Synthesis of Model Compounds for the Formation of Self-Assembled Monolayers on a Silicon Surface

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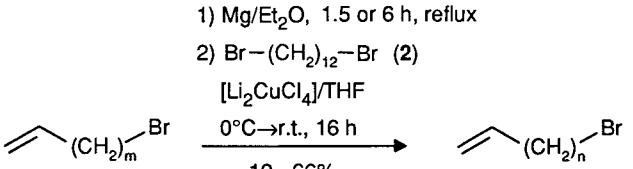
The synthesis of terminally functionalized alkanes, which represent potential compounds for formation of self-assembled monolayers, is reported. The alkanes described are substituted at one end with a trichloro- or trialkoxysilyl group suitable for linkage to a hydroxylated silicon surface and at the other end with a vinyl or amino group for further functionalization.

In recent years, numerous compounds have been proposed which may be applied in storage and transfer of information on a molecular level.[2,3] For a practical application in molecular electronics these compounds have to be organized in supramolecular structures and connected to electronic devices.[4,5] In terminally donor-acceptor substituted polyenes, which have been synthesized as model compounds for information transfer processes, an intramolecular energy transfer from the excited donor to the acceptor could be proved.[6] With respect to their ability to form well-organized Langmuir-Blodgett (LB) films, conjugated polyenes with amphiphilic terminal groups have been prepared.[7] The transfer of these LB films onto solid supports, e.g. silicon, was possible but incomplete.[7] Due to these results and the fact that LB layers are thermally not very stable, we became interested in the preparation of self-assembled monolayers[8] on silicon surfaces for studying energy transfer processes on a molecular level.

In the present paper we report on the synthesis of terminally functionalized alkanes with chain lengths suitable for the formation of self-assembled monolayers. In these compounds, one end is substituted with a trialkoxy- or trichlorosilyl group for the reaction with the hydroxylated silicon surface, whereas the other end has a vinyl or amino group suitable for further functionalization and multilayer formation.

The synthesis of 1-trichlorosilyl-ω-alkenes **4** with different chain lengths is known in principle.[9,10] However, in the procedures described[9,11] the separation and elimination of unreacted undec-10-enyl bromide used as the starting compound causes difficulties. Therefore, we have prepared the 1-bromo-ω-alkenes **3a–c** by coupling 1-bromo-ω-alkenes **1a–c** with 1,12-dibromododecane **(2)** using Li_2CuCl_4 as a catalyst.[12] (Scheme 1, Table 1). Unreacted **1** and the excess of **2** could be easily separated in this case.



Scheme 1

The formation of 1-bromododecane as a byproduct in the coupling reaction could be suppressed by reducing the amount of the catalyst Li_2CuCl_4.

In the coupling reaction of **1c** with **2** the main product is 1-bromo-13-cyclopentyltridecane, formed by cyclization of **1c**,[13] whereas **3c** was obtained only in 12% yield. We were not able to improve the yield of **3c** by this route.

The bromides **3a** and **b**, now easily available, were coupled with silicon tetrachloride in a known procedure[9] to

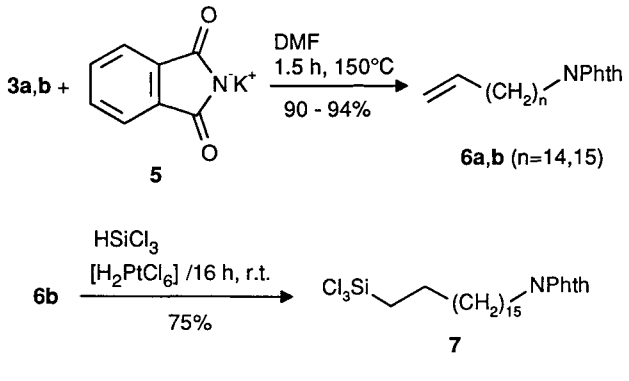
Table 1. Compounds **3** and **4** Prepared

