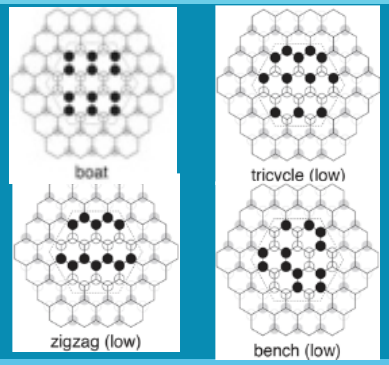
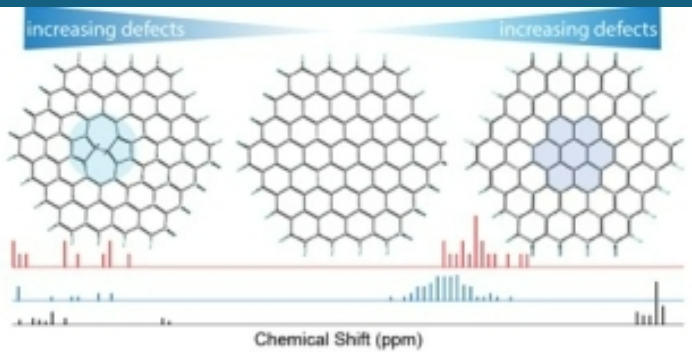
SAND2021-10324C

Characterizing Disorder and Defect Structures in Fluorinated Graphite Using NMR





Innovative Chemistry & Materials for Electrochemical Energy Storage, Fall 2021 American Chemical Society National Meeting
Aug. 24th, 2021

PRESENTED BY

Dr. Todd M. Alam

Organic Materials Science Department
Sandia National Laboratories
Albuquerque, NM 87185

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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SAND2020-11940 PE

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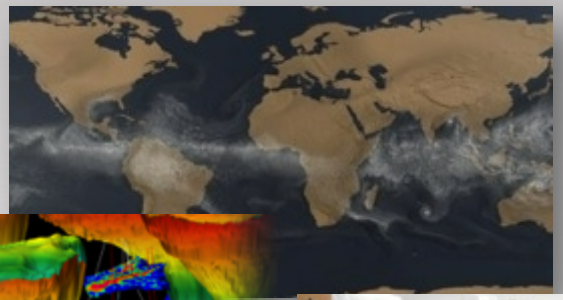
Energy Research at Sandia

Energy Research

ARPAe, BES Chem Sciences, ASCR, CINT, Geo Bio Science, BES Material Science

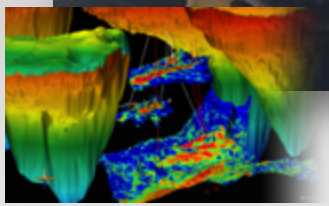
Climate & Environment

Measurement & Modeling, Carbon Management, Water & Environment, and Biofuels



Nuclear Energy & Fuel Cycle

Commercial Nuclear Power & Fuel, Nuclear Energy Safety & Security, DOE Managed Nuclear Waste Disposal

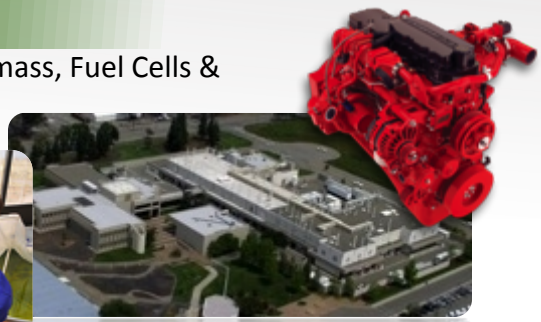


Renewable Systems & Energy Infrastructure

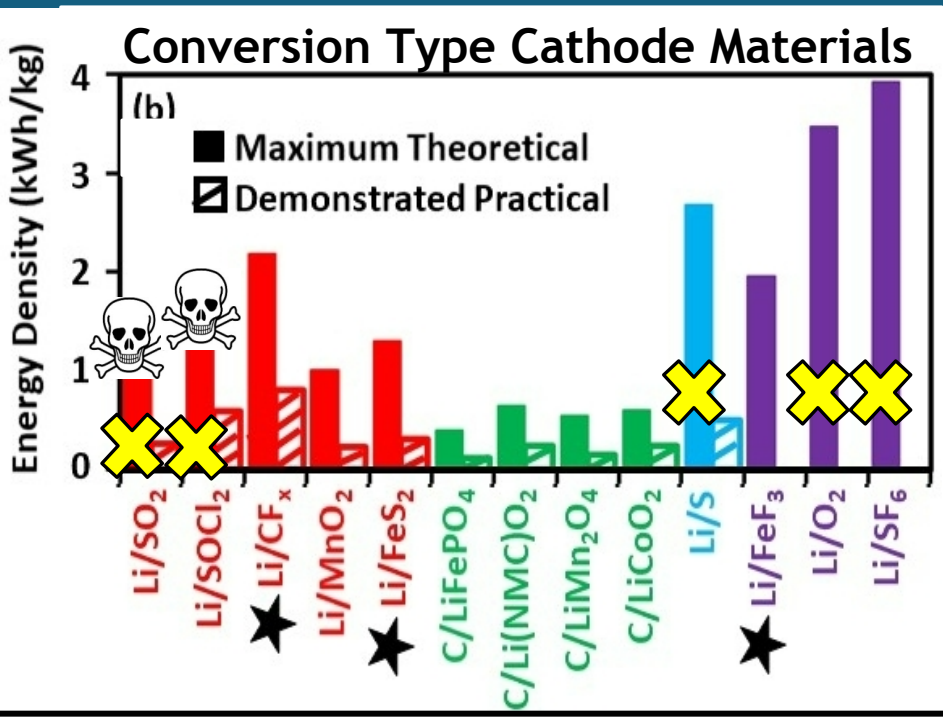
Renewable Energy, Energy Efficiency,
Grid and Storage Systems

Transportation Energy & Systems

Vehicle Technologies, Biomass, Fuel Cells & Hydrogen Technology



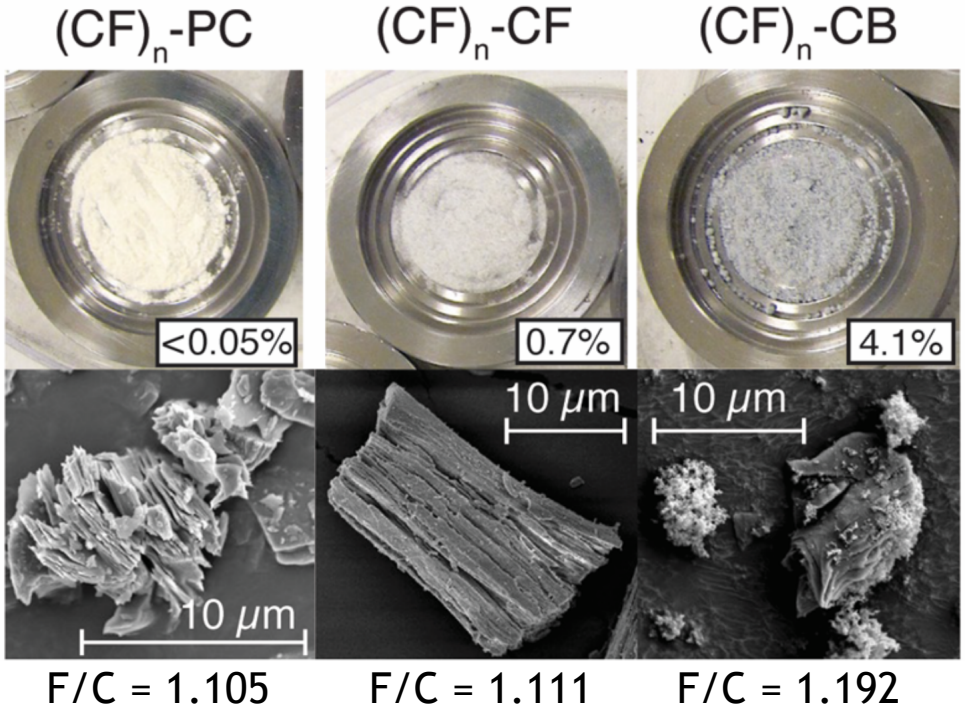
Li Batteries: CF_x Larger Theoretical Capacities

