Supplementary Information (SI) for Chemical Science.
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1. Materials

2-azidoethyl 2-bromoisobutyrate (98%), azide-fluor 545 Tetramethylrhodamine, tris(2-carboxyethyl) phosphine hydrochloride (TCEP), tris(2-pyridylmethyl)amine (TPMA, 98%), ascorbic acid (99%), and poly(ethylene glycol) methacrylate (OEGMA, M_n = 360) were purchased from Sigma Aldrich. 3-sulfopropyl methacrylate potassium salt (SPMA, 97%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%) were obtained from TCI. Gold-coated silicon wafer was purchased from Incole Union Tech Co., Ltd (Tianjin, China). 1H, 1H, 2H, 2H-perfluorooctyl trichlorosilane, acridine orange, and rhodamine B were obtained from Aladdin. Dimethyl sulfoxide (DMSO) and absolute alcohol were obtained from Chemical Reagent Co., Ltd. Polydimethylsiloxane (PDMS) and curing agent were purchased from Dow Corning.

2. Methods

Table S1: The sequences of oligonucleotide primers.

Primer	Sequence	5'-end	3'-end
A	CGACTCGCTGGTCTGGTTGAACG TCAGCCCTGCC	-	HS-$(CH_2)_6$-
B	GGCAGGGCTGACGTTCAACCAG ACCAGCGAGTCG	-	DBCO
C	GGCAGGGCTGACGTTCAACCAG ACCAGCGAGTCG	DBCO	HS-$(CH_2)_6$-

Preparation of PDMS stamps

Cleaned and patterned silicon wafer and 10 μL 1H,1H,2H,2H-perfluorooctyl trichlorosilane were placed in a sealed desiccator. Pumped to a low vacuum to volatilize 1H,1H,2H,2H-perfluorooctyl trichlorosilane and the wafer was fluorinated in the gas phase for 2 h at room temperature. PDMS and curing agent were poured onto the fluorinated silicon wafer and cured at 80 °C for 2 h. After cooling to room temperature, PDMS was gently peeled off from the silicon wafer to obtain PDMS stamps with different patterns.

Preparation of ssDNA ATRP initiator (ssDNA-Br)

2.4 mg of 2-azidoethyl 2-bromoisobutyrate was dissolved in 200 μL DMSO, and then 2 μL of the above 2-azidoethyl 2-bromoisobutyrate solution was added to 50 μL of 200 μM DBCO-modified DNA aqueous solution (sequences B in Table S1). The reaction

was allowed to proceed at room temperature for 2 h. By applying the above solution to an Amicon Ultra-15 Centrifugal Filter (Merck Millipore, MWCO = 3 kDa), unreacted 2-azidoethyl 2-bromoisobutyrate was centrifuged and washed away to obtain the ssDNA-Br initiator.

Immobilization of patterned ssDNA-Br ATRP initiator on gold substrates

ATRP initiator patterning on the surface of gold wafers was prepared by microcontact printing (μCP). Gold wafers (1.0×0.8 cm) were cleaned by ultrasonic treatment in alcohol, followed by 12 s of plasma treatment (70 W, air). 10 μL of TCEP solution (0.1 M) was reacted with 10 μL of 200 μM thiol-terminated ssDNA (sequence A, Table S1) for 1 h to reduce the disulfide bonds of ssDNA to free sulfhydryl groups for surface immobilization. Then the ssDNA solution was diluted with ethanol and dropped on the PDMS stamp to dry. PDMS stamp was brought into contact with the surface of the gold wafer and gently pressed for 10 min to obtain a patterned ssDNA-modified gold. Subsequently, the ssDNA-modified gold wafer was placed on a 10 μL ssDNA-Br solution (2 M NaCl and 20 mM $MgCl_2$), with the surface of the gold wafer facing the DNA solution and was incubated for 2 h for hybridization. Unhybridized DNA was removed by washing the gold substrates with deionized water.

