SUPPORTING INFORMATION

Single ether group in a glycol-based ultra-thin layer prevents surface fouling from undiluted serum

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I. Materials and methods

The following includes procedures for surface modifier synthesis, quartz cleaning, organic film formation and EMPAS measurements as well as film characterization by angle-resolved X-ray photo-electron spectroscopy (XPS) and contact angle goniometry. Glassware for organic film formation was pre-treated overnight with a 1/20 (v/v) solution of octadecyltrichlorosilane in anhydrous toluene. Quartz discs (AT-cut, 13.5 mm in diameter and 83 μm thick, 20 MHz fundamental frequency) were purchased from Laptech Precision Inc., Bowmanville, ON, Canada. Goat serum (45-75 mg protein/mL (Biuret)) and Dulbecco's phosphate buffered saline (PBS, pH = 7.4) were purchased from Sigma-Aldrich®. Other chemicals were also purchased from Sigma-Aldrich® and used as received unless otherwise noted. $H_2PtCl_6 \bullet 6H_2O$ (99.9%) was purchased from Strem Chemicals Inc.®. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer using $CDCl_3$ as the NMR solvent. ^1H and ^{13}C NMR spectra are referenced to the residual solvent peak: 7.27 ppm (^1H) and 77.23 ppm (^{13}C).

II. Surface modifier synthesis

MEG-TFA, MEG-OMe and OTS-TFA (OTS is commercially available from Sigma-Aldrich® and was redistilled prior to use) were prepared by Pt-catalyzed hydrosilylation of the corresponding alkene precursor (**Figure 1**), as follows: in a heavy-walled tube equipped with a magnetic stir bar, alkene precursors (1.0 equiv.) and $H_2PtCl_6 \bullet 6H_2O$ (1.0 mol%) were loaded. The tube was transferred into a glovebox and $HSiCl_3$ (2.0 equiv.) was added to the solution. The tube was tightly fastened then removed from the glovebox. The resulting solution was stirred at room temperature for 20h behind a protecting shield. Purification was achieved by Kugelrohr distillation under high vacuum to provide the desired surface modifier.

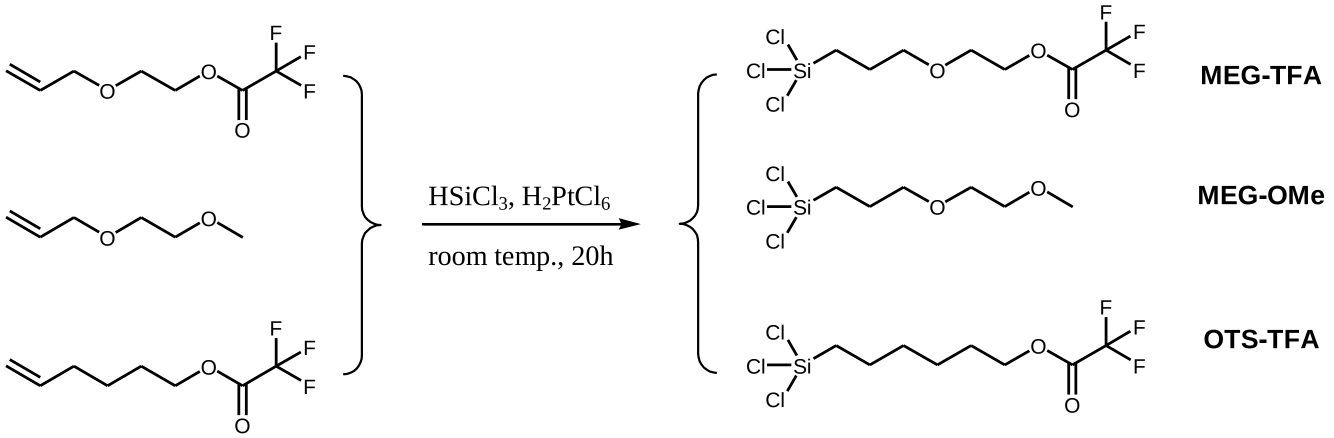

Figure 1 MEG-TFA, MEG-OMe and OTS-TFA surface modifier synthesis.

