

## Supplementary Information.

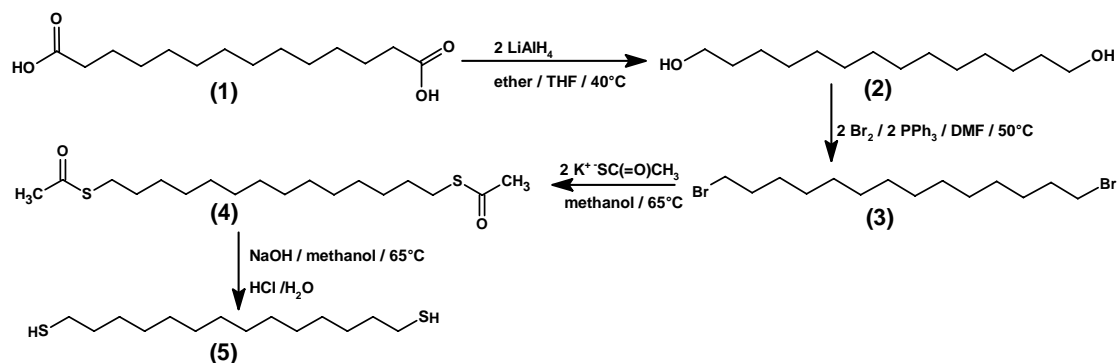
### Making molecular electronics a reality with large-area molecular junctions

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All solvents and chemicals were purchased from Sigma-Aldrich and used as received unless noted otherwise. THF was dried on Na/K alloy, ether on LiAlH<sub>4</sub> and DMF on 4 Å mol sieves. PEDOT:PSS (Baytron P HC V4) was purchased from H. C. Stark, Cr and Au from Umicore Materials AG, and 4'' silicon wafers with a 5000 Å thermally grown oxide from Silicon Quest International, Inc. Photolithography was done on a SUSS MA 1006 mask aligner. *I*-*V* curves were recorded with a Keithley 4200 Semiconductor Characterization System and a home-built probe station that was pressurized at typically 10<sup>-6</sup>-10<sup>-7</sup> mbar. In all measurements *I*-*V* scans were obtained by sweeping the voltage from 0 to 1 V, then from 1V to -1 V and finally from -1 to 0 V. To perform temperature dependent measurements, the sample table was cooled using liquid nitrogen and a temperature controller.

The length of the molecules was determined as the end-to-end distance using ACD labs software and includes 2.3 Å for the Au-S bonds.

Alkanedithiols (except 1,8-octanedithiol, Aldrich) were synthesized according to Scheme 1 and details are given below. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-300 with an internal lock on the <sup>2</sup>H signal of the solvent.



Scheme 1. Synthesis of 1,14-tetradecanediol, 1,14-dibromotetradecane, 1,14-dithioacetyl tetradecane, and 1,14-tetradecanedithiol.

**1,14-tetradecanediol (2):** 10.0 gr (= 39×10<sup>-3</sup> mol) of 1,14-tetradecanedioic acid (1) was dissolved in a 50/50 mixture of 300 ml dried ether/THF under nitrogen and cooled to 0 °C. After 78 ml of 1M LiAlH<sub>4</sub> in ether was added dropwise, the temperature was slowly increased and the solution was refluxed for 2 days. The mixture was poured out in 2.5 L of deionised water and the white precipitate was filtered, washed with copious amounts of water, 300 ml saturated NaHCO<sub>3</sub> (aq) and water. The remaining white solid was dissolved in hot methanol (500 ml) and the methanol was evaporated. The white product was recrystallised from 300 ml hot methanol to yield 7.26 gr of white crystals (2).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2 (m, 20H, -(CH<sub>2</sub>)<sub>10</sub>), 1.5 (m, 4H, HOCH<sub>2</sub>CH<sub>2</sub>-), 3.6 (t, 4H, HOCH<sub>2</sub>).

**1,14-dibromotetradecane (3):** Bromine (11.2 gr, 70×10<sup>-3</sup> mol) was added dropwise under nitrogen to an ice-cooled solution of 18.4 gr (=70×10<sup>-3</sup> mol) of triphenylphosphine in 150 ml of dried DMF. The resulting orange solution was added dropwise to a solution of 7.26 gr (=31.6×10<sup>-3</sup> mol) of 1,14-tetradecanediol (2) in 150 ml of dried DMF and stirred for 2 days at 50°C. After the solution was cooled down, it was poured out in 1 L deionised water. The white precipitate was filtered, washed with copious amounts of deionised water and dried. The white filtrate was dissolved in 400 ml hot hexane and the insoluble solid (Ph<sub>3</sub>PO) was filtered. Hexane was evaporated and the product was recrystallised from 200 ml methanol to yield 9.41 gr of white crystals (3).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.2–1.6 (m, 20H,  $-(\text{CH}_2)_{10}$ ), 1.8 (quintet, 4H,  $\text{BrCH}_2\text{CH}_2-$ ), 3.35 (t, 4H,  $\text{BrCH}_2$ ).

**1,14-dithioacetyltetradecane (4)**: 6.1 gr ( $=16.9 \times 10^{-3}$  mol) of 1,14-dibromotetradecane (**3**) was dissolved in 200 ml methanol, 4.2 gr ( $=36.7 \times 10^{-3}$  mol) potassium thioacetate was added and the solution was refluxed overnight. After cooling, the solution was extracted with  $3 \times 150$  ml ether and the ethereal phase was washed with  $3 \times 100$  ml hot saturated NaCl (aq). The ethereal phase was washed and dried on  $\text{Na}_2\text{SO}_4$ , filtered and evaporated, yielding 4.26 gr of white crystals (**4**).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.2 (m, 20H,  $-(\text{CH}_2)_{10}$ ), 1.5 (m, 4H,  $\text{CH}_3(\text{O}=\text{C})\text{-S-CH}_2\text{CH}_2-$ ), 2.25 (s, 6H,  $\text{CH}_3\text{C(=O)-S-}$ ), 3.8 (t, 4H,  $\text{CH}_3(\text{O}=\text{C})\text{-S-CH}_2$ ).

