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Monolayer Transformation by Nucleophilic Substitution: Applications to the Creation of New Monolayer Assemblies

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A series of new trichlorosilyl-terminated surfactants have been used to create a set of variously functionalized self-assembled monolayer surfaces. Transformations of these surfaces, with a focus on the use of nucleophilic substitution reactions for the creation and interconversion of surfaces with nitrogen- and sulfur-containing functionality, are reported. Approaches to the characterization of these surfaces and to the assessment of the efficacy of such in situ chemical transformations are explored. The use of such reactions to create new surface functionality and bridged monolayer structures is described.

Introduction

The report by Sagiv[1] of self-assembled (SA) organic monolayers, similar in organization and packing to Langmuir–Blodgett (LB) films[2] but anchored to hydroxyl-bearing surfaces by a cross-linked siloxane network, opened the door to the creation and study of new monolayer and multilayer films. The ease of preparation of the SA films and their relatively robust chemical and physical properties have allowed the study of such organized assemblies to move into areas that would not be accessible with classical LB systems.

To the chemist wanting to apply the tools of organic synthesis to the controlled creation of new kinds of functionalized surfaces, the stability of the SA films offers exciting opportunities. Despite their uniformity and well-developed physical characterization, LB films are limited in that their creation requires carefully controlled conditions and moderately sophisticated equipment. Moreover, once they are formed they are too fragile to be manipulated in a chemically meaningful way. Given the ability to readily deposit stable SA films on a variety of surfaces, two issues determine the utility of such assemblies for the creation of functionalized surfaces: the range of functionality that could be tolerated in the deposition process and the scope of chemical transformations that could be achieved within the monolayer environment.

It has been demonstrated that for siloxane-anchored films (and even more so for SA films of alkanethiols and alkyl disulfides on gold[3]), a range of functional groups (other than saturated hydrocarbon) could be present, remote from the anchoring functionality. These include olefins,[1] esters,[4] ethers,[5] thioethers,[6] and thioesters.[7] With these built-in functional groups, in situ transformations have included free radical halogenation;[8] terminal olefin to alcohol,[1] dibromide,[9] or acid;[9] ester to acid[9,10] or alcohol;[4]

(1) Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674–676.
(2) See, for example: Proceedings of the First and Second International Conference on Langmuir-Blodgett Films. *Thin Solid Films* **1983**, *99*; **1985**, *132–134*.
(3) (a) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3665. (b) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 6560. (c) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335. (d) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155–7164. (e) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164–7175. (f) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506.
(4) Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101–111.
(5) Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136–6144.
(6) Tillman, N.; Ulman, A.; Elman, J. F. *Langmuir* **1989**, *5*, 1020–1026.
(7) Wasserman, S. R.; Biebuyck, H.; Whitesides, G. M. *J. Mater. Res.* **1989**, *4*, 886–892.
(8) Sagiv, J. Personal Communication.
(9) Wasserman, S. R.; Tao, Y. T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074–1077.
(10) Maoz, R.; Netzer, L.; Gun, J.; Sagiv, J. In *New Technological Applications of Bilayers, Thin Films, and Vesicles*; Hayward, J. A., Ed.; Plenum Press: New York, 1986.

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thioether oxidation to sulfoxide;[6] thioether oxidation to sulfone;[11] and thioacetate hydrolysis to thiol.[7]

The goal of the work reported herein is to expand the scope of in situ reactions that can be reliably performed in a monolayer environment.[12] To this end, we have deposited siloxane-anchored monolayer films with Br, CN, SCN, and $SCOCH_3$ functionality. We have examined a variety of transformations and have assessed their efficiency. We have also obtained the same functionalized surface by using various reagents and various starting films. The scope of reactions employed has also allowed us to assess the usefulness of nucleophilic displacement chemistry (S_N2 reactions) in a monolayer environment. It has also allowed for the creation of a new kind of monolayer assembly: a structure wherein each surfactant monomer is bridged along the outer surface (remote from the anchoring network) to a neighbor, yielding a cyclic structure fused onto the substrate surface.

Experimental Section

General. NMR spectra are reported in units of δ and were recorded on a Varian XL-200 or Bruker MSL 400 spectrometer in $CDCl_3$ solvent. ^1H NMR spectra (200 MHz) are referenced to $CHCl_3$ at 7.24 ppm. ^{13}C NMR spectra (50, 100 MHz) are referenced to the center of the $CDCl_3$ solvent triplet at 77.0 ppm. Solution infrared spectra were recorded on a Mattson Cygnus 25 FTIR equipped with a water-cooled source and a TGS detector operating at a resolution of 4 cm^{-1}. High-resolution mass spectra (EI) were recorded on a Kratos MS 25RFA spectrometer. HPLC used a Waters 590 pump, a Rheodyne 7125 injector, and a Waters 401 differential refractometer. TLC was done on aluminum-backed 0.2-mm 60F254 plates from EM Science and used phosphomolybdic acid for visualization. Column chromatography (flash) was done with silica gel (Aldrich, 230–400 mesh). Dry THF and ether were distilled from Na. HPLC grade CH_2Cl_2 was used as received. Acetonitrile was dried over 3-Å molecular sieves. DMSO was distilled from CaH_2. Freshly opened bottles of DMF were used. Hexane for flash chromatography was distilled before use. HPLC grade hexane was used as received for HPLC. Hexane used as a reaction solvent was distilled from P_2O_5. Methanesulfonyl chloride was distilled. Et_3N was dried over CaH_2 and distilled. Undecenyl alcohol, 1,5-dibromopentane, and octadecyl mercaptan were used as received (Aldrich). $HSiCl_3$ (Petrarch) was distilled from quinoline. Hexadecane (Aldrich) and dicyclohexyl (Aldrich, vacuum distilled) were each passed through Brockman Activity I alumina (3% water by weight, 80–200 mesh, Fisher). Water was doubly distilled. $CHCl_3$ (Fisher, HPLC) was used as received. Octadecyltrichlorosilane (OTS, Aldrich) was distilled under vacuum before use.

