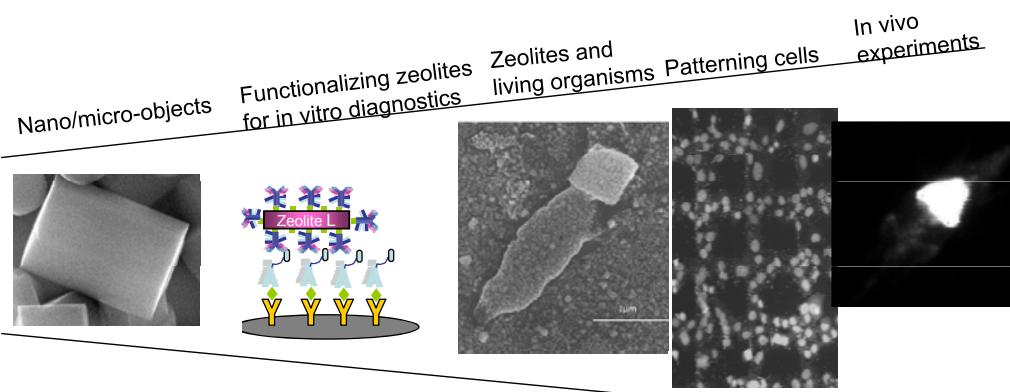


# Outline



## • 1756: A. F. Cronstedt

- History of zeolites starts with the discovery of Stilbite.
- Described behavior under fast heating conditions. The mineral seemed to boil because of the fast water loss.

$\zeta\epsilon\imath\nu$  = **zein** = to boil

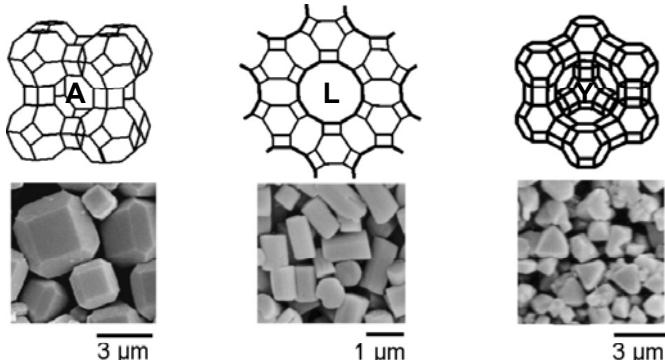
$\lambda\imath\vartheta\circ\varsigma$  = **lithos** = stone

→ **ZEOLITE**



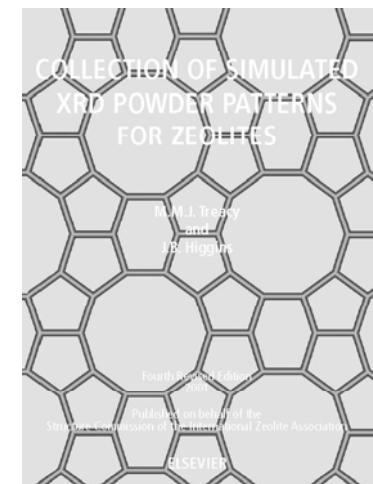
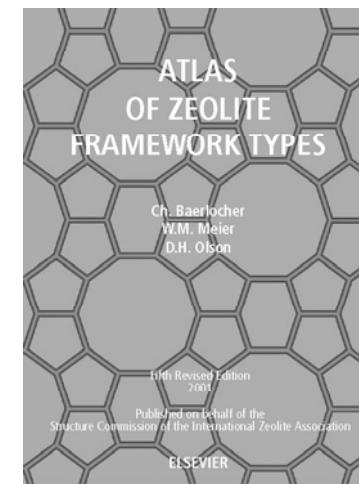
STILBITE:  
 $\text{NaCa}_2\text{Al}_5\text{Si}_{13}\text{O}_{36} - 14\text{H}_2\text{O}$

## Zeolites, a short introduction

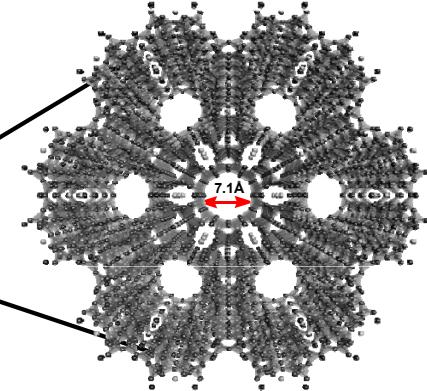
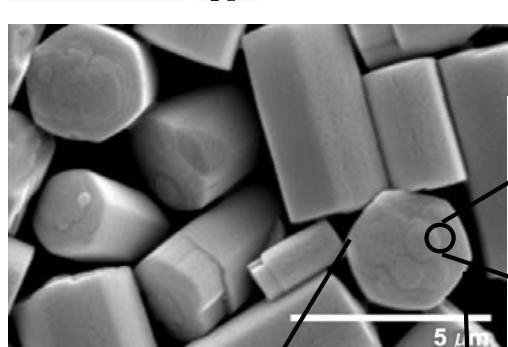


Zeolites are formed by the linking together tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  to give 3-dimensional anionic networks in which each oxygen of a given tetrahedron is shared between this tetra-hedron and one of the four others. Thus there are no unshared oxygen's in the frame- works. This means that  $(\text{Al} + \text{Si})\text{:O} = 1:2$ . For every  $\text{Si}^{+4}$  which is replaced in the framework by  $\text{Al}^{+3}$  a negative charge is created which is neutralized by a charge equivalent of cations. Additionally in zeolites but not in felspars the framework is sufficiently open to accommo-date water as well as cations. This openness imparts characteristic zeolite properties, e.g. their ability to lose and absorb water without damage to their crystal structures.

<http://www.iza-structure.org/databases>



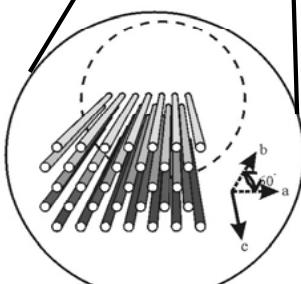
## Zeolites L, properties



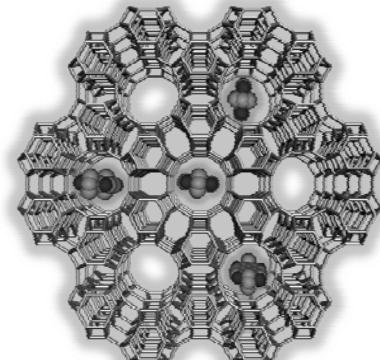
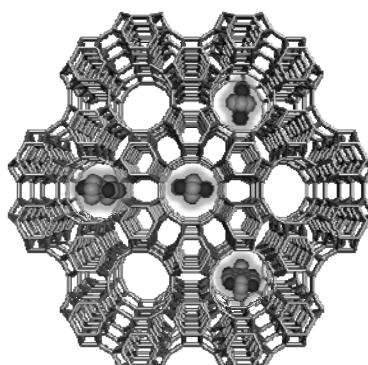
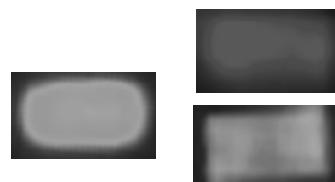
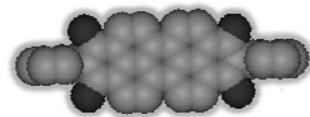
It belongs to the family of classical zeolites which are aluminosilicates.  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons are bridged three-dimensionally.

Zeolite L crystals consist of one-dimensional channels.

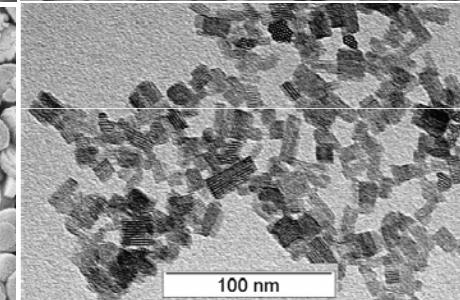
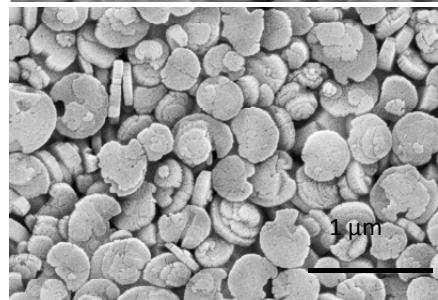
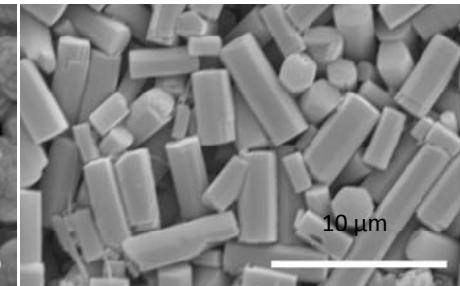
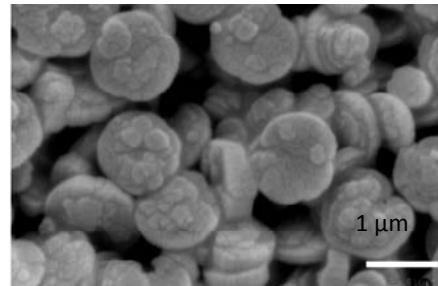
G. Calzaferri and N. Gfeller, J. Phys. Chem., **96** (1992) 3428  
G. Calzaferri, et. al. Angew. Chem. Int. Ed. **2003**, *42*, 3732.



