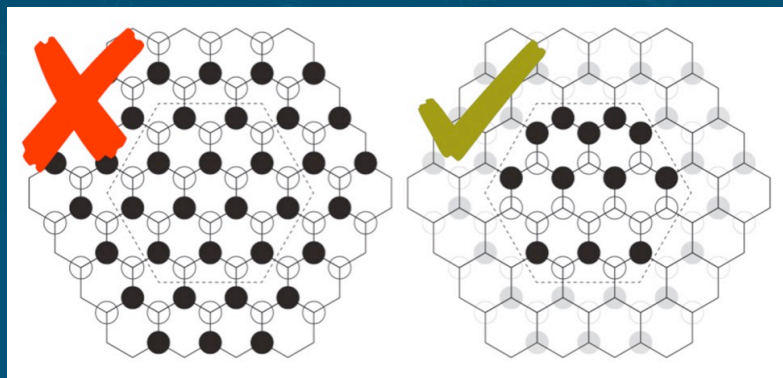
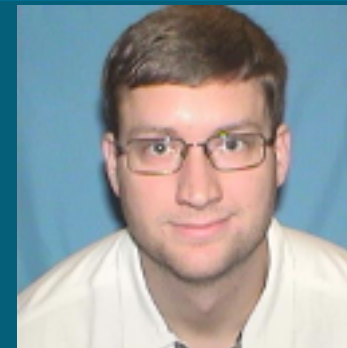




Sandia
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SAND2020-11893C

Penetrating the layers: $(\text{CF})_n$ and lithium electrochemistry



Contributors:

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- Dr. Jessica M. Rimsza
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- Dr. Noah B. Schorr
- Dr. Kevin Leung

PRESENTED BY

Dr. Brennan J. Walder

Fall 2020 NMR² virtual meeting

October 30, 2020



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2 Batteries: need no introduction

The slide is titled "What Is A Battery Cathode?". It features two main sections: "CATHODES ARE LIKE BOOKSHELVES" and "METAL COST MATTERS".

CATHODES ARE LIKE BOOKSHELVES: This section shows a diagram of a battery cathode structure. It consists of four horizontal layers, each containing a grid of dots representing atoms. Arrows point from the layers to labels: "NICKEL / COBALT MANGANESE / ALUMINUM" points to the top layer, and "LITHIUM" points to the bottom layer.

METAL COST MATTERS: This section is a scatter plot showing the cost of metals in \$/kWh. The y-axis is labeled "\$/kWh METALS" and ranges from 0 to 35. The x-axis is labeled "W" and ranges from 400 to 1400. Three data points are plotted: COBALT (at approximately 28 \$/kWh), NICKEL (at approximately 15 \$/kWh), and IRON (at approximately 5 \$/kWh).

The video player interface at the bottom shows the title "2020 Annual Shareholder Meeting and Battery Day", the view count "2,896,268 views • Streamed live on Sep 22, 2020", and the Tesla logo with "1.54M subscribers". A red "SUBSCRIBE" button is also visible.

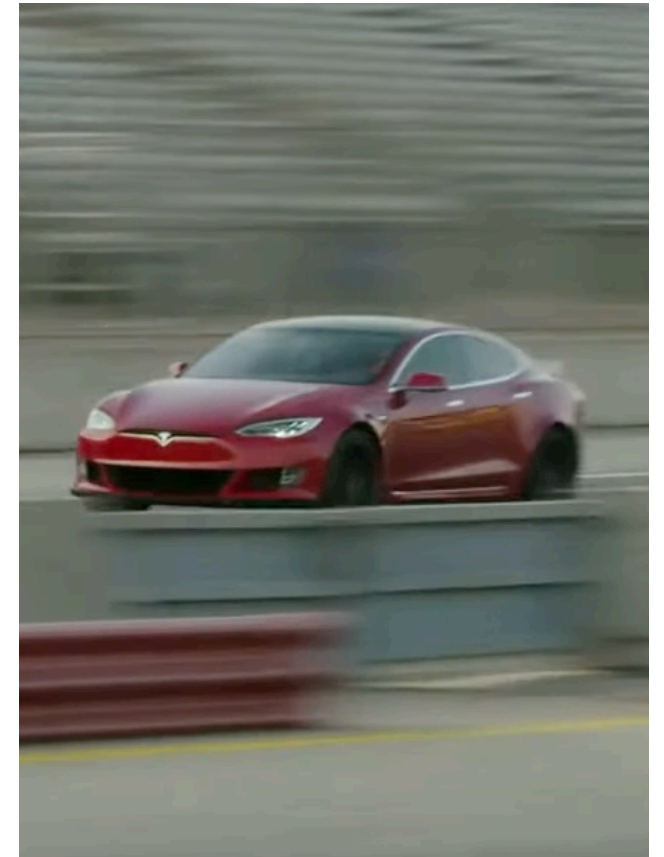
3 Batteries: we just want more, more, more



More power



More energy

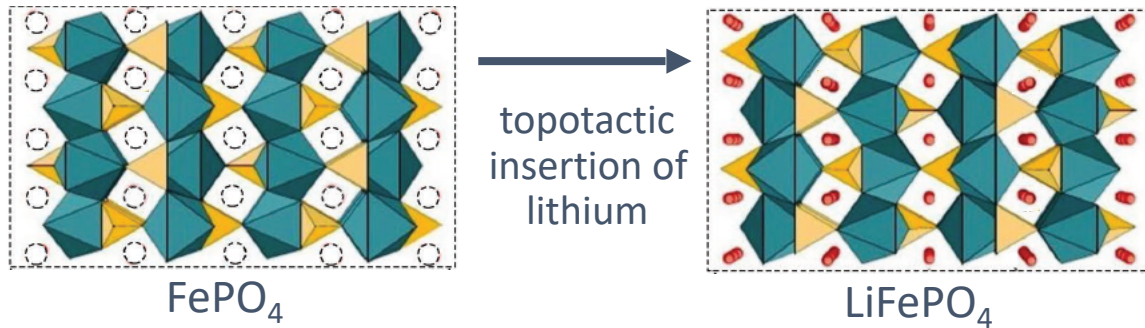


More fun

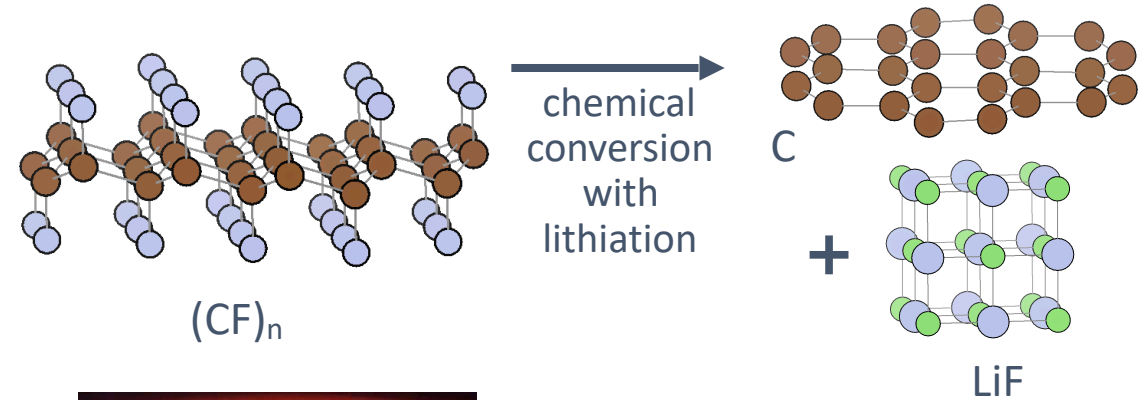
Getting more: lithium primary chemistries use conversion cathodes



Insertion cathode (Li-ion)



Conversion cathode (Li-primary)



Stable insertion cathodes
John B. Goodenough
Shared 2019 Nobel Prize in Chemistry
 CoO_2 (1980)
 FePO_4 (1997)



First commercial lithium primary battery
Matsushita Corporation
 Li/CF_x (1973)

Chemistry	Representative Reaction	Voltage	Capacity	Energy density
Li-primary	$n\text{Li} + (\text{CF})_n \rightarrow n\text{LiF} + (\text{C})_n$	3.4 V	701 mA·h/g	2.18 W·h/g
Li-ion	$\text{LiC}_6 + \text{FePO}_4 \rightarrow \text{C}_6 + \text{LiFePO}_4$	3.5 V	117 mA·h/g	0.40 W·h/g

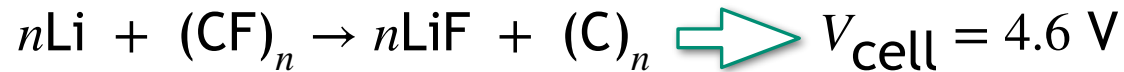
Insertion cathode figure courtesy of Dr. Katharine L. Harrison

Nobel images: nobelprize.org; Li/CF_x cells image: Nakajima T., *Prog. Fluor. Sci.* **2** 305–323 (2017)

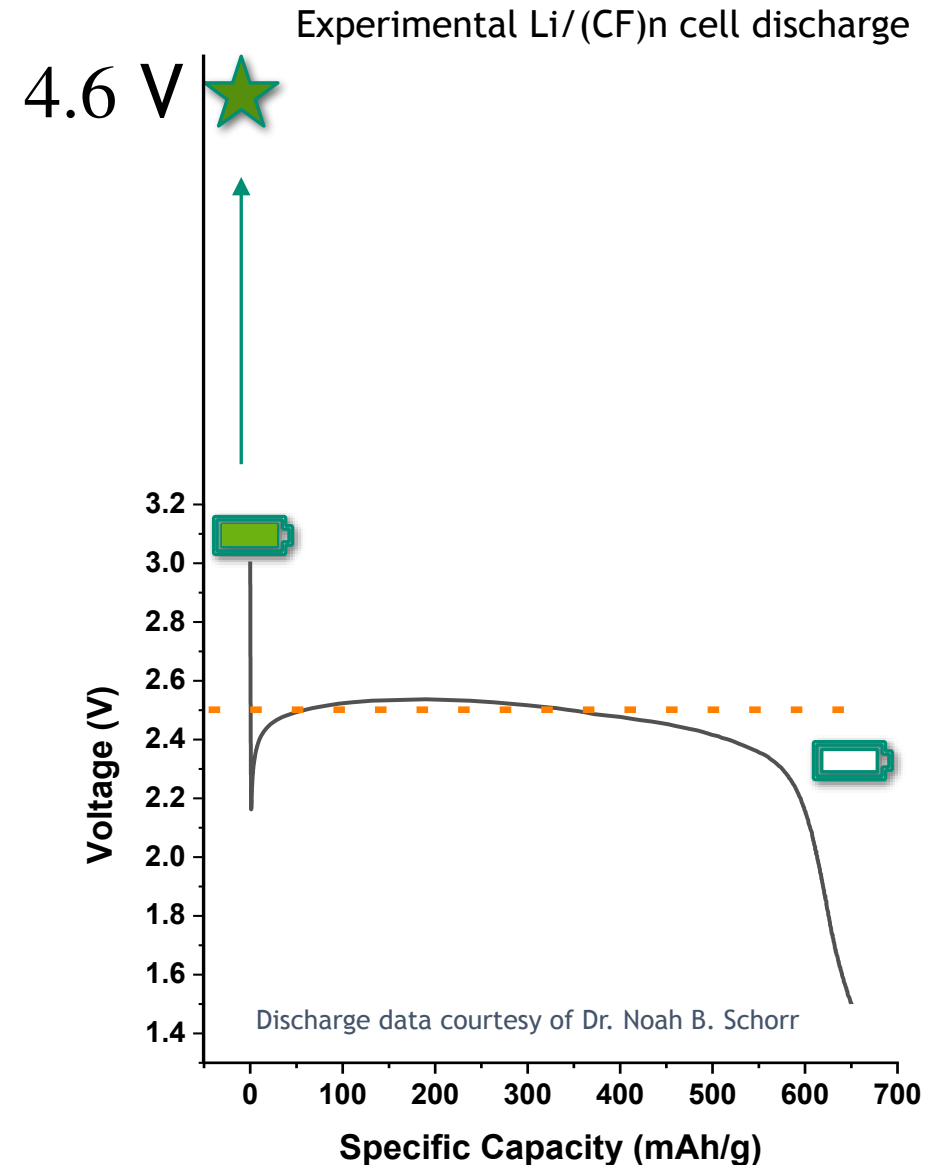
Much higher Li/(CF)_n cell voltages expected



From thermodynamic data:



Why not 4.6 V?

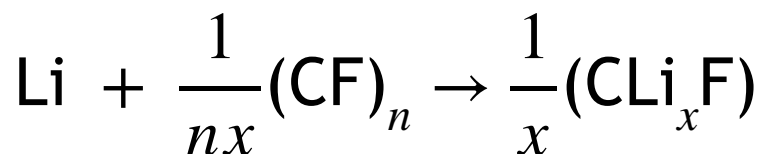


Why not 4.6 V?



A. Kinetic limitation: insufficiently rapid lithium and LiF diffusion

B. Intermediate phase: Ternary phase, “CLi_xF”



J. Electrochem. Soc. 122 526-527 (1975)
Mechanism of Reduction of the Fluorographite Cathode

M. Stanley Whittingham*

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

Graphite has a layered structure which on reaction with fluorine at elevated temperatures gives the compound (CF)_n in which the graphite lattice loses its

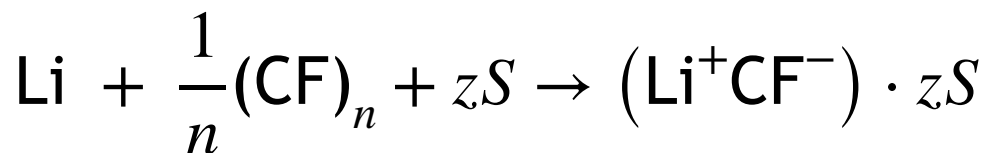
* Electrochemical Society Active Member.
 Key words: ternary phase, high energy density battery, carbon fluoride, cathode.

aromatic character and electronic conductivity (1). Ebert (2) has shown that the six membered carbon rings take up the boat configuration with the fluorine atoms between the carbon layers. The spacing between these layers expands from 3.35 to ~5.8Å on reaction. This carbon monofluoride is used as the cathode of

One year later...first rechargeable Li battery (TiS₂ cathode)



C. Solvent participation in electrochemistry

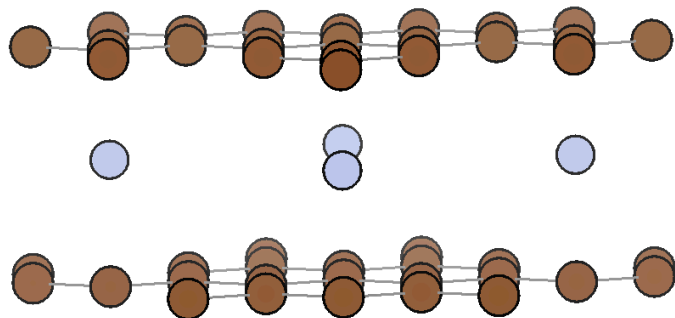


Watanabe N., Hagiwara R., Nakajima T., Touhara H., Kazuo U. *Electrochim. Acta* 27 1615-1619 (1982)

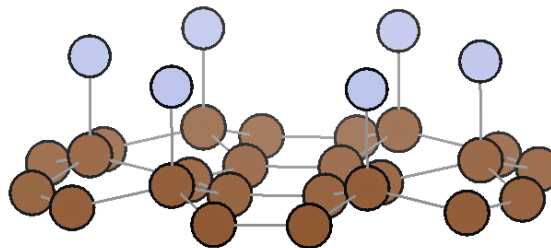
D. Structural property effectively increasing C-F bond dissociation energies?

7 Recognized C–F bonding motifs in graphite fluorides

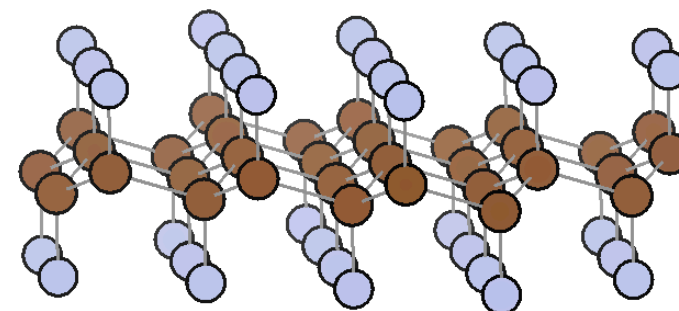
Panich, A. M., *Synth. Metals* **100** 169–185 (1999)



Metallic: $(C_8F)_n$

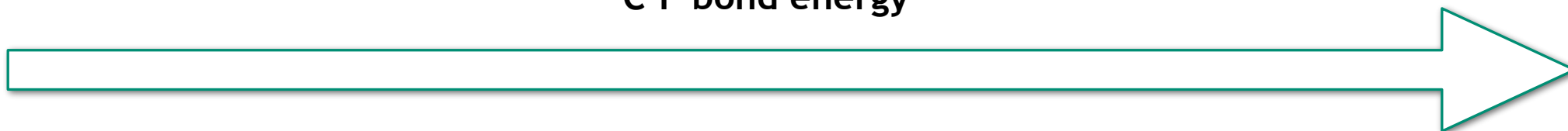


Semi-ionic: $(C_4F)_n$

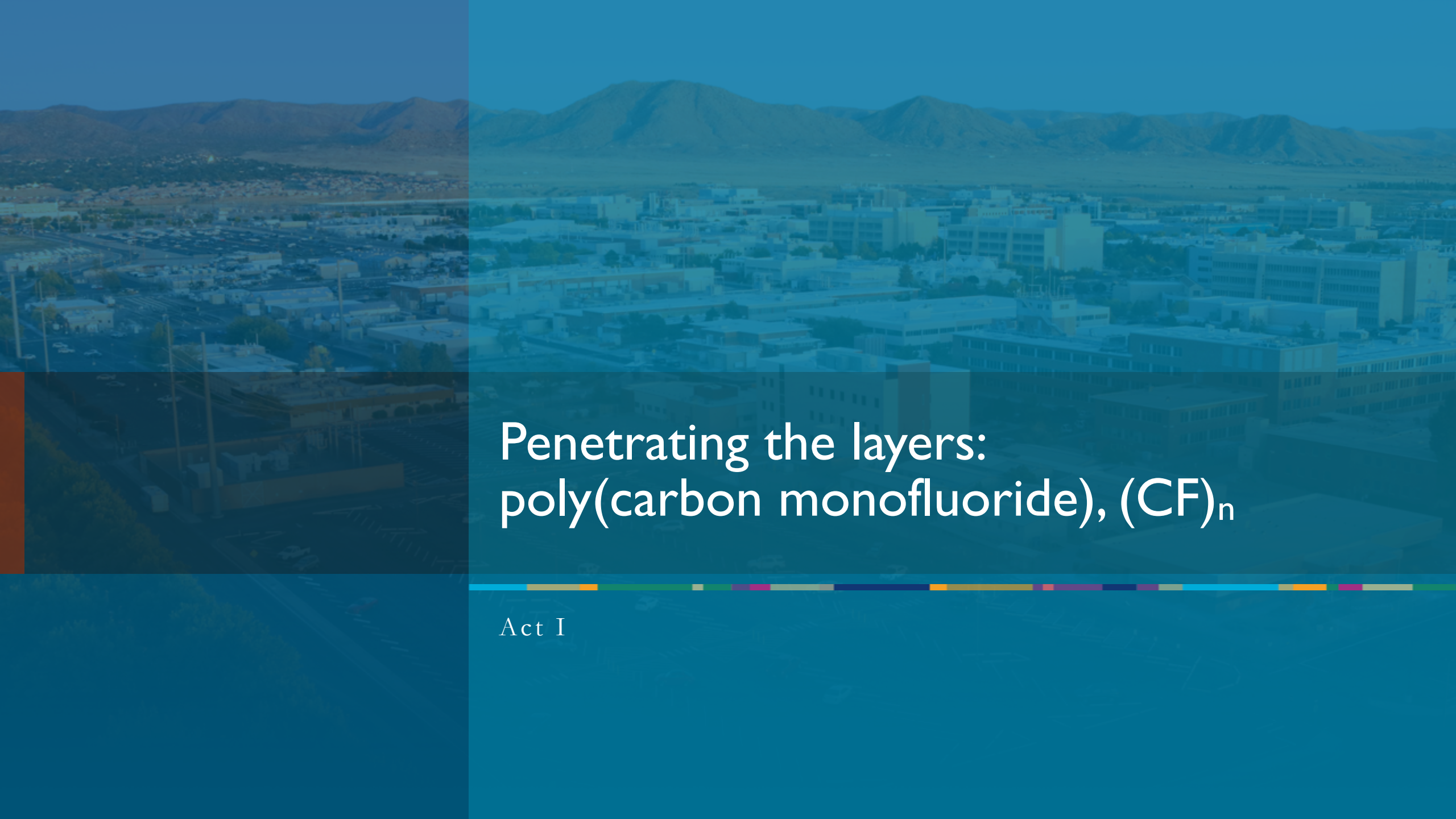


Covalent: $(CF)_n$

C-F bond energy



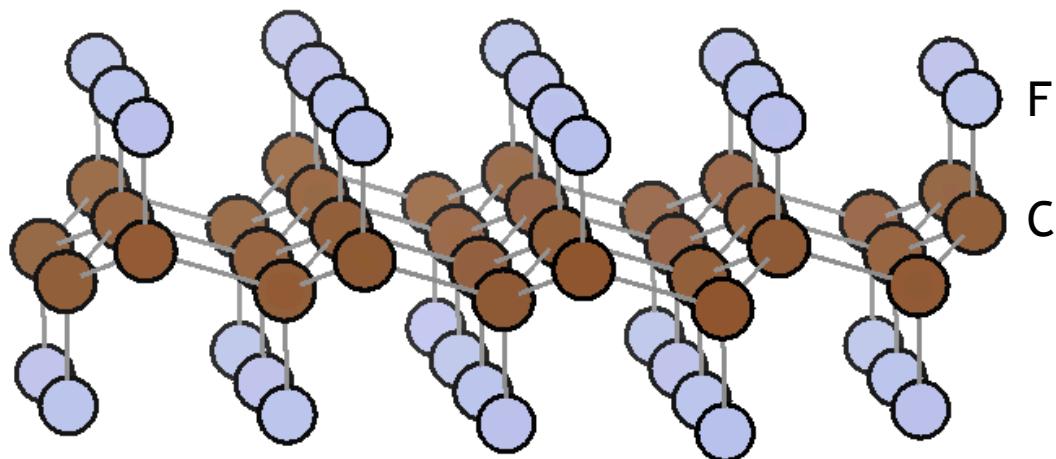
Could an unknown structural feature affect C-F bond energy in a single composition - $(CF)_n$?



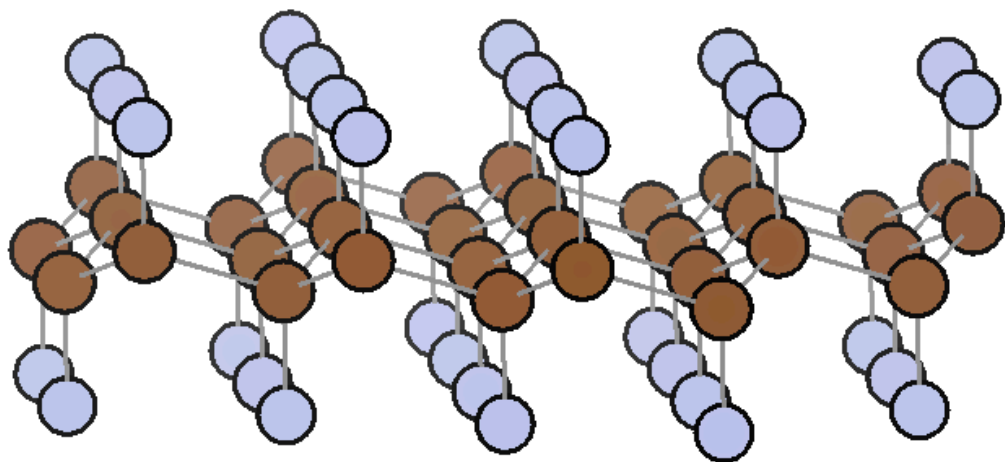
Penetrating the layers: poly(carbon monofluoride), (CF)_n

Act I

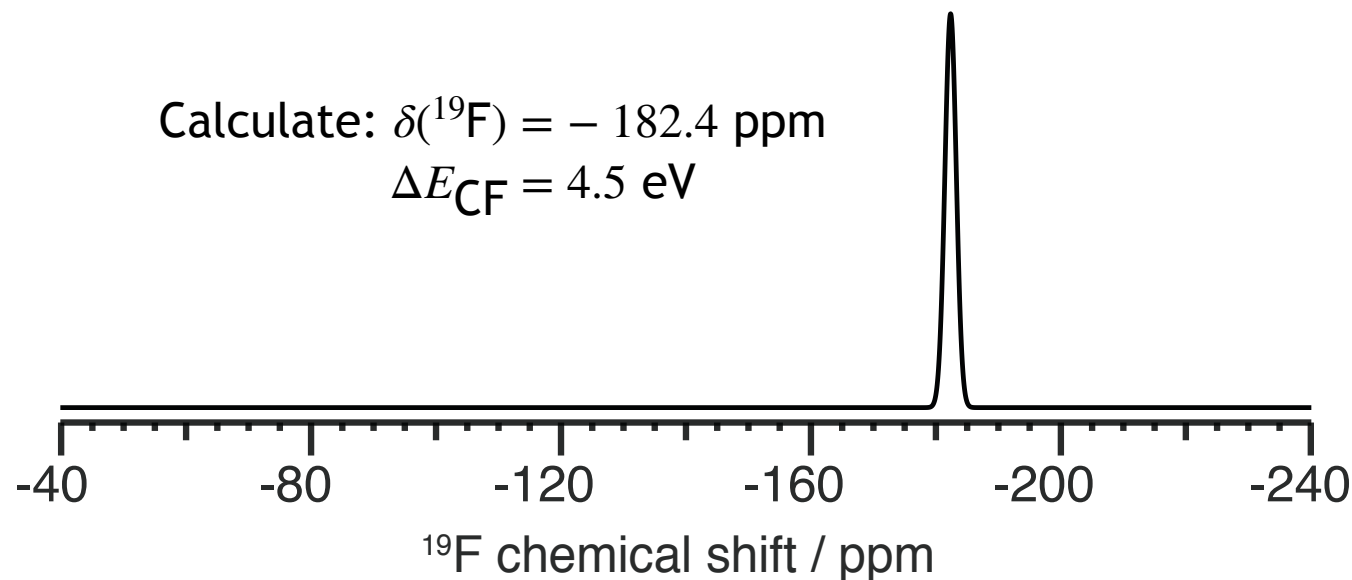
9 (CF)_n: ideal structure



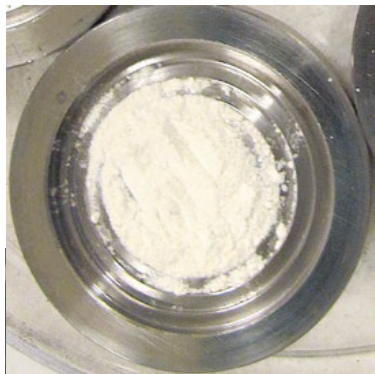
- Extended network of fused cyclohexane chairs (sp³)
- Van der Waals interactions between layers
- Alternating pattern of F neighbors above/below C layer
- All C, F are chemically equivalent



