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Silanol-Based Surfactants: Synthetic Access and Properties of an Innovative Class of Environmentally Benign Detergents

Natascha Hurkes,[a] Heike M. A. Ehmann,[b] Martina List,[b] Stefan Spirk,[b] Malte Bussiek,[a] Ferdinand Belaj,[b] and Rudolf Pietschnig*[a]

Dedicated to Prof. Dr. Volker Ribitsch on the occasion of his 65th birthday

Abstract: Herein, environmentally friendly surfactants based on new silanols as substitutes for the isoelectronic phosphonates were explored. Surface tensions of aqueous solutions are significantly reduced, particularly with those silanols that feature a high ratio of organic moiety to silanol. Besides their use as surfactants, their potential as coating agents for hydrophilic oxide surfaces was investigated for the example of glass substrates. In the solid-state sheet structures with silanol, double layers are present, in which the sheet spacing varies with the alkyl-chain length.

Introduction

Silanols are compounds analogous to alcohols containing one or more Si–OH groups.[1] Such functional groups are ubiquitous in nature, for example, in silicic acid, $Si(OH)_4$, found in low concentration in the aqueous environment, and on the surface of silicate rocks. Moreover, they are important in a variety of industrial transformations, such as the manufacture of silicones, sol–gel processes, and in silane coupling reactions in the functionalization of surfaces.[2] Unlike their carbon counterparts, several silanol functions can be attached to the same silicon atom, and the tendency to participate in hydrogen bonding increases with the number of silanol functions in the molecule. In the case of silanetriols ($RSi(OH)_3$), the maximum number of silanol functions is available for a neutral organosilanol. In fact, organosilanetriols are isoelectronic to the corresponding phosphonic and sulfonic acids. The salts of the latter have a prominent role as surfactants in science and technology,[3] and especially the phosphate-based detergents are the topic of continuing debates concerning their environmental impact.[4] In the light of these environmental issues combined with the predicted shortage of natural phosphate supplies in the future,[5–7] it would be attractive to have an alternative compound class available to replace phosphonates for certain applications. Therefore, we explored the potential of suitably substituted stable silanols in acting as surfactants in solution. The special appeal of this possibility is the fact that silanols are non-eutrophicating and environmentally benign,[8,9] and that silicon is a widely abundant element for which currently no supply shortage seems likely.

Results and Discussion

Owing to their strong tendency to undergo self-condensation reactions to give compounds containing the siloxane (Si-O-Si) linkage, silanols are in most cases intermediates of limited stability.[2] Recently, we investigated the aggregation behavior of silanetriols in solution and in the gas phase and found that *tert*-butyl-substituted silanetriols are stable under quite harsh conditions even in concentrated solutions.[10,11] Therefore, we wanted to combine the suitable steric protection provided by a *tert*-butyl group with a longer alkyl chain necessary for a more balanced amphiphilic character of the resulting silanetriols. Accordingly, a set of stable silanetriols with the general formula $CH_3(CH_2)_n(CH_3)_2CSi(OH)_3$ ($n = 0$–5) was prepared. This series was prepared following a synthetic route starting from acetone and alkylbromides of increasing chain length as outlined in Scheme 1. The critical point of this reaction sequence is the silylation step, in which the yield was found to be generally low for the reaction of the tertiary Grignard reagents of **2a**–**e** and 2-bromo-2-methylbutane **2f** with $SiCl_4$. Nevertheless, the yields could be increased from 0 to 3–14% in the presence of Cu^I catalysts.[12] Employing Knochel Grignard reagents[13] using LiCl and CuCN did not improve the yields of the trichlorosilanes. Switching to the more reactive organolithium reagents was prevented by the difficulty of preparing the corresponding compounds.