MEG-TFA:[1] 20.0 mmol scale, 5.46 g (82% yield), colourless oil, bp = 115-120ºC (0.09 Torr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (m, 2H), 3.76 (m, 2H), 3.56 (t, *J* = 6.2 Hz, 2H), 1.85 (m, 2H), 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7 (q, *J* = 42.3 Hz), 114.7 (q, *J* = 284.1 Hz), 71.8, 67.9, 67.0, 22.8, 21.0.

MEG-OMe: 4.5 mmol scale, 0.54 g (47% yield), colourless oil, bp = 90-100ºC (20 Torr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (m, 6H), 3.39 (s, 3H), 1.87 (m, 2H), 1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.1, 71.9, 70.3, 59.3, 22.8, 21.2.

OTS-TFA: 5.0 mmol scale, 1.29 g (78% yield), colourless oil, bp = 130-140ºC (20 Torr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (t, *J* = 6.6 Hz, 2H), 1.77 (m, 2H), 1.62 (m, 2H), 1.52-1.38 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8 (q, *J* = 42.0 Hz), 114.8 (q, *J* = 284.1 Hz), 68.2, 31.4, 28.1, 25.3, 24.4, 22.4.

III. Quartz cleaning procedure

The quartz discs were first sonicated in 20 mL of concentrated dishwashing soap for 30 min. The discs were then copiously rinsed with hot water followed by distilled water then gently dried with forced air. Next, the discs were individually soaked in 6 mL of Piranha solution (3:1 (v/v) mixture of H_2SO_4 and 30% H_2O_2) pre-heated to 90°C using a water bath (*CAUTION: Piranha solutions are corrosive. Handle with care*). After 30 min, the discs were thoroughly rinsed with distilled water (3x) followed by spectrograde methanol (3x). The discs were next sonicated in spectrograde methanol for 2 min then individually transferred into vials, which were subsequently placed in an oven maintained at 150°C for drying. After 2 h, the vials were rapidly transferred into a humidity-controlled chamber (magnesium nitrate hexahydrate) and set aside overnight.

IV. Organic film formation

MEG-TFA, MEG-OMe, OTS or OTS-TFA surface modifiers (10 μL) were first diluted with anhydrous toluene (10 mL), in a glovebox maintained under inert (N_2) and anhydrous (P_2O_5) atmosphere. The resulting solutions were portioned (1000 μL) in test tubes into which cleaned quartz discs were then individually soaked. The test tubes were then sealed with rubber stoppers, removed from the glovebox, and placed on a spinning plate for 60 min. Next, the discs were thoroughly rinsed with toluene (x3) then sonicated in toluene for 5 min. After a final rinse with toluene, the previous procedure was repeated with

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[1] S. Sheikh, J. C.-C. Sheng, C. Blaszykowski and M. Thompson, *Chem. Sci.*, 2010, **1**, 271.

chloroform. Finally, the discs were rinsed with chloroform (x2) then dried under a gentle stream of N_2. Immediately after, the discs were individually soaked in 3 mL of 1/1 (v/v) solution of methanol and Milli-Q water, overnight at room temperature on a spinning plate. The discs were then rinsed with spectrograde methanol (x3) and dry under a gentle stream of N_2.

V. EMPAS measurements

EMPAS measurements were performed at the ultra-high resonating frequency of 0.94 GHz (47th harmonic). After the standard set-up of EMPAS,[2] bare or film-coated quartz discs were individually inserted into the flow-through chamber and PBS buffer was flown at a rate of 50 μL/min. Once the frequency signal stabilized, 50 μL of undiluted goat serum were introduced into the flow-through system using an injection loop equipped with a low-pressure chromatography valve. Once the serum sample completely passed over the surface, the uninterrupted PBS buffer flow rinsed the surface of any loosely bound material. The frequency signal stabilized again, the experiment was stopped and the frequency shift calculated.

