Supplementary information

Crown Ether-Based Supramolecular Elastomer Exhibiting Reversible and Abundant Shape Programming

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Materials and methods

All reagents and solvents were purchased from commercial suppliers and used as received. The remote-controlled (RC) cars were commercially sourced and had their outer shells removed before experiment. The heat gun used for heating the connector in the assembly was commercially sourced. ^{1}H NMR spectra were acquired on a Bruker Avance III 400 MHz spectrometer (Bruker BioSpin GmbH, Germany). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded using a Bruker Alpha II spectrometer (BRUKER OPTICS, Germany) equipped with a diamond ATR accessory (Bruker Platinum ATR). Spectra were collected in the range of 4000–400 cm^{-1}. The thermogravimetric analysis and differential thermal analysis were performed using a Hitachi High-Tech TG/DTA6300 simultaneous thermal analyzer (Hitachi High-Tech, Japan) under a N_2 air flow at a heating rate of 10 °C·min^{-1} from 30 to 730 °C.

Tensile tests

The tensile tests of polymer materials were investigated using an electronic universal testing machine CMT4104 (SHENZHEN SUNS TECHNOLOGY STOCK CO., LTD, China) equipped with a 100 N load cell. The samples for uniaxial tensile test, heating/cooling uniaxial tensile test and uniaxial cyclic tensile test are prepared as long strips with length × width of 3 cm × 4 mm and the samples used for lap-shear experiments were prepared by overlapping elastomer strips with hydrogel strips, both of which have dimensions of 2 cm in length and 4 mm in width, with a contact length of 1 cm. These tensile tests were conducted with a tensile rate of 30 mm·min^{-1}. In the heating uniaxial tensile test, the strips were heated with a BOSCH GHG-16-50 heat gun (Robert Bosch Power Tools GmbH, Germany) for 30s at a distance of 15 cm. In the cooling uniaxial tensile test, the strips were cooled for different durations after being heated for 30 s.

Rheological tests

The dynamic oscillatory rheology tests were performed using a Kinexus Pro KNX2100 rotational rheometer (Malvern, Britain) equipped with a 2 cm parallel-plate geometry. The dynamic Frequency Sweep tests were conducted at 25 °C. The strain amplitude was fixed at 1%, with frequency ranging from 0.1 to 100 rad/s. The dynamic temperature sweep tests were conducted with a fixed frequency of 1 Hz and a strain amplitude of 1%. The temperature was ramped from 25 to 80 °C at a heating rate of 5 °C·min^{-1}.

The synthesis of B21C7 and DAAS

Synthesis of B21C7

The B21C7 was synthesized according to previously reported methods.[1-3]

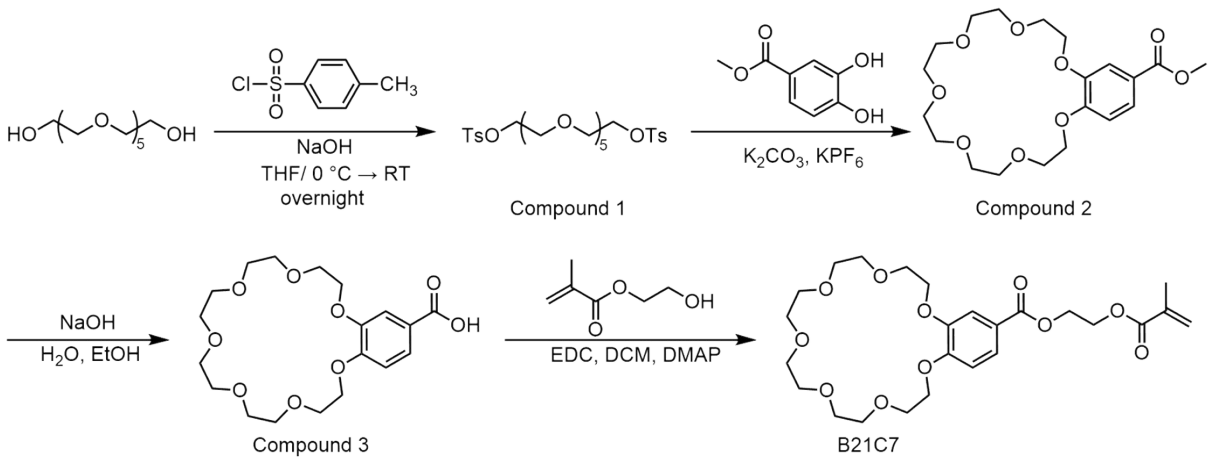

Fig. S1 The synthesis route of B21C7

Synthesis of compound 1

Hexaethylene glycol (15 g, 53.13 mmol) was dissolved in THF (75 mL) and placed in a round-bottomed flask and cooled to 0 °C. The mixture was then stirred for 30 min at 0 °C. NaOH (12.75 g, 318.75 mmol) was dissolved in deionized water (15 mL) and slowly added, and the mixture was stirred at 0 °C for 30 min. P-toluenesulfonyl chloride (40.5 g, 212.43 mmol) was dissolved in THF (75 mL) and slowly injected into the flask with syringe pump over 30 min and kept at 0 °C for 1 h. The reaction system was then warmed up to room temperature and stirred for 18 h. The reaction was concentrated under reduced pressure, then dissolved in DCM (300 mL) and washed with saturated brine (120 mL). The organic layer was collected and dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography and the product was obtained at V_{PE}: V_{EA}=2:3. The product fraction was collected and concentrated by rotary evaporation and dried under vacuum to give compound 1 (26.227 g, 83% yield) as a colorless viscous oily liquid. The ^{1}H NMR spectrum of compound 1 is shown in Fig. S2. ^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm) 7.78 (d, *J* =

8.4 Hz, 4H), 7.33 (d, J = 8.1 Hz, 4H), 4.17 – 4.09 (m, 4H), 3.66 (dd, J = 5.6, 4.0 Hz, 4H), 3.60 (s, 8H), 3.56 (s, 8H), 2.43 (s, 6H).

