Integrated Materials Design: Accelerating the Discovery of New Functional Materials

Sean Smith

Never Stand Still

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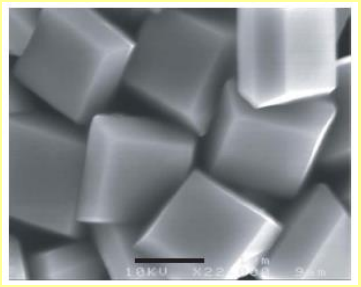
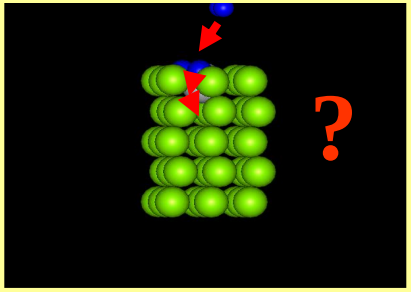
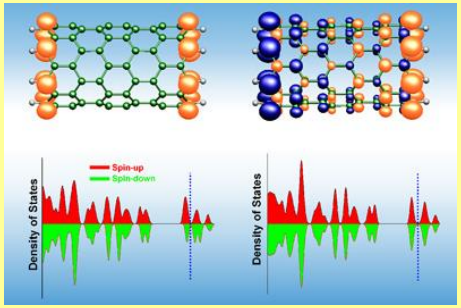
Smith team research (UQ/ORNL/UNSW): Computational Nano(bio)science and Engineering



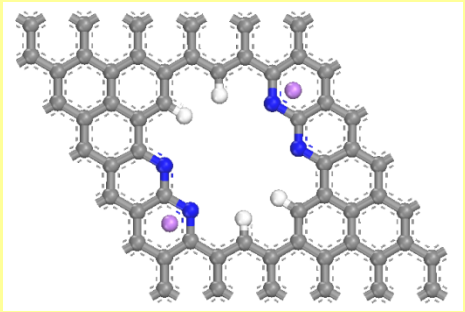
TiO_2 for photocatalysis



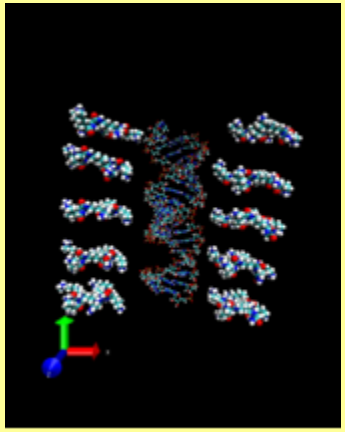
Catalysis in hydrogen storage



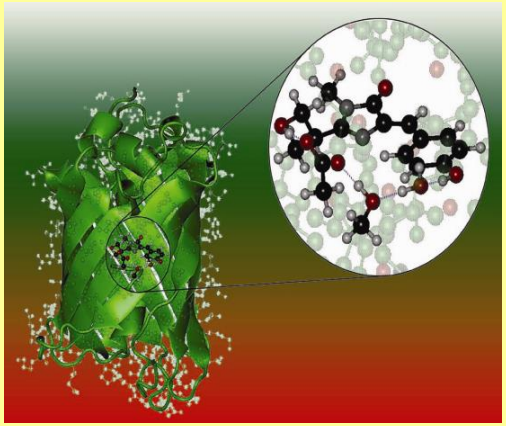
Functional 1D nano-architectures: electronics & light emission



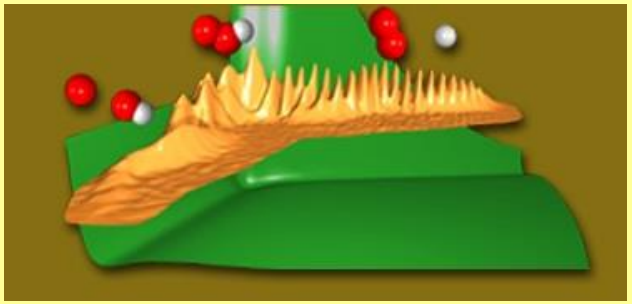
Functional 2D materials: membranes, supercapacitors, electronics, photovoltaics, catalysis



Vector-RNA interactions in gene delivery



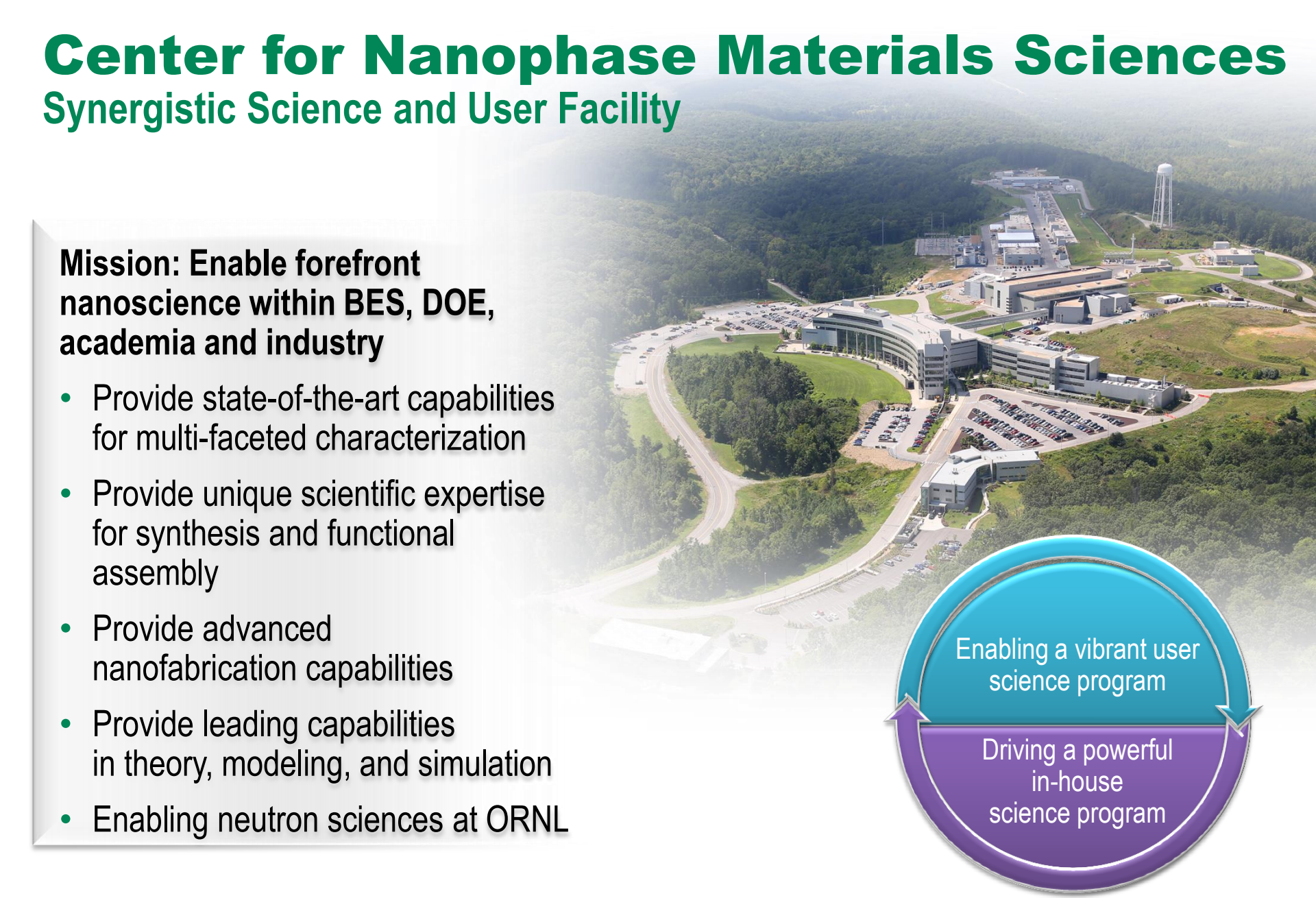
Fluorescent Proteins



Reaction Dynamics

Center for Nanophase Materials Sciences

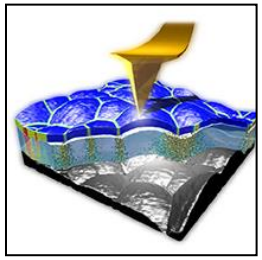
Synergistic Science and User Facility



Mission: Enable forefront nanoscience within BES, DOE, academia and industry

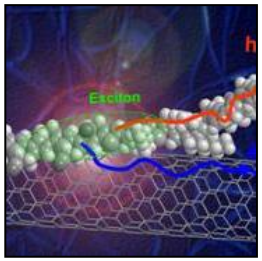
- Provide state-of-the-art capabilities for multi-faceted characterization
- Provide unique scientific expertise for synthesis and functional assembly
- Provide advanced nanofabrication capabilities
- Provide leading capabilities in theory, modeling, and simulation
- Enabling neutron sciences at ORNL

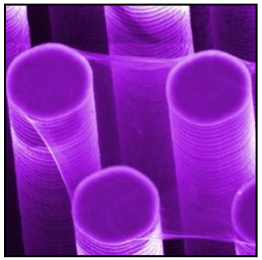
Center for Nanophase Materials Sciences
AT OAK RIDGE NATIONAL LABORATORY



Imaging and Nanoscale Characterization
Art Baddorf
Staff: 12
Postdocs/students: 11

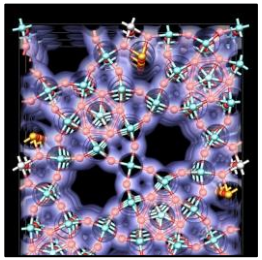
Nanomaterials Synthesis and Functional Assembly
Dave Geohegan
Staff: 24
Postdocs/students: 17





Nanofabrication
Mike Simpson
Staff: 14
Postdocs/students: 6

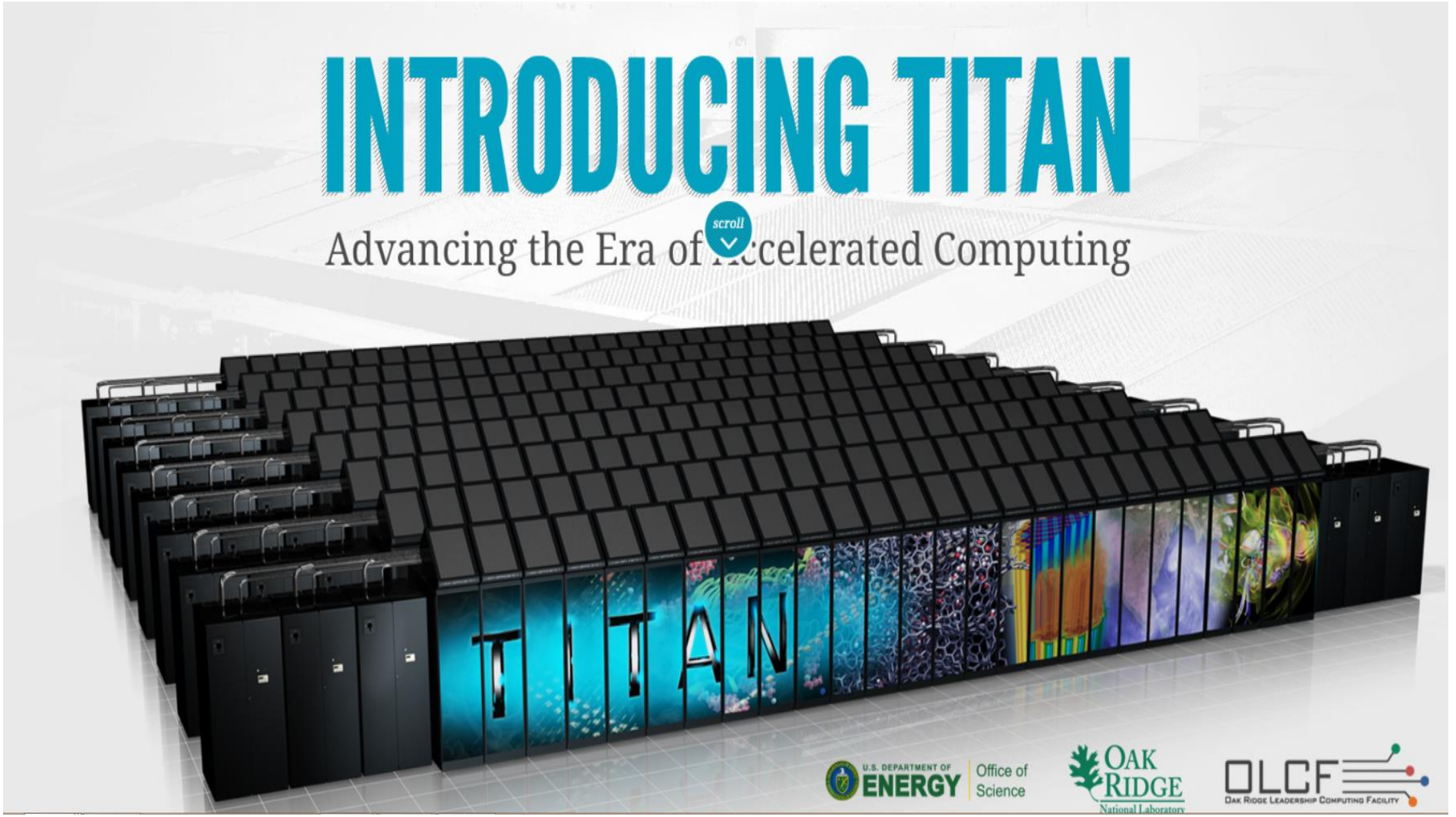
Nanomaterials Theory
Bobby Sumpter
Staff: 19
Postdocs/students: 7



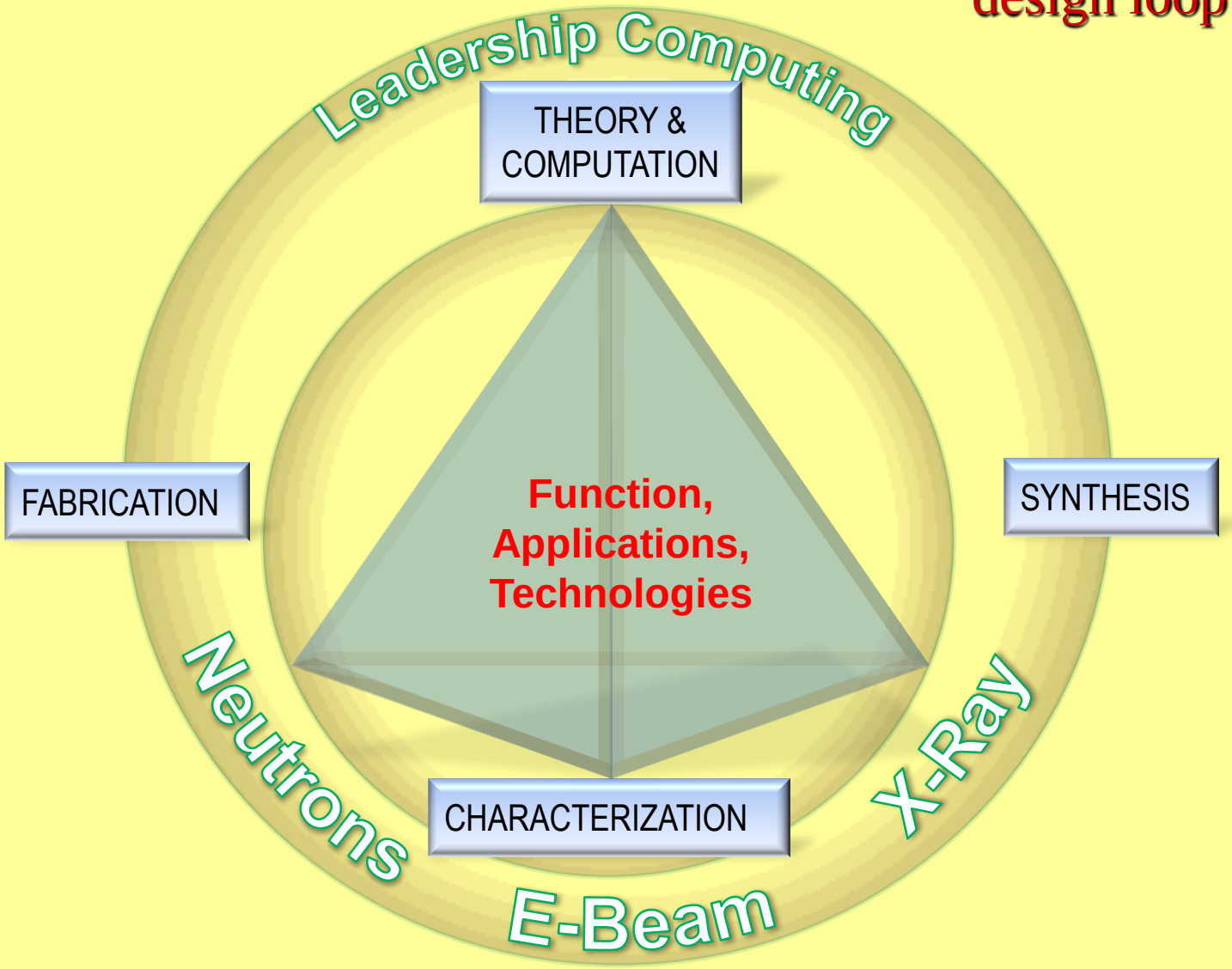
But, where to beyond the NNI?

- Mesoscale science
- Materials Genome

Computing power will be a major force towards accelerated discovery of new materials



FUTURE MATERIALS DISCOVERY: A powerfully integrated materials design loop



High throughput computing + Small volume material synthesis + High throughput characterization = Rapid Discovery of New Functional Materials

Computational Modelling has several major contributions to make here:

- Pre-screening of promising materials for different applications.
- Aiding development of synthetic routes to make new materials.
- Helping to interpret and understand experimental results.
- Making “blue sky” predictions of new materials and properties
- Helping understand molecular mechanisms where it is complex to figure it out any other way.

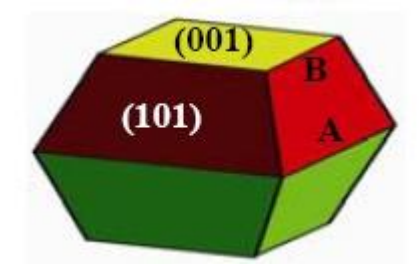
TiO_2 Single Crystals: Photocatalysis and Photoconversion

- *Many* applications for TiO_2 (nano)particles:
  - photocatalysis for water purification or water splitting
  - solar energy cells

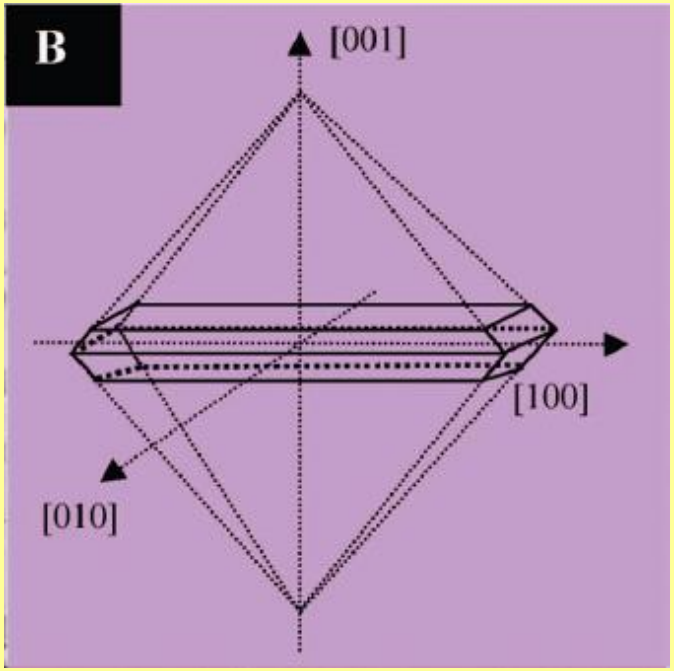
- Anatase TiO_2 single crystals with very large proportion of highly reactive surfaces – almost a contradiction of terms!!

- Synthesis and doping strategies to intrinsically modify TiO_2 spectral properties for *visible* light absorption (no dyes!).