Grignard Reaction						Coupling Reaction				Product	Yield g (%)	bp (°C)/0.01 Torr	
1, 3	g (mmol)	Mg, g (mmol)	Solvent	(mL)	Time (h)	**2**, $SiCl_4$	g (mmol)	Solvent	(mL)			found	reported[9-11]
1a	0.67 (5.0)	0.4 (16.4)	Et_2O	10	6.0	**2**	3.28 (10.0)	THF	10	**3a**	0.83 (54)	110	–
1b	1.49 (10.0)	1.1 (45.2)	Et_2O	20	1.5	**2**	6.56 (20.0)	THF	20	**3b**	2.10 (66)	124	–
1c	1.63 (10.0)	0.4 (16.4)	Et_2O	20	1.5	**2**	6.56 (20.0)	THF	10	**3c**	0.39 (12)[a]	–	–
3a	3.70 (12.2)	1.1 (45.2)	THF	25	0.5	$SiCl_4$	4.55 (26.8)	Et_2O	25	**4a**	2.84 (65)	106–112	–
3b	3.17 (10.0)	1.3 (53.5)	THF	25	2.0	$SiCl_4$	3.74 (22.0)	Et_2O	40	**4b**	2.12 (57)	110–116	105–115/0.005

[a] 1-Bromo-13-cyclopentyltridecane (37%) was isolated as the main product by chromatography (fraction 1, 1.23 g). Compound **3c** was isolated as fraction 2.
3c: ^1H NMR ($CDCl_3$): δ = 1.12–1.51 (26H, m, 3-15-H), 1.78–1.93 (2H, m, 2-H), 1.99–2.11 (2H, m, 16-H), 3.41 (2H, t, $J_{1,2}$ = 6.9 Hz, 1-H), 4.93 (1H, m_c, 18′-H), 4.99 (1H, m_c, 18-H), 5.82 (1H, dt, $J_{17,16}$ = 6.7, $J_{17,18}$ = 10.2, $J_{17,18'}$ = 17.0 Hz, 17-H).
$C_{18}H_{35}Br$ calc. C 65.24 H 10.65 Br 24.11
found 65.14 10.75 24.12

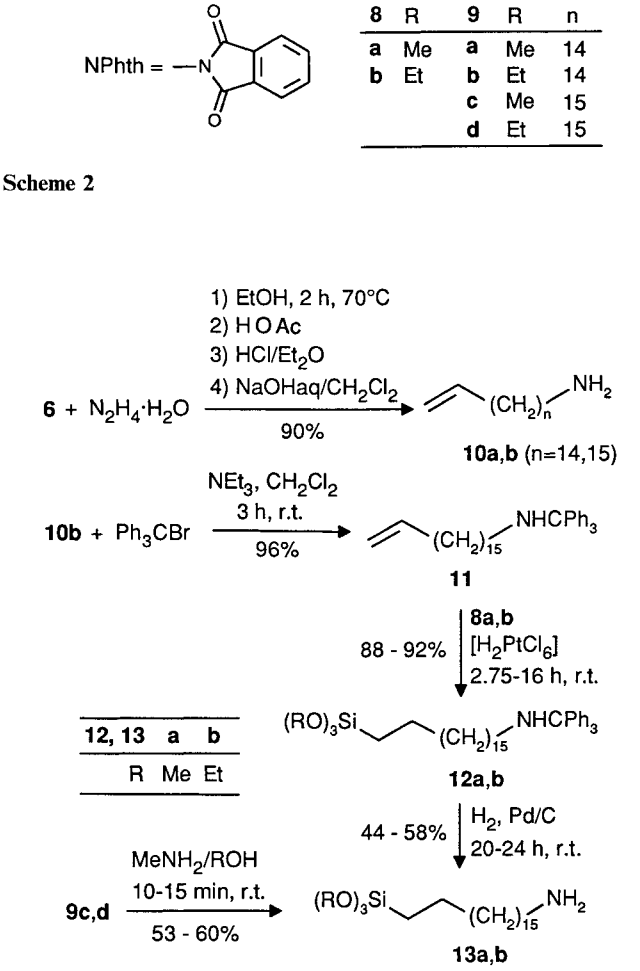
give the 1-trichlorosilyl-ω-alkenes **4a** and **b** (Scheme 1, Table 1).

