1	Ultra-tough self-healing hydrogel via hierarchical energy
2	associative dissipation
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13	Mechanical robustness is essential to the stability and lifetime of hydrogel based functional
14	materials. Owing to the water content and homogeneous texture, conventional hydrogels can hardly
15	reach satisfactory strength and elasticity ^{1,2} . Methods such as employing tensile-resistant groups ^{3,4}
16	and introducing structural heterogeneity ^{5,6} have been developed to fabricate tough hydrogels.
17	However, those techniques significantly increased the complexity and cost of material preparation,
18	and only had limited applicability. Here we show ultra-tough hydrogels can be obtained via a
19	unique hierarchical architecture composed of tightly coupled self-assembly units formed in one-
20	pot polymerization reaction. The associative energy dissipation among them exhibits clear
21	correlations with the structure of reactants, which may be rationally engineered to yield desired
22	robust gels. Tunable tensile strength, fracture strain and toughness of up to 19.6 MPa, 20000% and
23	135.7 MJ/cm ³ have been achieved, all exceed the best known records. The chemical nature of
24	intermolecular interactions involved in the self-assembly also enables self-healing capability and

high underwater stability. Our results demonstrate a universal strategy to synthesis libraries of super-robust hydrogels in a predictable and controllable manner. The superior simplicity, versatility and effectiveness of the present method hold great promise in industrial applications.

Hydrogels find broad applications in sensing⁷, energy storage⁸, smart materials⁹ and environmental 28 protection¹⁰. The mechanical property of hydrogels has great impact on their functions since real 29 30 devices usually work for extensive hours under load, impact or structural deformation. A stable 31 mechanical performance is the prerequisite to assure proper functioning. Nevertheless, native 32 structure of common hydrogel is not ideal to achieve high mechanical performance. Conventionally, hydrogels are hydrophilic polymeric networks that contain a significant portion of water¹¹. The 33 34 deficiency of solid materials making it difficult to form stiff structures. Meanwhile, the homogeneous texture does not support efficient energy dissipation¹². 35

36 To address the issue, a number of approaches have been proposed. One popular idea is to incorporate tensile-resistant units into hydrogel, such as micellar crosslinkers^{3,13}, force responsive 37 groups⁴, peptide crosslinkers¹⁴, covalent organic frameworks¹⁵, and ionic crosslinking points that 38 are usually found in double network hydrogels^{16,17}. During structural deformation, the tensile-39 40 resistant units are subject to quick chemical changes, which absorbs energy and converts into a 41 more extended state. Alternatively, introducing structural heterogeneity via molecular rearrangement is another feasible solution. Phase separation^{5,18}, partial polymer crystallization^{6,19} 42 and polymer alignment^{20,21} could take place during thermal annealing, freezing-thawing and 43 44 geometric constraint, leading to heterogeneous texture in the hydrogel. The stiffer portion in heterogeneous gels sustains the majority of stress while the softer portion dominates the 45 deformation^{12,22}. Such a combination results in simultaneous improvement in elasticity, strength, 46 and toughness. By employing multiple types of strengthening method, it is possible to further boost 47 48 the comprehensive property of hydrogels^{23,24}.

49 Nevertheless, many limitations still exist for current methods. The development of tensile-resistant groups usually requires extensive organic synthesis, which causes increased experimental 50 51 complexity and cost. Post-fabrication treatment is a necessity for the rearrangement of polymers 52 and the formation of most double network hydrogels. Not only does it consume additional time, 53 but it also has compatibility issues with certain samples. Bulky, mechanically unstable and 54 irregularly shaped objects, for example, would be very difficult to treat properly. Due to the irreversible nature of many force responsive groups and treating processes, a great portion of 55 existing ultra-tough hydrogels don't possess self-healing abilities, which has negative impact on 56 57 their working lifetime and long-term mechanical stability. Last but not least, previous ultra-tough 58 hydrogels were all developed in a try-and-error base. There lacks a universal strategy to correlate 59 the mechanical behavior and recipe of a hydrogel so as to rationally modulate its performance to 60 meet arbitrary needs.

Weak things united become strong. Here we devised a revolutionary strategy to obtain ultra-tough 61 62 hydrogels. By mixing hydrogen donor and acceptor with certain morphological features, unique 63 hierarchical architectures could be established in one-pot reaction driven by intermolecular self-64 assembly. Material characterizations revealed the as-prepared hydrogels consisted of three levels 65 of tightly coupled components that were able to withstand extreme stress and strain via hierarchical energy associative dissipation (HEAD). Combining experiments and simulations, structure-66 67 property relationships were established to guide the design of HEAD gels. It was possible to tune the mechanical performance of HEAD gels across a magnificent range by a predictable manner and 68 69 achieve record-breaking results. The self-healing ability, as well as underwater stability of HEAD 70 gel was also investigated to demonstrate their superior robustness.

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72 The formation and characteristics of HEAD gels

73 HEAD gels were obtained through spontaneous formation of hierarchical structures during the 74 curing and aging of precursors (Fig. 1a), which was driven by synergically worked intermolecular 75 interactions including hydrogen bonding, hydrophobic association, etc. This fabrication strategy is 76 distinctive from all previous ones as it only involves the self-assembly of macromolecules and 77 doesn't rely on new synthetic routes or post-fabrication treatment. In fact, HEAD gels could be 78 made from very simple reactants, such as acrylic acid and N,N,N',N'-tetramethylethylenediamine. 79 A wide variety of other species also worked, whose structures and corresponding recipes (A1-C2) 80 were included in Fig. S1 & Table S1.

81 A HEAD gel typically involved three levels of self-assembly, namely hydrogen bonding, 82 hydrophobic association and supramolecular clustering (Fig. 1a). Hydrogen bonding was the very first interaction formed between macromolecules. Carboxyl groups on the polymer chain acted as 83 84 hydrogen donors and amine groups were hydrogen acceptors. As multiple hydrogen bonds were established, the relative position and configuration of certain segments of polymers would be fixed, 85 yielding a 'core' to guide further self-assembly. Hydrophobic groups brought within an appropriate 86 87 distance started to associate and shape polymer chains into individual hydrophobic domains, e.g. densely packed granular phases. Multiple hydrophobic domains might aggregate via 88 89 supramolecular interactions and form the ultimate advanced structure.

90 The existence of structural heterogeneity could be visualized by fluorescent microscopy (Fig. 1b).
91 Network patterns presented in HEAD gel, whose threads were composed of micron-sized grains.
92 Compared with surrounding area, the network was much brighter, indicating a higher density in
93 organics. Such a discovery was verified by SEM (Fig. 1c). A number of nano-sized granules and
94 their clusters had been observed, which corresponded to the hydrophobic domains and the advanced
95 structure.

