Direct observation of patterned self-assembled monolayers and bilayers on silica-on-silicon surfaces

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Abstract: Self-assembled monolayers (SAMs) of organic molecules are widely employed in surface chemistry and biology, and serve as ultra-fine lithographic resists. Due to their small thickness of only a few nanometers, the analysis of patterned monolayer surfaces using conventional methods requires thorough point-by-point scanning using complicated equipment. In the work reported herein, patterned monolayers are simply and directly observed using a bright-field optical microscope. Features as narrow as 500 nm are properly recognized. The monolayers modify the spectral reflectivity pattern of a silica-on-silicon thin film, and introduce a contrast between bare and monolayer-coated regions of the substrate. The method can also distinguish between regions of single-layer and bi-layer coatings. The observations are supported by calculations, and by control experiments using atomic force microscopy, scanning Raman spectrometry and scanning reflection spectrometry. We show here that chemical reactions leading to the formation of a bi-layer of SAMs correspond to an optical contrast visible to the naked eye. This contrast, in turn, could provide a simple and effective differentiation between monolayers and adsorbed analytes, with possible applications in chemical and/or biological sensing. The method is also applicable to the study of graphene-on-SAM devices.

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References and links


1. Introduction

Self-assembled monolayers (SAMs) are ordered, single-molecular layers of organic materials which may form spontaneously on various surfaces, in solution or in the gas phase [1,2]. These thin films have proven to be powerful tools for controlling surface chemistry and are the basis of applications ranging from sensors [3–5] to controlling surface free energy and adhesion. The patterning of SAMs is of interest for diverse potential applications such as ultra-thin lithographic resists [6], positioning and attachment of different particles [7] and electronic molecular devices [8].

Many methods are routinely used for characterizing the thickness, composition and order of SAMs, such as ellipsometry [9], atomic force microscopy (AFM) [10], Fourier-transform infra-red spectroscopy (FTIR) [11], x-ray photo-electron spectroscopy (XPS) [12], and scanning tunneling microscopy (STM) [13]. Contact angle goniometry measurements are widely used in the estimation of surface free energy of the monolayers [14]. Some of these methods are inherently statistical, and are based on an averaging over large uniform surfaces, whereas others are extremely localized and require a thorough, nanoscale point-by-point sampling. In addition, these observation methods require sophisticated and expensive equipment. Some of them involve meticulous sample preparation, and/or could be destructive to the sample being examined. These characterization methods do not provide a rapid, convenient analysis of patterned SAM-coated surfaces.
Spectral analysis of reflections from thin film layers can resolve changes in optical path length on a sub-nanometer scale [15–19]. Gauglitz and associates employed spectral interferometry to monitor the swelling of thin polymer films exposed to different analytes, as well as antigen-antibody reactions [15]. A review of chemical and biological applications of spectral interferometry point-sensors is provided in [16]. Reflective interferometry was extended to the spatially resolved analysis of SAM patterns on a substrate, in a significant series of works by Rothberg and associates [17–19]. The deposition of molecular films could be observed with sub-Angstrom-level resolution based on relatively large contrast [17–19]. These experiments required polarization control, careful collimation and angular alignment of the interrogating beam, and/or narrow-band optical filtering. The lateral resolution of the measurements was limited to a length scale on the order of tens of microns. The direct imaging of sub-micron SAM patterns using a simple, readily available setup has not yet been reported.