Only decomposition was observed when the bromides **3** were reacted with potassium phthalimide **(5)** without solvent, according to the procedure described in the literature.[14] However, the substitution products **6** were obtained in very high yields by heating the bromides **3** with **5** in dimethylformamide[15] at 150°C (Scheme 2).



8	R	9	R	n
a	Me	a	Me	14
b	Et	b	Et	14
		c	Me	15
		d	Et	15

Scheme 2



Scheme 3

Hydrosilylation[16] of **6b** with trichlorosilane in the presence of H_2PtCl_6 as catalyst gives *N*-(17-trichlorosilyl)heptadecylphthalimide **(7)** in 75% yield, after distillation, as a colorless oil which slowly crystallizes (Scheme 2). Under analogous conditions the trialkoxysilyl compounds **9a–d** were synthesized in excellent yields by hydrosilylation of the alkenes **6a, b** with trialkoxysilanes **8a** and **b** (Scheme 2).

The removal of the phthalimido protecting group in compounds **6** using sodium borohydride[17] was not successful, since side products formed during the reaction could not be separated. With hydrazine hydrate[15,18] in ethanol, however, the amines **10** were obtained in very good yields (Scheme 3) and could be purified via the corresponding hydrochlorides.

The amines **10** could not be hydrosilylated directly according to the known procedure[19] since the catalyst H_2PtCl_6 was inactivated by salt formation. Therefore, the *N*-trityl protected amine **11**[20] was prepared first and hydrosilylated with **8a** and **b** to give the trialkoxysilanes **12** (Scheme 3). The *N*-trityl protecting group in **12** can be removed by catalytic hydrogenation in methanol/ethyl acetate (5:1) or ethanol yielding the amino compounds **13** (Scheme 3).

An alternative shorter route to **13** is the removal of the *N*-phthaloyl protecting group from the trialkoxysilanes **9** using methylamine in alcohol[21] (Scheme 3). To avoid the formation of mixtures in the trialkoxy moiety, the corresponding alcohols (methanol for **9a** and ethanol for **9b**) were used.

The application of compounds **4, 7** and **13** for the formation of self-assembled monolayers was investigated in cooperation with Professor M. Grunze (University of Heidelberg) and will be published separately.

^{1}H NMR spectra were recorded on a Bruker AC 250 F (250 MHz) with TMS as internal standard. Melting points were determined on a Büchi SMP 20 and are uncorrected. FAB mass spectrometric data were obtained with a Finnigan MAT 95 mass spectrometer. Preparative column chromatography was performed using glass columns of different size packed with silica gel S, grain size 0.032–0.063 mm (Riedel-de Haen). All solvents used were purified and dried. All experiments were performed under Ar as inert gas in flame-dried apparatus. The solution of catalyst H_2PtCl_6 was prepared from H_2PtCl_6 · aq (164 mg) in absolute *i*-PrOH (10 mL). The solution of $MeNH_2$ in MeOH (8.03 M) was obtained by passing $MeNH_2$ into absolute MeOH. Petroleum ether used had bp 40–60°C. Satisfactory microanalyses obtained for compounds **6a, b, 10a, b, 11, 12a, b, 13a, b**: C ± 0.25, H ± 0.15, N ± 0.14.

1-Bromo-ω-alkenes 3 and 1-Trichlorosilyl-ω-alkenes 4; General Procedure:

The corresponding Grignard reagent was prepared from the bromide **1** or **3** and Mg in Et_2O by refluxing for the given time (Table 1) (in the case of 3, dibromoethane was used as an entrainer). The Grignard solution was transferred to the dropping funnel of a second flask via cannula. In the case of **1**, the Grignard reagent was rapidly added dropwise to an ice-cooled solution of **2** in THF and Li_2CuCl_4 in THF[12] (100 μL, added via syringe). The mixture was warmed to r.t. (16 h), hydrolyzed with NH_4Cl solution, the organic phase was separated and the aqueous phase was extracted four times with CH_2Cl_2. The organic phases were combined, washed with sat. $NaHCO_3$ solution, water, and dried (Na_2SO_4). Evaporation and chromatography on silica gel with petroleum ether yielded **3**. For **4**, the Grignard reagent from **3** was added dropwise at r.t.