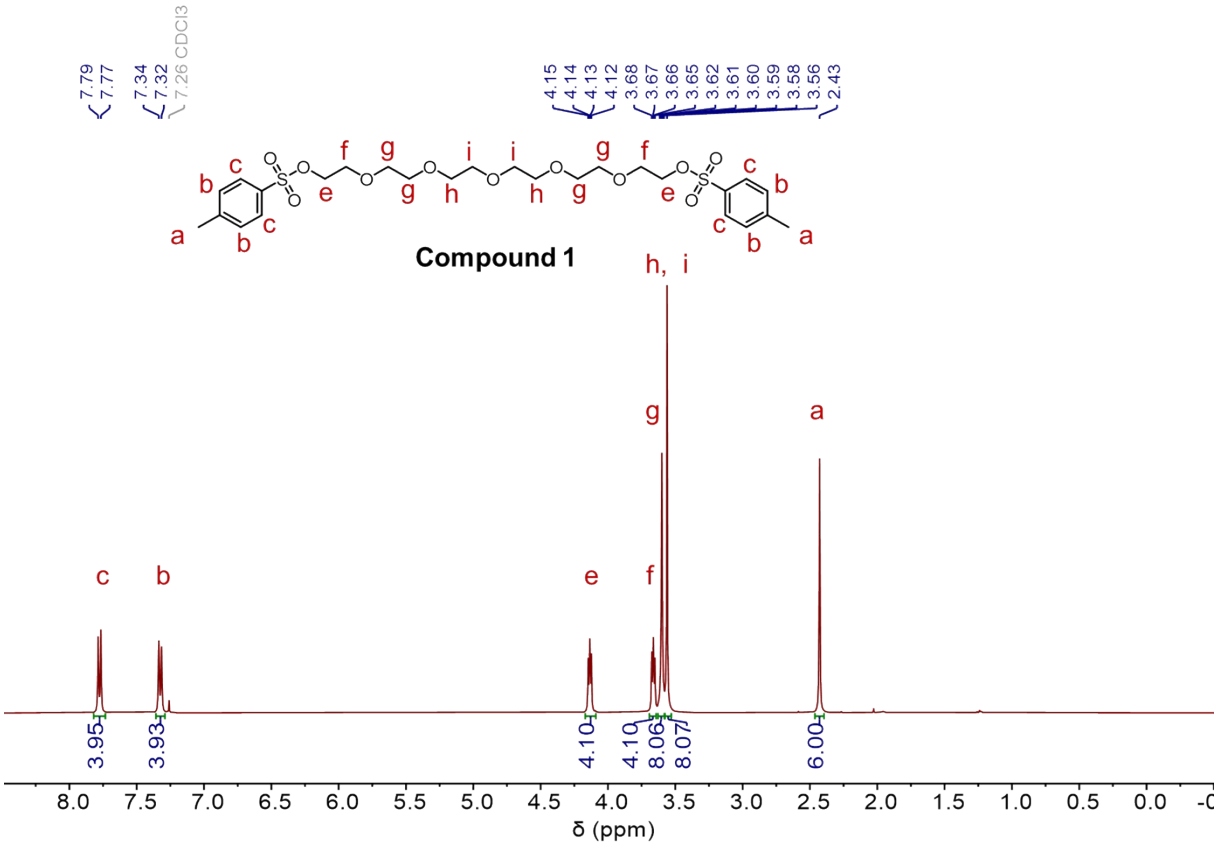

Fig. S2 The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of compound 1.

Synthesis of compound 2

Compound 1 (26.23g, 44.40 mmol,), K_2CO_3 (30.68g, 222.00 mmol) and KPF_6 (12.26g, 66.60 mmol) were dissolved in anhydrous CH_3CN (450 mL) in a round-bottomed flask, stirred vigorously and heated to reflux under an N_2 atmosphere. A solution of methyl 3,4-dihydroxybenzoate (7.466 g, 44.40 mmol) dissolved in CH_3CN (150 mL) was added dropwise to the suspension over 12 hours. The reaction mixture was stirred at reflux for 2 days. After cooling to room temperature, the suspension was filtered and washed with CH_2Cl_2 (500 mL), and the combined organic phases were concentrated by rotary evaporation. The residue was dissolved in DCM (500 mL) and washed three times with deionized water (500 mL). The aqueous phase was washed twice with DCM (250 mL × 2), and the organic phase was collected,

dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography, and the product was obtained at V_{PE}: V_{EA}=1:1. The product fraction was collected, concentrated by rotary evaporation and dried under vacuum to obtain compound 2 (5.78 g, 13.95 mmol, 31% yield), which was a colorless viscous oily liquid, and turned into a white crystalline solid after leaving it for a while. The ^{1}H NMR spectrum of compound 2 is shown in Fig. S3. ^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm) 7.64 (dd, J = 8.4, 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 4.20 (t, J = 4.4 Hz, 4H), 3.93 (q, J = 4.3 Hz, 4H), 3.87 (s, 3H), 3.80 (dq, J = 5.0, 3.2, 2.7 Hz, 4H), 3.77 – 3.71 (m, 4H), 3.70 – 3.61 (m, 8H).

