

# **Nanomaterials for bottom-up manufacturing**

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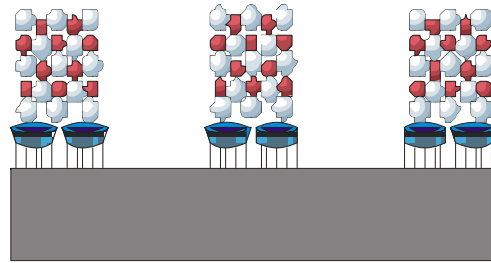


# General philosophy

Assembly: fundamental

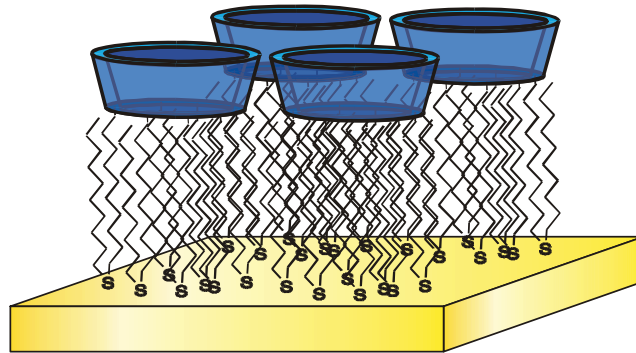
Patterning: fundamental

fundamental



3D nanostructures

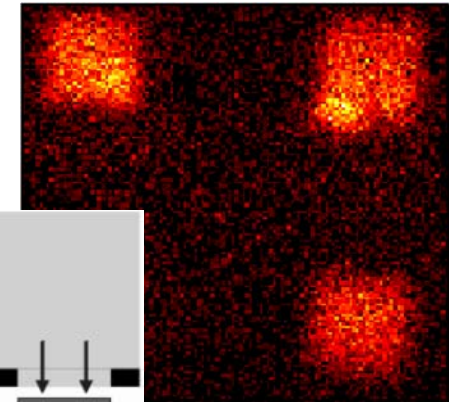
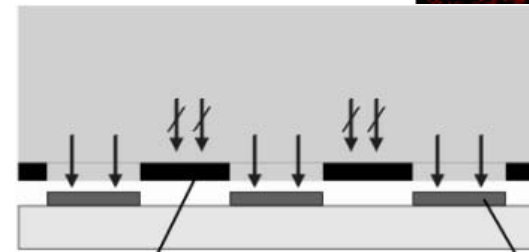
applied



printboards, multivalency, supramolecular nanolithography

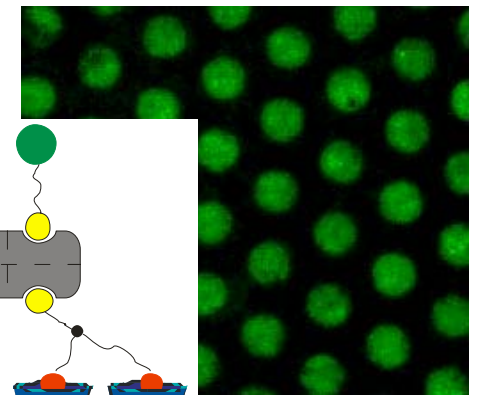
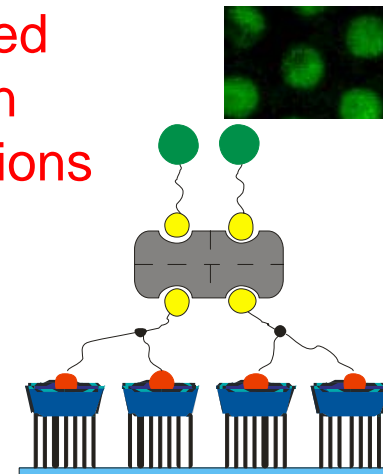
applied

flat stamps  
NIL patterning



50  $\mu$ m

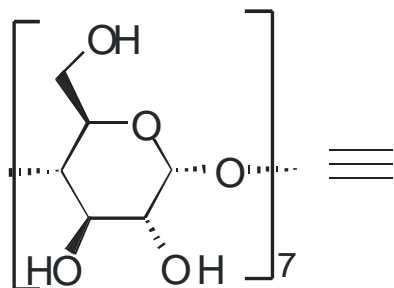
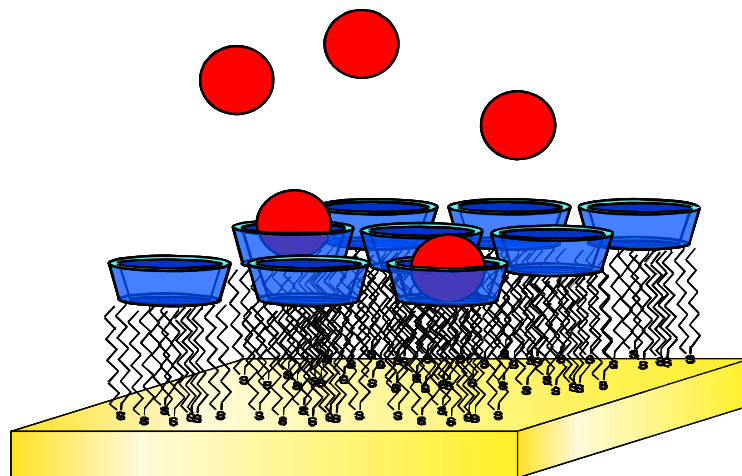
patterned  
protein  
constructions



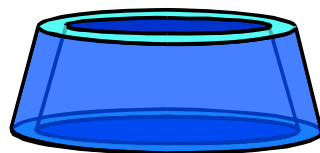


## Molecular printboards

CD monolayers on gold: **infinite 2D receptor lattices**:



$\beta$ -cyclodextrin (CD)



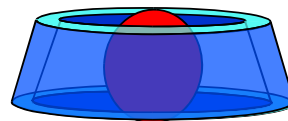
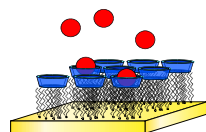
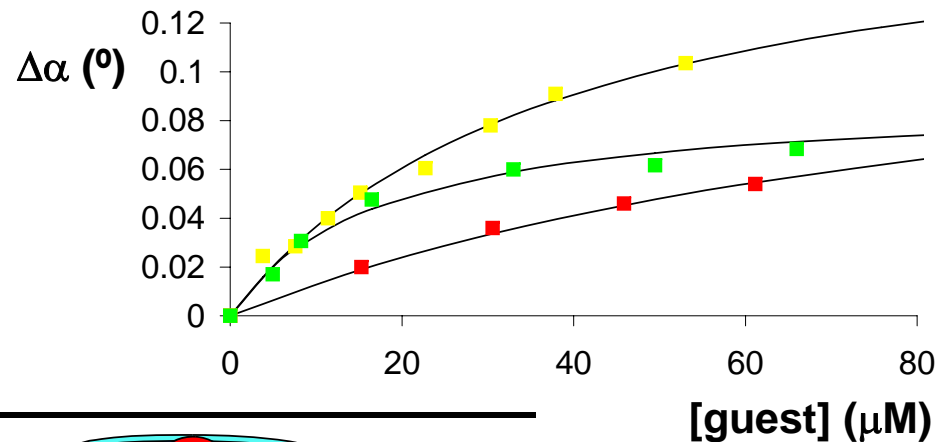
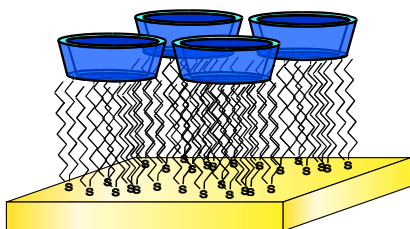
CA:	polarity:	$\theta_{adv} = 55^\circ$
EIS:	thickness:	2 - 3 nm
XPS:	bound sulfur:	65 %
SIMS:	molecular peaks:	(M+Au) <sup>+</sup>
AFM:	molecular order:	2.1 nm

M. W. J. Beulen, J. Bügler, M. R. de Jong, B. Lammerink, J. Huskens, H. Schönherr, G. J. Vancso, B. A. Boukamp, H. Wieder, A. Offenhäuser, W. Knoll, F. C. J. M. van Veggel, D. N. Reinhoudt, *Chem. Eur. J.* **2000**, 6, 1176



## Molecular printboards

Small guests at a CD monolayer:



	$K$ ( $M^{-1}$ )	$\Delta\alpha_{sat}$ ( $^{\circ}$ )	$K$ ( $M^{-1}$ )	$\Delta H$ ( $kcal\ mol^{-1}$ )	$T\Delta S$ ( $kcal\ mol^{-1}$ )
 <chem>Cc1ccc(cc1)C2=CC=CC=C2C3=CC=CC=C3C4=CC=CC=C4C5=CC=CC=C5C6=CC=CC=C6C7=CC=CC=C7C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10C11=CC=CC=C11C12=CC=CC=C12C13=CC=CC=C13C14=CC=CC=C14C15=CC=CC=C15C16=CC=CC=C16C17=CC=CC=C17C18=CC=CC=C18C19=CC=CC=C19C20=CC=CC=C20C21=CC=CC=C21C22=CC=CC=C22C23=CC=CC=C23C24=CC=CC=C24C25=CC=CC=C25C26=CC=CC=C26C27=CC=CC=C27C28=CC=CC=C28C29=CC=CC=C29C30=CC=CC=C30C31=CC=CC=C31C32=CC=CC=C32C33=CC=CC=C33C34=CC=CC=C34C35=CC=CC=C35C36=CC=CC=C36C37=CC=CC=C37C38=CC=CC=C38C39=CC=CC=C39C40=CC=CC=C40C41=CC=CC=C41C42=CC=CC=C42C43=CC=CC=C43C44=CC=CC=C44C45=CC=CC=C45C46=CC=CC=C46C47=CC=CC=C47C48=CC=CC=C48C49=CC=CC=C49C50=CC=CC=C50C51=CC=CC=C51C52=CC=CC=C52C53=CC=CC=C53C54=CC=CC=C54C55=CC=CC=C55C56=CC=CC=C56C57=CC=CC=C57C58=CC=CC=C58C59=CC=CC=C59C60=CC=CC=C60C61=CC=CC=C61C62=CC=CC=C62C63=CC=CC=C63C64=CC=CC=C64C65=CC=CC=C65C66=CC=CC=C66C67=CC=CC=C67C68=CC=CC=C68C69=CC=CC=C69C70=CC=CC=C70C71=CC=CC=C71C72=CC=CC=C72C73=CC=CC=C73C74=CC=CC=C74C75=CC=CC=C75C76=CC=CC=C76C77=CC=CC=C77C78=CC=CC=C78C79=CC=CC=C79C80=CC=CC=C80C81=CC=CC=C81C82=CC=CC=C82C83=CC=CC=C83C84=CC=CC=C84C85=CC=CC=C85C86=CC=CC=C86C87=CC=CC=C87C88=CC=CC=C88C89=CC=CC=C89C90=CC=CC=C90C91=CC=CC=C91C92=CC=CC=C92C93=CC=CC=C93C94=CC=CC=C94C95=CC=CC=C95C96=CC=CC=C96C97=CC=CC=C97C98=CC=CC=C98C99=CC=CC=C99C100=CC=CC=C100</chem>	$9.9 \cdot 10^3$	0.145	$1.0 \cdot 10^4$	-6.1	-0.7
 <chem>CC(=O)Nc1ccc(C(C)(C)C)cc1</chem>	$2.6 \cdot 10^4$	0.179	$3.0 \cdot 10^4$	-5.2	0.9
 <chem>CC(=O)Nc1c2c(c1)C3=CC=CC=C3C4=CC=CC=C4C5=CC=CC=C5C6=CC=CC=C6C7=CC=CC=C7C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10C11=CC=CC=C11C12=CC=CC=C12C13=CC=CC=C13C14=CC=CC=C14C15=CC=CC=C15C16=CC=CC=C16C17=CC=CC=C17C18=CC=CC=C18C19=CC=CC=C19C20=CC=CC=C20C21=CC=CC=C21C22=CC=CC=C22C23=CC=CC=C23C24=CC=CC=C24C25=CC=CC=C25C26=CC=CC=C26C27=CC=CC=C27C28=CC=CC=C28C29=CC=CC=C29C30=CC=CC=C30C31=CC=CC=C31C32=CC=CC=C32C33=CC=CC=C33C34=CC=CC=C34C35=CC=CC=C35C36=CC=CC=C36C37=CC=CC=C37C38=CC=CC=C38C39=CC=CC=C39C40=CC=CC=C40C41=CC=CC=C41C42=CC=CC=C42C43=CC=CC=C43C44=CC=CC=C44C45=CC=CC=C45C46=CC=CC=C46C47=CC=CC=C47C48=CC=CC=C48C49=CC=CC=C49C50=CC=CC=C50C51=CC=CC=C51C52=CC=CC=C52C53=CC=CC=C53C54=CC=CC=C54C55=CC=CC=C55C56=CC=CC=C56C57=CC=CC=C57C58=CC=CC=C58C59=CC=CC=C59C60=CC=CC=C60C61=CC=CC=C61C62=CC=CC=C62C63=CC=CC=C63C64=CC=CC=C64C65=CC=CC=C65C66=CC=CC=C66C67=CC=CC=C67C68=CC=CC=C68C69=CC=CC=C69C70=CC=CC=C70C71=CC=CC=C71C72=CC=CC=C72C73=CC=CC=C73C74=CC=CC=C74C75=CC=CC=C75C76=CC=CC=C76C77=CC=CC=C77C78=CC=CC=C78C79=CC=CC=C79C80=CC=CC=C80C81=CC=CC=C81C82=CC=CC=C82C83=CC=CC=C83C84=CC=CC=C84C85=CC=CC=C85C86=CC=CC=C86C87=CC=CC=C87C88=CC=CC=C88C89=CC=CC=C89C90=CC=CC=C90C91=CC=CC=C91C92=CC=CC=C92C93=CC=CC=C93C94=CC=CC=C94C95=CC=CC=C95C96=CC=CC=C96C97=CC=CC=C97C98=CC=CC=C98C99=CC=CC=C99C100=CC=CC=C100</chem>	$5.7 \cdot 10^4$	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