Even with finely dispersed Na/Li alloys with an increased Na content of 5%[14–16] prepared directly from the molten alkali metals by using an *ULTRA-TURRAX*®, we were not able to

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[a] Dr. N. Hurkes, Dr. M. Bussiek, Prof. Dr. R. Pietschnig
Universität Kassel, Institut für Chemie and CINSaT
Heinrich-Plett-Strasse 40, 34132 Kassel (Germany)
Fax: (+49) 561-804-4649
E-mail: pietschnig@uni-kassel.de

[b] Dr. H. M. A. Ehmann, M. List, Dr. S. Spirk, Prof. Dr. F. Belaj
Karl-Franzens-Universität Graz, Institut für Chemie, NAWI Graz
Schubertstrasse 1 and Heinrichstrasse 28, 8010 Graz (Austria)

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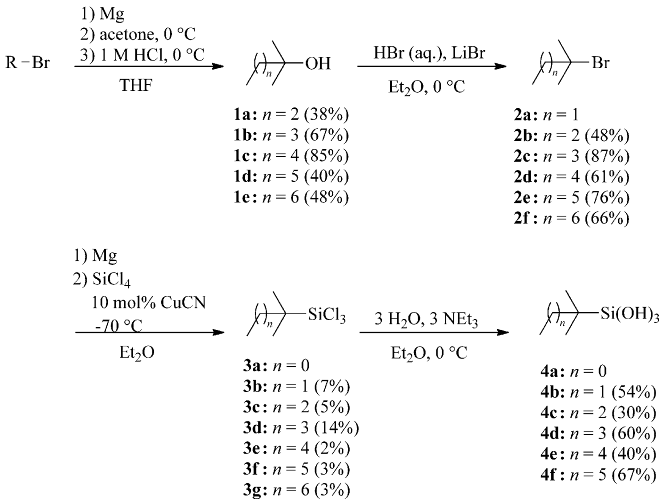

Scheme 1. Synthetic route to silanetriols **4a**–**f**; isolated yields are given in brackets.

obtain the organometallic species in significant yield. Following the Cu^I-catalyzed pathway, we were able to isolate the resulting trichlorosilanes **3b**–**g**. The ^{29}Si NMR chemical shifts range between $\delta = 16.7$ and 16.9 ppm and are comparable to literature known alkyl-substituted trichlorosilanes.[17] The smooth hydrolysis of the trichlorosilanes **3b**–**g** and *tert*-butyl-SiCl$_3$ **3a** by using stoichiometric amounts of water in the presence of triethylamine gave the new silanetriols **4b**–**f** in analogy to the literature known *tert*-butyl-Si(OH)$_3$ **4a**.[18,19] All compounds of this series were obtained as colorless solids, which are crystalline for $n = 0$–4 or waxy for $n = 5$. The identity of **4b**–**f** was established by using NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction. The ^{29}Si NMR spectra of **4b**–**f** showed characteristic chemical shifts between $\delta = -40$ and -43 ppm and are in agreement with their short-chain counterpart *tert*-butyl-Si(OH)$_3$ **4a**.[17,18] For compounds **4b**–**e**, crystals suitable for single-crystal X-ray diffraction were obtained. All compounds crystallize in the monoclinic space group $P2_1/c$ and showed a double-layer motif, in which the silanetriol units formed a hydrophilic double sheet consisting of hydrogen-bonded honeycomb-like hexagonal assemblies in the solid state.

A similar motif has already been observed in the solid-state structure of compound **4a**.[18] The structure of **4e** depicted in Figure 1 is exemplary for those of **4b**–**e**. The double-sheet spacing, which refers to the thickness of the hydrophilic layer (distance *A*, Figure 1) is just below 2 Å and almost invariant to the length of the alkyl chain (Table 1). In contrast, the interlamellar distance (distance *B*, Figure 1) between equivalent sheets increases continuously with the chain length. With increasing length of the alkyl chains, the latter are mutually interlocked owing to van der Waals interactions. As a result of this interlocking, the distances between the hydrophobic layers (distance *C*, Figure 1) decrease with increasing chain length.

