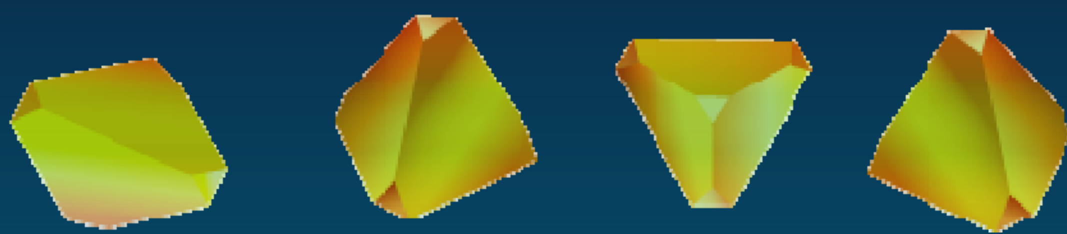
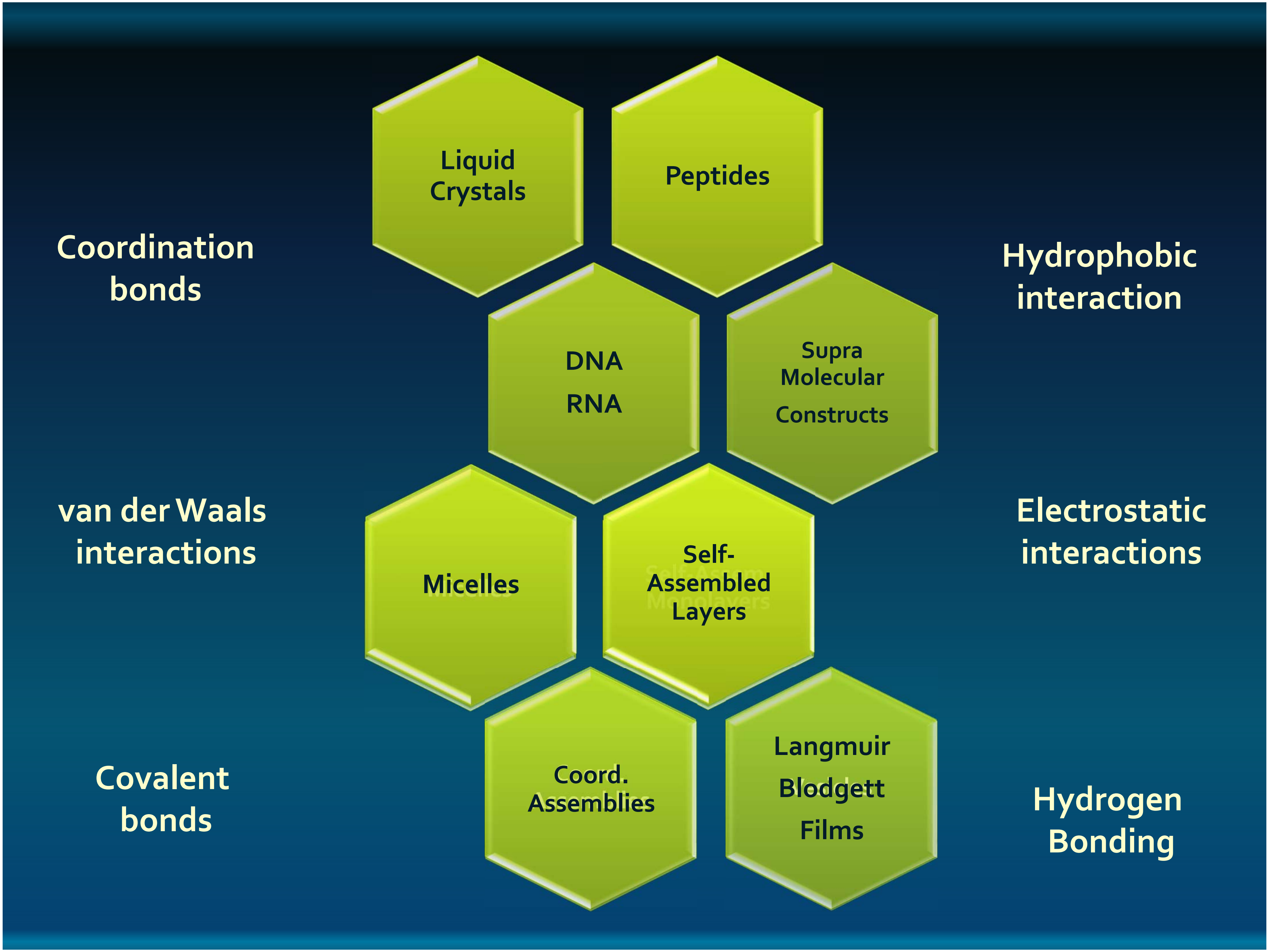
UNIVERSITY OF MICHIGAN, ANN ARBOR

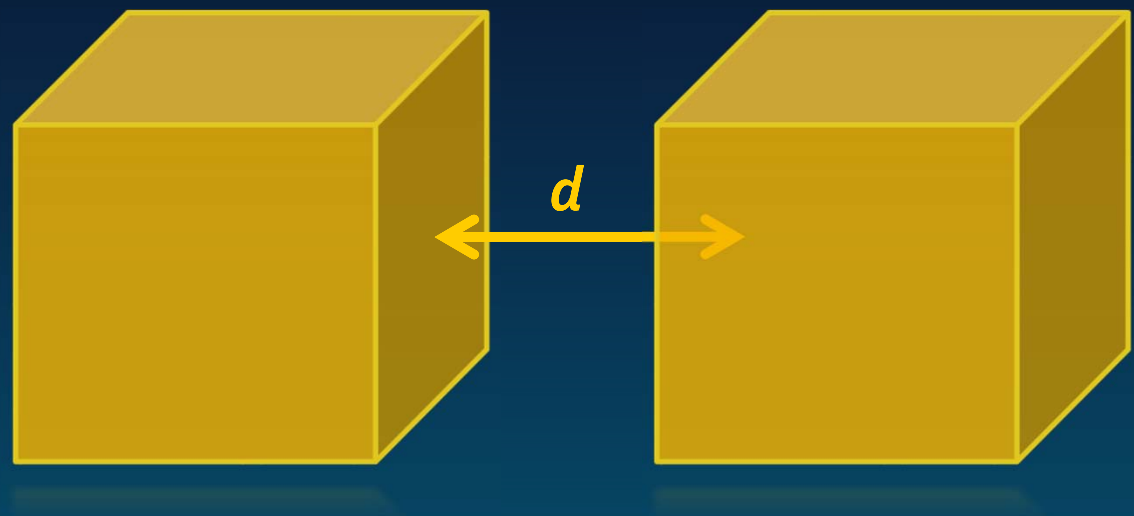
Hierarchical Assemblies of Inorganic Nanoparticles (NPs)



Nicholas A. Kotov

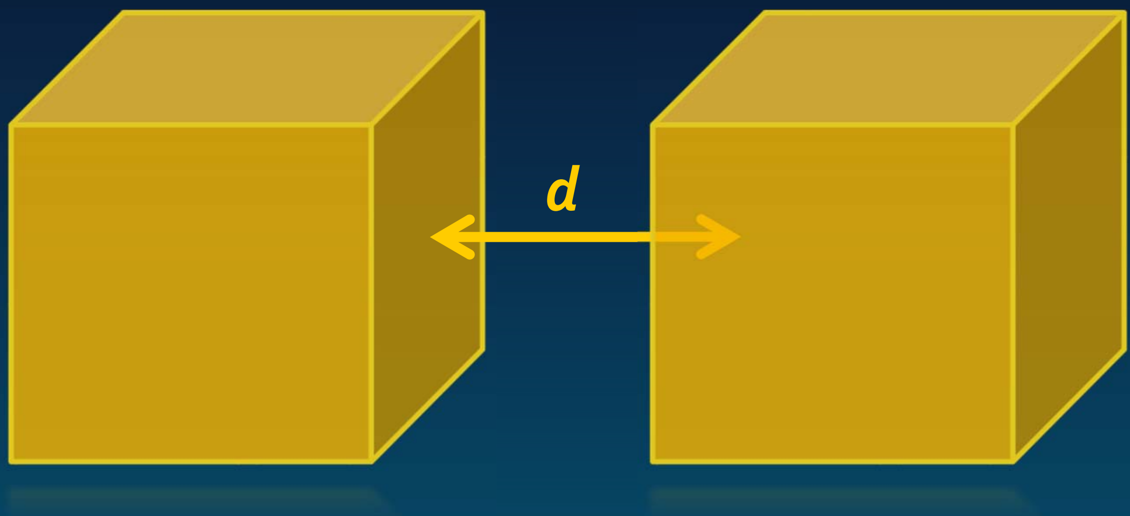

Coordination bonds
van der Waals interactions
Covalent bonds
Liquid Crystals
Peptides
DNA
RNA
Supra Molecular Constructs
Micelles
Self-Assembled Layers
Coord. Assemblies
Langmuir Blodgett Films
Hydrophobic interaction
Electrostatic interactions
Hydrogen Bonding

Interactions



London dispersion attraction $V_{LDF} = A_{121}/12 \cdot \pi \cdot d^2$

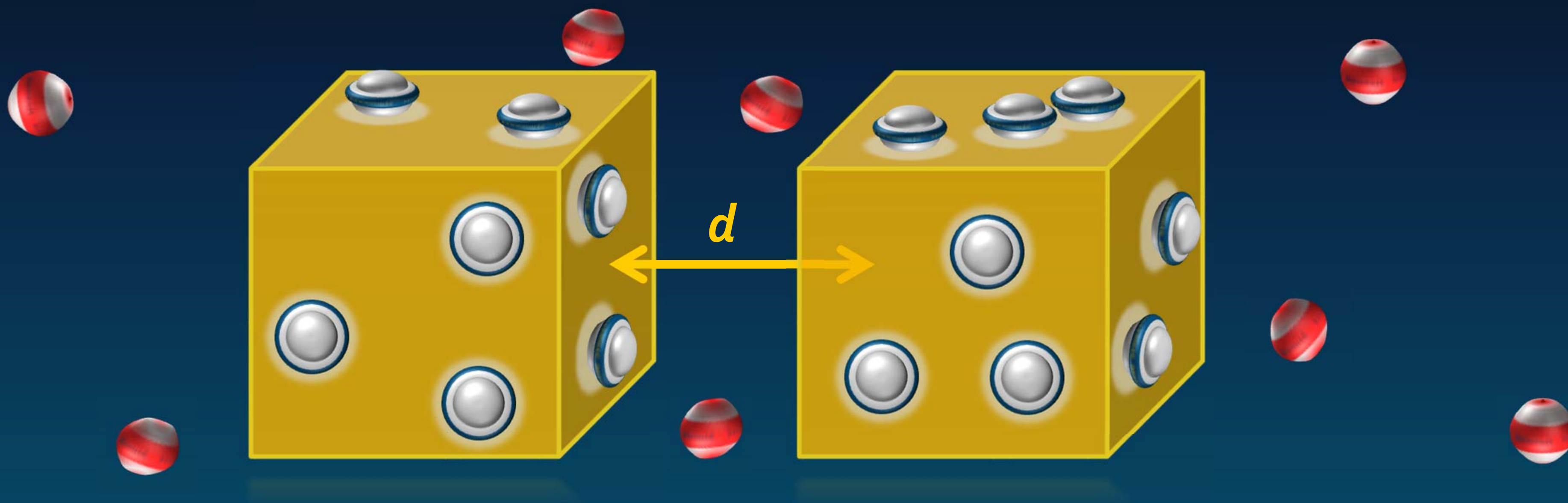
Interactions



A_{121}

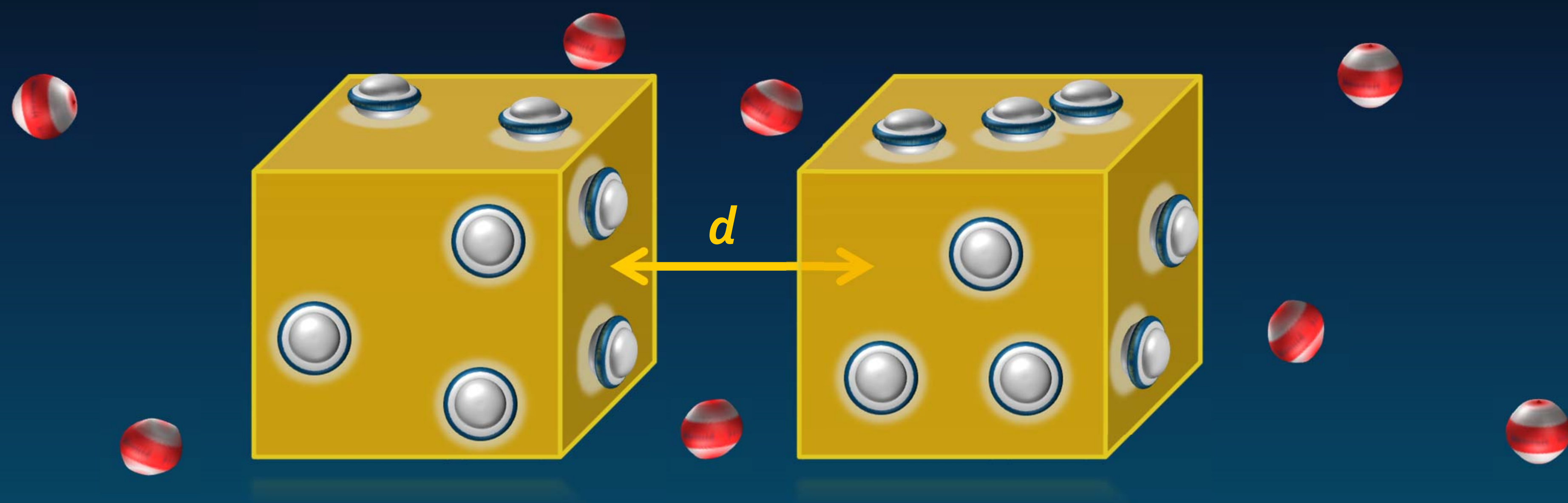
Metals and semiconductors	$10 — 40 \cdot 10^{-20}$ J
Organic molecules	$1 — 10 \cdot 10^{-20}$ J

Interactions



Electrostatic Repulsion: $V_{EL} = \dfrac{64 \cdot kT \cdot \sigma_o}{\varepsilon_o \varepsilon} \exp(-\kappa_D d)$