Patterned ATRP initiated on gold surfaces

Single pattern

For the polymerization of SPMA, 6.8 mg $CuCl_2 \cdot H_2O$, 116 mg TPMA and 88 mg ascorbic acid were dissolved in 1 mL MeOH/H_2O solution (*v/v* = 1/2). Then, 25 μL of the above solution was added to 1 mL SPMA solution (MeOH/H_2O, *v/v* = 1/2), [SPMA]/[$CuCl_2 \cdot H_2O$]/[TPMA]/[ascorbic acid] = 20000/1/10/1.2. Subsequently, dsDNA-Br modified substrates were immersed in the above reaction mixture for polymerization. The initiator immobilization only occurred in patterned areas, resulting in patterned polymer brushes.

Polymerization recipes for OEGMA and DMAEMA: 2 M OEGMA, [OEGMA]/[$CuCl_2 \cdot H_2O$]/[TPMA]/[ascorbic acid] = 10000/1/10/1.2, MeOH/H_2O, *v/v* = 4/1. 1 M DMAEMA, [DMAEMA]/[$CuCl_2 \cdot H_2O$]/[TPMA]/[ascorbic acid] = 2000/1/4/2, MeOH/H_2O, *v/v* = 1/2.

Binary and ternary patterns

By using the μCP method, the pattern of the first ATRP initiator was printed, and then

surface-initiated polymerization was performed. On the patterned surface of polymer brushes, ATRP initiator was re-printed. The initiator can only be printed onto the blank area of the gold wafer. After the second surface-initiated polymerization, binary polymer brushes can be obtained. Finally, ATRP initiator was pressed on the pattern surface of binary polymer brushes, and then surface polymerization was carried out to obtain the surface of the ternary polymer brushes.

Cleavage and regeneration of polymer brushes

PSPMA-modified patterned gold substrate (Au-PSPMA) was immersed in deionized water at 95 °C for 5 min and then quickly transferred to an ice bath. Dehybridization of dsDNA occurred and PSPMA with ssDNA was detached from the substrate. In order to realize the secondary modification of polymer brushes, gold substrate coated with ssDNA was co-incubated with ssDNA-Br solution for dsDNA ATRP initiator rehybridization, and the subsequent surface polymerization was performed following the same procedure as described previously.

3. Characterizations

The elemental compositions and chemical valence states of gold substrate surfaces were measured by Fourier transform infrared spectroscopy (FT-IR, Brooke Tensor II infrared spectrometer) and X-ray photoelectron spectroscopy (XPS, XPS, Ulvac-PHI, recorded by an Axis Supra X-ray using Al Kα radiation). The thickness of polymer brushes on gold substrates was measured by ellipsometry (equipped with a He-Ne laser source of λ = 632.8 nm and a fixed angle of incidence of 70°) and a three-dimensional optical profiler (Countour GT-K). Fluorescence micrographs of the stained DNA and polymer brushes on the gold surface were obtained using an Olympus BX51 microscope. The morphology of polymer brushes on the gold surface was observed using scanning electron microscopy (SEM, ZEISS Sigma 300). Molecular weights of polymer brushes were determined by gel permeation chromatography (GPC, Agilent GPC 50). ^{13}C-NMR was obtained from a solid-state nuclear magnetic resonance (Bruker Avance NEO 600 MHz). Monomer consumption was determined by liquid nuclear magnetic resonance (NMR, Bruker 400 MHz). The charge-to-mass ratio of DNA was measured by mass spectrometry.

4. Supplementary Figures

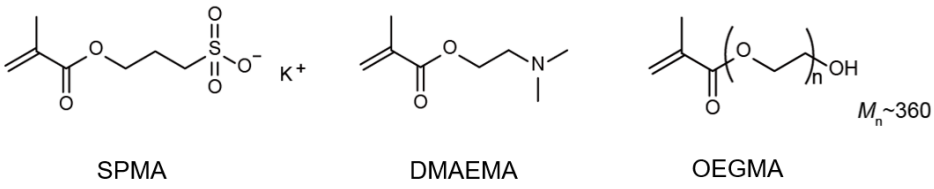

Fig. S1 Chemical structures of monomers.

