The Materials Genome …

… and the example of polymer dielectrics design

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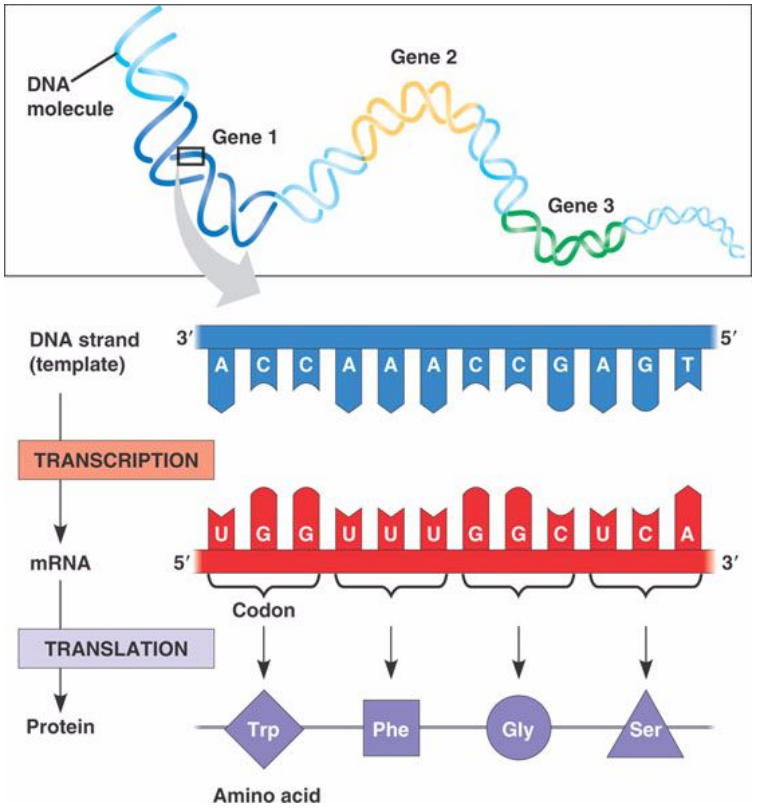
The "Original" Genome

"The molecular logic of the living state"

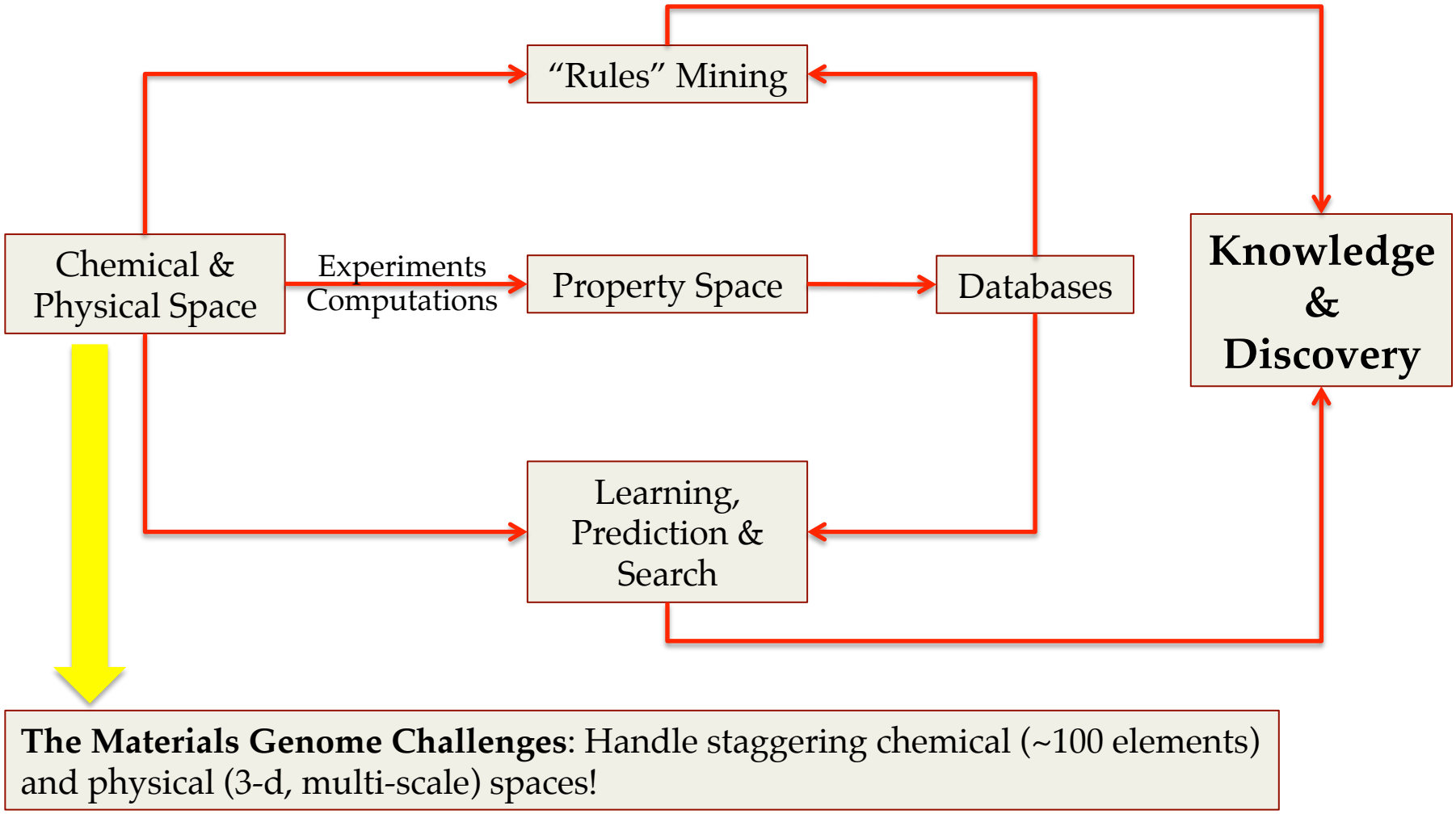


The Genetic Code

First Letter	Second Letter: U	C	A	G	Third Letter
U	Phenylalanine	Serine	Tyrosine	Cysteine	U
	Phenylalanine	Serine	Tyrosine	Cysteine	C
	Leucine	Serine	Stop	Stop	A
	Leucine	Serine	Stop	Tryptophan	G
C	Leucine	Proline	Histidine	Arginine	U
	Leucine	Proline	Histidine	Arginine	C
	Leucine	Proline	Glutamine	Arginine	A
	Leucine	Proline	Glutamine	Arginine	G
A	Isoleucine	Threonine	Asparagine	Serine	U
	Isoleucine	Threonine	Asparagine	Serine	C
	Isoleucine	Threonine	Lysine	Arginine	A
	Start Methionine	Threonine	Lysine	Arginine	G
G	Valine	Alanine	Aspartic acid	Glycine	U
	Valine	Alanine	Aspartic acid	Glycine	C
	Valine	Alanine	Aspartic acid	Glycine	A
	Valine	Alanine	Aspartic acid	Glycine	G

<u>Knowledge</u>: Structure ⇔ Function Relationship

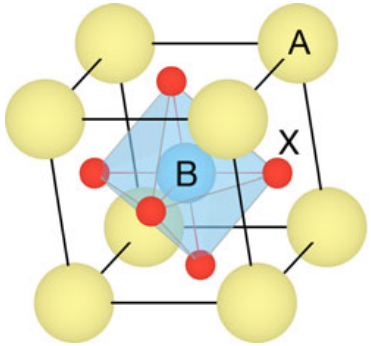
A Framework For Learning

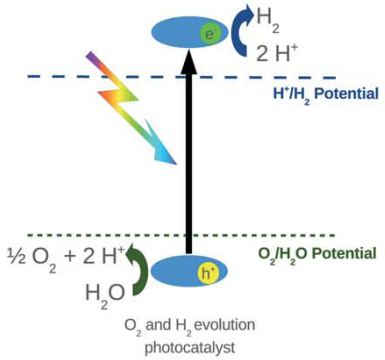


The Materials Genome Challenges: Handle staggering chemical (~100 elements) and physical (3-d, multi-scale) spaces!

The ABX_3 Genome

Castelli, et al, Energy Environ. Sci. 5, 5814 (2012); Energy Environ. Sci. 5, 9034 (2012).



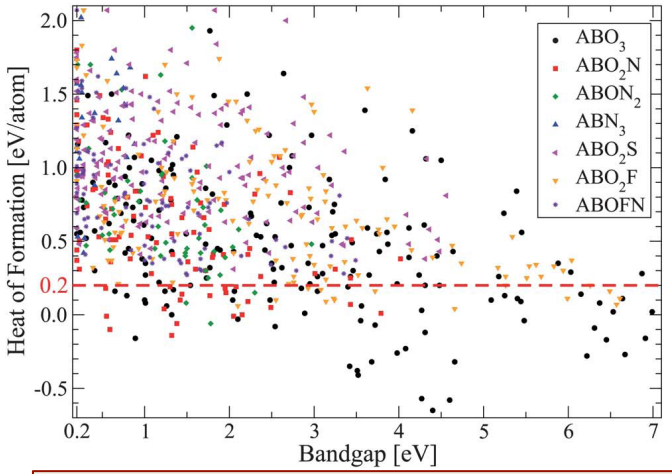


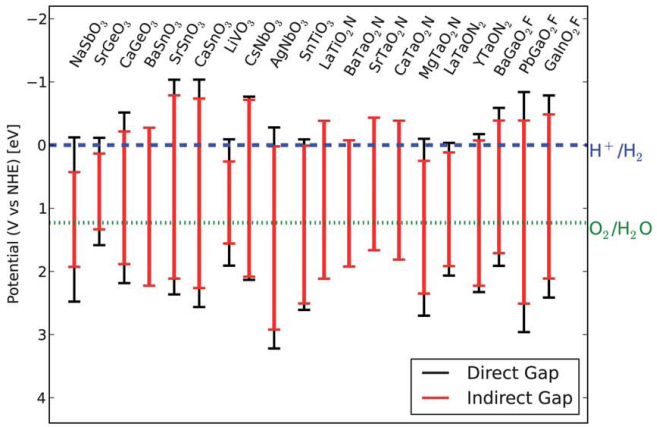
Screening parameters	One-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.5 \leq E_{gap} \leq 3$ eV
Band edges	$VB_{edge} > 1.23$ eV
(VB_{edge}, CB_{edge})	$CB_{edge} < 0$ eV

A, B : 52 metals

X_3 : O_3, O_2N, ON_2, N_3, O_2S, O_2F, OFN

~ 19,000 possibilities





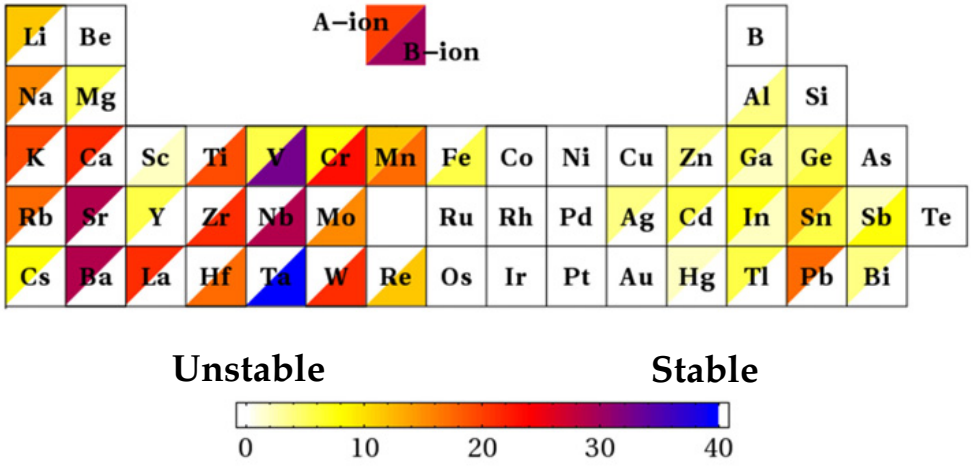
20 Candidates identified (out of ~19,000 cases)

Mining, Learning & Searching

Castelli, et al, Modelling Simul. Mater. Sci. Eg. 22 (2014); Jain, et al, J. Mater. Sci. 48 (2013).

