Electronic Supplementary Information for the manuscript

Dendritic polyglycerolamine as a functional antifouling coating of gold surfaces

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Spectroscopic Characterization of starting PG

^{1}H NMR (400 MHz, MeOD, δ): 4.05-3.45 (m, CH_2 and CH, PG backbone), 1.35 (m, CH_2 core), 0.86 (m, CH_3 core). **IR** (KBr) νmax = 3362s (OH), 2913m and 2877m (CH), 1651w, 1456w, 1106s and 1076s (C-OH).

Synthesis of polyglycerol derivatives

Synthesis of mesylpolyglycerol, PG-OMs (example given for 9% of conversion)

In a three-necked flask equipped with magnetic stirring, PG-OH (2.957g, 39.92 mmol -OH) was dissolved in pyridine (45 mL) and cooled to 0 °C. Then, MsCl (0.34 mL, 4.39 mmol, 0.11 eq.) was dissolved in pyridine (2 mL) and added dropwise through syringe. After stirring the solution for 1 h at 0 °C, it was allowed to reach room temperature and was stirred for 16 h. A yellowish-brown mixture was obtained. The solvent was removed under vacuum and the resulting mixture was dialyzed in MeOH to afford 3.13 g of PG-OMs as a honey-like product. Conversion = 9%, quantified by ^{1}H RMN. Yield= 97%. **^{1}H NMR** (400 MHz, MeOD, δ): 4.55-3.40 (m, CH_2 and CH, PG scaffold); 3.30-3.17 (m, CH_3 mesyl), 1.35 (m, CH_2 core); 0.87 (m, CH_3 core). **IR** (KBr) ν_{max} = 3376*s* (OH), 2929*m* and 2877*m* (CH), 1651*w*, 1456*w*, 1352*w* and 1173*w* (S=O mesyl), 1106*s* and 1076*s* (C-OH).

Synthesis of polyglycerolazide, PG-N_3

In a Schlenk tube equipped with magnetic stirring, PG-OMs (3.130 g, 3.82 mmol -OMs) was dissolved in DMF (20 mL). Then, NaN_3 (1.24 g, 19 mmol, 5 eq.) was added and the suspension was stirred for 72 h at 60 °C. The resulting reddish-brown mixture was filtered, and the supernatant was dialyzed in MeOH to afford 2.53 g of PG-N_3. Conversion: quantitative (determined by ^{1}H RMN and IR), yield = 86%. **^{1}H NMR** (400 MHz, MeOD, δ): 4.00-3.40 (m, CH_2 and CH, PG scaffold), 1.43 (m, CH_2 core), 0.91 (m, CH_3 core). **IR** (KBr) ν_{max} = 3375*s* (OH), 2915*m* and 2877*m* (CH), 2102*m* (-N_3), 1109*s* and 1078*s* (C-OH).

Synthesis of polyglycerolamine, PG-NH_2

In a one-necked flask equipped with magnetic stirring, PG-N_3 (0.700 g, 0.92 mmol -N_3) was dissolved in 50 mL of THF/water (70:30) and PPh_3 (0.72 g, 2.76 mmol, 3 eq.) was added. While stirring , the proportion of water was continuously increased in order to adjust the solubility of the partially reduced product. The resulting mixture was filtered, concentrated in vacuum, extracted three times with $CHCl_3$ and finally dialyzed in MeOH. 0.62 g of a pale yellow product, PG-NH_2, was obtained. Conversion: quantitative (determined by IR), yield = 92%. **^{1}H NMR** (400 MHz, MeOD, δ): 4.55-3.40 (m, CH_2 and CH, PG scaffold), 3.16-2.60 (m, OC*H*-NH_2 and CH_2-NH_2), 1.41 (m, CH_2 core), 0.91 (m, CH_3 core). **IR** (KBr) ν_{max} = 3364*s* (OH), 2915*m* and 2876*m* (CH), 1119*s* and 1088*s* (C-OH), 742*m* and 695*m*.

