Informatics guided nanomaterial design

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Outline

- QSAR type strategy for materials chemistry
- Crystal chemistry and nanoscience
- Descriptor development and data challenges
- Materials design and nanotoxicity

High Dimensional Data: materials functionality

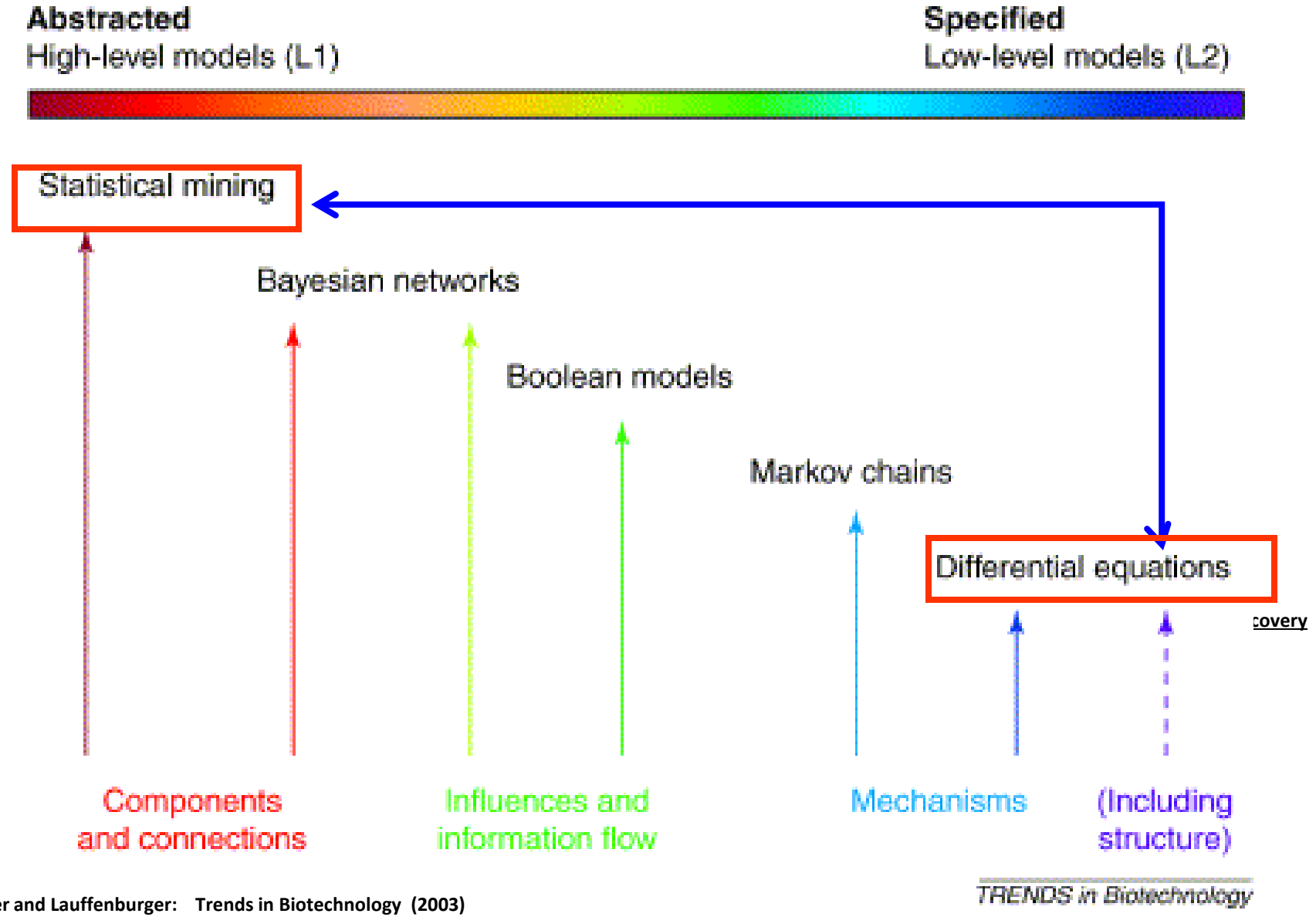
$$\text{Functionality} = \mathcal{F}\,(x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8 \ldots\ldots)$$

Issues:

- how many variables?
- which variables are important?
- classify behavior among variables
- making quantitative predictions ...relate functionality to variables ...
  - traditionally we describe them by empirical equations:
  - Quantitative Structure Activity Relationships (QSARs) are derived from data mining techniques not assuming a priori which physics is the most important

Need to build database with these variables

"Omics in Materials Science

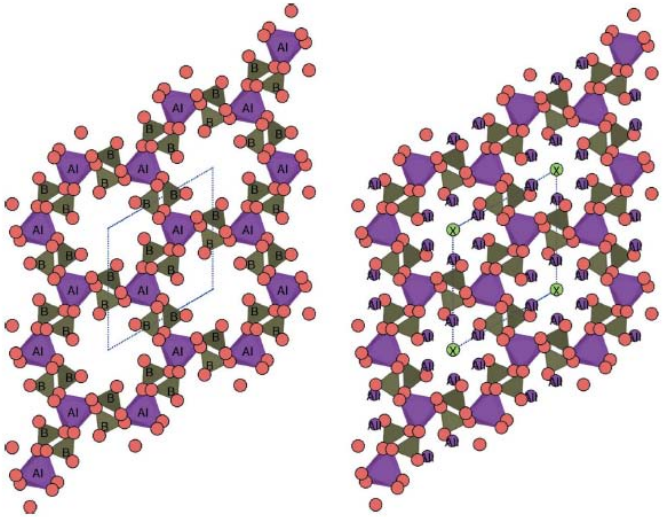


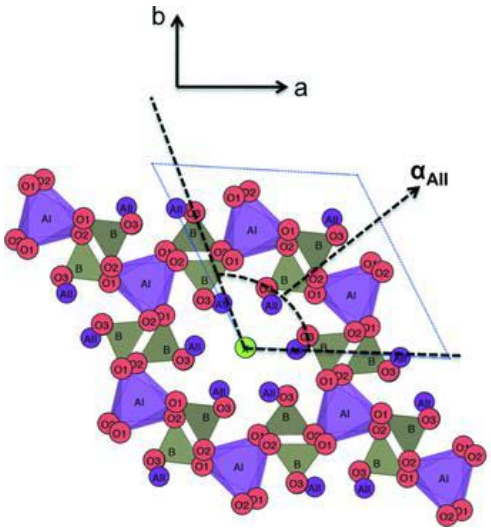
Ideker and Lauffenburger: Trends in Biotechnology (2003)

