Supporting Information

Covalent Surface Modification of Silicon Oxides with Alcohols in Polar Aprotic Solvents

Supplementary data for Covalent Surface Modification of Silicon Oxides with Alcohols in Polar Aprotic Solvents. Lee, A.W.H.; Gates, B.D., Langmuir, 2017, 33 (35), 8707-8715. https://doi.org/10.1021/acs.langmuir.7b00820

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This research was supported in part by the Natural Sciences and Engineering Research Council (NSERC) of Canada (Grant No. 1077758), the Canada Research Chairs Program (B.D. Gates, Grant No. 950-215846), and MNT Financial Assistance (CMC Microsystems, MNT Grant No. 4582). This work made use of the 4D LABS (www.4dlabs.ca) shared facilities supported by the Canada Foundation for Innovation (CFI), British Columbia Knowledge Development Fund (BCKDF), Western Economic Diversification Canada, and Simon Fraser University.

Formation of Alcohol Based Monolayers in Other Polar Aprotic Solvents

The formation of monolayers derived from 1-octanol was evaluated in a variety of additional polar aprotic solvents. These solvents were chosen based on their chemical structure and accessibility. Physical properties considered for potential solvents included their melting and boiling points. For example, the boiling point should be at least 150 °C to avoid significant evaporation of the solvent during the reaction. Solvents chosen for this comparative study included propylene carbonate (Sigma Aldrich, 99%, CAS no. 108-32-7), ethylene carbonate (Sigma Aldrich, 98%, CAS no. 94-49-1), diethylene glycol diethyl ether (Sigma Aldrich, 98%, CAS no. 112-36-7), and dibasic ester (DBE, Sigma Aldrich, dibasic ester mixture). Hydrophobicity of the substrate was evaluated at different time points of the reaction (e.g., 1, 3, 5, 24, 48, or 72 h) using a series of water contact angle (WCA) measurements (Figure S1). The reaction temperature (i.e. 100 °C) and concentration of 1-octanol (600 mM) were kept constant for each reaction.

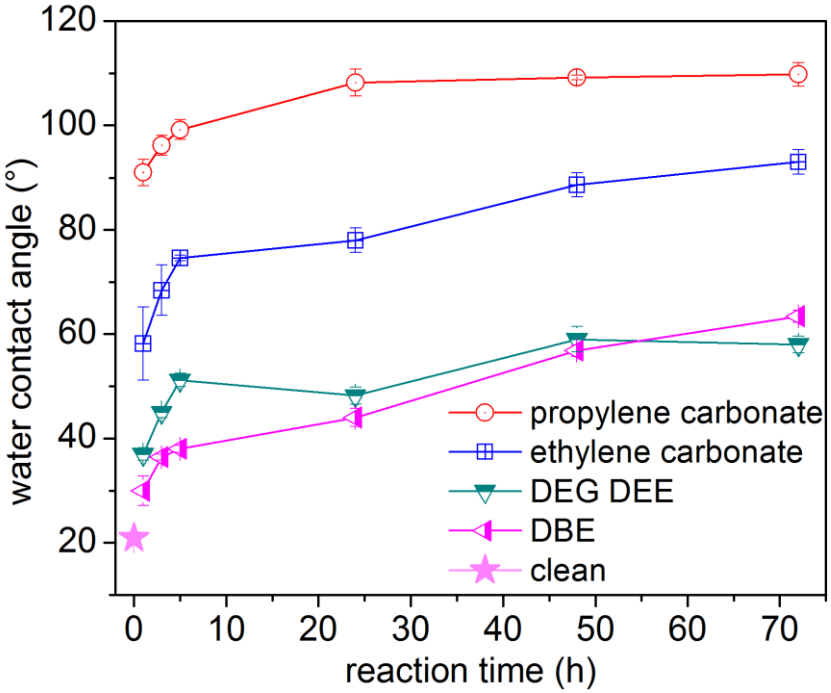

Figure S1. Water contact angle measurements for silicon substrates after reacting these at 100 °C in 600 mM solutions of 1-octanol in various solvents as indicated [i.e. propylene carbonate, ethylene carbonate, diethylene glycol diethyl ether (DEG DEE), and dibasic ester (DBE)].