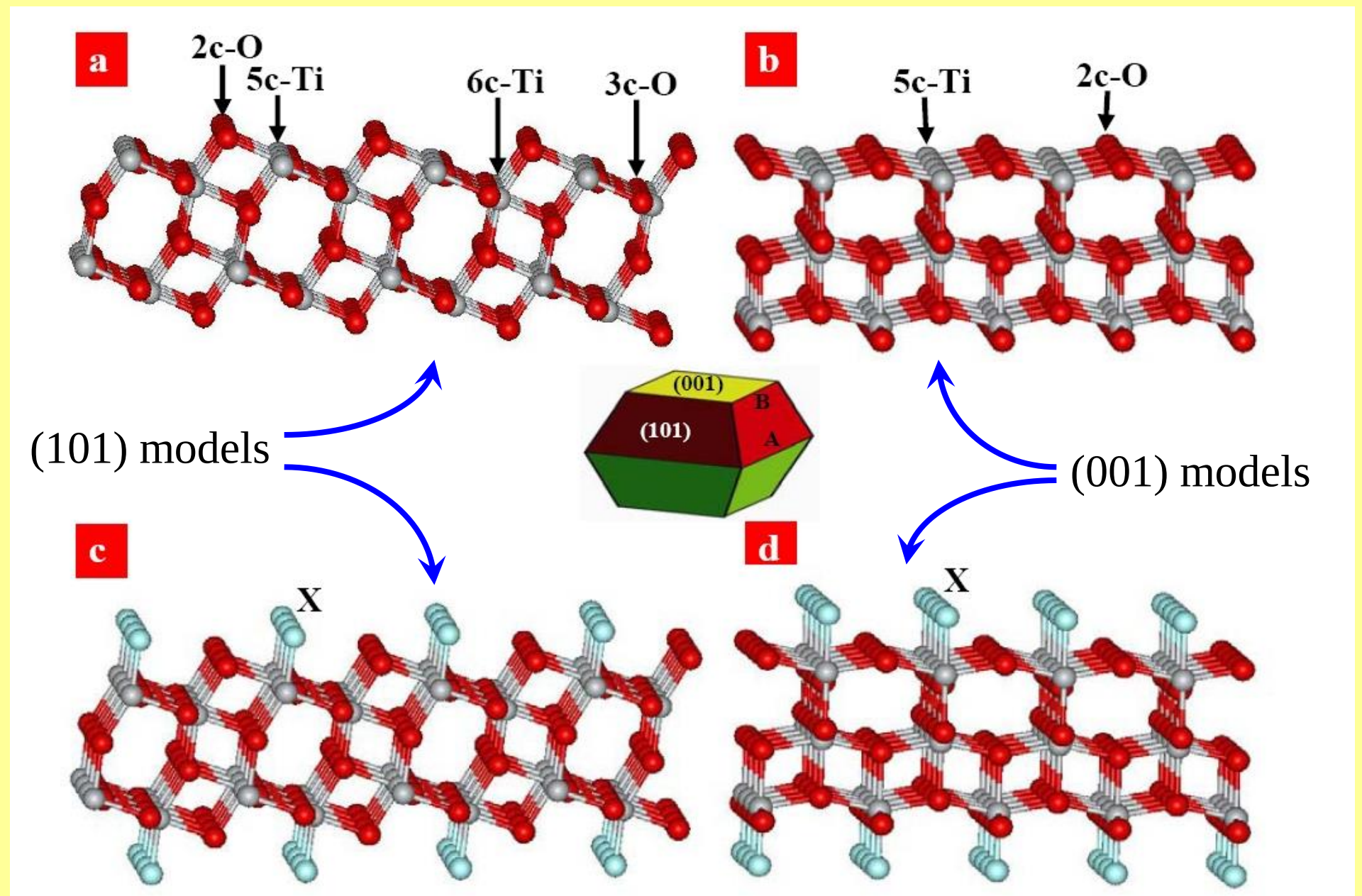
New Synthetic Approaches:



- TiO2 (101) surface is almost exclusively the most stable, meaning that it has a lower surface energy γ.
- Single crystals are not easy to grow with high purity. The usually inhomogeneous samples are dominated by the 101 facets.

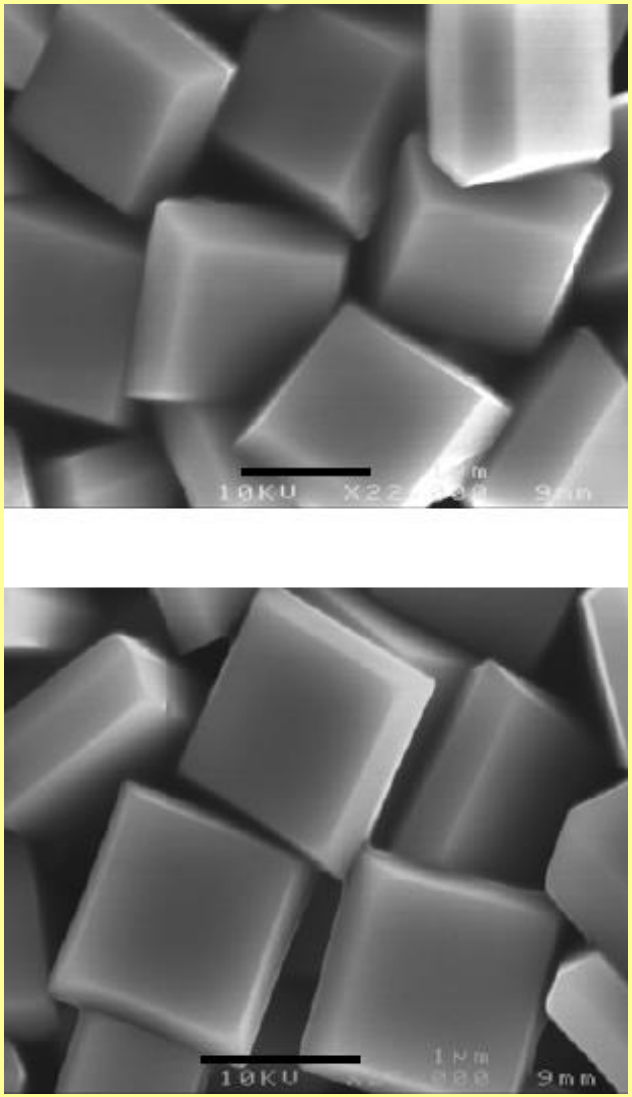


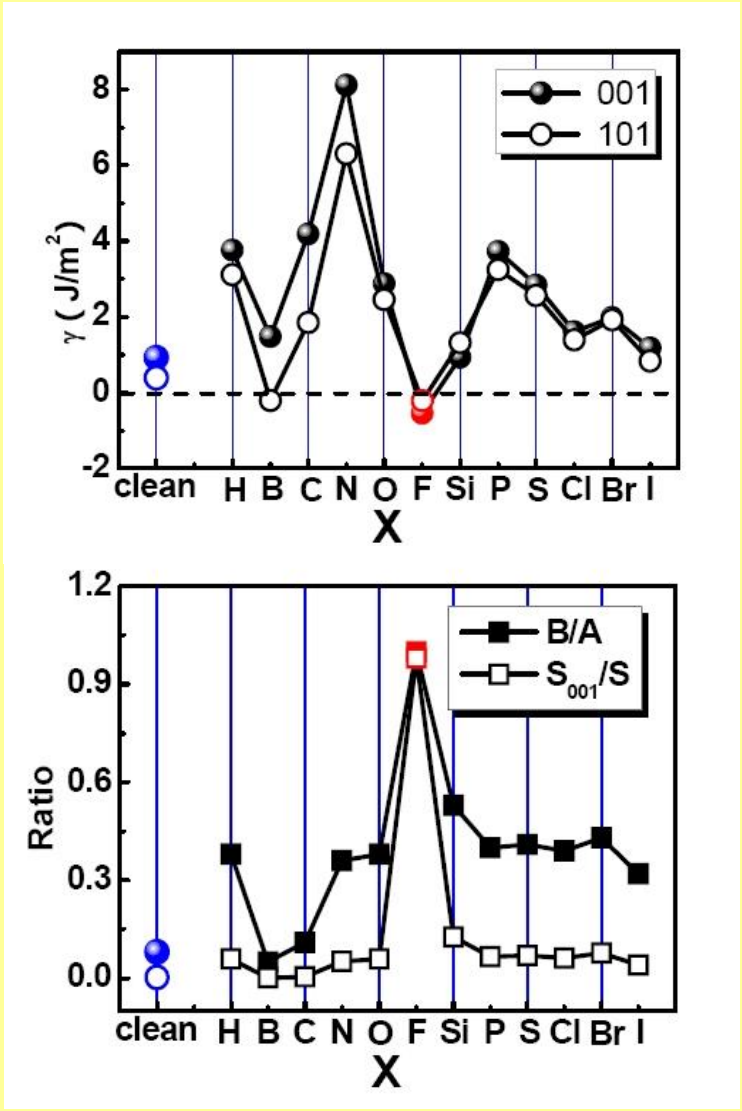
- There have been some hints in the literature that surface chemical modification might be able to alter the relative energetics. Fluorine has been implied in some studies.



Used DFT calculations to simulate surface modification energetics with X = H, B, C, N, O, F, Si, P, S, Cl, Br, I

Single TiO2 crystals with very large (001) facets!!





Yang, Sun, Qiao, Zhou, Smith, Cheng and Lu, ***Nature***, **453**, 638-641 (2008).

A new twist: hydrogenation of TiO2 to produce "black titania"!

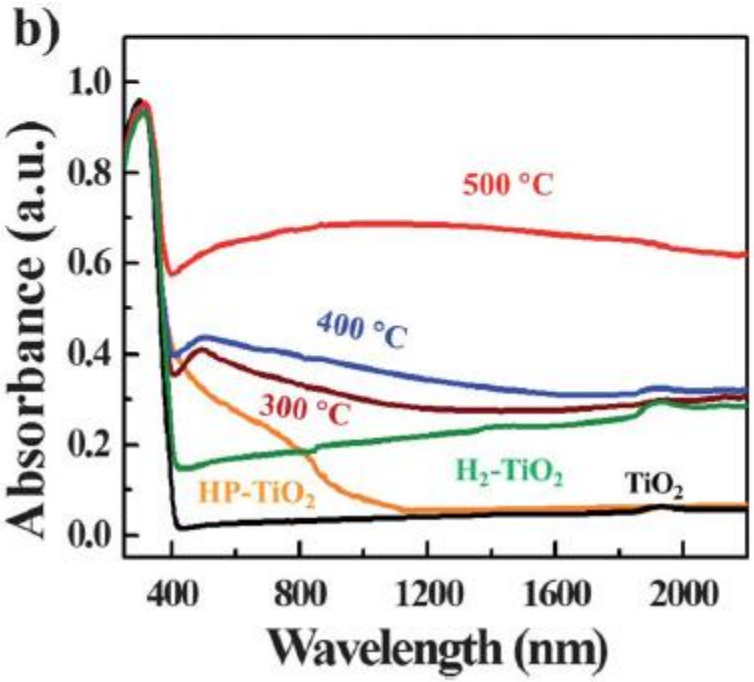
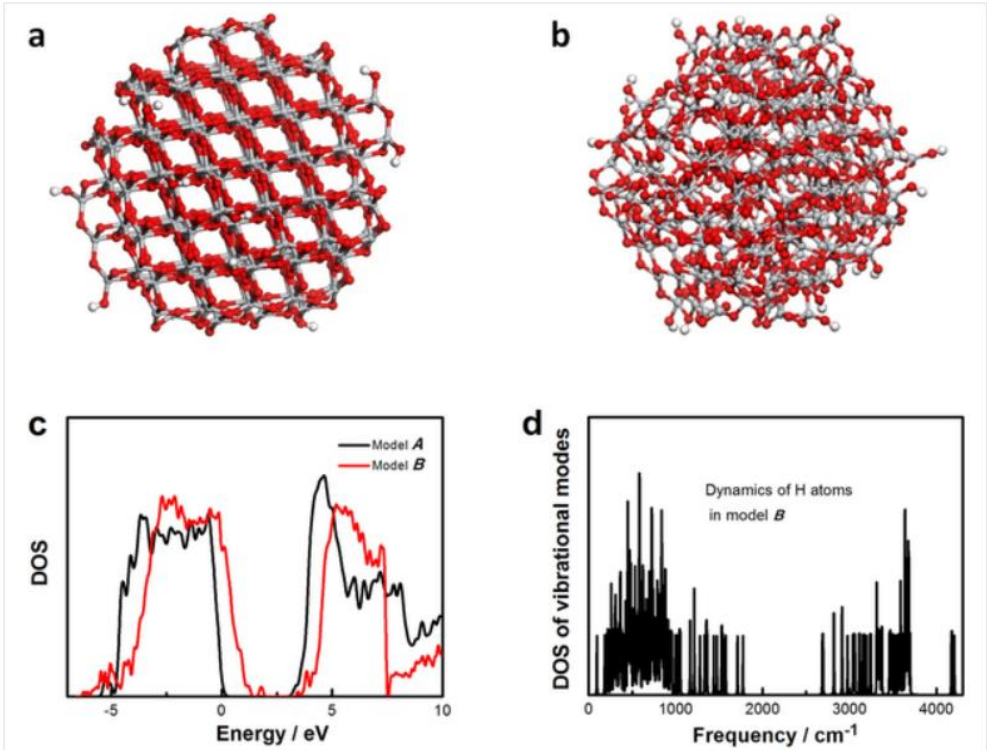


Figure 5: ab initio DFT calculation results on large TiO_2 clusters.

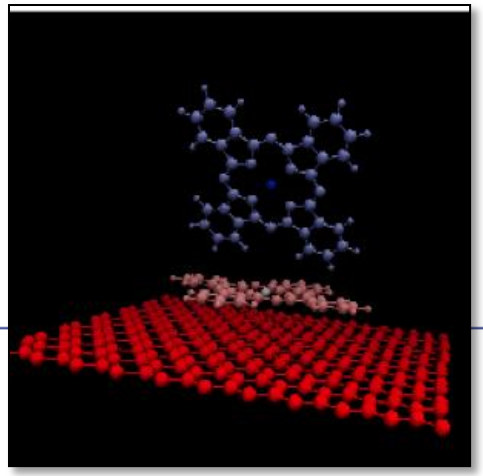


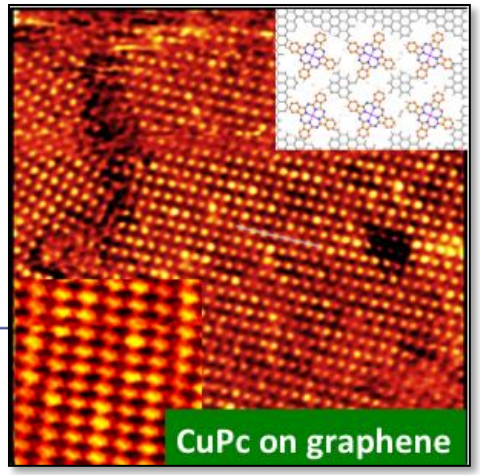
(a) model A structure of crystalline $Ti_{210}O_{420}H_{12}$. (b) model B structure of disordered $Ti_{218}O_{436}H_{70}$, Ti, O and H atoms are shown as grey, red and white balls, respectively. (c) The calculated electronic DOS of models A and B. The zero of the energy scale is set at the top of the valence band. (d) The calculated vibrational DOS of model B.

Jiang *et al.*, EES, **6**, 3007 (2013)

Interpreting and Understanding Self-Assembly on well-defined substrates:

Metal-organic CuPc on 2D silicon versus graphene





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Surface-Induced Orientation Control of CuPc Molecules for the Epitaxial Growth of Highly Ordered Organic Crystals on Graphene

Kai Xiao,*[,†] Wan Deng,[⊥] Jong K. Keum,[‡] Mina Yoon,[†] Ivan V. Vlassiouk,[§] Kendal W. Clark,[†] An-Ping Li,[†] Ivan I. Kravchenko,[†] Gong Gu,[⊥] Edward A. Payzant,[‡] Bobby G. Sumpter,[†] Sean C. Smith,[†] James F. Browning,[‡] and David B. Geohegan[†]

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[⊥]Department of Electrical Engineering and Computer Science, University of Tennessee at Knoxville, Knoxville, Tennessee 37931, United States

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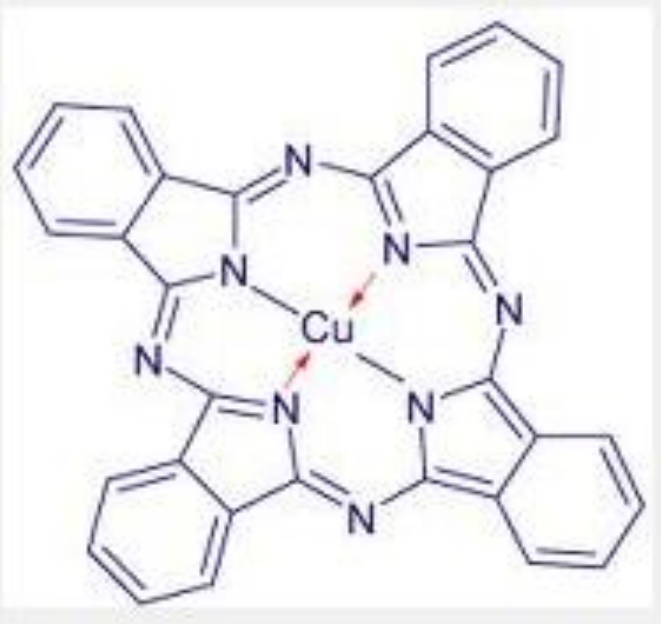
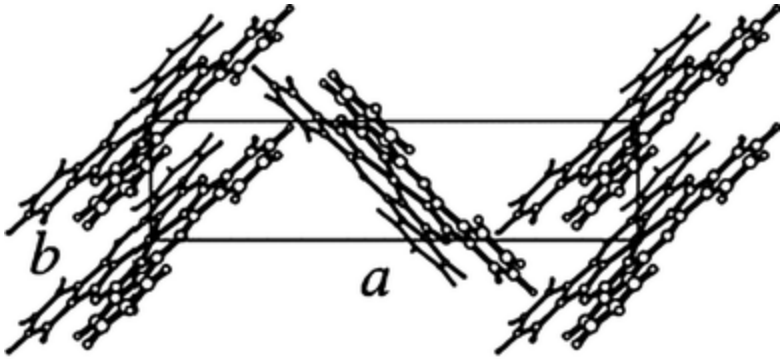
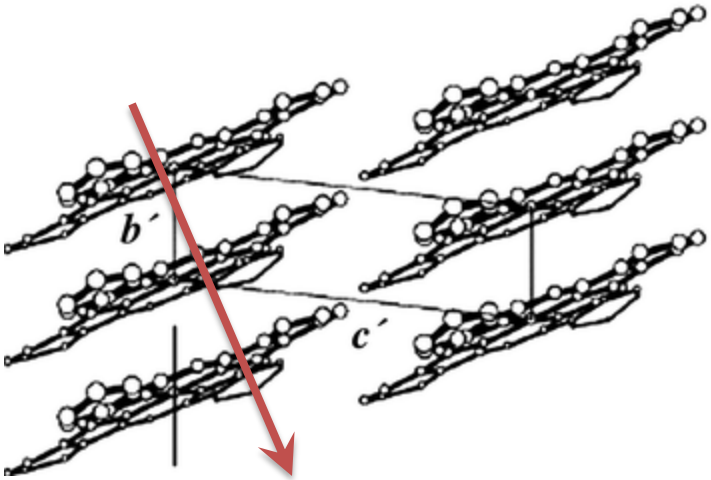
CuPc – stacking controls direction of electron transfer



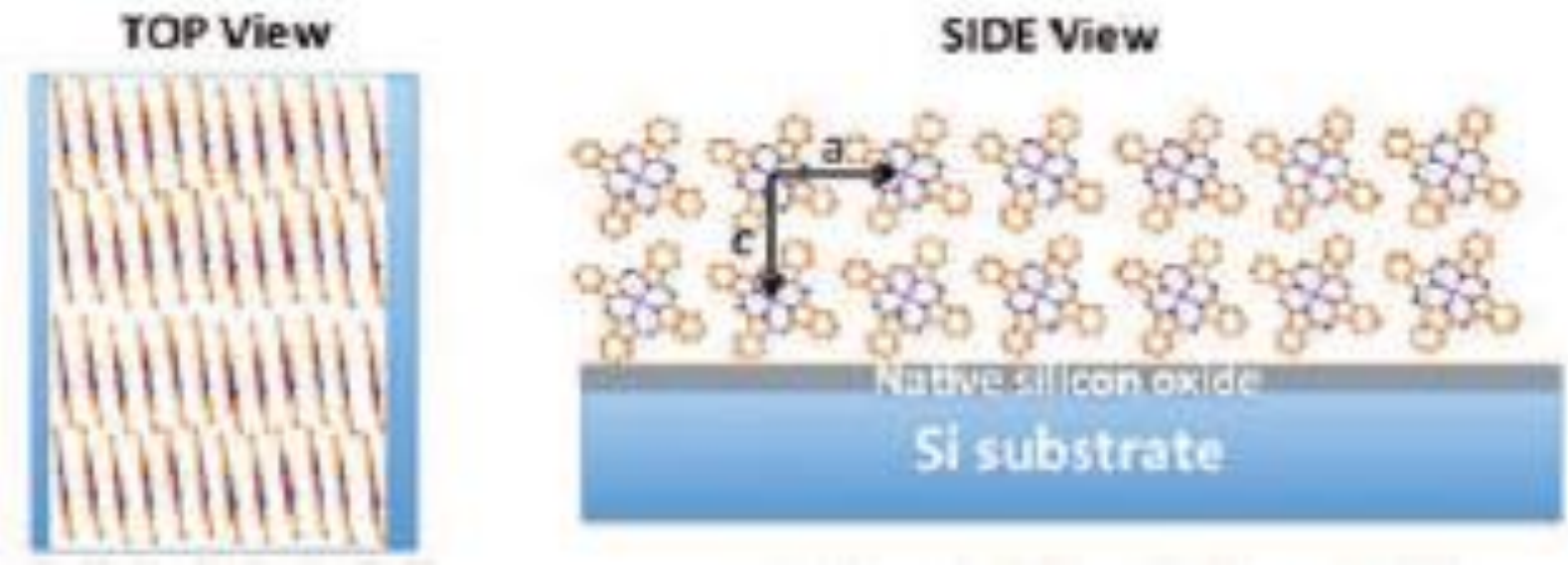
Copper pthaloocyanine (CuPc)



