Supramolecular Nanomaterials

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Molecular Nanofabrication group
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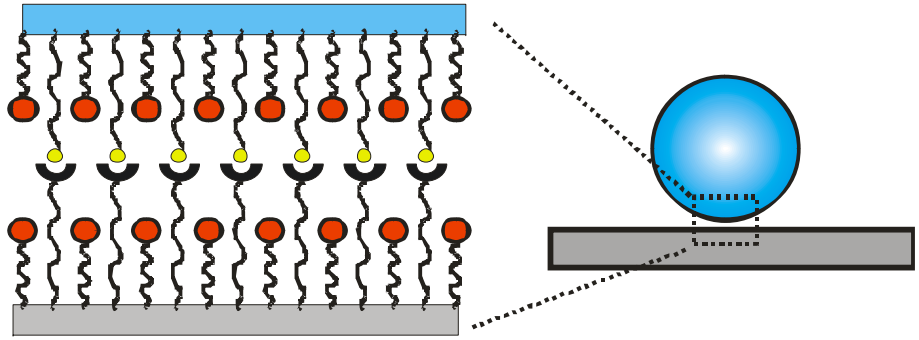
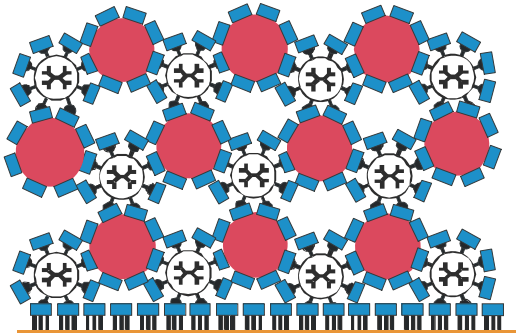
General philosophy

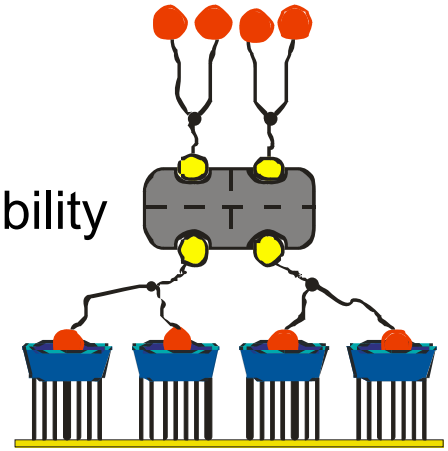
Engineering the interface: use of receptor-ligand interactions:

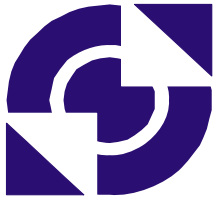




strength
(switchable/tunable)
specificity
competition
self-limiting

stability/cohesion
patterning/3D
specificity
regeneration/reversibility
multilayers
order



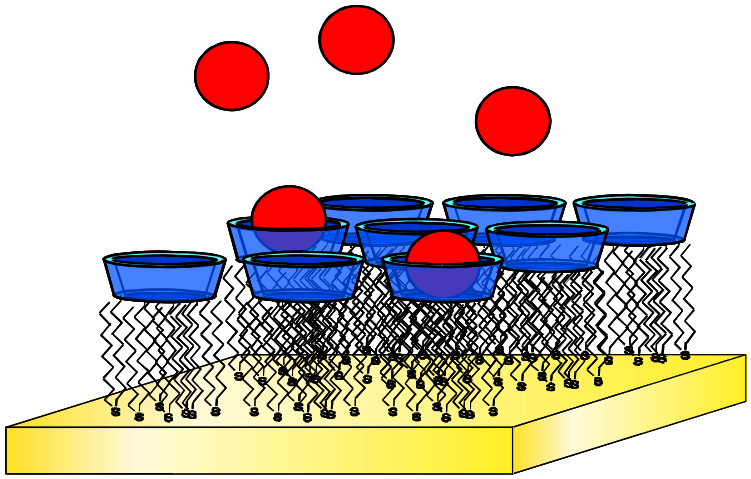


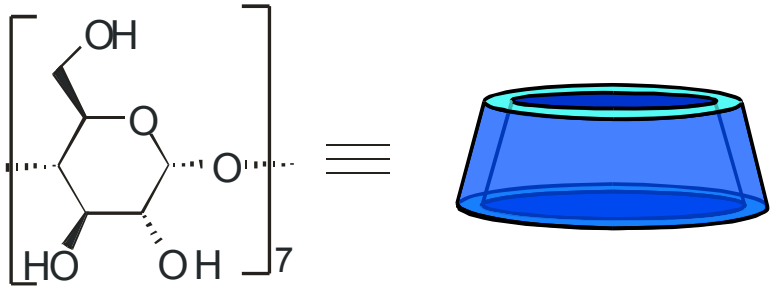
Part 1

Cohesion of Supramolecular Materials

Molecular printboards

CD monolayers on gold: infinite 2D receptor lattices:





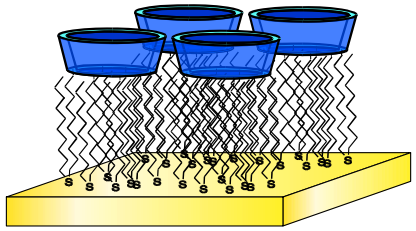
β-cyclodextrin (CD)

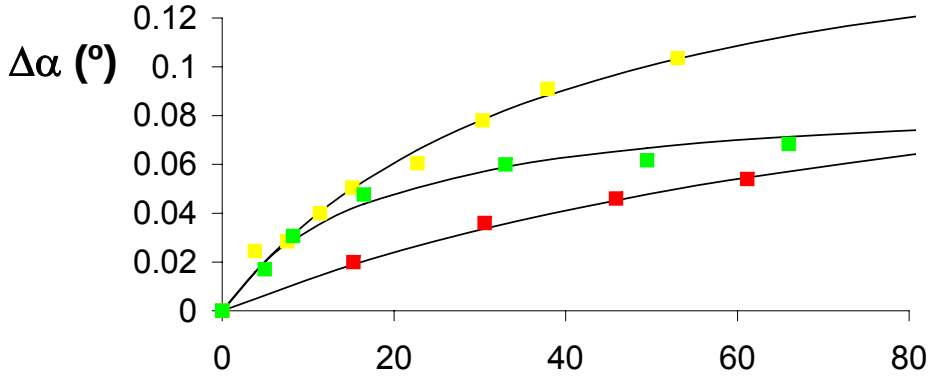
CA:	polarity:	θ_{adv} = 55°
EIS:	thickness:	2 - 3 nm
XPS:	bound sulfur:	65 %
SIMS:	molecular peaks:	$(M+Au)^+$
AFM:	molecular order:	2.1 nm

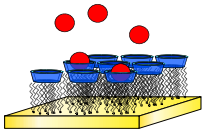
M. J. W. Ludden, D. N. Reinhoudt, J. Huskens, *Chem. Soc. Rev.* **2006**, *35*, 1122

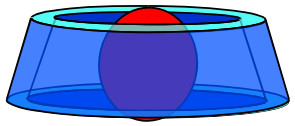
Molecular printboards

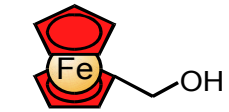
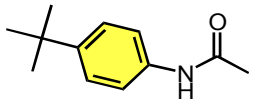
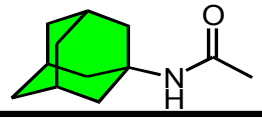
Small guests at a CD monolayer:









	K (M^{-1})	$\Delta\alpha_{sat}$ (°)	K (M^{-1})	ΔH (kcal mol^{-1})	$T\Delta S$ (kcal mol^{-1})
	$9.9 \cdot 10^3$	0.145	$1.0 \cdot 10^4$	-6.1	-0.7
	$2.6 \cdot 10^4$	0.179	$3.0 \cdot 10^4$	-5.2	0.9
	$5.7 \cdot 10^4$	0.090	$6.8 \cdot 10^4$	-5.9	0.7

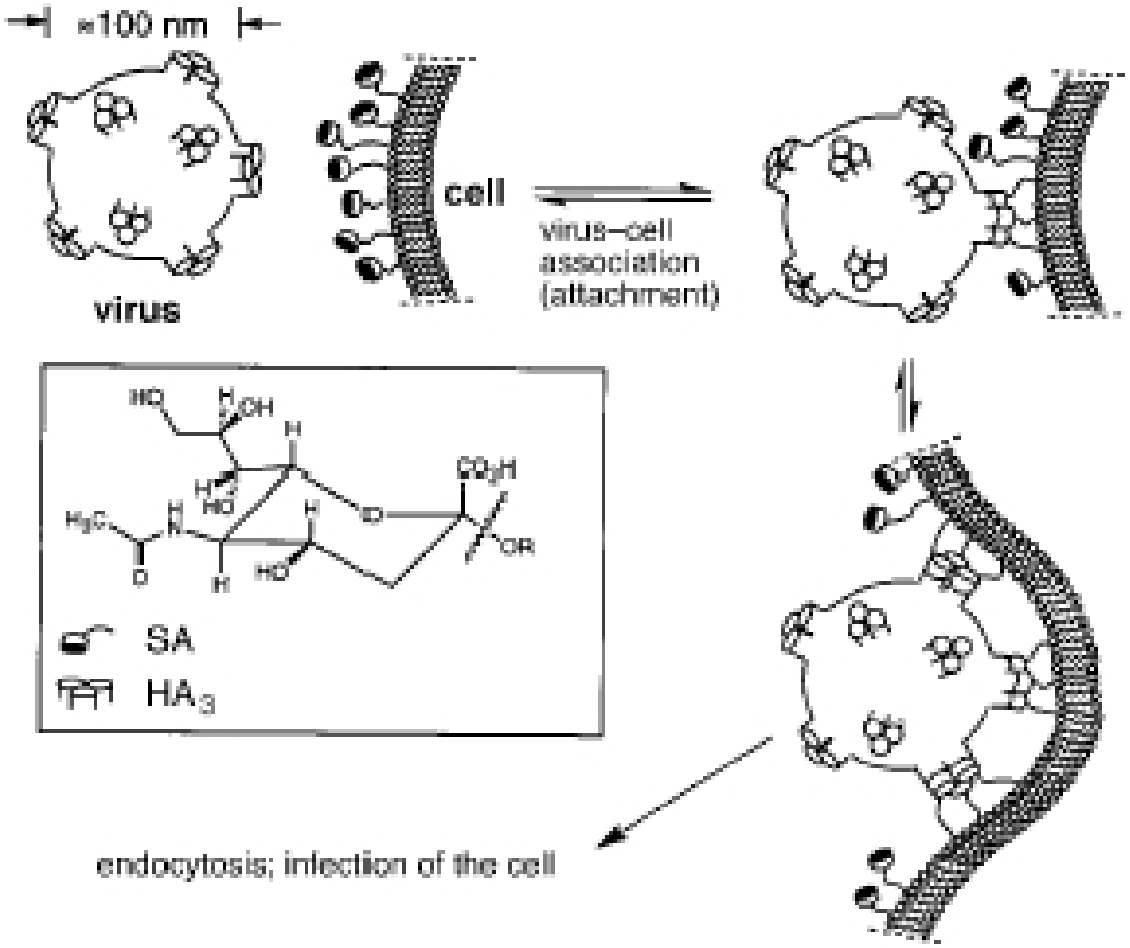
M. R. de Jong,
J. Huskens,
D. N. Reinhoudt,
Chem. Eur. J.
2001, *7*, 4164

General introduction to multivalency

Multivalency at interfaces:

Examples in Nature:

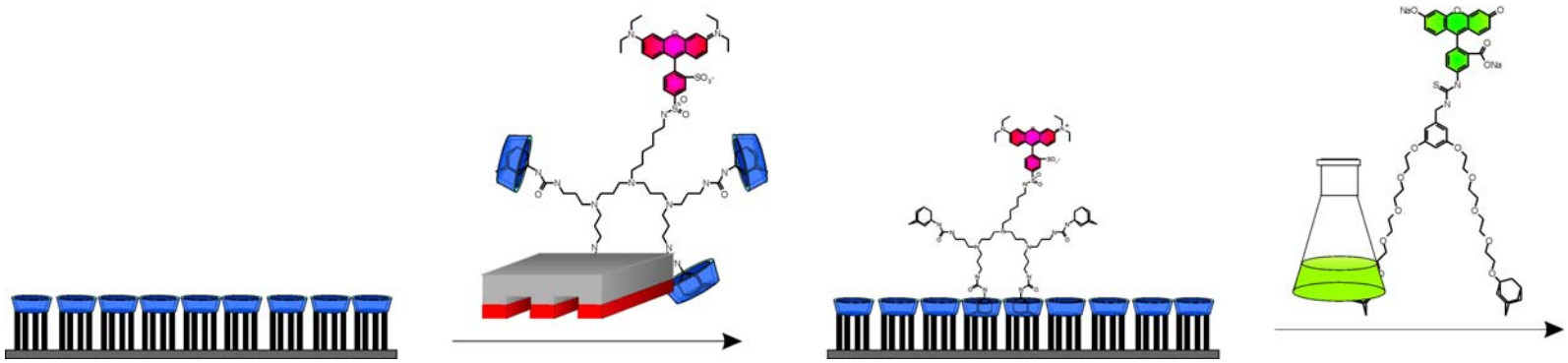
cell membrane interactions with bacteria and viruses:



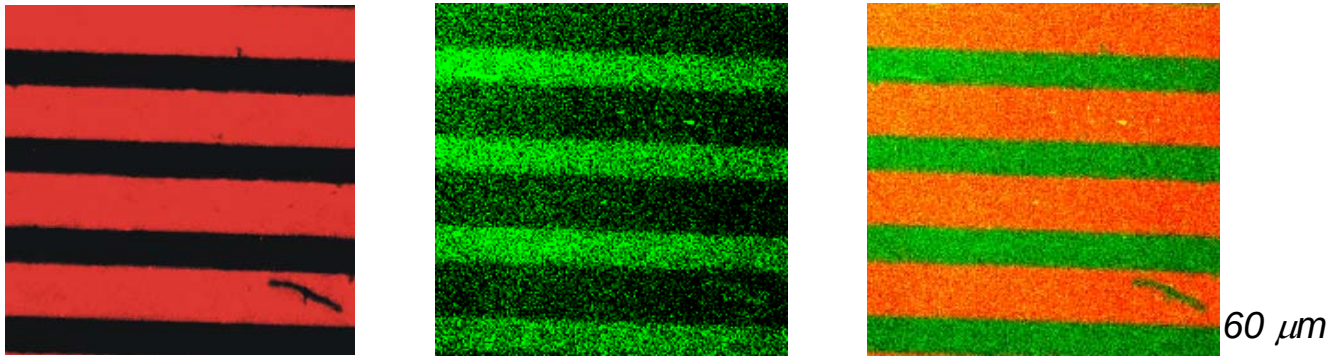
M. Mammen, S.-K. Choi, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 2754

μCP on SAMs

Patterning with multiple multivalent molecules:



Confocal microscopy images



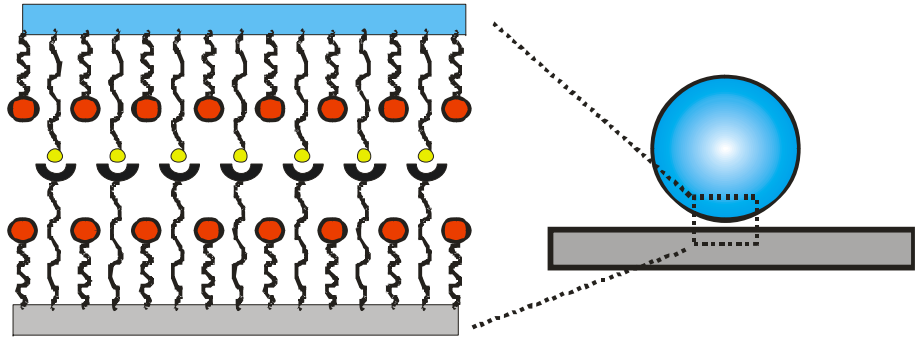
60 μm

Em > 600 nm *500 < Em < 530 nm* *Simultaneous*

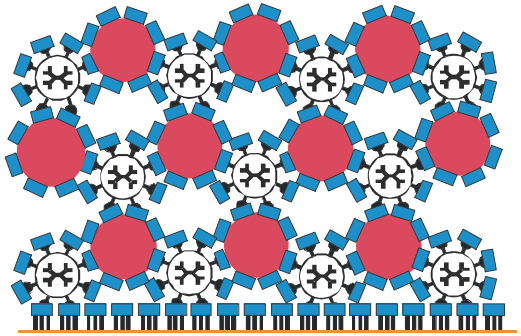
S. Onclin, A. Mulder, J. Huskens, B. J. Ravoo, D. N. Reinhoudt, *Langmuir* **2004**, *20*, 5460
A. Mulder, S. Onclin, M. Péter, J. P. Hoogenboom, H. Beijleveld, J. ter Maat, M. F. García-Parajó, B. J. Ravoo, J. Huskens, N. F. van Hulst, D. N. Reinhoudt, *Small* **2005**, *1*, 242

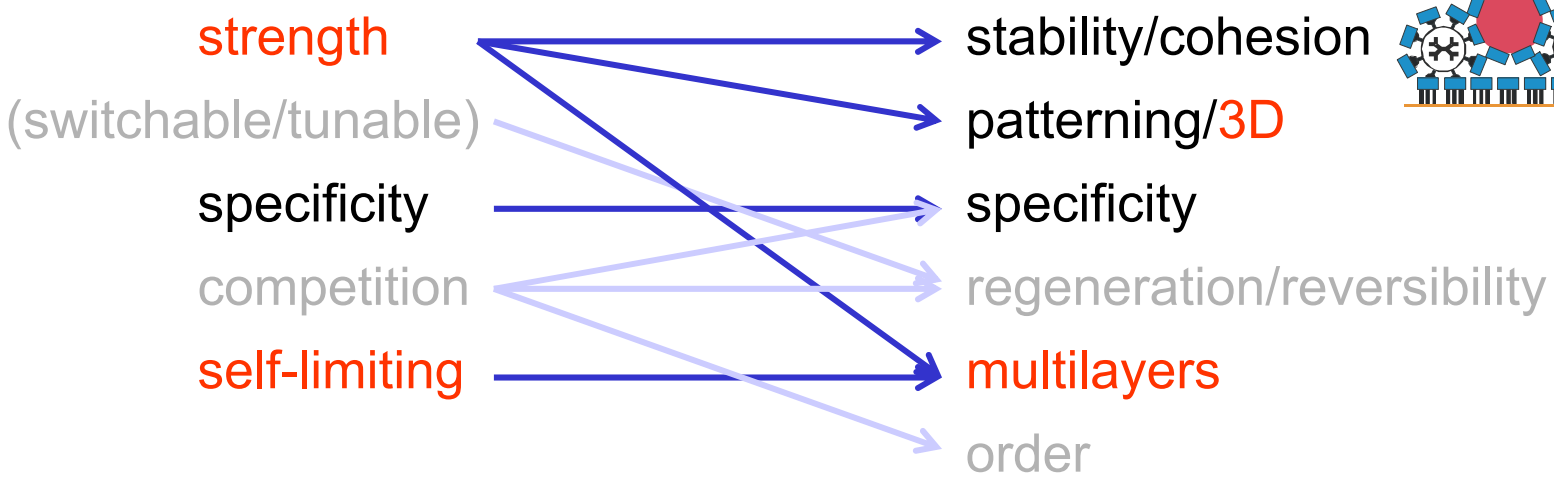
General philosophy

Engineering the interface: use of receptor-ligand interactions:



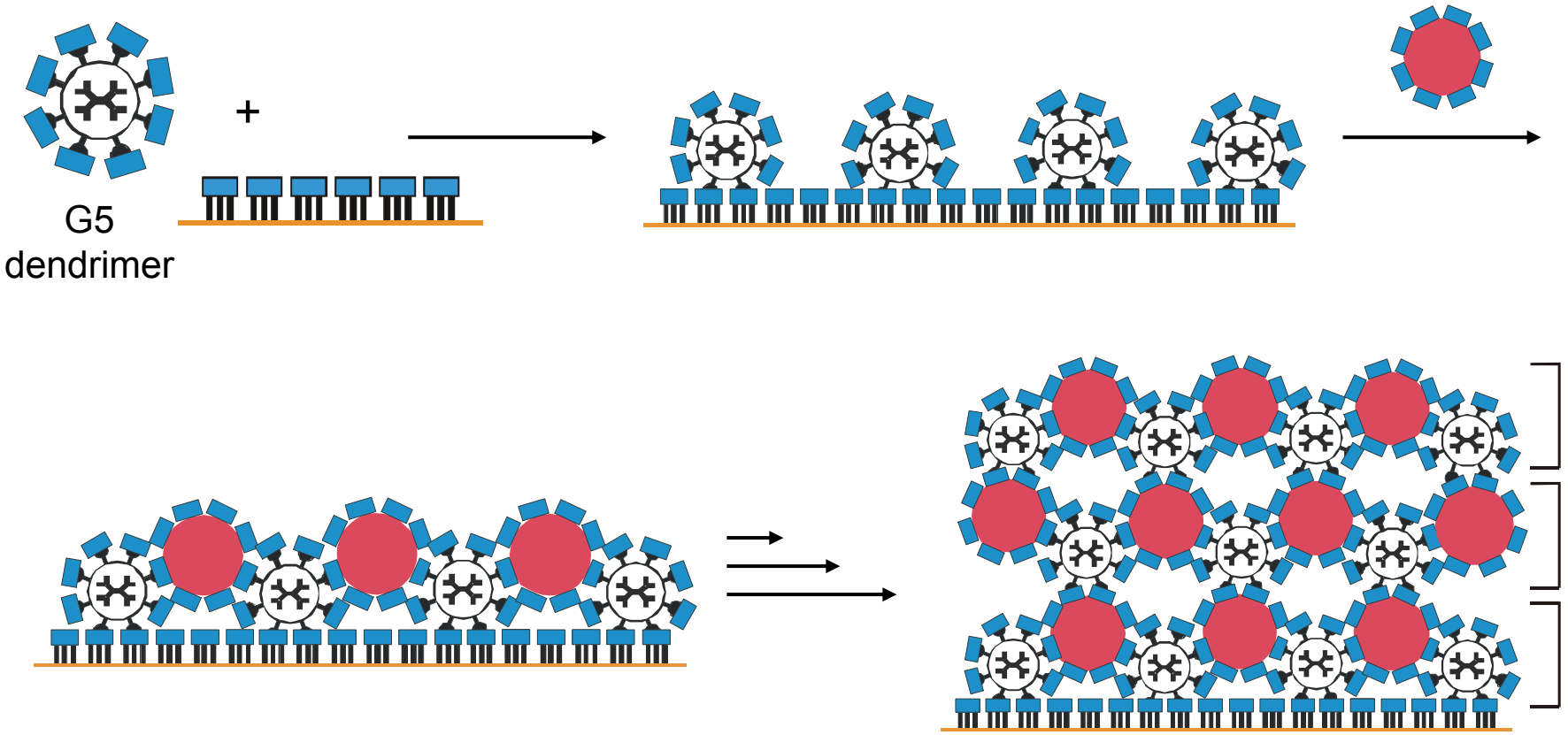
Supramolecular materials





Supramolecular materials

Supramolecular layer-by-layer assembly scheme using CD-Au colloids and adamantyl-functionalized dendrimers:



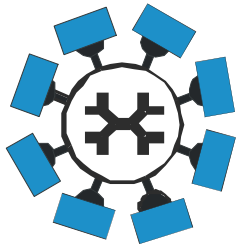
O. Crespo-Biel, B. Dordi, D. N. Reinhoudt, J. Huskens, *J. Am. Chem. Soc.* **2005**, *127*, 7594

Layer-by-layer assembly: G. Decher, *Science* **1997**, *277*, 1232

Supramolecular materials

Supramolecular building blocks for LBL assembly:

Adamantyl dendrimers:



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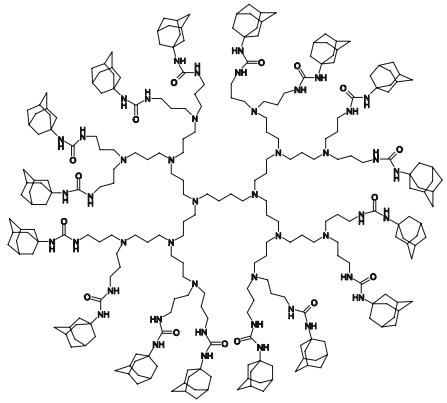
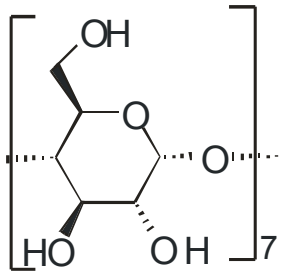


generation 3 dendrimer (*n* = 16)

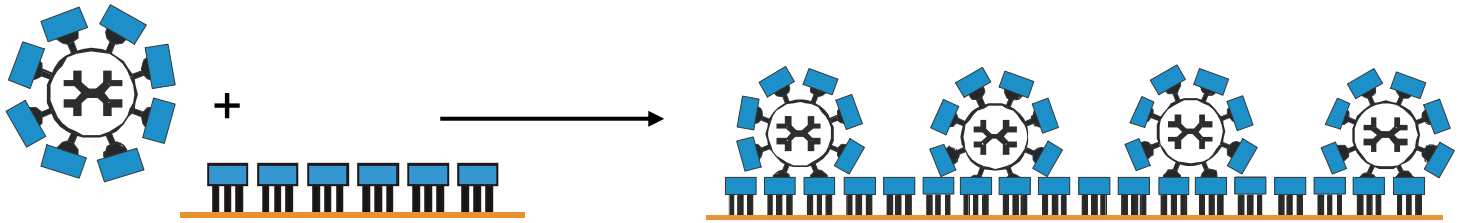


≡

β-cyclodextrin

J. J. Michels, M. W. P. L. Baars, E. W. Meijer, J. Huskens, D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, **2000**, 1914

Molecular printboards:

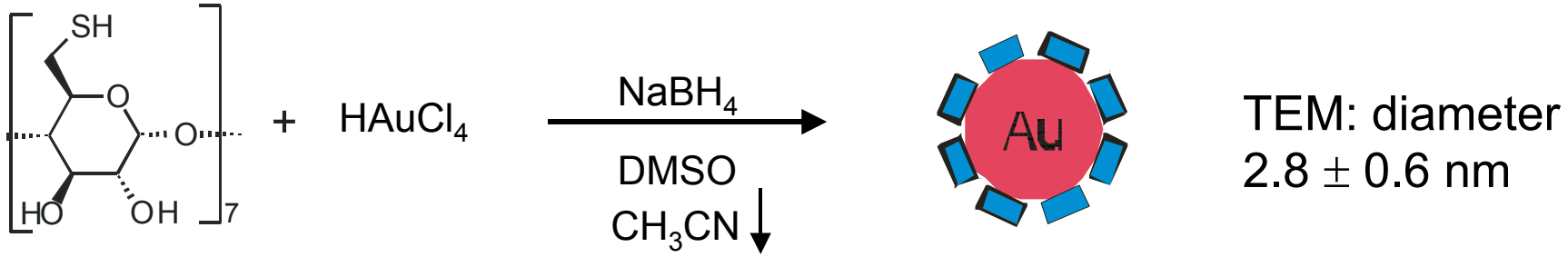


J. Huskens, M. A. Deij, D. N. Reinhoudt, *Angew. Chem. Int. Ed.* **2002**, *41*, 4467; T. Auletta, B. Dordi, A. Mulder, A. Sartori, S. Onclin, C. M. Bruinink, C. A. Nijhuis, H. Beijleveld, M. Péter, H. Schönherr, G. J. Vancso, A. Casnati, R. Ungaro, B. J. Ravoo, J. Huskens, D. N. Reinhoudt, *Angew. Chem. Int. Ed.* **2004**, *43*, 369

Supramolecular materials

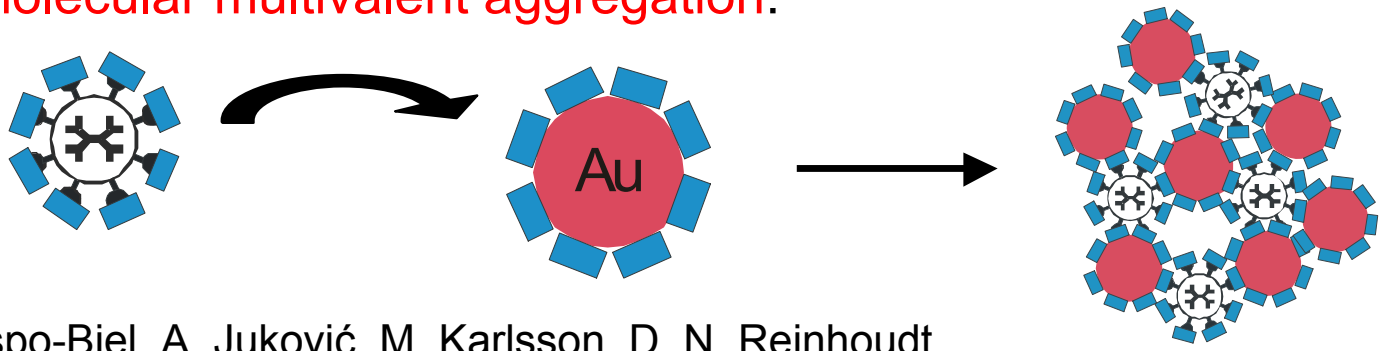
Supramolecular building blocks for LBL assembly:

Cyclodextrin gold nanoparticles:



J. Liu, W. Ong, E. Román, M. J. Lynn, A. E. Kaifer, *Langmuir* **2000**, *16*, 3000

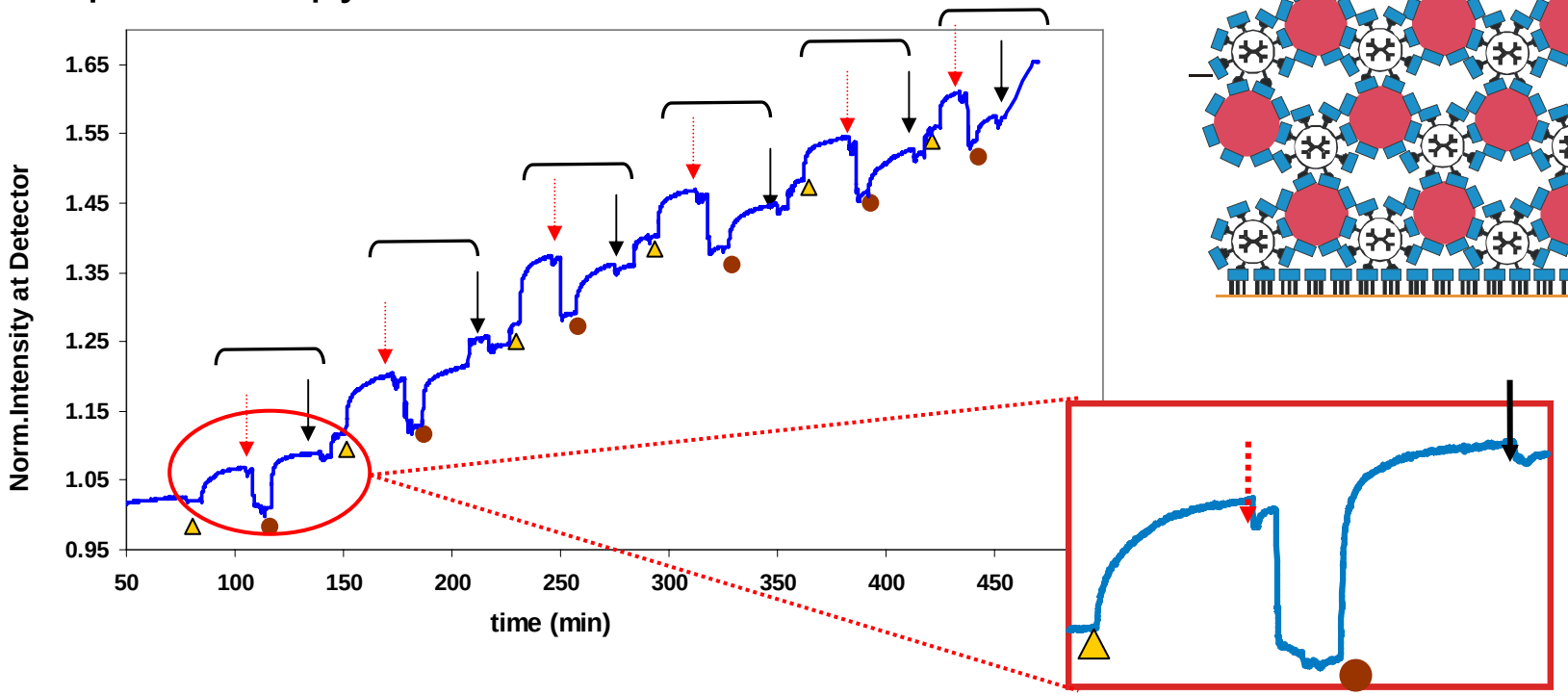
Supramolecular multivalent aggregation:



O. Crespo-Biel, A. Juković, M. Karlsson, D. N. Reinhoudt, J. Huskens, *Isr. J. Chem.* **2005**, *45*, 353

Supramolecular materials

Layer-by-layer assembly using CD-Au colloids and Ad dendrimers:
SPR spectroscopy:



Solutions: 6.5 μM CD-Au (H_2O) ●
0.01 mM Ad-G5 (1 mM CD pH 2) ▲

Rinse 1 mM CD pH 2
Rinse H_2O

O. Crespo-Biel, B. Dordi, D. N. Reinhoudt, J. Huskens, *J. Am. Chem. Soc.* **2005**, *127*, 7594

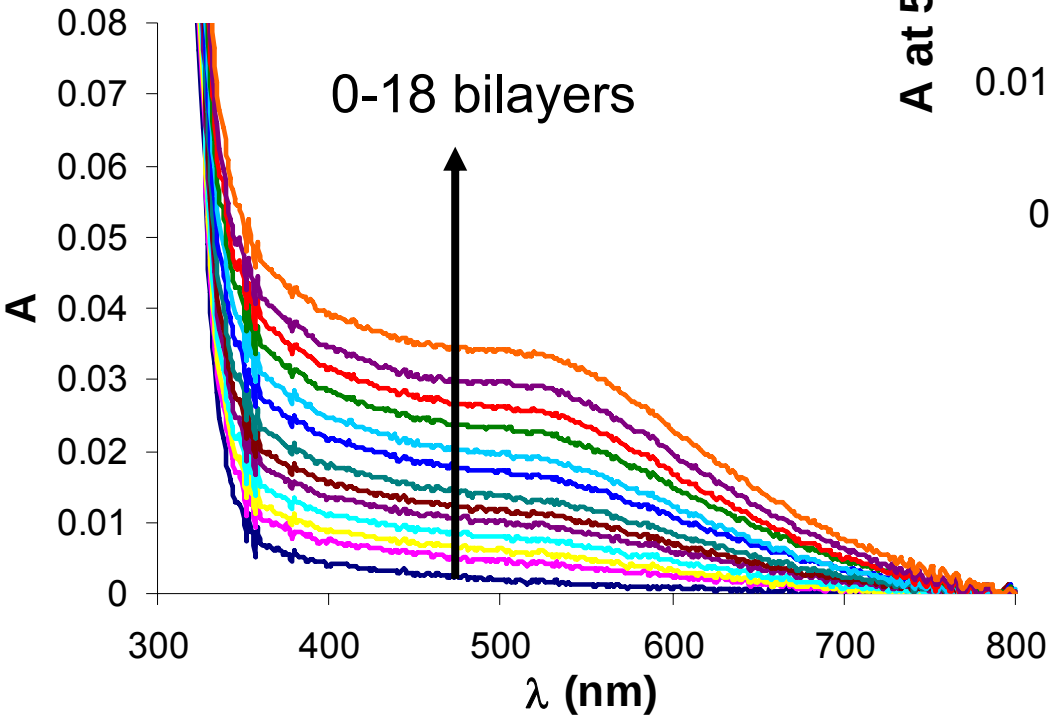
Supramolecular materials

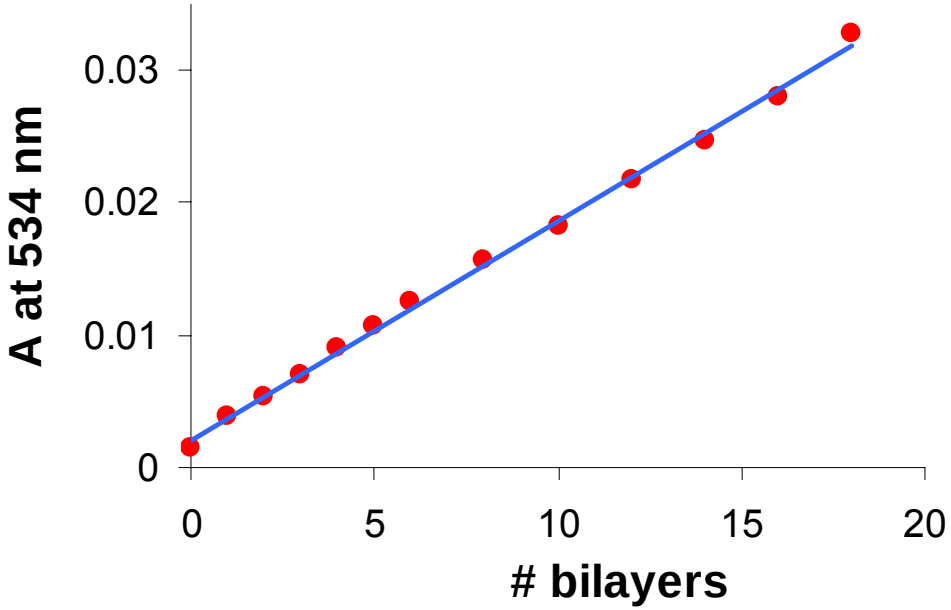
Layer-by-layer assembly using CD-Au colloids and Ad dendrimers:

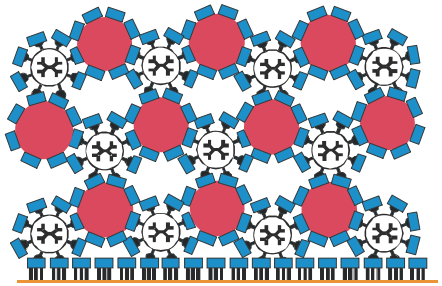
UV/Vis at glass substrates:

Quantitative interpretation possible:

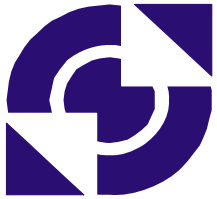
1 monolayer of particles per bilayer







O. Crespo-Biel, B. Dordi, D. N. Reinhoudt, J. Huskens, *J. Am. Chem. Soc.* **2005**, *127*, 7594

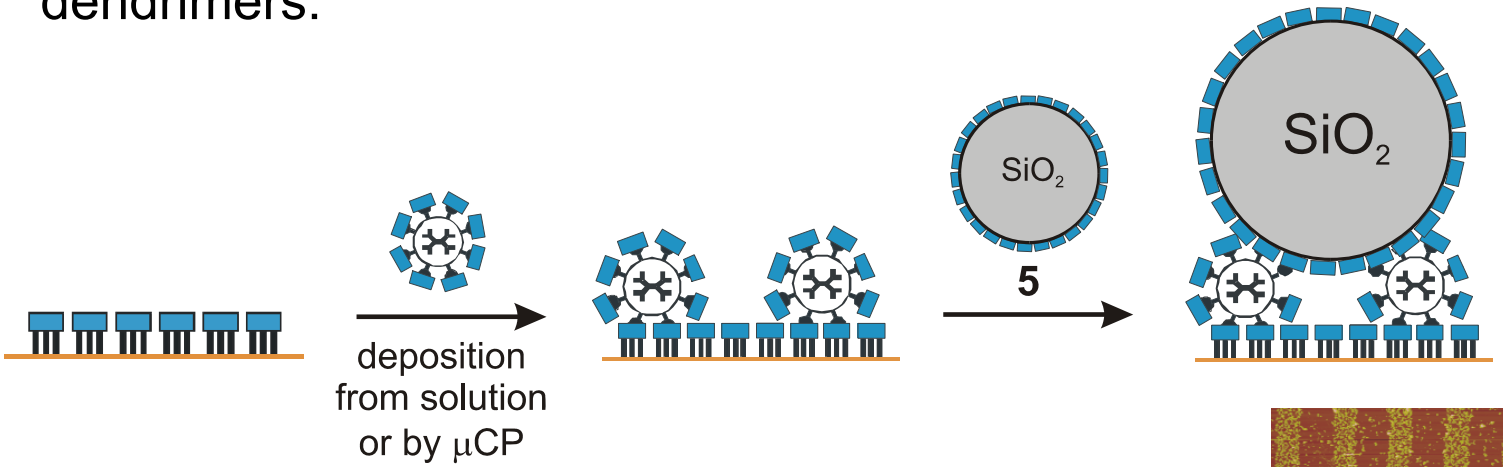


Part 2

Shaping Supramolecular Materials

Multivalent supramolecular materials

Directed assembly using CD-Au colloids and adamantyl-functionalized dendrimers:



V. Mahalingam, S. Onclin, M. Péter, B. J. Ravoo, J. Huskens, D. N. Reinhoudt, *Langmuir* **2004**, *20*, 11756

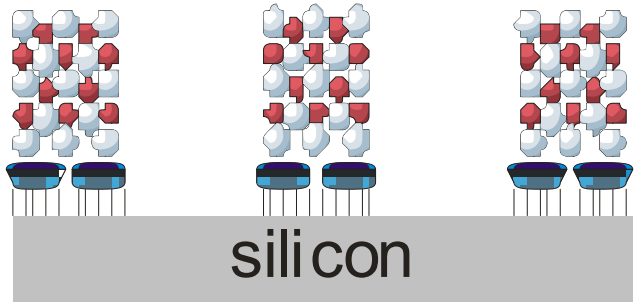
3D Supramolecular materials

Towards patterned LBL assemblies:

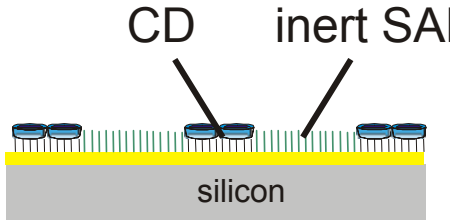
3D Nanofabrication:

x,y: top-down patterning

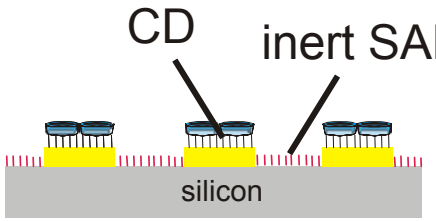
z: LBL assembly



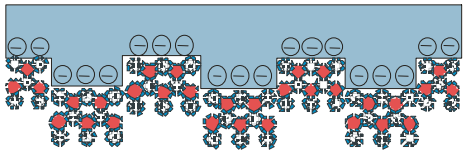
Patterned SAMs:
(μCP, NIL)



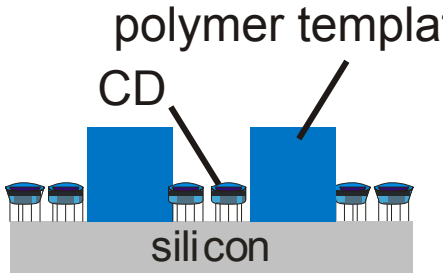
Patterned gold:
(μCP+etching,
NIL+metal lift-off,
sieve evaporation)



Structures on patterned stamp:
(μCP)

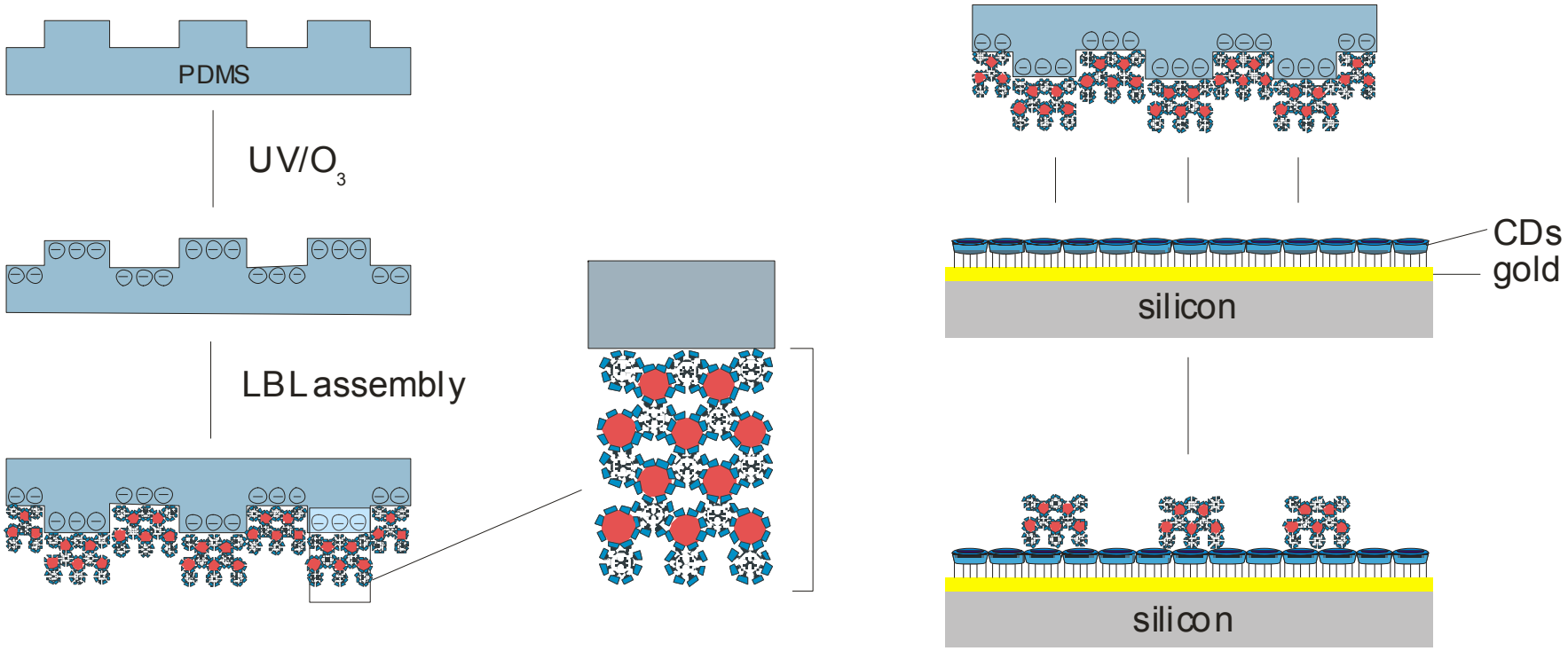


Patterned mask:
(NIL)



3D Supramolecular materials

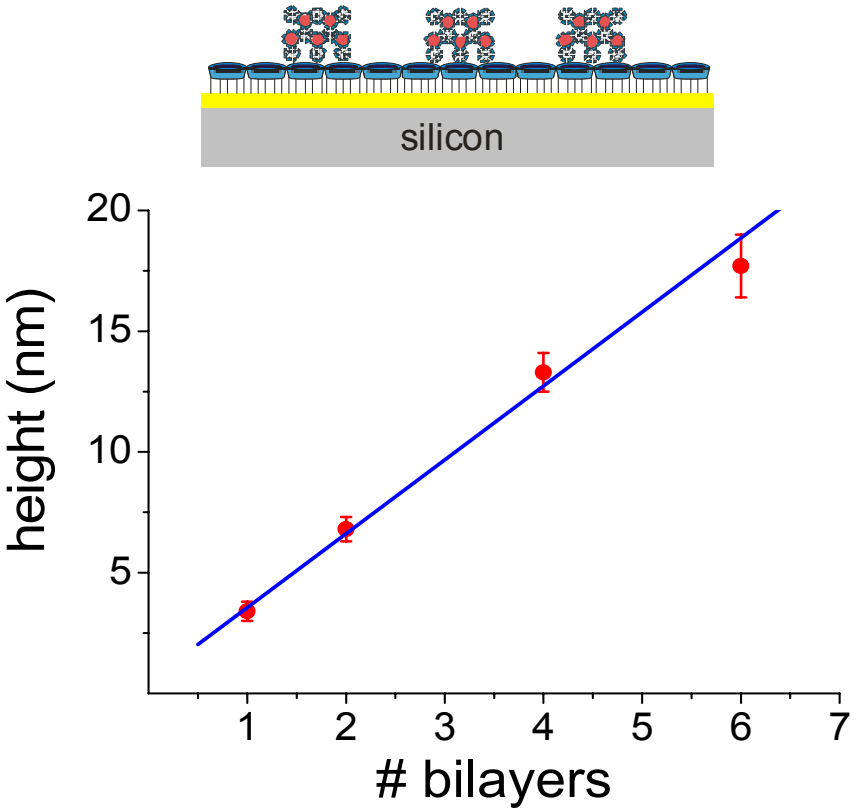
Alternative: LBL on PDMS stamp followed by assembly transfer by μCP:



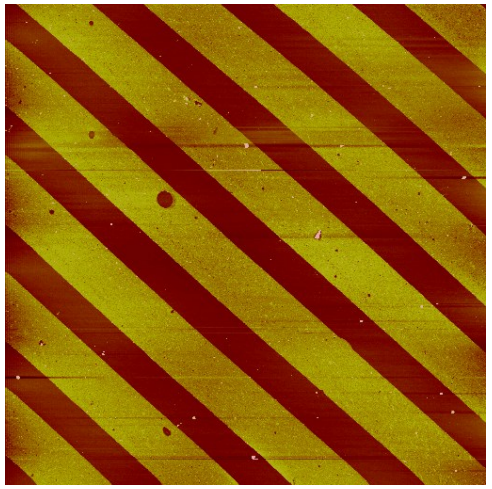
O. Crespo-Biel, B. Dordi, P. Maury, M. Péter, D. N. Reinhoudt, J. Huskens, *Chem. Mater.* **2006**, *18*, 2545
LBL in combination with μCP: J. Park, P. T. Hammond, *Adv. Mater.* **2004**, *16*, 520

3D Supramolecular materials

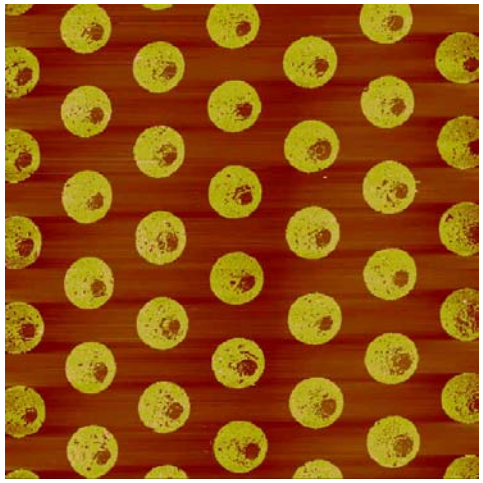
Patterned LBL assemblies by μCP:



Assemblies are stable against rinsing with competitive CD solutions



AFM height image
(80 x 80 μm²)
2 bilayers: 7 nm

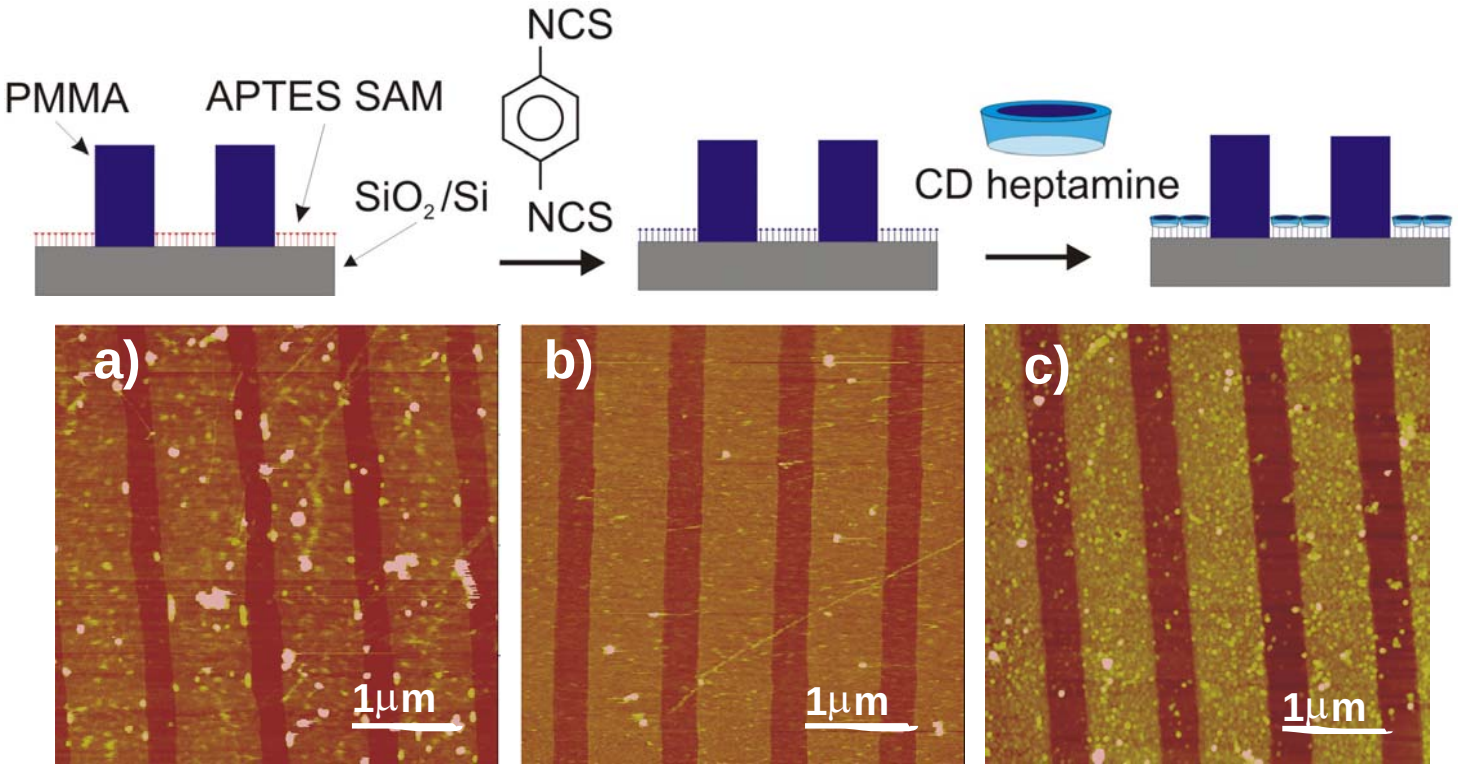


AFM height image
(60 x 60 μm²)
4 bilayers: 14 nm

O. Crespo-Biel, P. Maury, M. Péter, B. Dordi, D. N. Reinhoudt, J. Huskens, *Chem. Mater.* **2006**, *18*, 2545

NIL-patterned molecular printboards

NIL-patterned CD monolayers on SiO_2:
templates for multivalent supramolecular adsorption:

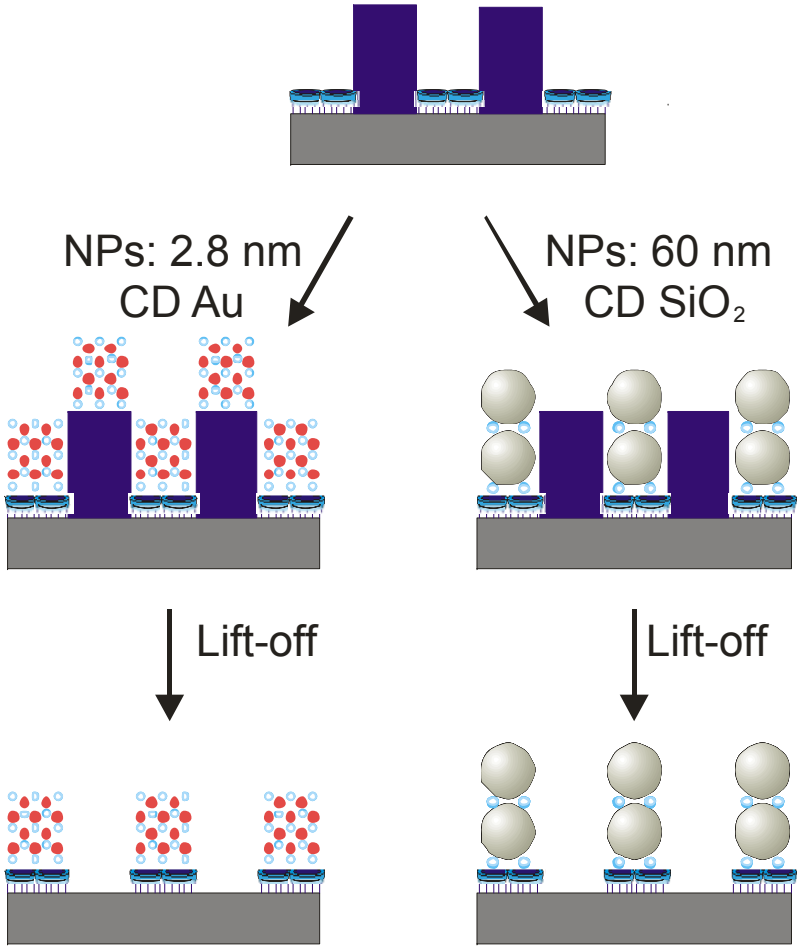


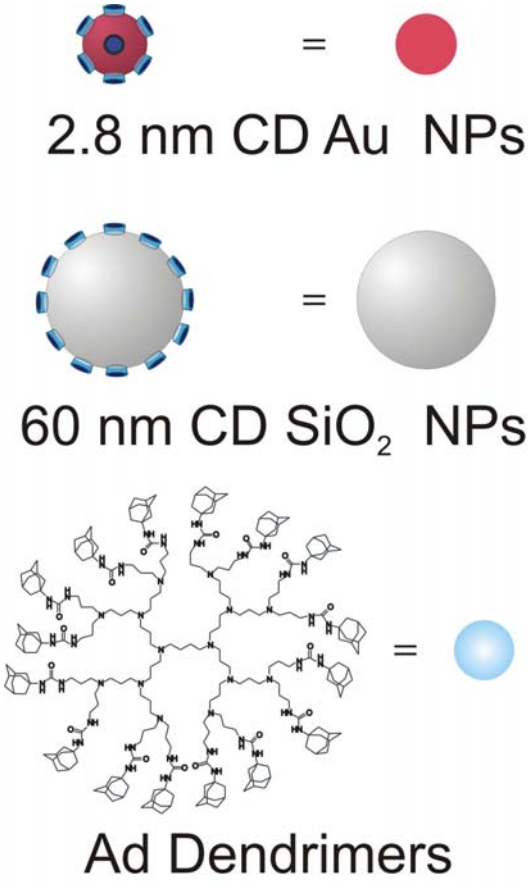
AFM height: 0.9 nm 0.9 nm 2.8 nm
(after polymer removal)

P. Maury, M. Péter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Nanotechnology* **2007**, *18*, 044007

3D Supramolecular materials

Integration with layer-by-layer (LBL) assembly:

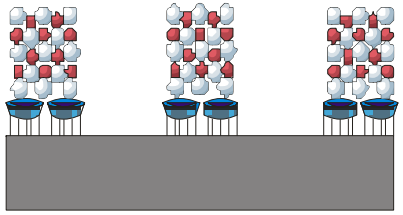




P. Maury, M. Péter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Nanotechnology* **2007**, *18*, 044007

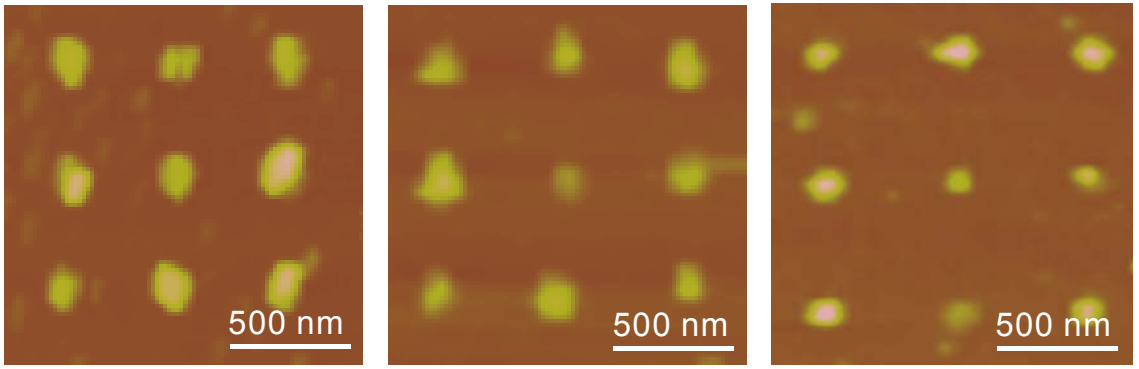
3D Supramolecular materials

NIL-patterned polymer masks for directed LBL:
results using an e-beam made master:

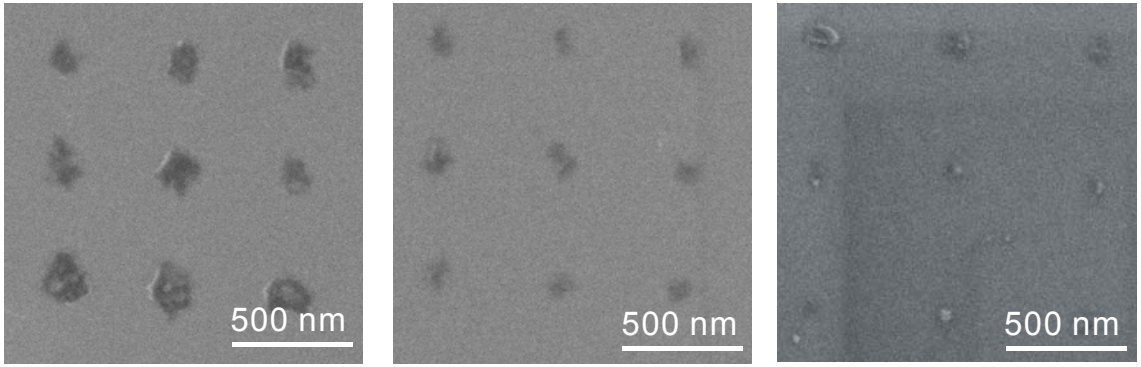


15 bilayers:
37 process steps !!