## Inserting fluorescent molecules

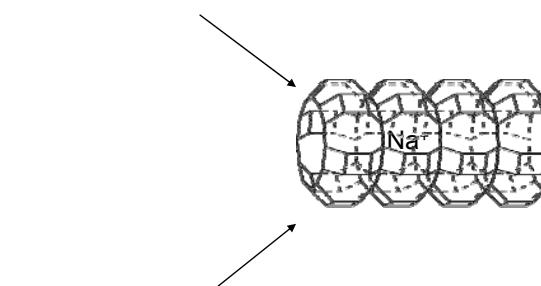
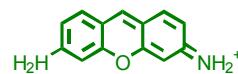


## Zeolite L Sizes and Shapes

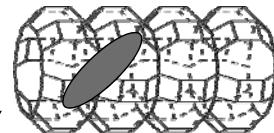


## Insertion of Molecules

### Ion Exchange



### Gas Phase



Molecules have preferred orientations and emission is polarised....

# Optical Imaging

- Confocal Microscopy

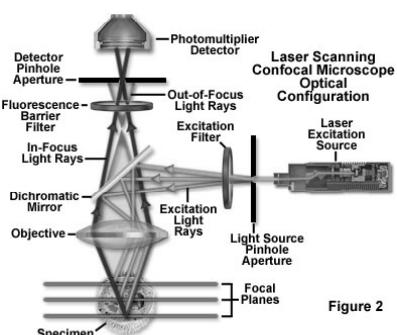
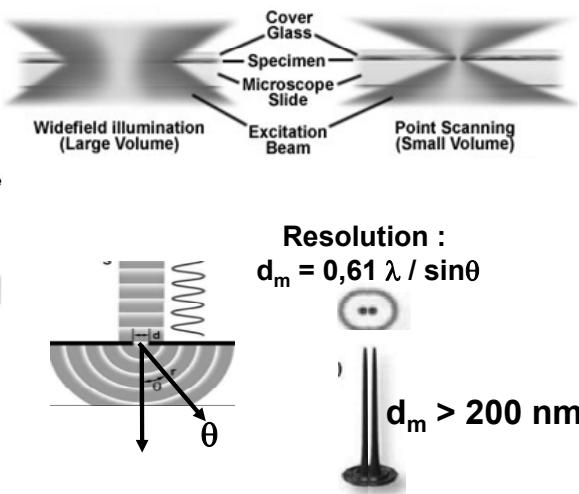
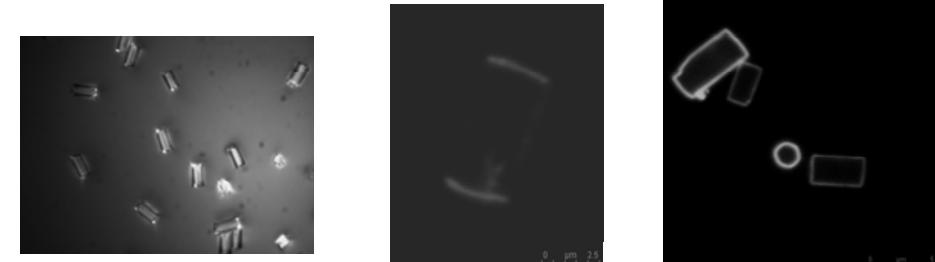


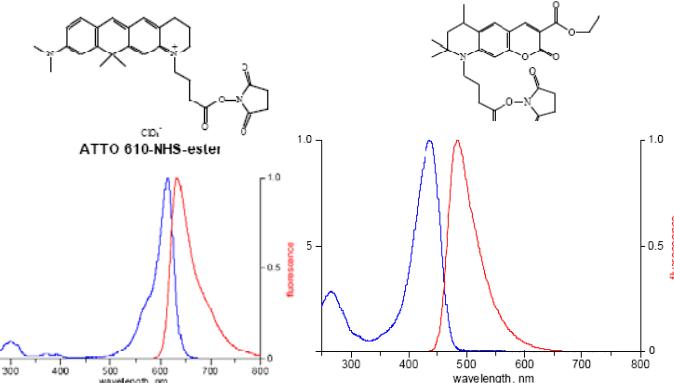
Figure 2



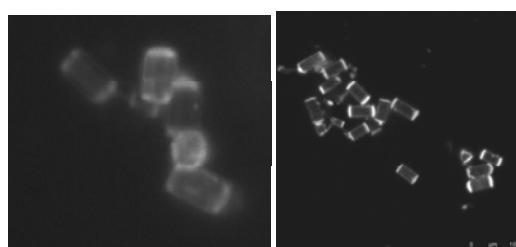
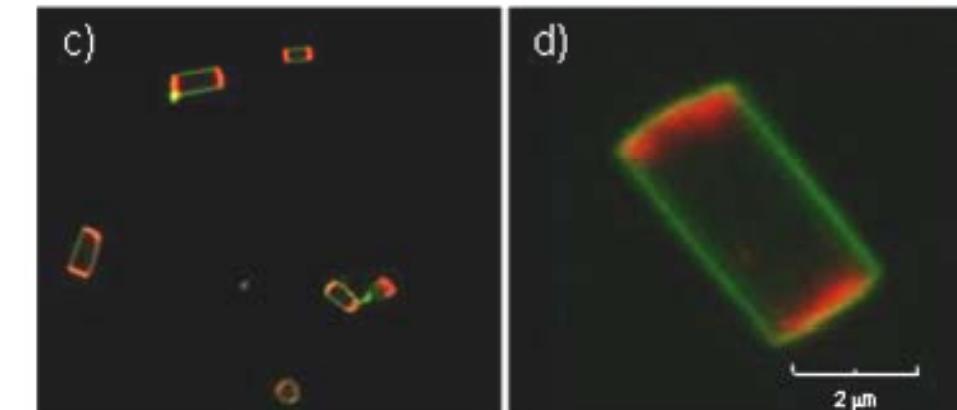
# Functionalization of Zeolites L



M. Busby, H. Kershbaum



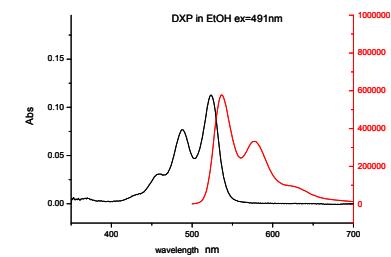
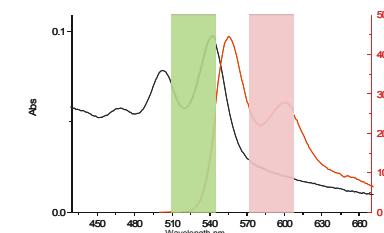
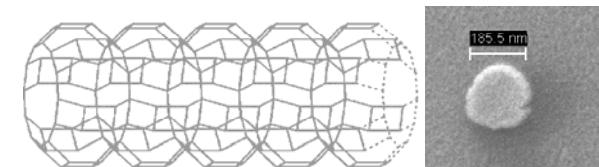
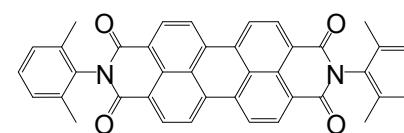
# Orthogonal functionalization



M. Busby, H. Kerschbaumer,  
G. Calzaferri, L. De Cola  
*Adv. Mat.*, **2008**, *20*, 1614.

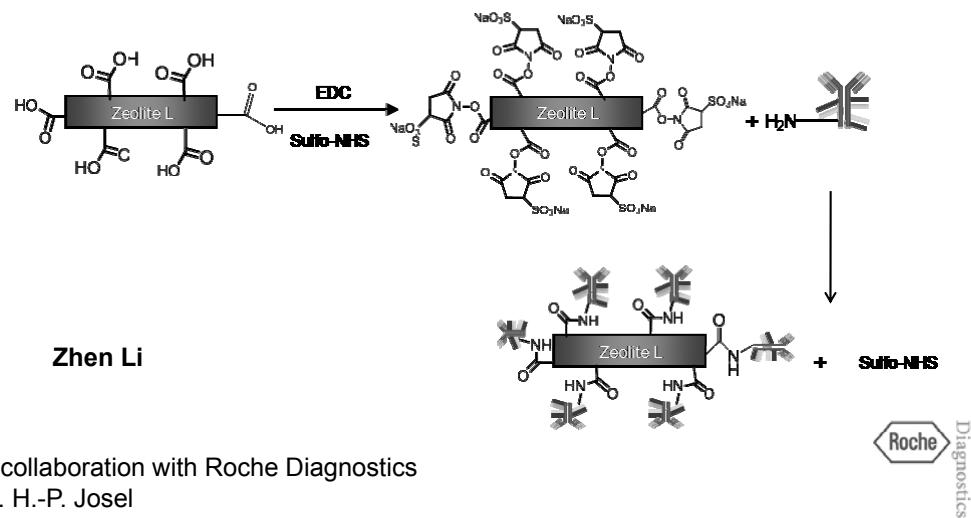
# DXP Filled Zeolites L

## DXP



## Zeolite L antibody (anti-dig) conjugates

Anti-DIGoxigenin (anti-DIG) and DIGoxigenin were chosen as universal immuno molecule pair for detection because of their high binding constant.