Following this trend, the precision of the structure determination in terms of *R* values (Table 4) and standard deviations (Table 1) increases with the chain lengths as well. This may be interpreted as a reduced tendency for disorder for the elongated chains concomitant with improved crystallinity in the solid state. The hydrogen-bonding interactions are similar to those in compound **4a**. Considering the distances and angles between the atoms involved, these interactions can be classified as moderate to strong hydrogen bonds according to Steiner.[20] The Si–O distances lie in between 1.626(2) and 1.647(3) Å. Combined with all other bond lengths and angles, these data are in agreement with **4a** and other silanetriols.[18,21] Interestingly, no folding of these chains can be observed, despite the steadily increasing alkyl chain length.

Surfactant properties

Despite the plethora of information available for the aggregation of silanetriols and silanols in the solid state,[21] little is known about their behavior in solution. For example, the am-

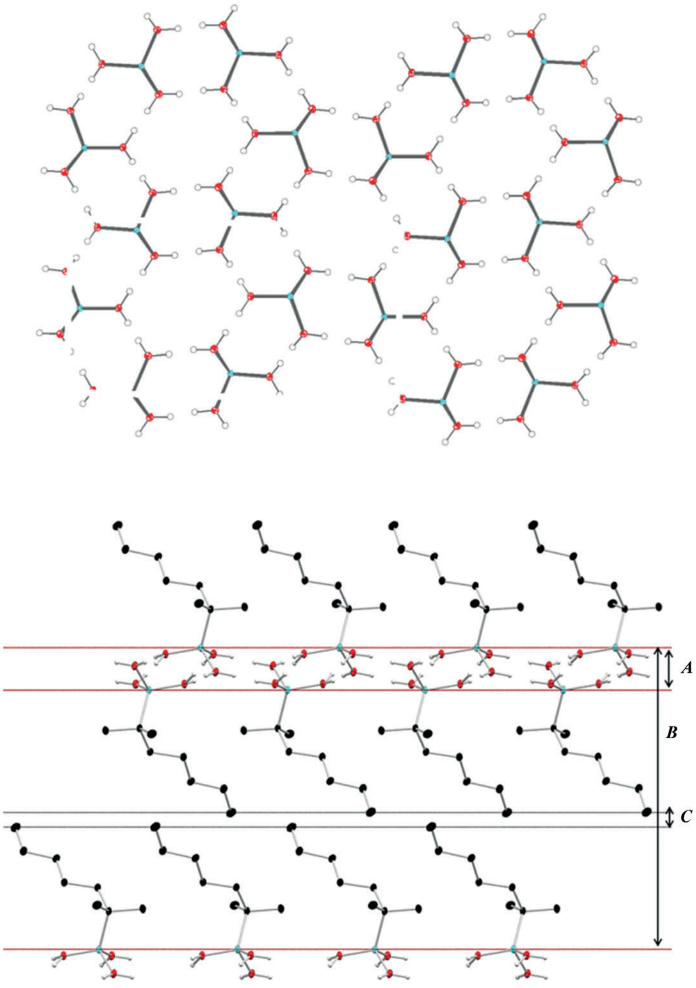

Figure 1. Crystal structure of **4e**. Top: top view of the hydrogen-bonded honeycomb sheet. Bottom: side view of the double-layer motif.

Table 1. Relevant geometric parameters in the crystal structures of **4b**–**e** in comparison to **4a**.[17,18]

