Surface modification of metal and metal oxide substrates by organic monolayers

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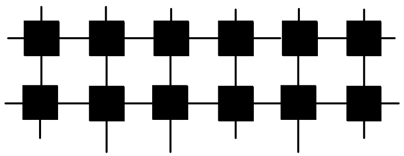
Surface modification



Inorganic surface

- metal
- oxide
- hydroxide
- carbonate
- phosphate
- nitride
- sulfide

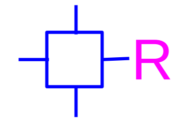
...

R

Organic

- alkyl
- functional group
- polymer
- metal complex
- proteine
- enzyme
- DNA

...



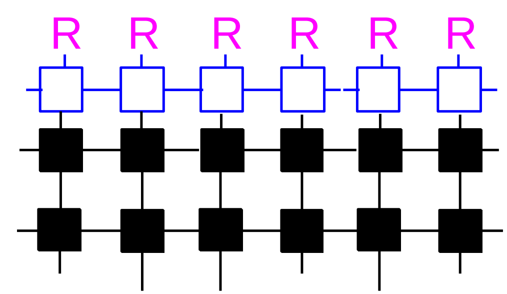
Coupling agent

- thiol
- organoalkoxysilane
- carboxylic acid
- phosphonic acid

...

Coupling Agent :

stable bonds with both **organic** and **inorganic** moieties



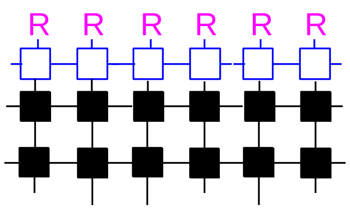
monolayer

Route to hybrid materials, complementary to Sol-Gel

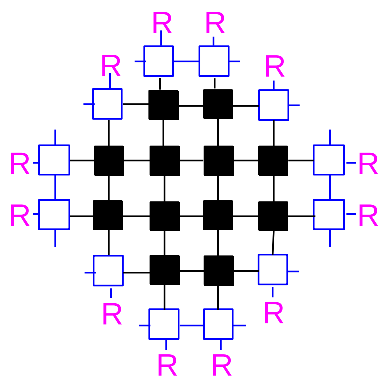
Surfaces

Composition: silicium, metal (Au, Ti...), oxide, hydroxide, carbonate, phosphate, nitrure, sulfure

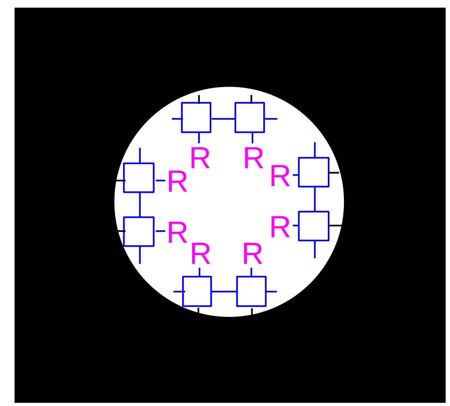
Amorphous, microcrystalline, monocrystalline



Flat



(Nano)particles



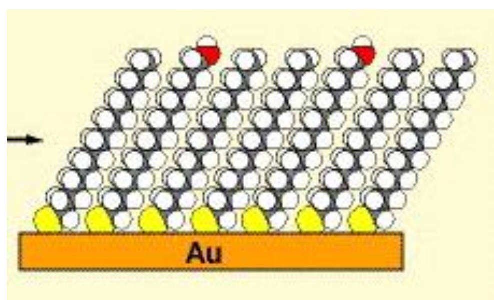
Porous

Monolayer or self-assembled monolayer?

Monolayer:
surface modification (chemical bonds with the surface)
no lateral interaction between coupling agent molecules
low or medium density, disordered

Self-Assembled Monolayer = SAM
surface modification + intermolecular interactions

Usually : long alkyl chains (10 to 20 CH_2 groups):
intermolecular van der Waals forces between methylene groups:
ordered chains, high grafting density (4-4.5 /nm^2)



Thiol and disulfide coupling agents

Alkylthiols, dialkyl disulfides...

Organic: stable S-C bonds

Surfaces:

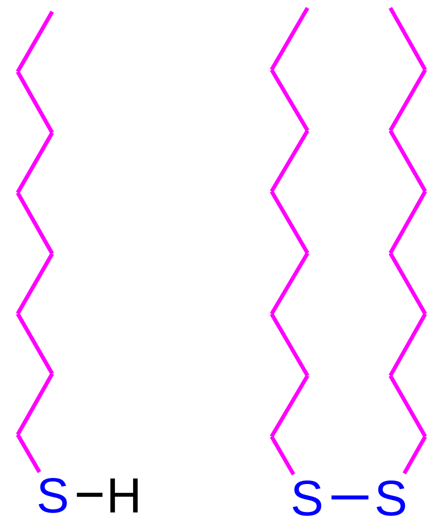
SAMs on Au(111), Pt, Ag, Cu, Hg, Fe,

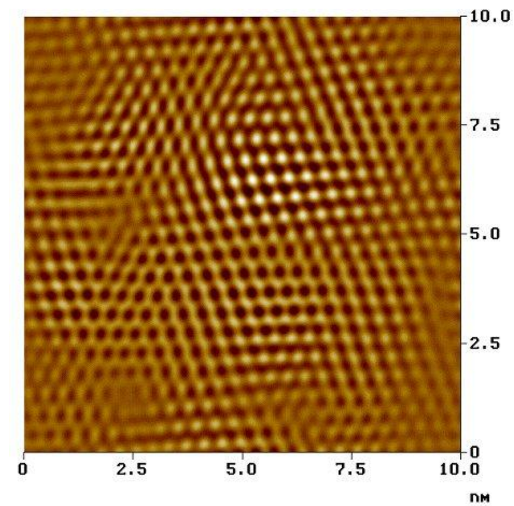
γ-Fe_2O_3, GaAs, ZnSe, InP

Coupling: M-S-C bonds

$$R\text{-}S\text{-}H + Au^0 \longrightarrow R\text{-}S^-Au^+ + \tfrac{1}{2} H_2$$

$$R\text{-}S\text{-}S\text{-}R + Au^0 \longrightarrow 2\ R\text{-}S^-Au^+$$



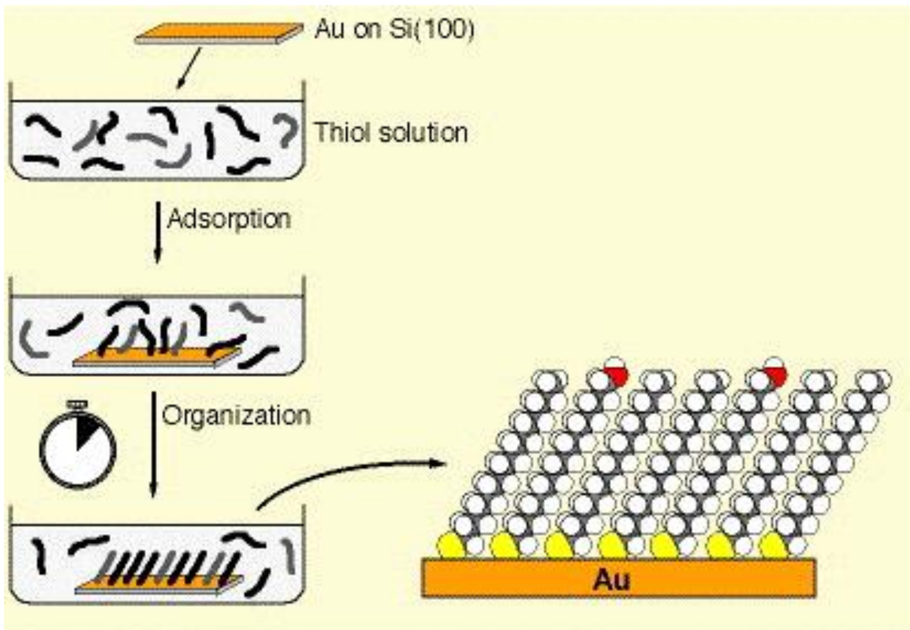


Deposition of Alkylthiol SAMs on Au

•Preferred crystal face for alkanethiolate SAM preparation Au (111)
- single crystal substrates: evaporation of thin Au films (200-400 nm) on flat supports (glass or silicon)

• Thiol concentrations: 1-2 mM, most common solvent ethanol.

• Time: a self-assembled monolayer forms very rapidly on the substrate, but it is necessary to use adsorption times of 15 h or more to obtain well-ordered, defect-free SAMs. Multilayers do not form, and adsorption times of two to three days are optimal in forming highest-quality monolayers.



Structure

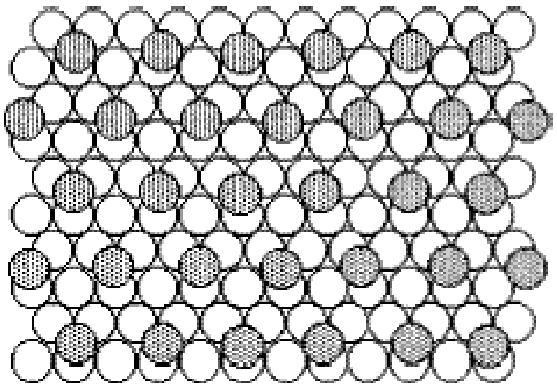


Figure 9. Hexagonal coverage scheme for alkanethiolates on Au(111). The open circles are gold atoms and the shaded circles are sulfur atoms.

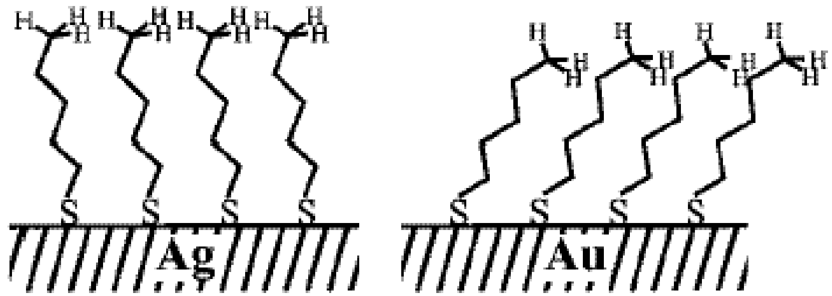


Figure 2. Schematics of alkanethiol SAMs on silver and gold substrates (showing tilt angles of 12° and 27°, respectively).

2-D packing

Tilt:

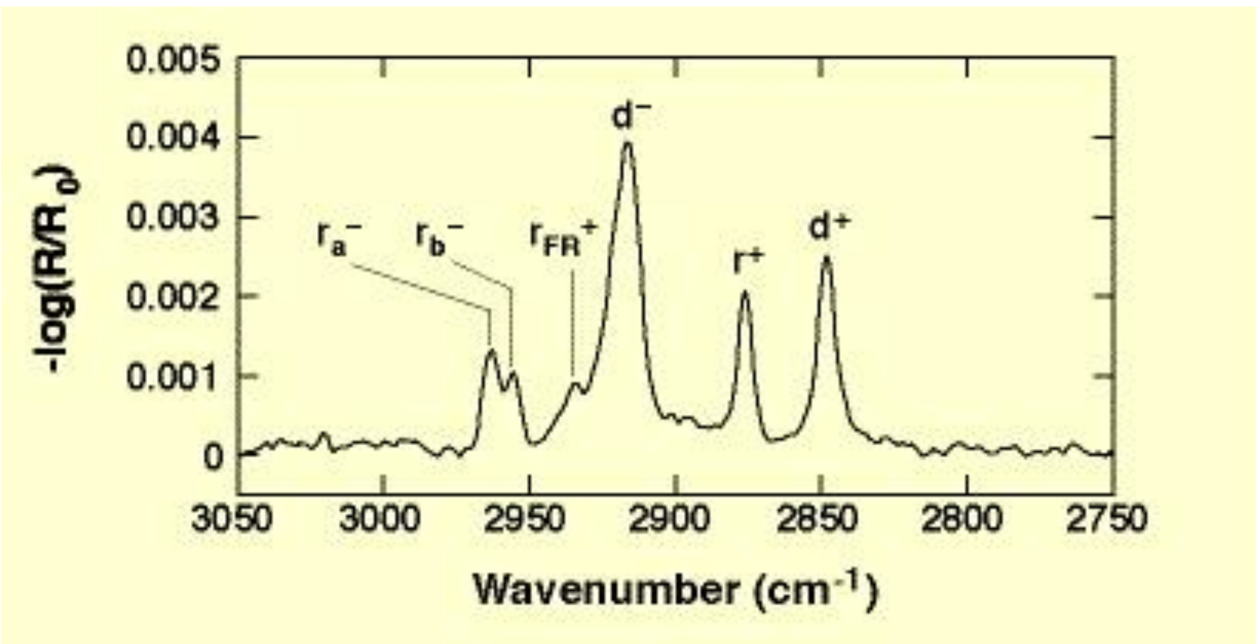
•to increase VdW contact alkyl chains of alkanethiol SAMs) surfactants are often tilted

•Depends on the metal (distance between M atoms)

Caracterization of density / ordering in alkyl SAMs

IR :CH stretching vib. very sensitive to packing density and gauche defects

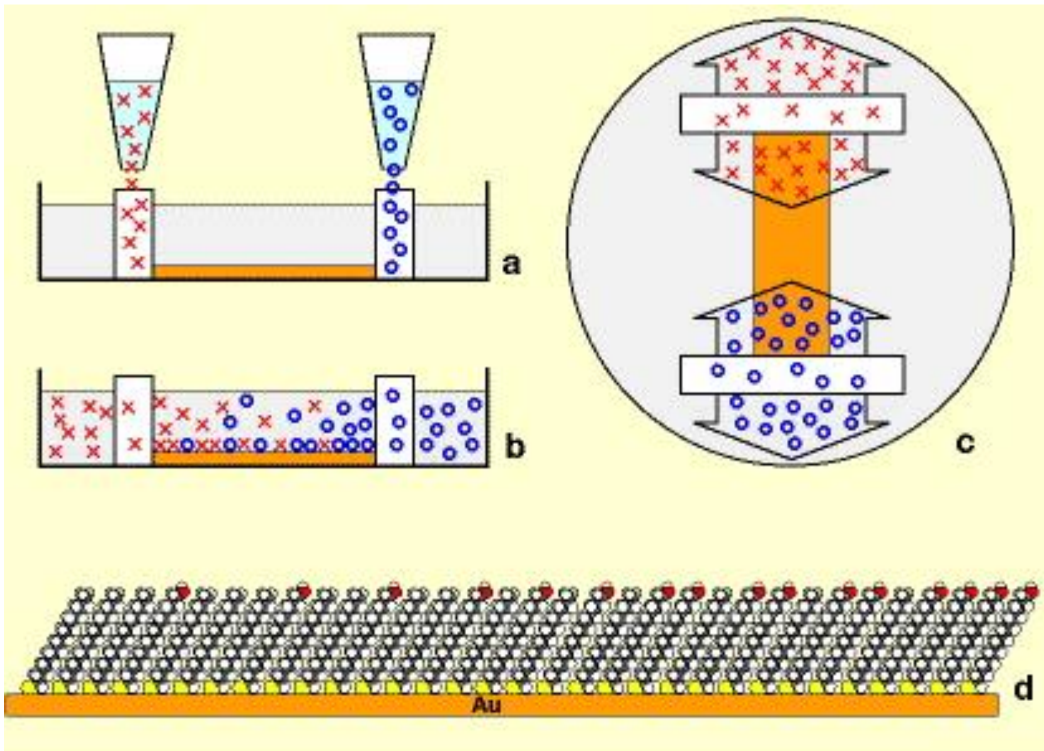
as CH_2 stretching vibration (d^-) :
2916 or 2917 cm^{-1} for SAMs of exceptional quality or cooled below RT
2918 cm^{-1} : normal value for a high-quality SAM,
~2926 cm^{-1} heavily disordered, "spaghetti-like" SAM.



IRAS spectrum of a hexadecanethiolate SAM.
d+ and d- are the s and as CH_2 stretches; r+ and r- s and as CH_3 stretches

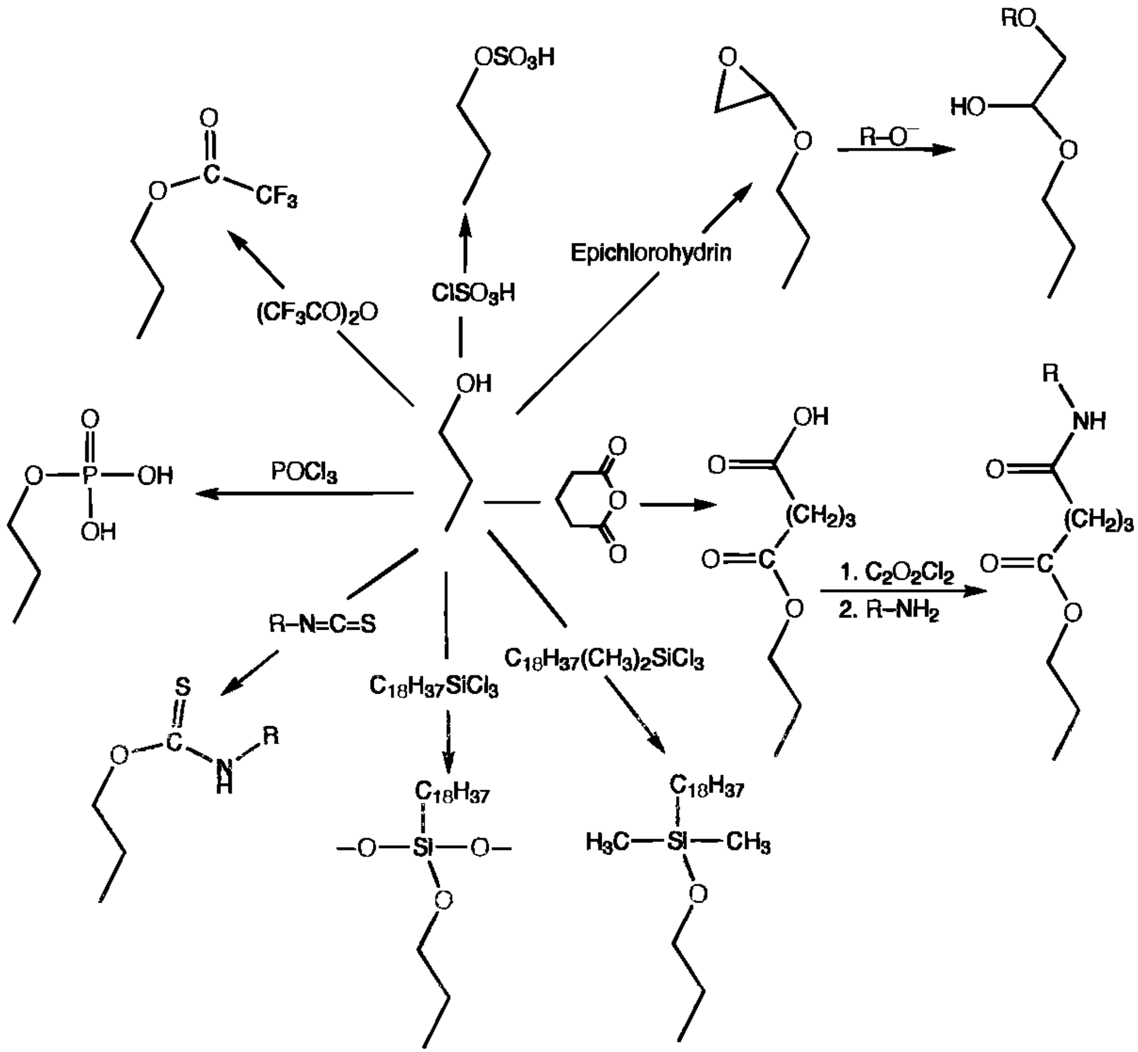
Mixed SAMs: two-component molecular gradients

Liedberg and Tengvall (*Langmuir* 11 (1995), 3821).
Cross-diffusion of two different thiols through an ethanol-soaked polysaccharide gel: formation of a continuous gradient of 10-20 mm length may be formed.



