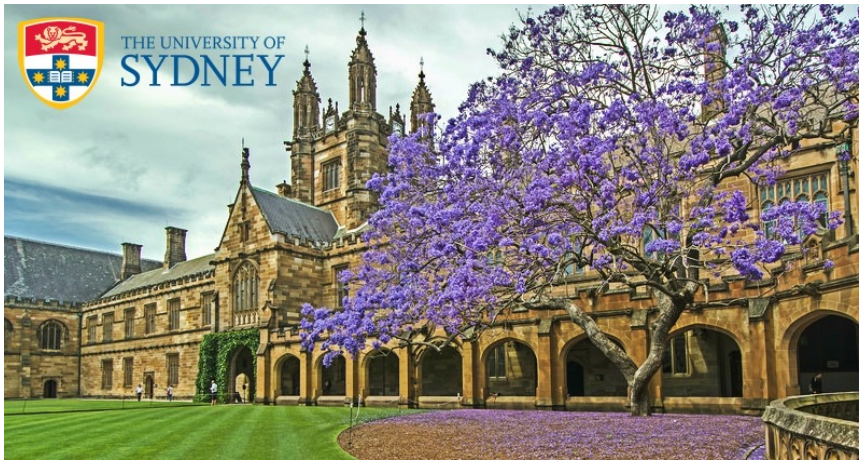
Ligand and Solvent Effects on the Colloidal Stability and Morphology of Apolar Nanoparticles

Asaph Widmer-Cooper

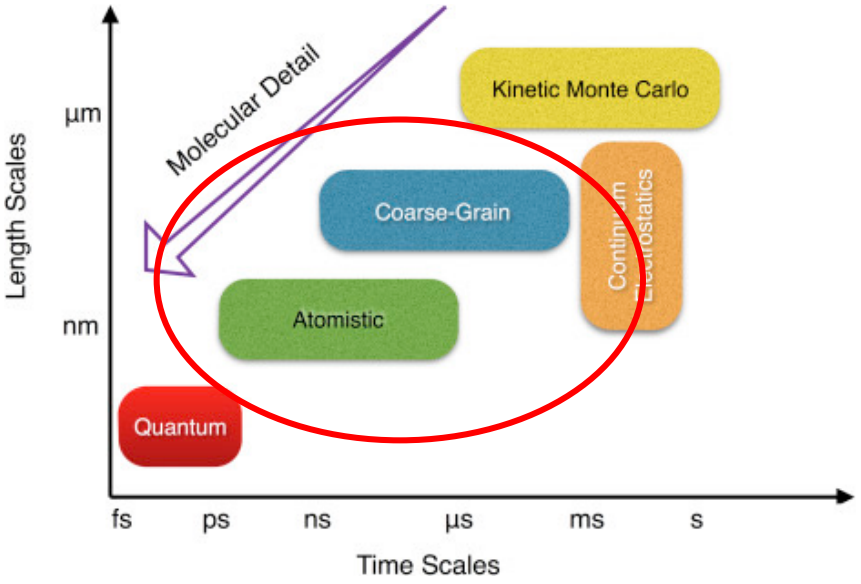
School of Chemistry

Australian Research Council Centre of Excellence in exciton science

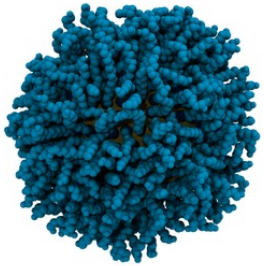


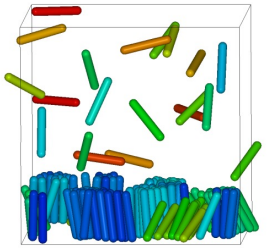
Soft Matter Theory and Simulation

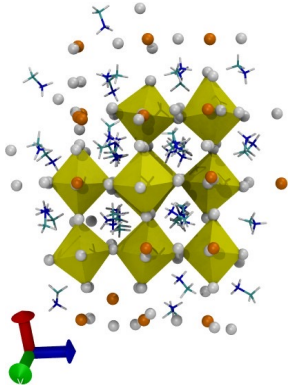
We study how atoms, molecules and nanoparticles spontaneously organise themselves – driven by intermolecular and surface forces and external driving forces – and how that order affects materials properties



- Molecular dynamics
- Monte Carlo simulations
- Free energy methods
- Dissipative particle dynamics
- Some quantum mechanics and continuum theory







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exciton science

THE UNIVERSITY OF MELBOURNE

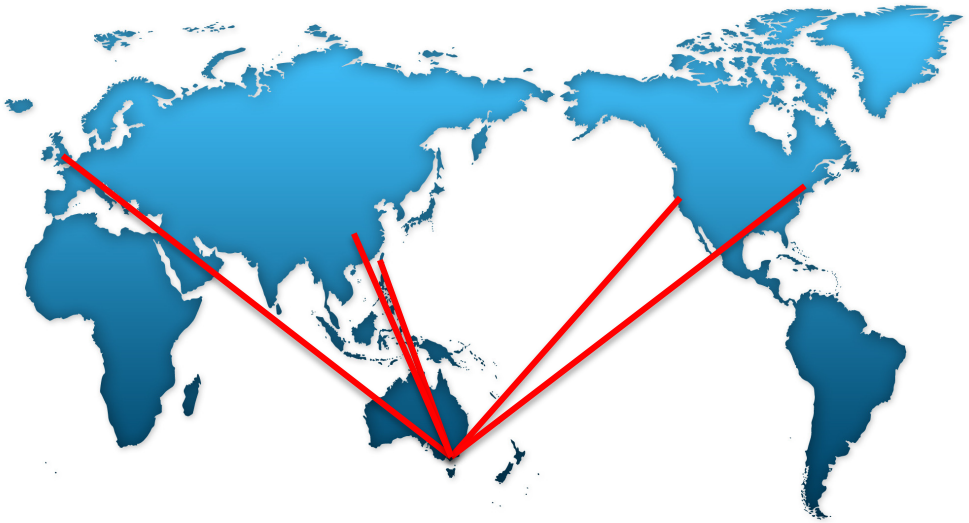
UNSW SYDNEY

MONASH University

THE UNIVERSITY OF SYDNEY

RMIT UNIVERSITY

>200 CIs, AIs, PIs, ECRs, students



CSIRO
Defence Science Technology Group
Reserve Bank of Australia

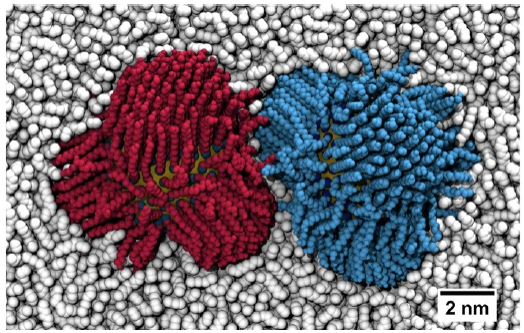
"Next-Generation Light Harvesting Materials for a Sustainable Energy Future"

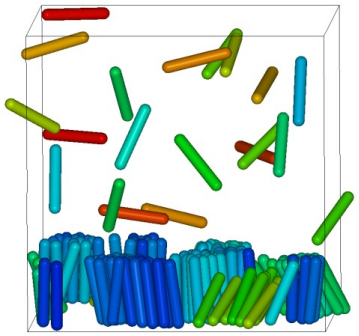
Formation and Properties of Nanomaterials

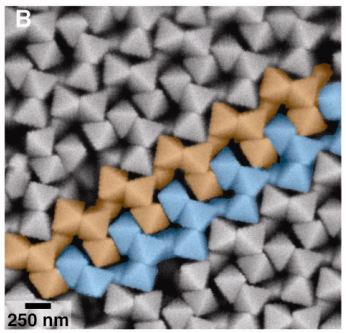
Colloidal properties of nanoparticles

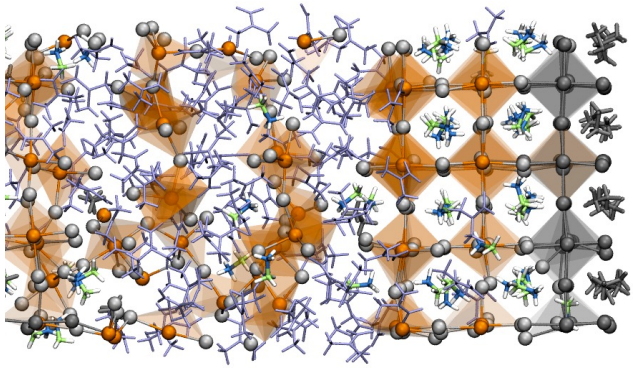
Nanoparticle assembly

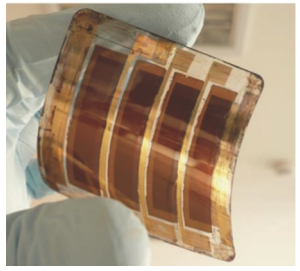
Formation and stability of metal halide perovskites



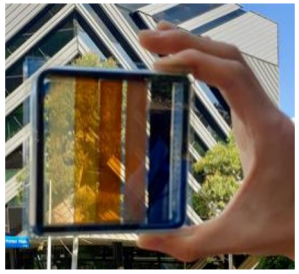






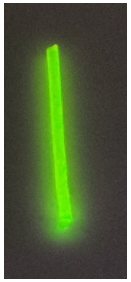


Printable solar



Solar windows

Luminescent solar concentrators

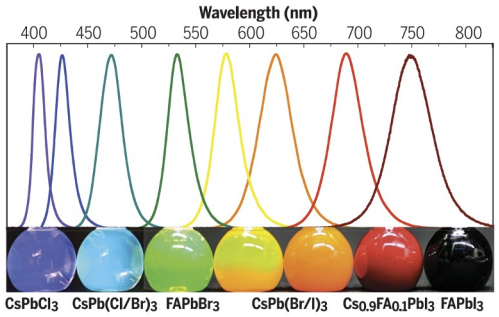


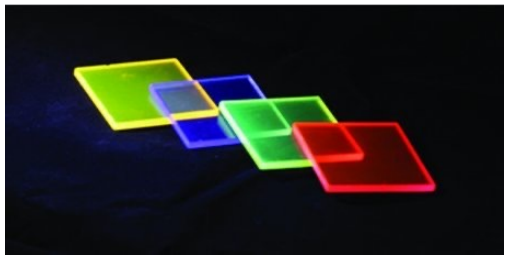
LEDs and lasers

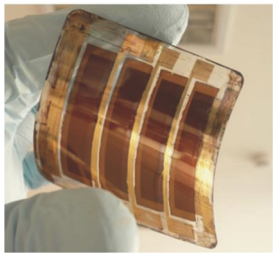
Outline

1) Colloidal stability of apolar nanoparticles

2) Morphology of nanoplatelets







1) Colloidal Stability of Apolar Nanoparticles

Debora Monego, Rashed Hasan

Tobias Kraus, Paul Mulvaney

Australian Research Council Centre of Excellence in exciton science

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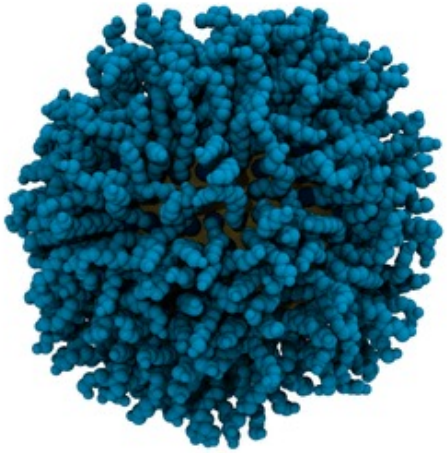
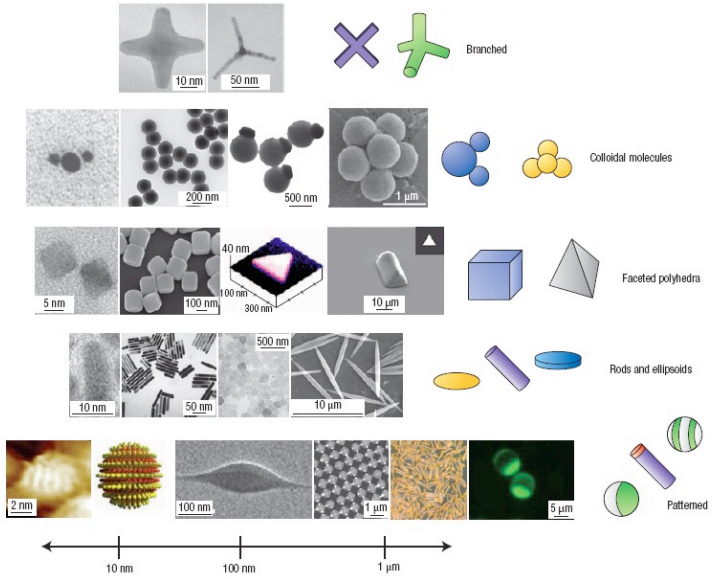


