

Supporting information

Synthesis and electrical properties of fullerene-based molecular junctions on silicon substrate

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1- Synthesis of organosilanes

Chemicals.

Buckminsterfullerene C₆₀ (sublimed, 99.9%), N-methylglycine (99 %), sulfuric acid (96 %), hydrogen peroxide (30 % in water), sodium azide (99.5 %), adogen 464, tetrabutylammonium hexafluorophosphate (99 %), anhydrous o-dichlorobenzene (99 %) were all purchased from Sigma Aldrich. N-[3-(triethoxysilyl)propyl]-2-carbomethoxyaziridine (97 %), triethoxysilylbutyraldehyde (90 %), 3-chloropropyltrimethoxysilane (95 %) were purchased from Gelest. Chloroform (99.9 %) and dichloromethane (99.9 %) were obtained from Scharlau. Anhydrous acetonitrile (99.8 %), toluene (99.9 %), ethyl acetate (99.5 %), isopropanol (99.7 %) were purchased from Carlo Erba. These chemicals were used as received without further purification, except dichloromethane and toluene that were distilled over calcium hydride then stored over freshly activated molecular sieves. For water-sensitive reactions, glassware was dried in an oven at 120 °C overnight prior to use.

¹H and ¹³C NMR spectra were recorded with AC 300 Bruker instrument. ¹H NMR spectra were recorded at 300 MHz and ¹³C NMR spectra at 75 MHz. Chemical shifts of NMR spectra are reported in ppm and referenced to tetramethylsilane.

FTIR spectroscopy of synthesized 3-azidopropyltrimethoxysilane was realized using a Perkin-Elmer Spectrum 2000 single-beam spectrophotometer by transmission IR spectroscopy in a sodium chloride crystal cell.

3-azidopropyltrimethoxysilane

3-azidopropyltrimethoxysilane was synthesized following the procedure developed by Karl et al.¹ by reaction of sodium azide with 3-chloropropyltrimethoxysilane in the presence of Adogen 464 catalyst. Let us precise that N₃-terminated SAMs is often also prepared by surface chemistry from halide-terminated monolayers^{2,3} but this method would have required one more chemical step in the reaction sequence and thus one more risk of pollution and decrease of yield.

All glassware was dried in an air oven at 120 °C overnight prior to use and the reaction was performed under nitrogen atmosphere. A solution of 3-chloropropyltrimethoxysilane (2.5 mL, 13.71 mmol), sodium azide (1 g, 15.4 mmol) in dry acetonitrile was refluxed for 16 h under stirring in the presence of the catalyst Adogen 464 (200 mg, 0.4 mmol). After filtration of the precipitated salt, then evaporation of the solvent, the resulting oil was purified by distillation

under reduced pressure (0.5 Torr). The first fraction (below 40°C) containing the unreacted halogenated precursor was eliminated then 3-azidopropyltrimethoxysilane was obtained at 80°C as a clear liquid in a yield of 60 % (1.7 g). *Caution: due to the excess of instable and highly toxic sodium azide, the oil should not be distilled to dryness.* ^1H NMR (300 MHz; CDCl_3 ; Me_4Si ; 20°C) : δ_{H} (ppm) 0.67 (2H, m, $-\text{CH}_2\text{Si}$), 1.68 (2H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 3.24 (2H, t, $^3J_{\text{CH}} = 6.95$ Hz, $-\text{CH}_2\text{N}_3$), 3.55 (9H, s, CH_3O). ^{13}C NMR (75.5 MHz; CDCl_3 ; Me_4Si ; 20°C) : δ_{C} (ppm) 6.27, 22.41, 50.50, 53.67. FTIR (in CCl_4) : λ_{max} 2098.8 cm^{-1} ($-\text{N}_3$).