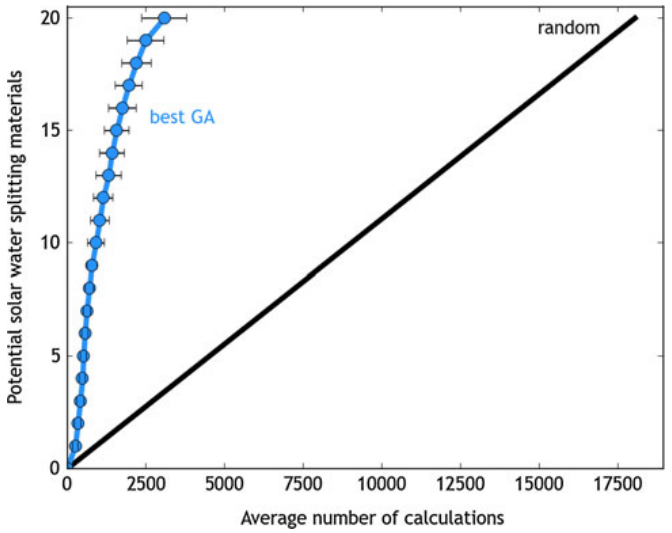
Rules for stable ABO_3 insulators:

1. Even number of electrons per unit cell
2. Sum of oxidation states zero
3. A-site element larger than B-site element

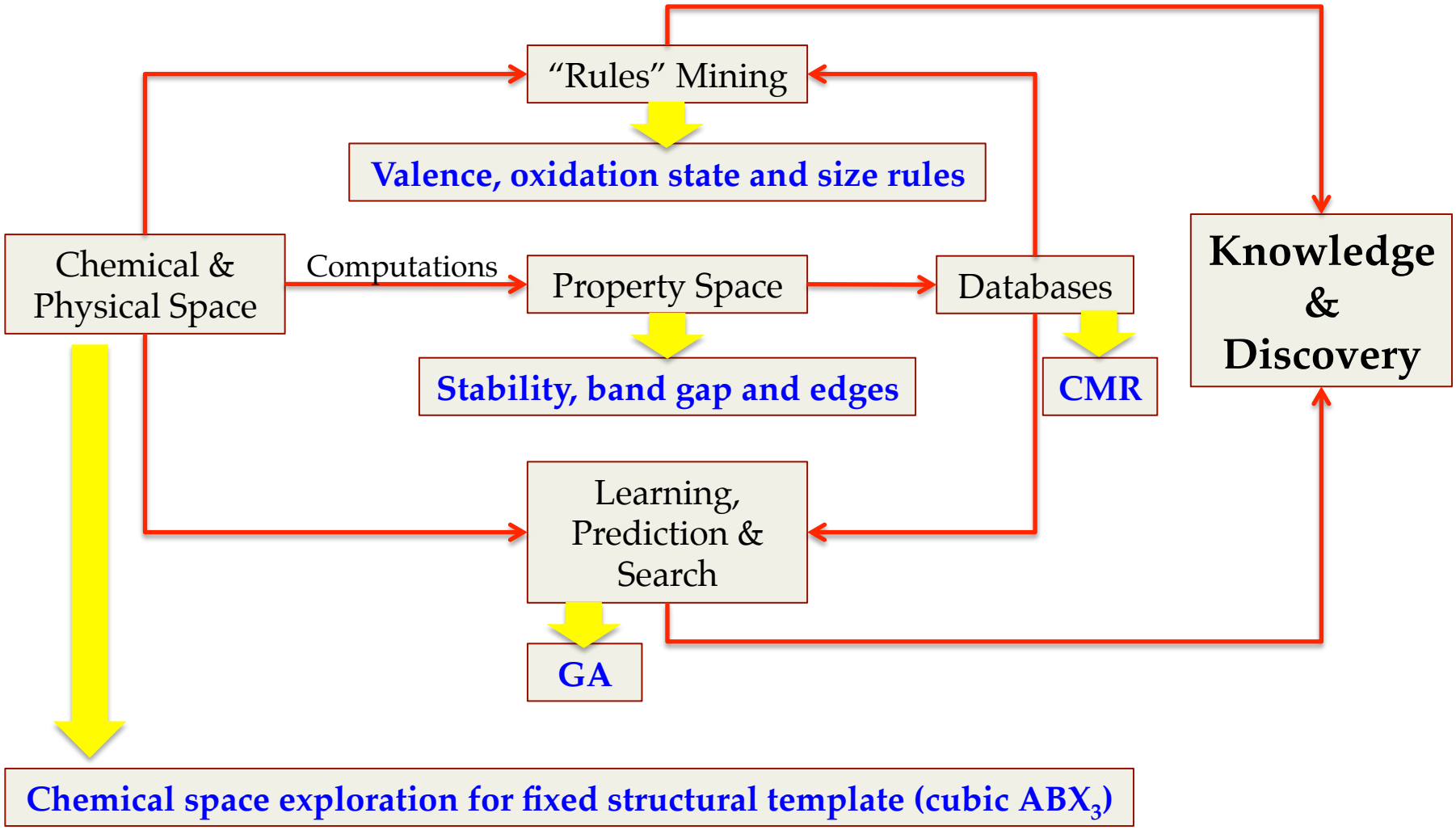


Do we need to do ~ 19,000 DFT calculations to identify 20?!

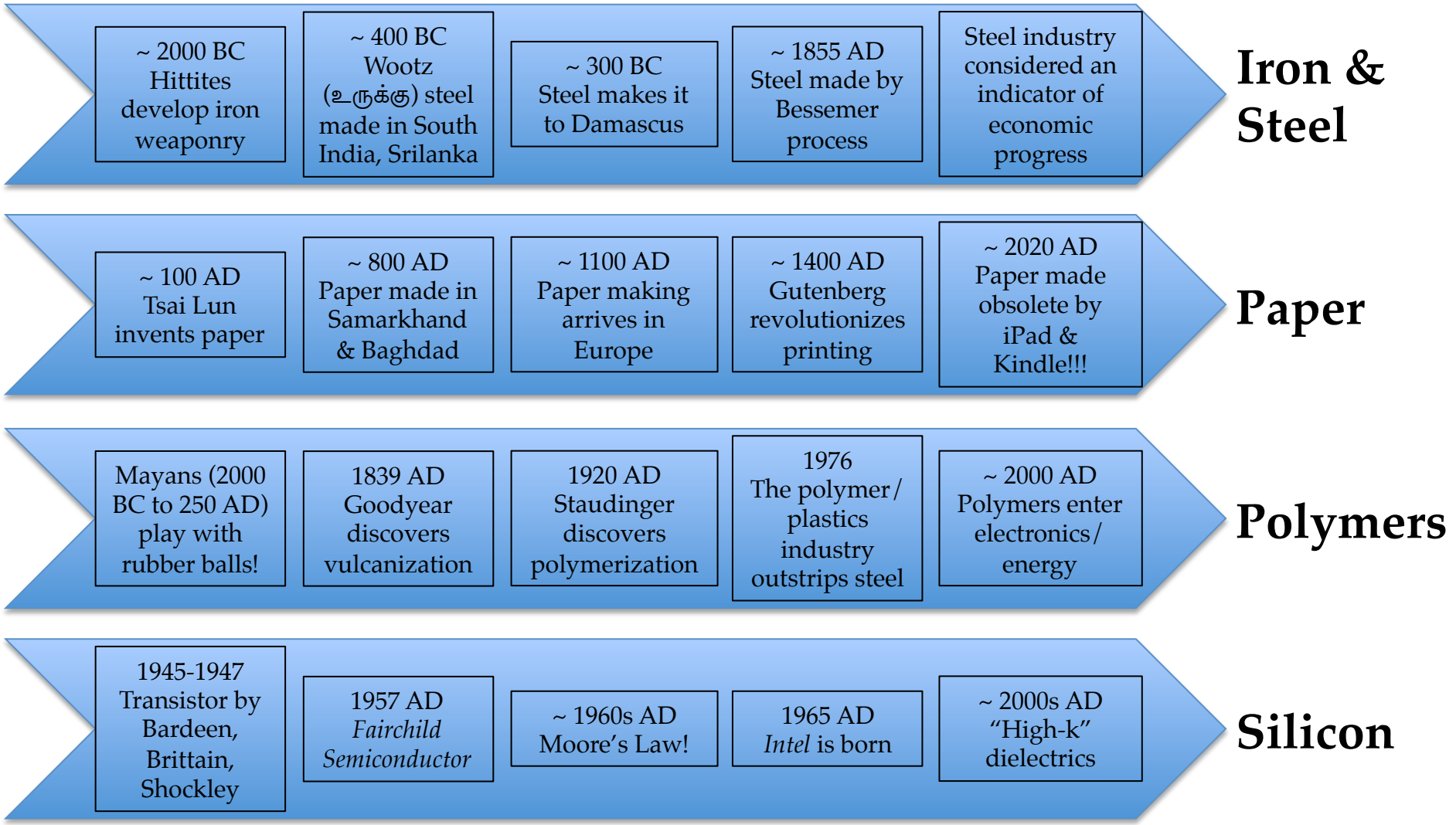
Evolutionary algorithm appears to work



A Framework For Learning



Materials That Rocked The World!



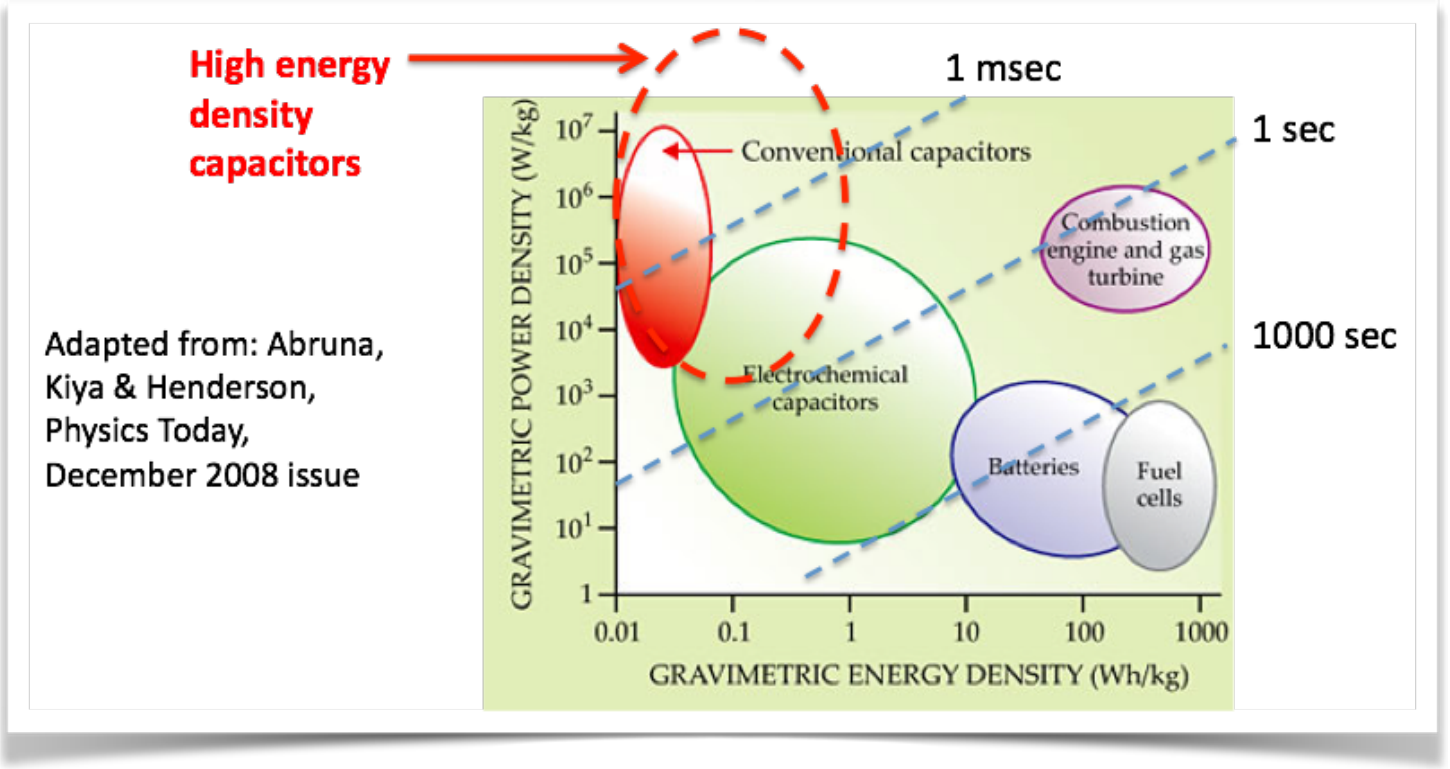
The "Materials" Genome Initiative

- Not just high-throughput computing/experiments (i.e., data generation)
- Not just database creation (i.e., data organization)
- Not just data mining
- All the above …
- … plus synergy between experiment, computation & theory, aimed at accelerated materials discovery