## Evaluation of Zeolite L antibody conjugates

Table 1 Fluorescent intensities of TSH immunoassay and calculated LDL values

TSH concentration $\mu\text{U}/\text{ml}$	Line1			Line2			Line3			Line4		
	mean counts	SD	CV	mean counts	SD	CV	mean counts	SD	CV	mean counts	SD	CV
control	10.76	3.52	32.74%	10.61	3.16	29.81%	12.91	2.67	20.68%	12.92	1.75	13.53%
0.046875	39.46	3.73	9.45%	38.72	2.79	7.20%	40.32	3.03	7.51%	37.10	2.53	6.83%
0.09375	39.6	6.02	15.20%	38.72	4.99	12.90%	40.38	2.77	6.87%	37.28	5.02	13.48%
0.125	110.68	5.34	4.83%	118.02	9.26	7.84%	113.22	10.83	9.57%	110.66	8.11	7.33%
0.1875	229.84	7.02	3.05%	238.20	9.42	3.95%	224.52	3.28	1.46%	211.80	4.26	2.01%
0.25	322.76	17.57	5.44%	342.72	22.35	6.52%	339.70	20.98	6.18%	307.88	12.40	4.03%
0.375	462.82	26.78	5.79%	474.22	21.37	4.51%	466.88	19.59	4.20%	425.44	21.12	4.97%
0.75	1181.46	60.71	5.14%	1235.56	72.13	5.84%	1,171.12	55.82	4.77%	1,090.94	52.87	4.85%
1.5	2374.58	112.32	4.73%	2,421.22	76.88	3.18%	2,325.46	61.46	2.64%	2,220.92	38.01	1.71%
LDL $\mu\text{U}/\text{ml}$	0.0042			0.0038			0.0033			0.0023		

The acronyms SD, CV and LDL represent standard deviation, coefficient of variation and lower detection limit. Mean counts represents fluorescent intensity.



## Evaluation of Zeolite L antibody conjugates

### On anti-TSH immobilized chip surface

TSH (Thyroid Stimulating Hormone) immunoassay which is useful in screening for both hyperthyroidism and hypothyroidisms, has been applied to evaluate the performance of this conjugate.

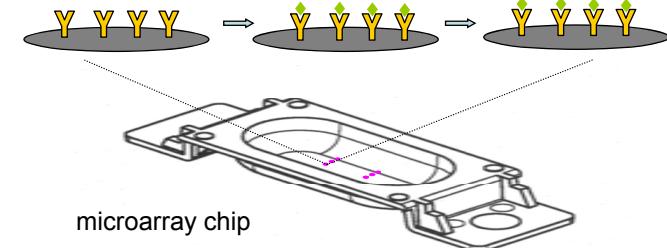
Y — Anti-TSH

♦ — TSH

— Anti-TSH and dig conjugates

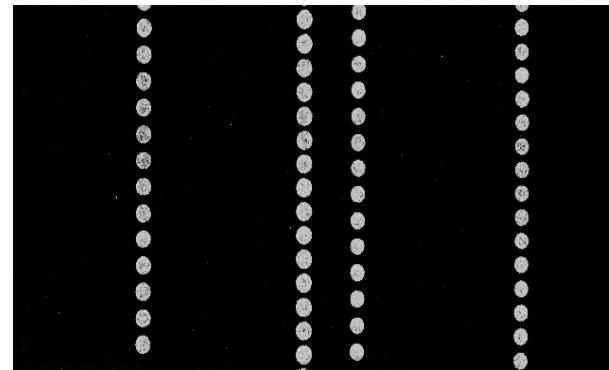
— Zeolite L

— Anti-dig zeolite L label



## Zeolite L antibody conjugates for microarrays

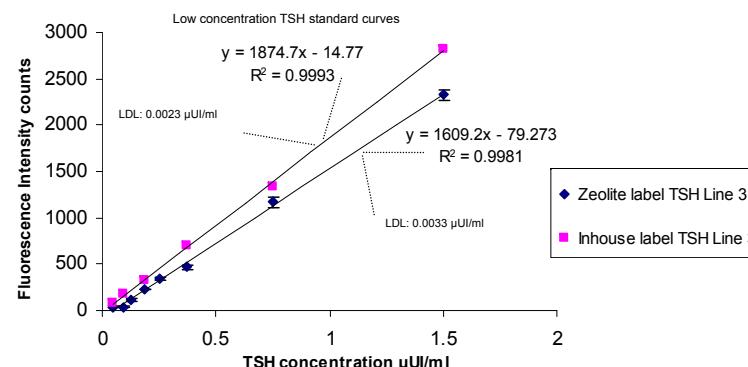
Fluorescent image of protein microarrays after probed with zeolite labels.



By varying the concentration of TSH while keeping the nanoparticle conjugate concentration constant, the standard calibration curve was obtained for each line

## Zeolite L antibody conjugates for microarrays

TSH assay Calibration curve of third line on the chips

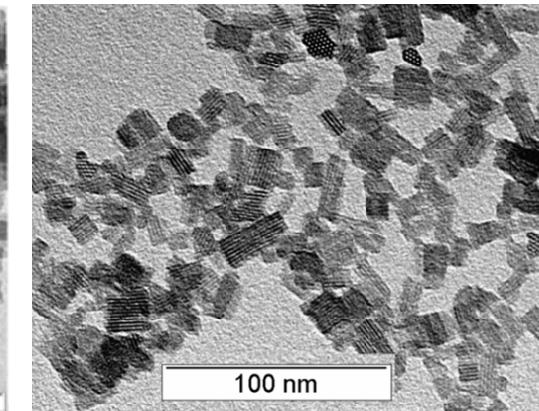
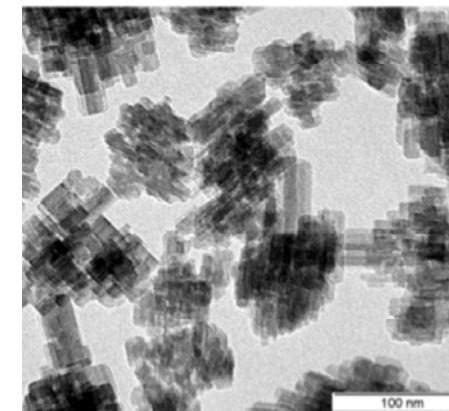


The coefficient of variation decreases as the analyte concentration increases.  
One of the most important parameter to evaluate an assay is lower detection limit (LDL), which is defined as:

$$\text{LDL} = 2 \times \text{standard deviation at zero concentration} / \text{slop of calibration curve}$$

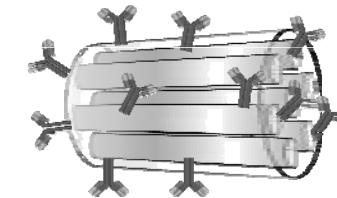
Z. Li, G. Luppi, A. Geiger, H.-P. Josel, L. De Cola submitted

## Nanozeolite Synthesis



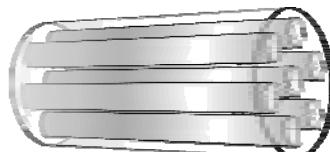
M. Tsotsalas, G. Luppi, U. Wiesner,  
L. De Cola to be submitted

In collaboration with Dr. Silvana Canevari  
Fondazione IRCCS  
Istituto Nazionale dei Tumori, Milano



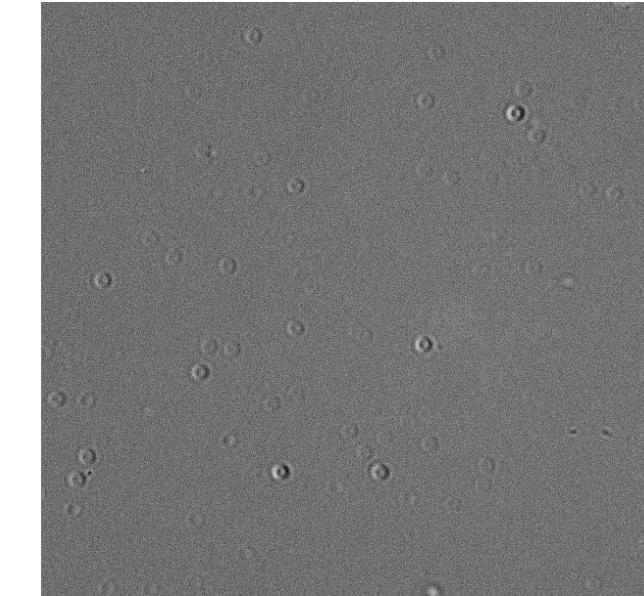
## Self-assembling zeolites and living systems

Could we imagine to have hybrid systems combining the material properties with living complex species?



