# 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

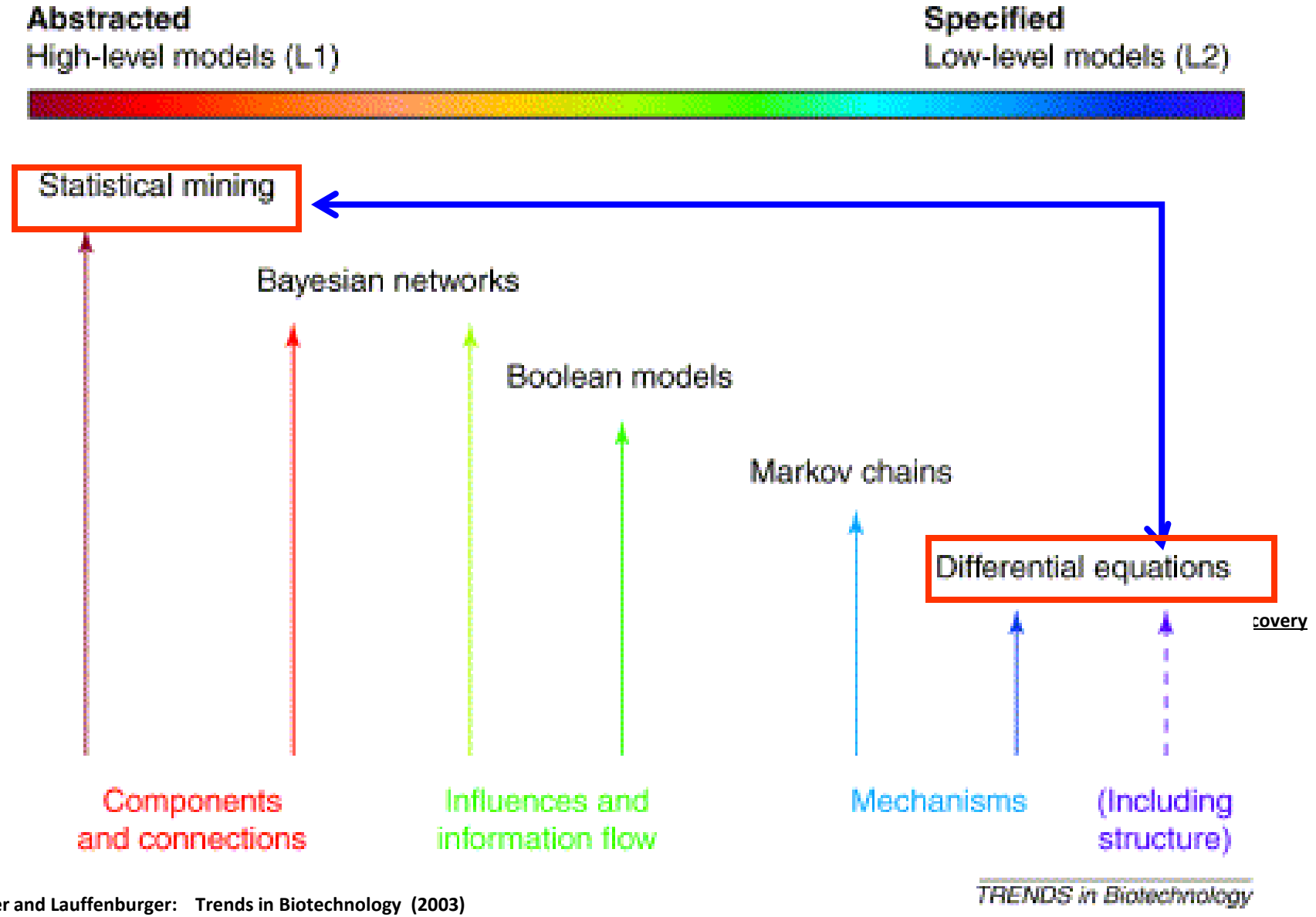
$$\text{Functionality} = \mathcal{F}\,(x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8 \ldots\ldots)$$

**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

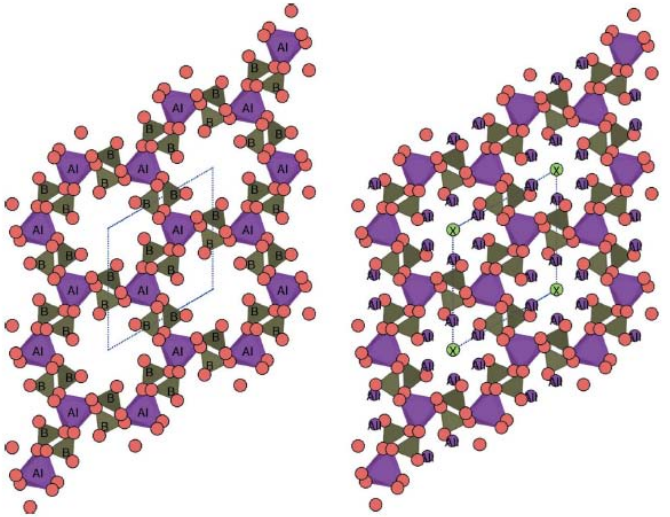


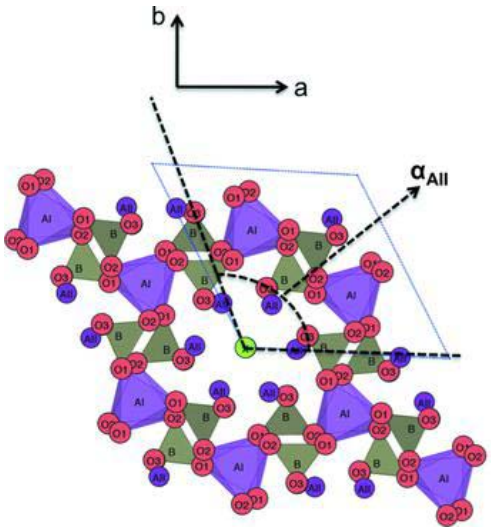

Ideker and Lauffenburger: Trends in Biotechnology (2003)

