Electronic Supplementary Information (ESI)

Molecular simulation, characteristic and mechanism of thermal-responsive acetylated amylose V-type helical complex

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1. Supporting methods

1.1. Materials

High amylose from corn, 1-methylimidazole, propofol and hexane were purchased from Aladdin Co., Ltd. (Shanghai, China). Iodine was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. acetic anhydride was purchased from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China).

1.2. The synthesis of acetylated amylose

The synthesis of acetylated amylose was according with literature early reported.[S1] Briefly, 2.0 g amylose dissolved in 100 mL DMSO at 0 °C for 30 min, then 195 μL of acetic anhydride and 164 μL of 1-methylimidazole were added. The reaction continued at 80 °C for 4 h. Finally, a large volume of ethanol was added into above reaction mixture and acetylated amylose was precipitated. The precipitate was centrifuged and washed twice with ethanol, and then dried at 50 °C to obtain acetylated amylose powder.

1.3. The preparation of acetylated amylose-guest V-type helical complex

100 mg acetylated amylose was dissolved in 20 mL pure water, then about 20 mg iodine, 20 μL propofol, 20 μL hexane or 20 μL 7-hydroxycoumarin solution (5 mg/mL) was added above solution, and then the mixture was stirred overnight. Finally, the complex solution was obtained by filtration using a 0.22μm filter.

2. Supporting data

Table S1.Strcuture parameters of acetylated amylose-guest V-type helix complex

Guest type	blank	iodine	propofol	hexane
Guest number	--	14	4	5
Diameter (nm)	1.477±0.064	1.248±0.034	1.211±0.064	1.338±0.077
Pitch (nm)	0.847±0.026	0.869±0.042	0.844±0.024	0.841±0.014

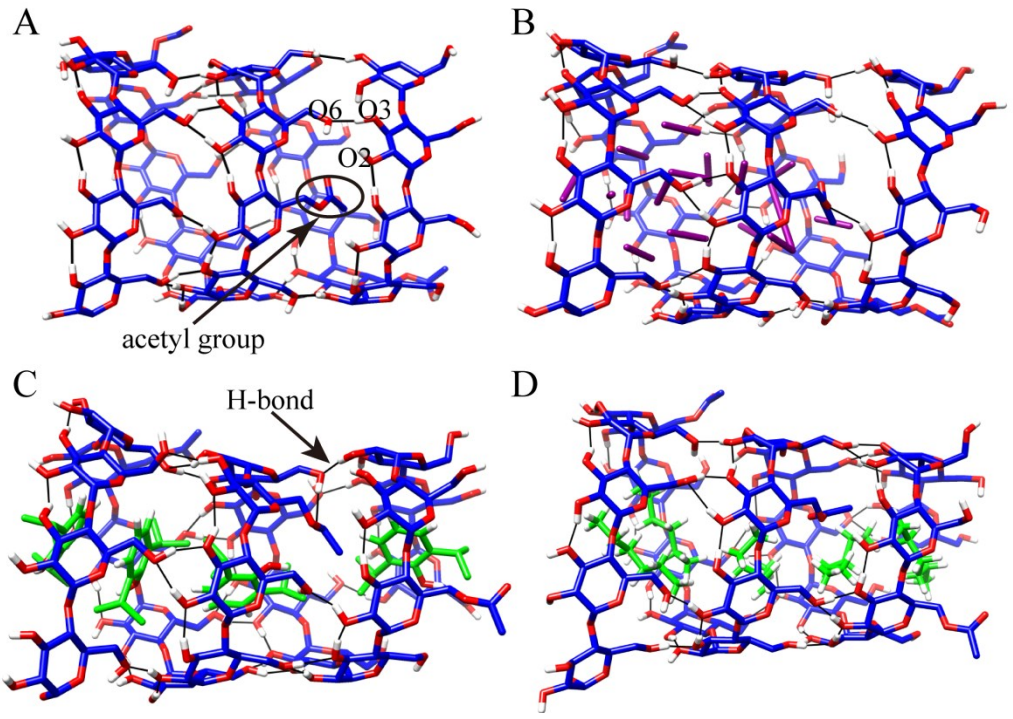

Fig. S1 Molecular structures of acetylated amylose V-type helical complexes. (A) Blank acetylated amylose helix; (B) acetylated amylose-iodine V-type helix complex; (C) acetylated amylose-propofol helix complex; (D) acetylated amylose-hexane helix complex.

