

Supplementary Information

Bioinspired Reversible Snapping Hydrogel Assembly

By Q. Zhao, X.X. Yang, C.X. Ma, D. Chen, H. Bai, T.F. Li, W. Yang, T. Xie

Supporting Videos

Video S1: A reversible snapping cycle in the convex-concave mode.

Video S2: Finite element simulation for the reversible snapping cycle in the convex-concave mode.

Video S3: A reversible snapping cycle in a bending mode.

Additional Data on Methods and Characterizations

Table S1. Mechanical properties of the individual hydrogels

Hydrogel samples	NRH	PRH	TRH
Elongation at break (%)	121±18	94±15	103±14
Young's Modulus (kPa)	10.3 ±0.7	18.4±2.3	13.5±1.4
Break Strength (kPa)	7.2±0.6	8.5±1.3	6.6±0.7

Table S2. Feed compositions and construction of the poly(AAm-co-Ad-AAm)

	Sample Label					
	Glue7	Glue5	Glue4	Glue3	Glue2	Glue1
Feed molar ratio of Ad-AAm to AAm	7%	5%	4%	3%	2%	1%
Calculated molar ratio of Ad-AAm to AAm ^a	6.9%	5.2%	4.2%	3.0%	2.1%	1.0%
Molecular weight ^b	8956	9079	8917	9041	9027	8865
Calculated number of Ad group per polymer chain ^c	7.6	5.6	4.7	3.4	2.3	1.2
Adhesive strength to bond NRG using the glue (kPa)	>7.2±0.5 ^d	>7.2±0.5 ^d	4.1±0.7	2.9±0.8	1.2±0.4	/ ^e

^aCalculated by ¹H-NMR from the integral area ratio (hydrogen atom labeled in a and b) in Figure S6.

^bMeasured by a MULDI-TOF mass spectrometer.

^cCalculated by the molar ratio of Ad-AAm to AAm and the number-average molecular weight.

^dCohesive failure

^eToo low to be detected

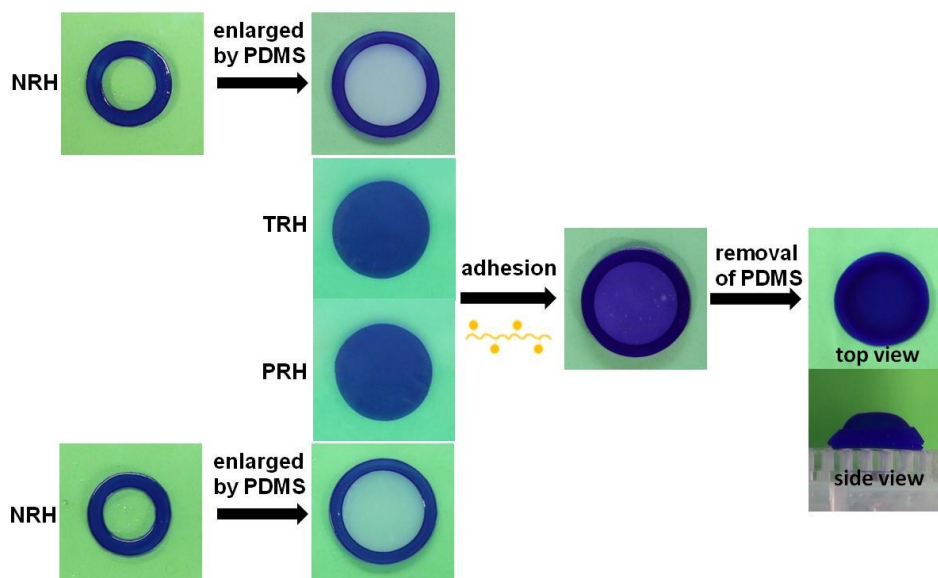


Figure S1. Detailed assembly procedure of the convex/concave-based hydrogel assembly.