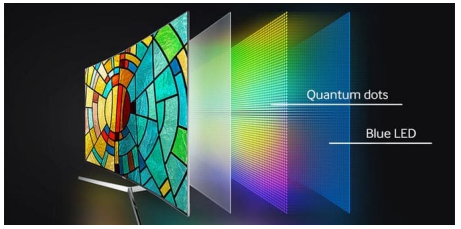
Leibniz Association

THE UNIVERSITY OF MELBOURNE

Colloidal stability is essential for processing and applications of nanoparticles



Glotzer & Solomon *Nature Mat.* 6, 2007



Long-term stability

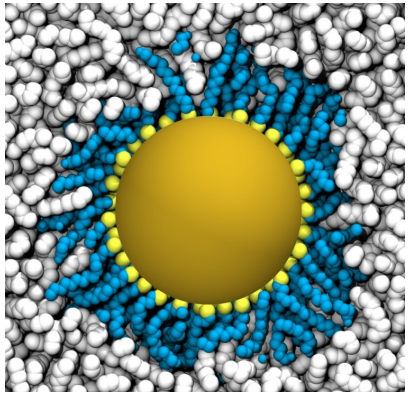
Dense inks for printing

Ordered assembly

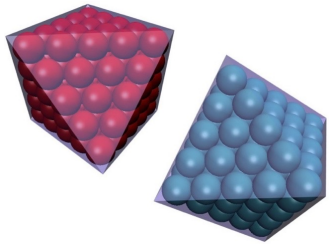
How particles interact is a key factor in stability and assembly

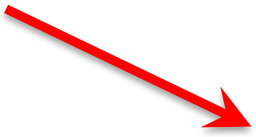
Ligand-coated (apolar) nanoparticles

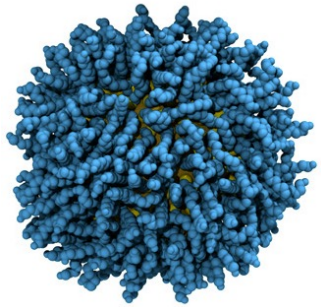
Inorganic core + organic ligands
- e.g. metals, semiconductors, oxides



Bare cores would agglomerate



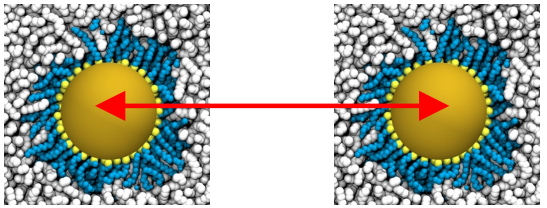




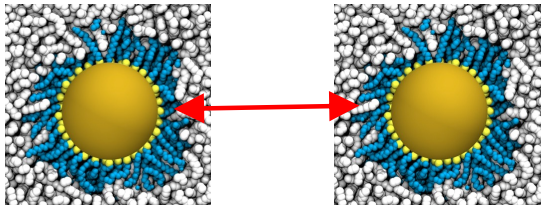
Add surface active molecules during synthesis or via exchange

Classical colloid theory approach

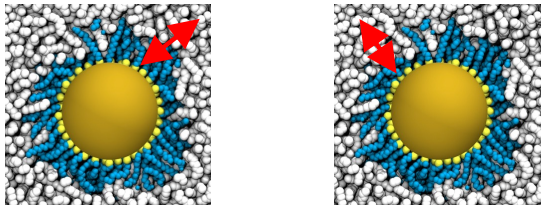
1) Core-core → Hamaker-Lifshitz theory



2) Ligand steric → Alexander-de Gennes theory



3) Ligand-solvent → Flory-Huggins theory

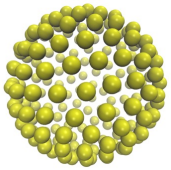


Langmuir **25** (2009) 13861

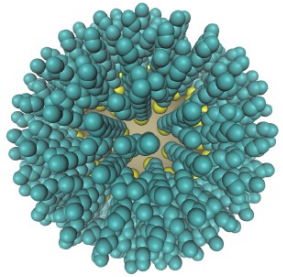
Fails in many cases

Our approach: SAXS + MD simulations

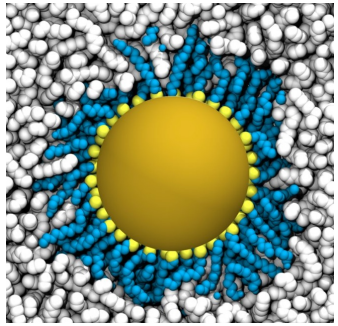
4-10 nm spherical core



3.6-5.5 ligands/nm^2



add tails (e.g. SC_{16})



add solvent

- United atom model (CH_x beads) for the ligand and solvent (TraPPE)

Martin and Siepmann *J. Phys. Chem. B* 102 (1998) 2569

$$u(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \qquad u_{\text{bend}} = k_\theta(\theta - \theta_0)^2/2 \qquad u_{\text{tors}} = c_1[1 + \cos\phi] + c_2[1 - \cos(2\phi)] + c_3[1 + \cos(3\phi)]$$

- Hamaker potential for core-core and core-CH_x interactions

- NPT or NVT molecular dynamics at the correct bulk solvent density

ACS Nano **12** (2018) 5969

Changing core diameter: Au-SC_{16} in decane

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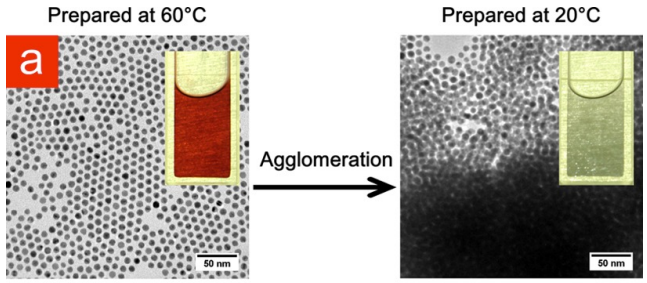
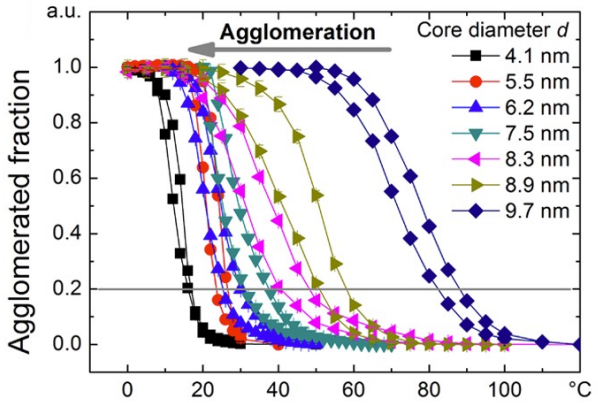
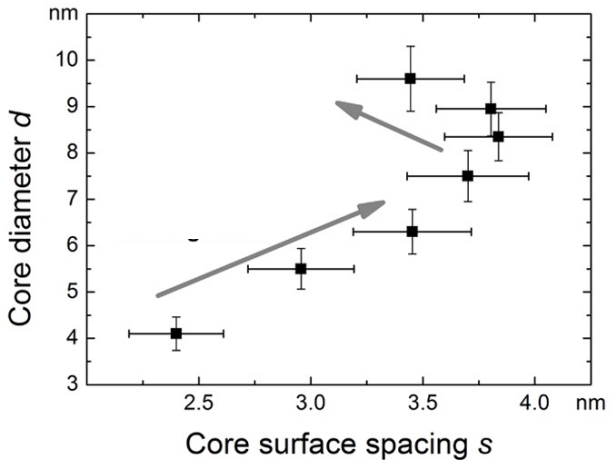
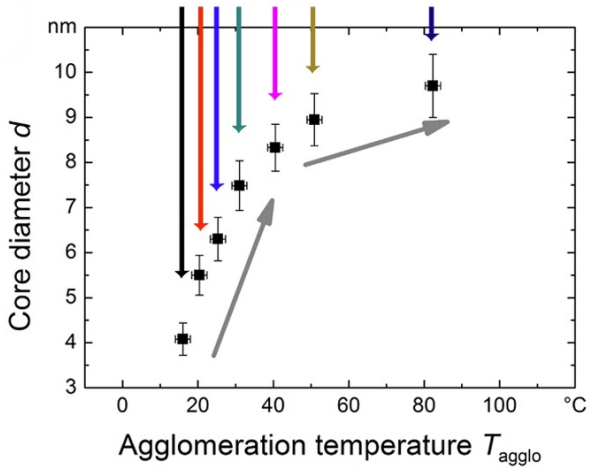


SAXS – Tobias Kraus' group

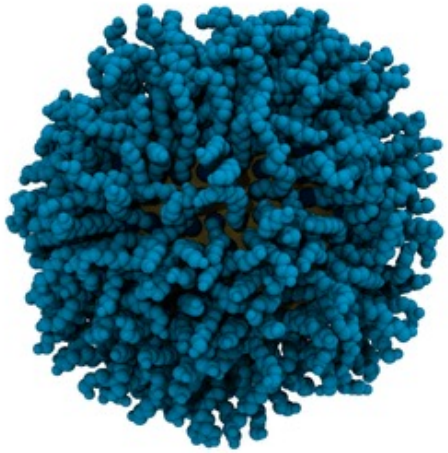


What is responsible for these trends?

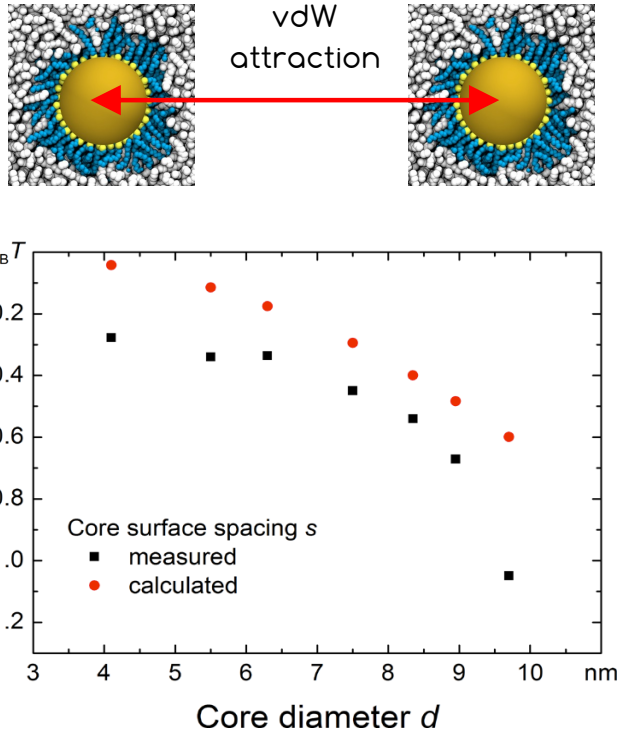




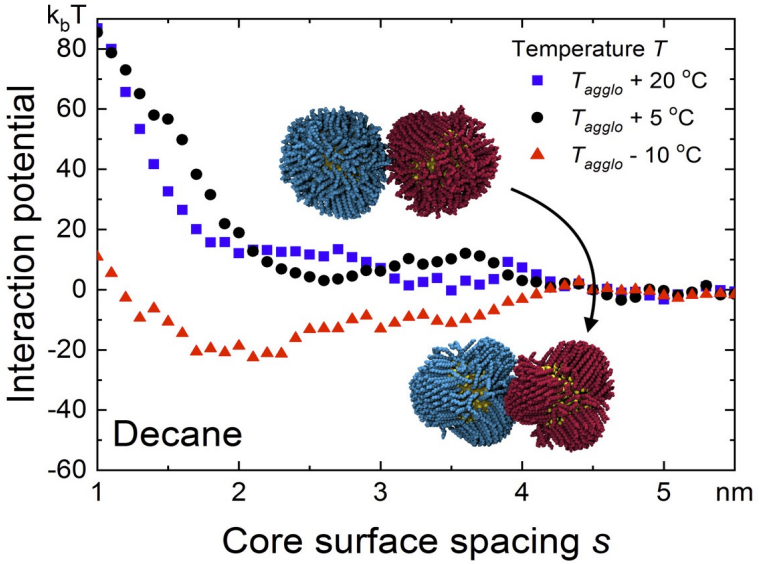
The conformational state of the ligand shell can change



