ICGM

Institut Charles Gerhardt Montpellier

CHEMISTRY: MOLECULES TO MATERIALS

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CMOS

CHEMISTRY: MOLECULES TO MATERIALS

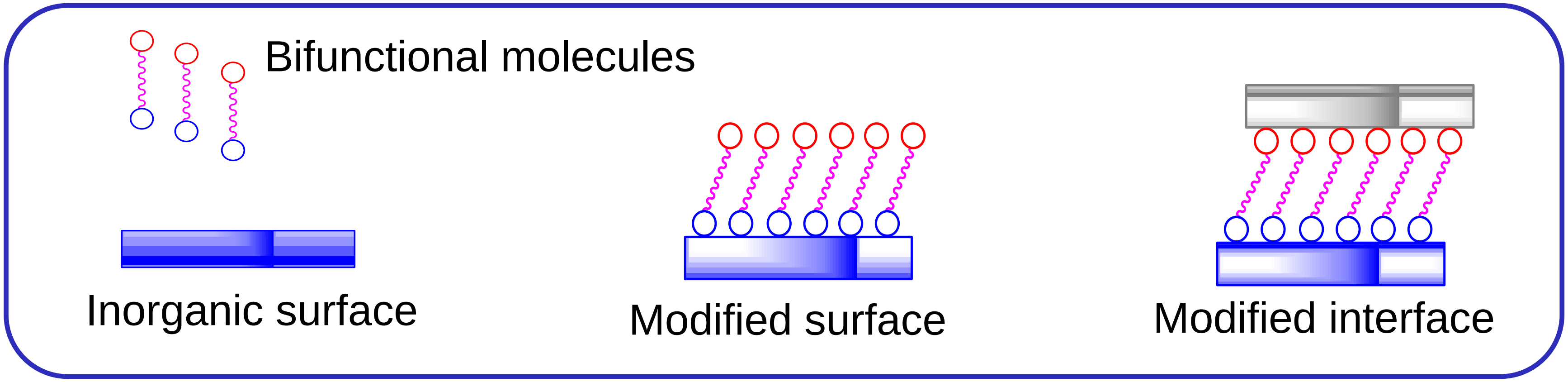
Hubert Mutin

Functionalization of metal and metal oxide surfaces with phosphonate coupling molecules

May 12, 2016 - Czech Chemical Society Lectures

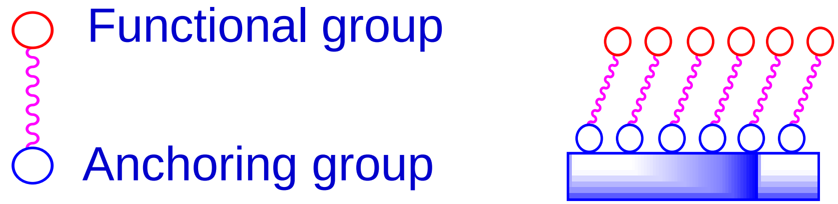
PÔLE chimie Balard
cnrs
ensCm CHIMIE Montpellier

Organic monolayers



- Molecular thickness: 1-2 nm, < 1 $nmol/cm^2$
- Control of surface and interface chemical and physical properties:
  - *charge, surface energy, reactivity, tribological properties...*
  - *electronic, mechanical, thermal properties...*
- Applications: *sensors, lab-on-a chip, hydrophobation, lubrication, catalysis, corrosion resistance, (nano)composite materials, photovoltaics,...*

Binding to the inorganic surface



Anchoring groups:

- **Thiols** R-SH : *coinage metals Au, Pt, Ag, Cu...,* M-S bonds
- **Silanes** R-Si(OEt)$_3$, R-SiCl$_3$ *: silica, metal oxides,* M-O-Si + Si-O-Si bonds
- **Carboxylic acids** R-CO$_2$H : *metal oxides, phosphates, carbonates...,* M-O-C bonds
- **Phosphonic acids** R-PO$_3$H$_2$: *metals, metal oxides, phosphates, carbonates, sulfides..,* M-O-P bonds

Today

Focus on: (native) oxide surfaces and phosphonic acids

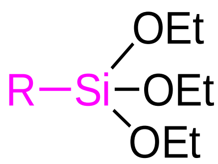
- **Background**:

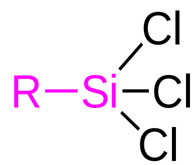
Reactivity, comparison between silanes and phosphonic acids

- **Examples:**

Surface modification of "flat" substrates, nanoparticles, layered materials

Organosilane monolayers





<u>SiO_2</u>, ZrO_2, Al_2O_3, TiO_2…

SiC, Si_3N_4

~~$CaCO_3$~~, ~~$Ca_{10}(PO_4)_6(OH)_2$~~

Hydrolysis: H_2O + Si-X → HX + Si-OH   X = Cl, OR

Heterocondensation: M-OH + Si-OH → Si-O-M + H_2O

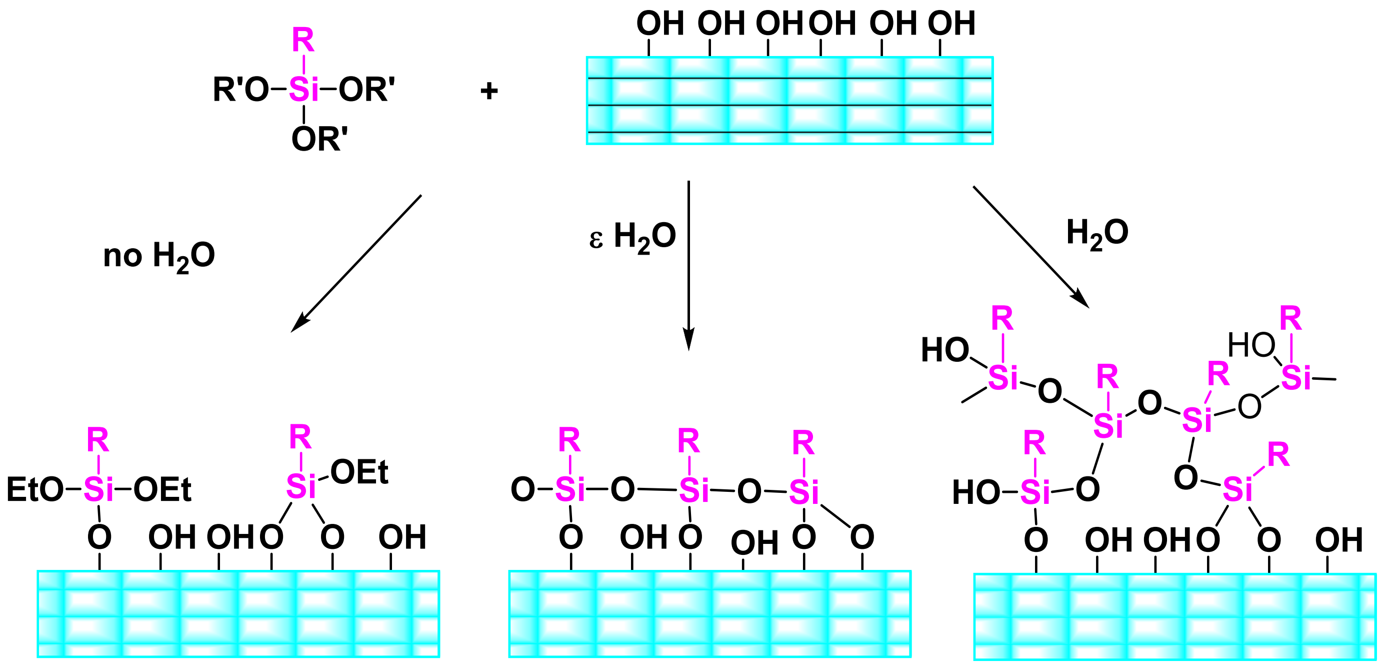
Homocondensation: Si-OH + Si-OH → Si-O-Si + H_2O

Competition heterocondensation / homocondensation: governs layer structure

Organosilane monolayers

Balance heterocondensation / homocondensation:

depends on the nature of the support and water content



only Si-O-M, partial monolayer

Si-O-M + Si-O-Si dense monolayer

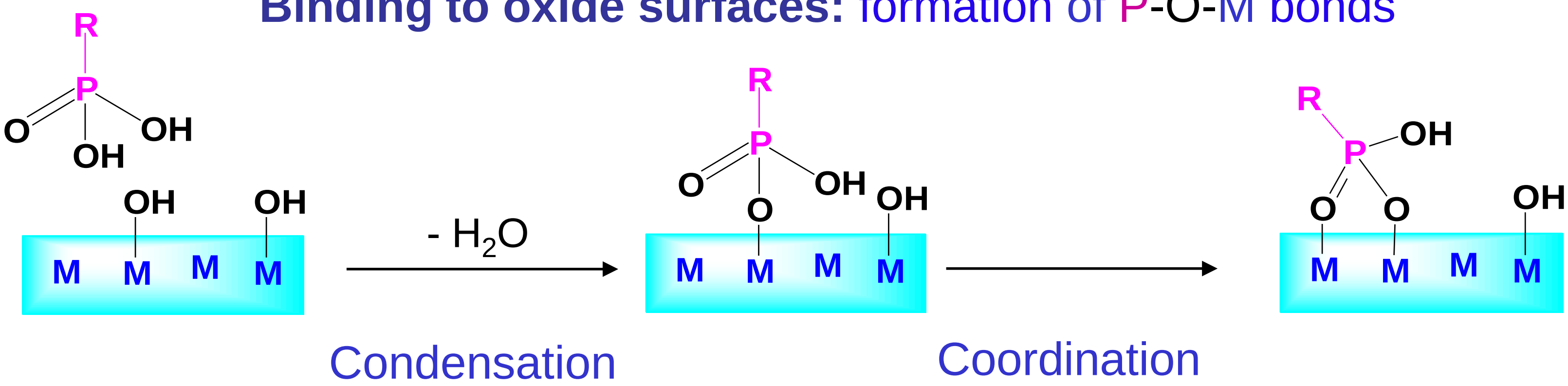
few Si-O-M, multilayer

Phosphonic acid monolayers

Ti, Al, Stainless steel, Mg, Ag, TiO_2, Al_2O_3, ZrO_2, SiO_2 …

$CaCO_3$, $Ca_{10}(PO_4)_6(OH)_2$, GaAs, CdS...