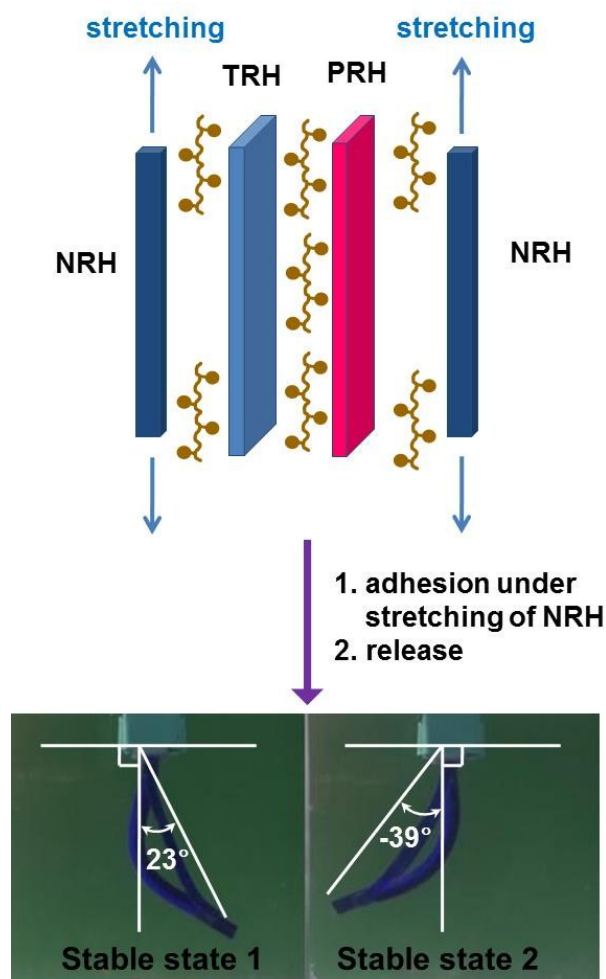


Figure S2. Schematic preparation method for the bending type buckling assembly and the measurement method for the bending angles.

