DNA-based Nanoscale Self-Assembly

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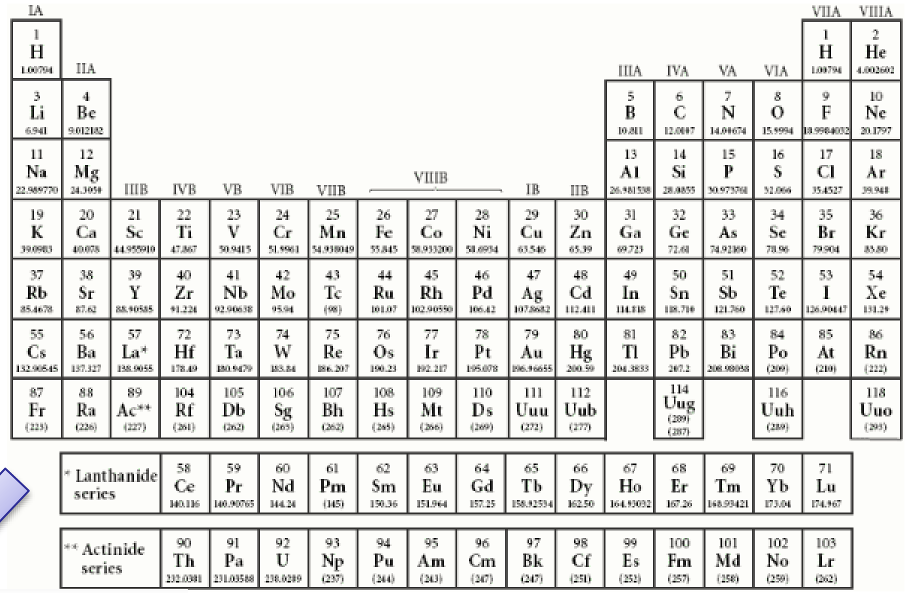
Lectures Outline

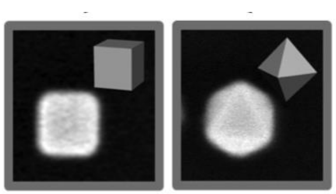
- Introduction: motivation, challenges, approaches
- DNA nanotechnology: from double helix to scaffolds and beyond
- Nanoparticles and DNA: functionalization, interactions and assembly approaches, arrays
- Building nanoparticle clusters with DNA: from structure to functions
- DNA-guided nanoparticle assemblies: structure, properties, phase behavior
- Towards designed lattice types
- Responsive lattices and transformation in DNA-assembled systems

Nanoscale objects

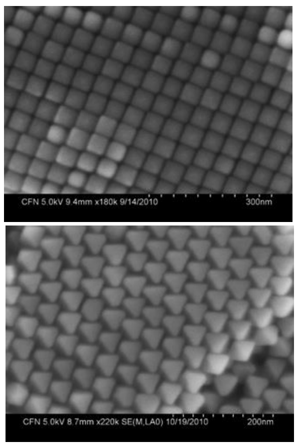


New Properties:
Optical
Electronic
Magnetic
Catalytic

Packaging atoms into nanoparticles

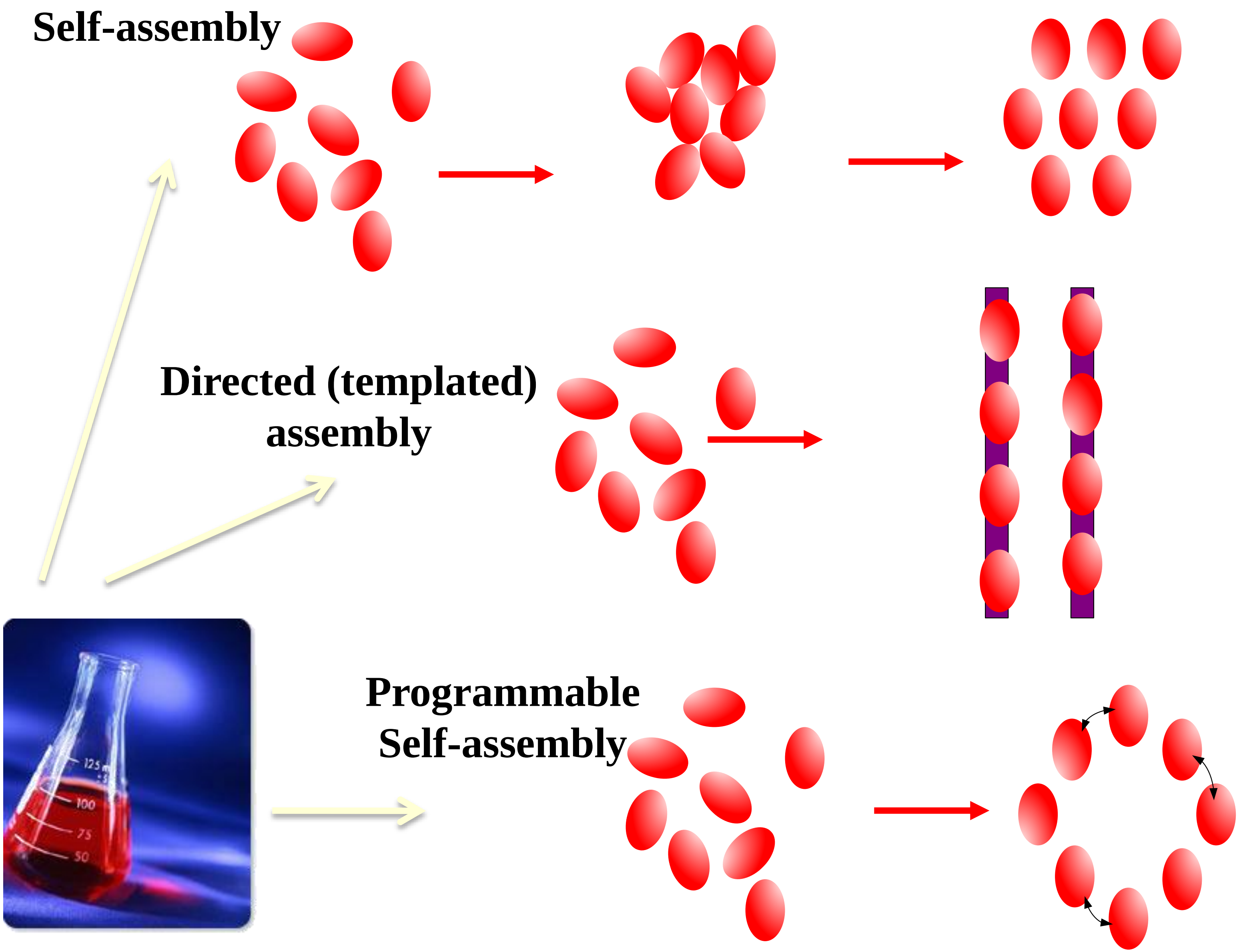


Nanoparticles

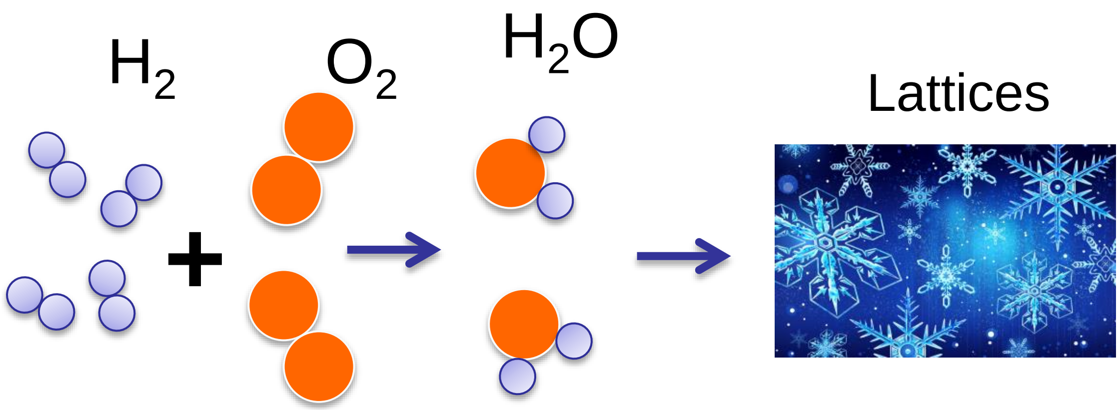


Novel Materials

Self-Assembly Strategies



Multicomponent Nanosystems: Bonds for Nanoparticles?



Nano-particles of different types → Well-defined Clusters → Large-scale organizations

Bonds

- **Programmable** (can be assigned specifically, to address multiple types of components)
- **Reversible** (allow for kinetic pathway to ordering)
- **Length-tunable** (control inter-particle separations)

Decoupling driving forces of assembly from the material specificity

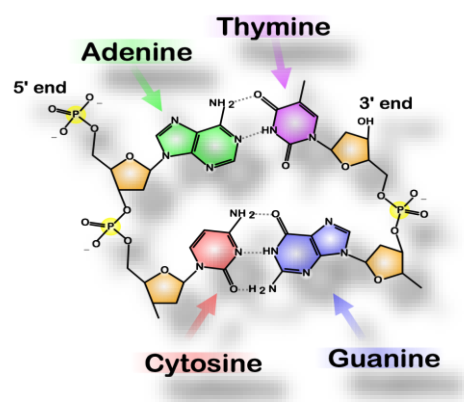
What is good about DNA?

i. Can store large amount of information
— enabling intricate designs

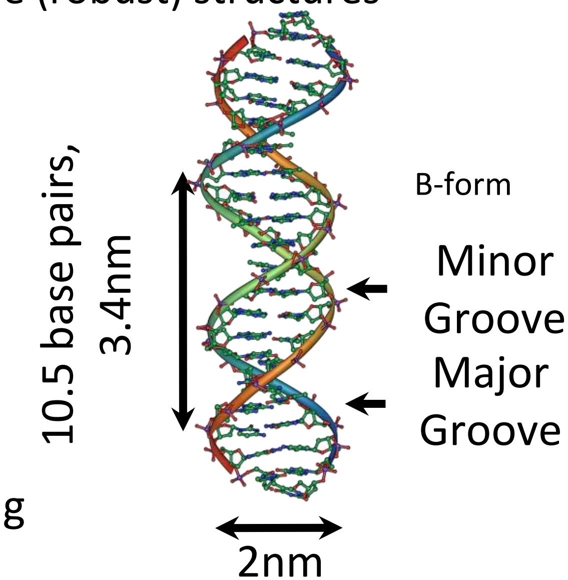
DNA sequences:

AGGATGTTGTTGCACCATCAGC
CGAAGTAGAACTGCGCGCGGCA
CCTCAACTTGCACCCGCATAGG
GTCCTCAATGCGATGCACGTCA
GGCCGAGGCATTTGAACCACCA
TCCGAAGATGGTCCCGAATAAC
ATCCACTAGAAGTAGAAGCGGG
AGAATCTC.......

ii. Programmability and predictability
— Simple interaction rules
— Predictable (robust) structures



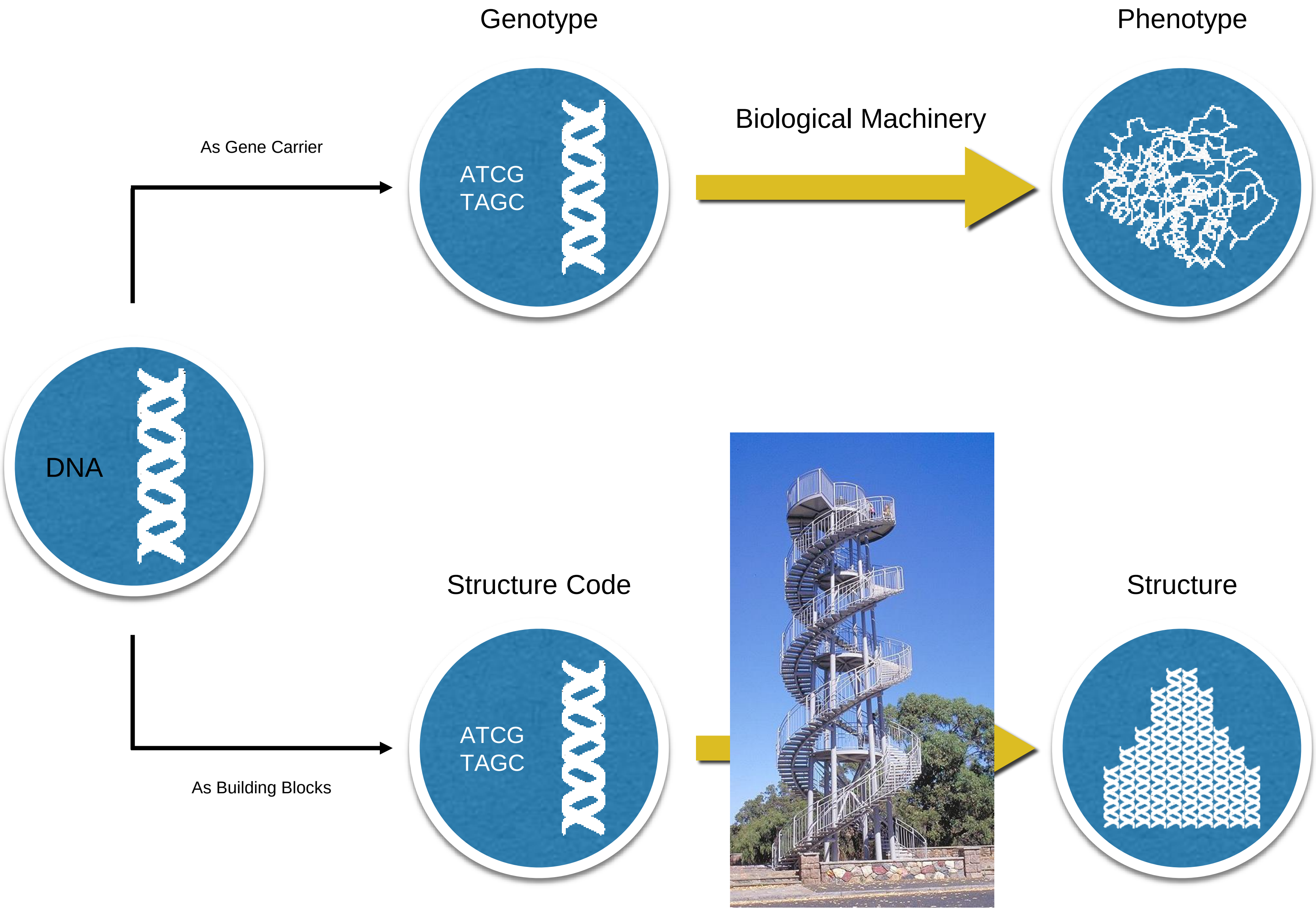
Watson-Crick base-pairing



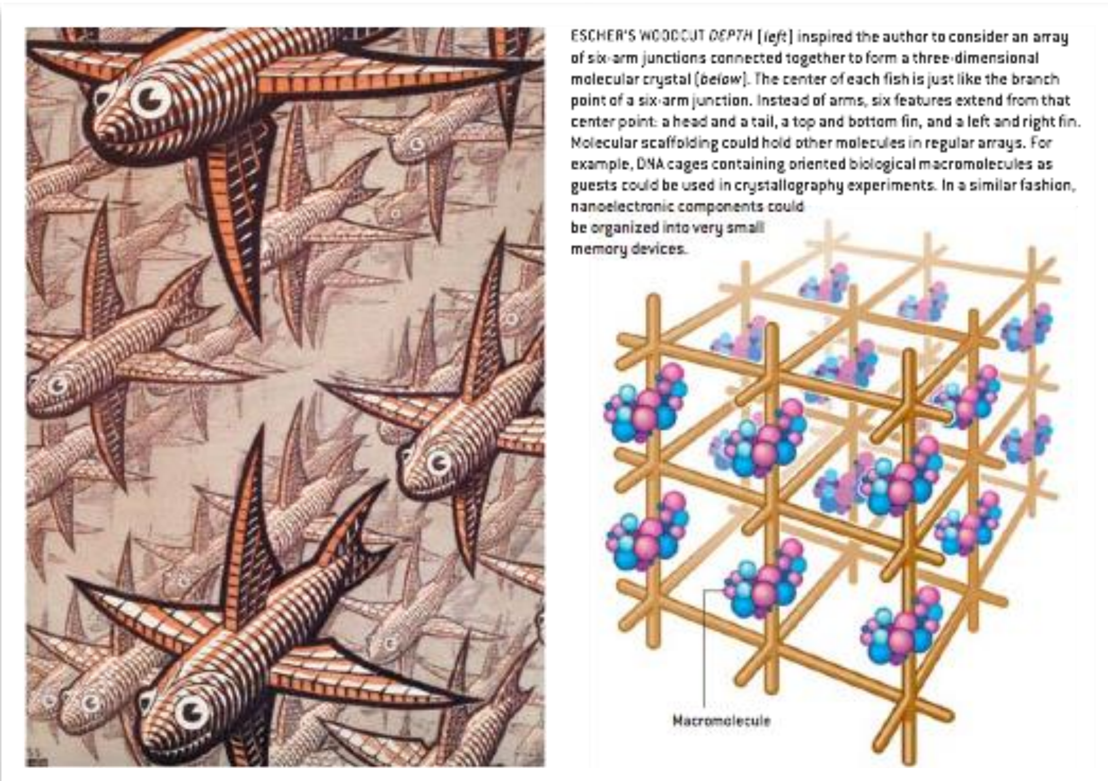
Right-handed twist with 10.5 basepairs per turn

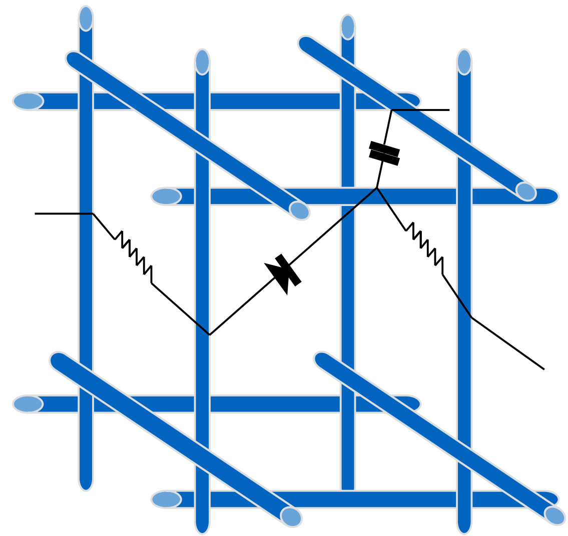
A pairs with T, C pairs with G

Can we use DNA directly for biomolecular programming?



The origin of structural DNA nanotechnology

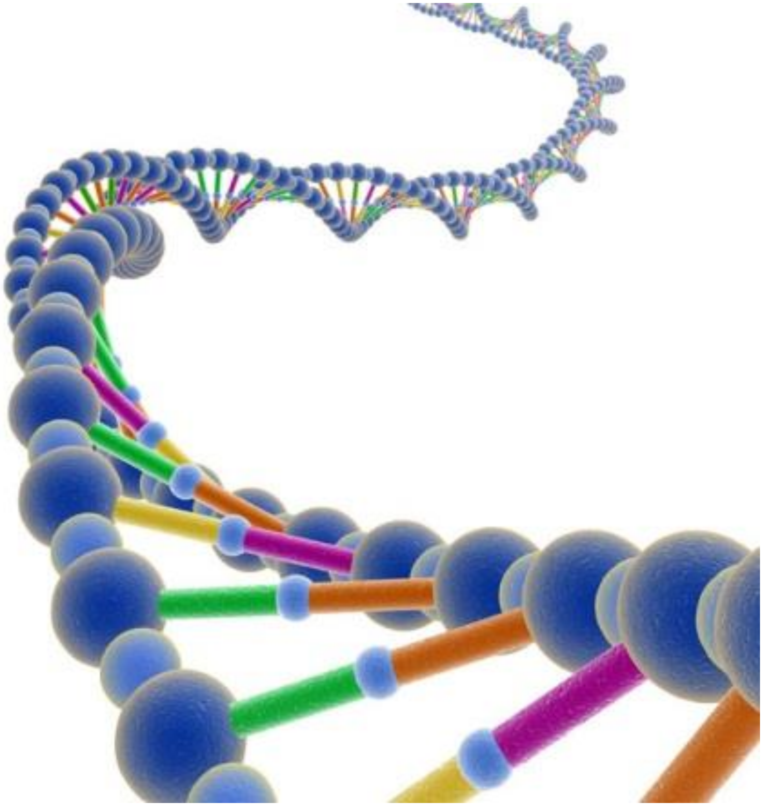




Seeman, N.C." *J. Theor. Biol*. 99, 237-247 (1982).

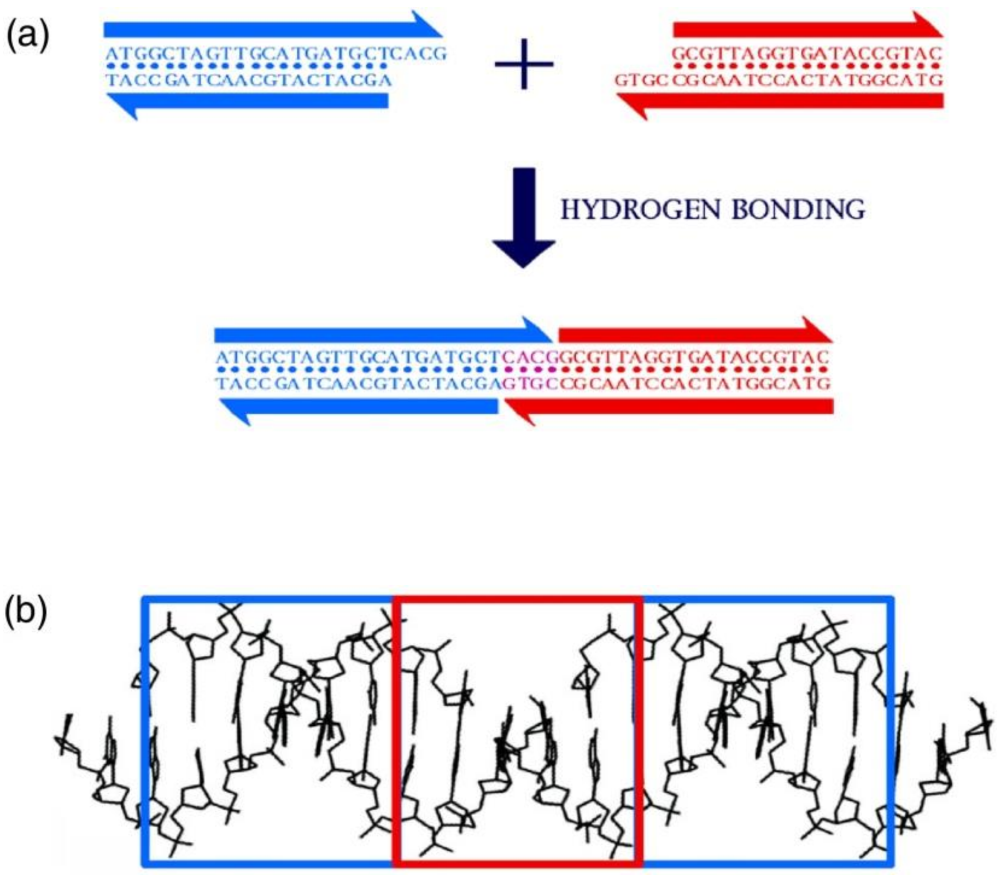
DNA nanostructures

DNA Molecule is Linear: how to build complex constructs?



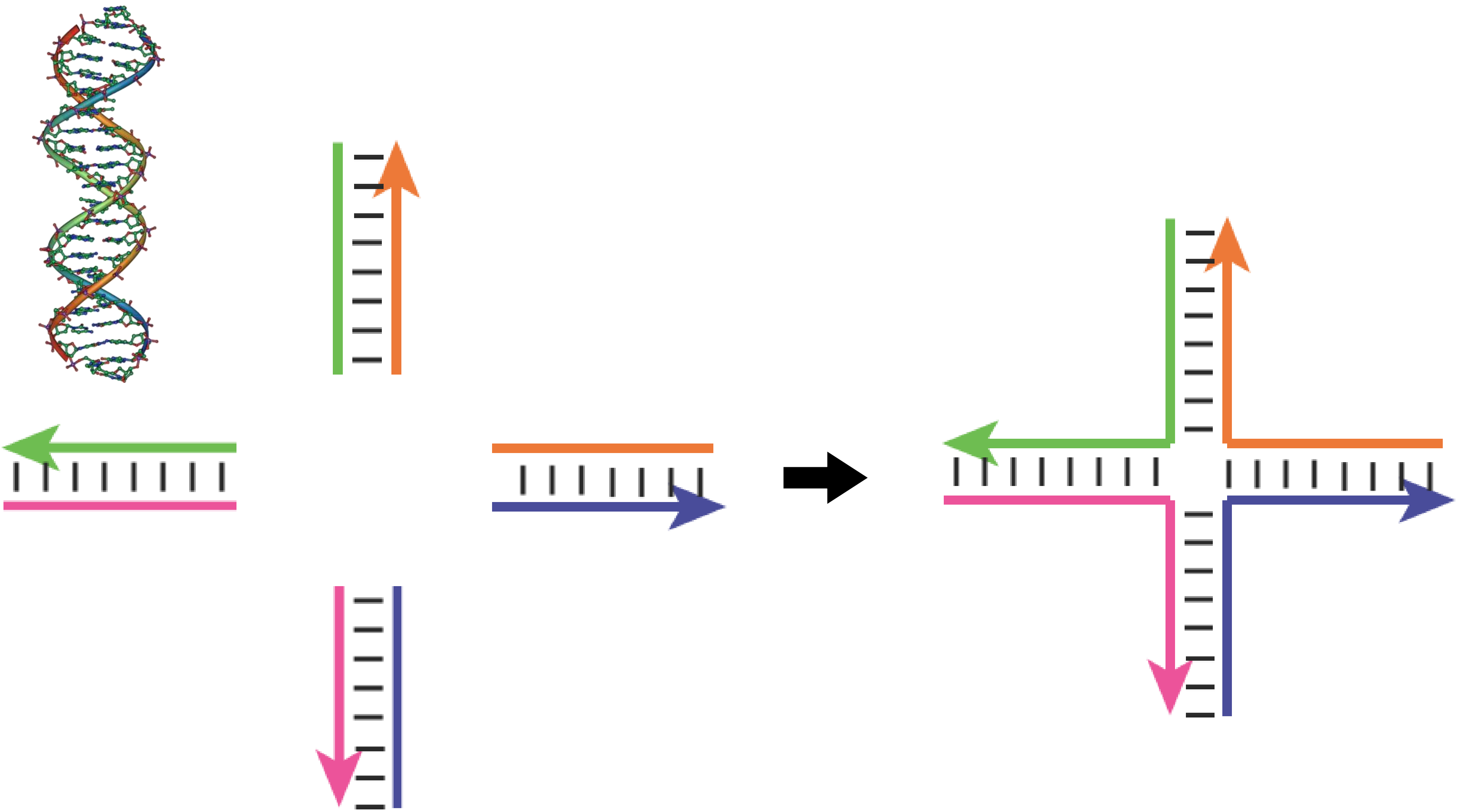
http://psychedelicadventure.blogspot.com/2010_04_01_archive.html

Sticky-Ended Cohesion

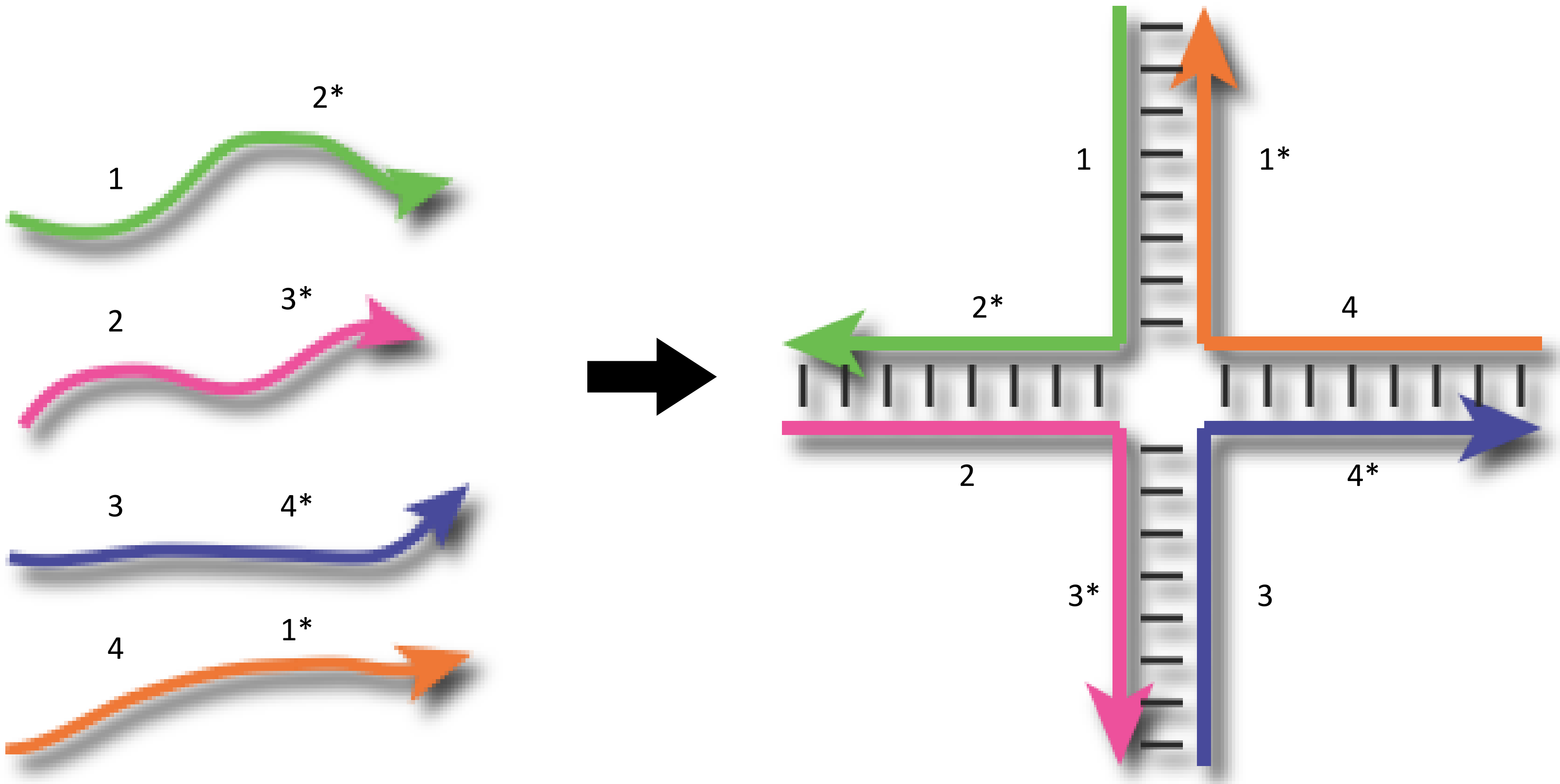


H. Qiu, J. C. Dewan, and N. C. Seeman, *J. Mol. Biol.* **1997**, 267, 881

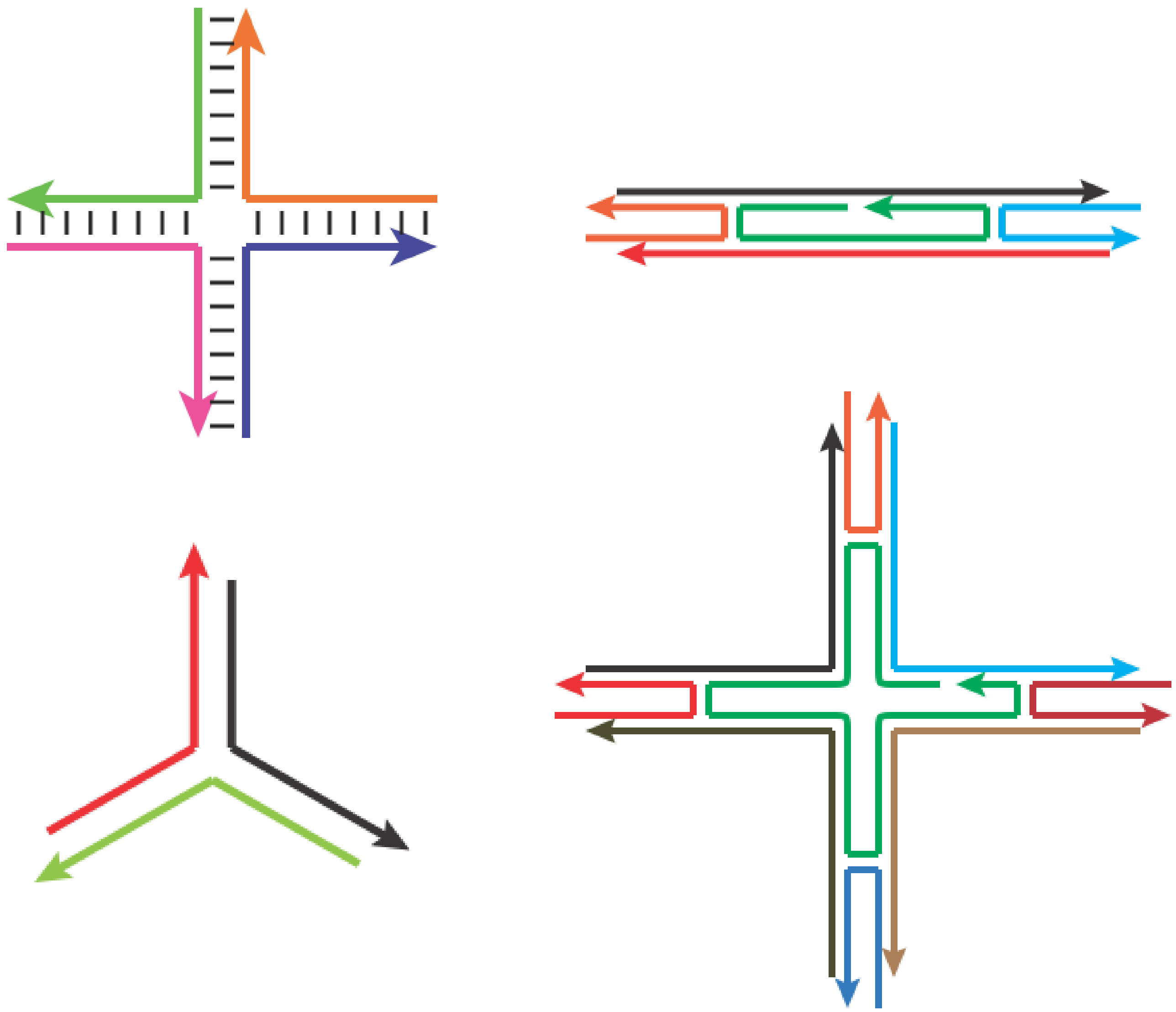
Double-helices as basic building-blocks



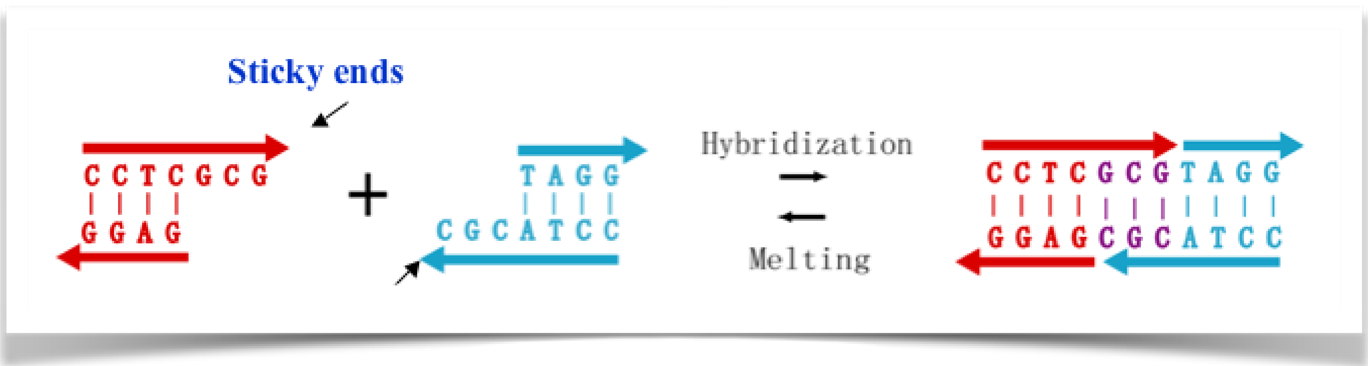
Single-stranded DNA as ‘smart molecules’ for self-assembly

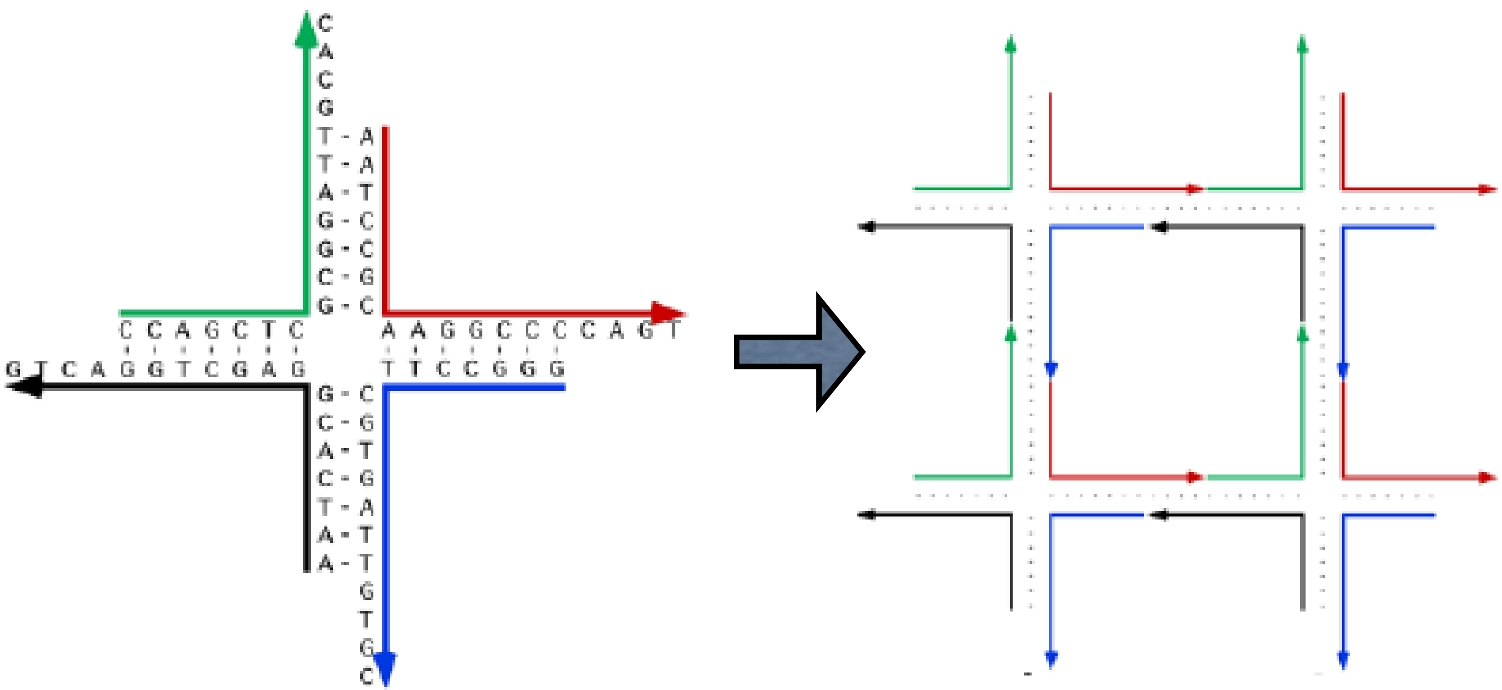


DNA tile self-assembly

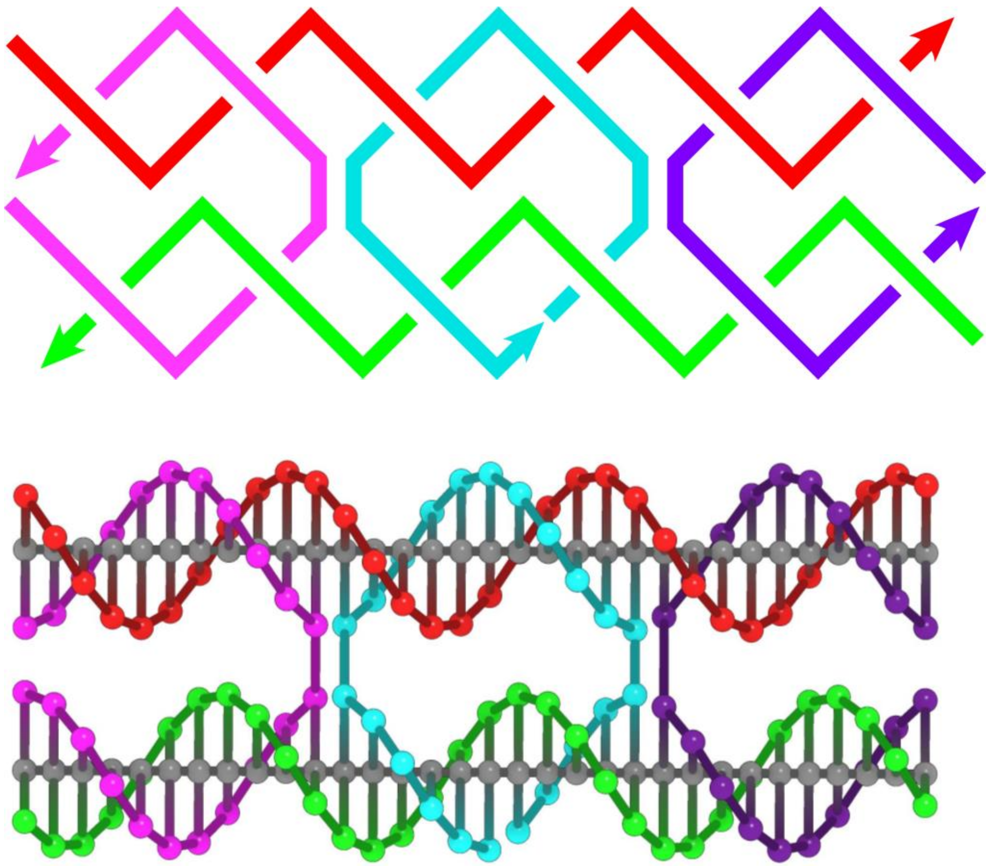


Connecting 'tiles' to form larger structures





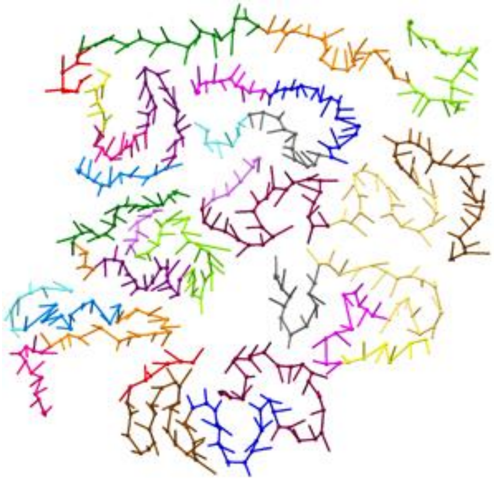
DNA Double Crossover (DX) Motif



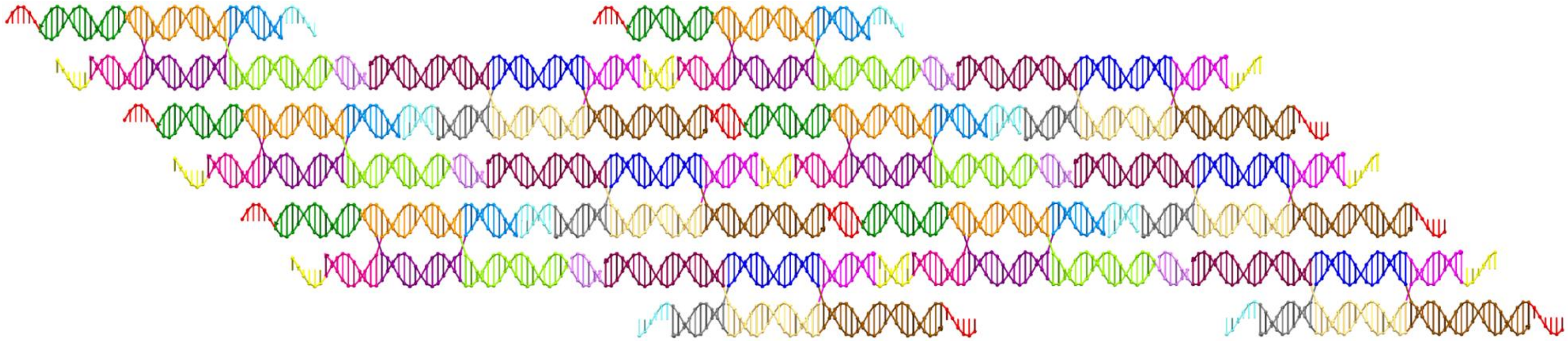
DNA Scaffolding

developed by N. Seeman

Step 1) Mix a bunch of strands of DNA together

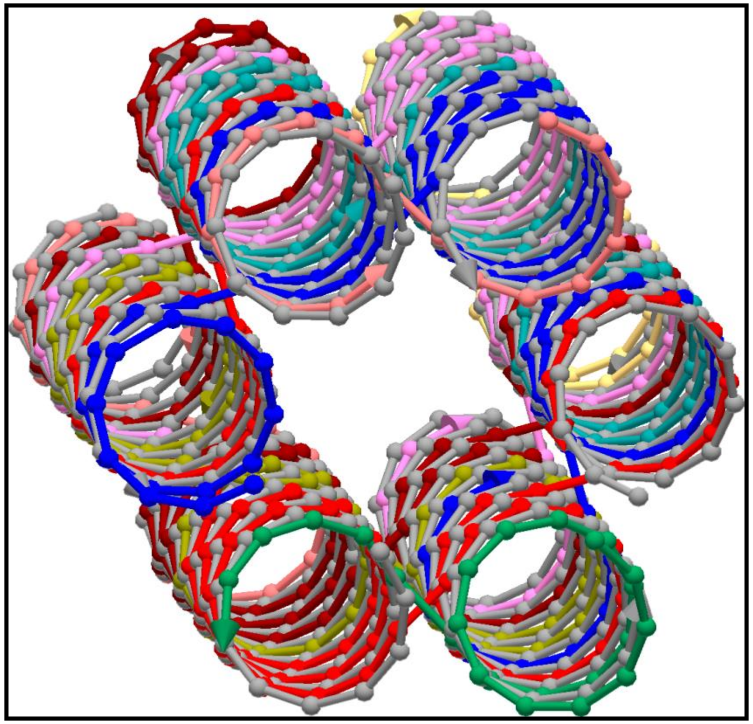


Step 2) Annealed strands self-assemble into tiles

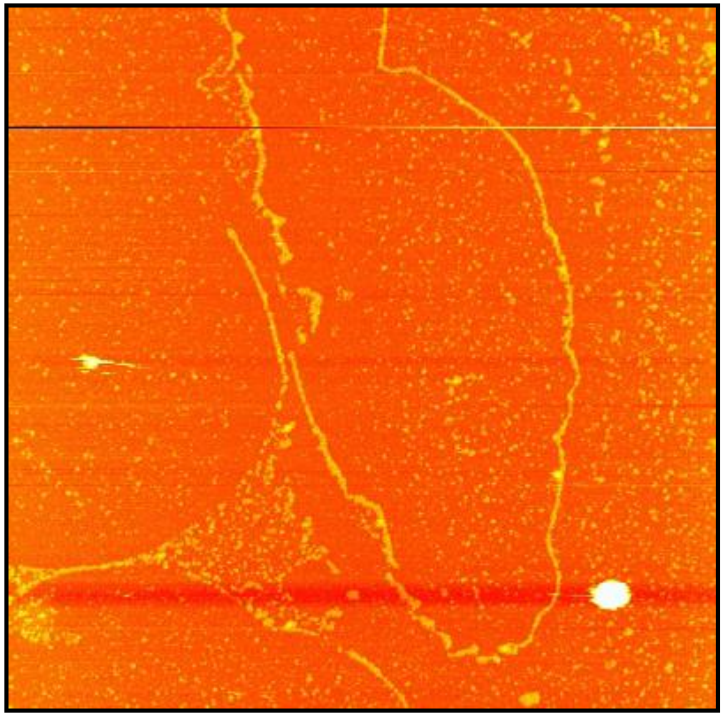


Step 3) Annealed tiles self-assemble into arrays

Six-Helix DNA Tube

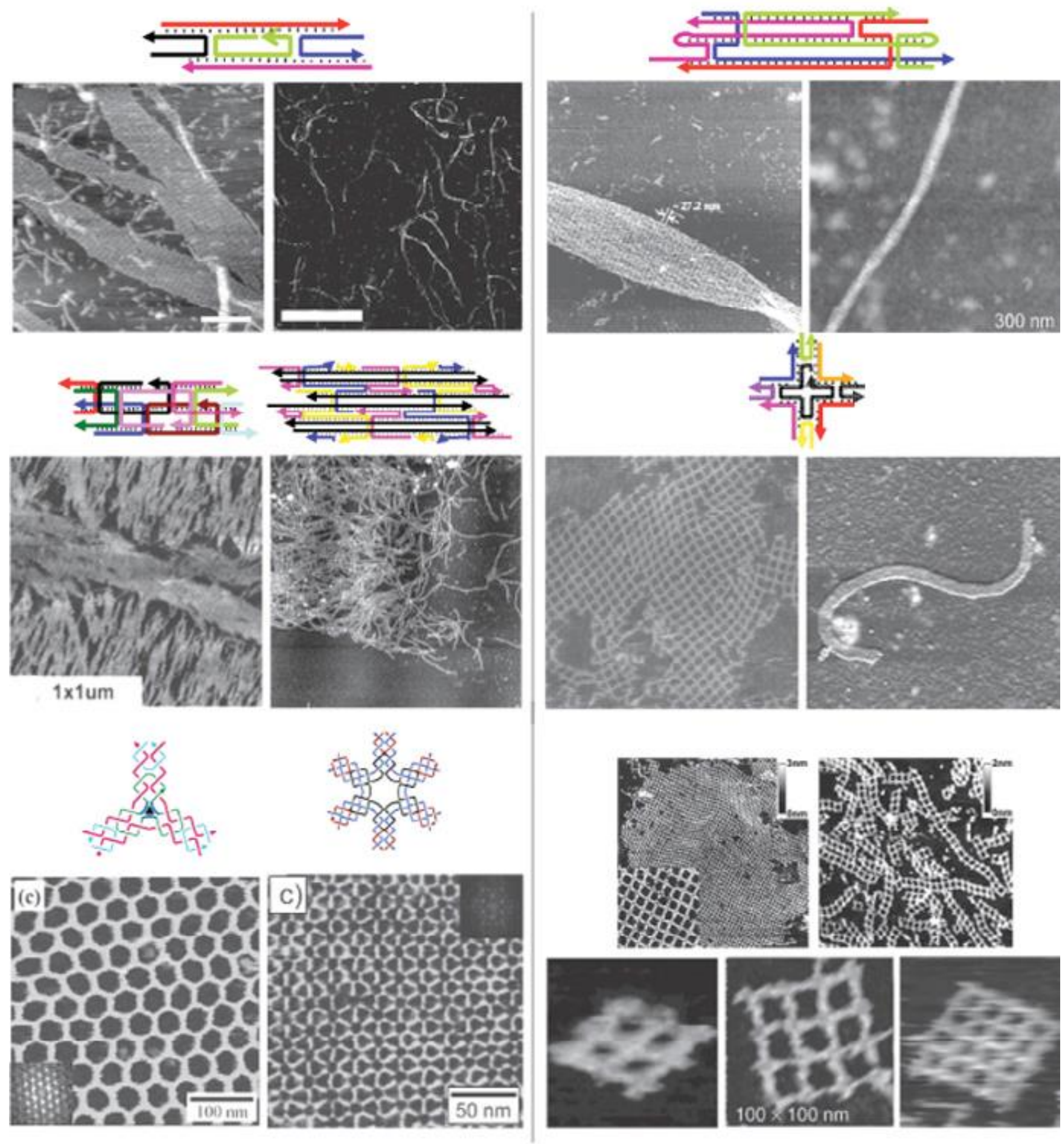


<-------------------7.3 Microns------------------->



Mathieu, F.; Liao, S. P.; Kopatsch, J.; Wang, T.; Mao, C.; Seeman, N. C. "Six-Helix Bundles Designed from DNA," *Nano Lett.* 5, 661-665 (2005)

Connecting 'tiles' to form larger structures

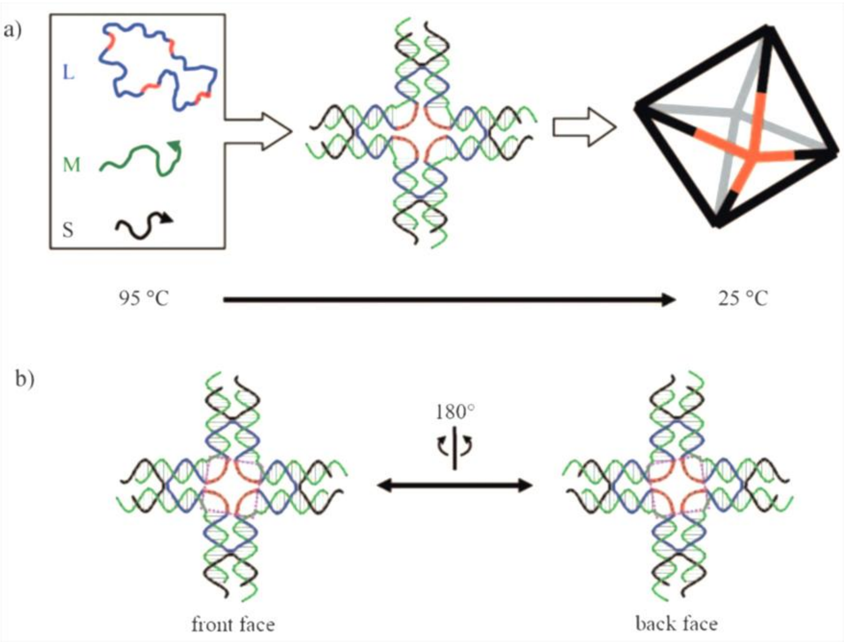


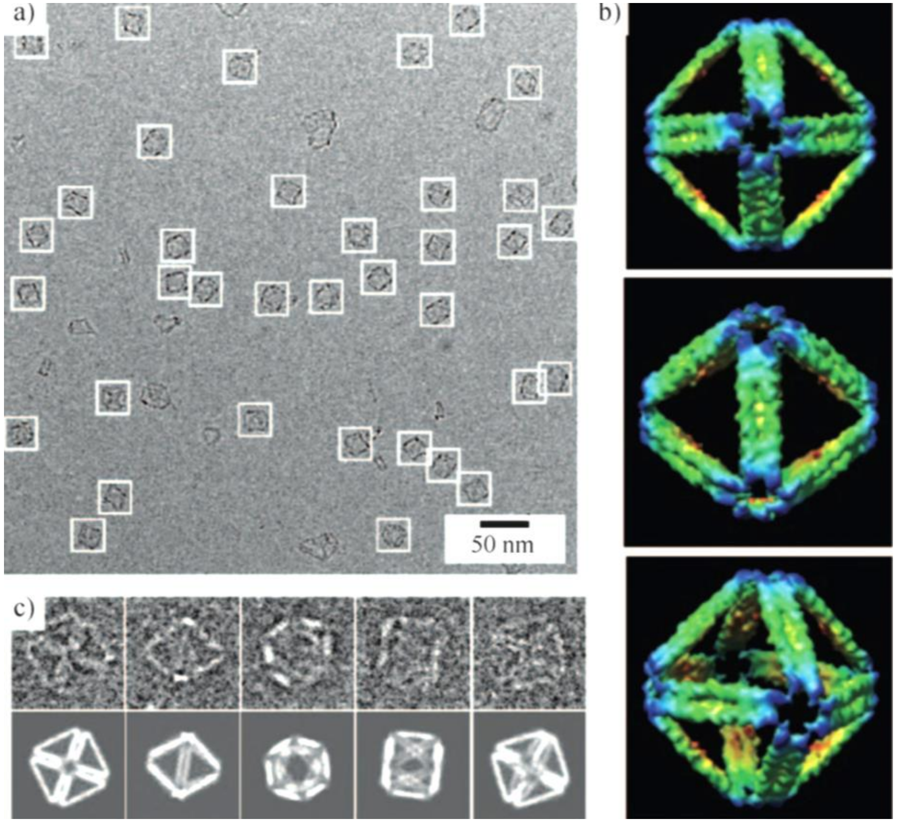
Li, Carter, Labean, *Materials Today* 2009.

