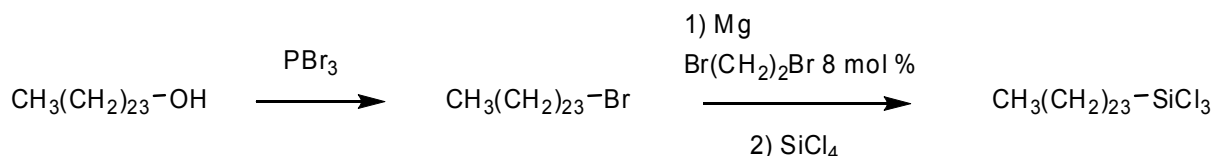


Supplementary Information

Synthesis of *n*-tetracosyltrichlorosilane

Chemicals. 1-tetracosanol (99 %), phosphorus tribromide (99 %), anhydrous hexamethylphosphoramide (99 %), anhydrous tetrahydrofuran (99.9%), silicon tetrachloride (99 %), magnesium (granular, 98%), 1,2-dibromoethane (98 %) were purchased from Sigma Aldrich. Chemicals were used as received without further purification except magnesium that was cleaned with diluted hydrochloric acid, washed with acetone then dried overnight in an oven at 120 °C. Glassware was dried in oven at 120 °C overnight prior to use.

¹H, ¹³C and ²⁹Si NMR spectra were recorded with Avance 300 or Avance 400 Bruker instruments. Depending on the instrument, ¹H NMR spectra were recorded at 300.1 or 400.3 MHz, ¹³C NMR spectra at 75.4 or 100.6 MHz and ²⁹Si at 79.5 MHz. Chemical shifts of NMR spectra are reported in ppm and referenced to tetramethylsilane.



Scheme 1.

1-bromotetracosane was synthesized from 1-tetracosanol similarly to procedure developed by Pomonis *et al.* for 1-bromodocosane (*J. Labelled Comp. Rad.*, 1987, **24**, 1077).

PBr₃ (18.3 mmol, 5 g) was added dropwise over 60 min to a stirred solution of 1-tetracosanol (13.9 mmol, 5 g) in dry HMPA (30 mL) at 50°C. The mixture was heated at 80°C for 4 h then stirred for an additional 60 h at room temperature. The medium was hydrolyzed in 400 mL of crushed ice. The solid was filtered, dried at room temperature then recrystallized from methanol in the presence of charcoal. 1-bromotetracosane (3.5 g, 8.4 mmol) was obtained in 60 % yield. ¹H NMR (300 MHz; CDCl₃; Me₄Si; 20°C) : δ_H(ppm) 0.88 (3H, t, ³J_{CH} = 6.72 Hz, CH₃), 1.25 (40H, m, CH₂), 1.39 (2H, t, ³J_{CH} = 7.23 Hz, CH₂), 1.85 (2H, quint, ³J_{CH} = 7.12 Hz, CH₂), 3.41 (2H, t, ³J_{CH} = 6.87 Hz, CH₂). ¹³C NMR (75.5 MHz; CDCl₃; Me₄Si; 20°C) : δ_C(ppm) 14.14, 22.71, 28.19, 28.78, 29.37, 29.45, 29.56, 29.71, 31.94, 32.85, 34.10.