Interactions



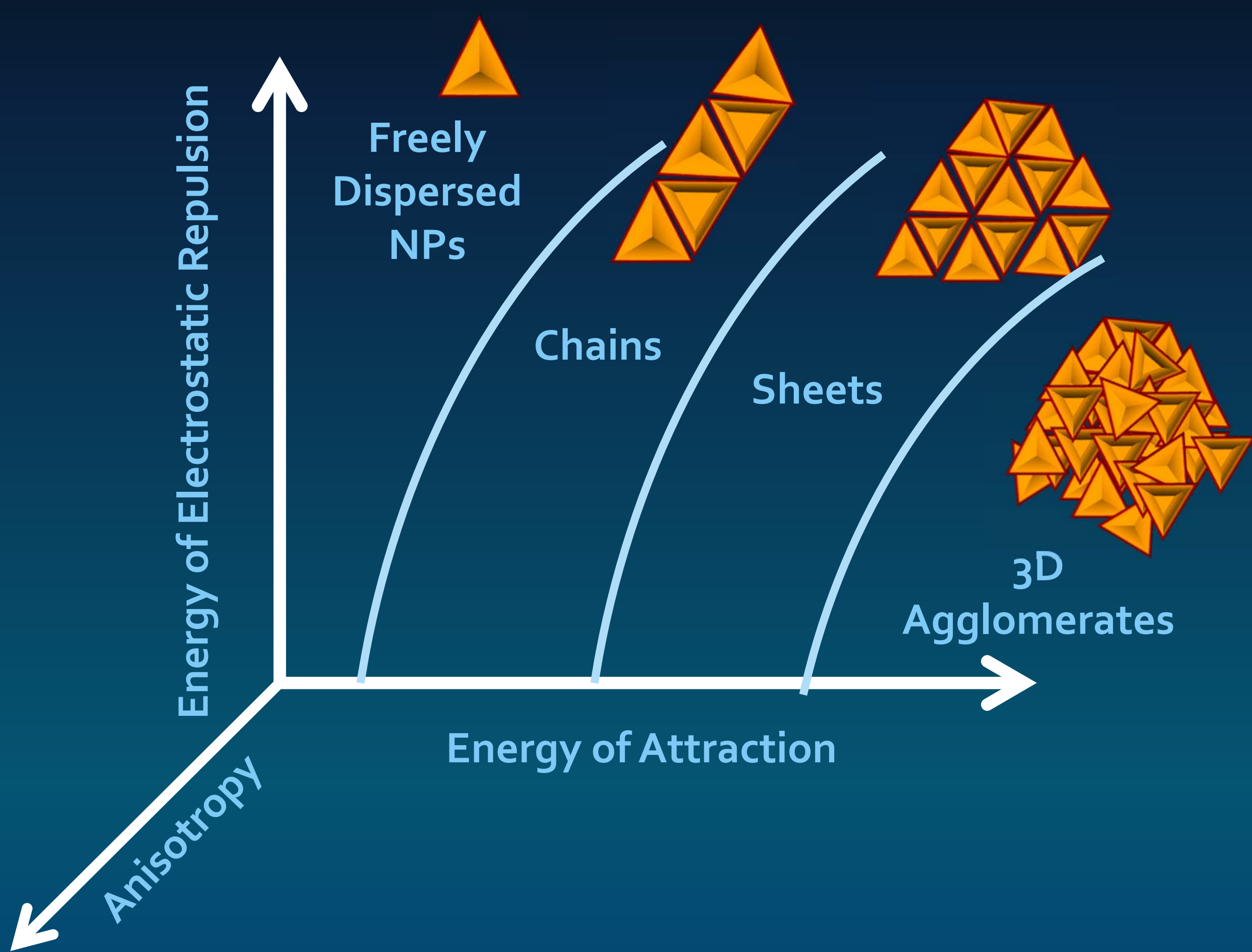
σ_0

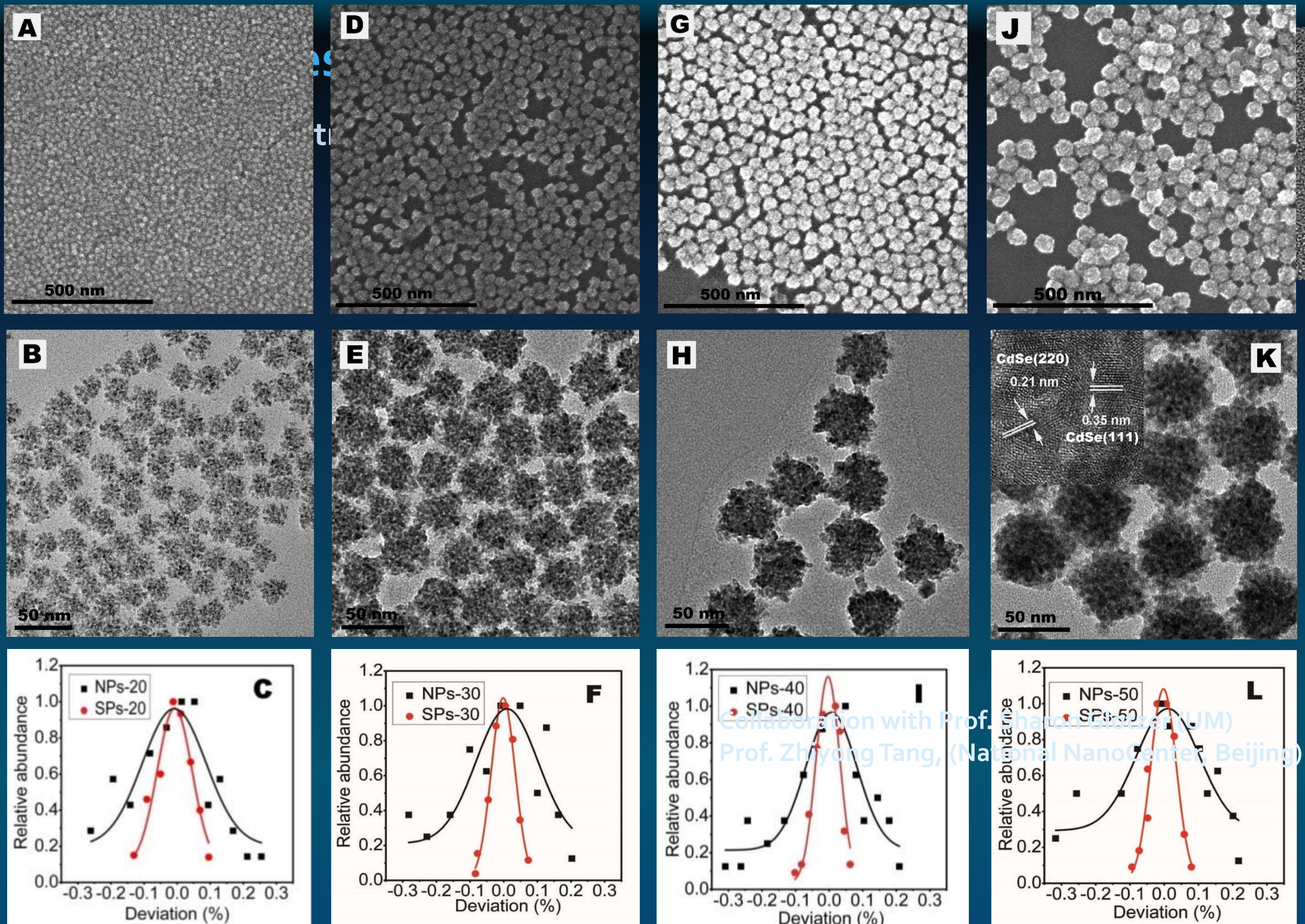
Metals and semiconductors	1 — 60 mC/m²
Organic materials, insulators	26 — 100 mC/m²

Simplicity

Wide range of experimental conditions and building blocks

Simple Phase Diagram

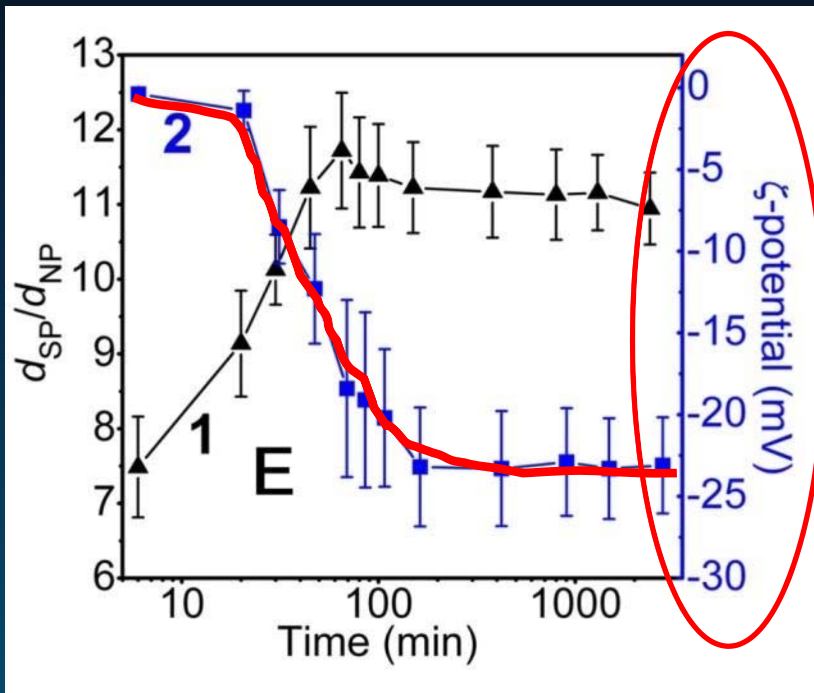


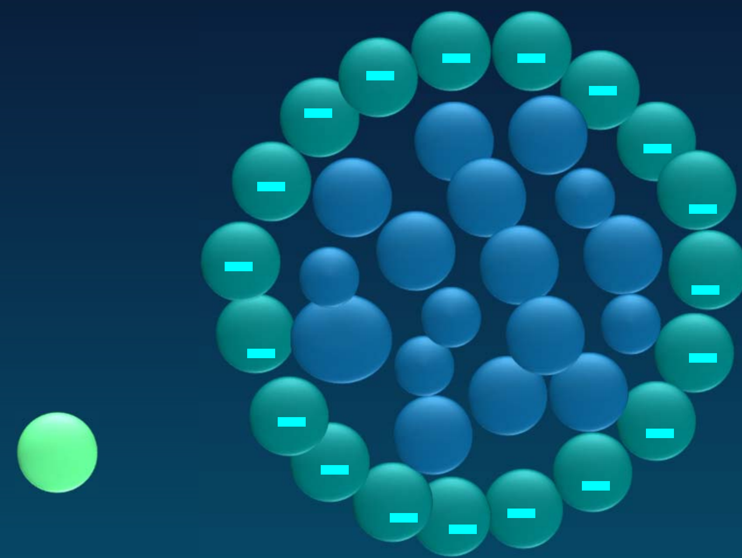


Collaboration with Prof. Sharon Glotzer (UM)
Prof. Zhiyong Tang, (National NanoCenter, Beijing)

Y. Xia, T. D. Nguyen, M. Yang, B. Lee, A. Santos, P. Podsiadlo, Z. Tang, S. C. Glotzer, N. A. Kotov,
Self assembly of virus-like self-limited inorganic supraparticles from nanoparticles, *Nature Nanotechnology*, 2011, 6, 580

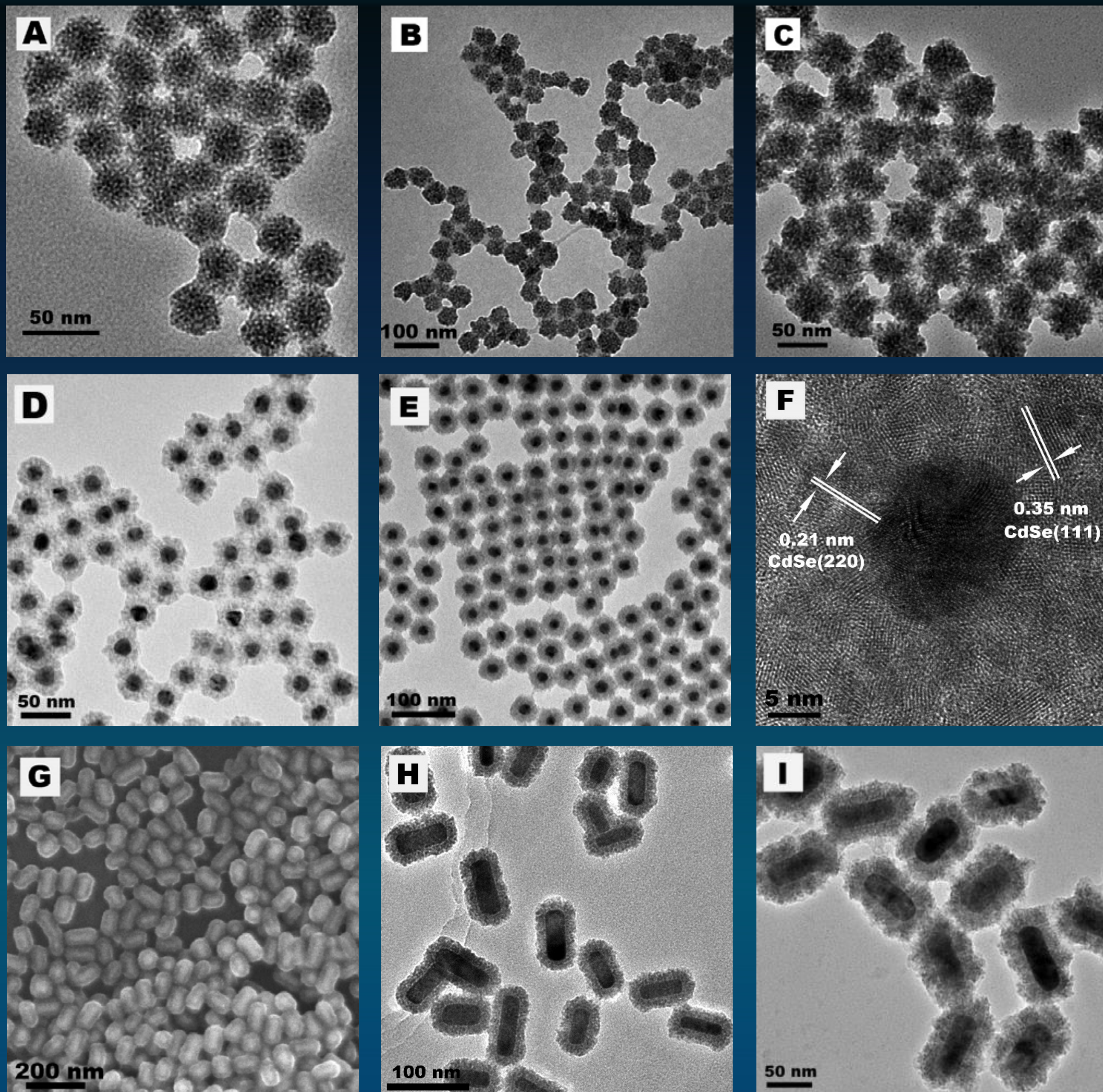
Mechanism of Supraparticle Self-Assembly





Supraparticle is formed due to balance of electrostatic repulsion and London dispersion attraction.

Y. Xia, T. D. Nguyen, M. Yang, B. Lee, A. Santos, P. Podsiadlo, Z. Tang, S. C. Glotzer, N. A. Kotov,
Self assembly of virus-like self-limited inorganic supraparticles from nanoparticles, *Nature Nanotechnology*, 2011, 6, 580

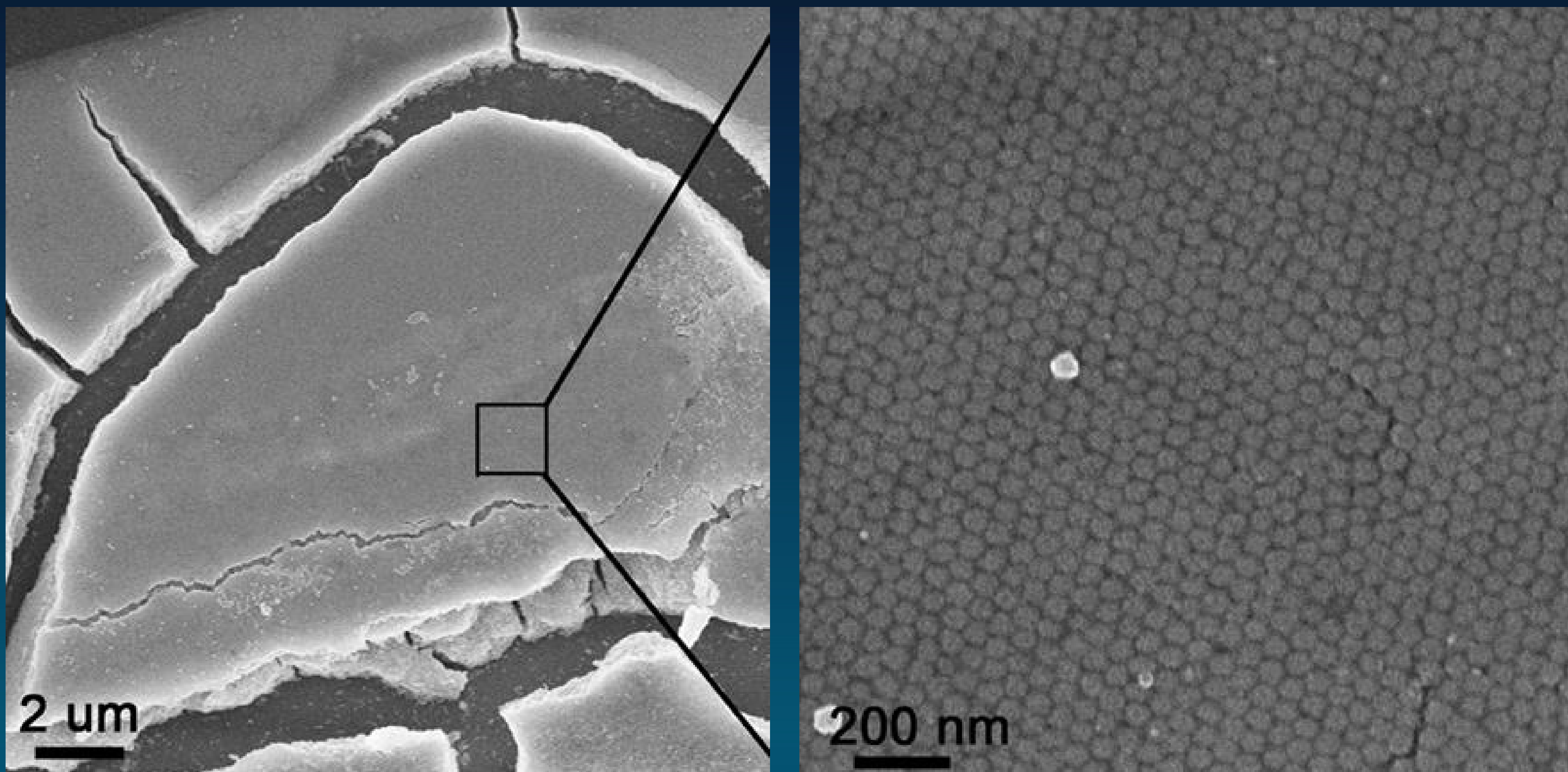


Other Assemblies
CdSe, PbS, PbSe

Complex Assemblies
with Au NP
in the center

Complex Assemblies
with Au NanoRods
in the center

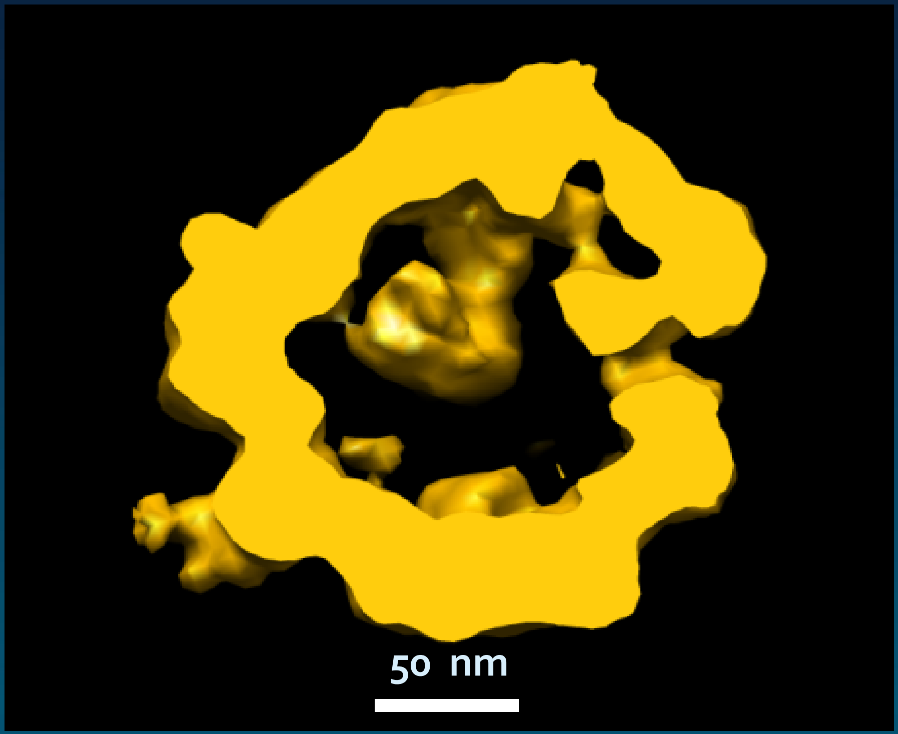
Colloidal Crystals from Supraparticles



Assembly combining the nanoscale and mesoscale structural motifs

Capsid-Like Biomimetic Nanoshells

Collaborations with
Prof. Petr Kral, U. Illinois Chicago
Prof. Peijun Zhang, U. Pittsburg

