Electronic Supplementary Material (ESI) for Materials Horizons.

Support Information

Small-scale soft grippers with environmentally responsive logic gates

*Xuan Zhang**, *Ya Wu, Yan Li, He Jiang, Qinglin Yang, Zichao Wang, Jiahao Liu, Yang Wang, Xiaodong Fan and Jie Kong**

MOE Key Laboratory of Materials Physics and Chemistry in Extraordinary Conditions, Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an, 710072, P. R. China.

*Corresponding Author, E-mail: zhangxuan@nwpu.edu.cn (X.Z.); kongjie@nwpu.edu.cn (J.K.)

1. Materials

2-hydroxyethyl methacrylate (HEMA, 96%), acrylamide (AAm, 99%), Acrylic acid (AAc, 99%), 2-acrylamido-2-methylpropanesulfonic acid (AMPS, 99%), Ethylene glycol dimethacrylate (EGDMA, 98%), *N, N*'-methylenebis (acrylamide) (BIS, 99%), *N*-isopropylacrylamide (NIPAm, 97%), 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, 99%), Phenylbis(2,4,6-trimethylbenzoyl) phosphineoxide (BAPO, 97%), 2,2′-Azobis (2-methylpropionamidine) Dihydrochloride (V50, 97%), Methanol, sodium chloride (NaCl) were purchased from Sigma-Aldrich. Iron (II, III) oxide particles (Fe_3O_4, 20 nm diameter) was purchased from Innochem. Silicon elastomer (Ecoflex 00-30) was purchased from Smooth-On. Silicon rubber (PDMS) prepolymer was purchased from Jinan Xingchi Chemical Co., LTD.

2. Fabrication of the grippers performing YES gate and NOT gate

Fabricating the YES gate. The ultraviolet (UV)-curable precursor solution for the temperature-responsive hydrogel (PNIPAm-1) layer was composed of NIPAm 120 mg, BIS 2.2 mg, BAPO 1.5 mg, DI water 150 μl, Methanol 210 μl and AAm 20 mg. The precursor solution for the pH responsive hydrogel (PAAc-1) layer was composed of AAc 0.41 g, HEMA 2.93 g, EGDMA 0.1 g and DMPA 0.1 g. The precursor solution for passive hydrogel (PHEMA) layer was composed of HEMA 3.2 g, EGDMA 0.07 g, DMPA 0.1 g and DI water 1.43 g. For varying the thickness of responsive layer and passive layer, appropriate ecoflex mold and spacer were selected. The mixture of the responsive layer was first introduced onto the ecoflex mold with pre-designed four-arm shaped wells (depth: 50μm). This mixture was polymerized under UV irradiation for 50s (at a wavelength of 365 nm and an intensity of 60 mW/cm^2). Next, for the UV polymerization of the passive layer, a four-arm shaped silicon rubber spacer (thickness: 25 μm) was attached to the ecoflex mold with pre-designed four-arm shaped wells. Subsequently, the mixture consisting of the passive part was added to the micromold and polymerized under UV irradiation for additional 1 min. The hydrogel bilayers were harvested from the micromold and washed with DI water. After the gripper was left in DI water overnight to dissolve and remove the un-polymerized monomer and initiator,

we obtained the final gripper with the PAAc and PHEMA bilayer (length of the gripper: 1.25mm, width of each arms: 0.25mm), and another final gripper with the PNIPAm and PHEMA bilayer (length of the gripper: 1.25mm, width of each arms: 0.25mm), as shown in Fig.1C.

The hydrogel bilayers fabricated in YES gate were composed of responsive and passive layers with similar equilibrium ratios (i.e., the responsive hydrogel layer contracted (input 0) and passive layer was at equilibrium), leading to the unbended arms (output 0). When the responsive layer expanded (input 1) in response to temperature or pH, whereas the passive layer, PHEMA, retained its equilibrium dimension, leading to bended arms (output 1).