There is a transition from core- to shell-driven agglomeration



vdW attraction between cores is too weak to drive agglomeration except for the largest particles



In this case, ordering of the ligand shell can drive agglomeration

$$\phi_{MF}(r) = \int_r^{\infty} F_{mean}(s) ds$$

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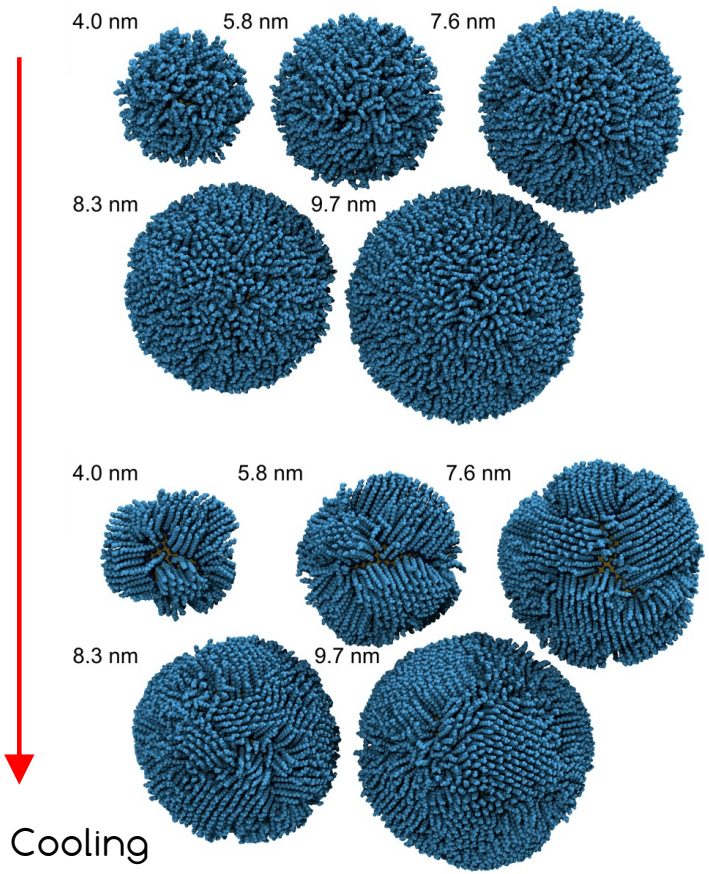
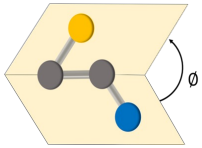
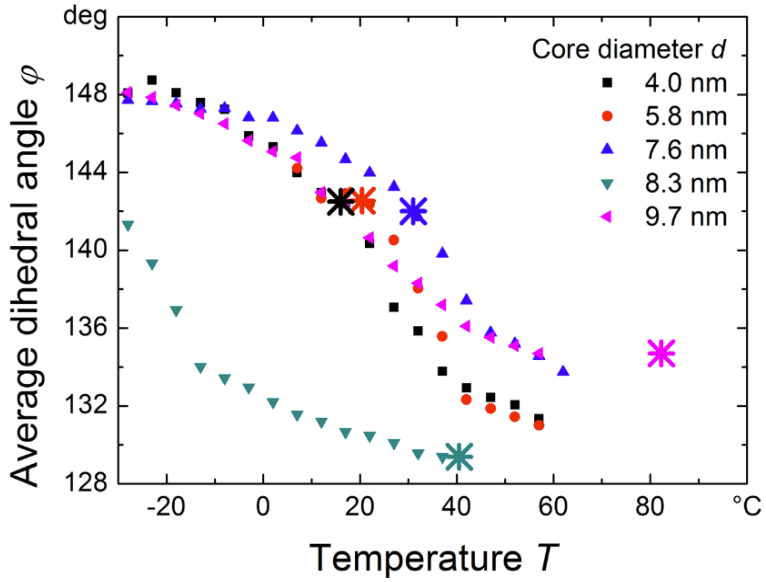
Smaller particles agglomerate when the ligands order







Ligand ordering precedes particle agglomeration (stars) only for particles smaller than ~9 nm

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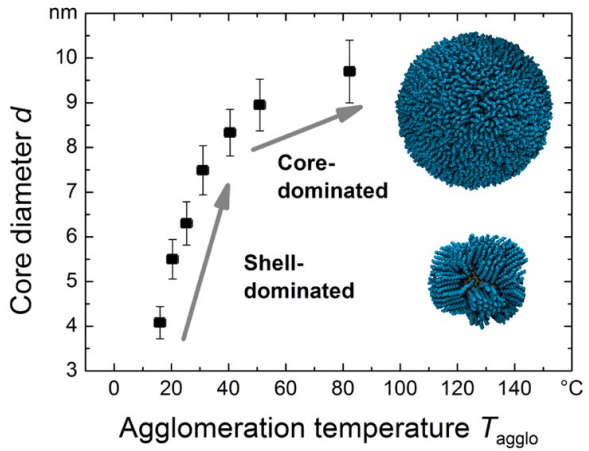
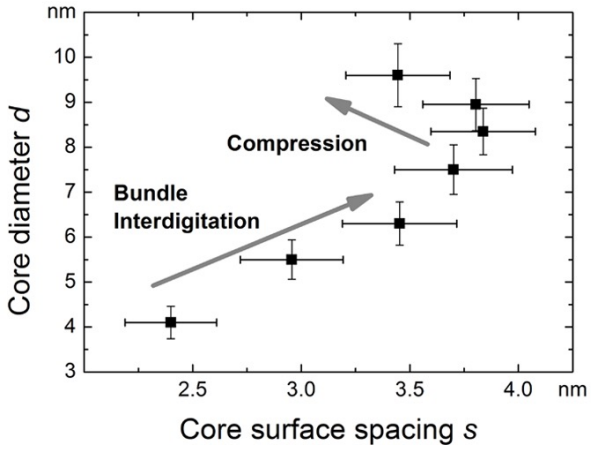
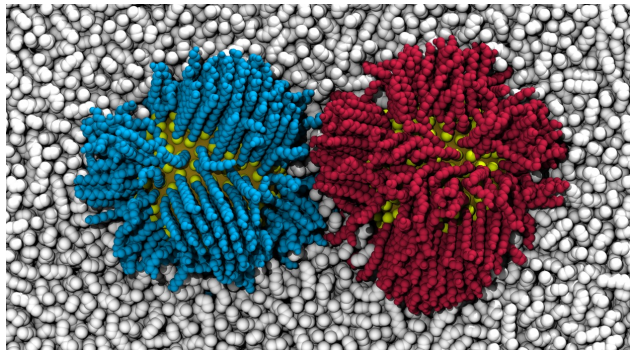
The ligand ordering transition …





Explains:

- non-linear dependence of T_{agglo} on d
- inversion of particle spacing



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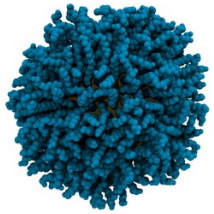
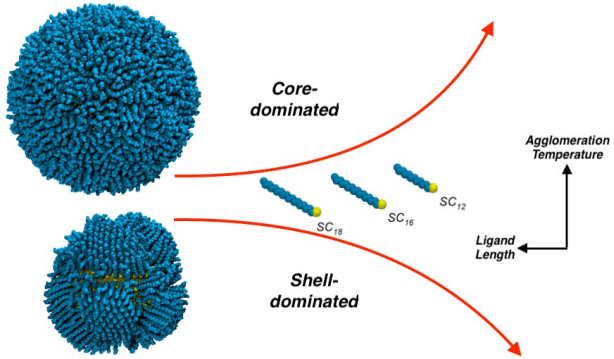


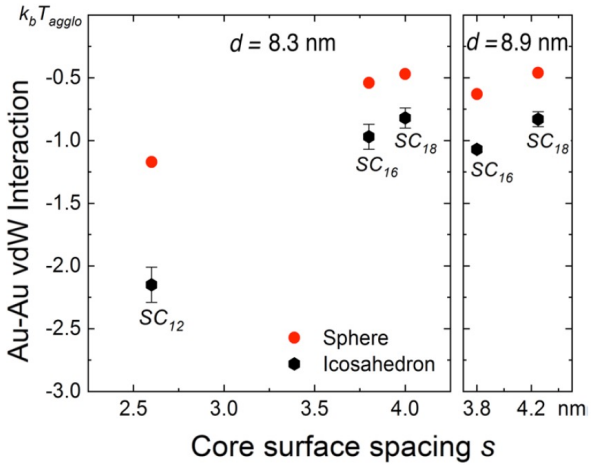
Earlier work (with Phill Geissler):

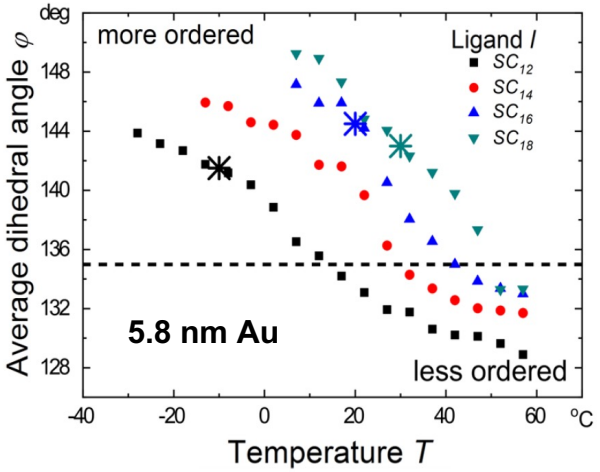
Nano Lett. **14** (2014) 57
ACS Nano **10** (2016) 1877

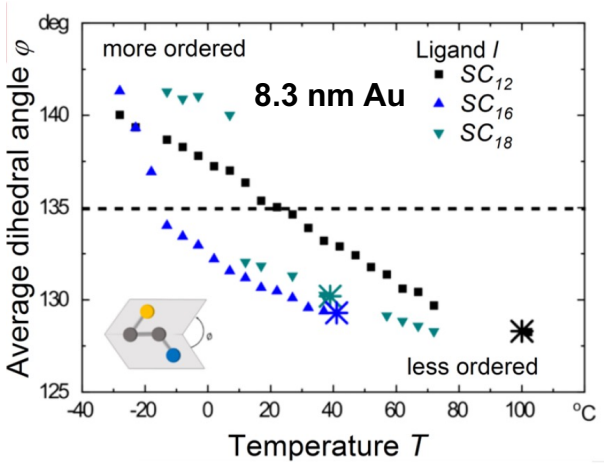
… inverts the effect of changing the ligand length



