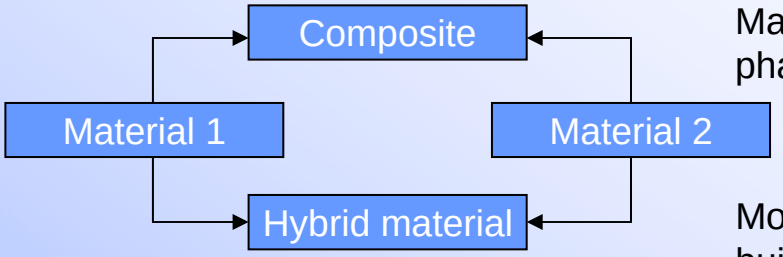
Progress in Inorganic-Organic Hybrid Materials by New Precursor Concepts

Ulrich Schubert

Institute of Materials Chemistry

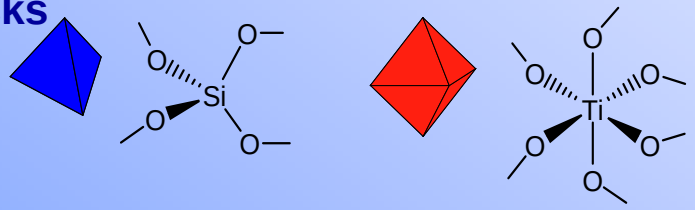
Hybrid Materials: Building Blocks



Macroscopic phases

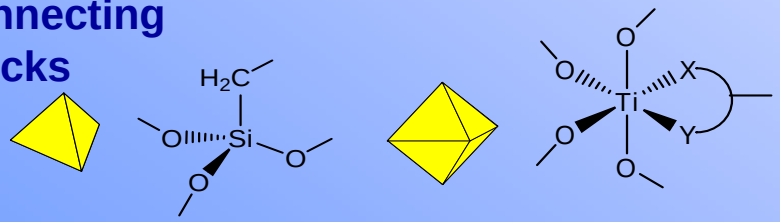
Molecular building blocks

Inorganic Building Blocks



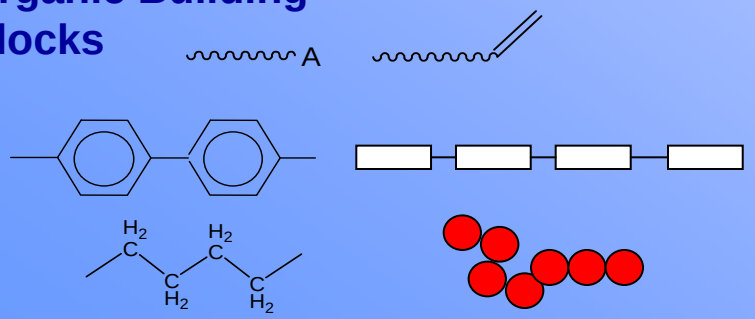
Mechanical, optical, electrical, magnetical properties

Connecting Blocks



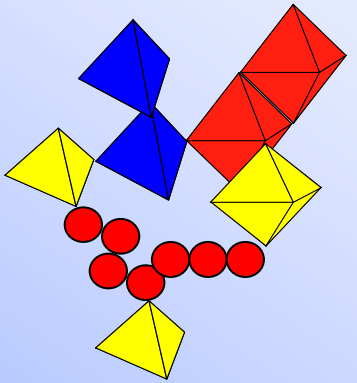
Reduction of the crosslinking density, coupling sites between inorganic / organic components

Organic Building Blocks

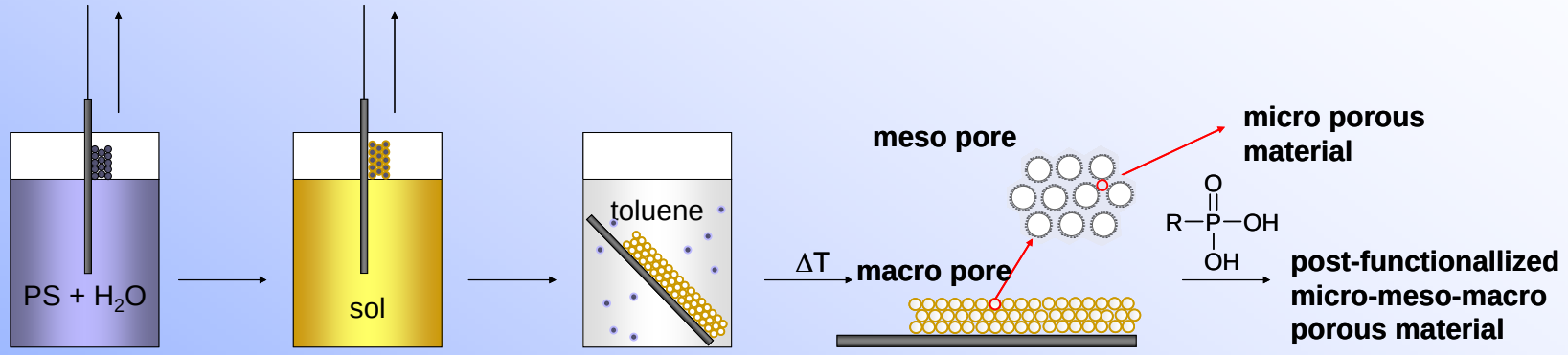


Functional groups, crosslinking, polymerizability

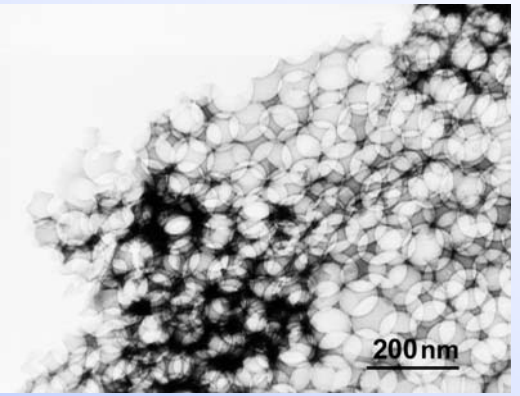
Flexibility, elasticity, processability



Films with Complex Compositions and Polymodal Pore Structure



polystyrene sphere dispersion | inorganic precursor + template | removal of polystyrene | micro-meso-macro porous hybrid material

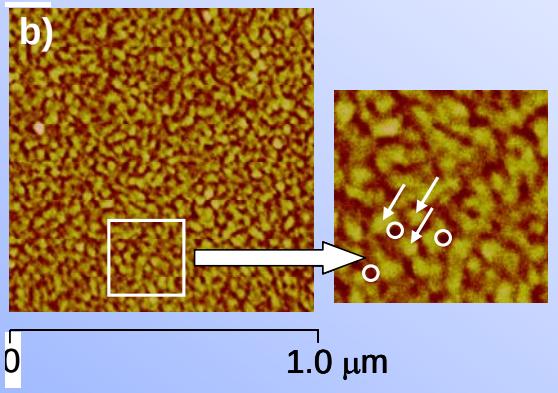


Trimodal pore size distribution:

- Macropores from polystyrene spheres (100 nm) as porogenes
- Meso- and micropores by removal of surfactant (as porogene) and organic groups

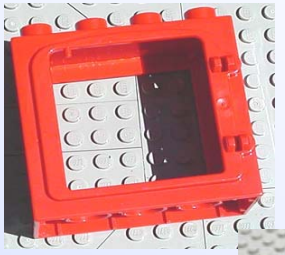
Complex composition

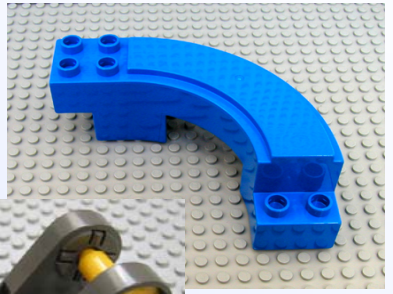
- Use of metal alkoxide mixtures
- 1st organic function from R'-Si$(OR)_3$ precursors
- 2nd organic function by post-synthesis functionalization of the metal oxide structures, e.g. with phosphonic acids

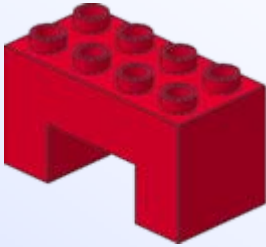


From Building Blocks to Preformed Modules

Shape
Function
Kind of linkage
Connector sites: number and geometrical arrangement



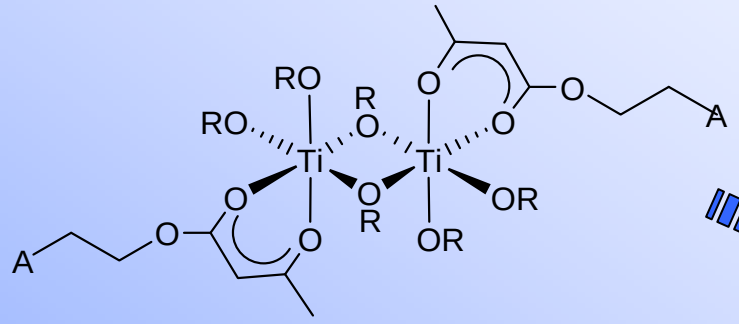


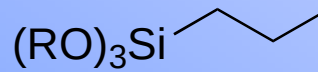


and arrangement “by chance”