Preparation of two-component alkanethiolate gradients.
(a) The two different thiols, represented by X and O, are injected into glass filters.
(b) They diffuse slowly through the polysaccharide gel and attach to the gold substrate.
(c) Top view showing the placement of the gold substrate between the filters.
(d) Schematic illustration of a fully assembled gradient.

Post-modification



Surface reactions of ω-hydroxyalkanethiolate monolayers on Au(111).

Monolayers on Au nanoparticles

MPCs (monolayer-protected clusters) = 3D analogs of 2D SAMs

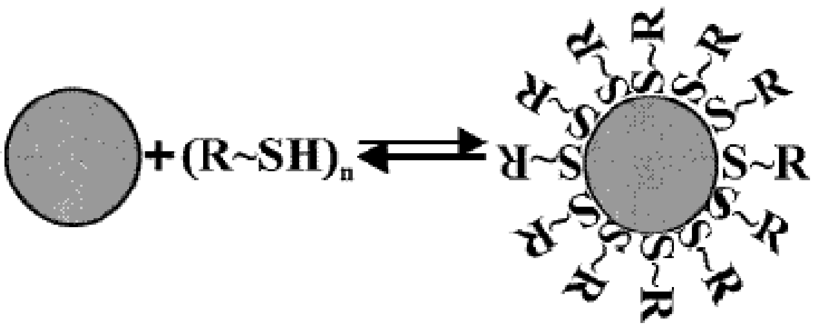


Figure 3. Schematics for the capping of a nanoparticle by alkanethiol molecules (i.e., the formation of MPCs).

monolayers on spherical nanoparticle substrate surfaces instead of monolayers on flat substrate surfaces

capping agents (citrate ions, thiol ligands) on gold nanoparticle surfaces can be exchanged by thiol ligand

•chemical functionalization of the nanoparticles

• transfer from solvent to solvent, storage in the dried state

• organization (and self-organization) into 2D arrays or 3D networks on solid substrates

Silane coupling agents

$R\text{-}SiX_3$ X = Cl, OEt...

easy nucleophilic attack at Si

Hydrolysis: $H_2O + Si\text{-}X \rightarrow Si\text{-}OH + HX$

Heterocondensation: $M\text{-}OH + Si\text{-}X \rightarrow Si\text{-}O\text{-}M + HX$

Si-O-M bonds $M\text{-}OH + Si\text{-}OH \rightarrow Si\text{-}O\text{-}M + H_2O$

Homocondensation: $Si\text{-}OH + Si\text{-}OH \rightarrow Si\text{-}O\text{-}Si + H_2O$

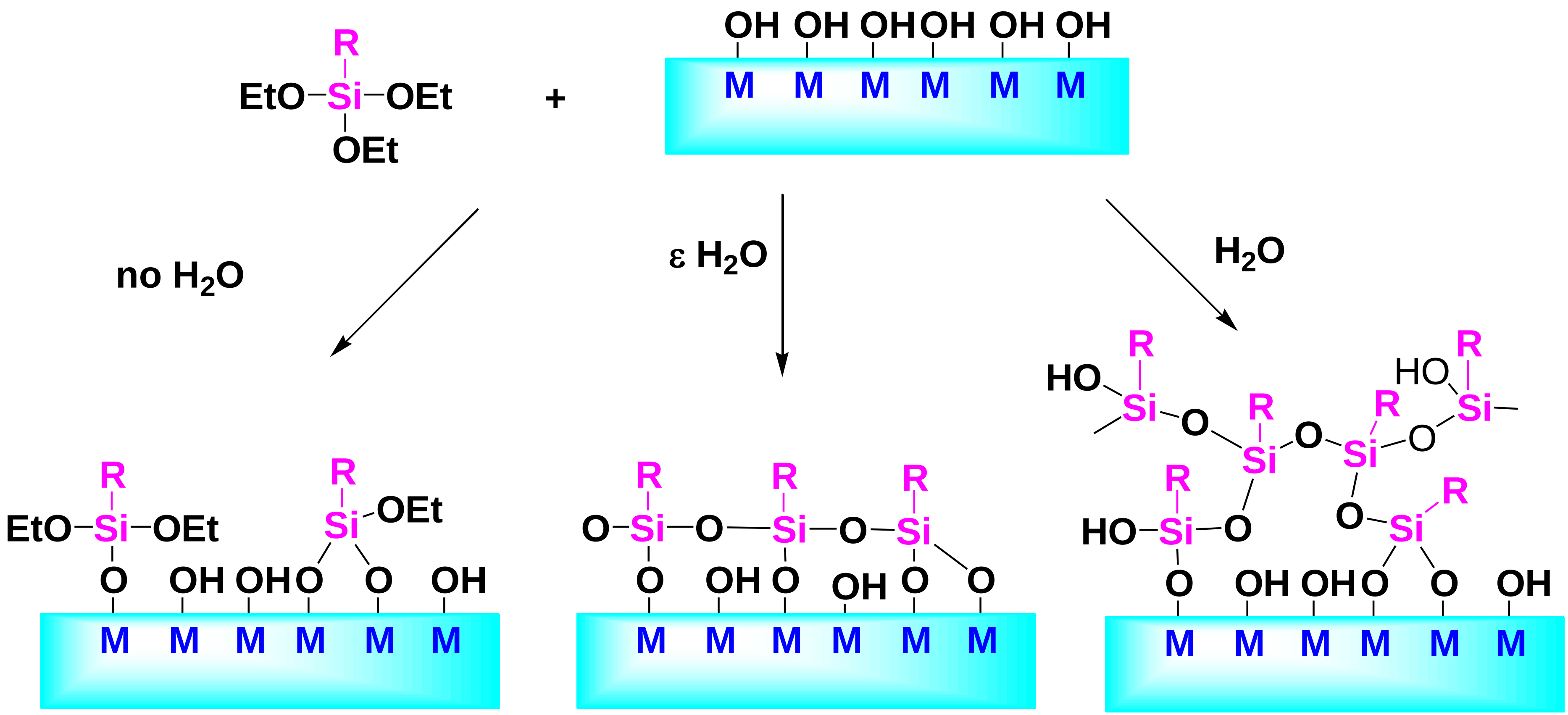
Si-O-Si $Si\text{-}OH + Si\text{-}X \rightarrow Si\text{-}O\text{-}Si + HX$

Competition heterocondensation / homocondensation

Surface modification by trialkoxysilanes:

Competition heterocondensation / homocondensation

Depends on the amount of water (adsorbed, in the solvent...)

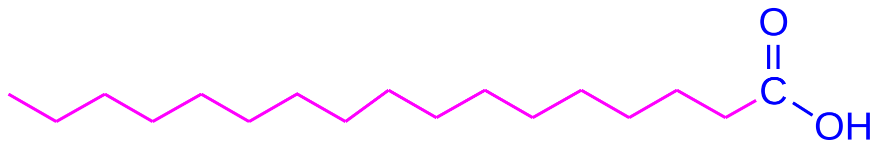


only **Si-O-M**,	**Si-O-M + Si-O-Si**	few **Si-O-M**,
Partial monolayer	**Dense monolayer**	**multilayer**

Carboxylic acids

- RCOOH

saturated fatty acids : $C_nH_{2n+1}COOH$...



Surfaces:

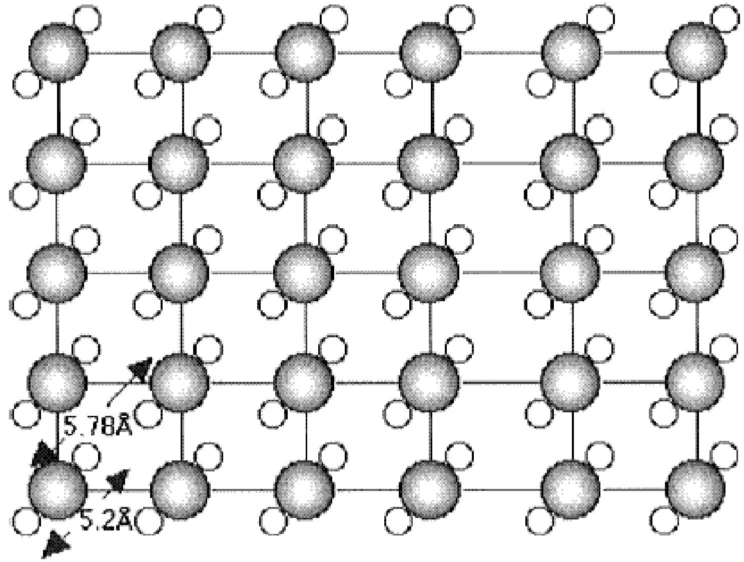
- oxides (Al_2O_3, AgO)
- oxidized metals(Ag, Au...)
- carbonates ($CaCO_3$)

Coupling: ionic bonds

Formation of a « surface salt » $RC(O)O^- M^+$

Bonding mode: mono- or bidentate

Carboxylic acids

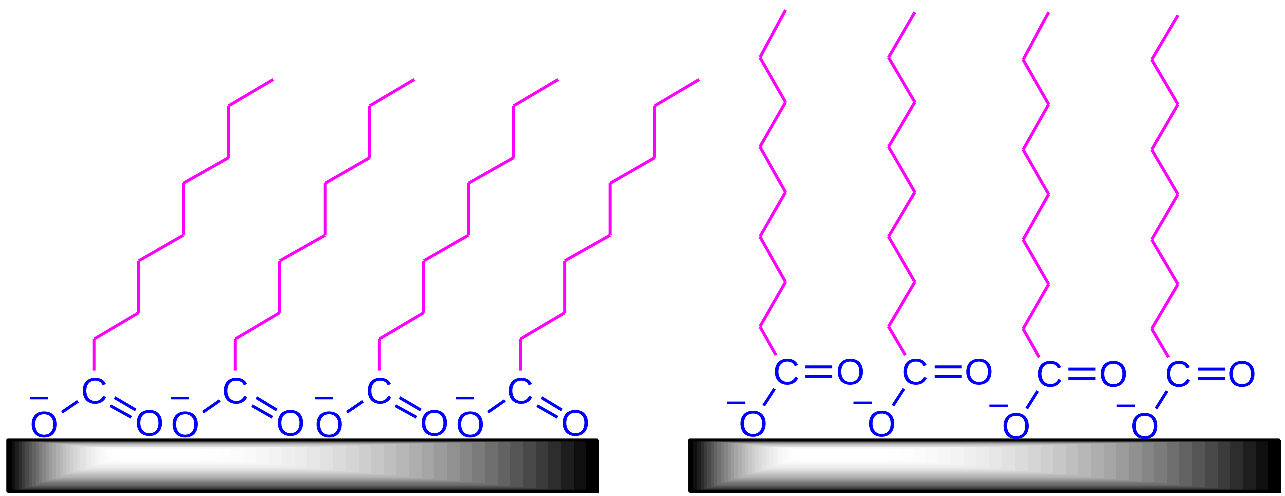


Adsorbed fatty acids on AgO.

Samart, M. G. et al

Langmuir **1993**, *9,*1082.

Y.-T. Tao et al.,
J. Am. Chem. Soc.
1993, *115,* 4350.



Carboxylic acids

Ex.: PP/ $CaCO_3$/ stearic acid system

Surface $CaCO_3$ not compatible with PP

→ melt of PP + $CaCO_3$: extremely high viscosity, extremely difficult mixing,

→ poor dispersion of $CaCO_3$ filler

Surface modification of $CaCO_3$ by stearic acid ($C_{17}H_{35}COOH$):

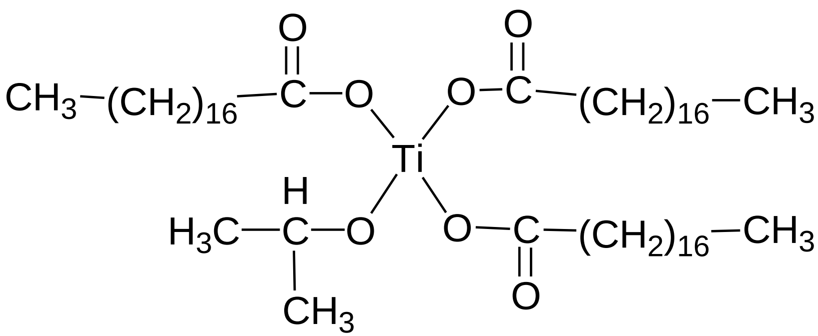
→ alkyl chains at the surface of particles

→ hydrophobic particles, good wettability by melt PP, incorporation and dispersion easier **Compatibilizer**

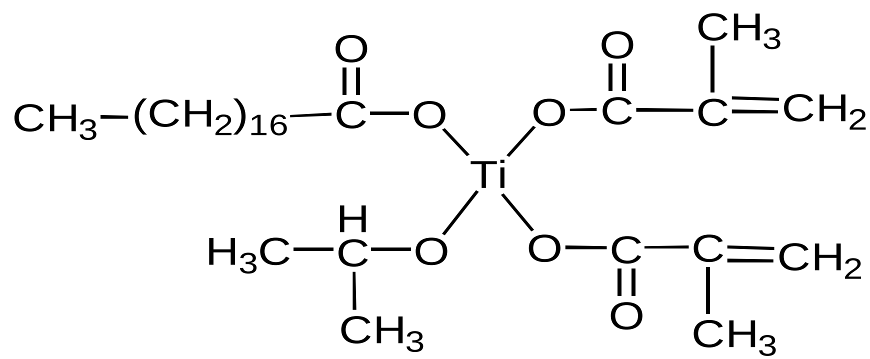
→ Improved mechanical properties (shock resistance)

Organotitanates

Titanium alcoxides *(also Zr, Al)*, **modified** by carboxylic acids or chelating groups (β-dicétones, cétoesters, glycols, hydroxyacides, phosphates).



Non réactif (dispersant)



Réactif

- Commercial, goods results with $CaCO_3$ or oxide fillers
- 1300 patents + 400 technical articles
- Mecanism? M-OH + Ti-OR $\rightarrow$ M-O-Ti ? source of carboxylic acid?
- Real composition and structure ?????

Titanium oxoalcoxydes

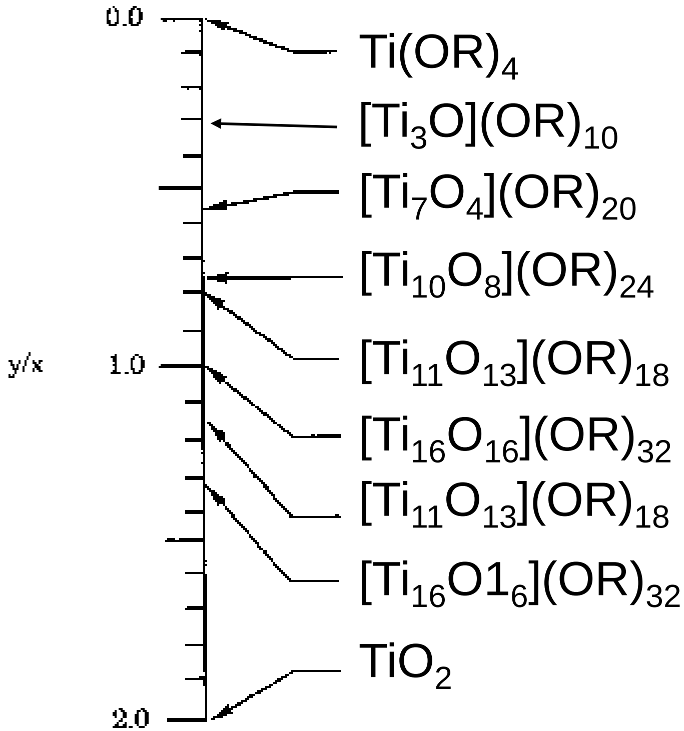
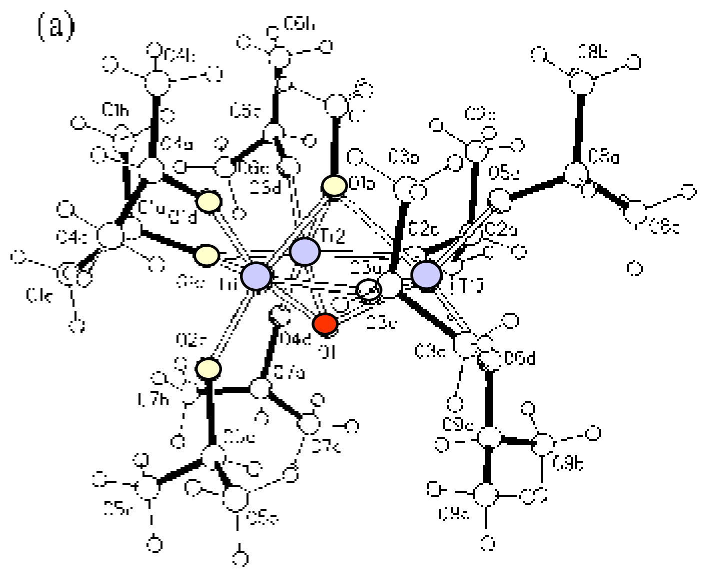
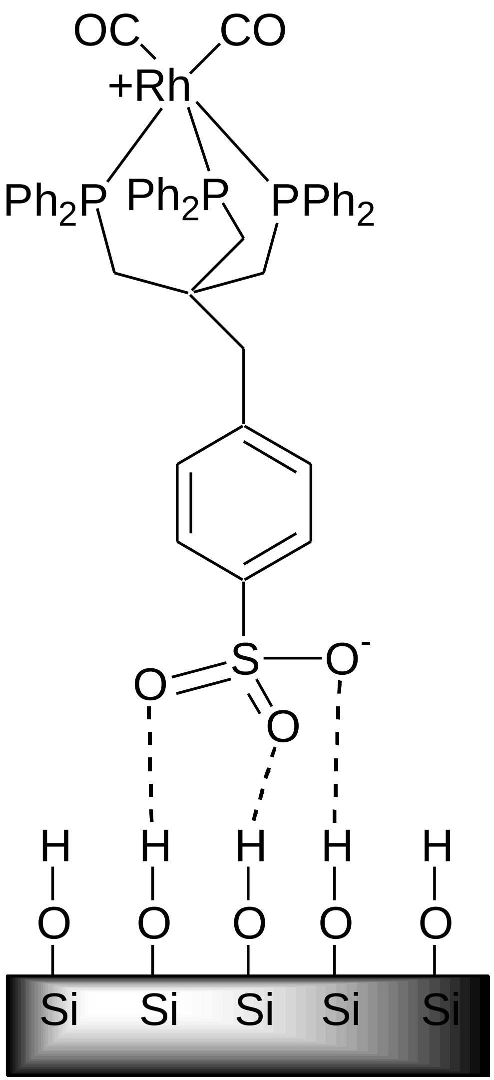


Fig. 1. Formulas of structurally-characterized titanium(IV) polyoxo-alkoxides $[Ti_xO_y](OR)_{4x-2y}$ arranged in order of their degrees of condensation relative to $Ti(OR)_4$ and TiO_2.