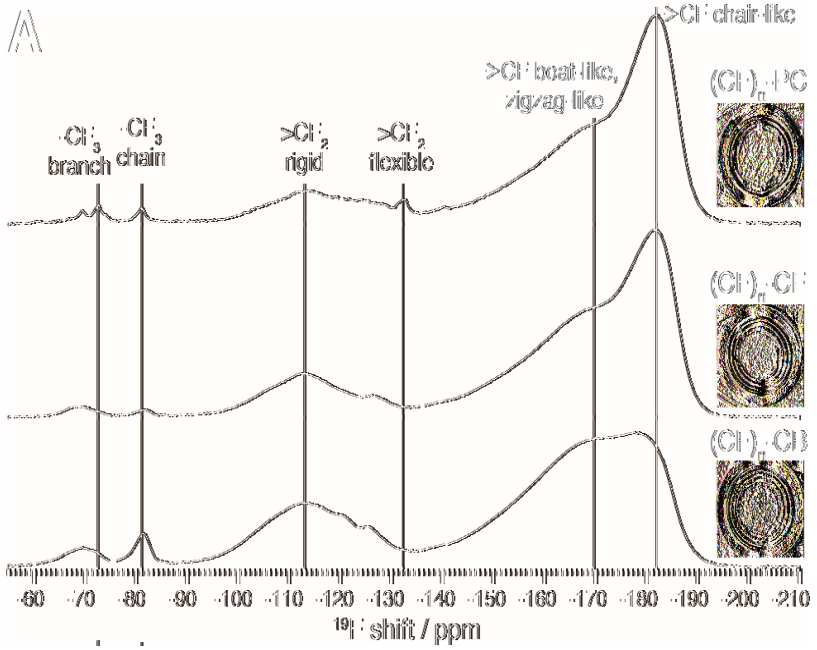


Li-primary Li-ion Next-generation R&D systems

System	Overall Reaction	Theoretical Voltage (V)	Capacity (mAh/g)	Energy Density kWh/kg	Energy Density (kWh/L)
Li/CF_x	$xLi+CF_x \rightarrow xLiF+C$, x=1	3.1	703	2.18	3.26

Understanding CF_x Material Lot-Lot Variations





- Carbon source plays an important role in material performance.

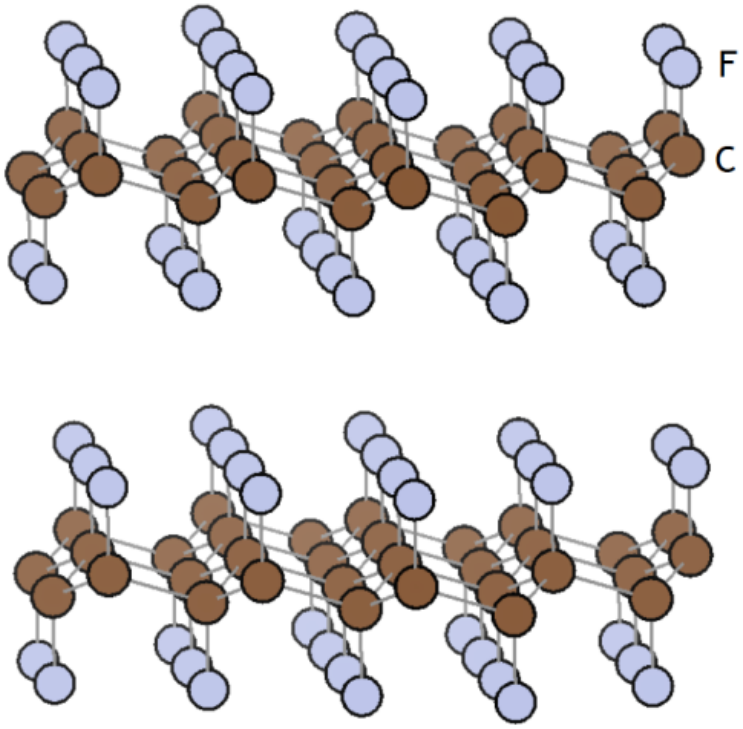
PC = petroleum coke; CF = carbon fiber; CB = carbon black

Advance Research Chemicals, Inc. (Catoosa, OK)

Brennan J. Walder and Todd M. Alam, "Modes of Disorder in Poly(carbon monofluoride)", *J. Am. Chem. Soc.*, **143(30)**, 11714-11733 (2021)

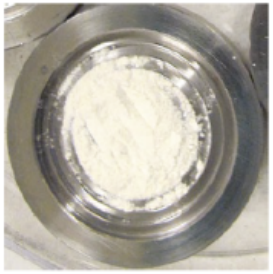
Do we really understand the $(CF)_n$ structures?

Ideal



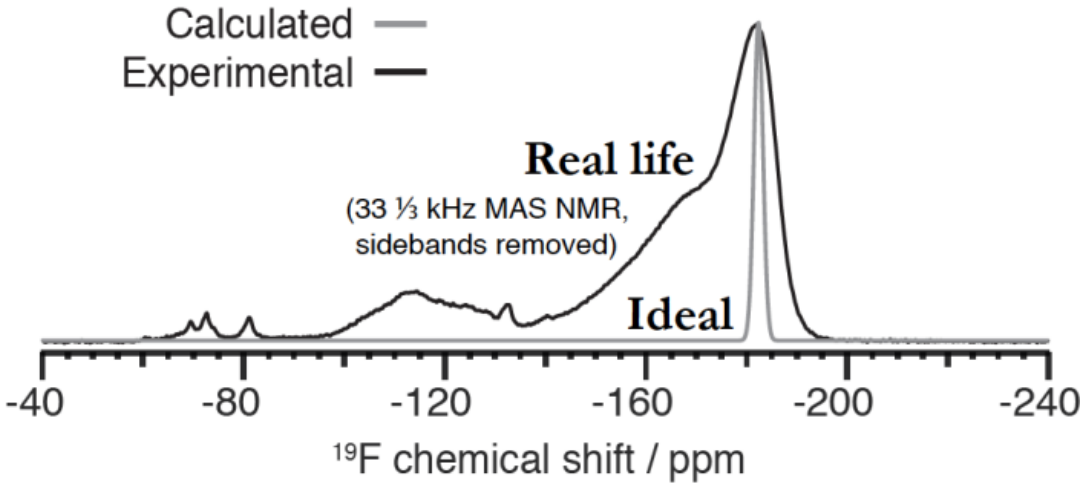
Rüdorff, W., Rüdorff, G. *Z. Anorg. Chem.* **253** 281–296 (1944)
Hagiwara R., Sato Y. *Prog. Fluor. Sci.* **2** 283–303 (2017)

vs.



