Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supplementary Information (ESI) for

Macroscopic supramolecular assembly of rigid hydrogels assisted by a flexible spacing coating

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S1. Characterization of mechanical performance of PDMAA/Gel hydrogels

We measured the elastic modulus of PDMAA/Gel hydrogels with varied crosslinker content through a universal tester with a compression mode at room temperature. The obtained results have been summarized in **Fig. S1a**. The elastic modulus values are 0.36 ± 0.04, 0.71 ± 0.08, 1.07 ± 0.06, 1.21 ± 0.05, 1.54 ± 0.05 and 2.46 ± 0.2 MPa, corresponding to the crosslinker contents of 1.52 wt%, 3.04 wt%, 3.80 wt%, 4.56 wt%, 6.08 wt% and 9.12 wt%, respectively, which presents a positive correlation between modulus and crosslinker content.

We have further increased the crosslinker content of MBA to 15.2% and 21.3%, which led to increased elastic moduli of 4.51 and 7.06 MPa, respectively.

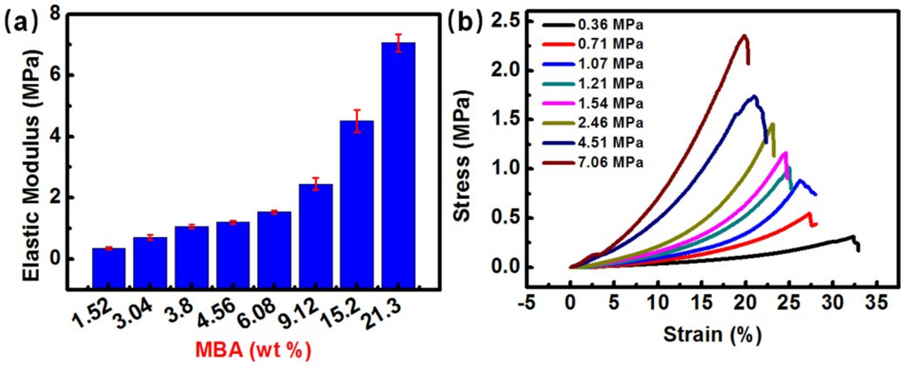


Fig. S1. (a) Elastic modulus of the PDMAA/Gel hydrogels versus the crosslinker (MBA) content. (b) Stress-strain curves (compression mode) of PDMAA/Gel hydrogels with varied elastic modulus of 0.36, 0.71, 1.07, 1.21, 1.54, 2.46, 4.51 and 7.06 MPa (curves from bottom-up).

The mechanical stability of the PDMAA/Gel of varied modulus is evaluated by the stress-strain curve under a compression mode (**Fig. S1b**). With the growing modulus of the hydrogels from 0.36 MPa to 7.06 MPa, the breaking strain reduces from 32% to 20% while the breaking stress increases from 0.3 MPa to 2.3 MPa, indicating that the hydrogel elasticity declines while the rigidity improves. As for the stability of the PDMAA/Gel assemblies after MSA experiments, we did not observe any disassembly or fracture phenomena.

S2. UV-visible spectra of (PDDA/PAA-Azo)$_{10}$ multilayer on PDMAA/Gel hydrogels

We applied UV-visible spectra for stepwise characterization of the film formation process of (PDDA/PAA-Azo)$_n$ multilayer because the azobenzene group has a strong absorption on its UV-visible spectrum. The results have been summarized in **Fig. S2**. We can observe that with the increasing deposition cycle number, i.e., number of bilayers, the absorbance of PAA-Azo at 345 nm grow linearly, indicating a good control over the content of PAA-Azo through the layer-by-layer (LbL) assembled technique. The PDMAA/Gel hydrogel after LbL assembled with a (PDDA/PAA-Azo)$_{10}$ multilayer turned from a transparent appearance to a yellowish color as shown in the insets of **Fig. S2a**, which is caused by the color of PAA-Azo. Moreover, we compared the absorbance of (PDDA/PAA-Azo)$_{10}$ multilayers modified on PDMAA/Gel hydrogels with varied modulus from 0.36 MPa to 2.46 MPa in **Fig. S2b**, and found all absorbance values kept at a similar level, indicating that the PAA-Azo content within each multilayer should be similar after LbL modification regardless of varied hydrogel modulus.

