

Supporting Information for "Large-Scale Atomistic Simulations of Environmental Effects on the Formation and Properties of Molecular Junctions"

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The details of the hybrid MD-MC method for simulating the elongation of a BDT-coated Au NW are described in our previous work.¹ We direct the reader to this publication for details on the energy terms and parameters for chemically bonded interactions within BDT, nonbonded interactions between BDT molecules and BDT and Au, and BDT partial charges. We follow the details and procedure outlined in this prior work, with a few important additions to improve the accuracy and efficiency of the simulations. As described below, these additions apply to both the MD-MC hybrid simulations as well as to the subsequent MC-based molecular junction formation simulations. In the first two sections we describe the additions we have made to the simulation models and the implementation of BDT identity swap moves.

In the last two sections we present additional results from those of the main article. The third section presents results for the bonding geometry of BDT on the Au (111) surface. In the final section we present snapshots of the twenty ruptured Au NWs employed in this study.

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Simulation Models

The first important addition to our simulation protocol is the inclusion of potential energy terms for more accurately describing the BDT-Au chemically bonded interaction. The functional forms of these additional terms are the following:

$$U_{bend}(\phi) = \frac{k_\phi}{2\sin^2\phi_0}(\cos\phi - \cos\phi_0)^2 \quad (S1)$$

$$U_{tors}(\varphi) = \frac{E_\varphi}{2}(1 - \cos 2\varphi_0 \cos 2\varphi) \quad (S2)$$

where U_{bend} and U_{tors} are the Au-S-C angle bending and Au-S-C-C torsion energies, respectively. U_{bend} is a function of the Au-S-C bond angle, ϕ , while U_{tors} is a function of the torsion angle, φ , about the S-C axis. k_ϕ and E_φ are force constants, and ϕ_0 and φ_0 are the bond and torsion angles, respectively, at equilibrium. The parameter values were obtained through fits to density functional theory (DFT) calculations in our previous work,² which included three separate DFT functionals; the values listed in Table S1 reflect the average of these three functionals. We incorporate both U_{bend} and U_{tors} into the MD calculations, and U_{bend} into MC sampling.

During MC sampling, the S-Au bond creation and destruction processes are realized using a bond cutoff, r_{cut} . To ensure a smooth transition between S-Au bonded and unbonded states, we slightly modify the S-Au bond stretching terms used in our previous work.¹ We now describe the potential energy between a S and Au atom using

$$U_{S-Au}(r) = \begin{cases} -\int_r^{r_{cut}} \nabla U_{Morse}(r) dr - \int_{r_{cut}}^{\infty} \nabla U_{LJ}(r) dr & \text{for } r < r_{cut} \\ U_{LJ}(r) & \text{for } r \geq r_{cut}, \end{cases} \quad (S3)$$

where

$$U_{Morse}(r) = D_e e^{-\alpha(r-r_e)} \left[e^{-\alpha(r-r_e)} - 2 \right] \quad (S4)$$

and

$$U_{LJ}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right]. \quad (\text{S5})$$

U_{Morse} is the Morse bonding potential, which we previously³ fit to DFT calculations using three different functionals to accurately describe BDT chemisorption at on-top and on-bridge sites. D_e is the Morse potential well depth, r_e is the equilibrium bond length, and α is a third fitting parameter. Values reflecting the averages of the three DFT functionals are listed in Table S1. Note, we have adopted the notation D_{S-Au} to represent r_e for on-top bonding in the body of the paper. U_{LJ} is the Lennard-Jones (LJ) interaction energy between a S atom and Au atom, with the parameters ϵ_{ij} (the potential well depth) and σ_{ij} (the inter-atomic distance at which the energy between a S and Au atom is zero) for S and Au taken from the universal force field.⁴ For predicting S-Au bond formation and breakage, we choose a value of $r_{cut} = 3.66$ Å. This value corresponds to the minimum on the S-Au LJ curve, and ensures a relatively smooth transition in both the energy and force between a S-Au pair at r_{cut} .

Table S1: BDT-Au bonding parameters.