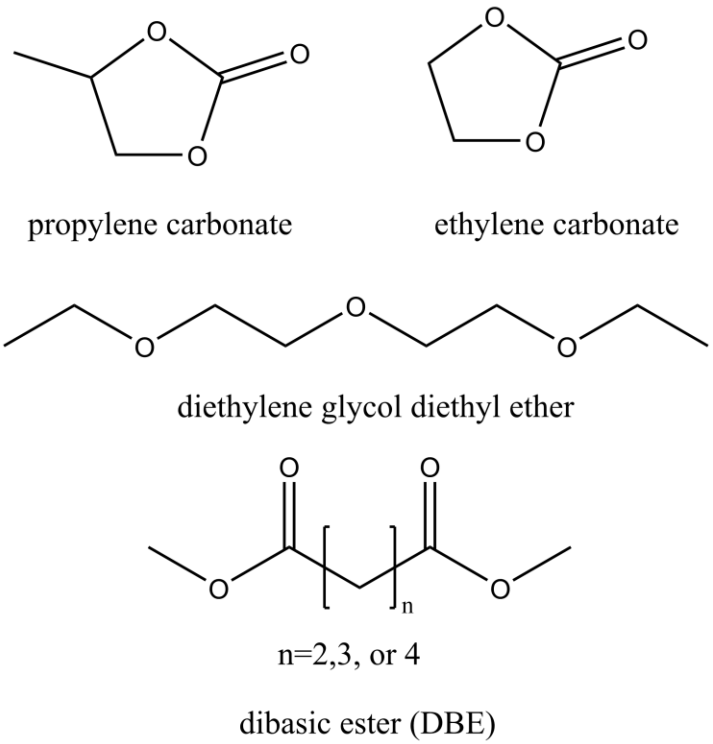

Figure S2. Chemical structures of polar aprotic solvents evaluated for the reaction of 1-octanol with piranha cleaned silicon substrates.

Formation of Alcohol Based Monolayers in Propylene Carbonate

Results are tabulated below for the water contact angle values reported in Figure 3.

Table S1. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 600 mM 1-Octanol in Propylene Carbonate at a Reaction Temperature of 50 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	58	1.5	54	2.2	4
3	70	1.5	64	1.0	6
5	82	3.1	78	2.2	4
24	102	2.7	99	1.7	3
48	107	1.9	105	1.7	2
72	110	1.5	108	1.0	2

Table S2. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 600 mM 1-Octanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	91	2.5	90	4.0	1
3	96	1.9	94	2.4	2
5	99	1.9	97	1.5	2
24	108	2.6	106	2.4	2
48	109	0.4	108	1.4	1
72	110	2.3	108	1.8	2

Table S3. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 600 mM 1-Octanol in Propylene Carbonate at a Reaction Temperature of 120 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	49	1.6	45	3.1	4
3	75	11	65	5.7	10
5	73	2.9	65	1.9	8
24	92	1.2	74	3.2	18
48	91	1.9	80	3.2	11
72	88	3.9	76	1.3	12

Results are tabulated below for the water contact angle values reported in Figure 5A.

Table S4. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 60 mM 1-Octanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	58	2.1	49	2.6	9
3	73	0.8	70	0.8	3
5	83	2.0	79	3.3	4
24	98	1.1	96	1.4	2
48	98	3.8	94	1.4	4
72	99	1.5	94	1.7	5

Table S5. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 6 mM 1-Octanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	36	1.7	19	6.8	17
3	47	1.6	32	3.5	15
5	47	3.6	28	10.0	19
24	61	2.4	42	4.1	19
48	61	2.6	51	3.0	10
72	67	2.2	65	0.8	2

Results are tabulated below for the water contact angle values reported in Figure 5B.

Table S6. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 600 mM 1-Octanol in Propylene Carbonate with the Additional of 0.6 M Water at a Reaction Temperature of 50 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	37	5.7	19	5.8	18
3	38	2.3	24	2.9	14
5	39	1.6	35	2.6	4
24	63	4.0	64	3.9	-1
48	94	1.5	94	1.4	0
72	95	1.6	92	2.9	3

Table S7. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 600 mM 1-Octanol in Propylene Carbonate with the Additional of 6.0 M Water at a Reaction Temperature of 50 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	25	4.0	5	5.1	20
3	21	1.1	8	4.9	13
5	22	0.5	5	7.9	17
24	12	0.9	5	4.6	7
48	16	1.4	5	3.9	9
72	11	1.5	4	2.9	7

Results are tabulated below for the water contact angle values reported in Figure 6.

