

# Supramolecular Materials & Hand-Operating Nanotechnology for Novel Functions

*Katsuhiko Ariga*

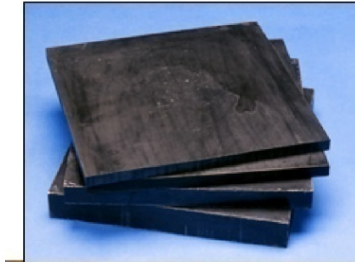
*World Premier International (WPI) Research Center  
for Materials Nanoarchitectonics (MANA),  
National Institute for Materials Science (NIMS)*



# Materials



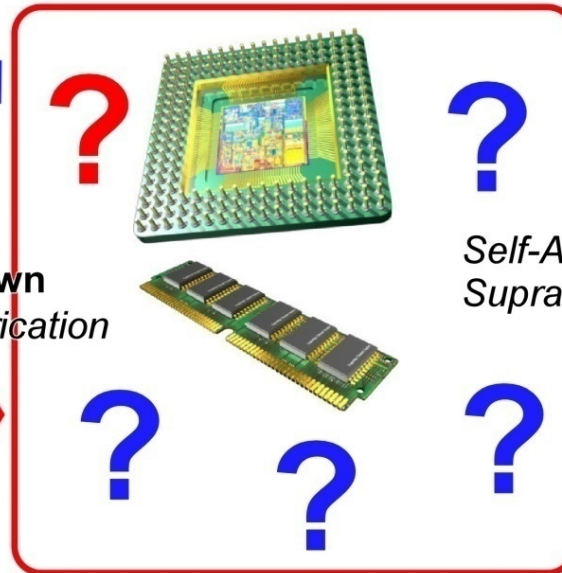
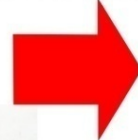
# ~~Molecules~~



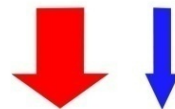
Bulk Materials

**Assembled  
Materials**

Top-Down  
Microfabrication

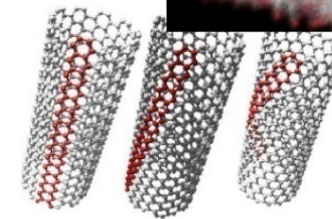
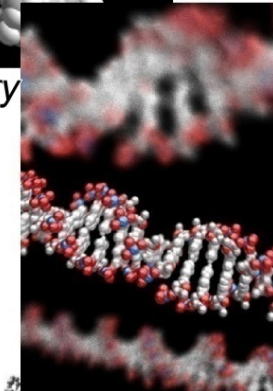
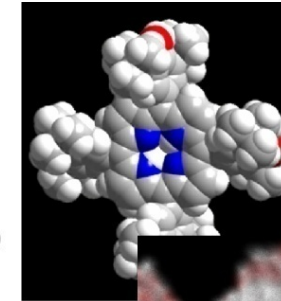
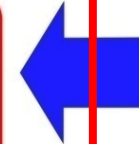


Functional Structures



Devices

Bottom-Up  
Self-Assembly  
Supramolecular Chemistry



~~Unit Molecules~~

Organic  
Inorganic  
Bio- Units

# Today's Menu

## 1) **Richness** of Assembled Materials

*Brief Summary of Our Recent Researches*

## 2) Novel Materials: **Feedback & Regulation**

*Auto-Modulated Materials Release*

*from Mesoporous Nanocompartment Film*

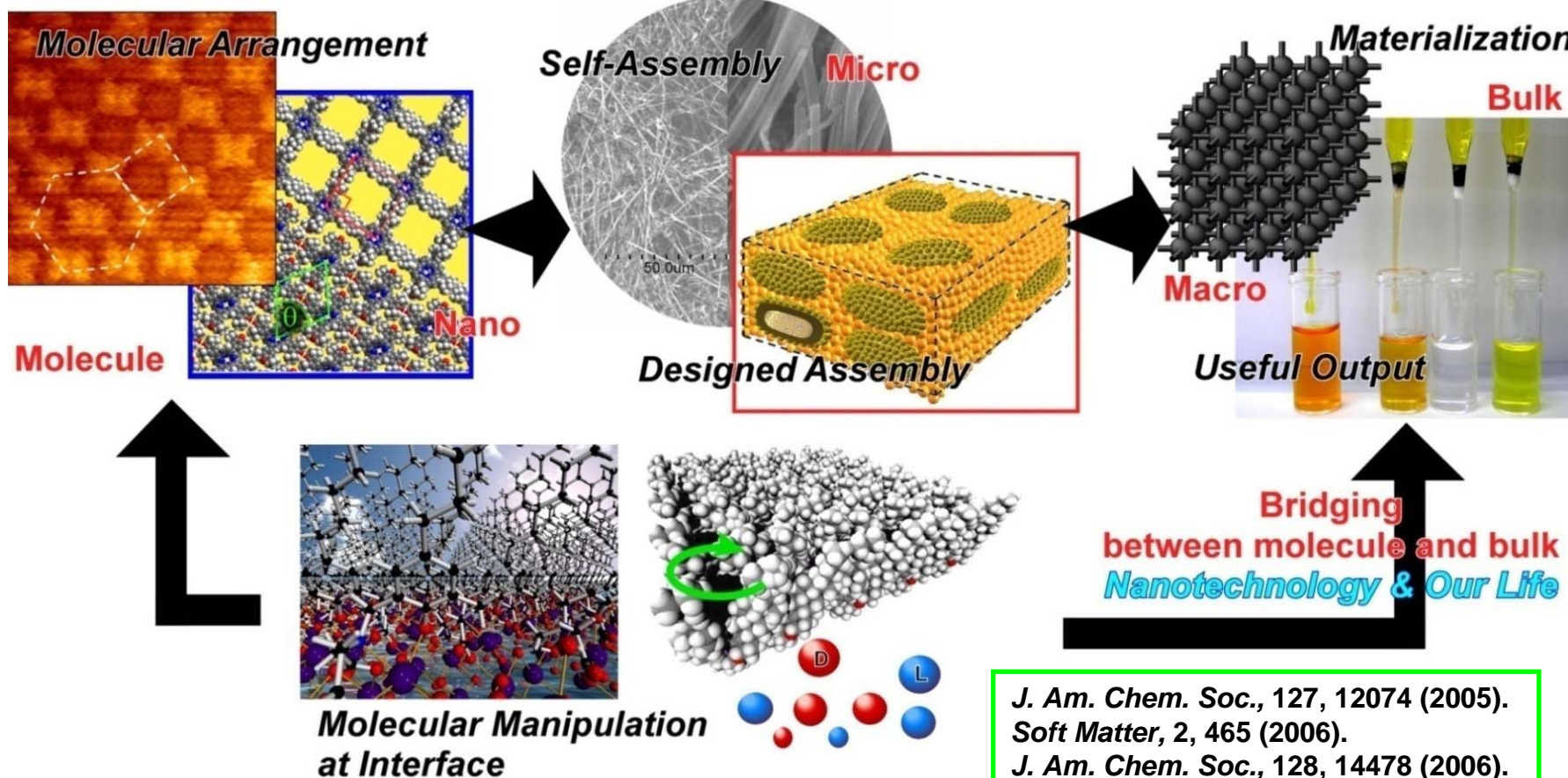
## 3) New Concept

*Hand-Operating Nanotechnology*

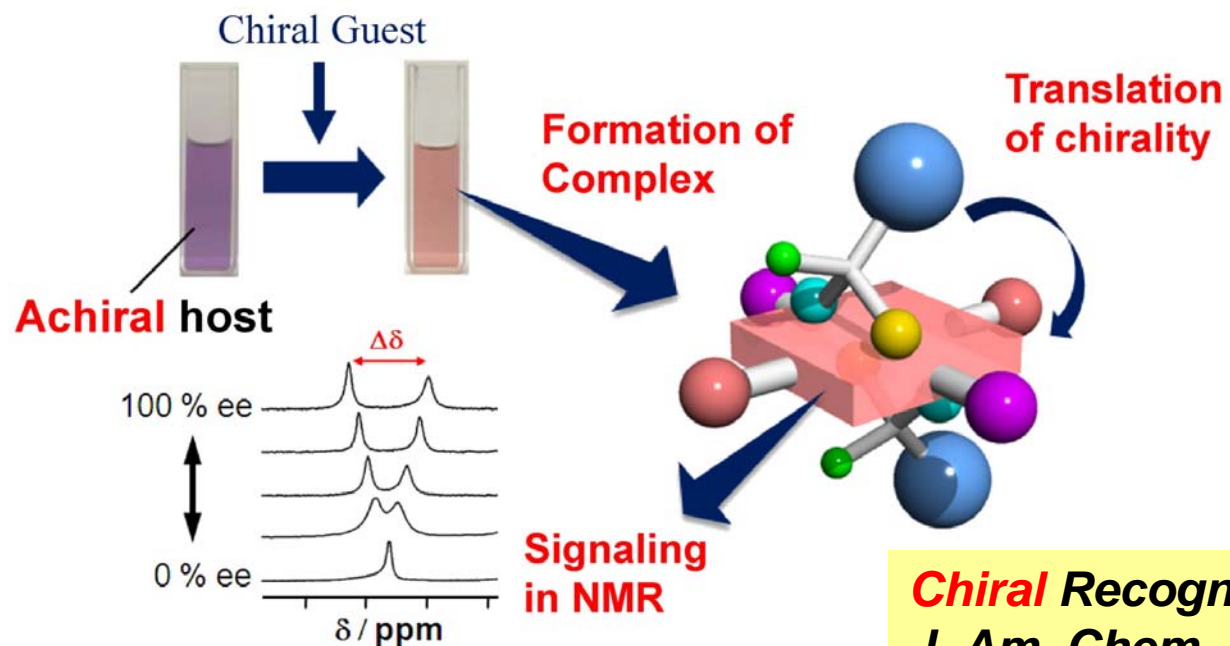
*J. Am. Chem. Soc.*, 128, 6328 (2006).  
*Appl. Phys. Lett.*, 92, 163301 (2008).  
*Chem. Eur. J.*, 15, 2486 (2009).  
*Phys. Chem. Chem. Phys.*, 11, 6038 (2009).  
*J. Am. Chem. Soc.*, 131, 9494 (2009).  
*J. Am. Chem. Soc.*, 131, 11282 (2009).  
*J. Am. Chem. Soc.*, 131, 16138 (2009).

*J. Am. Chem. Soc.*, 130, 2376 (2008).  
*J. Am. Chem. Soc.*, 130, 4594 (2008).  
*Adv. Mater.*, 20, 443 (2008).  
*Adv. Mater.*, 20, 4027 (2008).  
*Adv. Mater.*, 21, 989 (2009).  
*Adv. Funct. Mater.*, 19, 1792 (2009).  
*J. Am. Chem. Soc.*, 131, 4220 (2009).  
*J. Am. Chem. Soc.*, 131, 6372 (2009).  
*J. Am. Chem. Soc.*, 131, 18030 (2009).  
*J. Am. Chem. Soc.*, 132, 1212 (2010).

*J. Am. Chem. Soc.*, 128, 10384 (2006).  
*J. Am. Chem. Soc.*, 129, 11022 (2007).  
*Chem. Commun.*, 383 (2008).  
*Angew. Chem. Int. Ed.*, 47, 7254 (2008).  
*Angew. Chem. Int. Ed.*, 48, 7358 (2009).  
*Chem. Eur. J.*, 15, 2763 (2009).  
*Soft Matter*, 5, 3562 (2009).  
*Adv. Mater.*, 22, 323 (2010).  
*Angew. Chem. Int. Ed.*, 49, 5961 (2010).



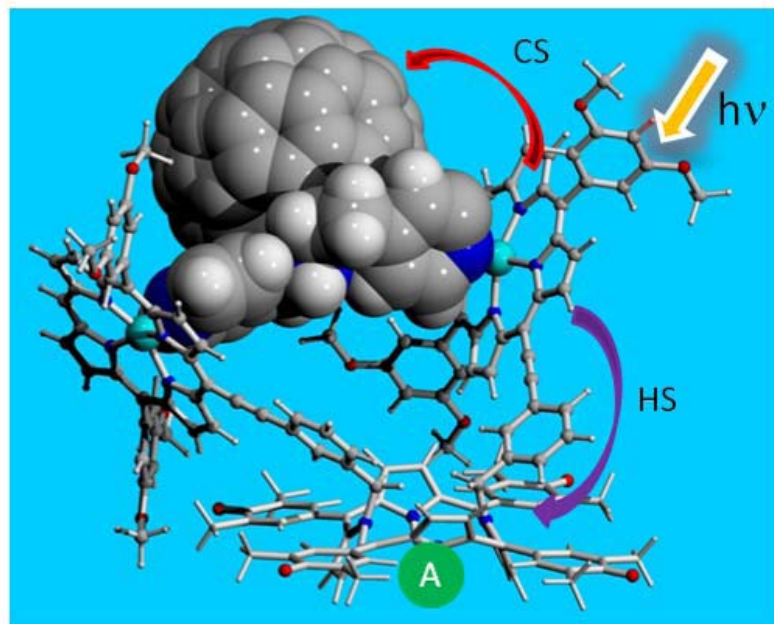
*J. Am. Chem. Soc.*, 127, 12074 (2005).  
*Soft Matter*, 2, 465 (2006).  
*J. Am. Chem. Soc.*, 128, 14478 (2006).  
*Adv. Mater.*, 21, 2959 (2009).  
*J. Am. Chem. Soc.*, in press.



Dr. Hill

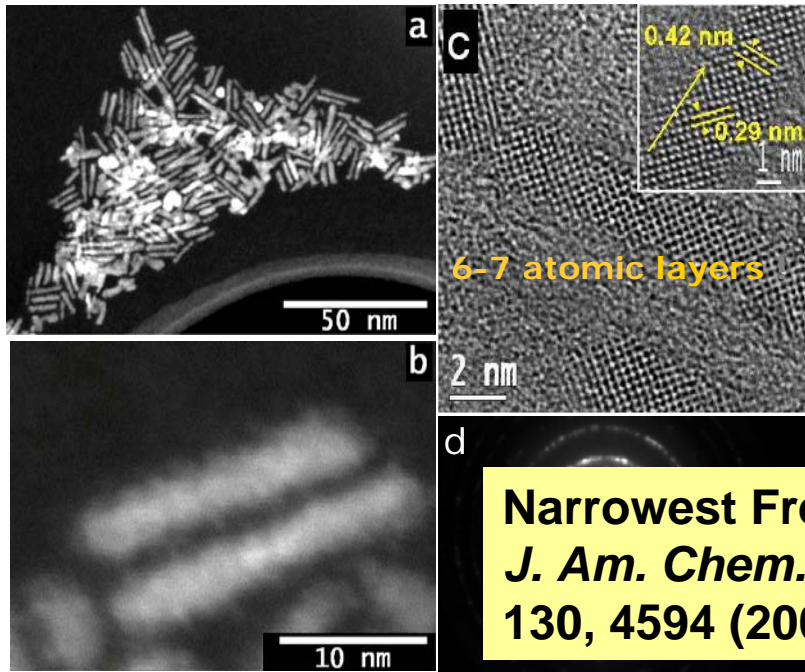
Dr. Shundo

**Chiral Recognition by Achiral Reagent**  
*J. Am. Chem. Soc.*, 131, 9494 (2009).  
 (Highlighted in *Nature Chemistry*)