Binding to oxide surfaces: formation of P-O-M bonds



- **Phosphonic acids stable in water**

⇒ *No need to control the water content*

⇒ *Surface modification in water*

- **No homocondensation**

P-OH + P-OH $\nrightarrow$ P-O-P + H_2O

⇒ easy access to monolayers

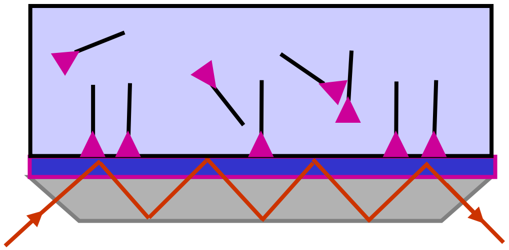
Growth of $C_{18}H_{37}PO_3H_2$ SAMs on titanium

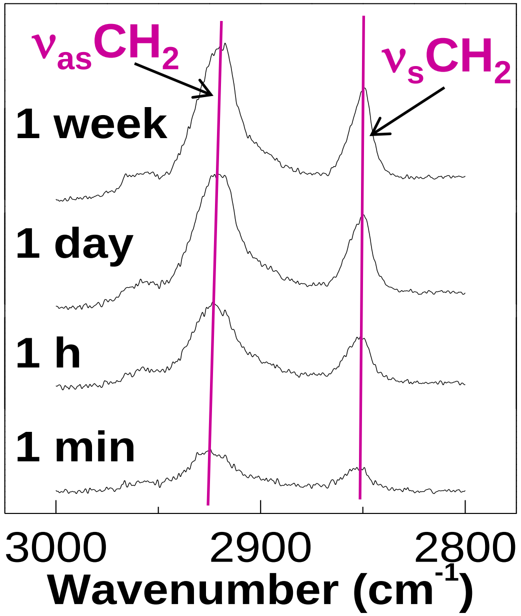
in situ **multireflexion ATR FTIR**

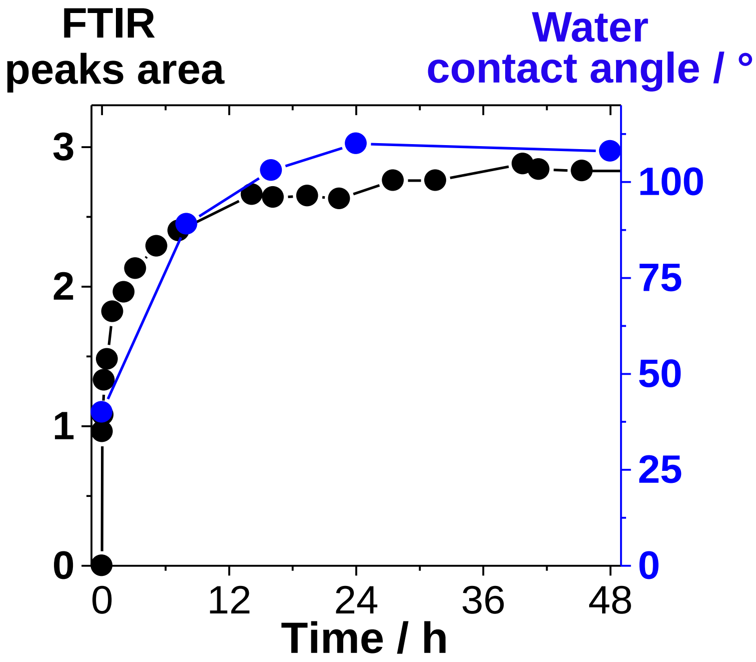
ex situ **water contact angle**

Substrate: 20 nm Ti on a silicon ATR crystal

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





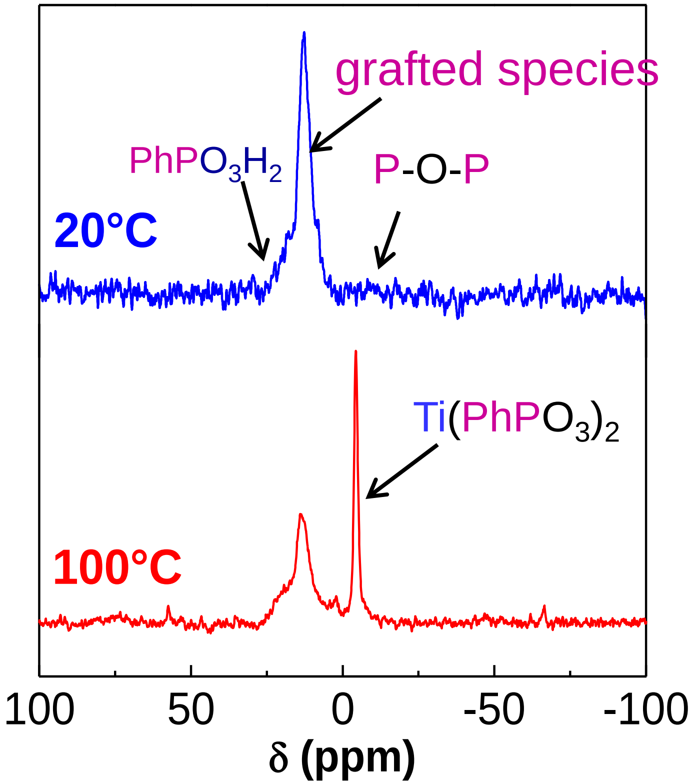


• No need to control the water content, simple and reproducible!

Surface Modification of TiO_2 Particles

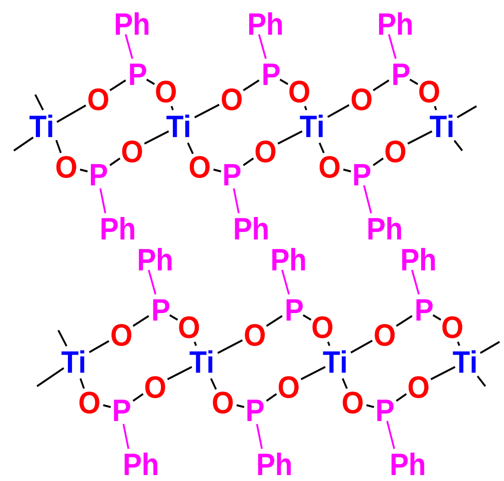
TiO_2 (50 m^2/g) + $PhPO_3H_2$ (22 P / nm^2) —[H_2O, pH 2.5; 3 d, T]→ —[washing; drying]→

^{31}P MAS-NMR



20°C, 2.8 mM: no P-O-P ⇒ monolayer

100°C, 40 mM ⇒ $Ti(PhPO_3)_2$ phase



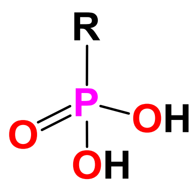
Chem. Mater. **2001**, *13*, 4367

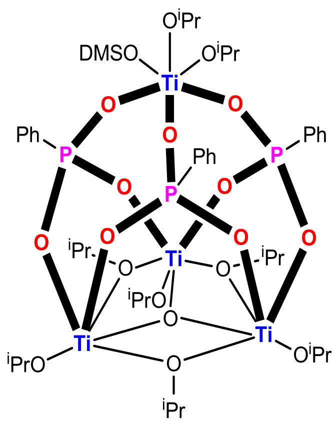
Evidencing P-O-M bonds: ^{17}O NMR

Collaboration F. Babonneau, C. Gervais (UPMC)

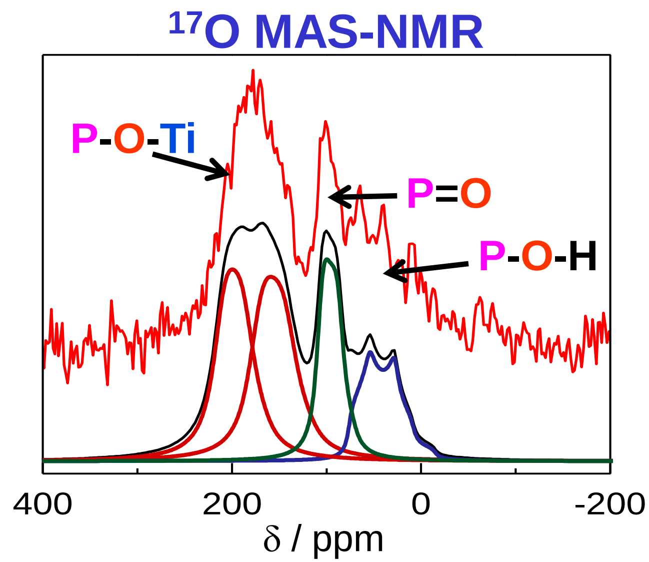
$C_{12}H_{25}PO_3H_2$ monolayer on TiO_2 (100 m^2/g)