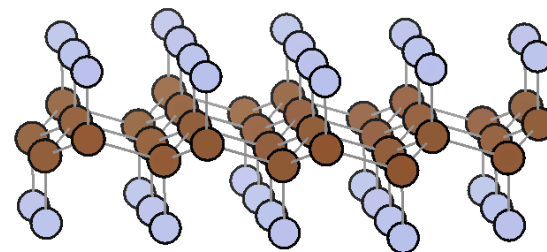
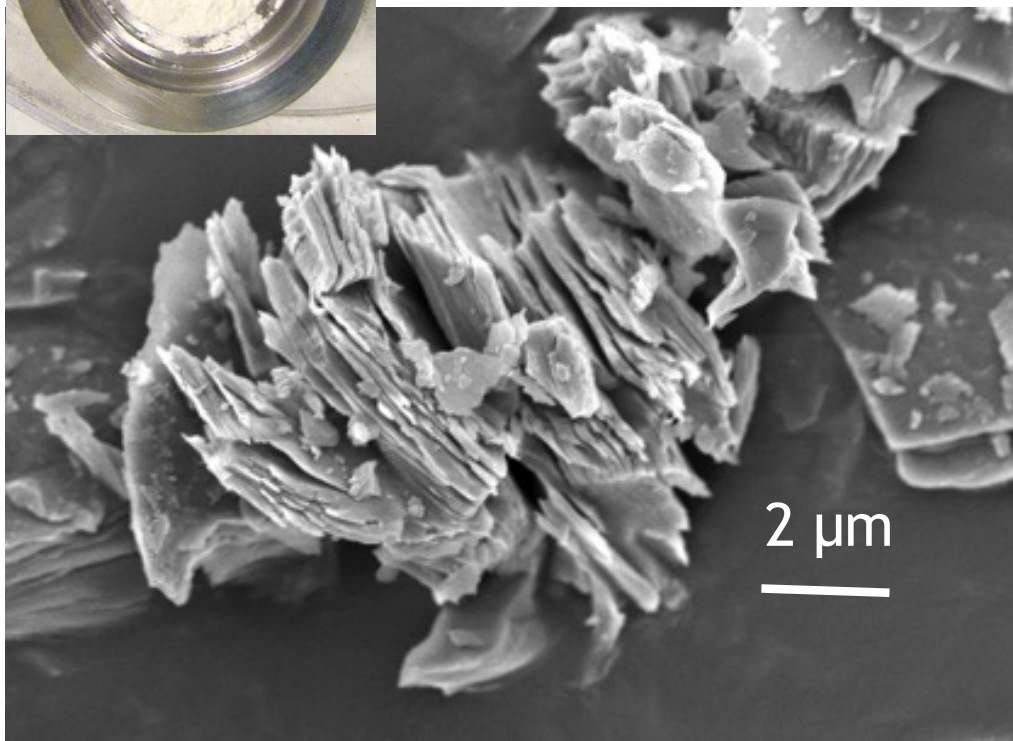
Calculate: $\delta(^{19}\text{F}) = -182.4 \text{ ppm}$
 $\Delta E_{\text{CF}} = 4.5 \text{ eV}$



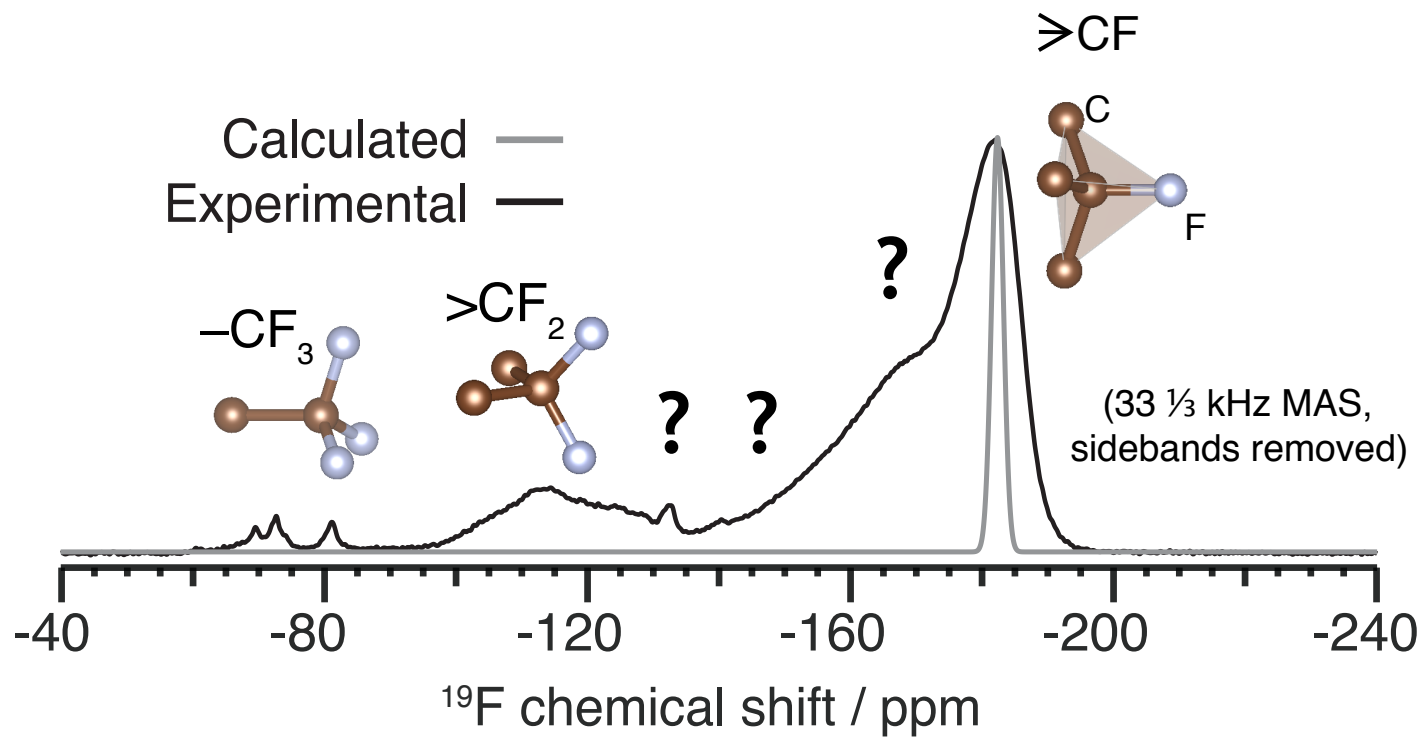
$(\text{CF})_n$: solid-state ^{19}F MAS NMR



poly(carbon monofluoride)
from petroleum coke
“(CF)_n-PC”



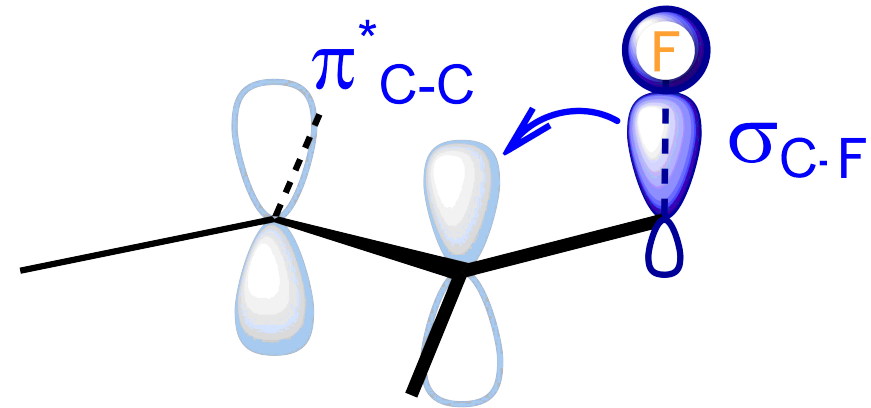
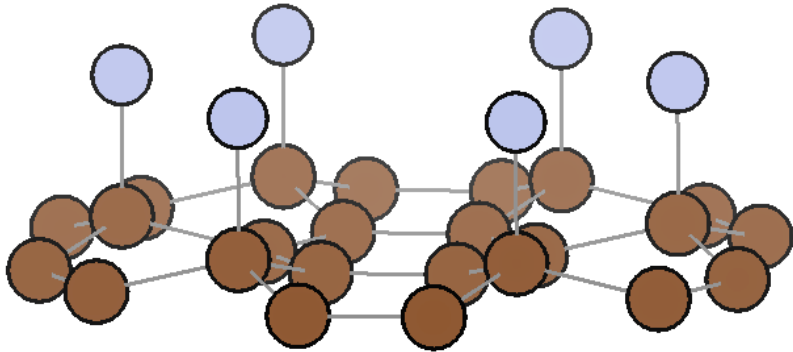
(XRD: very broad)



The conventional explanation: weakened covalence (“semi-ionic” bonds)

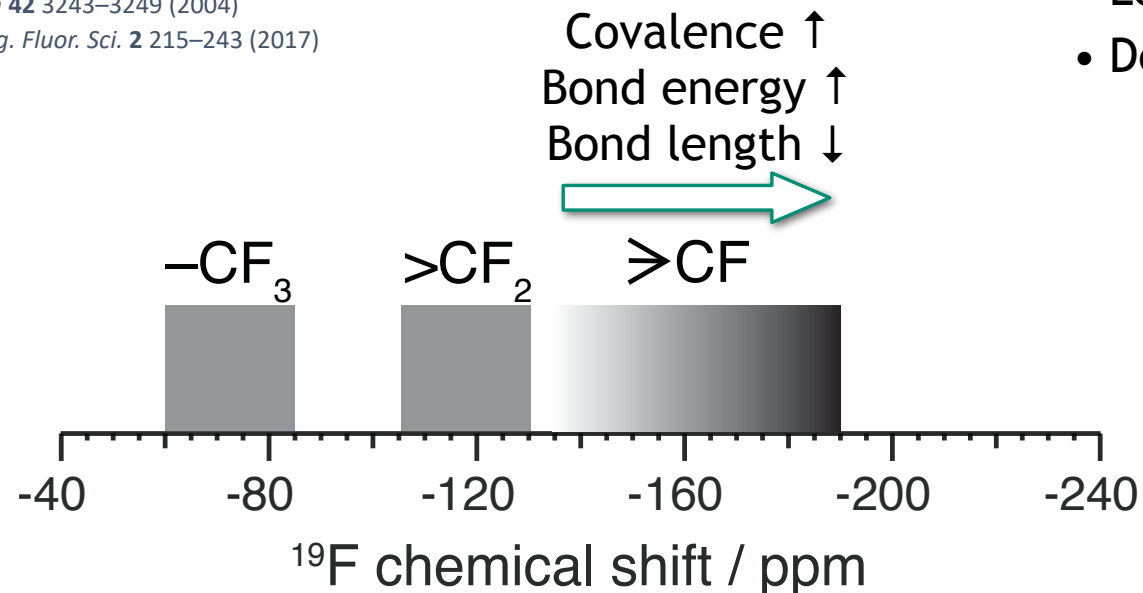


poly(tetracarbon fluoride), $(C_4F)_n$



- Hyperconjugation decreases C-F bond order
- Lengthens C-F bond
- Decreases ^{19}F shielding

Pischedda V., et al. *Carbon* **127** 384–391 (2018)
 Sato, Y., et al. *Carbon* **42** 3243–3249 (2004)
 Dubois M., et al. *Prog. Fluor. Sci.* **2** 215–243 (2017)



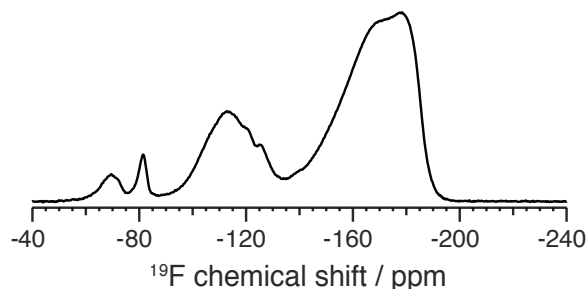
**Problem: $(\text{CF})_n$
 framework is fully
 saturated! (or is it?)**

Solid-state NMR

Functional groups

Quantification

Spatial relationships

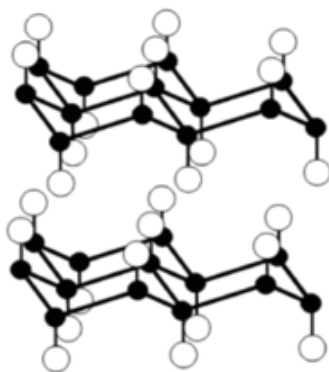
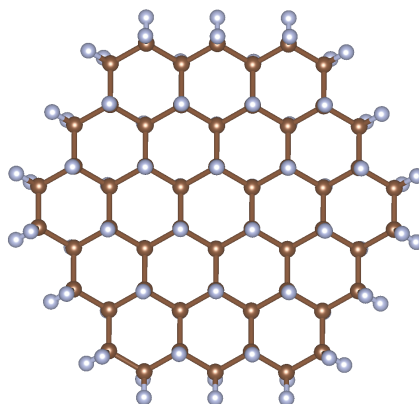
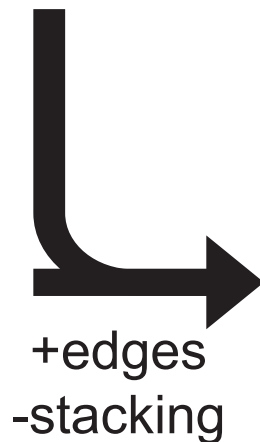
**DFT refinement**

Structure-based prediction of NMR parameters

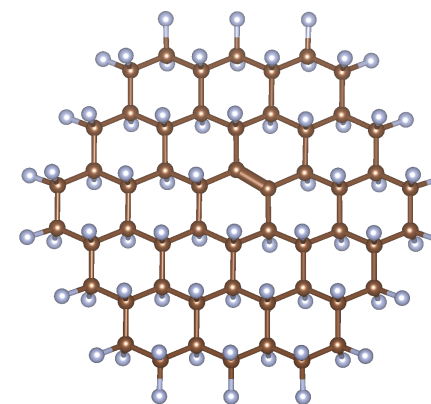
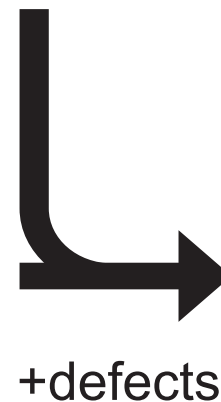
Bond dissociation energies

Analysis of periodically extended structures

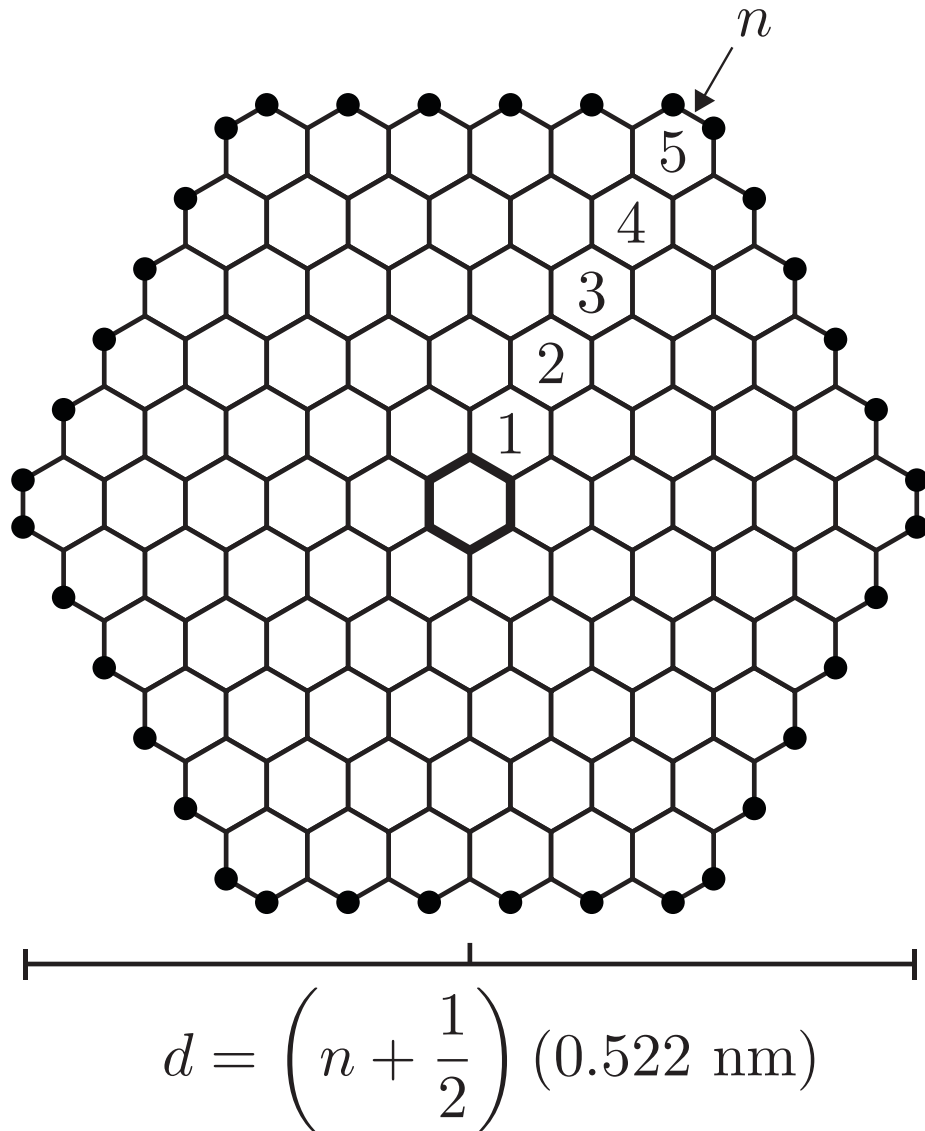
$$H\psi_i = \left\{ -\frac{\hbar}{2m} \nabla^2 + V[\rho] \right\} \psi_i$$

Initial $(\text{CF})_n$
model

Platelet model

Functional
structural model

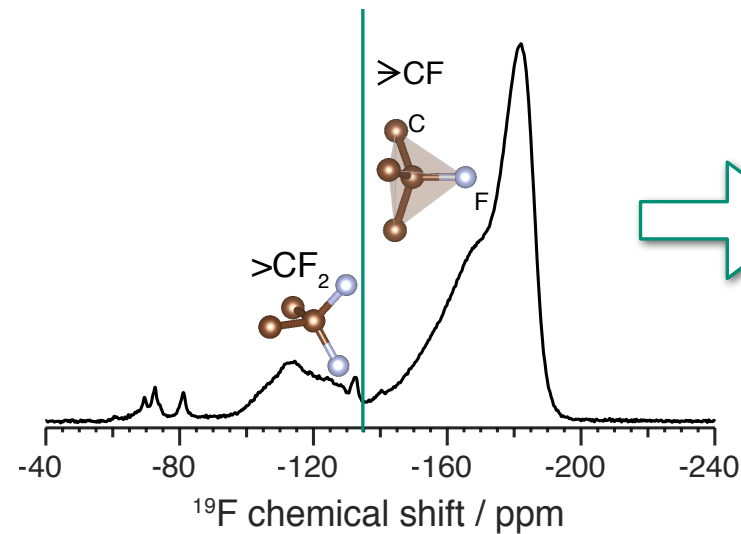
Crowned perfluoroperhydrocoronene platelet model



“5-crown ring perfluorocyclohexane”
5-PFCH

n = Number of crown rings

n = CF : CF₂ ratio



$n \approx 11$
 $d \approx 6 \text{ nm}$

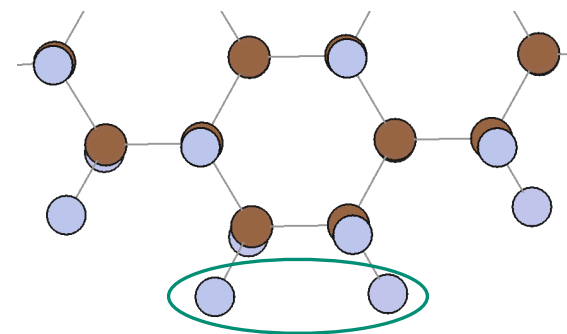
Expected: 1 - 10 nm

Does size matter?

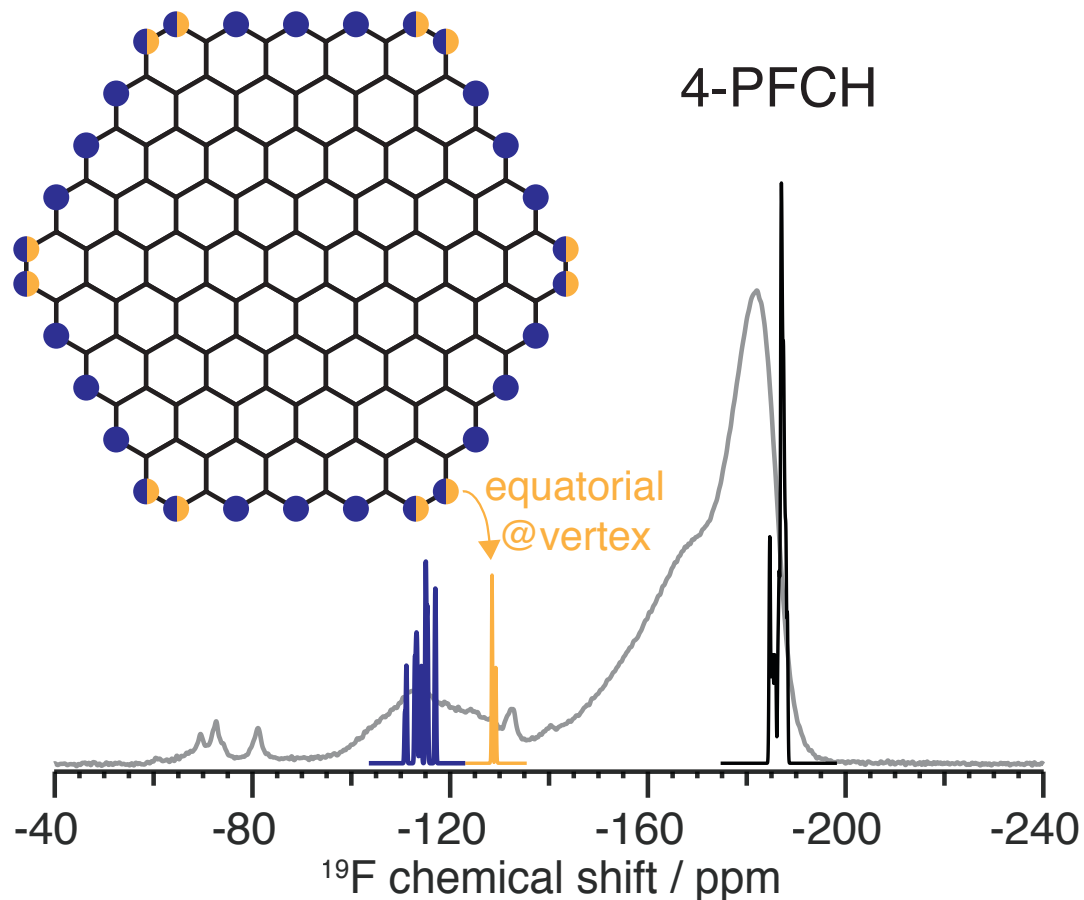


Emsley, J. W., Phillips, L. *Prog. Nucl. Magn. Reson. Spec.* **7** 1–520 (1971)

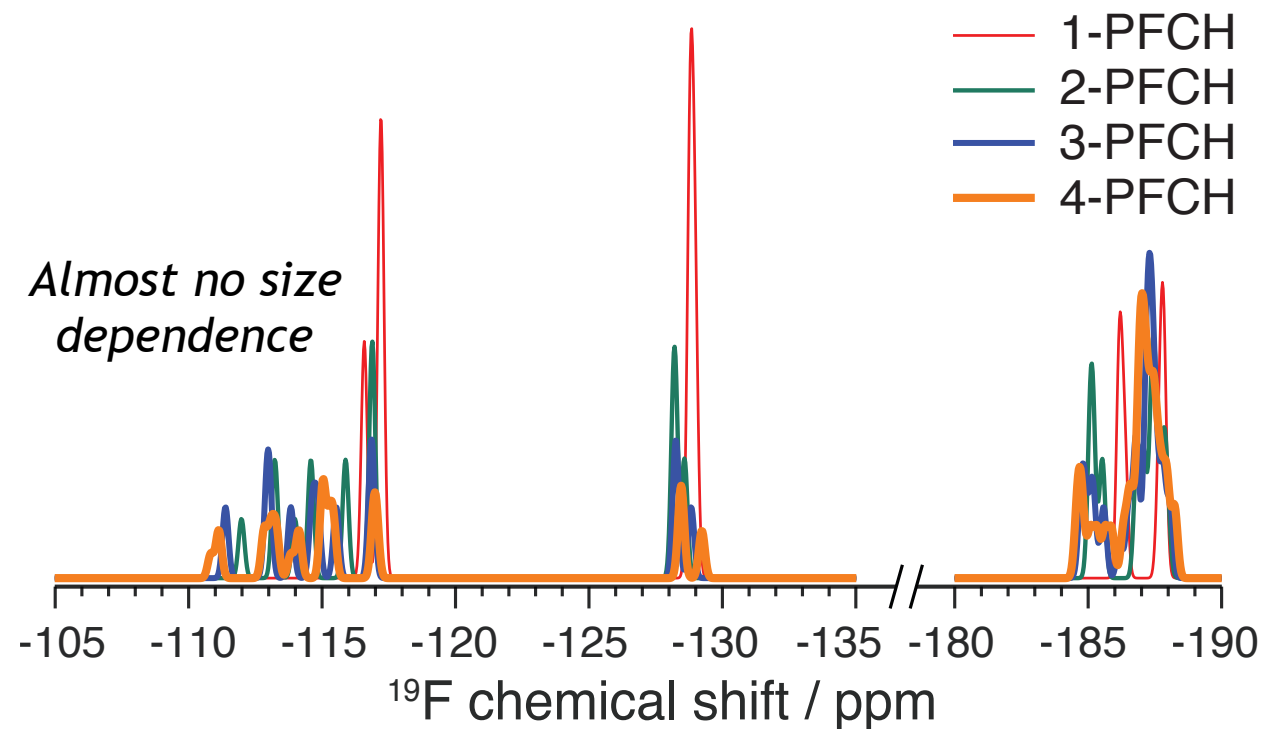
Back-to-back
equatorial $>\text{CF}_2$:



4-PFCH



Almost no
size
dependence

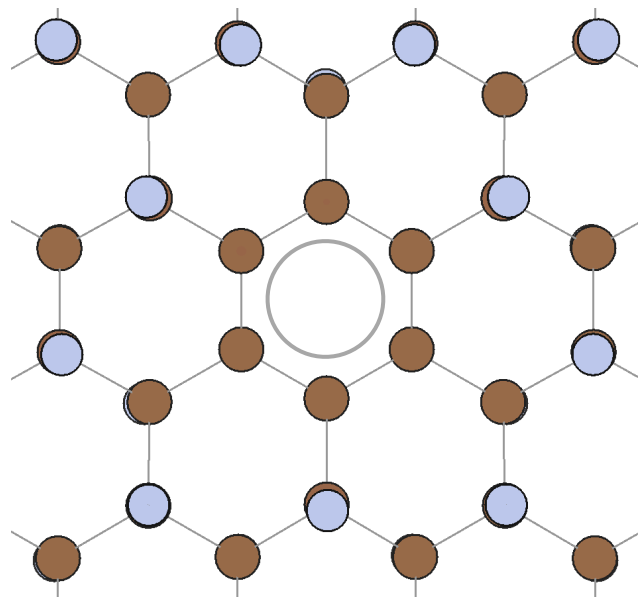


Fluorine-poor point defects

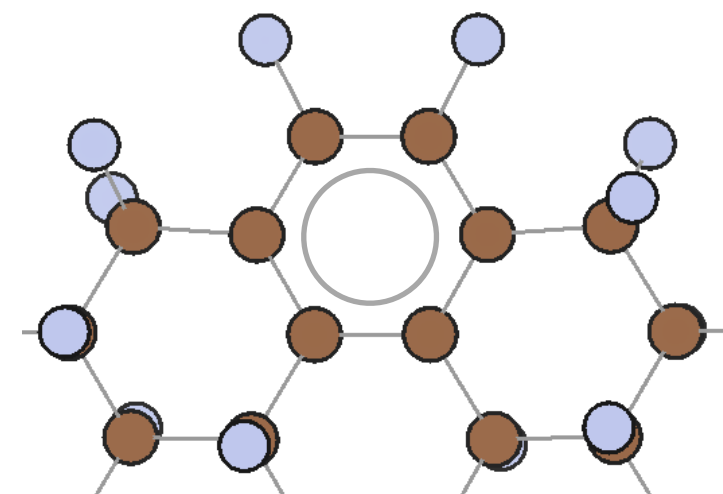


Core

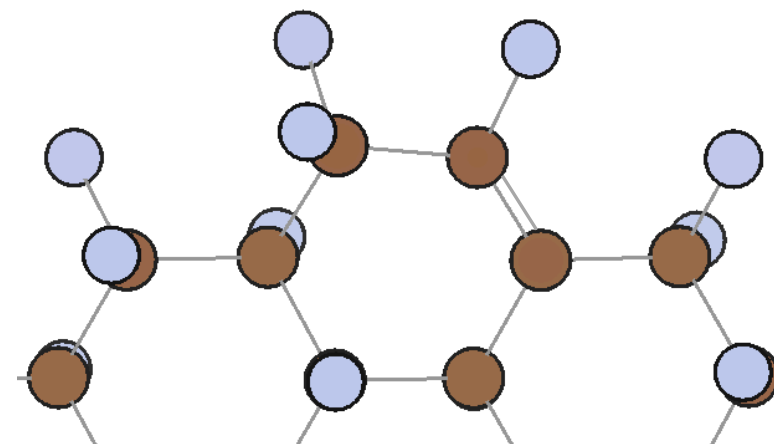
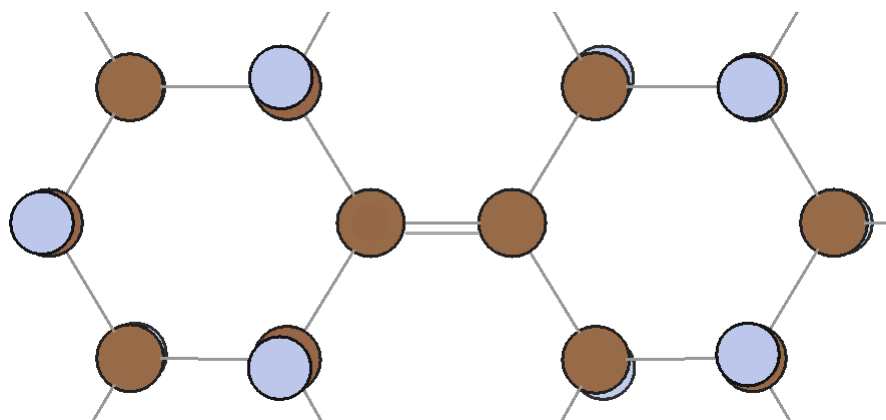
Aromatic