**1,14-tetradecanedithiol (5)**: 4.26 gr ( $=12.3 \times 10^{-3}$  mol) 1,14-dithioacetyltetradecane (**4**) was dissolved in 150 ml methanol, 6 ml NaOH (aq) was added dropwise and the mixture was refluxed overnight. After cooling, the mixture was poured out in 150 ml ice/15 ml HCl (37%)/300 ml ether and stirred for a few hours. The layers were separated, and the ethereal phase was dried on  $\text{Na}_2\text{SO}_4$ , filtered and evaporated. The product was obtained by Kugelrohr distillation and recrystallised from hexane to yield 2.66 gr of white crystals (**5**).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.2–1.4 (m, 20H,  $-(\text{CH}_2)_{10}$ ), 1.55 (quintet, 4H,  $\text{HS-CH}_2\text{CH}_2-$ ), 2.45 (quartet, 4H,  $\text{HSCH}_2$ ).

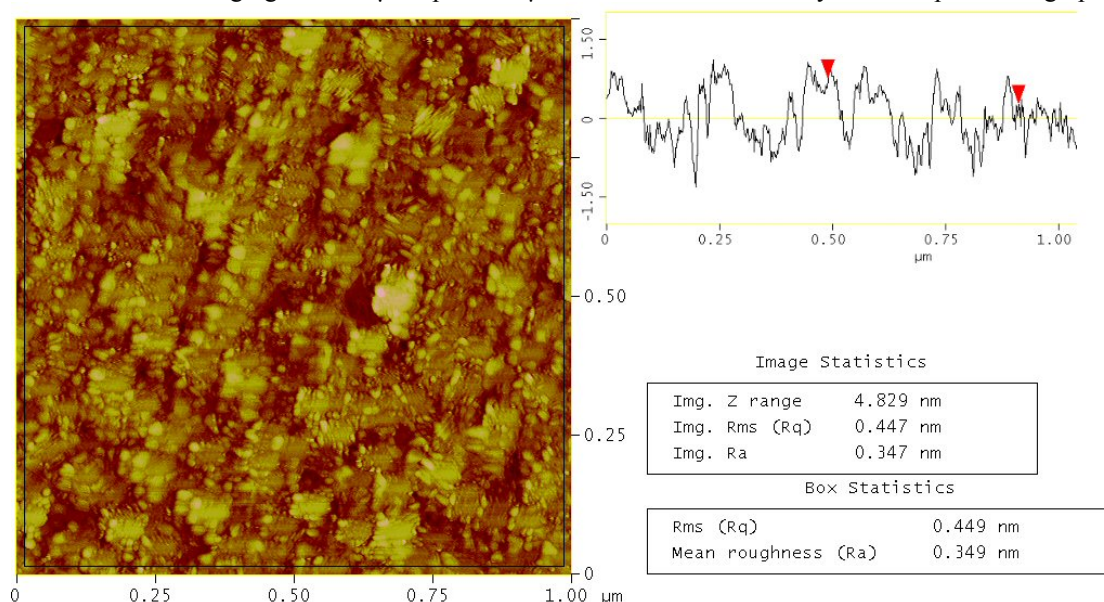
**1,12-dodecanedithiol**: This compound was synthesized similarly to 1,14-tetradecanedithiol, starting from 1,12-dibromododecane (Sigma-Aldrich).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.2–1.4 (m, 20H,  $-(\text{CH}_2)_8$ ), 1.55 (quintet, 4H,  $\text{HS-CH}_2\text{CH}_2-$ ), 2.45 (quartet, 4H,  $\text{HSCH}_2$ ).

**1,10-decanedithiol**: This compound was synthesized similarly to 1,14-tetradecanedithiol, starting from 1,10-dibromodecane (Sigma-Aldrich) and was obtained as a colourless liquid.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.2–1.4 (m, 20H,  $-(\text{CH}_2)_6$ ), 1.55 (quintet, 4H,  $\text{HS-CH}_2\text{CH}_2-$ ), 2.45 (quartet, 4H,  $\text{HSCH}_2$ ).

**Photolithography**: On top of a 4" silicon wafer with 5000 Å thermally grown oxide, a 1 nm chromium adhesion layer and a 40 nm gold bottom contact are thermally evaporated with a typical RMS roughness of about 0.5 nm for  $1 \mu\text{m}^2$  as measured with STM (see image below). Photoresist is spin coated and holes ranging from 10  $\mu\text{m}$  up to 100  $\mu\text{m}$  in diameter are made by standard photolithography.



STM image of the bottom gold electrode.

**SAM formation**: The self-assembling molecules were dissolved in ethanol ( $\sim 3 \times 10^{-3}$  M). The plasma cleaned gold substrates were immersed into the solution for at least 2 days. The substrates were thoroughly rinsed with ethanol, toluene and 2-propanol, dried with a  $\text{N}_2$  flow, and used immediately for spin coating of PEDOT:PSS (Baytron P HC V4).

**Reactive Ion Etching:** After deposition of a 150 nm Au top contact, the substrate was exposed for 5 minutes to a 40 Watts oxygen plasma (pressure: 0.009 mbar; flow: 9 sccm) to remove excess PEDOT:PSS using the gold top electrode as a etching mask.