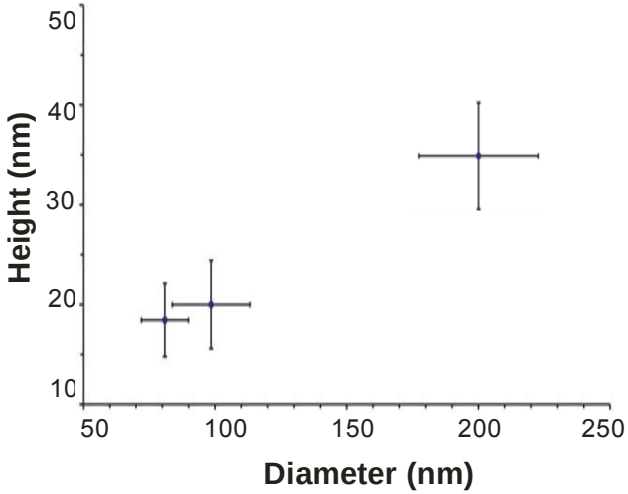
AFM



SEM



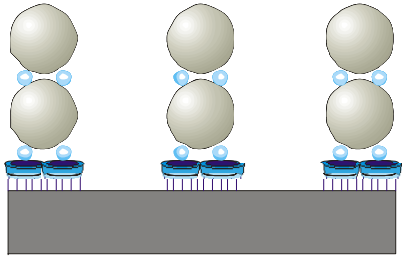
dot width: 200 nm 100 nm 50 nm



P. Maury, M. Péter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Nanotechnology* **2007**, *18*, 044007

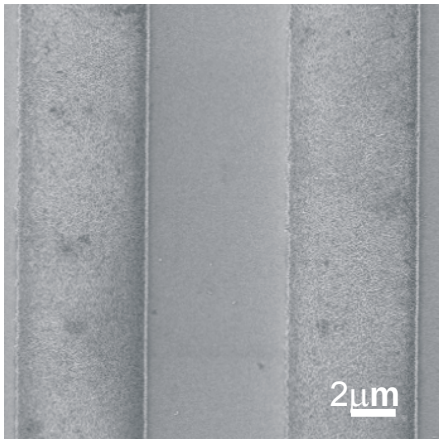
3D Supramolecular materials

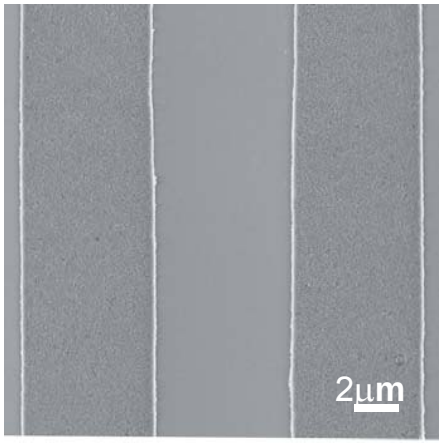
NIL-patterned polymer masks for directed LBL:
LBL with 60 nm CD SiO_2 NPs:

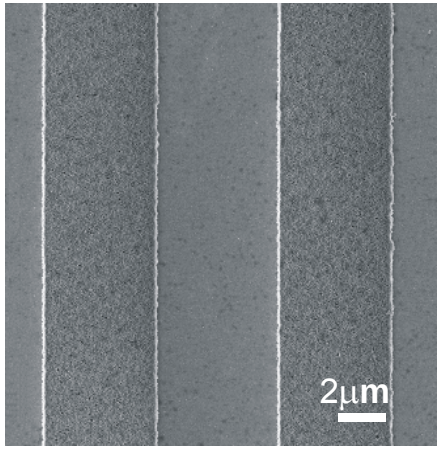


1-3 bilayers:
height = n x 60 nm

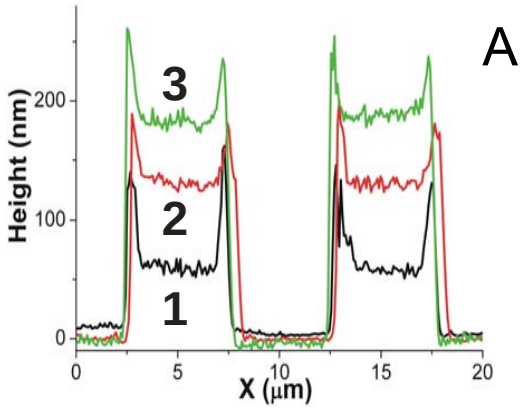
SEM







AFM



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3D Supramolecular materials

NIL-patterned polymer masks for directed LBL:
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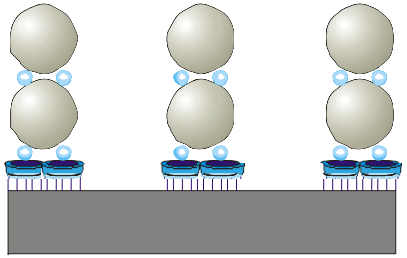
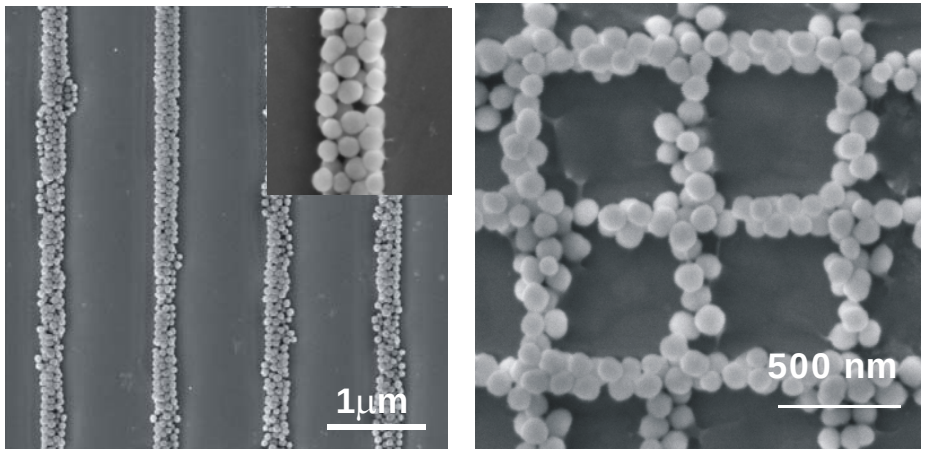
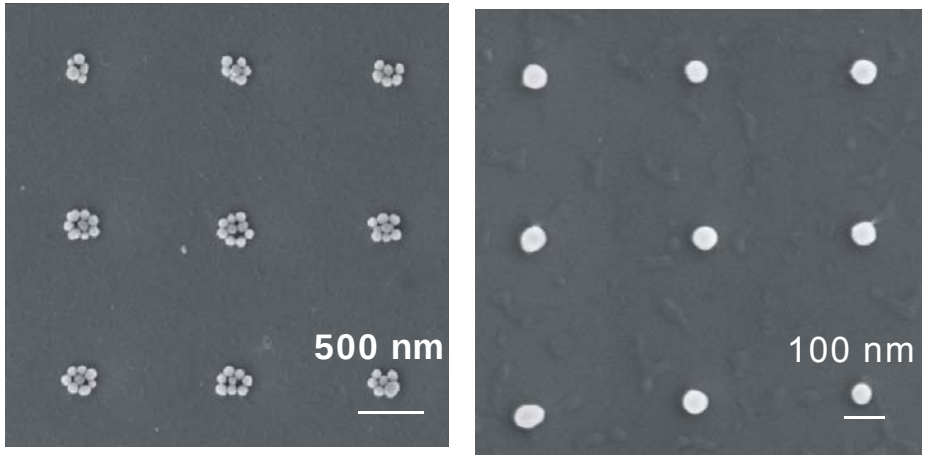


2 bilayers on line and grid patterns

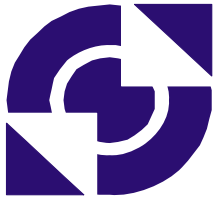


1 bilayer on dot patterns



SEM

P. Maury, M. Péter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Nanotechnology* **2007**, *18*, 044007

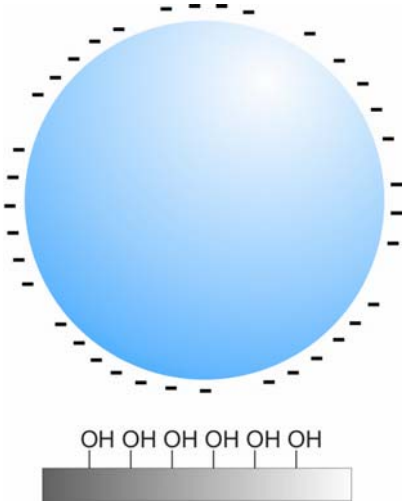


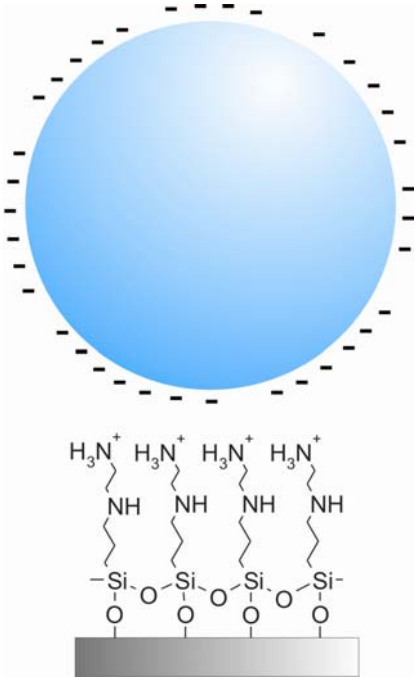
Part 3

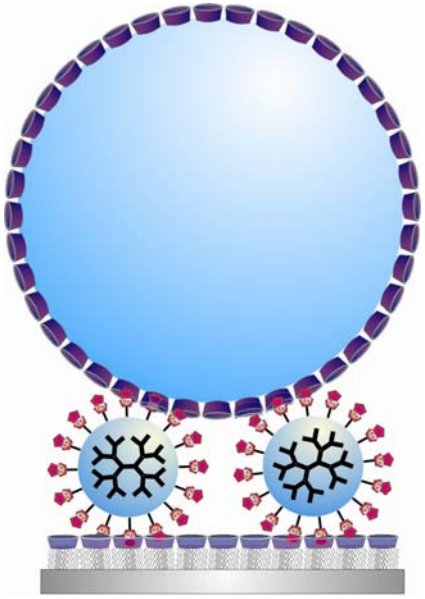
Bringing Order to Supramolecular Materials

Nanoparticle-substrate interface chemistry

Key question: What is the role of the interface chemistry on the assembly (order, reversibility) of large nanoparticles?
Case study: 500 nm polystyrene NPs:







physisorption electrostatic host-guest

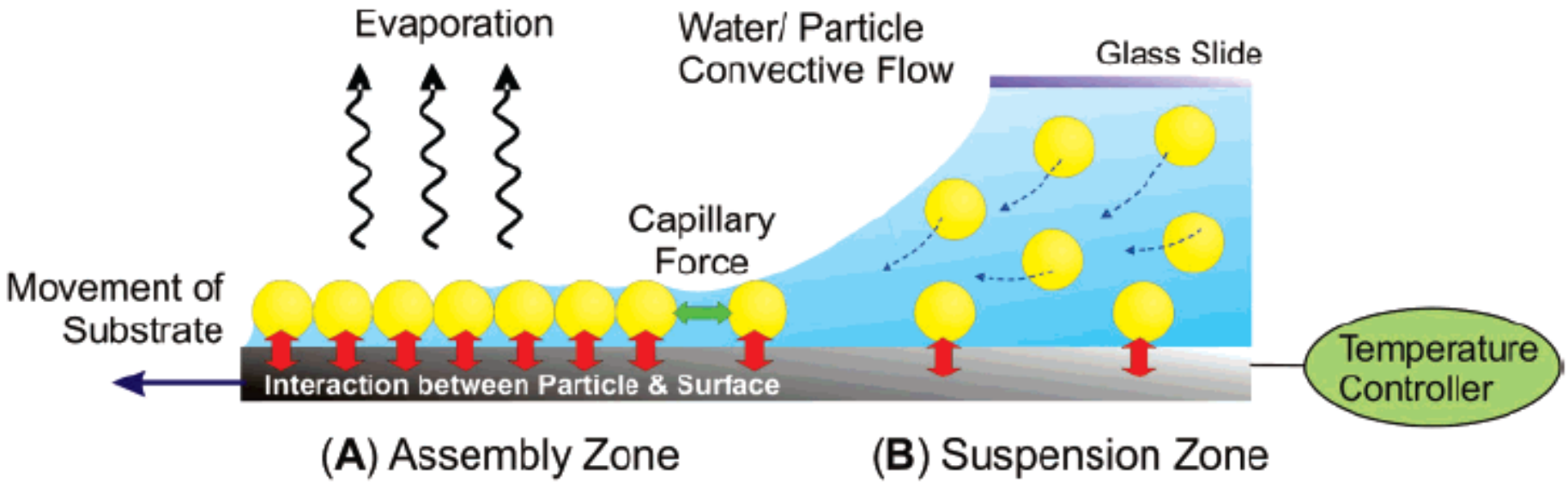
X. Y. Ling, L. Malaquin, D. N. Reinhoudt, H. Wolf, J. Huskens, *Langmuir* **2007**, *23*, 9990

Nanoparticle-substrate interface chemistry

NaPa
Emerging Nanopatterning Methods

Key question: What is the role of the interface chemistry on the assembly (order, reversibility) of large nanoparticles?

Setup:

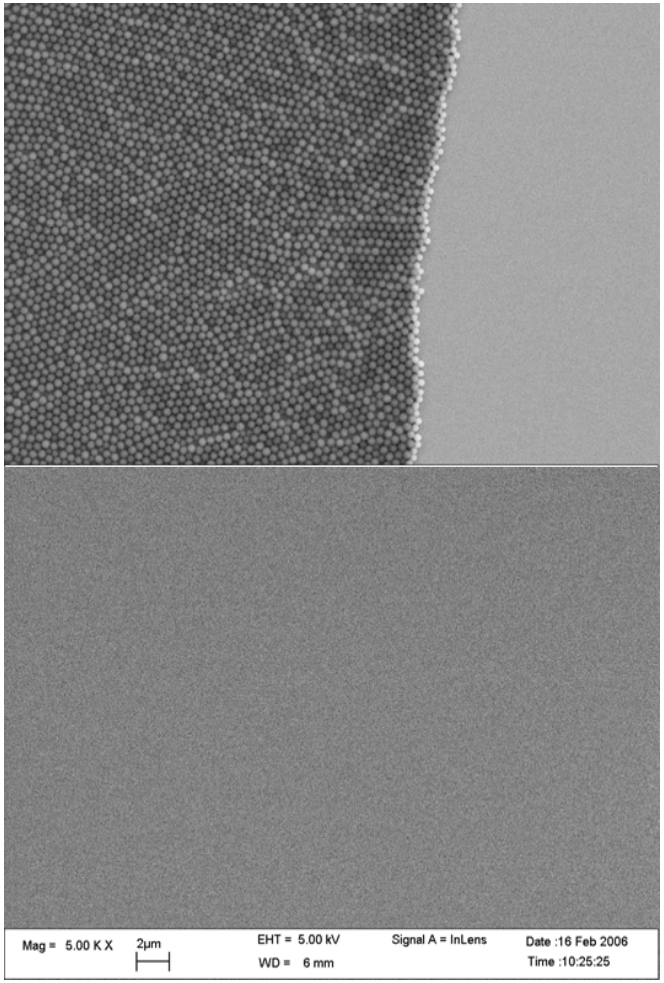


X. Y. Ling, L. Malaquin, D. N. Reinhoudt, H. Wolf, J. Huskens, *Langmuir* **2007**, *23*, 9990

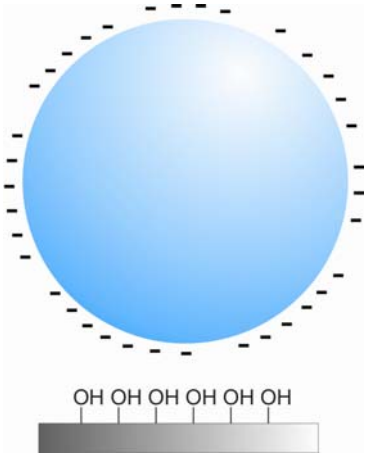
Nanoparticle-substrate interface chemistry

NaPa
Emerging Nanopatterning Methods

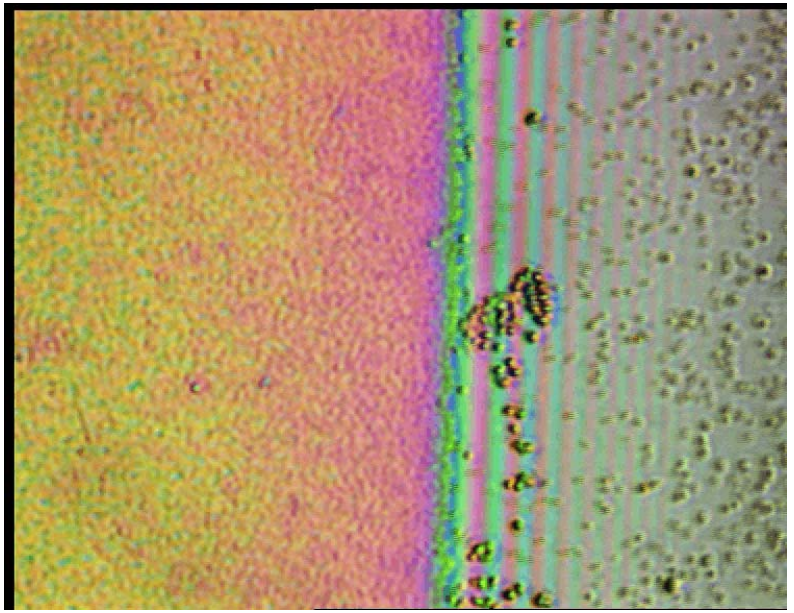
Physisorption: PS-COOH NPs on clean SiO_2:



Assembly zone



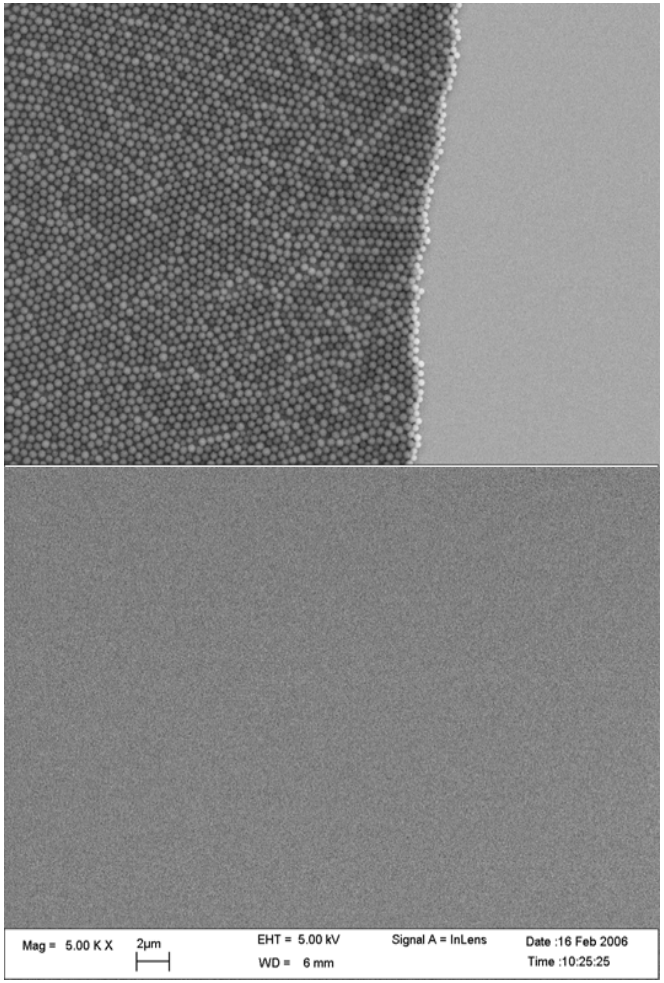
Solution zone



Nanoparticle-substrate interface chemistry

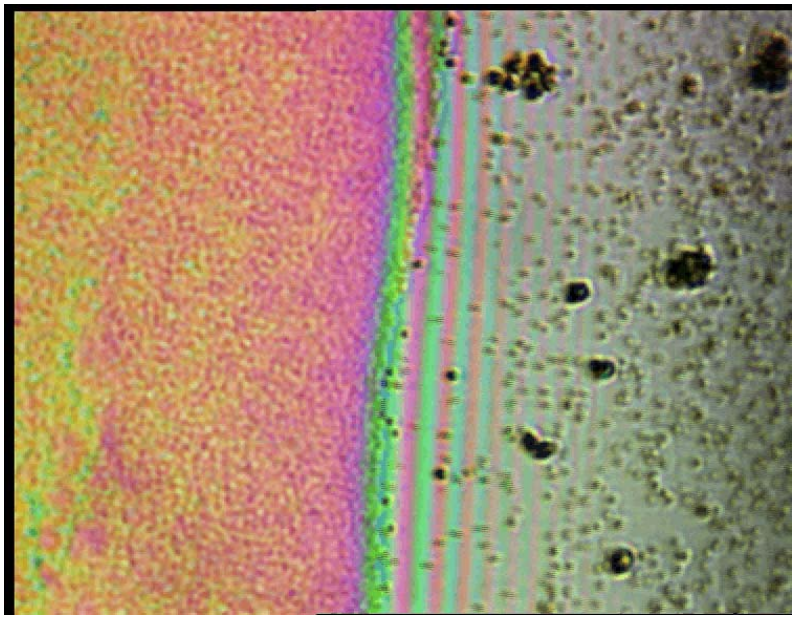
NaPa
Emerging Nanopatterning Methods

PS-COOH NPs on clean SiO_2: desorption when cooling down below dewpoint:



Assembly zone

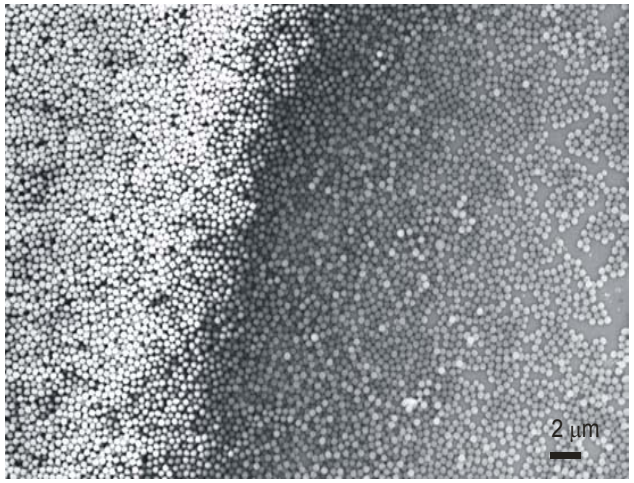
Solution zone

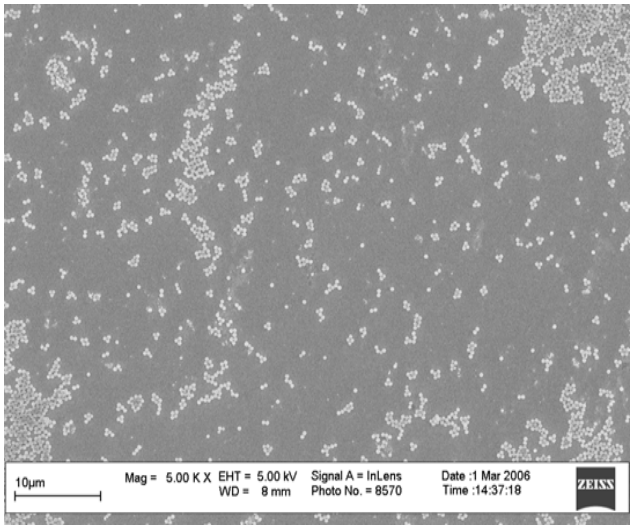


Nanoparticle-substrate interface chemistry

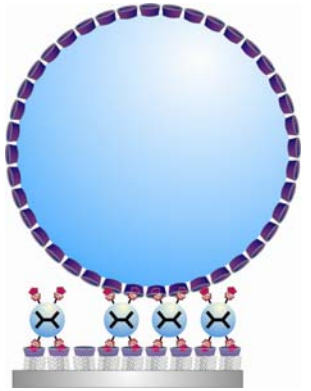
NaPa
Emerging Nanopatterning Methods

Host-guest interaction: PS-CD NPs on CD SAMs with G1 Fc dendrimers:

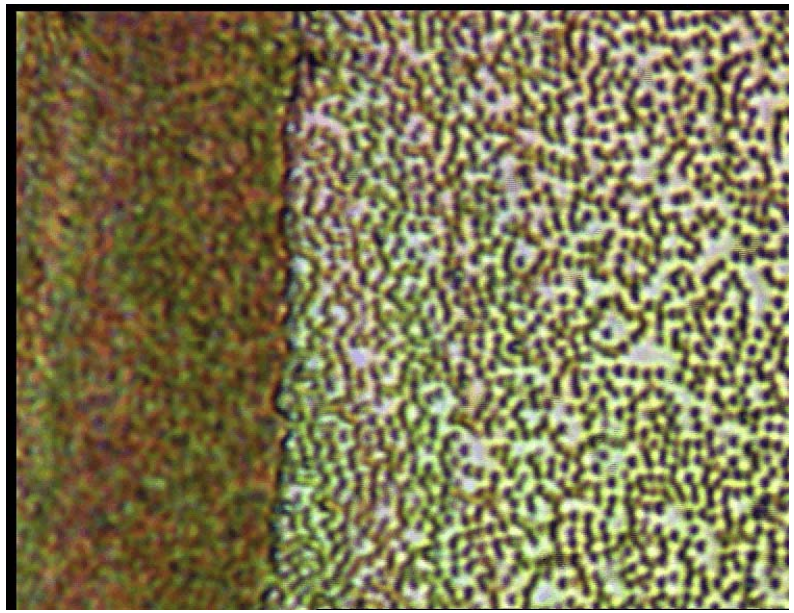




Assembly zone



Solution zone



Nanoparticle-substrate interface chemistry

NaPa
Emerging Nanopatterning Methods

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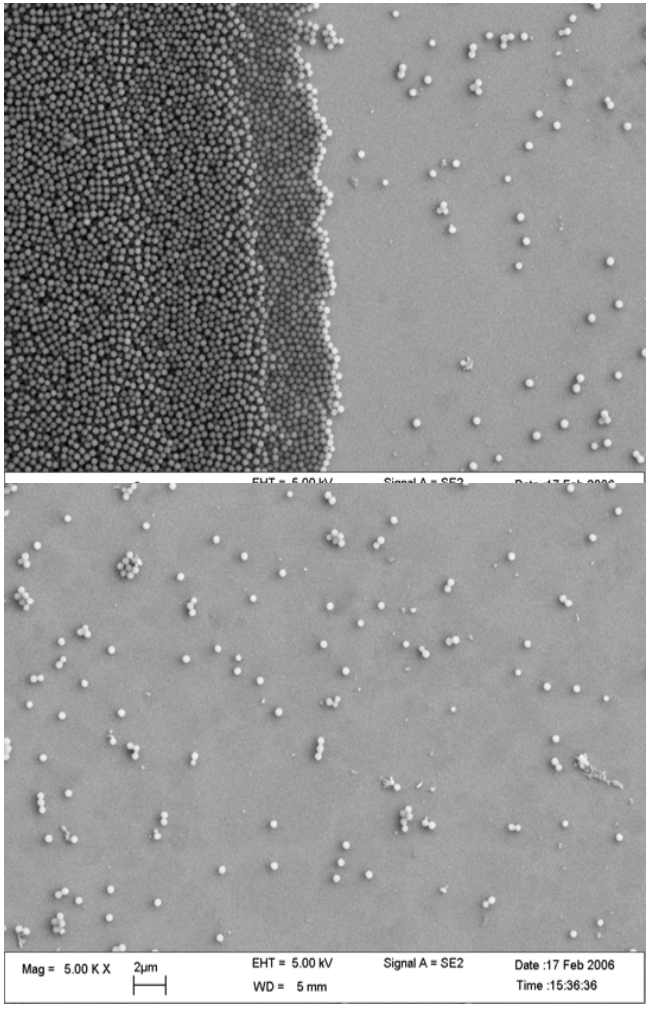
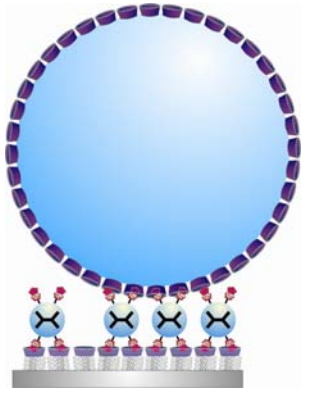
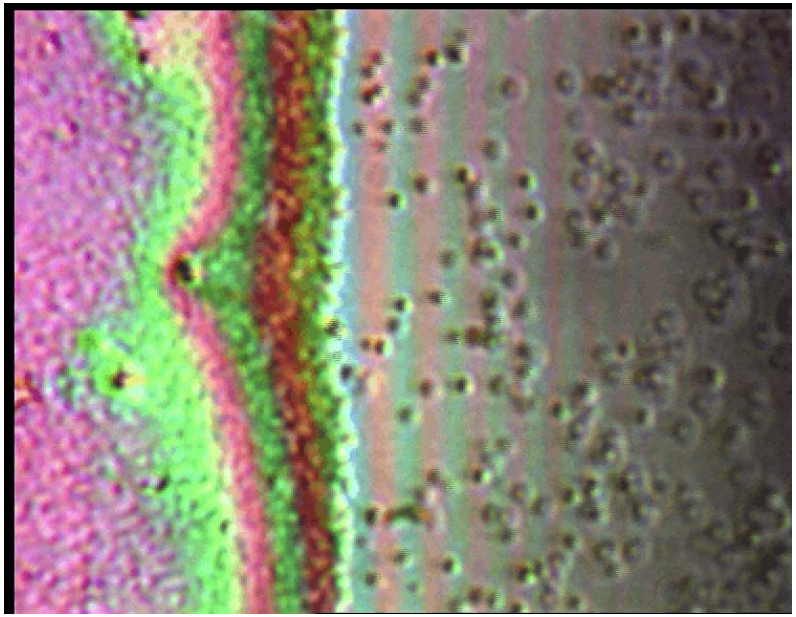


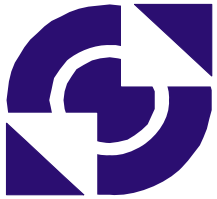
competition by CD in solution



Assembly zone

Solution zone



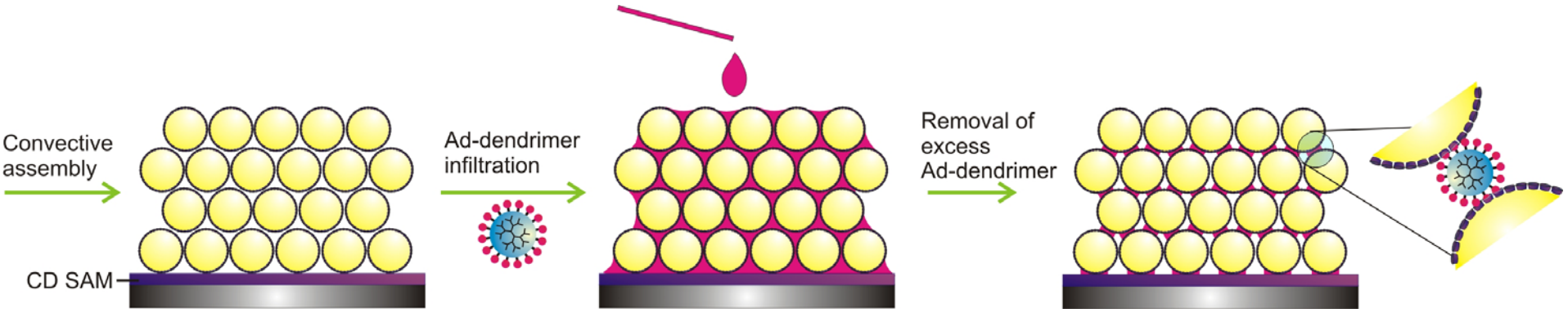


Part 4

Stability, Shape, and Order in 3D Supramolecular Nanomaterials

3D Supramolecular materials

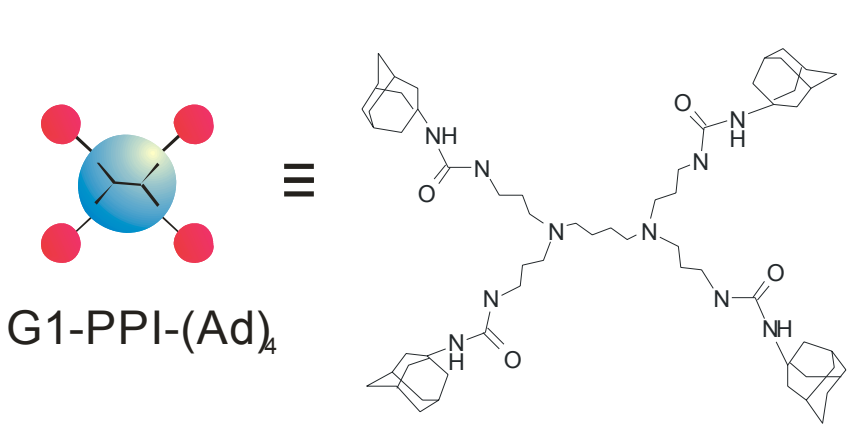
Can we decouple order and stability of nanoparticle assembly??

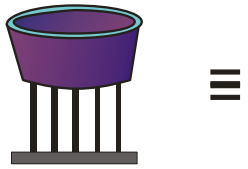


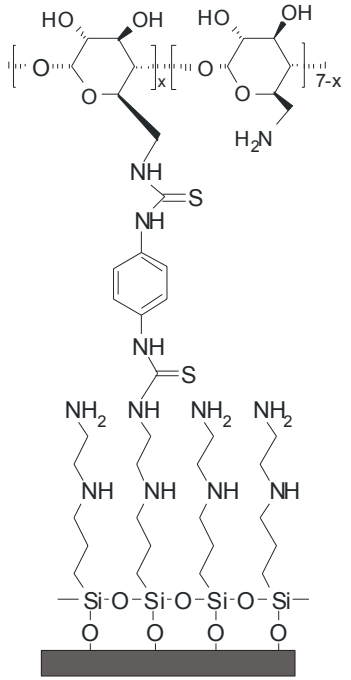
X. Y. Ling, I. Y. Phang, W. Maijenburg, H. Schönherr, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Angew. Chem. Int. Ed.* **2009**, *48*, 983; X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *ACS Appl. Mater. Interf.* **2009**, *1*, in press

3D Supramolecular materials

Building blocks:

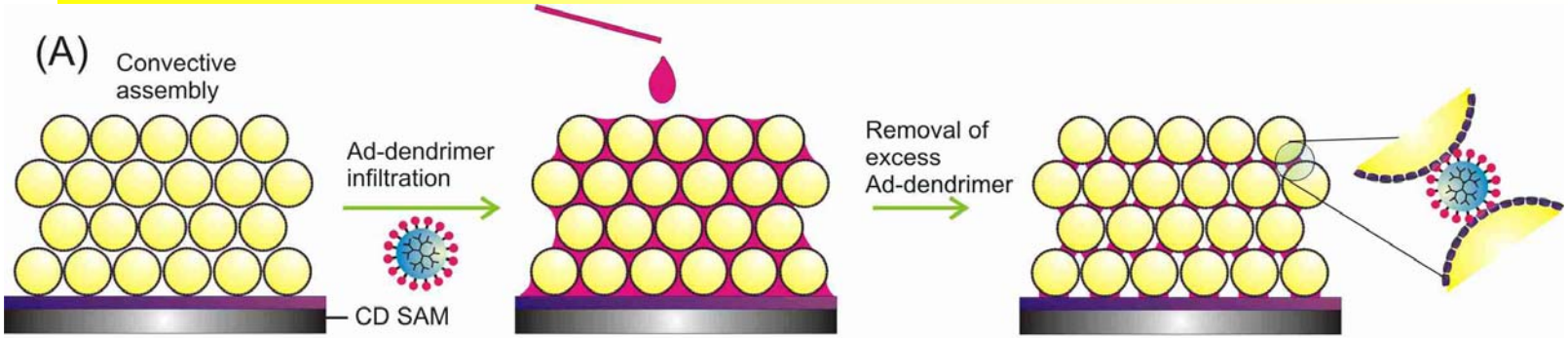


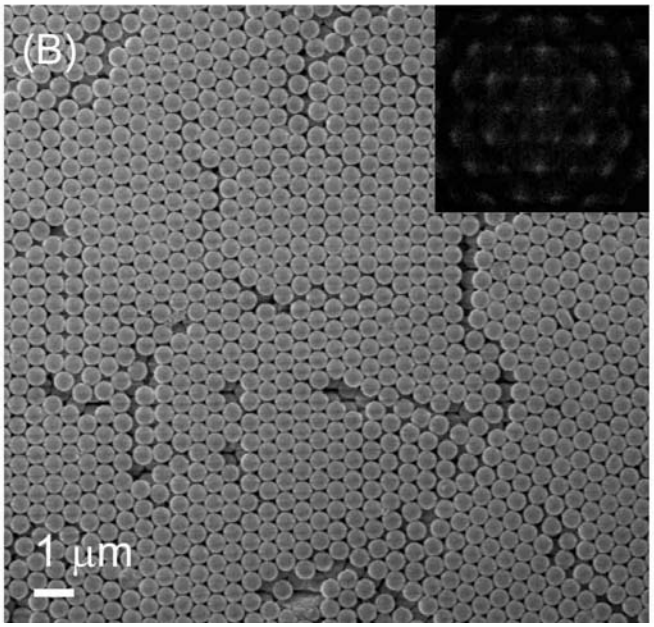




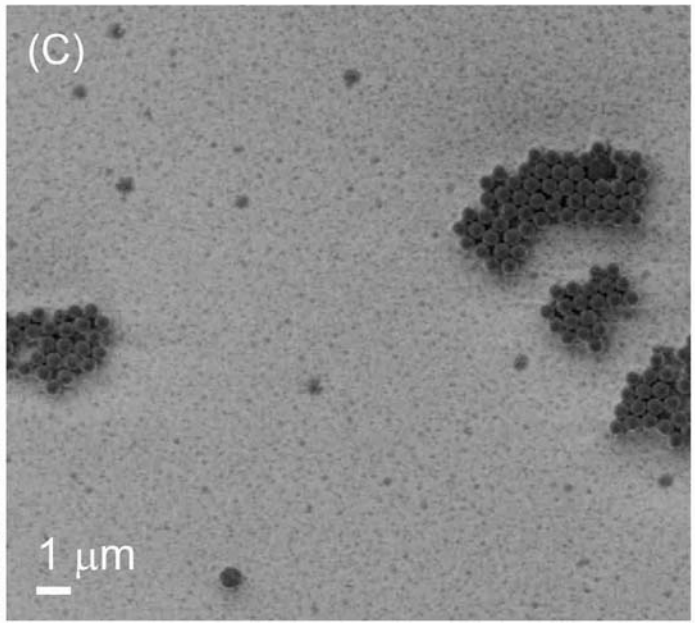
X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *ACS Appl. Mater. Interf.* **2009**, *1*, in press

3D Supramolecular materials





with infiltration of dendrimer



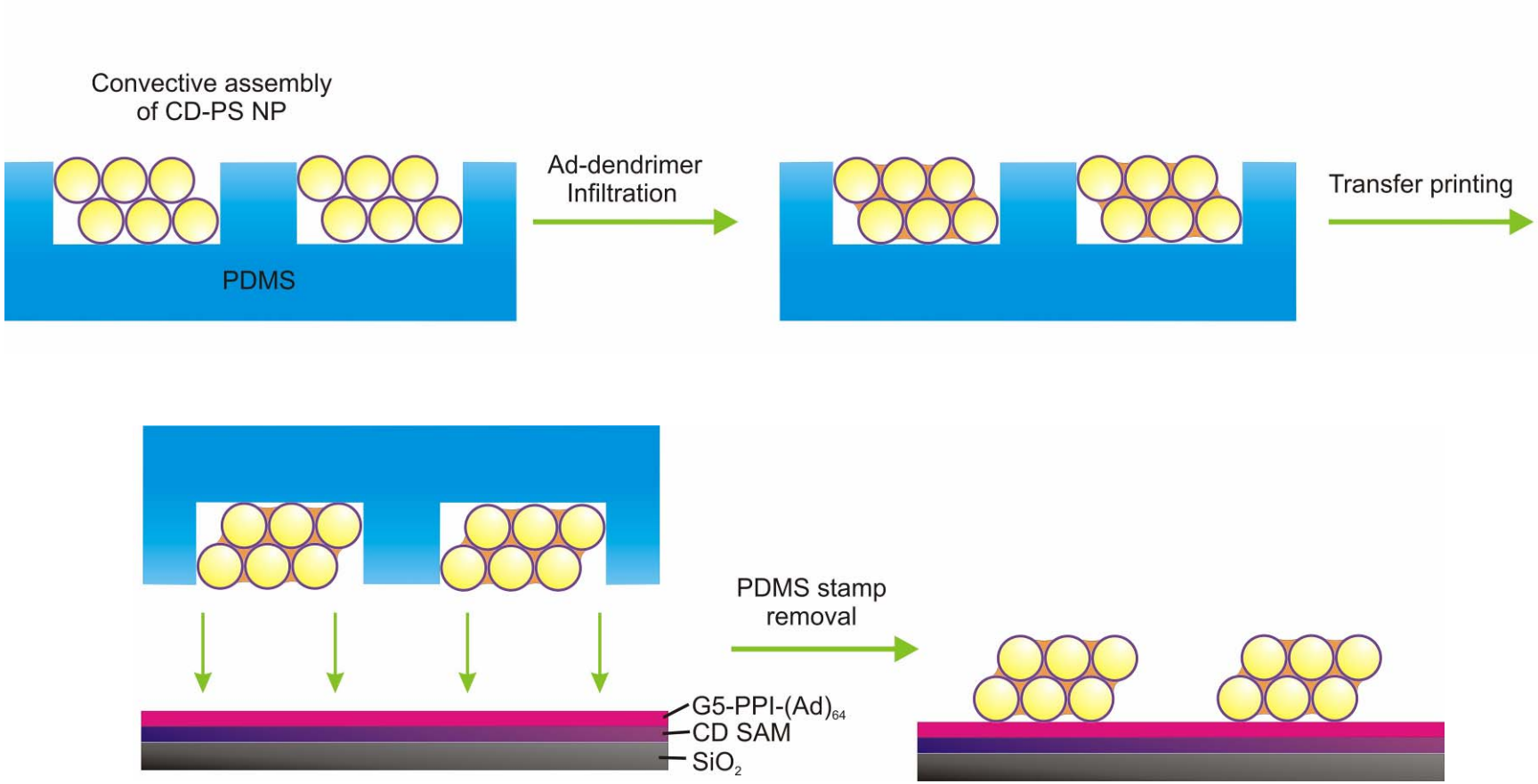
without infiltration

After ultrasonication

X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *ACS Appl. Mater. Interf.* **2009**, *1*, in press