Fabricating the NOT gate. The hydrogel bilayer grippers with NOT gate were prepared using the same technique as used in the YES gate. The precursor solution for the temperature-responsive hydrogel (PNIPAm-2) layer was composed of NIPAm 373 mg, BIS 5.4 mg, DI water 1.43 g, V50 7.8 mg. The precursor solution for the pH-responsive hydrogel (PAAc-1) layer was composed of AAc 0.41 g, HEMA 2.93 g, EGDMA 0.1 g and DMPA 0.1 g. The precursor solution for passive hydrogel PAAm layer was composed of AAm 0.9 g, BIS 7 mg, V50 20 mg and DI water 3 g. The detail procedure for preparing bilayer grippers with NOT gate was similar to that for fabricating grippers with YES gate. We obtained the final gripper with the PAAc (thickness 25μm) and PAAm (thickness 50μm) bilayer (length of the gripper: 1.25mm, width of each arms: 0.25mm) and another final gripper with the PNIPAm (thickness 75μm) and AAm (thickness 50 μm) bilayer (length of the gripper: 1.25mm, width of each arms: 0.25mm), as shown in Fig.1D.

The hydrogel bilayers fabricated in NOT gate were composed of responsive and passive layers with similar swelling ratios (i.e., the responsive hydrogel layer expanded (input 1) and passive layer was at equilibrium), leading to the unbended arms (output 0). When the responsive layer contracted (input 0) in response to temperature or pH, whereas the passive layer, PAAm, retained its equilibrium dimension, leading to bended arms (output 1).

3. Fabrication of grippers performing different logic operations

Fabricating the XOR gate. The hydrogel bilayer grippers performing XOR gate were prepared using the micromolding technique by designing two responsive layers. The precursor solution for the temperature-responsive hydrogel (PNIPAm-3) layer was composed of NIPAm 120 mg, BIS 2.2 mg, BAPO 1.5 mg, water 150 μl and Methanol 210 μl. The precursor solution for the pH-responsive hydrogel (PAAc-2) layer was composed of HEMA 3.2 g, AAc 0.215 g, EGDMA 0.14 g, DMPA 0.1 g and DI water 1.43 g. The mixture of the pH-responsive layer was first introduced onto the ecoflex mold with pre-designed four-arm shaped wells (depth: 200 μm). This mixture was polymerized under UV irradiation for 50s. Next, for the UV polymerization of the temperature-responsive layer, a four-arm shaped silicon rubber spacer (thickness: 300 μm) was attached to the ecoflex mold. Subsequently, the mixture consisting of the temperature-responsive part was added to the micromold and polymerized under UV irradiation for additional 1 min. After the gripper was left in DI water overnight to dissolve and remove the un-polymerized monomer and initiator, we obtained the final gripper with the PNIPAm and PAAc bilayer (thickness 500 μm, length of the gripper: 6 mm, width of each arms: 1 mm).

Fabricating the AND gate. The gripper with AND gate was prepared using the same hydrogels and similar micromolding technique as used in the YES gate (Fig.S1). The mixture of the temperature-responsive layer was first introduced onto the two arm shaped wells of ecoflex mold with pre-designed four-arm shaped wells (depth: 200 μm). The other two arms shaped wells of ecoflex mold were blocked by two pieces of PDMS blocks. This mixture was polymerized under UV irradiation for 50s (at a wavelength of 365 nm and an intensity of 60 mW/cm^2). Next, two pieces of PDMS blocks were taken out from the wells, and the mixture of the pH-responsive layer was introduced onto the other two arm shaped wells of ecoflex mold (depth: 200 μm). This mixture was polymerized under UV irradiation for 50s. For the UV polymerization of the passive layer, a four-arm shaped silicon rubber spacer (thickness: 100μm) was attached to the ecoflex mold. Subsequently, the mixture consisting of the passive part was added to the micromold and polymerized under UV irradiation for additional 1 min. After the gripper was left in DI water overnight to dissolve and remove the un-polymerized

monomer and initiator, we obtained the final gripper (thickness 300 μm). One pair of arms of the gripper was PAAc and PHEMA bilayer, and another pair of arms was PNIPAm and PHEMA bilayer.

