Supporting Information for

Nanopatterned Monolayers of Bioinspired, Sequence-Defined Polypeptoid Brushes for Semiconductor/Bio Interfaces

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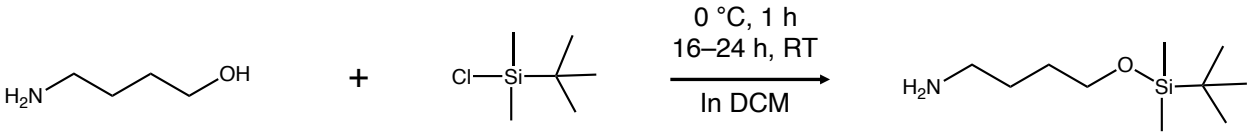
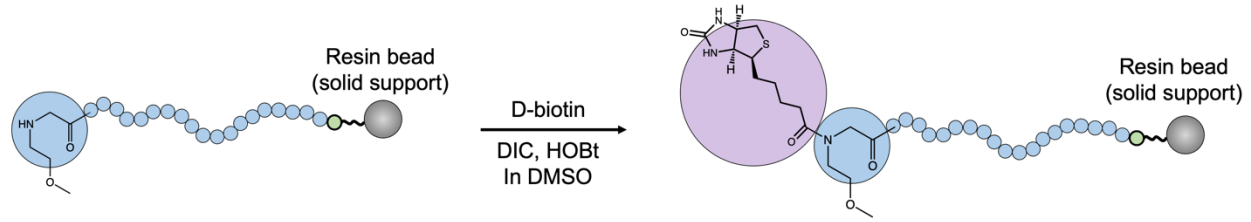
Addition Information on Material Synthesis

4-[(*tert*-butyldimethylsilyl)oxy]butan-1-amine. Tert-butyldimethylsilyl (tBDMS) protection of 4-amino-1-butanol was carried out following a similar protocol reported previously.[1] A solution of tert-butyldimethylsilyl chloride (tBDMS-Cl, 2.1 g, 14 mmol) in dichloromethane (DCM, 2.6 mL) was added dropwise at 0 °C to a vigorously stirred solution of 4-amino-1-butanol (5 g, 56 mmol) in DCM (1.3 mL), and stirring was continued for 1 h at 0 °C. The mixture was allowed to warm to room temperature and stirred for an additional 16–24 h. The crude mixture was poured into water (20 mL), and the layers were separated. The organic layer was washed with water (2 × 20 mL), and the aqueous layers was re-extracted with DCM (2 × 20 mL). The combined organic extracts were dried over Na_2SO_4, then the solvent was removed *in vacuo*, yielding 2.69 g (94%) product of a colorless oil.



Scheme S1. Tert-butyldimethylsilyl (tBDMS) protection 4-amino-1-butanol.

Biotinylation of polypeptoids. Rink amide resin with polypeptoid (25 µmol) was re-swelled in *N*,*N*-dimethylformamide (DMF) for 20–30 min, drained. D-biotin (0.4 M, 16 equiv.) and hydroxybenzotriazole hydrate (HOBt · xH_2O, 0.4 M, 16 equiv.) in dimethyl sulfoxide (DMSO, 1 mL) were added, followed by diisopropylcarbodiimide (DIC) (0.4 M, 16 equiv.) in DMSO. The syringe reaction vessel was allowed to mix on a rocker for 20–24 h. The resin was washed with DMF, then dichloromethane (DCM), and dried with a nitrogen flow.



Scheme S2. Biotinylation of polypeptoids at the N-terminus.

Polypeptoid Characterization

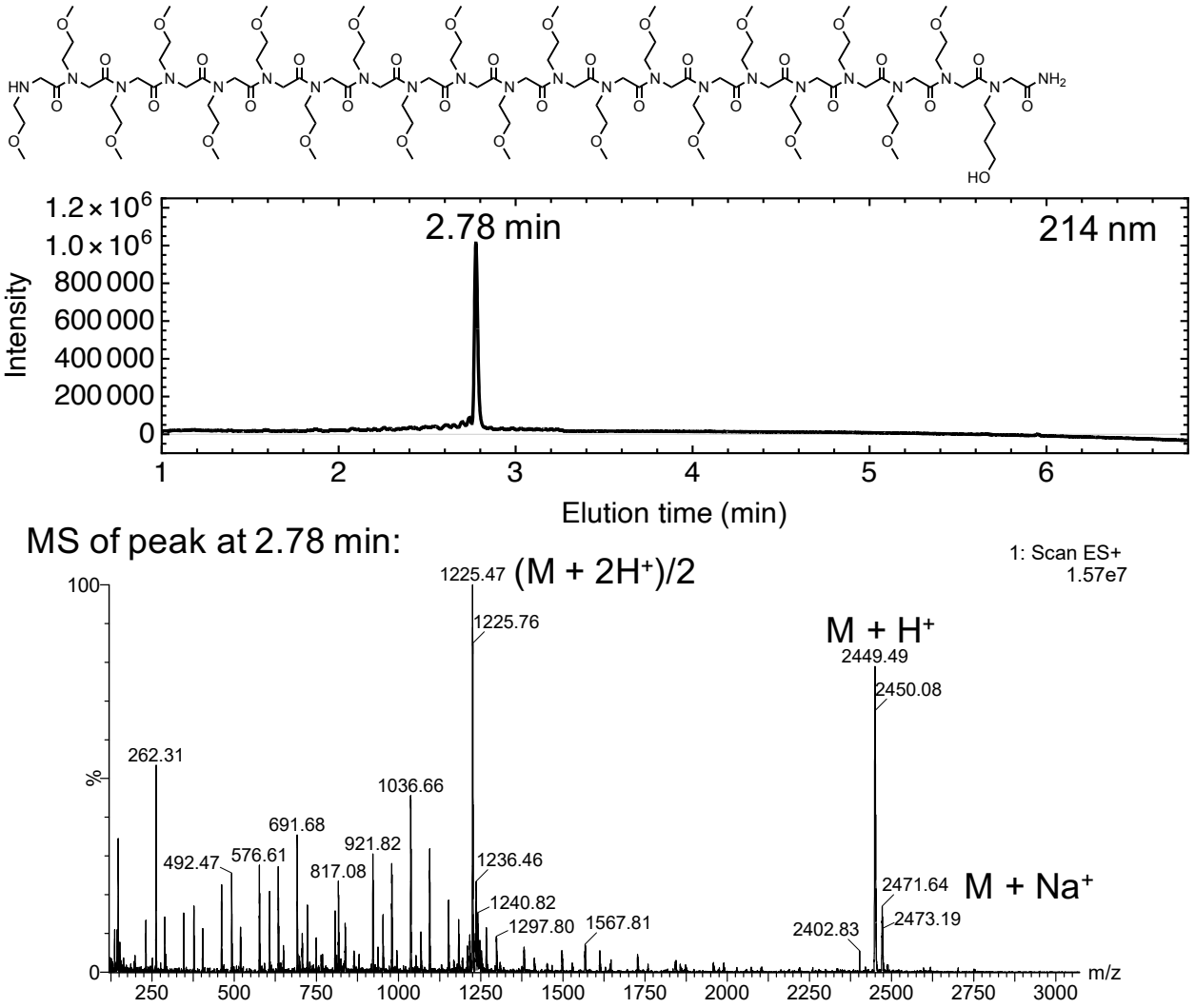


Figure S1. UPLC-MS (C18 column) of PP1, $Nme_{20}Nhb$, theoretical molecular weight: 2448.8 g mol^{-1}.