$[Ti_3O](OMe)(OiPr)_9$

Sulfonates coupling agents / SiO_2 H-bonding JACS 1999, 121, 5961



•SiO_2: pretreated at 300°C

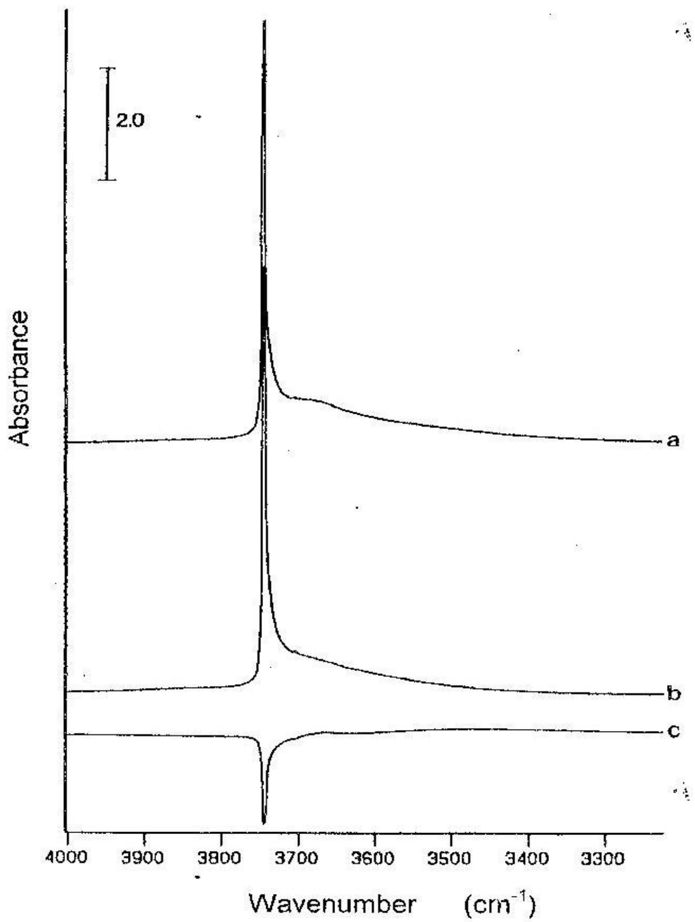
•Rh complex: dissolved in CH_2Cl_2

•Washing with CH_2Cl_2no loss of Rh

• Washing with MeOH: Rh complex dissolved

• Catalysis: hydrogenation and hydroformylation of alkenes, recyclable, Rh en solution < 1 ppm

Sulfonates / SiO_2: FTIR



Conditions:
SiO_2: 370 m_2/g
Pellets dried at 300°C / 10^{-5} mm Hg, 16h

dried SiO_2 + sulfonate

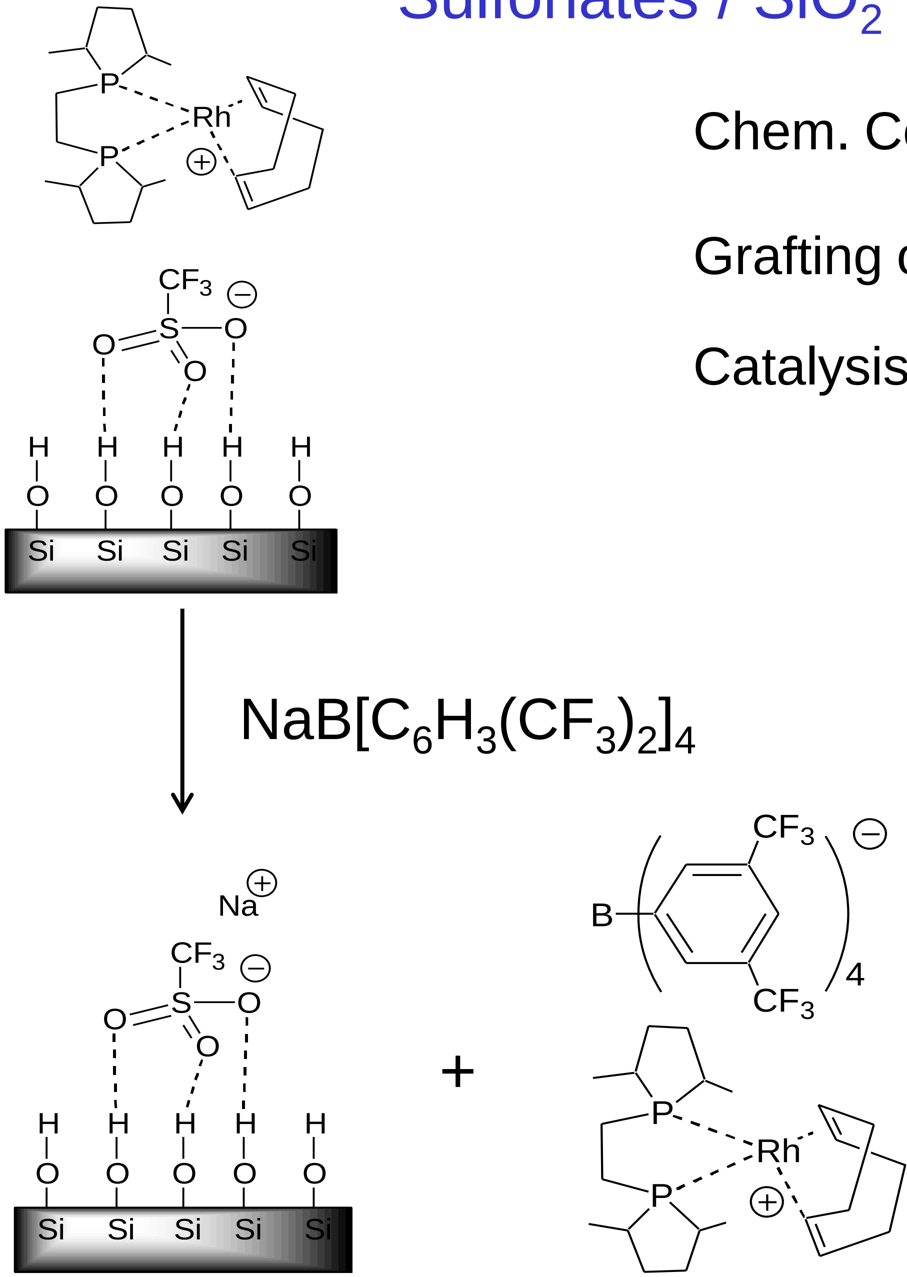
dried SiO_2

difference spectrum

- decrease of free OH
- increase bonded OH

⇒ **H-bonding**

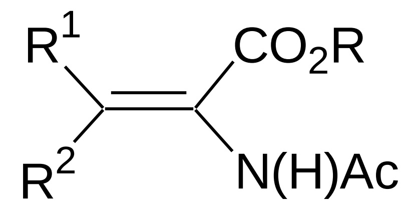
Sulfonates / SiO_2 **H-bonds + electrostatic bonds**



Chem. Comm. 2000, 1797

Grafting onto MCM-41

Catalysis: hydrogénation of enamides

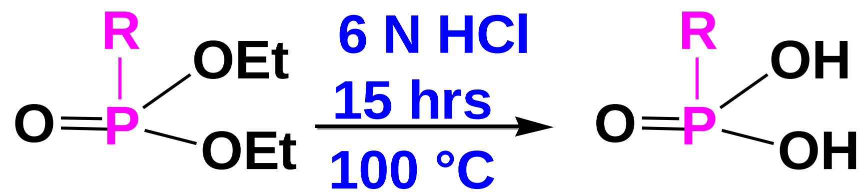


Characterization:
^{31}P, ^{19}F NMR

Organophosphorus coupling agents

Nucleophilic attack at P: difficult:

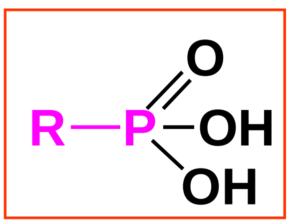
- Hydrolysis of P-OC : harsh conditions

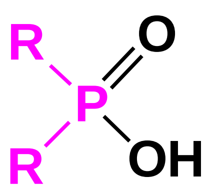


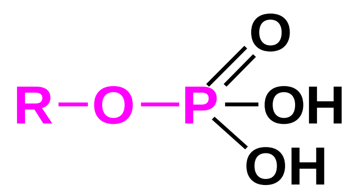
- No homocondensation of P-OH:

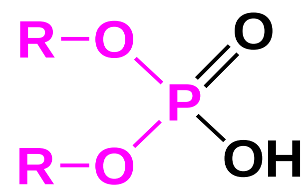
$$\text{P-OH} + \text{P-OH} \nrightarrow \text{P-O-P} + H_2O$$

⇒ **Possible coupling agents :** organophosphorus acids (or salts)









phosphonic acids

phosphinic acids

Mono- or di- esters of phosphoric acid

Phosphonic acids coupling agents

P-OH + P-OH $\nrightarrow$ P-O-P + H_2O ⇒no homocondensation

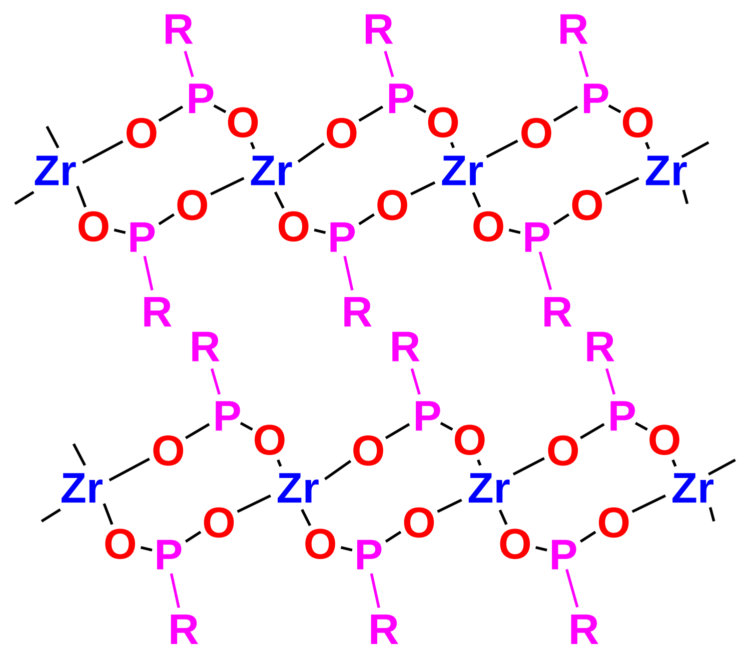
Heterocondensation

P-OH + M-OH → P-O-M + H_2O

Acids stable in water:

⇒ **surface modification in water**

Ex.: metal phosphonates



Great affinity for metal oxides :

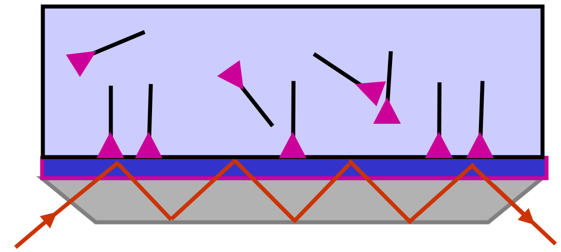
TiO_2, ZrO_2, Al_2O_3, Fe_2O_3 etc.

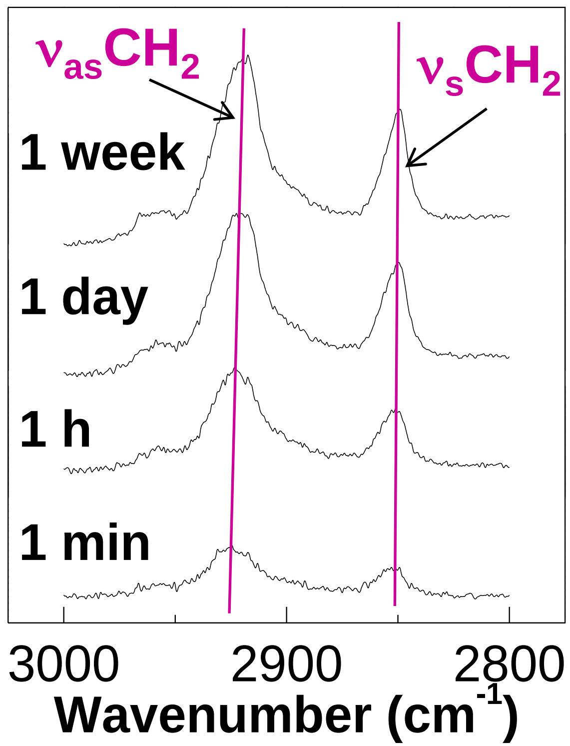
Growth of $C_{18}H_{37}PO_3H_2$ SAMs on titanium

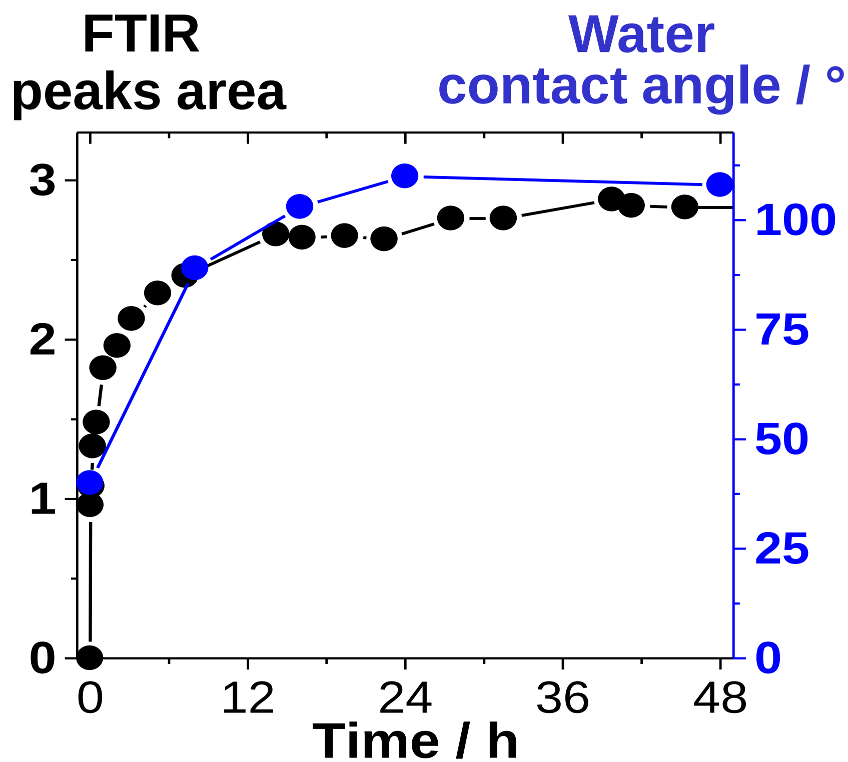
***in situ* multireflexion ATR FTIR**

Substrate: 20 nm Ti on a silicon ATR crystal

1 mM $C_{18}H_{37}PO_3H_2$ in CD_3CD_2OD, 15 °C







• **No need to control the water content, simple and reproducible!**

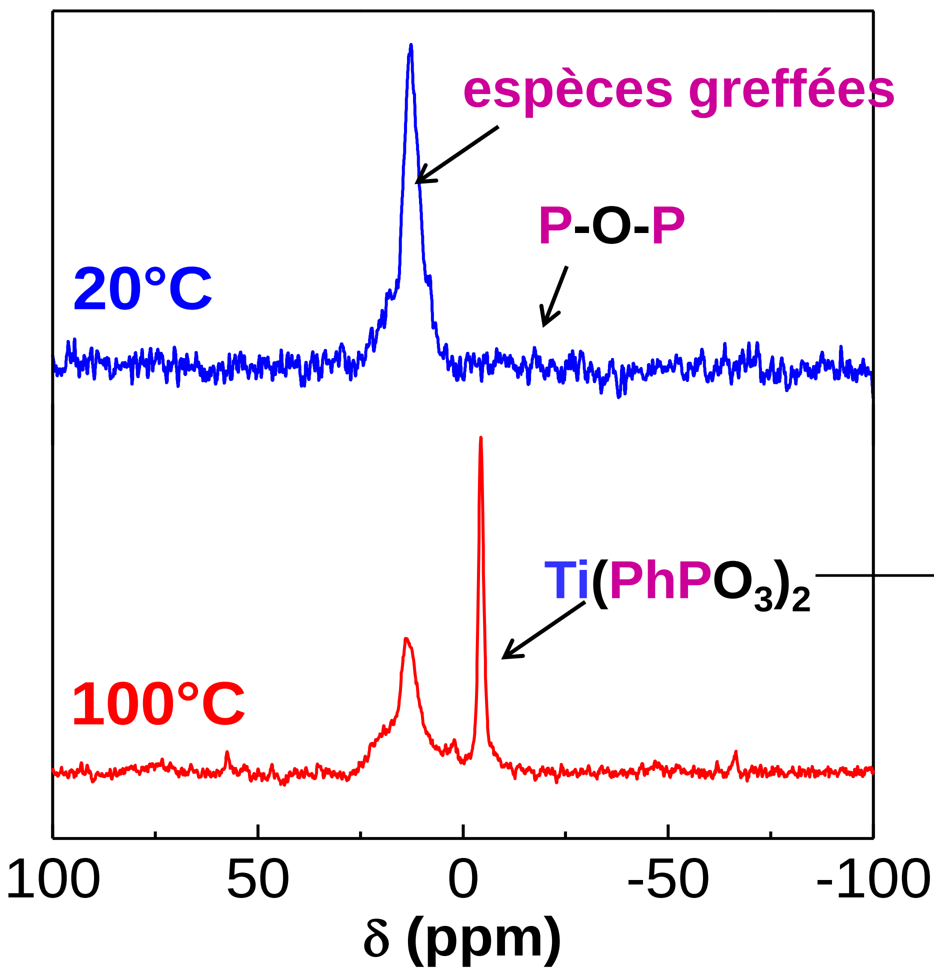
Surface modification of TiO_2 particles

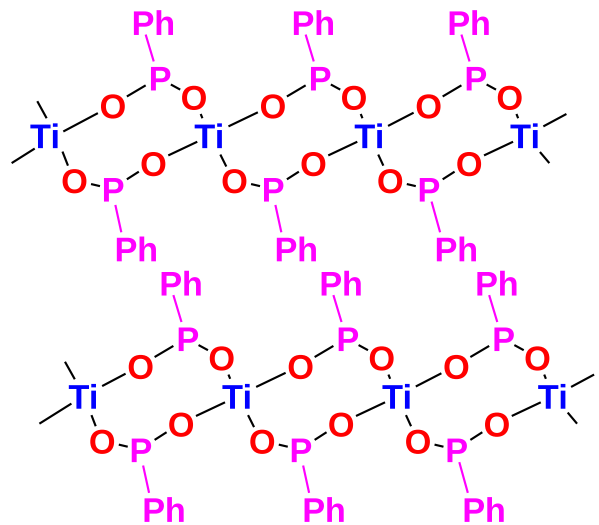
$$TiO_2 + PhPO_3H_2 \xrightarrow[T]{H_2O}$$

20°C: no P-O-P ⇒ **monolayer**

100°C: no P-O-P, but **dissolution/precipitation**

^{31}P MAS-NMR





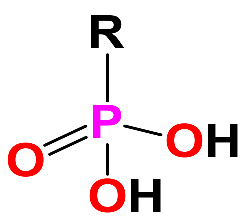
Chem. Mater. 2001, *13*, 4367-4373

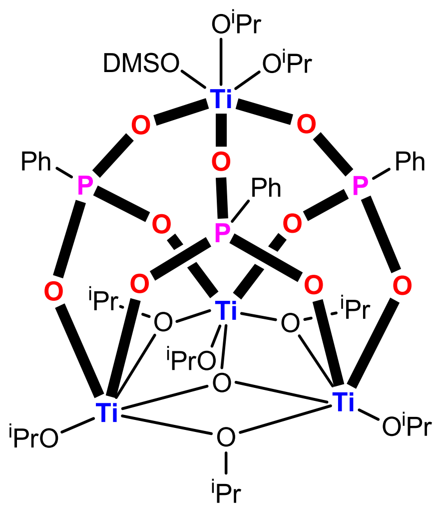
^{17}O NMR of phosphonate monolayers

collaboration F. Babonneau, C. Gervais (UPMC)