Zoran Popovic and Matthias Otter

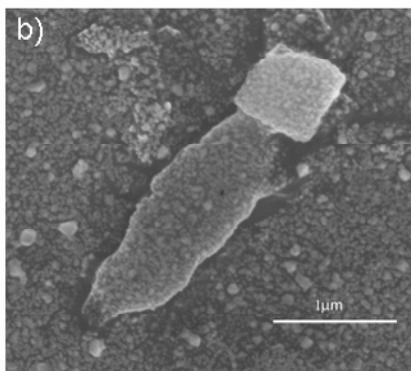
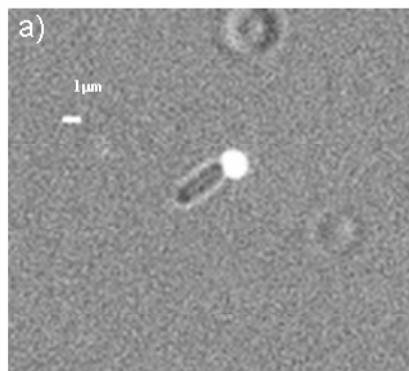
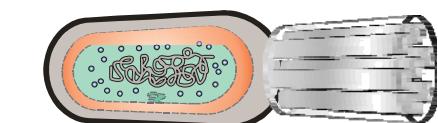
## Self-assembling zeolites and living systems



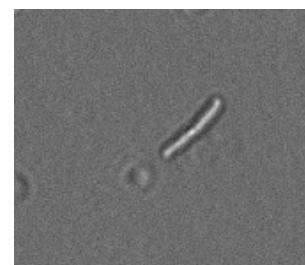
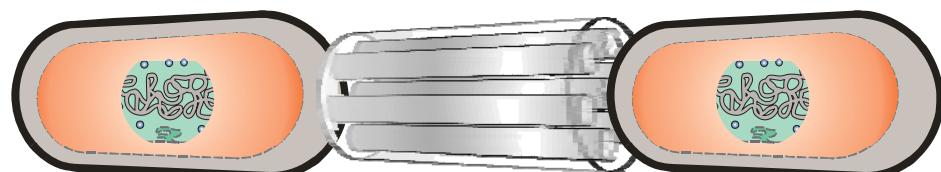
Z. Popovic, M. Otter, G. Calzaferri, L. De Cola *Angew. Chem. Int. Ed.* **2007**, *46*, 6188

Nanowissenschaftenpreis Z. Popovic 2007

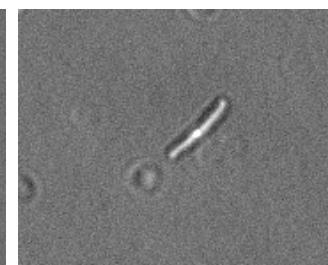
## Self-assembling zeolites and living systems



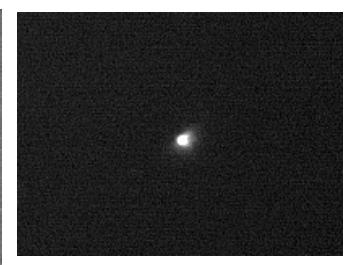
## Self-assembling zeolites and living systems



white light



white light and blue light

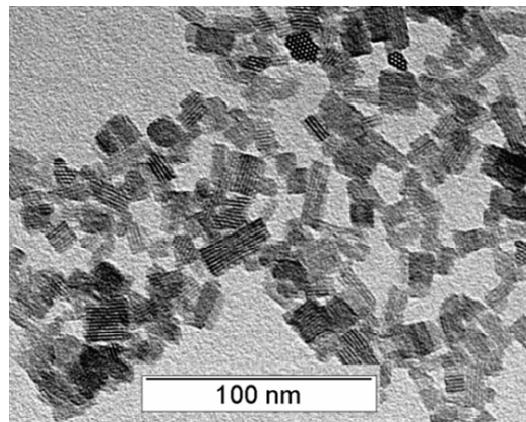
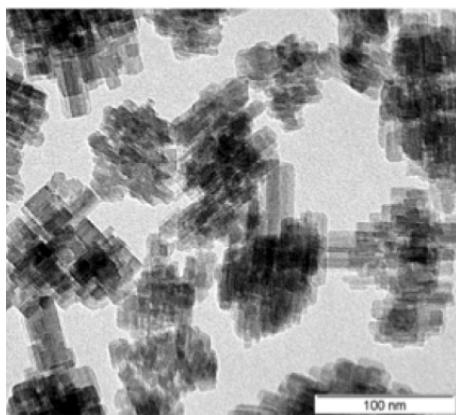


blue light

*Angew. Chem. Int. Ed.* **2007**, *46*, 6188

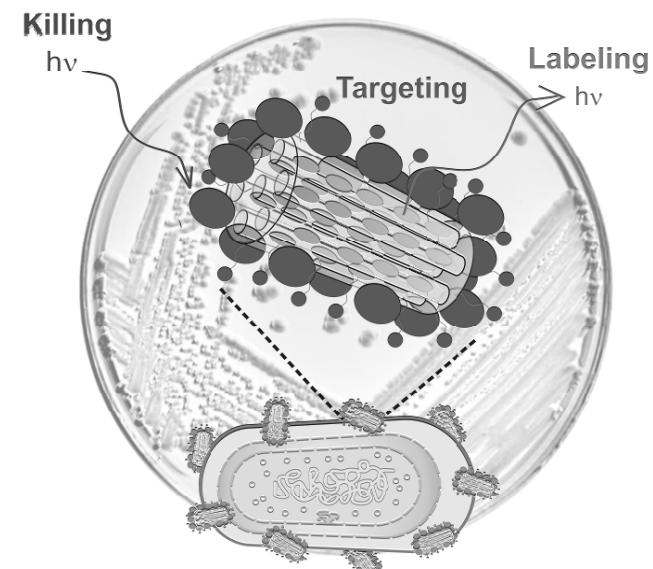
Z. Popovic, M. Otter

## Nano-zeolites Synthesis



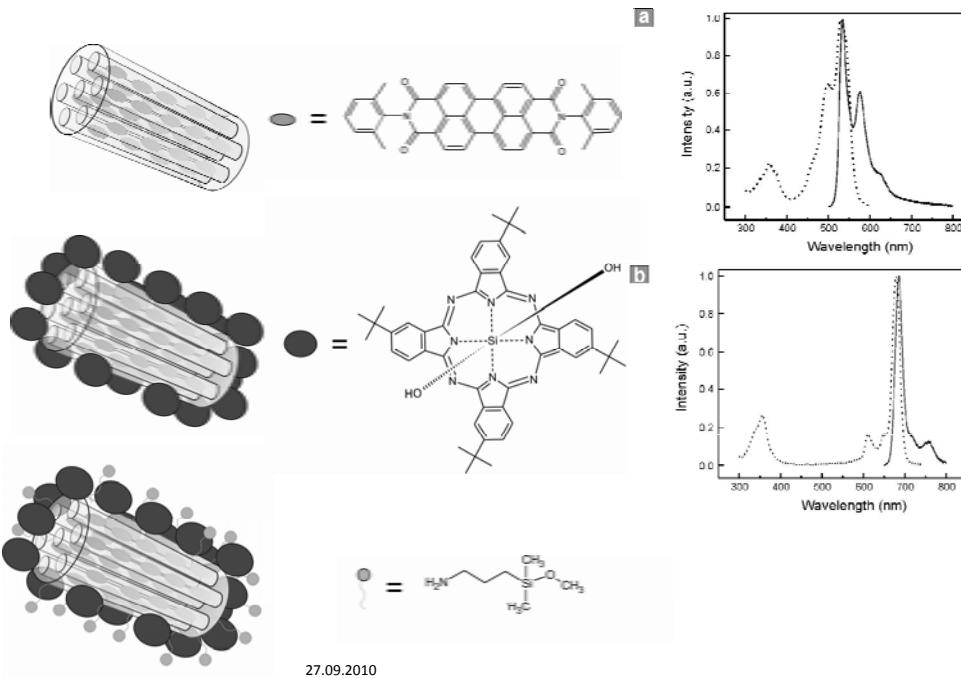
M. Tsotsalas, G. Luppi, et al. to be submitted