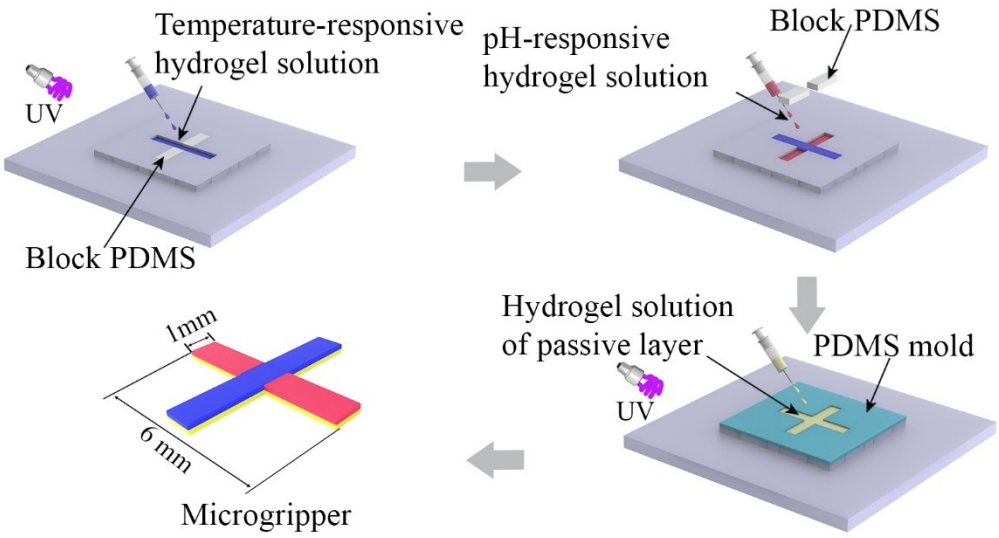


Fig.S1 The preparation of gripper with AND gate

Fabricating the OR gate. The hydrogel bilayer grippers with OR gate were prepared using the same hydrogels and similar micromolding technique as used in the AND gate (Fig.S2). The mixture of the temperature-responsive layer was first introduced onto the three arm shaped wells of ecoflex mold with pre-designed six-arm shaped wells (depth: 200 μm). The other three arms shaped wells of ecoflex mold were blocked by three pieces of PDMS blocks. This mixture was polymerized under UV irradiation for 50s (at a wavelength of 365 nm and an intensity of 60 mW/cm^2). Next, three pieces of PDMS blocks were taken out from the wells, and the mixture of the pH-responsive layer was introduced onto the other three arms shaped wells of ecoflex mold (depth: 200 μm). This mixture was polymerized under UV irradiation for 50s. For the UV polymerization of the passive layer, a six-arm shaped silicon rubber spacer (thickness: 100 μm) was attached to the ecoflex mold. Subsequently, the mixture consisting of the passive part was added to the micromold and polymerized under UV irradiation for additional 1 min. After the gripper was left in DI water overnight to dissolve and remove the un-polymerized monomer and initiator, we obtained the final

gripper (thickness 300 μm). Three arms of the gripper were PAAc and PHEMA bilayer, and the other three arms were PNIPAm and PHEMA bilayer.