Synthesis of thioctic-polyglycerolamine, TA-PG-NH_2

In a two-necked flask equipped with magnetic stirring, PG-NH_2 (0.300 g, 0.40 mmol -NH_2) was dissolved in DMF (10 mL) and cooled to 0 °C. Then, DMAP (1 mg, 8 µmol dissolved in 1 mL of DMF), thioctic acid (6.8 mg dissolved in 3 mL of DMF, 33 µmol, 0.08 eq.) and DCC (6.8 mg, 33 µmol, 0.08 eq.) were added. After stirring the solution for 1 h at 0 °C, it was allowed to reach room temperature and was stirred for 59 h. The resulting yellow solution was concentrated in vacuum and then dialyzed in MeOH to afford 0.295 g of TA-PG-NH_2 as a pale yellow product. **^{1}H NMR** (400 MHz, MeOD, δ): 4.55-3.40 (m, CH_2 and CH, PG scaffold), 3.16-2.60 (m, OC*H*-NH_2 and CH_2-NH_2), 2.55-1.15 (m, overlaid signals corresponding to AT and CH_2 core), 0.92 (m, CH_3 core). **IR** (KBr) ν_{max} = 3364*s* (OH), 2918*m* and 2876*m* (CH), 1651*w* and 1570*w*, 1103*s* and 1076*s* (C-OH).

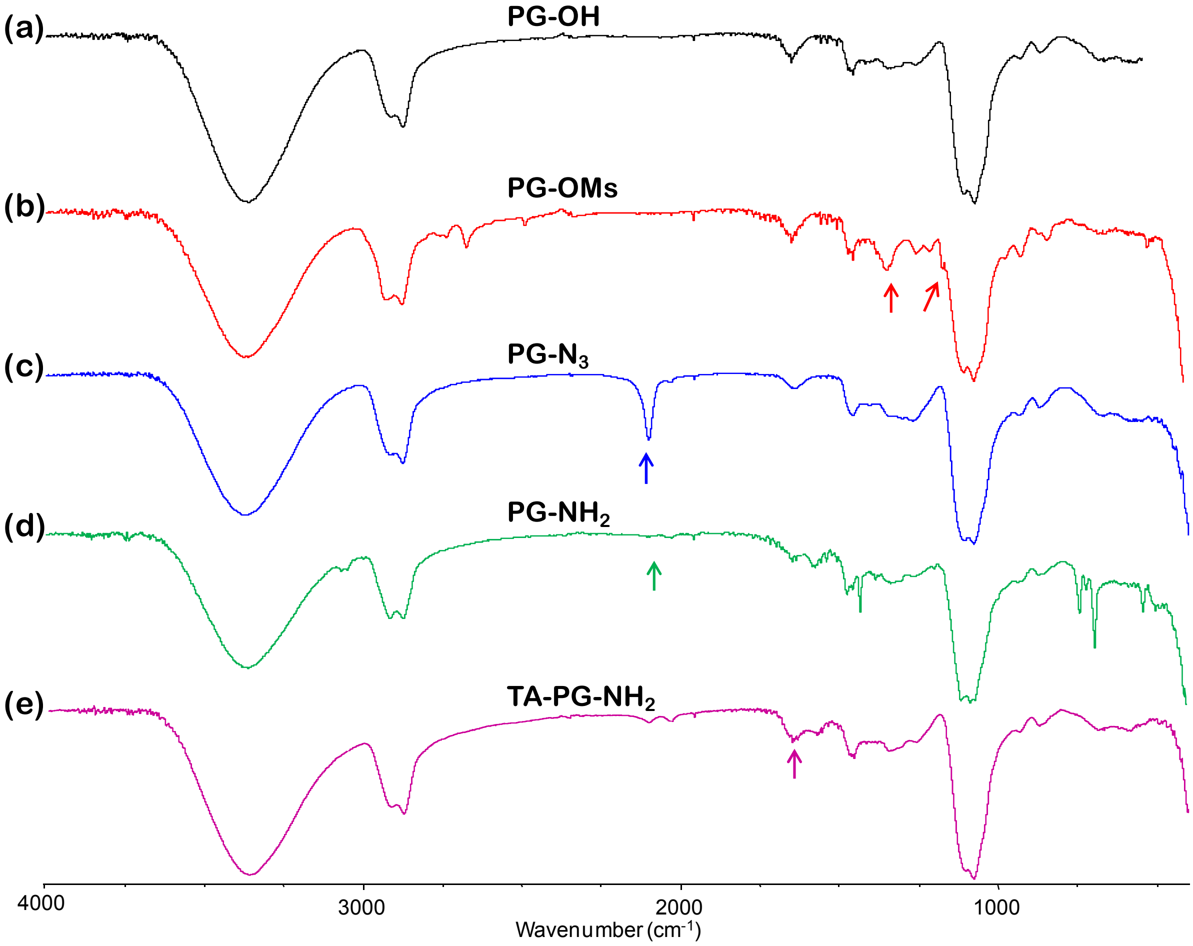

Figure S1. IR spectra of: (a) starting PG, (b) mesylpolyglycerol, (c) polyglycerolazide, (d) polyglycerolamine and (e) thioctic-polyglycerolamine, corresponding to a 9% of conversion of -OH groups into -NH_2 groups. The colored arrows indicate the appearance or disappearance of relevant signals.