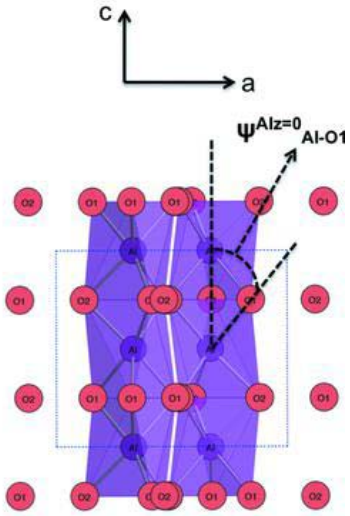
Structure maps for $A^{I}_{4}A^{II}_{6}(BO_4)_6X_2$ apatite compounds *via* data mining

Prasanna V. Balachandran and
Krishna Rajan*

Acta Crystallographica Section B
Structural
Science *Acta Cryst.* (2012). B**68**, 24–33





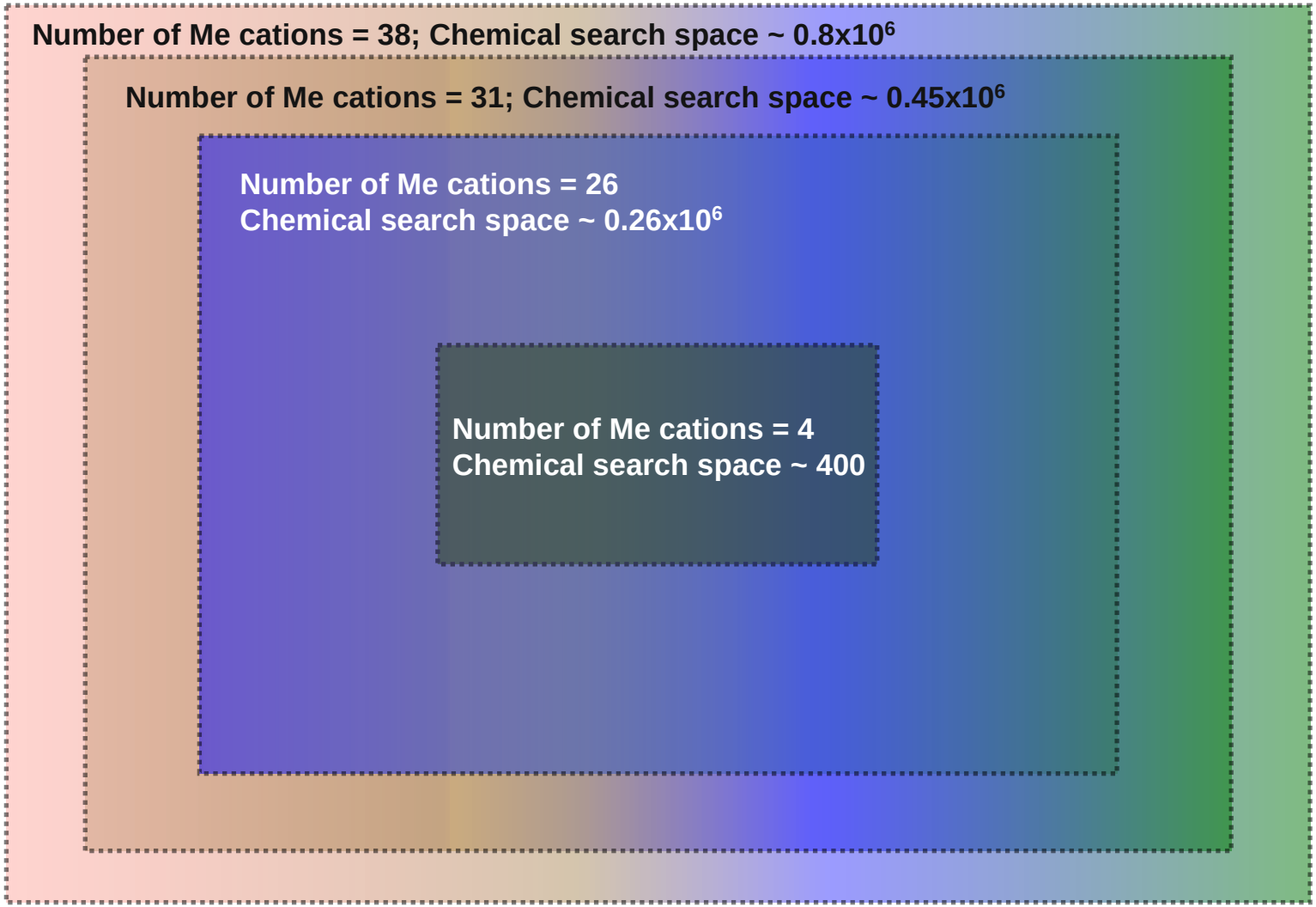


Chemical search space for informatics

Stoichiometric space: $xBi(Me1_pMe2_qMe3_r)O_3$-$(1-x)PbTiO_3$

Number of Me cations = 38

4	Abundant	22	Limited availability future risk to supply	5	Rising threat from increasing use	7	Serious threat in next 100 years



The schematic shows how the chemical search space shrinks, when we account for the scarcity information.