Binding of phosphonic acids to oxide surfaces: evidencing P-O-M bonds

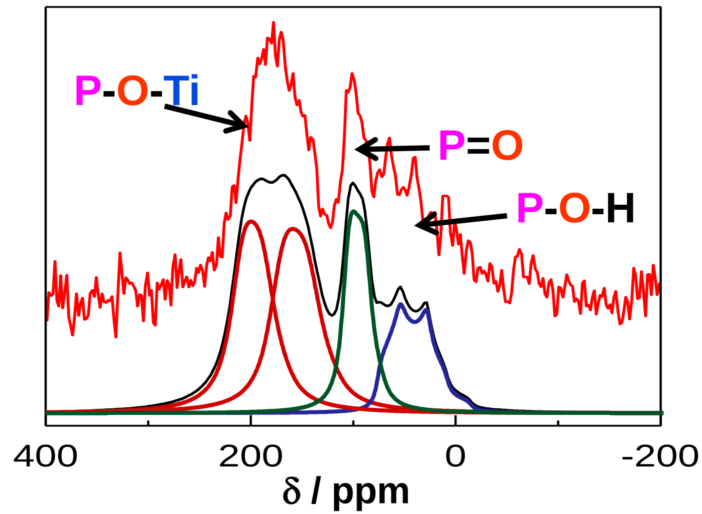
^{17}O-enriched
- phosphonic acids
- model compounds
- monolayers



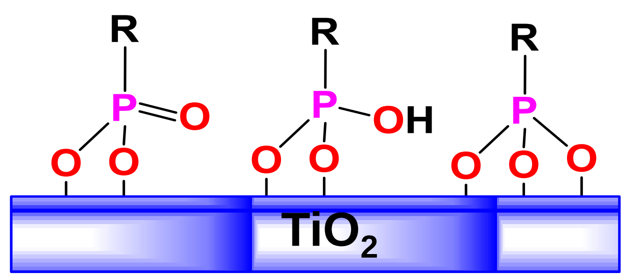


$C_{12}H_{25}PO_3H_2$ monolayer on TiO_2

^{17}O MAS-NMR

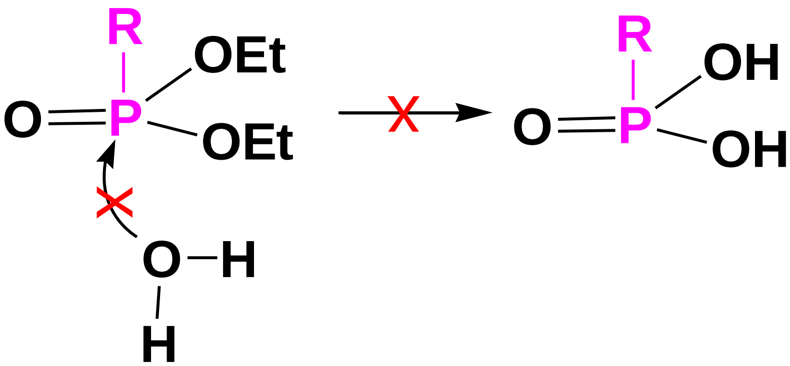


60% P-O-Ti
20% P=O
20% P-O-H

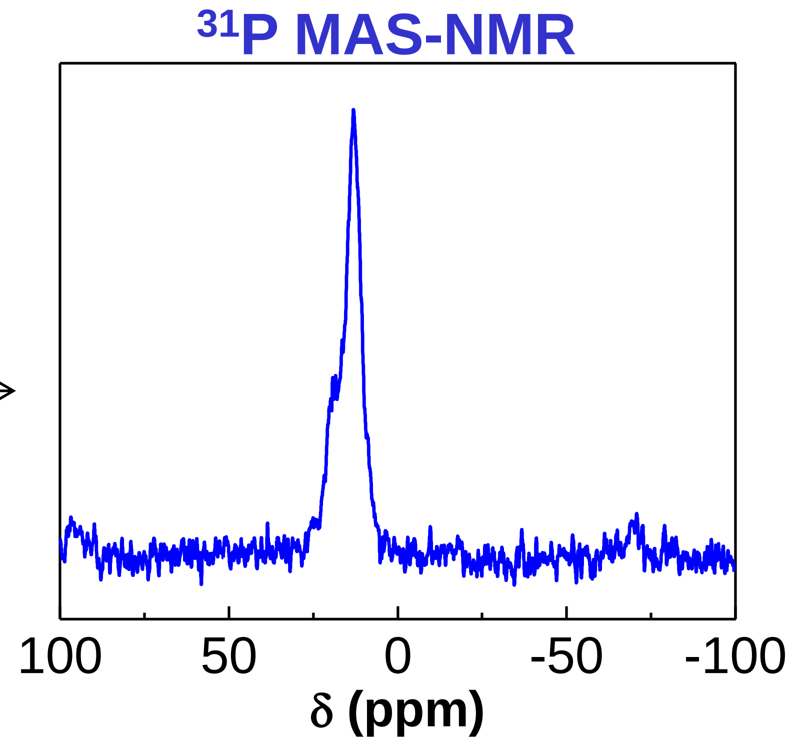


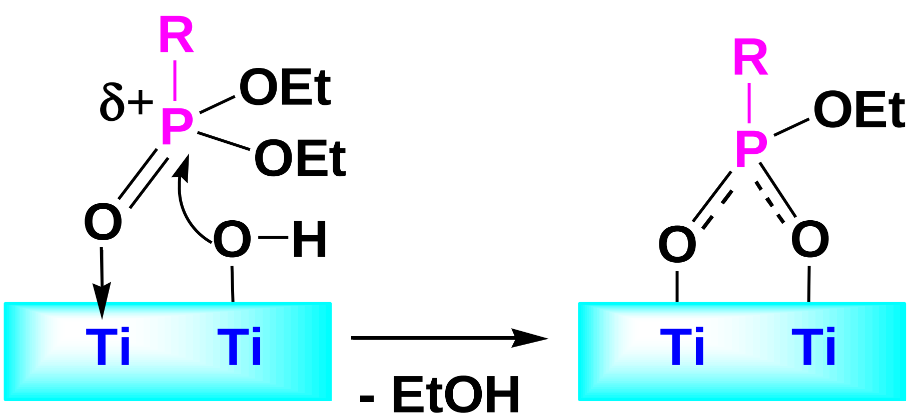
Chem. Mater. 2008

Surface modification by phosphonate esters



TiO_2 + PhPO(OEt)$_2$ $\xrightarrow[40\ °C]{CH_2Cl_2}$

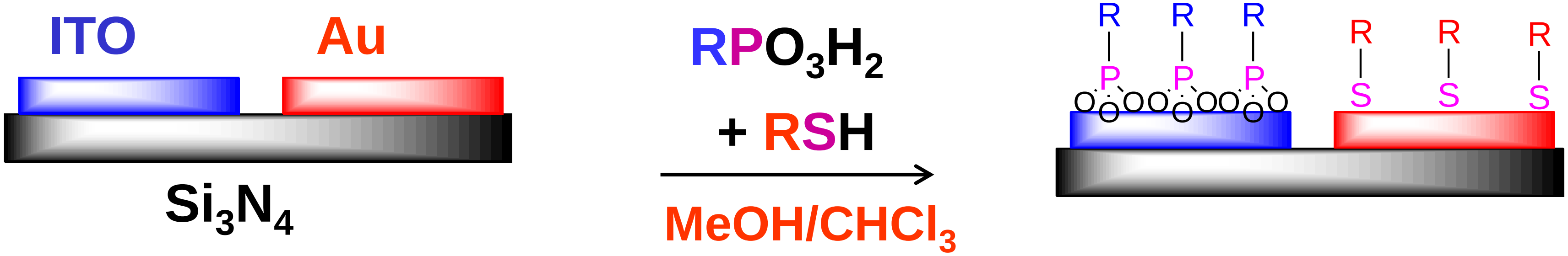


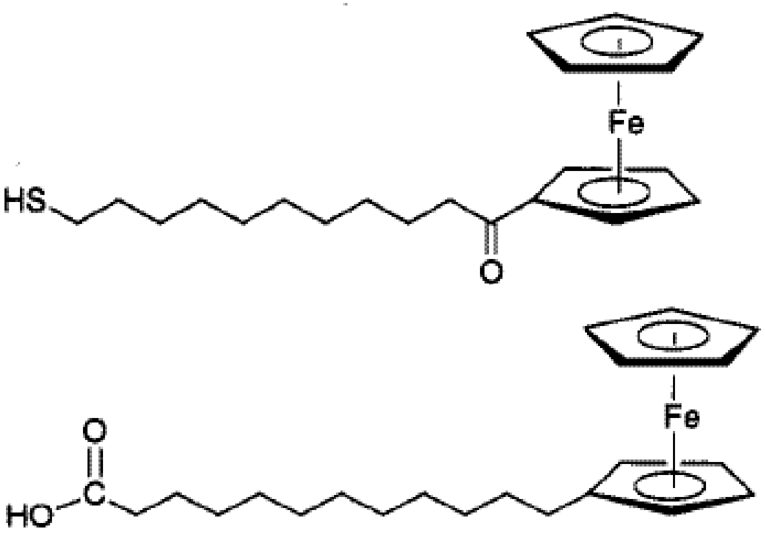


Surface catalyzed condensation

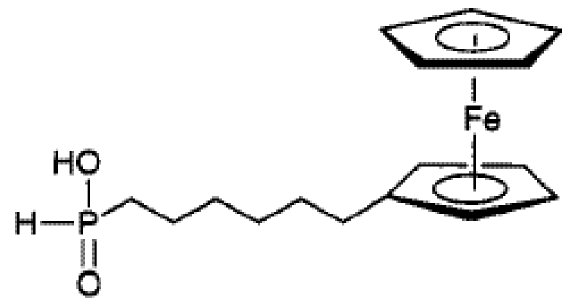
Controlled bifunctionalization

1-step: Orthogonal Self-Assembly (Gardner et al, JACS 1995)





III



V

RPO_3H_2/RSH : 0.1 mM in $MeOH/CHCl_3$ (1:3)

RCOOH/RSH : 0.1 mM in EtOH/hexane (1:20)

Selectivity >60

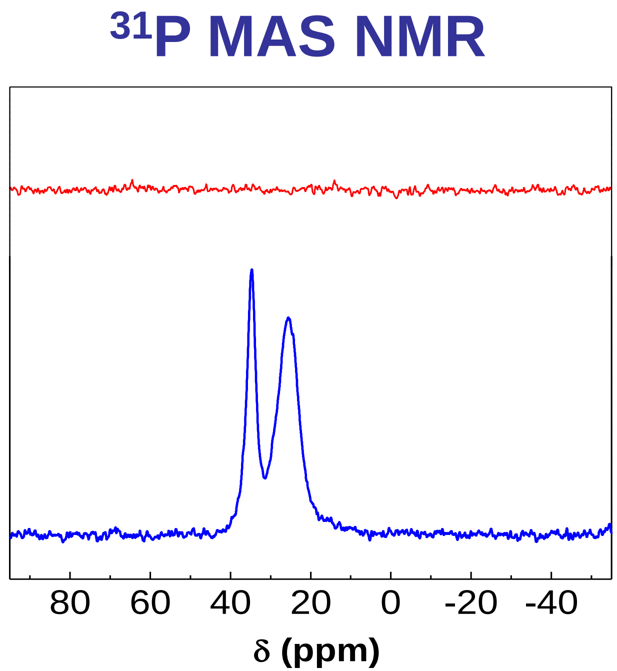
Hydrolytic stability of M-O-P

Basic conditions : stability of Ti-O-P , Zr-O-P >> Ti-O-Si , Si-O-Si

but Si-O-P + H_2O ⟶ Si-OH + P-OH

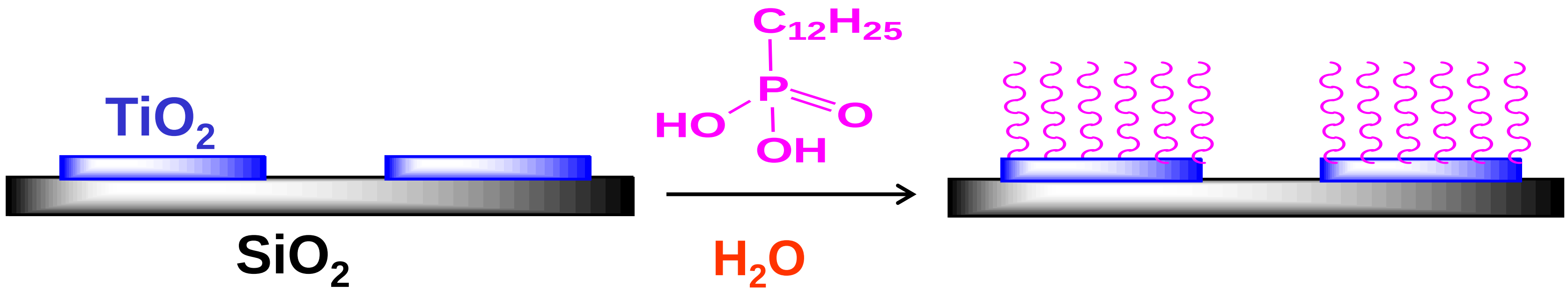
$SiO_2 + C_{12}H_{25}PO_3H_2$ —(MeOH/H_2O, 1 d)→

$SiO_2 + C_{12}H_{25}PO_3H_2$ —(Toluene., 1 d)→



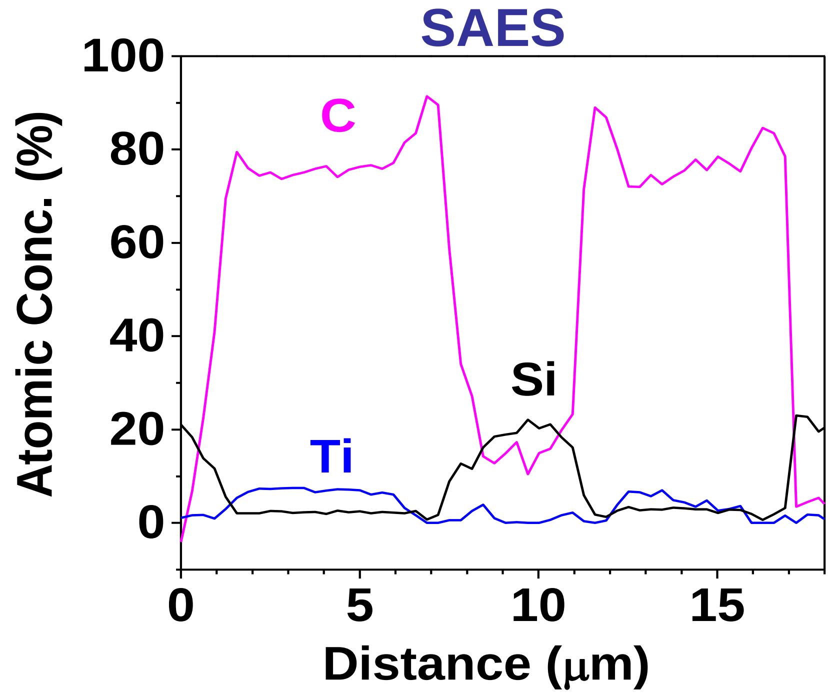
⇒ selective surface modification

Selective surface modification



substrate prepared
by microlithography

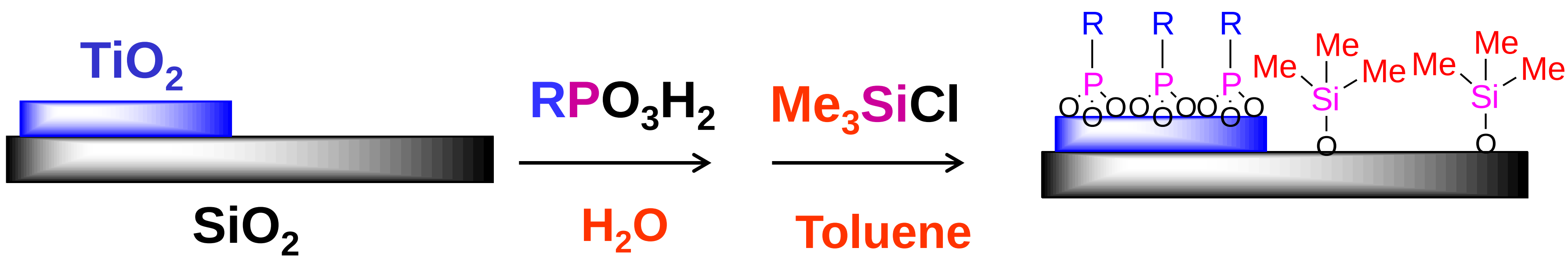
Repartition of organic groups controlled by the inorganic support



Chem. Mater. 2004, *16*, 5670-5675

Controlled bifunctionalization

2-step



- patterning substrates made by microlithography
- selective bifunctionalization of mesoporous SiO_2-TiO_2 mixed oxides prepared by sol-gel

Chem. Mater. 2004 *16*, 5670

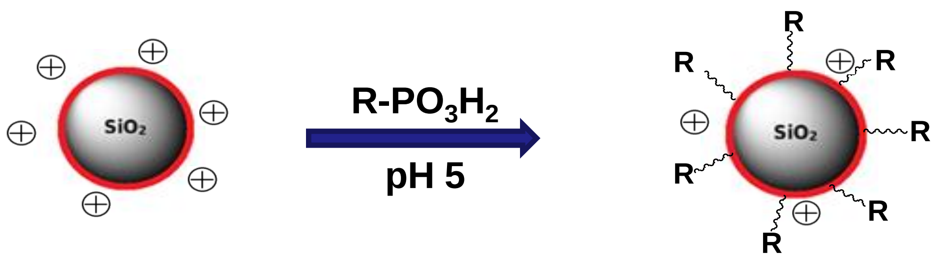
Grafting oxide NPs in aqueous colloidal solutions

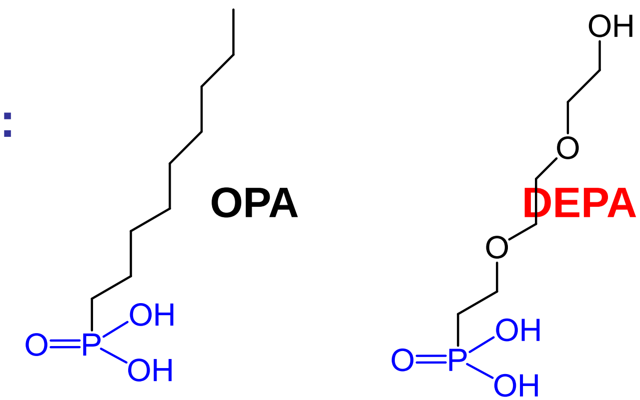
collaboration J. Oberdisse, C. Genix L2C

Silica colloids: ***used in ceramics, composite materials, cements, catalysts, polishing pastes, paper, textile...***

Levasil® 200S/30: "cationic silica sol"
= alumina-coated silica NPs

Modification of the NPs in the aqueous sol :