"The Materials Genome Initiative, the interplay of experiment, theory and computation", de Pablo, Jones, Kovacs, Ozolins and Ramirez, Current Opinion in Solid State and Materials Science (2014)

The Polymer Genome

Energy Storage Technologies



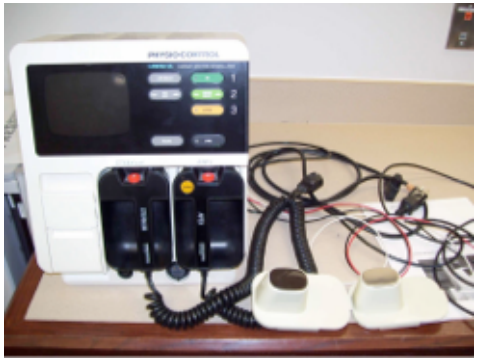
Capacitors are the only option for rapid (dis)charge applications

Maximum energy density ≈ (dielectric constant).(breakdown field)^2

Capacitor Options

- Ceramics (planar & multilayer), but breakdown is catastrophic
- Polymer films
  - Preferred for large area applications
  - Display graceful failure

Toyota Prius Capacitor Bank



Medical Defibrillators

The Current "Standard"

- Biaxially oriented polypropylene (BOPP)
  - Purely hydrocarbon based
  - Large breakdown field (700 MV/m); Low loss (0.0001); Cheap; Easily processable
  - But, low dielectric constant (2.2)
  - Energy density of 5 J/cc

- How to surpass BOPP?

Our "MGI" Effort & Team

- Search the organic & organometallic chemical space …
- … for materials with
  - High dielectric constant
  - High breakdown field (large band gap?)
  - Low loss (large band gap?)
  - High temperature stability
  - Easy processablity

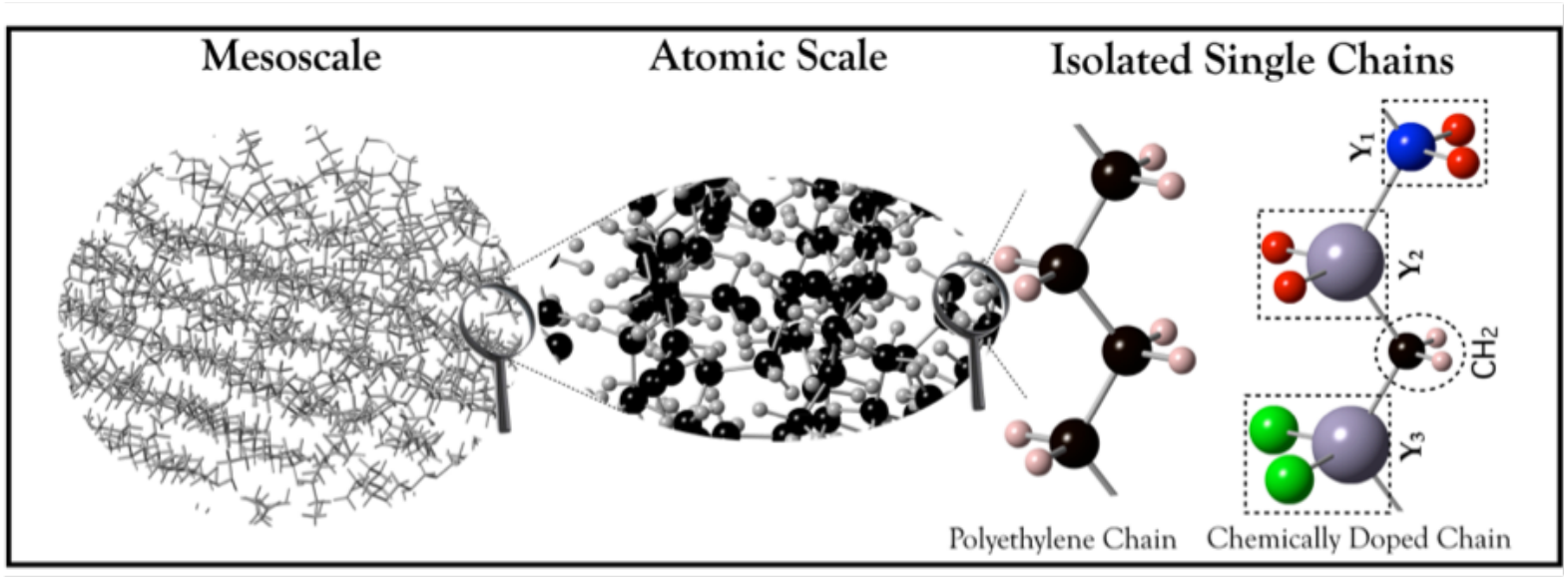
The University of Akron | Columbia University in the City of New York | University of Connecticut | Penn State | Rensselaer

Rational Design of Advanced Polymeric Capacitor Films

www.ims.uconn.edu/MURI

Multidisciplinary University Research Initiative (MURI)

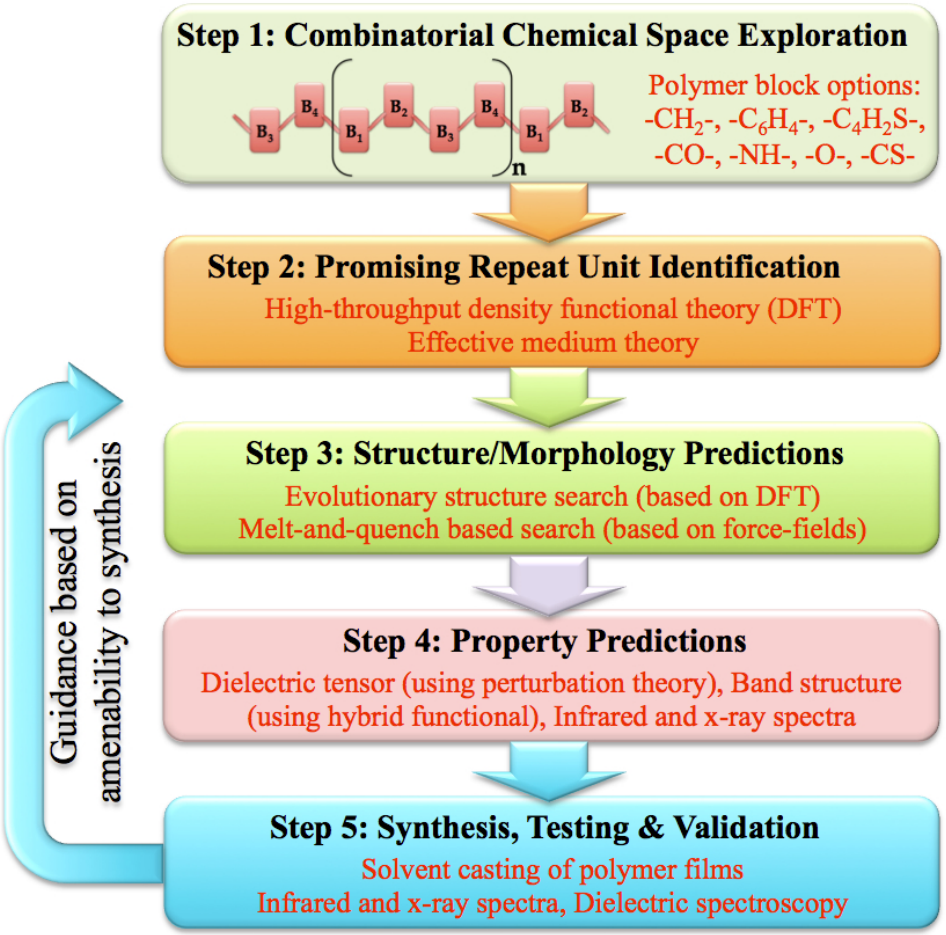
The Length Scale Challenge



DFT computations, effective medium theory, 3-D structure searches (evolutionary algorithms, minima hopping, melt-and-quench, force fields), data mining, machine learning

"Computational Strategies for Polymer Dielectrics Design", Wang, et al, Polymer 55, 979 (2014)

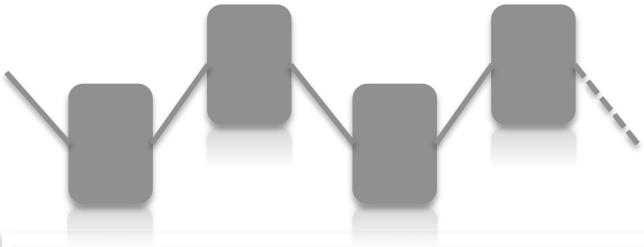
Our Strategy



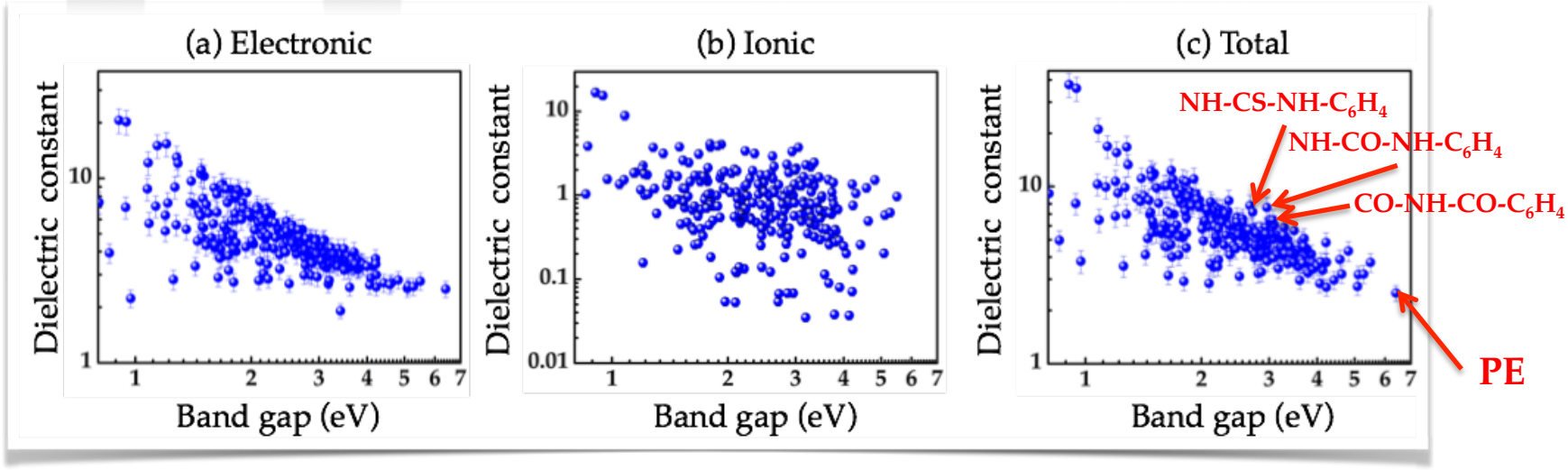
"Rational Design of All-Organic Polymer Dielectrics", Sharma, et al, accepted (Nature Communications)