Langmuir **34** (2018) 12982

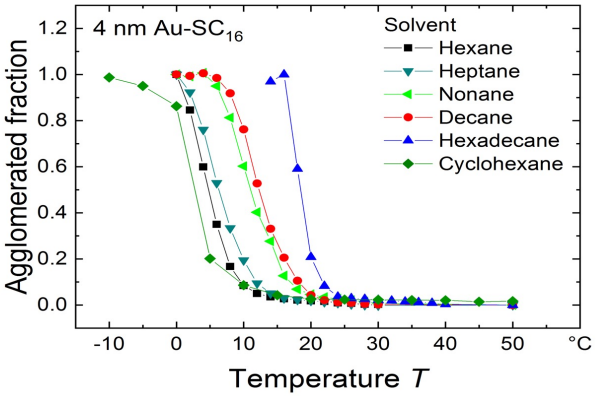


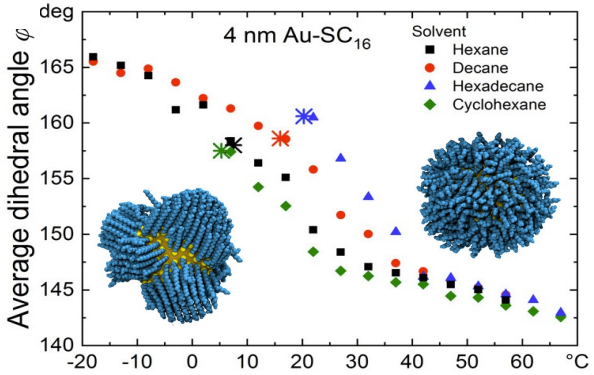




… and explains surprising solvent effects

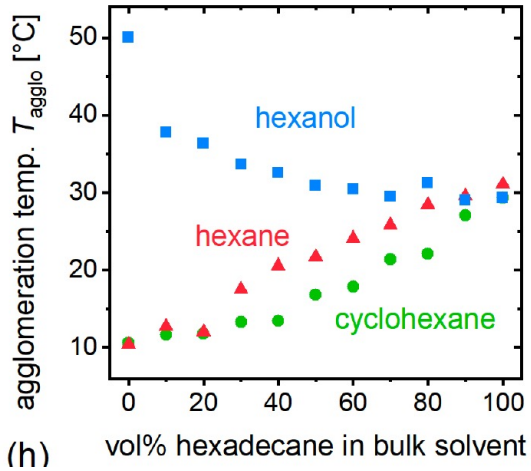
Stability trends inconsistent with simple solvation models

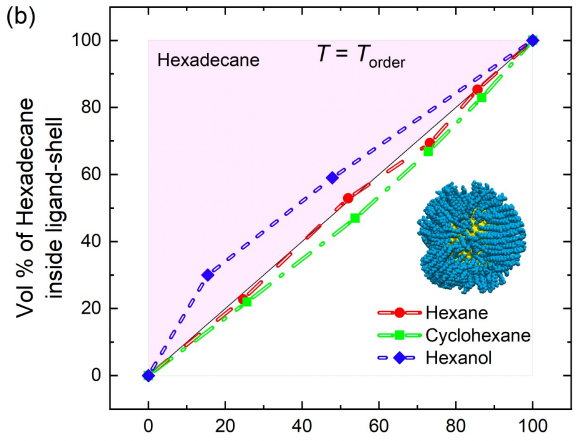




ACS Nano **14** (2020) 5278

Non-linear stability trends in solvent mixtures





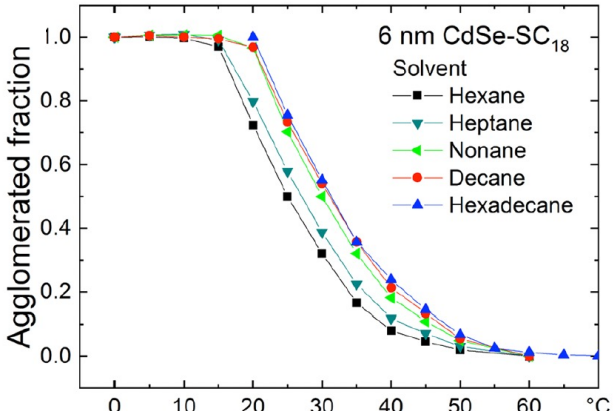
ACS Nano (2023) to appear

Rashed Hasan

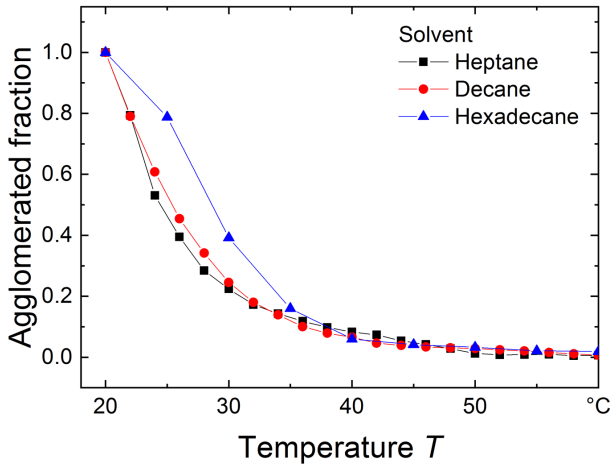
Effect of changing solvent structure

SAXS
Tobias Kraus' group

6 nm
CdSe-SC_{18}



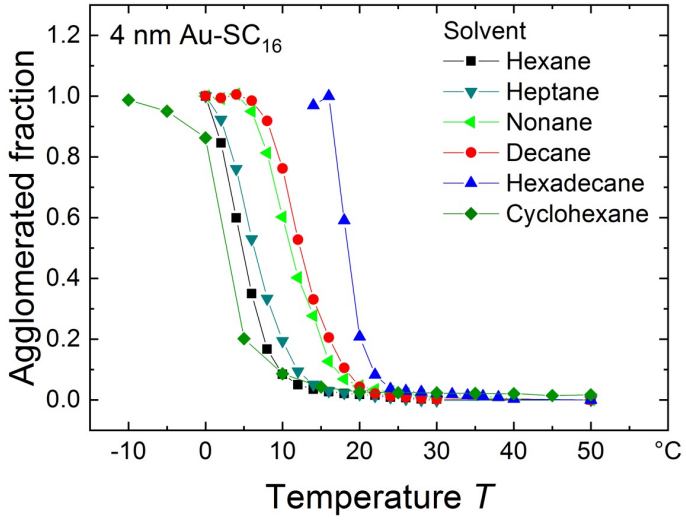
7.4 nm
Au-SC_{16}



Opposite to 'like dissolves like' – why?

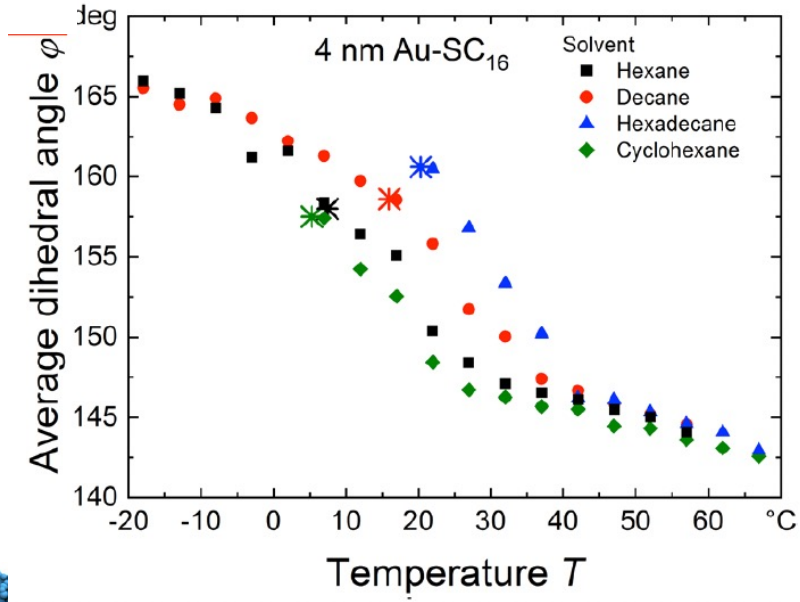
Solvent	Hildebrand Parameter ($Pa^{1/2}$)
	solvent
Hexane	14900
Decane	15800
Hexadecane	16300
Cyclohexane	16732

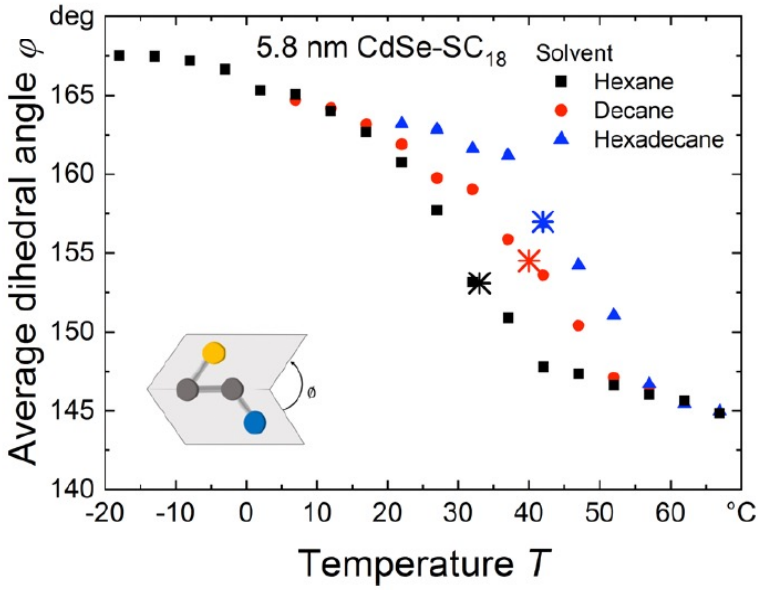
$$\chi = \frac{V_S}{RT}(\delta_L - \delta_S)^2 + 0.34$$

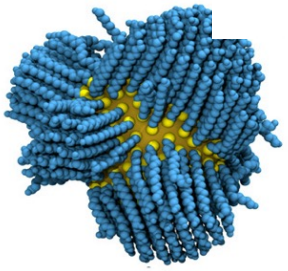


4 nm
Au-SC_{16}

Ligand ordering and particle agglomeration exhibit the same trend

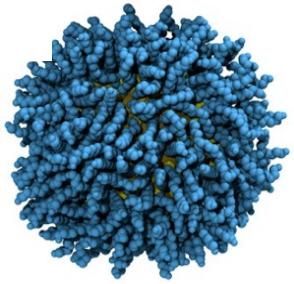






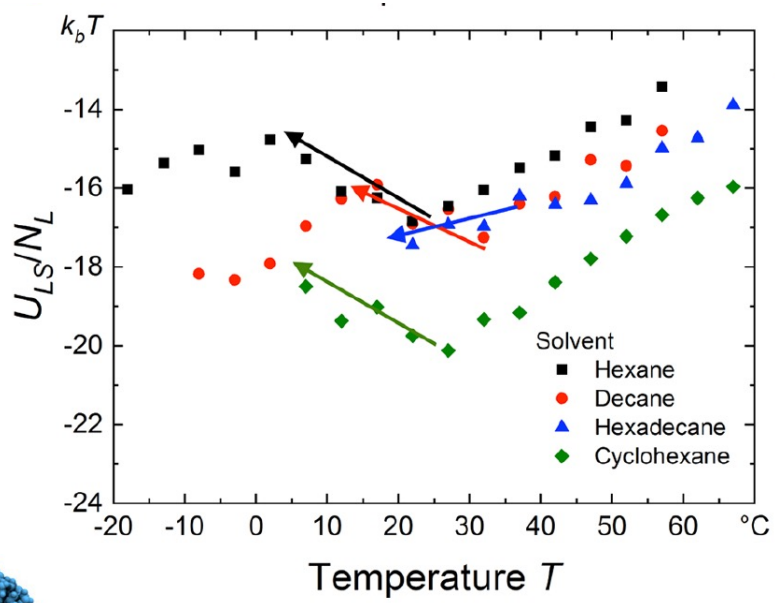
Why do the ligands order at different temperatures?

What is affecting the free energy difference?

