In Quest of a Systematic Framework For Unifying and Defining Nanoscience

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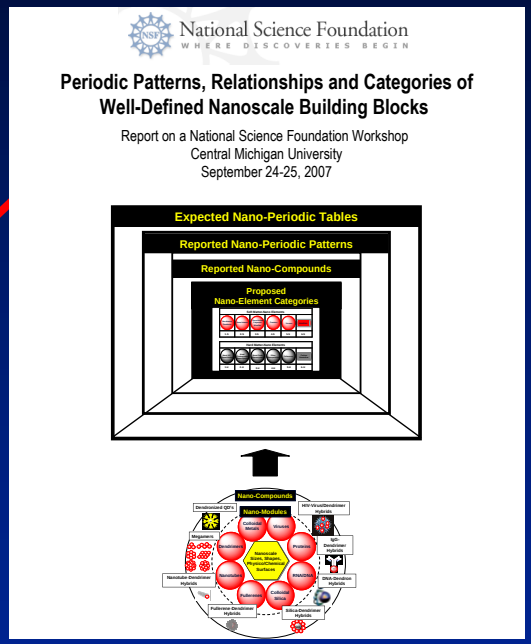
National Science Foundation
WHERE DISCOVERIES BEGIN

Periodic Patterns, Relationships and Categories of Well-Defined Nanoscale Building Blocks

Report on a National Science Foundation Workshop
Central Michigan University
September 24-25, 2007

CMU
CENTRAL MICHIGAN UNIVERSITY

Newly Established Ph.D. Program –(2008) Nanotechnology/ Science of Advanced Materials

http://www.nsf.gov/crssprgm/nano/GC_Charact08_Tomalia_nsf9_29_08.pdf

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The Concept

A systematic framework is proposed for unifying and defining nanoscience.

This systematic framework is based on the same "first principles" initiated by Lavoisier, Dalton, Mendeleev and others that led to a "periodic system and central paradigm" for traditional elemental atom and small molecule chemistry.

I. Introduction
Background and Historical

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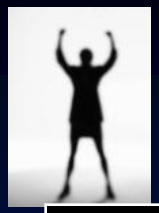
Brief Historical Overview



10^{0}

Macroscale

10^{-2}

10^{-3}

10^{-4}

10^{-5}

Microscale

10^{-6}

10^{-7}

Nanoscale

10^{-9}

10^{-10}

Picoscale

10^{-11}

10^{-12}

Nanostructures Assemblies

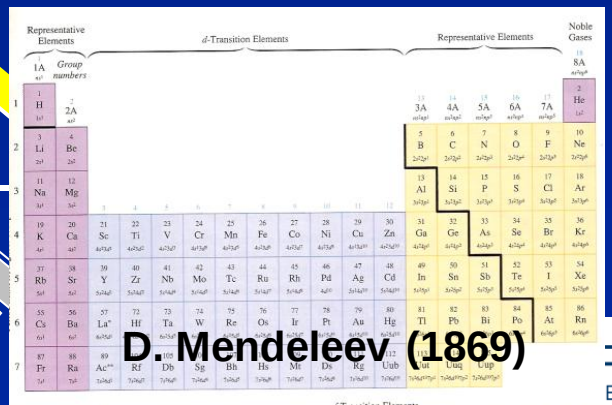
R. Feynman (1959)

Nano-Alchemy (1959-Present)

Molecular Structures

19th/20th Century Chemists/Physicists

Atom Periodicity



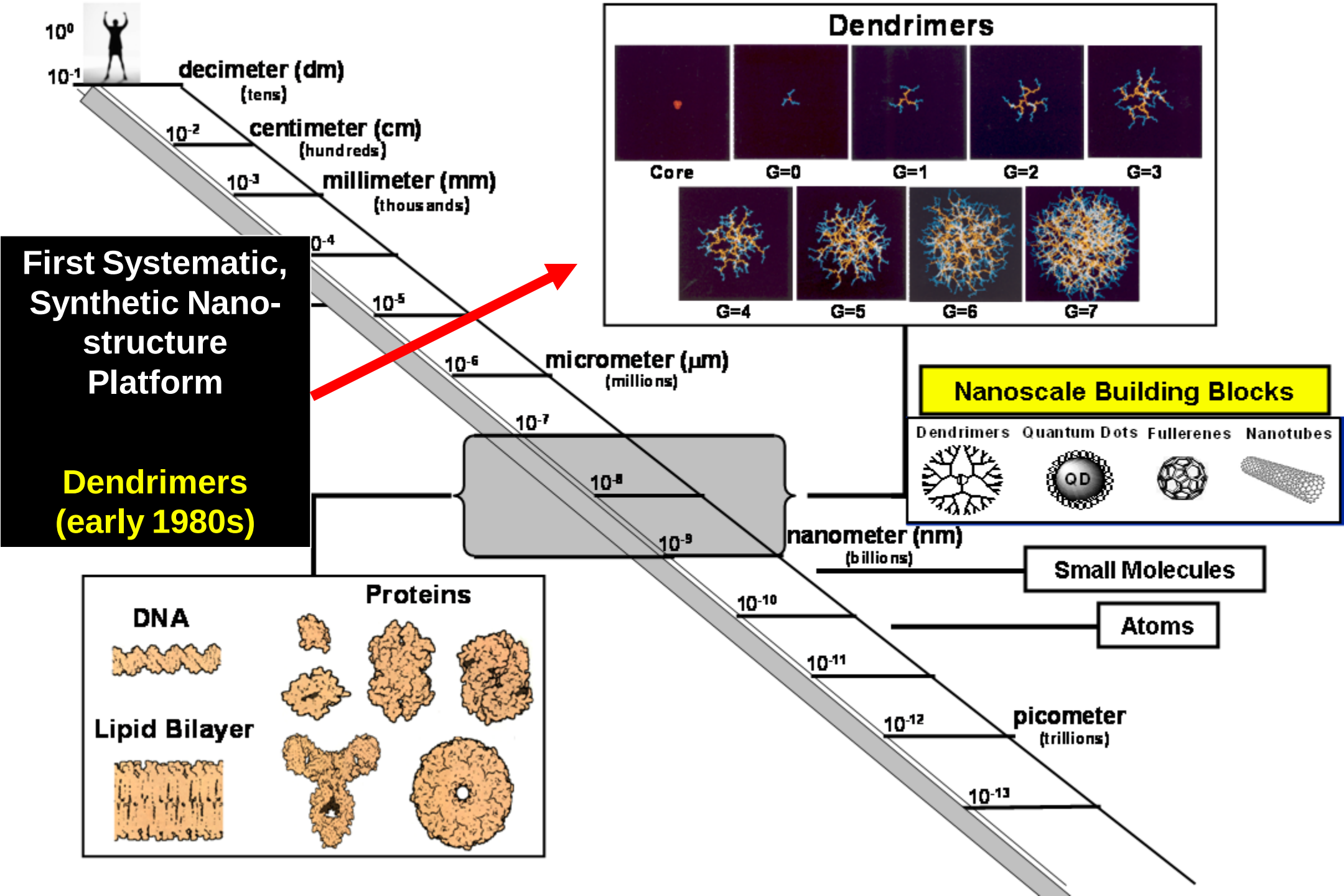
D. Mendeleev (1869)

Atoms

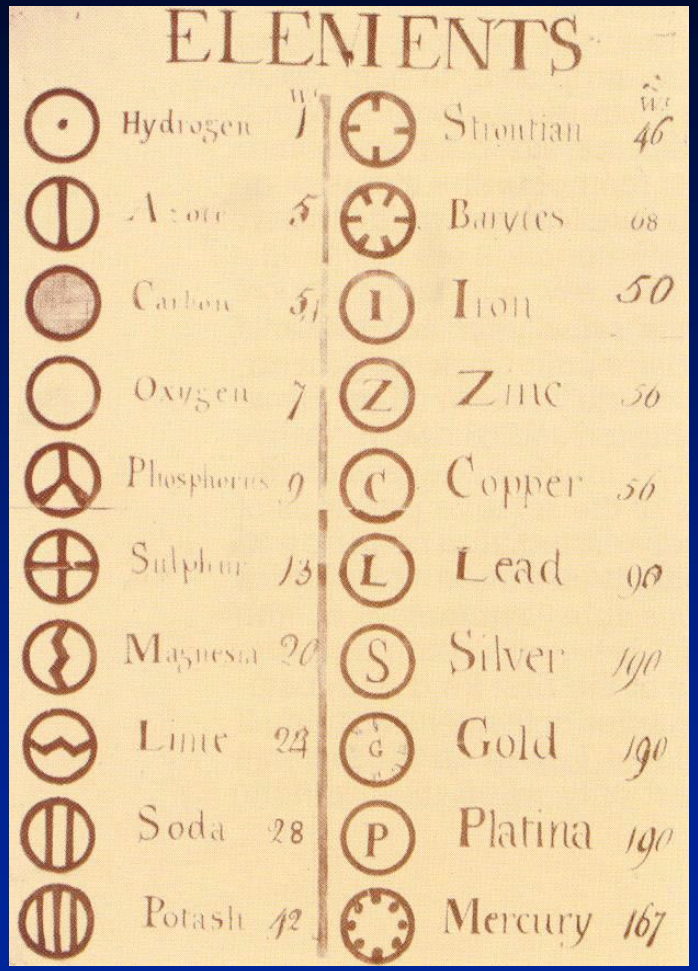
A. Lavoisier (1789)
J. Dalton (1808)

Alchemy

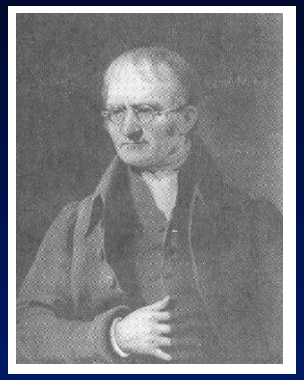
Pre-1789


First Systematic, Synthetic Nano-structure Platform
Dendrimers (early 1980s)
Dendrimers
Core
G=0
G=1
G=2
G=3
G=4
G=5
G=6
G=7
Nanoscale Building Blocks
Dendrimers
Quantum Dots
Fullerenes
Nanotubes
QD
Small Molecules
Atoms
DNA
Proteins
Lipid Bilayer
10^{0}
10^{-1}
decimeter (dm)
(tens)
10^{-2}
centimeter (cm)
(hundreds)
10^{-3}
millimeter (mm)
(thousands)
10^{-4}
10^{-5}
10^{-6}
micrometer (µm)
(millions)
10^{-7}
10^{-8}
10^{-9}
nanometer (nm)
(billions)
10^{-10}
10^{-11}
10^{-12}
picometer
(trillions)
10^{-13}

Traditional Chemistry – "Central Dogma" First Principles

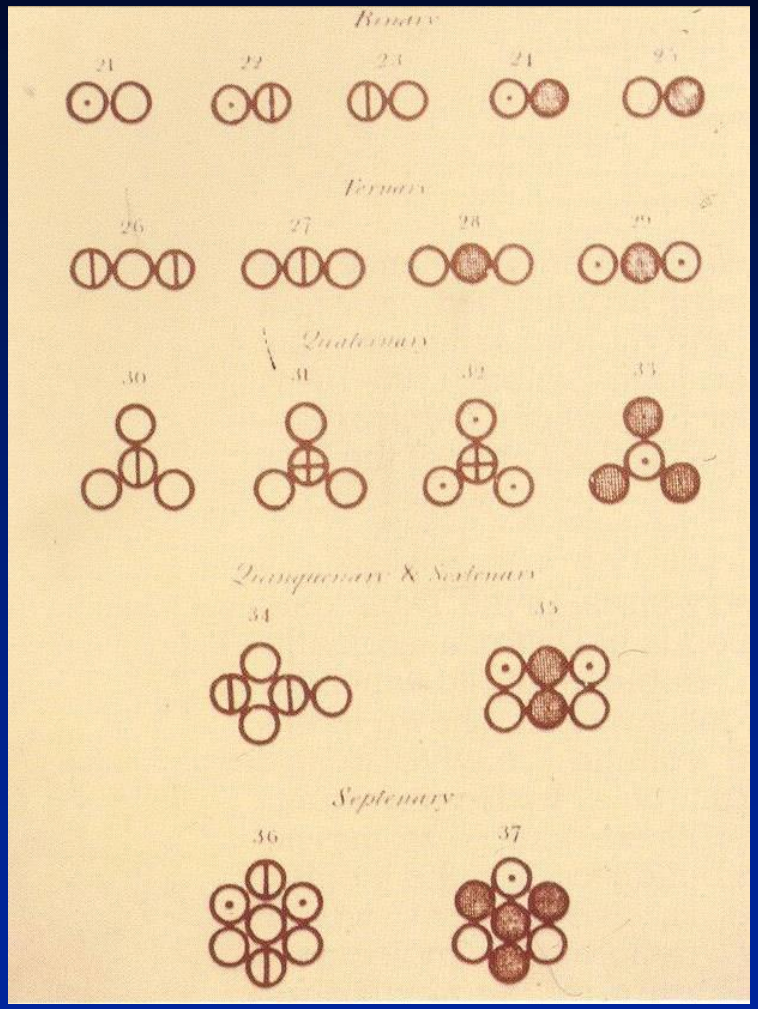


Atoms



John Dalton
(1808)

- Atoms Form Chemical Bonds
- Atoms Bond with Discrete Stoichiometries, Valency and Combining Weights
- Atoms Bond with Discrete Directionality
- Atoms Exhibit Periodic Properties



Compound Atoms

Atom Mimicry:

(a) Core-Shell Architecture
(b) Outer Shell Reactivity

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Comparison of Atoms with Hard and Soft Nanoparticles

Picoscale Matter (Atoms)