Parameter	units	Top Site	Bridge Site ^a
D_e	kcal/mol	49.4	28.7
α	1/Å	1.72	1.67
r_e	Å	2.29	2.44
k_ϕ	kcal/(mol rad ²)	145.5	71.5
ϕ_0	degree	105.4	110.8
E_ϕ	kcal/mol	2.92	1.23
φ_0	degree	90	90

^aFor a single S-Au pair involved in on-bridge bonding.

BDT Identity Swap Moves

The next important addition is a new MC move type designed to improve sampling efficiency. During MC sampling, on-top and on-bridge bonding of BDT to a NW surface is realized by performing the simulations within the semigrand canonical ensemble.⁵ In our previous work, MC sampling was performed in the grand canonical ensemble (constant μVT , where μ is chemical potential, V is volume, and T is temperature), with the Au NW surface in equilibrium with a bulk solution of BDT. Semigrand canonical Monte Carlo (SGCMC) simulations are akin to grand canonical Monte Carlo (GCMC) simulations in all respects except that in SGCMC simulations the composition of a mixture is sampled. Thus, in addition to the BDT center-of-mass (COM) displacement, COM rotation, insertion, and deletion moves of GCMC, the identity of a BDT may be swapped between those capable of bonding on-top and on-bridge. The identity of a newly created BDT molecule is chosen at random, with equal probability of bonding at on-top or on-bridge sites. We consider bridge sites to be those pairs of Au surface atoms separated by a distance of 2.51-3.25 Å. The main advantage of performing simulations in the semigrand canonical ensemble is that molecule swap moves ensure more efficient and complete sampling of the S-Au bonding geometry. The acceptance probability for a swap move is

$$p_{acc} = \min[1, \frac{f_1}{f_2} e^{-\beta \Delta U}] \quad (\text{S6})$$

where $\beta = \frac{1}{kT}$ (k is Boltzmann's constant and T is temperature), ΔU is the change in energy due to the molecule identity swap, and f_i represents the fugacity of species i . Since the two BDT species are considered thermophysically equivalent, $f_1 = f_2$ and eq. 6 reduces to a simple expression reminiscent of the acceptance criterion for a standard molecule COM displacement or rotation.

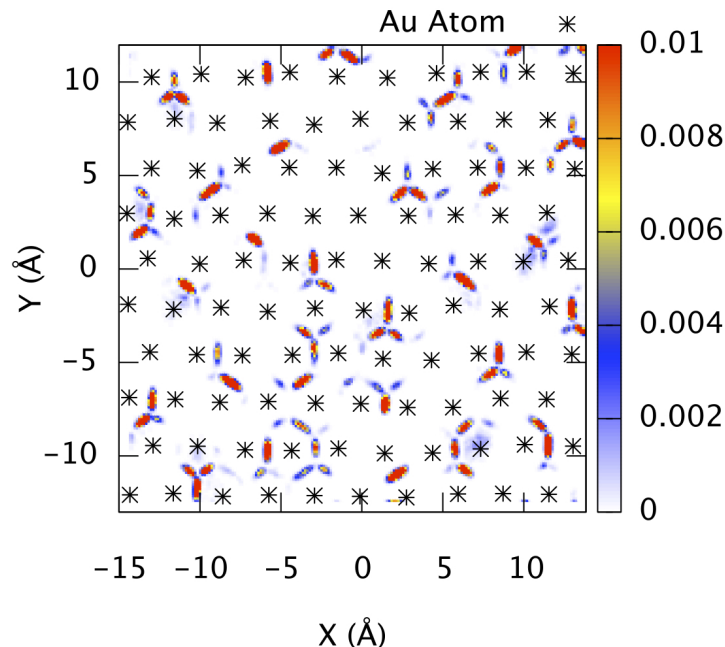


Figure S1: The distribution of the positions of BDT S atoms bonded to the Au (111) surface, for surface coverage 0.27. The color bar indicates the relative frequency of a particular $x - y$ position for each of the bonded S atoms. The black stars indicate the positions of the Au atoms on the first layer of the surface.