Similar methodology has been applied to the characterization of exfoliated graphene films [20], in which small regions of single-atomic layers must be identified. Over the last few years, several groups reported the direct observation of single-layer graphene using standard, bright-field microscopy, when the films are deposited on silica-on-silicon substrates [21–23]. The thickness of the silica layer is designed to provide wavelength-varying reflectivity within the visible range. The presence of a graphene monolayer slightly modifies the spectral reflectivity pattern. Although small, these spectral variations can be recognized by the naked eye [20,24]. The technique can also distinguish between regions containing different numbers of graphene layers [20,24]. The direct observation of nanometric coatings of lossy materials using visible light was recently reported as well [25]. A similar technique was used by Daaboul et al. in the sizing of micro-spheres with 70-200 nm diameters on a silica-on-silicon substrate [26], and in the detection and classification of viruses of a similar size [27]. However, the method had not yet been applied to the examination of patterned organic SAMs. Several recent reports have employed buffer layers of organic SAMs to reduce intrinsic doping in graphene and MoS$_2$ films, and to improve the performance of graphene-based devices [28–35]. The deposition of organic SAMs on top of graphene is also being investigated [36–39]. The observation of patterned SAMs adds an important capability to the fabrication and study of such hybrid SAM-graphene structures.

In this work, we employ reflective interferometry in the analysis of patterned SAMs on a silica-on-silicon substrate. We show that the method, which was previously proposed for graphene that is characterized by particularly pronounced light-matter interactions, is also applicable to organic SAMs. 500 nm-wide features are recognized in a standard bright-field microscope image, operating at normal incidence without polarization control or narrowband spectral filtering. The interferometry contrast is sufficient to resolve single layers and bilayers of SAM-forming molecules using a simple CMOS imaging sensor. The direct observation is compared with, and validated by, AFM analysis, Raman scattering microscopy and position-dependent reflection spectrometry. These observations are unequivocally related to the presence of a monolayer and can, with simple visible light detection, 'see' organic layers that are only a few nanometers thick.

2. Theory

Reflection from a SAM deposited on a silica-on-silicon substrate is illustrated in Fig. 1. The monolayer and the sub-micron silica layer are treated as non-absorbing, dielectric materials. Normal incidence is assumed throughout this work, for convenience and simplicity.
The reflectivity of the composite structure can be expressed in terms of cascaded elementary transmission matrices of individual thin films. The transverse electric and magnetic fields reflected from the thin film assembly are given by [40,41]:

\[
\begin{bmatrix}
    B \\
    C
\end{bmatrix} =
\begin{bmatrix}
    \cos \delta_1 & i \sin \delta_1 \eta_1 \\
    i \eta_1 \sin \delta_1 & \cos \delta_1
\end{bmatrix}
\begin{bmatrix}
    \cos \delta_2 & i \sin \delta_2 \eta_2 \\
    i \eta_2 \sin \delta_2 & \cos \delta_2
\end{bmatrix}
\begin{bmatrix}
    1 \\
    1
\end{bmatrix}
\]

Here \(B\) and \(C\) denote the electric and magnetic fields at the interface between air and the upper SAM layer. \(\delta_{1,2} = 2 \pi n_{1,2} d_{1,2} / \lambda\) are the optical phases acquired in the passing of light through the SAM and the SiO\(_2\) layer, respectively, \(n_{1,2}\) denote the refractive indices of the two media, \(d_{1,2}\) indicate their thicknesses, and \(\lambda\) is the vacuum wavelength of the incident light. \(\eta_{1,2,3} = n_{1,2,3} \eta_0\) denote the optical admittances of the monolayer, silica layer, and bulk silicon, respectively, defined as the ratio between the magnitudes of magnetic and electric fields components in each medium. The admittance of vacuum is noted by \(\eta_0\). The admittance of the composite thin film assembly is given by [40,41]:

\[
Y = \frac{C}{B}
\]

The overall power reflectivity coefficient of the three-layer stack can be expressed as:

\[
R = |R|^2 = \left| \frac{\eta_0 - Y}{\eta_0 + Y} \right|^2
\]

Direct observation of SAM patterns relies on the contrast in reflectivity between regions where a monolayer is deposited, and regions which are monolayer-free:

\[
\Delta R(\lambda, d_2) = \frac{R(\lambda, d_2 = 0) - R(\lambda, d_2)}{R(\lambda, d_2 = 0)}
\]

