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CUI THE HAMBURG CENTRE FOR ULTRAFAST IMAGING

Water in Nanopores

Phase behavior of confined water in ordered nanoporous organosilica hybrid materials with periodically modulated surface polarities

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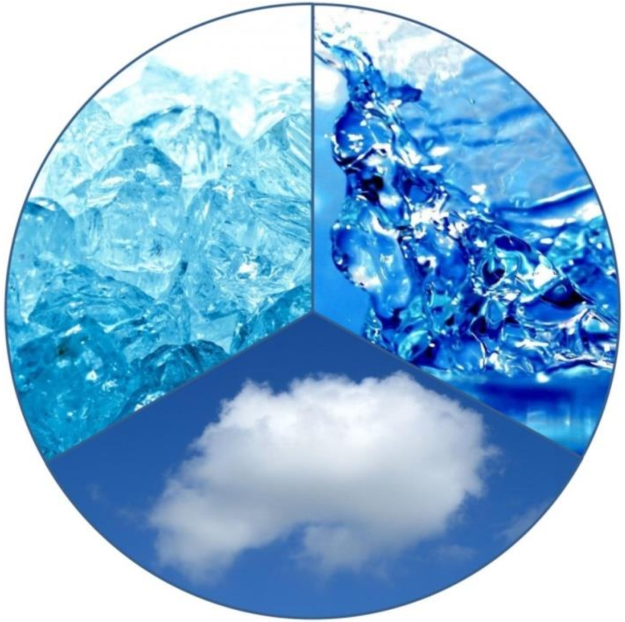
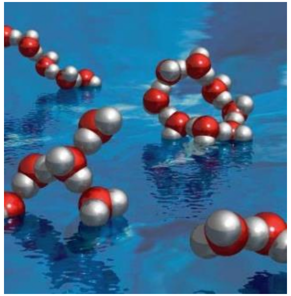
Contents

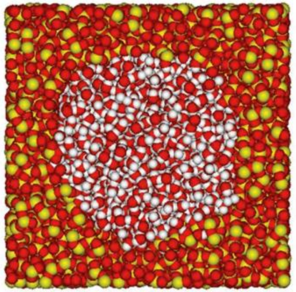
- **Water**
  properties, anomalies

- **Nanoporous solids**
  synthesis and properties

- **Confined water in nanoporous solids**
  phase behaviour







Water
Properties and anomalies

Anomalies of water – hydrogen bonding

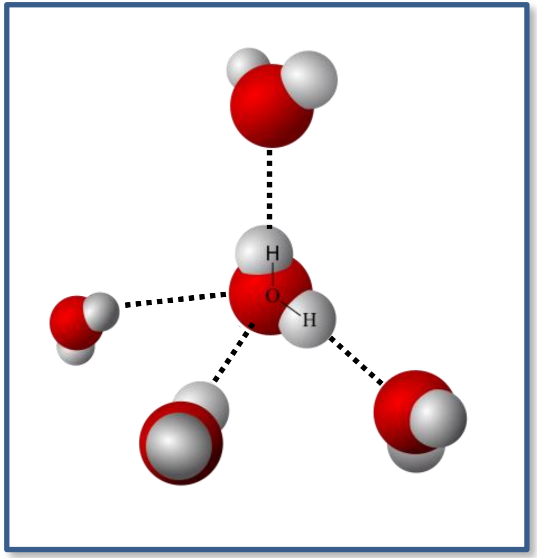
Hydrogen bonding is very efficient in liquid water and ice

- up to 4 hydrogen bonds per H_2O molecule (2 lone pairs, 2 hydrogen atoms)
- resulting in tetrahedral geometry and a three-dimensional network of hydrogen bonds

Only two bonds per molecule in HF and NH_3

- HF: 3 lone pairs, 1 hydrogen atom
- NH_3: 1 lone pairs, 3 hydrogen atoms

➡ Hydrogen bonding also responsible for **high viscosity, surface tension, heat of vaporization (melting, sublimation), heat capacity** etc.



H–F····H–F····H–F····H–F····H

Anomalies of water – consequences of hydrogen bonding

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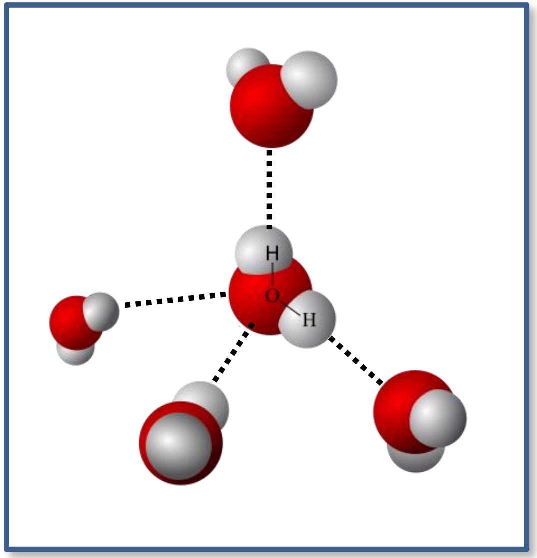
- Unusually high boiling temperature
- Unusually high melting temperature
- Unusually high heat of vaporization
- Unusually high heat of melting
- Unusually high heat of sublimation
- Unusually high viscosity (low mobility)
- Unusually high surface tension
- Low compressibility
- Low thermal expansion



→ 3D network of hydrogen causes very high intermolecular forces

Anomalous properties of water in the bulk state

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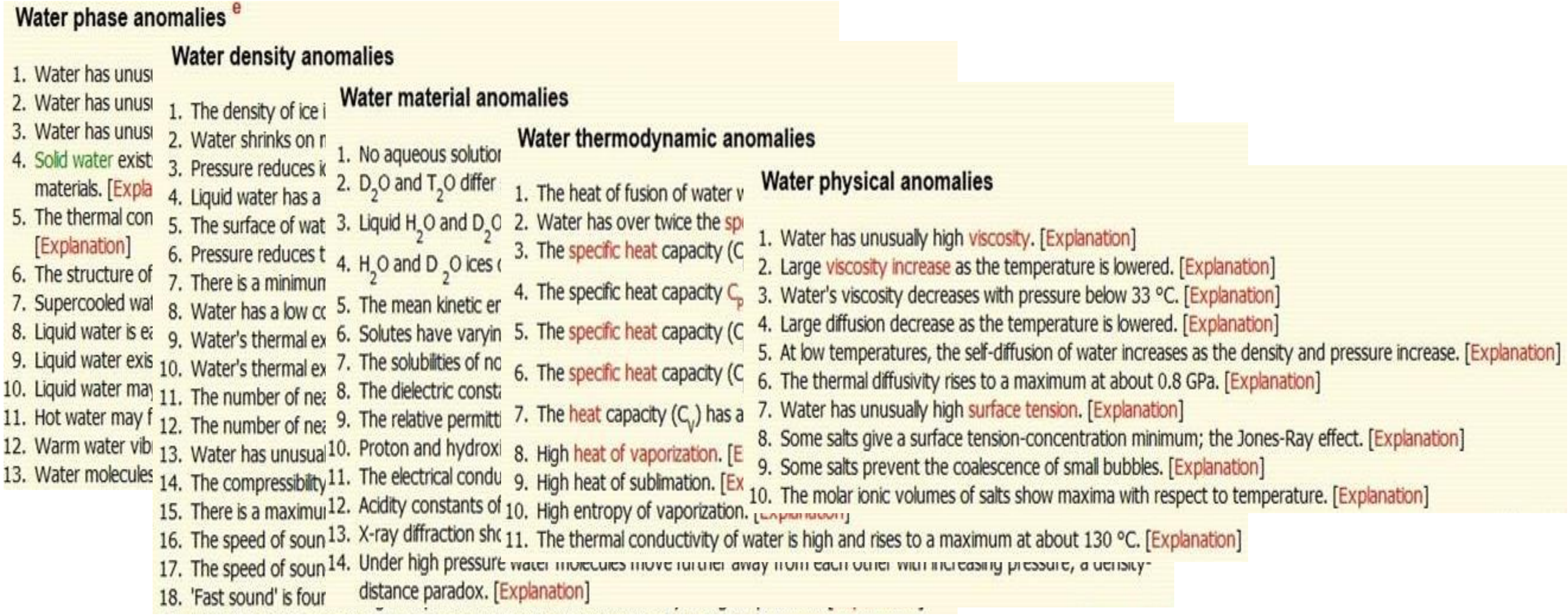
- Water exhibits more than 60 anomalies



Water phase anomalies

1. Water has unus
2. Water has unus
3. Water has unus
4. Solid water exist materials. [Expla
5. The thermal con [Explanation]
6. The structure of
7. Supercooled wat
8. Liquid water is ea
9. Liquid water exis
10. Liquid water may
11. Hot water may f
12. Warm water vib
13. Water molecules

Water density anomalies

1. The density of ice i
2. Water shrinks on m
3. Pressure reduces ic
4. Liquid water has a
5. The surface of wat
6. Pressure reduces t
7. There is a minimum
8. Water has a low co
9. Water's thermal ex
10. Water's thermal ex
11. The number of nea
12. The number of nea
13. Water has unusual
14. The compressibility
15. There is a maximu
16. The speed of soun
17. The speed of soun
18. 'Fast sound' is four

Water material anomalies

1. No aqueous solution
2. D_2O and T_2O differ
3. Liquid H_2O and D_2O
4. H_2O and D_2O ices
5. The mean kinetic er
6. Solutes have varyin
7. The solubilities of no
8. The dielectric const
9. The relative permitt
10. Proton and hydroxi
11. The electrical condu
12. Acidity constants of
13. X-ray diffraction sho
14. Under high pressure water molecules move further away from each other with increasing pressure, a density-distance paradox. [Explanation]

Water thermodynamic anomalies

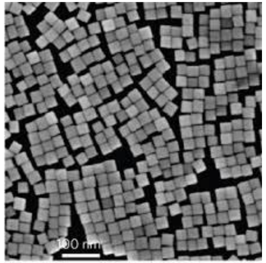
1. The heat of fusion of water v
2. Water has over twice the sp
3. The specific heat capacity (C
4. The specific heat capacity C_P
5. The specific heat capacity (C
6. The specific heat capacity (C
7. The heat capacity (C_V) has a
8. High heat of vaporization. [E
9. High heat of sublimation. [Ex
10. High entropy of vaporization. [Explanation]
11. The thermal conductivity of water is high and rises to a maximum at about 130 °C. [Explanation]

Water physical anomalies

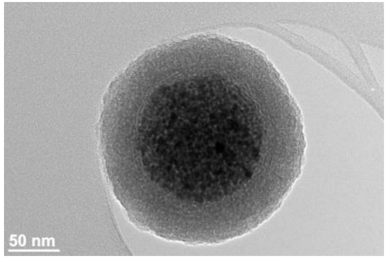
1. Water has unusually high viscosity. [Explanation]
2. Large viscosity increase as the temperature is lowered. [Explanation]
3. Water's viscosity decreases with pressure below 33 °C. [Explanation]
4. Large diffusion decrease as the temperature is lowered. [Explanation]
5. At low temperatures, the self-diffusion of water increases as the density and pressure increase. [Explanation]
6. The thermal diffusivity rises to a maximum at about 0.8 GPa. [Explanation]
7. Water has unusually high surface tension. [Explanation]
8. Some salts give a surface tension-concentration minimum; the Jones-Ray effect. [Explanation]
9. Some salts prevent the coalescence of small bubbles. [Explanation]
10. The molar ionic volumes of salts show maxima with respect to temperature. [Explanation]

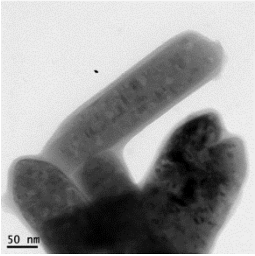
Nanoporous solids
Synthesis and properties

