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Supporting Information

Contact printing biomimetic catecholic monolayer on a variety

of surfaces and derivation reaction

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Materials

3-Hydroxytyramine hydrochloride (dopamine HCl), 5-norbornene-2-carboxylic acid. 1H,1H-perfluoro-1-octanol, Generation, Grubbs Catalyst 2nd 1,3-Bis(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)(dichlorophenylmethylene)(t ricyclohexylphosphine)ruthenium, and monomer dimethylaminoethyl methacrylate (DMAEMA), N-isopropylacrylamide (NIPAm), and 3-sulfopropyl methacrylate potassium salt (SPMA) were obtained from Sigma-Aldrich. Biotin and FITC conjugated streptavidin obtained from Alfa-Aesar. were 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) and N-hydroxysuccinimide (NHS) were purchased from Shanghai Fine Chemical Co. Ltd.

(Shanghai, China). Copper (I) bromide (CuBr) was purified by reflux in acetic acid. All other chemicals used in this work were analytical grade and used as received.

Gold film was deposited on freshly cleaned Si wafers (100) by Magnetron sputtering, the thickness of Au film was 100 nm (5 nm underlayer of Ti), and 150 nm of Ti film was obtained with the same method. Fe surface was obtained by polishing the iron disk with 2000 emery paper and 0.5 μ m alumina–water slurry, then degreased with acetone, and ethanol in ultrasonic bath. All the substrates, which used for printing the biomimetic binding chemistry, were cleaned and hydroxylated by exposure to oxygen plasma (Femto, diener electronic) for 3 min (at a power of 99 W).

Instrumentation

AFM measurements were performed using a commercial Multimode AFM (Nanoscope IIIa, Veeco Instrument, Santa Barbara, CA) under ambient laboratory conditions of 20–25 °C. The surface morphology and film thickness of polymer brushes were obtained in tapping mode using a pyramidal Si tip. The Optical and fluorescent images were taken with a fluorescence microscope (Olympus BX51). Chemical composition information about the samples were obtained by X–ray Photoelectron Spectroscopy (XPS), the measurement was carried out on a PHI–5702 multi–functional spectrometer using Al K α radiation. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The attenuated total reflection infrared spectra (ATR–FTIR) were detected on a Nicolet (iS10) infrared spectrometer equipped with a smart ATR accessory. The static water contact angles were measured by the sessile drop method in a DSA100 (Kruss) telescopic goniometer.

Experimental details

Protein patterning. Firstly, 7.6 mg 3–Hydroxytyramine hydrochloride, 4.2 mg (4 mM) Na₂CO₃ and 13.7 mg (4 mM) NHS–Biotin were added to 10mL DMF under N₂ atmosphere for 12 h to form DOPA–Biotin. Patterned DOPA–Biotin was obtained

on Ti substrates using microcontact printing. Then, patterned DOPA–Biotin was incubated with 10 mM FITC–Streptavidin buffer solution (pH 7.4) for 1 h. After being rinsed for several times to remove free streptavidin, the substrates were imaged under a fluorescence microscope.

Polymer brushes patterning by ATRP. The general polymerization procedure involved dissolving the monomer in water or water/methanol mixed solvent at room temperature and purged with N₂ during stirring (30 min). Bipyridyl or pentamethyldiethylenetriamine (PMDETA), and CuBr were added successively into this solution. The mixture was further stirred and degassed with N₂ flow until a clear solution was obtained. Thereafter, the initiator-patterned substrates were immersed in the mixture for polymerization under N₂ protection. Polymerization recipes for for SI-ATRP are as follows: (1) NIPAm 2.52 g, the three monomers water/methanol (4 mL, 1/1 v/v), CuBr 0.032 g, PMDETA 140 µL, 1, 5, 10, 20, 30, 60 and 120 min; (2) DMAEMA 0.5 mL, water/methanol (5 mL, 1/1 v/v), bipyridyl 0.031 g, CuBr 0.015 g, 60 min; (3) SPMA 1.23 g, water/methanol (3 mL, 1/2 v/v), bipyridyl 0.039 g, CuBr 0.012 g, 30 min. After polymerization, the polymer brushes were copiously rinsed with a mixture of methanol and water.