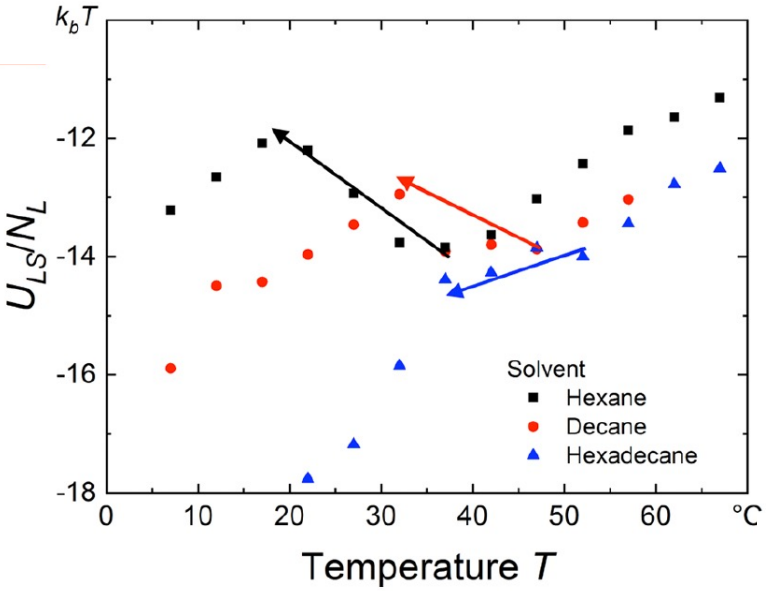


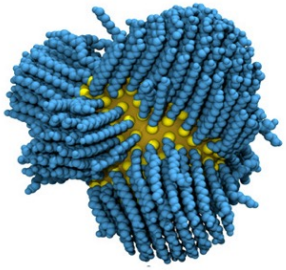
The ligand-solvent interactions differ

4 nm Au-SC_{16}

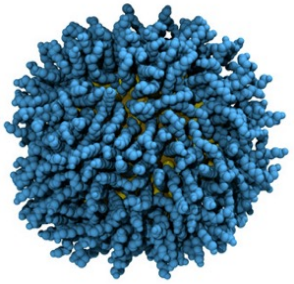


5.8 nm CdSe-SC_{18}

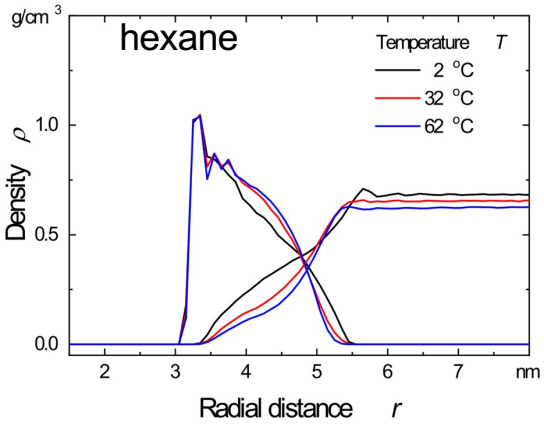


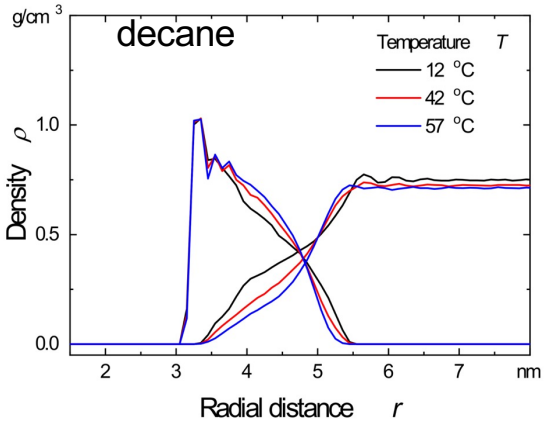


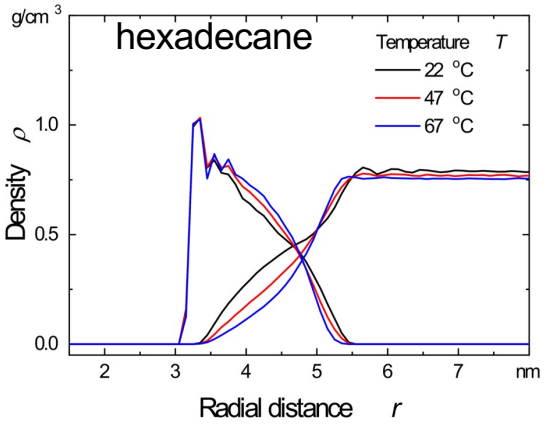
Hexadecane is energetically stabilizing the ligand ordered state – why?



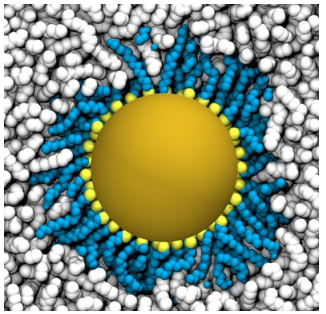
Due to details of ligand-solvent packing

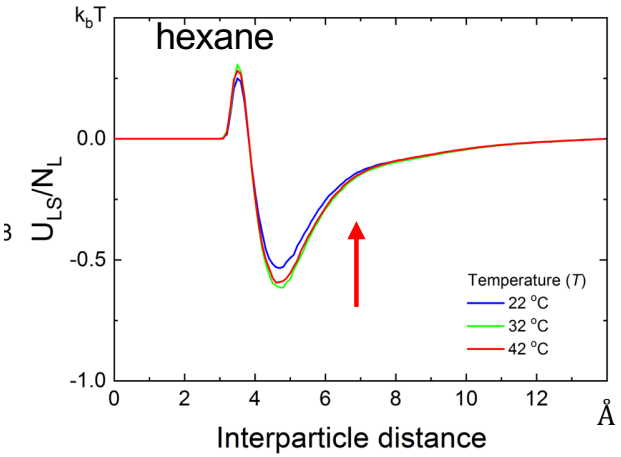


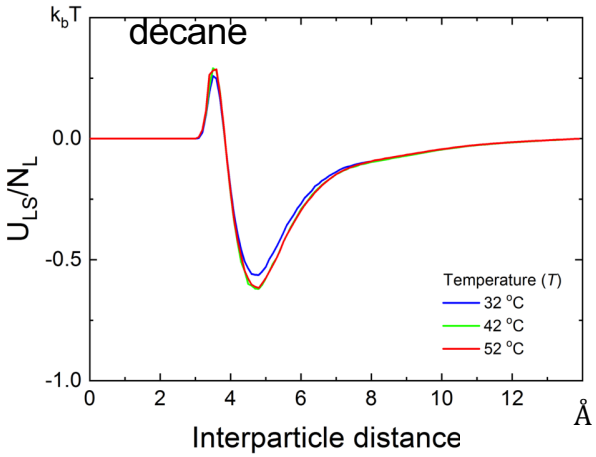


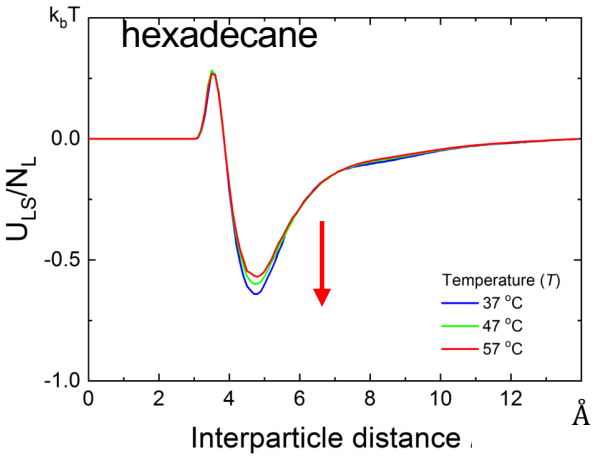


5.8 nm CdSe-SC_{18}









The longer chain solvents pack better with the ligands in the ordered state

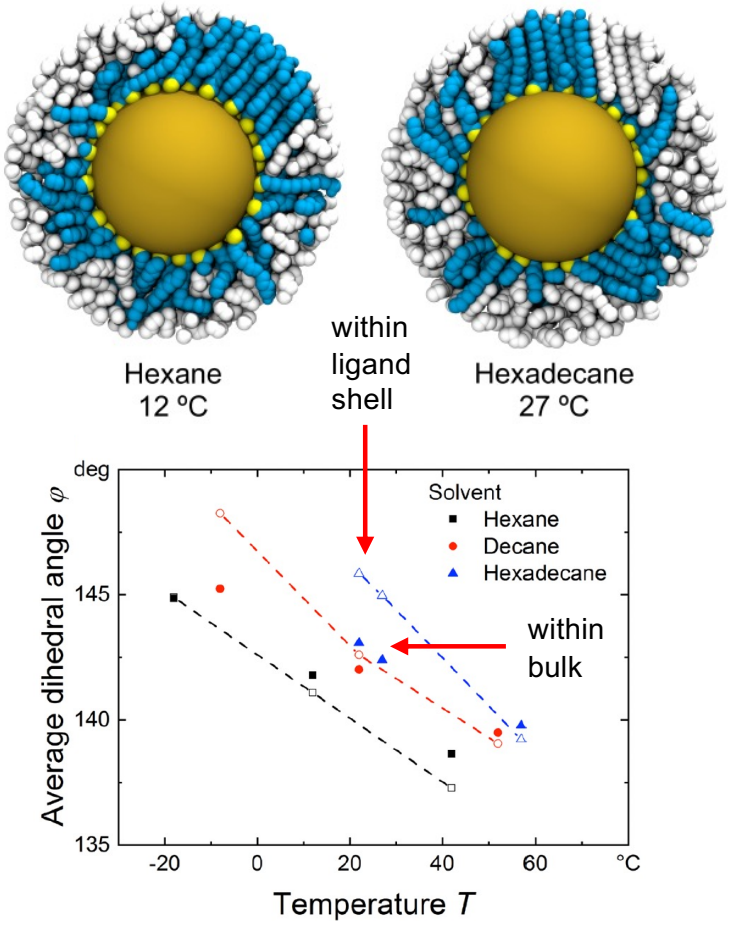
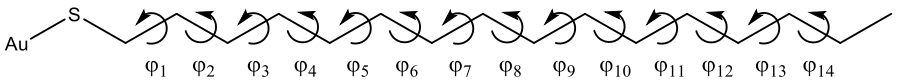


Table 1. Major Enthalpic and Entropic Contributions to the Difference in Free Energy between the Ordered and Disordered Ligand States[a] k_bT/ligand

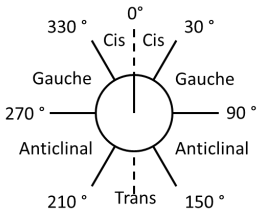
4 nm Au-SC_{16}			
solvent	hexane	decane	hexadecane
T_{order}	290	295	300
ΔU_{LL}	−3.8	−3.7	−3.5
ΔU_{LS}	**4.0**	**2.3**	**1.0**[b]
ΔU_{dih}^{lig}	−2.6	−2.3	−1.8
$-T\Delta S_{mix}$	**0.32**	**0.22**	**0.14**
$-T\Delta S_{conf}^{lig}$	2.5	3.0	2.5
$-T\Delta S_{conf}^{solv}$	0.00	0.00	0.30
5.8 nm CdSe-SC_{18}			
solvent	hexane	decane	hexadecane
T_{order}	300	310	320
ΔU_{LL}	−4.4	−3.5	−3.1
ΔU_{LS}	**4.3**	**2.6**	**1.3**
ΔU_{dih}^{lig}	−1.9	−1.8	−1.3
$-T\Delta S_{mix}$	**0.54**	**0.37**	**0.25**
$-T\Delta S_{conf}^{lig}$	2.2	2.8	2.2
$-T\Delta S_{conf}^{solv}$	−0.17	0.12	−0.09