Nanoparticle world

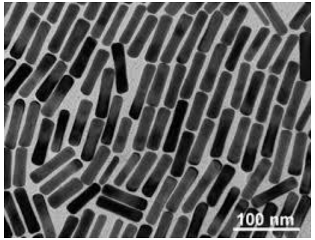


nanocubes





core/shell
systems

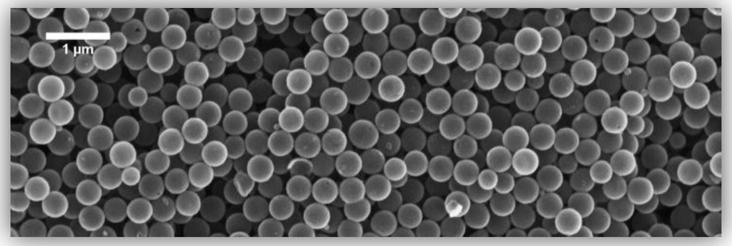


nanorods

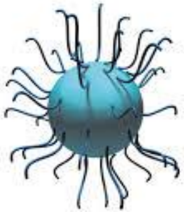
size-dependent properties

quantum-confinement

but:
single objects, stabilization necessary
limited to the solid state



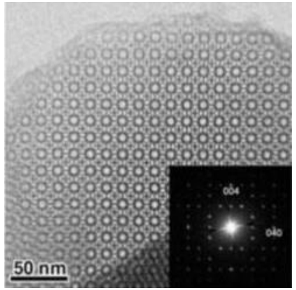
nanospheres

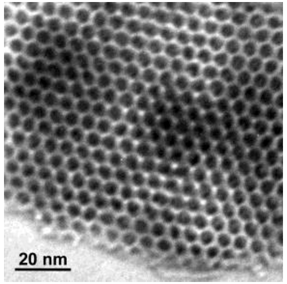


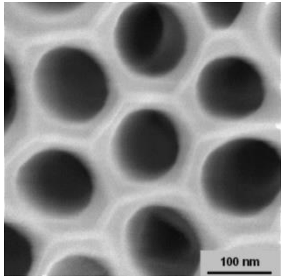
Steric stabilization

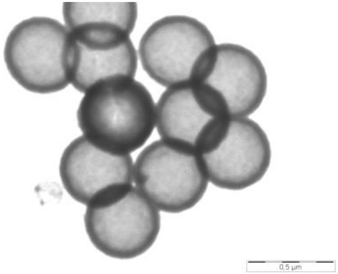
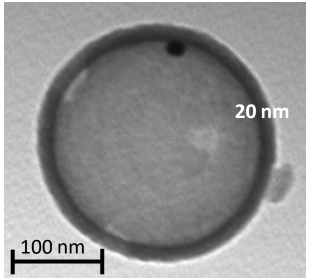
Electrostatic stabilization

Nanopore world



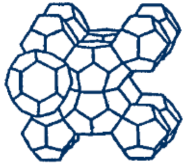
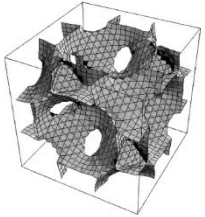
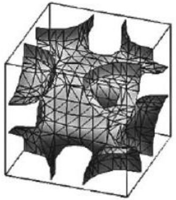
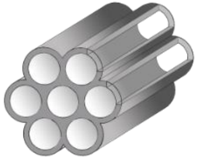
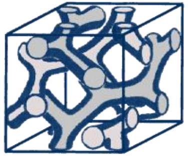




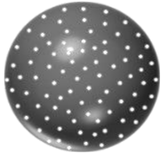
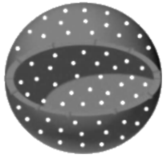
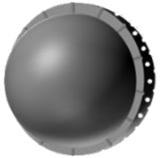
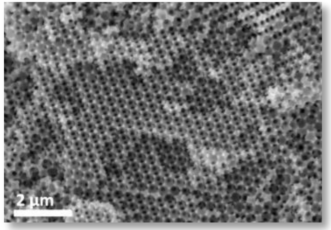
different pore geometries and diameters

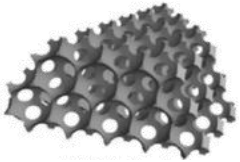
different morphologies

pore determines confined space
guest/guest interactions
guest/wall interactions
hierarchical or multimodal
porosity possible
not limited to single guest species

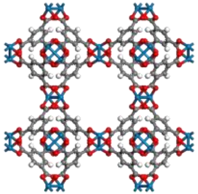
advantages:
not limited to the solid state
gaseous, liquid and solid phases as well as mixtures of them can be confined

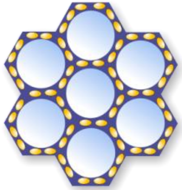


Research

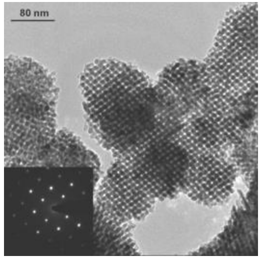
Metal-Organic Frameworks



Nanoporous Organosilicas

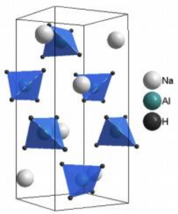


Metal oxides, phosphates, polymers and carbons

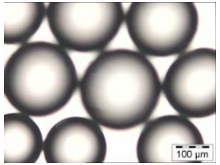


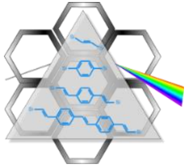
Functional Porous Materials

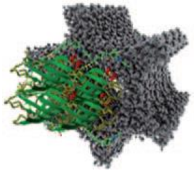
Light Metal Hydrides



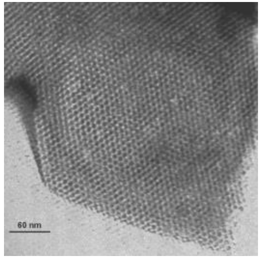
Hydrogen Storage





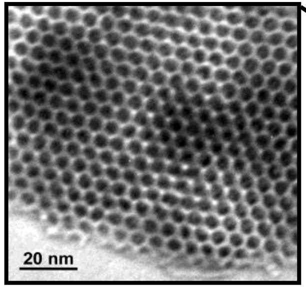


Separation, „Optical“ Materials and Biocatalysis

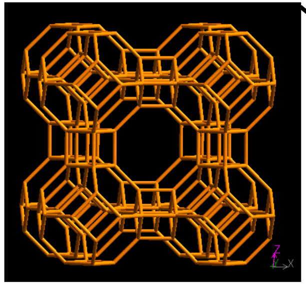


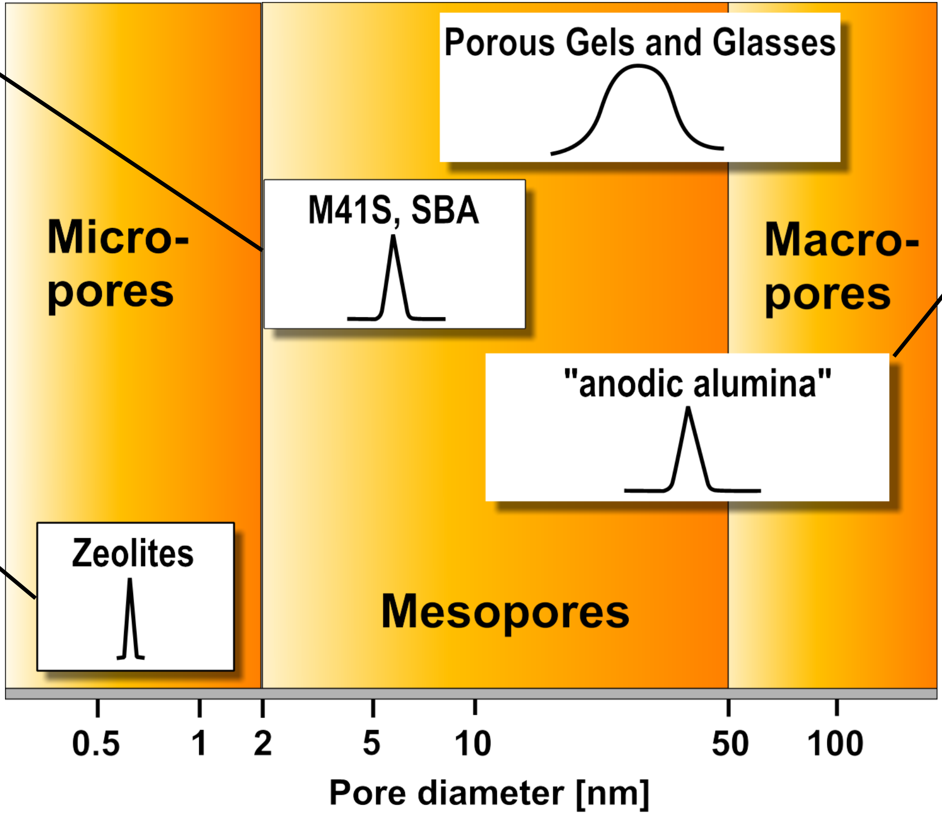
Batteries, Supercapacitors and Thermal Storage

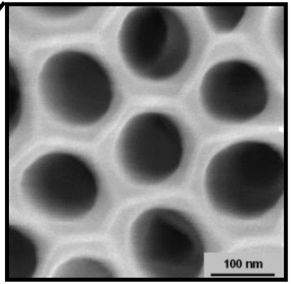
Porous solids – Pore diameters



supermicropores: > 0.7 nm
ultramicropores: < 0.7nm





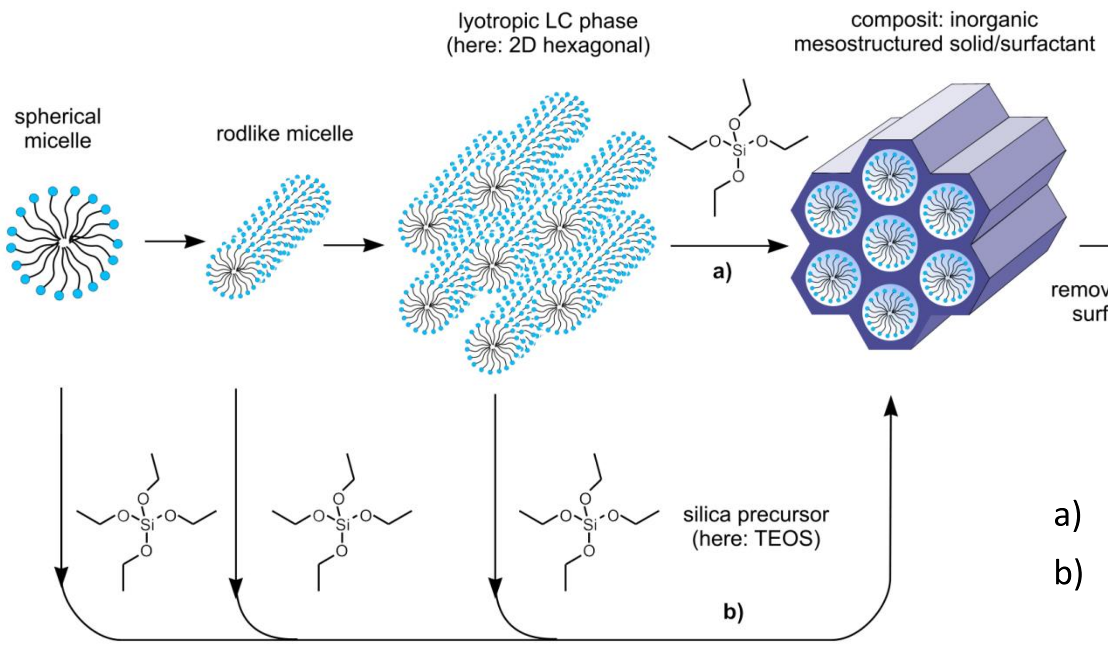


- after IUPAC

Sing, Everett, Haul, Mouscou, Pierotti, Rouquerol, Siemieniewska, *Pure & Appl. Chem.* **1985**, *57*, 603.

Mesoporous silica

- schematic illustration of the synthesis pathway to mesoporous silica



„endo templating"