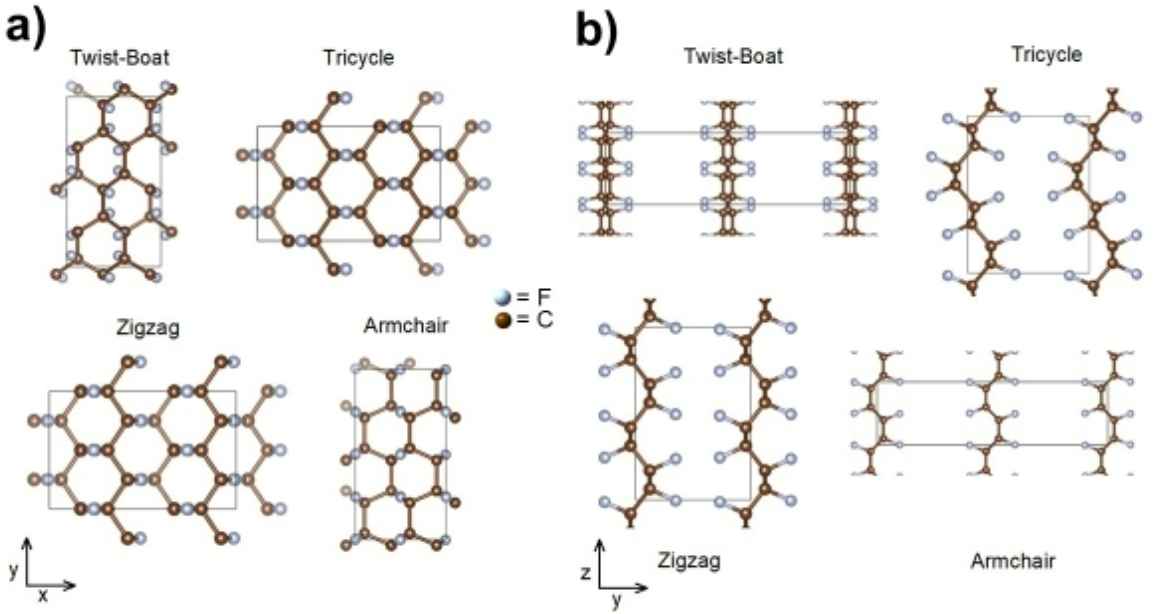
Real life

poly(carbon monofluoride)
from petroleum coke
"$(CF)_n$-PC"

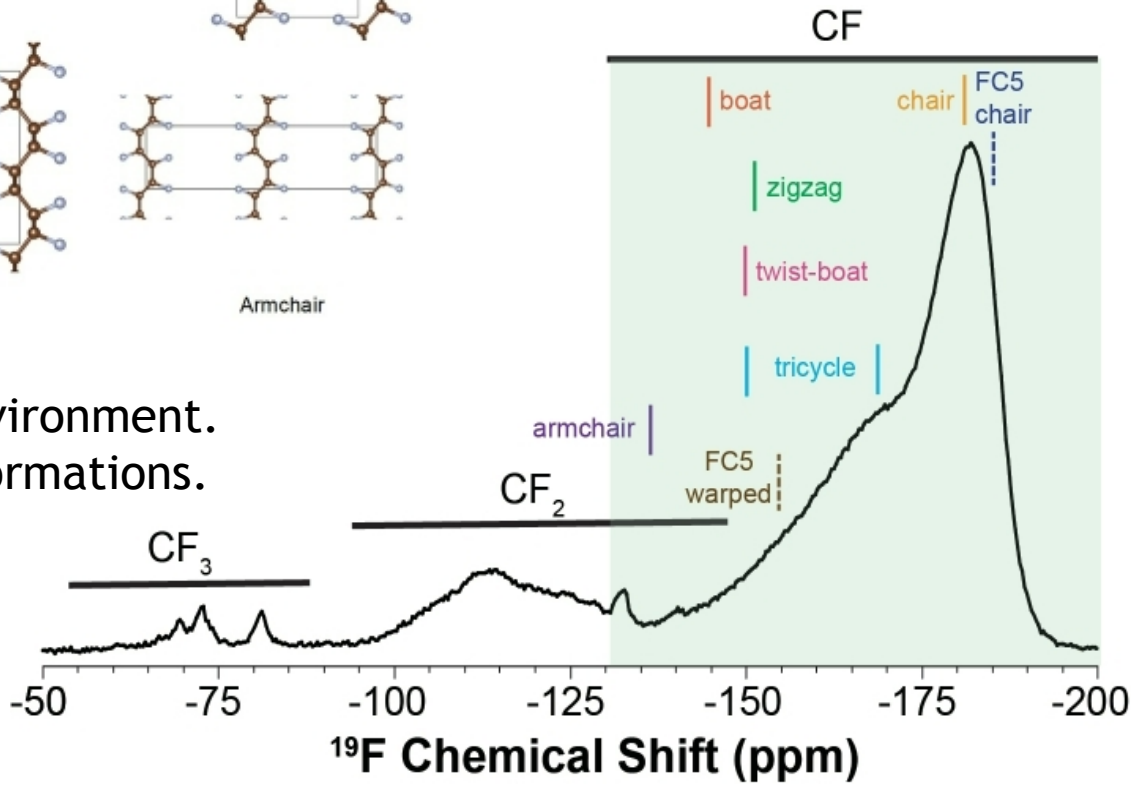


- Need to understand what is the actual structural motif in these different materials.

$(CF)_n$ Crystal Polymorphs

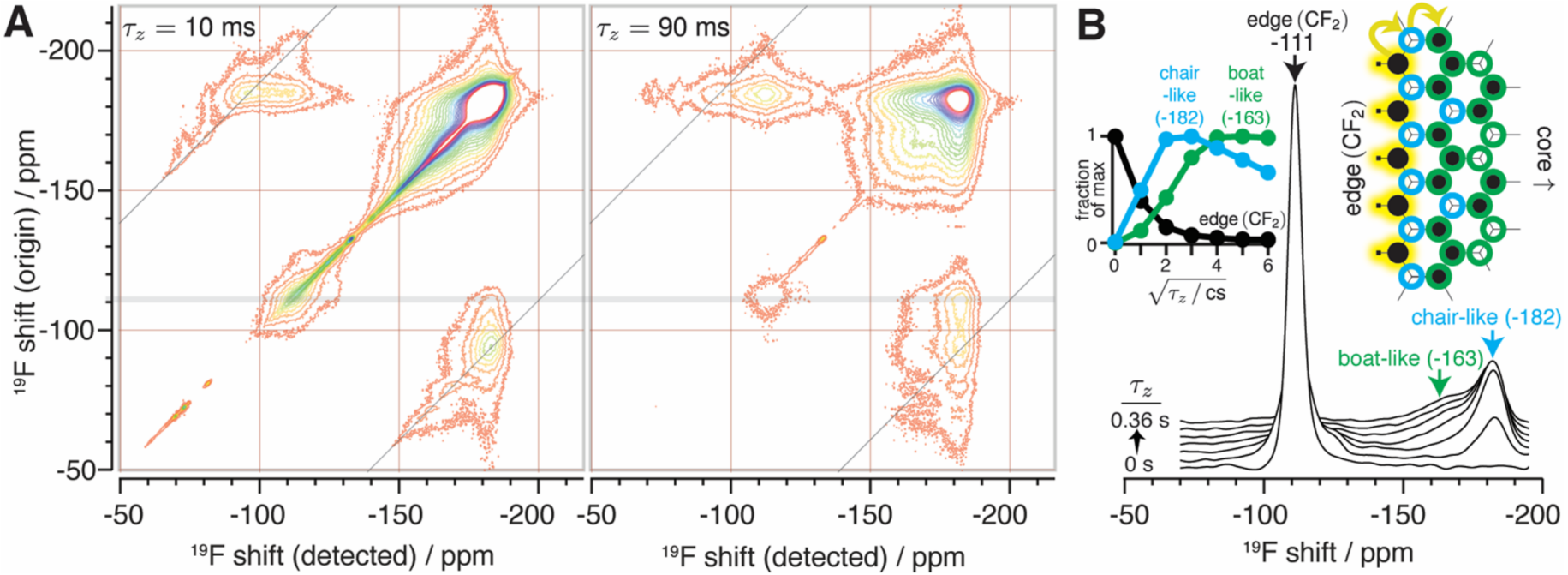


- ^{19}F MAS NMR reveals rich F environment.
- Mixture of different ring conformations.



Rimsza, J. M.; Walder, B. J.; Alam, T. M. Influence of Polymorphs and Local Defect Structures on NMR Parameters of Graphite Fluorides. J. Phys. Chem. C, 125, 2699-2712 (2021).