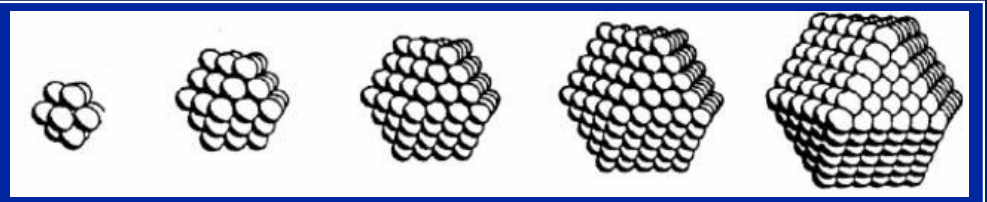
Elements Exhibiting Noble Gas Configurations

Shell Components n (Electrons)

	He	Ne	Ar	Kr	Xe
Electron shell levels:	1	2	3	4	5
Diameters:	.064 nm	.138 nm	.194 nm	.220nm	.260 nm
Saturation values (n):	2	10	18	36	54
Atomic weights:	4.00	20.17	39.94	83.80	131.30

Hard Nano-Matter (Gold Nanoclusters)

Full-Shell "Magic Number" Clusters

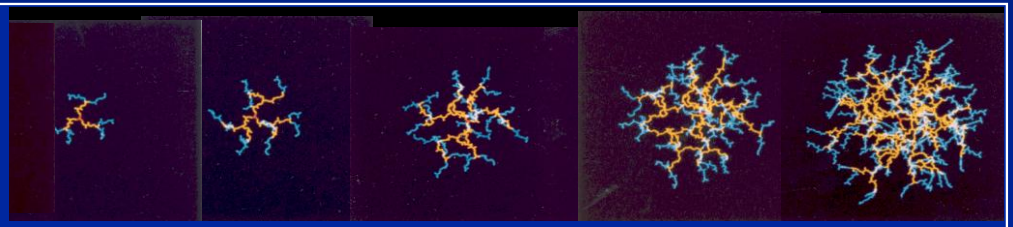


Shell Components n (Au Atoms)

Atom shell levels:	1	2	3	4	5
Diameters:	.864 nm	1.44 nm	2.02 nm	2.59 nm	3.17 nm
Saturation values (n):	12	54	146	308	560
Nano-cluster weights:	2560	10833	28953	60861	110495

Soft Nano-Matter (Dendrimers)

Saturated Monomer Shells



Shell Components n (Monomers)

Monomer shell levels:	G=1	G=2	G=3	G=4	G=5
Diameters:	1.58 nm	2.2 nm	3.10 nm	4.0 nm	5.3 nm
Saturation values (n):	9	21	45	93	189
Nanostructure weights:	144	2414	5154	10632	21591

D.A. Tomalia, *J. of Nanoparticle Research*, 11. 1251-1310 (2009)

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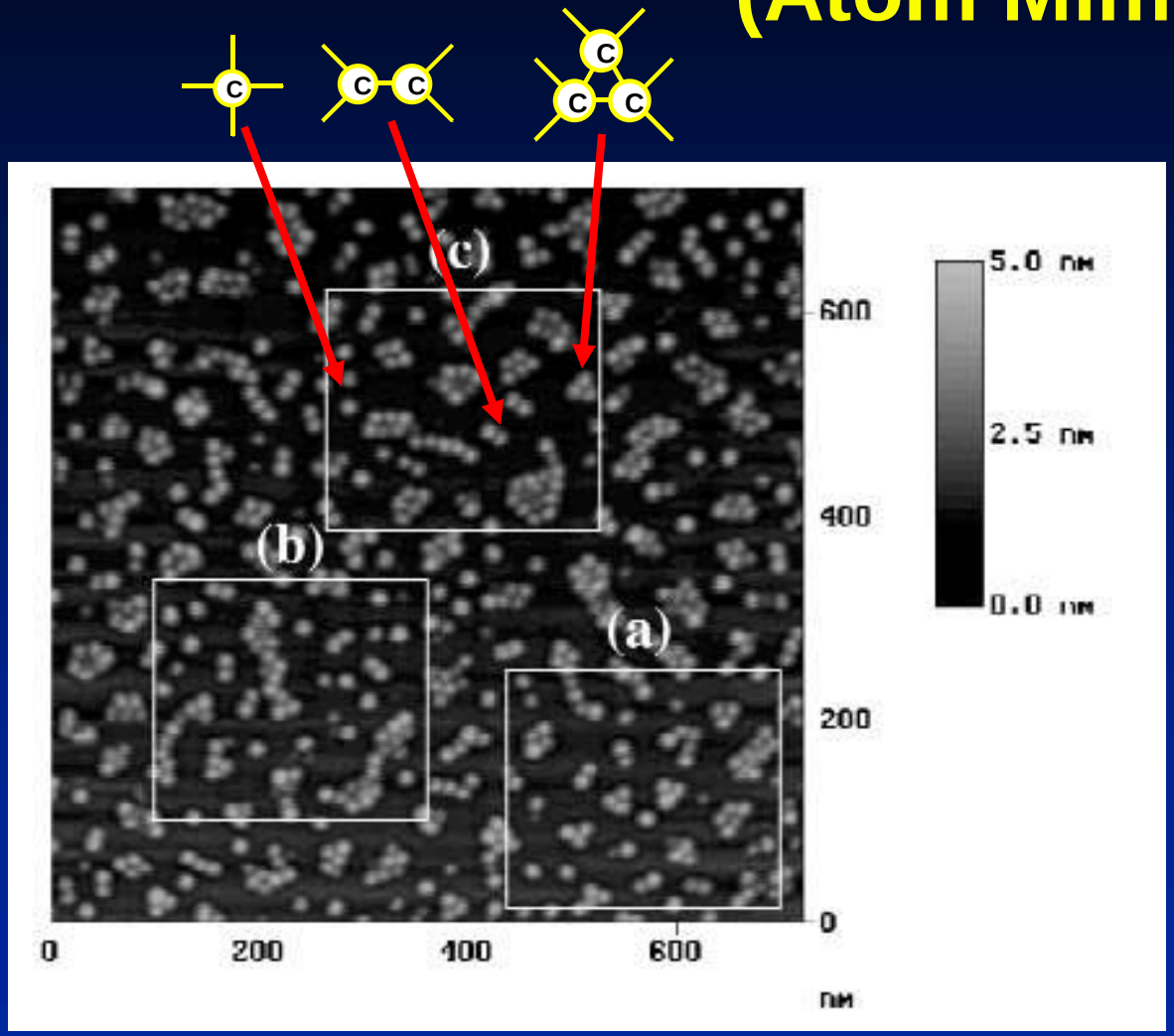
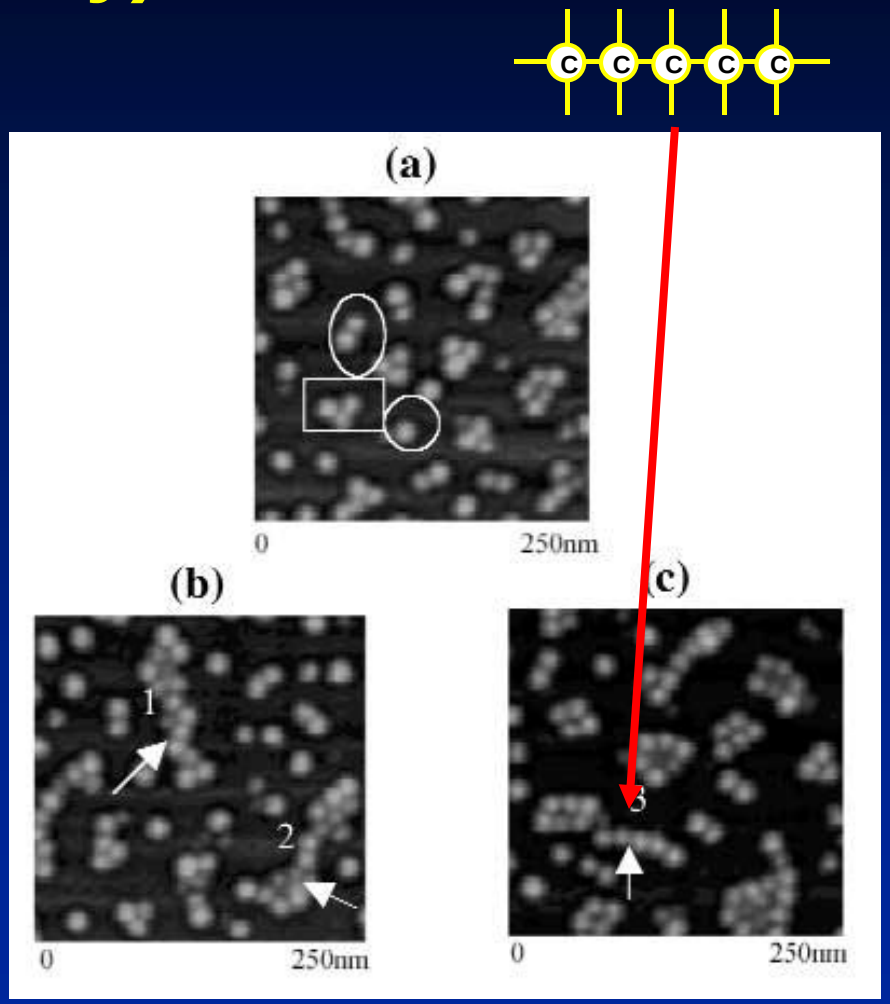
Self-Assembly of PAMAM Dendrimers (G9) (Atom Mimicry)





D.A. Tomalia, *et al., Pure and Applied Chem., 72*, 2343 (2000).

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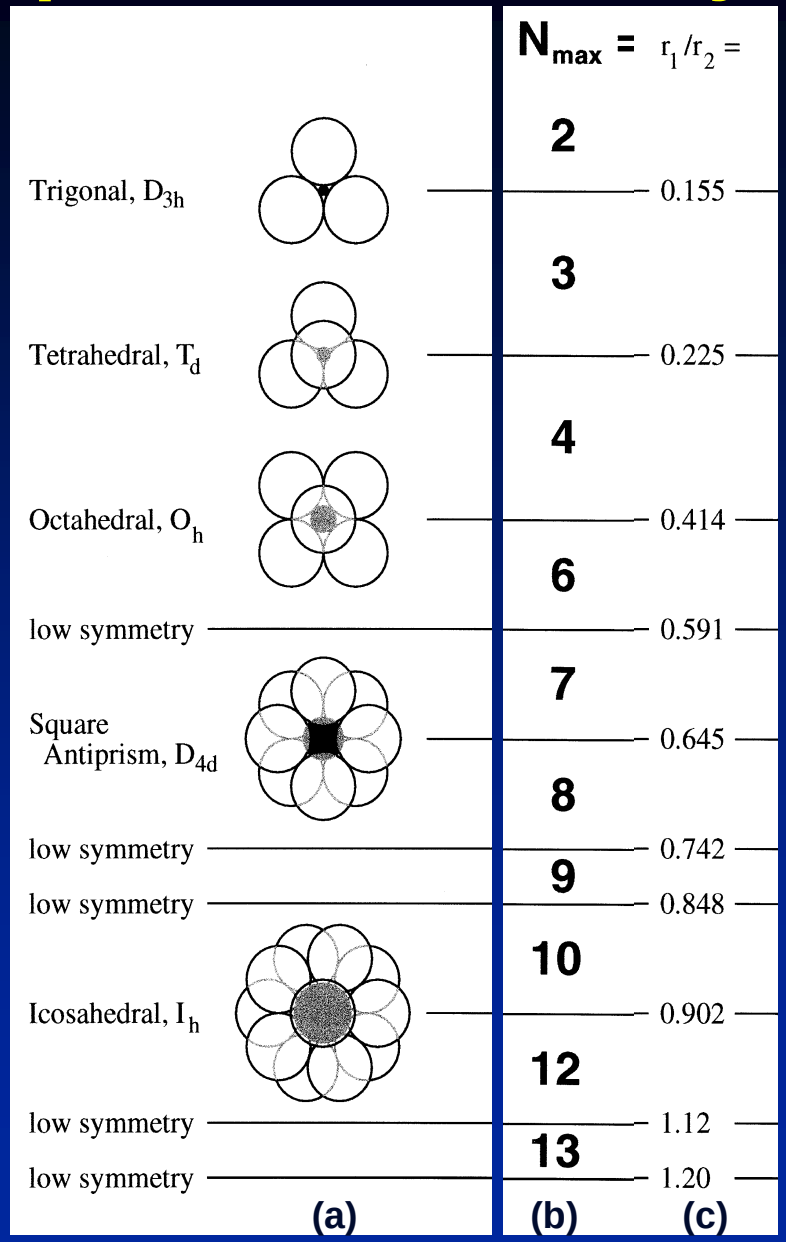
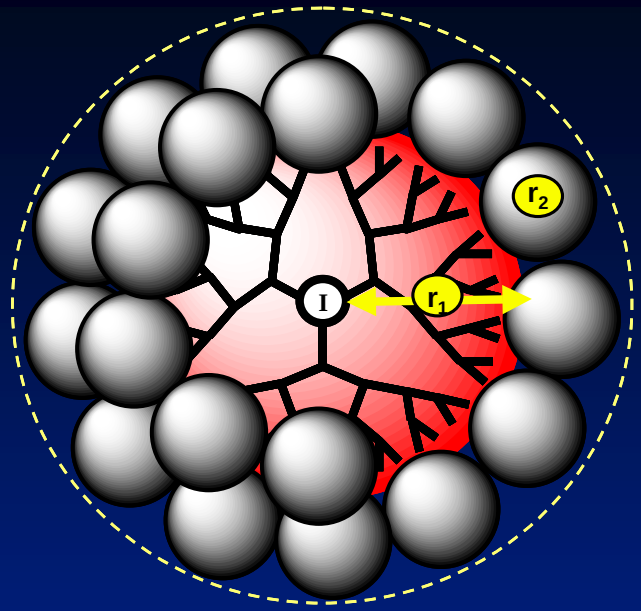
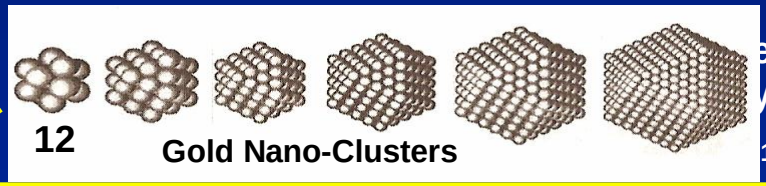
Spheroidal Valency Defined by Nano-Sterics





r_1 = radius of core dendrimer
r_2 = radius of shell dendrimer



Mansfield-Tomalia-Rakesh Equation

$$N_{max} = \frac{2\pi}{\sqrt{3}} \left(\frac{r_1}{r_2} + 1 \right)^2$$

When: $r_1/r_2 > 1.20$

D.A. Tomalia, et al., *J. Chem. Phys.* 105 (8), 3245 (1996).