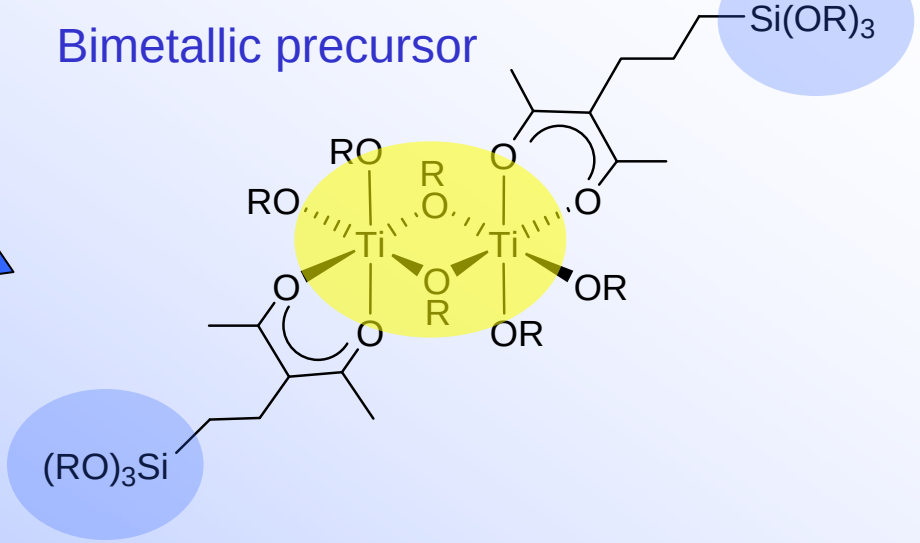
and arrangement according to a master plan

From Simple Molecular Building Blocks to Modules

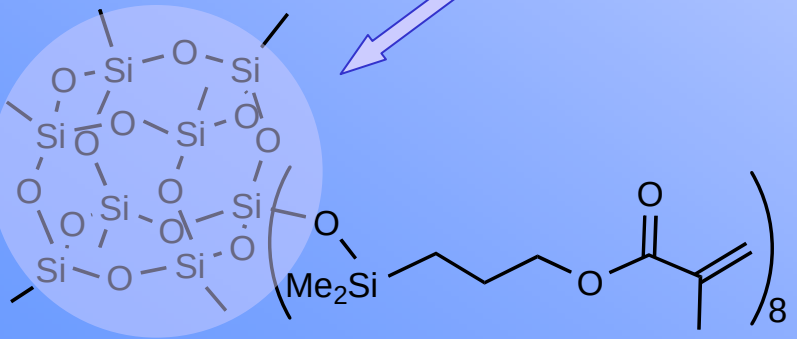




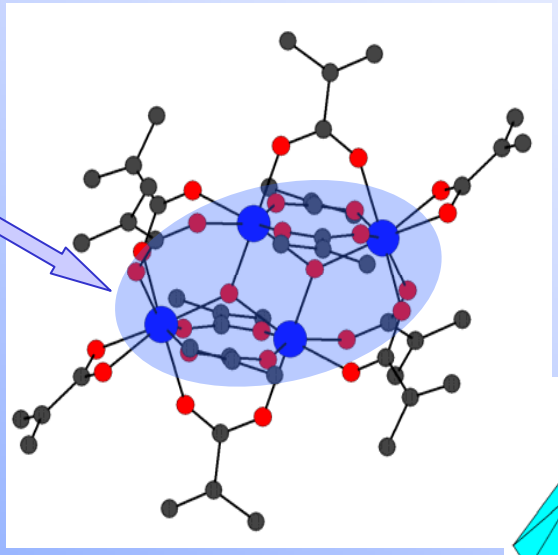
Bimetallic precursor

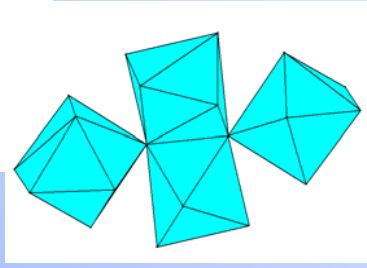


Inorganic nano building blocks (NBB)



Spherosilicates or POSS



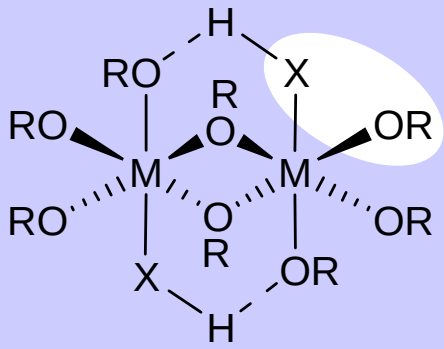


$Zr_4O_4(methacrylate)_{12}$

New Approaches

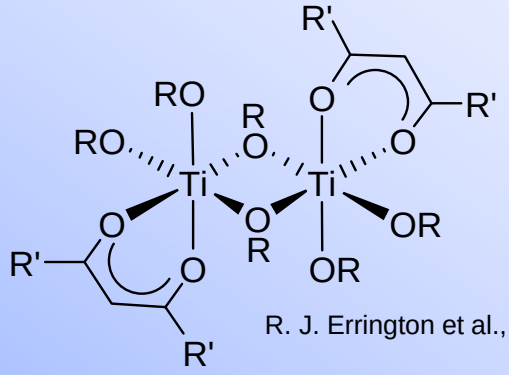
- New precursor concepts
- Organo-bridged bimetallic precursors
- Pre-formed modules

Coordination Chemistry of $Ti(OR)_4$: Chelating Ligands (CL)

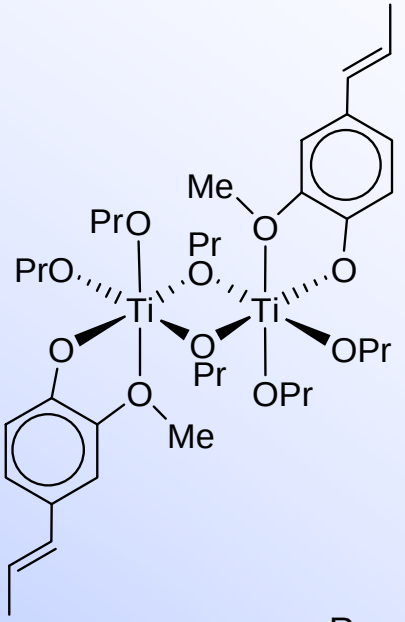


X = OR or NHR

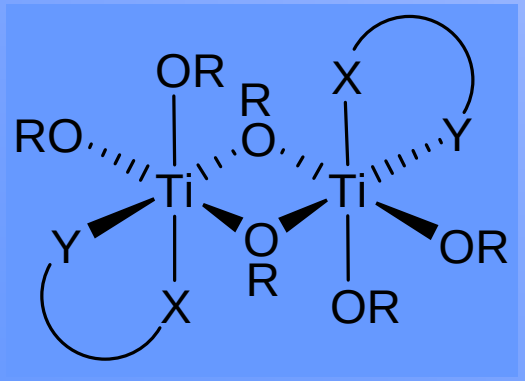
$$Ti(OR)_4 + CL\text{-}H \longrightarrow Ti(OR)_3CL + ROH$$

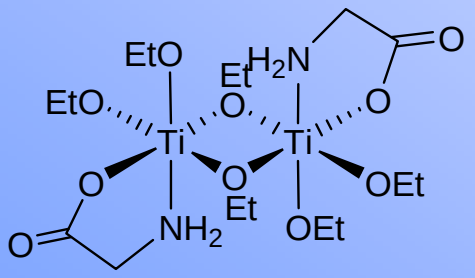


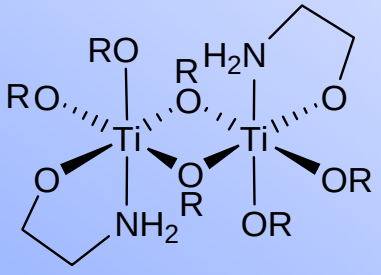
R. J. Errington et al., 1998

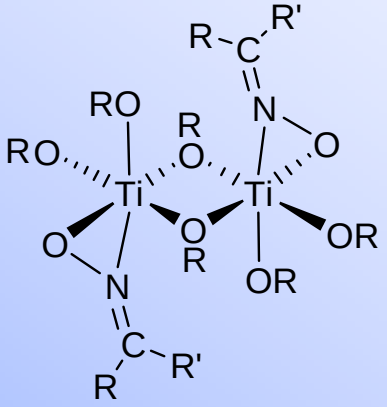


Chelating ligands:





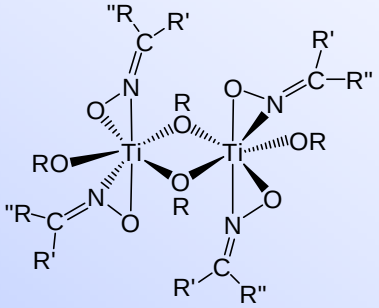




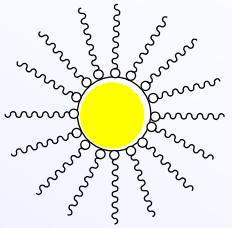
Organic Modification of $Ti(OR)_4$ by Acetaldoxime

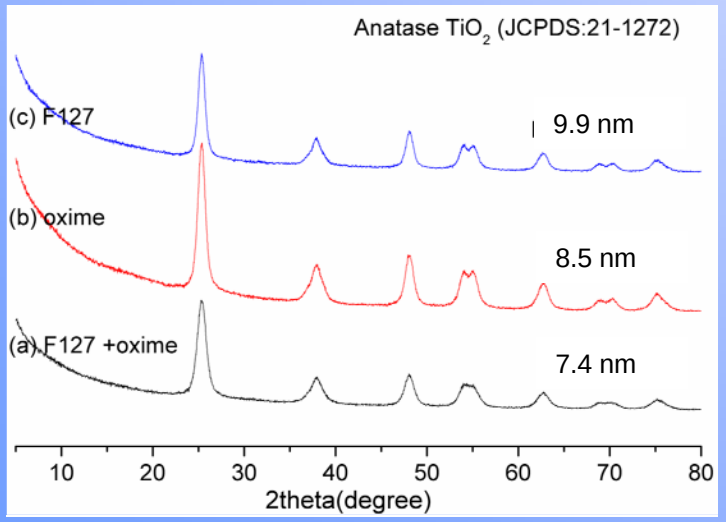
Acid-catalyzed hydrolysis of

- $Ti(O^iPr)_4$ + Pluronics F127
- $Ti_2(O^iPr)_4(ON{=}CHMe)_4$
- $Ti_2(O^iPr)_4(ON{=}CHMe)_4$ + Pluronics F127