$H_3C(CH_2)_nC(CH_3)_2Si(OH)_3$	**4a**[17,18],	**4b**	**4c**	**4d**	**4e**
n	0	1	2	3	4
A [Å]	1.97	1.97	1.89	1.88	1.93
B [Å]	9.67	10.29	11.49	12.24	13.68
C [Å]	2.20	2.93	1.79	1.78	0.66
Si–OH [Å]	1.635(1)–1.640(1)	1.632(3)–1.643(3)	1.626(2)–1.632(2)	1.633(1)–1.641(1)	1.6344(8)–1.6402(8)
Si–C [Å]	1.864(2)	1.867(4)	1.866(3)	1.867(2)	1.8668(12)
O–H [Å]	0.85	0.84	0.84	0.84	0.84
O–H···O [Å]	1.83–1.85	1.82–1.85	1.83–1.91	1.83–1.87	1.83–1.87
O···O [Å]	2.68	2.649(3)–2.669(3)	2.659(3)–2.674(3)	2.671(2)–2.696(2)	2.672(1)–2.704(1)
O–H···O [°]	165–173	164–174	147–172	168–175	174–180
O-Si-O [°]	108.3(1)	106.67(13)–108.66(12)	106.76(9)–108.51(10)	106.60(6)–108.42(6)	106.70(4)–108.60(4)
C-Si-O [°]	110.89(5)–111.01(8)	109.92(15)–112.92(14)	110.13(11)–113.45(11)	109.95(7)–113.53(7)	110.02(5)–113.41(5)
H_3C-C-CH_3 [°]	109.2(1)–109.9(2)	108.7(3)	108.2(2)	108.63(14)	108.26(9)
Si-C-C-C [°]	–	−53.9(4)	57.3(3)	72.94(17)	69.92(12)
C-C-C-C [°]	–	–	173.1(2)	178.69(15), 177.18(16)	175.02(10)–179.32(11)

phiphilic properties of cage-like polyhedral oligomeric silsesquioxane (POSS) trisilanols have been investigated.[22–24] For silanetriols, in which the maximum number of hydrophilic OH groups per Si atom is present in a neutral organosilanol, to the best of our knowledge, there are only two reports in the literature dealing with the aggregation behavior of **4a** in solution and the gas phase from our group.[10,11] In compound **4a**, the amphiphilic character is however rather imbalanced due to the dominance of the hydrophilic silanol units over the hydrophobic alkyl unit. Therefore, we wanted to explore the surfactant properties of the amphiphilic silanetriols **4b**–**f** in solution, in which the length of the hydrophobic chain is continuously increased. Due to their moderate to excellent water solubility, the surface tension of aqueous solutions of **4b**–**f** was explored by using the pendant-drop technique. Silanetriol **4a** was included as a reference compound. As depicted in Figure 2, the surface tension at 25 °C decreases with increasing length of the alkyl chains at the same concentration, similar to other surface active compounds, such as *n*-alkyl alcohols.[25]

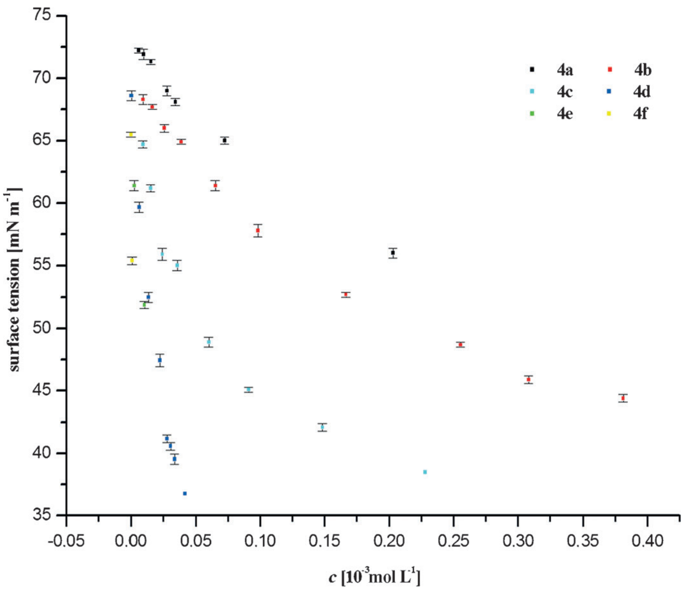

Figure 2. Surface tension of aqueous solutions of **4a**–**f**.

In the concentration range $0.2–308\times10^{-3}$ mol L^{-1}, we found a steady decrease of the surface tension with an increase in chain length at room temperature (Figure 2 and the Supporting Information). At a given concentration of 10×10^{-3} mol L^{-1}, the surface tension decreases by about 5 mN m^{-1} per additional methylene unit. The lowest value for surface tension (γ=36.7 mN m^{-1}) was determined for an aqueous solution of compound **4d** at a concentration of 41.6×10^{-3} mol L^{-1}. In comparison to sodium dodecylsulfate ($c=50\times10^{-3}$ mol L^{-1}; $\gamma=20$ mN m^{-1}),[26,27] a common surfactant in washing formulations, these results are remarkable.