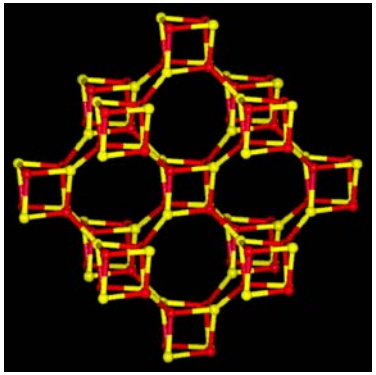
Krishna Rajan

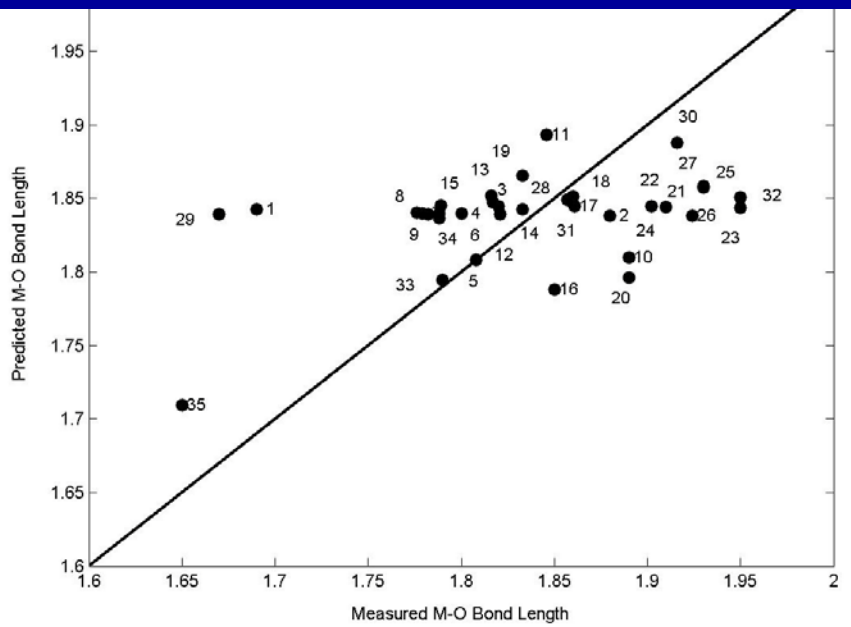
Materials parameters and nanotoxicty

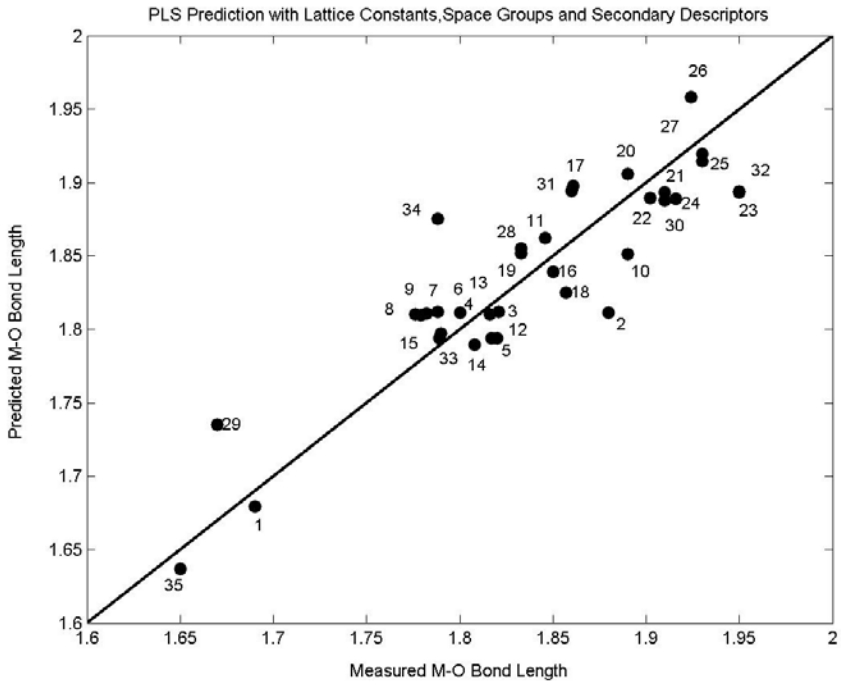
Descriptor	Brief description
a (Å)	Lattice constant of the hexagonal unit cell
c (Å)	Lattice constant of the hexagonal unit cell
c/a	Variable axial ratio (no unit)
r_{AI} (Å)	Shannon's ionic radii of A^{I}-site ion (nine-coordination)
r_{B} (Å)	Shannon's ionic radii of B-site ion
r_{AII} (Å)	Shannon's ionic radii of A^{II}-site ion (seven-coordination for F^{-} and eight-coordination for Cl^{-} and Br^{-}; Đordević *et al.*, 2008)
r_{X} (Å)	Shannon's ionic radii of X-site ion
Av CR (Å)	Average crystal radius = $[(r_{AI}x4) + (r_{AII}x6) + (r_{B}x6) + (r_{O}x24) + r_{X}x2)]/42$
$A_{EN} - O_{EN}$	Electronegativity difference A atom and O atom
$B_{EN} - O_{EN}$	Electronegativity difference B atom and O atom
$A_{EN} - X_{EN}$	Electronegativity difference A atom at A^{II} site and X atom
$A_{EN} - B_{EN}$	Electronegativity difference A atom at A^{I} site and B atom