Table S8. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 50 mM 1-Dodecanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	68	1.1	67	1.9	2
3	79	1.8	76	1.0	4
5	89	1.1	86	1.0	3
24	100	1.1	95	2.5	5
48	103	2.4	97	2.1	5
72	109	1.1	103	0.8	6

Table S9. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 50 mM 1-Tetradecanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	75	0.5	72	1.7	3
3	95	2.1	91	1.4	4
5	101	2.0	99	1.3	3
24	106	0.8	104	2.1	2
48	110	1.5	108	2.1	2
72	109	1.3	107	1.3	2

Table S10. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 50 mM 1-Hexadecanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	87	1.8	85	2.5	2
3	100	1.7	98	0.8	2
5	105	1.1	103	0.8	2
24	110	0.8	109	1	2
48	110	1.1	107	1.6	2
72	110	0.4	110	0.5	0

Table S11. Water Contact Angle Values for Silicon Oxide Surfaces after Reacting with 50 mM 1-Octadecanol in Propylene Carbonate at a Reaction Temperature of 100 °C

reaction time (h)	average advancing WCA (°)	standard deviation (°)	average receding WCA (°)	standard deviation (°)	hysteresis (°)
1	98	4.0	93	2.1	5
3	103	2.1	99	1.9	5
5	105	2.1	103	1.3	3
24	111	1.2	111	0.6	1
48	110	0.9	109	1.0	1
72	111	1.1	111	1.3	0

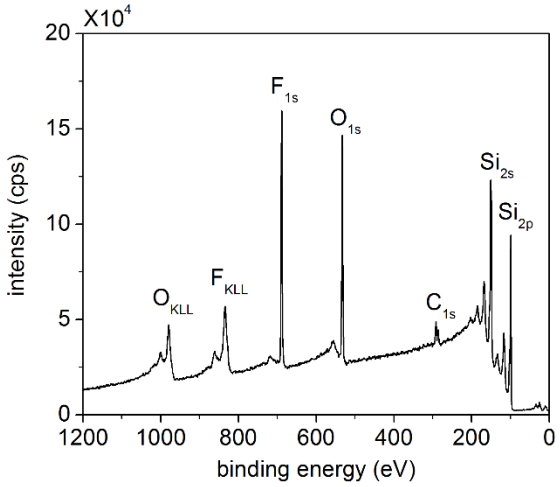

Figure S3. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol dissolved in propylene carbonate at 50 °C for 24 h.

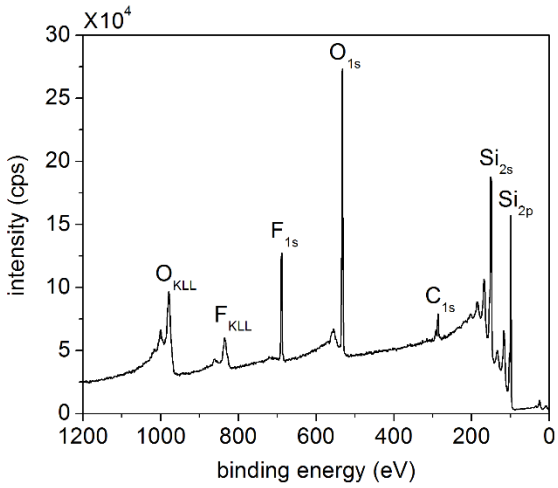

Figure S4. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with Zonyl fluorosurfactant dissolved in propylene carbonate at 50 °C for 24 h.

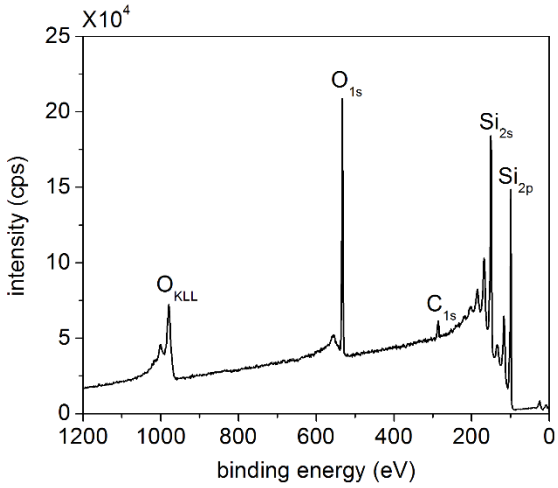

Figure S5. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with glycolic acid dissolved in propylene carbonate at 50 °C for 24 h.