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

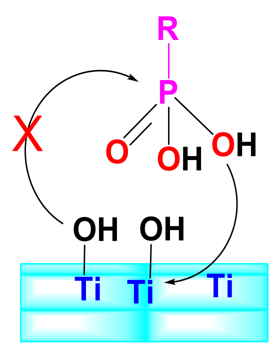




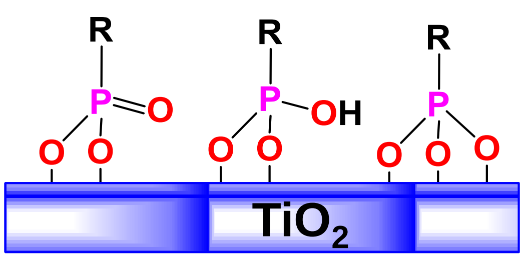
Chem. Mater. **2003, 2008**



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



Mechanism



Surface species

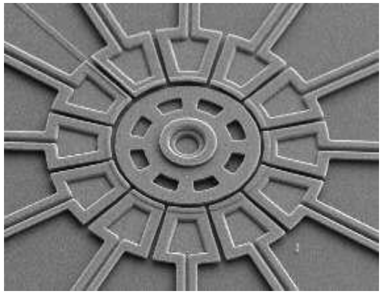
Protective boundary layer lubricants

Collaboration Ph. Tordjeman LAIN

Applications of SAMs:

- corrosion protection
- non-volatile lubricants


hard-disks


MEMS


electrical contacts

$C_{18}H_{37}PO_3H_2$ SAMs as lubricant coatings stable in alkaline media

Substrates: 20 nm Ti on Si

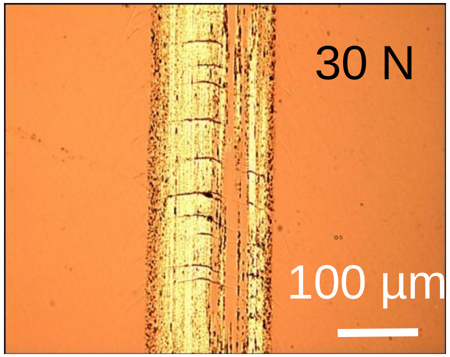
grafting with $C_{18}H_{37}PO_3H_2$

in EtOH, 2d.

Friction: stainless steel ball

D = 2 mm, 260 HV,

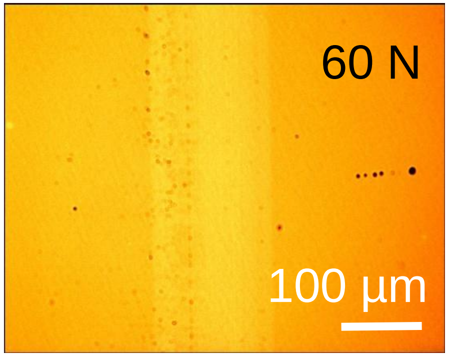
normal force up to 60 N



Ti/Si untreated

Contact angle 11°

Friction coeff. 0.6



ODPA/Ti/Si

Contact angle 102°

Friction coeff. 0.1

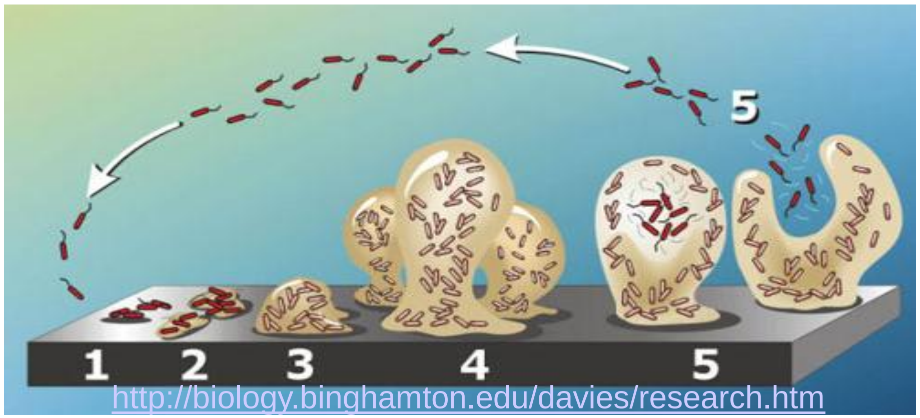
MRS Symp. Proc. 2004

Lubrication maintained after 100 min pH 14, 65 °C

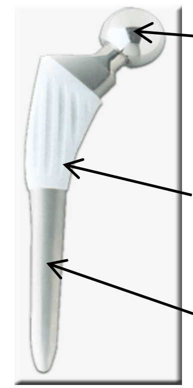
Antibacterial phosphonate monolayers

Collaboration J.-Ph. Lavigne CHU; Danièle Noël INM

Bacterial adhesion / biofilm formation: major cause of nosocomial infections



Biofilm formation



Inorganic biomaterials:

metals, metal oxides, phosphates…

Phosphonate monolayers as coatings for medical devices:

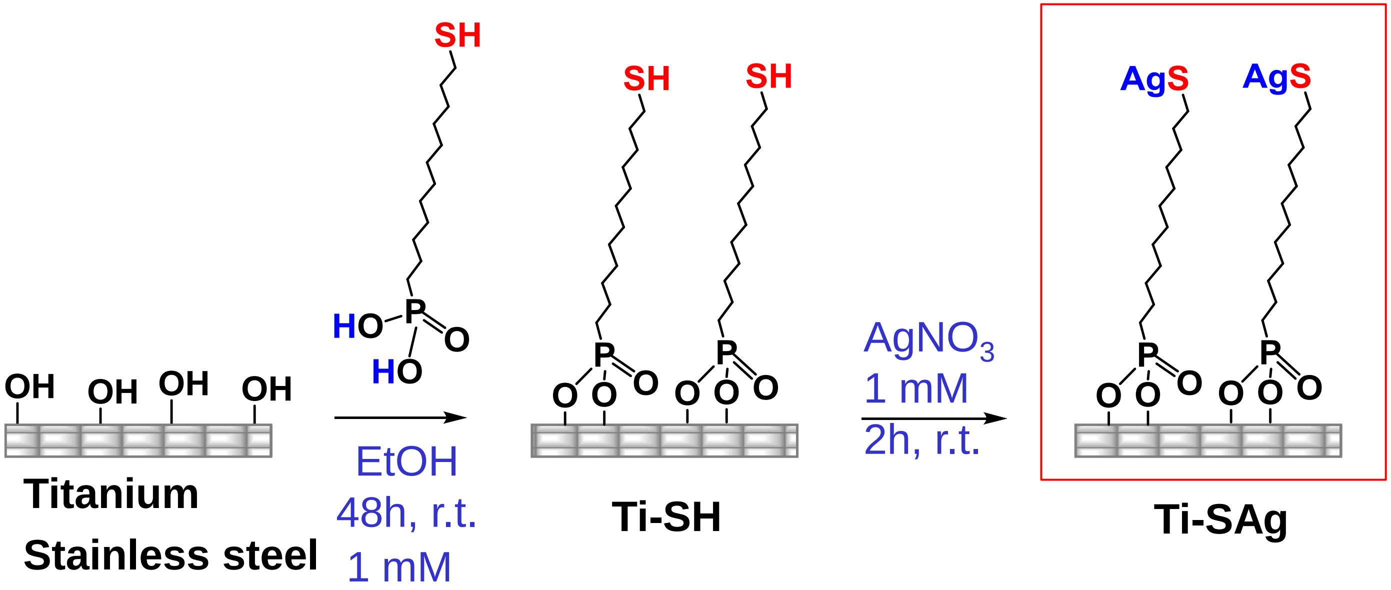
- high affinity for most inorganic biomaterials
- good thermal and hydrolytic stability

Antibacterial phosphonate monolayers

Strategy: **grafting of silver thiolate groups**

Ag+: good bactericidal activity over a wide range of bacteria

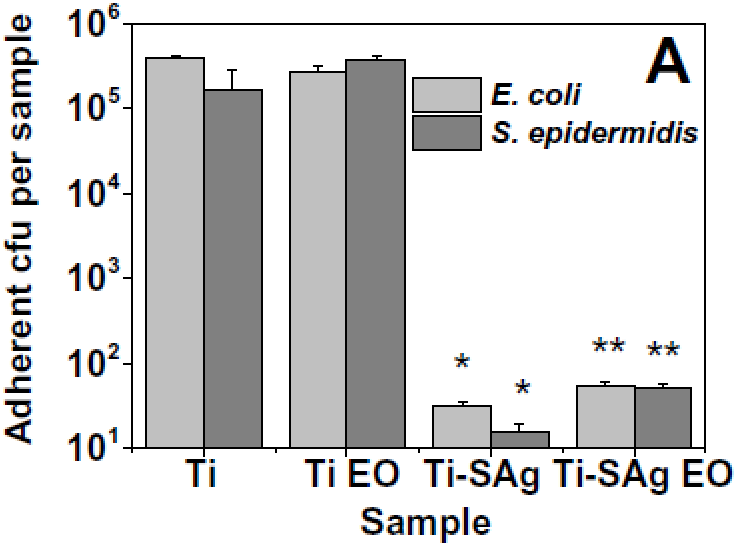
Ag thiolates: very high hydrolytic stability



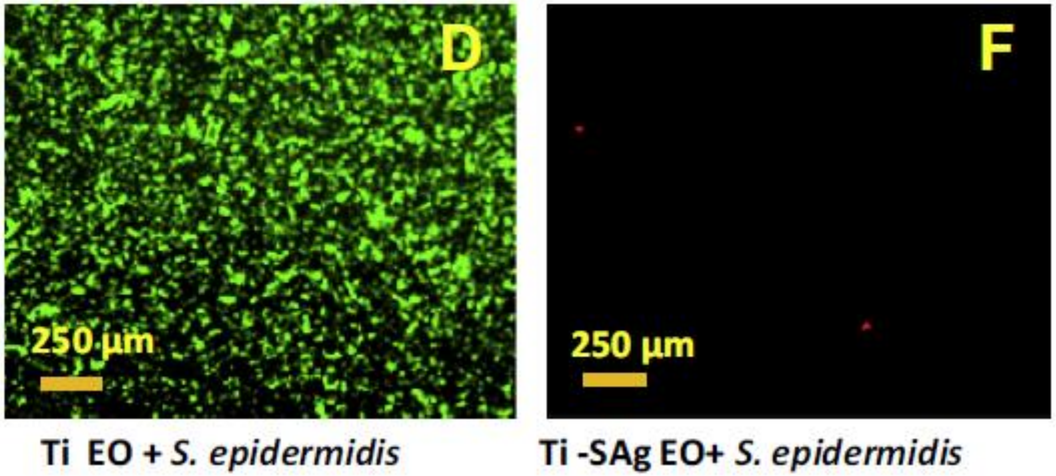
J. Mater. Chem. **2009**, *19*, 141 - 149
WO 2007080291