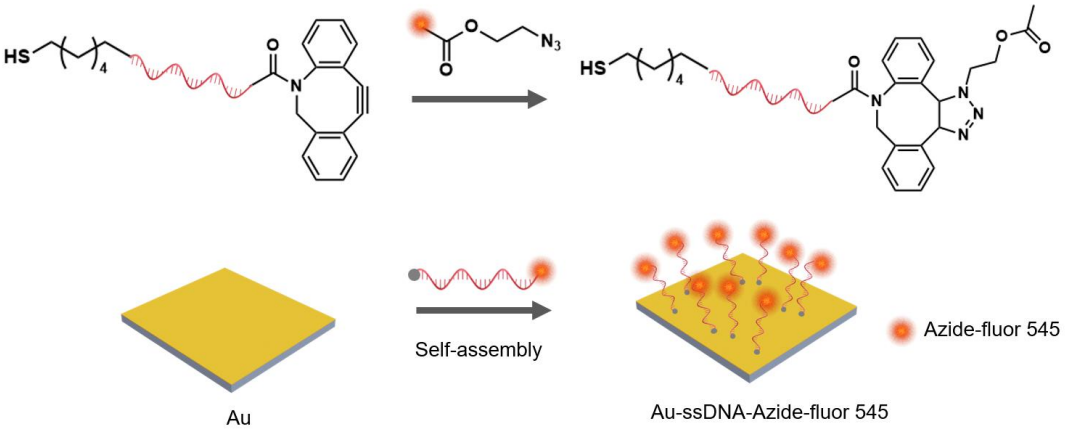

Fig. S2 Schematic diagram of the preparation of azide-fluorine 545-labeled ssDNA and its assembly on a gold substrate.

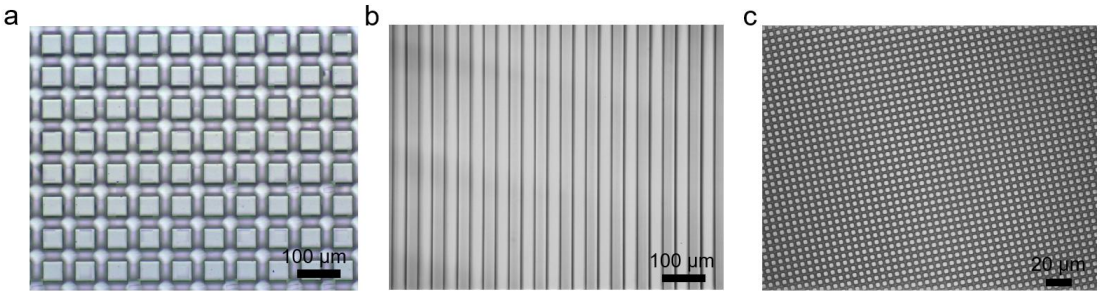

Fig. S3 Optical images of PDMS stamps with different patterns.

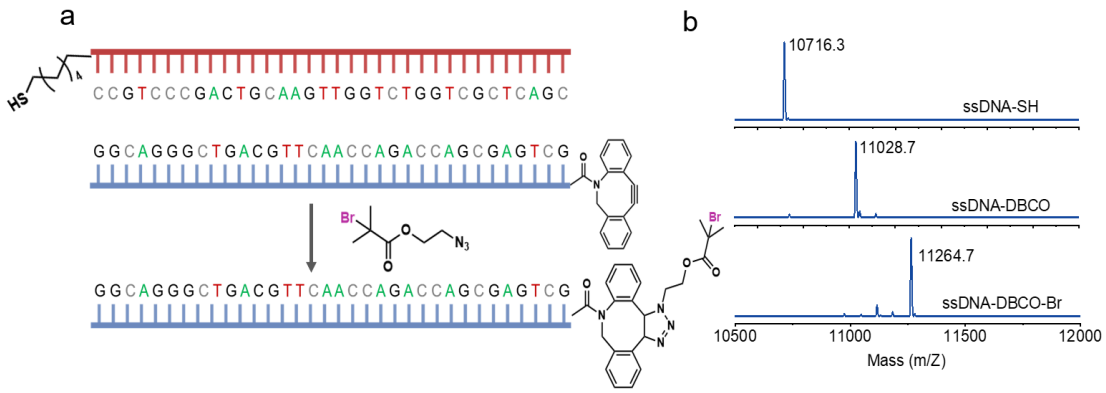

Fig. S4 (a) Preparation and (b) mass spectra of ssDNA-SH, ssDNA-DBCO, and ssDNA-Br.