Surfactant for particle stabilization

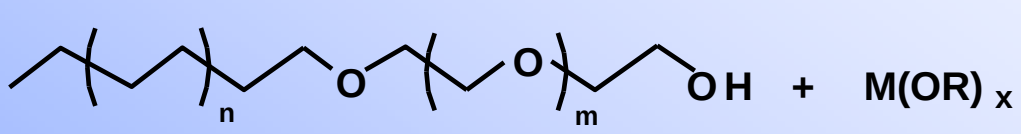




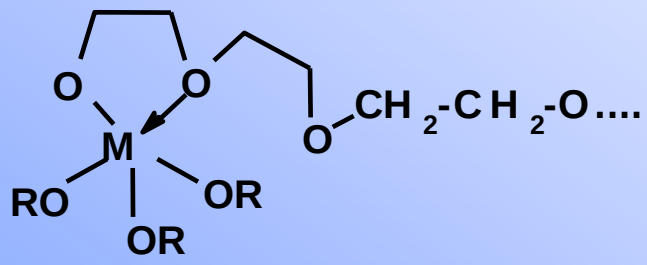
calcination at 400 °C for 2h

		Calcination temperature				
		250° C	300° C	350° C	400° C	500° C
(a) F127 + oxime	BET (m^2/g) D_{BJH} (nm)	151 6.7	110 10.4	**219** **6.7**	197 4.2	77 14.7
(b) only oxime	BET (m^2/g) D_{BJH} (nm)	17 13	**154** **3.9**	**154** **4.4**	82 4.1	39 6.7
(c) only F127	BET (m^2/g) D_{BJH} (nm)	180 5.4	**178** **3.9**	147 4.2	106 5.6	64 12.5

Ligand-assisted Template Syntheses

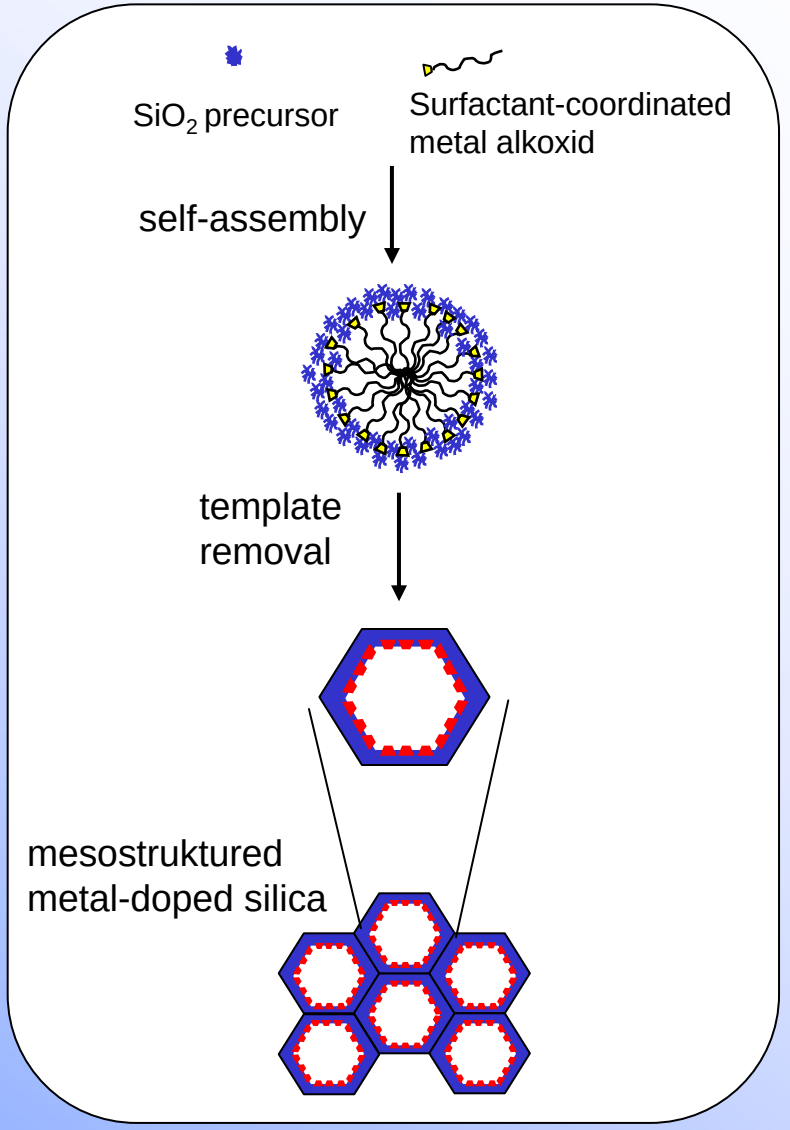


Toluene



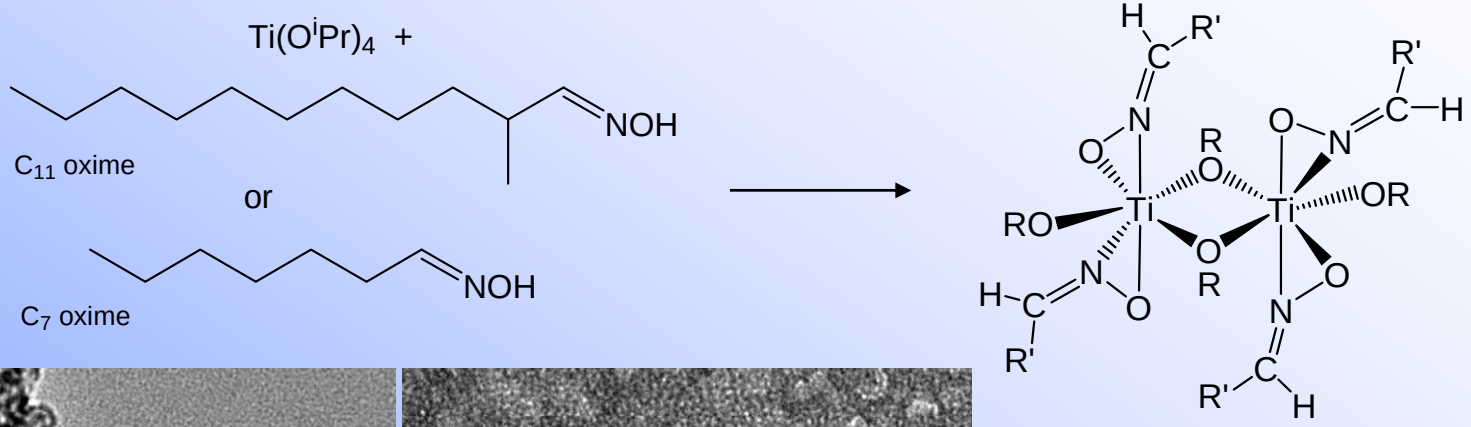
M - Surfactant Complex

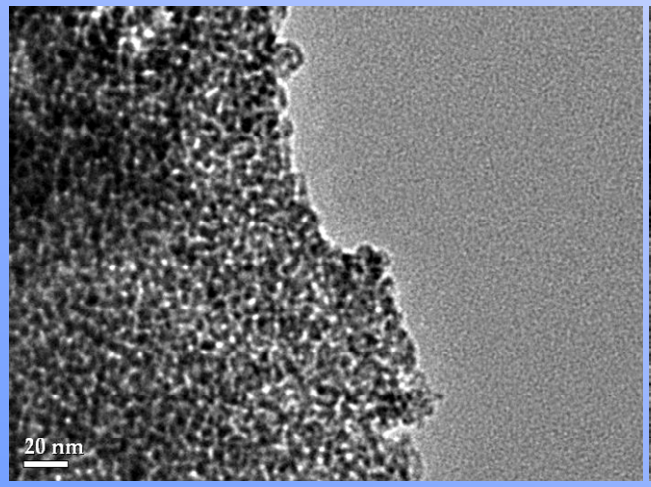
M = Ti, Zr, Zr, Hf, Fe, etc



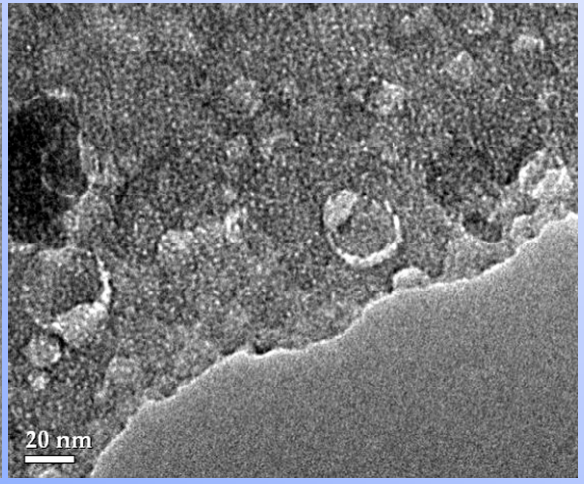
Hüsing et al., *Chem. Mater. 2002; Appl. Catal.* 2003

Long-Chain Oximates as Reaction Moderators + Surfactants





C_7



C_{11}

after calcination at 350°C

Sample	S^{BET} [m²/g]	D^{BJH} [nm]
C_7 oximate-modified $Ti(O^iPr)_4$	175	4.7
C_{11} oximate-modified $Ti(O^iPr)_4$	175	3.3
$Ti(O^iPr)_4$ + Pluronics	147	4.2
$Ti(O^iPr)_4$ + Brij56	193	3.3