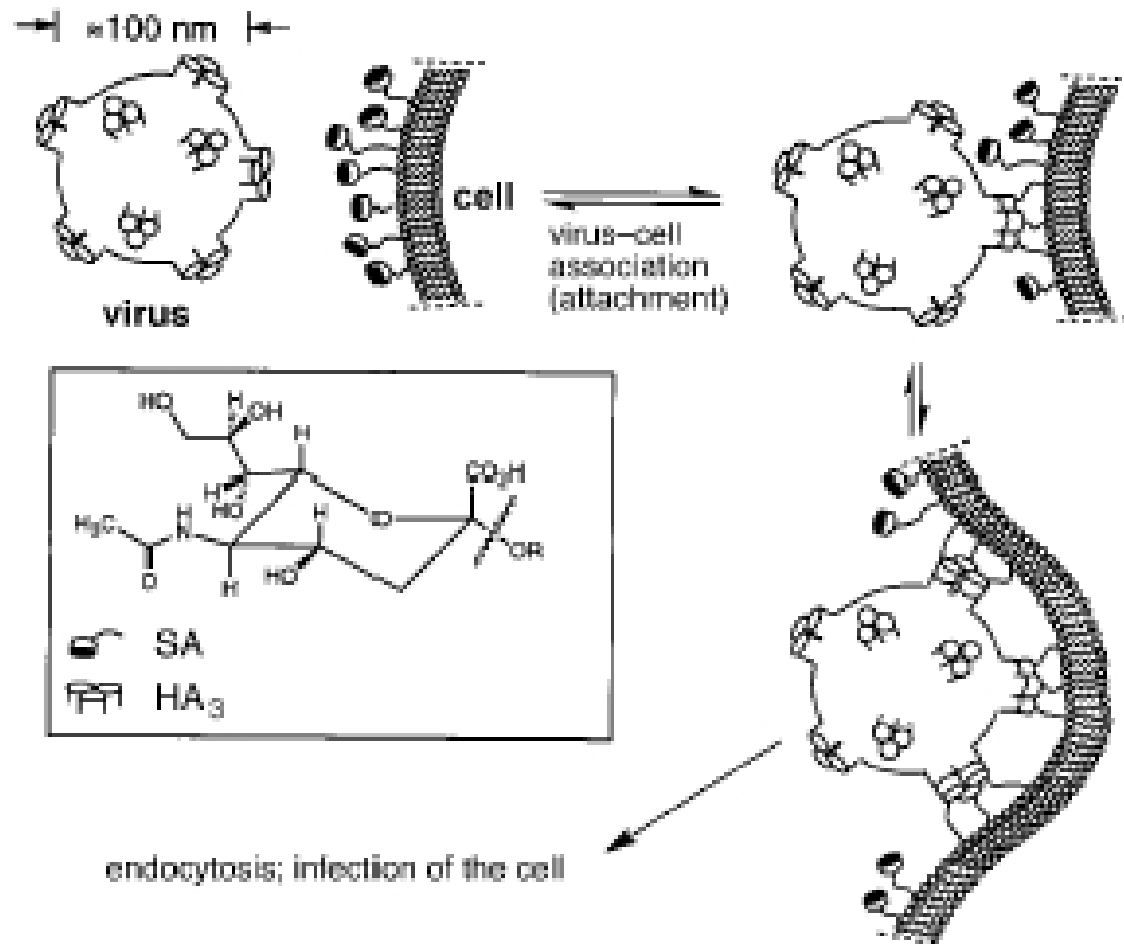


# General introduction to multivalency

Multivalency **at interfaces**:

Examples in Nature:

cell membrane interactions  
with bacteria and viruses:

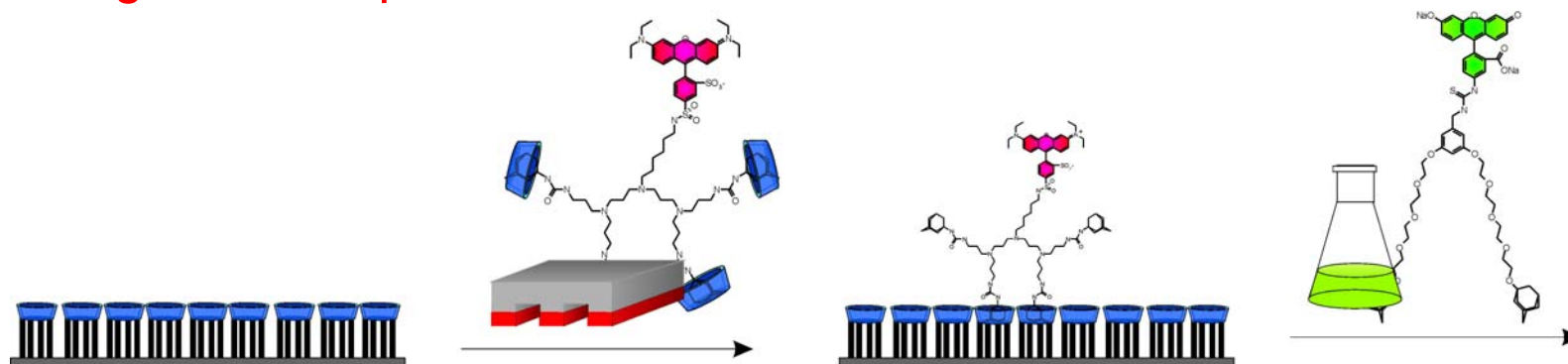


M. Mammen, S.-K. Choi, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, 37, 2754



## $\mu$ CP on SAMs

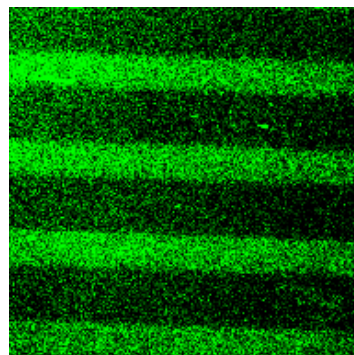
Patterning with **multiple** multivalent molecules:



Confocal microscopy images



$E_m > 600 \text{ nm}$



$500 < E_m < 530 \text{ nm}$



Simultaneous

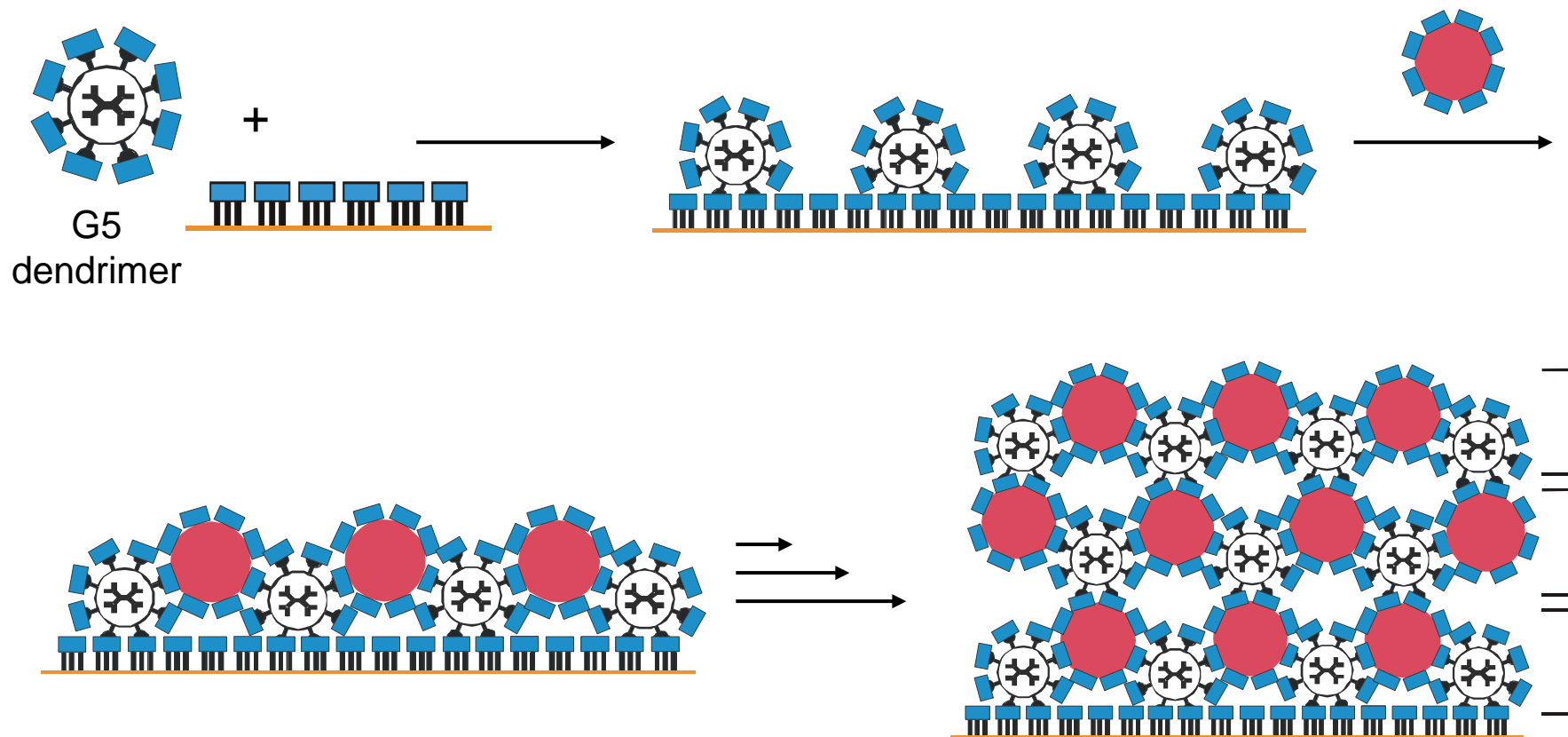
60  $\mu\text{m}$

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



## 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

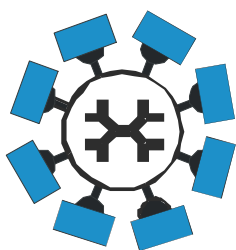
Layer-by-layer assembly: G. Decher, *Science* **1997**, 277, 1232



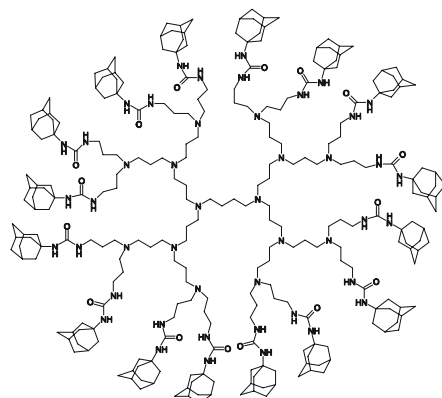
# Supramolecular materials

Supramolecular building blocks for LBL assembly:

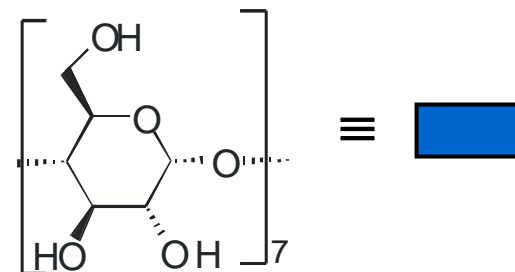
Adamantyl dendrimers:



≡



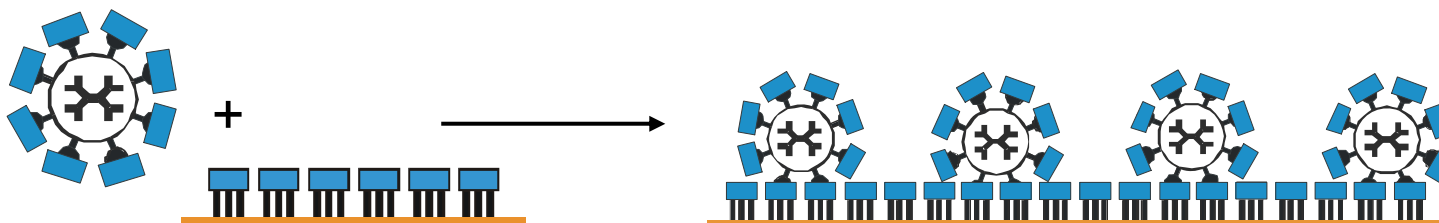
generation 3 dendrimer ( $n = 16$ )



$\beta$ -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

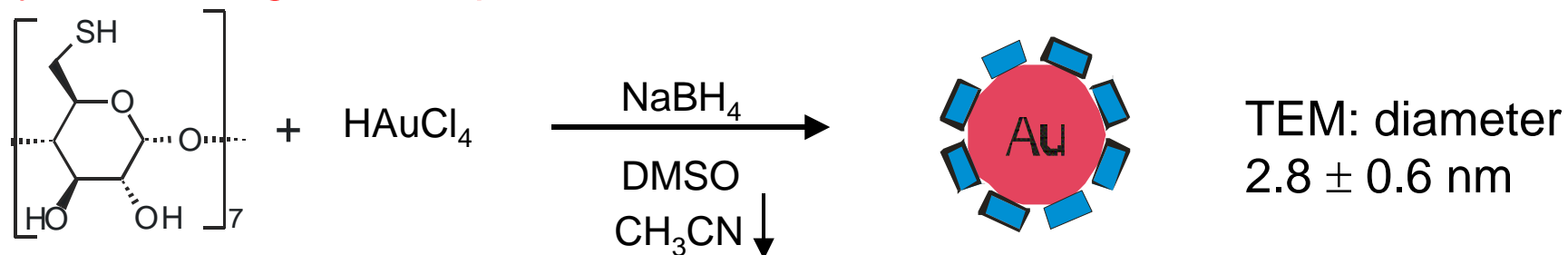




## Supramolecular materials

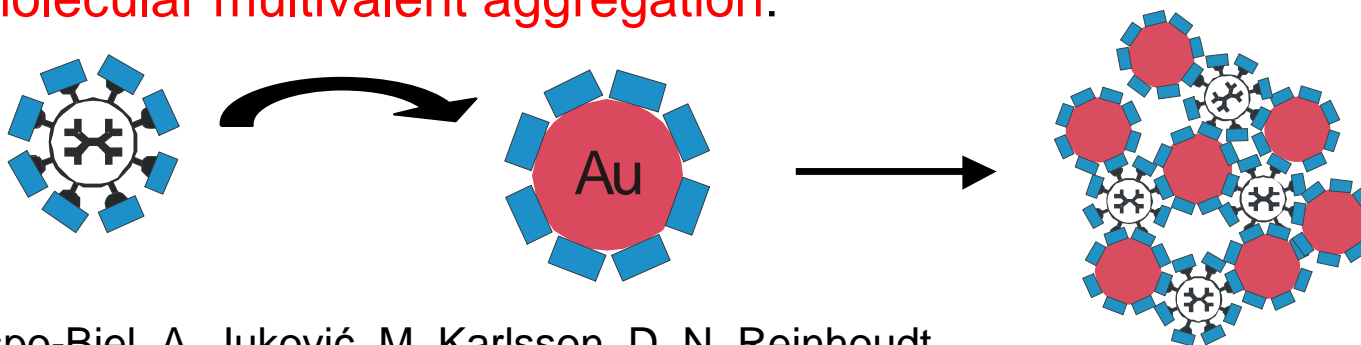
Supramolecular building blocks for LBL assembly:

Cyclodextrin gold nanoparticles:



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

Supramolecular multivalent aggregation:



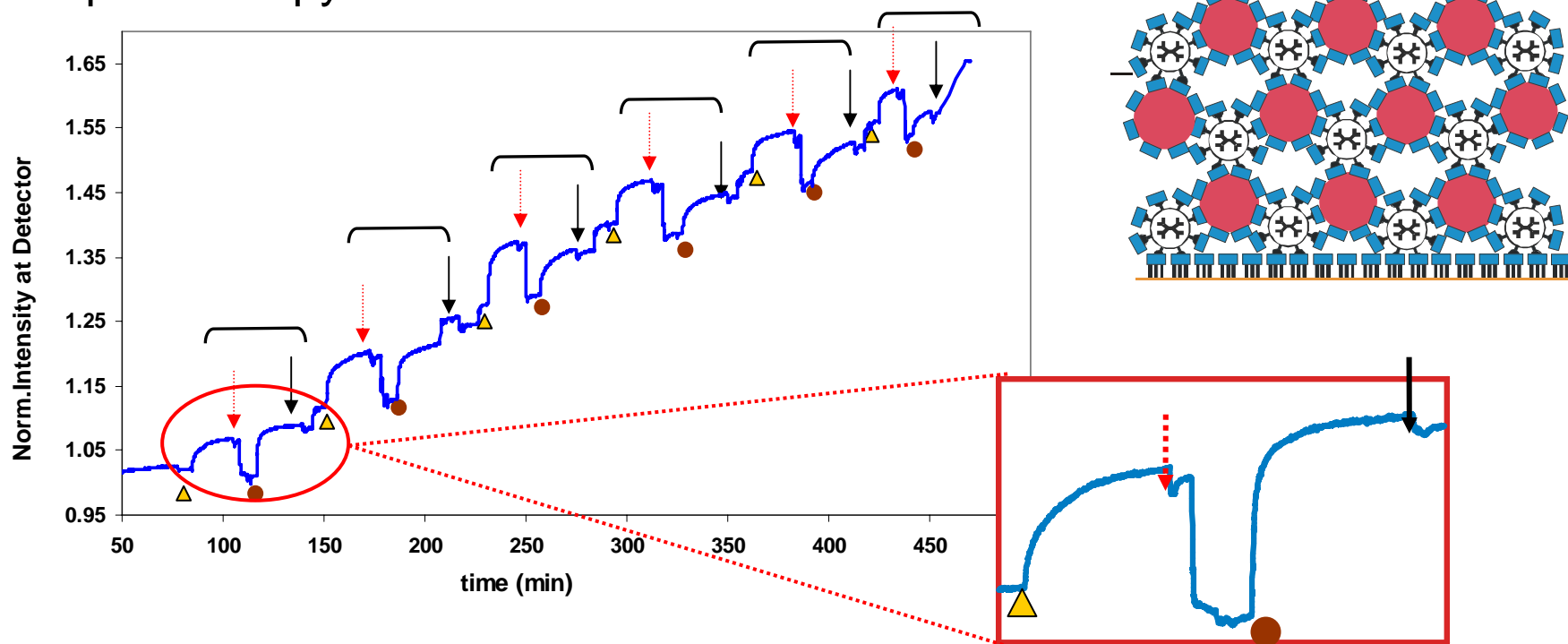
O. Crespo-Biel, A. Juković, M. Karlsson, D. N. Reinhoudt, J. Huskens, *Isr. J. Chem.* **2005**, 45, 353



# Supramolecular materials

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

SPR spectroscopy:



Solutions: 6.5  $\mu$ M CD-Au (H<sub>2</sub>O) ●

0.01 mM Ad-G5 (1 mM CD pH 2) ▲

→ Rinse 1 mM CD pH 2

→ Rinse H<sub>2</sub>O

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

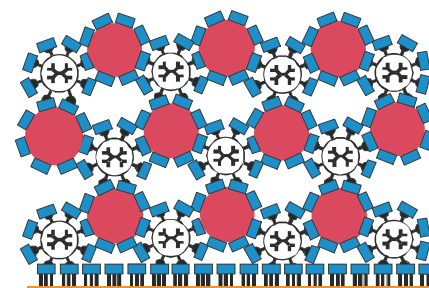
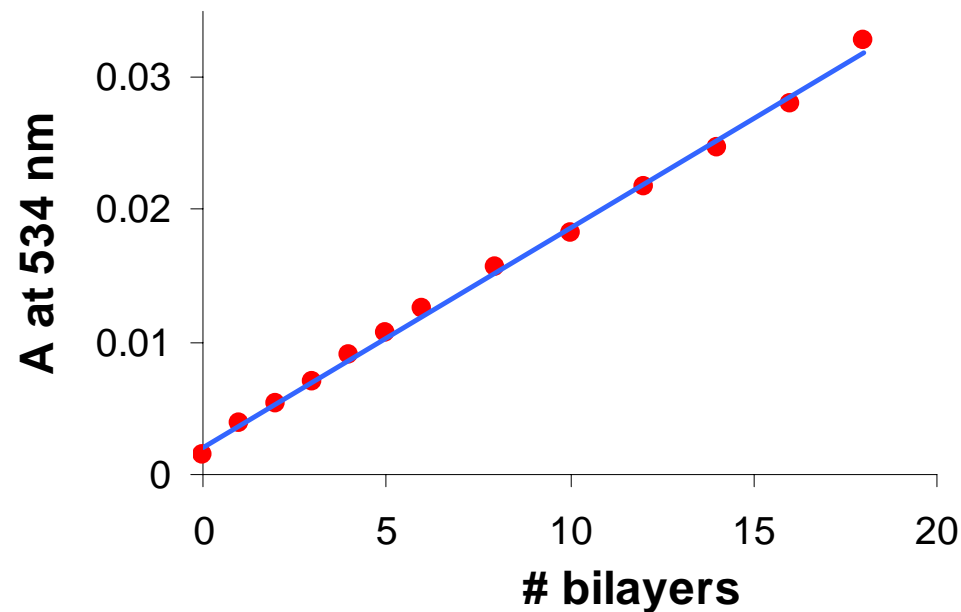
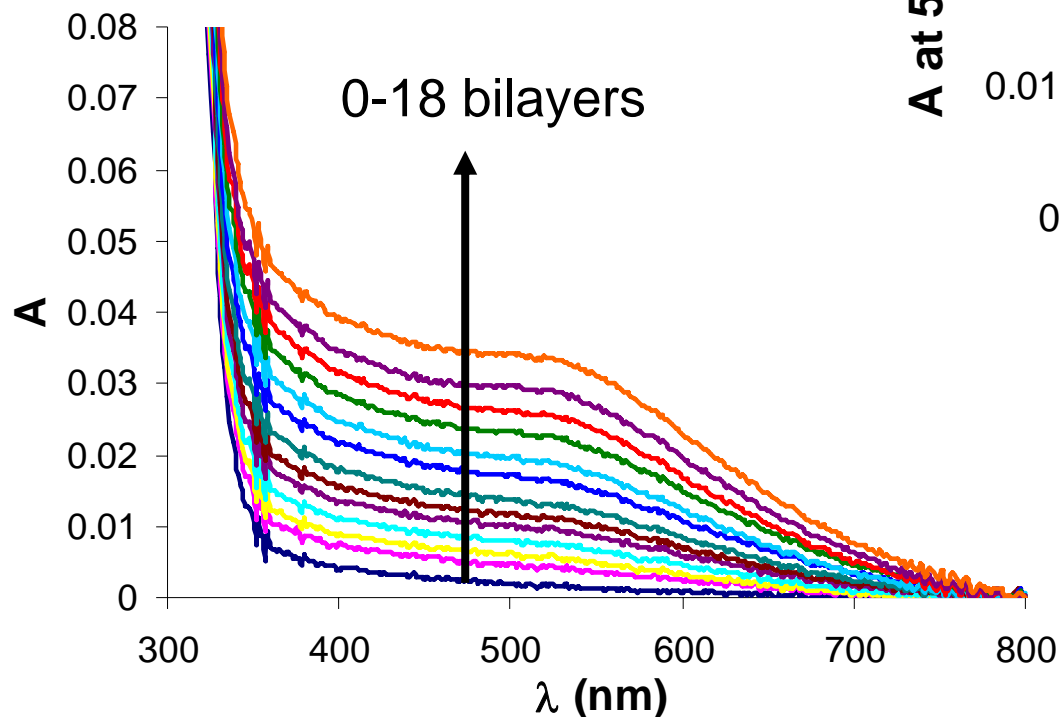


# Supramolecular materials

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

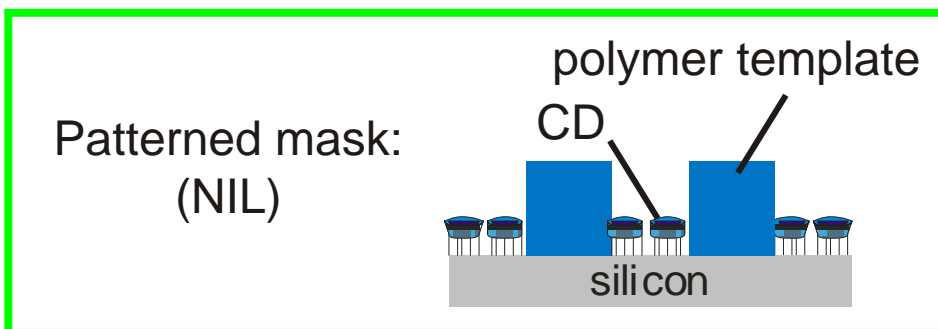
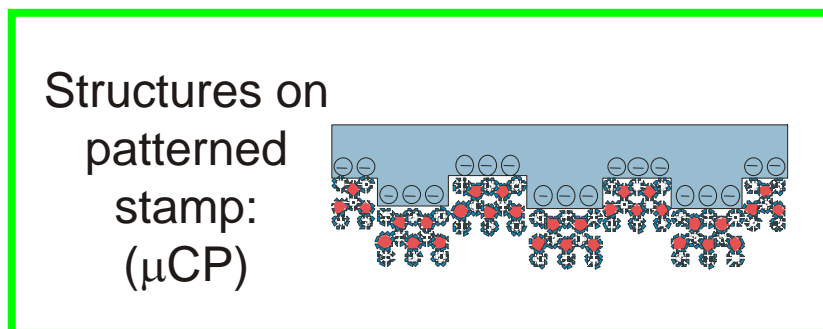
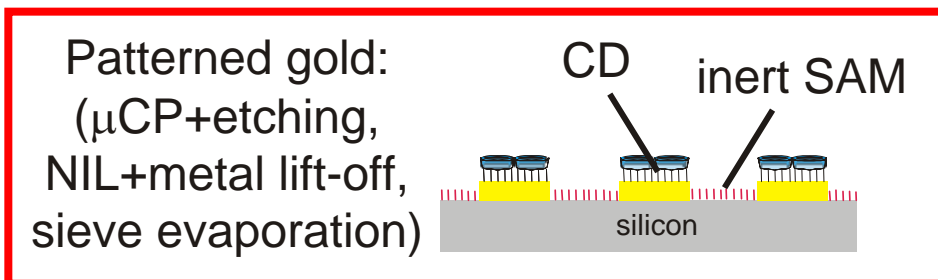
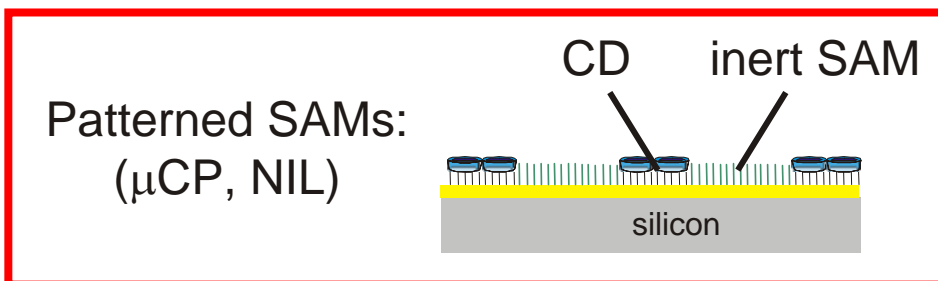
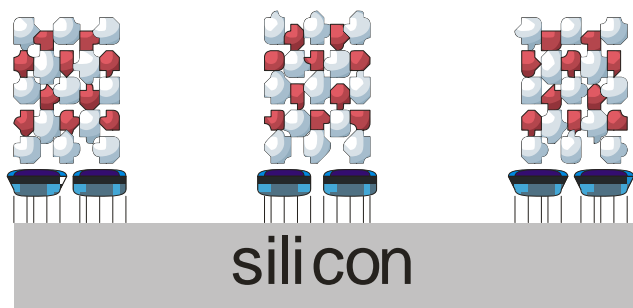


# 3D Supramolecular materials

Towards **patterned LBL assemblies**:

## 3D Nanofabrication:

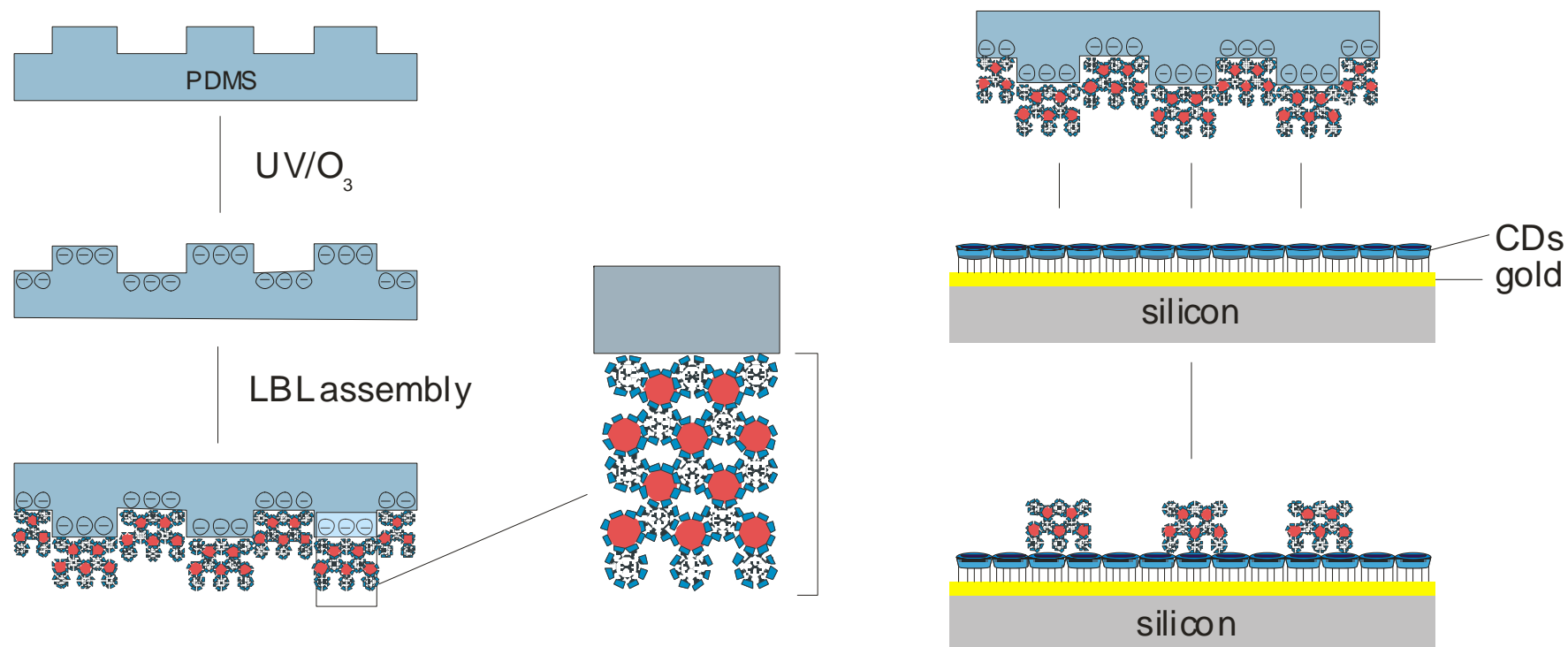
x,y: top-down patterning  
z: LBL assembly