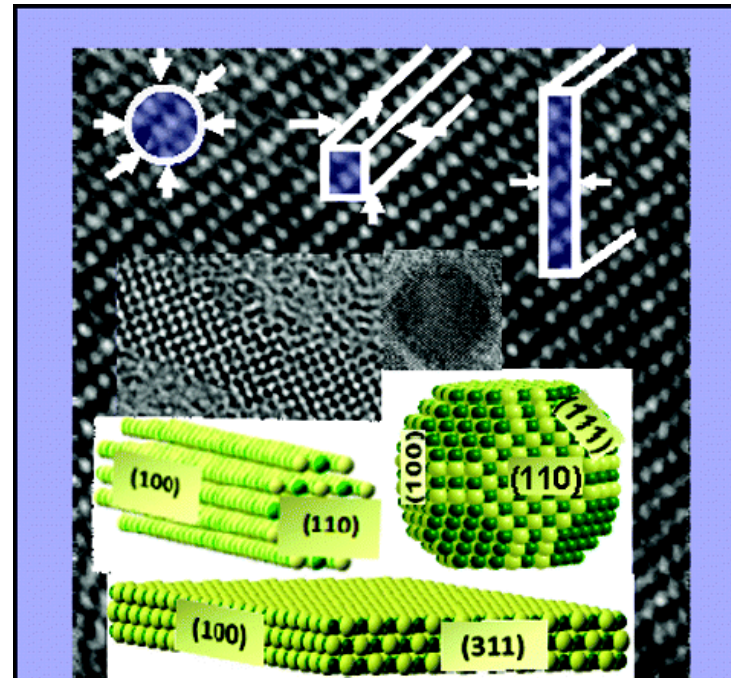


## Molecular Systems

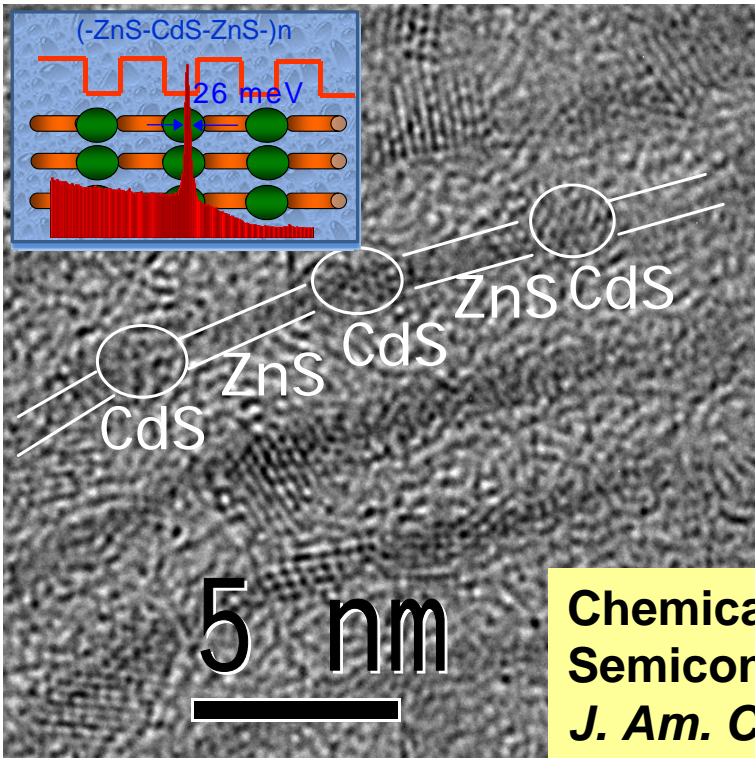
**Anion-Complexation-Induced Stabilization of Charge Separation**  
*J. Am. Chem. Soc.*, 131, 16138 (2009).  
 Collaboration with  
 Prof. Francis D'Souza (Wichita State Univ.)  
 Prof. Shun-ichi Fukuzumi (Osaka Univ.)



**Narrowest Freed Rod**  
*J. Am. Chem. Soc.*,  
 130, 4594 (2008).



**Shape-Dependent Confinement in 0D, 1D, and 2D PbS Nanostructures**  
*J. Am. Chem. Soc.*, 131, 11282 (2009).



**Chemically Programmed 2D Semiconductor Superlattice Array**  
*J. Am. Chem. Soc.*, 132, 1212 (2010).

**Nanomaterials**



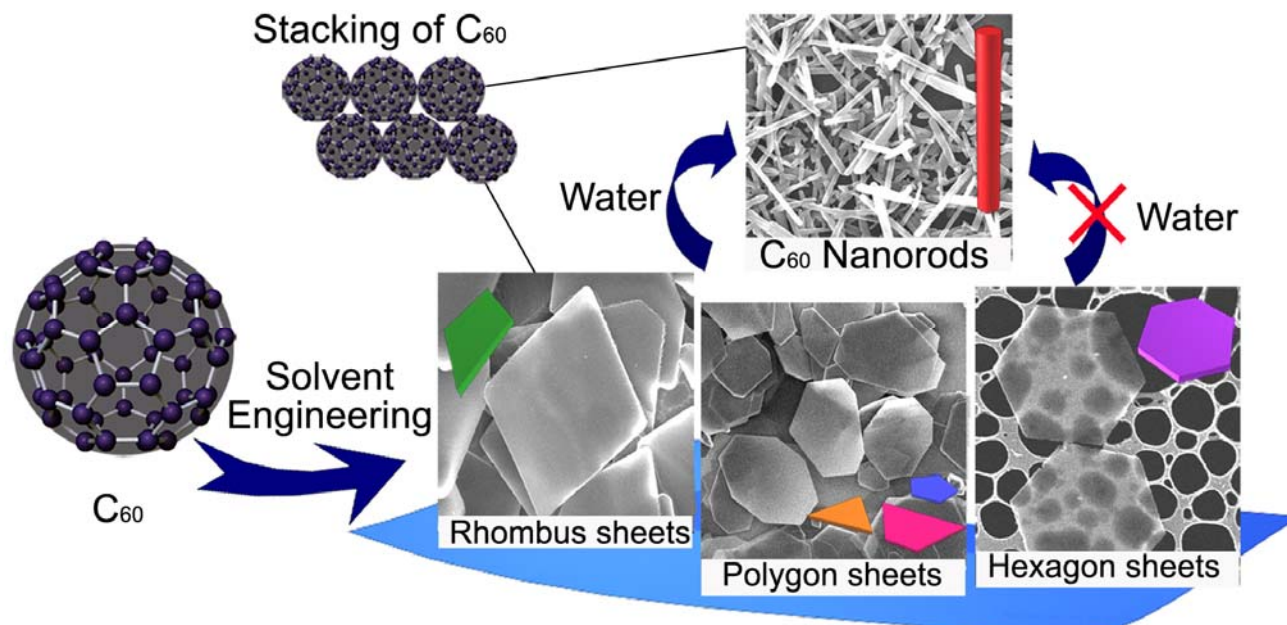
**Dr. Acharya**

**Solvent-Engineering for *Shape-Shifter Pure Fullerene (C<sub>60</sub>)***  
*J. Am. Chem. Soc.*, 131, 6372 (2009).



**Dr. Sathish**

Collaboration with  
 Dr. Miyazawa (NIMS)



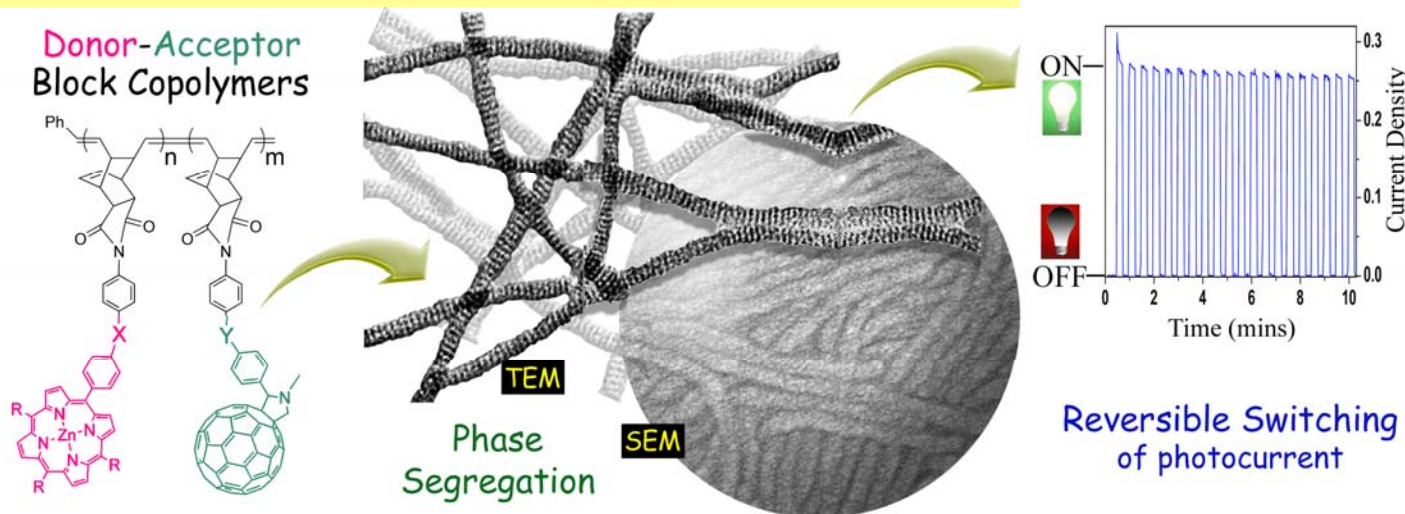
**Self-Assembly**



**Dr. Charvet**

Collaboration with  
 Prof. Seki  
 (Osaka Univ.)

***Zebra Nanowire* for Photo-Current Switching**  
*J. Am. Chem. Soc.*, 131, 18030 (2009).



**Perfect Materials Separation by Carbon Nanocage**  
*J. Am. Chem. Soc.*, 129, 11022 (2007).

Original Solution

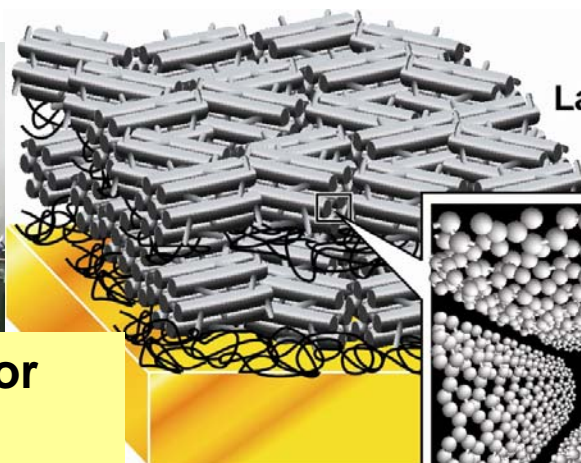
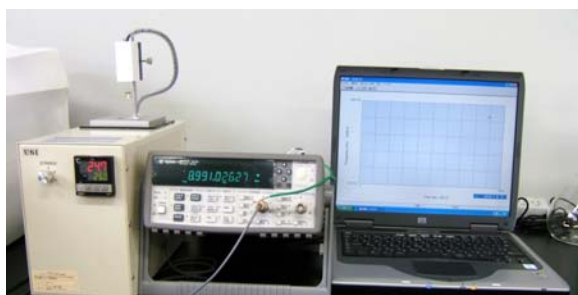
Filtered with Activated Carbon    Filtered with Carbon Nanocage    Filtered with Mesoporous Carbon

original    AC    CNC    CMK  
 after filtration

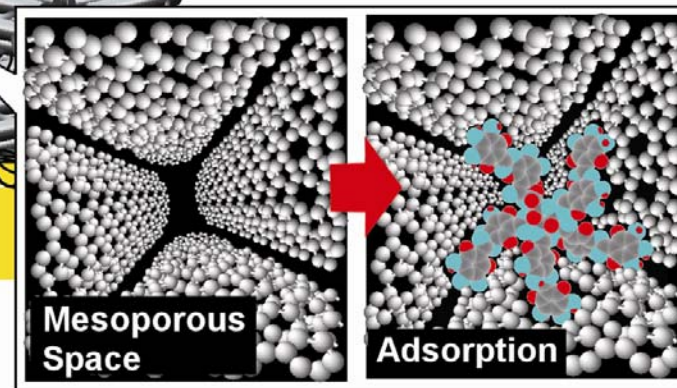
**Materials**

**Dr. Vinu**  
 Leader of Functional Nanoporous Materials Group

**Layered Mesoporous Carbon Sensor Based on Nanopore-Filling Cooperative Adsorption**  
*Angew. Chem. Int. Ed.*, 47, 7254 (2008).



Layer-by-Layer Film





**Novel Materials: *Feedback & Regulation***  
***Auto-Modulated Materials Release***  
***from Mesoporous Nanocompartment Film***

# Mesoporous Nanocompartment Film



**Dr. Ji**

Dr. Qingmin Ji

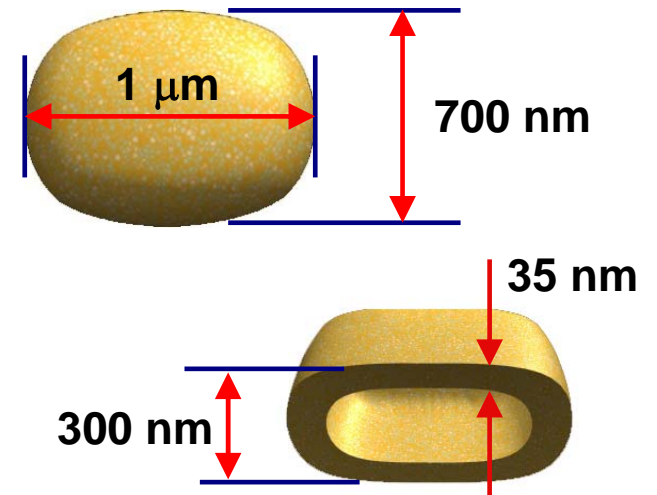
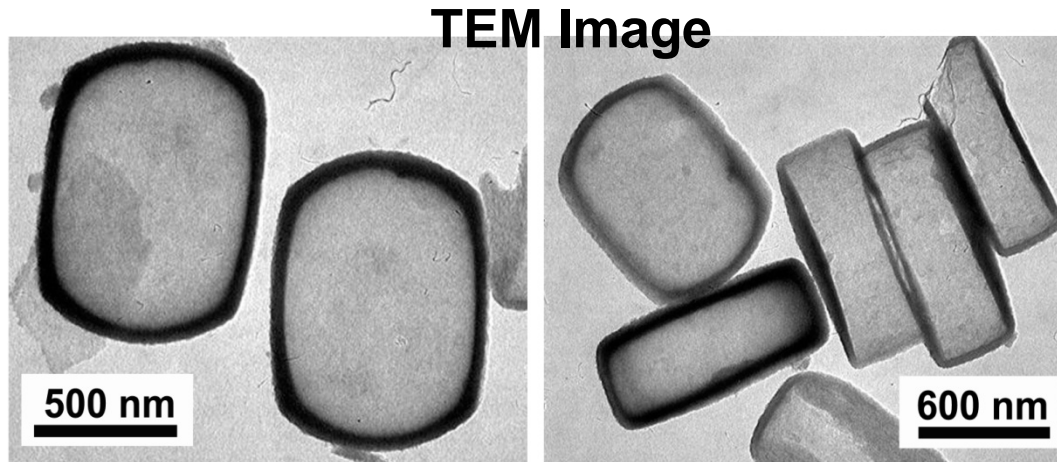
Collaboration with  
Prof. Jong-Sung Yu  
(Korea University)