New Approaches

- New precursor concepts
- Organo-bridged bimetallic precursors *
- Pre-formed modules

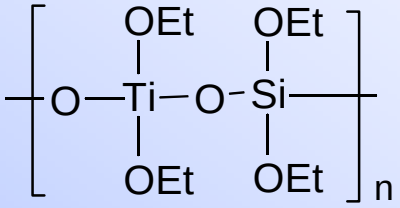
* Chemical link between two metal alkoxide moieties:
- to avoid macroscopic phase separation
- to pre-organize the inorganic structures

Bimetallic Metal Alkoxide Precursors

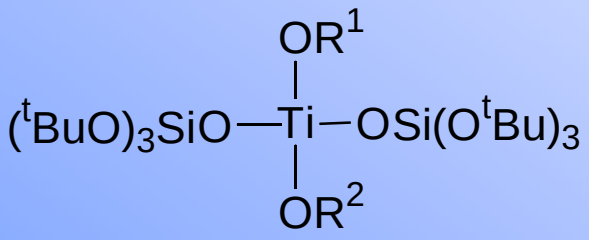
(Excluding precursors with OR-bridges between the metals)

$(EtO)_3Si\text{-}O\text{-}Al(OBu)_2$

J. C. Pouxviel et al.

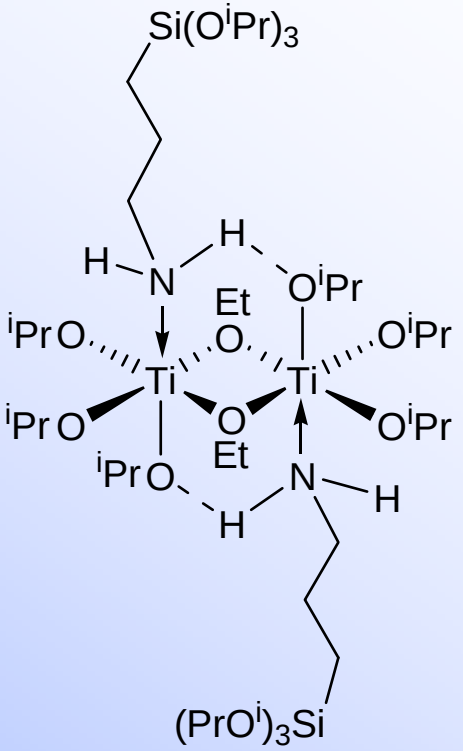


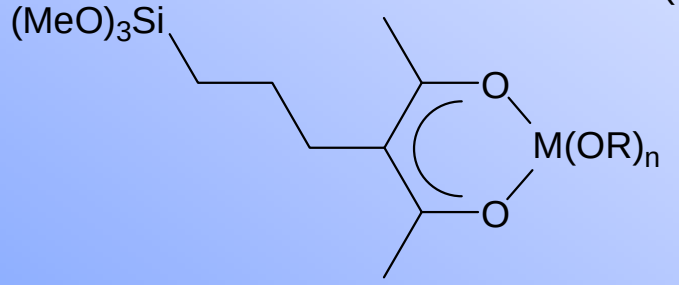
E. L. Ko et al.



$R^1 = R^2 = Si(O^tBu)_3$ T. D. Tilley et al.

$R^1 = {}^iPr$, $R^2 = {}^iPr$ or $Si(O^tBu)_3$ Y. Abe et al.





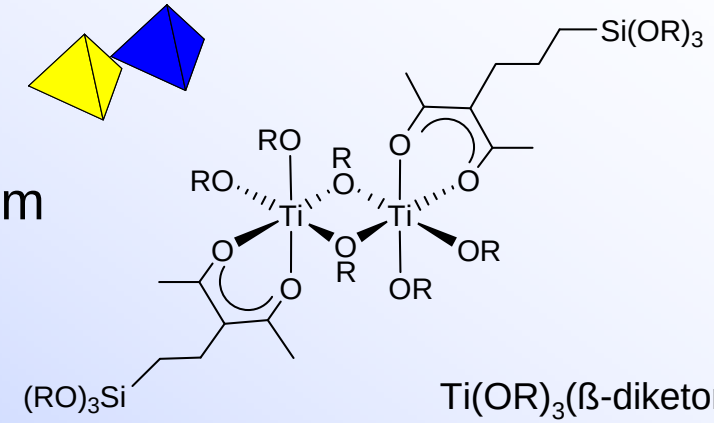
M = Al, Ti, Zr, etc.

Gelation of Silica / Titania Systems

Sol-gel processing of
$Si(OR)_4$ + $Ti(OR)_4$

immediate precipitation of
titania gels
(higher reactivity of $Ti(OR)_4$
towards water)

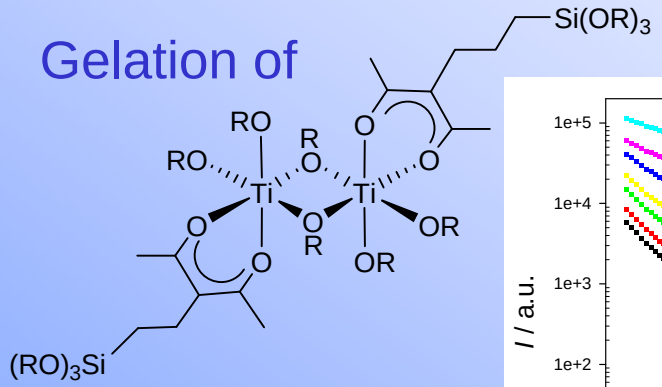
Gels from

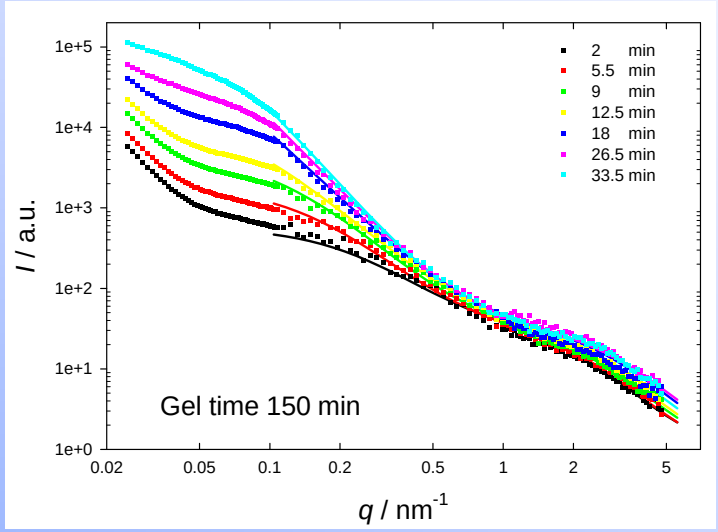


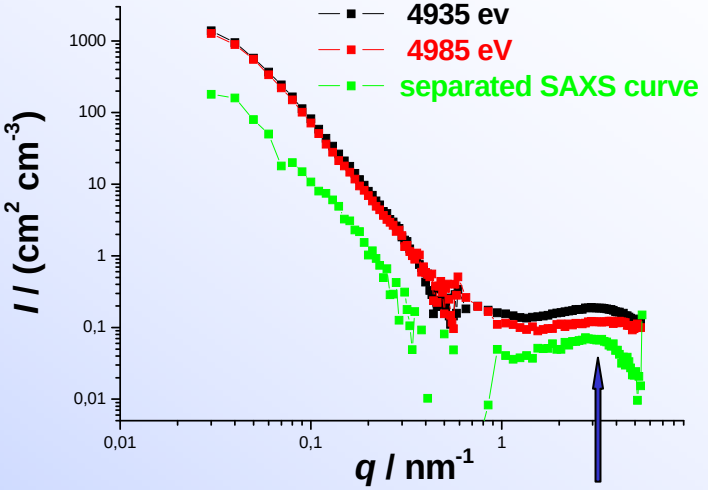
$Ti(OR)_3$(ß-diketonate)

SAXS Studies of Gelation Process

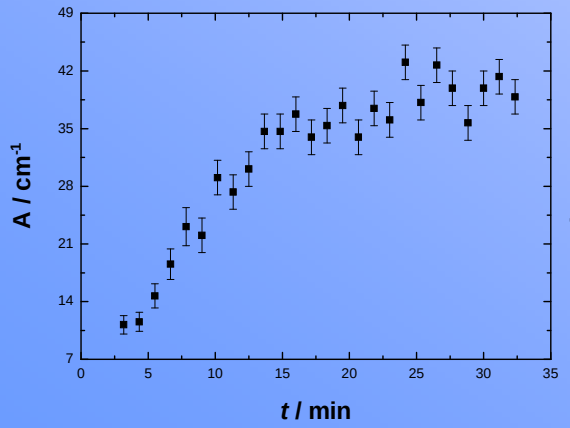
Gelation of



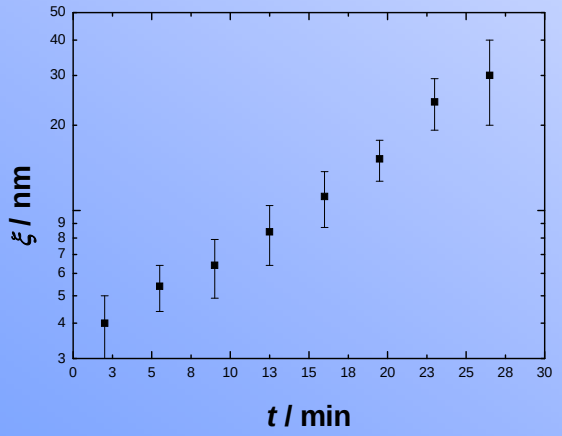




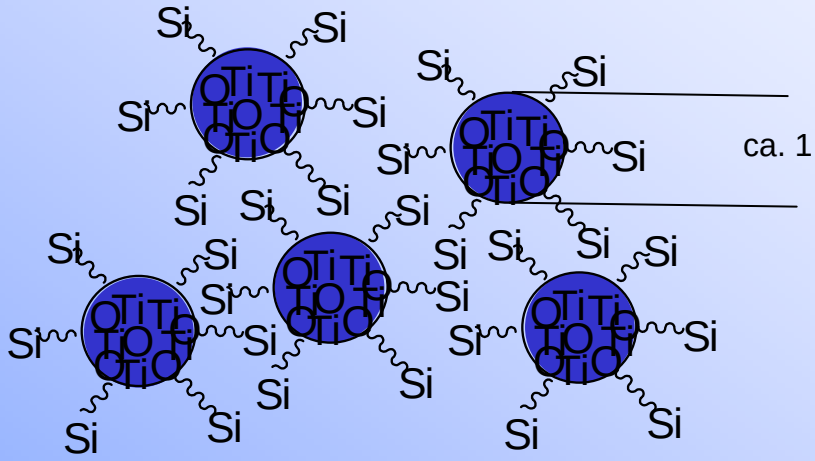
Scattering feature caused by Ti
(characteristic radius ≈ 0.5 nm)