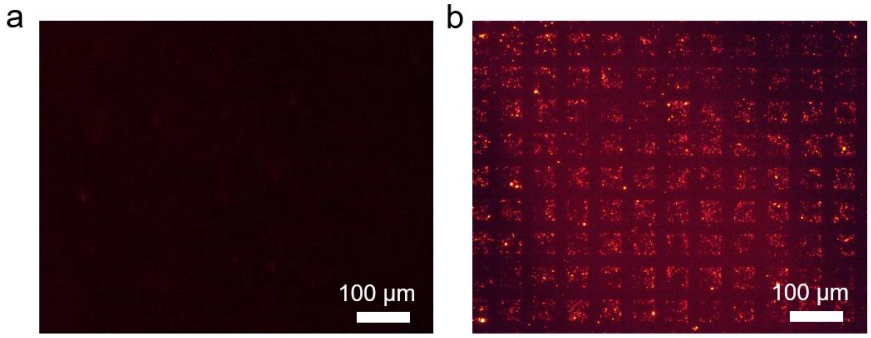

Fig. S5 Fluorescent image of Alexa Fluor 545-labeled SH-ssDNA modified gold substrate, showing red fluorescence (right).

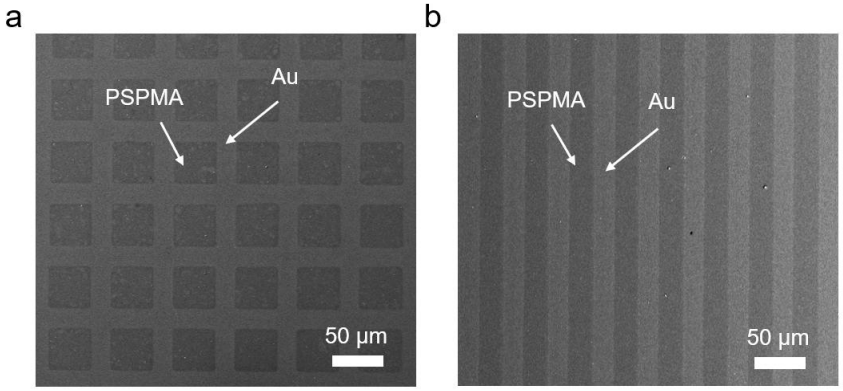

Fig. S6 SEM images of PSPMA with different patterns.

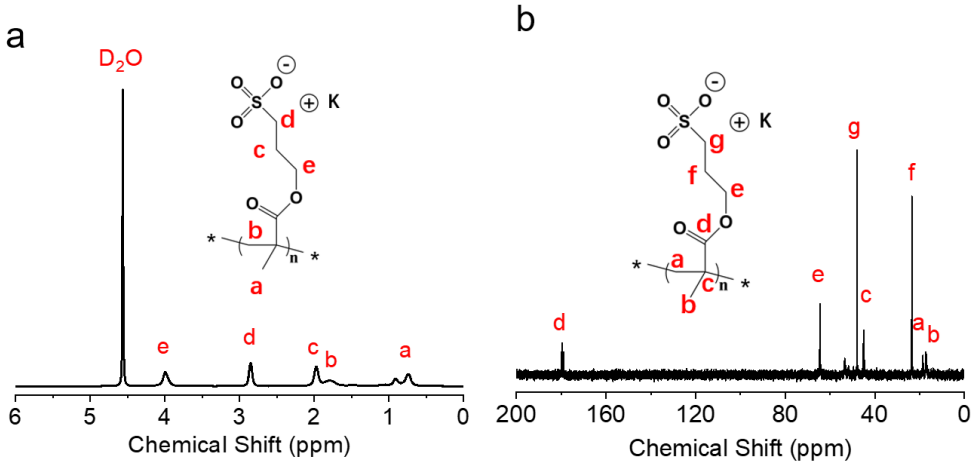

Fig. S7 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of PSPMA.