Surface modification

Recently, we have shown that surface modifications of silicon-based surfaces employing the sterically hindered *tert*-butyl-$Si(OH)_3$ **4a** under neutral aqueous conditions are feasible.[28] In comparison to acid-treated coatings, the modified surfaces showed improved hydrophobic and oleophobic character, with water-contact angles up to 90°. Similarly, McCarthy and co-workers demonstrated that various metal-oxide surfaces (TiO_2, Al_2O_3, NiO) can be modified by using a stable silanediol ($Me_2Si(OH)_2$), which allows improved hydrophobization compared to the corresponding alkoxy- or chlorosilanes.[29] Due to the availability of the stable silanetriols **4b**–**f** with increased chain length, we became interested how an increase in the hydrophobic part of the silanol agent affects the surface hydrophobicity. To explore this aspect, static contact angles (CA) were determined on substrates (glass and silicon wafer) dip coated with aqueous solutions of **4b**–**f** and in addition **4a** as a reference. Even when concentrations for dip coating as low as 0.02 wt % were used, the modified glass surfaces showed water-contact angles between 90–101°. Although the highest contact angle was obtained for the silanetriol with the longest alkyl chain in this series, no simple correlation between alkyl chain and CA could be derived (Table 2). The determination of the contact angles of different test liquids (water, formamide,

Table 2. Comparison of the static contact angles θ_K [°(± sd)] of different wetting liquids on glass slides dip coated with aqueous solutions of **4a**–**f** (c = 0.02 wt%).

Solvent	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**
water	90 (±3)	92 (±2)	98 (±2)	91 (±3)	97 (±3)	101 (±3)
CH_2I_2	55 (±2)	60 (±1)	63 (±2)	58 (±2)	60 (±2)	63 (±2)
formamide	65 (±1)	66 (±1)	65 (±1)	63 (±2)	63 (±2)	64 (±2)

diiodomethane) of defined polar and dispersive attributes allowed the calculation of the surface free energies (SFE) by using different theoretical models. All investigated models (equation-of-state, OWRK model,[30–32] Wu theory[33]) showed the same trends (for details, see the Supporting Information), therefore, in the following, we will discuss only the results derived from the van Oss model,[34,35] enabling the determination of Lewis-donor and Lewis-acceptor properties of the surface.

For this purpose, the contact angles of three liquids, namely, water, formamide, and diiodomethane, were used for SFE determinations (Table 3). In comparison to unmodified glass slides, the SFE of the surfaces dip coated with silanetriols **4a**–**f** were significantly lower with differences of 25 to 32 mJ m^{-2}. Herein, the lowest values of γ^{total} were observed for the longer alkyl chain silanetriols. When looking at the nature of contributions, the dispersive (γ^{LW}) and the acidic (γ^+) parts of the SFE remained nearly unaffected by the coating (($\Delta\gamma^{\text{LW}}$) 3–9 mJ m^{-2}, ($\Delta\gamma^+$) 2–3 mJ m^{-2}), whereas the basic contributions, γ^-, showed a strong decrease (($\Delta\gamma^-$) 48–50 mJ m^{-2}) compared to glass. Generally, on these modified surfaces, adsorption of hydrated OH$^-$ is preferred in comparison to hydrated H$^+$ ions, due to their larger adsorption enthalpy.

Table 3. Surface free energies [mJ m^{-2}] of the modified surfaces (glass, dip coated with aq. **4a**–**f** (c = 0.02 wt%)) calculated by using the van Oss model.