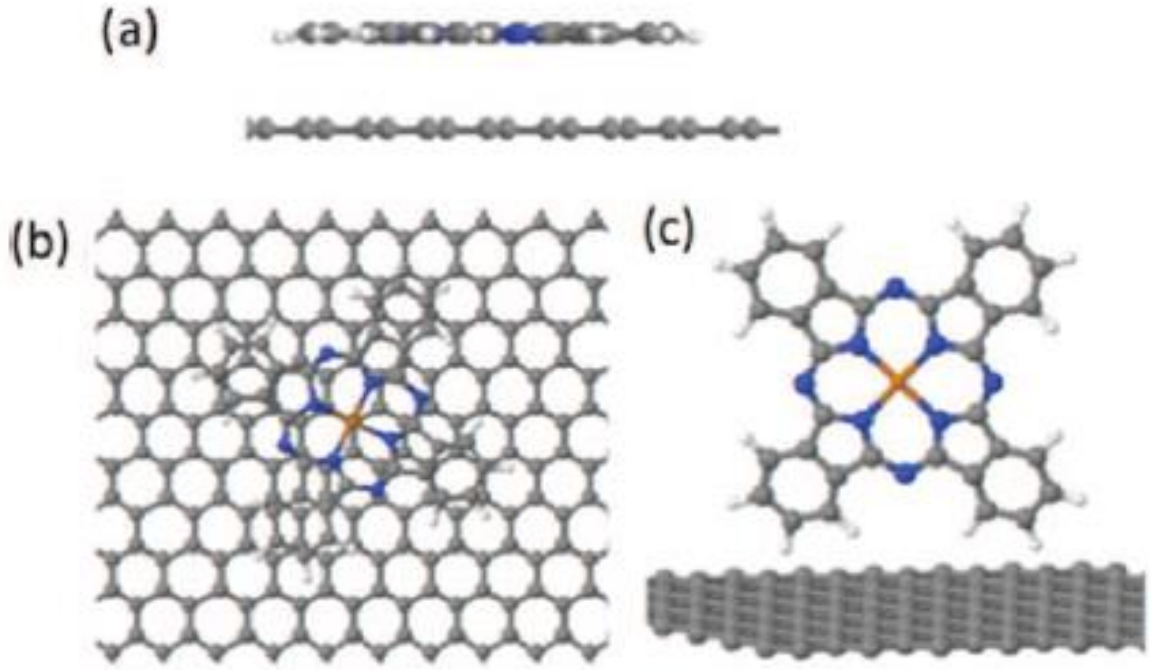


The orientation of pi-stacking that results from epitaxial growth of metal organics such as CuPc on substrates critically impacts the type of electronic application they can be used for.

Silicon or silicon oxide substrate: perpendicular alignment to surface is preferred



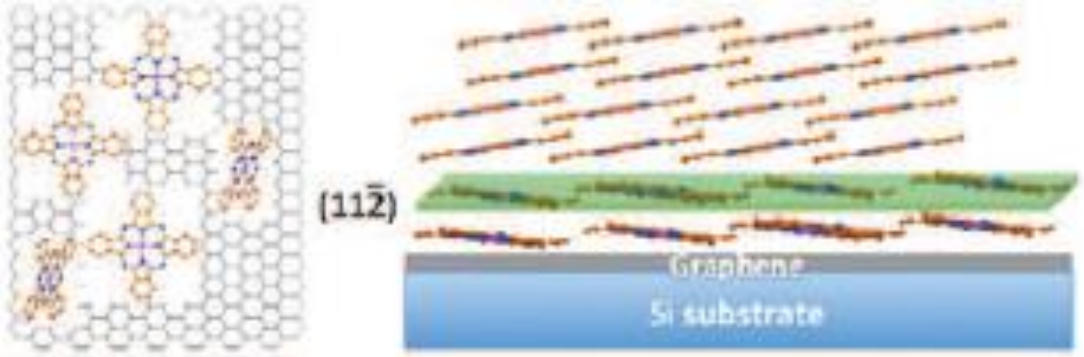
DFT + VdW calculations indicate preferred orientation on graphene is parallel to the substrate:



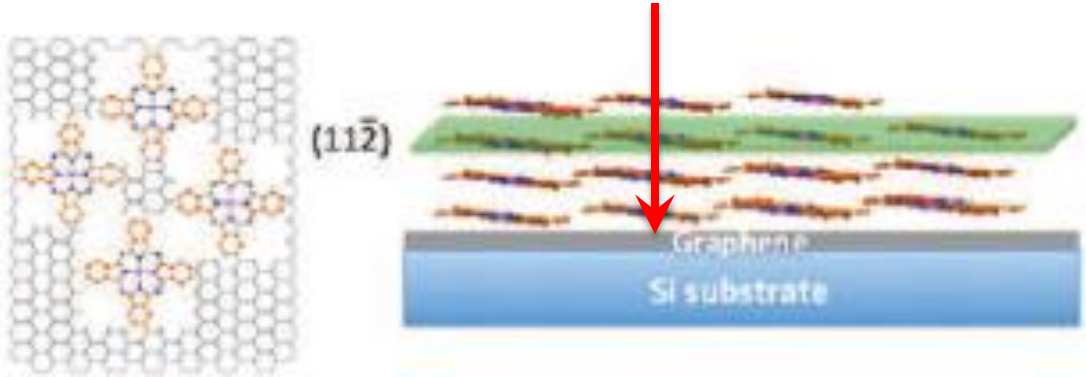
Why the difference?

Charge transfer from graphene to CuPc favors the parallel alignment to the surface

Higher temperature process enhances annealing to the lowest energy structure:



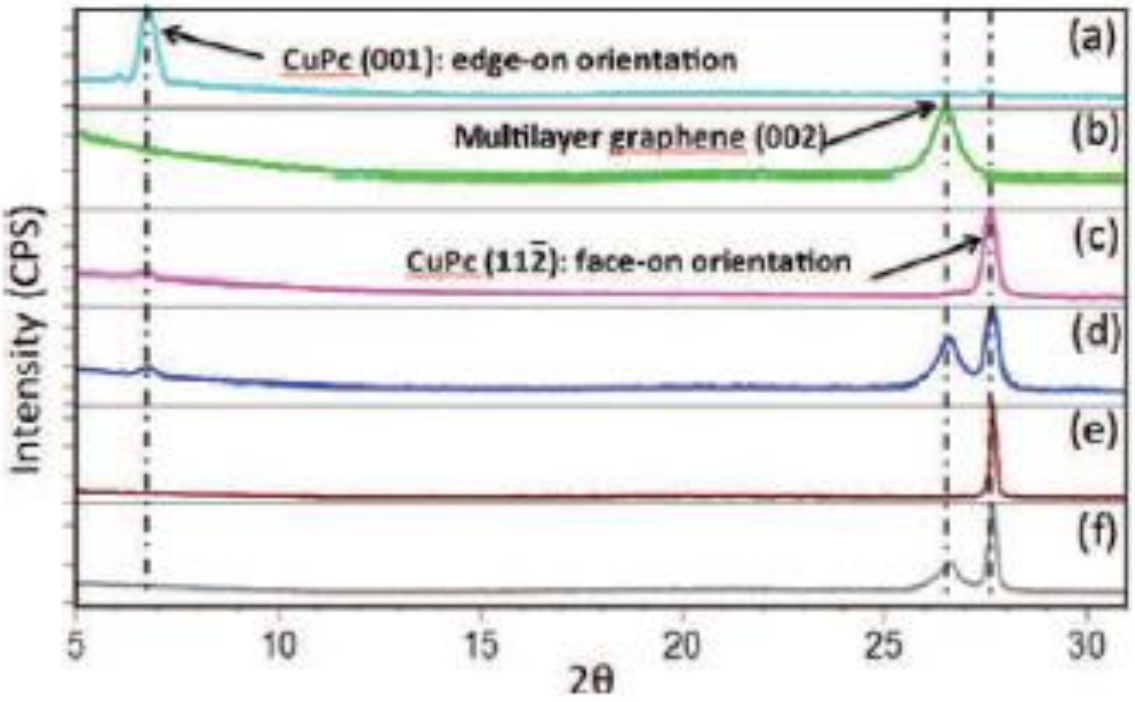
Room Temperature



130°C

- This orientation is superior for organic photovoltaic applications, since the direction of e^- transfer is towards the conducting graphene substrate
- Can be achieved at least up to 50nm thickness!

Single layer graphene (SLG) gives enhanced orientation properties!

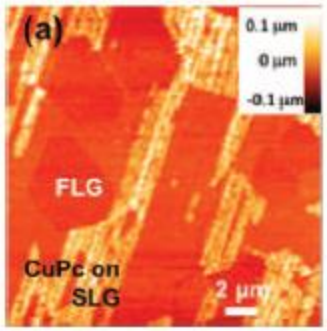


SLG: room temp

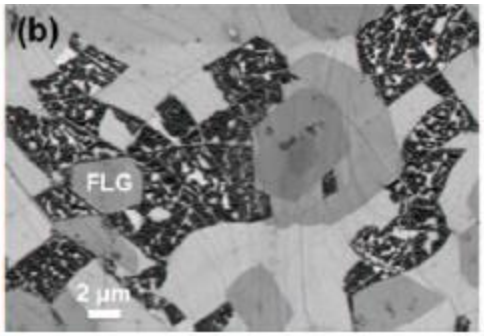
Few layer graphene (FLG): room temp

SLG: 130°C

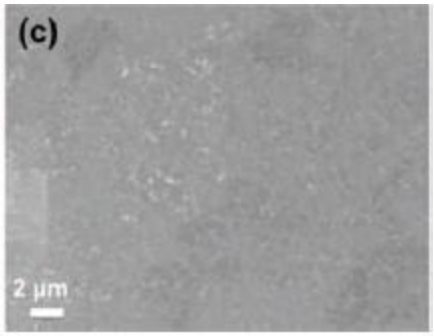
FLG: 130°C



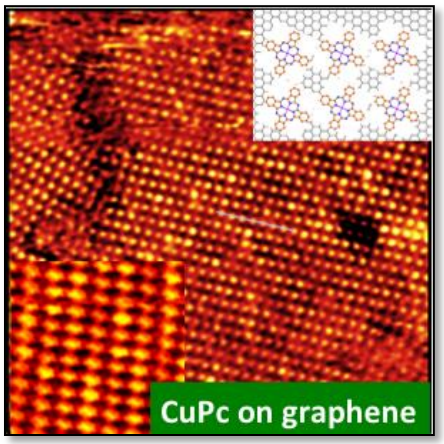
STM: 130°C



SEM: 130°C



SEM: room temp



Hydrogen Storage in Novel Light-Metal Nanostructured Materials

Key Criteria for Mobile Storage:

- High storage capacity: minimum 6.5 wt %
- Desorption Temperature 60-120 ° C.
- Reversibility of the thermal absorption and desorption cycle
- Low-toxicity and non-explosive
- Low cost, low weight.

Magnesium Hydride as a Storage Medium

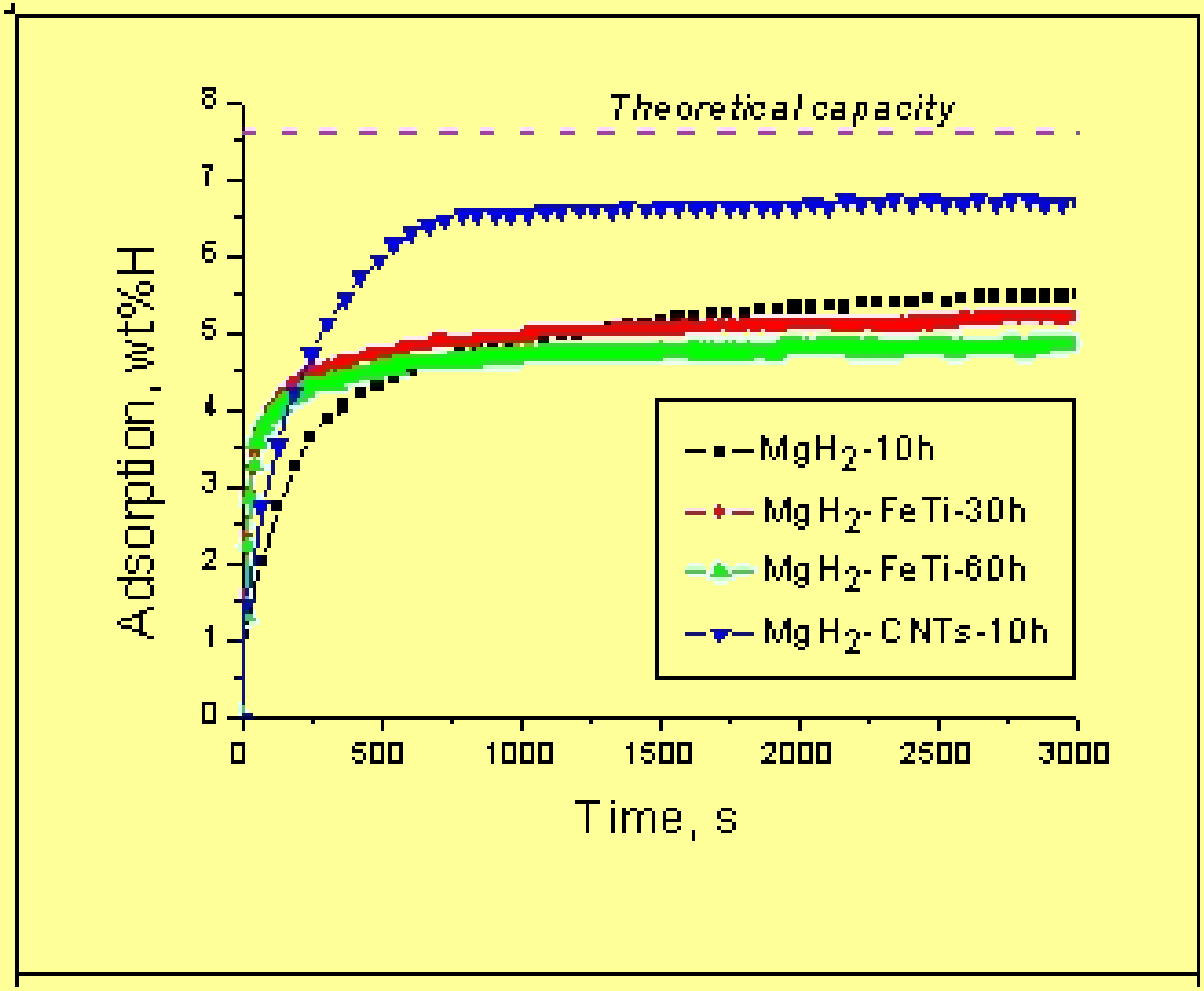
- Magnesium hydride, A very promising candidate for H_2 energy carrier in mobile vehicles.
- In MgH_2, the storage capacity of hydrogen is 7.6 wt%.
- Lightweight, low cost, easy to make

Main problems :

Slow kinetics and very high hydrogenation and dehydrogenation temperature !!

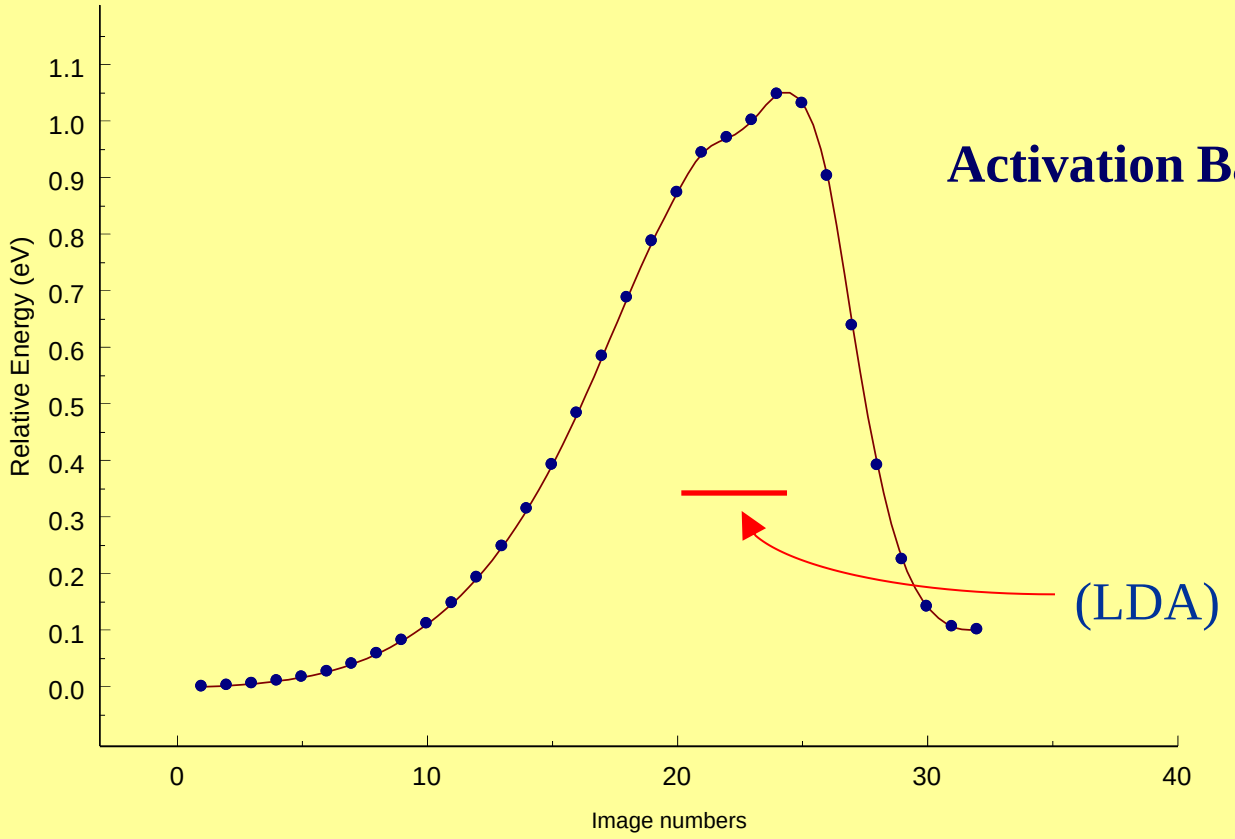
Recent Experimental Findings on Hydrogenation of Mg:

- **Ball-milling of Mg nanocomposite materials (start with hydride since it is more brittle).**
- **Can improve the adsorption kinetics through addition (≤5wt%) of transition metals such as Ti, Fe, V, Pd …**
- **Can improve the hydrogen storage capacity (closer to the stoichiometric limit) by addition of carbon graphite or nanotubes.**
- **Experimental motivation for addition of carbon related largely to physical factors …**



- Carbon is seen to increase the absorption capacity
- Transition metals (often in combination) enhance kinetics