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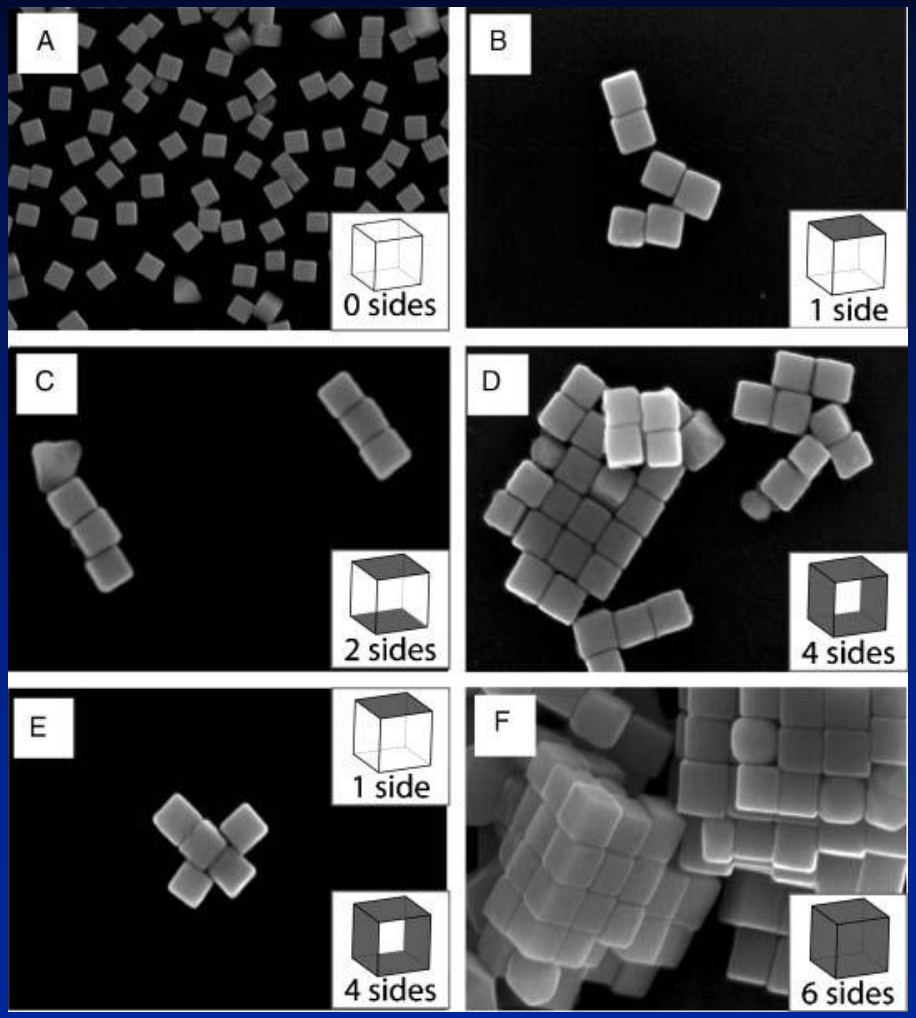
Nano-Element Valency :[H-1] type; [*Cubic*-$(Ag)_n$]

$[Metals]^0$ =

$-(CH_2)-_{n=3,4}$ =

CH_4 =



= H_2 , Cl_2, O_2

= 2-D Assembly

= 3-D Assembly

M. Rycenga, J. M. McLellan, Y. Xia; *Adv. Mater.*,(2008), 20, 2416-2420

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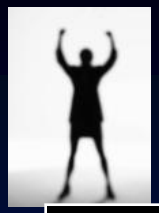
Critical Hierarchical Design Parameters



10^{0}

Macroscale

10^{-2}

10^{-3}

Conservation of Hierarchical Design Parameters?
(Atom → Molecular → Nano Structures)

Atom Mimicry

10^{-5}

Microscale

10^{-6}

10^{-7}

10^{-8}

10^{-9}

Nanoscale

10^{-10}

10^{-11}

Picoscale

10^{-12}

Architecture (Symmetry)

Size

Shape

Surface Chemistry

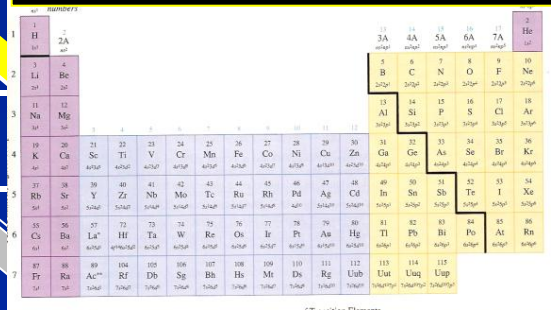
Flexibility

Nanostructures Assemblies
(CNDP)

Molecular Structures
(CMDP)

Atoms
(CADP)

Atom Periodicity



Conservation of Hierarchical Design Parameters?
(CADP → CMDP → CNDP)

Rudiementary Atomic Element Property Patterns Observed before Mendeleev

Physical Properties:

- ***Dependent on element mass (i.e., At. wt.)***

Chemical Properties:

- ***Dependent on element valency***

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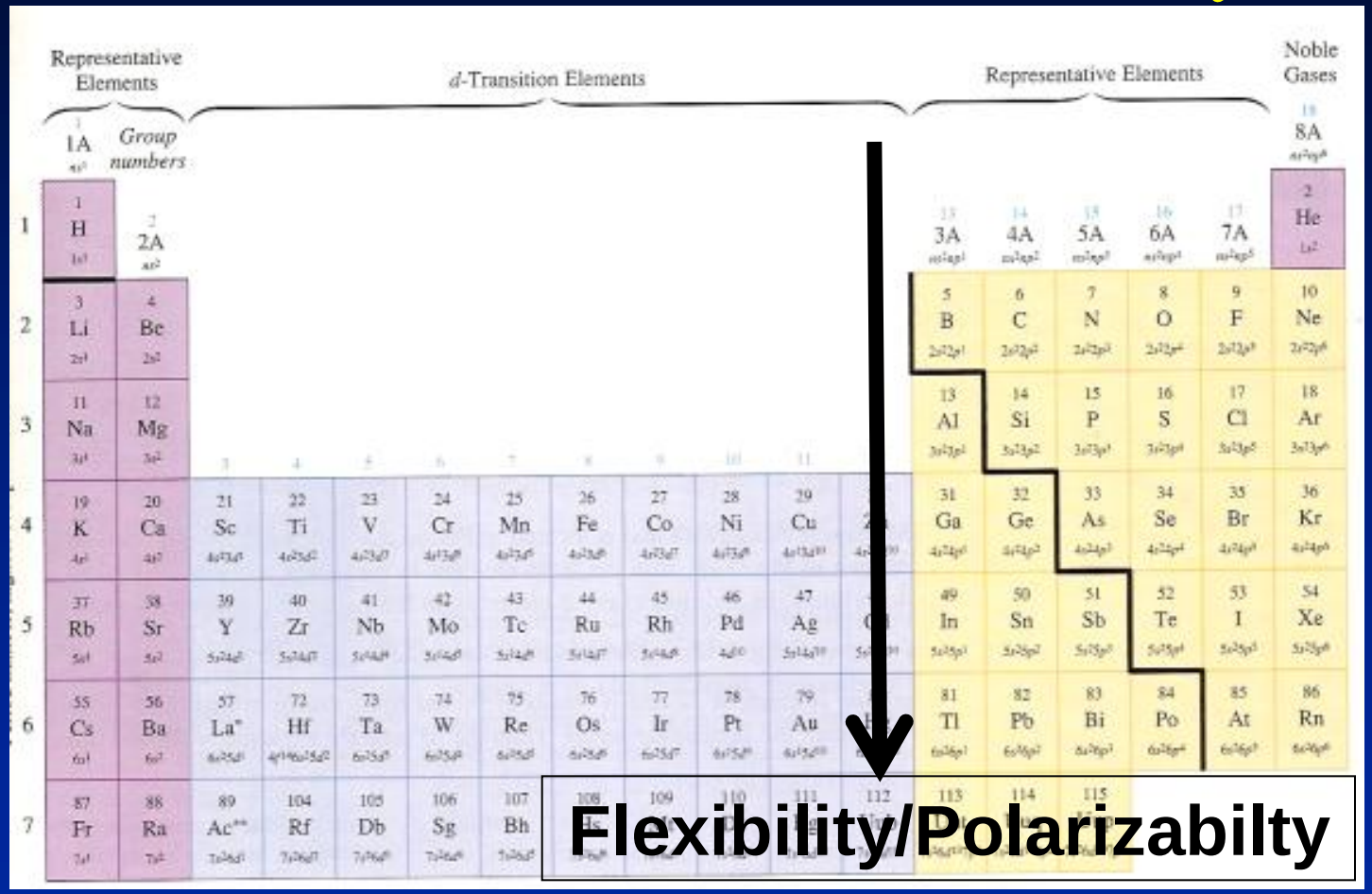
Critical Atomic Design Parameters (CADP's)

Reactive Surface Chemistry

Size



Inert

Shape

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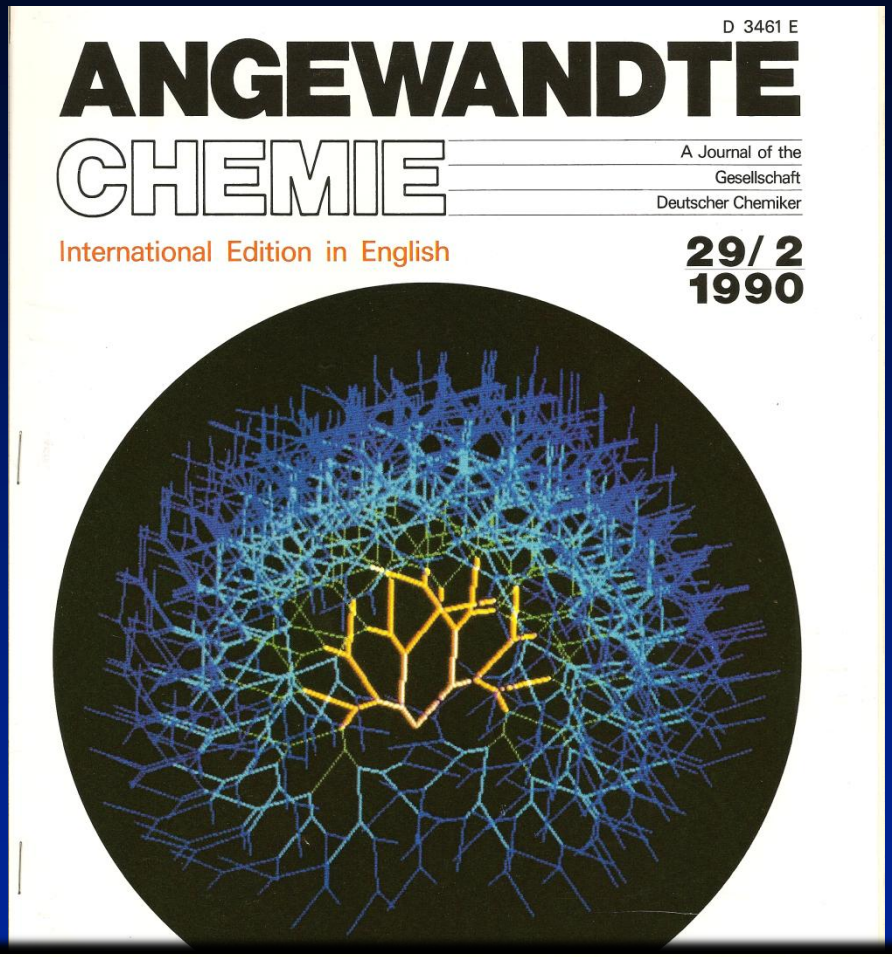
Critical Nanoscale Design Parameters (CNDP's)



Starburst Dendrimers:
Molecular-Level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter**

By Donald A. Tomalia,* Adel M. Naylor, and William A. Goddard III

ISI Citations
2126

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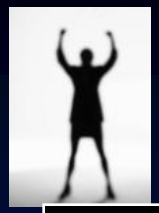
Critical Hierarchical Design Parameters



10^0 decimeter (dm) (tens)

Macroscale

10^{-2}

10^{-3}

Atom Mimicry

Microscale

10^{-6}

10^{-7}

10^{-8}

10^{-9}

Nanoscale

10^{-10}

10^{-11}

Picoscale

10^{-12}

Architecture (Symmetry)

Size

Shape

Surface Chemistry

Flexibility

Nanostructures Assemblies

(CNDP)