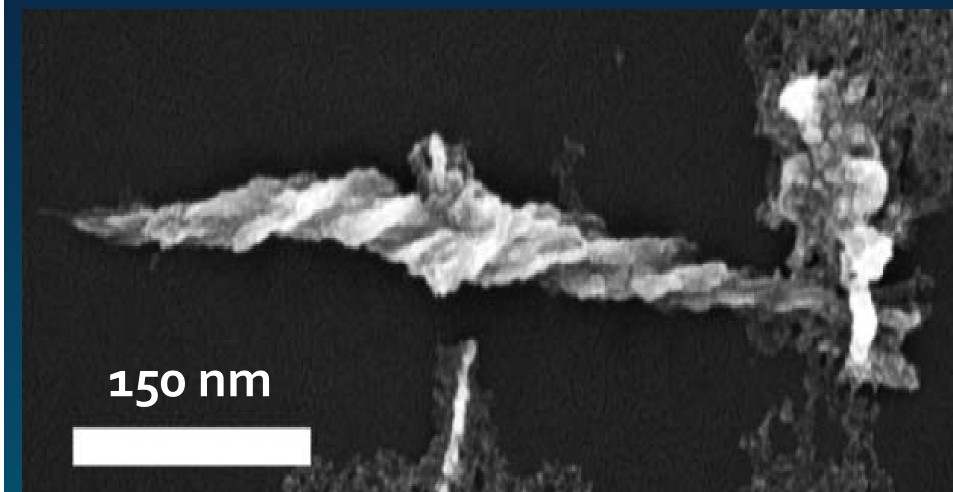


Cryo-TEM
Tomography

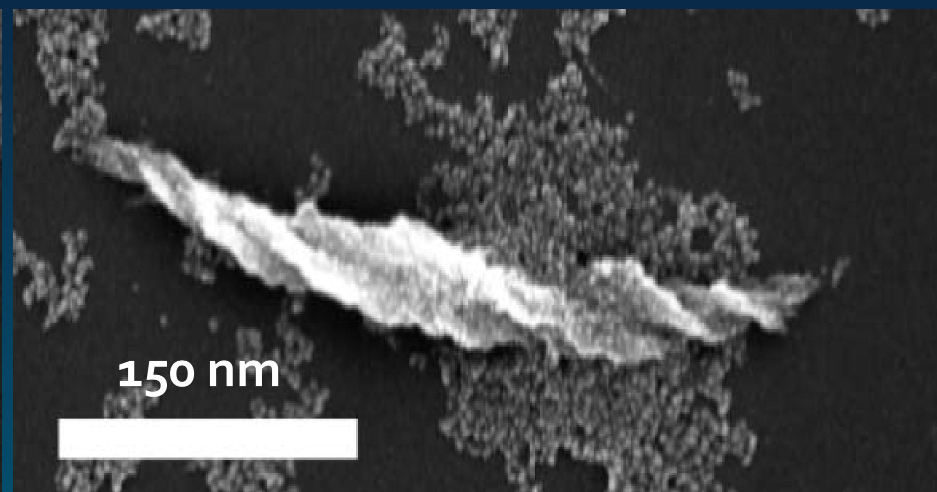
M. Yang, H. Chan, G. Zhao, J.H. Bahng, P. Zhang, P.Král, N. A. Kotov, Self-Assembly of Nanoparticles into Biomimetic Capsid-Like Nanoshells, *Nature Chemistry*, 2017, 9, 287–294.

Assemblies of Chiral NPs into Nanohelixes

CdTe NP stabilized with D-CYS

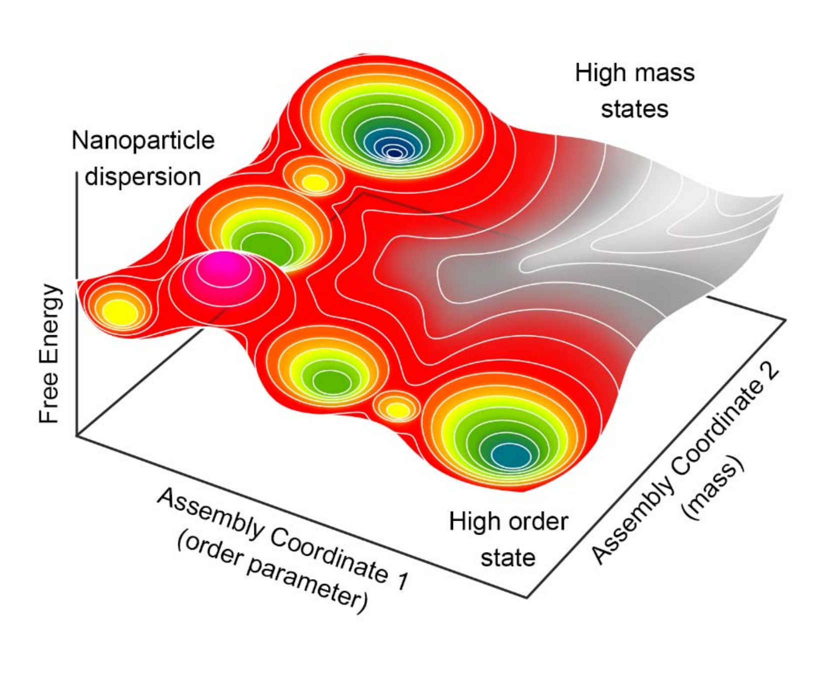


CdTe NP stabilized with L-CYS



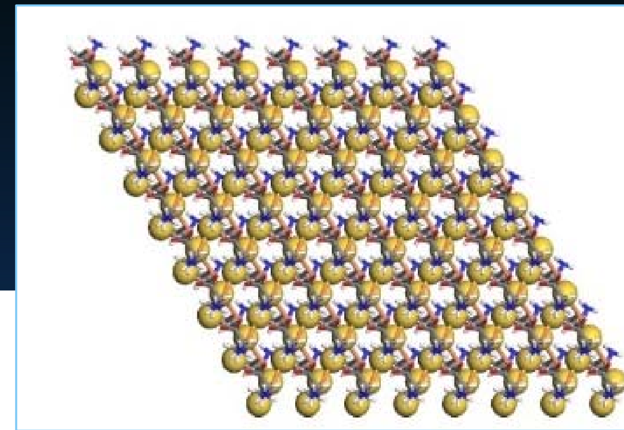
J. Yeom, B.Yeom, H. Chan, K.W. Smith, S. Dominguez-Medina , J.H.Bahng, G. Zhao, W.-S.Chang, S.J.Chang, A. Chuvilin, D. Melnikau,A.L. Rogach, P. Zhang, S.Link, P.Král, N. A. Kotov, *Nature Materials*, 2015, 14, 66–72

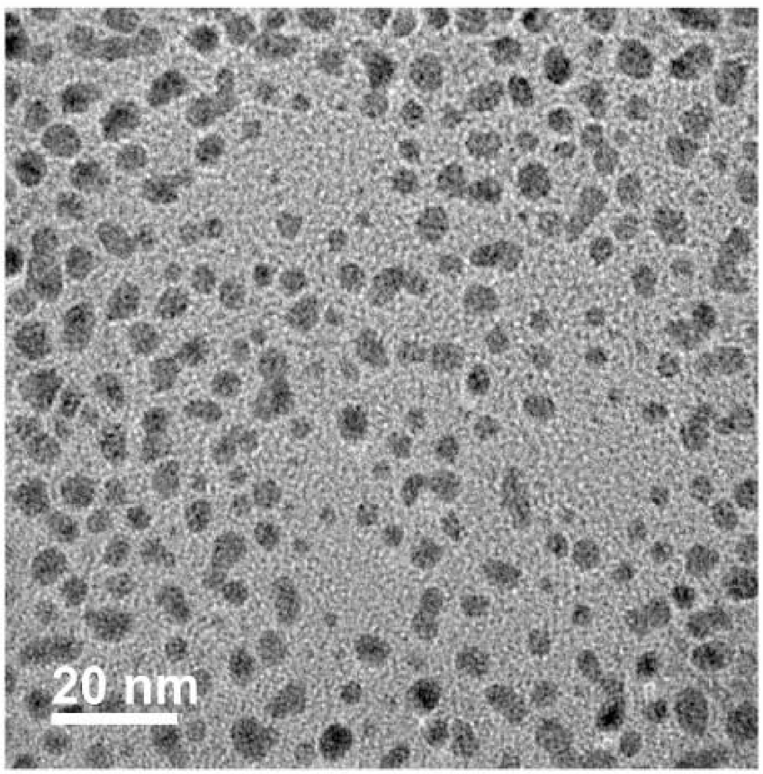
Does self-assembly of complex systems require monodispersity?

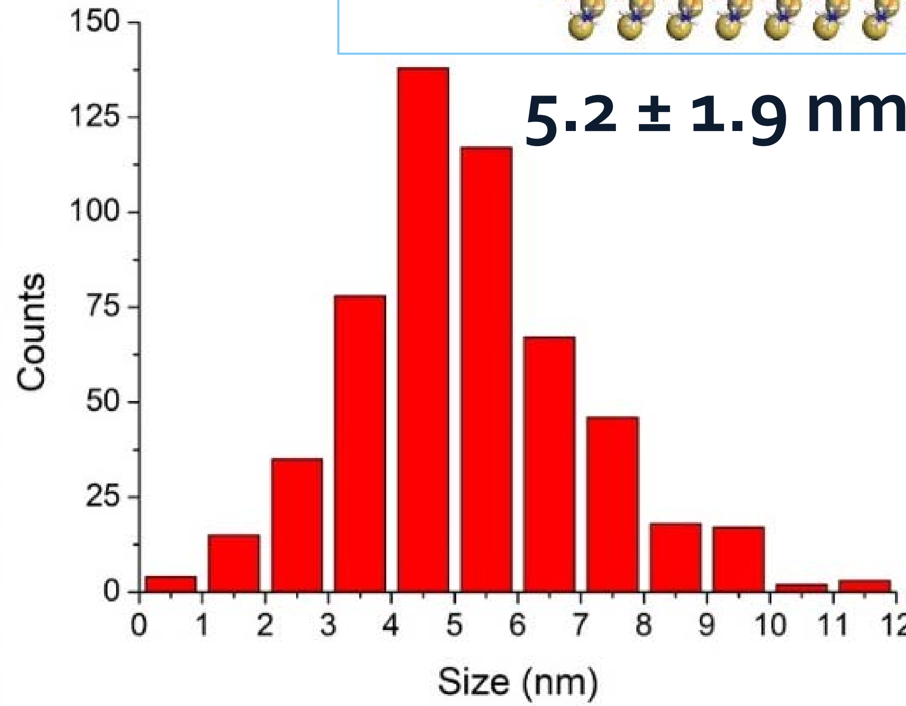


Energy landscape of self-assembly

Polydispersed Building Blocks Au-S nanosheets

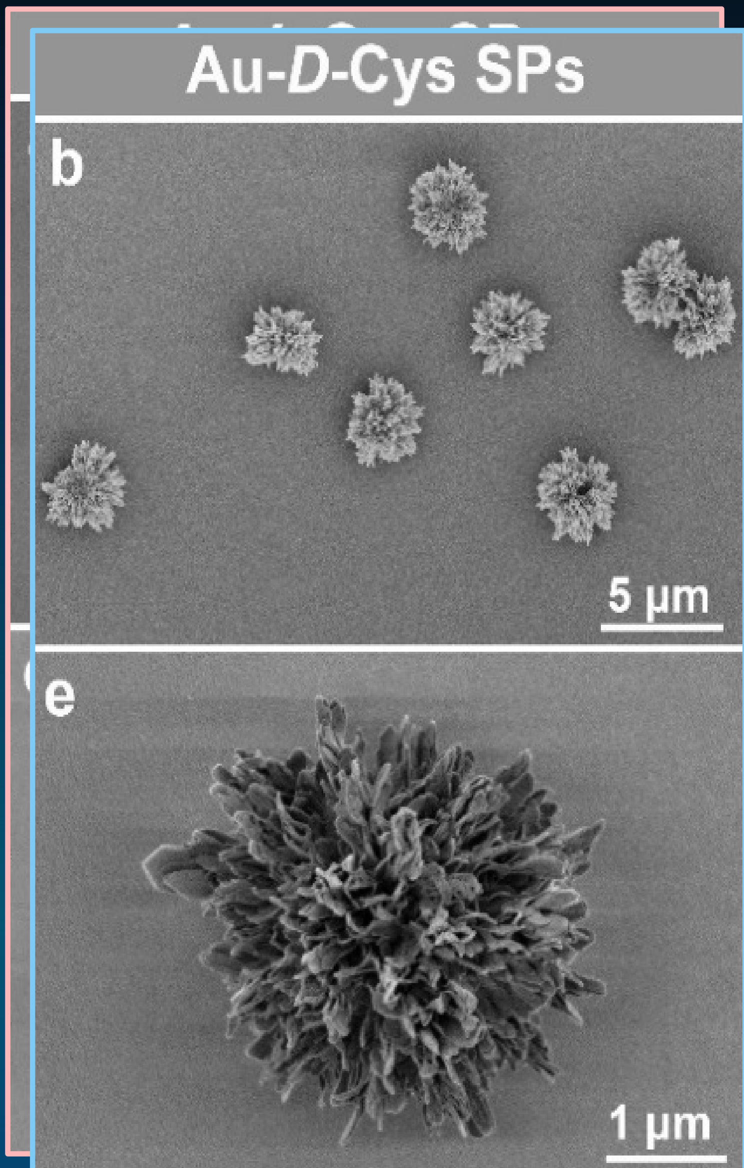


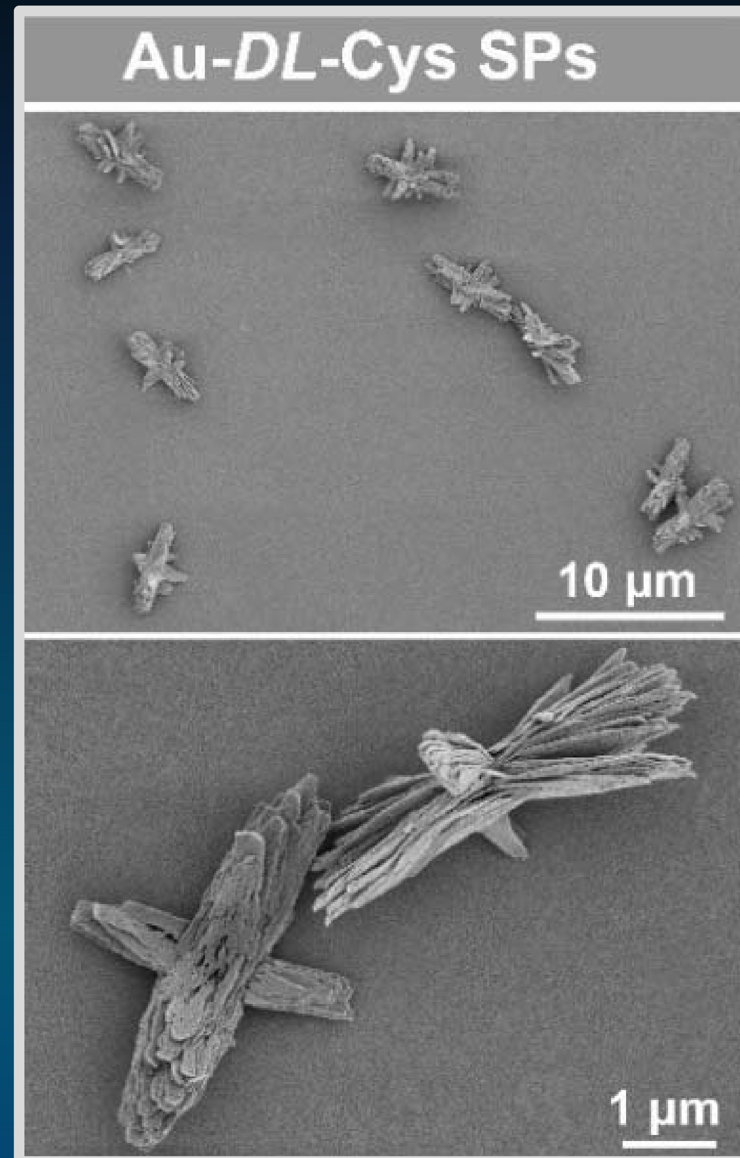




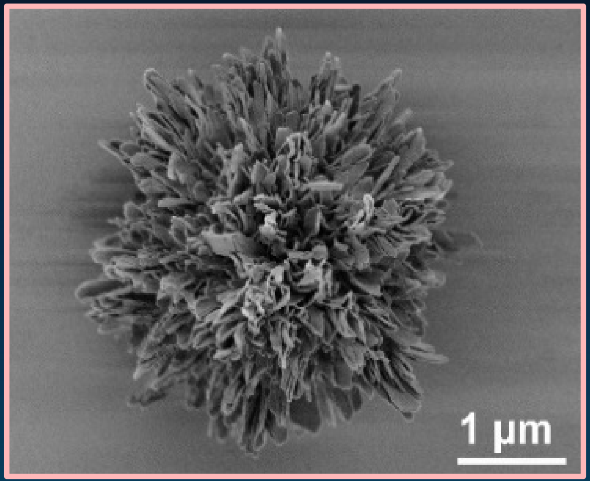
Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