Edge

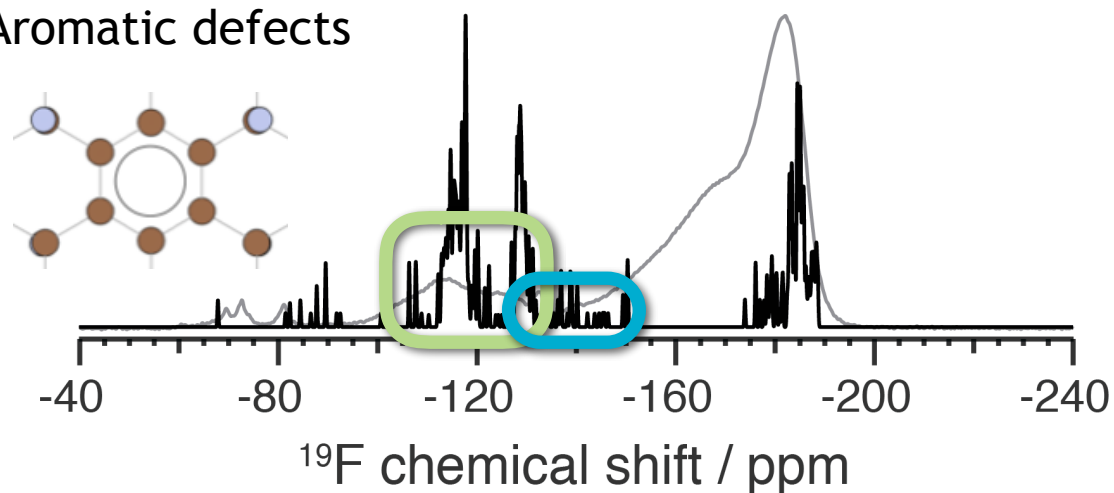


Alkenyl

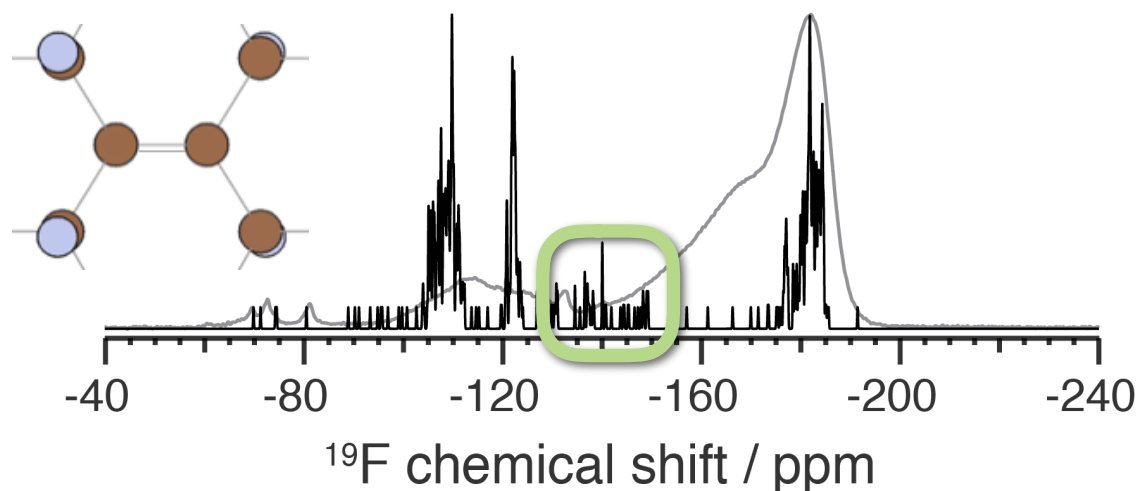


16 Fluorine-poor defects

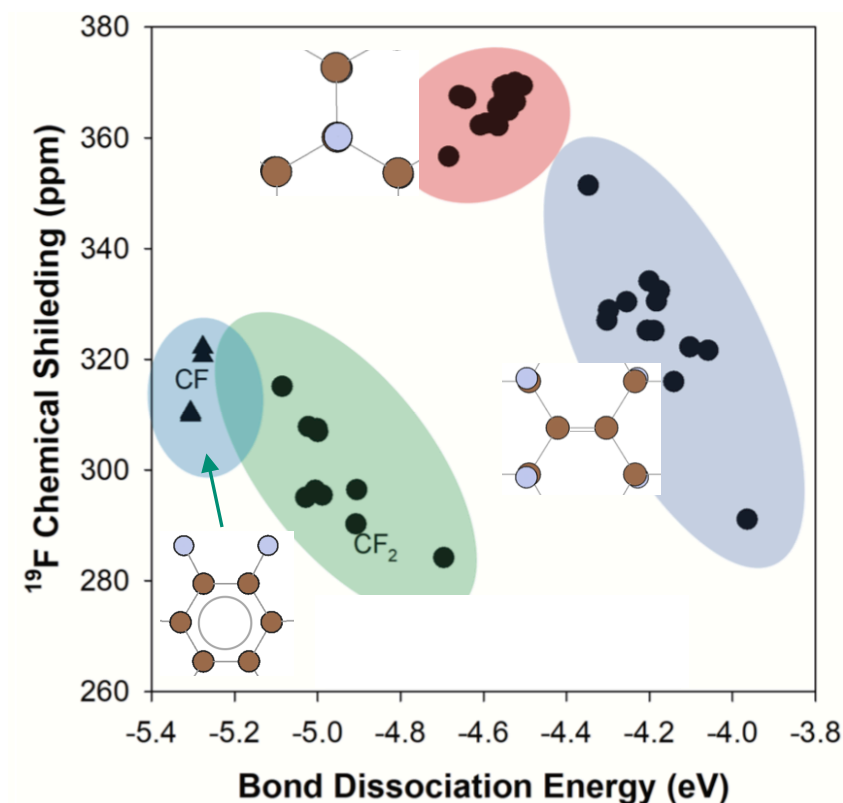
Aromatic defects



Alkenyl defects

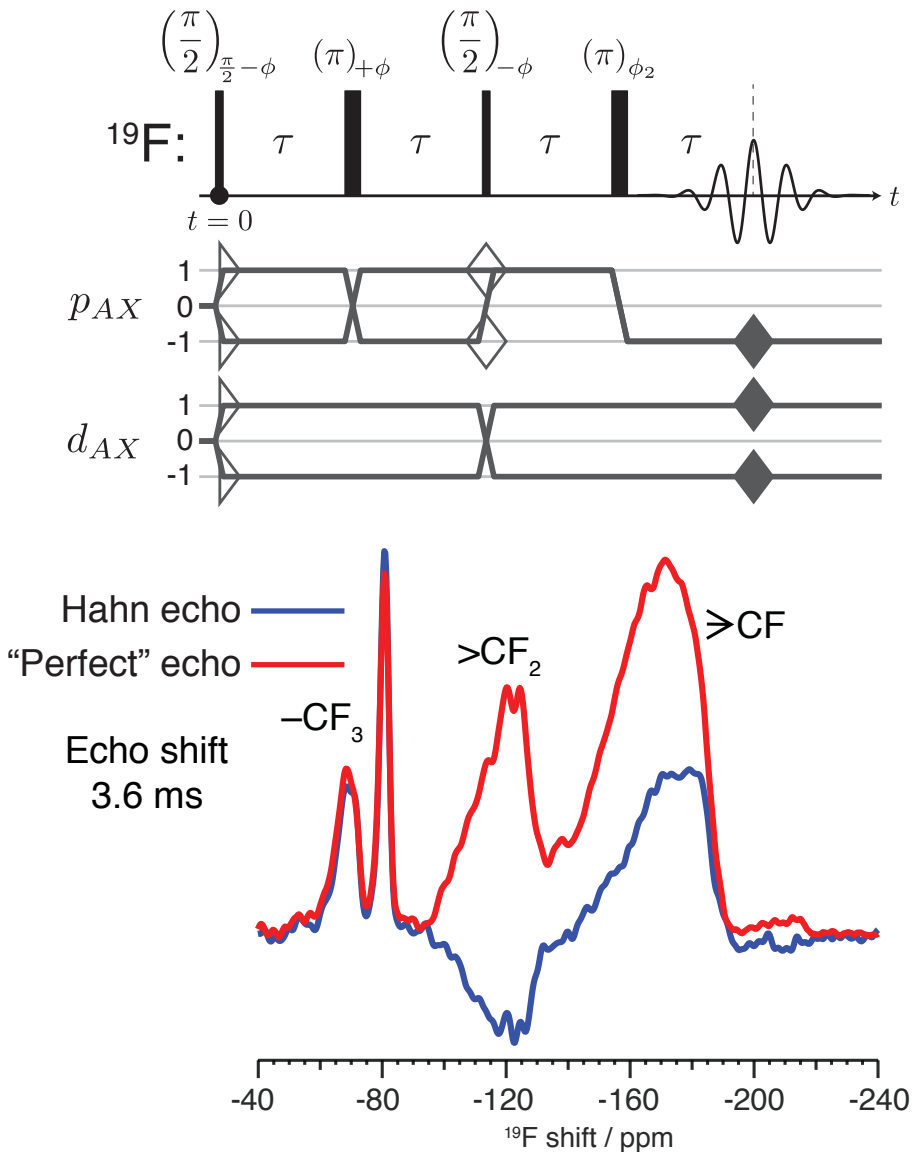
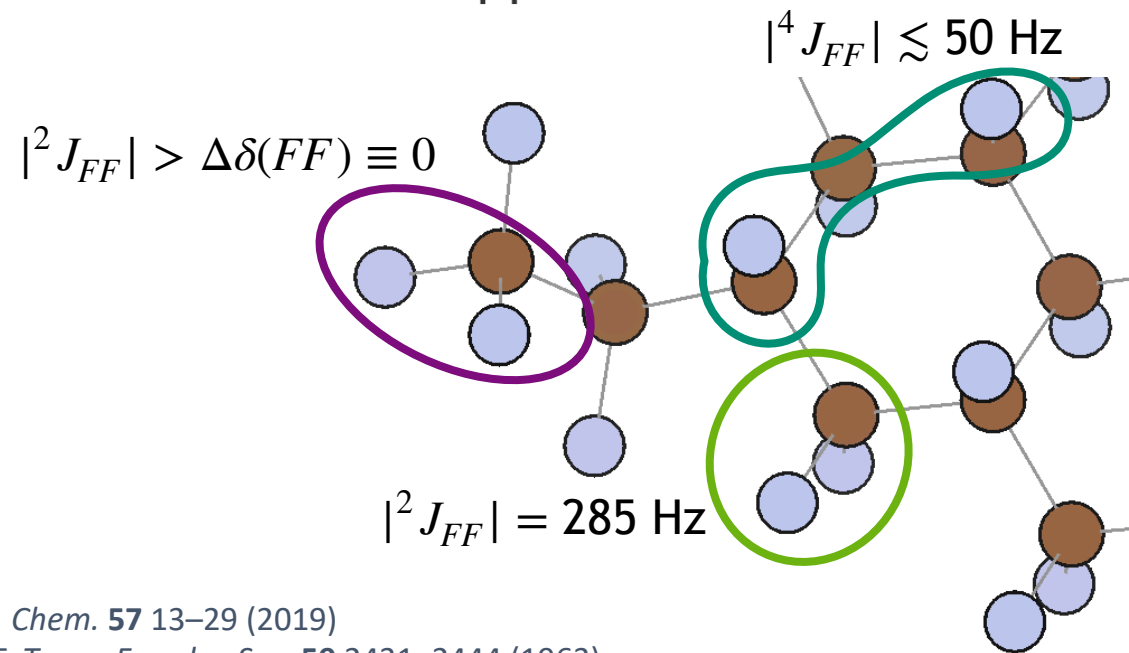
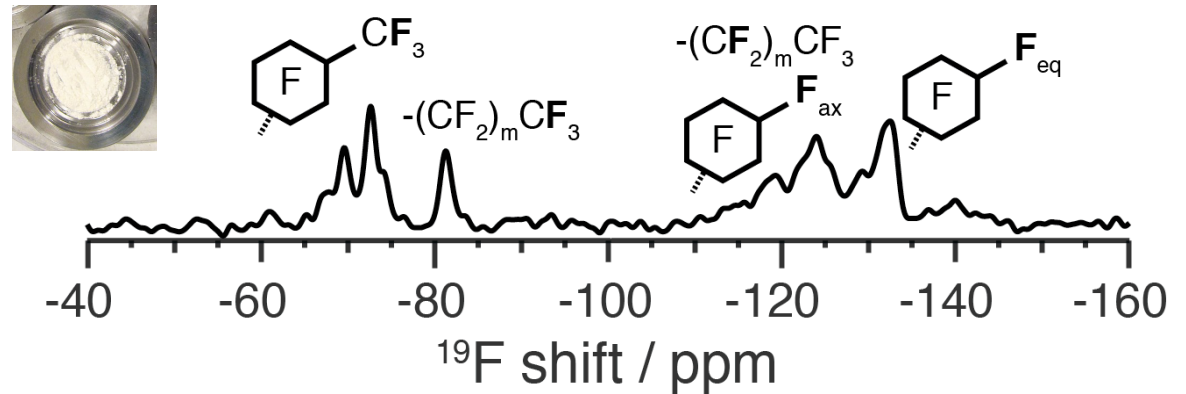


- Aggregated over edge and core
- Conjugated defects included
- Consistently larger deshielding by aromatic defects (overlaps $>\text{CF}_2$ mostly, edge arom overlap alkenyl)



But does NOT explain -170 ppm shoulder

“Perfect” echo

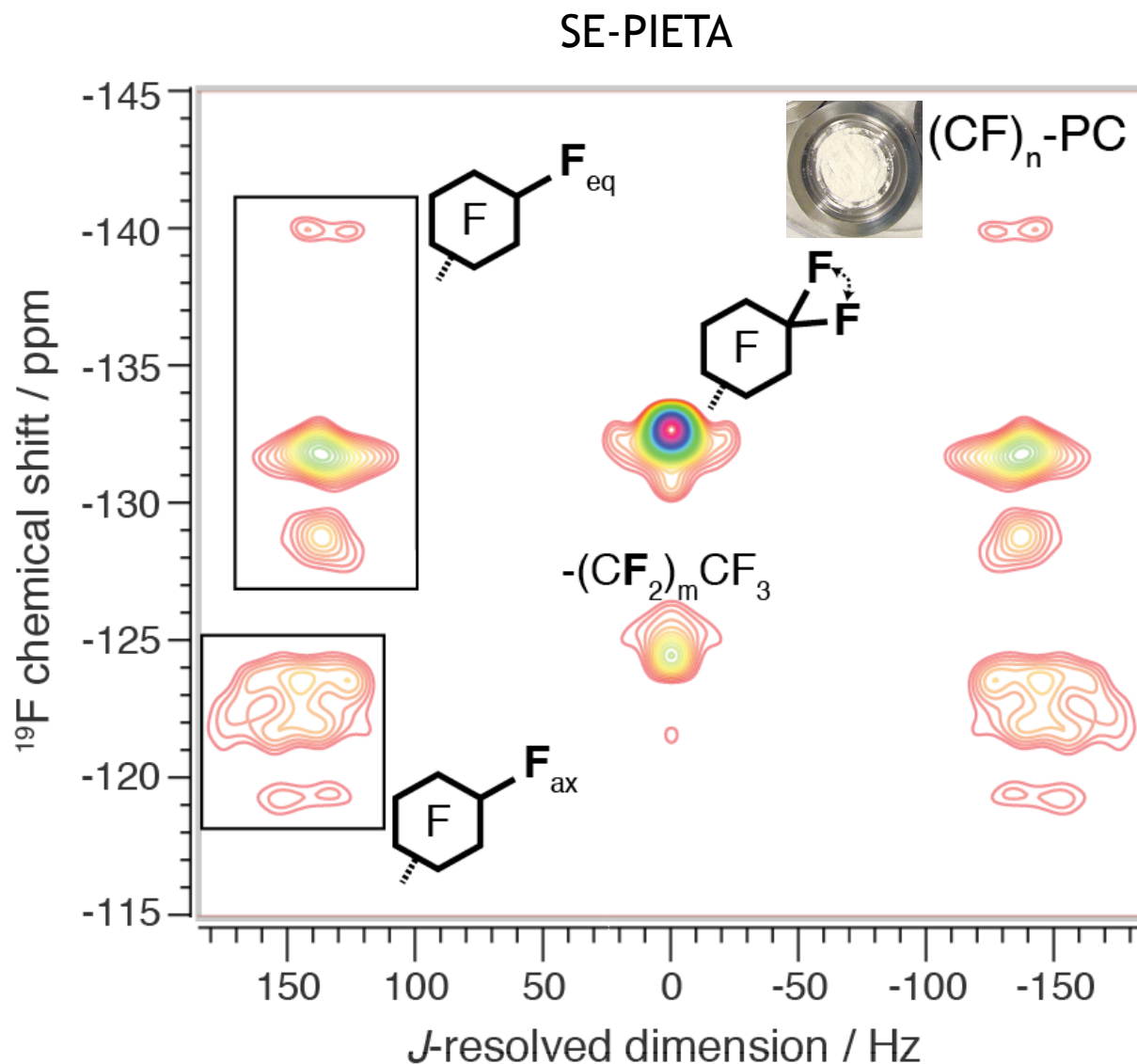
“Perfect” echo, 12 ms echo shift $\rightarrow$ mobile groups

Teodor, P. *Mag. Reson. Chem.* **57** 13–29 (2019)

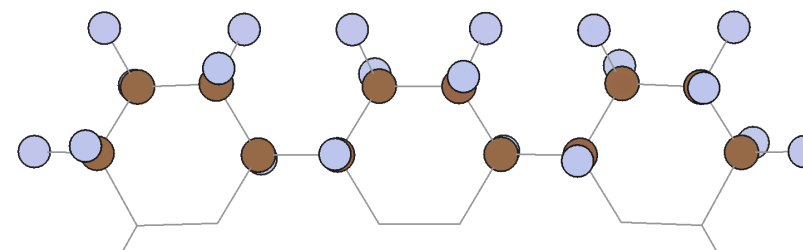
Homer, J., Thomas, L. F. *Trans. Faraday Soc.* **59** 2431–2444 (1963)

Walder, B. J., Rimsza, J. M., Alam, T. M. *In Prep.* (2020)

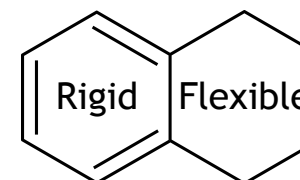
J-resolved spectroscopy: mobile groups



- SE-PIETA: Train of π pulses after perfect echo
- Shift refocused, J-modulated echoes
- Filters for flexible/mobile species
- Suggests crenellated edge groups exist



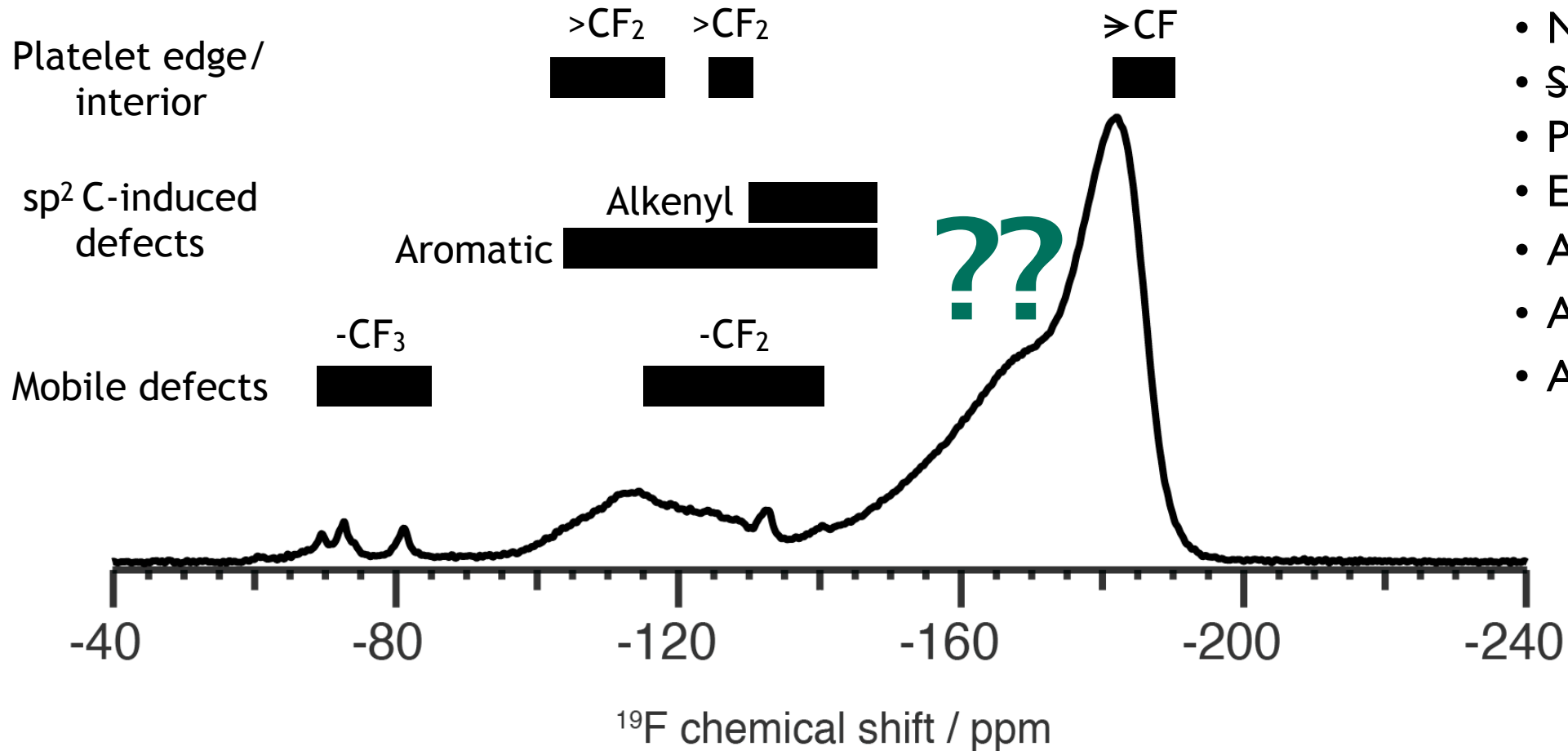
- Model for flexibility: tetralin



Srivastava, D. J., et al. *Phys. Rev. B* **98** 134202 (2018)

Walder, B. J., Rimsza, J. M., Alam, T. M. *In Prep.* (2020)

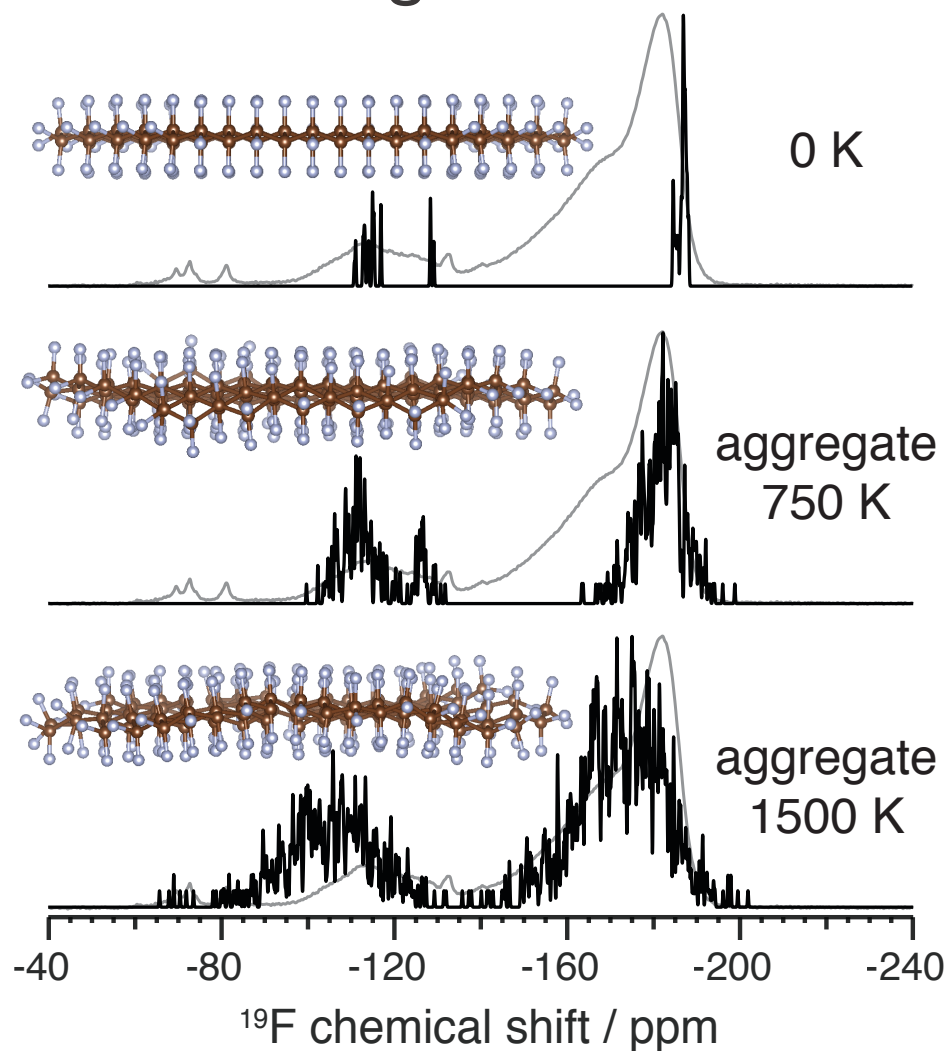
Defect disorder does not explain the “semi-ionic” signals



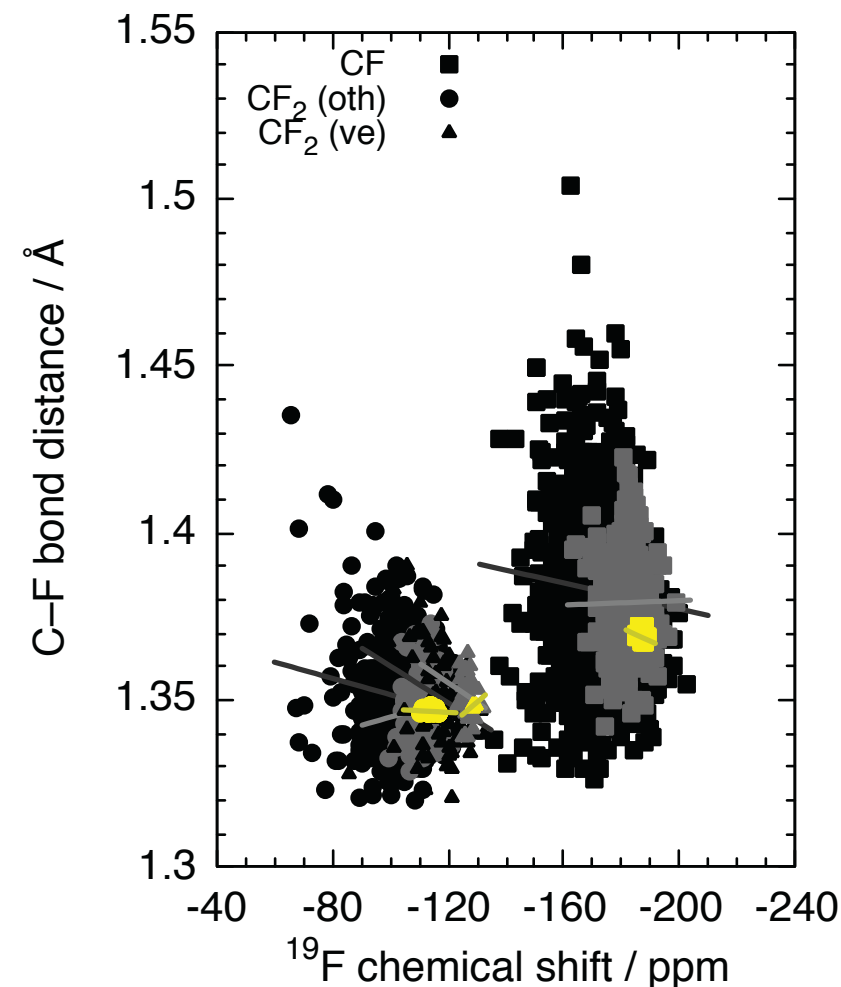
- Nanoplatelets ✓
- Size dependence
- Perfluoroalkyls ✓
- Edge crenellation ✓
- Alkenyl-adjacent CF ?
- Aromatic-adjacent CF ?
- Aromatic edge CF ?