Figure 2 shows the calculated contrast map \(\Delta R(\lambda, d_2)\). The refractive indices of silica and silicon as a function of \(\lambda\) were taken from known references [42,43]. The refractive index of a molecularly thin organic monolayer created using octadecyltrichlorosilane (OTS) was estimated as \(n_1 = 1.47\) using the group contribution method [44]. The thickness of an OTS monolayer is typically measured by ellipsometry to be around 2.5 nm [45]. The calculated contrast reaches \(\pm 7\%\). For each thickness of the silica layer, the contrast reaches a maximum at different wavelengths.
3. Results

The monolayers used in our work were fabricated using OTS and methyl 11-(trichlorosilyl)undecanoate. OTS is known to readily form dense and well-ordered monolayers [46]. The methyl 11-(trichlorosilyl)undecanoate SAMs are the basis for a simple method for bi-layer assembly whose basic principles were first demonstrated by Ulman and associates [47] and that we have adapted for use with a shorter, more readily available SAM forming material. Details of monolayer synthesis and deposition are provided in the Appendix.

Monolayers were patterned through lithography and lift-off processes. Both point-by-point electron-beam lithography and photo-lithography through pre-patterned masks were employed (details of the lithography are provided in the Appendix). Monolayers were deposited on a silica-on-silicon substrate, with a silica layer thickness of 298 ± 6 nm as measured by ellipsometry.

Figure 3(a) shows an optical microscope image of an OTS-coated substrate, taken with an objective lens of 100X magnification and with no optical filters. The SAM consists of multiple features, between 200 nm and 10 µm in size, which were patterned using electron-beam lithography. Patterns 500 nm or wider are clearly recognized by direct observation through the bright-field microscope. A dark-field microscope image of the patterns is shown in Fig. 3(b). The edges of the monolayer patterns are visible in the dark-field image due to diffraction of light at the boundaries. Diffraction does not contribute, however, to differences between SAM-coated and bare areas in the bright-field image. A line scan of the sensor pixel readings of the bright-field image of panel (a), crossing from a SAM-coated square region to an uncoated region, is shown in Fig. 3(c). The trajectory of the line scan is noted on Fig. 3(a). The trace was averaged over 60 scans along parallel lines. The boundary between regions is characterized by a discontinuity of 6 gray levels (GLs) in the sensor readout.

Figure 4 shows AFM scans of the finer patterns of Fig. 3(a), having feature widths of 200 nm and 500 nm. The profile maps obtained by the AFM match the designed patterns as well as the direct microscope observations. The height of the patterns is approximately 2.5 nm, in good agreement with the expected height of an OTS monolayer [45].
Fig. 3. (a) - Bright-field microscope image of multiple patterns, defined in an OTS monolayer through electron-beam lithography. Scales are noted in the image. The magnification of the microscope was 100X. No filters were used in the optical path. The dashed line indicates the trajectory of a line-scan of the sensor output readout, shown in panel (c). The arrow indicates the scanning direction. (b) – Dark-field microscope image of the same monolayer patterns. (c) - Readout of the sensor output values, taken from the image of panel (a), as a function of position (in pixels). The sensor output readings (in gray levels, GLs) were extracted along a line that is drawn for illustration on panel (a). The line scan crosses the boundary between the 10 X 10 µm² SAM-coated square and an uncoated region. Data was averaged over scans of 60 parallel lines.

Fig. 4. AFM images and height scans of multiple patterns, defined in an OTS monolayer through electron-beam lithography. Top row: feature width of 200 nm. Bottom row: feature width of 500nm.

The observation of patterned monolayers was further demonstrated using 2.8 X 2.8 mm² diamond-shaped features in an OTS monolayer, patterned by photo-lithography (Fig. 5(a)). The patterns were characterized using direct observation, and also by position-dependent Raman spectroscopy and position-dependent visible light reflection spectroscopy. Figure 5(b) shows an image of a patterned sample, taken by a regular CMOS camera. The image shows a discernible pattern that matches the design layout.
Fig. 5. (a) – Illustration of a diamond-shaped monolayer pattern, defined using a photolithography and lift-off process. The yellow dashed square indicates the region shown in the image of panel (b). (b) – CMOS camera image of OTS SAM-coated and uncoated regions in the sample.