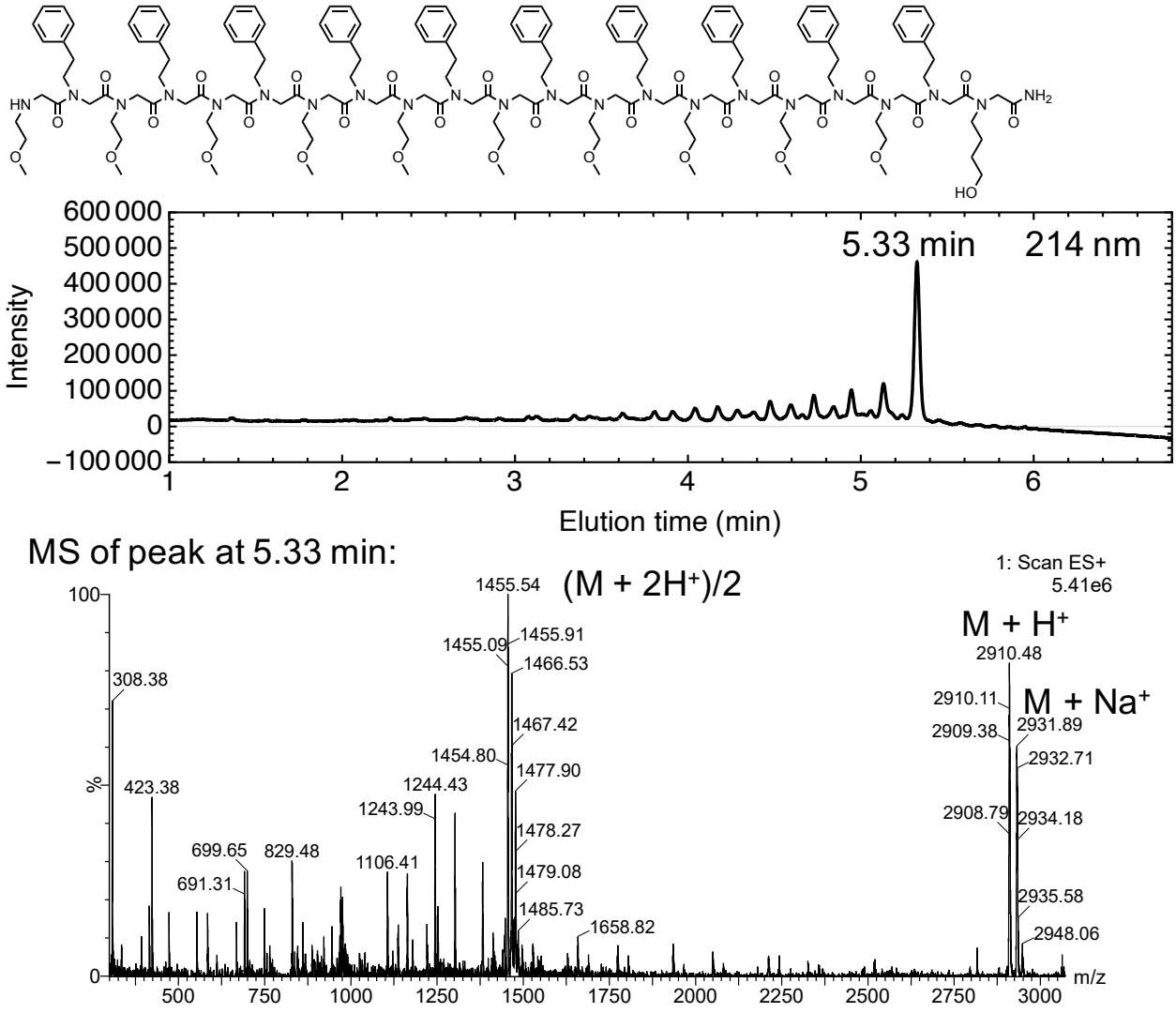


Figure S2. UPLC-MS of PP2 (C18 column), $(NmeNpe)_{10}Nhb$, theoretical molecular weight: 2909.6 g mol^{-1}.

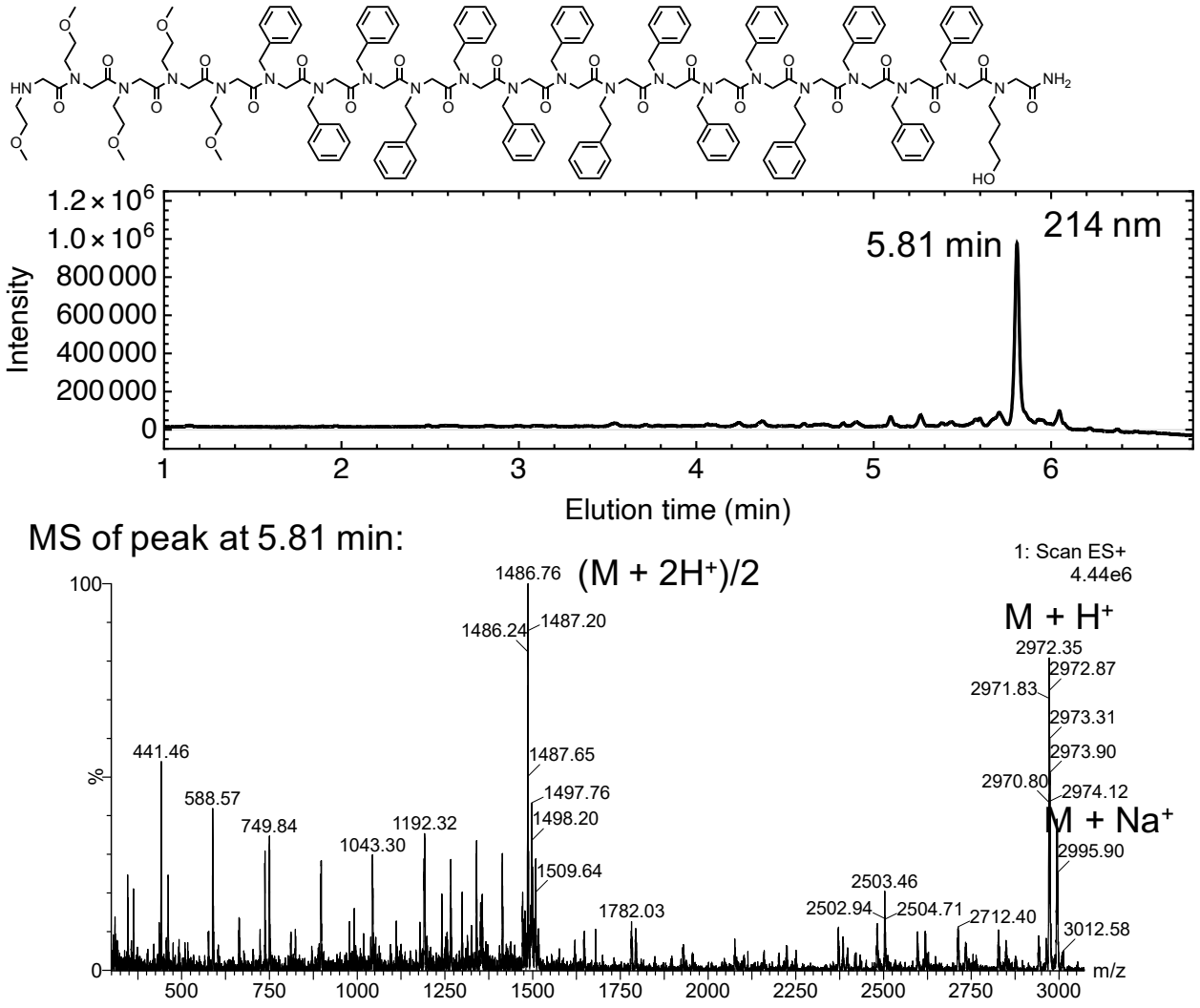


Figure S3. UPLC-MS of PP3 (C18 column), $Nme_5(Npm_3Npe)_3Npm_3Nhb$, theoretical molecular weight: 2971.6 g mol^{-1}.