Need to peer into the bulk

Thermal disorder/glassiness?

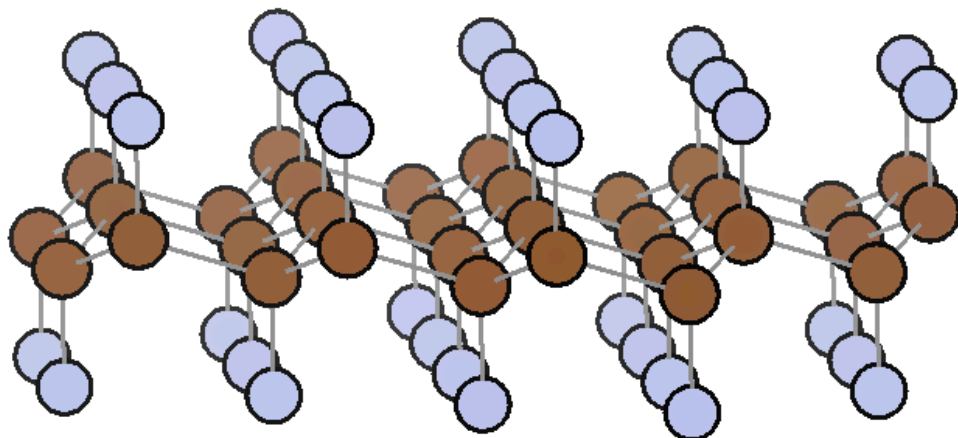


Broadening
Fails to replicate finer details



No evidence of
hyperconjugation

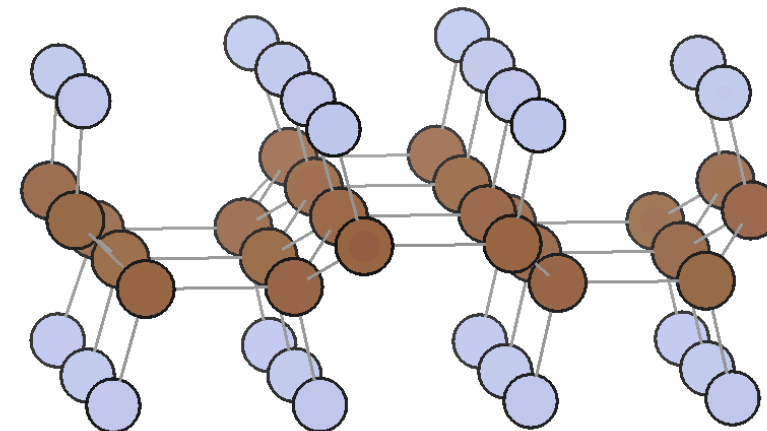
Chairs



Rüdorff, W., Rüdorff, G. *Z. Anorg. Chem.* **253**
281-296 (1947)

Kita, Y., Watanabe, N., Fujii, Y. *J. Am. Chem. Soc.* **101** 3832-3841 (1979)

Boats: $\Delta E_{\text{rel}} = 0.169$ eV per CF



Ebert, I. B., Brauman, J. I., Huggins, R. A. *J. Am. Chem. Soc.* **96** 7841-7842 (1974)

Clark, D. T., Peeling, J. *Poly. Sci. Poly. Chem. Ed.* **14**
2941-2967 (1976)

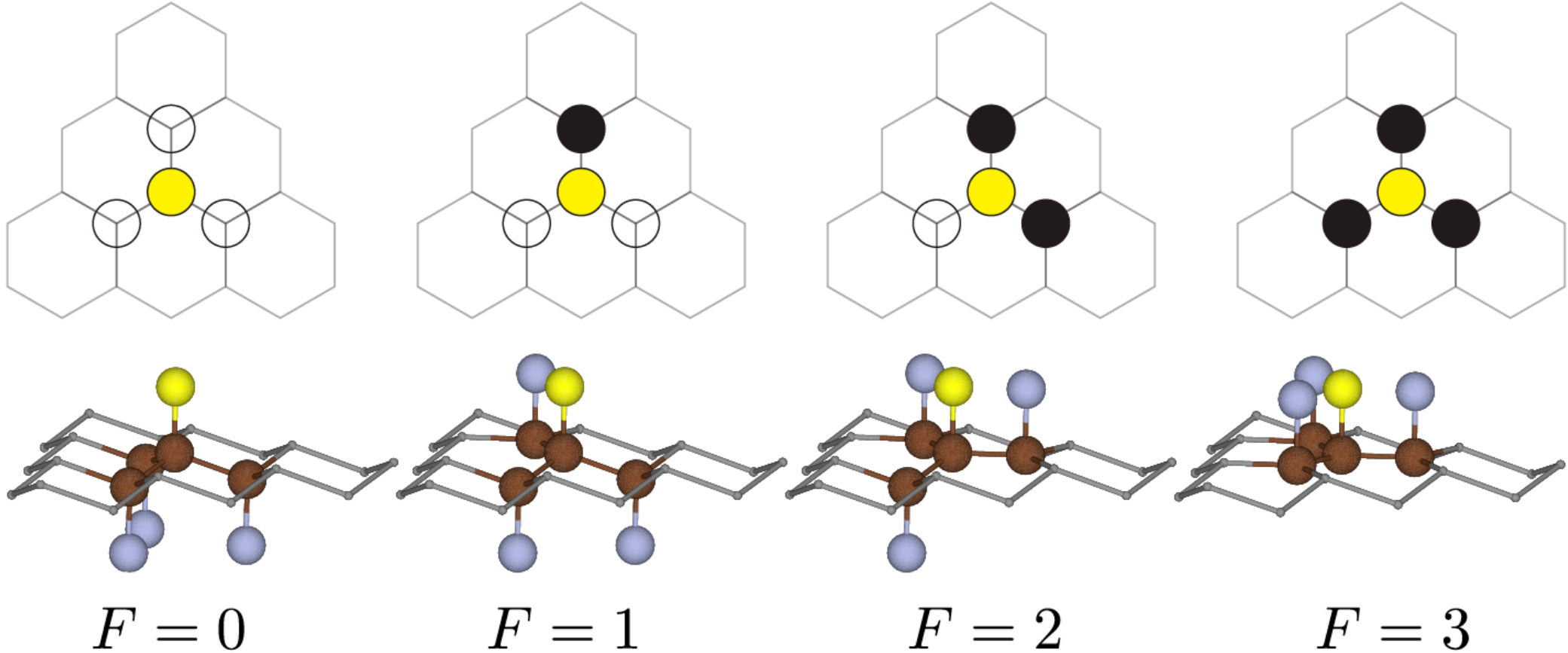
It depends: Charlier, J.-C., et al. *Phys. Rev. B* **47** 16162-16168 (1993)

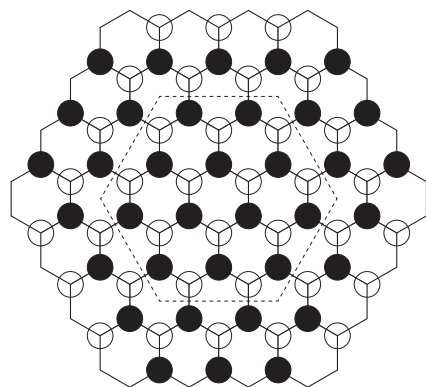
The last say: Giraudet, J., et al. *J. Phys. Chem. B* **109** 175-181 (2005)



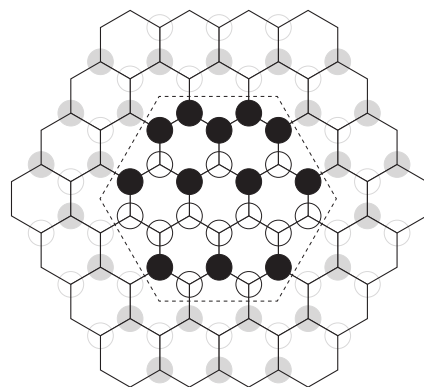
***Lots of NMR – but
no consideration of
 ^{19}F chemical shifts!***

Generalizing conformational disorder

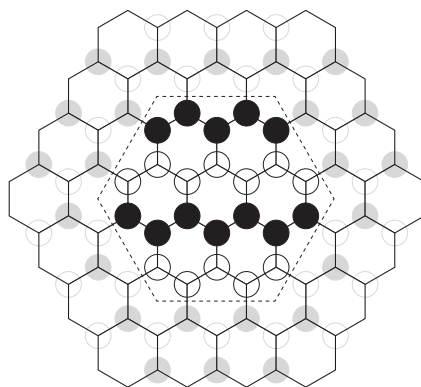


Ordered
core

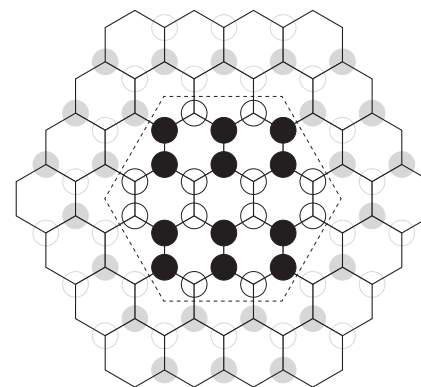
Name chair
 ΔE_{rel} 0.00 eV



tricycle (low)
4.18 eV

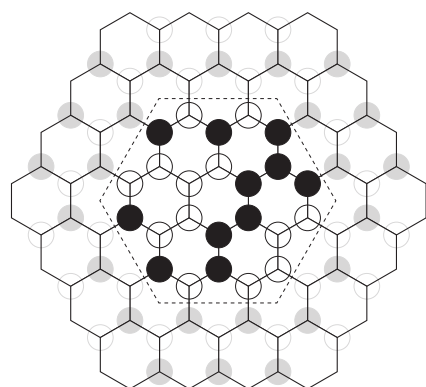


zigzag (low)
5.26 eV

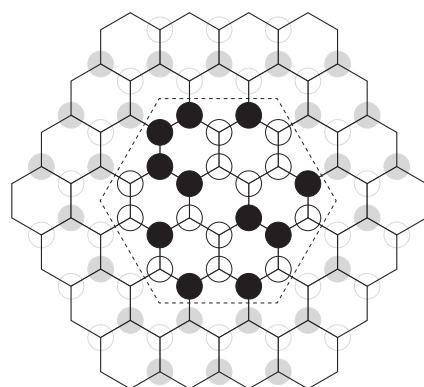


boat
7.08 eV

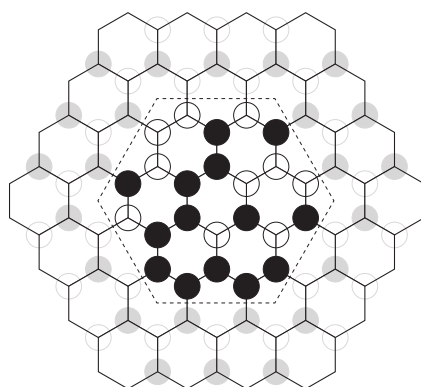
+7 more
4.2 eV to 10.7 eV

Random
core

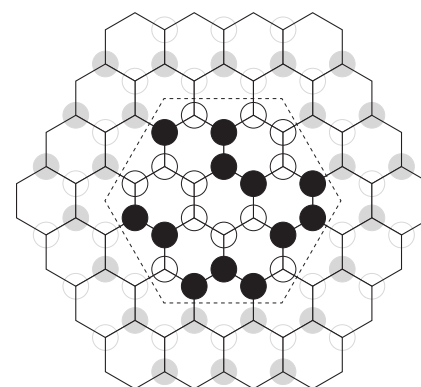
Name random_1
 ΔE_{rel} 9.28 eV



random_2
10.59 eV



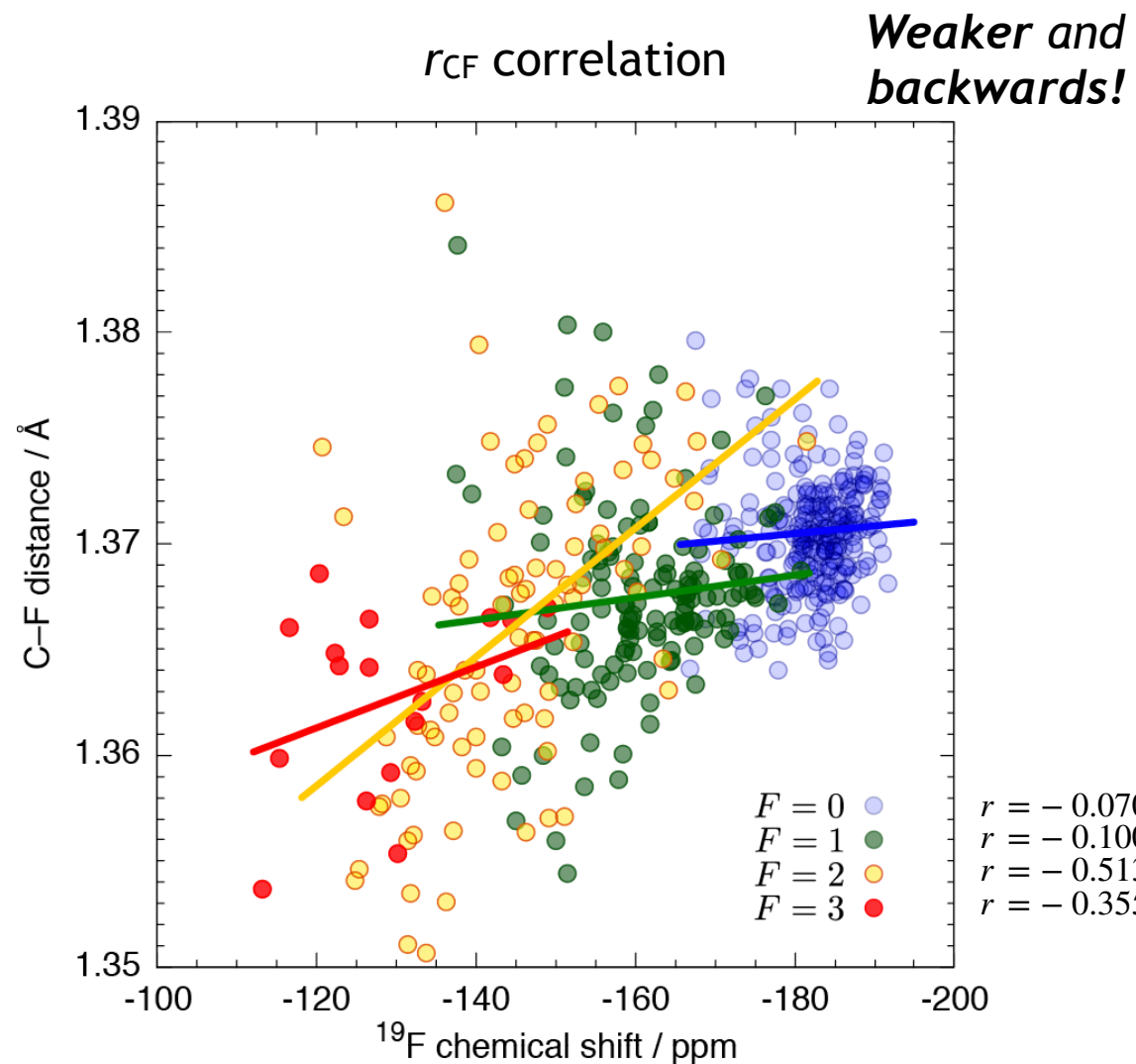
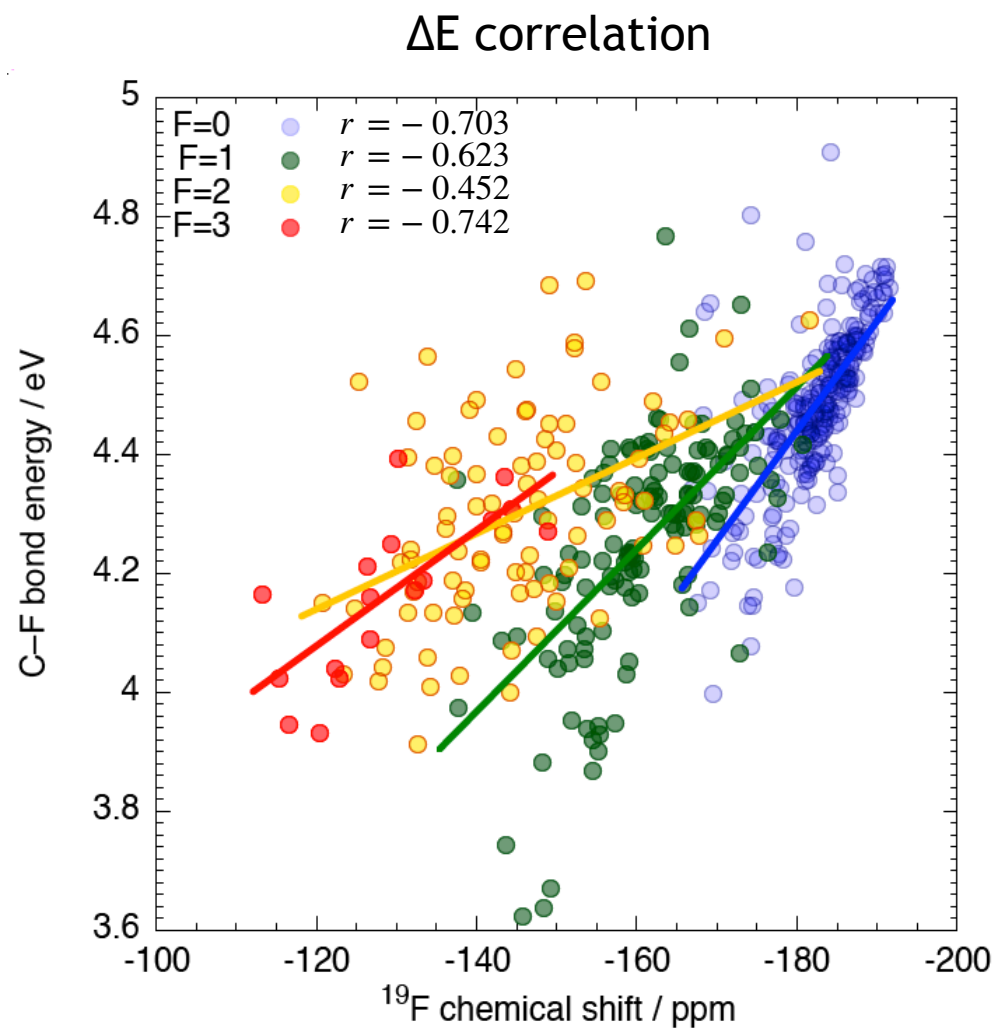
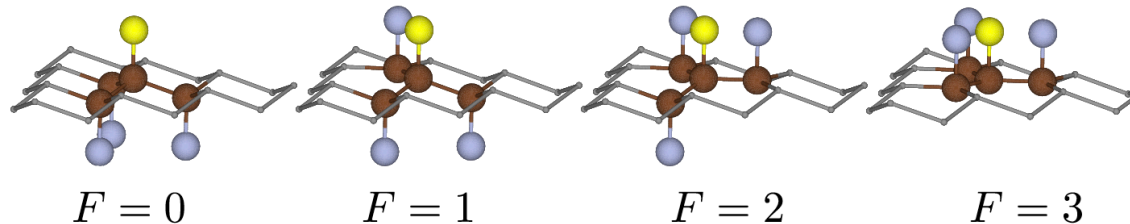
random_3
11.89 eV



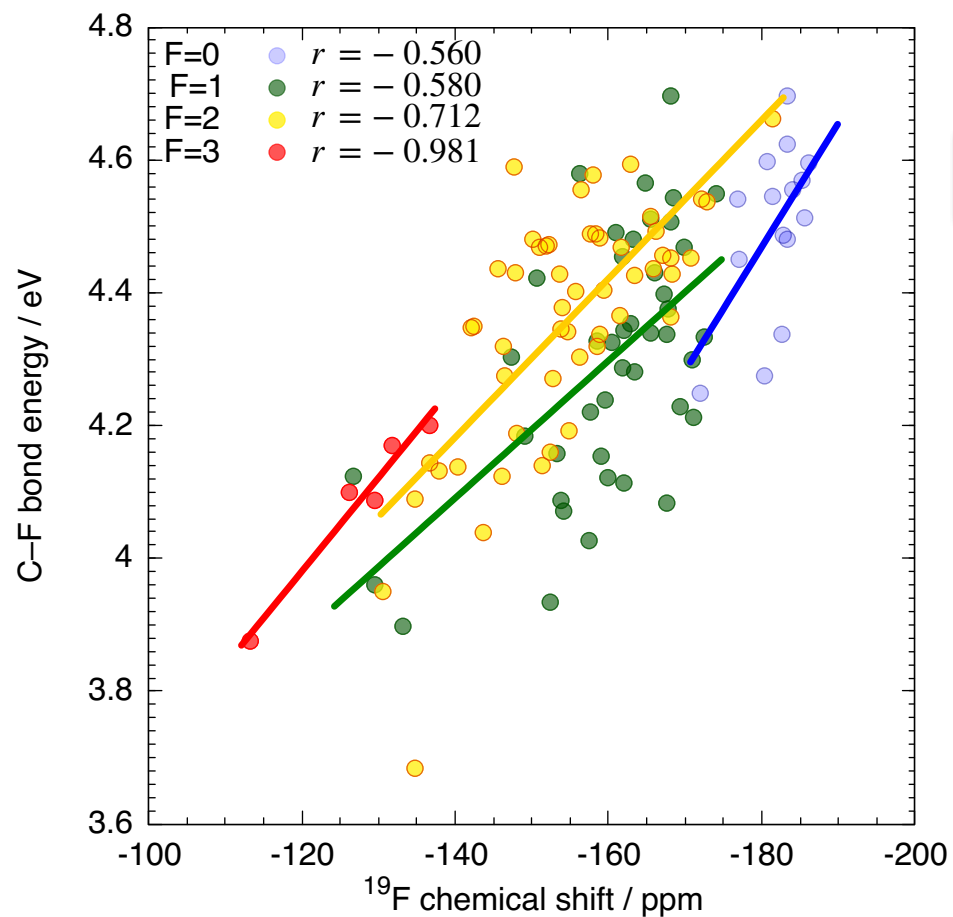
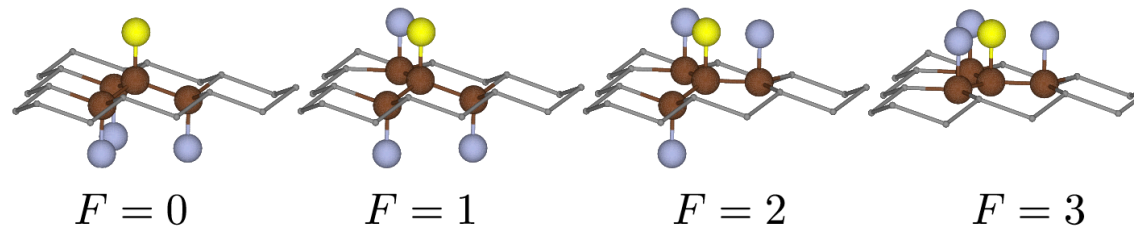
random_4
11.25 eV

+5 more
8.8 eV to 12.2 eV

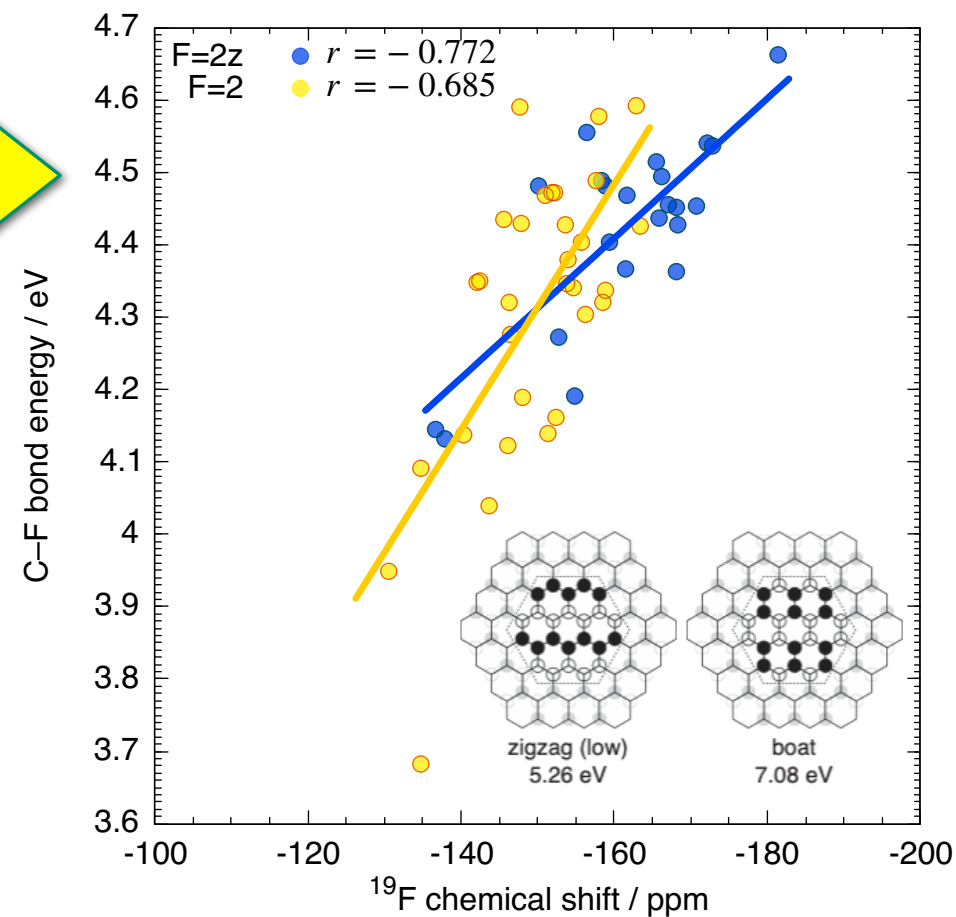
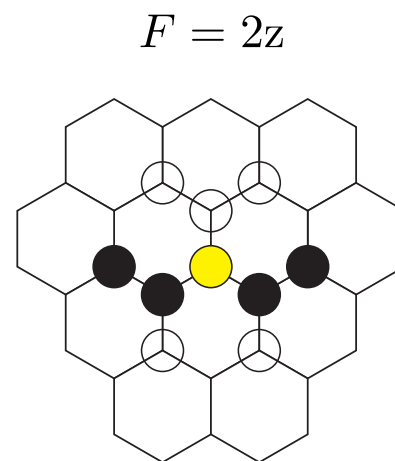
Random cores