time evolution of parameter A
(corresponds to primary particle volume ⇒ r = 0.5 ± 0.1 nm)



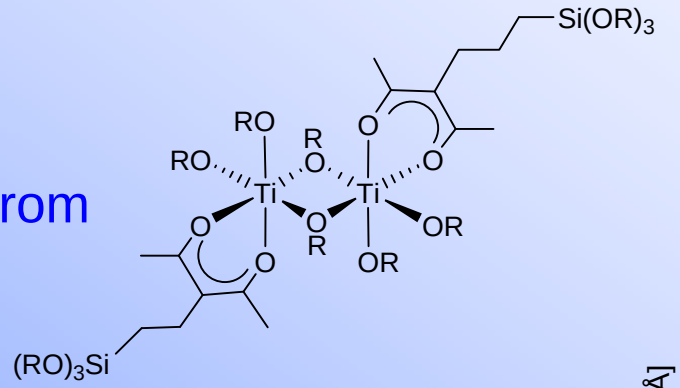
time evolution of parameter ξ
(corresponds to aggregate size)



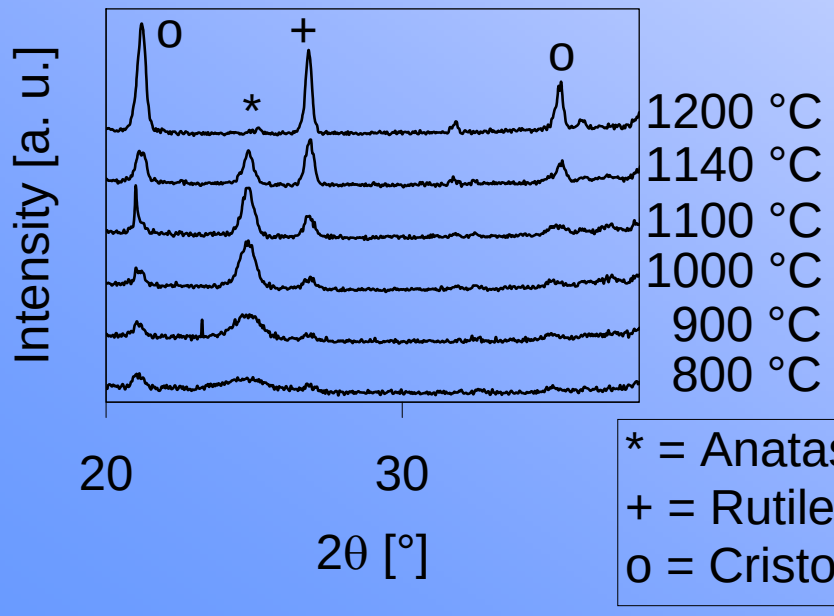
SAXS: Prof. Herwig Peterlik, Univ. of Vienna

Metal Oxide Nanoparticles in a Silica Matrix I

SiO_2/TiO_2 from

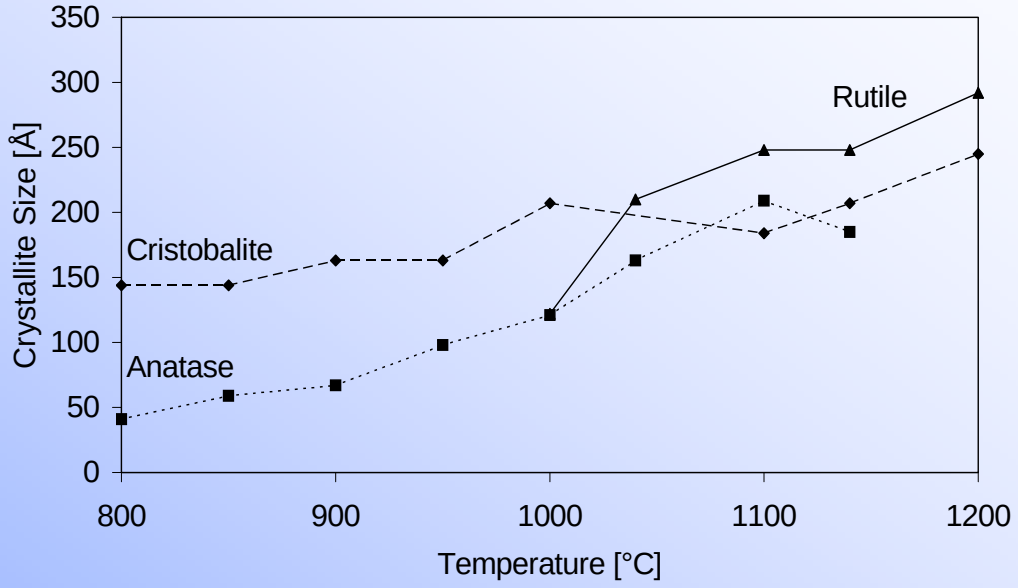


Phase development



* = Anatase
\+ = Rutile
o = Cristobalite

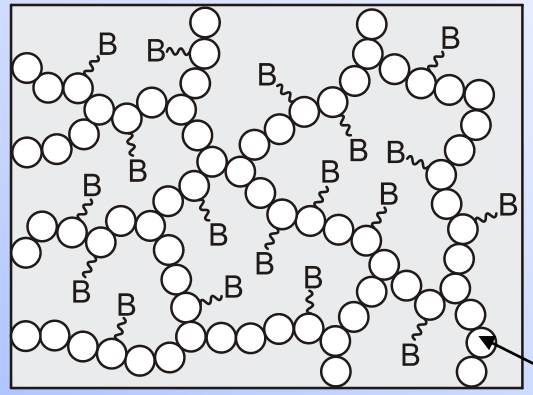
Crystallite diameters



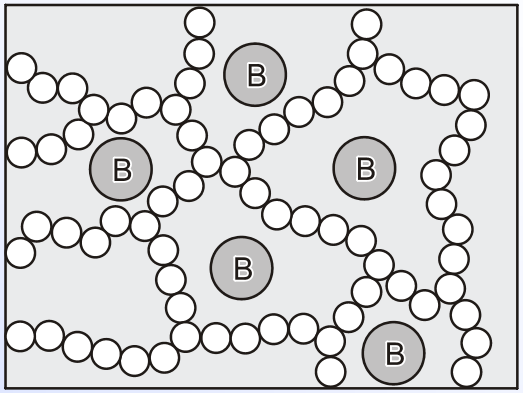
Nanoparticles by Post-Synthesis Treatment of Gels