3D DNA cages

Seeman, *Annu. Rev. Biochem.* 2010.

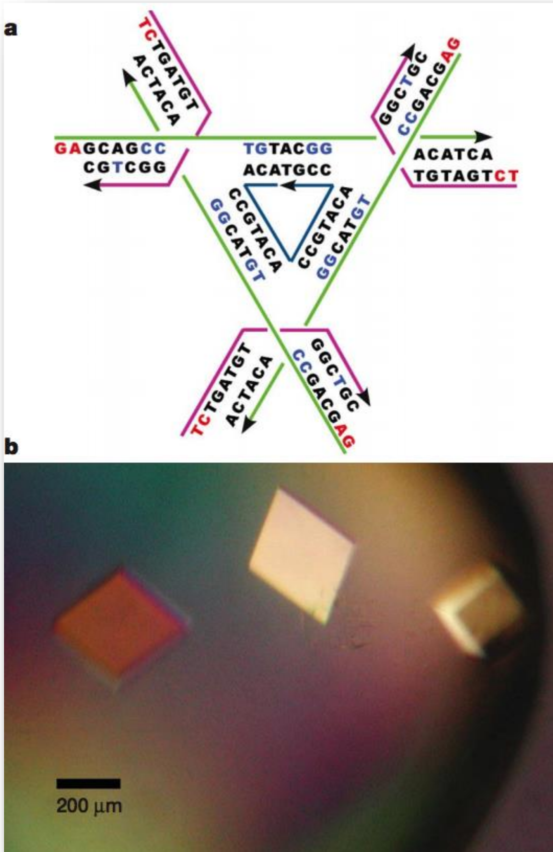
On the Chirality of Self-Assembled DNA Octahedra

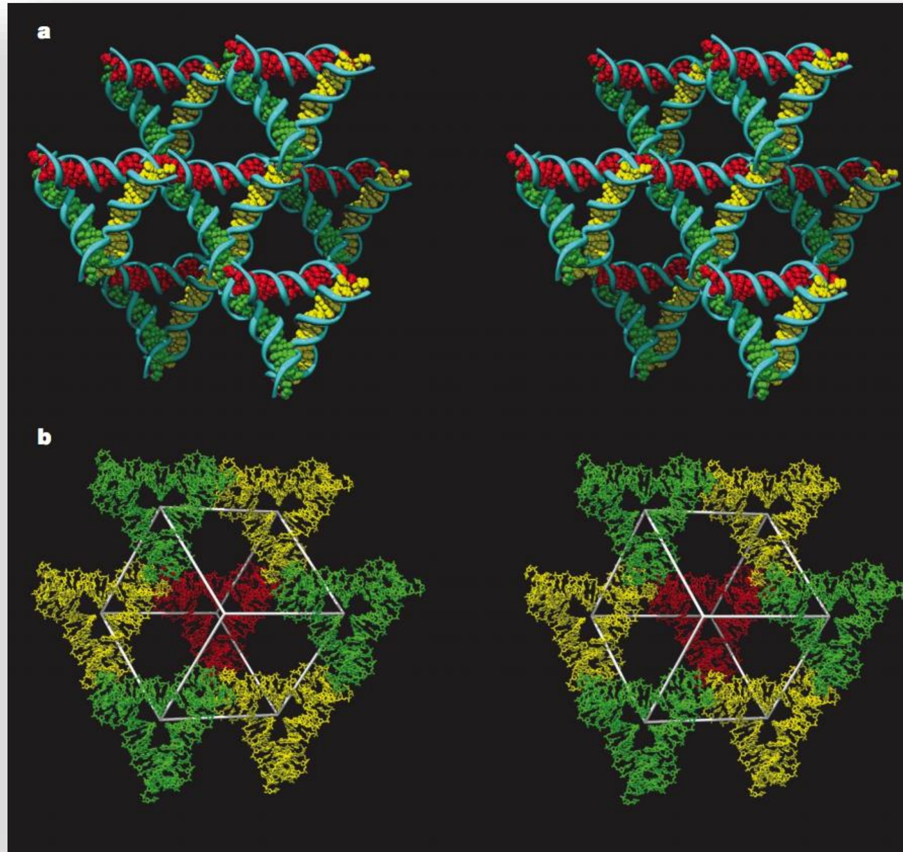




He, Y. *et al. Angew Chem Int Edit* **49**, 748 (2010)

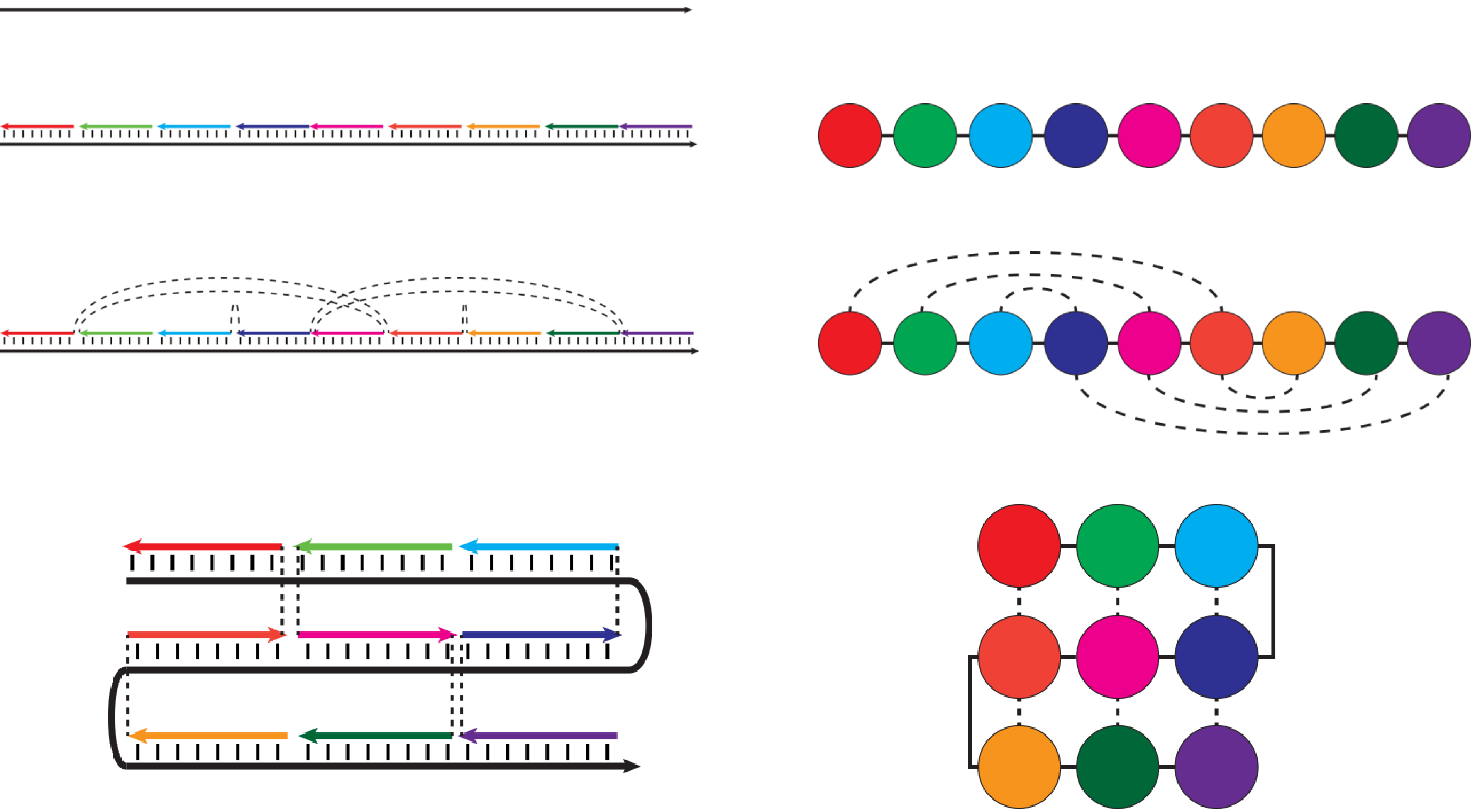
DNA Tile-Based Assembly-3D Crystal



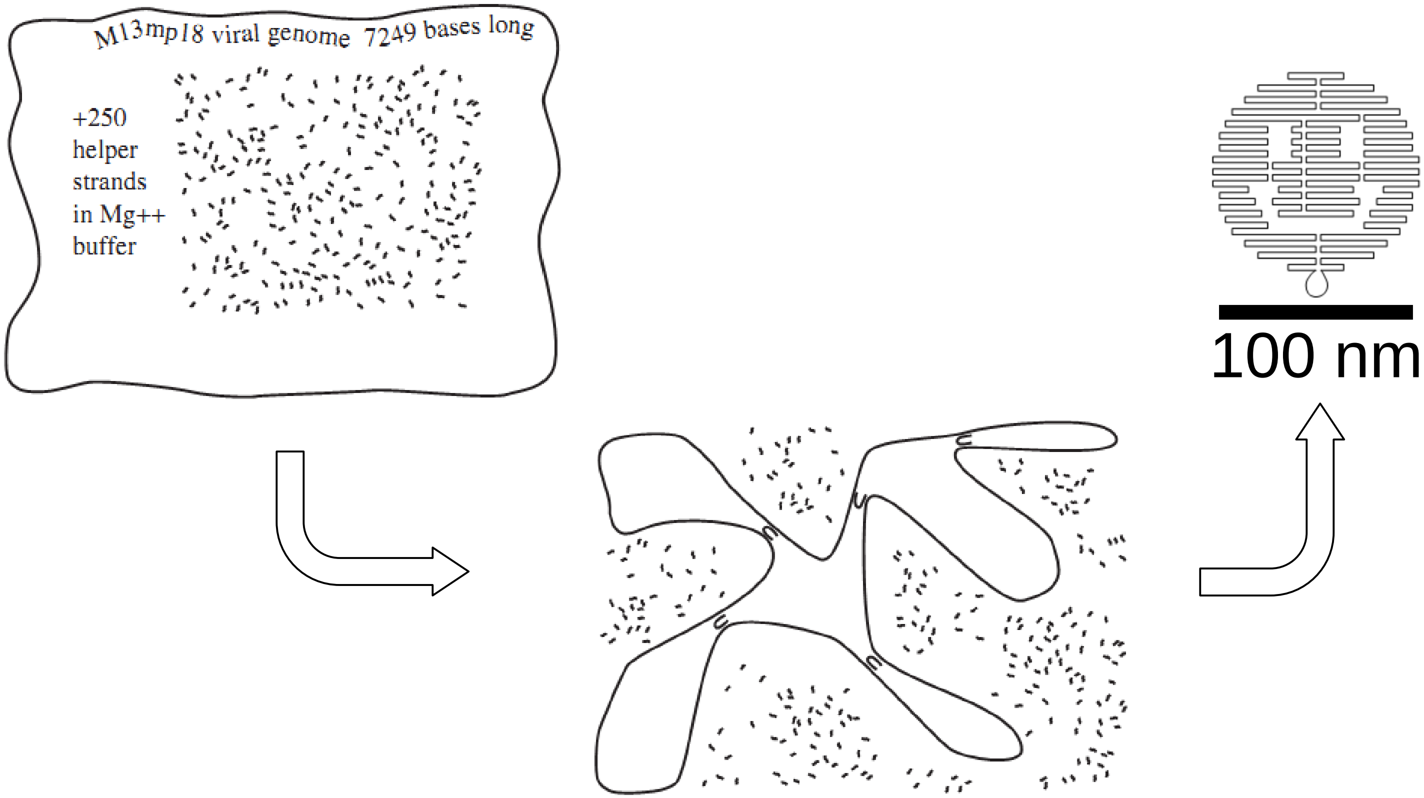


J. Zheng,J. J Birktoft, Y. Chen, T. Wang, R. Sha, P. E. Constantinou, S. L. Ginell, C. Mao, N. C. Seeman, *Nature.* **2009**, 461, 74

Complex ‘folding’ method — ‘DNA origami’



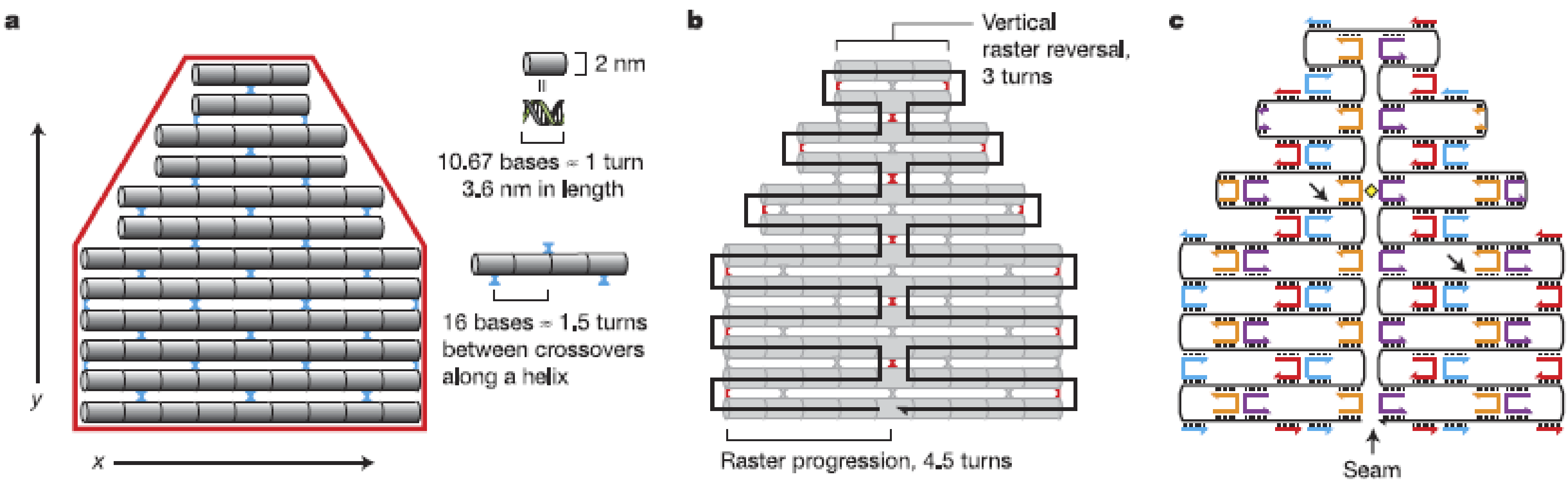
DNA Origami Technique



A method for folding a long circular single-stranded genomic DNA (M13, 7249 nucleotides) into arbitrary 2D and 3D target shapes in raster fill fashion.

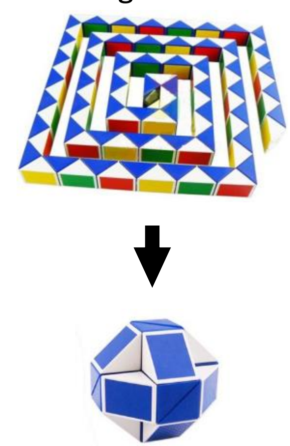
P. W. K. Rothemund, *Proc. Int. Conf. Comput. Aided Des.* **2005**, pp. 471

DNA Origami



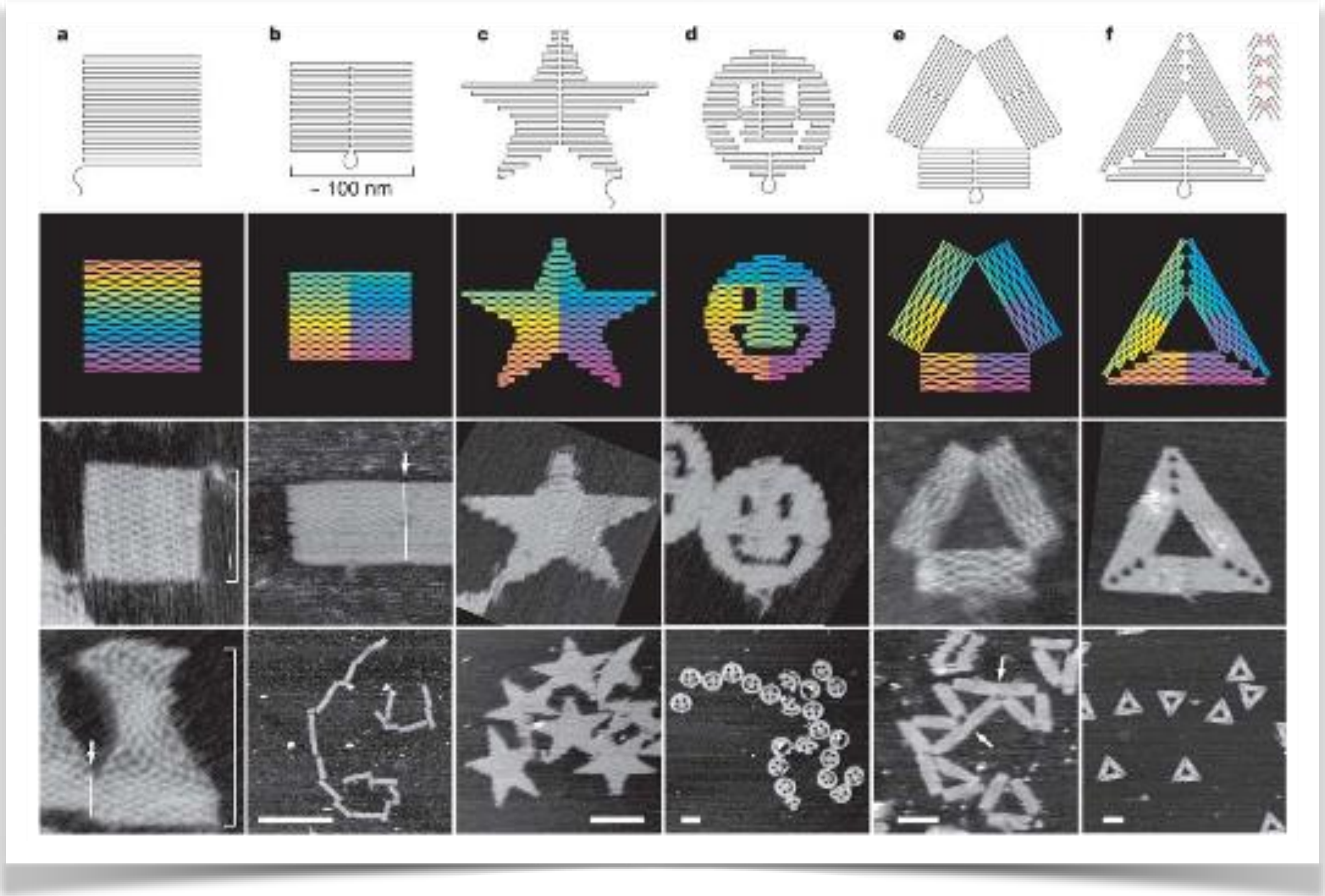
P. Rothemund, Nature, 440, 297 2006

Magic ruler



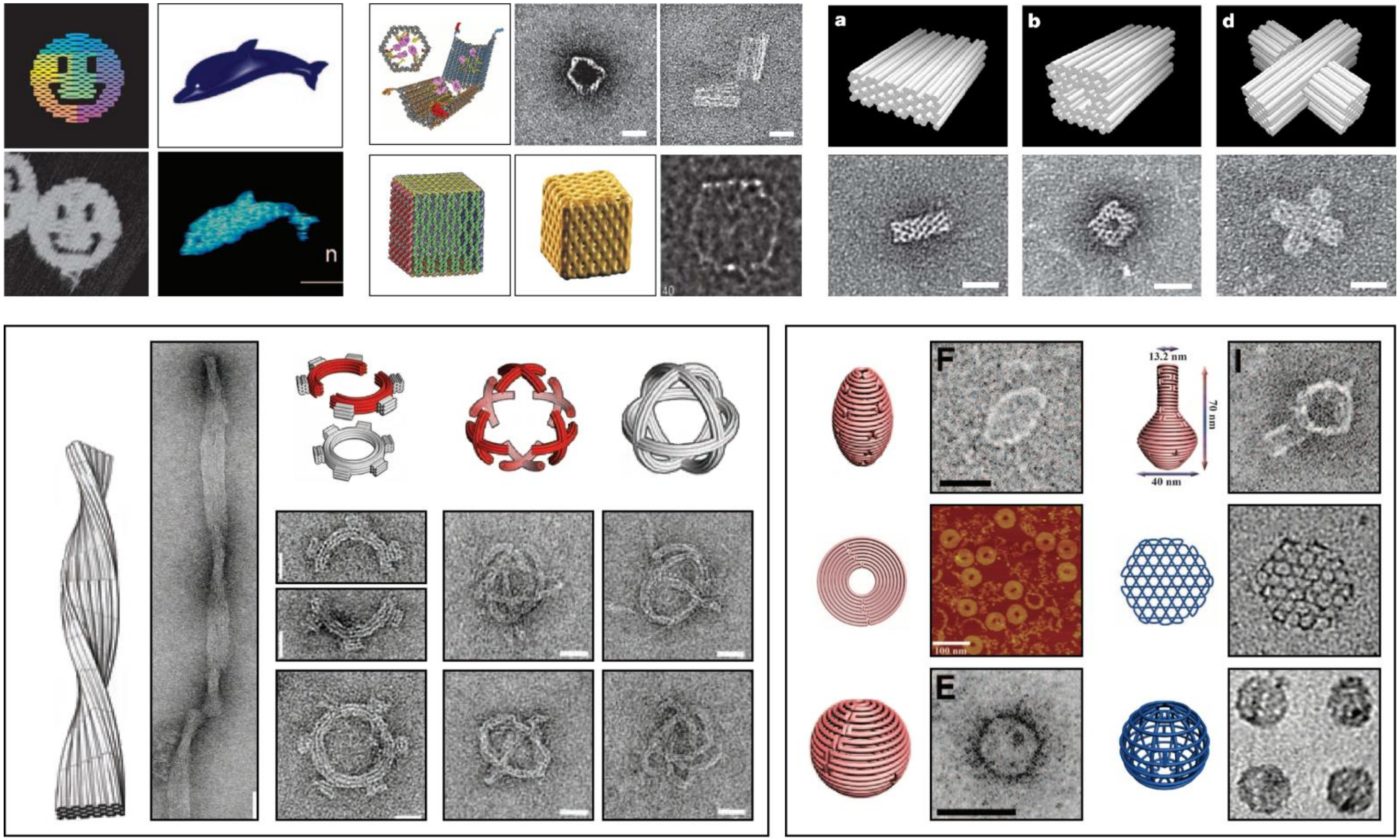
•Use of long (thousands of base-pairs) ssDNA
• Arbitrary overall shape
• short ssDNA are “staples”

DNA origami



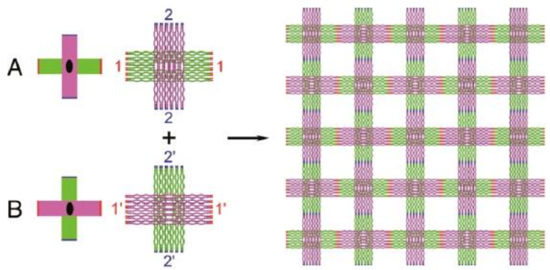
Rothemund, *Nature* 440, 297 2006

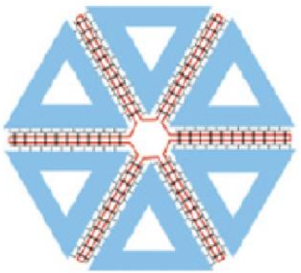
DNA Origami Shapes

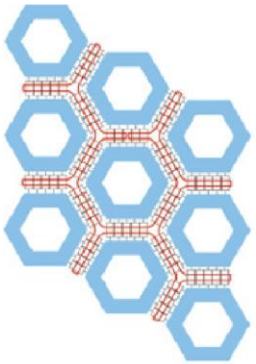


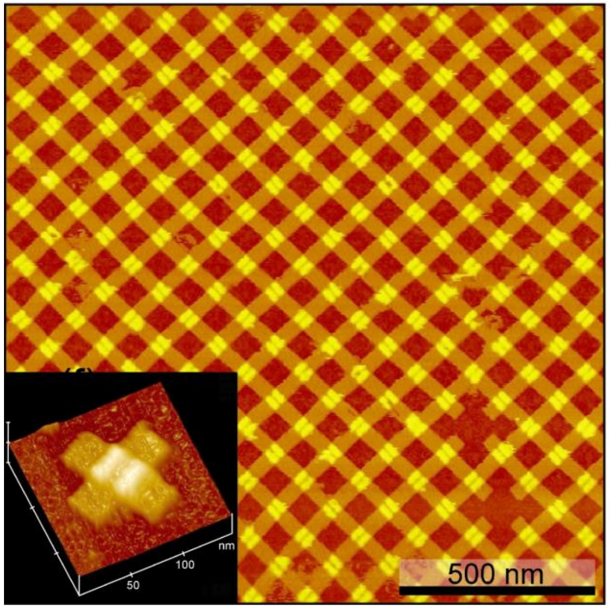
Rothemund, P. W. K. *Nature* **440**, 297-302 (2006); Andersen, E. S. *et al. Acs Nano* **2**, 1213 (2008)
Douglas, S. M., Bachelet, I. & Church, G. M. *Science* **335**, 831-834 (2012); Andersen, E. S. *et al. Nature* **459**, 73 (2009)
Douglas, S. M. *et al. Nature* **459**, 414-418 (2009); Dietz, H., Douglas, S. M. & Shih, W. M. *Science* **325**, 725 (2009)
Han, D. R. *et al. Science* **332**, 342-346 (2011); Han, D. R. *et al. Science* **339**, 1412 (2013)

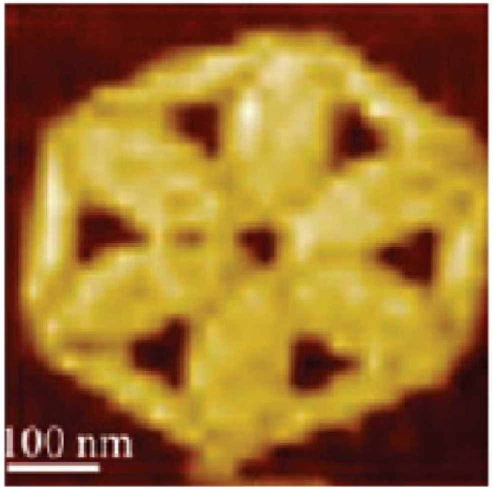
DNA Origami Arrays

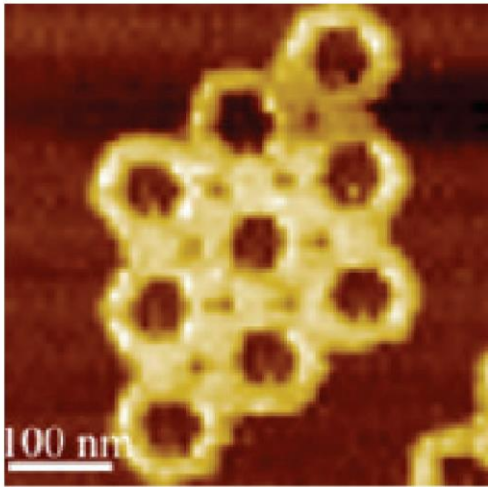






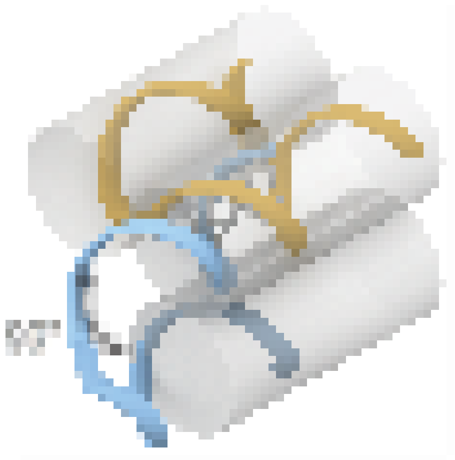






W. Liu, H. Zhong, R. Wang, and N. C. Seeman, *Angew. Chem. Int. Ed.* **50**, 264 (2011)
Zhao, Z., Liu, Y. & Yan, H. *Nano letters* **11**, 2997 (2011)

DNA bricks



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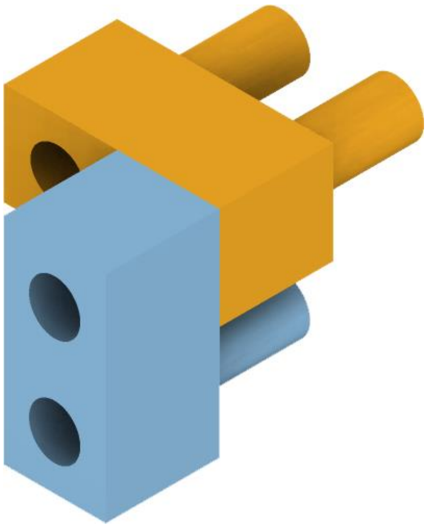
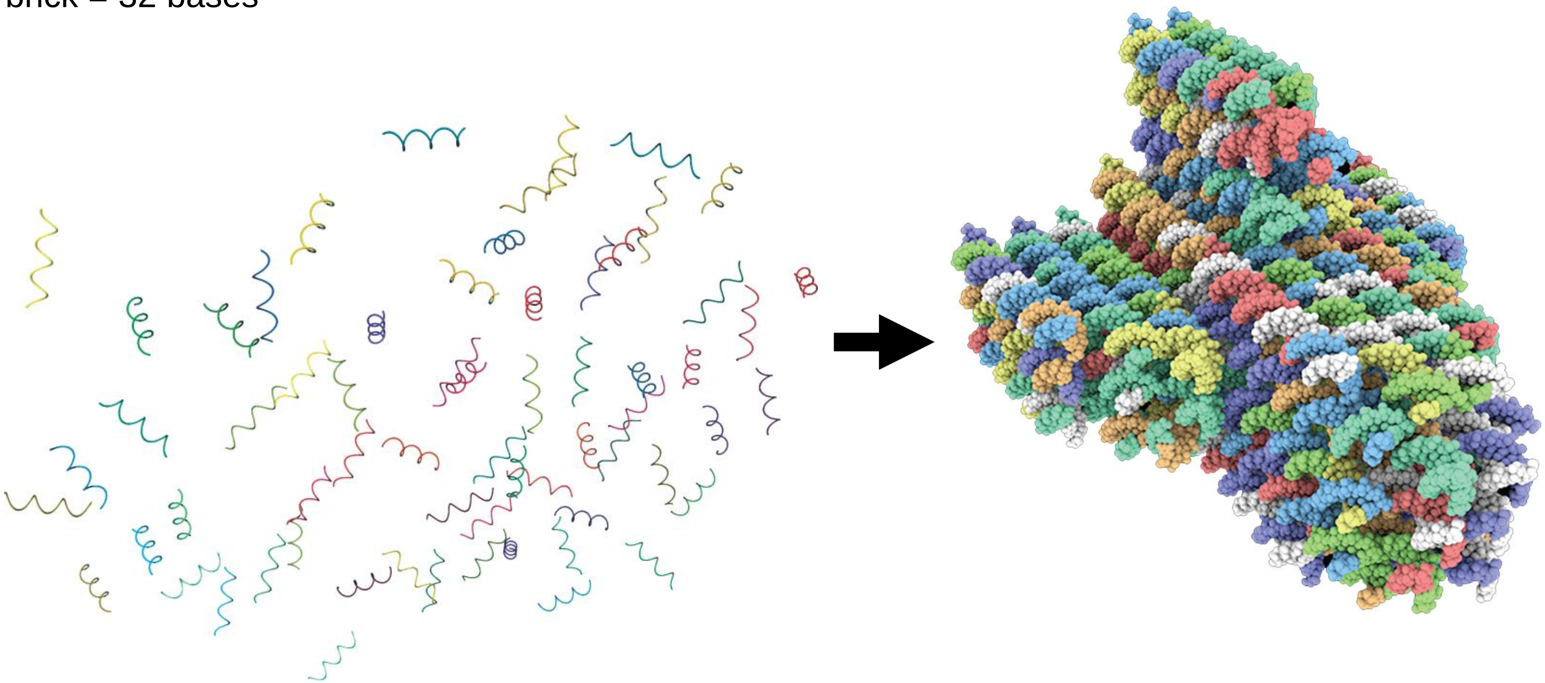
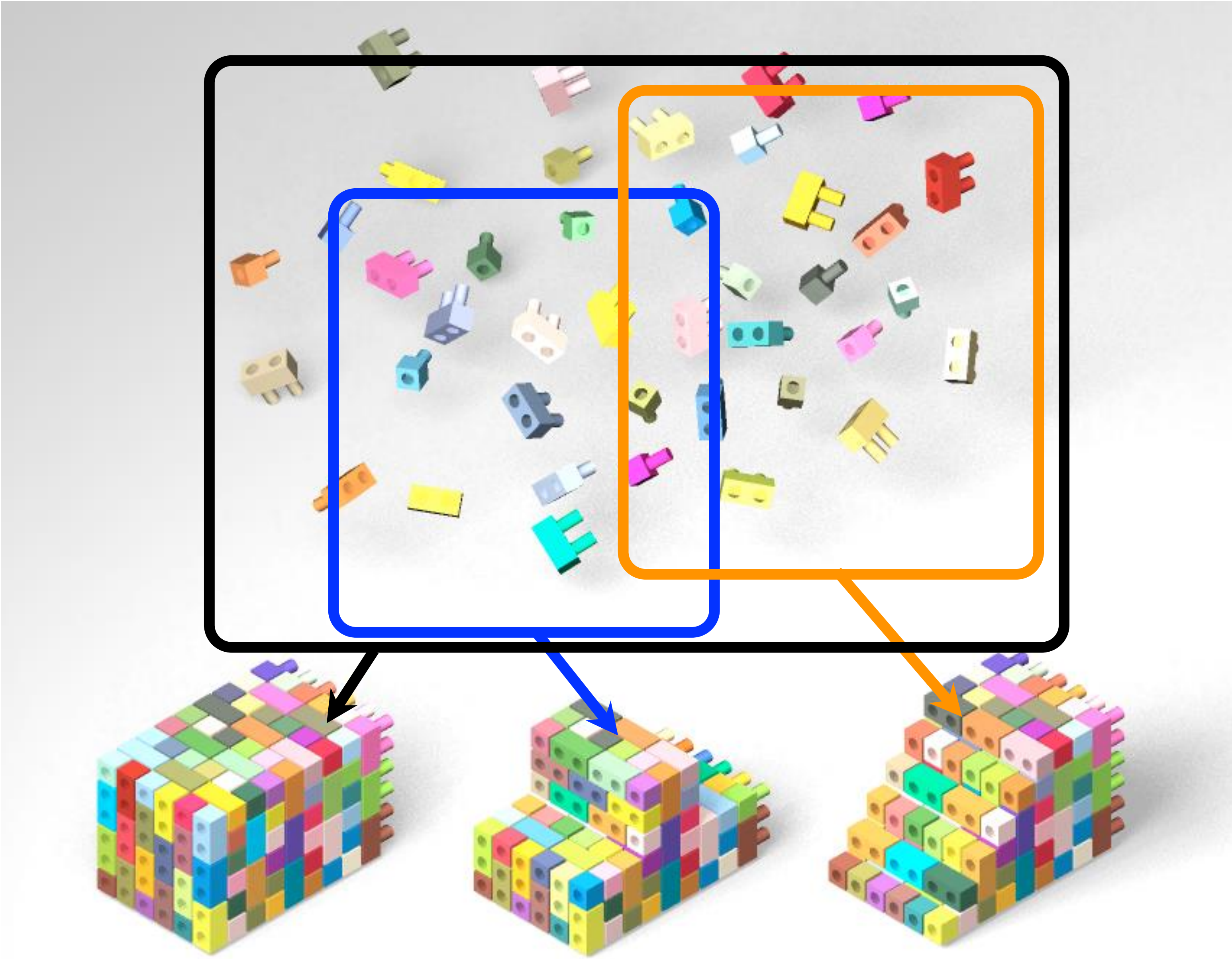


A brick = 32 bases



Ke, Ong, Shih, Yin, ***Science*** 2012

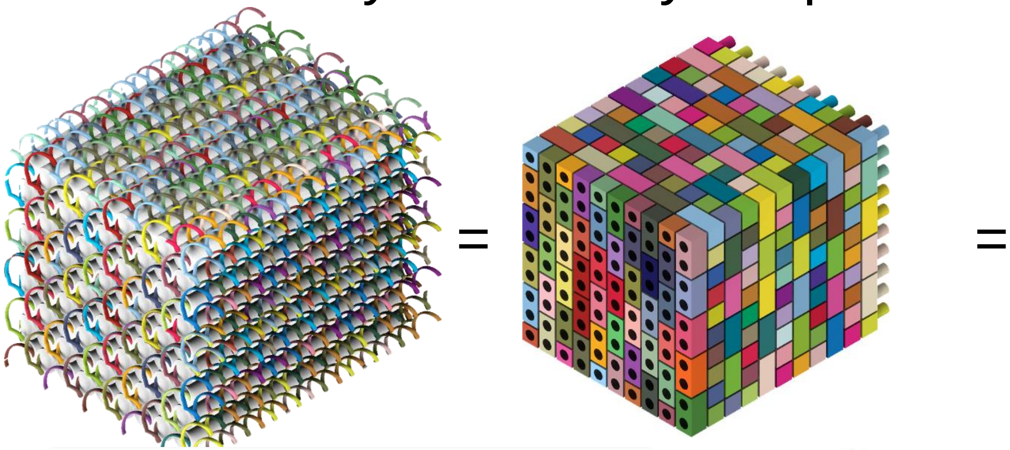
DNA bricks

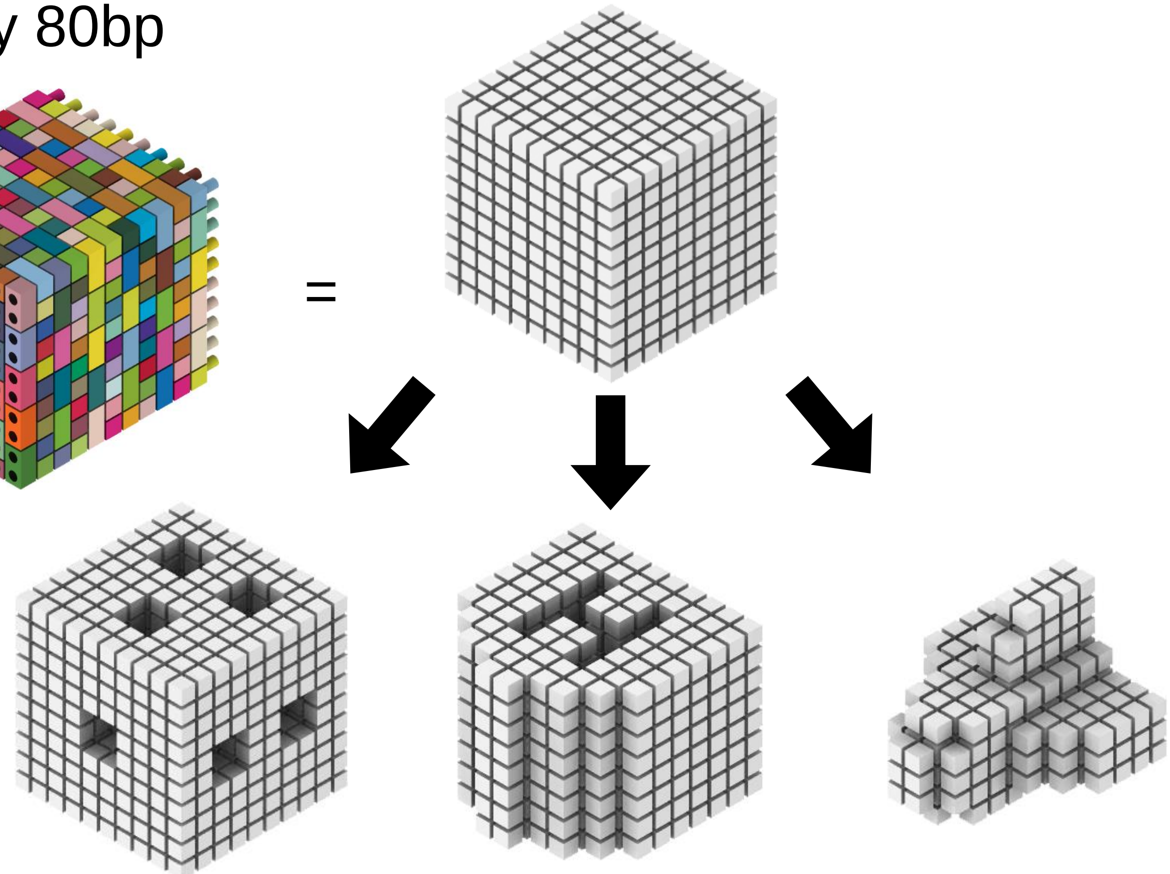


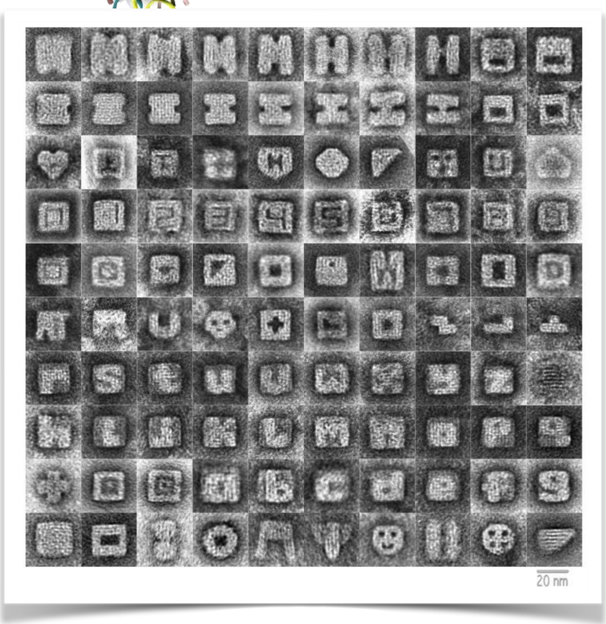
Ke, Ong, Shih, Yin, ***Science*** 2012

DNA bricks

10 helix by 10 helix by 80bp



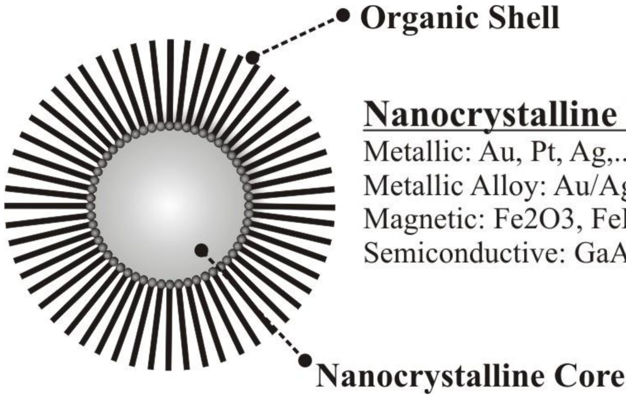




Ke, Ong, Shih, Yin, ***Science*** 2012

DNA-assembly of Nanoparticles

Nanoparticles

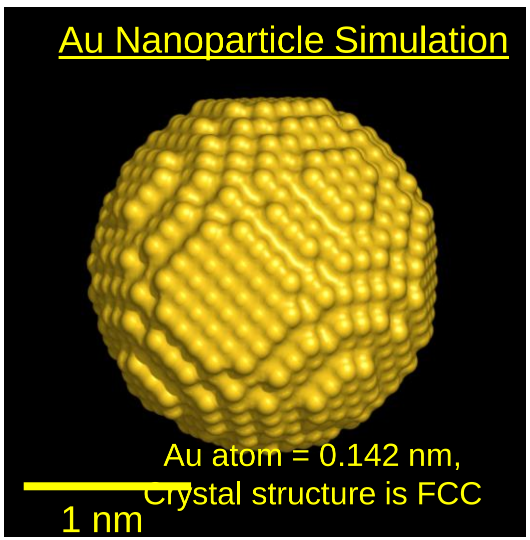


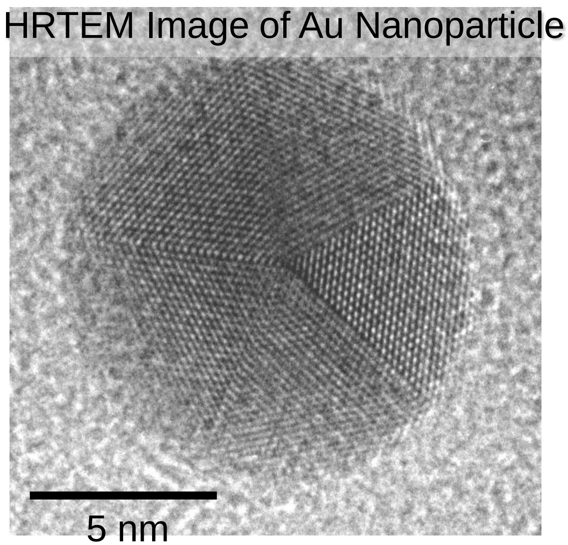
Nanocrystalline Core
Metallic: Au, Pt, Ag,...
Metallic Alloy: Au/Ag, PtRu,..
Magnetic: Fe_2O_3, FePt,..
Semiconductive: GaAs, CdTe..