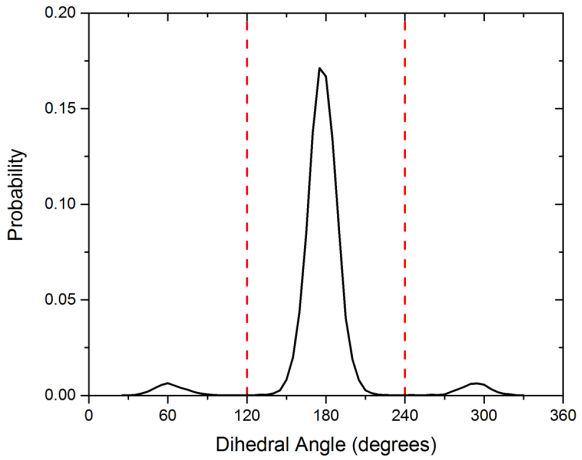
Estimating conformational entropy of ligands and solvent

$$S = -k_B \sum_r p(r) \ln[p(r)]$$

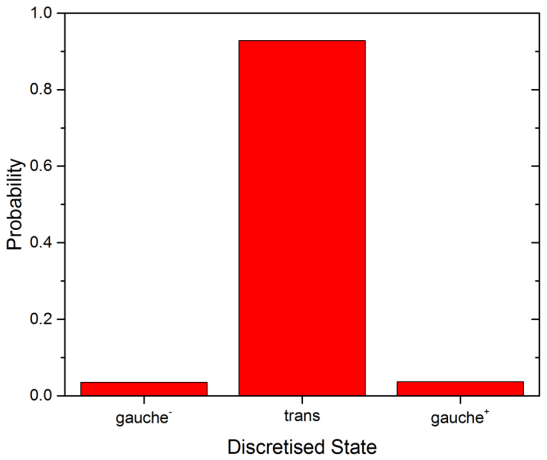


- Treat each ligand independently (will overestimate more in ordered state)
- Discretise data





discretisation

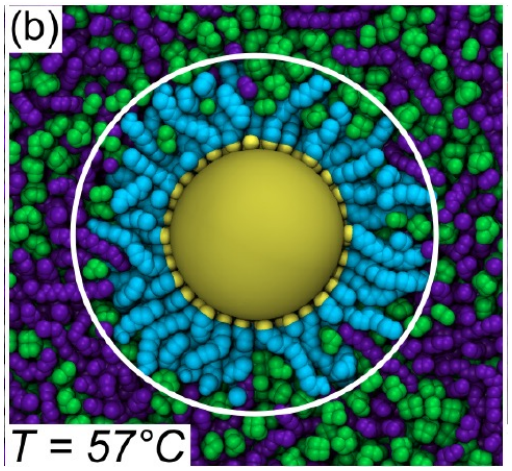


- # of ligand microstates = $3^{14} \approx 10^7$
- Estimate using the Cencalc CC-MLA method (converges rapidly)

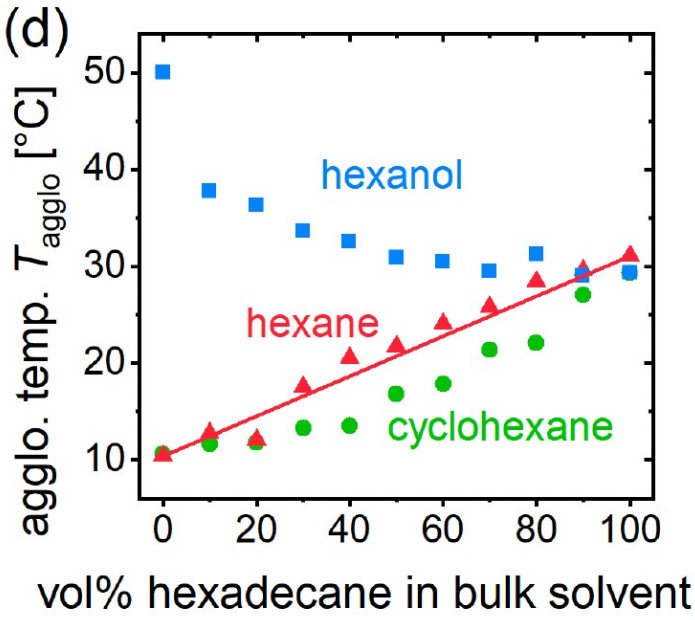
JCP **137** (2012) 084115

Effect of mixing solvents – solvent engineering

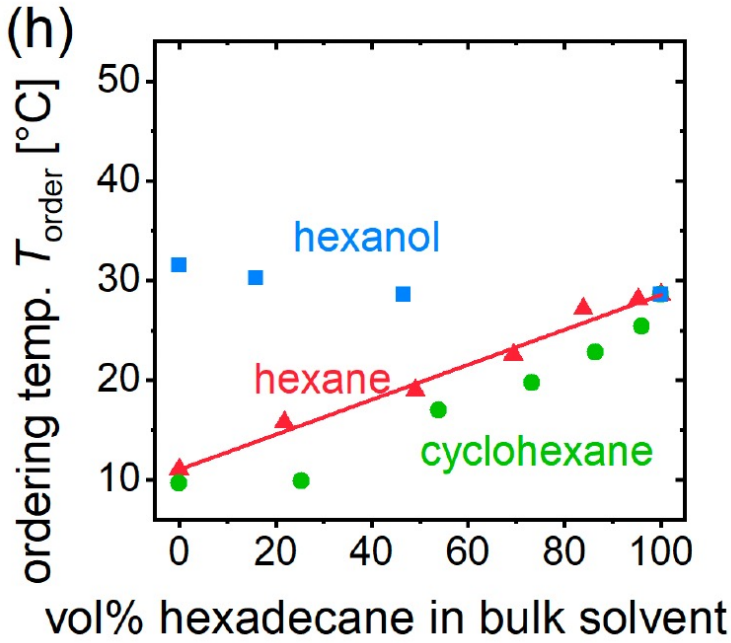
4 nm
Au-SC_{16}



SAXS



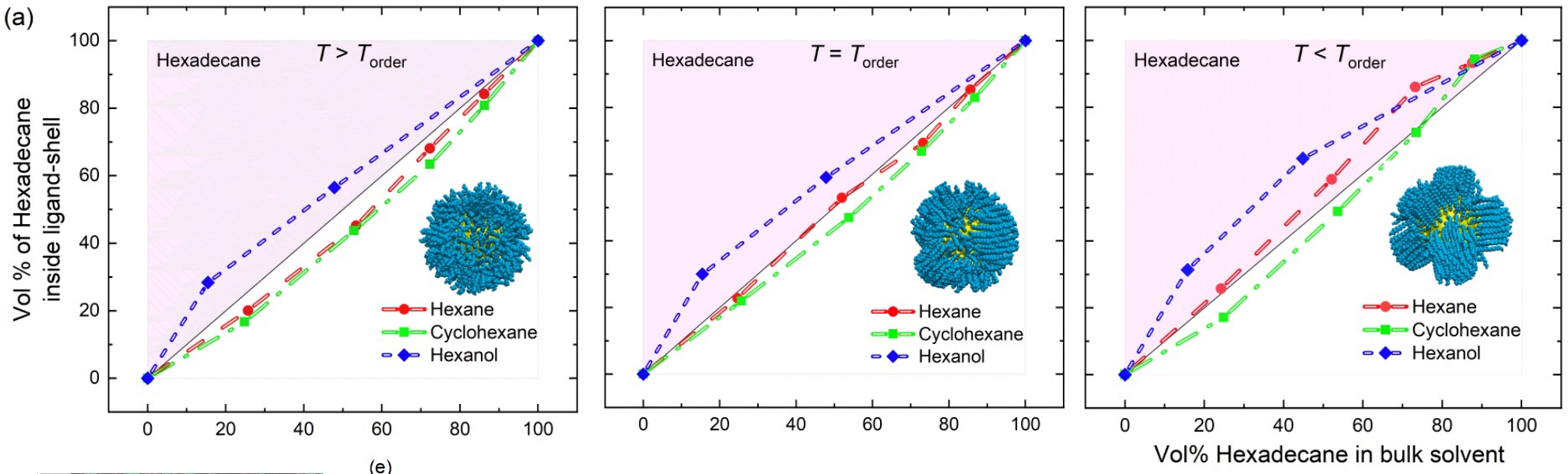
Simulation

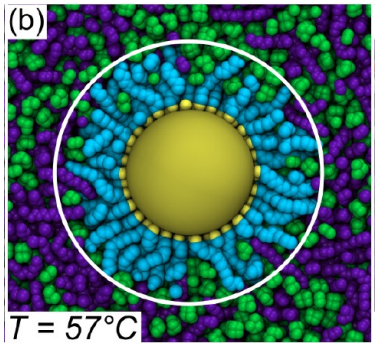


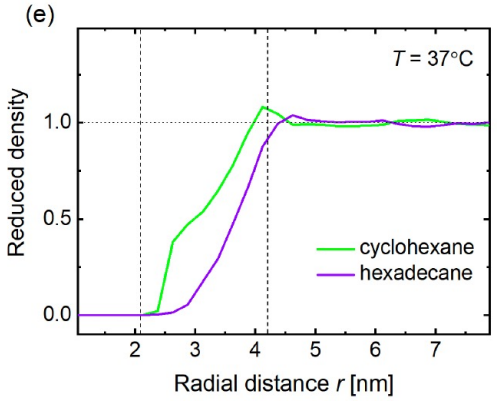
1) Hexadecane + hexane
2) Hexadecane + cyclohexane
3) Hexadecane + hexanol

What is responsible for the non-linear trends?

Solvent composition near ligand shell can differ from the bulk

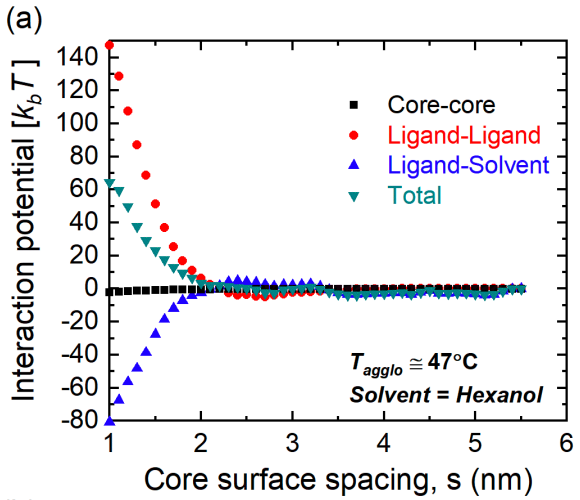


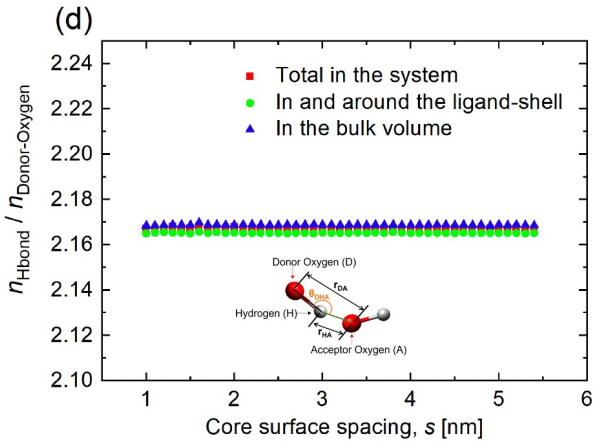


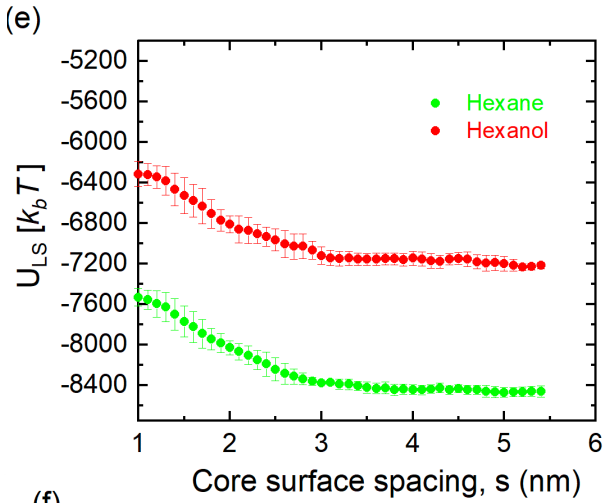


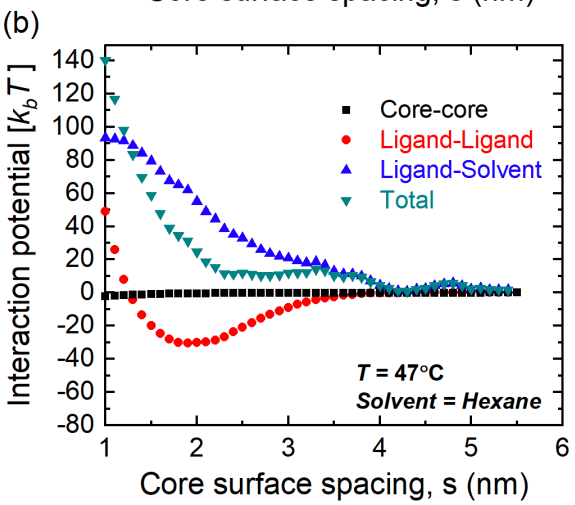
Ligands see solvent enhanced in one component, which can differ depending on the ligand state

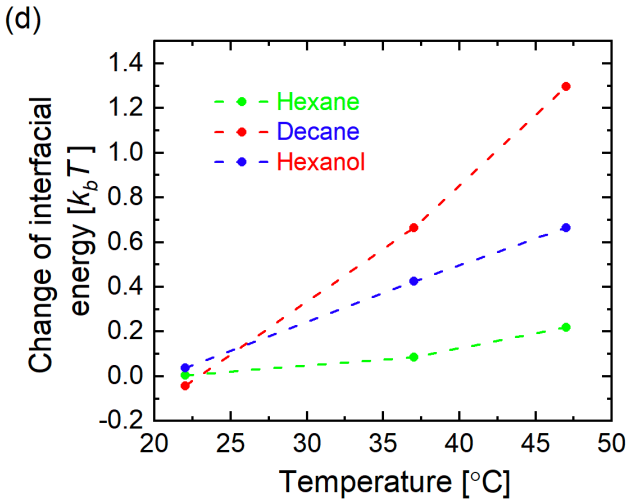
Why is T_{agglo} >> T_{order} in pure hexanol?

