Cucurbit[8]uril Directed Stimuli-Responsive Supramolecular Polymer Brushes for Dynamic Surface Engineering

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Materials

All starting materials and gold coated silicon wafers (layer thickness = 1000 Å, titanium as adhesion layer) were purchased from Sigma Aldrich and used as received unless stated otherwise. CB[8]-rotaxane-functionalised Au surfaces were prepared as documented previously by our group.¹

Instrumentation

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance QNP 400 MHz. ESI-MS was performed on a Fischer Thermo Scientific LTQ Velos Ion Trap Mass Spectrometer. Fluorescence microscopy was performed on a Leica DMI 4000B microscope. Photoirradiation was performed on a LZC-ORG photoreactor with both 350 and 420 nm wavelength lamps. Contact angle (CA) measurements were performed on a First Ten Ångstroms FTÅ200 machine. All the CA data reported in this work were average values from nine independently repeated experiments. CA data were collected on nonpatterned substrates after sufficient washing with corresponding solvents and drying with a flow of nitrogen. AFM image and force-distance curves were recorded on an Agilent 5500 AFM (Santa Clara, CA, USA, now Keysight Technologies).

Experimental

Synthesis of Np-PEG

Np-PEG was synthesised in analogy to literature procedure.² Poly(ethylene glycol) monomethyl ether (average $M_n = 5000$ g/mol) was dried by azeotropic distillation in toluene. A solution of poly(ethylene glycol) 5000 monomethyl ether (1.0 g, 0.2 mmol) in anhydrous DCM (30 mL) was added with 2-naphthol isocyanate (101.5 mg, 0.6 mmol). Two drops of dibutyltin dilaurate (TDL) was added at once and the mixture was stirred for 24 h at room temperature. The mixture was diluted with DCM (100 mL) and the slurry was sonicated for 5 min. The remaining solid was filtered

off and the solvent was removed under pressure to yield yellowish solid. The yellowish solid was redissolved in DCM (20 mL), filtered and precipitated in cold diethyl ether (2x). Suction filtration yielded Np-PEG (1.00 g, 97%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.03 (s, 1H), 7.79-7.77 (m, 3H), 7.45-7.38 (m, 4H), 4.39 (t, 2H), 3.85-3.45 (m, PEG backbone), 3.39 (s, 3H). The purity of the sample was confirmed by THF-GPC.



Figure S1: Approach and retract force curves of Np-PEG brushes with different grafting densities on the CB[8]-rotaxane-functionalised Au surface. The profile of the brushes prepared by (A) the addition of 100 % Np-PEG (5 mM) to the functional surface, (B) adding a mixture of Np-PEG (5 mM) and Np (20 mM) to the surface, and (C) immersing the functional surface in a mixture of Np-PEG (5 mM) and PEG (20 mM) in water for 30 min.

As shown in Figure S1A, AFM force-distance curves show the approach and retract profiles obtained in water (a good solvent for Np-PEG) between a Si_3N_4 AFM tip and the Np-PEG brushes. In order to show the necessity of having the Np group on the polymer chain, CB[8] rotaxane-terminated Au surface was immersed in a mixture of PEG and Np-PEG ([PEG] = 20 mM, [Np-PEG] = 5 mM) for 30 min. The force-distance curves in Figure S1B, don't show much difference compared to the curves for the brushes prepared by 100% Np-PEG. By comparing the three sets of force-distance curves, it shows that the attachment of polymers onto the substrate is completely through controlled host-guest recognition of the CB[8]-rotaxanes on the surface, rather than by random physical adsorption.

Synthesis of Azo-PEG

p-Azobenzene isocyanate and Azo-PEG ($M_n = 5000$ g/mol) was synthesised in analogy to literature procedure.² To a solution of p-azobenzene isocyanate (0.5 g, 2.2 mmol) and poly(ethylene



Figure S2: SEM image of patterned Np-PEG brushes on the surface after extensive wash with toluene for 2 days. The brushes are located all over the surface except the ring areas which were protected with dodecanethiol.