Antibacterial phosphonate monolayers

Bacterial adhesion and biofilm assays:



huge decrease of bacterial adhesion after 2-h incubation



inhibition of biofilm growth after 3-day incubation

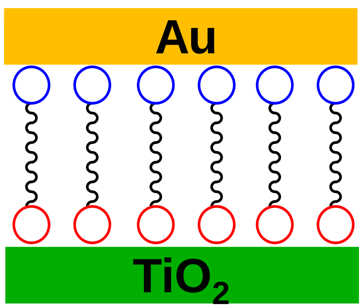
- good antibacterial activity *in vitro* and *in vivo* with less than 1 nmol Ag/cm^2
- maintained after ethylene oxide sterilization
- excellent biocompatibility *in vitro* (MCT3T3 cells) and *in vivo*

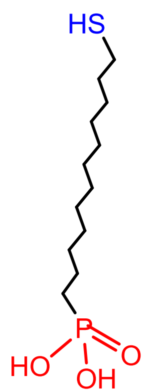
Acta Biomaterialia, **2015**, 154, 266-277

Dielectric / metal interfaces

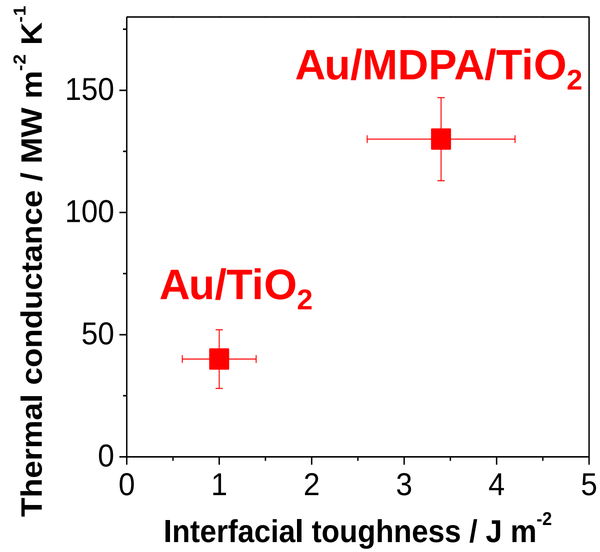
Collaboration Ganpati Ramanath RPI

Tuning interface mechanical and thermal properties





MDPA



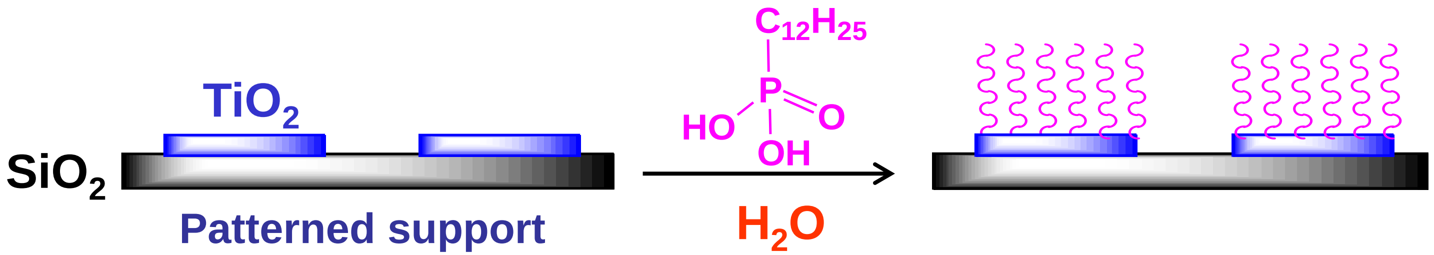
Modification of the interface by a MDPA monolayer:

- interfacial toughness: x3
- thermal conductance: x3

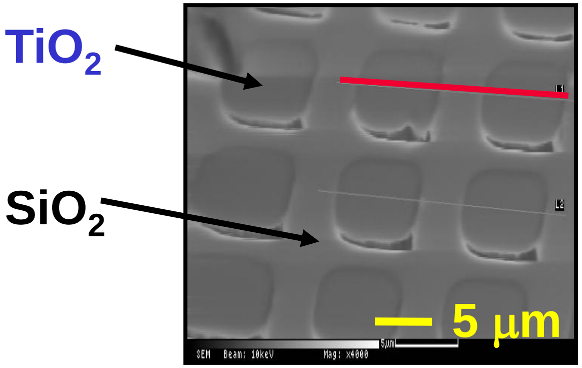
Nature Mater. **2013**

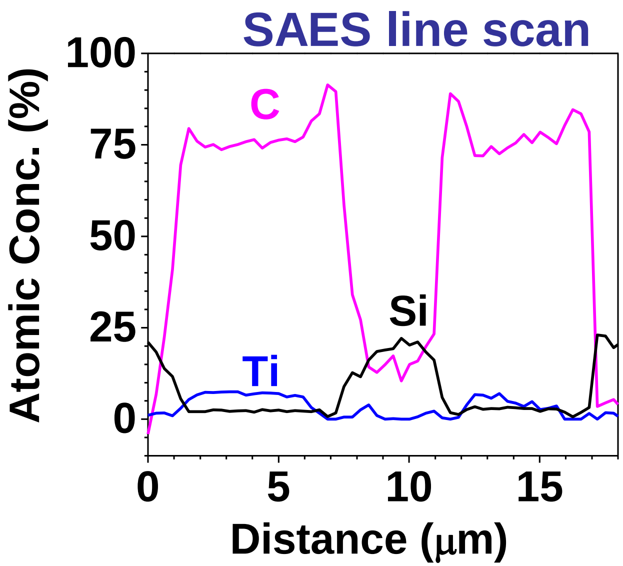
Selective surface modification

Ti-O-P : stable / hydrolysis **Si-O-P :** fast hydrolysis



SEM





Repartition of organic groups controlled by the inorganic support

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

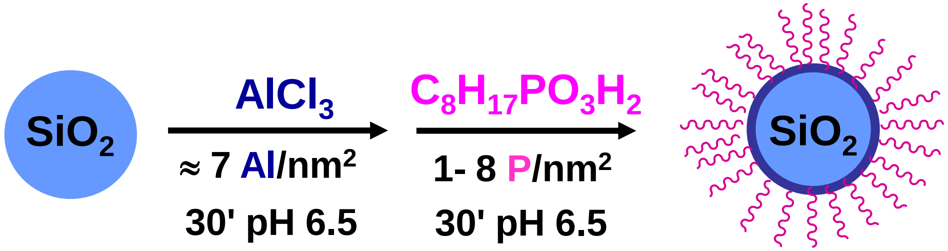
Surface modification of silica

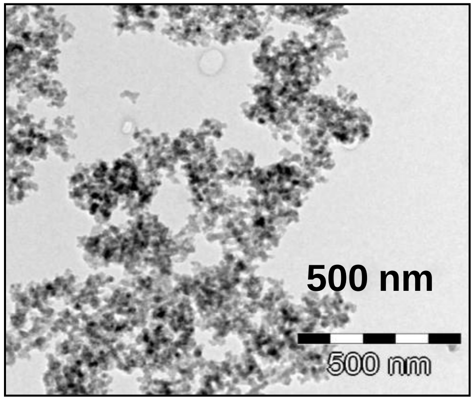
collaboration Rhodia, MACS (ICGM)

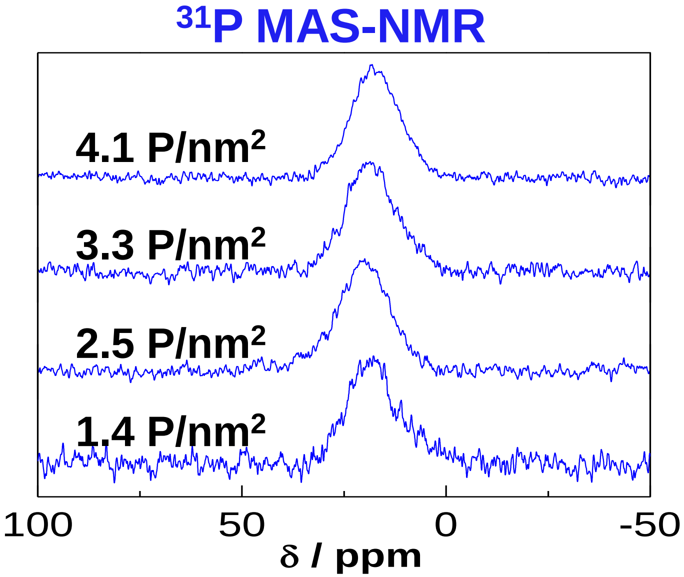
Compatibilization of silica nanofillers with hydrophobic polymers

Surface modification in aqueous medium?