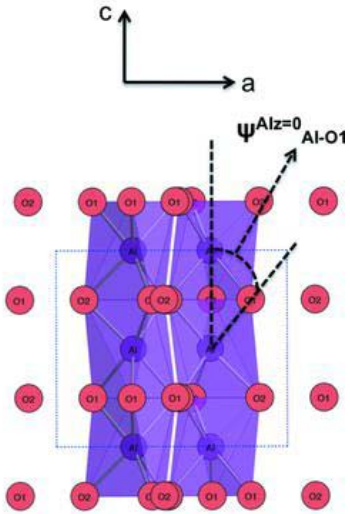

# Structure maps for $A^{I}_{4}A^{II}_{6}(BO_4)_6X_2$ apatite compounds *via* data mining

Prasanna V. Balachandran and
Krishna Rajan*

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





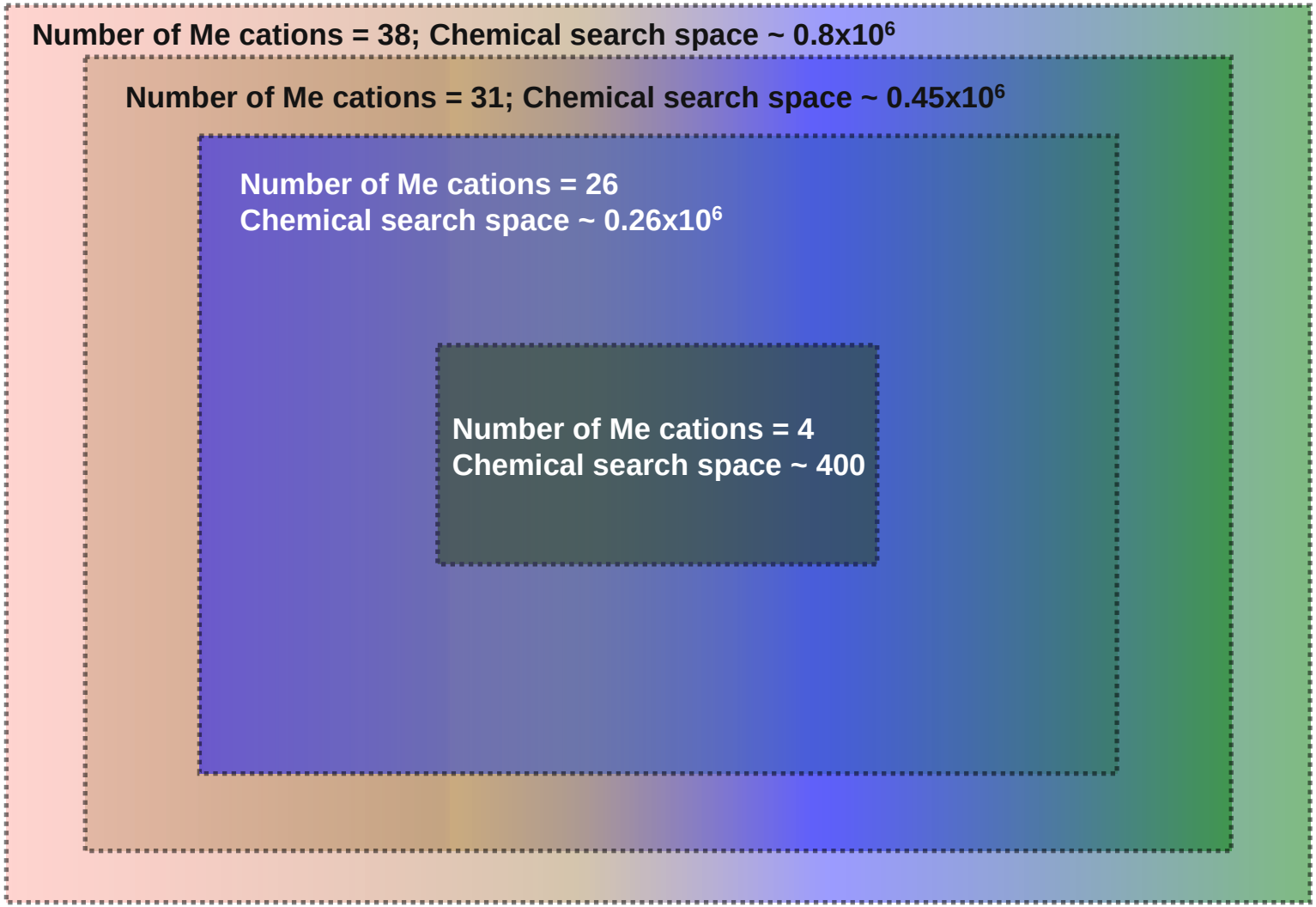



# Chemical search space for informatics

**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.

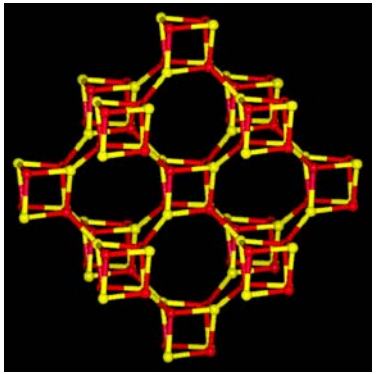
Krishna Rajan

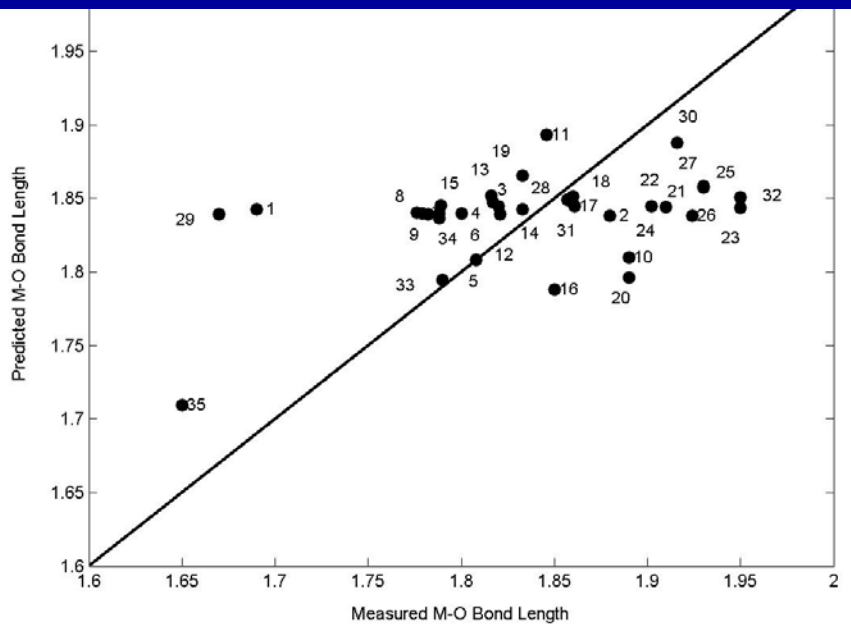
# Materials parameters and nanotoxicty

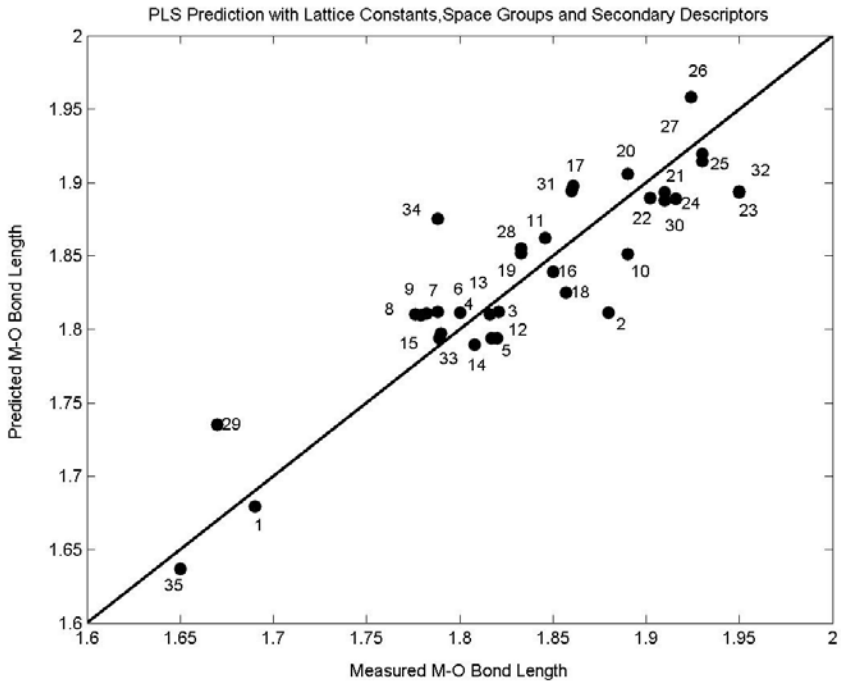
| Descriptor | Brief description |
|---|---|
| $a$ (Å) | Lattice constant of the hexagonal unit cell |
| $c$ (Å) | Lattice constant of the hexagonal unit cell |
| $c/a$ | Variable axial ratio (no unit) |
| $r_{AI}$ (Å) | Shannon's ionic radii of $A^{I}$-site ion (nine-coordination) |
| $r_{B}$ (Å) | 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 |

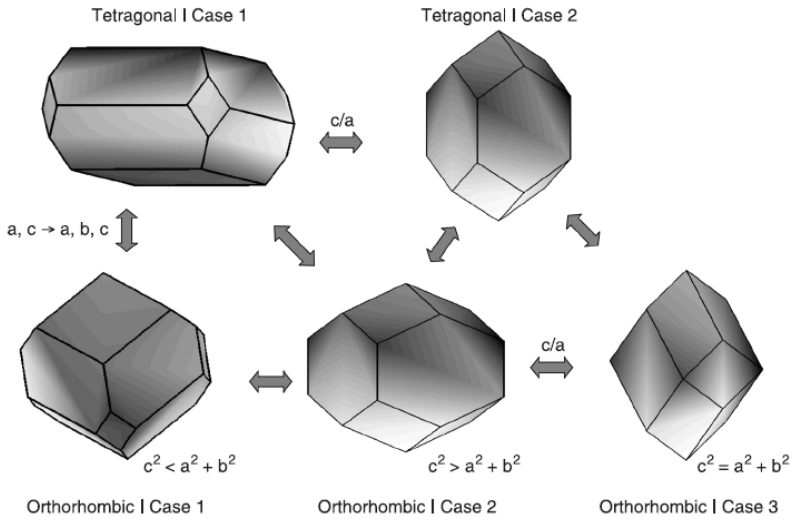
| Descriptor | Brief description |
|---|---|
| $A^{I}$—O1 (Å) | Distance between $A^{I}$ and O1 atom |
| $A^{I}$—O1$^{AIz=0}$ (Å) | Distance between $A^{I}$ and O1 atom with the constraint $z = 0$ at $A^{I}$ |
| $\Delta_{AI-O}$ (Å) | Difference in the lengths $A^{I}$—O1 and $A^{I}$—O2 |
| $\Delta_{AI-O}^{AIz=0}$ (Å) | Difference in the lengths $A^{I}$—O1 and $A^{I}$—O2 with the constraint $z = 0$ at $A^{I}$ |
| $\psi_{AI-O}$ (°) | 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 $A^{I}$ |
| $\delta_{AI}$ (°) | Counter-rotation angle of $A^{I}O_6$ structural unit |
| $\varphi_{AI}$ (°) | Metaprism twist angle ($\pi/3 - 2\delta_{AI}$) |
| $\alpha_{AI}$ (°) | 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 |
| $\rho_{AII}$ (Å) | $A^{II}$—$A^{II}$ triangular side length |
| $A^{II}$—$X$ (Å) | Distance between $A^{II}$ and $X$ atom |
| $\alpha_{AII}$ (°) | 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