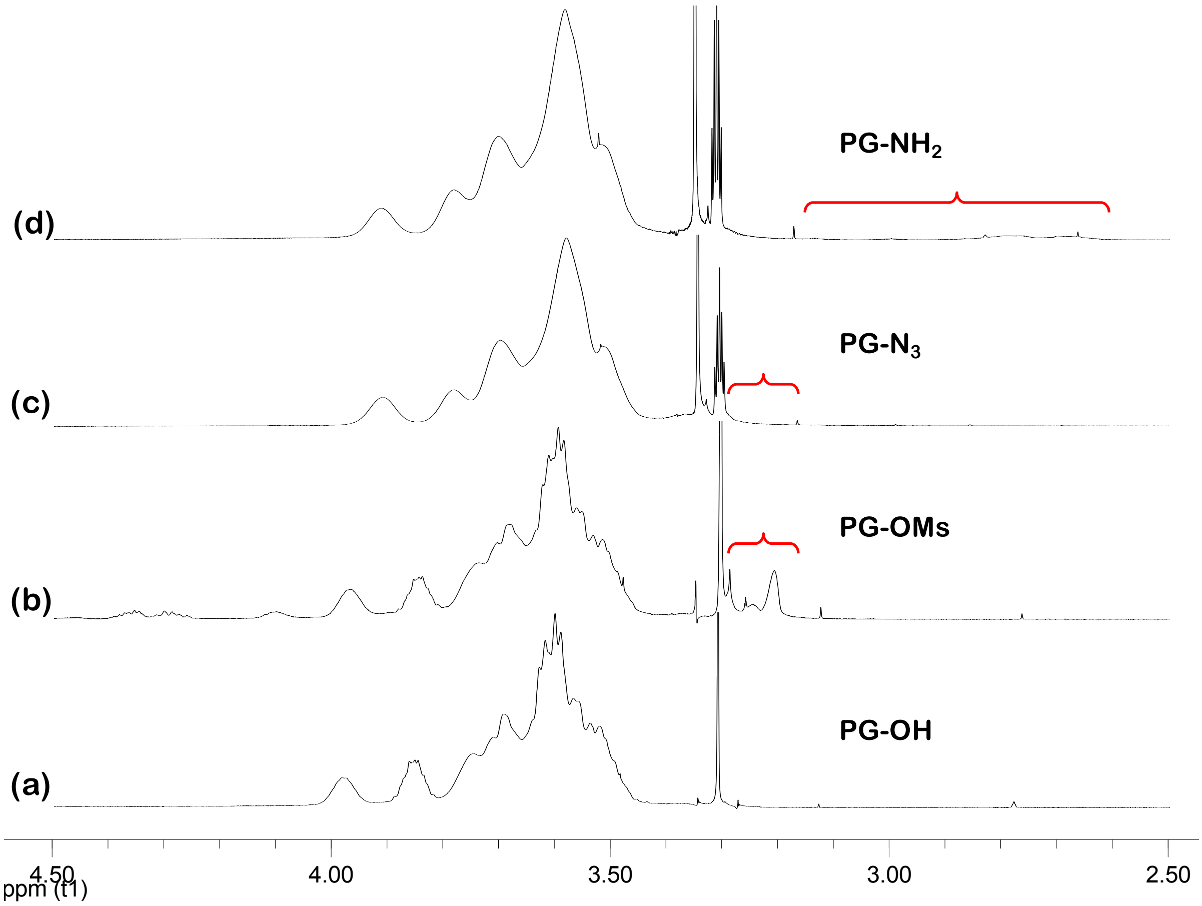

Figure S2. ^{1}H NMR spectra of: (a) starting PG, (b) mesylpolyglycerol, (c) polyglycerolazide, and (d) polyglycerolamine, corresponding to a 9% of conversion of -OH groups into -NH_2 groups. The colored brackets indicate the appearance/disappearance of relevant signals.