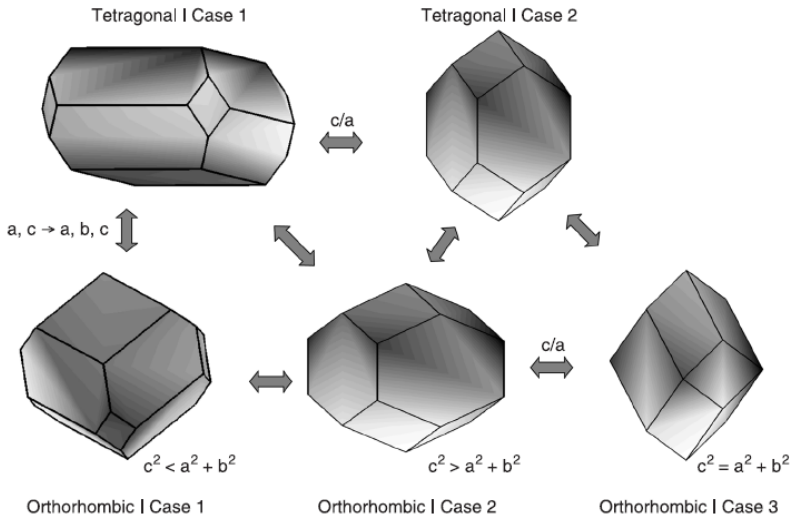
Descriptor	Brief description
A^{I}—O1 (Å)	Distance between A^{I} and O1 atom
A^{I}—O1$^{AIz=0}$ (Å)	Distance between A^{I} and O1 atom with the constraint $z = 0$ at A^{I}
Δ_{AI-O} (Å)	Difference in the lengths A^{I}—O1 and A^{I}—O2
$\Delta_{AI-O}^{AIz=0}$ (Å)	Difference in the lengths A^{I}—O1 and A^{I}—O2 with the constraint $z = 0$ at A^{I}
ψ_{AI-O} (°)	The angle that the A^{I}—O1 bond makes with respect to c
$\psi_{AI-O}^{AIz=0}$ (°)	The angle that the A^{I}—O1 bond makes with respect to c with the constraint $z = 0$ at A^{I}
δ_{AI} (°)	Counter-rotation angle of $A^{I}O_6$ structural unit
φ_{AI} (°)	Metaprism twist angle ($\pi/3 - 2\delta_{AI}$)
α_{AI} (°)	Orientation of $A^{I}O_6$ unit with respect to a
$\langle B—O \rangle$ (Å)	Average B—O bond length
$\langle \tau_{O-B-O} \rangle$ (°)	Average O—B—O bond-bending angle
ρ_{AII} (Å)	A^{II}—A^{II} triangular side length
A^{II}—X (Å)	Distance between A^{II} and X atom
α_{AII} (°)	Orientation of A^{II}—A^{II}—A^{II} triangles with respect to a
A^{II}—O3 (Å)	Distance between A^{II} and O3 atom
$\Phi_{O3-AII-O3}$ (°)	O3—A^{II}—O3 angle
E_{total} (eV)	Total energy calculated from *ab initio* calculations

