修学院離宮
Shugaku-in Imperial Villa

Eiichi Nakamura

Office of the President and
Department of Chemistry
The University of Tokyo

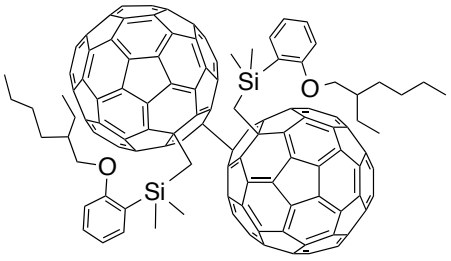
Atomic Resolution Electron Microscopy for Organic Chemists

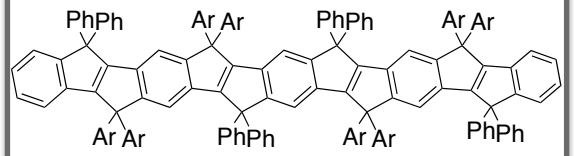
A Major Problem in Chemistry

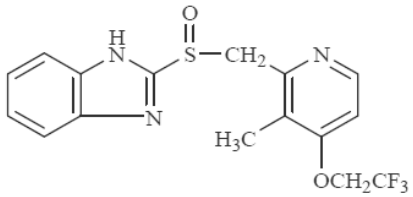
Molecular Design
≠
Real World Functions

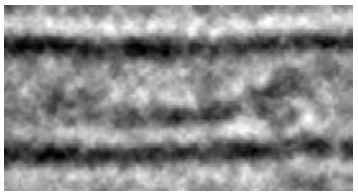
From Molecular World to Real World

Quantum Mechanical



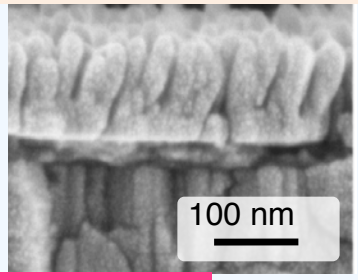




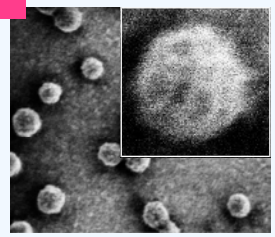


Nano•meso sized boundary

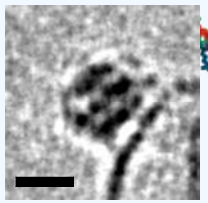
1. Heterogeneous solid

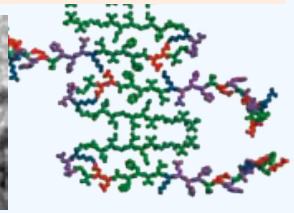


2. Interface



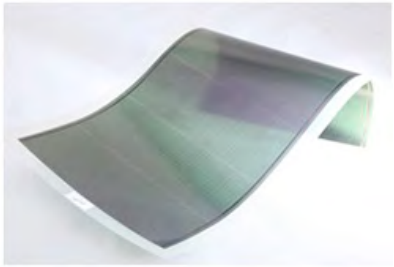
3. Fluctional systems





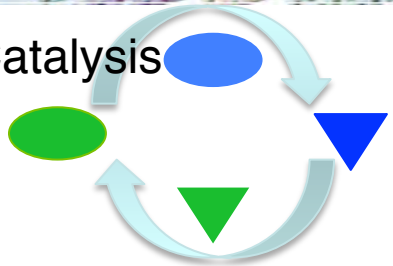
Classical Mechanical

plastic solar cells



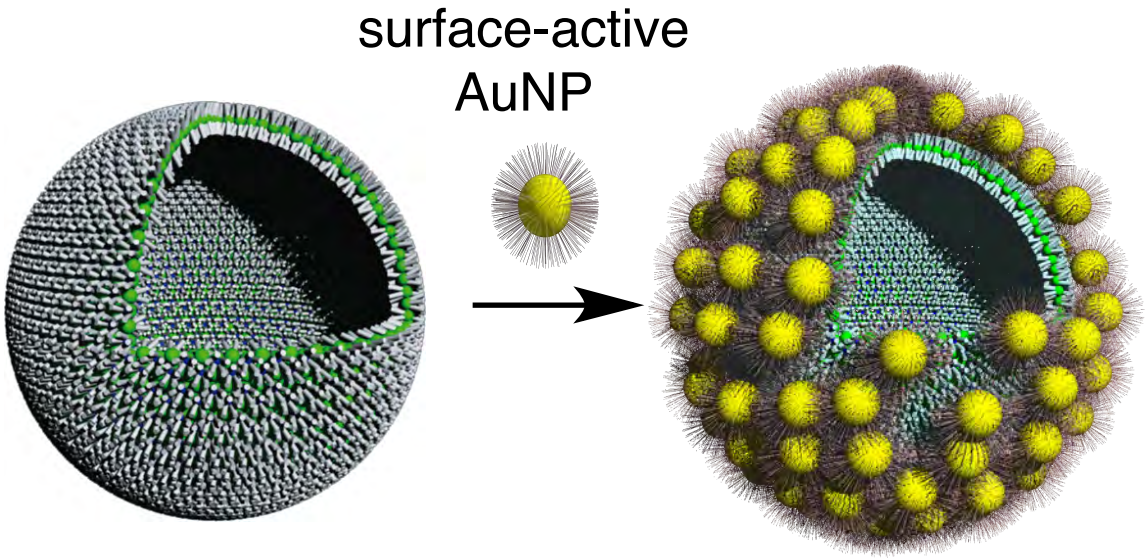
Pharmaceuticals

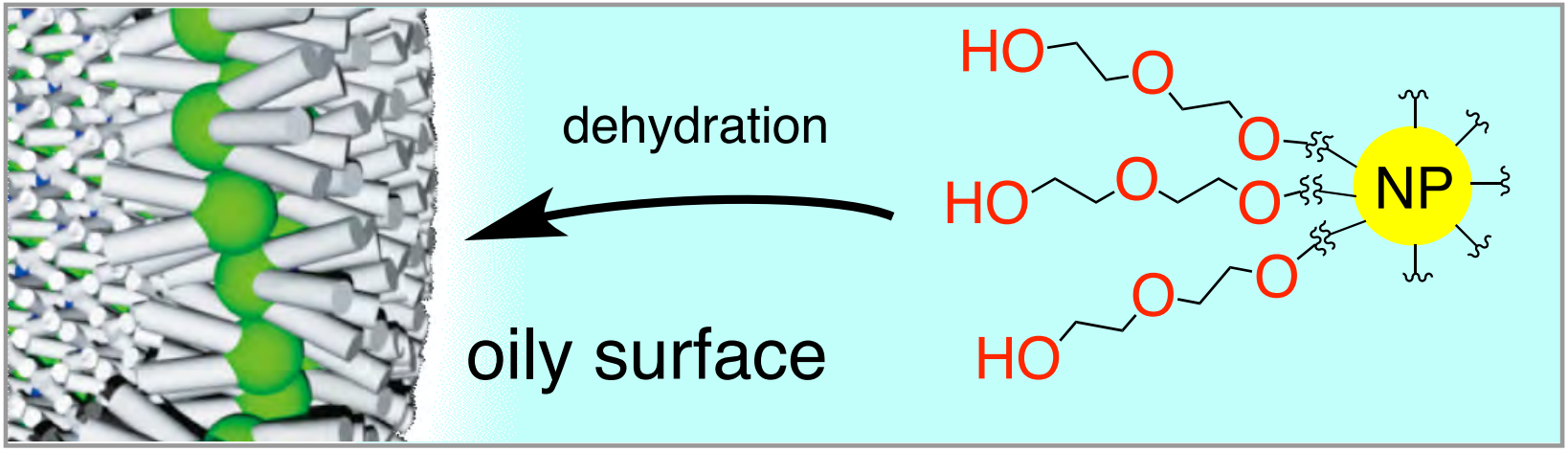
Catalysis



1 nm 5 nm 50 nm 500 nm 1 mm

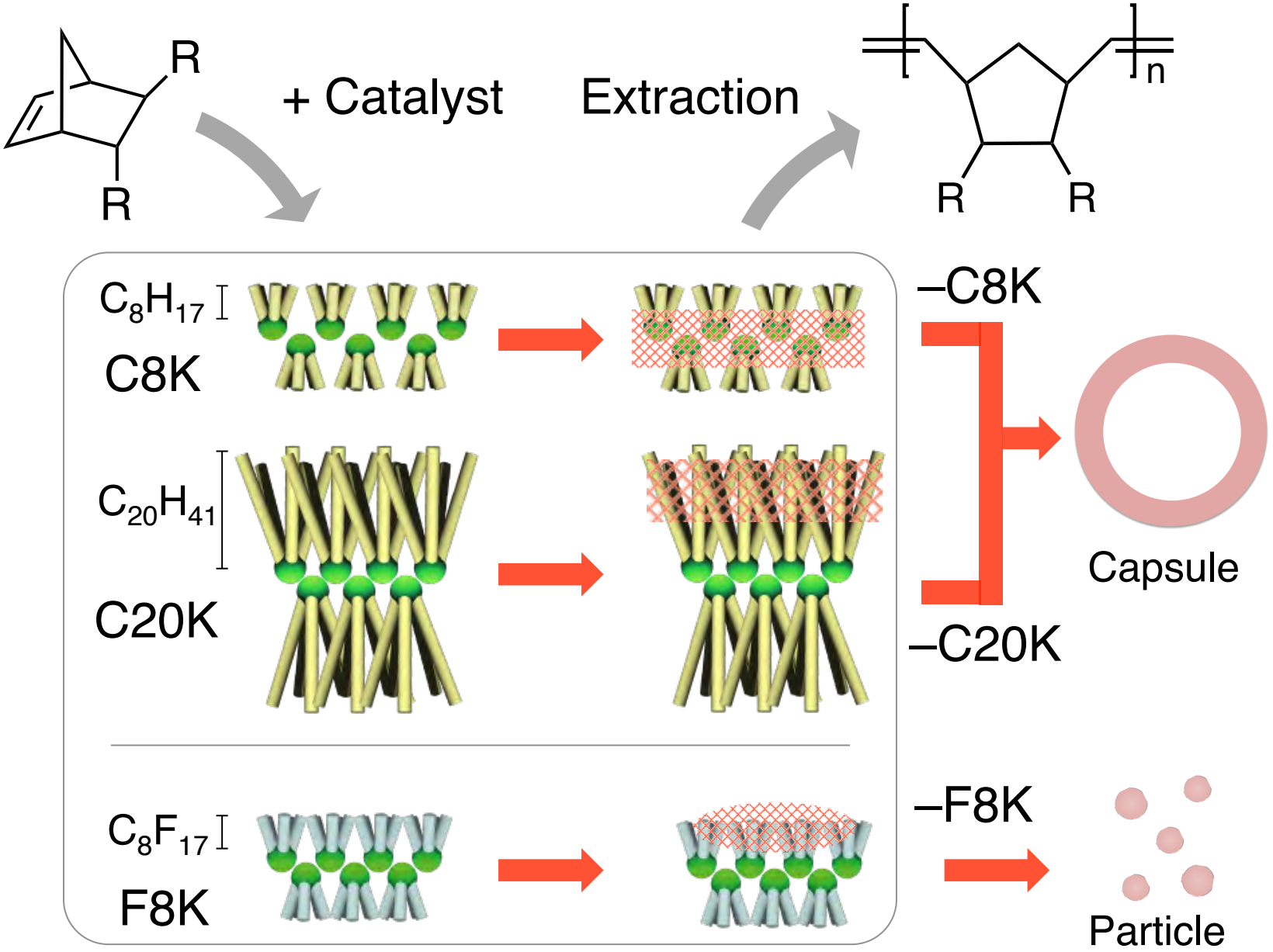
Spontaneous Self-Assembly of NP-1





J. Am. Chem. Soc. (2015) with Koji Harano, Ricardo Gorgol Mizoguchi

Control of Polymer Growth in Fullerene Bilayers



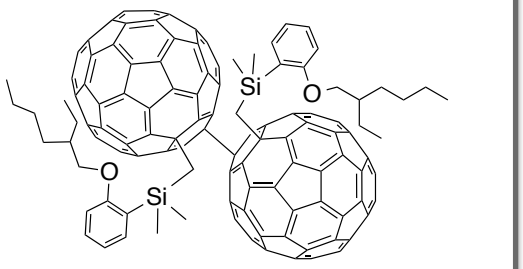
J. Am. Chem. Soc. (2016)

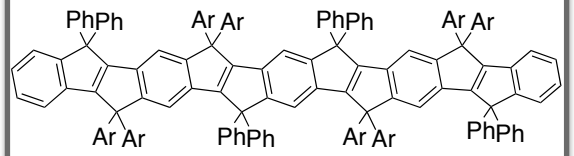
with Koji Harano, Ricardo Gorgol Mizoguchi

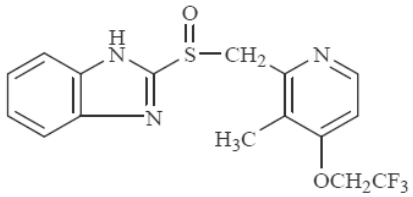

Our own
SOLAR CELL
PROJETCT

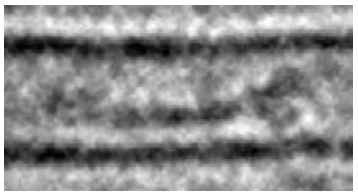
From Molecular World to Real World

Quantum Mechanical → Nano•meso sized boundary → Classical Mechanical









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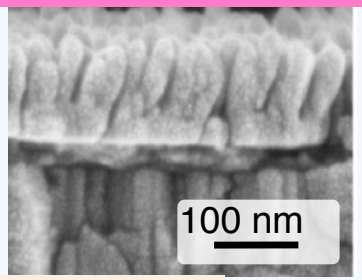