96 With the presence of hierarchical structure, HEAD gel was able to achieve superior toughness. First,

97 it is necessary to simultaneously overcome all three levels of chemically interlocked interactions to

98 finally break the material, which demands great energetic input. In addition, the intermolecular 99 interactions were all reversible in nature. Their dynamic regeneration during mechanical 100 deformation would consume even more energy, making the gel extremely difficult to destroy. 101 Tensile test (Fig. 1d) revealed that HEAD gels could reach extraordinary tensile strength (19.6 MPa) 102 and elasticity (strain level of ~8000%). In comparison, conventional homogeneous hydrogels with 103 chemical crosslinkers had much poorer properties^{2,25}.





Fig. 1 Formation of HEAD gels. a. Scheme showing the formation mechanism and characteristic structure of HEAD gels. Black arrows point to the position of bidentate hydrogen bonding. b. A representative microscopic image of HEAD gel. Inset: a magnified image of a single thread. c. A representative SEM image of HEAD gel. Inset: a locally magnified picture of c. d. Representative tensile curves showing the extraordinary strength and elasticity of HEAD gels.

111 Design appropriate core component in HEAD gels

To prepare HEAD gels, the reaction system should be designed following specific principles. The 112 113 most preferred hydrogen bonding existing between polyacid chains and amines involved 1,2-114 diamine unit (Fig. 2a). Polyacid chains were formed through the radical polymerization of acrylic 115 acid and its derivatives. Therefore, the carboxyl groups were evenly separated by three carbon 116 atoms. The specific geometry of polyacid chains and 1,2-diamine moiety allowed them to 117 efficiently associate into a zipper like core (z-core). When their association was partially destructed, 118 molecular rotation could quickly rebuilt the bonding at a neighboring position, leading to sliding, 119 instead of dissociation, among polymers (Fig. 2b-2c). This working process was similar to that of 120 actual zippers, with carboxyl groups acting as the teeth and 1,2-diamine as the slider. Such a 121 construction could tremendously enhance the ductility of hydrogels.

122 The necessity of having 1,2-diamine unit had been studied. Mixing MAAc and TEMED were able to yield HEAD gels. When TEMED was replaced by TMA, no gel would form (Fig. 2d). Increasing 123 124 the distance between amine groups also led to a quick drop in gelation efficiency. For example, it is possible to prepare MAAc based HEAD gels using 0.46 mol/L EDA. Employing BDA and HDA 125 126 of the same concentration resulted in incomplete and almost no gelation, respectively (Fig. 2d). The results demonstrated that 1,2-diamine unit yielded the most stable z-core. Compared with 127 128 monodentate amines, diamine unit bound polyacid chains with a much higher strength owing to the chelation effect²⁶. The greater binding affinity of EDA to polyacid chains over BDA and HAD had 129 been attributed to the chelation ring size effect^{27,28}. With the increase in size of chelation ring, the 130 131 relatively fixed binding geometry became more and more entropically unfavorable. Additional tests 132 demonstrating the geometric adequacy of 1,2-diamine structure were included in Extended Data Fig. 1. It is worthwhile to note that the diamine unit has to be incorporated into polymers so that 133 134 the z-core could function as a crosslinker. This might be readily achieved during radical

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polymerization, as demonstrated by previous researches^{29,30} (Extended Data Fig. 1). In contrast, no
gel would form if only free amines were added (Extended Data Fig. 1). The number of polymers
attached to the amine was not critical to gelation. Therefore, all schemes in this manuscript only
showed one possible structure.

139 The establishment of z-core was also affected by several other factors. The strength of hydrogen bonds could be enhanced by adding electron withdrawing groups on hydrogen donors, which 140 141 greatly facilitated the formation of z-core. Hydrophobic groups in the vicinity of hydrogen bonds 142 could serve as a shield to repel water and improved the stability of z-core. MD simulations (Fig. 143 2e) showed that compared with pAAc, diamine unit bound to pFAAc more tightly, as demonstrated 144 by simulated molecular configurations and the radial distribution g(r) of N-O distances (r). A 145 similar phenomenon was observed when methyl groups were on the amine. Two well-resolved 146 peaks with the shortest r values showed up, indicating the formation of tight and regular hydrogen binding. Our experimental results well matched the simulations (Fig. 2f). When the concentration 147 of acidic monomers and amines was constant, FAAc-EDA system and AAc-TEMED system could 148 149 be cured. In contrast, AAc-EDA based precursor wouldn't solidify. It was also noted that the 150 efficiency of gelation generally increased with the number of methyl groups (Fig. 2f). MMED 151 showed a better gelation efficiency than DMED, which further confirmed the presence of bidentate hydrogen bonding (Fig. 2a). Adding methyl groups to only one of the amines wouldn't improve 152 153 binding strength much. Importantly, hydrophobic groups on the acidic monomer had to attach to the same carbon as the carboxyl group otherwise an energetically unfavorable configuration would 154 155 form (Extended Data Fig. 2).

The conformation of diamine significantly affected reaction dynamics. When cis- and trans-CHDA were used to prepare HEAD gels, trans-CHDA containing precursor cured at least 2 times faster than the cis-CHDA containing ones (Fig. 2g). Apparently, the trans-conformation better matched the most probable configuration of the polyacid chain. Meanwhile, polyacid chains could change their configuration via rotating C-C bonds to fit cis-CHDA. As a result, both reagents were able to yield HEAD gels and the products exhibited similar appearance (Fig. 2h). Tensile tests revealed that trans-CHDA containing gels were more flexible while their cis-CHDA containing counterparts were harder (Fig. 2i). This was also attributed to the reason that trans-diamines facilitated the dynamic regeneration of z-core due to a higher matching degree in geometry. In comparison, cisdiamines tended to induce molecular rearrangement and lead to more heavily entangled, rigid polymer network.

167 It is easy to imagine that hydrogen acceptors with multiple diamine units could greatly boost the 168 overall strength of hydrogen bonding. For example, when AAc was mixed with EDA, DETA and 169 PEHA, the latter two precursors were able to get cured at an amine concentration of 0.46 mol/L 170 while the EDA containing precursor remained uncured (Extended Data Fig. 2).



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Fig. 2 Principles to design z-core. a-c. Scheme showing the origin of ductility of z-core. d.
Pictures of several precursors after incubation. Top: M1 and M18. Bottom: M4, M13 and M14. e.
Snapshots of simulated structure and radial distribution of N-O distances of three representative
systems. f. Pictures of several gel precursors after incubation. From left: F1, A1, A13, A14, A15
and A17. g. Measured curing time as a function of added amine. h. Pictures of cis- (M57-M61) and
trans-CHDA (M62-M66) gels with different amount (µL) of amine. i. Differences in the tensile
behavior of cis- (M61) and trans-CHDA (M66) gel.