- Organotrialkoxysilanes: not stable in water
- Phosphonic acids: stable in water but **Si-O-P** not stable in water ⇒ **Si-O-Al-O-P**







- fast, one-pot method
- no organic solvent: "green"
- no precipitation of Al phosphonate
- controlled surface coverage

J. Mater. Chem. **2011**

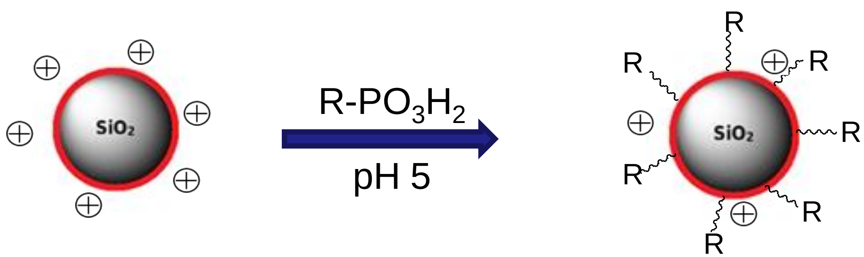
Grafting oxide NPs in aqueous colloidal solutions

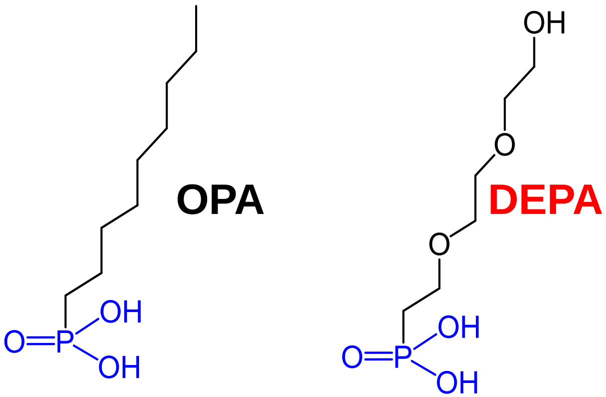
collaboration J. Oberdisse, C. Genix L2C

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 :



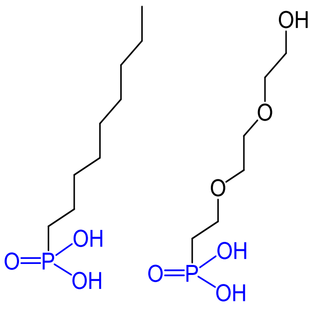


OPA *: hydrophobic R group*

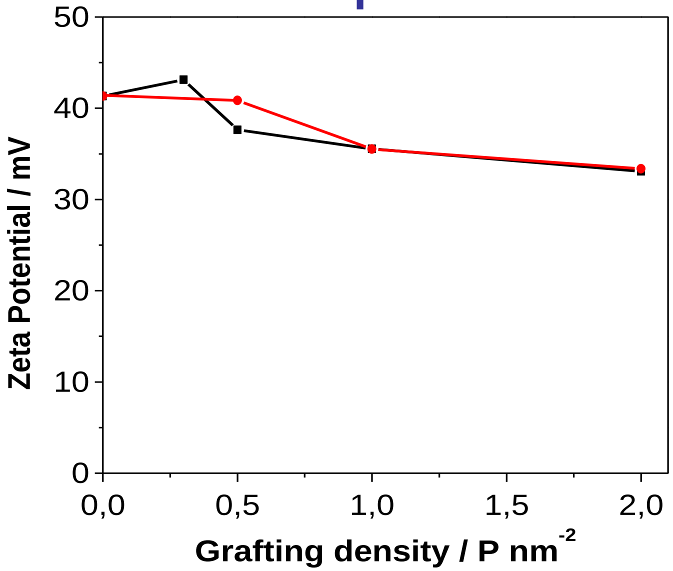
DEPA *: hydrophilic R group*

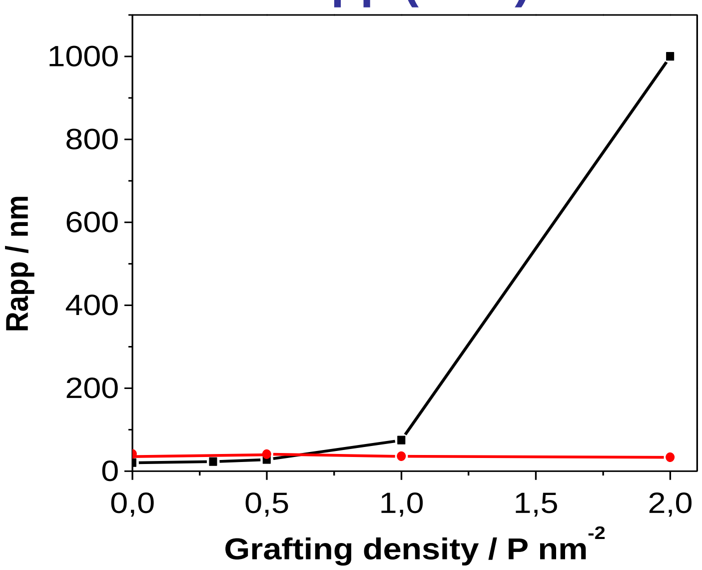
→Tuning interactions between nanoparticles in aqueous solutions

Grafting oxide NPs in aqueous colloidal solutions

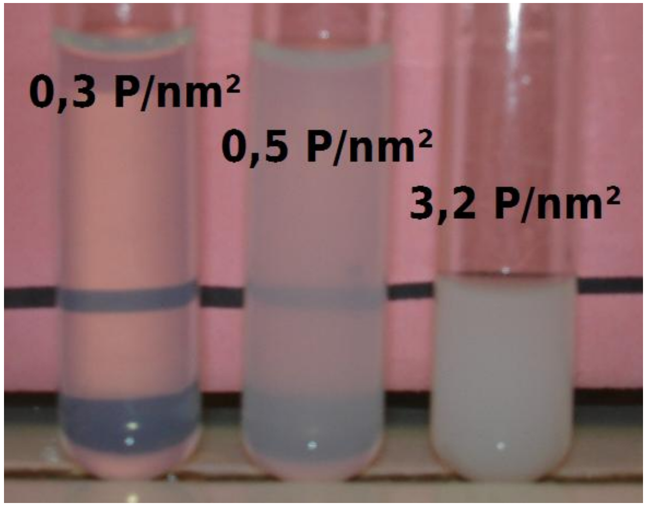


OPA **DEPA**





OPA



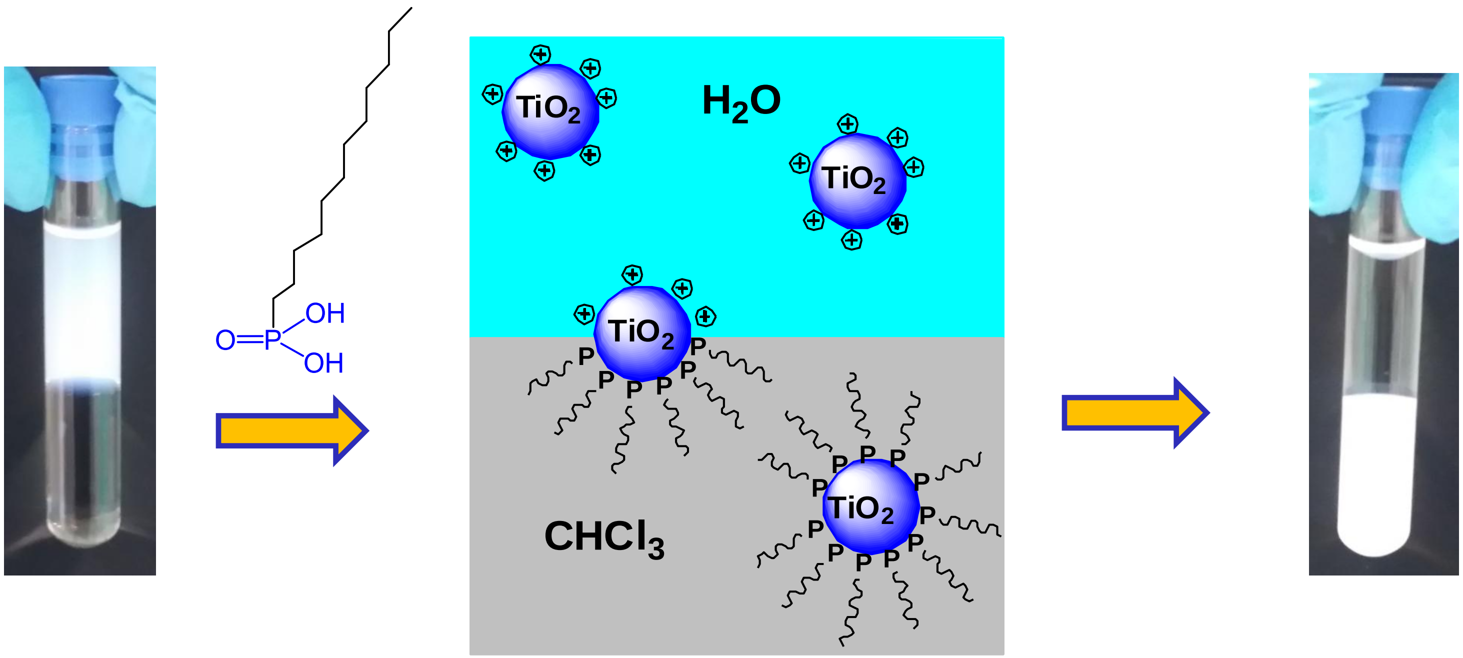
- **OPA**, **DEPA**: slight decrease of ZP
- **OPA:** aggregation increases with grafting density