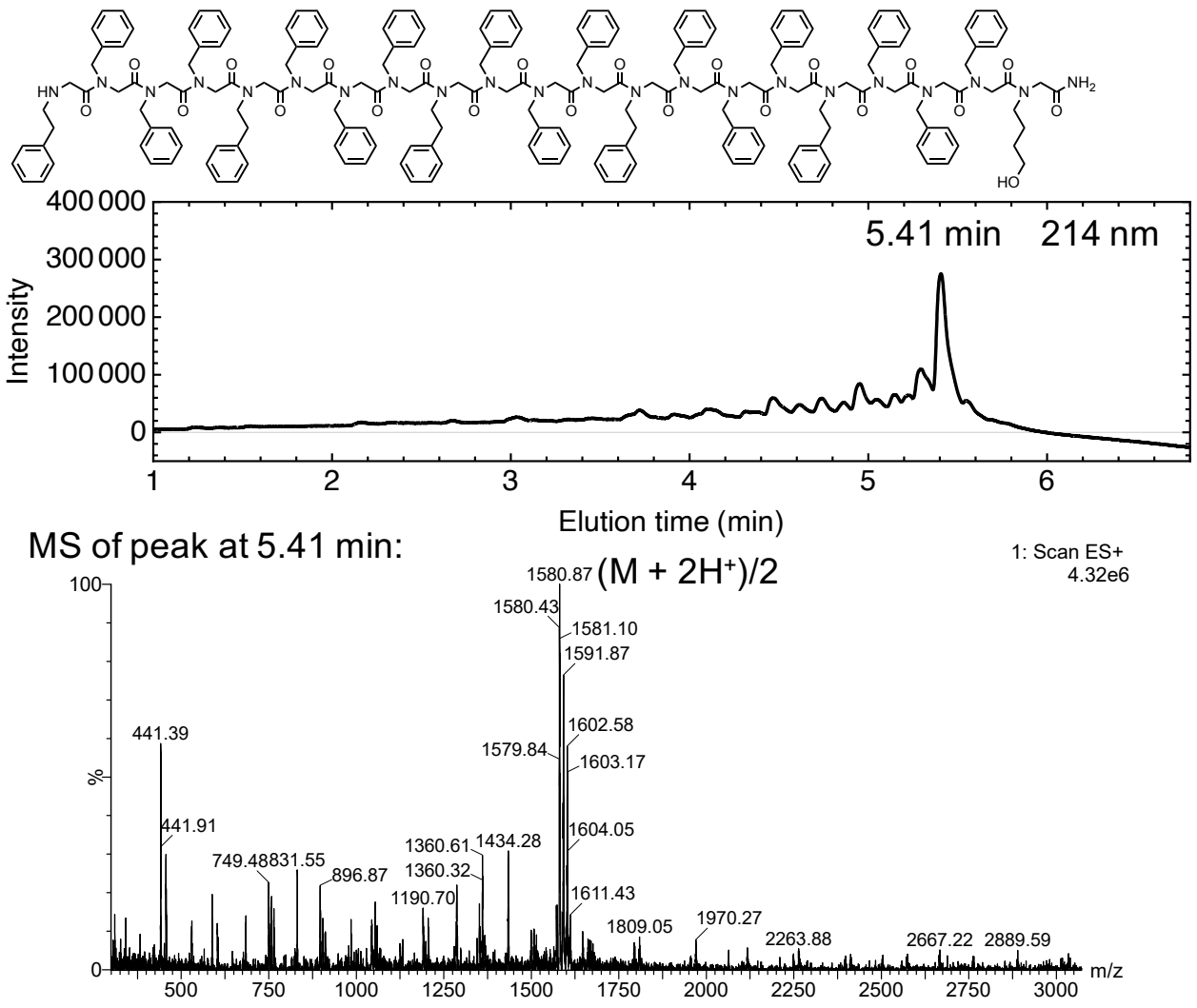


Figure S4. UPLC-MS (C4 column) of PP4, $(NpeNpm_3)_5Nhb$, theoretical molecular weight: 3159.9 g mol^{-1}.

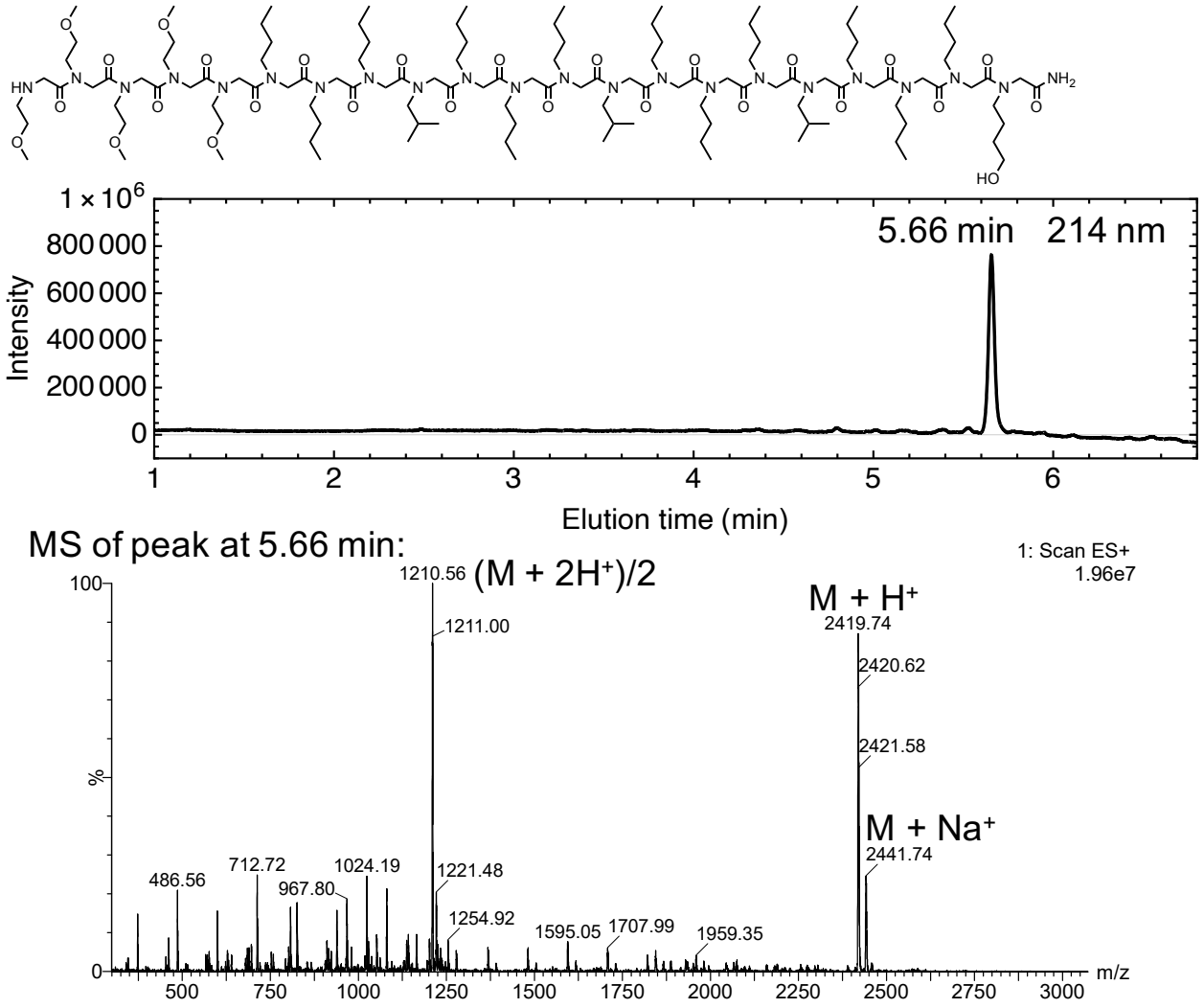


Figure S5. UPLC-MS of PP5 (C18 column), $Nme_5(Nbu_3Nib)_3Nbu_3Nhb$, theoretical molecular weight: 2419.3 g mol^{-1}.