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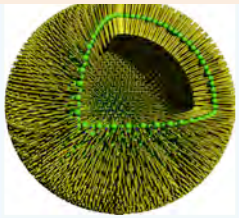
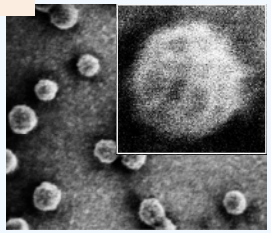
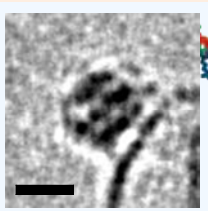
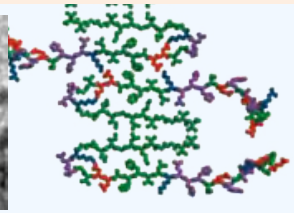


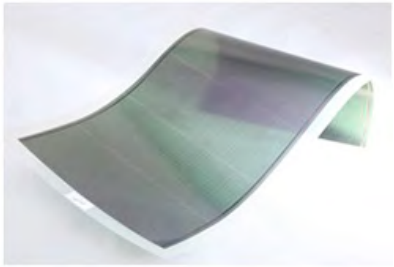


3. Non-equilibrium liquid



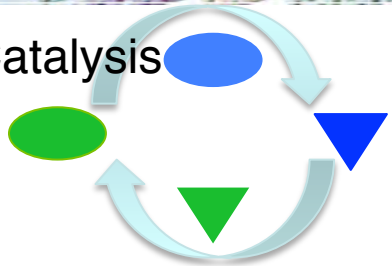


plastic solar cells



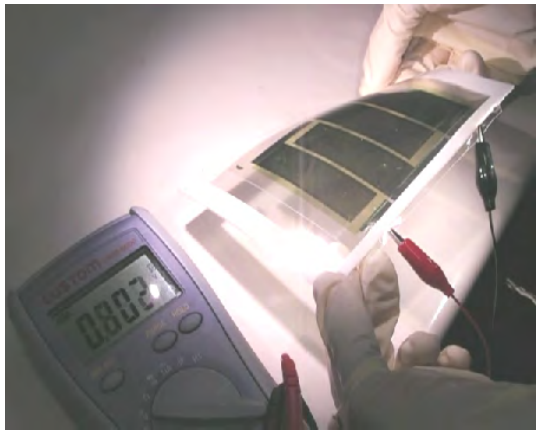
Pharmaceutrical

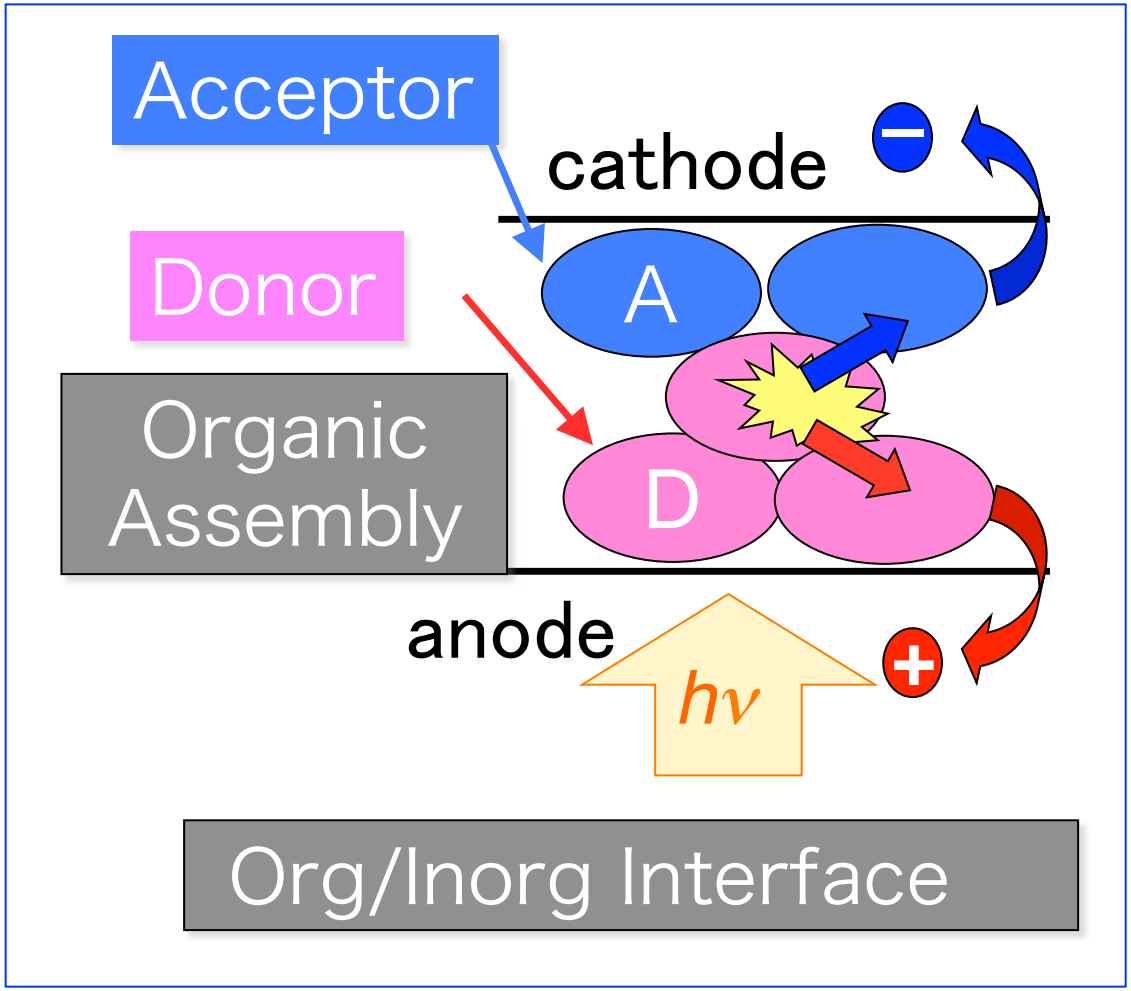
Catalysis



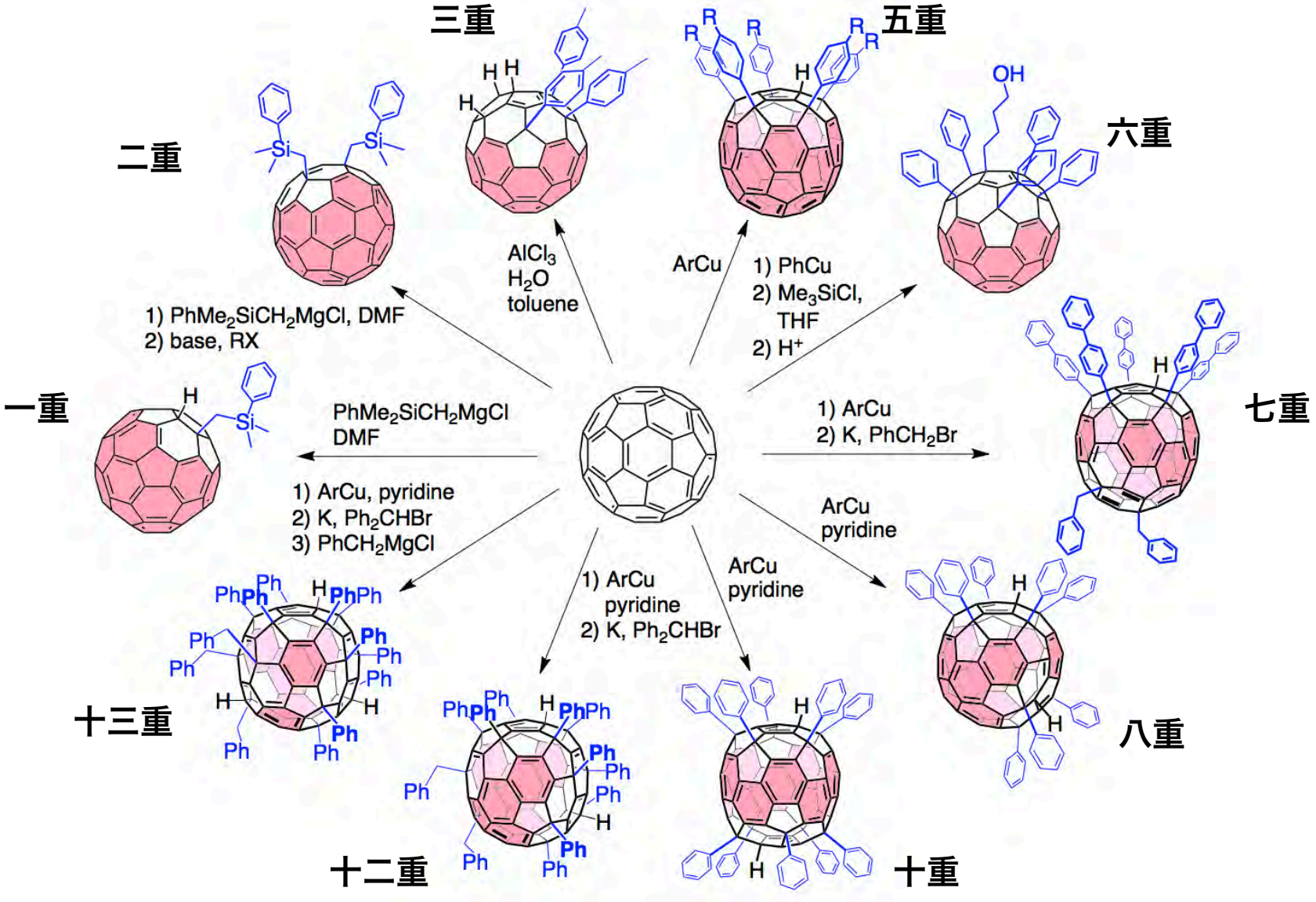
1 nm — 5 nm — 50 nm — 500 nm — 1 mm

Organic Solar Cells is a Device to Extract e^- and h^+ from a Photo-excited Donor/Acceptor Molecular Assembly





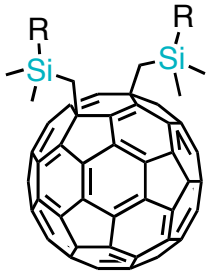
Screening of >800 n-Type Semiconductors



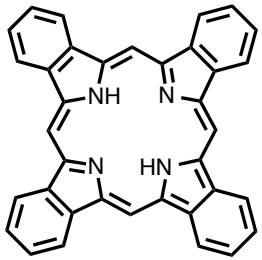
Y. Matsuo, E. Nakamura, *Chem. Rev.* **2008**, *108*, 3016-3028.

Chemistry solves energy problems!

Univ of Tokyo (2004-10) → Mitsubishi Chemical's window solar cells (2015)



R = Me, Ph



BP

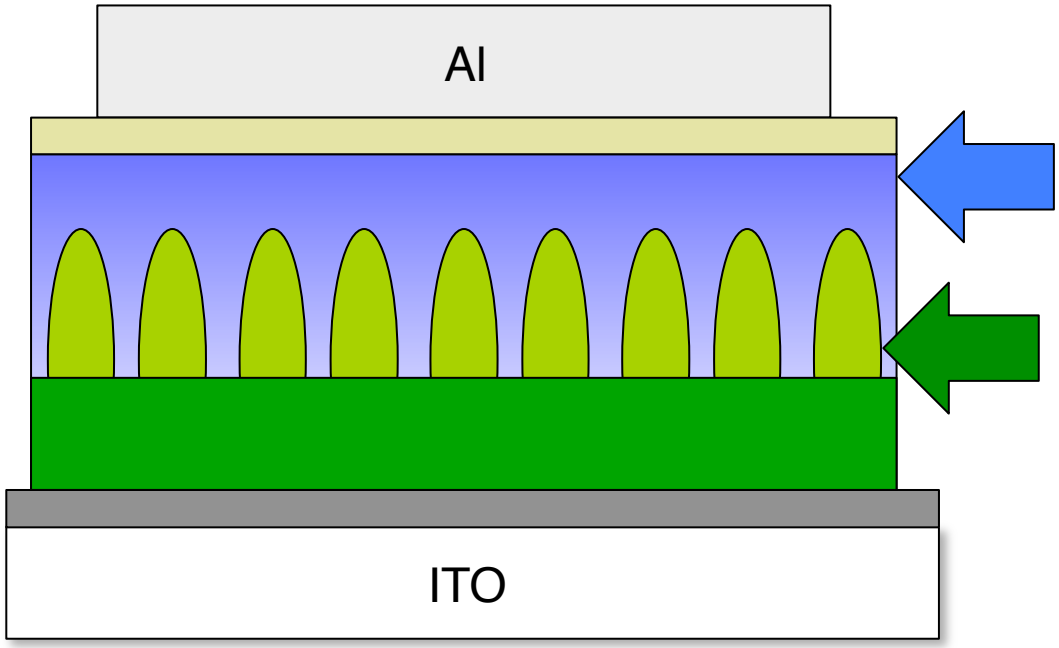
Nakamura, JACS (2009)

from Mitsubishi Chemical home page

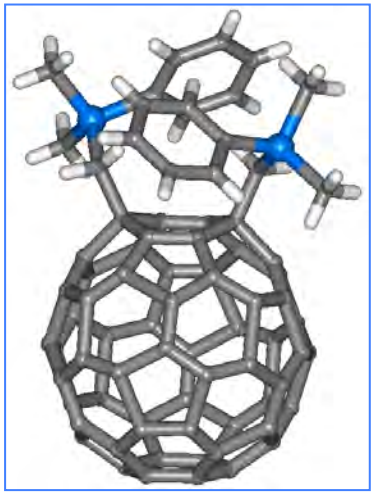
"Zero Energy Building" by Taisei Corporation

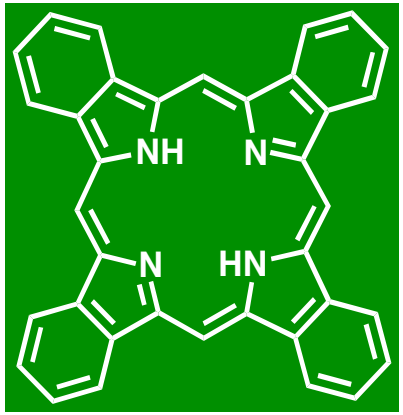
from Taisei home page

Our ERATO Device has a Column/Canyon Structure (2009)