H_2 Dissociation Barrier on Mg(0001) Surface – GGA(PBE) with PAW



Activation Barrier =1.05 eV

Ti-incorporated Mg(0001) Surface

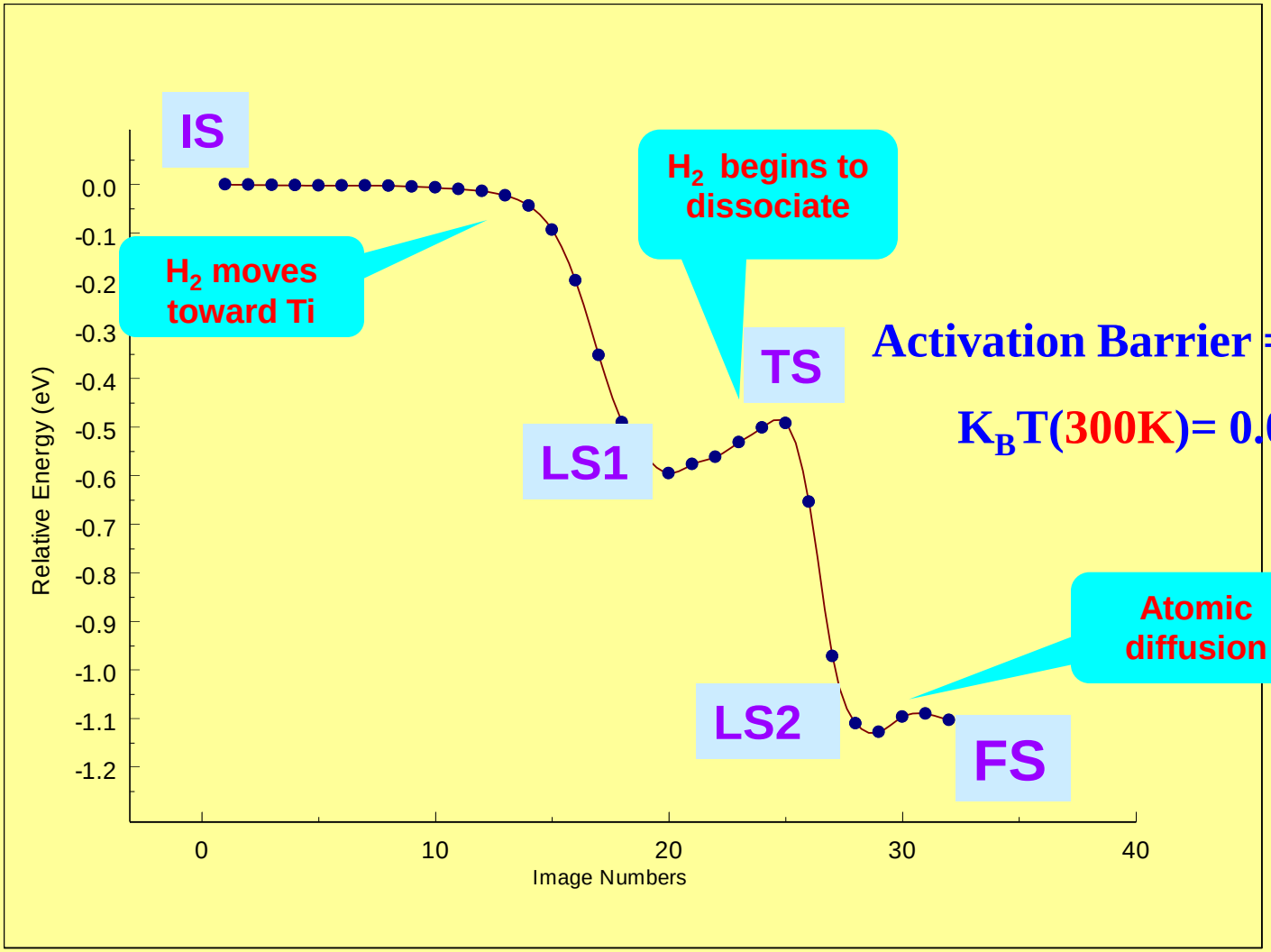
- **The formation energy of Ti@Mg(0001) surface involves the creation of a Mg vacancy on Mg(0001) surface in the first step and the vacancy is then occupied by a Ti atom.**

$$E_{ad}^{subs} = E_{Ti/Mg(0001)-subs} + E_{Mg} - E_{Ti-atom} - E_{Mg(0001)}$$

- **E_{ad}^{subs}= -4.09 eV**

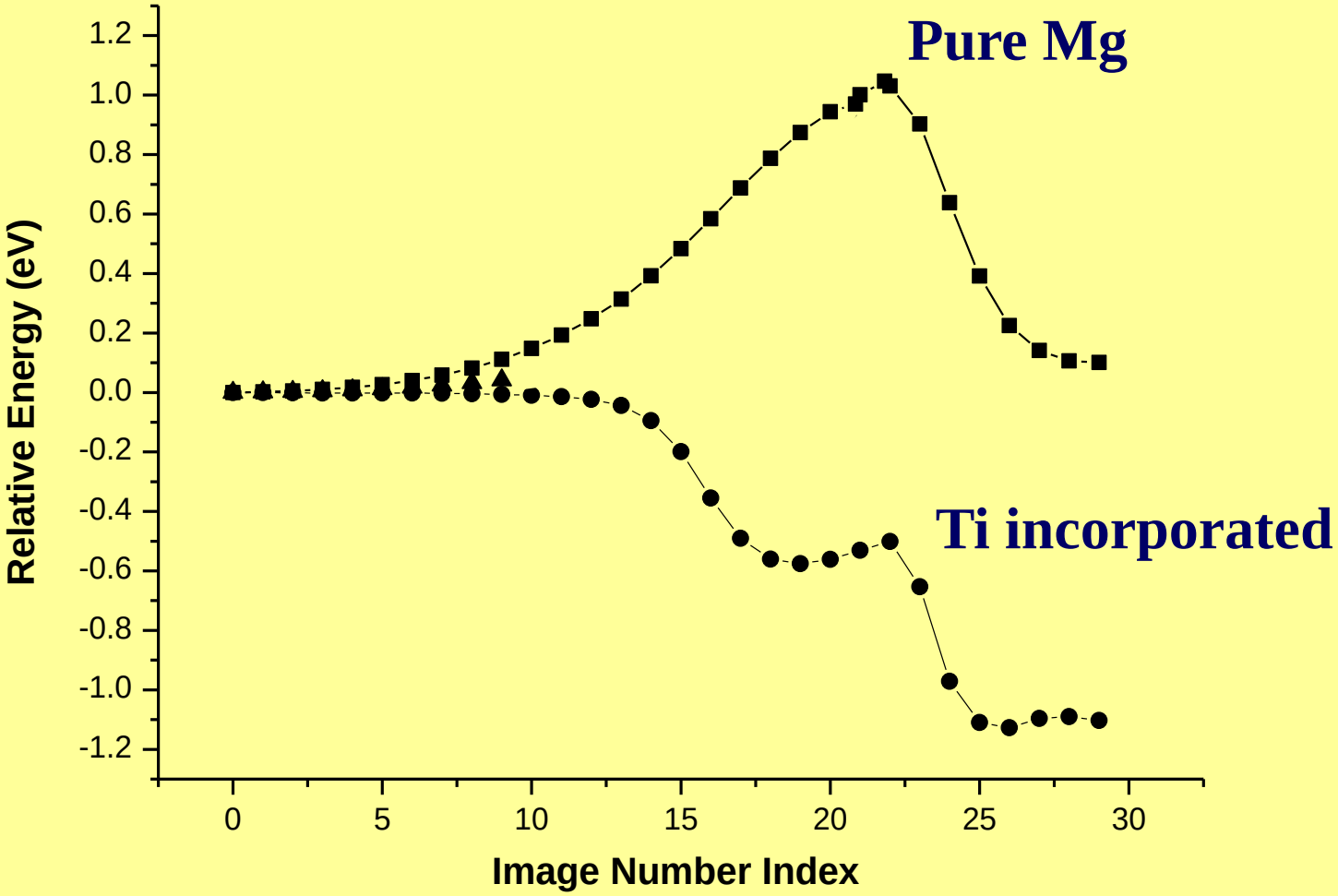
- **There are strong interactions between the molecular orbital of H2 with d metal states of Ti. (Charge is donated from H2 s-orbital to d-states, accompanied by a back–donation from the d-states to the H2 anti-bonding state)**

Barrier Calculation for Ti-incorporated Mg(0001) Surface – GGA (PBE) with PAW

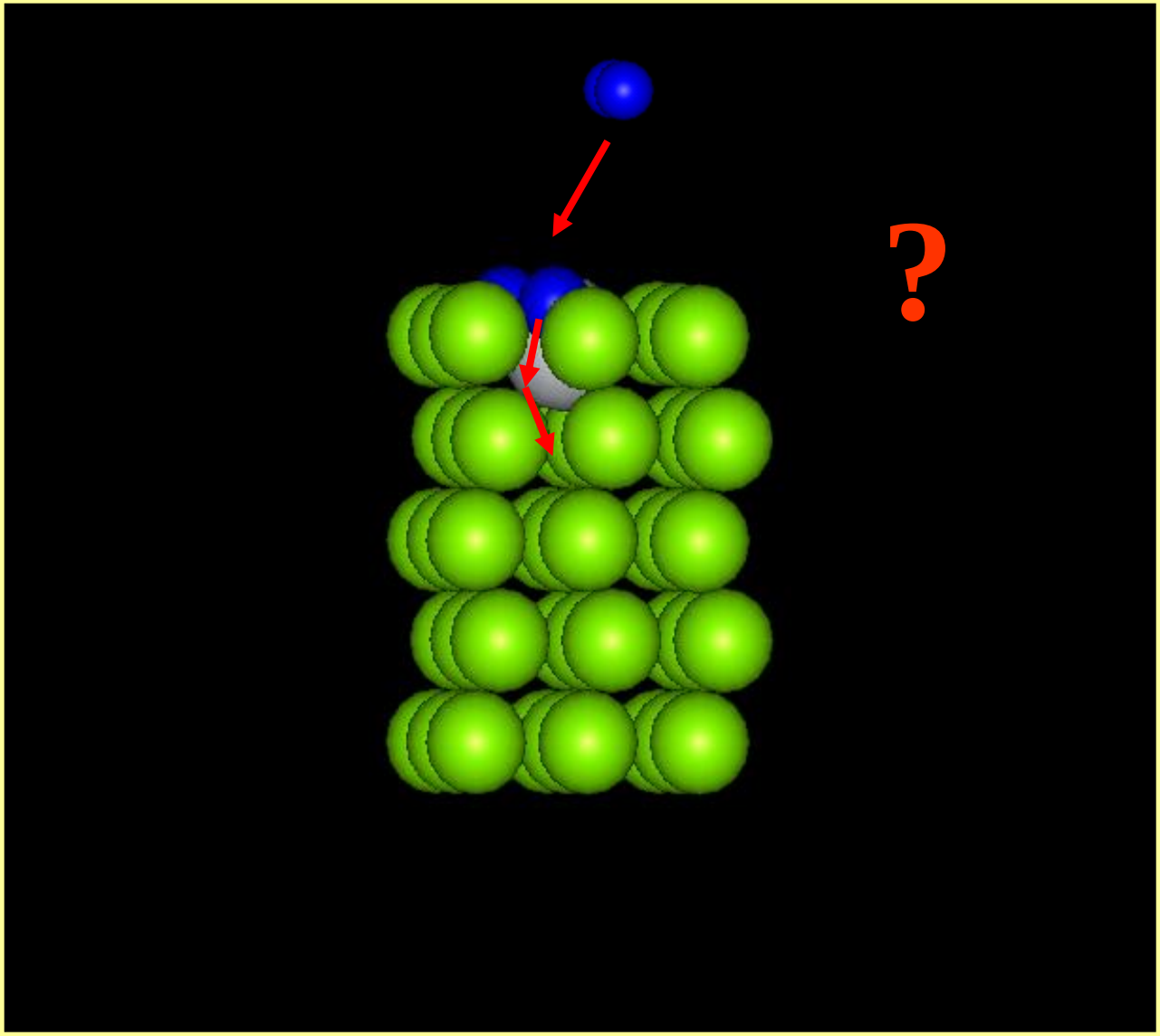


Activation Barrier =0.1034 eV

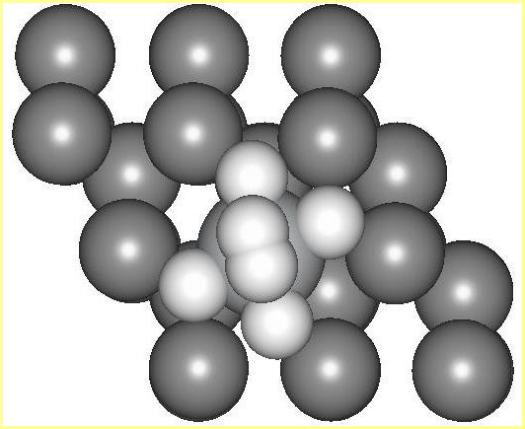
K_BT(300K)= 0.025 eV

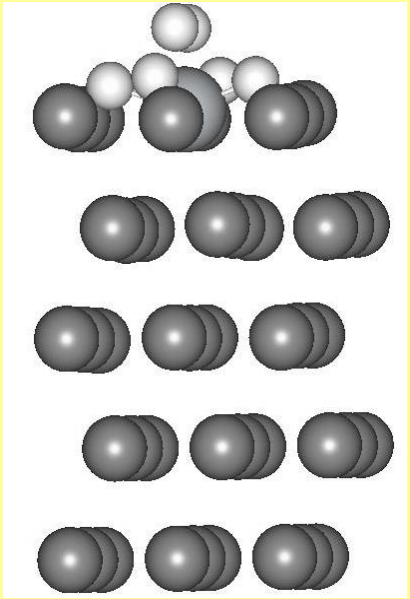


A.J. Du, S.C. Smith, X.D. Yao and G.Q. Lu, *J. Phys. Chem. B*, **109**, 18037 (2005)



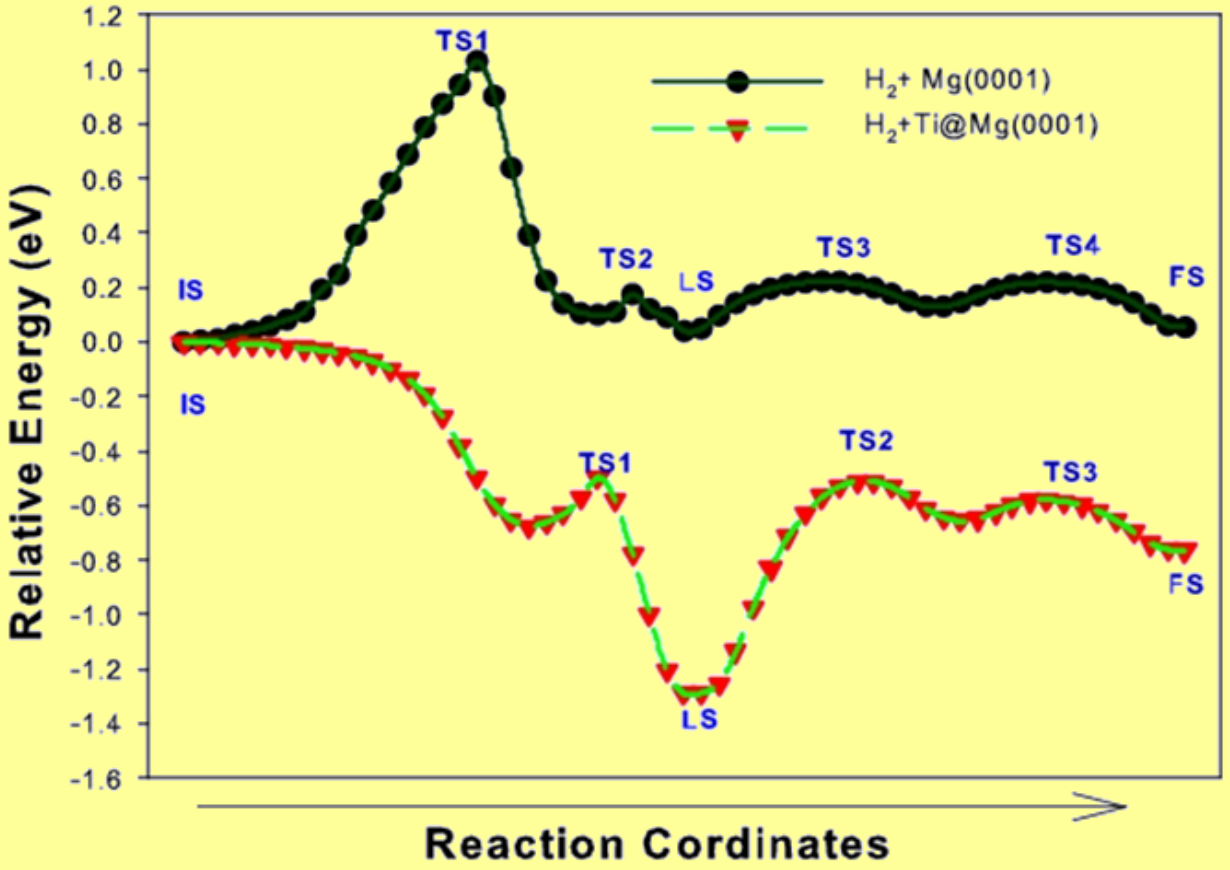
Further Dressing Ti with Hydrogen …





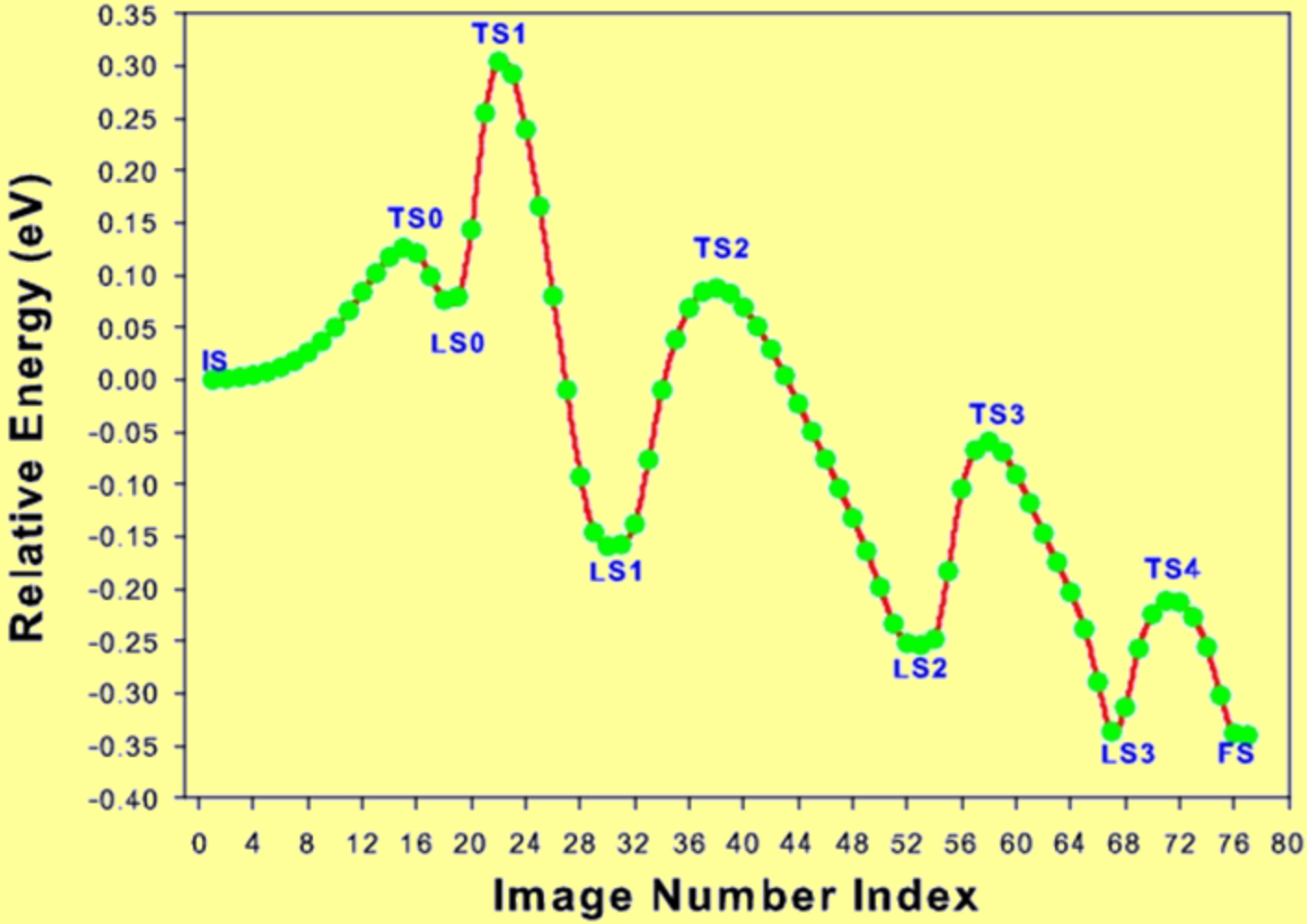
A. Du, S.C. Smith, X.D. Yao and G.Q. Lu, *J. Phys. Chem*. B, **110**, 21747 (2006).