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180 Engineer phase separation and supramolecular self-assembly in HEAD gels

181 The z-core shortened the relative distance among polymers thus enabled further hydrophobic interactions and phase separation. Neighboring hydrophobic moieties could associate tightly and 182 rearrange polymer chains, yielding different phases inside the hydrogel. This process was highly 183 184 dependent on the concentration of amines (Fig. 3a). At low amine concentrations, no phase separation took place and the hydrogel looked clear (Fig S2a). As the amine concentration increased, 185 186 submicron-sized hydrophobic domains appeared, which turned the gel into an opaque appearance due to light scattering. If the concentration of amine kept growing, hydrophobic domains would 187 disappear (Fig S2b). The phase separation was confirmed by both microscopic and SEM 188 characterizations (Fig. 3b-3c). Fluorescent image indicated that hydrophobic phases had a higher 189 190 material density, as revealed by their brighter color. Each individual hydrophobic domain was a 191 few hundred nanometers in diameter. Time-lapsed structural evolution could be told by 192 spectroscopy (Fig. 3d). Precursor with moderate amine concentrations underwent a quick drop in 193 transmission after its solidification. In comparison, other systems remained transparent.

194 The amine-concentration dependence of phase separation was attributed to the following reasons195 (Fig. S2). When amine concentration was low, the number of z-cores was not sufficient to bring

196 the majority of hydrophobic moieties into close contact to trigger phase separation. As the amine 197 concentration increased, polymeric rearrangement and phase separation happened spontaneously. Notably, hydrophilic shells were required to stabilize hydrophobic phases in aqueous media^{31,32}. At 198 199 high amine concentrations, free carboxyl groups were too rare to cover hydrophobic cores. Besides, 200 the pH of precursor rose at high amine concentrations (Fig. S3), leading to ionic COO⁻⁺NR₃ 201 bonding that was prone to hydrolysis. FT-IR spectra showed as the amine concentration increased, 202 the intensity of carboxyl C=O stretching (1698 cm⁻¹) got reduced while the asymmetric (1562 cm⁻¹) ¹) and symmetric (1398 cm⁻¹) COO⁻ stretching became stronger (Fig. 3e). Meanwhile, the spectral 203 variation within 960-1124 cm⁻¹ showed a distinctive trend, whose magnitude exhibited obvious 204 205 correlations with the presence of phase separation (Fig. 3a). This spectral region mainly contained C-N stretching, N-H rocking and C-O-H bending bands^{33,34}. The phenomenon above indicated 206 207 interactions between carboxyl groups and amine groups were likely strengthened due to denser 208 molecular packing in hydrophobic domains.

The phase separation was also regulated by other factors. Extending the length of amine would dramatically enhance the tendency of phase separation (Fig. 3f). Having electron withdrawing groups or hydrophobic groups on the polyacid chain helped broaden the phase separation window while hydrophobic groups on the amine narrowed it down (Extended Data Fig. 3). The corresponding mechanism was described in supplementary information. Additional IR tests revealed enhanced bands within 960-1124 cm⁻¹ were generally seen when obvious phase separation happened, regardless of the composition of hydrogel (Extended Data Fig. 3).

The presence of hydrophobic domains was not a necessity for successful gelation. However, it significantly boosted the mechanical strength (Fig. 3g). Compared with transparent gels, opaque gels possessed a much higher tensile strength. The mechanical properties of opaque gels, in comparison, didn't vary as significantly.



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221 Fig. 3 Phase separation in HEAD gels. a. A picture of AAc gels with various amount (µL) of TEMED addition (A16-A26). b. Fluorescent image of A20 gel (60 in a). c. SEM images of A20 222 223 gel (60 in a). d. Timed lapsed transmission of several AAc gels in a. Black arrows indicate the completion of gelation. e. IR spectra of several AAc gels in a. The 960-1124 cm⁻¹ region locates 224 225 between red dashed lines. f. Amine concentrations suitable for phase separation for AAc-EDA, -DETA, and PEHA systems. g. Tensile tests and corresponding pictures of several FAAc hydrogels. 226 227 Under proper amine concentrations, the hydrophobic phases might further assemble into advanced structures via supramolecular interactions (Extended Data Fig. 4). Several types of advanced 228 229 structures had been identified, including giant agglomeration, uniform porous network and hetero-230 porous network (Fig. 4a1-b3). The uniform porous network featured pores of similar sizes (Fig. 231 4a2 & 4b2) while the hetero-porous network had diversified pore sizes from tens of microns (Fig.

4a3) to a few micrometers (Fig. 4b3). Regardless of their morphology, advanced structures were
all composed of tightly associated hydrophobic domains. The presence of advanced structures
further enhanced the toughness of HEAD gels (Extended Data Fig. 4) since energy had to be
consumed to destroy them.

Compared with z-core and hydrophobic domains, advanced structures had a much slower formation dynamics due to the enormous groups participated in self-assembly (Fig. S4). Consequently, their mechanical behavior showed an obvious dependence on deformation rate (Fig. 4c). Upon prompt stretching, a sharp stress peak showed up at very low strain, followed by a clear drop in stress at moderate strains. As the strain kept increasing, the stress finally reached up to maximum values. When the stretching speed slowed down, the initial stress peak became less significant while the measured fracture strain rose.

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244 Synergize energy dissipation pathways to yield desired products

245 In order to achieve desired comprehensive properties, it is critical to balance and synchronize the 246 energy dissipation in each level of self-assembled units. Ideally, z-core could slide along polymer 247 chains as long as there was single-molecular continuity, leading to almost infinite flexibility. However, the strength of z-core was very tiny because of the limited number of hydrogen bonding. 248 249 The strength of hydrophobic domains and advanced structures were much greater due to the vast 250 number of intermolecular interactions within them. Meanwhile, their flexibility was weakened because those characteristic interactions only took effect in localized range^{35,36}. To withstand large 251 252 deformation, multiple hydrophobic domains or advanced structures had to unite properly. The mechanical behavior of HEAD gels could be represented by a spring model (Fig. S5). 253

A matched hydrophobicity among hydrogen donors and acceptors resulted in higher strength.
 According to law of matching water affinity^{37,38}, such a combination was energetically favorable

and stable. Dissimilar hydrophobicity of hydrogen donors and acceptors caused reduced strength,
but might greatly enhance the elasticity. In this case, intermolecular interactions were more
dynamically reversible and grouped different energy dissipation units efficiently so structural
deformation could be transferred across the entire material. For example, the ultimate strength of
AAc-EDA gel and MAAc-TEMED gel were much greater than AAc-TEMED gel and MAAc-EDA
gel, respectively. In contrast, their fracture strain showed an inverse trend (Extended Data Fig. 5).