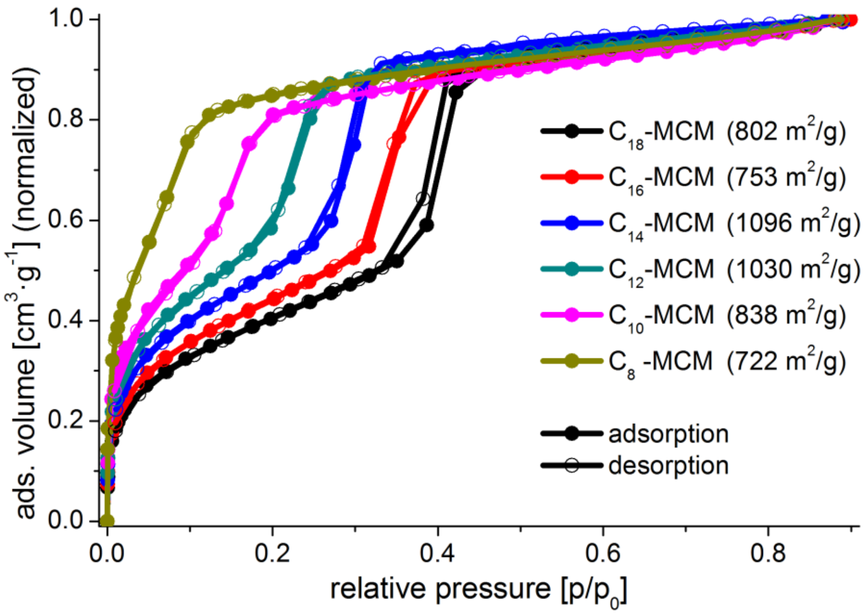
a) liquid crystal initiated

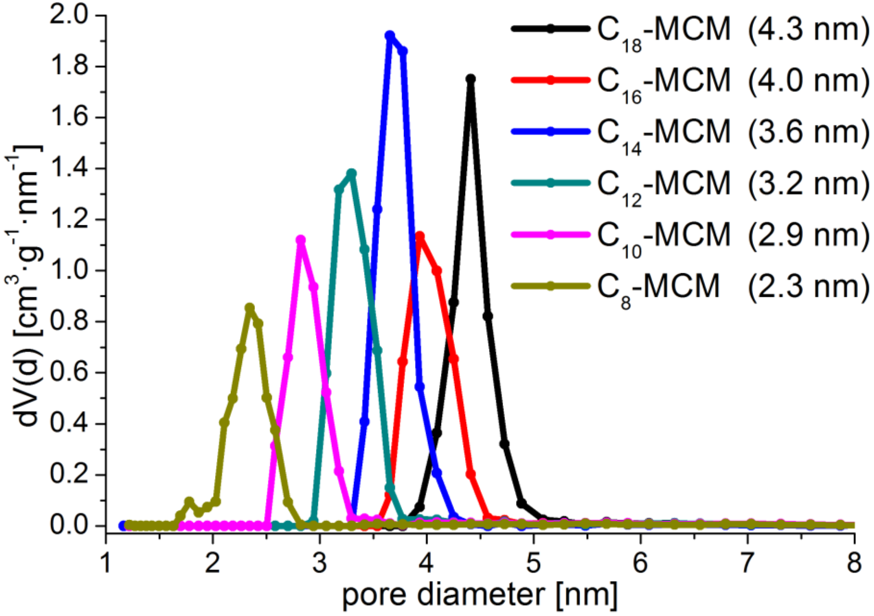
b) silicate anion initiated

cooperative mechanism

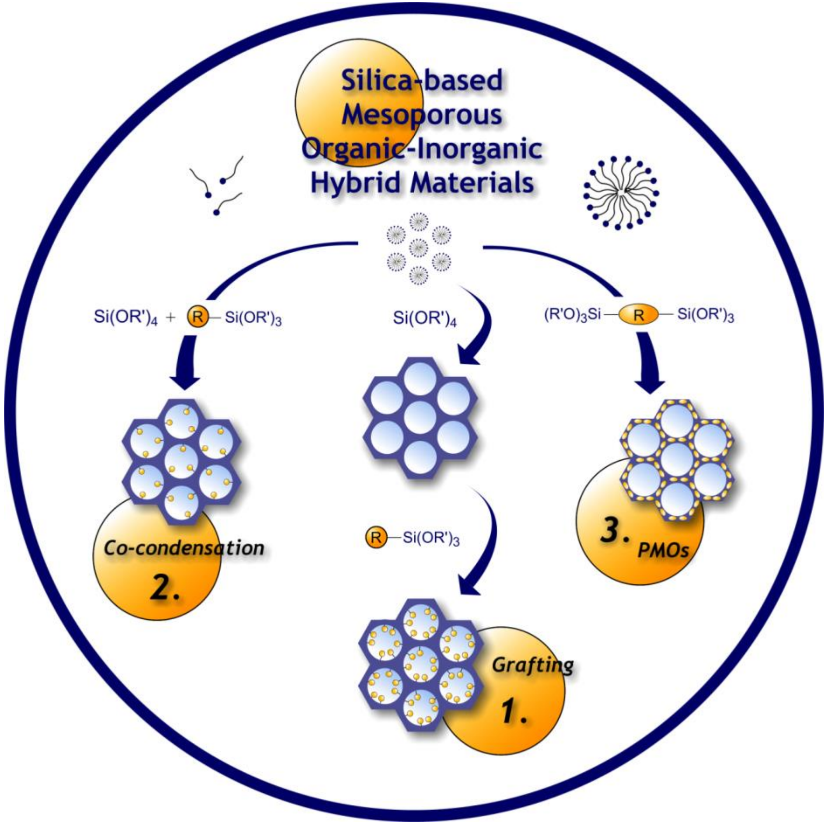
Mesoporous silica (MCM-41 type)

- Nitrogen physisorption (77 K)





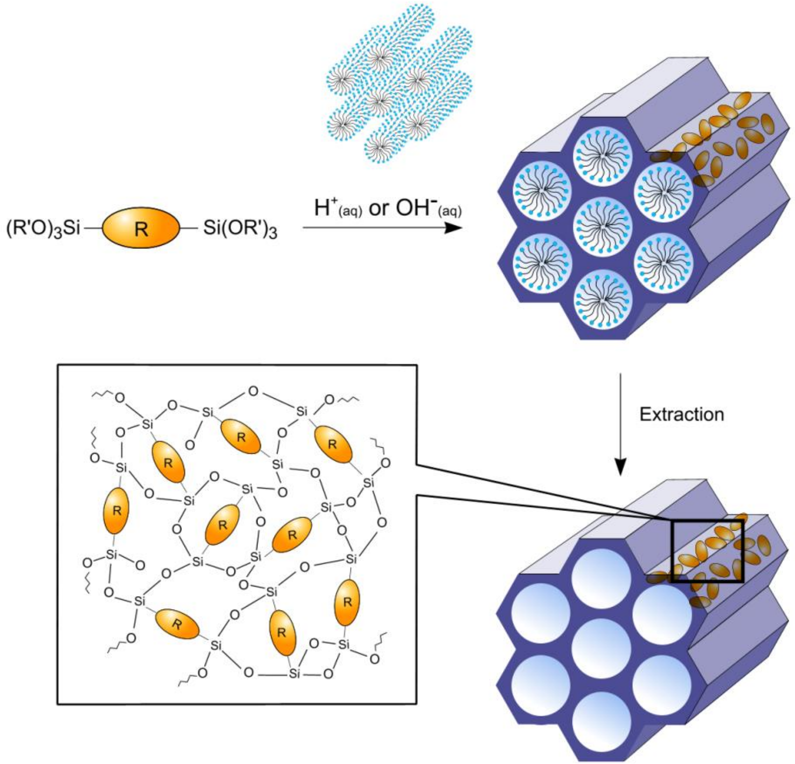
Mesoporous organosilicas – Synthesis



F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed.* **2006**, *45*, 3216-3251.

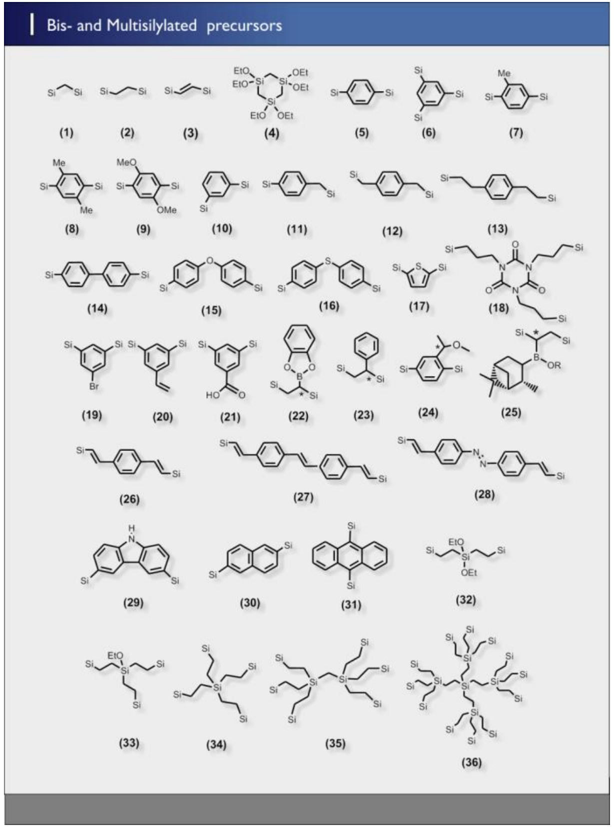
Mesoporous organosilicas – Synthesis

- Periodic Mesoporous Organosilicas (PMOs)
  - no pore blocking
  - highest degree of loading
  - hybrid pore wall structure !
  - ordered pore structure
  - synthesis of the precursor might be difficult
  - cleavage of Si-C bond ?



S. Inagaki et al. *J. Am. Chem. Soc.* **1999**, *121*, 9611; A. Stein et al., *Chem. Mater.* **1999**, *11*, 3302; G. A. Ozin et al., *Nature* **1999**, *402*, 867.

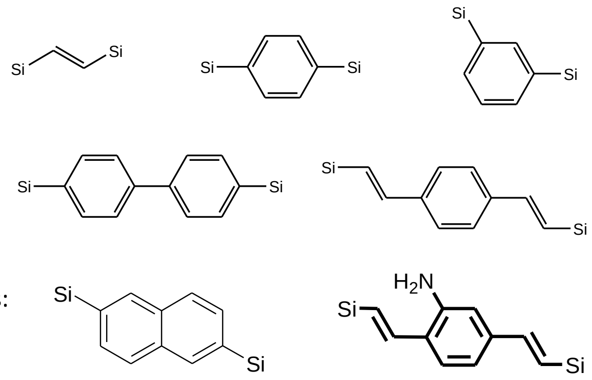
Periodic mesoporous organosilicas – Organic moieties



for terminal Si-groups:
Si = $Si(OR)_3$
R = CH_3, C_2H_5

Periodic mesoporous organosilicas – Wall structure

- Periodic Mesoporous Organosilicas (PMOs) *with crystal-like pore walls*
  - high thermal stability
  - only observed for rigid organic bridges (all C sp^2 hybridized)



for terminal Si-groups:
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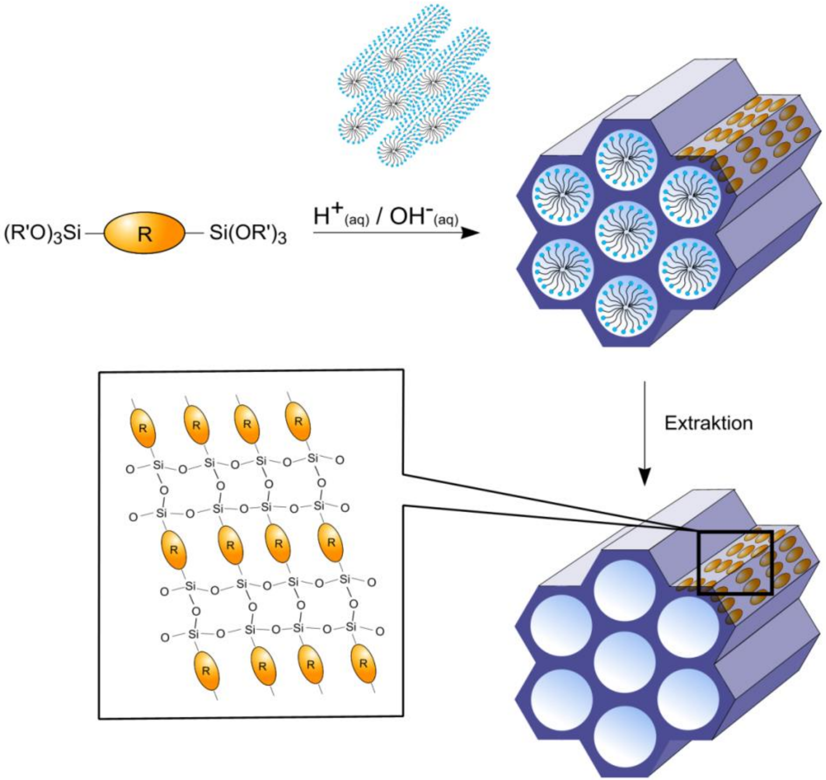
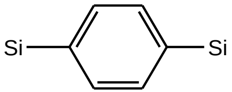
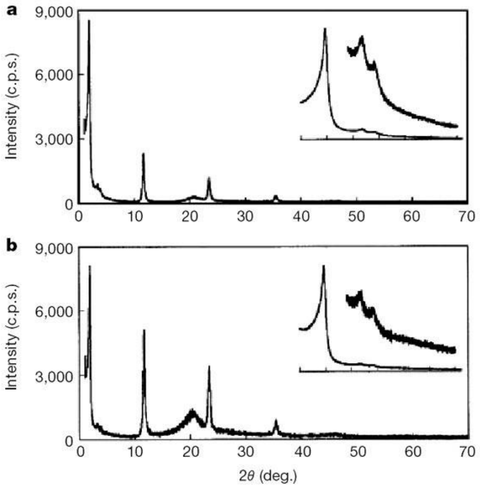


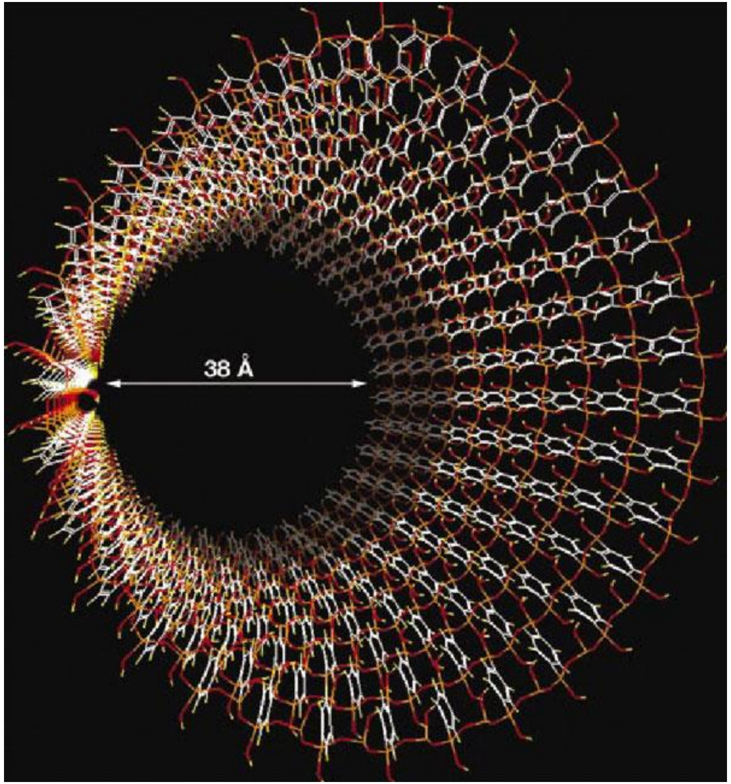
Periodic mesoporous organosilicas – Wall structure