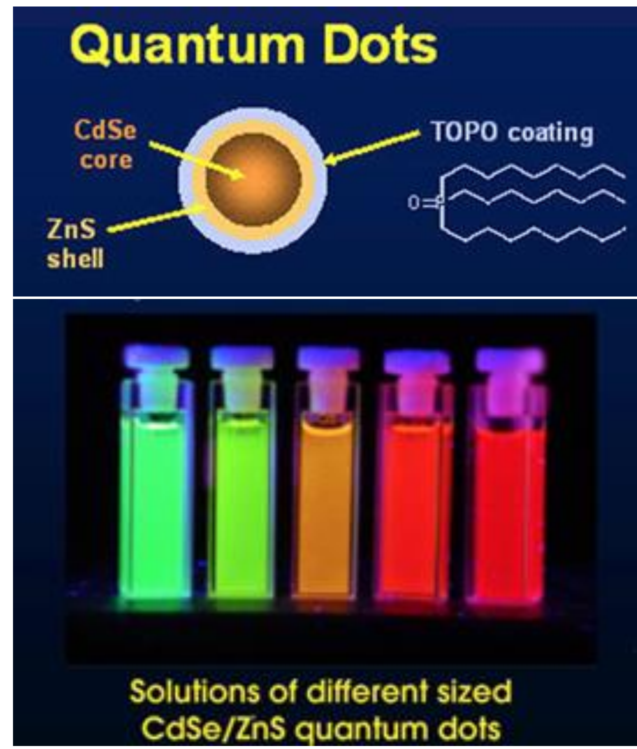
Organic Shell
Thiols: RSH, HSRCOOH,..
Amines: RNR, R_3N
Surfactants: $R_4N^+Br^-$
Acids: RCOOH

Properties Related to:

Core: Material, Size & Shape
Shell: Chemistries & Reactivities



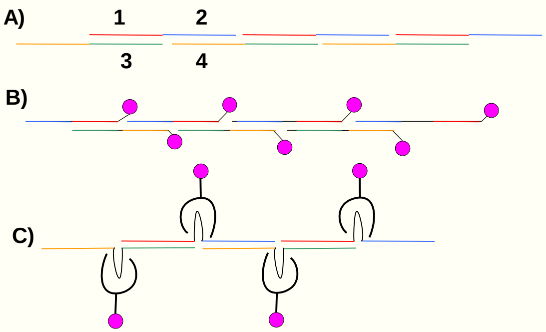




Particle Assembly Approaches with DNA

Scaffolding

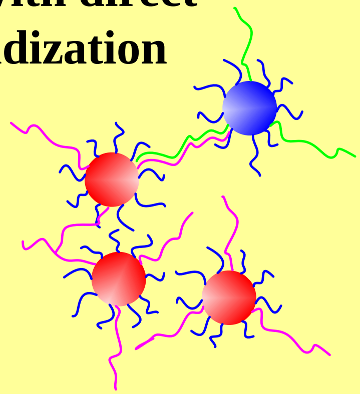
Particle incorporation into DNA scaffolds



Information-intensive: prescribe each particle position

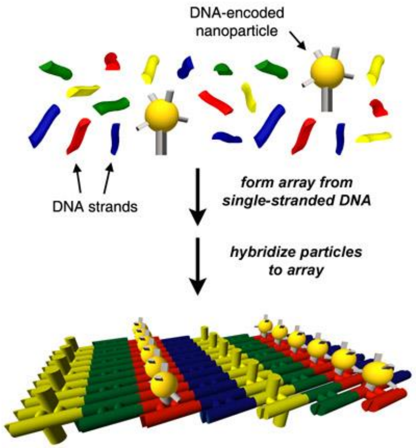
Encoded interactions

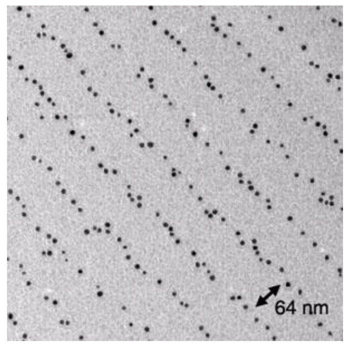
A-B particles with direct ss-DNA hybridization

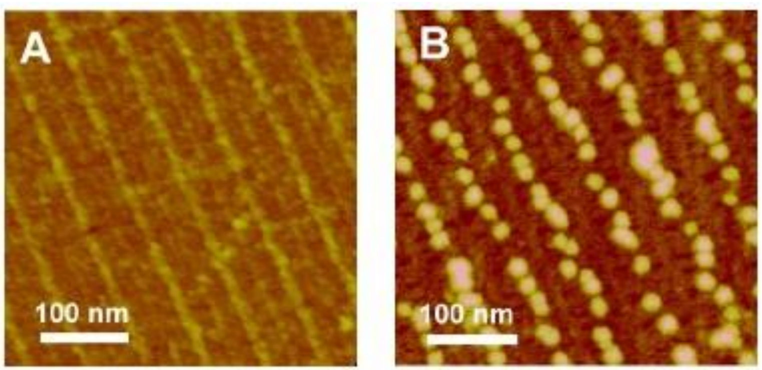


Information-minimalistic, but particle position is a result of many factors

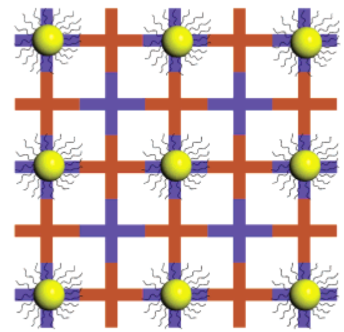
Nanoparticle positioning using DNA scaffolds

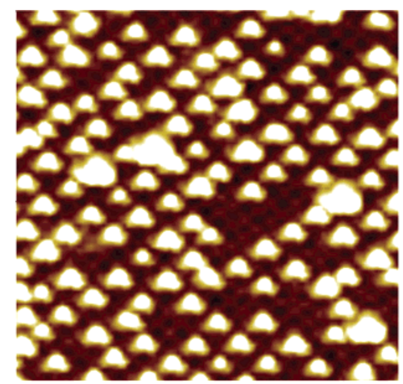






Seeman, Kiehl et al , NanoLett, 4, 2343, 2004



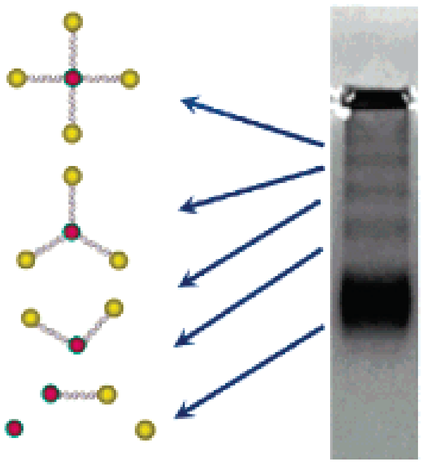


500x500 nm

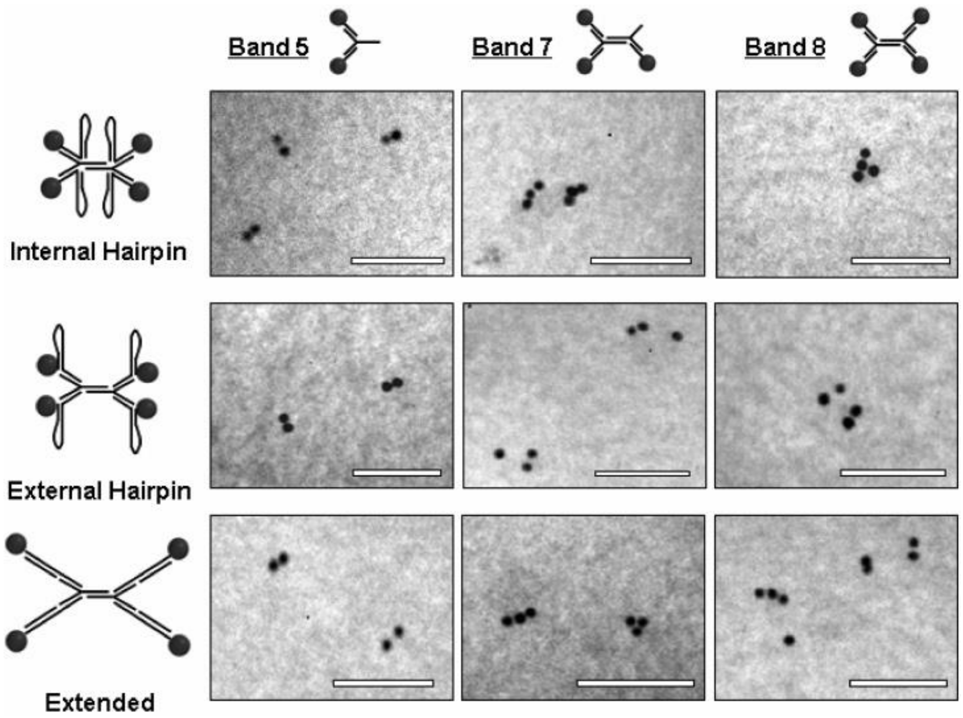
Hao et al Nano Lett 2006

Cluster Assembly

Building Nano-"molecules"

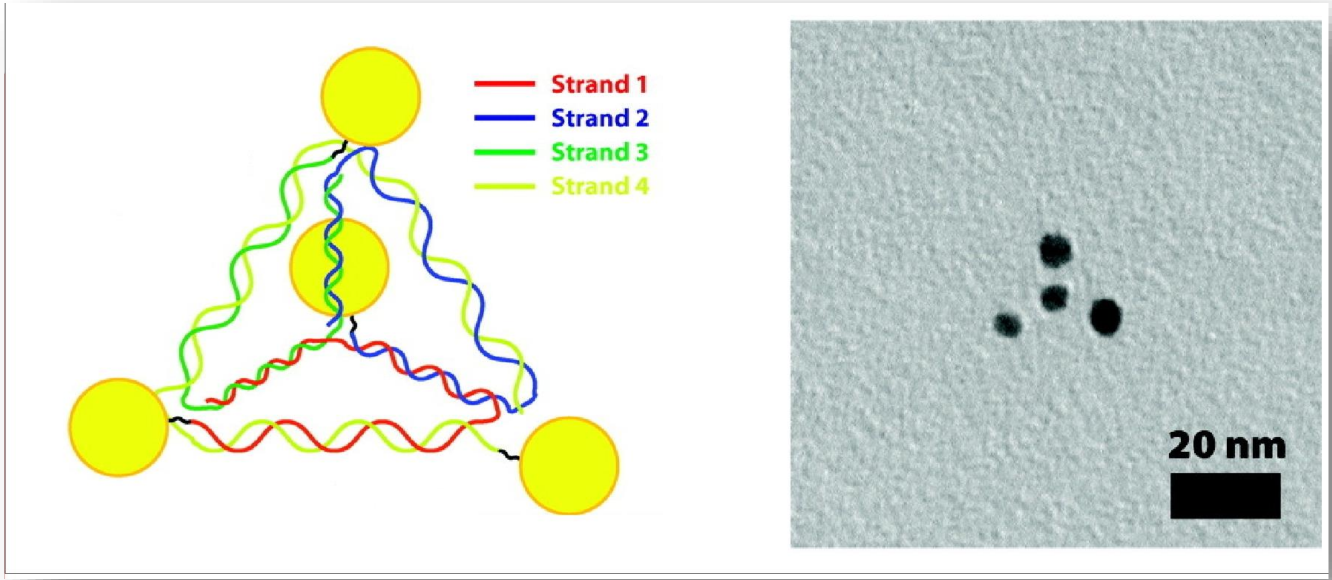


Fu et al, JACS, 10832 2004



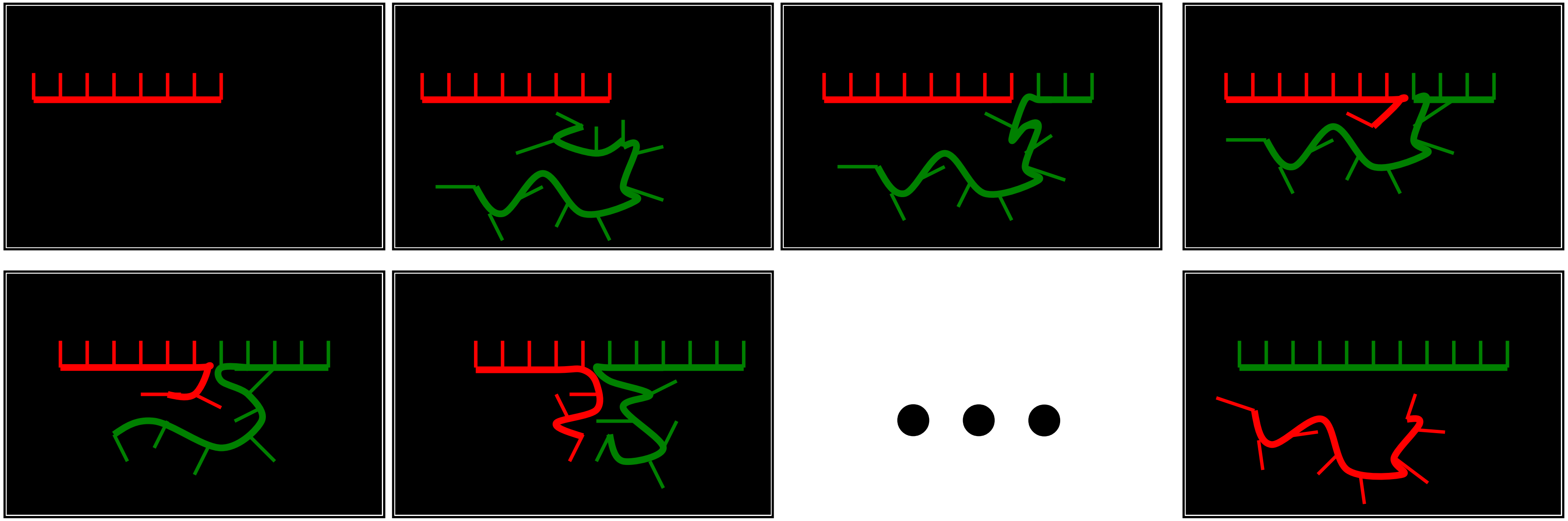
Sönnichsen, C.; Reinhard, B. M.; Liphardt, J.; Alivisatos, A. P. *Nature Biotech.* 2005,

S.A. Claridge & A. P. Alivisatos *Chem. Mater.* 2005



Mastroianni, A. J., Claridge, S. A. & Alivisatos, A. P. *Journal of the American Chemical Society* **131**, 8455 (2009)

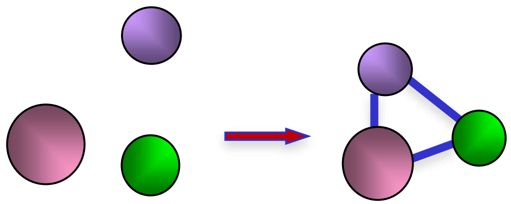
Fuel Strands



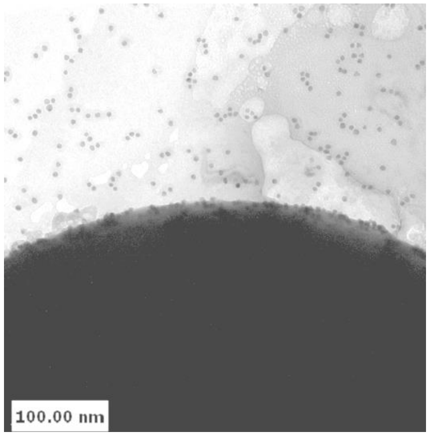
- A red strand can be removed from its compliment (black) by the introduction of an unset strand (green) which is a more complete mate for the black strand.
- Fuel strands are sequence sensitive, thus control is sequence specific.

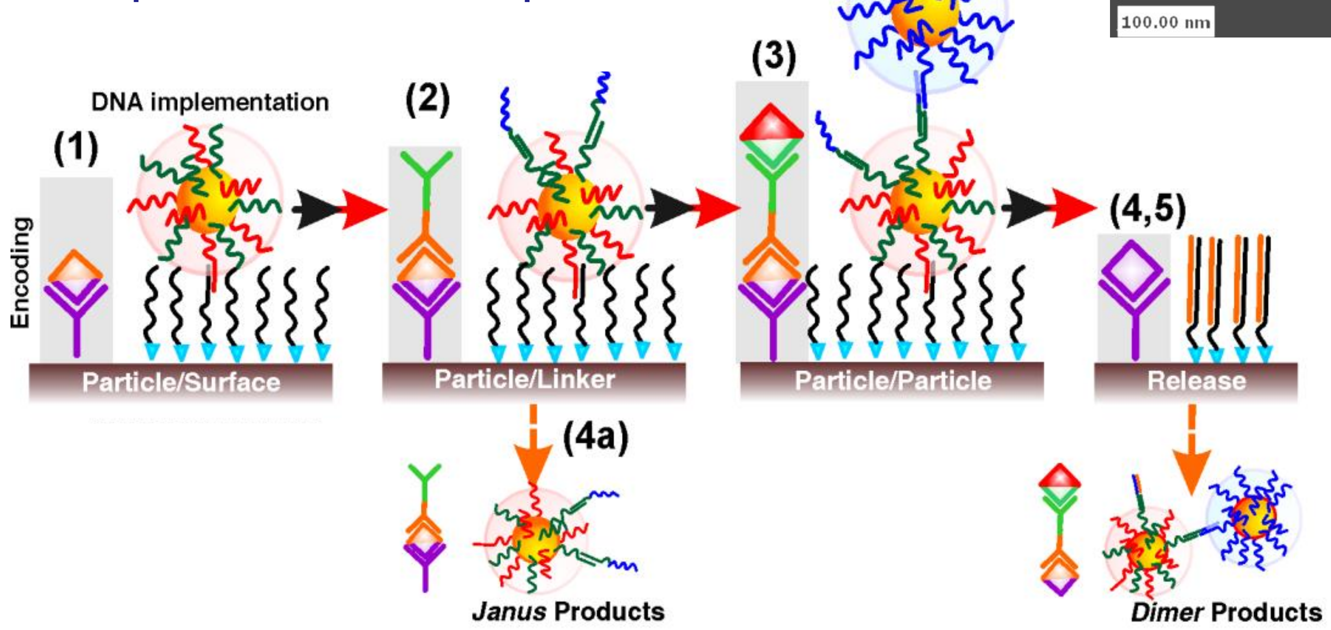
Yurke, B.; Turberfield, A. J.; Mills, A. P., Jr.; Simmel, F. C.; Neumann, J. L. *Nature* 406, 605 (2000).

Cluster Assembly



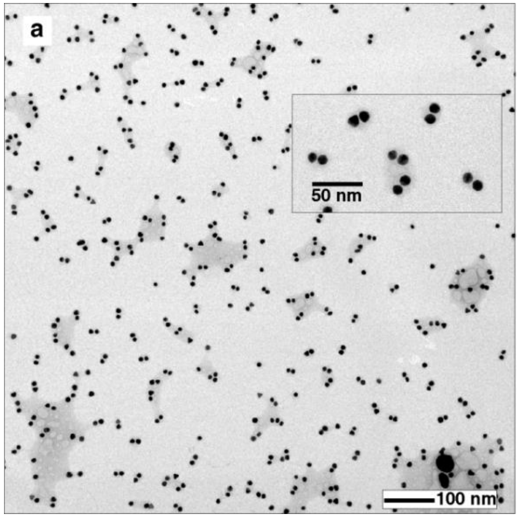
- Conventional solution-based approaches lead to multimers
- Extensive purification is required

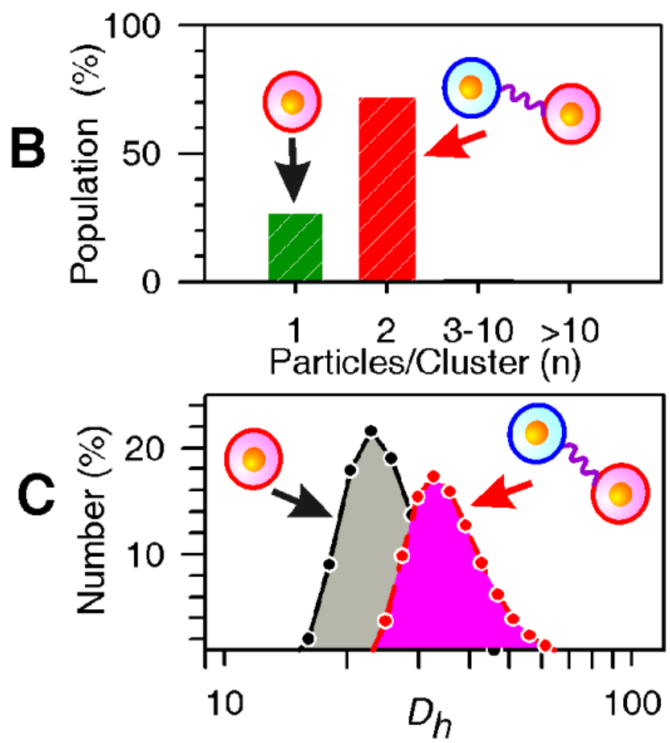


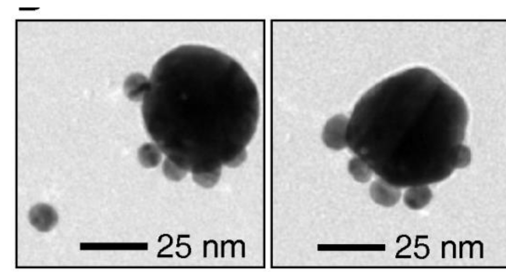


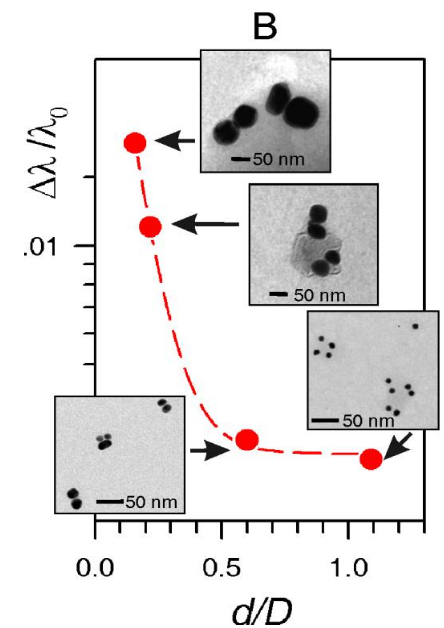
M. Maye et al, Nature Materials, 8, 365 (2009)

Building Nano-”molecules”









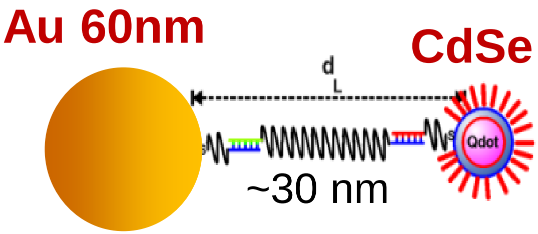
- Dimers formation with ~75% yield without additional purification
- Fabrication of symmetric and asymmetric clusters, Janus particles

Dl/l_0=exp (-x/t)+c, x=d/D, t=0.14

M. Maye et al, Nature Materials, 8, 365 (2009)

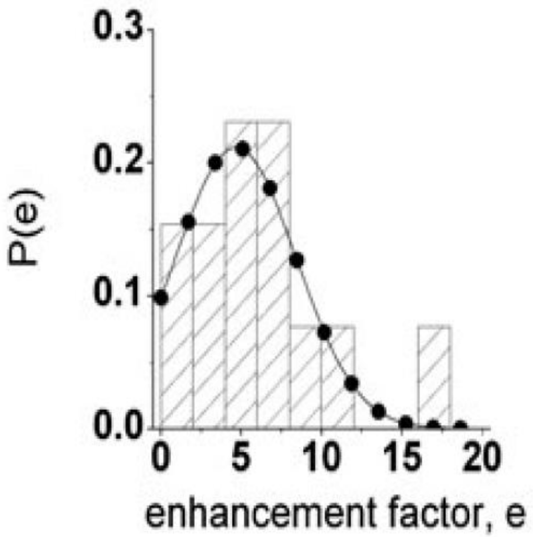
Cluster Assembly

Photoluminescent enhancement
in quantum dot (QD,CdSe)-Au dimer



Fluorescent Enhancement
(absorption normalized)

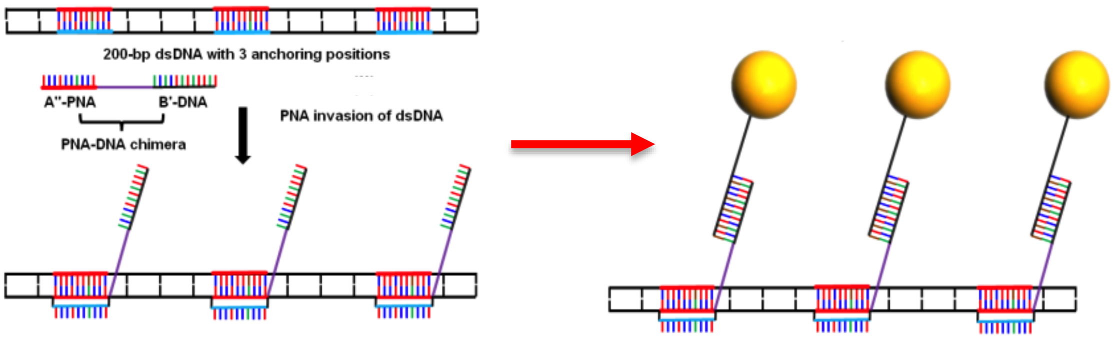
e = OD(457nm)/OD(543nm)*I_{fluo}(543)/I_{fluo}(457)



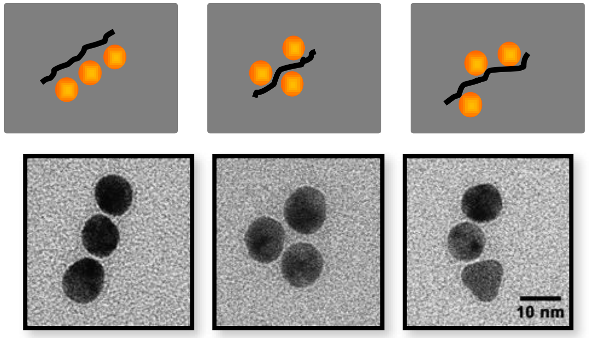
M. Maye, O. Gang, M. Cotlet, ChemComm, 46, 6111, (2010)
D. Sun et al, ACS Nano, 2015

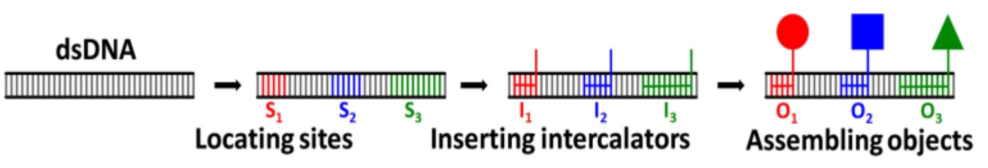
Assembly of designed clusters

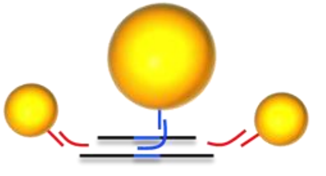
Nano-object attachment to double stranded DNA via molecular intercalators, PNA "invasion"

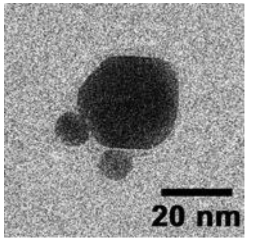


~25% yield of trimer formation



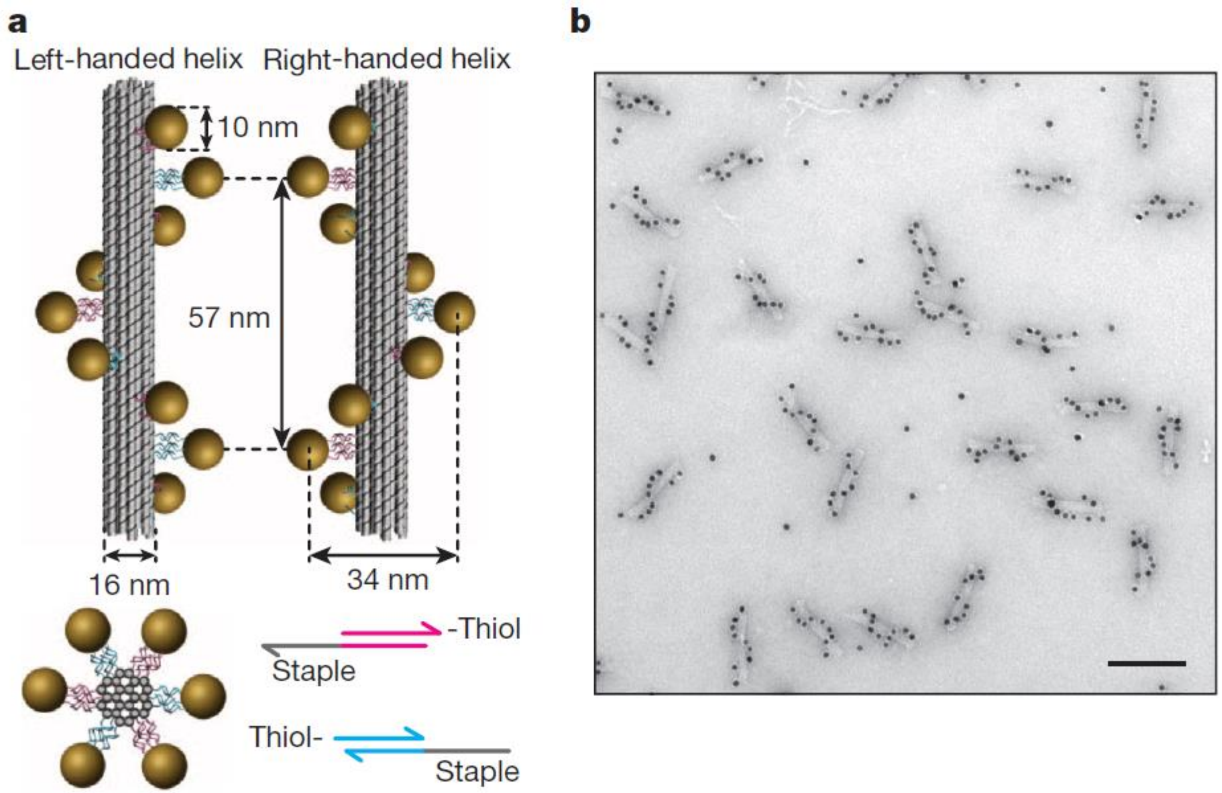






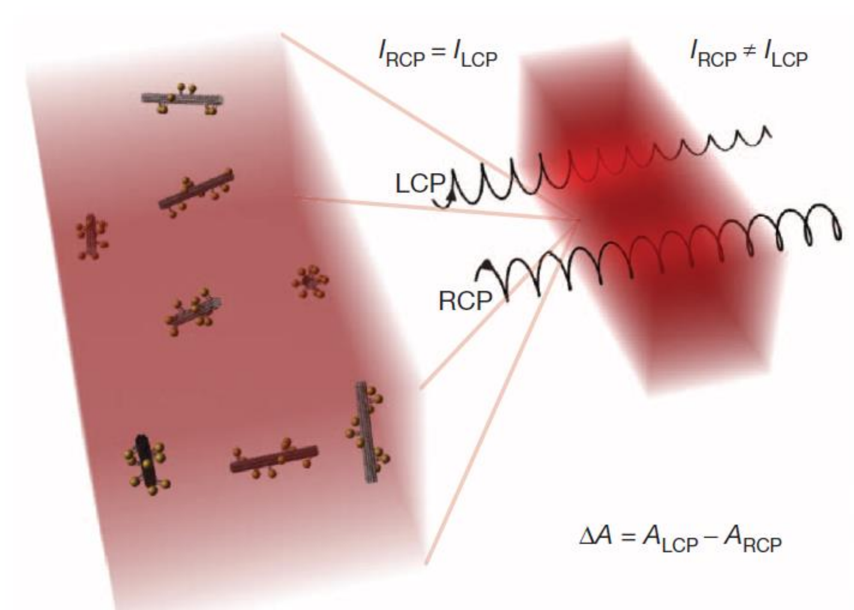
A.Stadler et al, ACS Nano 5(4):2467 (2011), P. Sun et al, Nanoscale, DOI: 10.1039/C2NR31908J (2012)

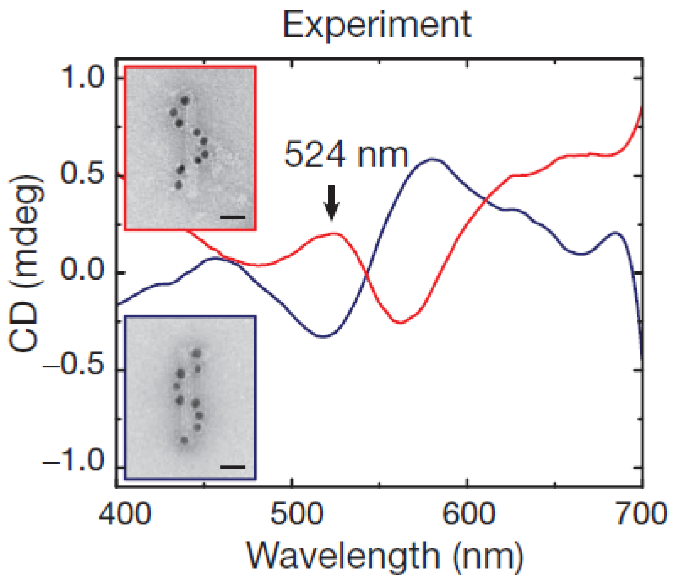
Assembly of Chiral Clusters with DNA Origami



Kizuk et al, Nature 483, 313, 2011

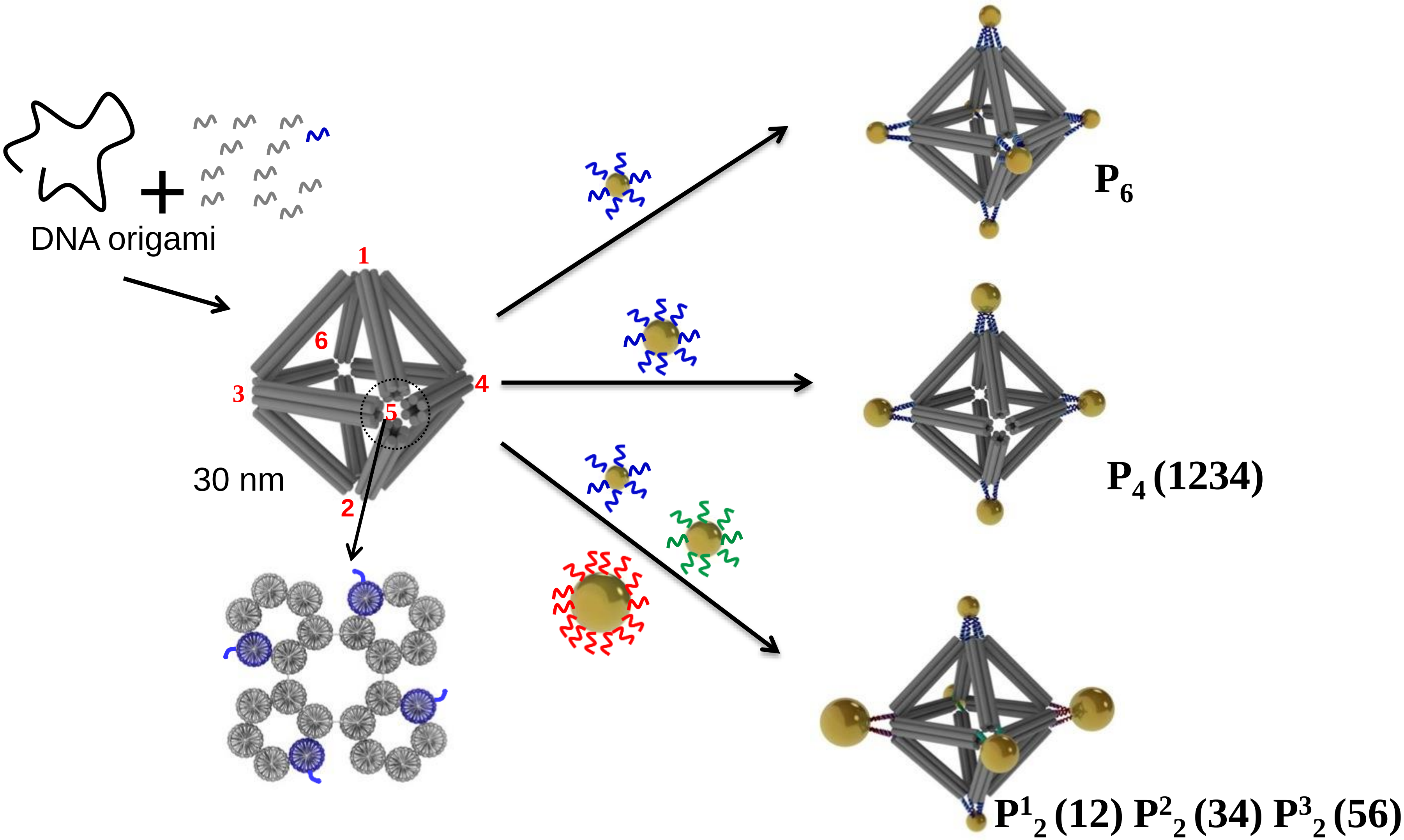
Optical Properties of Chiral Clusters





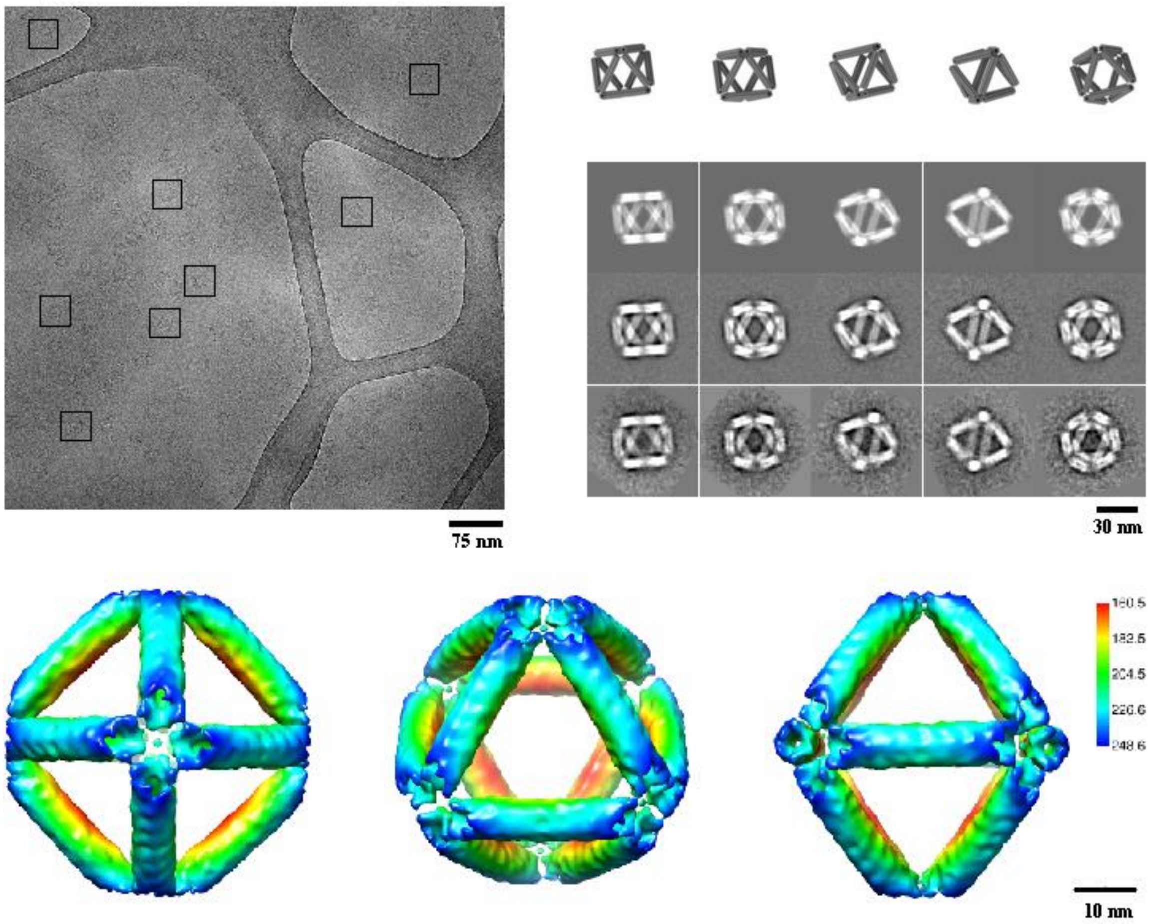
Kizuk et al, Nature 483, 313, 2011

Designed Clusters via DNA Frame

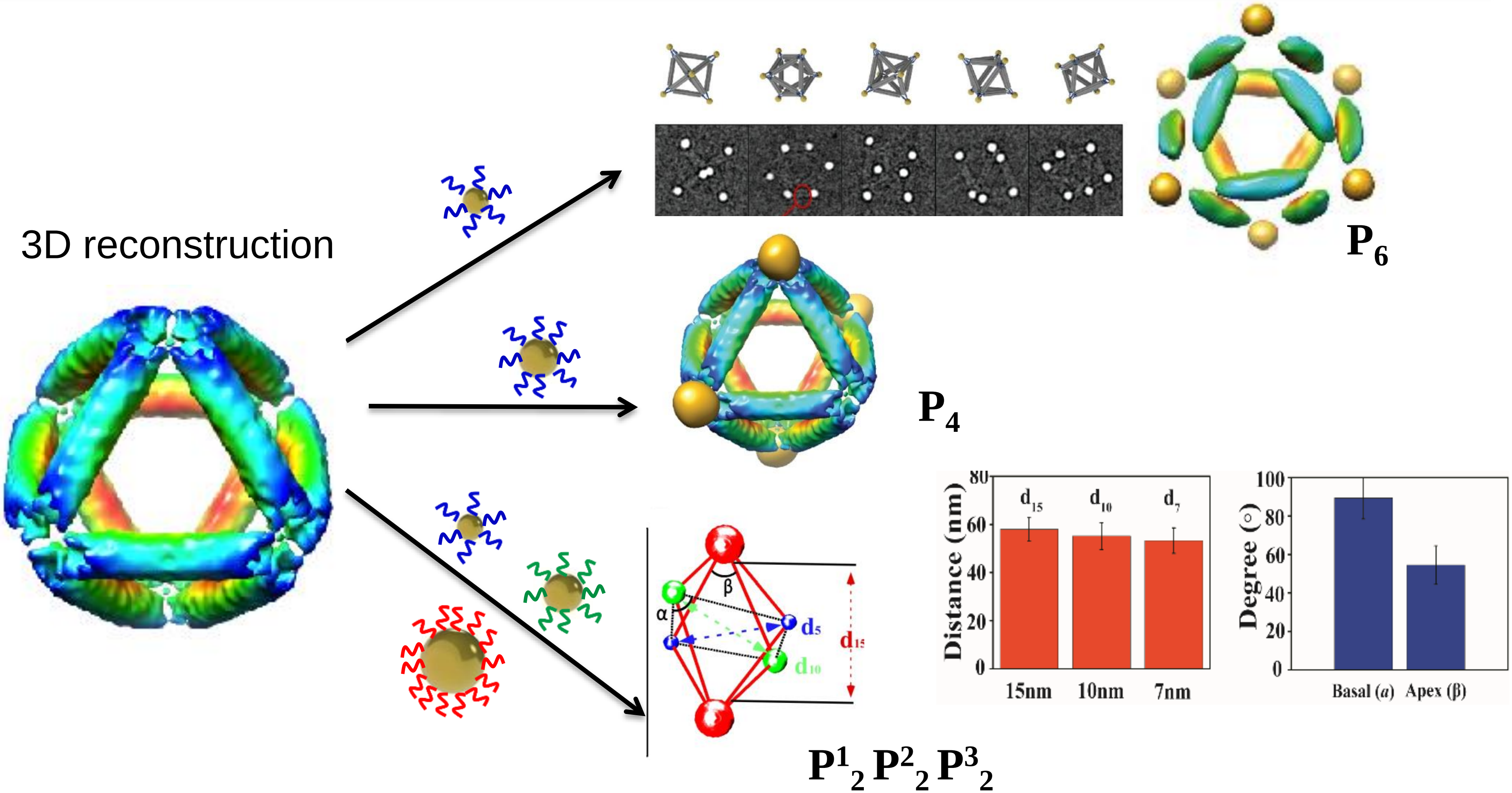


Y. Tian et al., Nature Nanotechnology, 10, 637, 2015

DNA Octahedra by cryo TEM



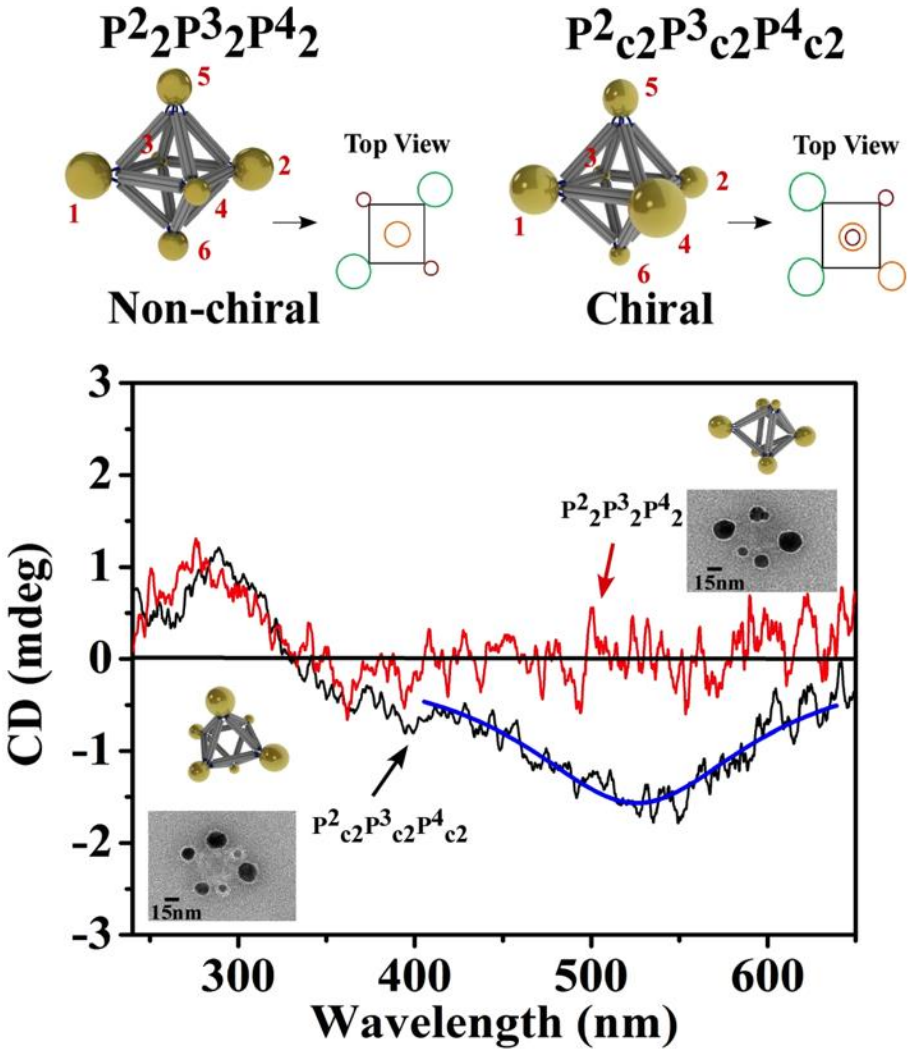
Designed Clusters



- 3D cluster structure by Cryo-TEM (~2 nm resolution
- 60-80% yield

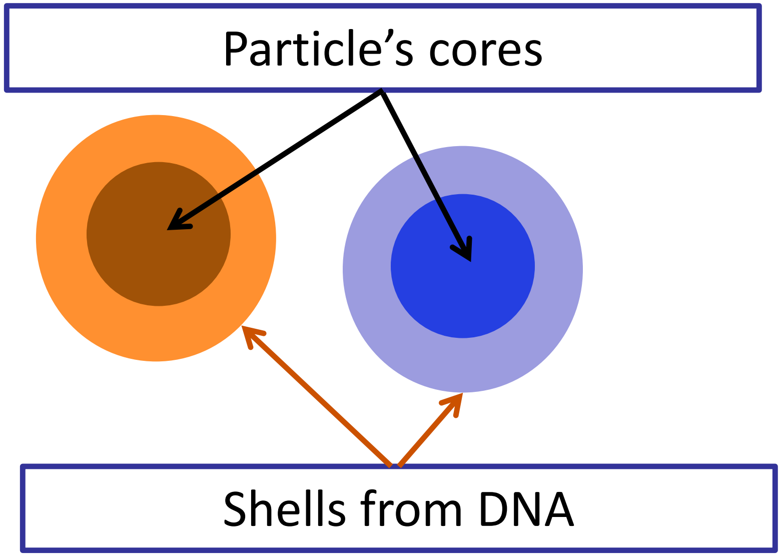
Y. Tian et al., Nature Nanotechnology, 10, 637, 2015

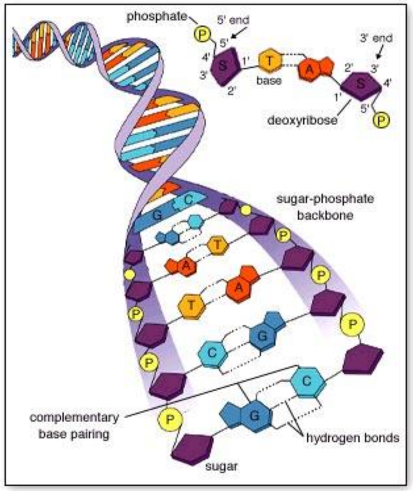
Chirooptical Response of Clusters via Vertex Encoding



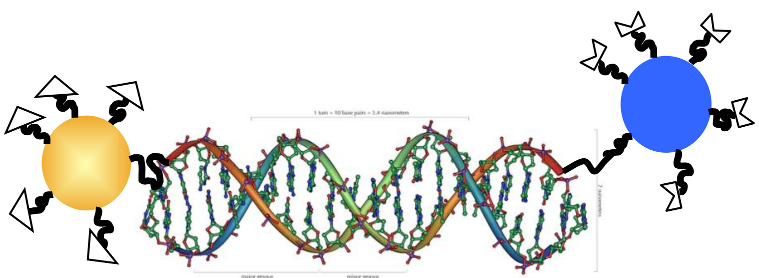
Y. Tian et al., Nature Nanotechnology, 10, 637, 2015

Large-scale Assembly of Nanoparticle with DNA





http://www.mhhe.com/biosci/esp/2001_gbio/folder_structure/ge/m4/s1/

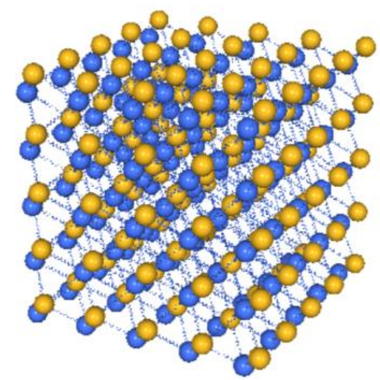


http://en.wikipedia.org/

Challenges

→

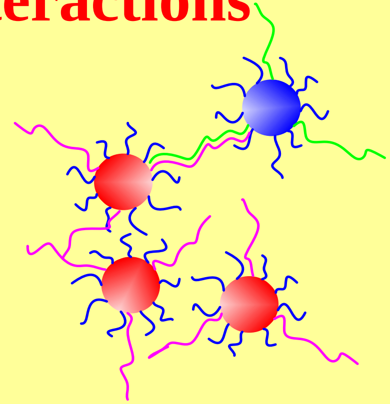
?