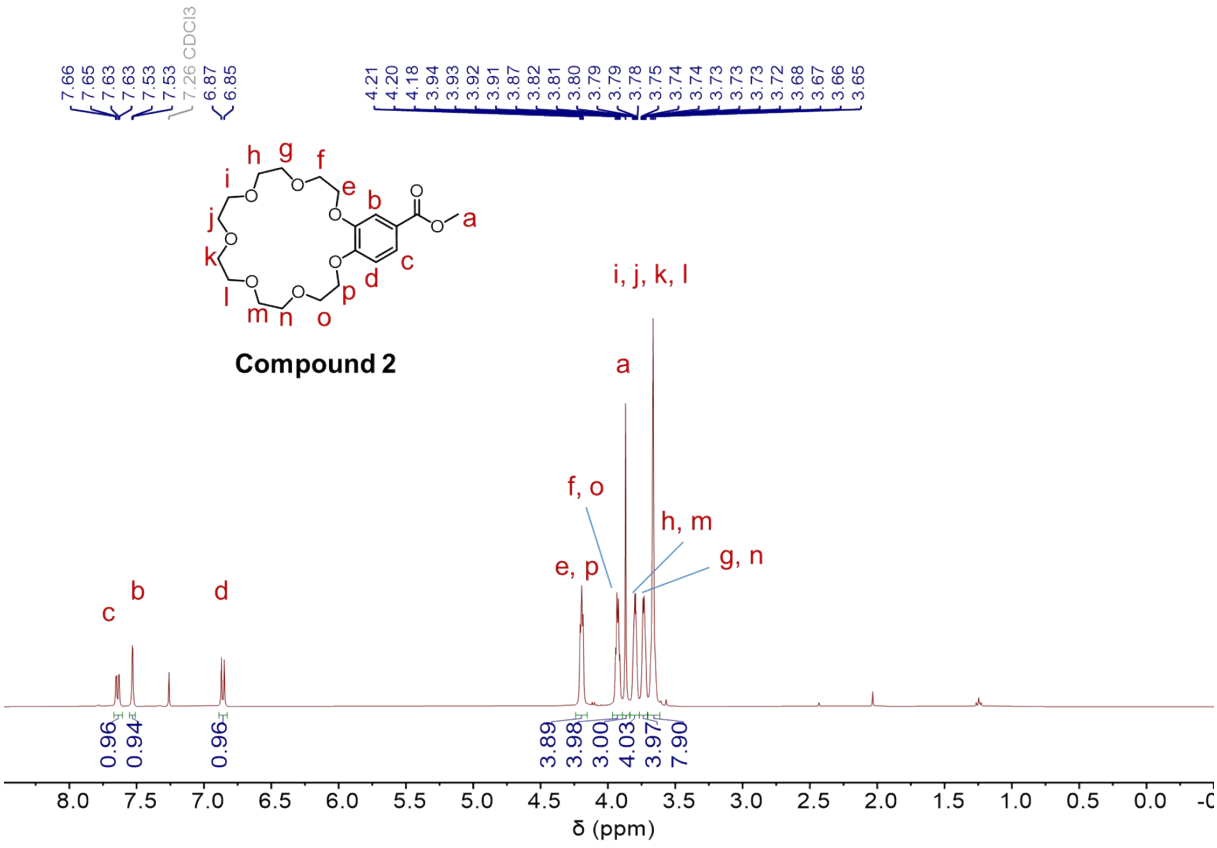

Fig. S3 The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of compound 2.

Synthesis of compound 3

Compound 2 (7.72 g, 18.63 mmol) was dissolved in EtOH (135 mL) and placed in a round-bottomed flask, followed by the addition of aqueous solution of NaOH (5.96 g, 149.02 mmol)

and the resulting mixture was refluxed overnight and then slowly cooled to room temperature. EtOH was removed by rotary evaporation and water (100 mL) was added and concentrated hydrochloric acid was slowly added to the solution until pH=1. The mixture was extracted three times with DCM (135 mL × 3), the organic phase was collected and dried with Na_2SO_4 and evaporated to dryness under reduced pressure to give compound 3 (7.03 g, 17.56 mmol, 94% yield) as a white powder. The ^{1}H NMR spectrum of compound 3 is shown in Fig. S4. ^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm) 10.76 (s, 1H), 7.73 (dd, J = 8.4, 2.0 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 4.22 (q, J = 4.3 Hz, 4H), 3.94 (q, J = 4.6 Hz, 4H), 3.82 (dt, J = 5.0, 2.9 Hz, 4H), 3.77 – 3.72 (m, 4H), 3.68 (d, J = 1.8 Hz, 8H).

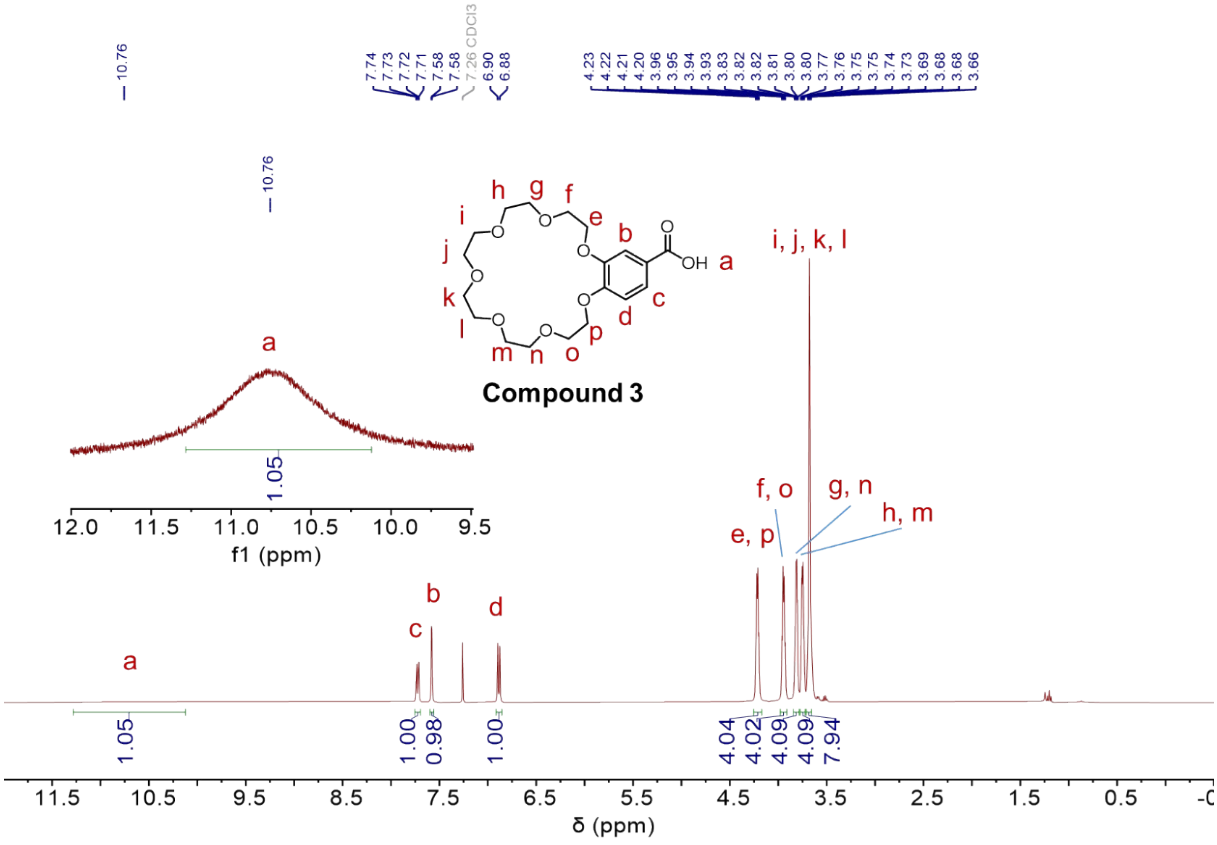

Fig. S4 The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of compound 3.