Organic Polymers

High-throughput density functional theory



Blocks: CH_2, CO, CS, O, NH, C_6H_4, C_4H_2S

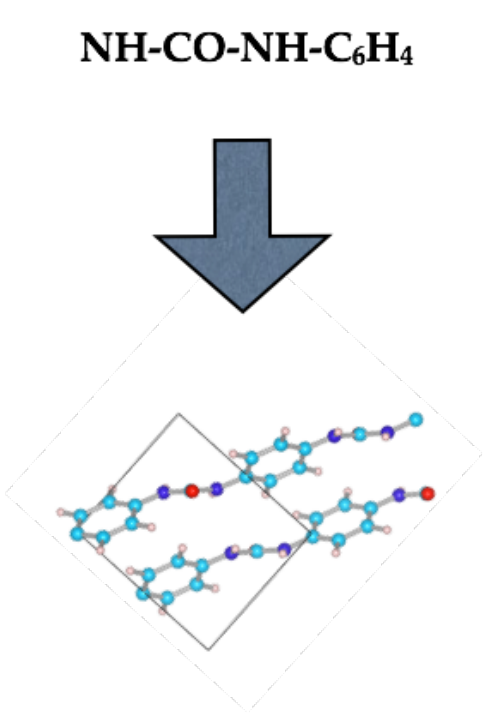


- Electronic part of dielectric constant is strongly related to band gap; but ionic part is not!
- "Sweet spot" dominated by NH, CO or CS, and at least one aromatic group

Pilania, et al, J. Chem. Inf. Model 53, 879 (2013); Wang, et al, Phys. Rev. B 87, 035103 (2013)

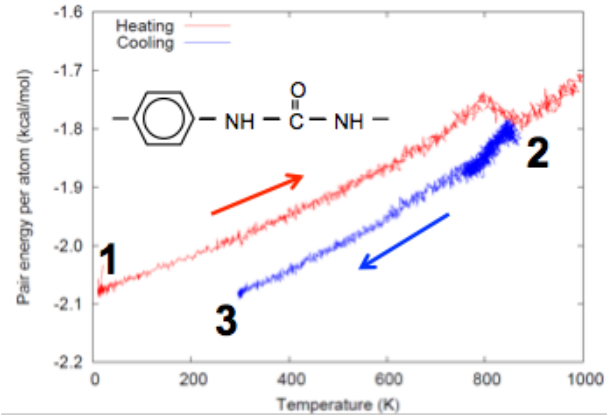
3D Structure Prediction

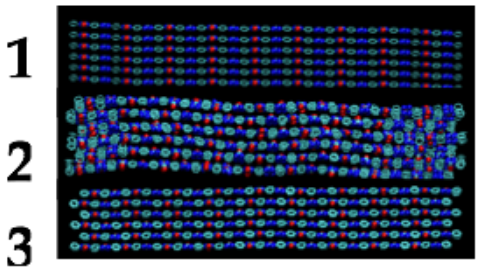
Constrained evolutionary search (based on DFT energies)



Courtesy: Artem Oganov (SUNY, Stony Brook)

Melt-and-quench based search (based on force-fields)





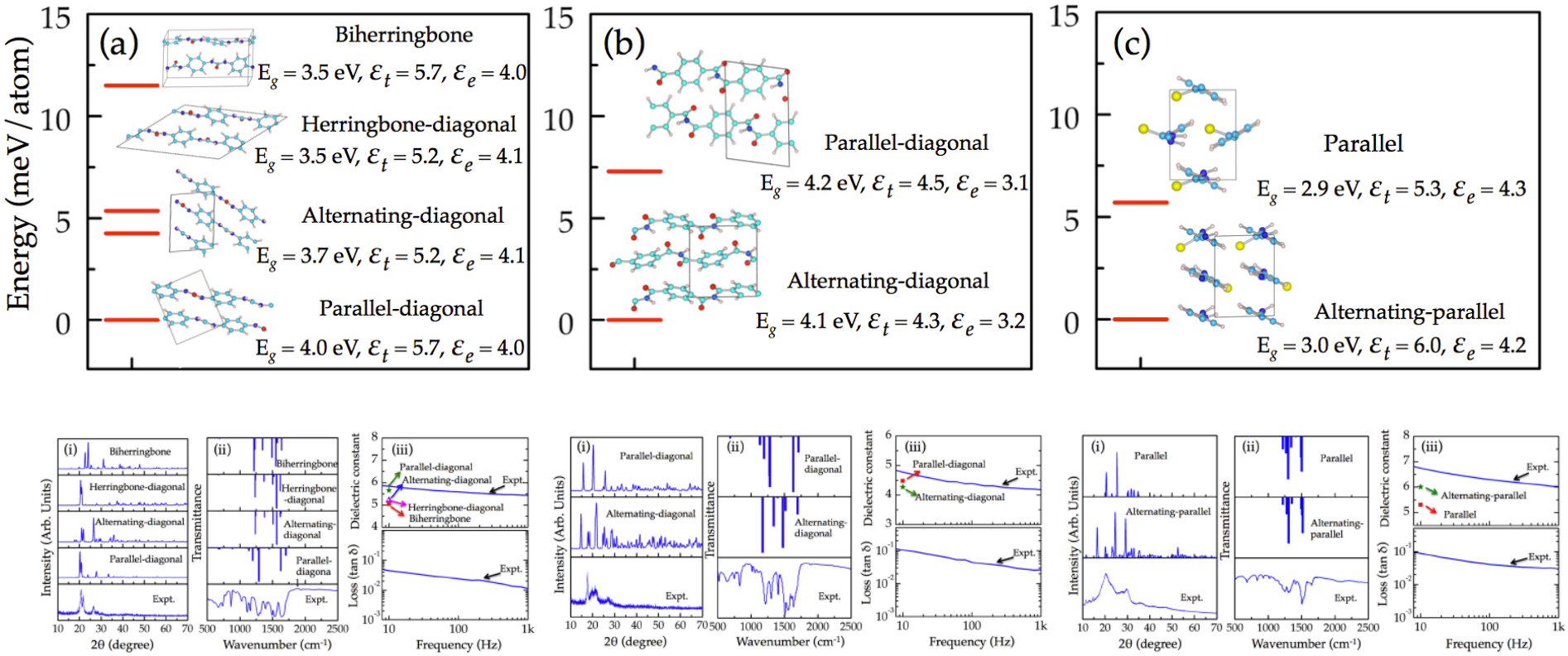
Courtesy: Sanat Kumar (Columbia University)

3D Structure & Properties

$NH\text{-}CO\text{-}NH\text{-}C_6H_4$ (polyurea)

$CO\text{-}NH\text{-}CO\text{-}C_6H_4$ (polyimide)

$NH\text{-}CS\text{-}NH\text{-}C_6H_4$ (polythiourea)

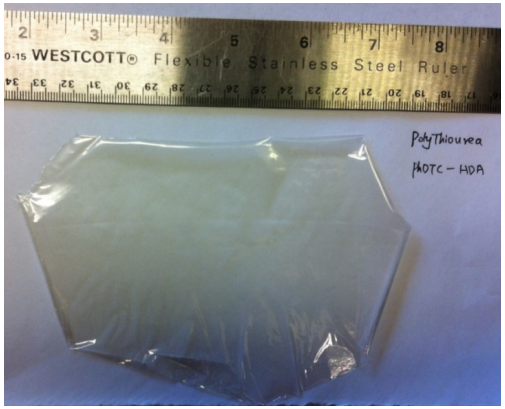


But none of them is "processable", i.e., flexible thin films cannot be made!

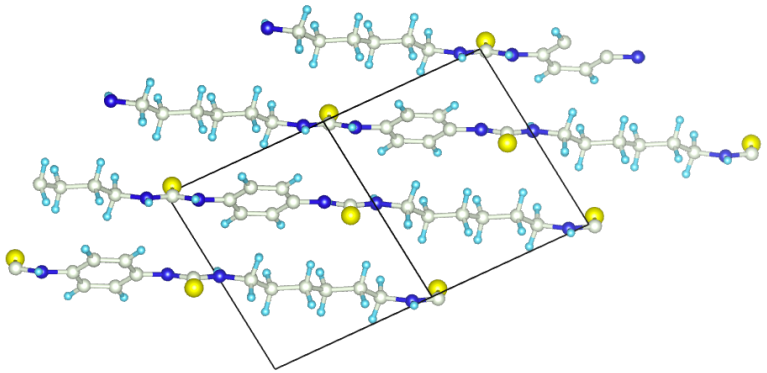
A Processable Variant

$$[\text{-NH-CS-NH-C}_6\text{H}_4\text{-NH-CS-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}]_n$$