LWAB	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**
γ^{total}	32.2	31.8	28.3	30.6	28.2	25.7
γ^{LW}	31.2	31.1	27.8	30.1	28.2	25.2
γ^+	0.4	0.5	0.1	0.1	0.1	0.1
γ^-	2.4	1.1	2.1	2.1	1.2	2.9

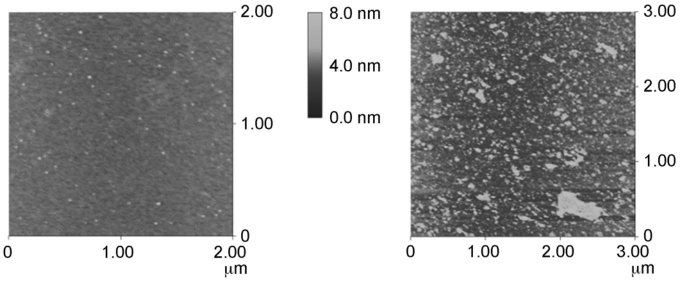

Figure 3. AFM image of Si wafer coated with aqueous **4c** (left 0.10 wt%; right 0.25 wt%).

Contact angles were determined on silicon wafers dip coated with aqueous solutions of **4b**–**f**. The results are very similar to those obtained for glass substrates (see the Supporting Information) showing the same trends for the components of the SFE. Unlike glass, the regular surface morphology of the silicon wafers allows the influence of the silanetriol coating on the surface morphology to be assessed. Therefore, silicon wafers with a 100 nm SiO_x surface layer were dip coated with solutions **4b**–**f** and analyzed by using AFM. The resulting surface roughness root-mean-squared roughness (R_q) clearly depends on the concentration of the respective silanetriol in solution. As a typical example, R_q is 0.2 nm obtained from a coating solution with 0.10 wt% of **4c**, whereas R_q increases to 1.1 nm by coating with a solution containing 0.25 wt% of **4c** (Figure 3).

In addition to increasing the surface roughness, the formation of islands increases with the silanetriol concentration, which may be a consequence of micellar aggregation in the coating solution above the critical micelle concentration, as was reported for silanetriol **4a**.[11]

Conclusion

We have shown that surfactants based on stable silanols are synthetically accessible and are capable of reducing the surface tension in water comparable to established detergents without exhibiting the eutrophicating potential of the latter. Their structural chemistry is driven by their tendency to assemble according to their amphiphilic character, which leads to alternating hydrophilic layer structures for which the spacing can be varied. Moreover, these surfactants can be used to modify surfaces by using simple dip-coating procedures. As was previously mentioned, silanols are the silicon analogues of alcohols and important intermediates in the manufacturing of silicones. This means in turn that the large-scale manufacturing of silanol-based surfactants in fact would be feasible and realistic with the current industrial manufacturing infrastructure. In addition, the cytotoxicity of the parent tertiary silanetriol *tert*-butyl-$Si(OH)_3$ was shown to be negligible, which corroborates the potential for application of this series of new silanetriols presented herein.[8]

Experimental Section

All manipulations were carried out under an inert argon atmosphere by using standard Schlenk techniques. All solvents were dried and freshly distilled over Na/K alloy (Et_2O, THF, pentane, heptane, C_6D_6), CaH_2 (NEt_3), or P_4O_{10} (acetone). $SiCl_4$ was freshly distilled before use. The *n*-alkylbromides, *tert*-butyl-$SiCl_3$ **3a**, 2-bromo-2-methylbutane **2a**, LiBr, and HBr (48%) were purchased and used without further purification. The tertiary alcohols **1a**–**e** and the tertiary bromides **2b**–**f** were prepared according to literature procedures; boiling points and NMR data fit to the published data.[36–43] ^{1}H and ^{13}C NMR data were recorded on a Bruker Avance III 300 MHz spectrometer (operating at 300 MHz, 75.4 MHz) or a Varian MR-400 MHz spectrometer (operating at 400 MHz, 100.5 MHz). ^{29}Si NMR data were recorded on a Bruker Avance III 300 MHz spectrometer (operating at 59.6 MHz) or a Varian VNMRS-