VI. Surface analyses

VI. A. Contact angle measurements

Contact angle measurements (static) were performed in the Department of Chemistry, University of Toronto, Toronto, ON, Canada. The surfaces were analyzed with the KSV contact angle measurement instrument (KSV Instruments Ltd.) and Milli-Q water as the test liquid. Contact angle values were generated using the CAM101 software (**Table 1**).

Surface	**Contact angle**
Cleaned bare quartz	16°
MEG-TFA	90°
MEG-OMe	58°
MEG-OH	30°
OTS-OH	57°
OTS	73°

Table 1 Static contact angle measurements for bare and derivatized quartz surfaces with Milli-Q water.

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[2] S. M. Ballantyne and M. Thompson, *Analyst*, 2004, **129**, 219.

VI. B. XPS analysis

Angle-resolved XPS was performed with a Theta probe ThermoFisher Scientific Instrument (East Grinstead, UK) located at *Surface Interface Ontario*, University of Toronto, Toronto, ON, Canada. The samples were analyzed with monochromated Al Kα X-rays (elliptical spots of 400 μm along the long axis), with take-off angles of 27.5°, 42.5°, 57.5° and 72.5° relative to the normal. The binding energy scale was calibrated to the main C_{1s} signal at 285 eV. Peak fitting and data analysis were performed using *Avantage* software provided with the instrument.

The successful deposition of MEG-TFA surface modifier onto bare quartz and subsequent complete removal of the labile TFA terminal groups was determined following the appearance (respectively the loss) of a peak for fluorine at 689 eV, the one element unambiguously attributable to MEG-TFA, as shown in the following XPS surveys (**Figure 2**). Unlike fluorine however, the signal for carbon (at 285 eV) was not affected by the following mild aqueous treatment, clearly demonstrating that the latter had effectively cleaved the TFA groups without etching the organic backbone from the quartz substrate.