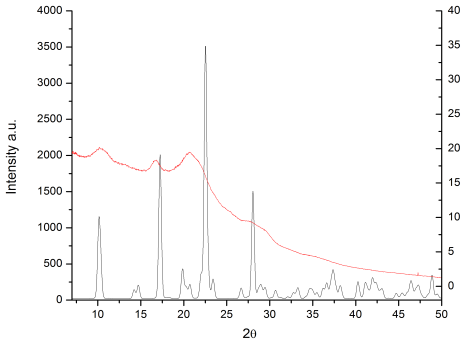
Synthesized Film



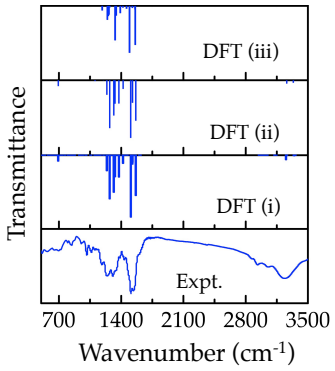
Predicted Structure



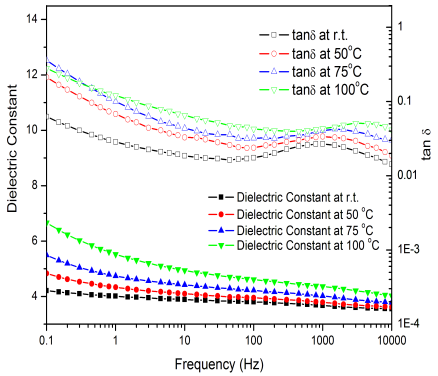
XRD



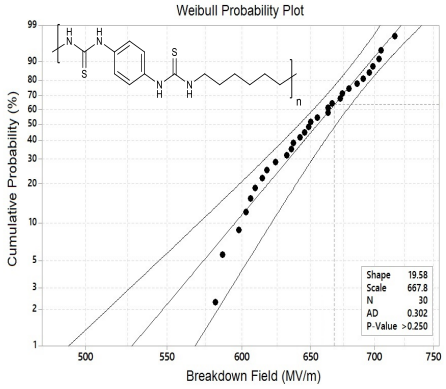
IR



Dielectric

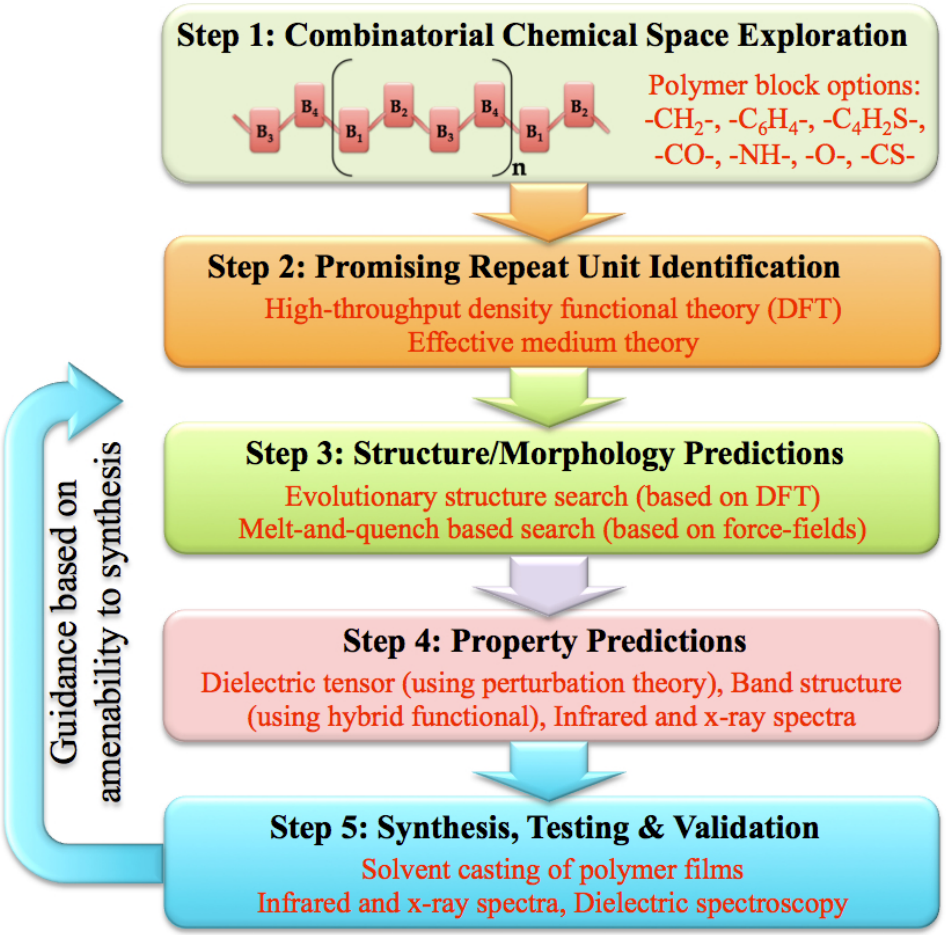


Breakdown



Courtesy: Greg Sotzing, Yang Cao (UCONN)

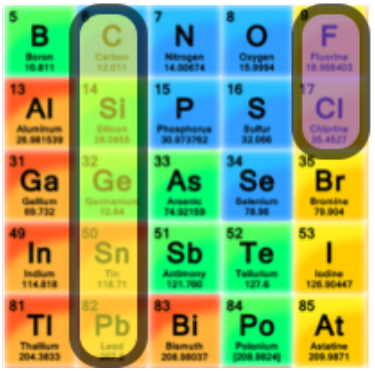
The Story So Far



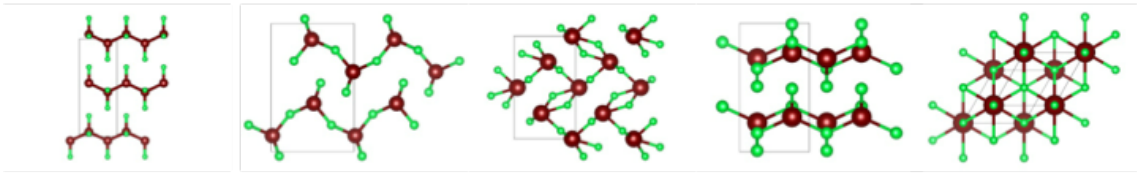
"Rational Design of All-Organic Polymer Dielectrics", Sharma, et al, accepted (Nature Communications)

Can We Do Better?!

... by ushering in Group 14 elements?



Coordination chemistry across Group 14 hydrides and halides!



TYPE- A

CH_2 CCl_2 CF_2 SiH_2 $SiCl_2$ SiF_2 GeH_2 SnH_2 PbH_2
CN = 4

TYPE- B

GeF_2 $GeCl_2$
CN = 5

TYPE- C

SnF_2
CN = 6

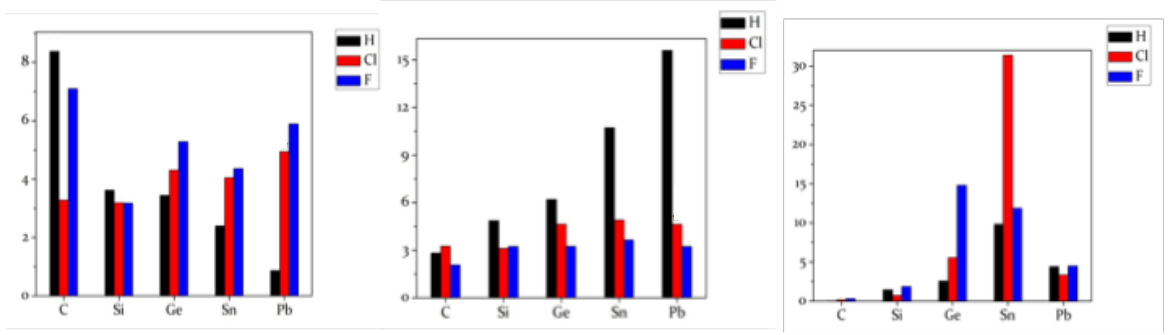
TYPE- D

$SnCl_2$ $PbCl_2$
CN = 6/7

TYPE- E

PbF_2
CN = 8

Property variation across Group 14 hydrides and halides!



HSE Band Gaps (eV)

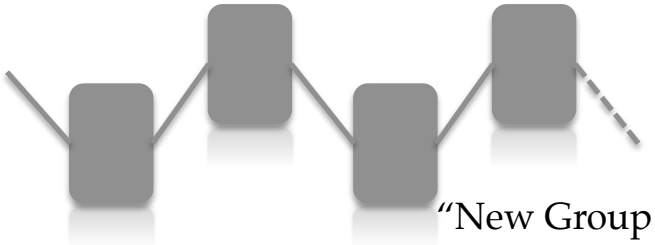
Electronic Dielectric Constant

Ionic Dielectric Constant

Wang, et al, Phys. Rev. B 87, 035103 (2013); Mannodi-Kanakkithodi, et al (under review)

Polymers Based on Group 14 Elements

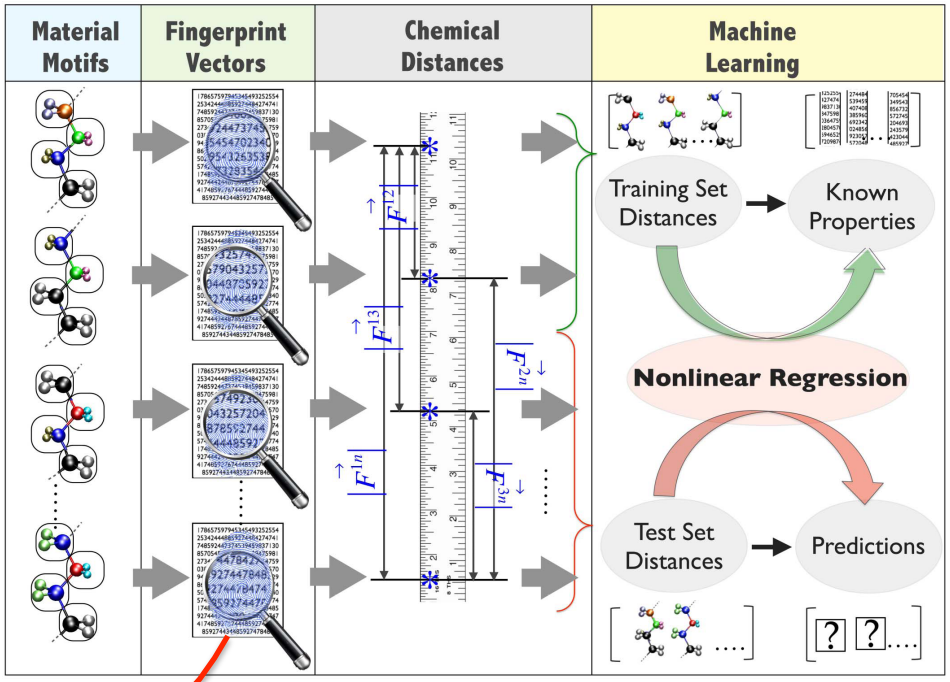
High-throughput density functional theory + Machine Learning



Blocks: CH_2, SiF_2, GeF_2, SnF_2, $SiCl_2$, $GeCl_2$, $SnCl_2$

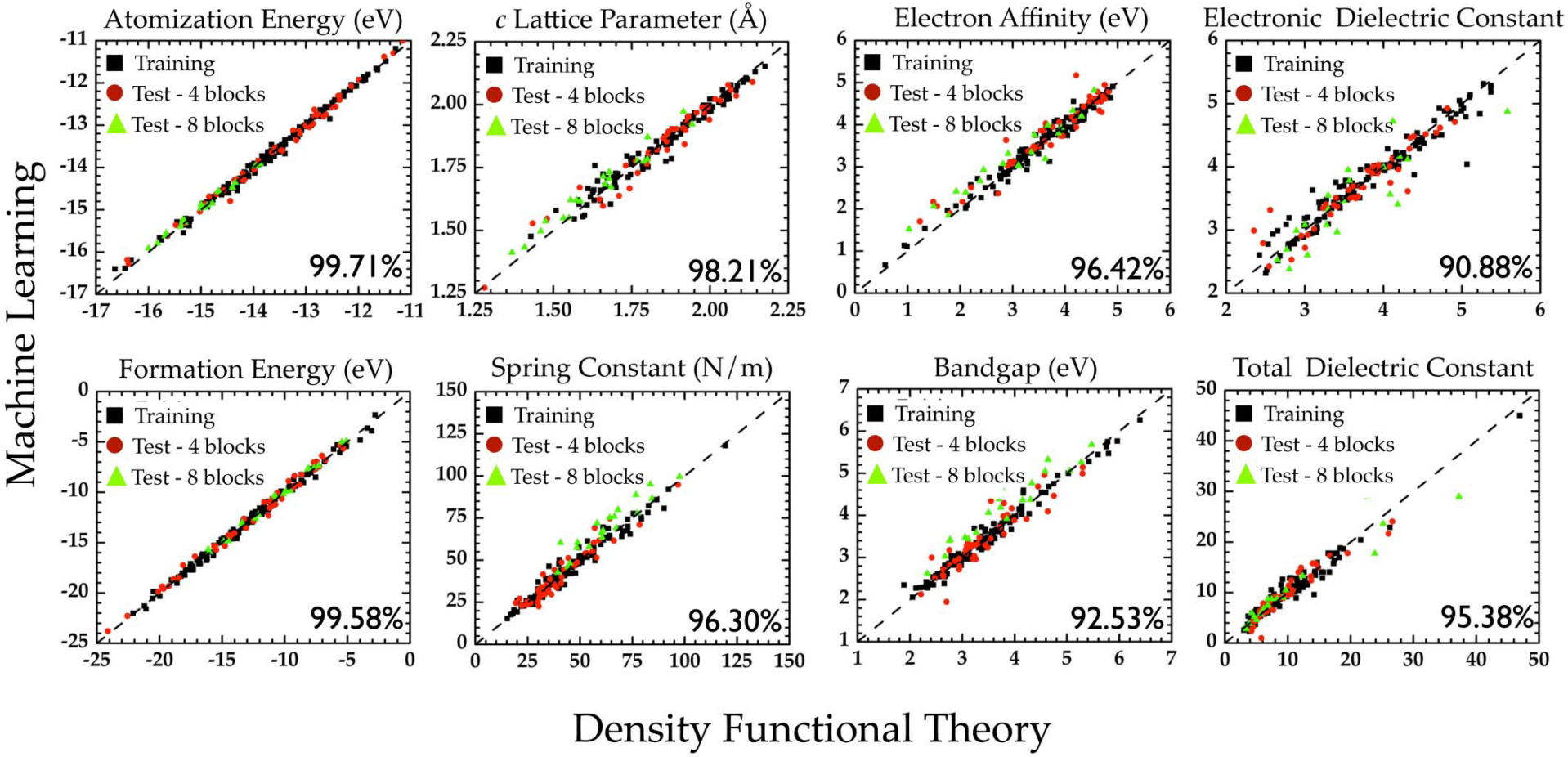
"New Group 4 chemical motifs for polymeric dielectrics with high energy density", Pilania, et al, J. Chem. Inf. Model 53, 879 (2013)