Figure 6(a) marks the region within a sample coated with a patterned OTS monolayer that was mapped by position-resolved Raman spectroscopy. Figure 6(b) shows an example of the Raman scattering spectrum, collected within the OTS-covered region. The line at 2847 cm\(^{-1}\) is characteristic of the symmetric \(\text{CH}_2\) stretch in OTS [48]. A two-dimensional map of the strength of the 2847 cm\(^{-1}\) peak, as a function of position across the sample, is shown in Fig. 6(c). The expected diamond-shaped pattern appears in the positional Raman scan. This result further indicates that the observed pattern is indeed due to the presence of the OTS SAM. The two black spots within the diamond-shaped pattern in Fig. 6(c) correspond to regions in which the overall collected intensity was weak. The scattering spectrum observed in these regions is a scaled down replica of that of Fig. 6(b), suggesting the presence of the OTS monolayer in these regions as well.

Fig. 6. (a) – Illustration of a diamond-shaped monolayer pattern, defined using a photolithography and lift-off process. The yellow dashed square indicates the region scanned in position-dependent Raman spectrometry. (b) – Raman scattering spectrum collected from within the OTS-coated region of the sample under test. A characteristic peak at 2847 cm\(^{-1}\) is evident. (c) – Map of the strength of the 2847 cm\(^{-1}\) Raman peak as function of position (in \(\mu\)m) across the sample. The expected diamond-shaped pattern, defined by photo-lithography, is apparent.

Direct observation of control experiment samples, that either left out the OTS from the deposition solution or that replaced the silica-on-silicon sample by a bulk silicon sample with a 2 nm-thin native oxide layer, did not reveal any spatial patterns. This further asserts that the observed patterns were due to the presence of the monolayer, and the significance of the multiple reflections in the layer stack as discussed above.
Next, the spectral reflectivity of the patterned sample was measured as a function of position, using a specialized scanning spectral reflectometer [49]. The spatial resolution of the measurements was 1 mm. Figure 7 shows the contrast between measured reflectivities of locations within (SAM-covered) and outside of (bare regions) the diamond-shaped pattern, as a function of wavelength. The corresponding, calculated spectral contrast is shown as well. A qualitative agreement between measurement and simulation is obtained, although the experimentally observed contrast is somewhat larger than expected.

Figure 8 shows bright-field microscope images of the sample, filtered at 640 nm and 540 nm wavelengths, which correspond to maximum and minimum reflectivity of the monolayer coated region, respectively. Bare and coated regions are identified in both images, with opposite signs of contrast. Line scans of the sensor pixel readings, crossing from bare to coated regions in Figs. 8(b) and 8(c), are shown in Fig. 9. The trajectories of line scans are noted on the two panels of Fig. 8. The boundaries between regions are characterized by discontinuities of 15 GLs in the sensor readout. The standard deviation of the sensor readout noise was 5 GLs. The traces shown in Fig. 9 were averaged over 200 scans along parallel lines. The gradual, low-spatial-frequency variability in both images of Fig. 8 and the traces of Fig. 9 is due to a spatial non-uniformity of the illumination module.

Fig. 7. Measured (red) and simulated (blue) contrasts between the reflectivities of an OTS SAM-coated region and an uncoated region of a silica-on-silicon sample, as a function of incident wavelength. Calculations were performed for a silica layer thickness of 298 nm.