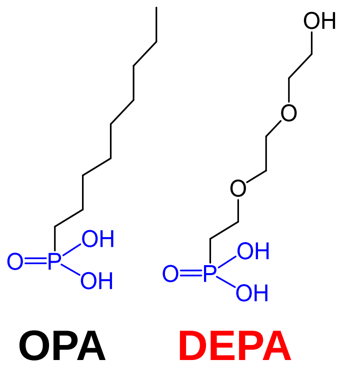


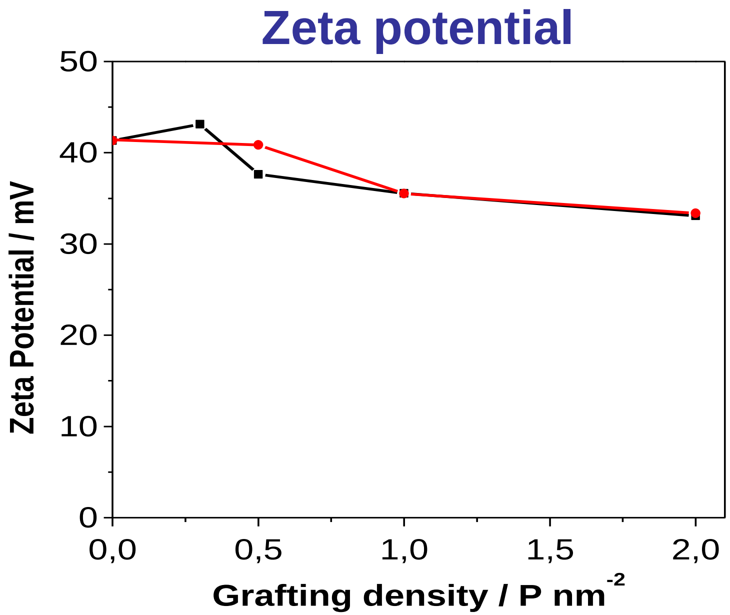
OPA *: hydrophobic R group*

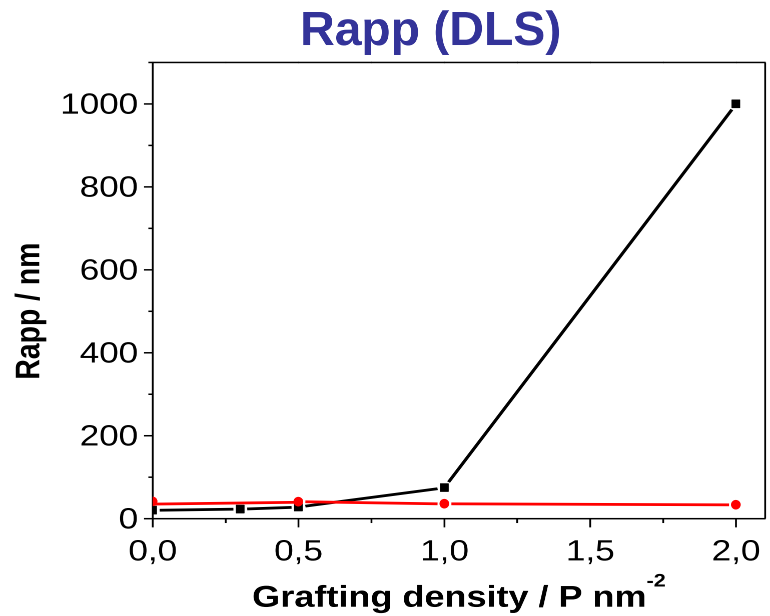
DEPA *: hydrophilic R group*

→Tuning interactions between nanoparticles in aqueous solutions

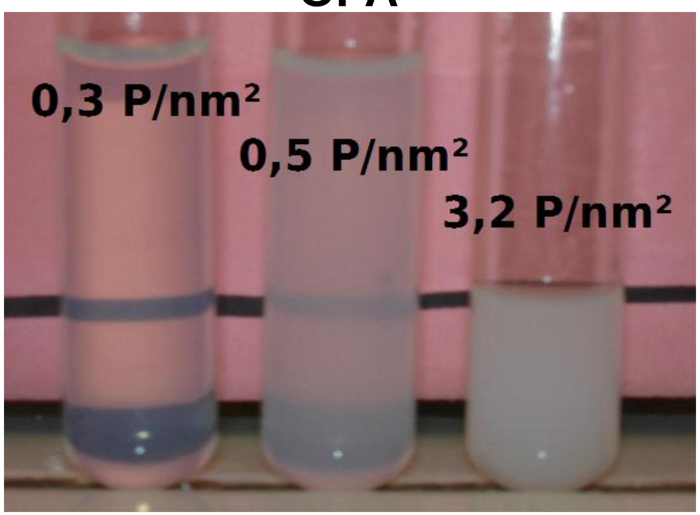
Grafting oxide NPs in aqueous colloidal solutions







OPA



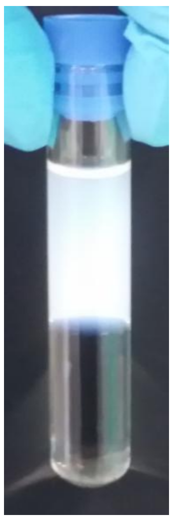
- OPA, DEPA: slight decrease of ZP
- OPA: aggregation increases with grafting density

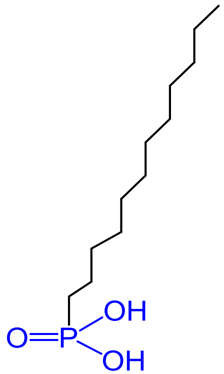
➢hydrophobic interactions

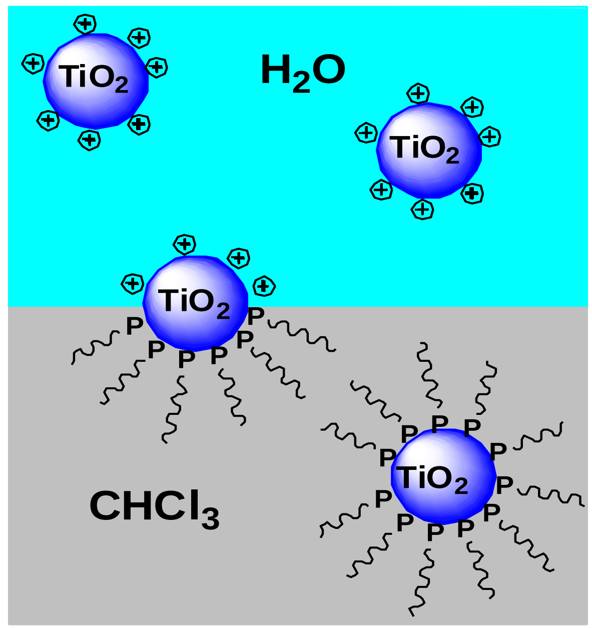
Phase transfer of TiO_2 particles

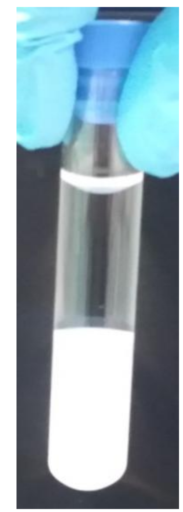
- **Oxide nanoparticles:** ***cheap, "green" syntheses in aqueous media, sols stabilized by electrostatic repulsion***

- **Inks, paints, nanocomposites:** ***need for organosoluble nanoparticles***







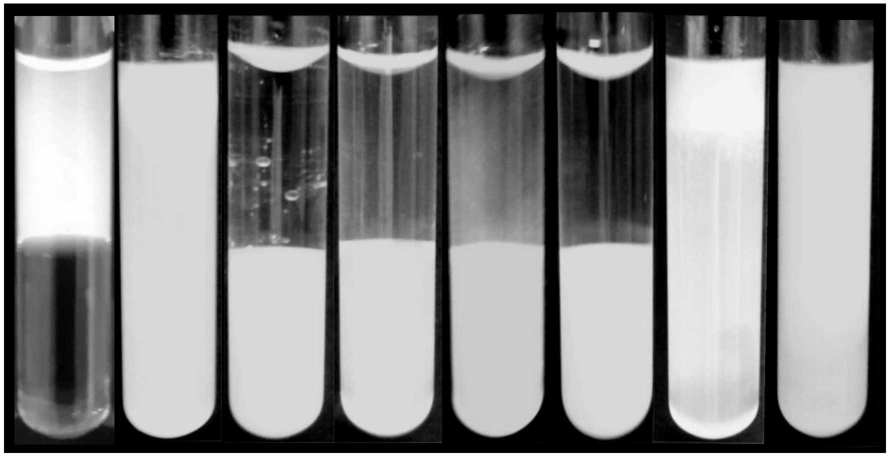


- **Simultaneous grafting / phase transfer (FTIR, NMR)**

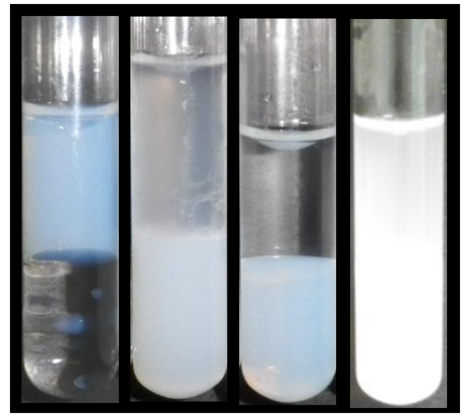
***Langmuir* 2015, 31, 10966-10974**

Phase transfer of TiO_2 particles

Parameters influencing the transfer

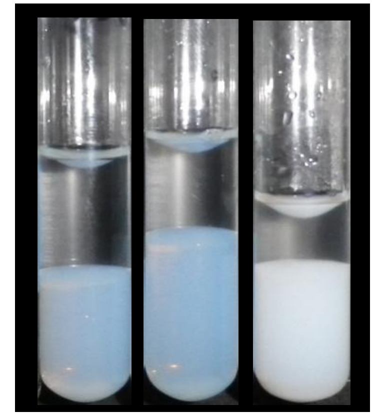


None, C_3PA, C_5PA, C_8PA, $C_{12}PA$, $C_{18}PA$, tBuPA, PPA



0 0.8 1.7 2.4

PA concentration (mmol/g)



1 5 23

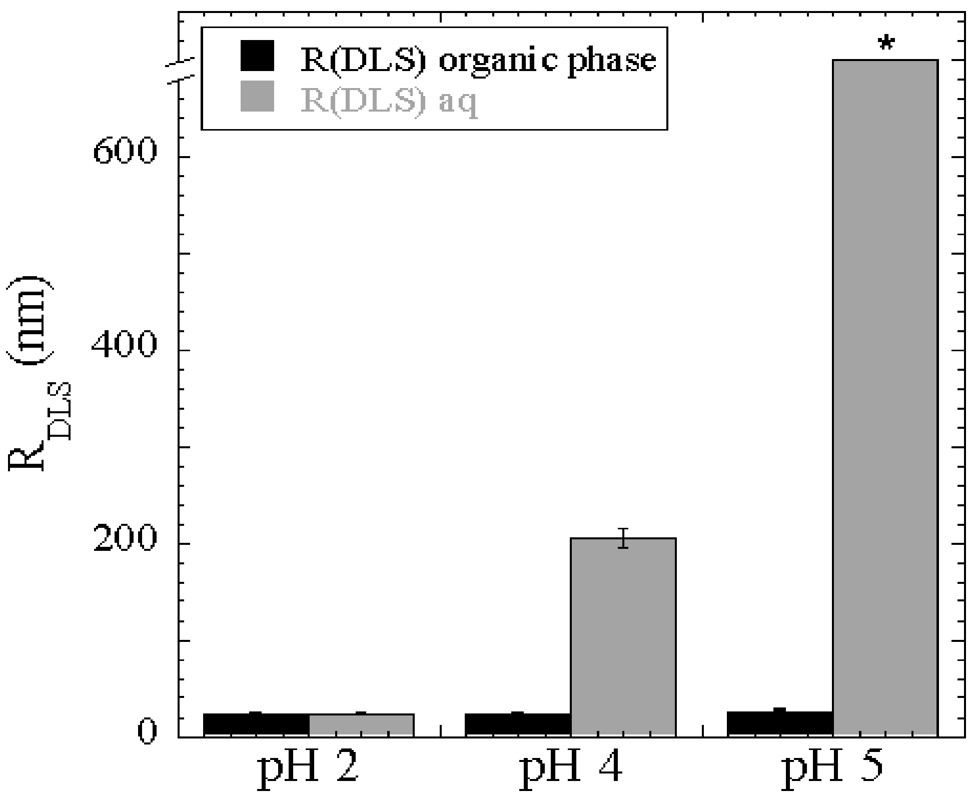
Sol concentration (wt%)

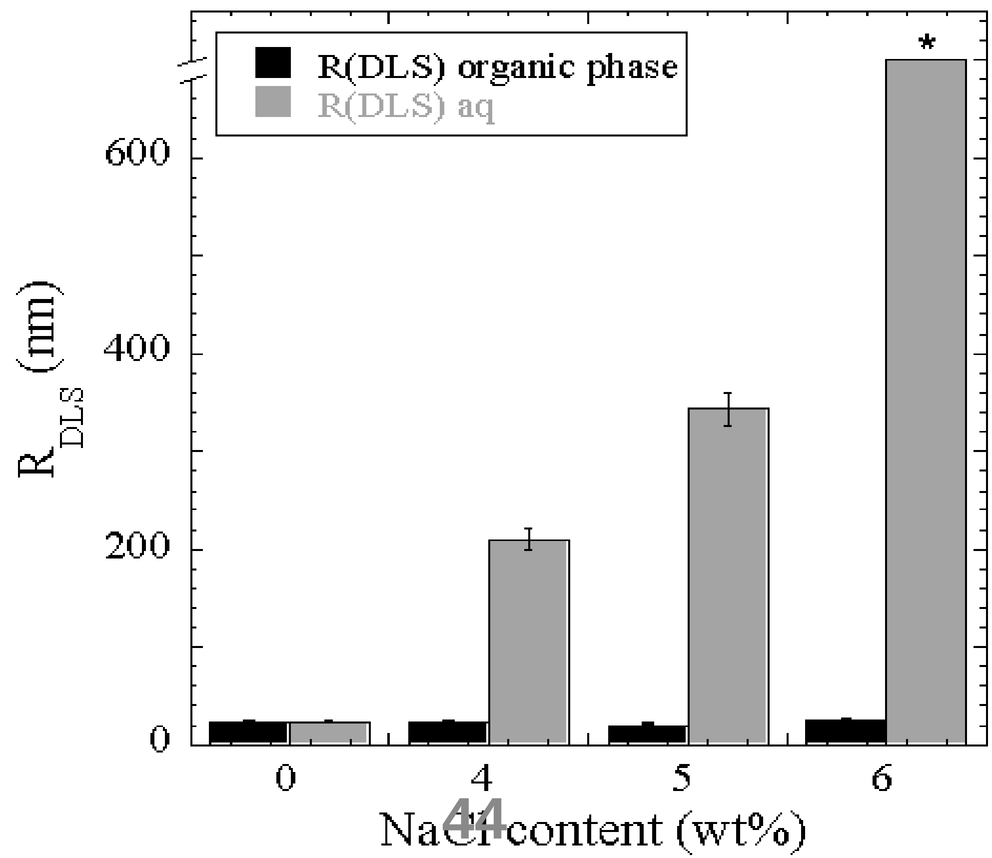
- Alkylphosphonic acids with chain ≥ 5 Carbons
- ca 4-5 P/nm^2
- Works even for high sol concentration

Langmuir 2015, 31, 10966-10974

Transfer of aggregated nanoparticles

Deaggregation during phase transfer / surface modification

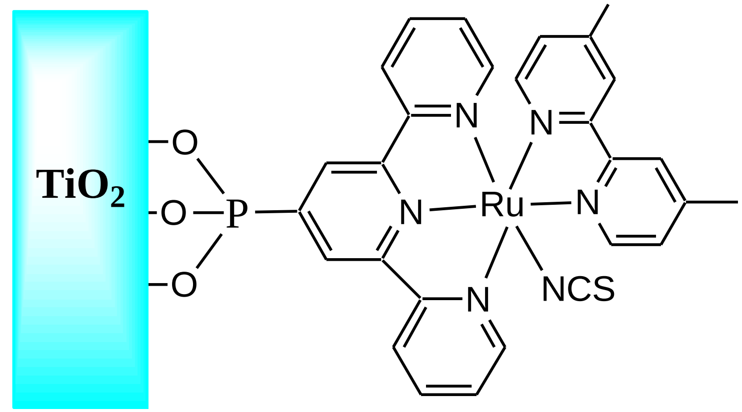




Applications

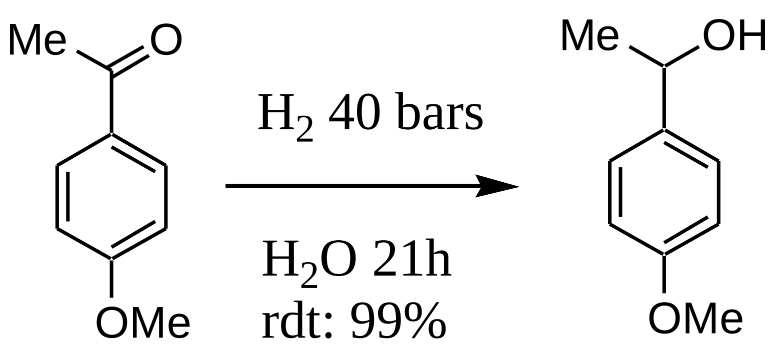
• Photovoltaic cells

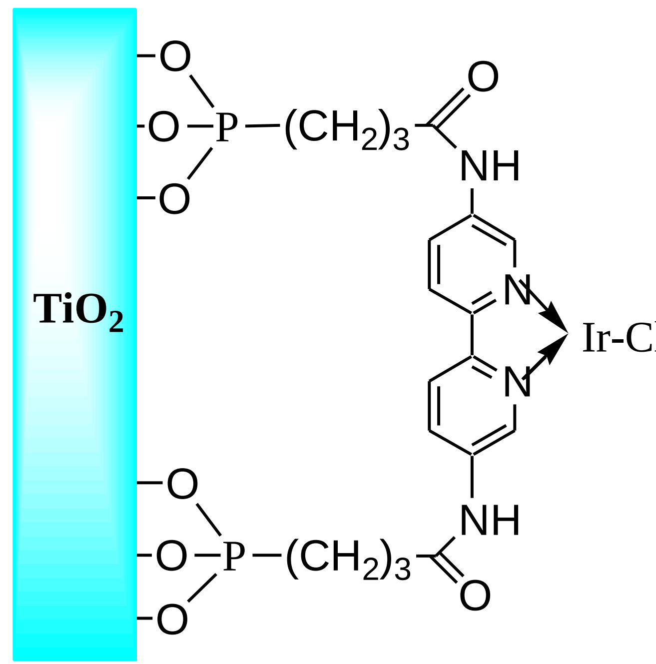
Complex absorbs visible light. Injection of é⁻ in the conduction band of the metal



