Electronic Supplementary Information (ESI) for

Polyelectrolyte chain conformation matters in macroscopic supramolecular self-assembly

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S1. Materials & instruments

Materials. The following chemicals were used as supplied: PEI (branched, Mw 1800), PAA (Mw 240000, aq, 25 wt%) from Alfa Aesar; PSS (Mw 70000) from Acros Organics; PDDA (Mw 100000~250000, aq, 20 wt%) and (11-Mercaptoundecyl)-N,N,N-trimethylammonium bromide from Sigma-Aldrich; urea (> 99%) from Xilong Chemical Co., Ltd; Ethanol (> 99.97%) from Beijing Chemical works; PDMS pre-polymer of Sylgard 184 silicone elastomer from Dow Corning.

Instruments. Force measurements were performed on a Dynamic Contact Angle Measuring Device and Tensionmeter (DCAT21) from DataPhysics Instruments. The SMFS characterization was measured in deionized water with an atomic force microscope (JPK Nanowizard 4, Bruker, Germany). The assembly behaviors were investigated on a rotating shaker (WS-50D, WIGGENS, Germany). Polymethyl methacrylate (PMMA) molds with arrays of cubic cavity of $3 \times 3 \times 3$ mm3 were obtained through commercially available micro-machining from Shenzhen Sanze Hardware Plastic Products Co., Ltd.

S2. Fabrication and modification of PDMS building blocks
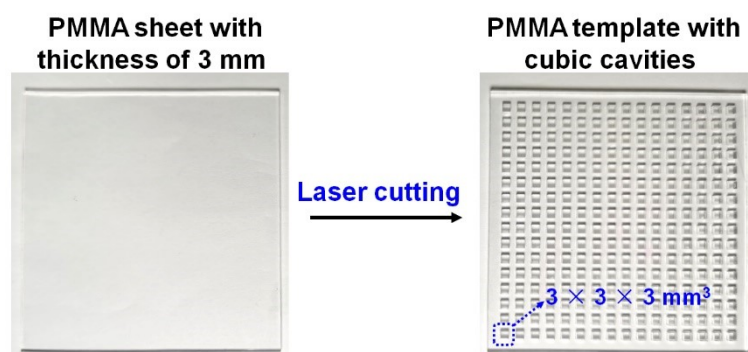
Fig. S1. Fabrication of PMMA template with cubic cavities with size of $3 \times 3 \times 3$ mm^3.

The PDMS building blocks for MSA were prepared with a polymethyl methacrylate template, which is commercially manufactured with arrays of cubic cavities ($3 \times 3 \times 3$ mm^3) by laser cutting (**Fig. S1**). The PDMS pre-polymer and its curing agent were mixed, degassed, and poured into the template, which was sandwiched between two hydrophobic glass substrates. After curing at 65 °C for 6 h and demolding, we obtained cubic PDMS building blocks with a dimension of $3 \times 3 \times 3$ mm^3(**Fig. S2**).
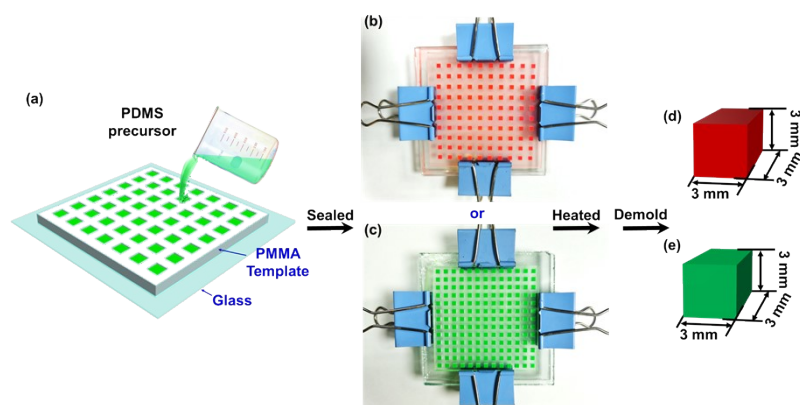
Figure S2. Illustration of the fabrication processes of cubic PDMS cubes. (a) The PDMS precursors were poured into PMMA template, then (b, c) sealed with a sandwich structure between two glass substrates. (d, e) PDMS building blocks were obtained after curing and demolding.