SIMEF





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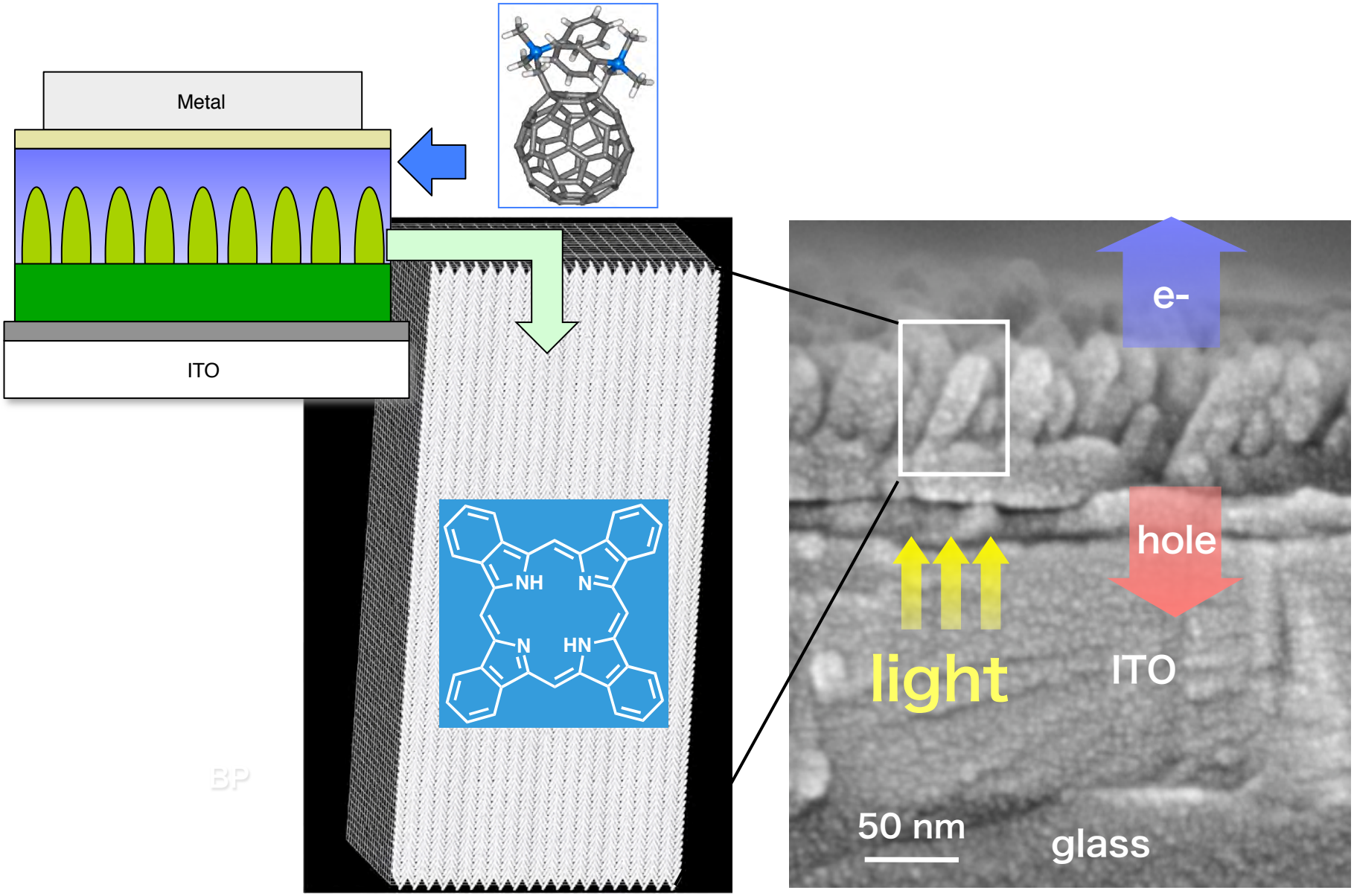
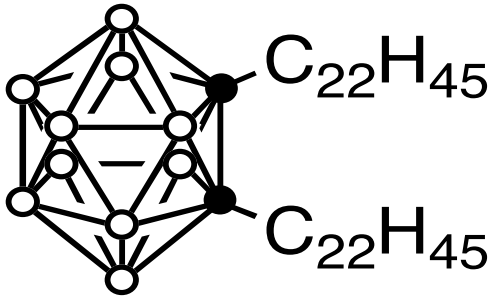
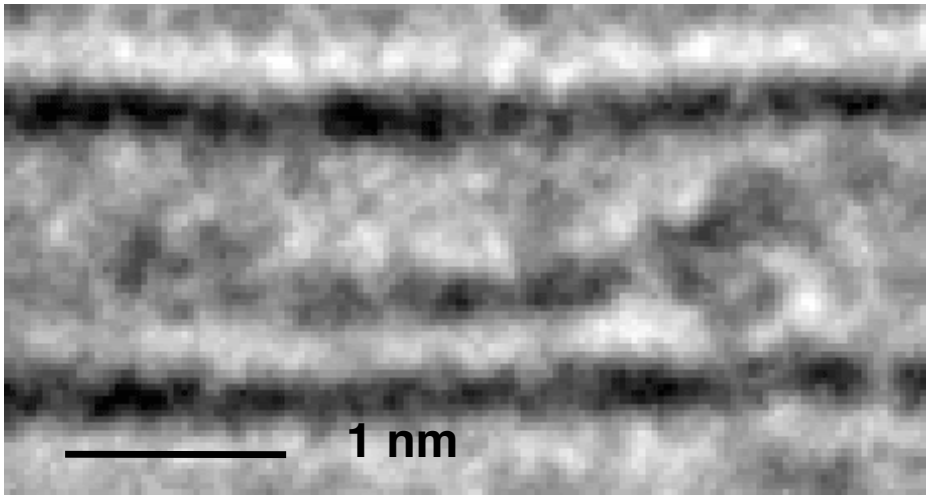


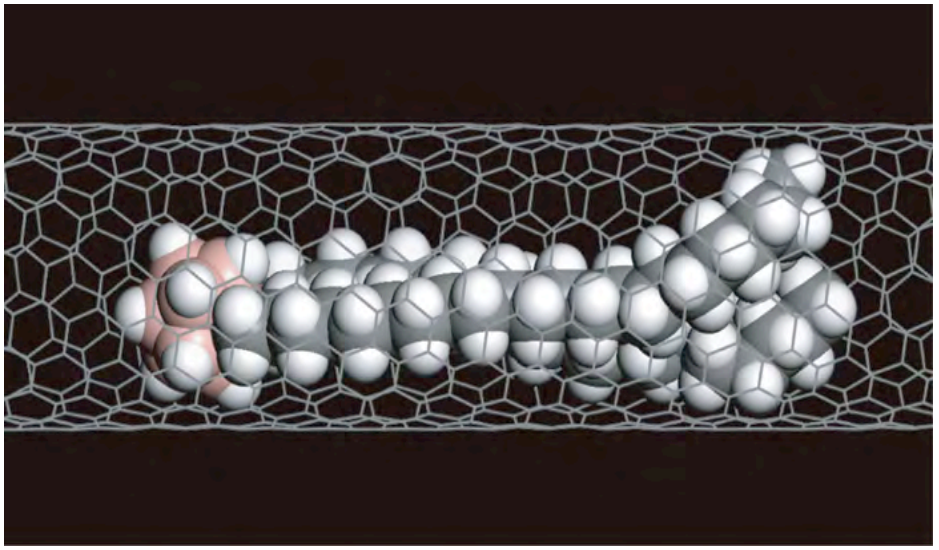

修学院離宮
Shugaku-in Imperial Villa
How do crystals grow?
How do molecules phase separate?

Movie of a Single Molecule in 2007
- Single-molecule, Atomic-resolution Real-time (SMART) TEM Imaging -



