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Ferrocenealkylsilane molecular rectifiers

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ABSTRACT

We developed four new ferrocene containing alkylated silane self-assembled monolayers (SAMs), and evaluated their electrical properties in a metal/SAM/metal configuration. The ferrocenyl silanes used in this work can be prepared in one to two simple chemical steps from readily available ferrocene carboxaldehyde. We found that the molecular diodes obtained from these molecules can exhibit current rectification ratios as high as 150. The ease of processing coupled with the excellent rectification behavior makes these compounds very attractive for molecular electronics applications.

1. Introduction

As the length scales relevant to commercial electronics continue to shrink, great effort has been expended to explore the feasibility of devices with dimensions approaching that of a single molecule [1–8]. The molecular junctions, or molecular diodes, represent the simplest devices based on single molecule or an array of molecules sandwiched between two electrodes. In these devices the current versus voltage behavior is highly dependent on the polarity of the applied bias, i.e. they can rectify the current, similar to a pn junction. The magnitude of rectification depends on the structure and order of the monolayer, as well as the choice and quality of contacts [9–14]. Recently, we reported on organosilicon molecules which can be easily prepared and perform as molecular rectifiers when deposited as a self-assembled monolayer (SAM) [15]. When incorporated in molecular rectifier devices, these compounds perform the same function as a diode in which current is allowed to pass through at one bias while a significantly decreased current passes at the opposite bias. We found that the rectification strength depends both on the length of the molecule and its internal molecular dipole, and we were able to reach rectifications ratios as high as 200 by controlling the molecular structure and the order of the molecular layer. In a recent paper, Nijhuis and co-workers prepared ferrocene-terminated alkanethiols with different connector groups for attaching the ferrocene to the alkanethiol and explored their rectification properties [16]. While acknowledging that it is difficult to separate electronic molecular structure changes from supramolecular structure changes on the electrical characteristics of molecular junctions, they nevertheless observed that ferrocenes substituted with electron donating groups generally assembled to provide molecular rectifiers with rectification ratios superior to those of ferrocenes substituted by electron withdrawing groups. Similarly, ferrocene redox potentials have also been correlated with ring substituent structure in the past [17]. While these molecules present tremendous potential for molecular electronic devices, exhibiting rectification ratios as high as 200, the ferrocene precursors to the SAMs used in that work require a complex manufacturing process which involves a five to six step synthesis. In addition, a thiol anchoring group characteristic to the ferrocene SAMs utilized in these studies requires metal surfaces for self-assembly. Nevertheless, the inherent roughness of evaporated metals can be on the same length scale as the molecules forming the monolayer. To allow for a well-ordered monolayer on a metal surface, samples must be prepared by the template-stripping method, a time- and cost-intensive process [18–20]. In order to make devices which are compatible with the nearly ubiquitous methods used in silicon-based technologies, we chose to use a triethoxysilane anchoring group which covalently bonds to the native oxide present on a silicon wafer. The choice of this anchoring group facilitates the use of silicon wafers, which are nearly atomically flat as grown, with no additional fabrication steps [15]. In addition, the imine and amine

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ferrocene molecules we propose are obtained via a one to two step synthesis, in a fast and effective process. We incorporate these compounds in molecular devices and explore how several ferrocene substituents affect the rectification behavior in these compounds.

2. Experimental

2.1. General procedures

The proton nuclear magnetic resonance (1H NMR) spectra were obtained using a Bruker Avance 300 MHz spectrometer operating at 300.1 MHz or a Bruker Avance 500 MHz spectrometer operating at 500.1 MHz ^{13}C NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer operating at 75.5 MHz or a Bruker Avance 500 MHz spectrometer operating at 125 MHz. ^{1}H and ^{13}C NMR spectra were referenced to the residual proton or carbon signals of the respective deuterated solvents. High-resolution mass spectrometry was performed at the Mass Spectrometry Facility at Wake Forest University. All reactions were carried out under an atmosphere of argon. Aminoundecyltriethoxysilane was purchased from Gelest and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Aminopropyltriethoxysilane and lithium aluminium hydride (2 M in THF) were purchased from Aldrich Chemical Company and used as received. Anhydrous sodium sulfate was purchased from Fisher/Acros and used as received. Ferrocene carboxaldehyde was purchased from Strem Chemicals and used as received.