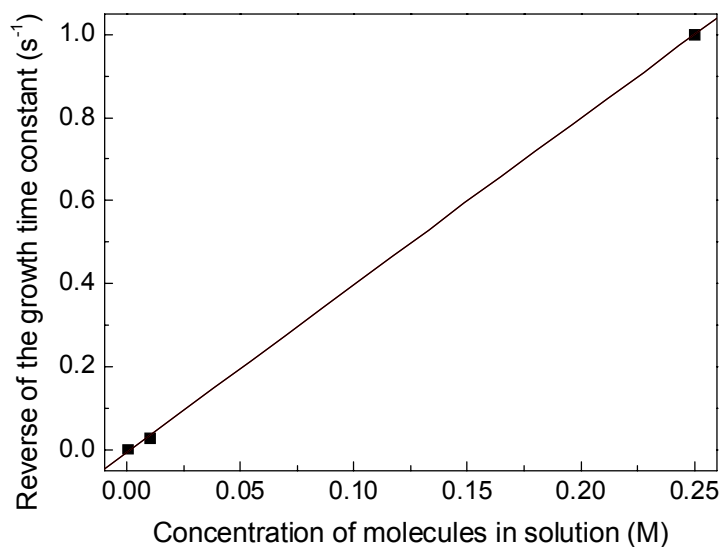
Synthesis of *n*-tetracosyltrichlorosilane was similar to that of long-chain alkenyltrichlorosilanes described by Nguyen *et al.* (*Tetrahedron* 2006, **62**, 647).

1-bromotetracosane (1 g, 2.4 mmol) and precleaned metallic magnesium (147 mg, 6.0 mmol) were added to 20 mL of anhydrous THF under nitrogen. Addition of 40 μL of 1,2-dibromoethane (8 mol % relative to magnesium) and heating at 50°C was necessary to activate the formation of the Grignard. The mixture was stirred overnight at room temperature. The organomagnesium solution was added dropwise under nitrogen into a flask containing tetrachlorosilane (1.1 mL, 9.6 mmol) in dry THF (20 mL). The resulting mixture was stirred overnight at room temperature. The solvent and residual tetrachlorosilane were removed by distillation and the residue was triturated under nitrogen with anhydrous hexane (3 × 20 mL). The supernatant solution was collected then the solvent was evaporated.

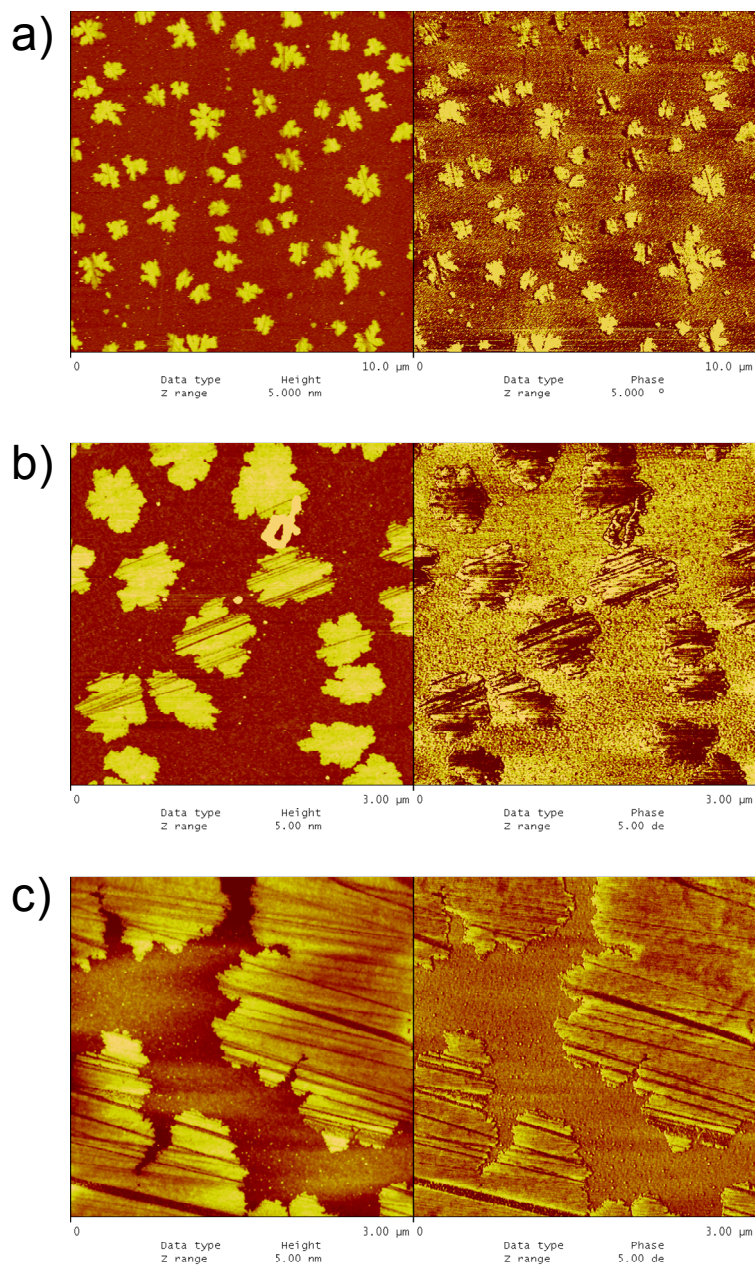
Purification of the residue by bulb-to-bulb vacuum distillation (fraction in the range 200-250°C / 0.1 Torr) afforded *n*-tetracosyltrichlorosilane as a white wax (0.65 g, 57 %).