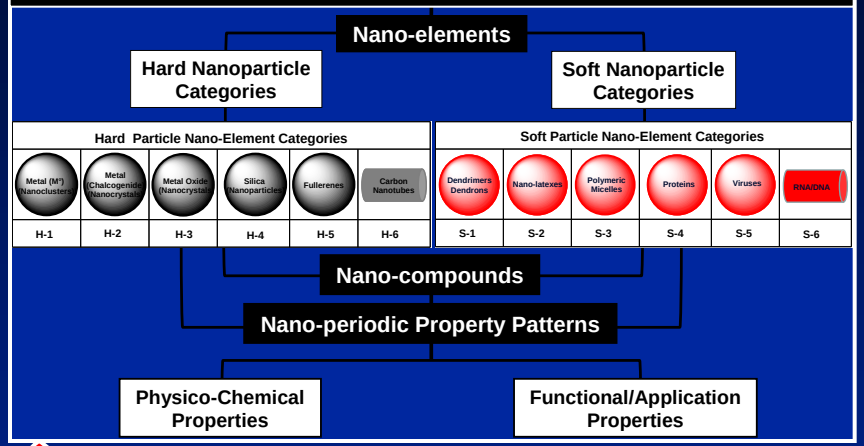
Molecular Structures

(CMDP)

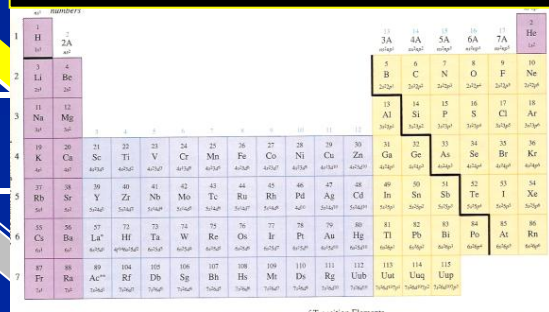
Atoms

(CADP)

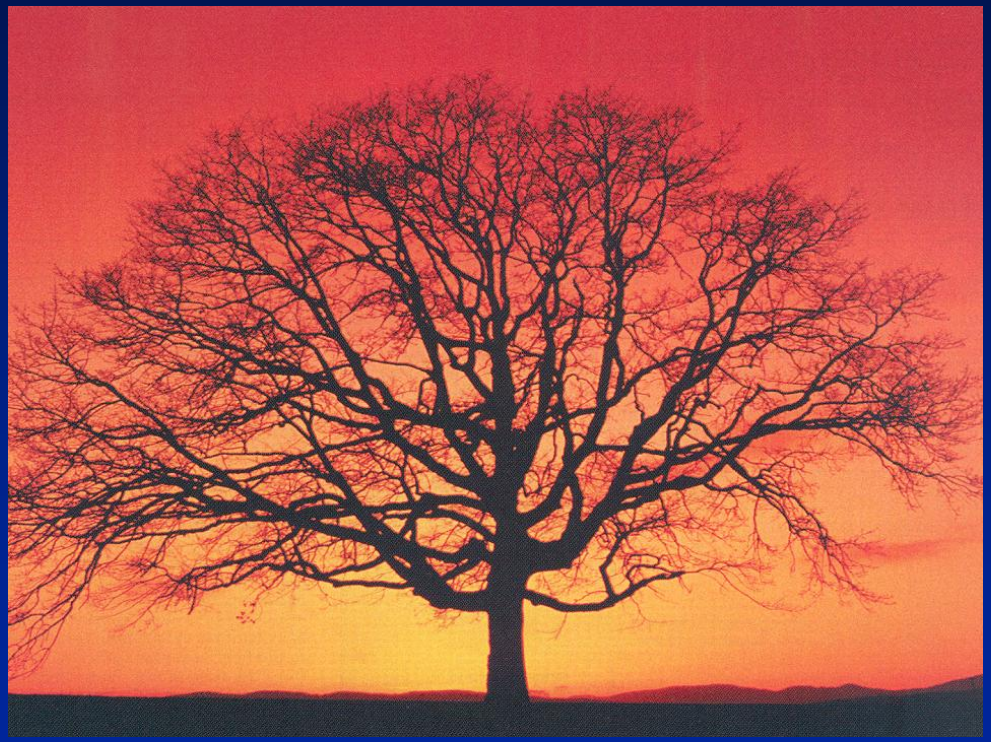
Nano-Periodicity



Atom Periodicity



II.
Proposed Nanomaterials Classification Roadmap



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Nano-Element (Module) Categories (Selection Criteria)

1. **Exhibit Well-Defined Monodispersity:**

   (>90% monodisperse as a function of size and/or mass)

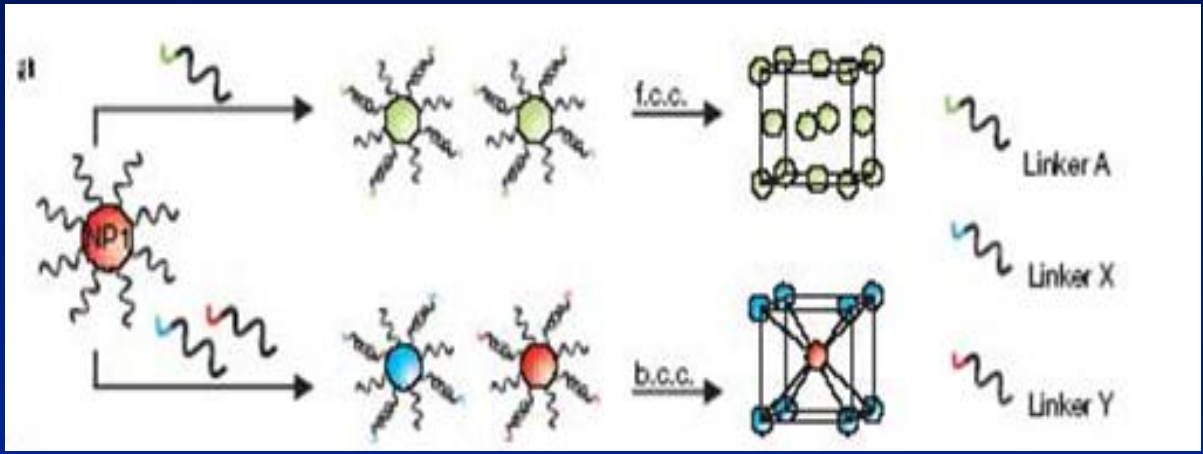
2. **Well-Defined Nanostructures, Assemblies or Particles that Mimic / Behave Like Atoms:**

   (They react, assemble and exhibit controlled Critical Nanoscale Design Parameter (CNDP) properties as a unit.)

3. **Exhibit Well-Defined Stoichiometries and Mass Combining Ratios**

4. **Exhibit Nano-Periodic Property Patterns**

Monodispersity Criteria:
Atom-Like, 3-D Nano-cluster Super Lattices



>90% monodisperse gold nanoclusters required to obtain well defined X-ray patterns

S.Y. Park, C. Mirkin et al., *Nature*, 451, 553-556 (2008).

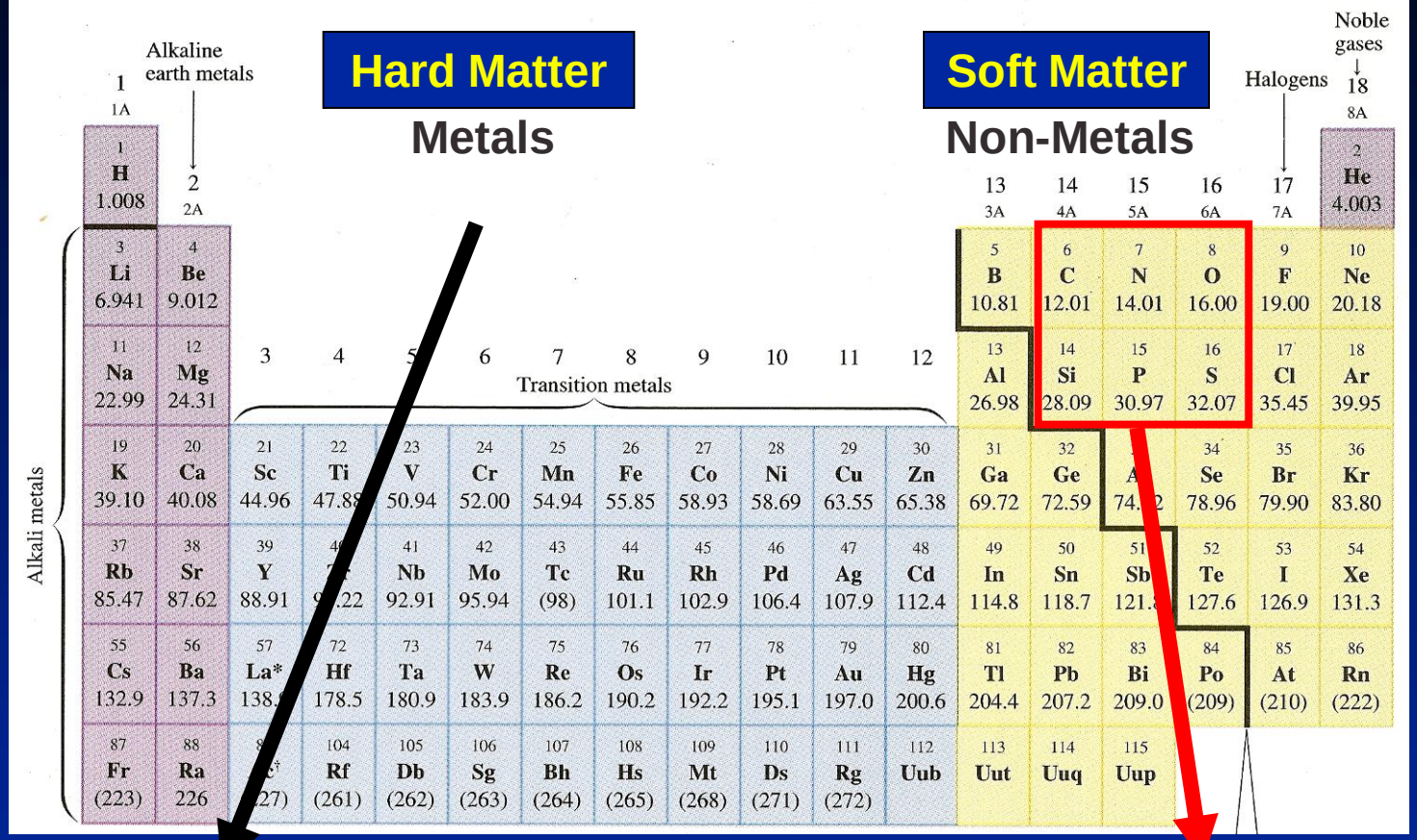
Periodic Table of the Elements

Hard Matter

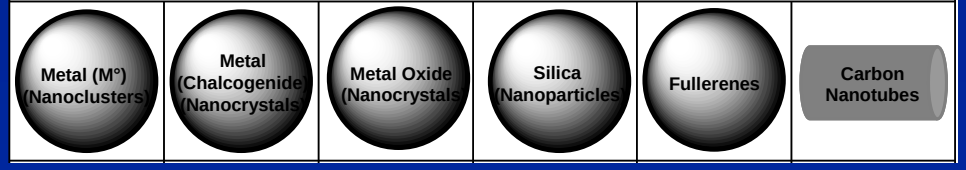
Metals

Soft Matter

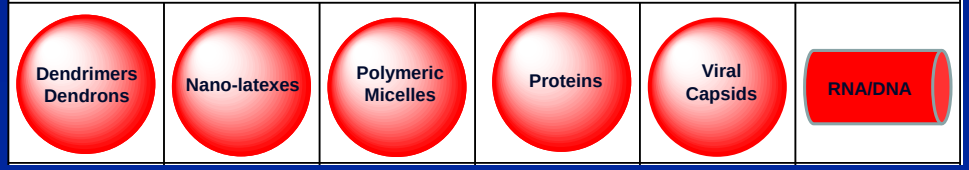
Non-Metals



HARD PARTICLE NANO-ELEMENT CATEGORIES



SOFT PARTICLE NANO-ELEMENT CATEGORIES



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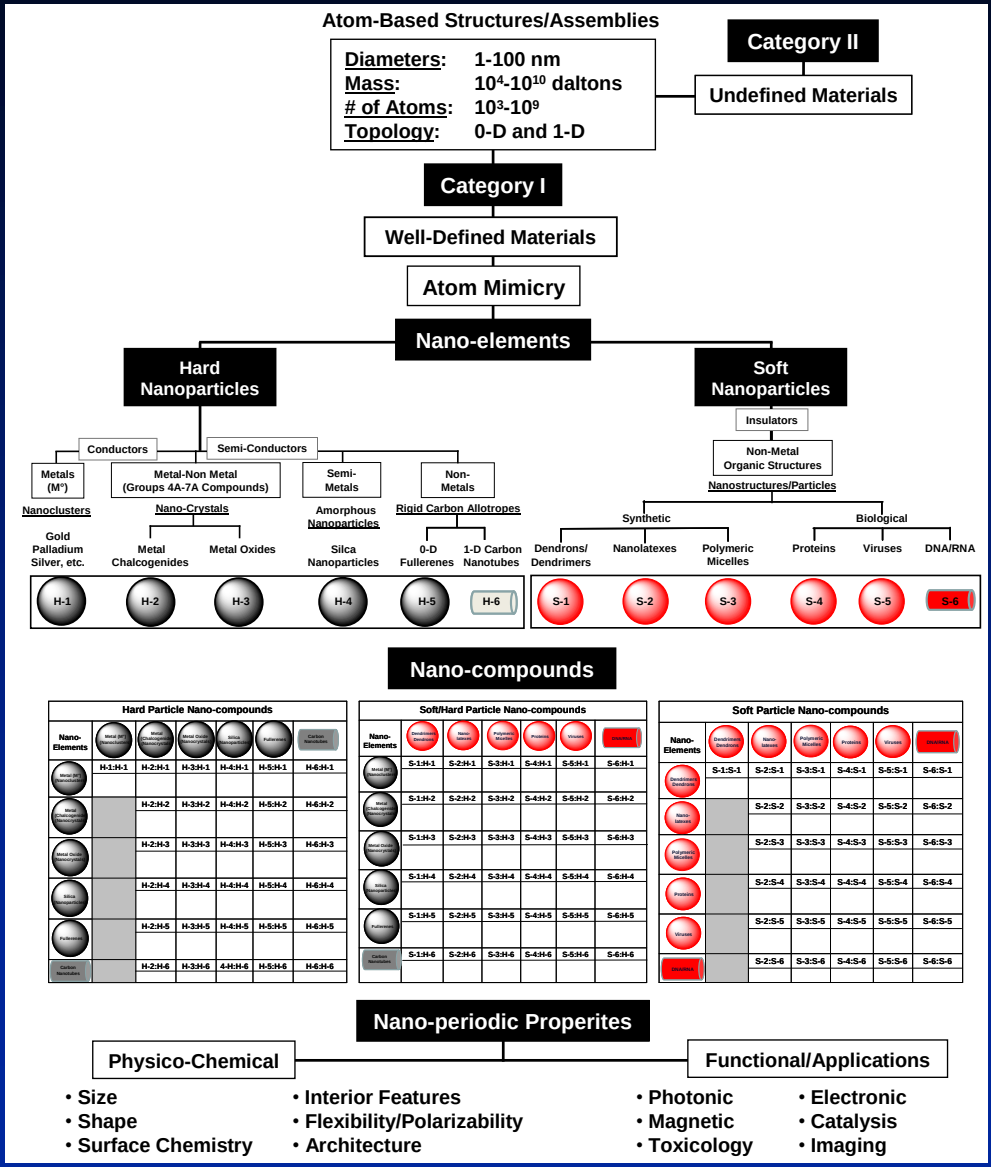
Nanomaterials Classification Roadmap



