

**Supporting Information**

**for**

**Bioinspired Nucleobase-Containing  
Polyelectrolytes as Robust and Tunable  
Adhesives by Balancing the Adhesive and  
Cohesive Properties**

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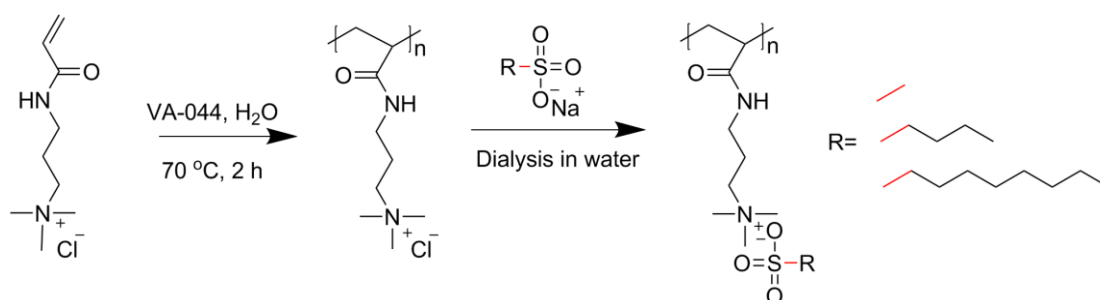
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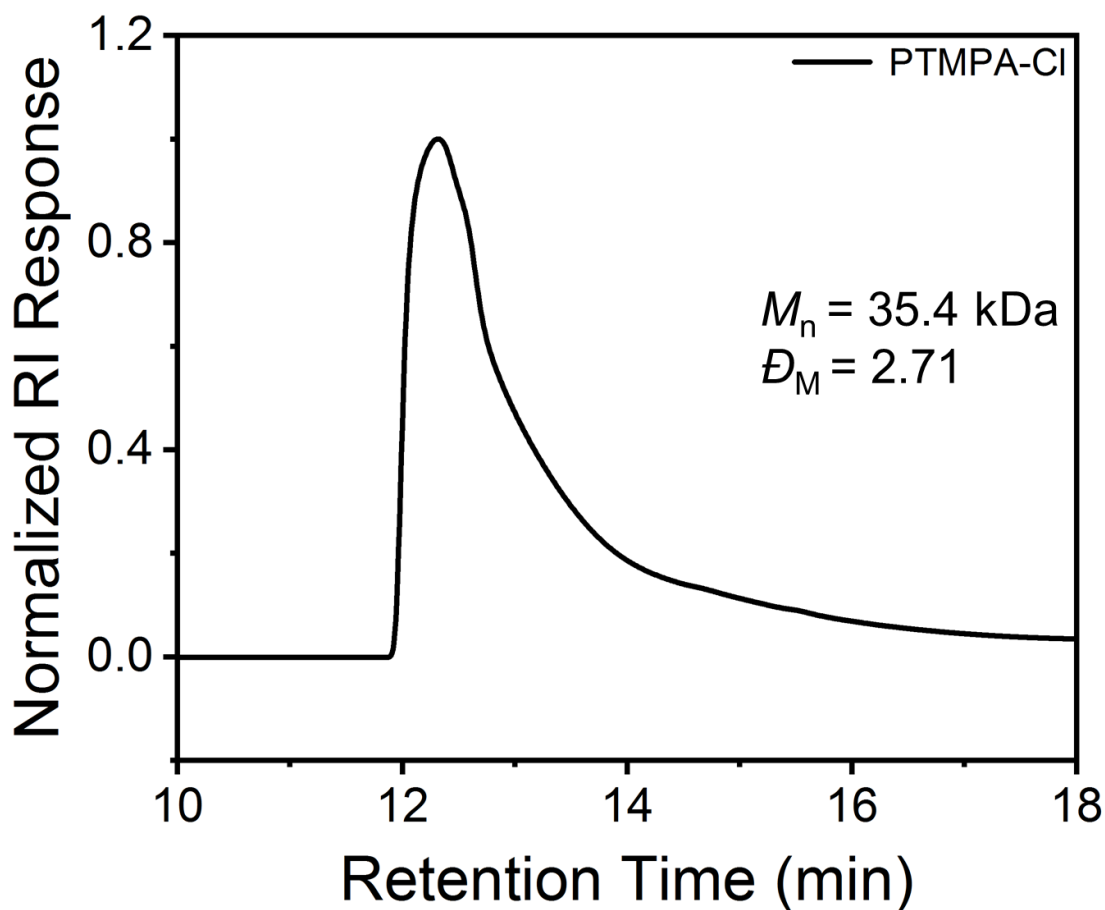
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**Syntheses and characterization of poly(3-acrylamidopropyltrimethylammoniumchloride) (PTMPA-Cl) and PTMPAs with different sulfonate counterions**