Systems with DNA Mediated Interactions

Encoded interactions

Binary systems

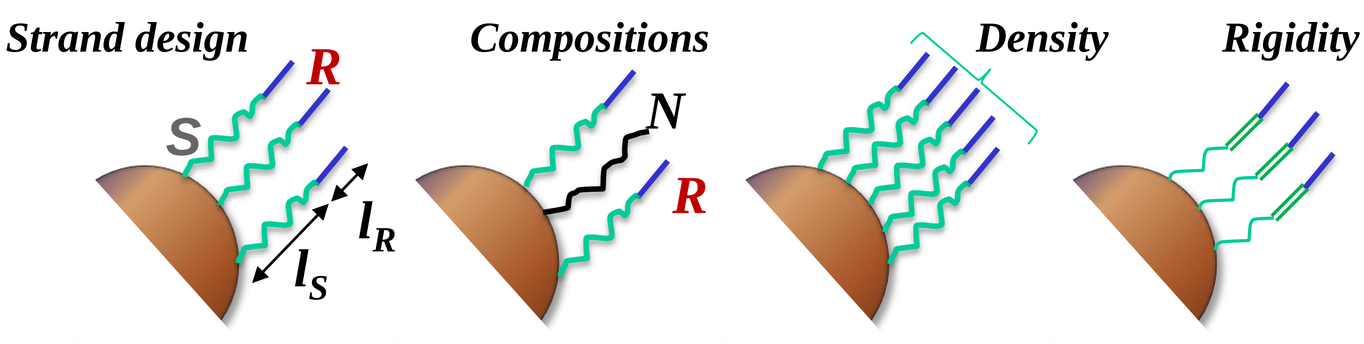


Interaction control

Addressability of interaction

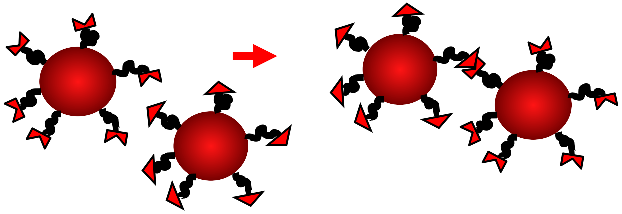
→ **Structure control of Multicomponent systems**

• A combination of physical interactions and addressability of particle/DNAs allow for tuning interparticle potential

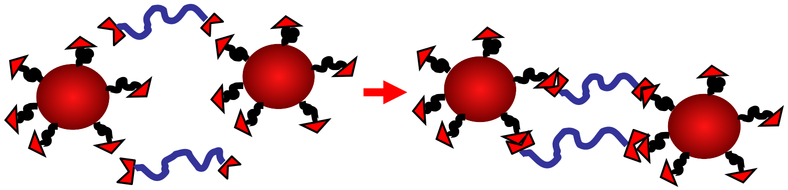


Typical DNA mediated particle assembly

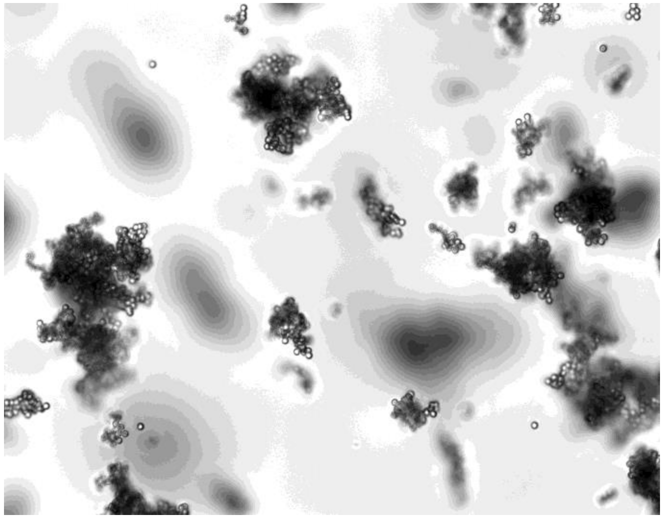
Direct particle hybridization



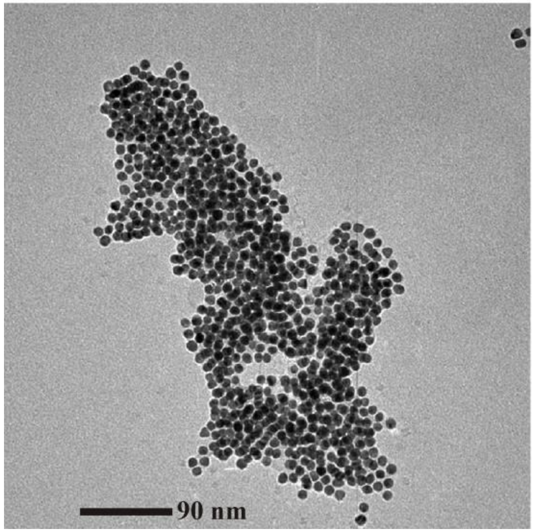
Linker induced hybridization



Micron-sized Colloids



Nano-sized Particles



Energy Landscape

Type	*Dependence*	*Energy kcal/mol*
Temperature	kT	0.6
Van der Waals (vdW)	complex	0.1-10
Steric	complex	0.1-10
Hydrogen bonds (HB)	Electrostatic origin + dispersion + …	2-10
Complex Steric	System dependent	???
DNA elasticity	$E_{cir}/kT = 2\pi^2 A/L$ and more	0.01-12
Ionic strength	Affect hybridization $T_m \sim \log[A^+]$	
Entropic and topological effects	System dependent	???
DNA-DNA DNA-protein	Ionic strength dependent ~HB	1-30

Addressable Interactions: 3D phases

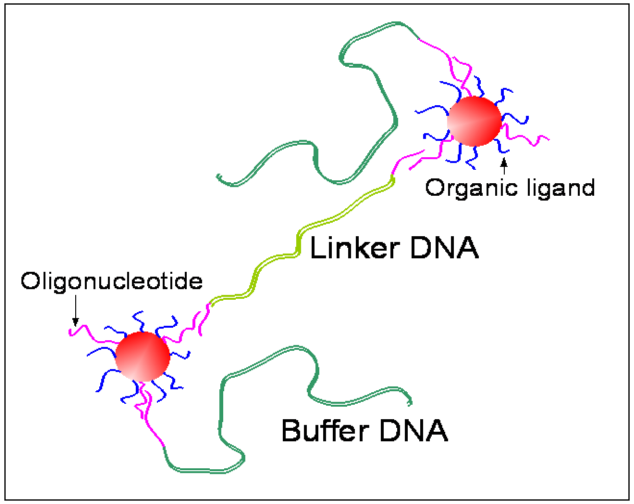
Assembly requires a balanced interaction to overcome random aggregation

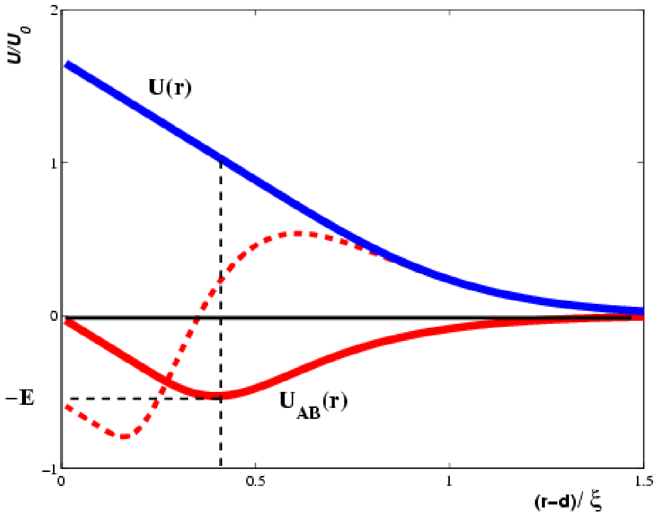
Particle-particle potential is tuned by DNAs

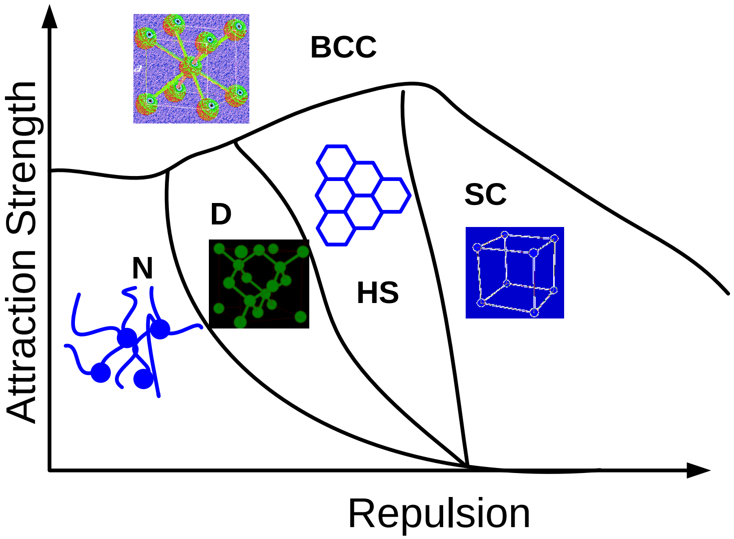
- **Relative concentration of linker and buffer DNAs**
- **Through DNAs lengths (nm to μ)**

$$U_{total}(r) = U_r(W_{st}, W_{dep}) + U_{AB}(W_{el}, W_h)$$

Repulsion **Interparticle attraction**





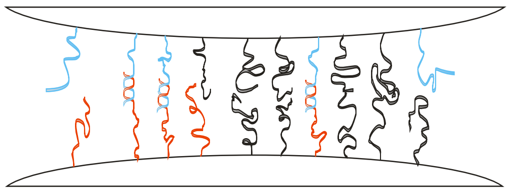


A. V. Tkachenko, PRL 89, 148303 (2002)

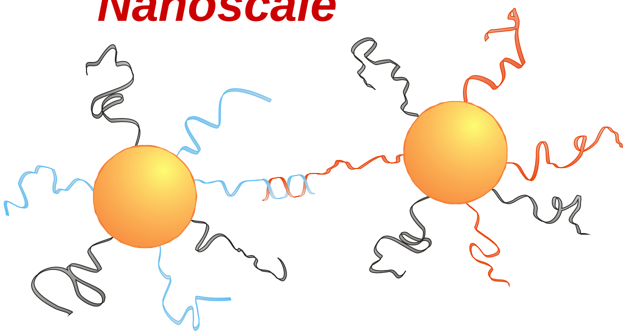
DNA mediated interaction between Micro and Nanoparticles

DNA for controlling attraction and repulsion between particles

Microscale



Nanoscale



Colloidal particles (~1 micron):
- "short-range" potential
- large number of DNA per particles (~10^5)
- flexibility in "construction" of the inter-particle interactions

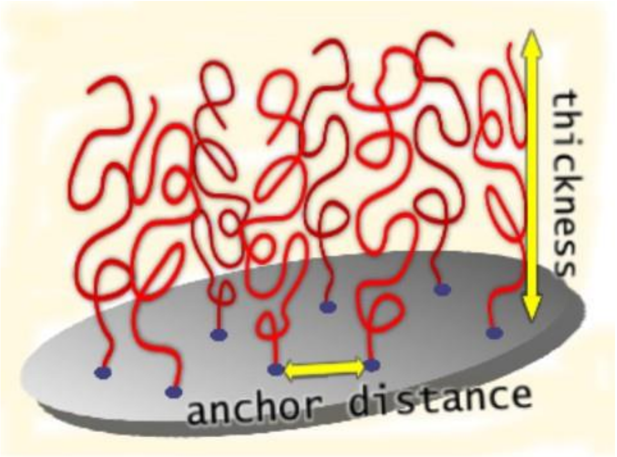
Nanoparticles (3-15 nm)
- "long-range" interactions
- small number of DNA per particles (1 to 10^2)

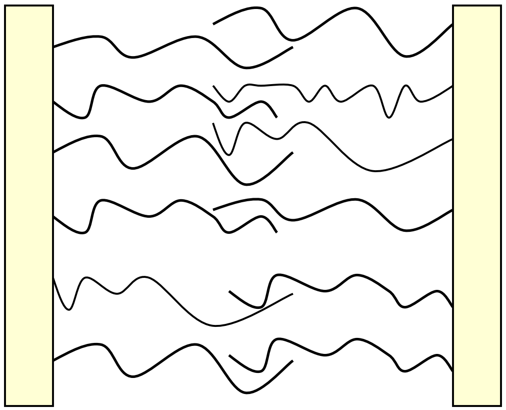
- Similar particle-design principles can be applied to micro- and nanoscales.
- The details of physical interactions will dictate behavior on specific scales.

Balancing particles interaction

$$L = klN\sigma^{1/3}$$

N – number of segments
σ - grafted polymers surface density
l - size of one monomer
k - a constant of order unity



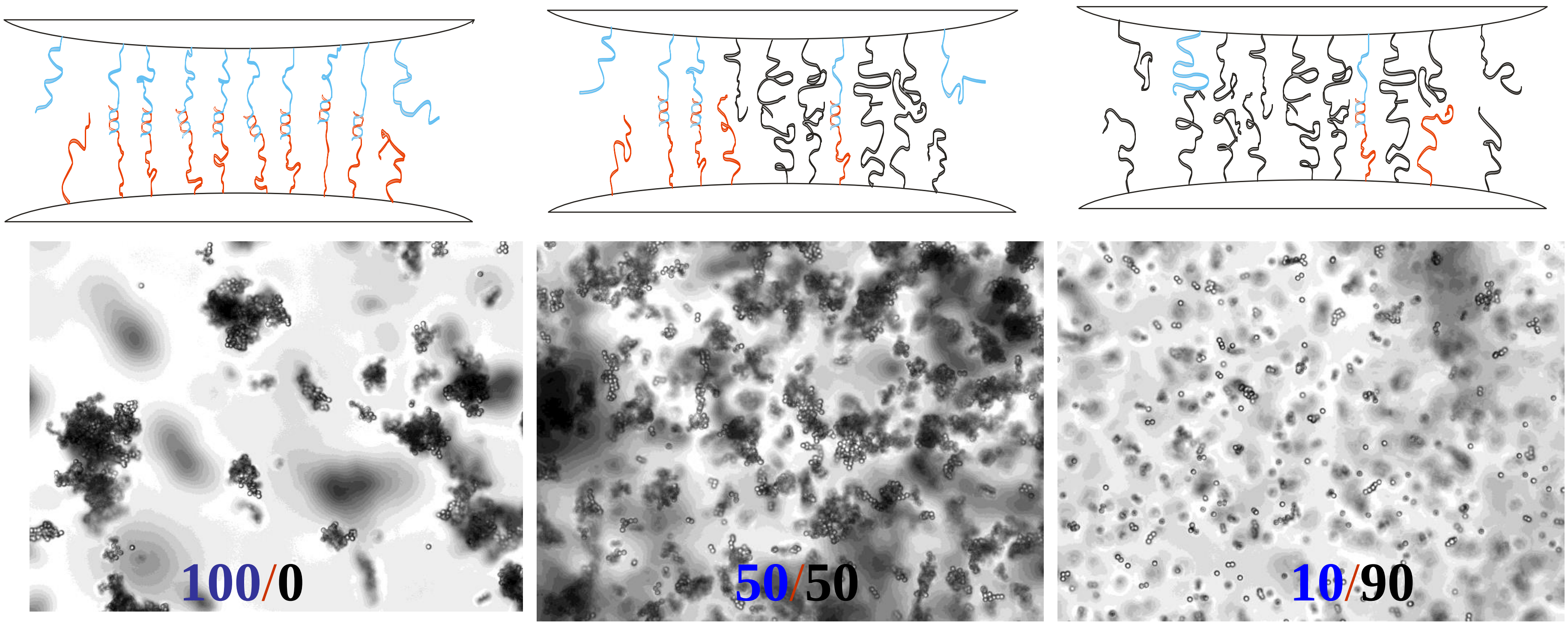


- Polymer chains tethered to a surface at a high density are stretched perpendicular to the surface - the loss of possible conformations

- Different regimes depending on the anchor distance D: mushrooms D> R_g, cross-over D~R_g, brushes D< R

- Surfaces with grafted polymer repeal due to the loss of chain entropy

Tuning the morphology of assembling through the "neutral" DNA



complementary/non-compl. ss DNA concentration

Optical microscopy images after 24 hours of mixing

D. Nykypanchuk, M. Maye, D. Van der Lelie, O. Gang, Langmuir (2007), 23(11):6305

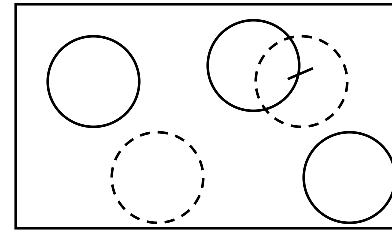
Energy profiles

attraction

$$E_a(d,f) = E_h \int_0^{R(d)} 2\pi r f \rho_0 P(d,r,f)\,dr + E_w(d)$$

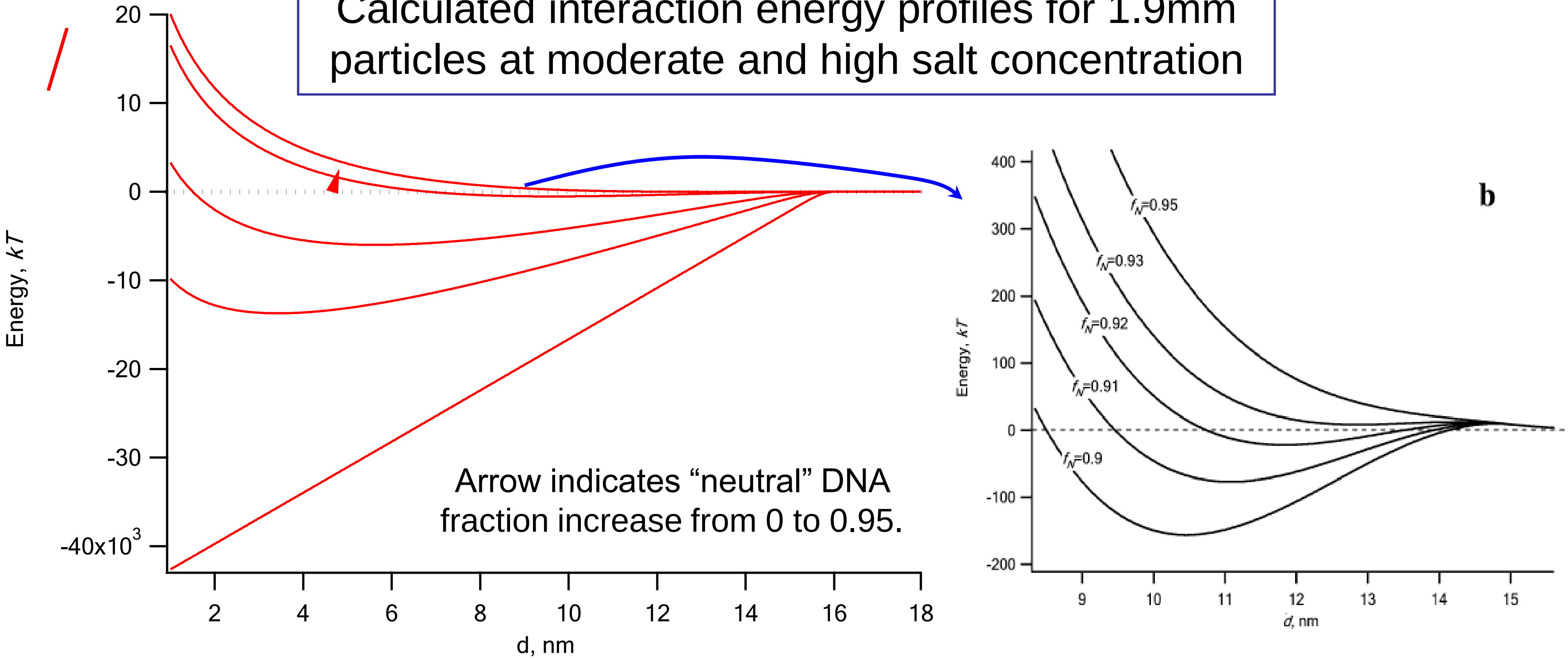
repulsion

$$E_r(d,f) = \int_0^{R} 2\pi r \rho_0 E_{ou}(d)(1 - fP(d,r,f))\,dr + E_{oh}(d,f) + E_{el}(d-2b_0)$$



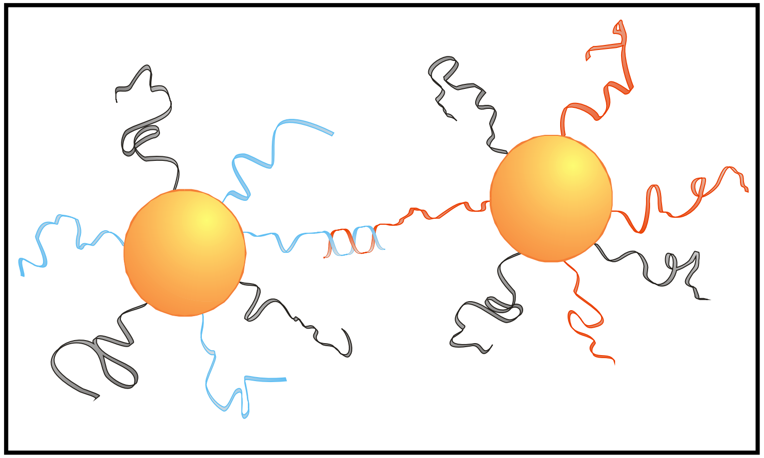
P (d,r,f) – the probability of overlap: $P(d,r,f) = \left(1 - \left(\left(1 - \pi a^2(d,r) f \rho_0\right) \exp\left(\frac{-3\pi a^2(d,r) f \rho_0}{1 - 2\sqrt{3}a^2(d,r) f \rho_0}\right)\right)\right)$

Calculated interaction energy profiles for 1.9mm particles at moderate and high salt concentration



D. Nykypanchuk, M. Maye, D. Van der Lelie, O. Gang, Langmuir (2007), 23(11):6305

Nanoscale



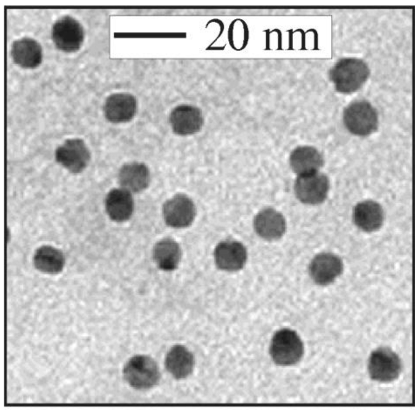
- DNA is comparable with particle size- “long-range” interactions
- Small number of DNA per particles (1 to 10^2). Can we average interactions?
- How to probe structure?

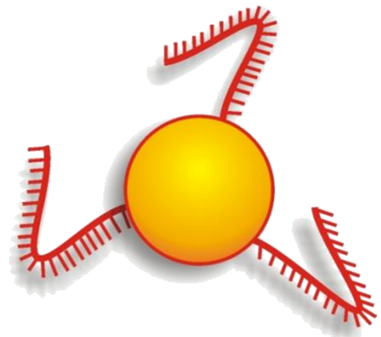
Oligonucleotide-Modified Au Nanoparticles

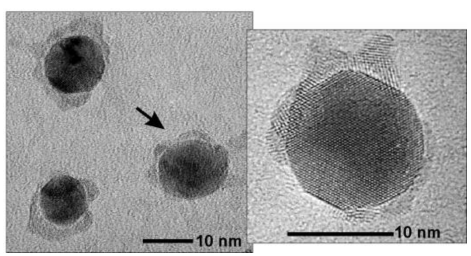
<u>Oligonucleotide Sequence (5' to 3')</u>

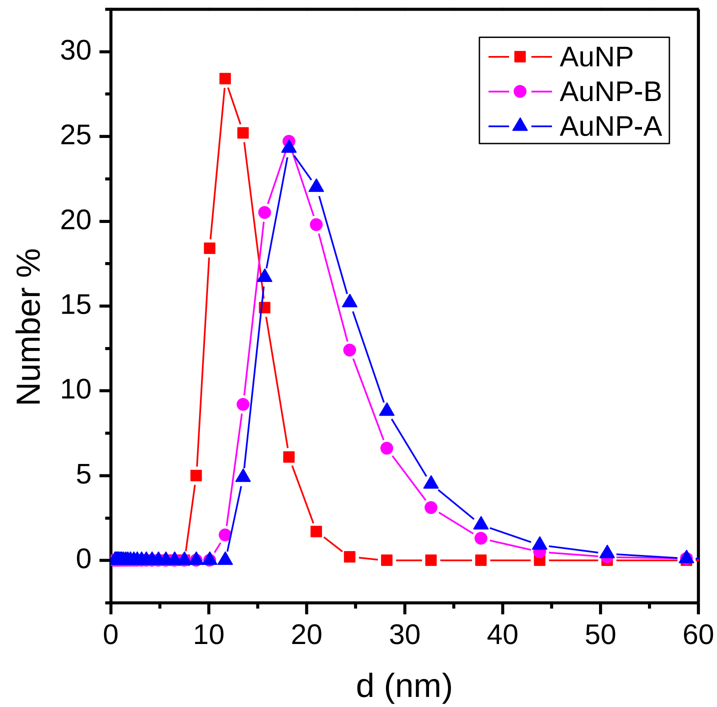
TAC TTC CAA TCC AAT- $(T)_{15}$-C_3H_6-S-(Au

TEM

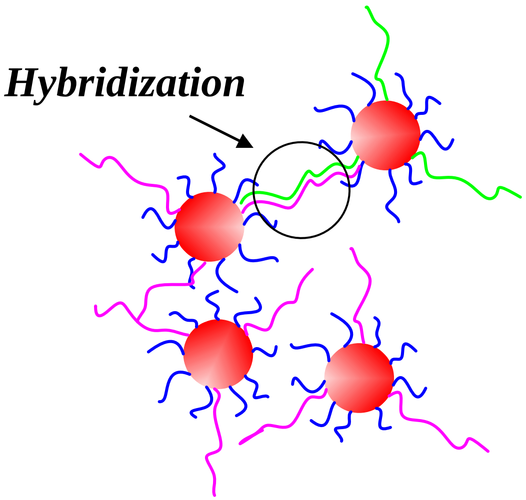






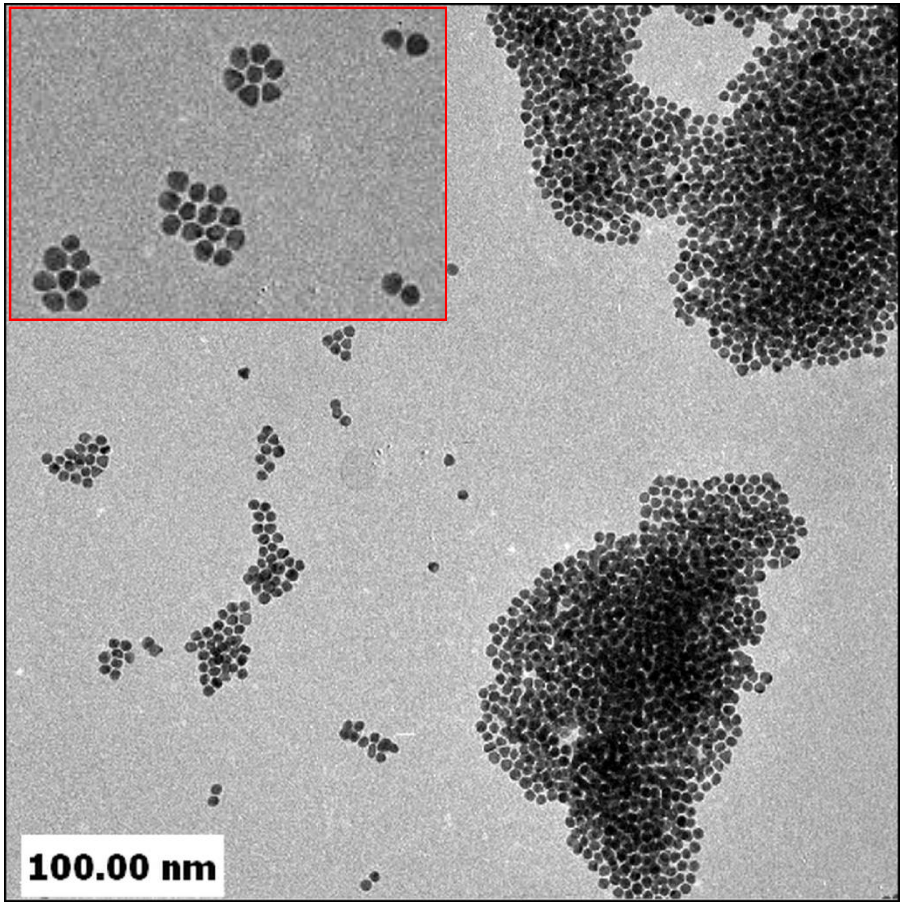


Aggregation of particles with complementary DNAs



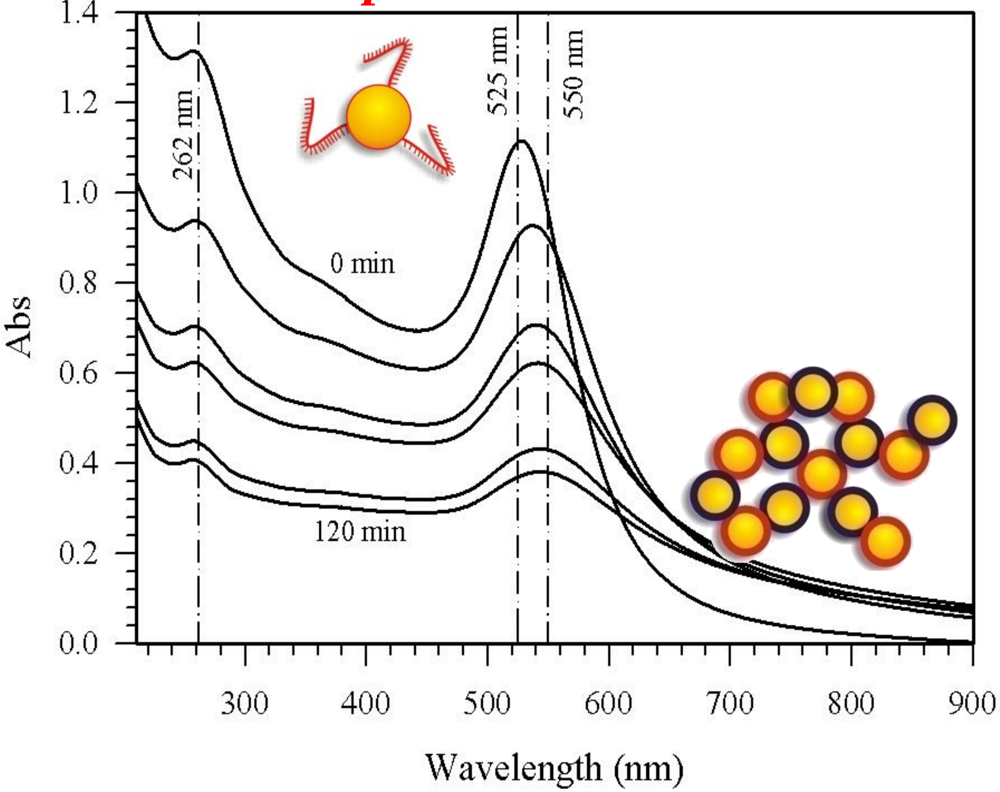
-Hybridization induce the aggregation of Au particles

-Formation of jammed structures is observed by TEM



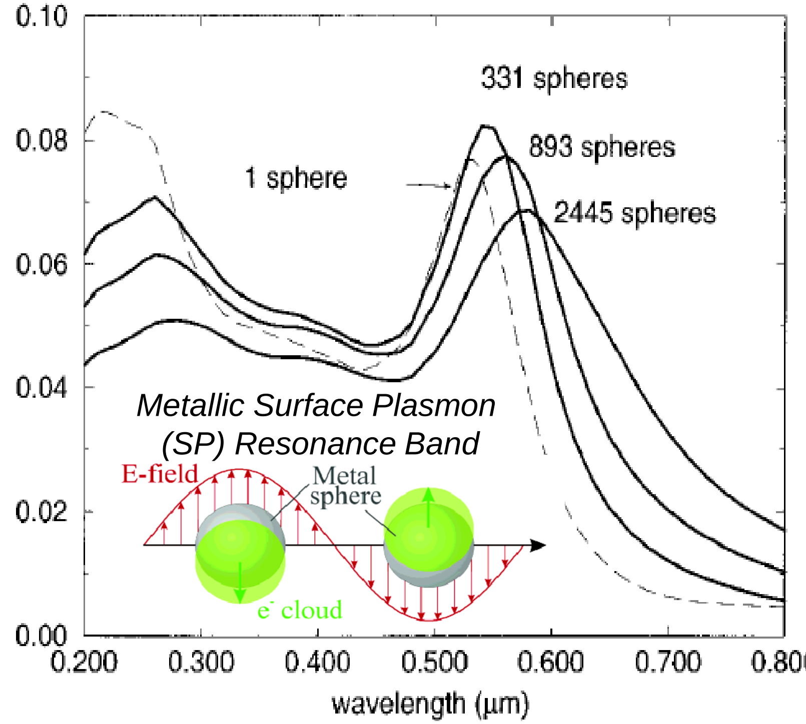
Monitoring Assembly via Optical Measurements

Experimental Results



[$\mathbf{Au_{nm}}$] = 5.9 nM, 0.3 M PBS, pH = 7

Theoretical Calculation

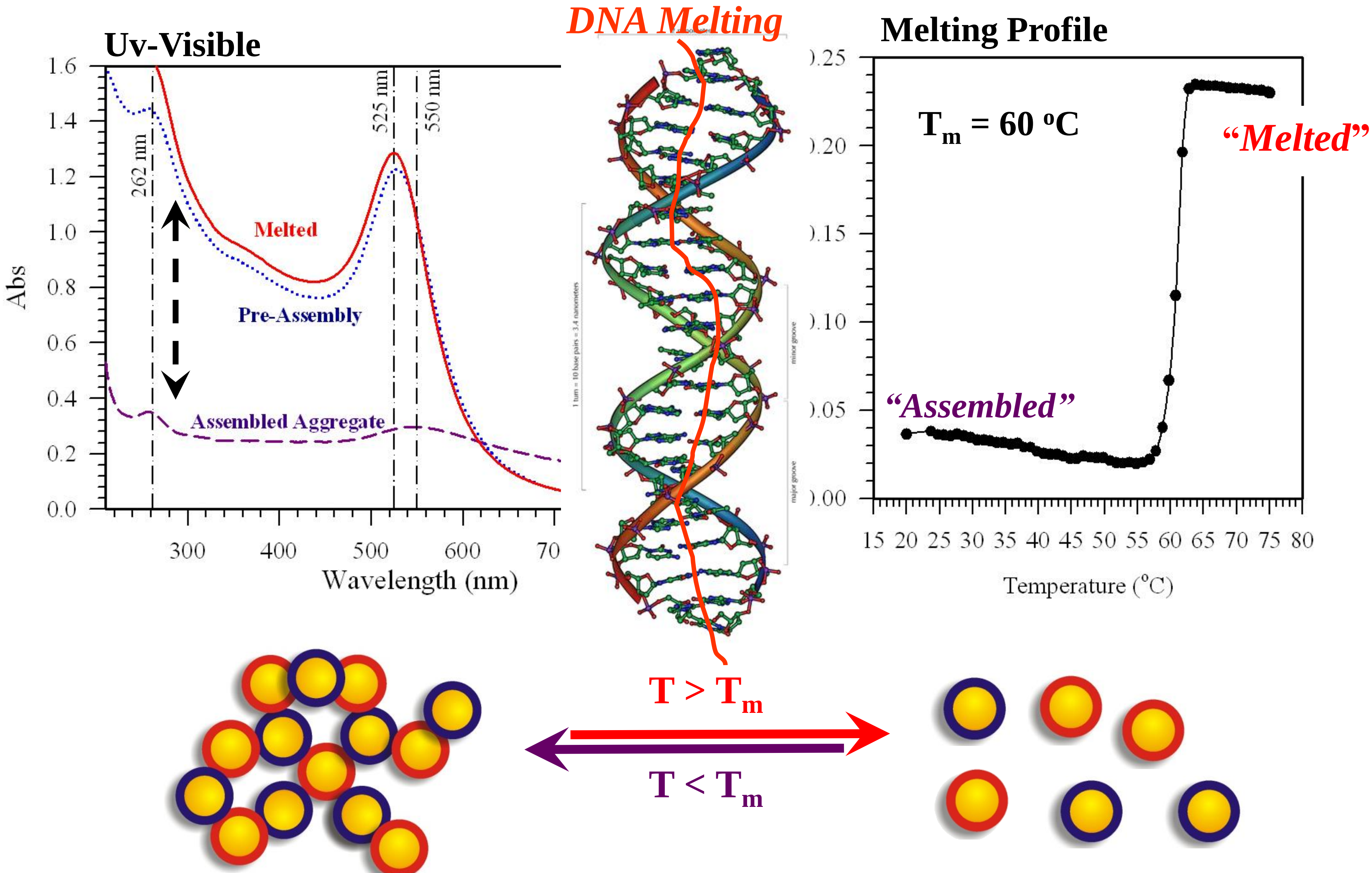


A. Lazarides and G. Schatz,
J. Phys. Chem. B **2000**, *104*, 460

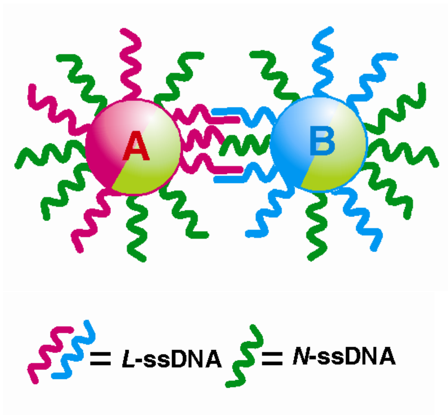
<u>**Optical Properties of Assembly dominated by:**</u>

Interparticle Distance, Aggregate Size/Shape

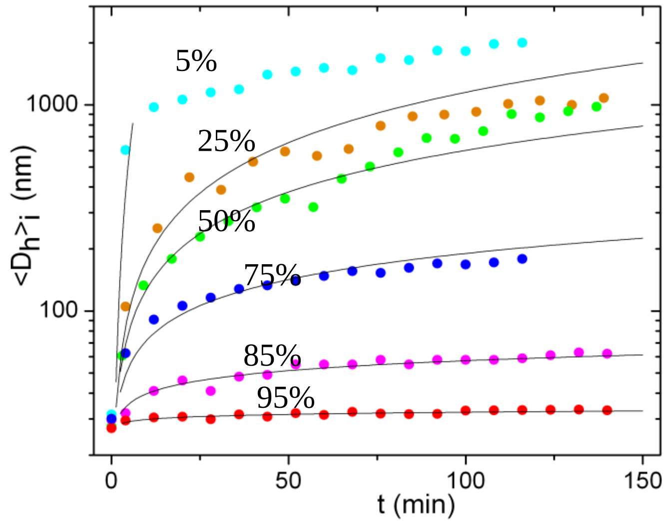
Assembling and Disassembling via DNA Melting



Tailoring interparticle interactions with DNA



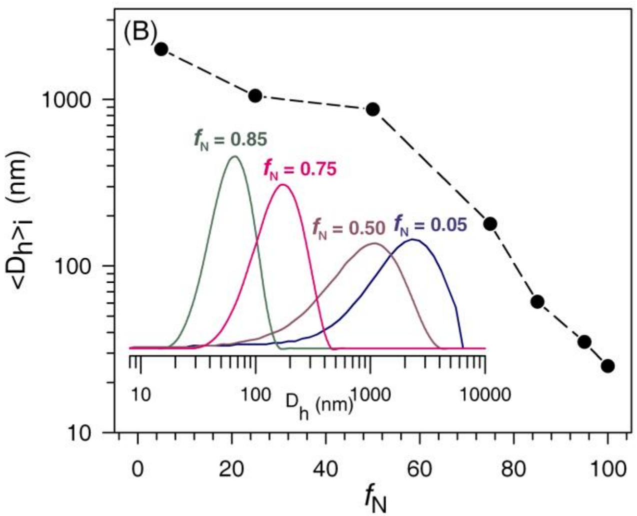
Assembly Kinetics DLS



$<D_h>_i \sim (t/\tau)^\gamma$

τ characteristic time, ~ doublet formation, increases from fraction of minute to tens minutes with the fraction of “neutral” DNA, f_N from 5% to 95%

Aggregate size, DLS after ~120 min

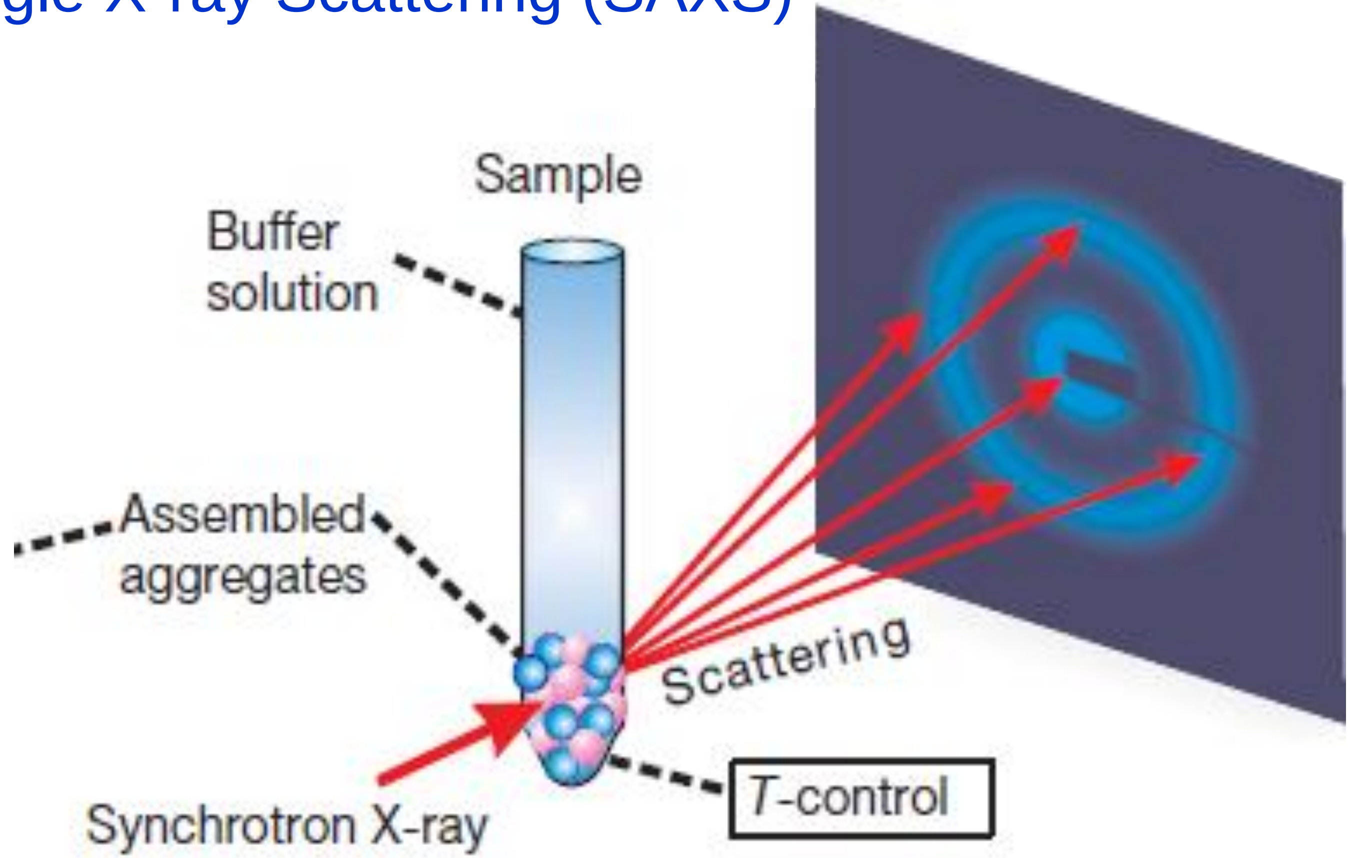


The transition from strongly aggregating regime to stabilization is observed with f_N increase

M.M. Maye, D. Nykypanchuk, D. van der Lelie, O. Gang, *Small* 3, 1678 (2007)

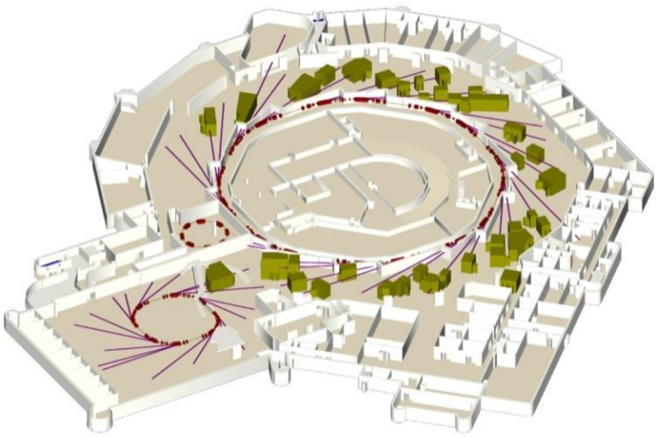
How to probe the 3D structures in-situ?

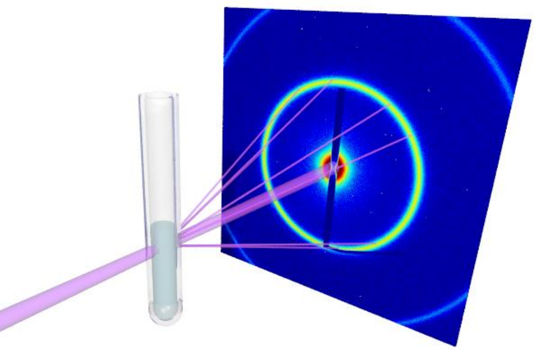
Small Angle X-ray Scattering (SAXS)

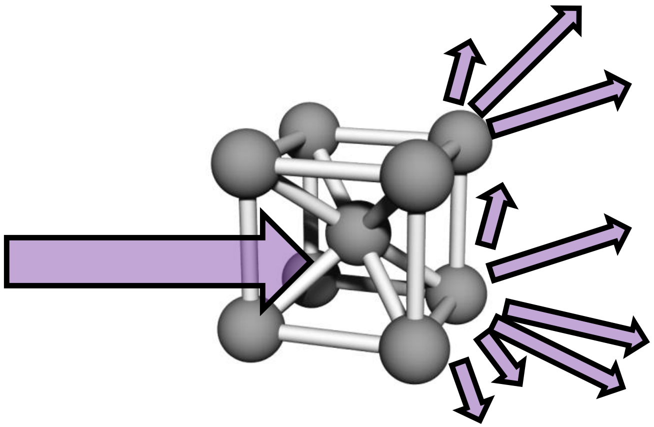


X-ray Scattering

- Electrons accelerated in synchrotron ring
- “Insertion devices” emit bright x-ray beams
- X-rays scatter off of all the atoms/particles in the sample

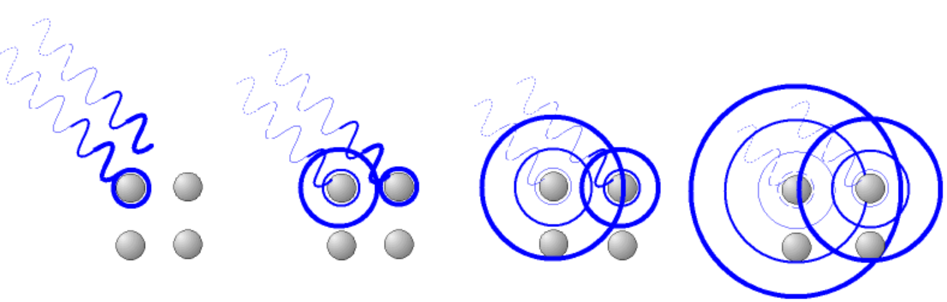


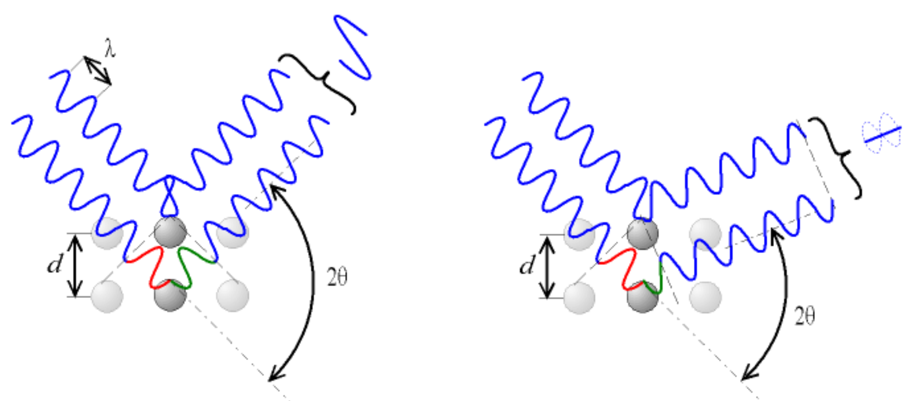




- The scattered waves interfere, which produces distinct spots or rings at specific angles…

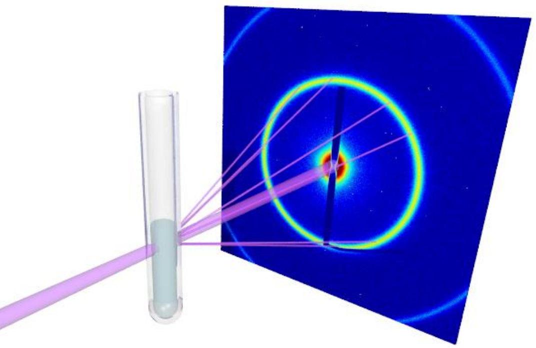
$$n\lambda = 2d\sin\theta$$





X-ray Scattering

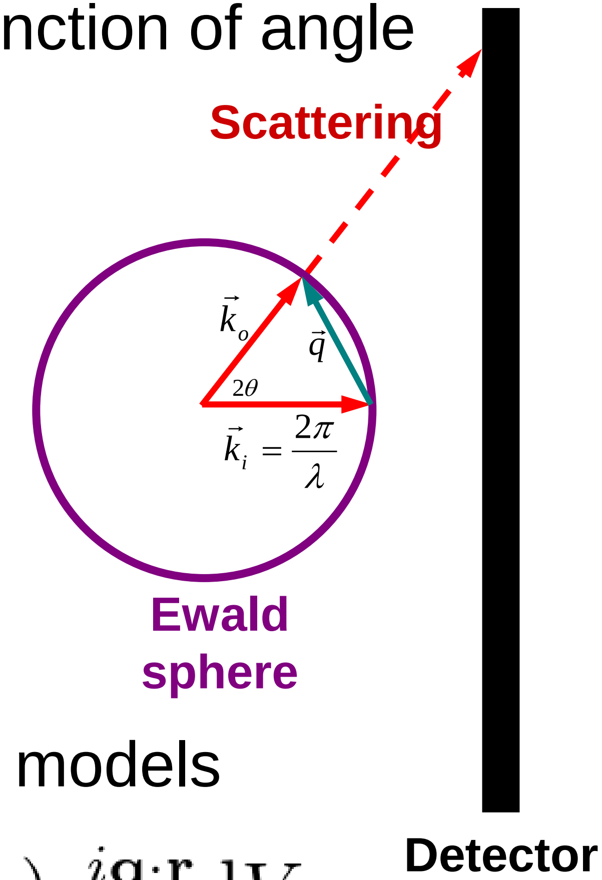
- Measure intensity of x-ray scatter as a function of angle
- Convert from angle to “reciprocal space”



$$\left|\vec{k}_i\right| = \frac{2\pi}{\lambda}$$

$$\vec{q} = \vec{k}_o - \vec{k}_i$$

$$\left|\vec{q}\right| = q = \frac{4\pi}{\lambda}\sin\theta$$



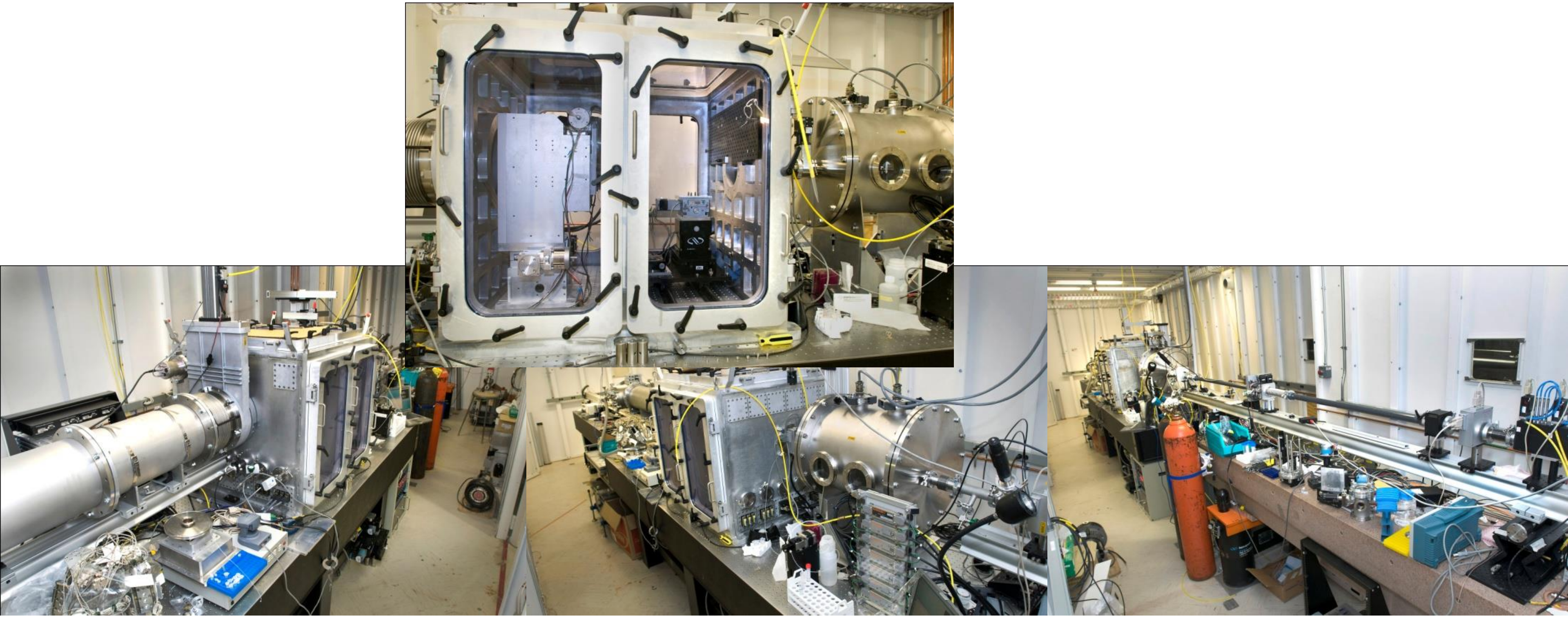
- Interpret data by comparing to candidate models