2D ^{19}F-^{19}F Exchange Spectrscopy (EXSY)

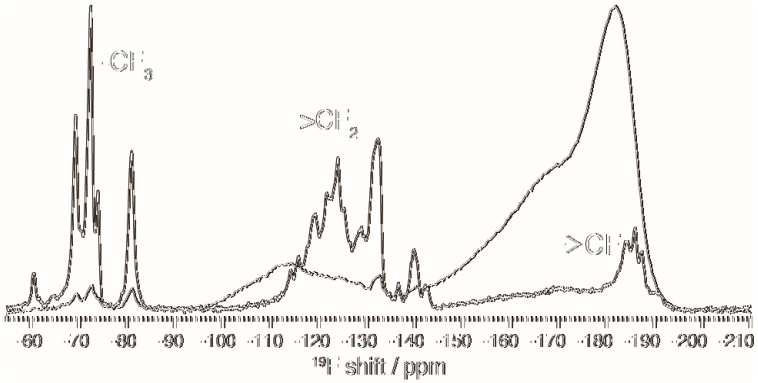


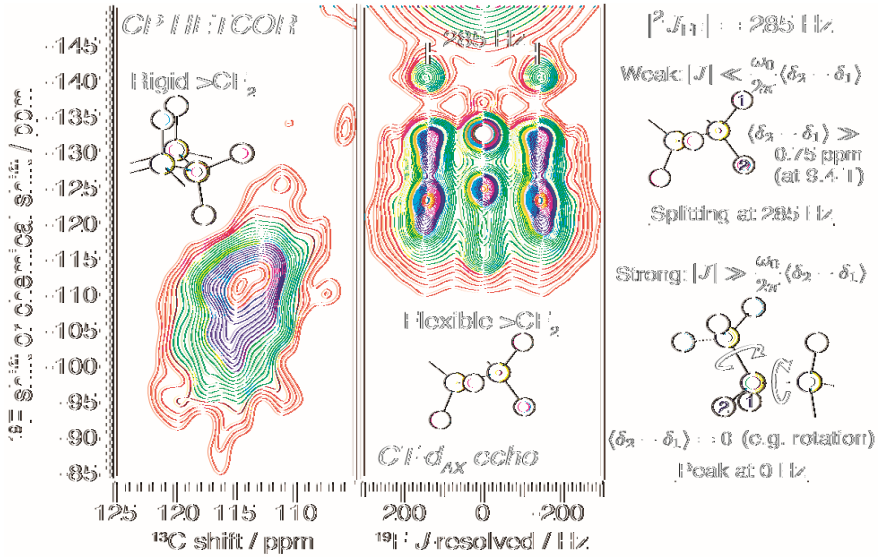
- Magnetization exchange between F environments through F-F dipolar coupling.
- Allows spatial structure to be determined.
- Different ring conformations (i.e. structures) inter-mixed.
- Very disordered structure - not a single CF_n polymorph.
- Also reveals CF_2 edge effects with evolution of structure across platelet.

Brennan J. Walder and Todd M. Alam, “Modes of Disorder in Poly(carbon monofluoride)”, *J. Am. Chem. Soc.*, **143(30)**, 11714-11733 (2021) https://doi.org/10.1021/jacs.1c05234 .

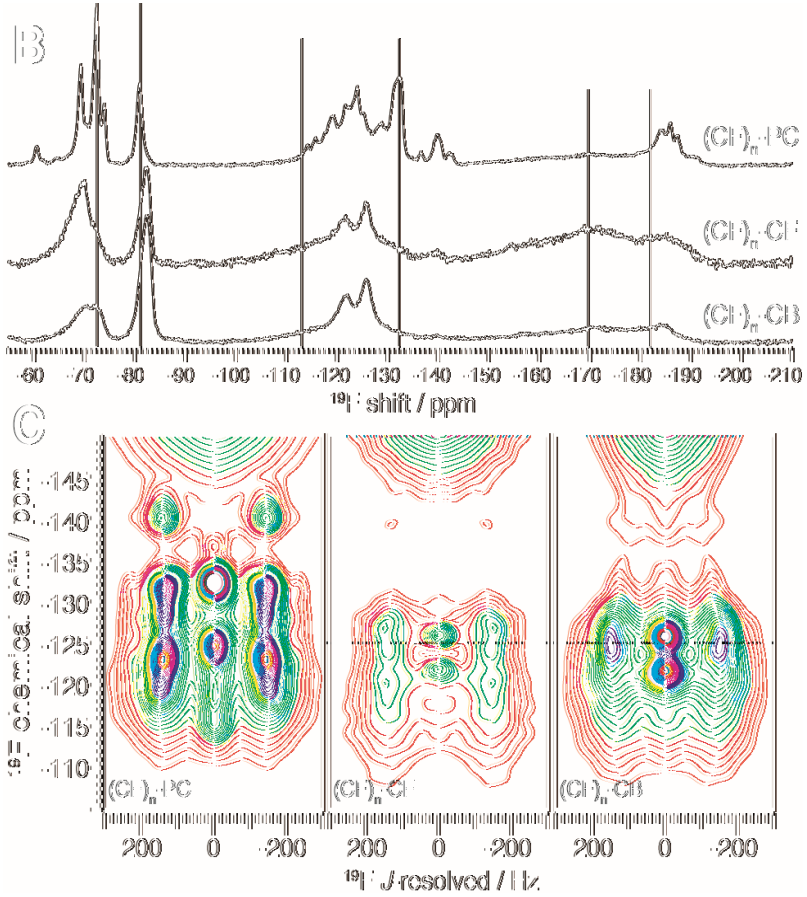
^{19}F MAS NMR Dynamic Spectral Filtering

1D ^{19}F MAS NMR versus CT-d_{AX} echo





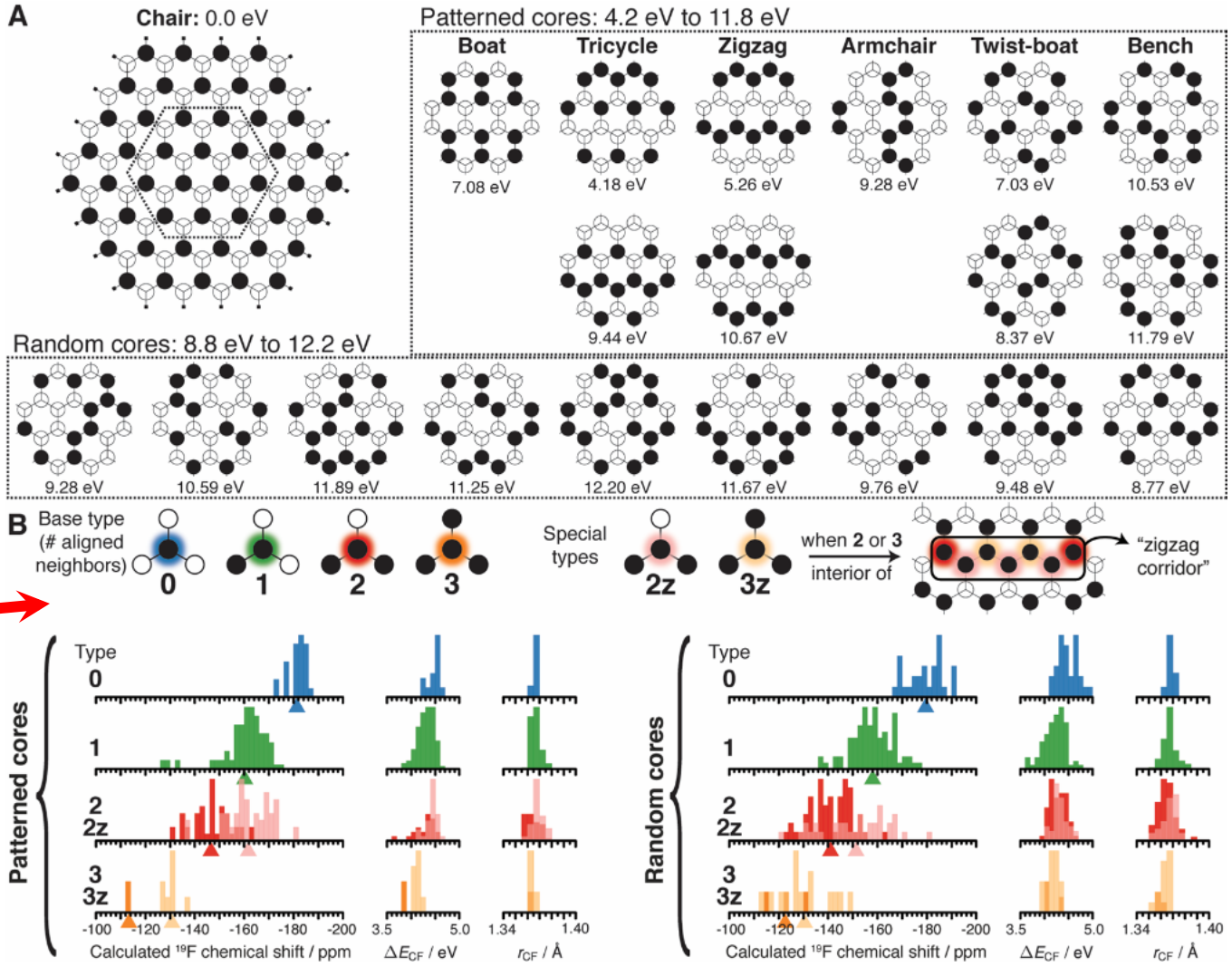
Each sample has different ring flexibility