Surfactant Syntheses. ω-Undecenyl Mesylate. In a dry two-neck 1-L flask equipped with a magnetic stirring bar, pressure-equalizing addition funnel, and a N_2 inlet was placed 600 mL of CH_2Cl_2. To the flask was added ω-undecenyl alcohol (60.9 g, 0.38 mol) and triethylamine (57.7 g, 0.57 mol), and the solution was cooled to 0 °C. The addition funnel was charged with a solution of methanesulfonyl chloride (48 g, 0.57 mol) in 100 mL of CH_2Cl_2 which was added to the reaction over 30 min. The reaction mixture was then stirred for an additional 30 min. It was transferred to a separatory funnel and washed with cold water, 5% HCl, 20% $NaHCO_3$, and saturated aqueous NaCl. The resulting solution was dried with $MgSO_4$, filtered, and concentrated on a rotovap. The product was obtained as a yellowish liquid and used without further purification: yield 92.5 g (98%); ^1H NMR 1.22–1.50 (m, 10 H), 1.74 (m, 2 H), 2.04 (m, 2 H), 2.98 (s, 1 H), 4.20 (t, J = 7 Hz, 2 H), 4.88–5.04 (m, 2 H), 5.80–5.92 (m, 1 H); IR (neat) 2928, 2856, 1641, 1467, 1355, 1176, 975, 951, 913, 822 cm^{-1}.

ω-Undecenyl Bromide. In a dry two-neck 1-L flask equipped with a pressure-equalizing addition funnel, a reflux condenser, a N_2 inlet, and a magnetic stirring bar were placed LiBr (24.66 g, 0.28 mol) and 300 mL of acetonitrile. The mixture was stirred until all the LiBr dissolved (10 min). The addition funnel was charged with a solution of ω-undecenyl mesylate (34.6 g, 0.14 mol) in 100 mL of acetonitrile, which was added to the reaction over 15 min. The reaction was heated at reflux for 1 h and monitored by TLC (hexane:THF 70:30; R_f(mesylate) = 0.39, R_f(bromide) = 0.87). It was cooled to room temperature and transferred to a separatory funnel, and ether (200 mL) was added. This solution was washed with water, 20% $NaHCO_3$, and brine, dried with $MgSO_4$, concentrated on a rotovap, and purified by passing through a short column of SiO_2 (hexane): yield 29 g (89%); ^1H NMR 1.14–1.54 (m, 10 H), 1.84 (m, 2 H), 3.38 (t, J = 7 Hz, 2 H), 4.88–5.02 (m, 2 H), 5.80–5.92 (m, 1 H); IR (neat) 2929, 2855, 1641, 1465, 1437, 993, 909, 721 cm^{-1}.

ω-Hexadecenyl Bromide. A flame-dried three-neck 100-mL flask equipped with a pressure-equalizing addition funnel, a reflux condenser with a N_2 inlet, and a magnetic stirring bar was charged with Mg turnings (3 g, 125 mmol). The addition funnel was charged with a solution of ω-undecenyl bromide (11.6 g, 50 mmol) in 50-mL of dry THF. A portion of this solution (10 mL) was added to the flask, and it was gently warmed. Once Grignard formation began, the rest of the solution was added over a period of 30 min. After the contents of the flask was heated at reflux for an additional 1 h, it was cooled to room temperature.

To another two-neck 500-mL flame-dried flask, fitted with a pressure-equalizing addition funnel, magnetic stirring bar, and N_2 inlet was added 200 mL of THF and 1,5-dibromopentane (25.3 g, 150 mmol). This solution was cooled in an ice/salt bath to −10 °C. The Grignard reagent from the first flask was transferred to the addition funnel by syringe. It was then added to the flask. A 0.2 M solution of LiCl and $CuCl_2$ in THF (1.8 mL) was added to the reaction flask. The resulting mixture was stirred at −10 °C for 12 h. Ether (150 mL) was added to the flask, and the entire contents transferred to a separatory funnel. The organic solution was washed twice with saturated aqueous NH_4Cl and once with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated on a rotovap. The excess 1,5-dibromopentane was removed by Kugelrohr distillation at 30–60 °C at 0.1 mm. The product was then subjected to flash chromatography (hexane) and final purification by HPLC (Whatman Magnum 20 column, hexane, 15 mL/min): yield 7 g (46%); MS m/e 302.1610 (calcd), 302.1619 (found); ^1H NMR 1.14–1.48 (m, 22 H), 1.8 (m, 2 H), 1.98 (m, 2 H), 3.36 (t, J = 7 Hz, 2 H), 4.88–5.04 (m, 2 H), 5.80–5.92 (m, 1 H); ^{13}C NMR 28.38, 28.97, 29.14, 23.35 (3C), 29.82 (5C), 33.04, 34.02, 34.20, 114.25, 139.4; IR (neat) 2925, 2855, 1641, 1465, 1437, 993, 909, 722 cm^{-1}.

