

Supporting Information for “Functionalization of glass substrates: Mechanistic insights into the surface reaction of trialkoxysilanes.”

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Experimental Methods:

Unless otherwise noted, reagents were used without further purification. All reactions were run under an argon atmosphere in dry glassware. Trimethoxysilane (95%), Karstedt's catalyst (3% platinum(0) in tetramethyldivinyldisiloxane), *m*-xylene (anhydrous, +99%), and toluene (91.5%, ACS) were obtained from Sigma-Aldrich, 1-eicosene from TCI America, triisopropoxysilane from Gelest, Inc., and flash silica gel 60, 230-400 mesh from Sorbent technologies. Dry tetrahydrofuran (THF) was used from J. T. Baker Cycletainers™. Eicosene was fractionally distilled under reduced pressure prior to use. Glass substrates were cut from Fisherbrand™ plain precleaned microscope slides.

¹H NMR and ¹³C NMR spectra were obtained on a Varian 300 MHz NMR spectrometer. Chemical shifts are reported in ppm relative to CHCl₃ at $\delta = 7.26$ (¹H NMR) and $\delta = 77.23$ (¹³C NMR). Mass spectra were obtained using a Kratos MS-50 mass spectrometer (Kratos, Manchester, England). Plasma oxidation was carried out using a Diener Electronic Femto plasma etcher at 50% power with oxygen gas (6 L / min). Infrared spectra were collected on a Perkin-Elmer Spectrum BX FT-IR spectrometer.

Eicosyltrimethoxysilane (1). 1-Eicosene (0.454 g, 1.62 mmol) was dissolved in dry THF (15.0 mL) and trimethoxysilane (1.09 g, 9.72 mmol, 1.20 mL) was added to the reaction mixture. A catalyst solution was prepared by dissolving Karstedt's catalyst (15 mol%, 0.10 mL) in dry *m*-xylene (0.80 mL),

followed by trimethoxysilane (0.10 mL). The catalyst solution was allowed to react with the trimethoxysilane until gas evolution ceased (~2 min). The resulting catalyst solution was pale yellow. An aliquot (0.25 mL) of catalyst solution was added to the reaction mixture and the reaction mixture was refluxed under argon. After refluxing for 30, 60 and 90 minutes, additional aliquots of trimethoxysilane (5.70 mmol, 0.7 mL) and catalyst solution (0.25 mL) were added. The reaction mixture was purified by flash chromatography on silica gel with elution using chloroform to afford a colorless oil (0.157 g, 0.390 mmol, 24%). ^1H NMR (300 MHz, CDCl_3): δ 3.57 (s, 9H), 1.10-1.30 (m, 36H), 0.88 (t, 3H, J = 6.6 Hz), 0.65 (m, 2H) ppm. ^{13}C NMR (300 MHz, CDCl_3): δ 50.78, 33.45, 32.21, 29.98, 29.83, 29.64, 29.55, 22.98, 22.88, 14.41, 9.42 ppm. MS (FAB): m/z calcd. for $\text{C}_{23}\text{H}_{50}\text{O}_3\text{Si}$ ($M + \text{H}$): 403.4, found 403.3.

Eicosyltriisopropoxysilane (2). 1-Eicosene (1.11 g, 3.97 mmol) was dissolved in dry THF (15.0 mL) and triisopropoxysilane (5.69 mmol, 1.45 mL) was added to the reaction mixture. A catalyst solution was prepared by dissolving Karstedt's catalyst (15 mol%, 0.10 mL) in dry *m*-xylene (0.80 mL), followed by triisopropoxysilane (0.10 mL). The catalyst solution was allowed to react with the triisopropoxysilane until gas evolution ceased (~2 min). The resulting catalyst solution was dark yellow. An aliquot (0.25 mL) of catalyst solution was added to the reaction mixture and the reaction mixture was refluxed under argon. After refluxing for 30, 60 and 90 minutes, additional aliquots of triisopropoxysilane (5.69 mmol, 1.45 mL) and catalyst solution (0.25 mL) were added. The reaction was allowed to proceed for 72 hours and purified by flash chromatography on a silica gel with stepwise elution using 9:1 hexanes/chloroform followed by 1:1 hexanes/chloroform to afford a viscous, colorless oil (0.370 g, 0.767 mmol, 19%). ^1H NMR (300 MHz, CDCl_3): δ 4.20 (septet, 3H, J = 10.5 Hz), 1.10-1.30 (m, 36H), 1.19 (d, 18H, J = 10.0 Hz), 0.88 (t, 3H, J = 6.6 Hz), 0.58 (m, 2H) ppm. ^{13}C NMR (300 MHz, CDCl_3): δ 65.03, 32.59, 32.21, 29.98, 29.94, 29.87, 29.65, 29.55, 23.24, 22.97, 14.40, 12.24 ppm. MS (FAB): m/z calcd. for $\text{C}_{29}\text{H}_{62}\text{O}_3\text{Si}$ ($M + \text{H}$): 486, found 485.4.

Glass Substrate Preparation. Microscope slides were cut into 2.5 cm x 2.5 cm squares, cleaned in boiling methanol (3 times, 1 min) and dried with air. The slides were then plasma oxidized 5 minutes per side, rinsed with absolute ethanol, and dried with air. Clean slides were used immediately.