➢**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*

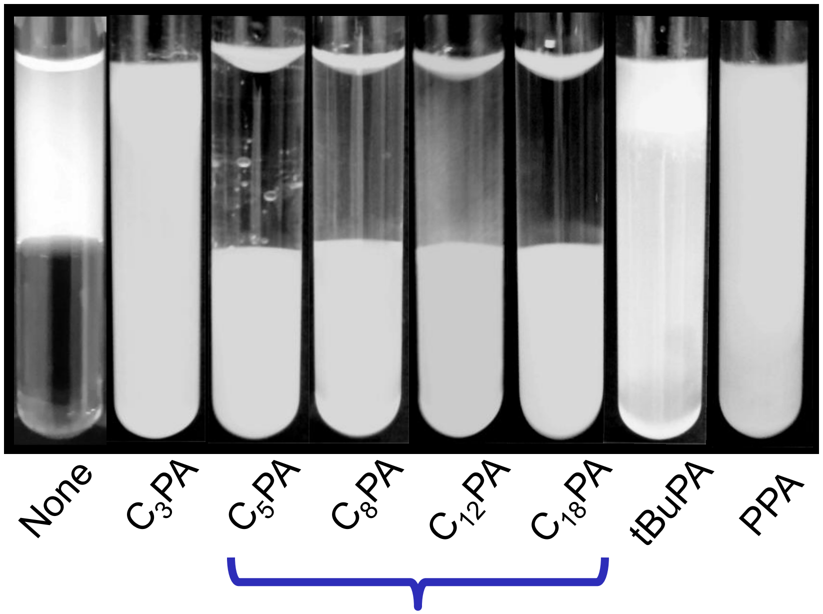


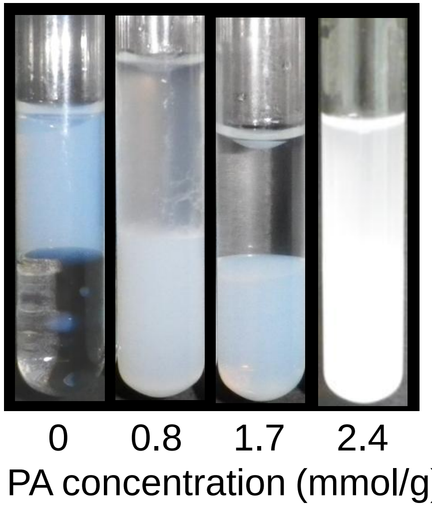
- **Simultaneous grafting / phase transfer (FTIR, NMR)**