Fig. 8. (a) – Illustration of a diamond-shaped monolayer pattern, defined using a photolithography and lift-off process. The yellow dashed square indicates the region imaged in a bright-field microscope; (b), (c) - Microscope images of a silica-on-silicon sample, filtered at 640 nm (panel b) and 540 nm (panel c) wavelengths. The edge of the region covered by an OTS SAM can be observed in the images. The coated region is characterized by a weaker reflectivity than that of its surroundings at 640 nm, and by a stronger reflectivity at 540 nm. Dashed lines in panels (b) and (c) indicate the trajectories of line-scans of the sensor output readout, shown in Fig. 9 below. The arrows indicate the scanning direction.
Fig. 9. Readout of the sensor output values, taken from the images of Fig. 8, as a function of position (in pixels). The sensor output readings (in gray levels, GLs) were extracted along lines that are drawn for illustration on panels (b) and (c) of Fig. 8. The line scans cross the boundaries between SAM-coated and bare regions of the imaged silica-on-silicon sample. Data was averaged over 200 parallel line scans. When the illumination is filtered at 640 nm, the line scan shows an increase in GL reading when moving from coated to bare areas of the sample. The opposite is true for 540 nm wavelength. The gradual decrease in GL as a function of position is due to non-uniformity of the illumination.

In order to investigate the contrast variations with thickness change, we fabricated two partially overlapping square patterns using a well-defined bilayer. An illustration describing the geometrical organization of the bilayer is given in Fig. 10. A bilayer is only formed in the region in which the two patterns overlap. Figure 11(a) shows an optical image, using a regular CMOS camera, of a patterned sample containing regions of a single and double layers of methyl 11-(trichlorosilyl)undecanoate, following the schematic in Fig. 10. Figure 11(b) shows a magnified bright-field microscope image of a region containing patterns with zero, one or two layers; the magnified region is located on the upper right-hand corner of Fig. 11(a). An optical filter with a bandwidth of 10 nm and a central transmission wavelength of 520 nm was applied to the magnified image. The transmission wavelength was chosen to match the maximum contrast between monolayer-coated and bare regions. Regions of a single layer and a bi-layer are clearly observed.

Figure 11(c) shows scans of the image GL values as a function of position, along two lines that are indicated on Fig. 11(b). One line crosses from a bare region to a monolayer-coated area, whereas the other crosses from a monolayer-coated area to a bilayer-coated area. The traces shown were averaged over 200 scans along parallel lines. GL discontinuities at region boundaries are seen in both traces.

Fig. 10. Illustration of the bi-layer deposition layout. The area of overlap between monolayers is the region in which the bi-layer is formed.
Fig. 11. (a) - a CMOS camera image of a silica-on-silicon sample, containing patterned regions of self-assembled single-layers and double-layers of methyl 11-(trichlorosilyl)undecanoate. (b) - enlarged bright-field microscope image of the upper right-hand corner of the sample (see Fig. 10). A 10 nm-wide optical bandpass filter, centered at 520 nm, was used to enhance the contrast between regions. Dashed lines indicate the trajectories of line-scans of the sensor output readout, shown in panel (c). The arrows indicate the scanning direction. (c) - Readout of the sensor output values, taken from the image of panel (b), as a function of position (in pixels). The sensor output readings (in gray levels, GLs) were extracted along lines that are drawn on panels (b), for illustration. The line scans cross the boundaries between a bare and a monolayer-coated region, and between a monolayer-coated and a bilayer-coated region. Data was averaged over 200 parallel line scans. The gradual decrease in GL as a function of position is due to non-uniformity of the illumination.

4. Discussion and summary

The direct observation of 2.5 nm-thick, single molecular layers of organic materials, using standard optical microscopy, has been convincingly demonstrated. The deposition of monolayers modifies the reflectivity spectrum of a silica-on-silicon substrate, providing distinguishable contrast between the exposed regions of the substrate and domains coated with various monolayers. Monolayer patterns are also observed by the naked eye, and in the images of a standard CMOS sensor.