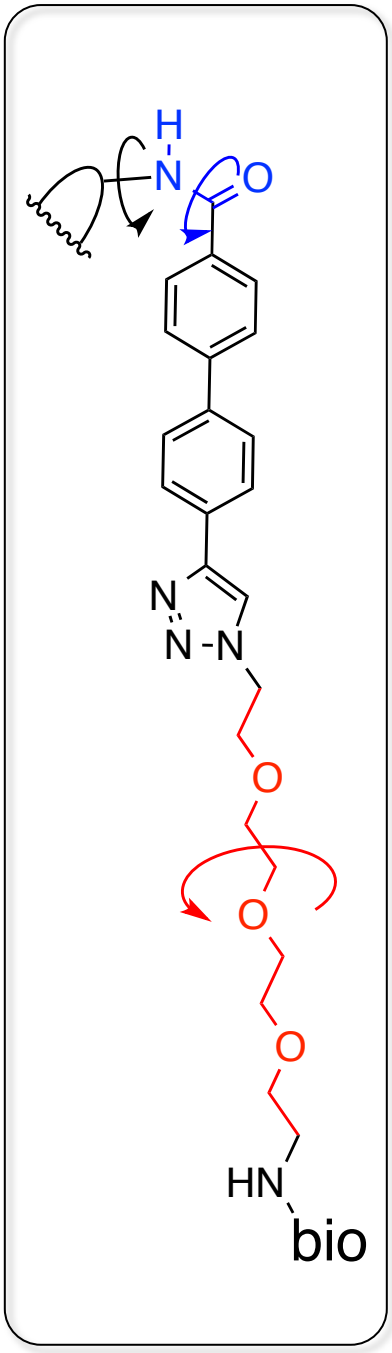
Alkylcarborane

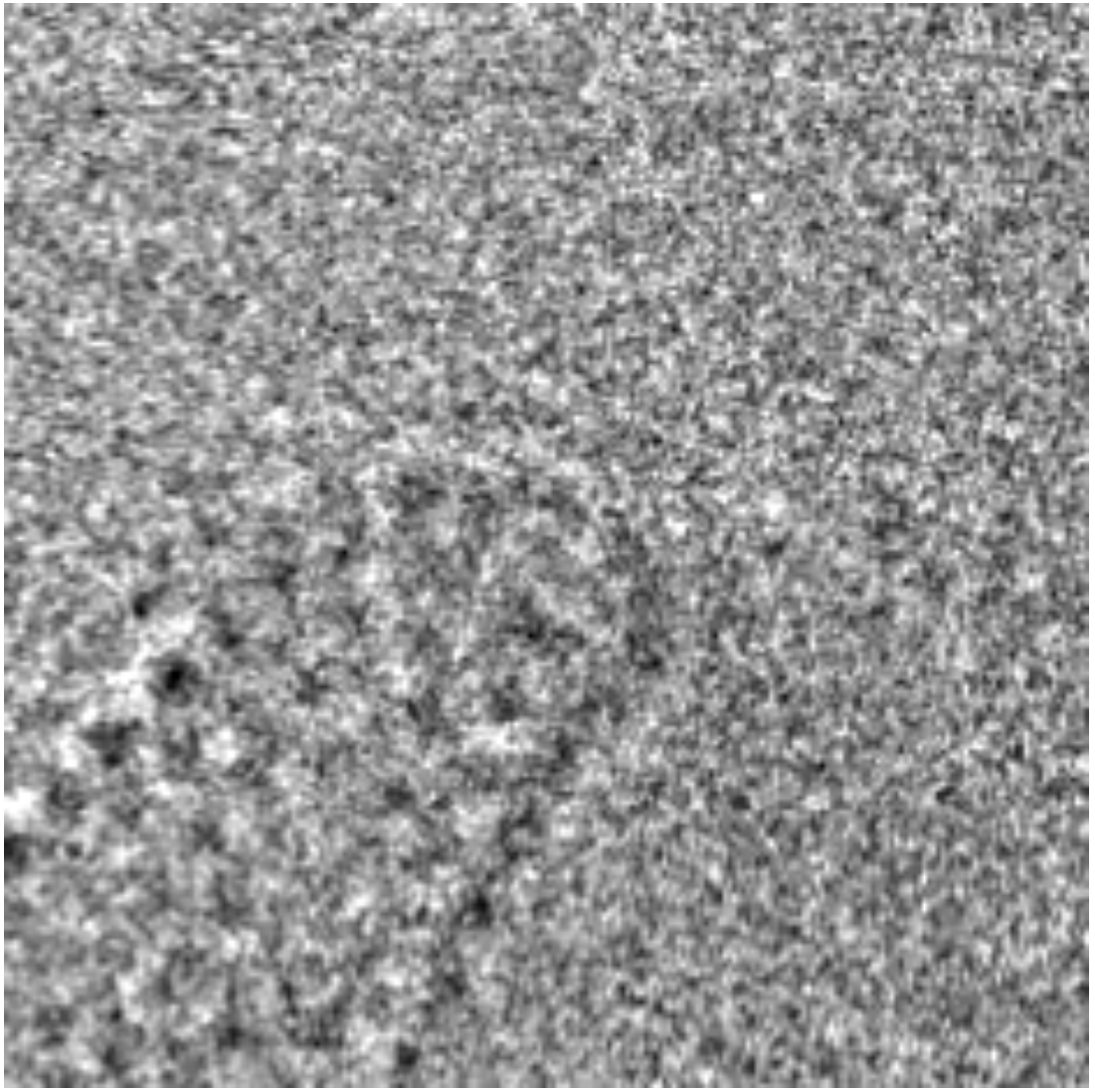




Science **2007,** *316*, 853

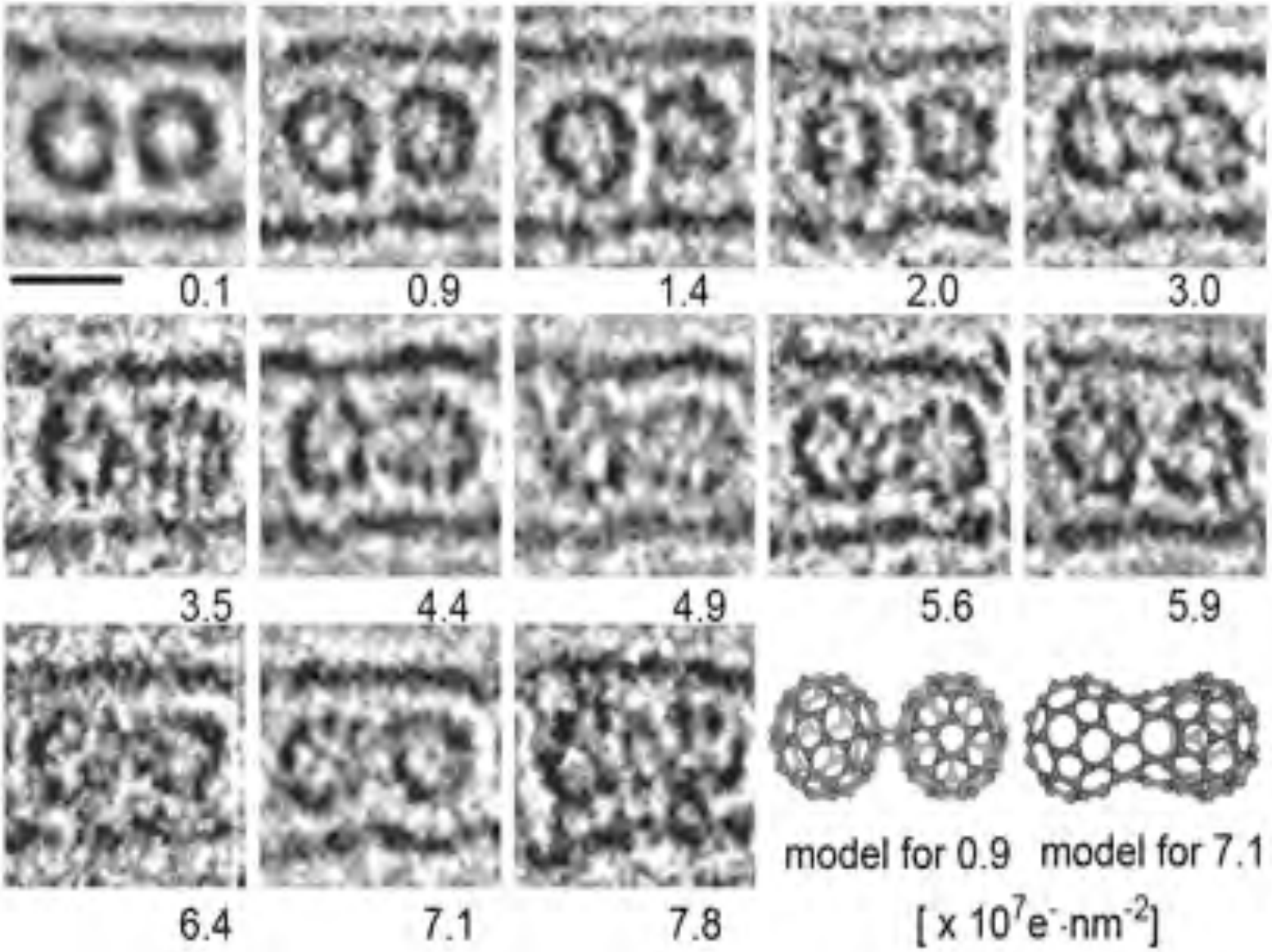
Atomic Resolution Movie of A Molecule





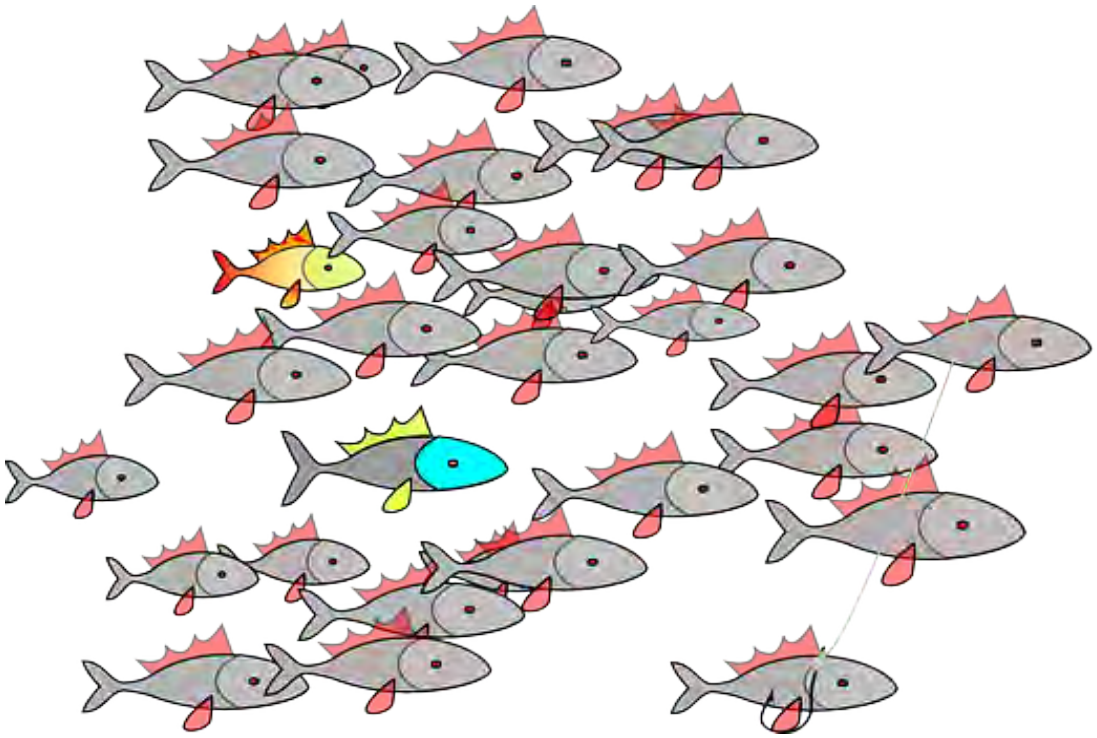
JACS (2015)

TEM Observation of Fullerene Dimerization



Nat. Chem. (2010)

Our Key Discovery: Design/synthesis of "Chemical Hooks" for Fishing Molecules



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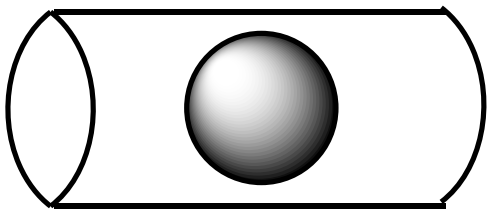
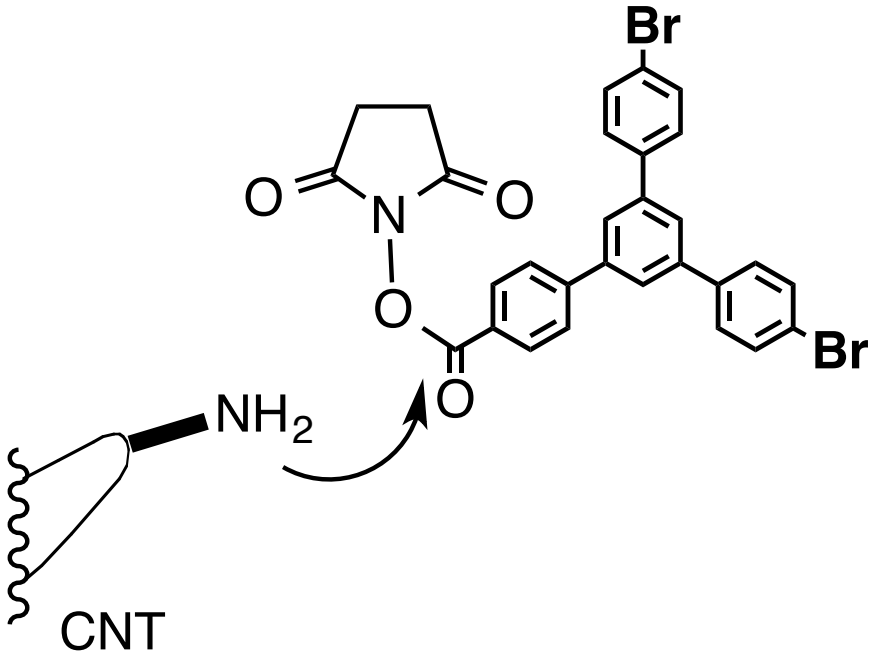


Eel Trap



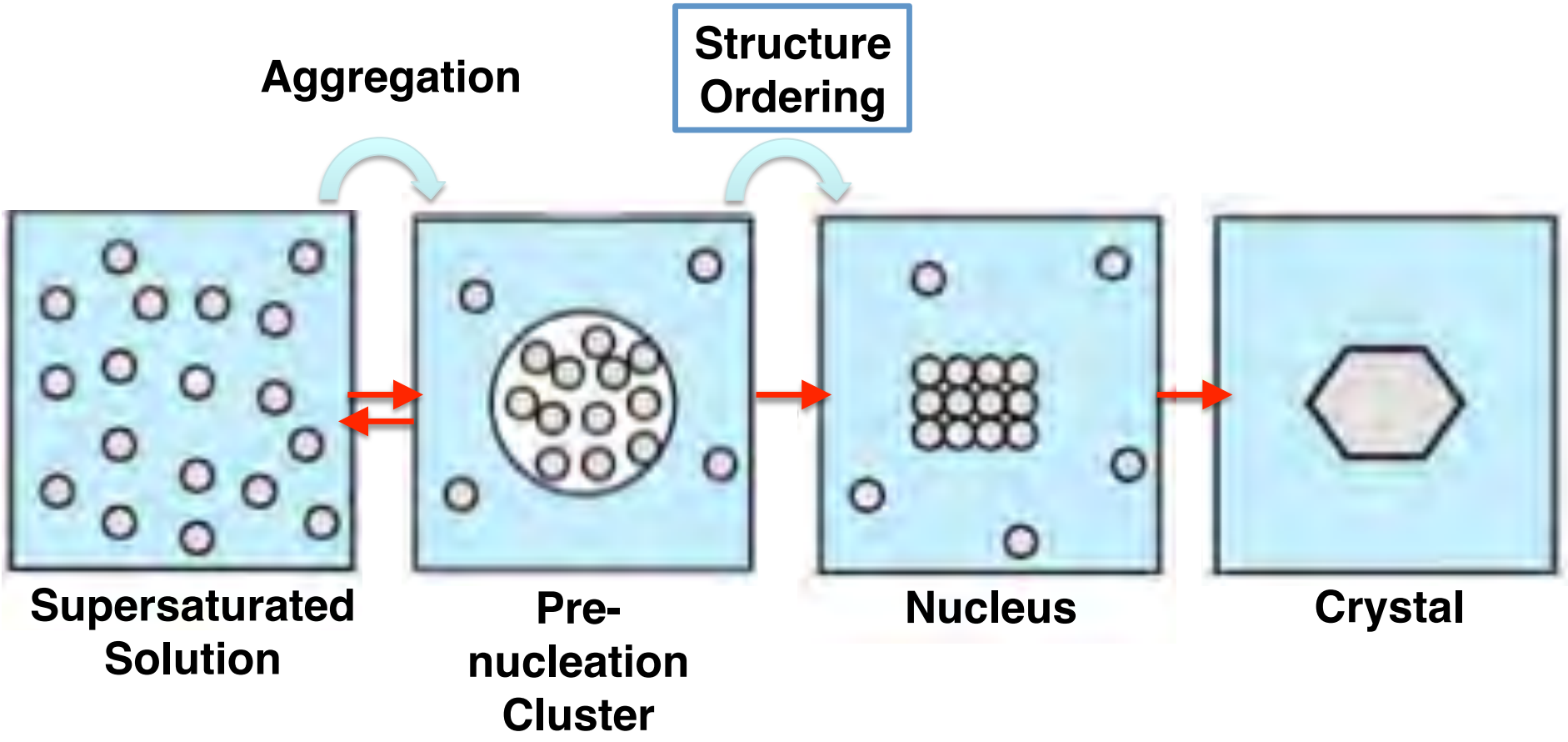
Chemical Hook

Mechanism of Crystal Nucleation

with Harano, Homma, Niimi, Koshino, Suenaga, Leibler

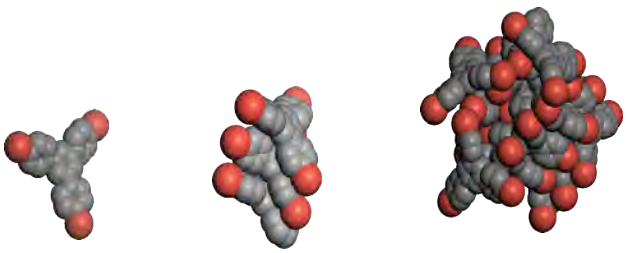
Nat. Mater., 11, 877-881 (2012)