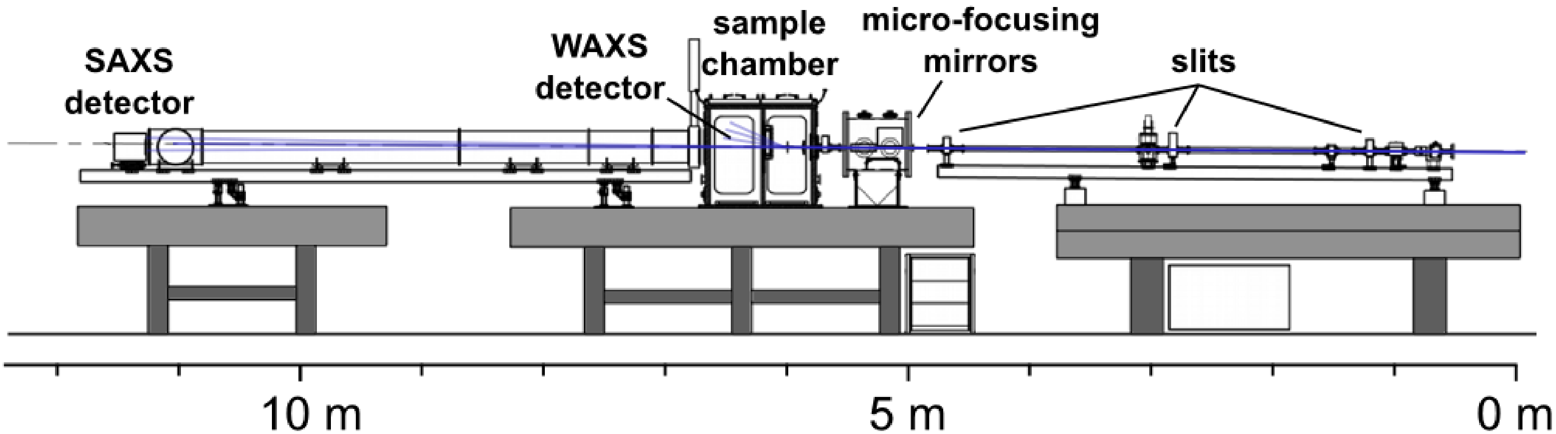
$$s(\mathbf{q}) = \sum_n f_n e^{i\mathbf{q}\cdot\mathbf{r}} \qquad f_n(\mathbf{q}) = \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \mathrm{d}V$$

- Can determine: symmetry, size, spacing, orientation, grain size, order/perfection, unit cell, …

NSLS-II at Brookhaven National Lab

X9 beamline at NSLS



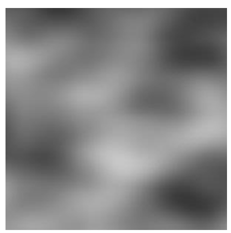
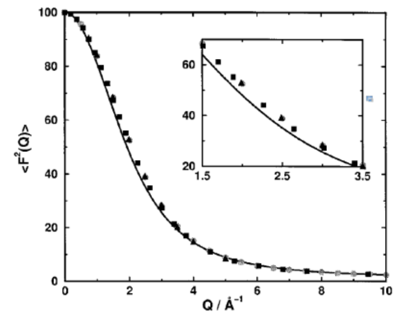


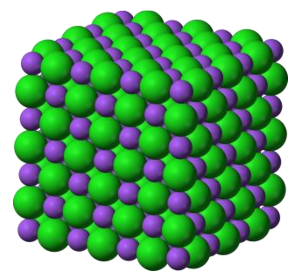
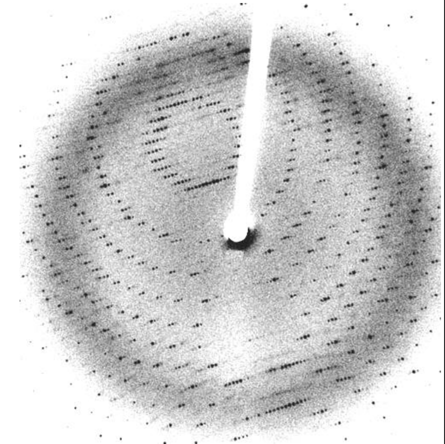
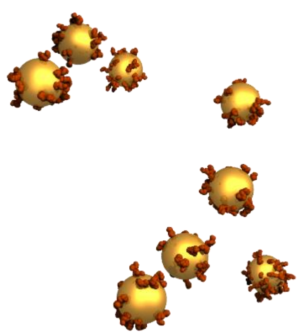
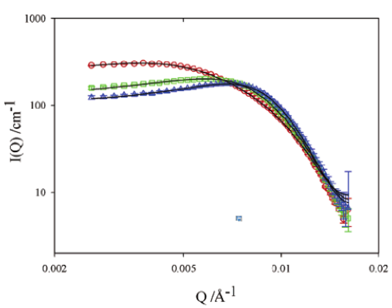
Different “kinds” of Scattering

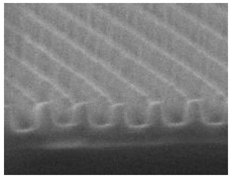
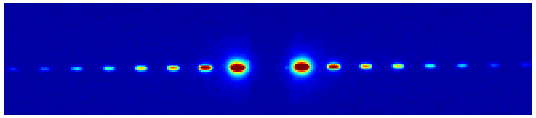
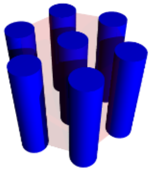
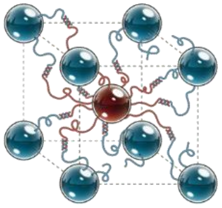
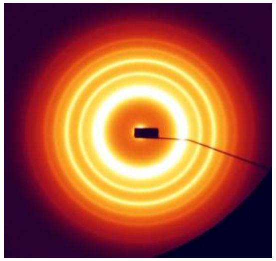
Organization of constituents (“Structure Factor”)

Constituents (“Form Factor”)

	Random	Periodic
Simple	Gases, liquids, glasses, …	Crystals, …
Arbitrary	Colloids, proteins in solution, …	Lithography, nano-particle lattices,

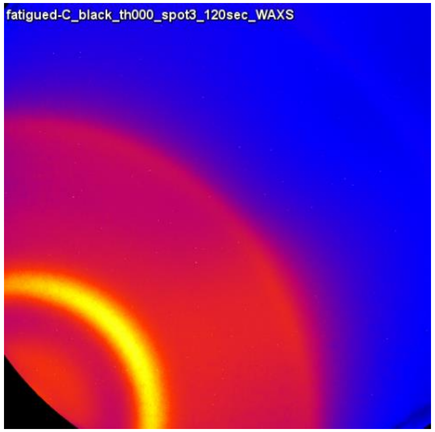





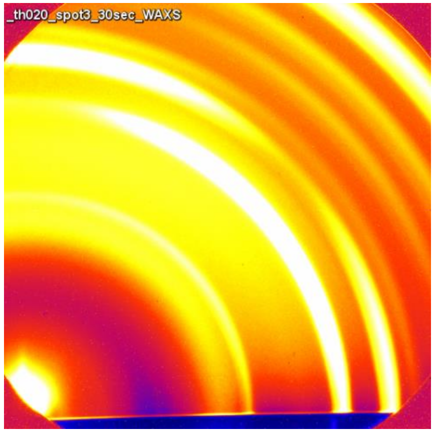
X-ray scattering Examples

BROOKHAVEN NATIONAL LABORATORY

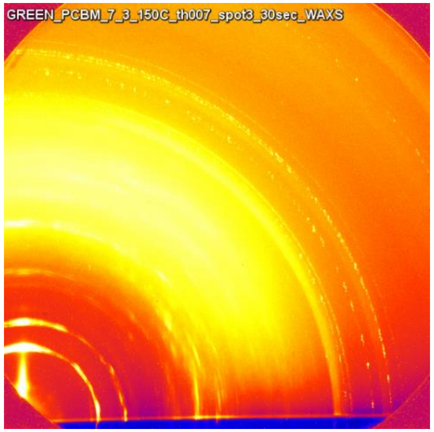
- Can easily infer amount of order:
  - Amorphous
  - Polycrystalline
  - Single crystal



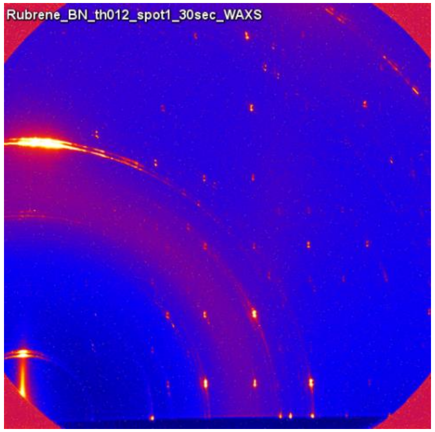
disordered



ordered, polycrystalline



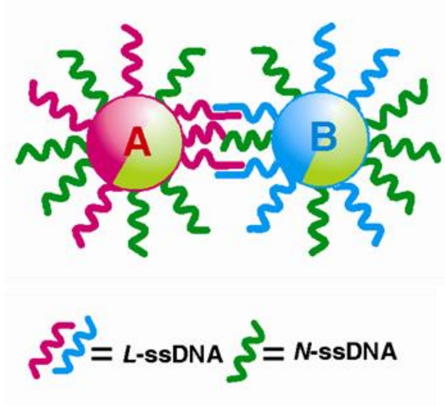
oriented, textured



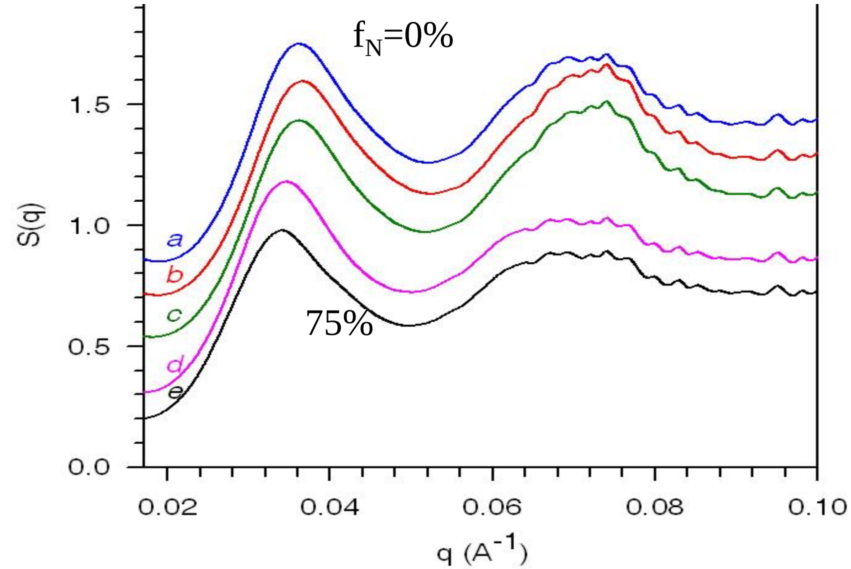
single crystal

less order ↔ **more order**

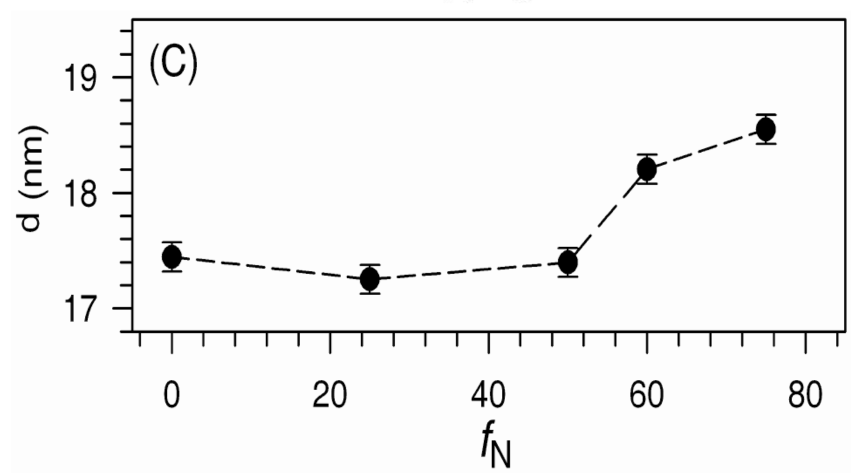
Small Angle X-Ray Scattering (SAXS)



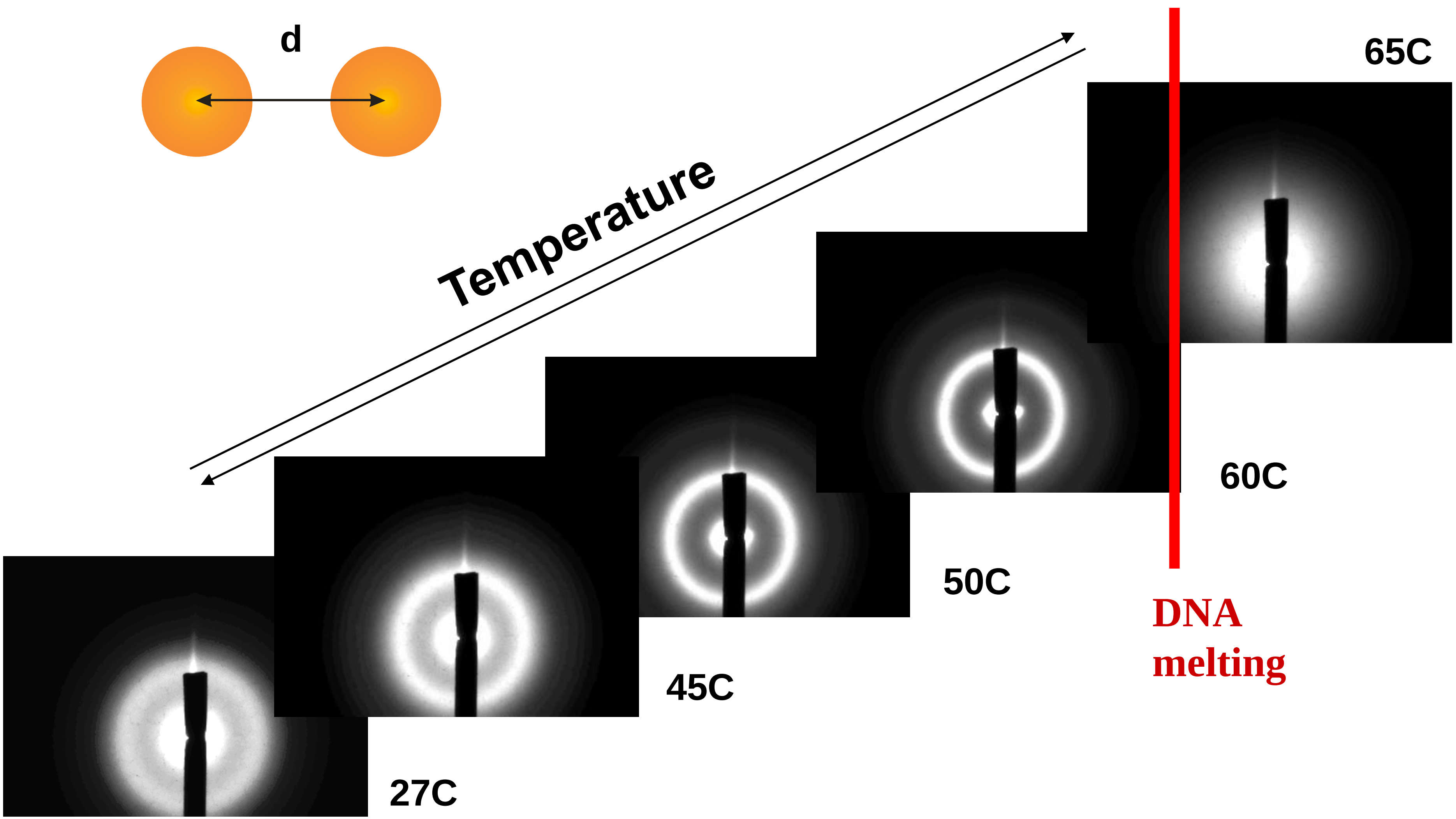
SAXS probing large length scale structures



- *d* increase from ~17.3 nm to 18.6 nm at f_N~50%
- stronger interparticle repulsion results in *d* increase at f_N>0.5

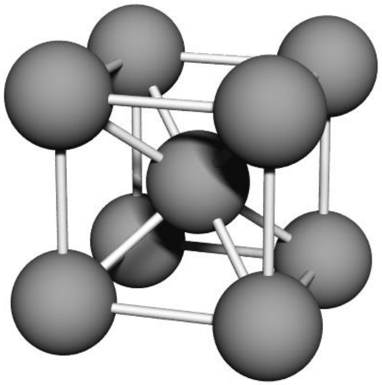


Small Angle x-ray scattering

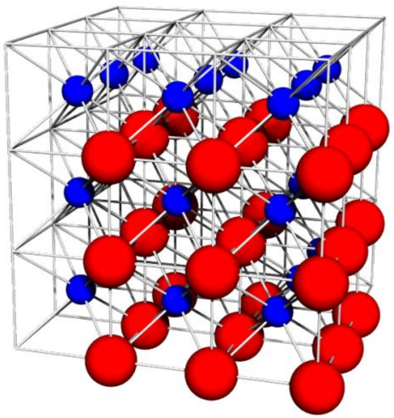


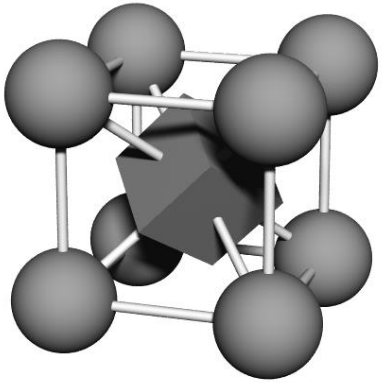
3D Assembly of Nano-objects into Superlattices

Lattice symmetry

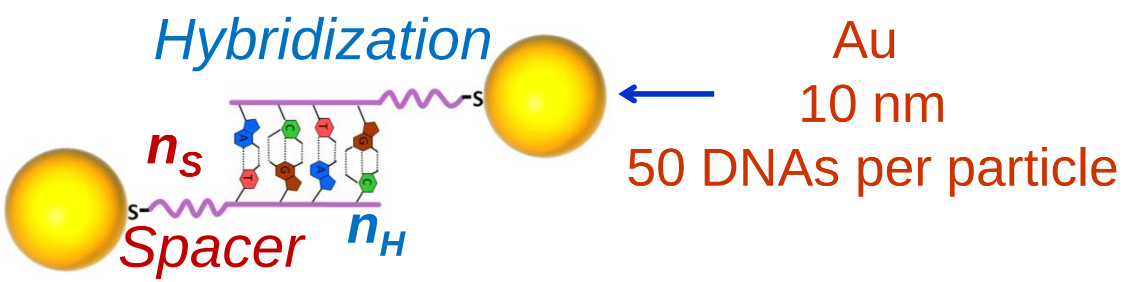


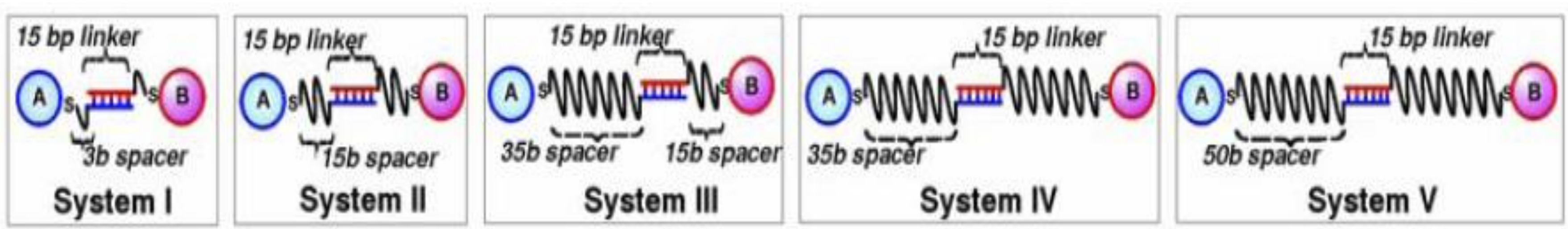
Heterogeneous lattices





DNA-guided 3D Ordering of Nanoparticles





Softness of repulsion

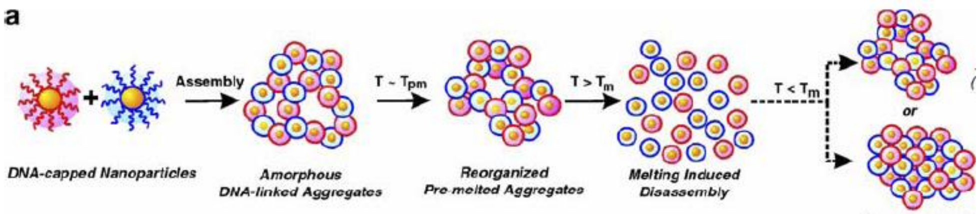
Attraction: $E_a \sim N_a$

Repulsion: $E_r \sim N^{3/5}/(N^{3/5} - cN_a)$

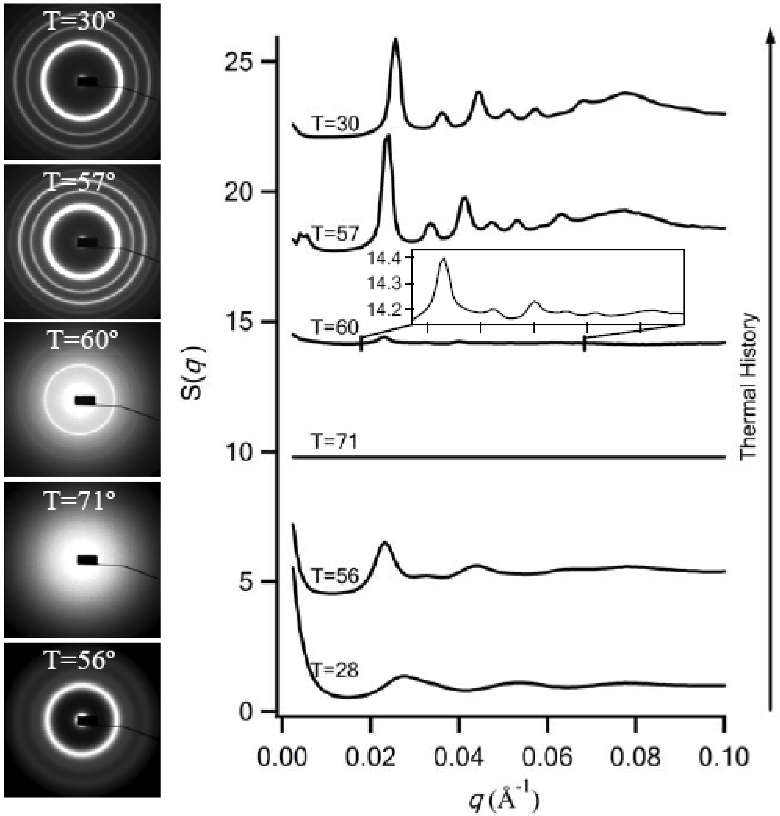
c is defined by persistence length and surface density

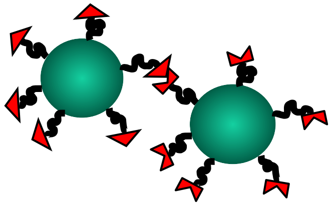
repulsion range $d_r \sim N^{3/5}$

DNA-guided 3D Ordering of Nanoparticles



- **Even for the "right" potential assembly is locked in disordered metastable state**





Ordered

Order onset

Molten

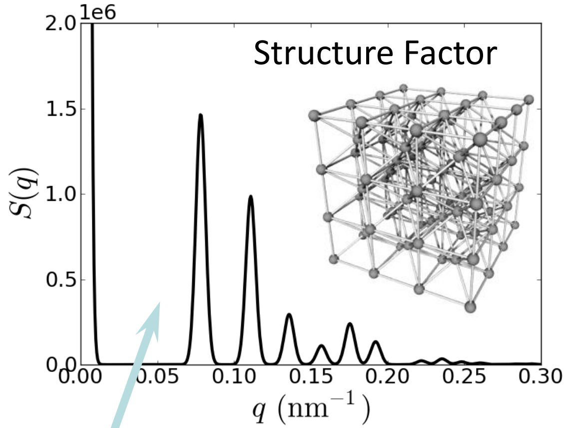
Reorganization at $T<T_m$

Disordered, as assembled

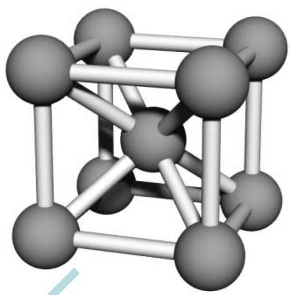
D. Nykypanchuk, M. Maye, D. Van der Lelie, and O. Gang, *Nature, 451, 549 (2008)*

Formalism of SAXS Analysis for Superlattices

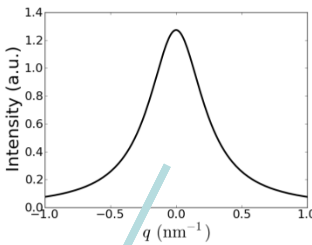
Structure Factor



Lattice Unit Cell



Peak Shape

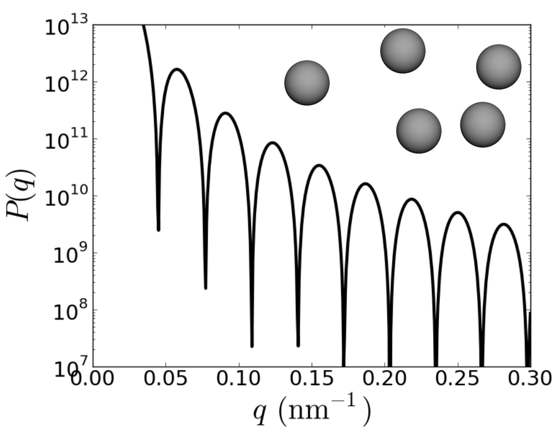


Debye-Waller (thermal disorder)

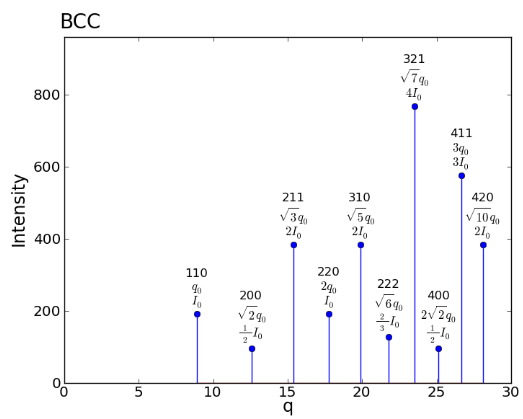
Plane Wave

$$S(q) = \frac{c}{q_{hkl}^2 P(q_{hkl})} \sum_{\{hkl\}}^{m_{hkl}} \left| \sum_{j=1}^{n_c} F_j(M \cdot \mathbf{q}_{hkl}) e^{2\pi i(x_j h + y_j k + z_j l)} \right|^2 e^{-\sigma_D^2 q_{hkl}^2 a^2} L_{hkl}(q - q_{hkl})$$

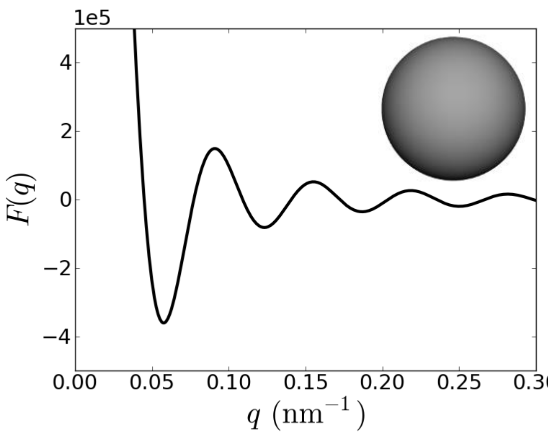
Isotropic Form Factor



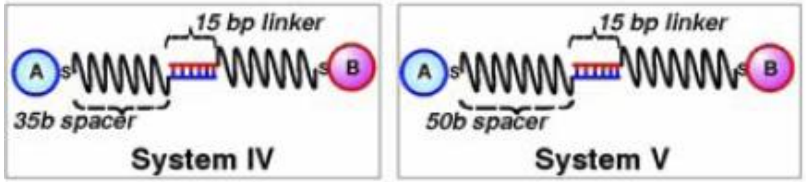
Reciprocal-space Peaks

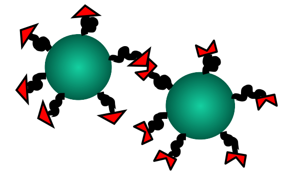


Particle Form Factor



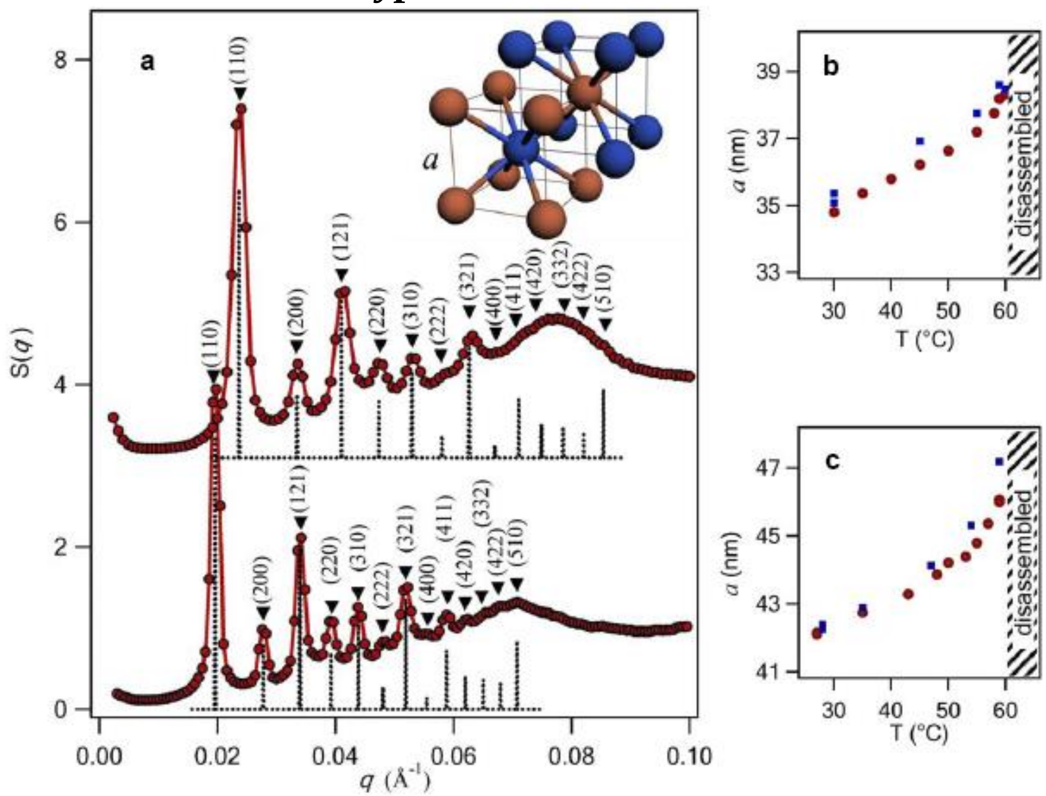
DNA-guided 3D Ordering of Nanoparticles





Direct particles hybridization

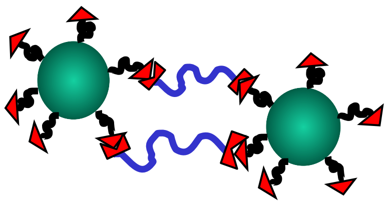
CsCl type

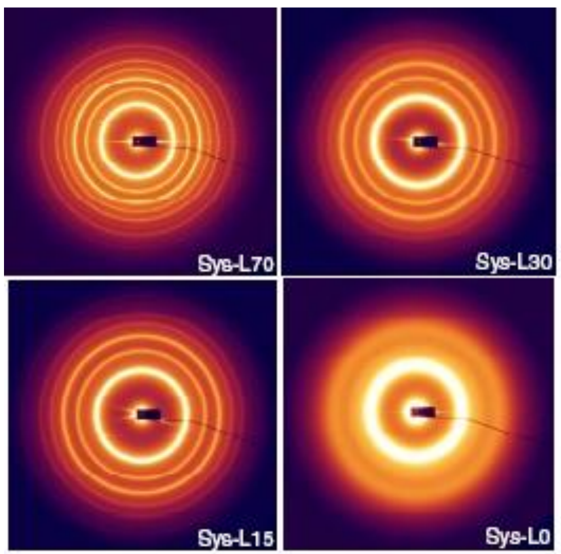


- **BCC structure, resolution limited diffraction peaks correlation lengths ~micron**
- **Remarkably open structure: Nanoparticles and DNA occupy ~3-4% and 6-8% volume respectfully**
- **Thermal extension coefficient ~3 $10^{-3}K^{-1}$, ~100 larger than conventional materials**

D. Nykypanchuk, M. Maye, D. Van der Lelie, and O. Gang, ***Nature, 451, 549 (2008)***

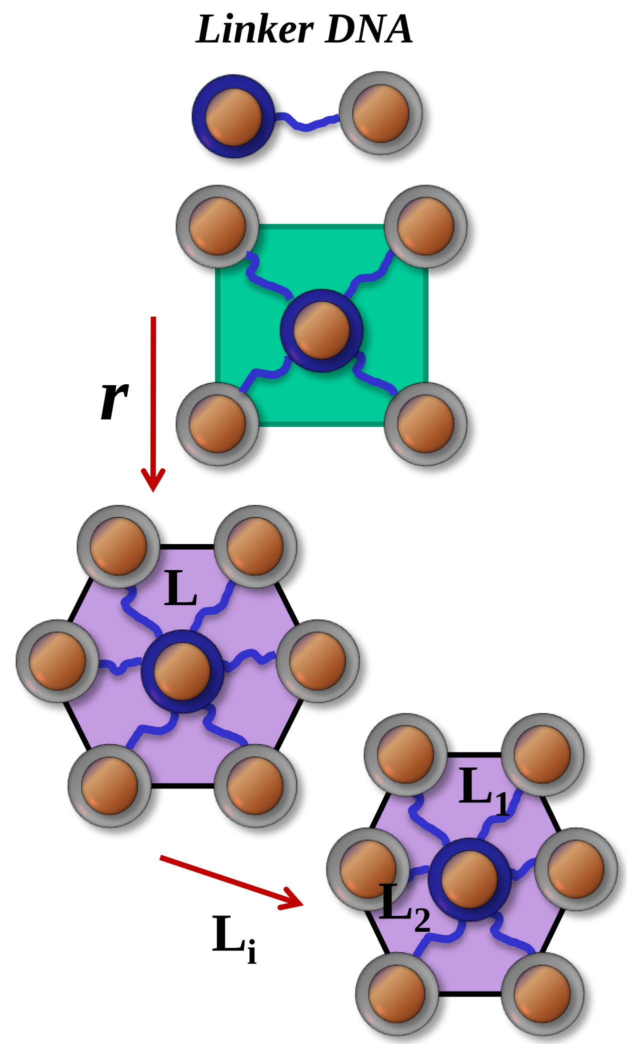
Assembly via DNA-Linkers





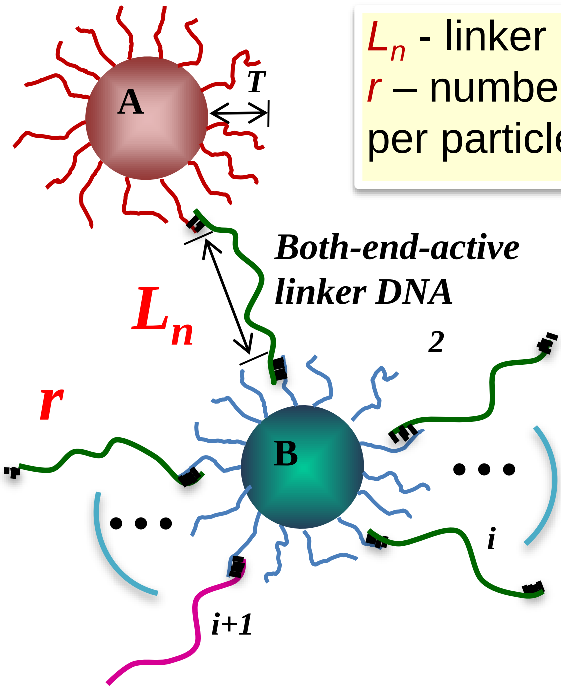
- Linker length L_n determines “softness“ of the interactions,
- Crystalline (bcc) phases are observed

- **Relative concentration *r* of DNA linkers vs. particle has a dramatic effect on phase formation.**
- **How coordination number, controlled by *r*, influence a phase formation, dependence on linker length ?**
- **Linker with more than one length: *Distance Encoded phase formation***

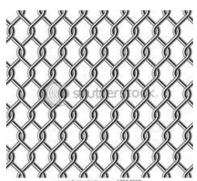


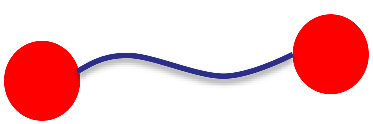
H. Xiong, D. Van der Lelie, and O. Gang, ***Jour. Amer. Chem. Soc., 130 (8), 2442 (2008)***

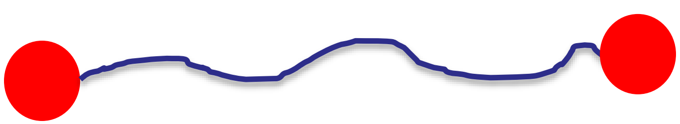
DNA Linker Mediated Assembly

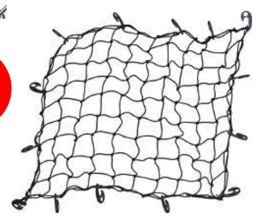


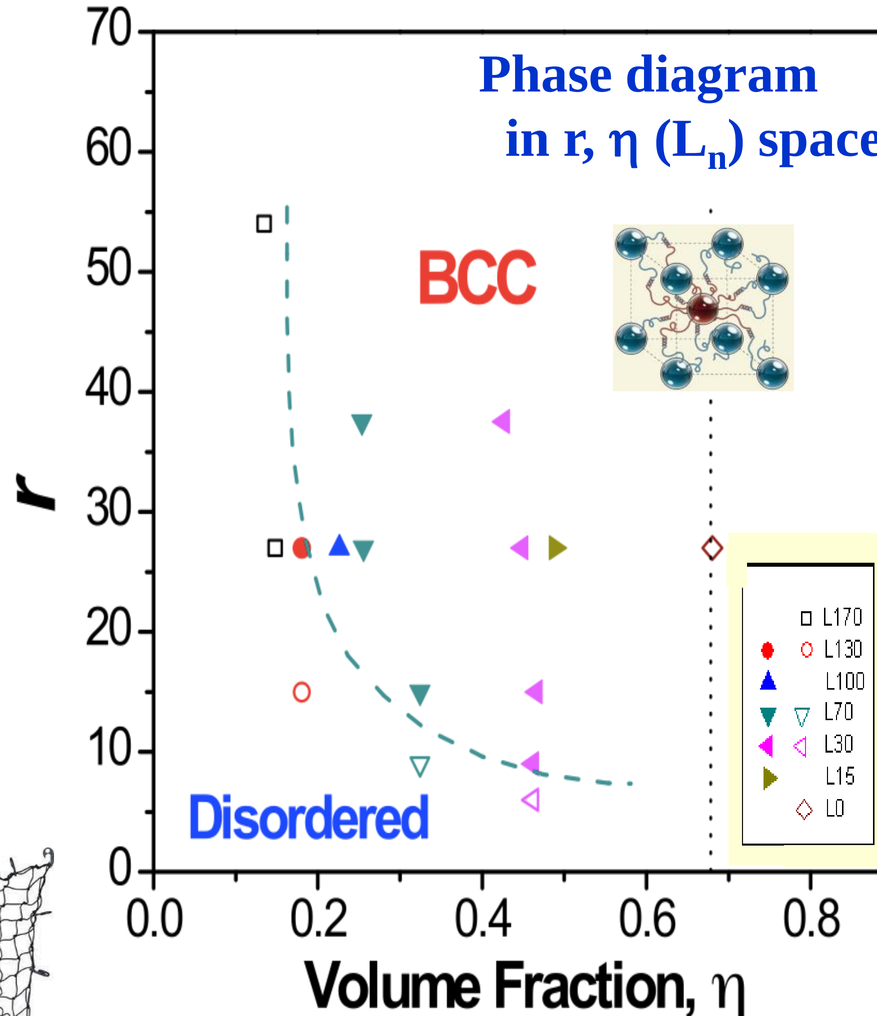
L_n - linker length
r – number of linkers per particle







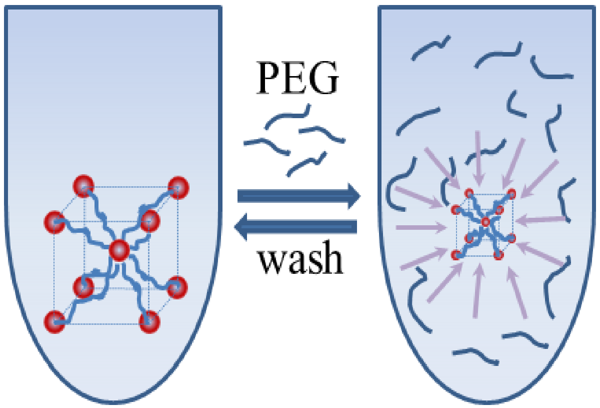


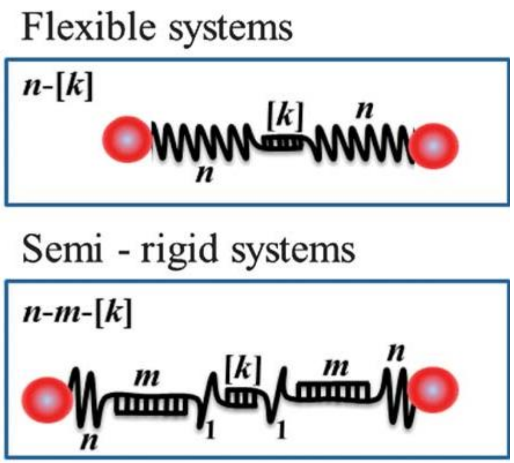


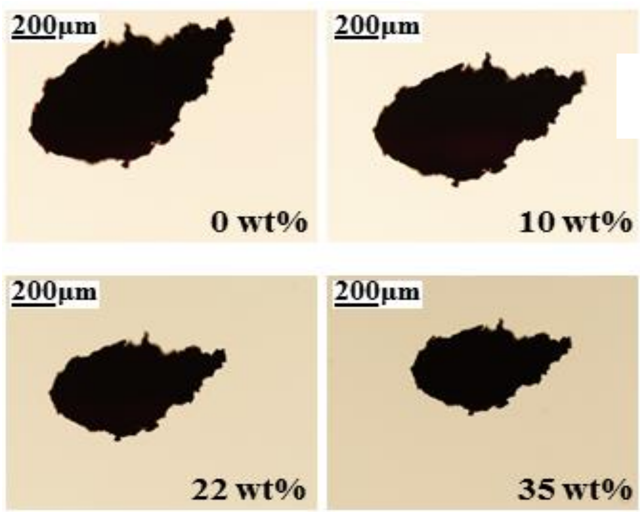
$\leftarrow$ ***L_n increase***

H. Xiong, D. Van der Lelie, and O. Gang, *Jour. Amer. Chem. Soc., 130 (8), 2442 (2008)*
H. Xiong, D.van der Lelie and O. Gang, Phys. Rev. Lett., 102 *(2009)*

Super-Compressible Nanoparticle Lattices

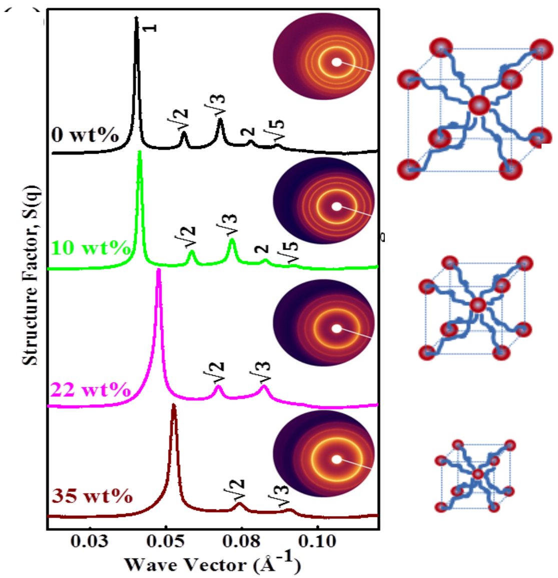


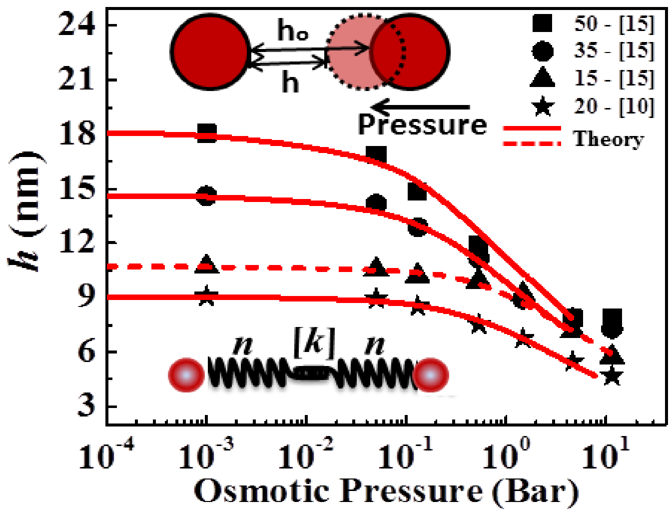


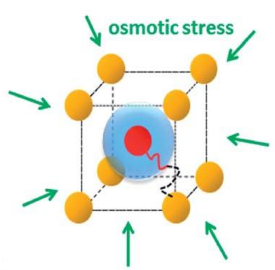


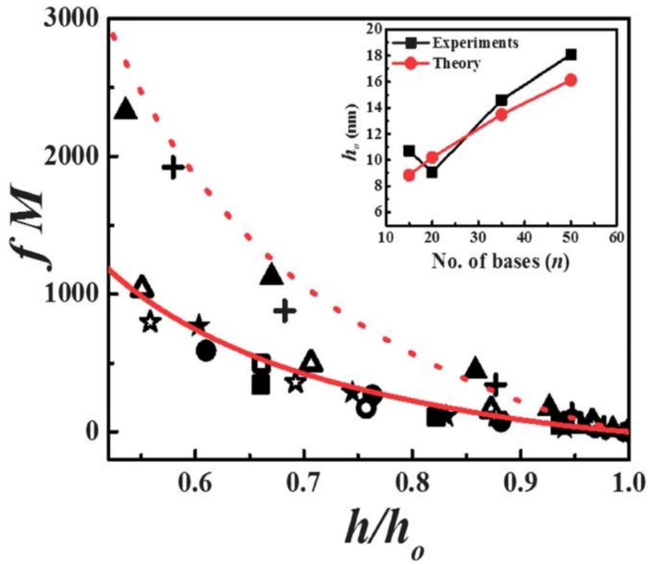
S. Srivastava et al, Soft Matter (2013)

Super-Compressible Nanoparticle Lattices







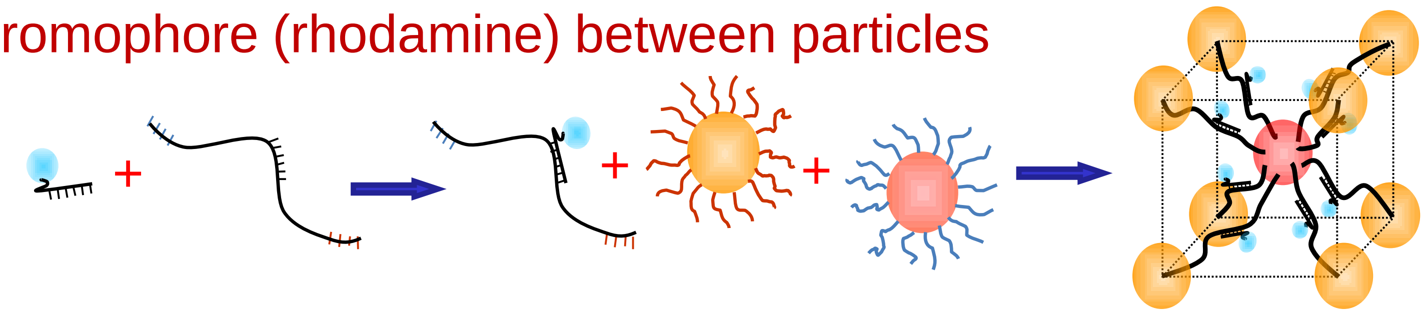


- **Lattice volume up to ~ 6-8 X at 20 bar, crystalline structure is preserved**
- **Macroscopic size changes are determined by DNA linkers**

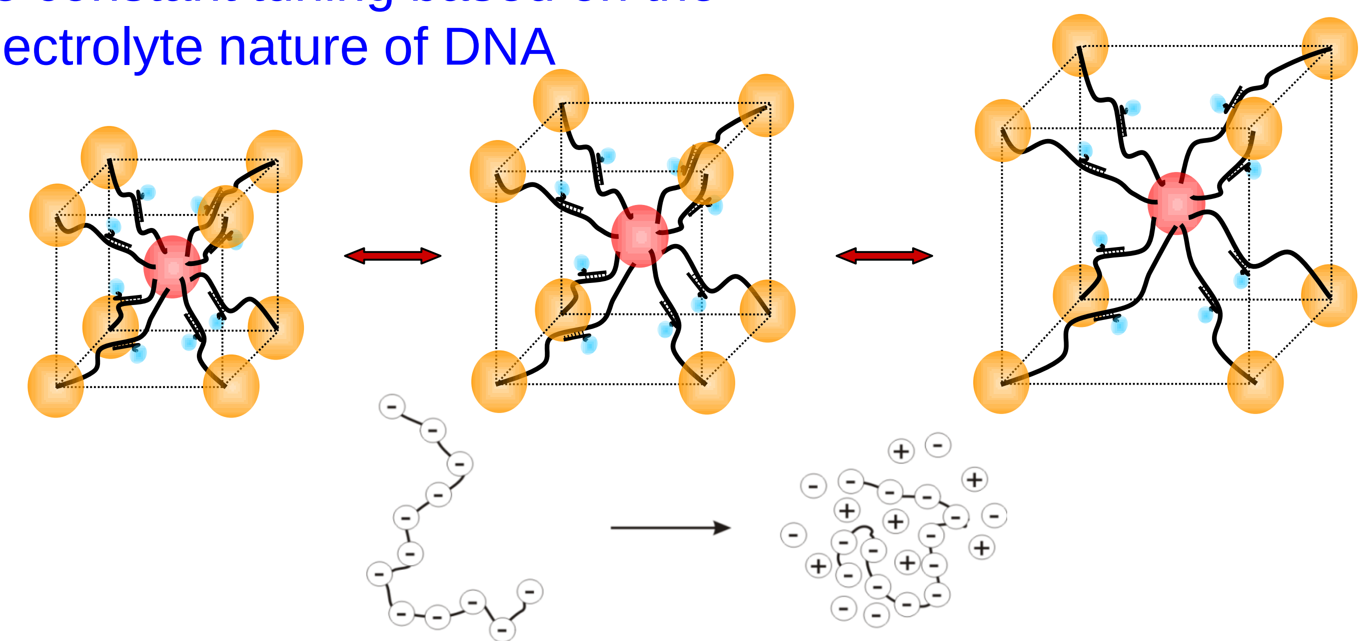
S. Srivastava et al, Soft Matter (2013)