Based on number of singles, doubles and triples



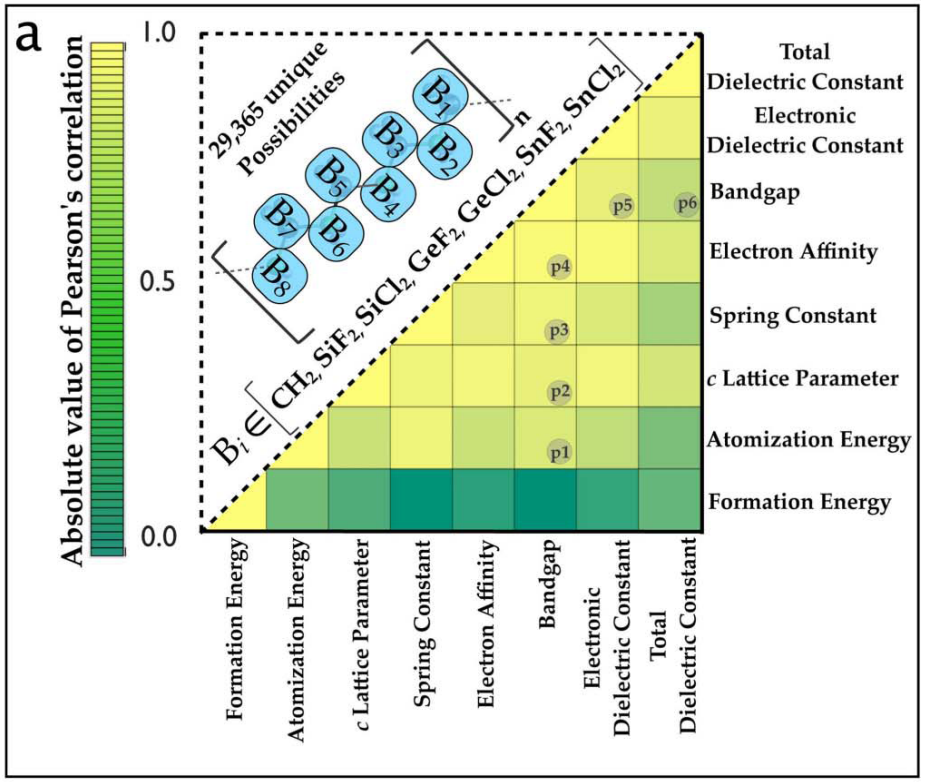
"Accelerating materials property predictions using machine learning", Pilania, et al, Sci. Rep. 3, 2810 (2013)

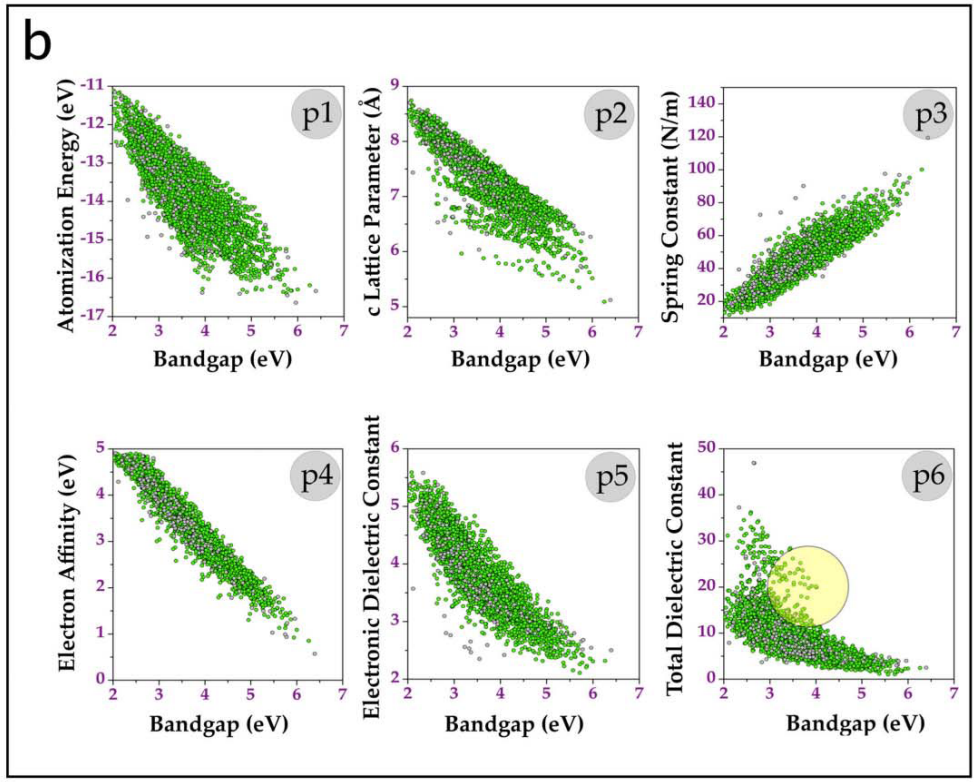
Prediction By Machine Learning



"Accelerating materials property predictions using machine learning",
Pilania, et al, Sci. Rep. 3, 2810 (2013)

Correlations & Insights

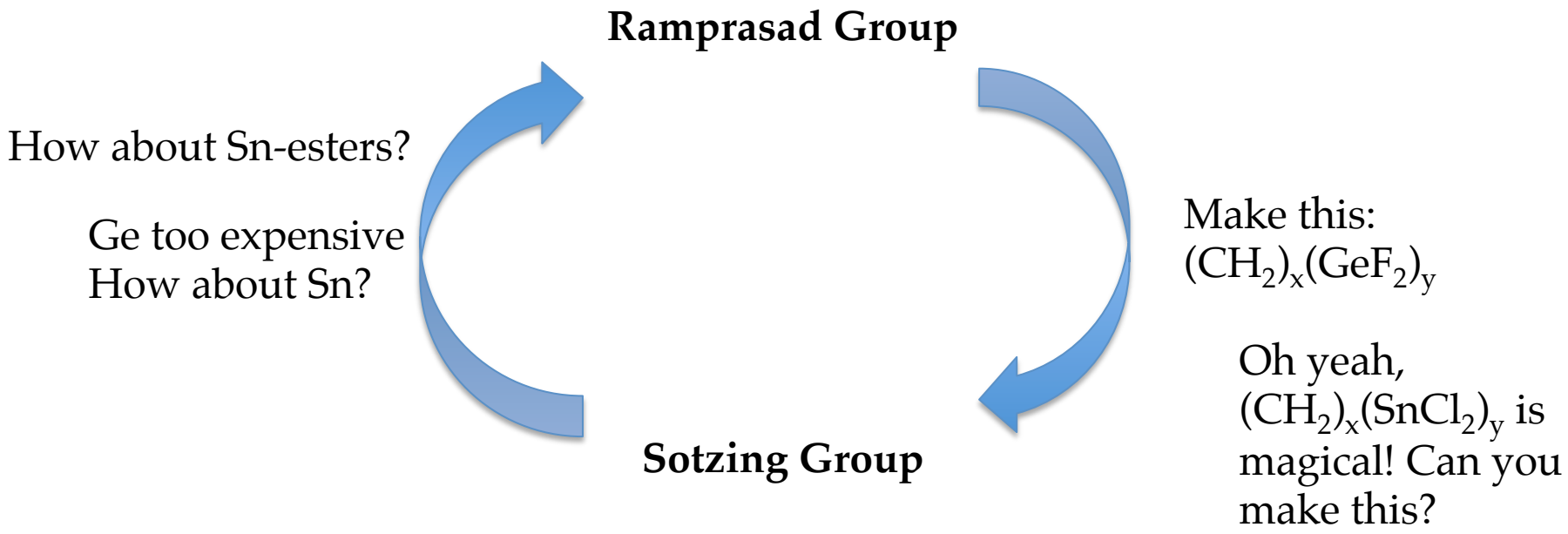




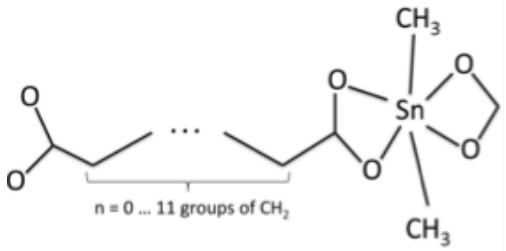
- Ionic part dominates dielectric constant
- Sn-containing groups occupy "sweet spot"

"Accelerating materials property predictions using machine learning",
Pilania, et al, Sci. Rep. 3, 2810 (2013)