Designing Molecular Architecture



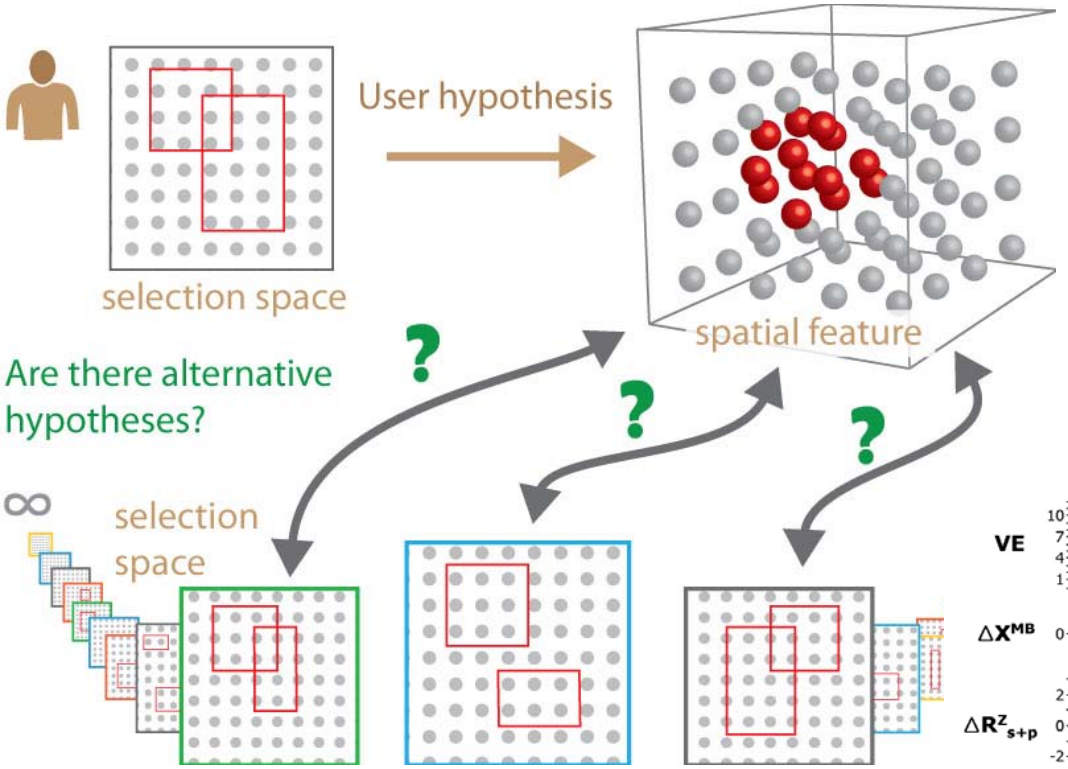






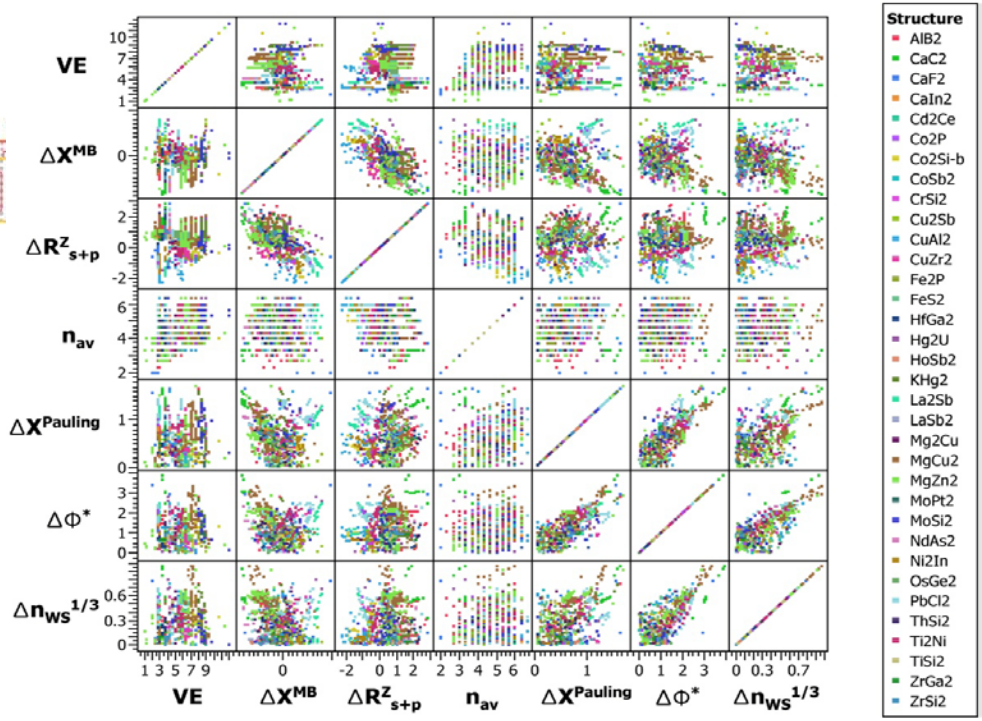
Rajagopalan & Rajan (2005)

Dimensionality and Complexity

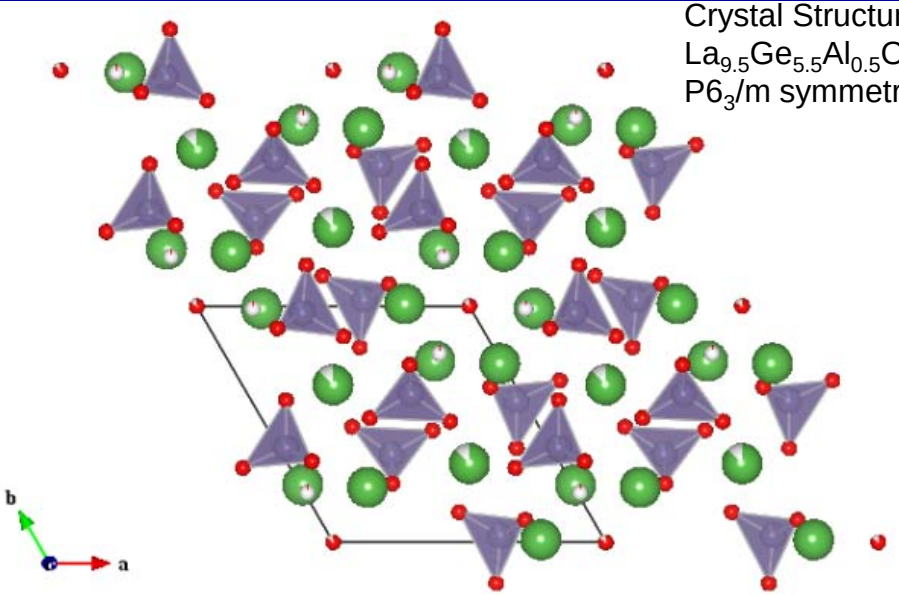


N point correlation

Kong & Rajan- 2009/ 2012



Searching an informatics based combinatorial space



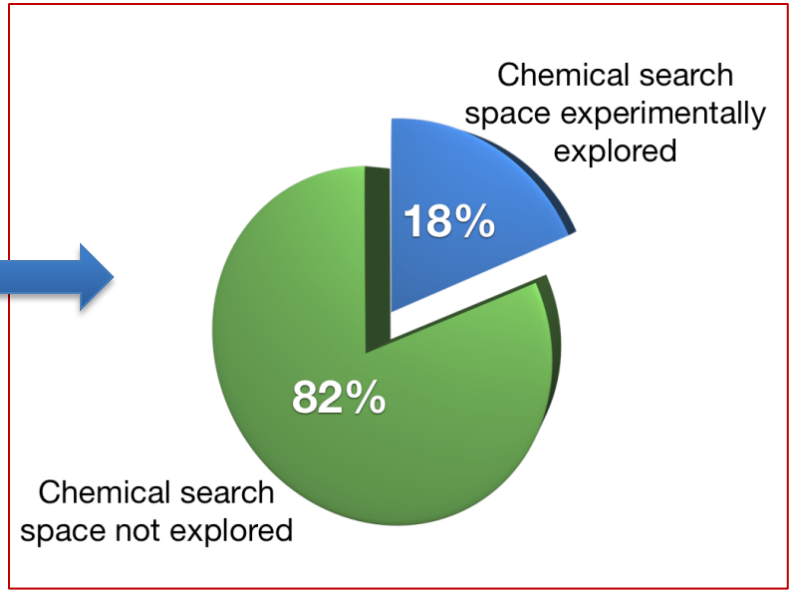
Crystal Structure of $La_{9.5}Ge_{5.5}Al_{0.5}O_{26}$ Apatite – $P6_3/m$ symmetry

Stoichiometric Space: $A^{I}A^{II}BO$

of (A) La-site substitutions=22
of (B) Ge-site substitutions=18

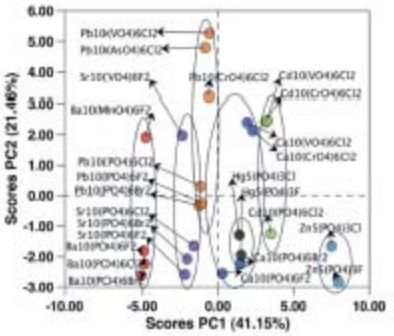
Total possibilities:

~ 10,000 chemical compositions



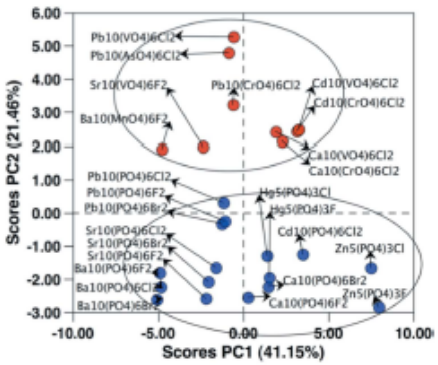
Blachandran & Rajan (2012)

