Supporting information for:

The Contribution of Lateral Packing Density to Albumin Adsorption on Monolayers

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Synthesis of LD-SAM adsorbates

The alkyne moiety with desired terminal group is mixed with 1,10-decanedithiol at a molar ratio of 1:4 in dichloromethane. Excess 1,10-decanedithiol was used to ensure the reaction would go to completion and limit cyclization. Irgacure-184 photoinitiator was added at 3% the weight of the 1,10-decanedithiol. Just enough solvent was used to dissolve the reagents and the photoinitiator. The solution was then exposed to 12 mW/cm^2, 365 nm light (THORLabs LED, Model M365L2) for 1.5 h at room temperature. Intensity was measured by UV radiometer (SPER SCIENTIST DIRECT, Model 850009). Reaction progress was monitored with thin layer chromatography. The mobile phase for each TLC and the associated R_f value of the product are in Table SI-1. After the completion of reaction, the solvent was evaporated under a stream of nitrogen, leaving only an oily liquid. The product was purified by silica gel column chromatography using the mobile phase in Table S.1, and the solvent was evaporated to yield a product.

Table SI-1. Synthesis details for formation of adsorbates used in this work

Compound	Alkyne	Mobile Phase	R_f
10,11-Bis(10-mercaptodecylthio) undecanoic acid	11-MUA	Hexane/Dichloromethane (85:25) vol%	0.44
5,6-Bis(10-mercaptodecylthio) hexan-1-ol	5-Hexyn-1-ol	Hexane:Acetone (80:20) vol%	0.36
5,6-Bis(10-mercaptodecylthio) hexane	1-hexyne	Hexane:Acetone (95:05) vol%	0.48

Characterization of 10,11-Bis (10-mercaptodecylthio) undecanoic acid

Complete details of the synthesis and chemical analysis are reported in previous work.[1] The chemical structure of the purified product was analyzed with ^{1}H NMR, ^{13}C NMR, and gas chromatography coupled with mass spectroscopy.

^{1}H NMR ($CDCl_3$): δ 1.2-1.5 ppm (36 H), 1.5-1.8 ppm (12H), 2.34 ppm (2H), 2.45 ppm (8H), 2.5-2.8 ppm (3H).

^{13}C NMR confirmed the presence of the branched point with a peak at 46 ppm. The use of an HSQC pulse sequence linked this 46 ppm carbon shift with the proton shift of 2.64 ppm.

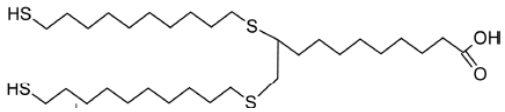

Figure SI-1. Structure of 10,11-Bis (10-mercaptodecylthio) undecanoic acid.

Characterization of 5,6-Bis [10-mercaptodecylthio) hexan-1-ol

5,6-Bis [10-mercaptodecylthio) hexan-1-ol was synthesized as described above with a yield of 85%. The chemical structure of the purified product was analyzed with ^{1}H NMR, ^{13}C NMR, and gas chromatography coupled with mass spectroscopy.

^{1}H NMR ($CDCl_3$): δ 1.2−1.42 (30H), 1.5−1.7 (10H), 2.46-2.6 (8H), 2.6−2.9 (3H), 3.62-3.72 (2H).

^{13}C NMR confirmed the presence of the branched point with a peak at 45.70 ppm. The use of an HSQC pulse sequence linked this 45.70 ppm carbon shift with the proton shift of 2.72 ppm.

Gas chromatography coupled with mass spectrometry (GC-MS) confirmed the presence of a species of 510 Da molecular weight, consistent with the expected structure of the 5,6-Bis[10-mercaptodecylthio) hexan-1-ol adsorbate.

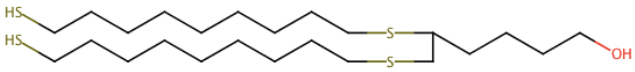

Figure SI-2. Structure of 10,11-Bis (10-mercaptodecylthio) hexan-1-ol adsorbate.

Characterization of 5,6-Bis [10-mercaptodecylthio) hexane

5,6-Bis [10-mercaptodecylthio) hexane was synthesized as described above with a yield of 87%. The chemical structure of the purified product was analyzed with ^{1}H NMR, ^{13}C NMR, and gas chromatography coupled with mass spectroscopy.

^{1}H NMR ($CDCl_3$): δ 0.86-0.98 (3H), 1.2−1.44 (30H), 1.52−1.76 (10H), 2.48-2.6 (8H), 2.62−2.9 (3H).

^{13}C NMR confirmed the presence of the branched point with a peak at 45.82 ppm. The use of an HSQC pulse sequence linked this 45.82 ppm carbon shift with the proton shift of 2.70 ppm.

Gas chromatography coupled with mass spectrometry (GC-MS) confirmed the presence of a species of 490 kDa molecular weight, consistent with the expected structure of 5,6-bis [10-mercaptodecylthio) hexane.

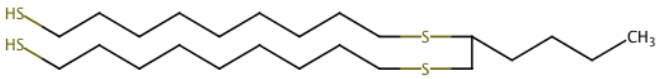

Figure SI-3. Structure of 10,11-Bis (10-mercaptodecylthio) hexane adsorbate.

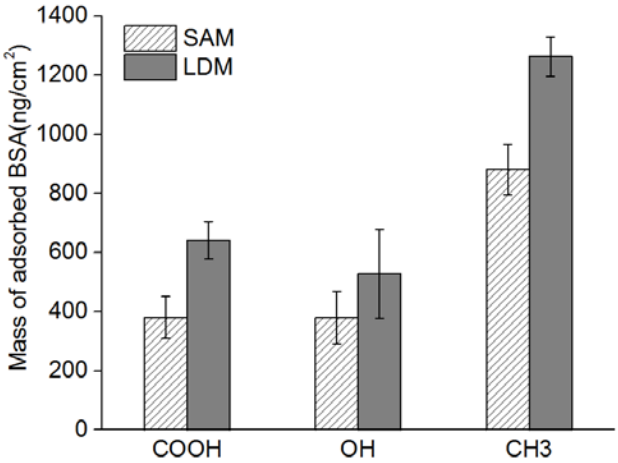

Figure SI-4. Mass of adsorbed BSA on well-packed self-assembled monolayers and their corresponding loosely packed monolayer, measured by ellipsometry. Data points and error bars represent the mean and standard deviation of at least 9 measurements.

References for Supporting Information:

1. Stevens, C. A.; Safazadeh, L.; Berron, B. J., Thiol-Yne Adsorbates for Stable, Low-Density, Self-Assembled Monolayers on Gold. *Langmuir* **2014,** 30, (8), 1949-1956.