To obtained superior comprehensive property, matched and unmatched hydrophobicity should be simultaneously introduced (Fig. 4d). Employing hydrogen acceptors with alternating hydrophobic and hydrophilic segments was one possible solution. MAAc-TEDETA based HEAD gels were found to be much tougher than MAAc-TEEED gels (Extended Data Fig. 5). Alternatively, using partially substituted amines, such as cis-CHDA and trans-CHDA would also work. In this case, the substitutional group had to be relatively bulky so that the hydrophilic side and hydrophobic side were chemically distinguishable.

269 When the hydrophobicity of reactants was fixed, altering the number of 1,2-diamine unit in amines 270 would significantly influence the comprehensive property. Apparently, this factor primarily 271 affected the multivalency of hydrogel bonding, which determined the strength and mobility of z-272 core. The longer the amine was, the stronger and more stretchable the z-core behaved. For hydrophilic reactants, the major contribution of toughness came from hydrogen bonding (z-core). 273 274 Therefore, extending the length of amine led to increased strength, elasticity, and toughness (Fig. 275 4e). For hydrophobic systems, the ultimate toughness was largely determined by hydrophobic 276 interactions. Therefore, the length of amine slider didn't necessarily enhance strength. However, 277 the elasticity of gel could still be improved (Extended Data Fig. 5).

Of course, simultaneously increasing the concentration of all reactants improved mechanicalproperties. This improvement was not universal, but focused on tensile strength more than elasticity

280 (Extended Data Fig. 5). A flow chart describing how to formulate desired HEAD gel was shown in



281 Fig. S6.

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Fig. 4 Engineer advanced structures and the performance of HEAD gels. a1-a3. Fluorescent images of different advanced structures (M37, M27 and F14). b1-b3. Fluorescent images of different advanced structures (M37, M27 and F14). Inset: magnified SEM images. Scale bars: 1 μm. c. Tensile behavior of M52 gel as a function of stretching speed (mm/min). d. Structural characters desired for high comprehensive properties. Red and blue circles indicate hydrophobic and hydrophilic segments. e. Tensile behavior of HEAD gels as a function of the length of amine (A51, A53 and A54).

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291 Robustness, tunability, self-healing and underwater stability

The greatest advantage of HEAD gels lay in their highly predictable, well-modulated mechanical properties. By doing a rational design according to previously mentioned principles, libraries of gelatinous materials with superior comprehensive properties could be readily obtained.

295 Tensile tests of representative HEAD gels were summarized in Fig. 5a. Combining MAAc and cis-296 CHDA yielded extremely hard gels with a tensile strength of 19.6 MPa, strain level of 540% and 297 toughness of 81.8 MJ/cm³. Lowing the concentration of cis-CHDA led to samples with superior 298 comprehensive properties, whose tensile strength, strain level and toughness were 14.5 MPa, 1310% and 135.7 MJ/cm³, respectively. By replacing cis-CHDA with trans-CHDA, HEAD gels with 299 300 balanced hardness and elasticity was fabricated. The tensile strength, fracture strain and toughness 301 was 6.7 MPa, 2360% and 98.7 MJ/cm³. AAc-PEHA gels exhibited great ductility, whose fracture 302 strain reached 7950%. The corresponding tensile and toughness was 632 kPa and 29.3 MJ/cm³.

303 HEAD gels outperformed the majority of known natural polymers as well as synthetic hydrogels in their comprehensive mechanical performance (Fig. 5b)^{3,6,13,14,16,18,39-43}. For example, HEAD gels 304 could reach a comparable toughness as spider silk, but was 40 times more flexible. Moreover, the 305 306 mechanical property of HEAD gels could be tuned in a record-breaking scope (Fig. 5c). The tensile 307 strength and fracture stain was able to vary across 0.04-19.6 MPa and 150%-20000% (Extended 308 Data Fig. 6), respectively, which had never been achieved before. Correspondingly, HEAD gels could satisfy almost arbitrary demands on tough hydrogels. Notably, the entire strain-stress curve 309 310 of the most stretchable HEAD gels were not able to be recorded completely by available instrument 311 (Extended Data Fig. 6). Manual tests demonstrated the strain level of those gels exceeded 20000% 312 (Fig. 5d & Video S1). The final diameter of deformed region could be as thin as $\sim 60 \mu m$, which equaled to a >2000 time shrinkage compared with the original cross-section (3 mm \times 2 mm). The 313 314 great toughness of HEAD gels might also been demonstrated by poking trials (Fig. 5e). As can be 315 seen, a 0.5 mm thick film made by AAc and PEHA could withstand extremely concentrated deformation. Drop-ball tests (Fig. 5f & Video S2) revealed that a falling ball of 0.82 J kinetic energy
could be easily captured by the film.

318 Another merit of HEAD gel was its self-healing ability. The hierarchical network was founded on reversible physical interactions, which allowed it to spontaneously recover from damages. As 319 320 shown in Fig. 5g, freshly sliced hydrogel pieces could recombine into continuous material in hours. 321 The bonding strength at interfaces in self-repaired material was strong enough to withstand extreme 322 stretching (e.g. >20000%). Tensile test (Fig. 5h) revealed that the recovered gel maintained up to 100% of its original strength and toughness. The optimal self-healing conditions varied among 323 different gels, which were summarized in Table S2. Self-healing ability is known to be critical to 324 325 practical applications, which extended the lifetime and stability of hydrogel materials⁴⁴. Many 326 previously developed ultra-tough hydrogels didn't possess such a capability due to the application 327 of irreversible chemical crosslinks or phase separation.

Conventional hydrogels severely lost mechanical strength in water due to swelling⁴⁵. The unique structure and compositional simplicity of HEAD gels made them highly stable under water. First, the hydrophobic domains were able to protect vulnerable z-cores from hydrolysis. In addition, HEAD gels didn't rely on external chemicals (e.g. salts) to maintain the structural heterogeneity therefore had little risk of material leaching in water. As shown in Extended Data Fig. 6, the mechanical toughness of HEAD gels varied little before and after soaking, which was strong enough to support objects that were more than 16000 times of their own weight (Fig. 5i & Fig. S8).