## 3D Supramolecular materials

Alternative: **LBL on PDMS stamp** followed by assembly transfer by  $\mu$ CP:

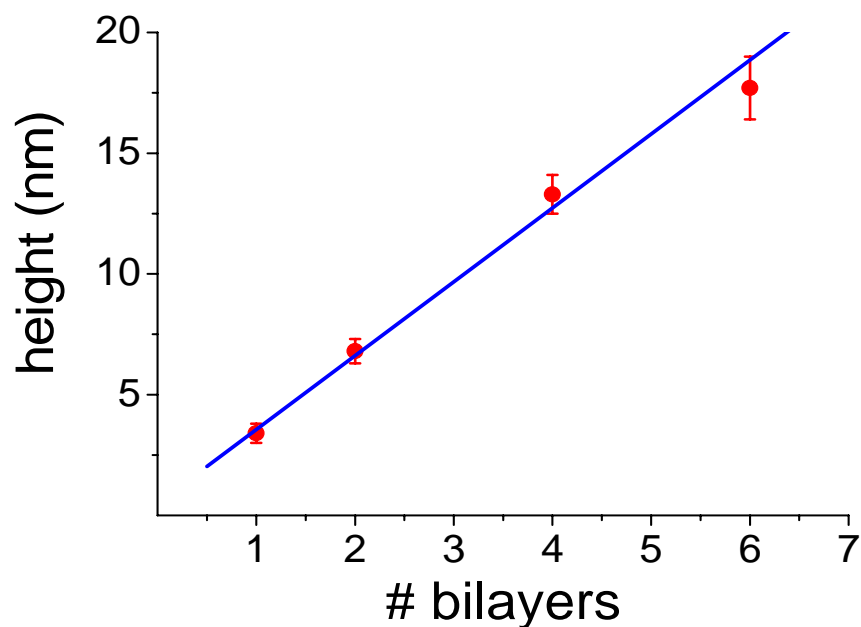
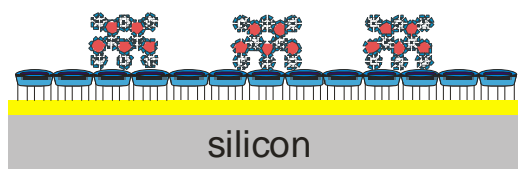


O. Crespo-Biel, B. Dordi, P. Maury, M. Péter, D. N. Reinhoudt, J. Huskens, *Chem. Mater.* **2006**, *18*, 2545  
LBL in combination with  $\mu$ CP: J. Park, P. T. Hammond, *Adv. Mater.* **2004**, *16*, 520

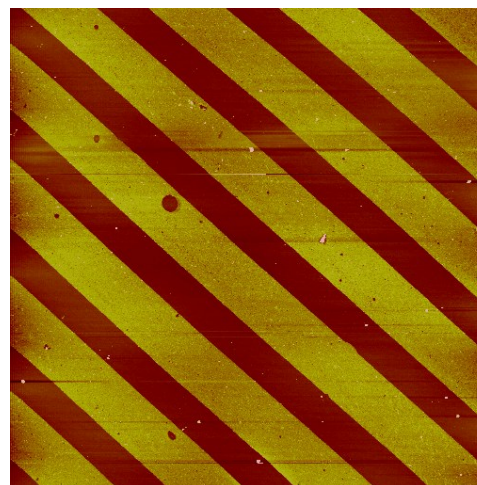


## 3D Supramolecular materials

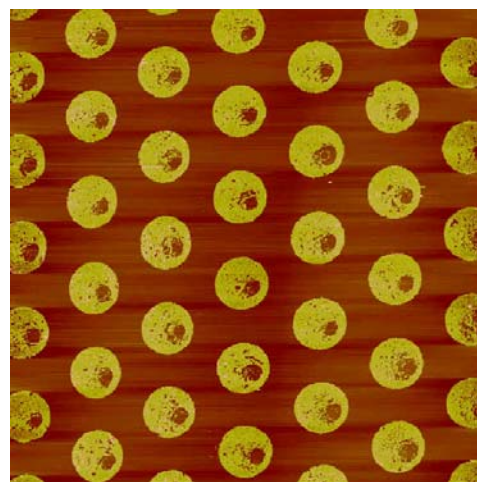
Patterned LBL assemblies by  $\mu$ CP:



Assemblies are stable against rinsing with competitive CD solutions



AFM height image  
(80 x 80  $\mu\text{m}^2$ )  
2 bilayers: 7 nm



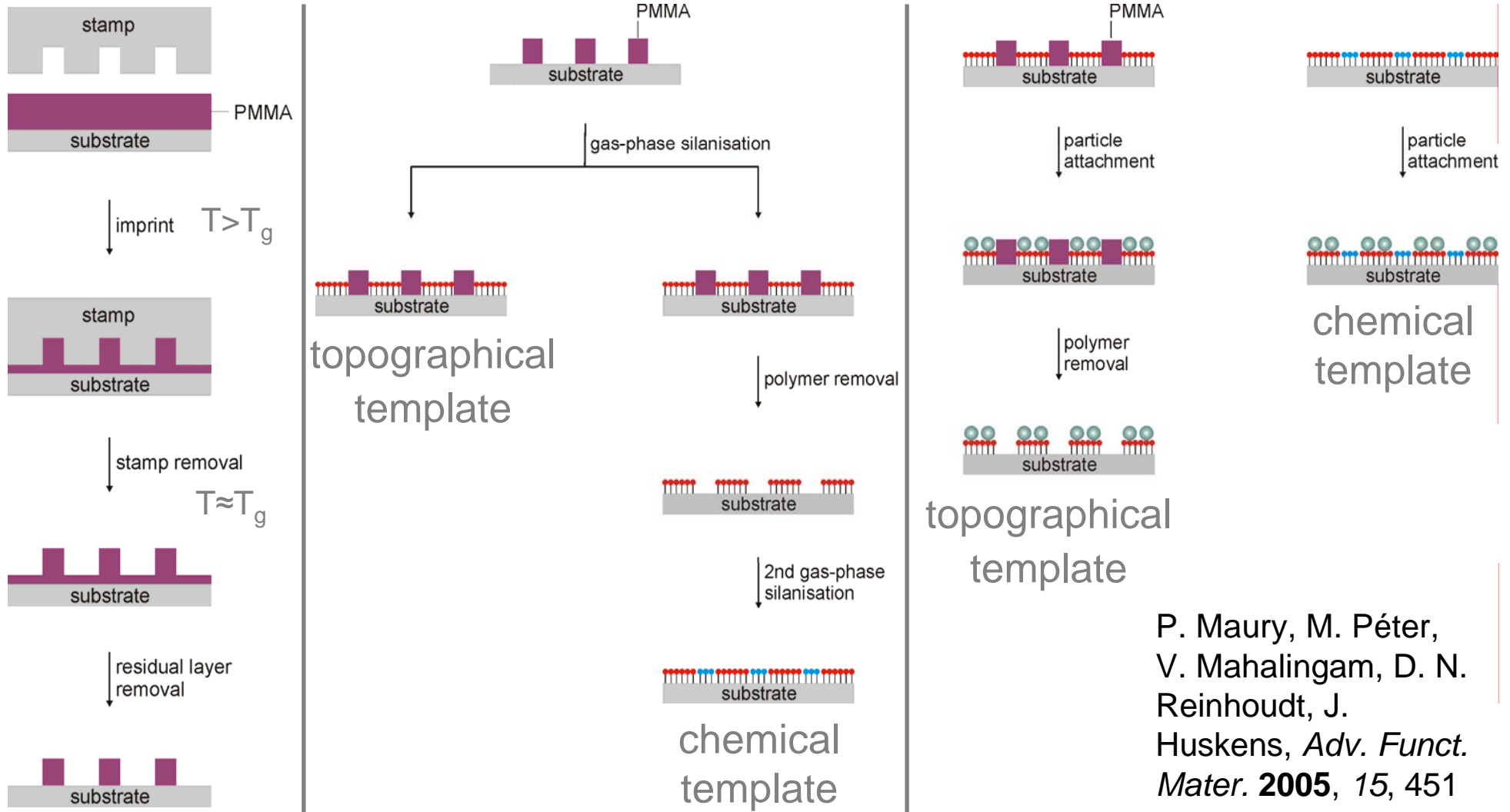
AFM height image  
(60 x 60  $\mu\text{m}^2$ )  
4 bilayers: 14 nm

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



# Directed nanoparticle assembly on NIL templates

Nanofabrication scheme including NIL and directed nanoparticle deposition:

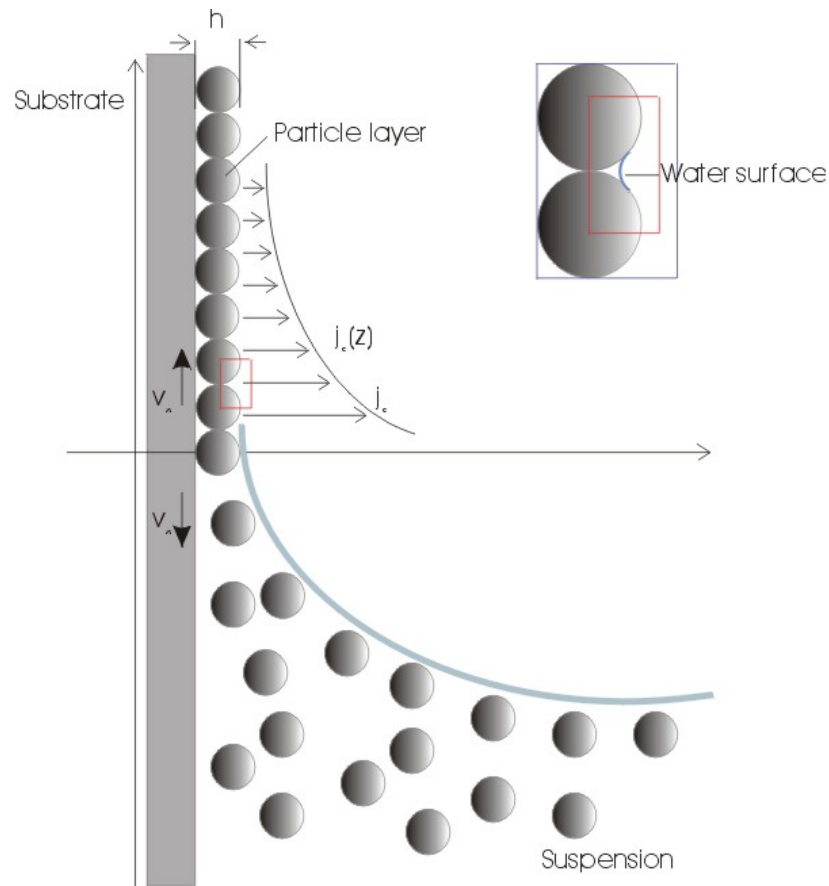


P. Maury, M. Péter,  
V. Mahalingam, D. N.  
Reinhoudt, J.  
Huskens, *Adv. Funct.  
Mater.* **2005**, 15, 451

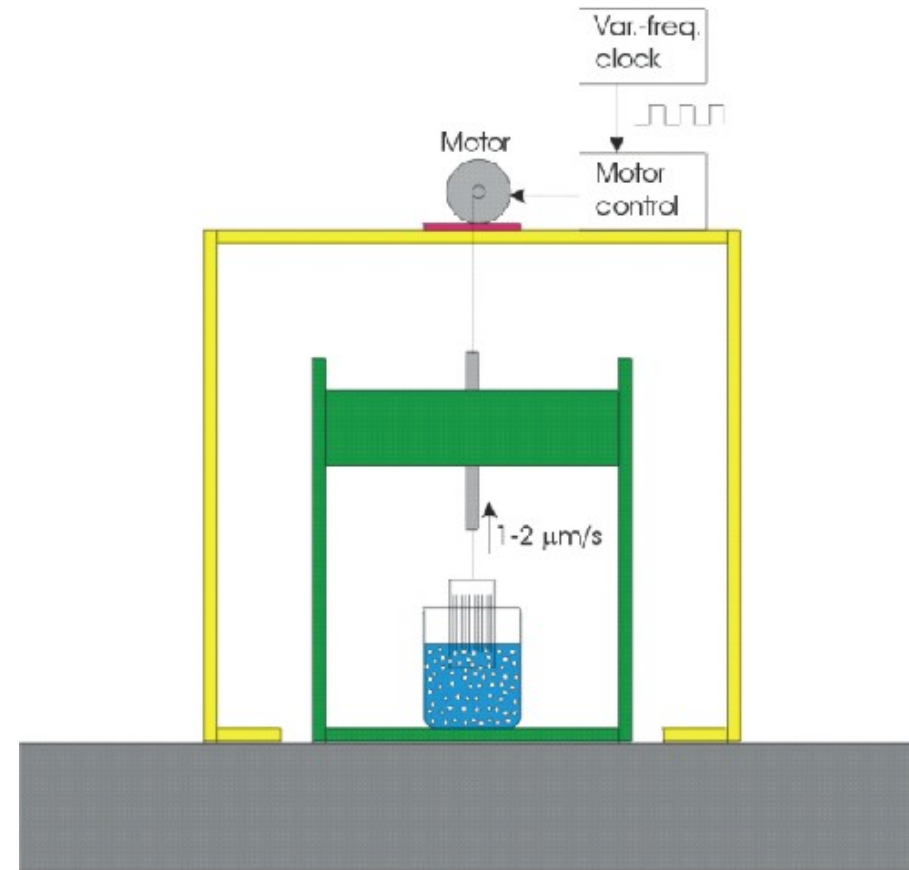


## Directed nanoparticle assembly on NIL templates

Improved particle deposition process: **controlled wetting and capillary forces:**



physical principle



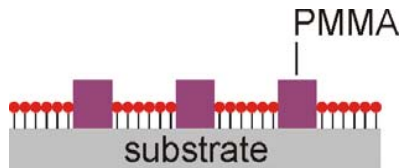
vertical NP deposition tool



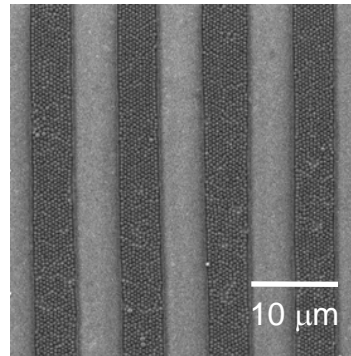
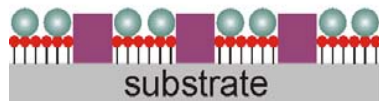