The as-prepared PDMS cubes were modified with composite polyelectrolyte multilayers through a facile layer-by-layer (LbL) method with the following procedure. The PDMS were washed with ethanol and deionized water, followed by plasma treatment for 2 min and immersion in a poly(ethyleneimine) (PEI) (aq, 1 mg/mL) solution overnight to absorb a layer of positively charged polyelectrolyte. Subsequently, the PDMS cubes were immersed in a PAA solution (aq, 1 mg/mL) and PEI (aq, 1 mg/mL) for 1 min each in a cycled manner; between each immersion, they were washed with copious water and immersed in water for another 1 min. Until 15 bilayers of PEI/PAA films were introduced, the PDMS building blocks then alternately dipped in poly-(diallyldimethylammonium chloride) (PDDA) (aq, 1 mg/mL) and poly(sodium-p-styrenesulfonate) (PSS) (aq, 1 mg/mL) for 5 min each for 25 cycles. Thus the PDMS building blocks were modified with $(PEI/PAA)_{15}$-$(PDDA/PSS)_{25}$ as flexible spacing coating. Finally, the PDMS cubes (dyed red) were immersed in PDDA solution (aq, 1 mg/mL) for 5 min to obtain positively charged building blocks (noted as 'PDDA-PDMS'), and the green PDMS cubes were immersed in PAA solution (aq, 1 mg/mL, pH=6.8) or PSS solution (aq, 1 mg/mL) for 5 min to obtain nagetively charged macroscopic building blocks (noted as 'PAA-PDMS' and 'PSS-PDMS', respectively).

S3. MSA behaviors of the PDMS building blocks

For each MSA event, we aligned 50 beakers containing 10 mL water in a 10 ×

5 array and placed one pair of PDMS building blocks into each beaker. The 50 beakers were shaken simultaneously on the same rotating shaker at 160 r/min for 5 min. Before and after shaking, we took photos of all beakers (**Fig. S3**) and cut the contours of assembled structures to be displayed in **Figure 1b**. For PDDA-PDMS and PAA-PDMS, no self-adhesion was observed in the control experiments (**Fig. S3a**), and 50 pairs oppositely charged building blocks assembled into red-green dimers (**Fig. S3b**). And we observed no dimer formed in ethanol (**Fig. S4**) because polyelectrolytes cannot be ionized and thus no surface charges for electrostatic interaction.
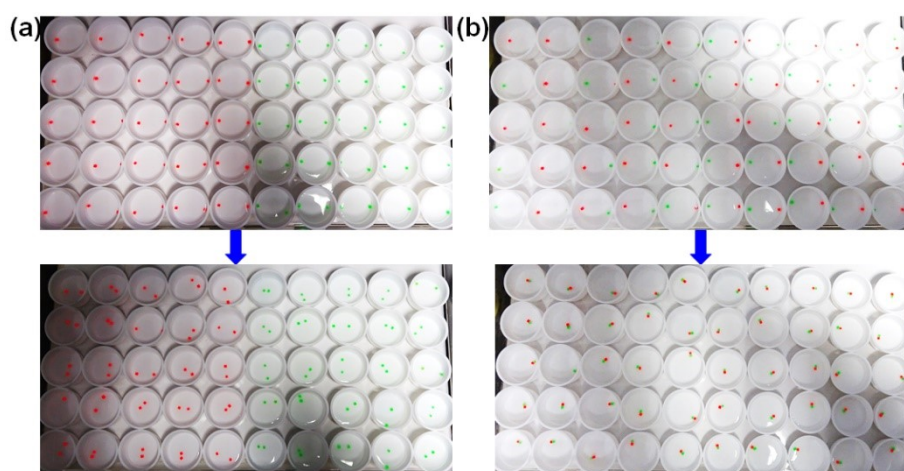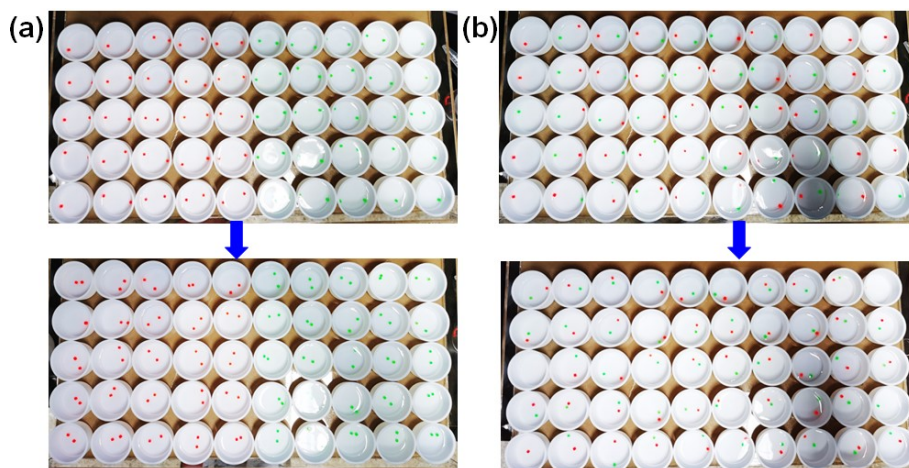