- *with crystal-like pore walls*



- XRD - high order reflections

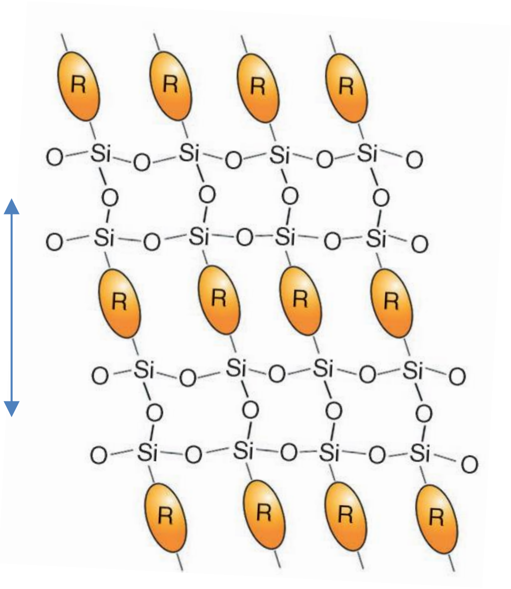


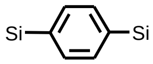
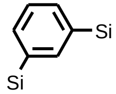
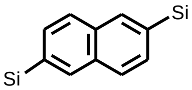
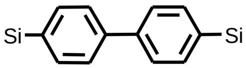
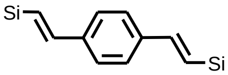
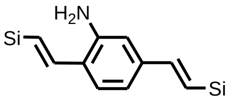


Periodic mesoporous organosilicas – Wall structure

- Periodic Mesoporous Organosilicas (PMOs) *with crystal-like pore walls*

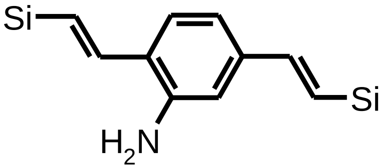
periodicity



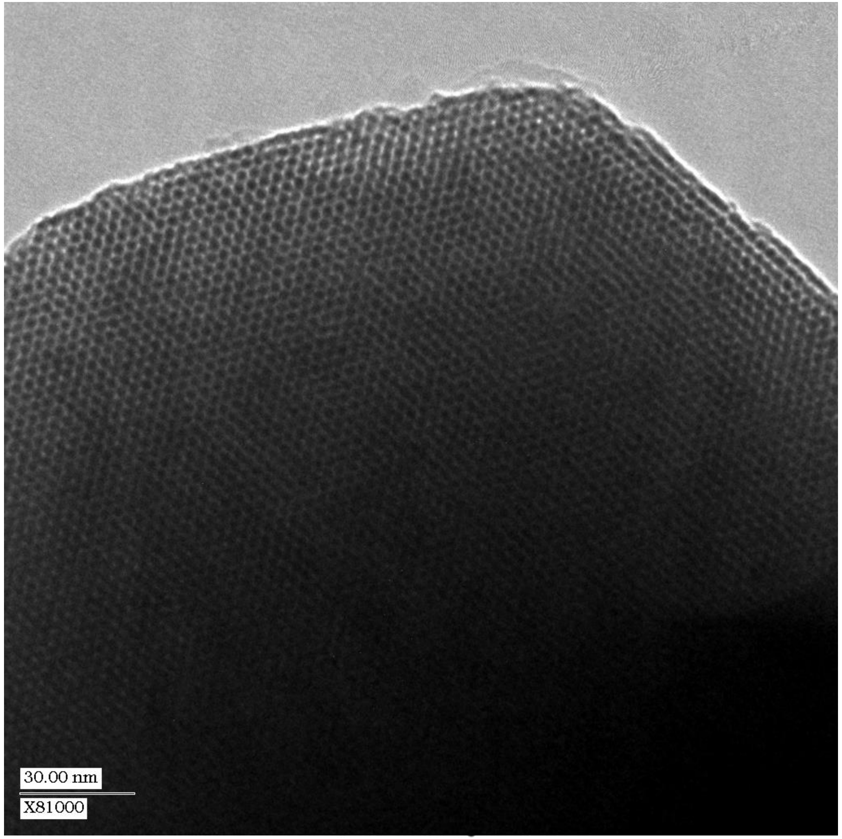
precursor	periodicity
	5.6 Å
	7.6 Å
	7.6 Å
	9.8 Å
	11.8 Å
	11.8 Å
	11.8 Å

Periodic mesoporous organosilicas

- *with heteroatom and crystal-like pore walls*



- XRD - high order reflections
- Nitrogen sorption
  - pore diameter: 2 - 4.5 nm
  - specific surface: 900 - 1400 m^2/g



M. Baretta, J. Morell, P. Sozzani, M. Fröba, *Chem. Commun.*, **2010**, *46*, 2495-2497.

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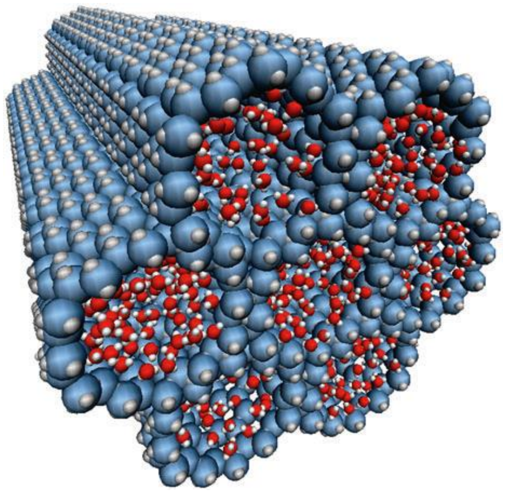
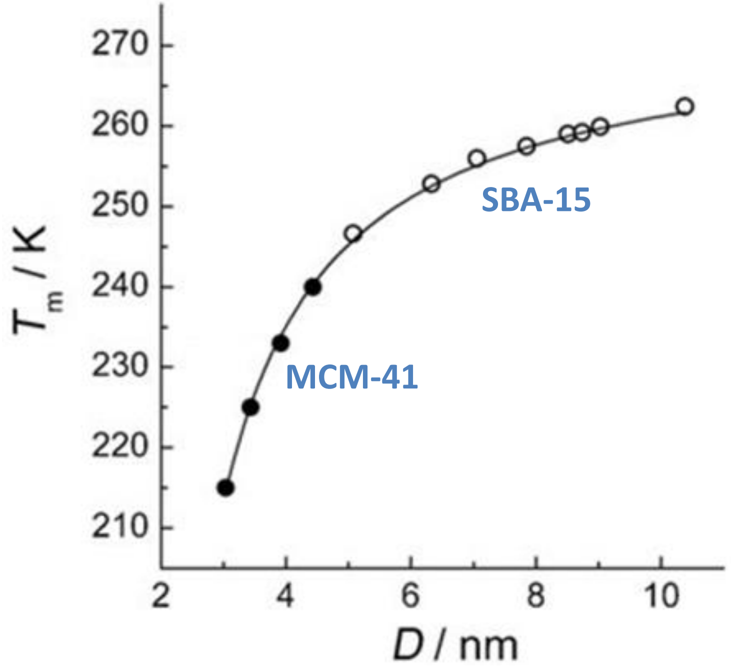
Confined water in nanoporous solids
Phase behaviour

Water/ice in mesoporous silica

- Melting point of confined water
  - **smaller** pore diameter → **lower** melting point
  - no freezing in pores < 3 nm





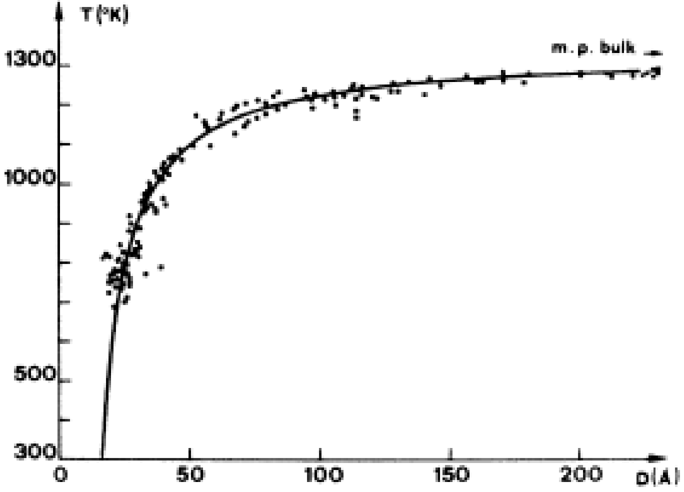
Gibbs–Thomson equation

- Shift of the melting point of small spherical solid
  - particle with the radius r

$$\Delta T_m(r) = T_0 - T(r) = \frac{2T_0 \cdot \gamma_{SL} \cdot V_S}{\Delta_m H} \cdot \frac{1}{r}$$

$$= C \cdot \frac{1}{r}$$

T	melting point of the small spherical particle
T_0	melting point of the bulk
γ_{SL}	solid-liquid surface free energy
V_S	molar volume of the solid
$\Delta_m H$	enthalpy of melting



melting temperature of gold nanoparticles

Water/ice in cylindrical nanopores

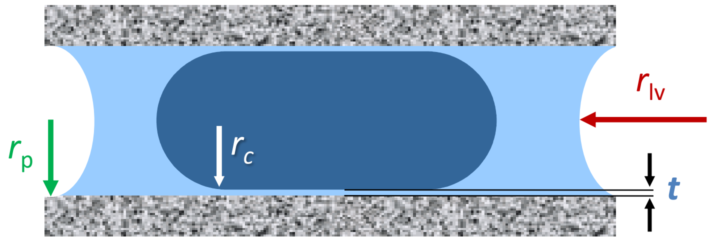
- Solid/liquid phase transition in confined geometries
  - in cylindrical pores of radius r_p
  - shift of the melting temperature

$$\Delta T_m(r_p) = T_0 - T(r_p) = \frac{2T_0 \cdot \gamma_{SL} \cdot V_S}{\Delta_m H} \cdot \frac{1}{r_p - t}$$

modified Gibbs-Thomson equation

$$= C \cdot \frac{1}{r_p - t}$$

T	melting point of the small spherical particle
T_0	melting point of the bulk
γ_{SL}	solid-liquid surface free energy
V_S	molar volume of the solid
$\Delta_m H$	enthalpy of melting
t	thickness of liquid film (**non-freezing water**)



r_p pore radius

r_{lv} radius of curvature (air–solution interface)

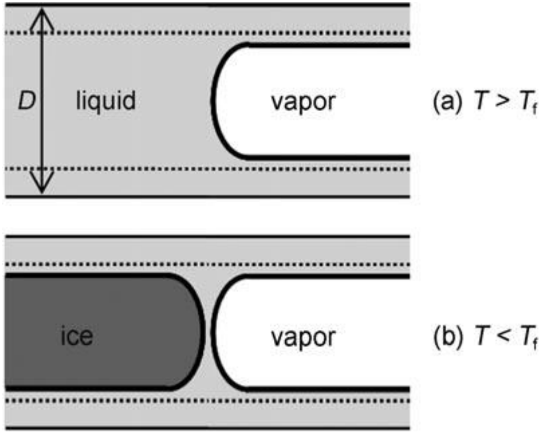
r_c radius of curvature (crystal–solution interface)

$r_c = r_p - t$

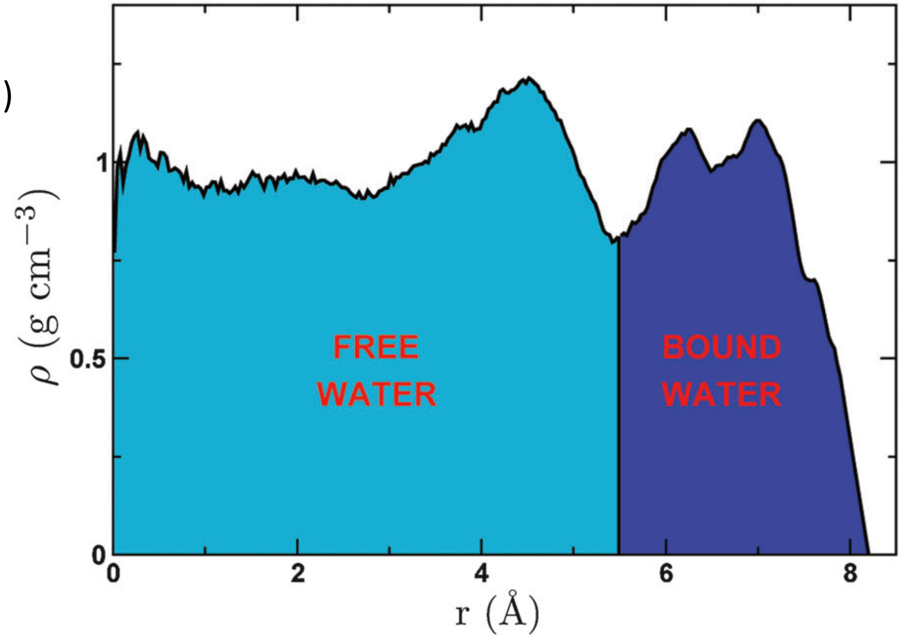
Water/ice in mesoporous silica

- Molecular dynamics (MD) simulations
  - liquid-like layer of "non-freezing water" on the pore wall