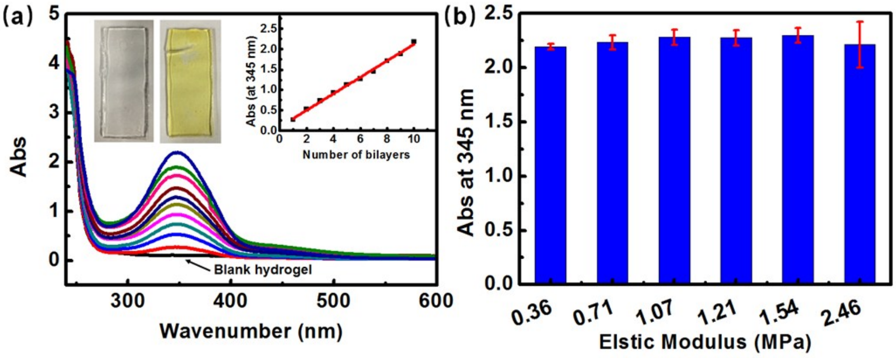


Fig. S2. (a) UV-visible spectra of the PDDA/PAA-Azo multilayer on PDMAA/Gel hydrogel (0.36 MPa) after each alternate immersion in PDDA and PAA-Azo (one bilayer). The inset optical photographs are the PDMAA/Gel hydrogels before (transparent) and after (yellow) modified with a (PDDA/PAA-Azo)$_{10}$ multilayer; the inset diagram is the absorbance at 345 nm versus number of bilayers. (b) Absorbance at 345 nm of hydrogels with (PDDA/PAA-Azo)$_{10}$ multilayers versus hydrogel modulus.

S3. MSA behavior of PDMAA/Gel hydrogels with varied elastic modulus

PDMAA/Gel hydrogels dyed blue were modified with a (PDDA/PAA-CD)$_{10}$ multilayer and those dyed red were modified with a (PDDA/PAA-Azo)$_{10}$ multilayer through an LbL assembled technique. 100 identical pairs of CD versus Azo hydrogels were separately placed in a 10 × 10 square array (**Fig. S3a**). All of these beakers were shaken together on a rotator shaker at a set speed of 160 rpm for 5 min. When using hydrogels of different modulus, we conducted the MSA experiments with the same above procedure. MSA results of hydrogels with different moduli were summarized in **Fig. S3**.

