Supporting Information

Vertically Stacked Molecular Junctions: Toward a Three-Dimensional Multifunctional Molecular Circuit

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Fabrication Process of the Molecular Circuit

a. The first floor, consisting of compound 1, was constructed with the use of a previously-described recipe1, followed by indirect evaporation of a gold layer on top of a palladium electrode.

b. The fabrication process of the second floor was initiated by a cold evaporation of a 100nm alumina layer followed by the definition of microcavities and pads in this layer.

c & d. Each second-floor cavity was set between two first-floor junctions with the use of standard etching and lift-off recipes (see Figure 3).

e. The top electrodes of the second floor were defined with the use of a low-temperature S1818 photolithography–based recipe, followed by the deposition of an Az-based SAM inside the second-floor cavities (f).

The Az protein, originating from Pseudomonas aeruginosa, was purchased from Sigma and used without further purification. The natural form of Az contains a disulfide group that serves to anchor the protein to gold surfaces after the gold substrate is activated by a previously-published technique.1 The Az monolayer was prepared by incubation of a solution of Az in 50mM ammonium acetate at pH 5 for about 48 hours. The sample was then rinsed with ultrapure water and dried in a stream of pure nitrogen.

The process was completed by the indirect evaporation and lift-off of the Pd upper contact (g,h).

Figure S1 shows optical images of the circuit taken at different focal length clearly demonstrating the 3D architecture of the circuit.

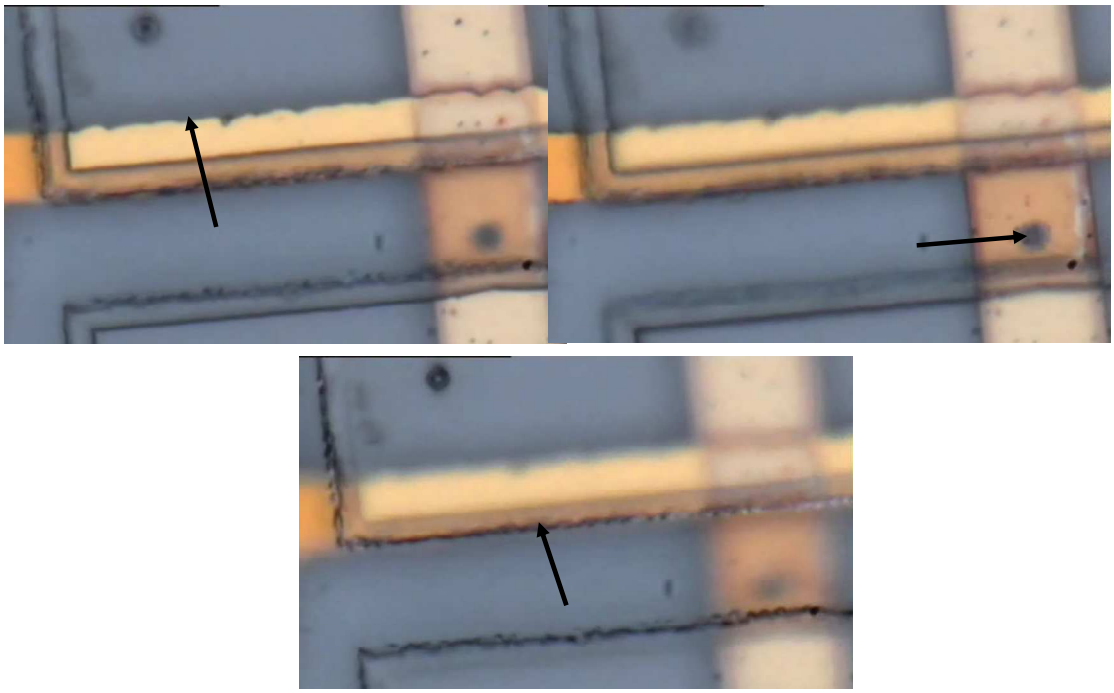

Figure S1- optical images of the circuit. Top (left) focus taken on the bottom electrode. Top (right) adjusted on a cavity and bottom – focus taken on the top electrode.

Preparation and Characterization of Self-Assembled Monolayer of Azurin protein

Sample preparation- A gold substrate was prepared by evaporation of a 120nm layer of gold on top of a 5nm titanium adhesion layer covering an oxidized-silicon wafer. The sample was thoroughly cleaned with UV-Ozone cleaner and ethanol and dried with nitrogen gas. The substrate was then immersed in an Az solution for 48 hours, rinsed with ultrapure water and dried in a stream of pure nitrogen. A 2cm x 2cm SAM sample

was characterized by polarization-modulated infrared absorption spectroscopy and spectroscopic ellipsometry.