ω-Hexadecenenitrile. A dry, two-neck 50-mL flask fitted with a N_2 inlet and a magnetic stirring bar was charged with NaCN (300 mg, 6 mmol) and 20 mL of DMSO. The mixture was heated to 80 °C, ω-hexadecenyl bromide (1.51 g, 5 mmol) was slowly added over a period of 30 min, and the mixture was maintained at 80 °C. The progress of the reaction was monitored by noting the disappearance of the bromide by TLC (hexane). The reaction mixture was cooled to room temperature, H_2O (100 mL) was added, and the product was extracted with three 50-mL portions of ether. The combined ether extracts were dried with $MgSO_4$ and concentrated on a rotovap. The crude product was purified by chromatography (silica gel/hexane): yield 900 mg (73%); MS m/e 249.2456 (calcd), 249.2463 (found); ^1H NMR 1.2–1.5 (m, 22 H), 1.53–1.67 (m, 2 H), 1.90–2.03 (m, 2 H), 2.31 (t, J = 7 Hz, 2 H), 4.88–5.02 (m, 2 H), 5.80–5.92 (m, 1 H); ^{13}C NMR 17.9, 25.56, 26.84, 28.95, 29.13, 29.34, 29.50, 29.70 (2C), 29.81 (4C), 34.01, 114.25, 120.00, 139.37; IR (neat) 2920, 2855, 2247, 1466, 993, 909 cm^{-1}.

ω-Hexadecenyl Thiocyanate. To a 50-mL round-bottom flask containing KSCN (490 mg, 6 mmol) and 30 mL of DMF was added ω-hexadecenyl bromide (1.5 g, 5 mmol), and the mixture was stirred at room temperature for 16 h with monitoring by TLC (hexane). Upon completion of the reaction, 50 mL of water was added and the product was extracted with three 50-mL portions of ether. The ether layer was dried with $MgSO_4$ and concentrated by evaporation. The crude product was sub-

(11) Reported in ref 30 of ref 6 above.

(12) A preliminary report of a portion of this work can be found in: Balachander, N.; Sukenik, C. N. *Tetrahedron Lett.* **1988**, *29*, 5593–5594.

jected to flash chromatography (10% EtOAc, 90% hexane): yield 1 g (72%); MS m/e 281.2179 (calcd), 281.2178 (found); ^{1}H NMR 1.2–1.45 (m, H), 1.8 (m, 2 H), 2.00 (m, 2 H), 2.93 (t, J = 7 Hz, 2 H), 4.85–5.03 (m, 2 H), 5.80–5.90 (m, 1 H); ^{13}C NMR 27.46, 28.42, 28.63, 29.10, 29.36, 33.30, 33.56, 111.85, 113.56, 138.7; IR (neat) 2926, 2855, 2155, 1641, 1467, 993, 909, 722 cm^{-1}.

ω-Hexadecenyl Thioacetate. In a dry 50-mL two-neck round-bottom flask equipped with a magnetic stirring bar and a reflux condenser was placed 25 mL of ethanol and potassium thioacetate (1.71 g, 15 mmol). To this was added ω-hexadecenyl bromide (3 g, 15 mmol), and the mixture was heated at reflux while the progress of the reaction was monitored by TLC (hexane). After about 6 h, the reaction mixture was cooled and 100 mL of water was added. The product was extracted with three 50-mL portions of ether. The combined ether extracts were dried over $MgSO_4$, and the solvent was removed on a rotovap. The crude product was purified by flash chromatography (10% EtOAc, 90% hexane): yield 2.65 g (90%); MS m/e 298.2332 (calcd), 298.2334 (found); ^{1}H NMR 1.2–1.6 (m, 24 H), 2.01 (m, 2 H), 2.84 (t, J = 7 Hz, 2 H), 4.88–5.01 (m, 2 H), 5.80–5.90 (m, 1 H); ^{13}C NMR 28.99, 29.12, 29.32 (2C), 29.69 (4C), 29.80 (3C), 30.80, 34.00, 114.23, 139.40, 196.19; IR (neat) 2925, 2855, 1696, 1641, 1465, 1353, 1134, 1109, 993, 954, 909 cm^{-1}.

ω-Hexadecenyl Azide. To a 50-mL round-bottom flask equipped with an N_2 inlet, containing NaN_3 (340 mg, 5 mmol) and 25 mL of dry DMF, was added ω-hexadecenyl bromide (1 g, 3.3 mmol). The mixture was stirred at room temperature for 12 h. The contents of the flask were transfered to a separatory funnel along with 100 mL of ether and 100 mL of water. The organic layer was washed 3 times with water to remove the DMF and was then dried over $MgSO_4$ and concentrated on a rotovap: yield 810 mg (93%); ^{1}H NMR 1.2–1.6 (m, 24 H), 2.04 (m, 2 H), 3.24 (t, J = 7 Hz, 2 H), 4.88–5.01 (m, 2 H), 5.8–5.9 (m, 1 H); IR (neat) 2927, 2856, 2096, 1642, 1465, 1349, 1281, 1259, 909 cm^{-1}. Attempted transformation of this material into the corresponding trichlorosilyl compound was unsuccessful.

1-Cyano-16-(trichlorosilyl)hexadecane. In a 20-mL pressure tube containing a magnetic stirring bar were placed ω-hexadecenenitrile (1 g, 4 mmol), $HSiCl_3$ (5 mL), and 10–20 μL of a 4% solution of $H_2PtCl_6 \cdot 6H_2O$ in i-PrOH. These reagents were all manipulated in an argon atmosphere glove bag. The tube was sealed and transferred to an oil bath maintained at 60 °C and heated for 10–16 h. The progress of the reaction was monitored by the disappearance of olefinic protons by ^{1}H NMR. After the reaction was complete, the contents of the tube were transferred to a 50-mL round-bottom flask in an argon-atmosphere glove bag. Excess $HSiCl_3$ was distilled off, and the product was isolated by Kugelrohr distillation at 110–120 °C at 0.01 mm: yield 1 g (66%); ^{1}H NMR 1.24–1.64 (m, 30 H), 2.31 (t, J = 7 Hz, 2 H); ^{13}C NMR 17.29, 25.56, 28.56, 28.84, 28.95, 29.14, 29.34, 29.50, 29.70 (2C), 29.82 (4C), 114.26, 120.00, 139.37; IR (neat) 2925, 2855, 2247, 1466, 766, 721, 692 cm^{-1}.