336 Fig. 5 Extraordinary performance of HEAD gels. a. Tensile curves of representative HEAD gels. **b.** Strain level and toughness of ultra-tough hydrogels prepared by different methods. **c.** Tunability 337 in fracture strain and stress (the encompassed area) of ultra-tough hydrogels prepared by different 338 methods. d. Pictures showing the superior ductility of HEAD gels (A56). e. Pictures of a poking 339 test of A54 gel. Scale bars: 2 cm. f. Pictures of a drop-ball test of A54 gel. g. The self-healing of 340 A56 gel. h. Tensile curves of pristine and self-repaired (SR) HEAD gels. i. Pictures showing a 3.2 341 g M53 gel scaffold (pointed by the arrow) can support a 50 kg person. Insets: pictures of the scaffold 342 343 sandwiched between two boards. Scale bar: 2 cm.

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345 Conclusion

346 In summary, a revolutionary strategy to construct ultra-tough hydrogels had been demonstrated. Unlike previously developed counterparts, HEAD gels were founded on hierarchical self-347 348 assemblies that were able to dissipate energy in a synergic way. Experimental investigations 349 confirmed HEAD gels consisted three levels of energy dissipation units, namely the z-core, the hydrophobic phase and the advanced structures, each of which possessed distinctive morphological 350 351 features and mechanical behaviors. By properly balancing the contribution of three components, record-breaking tensile strength, fracture strain and toughness of 19.6 MPa, 20000% and 135.7 352 MJ/cm³ had been achieved. 353

354 The present method exhibited several advantages over existing fabrication techniques for ultra-355 tough hydrogels. First, it only took an adequate mixing of reactants to obtain HEAD gels. No 356 additional synthetic reactions or post-fabrication treatment was required. The great operational 357 simplicity allowed HEAD gels to be prepared at high efficiency, low cost at arbitrary facilities by lightly trained personnel, which was ideal for industrial production. HEAD gels possessed peerless 358 tunability in mechanical properties and could serve as a universal solution for almost every existing 359 360 demands in tough hydrogels. This avoided the try-and-error based developing protocol for hydrogel precursors and could save tremendous research time. Through the combination of self-healing 361 362 ability, underwater stability and superior toughness, HEAD gels were extremely robust, which held great promise for practical applications under extreme serving conditions. Last but importantly, the 363 364 mechanical behavior of HEAD gels could be well predicted and well via clear rules. Further improvement of HEAD gels might be significantly facilitated under the guidance of those principles. 365 366 Therefore, it is expected that HEAD-gel system is full of potentials and can evolve constantly with 367 the progresses on material sciences.

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Methods

Materials

Methacrylic acid (MAAc, 99%), acrylic acid (AAc, 99%), crotonic acid (CAc, 98%), acrylamide (AAm, 99%) and dimethylsulfoxide (DMSO, ≥99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Ethylenediamine (EDA, >98%), 2-fluoroacrylic acid (FAAc, 98%), N,N,N'trimethylethylenediamine (DMMED, 98%), hexamethylenediamine (HDA, 98%), N,N'methylenebisacrylamide (Bis. 99%). ammonium persulfate (APS, 99.99%), tetramethylethylenediamine (TEMED) and fluorescein O-methacrylate (97%) were purchased from Beijing MREDA Technology Co., Ltd. Trimethylamine (TMA, 98%) and N,N'-dimethyl-1,2ethanediamine (MMED, 98%) purchased Chemical. were from Energy N.Ndimethylethylenediamine (DMED, 98%) N,N,N',N'-tetraethyldiethylenetriamine (TEDETA, \geq 97%), 1,4-diaminobutane (BDA, 98%), pentaethylenehexamine (PEHA, 98%) and diethylenetriamine (DETA, 99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Cis-cyclohexane-1,2-diamine (cis-CHDA, 98%) and trans-cyclohexane-1,2-diamine (trans-CHDA, 98%) were purchased from Bidepharm. N,N,N',N'-tetraethylethylenediamine (TEEED, 98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 98+%), N,N,N',N'tetramethyl-1,3-propanediamine (TEMPD, ≥98%) and N,N,N',N",N"pentamethyldiethylenetriamine (PMDETA, ≥98%) were purchased from Shanghai D&B Laboratory Equipment Co., Ltd. Methenamine (HMTA, AR) was purchased from Sigma-Aldrich. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure819, 99+%) was purchased from Beijing Hawk Science & Technology Co., Ltd.

Sample preparation

Hydrogel samples were obtained by mixing curable acidic monomers with proper amines. Stock solutions were first prepared by dissolving acidic monomers in deionized water (18.2 M Ω /cm).

CAc stock solution needed to be prepared and maintained at 60 °C. To those stock solutions, a variety of amines were added, followed by the addition of a 10 wt.% APS solution to initiate insitu polymerization. Detailed recipes of all the precursors were listed in Table S1. The reaction mixtures were left untouched for 1-2 days to allow complete cuing and aging. For samples used in the mechanical tests, precursors were cast into various molds and cured to form desired shapes.

To demonstrate the necessity of incorporating 1,2-diamines into polymers, 3.94 M AAc stock solution was mixed with 10 wt.% APS to conduct polymerization. The precursor was incubated for 7 days before water and TEMED were added. The final composition of the mixture was the same as precursor A20, named as A20'. The mixture was left untouched for another 7 days to see if gelation happened.

Characterization methods

Microscopic characterizations were carried out on a Leica DM6 microscope. Hydrogels were molded into a \sim 60 µm thin layer prior to characterizations. To improve the visibility of hydrogels under microscope, fluorescein O-methacrylate was employed to label the samples. Fluorescein O-methacrylate was first dissolved in DMSO to yield a 50 mg/mL stock solution. This solution was then mixed with hydrogel precursors at a 1:100 volume ratio. After curing, the polymer chains were fluorescent labelled, whose structural details could be clearly seen under fluorescent imaging mode.

Infrared (IR) spectra of hydrogels were recorded by a FT-IR spectrometer in the total internal reflection mode (PerkinElmer B420). All samples were sliced into thin layers and completed dried prior to spectral measurements. The dried samples were then crushed into powders and tightly pressed onto the optical window of the spectrometer by an indenter.

The transmission spectra of hydrogels in the UV-Vis-NIR regime were recorded by a FLAME-S-XR1-ES spectrometer (Ocean Optics). Precursors of interest were injected into UV cuvettes with 1 cm path length and characterized in the transmission mode. Time-lapsed spectra were recorded. Fully cured samples with a maximum transmission below 10% was considered as 'having obvious phase separation'.

SEM characterizations were performed with a Nova NanoSEM 200 system. Prior to SEM analysis, all the sample was coated with a ~10 nm layer of gold by a metal evaporator (Bühler Leybold Optics) to improve the electrical conductivity.