1. Polarization-modulated infrared absorption spectroscopy (PMIRAS)

Measurements were performed with the use of a Bruker PMIRAS spectrometer inside a glove box (Vertex 70 and PMA 50 equipped with a photoelastic modulator and a lock-in amplifier with an LN_2-cooled MCT photovoltaic detector) . Figure S2 shows the spectrum of the Az-SAM taken in the relevant region.

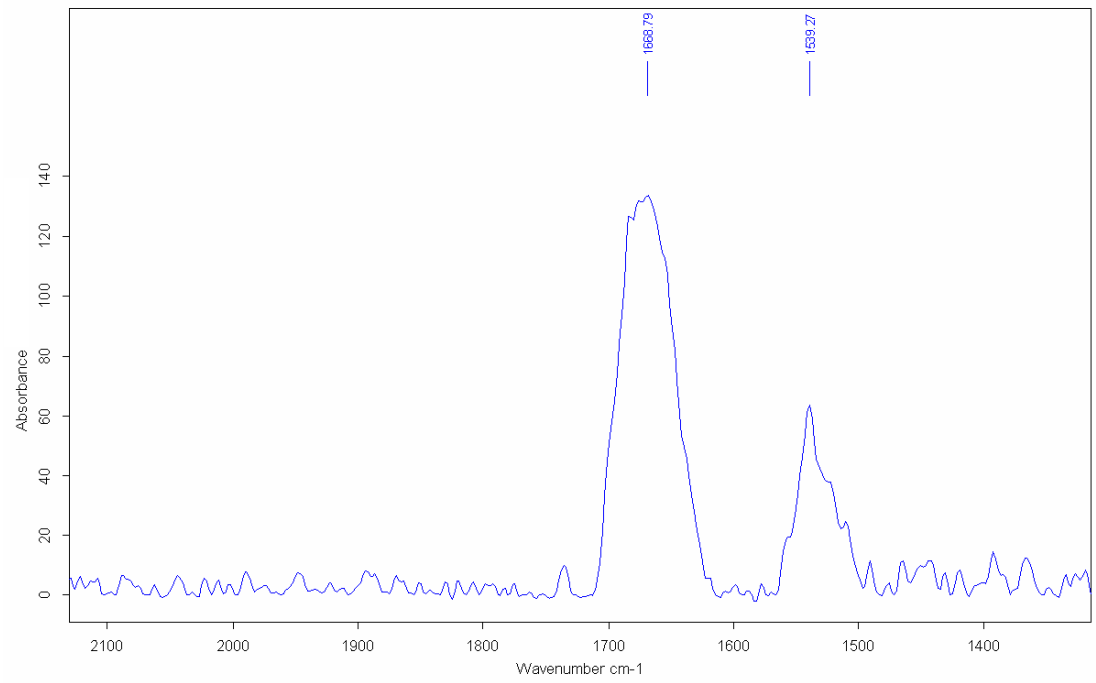

Figure S2 A PMIRAS spectrum of the AZ-SAM showing the distinct amide- 1 peak (1669 cm^{-1}).

Two distinct peaks were found in the region measured; a carbon peak near 1540cm^{-1} and a distinct amide-1 peak around 1669cm^{-1}). While the

carbon peak can originate from several sources, the amide peak is a clear indication of the existence of the protein[2].

2. **Characterization by spectroscopic ellipsometry**.

Measurements were made with the use of a spectroscopic ellipsometer (Woollam, alpha-SE) inside a glove box. The angle of incidence was 70° and measurements were carried out over the range of 380-900nm. Complete EASE analysis software was used for model fitting and analyzing the results. Figure S3 shows the measurement results and the Cauchy-model fitting of the results. We have found that the average thickness of the SAM is 2.2±0.3nm. This value agrees with previous measurements of Az SAM [3].