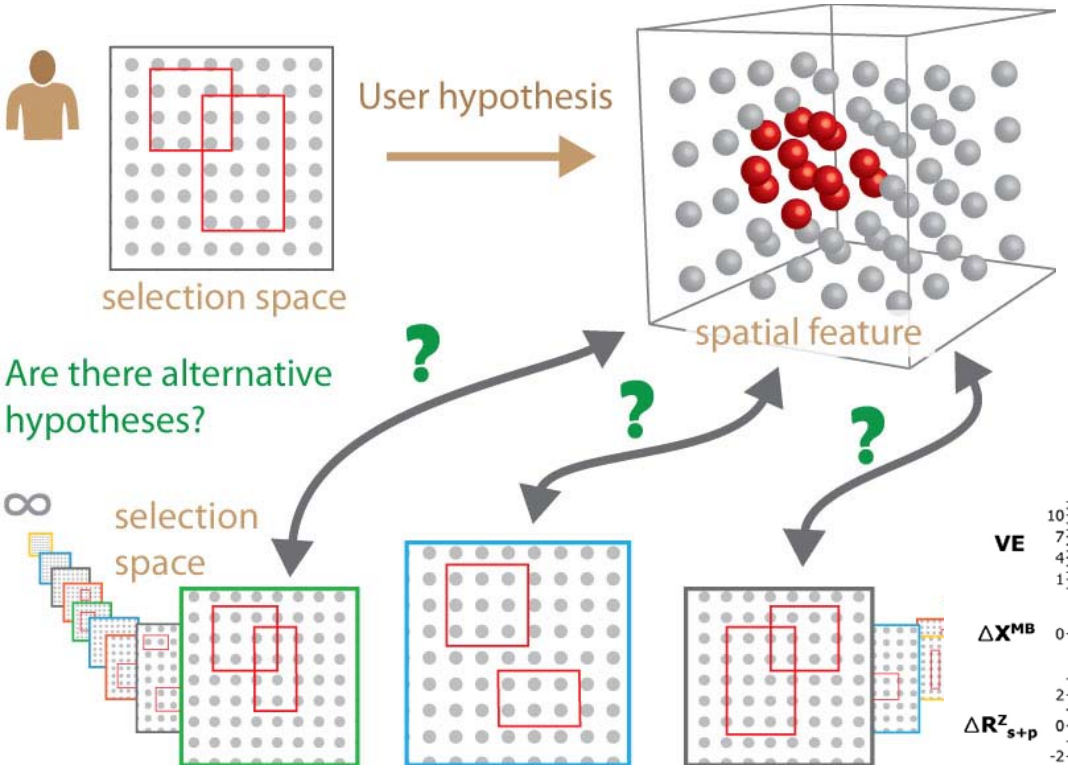


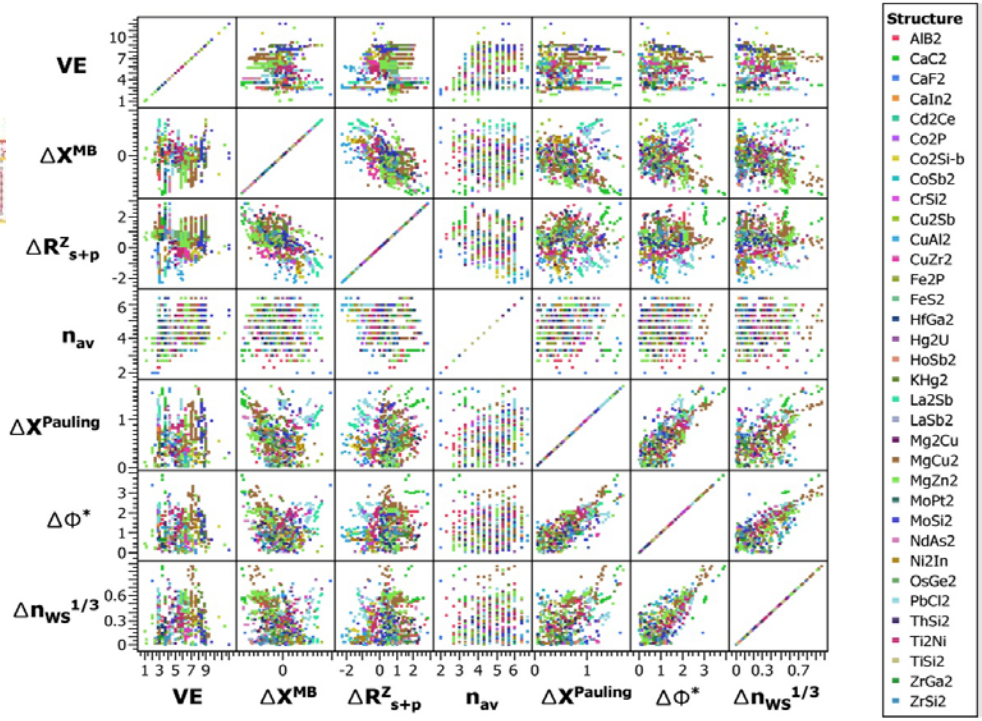

Rajagopalan & Rajan (2005)

