Supporting Information for

Conductance Based Characterization of Structure and Hopping Site Density in 2D Molecule-Nanoparticle Arrays

Cliff E. McCold †, Qiang Fu †, Jane Y. Howe §, Joshua Hihath ‡*

†Chemical Engineering and Materials Science, ‡Electrical and Computer Engineering, University of California, Davis, One Shields Ave., Davis, CA 95616

§Hiatchi High-Technologies Canada, Inc., Toronto, ON M9W 6A4, Canada

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I. Activation energies

**Figure S1.** Activation energies for the nanoparticle arrays for the four different average particle sizes, obtained via the temperature dependent conductance measurements in Fig 4. Error bars are the standard error of the mean of three measurements from the same sample sets (24 measurements total). Black corresponds to as-deposited oleylamine samples, and red corresponds to values measured after molecular exchange to hexanedithiol. The solid lines are charging energies calculated from a concentric spherical shell model,\(^1\) with an insulating shell thickness, \(s\), determined from the SEM images, and different relative permittivities \(\varepsilon_r\) corresponding to alkanethiols (2.7) and alkylamines (2.0).\(^2,3\) The spherical shell capacitance model in the fit above is

\[
C_{\text{shell}} = 4\pi \varepsilon_r \varepsilon_0 \left( \frac{r + s}{s} \right),
\]

with charging energy

\[
E_C = \frac{e^2}{2C}.
\]

The measured \(E_A\)'s are extracted from conductivities following the form

\[
\sigma(T) = \sigma_{\text{RT}} e^{-\frac{2E_A}{k_B T}},
\]

where \(\sigma_{\text{RT}}\) is the room temperature conductivity, and the 2 arising from both \(N\) (via Boltzmann statistics) and \(\mu\) (via activated hopping).
II. Size distribution

**Figure S2.** Particle sizes and dispersion for the four syntheses at different concentrations and mass. High-magnification SEM images (left) and particle size distribution from several lower magnification images (right). FFT insets on the left are from larger area images, and larger numbers on the right are peak diameters and widths from Gaussian fits (red). Scale bars are 20 nm. Each histogram comes from ~6-7 SEM images at 2,984,000X magnification, and each image contains approximately 35 nanoparticles, with the imaged areas coming from ~5 conducting junctions per synthesis. None of the devices showed significant size segregation effects.
III. Polydispersity and void density

Figure S3. Width of the particle size distribution (left axis) and average void percent (right) for the four syntheses at different Au precursor mass and concentrations, showing the relationship between particle polydispersity and microstructural void area. Error bars for size distribution are the uncertainty from the Gaussian fitting, while error bars for void percent are standard error of the mean void area. Void densities are for particles in the oleylamine-capped state. Void density measurements are obtained from an SEM image set with 12-14 images for each sample configuration, at 1,000,000X magnification, with ~300-500 nanoparticles per image.
IV. Effect of void density on activation energy

Figure S4. Activation energies versus void density for all 8 samples, showing no significant correlation of activation energy to void density over the observed range.
V. Dynamic light scattering

Figure S5. Dynamic light scattering (DLS) measured hydrodynamic diameter for the three 4x (23.5mM Au) syntheses in Fig 4. Bars represent average width of DLS diameter peaks from four DLS measurements for each synthesis. Toluene solvation shell was subtracted for $D_{CC}$ calculations. A Malvern Zetasizer Nano-S was used for DLS measurements.
References