Brennan J. Walder and Todd M. Alam, “Modes of Disorder in Poly(carbon monofluoride)”, *J. Am. Chem. Soc.*, **143(30)**, 11714-11733 (2021) https://doi.org/10.1021/jacs.1c05234 .

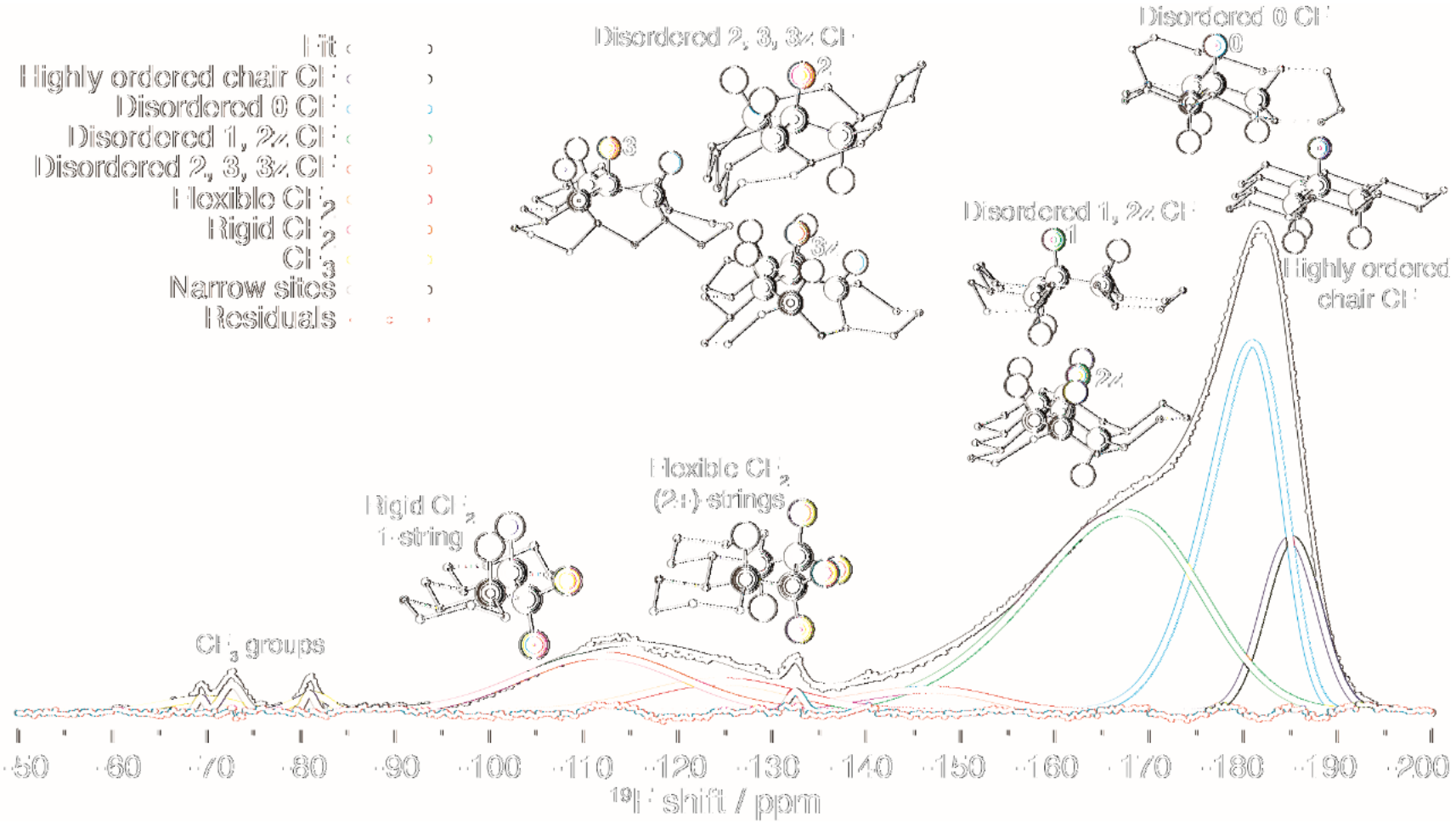
Disordered Structures – Chemical Shift Predictions

ID ^{19}F NMR environments based on nearest F neighbor orientation.



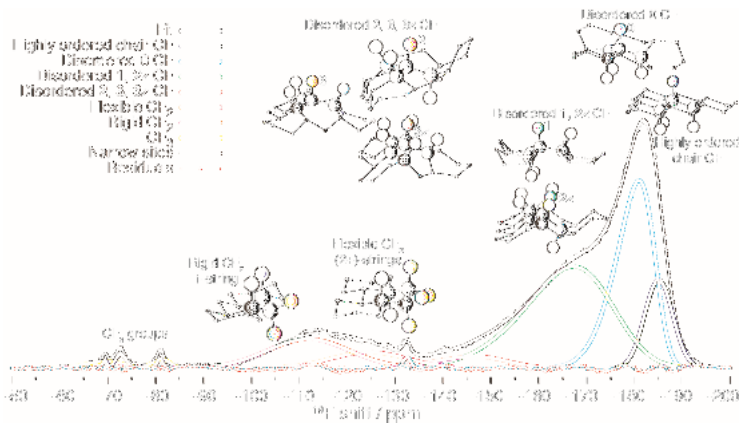
Brennan J. Walder and Todd M. Alam, "Modes of Disorder in Poly(carbon monofluoride)", *J. Am. Chem. Soc.*, **143(30)**, 11714-11733 (2021)

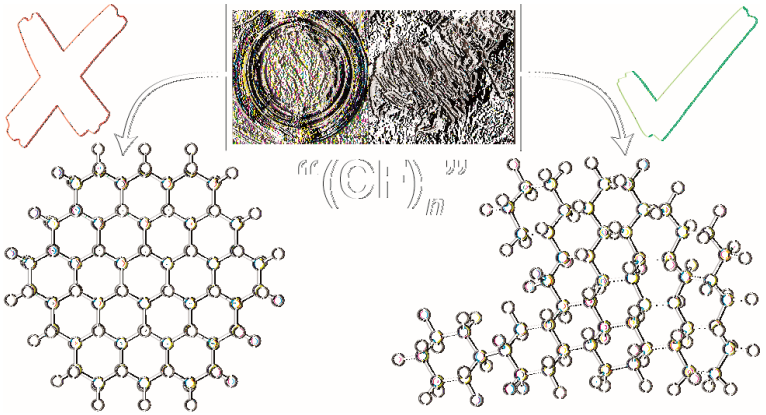
$(CF)_x$ Structures Reveal High Structural Disorder