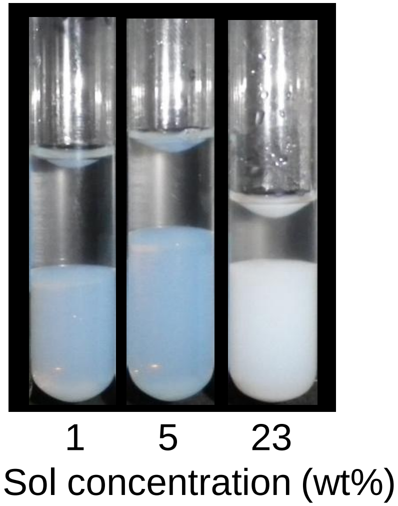
Langmuir **2015**, 31, 10966-10974

Phase transfer of TiO_2 particles

Parameters influencing the transfer







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

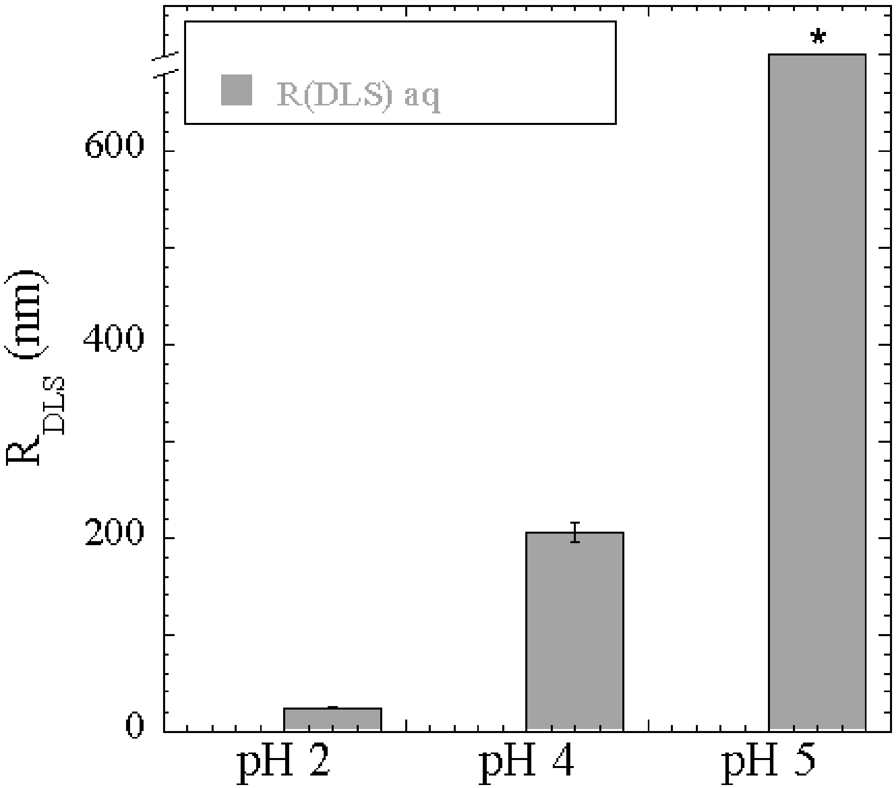
Langmuir **2015**, 31, 10966-10974

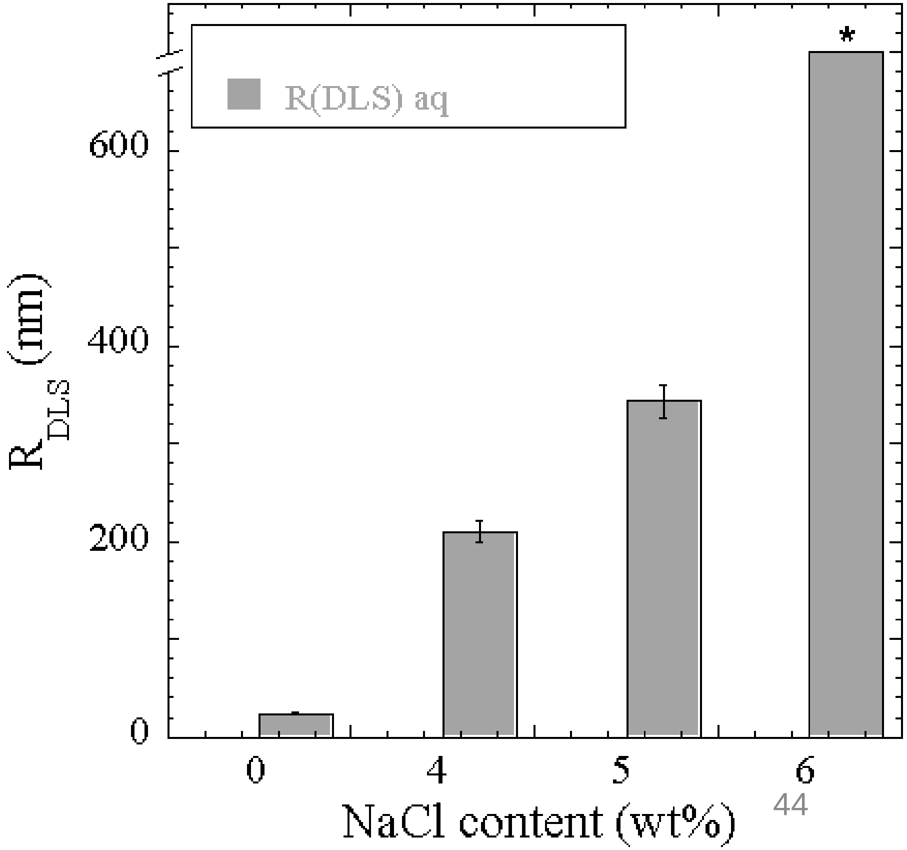
Phase transfer of TiO_2 particles

Transfer of aggregated nanoparticles

Variation of NP dispersion

pH variation | salt addition



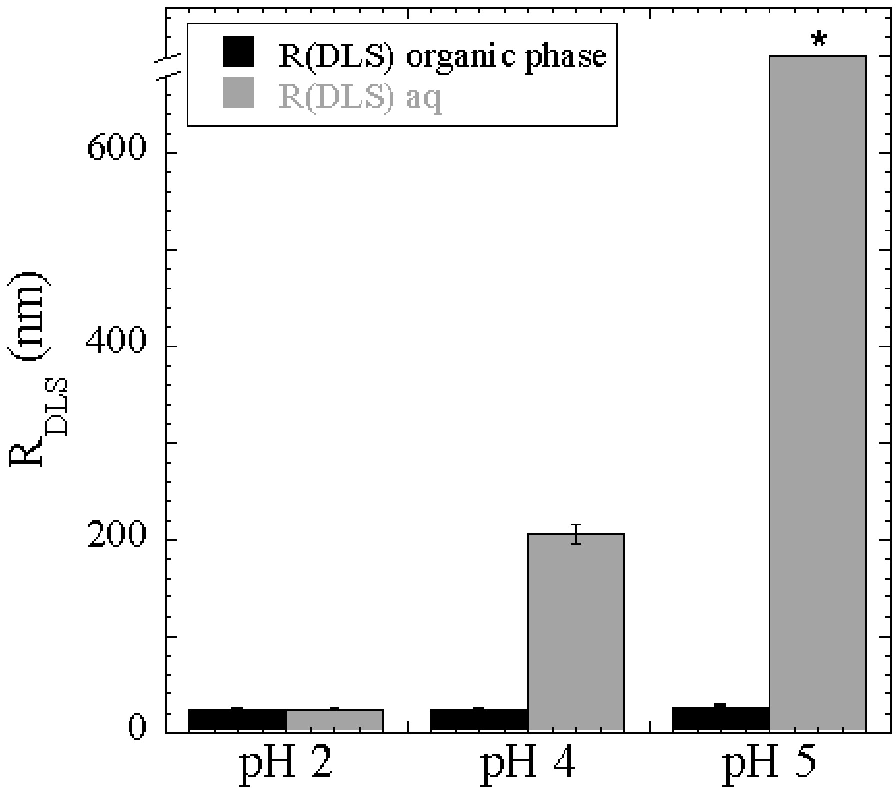


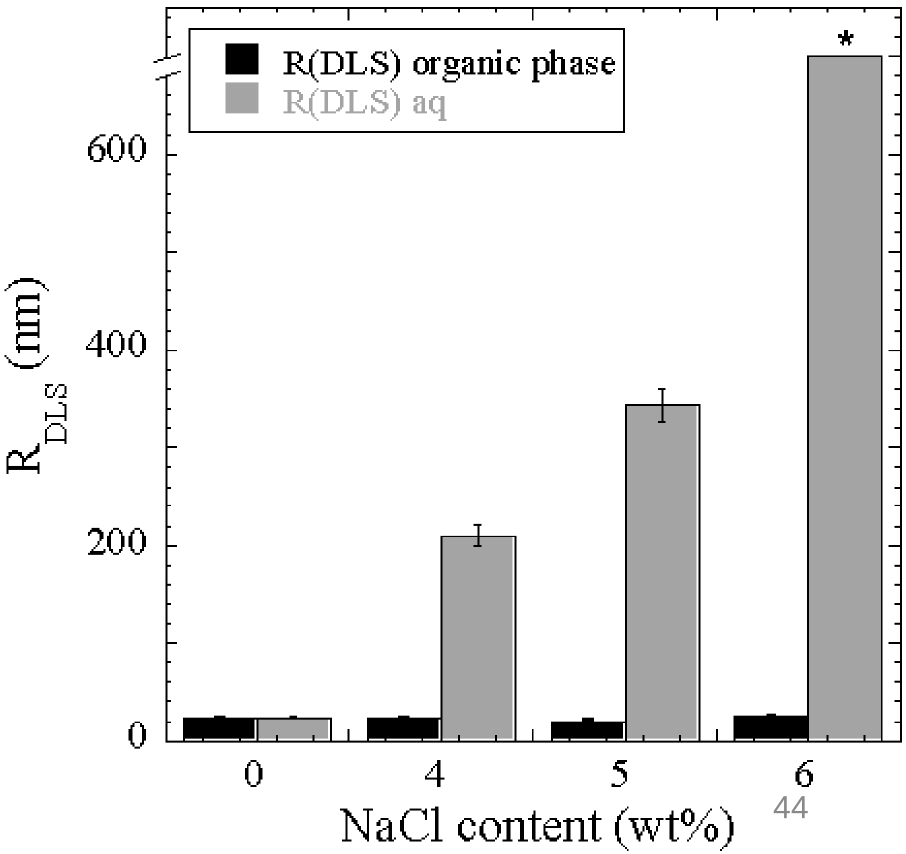
Transfer of aggregated nanoparticles

Variation of NP dispersion

pH variation

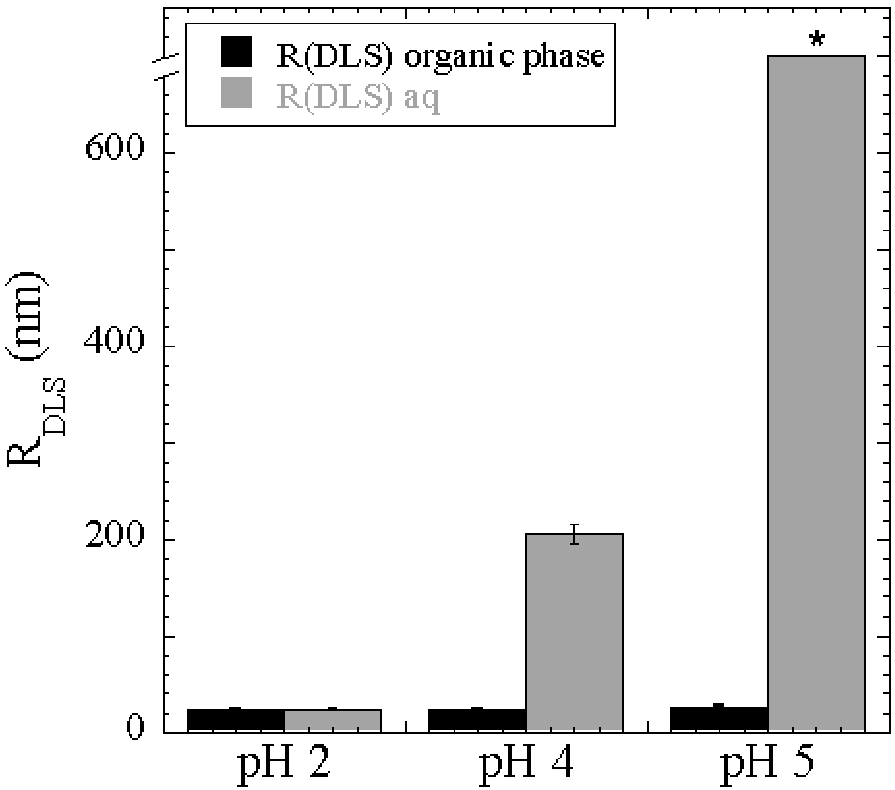
salt addition

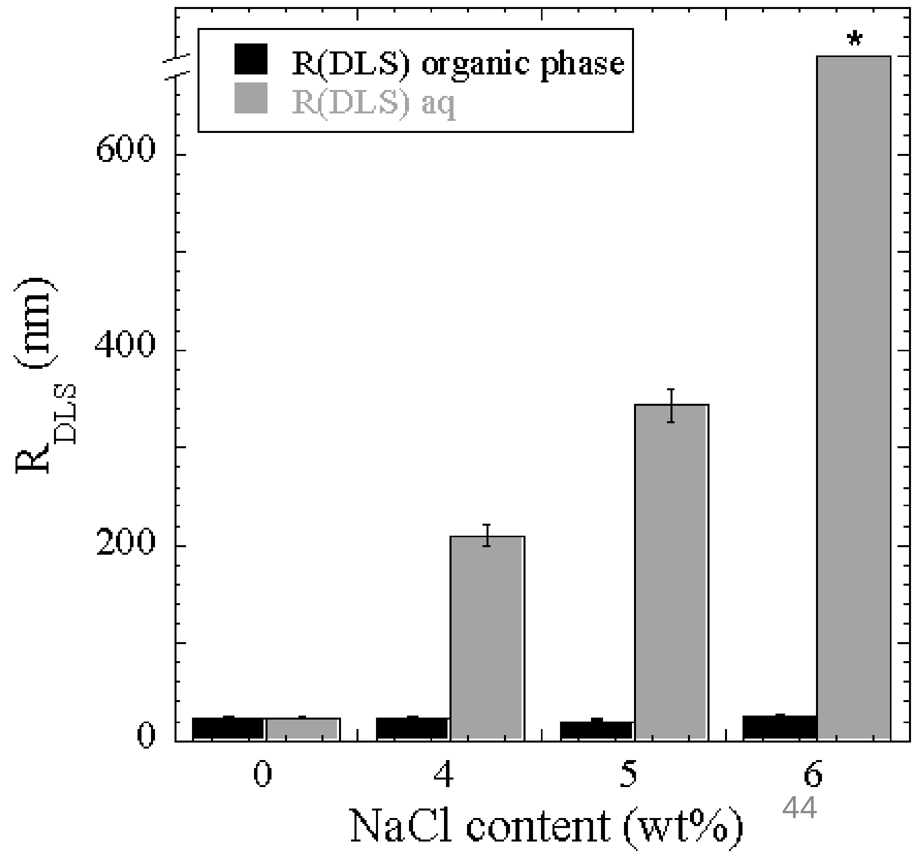




Transfer of aggregated nanoparticles

Deaggregation during phase transfer / surface modification

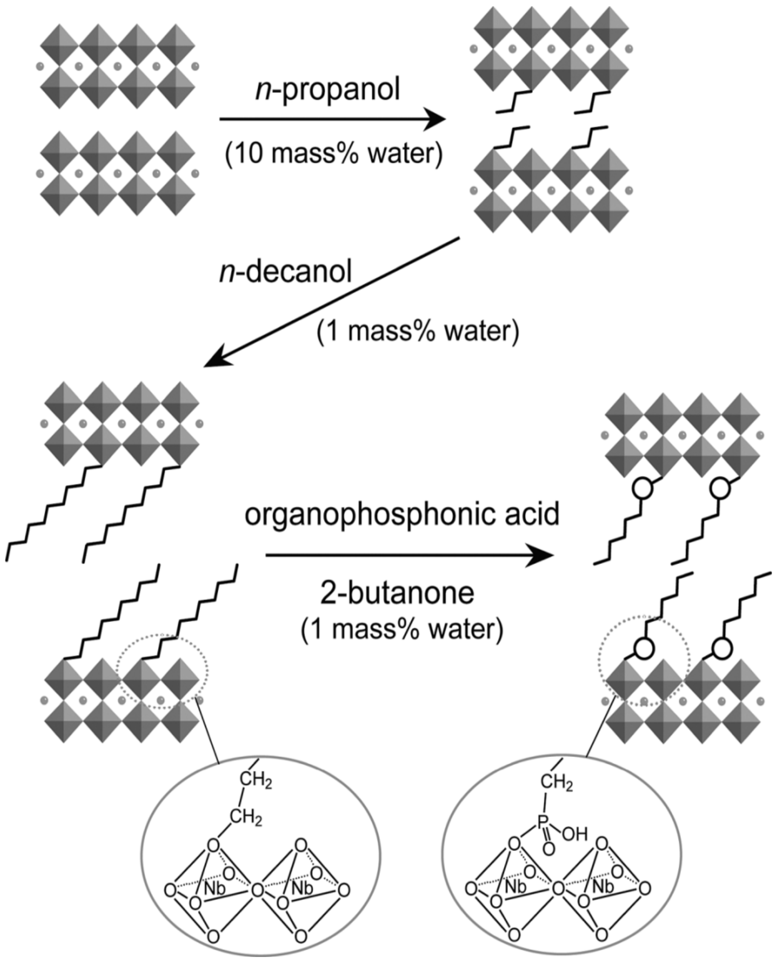




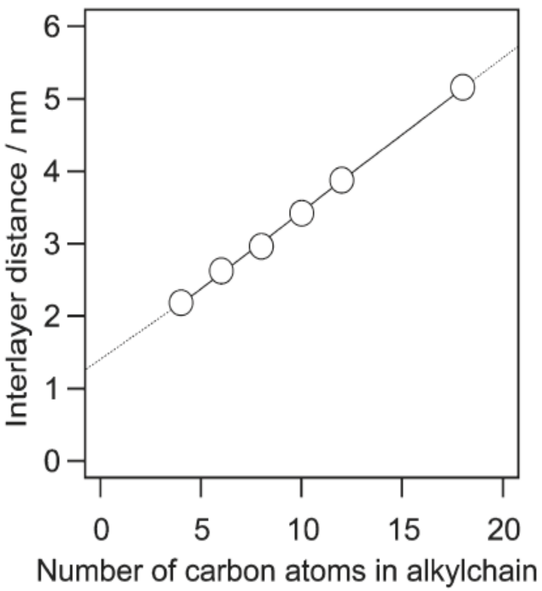
Interlayer grafting