Synthesis of B21C7

Compound 3 (9.87 g, 24.66 mmol), 2-hydroxyethyl methacrylate (6.42 g, 49.31 mmol) and DMAP (1.51g, 12.33 mmol) were dissolved in DCM (250 mL) and stirred at 0°C for 10 min.

To this solution was added EDC (4.73g, 24.66 mmol) and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered and concentrated by rotary evaporation. The crude product was purified by silica gel column chromatography and the product was obtained at V_{DCM}: V_{MeOH}=100:1. The product fraction was collected and evaporated to give white solid product (10.01g, 79% yield). The ^{1}H NMR spectrum of B21C7 is shown in Fig. S5. ^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm) 7.64 (dd, J = 8.5, 2.0 Hz, 1H), 7.52 (d, J = 2.1 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.12 (s, 1H), 5.57 (t, J = 1.7 Hz, 1H), 4.52 (dd, J = 6.4, 3.3 Hz, 2H), 4.46 (dd, J = 6.2, 3.3 Hz, 2H), 4.23 – 4.14 (m, 4H), 3.92 (q, J = 4.3 Hz, 4H), 3.79 (tt, J = 4.6, 2.2 Hz, 4H), 3.75 – 3.70 (m, 4H), 3.66 (s, 8H), 1.93 (s, 3H).

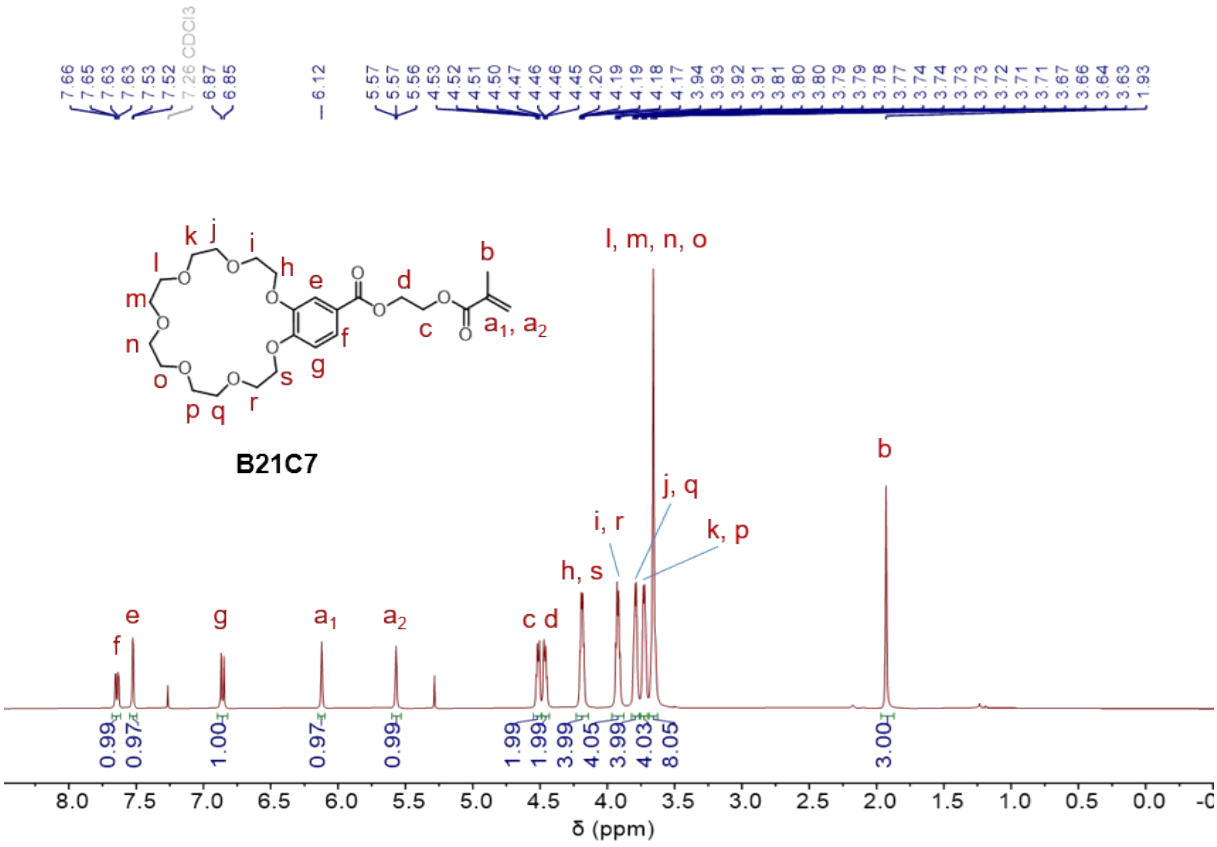

Fig. S5 The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of compound B21C7.

Synthesis of DAAS

The DAAS was synthesized according to previously reported methods.[4]

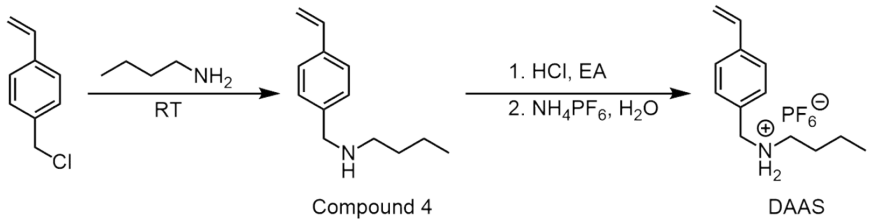

Fig. S6 The synthesis route of DAAS.

4-Vinylbenzyl chloride (10g, 65.52 mmol) and N-butylamine (4.79g, 652.22 mmol) were placed in a round-bottomed flask, and the mixture was stirred at room temperature for 24 hours. The excess N-butylamine was removed by rotary evaporation. The residue was dispersed in diethyl ether (mL) to precipitate the salt formed in the reaction, which was then removed by filtration. The organic phase was washed three times with water to remove the remaining salt, followed by dried with Na_2SO_4 and evaporated to remove the solvent. The crude product was purified by silica gel column chromatogram and the product was obtained at V_{DCM}: V_{MeOH}=50:1. The product fraction was collected and concentrated under reduced pressure to give the yellow oily product compound 4 (8.31 g, 67% yield).