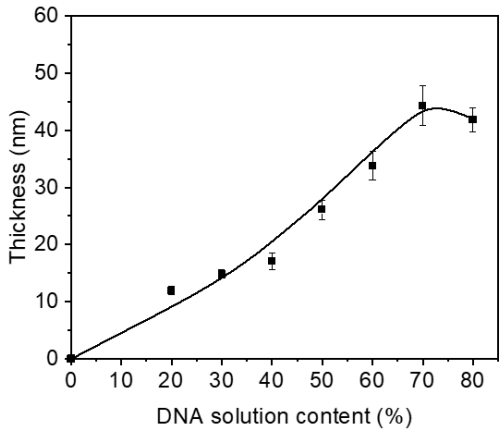

Fig. S8 Variation of PSPMA thickness with DNA solution content.

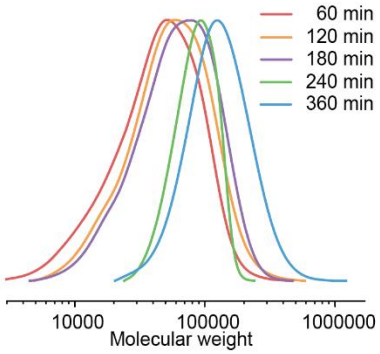

Fig. S9 Molecular weight versus polymerization time, as measured by GPC.

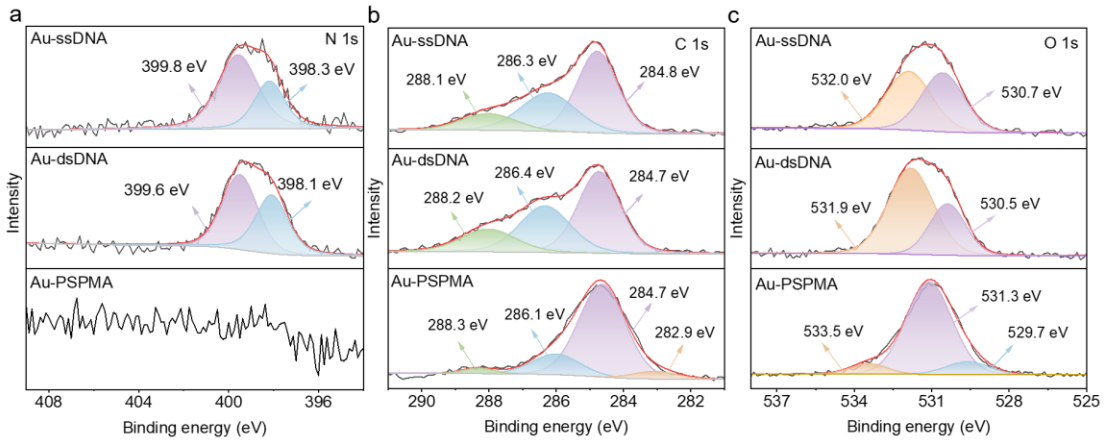

Fig. S10 XPS spectra of the ssDNA modified Au, dsDNA modified Au and PSPMA modified Au: (a) N 1s, (b) C 1s and (c) O 1s.

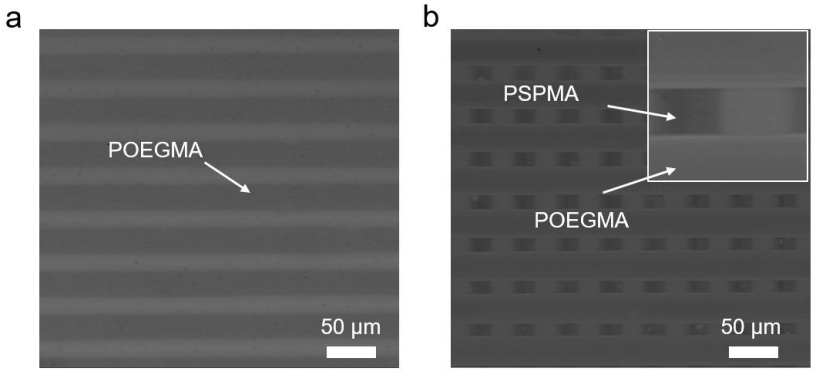

Fig. S11 SEM images of patterned (a) single POEGMA, and (b) binary POEGMA-PSPMA brushes.

