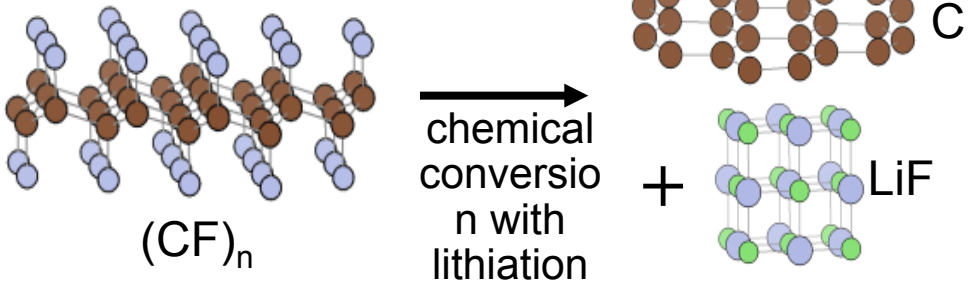
Tarascon, J.-M. *Nat. Chem.* **2010**, 2, 510.
Goodenough, J. B.; Park, K.-S., *J. Am. Chem. Soc.* **2013**, *135* (4), 1167–1176.
iPhone 11 (photograph). https://www.apple.com/shop/buy-iphone/iphone-11-pro (accessed Apr 6, 2020).
Tesla Model 3 (photograph). https://cars.usnews.com/cars-trucks/tesla/model-3 (accessed Apr 6

Can Li/CF_x be a secondary battery?

Li-primary Li-ion Next-generation R&D systems



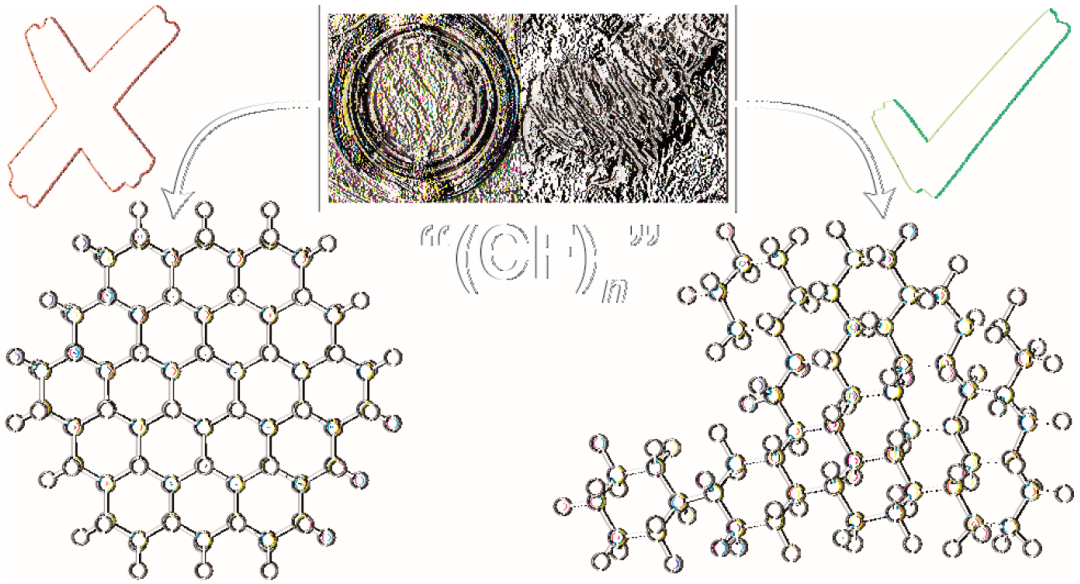
Conversion cathode (Li-primary)



Chemistry	Representative Reaction	Voltage	Capacity mA•h/g	Energy Density W•h/g
Li-ion	$LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$	3.4 V	701	2.18
Li-primary	$nLi + (CF)_n \rightarrow nLiF + (C)n$	3.5 V	117	0.40

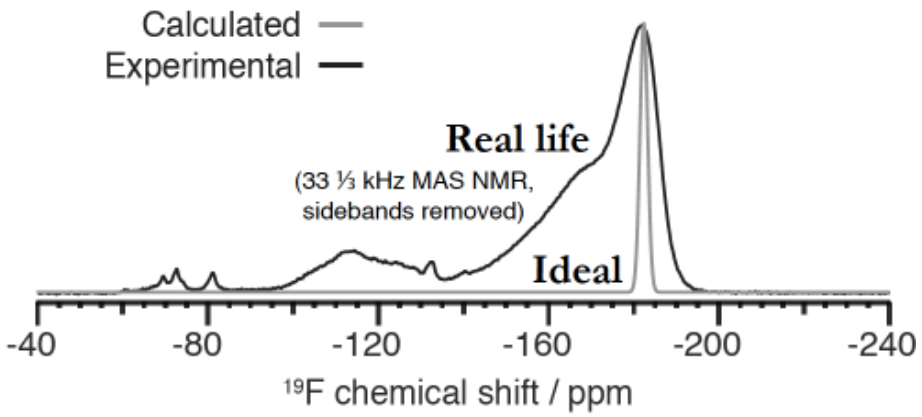
Insertion cathode figure courtesy of Dr. Katharine L. Harrison

Do we really know everything about $(CF)_n$ structures?



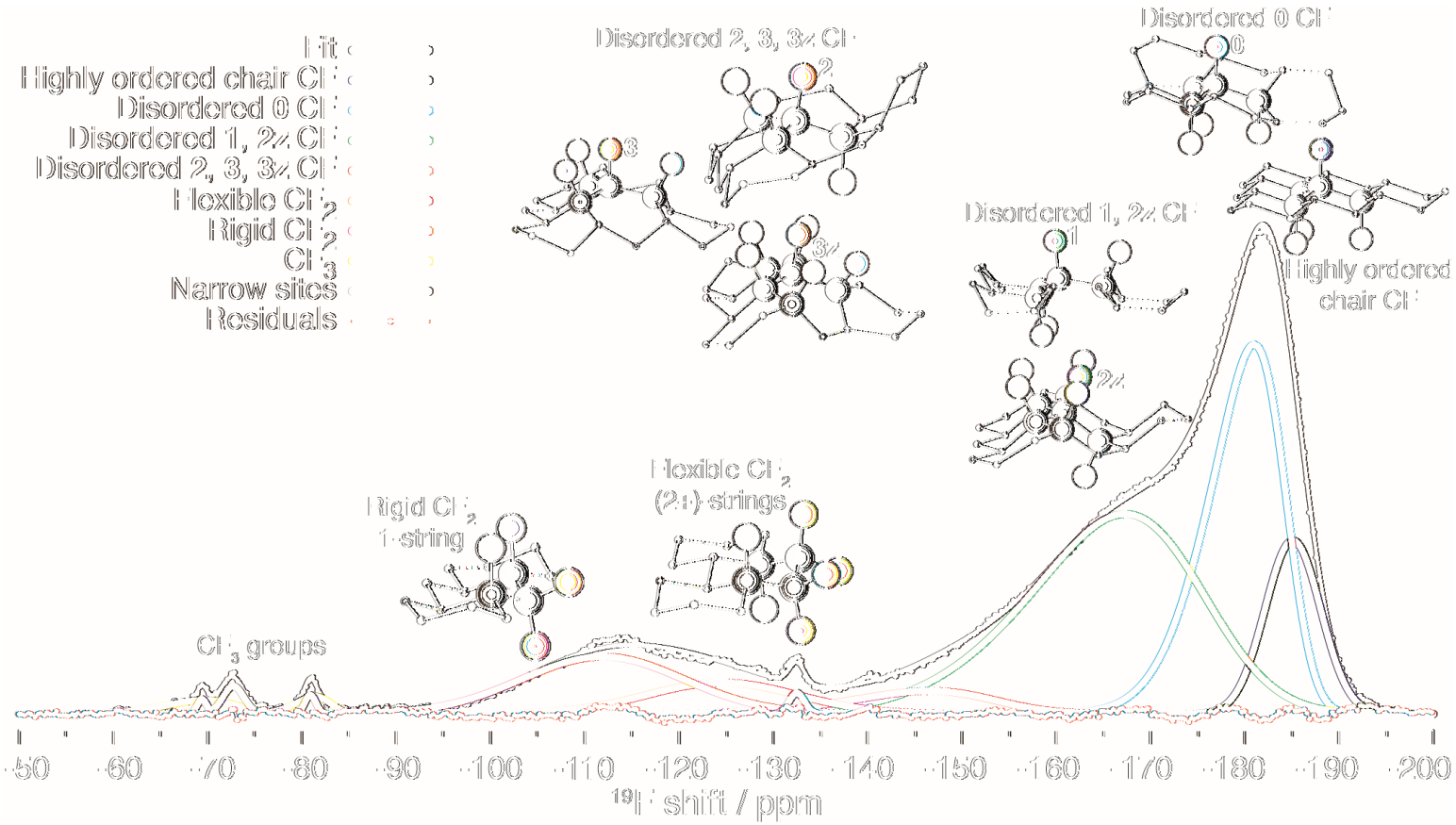
Ideal

Real Life



Walder, B. J.; Alam, T. M. *J. Am. Chem. Soc.*, **2021**, *XX*, (XXX), Just Published.