Tensile tests were performed with an Instron 5948 Micro Tester. The stretching speed was set at 20 mm/min for regular mechanical characterizations, and varied according to experimental purpose in other tests. Drop-ball tests were performed with an ASR-2000A drop ball tester. A 55.5 g steel ball was released from 1.5 m above the membrane, whose kinetic energy at impact was 0.82 J.

Self-healing and underwater stability tests

To study the self-healing ability of hydrogels, samples of interest were cut into pieces by a razor blade, which were then gently pressed together to allow a tight contact. After incubating for a few hours, the self-healing results were examined by tensile tests. To speed up the self-healing process, heating at a mild temperature could be applied. Details of the appropriate self-healing temperature and incubation time were included in Table S2.

Underwater stability of HEAD gels was examined by first soaking freshly prepared gel samples in DI water for 24 h. The fully swollen gel was then subjected to tensile tests or other characterizations.

Molecular dynamics (MD) simulations

MD simulations were performed by Material Studio software. The chemical structure of H₂O and all the reactants are built separately. Molecules being simulated were packed into an amorphous unit cell with a density of 1.0 g/cm³ using COMPASS force field. The lattice parameters for each unit cell was $a=b=c\approx 20$ Å, $\alpha=\beta=\gamma=90^{\circ}$. Condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS force-field) were applied to calculate the interactions among various atoms.⁴⁶ The "geometry optimization" function in the "forcite module" was employed to minimize structural energy, in which the convergence tolerance was set at 1×10^{-4} kcal/mol for energy convergence, 5×10^{-5} Å for displacement and 0.005 GPa for stress. Geometric optimizations was running automatically to tune the molecular structures until the total energy of the unit cell met the preset parameters. All MD simulations had been investigated by NVE ensembles controlled by Berendsen and Andersen's thermostat. Every cubic cell is analyzed at 298 K for 50 ps.

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Author contributions Z.Z. conceived the project and performed material synthesis and characterizations. Y.L. carried out calculation studies. Y.S. performed SEM characterizations. Z.Z. H.W and M.W. carried out mechanical tests. Z.Z., X.Z. and X.S. directed the research. All authors contributed to the writing and editing of the manuscript.

Competing interests The authors declare no competing interests.

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Extended Data Fig. 1 Additional tests on the formation of z-core. a. Curing tests showing 1,2diamine (TEMED), rather than 1,1-diamine (HMTA) or 1,3-diamine (TEMPD), was the most preferred structure in HEAD gels. From left: A49, A20, A50, M44, M18, and M45. **b.** The reaction mechanism of incorporating diamines into the polymer. **c.** Scheme and picture showing free diamines won't cure the gel (A20' in Methods).



Extended Data Fig. 2 Additional principles to design z-core. a. Having hydrophobic groups and carboxyl groups on different carbons results in an energetically unfavorable configuration (dash circled region) with regularly aligned hydrophobic groups facing towards aqueous media. **b.** Pictures of MAAc and CAc based precursors after incubation, demonstrating the selectivity on position of hydrophobic groups. **c.** Pictures reflecting the effect of the number of 1,2-diamine unit on gelation.



Extended Data Fig. 3 Additional characterizations on phase separation. a-c. Suitable amine concentrations for phase separation (the 'opaque window') in various systems. d. Picture (from left: A2, A3, A4, A5, A6, A8, A9, A10, A11, A12) and the corresponding IR spectra of AAc gels with various amount (μ L) of EDA. e. Picture (from left: M2, M3, M4, M5, M6, M7, M8, M10, M11, M12) and corresponding IR spectra of MAAc gels with various amount (μ L) of EDA. f. Picture (from left: F10, F11, F12, F13, F14, F15, F16, F17, F18, F20) and corresponding IR spectra of FAAc gels with various amount (μ L) of TEMED. g. Picture (from left: M15, M17, M18, M19,

M20, M21, M22, M23) and corresponding IR spectra of MAAc gels with various amount (μ L) of TEMED. **h.** Picture (from left: M24, M26, M27, M28, M29, M30, M31, M33) and corresponding IR spectra of MAAc gels with various amount (μ L) of TEEED. **i.** Picture (from left: M34, M36, M37, M38, M39, M40, M41, M43) and corresponding IR spectra of MAAc gels with various amount (μ L) of TEDETA.



Extended Data Fig. 4 Formation of advanced structures and their influence on mechanical properties. a1-a3. Microscopic morphology of three MAAc-TEBETA gels (M34, M37 and M39). **a4.** Tensile curves of MAAc-TEBETA gels. **b1-b3.** Microscopic morphology of three MAAc-TEEED gels (M24, M27 and M29). **b4.** Tensile curves of MAAc-TEEED gels. **c1-c3.** Microscopic morphology of three FAAc-TEMED gels (F10, F14 and F16). **c4.** Tensile curves of FAAc-TEMED gels.



Extended Data Fig. 5 Strategy to tune the property of HEAD gels. a-b. Effect of matching water affinity. **c.** Effect of introducing matched and unmatched hydrophobicity. **d.** Longer amines enhanced the elasticity in relatively hydrophobic reaction systems, but showed little correlation with the strength. **e.** Effect of concentration of reactants.



Extended Data Fig. 6 Additional characterizations of HEAD gels. a-b. Additional tensile results. Note the maximum measurable strain was 15000% due to instrumental limit. **c.** Pictures of a stretched A56 gel. Material appeared to be sliding out of the shoulder and extended into extremely thin thread, demonstrating the role of z-core. **d.** Tensile curves of M47 gel before and after swelling. **e.** Tensile curves of A54 gel before and after swelling. **f.** Pictures showing the load-bearing capacity of the scaffold in Fig. 5i in both air and water.

Supplementary Materials for

Ultra-tough self-healing hydrogel via hierarchical energy associative dissipation

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Supplementary Text

1. The influence of substitutional group on phase separation

As demonstrated by experiments, having electron withdrawing groups or hydrophobic groups on the polyacid chain helped broaden the phase separation window while hydrophobic groups on the amine narrowed it down (Extended Data Fig. 3). This discrepancy in the effect of substitutional group was likely caused by the structural character of hydrophobic domains. When hydrophobic domain formed, the z-core acted as a seed to integrate a few hydrophobic segments, rendering a hydrophobic inner sphere. The remaining hydrophilic moieties on the polymer then intertwined the inner sphere to create a hydrophilic shell as a stabilization layer in aqueous media (Fig. S2c).

The substitutional group on the polyacid chain enhanced interactions in the inner sphere, therefore reduced the number of required acidic monomers to form a single hydrophobic domain. Consequently, phase separation happened across a broader acid:amine range. In contrast, enhancing the hydrophobicity of amines made them stronger seeds so phase separation could happen at low amine concentrations and each inner sphere contained more hydrophobic segments. This led to a quick consumption of polyacid chains. No sufficient building blocks would be available at high amine concentrations to enable phase separation.