Both electron-beam lithography and optical lithography were used to make patterns of different sizes and shapes, and the observation of patterns as narrow as 500 nm was successfully demonstrated. Direct observation could also discern between regions of a single layer and of a bi-layer. The experimental observation is supported by numerical simulations, and corroborated by AFM analysis, scanning spectral reflection measurements, and scanning Raman scattering microscopy. Compared with previous reflective interferometry analyses of monolayers [17–19], the proposed setup is considerably simpler and provides order-of-magnitude higher spatial resolution, though it does compromise contrast and thickness sensitivity. The reflectivity spectrum is characterized by a broad resonance, whose spectral width is on the order of tens of nm. The observation of the reflectivity contrast between a SAM-coated and a bare region does not depend on narrow optical filters: simulations suggest that the increase of filter bandwidth from 10 nm to 50 nm, for example, reduces the contrast only slightly, from 0.07 to 0.06. These results extend the use of reflective interferometry,
beyond the observation of graphene [20,24], to the inspection of patterned organic SAMs. The extension will be of direct significance in the analysis of graphene layers that are deposited on top of SAMs [28–35].

The proposed observation method could be very useful for applications of patterned monolayers. The observed contrast between single and bi-layer regions paves the way for implementing a simple chemical sensor exhibiting a color change upon formation of a second layer on a monolayer interface. Such patterns of varying reflectivity would provide simple, real time and high-throughput biological and chemical sensors [16,27].

Appendix: Experimental procedures

Substrate preparation: Silica-on-silicon wafers with a silica layer thickness of about 300 nm were sonicated and scrubbed with acetone under cleanroom conditions. The wafers were then exposed to oxygen plasma cleaning for five minutes. Silicon wafers with native silica layer were cleaned in hexane, acetone and ethanol, blown dry in a filtered nitrogen stream and placed in a fresh piranha solution (H₂SO₄: H₂O₂, with 70:30 volume ratio at 80 °C) for 20 minutes. The wafers were rinsed 3 times with deionized, doubly-distilled water and dried with nitrogen.

Electron-beam lithography: Silica-on-silicon wafer dies of 1 X 1 cm² area were covered with a 250 nm-thick PMMA K950 A4 resist. Patterns were defined in the resist using a Crestec CABL-9500C electron-beam lithography machine. The lithography was performed at 50 KV with 1 nA current, and at 100 dots/µm resolution. Following the electron-beam writing, the samples were put in MIBK developer for 60 seconds and in isopropyl alcohol for 30 seconds, and then placed in a plasma chamber with 125 sccm flow of argon for duration of 30 seconds and at RF power of 100 Watts, for the cleaning of resist residues.

Photo-lithography: Silica-on-silicon wafer dies of 1 X 1 cm² area were spin-coated with Shipley 1813 photo-resist, baked for 2 minutes at 115 °C and exposed to UV light through a pre-patterned photo-lithographic mask. Illuminated areas of the photo-resist were developed in MF319 and doubly-distilled water, exposing the underlying silica layer.

Monolayer deposition and characterization: 10 mL of dicyclohexyl and either 50 µL of OTS or 20 µL of methyl 11-(trichlorosilyl)undecanoate were placed in a clean, dry test tube under positive pressure of nitrogen, together with a silicon or silica-on-silicon sample. The samples were immersed in the solution for 75 minutes at room temperature, sonicated in chloroform for 6 minutes, placed in hexane for 6 min at 80 °C, scrubbed with hexane at room temperature, and blown dry under a nitrogen stream. Silica-on-silicon samples which were previously covered by a lithographic resist were washed in acetone as well, to perform lift-off.

An OTS SAM on a silica-on-silicon substrate is illustrated Fig. 12. The oxide thickness was measured using an Accurion Nanofilm ep3 ellipsometer. Raman Spectra were measured using a Raman microscope (HORIBA Scientific LabRAM HR). The shifts were measured from a laser with an excitation wavelength of 532 nm. Contact angle goniometry was used to verify the surface wettability and AFM was used for verification of the monolayer height after fabrication of patterned SAM.

