## Supplementary Material for

## Nanometric Building Blocks for Robust Multifunctional Molecular Junctions

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## This document includes:

Materials and Methods Figure S1- AFM layer thickness determination Figure S2- AQ JV curves for different scan rates Figure S3- AQ/BTB JV curves for different scan rates Figure S4- AQ/BTB JV curves before and after one million cycles Figure S5- AQ/BTB/LiBA JV curves vs. scan rate in vacuum Figure S6- The dynamics of the trilayer device during a long negative pulse Figure S7- Two relaxation cycles for AQ/BTB/LiBA following voltage pulses

#### **Materials and Methods**

#### **Device** Fabrication

The MJ structure shown schematically in figure 1A was fabricated by established procedures<sup>1-3</sup> based on electrochemical reduction of diazonium reagents as follows. For bottom electrode preparation, clean quartz substrates (flame fused quartz (nano grade), Quartz Unlimited LLC) were placed in an electron beam deposition system (Kurt J. Lesker PVD 75) and pumped down in a vacuum chamber for a minimum of 3 hours ( $P < 1 \ge 10^{-6}$  Torr). Chromium (Kurt J. Lesker), gold (MRCS Canada) and carbon (spect pure graphite, SPI supplies) were then deposited respectively onto the clean Quartz substrate through a shadow mask with 250 µm vertical slits openings and employed as the bottom electrode. The resulting carbon layer (eC) is a conducting mixture of sp<sup>2</sup> and sp<sup>3</sup> carbon resembling glassy carbon which is very smooth (rms < 0.4 nm by AFM), making it ideal for diazonium grafting of molecular layers for use in molecular electronics. Electrochemical grafting of the molecular layers took place in a conventional 3 electrode cell with a 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>, 0.1 M, 99% Aldrich) electrolyte dissolved in acetonitrile. The eC bottom contacts acted as the working electrode, an Ag/Ag<sup>+</sup> reference electrode and a Pt wire as the counter electrode. The diazonium salts described in this section were synthesized using the diazotation reaction, as described previously. 2-Aminoanthraquinone (Sigma Aldrich), 4-Aminobenzoic acid (Sigma Aldrich), and 1-(bithien-2-yl)-4-aminobenzene (BTAB)<sup>4</sup> were used as precursors for the diazonium formation.

The first molecular layer was grafted to the eC bottom electrode by electrochemically reducing the 2-Anthraquinone (AQ) diazonium salt. The AQ diazonium salt (4.5 mg) and

tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>, 0.5 g, 99% Aldrich) electrolyte were dissolved in 11.7 g ACN (anhydrous, Caledon Laboratory Chemicals) to give 1 mM and 0.1 M concentrations, respectively. AQ was grafted on the carbon surface by linearly sweeping the electrochemical potential from +0.4 V to -0.65 V (vs. Ag/Ag<sup>+</sup>), for 10 cycles at a scan rate of 50 mV s<sup>-1</sup>. The samples were then rinsed with copious amounts of ACN and dried with nitrogen. This gave an AQ layer thickness of  $6.8 \pm 0.8$  nm. The subscripts in MJ descriptions designate the layer thicknesses in nm, e.g.  $eC_{10}/AQ_{6.8}/eC_{10}/Au_{20}$ .

Reduction of AQ diazonium ions in ACN results in covalent bonds to the eC and between molecular subunits. Since layer formation is mediated by aryl radicals, it is possible to form oligomer multilayers having thicknesses of 2 to >25 nm<sup>5-7</sup>. The layer thickness is well controlled by the electrochemical deposition parameters (sweep rate, potential and number of cycles) as well as the diazonium salt concentration and purity. Although diazonium-derived molecular layers are inherently more disordered than Au/thiol self-assembled monolayers, they have the advantage of stronger bonds between the substrate and the molecules, as well as between molecular subunits, thus greatly improving overall stability.