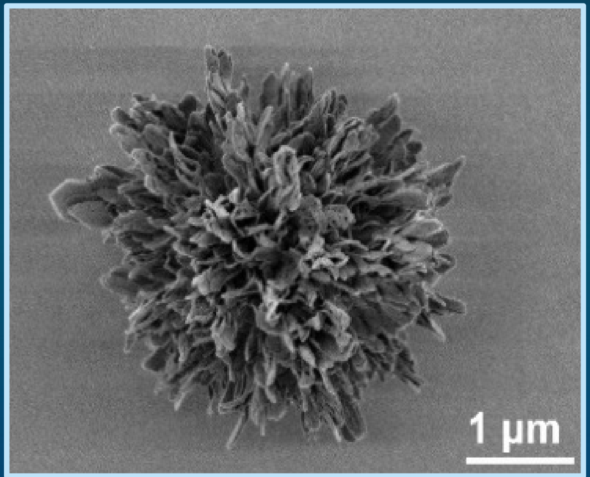
Self-Assembled Chiral Hedgehog Particles

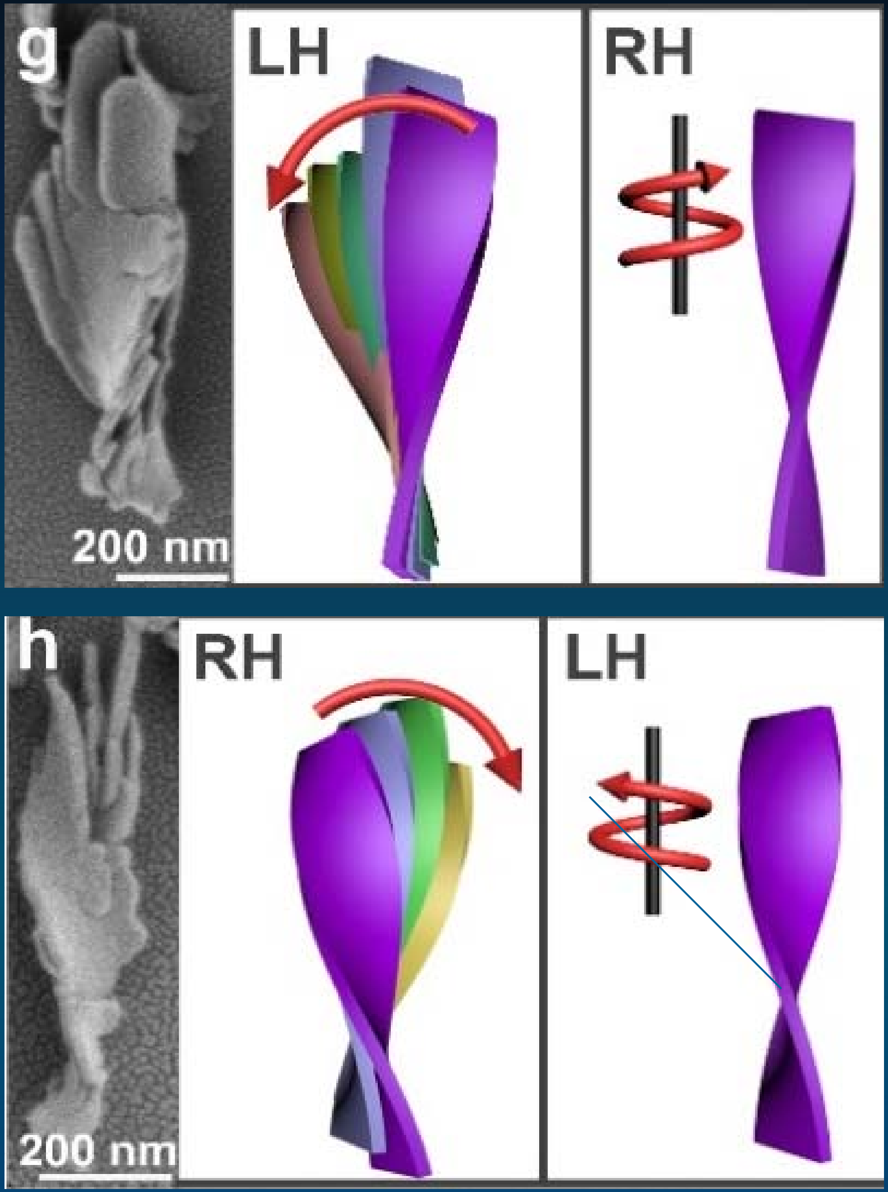




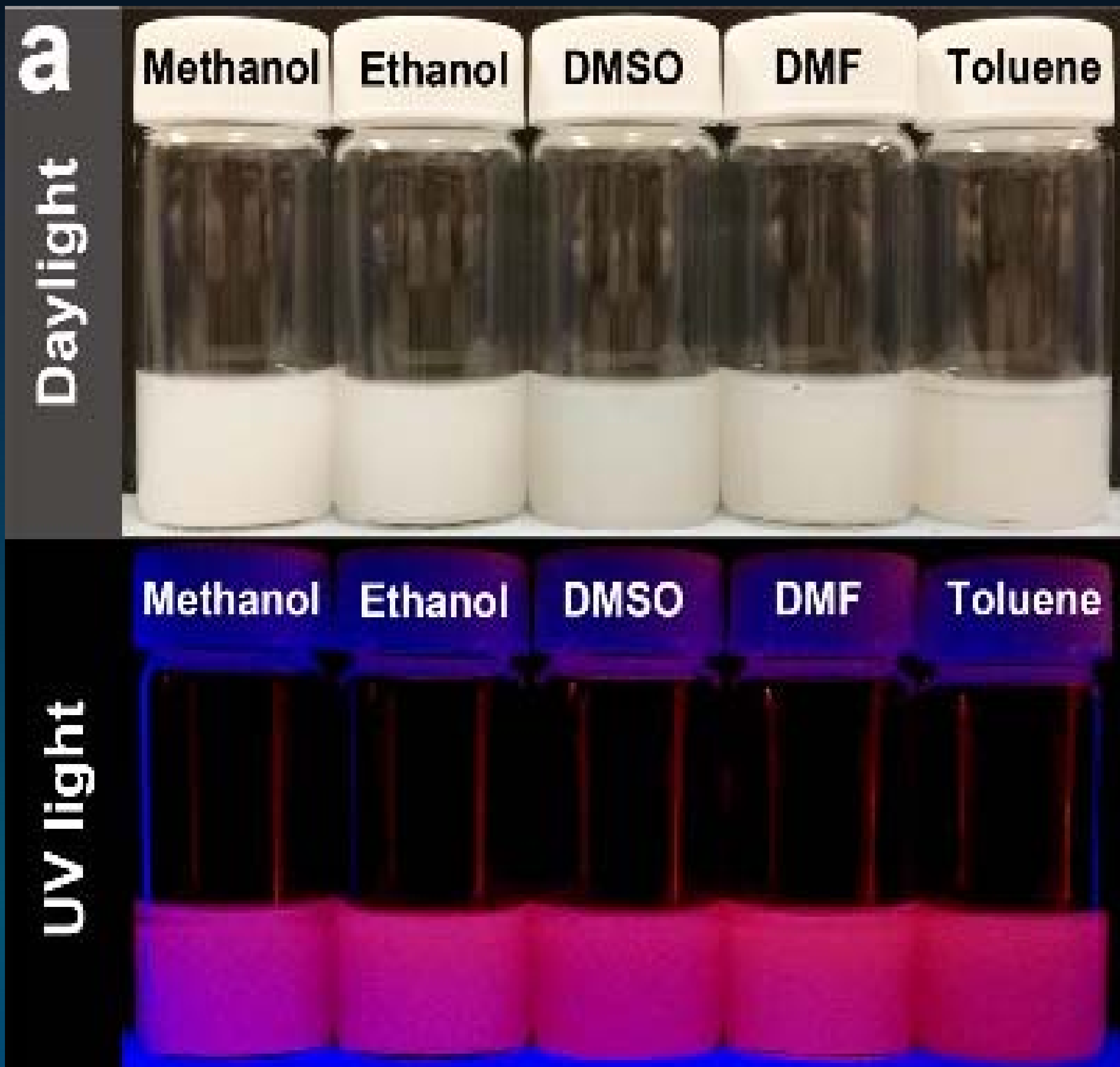
Chiroptically Active Hedgehog Particles

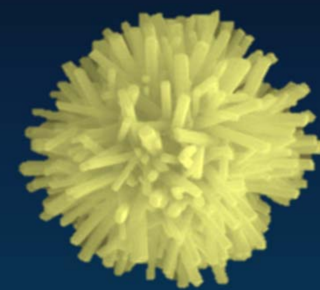


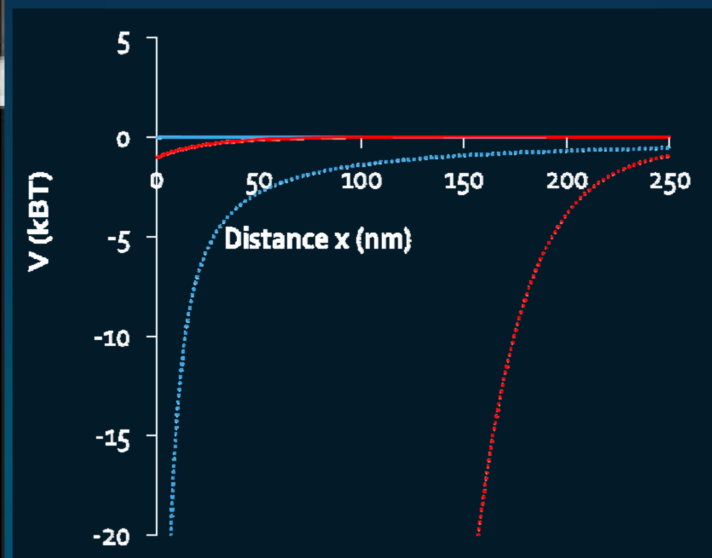




Self-Assembled Hedgehog Particles

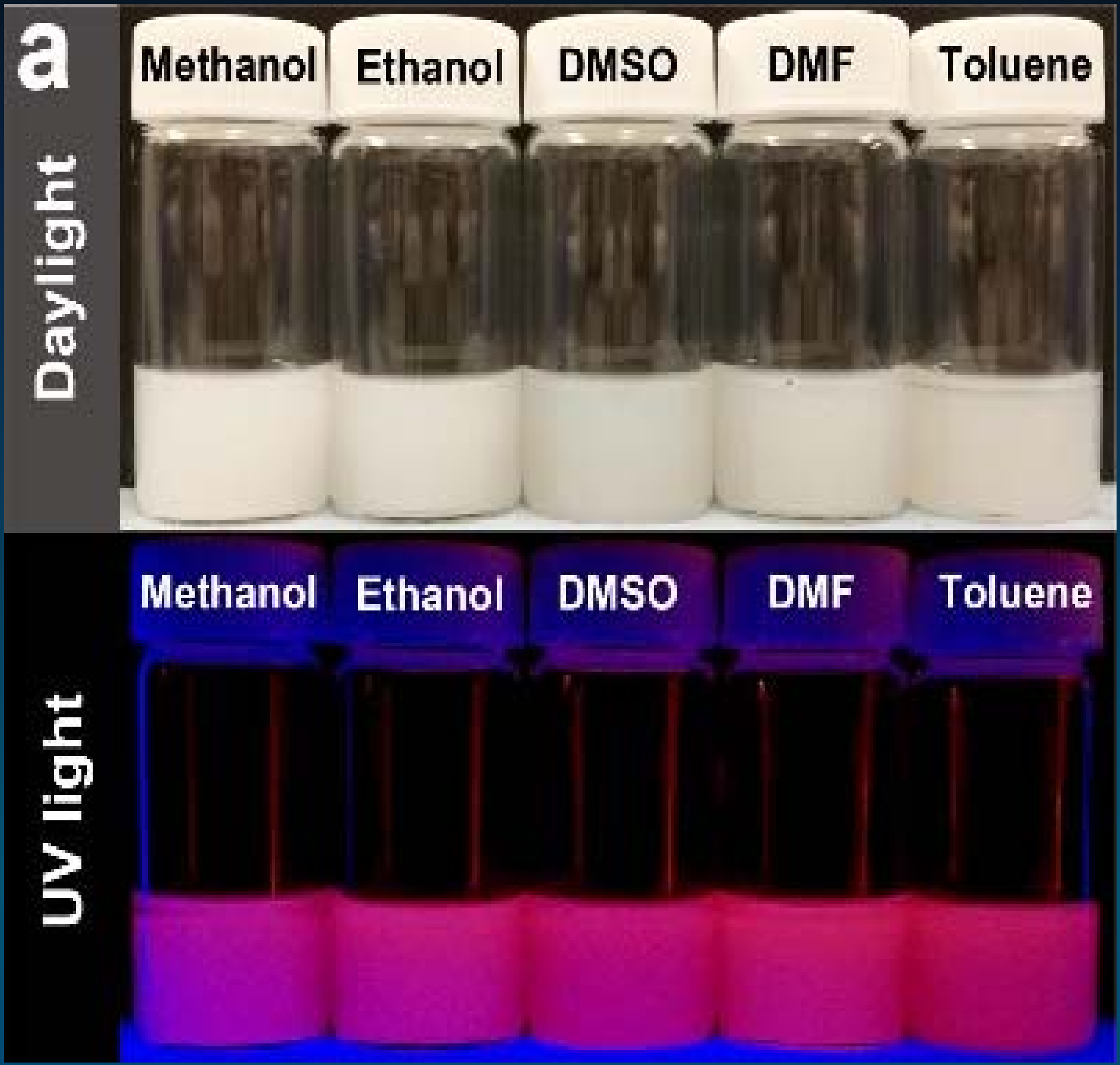






J. H. Bang, B. Yeom, Y. Wang, S. O. Tung, N.A. Kotov, Anomalous Dispersions of Hedgehog Particles, *Nature*, 2015, 517, 596

Self-Assembled Hedgehog Particles



Au-S
2D
Material

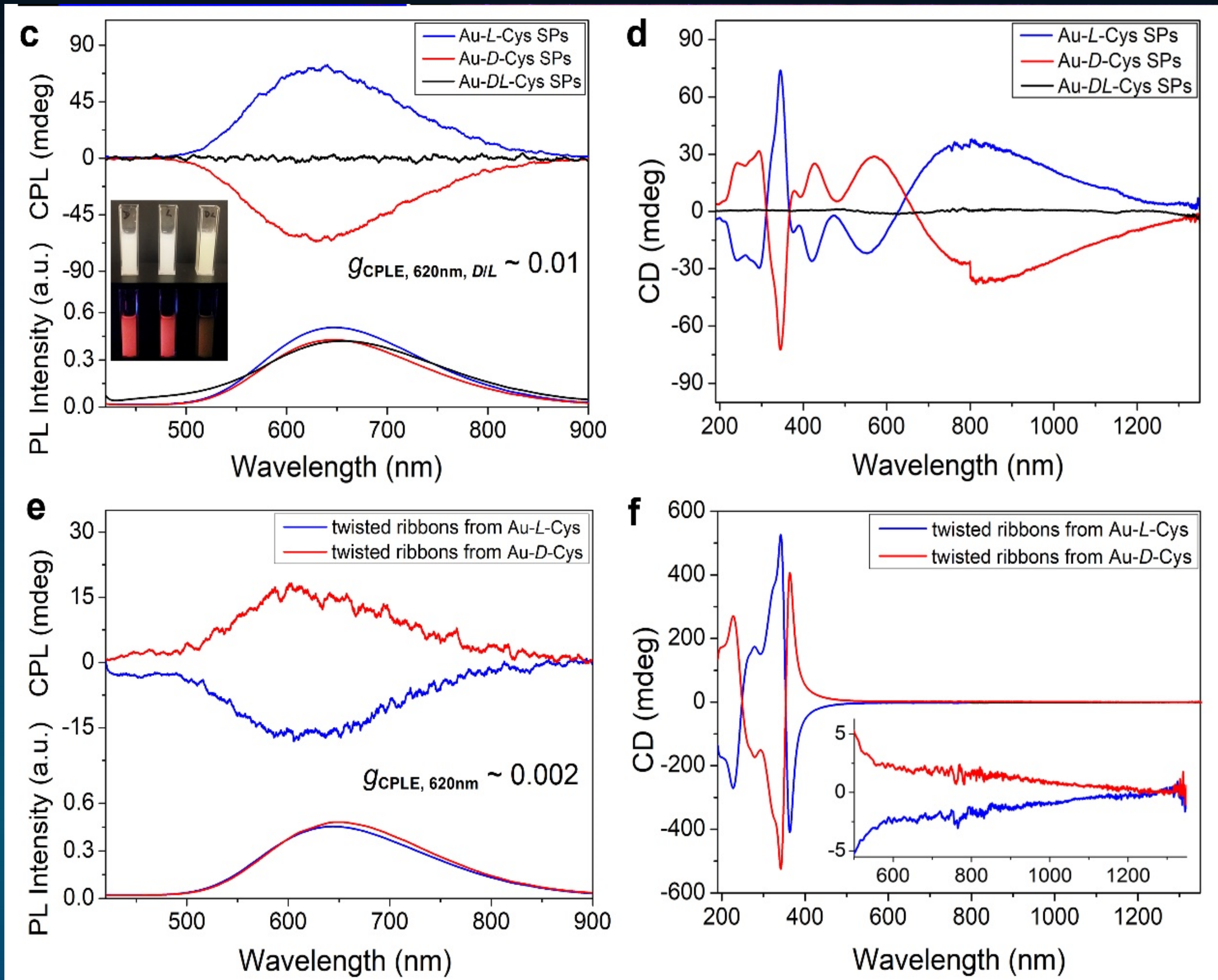
Strong
Optical
Emission

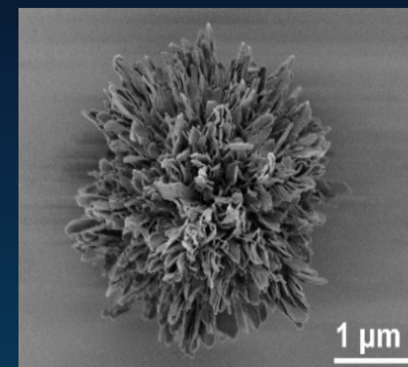
Jiang, W.; Qu, Z.; Kumar, P.; Vecchio, D.; Wang, Y.; Ma, Y.; Bahng, J. H.; Bernardino, K.; Gomes, W. R.; Colombari, F. M.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Second revision