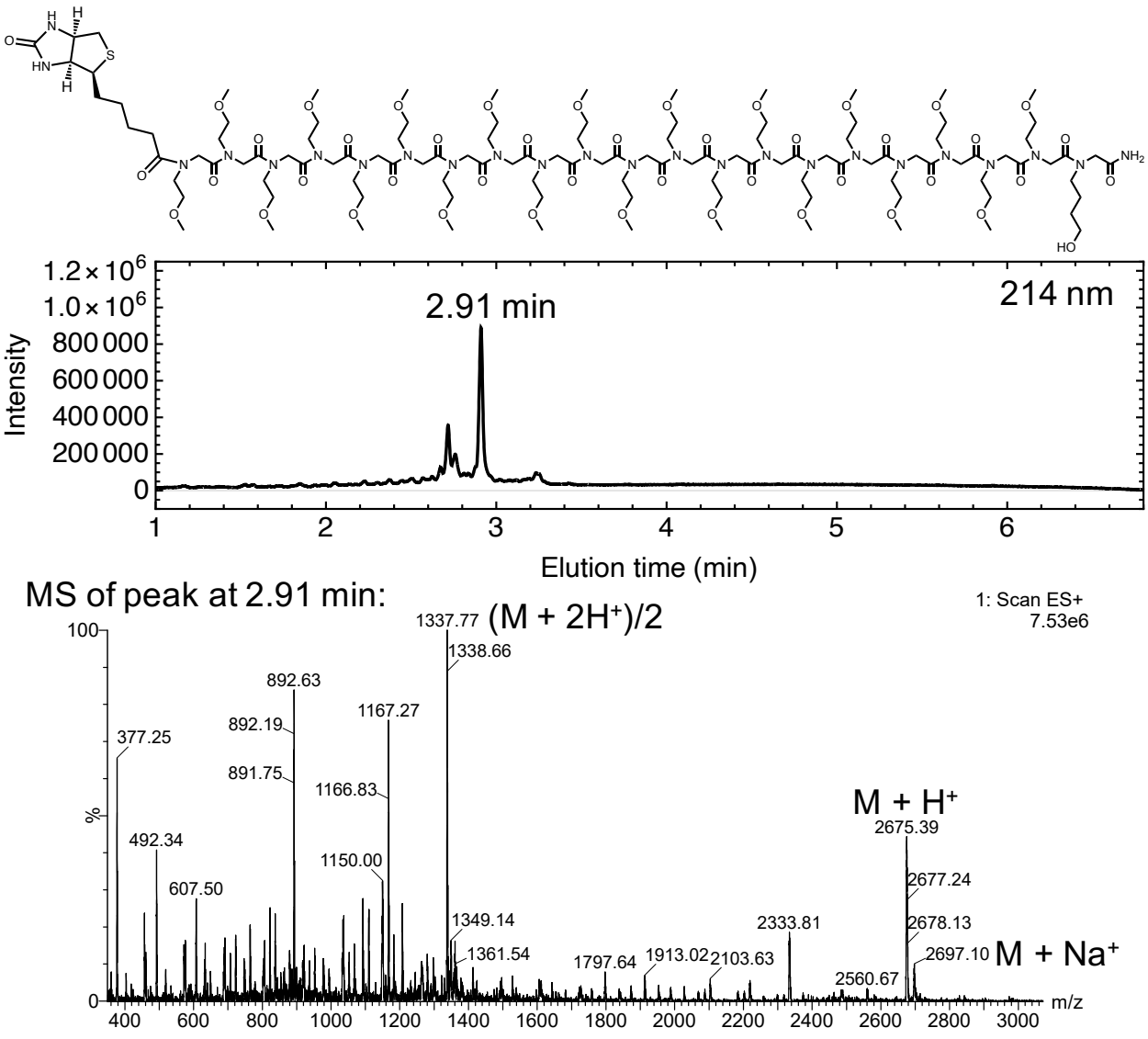
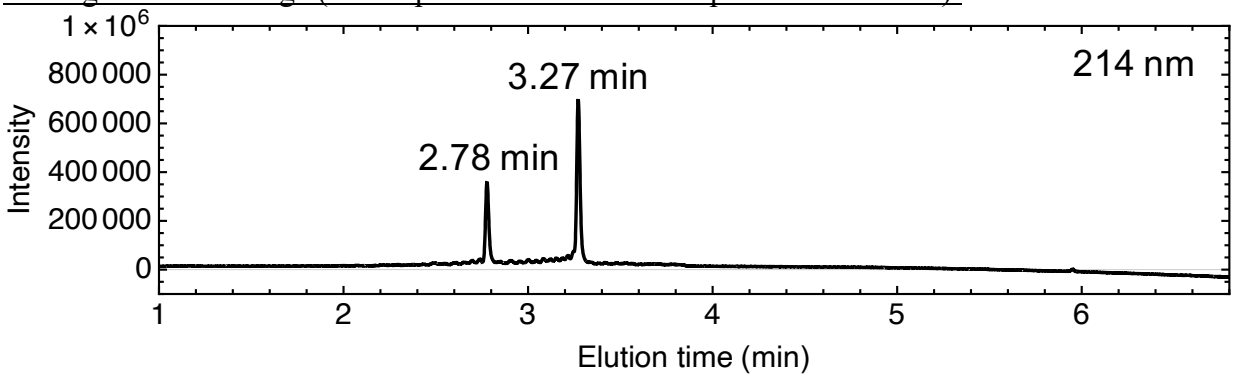
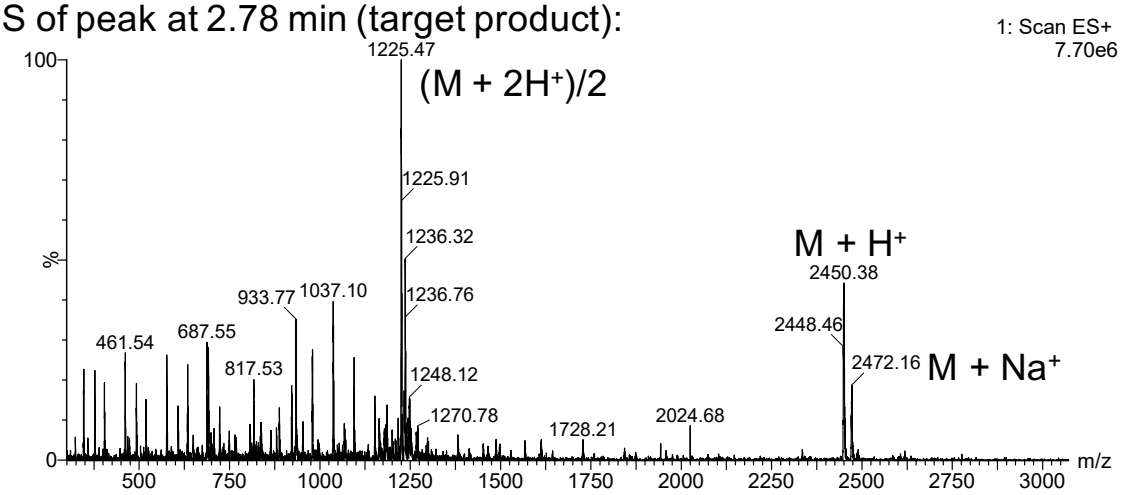


Figure S6. UPLC-MS of biotin-PP1 (C18 column), biotin-Nme$_{20}$Nhb, theoretical molecular weight: 2675.1 g mol^{-1}.