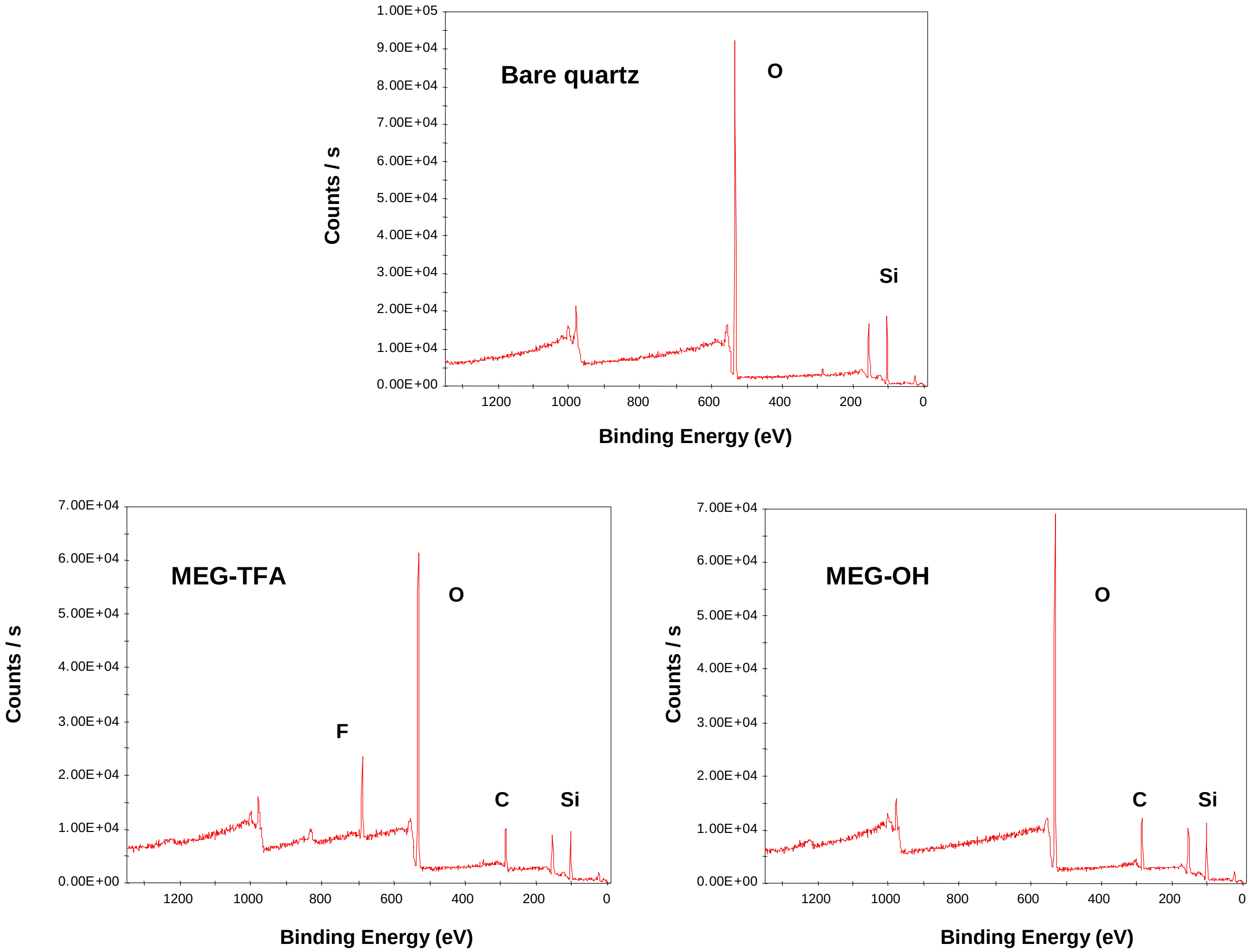

Figure 2 XPS surveys for bare quartz (top), MEG-TFA (bottom left) and MEG-OH (bottom right) films.

Relative atomic percentages and narrow XPS scans for the characteristic elements of MEG-TFA and MEG-OH organic films (fluorine and carbon) along with those for the elements mainly present in quartz (silicon and oxygen) are also available below (**Table 2** and **Figure 3**). Cleaned quartz discs only showed peaks for silicon (Si_{2p} at 102 eV) and oxygen (O_{1s} at 532 eV) as well as unavoidable adventitious carbon (C_{1s} at 285 eV). Upon deposition of MEG-TFA molecules, a signal for fluorine appeared (F_{1s} at 689 eV) and the signals for oxygen and silicon conversely decreased as expected for a now buried, underlying quartz substrate. With respect to carbon, the peaks expected for the TFA head functions (C-O, C=O and CF_3) are also clearly discernible on the narrow scan at ~ 288-295 eV[3] for MEG-TFA but absent for MEG-OH.

Surface	**Analysis angle**	**% C1s 285 eV**	**% F1s 689 eV**	**% O1s 532 eV**	**% Si2p 102 eV**
bare quartz	27.5°	2.6[a]	0.1	36.2	61.1
	42.5°	2.5[a]	0.1	34.2	63.2
	57.5°	3.9[a]	0.1	30.9	65.1
	72.5°	6.9[a]	0.0	30.3	62.8
MEG-TFA	27.5°	20.9	4.2	25.4	49.5
	42.5°	22.6	4.8	22.9	49.7
	57.5°	23.9	4.9	20.0	51.2
	72.5°	23.5	5.9	19.6	51.0
MEG-OH	27.5°	19.9	0.1	27.7	52.3
	42.5°	22.2	0.0	25.0	52.8
	57.5°	24.4	0.6	22.9	52.1
	72.5°	25.8	0.0	21.3	52.9

Table 2 Angle-resolved XPS analysis for bare, MEG-TFA and MEG-OH quartz surfaces. [a] This signal is due to unavoidable adventitious carbon.