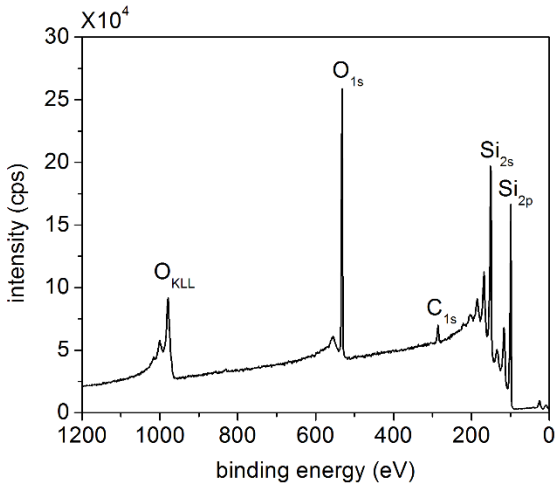

Figure S6. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 5-hydroxypentanal dissolved in propylene carbonate at 50 °C for 24 h.

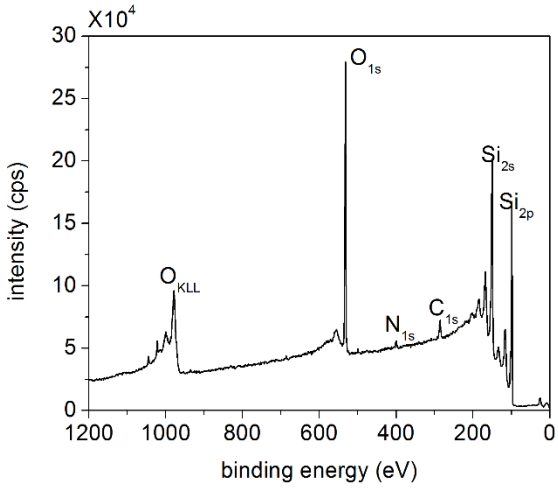

Figure S7. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with adenosine 5'-monophosphate dissolved in propylene carbonate at 50 °C for 24 h.

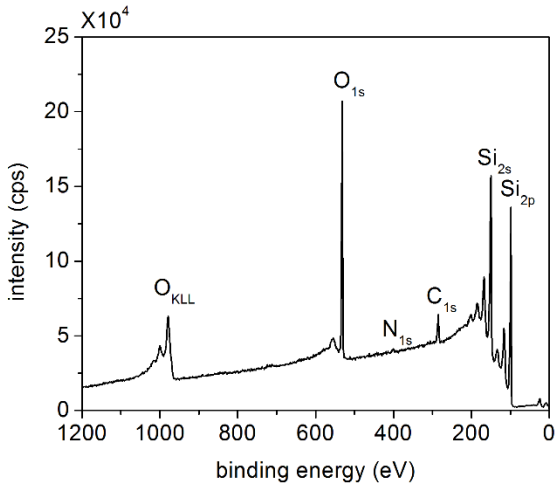

Figure S8. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with thiamine dissolved in propylene carbonate at 50 °C for 24 h.

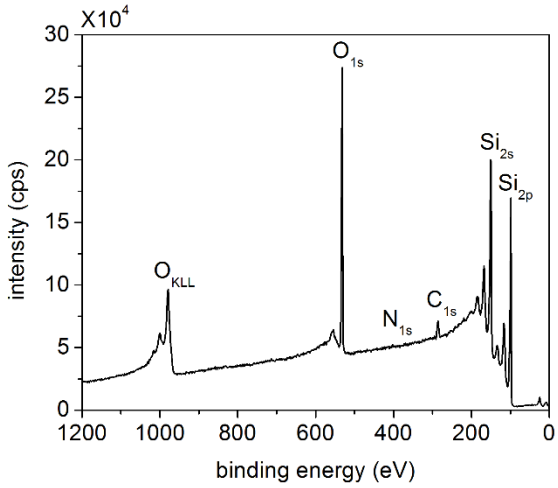

Figure S9. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with choline chloride dissolved in propylene carbonate at 50 °C for 24 h.