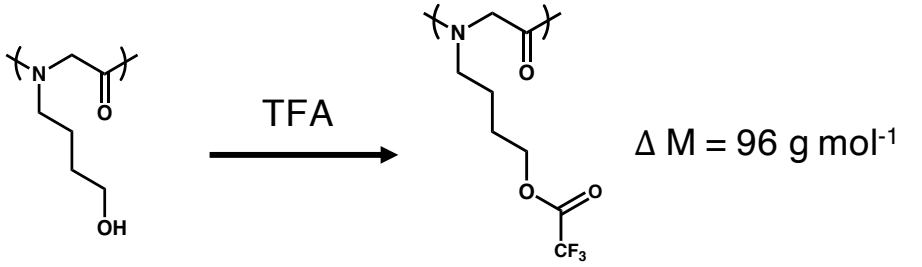
PP1 right after cleavage (with a potential esterification product with TFA):

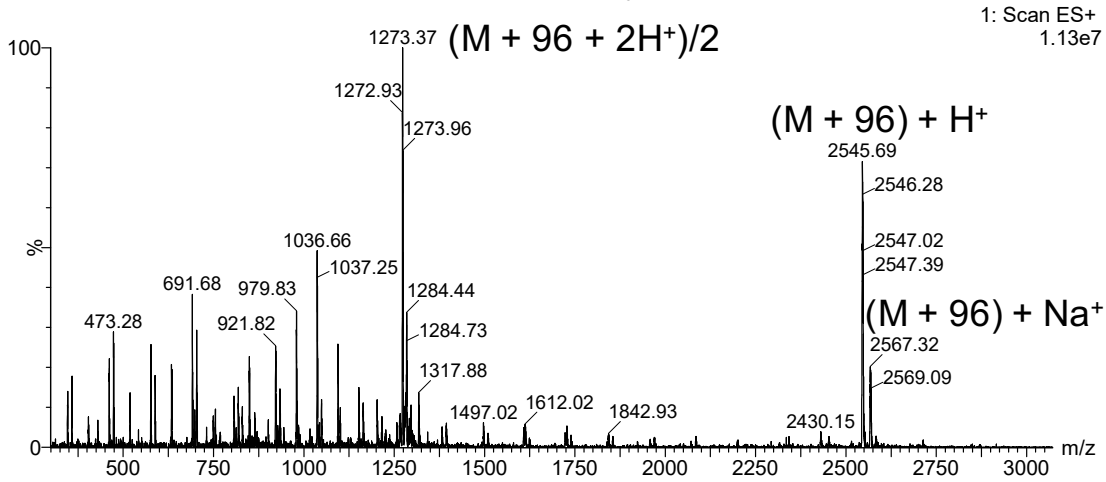


MS of peak at 2.78 min (target product):



MS of peak at 3.27 min (potential esterification product):





The same PP1 sample, after two days in ACN/H_2O solution:

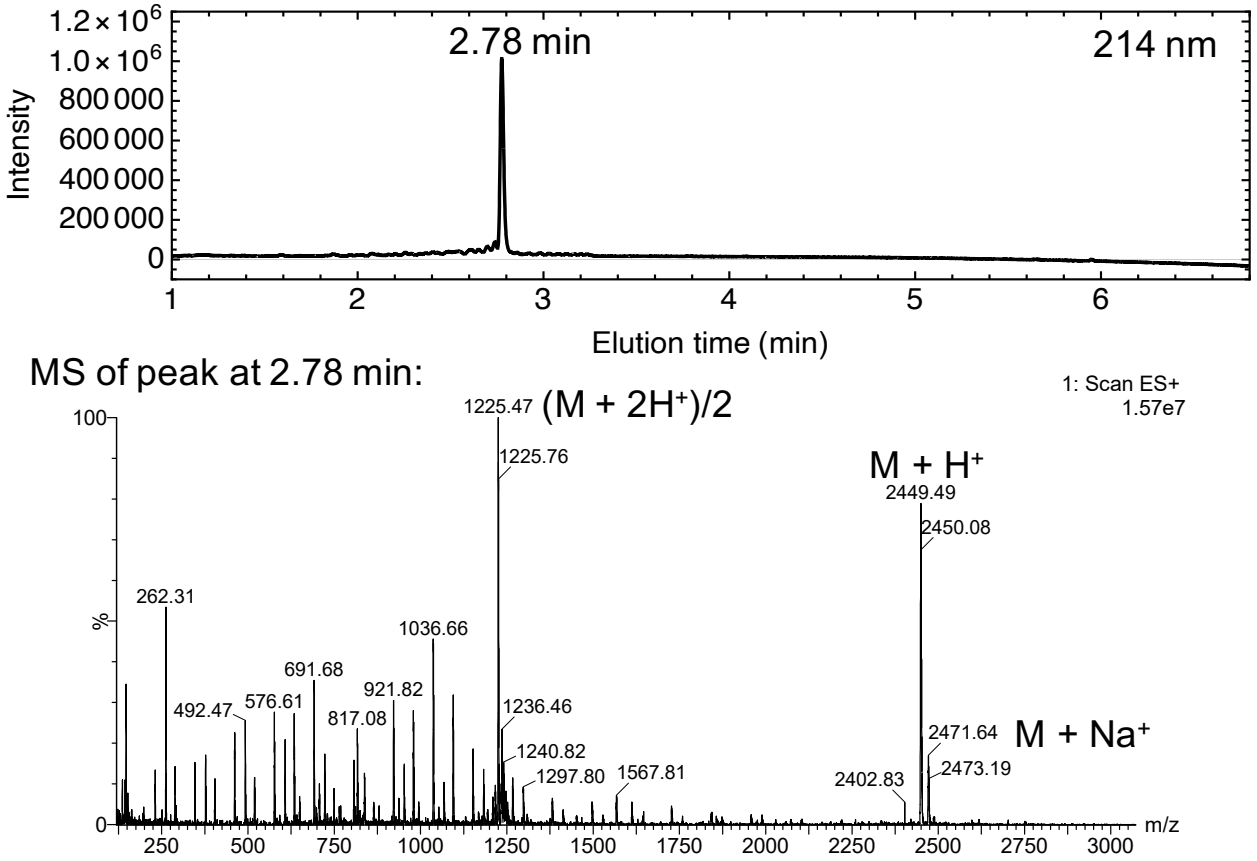


Figure S7. Potential esterification of the –OH group on the first monomer with TFA during cleavage (peak at 3.27 min observed in LC trace, with + 96 g mol^{-1} as compared to the theoretical molecular weight of PP1), which fully reverse after ~ two days in ACN/H_2O solution.