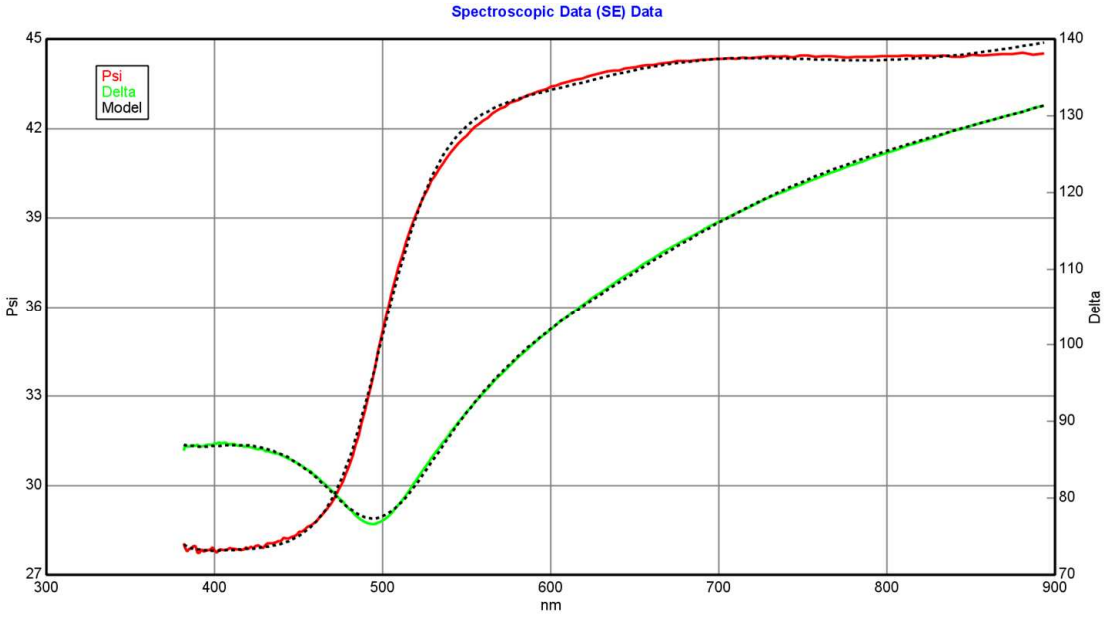

Figure S3. Spectroscopic ellipsometry measurements and fitting of the Az-SAM monolayer.

I/V curves of reference device

Figure S4 shows an I/V characteristics of a short-circuited reference device. The device was prepared by introduction of only the Az buffer solution without the protein itself. As expected, clear ohmic behavior was

measured, indicating on an electrical short-circuit between the top and bottom electrodes.

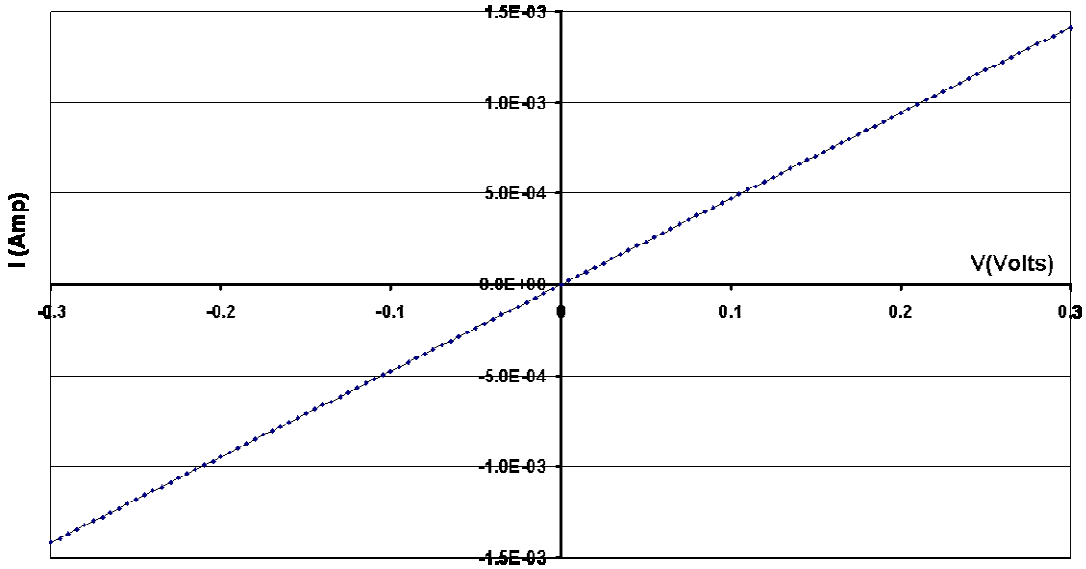

Figure S4. I/V characteristics taken for short-circuited reference second floor device. A clear Ohmic behavior is measured.

References

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(2) Surewicz, W. K.; Szabo, A. G.; Mantsch, H. H. ***Eur J Biochem*** **1987,** ***167***, **519-523.**

(3) Zhao, J. W.; Davis, J. J.; Sansom, M. S. P.; Hung, A. ***Journal of the American Chemical Society*** **2004,** ***126***, **5601-5609.**