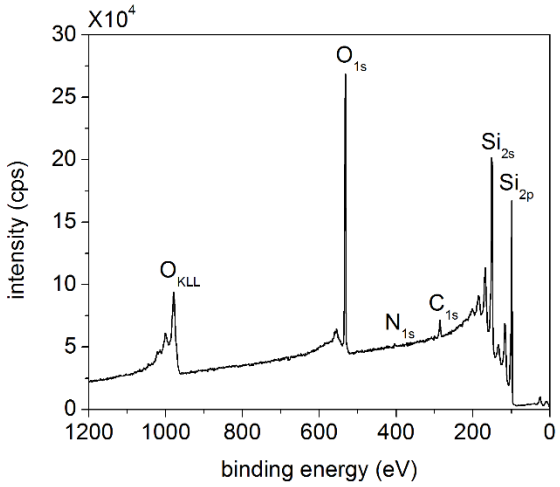

Figure S10. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 2-dimethylaminoethanol dissolved in propylene carbonate at 50 °C for 24 h.

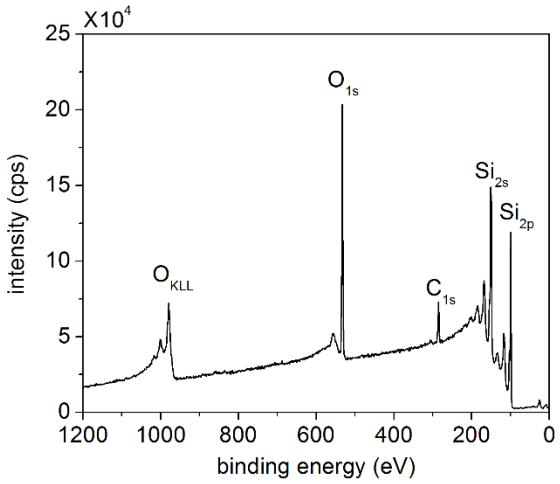

Figure S11. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 600 mM 1-octanol dissolved in propylene carbonate at 50 °C for 72 h.

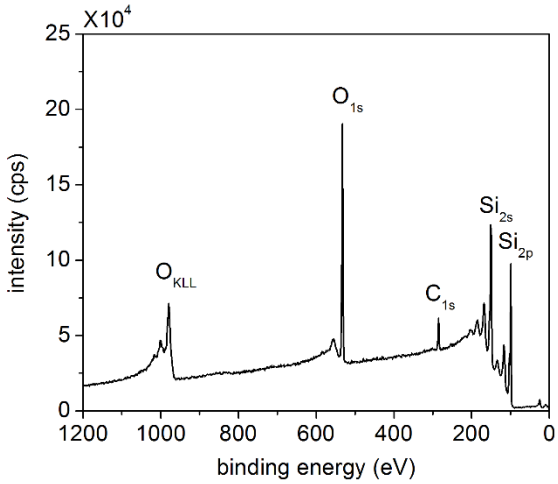

Figure S12. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 600 mM 1-octanol dissolved in propylene carbonate at 100 °C for 72 h.

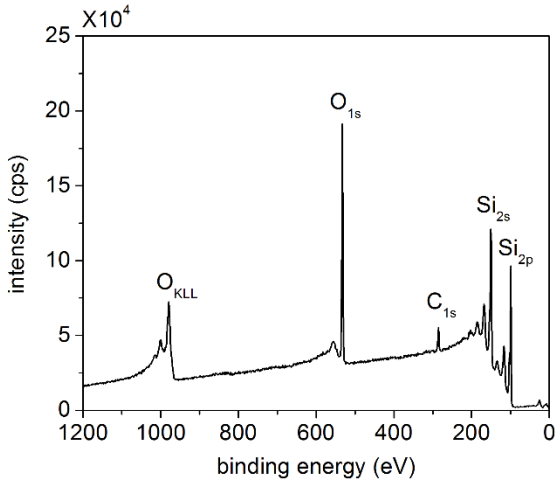

Figure S13. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 600 mM 1-octanol dissolved in propylene carbonate at 120 °C for 72 h.