N-methyl-2-(3-triethoxysilylpropyl)-3,4-fulleropyrrolidine

A solution of C_{60} (100 mg, 139 μmol), N-methylglycine (50 mg, 561 μmol), and triethoxysilylbutyraldehyde (150 μL , 553 μmol) in toluene (50 mL) was heated to reflux for 5 h. The solvent was evaporated then the crude product was purified by flash chromatography (SiO_2 , 40-63 μm) with toluene first to remove the unreacted C_{60} , then with a mixture of toluene/ethyl acetate v/v 9:1. The fulleropyrrolidine was isolated as a brown solid (32 mg, 22 %) by filtration after dissolution in a minimum of toluene then precipitation by the addition of acetonitrile. During the flash chromatography, 50 % of unreacted fullerene was also recovered. $R_{\text{f}} = 0.47$ in toluene/ethyl acetate, v/v 9:1. ^1H NMR (300 MHz; C_6D_6 ; Me_4Si ; 20 °C): δ_{H} (ppm) 0.85 (2 H, t, CH_2Si), 1.18 (9 H, t, $J = 6.9$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.34-1.58 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 2.65 (3H, s, CH_3N), 3.80 (6H, q, $J = 6.9$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 3.74 (1H, t, $J = 5.55$ Hz, CHCH_2), 3.87-3.92 (1H, m, CH_2 pyrrolidine), 4.34 (1H, d, $J = 9.78$ Hz, CH_2 pyrrolidine). ^{13}C NMR (75.5 MHz; C_6D_6 ; Me_4Si ; 20 °C): δ_{C} (ppm) 11.77, 15.71, 21.48, 34.62, 39.48, 58.47, 70.22, 70.76, 76.85, 78.11, 135.91, 136.31, 136.71, 137.66, 140.01, 140.14, 140.51, 140.58, 142.02, 142.06, 142.19, 142.39, 142.42, 142.46, 142.49, 142.50, 142.56, 142.58, 142.98, 143.01, 143.05, 143.44, 143.56, 144.72, 144.78, 144.94, 145.12, 145.51, 145.54, 145.57, 145.60, 145.65, 145.75, 145.77, 145.93, 145.94, 146.16, 146.26, 146.28, 146.36, 146.40, 146.52, 146.53, 146.59, 146.63, 146.75, 147.06, 147.31, 147.48, 147.52, 154.34, 154.95, 155.05, 157.19.

2- Synthesis of aldehyde, carbomethoxyaziridine and azide terminated SAMs

CHO-terminated SAM, carbomethoxyaziridine-terminated SAM and N_3 -terminated SAM were successfully prepared by classical silanization reactions immersing a freshly cleaned natively oxidized silicon substrate in a 10^{-3} M solution of the corresponding organosilane in toluene for several days.

Silicon substrate cleaning method. Substrates used for electrical characterizations were n-type degenerated silicon wafers purchased from Siltronix (resistivity of $\sim 10^{-3}$ $\Omega\cdot\text{cm}$) to avoid any voltage drop during electrical measurements. For FTIR spectroscopy, ATR silicon crystals (undoped) were used (45°, 10 mm \times 5 mm \times 1.5 mm). Surface of silicon substrates were covered with native oxide (10-15 Å thick) providing a dense array ($\sim 5 \times 10^{14}$ cm^{-2}) of reactive hydroxyl groups (-OH), which are anchoring sites for the alkyltrialkoxysilane molecules. All silicon substrates including ATR silicon crystals were first sonicated in chloroform for 5 min then dried under nitrogen. The polished side of the wafers was cleaned by ozonolysis for 30 min in a UV/ozone cleaner (wavelength at 185 and 254 nm). Then, the samples were dipped into a freshly prepared piranha solution ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ 2:1 v/v) at 100 °C for 15 min, were rinsed thoroughly with DI water then were dried under nitrogen stream. Finally, cleaning was ended by additional ozonolysis for 30 min. *Caution: the piranha solution violently reacts with organic chemicals; consequently, it should be handled with extreme care.*

N₃-terminated SAM

The reaction was carried out at room temperature in a glovebox under nitrogen atmosphere. A freshly cleaned silicon substrate was immersed for 48 h in a 10⁻³ M solution of 3-azidopropyltrimethoxysilane in anhydrous toluene (i.e. ~20 μL of organosilane in 20 mL of solvent). The substrate was removed, sonicated 5 min in toluene then in chloroform, and blown with dry nitrogen.