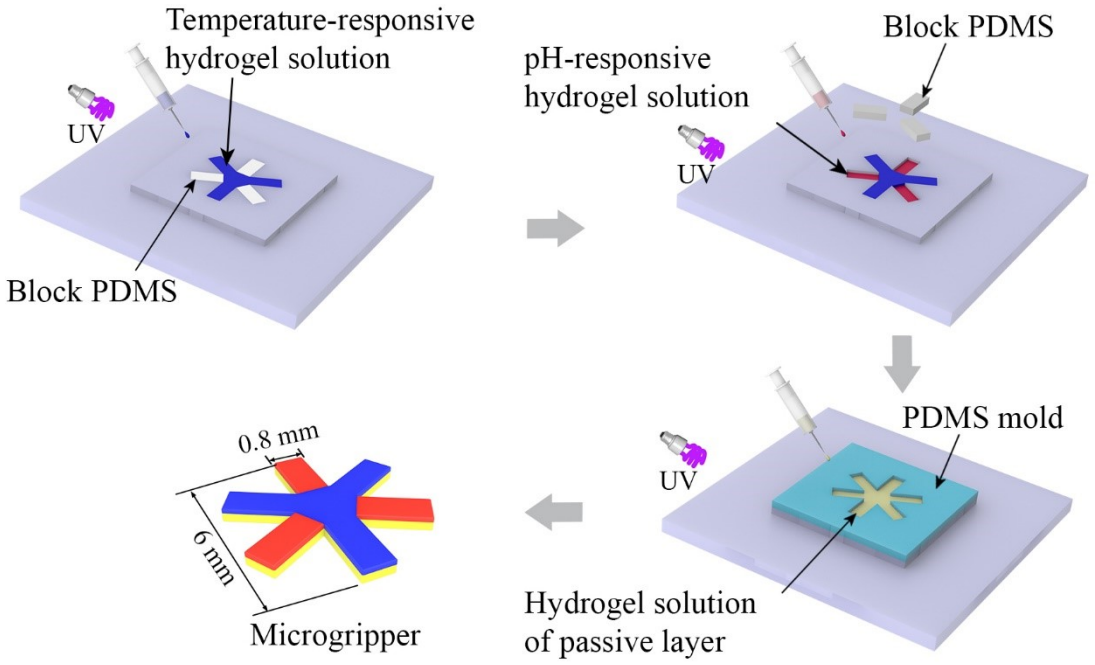


Fig.S2 The preparation of gripper with OR gate

Fabricating the NOR gate. The gripper with NOR gate was prepared using the same hydrogels and similar micromolding technique as used in the NOT gate. The mixture of the temperature-responsive layer was first introduced onto the two arm shaped wells of ecoflex mold with pre-designed four-arm shaped wells (depth: 300 μm). The other two arms shaped wells of ecoflex mold were blocked by two pieces of PDMS blocks. This mixture was polymerized under UV irradiation for 50s (at a wavelength of 365 nm and an intensity of 60 mW/cm^2). Next, two pieces of PDMS blocks were taken out from the wells, and the mixture of the pH-responsive layer was introduced onto the other two arm shaped wells of ecoflex mold (depth: 100 μm). This mixture was polymerized under UV irradiation for 50s. For the UV polymerization of the passive layer, a four-arm shaped silicon rubber spacer (thickness: 200μm) was attached to the ecoflex mold. Subsequently, the mixture consisting of the passive part was added to the micromold and polymerized under UV irradiation for additional 1 min. After the gripper was left in DI water overnight to dissolve and remove the unpolymerized

monomer and initiator, we obtained the final gripper (length of the gripper: 6 mm, width of each arms: 1 mm).

Fabricating the NAND gate. The gripper with NAND gate was prepared using the same hydrogels and similar micromolding technique as used in the NOT gate (length of the gripper: 6 mm, width of each arms: 0.8 mm). We obtained the final gripper with the PAAc (thickness 100μm) and PAAm (thickness 200μm) bilayer for three arms and the PNIPAm (thickness 300μm) and PAAm (thickness 200μm) bilayer for the other three arms.