## Labeling, targeting and killing bacteria

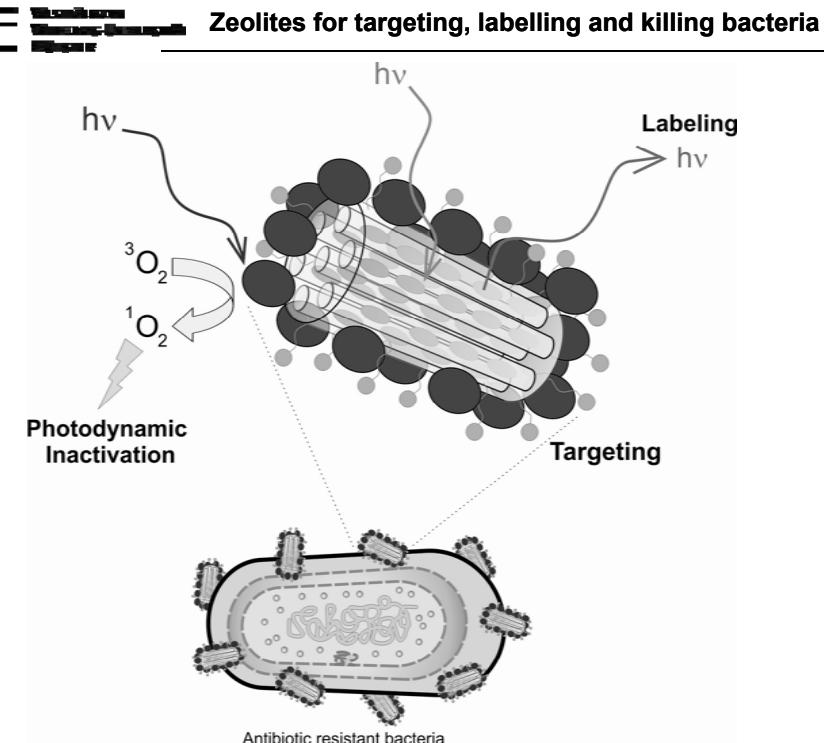


C. Strassert, M. Otter, R.Q. Albuquerque, A. Höne, Y. Vida, B. Maier, L. De Cola  
*Angew. Chem. Int. Ed.* **2009**, *48*, 7928 (VIP Paper), highlighted in *Nature Chemistry*

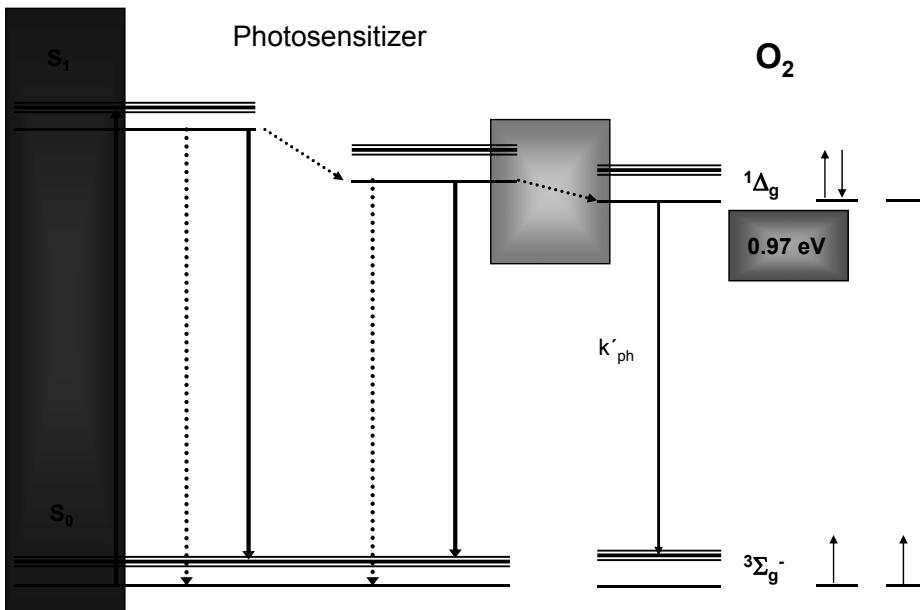
## Zeolites for targeting, labelling and killing bacteria



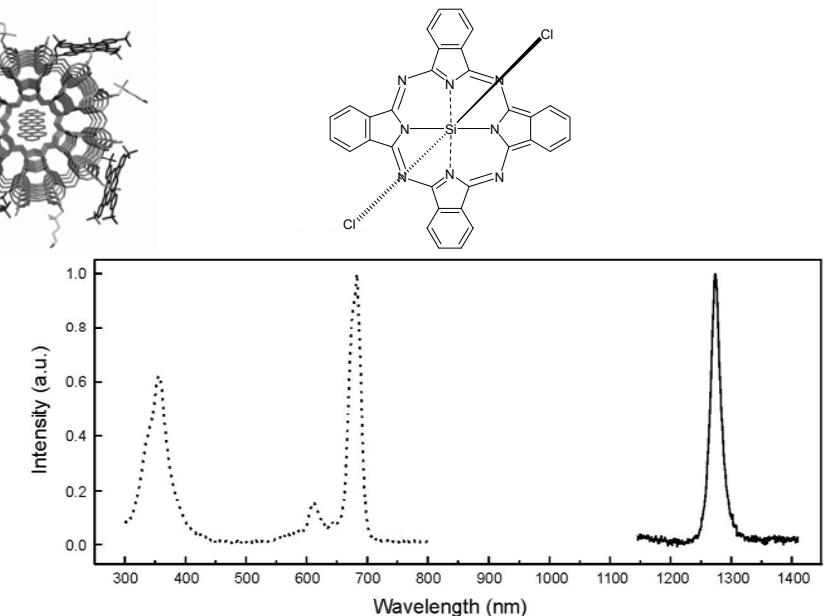
27.09.2010

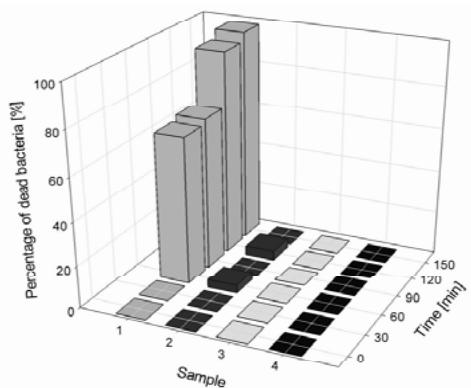
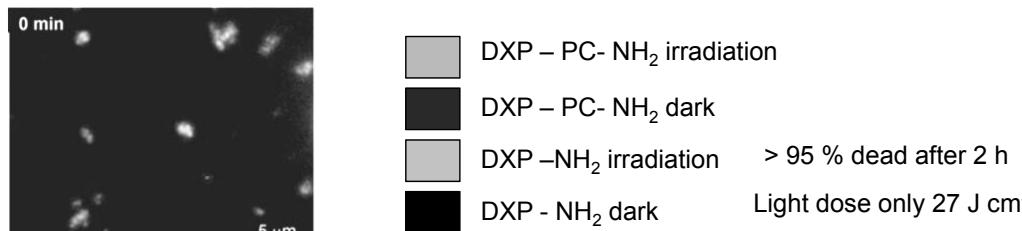
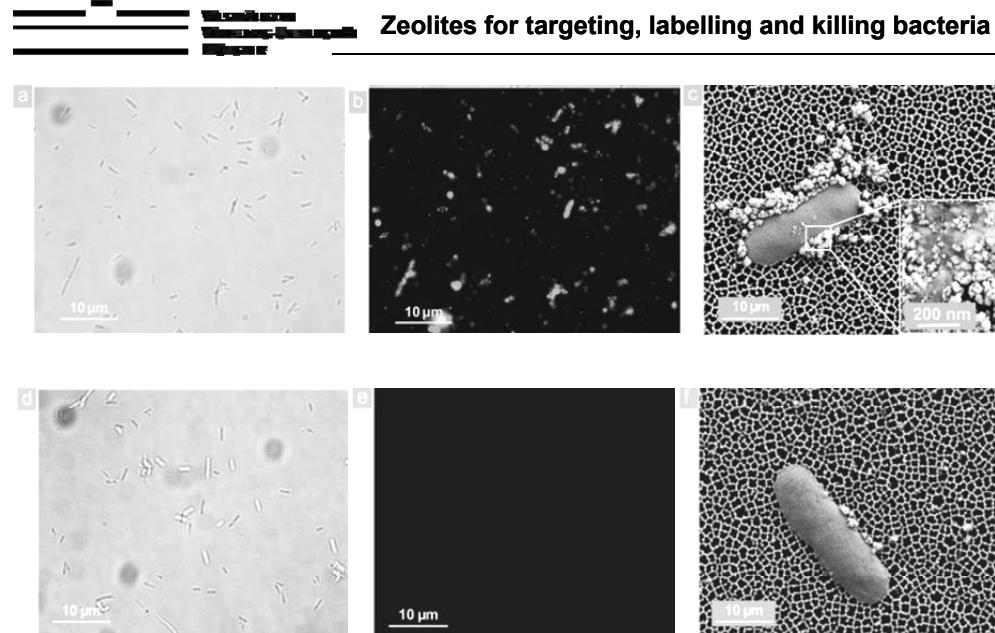
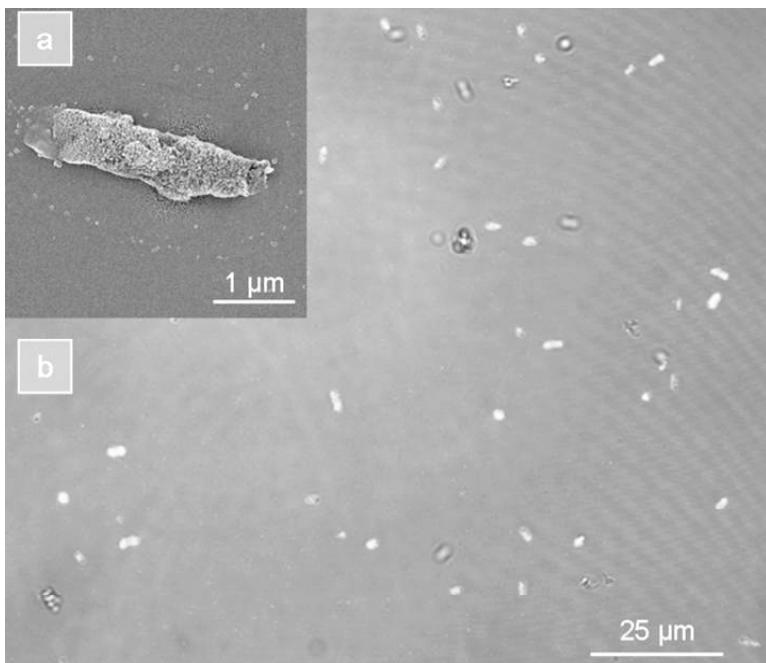