Monolayer Preparation. Substrates were soaked for 30 to 90 seconds in a THF containing monomer (5.0 mM). After soaking, excess solution was removed from substrates and the substrates were allowed to dry at room temperature. The substrates were then thermally annealed for 15 min at 150°C and rinsed sequentially with THF, methylene chloride, absolute ethanol, and water. Additional coatings were applied by repeating the steps described above.

Infrared Data Calculation. Single beam transmission spectra were collected as an average of 64 scans between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} and a data spacing of 2 cm^{-1} . Background spectra were obtained from clean, thermally annealed glass substrates. Percent transmission was calculated by dividing the sample spectrum by the background spectrum. Baseline correction was performed by the subtraction of the best-fit line obtained using the data from 3100-3050 cm^{-1} and 2750-2700 cm^{-1} . Peak positions were interpreted from the positions of 4 points nearest the maximum. Reported values are an average of 9-18 samples. Error is reported as standard error of the mean.

Monomer	Number of coats	Number of samples	Asymmetric Methylene Stretch			Symmetric Methylene Stretch		
			<i>Position</i>	<i>Width</i>	<i>Intensity</i>	<i>Position</i>	<i>Width</i>	<i>Intensity</i>
C ₂₀ SiOMe ₃ (1)	1	9	2920.6 ± 0.3	23 ± 1	99.58 ±0.02	2851.2 ± 0.1	16.0 ±0.3	99.76 ± 0.01
	2	9	2920.3 ± 0.1	21.3 ± 0.2	99.54 ±0.02	2850.7 ± 0.1	14.9 ± 0.3	99.74 ±0.01
	3	9	2919.8 ± 0.2	20.6 ± 0.3	99.51 ± 0.03	2850.6 ± 0.1	14.4 ± 0.3	99.70 ± 0.02
	4	9	2919.2 ± 0.1	19.6 ±0.2	99.50 ± 0.03	2850.02 ± 0.01	13 ± 1	99.72 ± 0.03
	5	12	2919.0 ± 0.1	20.2 ± 0.2	99.5 ± 0.2	2850.0 ± 0	13.3 ± 0.2	99.66 ± 0.01
	6	11	2918.7 ± 0.1	19.0 ± 0.3	99.5 ± 0.1	2850.05 ± 0.04	13.2 ± 0.2	99.66 ± 0.03
C ₂₀ Si(OPr) ₃ (2)	1	9	2922.3 ± 0.2	19 ± 1	99.87 ± 0.01	2852.1 ± 0.1	12.0 ± .3	99.90 ± 0.01
	2	7	2922.6 ± 0.3	16 ± 1	99.50 ± 0.08	2852.1 ± 0.1	19 ± 2	99.64 ± 0.03
	3	8	2923.0 ± 0.4	23 ± 1	99.88 ± 0.02	2852.9 ± 0.4	16 ± 1	99.94 ± 0.01
	4	7	2922.0 ± 0.2	26 ± 3	99.90 ± 0.01	2851.6 ± 0.1	23 ± 2	99.95 ± 0.01
	5	7	2923.2 ± 0.4	20 ± 1	99.84 ± 0.01	2854.0 ± 1	19 ± 1	99.91 ± 0.01
	6	8	2923.3 ± 0.3	22 ± 1	99.91 ± 0.01	2850.7 ± 0.4	17 ± 1	99.95 ± 0.01

Table S1: Average band positions, widths, and intensities of asymmetric and symmetric methylene stretches for eicosyltrimethoxysilane (1) and eicosyltriisopropoxysilane (2) SAMs on glass. Peak position and width are reported in inverse centimeters (cm⁻¹), peak intensity a percent transmission (%T), and error as standard deviation.

Coats	Silane	n	Asym. methylene stretch			Sym. methylene stretch		
			<i>Position</i>	<i>Width</i>	<i>Intensity</i>	<i>Position</i>	<i>Width</i>	<i>Intensity</i>
1	1	18	2922.9 ± 0.2	36 ± 3	99.89 ± 0.02	2852.6 ± 0.1	30 ± 4	99.91 ± 0.02
2	2	17	2922.1 ± 0.1	22 ± 1	99.80 ± 0.02	2851.8 ± 0.1	15 ± 1	99.86 ± 0.02
3	2	18	2921.4 ± 0.1	22 ± 1	99.69 ± 0.02	2851.8 ± 0.1	15 ± 1	99.84 ± 0.01
4	2	18	2921.4 ± 0.2	21.0 ± 0.5	99.80 ± 0.02	2851.9 ± 0.1	15.0 ± 0.5	99.86 ± 0.01
5	2	9	2920.9 ± 0.2	22.0 ± 0.3	99.67 ± 0.02	2851.6 ± 0.1	15 ± 1	99.81 ± 0.01

Table S2: Average band positions, widths, and intensities of asymmetric and symmetric methylene stretches for SAMs formed from 1 coating of eicosyltriisopropoxysilane (1) on glass then 4 subsequent coatings of eicosyltrimethoxysilane (2). The table is organized by coating number and the monomer used for that coating. Peak position and width are reported in inverse centimeters (cm^{-1}), peak intensity as percent transmission (%T), and error as standard deviation. The number of samples is represented by *n*.