Dissolve compound 4 (5 g, 26.41 mmol) with EA (50 mL) in a round-bottom flask, and 5 M HCl was added dropwise to the solution with stirring until the precipitate no longer generated, and was stirred for a moment. The precipitate was collected by filtration, washed 3 times with EA and dried under vacuum to obtain a white solid. The white solid was dissolved in a mixed solvent of deionized water and MeCN (V_{H2O}=50 mL, V_{MeCN}=35 mL), and saturated NH_4PF_6 solution was added to the solution under stirring conditions until the precipitate was formed. The reaction was stirred at room temperature for 4 h. The precipitate was collected by filtration, washed 3 times with deionized water and dried under vacuum to obtain a white solid DAAS (5.28 g, 56%). The ^{1}H NMR spectrum of DAAS is shown in Fig. S7. ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) 8.63 (s, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.9 Hz, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.90 (d, J = 17.6 Hz, 1H), 5.32 (d, J = 10.9 Hz, 1H), 4.13 (s, 2H), 2.92 (s, 2H), 1.58 (p, J = 7.6 Hz, 2H), 1.32 (q, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H).

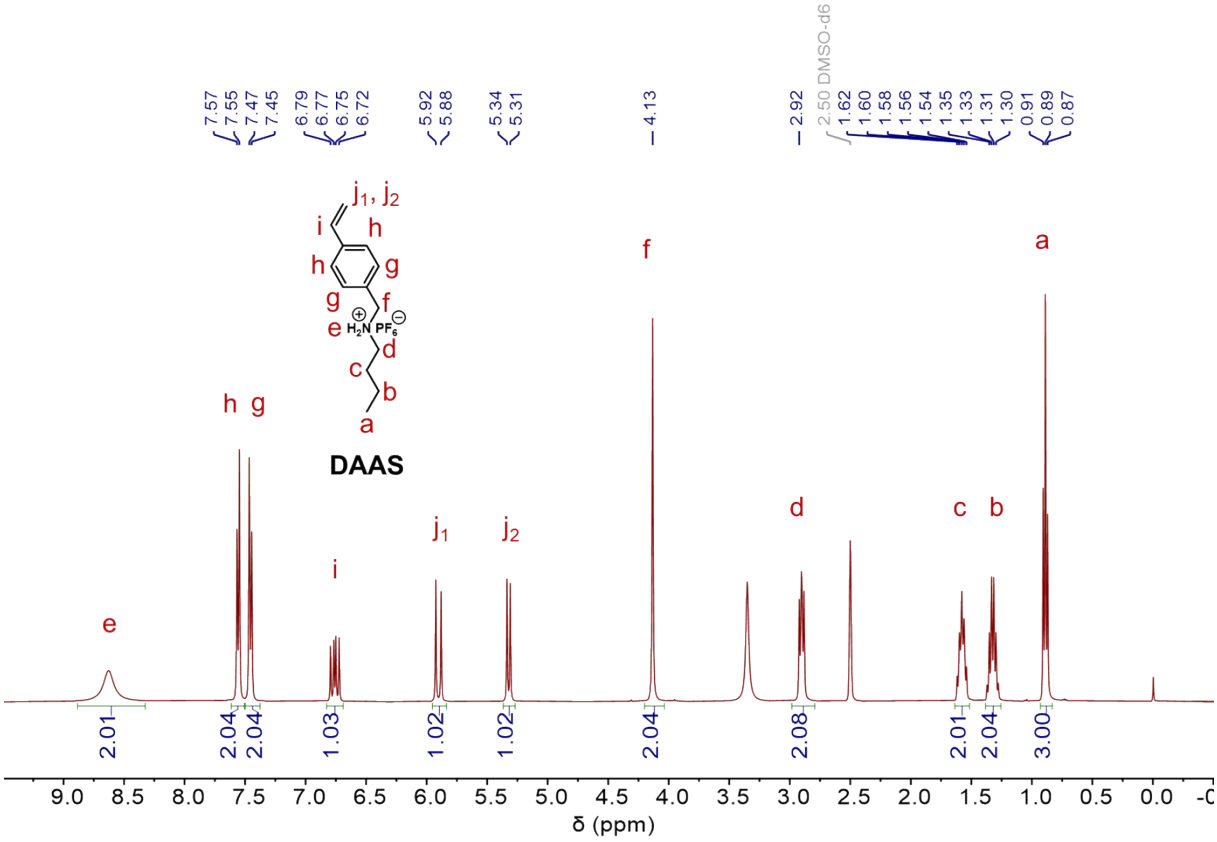

Fig. S7 The ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, 298 K) of DAAS.