4. Kinetics of gripper performing logic gates

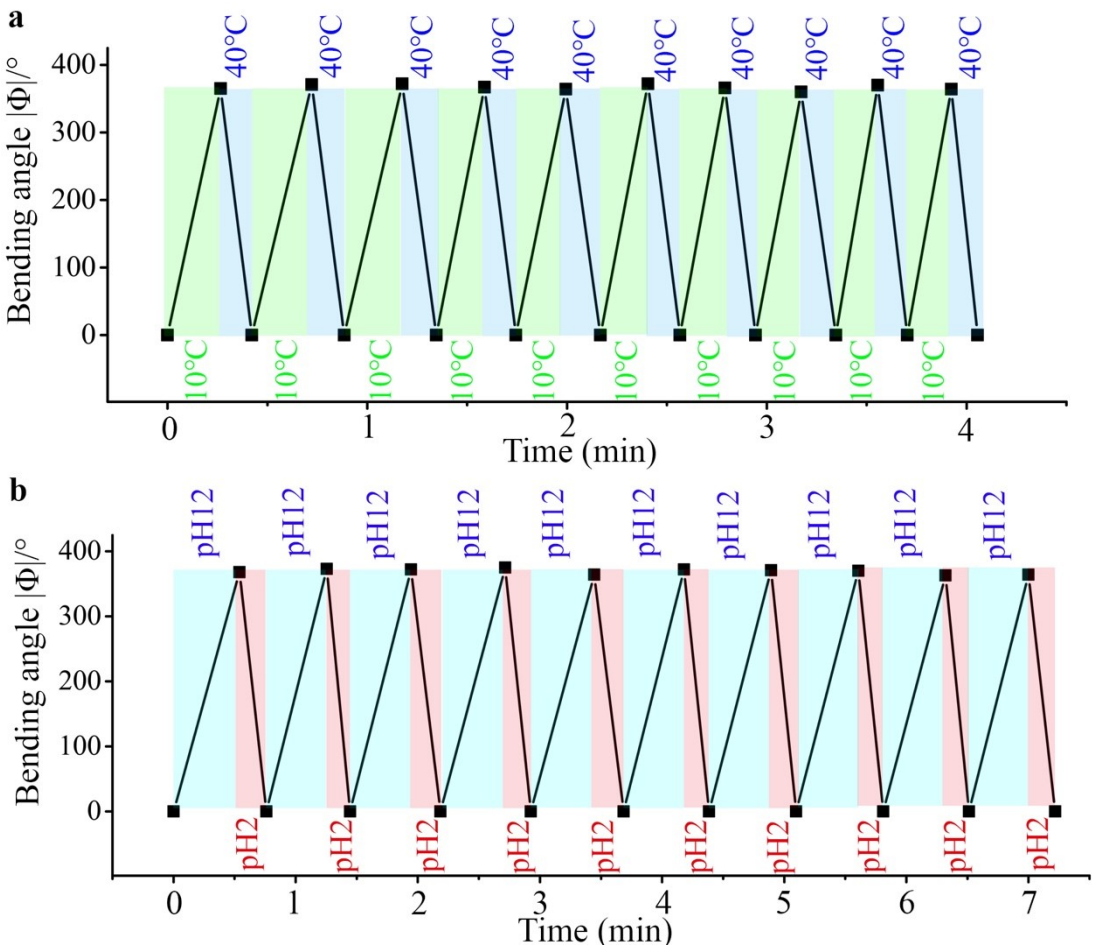


Fig.S3 Reversibility of grippers with YES gate. a) Grippers with YES gate actuated by temperature; b) grippers with YES gate actuated by pH.

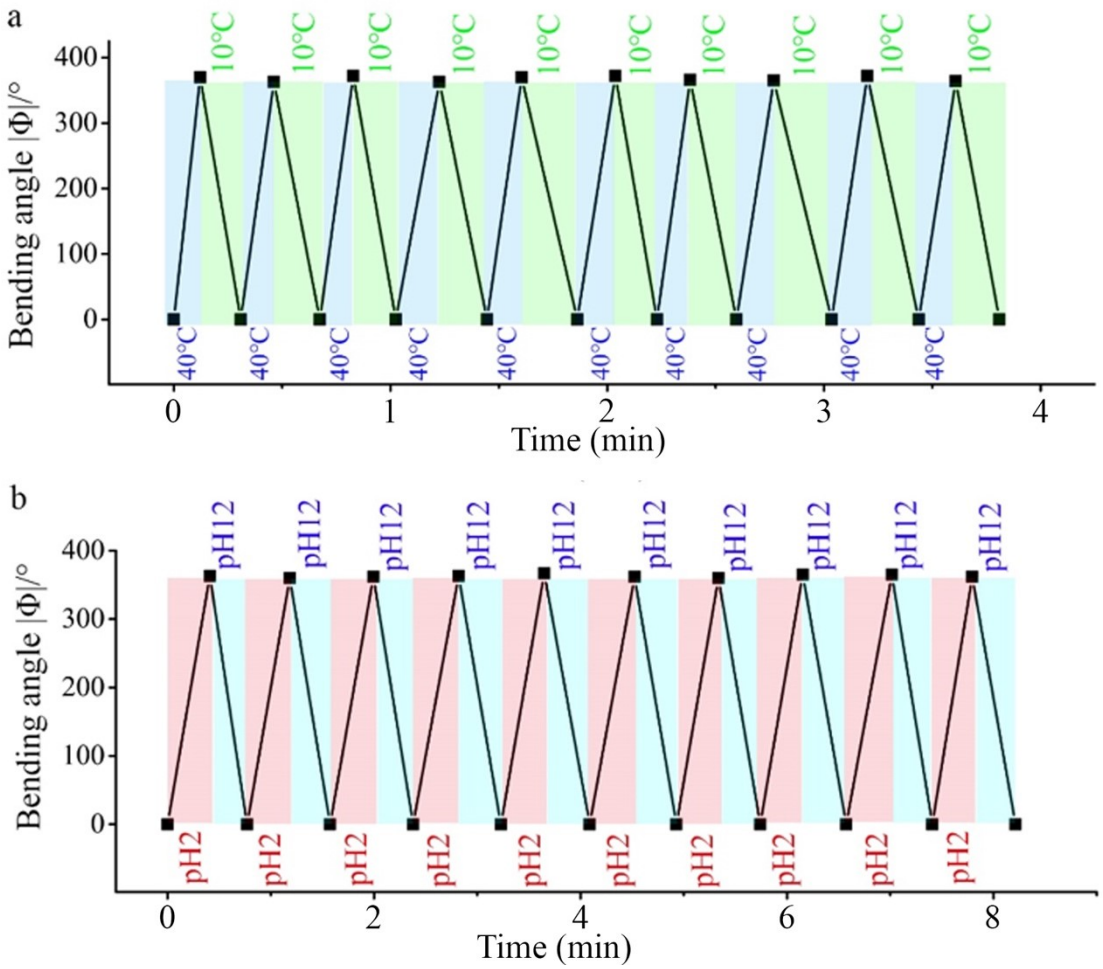


Fig.S4 Reversibility of grippers with NOT gate. a) Grippers with NOT gate actuated by temperature; b) grippers with NOT gate actuated by pH.