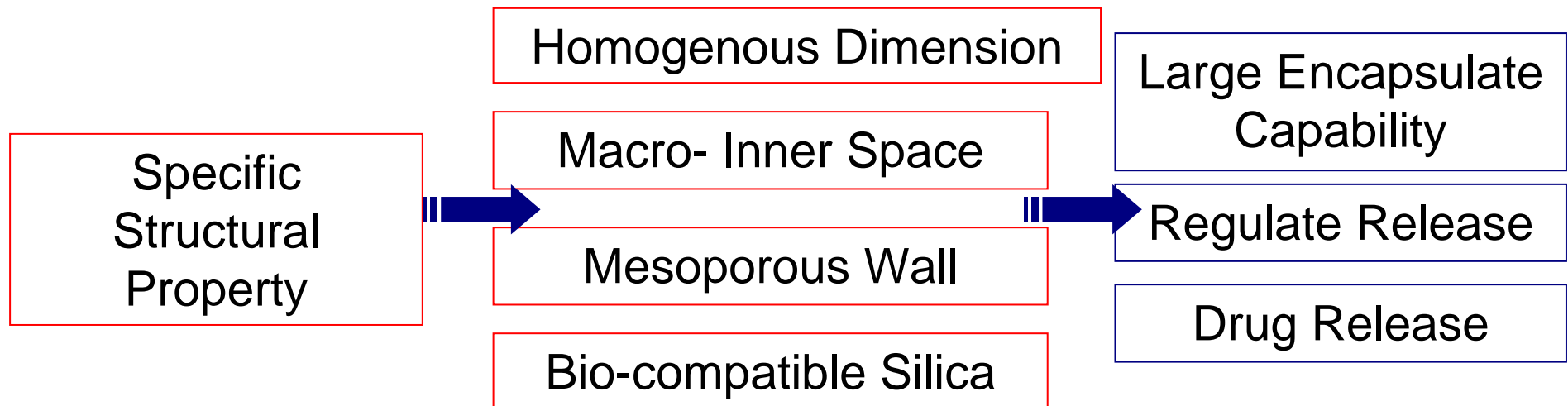
**Prof. Yu**

# Introduction

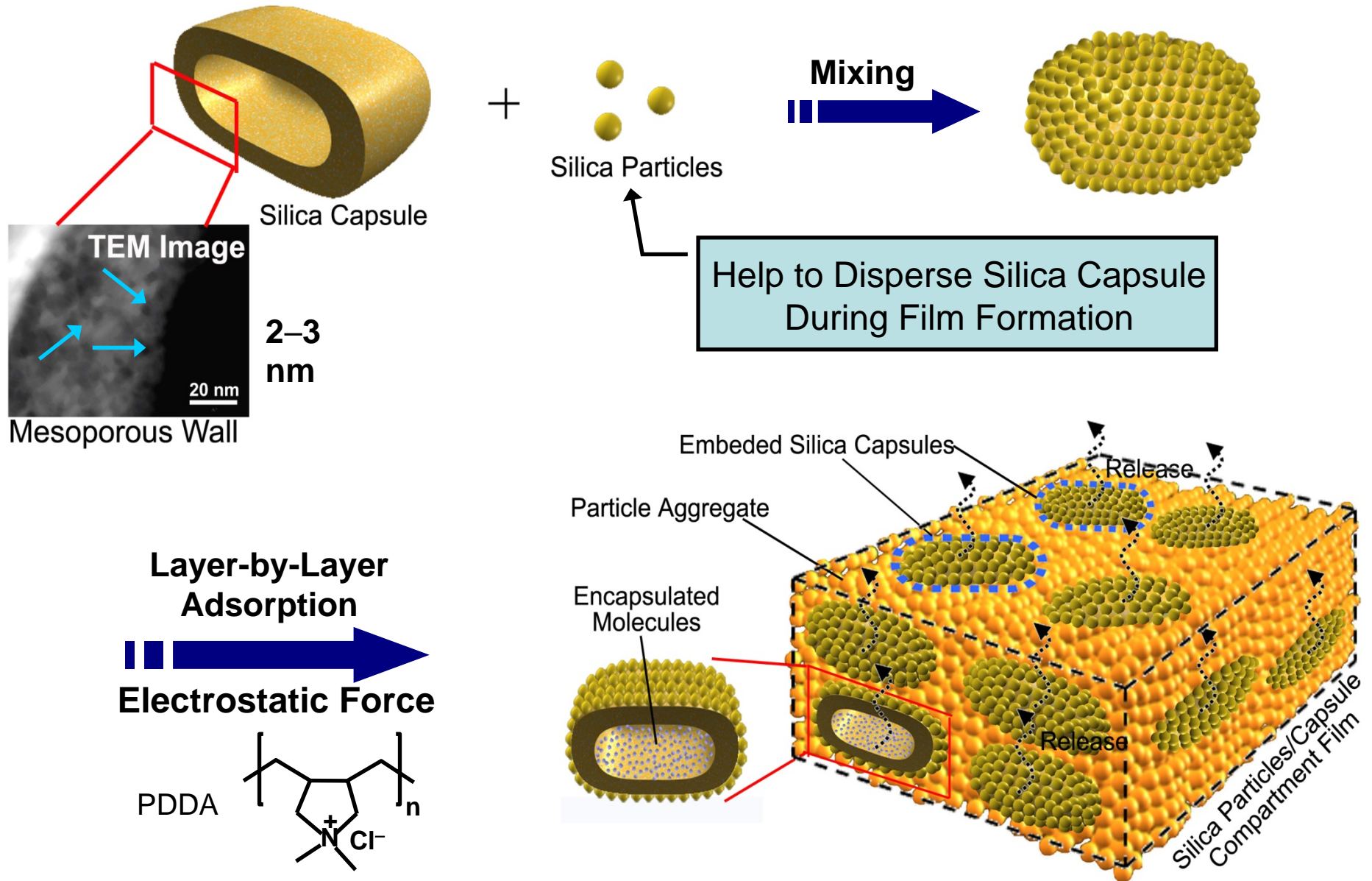
## Silica Capsule with Mesoporous Wall



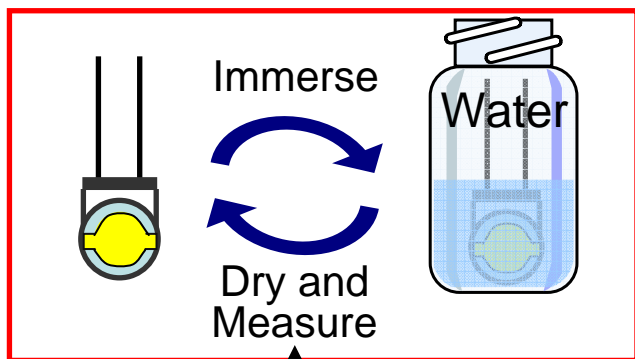
Yu, J. S. et. al. *J. Phys. Chem. B* **2005**, 109, 7040



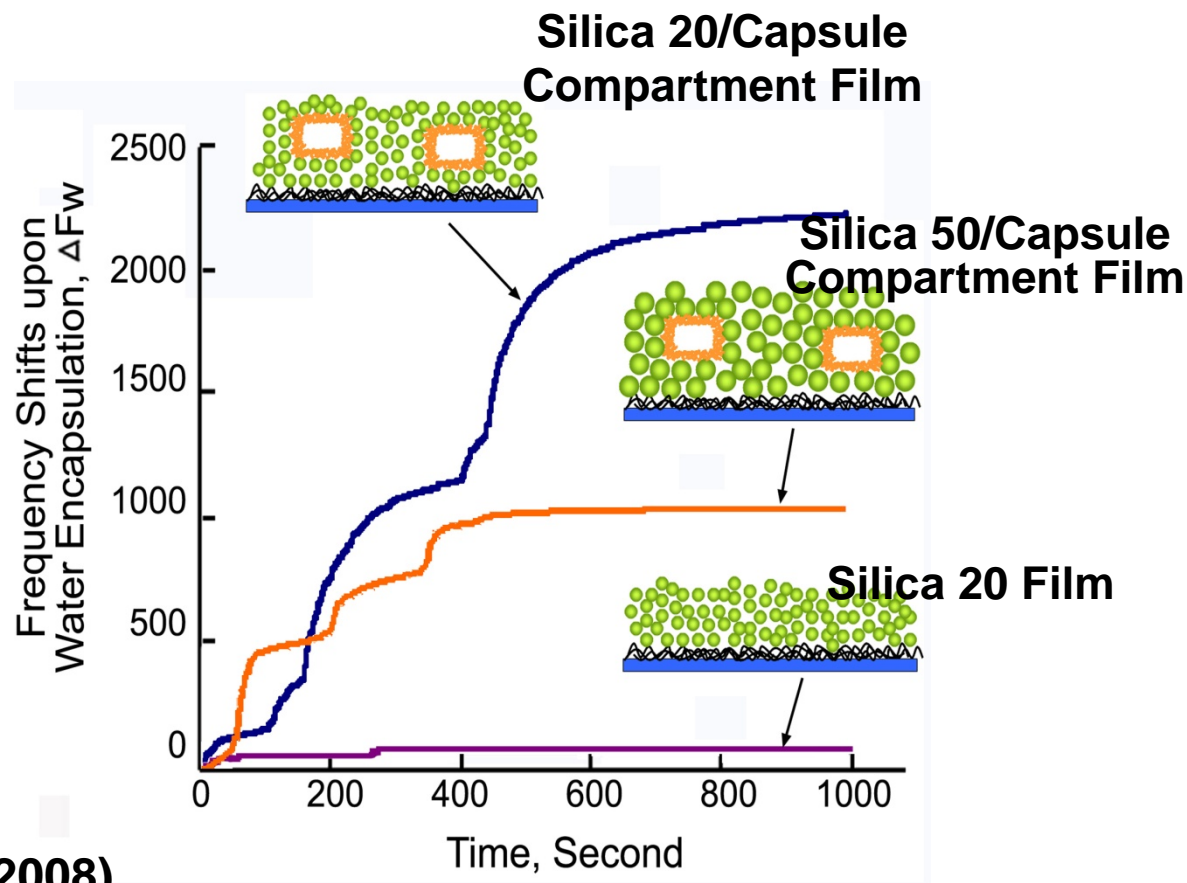
# Preparation Scheme



## Stepped Mode



Quartz Crystal Microbalance

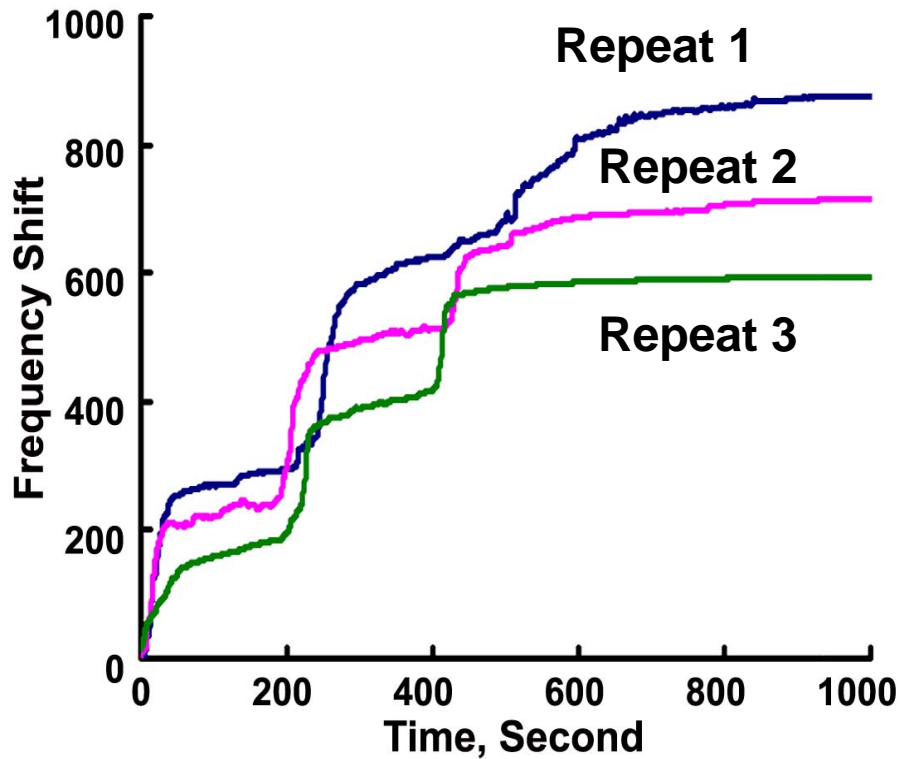


*J. Am. Chem. Soc.* 130, 2376 (2008).  
(Highlighted in **Nature Materials**)  
*Adv. Funct. Mater.*, 19, 1792 (2009).