The preparation of Elastomers and hydrogel

The preparation of elastomer SE-HG-Z

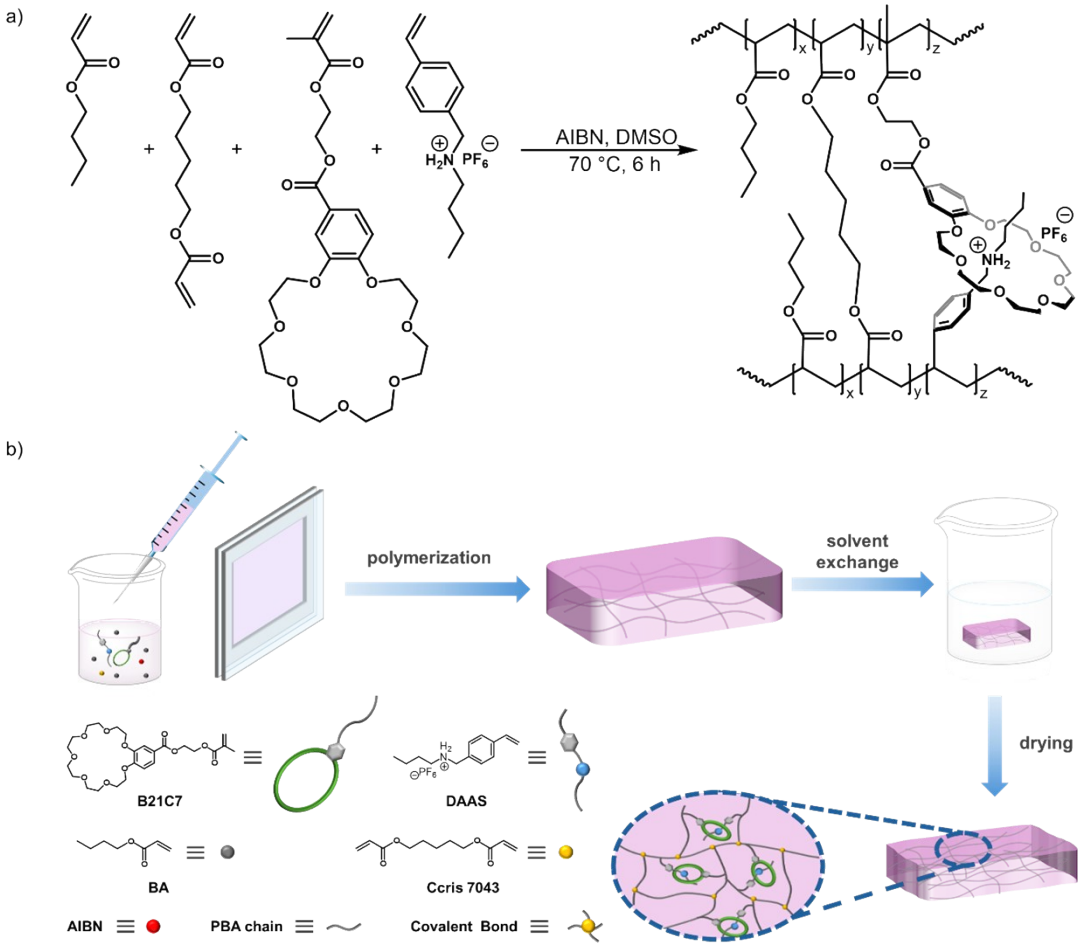

Fig. S8 (a) The synthesis of DMSO gels containing B21C7 and DAAS; (b) the preparation routine of SE-HG-Z.

A series of solutions were prepared according to Table S1 and subsequently injected into a mold with a length × width × height of 10 cm × 10 cm × 2 mm, which consisted of two glasses sandwiched a silicone pad. The mold was bubbled with N_2 for 15 min and then heated to 70 °C for 6 h. Then, the mold was cooled to room temperature and then demolded, and the obtained DMSO gel was immersed in DCM (200 mL × 3), and the DCM was renewed every 4 h. The DCM gel was then placed in a blast drying oven at 25 °C to evaporate the solvent for 6 h to obtain the elastomer SE-HG-Z.

Table S1. Recipes for the precursor solutions for the preparation of SE-HG-Z with different contents of B21C7 and DAAS.

Elastomer	BA(g)	DMSO (g)	B21C7 (mg)	DAAS (mg)	Ccris 7043 (mg)	AIBN (mg)
SE-HG-0	1.0	3.0	0	0	16.7	12.8
SE-HG-1	1.0	3.0	40.0	27.7	16.7	12.8
SE-HG-2	1.0	3.0	80.0	54.4	16.7	12.8
SE-HG-4	1.0	3.0	160.0	110.9	16.7	12.8
SE-HG-6	1.0	3.0	240.0	166.3	16.7	12.8
SE-HG-8	1.0	3.0	320.0	221.7	16.7	12.8
SE-HG-10	1.0	3.0	400.0	277.2	16.7	12.8

The preparation of elastomer E-G-Z

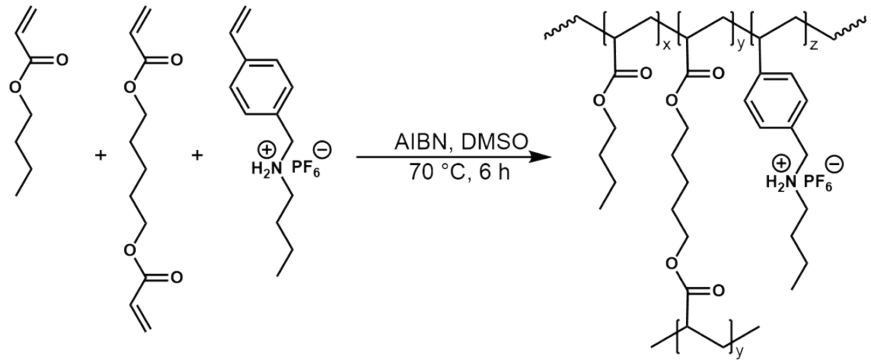

Fig. S9 The synthesis of DMSO gel containing DAAS.

A series of solutions were prepared according to Table S2 and subsequently injected into a mold with a length × width × height of 10 cm × 10 cm × 2 mm, which consisted of two glasses sandwiched a silicone pad. The mold was bubbled with N_2 for 15 min and then heated to 70 °C for 6 h. Then, the mold was cooled to room temperature and then demolded, and the obtained DMSO gel was immersed in DCM (200 mL × 3), and the DCM was replaced every 4 h. The DCM gel was then placed in a blast drying oven at 25 °C to evaporate the solvent for 6 h to obtain the elastomer E-G-Z.

Table S2. Recipes for the precursor solutions for the preparation of E-G-Z with different contents of DAAS.

Elastomer	BA (g)	DMSO (g)	DAAS (mg)	Ccris 7043 (mg)	AIBN (mg)
E-G-0	1.0	3.0	0	16.7	12.8
E-G-1	1.0	3.0	27.7	16.7	12.8
E-G-2	1.0	3.0	54.4	16.7	12.8
E-G-4	1.0	3.0	110.9	16.7	12.8
E-G-6	1.0	3.0	166.3	16.7	12.8
E-G-8	1.0	3.0	221.7	16.7	12.8
E-G-10	1.0	3.0	277.2	16.7	12.8

The preparation of PDAC hydrogel

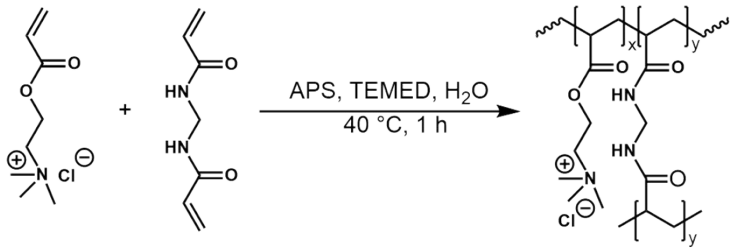

Fig. S10 The synthesis of PDAC hydrogel.

A precursor solution was prepared, which consisted of 80 wt % DAC aqueous solution (7.5 g, 30.98 mmol), MBA (2.4 mg, 15.49 μmol), APS (70.7 mg, 0.31 mmol), TEMED (35.8 mg, 0.31 mmol), and H_2O (2.5 mL). The solution was injected into a mold with a length × width × height of 10 cm × 10 cm × 2 mm, which was composed of two glasses sandwiched by a silicone gel pad. The reaction was heated to 40 °C for 1 h followed by demolding to obtain PDAC hydrogel.