500 MHz spectrometer (operating at 99.3 MHz). All measurements were performed at room temperature by using TMS as external standard. MS (EI) spectra were recorded on an Agilent Technologies 5975C inert XL MSD with SIS Direct Insertion Probe. ESI and APCI mass spectra were recorded on a Finnigan LCQ Deca (ThermoQuest). HRMS (ESI) spectra were recorded by using a micrOTOF (Bruker Daltonics) and an Apollo "Ion Funnel" ESI-ion source. IR spectra were recorded by using a Bruker Alpha Platinum ATR spectrometer. Elemental analysis data were obtained by using a Euro EA by HEKAtech.

X-Ray diffraction measurements

X-Ray diffraction measurements were performed on a Stoe IPDS2 or a BRUKER-AXS SMART APEX 2 CCD diffractometer by using graphite monochromatized $Mo_{K\alpha}$ radiation. Essential details of the crystal-data and structure refinement for **4b**–**e** are summarized in Table 4.

Table 4. Crystal data and structure refinement for **4b**–**e**.[17,18]

	4b	**4c**	**4d**	**4e**
formula	$C_5H_{14}O_3Si$	$C_6H_{16}O_3Si$	$C_7H_{18}O_3Si$	$C_8H_{20}O_3Si$
formula weight [$g\,mol^{-1}$]	148.24	164.28	178.30	192.33
T [K]	100	95	100	100
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
unit-cell dimensions				
a [Å]	11.1160(14)	11.657(6)	12.4316(10)	14.4406(8)
b [Å]	6.6685(8)	6.801(3)	6.6759(5)	6.5522(4)
c [Å]	12.3970(14)	12.249(8)	12.5082(9)	12.5218(7)
β [°]	113.433(6)	99.79(4)	100.143(2)	108.684(2)
V [Å^3]	843.16(17)	957.0(9)	1021.86(13)	1122.35(11)
Z	4	4	4	4
ρ_{calcd} [$mg\,m^{-13}$]	1.184	1.140	1.159	1.138
μ [mm^{-1}]	0.225	0.203	0.195	0.182
Θ range for data collected [°]	2.00–26.00	3.38–26.00	3.33–26.00	2.98–28.00
unique reflections	1646	1883	1994	2684
parameters	108	118	129	122
goodness-of-fit on F^2	1.161	1.138	1.078	1.038
R_1 (obs. data)$_1$	0.0644	0.0516	0.0370	0.0302
wR_2 (all data)	0.1549	0.1361	0.1023	0.0840

The structures were solved by using direct methods (SHELXS-97) and refined by full-matrix-least-squares techniques against F^2 (SHELXL-97). The nonhydrogen atoms were refined with anisotropic displacement parameters without any constraints. The hydrogen atoms of the OH groups are disordered over two sites. They were refined with one common isotropic displacement parameter. The bond lengths were fixed to 0.84 Å and some restraints were applied to these H atoms. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with approximately tetrahedral angles and C–H distances of 0.99 Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. CCDC-972002 (**4b**), CCDC-766344 (**4c**), CCDC-972003 (**4d**), and CCDC-972004 (**4e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Surface-tension measurements

Surface-tension measurements were performed on a Dataphysics OCA20 system by using the pendant-drop method. All manipulations were performed at room temperature. All data points are mean values calculated by using the Dataphysics SCA 20 software (DataPhysics Instruments GmbH, Filderstadt, Germany) from at least 20 independent measurements. Contact-angle measurements were performed on a Dataphysics (DataPhysics Instruments GmbH, Filderstadt, Germany) contact angle system (OCA15+) by using water, diiodomethane, and formamide as solvents with a drop volume of 5 µL. Solvent properties of the three testing liquids used for the calculation of the SFE can be found in the Supporting Information. At least three different glass slides were used for contact-angle determinations of each wetting liquid. On each slide, 7–10 drops were deposited. For the determination of the equilibrium structure of the liquid/solid/vapor interface, the sessile drop method was used. For the neat solvents, surface tensions of 72.75 (water), 50.80 (diiodomethane), and 58.20 $mJ\,m^{-12}$ (formamide) were used for further calculations.

