Supporting Information

Tunable interfacial adhesion based on orthogonal supramolecular forces

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1. Materials and instruments

All these materials were of analytical grade and were used without further purification. Compounds 1 and 2 were both synthesized according to literature procedures.\(^1\,^2\) For analysis of chemical structures, \(^1\)H NMR spectra and \(^13\)C NMR spectra were recorded through a Bruker Advance 400 MHz spectrometer. High-resolution electrospray ionization mass spectra (ESI-MS) was performed via using a Bruker microOTOF II. The molecular masses of polymers were recorded by using gel permeation chromatography (GPC) measurements which were conducted in tetrahydrofuran (THF) on an Elite P230pII HPLC system. Fourier transform infrared (FT-IR) spectra were collected by using an FT interferometer (Equinox 55, Bruker, Germany). The thermal properties of the polymer were examined through applying a thermogravimetric analyzer (TGA, 4000 PerkinElmer) under N\(_2\) at a heating rate of 10 °C min\(^{-1}\) ranging from 0 to 600 °C. Differential scanning calorimetry (DSC, Q2000, TA) was manipulated at a rate of 10 °C min\(^{-1}\) under N\(_2\). Scanning electron microscopic (SEM) images of freeze-dried gels were obtained using a Hitachi SU8010 instrument. The rheological properties of the gels were measured via using a rheometer MCR 302 (Anton Paar, Austria), with a 25 mm diameter parallel plate attached to a transducer. The frequency sweep was performed over the frequency range of \(\omega = 0.1 - 100\) rad s\(^{-1}\) at a fixed strain of 1% at 25 °C. The tensile tests of the gels were investigated using an electronic universal testing machine (CMT4104, Shenzhen Sans Testing Machine Co.) with a tensile rate of 6 mm min\(^{-1}\). The gels G1-G5 were prepared by immersing the P1, P3, P4 and P5 in Zn\(^{2+}\) solutions (MeCN/CHCl\(_3\): 1/10, vol/vol), while P2 was dissolved in pure CHCl\(_3\) solutions at room temperature. For these studies gels were all 20 mm long, 5 mm wide, and 1 mm in thick. As for adhesive gels (AG1-AG7), the detailed preparation steps were shown in below. Therein, the preparation steps of adhesive gels AG1, AG3, AG4 and AG5 were similar, thus, take AG1 as an example here. Firstly, adhesive gel AG1 was fabricated by contacting gel G1 together when Zn\(^{2+}\) solutions (MeCN/CHCl\(_3\): 1/10) was added onto the interface. Apart from this, adhesive gel AG2 was produced via mutual adhesion of gel G2. With regard to adhesive gels AG6 as well as AG7, they were generated through adding distinct types of competitive molecules. Cyclen solutions (1.74×10\(^{-4}\) mol/L, dissolved in CHCl\(_3\)) was injected into adhesive gel AG3 by using needles, adhesive gel AG6 was thus produced. Besides, adhesive gel
AG7 was generated upon the addition of UPy monomer solutions (2.50×10⁻⁴ mol/L, dissolved in CHCl₃), likewise, the solutions was injected into adhesive gel AG3.

2. Synthesis and characterization of compounds 2 and 3

Scheme S1 Synthetic routes of compounds 1 and 2.

2.1 Synthesis and characterization of compound 2

First, 4-hydroxybenzaldehyde (2.45 g, 20.0 mmol) and 4-vinylbenzyl chloride (3.58 g, 20.0 mmol) were dissolved in DMF (50.0 mL), then the solid KOH (1.12 g, 20.0 mmol) was added into the solution. At room temperature, the mixture was stirred for 12 h. To precipitate the product, the water (600 mL) was added, also used to wash the product. Next, the product was dried by the vacuum at 60 °C. While the redundant 4-vinylbenzyl chloride was eliminated via triturating the product in hexane (50.0 mL). The final product was washed with additional hexane, dried by positive air flow to give compound 2.

¹H NMR (400 MHz, CDCl₃) δ 8.82 – 8.61 (m, 6H), 7.87 (t, J = 6.9 Hz, 4H), 7.48 – 7.40 (m, 4H), 7.37 – 7.32 (m, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.74 (dd, J = 17.6, 10.9 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H), 5.13 (s, 2H). ¹³C NMR (101 MHz,
CDCl$_3$ δ 172.85, 167.33, 156.75, 154.48, 148.32, 136.11, 125.83, 106.69, 63.07, 38.76, 18.95, 18.29. HRMS (ESI$^+$) Calcd for $C_{30}H_{23}N_3O$ [M+H]$^+$: 442.1910, found: 464.1716.
Figure S1 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of 2.