1-Bromo-16-(trichlorosilyl)hexadecane. ω-Bromohexadecene (1 g, 3.3 mmol) was converted into 1-bromo-16-(trichlorosilyl)hexadecane (1.15 g, 80%) by using the above hydrosilylation procedure and isolation by Kugelrohr distillation: ^{1}H NMR 1.20–1.87 (m, 30 H), 3.39 (t, J = 7 Hz, 2 H); IR (neat) 2925, 2855, 1466, 1437, 765, 721, 692 cm^{-1}.

1-Thiocyanato-16-(trichlorosilyl)hexadecane. Similarly, ω-hexadecenyl thiocyanate (500 mg, 1.8 mmol) gave 1-(trichlorosilyl)hexadecyl thiocyanate (500 mg, 70%): ^{1}H NMR 1.20–1.70 (m, 28 H), 1.80 (m, 2 H), 2.93 (t, J = 7 Hz, 2 H); IR (neat) 2928, 2856, 2155, 1465, 765, 722, 693 cm^{-1}.

1-Thioacetato-16-(trichlorosilyl)hexadecane. As above, ω-hexadecenyl thioacetate (500 mg, 1.68 mmol) gave 16-(trichlorosilyl)hexadecyl thioacetate (700 mg, 60%): ^{1}H NMR 1.20–1.65 (m, 30 H), 2.4 (s, 3 H), 2.84 (t, J = 7 Hz, 2 H); ^{13}C NMR 21.78, 23.84, 28.37, 28.54, 28.68, 28.89, 29.17, 30.18, 31.35, 195.58; IR (neat) 2926, 2855, 1696, 1465, 1134, 1109, 765, 722, 692 cm^{-1}.

Preparation of Solid Substrates for Monolayer Coating. The glass slides used in this work were obtained from Fisher (22 × 22 mm^2 NO:1/2) and were cleaned by washing with doubly distilled water followed by cleaning with hot $CHCl_3$ in a Soxhlet extractor for about 1 h. The substrates were then dried in an oven at 140 °C. The Si ATR crystals were cleaned with hot $CHCl_3$ for 30 min in a Soxhlet extractor, and ZnSe ATR crystals were cleaned by washing with $CHCl_3$ followed by drying in air. Germanium was prepared by first sonicating in hot water (40–50 °C) for 4 h followed by washing successively with water, acetone, and chloroform. All the substrates were plasma cleaned for about 30 min in radio-frequency Argon plasma (Harrick PDC-3xG Plasma Cleaner), stored in fluorocarbon containers (Fluoroware Inc.), and used within 1–2 days.

Preparation and Use of Coating Solutions. All trichlorosilyl surfactants used in this work were used as (2–2.5) × 10^{-3} M solutions in dicyclohexyl. The surfactant (100 μL) was added to the dicyclohexyl solvent (10 mL) under inert atmosphere and transferred to the bench top. All the surfactant solutions were used within 1–3 h after their preparation. The monolayers were prepared by immersion of the substrate (using Teflon-coated tweezers) into a 10-mL beaker containing about 10 mL of the surfactant solution and a magnetic stirrer. The substrate is quickly withdrawn from the solution after 3 min, washed with $CHCl_3$ and water, and finally cleaned in hot $CHCl_3$ in a Soxhlet extractor for 15 min.

Contact Angle Measurements. Contact angles were measured by using a Rame-Hart Model 100 contact angle goniometer equipped with a controlled environment chamber. Advancing contact angles were determined by placing a drop of H_2O from a syringe, advancing the periphery of the drop by adding more liquid, withdrawing the syringe, and measuring the advancing contact angle within 30 s of application of the drop. Receding contact angles were measured by withdrawing part of the liquid from the drop and measuring the angle. The temperature of the measurements was not controlled but stayed within a range of 22 ± 2 °C. Reported values are averages of four to six measurements taken at different points on the surface.

X-ray Photoelectron Spectroscopy. XPS measurements were carried out on a Perkin-Elmer ESCA 5400. Analyses were done by using Mg Kα lines at a pressure of 10^{-9} Torr with a takeoff angle of 45°. Survey spectra were recorded on a 1-mm spot, using 150-eV pass energy, 200-W electron beam power, and an acquisition time of 7 min. High-resolution multiplex spectra of the individual elements were done on a 1-mm spot, using 50-eV pass energy and an acquisition time of 30 min. Peak positions were assigned by referencing the C 1s peak at 285 eV.

Infrared Spectroscopy of SA Monolayers. FTIR measurements of monolayers were done by using an IBM FT-IR98A or a Mattson Sirius 100 single-beam spectrophotometer equipped with a He–Ne laser and a liquid N_2 cooled MCT detector. The internal reflection elements used were Si or ZnSe single-pass crystals (45°, 25 mm × 10 mm × 5 mm, Harrick). All measurements were made after purging the sample chamber for 30 min with N_2 or evacuating the chamber for 20 min with a vacuum pump. Spectra were recorded at 4-cm^{-1} resolution, and 1000–5000 scans were coadded. Reference spectra were recorded each day. Absorption spectra were obtained by subtracting the reference spectrum from the absorbance spectrum of the coated substrate.

Solution Reactions Used as Models for in Situ Transformations. The above preparations of ω-hexadecenyl thiocyanate and ω-hexadecenyl azide from ω-hexadecenyl bromide guided the corresponding monolayer-bound reactions. The reactions of Na_2S and Na_2S_2 with ω-hexadecenyl bromide were both done as per literature procedures[13] and proceeded in near quantitative yield. The oxidation of octadecyl mercaptan with Br_2 (as per ref 14) served as a model for such an in situ reaction; this reaction could not be done on the thiol derived from ω-hexadecenyl bromide due to its double bond.