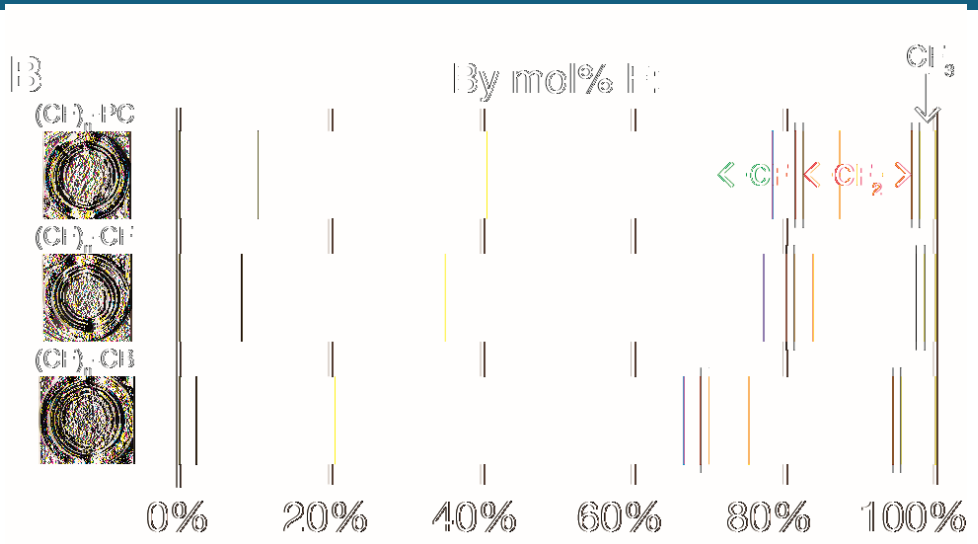


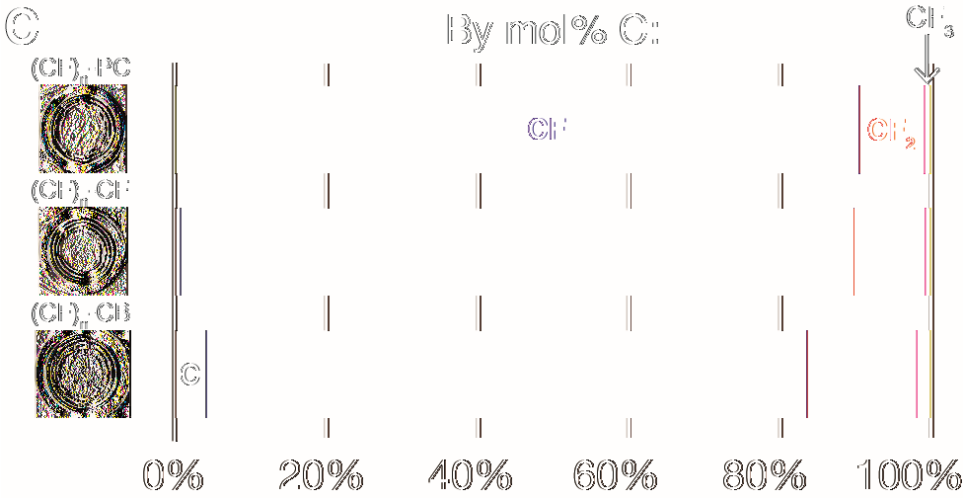
Brennan J. Walder and Todd M. Alam, "Modes of Disorder in Poly(carbon monofluoride)", *J. Am. Chem. Soc.*, **143(30)**, 11714-11733 (2021) https://doi.org/10.1021/jacs.1c05234 .