Two-Step Mechanism of Nucleation

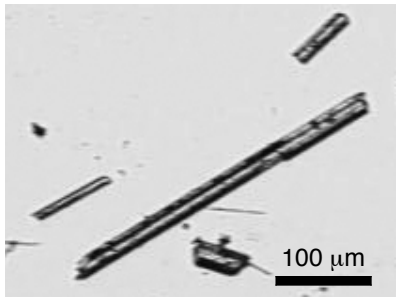


A. S. Myerson, *et al. Acc. Chem. Res.* **2009**, *42*, 621.

Gibbs Proposal of Nucleation/Crystallization



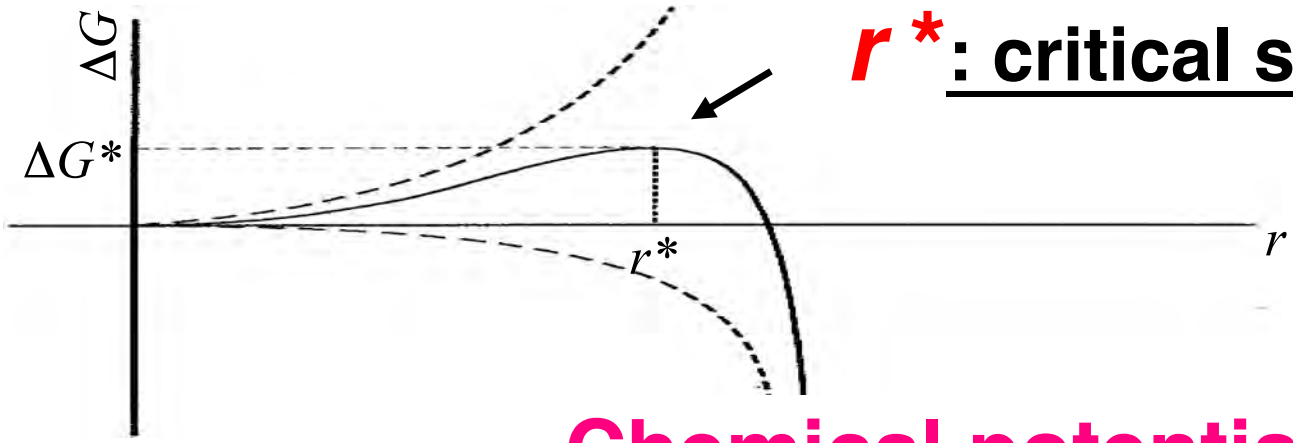
Embryo or Nucleus



Pre-nucleation

Nucleation/ Crystal Growth

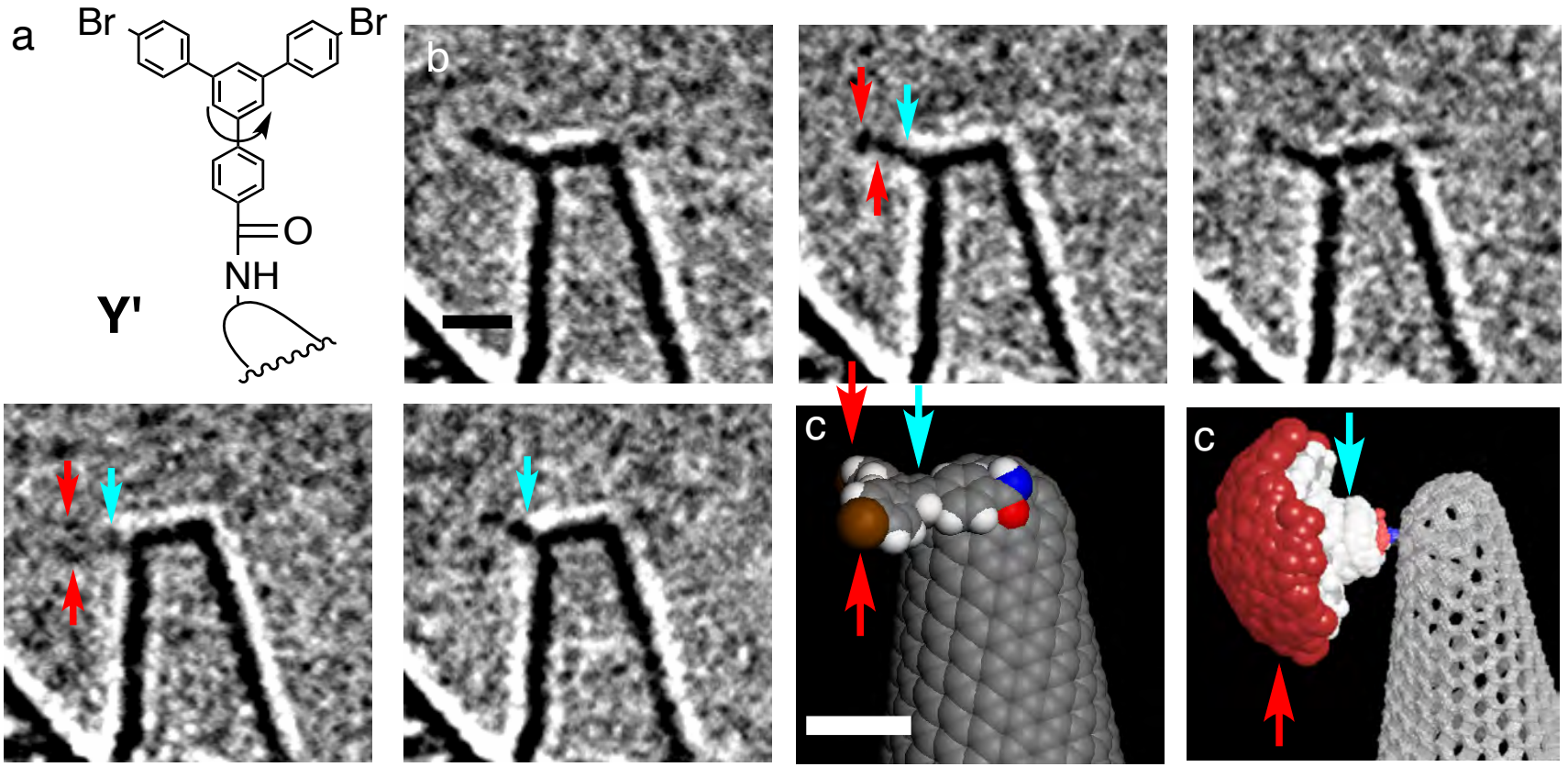
Surface energy (r^2)



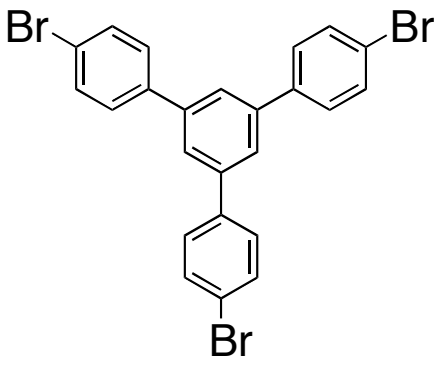
r*: critical size*

Chemical potential (r^3)

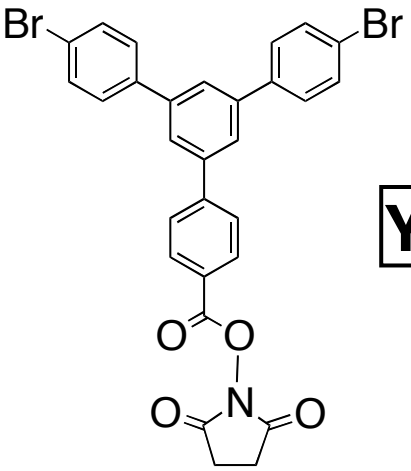
Single Molecule Template for Nucleation



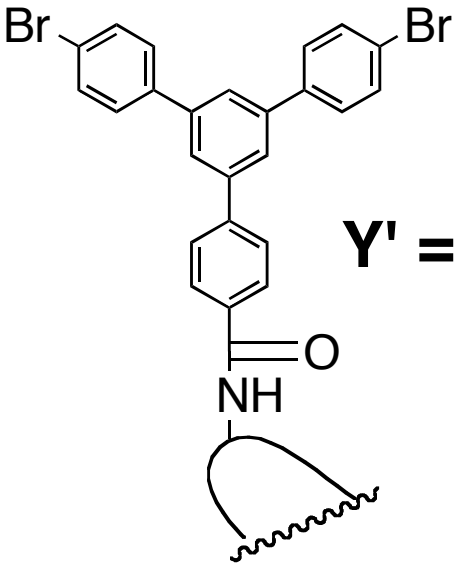
We Recrystallized Two Compounds
on the same Single-molecule Nucleation Site



Y

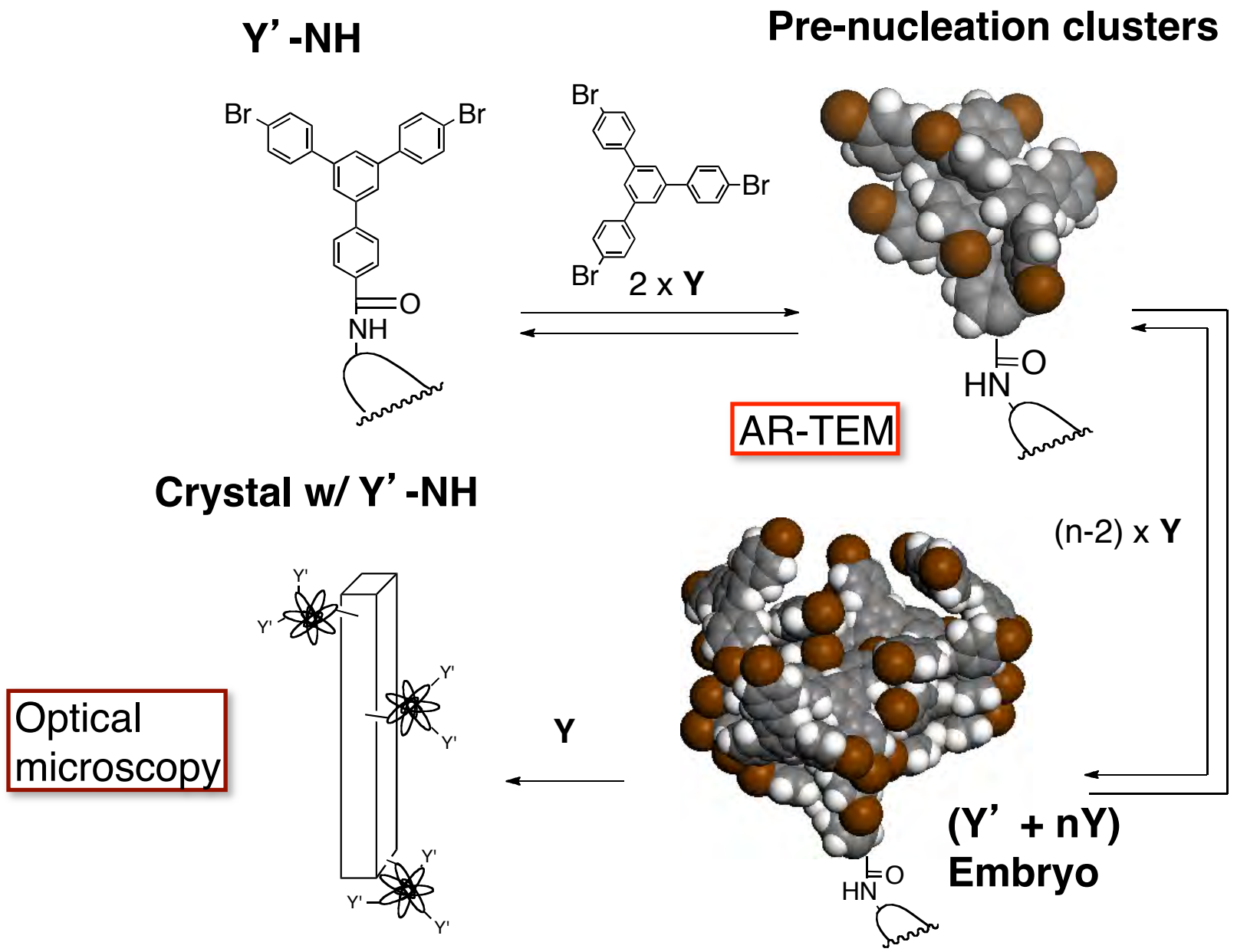


Y' -imide



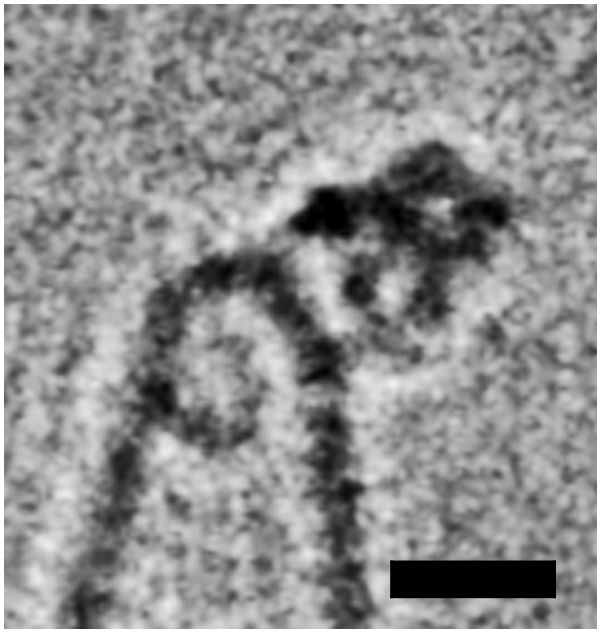
Y' = Template

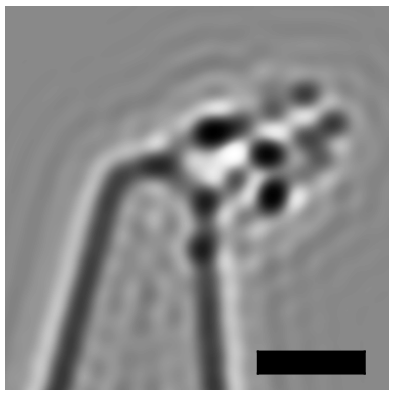
Summary of Macro- and Microscopic Studies

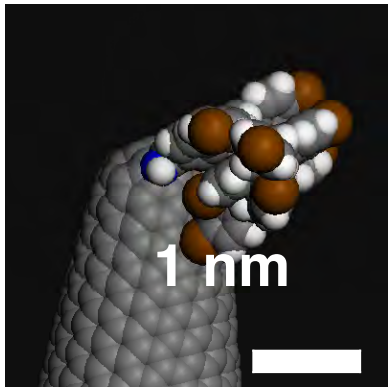


A Termolecular Pre-nucleation Cluster Standing Upright on CNH Surface

(Y’ + 2•Y)