In Situ Transformations of Monolayer Functionality. Transformations were carried out by dipping the monolayer coated substrate (glass slides or ATR crystals) in the reagent solution under the indicated reaction conditions for the indicated time and then rapidly withdrawing it with Teflon-coated tweezers. The stability of the siloxane anchor of the monolayer to a given set of reaction conditions was verified by car-

(13) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic Press: New York, 1983; Vol. 1.
(14) Drabowicz, J.; Mikolajczyk, M. *Synthesis* **1980**, 32–33.

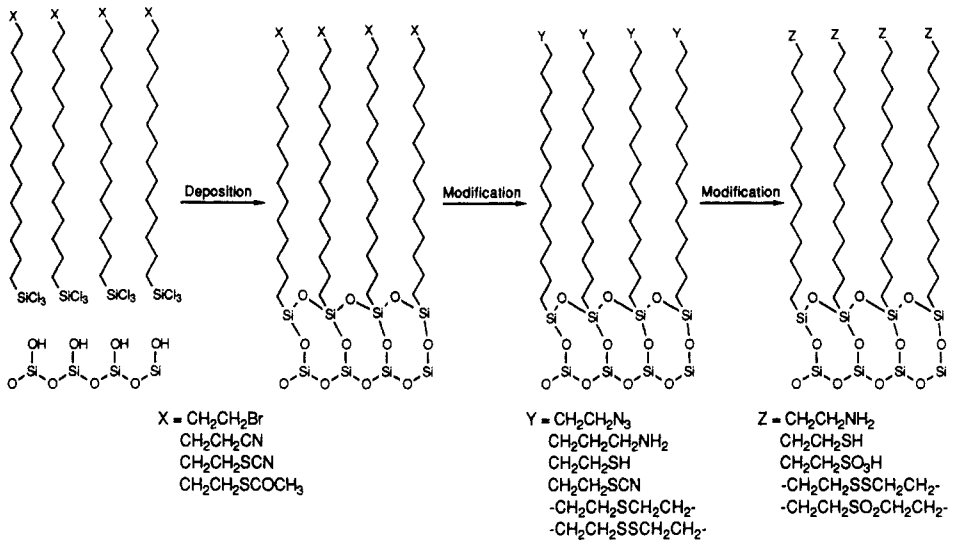

Figure 1. Monolayer deposition (X-surfaces) and transformation (Y/Z surfaces).

rying out the reaction with an unreactive monolayer surface (OTS) and checking its water contact angles before and after the reaction. We also verified that the monolayer substrate was unaffected by the reaction conditions in the absence of the nucleophile or oxidizing or reducing agent. Unless stated otherwise, all monolayer-coated substrates were cleaned after they were withdrawn from the reaction medium by washing with water, acetone, and chloroform before finally cleaning with hot $CHCl_3$ in a Soxhlet extractor. Characterization of the modified films involved contact angle measurements, IR, and XPS.

In Situ Displacement of Br by N_3. In a dry 125-mL Erlenmeyer flask containing a small magnetic stirring bar were placed 200 mg of NaN_3 and 25 mL of dry DMF. The substrate coated with the bromide-terminated monolayer was placed in the flask, and the mixture was stirred at room temperature overnight. The substrate was removed and cleaned.

In Situ Reduction of RN_3 and RCN with $LiAlH_4$. A stock solution of $LiAlH_4$ in ether was prepared by stirring a mixture of 10 g of $LiAlH_4$ in 1 L of ether for 2 h and allowing the mixture to stand. The clear supernatant was carefully removed with a syringe whenever required. The homogeneous $LiAlH_4$ solution (25 mL) was transferred into an oven-dried 50-mL round-bottom flask containing the substrate and was stirred overnight. The ether solution was then withdrawn and replaced with 25 mL of ether and then 25 mL of 10% HCl solution. The substrate was then withdrawn and cleaned. IR analysis showed complete disappearance of the distinctive CN or N_3 bands. The amine surface thus formed was present in a protonated form. The free amine was generated by dipping the substrate in dry Et_3N for 2 h followed by washing with $CHCl_3$. The interconversion of the free amine and the protonated amine was reversible and could be easily monitored by measuring water contact angles.

In Situ Reduction of RN_3 with $SnCl_2$/MeOH. The azide-containing surface was placed in a stirred solution of 100 mg of $SnCl_2$ in 25 mL of MeOH. The substrate was withdrawn after 4 h and dipped in 10% HCl and cleaned. Comparison of contact angle measurements with those obtained above indicated complete reduction.

In Situ Reduction of CN with BH_3. A glass substrate coated with a CN-terminated monolayer was dipped into a 1 M BH_3/THF solution for 4 h under an inert atmosphere. It was withdrawn and dipped into MeOH for an additional hour. It was finally dipped into 10% HCl solution for 15 min and then cleaned. Comparison of contact angle measurements with those obtained above indicated complete reduction.

In Situ Displacement of Br with SCN. A solution of KSCN (100 mg) was prepared in dry DMF (10 mL), and the substrate was kept in this solution for 20 h. The substrate was then withdrawn and cleaned.

In Situ Reduction of RSCN or $RSCOCH_3$ with $LiAlH_4$. The thiocyanate surface derived from the bromide-terminated monolayer as well as both thiocyanate and thioacetate surfaces obtained by the direct deposition of their respective (trichlorosilyl)hexadecyl compounds were reduced (for 4 h) with $LiAlH_4$ as described above. Disappearance of the distinctive IR bands and the loss of the nitrogen signal of the SCN in the XPS indicated complete reaction.