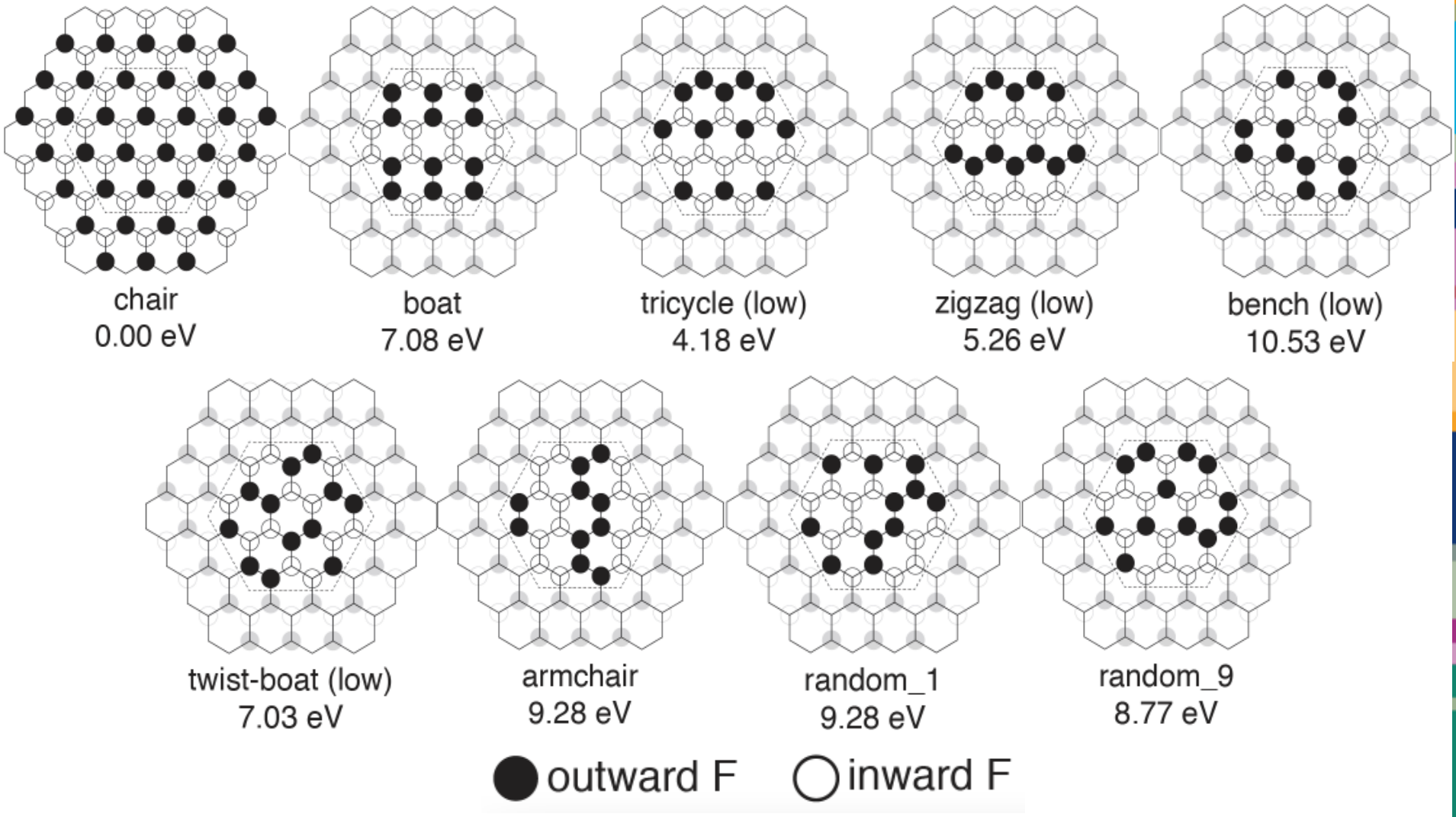
$(CF)_x$ Structures are Rich in Disorder



How does disorder impact the energetics of the C-F bond?

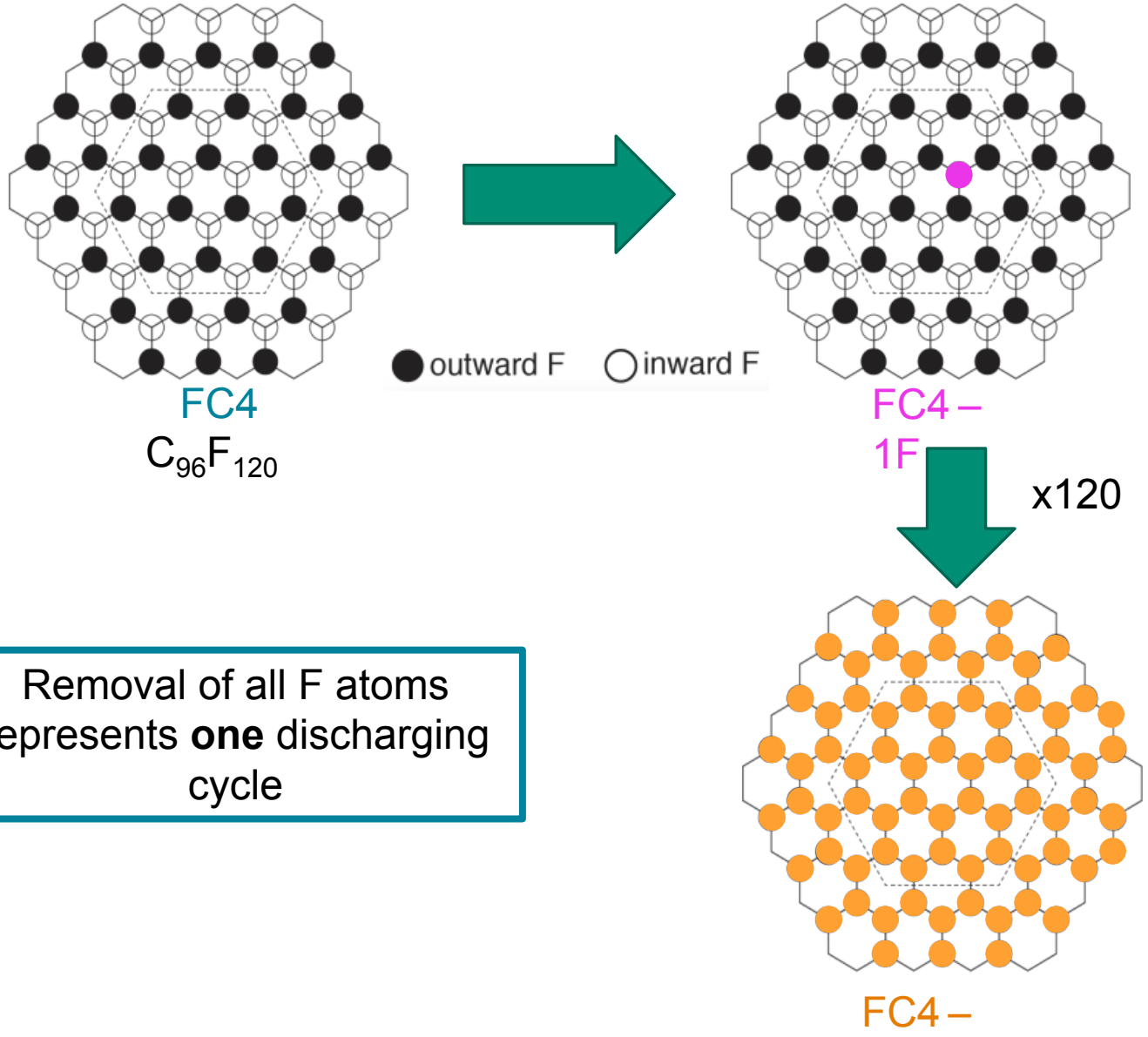
Walder, B. J.; Alam, T. M. *J. Am. Chem. Soc.*, **2021**, *XX*, (XXX), Just Published.

Representative Disordered Structures



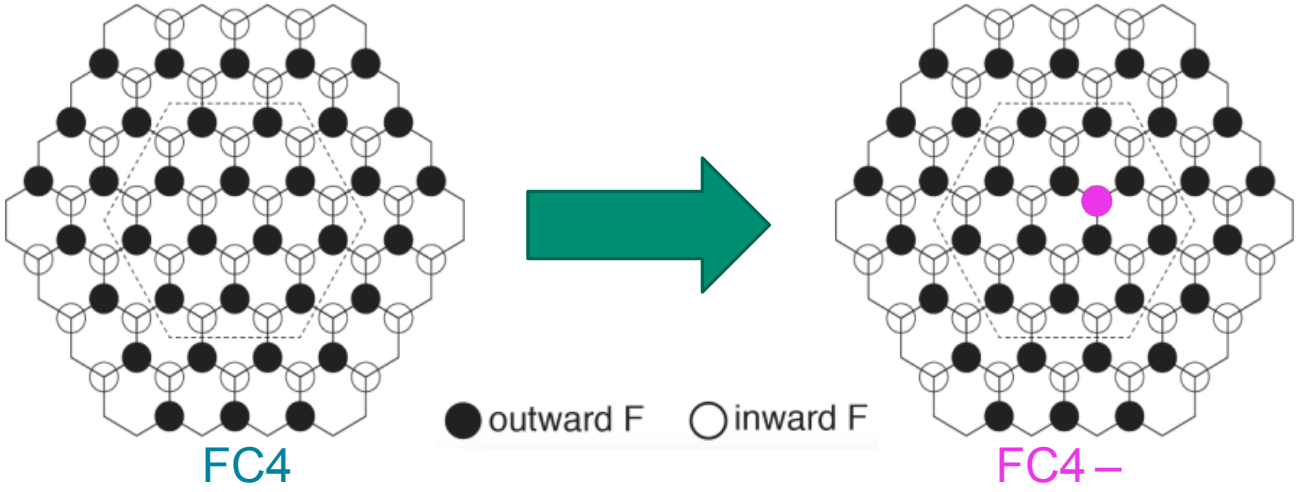
Walder, B. J.; Alam, T. M. *J. Am. Chem. Soc.*, **2021**, *XX*, (XXX), Just Published.