Polymer brushes patterning by ROMP. First, PDMS stamp soaked with catechol-based initiator 2 (4 mM, water:ethanol = 4:1), and Ti substrates were contact printed with the initiator under ambient conditions. The primed substrates were then transferred into a solution of 20 mg of Grubbs 2nd catalyst in 4 mL of dry dichloromethane mixture, which were placed in a flask under N₂ flow for 30 min at room temperature. After the Ru catalyst functionalizes with the resulting patterned initiator, the substrates were then carefully rinsed with pure dichloromethane (three times) in order to remove the excess catalyst, and immersed in 5 mL of freshly prepared solutions of 0.3 M NCA-F15 in dichloromethane under N₂ protection. The

reaction was carried out at room temperature for 30 min. Last, the samples were removed from the reaction medium, extensively washed with pure dichloromethane.

A curve of thickness versus polymerization time. Figure S1 shows the evolution of PNIPAm thickness (as measured by AFM in the dry state) with the polymerization time on Ti substrates. It can be seen from the image that the growth of PNIPAm is very fast in the initial stage. The thickness can reach around 18 nm within 1 min, and the thickness of the polymer brushes increases by increasing of the polymerization time.



Figure S1. The evolution of brush thickness with the polymerization time. The line was added to guide the eye.

Characterization

ATR-FTIR Spectra. Figure S2 shows the ATR-FTIR spectra of patterned polymer brushes fabricated by SI-ATRP and SI-ROMP on Ti substrate.



Figure S2. ATR–FTIR spectra of patterned polymer brushes fabricated by ATRP (a) PNIPAm, (b) PDMAEMA, (c) PSPMA, and by ROMP (d) PNCA-F15.

Figure S2a demonstrates ATR–FTIR spectrum of PNIPAm polymer brushes. It can be seen that two sharp absorption peaks appearing at 1646 cm⁻¹ (C=O stretching) and 1540 cm⁻¹ (N–H bending) are both the exact proofs that PNIPAm has grown from the patterned initiator monolayers successfully. Figure S2b demonstrates ATR–FTIR spectrum of PDMAEMA polymer brushes. Typical features of the PDMAEMA backbone include absorptions at 1729 cm⁻¹ (a sharp peak) from C=O stretch in the ester group, and a peak at 1471 cm⁻¹ from CH₂ bending and 1268 cm⁻¹ from C–N stretching of –N(CH3)₂ groups. Figure S2c demonstrates ATR–FTIR spectrum of PSPMA polymer brushes. Typical features of the PSPMA backbone include absorptions at 1704 cm⁻¹ from C=O stretch in the ester group, and a peak at 1471 stretching vibrations of the S=O groups. Figure S2d demonstrates ATR–FTIR spectrum of PNCA–F15 polymer brushes by ROMP. Typical features of the PNCA–F15 backbone include a sharp absorptions peak at 1750

cm⁻¹ from C=O stretch in the ester group; the IR spectrum for PNCA–F15 exhibits absorbance peaks for perpendicular C–F stretching modes at 1234, 1201, and 1142 cm⁻¹. The CF₂ stretching modes absorb strongly from 1100 to 1400 cm⁻¹.

XPS Spectra. Successful grafting of patterned polymer brushes fabricated by SI–ATRP and SI–ROMP was further confirmed by XPS analysis (Figure S3–10).



Figure S3. XPS spectra of Ti (a), patterned PNIPAm (b) and PDMAEMA (c) polymer brushes on Ti surfaces.





Figure S4. XPS spectra of Si (a), patterned PNIPAm (b) and PDMAEMA (c) polymer brushes on Si surfaces.



Figure S5. XPS spectra of patterned PNIPAm polymer brushes on stainless steel.



Figure S6. XPS spectra of patterned PNIPAm polymer brushes on Au surface.



Figure S7. XPS spectra of patterned PNIPAm polymer brushes on quartz surface.



Figure S8. XPS spectra of patterned PNIPAm polymer brushes on glass surface.



Figure S9. XPS spectra of patterned PSPMA polymer brushes on Ti surface.



Figure S10. XPS spectra of Ti (a), patterned initiator 2 (b) and further grafted PNCA-F15 polymer brushes (c) on Ti surfaces.