In Situ Oxidation of RSH to RSSR. The thiol-covered glass substrate was dipped into a solution containing 25 mL of a 10% solution of aqueous $KHCO_3$. About 100 μL of Br_2 was added. The substrate was withdrawn after 20 min and cleaned.

In Situ Reduction of RSSR with $LiAlH_4$. The coated glass substrate was treated with the $LiAlH_4/Et_2O$ solution overnight at room temperature and then dipped into 10% HCl as described above. This reaction was monitored by careful measurement of both advancing and receding water contact angles.

In Situ Reaction of RBr with Na_2S To Yield Surface-Bound RSR. $Na_2S{\cdot}9H_2O$ (240 mg, 1 mmol) was mixed with 25 mL of DMF in a 50-mL round-bottom flask, and the substrate was placed in the flask. After 12 h, the substrate was withdrawn and cleaned.

In Situ Reaction of RBr with Na_2S_2 To Yield Surface-Bound RSSR. Equimolar quantities of $Na_2S{\cdot}9H_2O$ (240 mg, 1 mmol) and elemental sulfur (32 mg, 1 mmol) were placed in a 50-mL round-bottom flask containing 25 mL of ethanol. The mixture was heated at reflux for 30 min; the sulfur dissolved and the solution turned deep yellow. The substrate was then placed into this solution, and the contents of the flask were heated to reflux for a further 2 h. The contents of the flask were then cooled to room temperature, and the substrate was withdrawn and cleaned.

Oxidation of Surface-Bound RSH or RSR with 30% H_2O_2/HOAc.[11] The sulfide-containing surface was placed in a 10-mL beaker containing a solution of 30% H_2O_2/HOAc (1:5 v/v) maintained at 40–50 °C. The substrate was withdrawn after 30 min and cleaned.

Results

The functionalized surfaces discussed in this study are schematically represented in Figure 1. They are each deposited by using a 16-carbon, trichlorosilyl surfactant (synthesized from ω-hexadecenyl bromide) as a dilute solution in dicyclohexyl. Initially formed monolayers (X terminated) include a standard hydrocarbon surface formed from octadecyltrichlorosilane (OTS) as well as the Br-, CN-, SCN-, and $SCOCH_3$-terminated surfaces, each made from the appropriately functionalized surfactant. Treatment of these surfaces with appropriate reagent(s) allowed their transformation into the various Y- and Z-terminated surfaces. The reagents used and the specific transformations are summarized in Table I.

Table I. Reagents for in Situ Transformations of Monolayers

entry	reagent	transformation (X/Y → Y/Z per Figure 1)
1	NaSCN	$(CH_2)_{16}Br \rightarrow (CH_2)_{16}SCN$
2	NaN_3	$(CH_2)_{16}Br \rightarrow (CH_2)_{16}N_3$
3	$LiAlH_4$	$(CH_2)_{16}SCN \rightarrow (CH_2)_{16}SH$ $(CH_2)_{16}SCOCH_3 \rightarrow (CH_2)_{16}SH$ $((CH_2)_{16}S)_2 \rightarrow (CH_2)_{16}SH$
4	$LiAlH_4$ or BH_3	$(CH_2)_{16}CN \rightarrow (CH_2)_{17}NH_2$
5	$LiAlH_4$ or $SnCl_2$	$(CH_2)_{16}N_3 \rightarrow (CH_2)_{16}NH_2$
6	Na_2S	$(CH_2)_{16}Br \rightarrow ((CH_2)_{16})_2S$
7	Na_2S_2	$(CH_2)_{16}Br \rightarrow ((CH_2)_{16}S)_2$
8	H_2O_2	$((CH_2)_{16})_2S \rightarrow ((CH_2)_{16})_2SO_2$ $(CH_2)_{16}SH \rightarrow (CH_2)_{16}SO_3H$
9	Br_2	$(CH_2)_{16}SH \rightarrow ((CH_2)_{16}S)_2$

Each of these films was characterized in the following ways. Those with IR-active chromophores were deposited on Si ATR elements. Their IR spectra showed the polymethylene signals and the expected individual chromophores (CN, 2247; SCN, 2157; $SCOCH_3$, 1695; N_3, 2098 cm^{-1}). By use of samples of each of these films on glass, the water contact angle for each surface and its XPS were measured. The advancing and receding contact angles and the characteristic electron binding energies of the heteroatoms (relative to C 1s at 285 eV) are reported in Table II.

The interconversion of surfaces provides access to otherwise unobtainable surface functionality as well as the ability to generate the same surface from a number of different routes. This in turn should allow for a clearer assessment of monolayer integrity and of the efficacy of the various transformations.

The same amine surface is obtained from a CN-terminated monolayer whether $LiAlH_4$ or BH_3[15] is used as the reducing agent. Similarly, whether an amine surface is obtained in this way or by in situ N_3 displacement of Br, followed by reduction with either $LiAlH_4$ or $SnCl_2$,[16] the spectral and physical properties are the same. This is true despite the fact that the CN route leads to an amine surface on a 17-carbon, rather than a 16-carbon, monolayer assembly.

Independent generation of identical surfaces is extended to the sulfur-containing functional groups by creating initially deposited SCN and $SCOCH_3$ surfaces, matching the SCN surface with that created by in situ Br displacement and by transforming all such surfaces into the same SH-terminated films. Other sulfur nucleophiles provide further corroboration of the above results and have been used to create bridged monolayer assemblies. Treatment of the Br-terminated surface with Na_2S gives[13] a surface where two surface-anchored polymethylene chains are bridged by a single sulfur atom. Oxidation[11] of this new surface yields a film where the bridge is now an SO_2 group. Similarly, using Na_2S_2 as the nucleophile[13] creates the same surface that is obtained from the oxidation of an SH-terminated film with Br_2.[14] Also, $LiAlH_4$ reduction of the disulfide surface generates a thiol surface identical with that obtained by the reduction of either the SCN or $SCOCH_3$ films. This thiol/disulfide interconversion and the amine protonation/deprotonation of functionalized films are both completely reversible.