Ordered cores

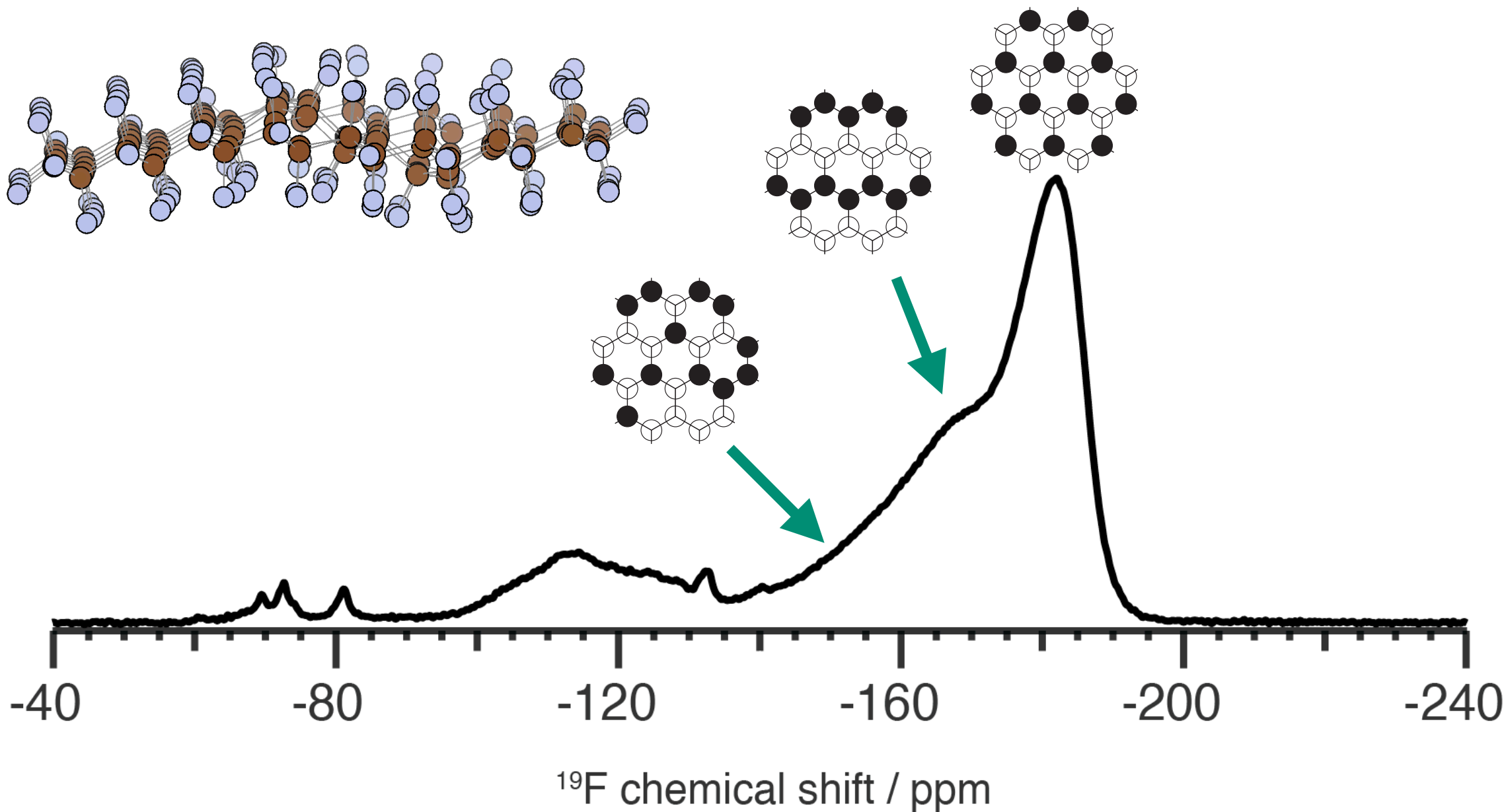


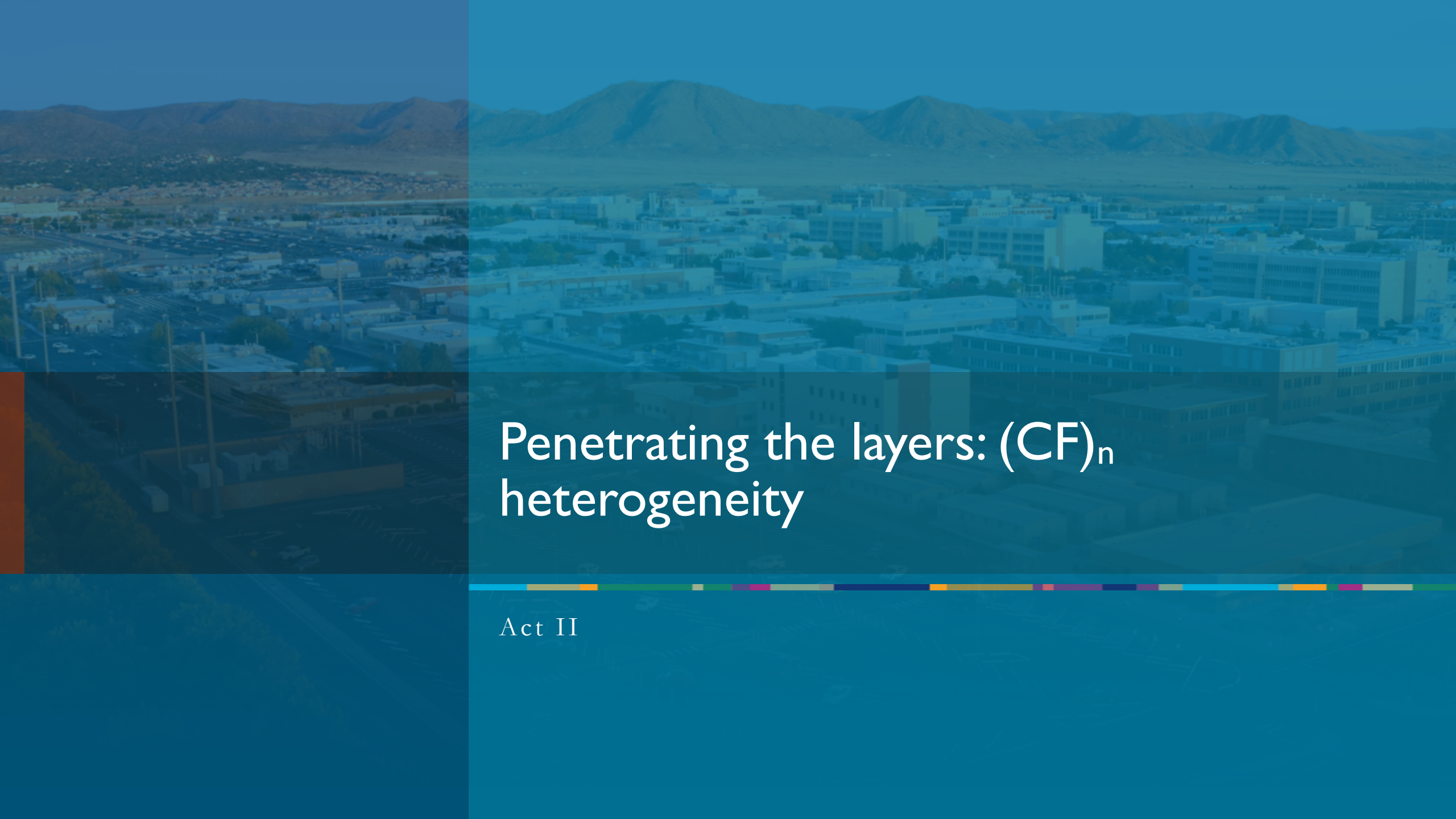
Subclassify “zigzags”



Precedent for zigzags in $(\text{C}_y\text{F})_n$, $y \approx 2.5$: Vyalikh, A., et al. *J. Phys. Chem. C* **117** 7940–7948 (2013)

Shoulder is due to conformational disorder

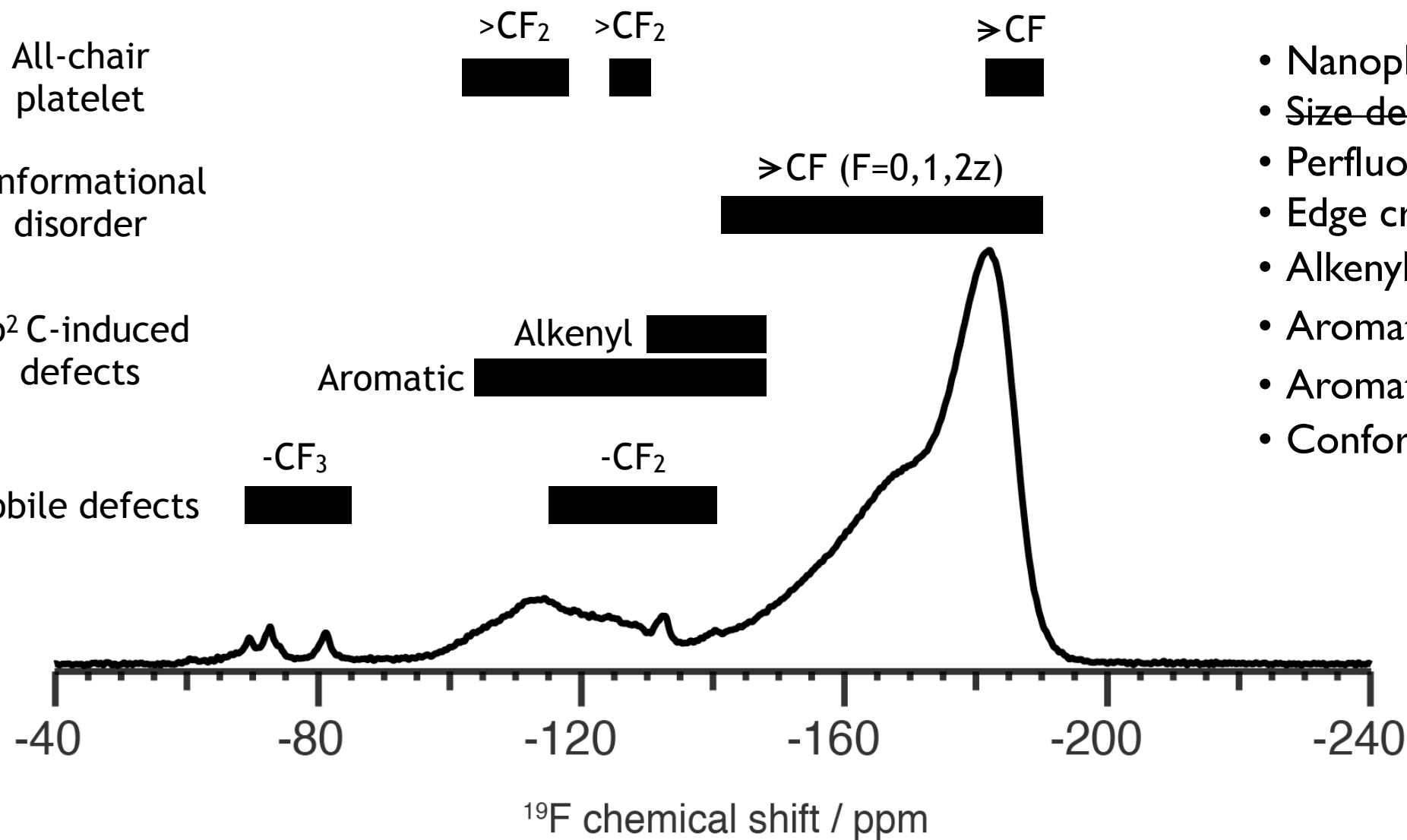




Penetrating the layers: $(CF)_n$ heterogeneity

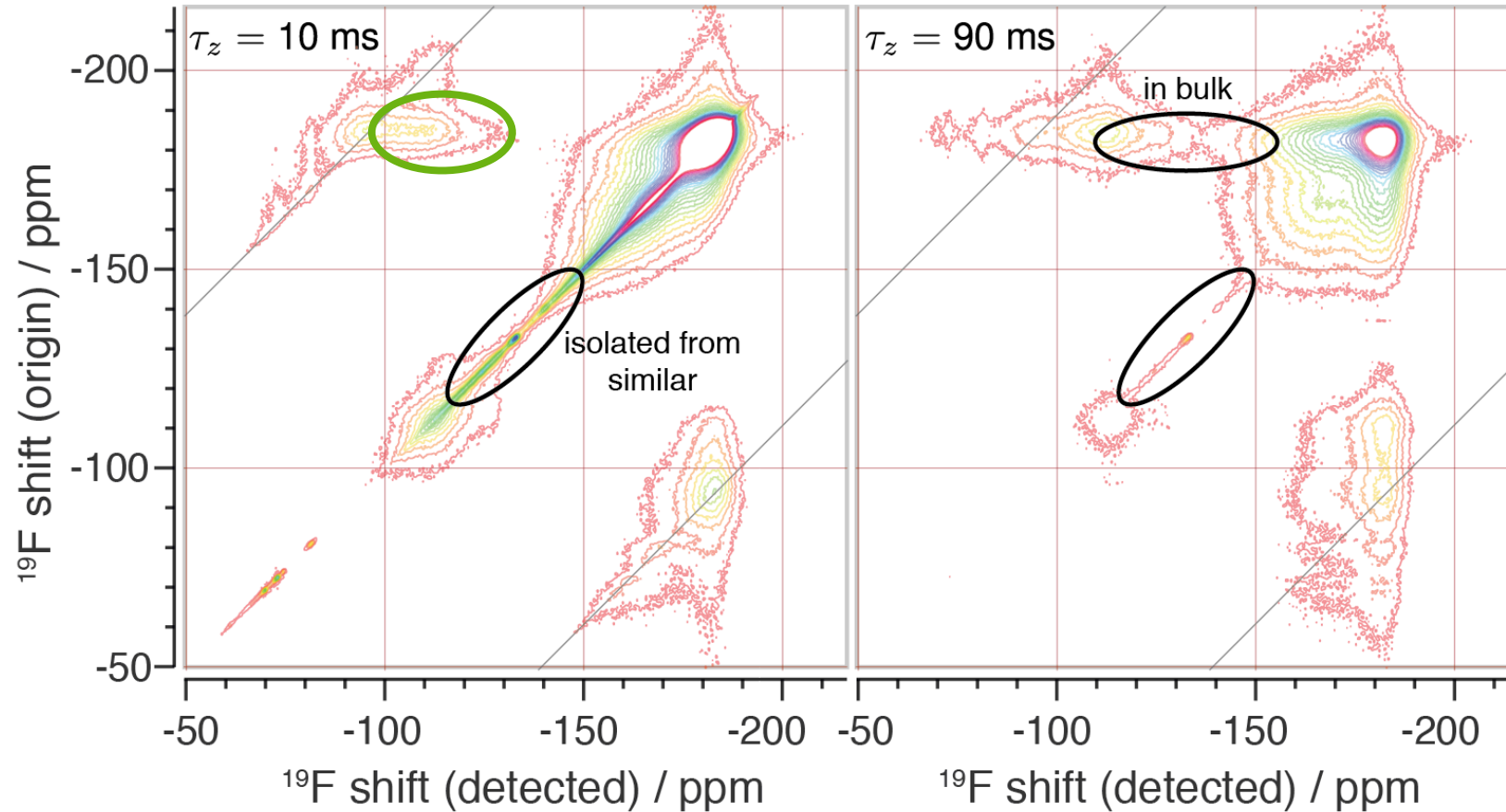
Act II

Assignments from ^{19}F chemical shift analysis

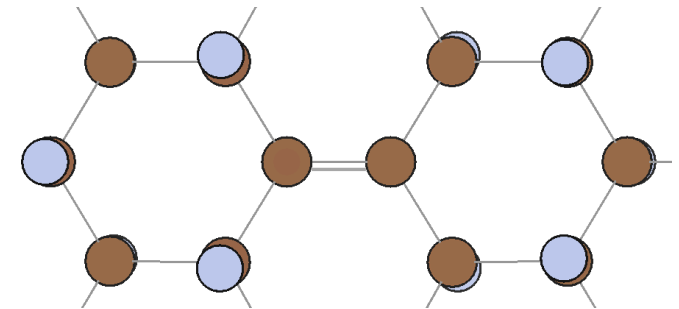


- Nanoplatelets ✓
- ~~Size dependence~~
- Perfluoroalkyls ✓
- Edge crenellation ✓
- Alkenyl-adjacent CF ?
- Aromatic-adjacent CF ?
- Aromatic edge CF ?
- Conformational disorder ✓ ✓

Probing spatial correlations by $\{^{19}\text{F}\}^{19}\text{F}$ EXSY



- Narrow ridge feature
- Ridge avoids $>\text{CF}_2$ region
- Transfer to $>\text{CF}$, avoids $>\text{CF}_2$
- Implies interior point defects

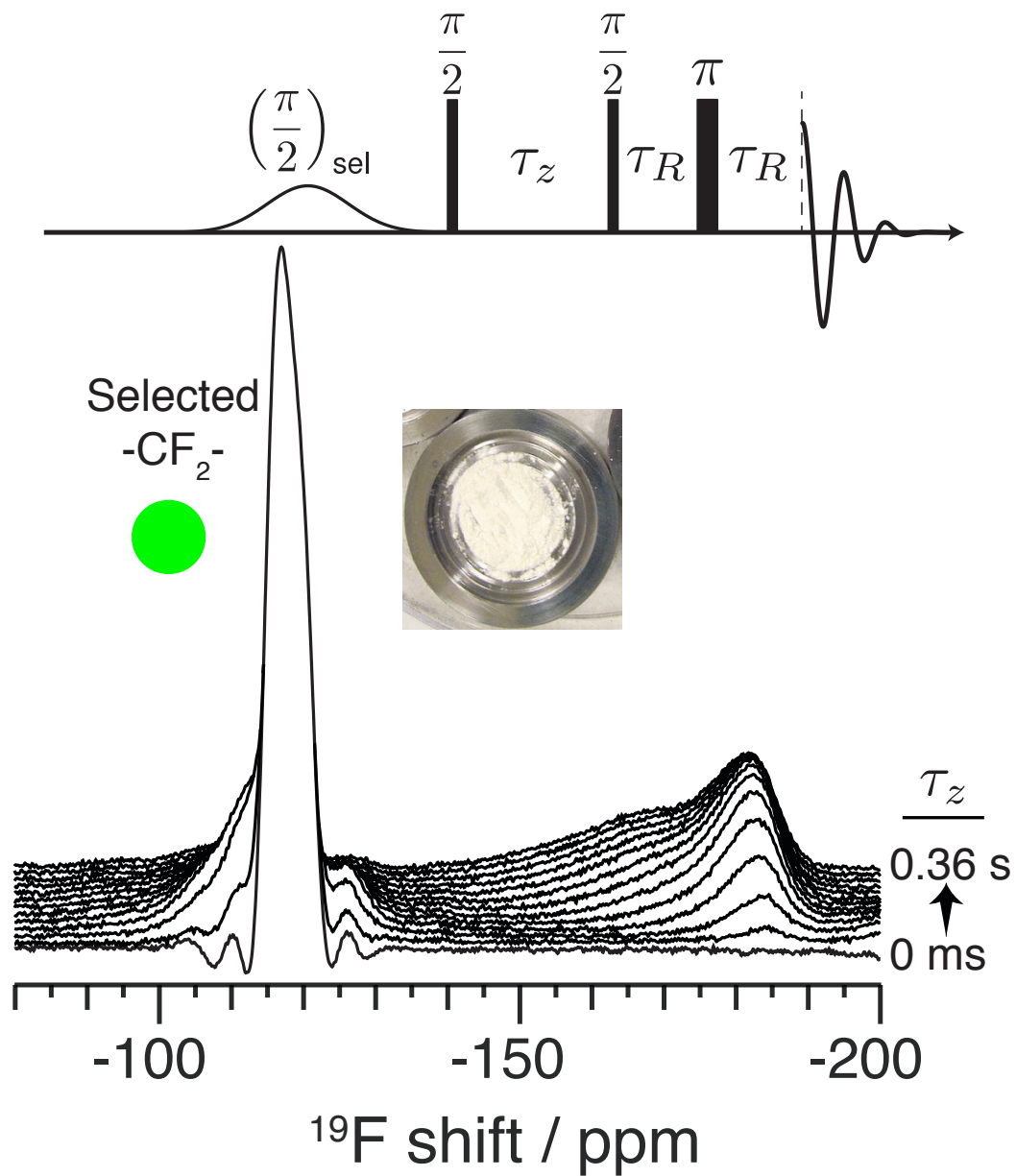


33 $\frac{1}{3}$ kHz MAS

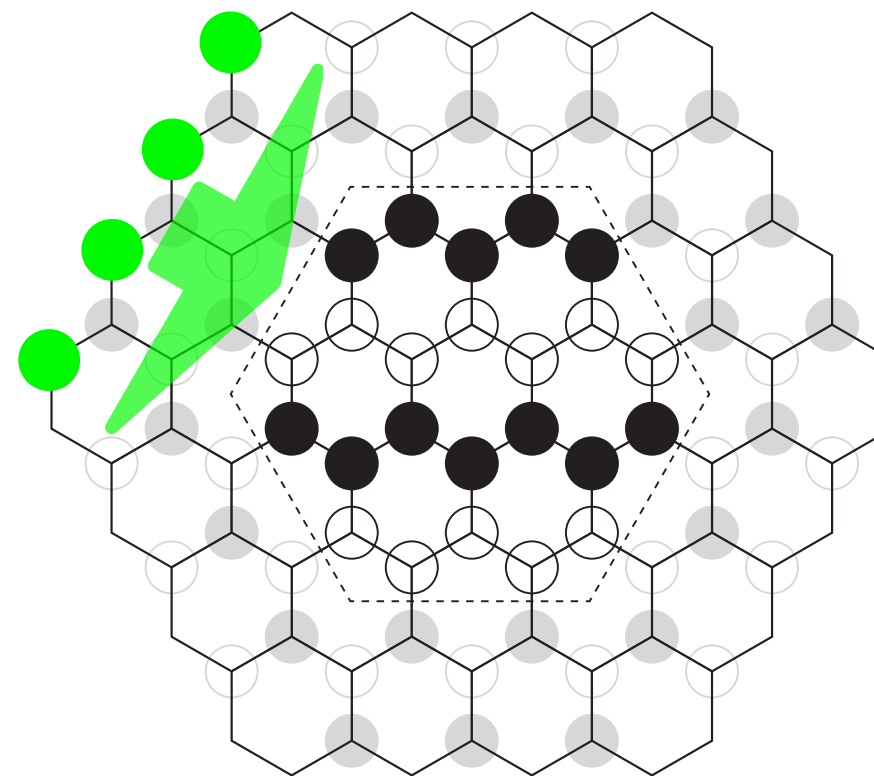


Most rapid diffusion: $>\text{CF}_2 \rightarrow \text{chair } >\text{CF}$

Why core/crown model?



Well defined flow
 $\text{>CF}_2 \rightarrow \text{chair} \text{>CF} \rightarrow \text{disordered} \text{>CF}$



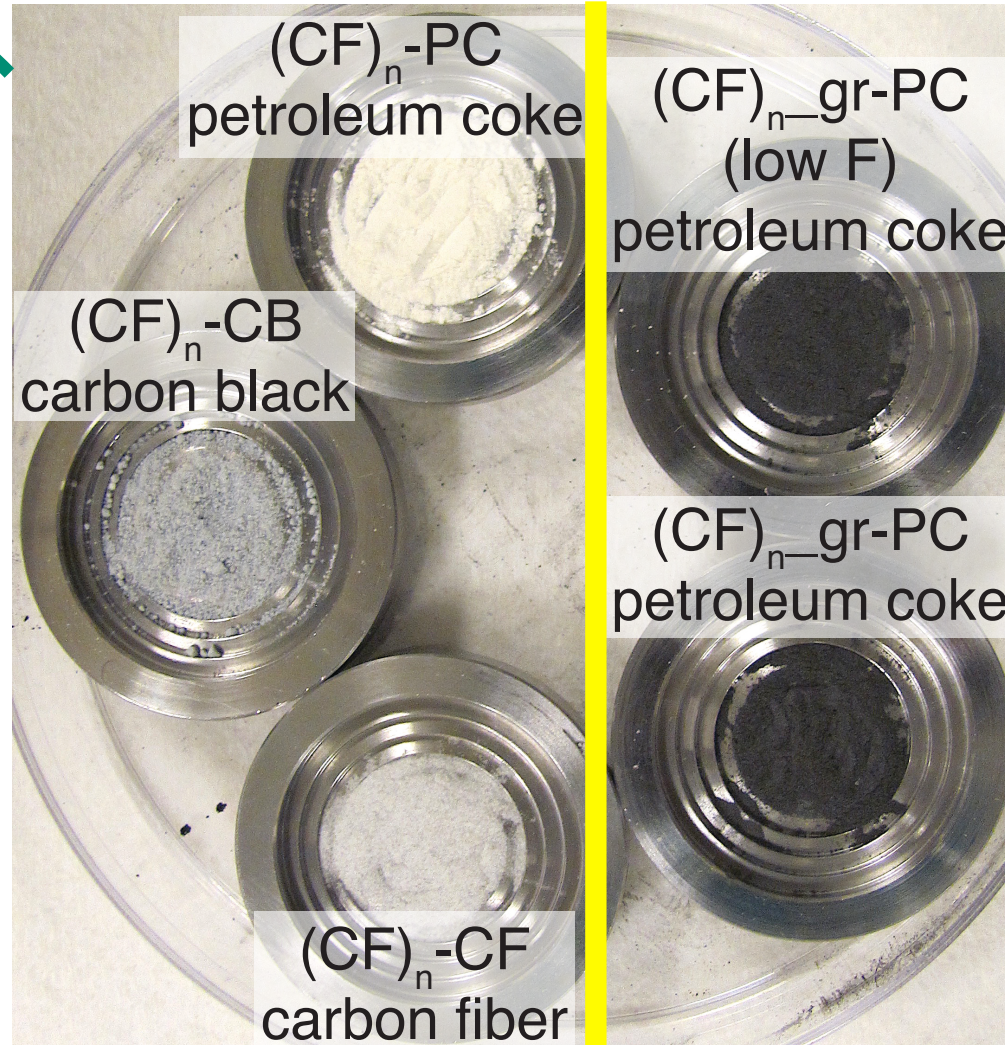
Precedent for ordered near-edge behavior:

Sheka, E. F. *Int. J. Quant. Chem.* **114** 1079–1095 (2014)

