ADVANCED
MATERIALS

Supporting Information

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Preparation of 2-Amino-2'-[(2-hydroxy ethyl propargyl ether)amino]ethylene Glycol Diethyl Ether (1). Glycidyl propargyl ether (5.000 mL, 5.200 g, 4.64×10^{-2} mol) was added dropwise to a solution of 2,2'-(ethylenedioxy)bis(ethylamine) (6.768 mL, 6.869 g, 4.64×10^{-2} mol) in dichloromethane (300 mL) at ambient temperature over 1 h. The mixture was allowed to stir for 24 h and concentrate. Water (200 mL, 18 MΩ-cm) was added and the solution was extracted three times with 100 mL of dichloromethane. The combined organic layer was dried over $MgSO_4$ and concentrated to give 8.207 g (68 %) of the crude product. It was purified via flash column chromatography (hexane: dichloromethane: methanol 85:10:5) Yield: 52 %. Matrix assisted laser-desorption ionization (MALDI) (261.17, M+H); ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ 2.41 (s, $C{\equiv}C\boldsymbol{H}$), 2.80 (t, 2H, $H_2NC\boldsymbol{H}_2CH_2O$), 2.90 (d, 2H, $CH_2NHC\boldsymbol{H}_2CH(OH)CH_2$), 2.95 (m, 1H, $CH_2NHCH_2C\boldsymbol{H}(OH)CH_2$), 3.58 (t, 2H, $H_2NCH_2C\boldsymbol{H}_2O$), 3.60 (d, 2H, $CH(OH)C\boldsymbol{H}_2OCH_2$), 3.70 (s, 4H, $OC\boldsymbol{H}_2C\boldsymbol{H}_2O$), 4.11 (t, 2H, $OC\boldsymbol{H}_2C{\equiv}CH$), 4.40 (br, 4H, $OC\boldsymbol{H}_2C\boldsymbol{H}_2NHCH_2$) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 41.53, 49.08, 52.22, 58.50, 68.49, 70.22, 72.80, 72.95, 74.65, 79.71 ppm.

GRGDS Azide-derivatized Peptide Synthesis (2) The GRDGS peptide was synthesized by solid phase synthesis using Fmoc chemistry and further derivatized (3:1 molar ratio to peptide) with O-(2-Azidoethyl)-O'-(N-diglycolyl-2-aminoethyl)-hexaethyleneglycol (FW = 554.6, NovaBiochem, San Diego CA). Following standard trifluoroacetic acid (TFA): triisopropyl silane (TIS): H_2O (95:2.5:2.5) cleavage conditions and reverse-phase high performance liquid chromatography (HPLC) purification, the linker derivatized peptide was characterized by liquid chromatography-mass spectrometry (LC-MS), MALDI (1043.51, M+H), and Fourier transform infrared spectroscopy (FT-IR).

SAM Derivatization with Alkyne Linker. **1** (1.000 g) in DMSO (15 mL) and N,N-dimethylaminopyridine (100 mg) were added to a glass 15 cm petri dish containing an gradient treated glass cover slip (9.60 cm^2 per cover slip). This was followed by the sequential addition of 2.00 mL diisopropylcarbodiimide with the above mixture. The vial was stirred at ambient temperature for 48 h. After the reaction time, the slides were washed three times each with methanol and deionized water and blown dry with nitrogen.

Click immobilization of 2 onto Gradient SAM Derivatization with Alkyne Linker. A total of 50 mL of a 4:1 H_2O:DMSO solution with 40 mM sodium ascorbate and 20 mM Cu^{II} sulfate was added to a glass 15 cm petri dish containing 8 alkyne gradient derivatized glass cover slips (9.60 cm^2 per cover slip, 76.80 cm^2 total). This was followed by the sequential addition of **2** (550.2 mg) in 1.00 mL of DMSO. The solution was stirred for 48 h at 50 °C. The reaction solution which turned a dark blue due to oxidation was removed and the cover slips were washed three times each with 18 MΩ-cm H_2O and ethanol followed by drying with nitrogen stream.

Figure S1. ^{13}C NMR

^{13}C Spectra - 2-Amino-2‘-[(2-hydroxy propyl propargyl ether)amino]ethylene Glycol Diethyl Ether - 76.5 MHz, $CDCl_3$