Tunable Superlattice with Optical Activity

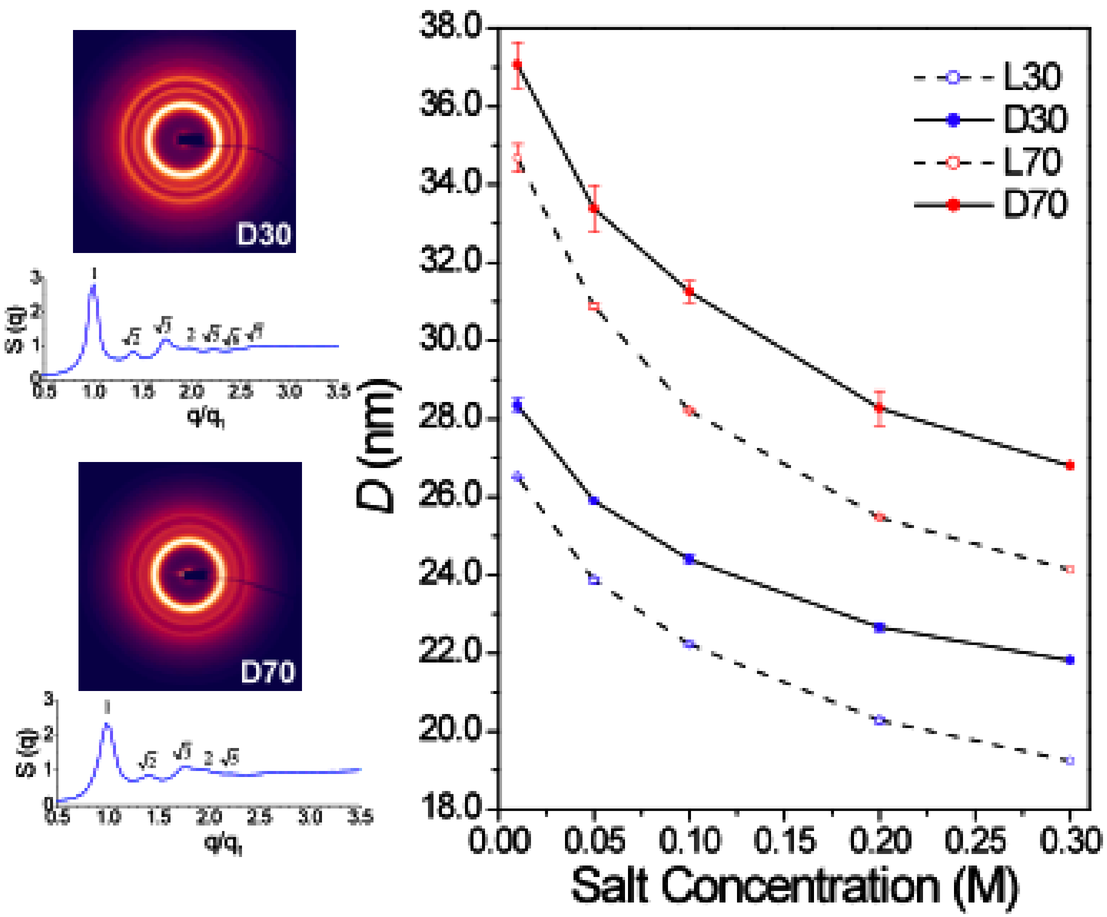
Assembly: DNA site-selectivity for positioning of chromophore (rhodamine) between particles

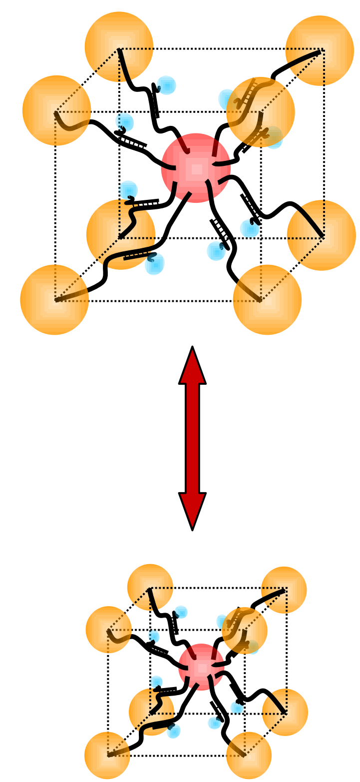


Lattice constant tuning based on the polyelectrolyte nature of DNA



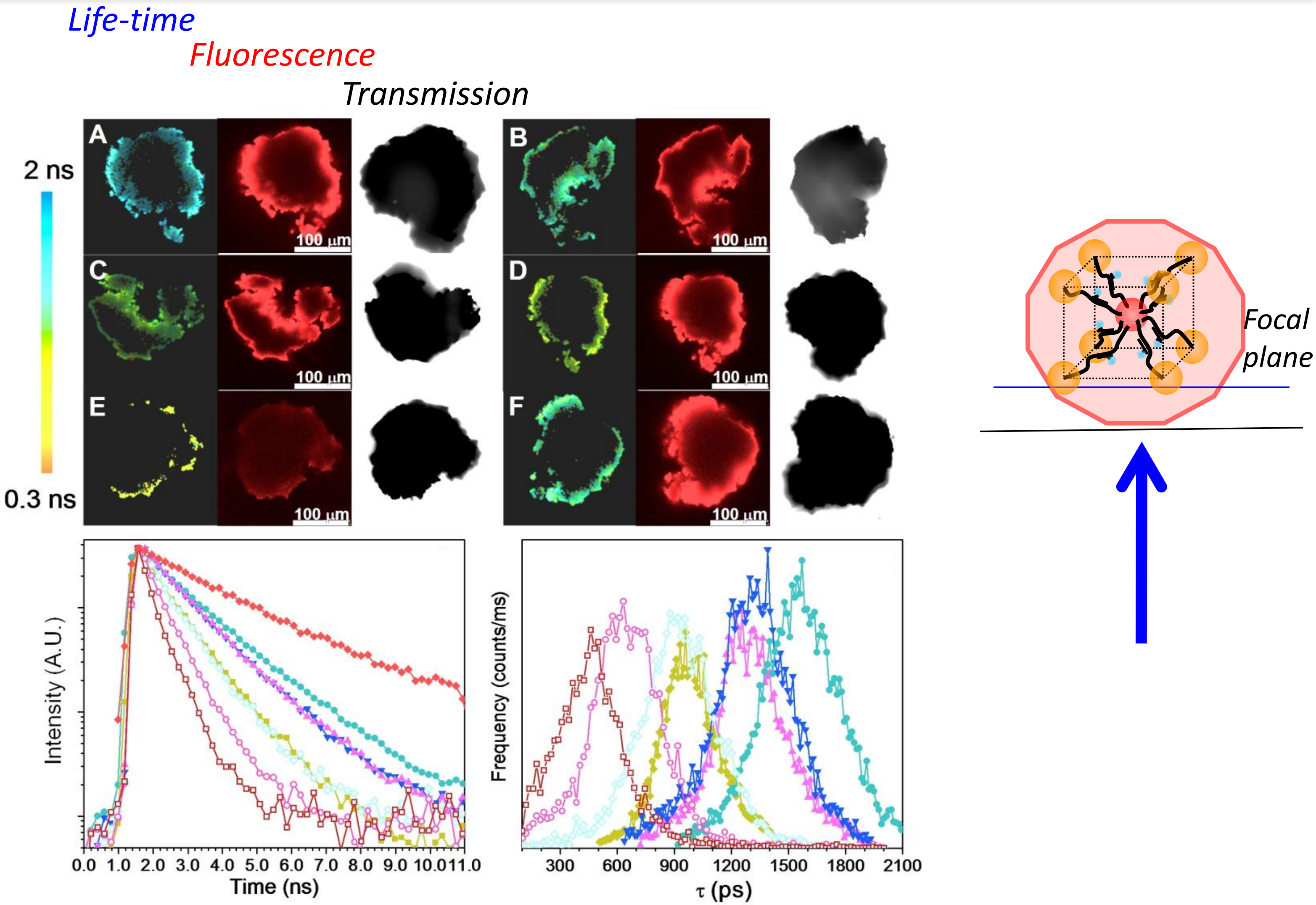
Structure of Particle-Chromophore Superlattices Assembled with DNA





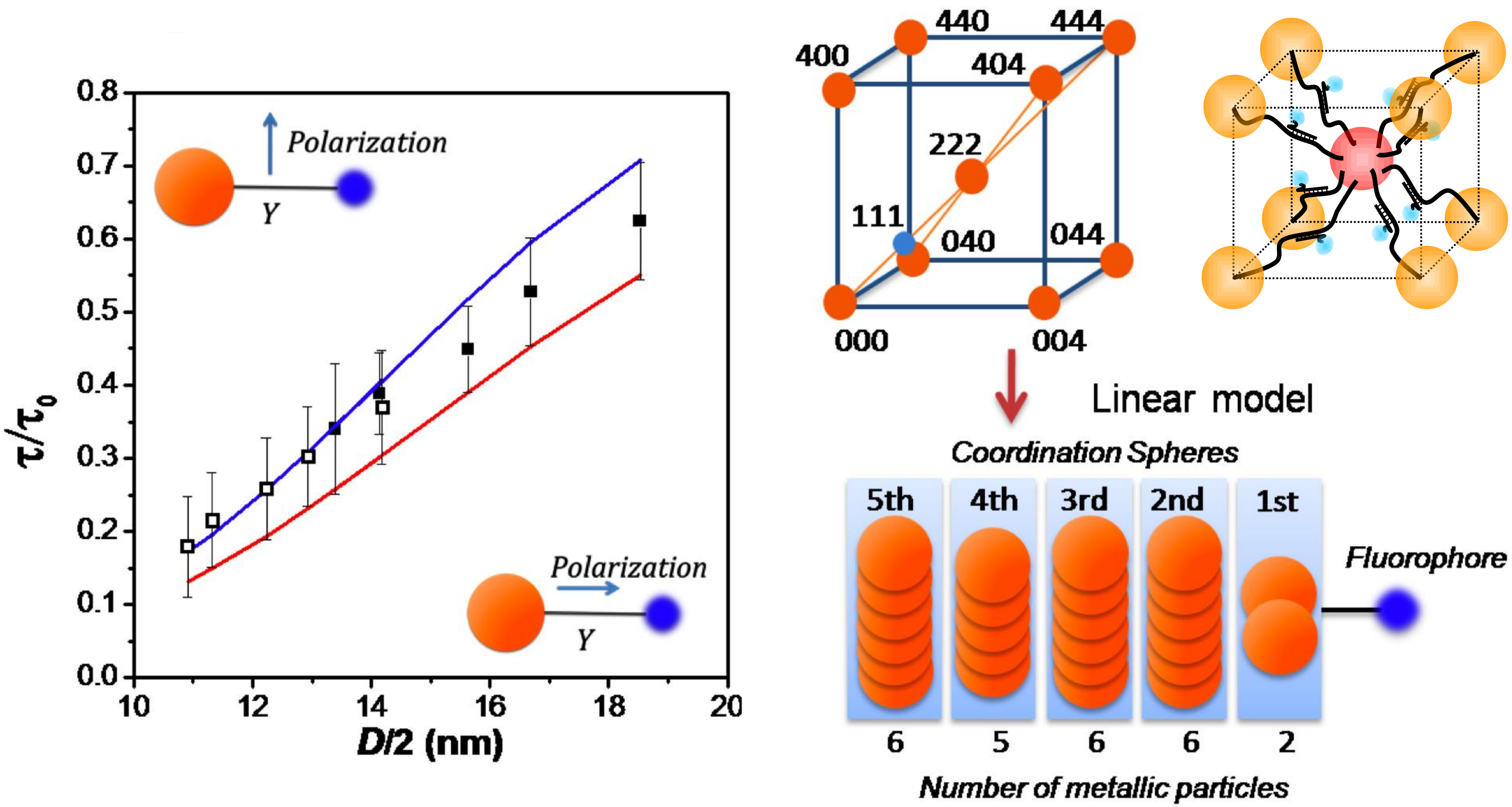
H. Xiong, M. Sfeir, O. Gang, Nano Letters, 10, 3933 (2010)

Optical Response of Particle-Chromophore Superlattices Assembled with DNA



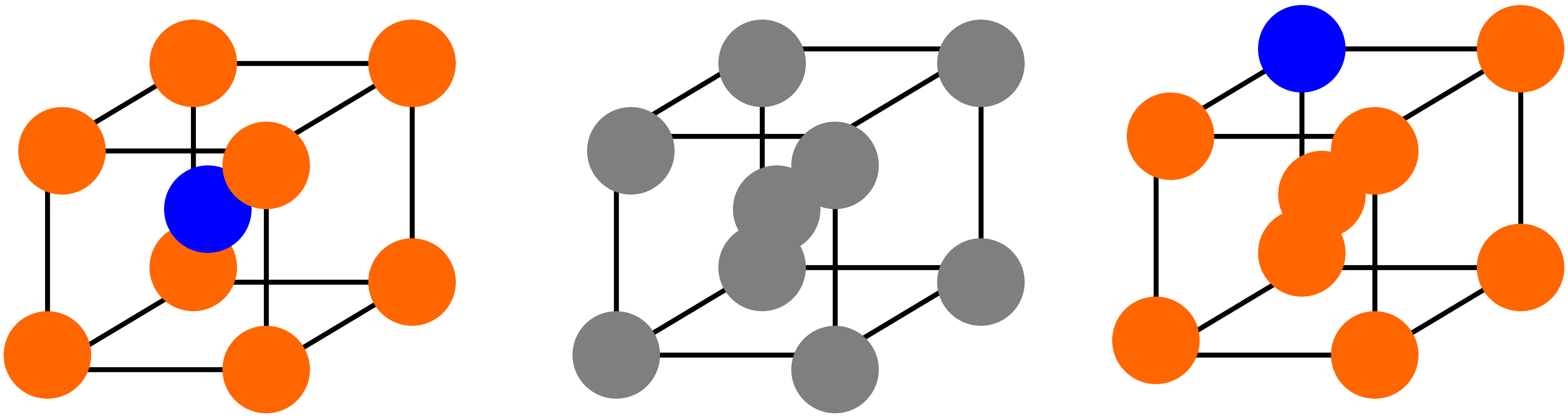
Average Life-time and image histogram at different salt concentrations

Fluorescent lifetimes for tunable superlattices



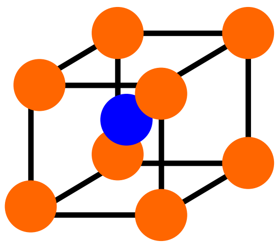
H. Xiong, M. Sfeir, O. Gang, Nano Letters, 10, 3933 (2010)

Multicomponent systems: Compositional Disorder?

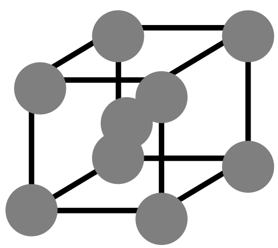


Compositional Order in Binary Systems

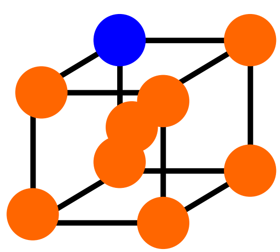
CsCl structure

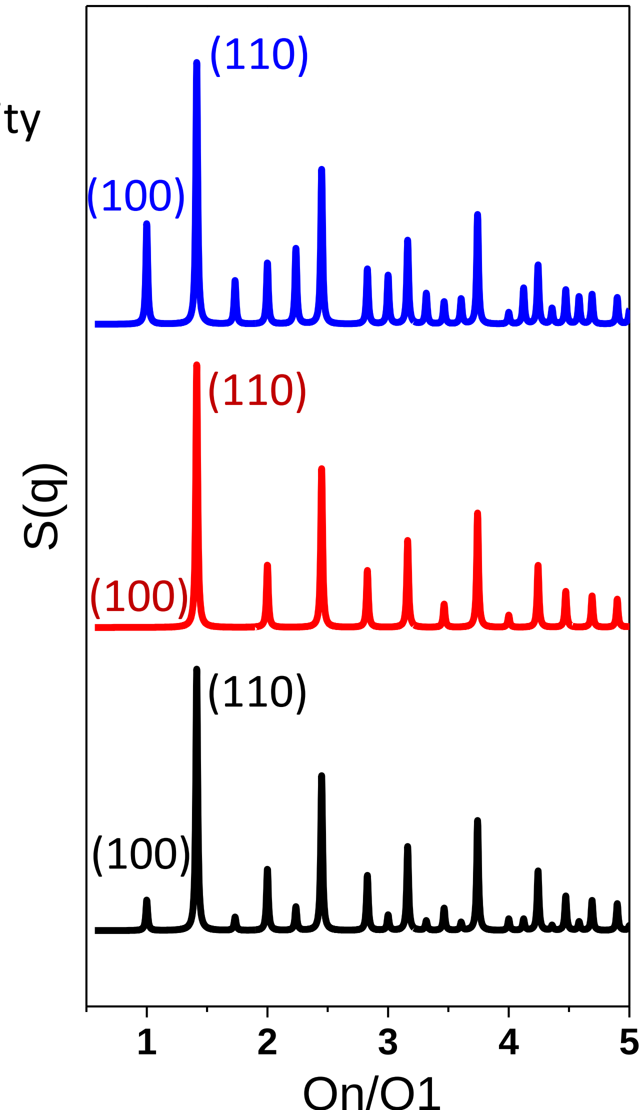


Different electron density



Positional Order -> Correlation length ξ

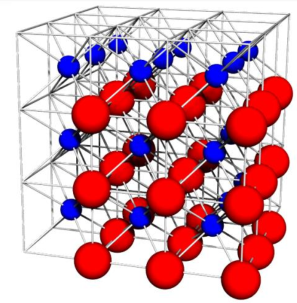


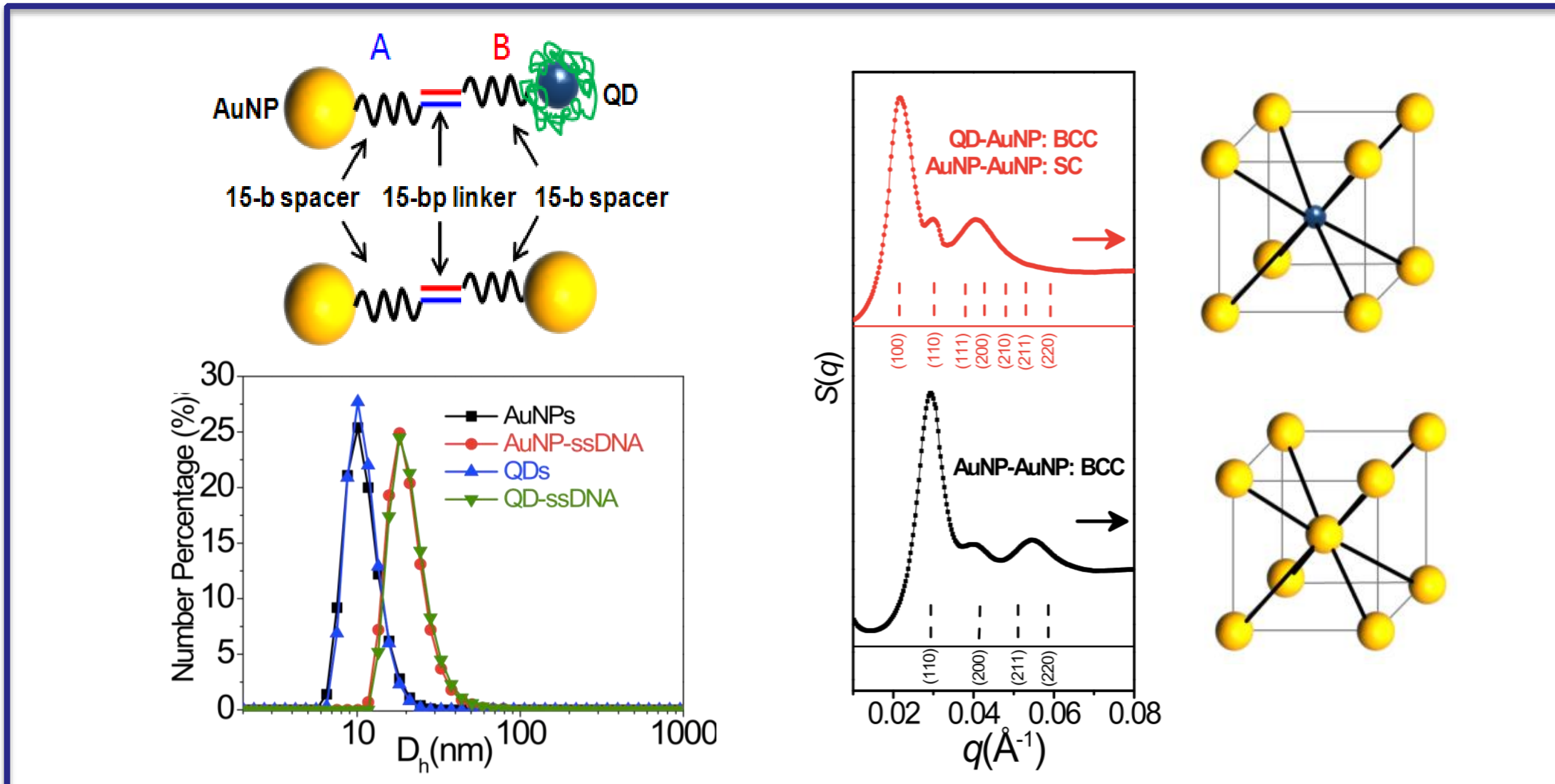


Compositional Order ?

Binary Superlattices from CdSe and Au particles

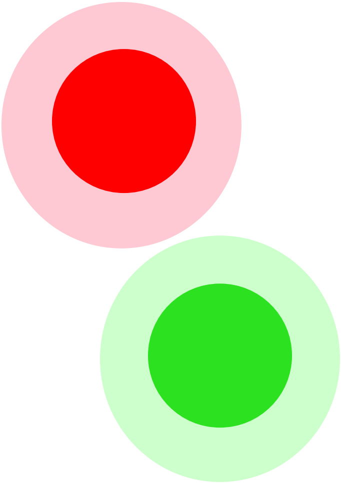
- **Assembly of gold-semiconductor (CdSe, quantum dot, QD) lattice**



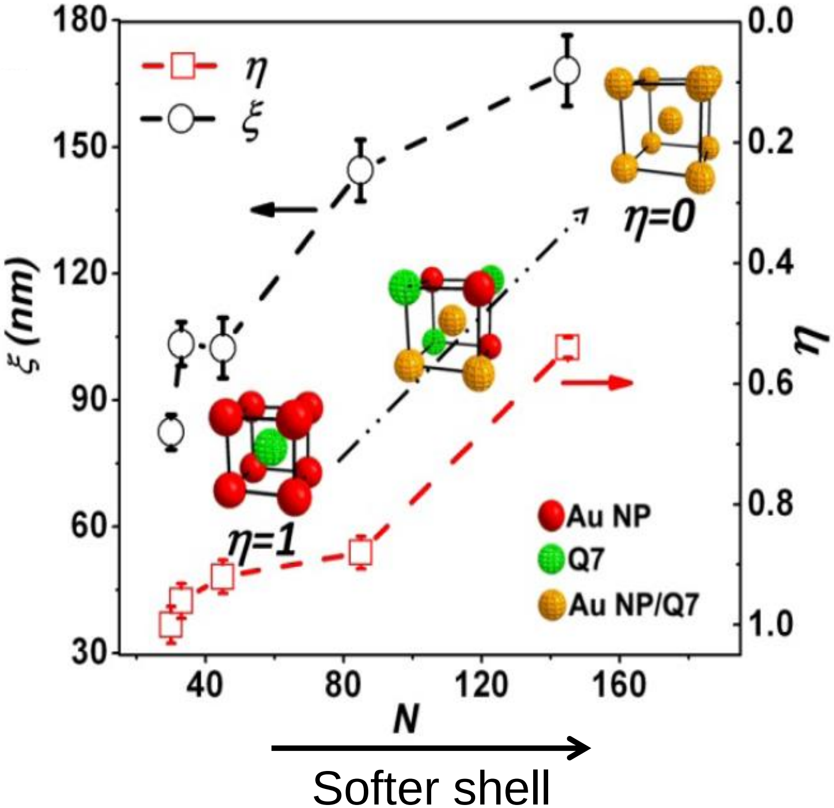


D. Sun and O. Gang, JACS (2011), *33* (14), 5252

Soft Shells and Compositional Disorder



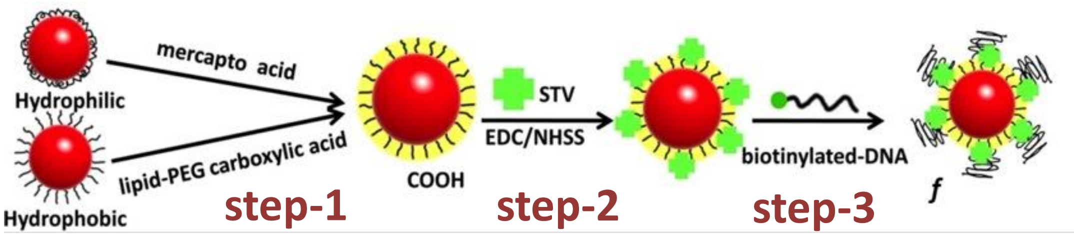
Binary QD and Au



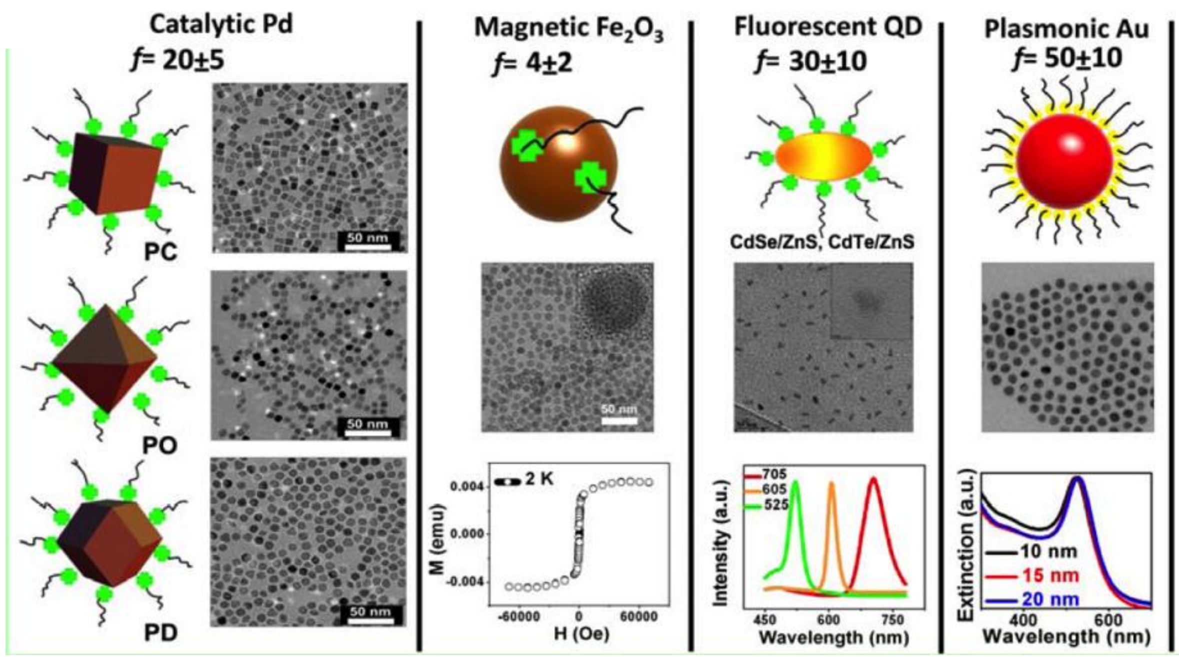
$\eta = (r_A - F_A)(1 - F_A)$

Compositional disorder increases with the shell softness

Nanoparticle Functionalization with DNA



- ❑ carboxylic group grafting
- ❑ streptavidin (STV) conjugation
- ❑ biotin-DNA attachment

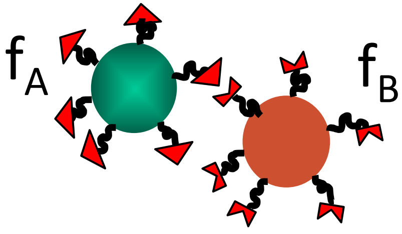


Material	Catalytic Pd	Magnetic Fe_2O_3	Fluorescent QD	Plasmonic Au
Surfactant	PVP	Oleic acid	TOPO	Citrate
Surface property	hydrophilic	hydrophobic	hydrophobic	hydrophilic

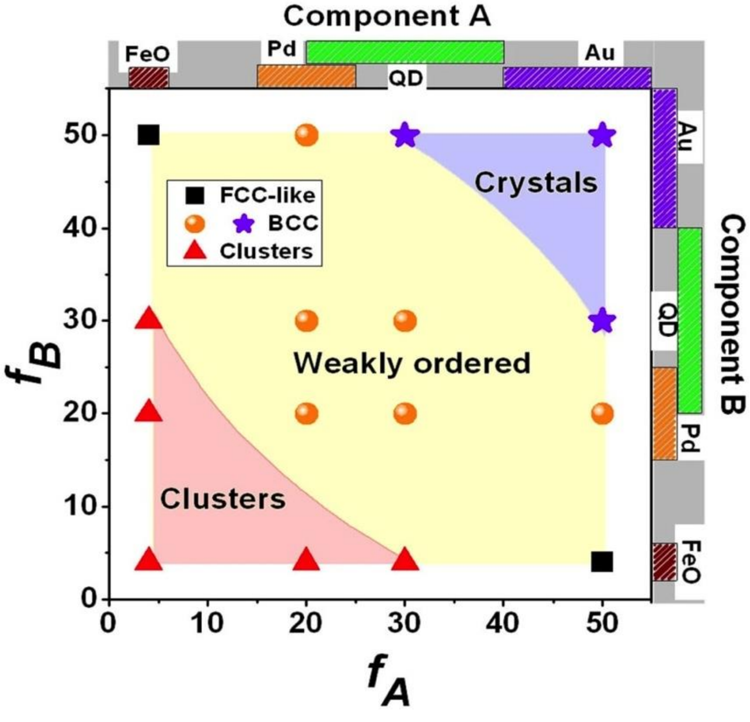
Y. Zhang et al., Nature Nanotechnology, 2013, 8, 865

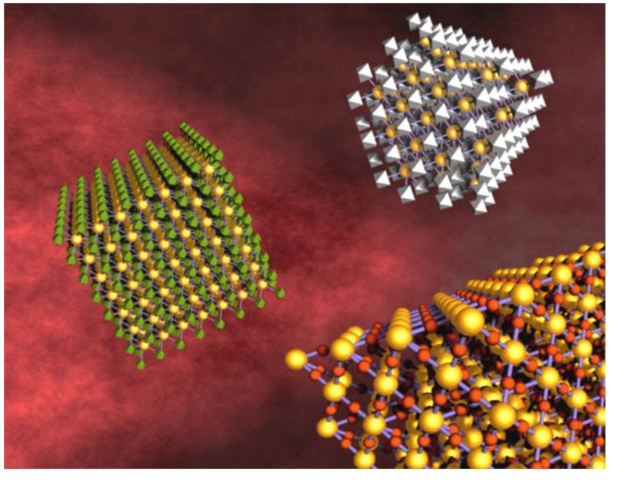
Heterogeneous 3D Lattices: Structural and Functional Diversity

Binary 3D systems with regulated inter-particle distances, 10 to sub-100 nm



Mix-and-Match of catalytic, magnetic, and optically active nanoparticles



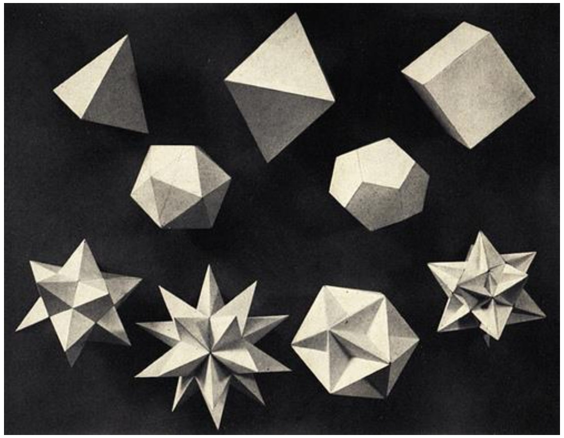


Y. Zhang et al., Nature Nanotechnology, 8 (11), p865 (2013)

Anisotropic shapes and interactions

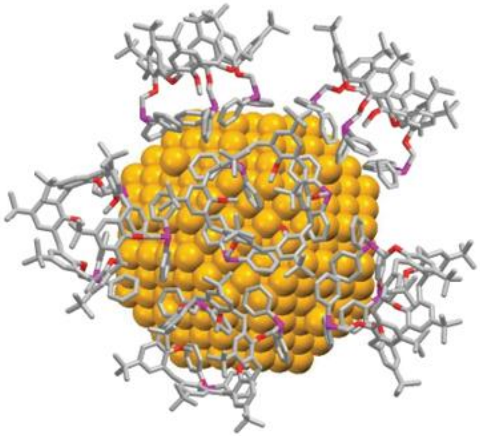
Packing of Solid Objects

Requirements for maximum packing fraction/entropy



Nanoscale shapes are different!

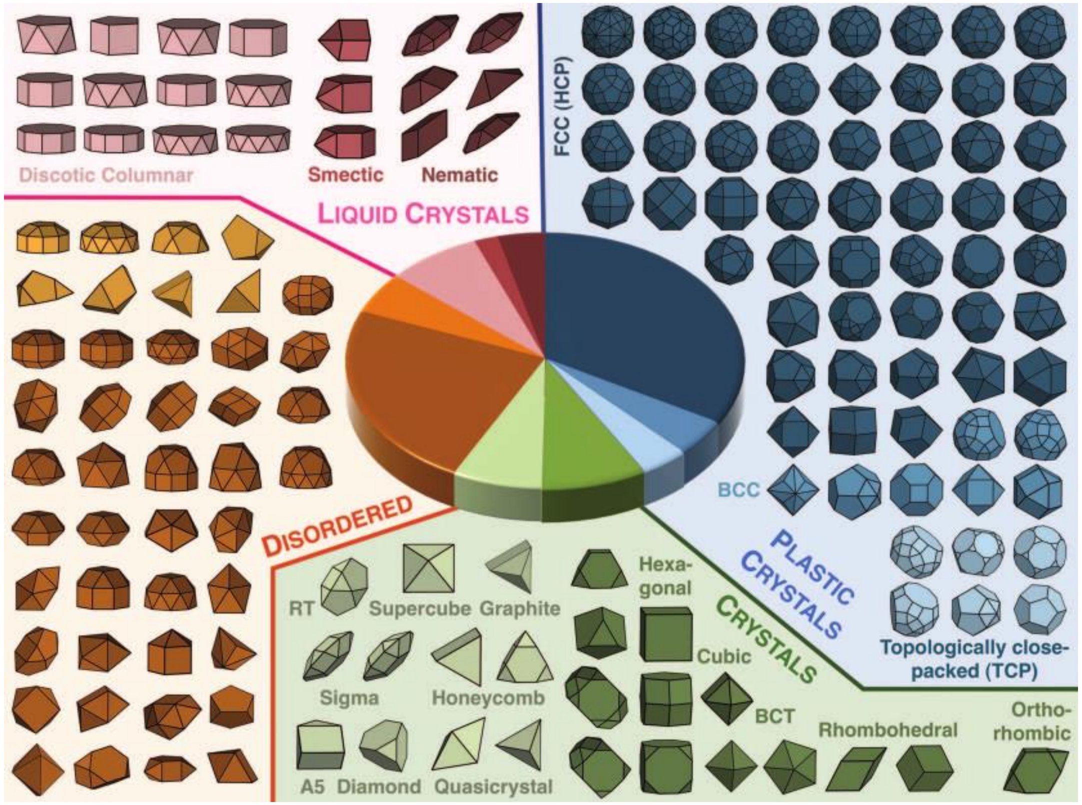
Interplay of particle shape and chains:
- directionality of interactions
- shell softness
- cooperative chain effects



Anisotropic shapes and interactions

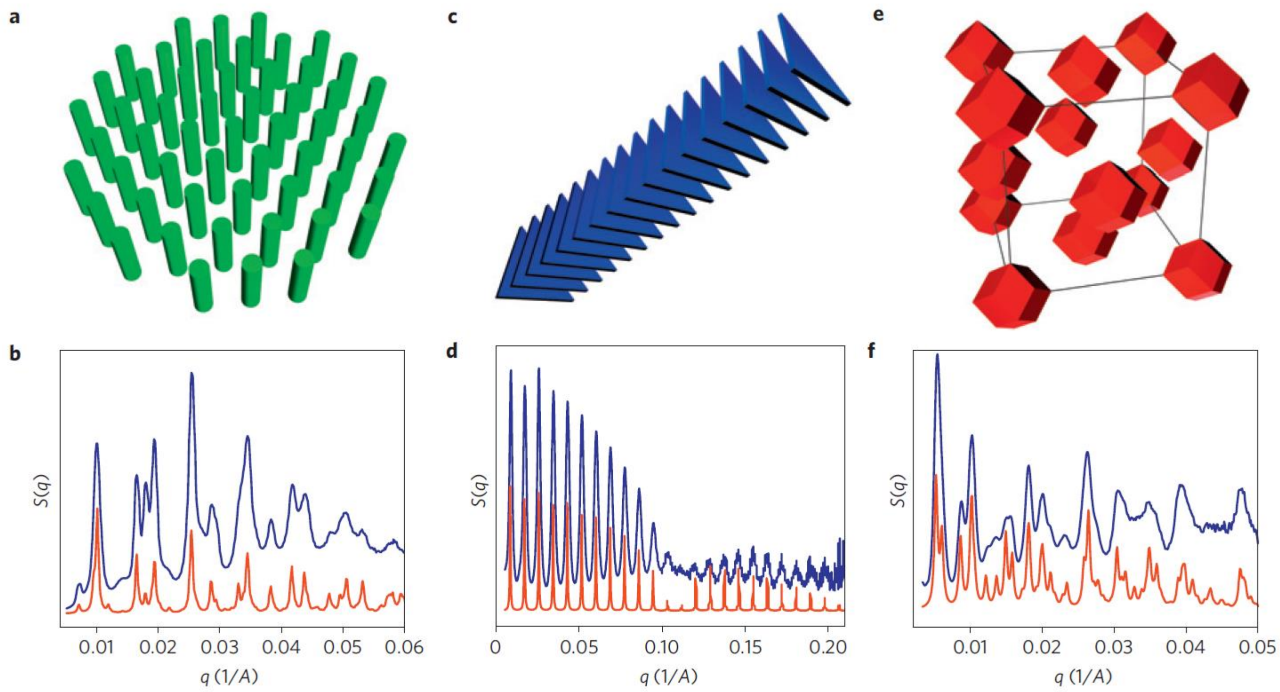
Packing of Solid Objects

Requirements for maximum packing fraction/entropy



Damasceno, Engel, Glotzer, Science, 337, 453 (2012)

Phases of nanoparticles (A-A systems) with rigid DNA shells resemble packing of solid shapes



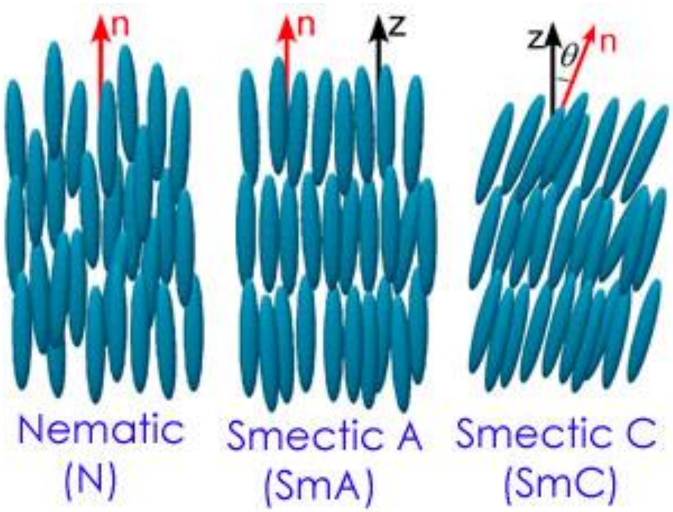
Rods- 2D hexagonal

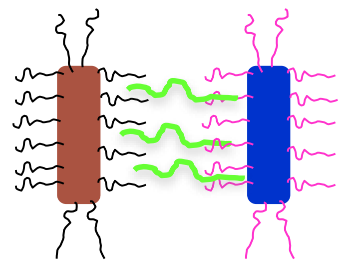
Prizms- Linear face to face

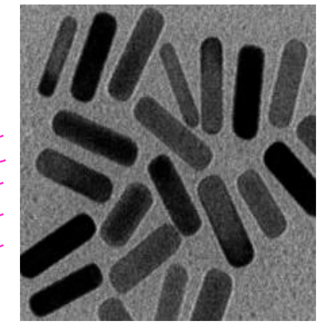
Rhombic dodedahedra- FCC

Mirkin’s group, Nature Materials,9,913, 2010

Assembly of Rods, A-B Systems





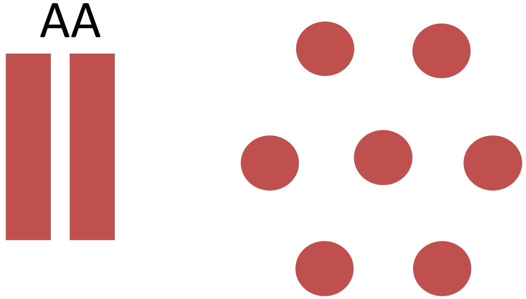


~ 10 nm X 40 nm

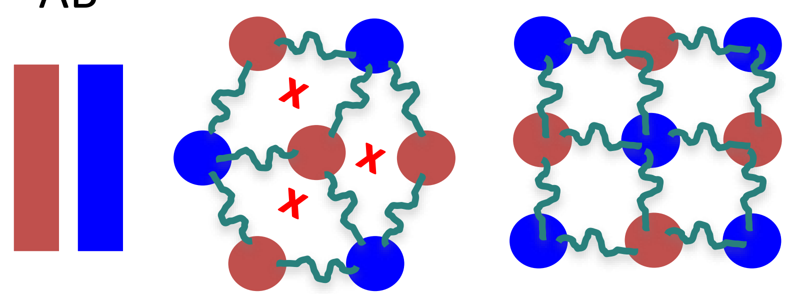
?

Hexagonal Phase

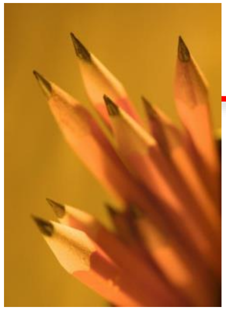
AA



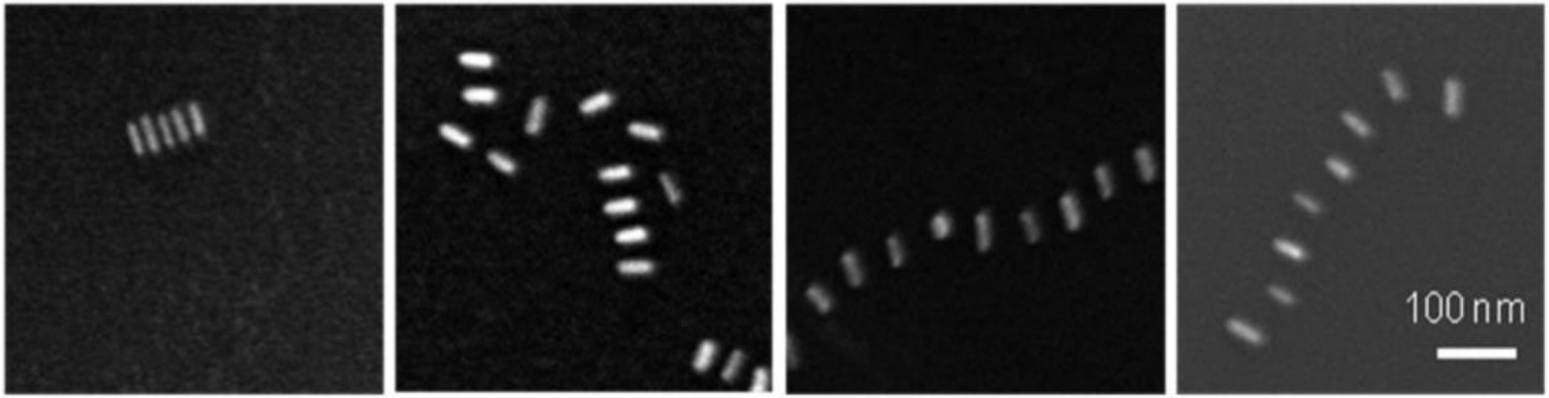
AB



Assembly of Rods

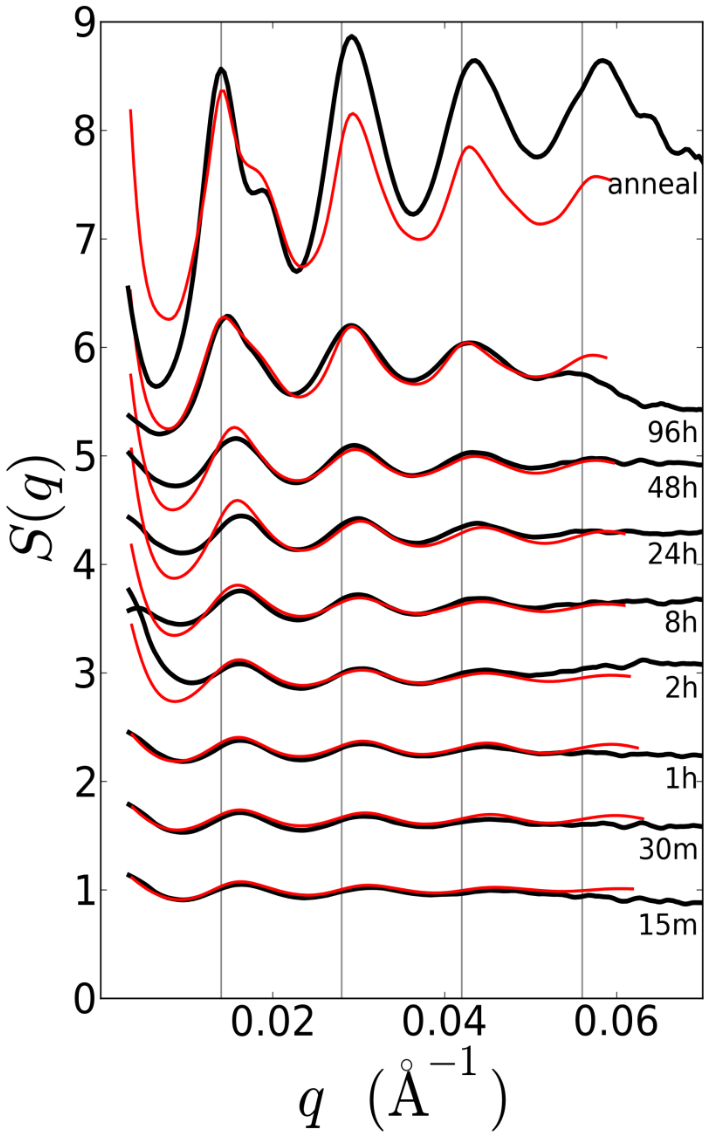


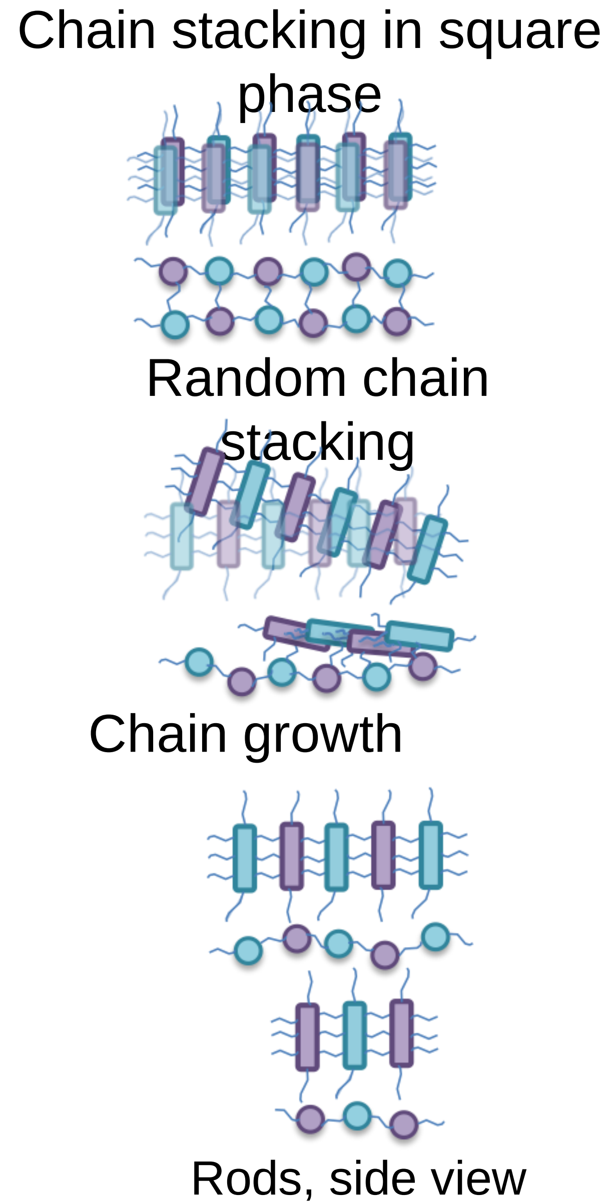
1D ribbons of parallel rods for different lengths of DNA linkers