**Scheme S1.** Syntheses of poly(3-acrylamidopropyltrimethylammonium chloride) (PTMPA-Cl) and PTMPAs with different sulfonate counterions.

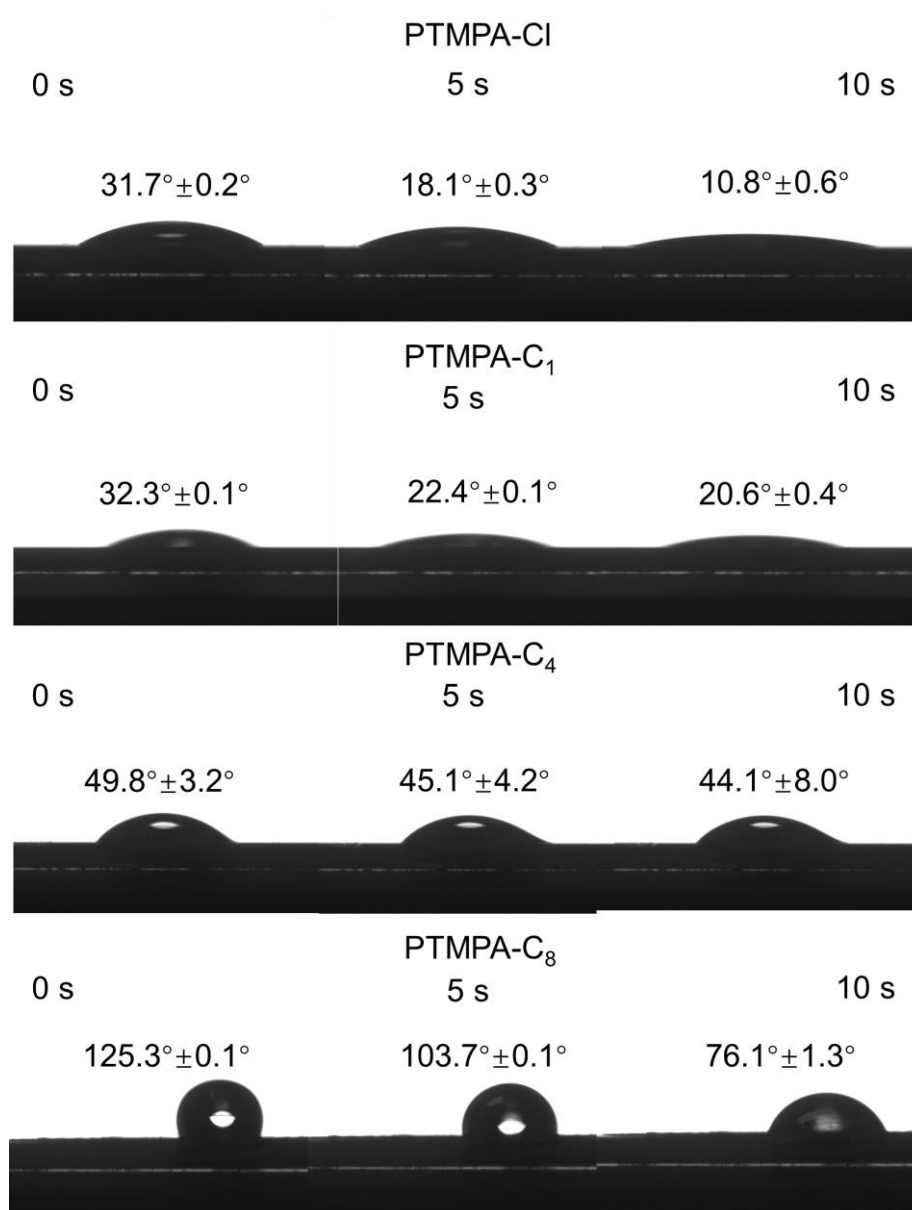


**Size exclusion chromatography (SEC) analysis of PTMPA-Cl**



**Figure S1.** SEC trace of PTMPA-Cl homopolymer with aqueous solution as the eluent.

**Wettability of coating surface with PTMPA-Cl and PTMPAs with different sulfonate counterions**



**Figure S2.