Table 2. Compounds **9** Prepared

Starting Materials		Product[a]	Yield mg (%)	bp (°C)/Torr	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)
6, mg (mmol)	**8**, g (mmol)				
a 369.5 (1.0)	**a** 0.96 (7.85)	**9a**	453 (92)	190/0.01	0.58–0.74 (2H, m, 1-H), 1.18–1.57 (26H, m, 2-14-H), 1.59–1.78 (2H, m, 15-H), 3.57 (9H, s, OCH_3), 3.67 (2H, t, $J_{16,15}$ = 7.3 Hz, 16-H), 7.78 (4H, m_c, ArH)
a 369.5 (1.0)	**b** 0.89 (5.43)	**9b**	484 (90)	210/0.01	0.55–0.72 (2H, m, 1-H), 1.12–1.52 (35H, m, 2-14-H, CH_3), 1.54–1.75 (2H, m, 15-H), 3.67 (2H, t, $J_{16,15}$ = 7.3 Hz, 16-H), 3.82 (6H, q, J = 7.0 Hz, OCH_2), 7.78 (4H, m_c, ArH)
b 767.0 (2.0)	**a** 1.92 (15.71)	**9c**	943 (93)	205/0.01	0.59–0.72 (2H, m, 1-H), 1.14–1.50 (28H, m, 2-15-H), 1.59–1.76 (2H, m, 16-H), 3.57 (9H, s, OCH_3), 3.65 (2H, t, $J_{17,16}$ = 7.3 Hz, 17-H), 7.79 (4H, m_c, ArH)
b 767.0 (2.0)	**b** 1.33 (8.10)	**9d**	1000 (91)	210/0.01	0.55–0.70 (2H, m, 1-H), 1.10–1.53 (37H, m, 2-15-H, CH_3), 1.54–1.74 (2H, m, 16-H), 3.68 (2H, t, $J_{17,16}$ = 7.3 Hz, 17-H), 3.82 (6H, q, J = 7.0 Hz, OCH_2), 7.78 (4H, m_c, ArH)

[a] Satisfactory microanalyses obtained: C ± 0.16, H ± 0.22, N ± 0.15.

to a solution of $SiCl_4$ in Et_2O within 1.5–2 h, the mixture was refluxed for 16 h and unreacted $SiCl_4$ and Et_2O were removed in vacuo. Under Ar hexane was added, the mixture stirred for 0.5 h and the remaining solid was filtered. The filtrate was concentrated and fractionally distilled through a Vigreux column in vacuo (Table 1).

N-(ω-Alkenyl)-1-phthalimides 6; General Procedure:
DMF was added to bromide **3** and potassium phthalimide **(5)**, and the mixture was heated to 150 °C for 1.5 h. The solvent was removed, the residue taken up in CH_2Cl_2 and stirred for 16 h. The remaining solid was filtered, and the filtrate was dried (Na_2SO_4). Evaporation and chromatography on silica gel with petroleum ether/EtOAc (9:1) afforded **6**.

N-(15-Hexadecenyl)-1-phthalimide **(6a)**: From **3a** (606 mg, 2.0 mmol), **5** (496 mg, 2.67 mmol) and DMF (20 mL); yield: 669 mg (90%); mp 59 °C.

^{1}H NMR ($CDCl_3$): δ = 1.12–1.48 (22H, m, 3-13-H), 1.58–1.79 (2H, m, 2-H), 1.98–2.12 (2H, m, 14-H), 3.67 (2H, t, $J_{1,2}$ = 7.3 Hz, 1-H), 4.92 (1H, m_c, 16′-H), 5.00 (1H, m_c, 16-H), 5.81 (1H, ddt, $J_{15,14}$ = 6.7, $J_{15,16}$ = 10.3, $J_{15,16'}$ = 17.0 Hz, 15-H), 7.78 (4H, m_c, ArH).

N-(16-Heptadecenyl)-1-phthalimide **(6b)**: From **3b** (7.20 g, 22.7 mmol), **5** (5.63 g, 30.4 mmol) and DMF (250 mL); yield: 8.20 g (94%); mp 68 °C.