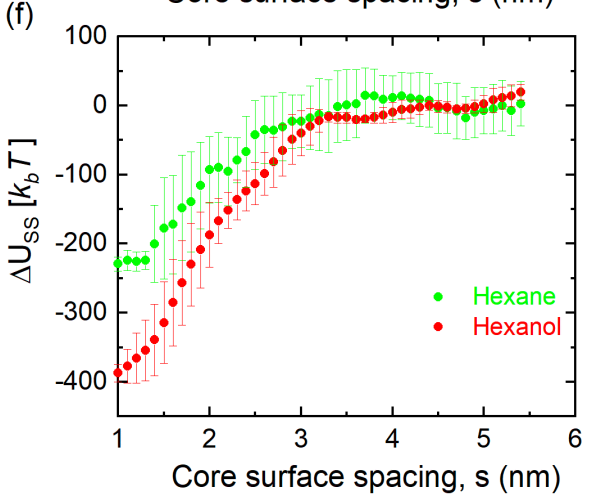






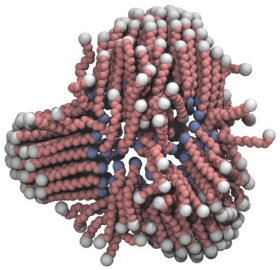




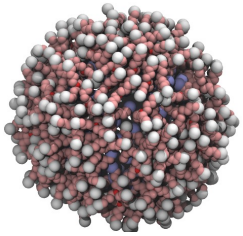


Ligands that inhibit ordering increase stability

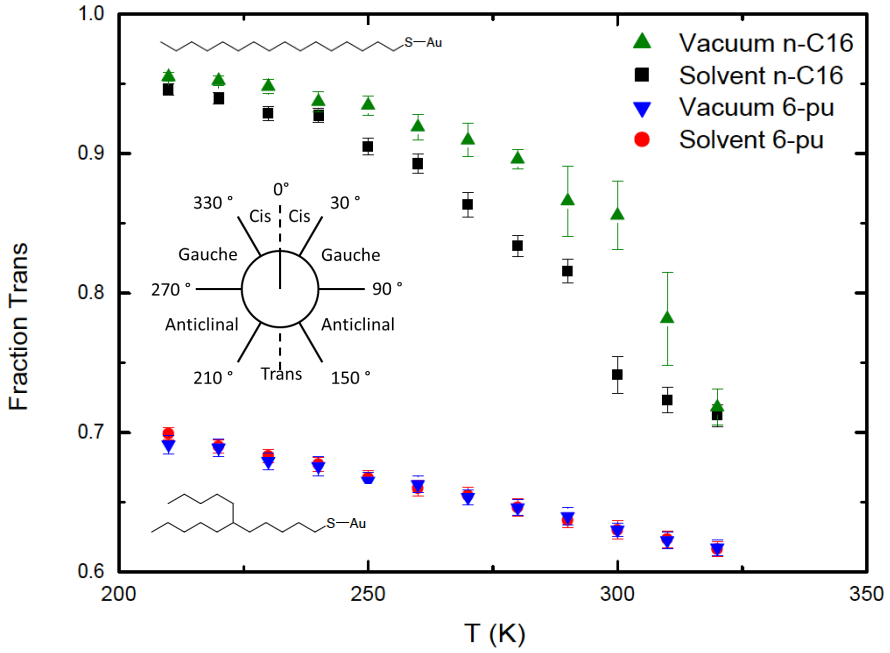
See e.g. Yang et al. *Nano Lett.* **16** (2016) 2127

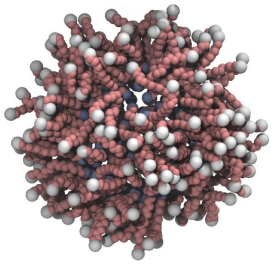


linear

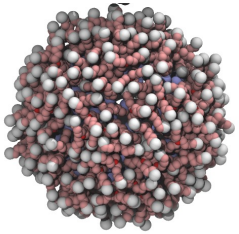


branched

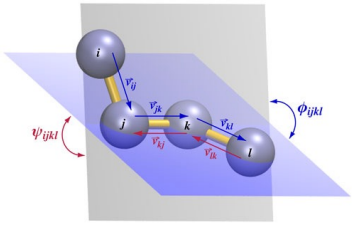




linear



branched

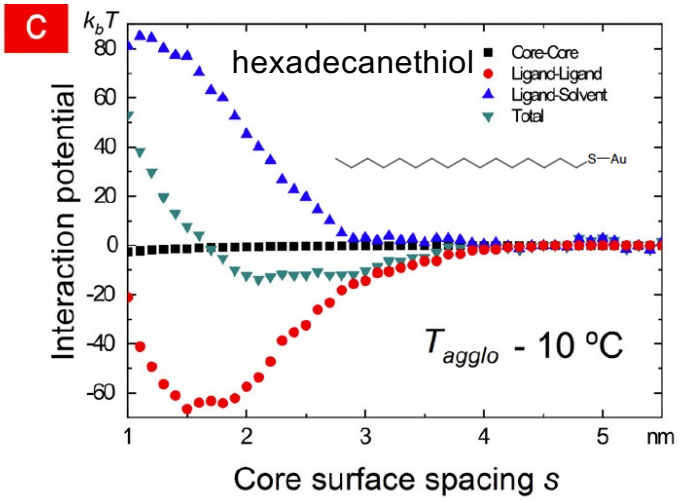


Changing the branch point or length yields similar results, as does adding a *cis* double bond

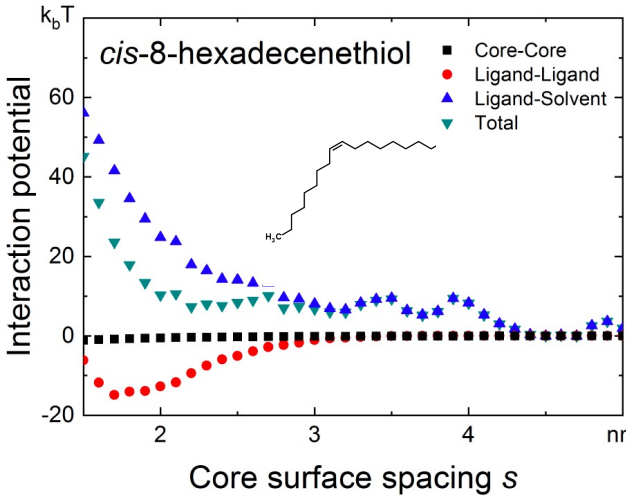
Ligands that inhibit ordering increase stability

4 nm AuNP in hexane

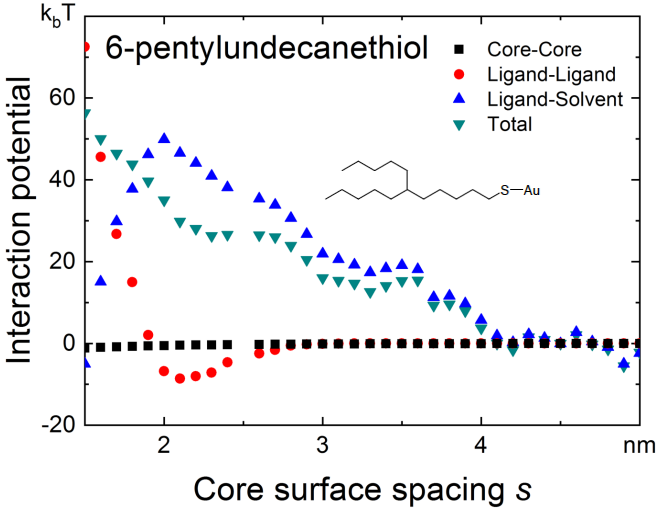
5 °C



-53 °C



-53 °C



Conclusions (1)

The ability of the ligand shell to order (or not) can explain colloidal stability in cases where classical colloid theory fails, including:

- Transition from core- to shell-dominated agglomeration
- Inversion of the effect of ligand length on stability
- Solvent trends inconsistent with simple solvation models
- Dramatic dependence on ligand structure

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- James Smith
- Leo Jiang

Leibnitz Institute for New Materials
- Prof Tobias Kraus
- Thomas Kister
- David Doblas

University of Melbourne
- Prof Paul Mulvaney
- Nick Kirkwood

2) Morphology of nanoplatelets

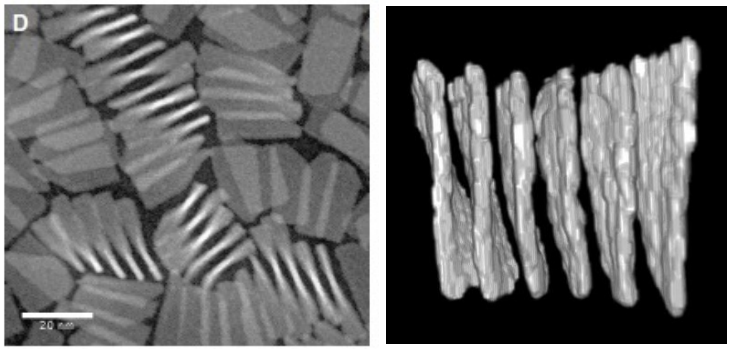
Asaph Widmer-Cooper

Marion Krapez, Debora Monego

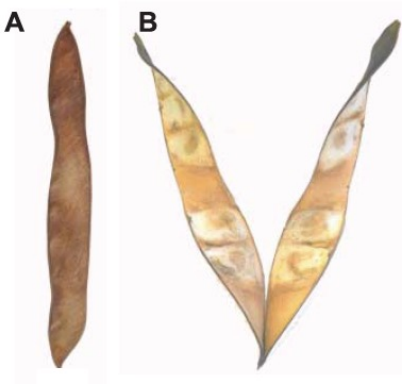
School of Chemistry, University of Sydney