How does disorder impact electrochemical performance?

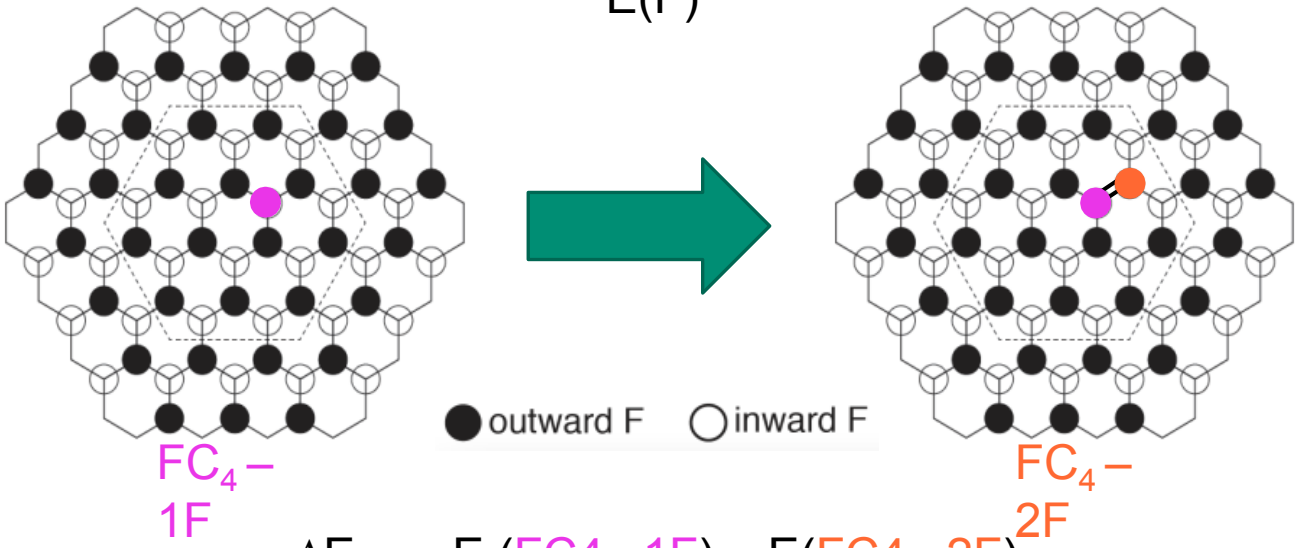


Removal of all F atoms represents **one** discharging cycle

How does disorder impact electrochemical performance?



$$\Delta E_{CF} = E\,(FC4) - E(FC4 - nF) - E(F)$$

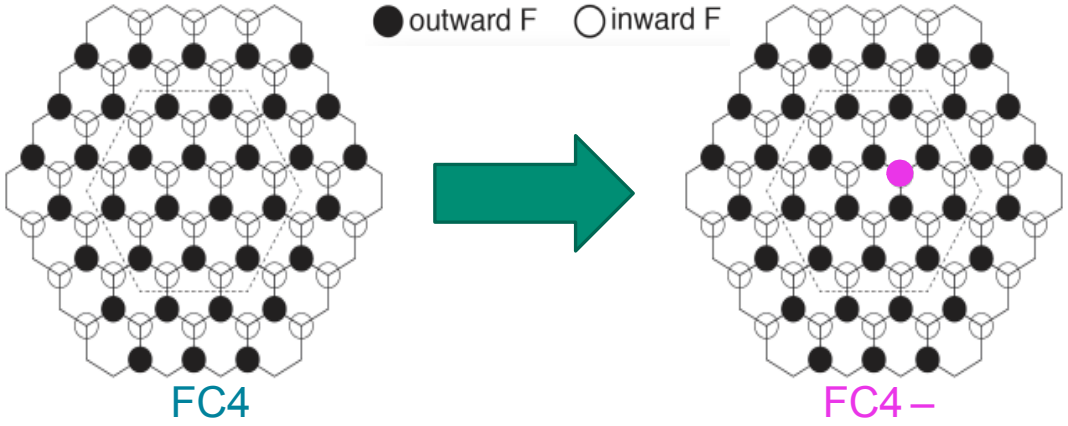


$$\Delta E_{CF} = E\,(FC4 - 1F) - E(FC4 - 2F) -$$

High-Performance Computing at SNL

HPC Clusters
- Attaway
- Sky Bridge
- Uno
- Ghost
- Eclipse
- Manzano

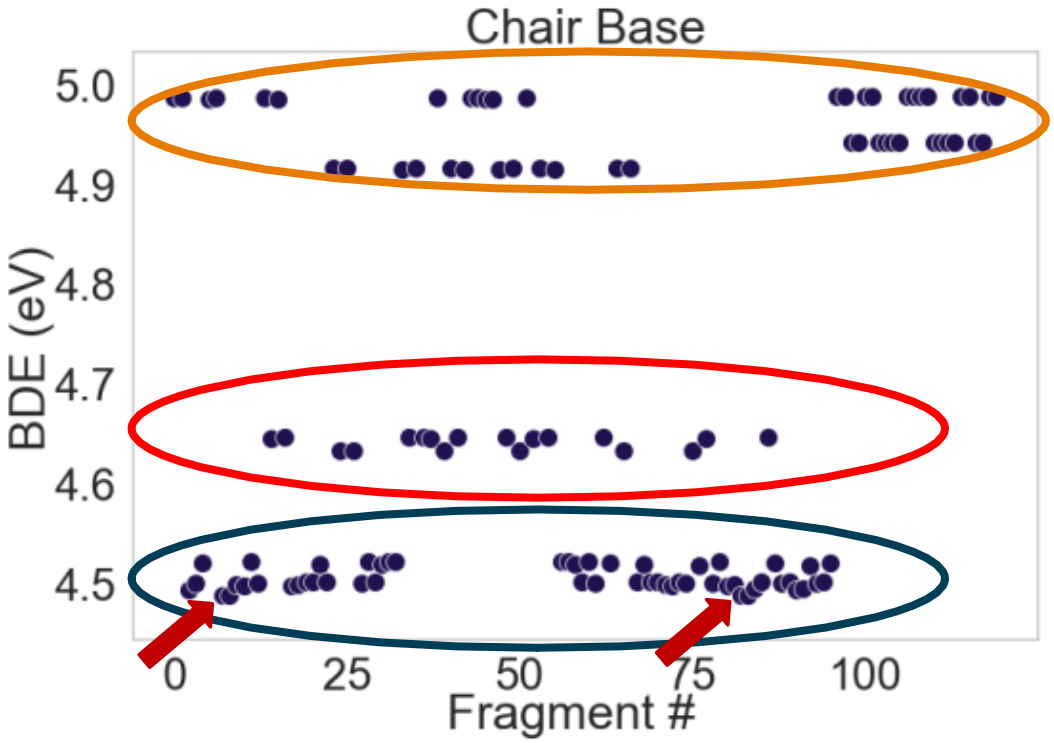
Gaussian16 Calculations

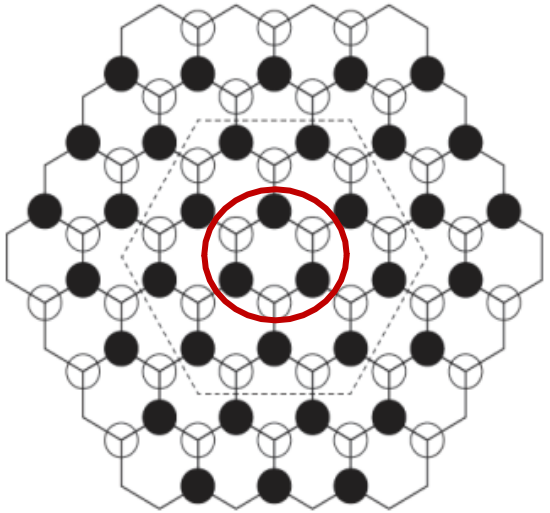


Optimization → Fragmentation → BDE calculation → Removal of next F atom → Optimization

Sky Bridge Cluster (photograph). https://hpc.sandia.gov/index.html (accessed July 26th,

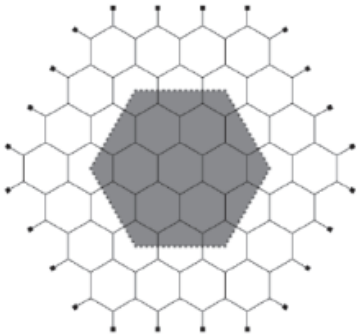
Distribution of BDEs in the Chair Structure