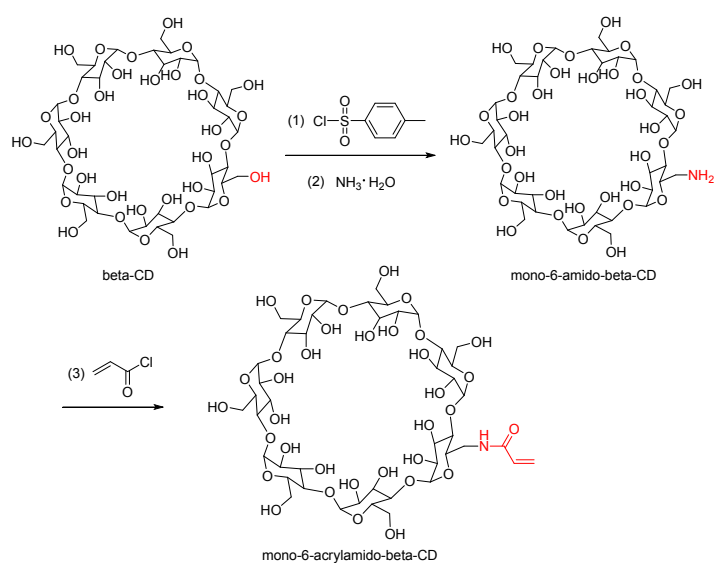


Figure S3. Synthesis process of β -CD-AAm

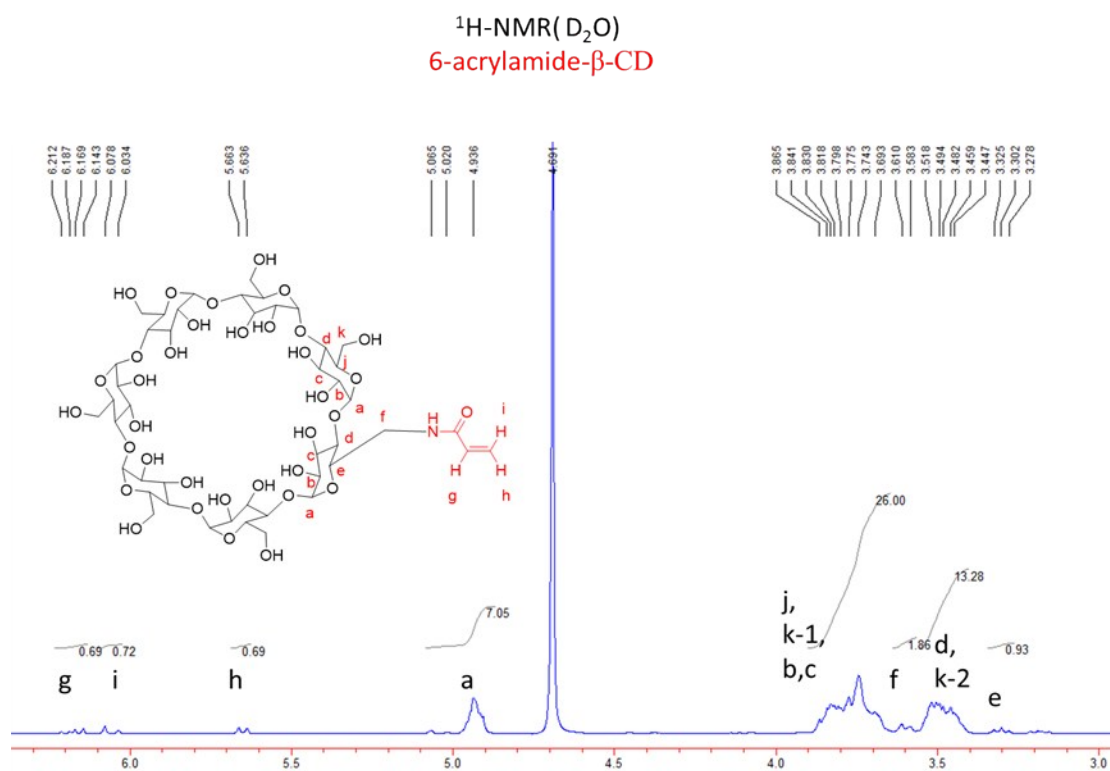


Figure S4. ¹H-NMR spectrum of β-CD-AAm

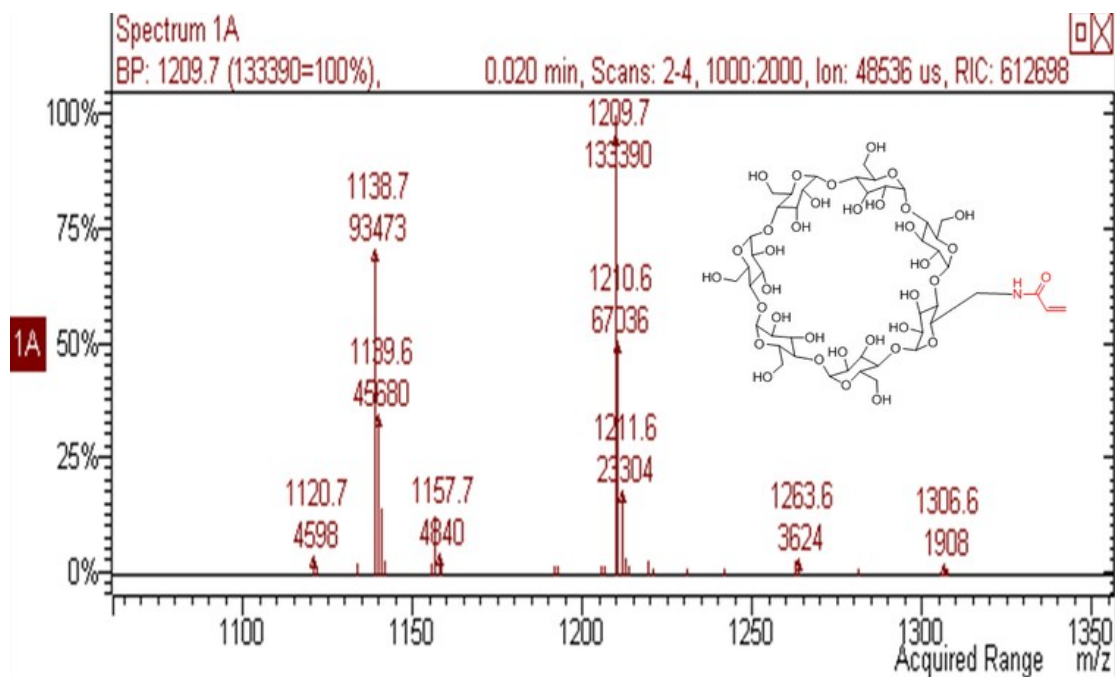


Figure S5. ESI-MS spectrum of β-CD-AAm

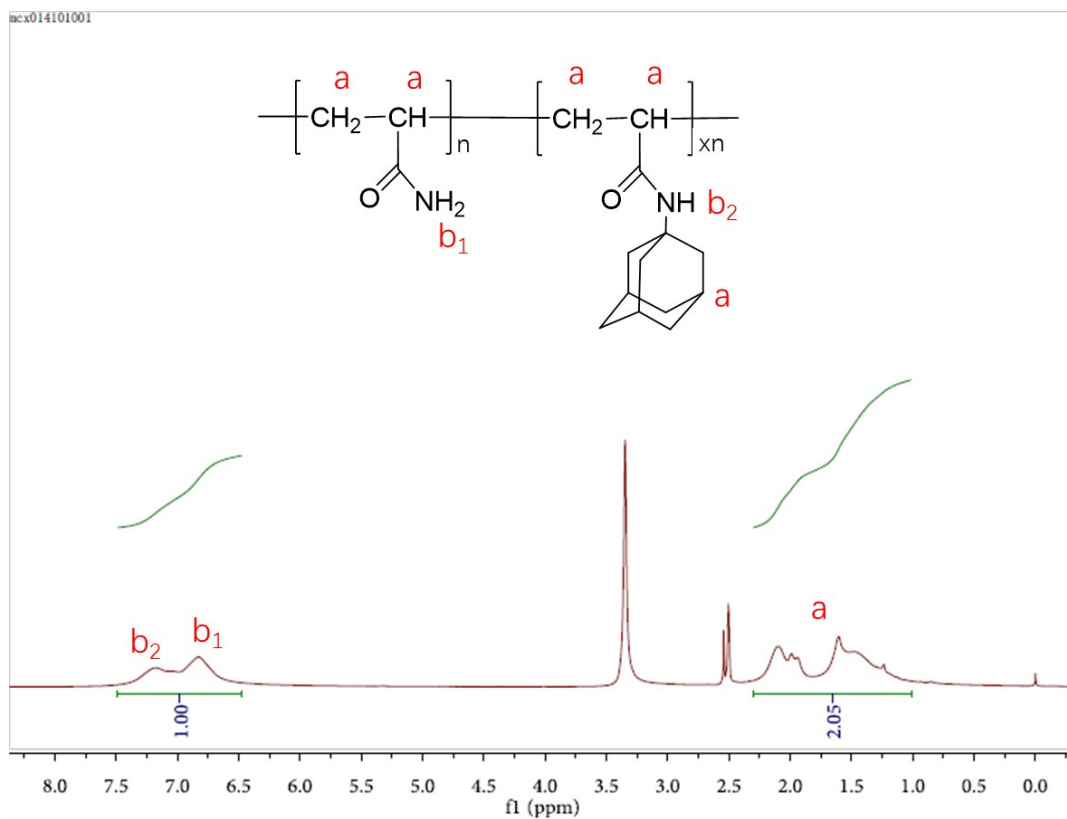


Figure S6. ¹H NMR spectra of poly(AAm-co-Ad-AAm) (the glue) in DMSO-D₆ taking Glue7 for example. Integral area ratios (a:b) for Glue7, Glue5, Glue4, Glue3, Glue2, and Glue1 are respectively 2.05, 1.92, 1.84, 1.74, 1.67, and 1.58.

Measurement of hydrogel swelling ratio

The room temperature swelling ratios of PRH were measured gravimetrically. Before each measurement, the gel sample was immersed in a buffer solution (IS = 100 mmol/L) for at least 12 hours at the corresponding pH value (between 2.0 and 12.0). The swelling ratio was calculated as W_s/W_d , where W_s is the weight of the swollen gel at a given pH value and W_d is the weight of the sample in the dry state. The swelling ratios of TRH samples were determined accordingly except that the temperature was varied while the pH was maintained neutral with PBS buffers.

Finite element simulation

The bi-stability of the model is due to the contraction of the pre-stretched NRH rings (layer 1 and 4 in **Figure 3a**). This mode of loading is similar to a thin rod hinged on its ends, the free end of the structure can deflect and store the elastic energy of the deformed hydrogel structure. In the FEM simulation, we first induce the shrinking of the TRH part, which corresponds to the shrinking of the TRH hydrogel by rising temperature in the experiment. The dimensions of hydrogel blocks in the simulation are identical to those in the experiments. Layers 1 and 4 are two NRH rings with an inner diameter