J. of Nanoparticle Research, 11, 1251-1310 (2009).

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Abbreviated Nanomaterials Classification Roadmap

Nanomaterials

Size:	1-100 nm
# Atoms:	10^3-10^9 atoms
Mass:	10^4-10^{10} daltons

Category I

Well Defined
Monodisperse
a) size
b) mass

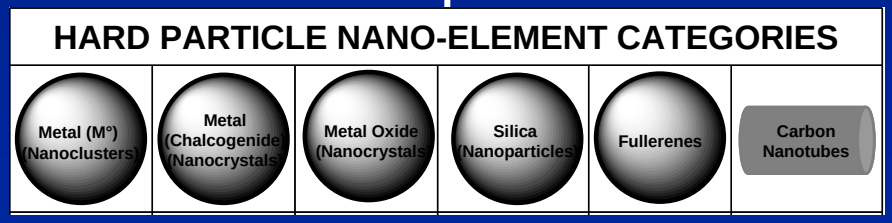
Category II

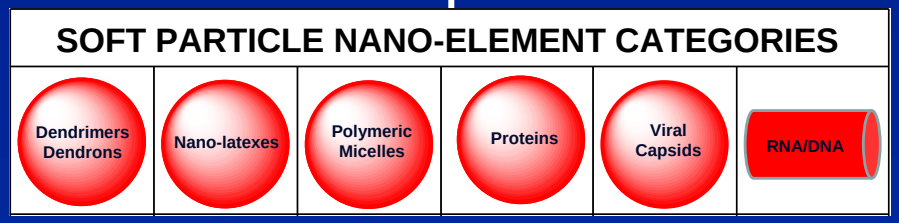
Undefined
Statistically Polydisperse
a) size
b) mass

Atom Mimicry

Hard Nanoparticle Categories

Soft Nanoparticle Categories





J. of Nanoparticle Research, 11, 1251-1310 (2009).

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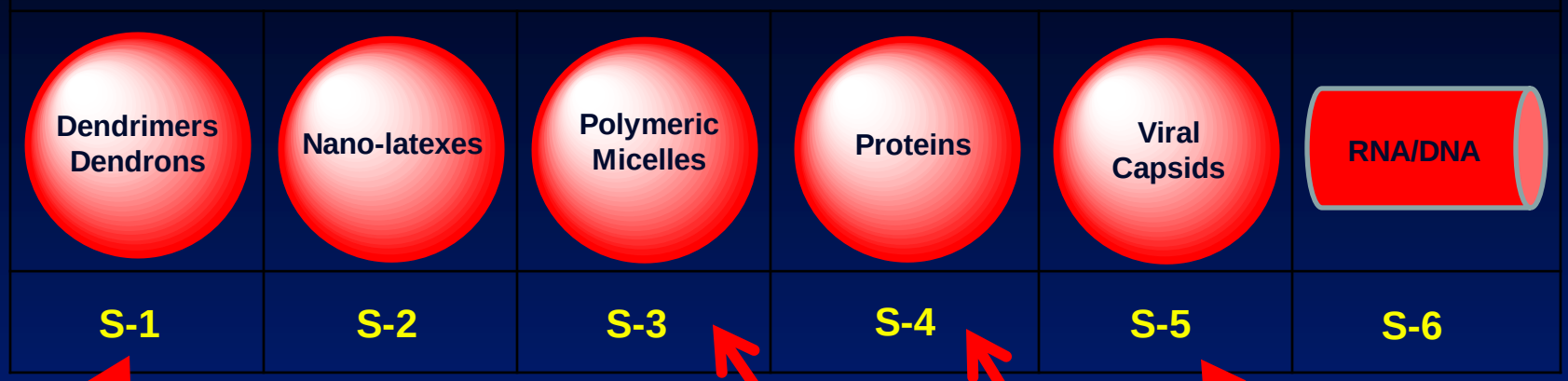
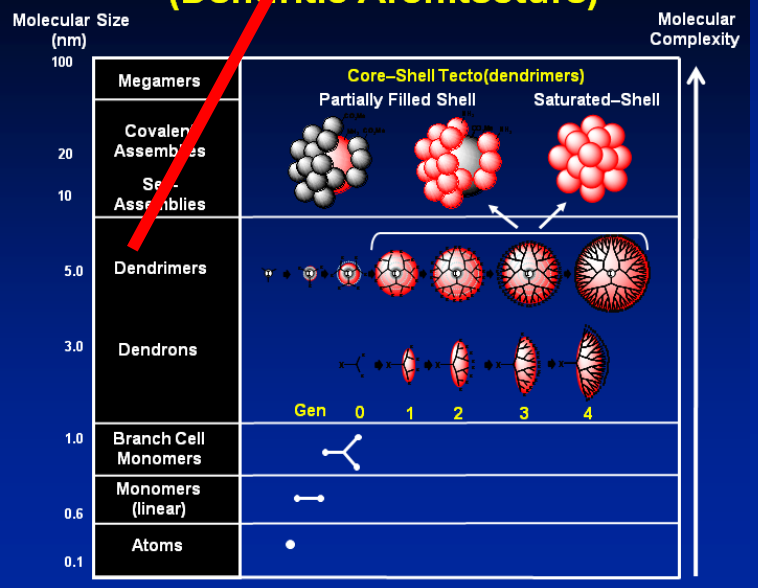
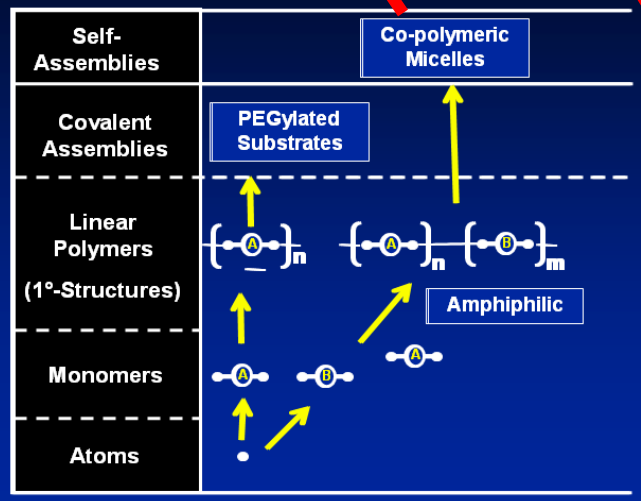
SOFT PARTICLE NANO-ELEMENT CATEGORIES



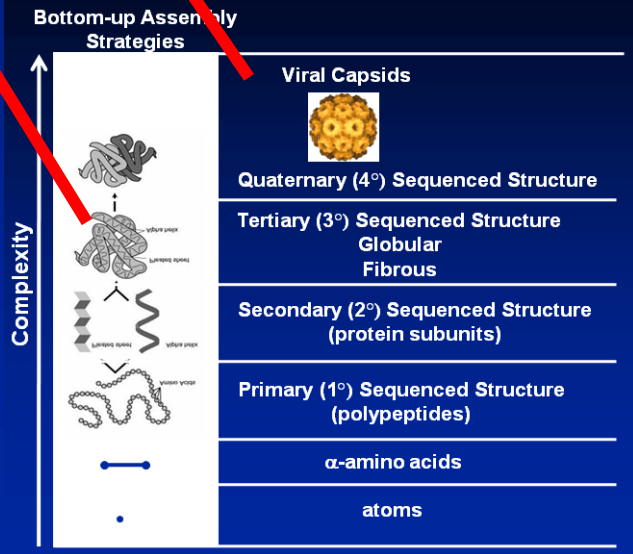
Synthetic Polymers (Dendritic Architecture)



Synthetic Polymers (Linear Architecture)



Bio-Polymers (Linear Architecture)



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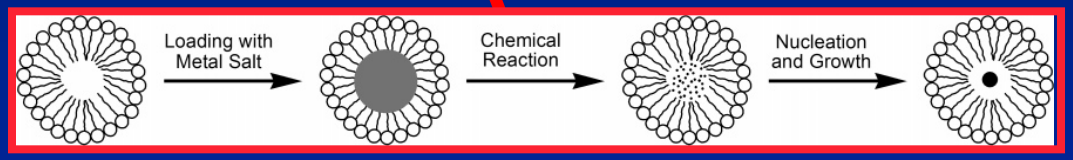
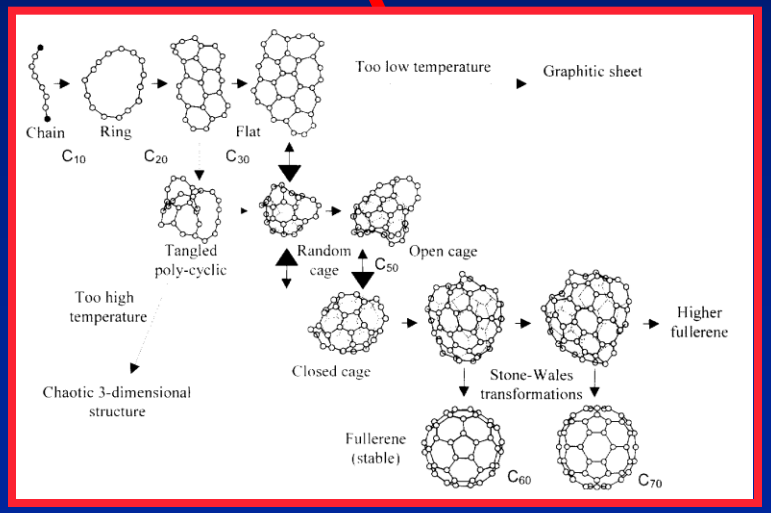
Hard Particle Nano-Element Categories

Metal (M°) (Nanoclusters)	Metal (Chalcogenide) (Nanocrystals)	Metal Oxide (Nanocrystals)	Silica (Nanoparticles)	Fullerenes	Carbon Nanotubes
H-1	H-2	H-3	H-4	H-5	H-6





J.P. Wilcoxon, et al., *Chem. Soc. Rev.* 35, 1161-1194 (2006).

S. Maruyama, Y. Yamaguchi, *Chemical Physics Letters*, 286, 343-349 (1998).

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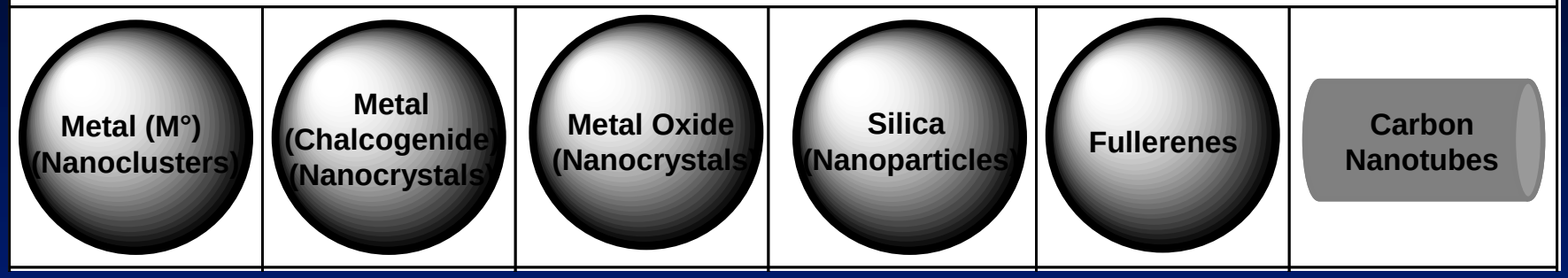
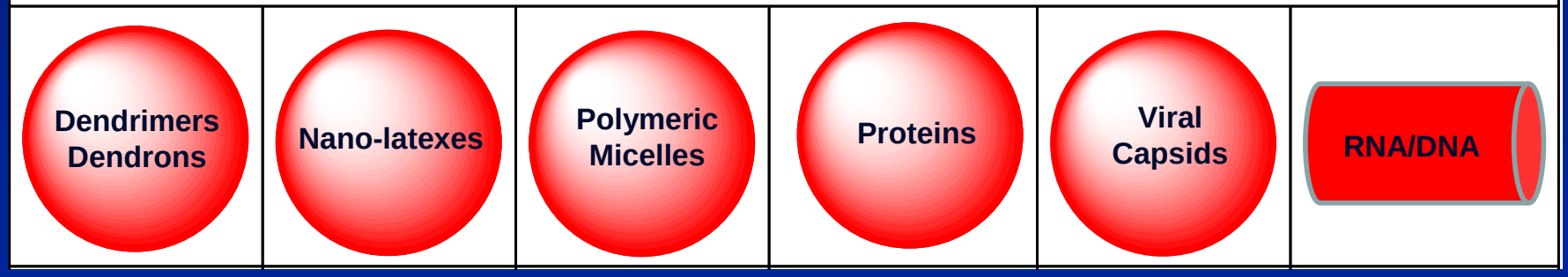
Nano-Element Categories