Pulling atomic H away from Ti across the Mg surface:

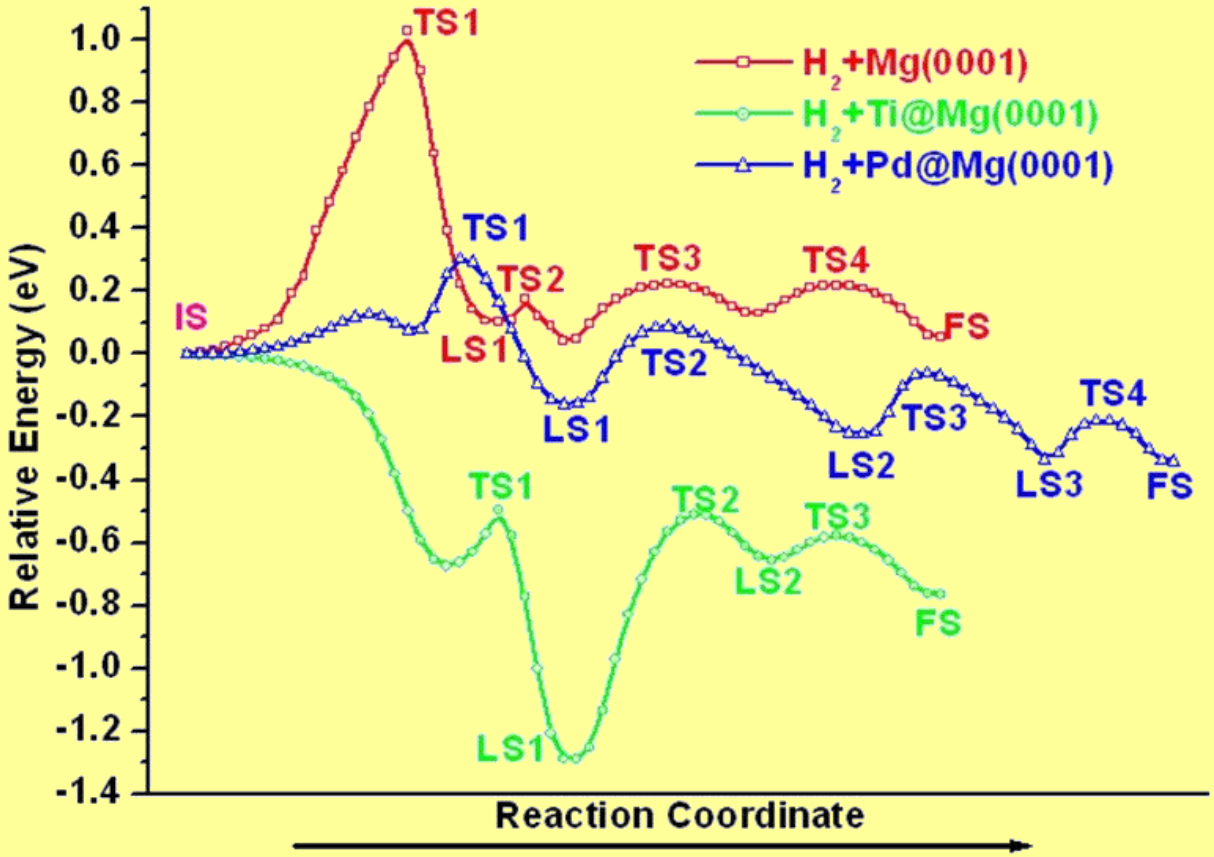


Hydrogen is too strongly bound to Ti – it will not easily diffuse away and so will block the site!

Palladium catalyst – first ab initio validation of the "spill-over" catalytic effect in hydrogen storage

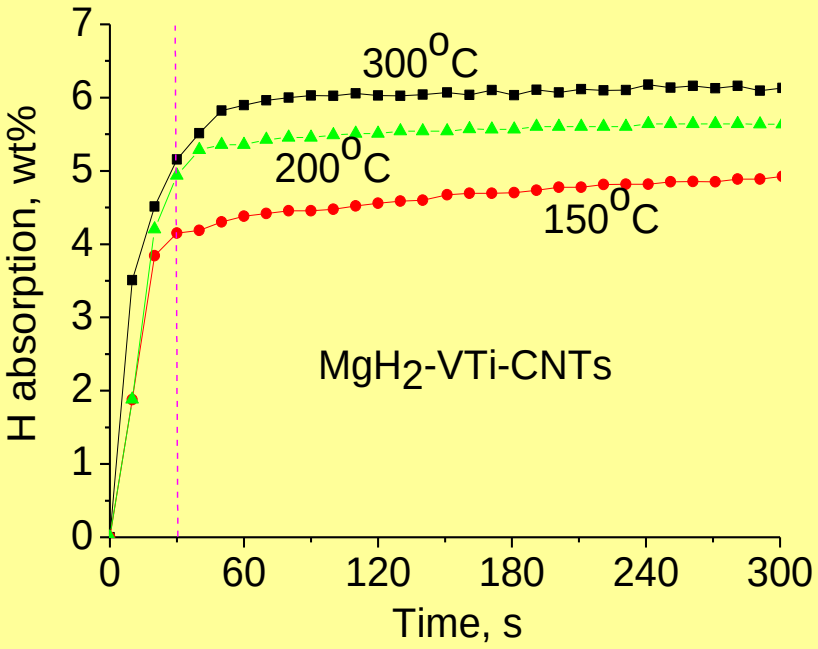


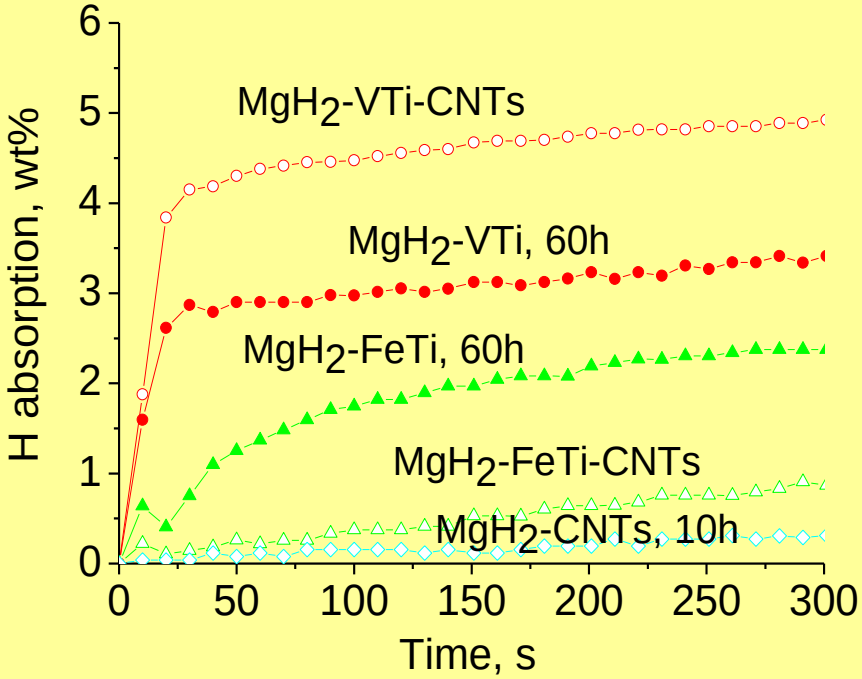
Pd dopant: effective catalysis is a delicate balance of properties!!



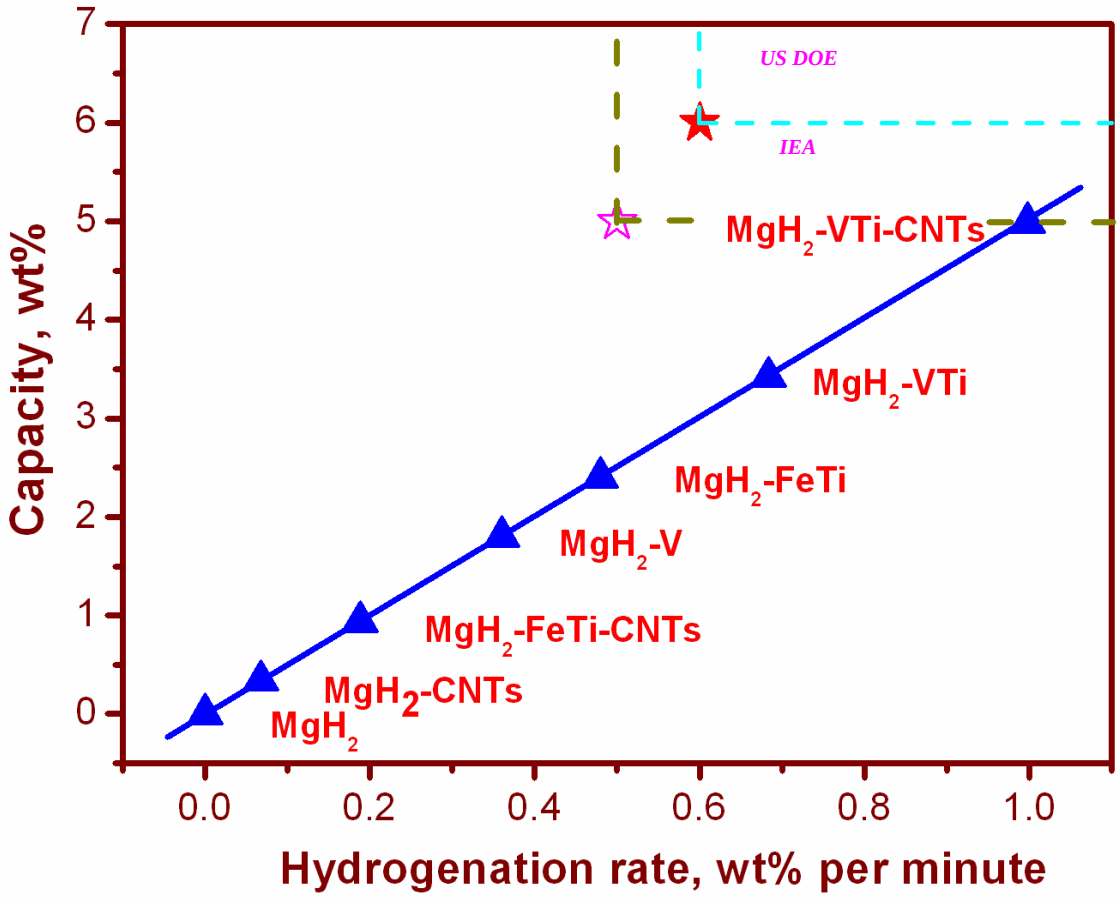
A. Du, S.C. Smith, X.D. Yao and G.Q. Lu, *J. Amer. Chem. Soc*., **129**, 10201 (2007)

The Future: Improved Catalysis for multi-functional performance (absorption, desorption, cyclying stability, etc.)

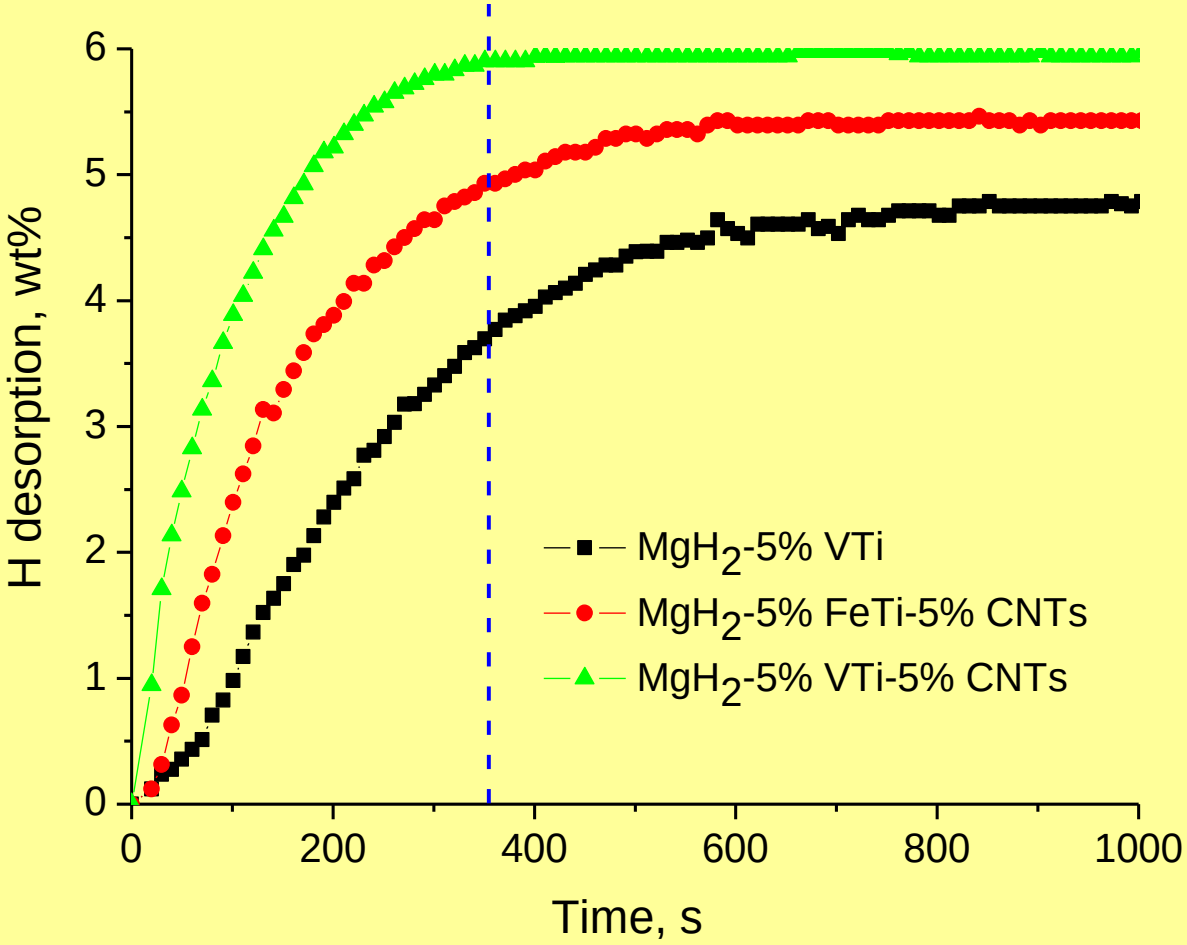




X. Yao, C.Z. Wu, A.J. Du, J. Zou, Y. He, Z.H. Zhu, P. Wang, H.M. Cheng, S.C. Smith, G.Q. Lu, *J. Amer. Chem. Soc.*, **129**, 15650-15654 (2007)

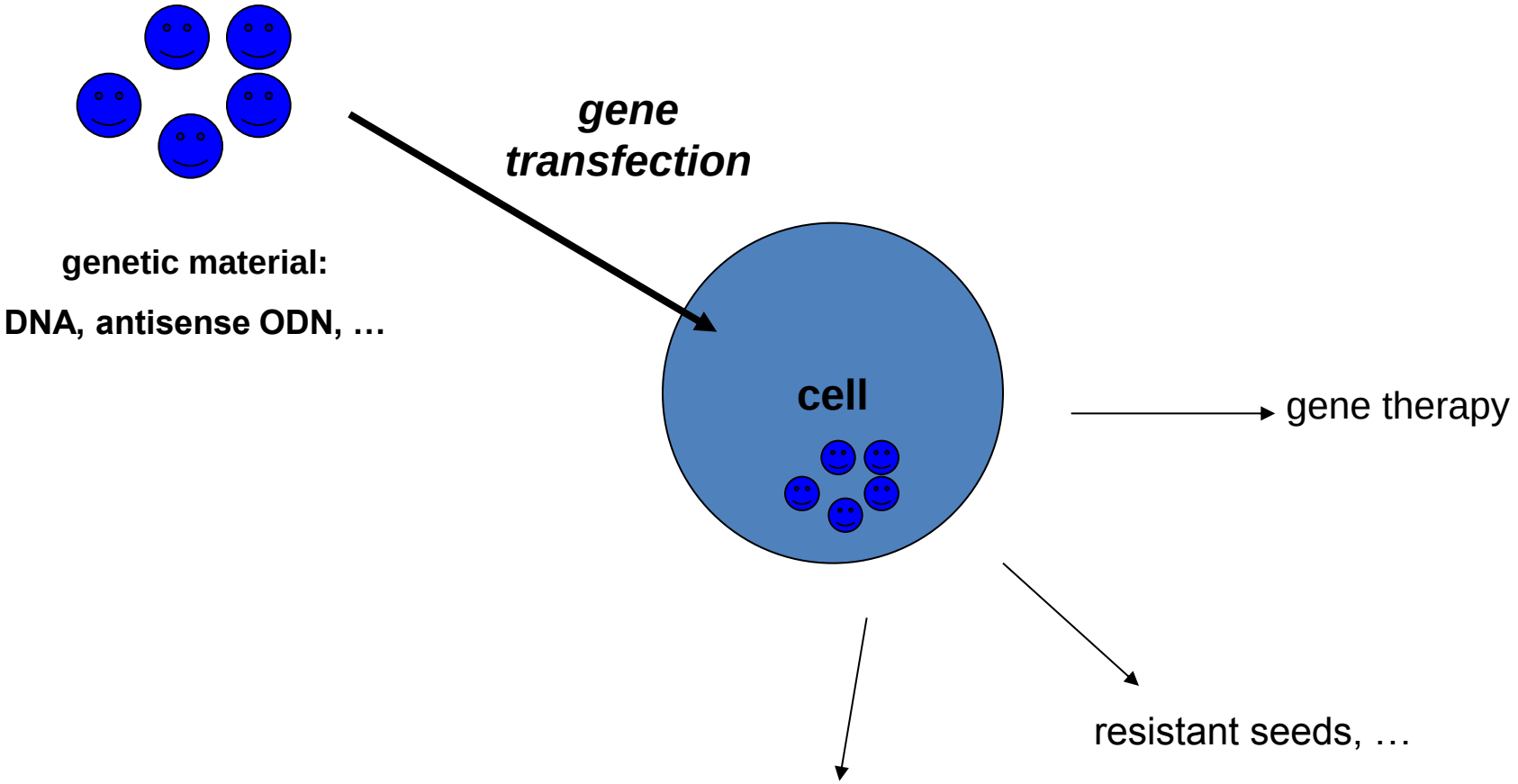

US DOE
IEA
MgH2-VTi-CNTs
MgH2-VTi
MgH2-FeTi
MgH2-V
MgH2-FeTi-CNTs
MgH2-CNTs
MgH2
Capacity, wt%
Hydrogenation rate, wt% per minute
0
1
2
3
4
5
6
7
0.0
0.2
0.4
0.6
0.8
1.0

Desorption Remains a Challenge

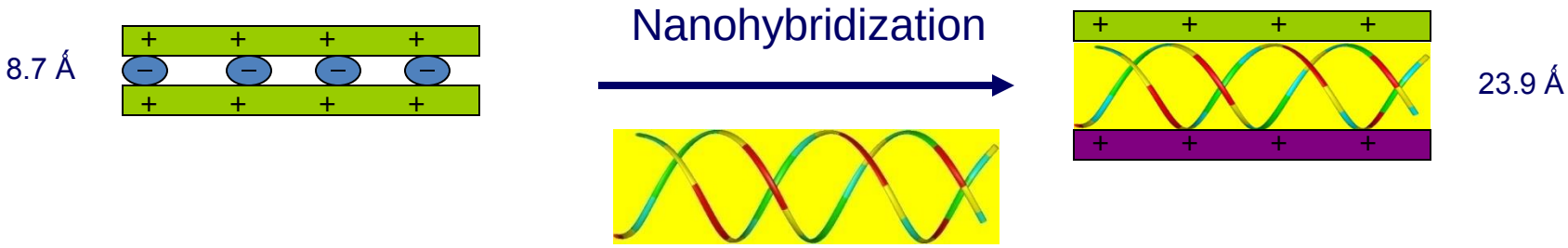


Cellular delivery:

DNA / RNA delivery is a central problem in biomanufacturing, gene therapy, biopharmaceuticals and drug delivery.