# Dimensionality and Complexity

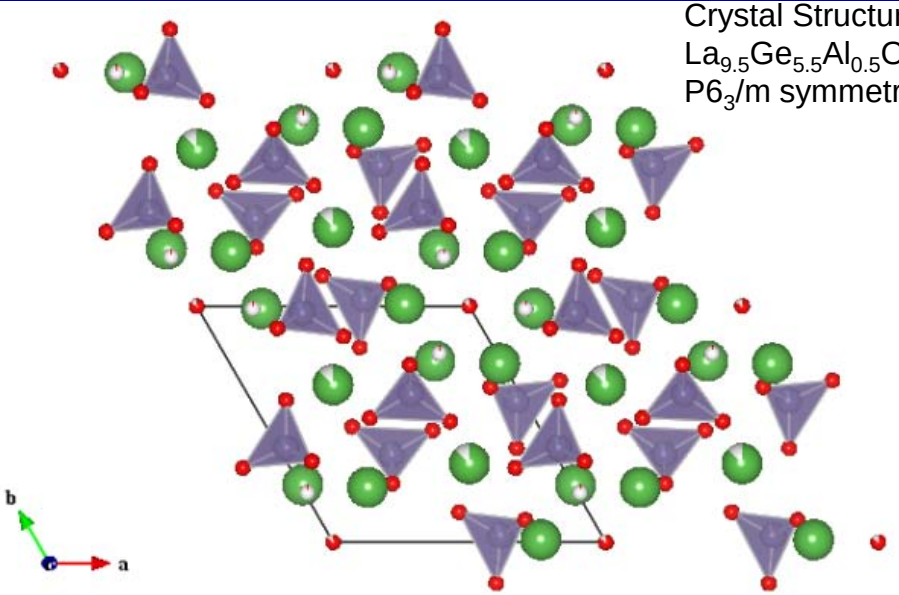



## N point correlation

Kong & Rajan- 2009/ 2012



# Searching an informatics based combinatorial space



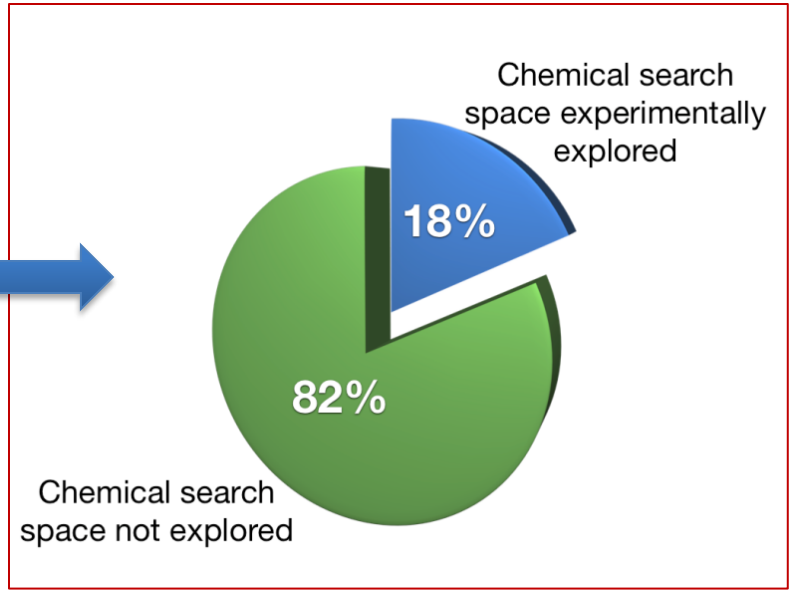

Crystal Structure of $La_{9.5}Ge_{5.5}Al_{0.5}O_{26}$ Apatite – $P6_3/m$ symmetry

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

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

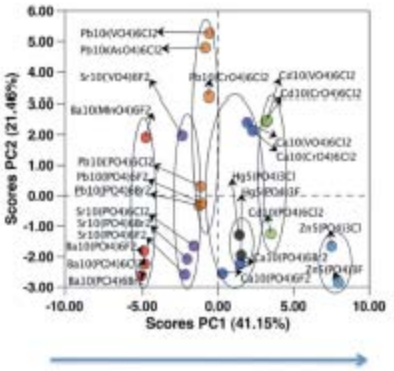
**Total possibilities:**

**~ 10,000 chemical compositions**



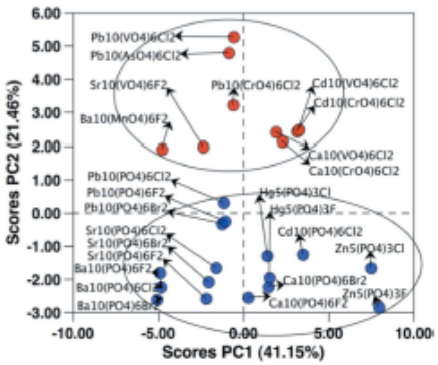

Blachandran & Rajan (2012)