Unusual pH Stability

Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

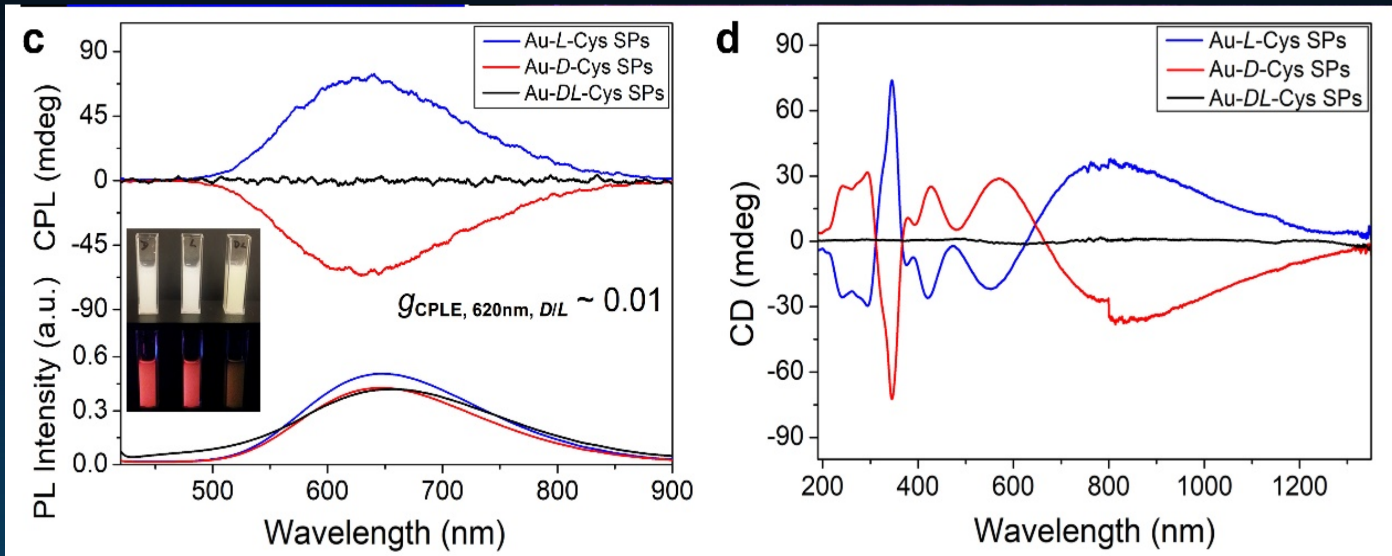
Chiroptically Active Hedgehog Particles

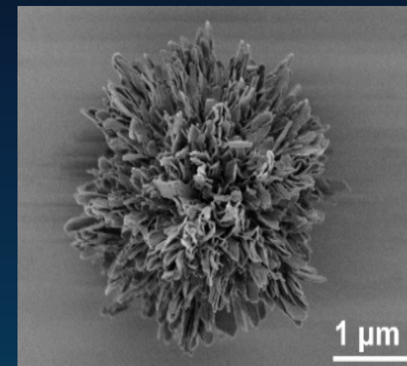


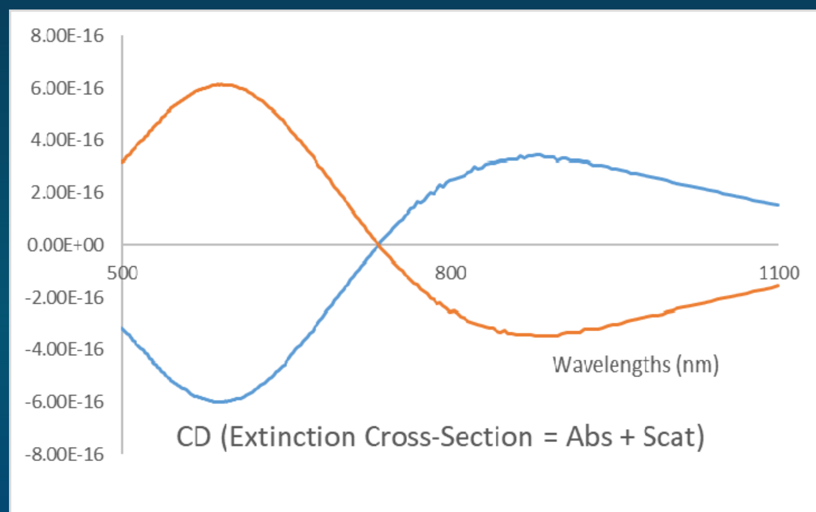


Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

Chiroptically Active Hedgehog Particles

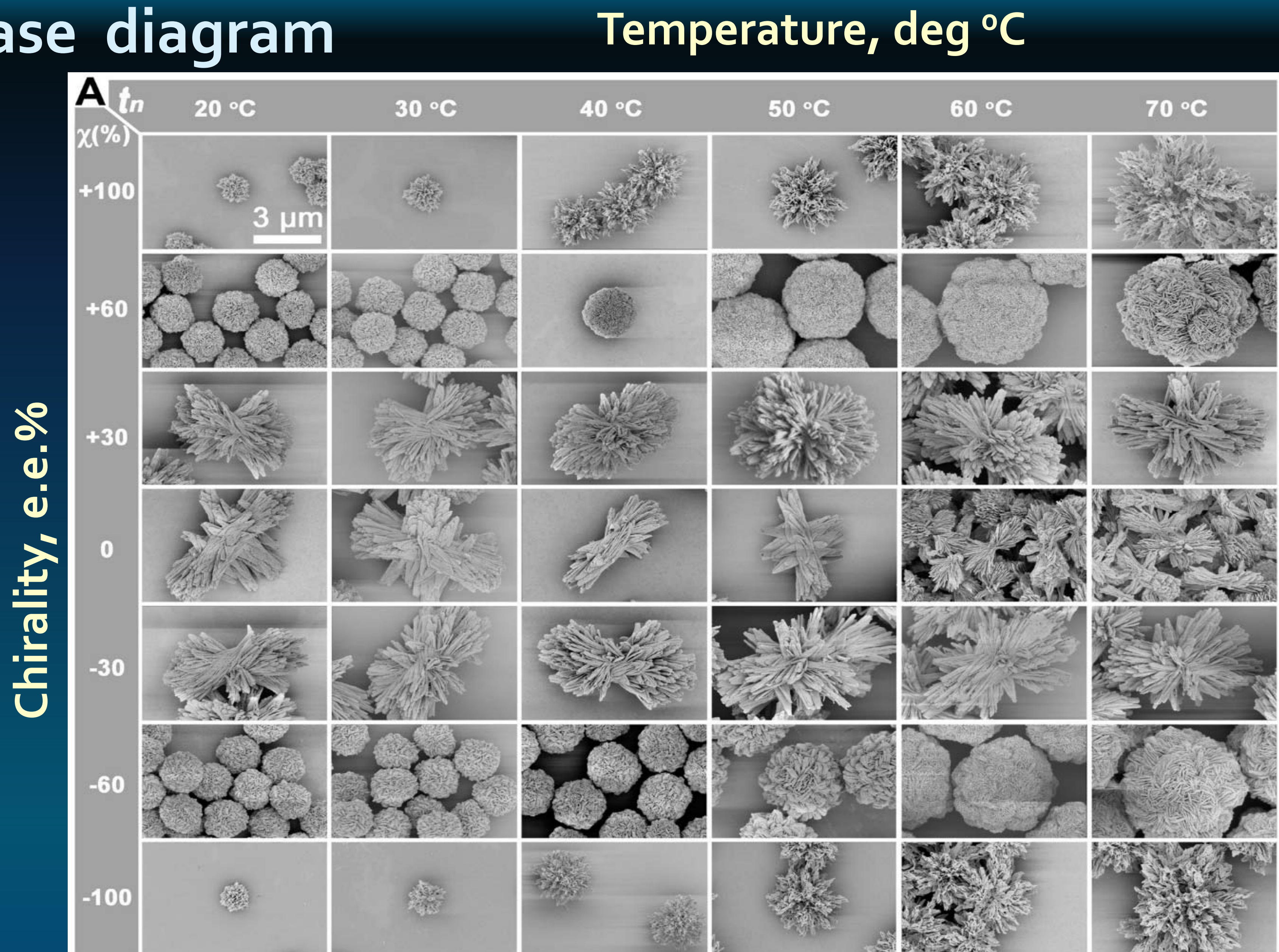






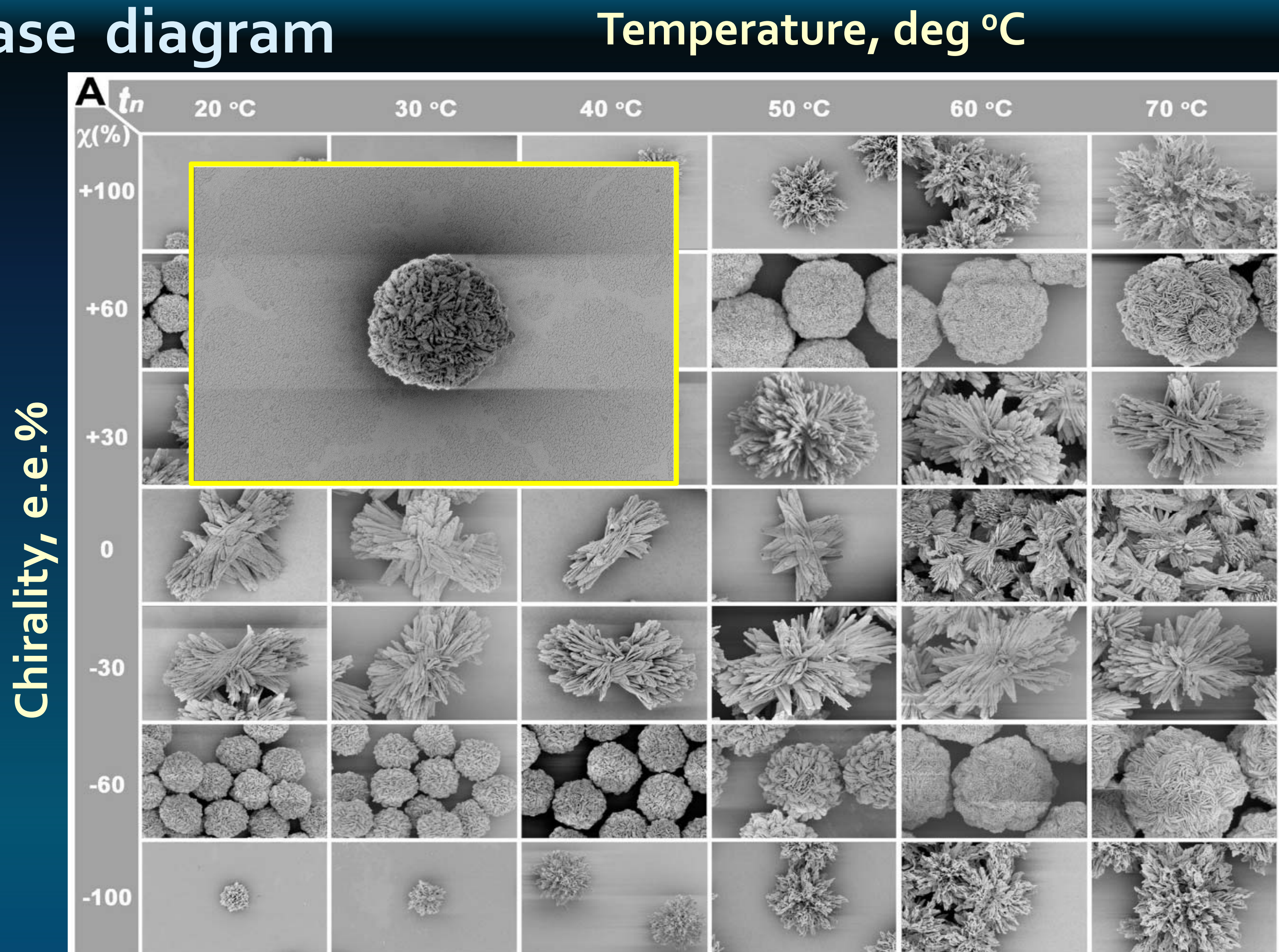
Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

Phase diagram



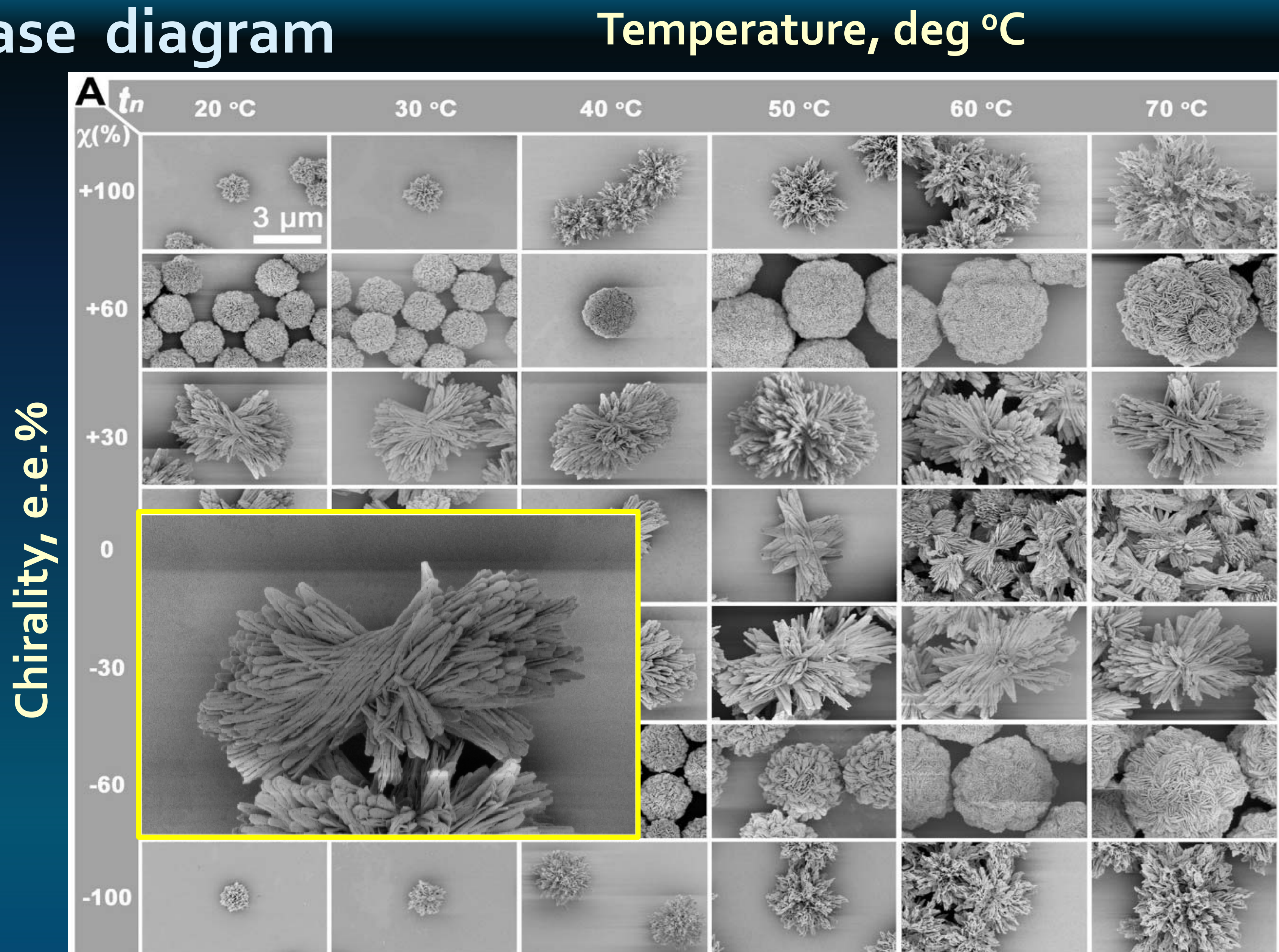
Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