# Directed nanoparticle assembly on NIL templates

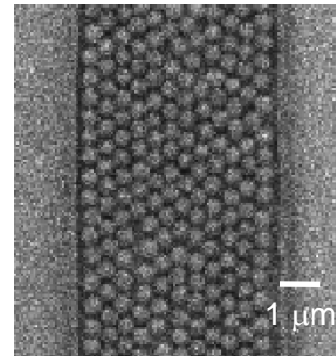
Particle adsorption **in PMMA templates** using **vertical colloidal deposition**:



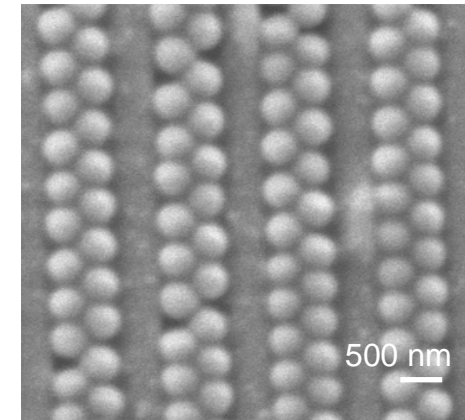
particle attachment



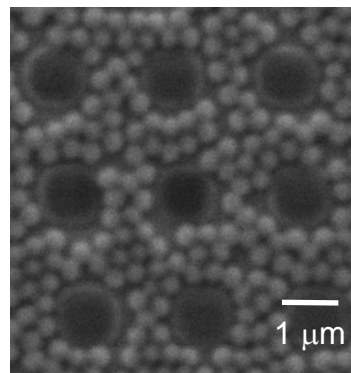
5  $\mu\text{m}$  lines



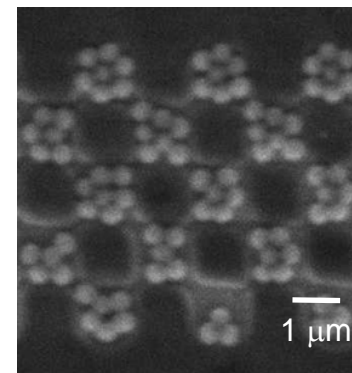
1  $\mu\text{m}$  holes



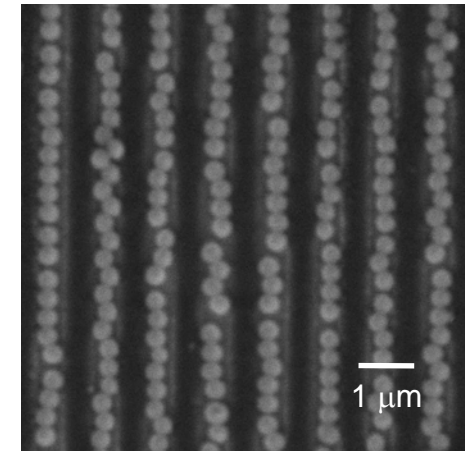
600 nm lines



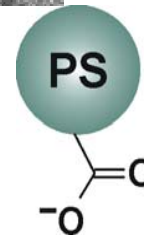
1  $\mu\text{m}$



1  $\mu\text{m}$



500 nm lines

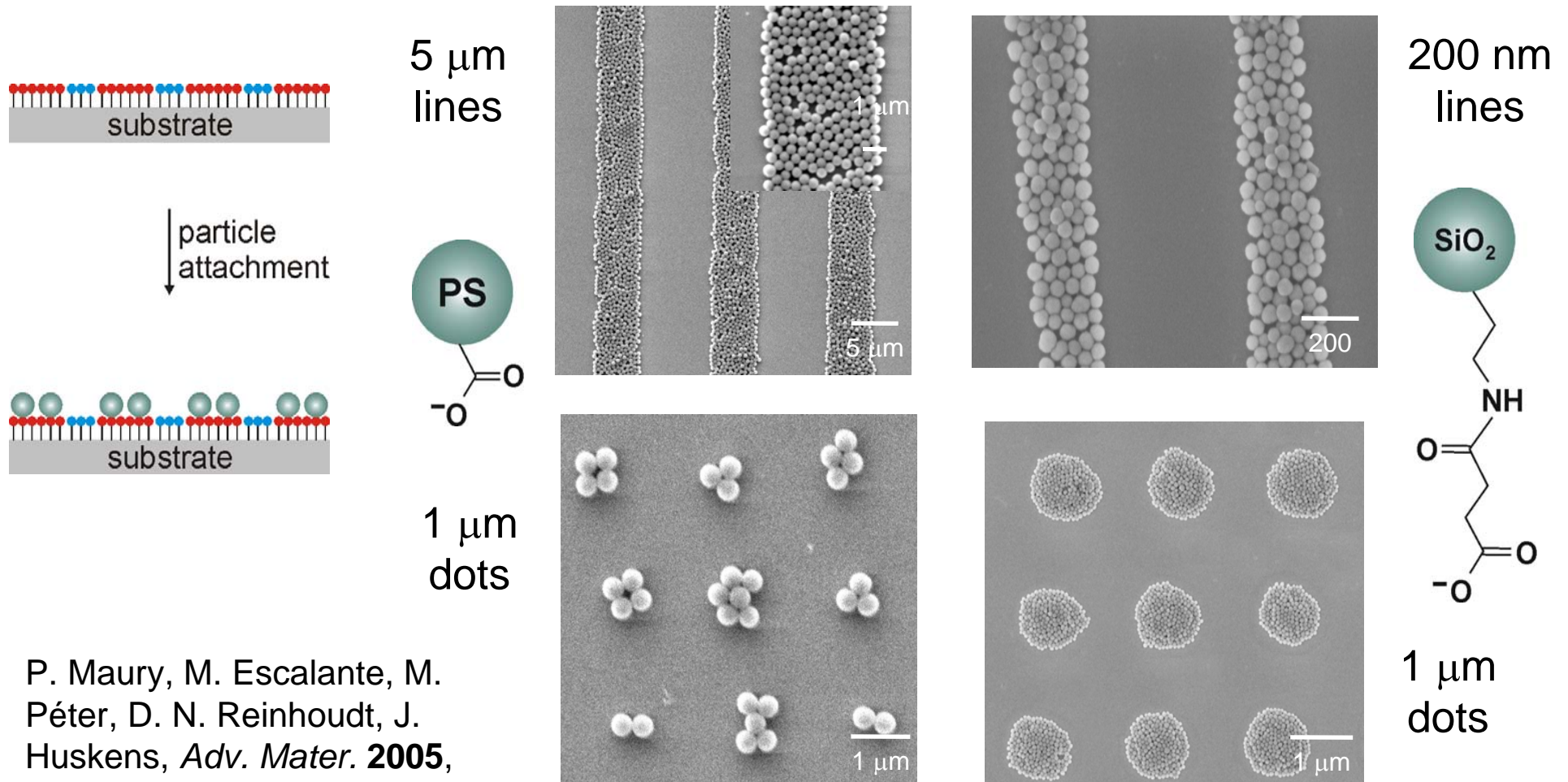


P. Maury, M. Escalante, M. Péter, D. N. Reinhoudt, J. Huskens, *Adv. Mater.* **2005**, *17*, 2718



# Directed nanoparticle assembly on NIL templates

Particle adsorption on NIL-patterned SAMs using vertical colloidal deposition:

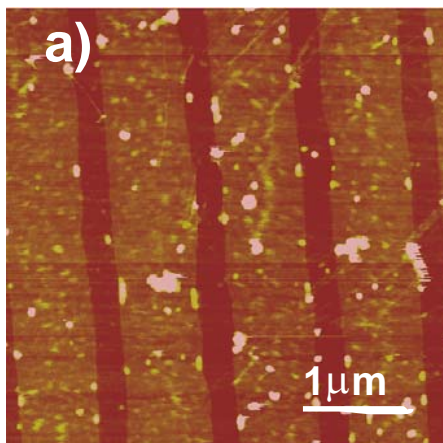
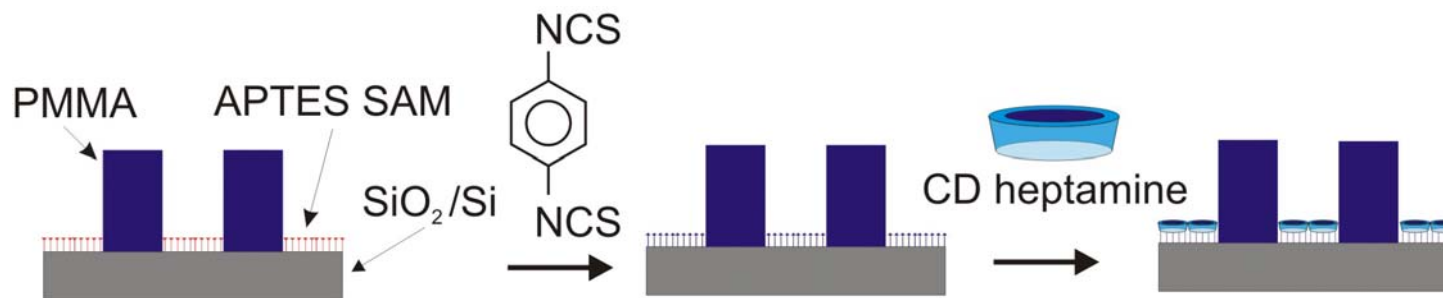


P. Maury, M. Escalante, M. Péter, D. N. Reinhoudt, J. Huskens, *Adv. Mater.* **2005**, *17*, 2718

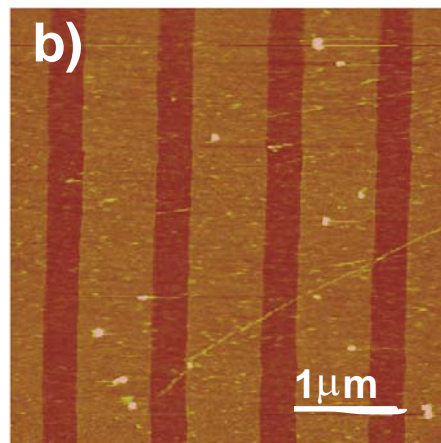


## NIL-patterned molecular printboards

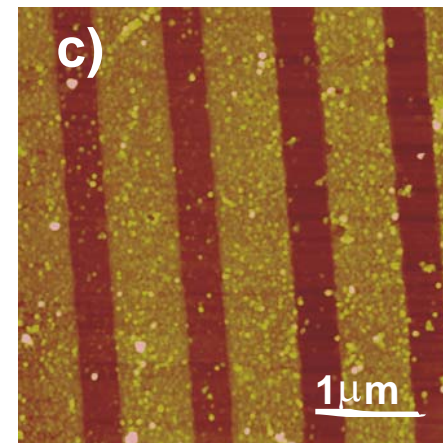
NIL-patterned CD monolayers on SiO<sub>2</sub>:  
templates for **multivalent supramolecular adsorption**:



AFM height: 0.9 nm  
(after polymer removal)



0.9 nm



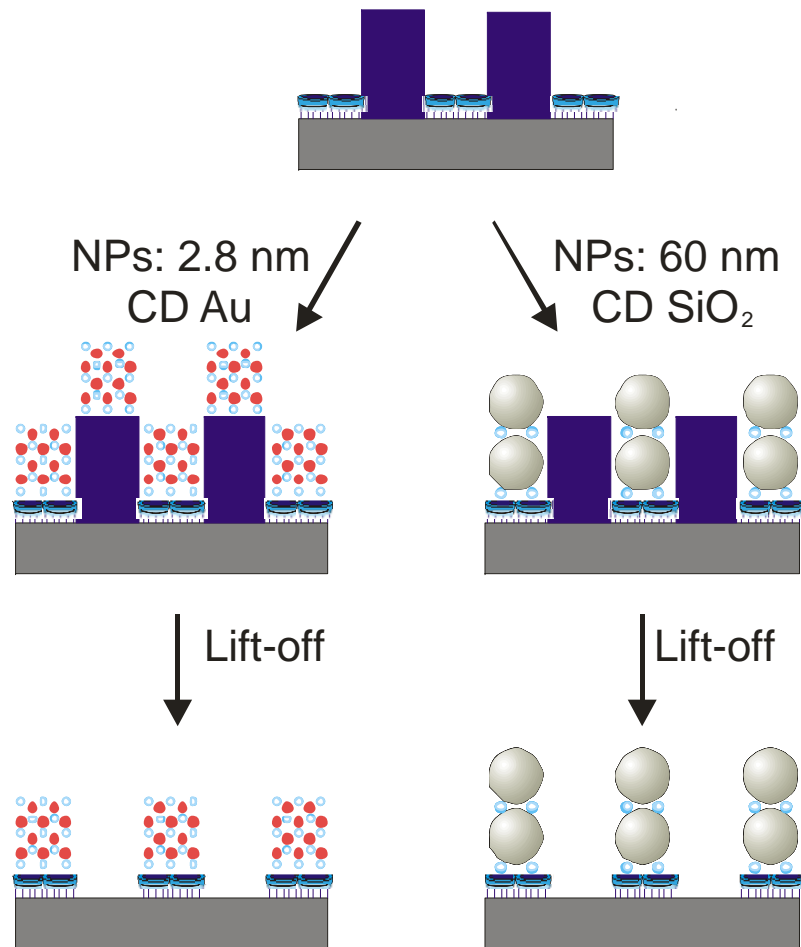
2.8 nm

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:



=



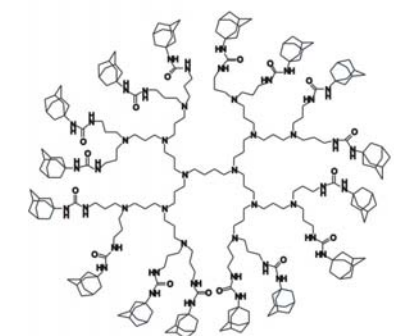
2.8 nm CD Au NPs



=



60 nm CD SiO<sub>2</sub> NPs



=



Ad Dendrimers

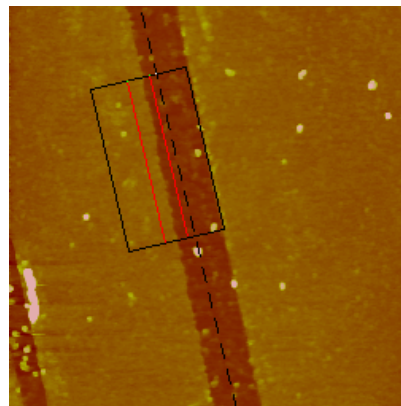
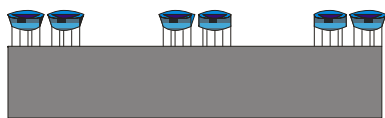
P. Maury, M. Péter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Nanotechnology* **2007**, *18*, 044007