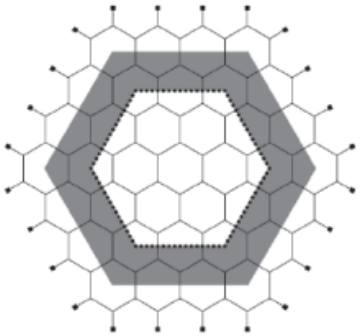


chair
0.00 eV

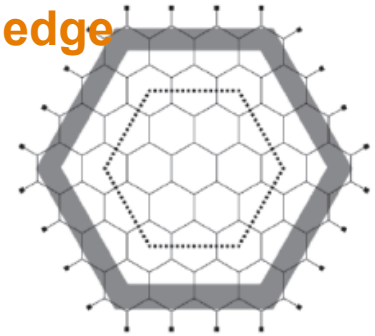
Core



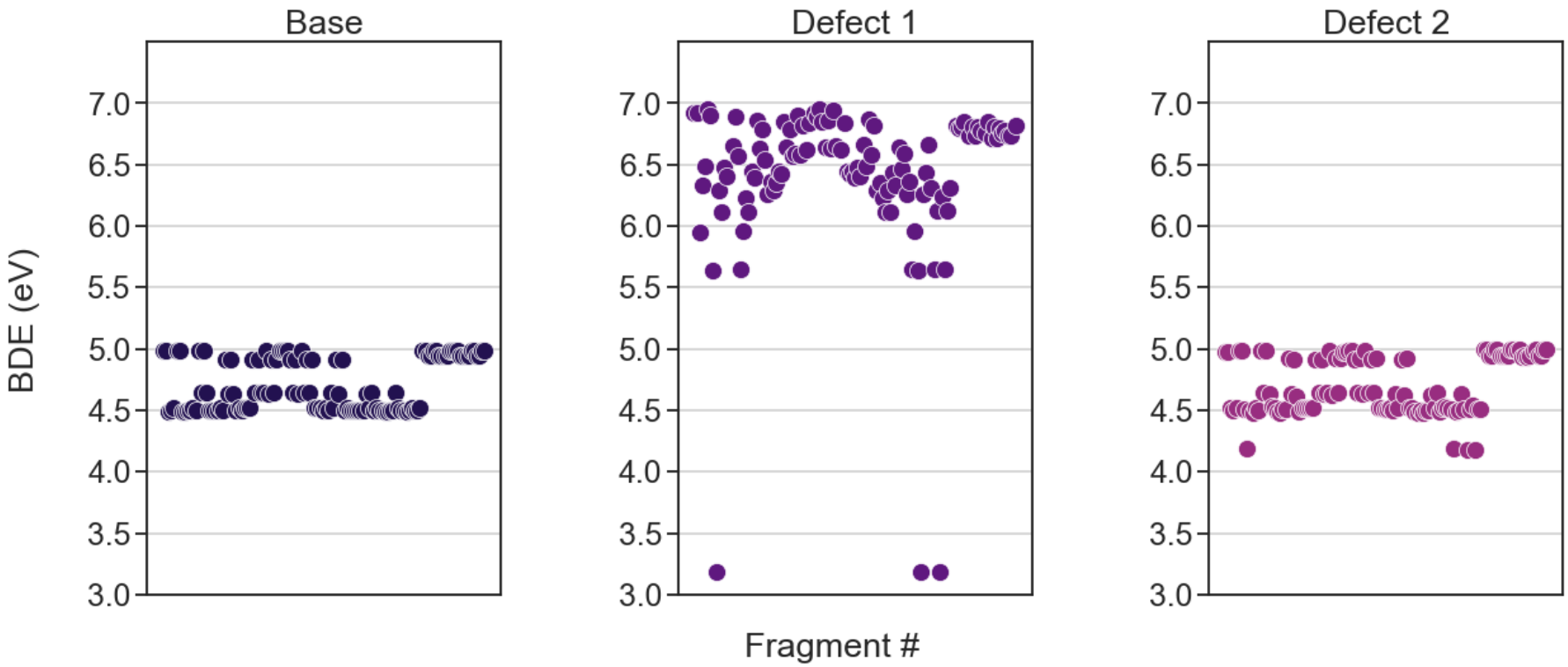
Core Adjacent

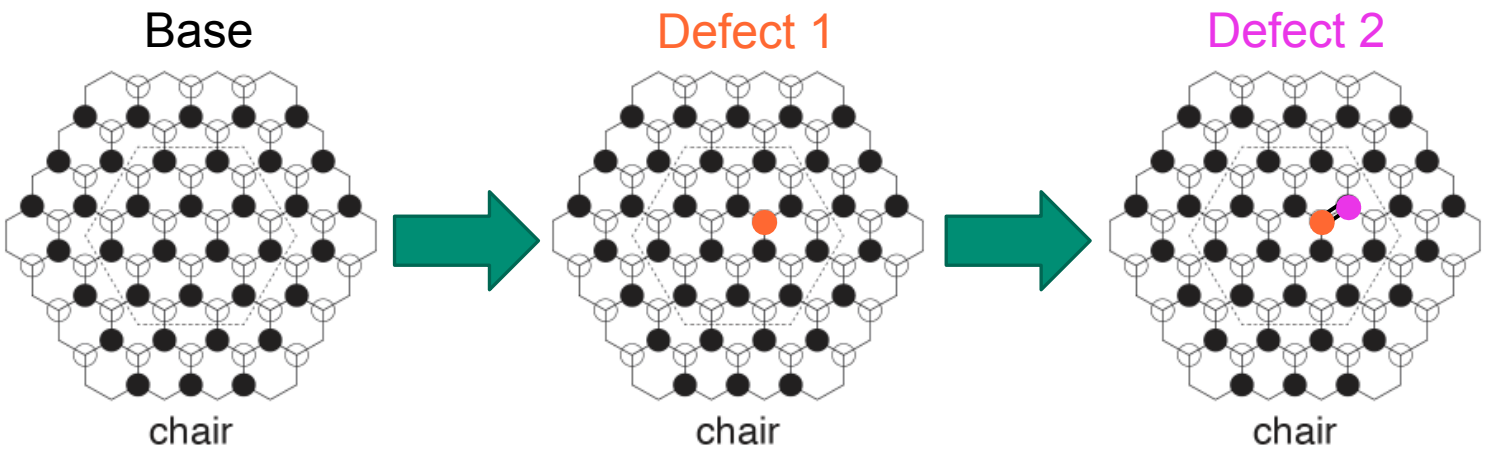


Hexagonal edge

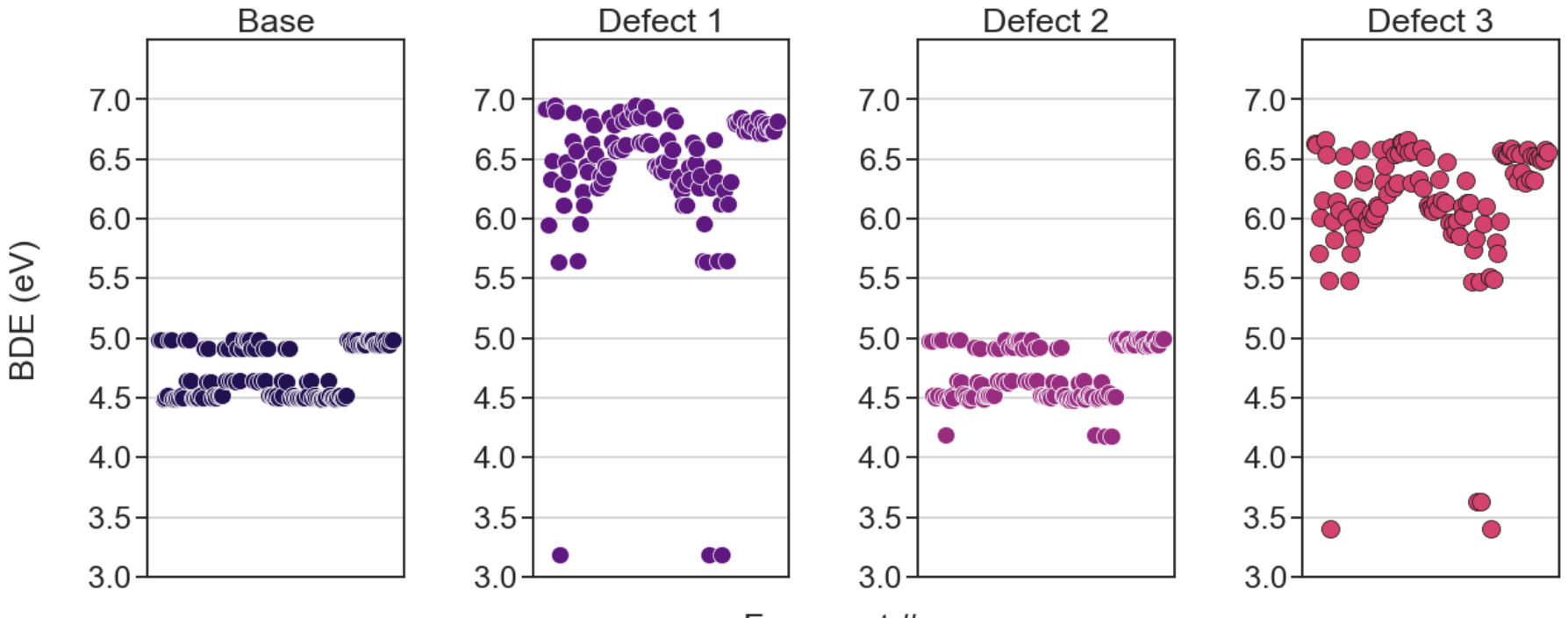


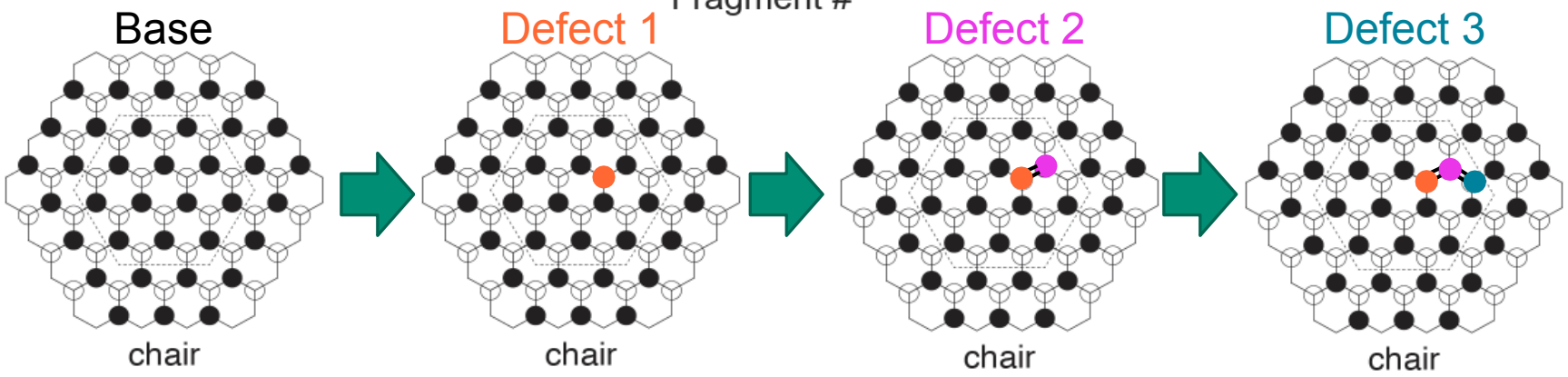
Defluorination Pathway of Chair Structure