Fig. 12. Illustration of octadecyltrichlorosilane (OTS) monolayer on silica on silicon wafer.
Bilayer formation (modeled after [47]): 10 mL of lithium aluminum hydride (LiAlH₄) solution (1 M in THF) were placed in a dry, clean test tube under a nitrogen stream. A methyl 11-(trichlorosilyl)undecanoate-modified sample was placed in the test tube for 10 minutes. Next, the sample was removed and placed in a 10% solution of hydrochloric acid for 5 minutes. The sample was then rinsed with hexane at room temperature and dried under a filtered nitrogen stream. A second layer of methyl 11-(trichlorosilyl)undecanoate was then deposited as illustrated in Fig. 13. FTIR traces of a silicon wafer, taken at different stages of a two-layer deposition process, are shown in Fig. 14.

![Fig. 13. Illustration of methyl 11-(trichlorosilyl)undecanoate bilayer formation on a silica-on-silicon sample. (a) denotes LiAlH₄, (b) denotes second layer of methyl 11-(trichlorosilyl)undecanoate.](image)

![Fig. 14. FTIR monitoring of the construction of a bi-layer film. The appearance and disappearance of the peak at ~1740 cm⁻¹ indicates the deposition of the methyl 11-(trichlorosilyl)undecanoate and its subsequent reduction.](image)

Synthesis of methyl undec-10-enoate [50]: Undec-10-enoic acid (7 g, 37.9 mmole), methanol (70 mL) and 2-3 drops of H₂SO₄ were placed into a 250 mL flask equipped with a magnetic stirring bar. The reaction mixture was stirred under reflux for 1-2 hours until the reaction was complete (monitored by TLC: silica gel/ hexane: ethyl acetate 2:1). The crude product was isolated by evaporating the excess methanol using a rotary evaporator. No further purification was needed before hydroxylation. (yield: 7.53 g, 100%). ¹H-NMR: 5.8 (m, 1H, CH₂=CH), 4.7 (m, 2H, CH₂=CH), 3.66 (s, 3H, OCH₃), 2.3 (t, J = 8 Hz, 2H, CH₂C=O), 2.05 (m, 2H, CH₂=CH-CH₂), 1.6 (m, 2H, CH₂CH₂C=O), 1.21-1.4 (m, 10H). ¹³C-NMR: 25.084 (CH₂CH₂C=O), 29.01, 29.273 (2C), 29.352 (2C), 33.24 (CH₃C=O), 34.235 (CH₂=CHCH₂), 51.535 (OCH₃), 114.2 (CH₂=CH), 139.102 (CH₂=CH), 175.1 (C=O).
Synthesis of methyl 11-(trichlorosilyl)undecanoate [50]: Methyl undec-10-enoate (2 g, 10.08 mmole), HSiCl₃ (6 mL), and 2 drops of 4% solution of H₂PtCl₆·6H₂O in dry i-PrOH were placed into a 20 mL oven-dried pressure tube containing a magnetic stirring bar. The contents of the tube were stirred at room temperature overnight. The progress of the reaction was monitored by the disappearance of the olefinic protons in the ¹H-NMR. After the reaction was complete, the contents of the tube were transferred (under nitrogen) to a 25 mL oven-dried round bottom flask. Excess HSiCl₃ was evaporated using a stream of nitrogen and the product was isolated by Kugelrohr distillation at 130 °C and 0.05 mm Hg pressure (yield: 2.35 g, 70%). The synthesis is illustrated in Fig. 15. ¹H-NMR: 3.66 (s, 3H, OCH₃), 2.3 (t, J = 8 Hz, 2H, CH₂C=O), 1.6 (m, 4H, CH₂CH₂C=O and Cl₃SiCH₂), 1.21-1.4 (m, 14H, aliphatic). ¹³C-NMR: 22.40, 24.52, 25.13, 29.19, 29.35 (2C), 29.48, 29.56, 34.23 (CH₂C=O), 51.53 (OCH₃), 175.10 (C=O).

Fig. 15. Synthesis of methyl 11-(trichlorosilyl)undecanoate.

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