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Reply to Comment on “Extent of conjugation in diazonium-derived layers in molecular junction devices determined by experiment and modelling”, [PCCP 2019, 21, 16762] By: Richard L. McCreery,* Shailendra K. Saxena, Mustafa Supur, Ushula Tefashe

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Abstract

Our paper [PCCP 2019, 21, 16762] is the subject of a comment that clarifies a flaw in analysis of STM data. We accept the comment in regard to the aspect ratio considerations, but we also further clarify the main conclusions of our paper, and provide a molecular scale schematic using the data presented in the comment to help refine the original conclusions. Taken together, this shows that models presented in the literature may benefit from including more fine structure details, as better understanding may emerge from such considerations. This was the intent of our original article, and we thank the comment authors for the chance to clarify these points.

Main Text

We thank the authors for their thoughtful comment [REF] on our paper [PCCP 2019, 21, 16762]. The authors did not seem to dispute one of our main conclusions, stating that “We agree with one conclusion of the paper, that diazonium-derived molecular layers on carbon surfaces have weak intermolecular electronic interactions between oligomer subunits, and came to that conclusion in 2017 [1].” However, they do argue that the STM data we presented is not representative of many samples used, and that our analysis of the height variations was flawed. While we agree with some aspects of their analysis, we will reiterate here that we are calling for a refinement of the models used in literature, especially with respect to molecular layer structure and the characterization of the surface upon which they are built. This analysis is based on experimental optical absorption data and DFT models, but as shown here, a to-scale roughness analysis still necessitates consideration of the detailed molecular structure features of these devices. Our hope is that discussions such as the comment in question and its author's large body of work on the subject, together with new perspectives offered in works like ours, will lead to a refinement of the models used in the literature so that the understanding of molecular nanolayers and devices derived from them can be advanced.

We agree with the authors that our scanning tunneling microscopy analysis of substrates on which molecular layers are built should have taken into account the aspect ratio and that our characterization of the substrate as having "sharp undulations" was flawed. We therefore agree with the statement:

> "By magnifying the Z axis relative to the X and Y axes to highlight topography, the height variations appear "sharp" and severe compared to the length of the azobenzene molecules used in the PCCP2019 study (i.e. 1.12 nm). However, when plotted with a 1:1 Z:X aspect ratio in Figure 2B, the picture is very different, with height variations resembling "rolling hills" with the rate of height changes being gradual over the length of an AB molecule."

The topology (~0.5 nm or less RMS roughness) of our surface is similar to that presented in many previous works [2]. We also agree with the fact that the long-range variation in surface topography remains very low for these surfaces, including the one we presented despite the fact that we did not present these data with the appropriate aspect ratio.

We believe it is important to note that in the simple schematics that have been used to represent azobenzene (and other) layers within molecular junction devices [2] [3] [4], the layer is generally shown as being composed of para-linked molecules. If molecular layers were indeed composed of *para*-linked molecules, a shift in absorbance maxima to lower energies with layer thickness (i.e. increased molecular conjugation) would be observed. However, experimental measurements show conclusively that absorbance maxima of molecular layers are largely independent of layer thickness, and our paper showed some possible alternative molecular structures that are consistent with these observations. While dihedral angles between *para*-linked units can account for some degree of the effect (as mentioned in the comment), we showed why other possible linkages must also be considered.

Figure 2 presented in the comment shows several line scans of surfaces that have undulations on the order of the molecular length of the molecule used to build layers. This is consistent with the underlying hypothesis presented in our paper, which is that the surface topology is such that the layer growth can occur through substitutions other than at the *para* site of deposited azobenzenes. Layer growth through *ortho*- and *meta*-sites of deposited molecules would result in layers that have optical properties that are consistent with the optical measurements. In Figure 1 below, we demonstrate how the undulations in the surface allow for radical addition reactions at different sites on deposited azobenzene molecules, using a set of line scan data provided in the comment. It can be seen from the figure than even the mild undulations described in the comment provides the opportunity for the formation of molecular layers composed of variously linked azobenzene molecules. Our conclusions in this connection are not disputed by the authors, who state "We agree that radical-mediated oligomer growth will result in a variety of structures (i.e. para-, ortho, and meta linked), determined in part by the molecular structure of the monomers." Thus, we conclude that the model of the devices shown should be refined to include more complex layer structures than are commonly shown.