The second molecular layer was grown by electrochemically reducing bis-thienylbenzene (BTB) diazonium ions. To generate the BTB diazonium ions, 1-(bithien-2-yl)-4-aminobenzene (BTAB, 2.8 mg) and TBABF<sub>4</sub> were dissolved in ACN (similar to the previously described procedure<sup>6</sup>). However, 30  $\mu$ L of tert-butyl nitrite (Fluka Analytical) was then added to the BTAB solution in situ to convert the amino moiety of the molecule to a diazonium ion (R-N<sub>2</sub><sup>+</sup>) as described previously. The BTB diazonium ion was then grafted to the eC/AQ surface by sweeping from 0 V to -0.8 V (vs. Ag/Ag<sup>+</sup>), for 8 cycles at a scan rate of 100 mV s<sup>-1</sup>. The samples

were then rinsed with copious amounts of ACN and dried with nitrogen. Taking the difference between the total thickness and the 6.8 nm AQ layer resulted in a BTB layer thickness of 8.0 nm.

The third molecular layer was grown by electrochemically reducing the benzoic acid (BA) diazonium salt. BA diazonium salt (3.5 mg) and TBABF<sub>4</sub> (0.5 g) electrolyte were dissolved in ACN (11.7 g) to give 1 mM and 0.1 M concentrations, respectively. BA was grafted to the eC/AQ/BTB surface by sweeping the potential from 0 V to -1.7 V (vs. Ag/Ag<sup>+</sup>), for 8 cycles at a scan rate of 200 mV s<sup>-1</sup>. The solution was continuously purged with Ar throughout the electrochemical grafting procedure to reduce the possibility of oxygen reduction in the solution at very negative potentials. The samples were then rinsed with copious amounts of ACN and dried with nitrogen. Taking the difference between the total thickness and the AQ<sub>6.8</sub>/BTB<sub>8.0</sub> layer gave a BA layer of 1.1 nm.

To interchange the hydrogen of the benzoic acid top layer with lithium, the devices were incubated in a solution of lithium hydroxide (0.1 M, Sigma-Aldrich) in anhydrous ethyl alcohol (200 mL, Commercial Alcohols) for 10 minutes with constant stirring. The substrates were then rinsed with copious amounts of ethyl alcohol and ACN to remove excess lithium cations.

A shadow mask with horizontal line openings of 250  $\mu$ m was placed on the chips for deposition of the top contact and the modified devices were pumped down in the vacuum chamber for no longer than 1.5 hours. The top electrodes consisted of 10 nm of evaporated carbon (eC) followed by 20 nm of Au at deposition rates of 0.2 and 0.5 Å s<sup>-1</sup>, respectively. This arrangement formed a cross-bar junction with an active junction area of 0.000625 cm<sup>2</sup>. The eC/Au top contact combination reduces gold penetration into the molecular layer and resists breakdown by electromigration<sup>2</sup>.

#### **Determination of Molecular Layer Thickness**

The thickness of each molecular layer was independently measured using a combination of contact and tapping modes of Atomic Force Microscopy (AFM, Digital Instruments 3100) using a silicon AFM cantilever probe (with Al backside) with a tip radius of 8 nm (MikroMasch). This method was previously described in detail<sup>8</sup>. Briefly, a 1x1 µm area trench was formed on the eC/molecule bottom contact near the active junction using contact mode (Figure S1A). A 0.7 to 0.8 V set point was used to remove the entire molecular layer in the scratched area without observable damage to the eC bottom contact. After removal of the molecule, tapping mode was used to view a 5x5 um image of the scratched area. The 5x5 um area was imaged using tapping mode with a low scan rate (0.5 Hz) and high resolution (1024) iterations/line). The trenched area of 1x1 µm was centered in the tapping mode image (Figure S1A). A "depth" analysis was performed in which a rectangular box was placed evenly across the trench and undisturbed molecular layer (bottom of Figure S1A). The depth profile fit two Gaussian functions that represented the average height of the scratched and unscratched areas (Figure S1B). The difference between the centers of the Gaussian curves determined the thickness of the molecular layers.

The total thickness of the molecular layers of AQ, the bilayer (AQ/BTB) and trilayer (AQ/BTB/LiBA) devices described in this paper were found to be  $6.8 \pm 0.8$  nm,  $14.8 \pm 1.4$  nm and  $15.9 \pm 1.2$  nm respectively.