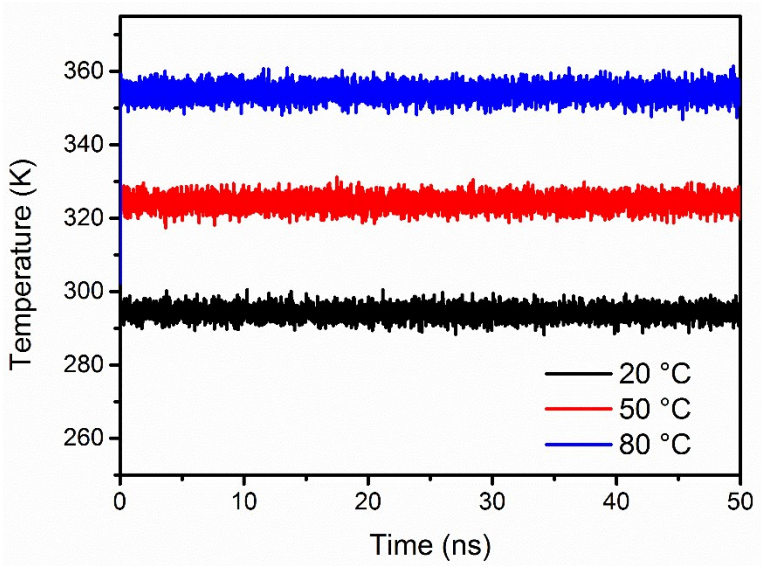

Fig. S2 The temperature fluctuation during molecular dynamic simulation.

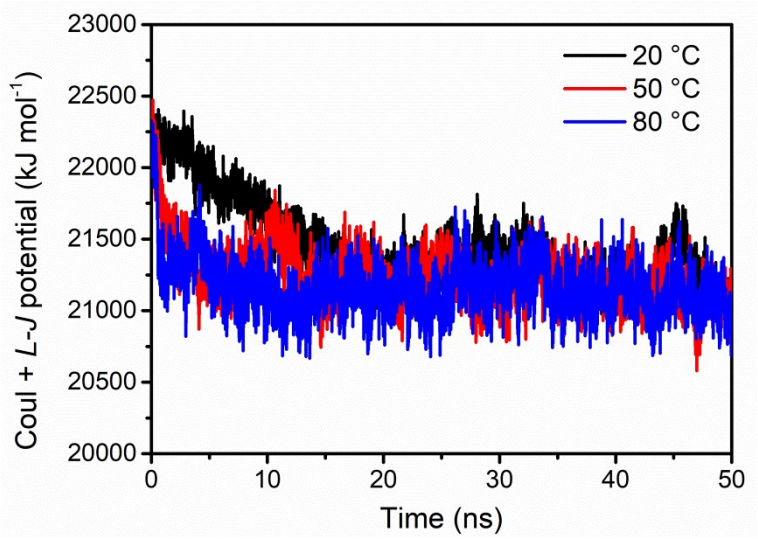

Fig. S3 The energy fluctuation (The sum of coulomb and *L-J* potential) of acetylated amylose during molecular dynamic simulation.

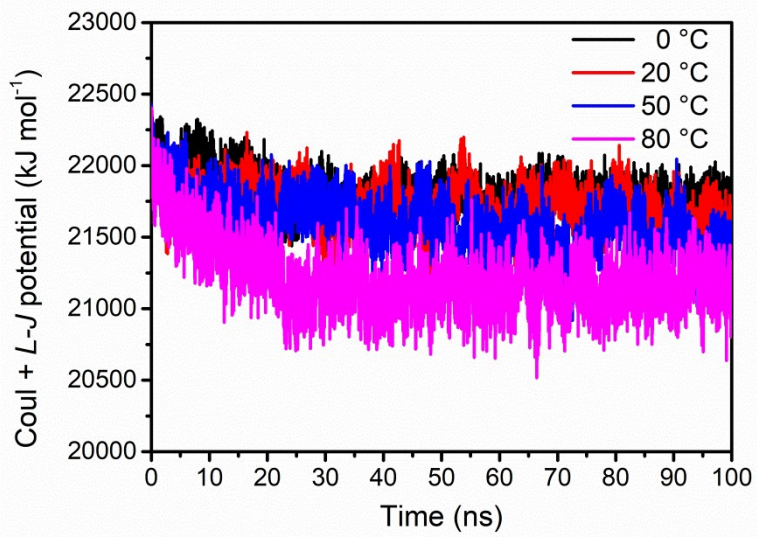

Fig. S4 Energy fluctuation of acetylated amylose in AAIHC during molecular dynamic simulation.