BDT on Au (111) Surface

As described in the previous section, performing simulations in the semigrand canonical ensemble allows BDT molecules to explore preferred adsorption sites. To validate this, we perform constant NVT moves for a BDT monolayer on the Au (111) surface, with surface coverage 0.27. After reaching equilibrium, we perform 10 million MC moves, saving configurations every 5,000 steps. In Figure S1 we present the distribution of positions of BDT S atoms bonded to the relaxed Au (111) surface. The Au (111) surface is a frequently used substrate for preparing self-assembled monolayers composed of thiol-terminated organic molecules.⁶⁻⁹ Among the challenges of modeling the S-Au interface includes capturing the strong chemical bonding and mobility of S atoms around numerous possible bonding sites. Previous work has demonstrated that on-bridge and on-

top sites are the relevant bonding sites for BDT and other thiol-terminated organic molecules,^{3,6–9} with the on-bridge site being energetically favored.^{3,7–9} The results in Figure S1 demonstrate that our MC simulation protocol predicts S atom pathways predominantly along the energetically preferred on-bridge sites, with areas of red, orange, and yellow appearing between two Au atoms. Adsorption at on-top sites occurs to a limited degree, as evidenced by a few light blue areas directly above (or close to) a single Au atom. Thus, we conclude that our MC method predicts reasonable bonding geometries, in agreement with previous experimental and theoretical results.

Ruptured Au NW Tips

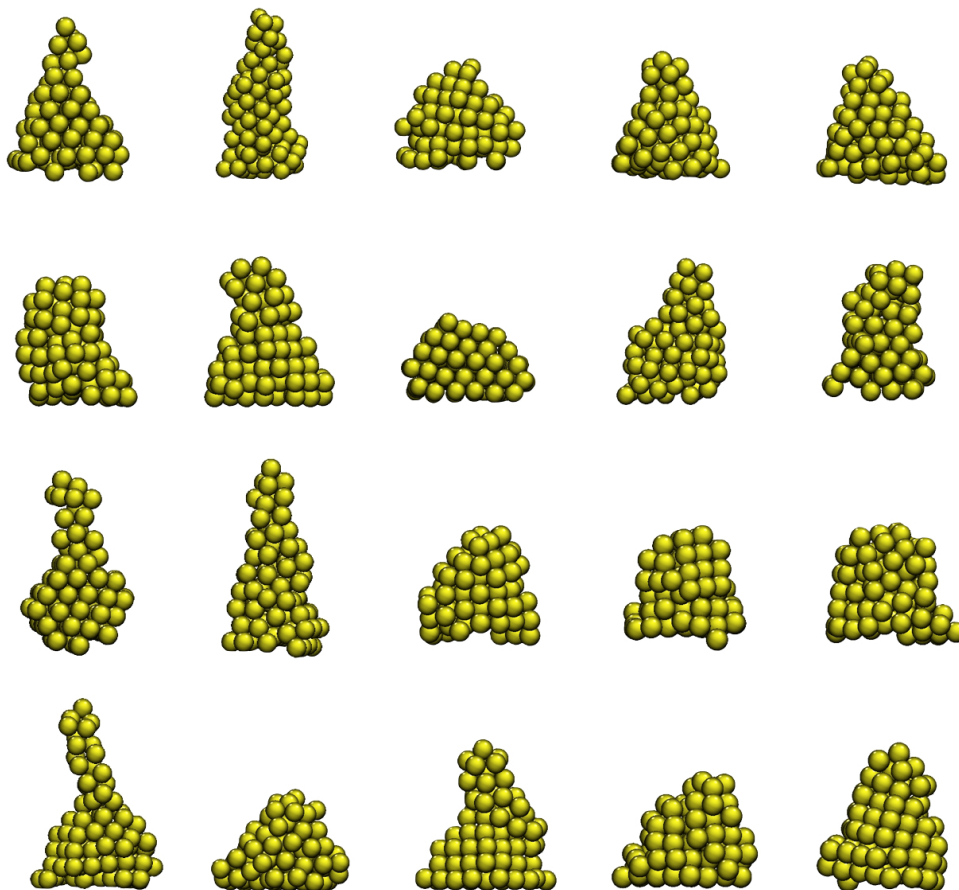


Figure S2: Snapshots of the twenty ruptured Au NW tips used in this study.

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