Carbomethoxyaziridine-terminated SAM

The SAM was prepared by treating the freshly oxidized silicon substrate with N-[3-(triethoxysilyl)propyl]-2-carbomethoxyaziridine in the same conditions as N₃-SAM. The immersion duration in toluene was 3 days.

CHO-terminated SAM

Freshly cleaned silicon substrate was immersed for 3 days in a 10⁻³ M solution of triethoxysilylbutyraldehyde in anhydrous toluene in the same conditions as N₃-SAM.

As can be seen in table 1, precursor SAMs thicknesses measured by ellipsometry were conform to theoretical values (MOPAC, PM3 optimization) calculated considering the molecules in their all-trans conformation and almost standing perpendicular to the surface. Measured water contact angles (see table 1) were slightly lower than those of analogous monolayers published in literature. In the present work, the molecule lengths are much smaller than those previously described, and it is known⁴ that SAM of short chains are more disordered than long ones, thus explaining the lower contact angles.

Precursor SAMs	thickness (Å)		contact angle (°)	
	exp.	theo.	exp.	ref.
CHO-SAM	7.0	7.8	67±1	80 ⁵
Aziridine-SAM	12.0	12.1	55±1	NR
N ₃ -SAM	8.0	8.8	68±1	77 ⁶

Table 1. Thickness and wettability of precursor SAMs selected for sequential methods. NR : no found reference in literature.

3- Instrumentation and methods for the physicochemical characterizations of self-assembled monolayers

FTIR spectroscopy. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000 single-beam spectrophotometer equipped with a tungsten-halogen lamp and a liquid nitrogen cooled MCT detector. The functionalized silicon surfaces were characterized by reflection IR spectroscopy, method also called attenuated total reflection (ATR).⁷ For the IR studies, all substrates were ATR silicon crystals (45°, 10 mm×5 mm×1.5 mm). All measurements were made after purging the sample chamber for 30 min with dry N₂. Spectra were recorded at 4 cm⁻¹ resolution, and 200 scans were averaged. Background spectra of the freshly cleaned crystal (with SiO₂ layer) were recorded before any chemical treatment. After the chemical reactions, the sample spectra were recorded in the same conditions. The monolayer transmittance spectrum was obtained by dividing the sample spectrum by the background spectrum.

Contact angle measurements were done using a remote computer-controlled goniometer system (DIGIDROP by GBX, France). These measurements were carried out in a clean room (class 1,000) where humidity, temperature, and pressure were controlled. Deionized water (18 M Ω /cm) was used for these characterizations. Static drops (in the range 1-10 μ L) of liquid were applied to the modified surfaces with a micropipette and the projected image was acquired and stored by the remote computer. Several measurements were taken on each region of a given substrate. Contact angles were then extracted by contrast contour image analysis software. These angles were determined 5 s after application of the drop. Measurements made across the functionalized surfaces were within 2°.