Polymer/Polypeptoid Thin Film and Monolayer Characterization

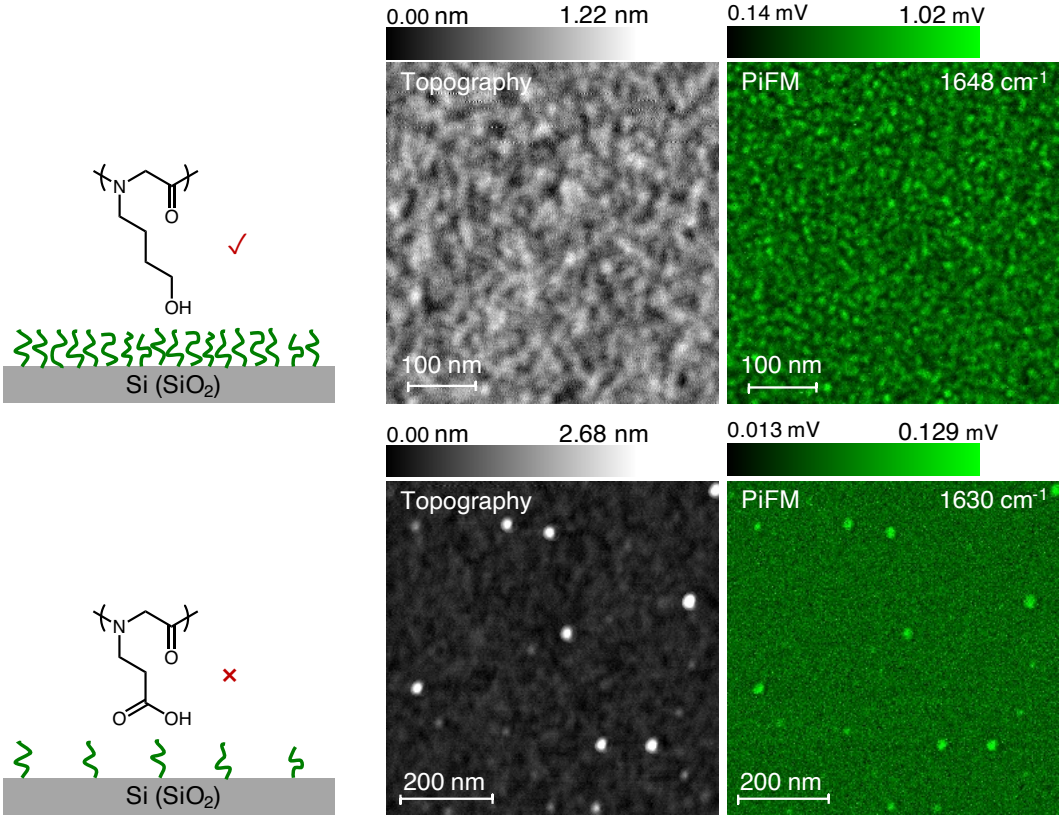


Figure S8. Topography and PiFM images of prepared polypeptoid brush monolayers on Si substrates with –OH vs. –COOH functionalized polypeptoids ($Nme_5(Npm_3Npe)_3Npm_3\underline{Nhb}$ vs. $Nme_5(Npm_3Npe)_3Npm_3\underline{Nce}$).

Table S1. Comparison of brush monolayer thickness and water contact angle of the correspondingly modified Si substrate surface between –OH and –COOH functionalized polymers.

	M_n (g mol^{-1})	Monolayer thickness (nm)[a]	Water contact angle
PS–OH	10,000	5.70	(89.5 ± 0.1)°
PS–COOH	10,000	0.48	(56.0 ± 0.0)°
PMMA–OH	6300	3.89	(63.9 ± 0.6)°
PMMA–COOH	8400	< 0	(39.7 ± 3.9)°

[a]Polymer brush monolayers are prepared on Si wafers with a 250 nm thermal oxide layer, with the thermal oxide layer thickness measured via ellipsometry before polymer grafting.

Table S2. Surface free energy (SFE) of Si substrates modified by different polypeptoid brush monolayers.

	Water	Diiodomethane	SFE (total) (mN/m)	SFE (disperse) (mN/m)	SFE (polar) (mN/m)
PP**1**	(37.6 ± 0.3)°	(40.2 ± 0.6)°	64.8 ± 0.5	39.5 ± 0.3	25.3 ± 0.2
PP**2**	(67.6 ± 0.4)°	(35.7 ± 0.4)°	49.7 ± 0.4	41.7 ± 0.2	7.9 ± 0.2
PP**3**	(70.6 ± 0.1)°	(33.2 ± 0.1)°	49.2 ± 0.1	42.9 ± 0.1	6.3 ± 0.1
PP**4**	(72.5 ± 0.1)°	(31.0 ± 0.2)°	49.1 ± 0.1	43.8 ± 0.1	5.3 ± 0.1
PP**5**	(81.9 ± 0.5)°	(56.4 ± 0.3)°	35.5 ± 0.4	30.6 ± 0.2	4.8 ± 0.2

Surface free energy is calculated using a "two-liquid geometric approach"[2-4] based on static contact angles of two liquids, water (polar) and diiodomethane (nonpolar), measured immediately after dispensing a 2 μL drop of the liquid with an automated dispenser.

We note here that the polypeptoids are soluble in water (PP**1**) or diiodomethane (PP**2**-PP**5**) to some degree. While measurements were possible on the (insoluble) grafted brush monolayers, it was not possible to verify the trend on thicker polypeptoid films. We also note that thicker films of polystyrene were observed to be soluble in diiodomethane, which made it not possible to measure and calculate surface free energy using the water-diiodomethane pair. However, we did not find acknowledgements of the difficulty of performing the such measurements with the water-diiodomethane when the polymers are soluble in the polar or nonpolar liquids.[2-4]

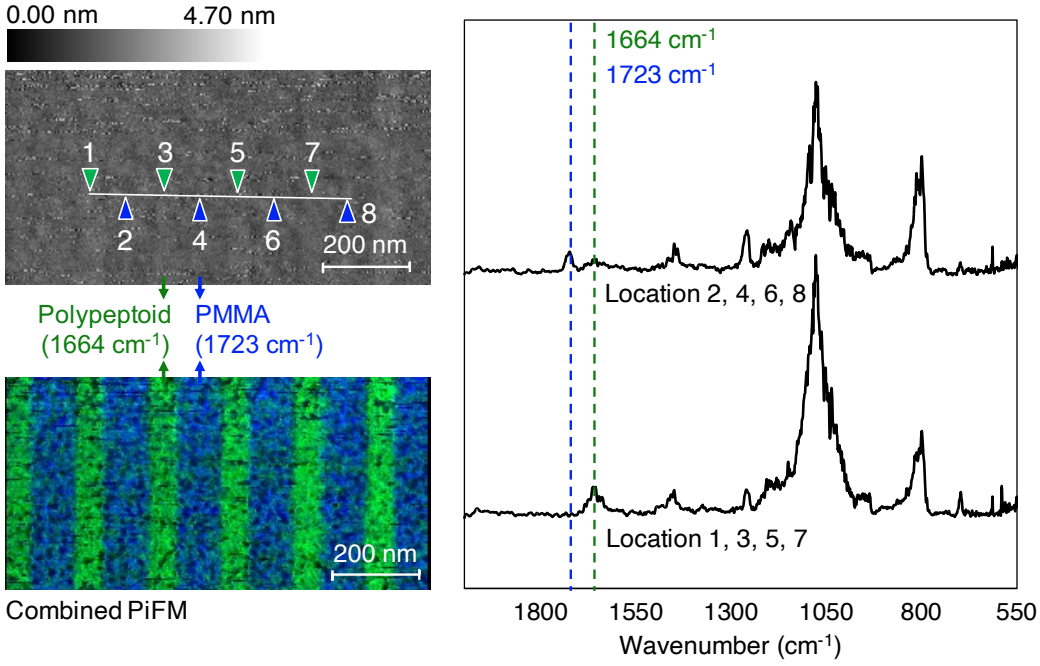


Figure S9. IR PiFM of PMMA–polypeptoid nanopattern.