HARD PARTICLE NANO-ELEMENT CATEGORIES



H-1 H-2 H-3 H-4 H-5 H-6

SOFT PARTICLE NANO-ELEMENT CATEGORIES



S-1 S-2 S-3 S-4 S-5 S-6

(Synthetic Polymers) (Biological Polymers)

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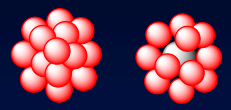
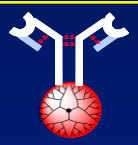
Soft Nanoparticle Compounds



Dendrimer-Cluster Compounds Tomalia, et al. Adv. Mater. (2000)

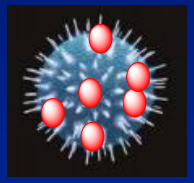


IgG-Dendrimer Compounds (Stratus®) Siemens Germany

Tobacco Mosaic Virus Compound

Nano-Elements	Dendrimers Dendrons	Nano-latexes	Polymeric Micelles	Proteins	Viral Capsids	DNA/RNA
Dendrimers Dendrons	S-1:S-1	S-2:S-1	S-3:S-1	S-4:S-1	S-5:S-1	S-6:S-1
Nano-latexes		S-2:S-2	S-3:S-2	S-4:S-2	S-5:S-2	S-6:S-2
Polymeric Micelles		S-2:S-3	S-3:S-3	S-4:S-3	S-5:S-3	S-6:S-3
Proteins		S-2:S-4	S-3:S-4	S-4:S-4	S-5:S-4	S-6:S-4
Viral Capsids		S-2:S-5	S-3:S-5	S-4:S-5	S-5:S-5	S-6:S-5
DNA/RNA		S-2:S-6	S-3:S-6	S-4:S-6	S-5:S-6	S-6:S-6

DNA-Dendrimer Compounds (Superfect®) Qiagen, Ger.



HIV-Virus-Dendrimer Compounds (VivaGel®) Starpharma, AU

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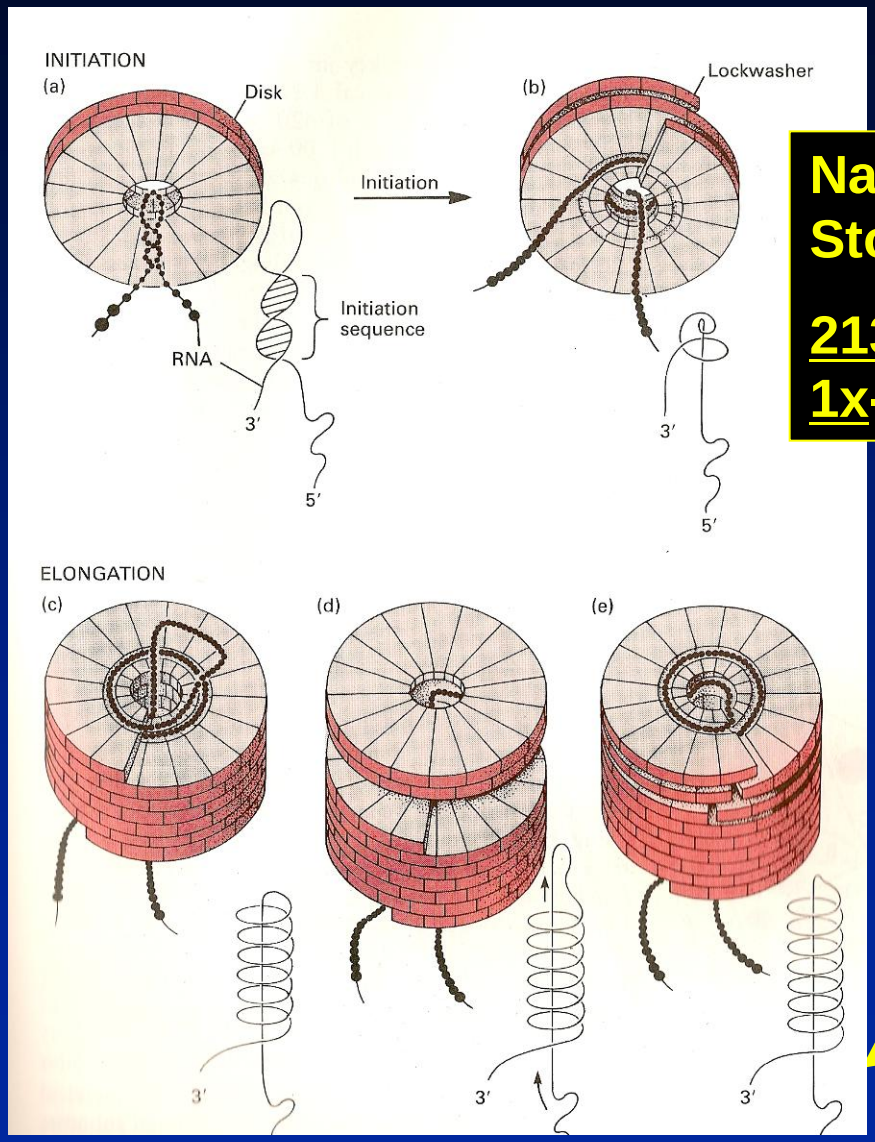
Viral Capsid-RNA [S-5:S-6] Core-Shell Type, Nano-Compound

Tobacco Mosaic Virus



Nano-Compound Stoichiometry:

2130x-Protein Subunits [S-5]; 1x-ss-RNA [S-6]

Subunits: 158 amino acids

[S-5]

ss-RNA: 6400 nucleotide units

[S-6]

Diameter: 18 nm
Length: 300 nm
Helical Symmetry

P.J.G. Butler, A. Klug, *Sci. Amer.* 239 (5) 62-69, (1978).

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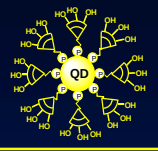
Soft/Hard Nanoparticle Compounds

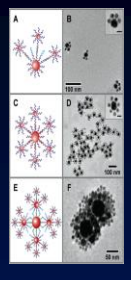


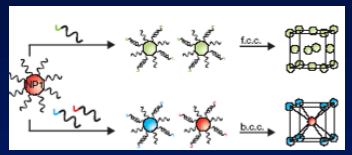
Tomalia et.al.
J. Luminescence
(2005)

Wiesner, et al.,
Chem. Mater.
(2007)

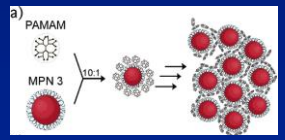
Jensen, et al.
Nano Lett. (2005)

Nano-Elements	Dendrimers Dendrons	Nano-latexes	Cross-linked Polymeric Micelles	Proteins	Viruses	DNA/RNA
Metal (M°) (Nanoclusters)	S-1:H-1	S-2:H-1	S-3:H-1	S-4:H-1	S-5:H-1	S-6:H-1
Metal (Chalcogenide) (Nanocrystals)	S-1:H-2	S-2:H-2	S-3:H-2	S-4:H-2	S-5:H-2	S-6:H-2
Metal Oxide (Nanocrystals)	S-1:H-3	S-2:H-3	S-3:H-3	S-4:H-3	S-5:H-3	S-6:H-3
Silica (Nanoparticles)	S-1:H-4	S-2:H-4	S-3:H-4	S-4:H-4	S-5:H-4	S-6:H-4
Fullerenes	S-1:H-5	S-2:H-5	S-3:H-5	S-4:H-5	S-5:H-5	S-6:H-5
Carbon Nanotubes	S-1:H-6	S-2:H-6	S-3:H-6	S-4:H-6	S-5:H-6	S-6:H-6

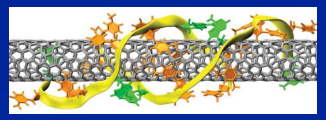




Mirkin, et al.
Nature, (2008)



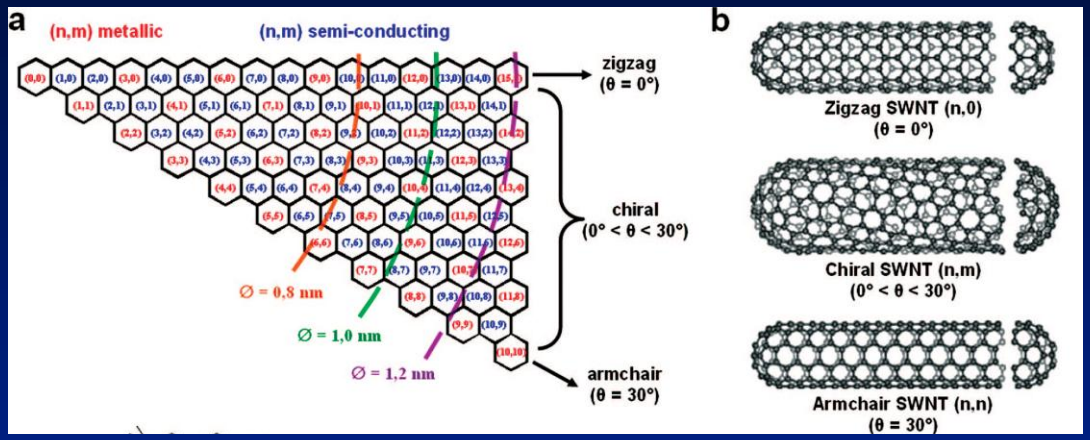
Rotello, et al.
J.A.C.S. (2005)



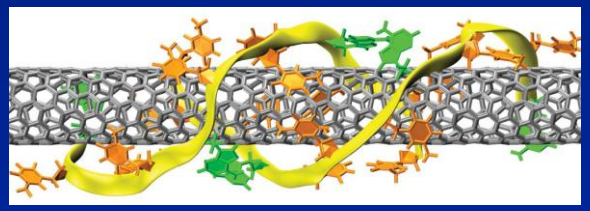
X. Tu, et al.,
Nature (2009)

Barrel Shaped, SWNT:DNA -[H-6:S-6]; Core-Shell Type Nano-Compound Series

SWNT; [S-6]



DNA; [S-6]



Core-Shell; [H-6:S-6] Type Nano-Compounds

Nano-Compound Synthesis, Yields and Purities

Table 2 | Experimental conditions and quantification

Chirality (n,m)	Sequence	Dispersion solution*	Incubation period†	Yield‡ (μg per 100 μg)	Purity§ (%)
(9,1)	$(TCC)_{10}$	0.1 M NaCl	None	0.1	80
(8,3)	$(TTA)_3TTGTT$	0.1 M NaCl	1 day	0.1	70
(6,5)	$(TAT)_4$	0.1 M NaCl	None	0.5	90
(7,5)	$(ATT)_4AT$	0.1 M NaCl	None	0.2	90
(10,2)	$(TATT)_2TAT$	0.1 M NaCl	None	0.1	90
(8,4)	$(ATTT)_3$	0.1 M NaCl	None	0.3	90
(9,4)	$(GTC)_2GT$	0.1 M sodium acetate pH 4.5	2 days	0.5	60
(7,6)	$(GTT)_3G$	0.1 M NaCl	None	0.4	90
(8,6)	$(GT)_6$	0.1 M NaCl	1 day	0.8	90
(9,5)	$(TGTT)_2TGT$	0.1 M NaCl, 10% glycerol	None	0.3	70
(10,5)	$(TTTA)_3T$	0.1 M sodium acetate pH 4.5	2 days	0.5	90
(8,7)	$(CCG)_2CC$	0.1 M NaCl, 10% glycerol	None	0.4	80

The experimental conditions listed here are used to obtain the results shown in Fig. 1.
* Solution in which DNA and raw HiPco material are mixed and sonicated.
† Time period between the end of sonication dispersion and the beginning of the IEX separation.
‡ The mass of (n,m) tubes obtained from 100 μg SWNTs loaded on to the IEX column in each run.
§ Estimated error ±10%, due to extinction coefficient difference among different semiconducting tubes, the presence of baseline and phonon side-bands near E_{11} peaks[28].