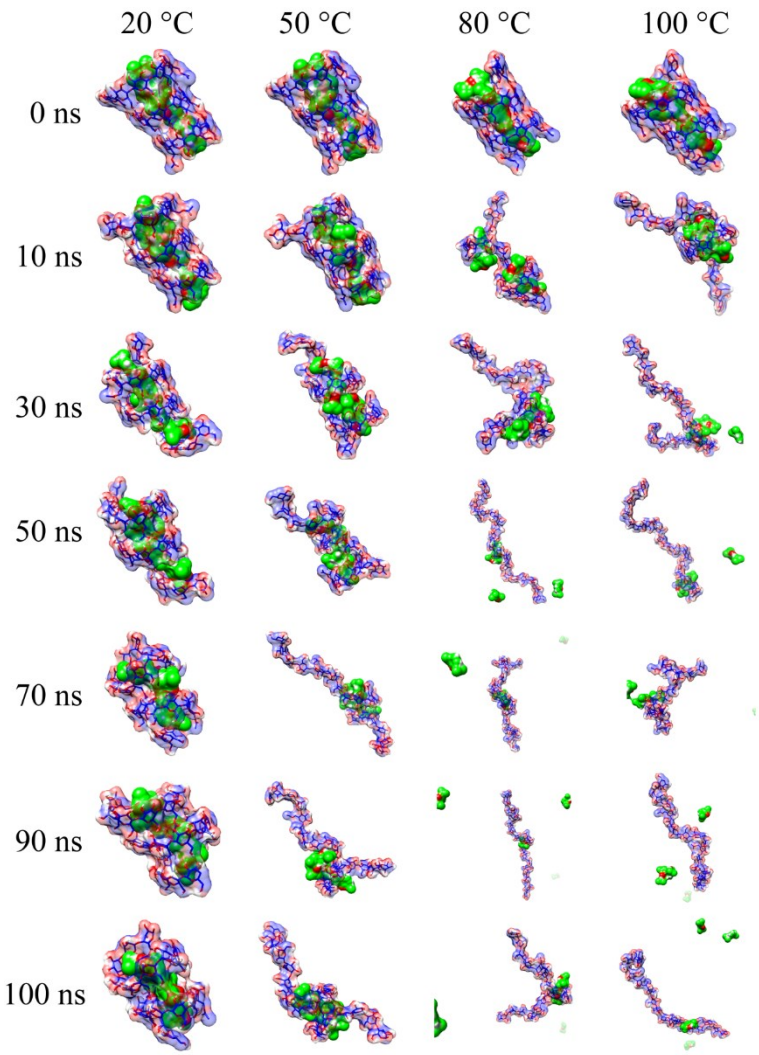

Fig. S5 Thermal-responding unfolding and releasing snapshots of AAPHC at different time-points.