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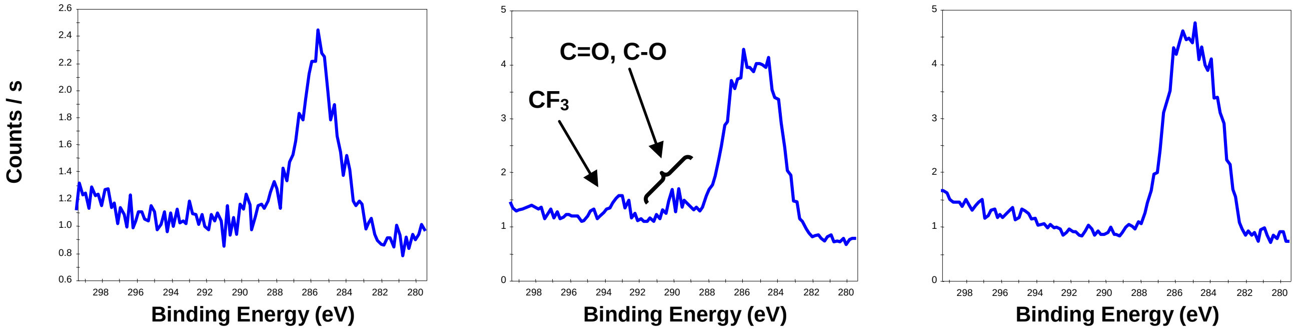
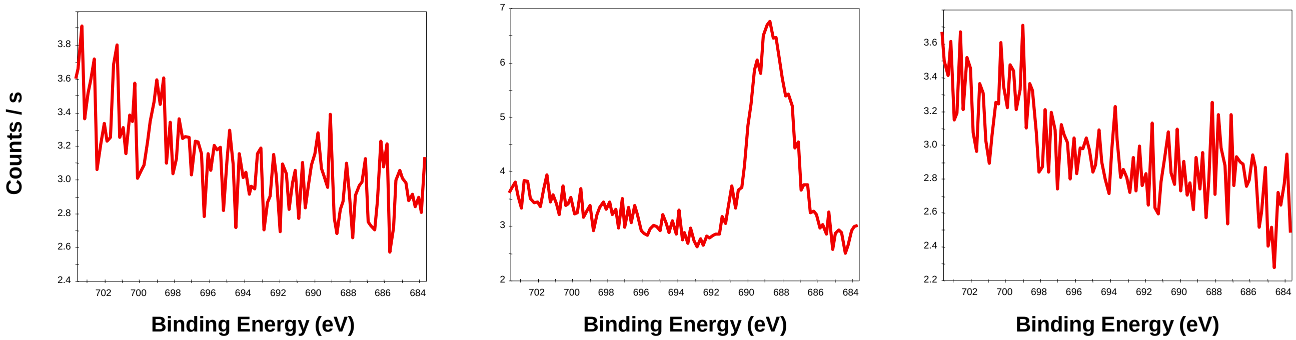
[3] (a) T. Strother, W. Cai, X. Zhao, R. J. Hamers and L. M. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 1205; (b) Q.-Y. Sun, L. C. P. M. de Smet, B. van Lagen, A. Wright, H. Zuilhof and E. J. R. Sudhölter, *Angew. Chem.*, 2004, **116**, 1376.