    ~ 0.3 nm (theo.); 0.5-0.6 nm (exp.)
  - double layer of water molecules (radius: 0.19 nm)



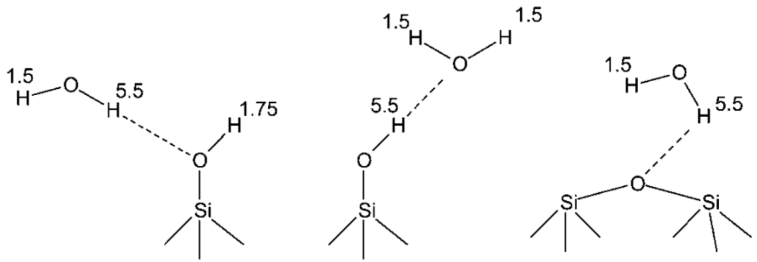
T_f : pore freezing temperature



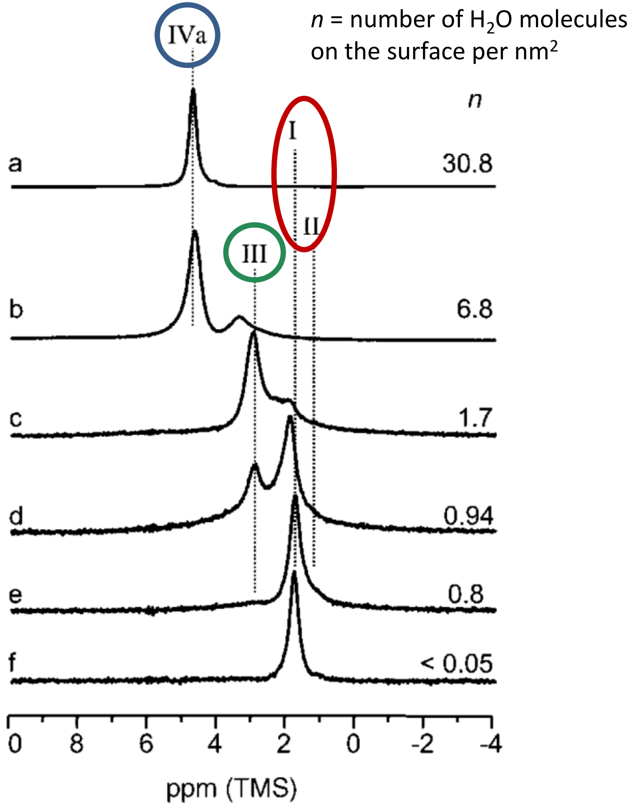
G.H. Findenegg, S. Jähnert, D. Akcakayiran, *Chem. Phys. Chem.* **2008**, *9*, 2651–2659; P. Gallo, M. Rovere, S.-H. Chen, *J. Phys. Chem. Lett.* **2010**, *1*, 729–733

Water/ice in mesoporous silica

- ^{1}H MAS solid state NMR measurements
  - **I,II:** surface –SiOH protons (1.7-1.8 ppm)
  - **III:** proton exchange process between water molecules and silica surface (2.8-2.9 ppm)

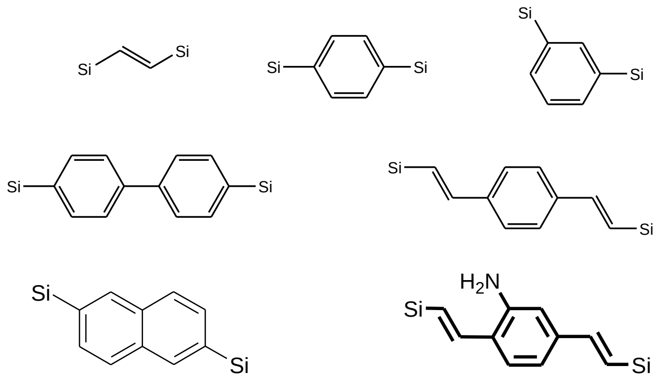


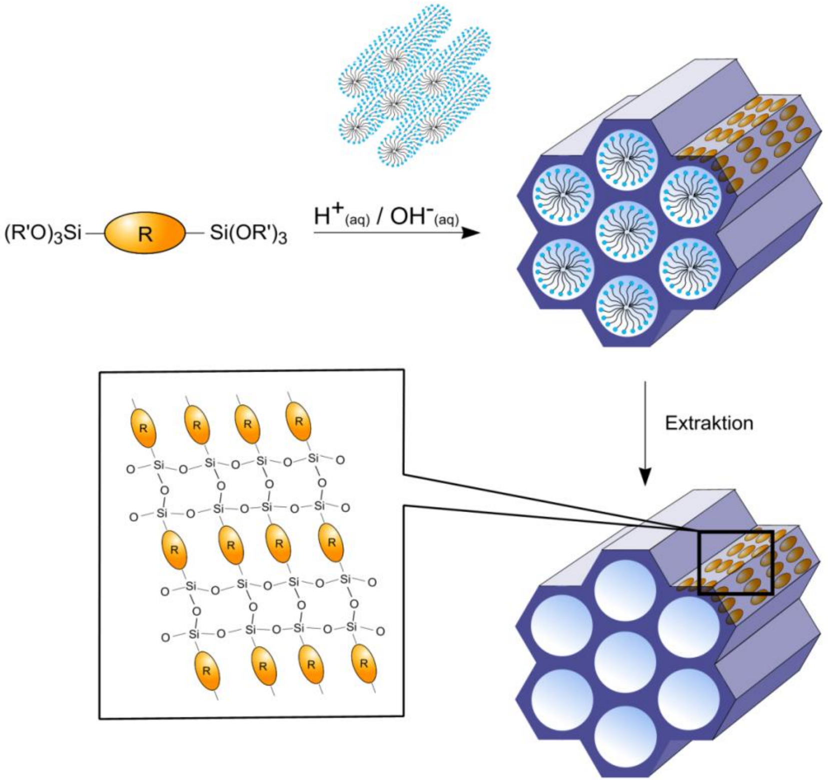
  - **IV:** inner-water molecules (4.7 ppm)
    (free water clusters: 5.5 ppm)



Periodic mesoporous organosilicas – Wall structure

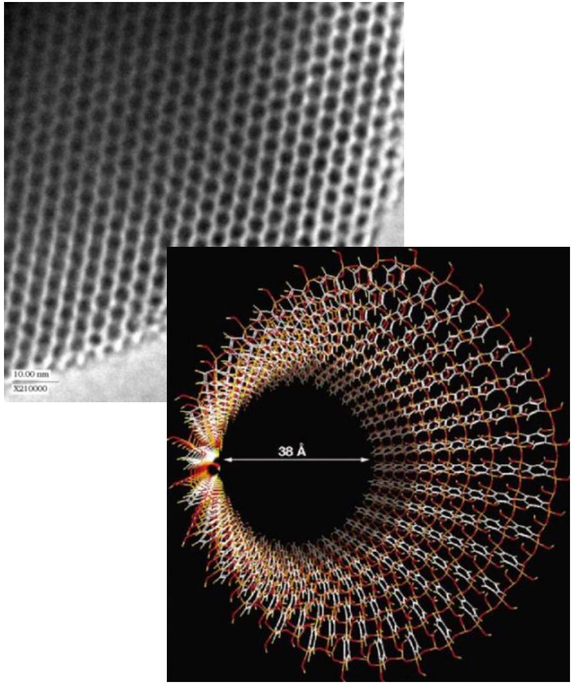
- Periodic Mesoporous Organosilicas (PMOs) *with crystal-like pore walls*
  - high thermal stability
  - only observed for rigid organic bridges (all C sp^2 hybridized)

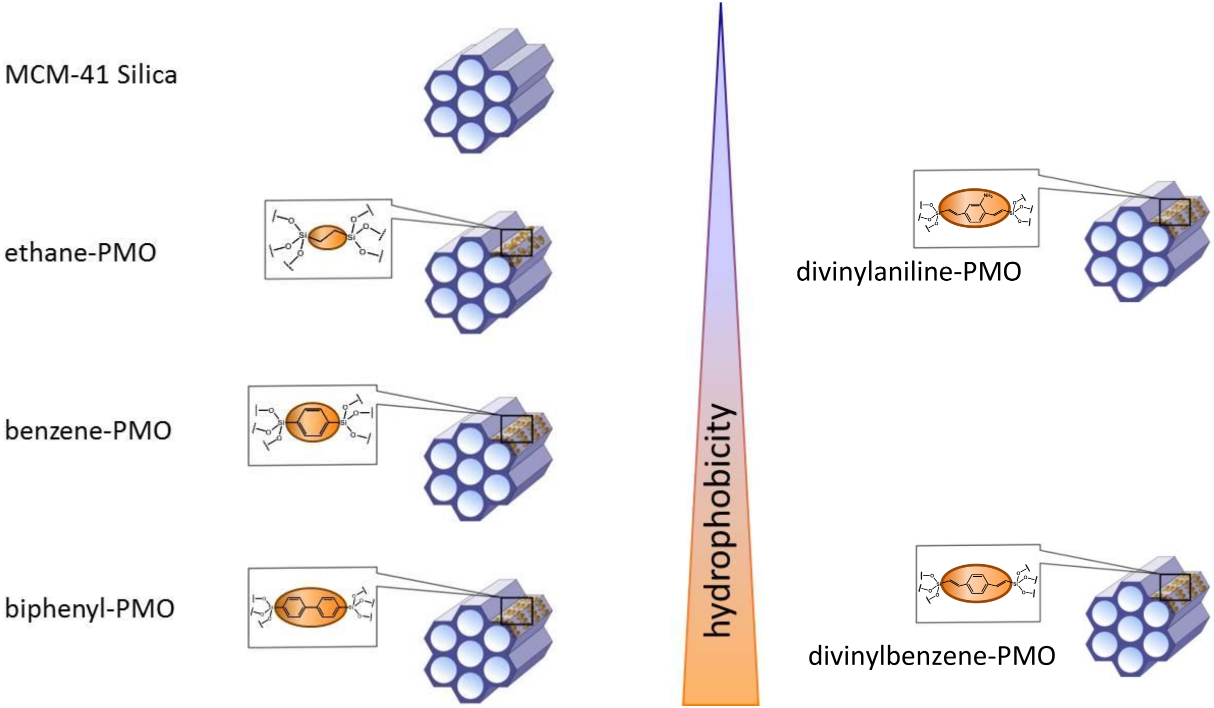




Periodic mesoporous organosilicas (PMOs)

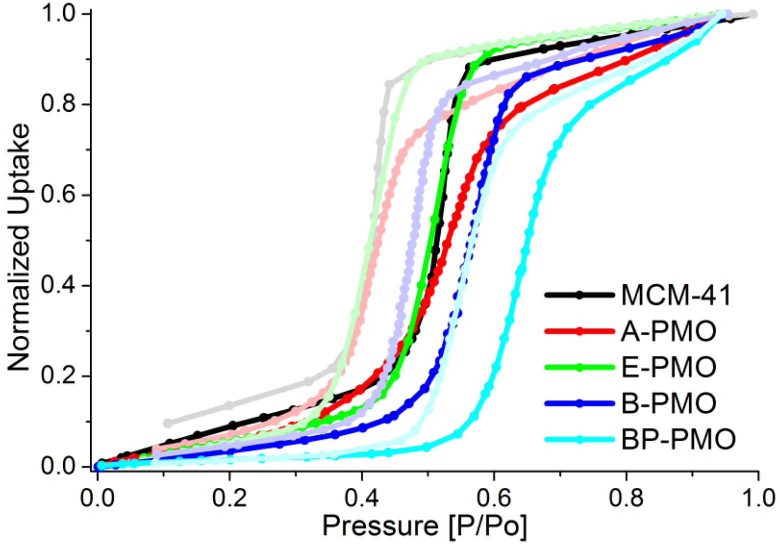
- PMOs with cylindrical pores (MCM-41 type) and modulated surface polarity



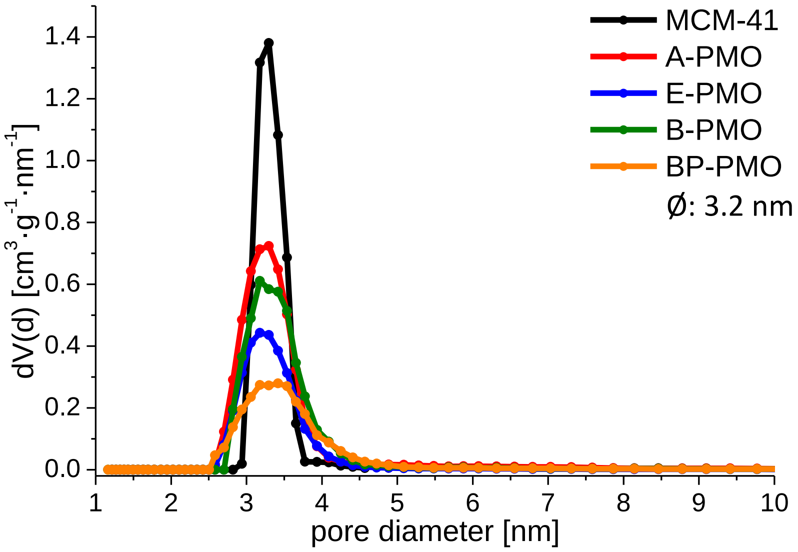


Mesoporous silica vs. organosilicas (PMOs)

- Water vapor sorption (298 K)
  - isotherms are shifted to higher relative pressure (humidity)
  - effect of surface polarity!