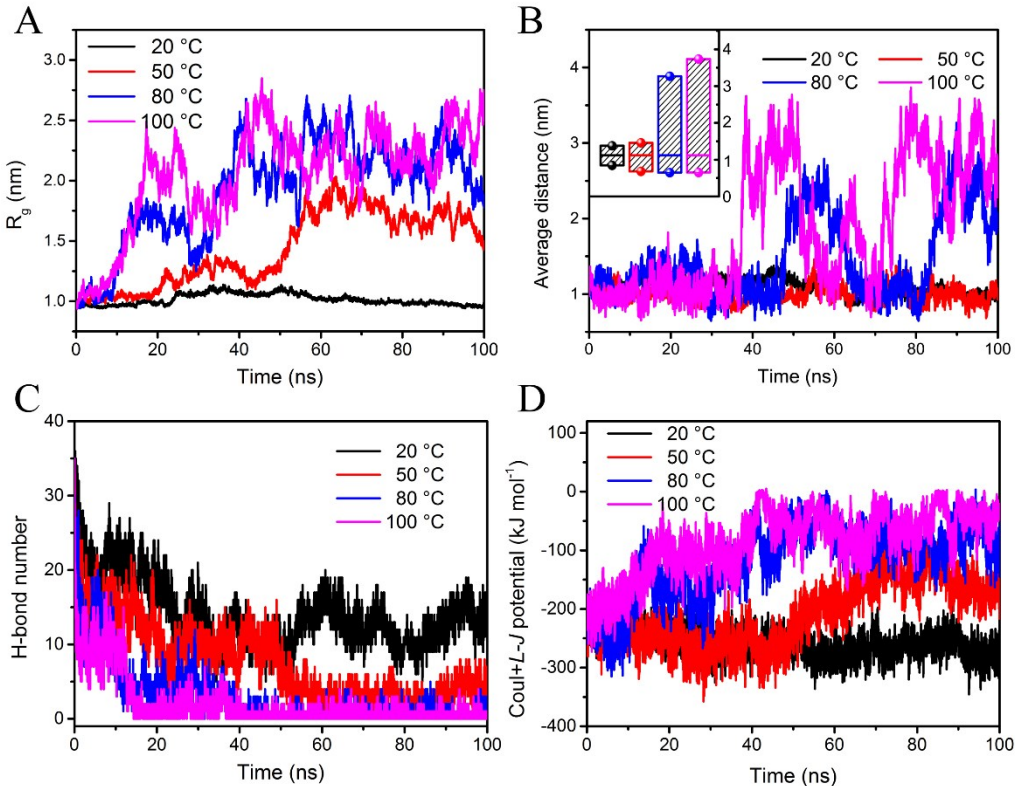

Fig. S6 Thermal-responsive helix-unfolding and guest-release characteristics in AAPHC. (A) The R_g of acetylated amylose in helix complex at different temperatures. (B) The average distance between propofol molecules and the center atom of acetylated amylose at different temperatures (inserted data is the maximum and minimum average distance at different temperatures). (C) The H-bond number of acetylated amylose-propofol V-type complex at different temperatures. (D) The binding energy between propofol molecules and acetylated amylose.

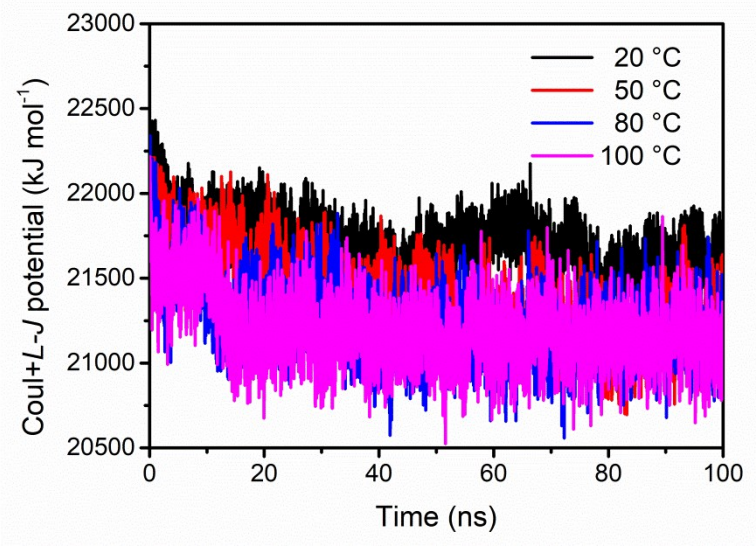

Fig. S7 Energy fluctuation of acetylated amylose in AAPHC during molecular dynamic simulation.