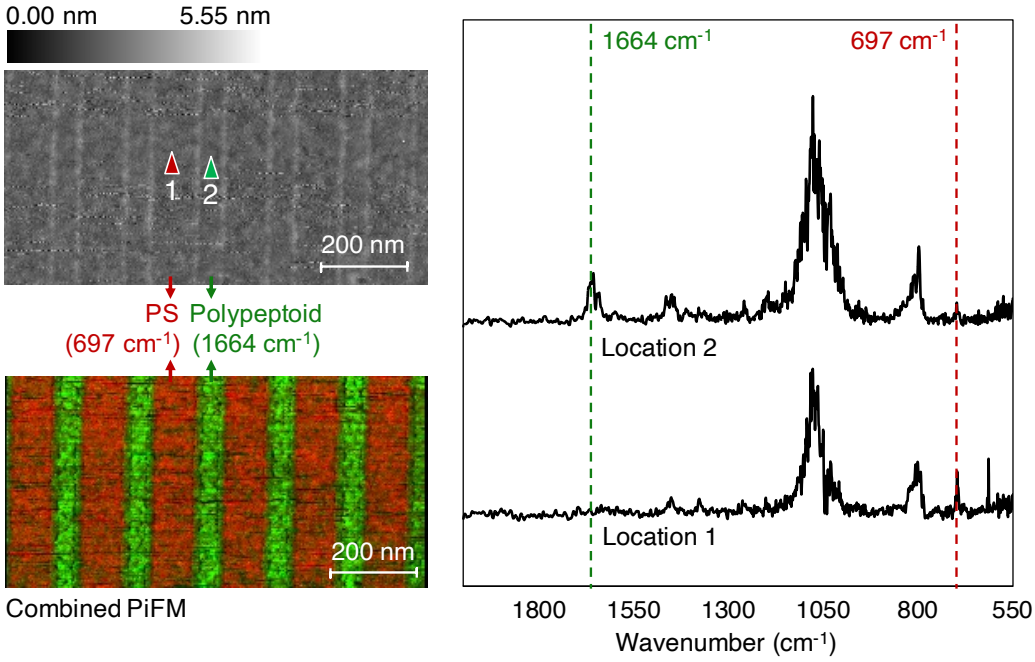


Figure S10. IR PiFM of PS–polypeptoid nanopattern.

DNA Origami and Streptavidin Immobilization on Polymer Brush Modified Surfaces and Chemical Contrast Nanopatterns

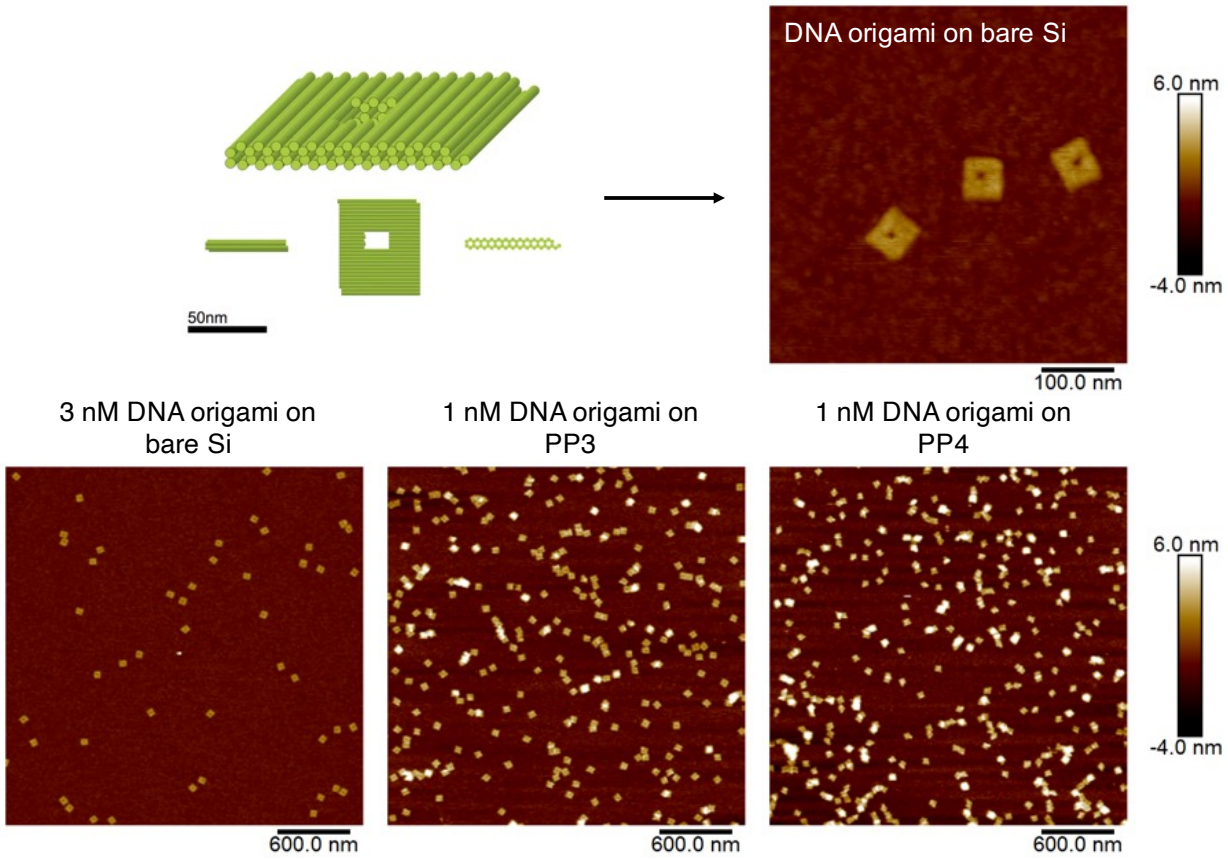


Figure S11. Top: Schematic of the DNA origami nanostructure (from tilibit nanosystems) and morphology of deposited DNA origami nanostructures on bare Si substrates. Bottom: DNA origami binding density on bare Si (3 nM) vs. on PP3 brush monolayer and PP4 brush monolayer modified Si substrates (1 nM).