Phase diagram



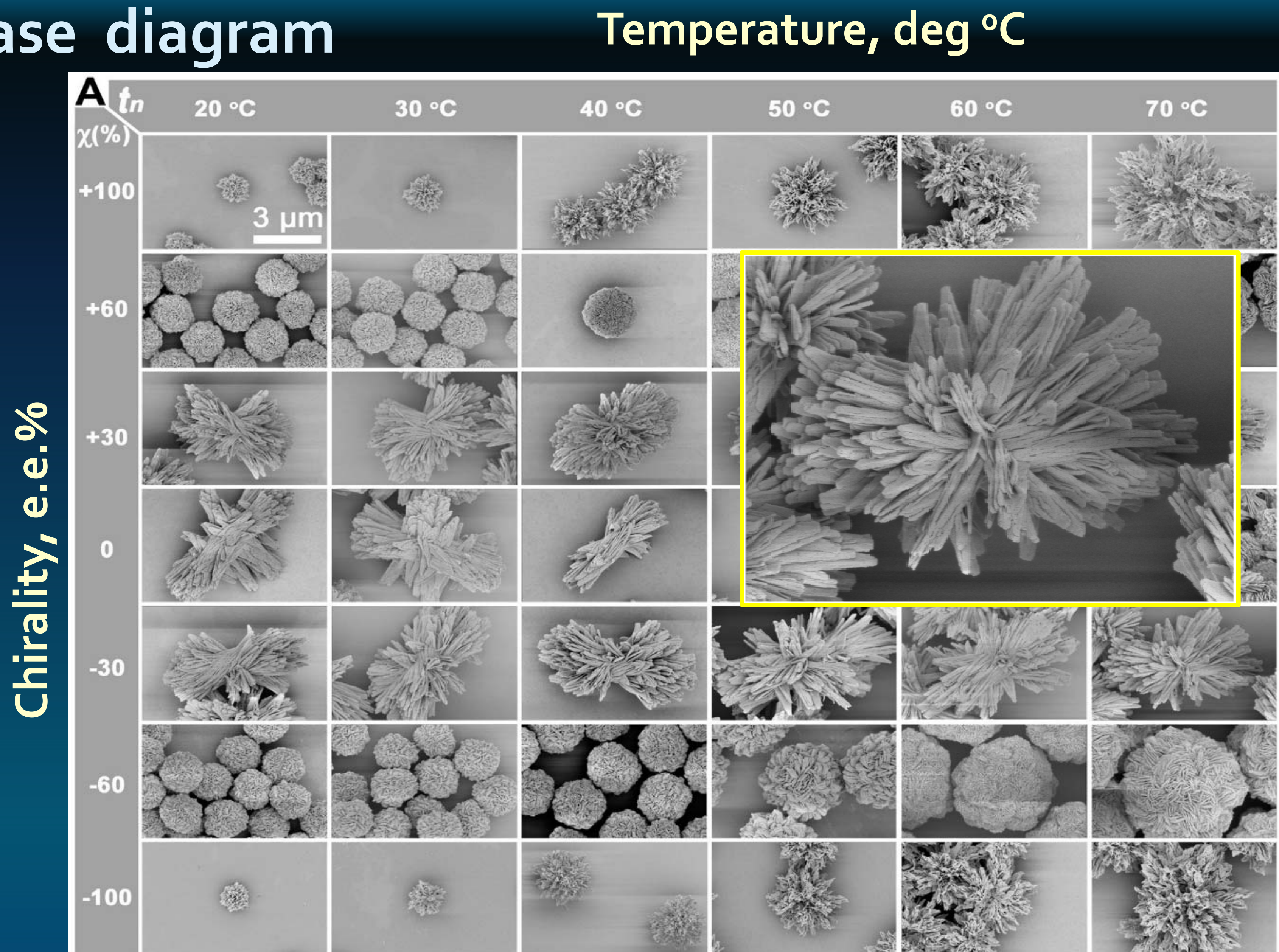
Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

Phase diagram



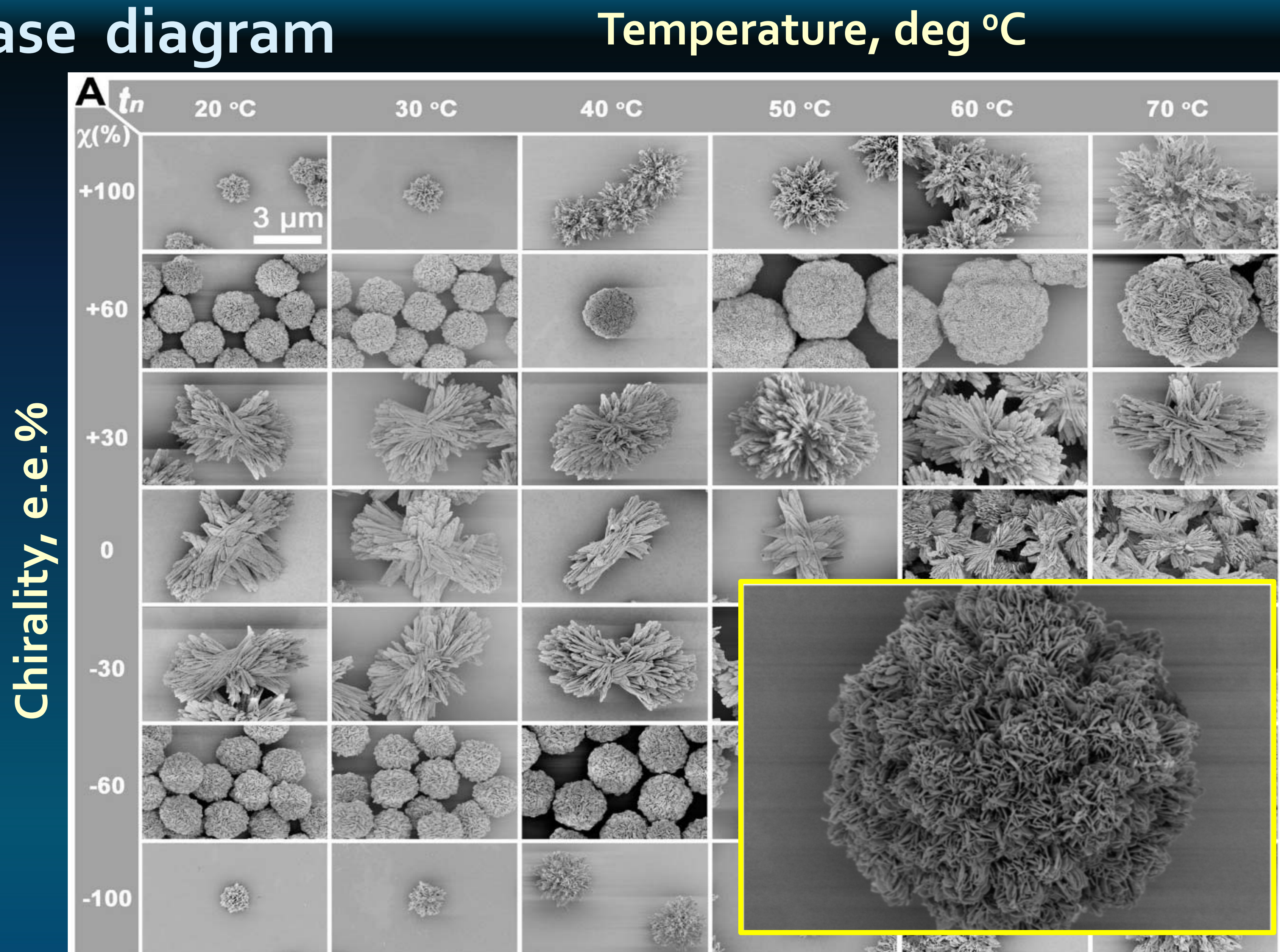
Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

Phase diagram



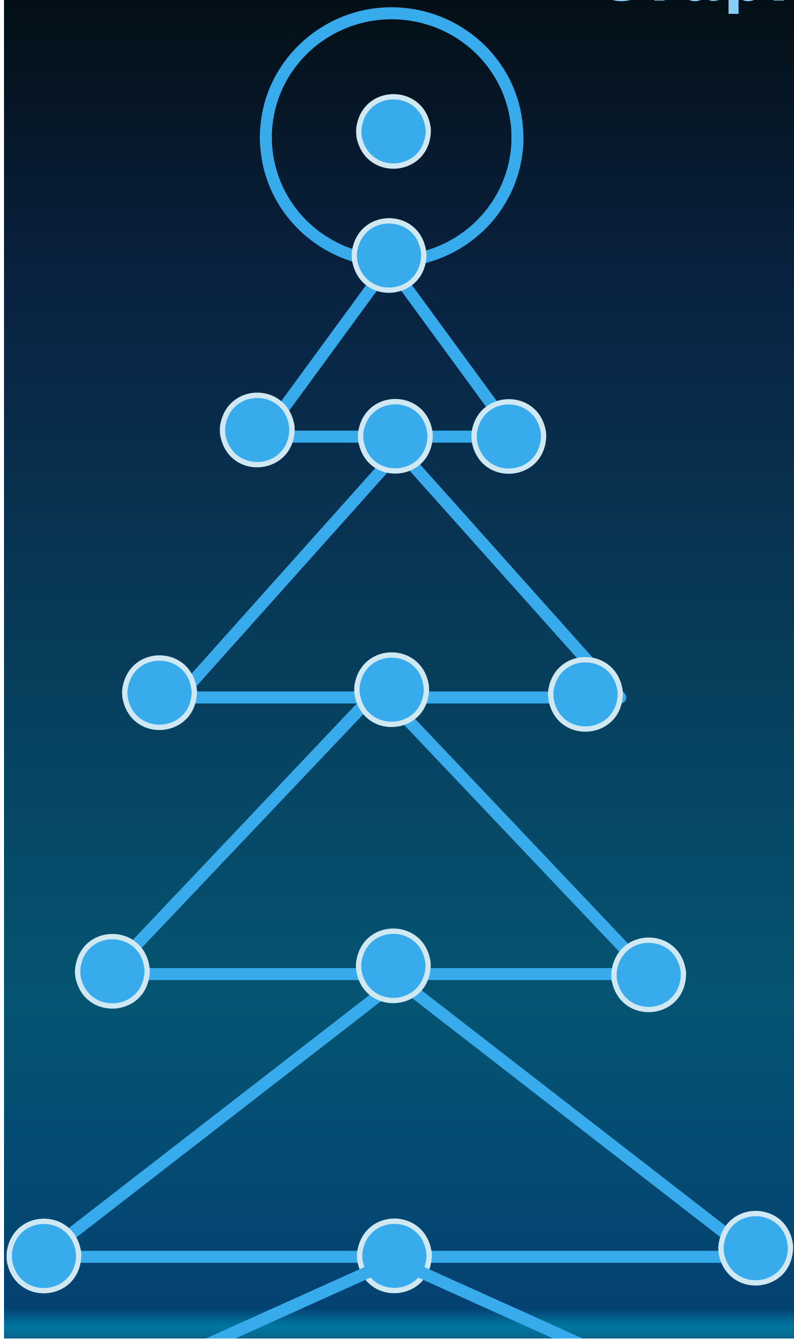
Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

Phase diagram



Jiang, W.; *et al.* Emergence of Complexity in Hierarchically Organized Chiral Particles. Science, 2020, 368, 6491, 642

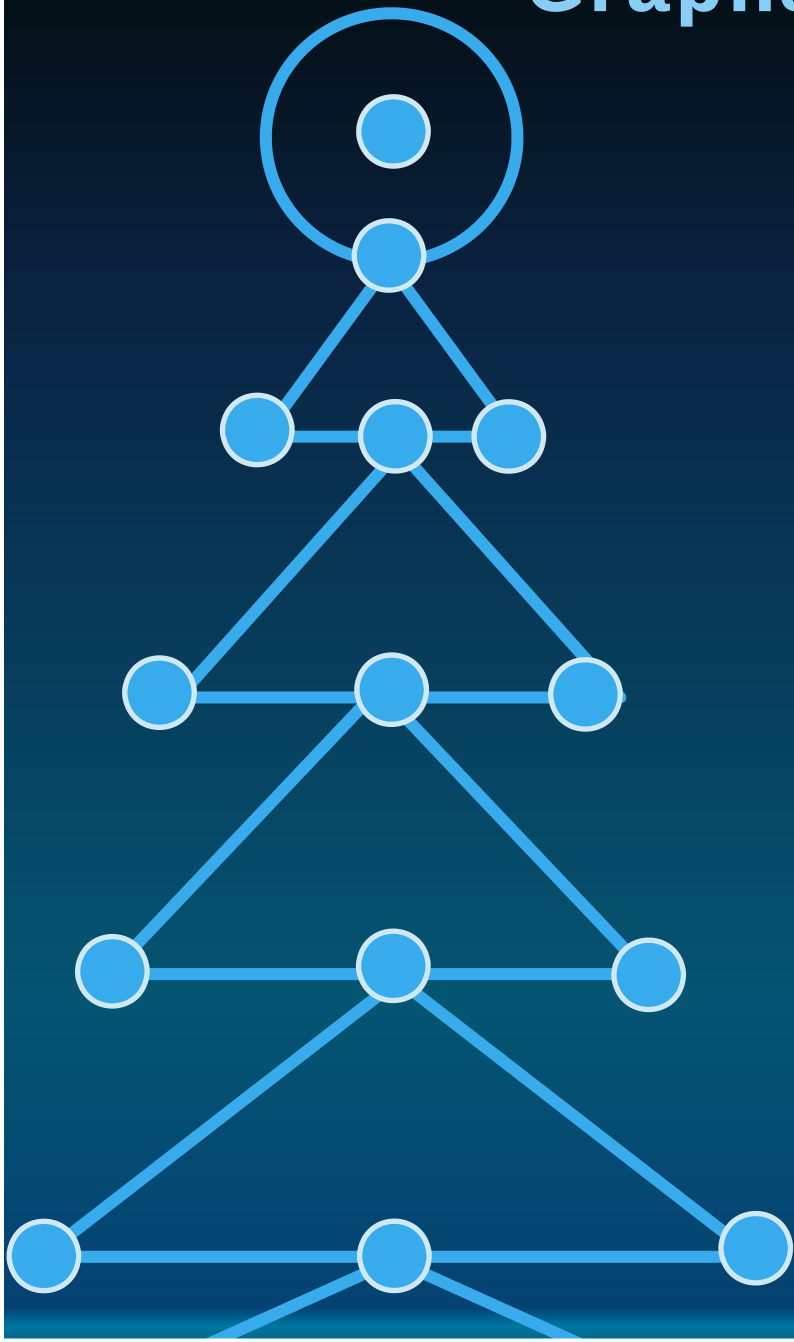
Graphs and Complexity



GRAPH - a set of nodes and edges

COMPLEXITY - information content

Graphs and Complexity



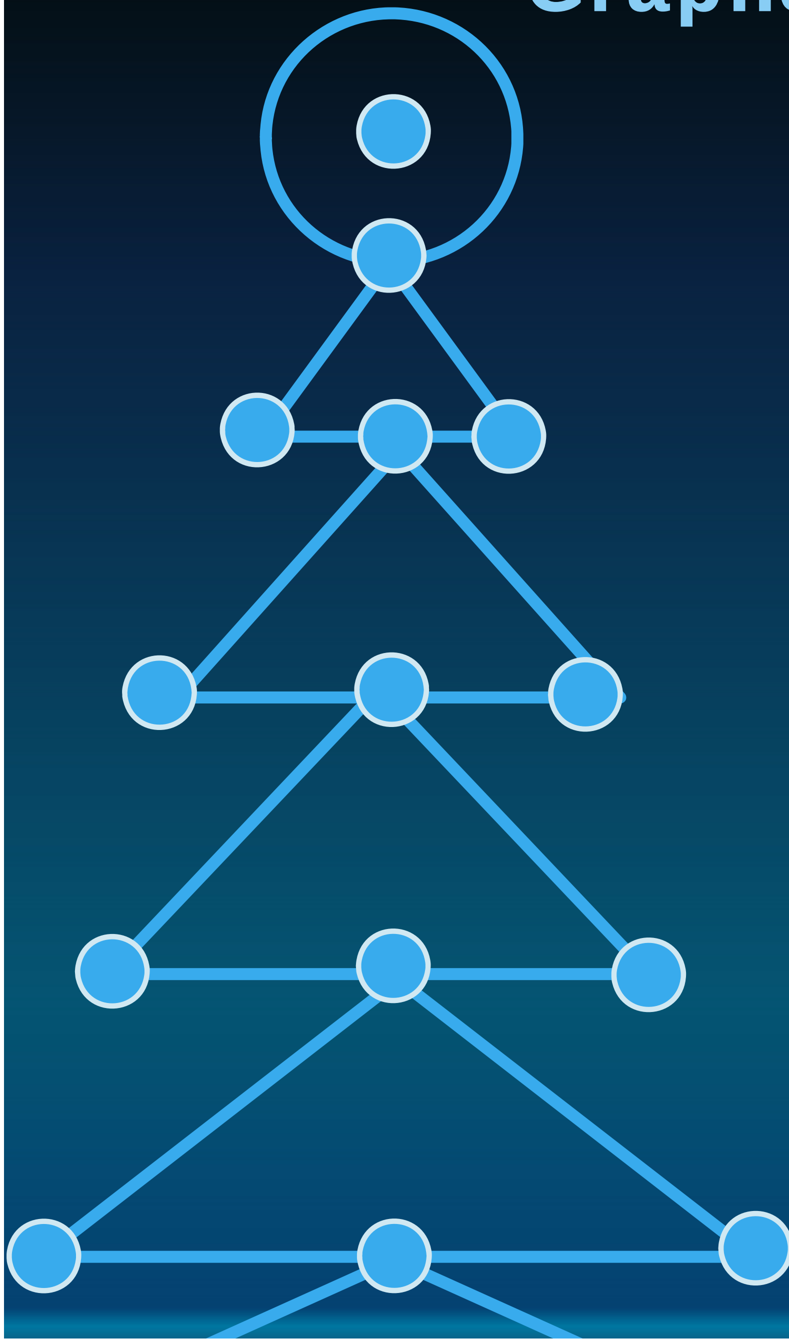
Measures of Complexity

Multifractal parameters

Connectivity index

Complexity index (*CI*)