Classification: Structure-Chemistry relationships

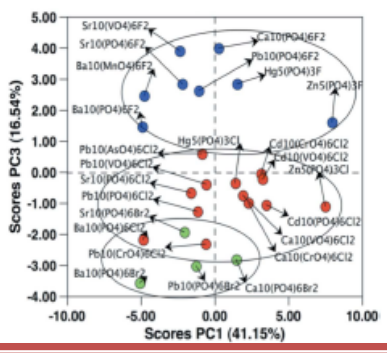


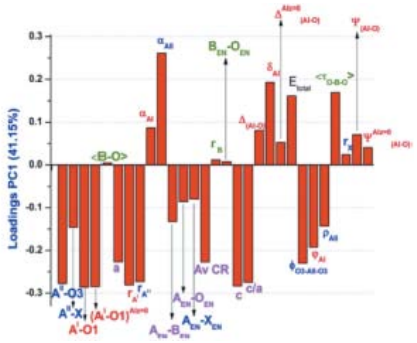
Ionic radius of A-site element decreases in this direction

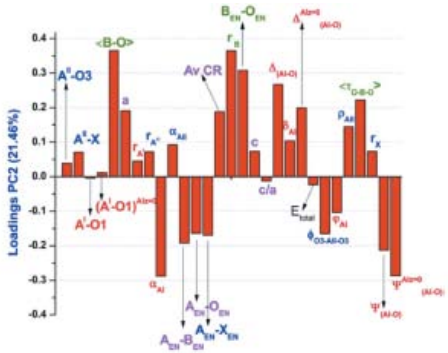
Ionic radius of B-site element decreases in this direction