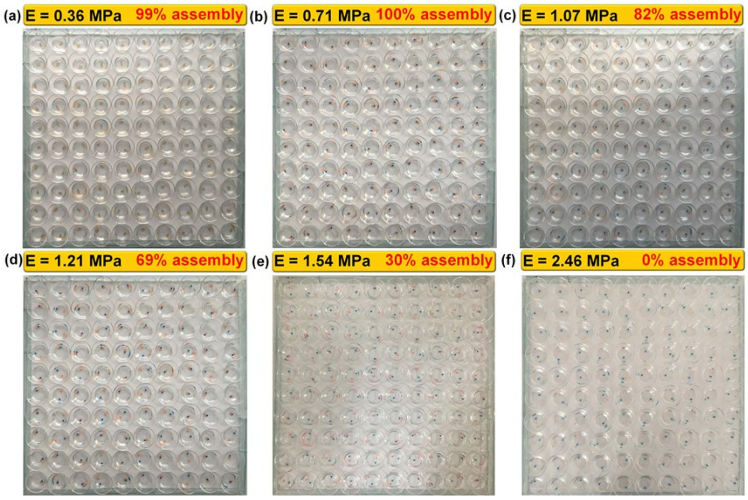
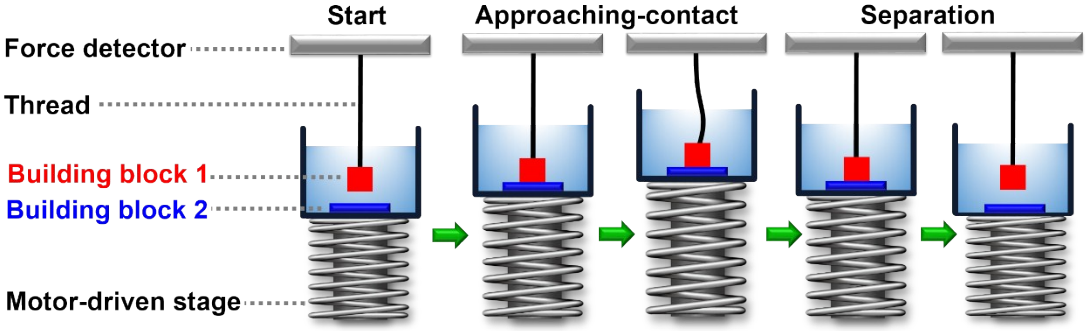


Fig. S3. Photographs of 100 pairs of interactive PDMAA/Gel hydrogels separately put in beakers aligned in a 10 × 10 square array for hydrogel moduli of (a) 0.36 MPa, (b) 0.71 MPa, (c) 1.07 MPa, (d) 1.21 MPa, (e) 1.54 MPa and (f) 2.46 MPa after shaking in water for 5 min.

S4. In situ force measurement



Scheme S1. Schematic illustration of the *in situ* measurement process of interactive forces between hydrogel building blocks.

The interactive forces versus different surface chemistry have been summarized in **Fig. S4**. The CD/Azo combination exhibited a force value as high as 393.3 ± 34.8 N/m^2, which is remarkably larger than those in control experiments, including Azo/Azo (10.1 ± 8 N/m^2), CD/CD (24.5 ± 2.1 N/m^2), Blank-Blank (2.6 ± 1.1 N/m^2) and CD/Azo in an Ad-NH$_2$ solution (19.1 ± 3.5 N/m^2). For the force tests with Ad-NH$_2$, we used an Ad-NH$_2$ solution (aq, 0.05 mM) as replacement of water before CD and Azo hydrogels contact.

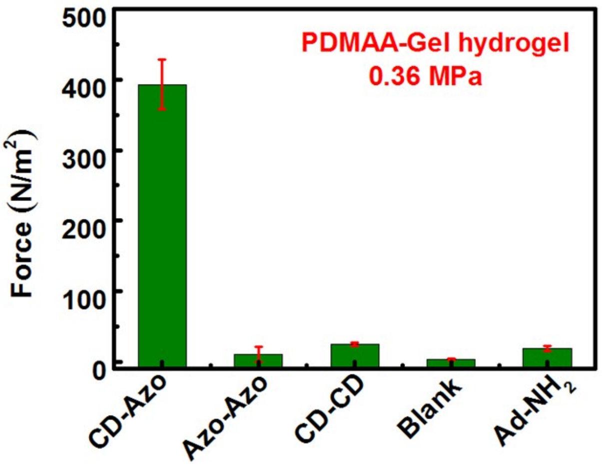


Fig. S4. Normalized interactive forces between PDMAA/Gel hydrogels (0.36 MPa) modified with (PDDA/PAA-CD)$_{10}$ and (PDDA/PAA-Azo) multilayers, which is marked as 'CD-Azo'. Similarly, 'Azo-Azo' and 'CD-CD' represent interactions between identical hydrogels. 'Blank' means interactions between two blank PDMAA/Gel hydrogels. 'Ad-NH$_2$' indicates the condition of 'CD-Azo' after adding an Ad solution (aq, 0.05 mM)

Control MSA experiments were conducted in **Fig. S5**: assembly of CD-Azo hydrogels together with their disassembly in Ad solution, assembly of CD-CD hydrogels and Azo-Azo hydrogels.