Quantification of Structure in Different CF_n Lots



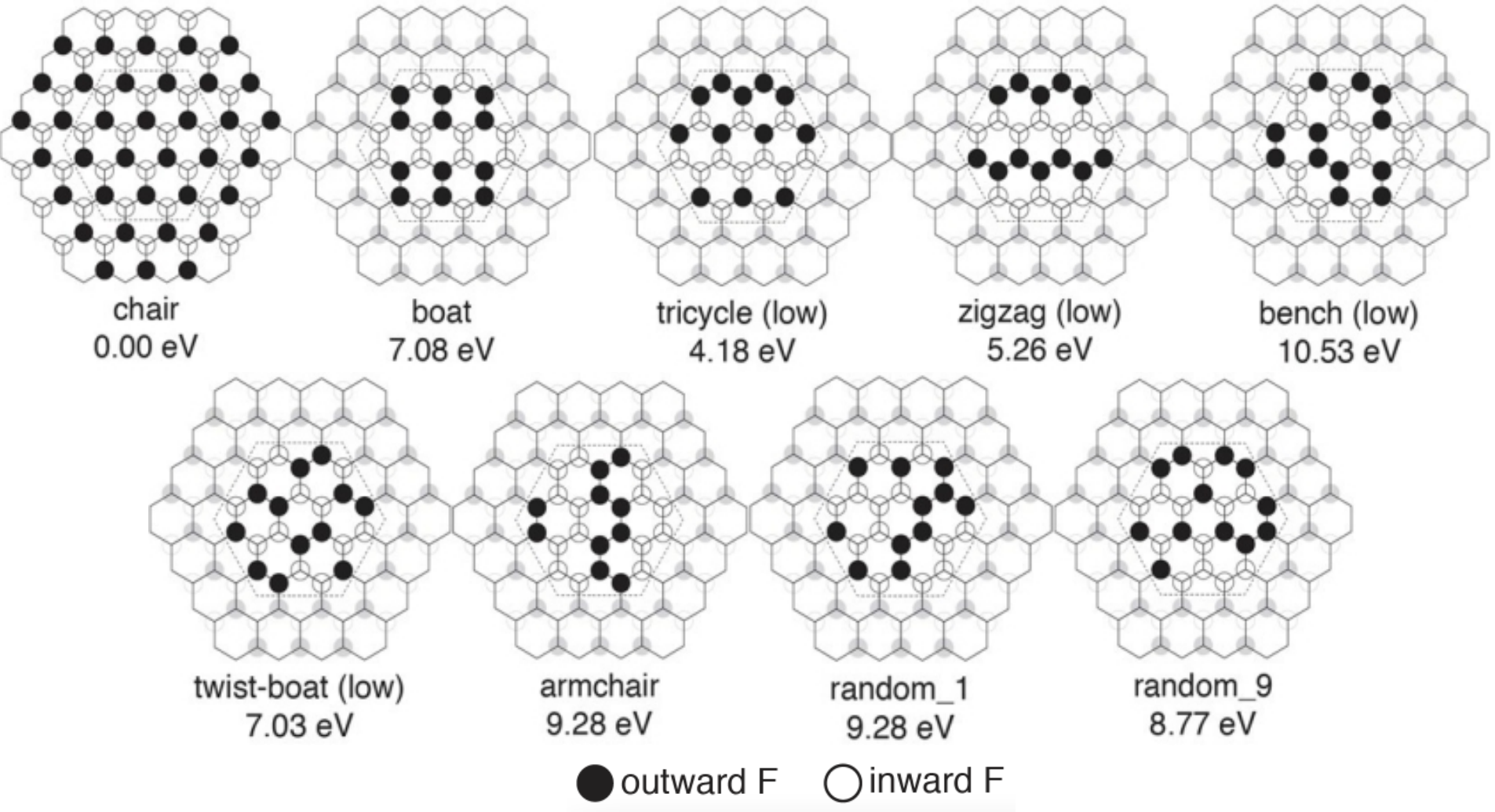






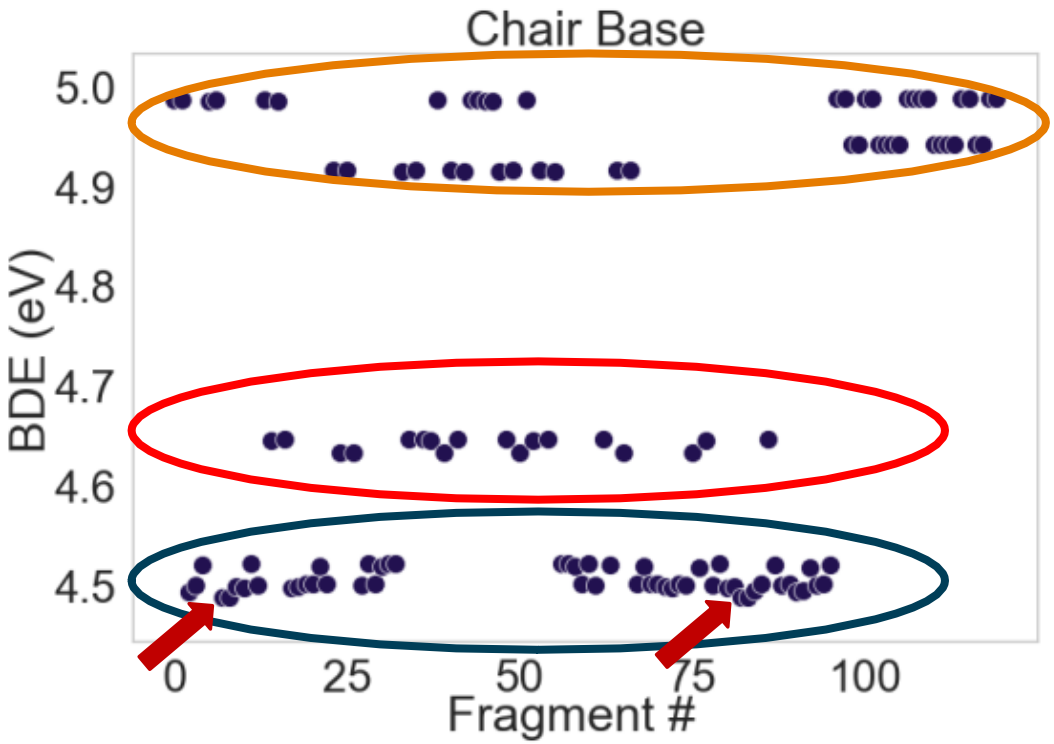
Brennan J. Walder and Todd M. Alam, “Modes of Disorder in Poly(carbon monofluoride)”, *J. Am. Chem. Soc.*, **143(30)**, 11714-11733 (2021)