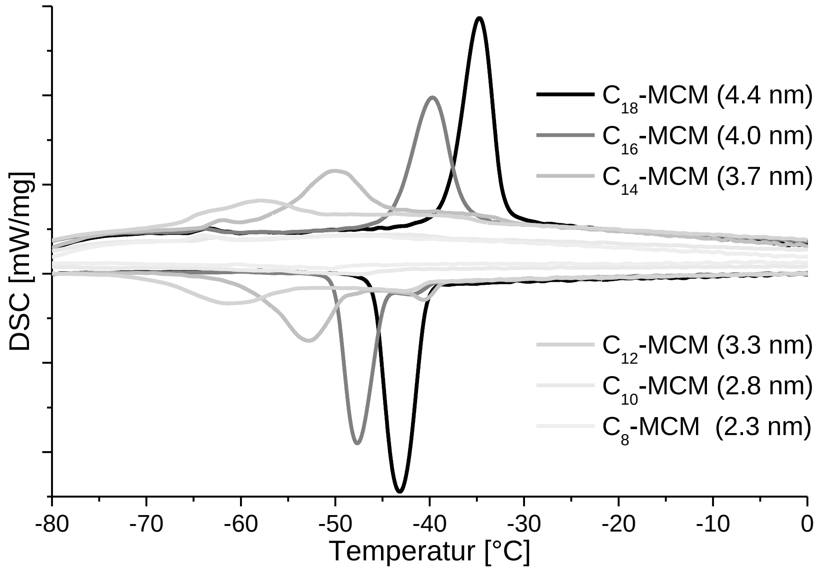


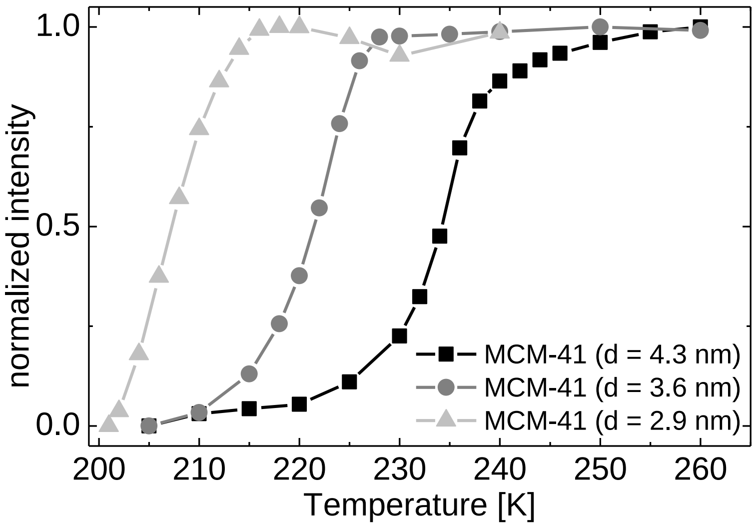
rel. humidity



Water/ice in MCM-41 silica mesopores

- Melting point of confined water (DSC vs. NMR cryoporometry)
  - DSC does not provide reliable data for pores smaller than 3.0 nm in diameter





J.B. Mietner, Y.J. Lee, F. J. Brieler, M. Fröba, *Angew. Chem. Int. Ed.* **2017**, accepted.

Mesoporous silica vs. organosilicas (PMOs)

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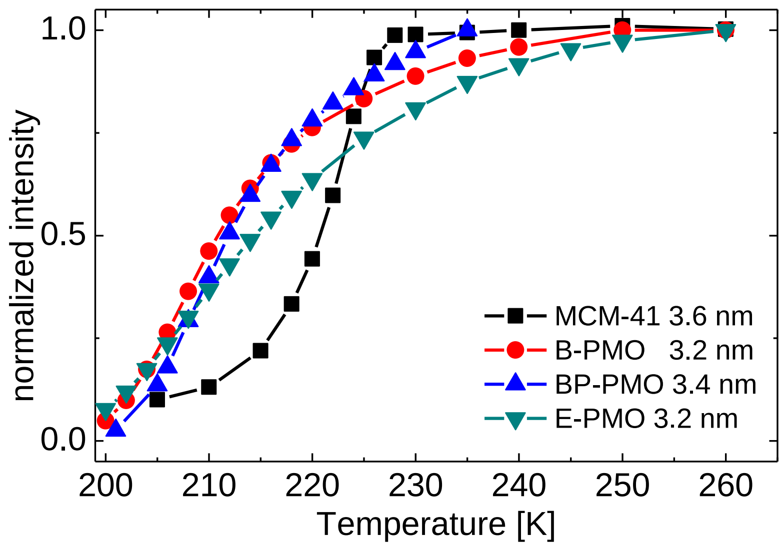
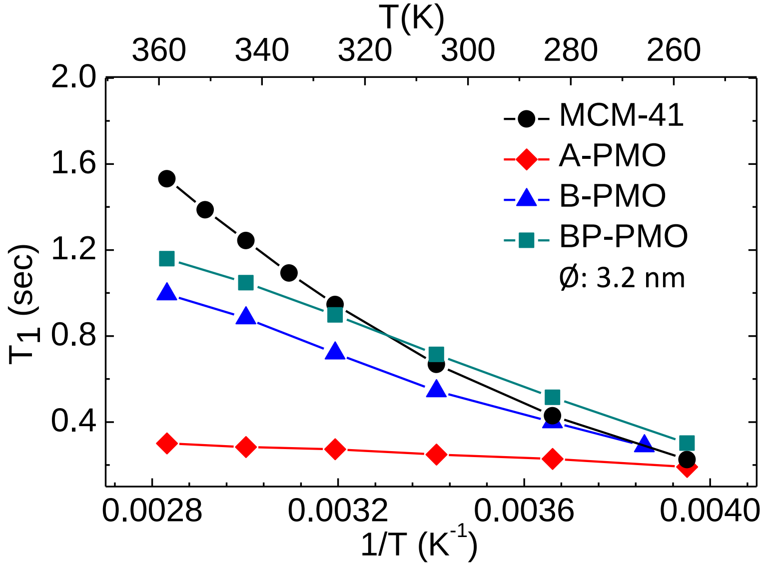
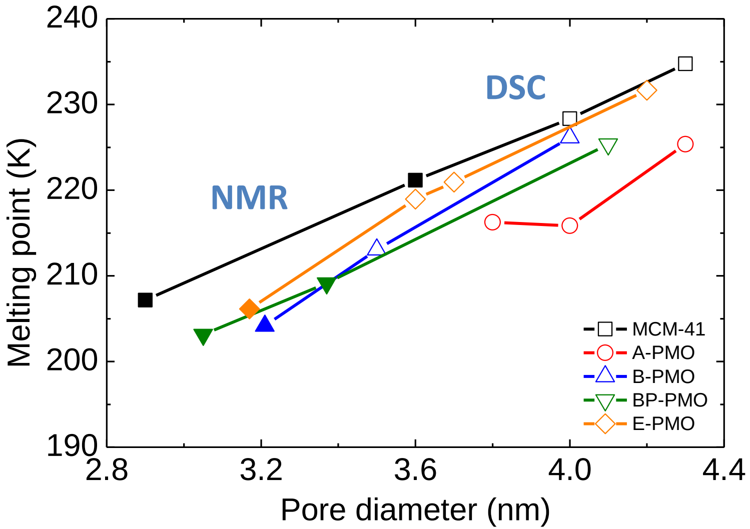
- Melting point and water/pore interaction of confined water
  - NMR cryoporometry: spin-echo sequence with an echo delay time of τ = 0.5 ms
- ^1H T_1 (spin-lattice) relaxation times
  - molecular mobility and proton exchange
  - sensitive to fluid-wall interactions

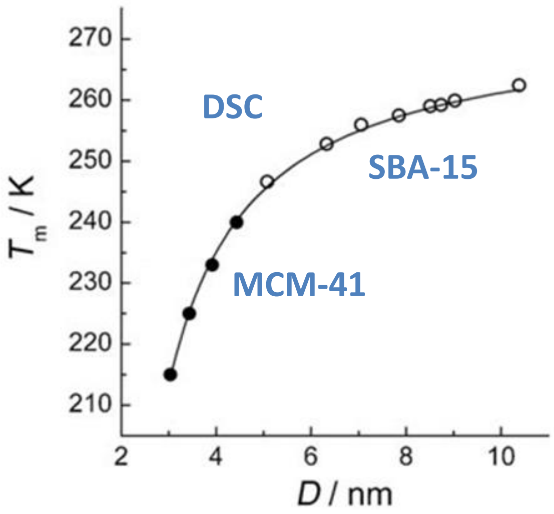




Water/ice in mesoporous silica and organosilicas

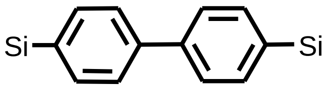
- Melting point of confined water
  - melting point of PMOs lower than that of silica (similar pore diameter)
  - thickness of liquid-like layer ("nonfreezing water“) is increasing



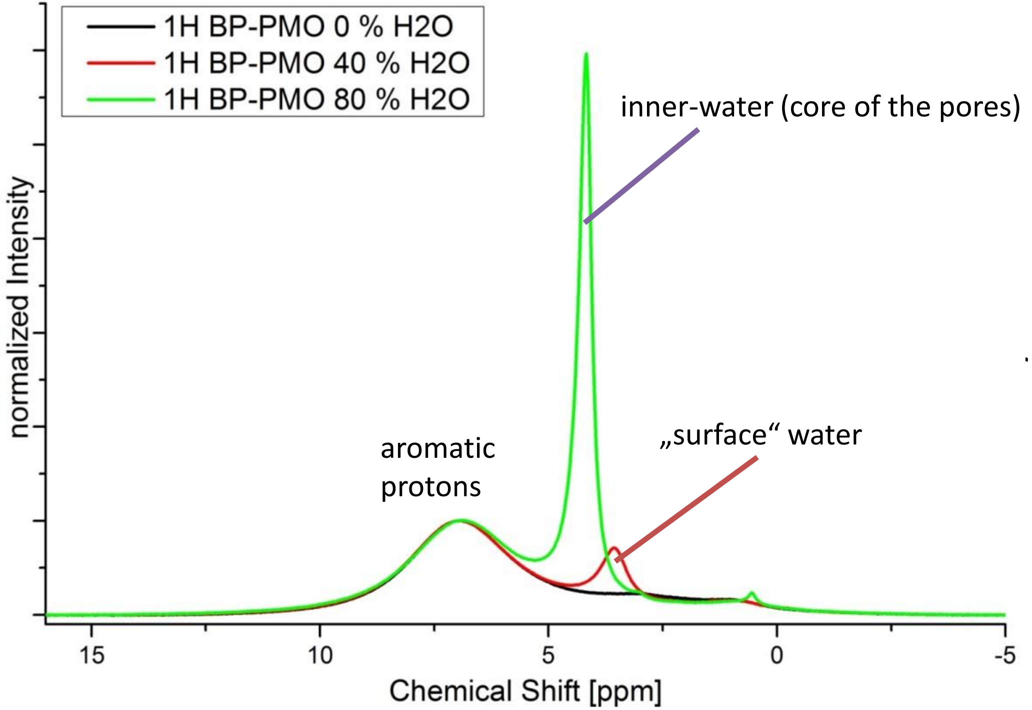


Water in periodic mesoporous organosilicas

- ^{1}H MAS solid state NMR measurements
  - biphenyl-PMO with **2.6 nm pores**

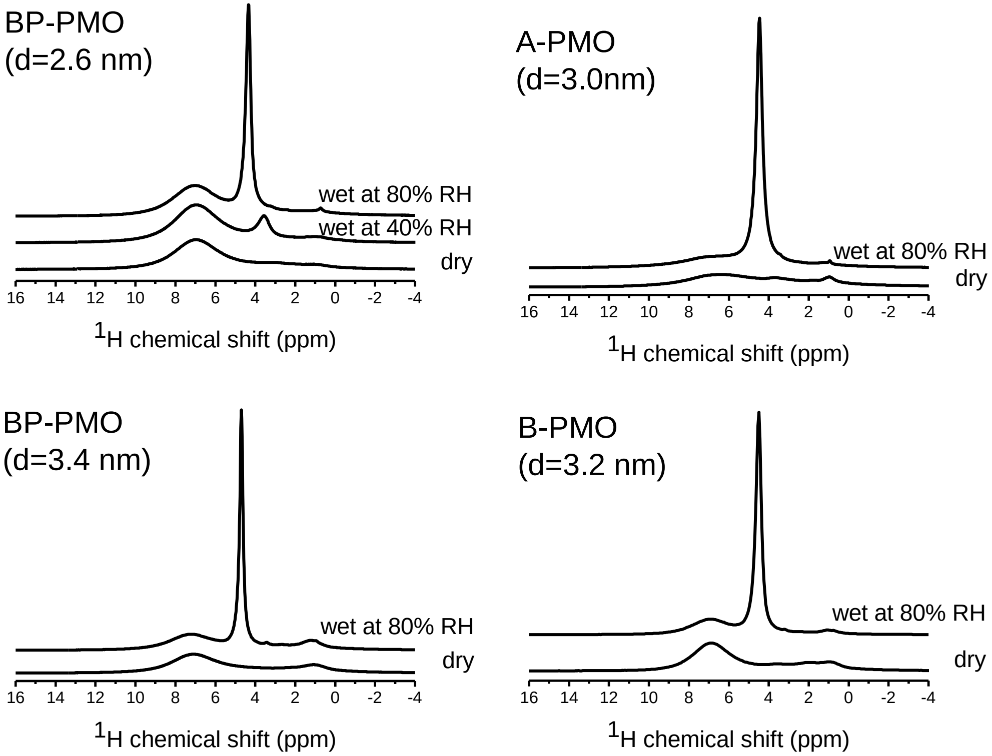


  - **dry sample:** only aromatic protons
  - **40 % r.h.:** aromatic protons + "surface" water
  - **80 % r.h.** (completely filled): aromatic protons + inner-water in the core of the pores + very small amount of –SiOH protons