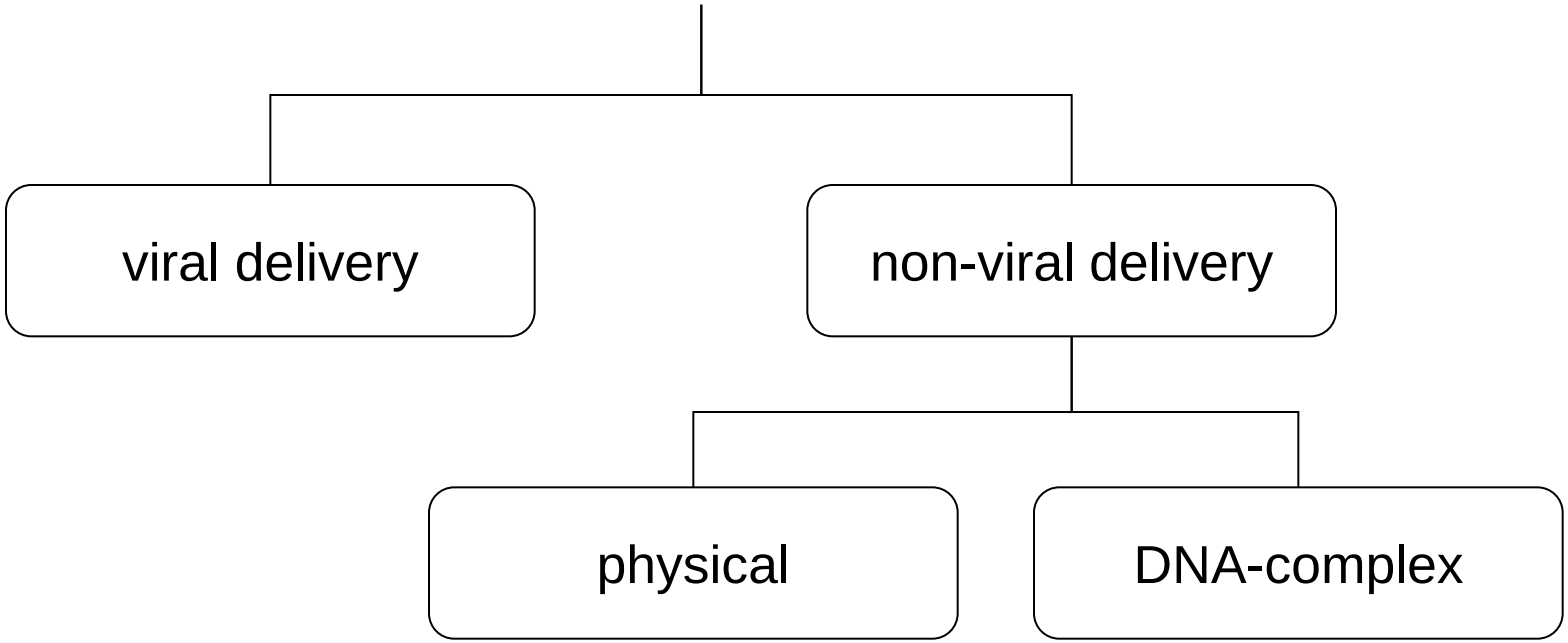


General Mechanism



Choy, J.-H.; Park, J.-S.; Kwak, S.-Y.; Jeong, Y.-J.; Han, Y.-S.
Molecular Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals **2000**, *341*, 425-429

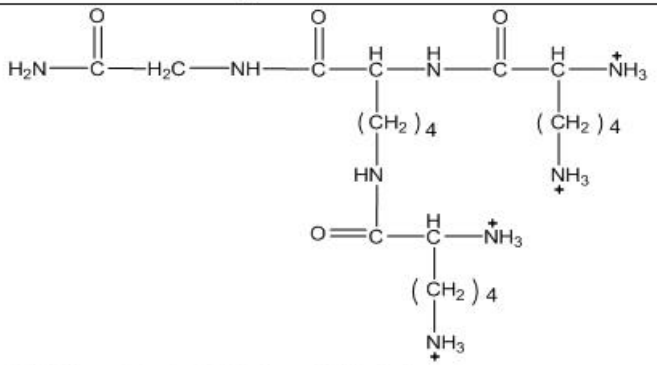
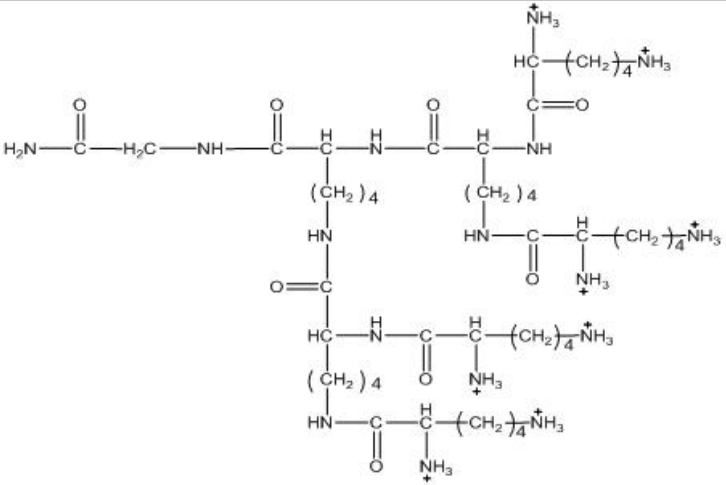
Currently available cellular delivery agents



- electroporation
- microinjection
- biolistics
- …

- cationic liposomes
- polymers/ dendrimers
- $CaPO_4$, inorganic carriers
- …

Biodendrimers as carrier particles

3 4+dendrimer	 Molecular Weight: 458.60
4 8+dendrimer	 Molecular Weight: 971.29

Dr Harry Parekh (Pharmacy, UQ) and Ouyang Defang

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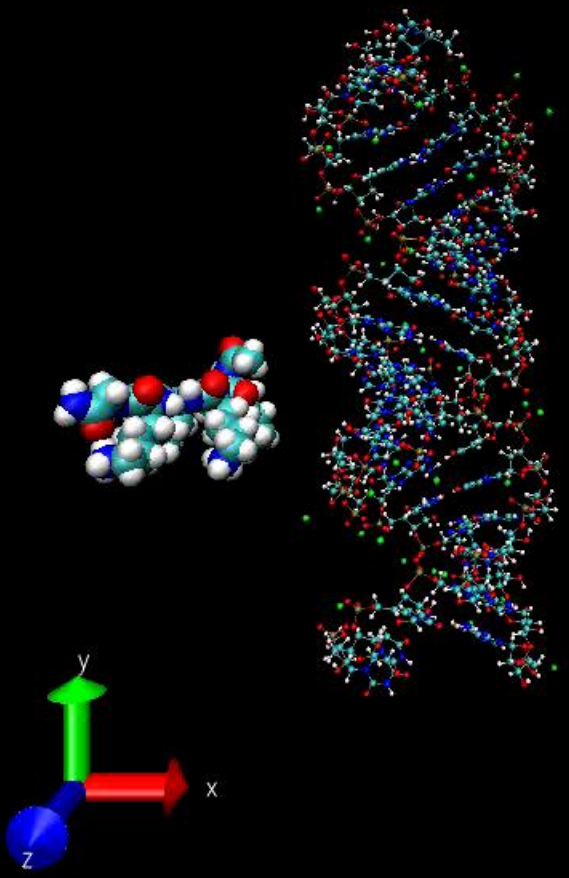
4+ dendrimer: Minor Groove simulation

The example sequence chosen is a 21 base pair siRNA of relevance in clinical studies of cervical cancer.

MD simulations used the AMBER9 software package with the all-atom AMBER99 force field (ff99) for RNA .

5'- GCAACAGUUACUGCGACGUUU-3'
3'- UUCGUUGUCAAUGACGCUGCA -5'



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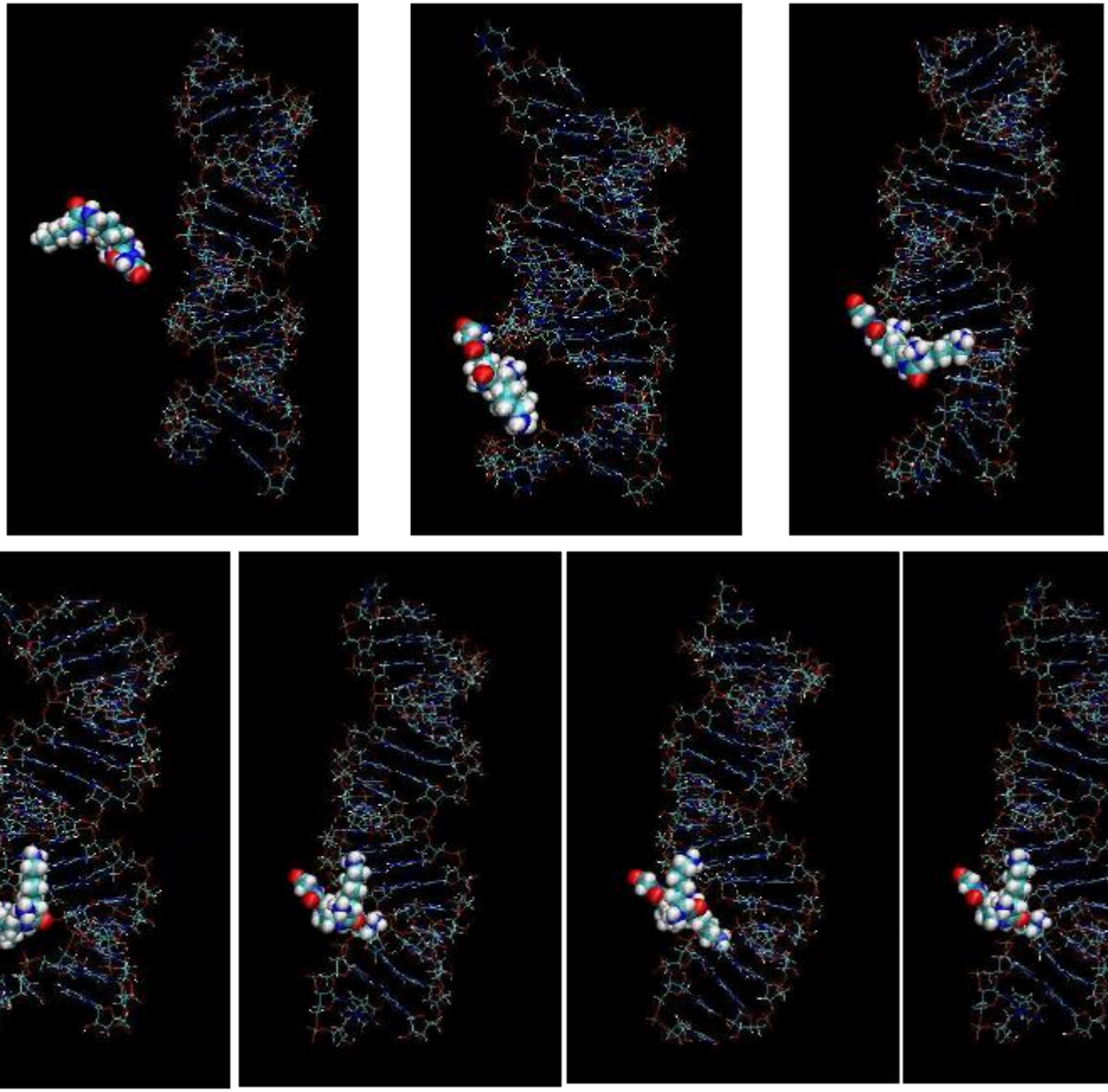

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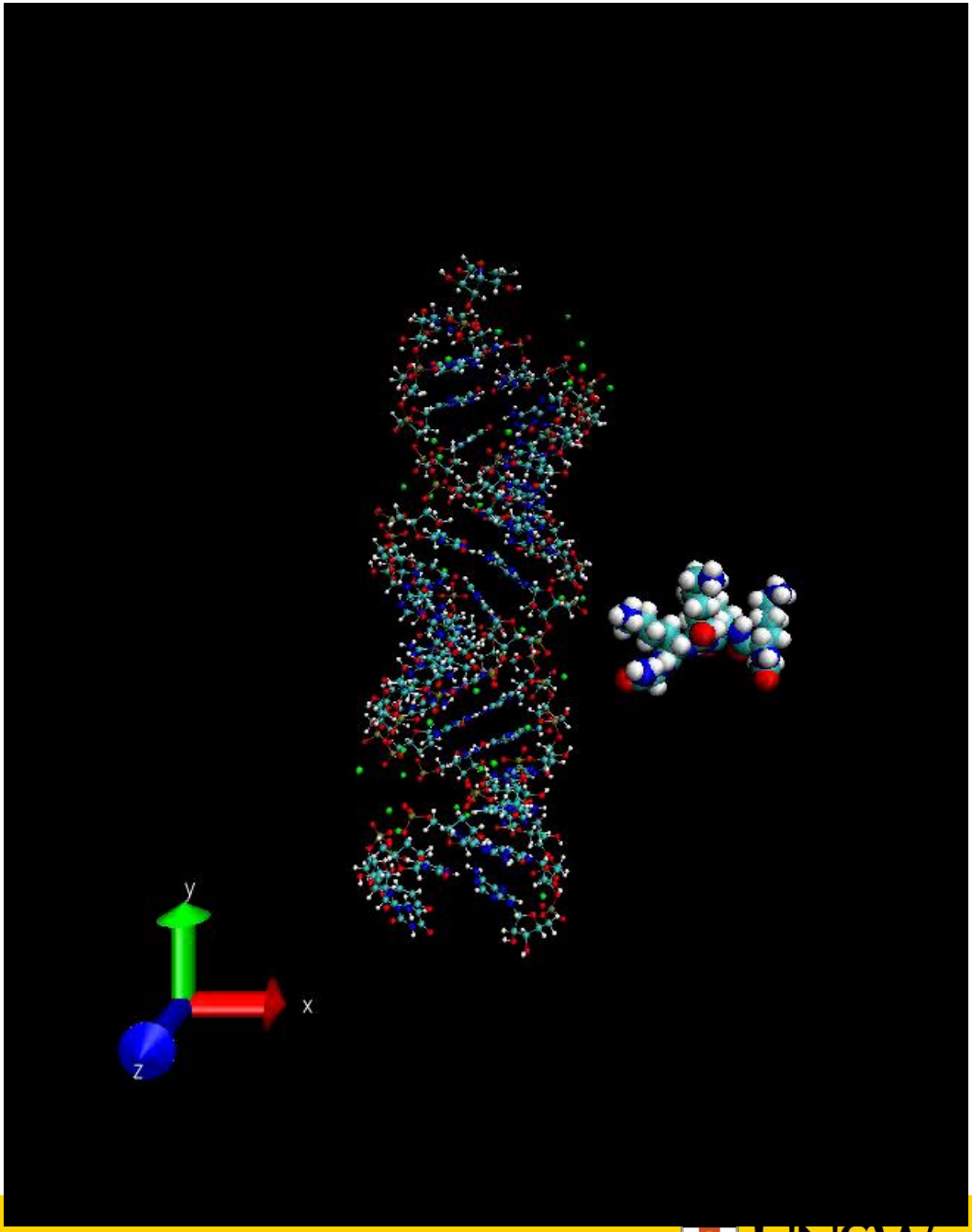
4+ dendrimer: Major Groove simulation



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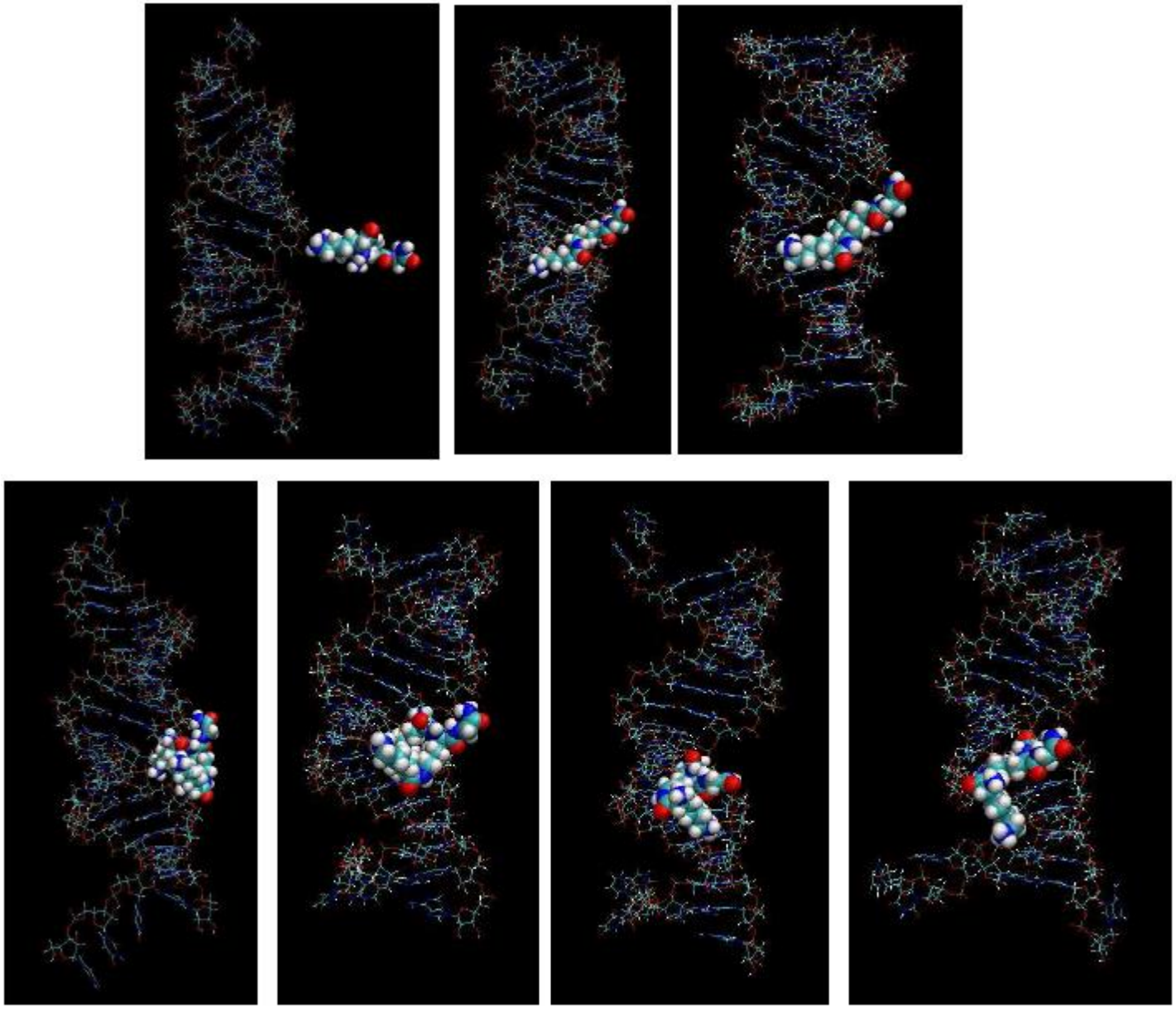

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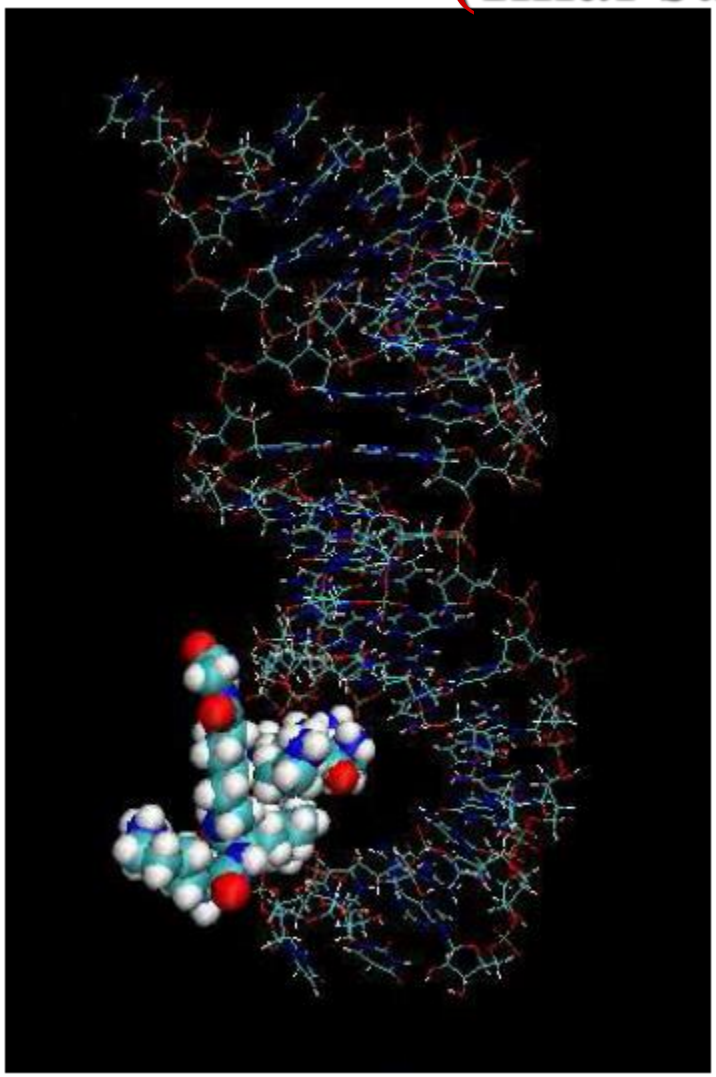
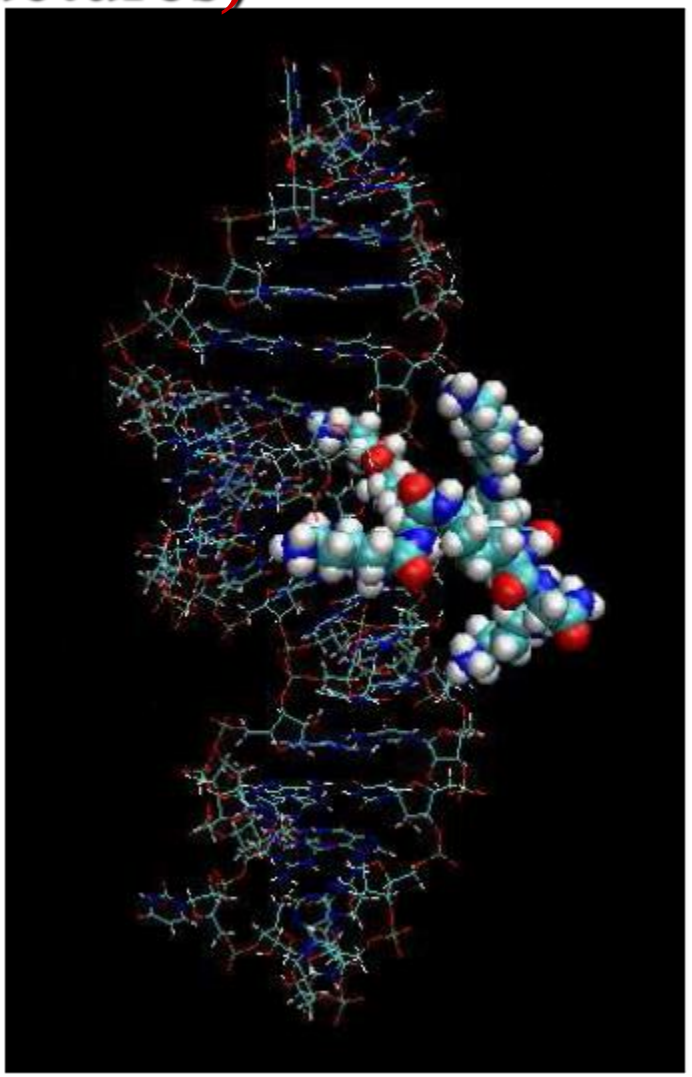
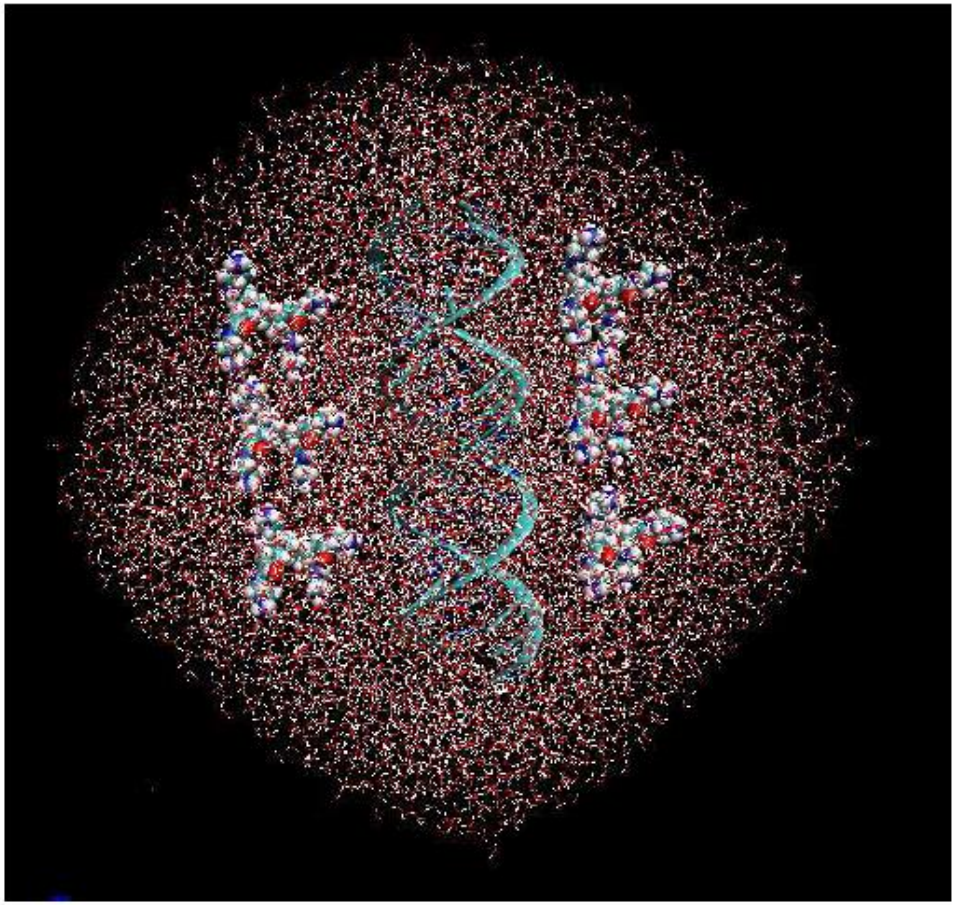
8+ dendrimer: Minor & Major Groove simulations (final structures)