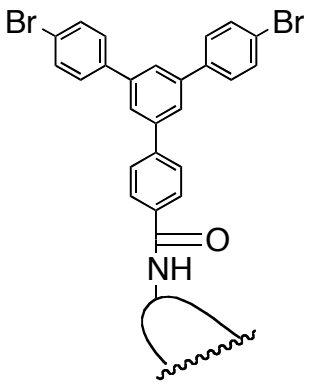




Probability of Growth of a Cluster to a Crystal

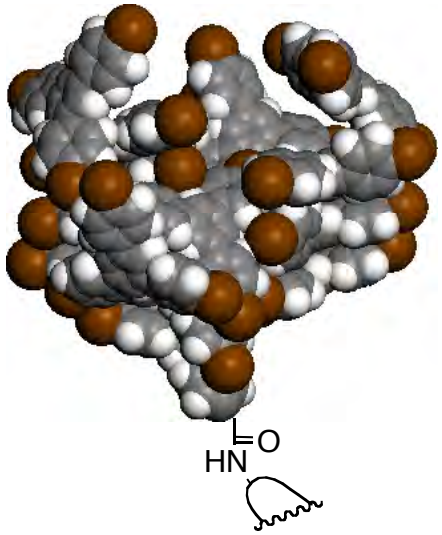
pre-nuclation cluster

Y' -NH



1

1/300

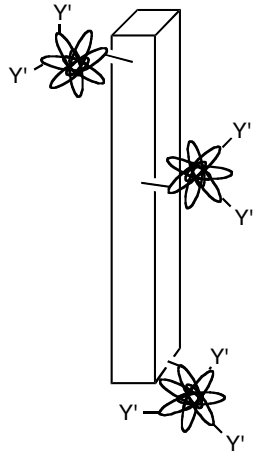


3 x 10^{-3}

1/30,000,000 to 1/3,000,000,000

3^{-15}–4^{-15}

crystal



10^{-9} – 10^{-11}

3^{-15}–4^{-15}:15 molecules in one cluster **with 3-4 possible orientations take the best orientation at the same time.**

Disordered to Ordered Transition is a Stochastic Process,

depending on the cluster size, mobility of the molecules and temperature

erratic

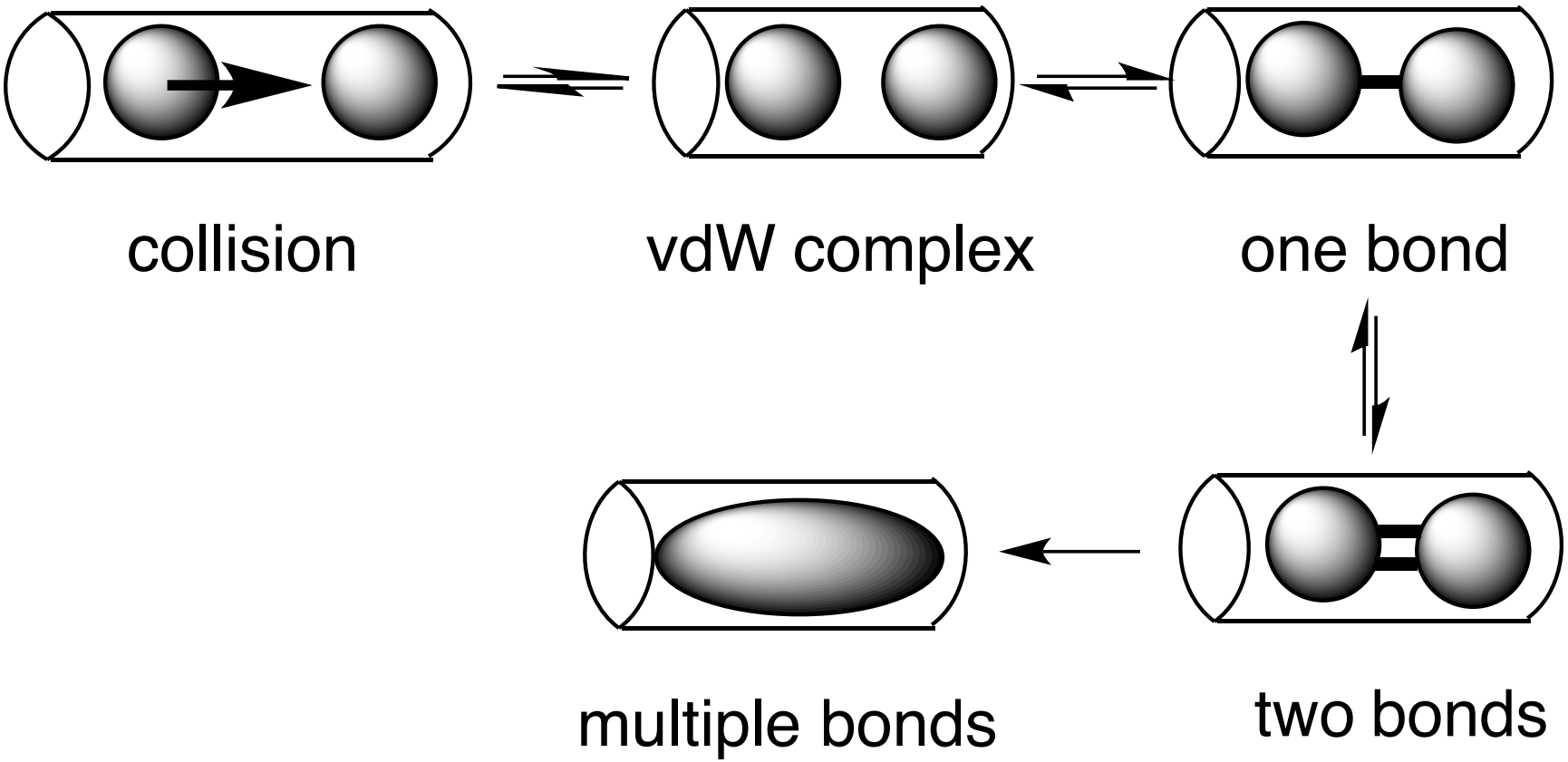
slow cooling

flexible molecules vs. rigid molecules

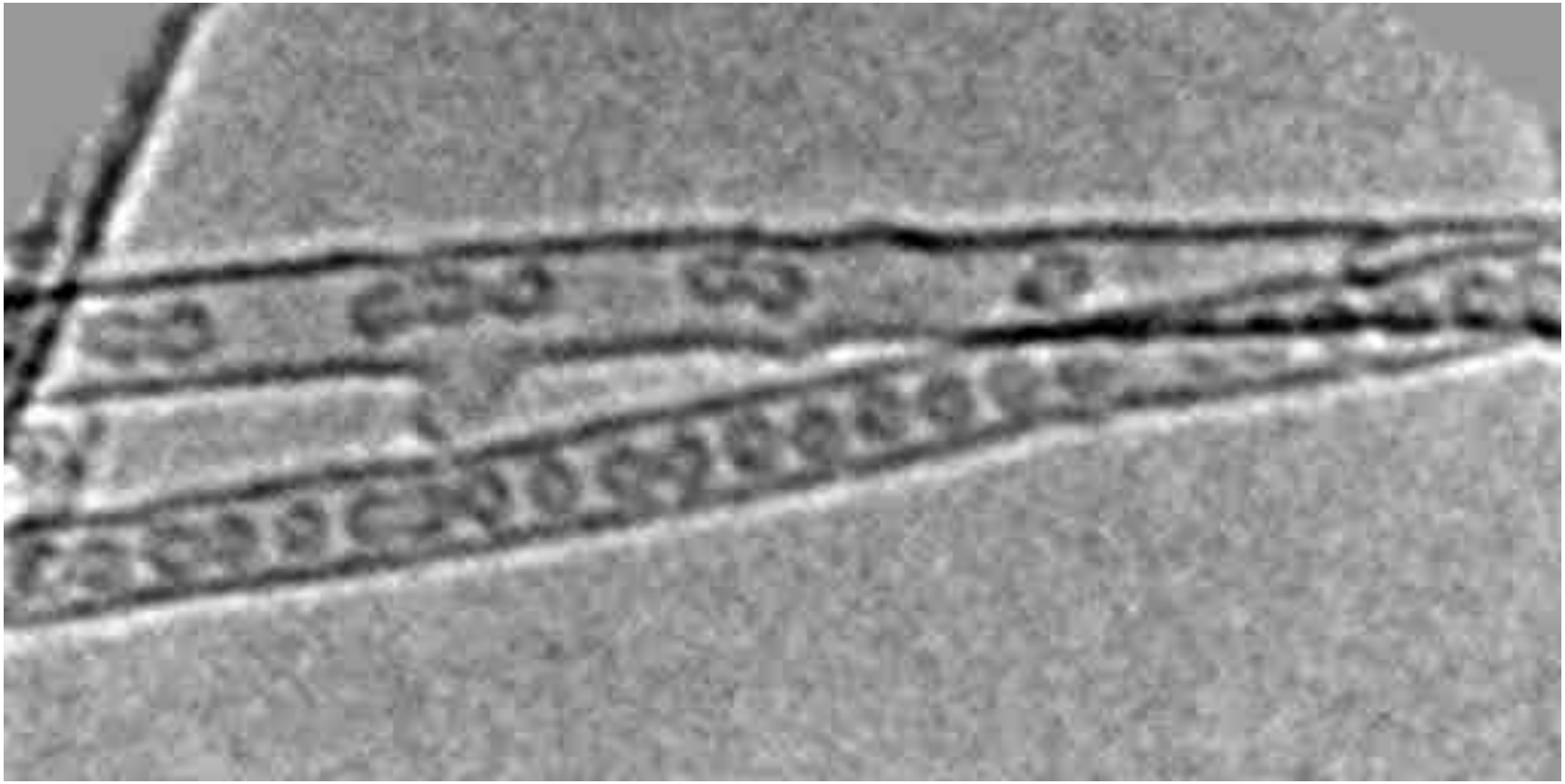
Kinetic Analysis of Individual Events of C60 Dimerization by Atomic Resolution Electron Microscopy

Manuscript in preparation
with Satoshi Okada,
Prof. Koji Harano, and Prof.
Kaoru Yamanouchi

1–D Model of Collision, van der Waals Complex, Reaction

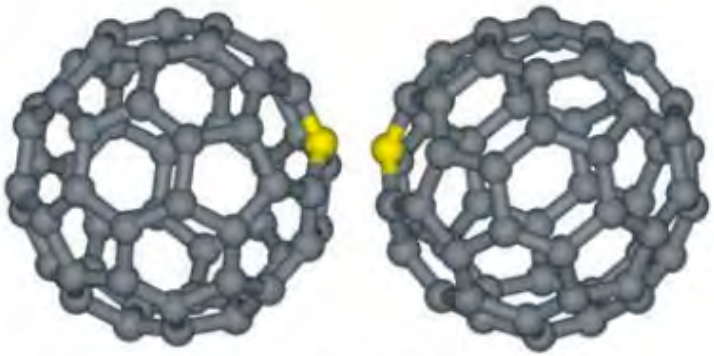


Collision, van der Waals Complex, Bond Formation at 793K

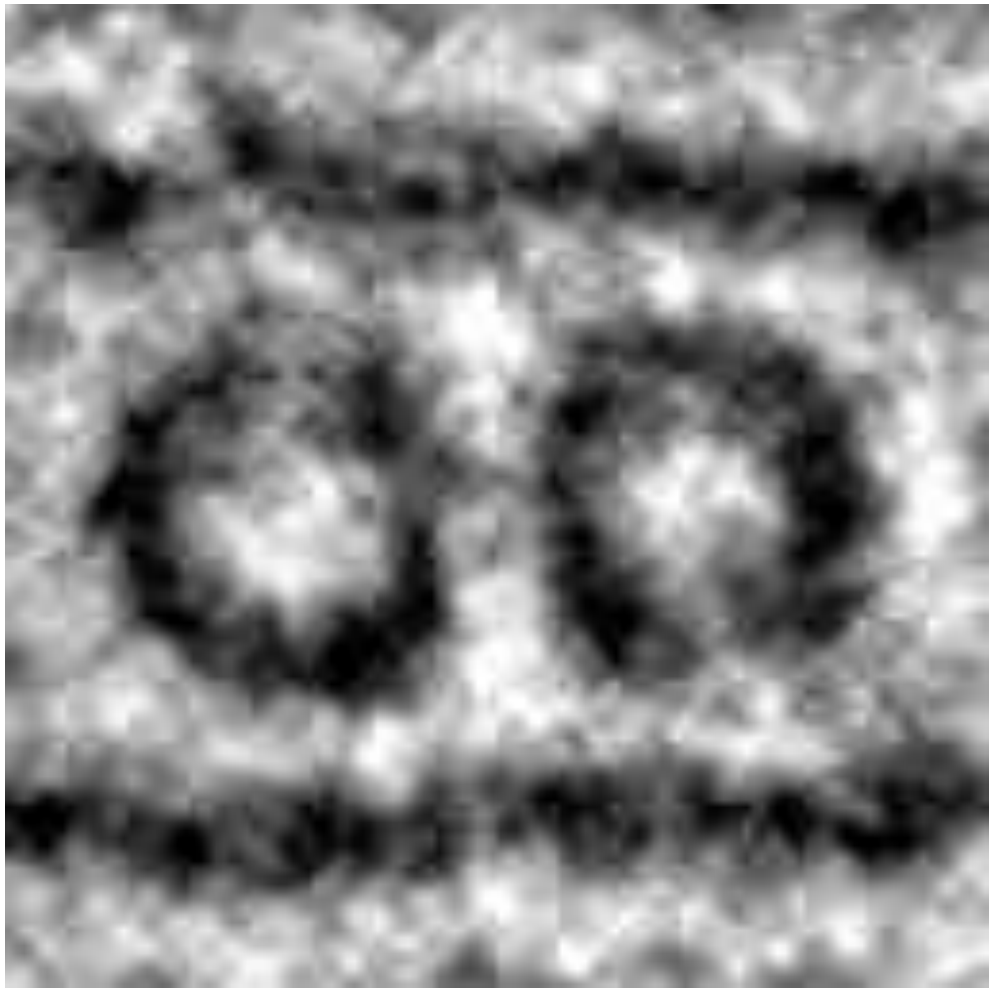


Nature Chem. (2010)