of 24 mm, an outer diameter of 30 mm and a thickness of 0.43 mm (the original thickness of the NRH is 0.8 mm, and the pre-stretch of the NRH in circumferential direction is 1.85, considering the NRH as incompressible material and ignore the strain in radial direction, the thickness of NRH becomes 0.43 mm). Layer 2 is the DRH layer with a thickness of 0.3 mm and a diameter of 30 mm. Layer 3 is the TRH layer with the same size as layer 2. In the simulation, hydrogels are modeled as a hyperelastic material defined by Neo-hookean model (with the dimensionless shear modulus of 1). 660 CAX4RH elements are used in the simulation. Layers 1 and 4 were pre-stretched in the experiment to resemble the distributed axial forces within those two layers.

Theoretical analysis of bi-stable structure

During the actuation of the hydrogel structure, the free-energy function of the system can be expressed as

$$G = W_E - F_0 \times d \quad (s1)$$

The second term $F_0 \times d$ represents the work done by the driving force. Based on existing studies, the relationship between force-deformation can be simply approximated by:

$$F(d) = Ad + Bd^3 \quad (\text{s2})$$

Denote W_E as the elastic energy of the deformed hydrogel structure, whose value can be obtained by the integration of $F(d)$

$$W_E = \int F(d) \, d \quad (\text{s3})$$

The energy-deformation relation provides a 'landscape' to the possible states of the hydrogel structure. Pursuing the free energy analysis to the hydrogel reversible bi-stable case, one can have the expression of free energy as

$$G = W_E - F_0 \times d = \frac{1}{2}Ad^2 + \frac{1}{4}Bd^4 - F_0d \quad (\text{s4})$$

With Eq. s1 and s3 and qualitatively refer to experimental results, we chose the parameters $A=-48$ N/m³, $B=1$ N/m⁴.