The characterization of SE-HG-Z and PDAC hydrogel

The NOESY test of B21C7@DAAS complex and ATR-FTIR tests of SE-HG-Z

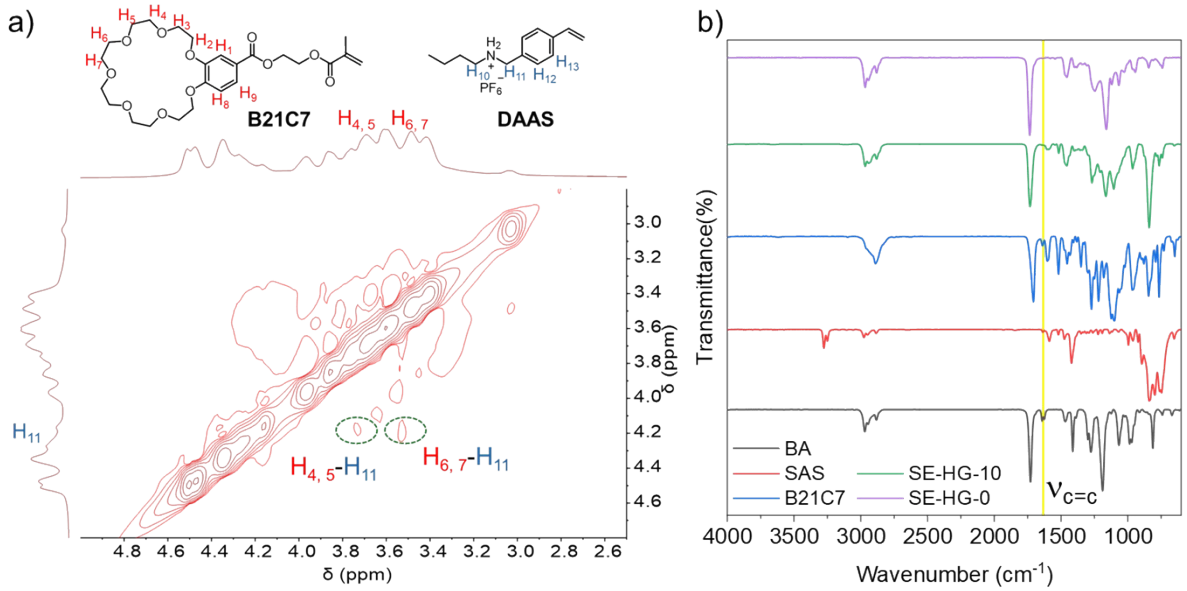

Fig. S11 (a) Partial NOESY spectrum ($CDCl_3/CD_3CN$, v/v = 1/1, 400 MHz, 298 K) of equal molar mixture of B21C7 and DAAS at 200 mM; (b) Comparison of the ATR-FTIR spectra of SE-HG-10, SE-HG-0, BA, DAAS and B21C7

The TGA test and DTA test of **SE-HG-Z**

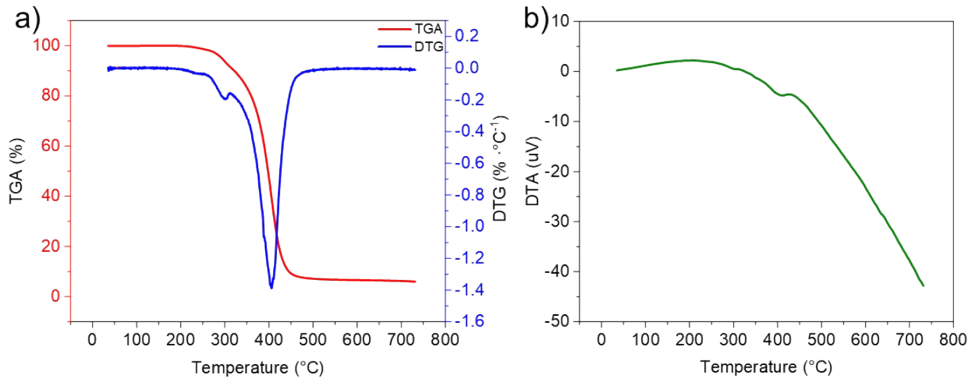

Fig. S12 (a) The TGA and DTG spectrum of SE-HG-6; (b) The DTA spectrum of SE-HG-6.

The uniaxial tensile test of TBACl-treated SE-HG-Z

To investigate the influence of competitive guests on host-guest complexes and the resulting mechanical properties of the material, we conducted competition experiments. The SE-HG-8 samples were immersed in DCM solutions of tetrabutylammonium chloride (TBACl) at various concentrations (3, 6, 9, and 12 mM) for 12 hours. Subsequently, the samples were thoroughly washed with DCM (three times, 4 hours each) to remove unbound guests and then dried prior to tensile testing. The original SE-HG-8 sample (without TBACl treatment) exhibited a fracture stress of approximately 7.8 MPa and a fracture strain of only about 30% (Fig. SR3a). After TBACl treatment, the mechanical properties of the material deteriorated significantly. For instance, following treatment with a 12 mM TBACl solution, the tensile strength decreased to approximately 1.5 MPa, while the fracture strain increased to over 600% (Fig. SR3a). This indicates that the host-guest interactions were severely disrupted, leading to a reduction in the crosslinking density of the polymer network. The underlying reason (Fig. SR3b) is that the charge-convergent chloride anions form intimate ion pairs with the ammonium cations; these ion pairs are too bulky to fit into the cavity of B21C7, thereby resulting in the dissociation of the host-guest complexes.[5]