3D Supramolecular materials

Nanotransfer printing of nanoparticle assemblies:



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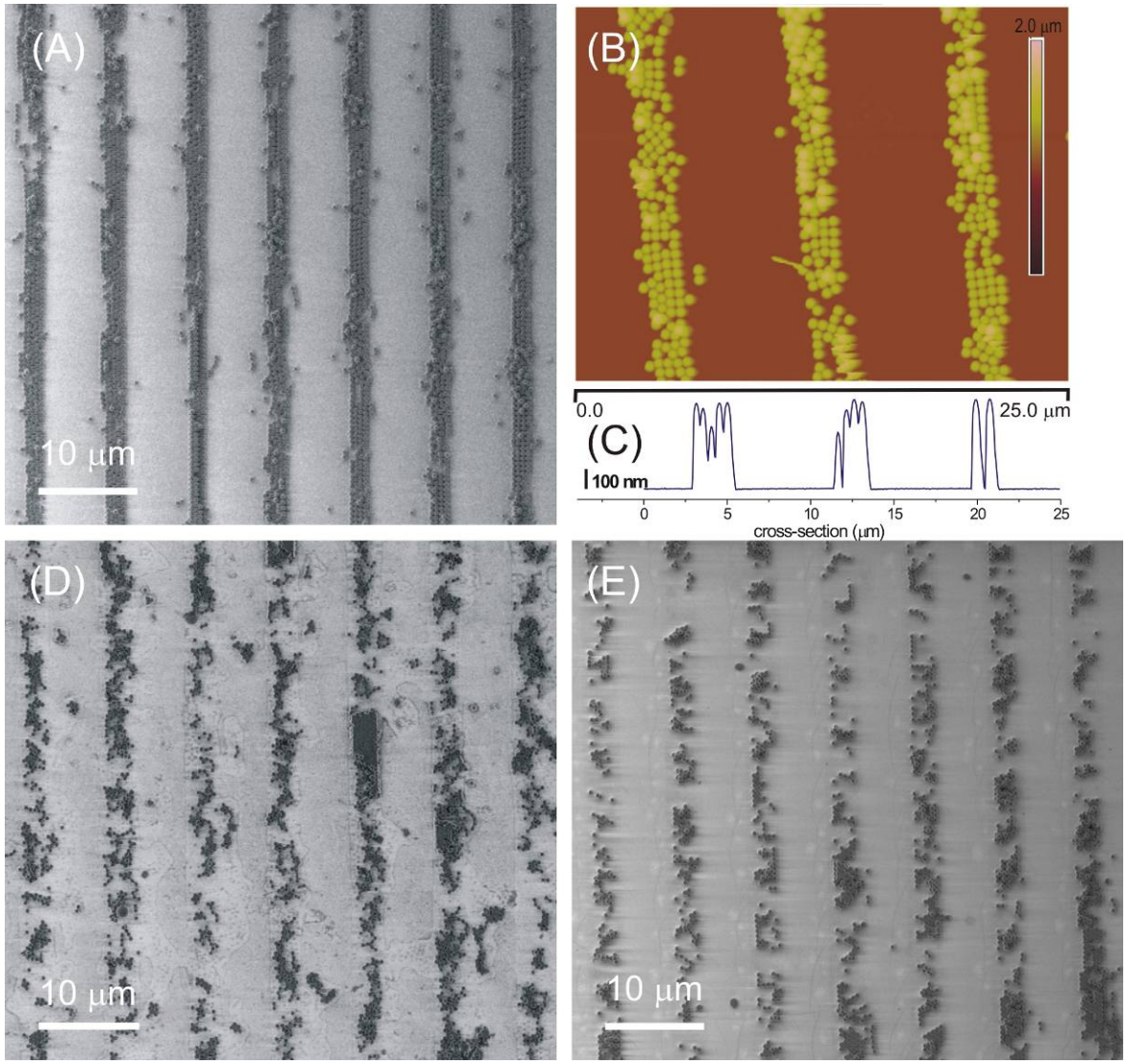
3D Supramolecular materials

Without infiltration with guest dendrimers:



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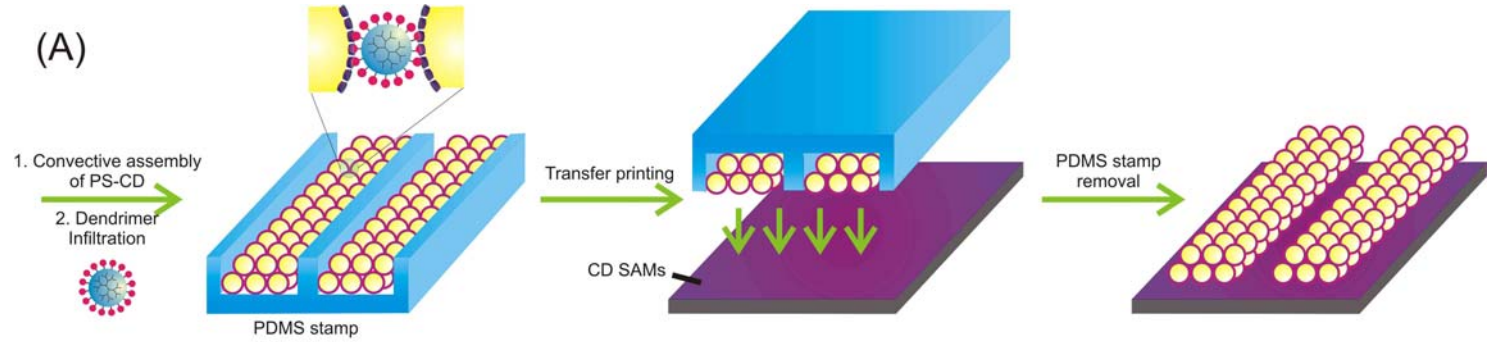
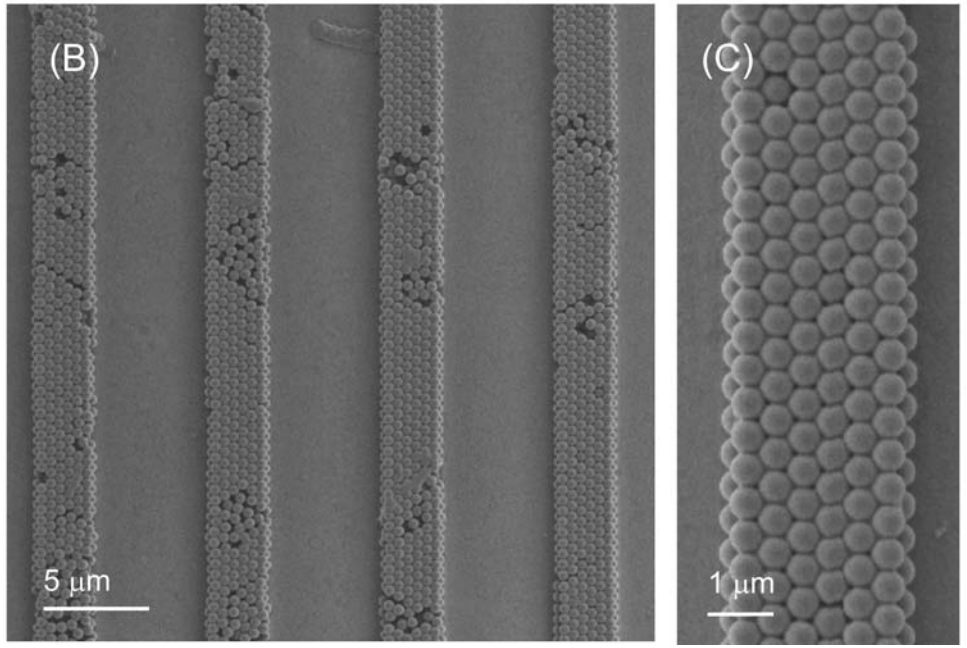
3D Supramolecular materials



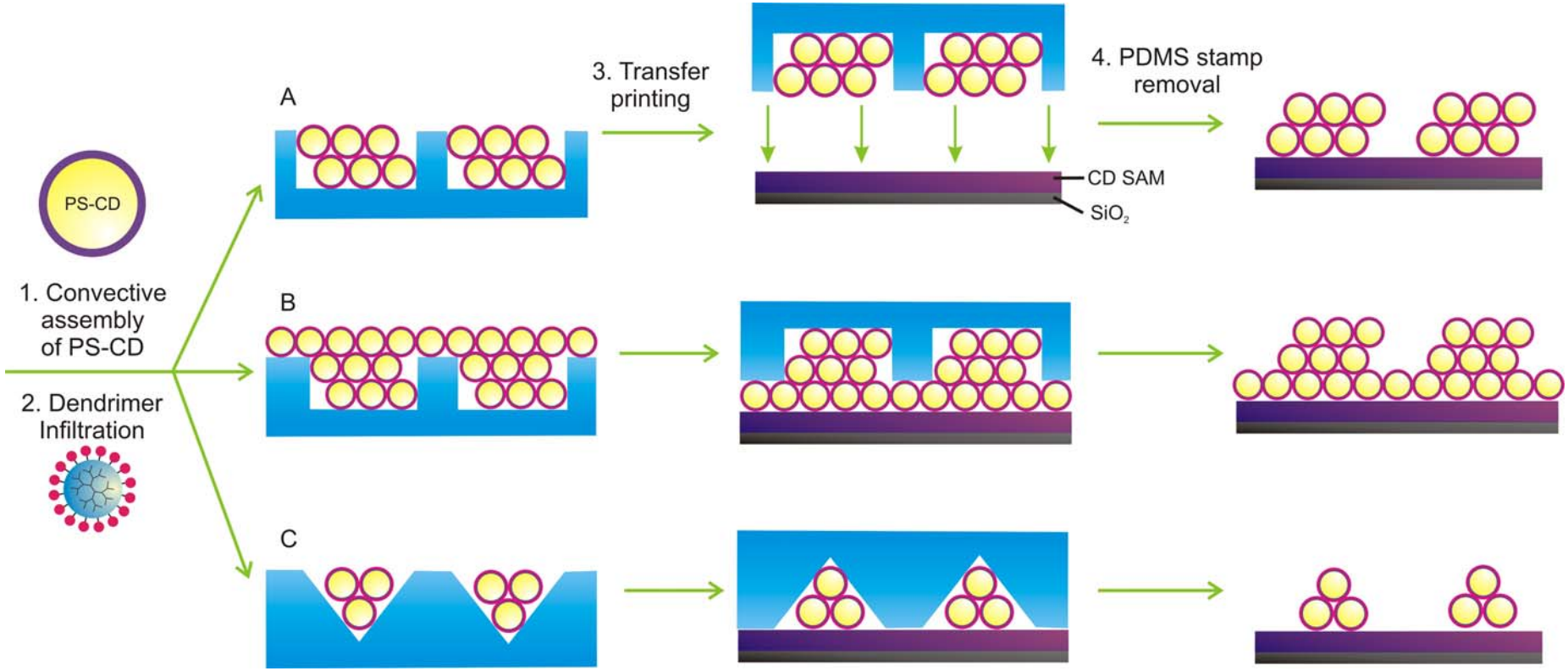
With infiltration with guest dendrimers:



X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *ACS Appl. Mater. Interf.* **2009**, *1*, in press

3D Supramolecular materials

Shape control by stamp variation:



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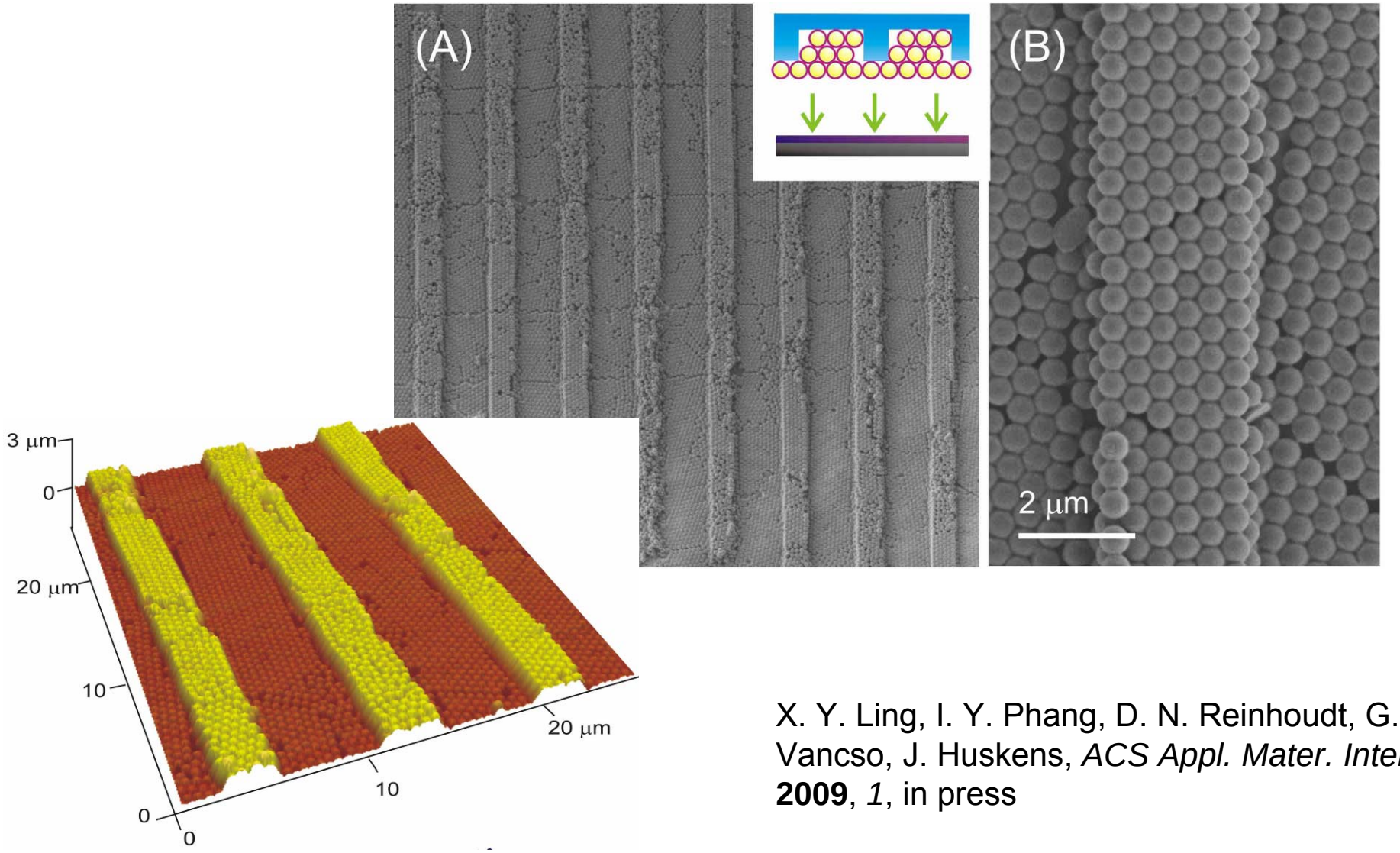
3D Supramolecular materials



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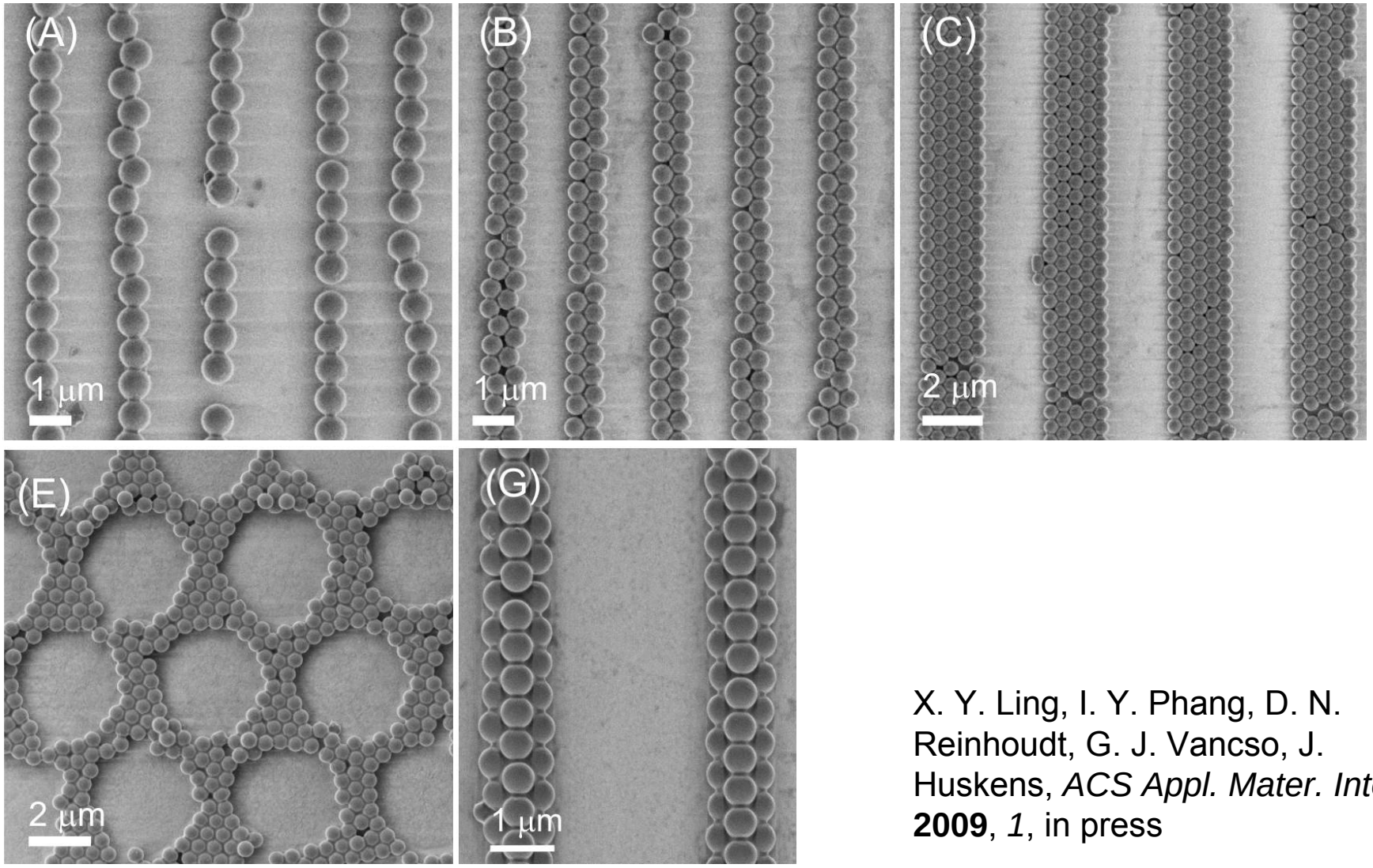
3D Supramolecular materials