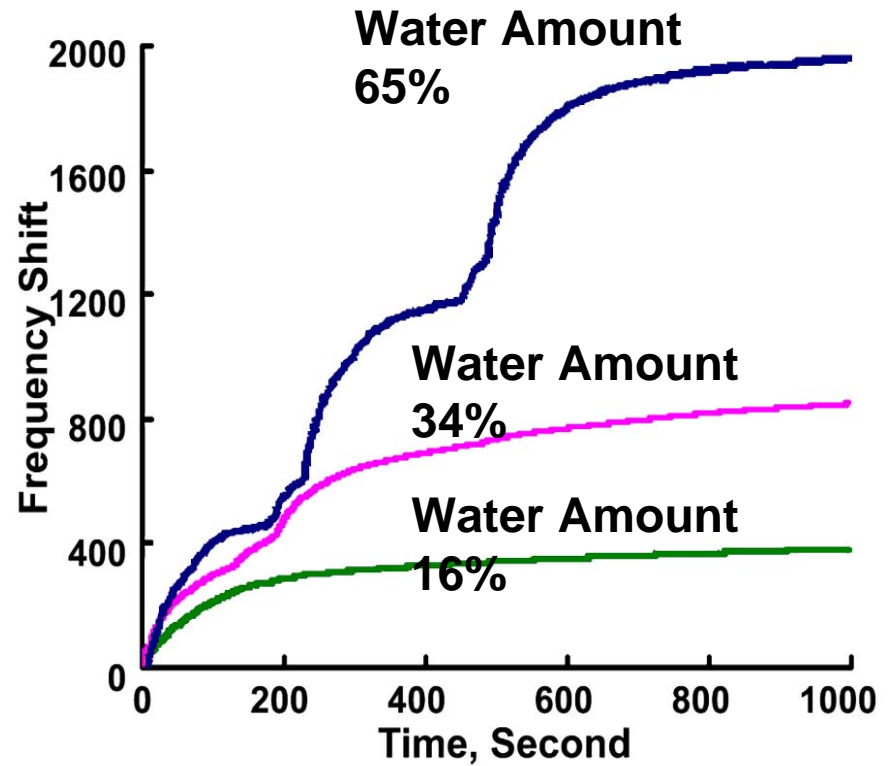
The Step not Related with Layer Numbers

# Study of the Release Mechanism

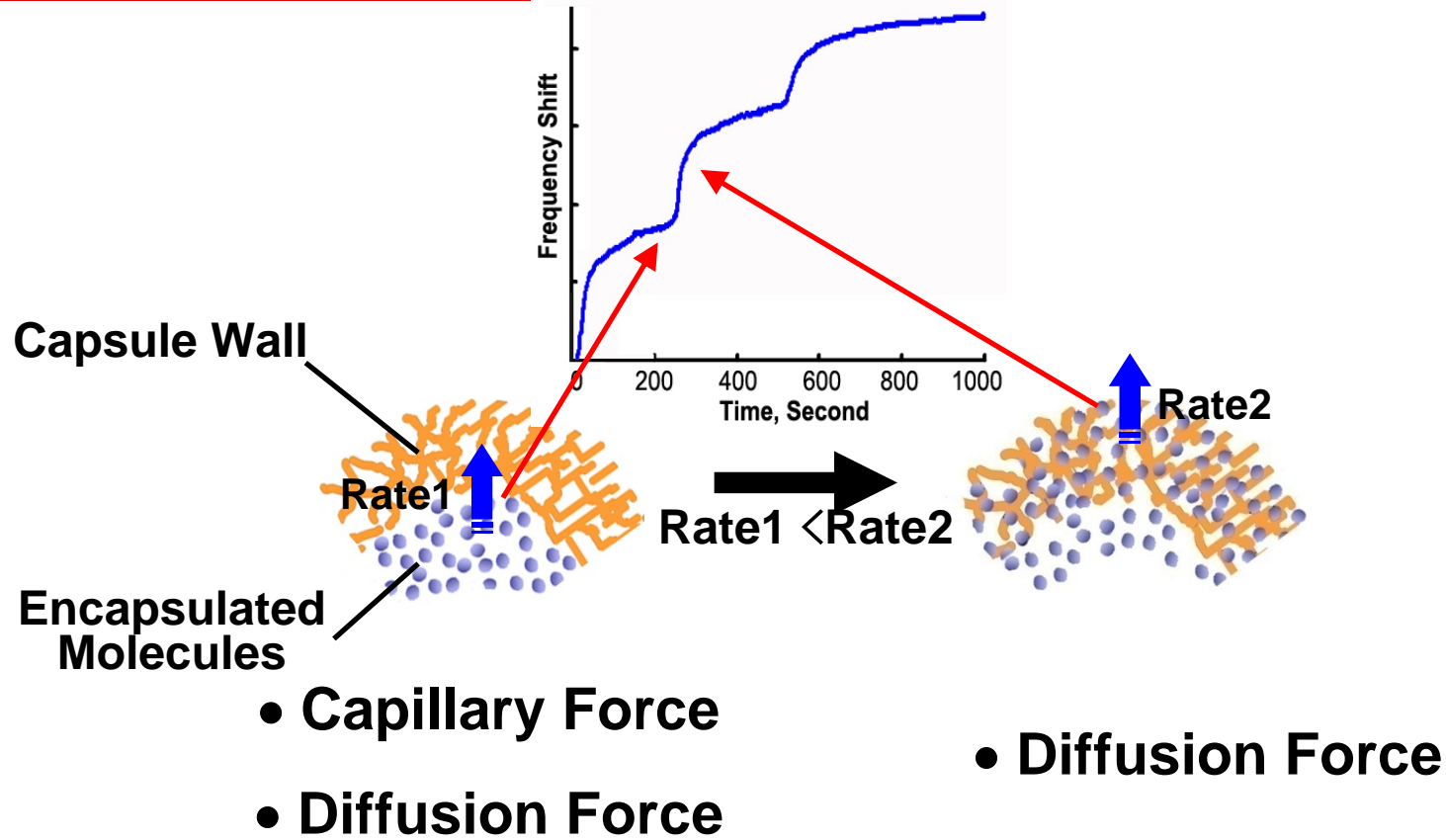
## Repeatable Behavior



## Controllable Behavior



# Driving Force for the Release Behavior

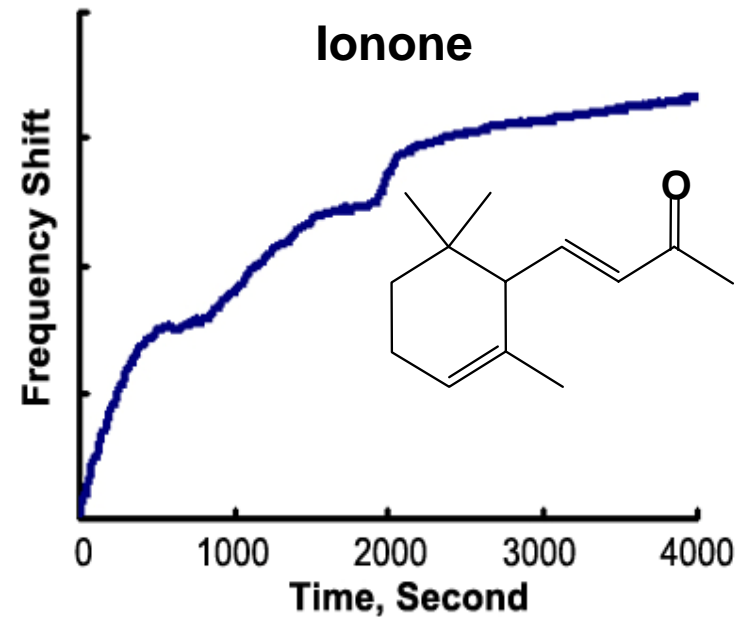
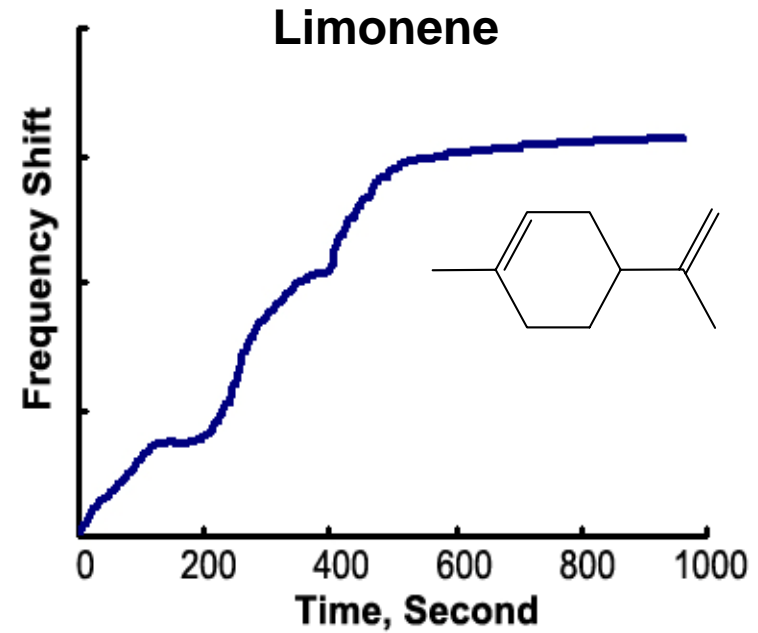
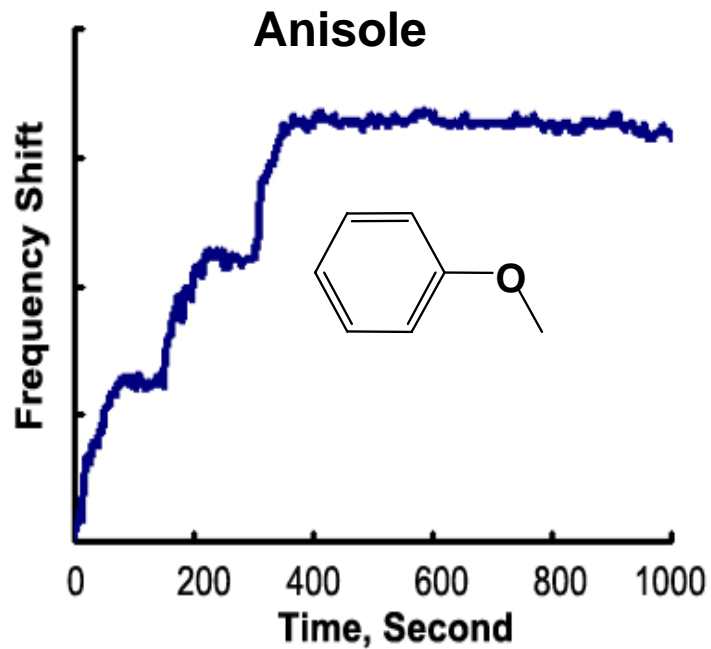


Change Rate



Change the Release Behavior

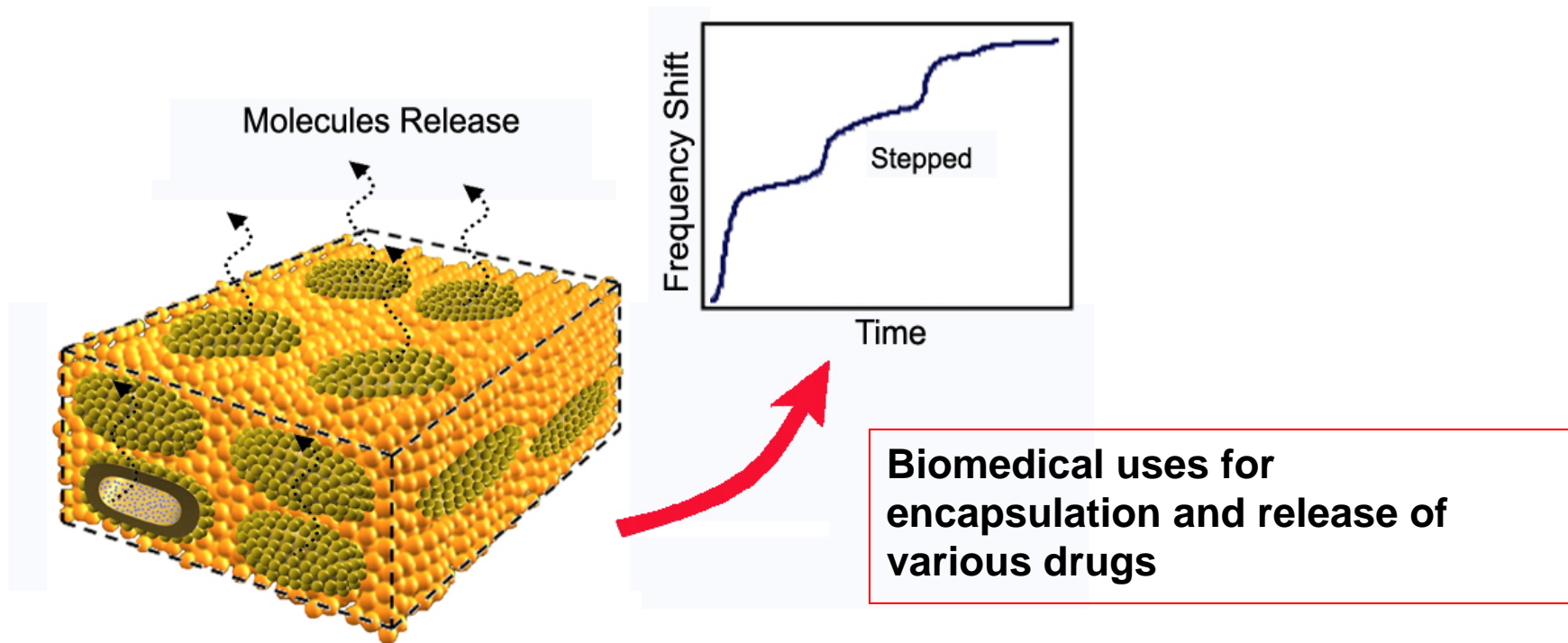
**Stepped Sustained Release of Liquid Fragrance Molecules**



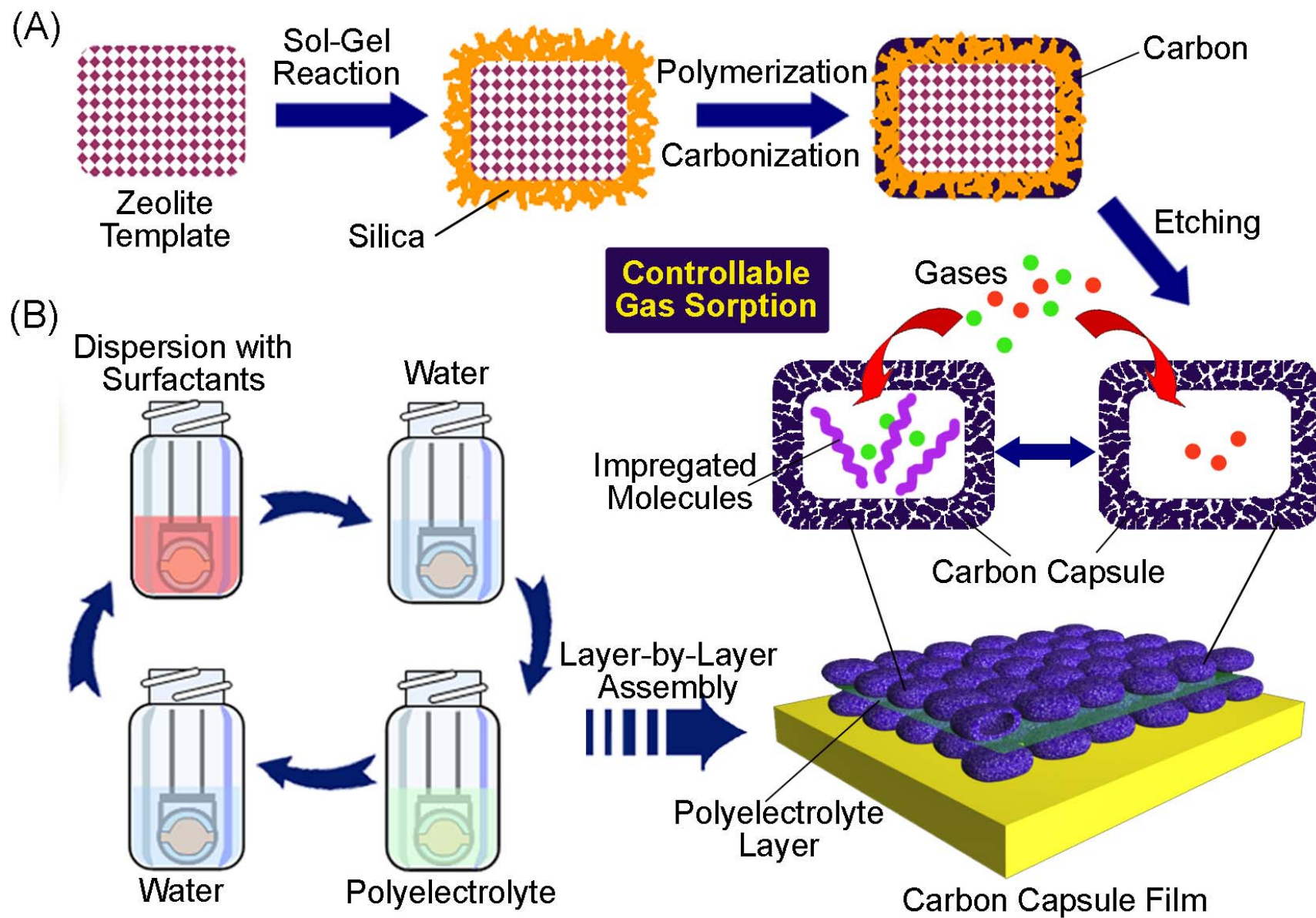


# Conclusion

- We have successfully prepared compartment films composed of **porous hollow silica capsules** using simple LbL technique.
- The compartment films exhibit **spontaneous materials release** in a **stepped auto-modulated mode** due to the special morphology of the silica capsule.



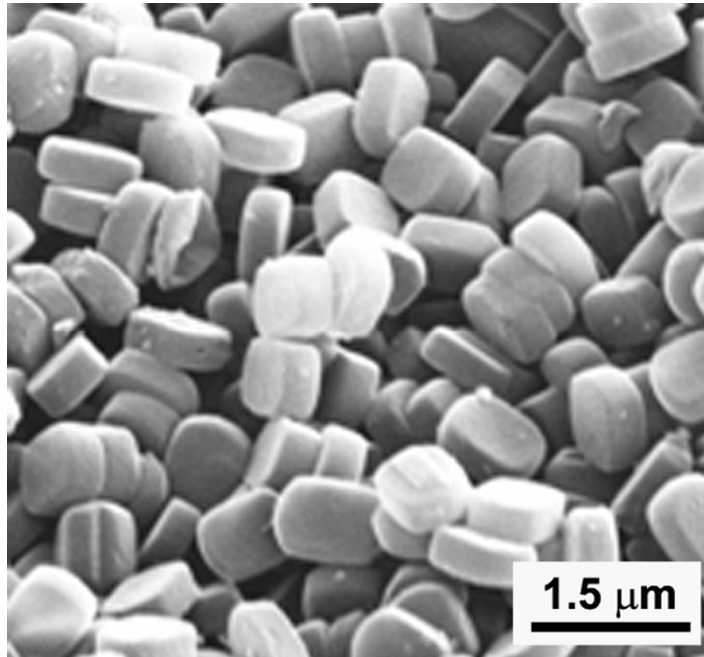
# Mesoporous Nanocompartment for Sensing



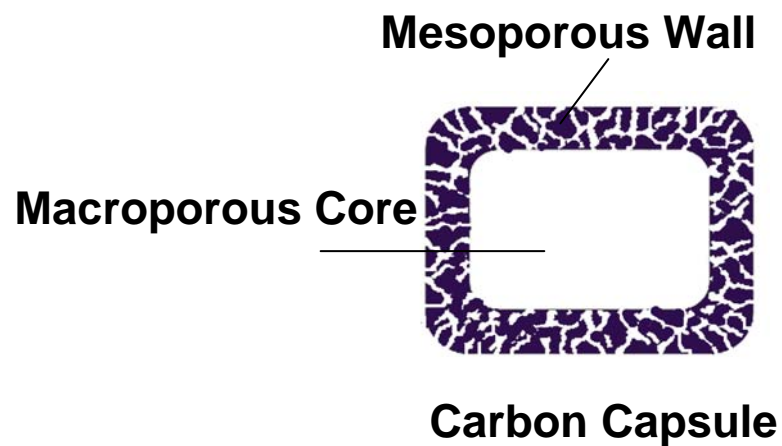
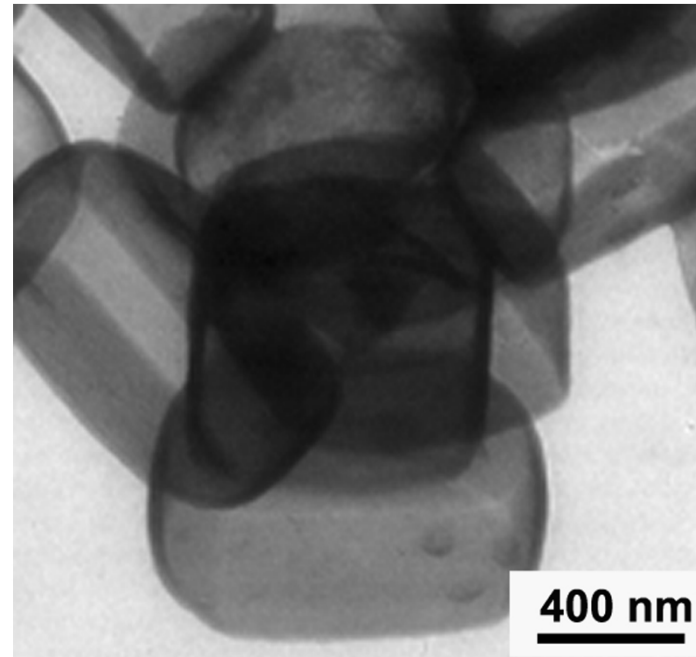
*J. Am. Chem. Soc.*, 131, 4220 (2009).