TEM Observation of Fullerene Dimerization

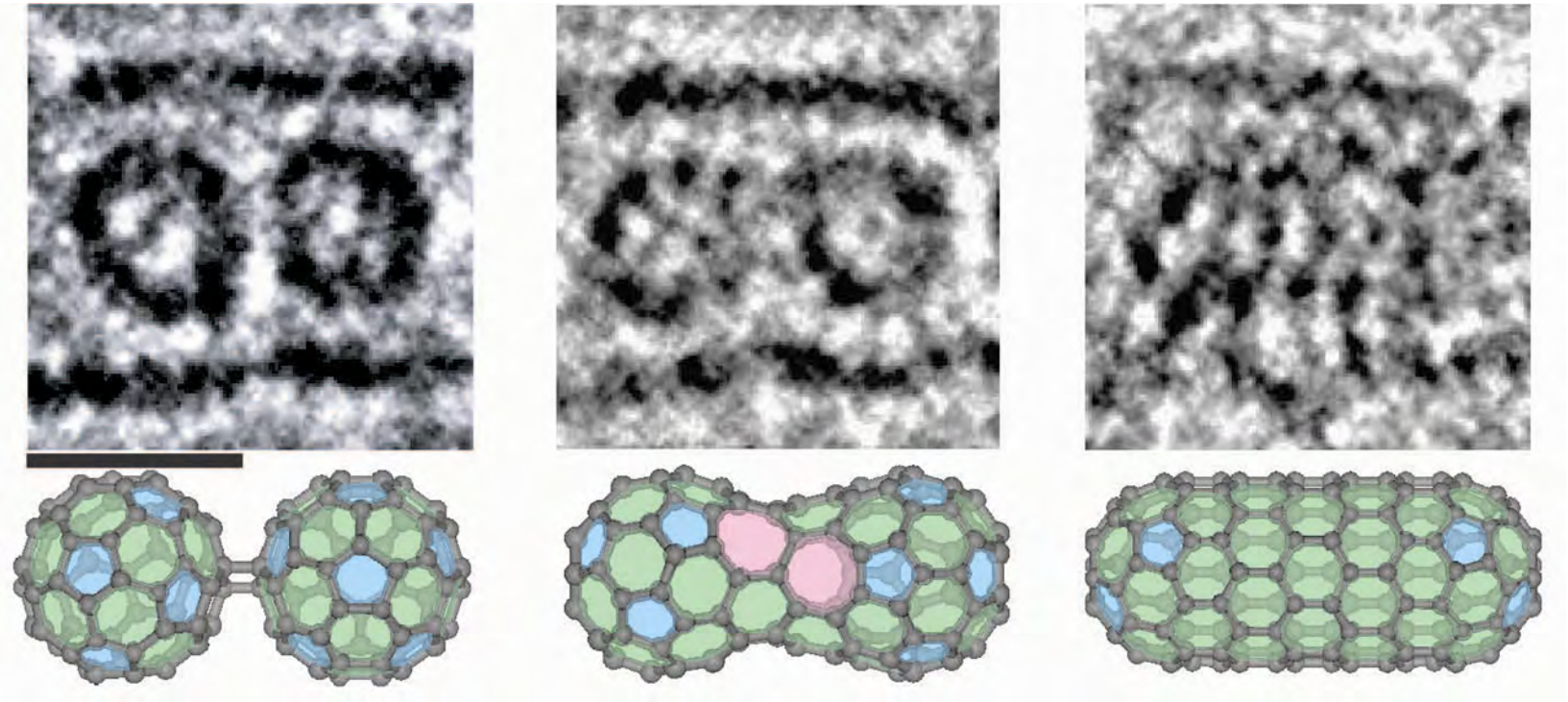


side view



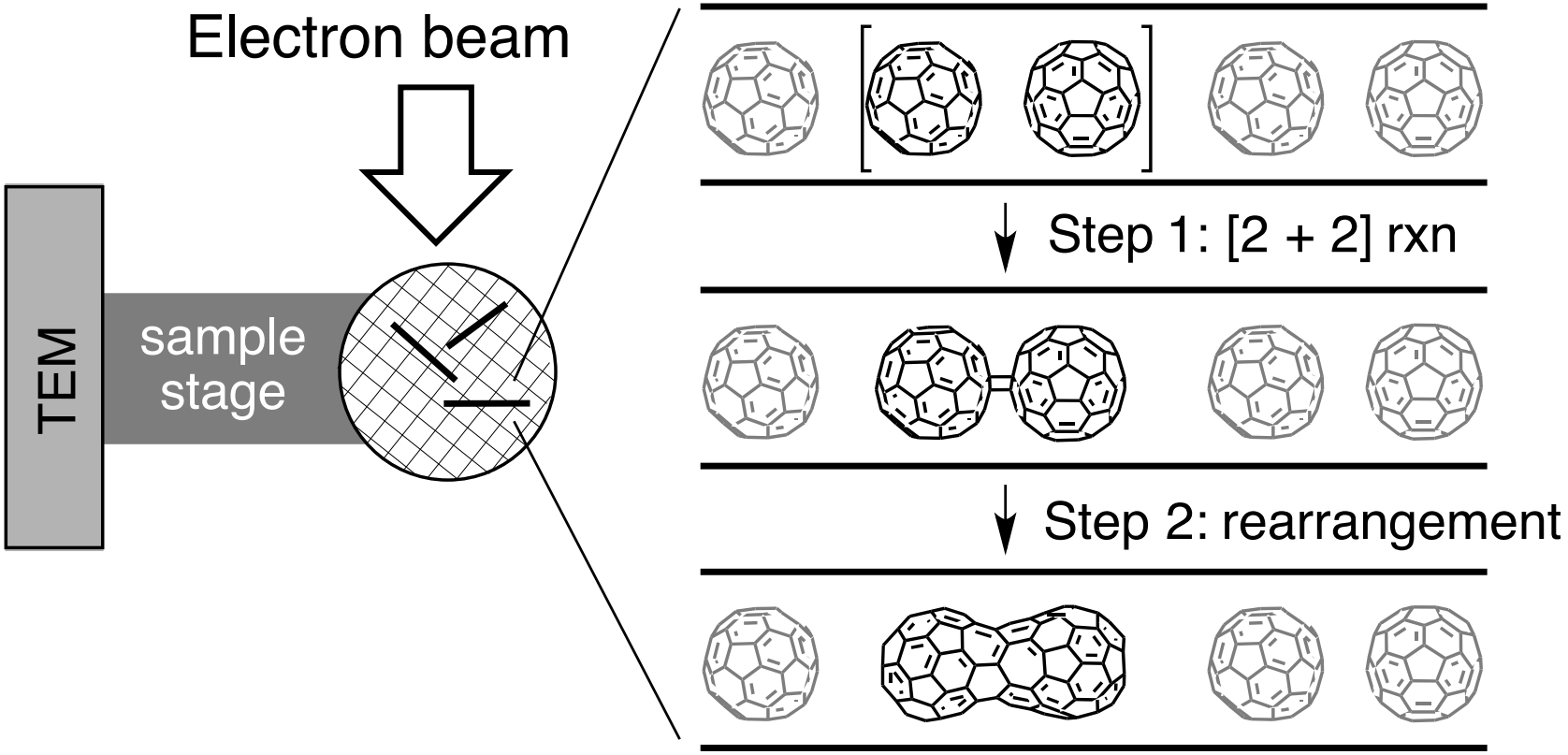
M. Koshino, et al., *Nature Chemistry* (2010).

Atom-level Analysis of Reaction Intermediates

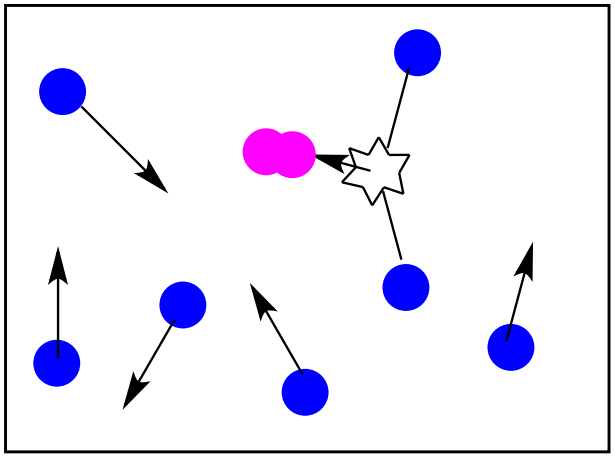


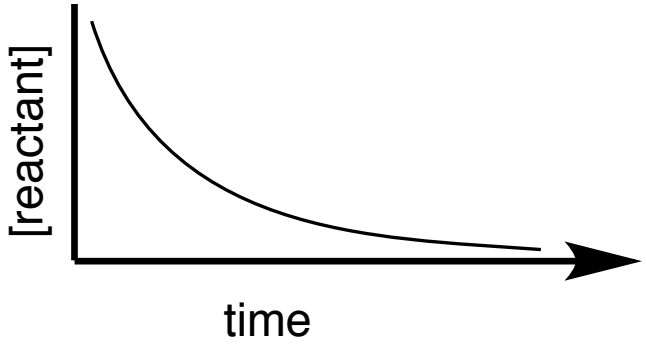
M. Koshino, et al., *Nature Chemistry* (2010).

[2 + 2] Dimerization
Followed by C–C Rearrangement



Conventional statistical kinetics



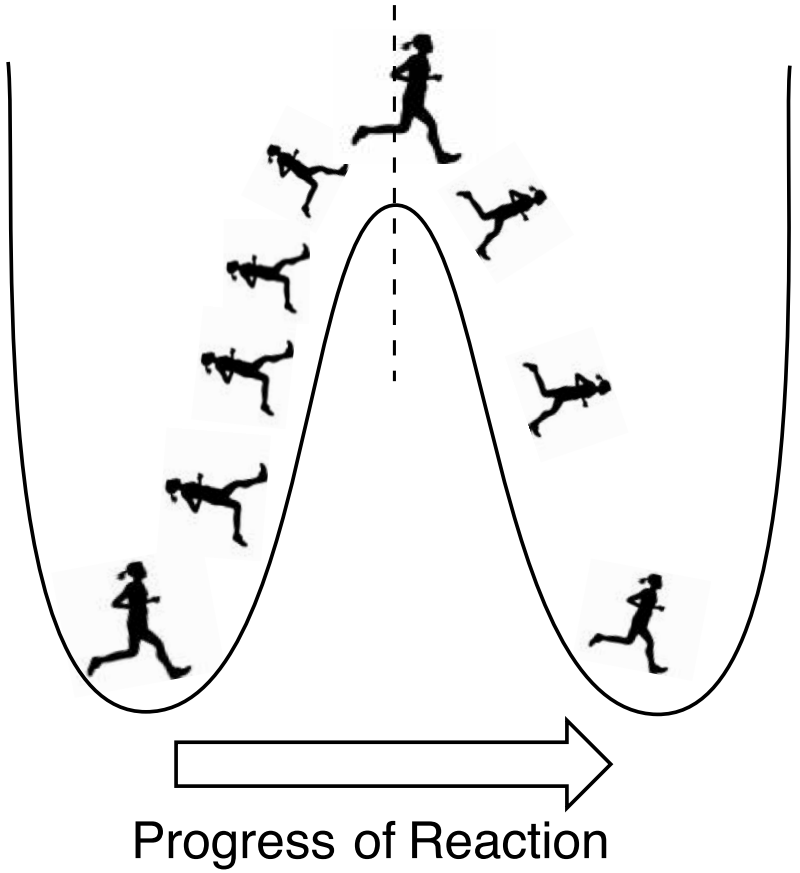


Reaction rate

k = (reaction) x (diffusion)

A Classical Transition State Theory

Constant Flux of Molecules through Dividing Surface

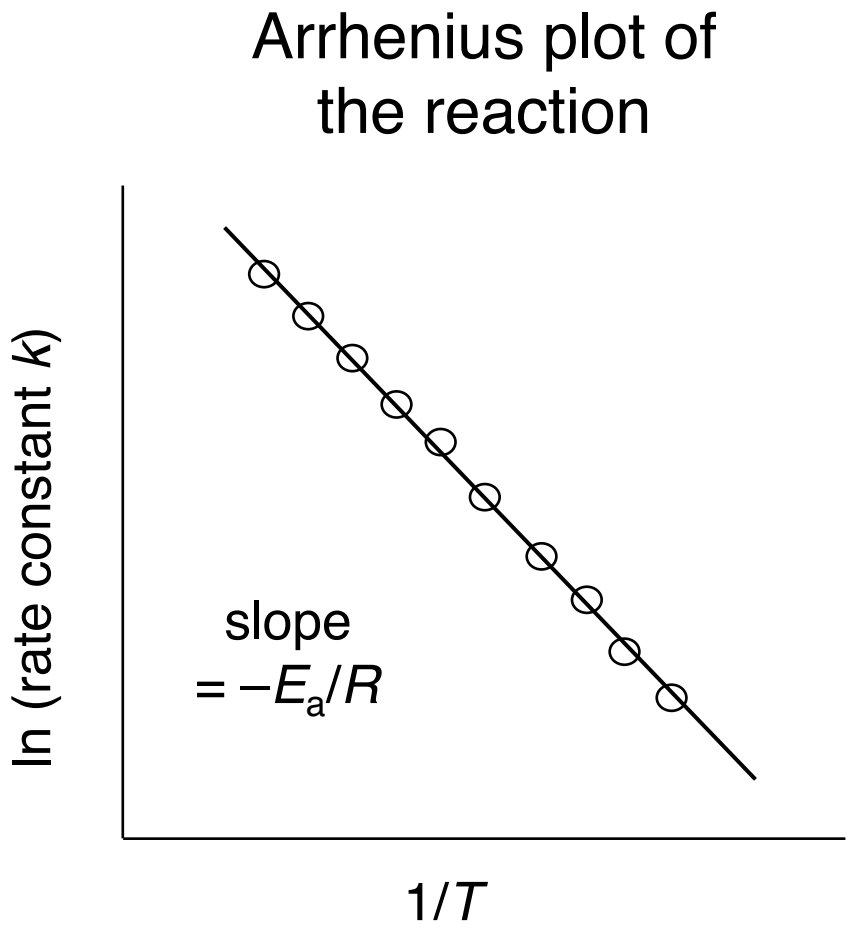


Eyring equation

$$k = \frac{k_B T}{h c^0} \exp\left(-\frac{\Delta H - T\Delta S}{k_B T}\right)$$

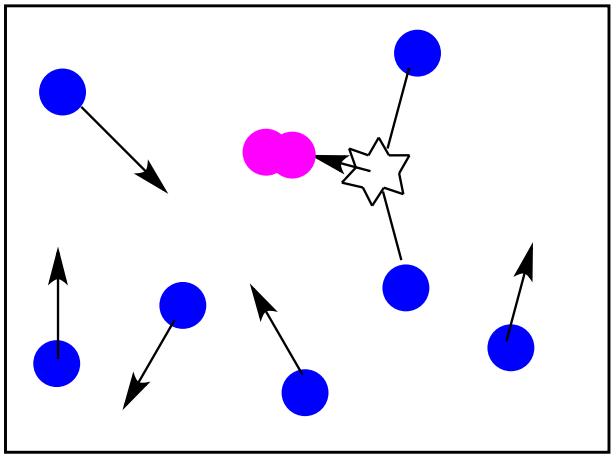
Dependent on conc. (c^0) & diffusion (ΔS)

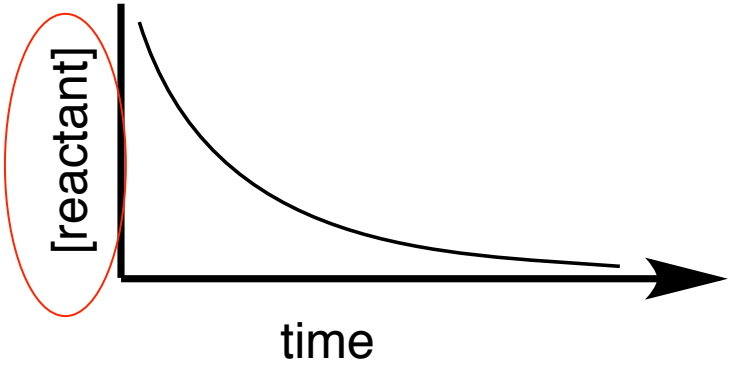
Experimentally...