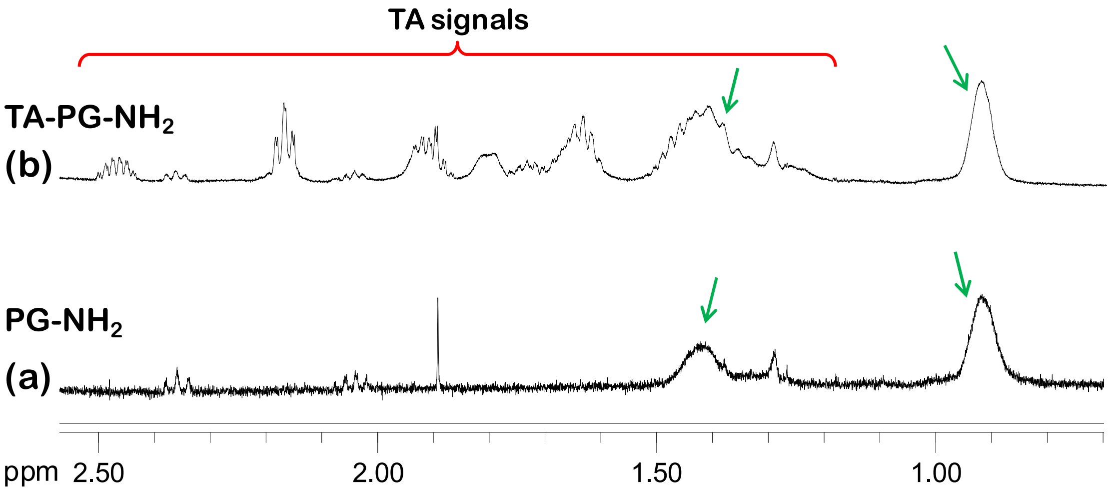

Figure S3. ^{1}H NMR spectra in the 2.6-0.7 ppm region of: (a) polyglycerolamine and (b) thioctic-poliglycerolamine corresponding to a 9% of conversion of -OH groups into -NH_2 groups. The relevant signals are indicated: PG core (TMP, green arrows) and signals corresponding to 10H of the incorporated TA (red bracket).

AFM characterization of Au/TA-PG-NH_2

Experimental part

The AFM measurements were performed using a Nanoscope Multimode IIIA (Veeco, now Bruker AXS, Mannheim). Measurements were conducted in laboratory air at room temperature. The microscope was operated in the tapping mode (TM-AFM) using silicone probes NST-NCLF (Nascatec, Stuttgart) with a size of 250 ± 10 µm and a tip radius of 7 ± 1 nm at resonance frequencies of 165 kHz under ambient conditions. The force constant was 30 N/m. The cantilever was forced to oscillate near its resonance frequency.

Pretreatment of the gold surface and functionalization by self-assembly

Before each experiment, the 12x12x0.7 mm gold substrate on borosilicate glass (Arrandee, Germany) was annealed (hydrogen flame length *ca.* 2-4 cm) by sweeping the substrate back and forth for about 30-60 s, keeping the small flame spot on the film a dim orange color. After annealing, the surface was cooled down under a stream of N_2. Then, it was functionalized by immersing the substrate overnight into a 1 mM solution of the corresponding PG derivative in MeOH. The modified gold surface was removed and rinsed copiously with MeOH for 1 min, and then with EtOH for another min before drying with N_2. The functionalized surface was used immediately for AFM measurements.

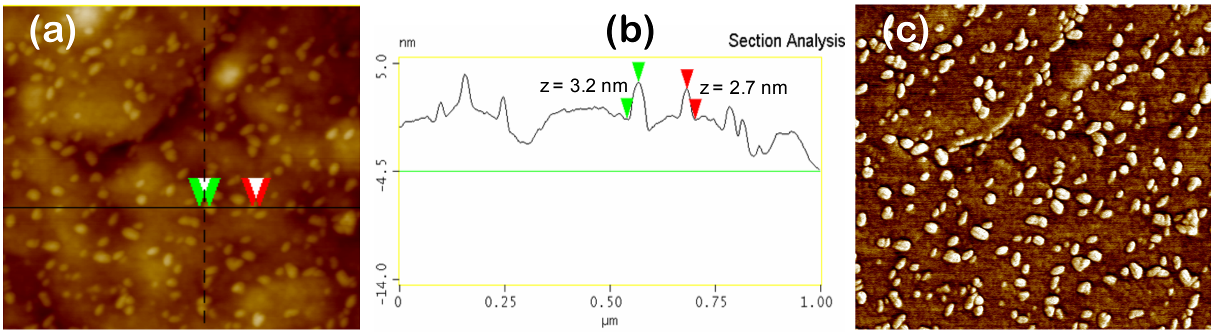

Figure S4. AFM measurements of Au/TA-PG-NH_2 9 %: (a) 1000 nm x 1000 nm topographical image; (b) cross-section profiles corresponding to the black solid line in (a); (c) 1000 nm x 1000 nm phase image showing an incomplete monolayer.