# Hollow Mesoporous Capsules

SEM Image

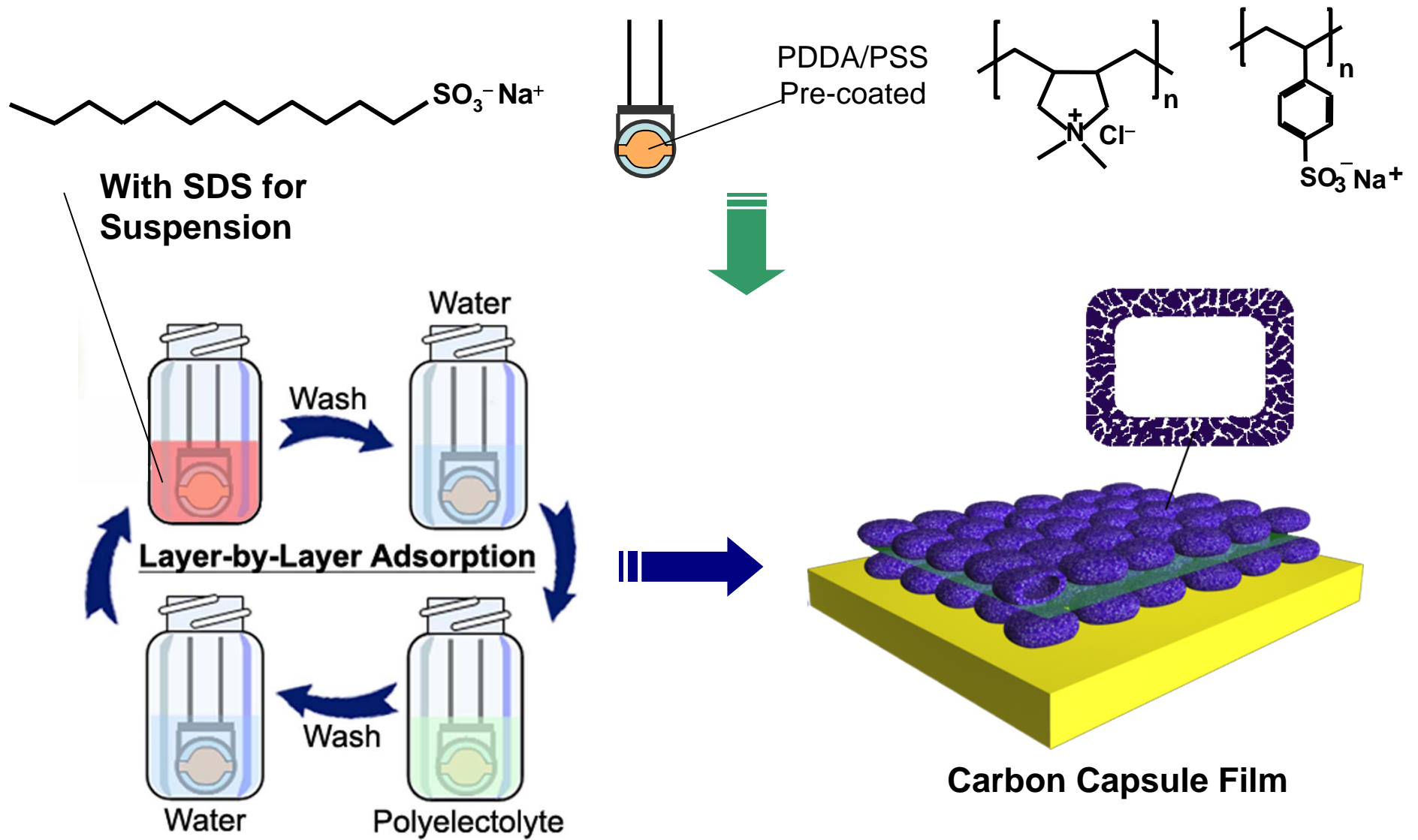


TEM Image

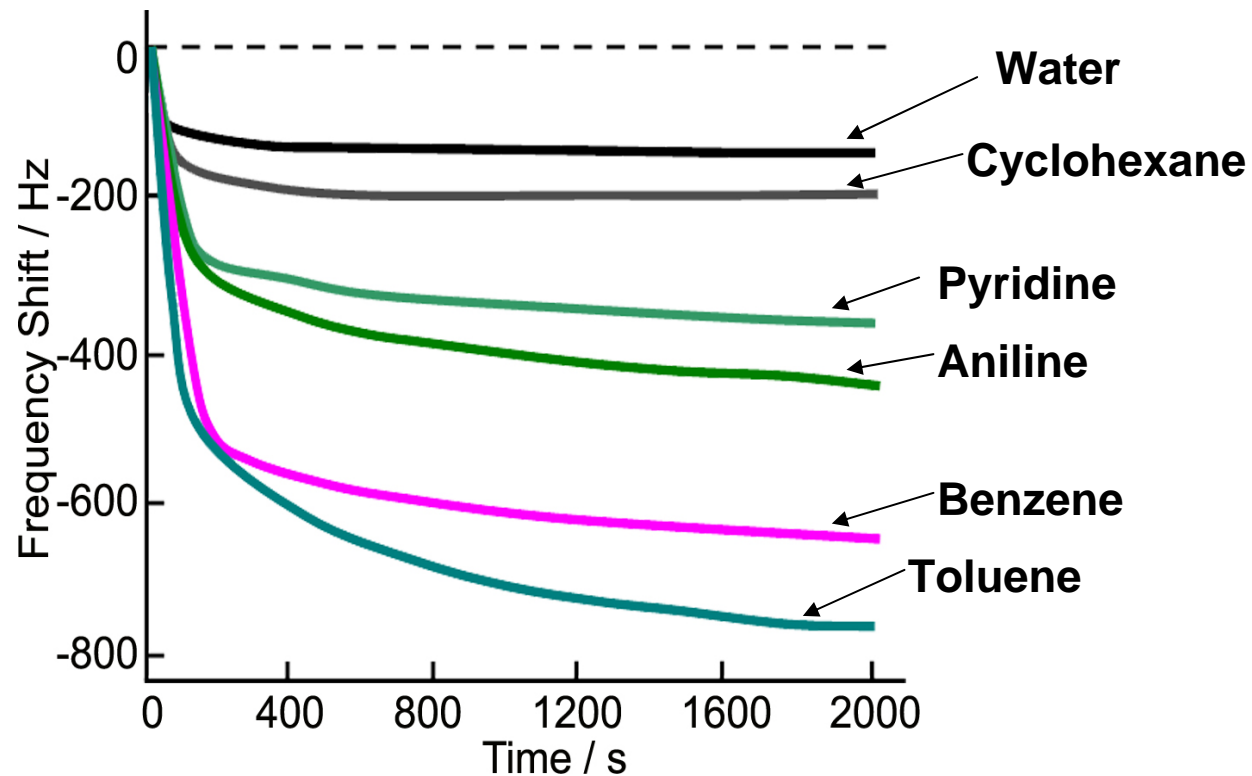
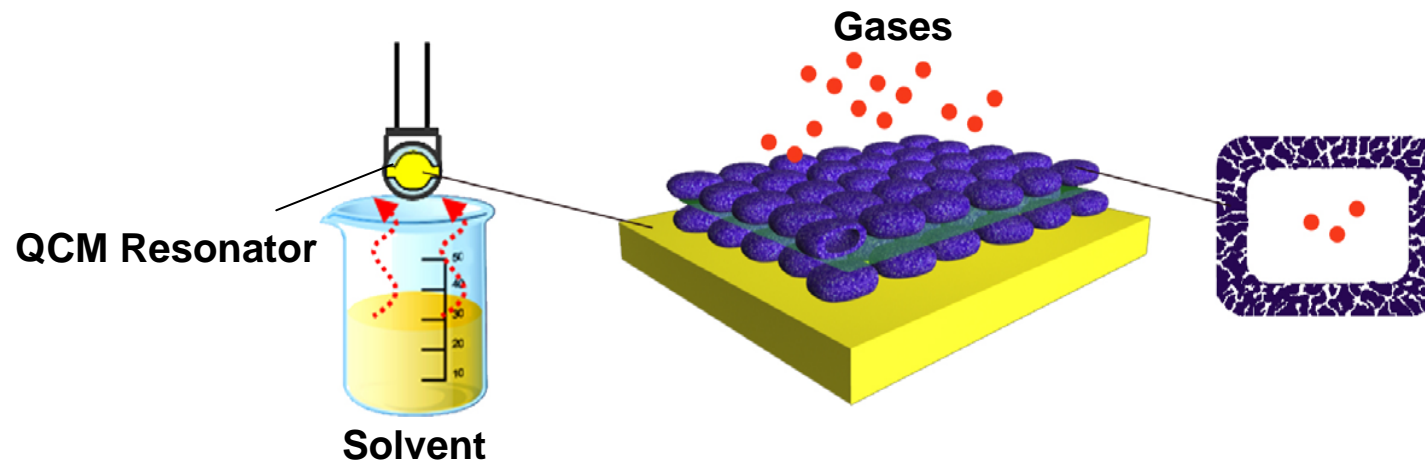


- Effective Adsorption
- Large Space for Storage

# Fabrication by Layer-by-Layer Technique

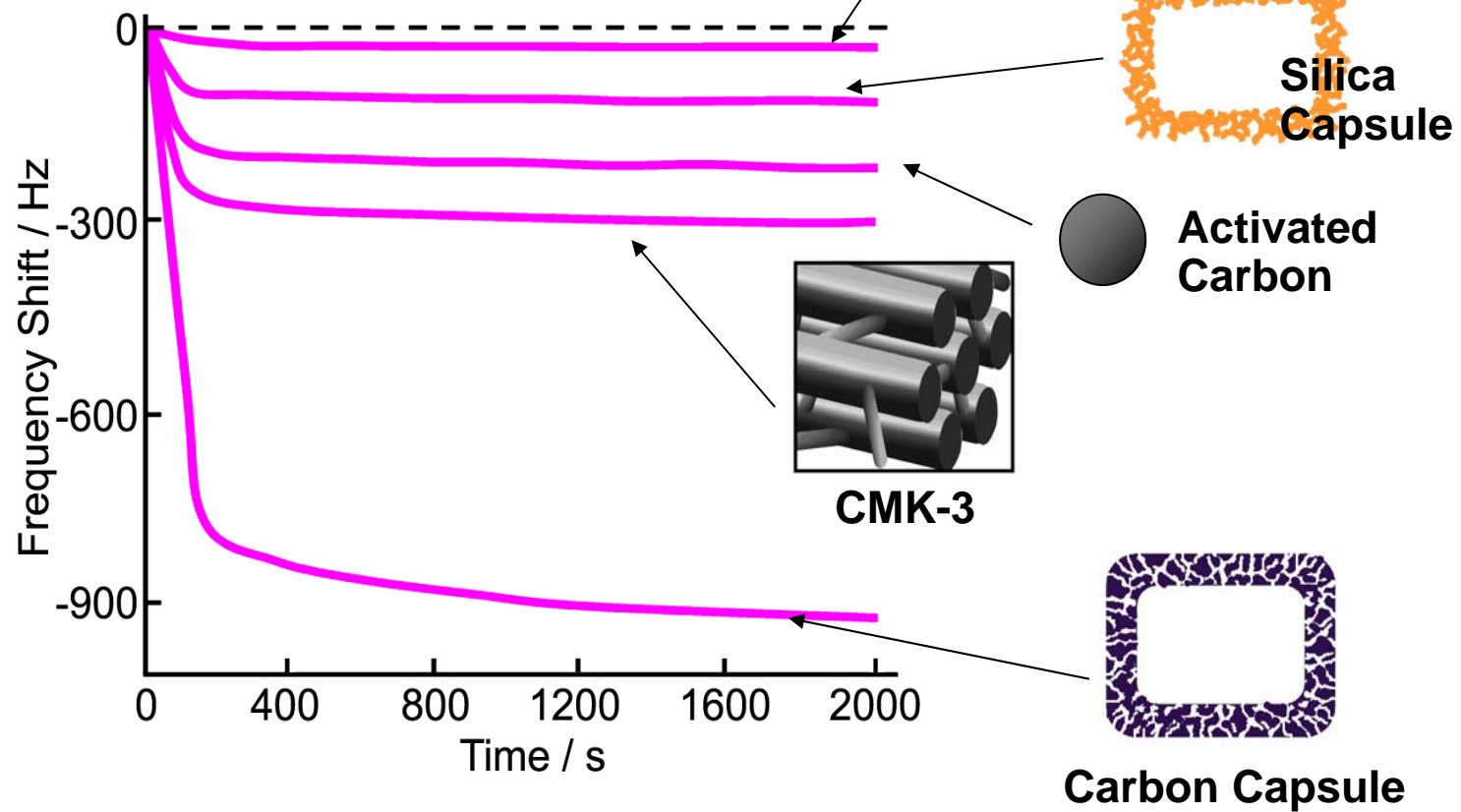
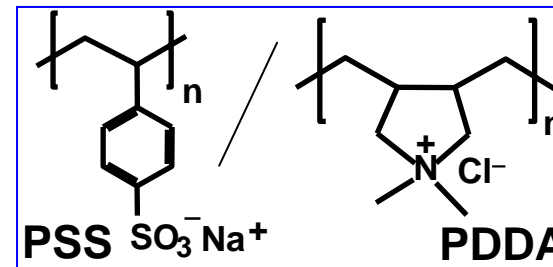


# Adsorption of Different Vapors

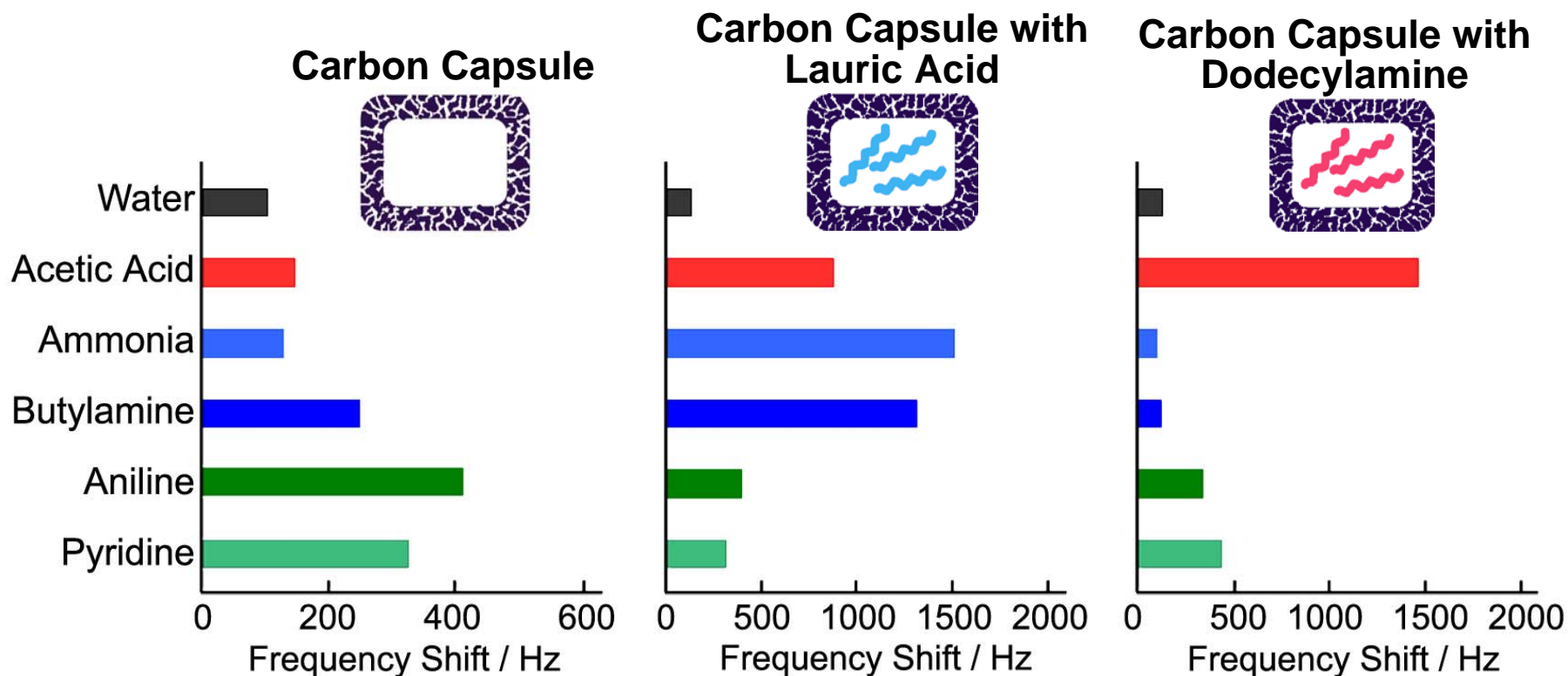
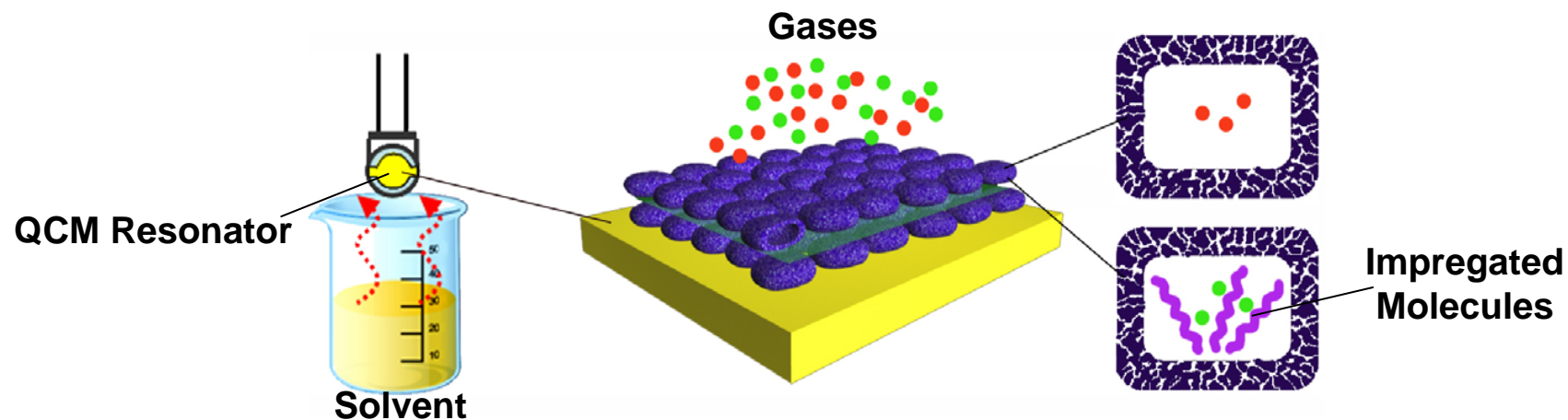