A ~~~~ B

Sol-gel processing



Degradation of organic groups

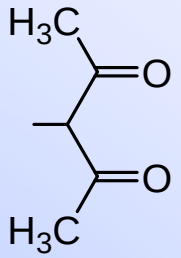


Matrix from the A part of the precursor mixture

A B

$(RO)_3Si\text{-}(CH_2)_n\text{-}X\text{-}M$

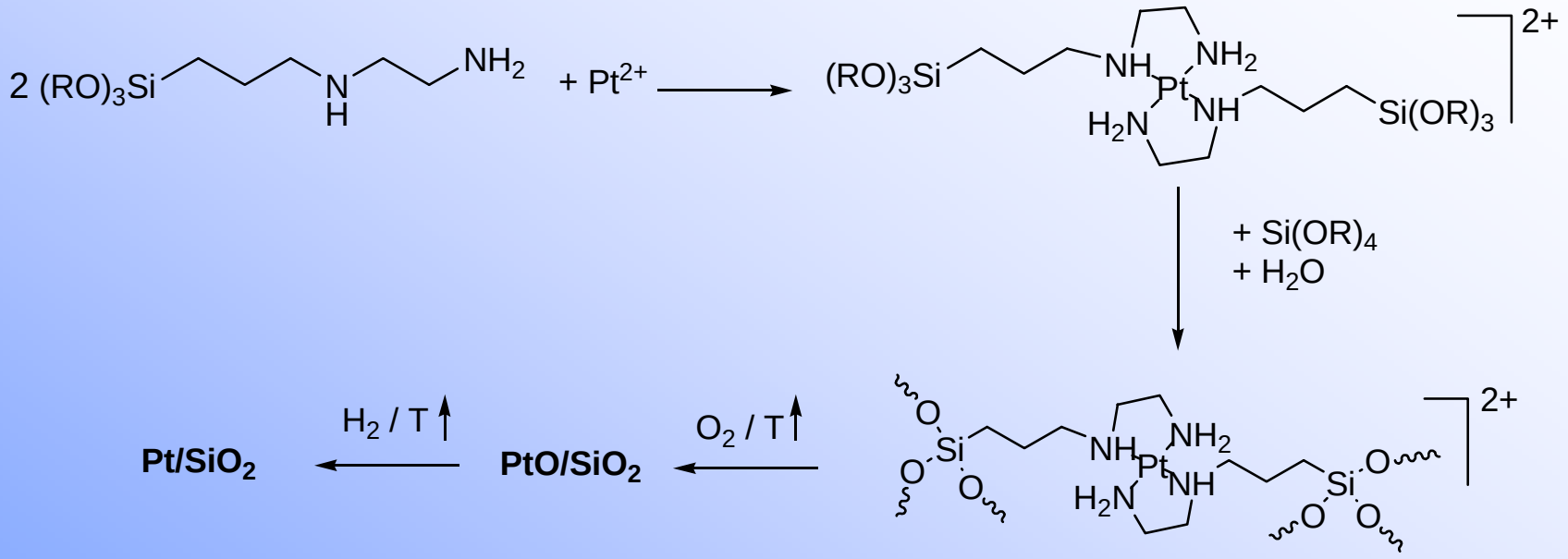
X = $-NH_2$ $-NH-NH_2$

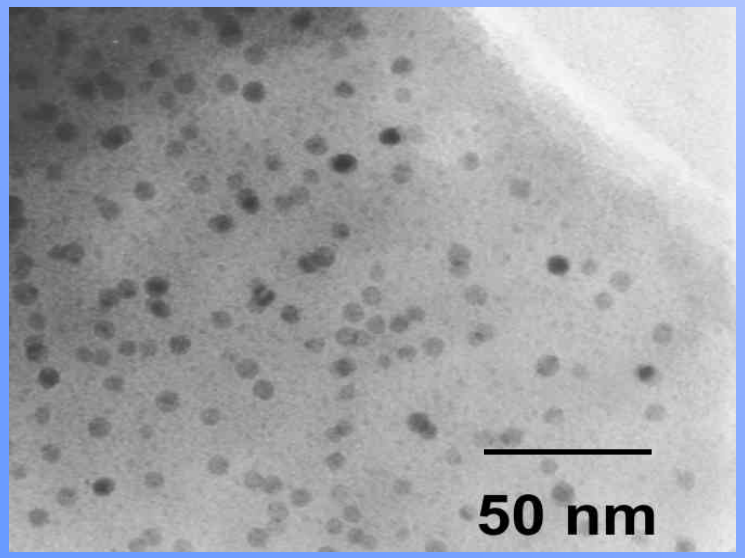


Coordinating organic group

Metal or metal-containing group

Metal or Metal Oxide Nanoparticles in a Silica Matrix II



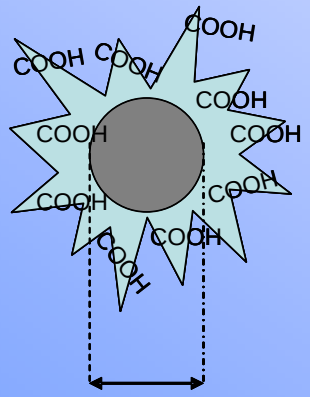


Pd

Metallic nanoparticles
Narrow particle size distribution
Variable particle sizes
Variable metal content (up to 50 mol%)
No aggregation of the particles
Homogeneous distribution in the SiO_2 matrix

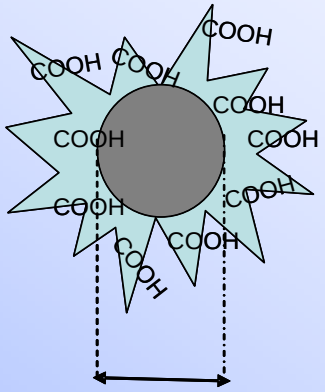
Core-Shell-Particles with Complex Structures

SiO_2 particle with Poly(*N*-dicarbazolyl-lysine) shell



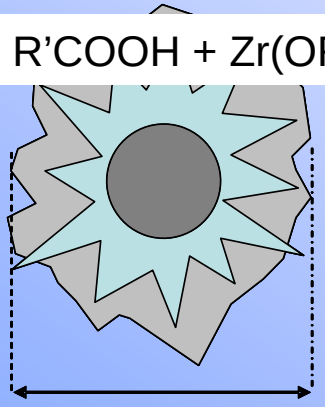
$Si(OEt)_4$
H_2O

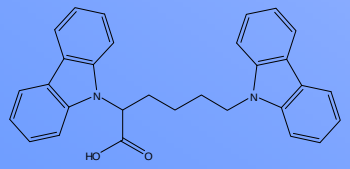
A



$M(OR)_n$
H_2O

M = Ti, Zr, Al

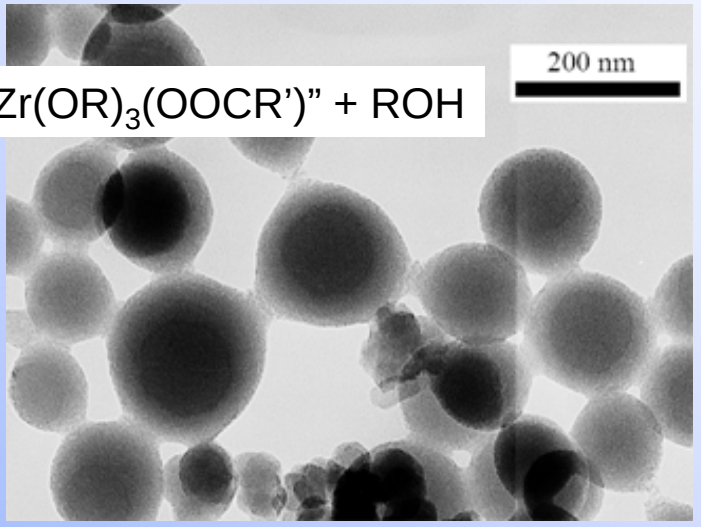




DCL

$R'COOH + Zr(OR)_4 \longrightarrow$ "$Zr(OR)_3(OOCR')$" + ROH

B

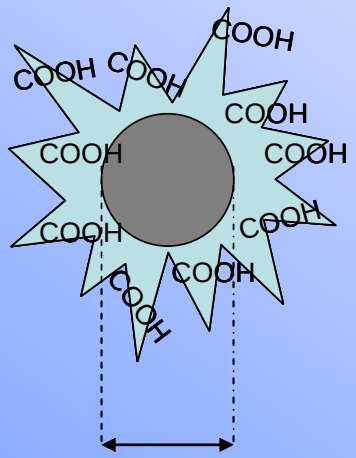


SiO_2@PDCL@Al_2O_3 composite particles

Cooperation with J.P.Lellouche, Bar-Ilan University, Israel

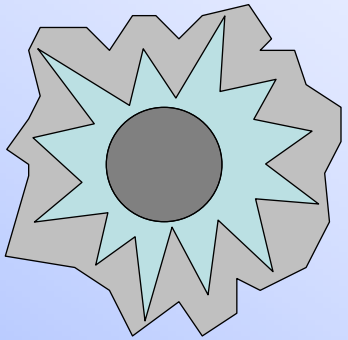
Application to Complex Particle Structures

SiO_2@PDCL



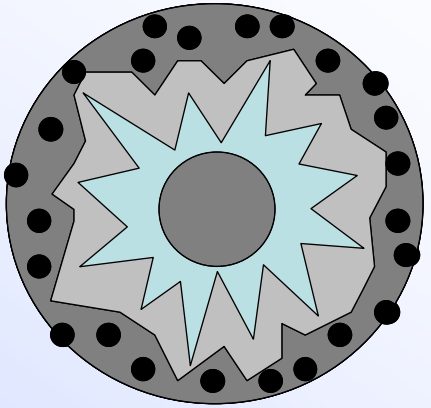
1) $Zr(OR)_4$
2) H_2O

SiO_2@PDCL-ZrO_2

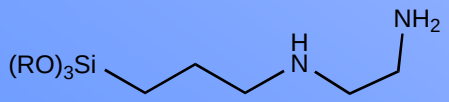


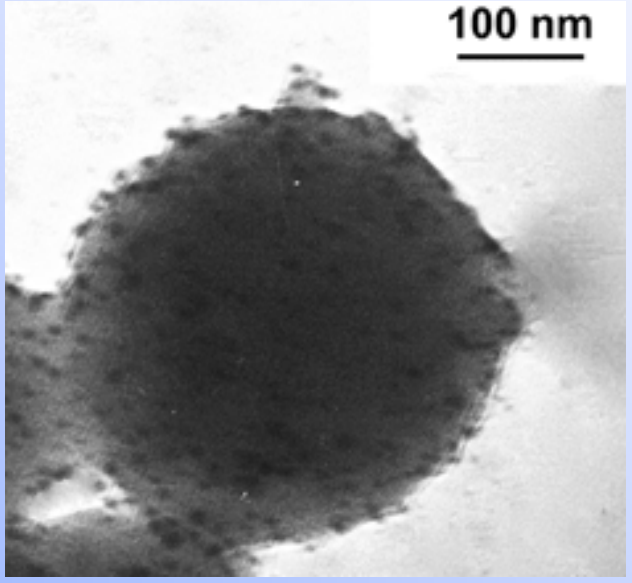
1) Ag^+ / AEAPTS
2) $Si(OEt)_4$, H_2O
3) hν

SiO_2@PDCL-ZrO_2@(Ag@SiO_2)