Water in periodic mesoporous organosilicas

- ^{1}H MAS solid state NMR measurements
  - water exists in various environments
  - isolated silanol group -SiOH at ~ 1.8 ppm
  - water hydrogen-bonded to the surface silanol groups at ~ 3.5 ppm
  - water clusters in the core of the pores at ~ 4.6 ppm
  - fast dynamic exchange between the water molecules themselves and the silanol groups
  - free water clusters (bulk) at 5.5 pm



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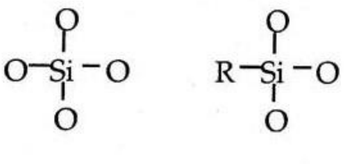
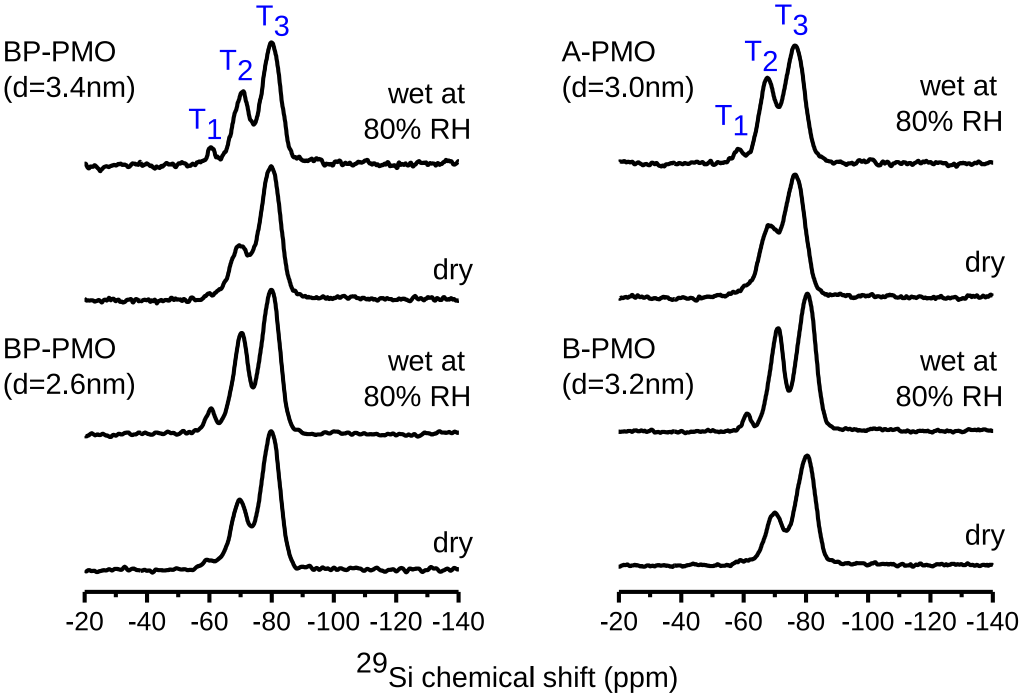
Water in periodic mesoporous organosilicas

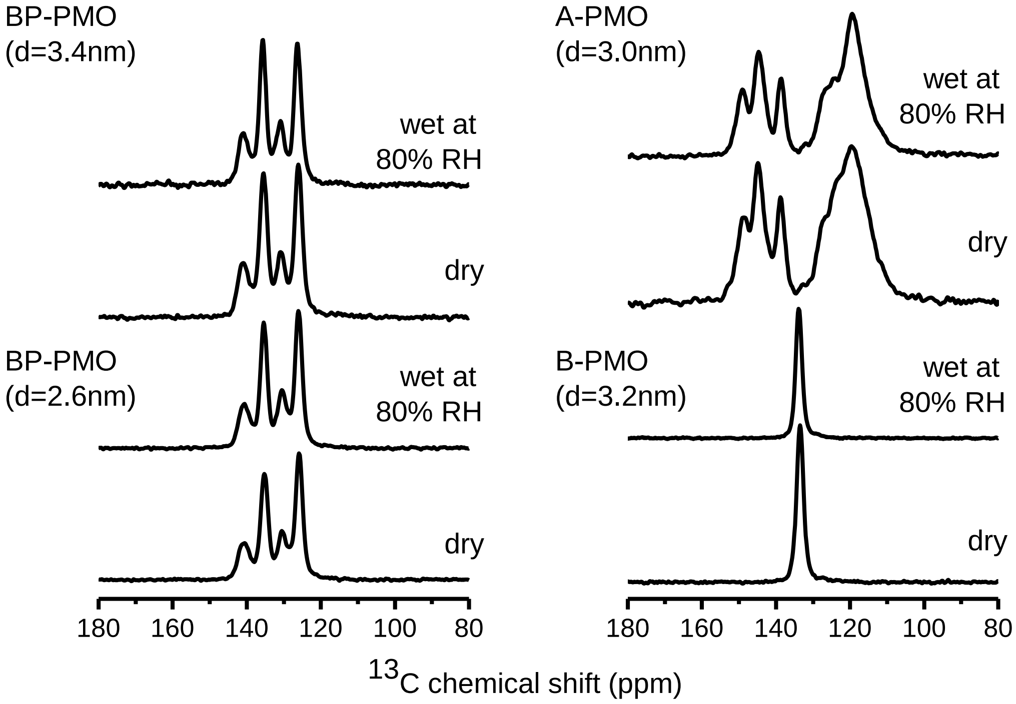
- ^{29}Si CP MAS solid state NMR measurements
  - only T signals
  - no Q signals between -90 and -120 ppm
    → **no cleavage** of the Si-C bond
  - T_3 unit: R**Si**(OSi)$_3$
  - T_2 unit: R**Si** (OSi)$_2$(OR'), R'= H or CH_3CH_2
  - T_1 unit: R**Si**(OSi)(OR')$_2$, R'= H or CH_3CH_2
  - strong T_3 signal: high degree of connectivity





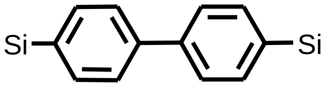
Water in periodic mesoporous organosilicas

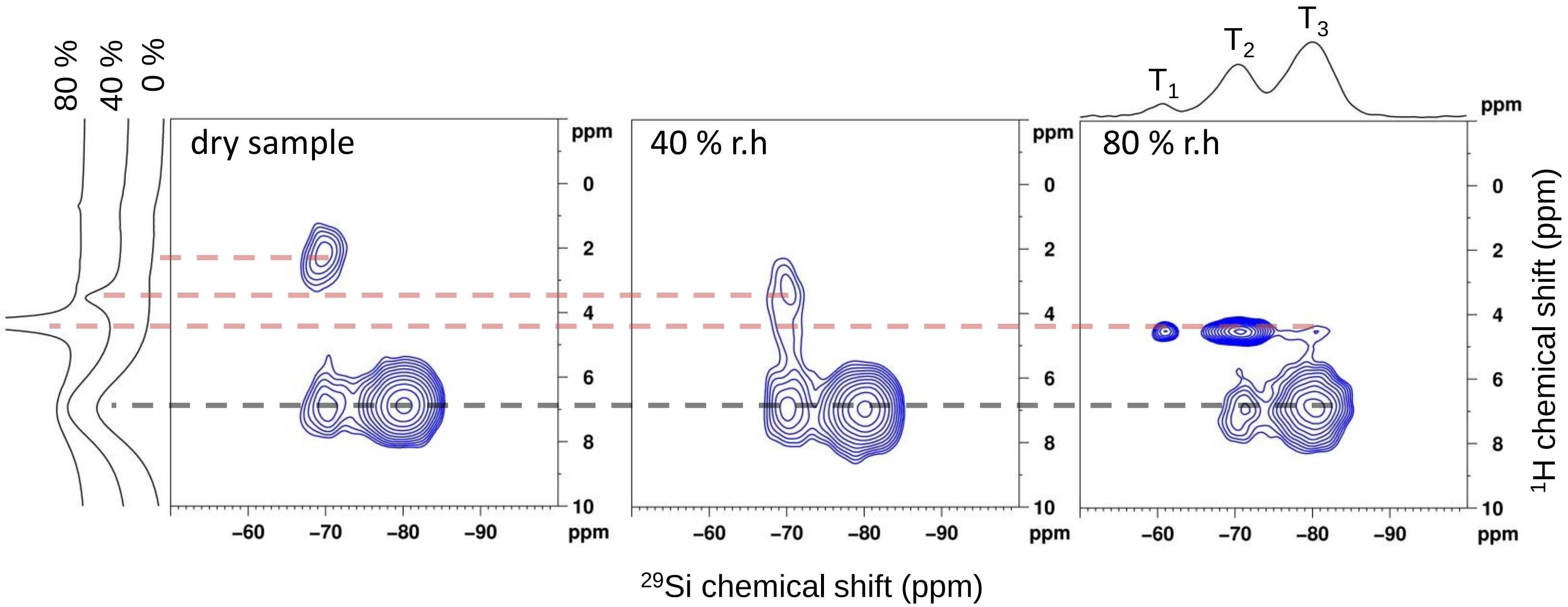
- ^{13}C CP MAS solid state NMR measurements
  - characteristic signals of the carbon atoms corresponding to the organic bridge groups
  - in contrast to ^{29}Si CP NMR, no intensity change is observed for B- and BP-PMO after water adsorption
  - however, that ^{13}C CP MAS NMR of the A-PMO exhibits clear differences in the signal intensities and linewidths between the dry and the fully loaded samples



Location of water in periodic mesoporous organosilicas

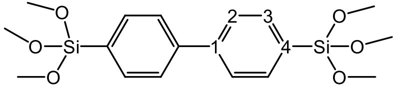
- 2D ^{1}H-^{29}Si HETCOR solid state NMR measurements
  - biphenyl-PMO with **2.6 nm pores**
  - water protons in the proximity to the silicon atoms