Surface free-energy calculations

In the van Oss or LWAB approach[34,35] the surface energy is expressed as sum of the apolar interactions, called Lifshitz–van der Waals (γi, LW, includes London dispersion, Debye induction (dipole-induced dipole), and Keesom orientation (dipole–dipole forces)) and the polar Lewis acid/base (γi, AB, often due to hydrogen bonding) interactions according to Equation (1),[30] in which γi,- is the electron donor and γi,+ the electron-acceptor component of the energy of the phases i. The work of adhesion W_H then can be defined according to the Young–Dupre equation:[35] for a solution of this equation and the determination of the surface-tension components of a solid, we employed diiodomethane ($\gamma_L = \gamma_{L,LW}$), formamide ($\gamma_L = \gamma_{L,LW} + \gamma_{L,-}$), and water ($\gamma_L = \gamma_{L,LW} + \gamma_{L,+} + \gamma_{L,-}$).

The substrates (glass slides and silicon wafers) were cleaned by treatment with Caro's acid, freshly prepared by carefully adding H_2O_2 (33%) to H_2SO_4 (conc.) in a ratio 3:7. After 30 min, the slides were rinsed three times with double distilled water and dried in a stream of nitrogen before performing the coating experiments. For the dip-coating experiments, solutions containing 0.02 wt% (glass slides) or 0.10 and 0.25 wt% (silicon wafers) of **4b**–**f** in double distilled water were prepared and used immediately. After the dip-coating experiments (30 min), the substrates were dried for 24 h at 60 °C in a drying oven and after cooling, they were washed with double distilled water.

Atomic force microscopy (AFM) images were recorded on a Nanoscope V Multimode AFM (Veeco) by using silicon cantilevers TESP7 from Veeco Instruments with an average spring constant of 40 $N\,m^{-1}$, tip radius of 8 nm, and resonance frequency of 320 kHz. Image processing, analysis, and root mean-square roughness calculations were performed with WSxA freeware[44].

Synthesis

Synthesis of the tertiary trichlorosilanes 3b–f

The corresponding tertiary bromide **2a**–**f** (1 equiv) was dissolved in Et_2O and slowly added to Mg turnings (1.1 equiv). Subsequently, the obtained Grignard solution was slowly added by cannula to a suspension of CuCN (0.01 equiv) and $SiCl_4$ (3 equiv) in Et_2O at −70 °C. The reaction mixture was slowly warmed to RT and stirred overnight. After evaporation of the solvent and excess $SiCl_4$, the remaining solid was extracted with *n*-pentane and filtered. Evaporation of the solvent and fractional distillation led to the isolation of the compounds **3 b**–**f**.

Synthesis of the tertiary silanetriols 4 b–f

The corresponding tertiary trichlorosilane **3 b**–**f** (1 equiv) was dissolved in Et_2O and slowly added to a solution of H_2O (3 equiv) and NEt_3 (3 equiv) in Et_2O at 0 °C. After the addition was complete, the reaction mixture was slowly warmed to RT and stirred for a further 3 h. The white precipitate was removed by filtration, and all volatiles were removed in vacuo. The remaining solid was washed with *n*-pentane and recrystallized from Et_2O/*n*-heptane (1:1). The tertiary silanetriols **4 b**–**f** were obtained in 30–67 % yield as white crystalline materials.

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Keywords: main-group elements · metalation · silanes · supramolecular chemistry · sustainable chemistry

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FULL PAPER

Soap from sand? A synthetic entry to surfactants based on stable silanols, which provide beneficial properties comparable to established detergents without sharing their eutrophicating potential, was established (see figure).

Supramolecular Chemistry

*N. Hurkes, H. M. A. Ehmann, M. List, S. Spirk, M. Bussiek, F. Belaj, R. Pietschnig**

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Silanol-Based Surfactants: Synthetic Access and Properties of an Innovative Class of Environmentally Benign Detergents