Bare quartz **MEG-TFA** **MEG-OH**

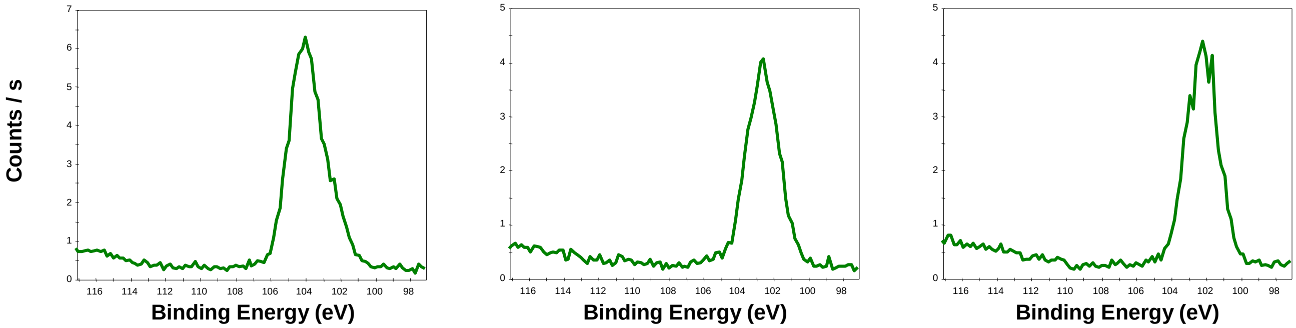
Carbon



Fluorine



Silicon



Oxygen

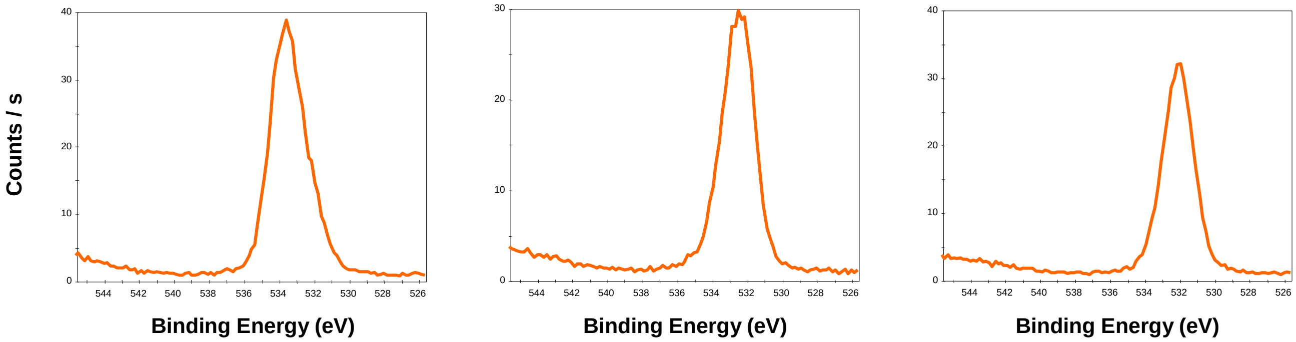


Figure 3 Narrow scans for (top to bottom) carbon, fluorine, silicon and oxygen for (left to right) bare quartz, MEG-TFA and MEG-OH films, at 72.5° relative to the normal (surface analysis).

VI. C. Ellipsometry

Ellipsometry measurements were performed with a HS-190 VASE ellipsometer (J. A. Woollam Co. Inc., Lincoln, Nebraska - USA) located in the McLennan Department of Physics and Institute for Optical Sciences, University of Toronto, Toronto, ON, Canada. The samples were analyzed with a 75W light source high speed monochromator system at 35°, 55° and 75° angles. Curve fitting and data analysis were performed using a Cauchy model (Figure 4) that provided a thickness of 0.51 ± 0.01 nm for MEG-TFA film, with a MSE of 0.47.