Understanding Disordered C-F Chemistry

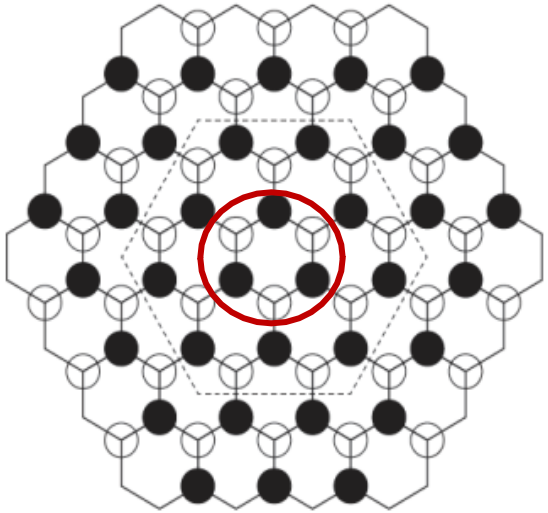


***How does disorder impact C-F bond energies*?**

Distribution of BDEs in the Chair Structure

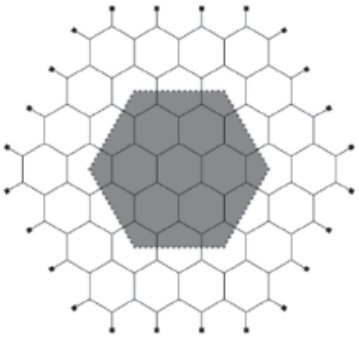


BDE = bond dissociation energy

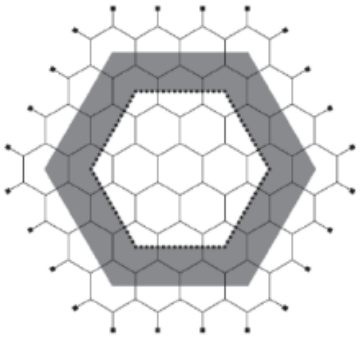


chair
0.00 eV

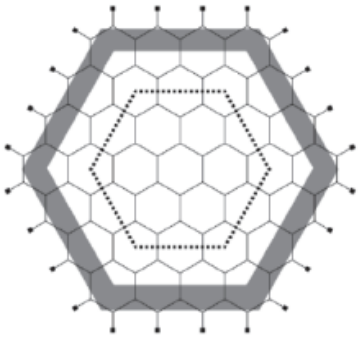
Core



Core Adjacent

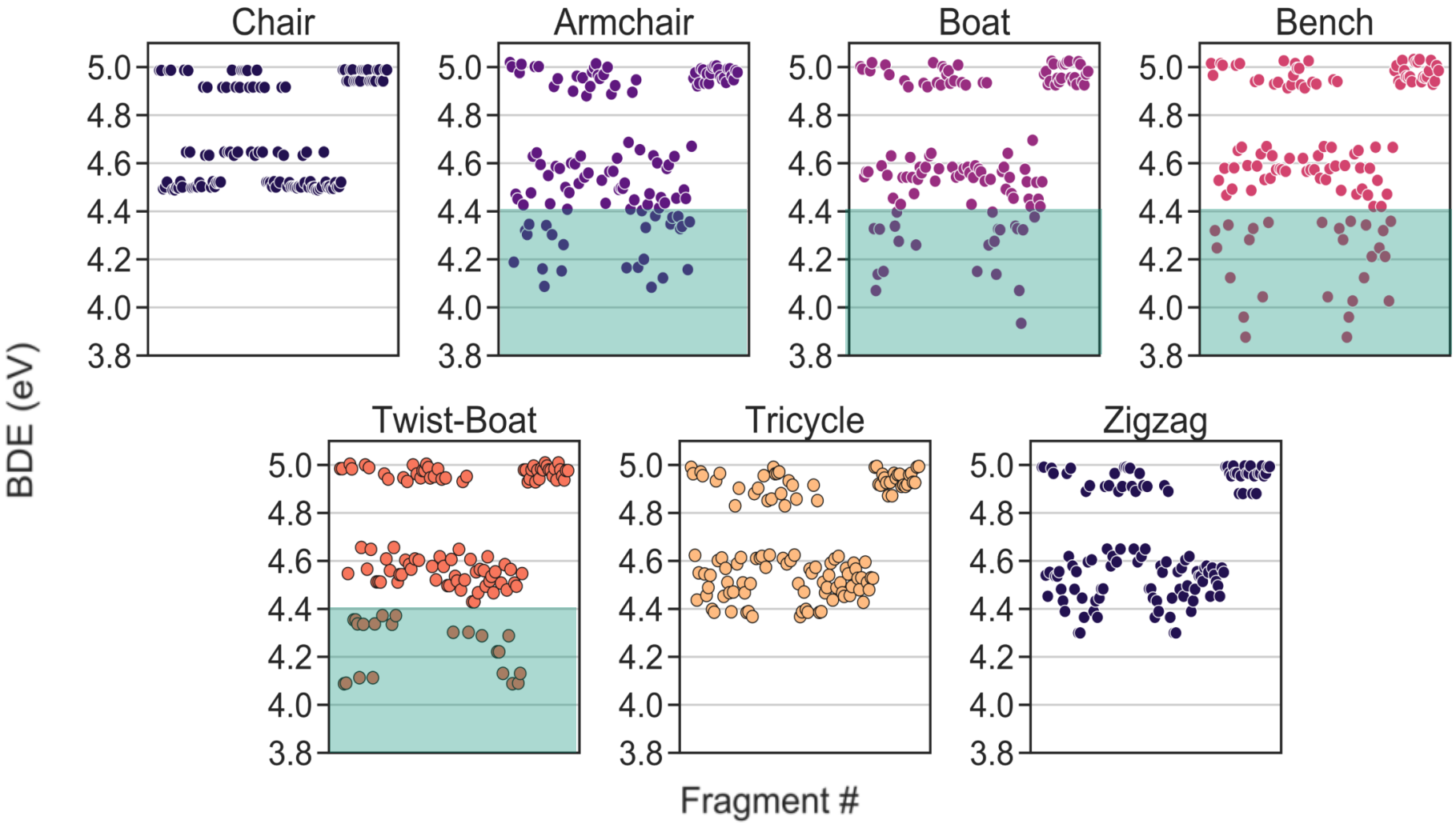


Hexagonal edge



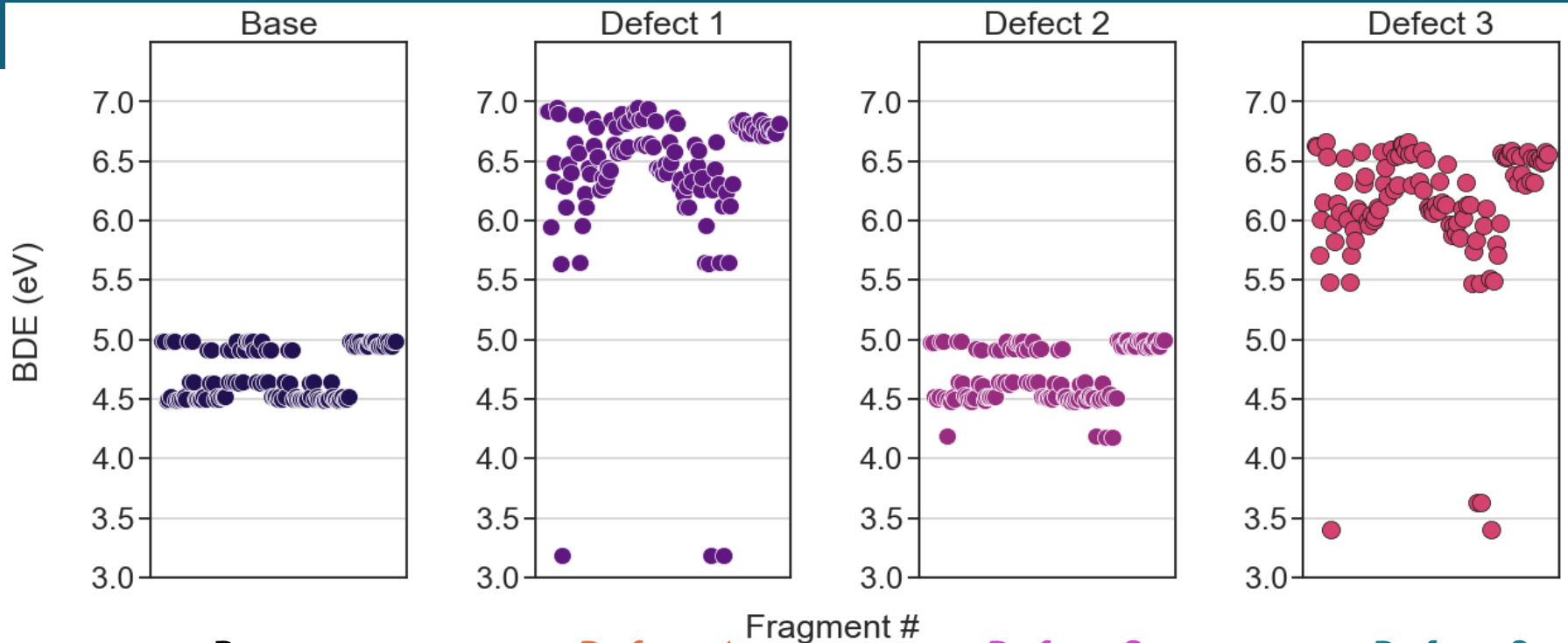
Kelly Nieto, Brennan J. Walder and Todd M. Alam, "Disorder and C-F Bond Energetics", *In preparation*

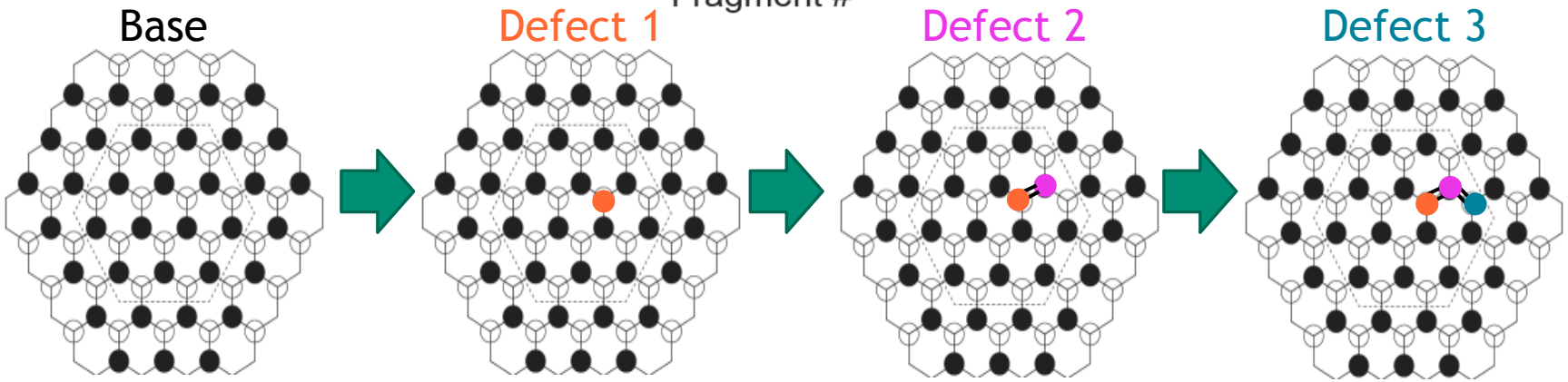
Base Disordered Structures Show BDE Differences



Disorder can reduce C-F bond energy up to 0.6 eV

Defluorination Pathway of CF_n Chair Structure





BDE = 4.49 eV
BL = 1.37 Å

BDE = 3.19 eV
BL = 1.38 Å

BDE = 4.18 eV
BL = 1.38 Å

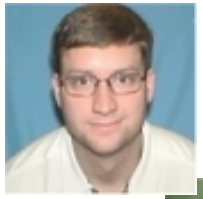
Conclusions

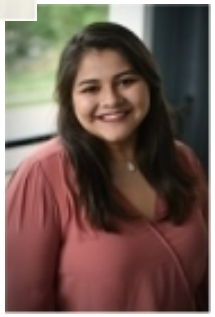
- ^{19}F MAS NMR provides unparallel information on CF_n disordered structure.
- Quantified C and F speciation.
- Structure dependent on carbon source and preparation methods.
- Simple picture of perfect chair structure *misguided*.
- Disorder impacts CF bond energetics – lowered by ~ 0.5 eV.
- F defects further lowers CF bond energetics.
- ^{19}F MAS NMR provides an excellent tool to follow defluorination.

Acknowledgements

Dr. Brennan Walder (SNL)

Kelly Nieto, EERE summer intern (CSU)





Thank you for your time….

This research was supported entirely through the Sandia Laboratory Directed Research Development (LDRD) program and EERE energy fellowship (K. Nieto). Sandia National Laboratories is a multi-mission laboratory managed and operated by the 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 No. DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in this paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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Project funding through the Sandia LDRD program

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