Graphs and Complexity



Measures of Complexity

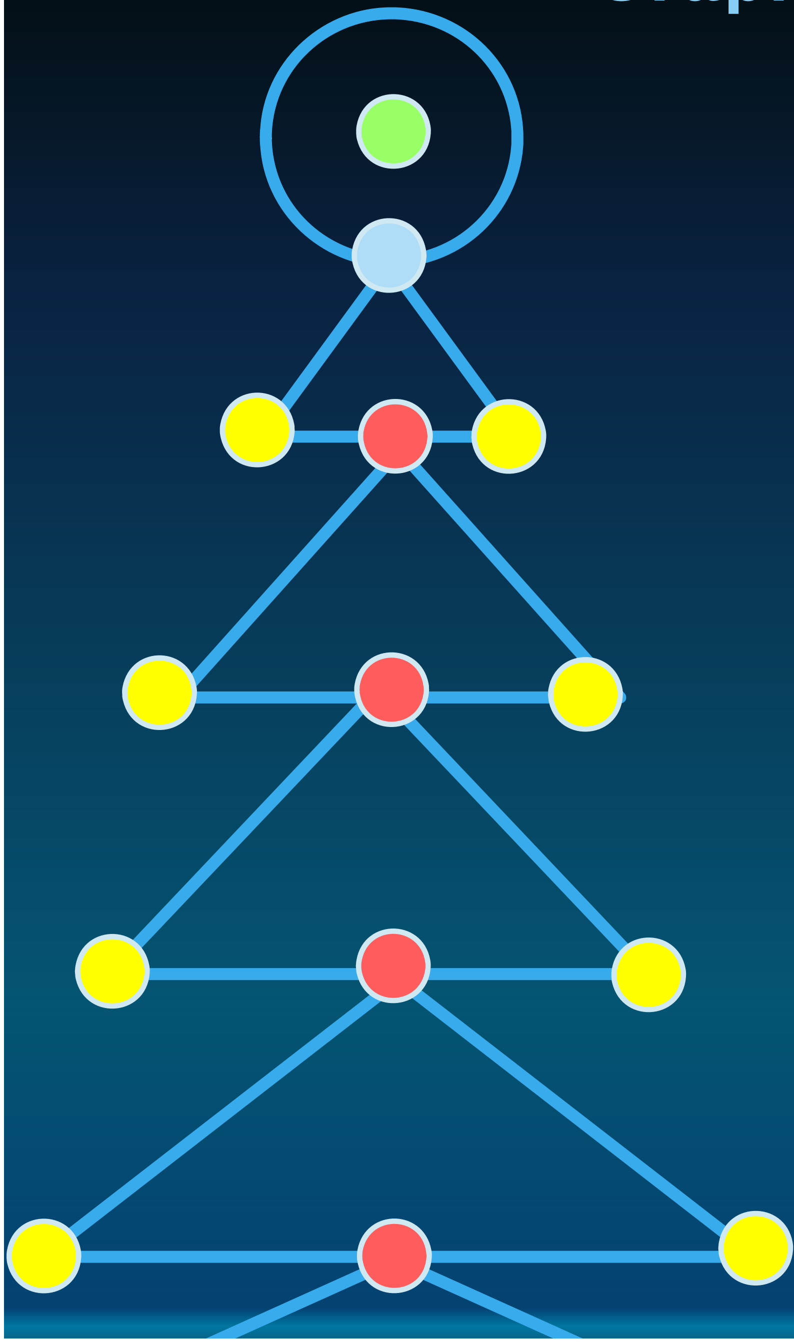
Multifractal parameters

Connectivity index

Complexity index (*CI*)

M. Randić, D. Plavšić On the Concept of Molecular Complexity *Croatica Chemica Acta*, 2002, 75 (1) 107

Graphs and Complexity



Measures of Complexity

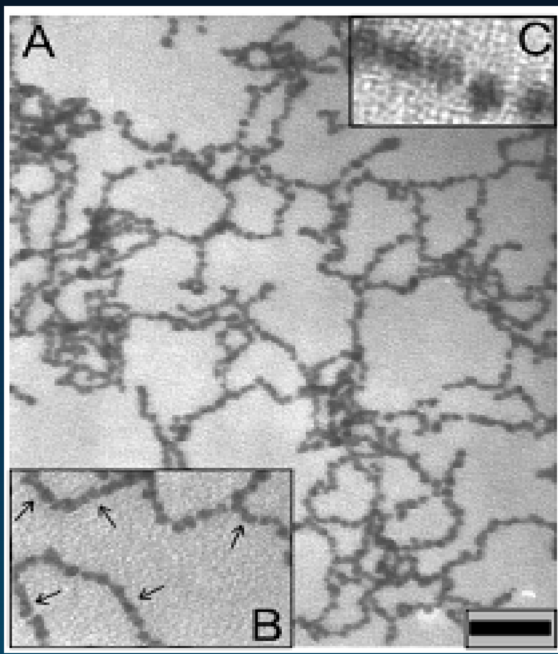
Multifractal parameters

Connectivity index

Complexity index (*CI*)

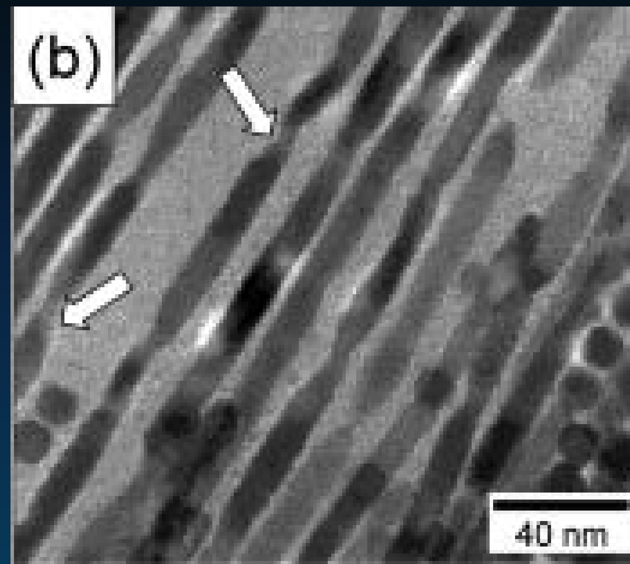
M. Randić, D. Plavšić On the Concept of Molecular Complexity *Croatica Chemica Acta*, 2002, 75 (1) 107

Nanoassemblies

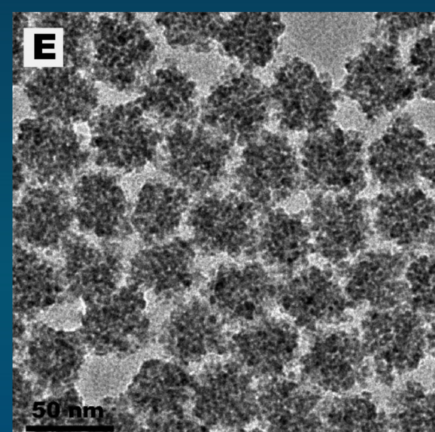


Tang, Z.; Kotov, N. A.; Giersig, M.; *Science*, 2002, 297, 237.

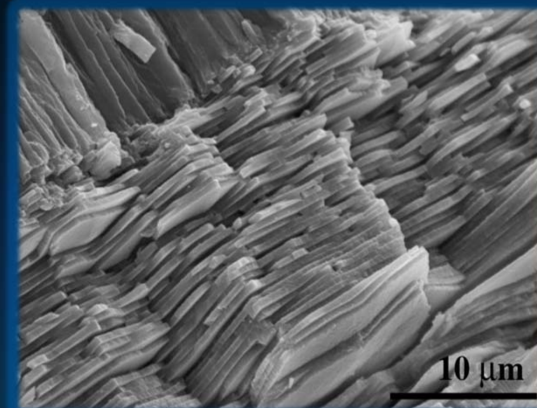
Kotov, N.A.; Dékány, I.; Fendler, J.H. *Adv. Mater.* 1996, *8*, 637.



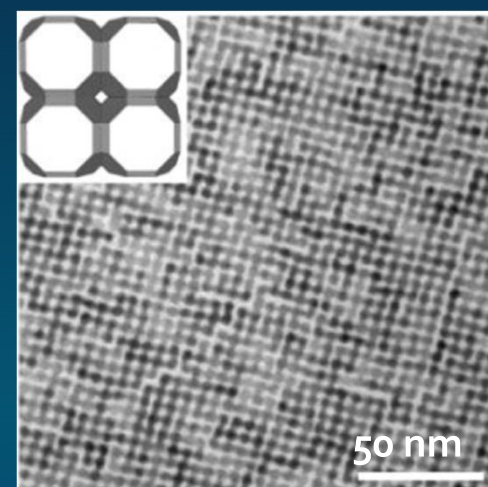
Cho, K.-S.; Talapin, D. V.; Gaschler, W. L.; Murray, C. B., *J. Am. Chem. Soc.*, 2005, 127, 7140



Y. Xia, T. D. Nguyen, M. Yang, B. Lee, A. Santos, P. Podsiadlo, Z. Tang, S. C. Glotzer, N. A. Kotov, *Nature Nanotech*, 2011, 6, 580



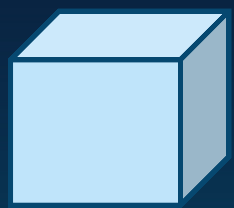
S. Blank, et al.. *J. Microsc.* 2003, 212, 280.



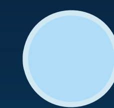
W. H. Evers, B.Goris, S. Bals, M.Casavola, J.de Graaf, R.van Roij, M. Dijkstra, D. Vanmaekelbergh, *Nano Lett.* 2013, *13*, *2317*

Graph Theory (GT) of Nanoassemblies

NODES – represent zero-dimensional nanoscale building blocks

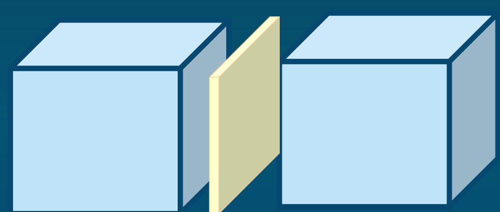


Generalized nanoparticle

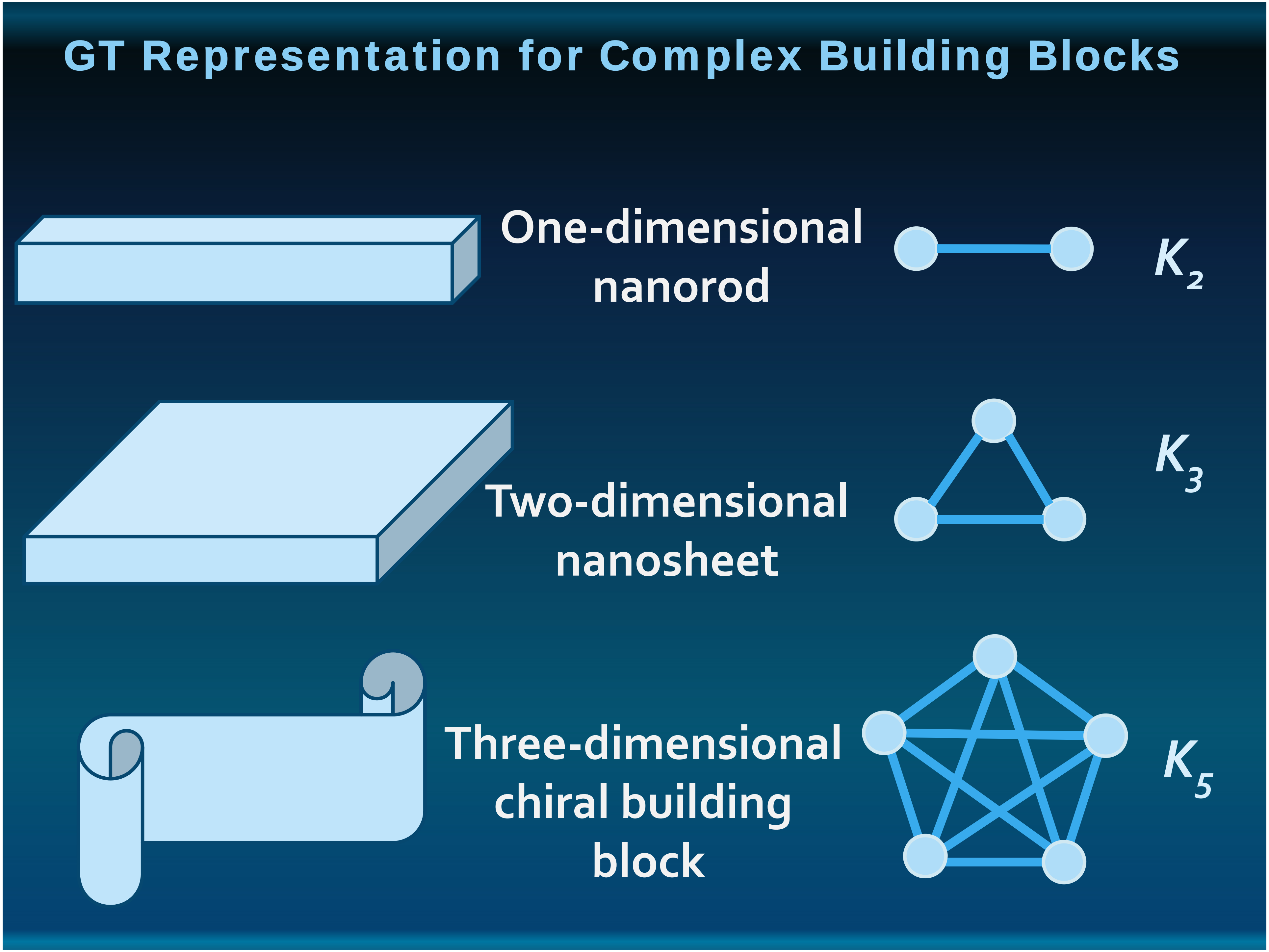


K_1 graph

EDGE - represents organic-inorganic interface

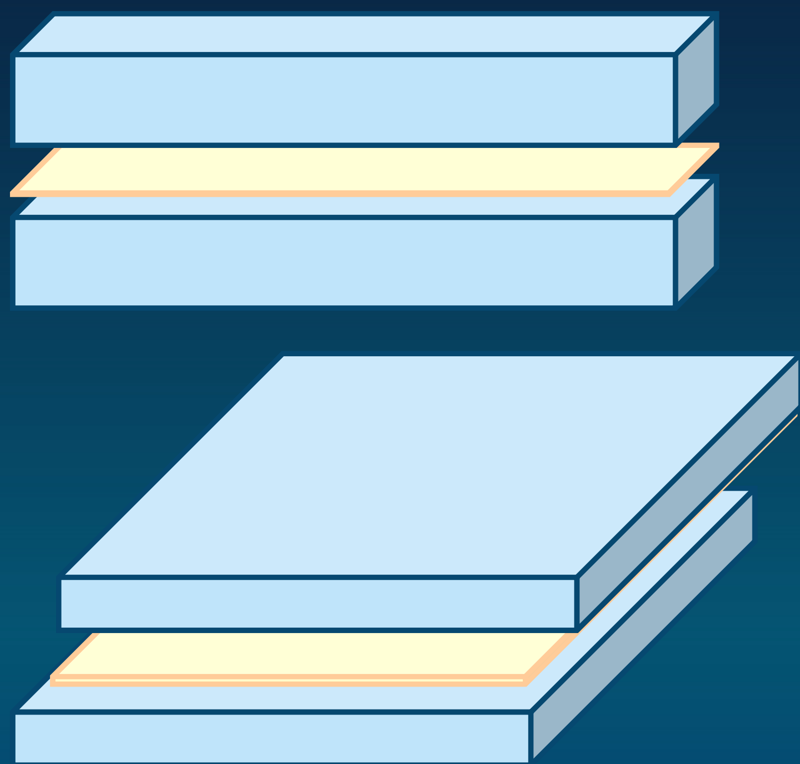


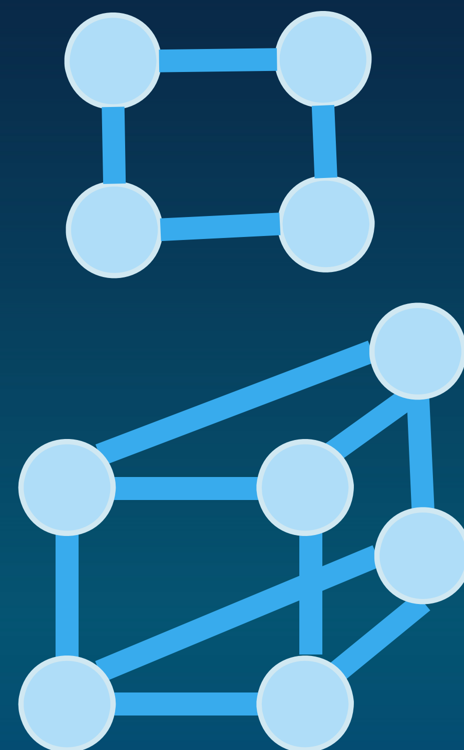
A generalized layer of organic ligands


GT Representation for Complex Building Blocks
One-dimensional nanorod
K_2
Two-dimensional nanosheet
K_3
Three-dimensional chiral building block
K_5