Transition from Classics to Quantum Mechanics

Statistical kinetics

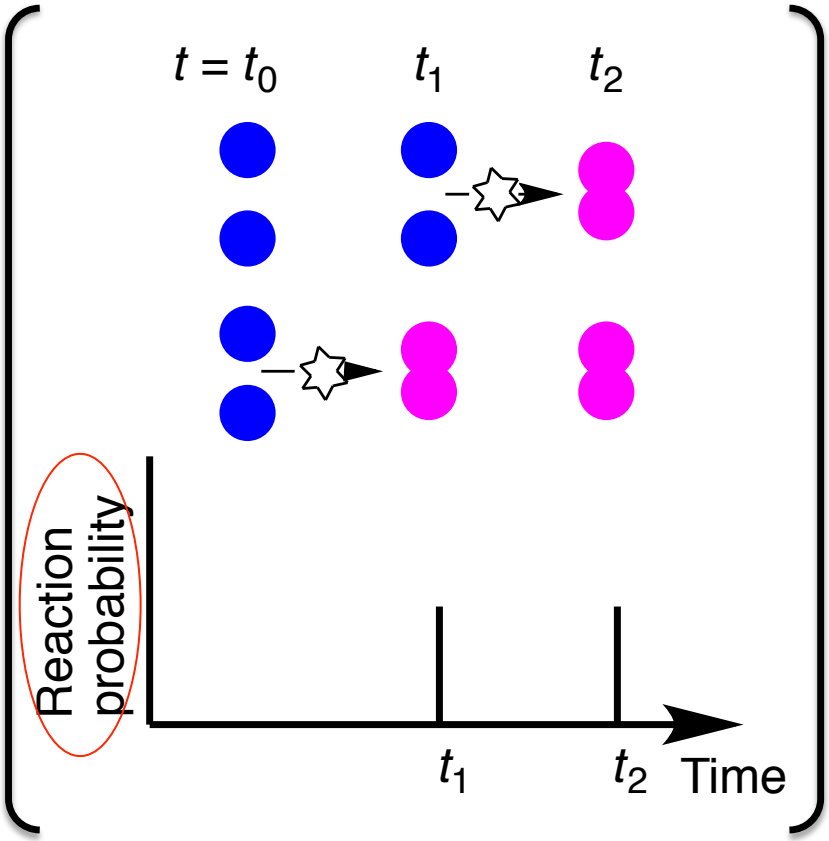




Reaction rate
k = (reaction) x (diffusion)

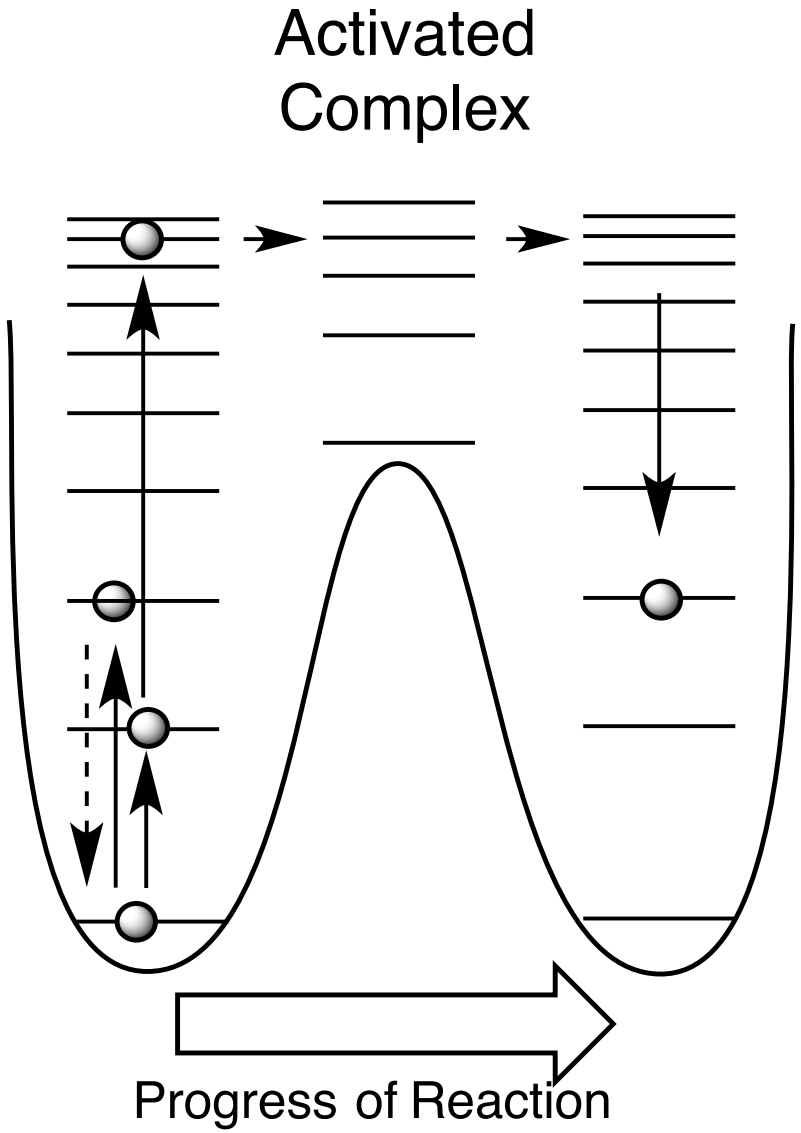
Single Molecule Kinetics

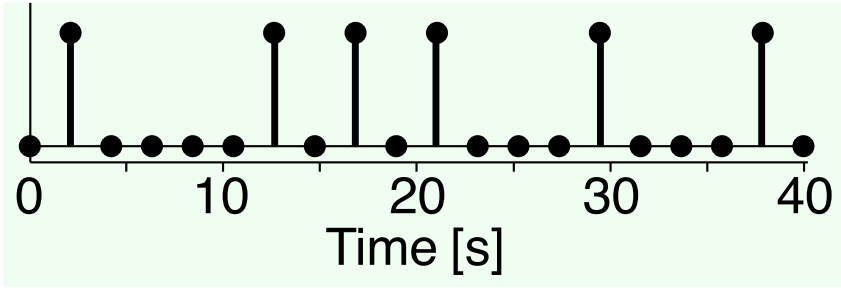
Σ



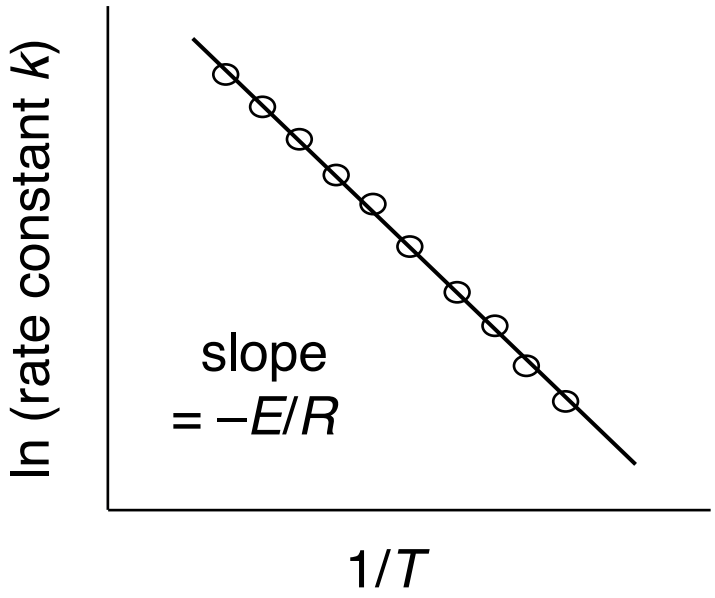
Reaction rate
k = (reaction)

A Quantum Mechanical Transition State Theory





RRKM theory



Observation of Single Molecular Reaction Events

Classics

Eyring equation

$$k = \frac{k_B T}{h c^0} \exp\left(-\frac{\Delta H - T\Delta S}{k_B T}\right)$$

Dependent on conc. (c^0) & diffusion (ΔS)

Quantum mechanics

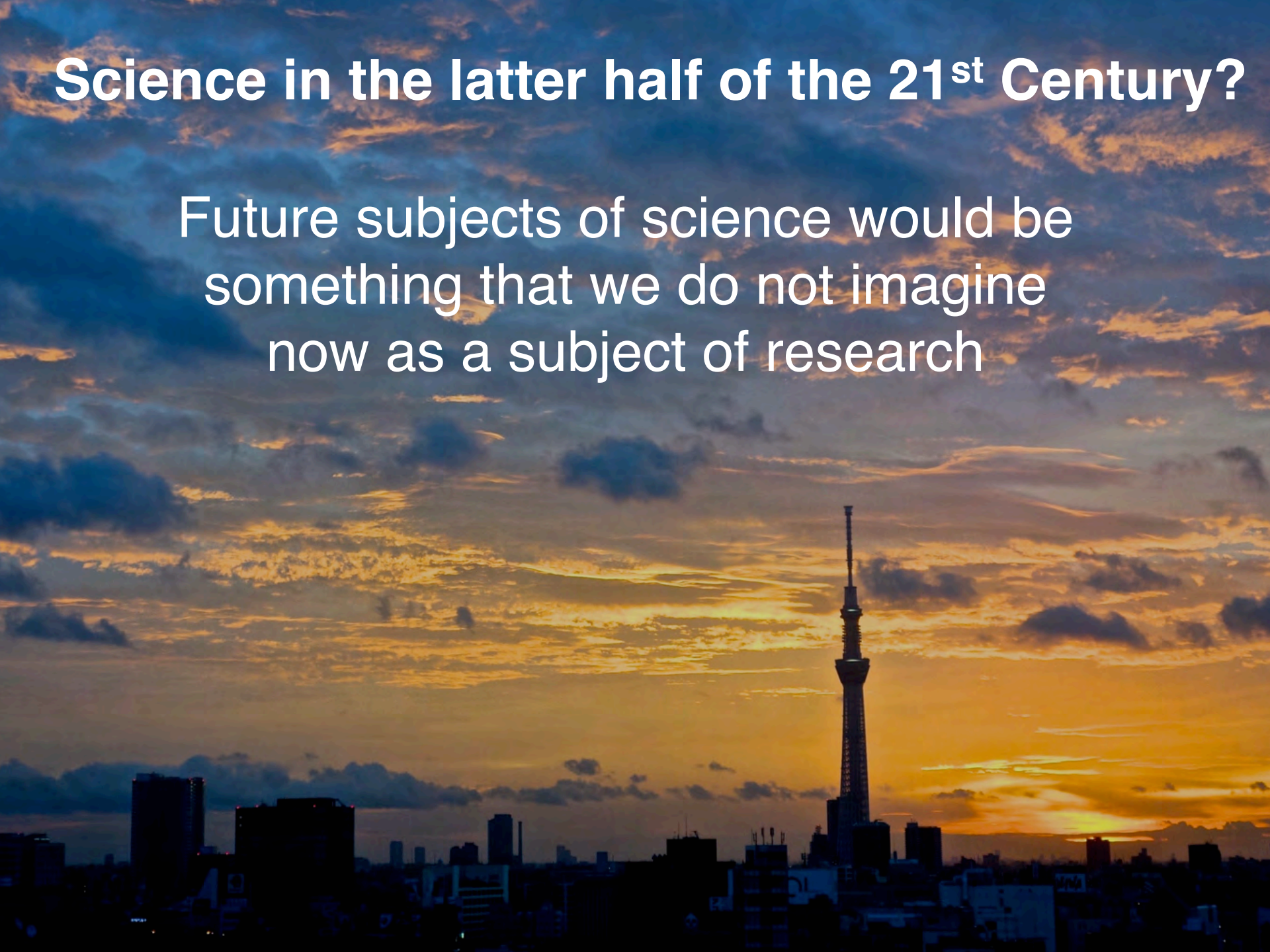
Rice–Ramsperger–Kassel–Marcus theory

$$k(\varepsilon) = \frac{\sum \rho\left(\varepsilon^{active}\right)}{hN(\varepsilon)}$$

The density of states of reactants (ρ) devided by those of activated complex (N)

Science in the latter half of the 21st Century?

Future subjects of science would be
something that we do not imagine
now as a subject of research



Thanks for All the Current Lab Members

(JSPS, JST, Mitsubishi Chemicals, Towa Pharmaceuticals, JEOL)