Discussion

The generation, interconversion, and characterization of functionalized monolayer surfaces require that we establish the integrity of monolayer packing and structure and determine the efficacy of in situ synthetic transformations. The following discussion will therefore first consider the extent to which our surfaces can be shown to be close-packed, defect-free monolayers with well-defined functionality. It will then assess our ability to perform and monitor chemical reactions that could be used to interconvert monolayer surface functionality. Finally, the use of such transformations to create novel, otherwise inaccessible, monolayer assemblies will be discussed.

Film Structure. The packing and integrity of both OTS (Figure 1, X = CH_2CH_3) and HTS (Figure 1, X = $CH{=}CH_2$) monolayers have been directly addressed in the literature. They have been shown to be close-packed, well-ordered, and nearly defect-free. This assessment is based on a combination of X-ray diffraction[17] and reflectivity studies,[18] ac impedance,[19] and ellipsometry.[18] These surfaces show relatively small contact angle hysteresis, as would be expected for well-packed, aprotic, surface functionality. Since none of our initially deposited surfaces has been the subject of such direct structural evaluation, various less direct approaches must be used to assess monolayer structural integrity.

Firstly, three of our terminal X groups (Figure 1; Br, CN, $SCOCH_3$) have been studied as terminal groups in SH-anchored films on gold. The integrity of the gold-bound films has been established,[20] and they serve as a reasonable reference for our study. Water contact angles of those SH-anchored films match those of our siloxy-anchored structures. This comparison, coupled with reasonable XPS and IR signal intensities, and the relatively small hysteresis that we see for each of these films (Table II) are all consistent with a well-packed film structure.

Film structure is also a factor in the extent to which identical surfaces can be generated by different routes. That SCN and $SCOCH_3$ films both reduce to identical SH-terminated surfaces requires both comparable film structure and comparable reaction efficiency. That the SH surface generated from either of these films matches (by contact angle and XPS) the surface generated from disulfide reduction and that generated from the hydrolysis of a thioacetate precursor[7] reinforces this.

The availability of a variety of transformations and functionality also raises the issue of how one can be certain of the identity of the surface group. This must be addressed before any assessment of reaction efficiency can be undertaken. Here too, a combination of evidence is needed. For those groups with distinctive IR chromophores (CN, SCN, N_3, $SCOCH_3$), ATR spectra are compared to the solution spectra of the ω-hexadecenyl compound bearing that functional group. In all cases, the peak position and its intensity relative to the polymethylene correlate well in the two spectra.

For other systems, a combination of XPS and contact angle measurements allows us to differentiate among various functionality. Among the nitrogen-containing functional groups, the differentiation provided by XPS is useful. Though all of the binding energies are within 1.7 eV, and despite relatively broad signals, the various kinds of nitrogens can be distinguished. While CN and N_3 need

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Table II. Water Contact Angles and Electron Binding Energies of Functionalized Monolayer Surfaces

surface group	advancing water contact angle, deg	receding water contact angle, deg	XPS, eV		
			Br 3_d	S 2_p	N 1_s
Br	82 ± 1	77 ± 2	70.2		
CN	72 ± 2	65 ± 2			399.9
N_3	77 ± 2	71 ± 2			399.5
NH_2	63 ± 2[a]	42 ± 4[b]			400.6–401.2
SCN	73 ± 2	70 ± 2		164.1/165.1	399.9
$SCOCH_3$	73 ± 3	65 ± 3		164.0/165.0	
SH	71 ± 3	49 ± 3		163.6/164.7	
-S-	68 ± 2	63 ± 3		163.6/164.7	
$-SO_2-$	50 ± 4	32 ± 3		168.3/169.4	
-S-S-	65 ± 3	52 ± 2		164.0/165.0	
SO_3H	30 ± 2	<10		168.1/169.2	

[a] NH_3^+, 42 ± 3. [b] NH_3^+, 24 ± 4.

not be distinguished from each other, they can each be distinguished from their amine reduction products. Assignment of the amine structure is strengthened by the pH dependence of its water contact angle, analogous to that reported for comparably functionalized polyethylene films.[21]

Assignment of the sulfur functionality required a combination of physical, chemical, and spectroscopic information. The $SCOCH_3$ group has its carbonyl as a clear IR diagnostic, and the SCN group has a distinct IR absorption and shows a CN-like N by XPS. The more oxidized RSO_2R and RSO_3H groups have distinctive sulfur XPS signals. They can be unequivocally assigned based on comparison to Ulman's values for sulfides, sulfoxides, and sulfones[6] (163.7, 166.3, and 168.1 eV, respectively, relative to C 1s at 285 eV) and by comparison to literature tabulations[22] of values for sulfone, sulfoxide, and sulfinic and sulfonic acids. However, the differentiation among R–SH, R–S–S–R, and R–S–R cannot be achieved by IR (neither the S–H nor the S–S signals can be seen in our ATR experiment) or XPS (signals too similar to be resolved). Moreover, the advancing contact angles of these surfaces are quite similar. Thus, characterizing these surfaces required the following. Firstly, the water contact angle hysteresis of the SH surface is particularly large, as would be expected for protic surface functionality.[3c] Secondly, oxidation of these surfaces yields new functionality with distinctly different properties; i.e., oxidation of SH with H_2O_2 yields sulfonic acid (distinctive XPS and contact angle), while the same treatment of the R–S–R surface yields sulfone (equally distinctive XPS and contact angle). The differentiation between the thiol and disulfide surfaces relies to some extent on their somewhat different advancing contact angles and more so on the hysteresis of the thiol contact angle. Moreover, the reversible redox chemistry ($LiAlH_4$ reduction, Br_2 oxidation[14]) of these surfaces is reliably reflected by their contact angles. Further study of the SH $\rightleftarrows$ SS equilibrium by higher resolution XPS is currently underway.[23]

In Situ Chemical Transformations. Despite the range of monolayer transformations reported in the literature, none utilizes S_N2 nucleophilic substitution chemistry. The interest in such systems stems from the simplicity and synthetic power of such reactions and from the question of whether monolayer packing will interfere with the preferred S_N2 transition state, requiring backside attack of the incoming nucleophile. The optimal utility of such reactions will be realized if they allow monolayer structure to be preserved and if quantitative conversion can be achieved.