The y-axis of "Bending angle |Φ|" represents the sum of absolute values of bending angles for all the arms of the gripper.

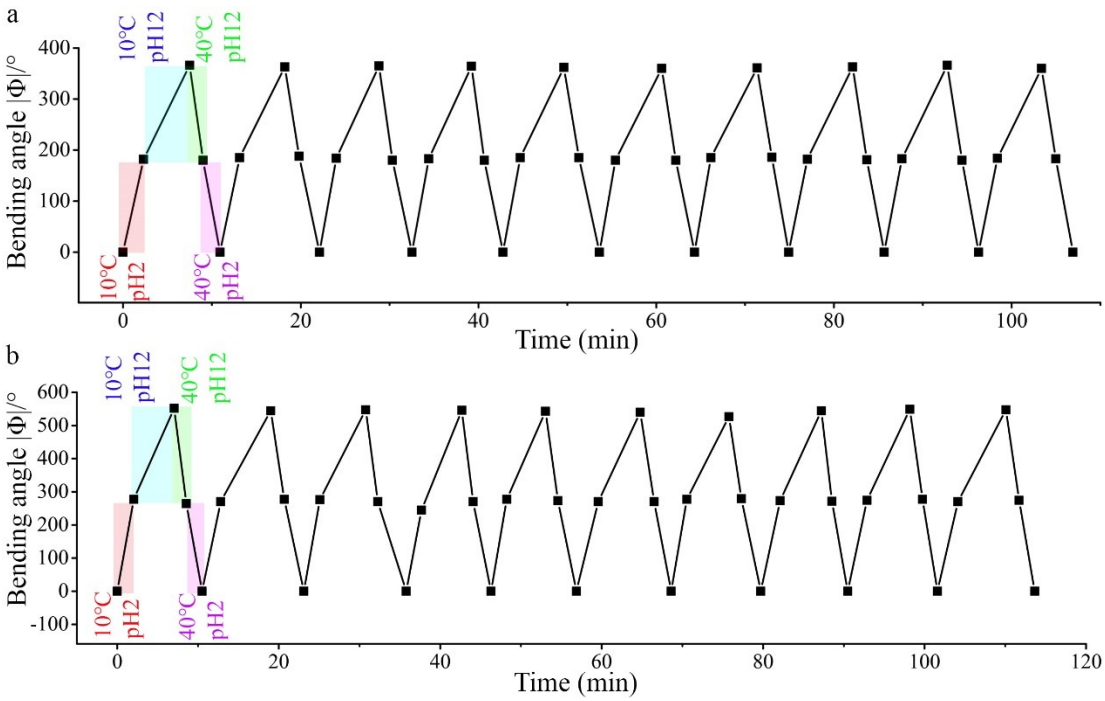


Fig.S5 Reversibility of grippers with AND (a) and OR (b) gate

5. Fabricating the AND-AND connected gate.

The gripper with AND-AND connected gate was prepared using the same hydrogels and similar micromolding technique as used in the AND gate (Fig.S6). The salt-responsive hydrogel included 2-acrylamido-2-methylpropanesulfonic acid (AMPS, 0.174 g), sodium hydroxide (0.03 g), deionized water (0.615 g), 2-hydroxyethyl methacrylate (2.51 g), ethylene glycol dimethacrylate (0.0478 g), 2,2-dimethoxy-2-phenyl-acetophenone (0.1024 g). After the preparation procedures, we obtained the final gripper (length of the gripper: 6 mm, width of each arms: 1 mm). The thickness of responsive layer was 200 μm. The thickness of passive layer was 100μm.