# Classification: Structure-Chemistry relationships

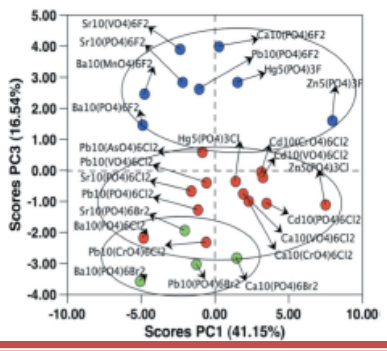


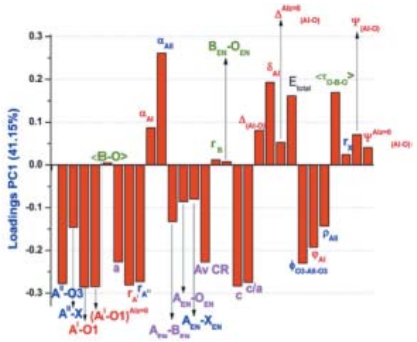

Ionic radius of A-site element decreases in this direction

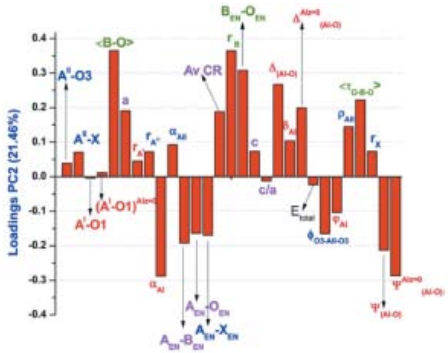
Ionic radius of B-site element decreases in this direction