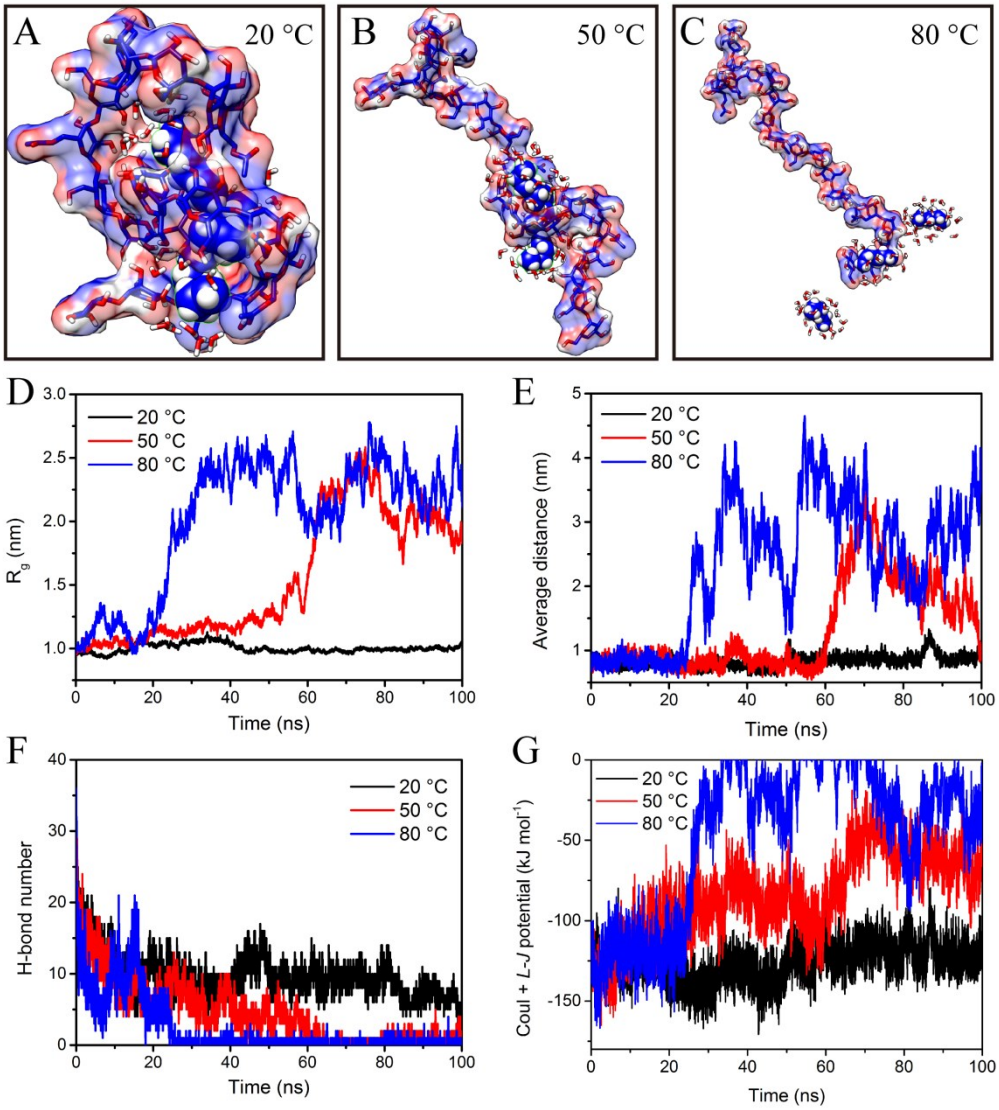

Fig. S8 Thermal-responsive helix-unfolding and guest-release characteristics in AAHHC. (A) The Rg value of AAHHC at different temperature. (B) The average distance between hexane molecules and the center atom of acetylated amylose at different temperature (inserted data is the maximum and minimum average distance at different temperature). (C) The H-bond number of AAHHC at different temperature. (D) The binding energy between hexane molecules and acetylated amylose.

