



# Aryl-Substituted Silanols – Synthesis, Properties and Condensation Behavior

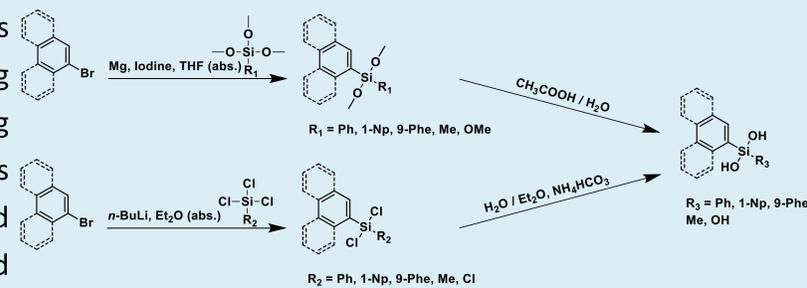
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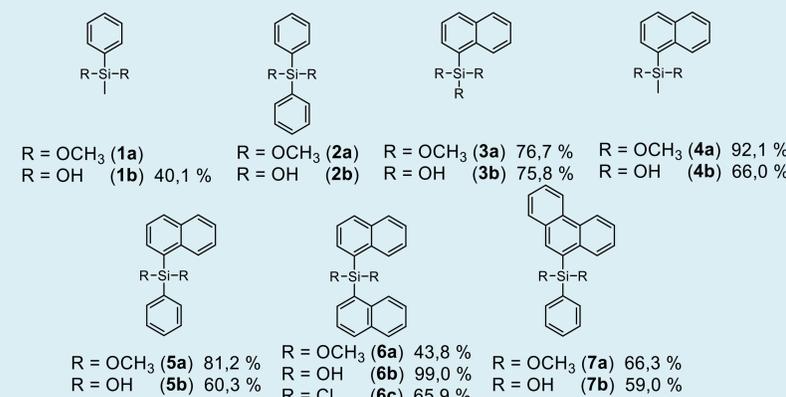
Silanols are the silicon analogues of alcohols/carbinols. However, unlike alcohols, geminal silanols are stable. Nevertheless, silanols exhibit a high condensation tendency. They are mainly found as unstable intermediates in polycondensation reactions such as the sol-gel process.<sup>[2]</sup> An outstanding property of silanols is their ability to form strong hydrogen bonds, as they are both very strong hydrogen bond acceptors and donors.<sup>[3,4]</sup> Potential applications of silanols include use as precursors for polysiloxanes<sup>[5]</sup> and polyhedral oligomeric silsesquioxanes<sup>[6]</sup>, silicon-based surfactants<sup>[7]</sup>, protease inhibitors<sup>[8]</sup>, cross-coupling reagents<sup>[9]</sup>, anion recognition systems<sup>[10]</sup>, and surface modification agents<sup>[11]</sup>.

Stable isolable silanols containing aromatic substituents were obtained by controlled hydrolysis of methoxysilanes or chlorosilanes.

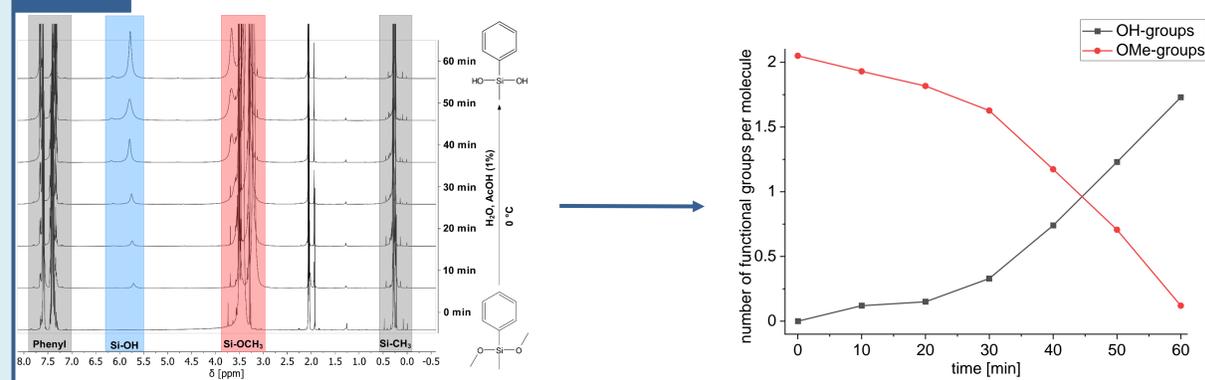
## Synthesis route<sup>[1]</sup>



## Isolated compounds<sup>[1]</sup>



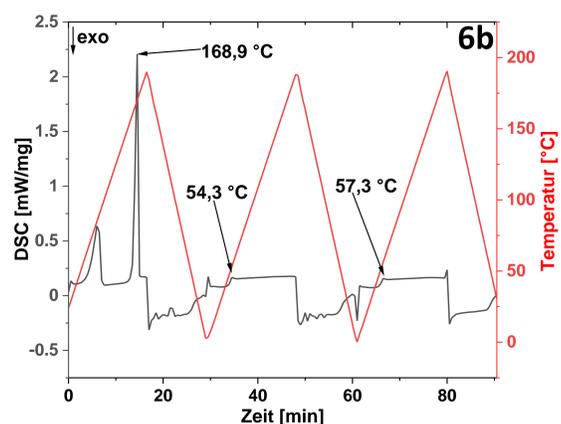
## NMR<sup>[1]</sup>



- Disappearance of methoxy signals with progressive reaction
- New signals of the hydroxy groups appear at approx. 6 ppm
- increasing reaction rate with progressive hydrolysis of this compound
- other alkoxy-silanes (e.g. **4a**, **5a**) show a more linear progression of hydrolysis
- <sup>29</sup>Si NMR showed only silanol formation (no condensation)