There's more: color suggests graphitic carbon domains

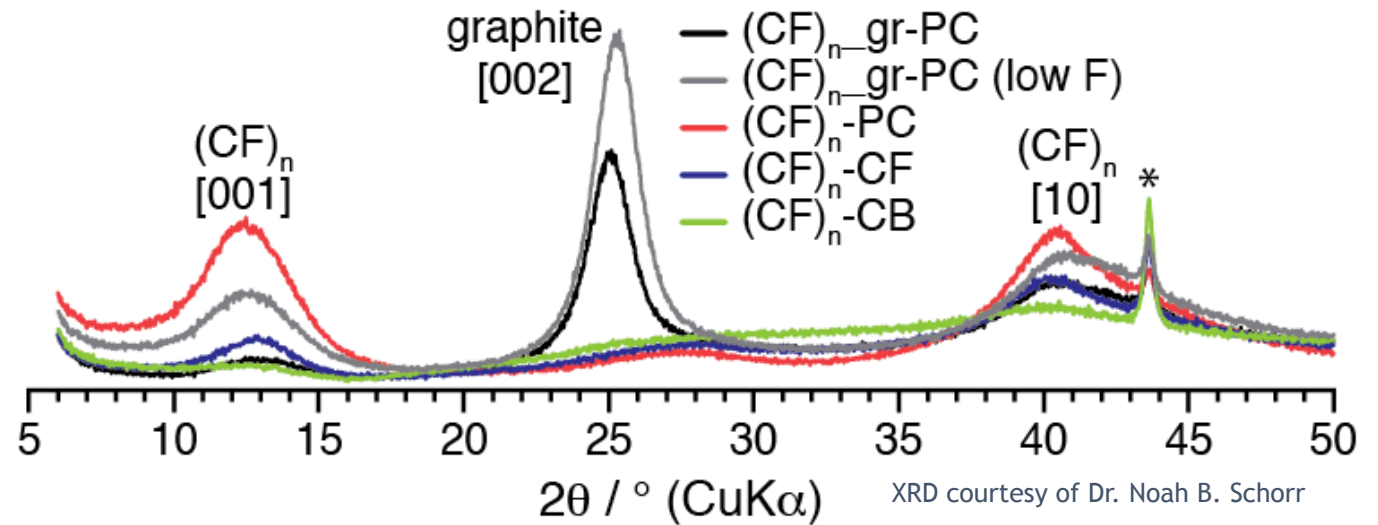
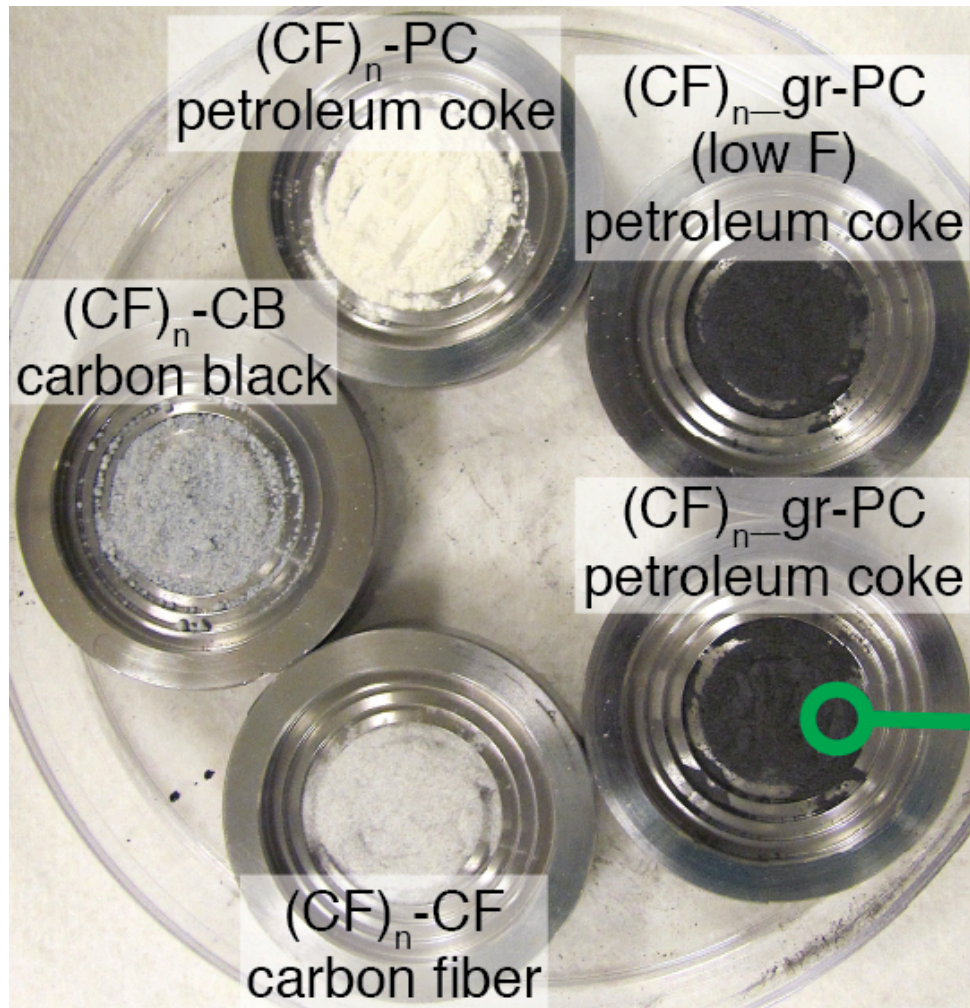


“Fully fluorinated $(CF)_n$ ”

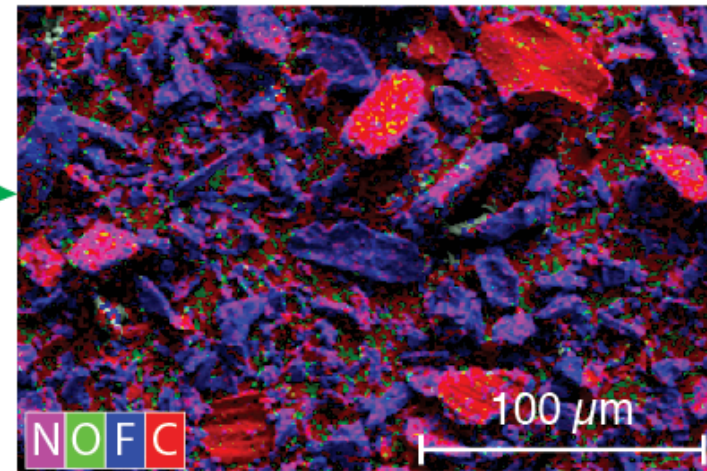


“Sub-fluorinated $(CF)_n$ ”

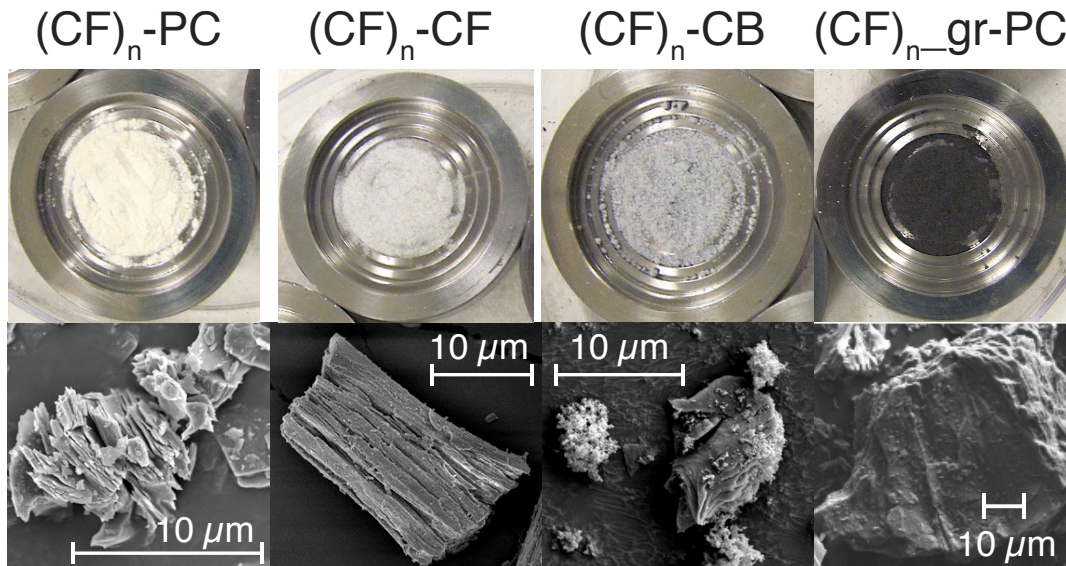
Graphitic carbon in the “sub-fluorinated” $(\text{CF})_n$ samples



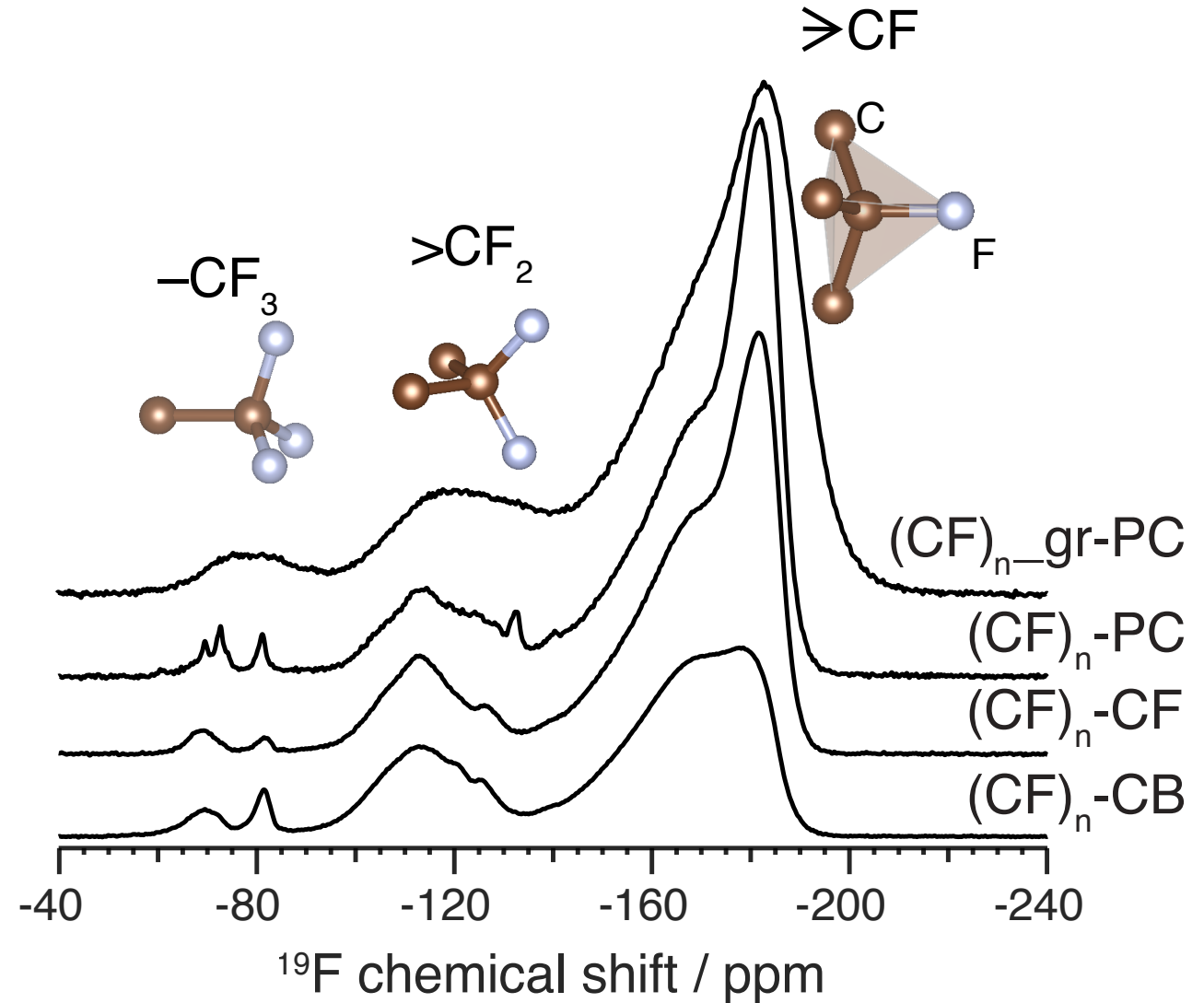
XRD courtesy of Dr. Noah B. Schorr



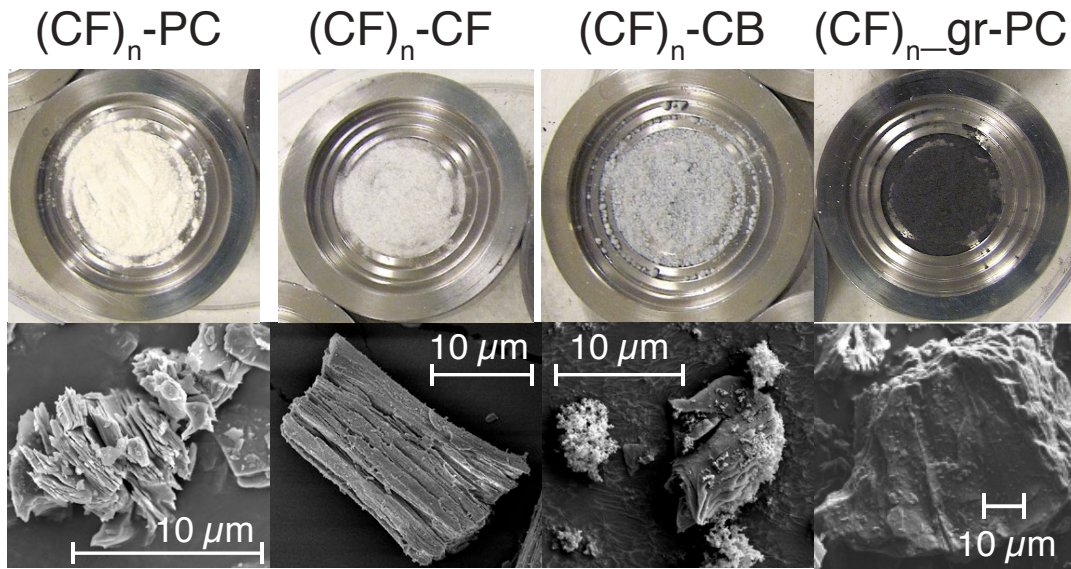
What causes the grayness of some of the “fully fluorinated” samples?



- Uniform particle morphology
- Essential features are the same
- $(\text{CF})_n\text{-gr-PC}$ is much broader

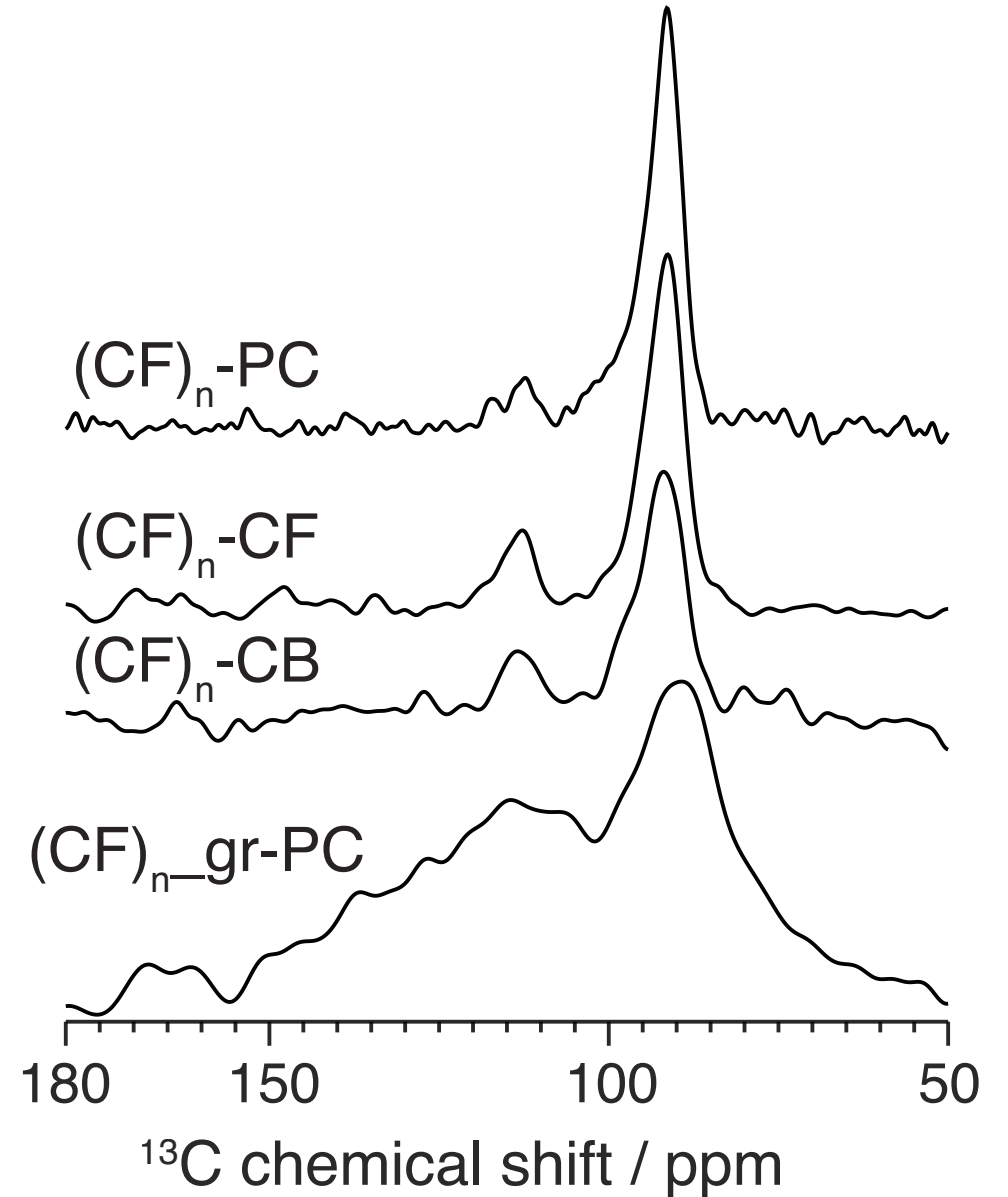


Quantitative ^{13}C MAS NMR

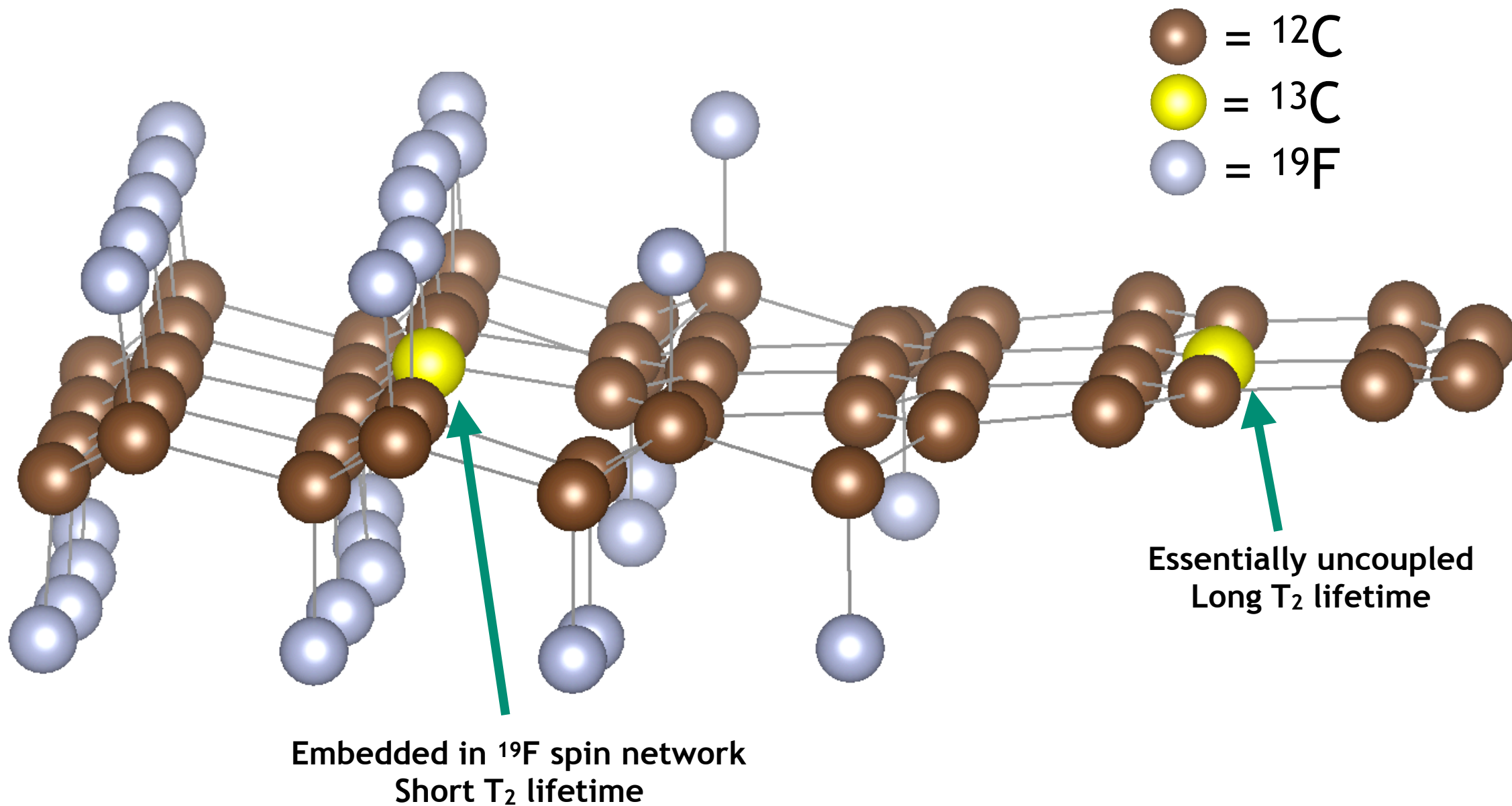


Except for $(\text{CF})_n\text{-gr-PC}$ only fluorinated ^{13}C
NMR signals can be discerned.

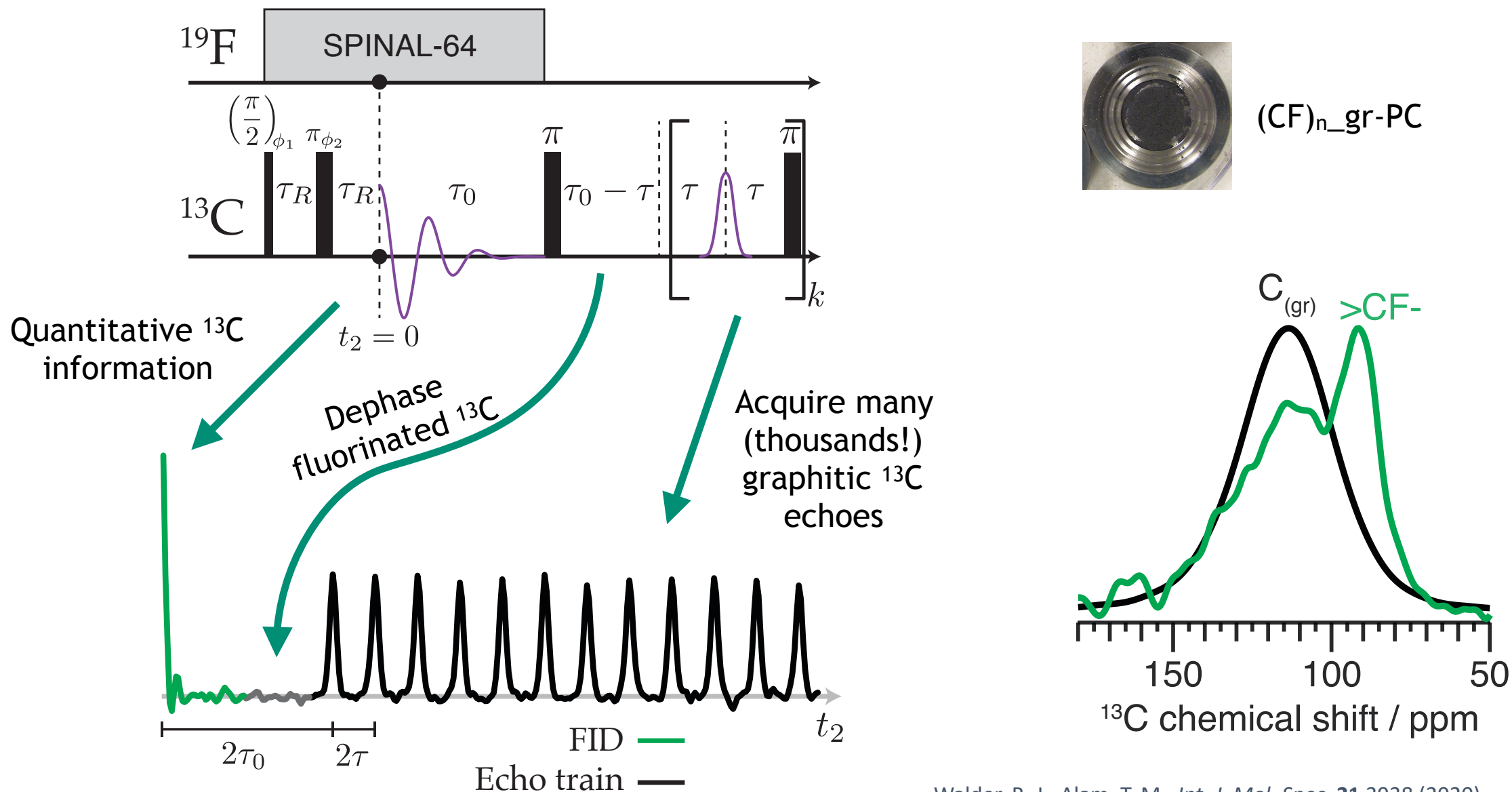
Can we do anything about this?