Figure S3: Schematic illustration (A) and AFM topography image (B) of Np-PEG brushes on CB[8]-functionalised Au surface in a mixture of acetonitrile and toluene (1 : 1 by volume, medium solvent).

glycol) 5000 monomethyl ether (1.0 g, 0.5 mmol) in 10 mL of anhydrous DCM was added a drop of TDL, and the mixture was stirred for 48 h at room temperature. The product was obtained by precipitation from cold diethyl ether. The solid was redissolved in ca. 30 mL DCM, filtered and reprecipitated in cold diethyl ether. Suction filtration yielded Azo-PEG (0.9 g, 0.2 mmol, 92%) as a yellow solid. ¹H NMR (400 MHz, d⁶-DMSO): δ = 7.90-7.84 (m, 3H), 7.76-7.69 (m, 2H), 7.60-7.52 (m, 3H), 4.25 (t, 2H, 4.4 Hz), 3.67-3.33 (m, PEG backbone), 3.24 (s, 3H) ppm. The purity of the sample was confirmed by THF-GPC.



Figure S4: Approach and retract force-distance curves of Azo-PEG brushes with different grafting densities on CB[8]-functionalised Au surface. The profile of the brushes prepared by (A) the addition of 100 % Azo-PEG (5 mM) to the functional surface, (B) adding a mixture of Azo-PEG (5 mM) and Azo (20 mM) to the surface, and (C) immersing the functional surface in a mixture of Azo-PEG (5 mM) and PEG (20 mM) in water for 30 min. (D) Approach and retract profiles of a force-distance curve for Azo-PEG brushes obtained in toluene between a Si₃N₄ AFM tip and the brushes on Au surface.

Synthesis of poly(MPAC-Azo)

For the synthesis of azobenzene monomer (Azo-mma), a solution of triethylene glycol azobenzene (13.7 g, 69.4 mmol) and triethylamine (14.5 ml, 104.0 mmol) in diethyl ether (150 ml) was cooled to -20 °C. To this a solution of methacryloyl chloride (8.06 ml, 83.2 mmol) in diethyl ether (50 ml) was added dropwise over 1 h. The mixture was then allowed to slowly warm to room temperature and stirred for 12 h. The triethylammonium chloride salt was removed by filtration and the volatiles *in vacuo*. The crude product was purified by flash chromatography (SiO₂, 30:1 ν/ν petroleum ether/ethyl acetate). The relevant fractions were collected, combined and condensed *in vacuo* to give an orange oil (12.5 g, 85%).³ ¹H NMR (400 MHz, d₆-DMSO, 298 K) 7.91 (t, 2H), 7.78



Figure S5: ¹H NMR spectrum of poly(MPAC-Azo)

(d, 2H), 7.56 (t, 2H), 7.32 (t, 1H), 7.07 (d, 2H), 6.4 (s, 2H), 4.31 (m, 4H), 3.77 (t, 2H), 3.63 (t, 2H), 3.52 (t, 4H), 2.12 (s, 3H).

Poly(MPAC-Azo) was synthesised *via* free radical polymerisation using the 4,4-azobis(4-cyano-valeric acid) (ACPA). To a two-neck round bottom flask was added [3-(methyacryloylamino)-propyl]trimethylammonium chloride 50 wt% solution (2.65 g, 6 mmol, 400 eq.), Azo-mma (0.060 g, 0.15 mmol, 10 eq.) and fluorescein O-methacrylate (0.0063 g, 0.015 mmol, 1 eq.) in methanol (6 ml). Oxygen was removed by bubbling argon through the solution for 20 min, followed by the subsequent addition of ACPA (4.2 mg, 0.015 mmol, 1 eq.). The flask was immersed in a preheated oil bath (70 °C) and the solution stirred at 400 rpm for the 24 h. The resultant polymer was precipitated into cold diethyl ether and dried *in vacuo* at 50 °C. The purified polymer was characterised

to give $M_w = 52.1$ kDa, PDI = 1.4 from Aqueous-GPC.