Connectivity Between Complex Blocks

EDGE - represents organic-inorganic interface



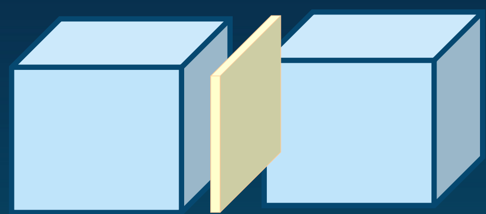


Jiang, W.; Qu, Z.; Kumar, P.; Vecchio, D.; Wang, Y.; Ma, Y.; Bahng, J. H.; Bernardino, K.; Gomes, W. R.; Colombari, F. M.; *et al.*
Emergence of Complexity in Hierarchically Organized Chiral Particles.. Second revision

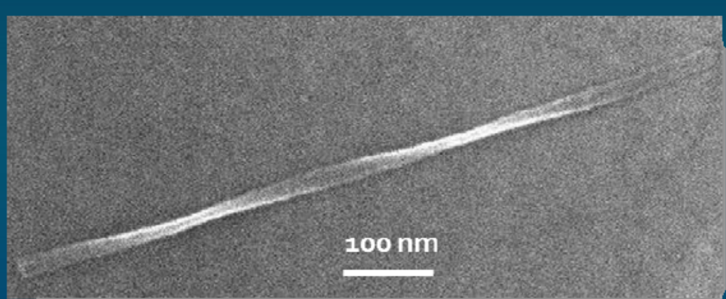
Calculations of Complexity Index

Number of edges for a node = N

$$CI = N + \Sigma N\ (\text{nearest neighbors})/2 + \Sigma N\ (\text{next neighbors})/4 + \ldots$$



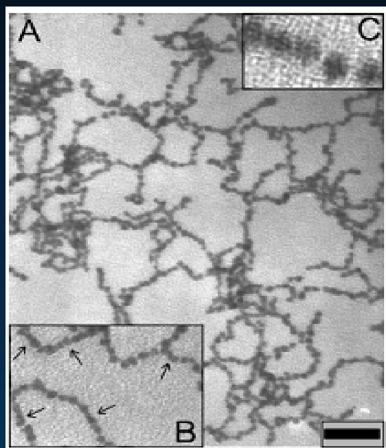
$CI = 1 + [1/2]$ **= 1.5**



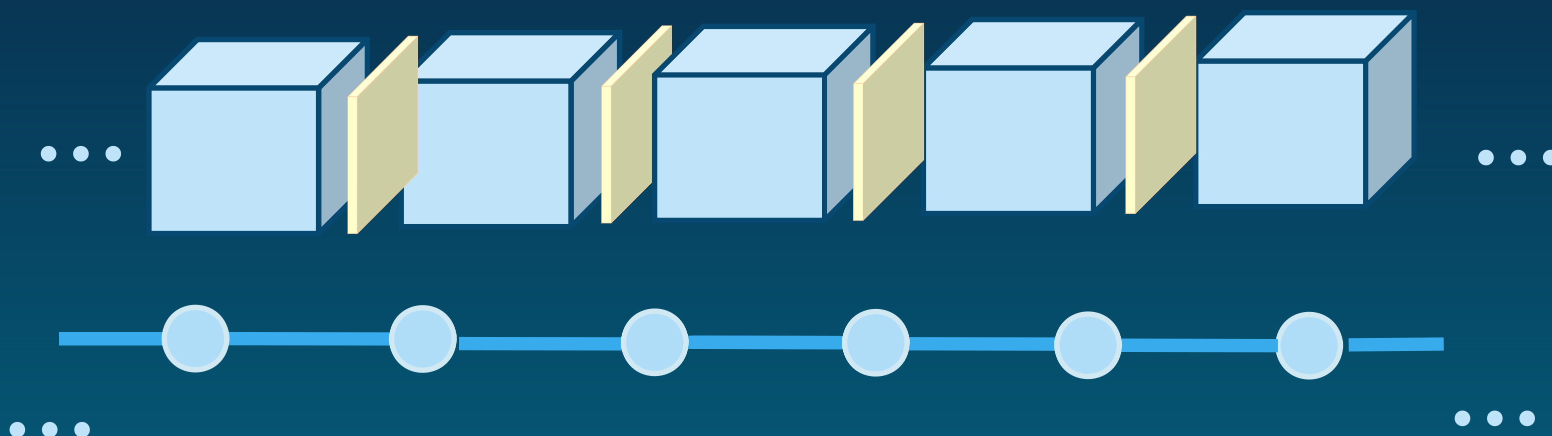
$CI = 4 + [16/2]$ **= 12**

Jiang, W.; Qu, Z.; Kumar, P.; Vecchio, D.; Wang, Y.; Ma, Y.; Bahng, J. H.; Bernardino, K.; Gomes, W. R.; Colombari, F. M.; *et al.*
Emergence of Complexity in Hierarchically Organized Chiral Particles.. Second revision

Calculations of Complexity Index

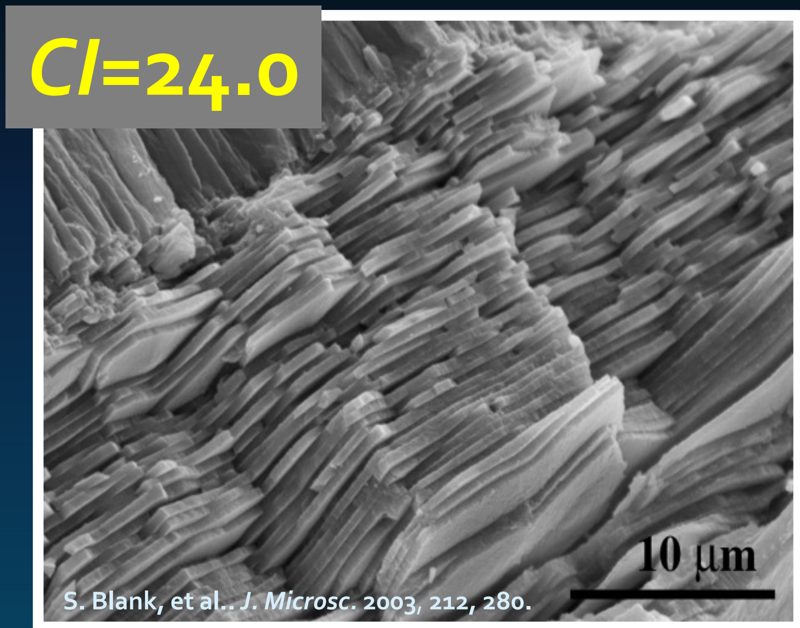


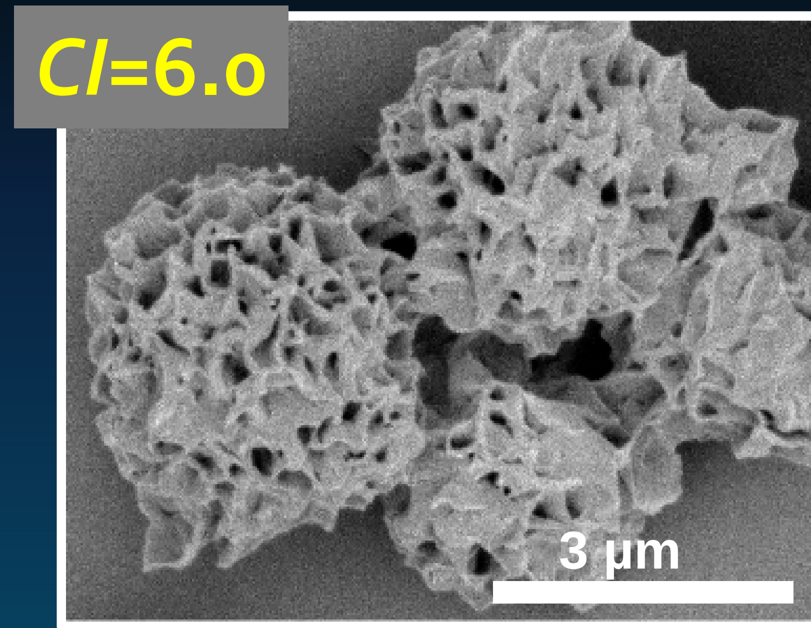
M. Li, S. Johnson, H. Guo, E. Dujardin
S. Mann, A Generalized Mechanism for
Ligand-Induced Dipolar Assembly of Plasmonic
Gold Nanoparticle Chain Networks *Advance Funct. Mater*, 2011, 21, 851

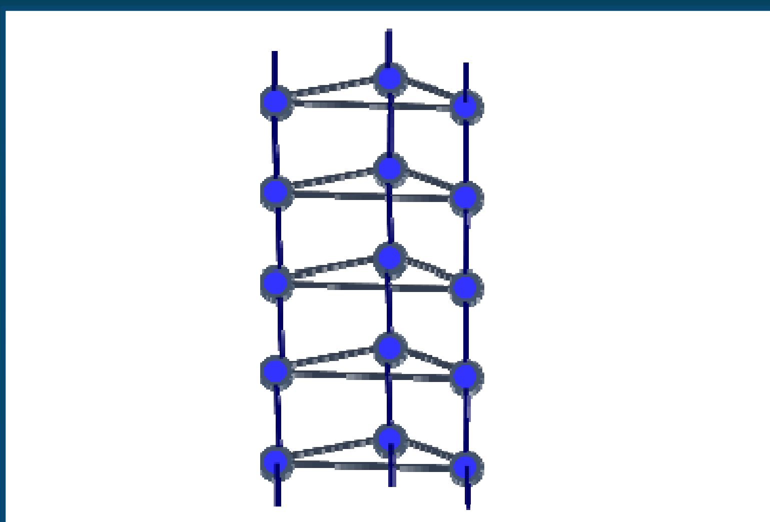


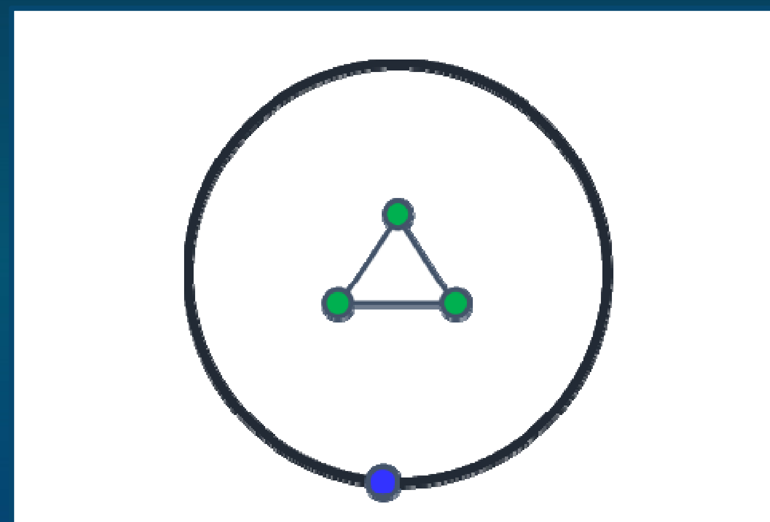
$$CI = 2 + [4/2] + [4/4] + [4/8] + \ldots = 2 + Lim(\Sigma\ 4/2^n) = 6$$

Graph Theory Models

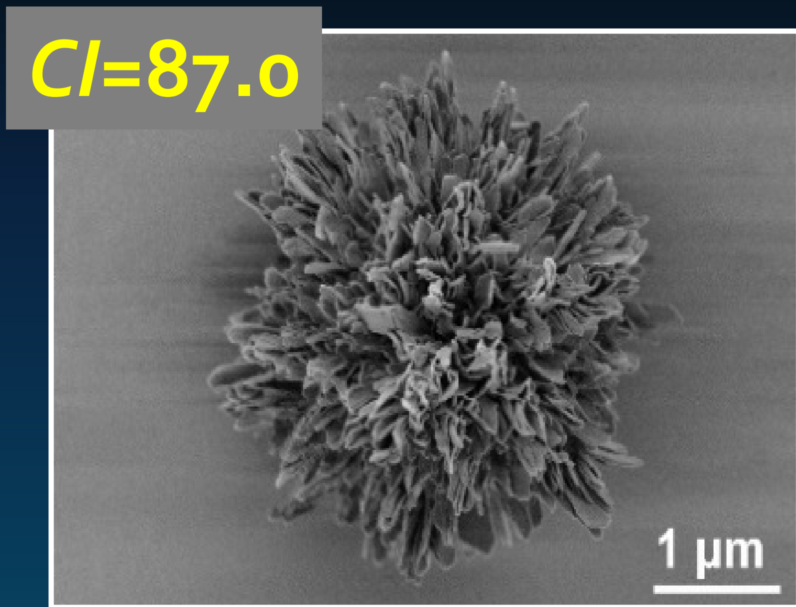


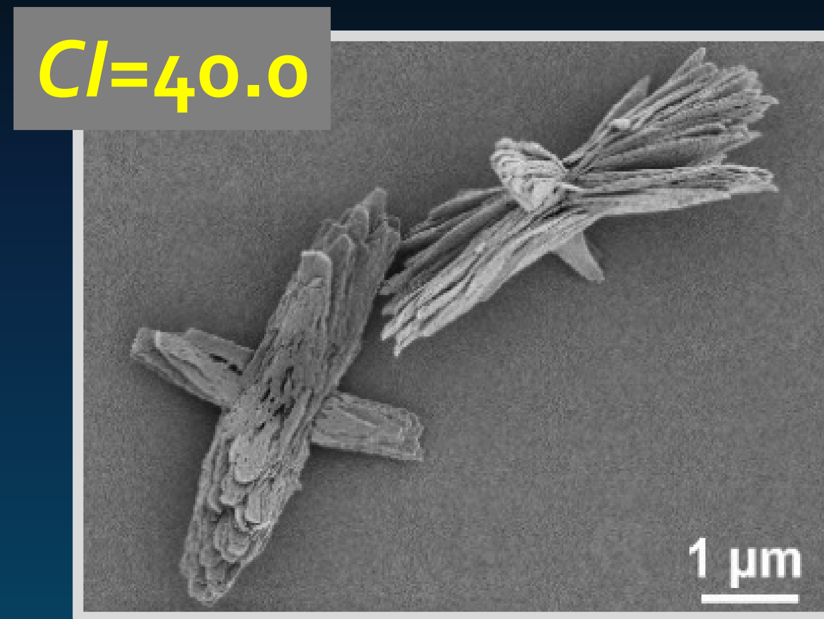


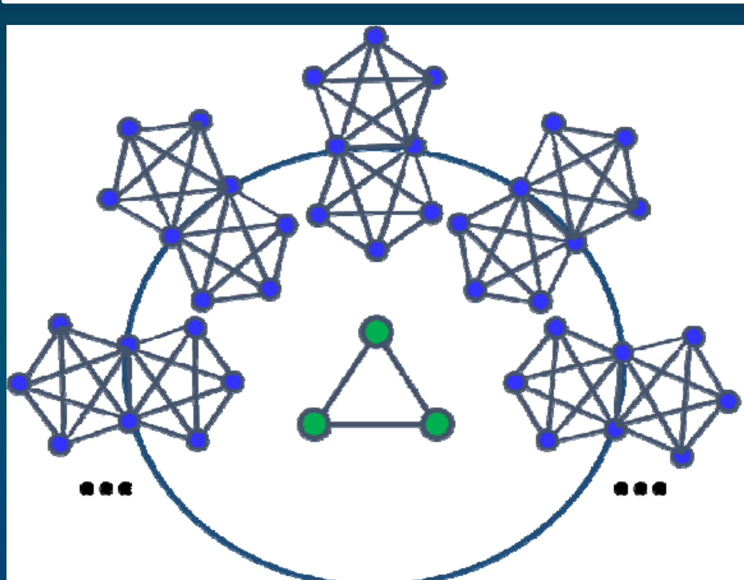


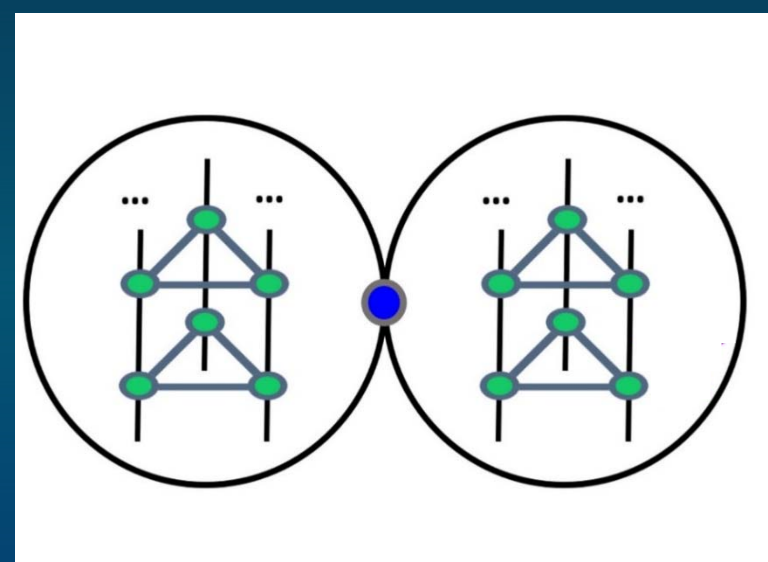


Graph Theory Models









Thank You!

NIH
NSF
DARPA
ONR

Dow Chemicals
Boeing
Dow Chemicals
3D Biomatrix

AFOSR
ARO
DOE
DTRA

IMRA
Nico Technologies
BASF
Hyundai

and other contributors for generous support