^{1}H NMR ($CDCl_3$): δ = 1.12–1.49 (24H, m, 3-14-H), 1.54–1.79 (2H, m, 2-H), 1.98–2.13 (2H, m, 15-H), 3.67 (2H, t, $J_{1,2}$ = 7.3 Hz, 1-H), 4.92 (1H, m_c, 17′-H), 4.99 (1H, m_c, 17-H), 5.81 (1H, dt, $J_{16,15}$ = 6.7, $J_{16,17}$ = 10.2, $J_{16,17'}$ = 17.1 Hz, 16-H), 7.78 (4H, m_c, ArH).

N-(17-Trichlorosilyl)heptadecylphthalimide (7):
$HSiCl_3$ (2.68 g, 19.8 mmol) was added to **6b** (767 mg, 2.0 mmol) via syringe followed by 4 drops of a solution of H_2PtCl_6 in *i*-PrOH, and the mixture was stirred at r.t. for 16 h. Unreacted $HSiCl_3$ was removed in vacuo in a trap, and the residue was distilled at 0.01 Torr. The main fraction was distilled once more at 0.01 Torr to give **7** as a colorless oil; yield: 778 mg (75%); bp 210–240 °C (0.01 Torr).

^{1}H NMR ($CDCl_3$): δ = 1.10–1.58 (32H, m, 1-16-H), 3.67 (2H, t, $J_{17,16}$ = 7.3 Hz, 17-H), 7.77 (4H, m_c, ArH).

MS: *m/z* (%) = 517.2 (96.8), 518.2 (34.0), 519.3 (100.0), 520.3 (31.7), 521.3 (37.4), 522.4 (10.5), 523.3 (6.0).

Trialkoxysilyl Compounds 9:
Prepared as described above for **7**, from **6a, b**, the trialkoxysilane **8a** and **b** and 3 **(9a, b)** or 6 drops **(9c, d)** of a solution of H_2PtCl_6 in *i*-PrOH (Table 2).

ω-Alkenyl-1-amines 10; General Procedure:
The alkenylphthalimide **6a** or **b** was dissolved in EtOH by warming, then $N_2H_4 \cdot H_2O$ was added, and the mixture was heated to 70 °C for the given time (see below). AcOH was added slowly to the warm solution, and heated at 70 °C for further 0.5 h. The mixture was diluted with water, made alkaline with 5 M NaOH and extracted four times with CH_2Cl_2. The combined extracts were washed with water, dried (Na_2SO_4) and evaporated. The crude amine was converted to the hydrochloride by dissolving in anhydr. Et_2O, and passing HCl into the ice-cooled solution for 10 min. After 16 h at 8 °C the hydrochloride was filtered, washed with Et_2O and dried. 1 M NaOH and CH_2Cl_2 were added via syringe to the hydrochloride, and the mixture was vigorously stirred at r.t. for 1 h. The organic phase was separated, and the aqueous phase extracted four times with CH_2Cl_2. The organic phases were combined, washed twice with water, and dried (Na_2SO_4). Evaporation and distillation in vacuo afforded the amine **10**.

15-Hexadecenyl-1-amine **(10a)**:

10a · HCl: From **6a** (1.19 g, 3.22 mmol), $N_2H_4 \cdot H_2O$ (480 µL, 9.68 mmol), EtOH (60 mL) and AcOH (8 mL); 2.5 h at 70 °C; yield: 814 mg (92%); white crystals; mp 183–187 °C.

^{1}H NMR (DMSO-d_6): δ = 1.13–1.45 (22H, m, 3-13-H), 1.45–1.62 (2H, m, 2-H), 1.93–2.10 (2H, m, 14-H), 2.74 (2H, t, $J_{1,2}$ = 7.5 Hz, 1-H), 4.93 (1H, m_c, 16′-H), 5.00 (1H, m_c, 16-H), 5.79 (1H, dt, $J_{15,14}$ = 6.7, $J_{15,16}$ = 10.2, $J_{15,16'}$ = 17.1 Hz, 15-H), 7.83 (3H, br s, NH_3).

10a: From hydrochloride (276 mg, 1.0 mmol), NaOH (5 mL) and CH_2Cl_2 (5 mL); yield: 235 mg (98%); white solid; bp 110 °C/0.1 Torr; mp 33.5 °C.