Figure S2 $^{13}$C NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of 2.
2.2 Synthesis and characterization of compound 3

First, with heating to 170 °C, 6-methylisocytosine (2.94 g, 23.5 mmol) was dissolved in DMSO. Then the flask containing solution was taken out. Upon the addition of 2-isocyanatoethyl methacrylate (ICEMA) (4.00 g, 21.8 mmol) into flask, the reaction became violently, then the water was used to quench it which inhibited the polymerization. The precipitated white solid was washed with cyclohexane. Finally, cyclohexane was employed to washed the product, then the compound 3 was dried under reduced pressure.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.96 (s, 1H), 11.95 (s, 1H), 10.50 (s, 1H), 6.17 (s, 1H), 5.78 (s, 1H), 5.54 (s, 1H), 4.26 (t, $J = 5.7$ Hz, 2H), 3.57 (q, $J = 5.7$ Hz, 2H), 2.23 (s, 3H), 1.93 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.85, 167.33, 156.75, 154.48, 148.32, 136.11, 125.83, 106.69, 63.07, 38.76, 18.95, 18.29. HRMS (ESI$^+$) Calcd for C$_{12}$H$_{16}$N$_4$O$_4$ [M+Na$^+$]: 303.1069, found: 303.1123.
Figure S4 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of 3.

Figure S5 $^{13}$C NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of 3.
3. Synthesis and characterization of polymers P1, P2, P3, P4 and P5

Scheme S2 Synthetic routes of polymers P1, P2, P3, P4 and P5
3.1 Synthesis and characterization of polymer P1

Polymer P1 was prepared from compound 2 and methyl methacrylate by free radical polymerization. The molar ratio of compound 2 to methyl methacrylate was controlled at 1:100. DMSO as solvent, then compound 2 (397 mg, 0.800 mmol) and methyl methacrylate (9.00 g, 900 mmol) was added. Meanwhile, azobisisobutyronitrile (AIBN) (22.0 mg, 0.130 mmol) acted as initiator was added. A stream of nitrogen (N$_2$) was bubbled through the reaction mixture for 15 min. Then the mixture was heated to 80 °C, stirred for 10 h. The polymerization was quenched by freezing the reaction mixture in ice water. Next, the resulting solution was added into methanol (500 mL), then the precipitated yellow solid was obtained through vacuum filtration. These two steps were repeated for three times, finally, polymer P1 was produced after being dried with vacuum.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.70 (d, $J = 20.4$ Hz, 1H), 7.89 (s, 3H), 7.06 (s, 2H), 5.06 (s, 2H), 3.59 (s, 59H), 2.61 (s, 62H), 2.07 – 1.50 (m, 49H), 1.42 (s, 6H), 1.20 (s, 4H), 1.05 – 0.45 (m, 58H).
Figure S7 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of P1.

Figure S8 GPC trace of P1.
The ratio of x/y was $(2)/(146.92/3)$, namely $2/48.97$, for polymer P1, as calculated based on the integrations of the peaks corresponding to protons $H^{1f}$, $H^{1e}$. According to $M_n$ and the ratio of x/y, the values of x and y were calculated to be 19.06 and 466.9.

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<td>466.9</td>
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Table S1 GPC analysis of P1.

Table S2. The calculated values of x and y for P1.

Figure S9 FT-IR spectrum of P1.
Figure S10 DSC spectrum of P1.

Figure S11 TGA trace of P1.
3.2 Synthesis and characterization of polymer P2

Polymer P2 was prepared from compound 3 and methyl methacrylate by free radical polymerization. The molar ratio of compound 3 to methyl methacrylate was also controlled at 1:100. DMSO as solvent, then compound 3 (252 mg, 0.800 mmol) and methyl methacrylate (9.00 g, 90.0 mmol) was simultaneously added. And azobisisobutyronitrile (AIBN) (22.0 mg, 0.130 mmol) acted as initiator was added. A stream of nitrogen (N₂) was bubbled through the reaction mixture for 15 min. Then the mixture was heated to 80 °C, stirred for 10 h. The polymerization was quenched by freezing the reaction mixture in ice water. The resulting solution was added into methanol (500 mL), then the precipitated white solid was obtained by using vacuum filtration. These two steps were again repeated for three times, then polymer P2 was produced after being dried with vacuum.

^1H NMR (400 MHz, CDCl₃) δ 12.95 (s, 1H), 11.95 (s, 1H), 10.46 (s, 1H), 5.82 (s, 1H), 4.07 (s, 1H), 3.58 (s, 400H), 2.73 – 0.50 (m, 848H).
Figure S12: $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of P2.
Figure S13 GPC trace of P2.

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Table S3 GPC analysis of P2.

The ratio of x/y was (0.9)/(1226.75/3), namely 2/408.92, for polymer P2, as calculated based on the integrations of the peaks corresponding to protons H$_2^i$, H$_2^f$. According to $M_n$ and the ratio of x/y, the values of x and y were calculated to be 2.78 and 569.2.

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<td>569.2</td>
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Table S4. The calculated values of x and y for P2.

Figure S14 FT-IR spectrum of P2.
Figure S15 DSC spectrum of P2.