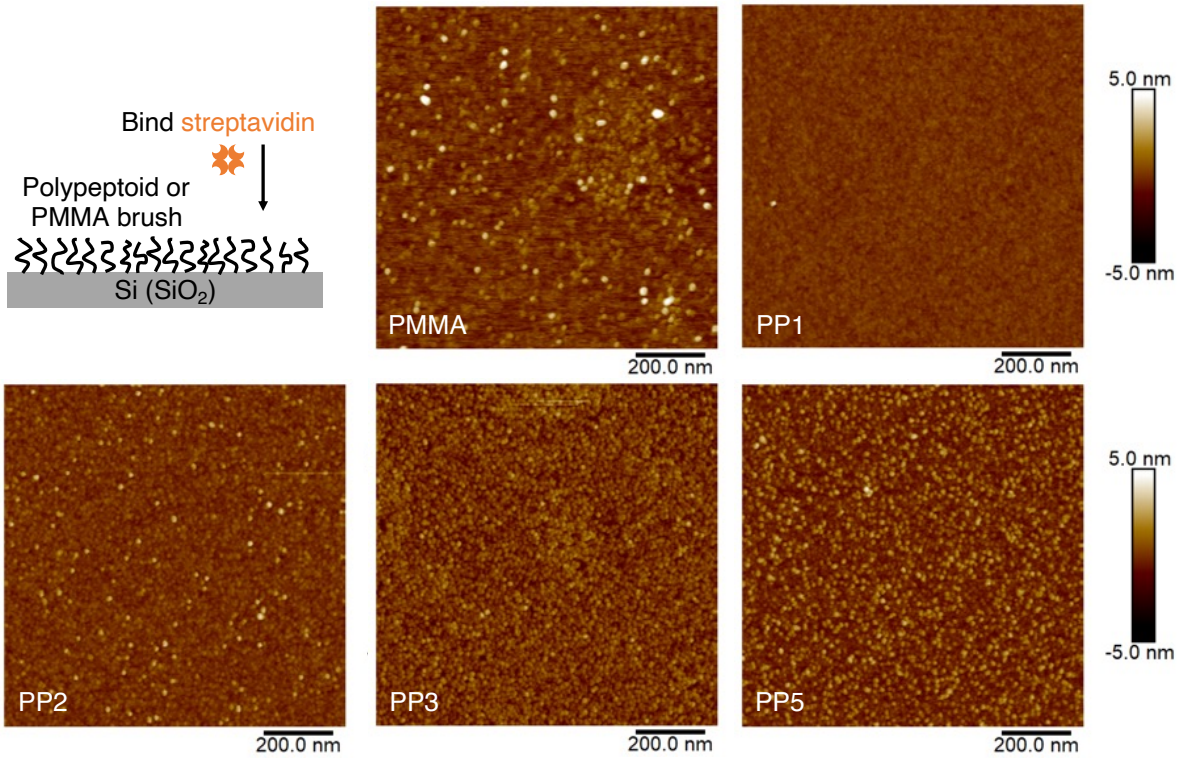


Figure S12. Passivation test against non-specific binding streptavidin (1 μM in 1× PBS buffer) on different polypeptoid brush and PMMA brush modified Si substrates.

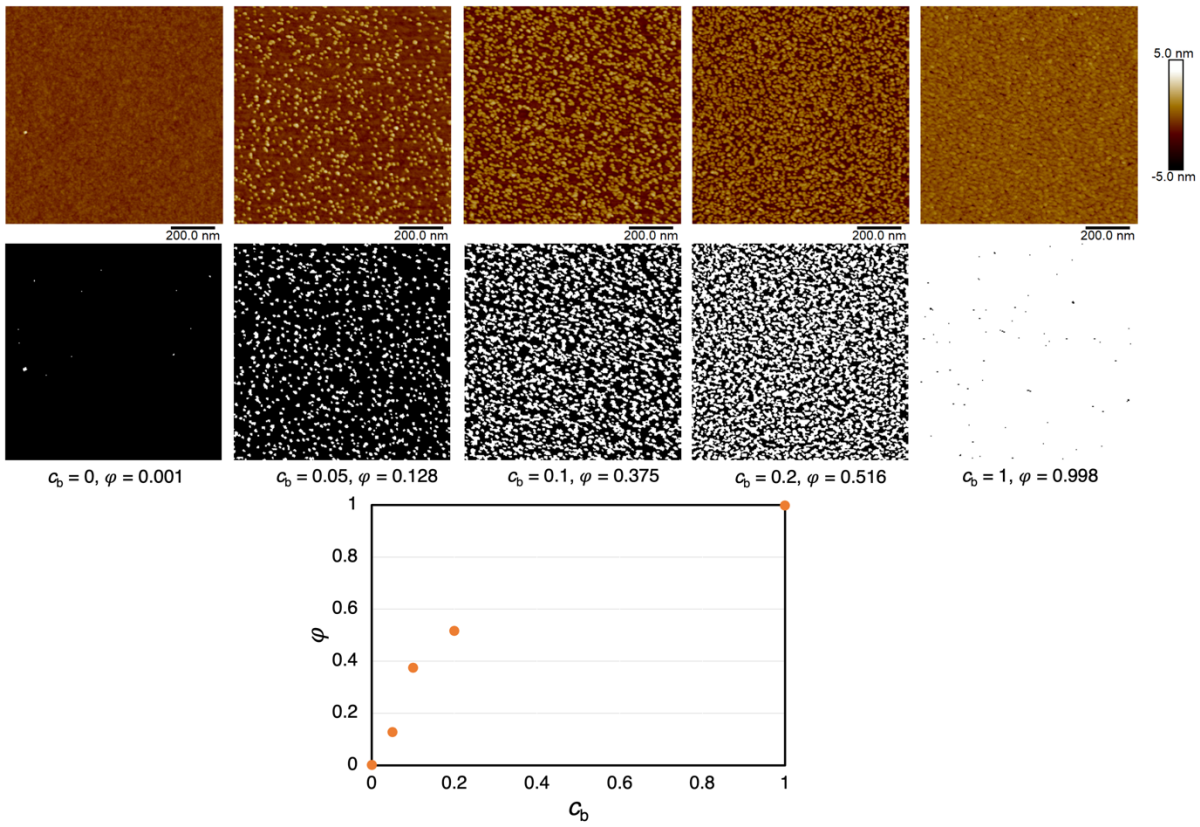


Figure S13. Different streptavidin binding density (quantified by streptavidin fractional surface coverage, φ) is achieved by controlling surface biotin group density through grafting biotin-PP**1** and PP**1** mixtures (relative concentration of biotin-PP**1** in PP**1**, c_b). Binarization of AFM images were performed by thresholding with either clustering with the "KMedoids" method (c_b = 0.05, 0.1, 0.2), or the "MinimumError" method (c_b = 0, 1) when the two height populations corresponding to streptavidin surface and polymer brush surface have minimum overlap in the height histogram.

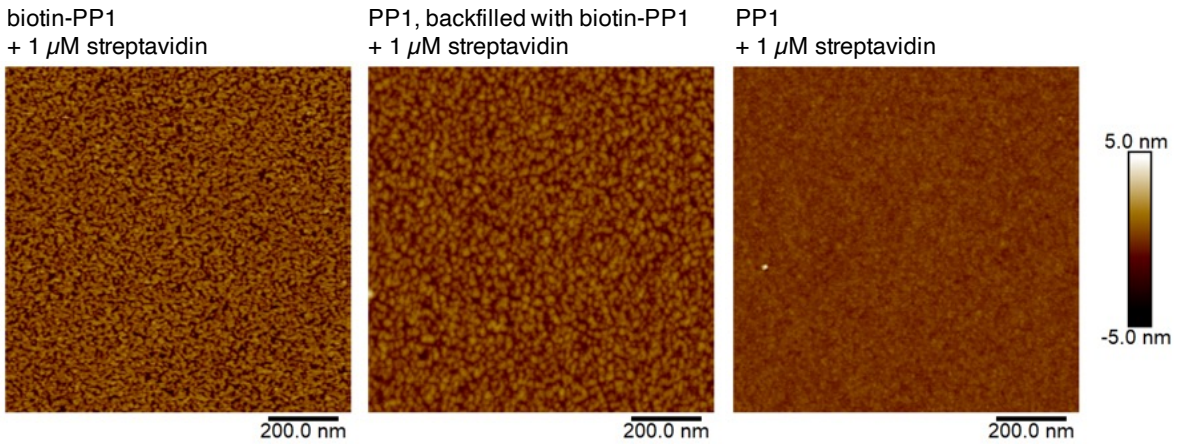


Figure S14. Backfill test with the biotinylated polypeptoid (biotin-PP1) brush, which demonstrates sufficient brush interpenetration happens during the backfill step, and the interpenetrated biotinylated polypeptoid brushes bind large amounts of streptavidin proteins.

References

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