Figure S6: ¹H NMR spectrum of poly(MPAC)



Figure S7: ¹³C NMR spectrum of poly(MPAC)

Poly(MPAC) was synthesised in analogy to poly(MPAC-Azo). To a two-neck round bottom

flask was added [3-(methyacryloylamino)propyl]trimethylammonium chloride 50 wt% solution (2.65 g, 6 mmol, 400 eq.) in methanol (6 ml). Oxygen was removed by bubbling argon through the solution for 20 min, followed by the subsequent addition of ACPA (4.2 mg, 0.015 mmol, 1 eq.). The flask was immersed in a preheated oil bath (70 °C) and the solution stirred at 400 rpm for the 24 h. The resultant polymer was precipitated into cold diethyl ether and dried *in vacuo* at 50 °C. ¹H NMR and ¹³C NMR spectra are shown in Figure S6 and S7. The necessity of having Azo derivatives on polymers for the assembly of poly(MPAC-Azo) brushes is proved by a control experiment, where poly(MPAC) was used instead of poly(MPAC-Azo). Ellipsometry confirmed that poly(MPAC) without second guest Azo can not be attached to the CB[8] functionalised Au surface.

General preparation method for supramolecular polymer brushes on Au surfaces

CB[8]-rotaxane functionalised Au surfaces were prepared according to a previously published paper by our group.¹ For unpatterned surfaces, CB[8]-rotaxane functionalised Au substrates were directly immersed into aqueous solutions of polymers and left on a shaker with 200 r.p.m. for 30 min. For patterned surfaces, polydimethylsiloxane (PDMS) stamps were wetted by EtOH solutions of 2-aminoethanethiol hydrochloride (20 mM) and then brought into contact with bare Au substrates for 30 s. After peeling away the stamps, the resulting substrates were washed with EtOH and immersed into solutions of dodecanethiol (2 mM) to backfill the bare areas. Surface-bound CB[8]-rotaxanes were subsequently prepared on the patterned areas where amino groups were present, with the method as the same as for the unpatterned surfaces. The resultant substrates with patterned CB[8]-rotaxanes were then immersed into aqueous solutions of polymers and left on a shaker with 200 r.p.m. for 30 min.

AFM force-distance measurements

AFM force-distance curves displayed in this work are averaged over 100 measurements from representative surfaces. A maximum trigger value of 0.5 nN was imposed on all force measurements to avoid damaging the tip. Rectangular-shaped silicon FESPA AFM-cantilevers (Bruker) with V-shaped tips were used for imaging. Rectangular-shaped Si₃N₄ AFM-cantilevers (HYDRA2R-50N Series, AppNano) with V-shaped tips were used for measuring all force-distance curves. The FESPA tips have a resonant frequency of 75 kHz, tip radius of 8 nm and nominal spring constant of 2.8 N/m. The HYDRA2R-50N tips have a resonant frequency of 77 kHz and nominal spring constant of 0.084 N/m. Spring constant of the AFM tips was calculated from dimensions (see Equation 1 and 2) and calibration typically fell within a 20% margin of error from the nominal spring constant.

$$k = \frac{Ew}{4} \left(\frac{t}{l}\right)^3 \tag{1}$$

$$f = \frac{(1.8751)^2}{2\pi} \cdot \frac{t}{l^2} \cdot \sqrt{\frac{E}{12\rho}}$$
(2)

k spring constant, E Young's modulus, w width, t thickness, l length, f resonance frequency, ρ mass density

The direct result of a force measurement is a photodiode current (*I*) vs. height position of the piezoelectric translator (*Z*) data. The linear part of the 'contact regime' (not the exponentially decaying part, see Figure S8) in the force-distance curve is assumed to be zero distance and its slope is the sensitivity $(\frac{\Delta I}{\Delta Z})$. This value is used to convert *I* into deflection distance in nanometer along the whole curve. Zero deflection is determined from the non-contact part at large distance, where surface forces are negligible. The contact point is extrapolated from the two linear regimes. Once the deflection of the cantilever is known as a distance (*x*), the spring constant (*k*) is needed



Figure S8: Schematic illustration of how the I vs. Z curve is converted to F vs. D curve, and the contact/non-contact regimes.

to convert this value into a force F, using the well-known Hooke's law:

$$F = kx = k \frac{I}{\frac{\Delta I}{\Delta Z}} \tag{3}$$

In order to convert Z to tip-sample distance (D), cantilever deflection x was subtracted from Z.⁴

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