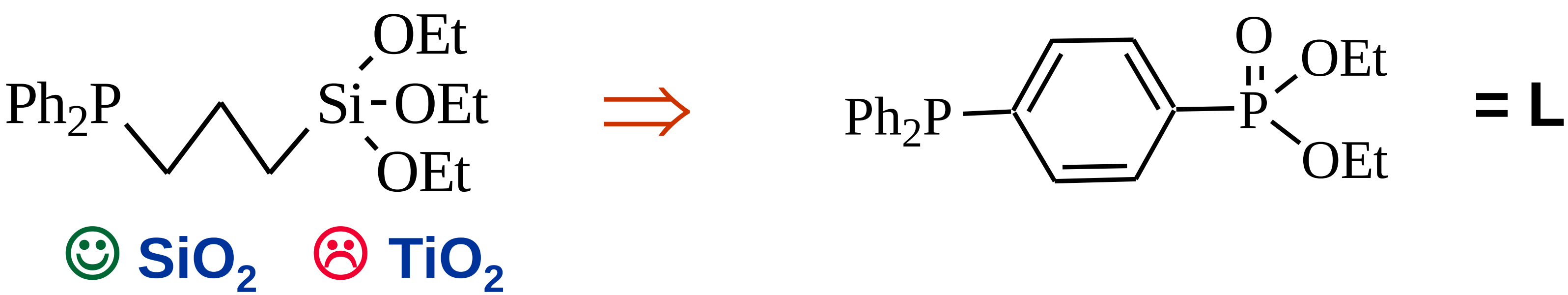
•Heterogeneous catalysis

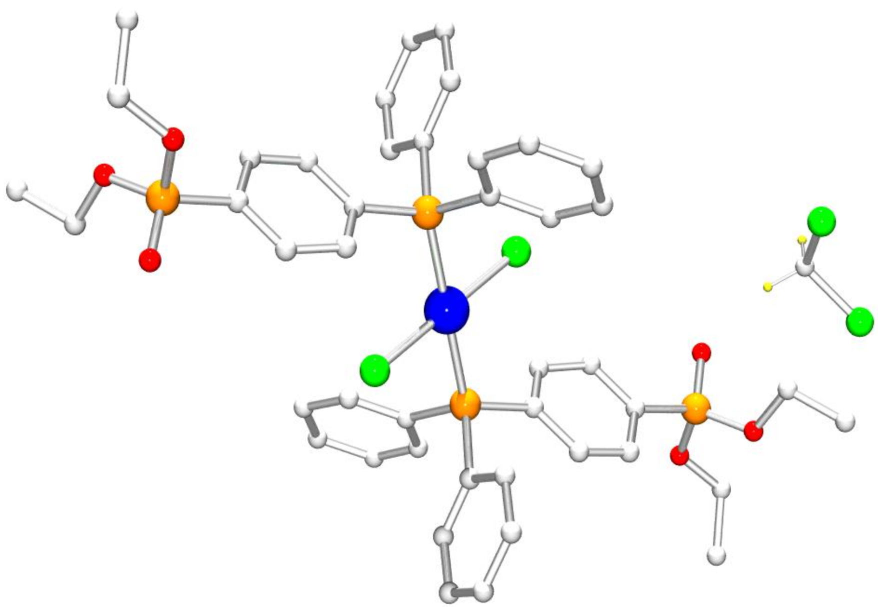
Reduction of aromatic ketones



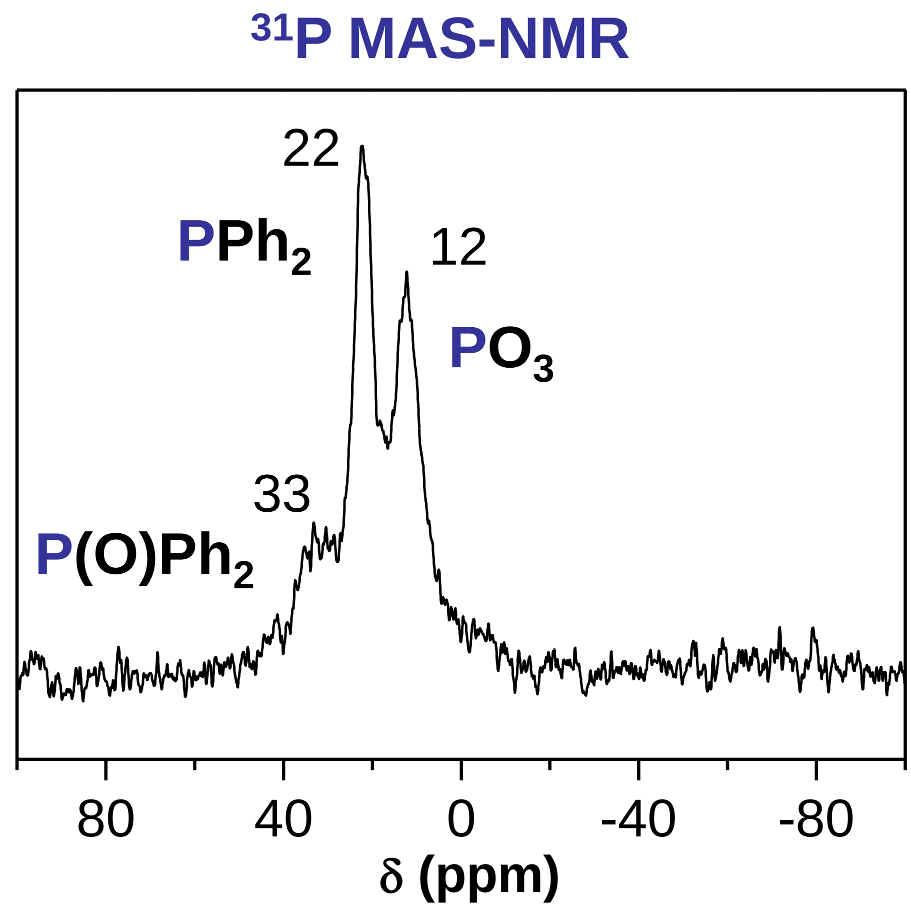


Immobilization of Catalyts on Metal Oxides

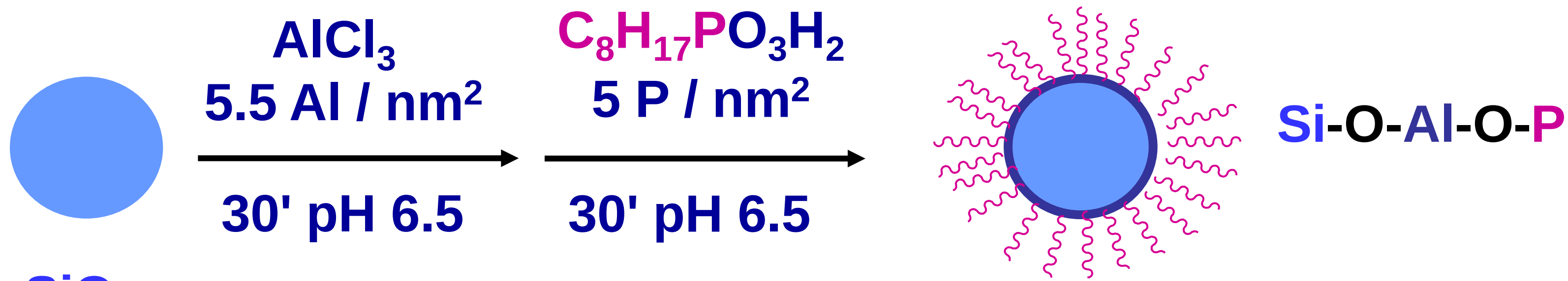




trans-$PdCl_2L_2.CH_2Cl_2$ —TiO₂, 40°C→

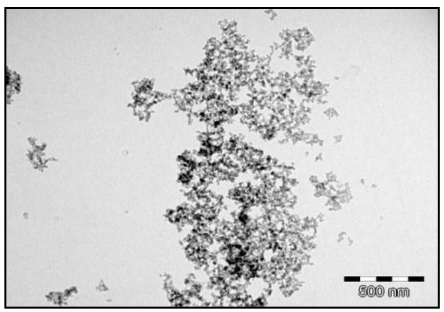


Modification of SiO_2 fillers in Water

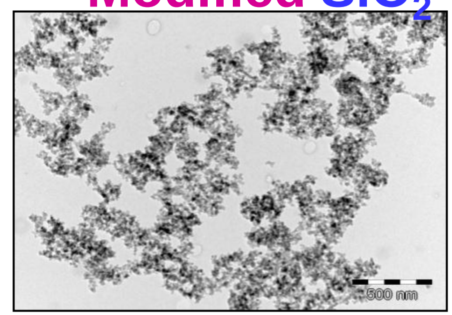


SiO_2

Modified SiO_2



125 m^2/g

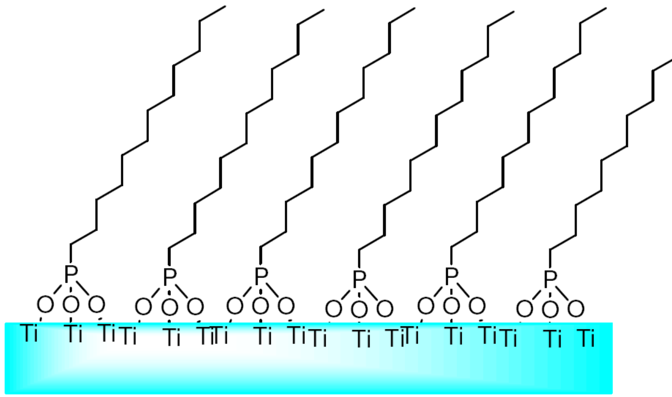


130 m^2/g

No change in morphology, 1-4 P/nm^2, hydrophobic

Fr. Patent **2005 Rhodia-CNRS**

$C_{18}H_{37}PO_3H_2$ SAMs as boundary layer lubricants



Long alkyl chains :

intermolecular forces between methylene groups

⇒ formation of Self-Assembled Monolayers

Application: lubrication

Substrates: 20 nm Ti on Si

grafting with $C_{18}H_{37}PO_3H_2$

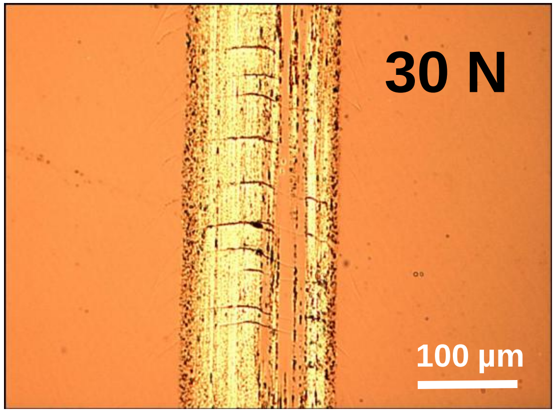
in EtOH, 2d.

Friction: stainless steel ball

D = 2 mm, 260 HV,

normal force up to 60 N

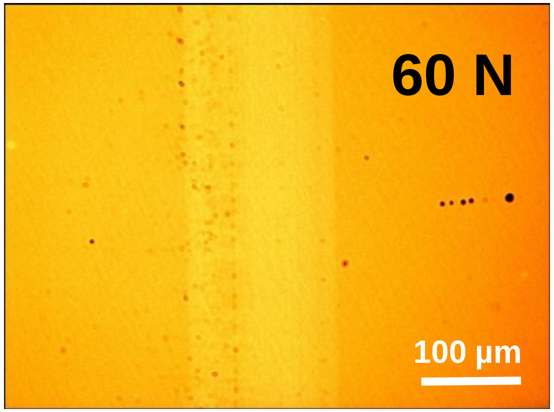
MRS Symp. Proc. **2004**



Ti/Si untreated

Contact angle 11°

Friction coeff. 0.6



ODPA/Ti/Si

Contact angle 102°

Friction coeff. 0.1

Antibacterial Monolayers for Biomaterials

Prevention of orthopedic implant infections:

Current approach: hinder bacterial adhesion and biofilm formation using "thick" antibacterial coatings : cationic polymers, polyelectrolyte multilayers, silver-releasing sol-gel coatings…

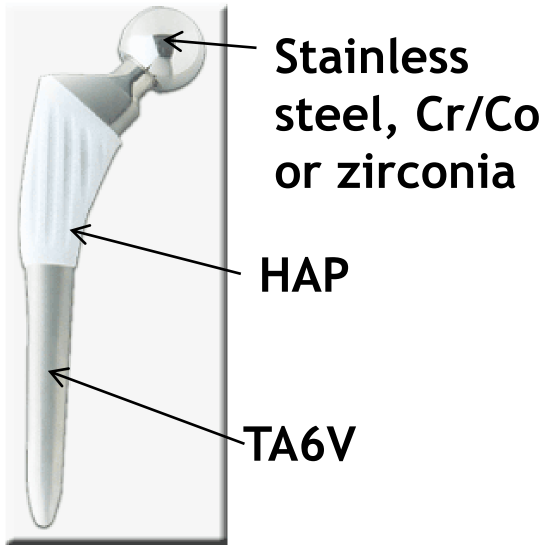
Monolayers ?

Inorganic implant materials:

- metals, metal oxides, phosphates…

Interest of phosphonates:

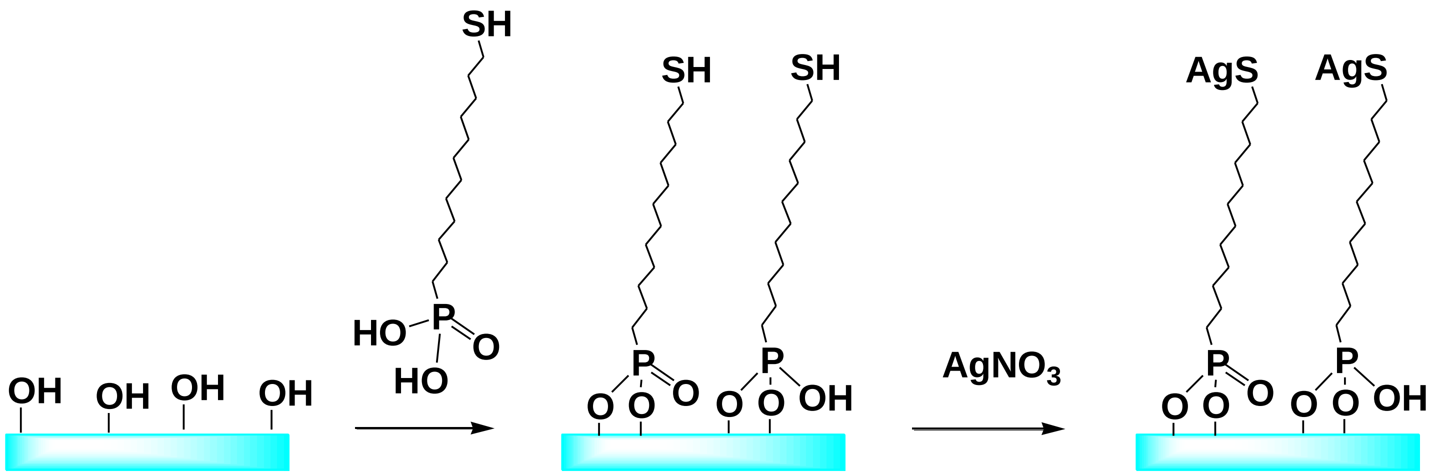
- high affinity for all these materials
- good thermal and hydrolytic stability



Hip prosthesis

Antibacterial monolayers

Proof of principle: silver release

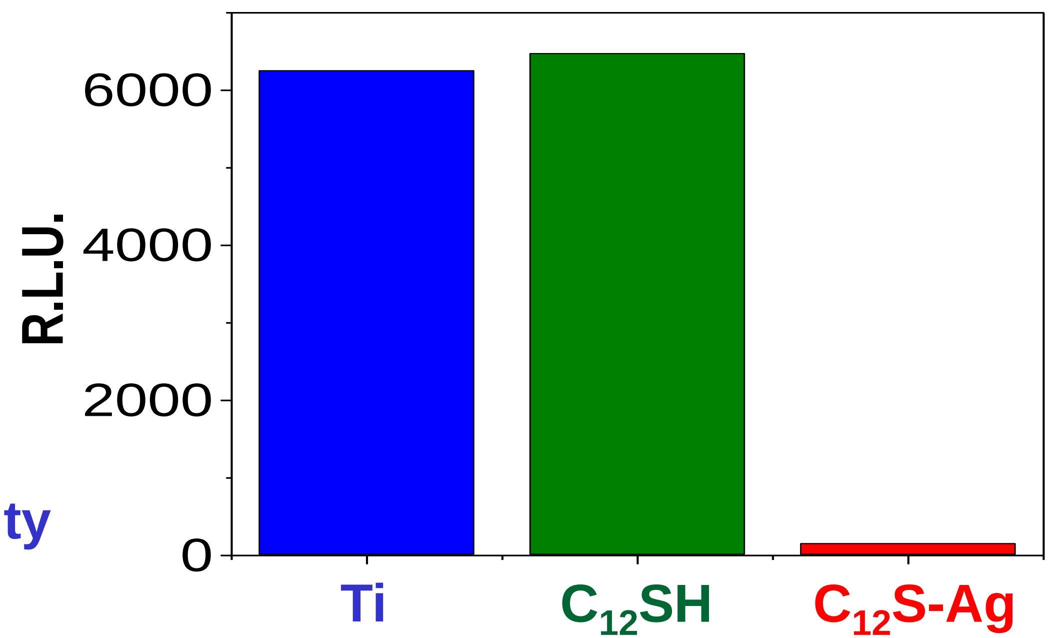


Biofilm assay:

samples immersed 3d at 37 °C in a culture of *E. Coli* GFP

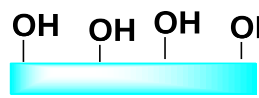
⇒ growth of the biofilm at the air-liquid interface.