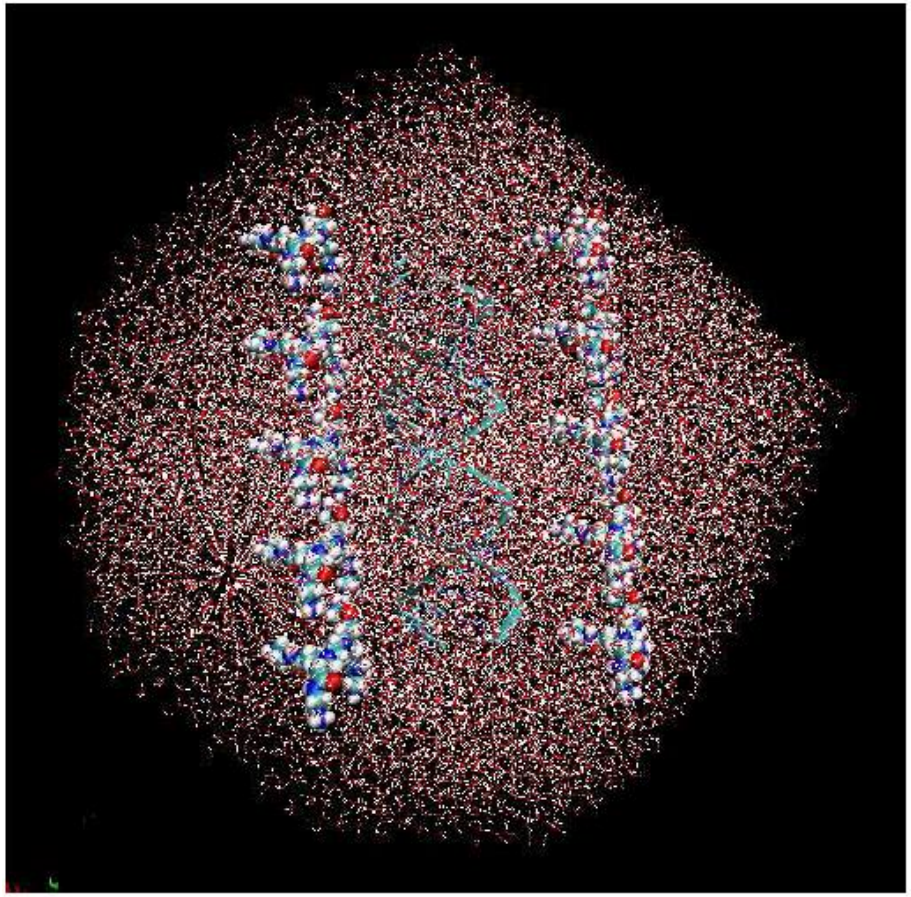


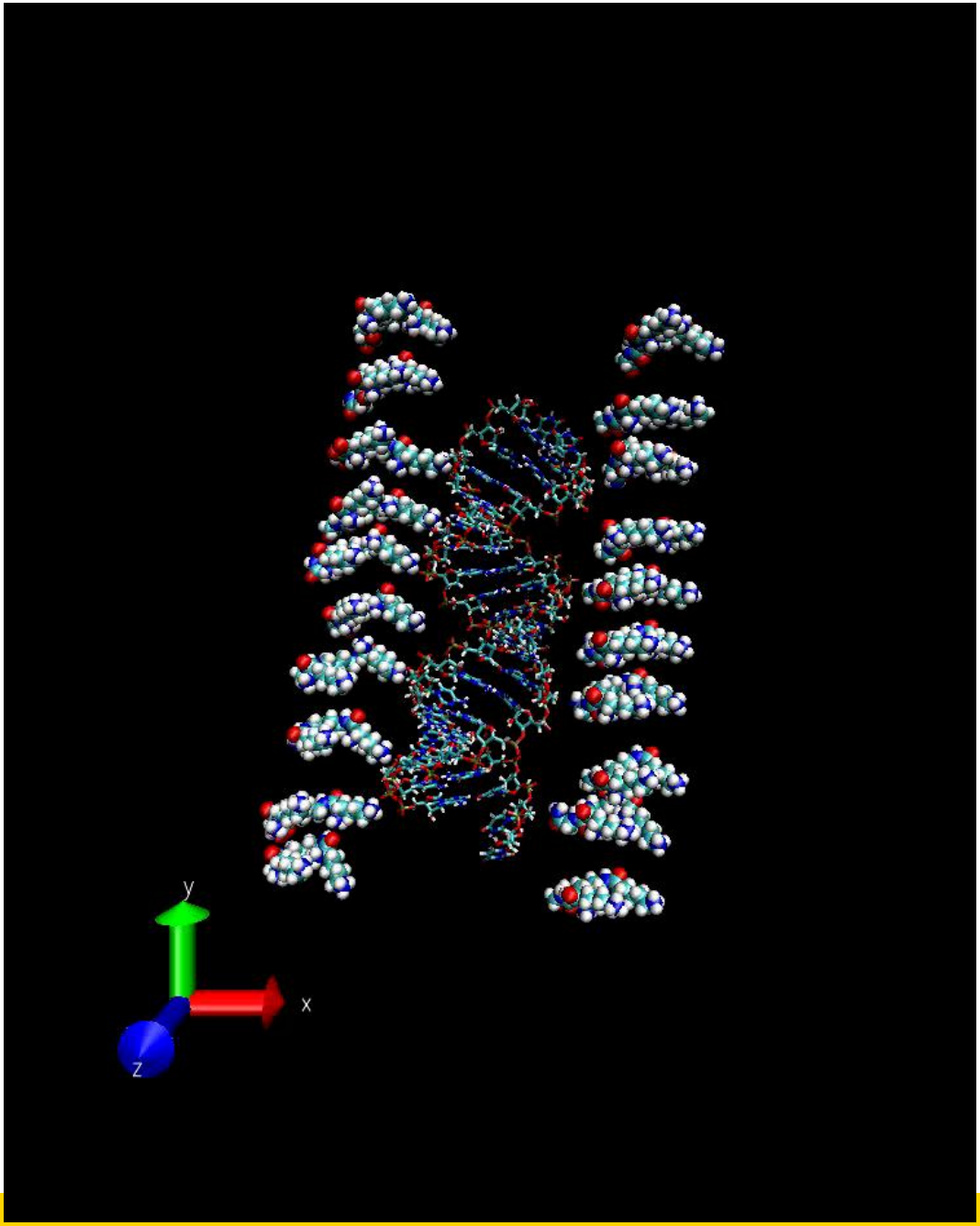
Dialing up the n/p charge ratio:

0.6:1



1:1





n/p charge ratio 2:1

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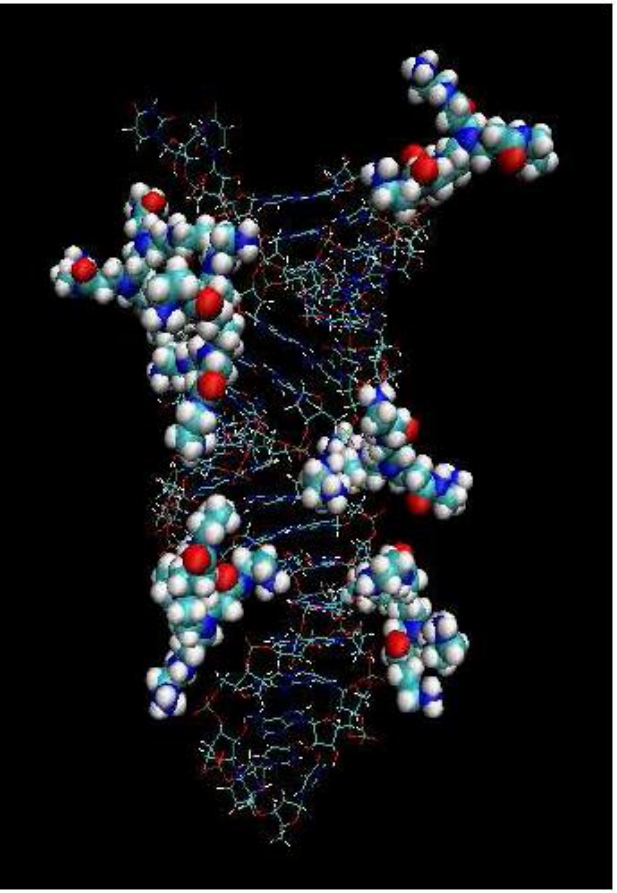
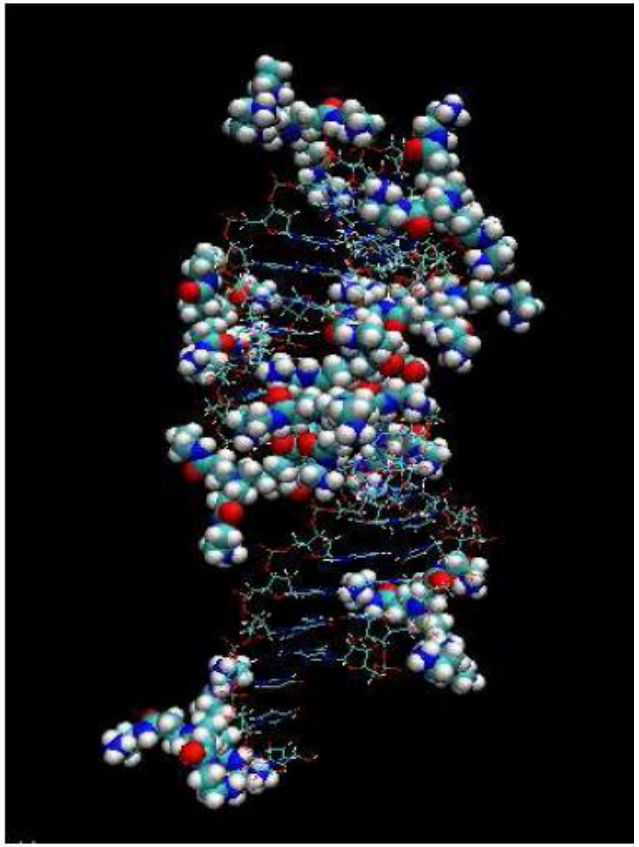
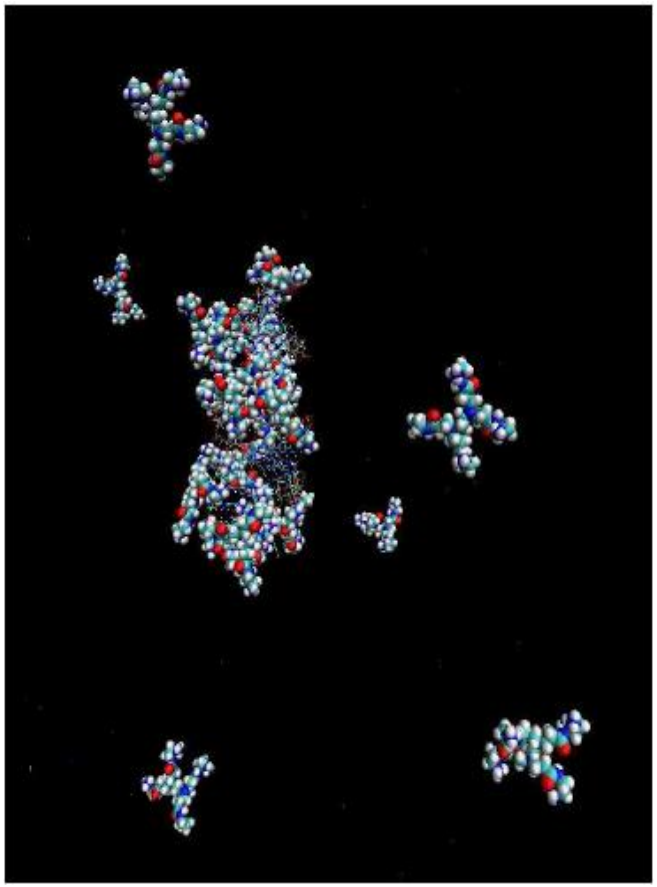




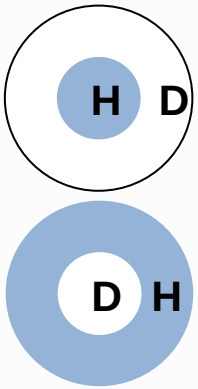


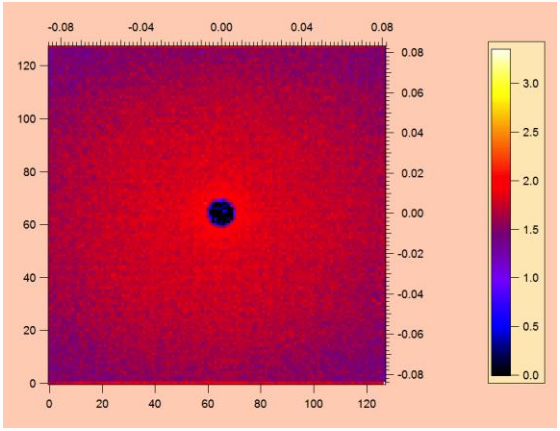
Structure of solvated dendrimers: Precision deuteration with neutron scattering resolves the debate

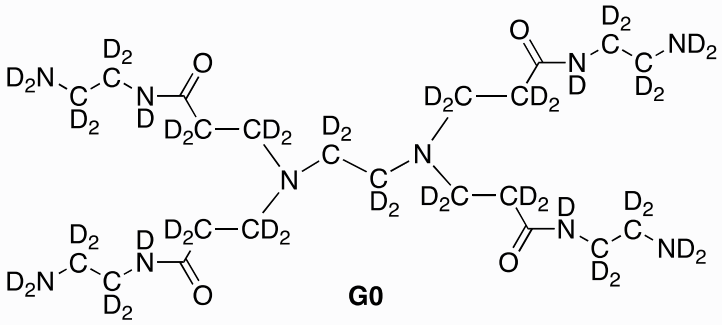
de Gennes et al., 1983: Dense shell

Likos et al., 2006: Theory supports dense-core model, but no convincing experimental evidence

Muthukumar et al., 1990: Dense core







Structure of deuterated G0 PAMAM

Wu et al. (Wei-Ren Chen group), 2011: SANS from selectively deuterated G5 PAMAM dendrimers proves segmental backfolding (dense core) **unambiguously** (*J. Chem. Phys.* 135, 144903)

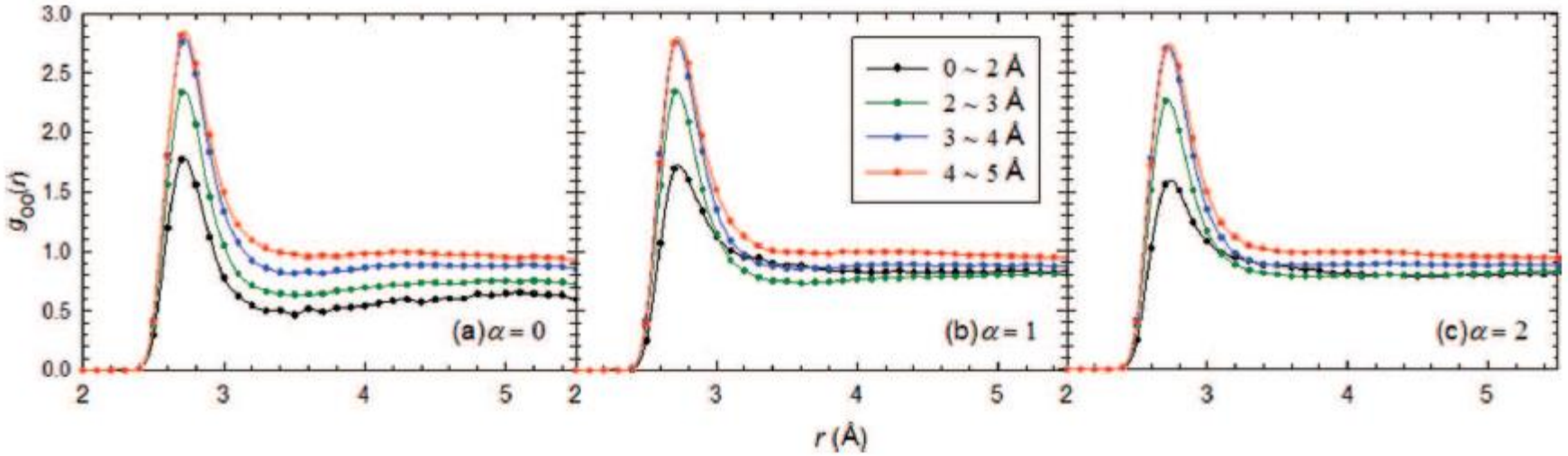
Wei-Ren Chen

Kunlun Hong

UNSW AUSTRALIA

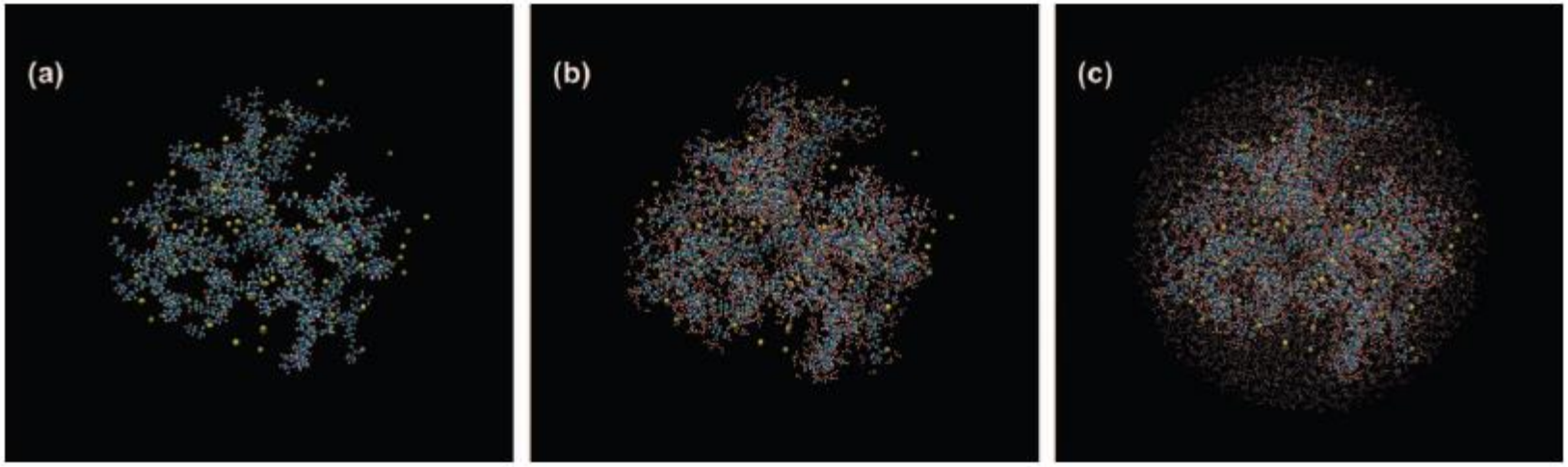
What about the water?