S. Vial et al., ACS Nano, 7, 5437, 2013

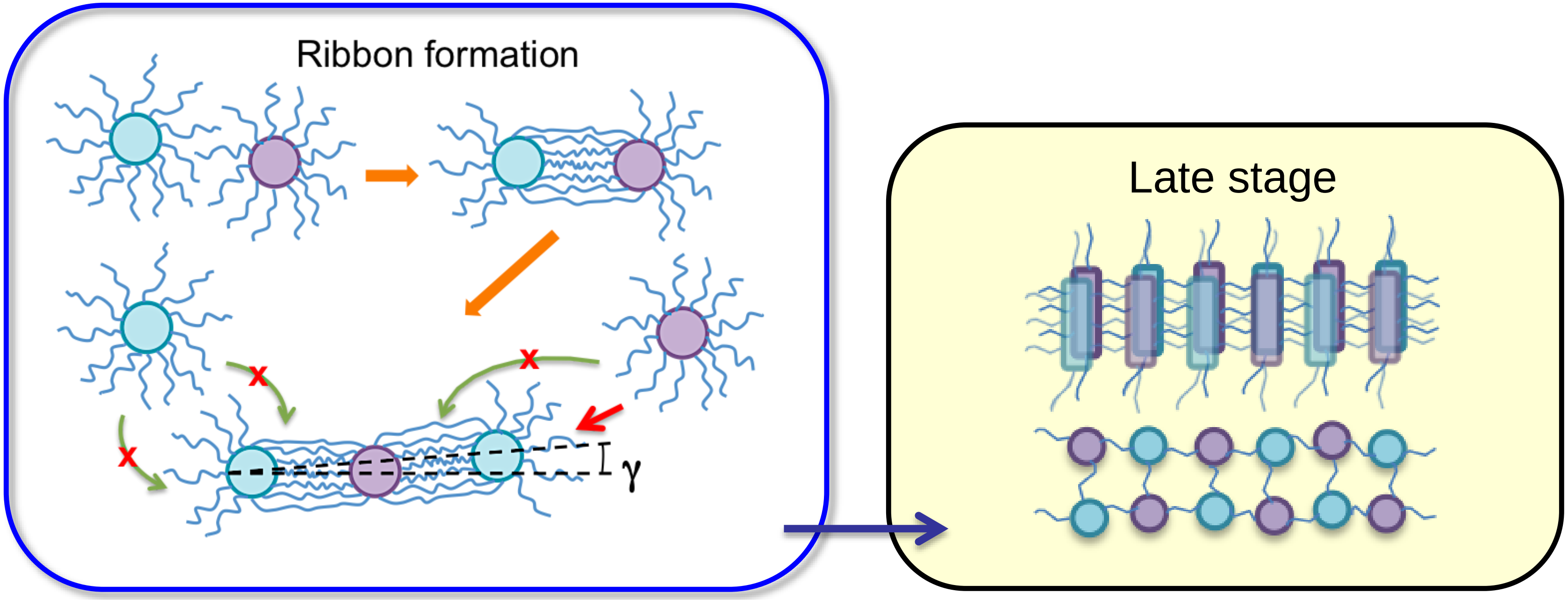
Kinetics of Rods Assembly





S. Vial et al., ACS Nano, 7, 5437, 2013

Assembly of Rods

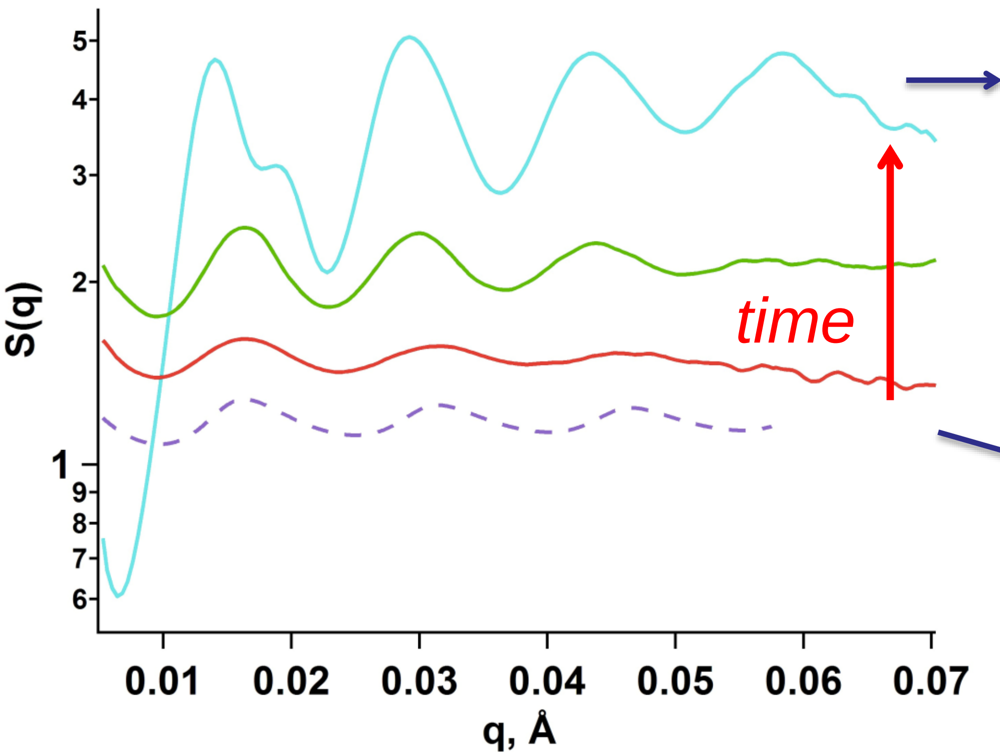


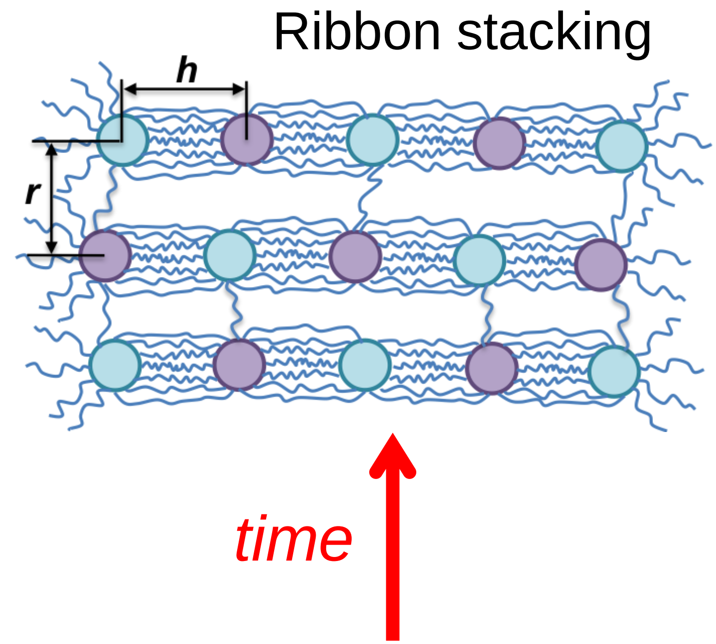
Side view of rods

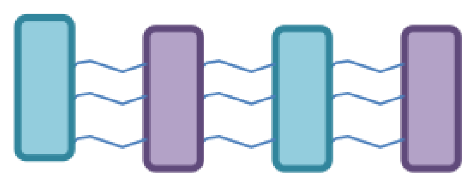
- Spontaneous symmetry break during assembly: flexibility of the chains and their collective effect
- Hierarchical assembly: time separated regimes for intra- and inter-ribbon assembly and the reversibility of DNA binding

Assembly of Rods, A-B systems

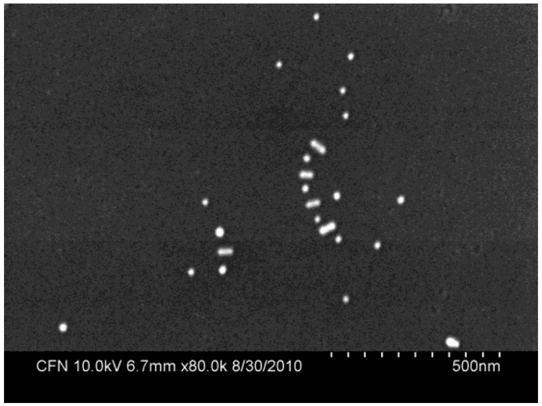
Kinetics of rods assembly (SAXS)

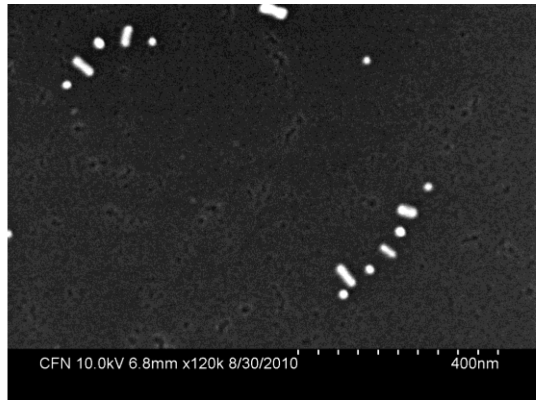




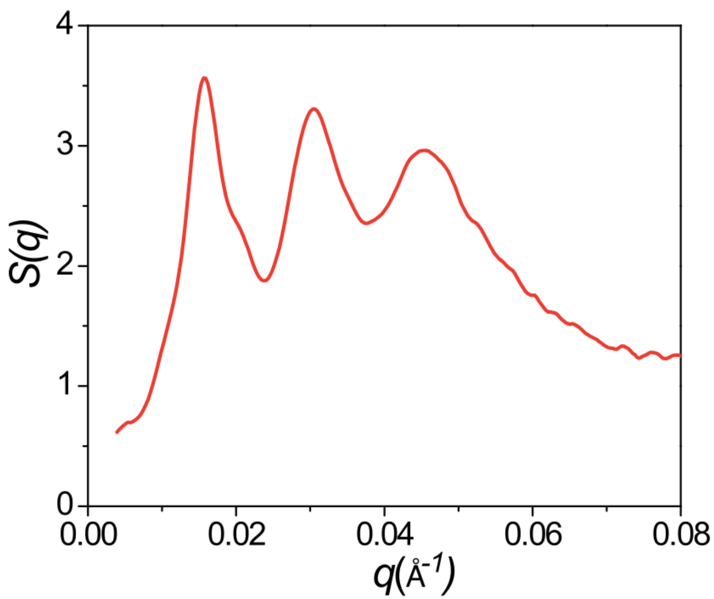


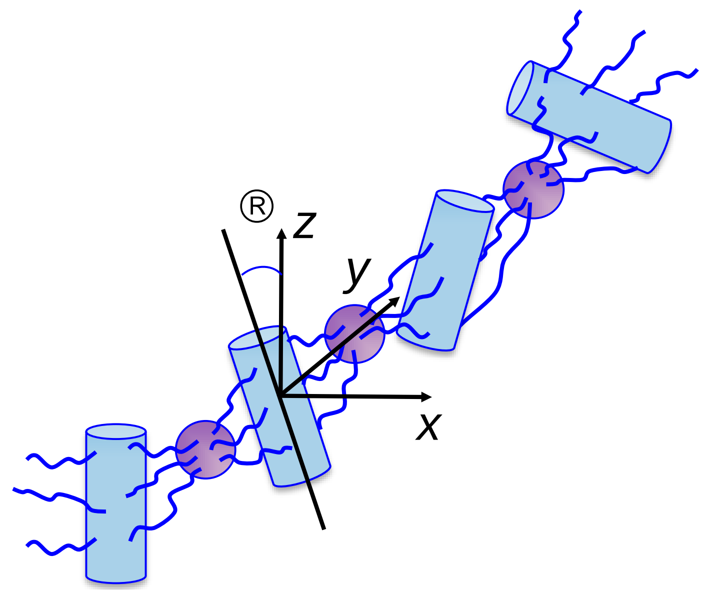
Assembly of Rods and Spheres



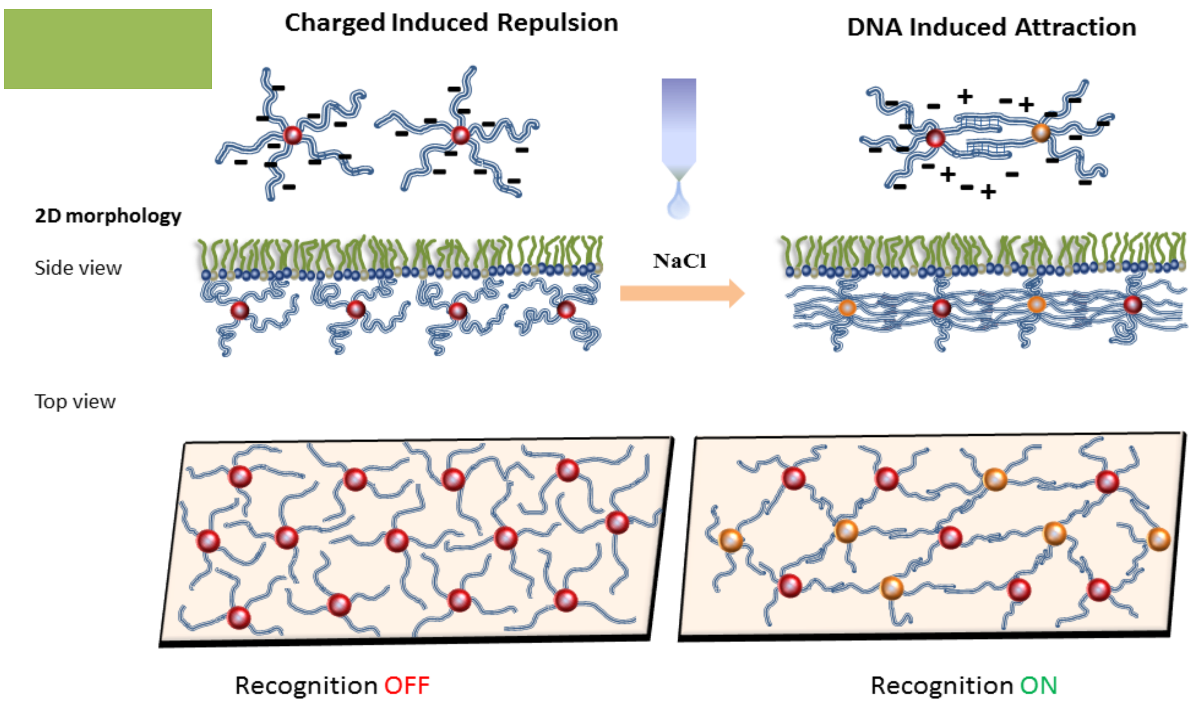


- Assembly of rods and spheres result in 1D alternating structures
- SAXS indicate distances are similar to rod-rod systems, however, no orientational correlation between rods (®is random)

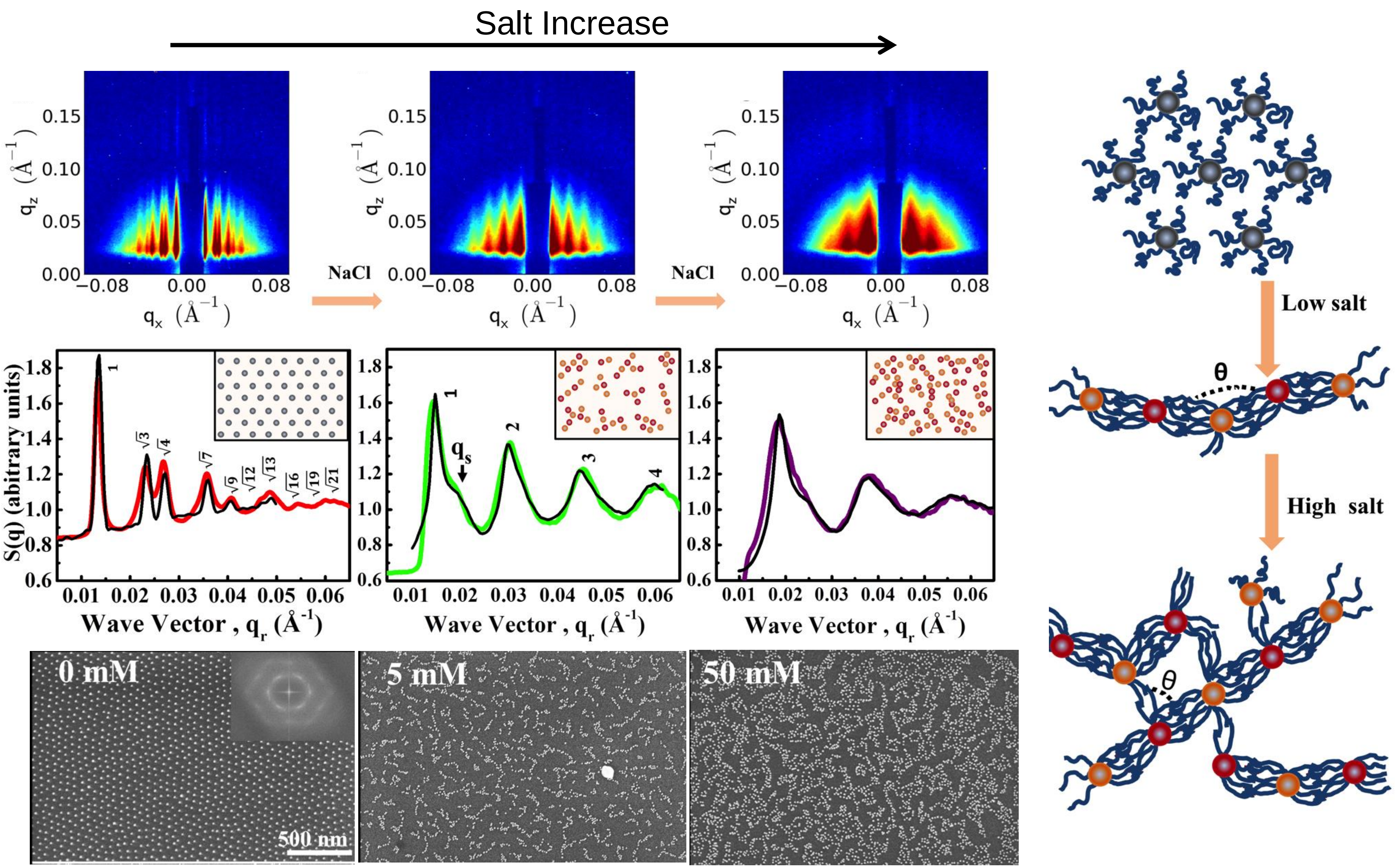




Assembly in 2D

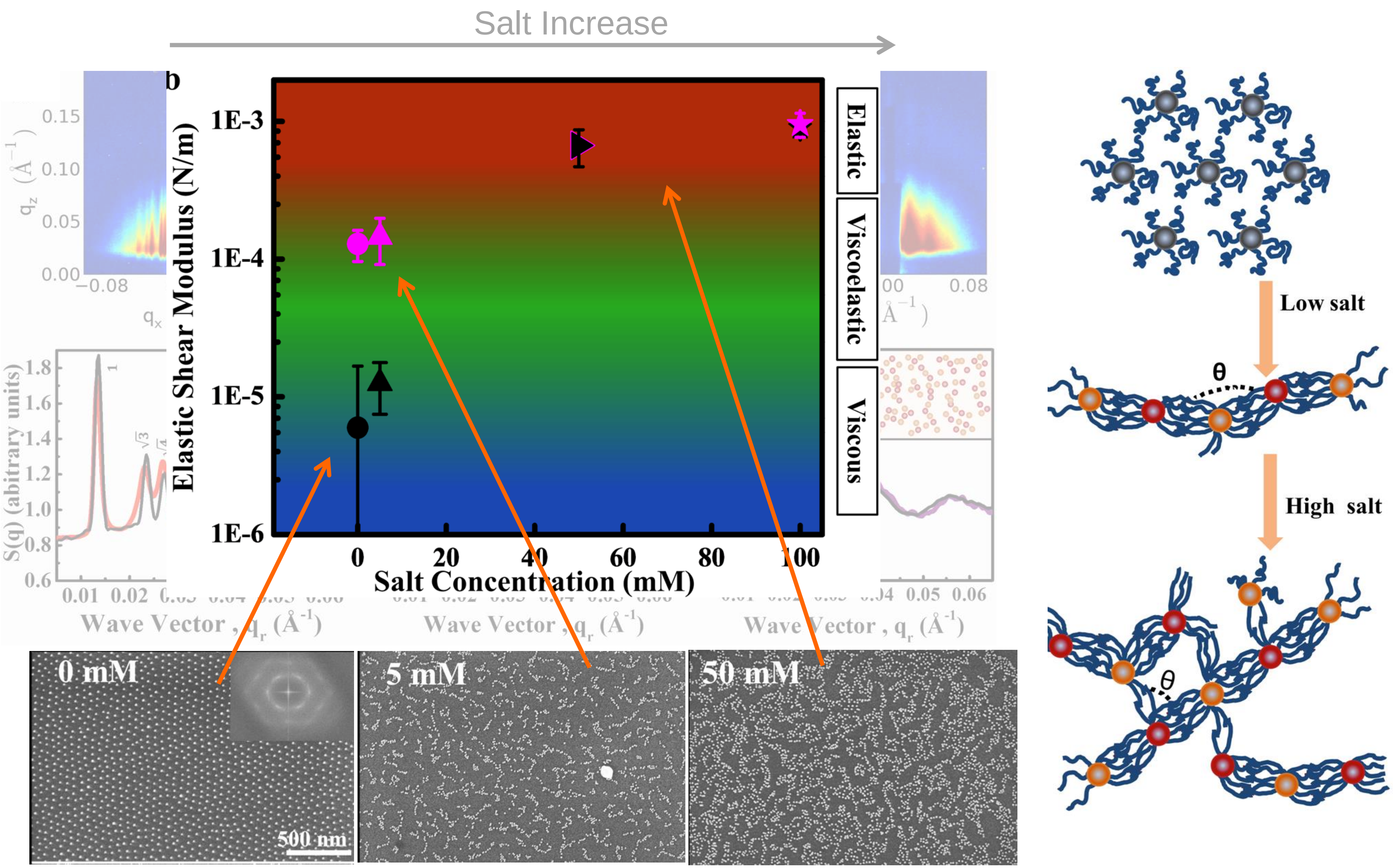


Programmable Assembly in 2D



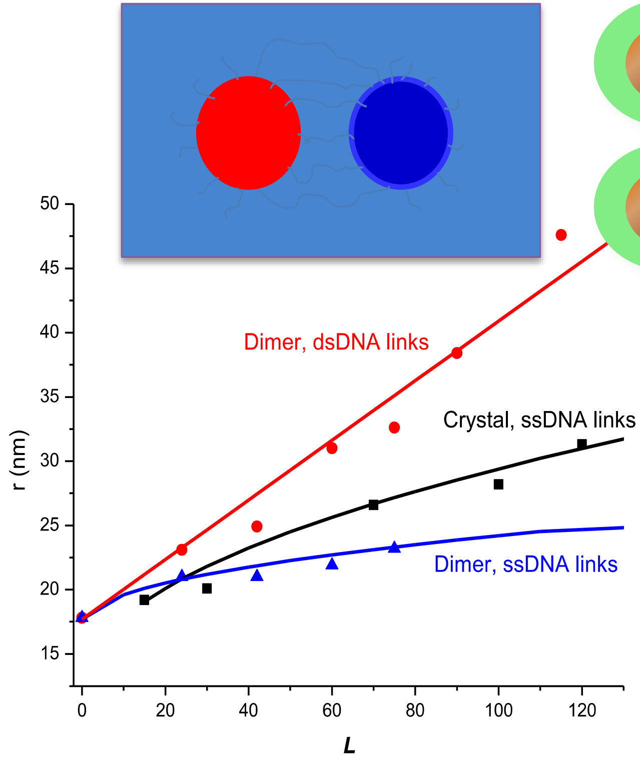
S. Srivastava et al, JACS, (2014), dx.doi.org/10.1021/ja501749b

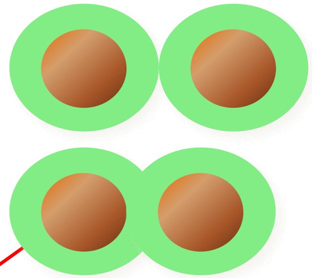
Programmable Assembly in 2D



S. Srivastava et al, JACS, (2014)

When molecules and nano-objects are similar in sizes:
Collective polymers effects in Shells of Dimer Clusters

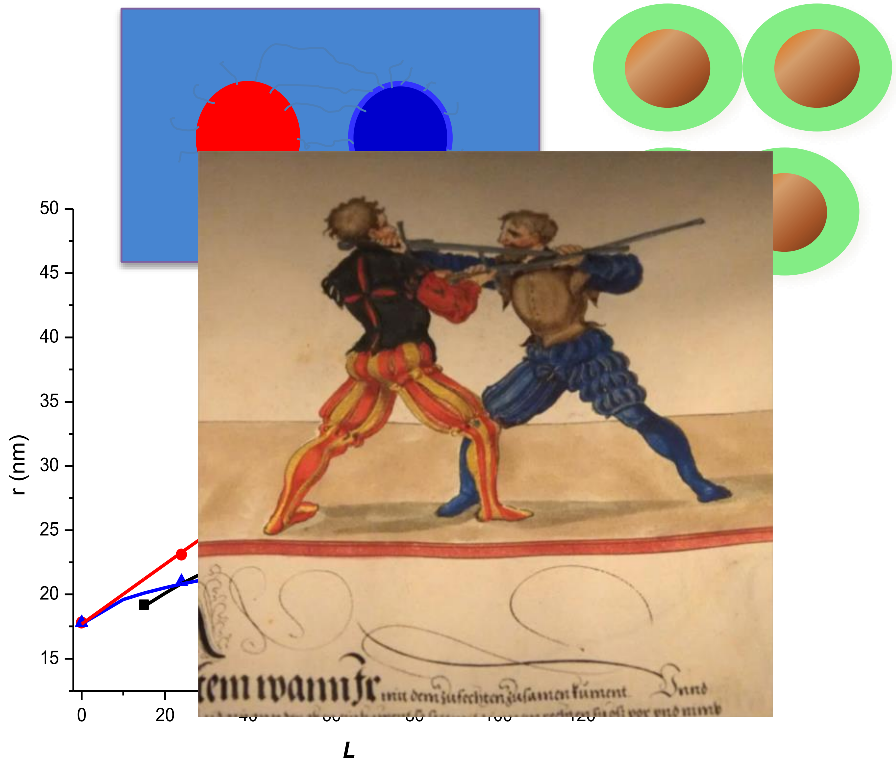




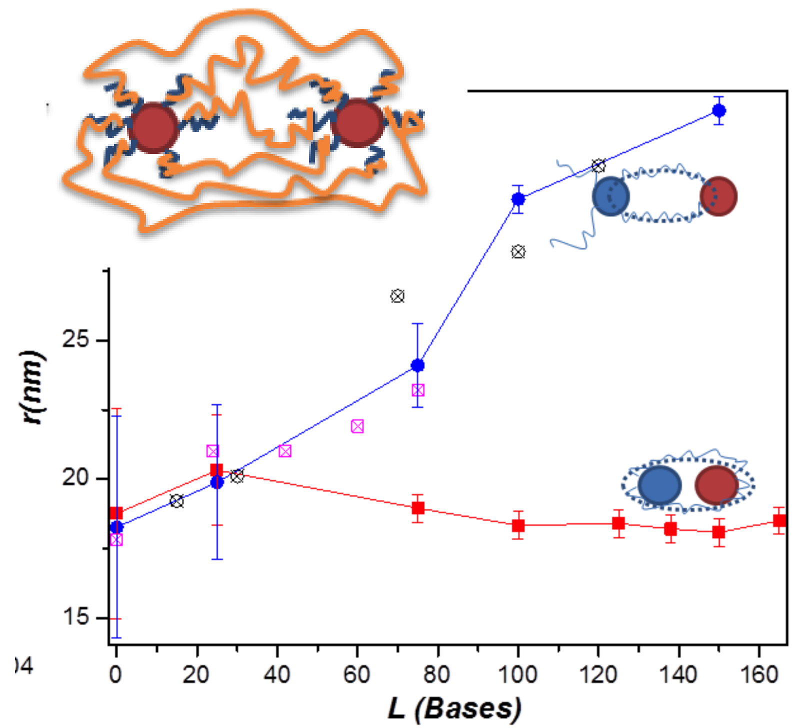
- Unrealistic persistence length (~0.4nm) is observed for dimers linked with multiple linkers
- Interplay of particle curvature and number of linkers plays major role, as shown by simulations and theory

Chi et al., ACS Nano, 6 (8), 6793 (2012)

When molecules and nano-objects are similar in sizes:
Collective polymers effects in Shells of Dimer Clusters



Self-limited dimers with "collapsed" structure for particular assembly pathways



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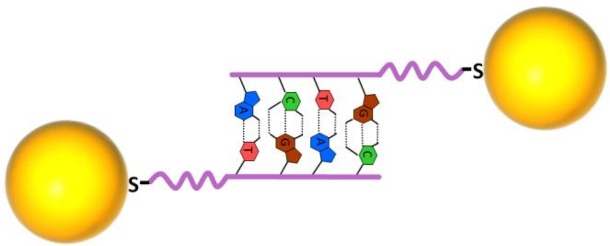
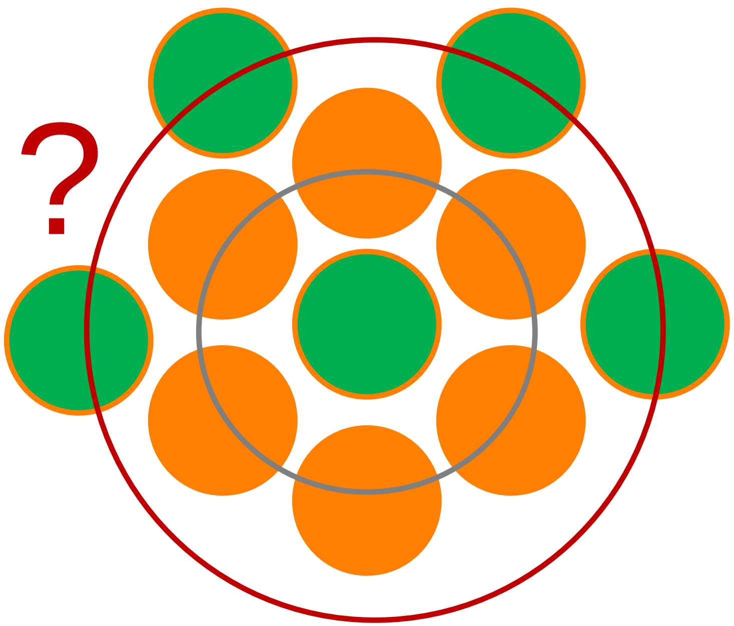
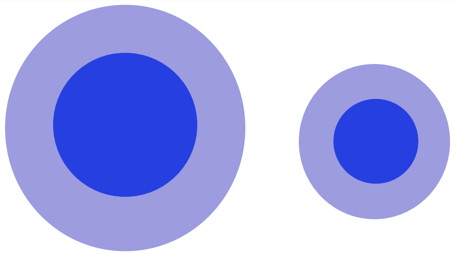
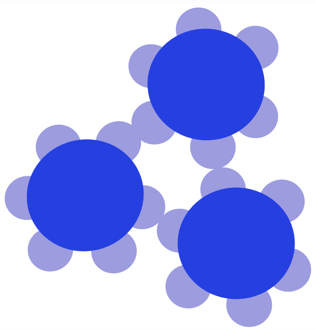
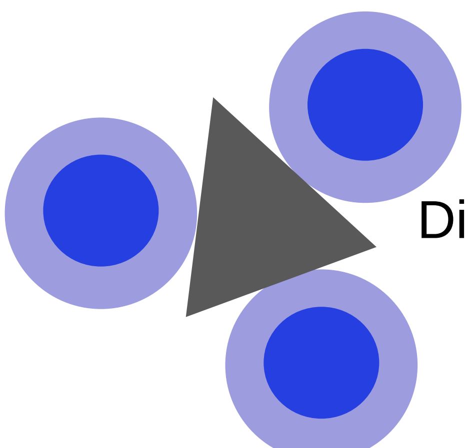
Chi et al., ACS Nano, 6 (8), 6793 (2012) and unpublished (right)

DNA recognition between components and phase control

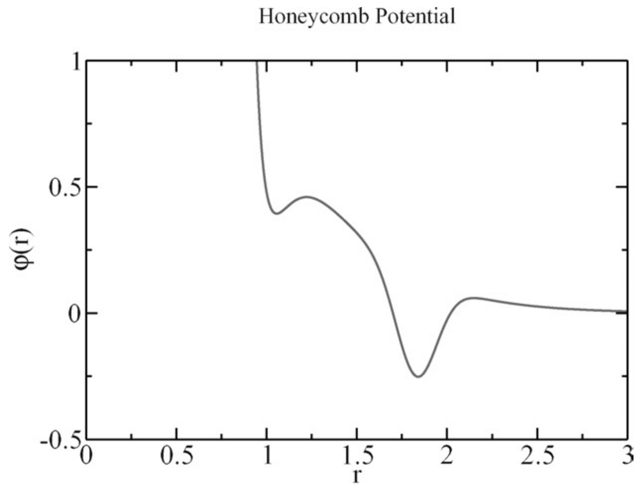


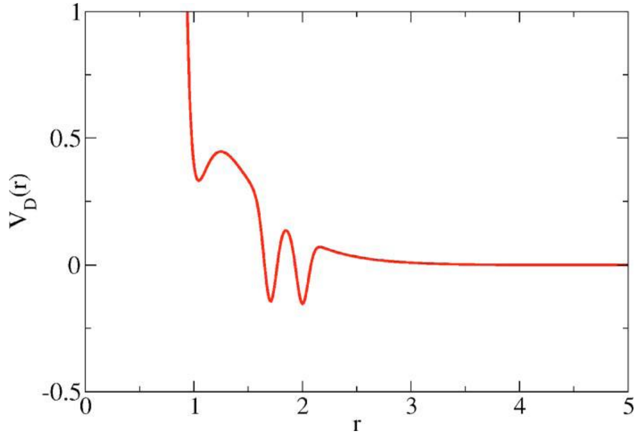


Assembly by Design: Strategies

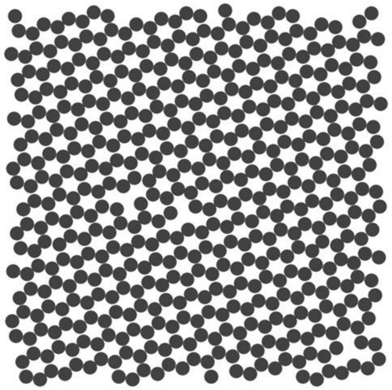
	Assembly Strategy	Determining Factor
	Uniform Shell	Packing + Interactions
	Patches	Symmetry of Patches
	Directional interactions	Block Symmetry

How to form a complex structure: Engineering isotropic interaction potential

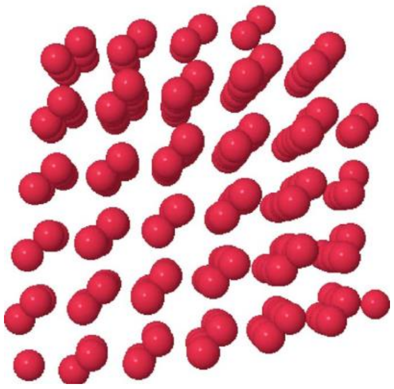




Honeycomb



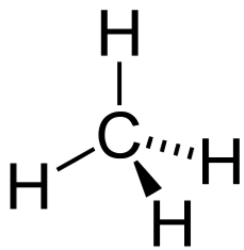
Diamond

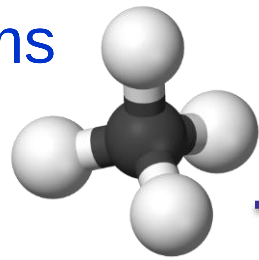


S. Torquato et al, Soft Matter, 5, 1157 (2009), PRE (2007)

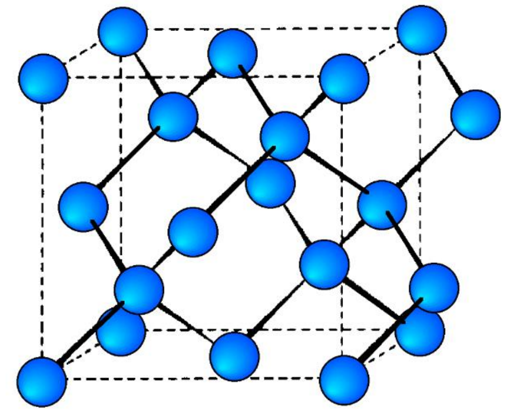
How to form a complex structure: Engineering Anisotropic Interactions

Atomic systems





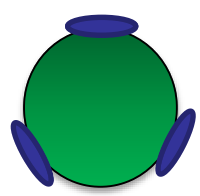
Molecular bonds determine crystalline structure

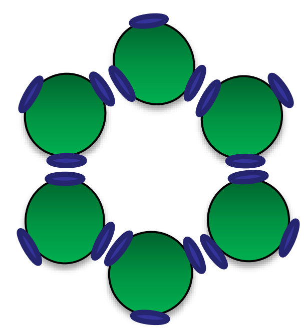


Particles systems

"Patchy" particles

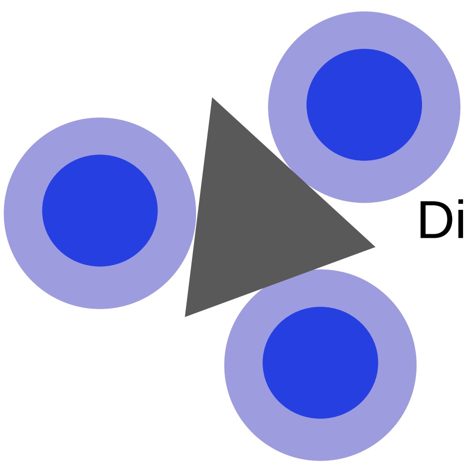
Patches provide bindings



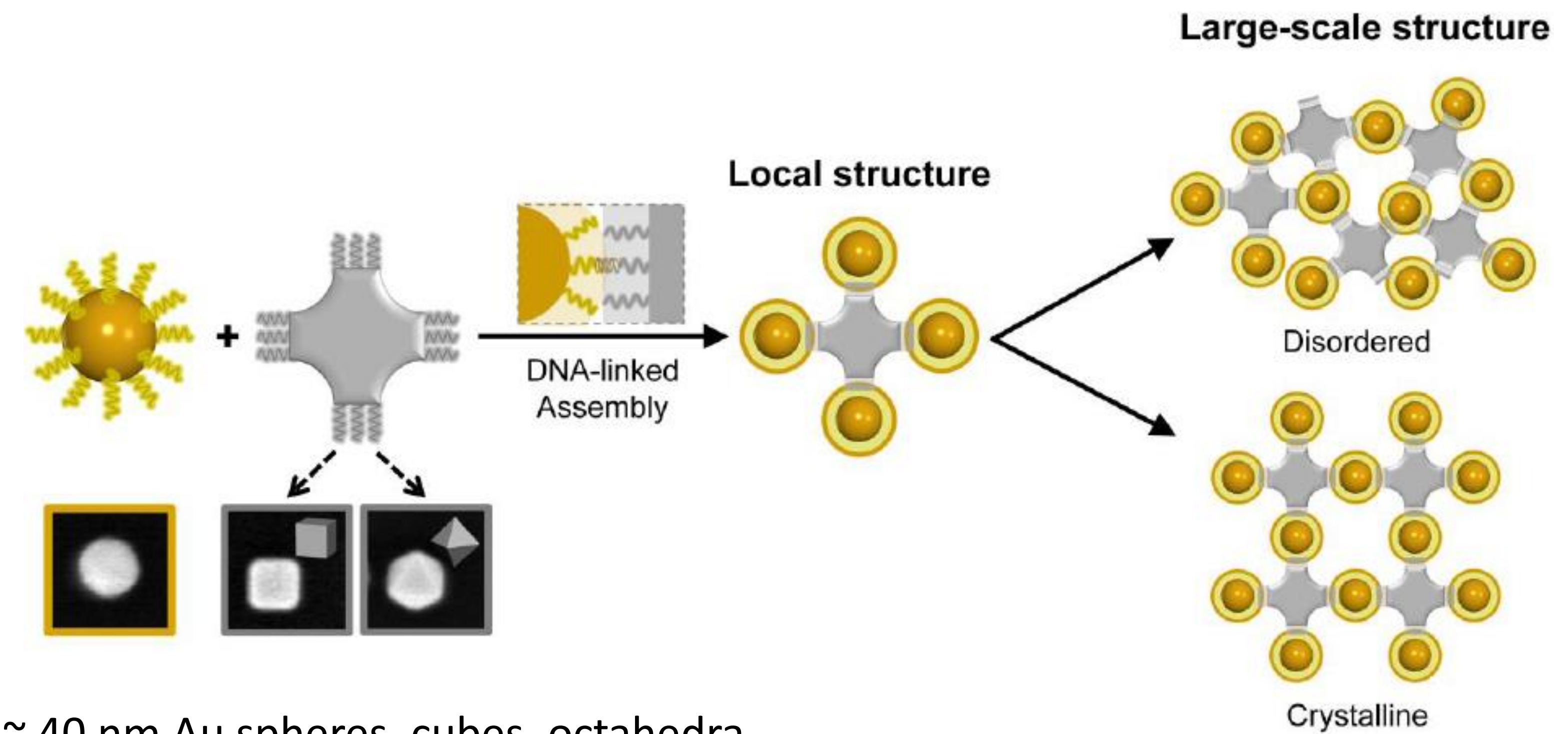


- Difficult to create on nanoscale
- Difficult to control uniformity and locations on particle

Assembly by Design: Strategies

	Assembly Strategy	Determining Factor
	Uniform Shell	Packing + Interactions
	Patches	Symmetry of Patches
	Directional interactions	Block Symmetry

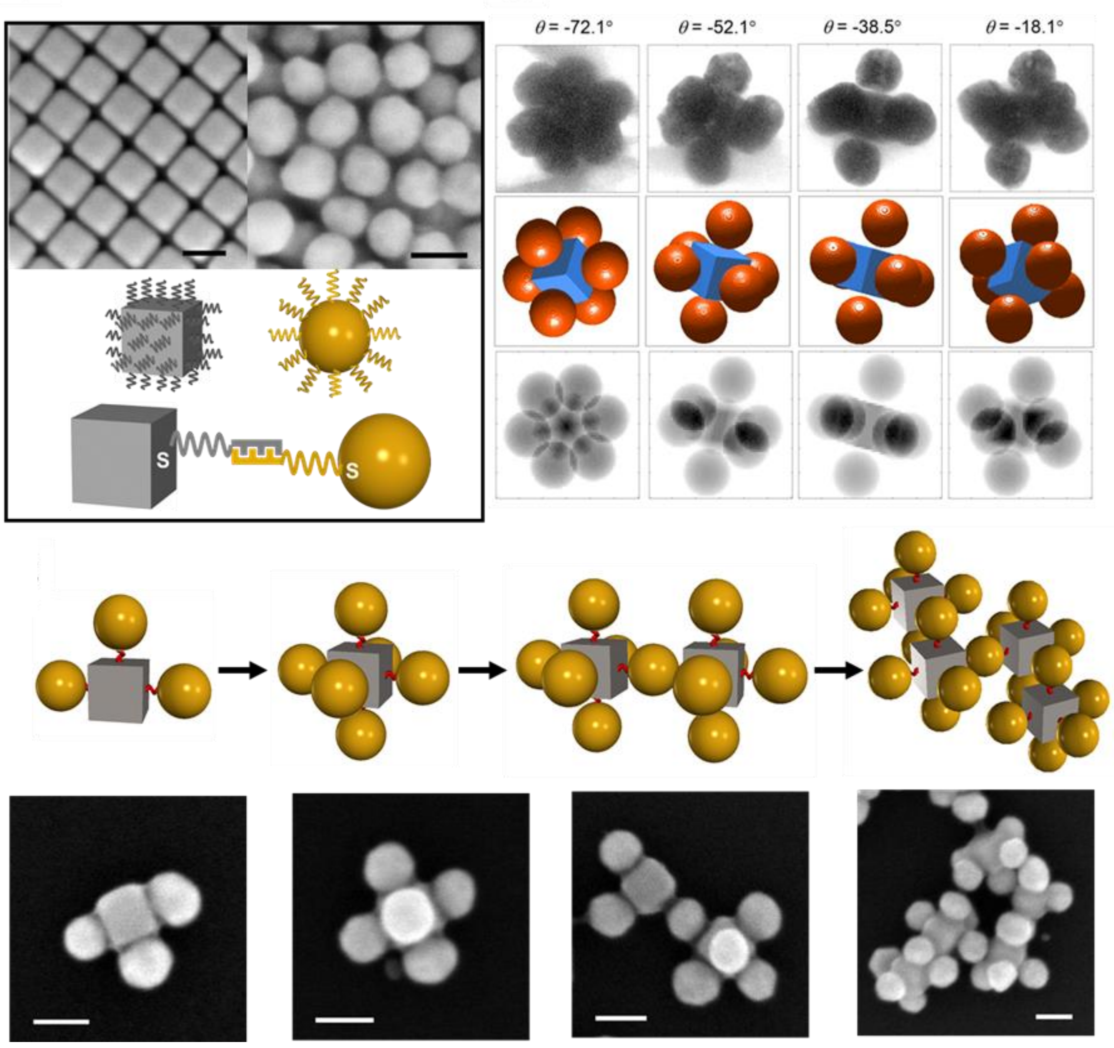
Shape-directed Assembly of Binary Lattices



~ 40 nm Au spheres, cubes, octahedra

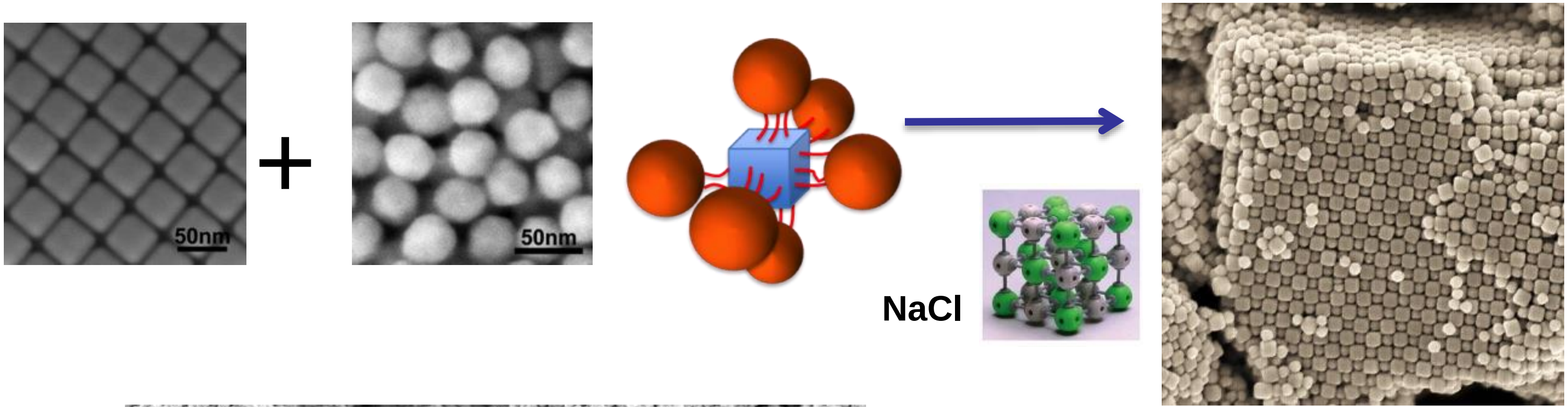
F. Lu, et al, Nature Communications, (2015), DOI:10.1038/ncomms7912

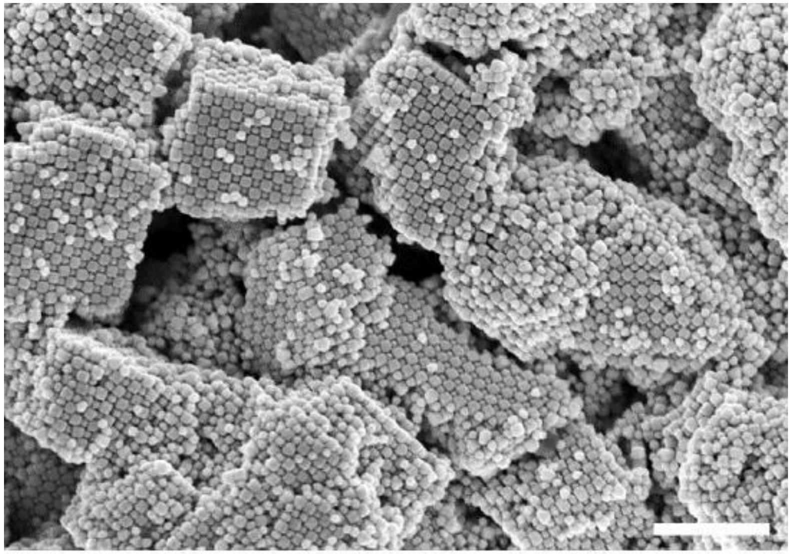
Shape-directed Assembly of Clusters

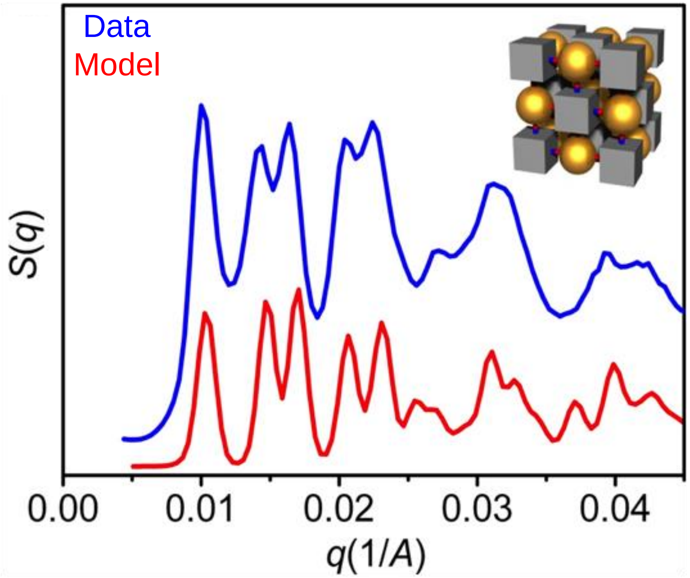


F. Lu, et al, Nature Communications, (2015)

Cube-Directed Assembly of Spheres

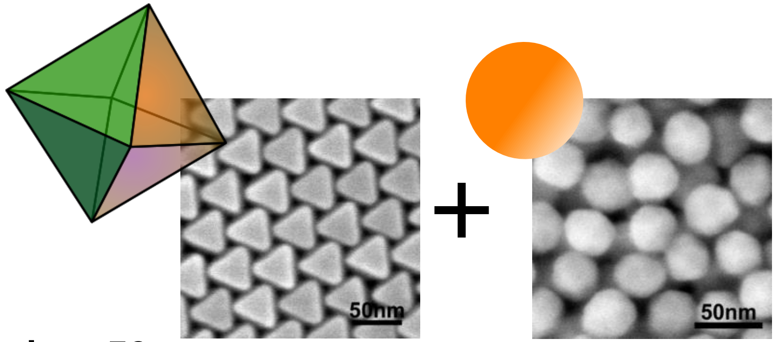


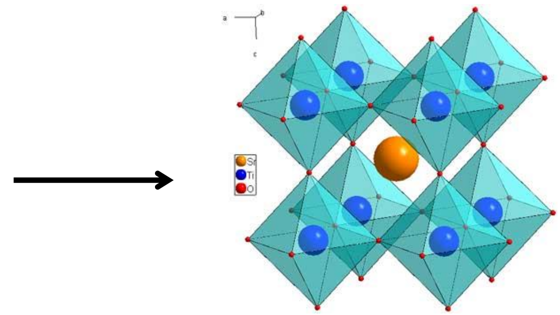




F. Lu, et al, (2015), Nature Communications

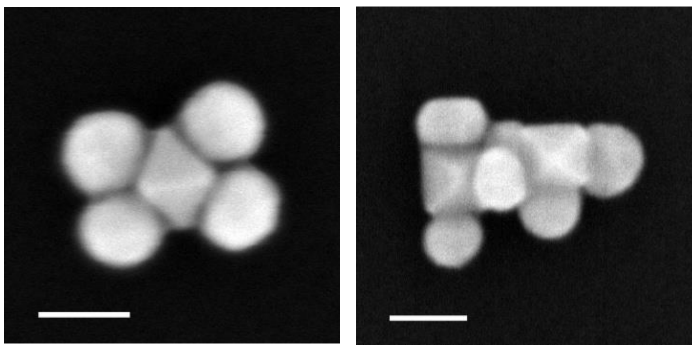
Designed Lattices: Octahedra as Linkers

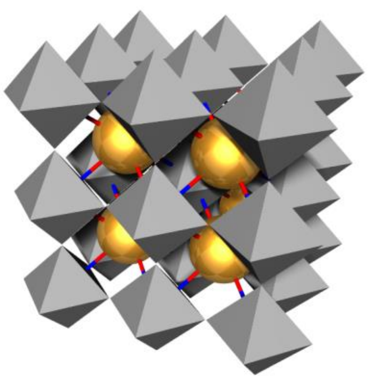


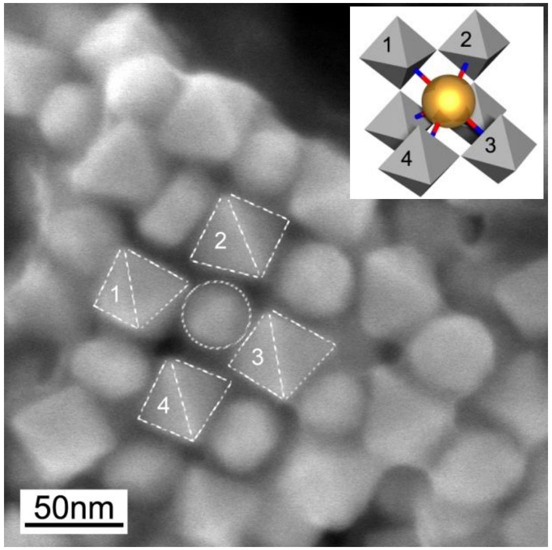


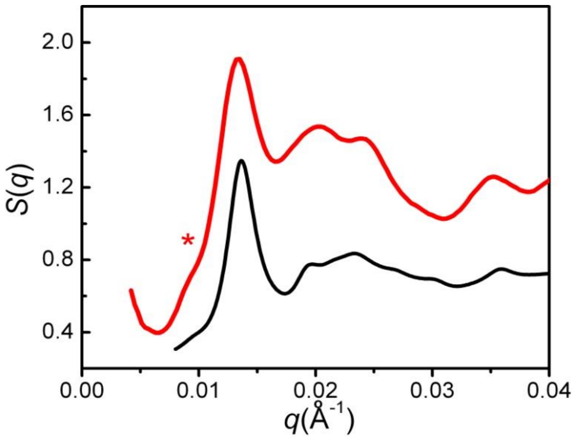
Cubic Perovskites ($SrTiO_3$)