## Photosensitization process



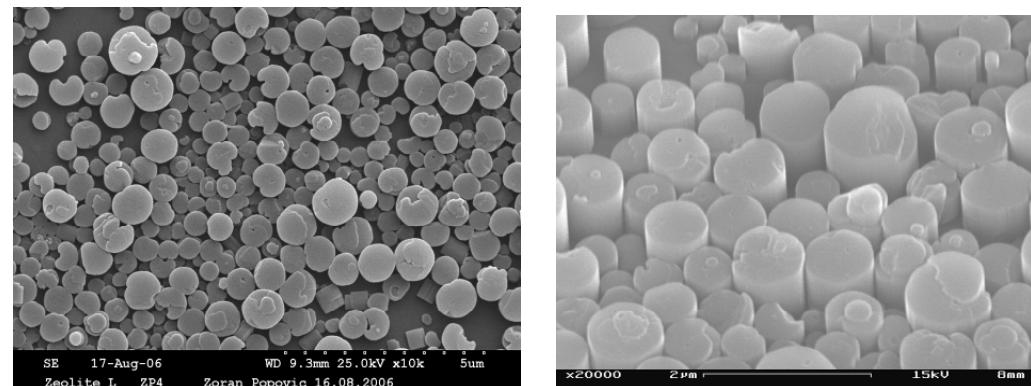
## Zeolites for targeting, labelling and killing bacteria





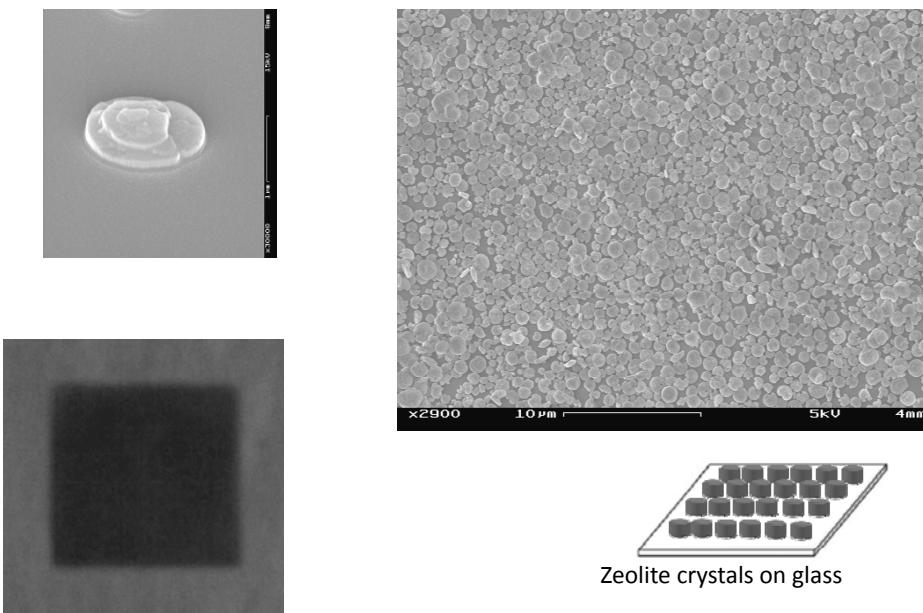
C. Strassert, M. Otter, R.Q. Albuquerque, A. Höne, Y. Vida,  
B. Maier, L. De Cola  
*Angew. Chem. Int. Ed.* **2009**, *48*, 7928 (VIP Paper)

## Organizing zeolites in monolayers

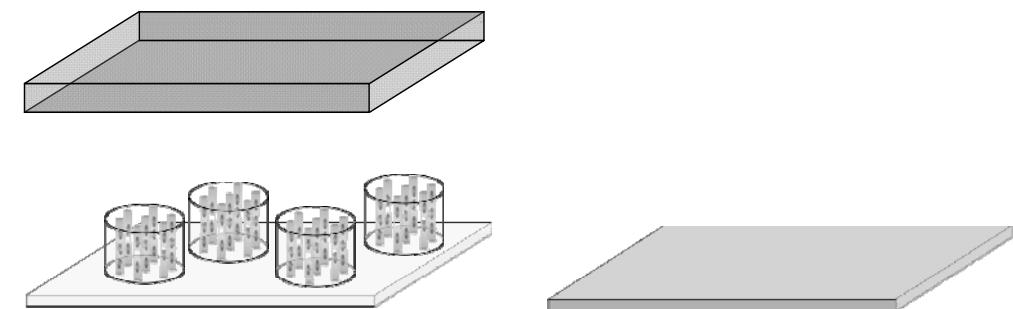


A. Z. Ruiz, H. Li, G. Calzaferri, *Angew. Chem. Int. Ed.* **2006**, *45*, 5282,  
J. S. Lee, H. Lim, K. Ha, H. Cheong, K. B. Yoon, *Angew. Chem. Int. Ed.* **2006**, *45*, 5288.