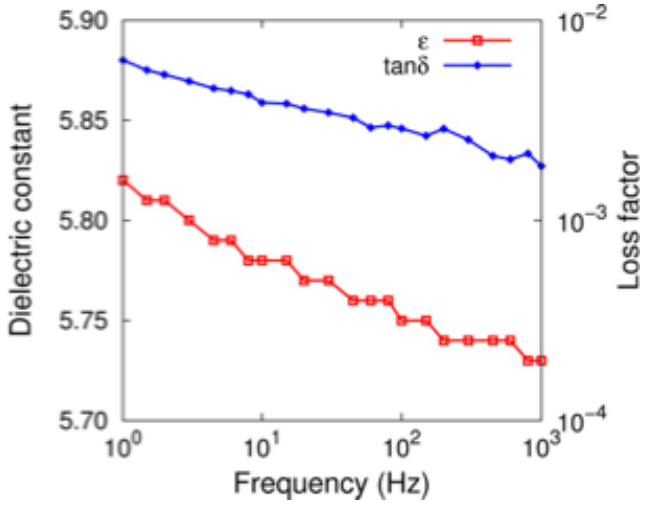
Synergy With Synthesis

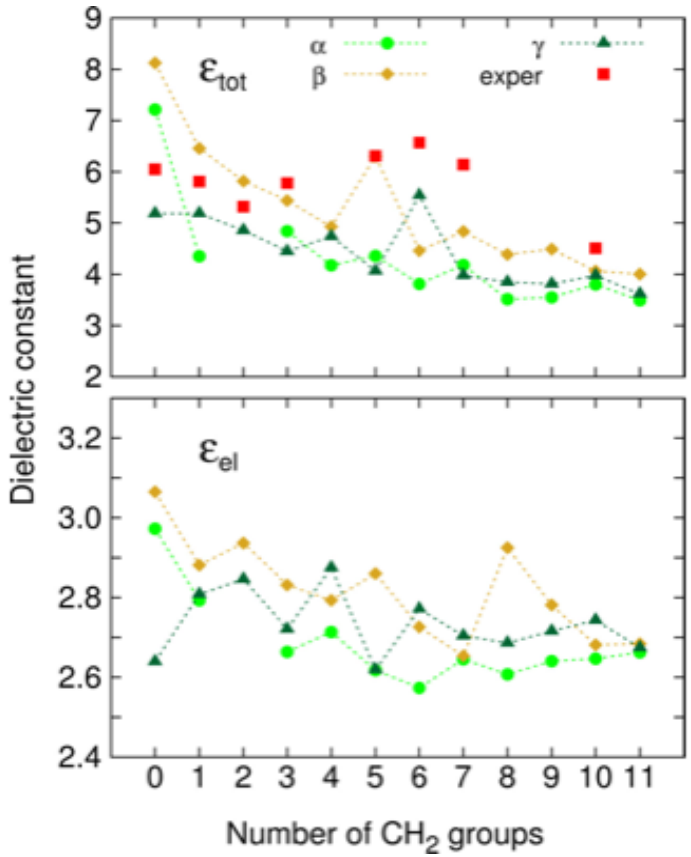


Organo-tin Ester Polymers



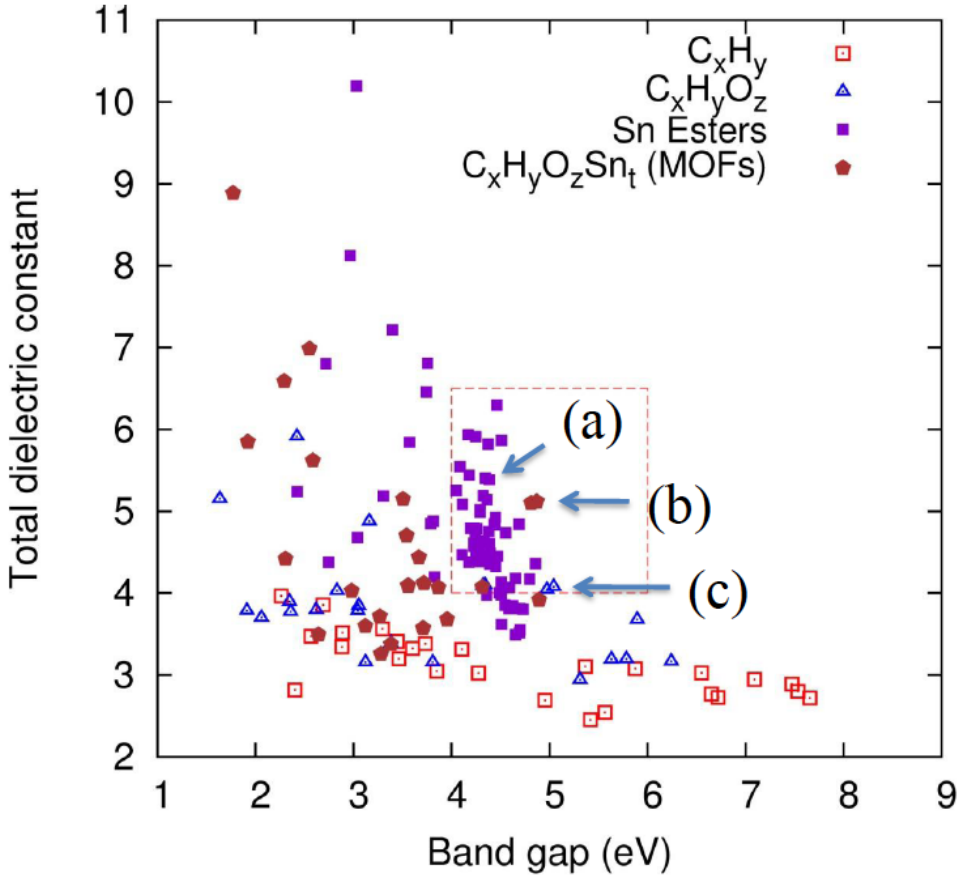
The whole series via minima hopping!

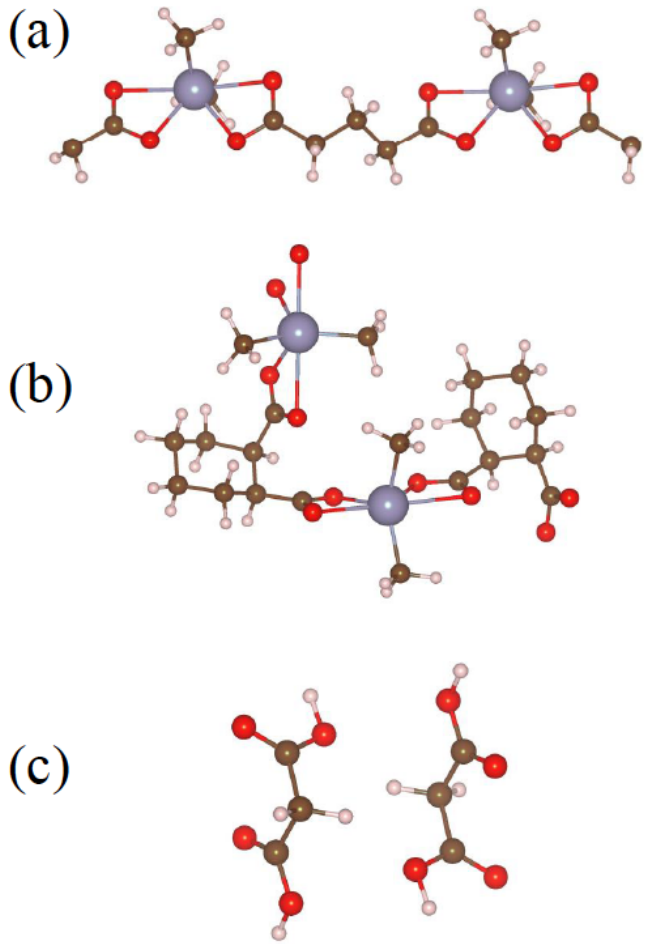




Baldwin, et al (under review)

Deeper into Organo-tin

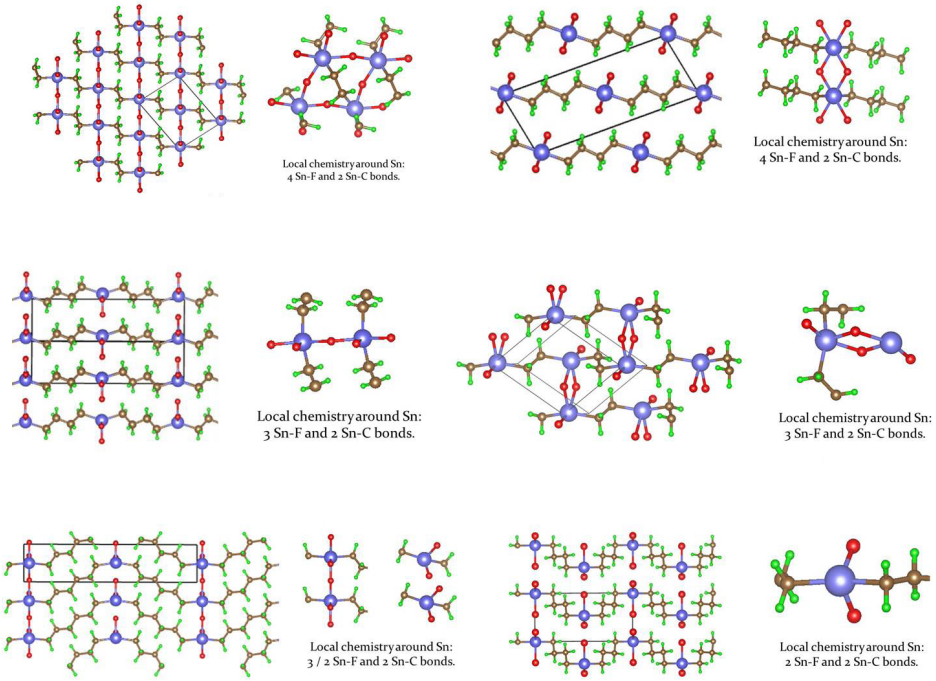


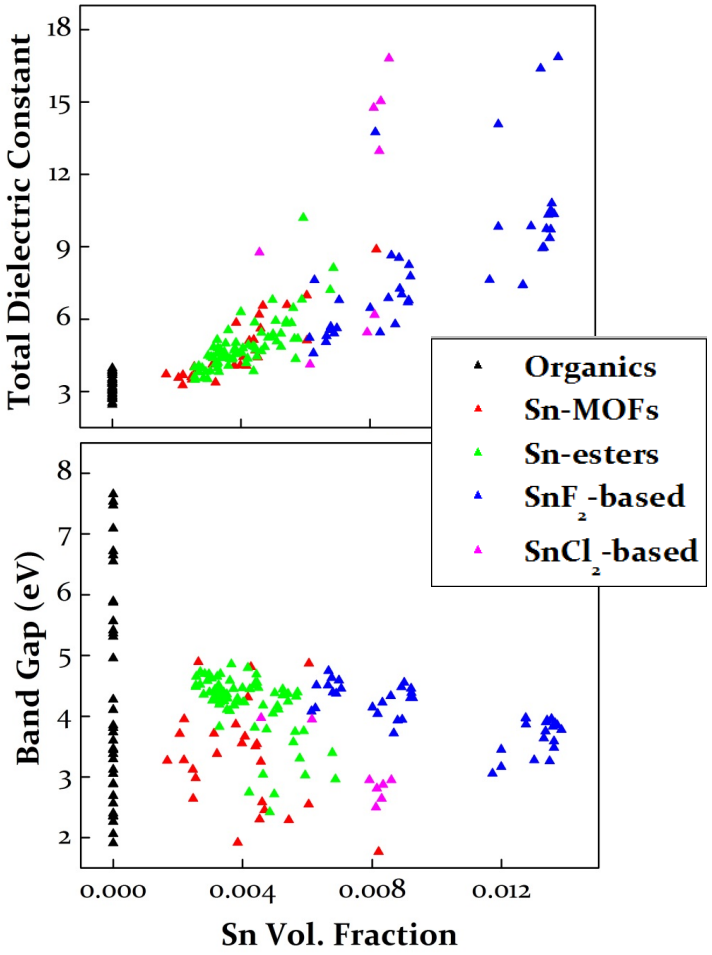


Tran, et al (in preparation)

Deeper into Organo-tin

$(SnF_2)_x(CH_2)_y$ and $(SnCl_2)_x(CH_2)_y$



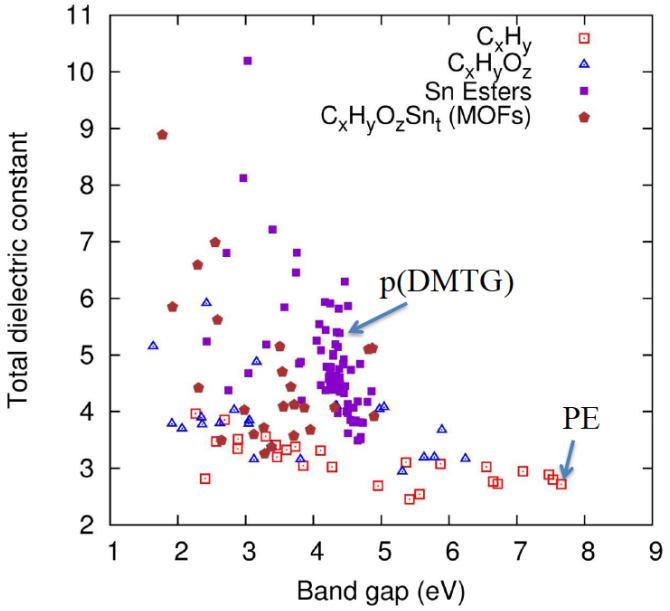


- Structures determined using the minima-hopping method
- 1D, 2D & 3D motifs, with 4-7 fold coordinated Sn

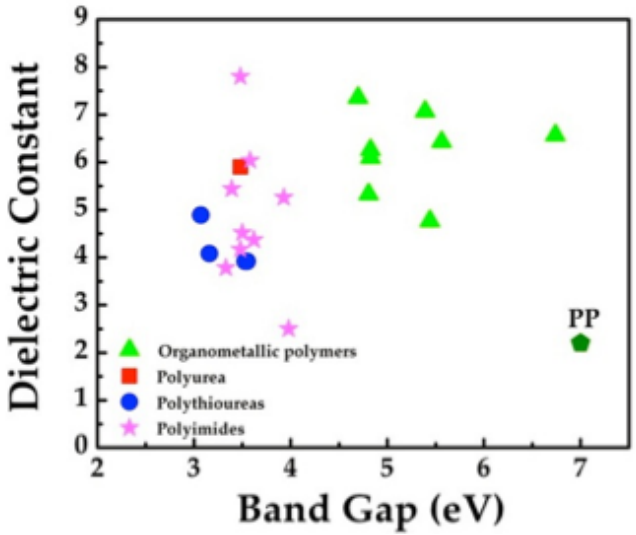
Mannodi-Kanakkithodi, et al (in preparation)