Figure S16 TGA trace of P2.
3.3 Synthesis and characterization of polymer P3, P4 and P5

Polymer P3, P4 and P5 was prepared from compound 2, compound 3 and methyl methacrylate by free radical polymerization. In P3, the molar ratio of compound 2, compound 3 and methyl methacrylate is 1:1:100. While in P4, the molar ratio changed to 0.6:1:100. And in P5, this molar ratio transformed to 0.3:1:100. The preparation steps of the three polymers are the same, so taking P3 as an example. DMSO as solvent, then compound 2 (397 mg, 0.800 mmol), compound 3 (252 mg, 0.800 mmol) and methyl methacrylate (9.00 g, 90.0 mmol) was simultaneously added. And azobisisobutyronitrile (AIBN) (22.0 mg, 0.130 mmol) acted as initiator was added. A stream of nitrogen (N₂) was bubbled through the reaction mixture for 15 min. Then the mixture was heated to 80 °C, stirred for 10 h. The polymerization was quenched by freezing the reaction mixture in ice water. The resulting solution was added into methanol (500 mL), then the precipitated white solid was obtained by using vacuum filtration. These two steps were again repeated for three times, then polymer P3 was produced after being dried with vacuum. P4 and P5 could be obtained in the same way.  

P3: ¹H NMR (400 MHz, CDCl₃) δ 12.92 (s, 1H), 11.88 (s, 1H), 10.42 (s, 2H), 8.67 (d, J = 15.0 Hz, 66H), 7.84 (s, 44H), 7.03 (s, 35H), 5.87 – 5.71 (m, 11H), 5.03 (s, 22H), 4.66 (d, J = 7.6 Hz, 26H), 4.03 (d, J = 7.9 Hz, 20H), 3.56 (s, 3580H), 2.88 – 0.02 (m, 13470H).

P4: ¹H NMR (400 MHz, CDCl₃) δ 12.92 (s, 1H), 11.93 (s, 1H), 10.41 (s, 1H), 8.66 (s, 3H), 7.85 (s, 2H), 7.03 (s, 2H), 5.79 (s, 1H), 5.05 (s, 2H), 4.04 (s, 3H), 3.56 (s, 214H), 2.92 – 0.51 (m, 591H).

P5: ¹H NMR (400 MHz, CDCl₃) δ 12.95 (s, 1H), 11.93 (s, 1H), 10.43 (s, 1H), 8.68 (s, 2H), 7.86 (s, 1H), 7.05 (s, 1H), 5.80 (s, 1H), 5.06 (s, 1H), 4.07 (s, 2H), 3.58 (s, 133H), 2.86 – 0.24 (m, 363H).
Figure S17 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of P3.

Figure S18 GPC trace of P3.
Table S5. GPC analysis of P3.
The ratio of m/x/y was \((4.2)/(22.2/2)/(3660.39/3)\), namely \(4.2/11.1/1220.13\), for polymer P3, as calculated based on the integrations of the peaks corresponding to protons H\(^3\)l, H\(^3\)k and H\(^3\)h. According to \(M_n\) and the ratio of m/x/y, the values of m, x and y were calculated to be 1.59, 4.2 and 462.06.

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<td>4.2</td>
<td>462.09</td>
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Table S6. The calculated values of x and y for P3.

Figure S19 FT-IR spectrum of P3.
Figure S20 DSC spectrum of P3.

Figure S21 TGA trace of P3.
Figure S22 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of P4.

Figure S23 GPC trace of P4.
Table S7 GPC analysis of P4. The ratio of m/x/y was (1.15)/(1.13/2)/(214.48/3), namely 1.15/0.56/71.5, for polymer P4, as calculated based on the integrations of the peaks corresponding to protons H^4l, H^4k and H^4h. According to $M_n$ and the ratio of m/x/y, the values of m, x and y were calculated to be 5.56, 2.7 and 345.3.

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<td>2.7</td>
<td>345.3</td>
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Table S8 The calculated values of x and y for P4.

Figure S24 FT-IR spectrum of P4.
Figure S25 DSC spectrum of P4.
Figure S26 TGA trace of P4.

Figure S27 $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of P5.
The ratio of m/x/y was (0.97)/(0.57/2)/(170.13/3), namely 0.97/0.285/56.71, for polymer P5, as calculated based on the integrations of the peaks corresponding to protons H$_{5l}$, H$_{5k}$ and H$_{5h}$. According to $M_n$ and the ratio of m/x/y, the values of m, x and y were calculated to be 9.9, 2.9 and 578.44.

Table S10 The calculated values of x and y for P5.

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Figure S29 FT-IR spectrum of P5.
Figure S30 DSC spectrum of P5.

Figure S31 TGA trace of P5.
4. Rheological properties and SEM images of adhesive gels AG4 and AG5

**Figure S32** Rheological behaviors of (a) AG4, and (b) AG5. SEM images of (c) AG4, and (d) AG5.

5. Supporting references