# Adsorption of Different Vapors

On Adsorption of Benzene Vapor

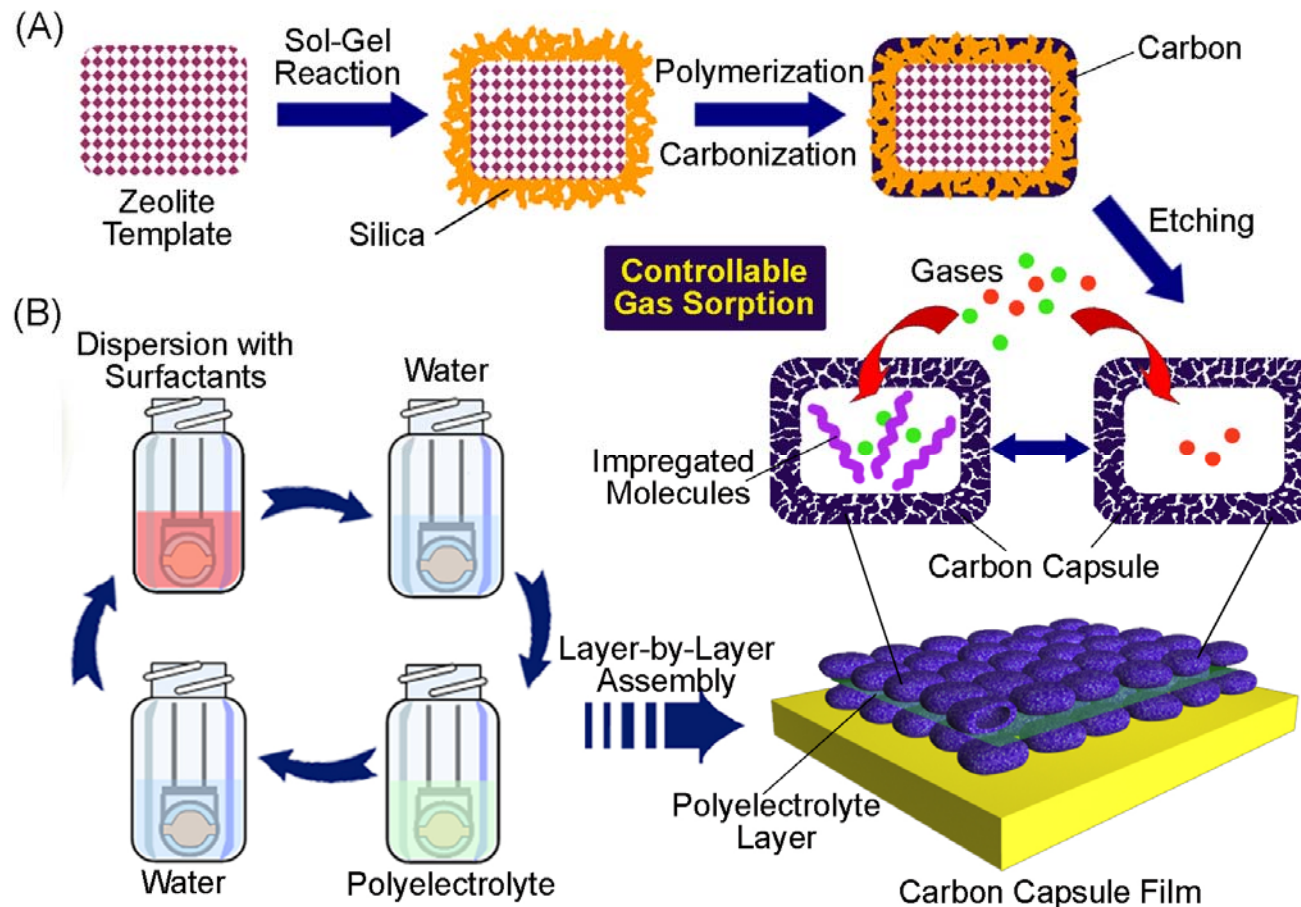


# Carbon Capsules With Imprinted Molecules



# In Summary

- LbL compartment films formed by carbon capsule have shown effective adsorption of organic solvent with phenyl group.
- By encapsulation of different molecules in the carbon capsule, it is possible to control the adsorption selectivity of different vapors.



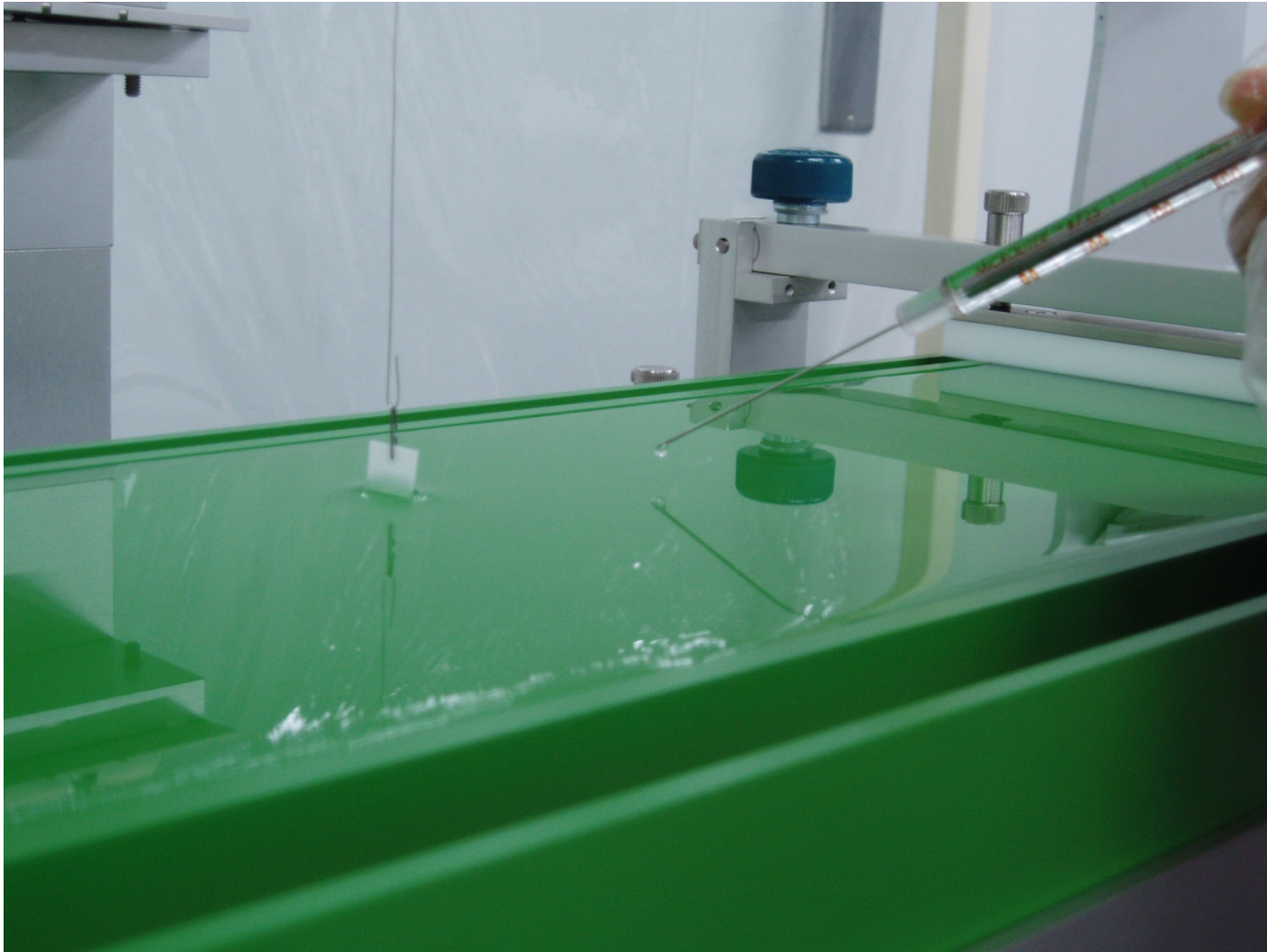


**New Concept**

***Hand-Operating Nanotechnology***

# *Hand-Operating Nanotechnology*

## Catch a Molecule!



# Hand-Operating Nanotechnology

## Molecular Machine at Interface

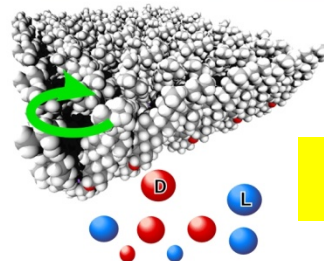
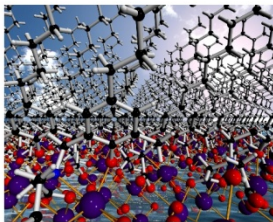
Bottom-up

Top-down

*Simple size-matching  
dose not result in  
anything.*

**New concept has  
to be established**

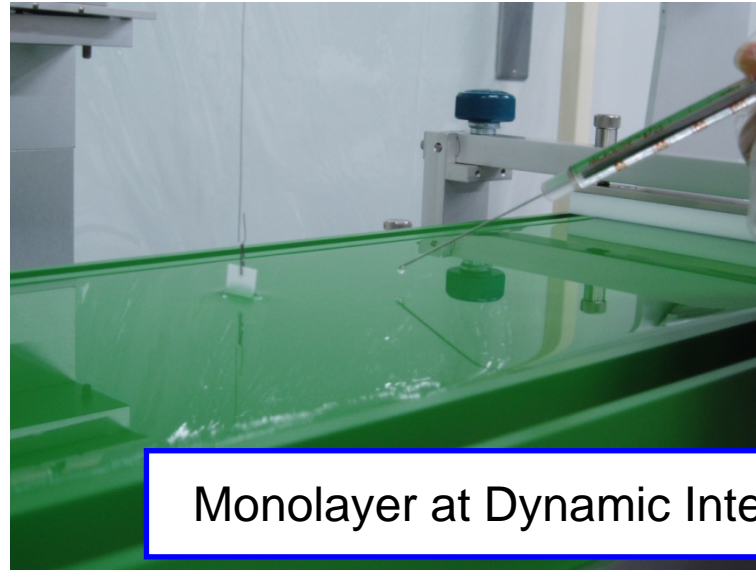
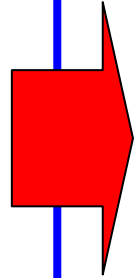
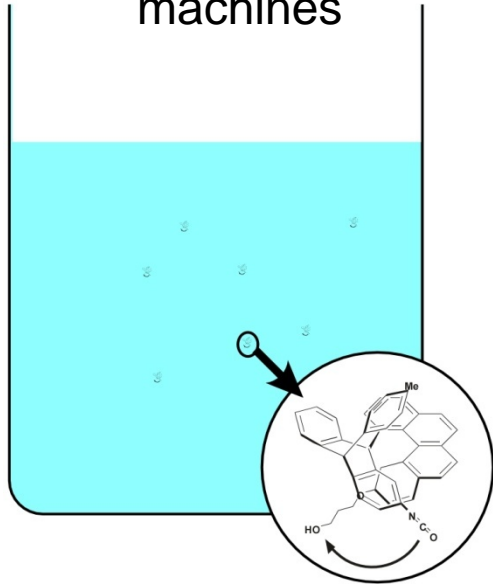
**Mechanism for connection between molecule (Nano) and real (Visible World)**



**Molecular Manipulation by Bulk Motion**

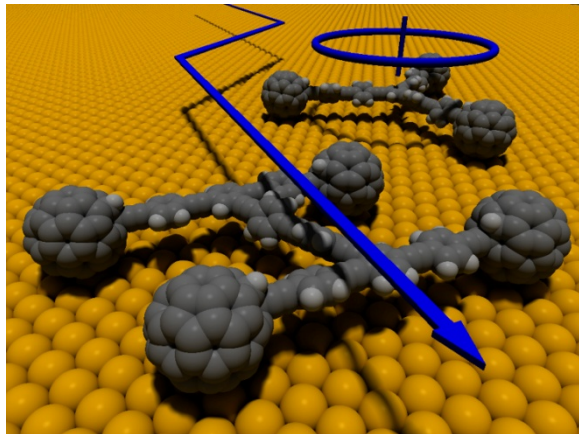
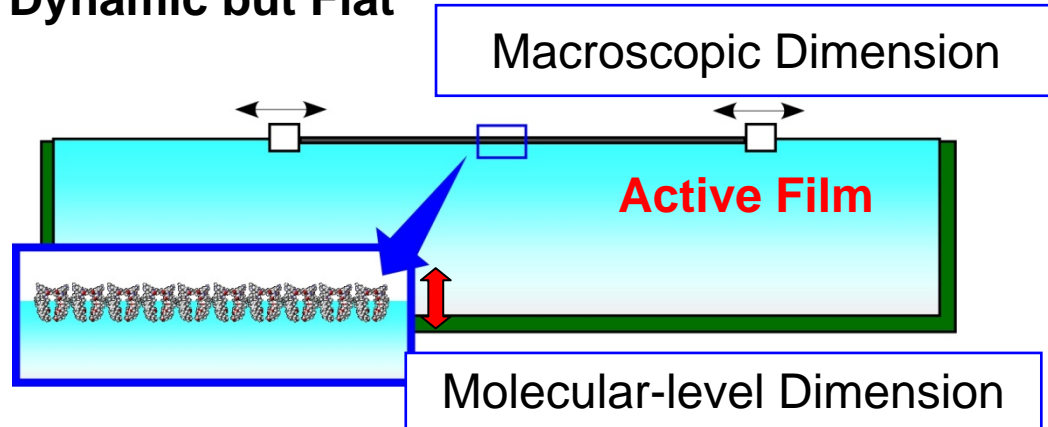
# Molecular Machine at Dynamic Interface