Fig. S3. Optical photos of 50 pairs of (a) PDDA-PDMS vs PDDA-PDMS or PAA-PDMS vs PAA-PDMS and (b) PDDA-PDMS vs PAA-PDMS before and after shaking in water.
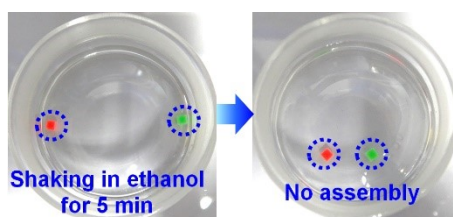
Fig. S4. Optical photos of PDDA-PDMS and PAA-PDMS before and after shaking in ethanol.

For PDDA-PDMS and PSS-PDMS, no self-adhesion was observed in the control experiments (**Fig. S5a**), and no MSA occurred pairs oppositely charged building blocks assembled into red-green dimers (**Fig. S5b**)

Fig. S5. Optical photos of 50 pairs of (a) PDDA-PDMS vs PDDA-PDMS or PSS-PDMS vs PSS-PDMS and (b) PDDA-PDMS vs PSS-PDMS before and after shaking in water.

S4. In situ force measurement

The interactive forces between building blocks were measured by a DCAT apparatus. The cubic PDMS building blocks with size of $3 \times 3 \times 3$ mm^3 were hanging to the above micro-balance through soft thread and the PDMS sheet with size of $10 \times 10 \times 3$ mm^3 were adhered at the bottom of the beaker containing water, thus keeping the contacting area constant to be the area of the cube, i.e. 3 mm × 3 mm. Initially, the cubic PDMS and sheet PDMS were separate and immersed within water both, and the scale value was automatically set to 0 g. Then, the motor was set to move upward to make the cubic PDMS and PDMS sheet get close and contact at a speed of 0.5 mm/s. Once the two building blocks contacted with each, the motor move upwards for another 2 mm to ensure that the building blocks contacted adequately. Afterwards, the motor moved downward back to its original position, resulting in the separation of the two PDMS. A typical mass-position curves was obtained during the above 'contact-separation' process as **Figure S6**. The peak value of indicates the force to break the interfacial interactions for the separation of the two PDMS building blocks. And the interactive force was calculated by normalizing by the interacted area.
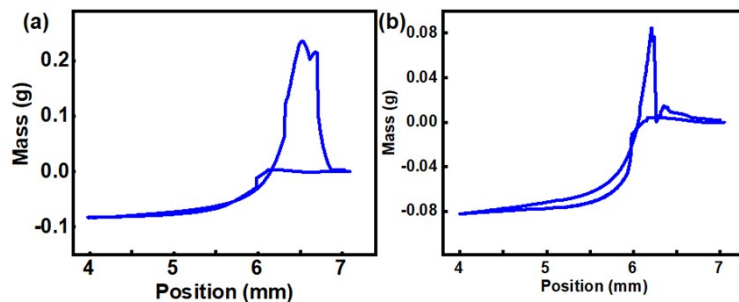
Fig. S6. a typical force curve for (a) PDDA-PDMS vs PAA-PDMS and (b) PDDA-PDMS vs PSS-PDMS.