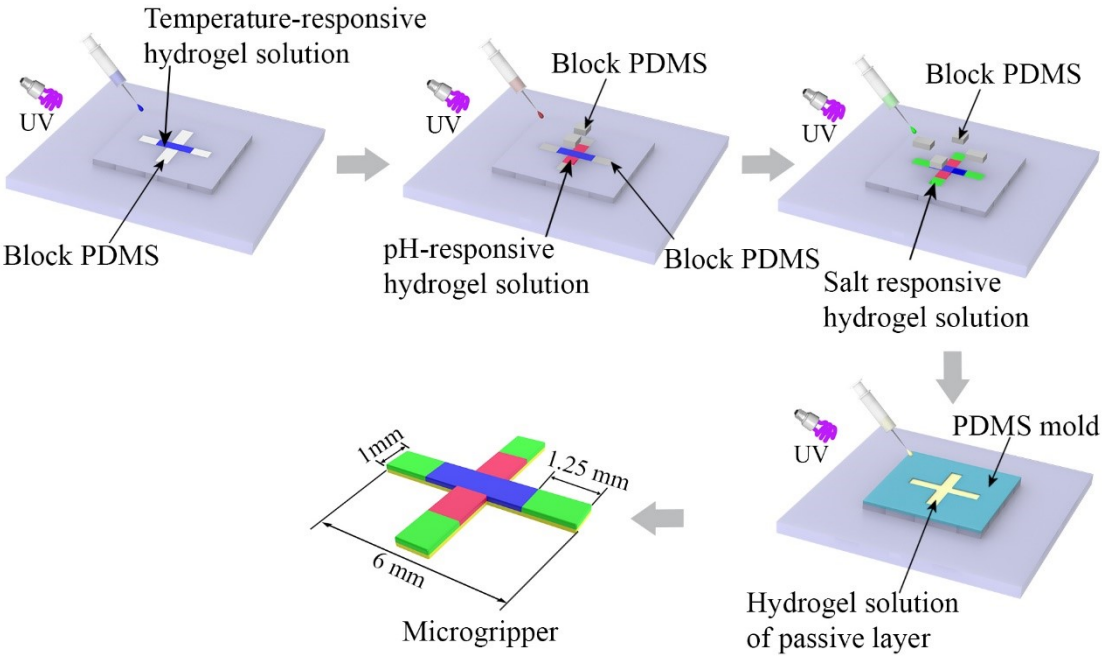


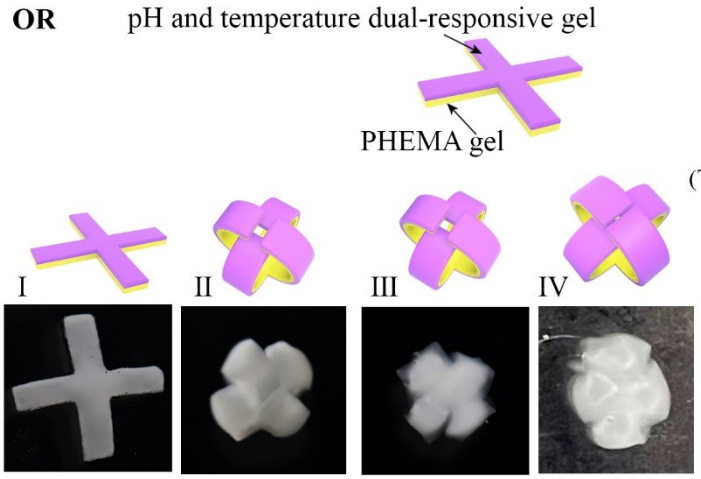
Fig.S6 The preparation of gripper with AND-AND connected gate

6. Fabricating the gripper using dual-responsive hydrogel.

The gripper with dual-responsive hydrogel was prepared using the similar micromolding technique. The precursor solution for the dual-responsive hydrogel layer was composed of AMPS, 0.174 g, sodium hydroxide (0.03 g), deionized water (4.615 g), 2-hydroxyethyl methacrylate (2.51 g), AAc 0.75 g, ethylene glycol dimethacrylate (0.03 g), 2,2-dimethoxy-2-phenyl-acetophenone (0.1024 g). The precursor solution for passive hydrogel layer was composed of HEMA 3.2 g, EGDMA 0.035 g, DMPA 0.1 g and DI water 2.4 g. The mixture of the dual-responsive layer was first introduced onto the ecoflex mold with pre-designed four-arm shaped wells (depth: 300 μm). This mixture was polymerized under UV irradiation for 5 mins (at a wavelength of 365 nm and an intensity of 60 mW/cm^2). Next, for the UV polymerization of the passive layer, a four-arm shaped silicon rubber spacer (thickness: 100μm) was attached to the ecoflex mold. Subsequently, the mixture consisting of the passive part was added to the micromold and polymerized under UV irradiation for additional 5 min. After the gripper was left in DI water overnight to dissolve and remove the unpolymerized monomer and initiator, we obtained the final gripper (length of the gripper: 6 mm, width of each arms: 1 mm).