That initially deposited films were stable to the necessary reaction conditions was readily demonstrated. Br films (the substitution substrate) were shown to be stable to the solvent and temperature of each reaction. The OTS film was used as a nonreactive model system and was subjected to each set of reaction conditions (including all reagents) and showed no change.

A strong case for the efficacy of our substitution chemistry can be made in two ways. Firstly, the SCN film that is deposited directly (as an X group, Figure 1) and the film obtained by in situ displacement of Br have identical contact angle behaviors and IR and XPS spectra (both peak positions and intensities). Once SCN and $SCOCH_3$ films are created, their SH reduction product is the same regardless of the source of the sulfur functionality. Also, such SH surfaces match those obtained from disulfide reduction. This last point speaks to both the simple displacements of Br with a monodentate nucleophile like SCN and to displacement by the bidentate S_2^{2-} nucleophile (see below). Similarly, displacement with a nitrogen-containing nucleophile like N_3 is a demonstrably efficient process, on the basis of the identical properties of the amine surface obtained from the various precursors (CN film reduction or Br displacement by N_3 followed by reduction).

A direct monitor of Br displacement by XPS provides, perhaps, the clearest way of assessing S_N2 efficiency. The XPS spectra of a Br-terminated film on a glass substrate show the expected peak at 70.2 eV, flanked by the Na 1s signals at 74.8 and 64.5 eV. As demonstrated in Figure 2, these Na peaks provide an internal reference that allows the semiquantitative assessment of Br disappearance. Br displacement by SCN^-, S^{2-}, S_2^{2-}, and N_3^- was monitored for each case, and the extent of Br loss could be established. While this approach measures Br loss and not nucleophile incorporation, the identical character (i.e., the same XPS peak positions and intensities and the same contact angle behavior) of the substitution-derived surfaces with those obtained by initial deposition of surfactants containing those same functional groups or by alternative routes, like thiol oxidation to disulfide, strongly supports quantitative displacement of surface functionality.

Bridged Monolayer Assemblies. Having successfully established the use of nucleophilic modification of monolayer functionality, the novelty and uniqueness of R–S–R and R–S–S–R monolayer assemblies where both R groups are surface-anchored deserve comment. They are each created by a pair of nucleophilic substitution reactions of

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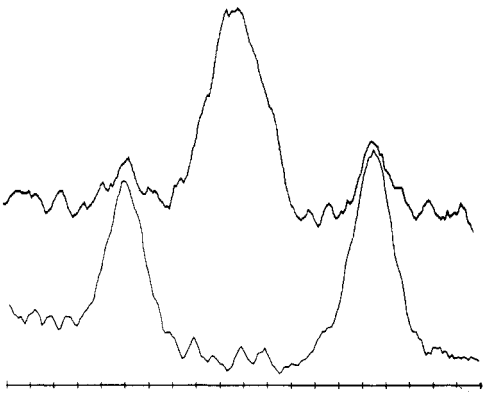

Figure 2. XPS monitoring of Br disappearance by nucleophilic substitution: top trace is of a 20-eV region of the XPS spectrum of a Br-terminated monolayer on glass showing a strong Br 3d peak flanked by the two Na 1s peaks on the glass. Bottom trace is of the same XPS spectral region after treatment with Na_2S, showing the disappearance of the Br 3d peaks.

a bidentate sulfur nucleophile on two alkyl bromide chains, and the RSSR surface can also be obtained by oxidation of thiol surfaces. The position and intensities of the XPS sulfur signals and the contact angle data suggest that the indicated functionality has been successfully, and quantitatively, installed.

Thioether functionality as a monolayer terminal group and its oxidation to a sulfoxide have been reported by Ulman.[6] Our bridged thioether and its oxidation to the bridged sulfone nicely complement that work. The surface properties and spectroscopy of such functionality, installed in both of these ways, deserve more detailed study and comparison. Furthermore, the thiol/disulfide interconversion described above provides an interesting arena in which to explore the effect of proximity and packing on such a redox couple. Such a study would, however, require a very sensitive probe to quantitatively look at the thiol/disulfide ratio under various conditions. Such a probe may be provided by high-resolution XPS.[23]

A novel aspect of such bridged structures is their cyclic nature. They are envisioned to be large polymethylene rings (with one or two hetero atoms) covalently fused onto the solid substrate by a pair of siloxane linkages. One implication of such a structure with a single-heteroatom bridge is that the functional group density in the film is half that of the more typical monolayers. This is qualitatively consistent with the sulfur XPS intensity data where the RSR and RSO_2R surfaces show a sulfur signal of approximately half the intensity of the RSH, RSSR, RSO_3H, RSCN, and $RSCOCH_3$ surfaces.

An intriguing question about the bridged films, that is not answered by our work, is the issue of whether the bridging that is required by our chemistry is among nearest-neighbor molecules or does it allow for (or perhaps even favor) bridging to a next-nearest or third-nearest neighbor. Moreover, are the types of bridges formed in an irreversible nucleophilic substitution reaction different from those that persist in the sulfide/disulfide equilibrium? New approaches to address such questions are currently being sought.

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