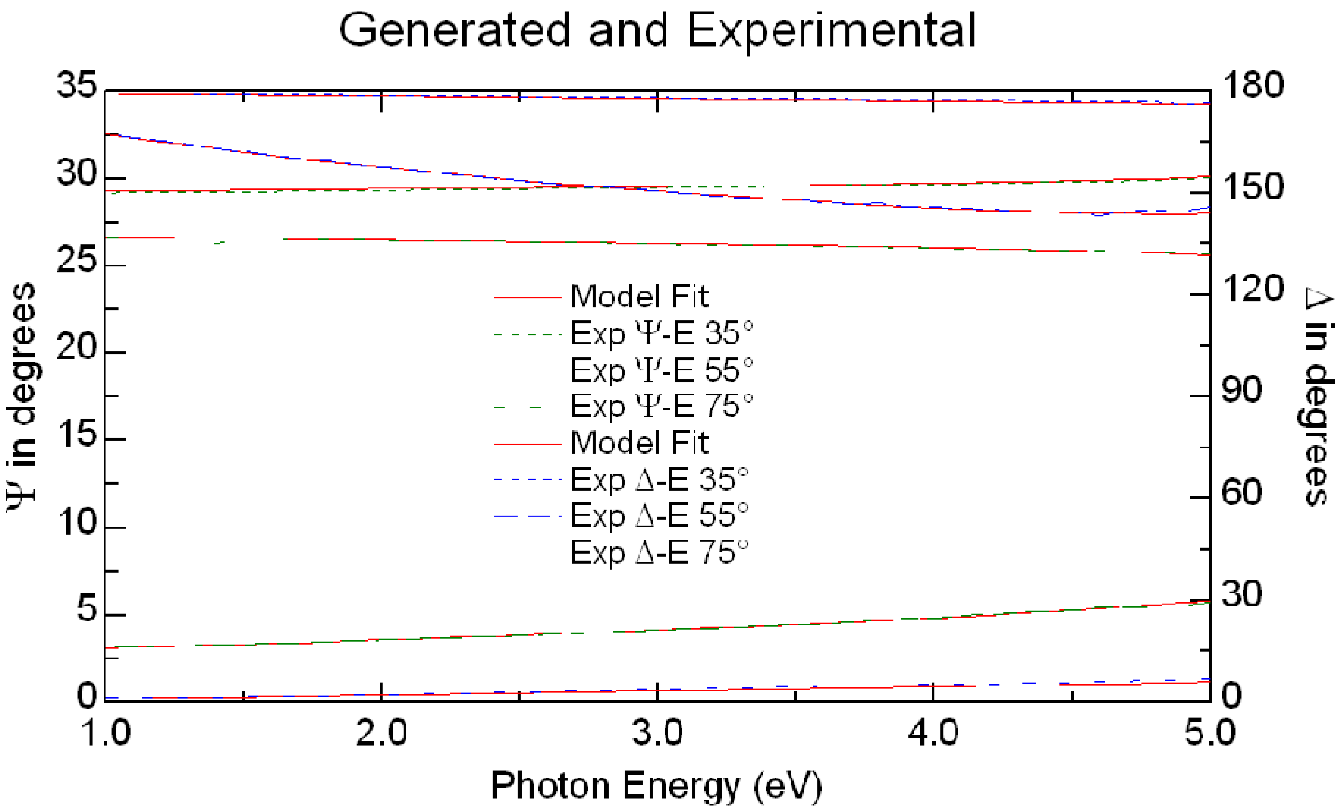
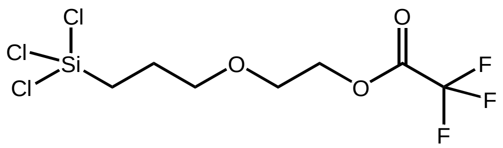


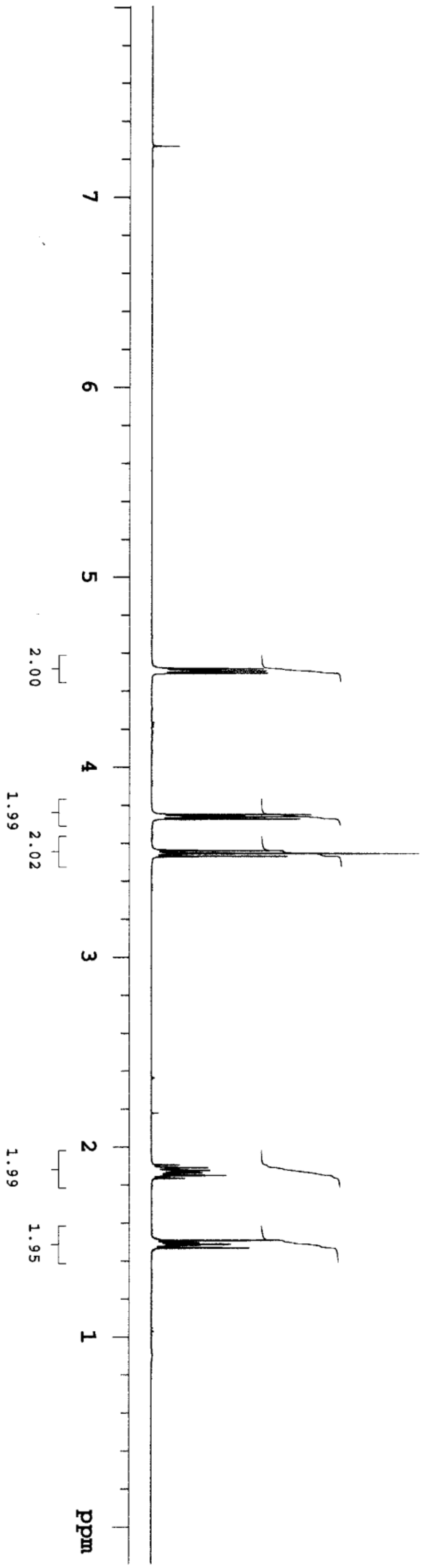
Figure 4 Ellipsometry data and curve fitting using a Cauchy model for MEG-TFA film.