X. Tu, S. Manohar, A Jagota and M. Zheng, *Nature,* (2009), 460, 250

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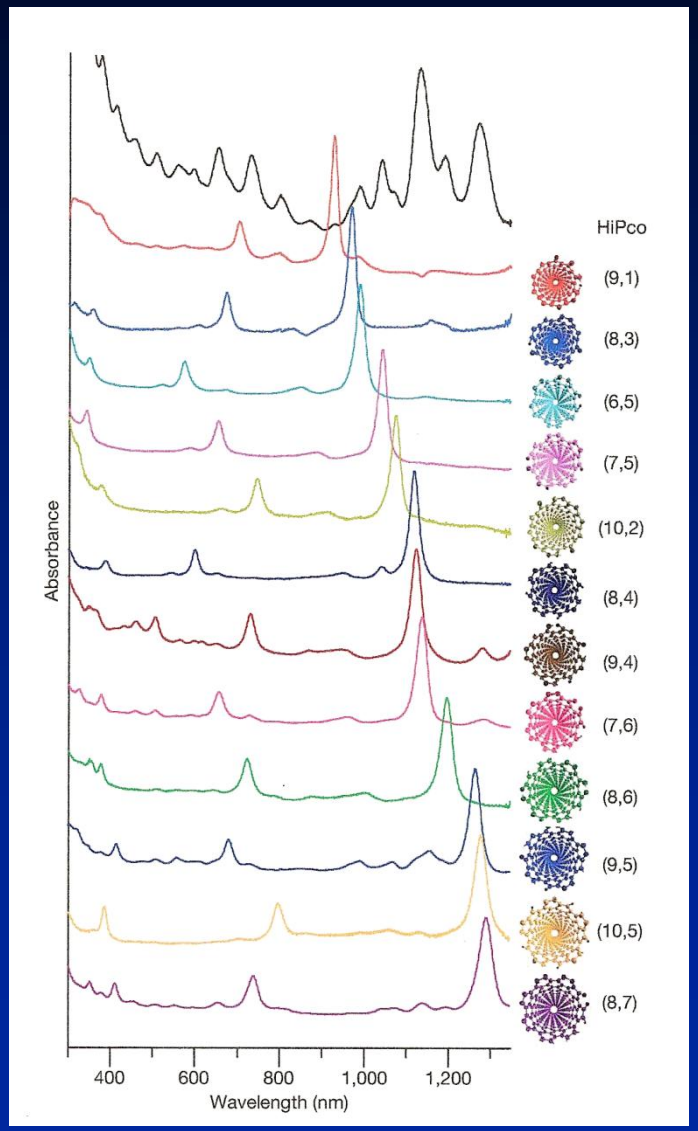
Nano-Periodic Property Patterns for a Series of [H-6:S-6] Nano-Compounds



SWNT [H-6]

DNA [S-6]

Table 1 | DNA sequence versus SWNT chirality

Chirality (*n*,*m*)	Sequences
(9,1)	$(TCC)_{10}$, $(TGA)_{10}$, $(CCA)_{10}$
(8,3)	$(TTA)_4TT$, $(TTA)_3TTGTT$, $(TTA)_5TT$
(6,5)	$(TAT)_4$, $(CGT)_3C$
(7,5)	$(ATT)_4$, $(ATT)_4AT$
(10,2)	$(TATT)_2TAT$
(8,4)	$(ATTT)_3$
(9,4)	$(GTC)_2GT$, $(CCG)_4$
(7,6)	$(GTT)_3G$, $(TGT)_4T$
(8,6)	$(GT)_6$, $(TATT)_3T$, $(TCG)_{10}$, $(GTC)_3$, $(TCG)_2TC$, $(TCG)_4TC$, $(GTC)_2$
(9,5)	$(TGTT)_2TGT$
(10,5)	$(TTTA)_3T$
(8,7)	$(CCG)_2CC$

DNA sequences enabling chromatographic purification of single chirality semiconducting SWNTs.

Optical Absorption Spectra versus SWNT (n,m) Chirality

X. Tu, S. Manohar, A Jagota and M. Zheng, *Nature,* 2009, 460, 250

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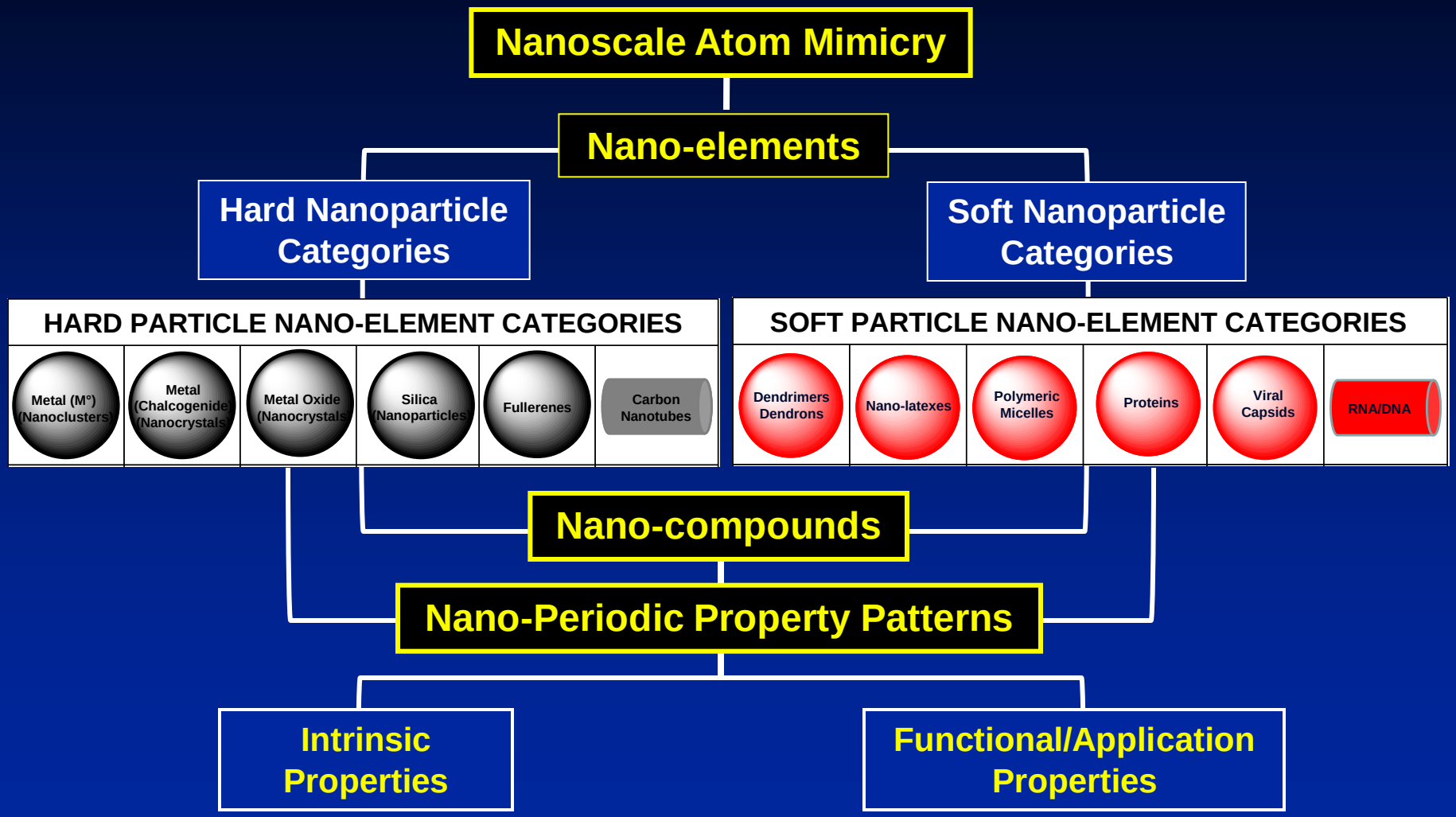
V.
Nano-(*Periodic*) Property Trends

Using Traditional "First Principles"



D.A. Tomalia, *J. of Nanoparticle Research*, 11. 1251-1310 (2009)

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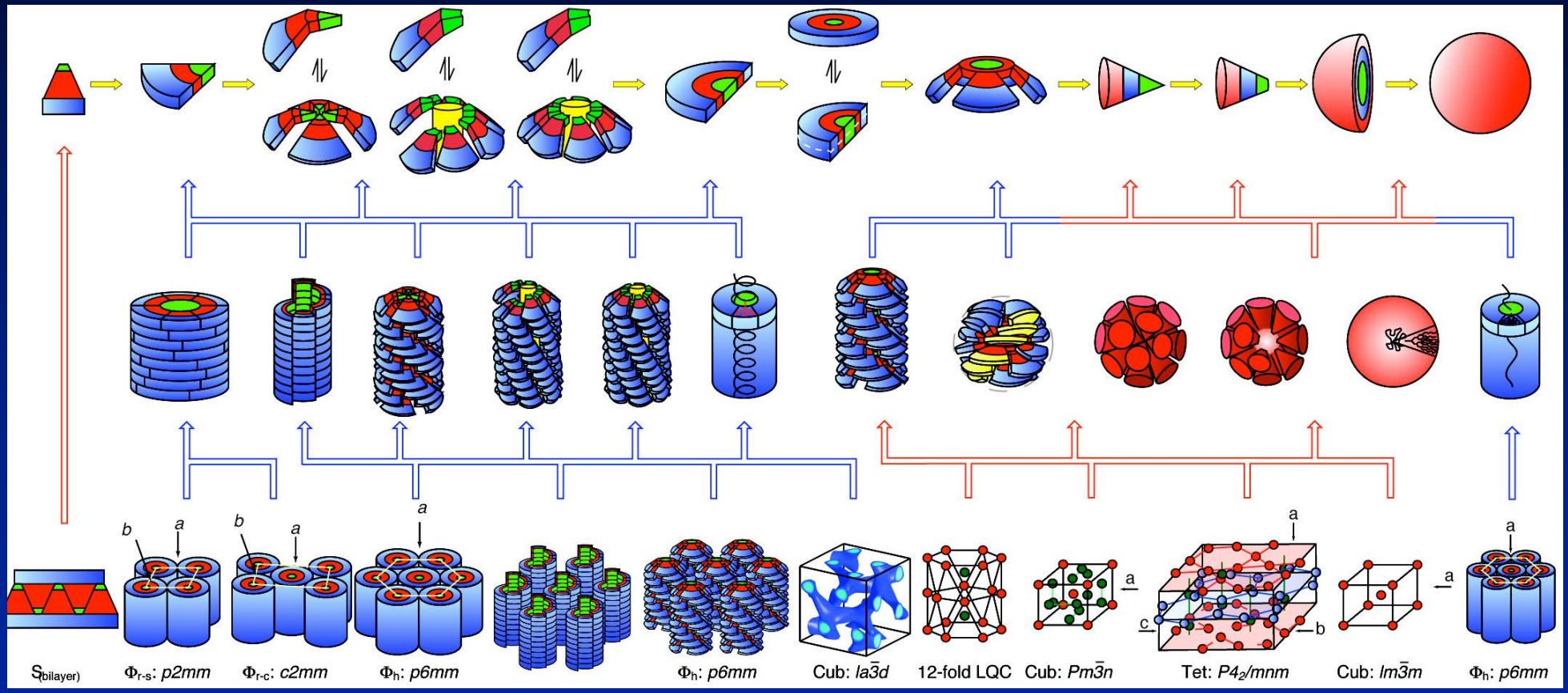
Nano-Periodic Trends of [S-1]-Type Nano-Elements (Dendrons)

(Size, Shape, Surface Chemistry Driven Self Assembly Patterns)



J.G. Rudick, V. Percec, *Accounts of Chemical Research*, 41,(12), 1641-1652 (2008)

First Demonstration of <u>Quasi-Equivalence</u> with Synthetic Nanostructures

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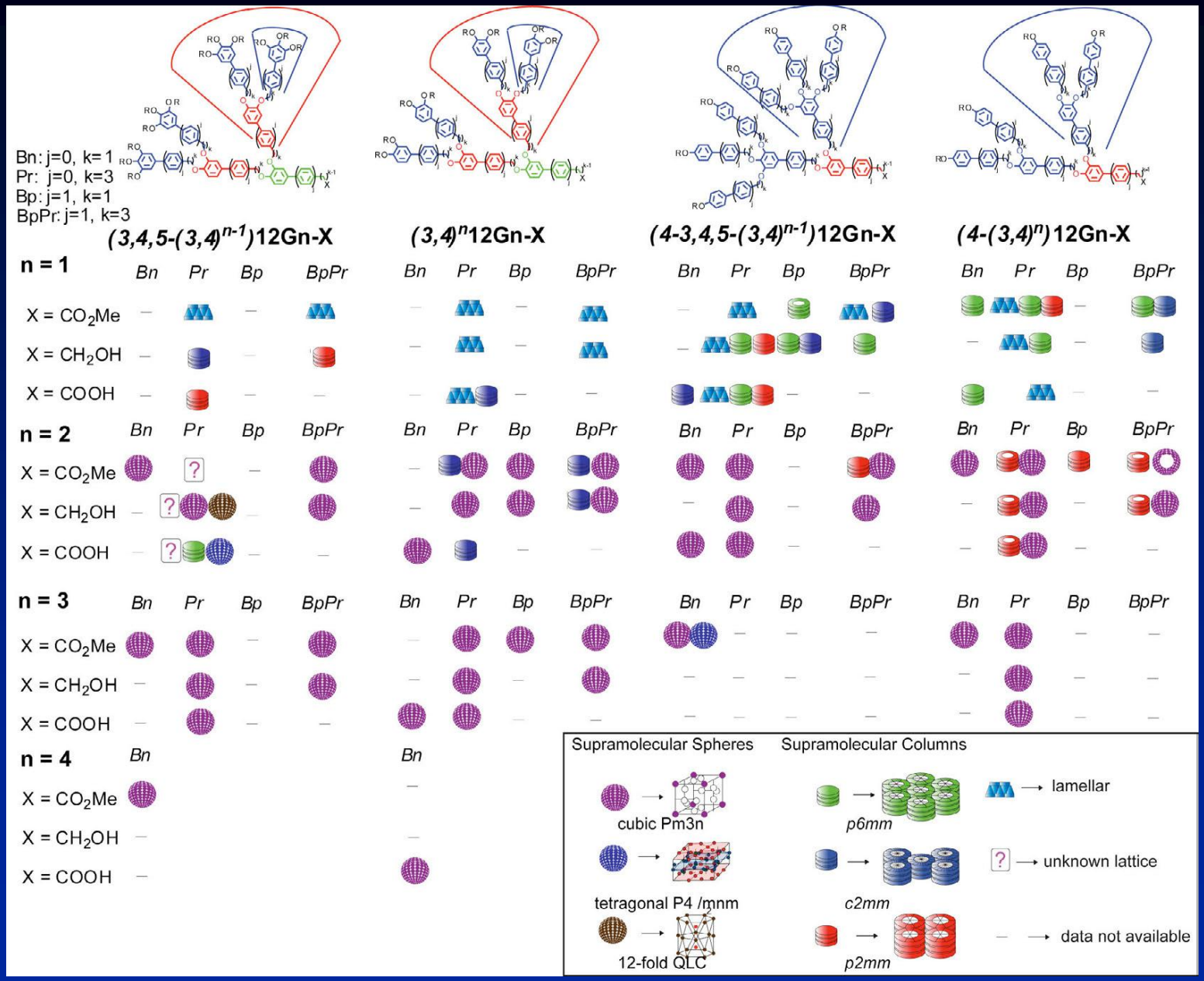
Percec's Nano-Periodic Self-Assembly Table