2. A spring model of HEAD gel

The role of each energy dissipation structure during mechanical deformation could be expressed by a spring model, in which the spring constant $k_1 << k_2 < k_3$ (Fig. S5a). The z-core featured the largest elastic range but the smallest spring constant. Hydrophobic domains had moderate elasticity and strength while the advanced structure was strong but rigid. To survive in large stretching, multiple hydrophobic domains and advanced structures had to be tightly connected to share the geometric deformation.

When the system was in lack of hydrophobic interactions, z-cores dominated the mechanical behavior. Although they could withstand large deformation, their low strength made the gel very soft. In contrast, if hydrophobic interaction was too overwhelming, molecular interactions tended to be localized within individual unit so connections among units were lost. In this case, the gel was hard but had very poor ductility. To reach superior comprehensive properties, a chemically balanced network was desired in which the elastic range of united hydrophobic domains and advanced structures was roughly the same as that of z-core (Fig. S5b).

The stretching-speed dependency of mechanical properties (Fig. 4c) could also been explained by the spring model. Under a sudden stretch, advanced structures didn't have time to deform and behaved more like a rigid body (increased effective k_3), which reached a great peak stress at low strains. Keep extending the material led to the damage of a great portion of advanced structures (effective k_3 dropped), resulting in reduced stress. When a low stretching speed was employed, the advanced structures were given enough time to change their shapes and absorb energy. Therefore, they behave more like normal springs and helped achieve a higher elasticity.

3. Self-repair behavior of various HEAD gels

The optimal self-repair condition varied among different HEAD gels (Table S2). In general, softer and elastic gels healed at a faster speed under RT owing to their z-core dominated structure. Tougher gels involving heavy hydrophobic interactions, on the other hand, required a longer healing time at elevated temperatures. For example, A55 and A56 gels could completely recover from damage after a 4 h incubation at RT (Fig. 5h). A53 and A54 gels required a higher self-healing temperature (40 °C) and elongated incubation time (Fig. S7a). Harder gels such as M47 had very slow self-repair dynamic. To speed up the process, the wound was first transiently heated at about 240 °C for 3 s by a hot plate or iron. The heated area quickly turned clear, indicating the loss of phase separation. The samples were then incubated at 40 °C for 1 day during which new hierarchical structures would form. The as-obtain self-repaired samples possessed partially recovered properties, as shown in Fig. S7b.



Fig. S1 Reactive species tested in the preparation of HEAD gels. The green and red color indicate preferred and undesirable reactants, respectively.



Fig. S2 Amine-concentration dependent phase separation a1-a2. Additional fluorescent image of some gels in Fig. 3a. b1-b2. Additional SEM image of some gels in Fig. 3a. c-e. Schemes showing the phase separation process at low amine concentration (c), moderate amine concentration (d) and high amine concentration (e).



Fig. S3 Variation of pH as a function of added TEMED (μ L) for a series of AAc-TEMED precursors (Axx-Axx).



Fig. S4 Scheme showing the formation dynamics of different structural components.



Fig. S5 A spring model of HEAD gels. **a.** Spring model of each structural component under static condition. Black circles indicate strong connections between different units. **b.** Mechanical behavior of various HEAD gels explained by the spring model. Black circles indicate strong connections between different units.



Fig. S6 A flow chart describing the design strategy of HEAD gels.



Fig. S7 Additional self-healing tests. **a.** Tensile test of pristine A56 gel and self-repaired (SR) A56 gels incubated for 4 h and 24 h. **b.** Tensile results of pristine and SR M47 gel.



Fig. S8 Pictures of the M53 scaffold before and after load tests. No obvious damaged was observed.

Dasina	Hydrgen donor			Hydrogen a	cceptor	Water	10 40/
No	Name	Concentration	Volume	Name	Volume	water (nL)	10 WT% APS (111)
110.		(M)	(mL)		(µL)	(μL)	Μο (μL)
A1	AAc	3.94	1	EDA	13	187	100
A2	AAc	3.94	1	EDA	20	180	100
A3	AAc	3.94	1	EDA	30	170	100
A4	AAc	3.94	1	EDA	40	160	100
A5	AAc	3.94	1	EDA	50	150	100
A6	AAc	3.94	1	EDA	60	140	100
A7	AAc	3.94	1	EDA	65	135	100
A8	AAc	3.94	1	EDA	80	120	100
A9	AAc	3.94	1	EDA	100	100	100
A10	AAc	3.94	1	EDA	120	80	100
A11	AAc	3.94	1	EDA	140	60	100
A12	AAc	3.94	1	EDA	200	0	100
A13	AAc	3.94	1	DMED	21	179	100
A14	AAc	3.94	1	MMED	21	179	100
A15	AAc	3.94	1	DMMED	26	174	100
A16	AAc	3.94	1	TEMED	20	180	100
A17	AAc	3.94	1	TEMED	30	170	100
A18	AAc	3.94	1	TEMED	40	160	100
A19	AAc	3.94	1	TEMED	50	150	100
A20	AAc	3.94	1	TEMED	60	140	100
A21	AAc	3.94	1	TEMED	80	120	100
A22	AAc	3.94	1	TEMED	90	110	100
A23	AAc	3.94	1	TEMED	100	100	100
A24	AAc	3.94	1	TEMED	120	80	100
A25	AAc	3.94	1	TEMED	140	60	100
A26	AAc	3.94	1	TEMED	200	0	100
A27	AAc	3.94	1	DETA	15	185	100
A28	AAc	3.94	1	DETA	21	179	100
A29	AAc	3.94	1	DETA	30	170	100
A30	AAc	3.94	1	DETA	40	160	100
A31	AAc	3.94	1	DETA	50	150	100
A32	AAc	3.94	1	DETA	60	140	100
A33	AAc	3.94	1	DETA	80	120	100
A34	AAc	3.94	1	DETA	100	100	100
A35	AAc	3.94	1	DETA	120	80	100
A36	AAc	3.94	1	DETA	140	60	100
A37	AAc	3.94	1	DETA	200	0	100
A38	AAc	3.94	1	PEHA	15	185	100
A39	AAc	3.94	1	РЕНА	25	175	100

 Table S1. A list of all the recipes of precursor.