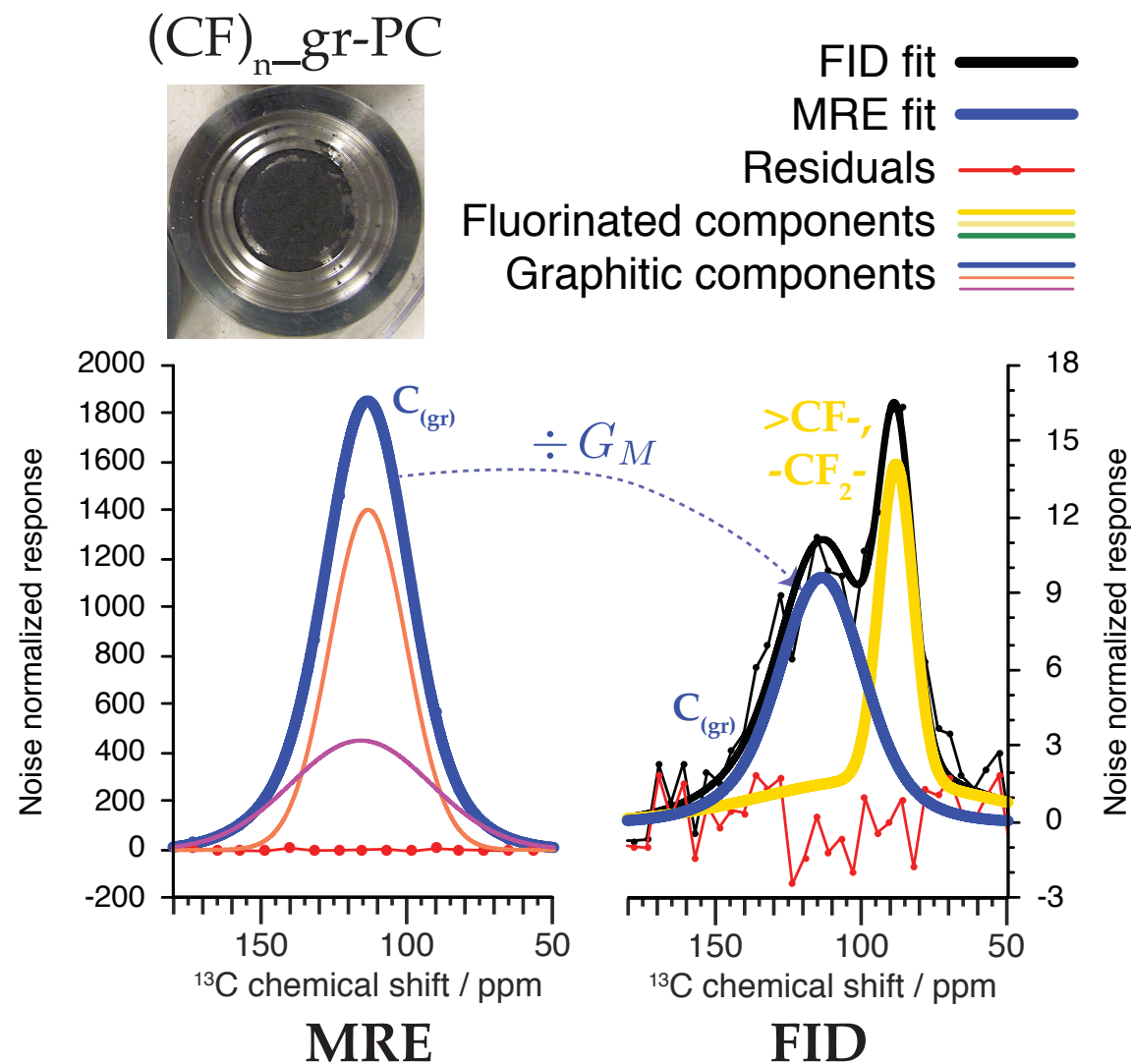
Nuclear spin densities: fluorinated vs. graphitic domains



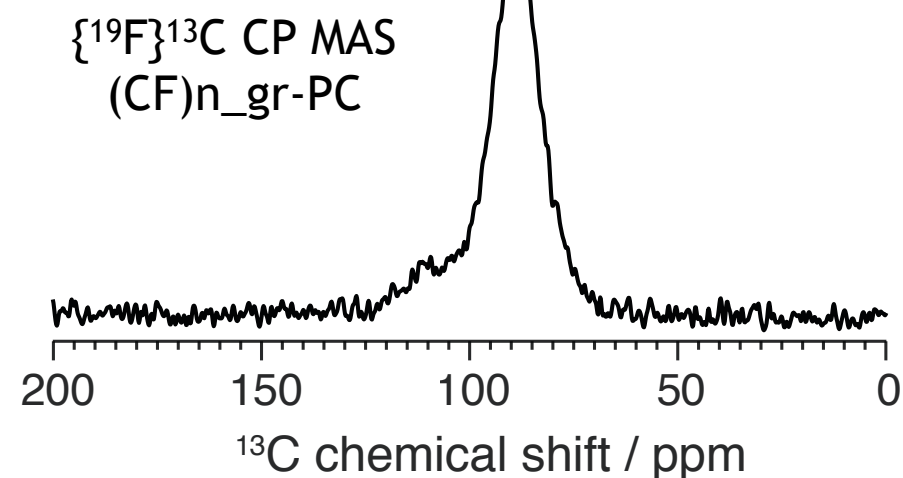
Uncoupled ^{13}C NMR signal enhancement using CPMG



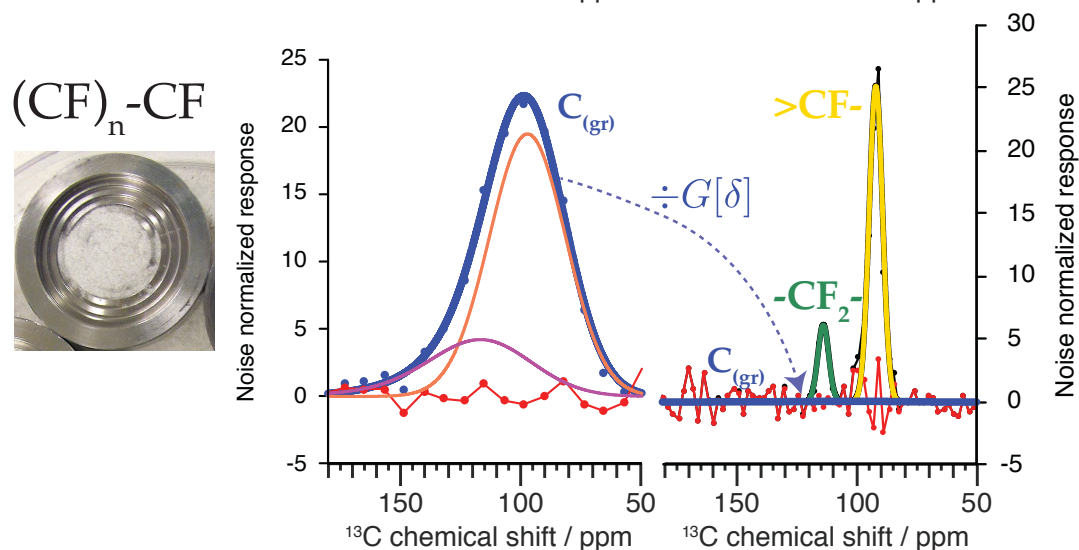
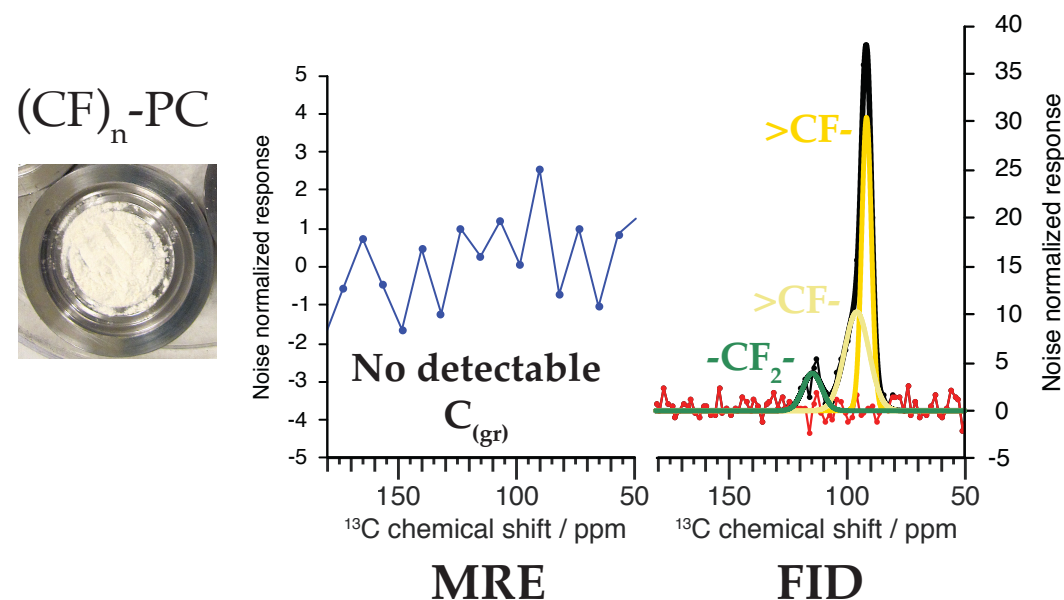
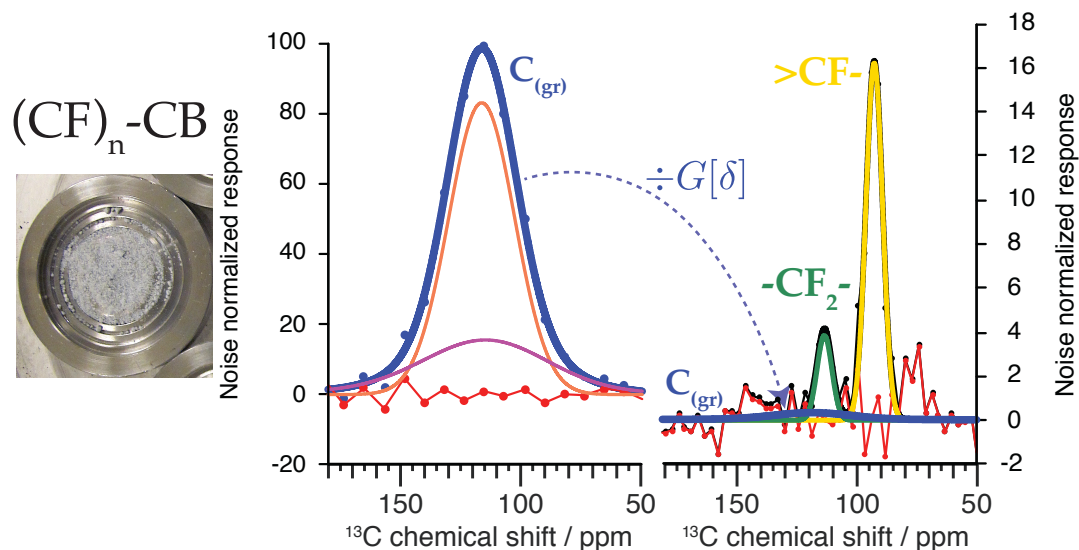
The gain by CPMG can be calculated



- Mapping of enhanced graphitic ^{13}C NMR signals onto FID with calculated gain factor is excellent
- Simultaneous constrained fit of MRE and FID
- Remaining signal (fluorinated components) an excellent match to CP MAS spectrum

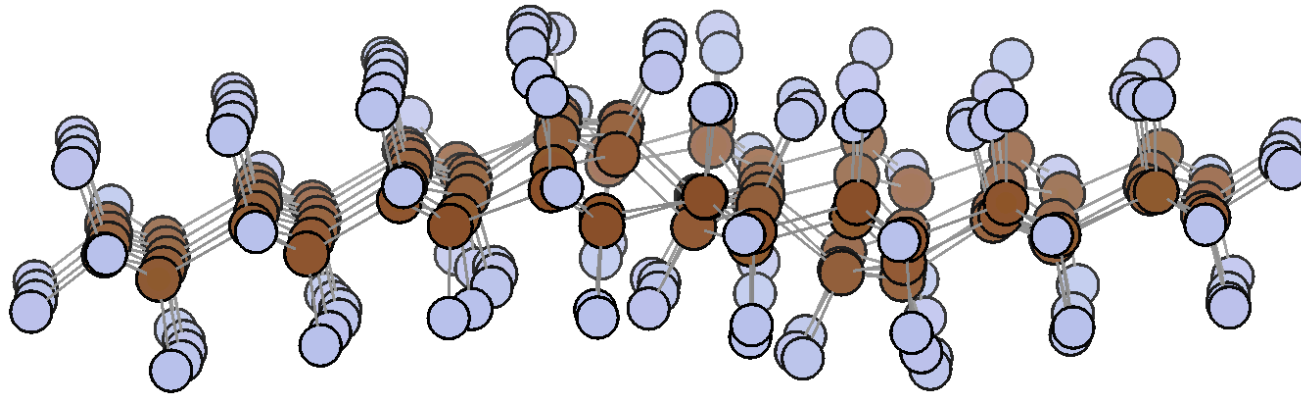


Quantification of graphitic carbon in “fully fluorinated” samples

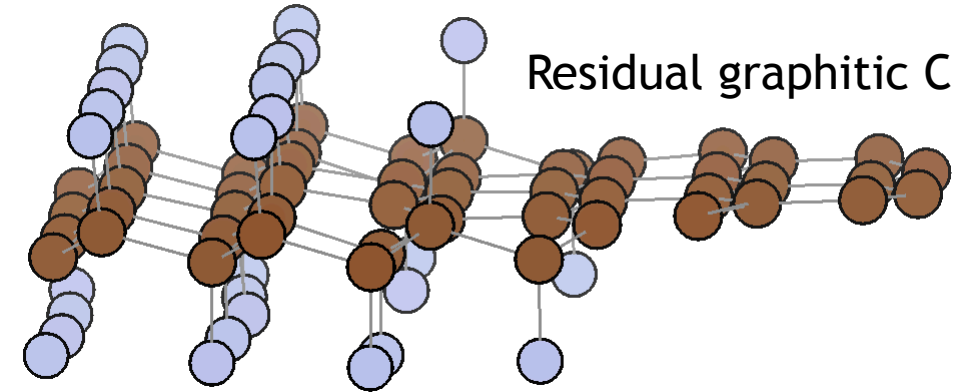


Sample	$x_{\text{gr}} / \text{mol}\%$
$(\text{CF})_{n_gr}\text{-PC}$	45.7 ± 2.7
$(\text{CF})_n\text{-CB}$	4.09 ± 0.40
$(\text{CF})_n\text{-CF}$	0.72 ± 0.43
$(\text{CF})_n\text{-PC}$	< 0.05

Many modes of disorder!

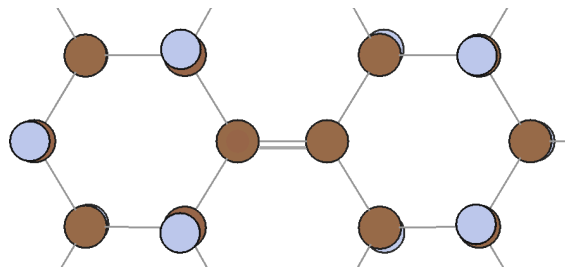


Sub-ordered cores

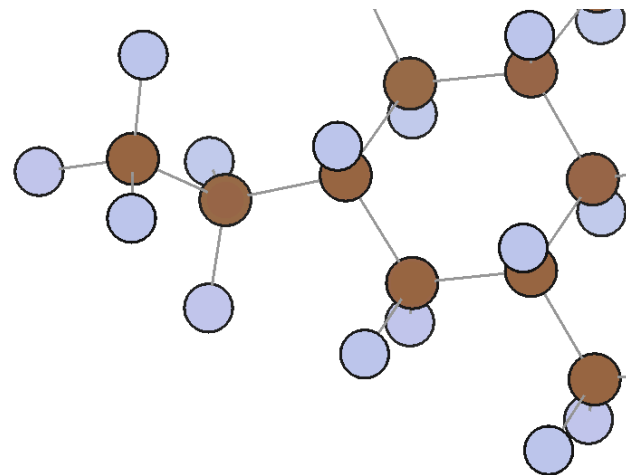


Residual graphitic C

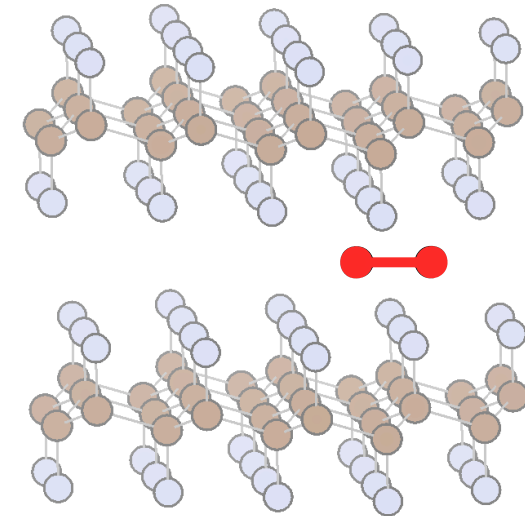
Fluorine-deficient point defects



Fluorine-rich mobile regions

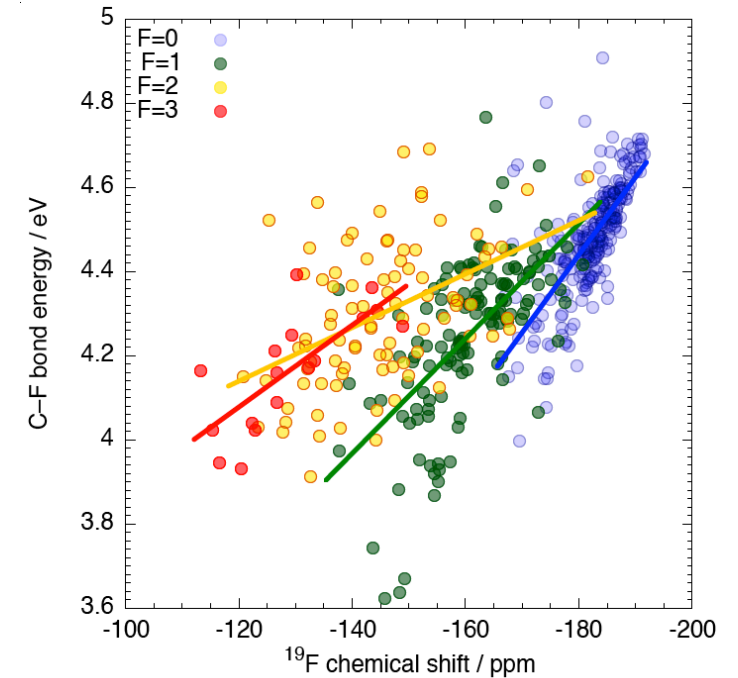
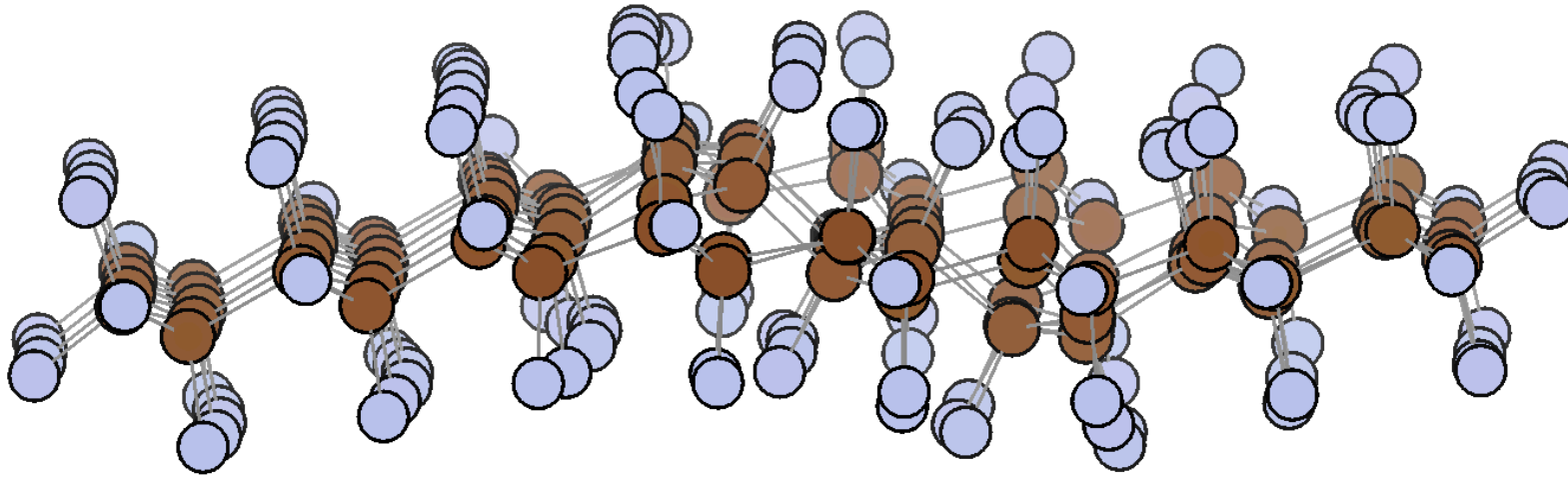


Intercalated O₂



(+ narrow line radicals...Giraudet J., et al. *J. Phys. Chem. Solids* **67** 1100-1105 (2006))

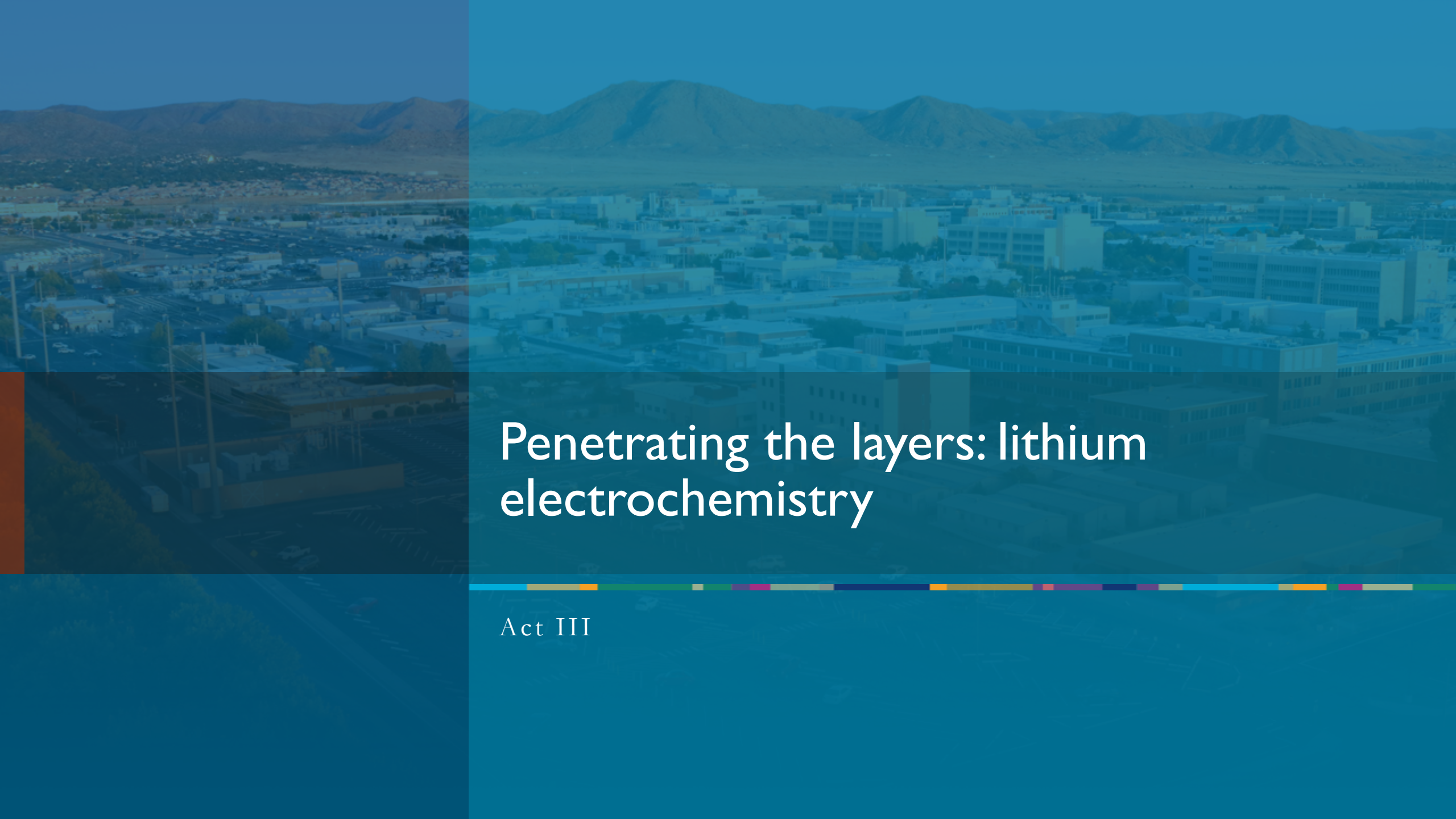
So why not 4.6 V?



- A. Kinetic limitation: insufficiently rapid lithium and LiF diffusion
- B. Intermediate phase: Ternary phase, “CLi_xF”
- C. Solvent participation in electrochemistry
- ~~D. Structural property effectively increasing C-F bond dissociation energies?~~

Conformational disorder → weaker C-F bonds → even HIGHER cell voltage

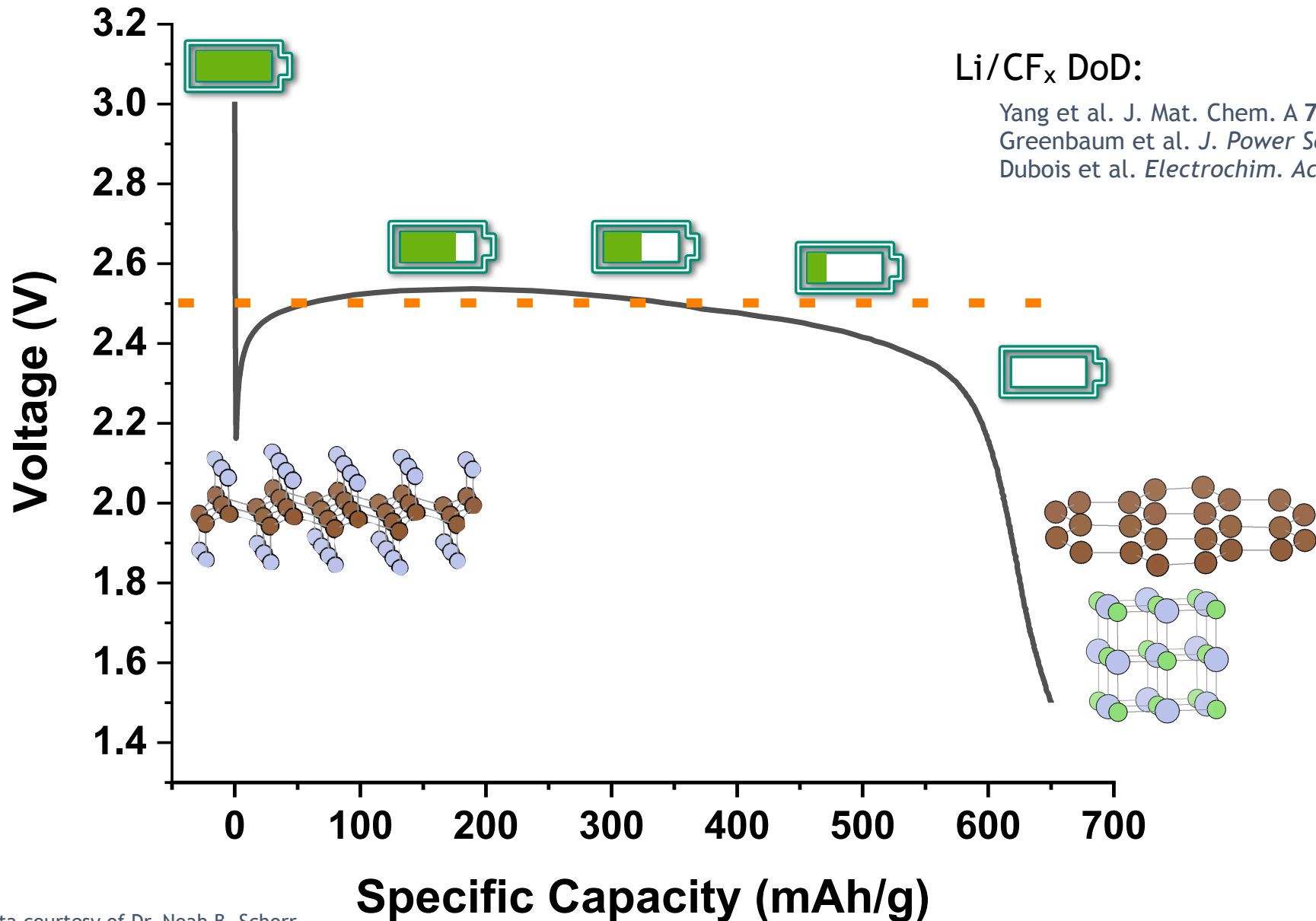
BUT have discovered new spectroscopic handles for delivering a molecular-level understanding of A, B, C



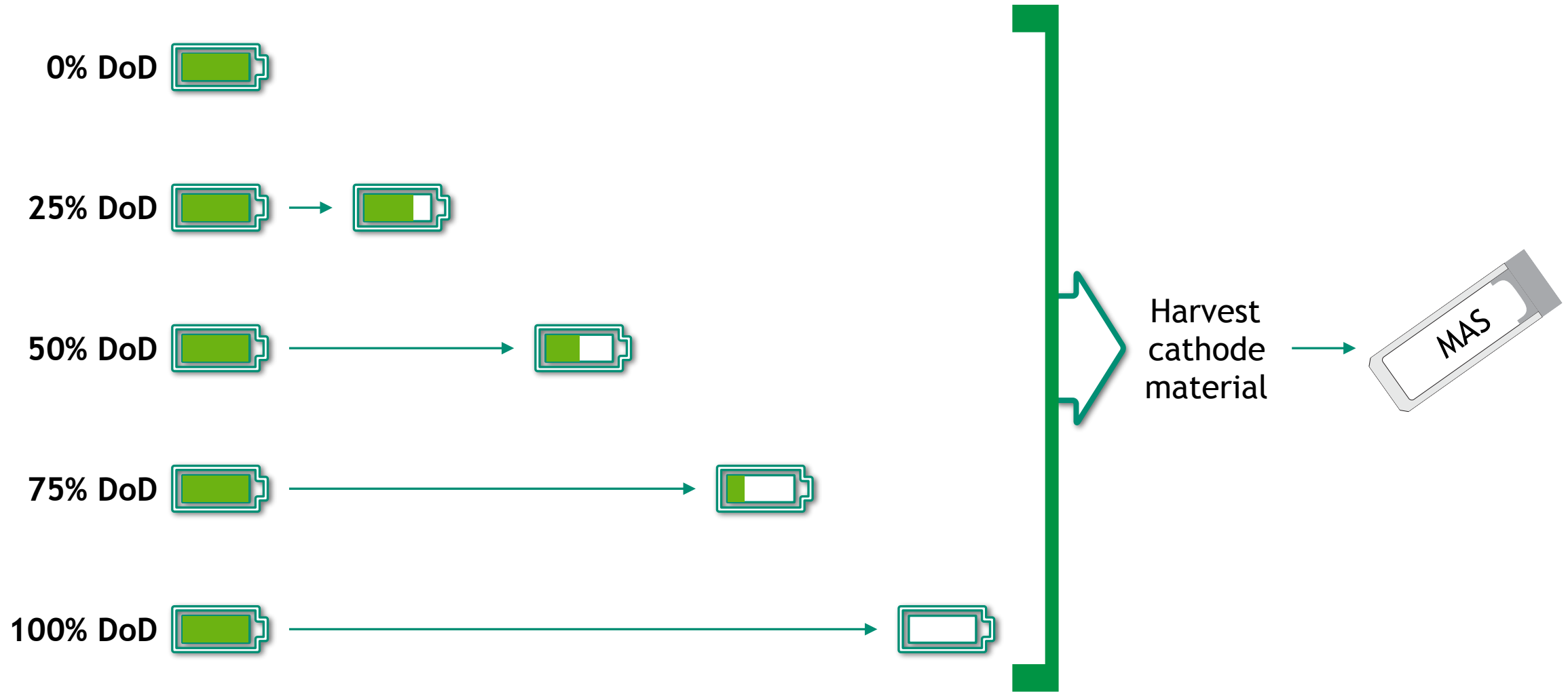
Penetrating the layers: lithium electrochemistry