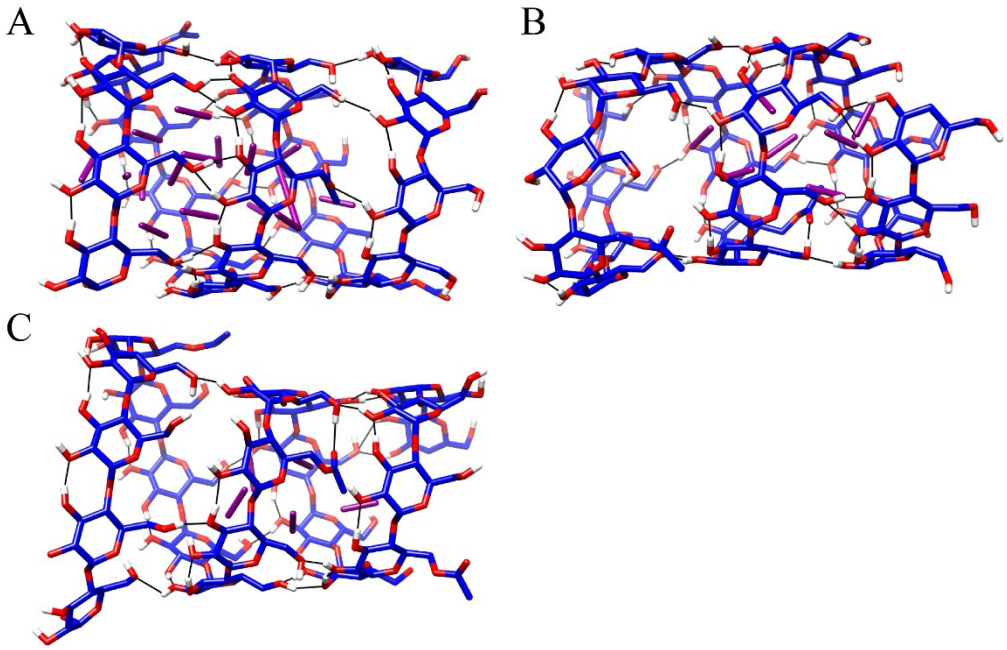

Fig. S9 Molecular structures of AAIHC with different iodine loaded. (A) 14; (B) 7; (C) 5.

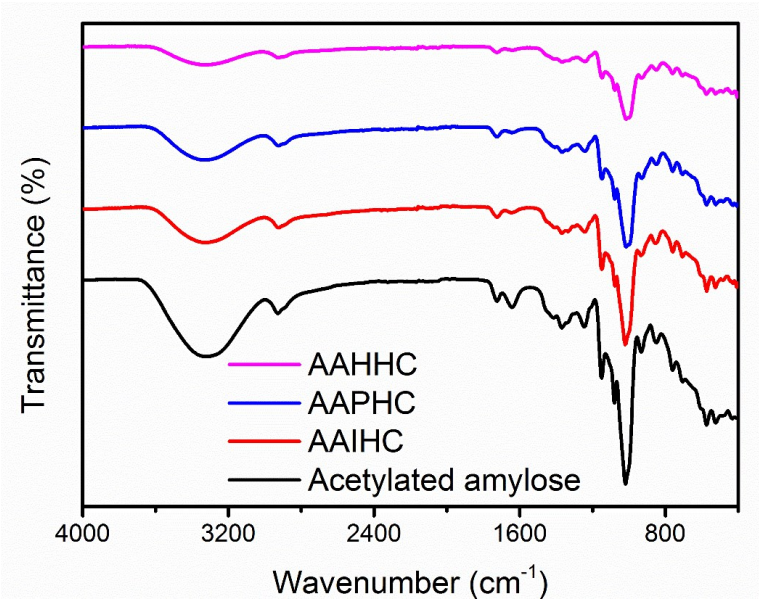

Fig. S10 The FT-IR spectra of AAGHCs.

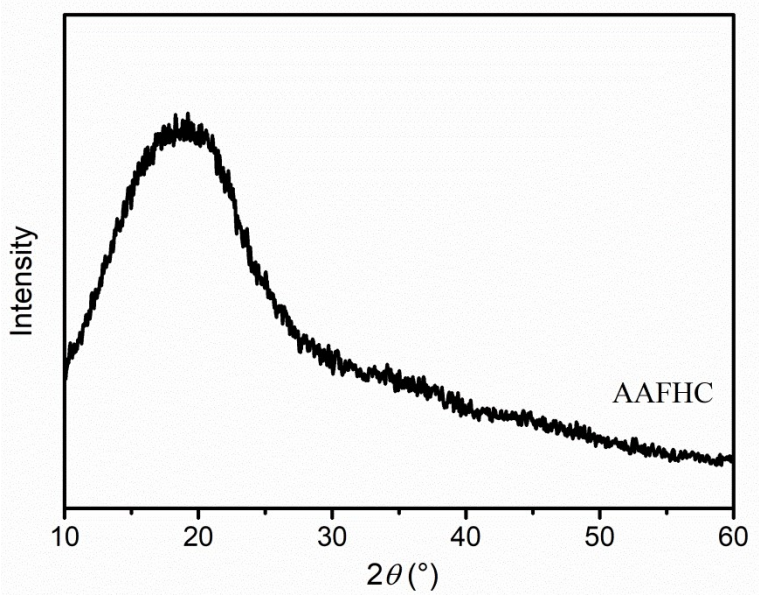

Fig. S11 The XRD pattern of AAFHC.