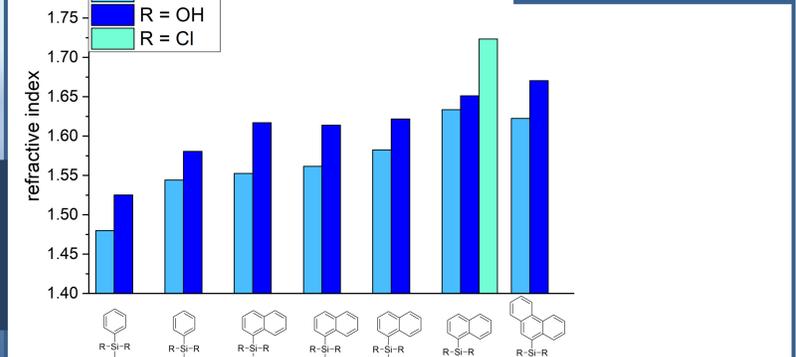
## DSC

- a large endothermic process (assumed melting point) can be seen
- process is not reversible
- After the first cycle, a glass transition point is found
- thermal condensation as they are melted and the diffusion barrier is thus significantly smaller
- NMR spectroscopic investigations confirm the condensation reaction



## Characterization

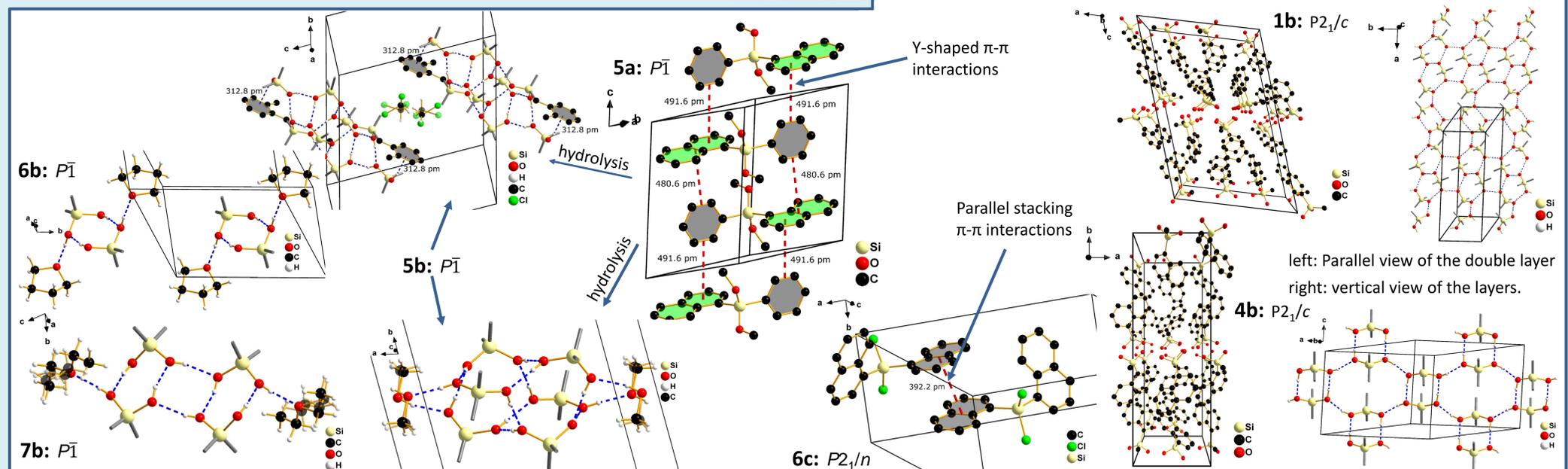
## Refractive Indices



- determined by a dilution calibration in solution
- refractive indices increase with increasing  $\pi$ -systems
- consistent with the Lorentz-Lorenz equation
- Silanols always have larger refractive indices than the corresponding alkoxy-silanes

## Single Crystal structure Analysis<sup>[1]</sup>

- $\pi$ - $\pi$ -interactions are dominating the crystal structures of the alkoxy- and chlorosilanes
- preferred perpendicular Y-shaped and parallel stacking interactions
- crystalline structures of the synthesized silanols were dominated by hydrogen bonds
- different structural motifs were formed, which became smaller and simpler the larger (more sterically demanding) the substituents on the silicon atom
- Dimers, tetramers, hexamers, octamers and bilayer structures were found



## Conclusion

Aromatic substituent containing di- and trisilanols were synthesized by hydrolysis of precursor compounds. The hydrolysis of the alkoxy-silanes was studied and different kinetic processes (consistent or increasing reaction rate) were found, although these are difficult to compare due to the widely different reaction conditions. DSC analysis showed thermally induced condensation to the corresponding polysiloxanes. Based on the polycyclic aromatic substituents the obtained silanols showed different refractive indices ranging from 1.525 - 1.671. Different hydrogen bond structural motifs were found in the single crystal structures depending on the composition of the molecules.

## References

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