Defluorination Pathway of Chair Structure



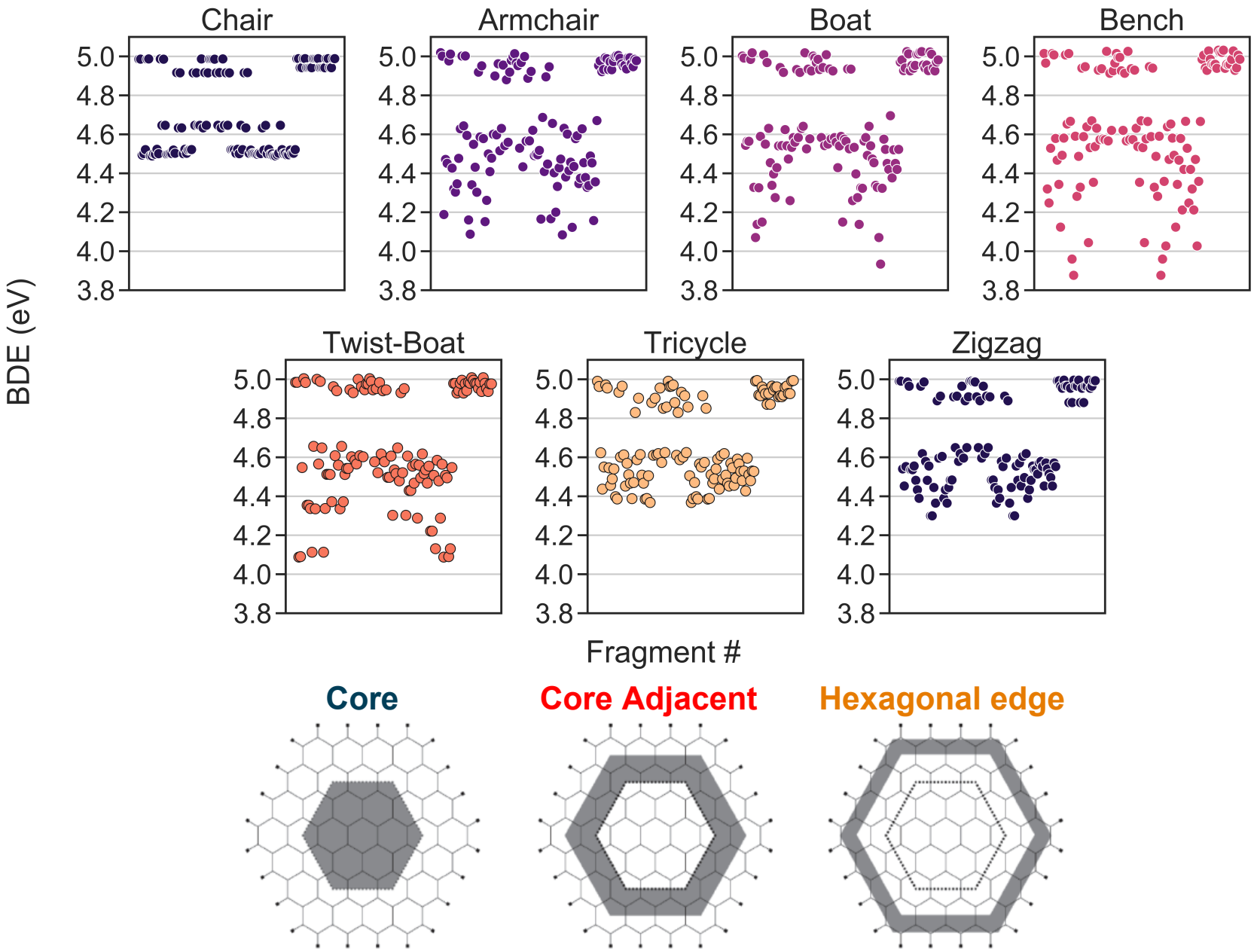


BDE = 4.92 eV
BL = 1.37 Å

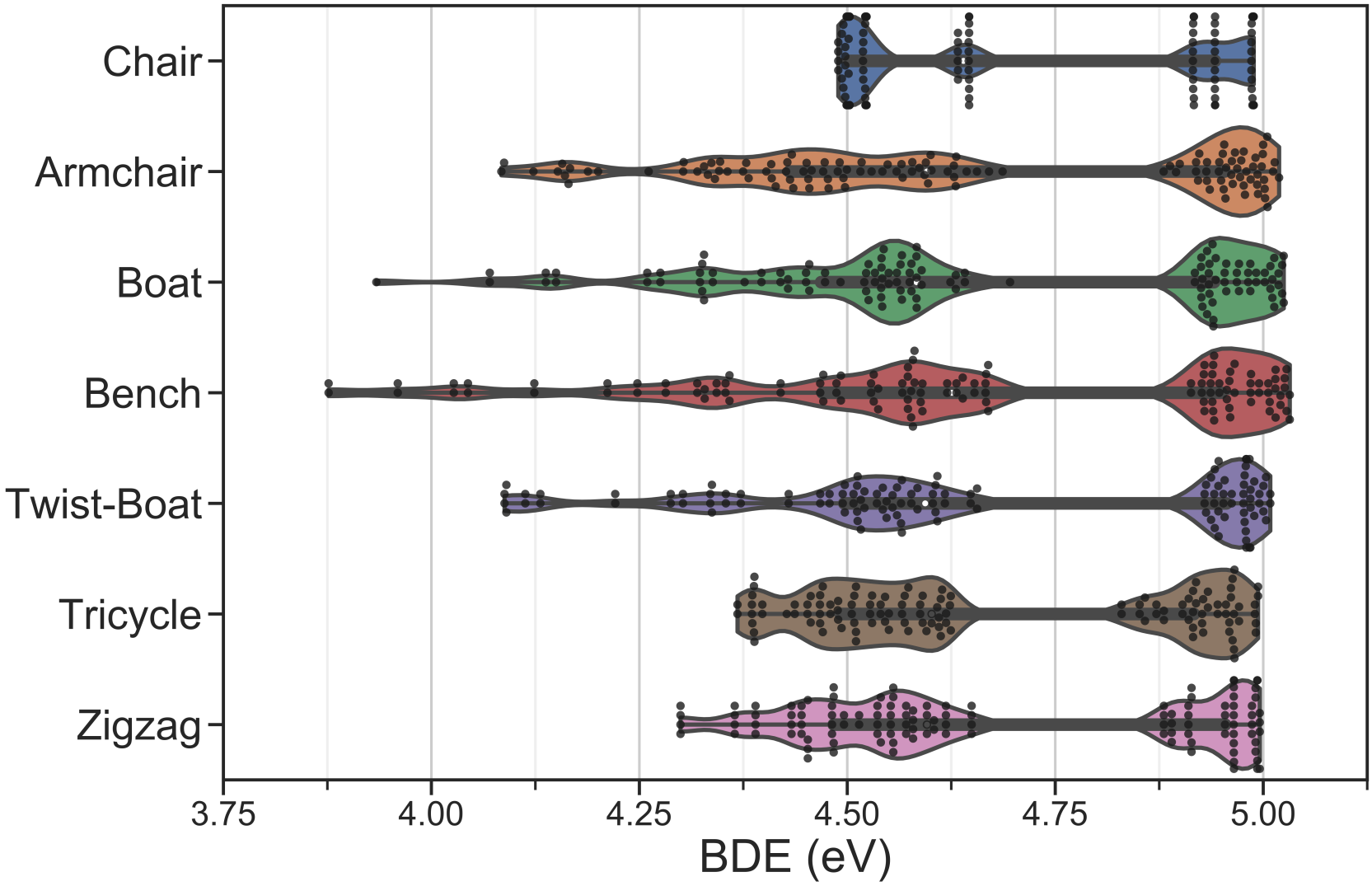
BDE = 3.19 eV
BL = 1.38 Å

BDE = 4.18 eV
BL = 1.38 Å

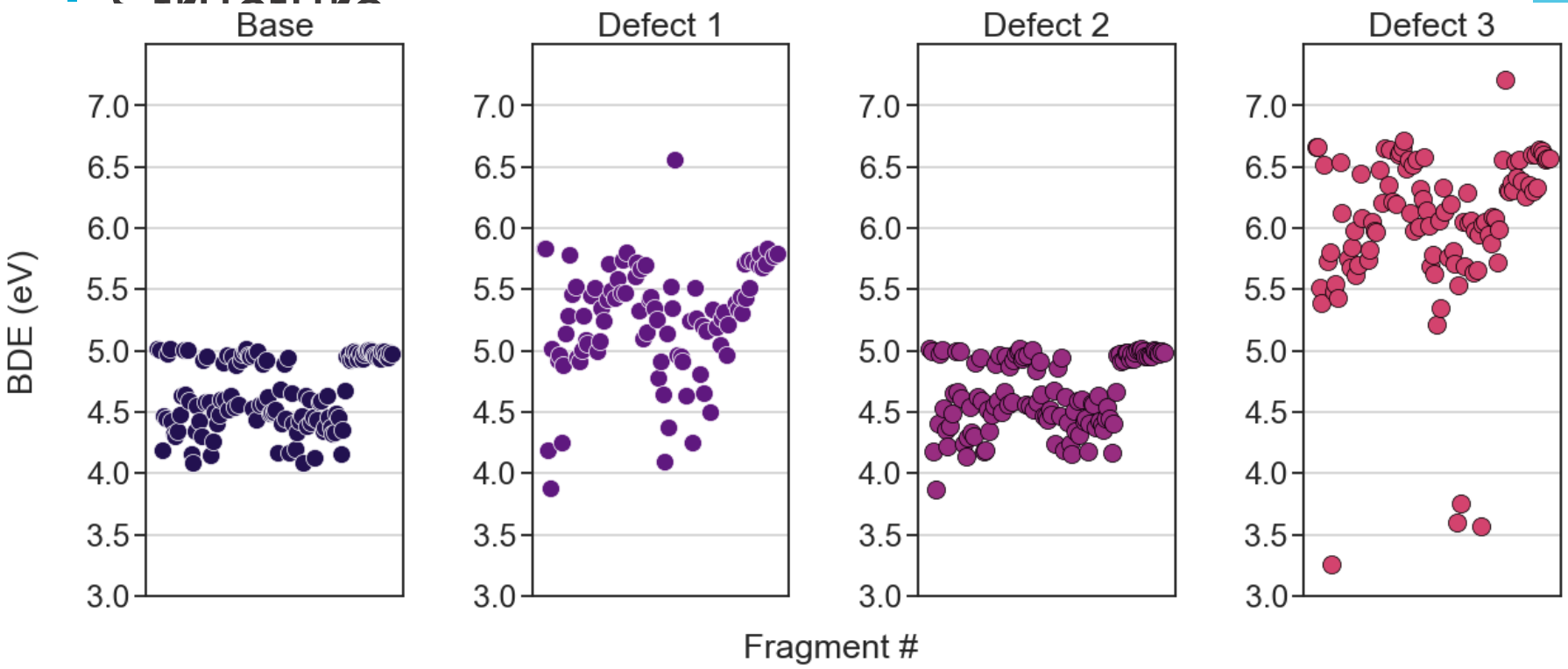
Base Structures show differences in BDEs