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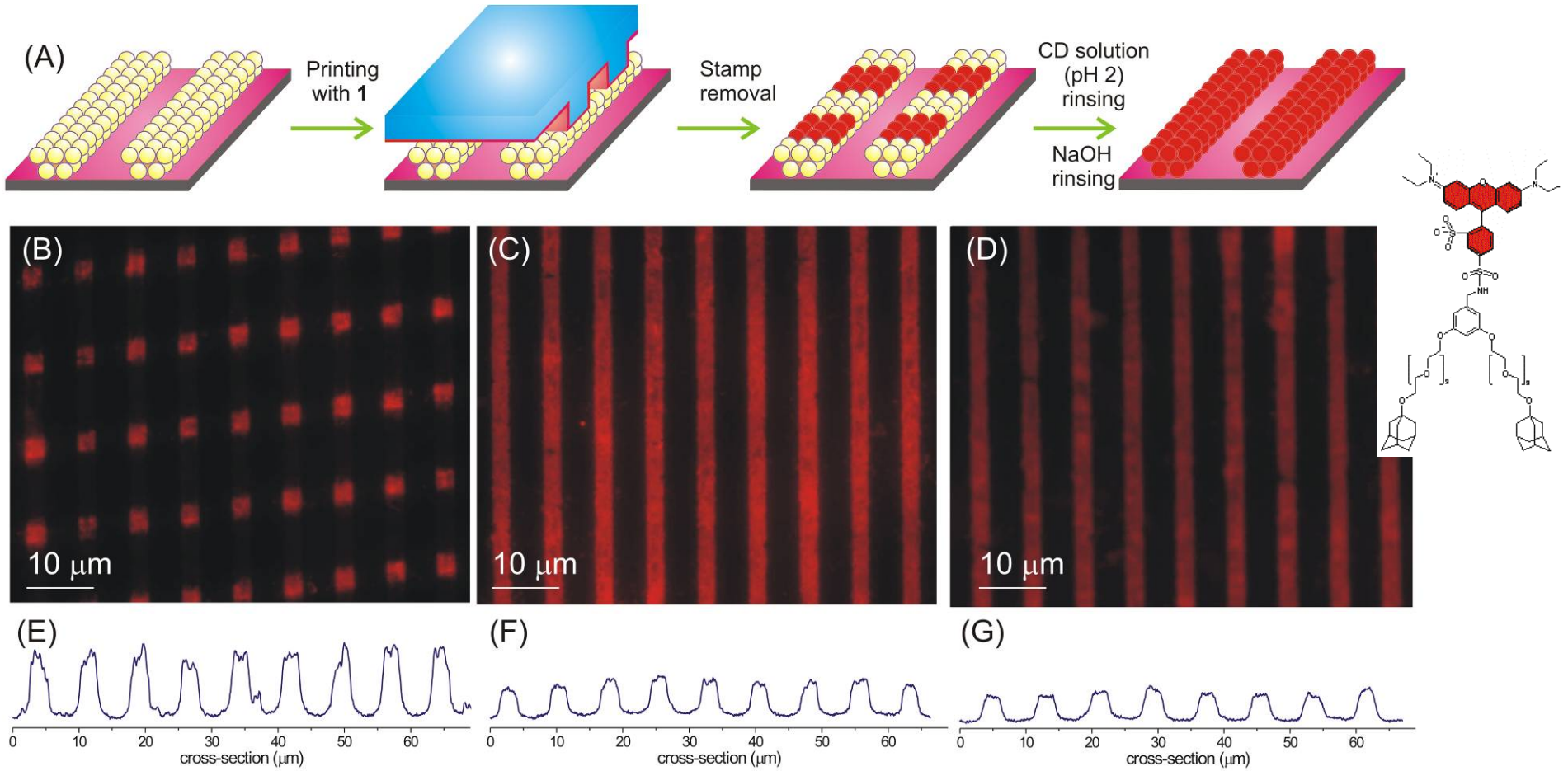
3D Supramolecular materials

Filling the 3D structures with fluorescent guests:



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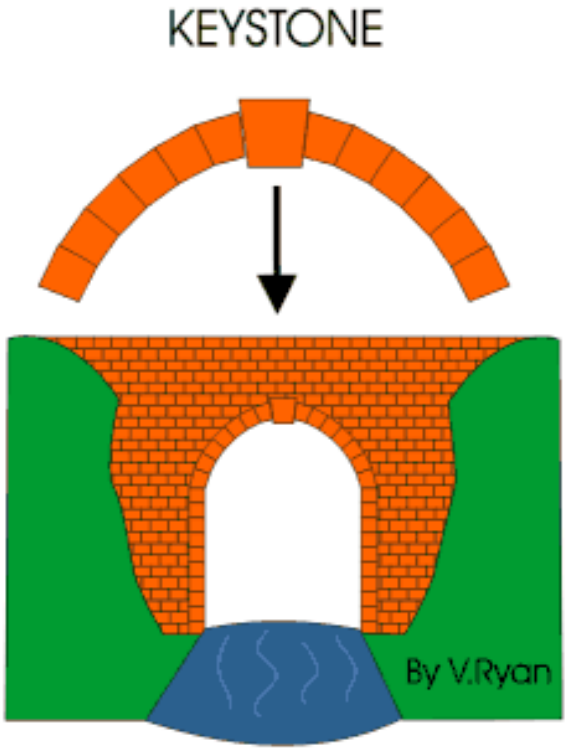
3D Supramolecular materials

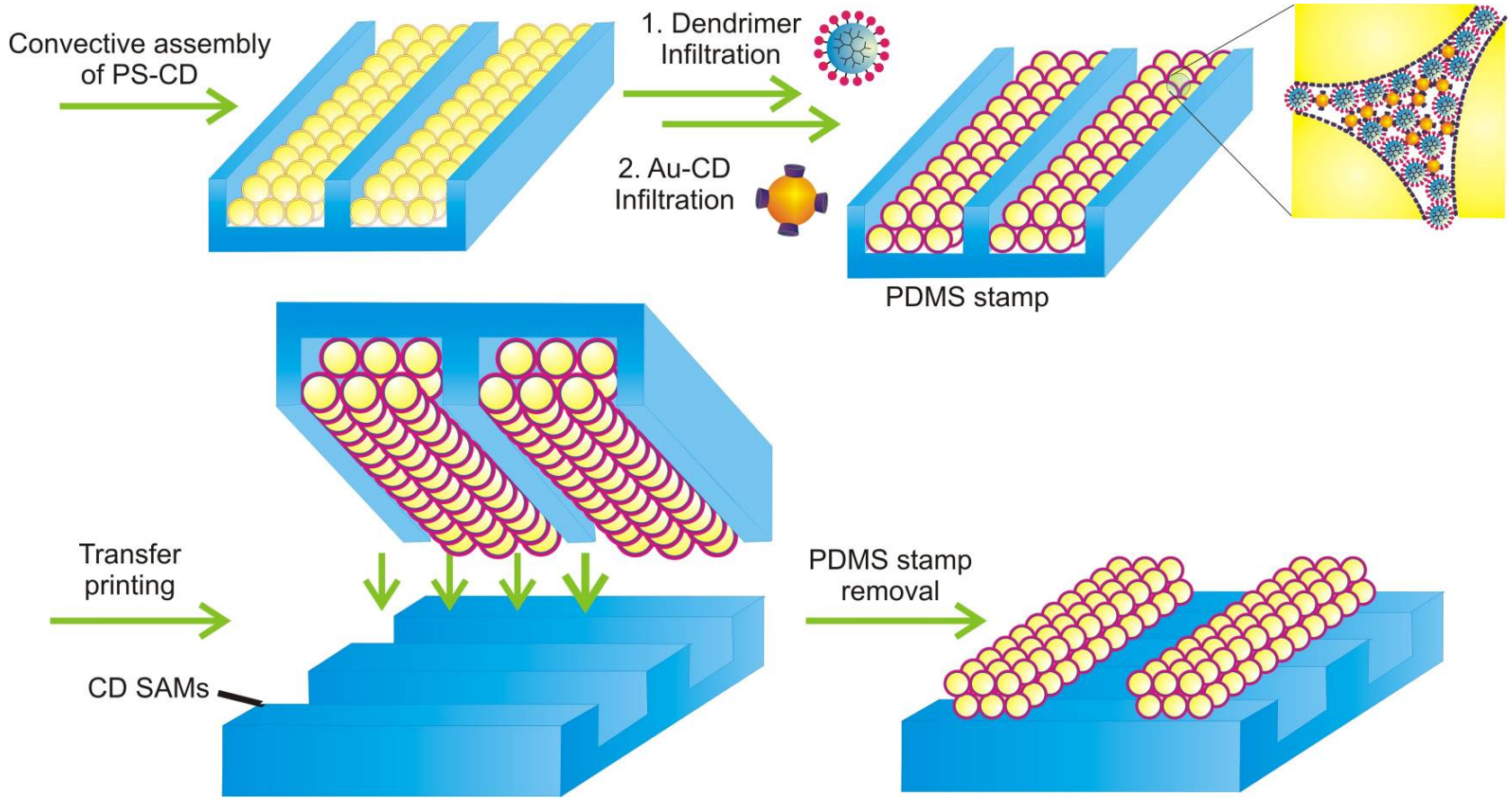
Are supramolecular materials strong enough to make free-standing bridges??

POND DE GARD (South of France):
Example of a Stone Arch Bridge - Built by the Romans over two thousand year ago.



3D Supramolecular materials

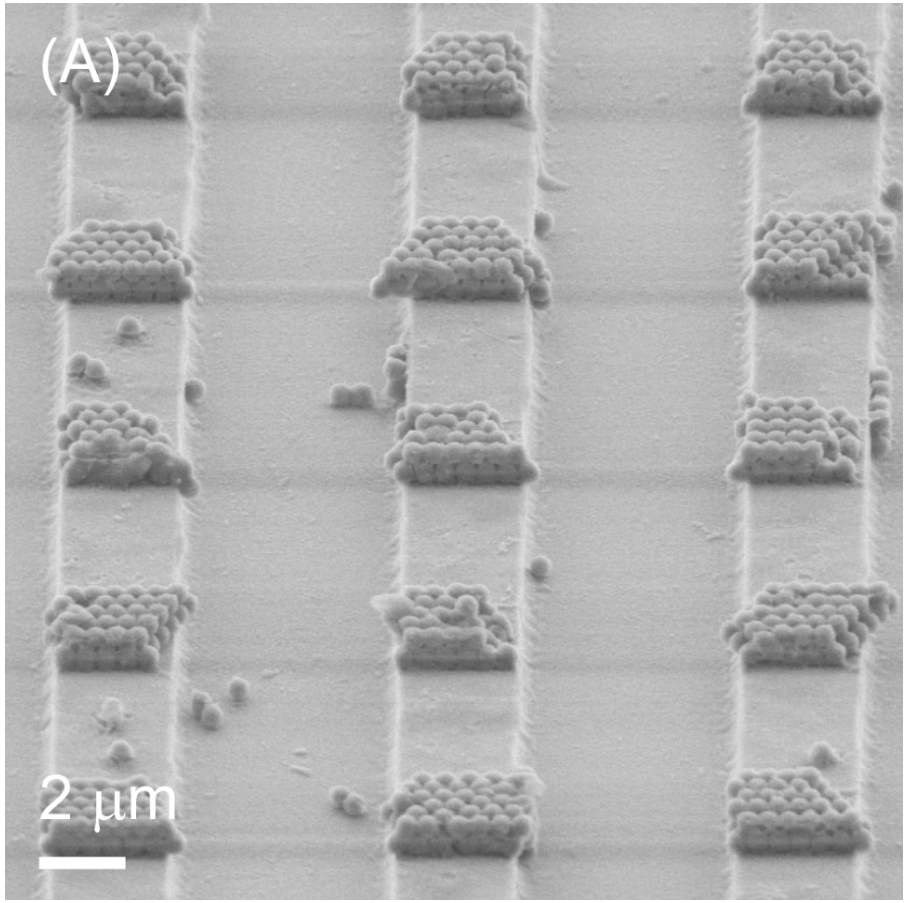
Are the structures stable enough to make free-standing bridges??
nTP onto NIL-patterned polymer lines:



X. Y. Ling, I. Y. Phang, W. Maijenburg, H. Schönherr, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Angew. Chem. Int. Ed.* **2009**, *48*, 983

3D Supramolecular materials

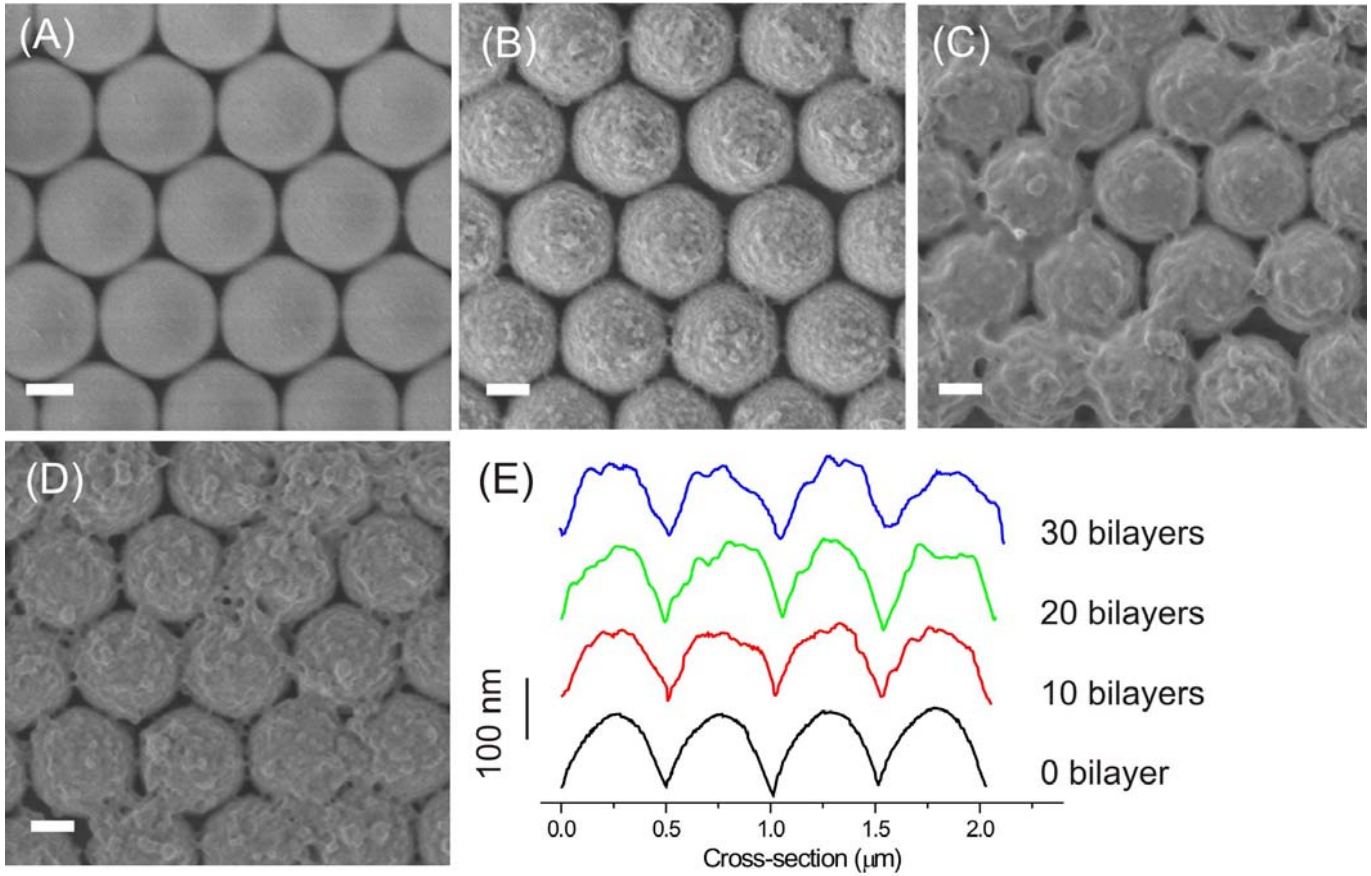
nTP onto NIL-patterned polymer lines: infiltration with dendrimers only:



X. Y. Ling, I. Y. Phang, W. Maijenburg, H. Schönherr, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Angew. Chem. Int. Ed.* **2009**, *48*, 983

3D Supramolecular materials

Filling the nanoparticle structures with LbL assemblies of dendrimers and CD gold nanoparticles:

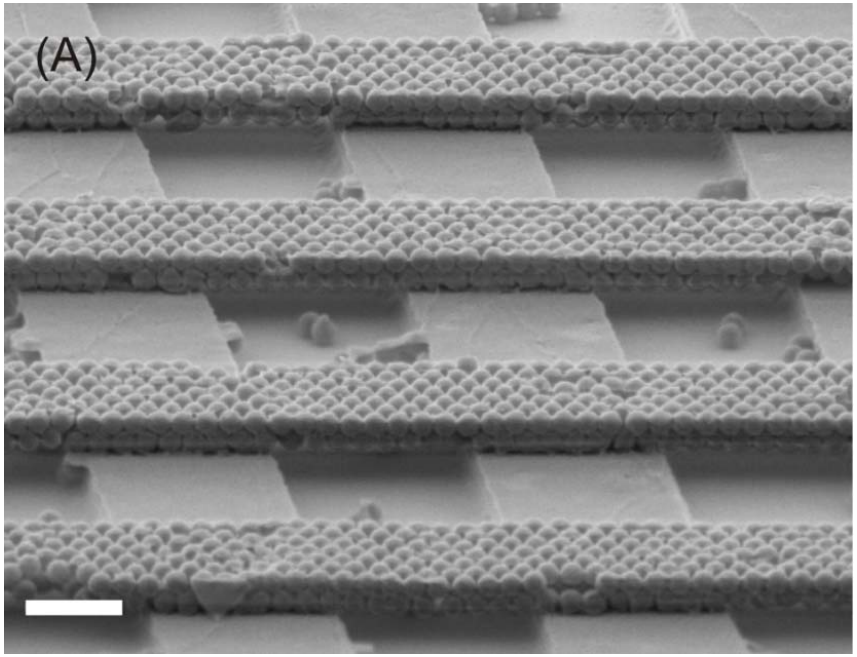


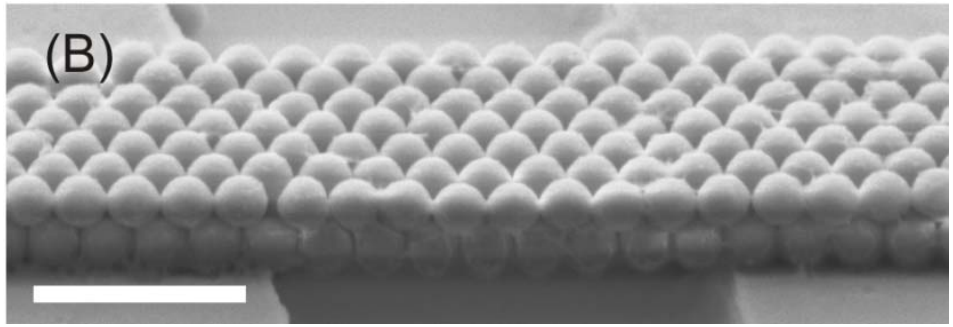
X. Y. Ling, I. Y. Phang, W. Maijenburg, H. Schönherr, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Angew. Chem. Int. Ed.* **2009**, *48*, 983

3D Supramolecular materials

nTP of LbL-filled nanoparticle structures onto NIL-patterned polymer lines:

free-standing bridges!!



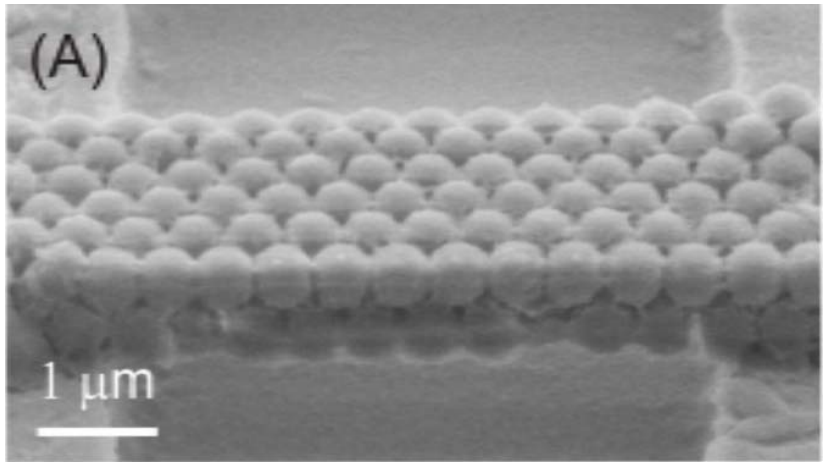


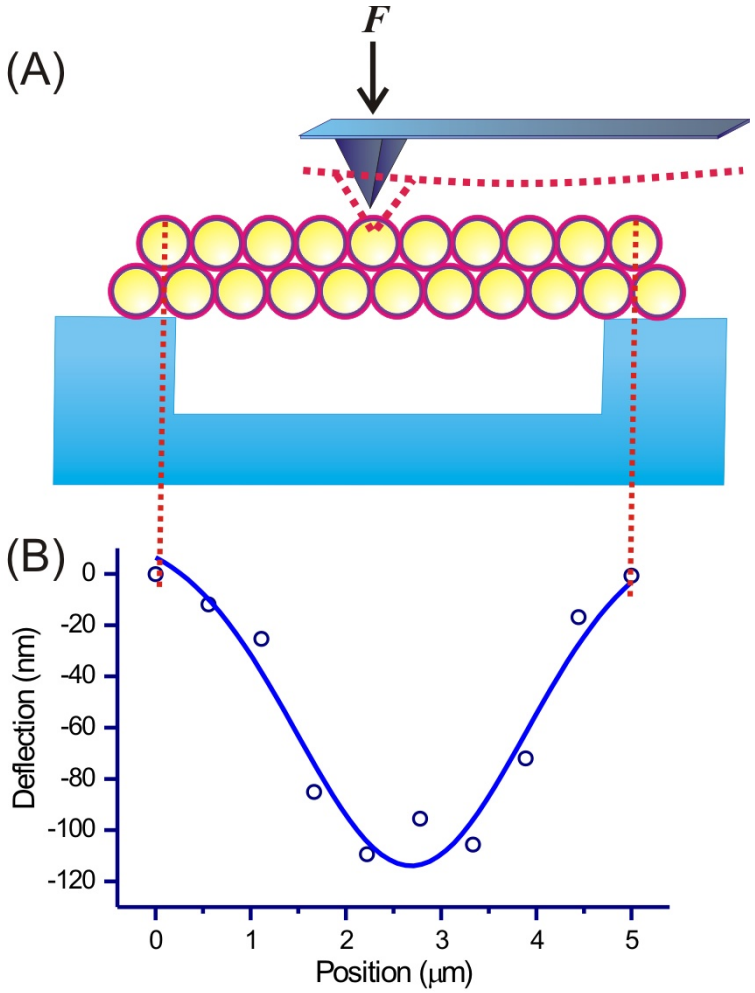
X. Y. Ling, I. Y. Phang, W. Maijenburg, H. Schönherr, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Angew. Chem. Int. Ed.* **2009**, *48*, 983

3D Supramolecular materials

AFM on a free-standing bridge:

Modulus comparable to PS !