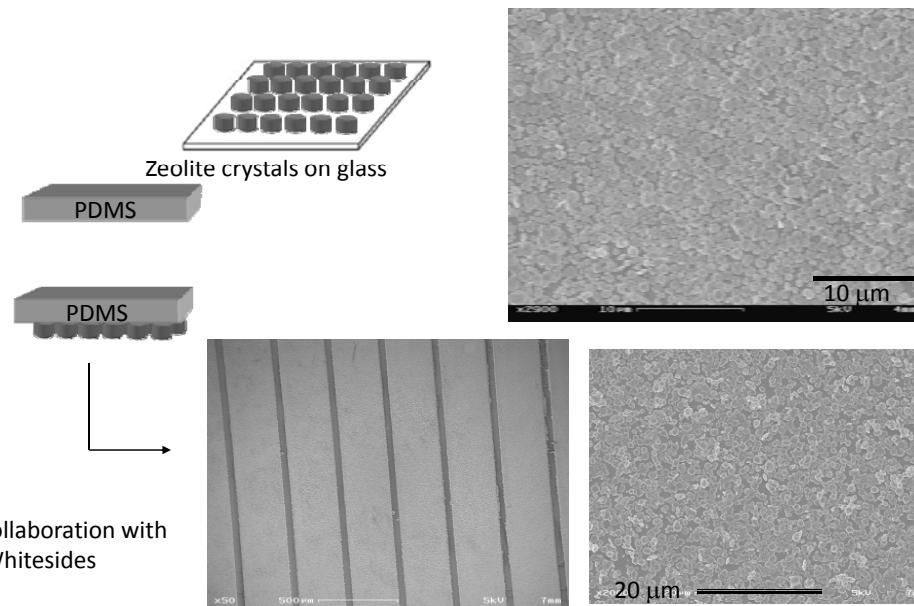
## Monolayer Formation



## Transferring zeolite monolayer

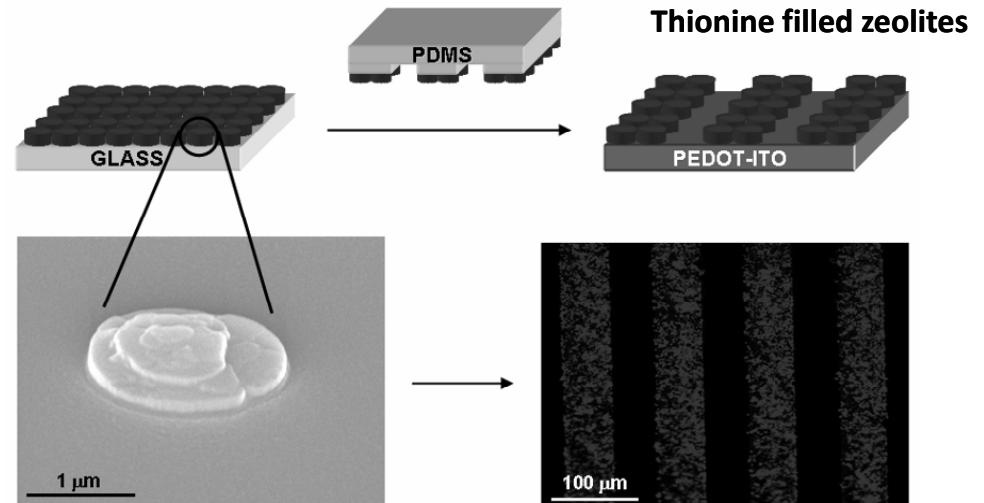


## Transfer of Zeolite monolayer



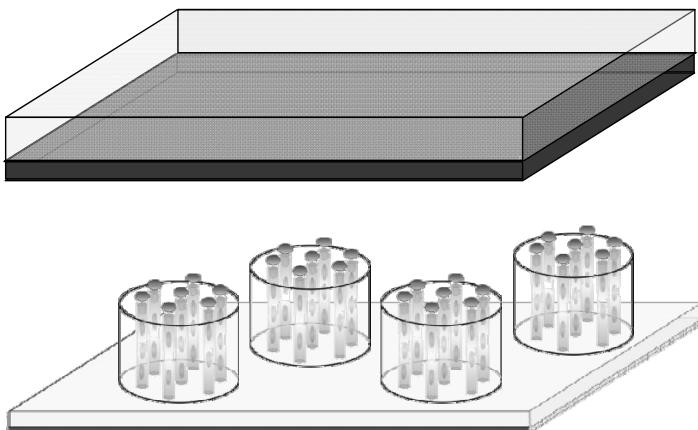
Xia, Y. and Whitesides, G.M. *Angew.Chem. Int. Ed. Engl.* 1998, 37, 551-575  
Quake, S. R. & Scherer, A. *Science*, 2000, 290, 1536 – 1540.

## Emitting patterned monolayer



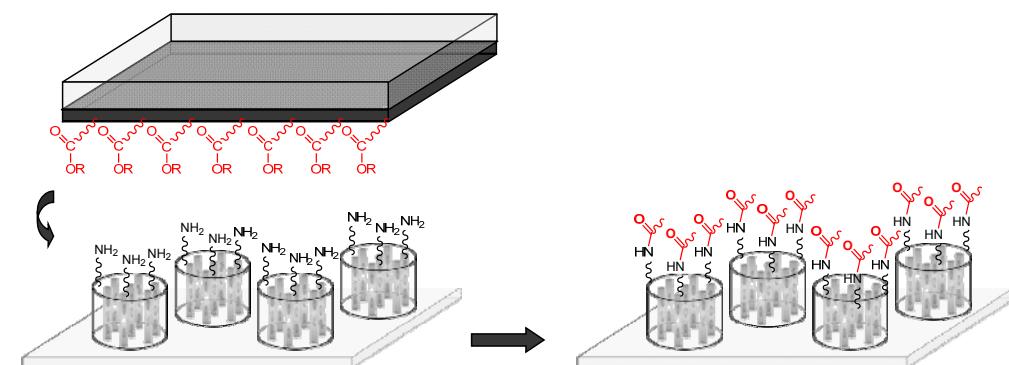
F. Cucinotta, Z. Popovic, E. Weiss, G. Whitesides, L. De Cola  
*Adv. Mater.* 2009, 21, 1142

## Micro-contact printing



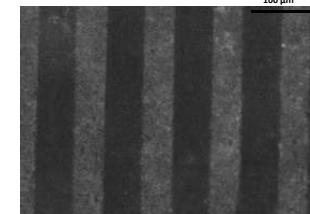
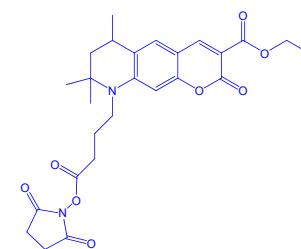
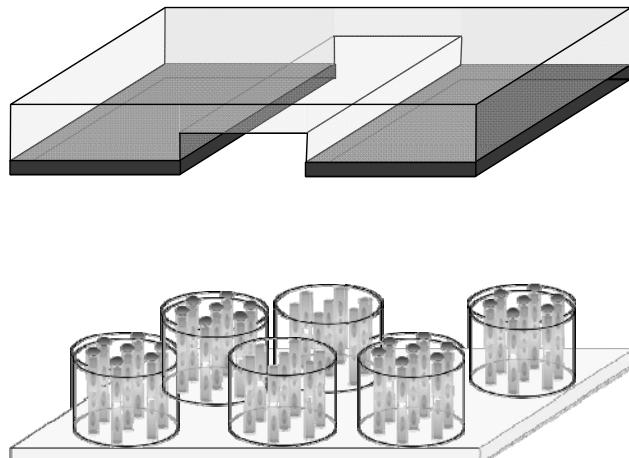
A. Kumar, G.M. Whitesides, *Appl. Phys. Lett.*, **1993**, 63, 2002

## Micro-contact printing



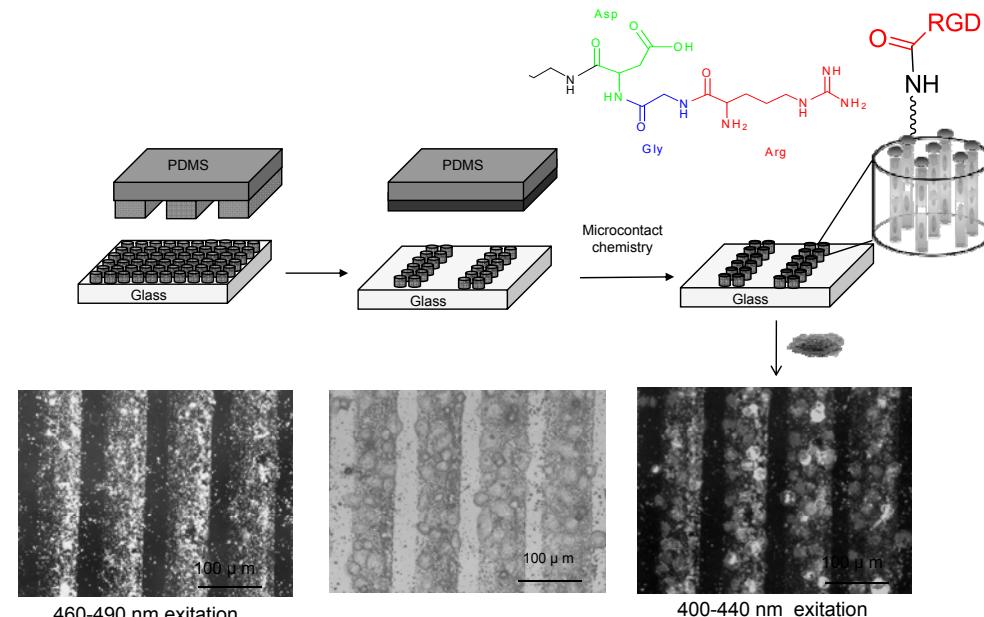
A. Kumar, G.M. Whitesides, *Appl. Phys. Lett.*, **1993**, 63, 2002

## Patterned micro-contact printing



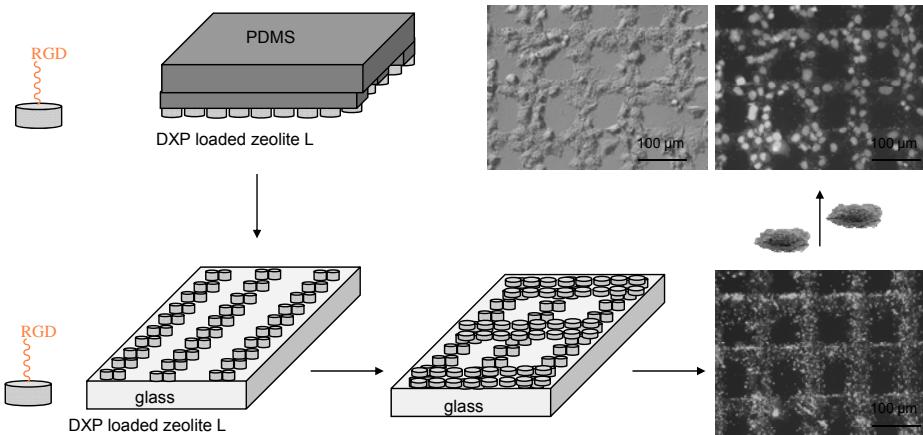
N. S. Kehr, A. Schäfer, B. J. Ravoo, L. De Cola *Nanoscale*, **2010**, 2, 601

## Cellular Patterning on Zeolite Monolayer



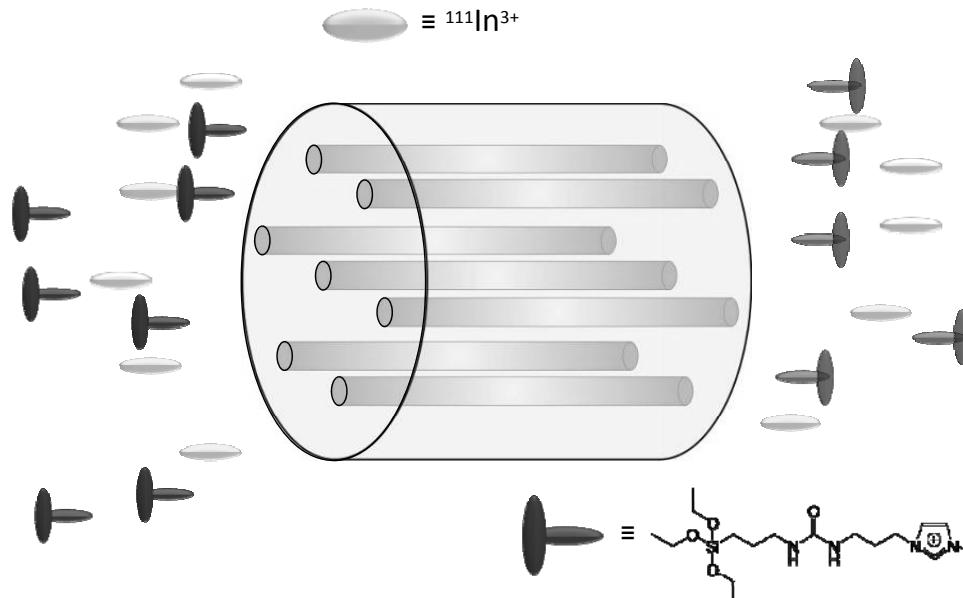
Kehr, De Cola, et. al., *Adv Funct. Mater.* **2010**, 20, 2248.