Organic Versus Organo-tin Polymers

Computational

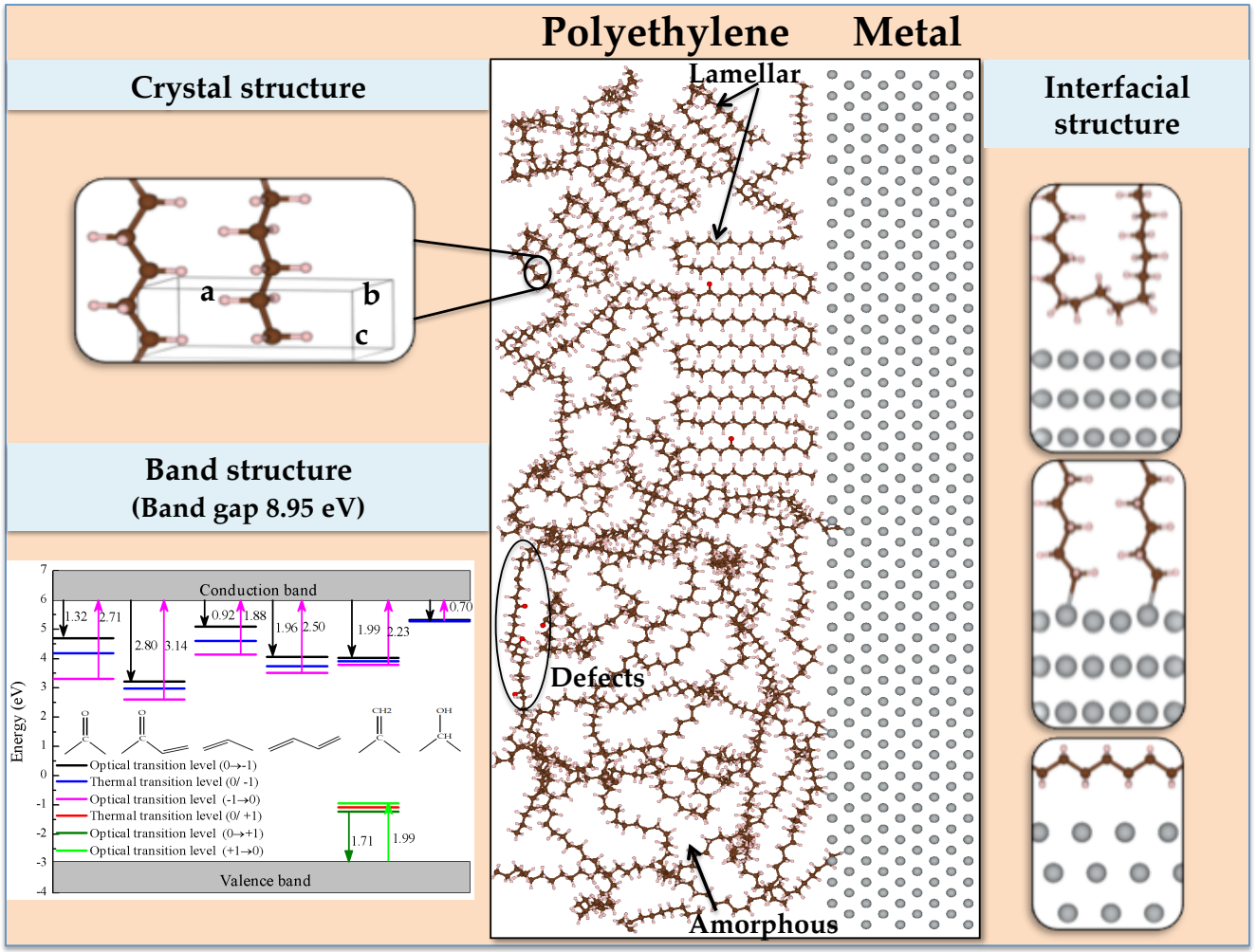


Experimental (Sotzing group)



- By carefully choosing organic blocks, one can improve upon polypropylene
- Organometallic polymers could lead us to an important part of the chemical/property space!
- But, there are other issues to contend with, of course!

Physical & Chemical Complexity

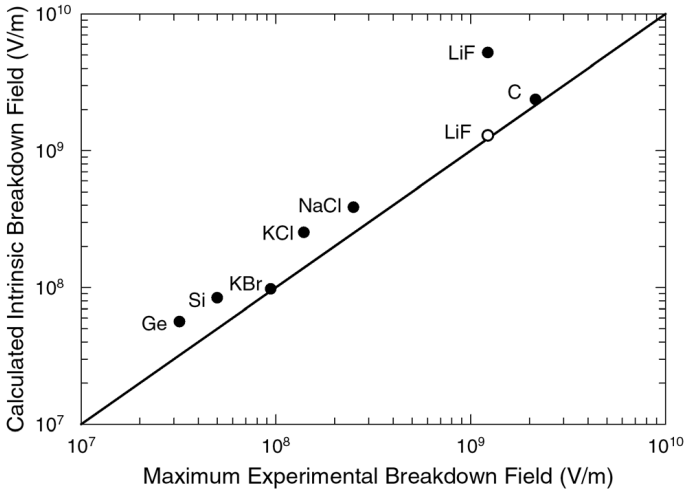


"New perspective on formation energies and energy levels of point defects in non-metals", Ramprasad, et al, Phys Rev. Lett. 108, 066404 (2012)

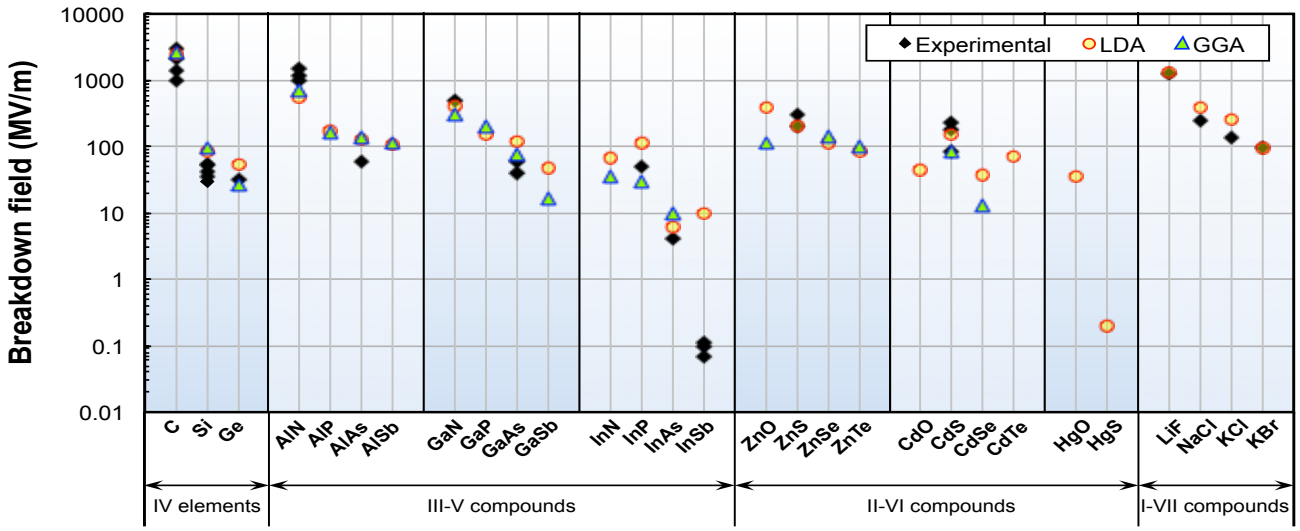
Chen, et al, (in preparation)

Dielectric Breakdown: A New Frontier?!

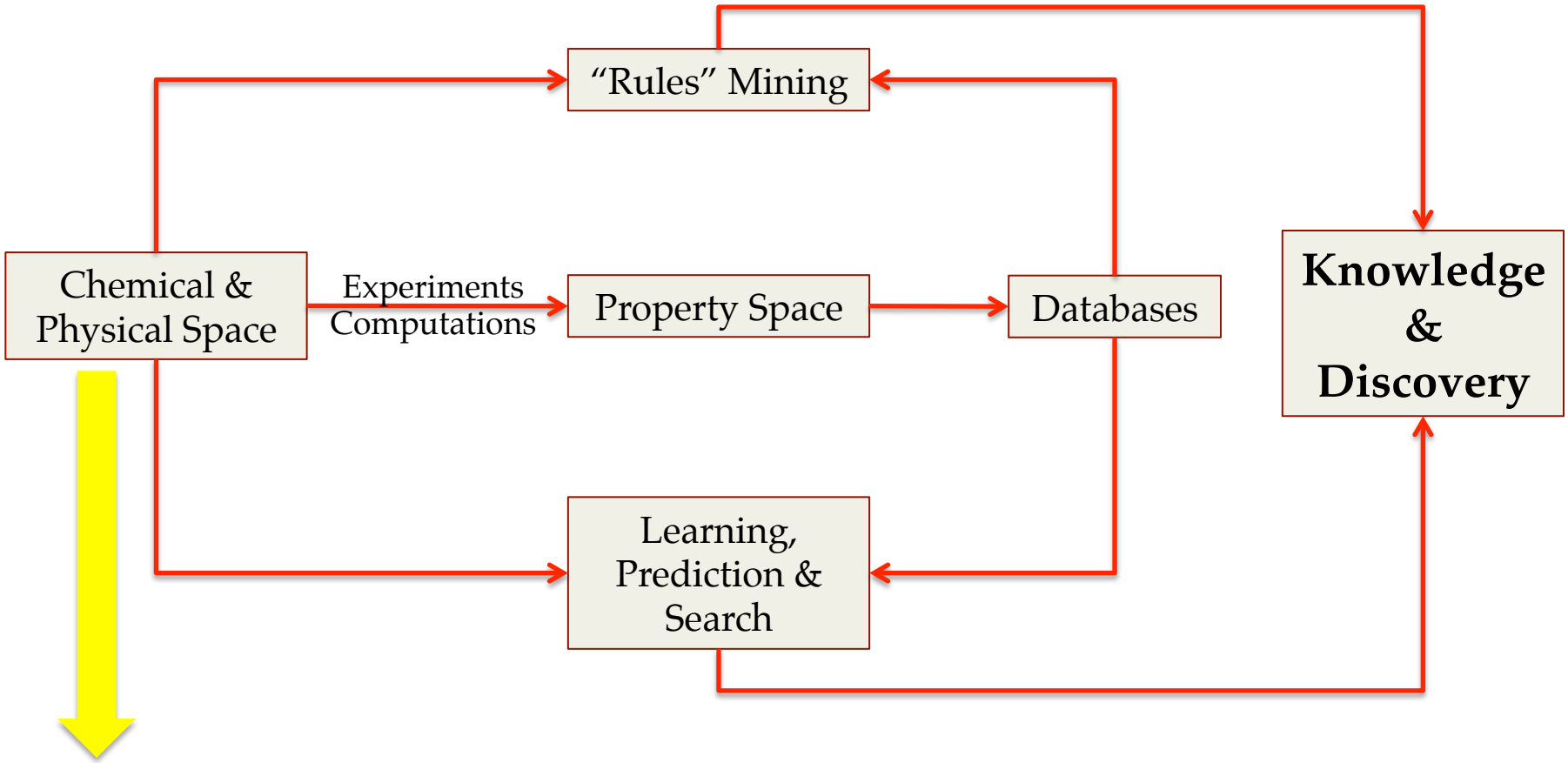
- The *intrinsic* breakdown field of a crystalline material is controlled by the scattering of charge carriers by phonons.
- How about extrinsic factors?!



"The intrinsic electrical breakdown strength of insulators from first principles"
Sun, et al, Appl. Phys. Lett. 101, 132906 (2012)
Kim, et al (in preparation)



A Framework For Learning



The Materials Genome Challenges: Handle chemical and physical spaces; accurate property prediction scheme development; synergize with experiments.

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