AEAPTS =





Cooperation with J.P.Lellouche, Bar-Ilan University, Israel

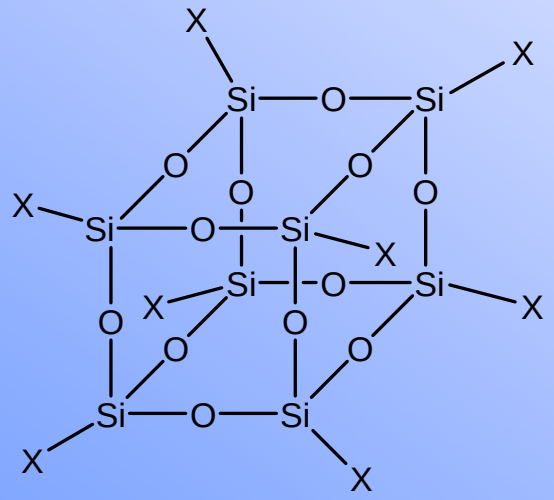
New Approaches

- New precursor concepts
- Organo-bridged bimetallic precursors
- Pre-formed modules

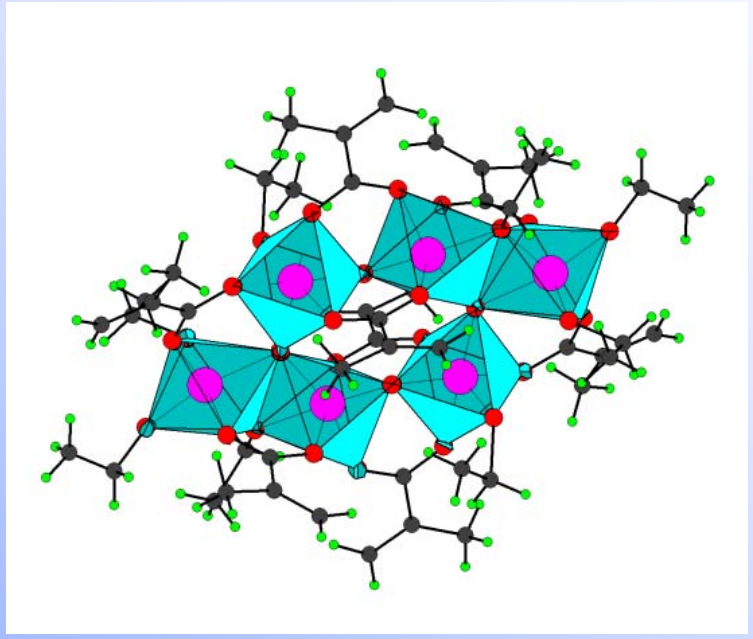
Pre-formed Modules: Clusters with Functional Ligands

Cage compounds as an alternative to network structures

(upon hydrolysis/condensation of metal alkoxides)



Silsesquioxanes (X = R)
and Spherosilicates (X = O^-)



$Ti_6O_4(OEt)_8(methacrylate)_8$

Cluster-Reinforced Organic Polymers

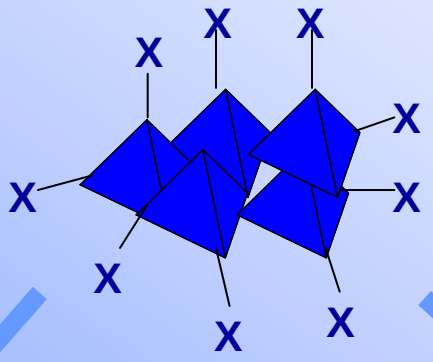
Clusters as pre-formed modules (nanosized building blocks) for the synthesis of class II inorganic-organic hybrid materials

Why clusters?

- Well defined structures
- Deliberate surface modifications
- High interface area
- Clusters are molecules

Why covalent bonds?

- No leaching
- Control of agglomeration
- No migration in the polymer

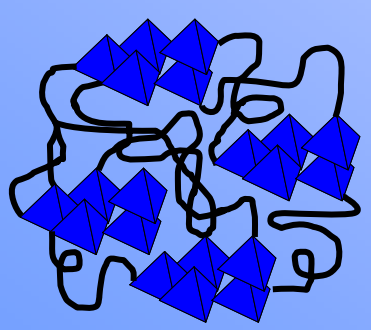


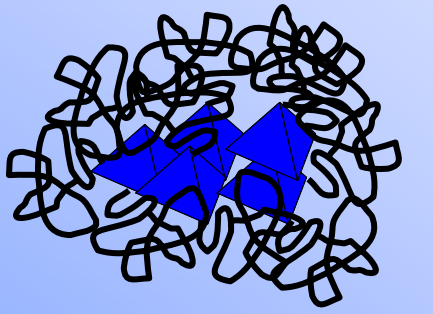
Polymerizable groups X

Free radical polymeryzation, ROMP, click reaction, thiol-en polymerization

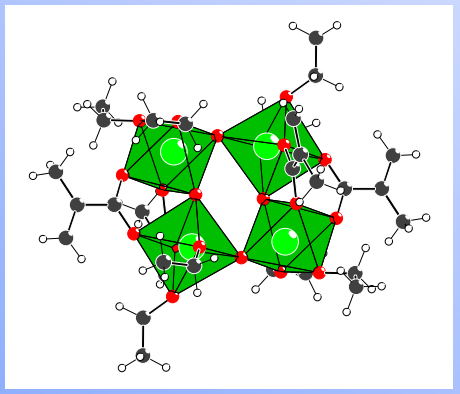
Initiator groups X

ATRP

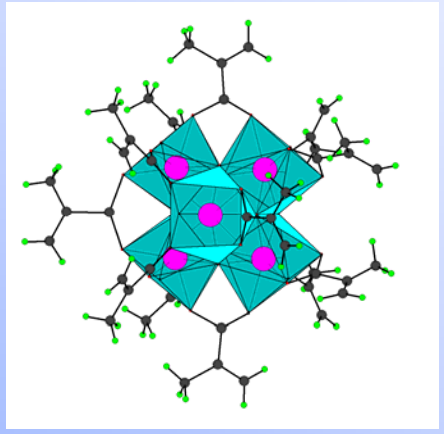




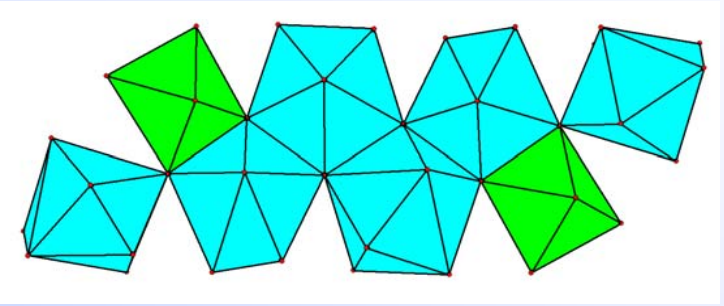
Methacrylate-Substituted Metal Oxide Clusters: Examples



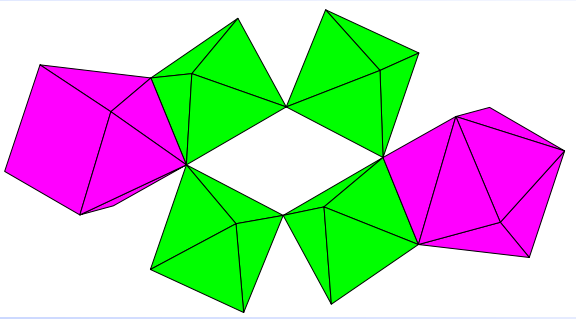
$Ta_4O_4(OEt)_8(OMc)_4$ *



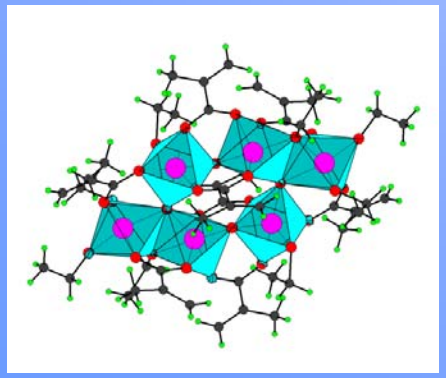
$M_6(OH)_4O_4(OMc)_{12}$
(M = Zr, Hf)



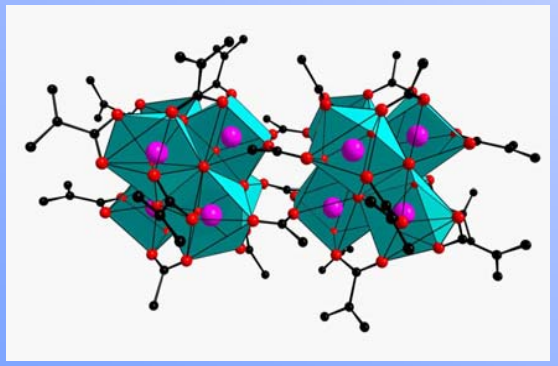
$Ti_2Zr_6O_6(OMc)_{20}$
$Ti_2HfZr_5O_6(OMc)_{20}$



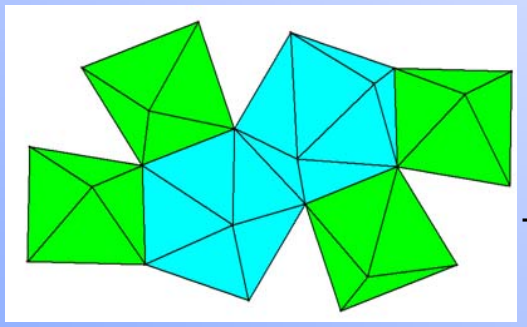
$Ti_4Y_2O_4(OMc)_{14}(HOCH_2CHOMe)_2$



$Ti_6O_4(OEt)_8(OMc)_8$



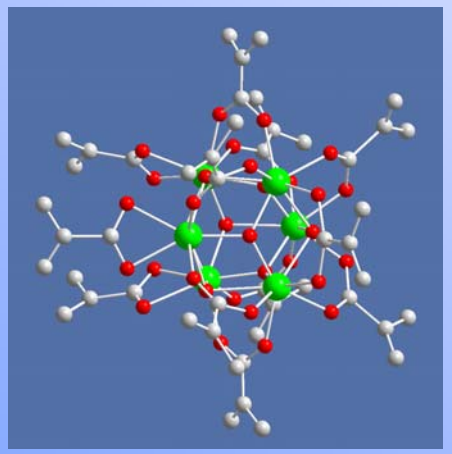
$[Zr_6(OH)_4O_4(OAcr)_{12}]_2$



$Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$

OMc = methacrylate

Carboxylate-Substituted Metal Oxide Clusters
Variation of the Functional Organic Groups



$Zr_6O_4(OH)_4(methacrylate)_{12}$

Fee radical polymerization

⇒ X = acrylate, methacrylate, styryl groups etc.