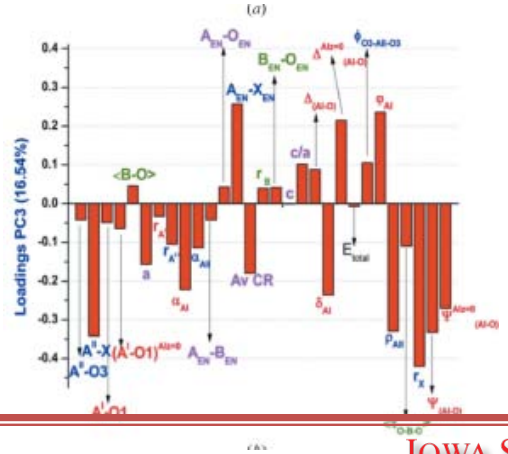


Ionic radius of X-site element decreases in this direction

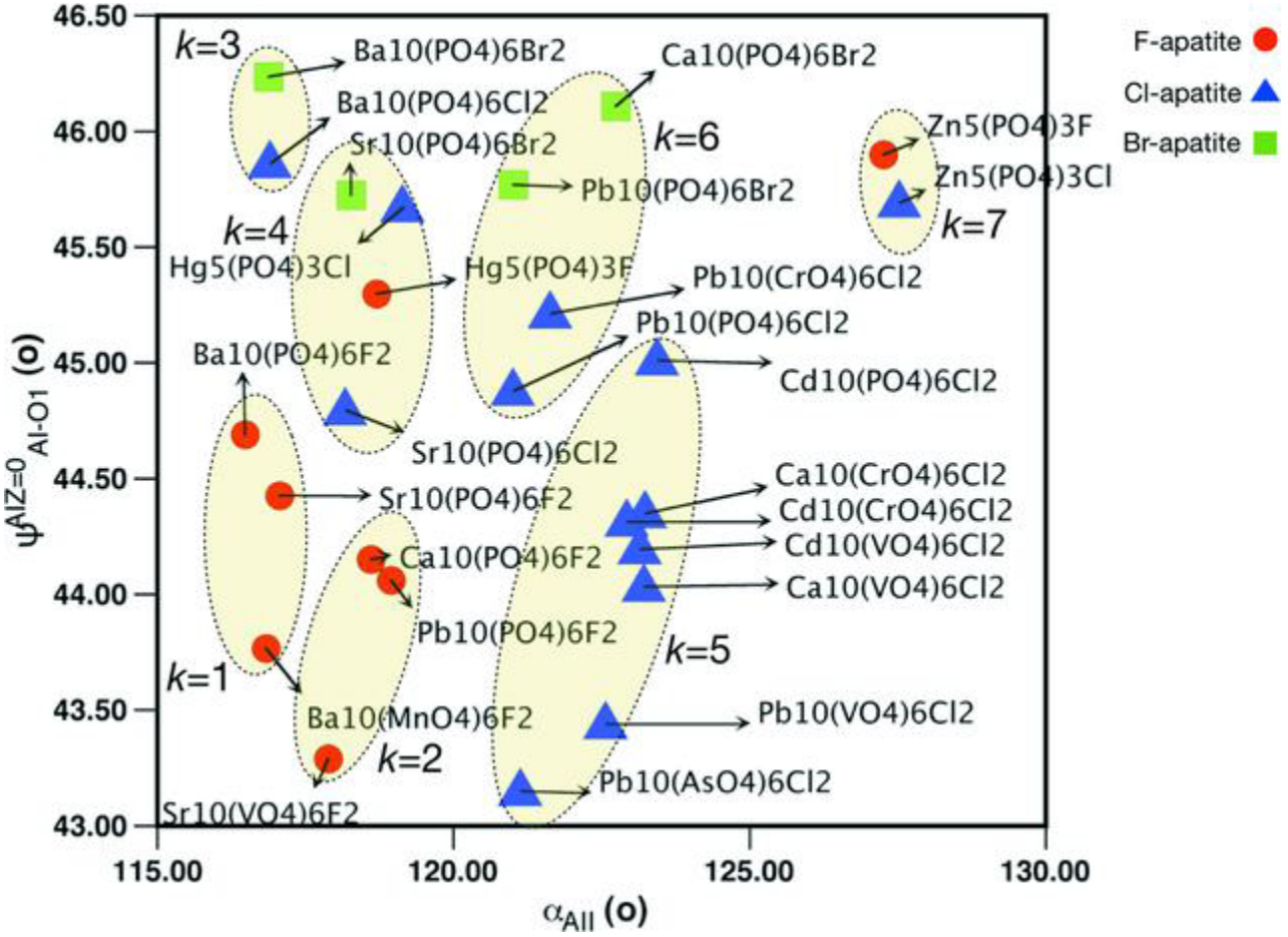




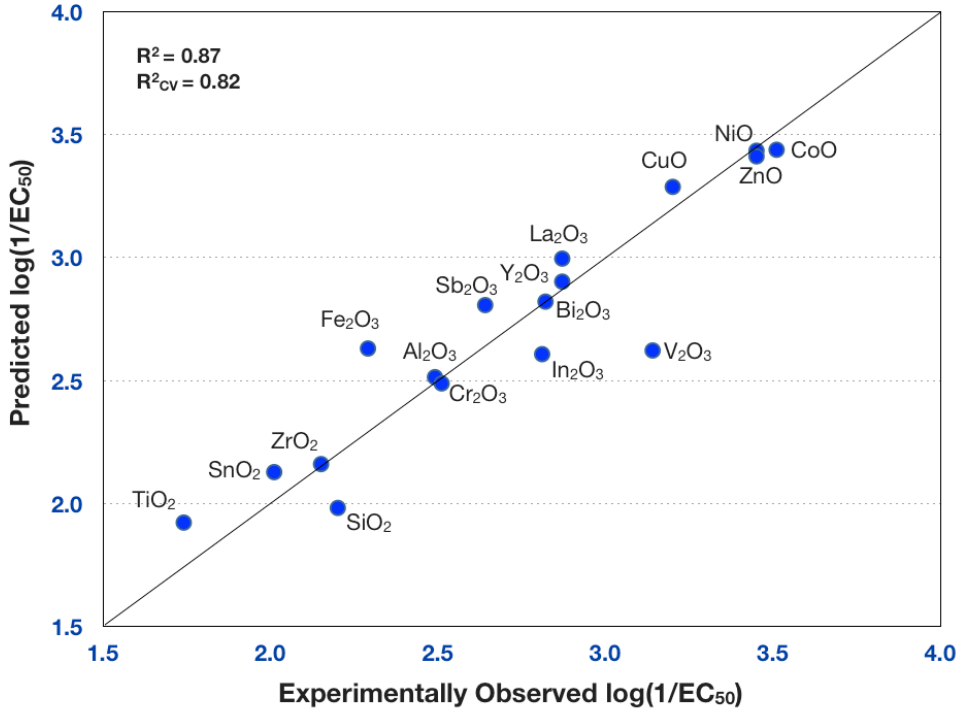


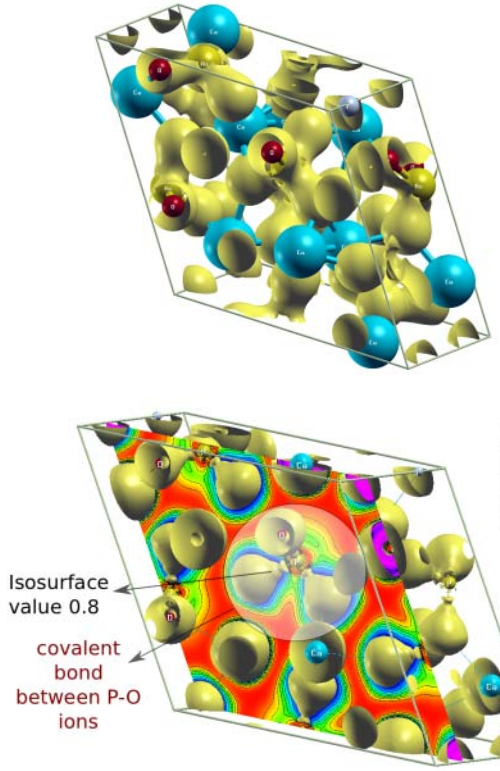


Chemical design



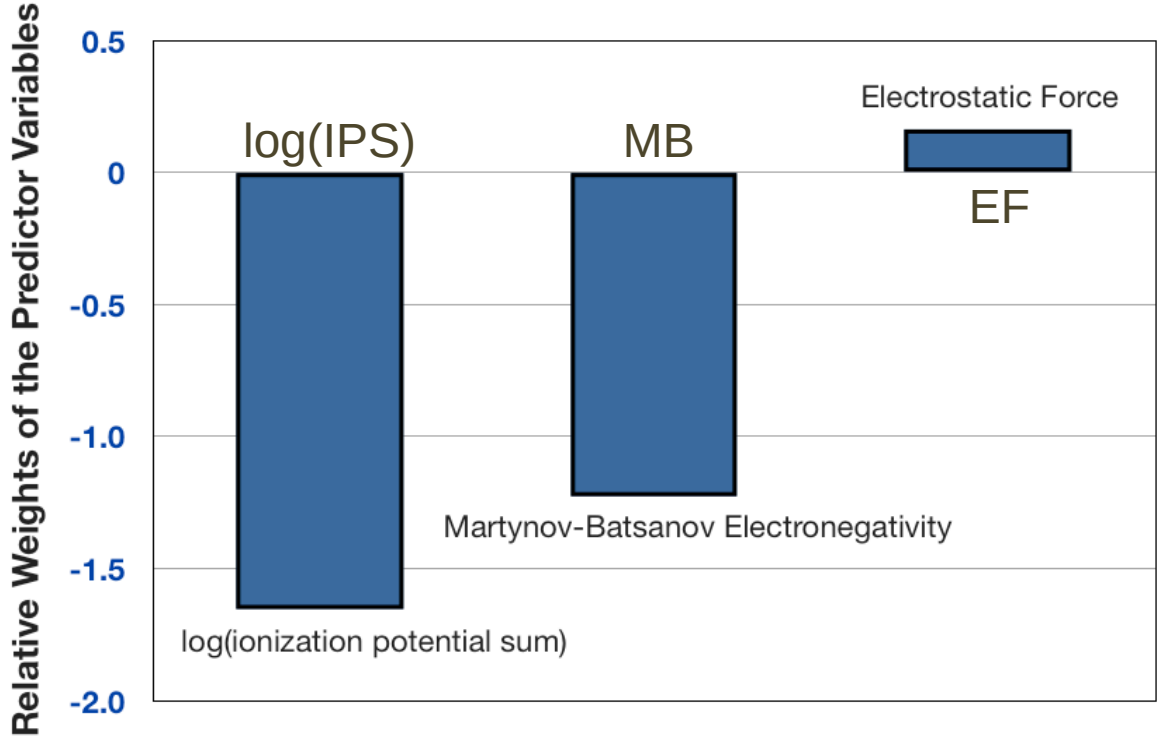
Predictive Nanotoxicology





Nanochemistry	Predicted log(1/EC_{50})	Classification
CeO_2	2.197	Harmful
FeO	3.45	Extremely Toxic
$(Zn_{0.95}Al_{0.05})O^{§}$ $(Cu_{0.95}Al_{0.05})O^{§}$	3.355	Extremely Toxic
$-(Zn_{0.9}Fe^{3+}{}_{0.1})O^{*}$	3.241	Very Toxic
Sc_2O_3	3.016	Very Toxic
MnO	2.741	Toxic
MnO_2	3.477	Extremely Toxic
	1.807	Harmful

Linking length scales



❖*log(IPS) describes the difference between enthalpy of formation of gaseous cation and enthalpy of sublimation [1].*