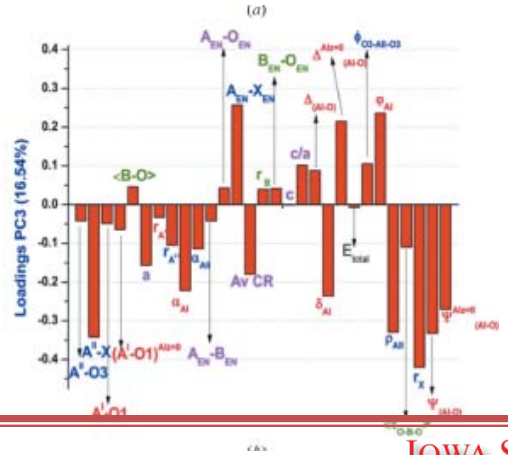



Ionic radius of X-site element decreases in this direction

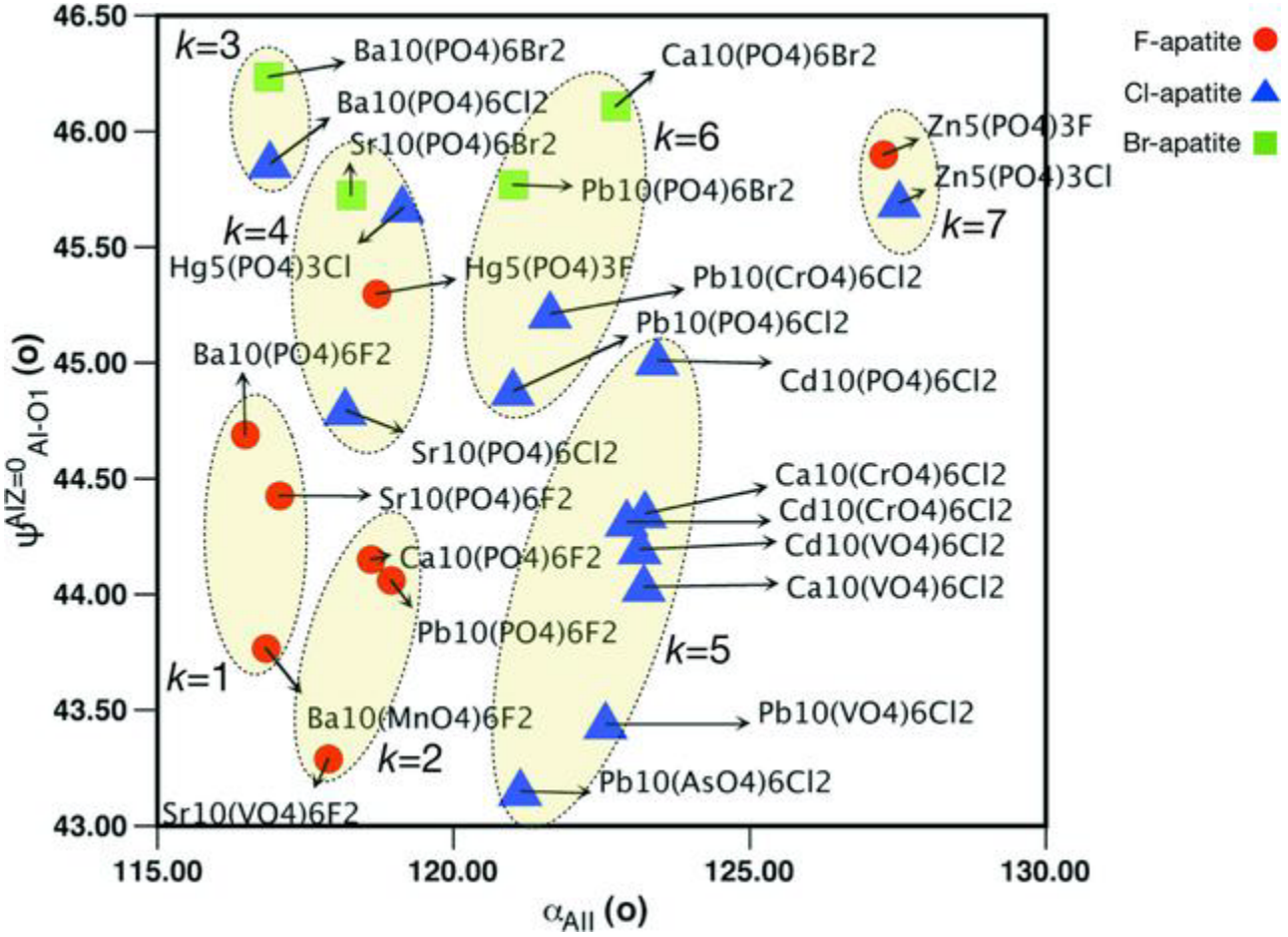


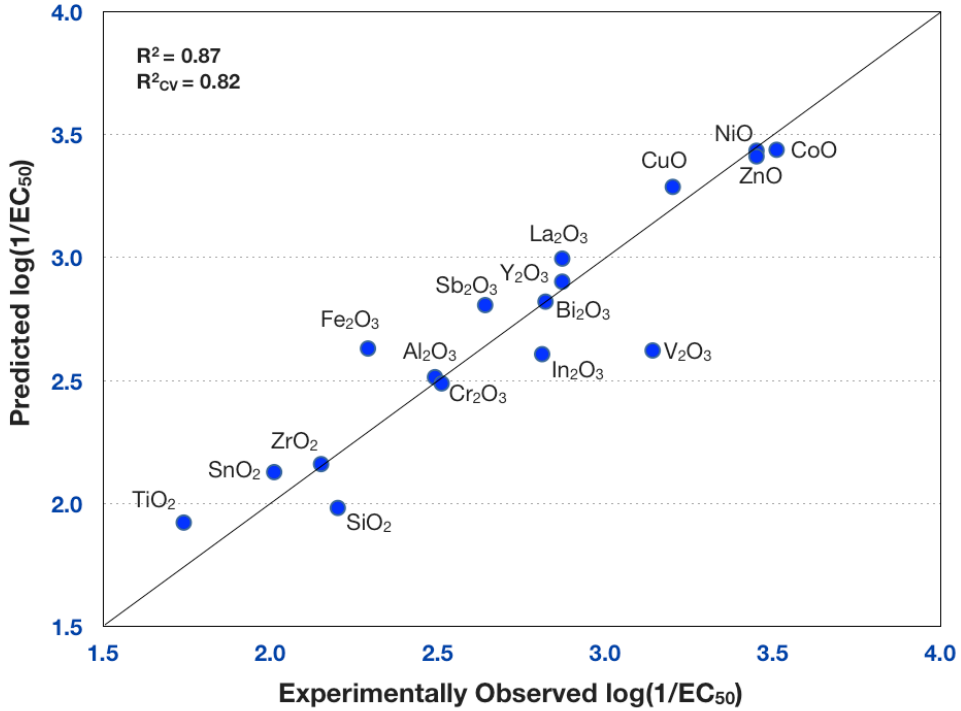



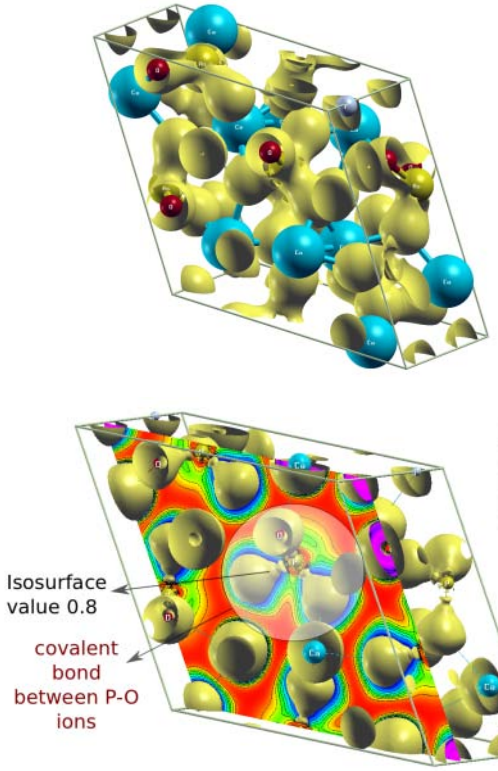



# Chemical design



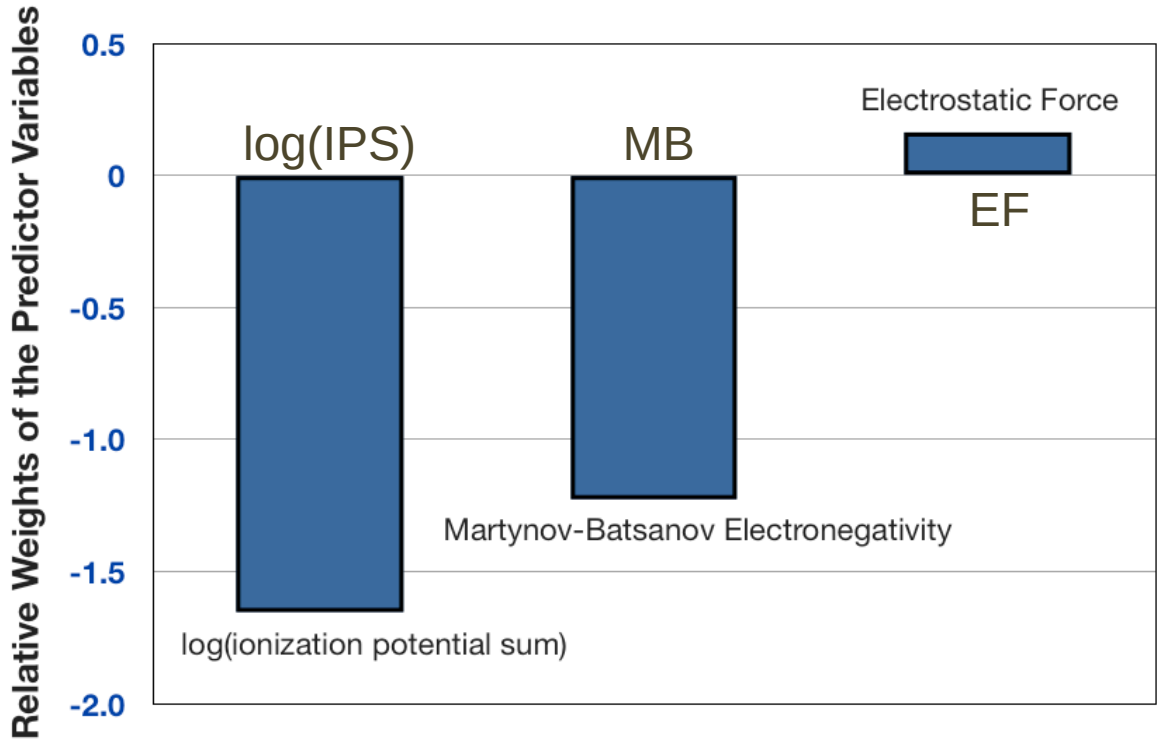