Decrease of ca 97 % of biofilm density

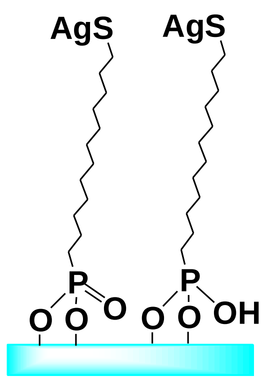


Fluorescence microscopy (*E. coli gfp*)

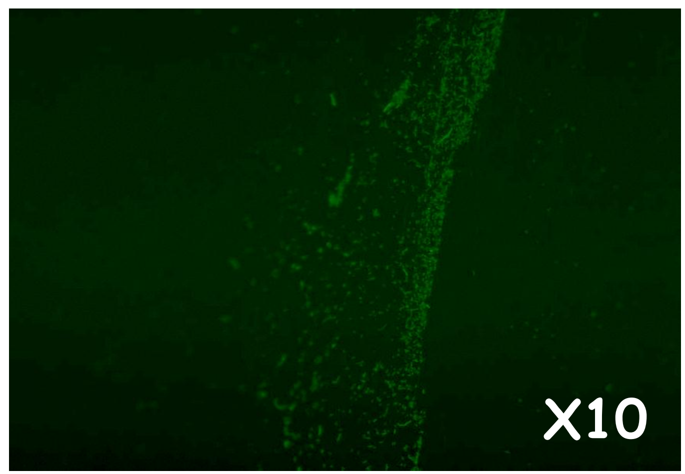
Immersion 3 days at 37 °C



Very dense biofilm



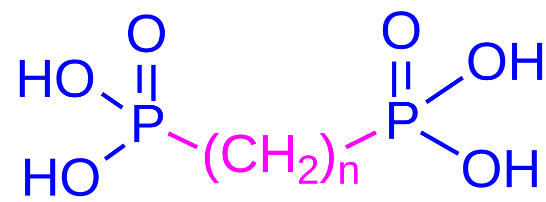
No real biofilm



Decrease of 95 % of biofilm density

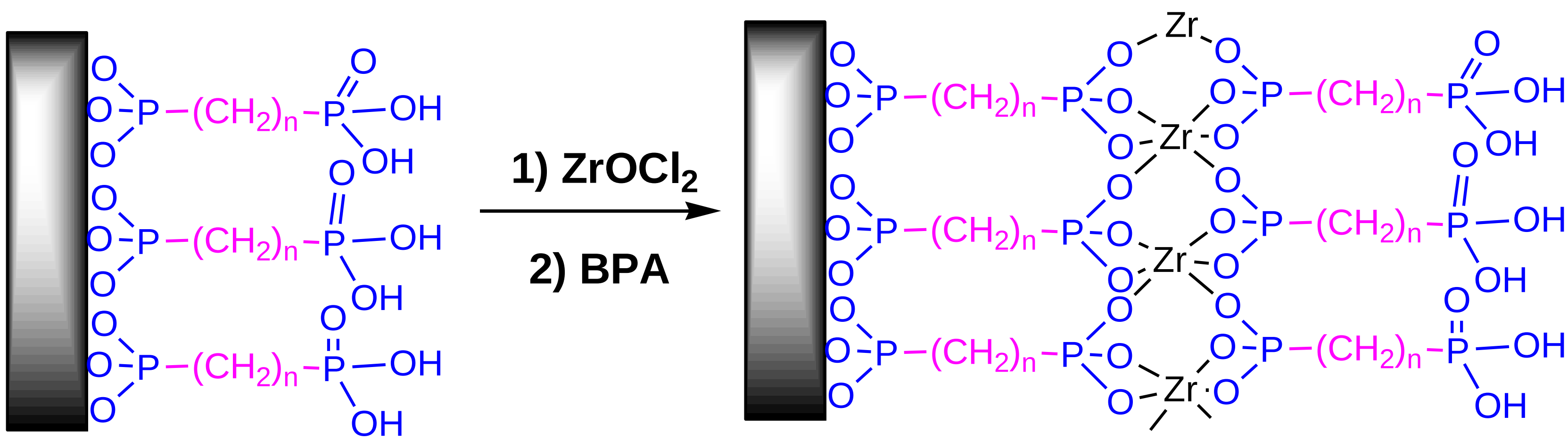
Bis-phosphonate multilayers

bis-phosphonic acids (BPA)



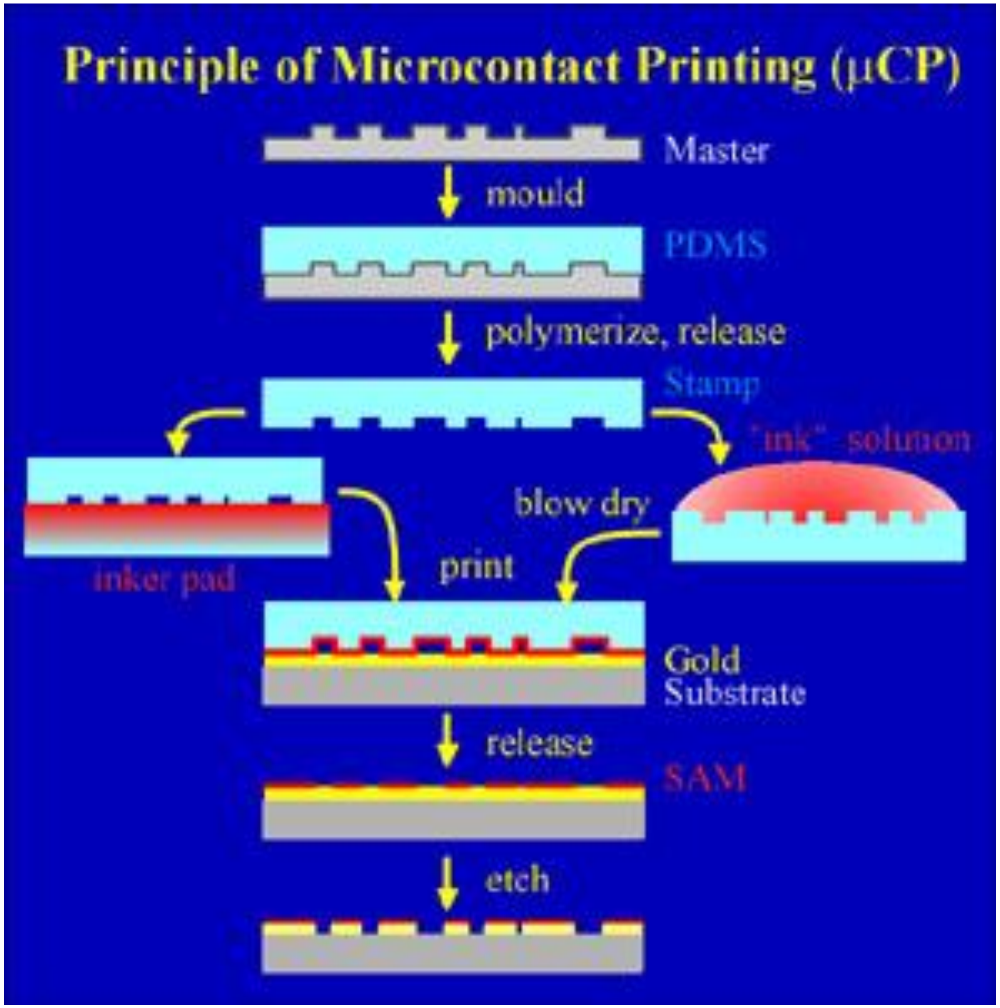
Controlled deposition of multilayers

- Ex.: BPA / Zr Mallouk et al., JACS 1993



Microcontact printing

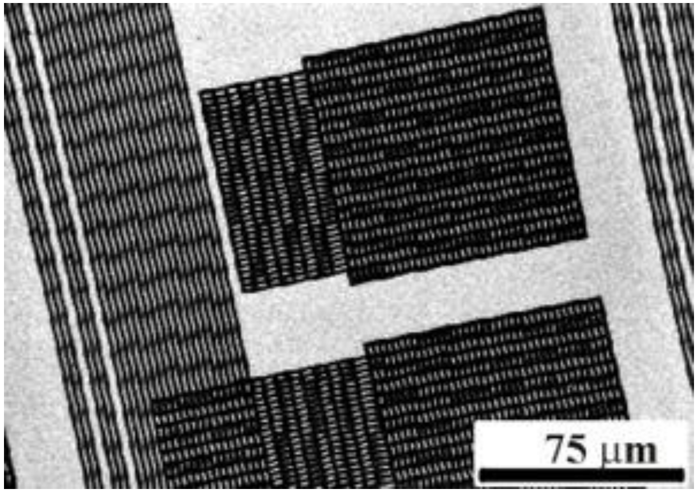
Chemical patterning of surfaces and high-resolution lithographies

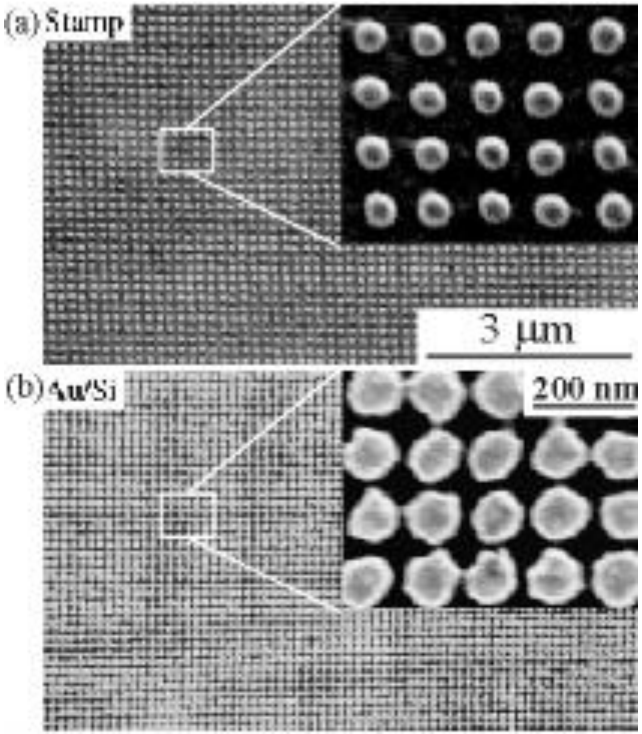


•alkanethiols on gold

•stamps made from polydimethylsiloxane (PDMS).

Microcontact printing





Scanning electron micrograph of a gold structures on silicon fabricated by µCP and a subsequent etch. Hydrophobic SAM protects the modified surface from etching

High-resolution µCP:

(a) SEM of a stamp with 60 nm dots.

(b) gold dots fabricated by printing and etching were slightly broadened due to ink diffusion and substrate roughness.

http://www.zurich.ibm.com/

Microcontact printing

Universal Ink for Microcontact Printing

Burdinski et al. Angew. Chem. 2006, 45, 4355

Surfaces routinely used in µCP: Au, Ag, Cu, Pd, SiO_x, AlO_x

Patterning of metal as well as metal oxide surfaces with a single ink composition:

octadecanethiol (ODT) + octadecylphosponic acid (ODPA) (PDMS stamps)

Conditions optimum: ODT (2 mm) and ODPA (10 mm)

[ODPA] sur le tampon PDMS << [ODPA] dans l'encre (hydrophilie)

Temps de contact: 15 s (Au), 300 s (Al)

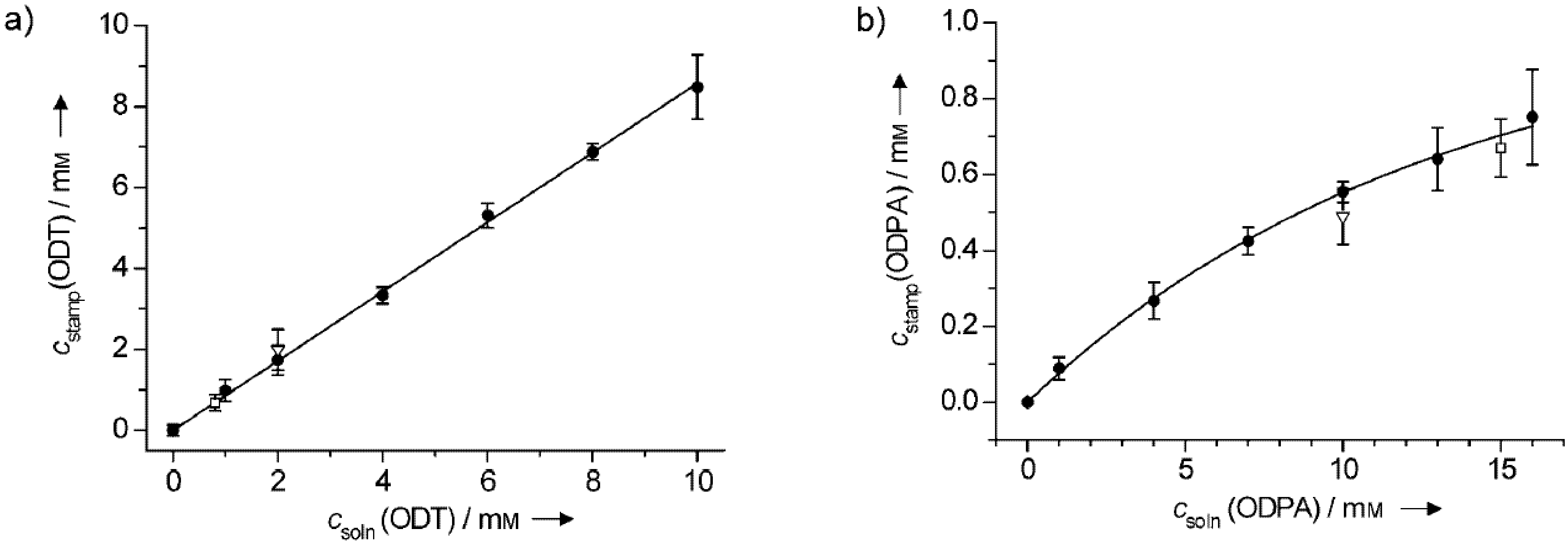
XPS:

sur Au: 3.6 S/nm^2 0.8 P/nm^2

sur Al: 0 S/nm^2 4.6 P/nm^2

Microcontact printing

Universal Ink for Microcontact Printing



Concentrations of ODT (a) and ODPA (b) in PDMS stamps after inking as a function of their concentration in:

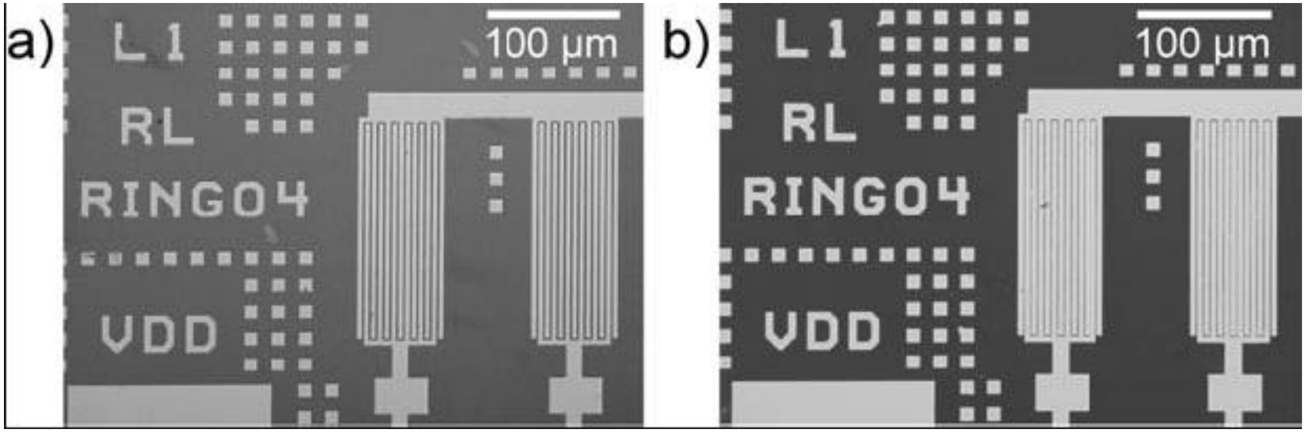
● pure ODT or ODPA solutions in ethanol

▽: csoln(ODT)=2.0 mm and csoln(ODPA)=10 mm,

□: csoln(ODT)=0.8 mm and csoln(ODPA)=15 mm).

Microcontact printing

Universal Ink for Microcontact Printing



Optical micrographs of gold (a) and aluminum substrates (b) after µCP with a solution of ODT (2 mm) and ODPA (10 mm) in ethanol followed by wet chemical etching.

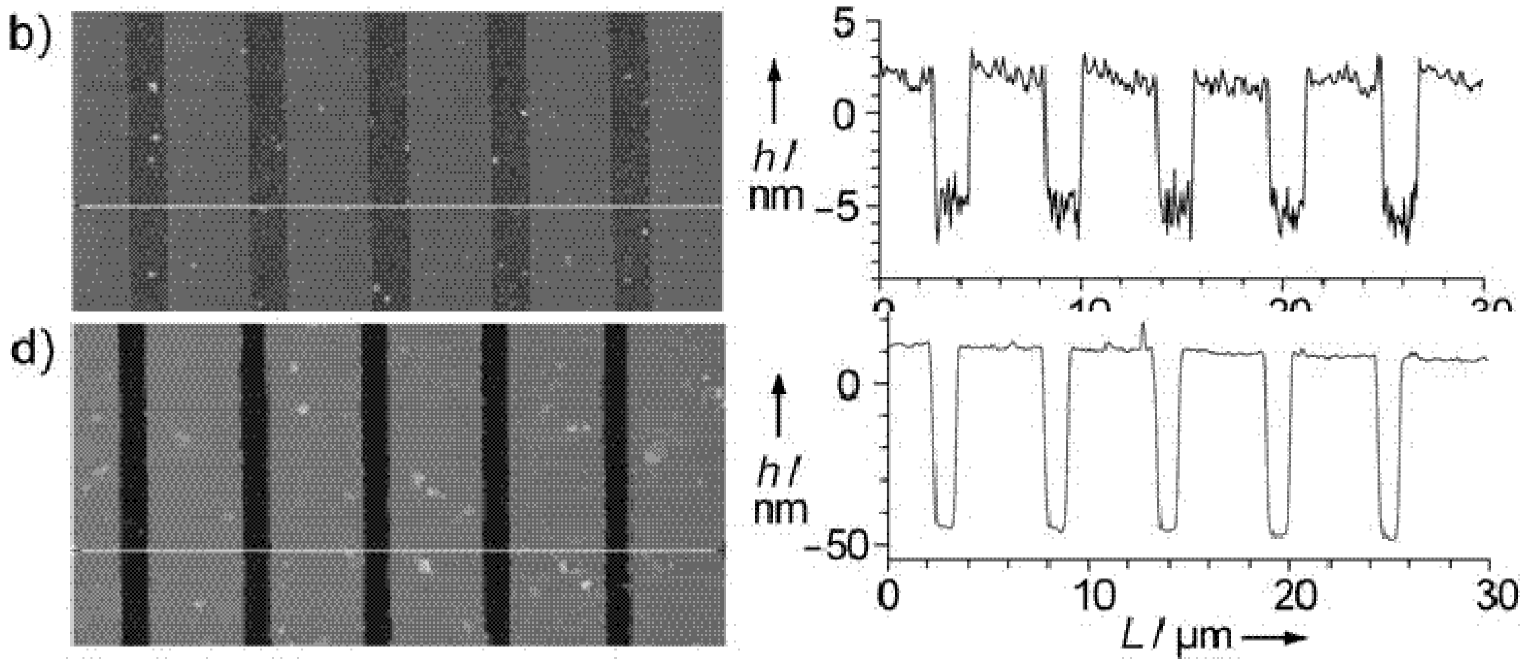
Etching bath:

Al : alkaline hydrogen peroxide

Au : alkaline thiosulfate

Microcontact printing

Universal Ink for Microcontact Printing

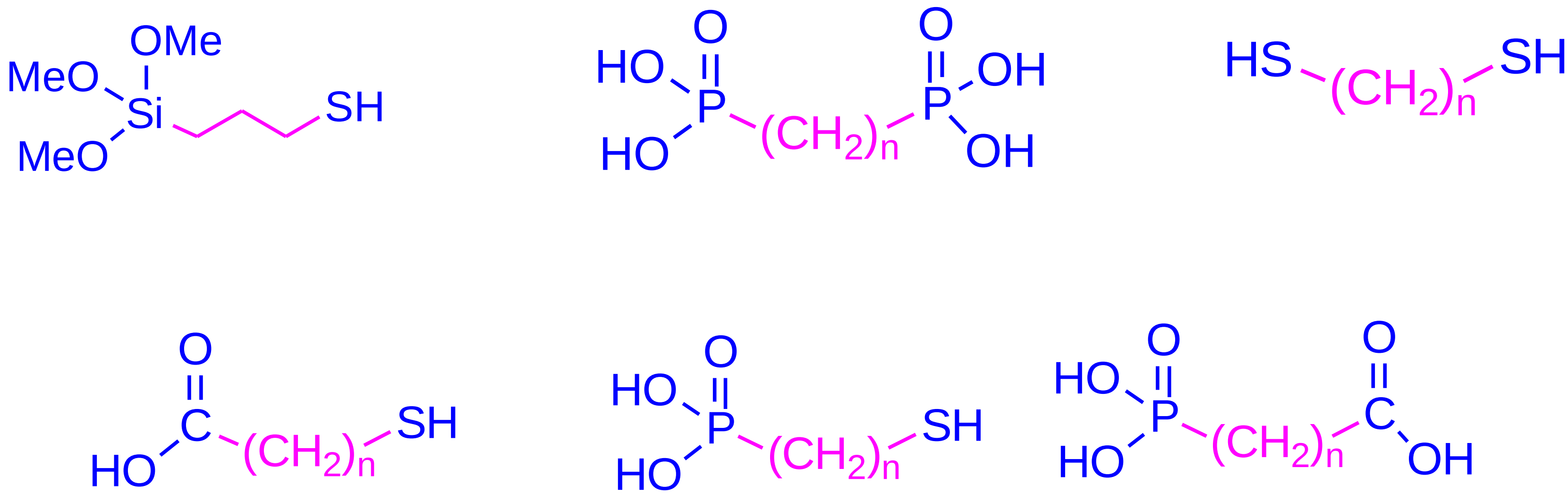


Tapping mode AFM micrographs and height profiles of

gold (b, 10 nm Au) and aluminum substrates (d, 50 nm Al)

patterned by µCP with mixed ODT/ODPA inks and subsequent wet etching.