(Primary) Dendron Structures

↓

(Tertiary) Supramolecular Dendrimers

↓

(Quaternary) Dendrimer Assemblies

V. Percec, et al., *J. Am. Chem. Soc.*, (in press)

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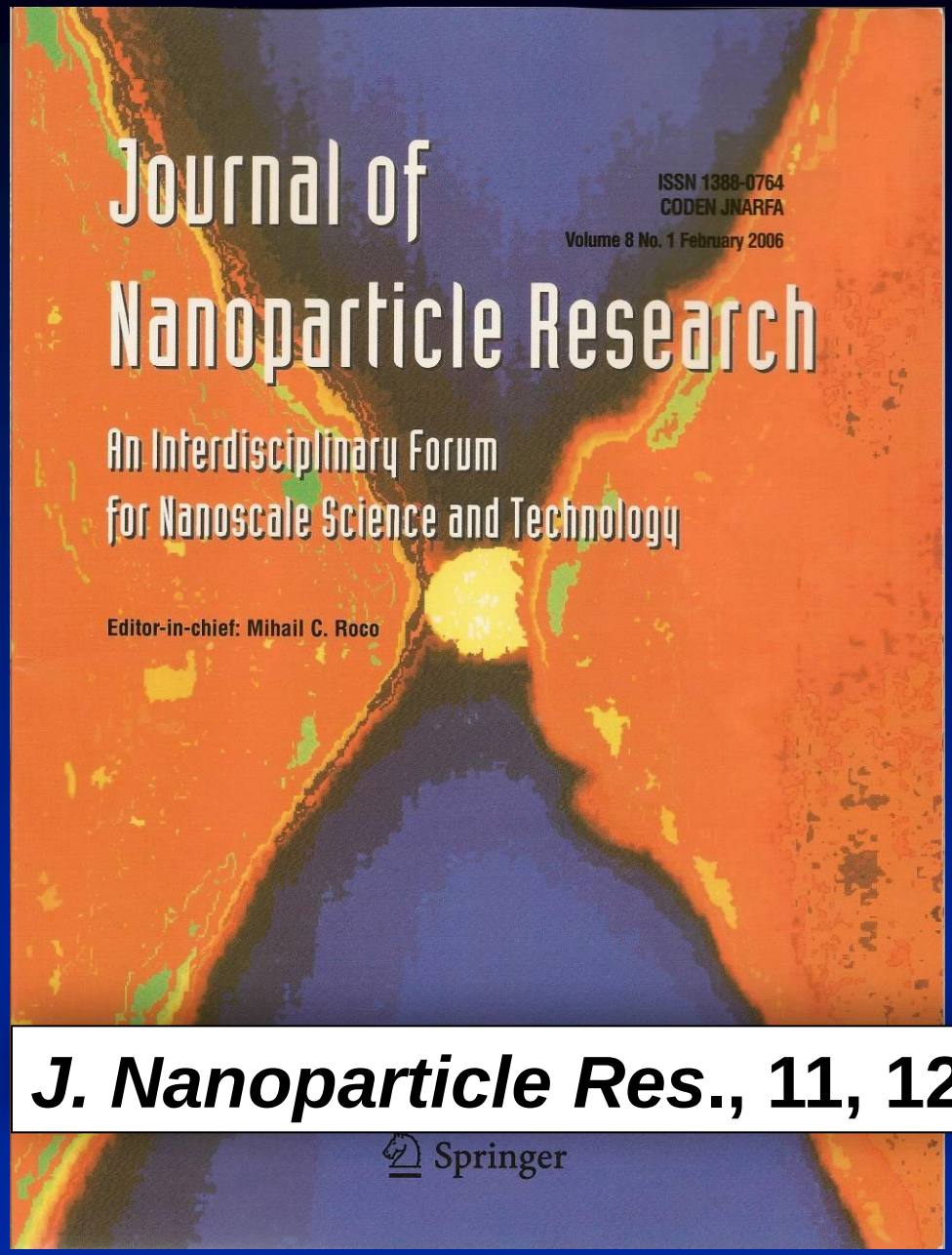

"The spirit of this perspective is not to disrupt any natural physico-chemical laws, but to encourage new and different thinking.

This is a works in progress! Much more remains to be done."

Donald A. Tomalia

J Nanopart Res (2009) 11:1251–1310
DOI 10.1007/s11051-009-9632-z

PERSPECTIVES

In quest of a systematic framework for unifying and defining nanoscience

Donald A. Tomalia

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Abstract This article proposes a systematic framework for unifying and defining nanoscience based on historic first principles and step logic that led to a "central paradigm" (i.e., unifying framework) for traditional elemental&small-molecule chemistry. As such, a *Nanomaterials classification roadmap* is proposed, which divides all nanomatter into Category I: discrete, well-defined and Category II: statistical, undefined nanoparticles. We consider only Category I, well-defined nanoparticles which are >90% monodisperse as a function of Critical Nanoscale Design Parameters (CNDPs) defined according to: (a) size, (b) shape, (c) surface chemistry, (d) flexibility, and (e) elemental composition. Classified as either hard (H) (i.e., inorganic-based) or soft (S) (i.e., organic-based) categories, these nanoparticles were found to manifest pervasive atom mimicry features that included: (1) a dominance of zero-dimensional (0D) core–shell nanoarchitectures, (2) the ability to self-assemble or chemically bond as discrete, quantized nanounits, and (3) exhibited well-defined nanoscale valencies and stoichiometries reminiscent of atom-based elements. These discrete nanoparticle categories are referred to as hard or soft particle nanoelements. Many examples describing chemical bonding/assembly of these nanoelements have been reported in the literature. We refer to these hard:hard (H-*n*:H-*n*), soft:soft (S-*n*:S-*n*), or hard:soft (H-*n*:S-*n*) nanoelement combinations as nanocompounds. Due to their quantized features, many nanoelement and nanocompound categories are reported to exhibit well-defined nanoperiodic property patterns. These periodic property patterns are dependent on their quantized nanofeatures (CNDPs) and dramatically influence intrinsic physicochemical properties (i.e., melting points, reactivity/self-assembly, sterics, and nanoencapsulation), as well as important functional/performance properties (i.e., magnetic, photonic, electronic, and toxicologic properties). We propose this perspective as a modest first step toward more clearly defining synthetic nanochemistry as well as providing a systematic framework for unifying nanoscience. With further progress, one should anticipate the evolution of future nanoperiodic table(s) suitable for predicting important risk/benefit boundaries in the field of nanoscience.

Keywords Dendrimers · Proteins · Nanoclusters · DNA/RNA · Metal (M^n) nanoclusters · Metal chalcogenides · Metal ligand/oxides · Fullerenes · Carbon nanotubes · Nanoelements · Nanocompounds · Nanoperiodic property patterns · Hard nanoparticles · Nanoperiodic table · Atom mimicry · Nanochemistry

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***J. Nanoparticle Res*., 11, 1251-1310,(2009)**

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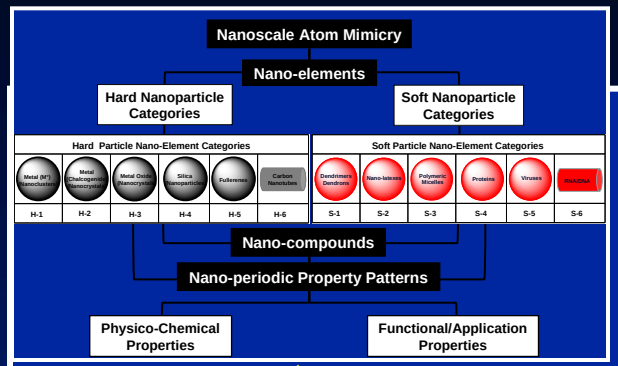
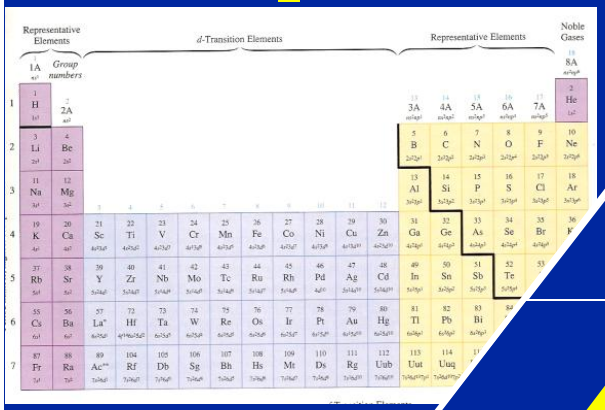
The Future

Complexity Staircase

Nano-Periodicity





Complex Organisms (Humans)

Organisms (Plants, Animals)

Simple Organisms (Bacteria)

Biological Cells

(100 nm)

Bio-assemblies (Viruses, Ribosomes)

Nanoscale Modules (Proteins, DNA, RNA)

(1 nm)

Complex Compounds (Palytoxin, C_{60})

Functional Groups ($-CO_2H$, $-NH_2$, $-OH$)

Sub-nano Modules (Aliphatic, Aromatic)

Simple Compounds (HCl, H_2O, NH_3, CH_4)

Atoms (Elements) (Periodic Table)

Quantized Building Blocks

Hard/Soft Nano-Elements

Synthetic Nano-Chemistry

Polypeptide Chemistry

Polymer Chemistry

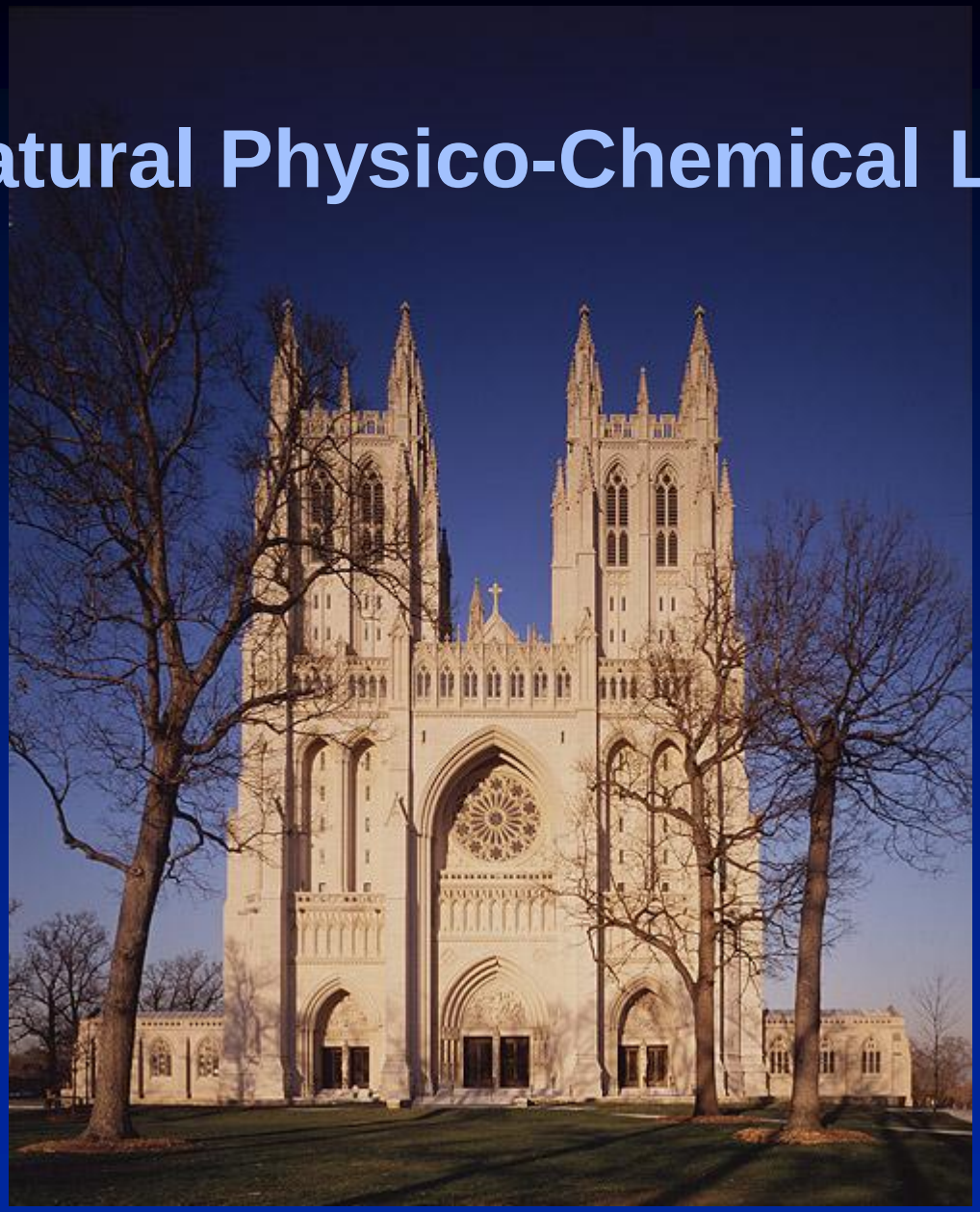
Organic Chemistry

Inorganic Chemistry

Monomers

Atoms

Natural Physico-Chemical Laws



We are not advocating changes in the gospel! We are merely proposing some new hymns--new thinking.

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