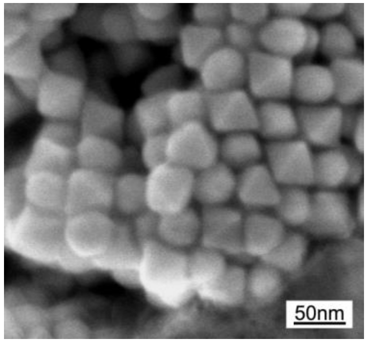
Scale bar: 50nm

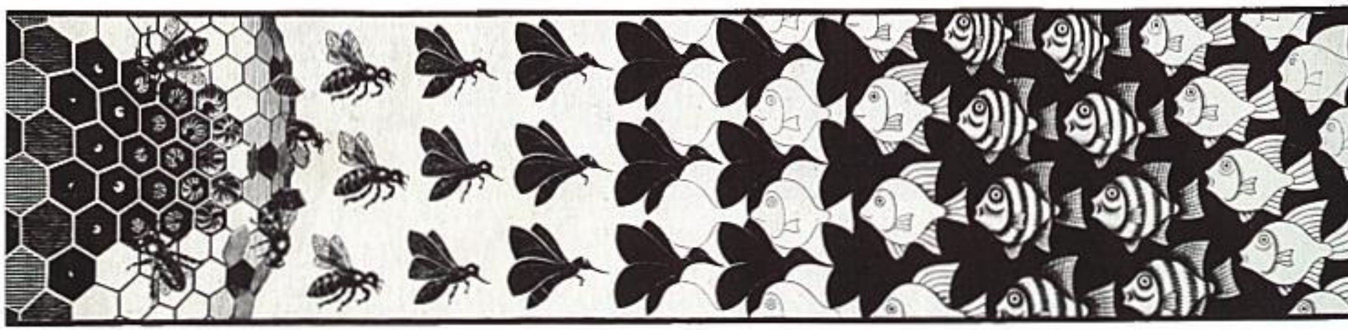




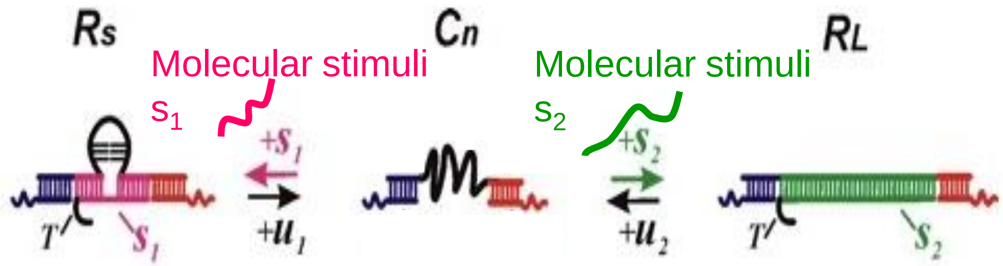








Superlattices with Switchable Lattice Constant

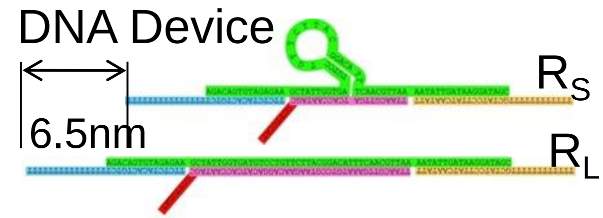


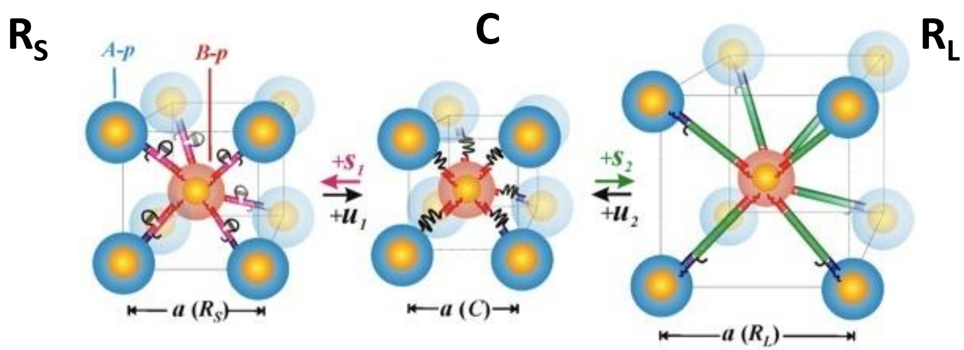
Rigid short (R_s) linker with a loop

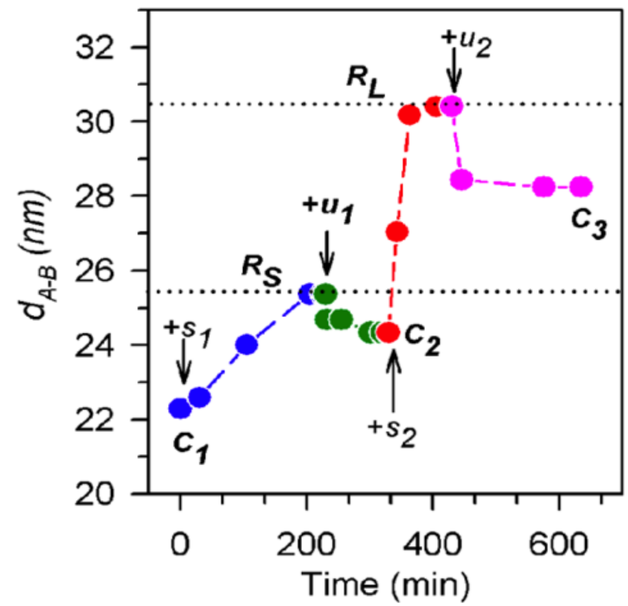
Coiled (C_n) linker

Rigid long (R_L) linker

DNA Device switches interparticle distances

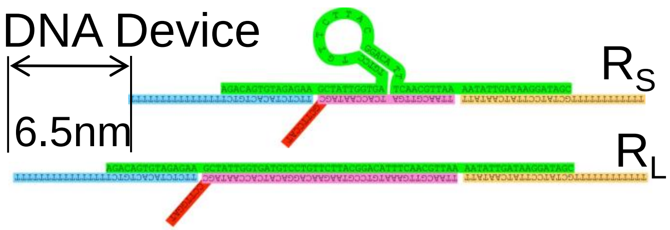






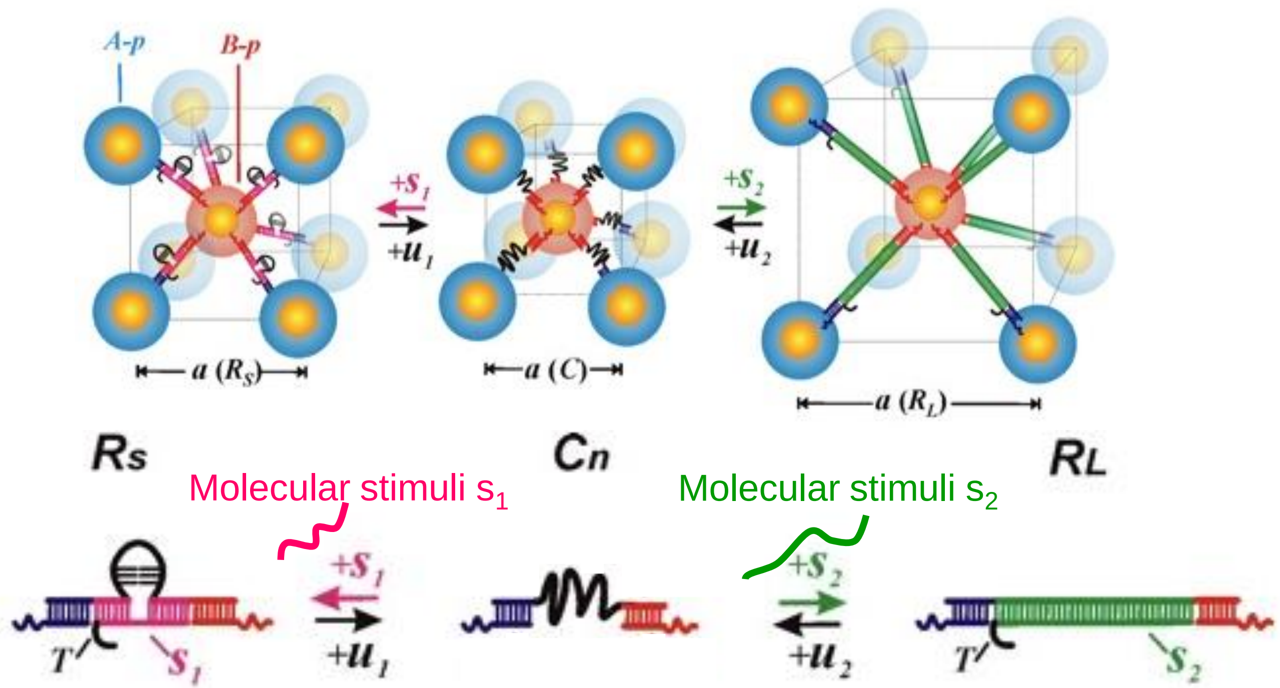
M. Maye et al, Nature Nanotechnology 6, 116, (2010)

Molecularly switchable nano-systems*



Switchable DNA Device

- Switches interparticle distances
- Assembles and manipulates 3D structures



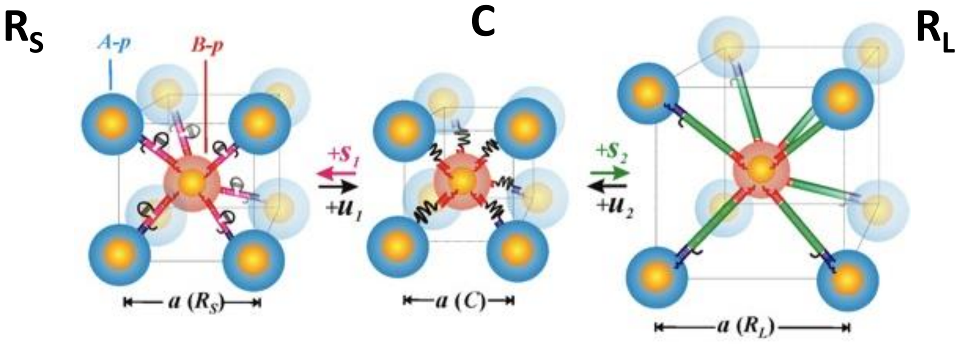
Rigid short (R_s) linker with a loop

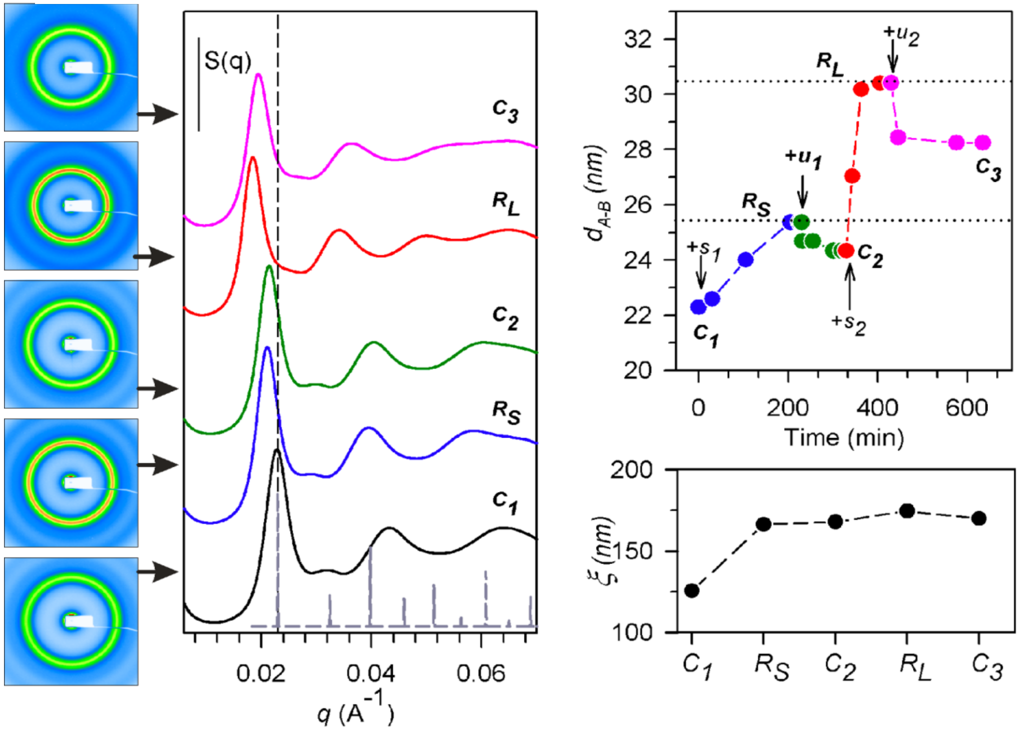
Coiled (C_n) linker

Rigid long (R_L) linker

Nature Nanotechnology 6, 116, (2010)

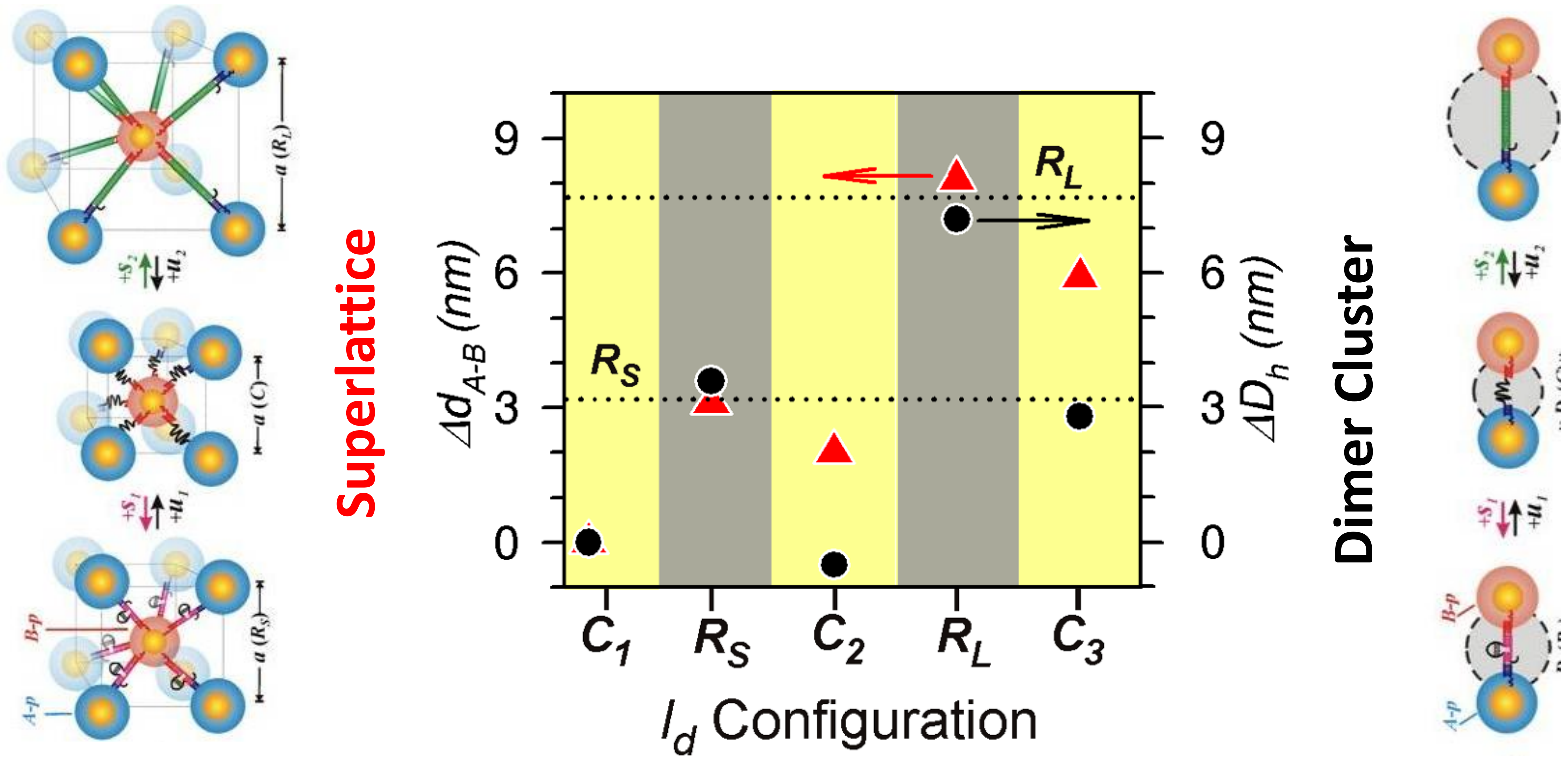
Switchable 3D Superlattices





Nature Nanotechnology 6, 116, (2010)

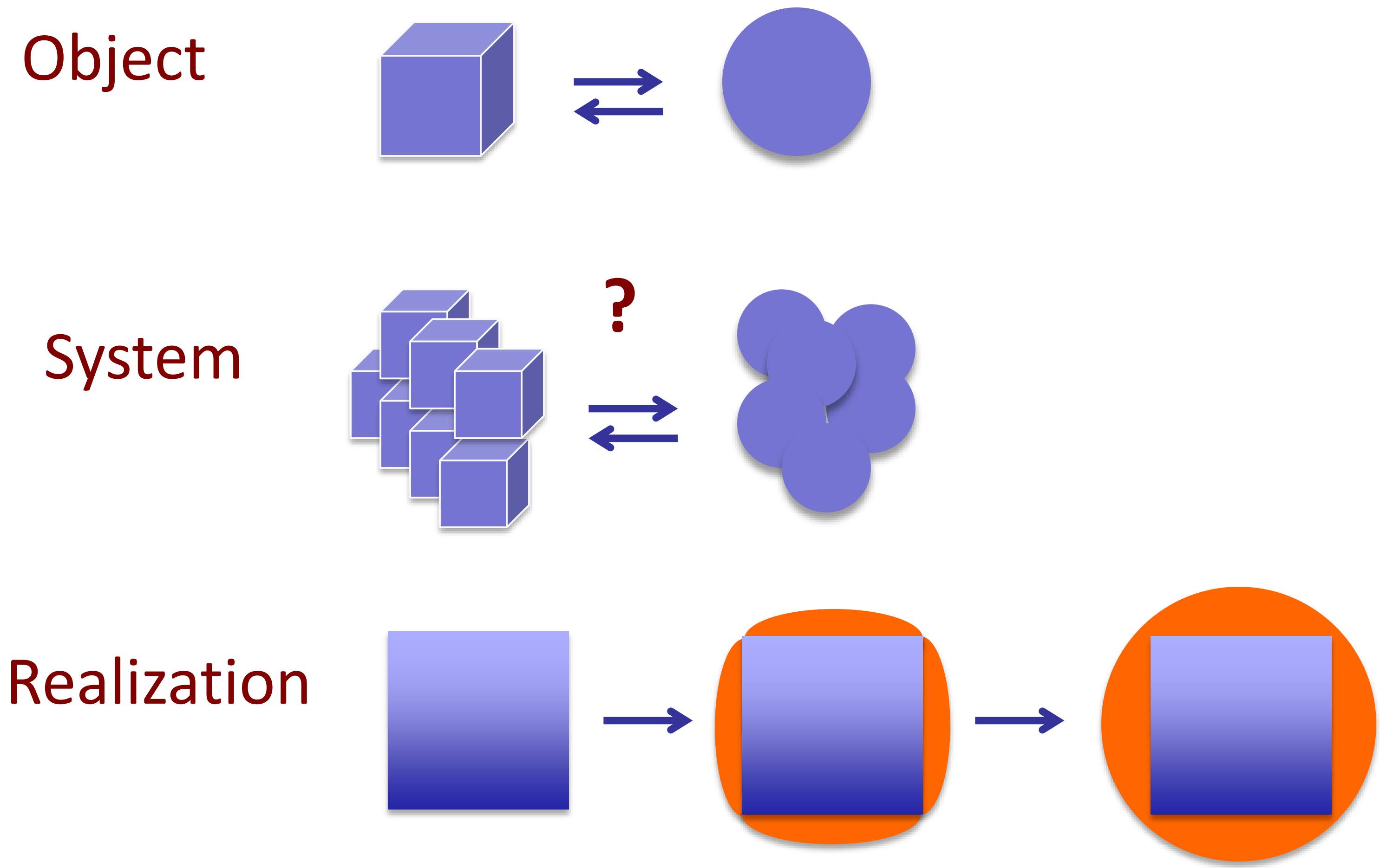
Switchable Nanosystems



- Reconfigurations of superlattice and cluster result in a similar distance change ~ 5 nm
- DNA device operates for 3D and cluster systems; kinetics for 3D is slower
- Hysteresis of coiled device configuration is more pronounced in 3D, might be attributed to confinement, multiple particle linkages, trapped ds-DNA fragments

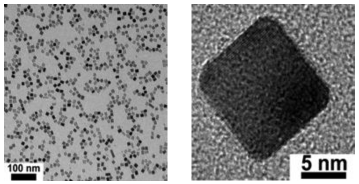
Nature Nanotechnology 6, 116, (2010)

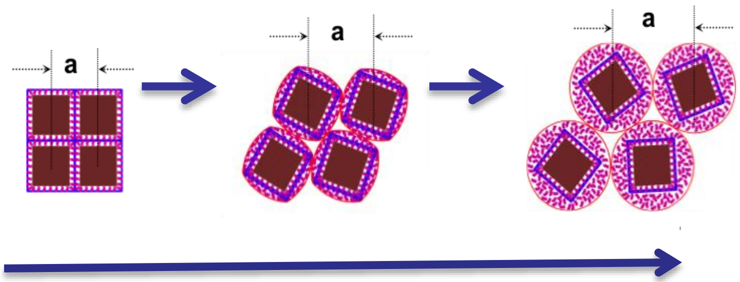
Anisotropy: shape-induced system transformation



Shape-induced system transformation

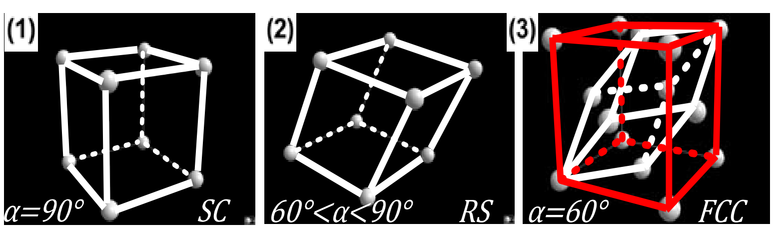
10 nm Pd cube



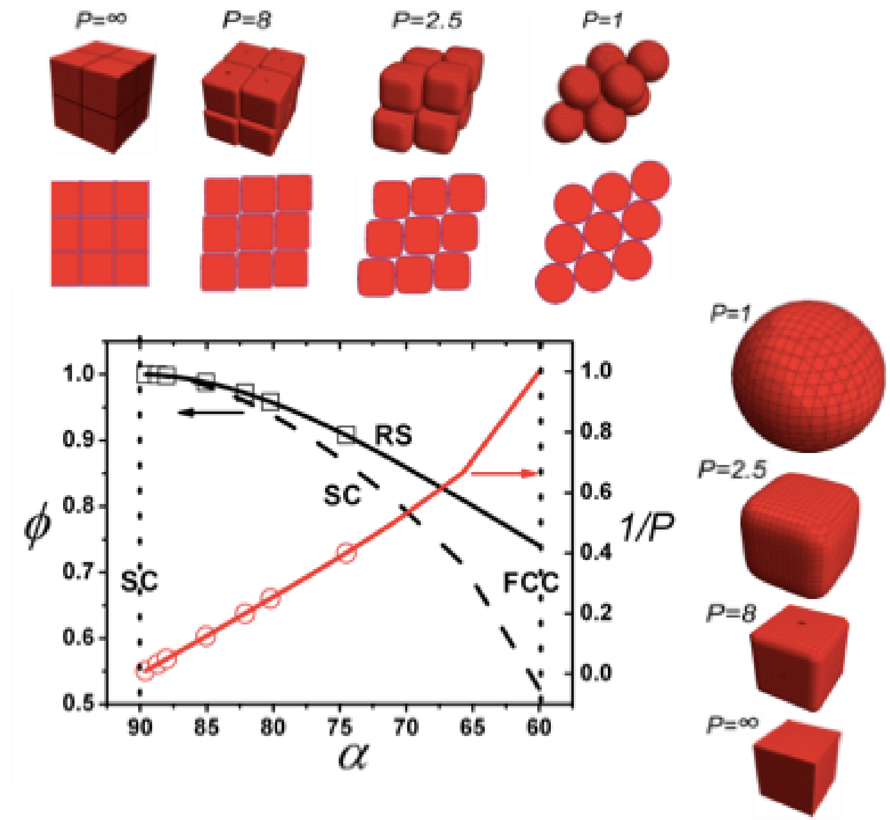


Ligand (dodecanthiol) layer adsorption
via solvent evaporation

In-situ SAXS

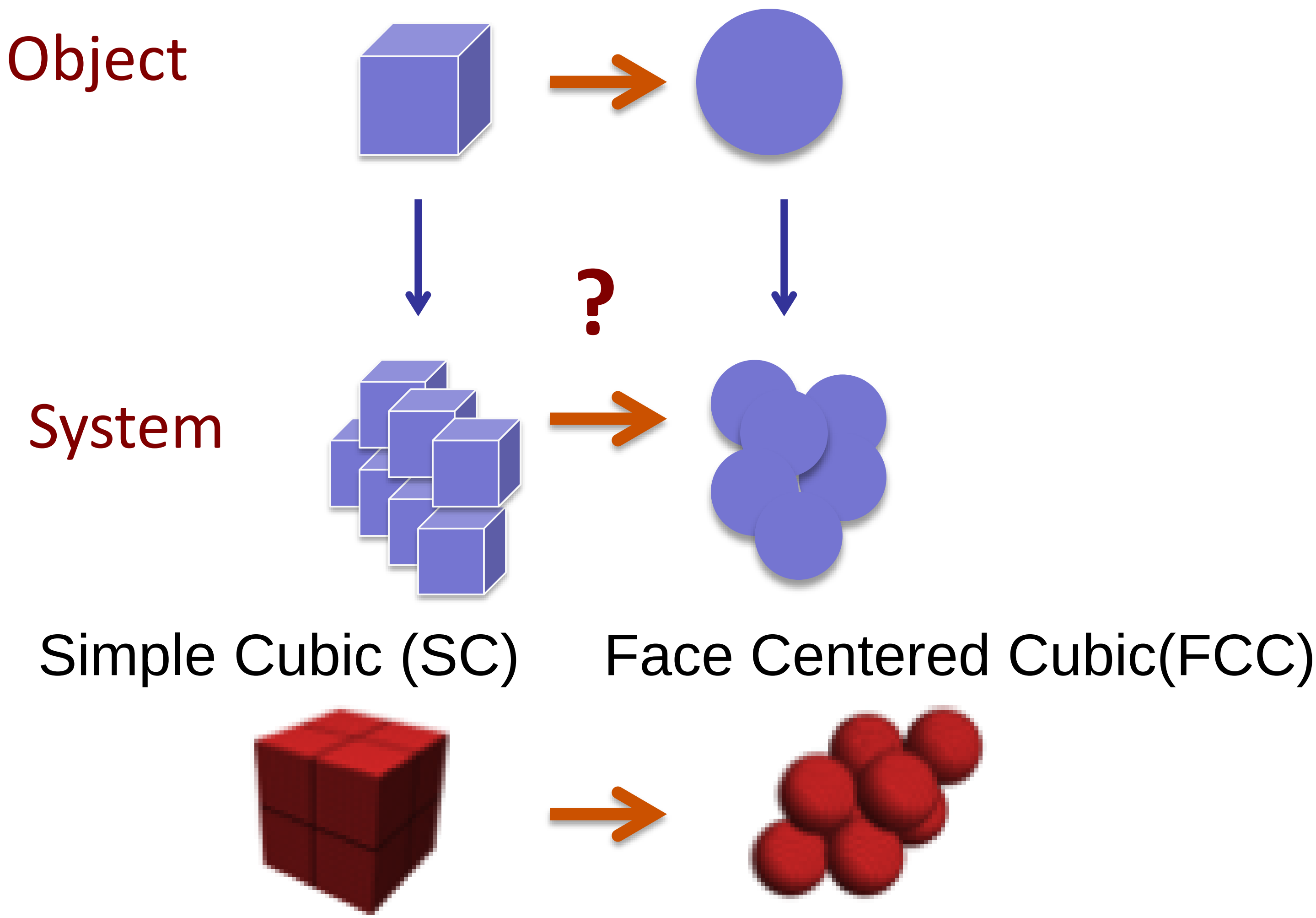


$$|x|^{2p} + |y|^{2p} + |z|^{2p} \leq 1$$

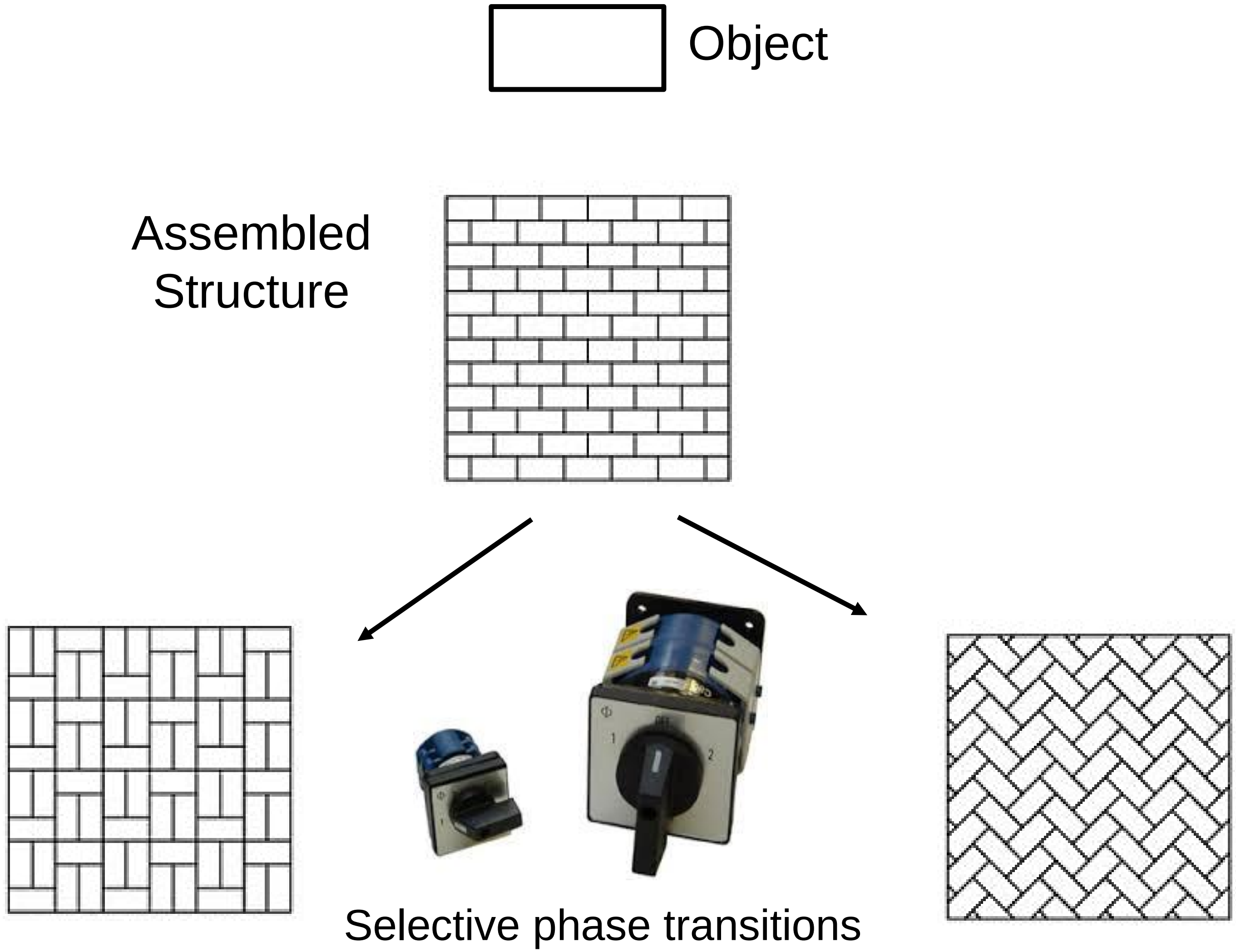


Y. Zhang, F. Lu, D van der Lelie, and O. Gang, Phys. Rev. Lett. 107, 135701 (2011)

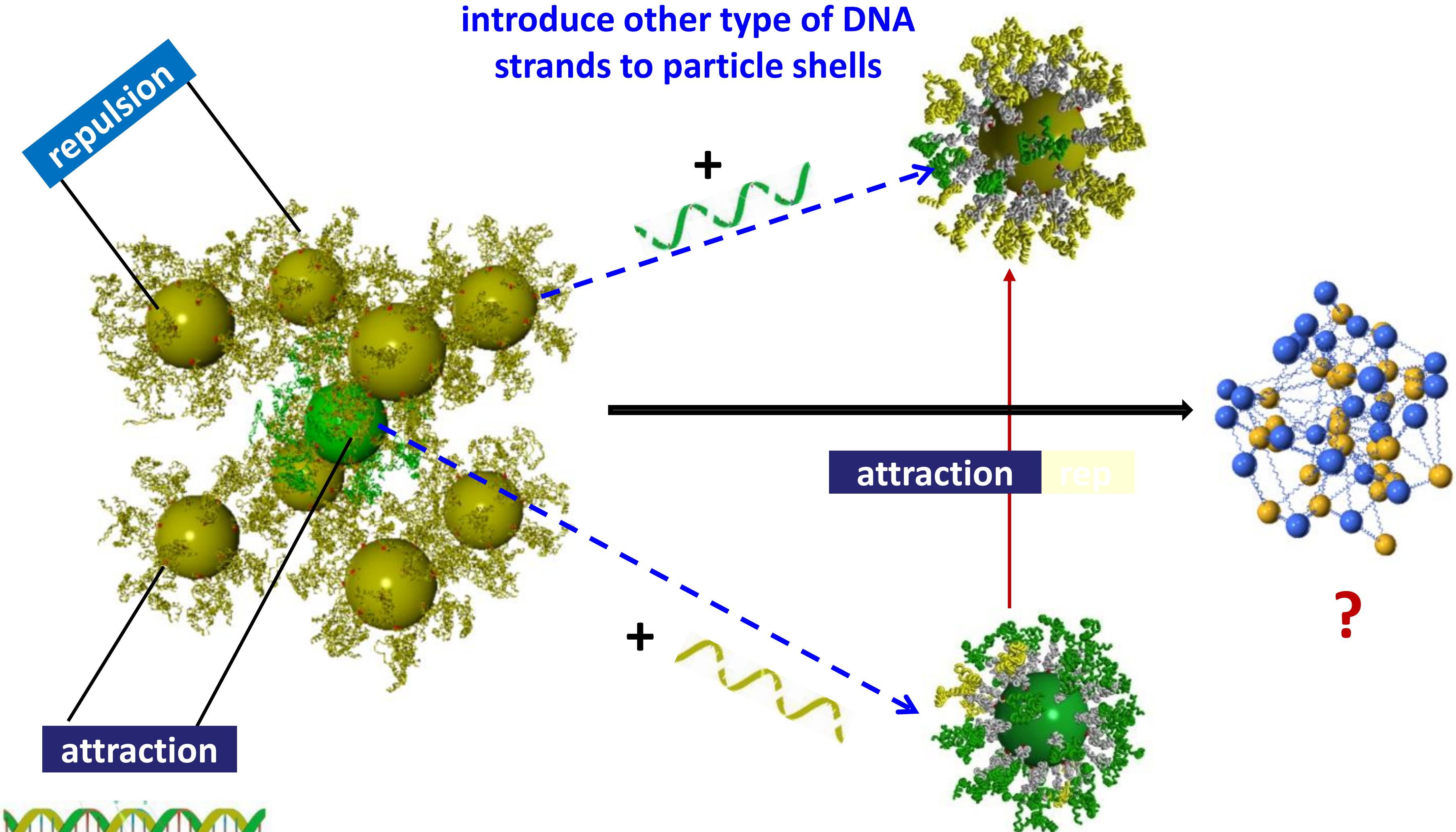
Shape-induced system transformation



Switching Material Structure Globally?

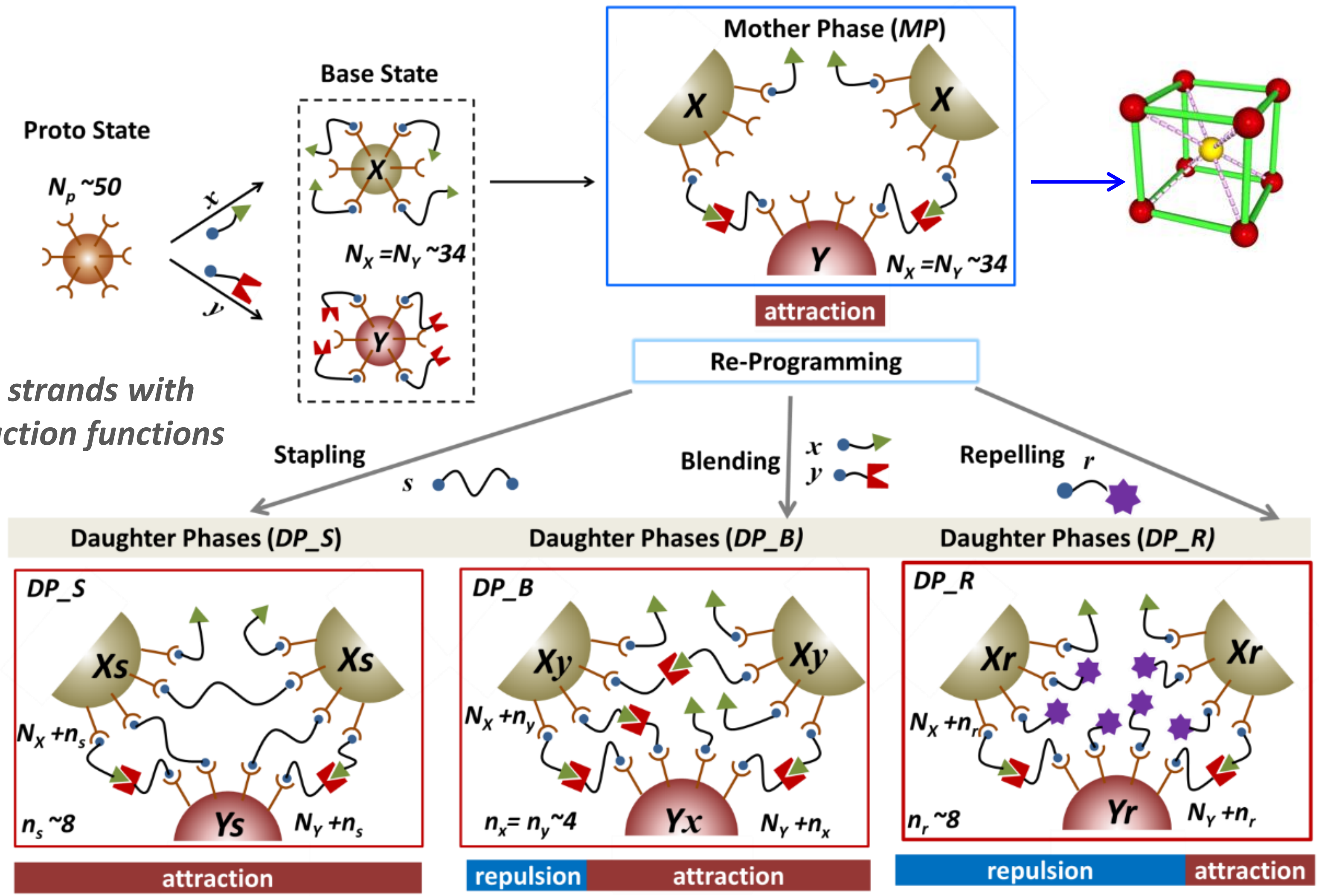


Programmable Transformations



Tuning the interactions in-situ, within the lattice

Programmable Transformations by Selective Interaction Tuning

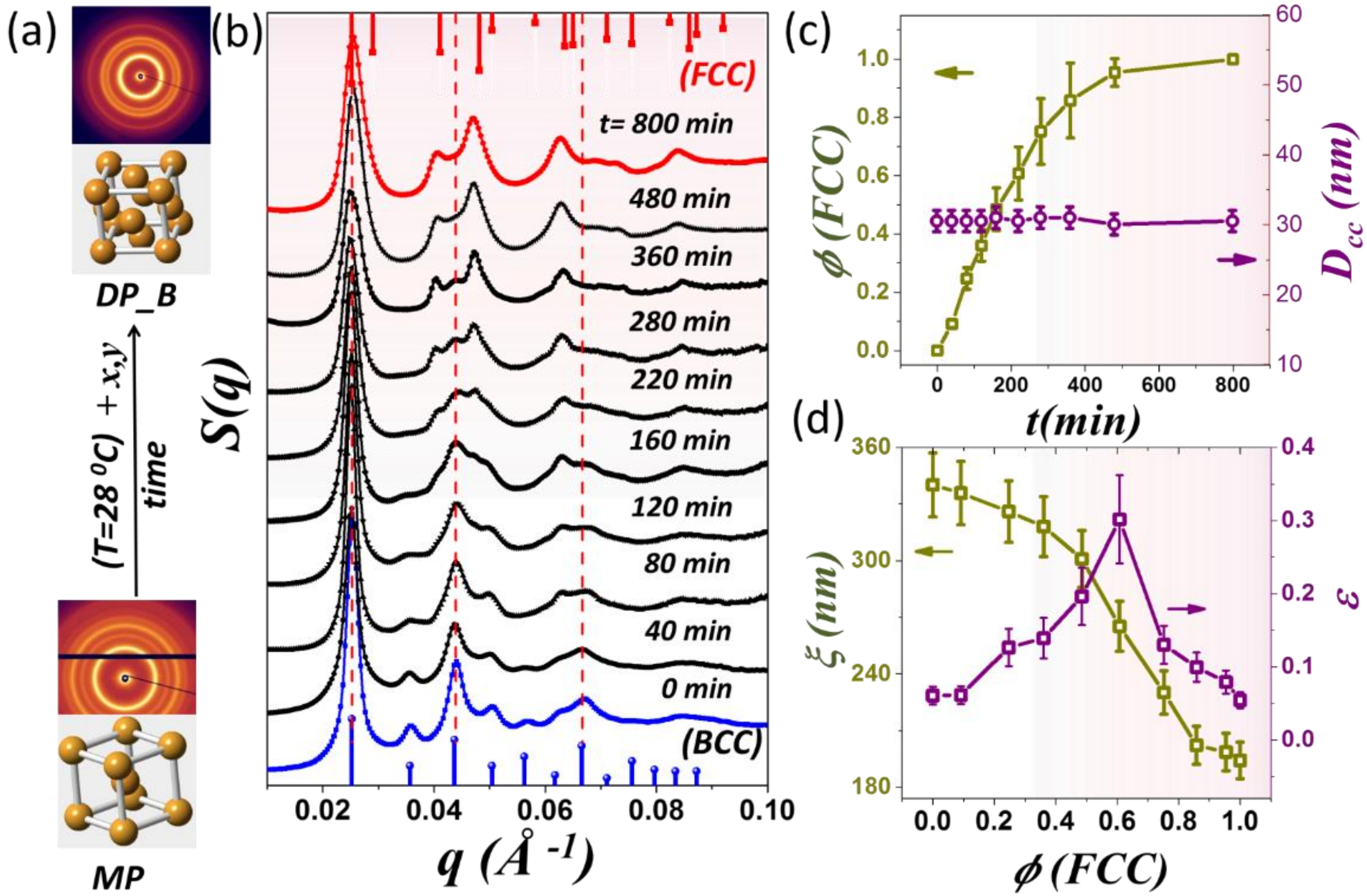


Input of DNA strands with different interaction functions

Y. Zhang, et al. Nature Materials (2015), *in press*

An Example for Blending-Interaction Case

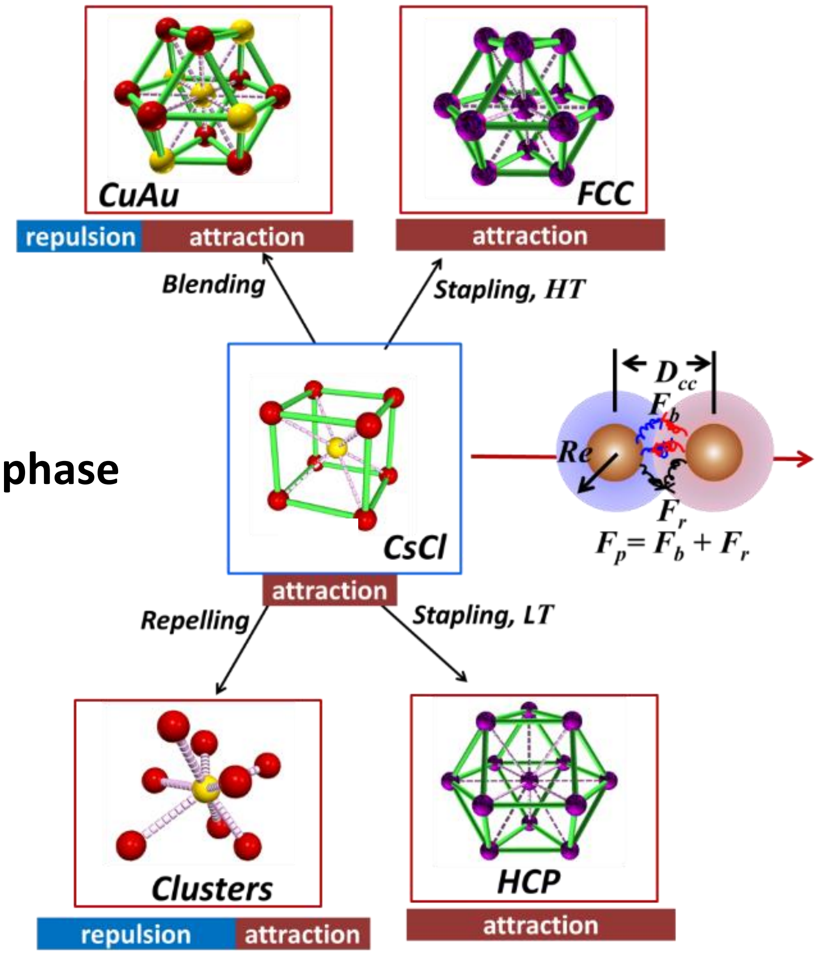
Phase transition from BCC to FCC upon introducing "blending" DNA strands



Y. Zhang, et al. Nature Materials (2015), *in press*

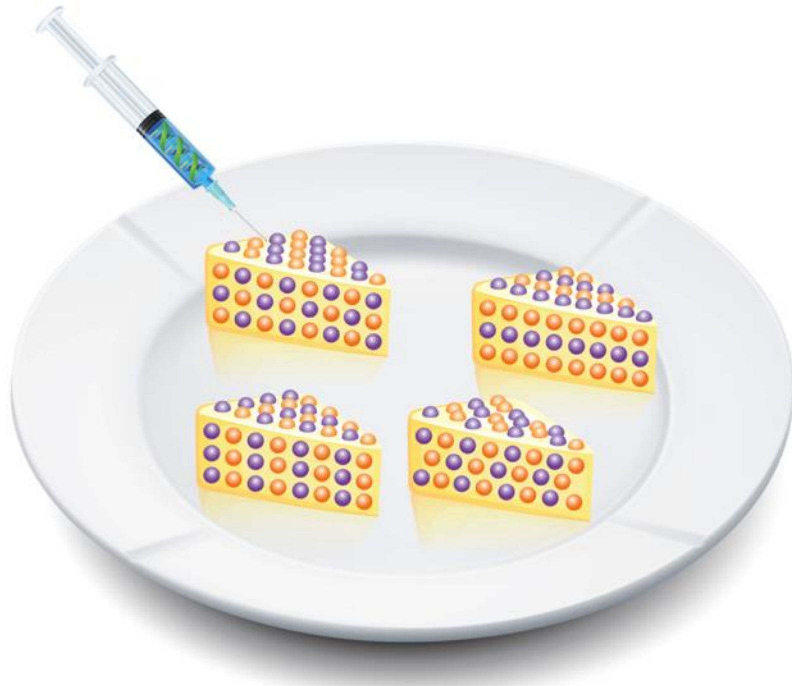
Programmable Transformations

BCC
Mother phase



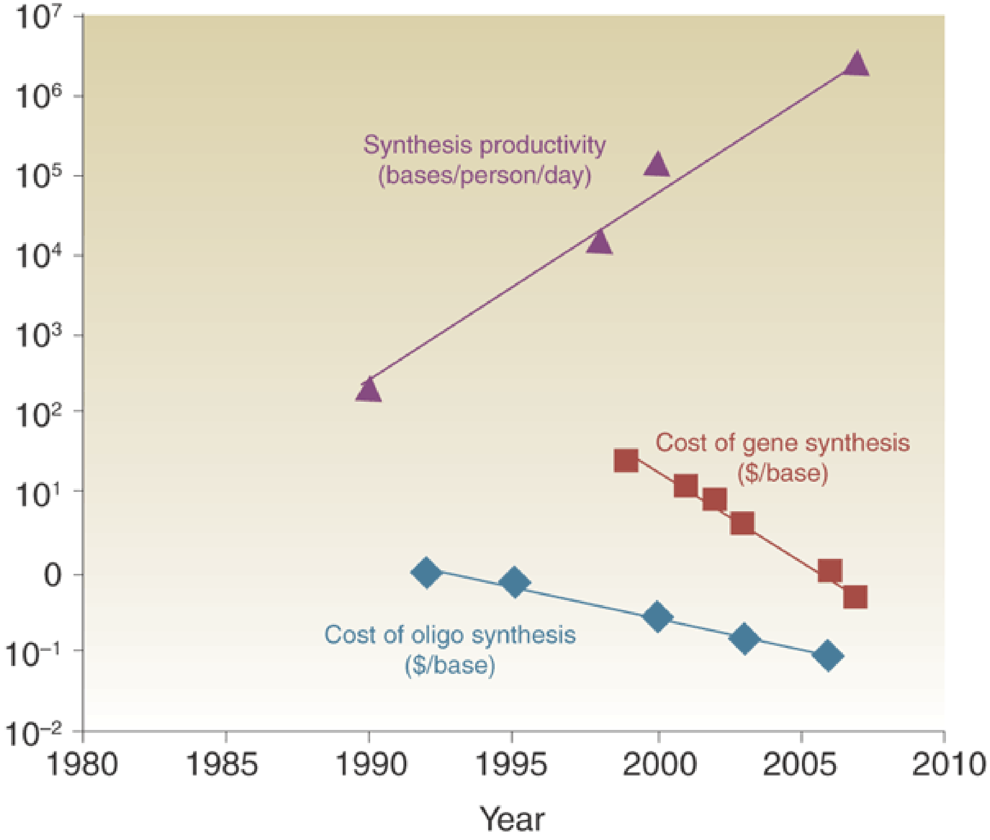
Y. Zhang, et al. Nature Materials (2015)

“Genetically” Modifiable Materials



Selective switching of material structures and functions on-demand by inputting highly specific DNA strands

DNA economics



R. Carlson, ***Nature Biotechnology 27, 1091 (2009)***

Perspectives

- Prescribed lattice symmetries?
- Self-assembly of non-periodic architectures?
- Systems with regulated transformation?