Act III

Ex situ depth of discharge (DoD) profiling



Ex situ depth of discharge (DoD) profiling



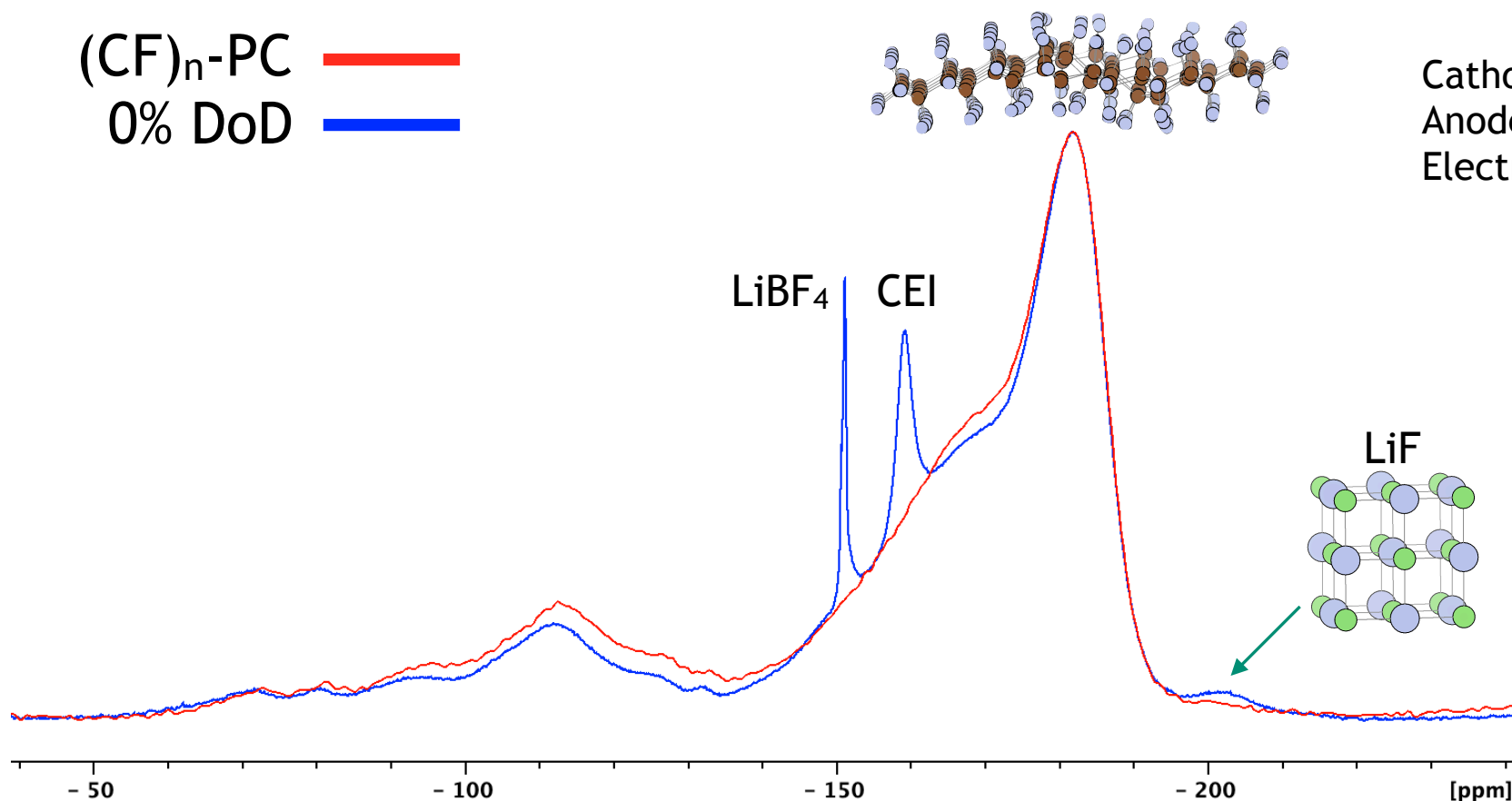
Ex situ ^{19}F MAS NMR, $\text{Li}/(\text{CF})_n$ cells: Pristine versus 0% DoD

$(\text{CF})_n\text{-PC}$ — (red line)
0% DoD — (blue line)

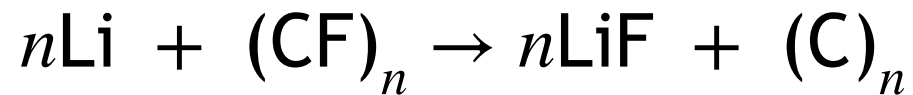
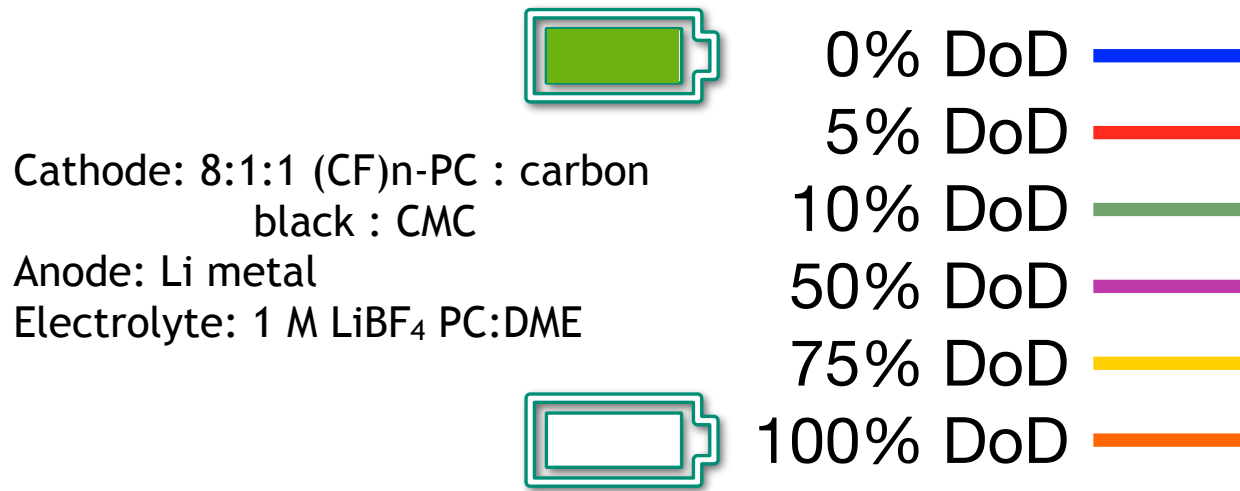
0% DoD



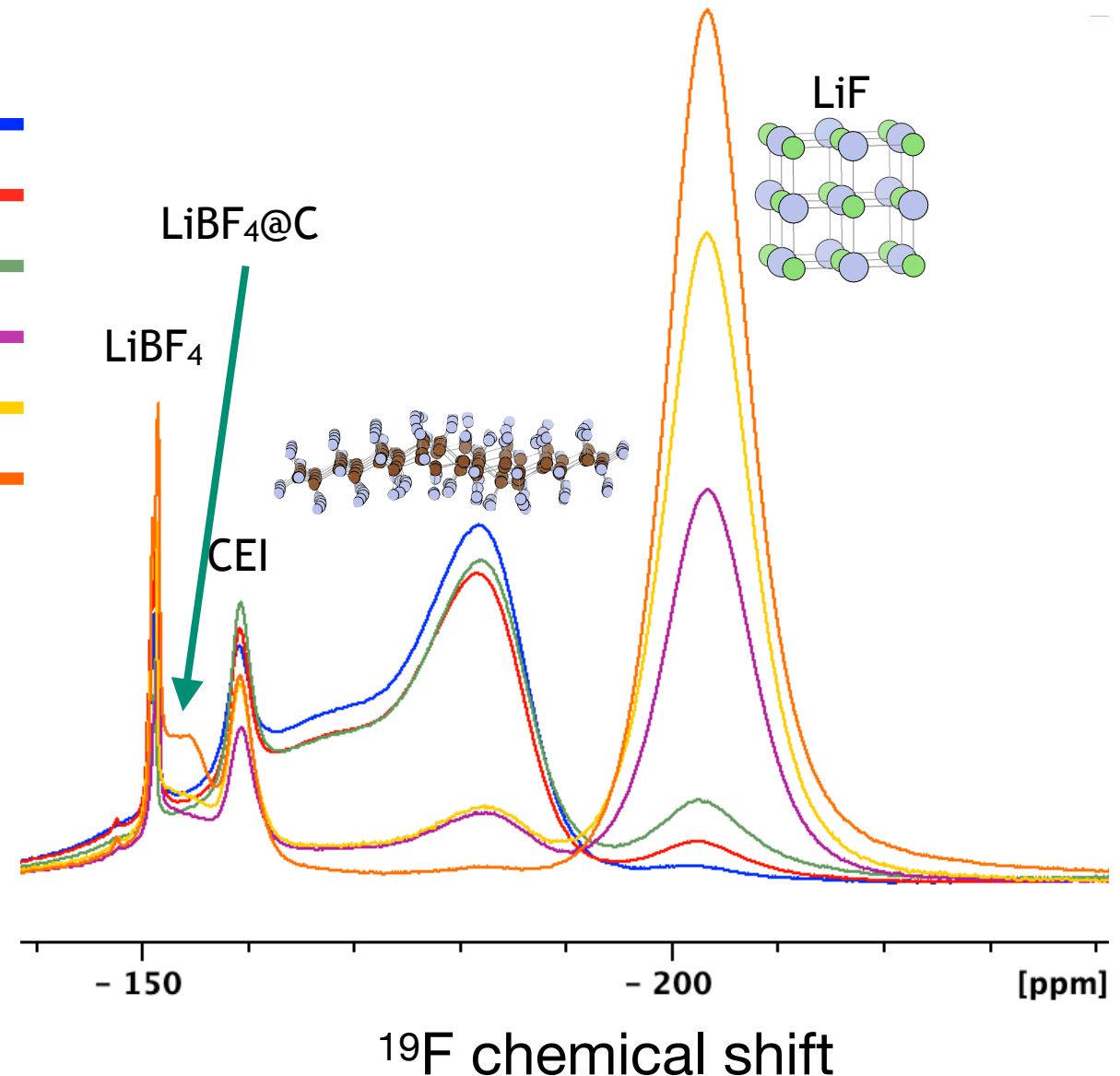
Cathode: 8:1:1 $(\text{CF})_n\text{-PC}$: carbon black : CMC
Anode: Li metal
Electrolyte: 1 M LiBF_4 PC:DME

 ^{19}F chemical shift

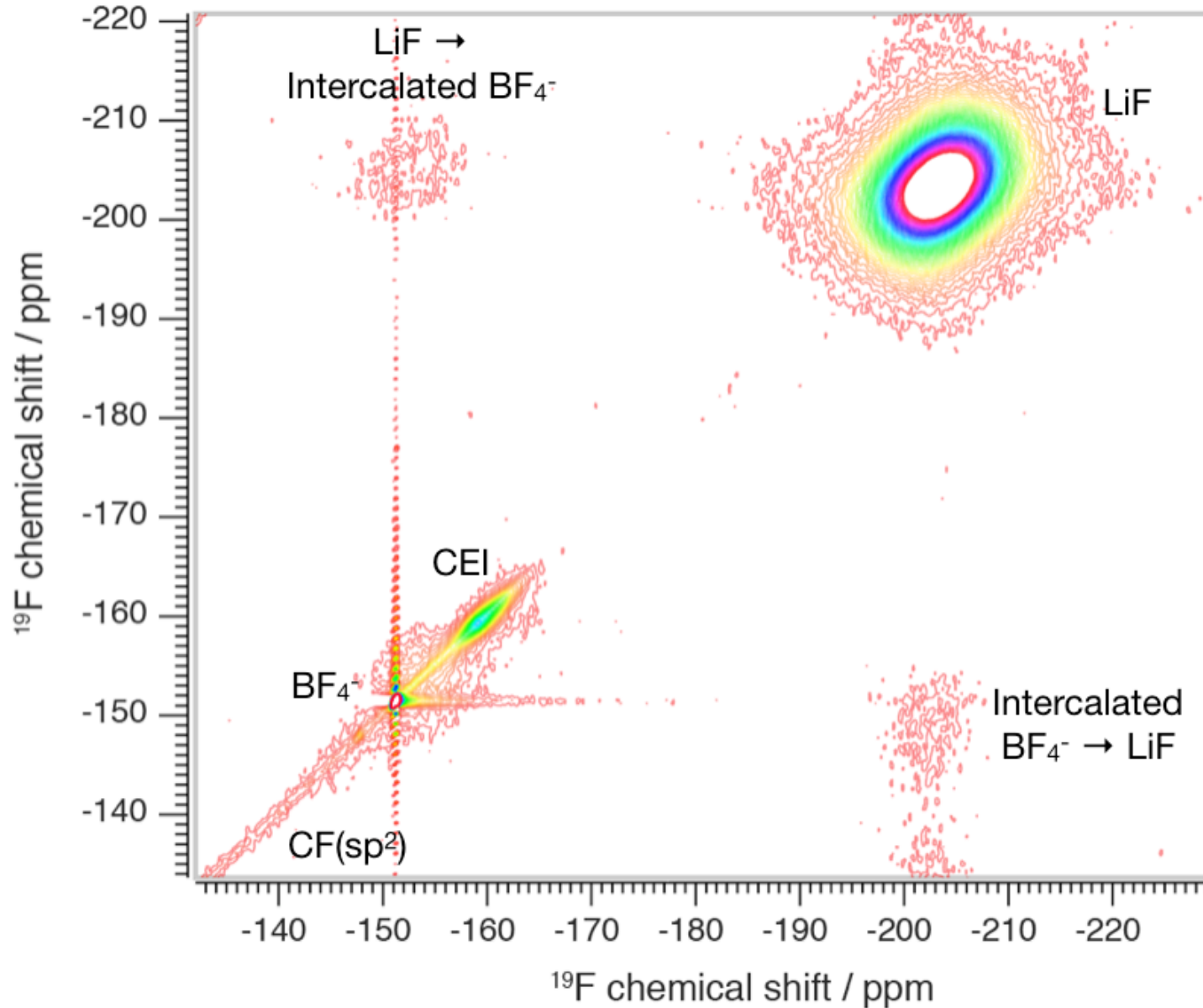
Ex situ ^{19}F MAS NMR, Li/(CF)_n cells: DoD series



- Logical progression of (CF)_n, LiF intensities
- CEI appears electrochemically inert
- Graphite intercalated LiBF₄ grows with DoD



Ex situ $\{^{19}\text{F}\}^{19}\text{F}$ MAS EXSY, Li/(CF)_n cells: LiF exchange observed

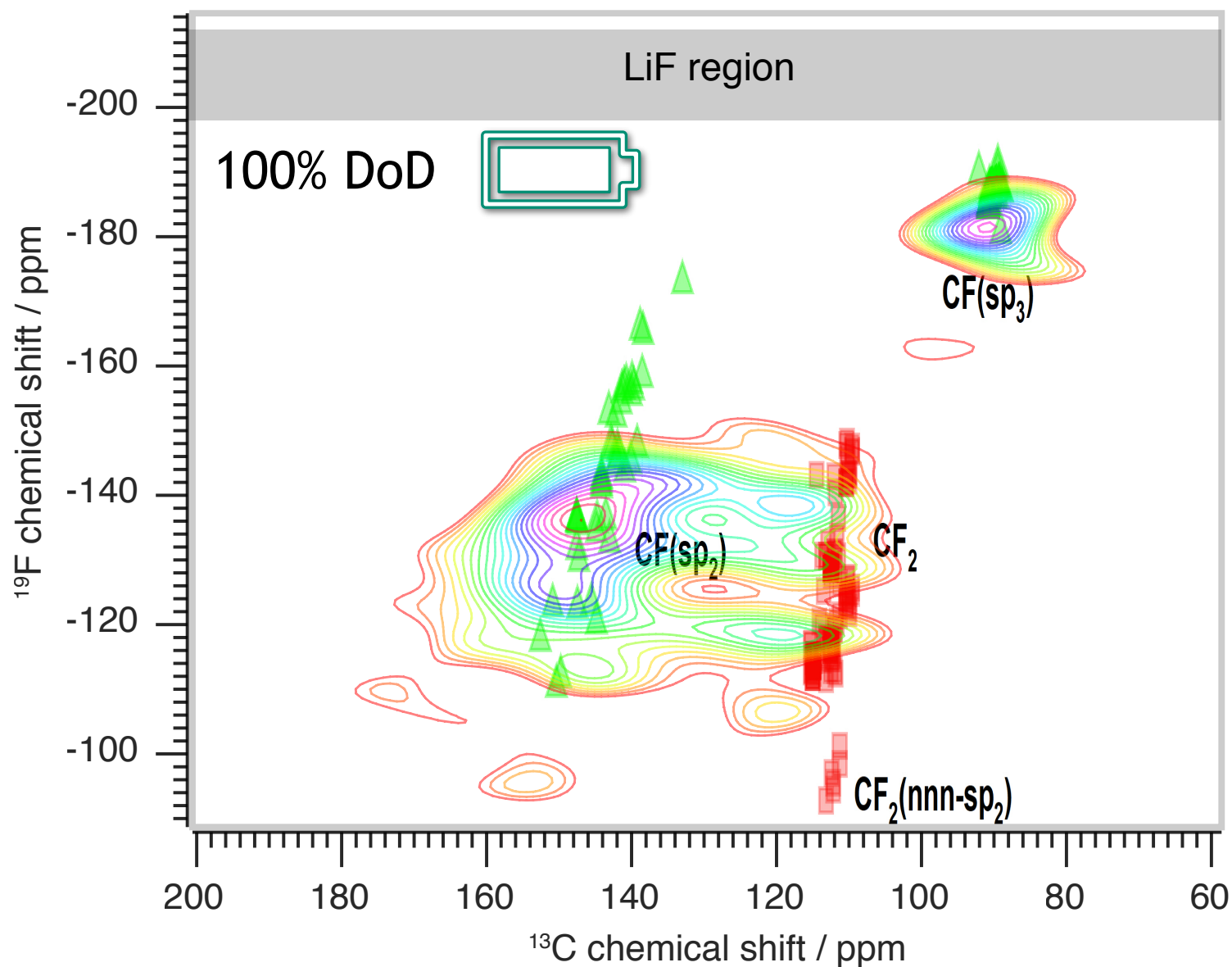


100% DoD

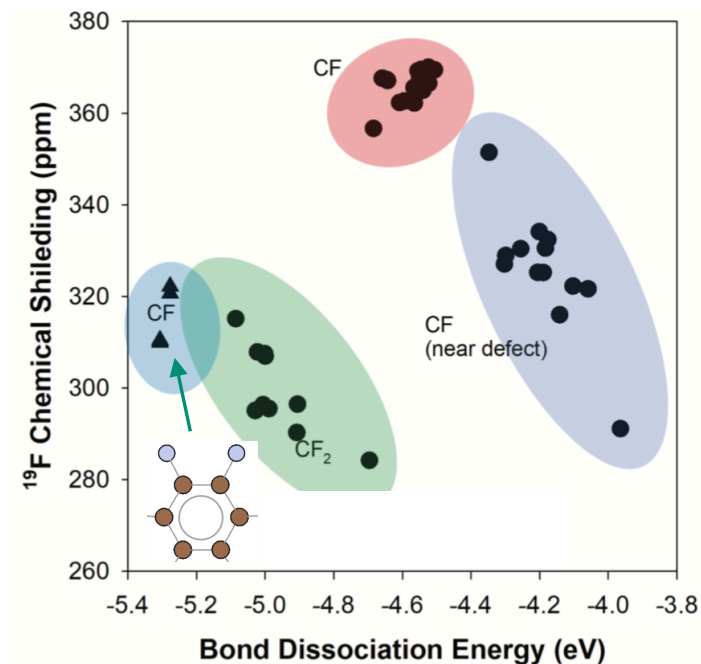


$$\tau_z = 40 \text{ ms}$$

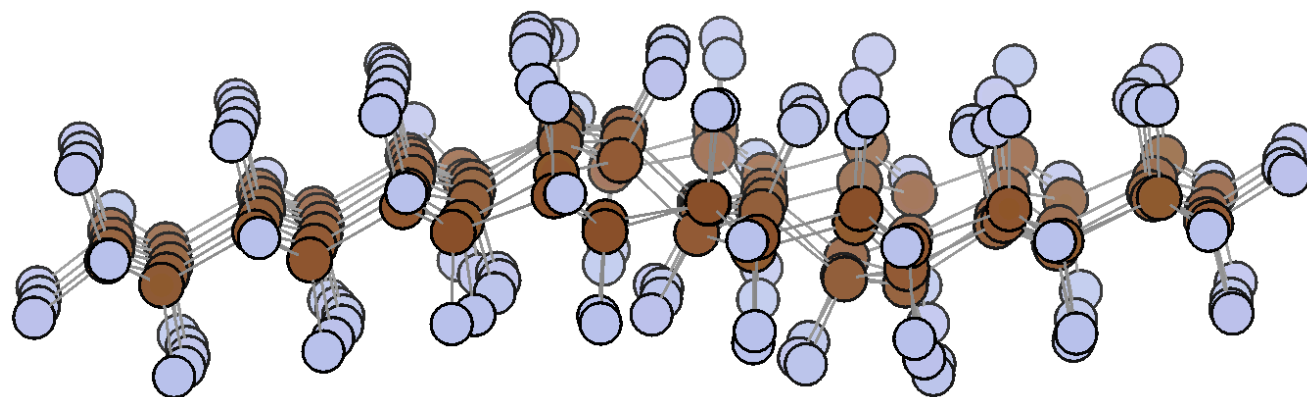
Electrochemically inactive groups



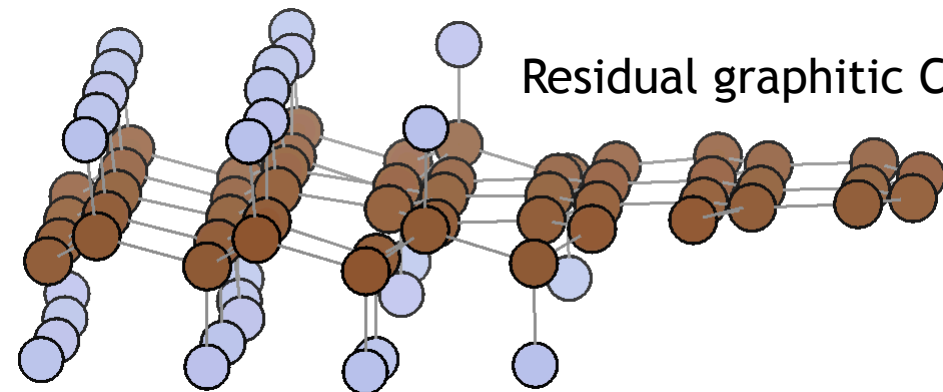
- $\{^{19}\text{F}\}^{13}\text{C}$ CP-HECTOR CPMG
- Short contact time (0.2 ms)
- Natural abundance ^{13}C , 33 $\frac{1}{3}$ kHz (so...)
- Observe “dead” (CF)_n
- sp² carbon-adjacent >C-F groups
- Likely edge located (energetics)



Many modes of disorder!

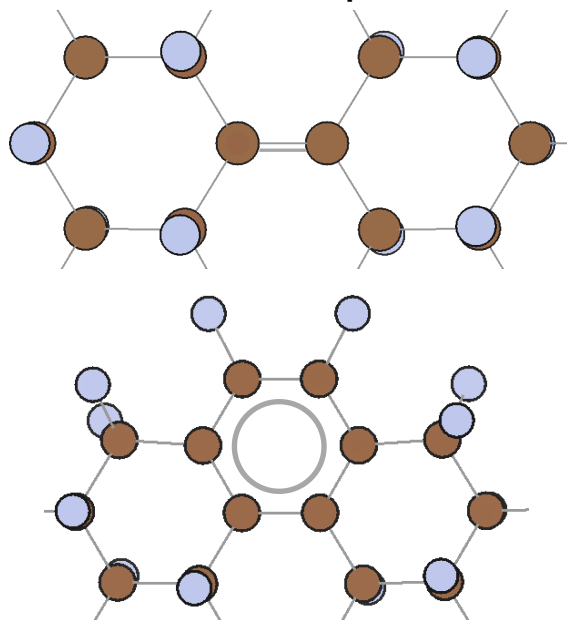


Sub-ordered cores

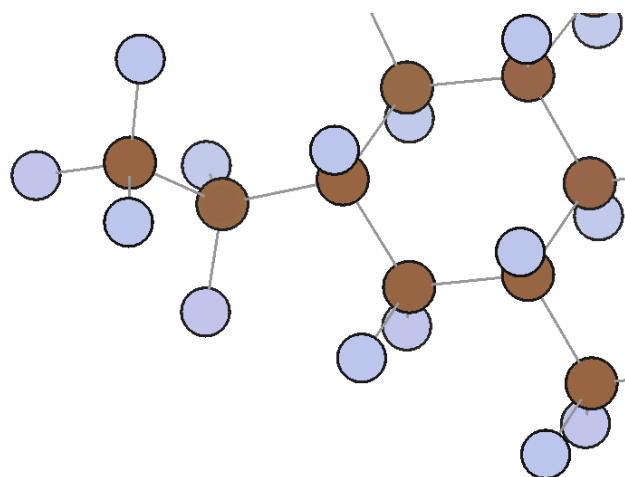


Residual graphitic C

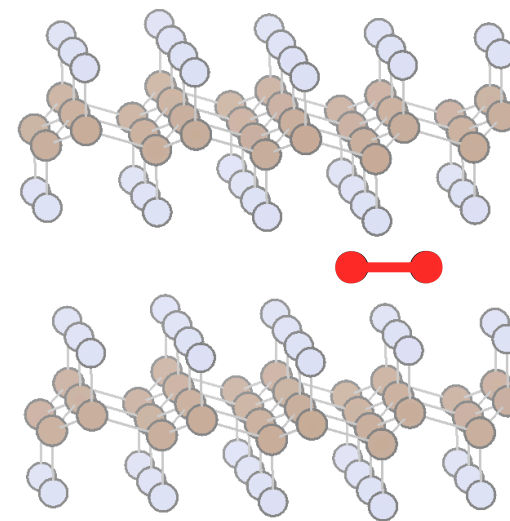
Fluorine-deficient point defects



Fluorine-rich mobile regions

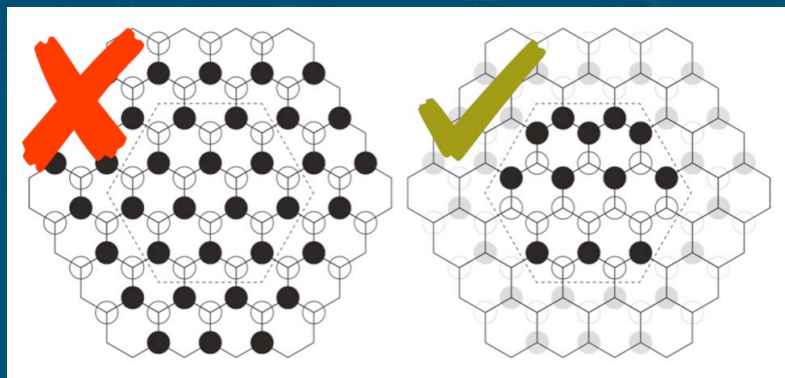
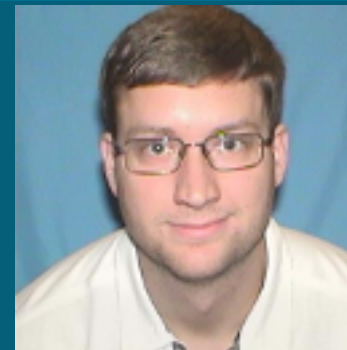


Intercalated O₂



(+ narrow line radicals...Giraudet J., et al. *J. Phys. Chem. Solids* **67** 1100-1105 (2006))

Penetrating the layers: $(\text{CF})_n$ and lithium electrochemistry



Contributors:

- Dr. Todd M. Alam
- Dr. Jessica M. Rimsza
- Dr. Katharine L. Harrison
- Dr. Noah B. Schorr
- Dr. Kevin Leung

PRESENTED BY

Dr. Brennan J. Walder

Fall 2020 NMR² virtual meeting

October 30, 2020