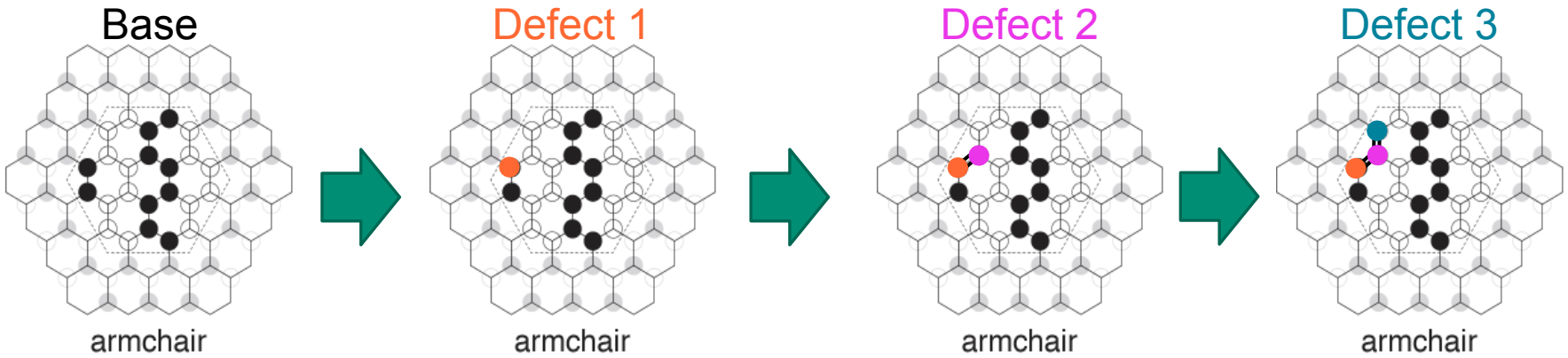


Disorder Leads to Wider Distributions of BDEs



Defluorination Pathway of Armchair Structure



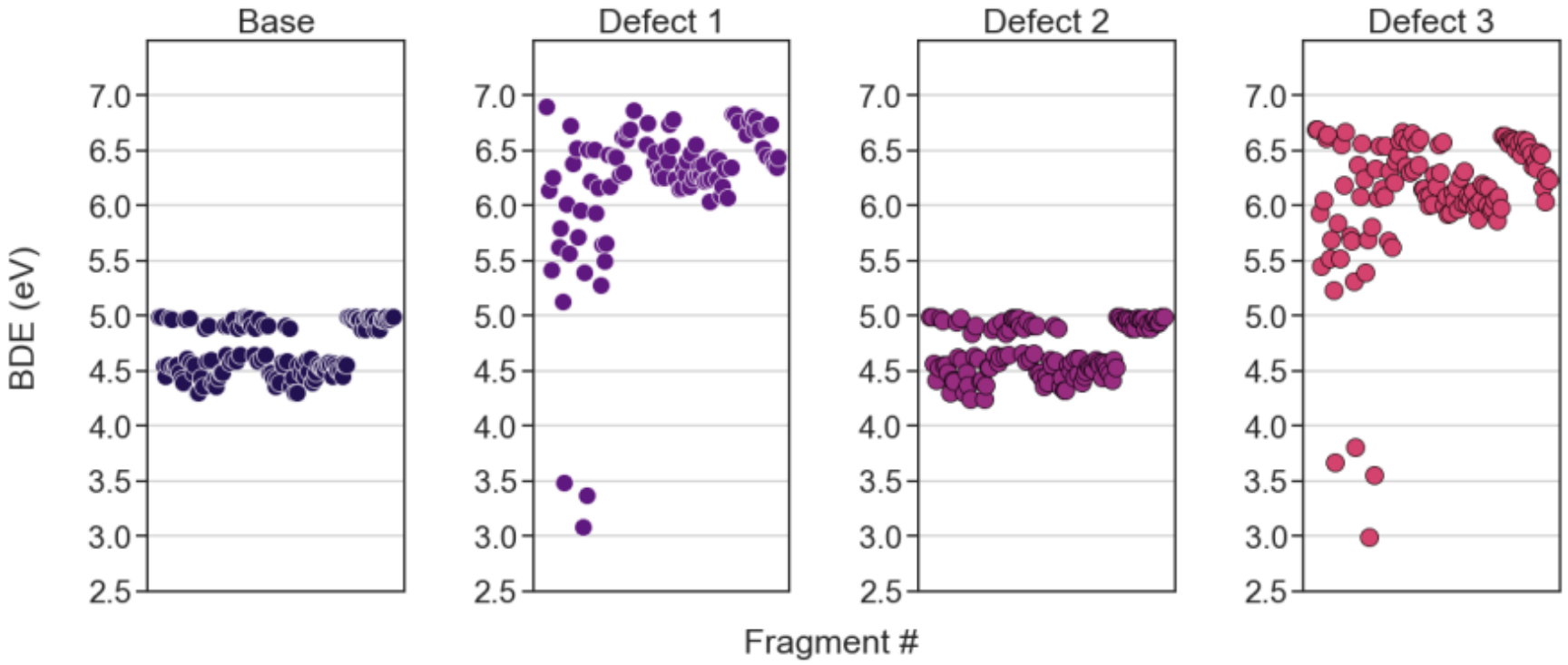


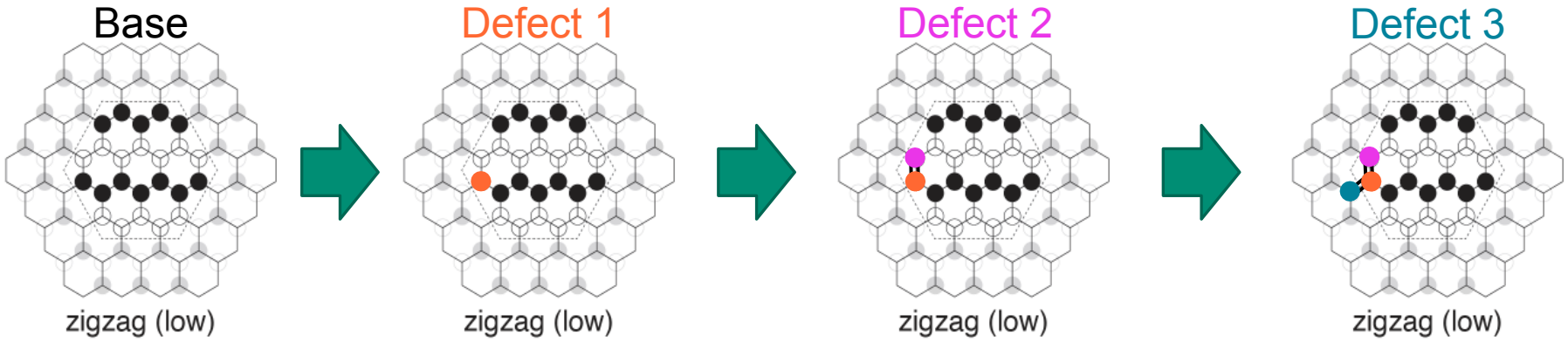
BDE = 4.08 eV
BL = 1.37 Å

BDE = 2.19 eV
BL = 1.38 Å

BDE = 3.87 eV
BL = 1.39 Å

Defluorination Pathway of Zigzag Structure





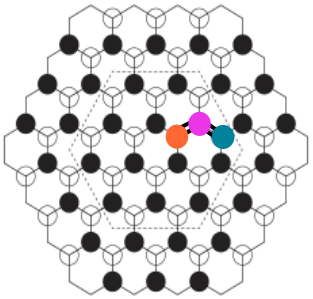
BDE = 4.30 eV
BL = 1.37 Å

BDE = 3.08 eV
BL = 1.38 Å

BDE = 4.24 eV
BL = 1.38 Å

Disorder Impacts BDEs of C-F Bonds

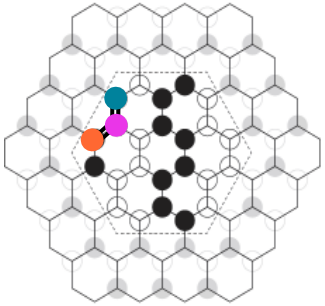
Defect 3



chair

BDE = 4.18 eV
BL = 1.38 Å

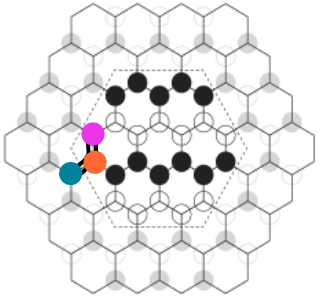
Defect 3



armchair

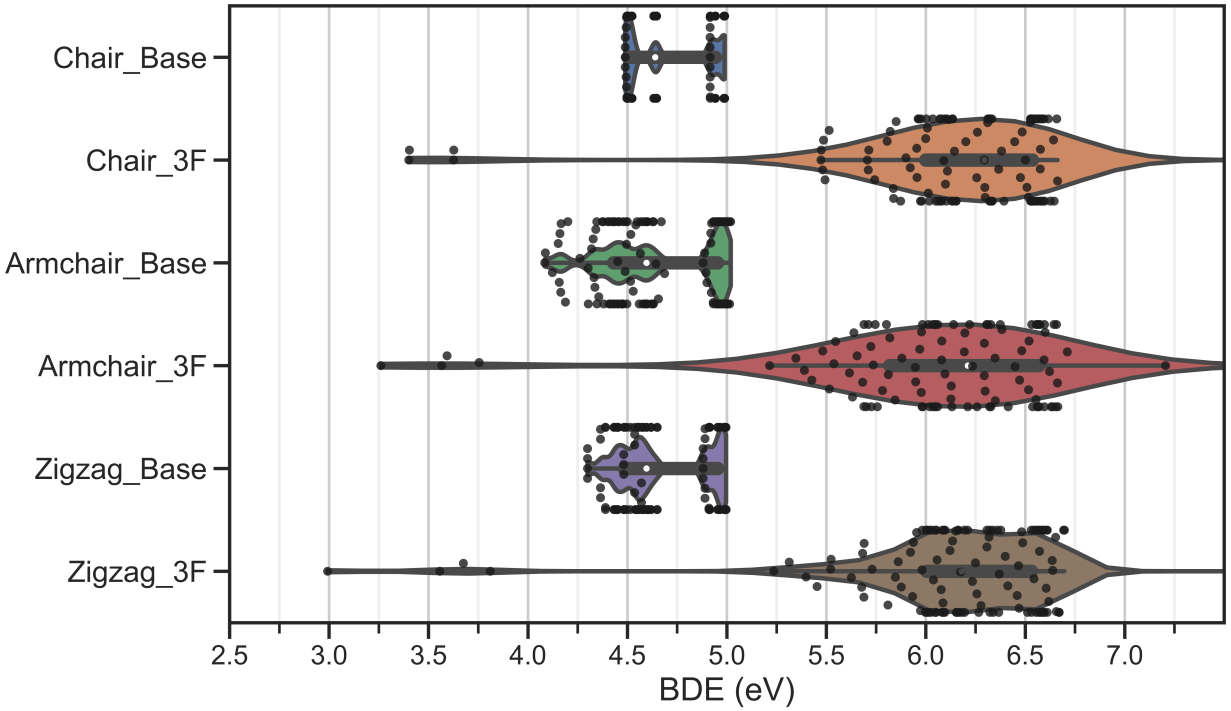
BDE = 3.87 eV
BL = 1.39 Å

Defect 3



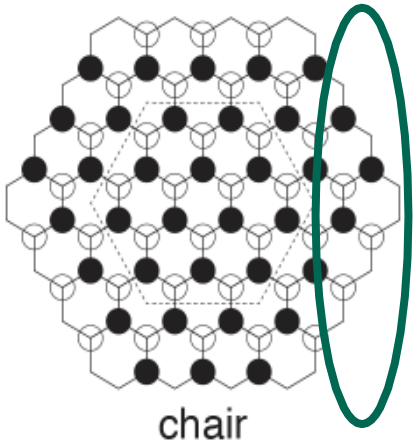
zigzag (low)