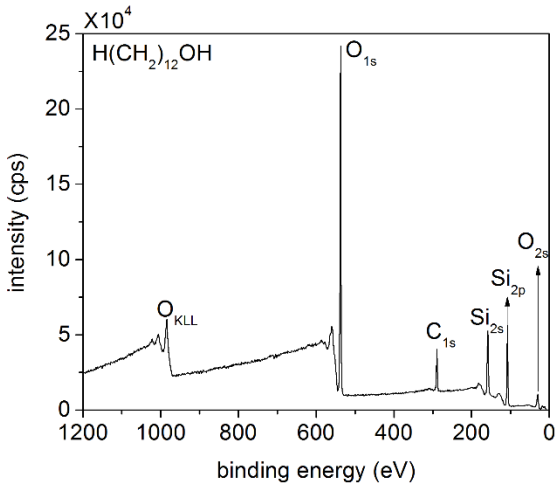

Figure S14. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 0.05 M 1-dodecanol dissolved in propylene carbonate at 100 °C for 72 h.

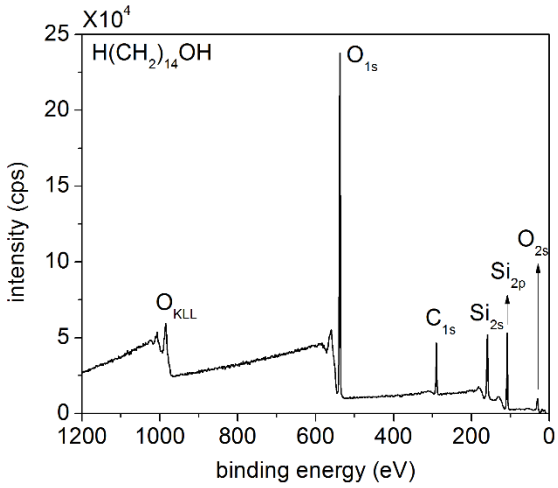

Figure S15. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 0.05 M 1-tetradecanol dissolved in propylene carbonate at 100 °C for 72 h.

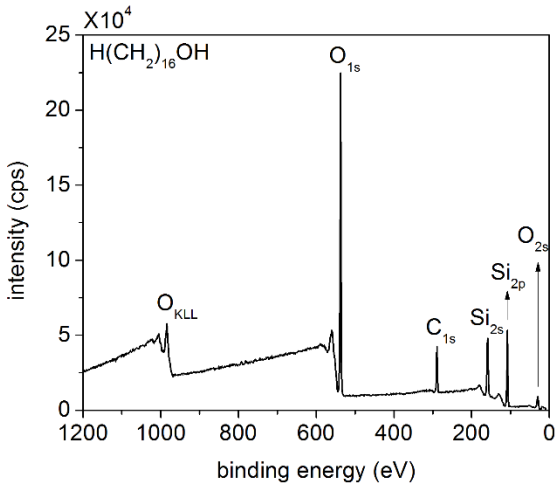

Figure S16. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 0.05 M 1-hexadecanol dissolved in propylene carbonate at 100 °C for 72 h.

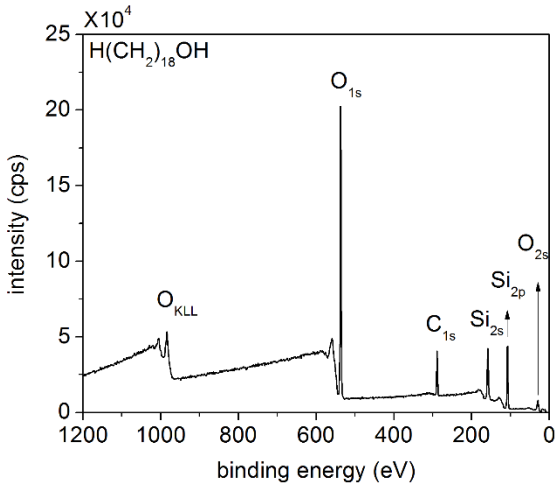

Figure S17. Survey scan obtained by XPS for a piranha cleaned silicon substrate after reacting with 0.05 M 1-octadecanol dissolved in propylene carbonate at 100 °C for 72 h.