Ring-opening metathesis polymerization (ROMP)

⇒ X = norbornenyl groups

Click reaction

⇒ X = alkinyl-substituted groups

Atom-transfer radical polymerization (ATRP)

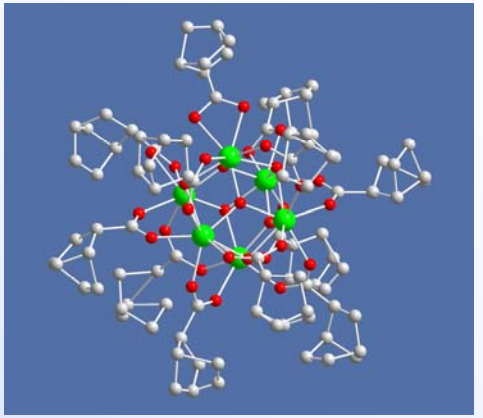
⇒ X = halogenated groups, (e.g. $OOC\text{-}CBrMe_2$)

G. Kickelbick

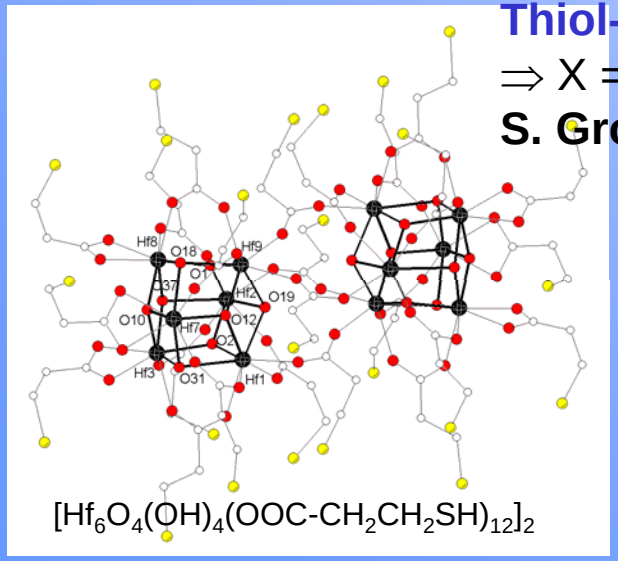
Thiol-ene reaction

⇒ X = SH-containg groups, (e.g. $OOC\text{-}CH_2CH_2SH$)

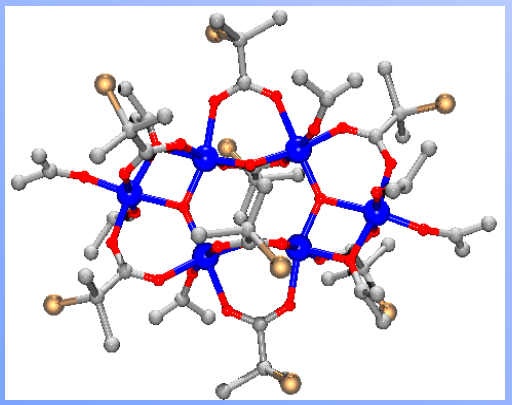
S. Gross



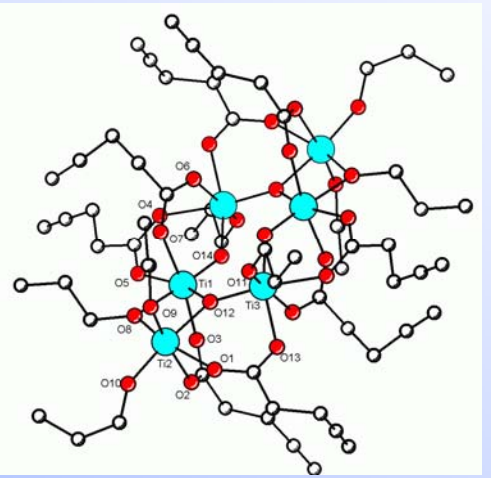
$Zr_6O_4(OH)_4$(5-norbornene-2-carboxylate)$_{12}$



$[Hf_6O_4(OH)_4(OOC\text{-}CH_2CH_2SH)_{12}]_2$



$Ti_6O_4(O^iPr)_8(OOCCBrMe_2)_8$

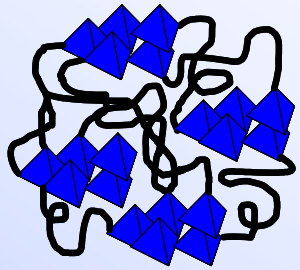


$Ti_6O_4(OPr)_8(OOC\text{-}CH_2CH_2C{\equiv}CH)_8$

Cluster-Reinforced Organic Polymers

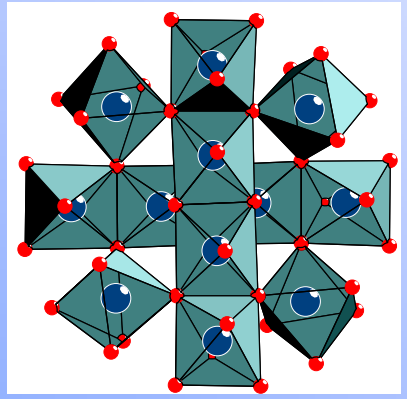
The properties of the cluster*-based hybrid materials orginate from the high **crosslinking** efficiency in combination with „**nanofiller**“ effects. The properties not only depend on the polymerization conditions and the cluster proportion, but also on the kind of employed cluster.

- Increased thermal stability
- Adjustable swelling in organic solvents
- Improvement of thermomechanical properties and tensile strength
- Modification of dielectric properties
- Incorporation of clusters with special intrinsic properties, e.g. superparamagnetic clusters



* Oxo clusters of Ti, Zr, Hf, Ta, Mn

Dispersion of $Mn_{12}O_{12}(acrylate)_{16}$ in Poly(ethylacrylate)



$$Mn_{12}O_{12}(OOC\text{-}CH_3)_{16} \xrightarrow[-\ CH_3COOH]{+\ CH_2{=}CH\text{-}COOH} Mn_{12}O_{12}(OOC\text{-}CH{=}CH_2)_{16}$$

Radical polymerization ↓ + CH_2=CMe-COOEt

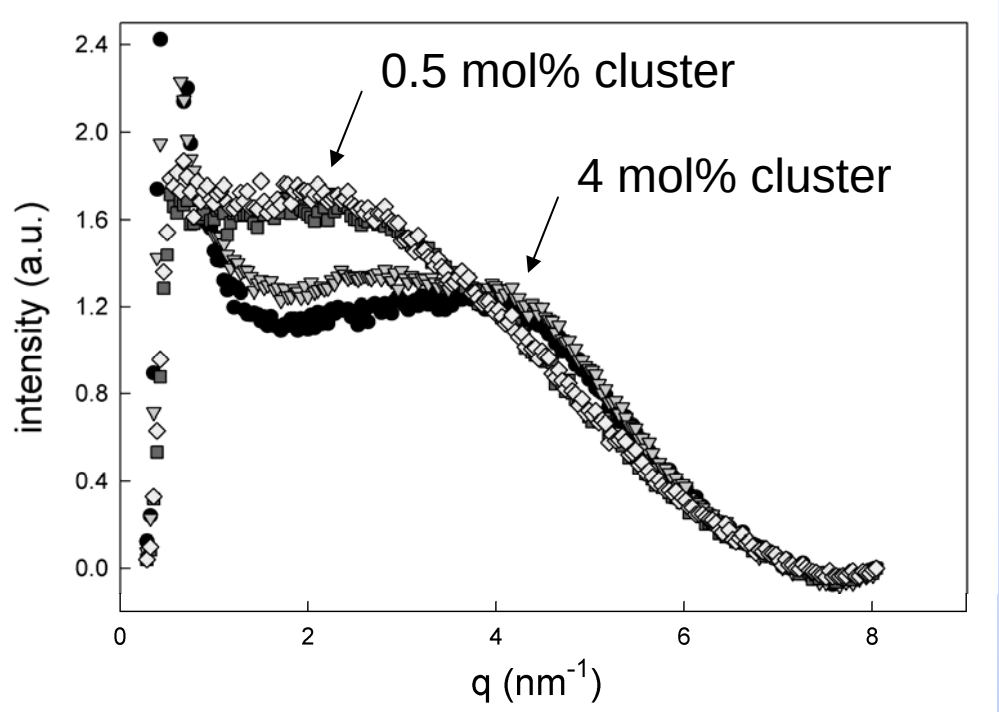
(Superparamagnetic) PMMA crosslinked by Mn_{12}

„**Mn_{12}**“: total cluster spin S = 10
(4 Mn^{IV}, S = $^3/_2$ + 8 Mn^{III}, S = 2)

SAXS:

One characteristic length

Cluster-cluster distance changes from 1.6 to 3.2 nm when cluster proportion is decreased



Acknowledgements

Money

Fonds zur Förderung der wissenschaftlichen Forschung