Water is structured differently within proximity of a charged dendrimer !



- α=0 (neutral); α=1 (primary amines protonated); α=2 (primary + tertiary amines protonated)
- Pair correlation functions for water do not stabilize to bulk-like behavior until about 5Å outside the exterior of the dendrimer
- Water is less dense and more ordered within / around the charged dendrimer

Modeling Neutron Scattering:
Should account for not just the polymer but also the invasive water and cavities!



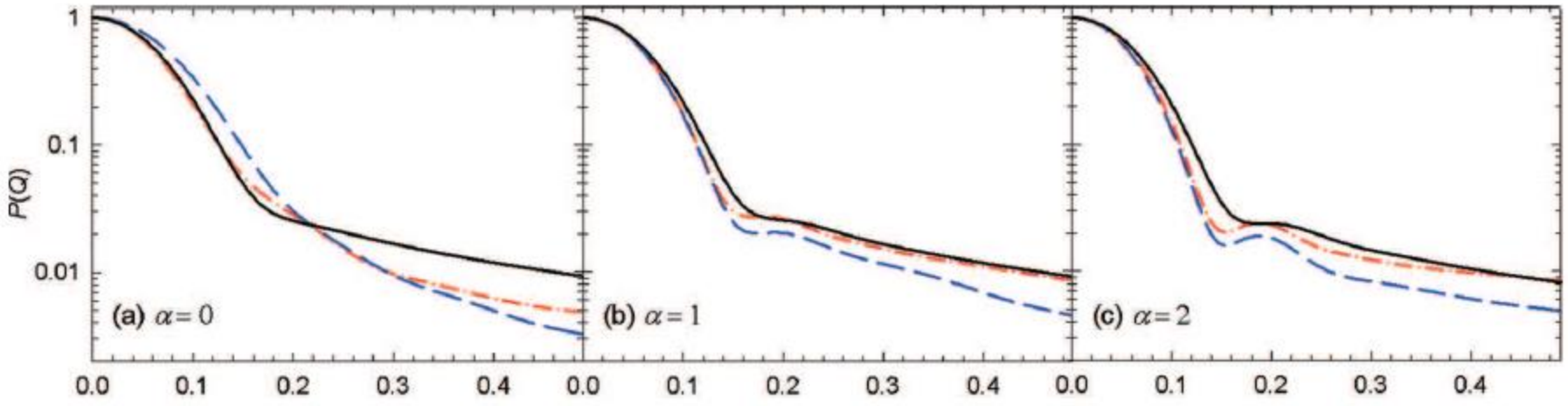
Dendrimer + counterions

Dendrimer + Counterions + invasive water

Dendrimer + Counterions + invasive water + non-bulk water corona

- To do this correctly requires atomistic molecular dynamics simulations

Improved prediction of scattering form factors



- This results in a significantly better fitting to the experimental scattering data
- So, for dendrimers and polymers solvated water is important, and differs from the bulk

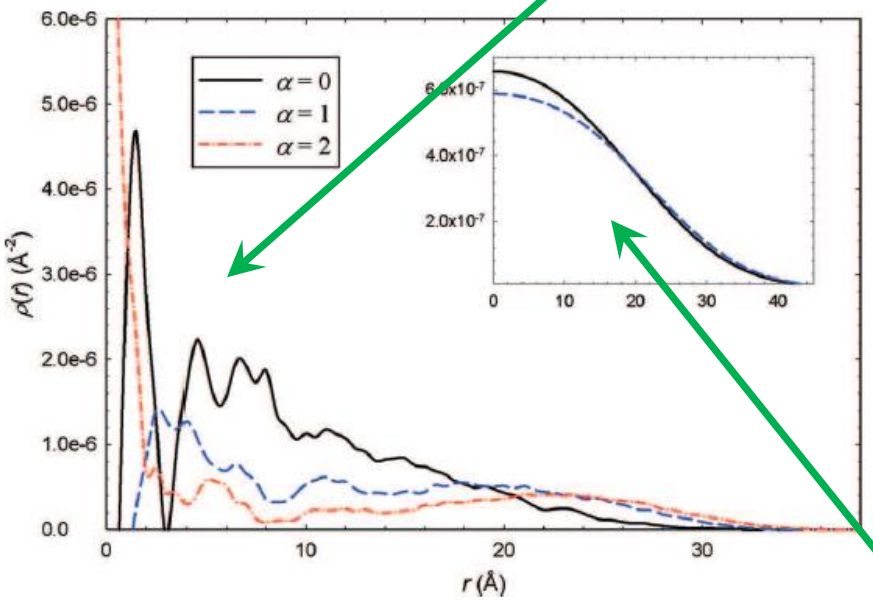
THE JOURNAL OF CHEMICAL PHYSICS **136**, 144901 (2012)

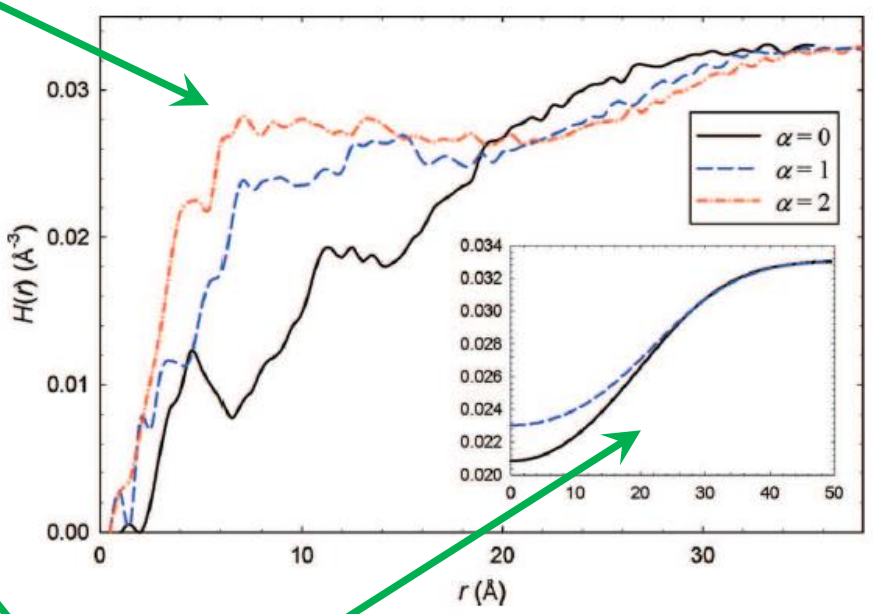
Structured water in polyelectrolyte dendrimers: Understanding small angle neutron scattering results through atomistic simulation

Bin Wu,[1,2,3] Boutheïna Kerkeni,[4] Takeshi Egami,[5,6] Changwoo Do,[1] Yun Liu,[7,8] Yongmei Wang,[9] Lionel Porcar,[10] Kunlun Hong,[2] Sean C. Smith,[2] Emily L. Liu,[3] Gregory S. Smith,[1] and Wei-Ren Chen[1,a)]

Charged dendrimers swell electrostatically: **Core becomes less dense; dendrimer extends further outward**

Molecular dynamics

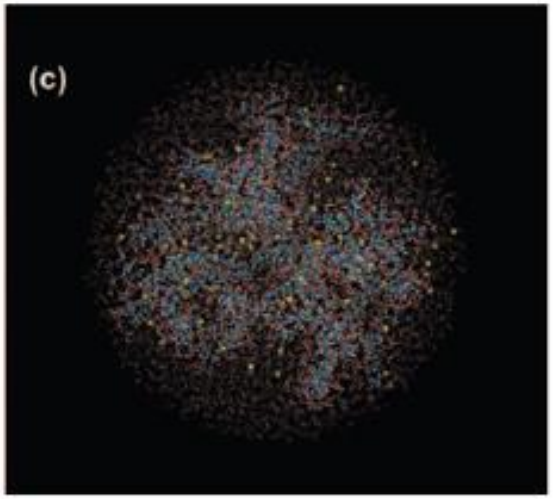




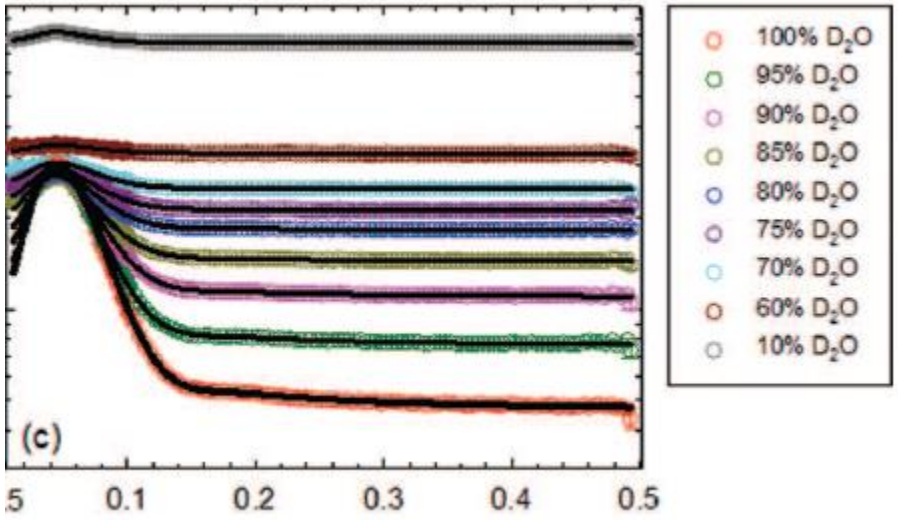
Experimental fitting

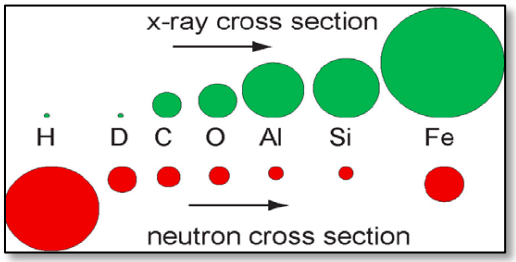
- Invasive water penetrates into the core to fill the extra voids that open up as the dendrimer swells due to electrostatic repulsion

How do we separate out the invasive water from the dendrimer experimentally?



Dendrimer +
Counterions +
invasive water +
non-bulk water corona

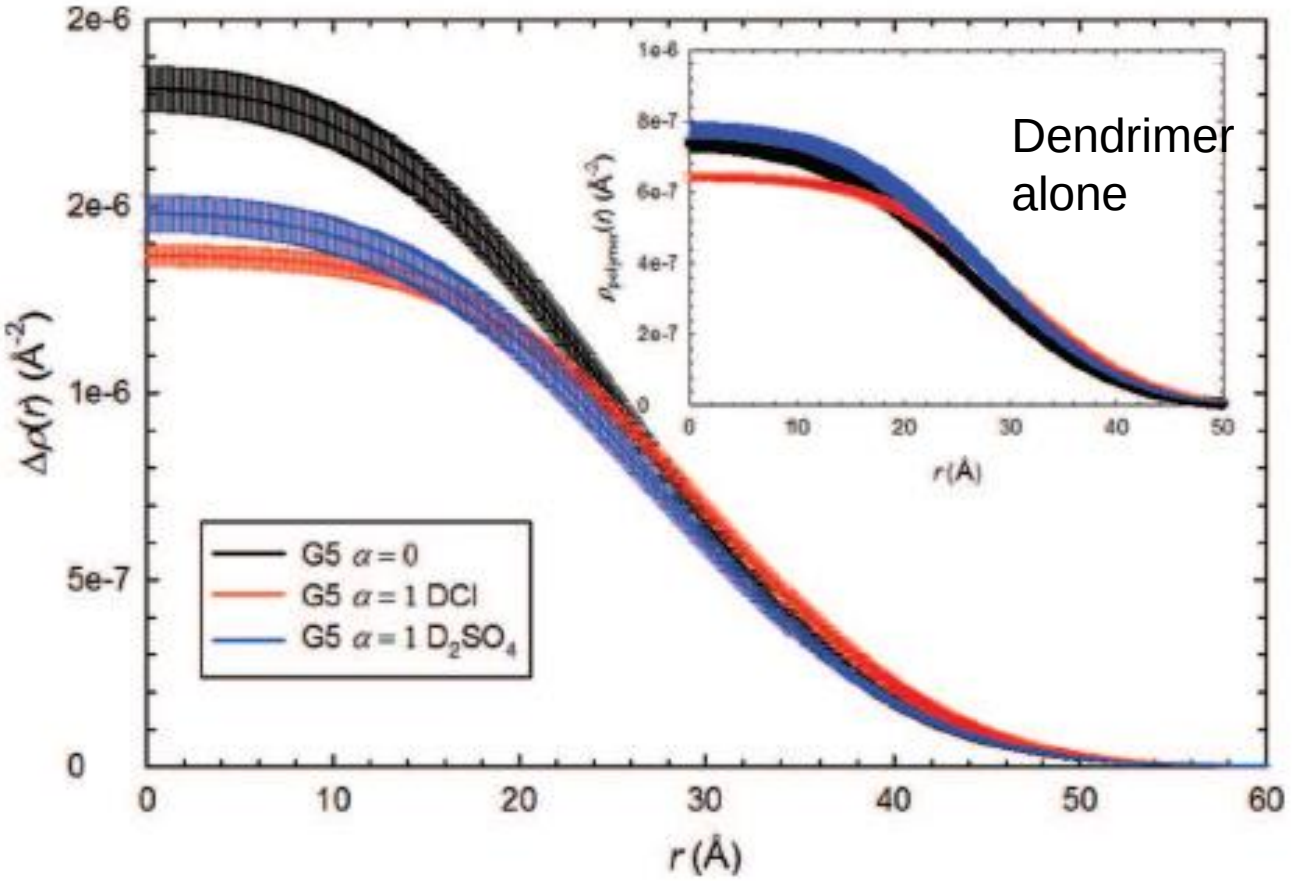




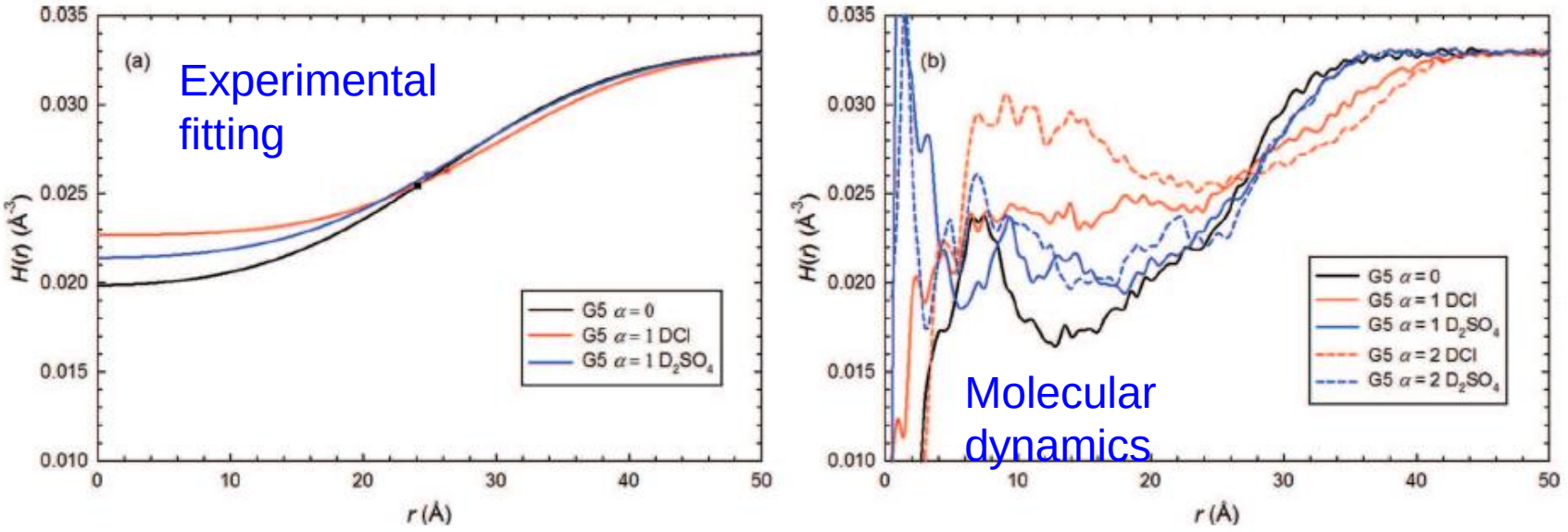
Contrast variation small angle neutron scattering:

- Altering the ratio of D_2O to H_2O allows to distinguish the invasive water from the actual dendrimer

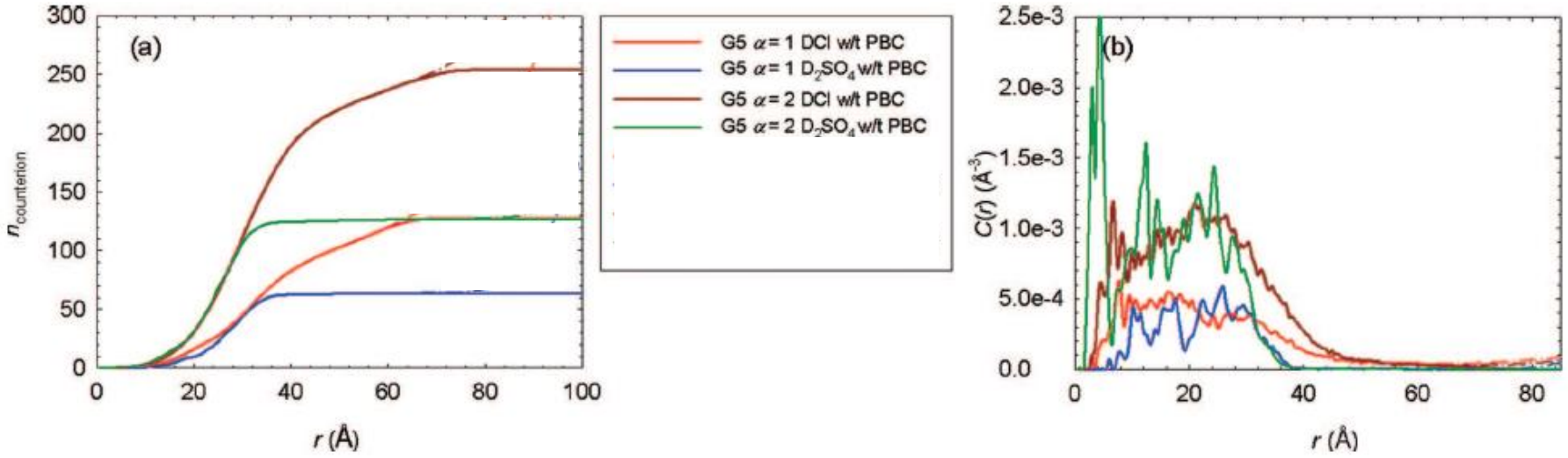
Electrostatic swelling of the dendrimer is dependent also on the nature of the counterion !



Solvating water adjusts to changes in the dendrimer structure – moves in to fill voids



Charge of the counterions mediates the electrostatic swelling



Multiple charge on sulphate SO_4^{2-} coordinates two protinated amine sites – tends to hold the structure together more and reduces the swelling effect.

Wei-Ren Chen
(ORNL)

Kunlun Hong
(ORNL)

Bin Wu
(RPI / ORNL)

Integrated Materials Design: Accelerating the Discovery of New Functional Materials

Sean Smith

Never Stand Still

School of Chemical Engineering, UNSW Australia

Ouyang Defang
(Aston)

Harry Parekh
(UQ)

Aijun Du
(QUT)

Chenghua Sun
(Monash)

Yan Jiao
(Adelaide)

UNSW
AUSTRALIA

Integrated Materials Design: Accelerating the Discovery of New Functional Materials

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