BDE = 4.24 eV
BL = 1.38 Å



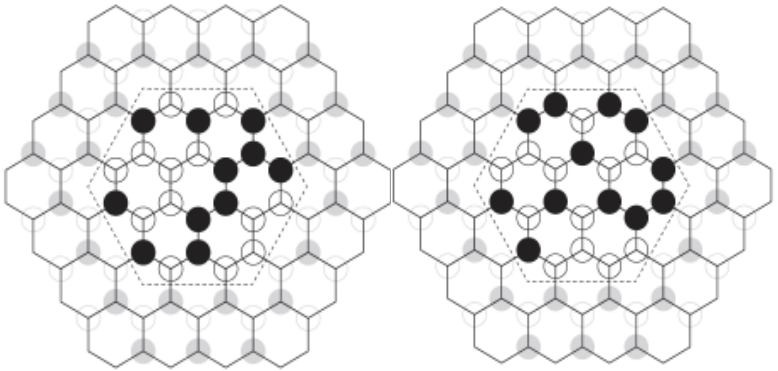
Future Directions

Edge Defluorination



chair
0.00 eV

Defluorination with greater disorder



random_1
9.28 eV

random_9
8.77 eV

Acknowledgments

Dr. Todd Alam

Dr. Brennan Walder

Dr. Keith Fritzsching

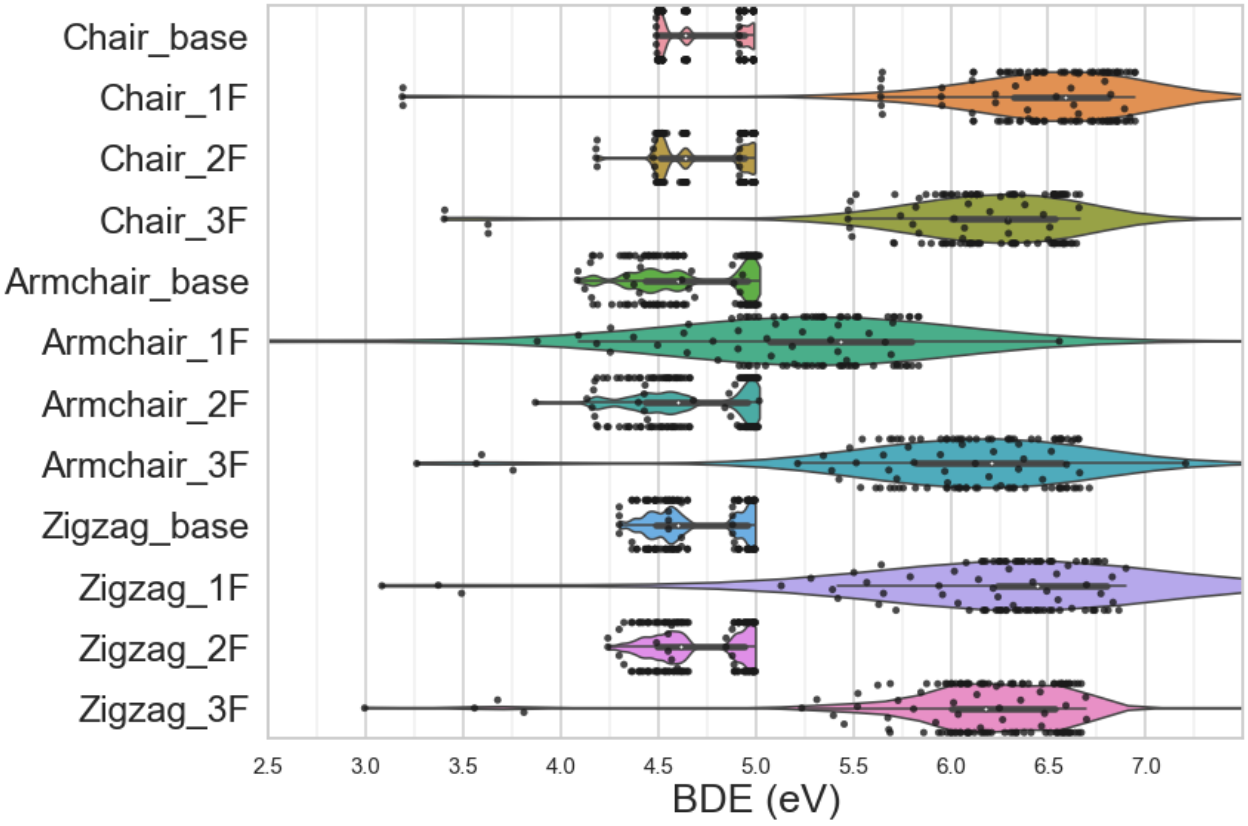
Josh Allers

Jane Keth

This research was supported entirely through the ***U.S Department of Energy, Advanced Manufacturing Office and the Energy Efficiency & Renewable Energy Storage Internship*** program.

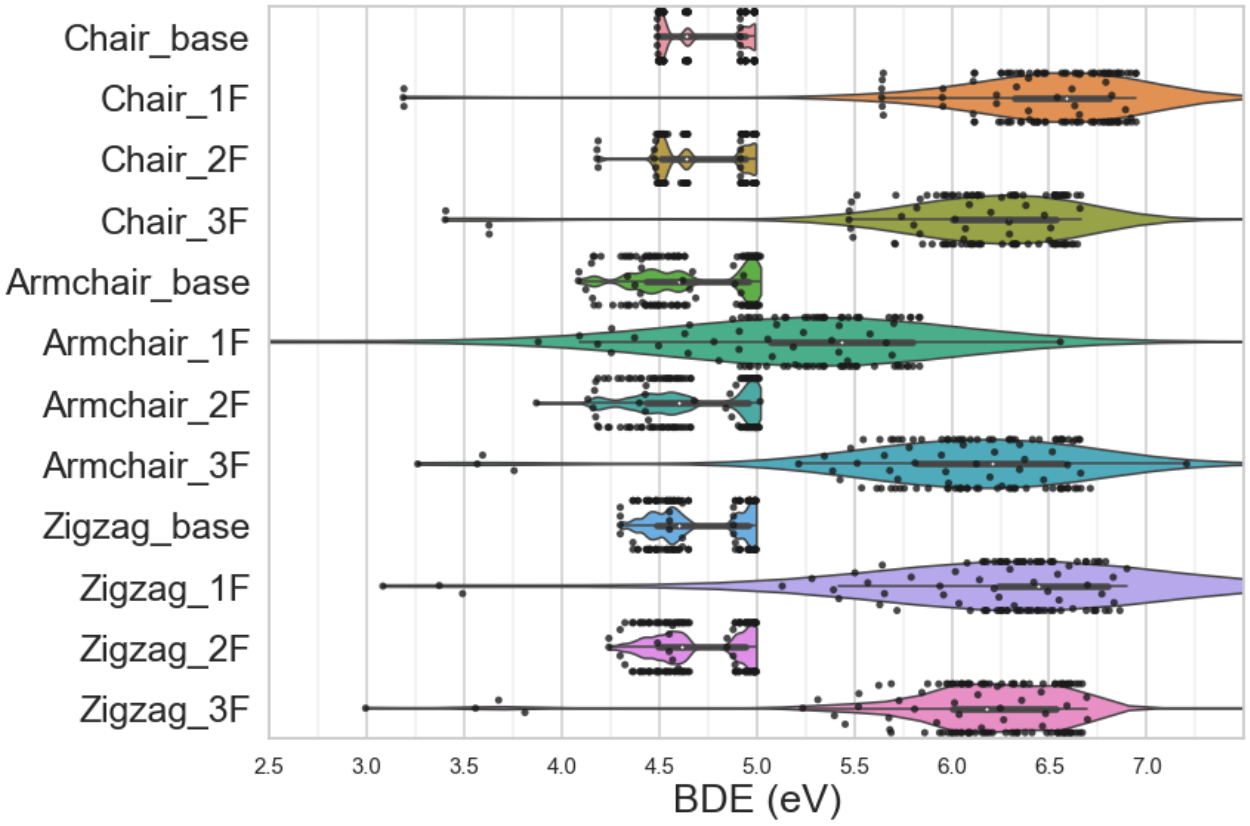
Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This presentation describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the presentation do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