#### **Electrochemical Instrumentation and Measurements**

All cyclic voltammetry and chronoamperometry experiments described in this work were carried out in a cryogenic vacuum probe station (Janis Research ST-500) using a custom

Labview setup with a PCI-6110 DAQ board and a SR570 current amplifier (Stanford Research Systems) paired with National Instrument software. All investigations employed a 4 wire-mode to correct for ohmic losses in the Au/eC films.

For acetonitrile (ACN) vapor experiments, ~5 mL of ACN (anhydrous) was placed in the cryogenic probe station's designated solvent holder. The solvent line was evacuated for 10 minutes prior to release of the vapor to ensure no residual air was in the line. The system was then closed off from the vacuum pump ( $P \le 1 \ge 10^{-5}$  torr prior to ACN vapor release) and the ACN vapor was allowed into the system. After 10 minutes of ACN exposure, the solvent line was closed off. An additional 30-60 minute wait period followed before experiments were carried out to ensure ACN had reach equilibrium with the molecular layer.



# Figure S1:

AFM images for molecular layer thickness analysis. A. (top and middle) Line profile across 1x1 cm trench illustrating the depth of the molecular layer, (bottom) rectangular area chosen for depth analysis calculations. B. (top) Gaussian curve analysis for AQ molecular layer thickness, (middle) Gaussian curve analysis for AQ/BTB bilayer thickness, and (bottom) Gaussian curve analysis for AQ/BTB/LiBA thickness.



## Figure S2:

4-wire cyclic voltammetry scans for quartz/Cr<sub>4</sub>/Au<sub>30</sub>/eC<sub>10</sub>/AQ<sub>6.8</sub>/eC<sub>10</sub>/Au<sub>20</sub> at scan rates of 1, 10, 100 and 1000 V s<sup>-1</sup> in **A.** Vacuum (P  $\leq$  1 x 10<sup>-5</sup> Torr,  $t_{min} >$  12 hours) and **B.** ACN vapor (exposed for 1 hour).



## Figure S3:

4-wire cyclic voltammetry scans for quartz/Cr<sub>4</sub>/Au<sub>30</sub>/eC<sub>10</sub>/AQ<sub>6.8</sub>/BTB<sub>8.0</sub>/eC<sub>10</sub>/Au<sub>20</sub> at scan rates of 1, 10, 100 and 1000 V s<sup>-1</sup> in **A.** Vacuum (P  $\leq$  1 x 10<sup>-5</sup> Torr,  $t_{min} >$  12 hours) and **B.** ACN vapor (exposed for 1 hour).



# Figure S4:

Lifetime test for  $eC_{10}/AQ_{6.8}/BTB_{8.0}/eC_{10}/Au_{30}$  in vacuum (P  $\leq 1 \ge 10^{-5}$  Torr,  $t_{min} = 12$  hours) at 1000 V s<sup>-1</sup> scan rate. Black line is first scan and the red line after an additional 1 million scans. Rectification ratio (RR) at 4V decreased from 47 to 9 after 1 million scans.



## Figure S5:

A. Scan rate dependence of the trilayer quartz/ $Cr_4/Au_{30}/eC_{10}/AQ_{6.8}/BTB_{8.0}/LiBA_{1.1}/eC_{10}/Au_{20}$  in vacuum (P  $\leq$  1 x 10<sup>-5</sup> Torr,  $t_{min} >$  12 hours) for scan rates between 1000 to 1 V s<sup>-1</sup>. **B**. Overlay of 1000 V s<sup>-1</sup> scans for the trilayer in vacuum and ACN vapor.



# Figure S6:

Comparison of the dynamics of  $AQ_{6.8}/BTB_{8.0}/LiBA_{1.1}$  device in ACN vapor (exposed for 1 hour) vs vacuum during a 1s, -4.5 V pulse.



#### Figure S7:

Relaxation experiment of  $AQ_{6.8}/BTB_{8.0}/LiBA_{1.1}$  in ACN vapor (exposed for 1 hour). Initial curve was taken before any bias applied. Scans labelled "0, 1, and 100" represent the time waited (in seconds) before running the CV scans (blue and red) after a 10s pulse of -4.5V. The red curves represent the first run and the blue curves represent the repeated run, performed a few minutes later. Small change in current observed between consecutive runs.

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