# Predictive Nanotoxicology




| 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].*

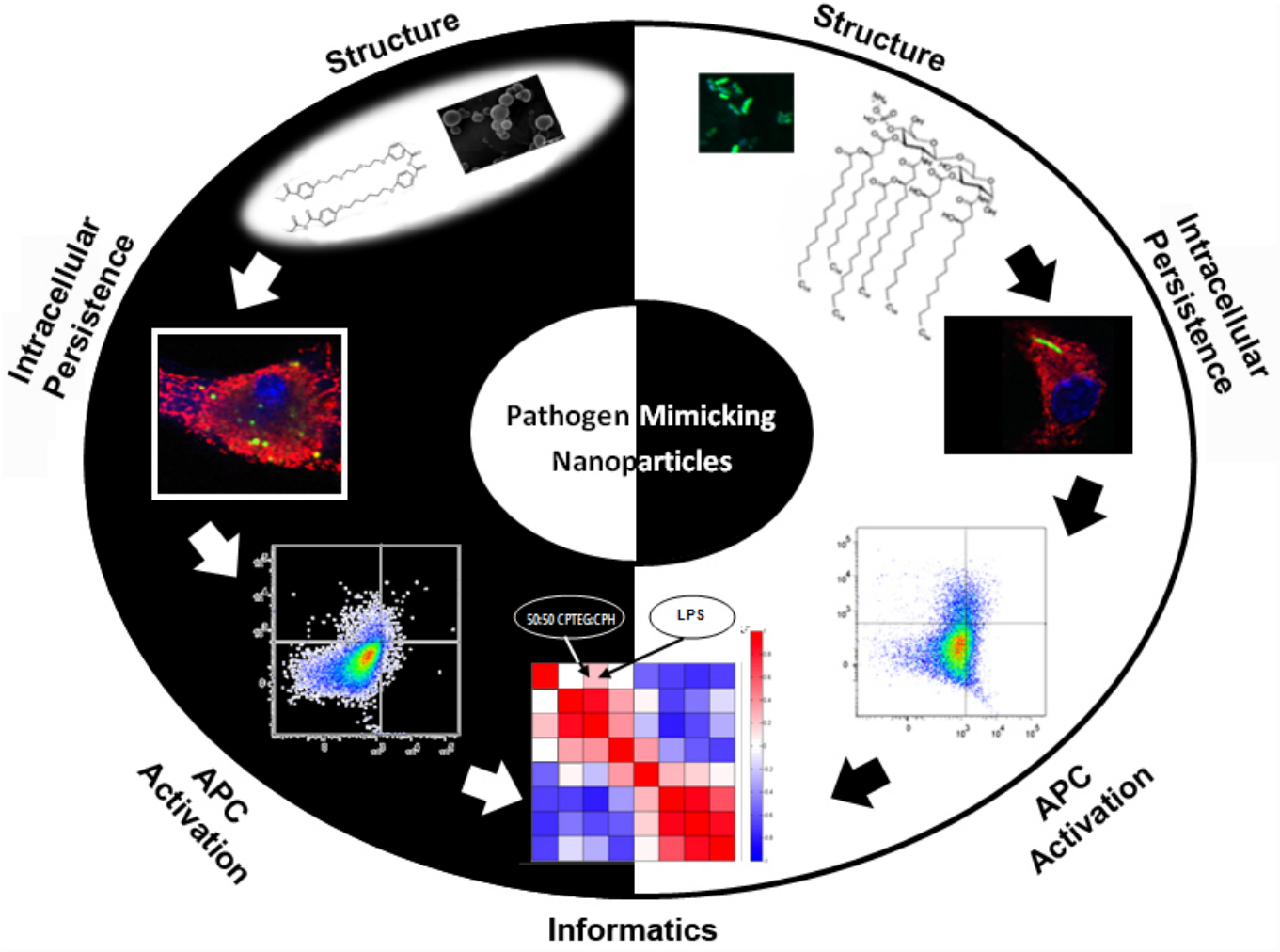
❖*MB electronegativity describes bonding associated with the relative ability of an atom in a nanoparticle to attract valence electrons [2].*

❖*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 !!**