^{1}H NMR ($CDCl_3$): δ = 1.12 (2H, br s, NH_2), 1.10–1.60 (24H, m, 2-13-H), 1.94–2.12 (2H, m, 14-H), 2.67 (2H, t, $J_{1,2}$ = 6.9 Hz, 1-H), 4.91 (1H, m_c, 16′-H), 4.98 (1H, m_c, 16-H), 5.81 (1H, dt, $J_{15,14}$ = 6.7, $J_{15,16}$ = 10.2, $J_{15,16'}$ = 17.1 Hz, 15-H).

16-Heptadecenyl-1-amine **(10b)**:

10b · HCl: From **6b** (547 mg, 1.43 mmol), $N_2H_4 \cdot H_2O$ (225 µL, 4.5 mmol), EtOH (20 mL) and AcOH (4 mL); 1.75 h at 70 °C; yield: 380 mg (92%); white crystals; mp 178–180 °C.

^{1}H NMR (DMSO-d_6): δ = 1.12–1.43 (24H, m, 3-14-H), 1.43–1.65 (2H, m, 2-H), 1.91–2.11 (2H, m, 15-H), 2.65–2.83 (2H, m, 1-H), 4.93 (1H, m_c, 17′-H), 5.00 (1H, m_c, 17-H), 5.79 (1H, dt, $J_{16,15}$ = 6.7, $J_{16,17}$ = 10.3, $J_{16,17'}$ = 17.1 Hz, 16-H), 7.97 (3H, br s, NH_3).

10b: From hydrochloride (435 mg, 1.5 mmol), NaOH (15 mL), and CH_2Cl_2 (15 mL); yield: 371 mg (98%); white solid; bp 110 °C/0.01 Torr; mp 36 °C.

^{1}H NMR ($CDCl_3$): δ = 0.90–1.62 (28H, m, 2-14-H, NH_2),

1.87–2.09 (2H, m, 15-H), 2.61 (2H, t, $J_{1,2}$ = 6.6 Hz, 1-H), 4.86 (1H, m_c, 17′-H), 4.92 (1H, m_c, 17-H), 5.74 (1H, dt, $J_{16,15}$ = 6.7, $J_{16,17}$ = 10.3, $J_{16,17'}$ = 17.0 Hz, 16-H).

16-Heptadecenyl-1-(*N*-triphenylmethyl)amine (11):
Method A: Et_3N (975 μL, 7.0 mmol) was added to a suspension of **10b** (1.69 g, 6.67 mmol) and bromotriphenylmethane (2.26 g, 7.0 mmol) in CH_2Cl_2 (40 mL), and the mixture was stirred at r.t. for 3 h. The solvent was removed, the residue dried in vacuo and chromatographed on silica gel with petroleum ether/EtOAc (9:1). Evaporation and bulb-to-bulb distillation of the residue gave **11** as a bright yellow oil; yield: 3.18 g (96%); bp 230°C/0.01 Torr.

^{1}H NMR ($CDCl_3$): δ = 1.10–1.65 (27H, m, 2-14-H, NH), 1.92–2.10 (2H, m, 15-H), 2.11 (2H, t, $J_{1,2}$ = 6.9 Hz, 1-H), 4.92 (1H, m_c, 17′-H), 4.98 (1H, m_c, 17-H), 5.81 (1H, dt, $J_{16,15}$ = 6.7, $J_{16,17}$ = 10.2, $J_{16,17'}$ = 17.0 Hz, 16-H), 7.00–7.35, and 7.36–7.59 (15H, 2 m, C_6H_5).

Method B: Et_3N (6.2 mL, 44.5 mmol) was added via syringe to a solution of bromotriphenylmethane (16.14 g, 50.0 mmol) in CH_2Cl_2 (350 mL) followed by addition of a solution of crude **10b**, prepared from **6b** (15.60 g, 40.67 mmol), $N_2H_4 \cdot H_2O$ (6.0 mL, 121 mmol), EtOH (400 mL) and AcOH (100 mL) as described above, in CH_2Cl_2 (50 mL). The mixture was stirred at r.t. for 16 h. Evaporation, chromatography on silica gel with petroleum ether/EtOAc (9:1) and distillation in vacuo afforded 17.5 g (86%) (based on **6b**).