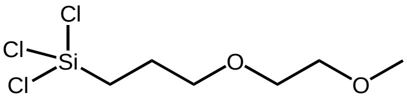
VII. ^{1}H NMR spectra



MEG-TFA

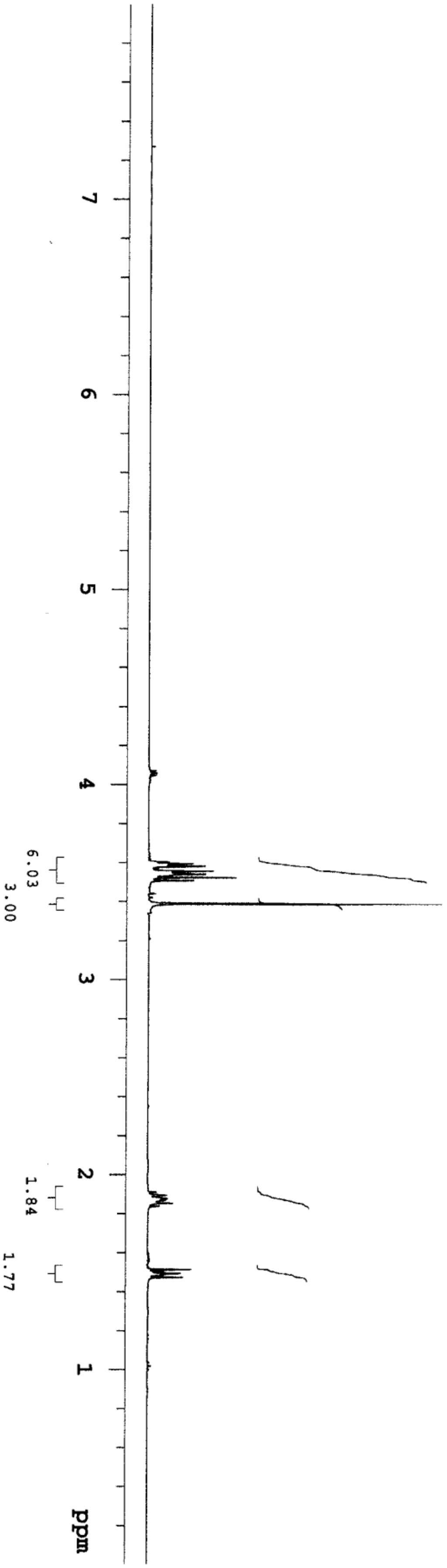
^{1}H NMR (400 MHz, $CDCl_3$)



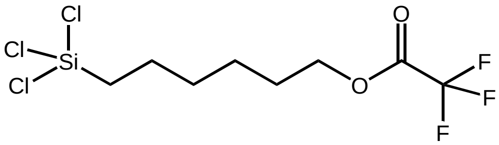


MEG-OMe

^{1}H NMR (400 MHz, $CDCl_3$)



VARIAN



OTS-TFA

^{1}H NMR (400 MHz, CDCl$_3$)