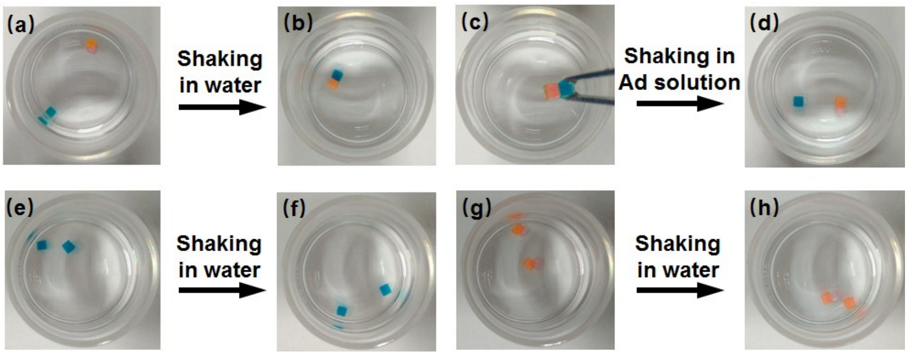


Fig. S5. Photographs of the PDMAA/Gel hydrogels (0.36 MPa) modified with (PDDA/PAA-CD)$_{10}$ (dyed blue) and (PDDA/PAA-Azo)$_{10}$ (dyed red) (a, e, g) before and (b, f, h) after shaking in water for 5 min. (c) The CD-Azo hydrogels assembled to a dimer in water but (d) disassembled in an Ad-NH$_2$ solution (0.05 mM).

To clarify contributions from other possible forces such as electrostatic interaction, hydrogen bonding etc. in MSA, we have conducted control experiments of *in situ* force measurements of interactive hydrogels pairs modified with multilayers of (1) (PDDA/PAA-CD)$_{10}$ versus (PDDA/PAA)$_{10}$, (2)

$(PDDA/PAA\text{-}Azo)_{10}$ versus $(PDDA/PAA)_{10}$, and (3) $(PDDA/PAA)_{10}$ versus $(PDDA/PAA)_{10}$, together with (4) forces between blank hydrogels. As control experiments of $(PDDA/PAA\text{-}CD)_{10}$ versus $(PDDA/PAA\text{-}Azo)_{10}$, the combinations of (1) to (3) are designed to clarify the contributions of electrostatic interaction or hydrogen bonding without molecular recognition; the interaction between blank hydrogels provides a reference without any surface modification.

The results of the above force measurements between hydrogels of all moduli have been summarized in **Fig. S6** and the interactive force of $(PDDA/PAA\text{-}CD)_{10}$ versus $(PDDA/PAA\text{-}Azo)_{10}$ is displayed as comparison. We can observe that the interactive force when the molecular recognition of CD/Azo is present exhibits remarkably higher values than those control groups. With the increasing modulus values of hydrogels, this force difference drops to a level of almost comparable with control groups. Meanwhile, the interactive forces of the control groups are almost at a similar level when the surface chemistry has been changed after removing the CD/Azo interaction. Taken together, we could attribute the strong binding force between the hydrogels in our experiments mainly to molecular recognition between the surface CD and Azo groups rather than other interactions, which contributed to some degree with a minor share.