A40	AAc	3.94	1	PEHA	40	160	100
A41	AAc	3.94	1	PEHA	50	150	100
A42	AAc	3.94	1	PEHA	60	140	100
A43	AAc	3.94	1	PEHA	80	120	100
A44	AAc	3.94	1	PEHA	100	100	100
A45	AAc	3.94	1	PEHA	120	80	100
A46	AAc	3.94	1	PEHA	140	60	100
A47	AAc	3.94	1	PEHA	160	40	100
A48	AAc	3.94	1	PEHA	200	0	100
A49	AAc	3.94	1	HMTA	21	179	100
A50	AAc	3.94	1	TEMPD	67	133	100
A51	AAc	6.1	1	EDA	60	140	100
A52	AAc	6.1	1	TEMED	80	120	100
A53	AAc	6.1	1	DETA	60	140	100
A54	AAc	6.1	1	PEHA	80	120	100
A55	AAc	6.1	1	PMDETA	70	130	100
A56	AAc	6.1	1	PMDETA	80	120	100
M1	MAAc	3.94	1	TMA	70	130	100
M2	MAAc	3.94	1	EDA	20	180	100
M3	MAAc	3.94	1	EDA	30	170	100
M4	MAAc	3.94	1	EDA	40	160	100
M5	MAAc	3.94	1	EDA	50	150	100
M6	MAAc	3.94	1	EDA	60	140	100
M7	MAAc	3.94	1	EDA	80	120	100
M8	MAAc	3.94	1	EDA	100	100	100
M9	MAAc	3.94	1	EDA	110	90	100
M10	MAAc	3.94	1	EDA	120	80	100
M11	MAAc	3.94	1	EDA	140	60	100
M12	MAAc	3.94	1	EDA	200	0	100
M13	MAAc	3.94	1	BDA	60	140	100
M14	MAAc	3.94	1	HDA	78	122	100
M15	MAAc	3.94	1	TEMED	20	180	100
M16	MAAc	3.94	1	TEMED	30	170	100
M17	MAAc	3.94	1	TEMED	40	160	100
M18	MAAc	3.94	1	TEMED	60	140	100
M19	MAAc	3.94	1	TEMED	80	120	100
M20	MAAc	3.94	1	TEMED	100	100	100
M21	MAAc	3.94	1	TEMED	120	80	100
M22	MAAc	3.94	1	TEMED	140	60	100
M23	MAAc	3.94	1	TEMED	200	0	100
M24	MAAc	3.94	1	TEEED	20	180	100
M25	MAAc	3.94	1	TEEED	30	170	100
M26	MAAc	3.94	1	TEEED	40	160	100
M27	MAAc	3.94	1	TEEED	60	140	100

M28	MAAc	3.94	1	TEEED	80	120	100
M29	MAAc	3.94	1	TEEED	100	100	100
M30	MAAc	3.94	1	TEEED	120	80	100
M31	MAAc	3.94	1	TEEED	140	60	100
M32	MAAc	3.94	1	TEEED	160	40	100
M33	MAAc	3.94	1	TEEED	200	0	100
M34	MAAc	3.94	1	TEDETA	20	180	100
M35	MAAc	3.94	1	TEDETA	30	170	100
M36	MAAc	3.94	1	TEDETA	40	160	100
M37	MAAc	3.94	1	TEDETA	60	140	100
M38	MAAc	3.94	1	TEDETA	80	120	100
M39	MAAc	3.94	1	TEDETA	100	100	100
M40	MAAc	3.94	1	TEDETA	120	80	100
M41	MAAc	3.94	1	TEDETA	140	60	100
M42	MAAc	3.94	1	TEDETA	160	40	100
M43	MAAc	3.94	1	TEDETA	200	0	100
M44	MAAc	3.94	1	HMTA	21	179	100
M45	MAAc	3.94	1	TEMPD	67	133	100
M46	MAAc	6.1	1	EDA	80	120	100
M47	MAAc	6.1	1	TEMED	80	120	100
M48	MAAc	6.1	1	TEEED	90	110	100
M49	MAAc	6.1	1	TEEED	114	86	100
M50	MAAc	6.1	1	TEEED	140	60	100
M51	MAAc	6.1	1	TEDETA	80	120	100
M52	MAAc	6.1	1	TEDETA	90	110	100
M53	MAAc	6.1	1	TEDETA	100	100	100
M54	MAAc	6.1	1	TEDETA	110	90	100
M55	MAAc	6.1	1	TEDETA	120	80	100
M56	MAAc	6.1	1	HMTETA	73	127	100
M57	MAAc	6.1	1	cis-CHDA	30	170	100
M58	MAAc	6.1	1	cis-CHDA	40	160	100
M59	MAAc	6.1	1	cis-CHDA	50	150	100
M60	MAAc	6.1	1	cis-CHDA	60	140	100
M61	MAAc	6.1	1	cis-CHDA	80	120	100
M62	MAAc	6.1	1	trans-CHDA	30	170	100
M63	MAAc	6.1	1	trans-CHDA	40	160	100
M64	MAAc	6.1	1	trans-CHDA	50	150	100
M65	MAAc	6.1	1	trans-CHDA	60	140	100
M66	MAAc	6.1	1	trans-CHDA	80	120	100
F1	FAAc	3.94	1	EDA	13	187	100
F2	FAAc	3.94	1	EDA	20	180	100
F3	FAAc	3.94	1	EDA	30	170	100
F4	FAAc	3.94	1	EDA	40	160	100
F5	FAAc	3.94	1	EDA	60	140	100

F6	FAAc	3.94	1	EDA	80	120	100
F7	FAAc	3.94	1	EDA	100	100	100
F8	FAAc	3.94	1	EDA	120	80	100
F9	FAAc	3.94	1	EDA	150	50	100
F10	FAAc	3.94	1	TEMED	20	180	100
F11	FAAc	3.94	1	TEMED	30	170	100
F12	FAAc	3.94	1	TEMED	40	160	100
F13	FAAc	3.94	1	TEMED	50	150	100
F14	FAAc	3.94	1	TEMED	60	140	100
F15	FAAc	3.94	1	TEMED	80	120	100
F16	FAAc	3.94	1	TEMED	100	100	100
F17	FAAc	3.94	1	TEMED	120	80	100
F18	FAAc	3.94	1	TEMED	140	60	100
F19	FAAc	3.94	1	TEMED	170	30	100
F20	FAAc	3.94	1	TEMED	200	0	100
C1	CAc	3.94	1	TEMED	80	120	100
C2	CAc	3.94	1	TEMED	140	60	100

Recipe No.	Optimal temperature (°C)	Time	Recovery of toughness
A55	RT	4 h	~100%
A56	RT	4 h	~100%
A53	40	24 h	90%±9%
A54	40	24 h	90%±9%
M47	240	3 s	250/ + 50/
1014 /	40	24 h	5570±570

 Table S2. Summary on self-healing conditions.