collaboration Y. Sugahara, Waseda, Tokyo

$HLaNb_2O_7.xH_2O$: ion-exchangeable layered perovskite



XRD

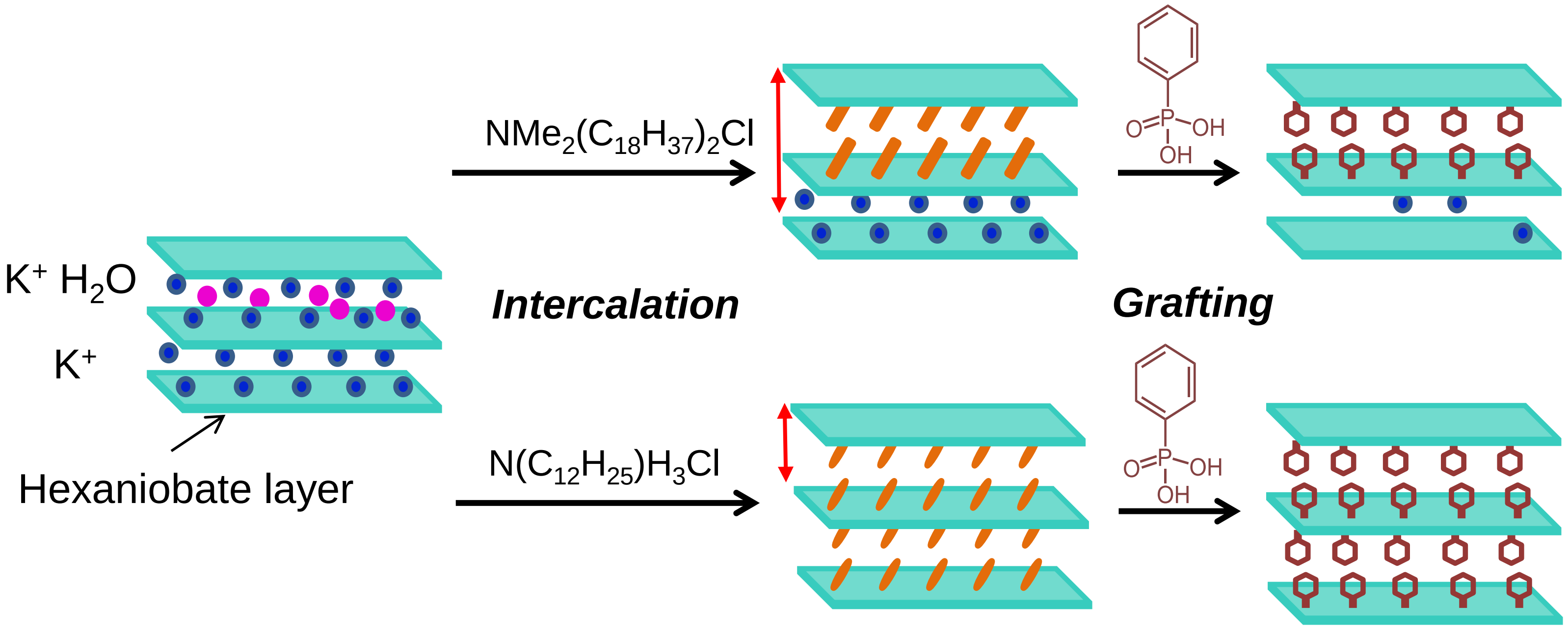


Chem. Mater. **2009**, *21*, 4155

Selective interlayer grafting

collaboration Y. Sugahara Tokyo

$K_4Nb_6O_{17}\cdot 3H_2O$: two distinct interlayers, selective intercalation

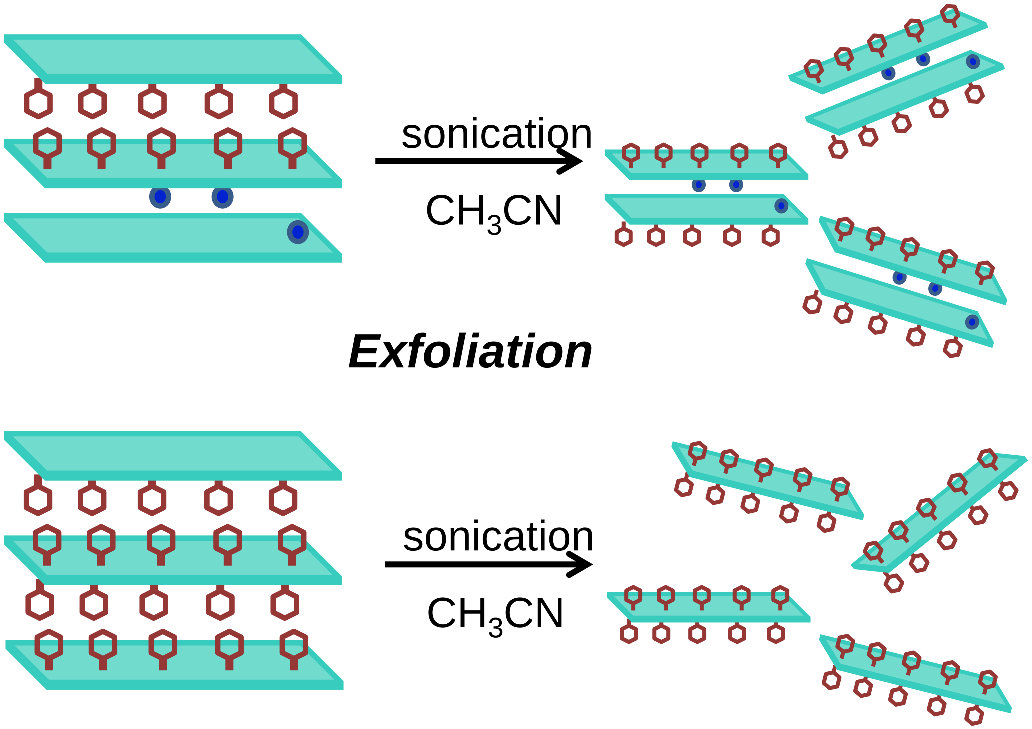


XRD: selective grafting

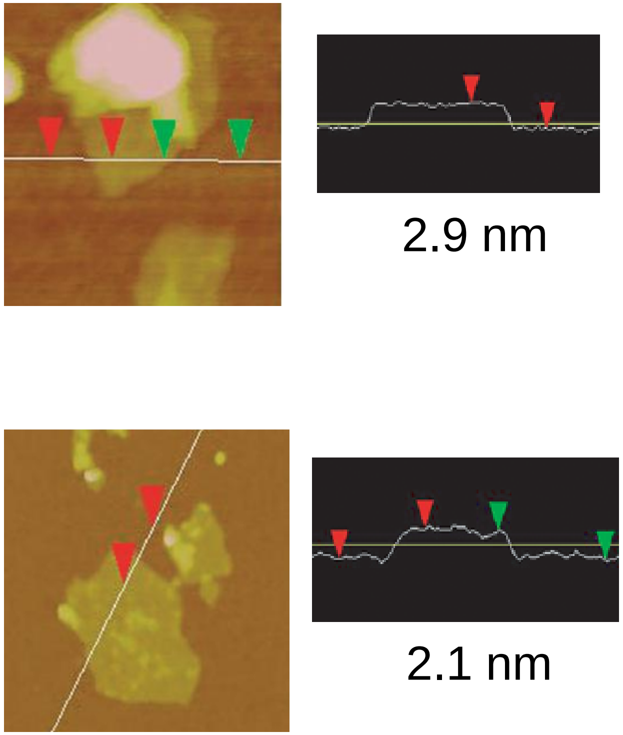
Langmuir **2014**, *30*, 1169

Selective interlayer grafting

Exfoliation in CH_3CN: leads selectively to hydrophobic mono- and bilayers



AFM



Janus monolayers?

Langmuir **2014**, *30*, 1169

Conclusions

Phosphonate coupling molecules

- complementary of silanes and thiols
- anchoring to the surface by M-O-P bonds only
- wide range of inorganic substrates and terminal groups

Powerful tool for the control of surface and interface properties

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