S5. SMFS characterization of PAA and PSS

The Au substrates were modified with (11-Mercaptoundecyl)-N,N,N-trimethylammonium bromide to obtain quaternary ammonium functionalized surface. Then 100 uL polyanion solution of PAA or PSS (aq, 0.1 mg/mL) was dropped onto the modified Au substrates, which were washed with deionized water after 1 h.

A commercial AFM (JPK Nonwizard 4) was used to perform SMFS experiments. Testing conditions were set as setpoint was 2 nN and Z length was 0.5 um. The bare AFM tip (SiNi, BudgetSensors) moved towards the PAA or PSS modified Au substrate and kept in contact at the force of 2 nN for 0.5 s, then retracted from the substrate at a pulling speed of 5 um/s. After completion of the above approach–detach cycles, the pulling force-extension traces were recorded.
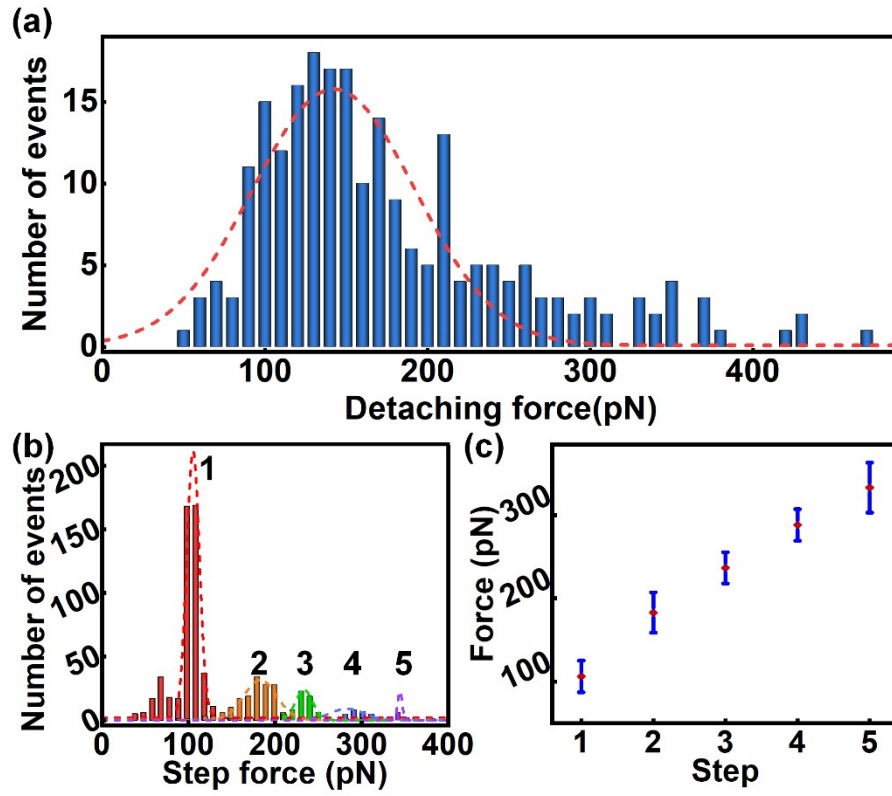
Fig. S7. The histogram of distributions detaching force of (a) PAA and (b) PSS, (c) pulling step dependence of detaching force of PSS.