Australian Research Council Centre of Excellence in exciton science

Sarit Dutta, Benjamin Abecassis, CNRS, ENS Lyon



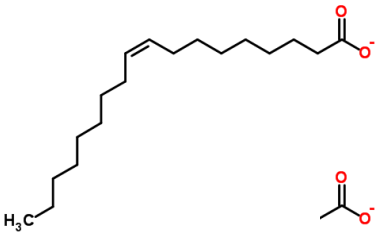
Science Advances 2017, 3, e1701483

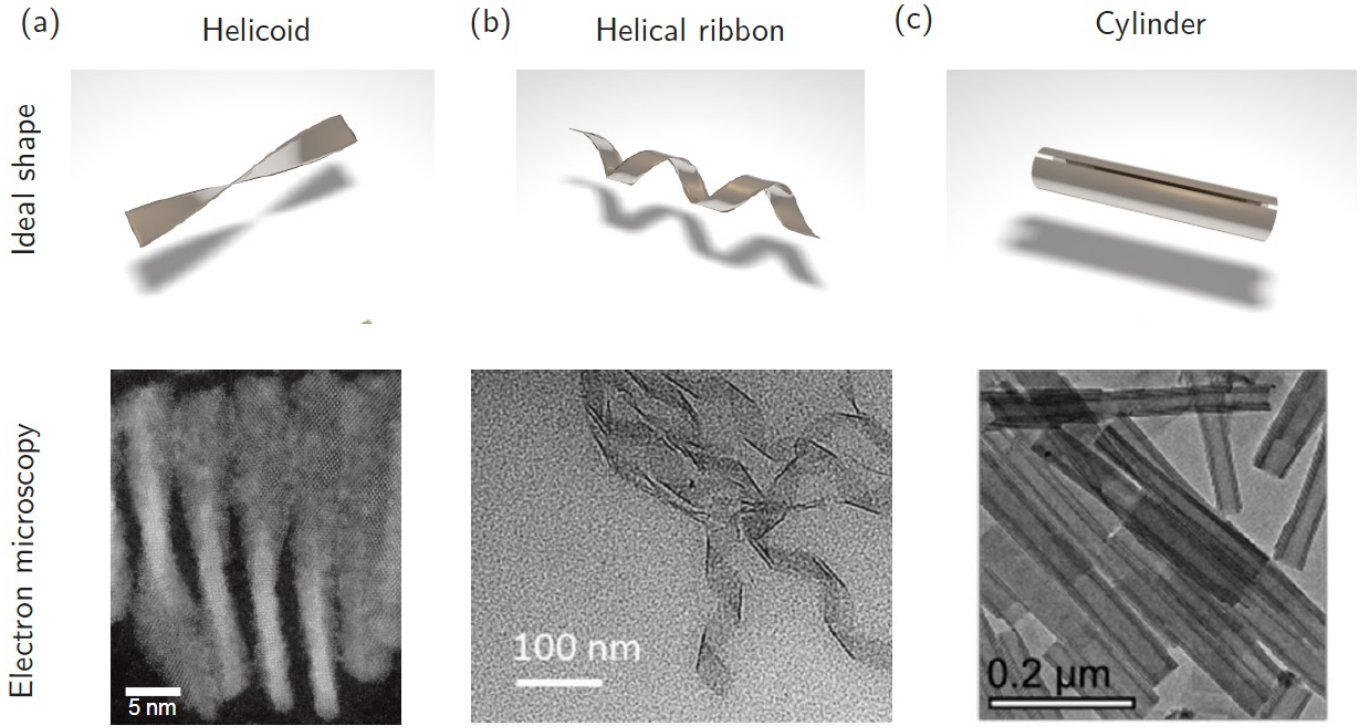


Science 2011, 333, 1726

CdSe nanoplatelets

- 7-15 atomic layers thick (Cd on top and bottom)
- 10s-100s nm side length
- Zincblende crystal structure (dots and rods are wurtzite)



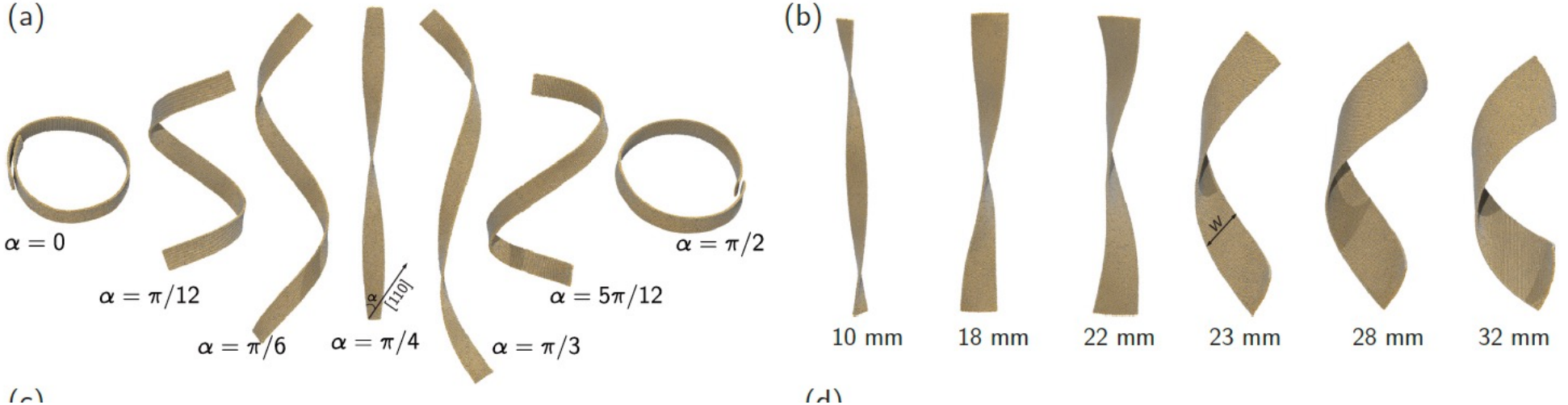


Simulation setup

- Considered 3 different shapes (7 atomic layers thick, ~10 nm in side length)
- Used OPLS-AA force field for the ligands (also LJ/coulomb type)
- No explicit solvent

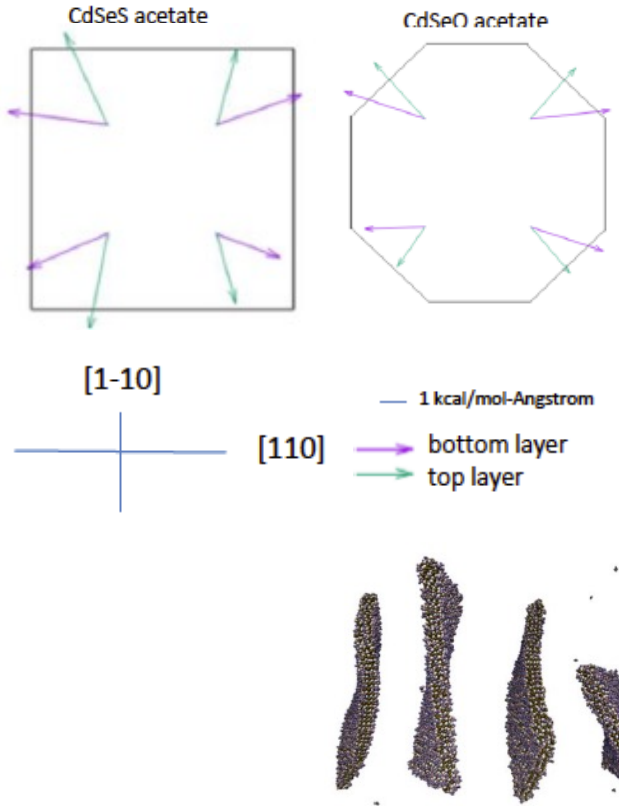
1. Add sufficient ligands to neutralise overall charge
2. Allow ligands to adsorb
3. Allow the full system to equilibrate

Results


(a)
α = 0
α = π/12
α = π/6
α = π/4
α
[110]
α = π/3
α = 5π/12
α = π/2
(b)
10 mm
18 mm
22 mm
23 mm
w
28 mm
32 mm

Universal origin of twisting

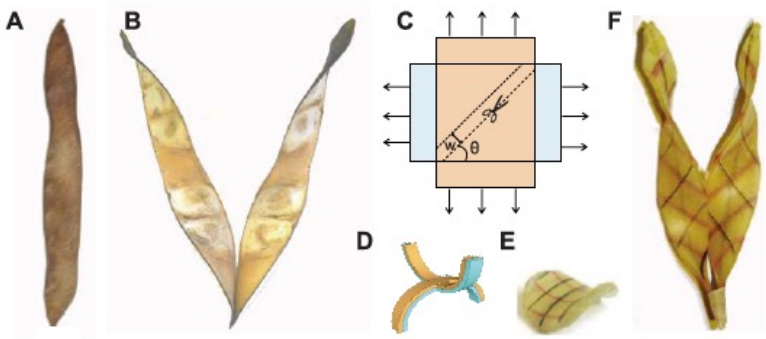
Stress anisotropy in NPLs

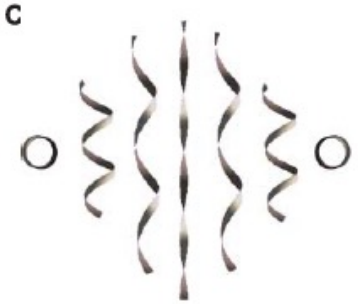


Geometry and Mechanics in the Opening of Chiral Seed Pods

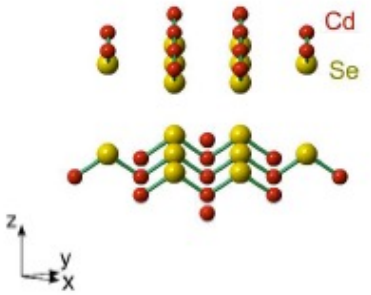
Shahaf Armon,[1] Efi Efrati,[1] Raz Kupferman,[2] Eran Sharon[1]*

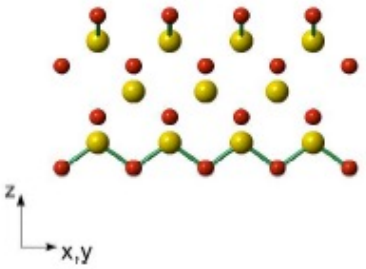
Science 2011, 333, 1726

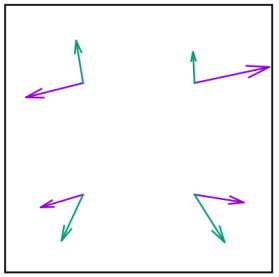




Chemical origin of twisting in CdSe NPLs

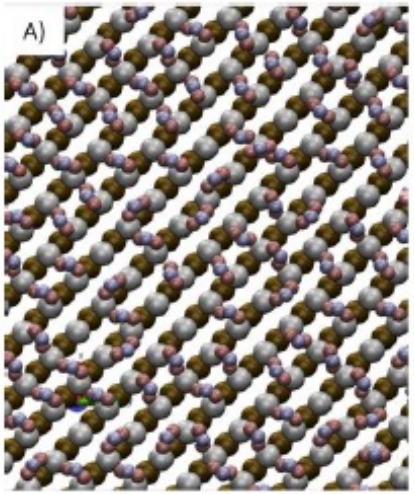


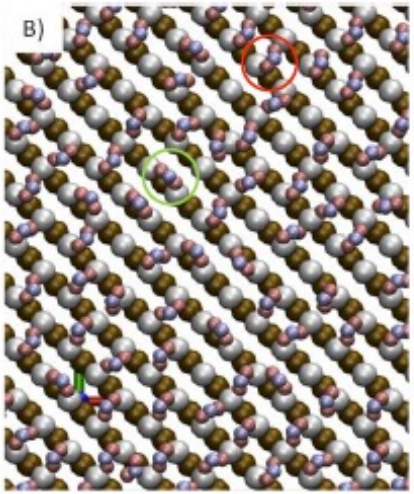


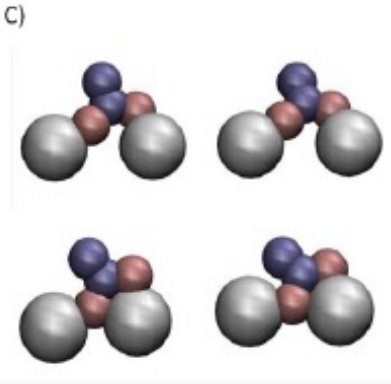


Bare crystal

With ligands







initial

final

Ligands hold the rows together

Conclusions (2)

- Rolling and twisting of NPLs is due to the same physical mechanism that causes some seed pods to twists open, i.e. directional stress anisotropy in the top and bottom surfaces
- For CdSe NPLs, the anisotropy arises due to the interaction of a directionally anisotropic crystal surfaces (zincblende) and ligands preferentially binding in such a way that the top and bottom surfaces want to expand in different directions

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