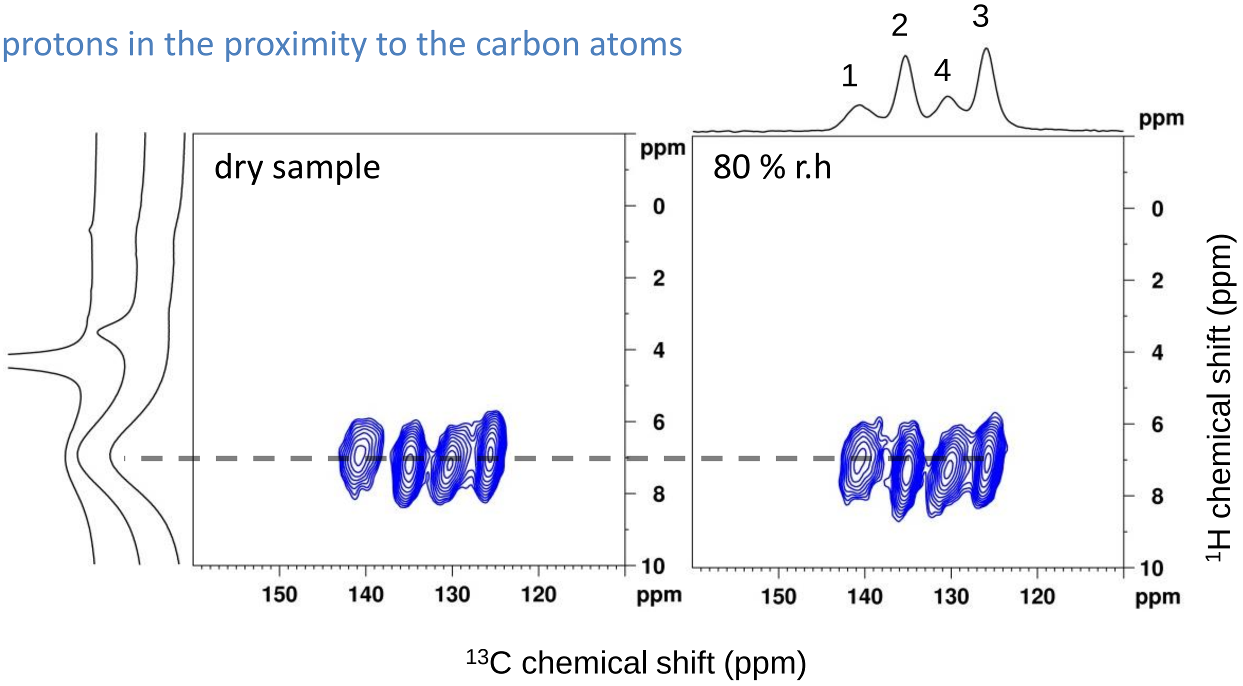




Location of water in periodic mesoporous organosilicas

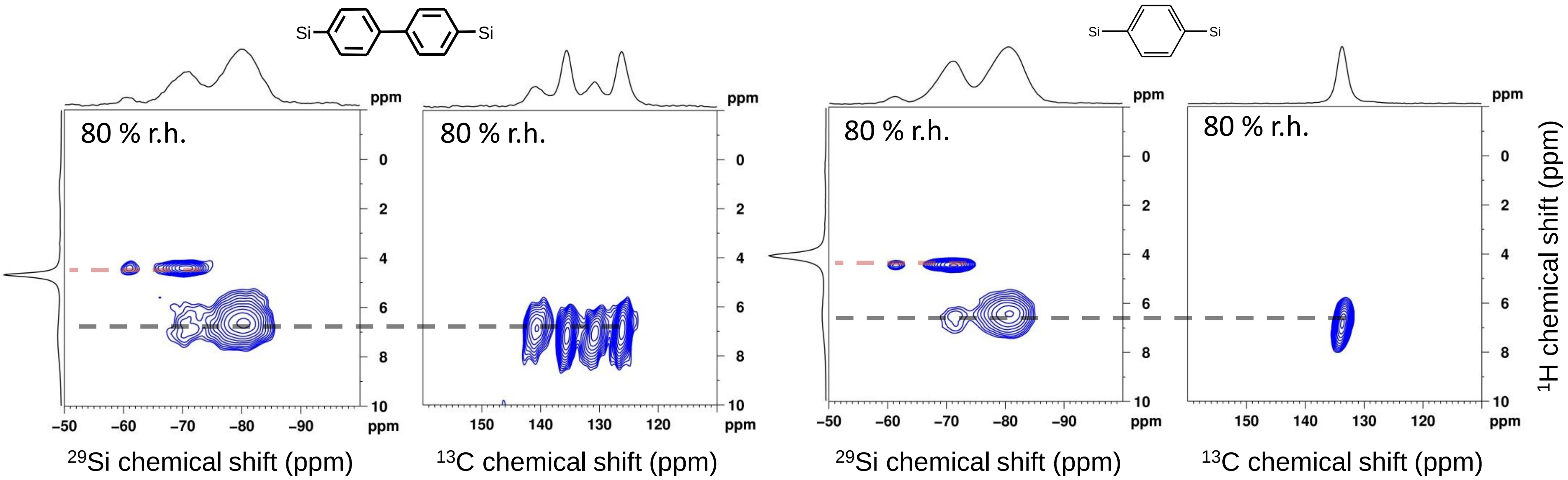
- 2D ^{1}H-^{13}C HETCOR solid state NMR measurements
  - biphenyl-PMO with **2.6 nm pores**
  - **no** water protons in the proximity to the carbon atoms





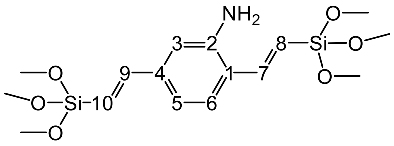
Location of water in periodic mesoporous organosilicas

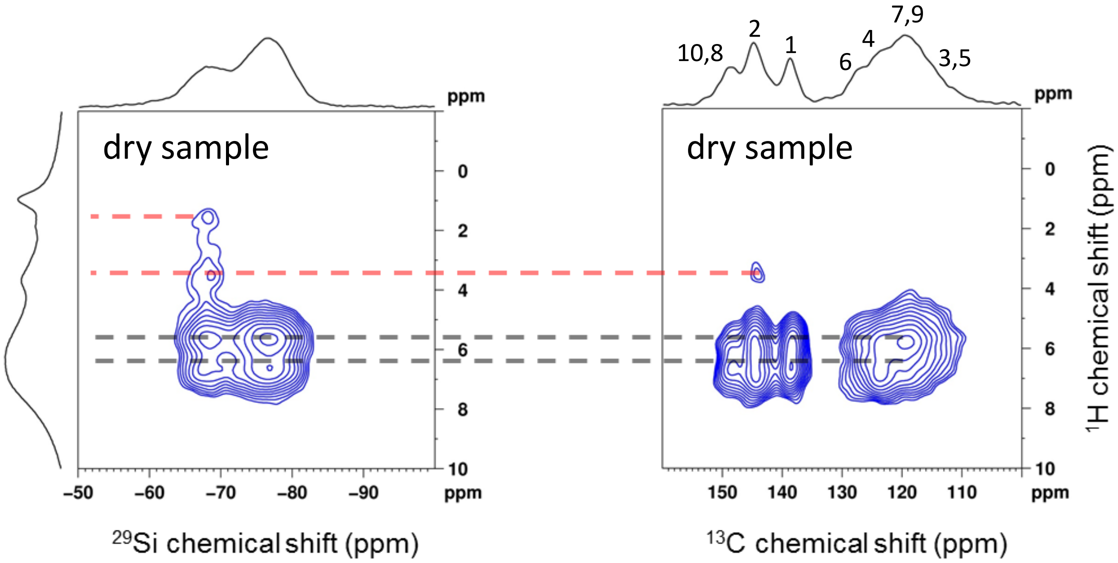
- 2D ^{1}H-^{29}Si and ^{1}H-^{13}C HETCOR solid state NMR measurements
  - biphenyl-PMO with **3.4 nm pores** and benzene-PMO with **3.2 nm pores**
  - water protons **only** in the proximity to the silicon atoms



Location of water in periodic mesoporous organosilicas

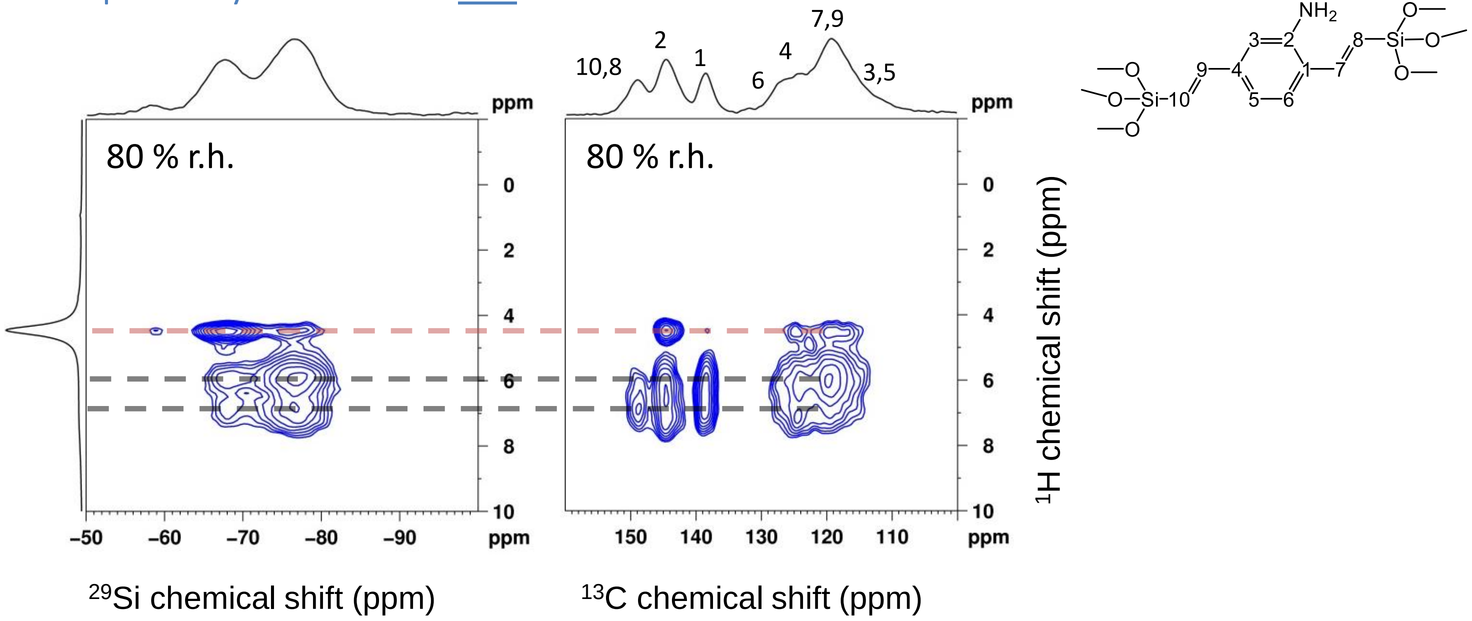
- 2D ^{1}H-^{29}Si and ^{1}H-^{13}C HETCOR solid state NMR measurements
  - aniline-PMO with **3.0 nm pores**
  - "surface" protons close to the carbon atoms





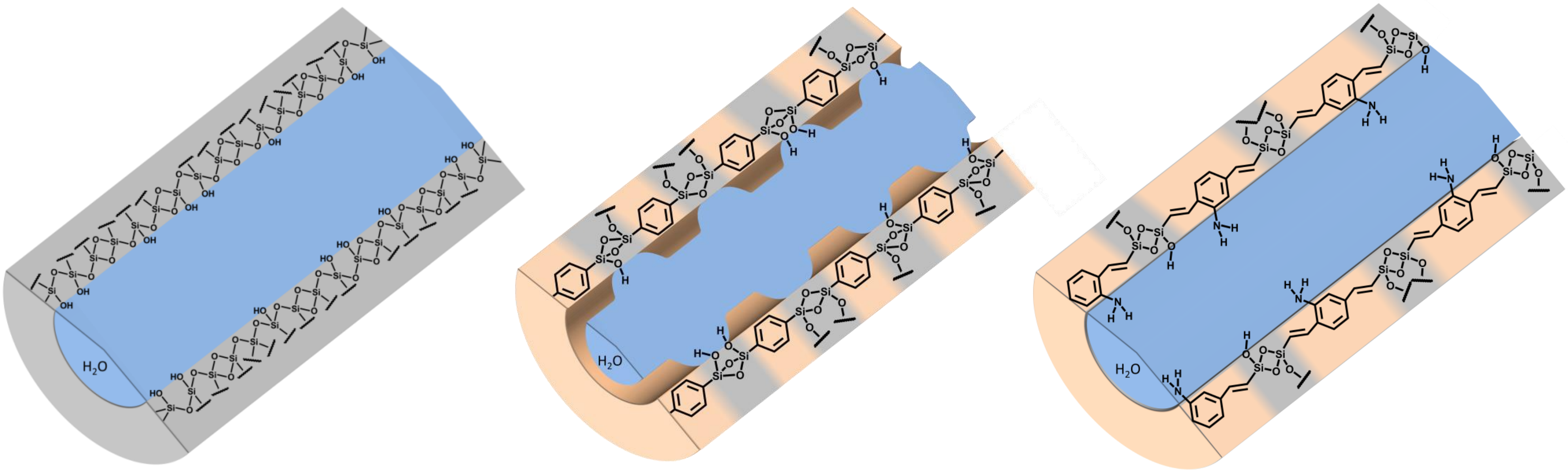
Location of water in periodic mesoporous organosilicas

- 2D ^{1}H-^{29}Si and ^{1}H-^{13}C HETCOR solid state NMR measurements
  - aniline-PMO with **3.0 nm pores**
  - water protons in the proximity to the silicon **and** carbon atoms



Location of water in periodic mesoporous organosilicas

- Proposed structure model



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Summary

- There is a strong decrease of the melting point (down to - 70 ^{o}C) of water within nanoporous host structures with diameter below 4 nm

- Periodic mesoporous organosilicas (PMOs) show a up to 10 K lower melting point than the corresponding silicas with the same pore diameter

- There is no wetting of a hydrophobic organic bridging unit except when a polar unit with the ability to form hydrogen bonds is present in the organic motif

- Not only the pore size with its confinement effect but also the surface polarity has an influence on the water properties at the same time

- Periodic mesoporous organosilicas (PMOs) with quasi-crystalline pore walls are ideal model host structures due to their defined pore size and tailored modulated surface polarity

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