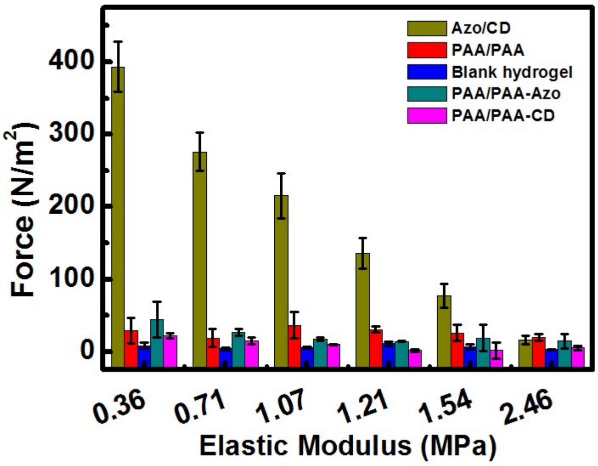


Fig. S6. In situ interactive force versus modulus when the interacted hydrogels were modified with $(PDDA/PAA\text{-}CD)_{10}$ versus $(PDDA/PAA\text{-}Azo)_{10}$ multilayers (noted as Azo/CD), $(PDDA/PAA)_{10}$ versus $(PDDA/PAA)_{10}$ multilayers (PAA/PAA), blank versus blank (Blank hydrogel), $(PDDA/PAA)_{10}$ versus $(PDDA/PAA\text{-}Azo)_{10}$ multilayers (PAA/PAA-Azo), and $(PDDA/PAA)_{10}$ versus $(PDDA/PAA\text{-}CD)_{10}$ multilayers (PAA/PAA-CD).

S5. MSA of high-modulus PDMAA/Gel hydrogels

The PDMAA/Gel hydrogel building blocks with modulus value of 2.46 MPa were modified with a composite polyelectrolyte multilayer through an LbL method with the following procedure. The PDMAA/Gel hydrogel building blocks were immersed in a PEI (aq, 1 mg/mL) solution for 2 h. Subsequently, the PDMAA/Gel hydrogels were alternately immersed in PAA (aq, 1 mg/mL) and PEI (aq, 1 mg/mL) solutions for 1 min each; after necessary cycles of PEI/PAA was completed, the hydrogels were alternately immersed in PDDA (aq, 1 mg/mL) and PSS (aq, 1 mg/mL) for 5 min each. Finally, the PDMAA/Gel hydrogel building blocks dyed red were modified with a composite multilayer of $(PEI/PAA)_{20}$-$(PDDA/PSS)_{10}$-$(PDDA/PAA\text{-}Azo)_{10}$ while those dyed blue with a $(PEI/PAA)_{20}$-$(PDDA/PSS)_{10}$-$(PDDA/PAA\text{-}CD)_{10}$ multilayer.

We compared the interactive forces between CD/Azo building blocks with and without the flexible spacing coating in **Fig. S7**. The interactive force value of the PDMAA/Gel hydrogels with the $(PEI/PAA)_{20}$-$(PDDA/PSS)_{10}$ multilayer reaches 408.8 ± 61.1 N/m^2, which is almost 20 times larger than that without this coating (19.1 ± 3.5 N/m^2).

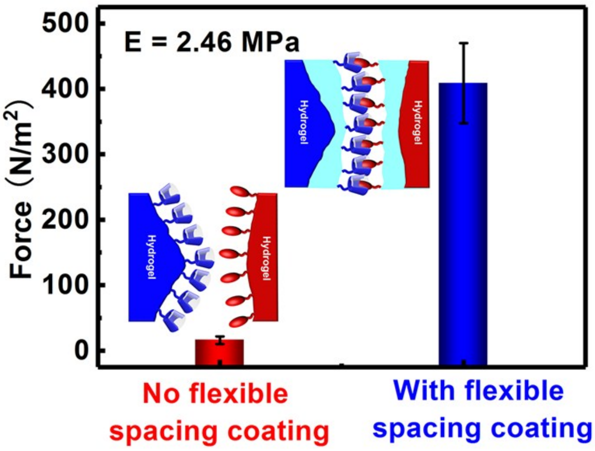


Fig. S7. *In-situ* interactive forces CD-Azo hydrogels (2.46 MPa) with (red bar) and without (blue bar) the flexible spacing coating.