Bifunctional coupling agents

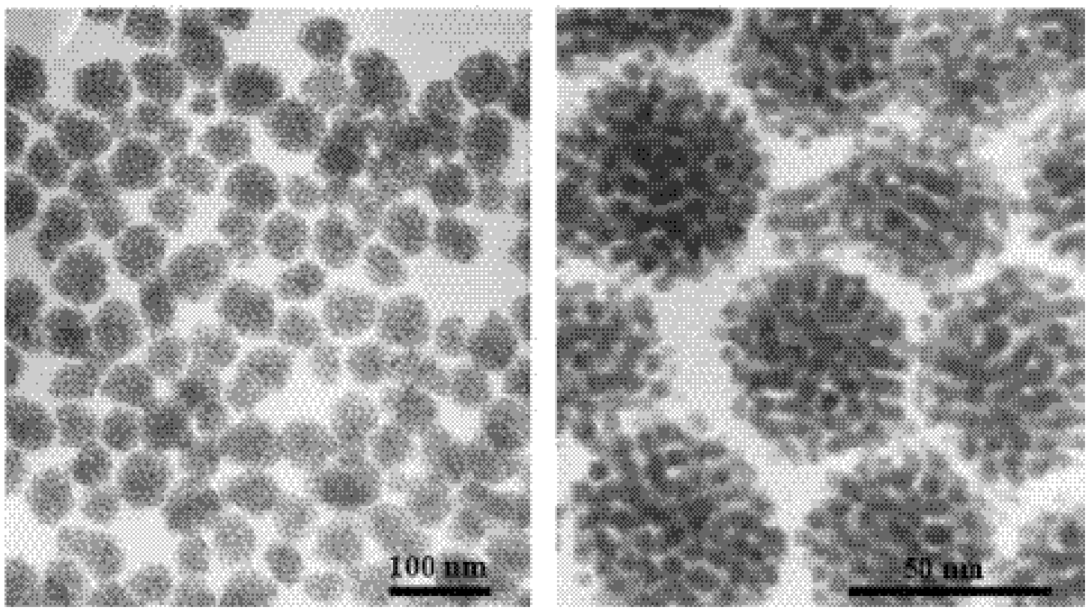


Inorganic-inorganic assemblies, interface modification

Bifunctional coupling agents

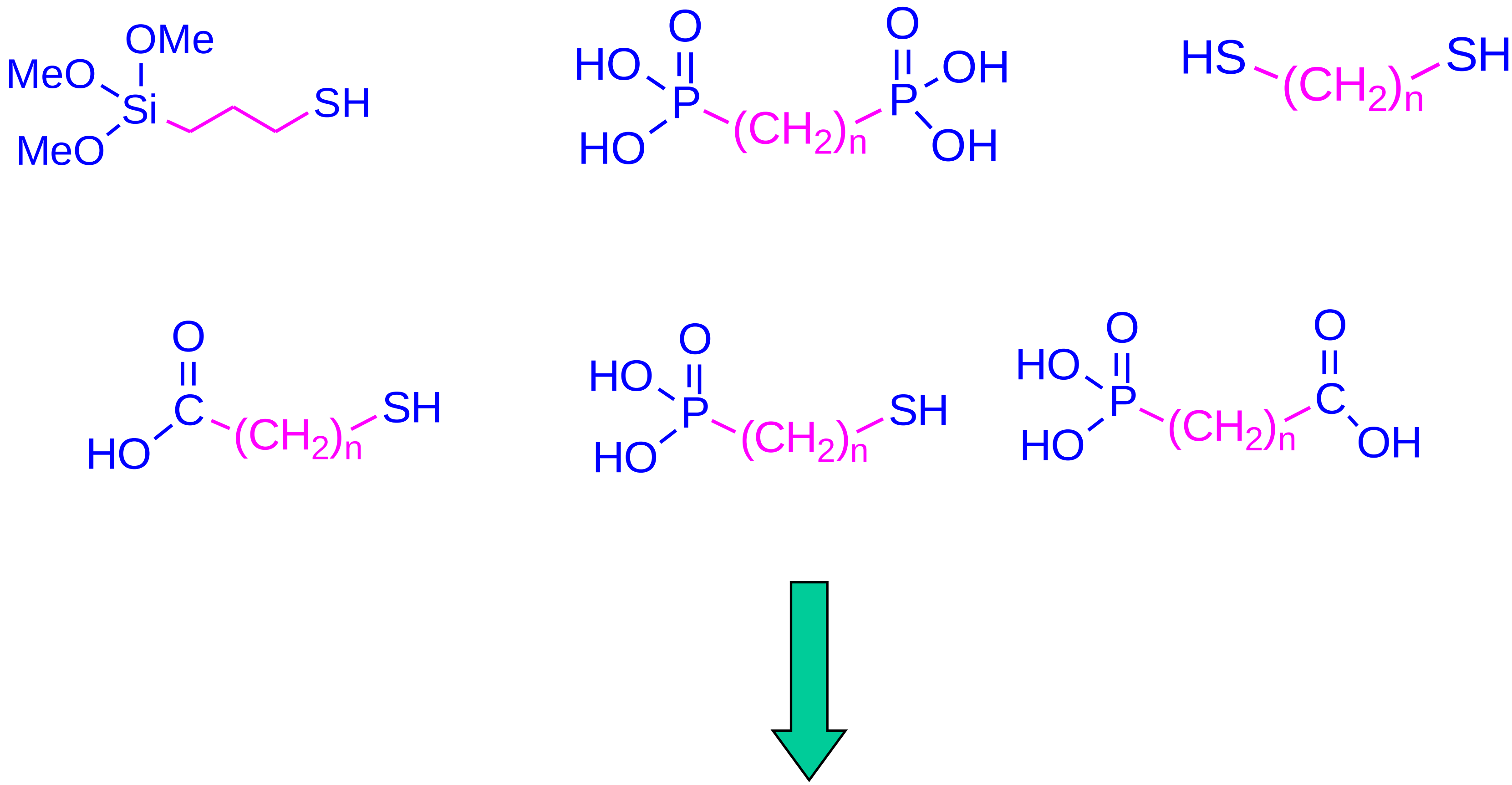
Tetraoctylammonium bromide-stabilized gold nanoparticles in toluene of ca. 5-8 nm diameter

+ dilute solution of 1,9-nonanedithiol in toluene (0.5 mL)



Transmission electron micrographs of solution-stable spherical assemblies formed at a molar ratio of 1,9-nonanedithiol to gold particles of 100.

Bifunctional coupling agents

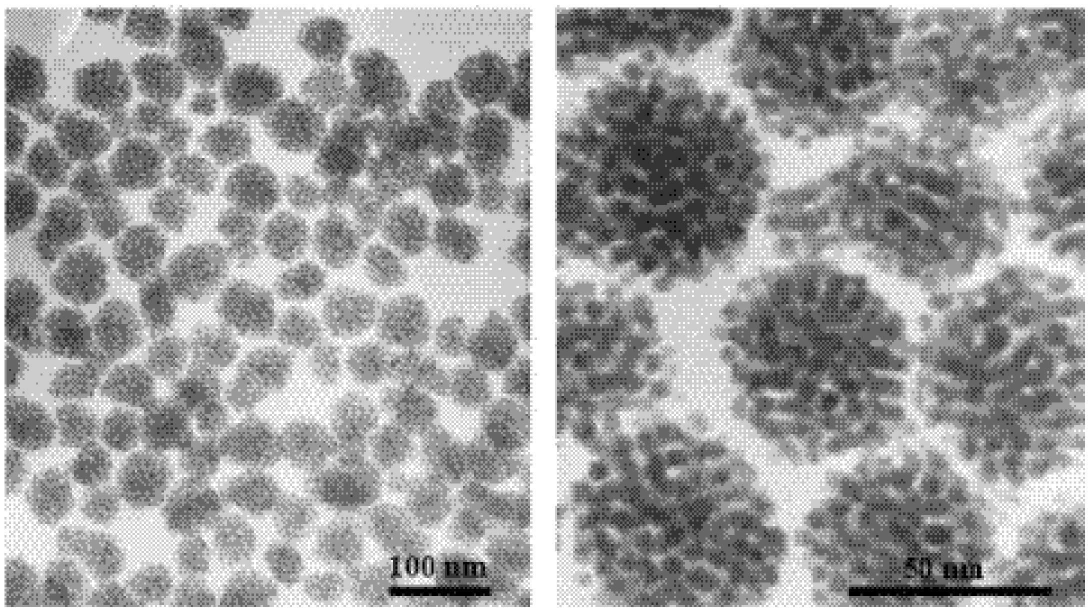


Assemblies inorganic-inorganic

Agents de couplage bi-fonctionnels

Tetraoctylammonium bromide-stabilized gold nanoparticles in toluene of ca. 5-8 nm diameter

+ dilute solution of 1,9-nonanedithiol in toluene (0.5 mL)

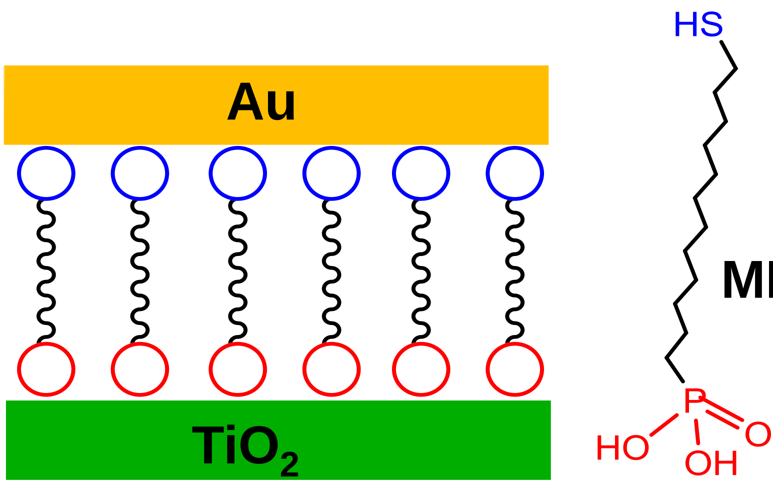


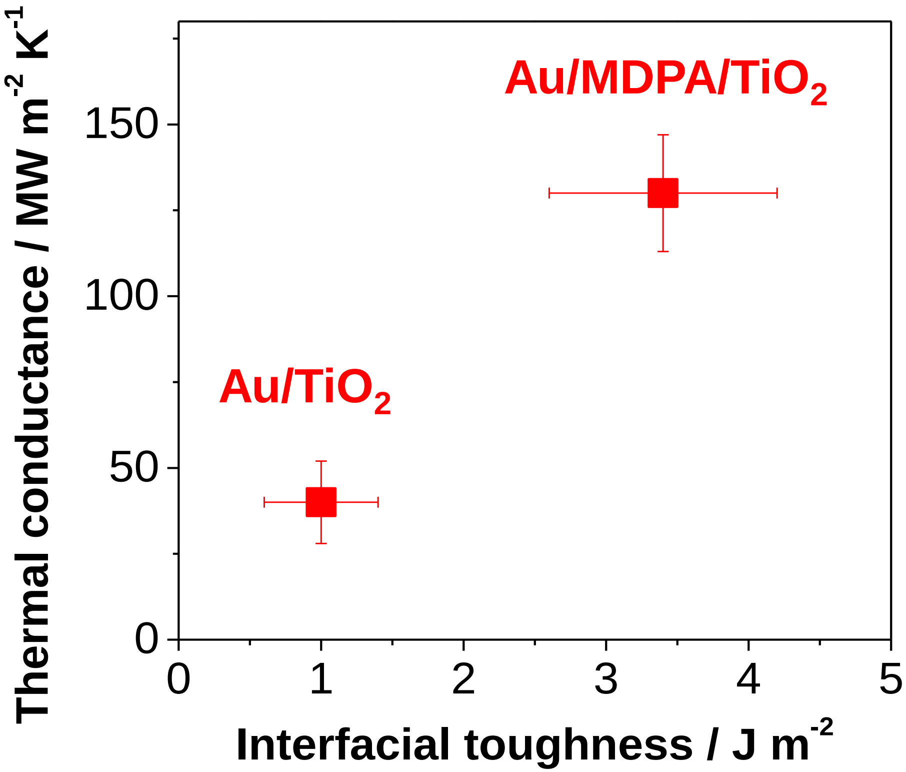
Transmission electron micrographs of solution-stable spherical assemblies formed at a molar ratio of 1,9-nonanedithiol to gold particles of 100.

Dielectric / metal interfaces

collaboration Prof. Ramanath RPI

Tuning mechanical and thermal properties



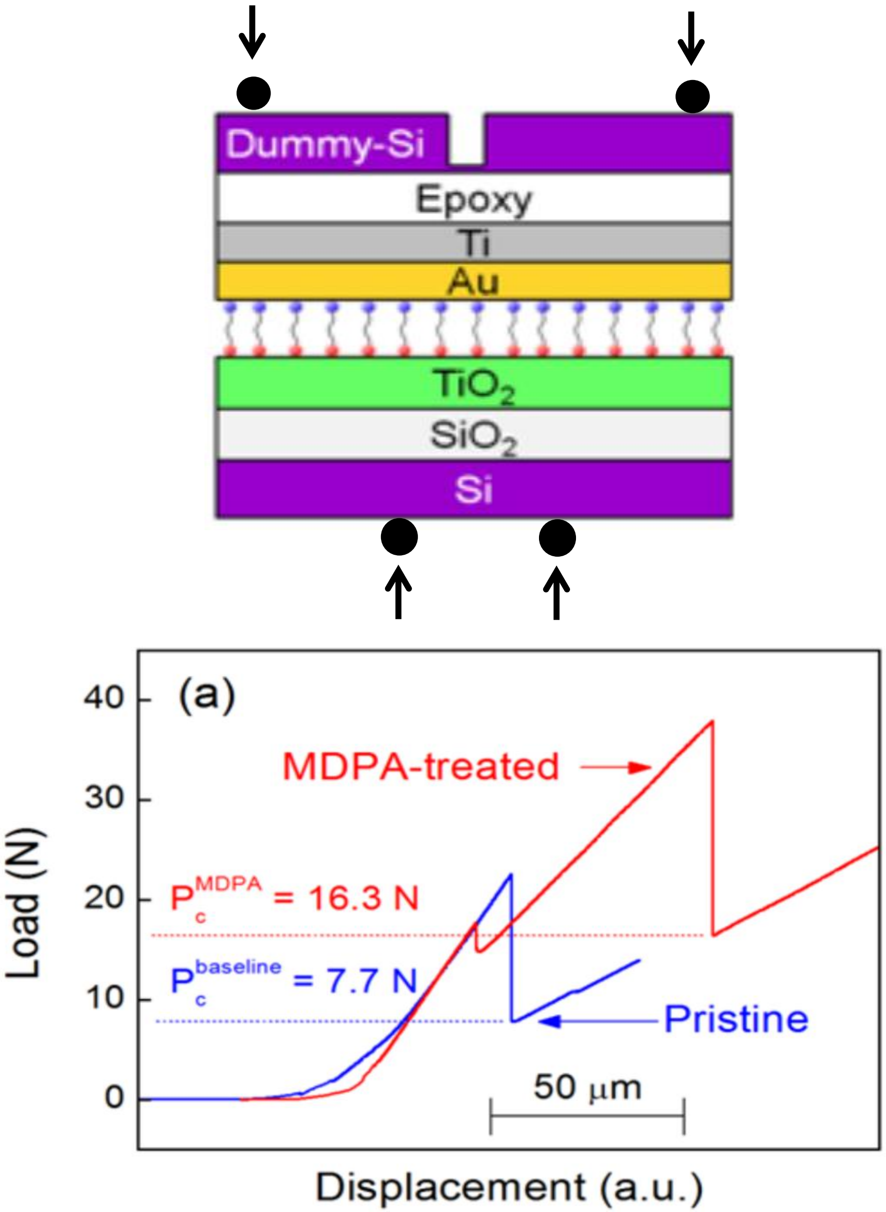


Modification of the interface by a MDPA monolayer:

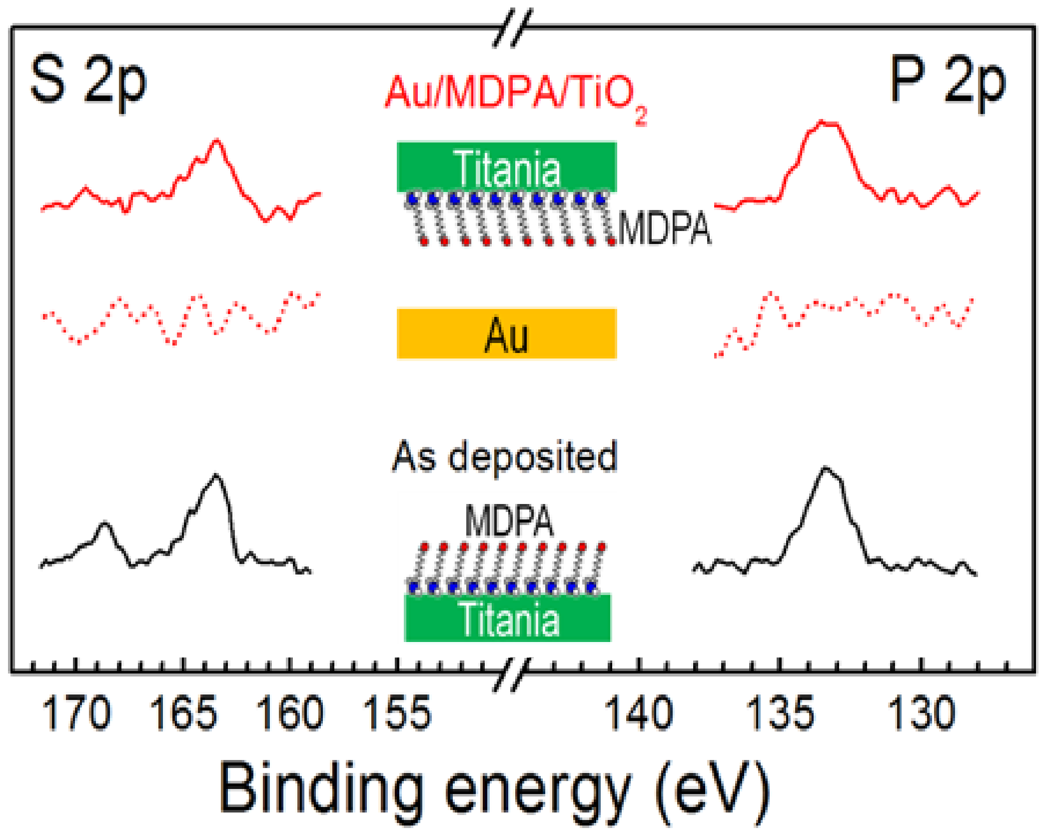
- **interfacial toughness: x3**
- **thermal conductance: x3**

***Nature Mater.* 2013**

Dielectric / metal interfaces



XPS of delaminated surfaces



⇒ Scission of Au-S bonds

Appl. Phys. Lett. 2013

Conclusions

Organic monolayers :

Different anchoring groups: SH, COOH, $SiCl_3$, PO_3H_2...

$\Rightarrow$ **complementary**

- **Modification/functionalization of inorganic surfaces**
- **Interface modification / assemblies**

• **organic-inorganic**

• **inorganic-inorganic**