7. Flexibility of designing the grippers with logic gates

In order to show the flexibility of this approach, we fabricate a gripper with OR gate by a pH and temperature dual-responsive hydrogel (Fig.S7). The dual-responsive hydrogel layer (thickness: 300μm) was composed of NIPAm 120 mg, AAc 6 μl, BIS 2.2 mg, BAPO 1.5 mg, DI water 150 μl and Methanol 210 μl. The passive hydrogel layer was PHEMA (thickness: 100μm; length of the gripper: 6 mm, width of each arms: 1 mm). In our notation, for input 1, we assign an input of 0 for the state when applied 40℃, and an input of 1 for the state when applied 10℃; for input 2, we assign an input of 0 for the state when applied pH 2, and an input of 1 for the state when applied pH 12. The output is the same as we defined in the main text. Whenever anyone (or both) type of responsive polymer network expanded under the influence of either one (or both) of the stimuli, four arms of the gripper fully folded; thus, the gripper could perform effective gripping.



	Input 1 (Temperature)	Input 2 (pH)	Output
I	0	0	0
II	1	0	1
III	0	1	1
IV	1	1	1

Fig.S7 Dual-responsive hydrogel grippers performing OR gate

8. Design of intelligent grippers with logic gates.

Intelligent Systems have the ability to sense their surroundings, analyze, and respond accordingly. In order to achieve more advanced and intelligent grippers, for example, performing similar functions like sensory neuron,[1] incorporating multiple functions within a gripper might be a promising pathway. Our strategy is using stimuli-

responsive materials as building blocks for constructing intelligent grippers. The strategy using stimuli-responsive hydrogels as building blocks to fabricate grippers with logic gates is flexible. According to requirement of specific applications, the types of stimuli-responsive hydrogels can be expanded to a large variety of hydrogels, which can respond to external stimuli such as temperature, pH, electric field, magnetic field, light, pressure, gases, ions, alcohol, glucose, DNA, enzymes and antigens.

Inspired by many biological systems, we categorized smart functions broadly into four classes: basic functions (changes in materials properties, e.g., stiffness, degradability, wettability), practical functions (e.g., targeting), regulatory functions (e.g., self-regulation), and analytical processing functions (e.g., memory and computing).[2] We will briefly discuss the proposal of several multifunctional grippers integrating above functions with logic gates.

For integrating biodegradability and logic gates for grippers. Small-scale soft grippers with environmentally responsive logic gates provide the possibility for pick and place of fragile biological cargo in hard-to-reach environments with potential applications in biomedical engineering, but there is a concern that such devices could get lost or left behind after their utilization in the human body. An attractive strategy to reduce the risks is to create grippers that are endowed with the biodegradability. The biodegradable grippers with logic gates can be designed enzymatically degradable[3] or fabricated by introducing disulfide bonds into hydrogel matrix that can be readily cleaved by reduction.[4]

For integrating targeting and logic gates for grippers. The combination of logic gates and targeting for grippers can be achieved by preparing biomolecule responsive hydrogel can respond to more specific physicochemical cues such as DNA, enzymes, or other biomolecular triggers.[5-7]

For integrating memory and logic gates for grippers. Memory and data storage are the processes of storing information in a medium. The ability to store information is one of the most important features in defining intelligence of an advanced biological system. Therefore, intelligent grippers can formally be achieved by having the ability to remember information and perform complex analysis of the information. For the

hydrogel grippers with logic gates present in this manuscript, the memory function can be integrated by introducing hysteresis of stimuli-responsive hydrogels or shape memory hydrogels. Hysteresis of a stimuli-responsive material is the property that allows the material to be in different states at the same condition depending on the stimulus that was previously applied. For example, when the stimuli-responsive hydrogels used in the grippers are endowed with hysteresis, the grippers are able to store the stimulus information that was previously applied and perform logical operations based on the history of stimulus.

9. Fabricating the magnetic actuated gripper with AND gate.

The magnetic actuated gripper was prepared by incorporating magnetic nanoparticles, 5wt% Fe_3O_4 nanoparticle, into the PHEMA layer. The preparation procedure and the hydrogel composition of PAAc and PNIPAm were the same as used in the AND gate (the detailed size of the gripper was the same as shown in Fig.S1). The H-shaped chamber was prepared by 3D printer. The inner surface of the chamber was coated with agarose gel to decrease the friction between the soft microrobot and the bottom surface of the chamber.

References:

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