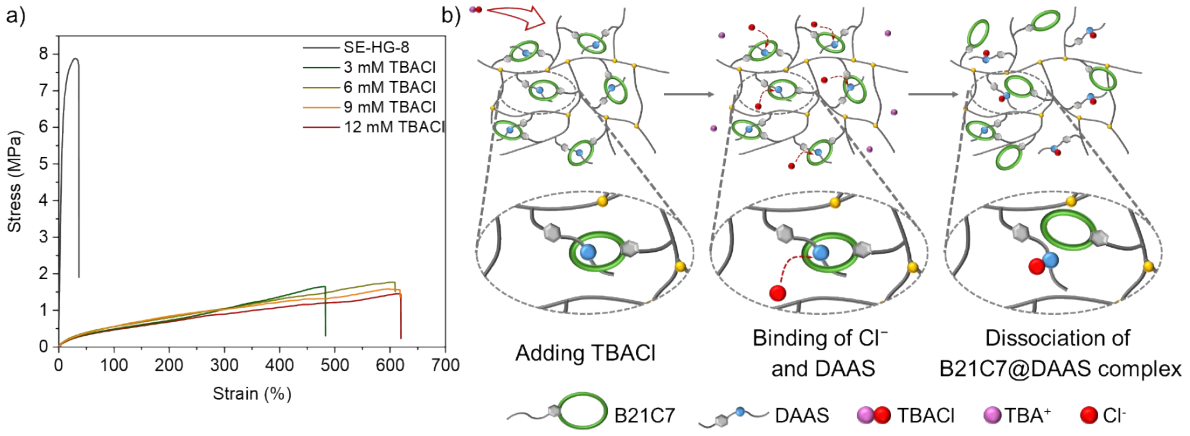

Fig. S13 (a) Stress-strain curves of the original SE-HG-8 sample and the samples treated with DCM solutions of TBACl at concentrations of 3, 6, 9, and 12 mM, respectively; (b) Schematic illustration of the dissociation mechanism of host-guest complexes in the SE-HG-Z polymer network upon treatment with TBACl

The uniaxial tensile test and uniaxial cyclic tensile test of PDAC hydrogel

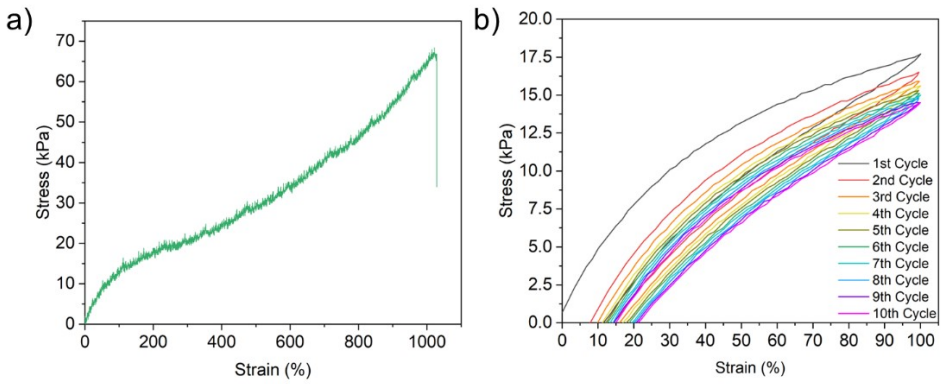

Fig. S14 (a) The stress-strain curves of PDAC hydrogel; (b) The cyclic stress-strain curves of PDAC hydrogel.

In order to characterize the mechanical strength of PDAC hydrogel, we cut it into long strips with a length × width × thickness of 3 cm × 4 mm × 2 mm for uniaxial tensile testing with a tensile rate of 30 mm/min. The fracture stress of the hydrogel was around 67 kPa, and the strain at fracture was about 1000%. Subsequently, to characterize the fatigue resistance of PDAC hydrogel, we performed uniaxial cyclic tensile tests with strips as described above, with a tensile rate of 30 mm/min and a constant maximum strain ε = 100%. The maximum stress decreased significantly from 17.7 kPa to 16.5 kPa from the first to the second cycle and then decreased steadily with a small magnitude; the area of the hysteresis loop decreases significantly from the first to the second loop and then decreases slowly from the second to the fourth loop and finally remains almost stable from the fifth loop onwards.

The assembly process and the dimension drawings

The G-PDAC precursor solution was prepared, and 25 mL of the solution was injected into a mold and reacted at 40 °C for 1 h. The G-PDAC hydrogel shell was obtained by removing the mold after cooling. The shell of the mini remote-controlled car was removed, and the hydrogel shell was assembled with the remaining parts to obtain the hydrogel car as shown in Fig. S13a. The SE-HG-6 elastomer was cut into an I-shaped strip as Fig. S13b shown size. The strip was heated for 15 s with a heat gun, then the two ends of the strip were bent to 90° on the same side, followed by cooling for 1 min to get the square bracketed connector.

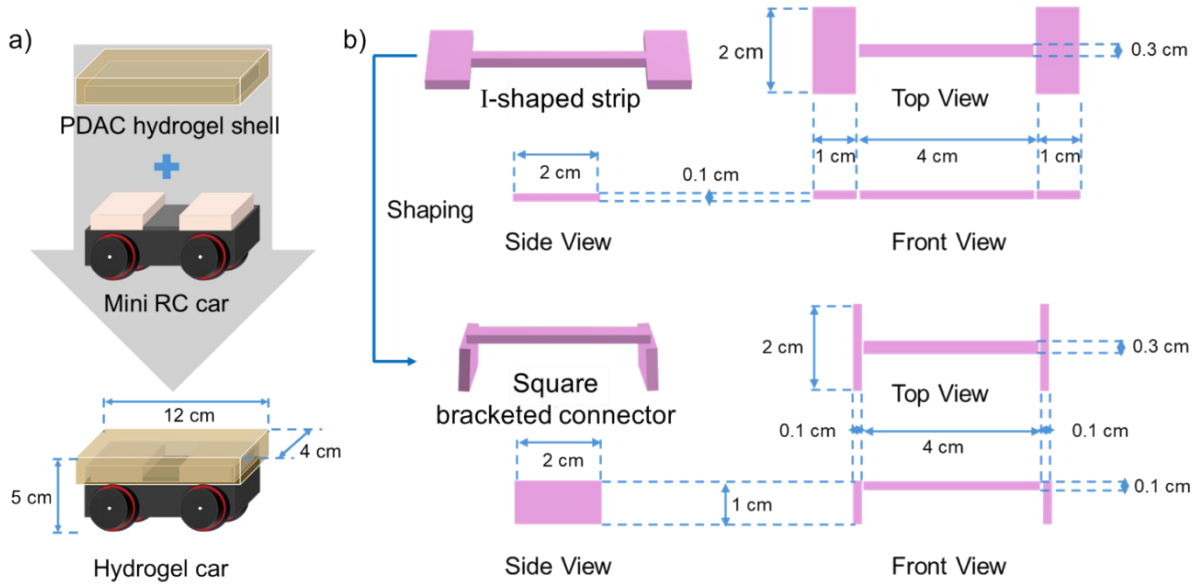

Fig. S15 (a) The assembly process and dimension of the hydrogel car; (b) The dimension drawing of the I-shaped strip and square bracketed connector.

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