^1H NMR (400.3 MHz; C_6D_6 ; Me_4Si ; 20°C) : δ_{H} (ppm) 0.88-0.95 (5H, m, CH_3CH_2), 1.07 (2H, quint, $^3J_{\text{CH}} = 3.54$ Hz, CH_2), 1.20 (2H, m, CH_2), 1.28-1.39 (40H, m, CH_2). ^{13}C NMR (100.6 MHz; C_6D_6 ; Me_4Si ; 20°C) : δ_{C} (ppm) 14.14, 22.22, 22.89, 23.93, 29.05, 29.54, 29.60, 29.81, 29.88, 29.91, 29.98, 31.74, 32.11. ^{29}Si NMR (79.5 MHz; C_6D_6 ; Me_4Si ; 20°C) : δ_{Si} (ppm) 13.51 (s, SiCl_3).

Reverse of the growth time constant of C_{18} SAM grown at LT-HH as a function of the concentration of the C_{18} solution used (■). Solid line represents the linear fit with a slope of $\sim 4 \pm 0.4 \text{ s}^{-1} \cdot \text{M}^{-1}$



Topography (left) and Phase (right) Tapping ModeTM AFM images of incomplete C₃₀ SAMs grown at various conditions of temperature and humidity: a) HT-HH (20 s), b) LT-LH (30 s), c) LT-HH (45 s)



Characteristic parameters (thickness, water and hexadecane contact angles) measured on the final monolayers of all molecules for all the conditions

		C₁₆	C₁₈	C₂₀	C₂₄	C₃₀
LT-LH	thickness (Å)		23.9±1.3	28.1±1.1	33.2±1.0	38
	θ _{H₂O} (°)		110.8±3	111.9±0.3	111.2±0.8	106.7
	θ _{HD} (°)		41.9±0.6	42.0±0.1	-	NM
LT-HH	thickness (Å)	23	25	28.1±1.1	32.6±0.6	41.3±1.5
	θ _{H₂O} (°)	108.8±0.2	112.0±0.3	110.8±0.8	112.0±1.2	107.4±0.5
	θ _{HD} (°)	40.8±0.2	41.2±0.1	42.4±0.4	-	NM
HT-LH	thickness (Å)	22.6±0.1	25	29		42±1
	θ _{H₂O} (°)	109.4±0.2	111	111.7		105.3±0.6
	θ _{HD} (°)	41.6±0.4	41.8	41.9		NM
HT-HH	thickness (Å)	22.1±0.8	25±1	27.5±1.5	33.0	41.1±3
	θ _{H₂O} (°)	112.9±0.5	111.9±0.9	110.5±2.2	113.2±0.3	107.6±1.5
	θ _{HD} (°)	42±0.7	40.9±0.4	41.5±0.5	41.5±0.4	NM
Theoretical thickness (Å)		23.7	26.2	28.7	33.8	41.3

Table 2. Thickness and contact angle values for all molecules in all conditions, given for full monolayers, *i.e.* a silanisation time of 1.5 h. NM stands for non measurable value.