Supplementary Information

Going Beyond The Self-Assembled Monolayer: Metal Intercalated Dithiol Multilayers and Their Conductance.

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The SAM formation protocol used in our BPD work is based on earlier work on BDMT. Here we describe briefly XPS and spectroscopic ellipsometry (SE) investigation of BDMT system for comparison with the BPD one.

XPS data for BDMT.

Figure S1 shows the S2p peaks regions of a BDMT-Au sample. The S2p spectra are decomposed into two doublets corresponding to S atoms bound to gold (S_{Au} at 161.2 eV) and “free” S_{H} atoms on top of the BDMT SAM (at 163.1 eV). The initial BDMT spectrum resembles the one reported previously (ref 23-24 in main paper), using this SAM preparation method and has the same relative intensities of the S_{Au} and S_{H} components as reported previously.

Figure S1. S2p, and C1s XPS spectra of BDMT.
Assuming an attenuation length of $\lambda=2.5\text{nm}$ and a thickness of 1.25nm, for the BDMT SAM, we obtain an attenuation of electrons from S adsorbed on Au ($S_{\text{Au}}$) by a factor of 0.6, which corresponds fairly well with the lesser intensity of the $S_{\text{Au}}$ peak in the figure S1.

The C 1s spectra of the BDMT, are compared to a dodecanethiol (C12) SAM and presented in Figure S2. The main peak at 284.9 eV of the BDMT SAM is a superposition of contributions from: the C-C moieties, and the C=C in the ring unit.

![Figure S2. C1s XPS spectra of BDMT and C12 molecules.](image)

When BDMT is immersed into the AgNO$_3$ solution Ag is adsorbed on top of the BDMT SAM and is observed in the Ag3d XPS spectra in fig. S3. Upon further BDMT adsorption one can see the attenuation of the Ag peak intensity consistent with an 0.6 factor corresponding to a 1.25nm SAM over layer thickness.

![Figure S3. Ag3d XPS spectra of BDMT with Ag and BDMT-Ag-BDMT.](image)
Spectroscopic ellipsometry

The SE data are shown in the 245-1000 nm range for a 65° angle of incidence. The shapes of BDMT $\delta \Psi$ and $\delta \Delta$ spectra resemble the one reported previously\textsuperscript{1} using the same preparation method. The $\delta \Psi$ BDMT curve for wavelengths less than 300 nm shows a dip, which was previously assigned to BDMT absorption, related to aromatic rings, eventually influenced by intermolecular interactions in the SAM. We also observe, as reported earlier for thiolate SAMs, that for wavelengths above about 550 nm the $\delta \Psi$ curve has a negative value and a minimum around 600 nm, attributable to the formation of a strong molecule-surface bond, leading to charge redistribution and chemisorption-induced structural and morphological changes which affect the mean free path of electrons.

Figure S4: SE measurements for the BDMT SAM, BDMT-Ag, BDMT-Ag-BDMT: (a) $\delta \Psi$ and (b) $\delta \Delta$. Data for C18 SH SAM is shown for comparison.

After immersion into the AgNO$_3$ solution the BDMT-Ag the $\delta \Psi$ and $\delta \Delta$ curves change and as for the BPD case described in the main text, we see an attenuation due to absorption for wavelengths below about 400 nm and subsequent growth of the second BDMT layer.

The $\delta \Psi$ BDMT-Ag-BDMT curve shows an increase in magnitude and the dip at $\sim$ 300 nm is much more pronounced as compared with the BDMT spectra. The $\delta \Delta$ curves have more negative values, due to an increase in thickness and to larger absorption because of the increase in the number of the aromatic rings in the BDMT-Ag-BDMT system.

A comparison with octadecanethiol: C18 is shown. The results for C18 are
compatible with earlier work and also show the slightly negative $\delta \Psi$ values for the larger wavelengths. The results for the C18 SAM and BDMT-Ag-BDMT are quite close, indicating that they have similar thickness. Thickness simulations in earlier works give a layer thickness of 2.5 nm for a C18 SAM and about 1.2 nm for BDMT (as in the above XPS estimate), which indicates that we are indeed dealing with a double BDMT layer in the BDMT-Ag-BDMT system.

**Conductance measurements for BPD.**

Fig.S5 shows a normalized plot of the resistance as a function of bias. The plot delineates similarities in the bias dependence for the BPD2 layers and the strong difference with BPD. Fig S6. Shows a Fowler Nordheim type plot for all the BPDn layers.

![Figure S5. Normalised resistance as a function of bias for the different layers.](image-url)
Figure S6 Fowler-Nordheim plot of \( J/V^2 \) versus \( 1/V \) for the different BPDn layers.