2.2. Procedures for preparation of ferrocene complexes

2.2.1. (E)- 1-(ferrocenyl)-N-(3-(triethoxysilyl)propyl) methanimine (2)

Anhydrous Na_2SO_4 (2.6 g) was added to a solution of ferrocenecarboxaldehyde (**1**) (0.200 g, 0.934 mmol) in anhydrous dichloromethane (4 mL). A solution of aminopropyltriethoxysilane (APTES) (0.206 g, 0.934 mmol) in anhydrous dichloromethane (4 mL) was added dropwise with stirring over 10 min. After 5 h under argon, the reddish orange mixture was filtered to remove Na_2SO_4 and dichloromethane was removed *in vacuo*. Compound **1** was isolated as a dark red viscous liquid (0.342 g, 0.819 mmol, 88%): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 4.62 (t, $J = 1.7$ Hz, 2H), 4.35 (t, $J = 1.9$ Hz, 2H), 4.18 (s, 5H), 3.83 (q, $J = 7.0$ Hz, 5H), 3.45 (t, $J = 6.9$ Hz, 2H), 1.77 (dt, $J = 15.0$, 7.0 Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 9H), 0.78–0.58 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.83, 80.83, 70.22, 69.05, 68.36, 64.60, 58.37, 24.29, 18.34, 8.08. HRMS (ESI-ion trap) *m*/*z*: $[M + H]^+$ Calc $C_{20}H_{31}FeNO_3SiH$ 418.1501; Found 418.1491.

2.2.2. (E)- 1-(ferrocenyl)-N-(3-(triethoxysilyl)propyl) methanamine (3)

Lithium aluminum hydride (2 M in THF) (2.56 mL, 5.12 mmol) was added dropwise to a solution of (E)- 1-(ferrocenyl)-*N*-(3-(triethoxysilyl)propyl)methanimine (**2**) (0.534 g, 1.28 mmol) in anhydrous THF (31 mL) at 0 °C. The mixture was stirred under argon at room temperature for 12 h and then quenched with 200 proof ethanol (4.48 mL) over ice bath (0 °C). The solvent was removed *in vacuo*. Anhydrous toluene (30 mL) was then added and the mixture was stirred at room temperature for 2 h. The oil was collected via filtration and the toluene was removed *in vacuo*. Compound **2** was isolated as a golden yellow oil (0.317 g, 0.756 mmol, 63%): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.18 (t, $J = 1.8$ Hz, 2H), 4.12 (s, 5H), 4.09 (t, $J = 1.8$ Hz, 2H), 3.82 (q, $J = 7.0$ Hz, 6H), 3.51 (s, 2H), 2.64 (t, $J = 7.3$ Hz, 2H), 1.70–1.50 (m, 2H), 1.22 (t, $J = 7.0$ Hz, 9H), 0.74–0.55 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 87.13, 68.41, 68.36, 67.70, 58.37, 52.44, 48.92, 23.30, 18.32, 8.00. HRMS (ESI-ion trap) *m*/*z*: $[M + H]^+$ Calc $C_{20}H_{33}FeNO_3SiH$ 420.1657; Found 420.1651.