base - 3F for Chair, Armchair, and Zigzag

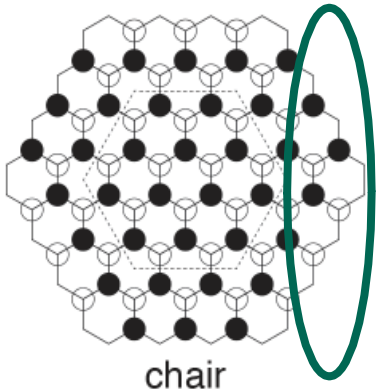


Future Directions
(I think I like this slide better)

Continuation of Defluorination

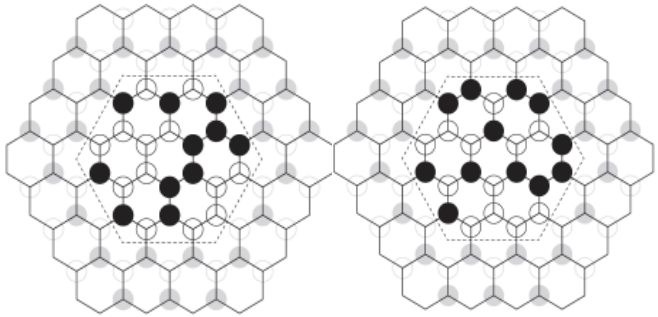


Edge Defluorination



chair
0.00 eV

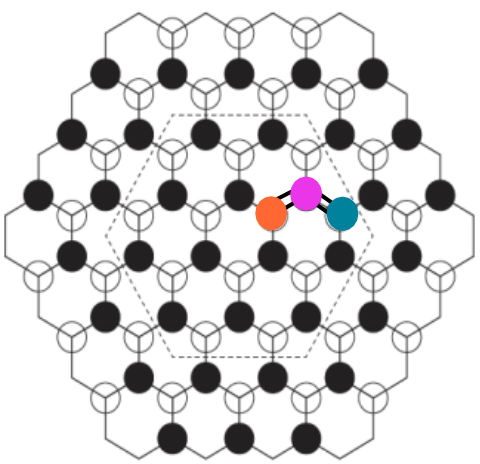
Defluorination with Greater Disorder



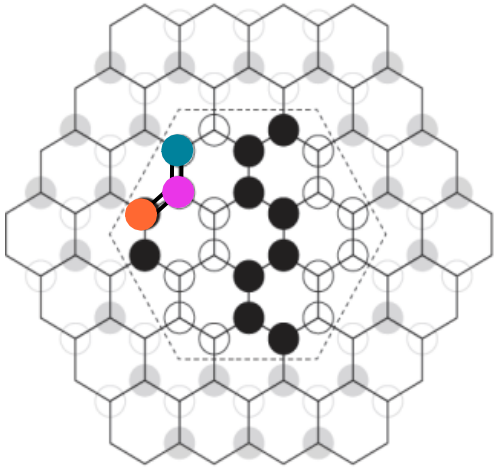
random_1
9.28 eV

random_9
8.77 eV

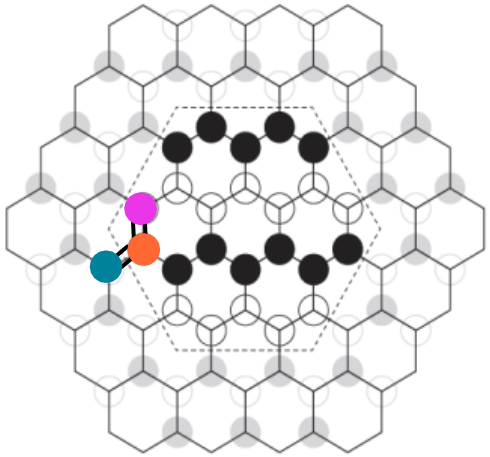
Possible images for intro slide



chair
3rd F removed
BDE = 4.18
eV



armchair
3rd F removed
BDE = 3.87
eV



zigzag (low)
3rd F removed
BDE = 4.24
eV