## Cellular Patterning on Zeolite Monolayer



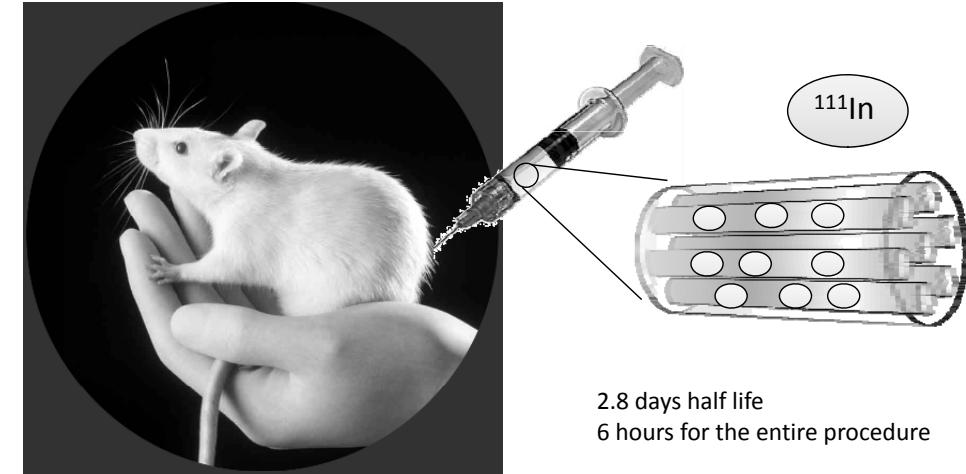
Dr. Seda Kehr unpublished results

## Loading of the zeolites



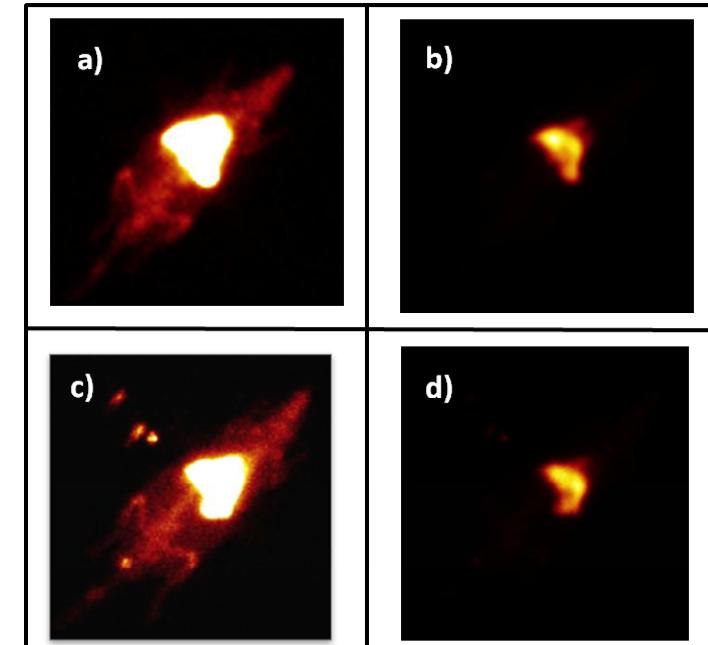
M. Tsotsalas, K. Kopka, G. Luppi, S. Wagner, M. Law,  
M. Schäfers, L. De Cola *ACS Nano* 2010, 4, 342-348

## In vivo experiments

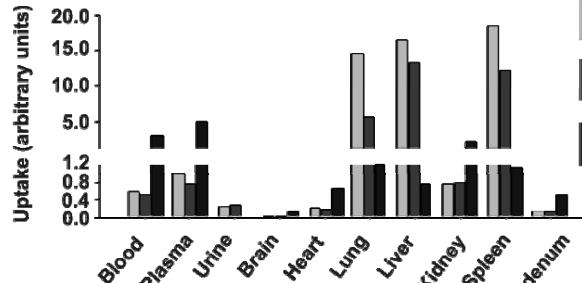


In collaboration with the Nuclear Medicine dept. UKM  
Prof. M. Schaefers, Dr. K. Kopka, Dr. S. Wagner

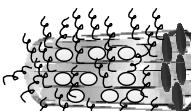
## In vivo experiments



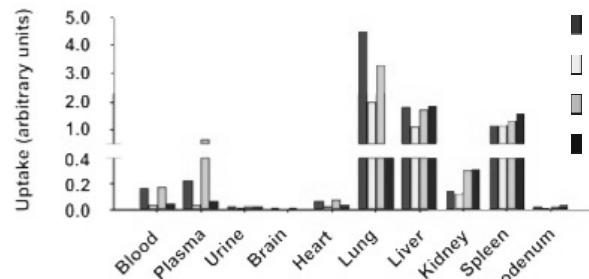
## Bio-distribution of the zeolites L



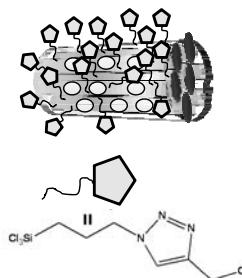
Rat 1: Zeolites L  
Rat 2: Zeolites L + PEG 500  
Rat 3:  $^{111}\text{InCl}_3$



= polyethyleneglycole



5 min  
20 min  
60 min  
24 h



M. Tsotsalas, K. Kopka, G. Luppi, S. Wagner, M. Law, M. Schäfers,  
L. De Cola *ACS Nano* 2010, 4, 342-348

## Thanks to my group



## Special Thanks to...



### MY GROUP

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De Paoli, M. Mauro, K. Schürmann, M.  
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Prof. B. Maier Micro Biology Institute WWUM  
Prof. Schäfers EIMI and WWUM  
Dr. H.-P. Josel Roche Diagnostics



SFB- TRR 61



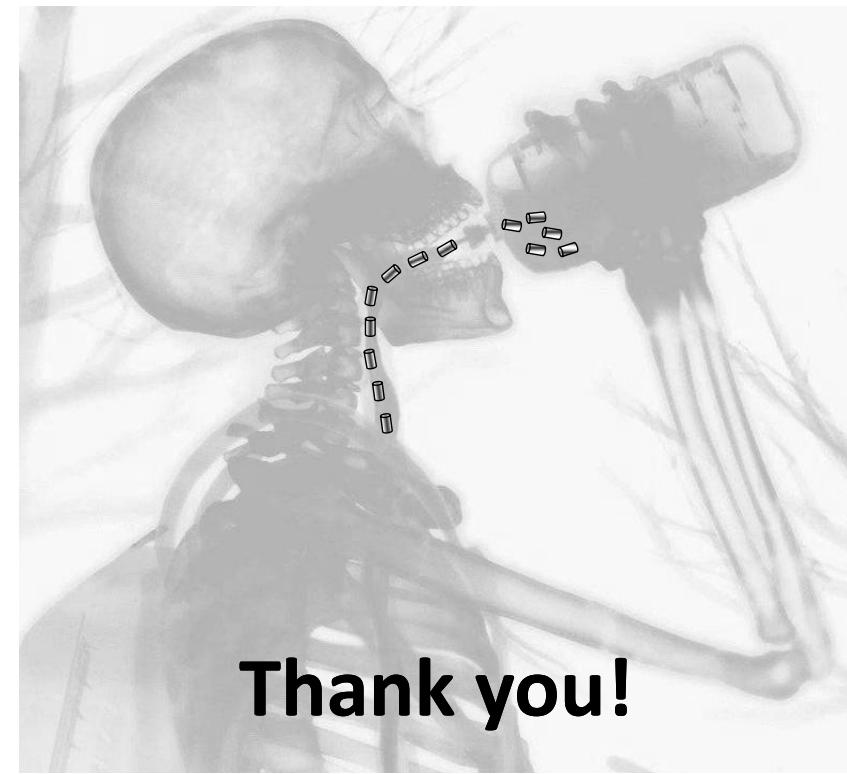
Alexander von Humboldt  
Stiftung/Foundation



Advanced Research Grant Award



Westfälische Wilhelms-Universität Münster



Thank you!