2.2.3. (E)- 1-(ferrocenyl)-N-(3-(triethoxysilyl)undecyl) methanimine (4)

Anhydrous Na_2SO_4 (1.3 g) was added to a solution of ferrocenecarboxaldehyde (**1**) (0.100 g, 0.467 mmol) in anhydrous dichloromethane (2 mL). A solution of 11-aminoundecyltriethoxysilane (AUDTES) (0.103 g, 0.467 mmol) in anhydrous dichloromethane (2 mL) was added dropwise with stirring over 10 min. After stirring under argon overnight, the red mixture was filtered to remove Na_2SO_4 and dichloromethane was removed *in vacuo*. Compound **3** was isolated as a dark red viscous liquid (0.229 g, 0.432 mmol, 93%): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 4.63 (t, $J = 1.8$ Hz, 2H), 4.35 (t, $J = 1.8$ Hz, 2H), 4.18 (s, 5H), 3.81 (q, $J = 7.0$ Hz, 6H), 3.44 (t, $J = 6.6$ Hz, 2H), 1.69–1.57 (m, 2H), 1.27–1.20 (m, 25H), 0.68–0.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.46, 70.24, 69.05, 68.37, 61.98, 58.28, 33.21, 30.98, 29.67, 29.63, 29.55, 29.51, 29.27, 27.38, 27.37, 22.76, 18.31, 10.39. HRMS (ESI-ion trap) *m*/*z*: $[M + H]^+$ Calc $C_{28}H_{47}FeNO_3SiH$ 530.2753; Found 530.2744.

2.2.4. (E)- 1-(ferrocenyl)-N-(3-(triethoxysilyl)undecyl) methanamine (5)

Lithium aluminum hydride (2 M in THF) (0.721 mL, 1.44 mmol) was added dropwise to a solution of (E)- 1-(ferrocenyl)-*N*-(3-(triethoxysilyl)undecyl)methanimine (**4**) (0.191 g, 0.361 mmol) in anhydrous THF (7 mL) at 0 °C. The mixture was stirred under argon at room temperature for 48 h and then quenched with 200 proof ethanol (1.26 mL) over ice bath (0 °C). The solvent was removed *in vacuo*. Anhydrous toluene (12 ml) was then added and the mixture was stirred at room temperature for 2 h. The oil was collected via filtration and the toluene was removed *in vacuo*. Compound **4** was isolated as a golden yellow oil (0.0310 g, 0.0583 mmol, 26%): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.18 (t, $J = 1.8$ Hz, 2H), 4.12 (s, 5H), 4.11–4.09 (m, 2H), 3.81 (q, $J = 7.0$ Hz, 6H), 3.50 (s, 2H), 2.62 (t, $J = 7.3$ Hz, 2H), 1.53–1.44 (m, 3H), 1.30–1.19 (m, 25H), 0.68–0.58 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 87.24, 70.24, 68.44, 68.40, 68.36, 67.68, 58.29, 49.79, 49.13, 33.21, 30.15, 29.63, 29.60, 29.55, 29.27, 27.42, 22.77, 18.32, 10.40. HRMS (ESI-ion trap) *m*/*z*: $[M + H]^+$ Calc $C_{28}H_{49}FeNO_3SiH$ 532.2909; Found 532.2916.

2.3. Procedures for SAM assembly

Polished, highly-doped silicon (100) wafers (1 cm × 1 cm) were cleaned in hot acetone followed by hot isopropanol (IPA) and dried in a stream of nitrogen. The wafers were then exposed to UV-ozone, which serves to remove organic contaminants as well as to increase the density of hydroxyl groups on the native SiO_2 surface, before rinsing with deionized water and drying in a stream of nitrogen. All SAM depositions were carried out in a nitrogen glovebox ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm) immediately after cleaning. As compounds 2–5 were solid at room temperature, the monolayers were prepared using solution deposition. Substrates were placed into a 4 mMol SAM solution in room-temperature chloroform and sealed for 16–24 h and then rinsed sequentially with chloroform and IPA three times each to remove any molecules physisorbed on top of the chemisorbed monolayer.

2.4. Electrical characterization

Electrical measurements were carried out using a 4155C Agilent Semiconductor Parameter Analyzer with a conical-tip eutectic gallium-indium (EGaIn) contact as a non-damaging top contact and the highly-doped silicon wafer as the bottom contact. EGaIn as a top contact is very well-studied in this application because it holds its shape while on a probe tip and deforms as a liquid upon application to a surface, greatly limiting the damage to the surface under study [20–23]. The bias was applied between the EGaIn contact and the