Invisible molecular machines



Monolayer at Dynamic Interface

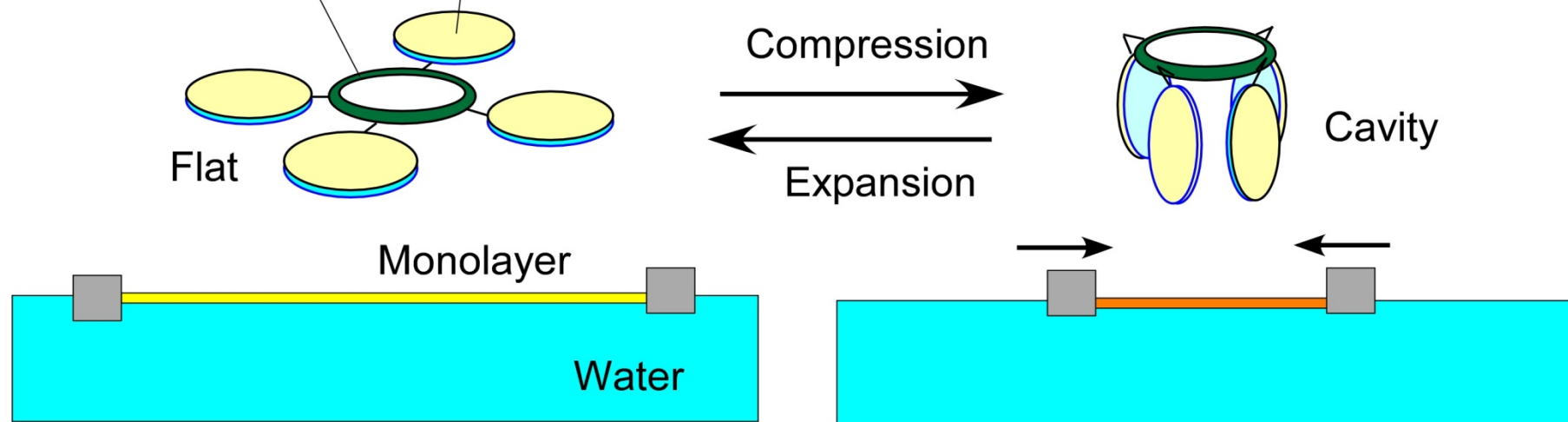
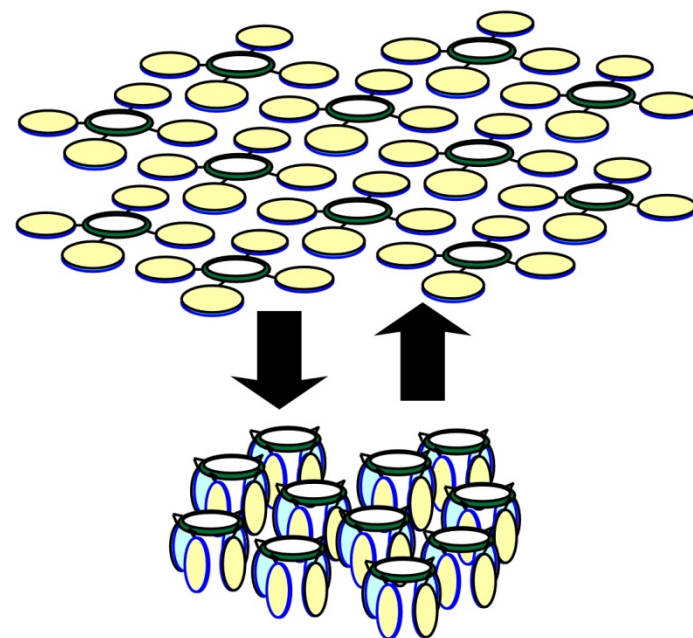
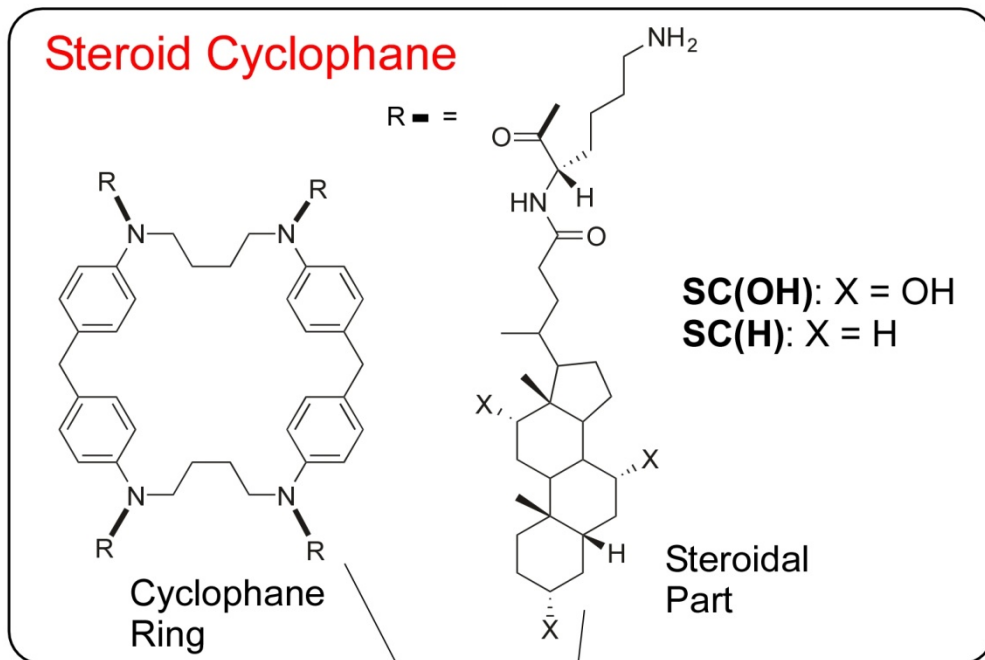
Dynamic but Flat



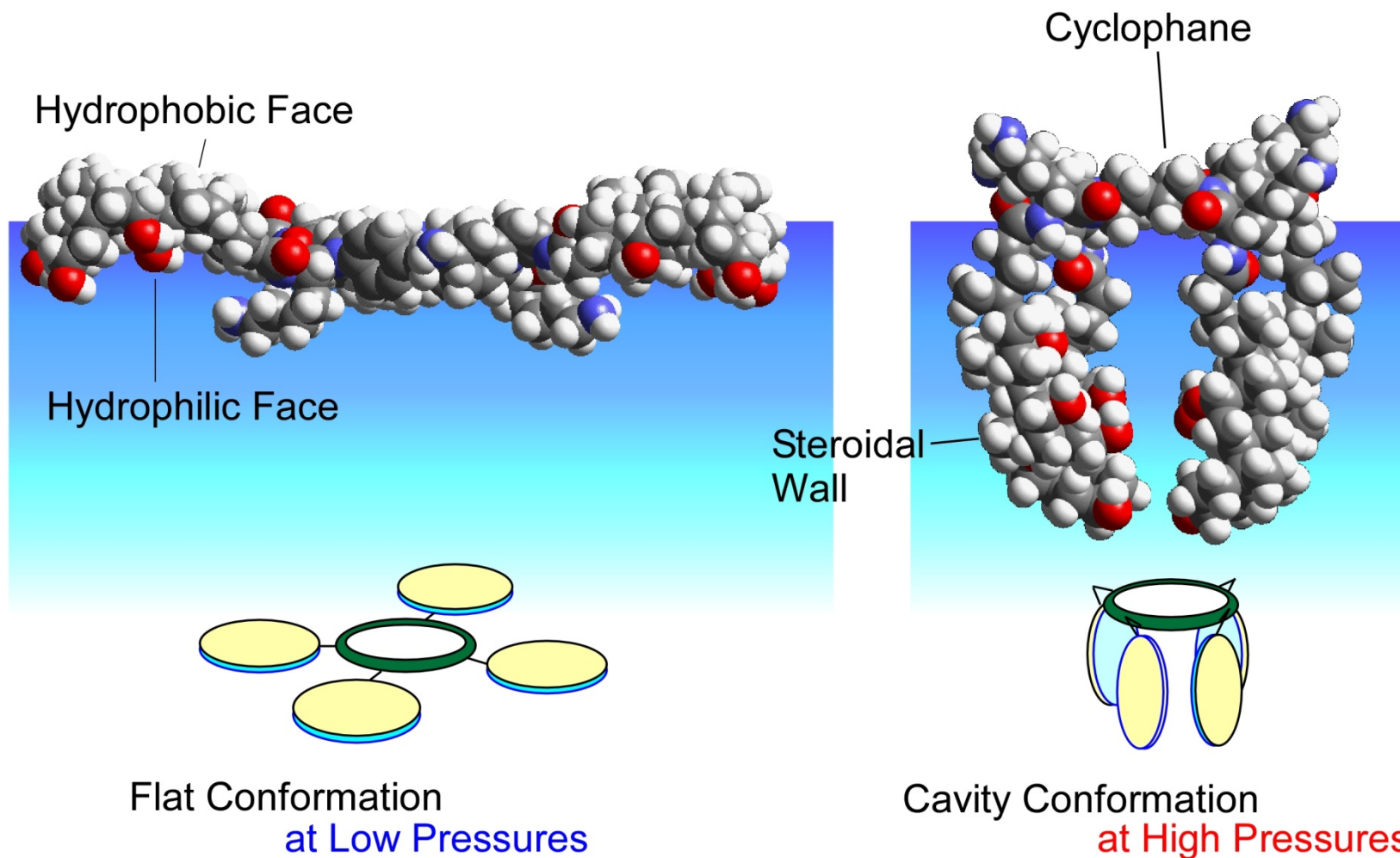
Useless!

*Environment with both molecular and macroscopic characteristics!*

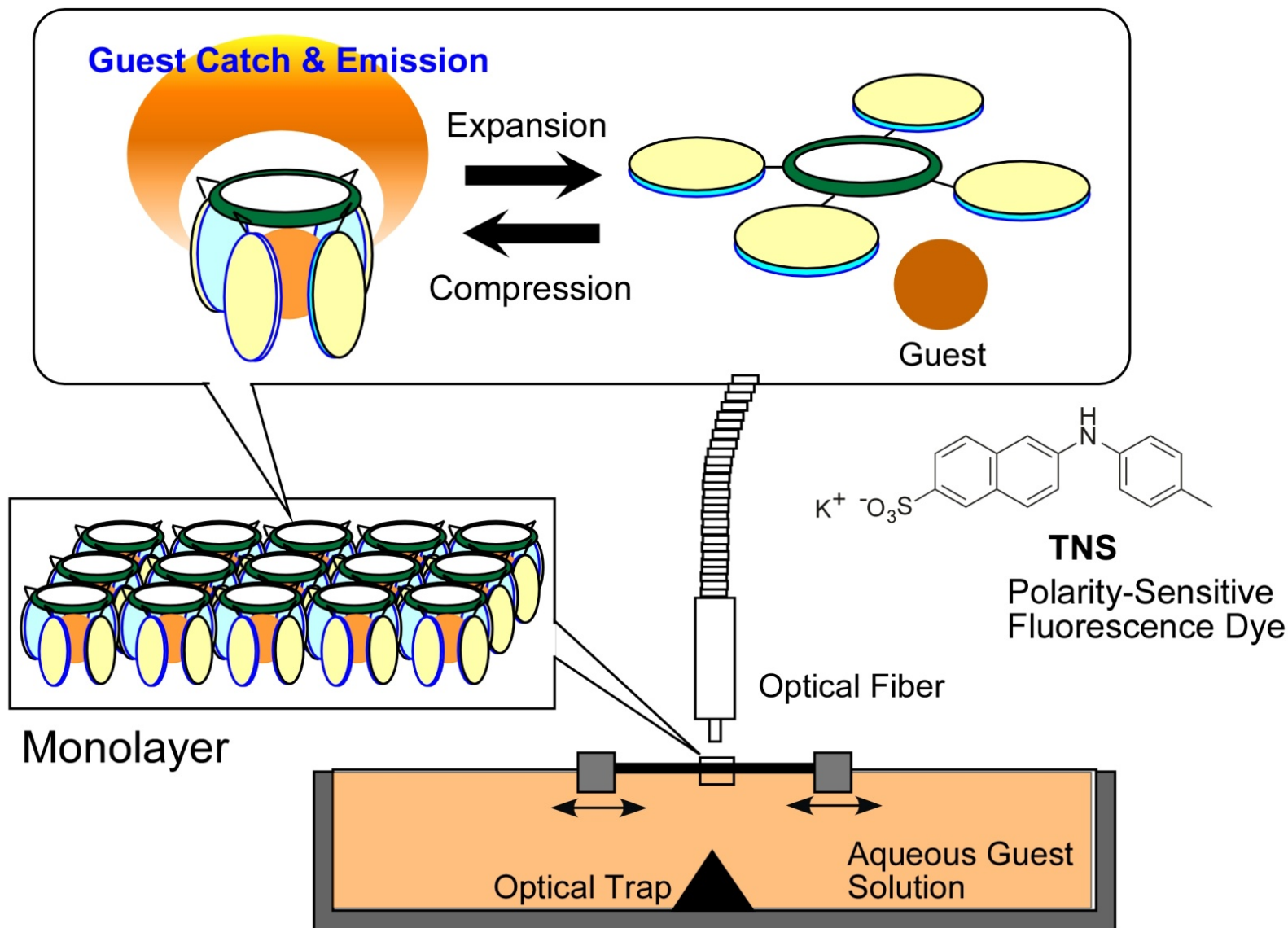
# Dynamic Function of Molecular Pattern at Air-Water Interface

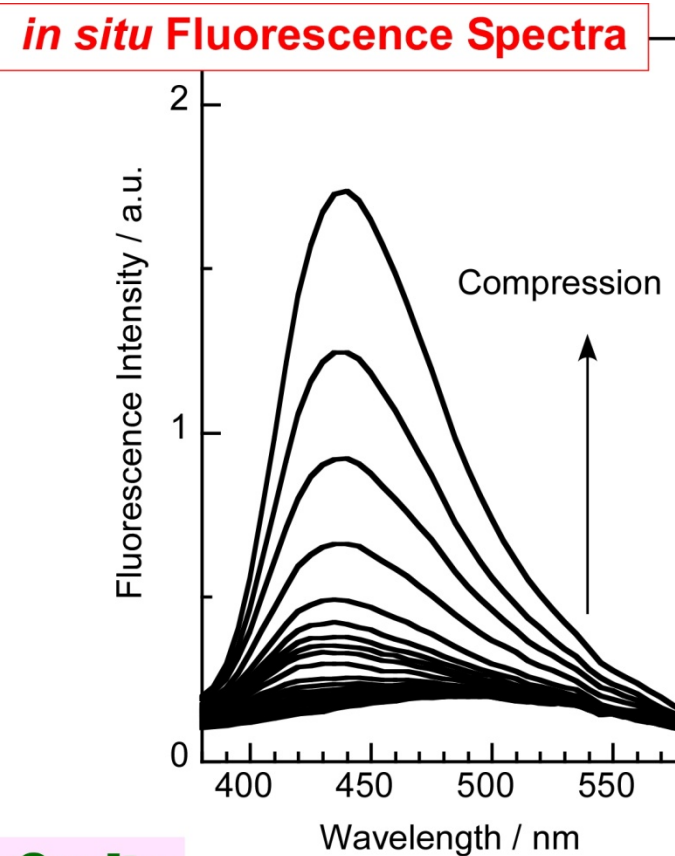
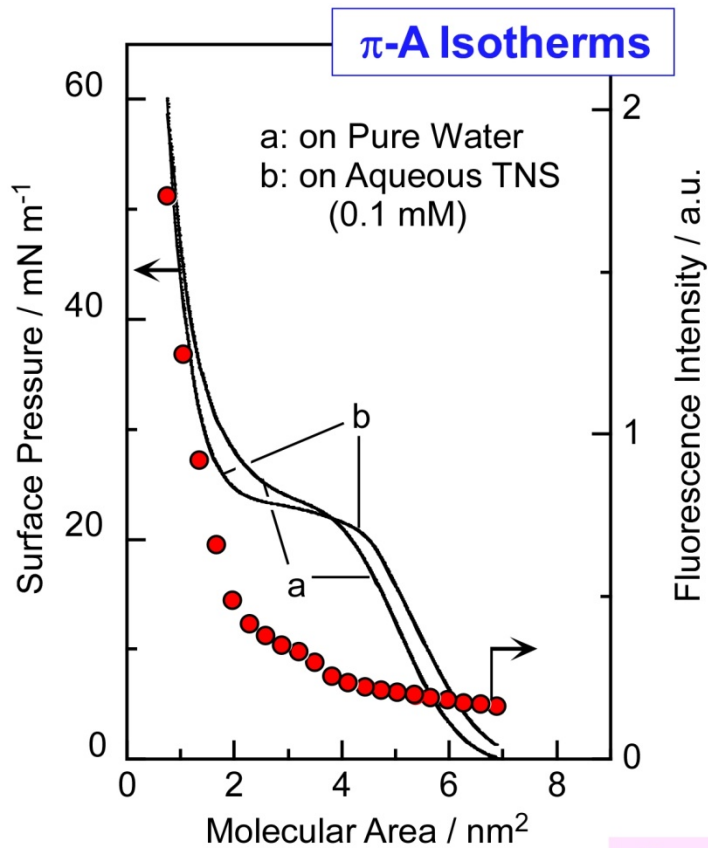