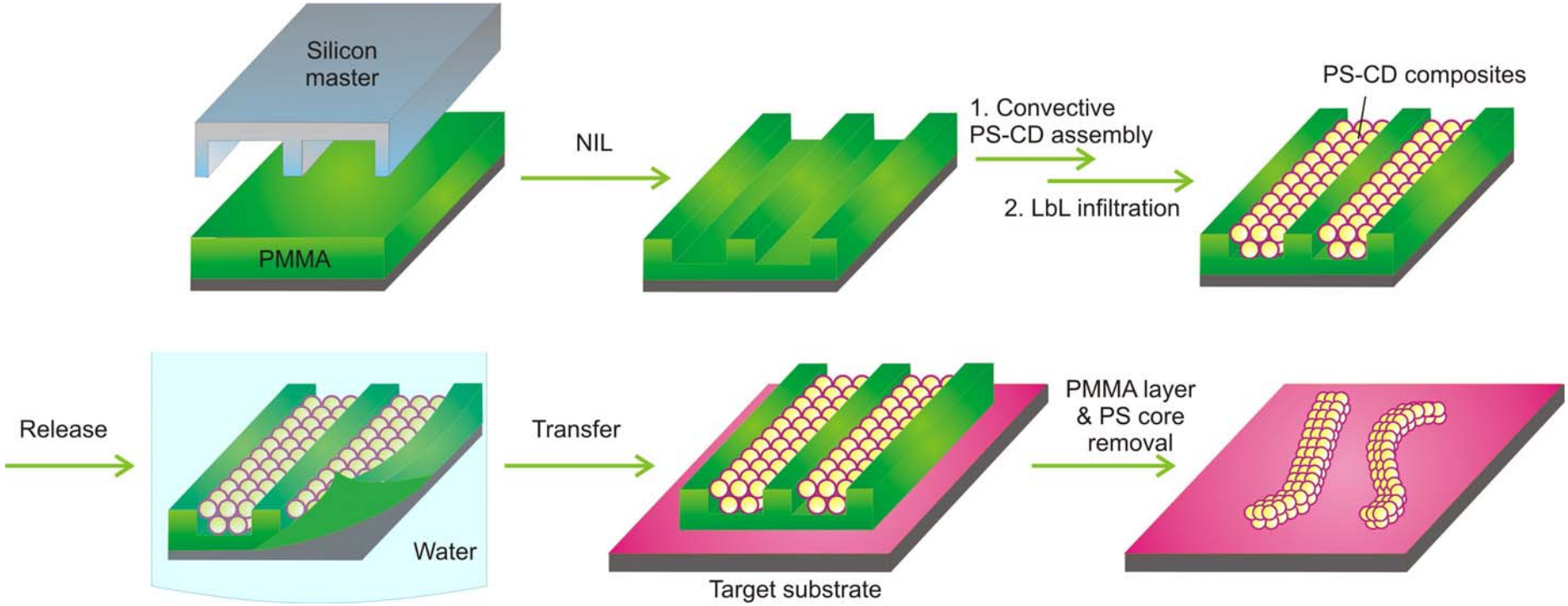
X. Y. Ling, I. Y. Phang, H. Schönherr, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Small* **2009**, *5*, in press

3D Supramolecular materials

Are supramolecular materials strong enough to make free-floating ribbons??

3D Supramolecular materials

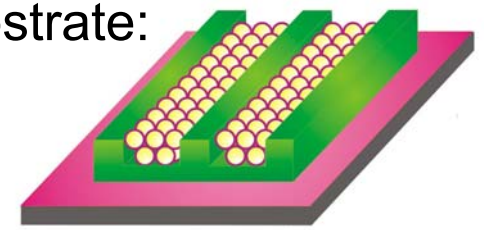
nTP of LbL-filled nanoparticle structures onto a sacrificial layer:
preparation of free-floating ribbons:

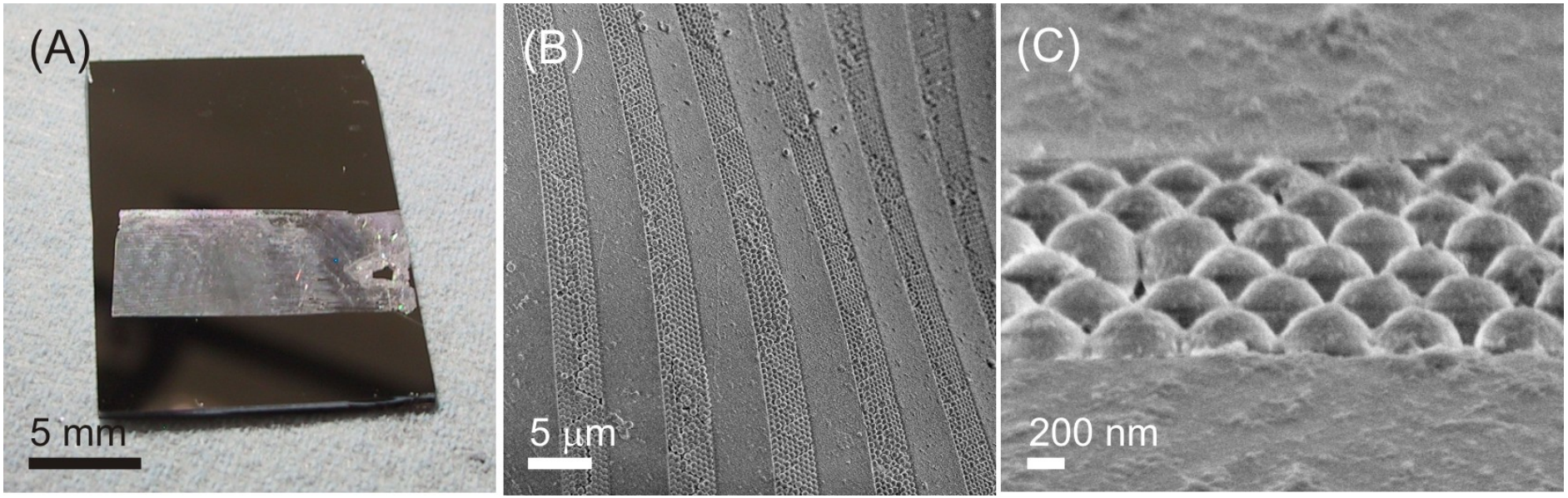


X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens,
Faraday Discuss. **2009**, *143*, in press

3D Supramolecular materials

nTP of LbL-filled nanoparticle structures onto a sacrificial layer:
After transfer of the embedded structures onto a target substrate:

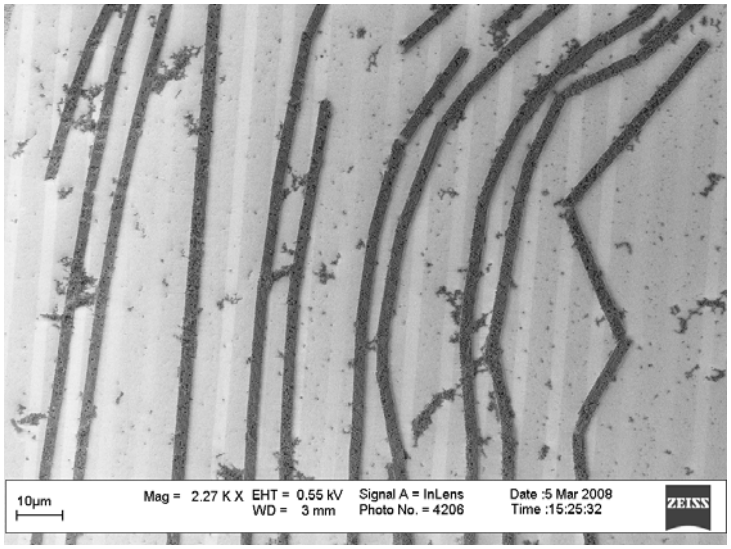


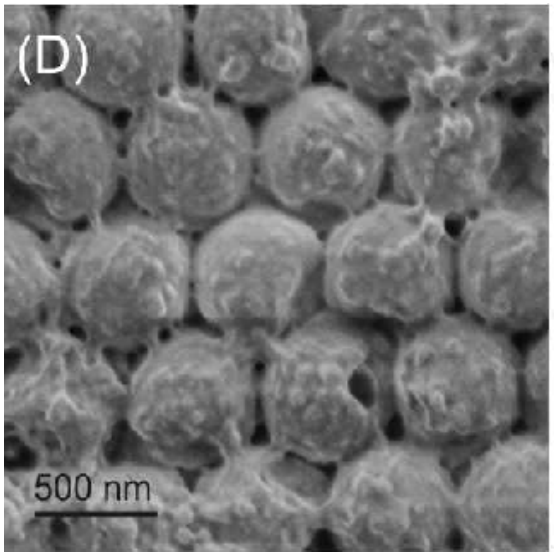


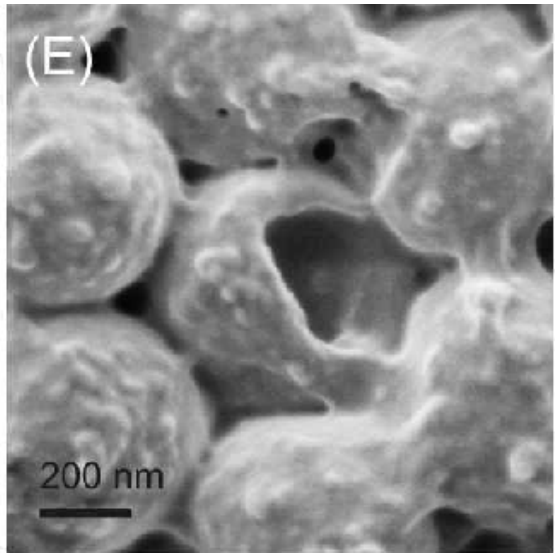
X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens,
Faraday Discuss. **2009**, *143*, in press

3D Supramolecular materials

nTP of LbL-filled nanoparticle structures onto a sacrificial layer:
After transfer and removal of template and core:



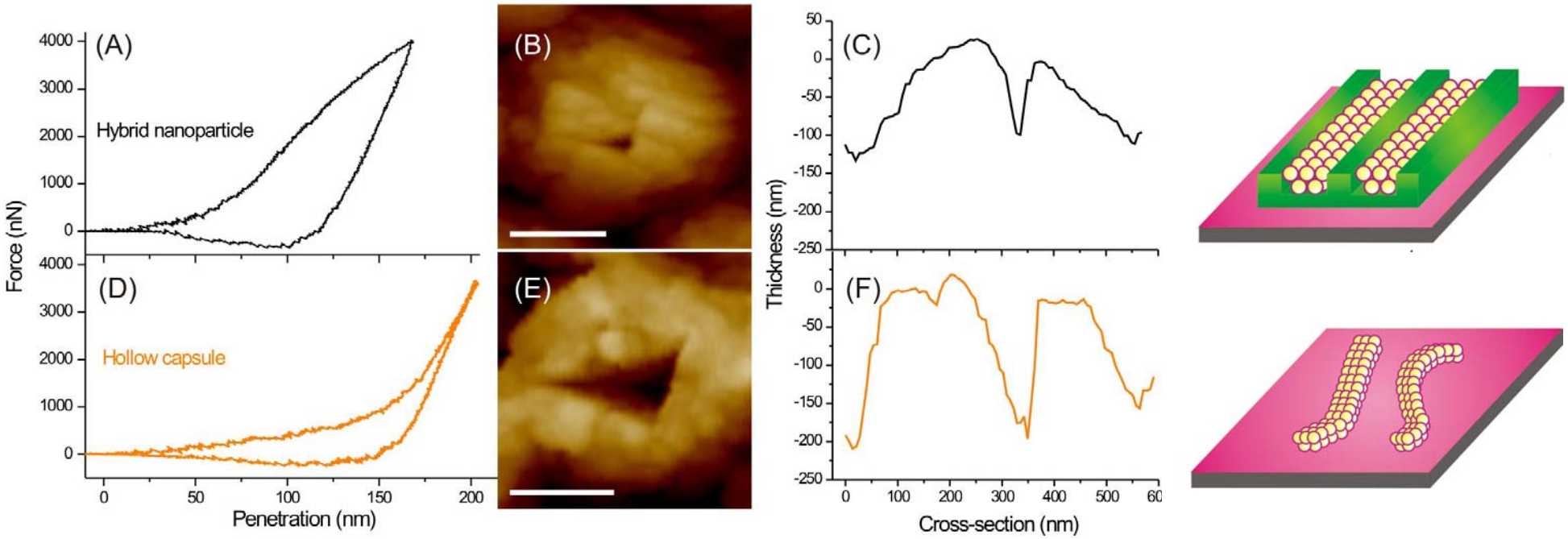




X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Faraday Discuss.* **2009**, *143*, in press

3D Supramolecular materials

AFM on filled and hollow capsules:

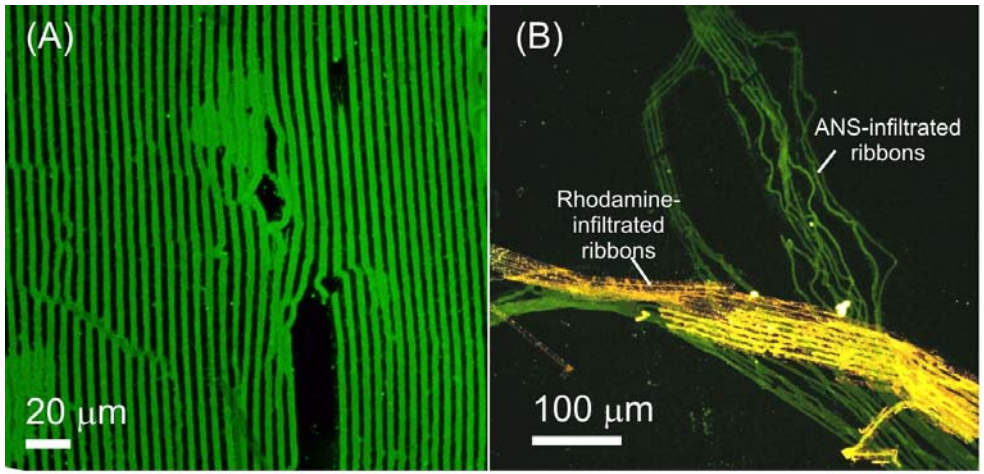


X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Faraday Discuss.* **2009**, *143*, in press

3D Supramolecular materials

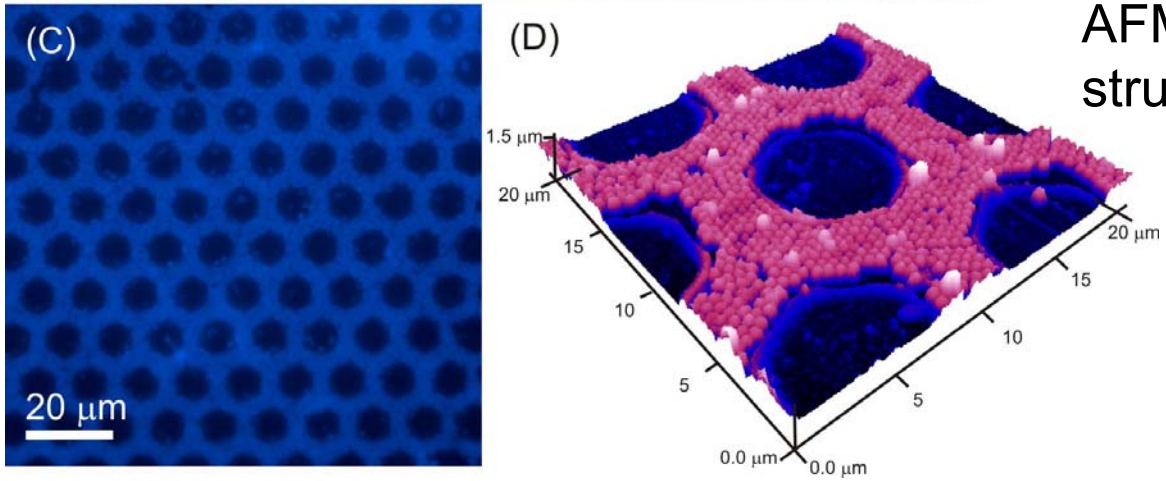
Colored free-floating ribbons:

ANS



ANS & lissamine rhodamine

naphthoic acid



AFM of network structure

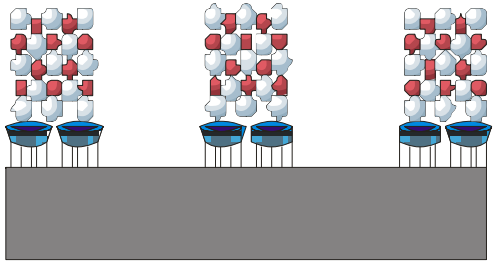
X. Y. Ling, I. Y. Phang, D. N. Reinhoudt, G. J. Vancso, J. Huskens, *Faraday Discuss.* **2009**, *143*, in press

Summary

Assembly: fundamental

Patterning:

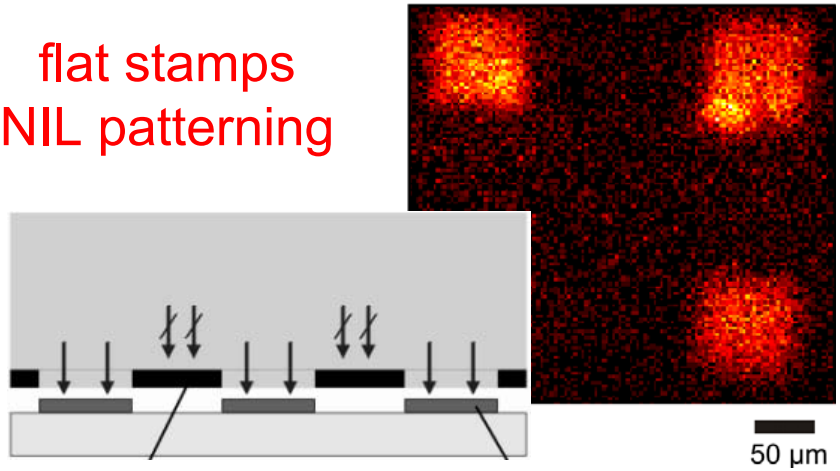
fundamental



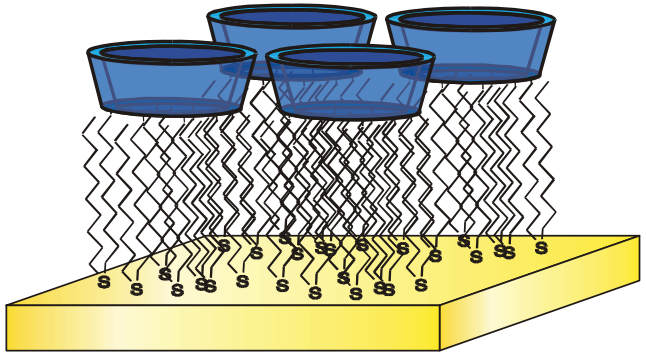
3D nanostructures

applied

flat stamps
NIL patterning

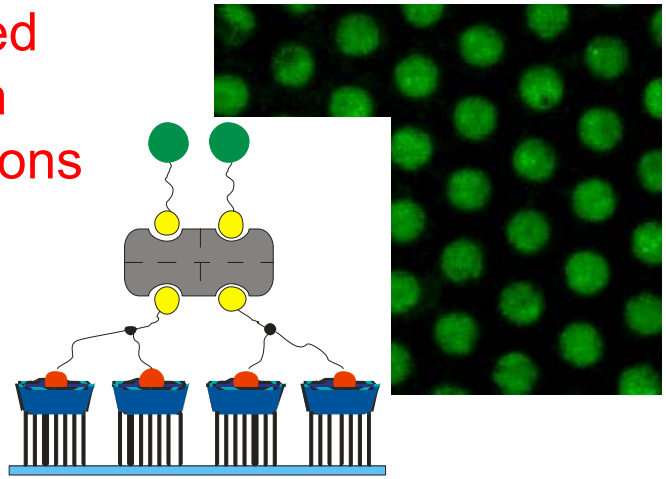


applied



printboards, multivalency,
supramolecular nanolithography

patterned
protein
constructions



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