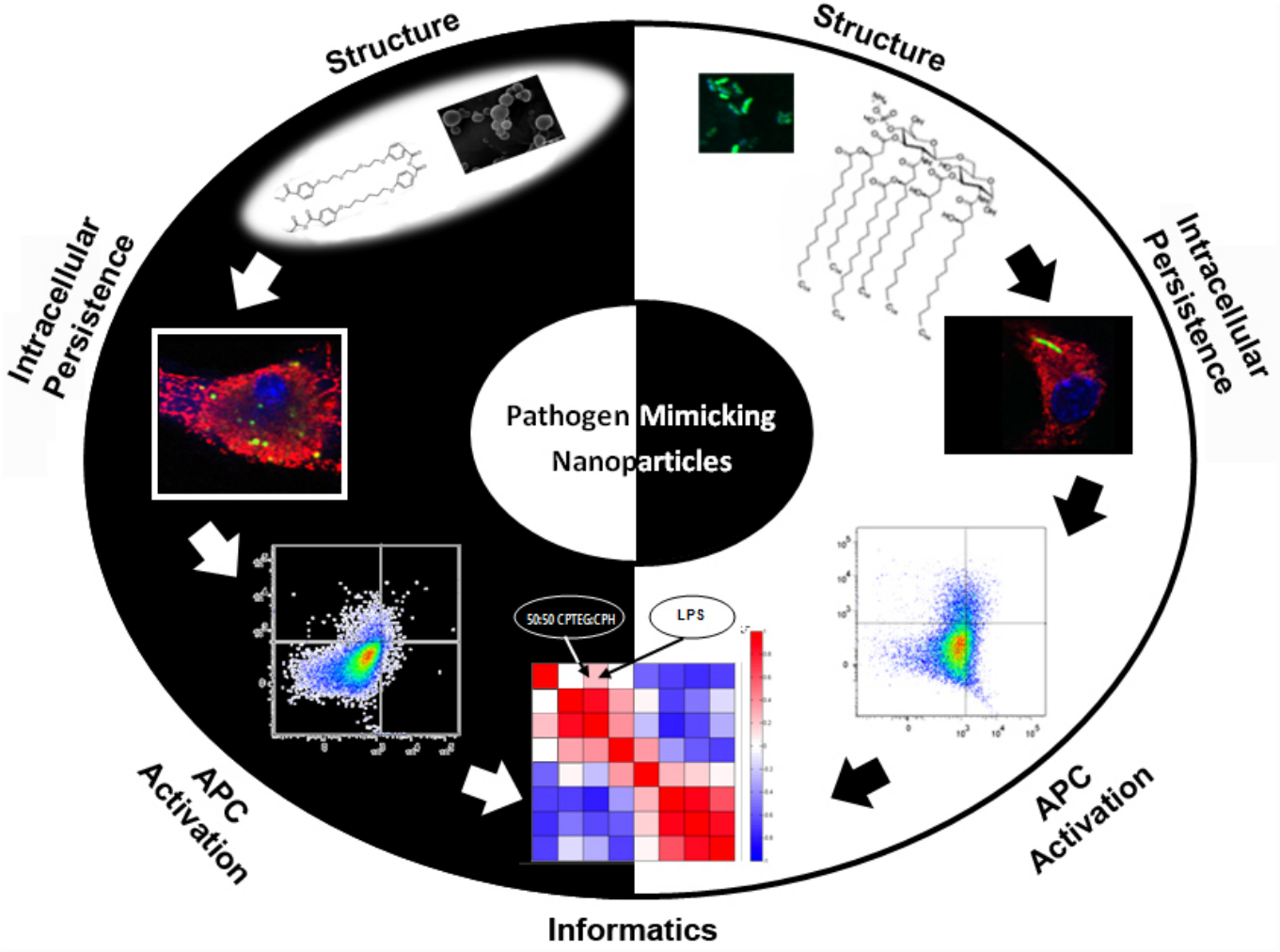
❖*MB electronegativity describes bonding associated with the relative ability of an atom in a nanoparticle to attract valence electrons [2].*

❖*EF describes the force exerted by the effective nucleus of metal cation on the valence electrons [3]*

SCIENTIFIC REPORTS

Rational Design of Pathogen-Mimicking Amphiphilic Materials as Nanoadjuvants

Ideal vaccine will mimic the way in which a naturally occurring infection induces a robust immune response yet avoid the undesirable effects of disease



Ulery et.al (2012)

Summary

- Data driven design of materials chemistry
- Nano-QSAR---linking chemistry to structure
- Nanotoxicity: chemical sequestration and chemical transport

Structure Matters !!