## 3D Supramolecular materials

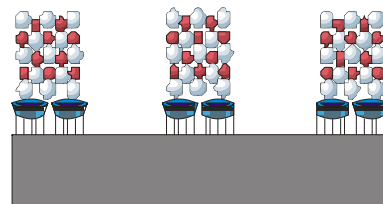
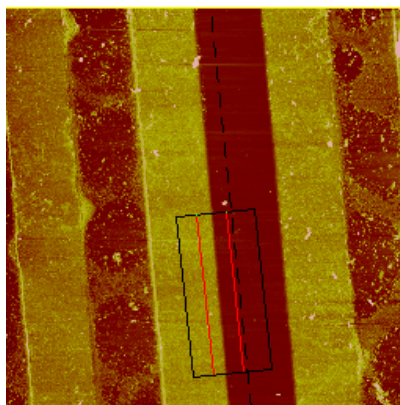
NIL-patterned polymer masks for directed LBL: results:

NIL-patterned CD SAMs:

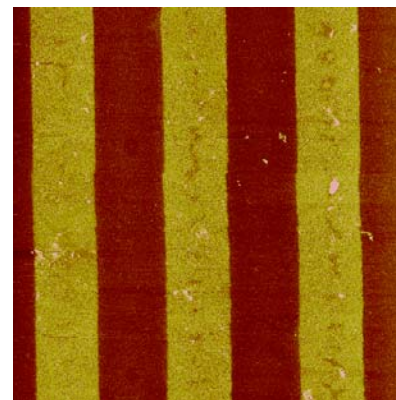


AFM height image  
(8 x 8  $\mu\text{m}^2$ )  
no bilayers: 2 nm  
(7 process steps)

NIL-patterned CD SAMs followed by LBL, then polymer removal:



AFM height image  
(30 x 30  $\mu\text{m}^2$ )  
2 bilayers: 6 nm



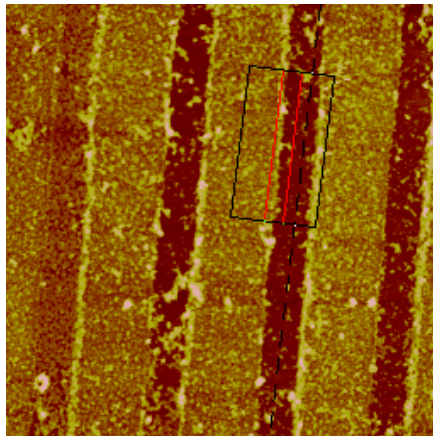
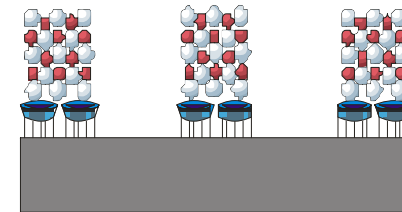
AFM height image  
(30 x 30  $\mu\text{m}^2$ )  
4 bilayers: 10 nm  
(15 process steps!)



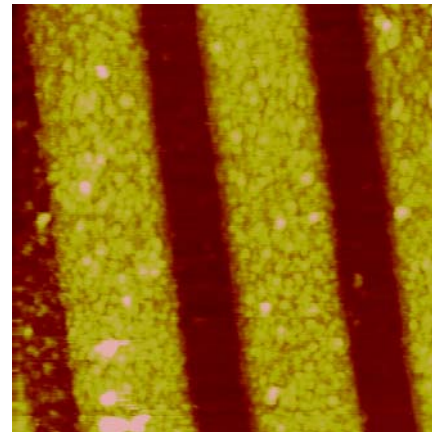
## 3D Supramolecular materials

NIL-patterned polymer masks for directed LBL: results:

NIL-patterned CD SAMs followed by LBL:  
submicron patterns:



AFM height image  
(4 x 4  $\mu\text{m}^2$ )  
2 bilayers: 5 nm  
line width: 700 nm



AFM height image  
(2.8 x 2.8  $\mu\text{m}^2$ )  
4 bilayers: 10 nm  
line width: 700 nm

15 process steps !

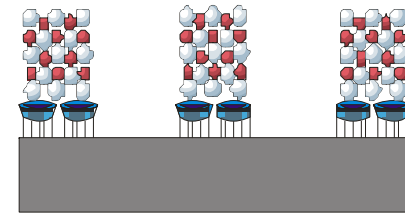
J. Huskens, P. Maury, O. Crespo-Biel, M. Péter, D. N. Reinhoudt, *Proceed. Instit. Mech. Engin. N: J. Nanoengin. Nanosys.* **2006**, 220, 157

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

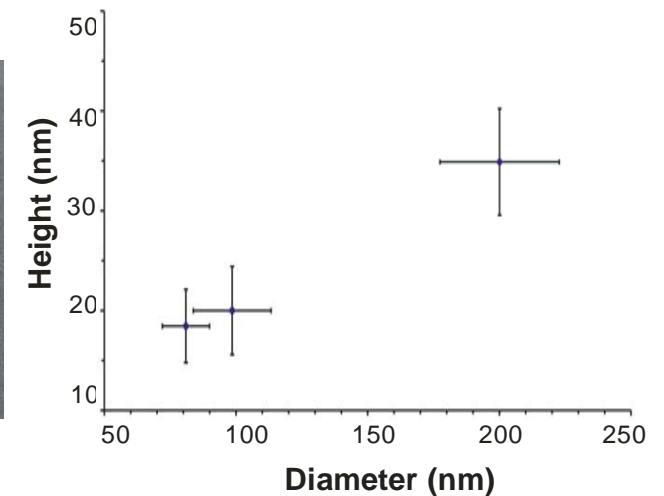
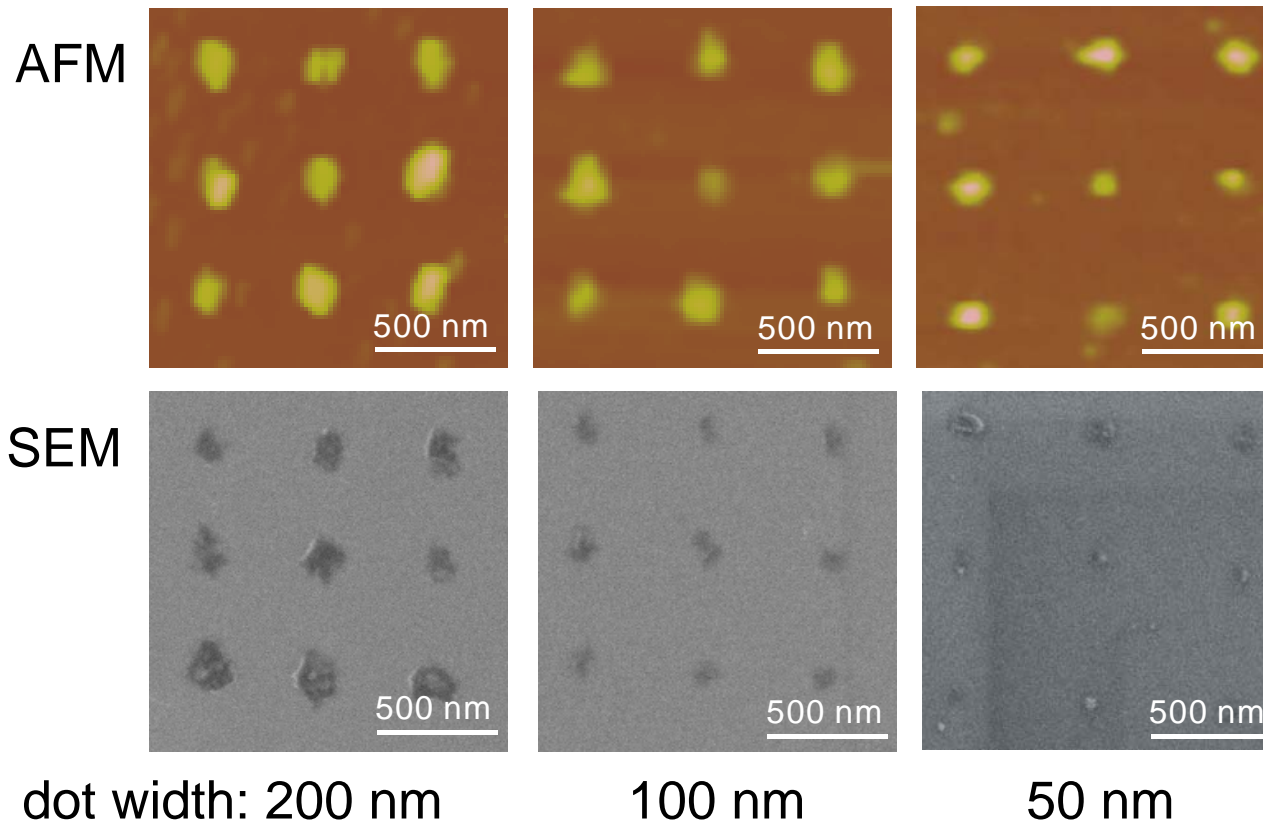


## 3D Supramolecular materials

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



15 bilayers:  
37 process steps !!



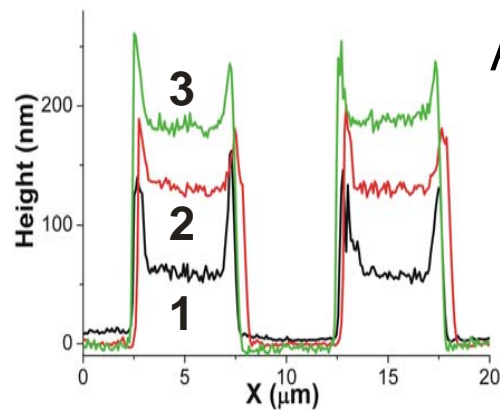
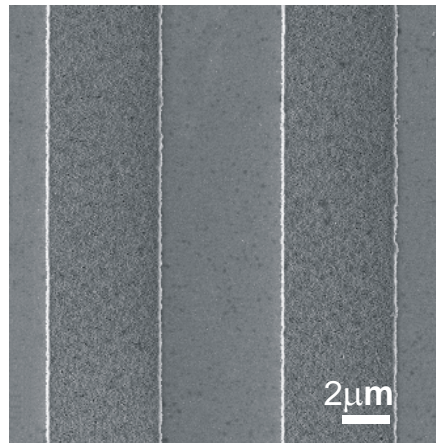
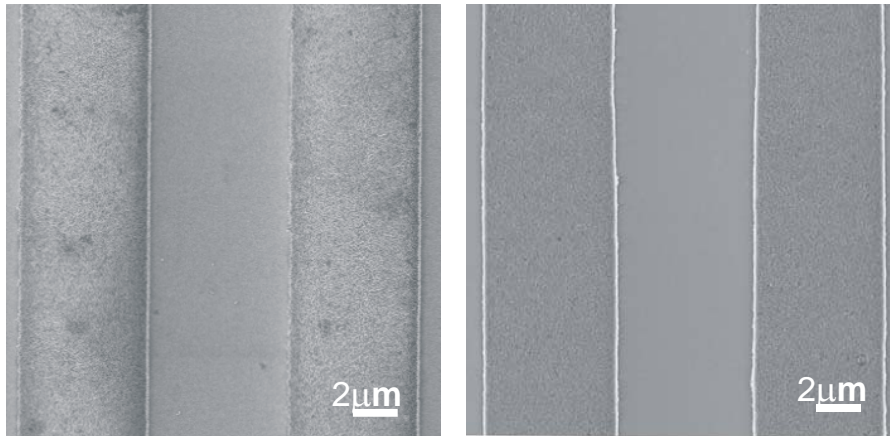
P. Maury, M. Péter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt,  
J. Huskens, *Nanotechnology* **2007**, 18, 044007



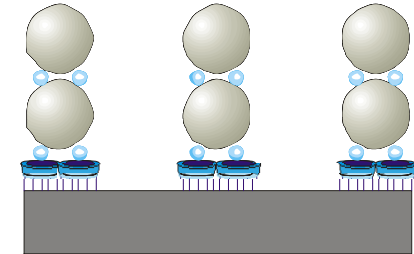
## 3D Supramolecular materials

**NIL-patterned polymer masks for directed LBL:**  
LBL with 60 nm CD SiO<sub>2</sub> NPs:

SEM



AFM



1-3 bilayers:  
height =  $n \times 60 \text{ nm}$

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



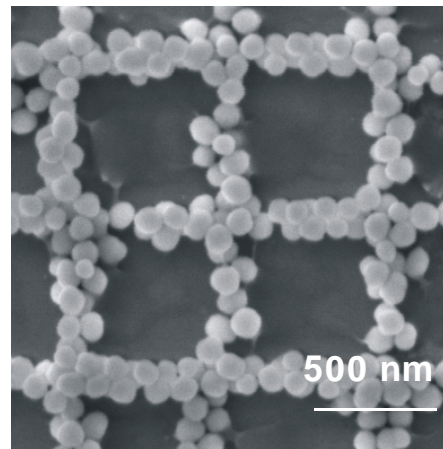
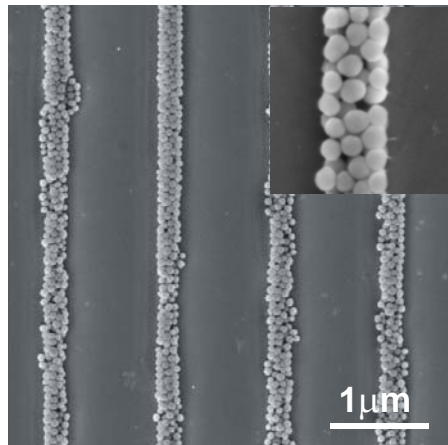


## 3D Supramolecular materials

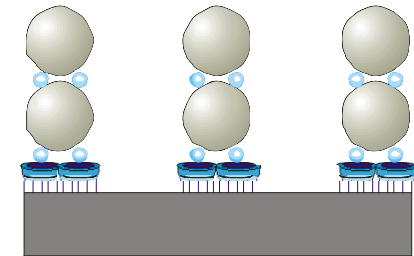
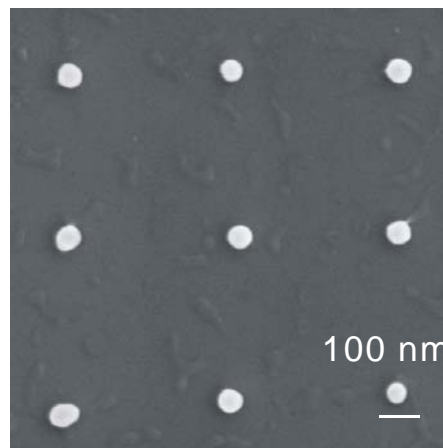
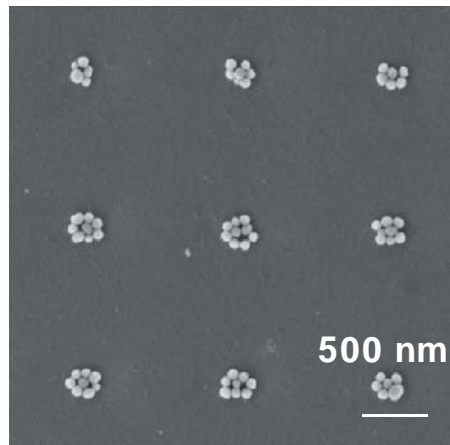
**NIL-patterned polymer masks for directed LBL:**