3. Appendix

1. The pdb and itp file of iodine

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[ exclusions ]
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    11     20      1
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     1      7      1
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     4      7      1
     4      8      1
     3      6      1
     3      7      1
     3      8      1
     7      9      1
     7     10      1
```

```
     7     11      1
     6      9      1
     6     10      1
     6     11      1
    10     12      1
    10     13      1
    10     14      1
     9     12      1
     9     13      1
     9     14      1
    13     15      1
    13     16      1
    13     17      1
    12     15      1
    12     16      1
    12     17      1
    16     18      1
    16     19      1
    16     20      1
    15     18      1
    15     19      1
    15     20      1
[ angles ]
;    ai     aj     ak    funct     angle         fc
     1      2      3      2      107.57     484.00
     1      2      4      2      107.57     484.00
     1      2      5      2      111.40     532.00
     3      2      4      2      107.57     484.00
     3      2      5      2      111.40     532.00
     4      2      5      2      111.40     532.00
     2      5      6      2      109.50     448.00
     2      5      7      2      109.50     448.00
     2      5      8      2      111.00     530.00
     6      5      7      2      106.75     503.00
     6      5      8      2      109.50     448.00
     7      5      8      2      109.50     448.00
     5      8      9      2      109.50     448.00
     5      8     10      2      109.50     448.00
     5      8     11      2      111.00     530.00
     9      8     10      2      106.75     503.00
     9      8     11      2      109.50     448.00
    10      8     11      2      109.50     448.00
     8     11     12      2      109.50     448.00
     8     11     13      2      109.50     448.00
```

```
   8    11    14     2      111.00    530.00
  12    11    13     2      106.75    503.00
  12    11    14     2      109.50    448.00
  13    11    14     2      109.50    448.00
  11    14    15     2      109.50    448.00
  11    14    16     2      109.50    448.00
  11    14    17     2      111.00    530.00
  15    14    16     2      106.75    503.00
  15    14    17     2      109.50    448.00
  16    14    17     2      109.50    448.00
  14    17    18     2      111.40    532.00
  14    17    19     2      111.40    532.00
  14    17    20     2      111.40    532.00
  18    17    19     2      107.57    484.00
  18    17    20     2      107.57    484.00
  19    17    20     2      107.57    484.00
[ dihedrals ]
; GROMOS improper dihedrals
;   ai    aj    ak    al   funct    angle        fc
[ dihedrals ]
;   ai    aj    ak    al   funct      ph0          cp        mult
    1     2     5     8      1          0.00        5.92      3
    2     5     8    11      1          0.00        5.92      3
    5     8    11    14      1          0.00        5.92      3
    8    11    14    17      1          0.00        5.92      3
   11    14    17    20      1          0.00        5.92      3
[ exclusions ]
;   ai    aj   funct   ;   GROMOS 1-4 exclusions
```

4. The mdp file for molecular dynamic simulation (take the protocol guest is iodine and temperature is 50 °C as example)

```
title                    = Yo
define                   =
integrator               = md
dt                       = 0.002       ;2 * 50000000 = 100000000 ps (100 ns)
nsteps                   = 50000000
nstxout        = 0       ; suppress .trr output
nstvout        = 0       ; suppress .trr output
nstenergy      = 5000    ; save energies every 2 ps
nstlog         = 5000    ; update log file every 2 ps
nstxtcout      = 5000    ; write .xtc trajectory every 2 ps
energygrps               = GLCA_GLCY IODI SOL
; Bond parameters
continuation       = yes             ; first dynamics run
```

constraint_algorithm = lincs ; holonomic constraints
constraints = all-bonds ; all bonds (even heavy atom-H bonds) constrained
nstlist = 10
cutoff-scheme = Verlet
ns-type = grid
rlist = 0.9
rlistlong = 1.4
nstcalclr = 1
coulombtype = Reaction-Field
rcoulomb = 0.9
epsilon-rf = 2.2
fourierspacing = 0.16
vdw-type = Cut-off
rvdw = 0.9
tcoupl = V-rescale
tc-grps = GLCA_GLCY IODI SOL
tau-t = 0.1 0.1 0.1
ref-t = 353 353 353
Pcoupl = Parrinello-Rahman
pcoupltype = isotropic
tau-p = 1.0
ref_p = 1.0
compressibility = 4.5e-7
pbc = xyz ; 3-D PBC
; Dispersion correction
DispCorr = EnerPres ; account for cut-off vdW scheme
; Velocity generation
gen_vel = no ; assign velocities from Maxwell distribution
noted: GLCA_GLCY means acetylated amylose; IODI means iodine; SOL means water molecule.

References

S1 Y. Liu, W. Gao, C. Zhang, P. Tang, Y. Zhao and D. Wu, *Chemical Communications*, 2017, **53**, 10680-10683.