# Conformational Changes of Steroid Cyclophane at Air-Water Interface

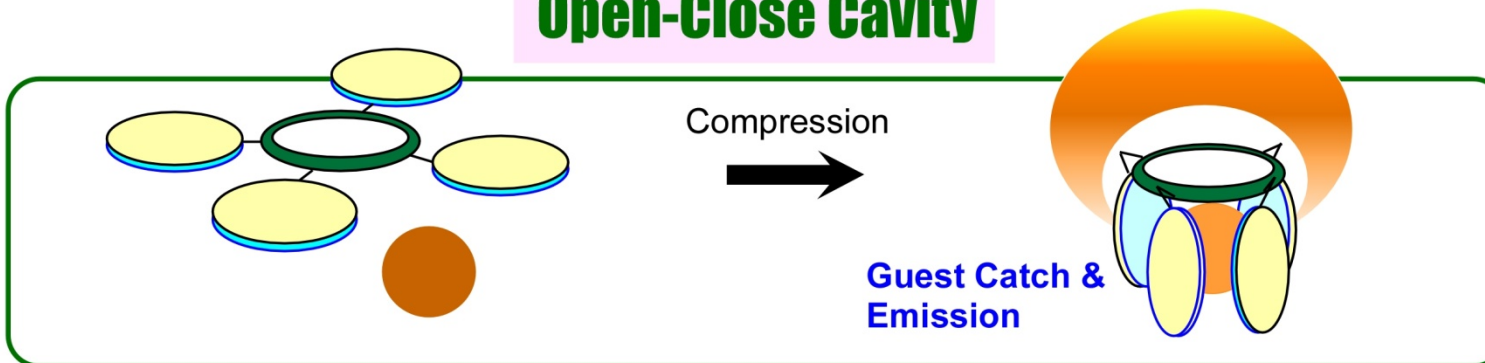


# Measurement of Piezoluminescence (Pressure to Light) Behavior

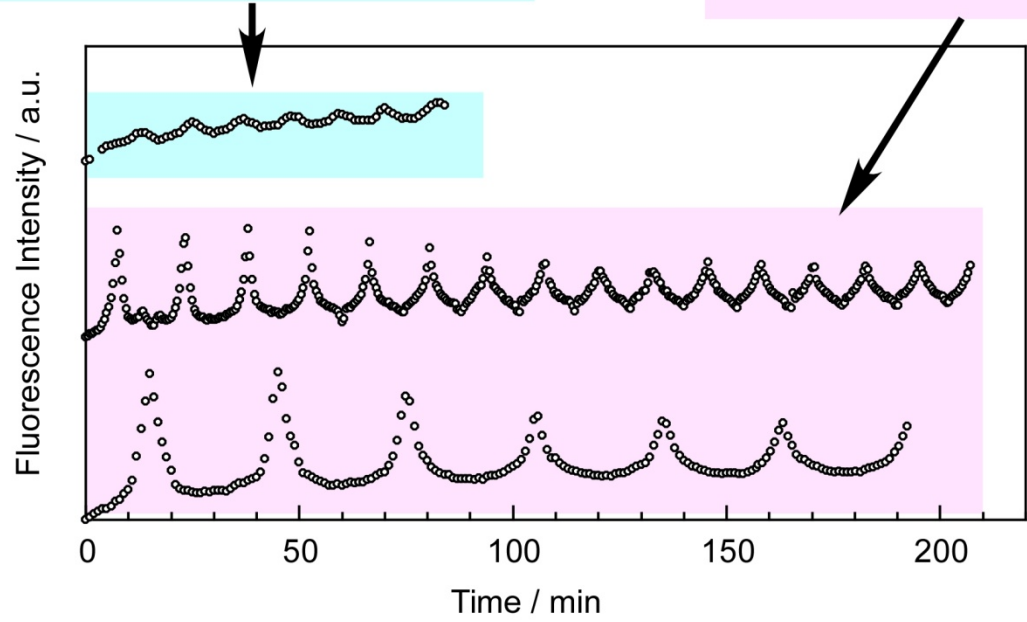
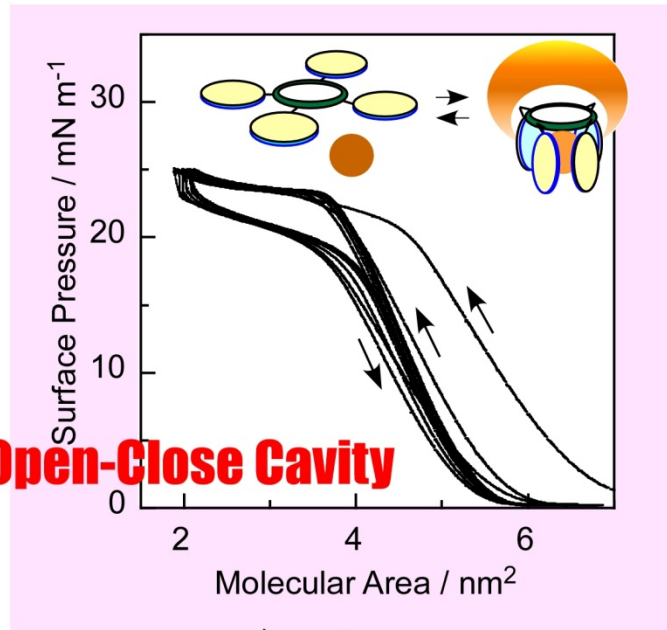
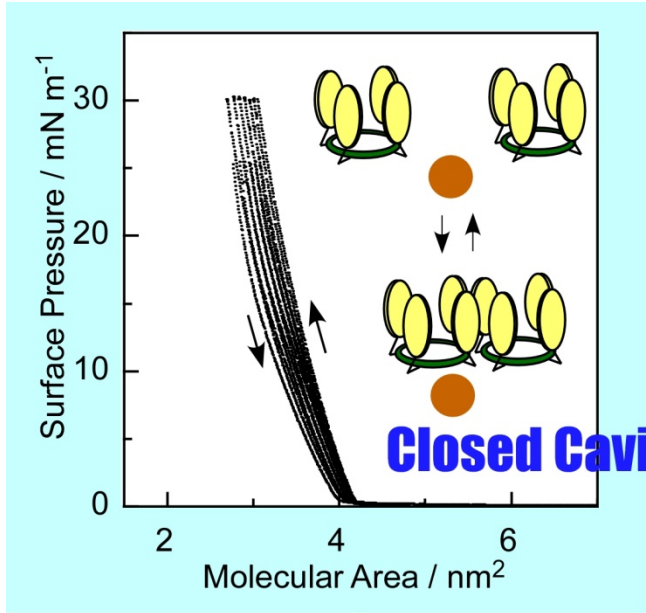




## Open-Close Cavity







**Repeated  
Piezoluminescence  
Based on Molecular  
Recognition**

**Bulk Operation**



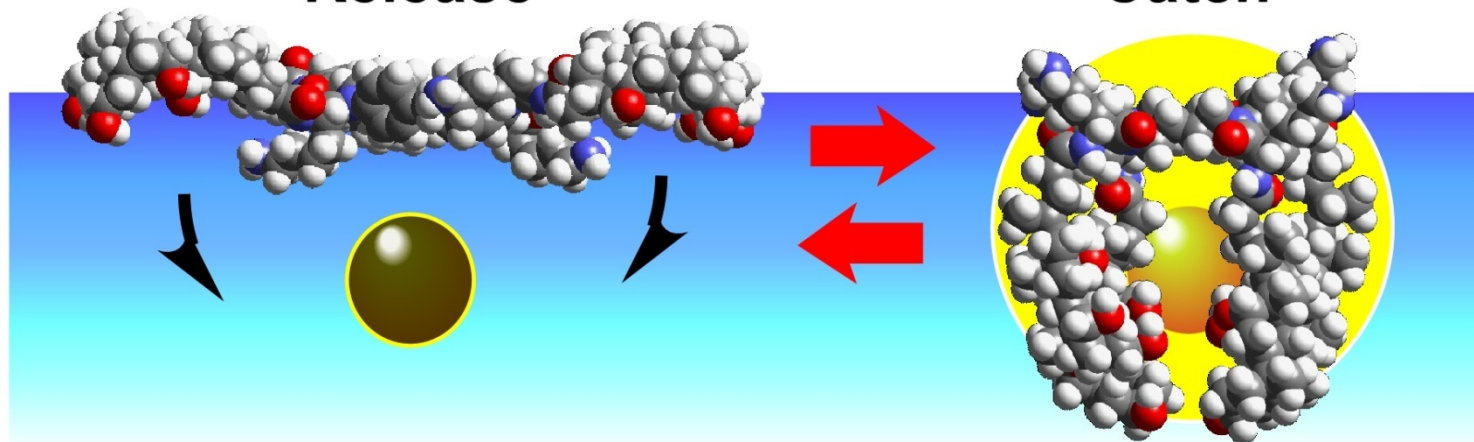
# ***Hand-Operating Nanotechnology*** **Molecular Machine at Interface**

***Connection between  
molecular (nano) world  
and real (visible) world***

**Access to  
Molecular World**

**Release**

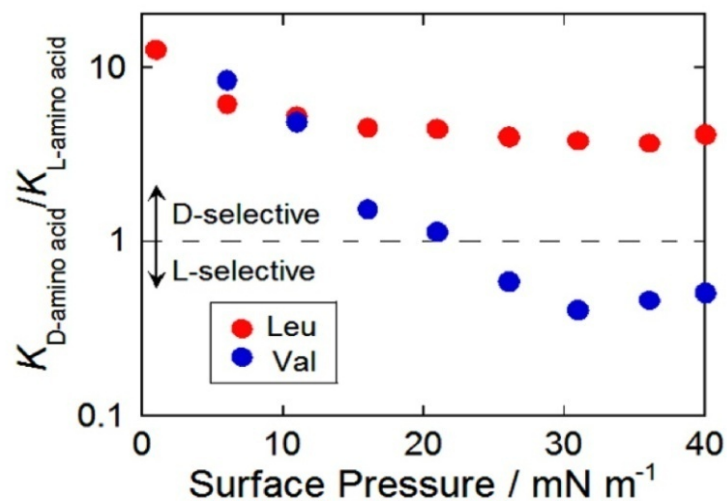
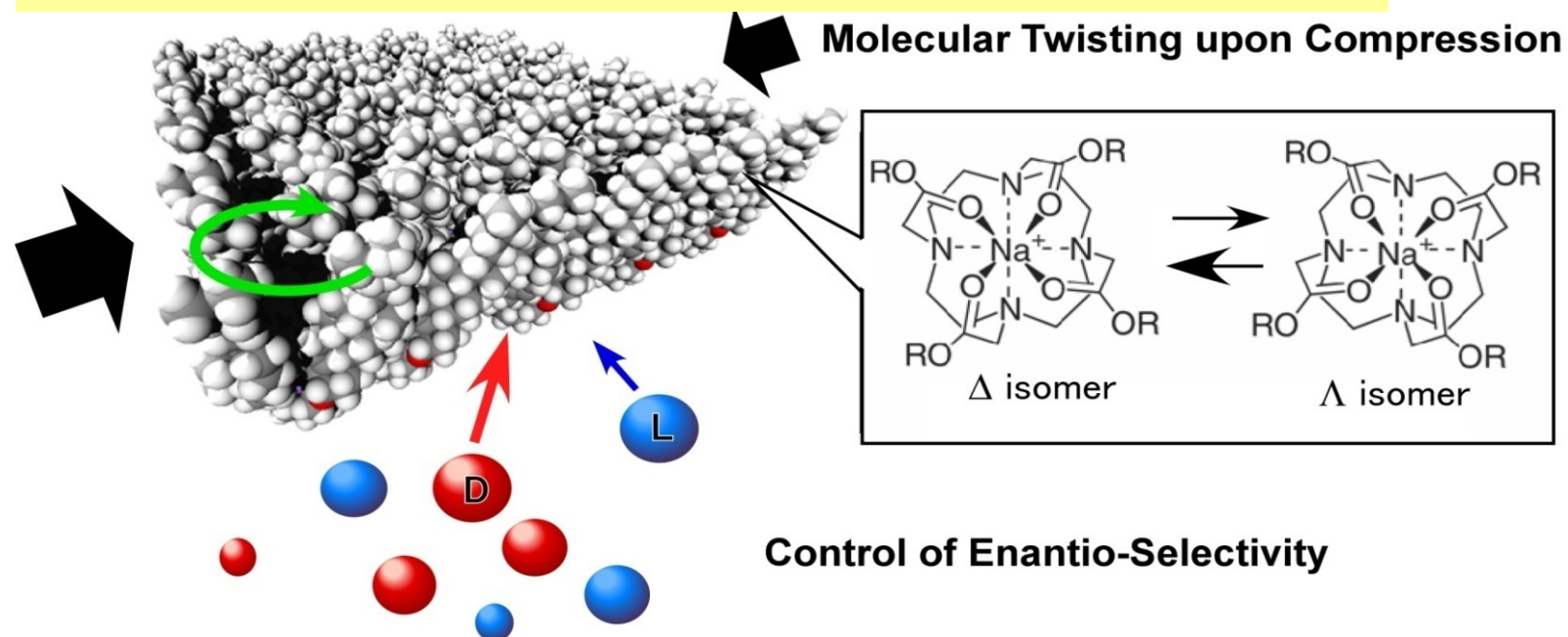
**Catch**



# Hand-Operating Nanotechnology

## Chiral Resolution by Hand Motion

First Achievement Since Dr. Pasteur



Collaboration with  
Prof. Tsukube and Prof. Shinoda  
(Osaka City University)

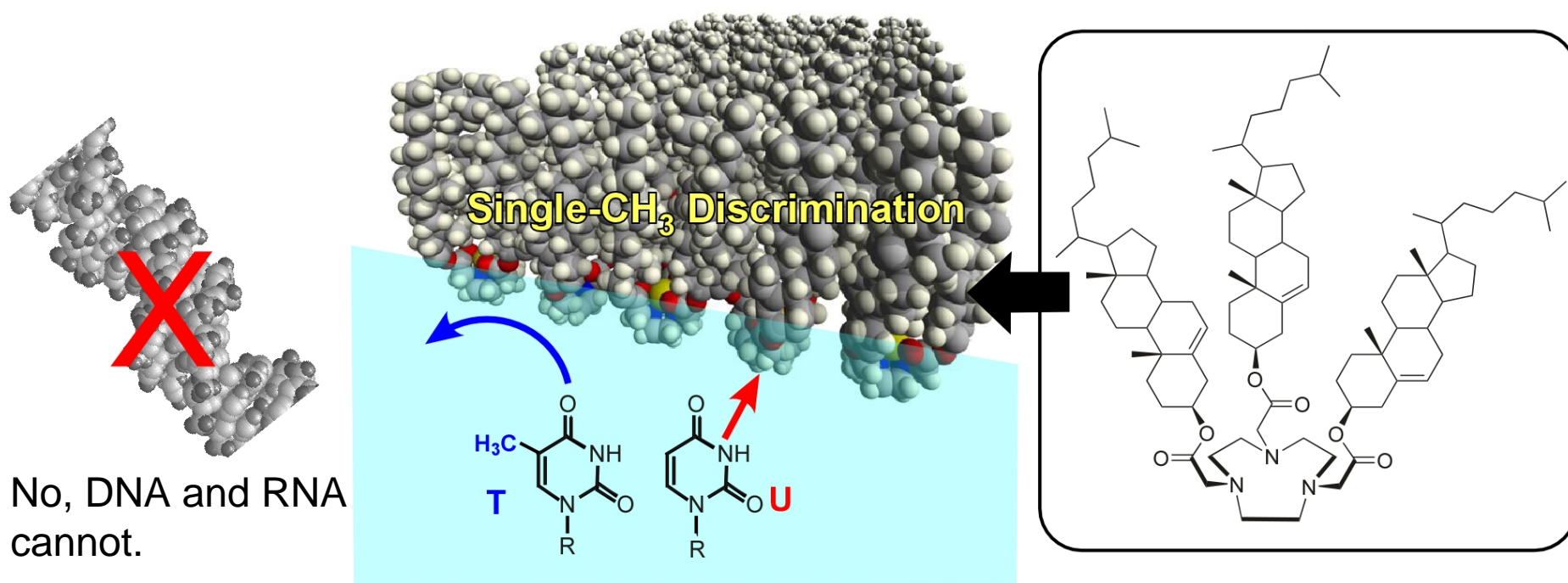
***J. Am. Chem. Soc.*, 128, 14478 (2006).**

# Hand-Operating Nanotechnology

## Discriminate the Single-Methyl-Group Difference between Thymine and Uracil

*Beyond Nucleic Acid Recognition*

**YES, monolayer can.**



# Thank you