LBL with 60 nm CD SiO<sub>2</sub> NPs:

2 bilayers on  
line and grid  
patterns



1 bilayer on  
dot patterns



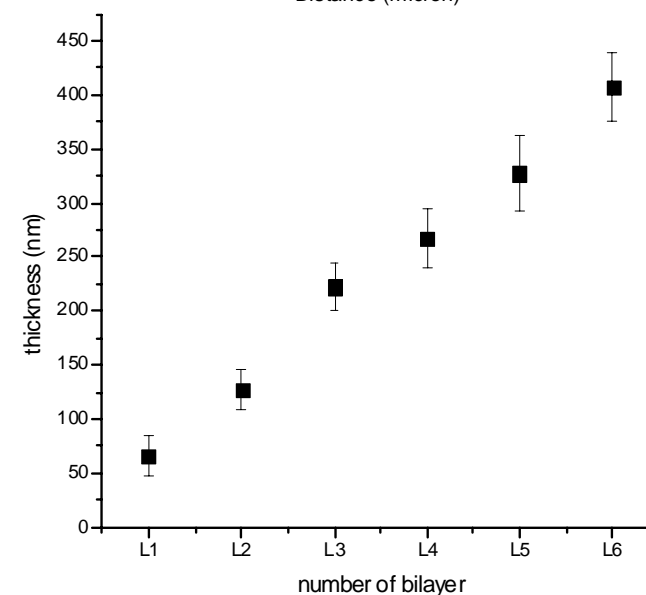
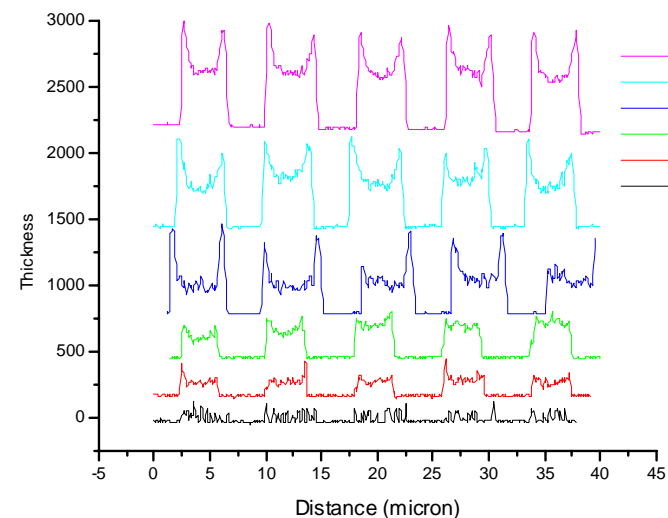
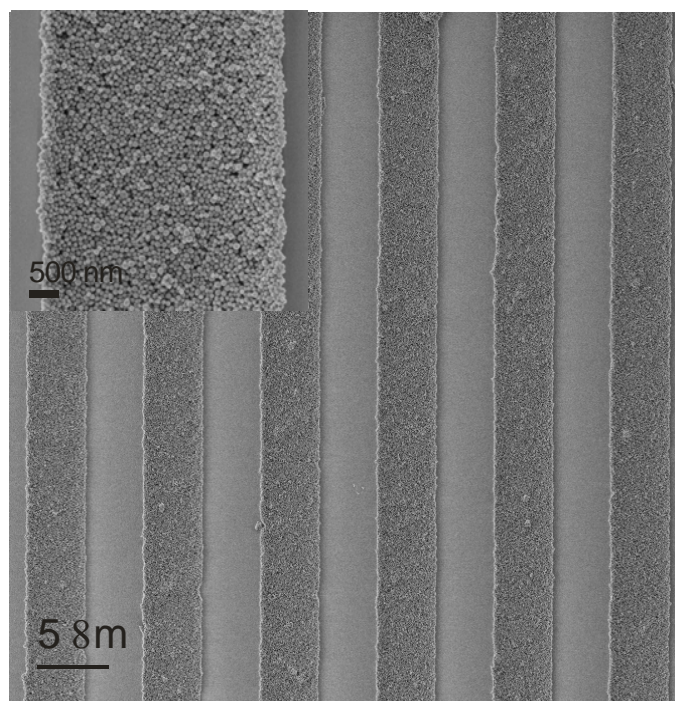
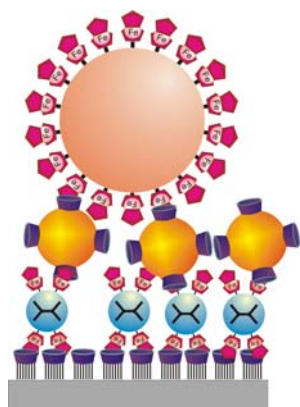
SEM

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



## 3D Supramolecular materials

NIL-patterned polymer masks for directed LBL:  
LBL with 3 nm CD Au and 60 nm Fc SiO<sub>2</sub> NPs:



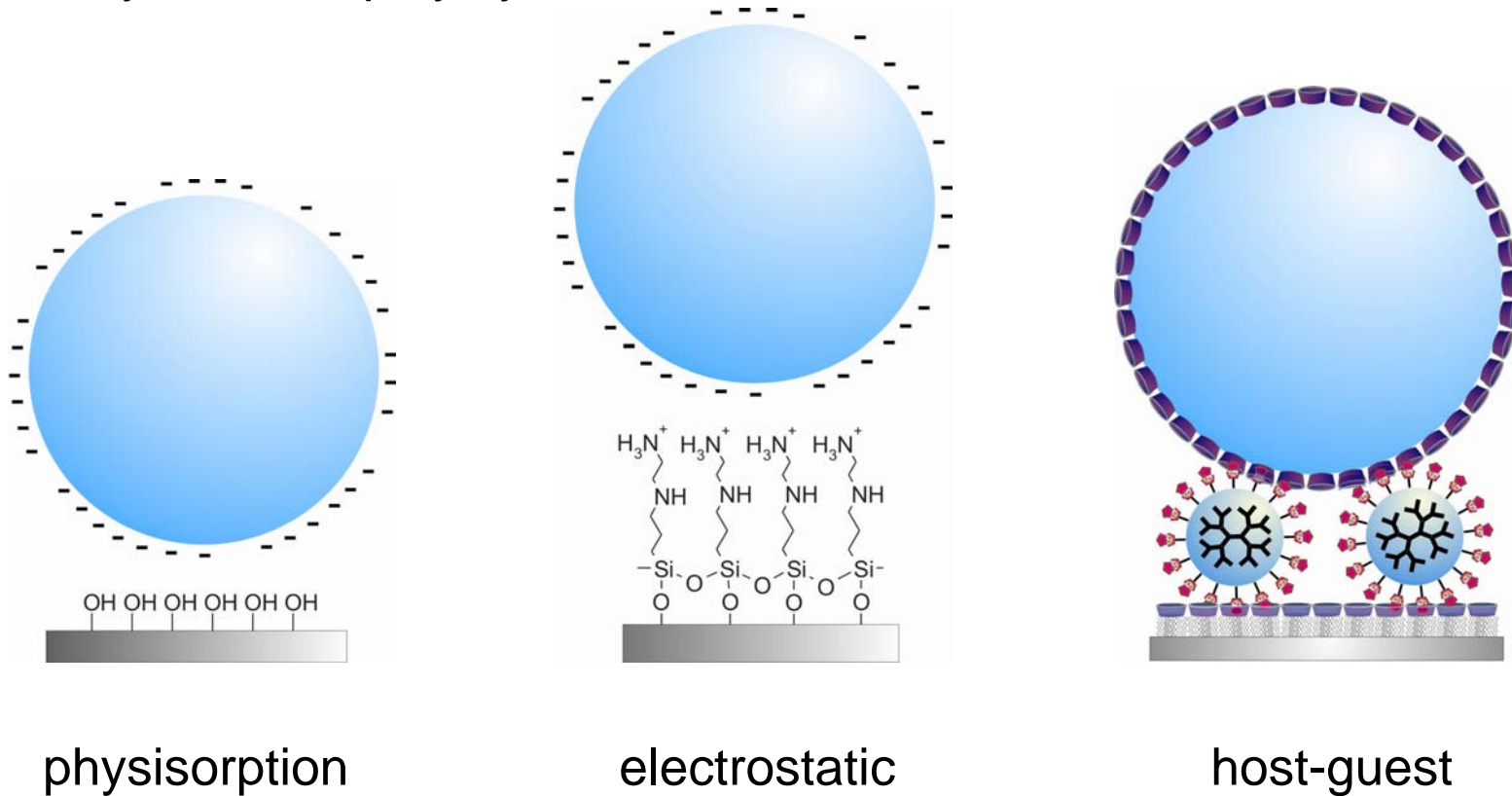
X. Y. Ling, I. Y. Phang, G. J. Vancso, D. N. Reinhoudt,  
J. Huskens, *Int. J. Mol. Sci.* **2008**, 9, 486



## 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:



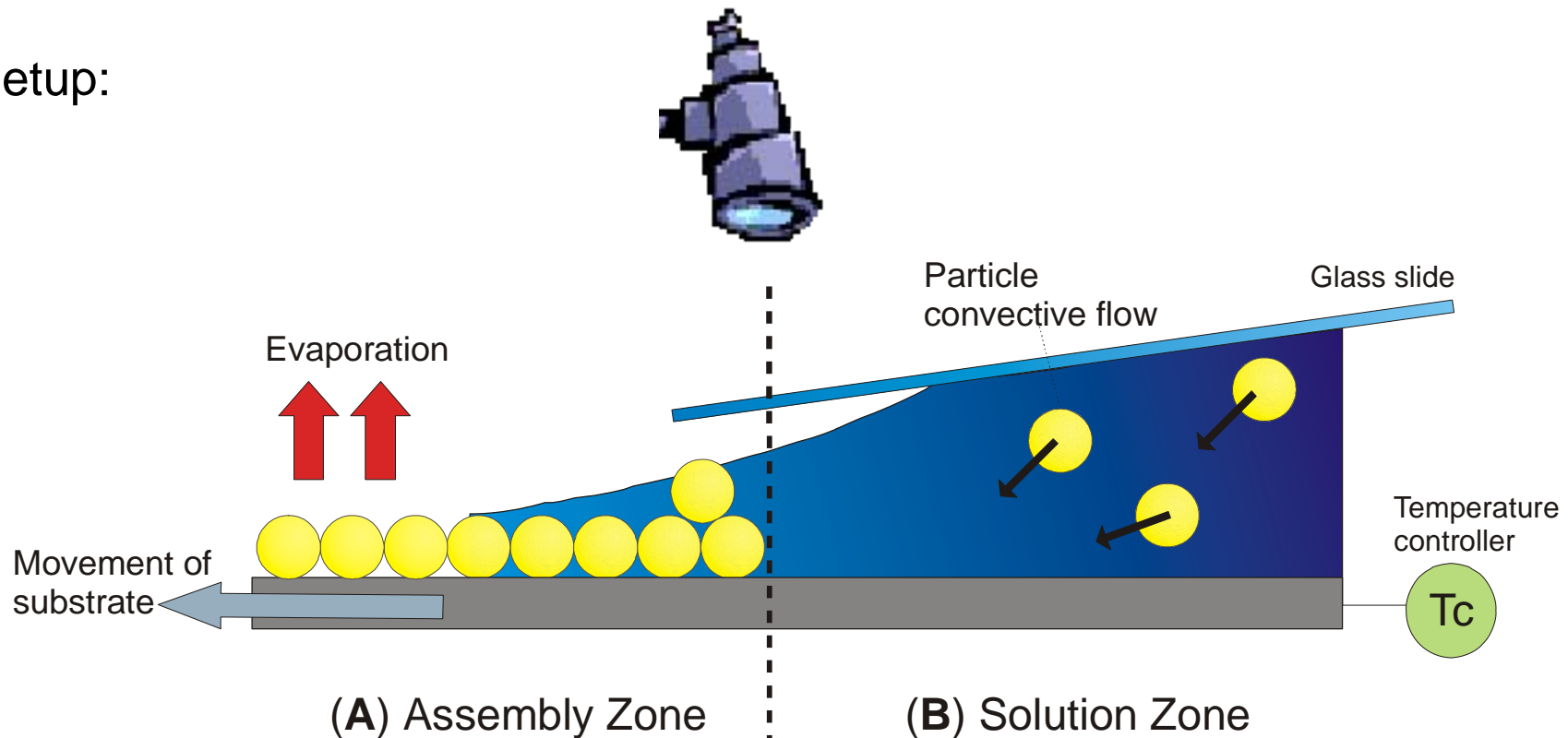
X. Y. Ling, L. Malaquin, D. N. Reinhoudt, H. Wolf, J. Huskens, *Langmuir* **2007**, 23, 9990



# Nanoparticle-substrate interface chemistry

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

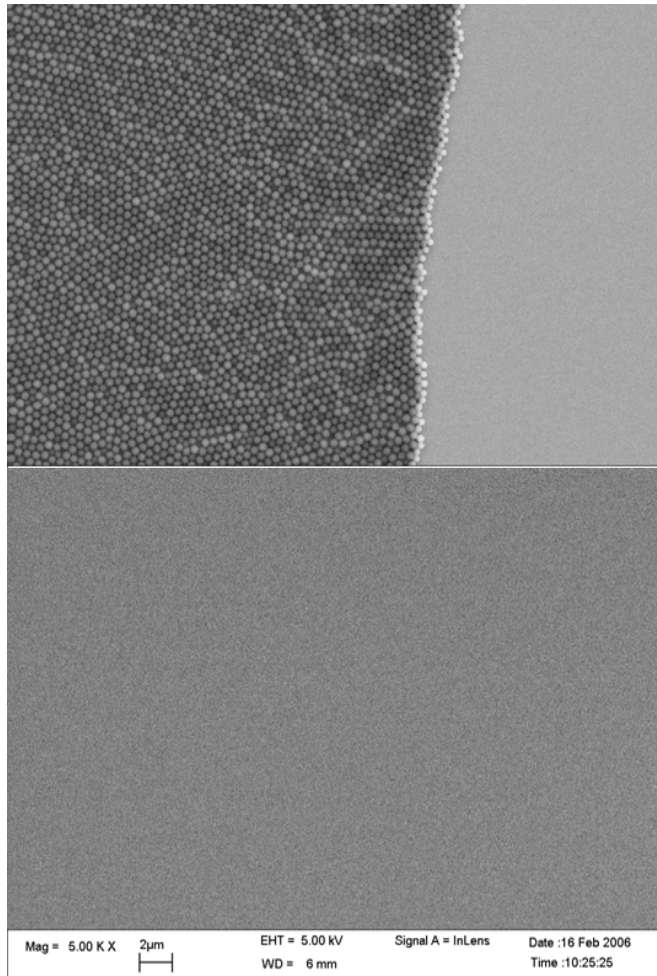
Setup:





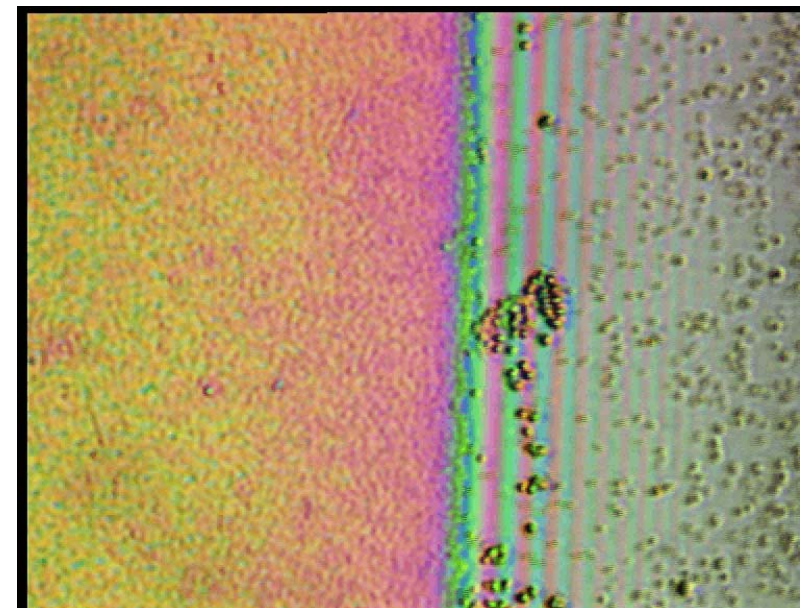
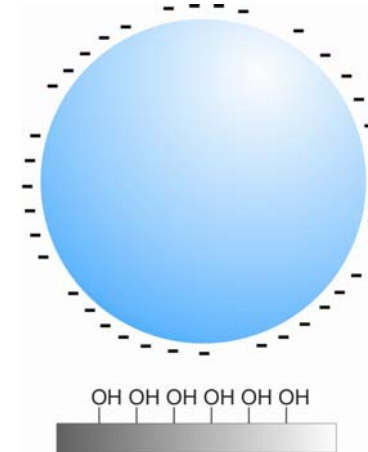
# Nanoparticle-substrate interface chemistry

**Physisorption:** PS-COOH NPs on clean SiO<sub>2</sub>:



Assembly zone

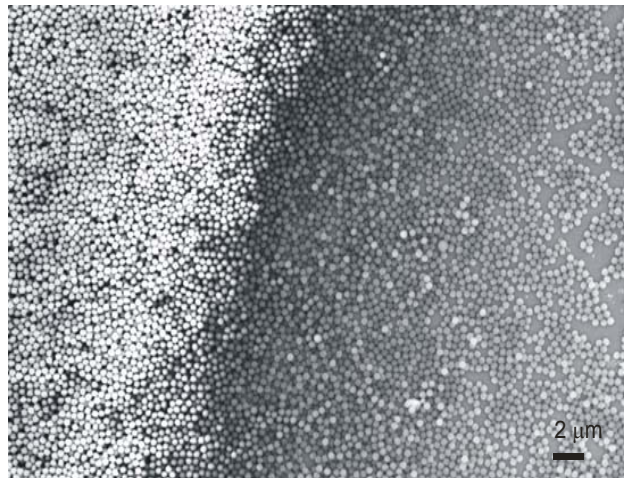
Solution zone



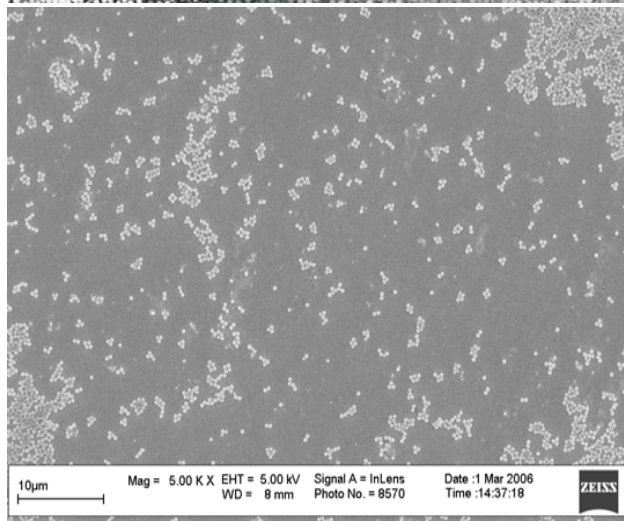
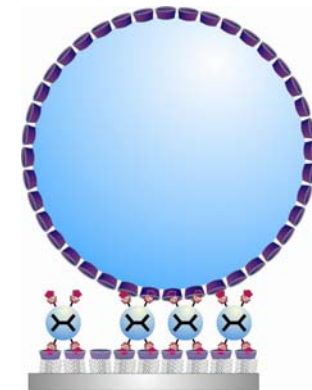


# Nanoparticle-substrate interface chemistry

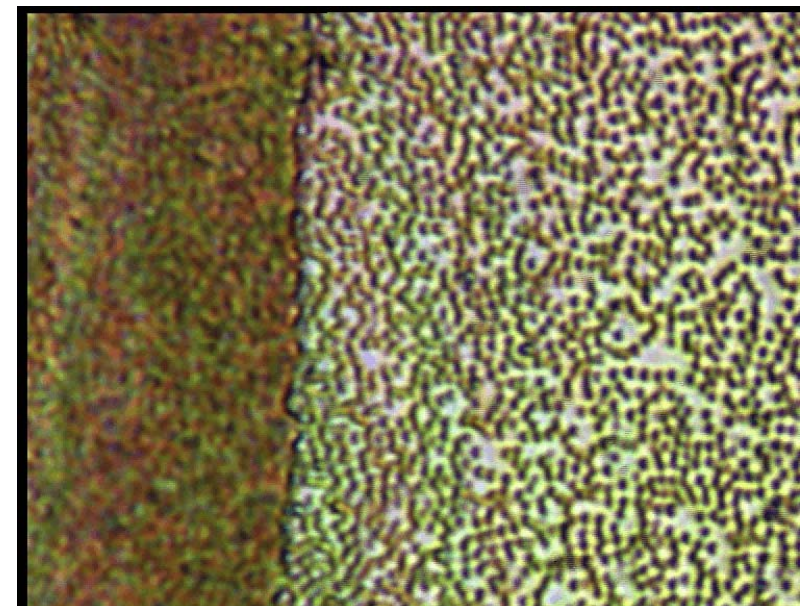
**Host-guest interaction:** PS-CD NPs on CD SAMs with G1 Fc dendrimers:



Assembly zone



Solution zone

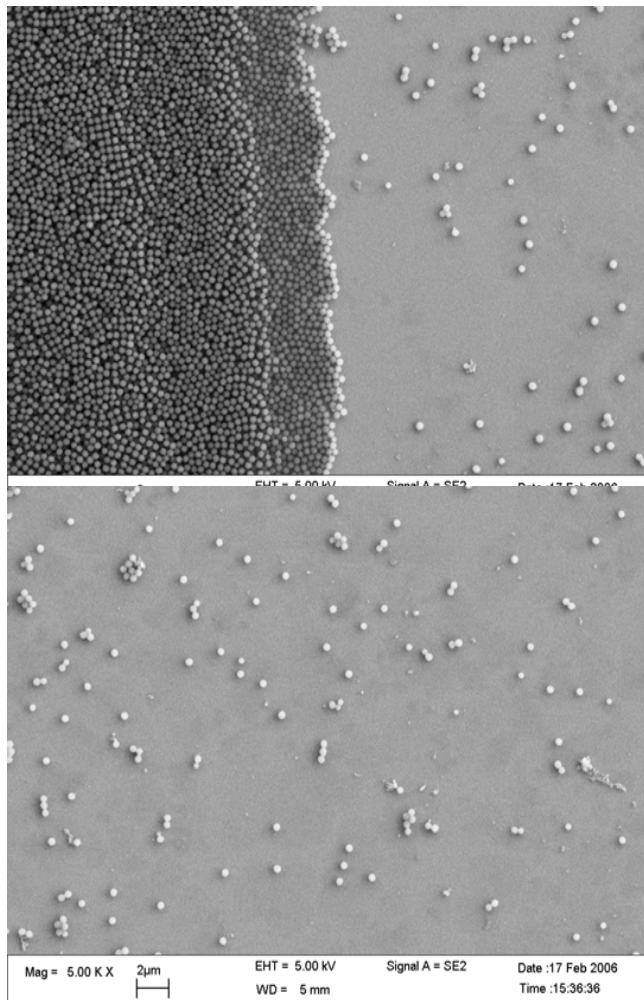




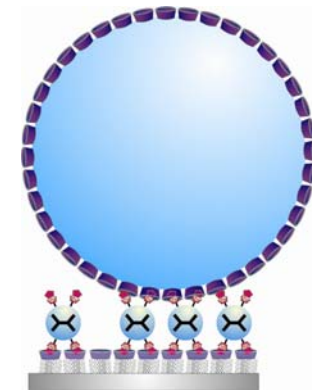
# Nanoparticle-substrate interface chemistry

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

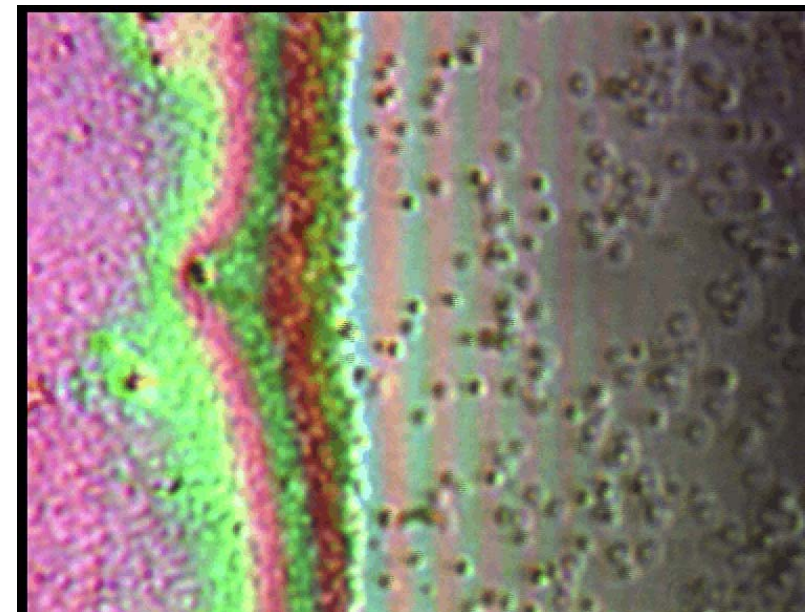
**competition** by CD in solution



Assembly zone



Solution zone



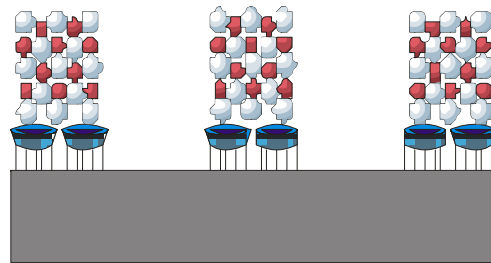


# Summary

Assembly: fundamental

Patterning:

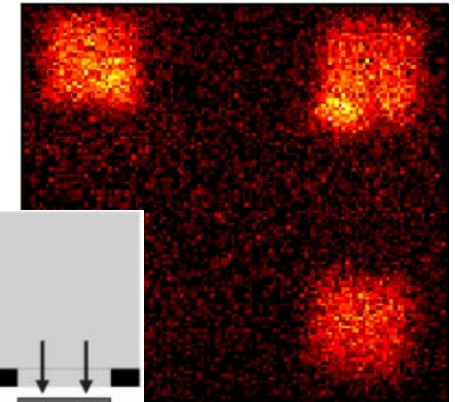
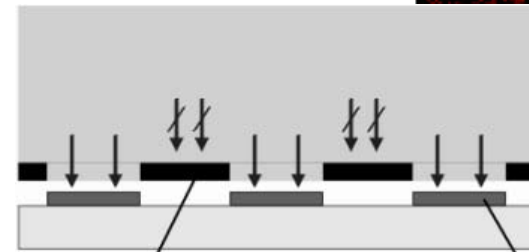
fundamental



3D nanostructures

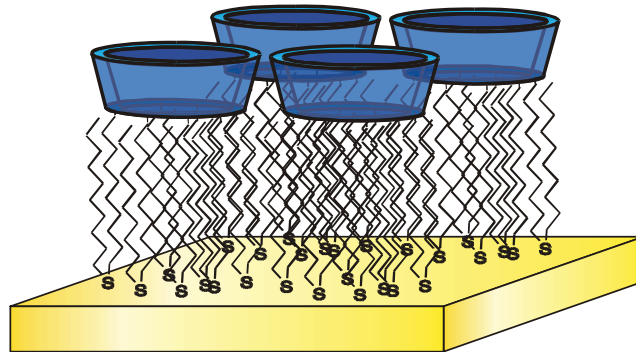
applied

flat stamps  
NIL patterning



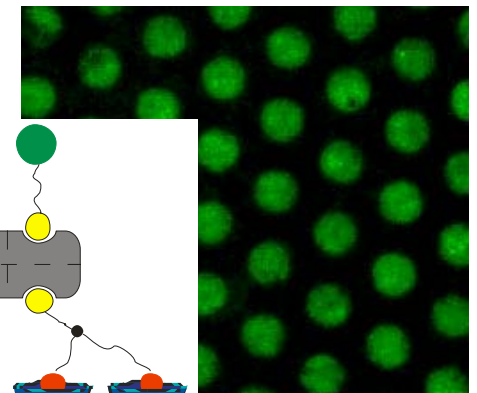
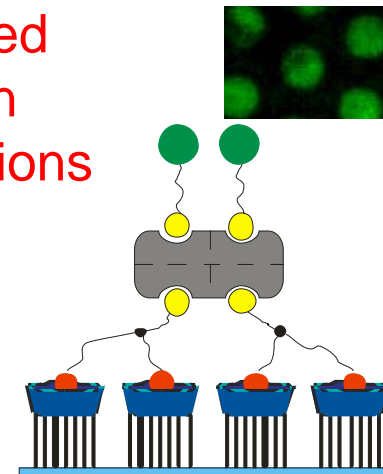
50  $\mu\text{m}$

applied



printboards, multivalency,  
supramolecular nanolithography

patterned  
protein  
constructions







## Acknowledgements



### Molecular Nanofabrication group:

Xing Yi Ling

Manon Ludden

Prof. David Reinhoudt

Dr. Olga Crespo-Biel

Dr. Pascale Maury

Dr. Maria Peter

Dr. Venkataramanan Mahalingam

Prof. Bart Jan Ravoo

IBM Zurich, Switzerland: Dr. Laurent Malaquin, Dr. Heiko Wolf

Transducer Science and Technology, MESA+, University of Twente:

Dr. Henri Jansen, Dr. Niels Tas, Prof. Miko Elwenspoek

Materials Science and Technology of Polymers, MESA+, University of Twente:

Dr. Mark Hempenius, Prof. G. Julius Vancso

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