17-(*N*-Triphenylmethylamino)heptadecyltrimethoxysilane (12a):
Prepared as described for **7**, from **11** (498 mg, 1.0 mmol), **8a** (0.96 g, 7.85 mmol) and 6 drops of a solution of H_2PtCl_6 in *i*-PrOH; reaction time 2.75 h; yield: 567 mg (92%); bright yellow oil, bp 210°C/0.01 Torr.

^{1}H NMR ($CDCl_3$): δ = 0.58–0.72 (2H, m, 1-H), 1.11–1.59 (31H, m, 2-16-H, NH), 2.10 (2H, t, $J_{17,16}$ = 6.9 Hz, 17-H), 3.57 (9H, s, OCH_3), 7.10–7.34, 7.40–7.54 (15H, 2 m, C_6H_5).

17-(*N*-Triphenylmethylamino)heptadecyltriethoxysilane (12b):
Prepared as described for **7**, from **11** (995 mg, 2.0 mmol), **8b** (1.79 g, 10.9 mmol) and 6 drops of H_2PtCl_6 solution; reaction time 16 h; three times bulb-to-bulb distillation; yield: 1.16 g (88%); bright yellow oil; bp 245°C/0.01 Torr.

^{1}H NMR ($CDCl_3$): δ = 0.57–0.71 (2H, m, 1-H), 1.10–1.60 (40H, m, 2-16-H, CH_3, NH), 2.10 (2H, t, $J_{17,16}$ = 6.9 Hz, 17-H), 3.81 (6H, q, J = 7.0 Hz, OCH_2), 7.10–7.34 and 7.40–7.55 (15H, 2 m, C_6H_5).

17-Aminoheptadecyltrialkoxysilanes 13; General Procedure:
Method A: A suspension of Pd/C in the given solvent was hydrogenated for 0.5 h. Then a solution of the corresponding compound **12** in the given solvent was added via syringe, and the hydrogenation was continued. The catalyst was filtered, the filtrate was concentrated and distilled in vacuo.

Method B: A solution of $MeNH_2$ in alcohol was added to a solution of phthalimide **9c** or **d** in alcohol, and the mixture was stirred at r.t. for 10–15 min. Unreacted $MeNH_2$ and solvent were removed, and the residue was purified by bulb-to-bulb distillation.

17-Aminoheptadecyltrimethoxysilane **(13a)**:

Method A: From **12a** (2.75 g, 4.45 mmol) in EtOAc (5 mL), MeOH/EtOAc (100:15 mL); reaction time 20 h; yield: 962 mg (58%); colorless oil, bp 135°C/0.01 Torr.

^{1}H NMR ($CDCl_3$): δ = 0.56–0.72 (2H, m, 1-H), 1.02–1.58 (32H, m, 2-16-H, NH_2), 2.68 (2H, t, $J_{17,16}$ = 6.8 Hz, 17-H), 3.57 (9H, s, OCH_3).

Method B: From **9c** (505 mg, 1.0 mmol), $MeNH_2$ (10 mL, 8.03 M in MeOH) and MeOH (5 mL); yield: 198 mg (53%).

17-Aminoheptadecyltriethoxysilane **(13b)**:

Method A: From **12b** (1.07 g, 1.62 mmol) in EtOH (5 mL), EtOH (25 mL); further addition of catalyst after 7 h; reaction time 24 h; yield: 296 mg (44%); colorless oil; bp 140°C/0.01 Torr.

^{1}H NMR ($CDCl_3$): δ = 0.58–0.70 (2H, m, 1-H), 1.00–1.61 (41H, m, 2-16-H, CH_3, NH_2), 2.68 (2H, t, $J_{17,16}$ = 6.9 Hz, 17-H), 3.82 (6H, q, J = 7.0 Hz, OCH_2).

Method B: From **9d** (720 mg, 1.31 mmol), $MeNH_2$ (20 mL, 8.03 M in EtOH) and EtOH (5 mL); yield: 330 mg (60%).

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