Spectroscopic ellipsometry data in the visible range was obtained using a UVISSEL by Jobin Yvon Horiba Spectroscopic Ellipsometer equipped with a DeltaPsi 2 data analysis software. The system acquired a spectrum ranging from 2 to 4.5 eV (corresponding to 300-750 nm) with 0.05 eV (or 7.5 nm) intervals. Data were taken using an angle of incidence of 70°, and the compensator was set at 45.0°. Data were fitted by regression analysis to a film-on-substrate model as described by their thickness and their complex refractive indices. First, before monolayer deposition the silicon oxide thickness was measured. In the software, the measured data were compared with the simulated data to determine this thickness. The simulated data were obtained with a 2-layer model (Si/SiO₂). In this model we use for the materials, the optical properties (complex refractive index for each wavelength) from the software library. Second, after the monolayer deposition we use a 3-layer model (Si/SiO₂/organic film). To determine the monolayer thickness, we use the oxide thickness previously measured, for silicon and oxide we use the optical properties from the software library, and for the monolayer we use the refractive index of 1.50. Usual values in the literature are in the range of 1.45-1.50.^{8,9} One can notice that a change from 1.50 to 1.55 would result in less than 1 Å error for a thickness less than 30 Å. As a function of the wafer used, the oxide layer thickness was between 10 and 15 Å (accuracy \pm 1 Å). The SiO₂ thickness is assumed unchanged after monolayer assembly on the surface. Accuracy of the SAM thickness measurements is estimated to be \pm 2 Å. All given values for the reaction sequence were measured from a same silicon substrate.

X-ray photoemission spectroscopy (XPS) experiments were performed to control the chemical composition of the SAMs and to detect any unremoved contaminant. Samples have been analyzed by XPS, using a Physical Electronics 5600 spectrometer fitted in an UHV chamber with a base pressure of about 3.10⁻¹⁰ Torr. The X-ray source was monochromatic Al K α ($h\nu$ = 1486.6 eV) and the detection angle was 45° with respect to sample surface normal. Intensities of XPS core levels were measured as peak areas after standard background subtraction according to the Shirley procedure.

Atomic force microscope measurements were conducted in ambient air using a tapping mode AFM (Veeco, model Dimension 3100 Nanoscope) equipped with a silicon cantilever (tip radius <20 nm).

Electrochemical investigations were carried out under nitrogen atmosphere, in anhydrous and degassed dichloromethane containing 0.1 M of tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Pieces of functionalized silicon surfaces (5 mm \times 10 mm) were used as working electrodes and a platinum wire was used as counter electrode. Cyclic voltammograms were recorded at 1 V.s⁻¹ with a potentiostat (Voltalab PGZ301) controlled by a computer. The potentials were measured *versus* a saturated calomel electrode (SCE). For sequential route 3 and direct grafting, indium tin oxide substrates (ITO) were employed as

working electrodes instead of Si/SiO₂ in order to amplify electrochemical signal. ITO was first cleaned by sonication in chloroform for 5 min then treated by UV/ozone cleaner for 15 min before being functionalized exactly in the same conditions as Si/SiO₂.

4- Experimental procedure for electrical characterizations of Si/SiO₂/σC₆₀/Hg and Si/SiO₂/σC₆₀/σHg molecular junctions

Measurements were performed at room temperature in a nitrogen purged glove box. The Si n⁺/SiO₂/σC₆₀ junctions were fixed onto copper substrates with silver paste. The wafer backside was stripped with a diamond tip to remove backside oxide and ensure a good electrical contact with the silver paste. These copper substrates were mounted onto a precision vertical translation stage and the top contact was realized by carefully approaching the sample surface towards a hanging mercury drop electrode. Mercury (99.9999 %) was purchased from Fluka. Calibrated mercury drops were generated by a controlled growth mercury electrode (CGME model from BASi). The contact area of the mercury drop with the sample surface was evaluated to 1,6×10⁻³ cm² with a microscope camera. Si/SiO₂/σC₆₀/σHg molecular junction was prepared contacting Si/SiO₂/σC₆₀ junction with an alkanethiol-protected mercury drop. This treatment was obtained by immersing a hanging mercury drop in a 10⁻³ M solution of hexadecanethiol (C6) or tetradecanethiol (C14) in hexadecane for 18 h. The thiolated drop was removed from the solution then directly applied on the Si/SiO₂/C₆₀ junction (see fig. 11). During measurements, the mercury drop electrode is protected by a film of the alkylthiol solution in hexadecane (this solvent does not evaporate). Electrical transport through the SAMs was determined by measuring the current density vs the applied direct current (dc) voltage with an Agilent 4155C picoammeter. Voltage was applied on the mercury drop, the silicon substrate being grounded.

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