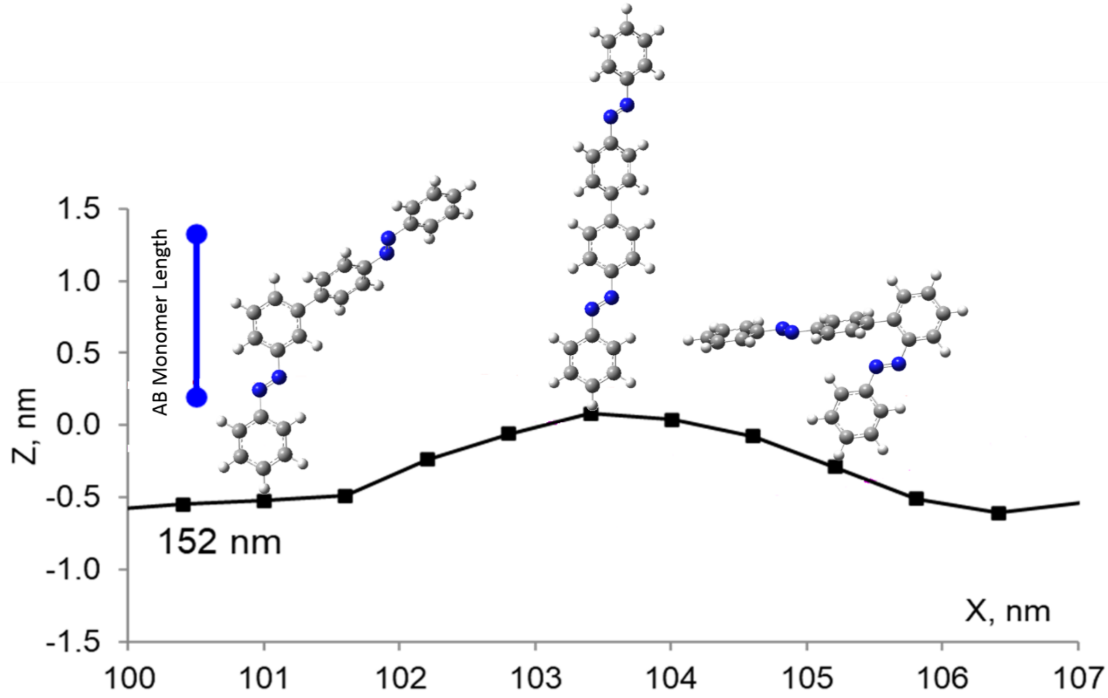

Figure 1. Overlay of a line scan with superimposed monomer molecules shown to scale, illustrating that the variety of motifs are indeed possible.

The authors suggest that the substrate we used may lead to differences in surface roughness in comparison to devices built with thicker substrates. We used optically transparent PPF (OTPPF), which indeed is different from the thicker films that have been used in other works. We were clear in our paper about the processes used to create the substrates, and the data we provided should be considered within that context. We obtained optical data on the same type of substrate as the STM image presented in Figure 3 of our original paper. The value of the RMS roughness for our sample was 0.5 nm, which is consistent with the vast literature cited in the comment. While there may be slightly more variation in heights for this particular sample (up to ~5 nm), taking the aspect ratio into consideration, there appears to be a “rolling hill” topology as shown by the comment authors. This suggests to us that there is little structural difference between the nature of the OTPPF and thicker samples.

In closing, we again thank the authors for pointing out the flaw in our STM image analysis. This important point should be considered when constructing a complete model for devices made using the techniques we described. What is clear is that the exact nature of 2-10 nm molecular layers in molecular junction devices such as those constructed by us and by the authors of the comment requires refinement. Indeed, this is the central conclusion of our work, which is supported by the comment authors’ statement: “We consider the distribution of oligomer isomers to be an open question, and agree with PCCP2019 that the molecular layers are mixtures of isomers.” We wish to underscore that our work does not invalidate the results of the many works that came before it. In fact, these works collectively demonstrate the robust nature of the molecular device platform based on diazonium-derived films on PPF surfaces. Indeed, this platform was the first molecular electronic device used in the commercial market, with robust performance and impressive application in the real world [5]. Our goal was to contribute to an understanding of the nature of the molecular layer structure in molecular junction devices. We hope our clarification here conveys the value in refining the models of molecular layer structure to improve understanding that could reveal rich and interesting device functionality.

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