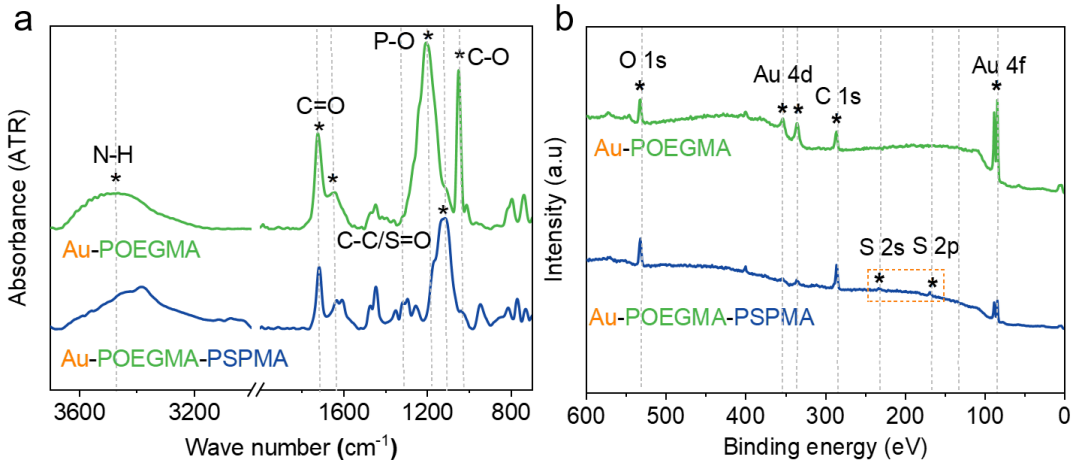

Fig. S12 (a) FTIR and (b) XPS spectra show the successful preparation of binary POEGMA-PSPMA brushes.

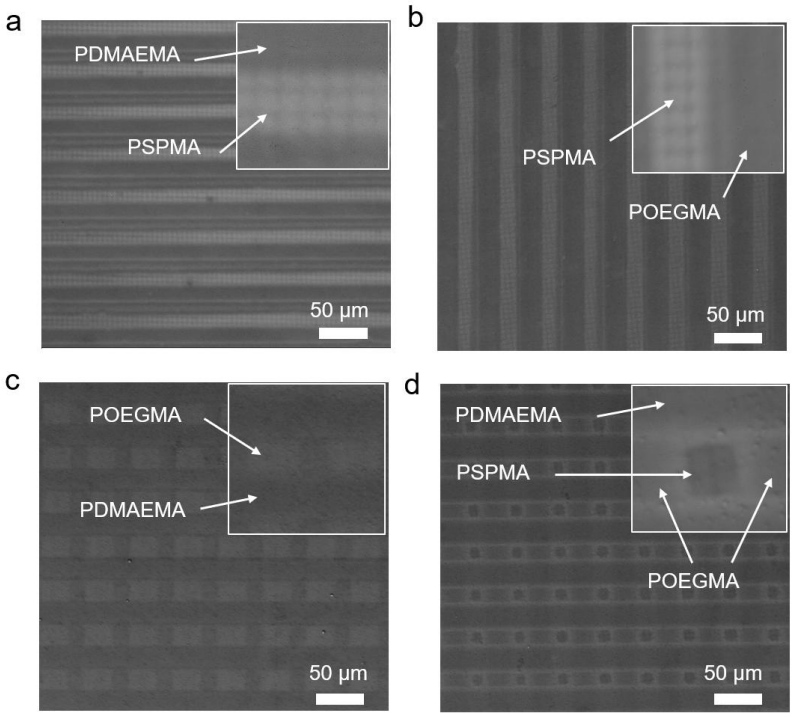

Fig. S13 SEM images of patterned binary brushes: (a) PDMAEMA-PSPMA, (b) POEGMA-PSPMA, (c) PDMAEMA-POEGMA. (d) Tertiary PDMAEMA-POEGMA-PSPMA brushes.