** Water contact angles (WCAs) of PTMPA-Cl, PTMPA-C<sub>1</sub>, PTMPA-C<sub>4</sub>, and PTMPA-C<sub>8</sub>, illustrating the successful exchange of counterions.

FT-IR spectra of PTMPA-Cl and PTMPAs with different sulfonate counterions

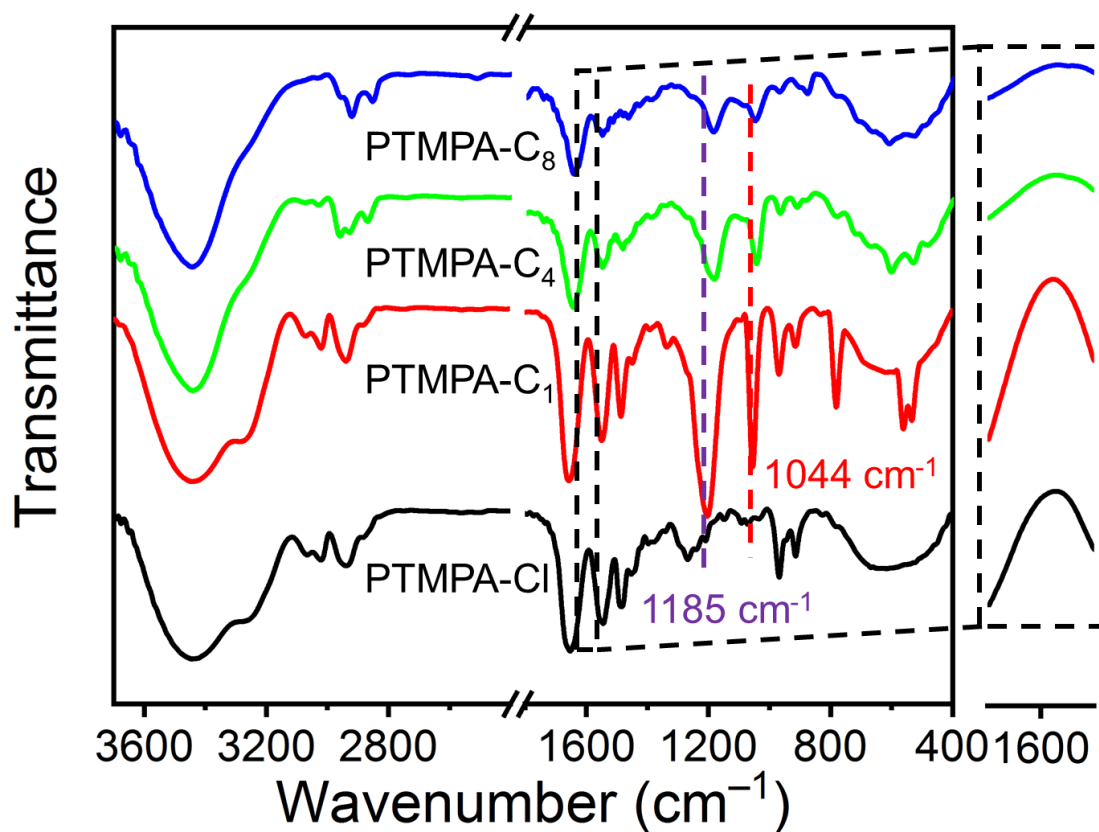


Figure S3. FT-IR spectra of PTMPA-Cl and PTMPAs with different counterions.

XPS spectra of PTMPA-Cl and PTMPAs with different sulfonate counterions

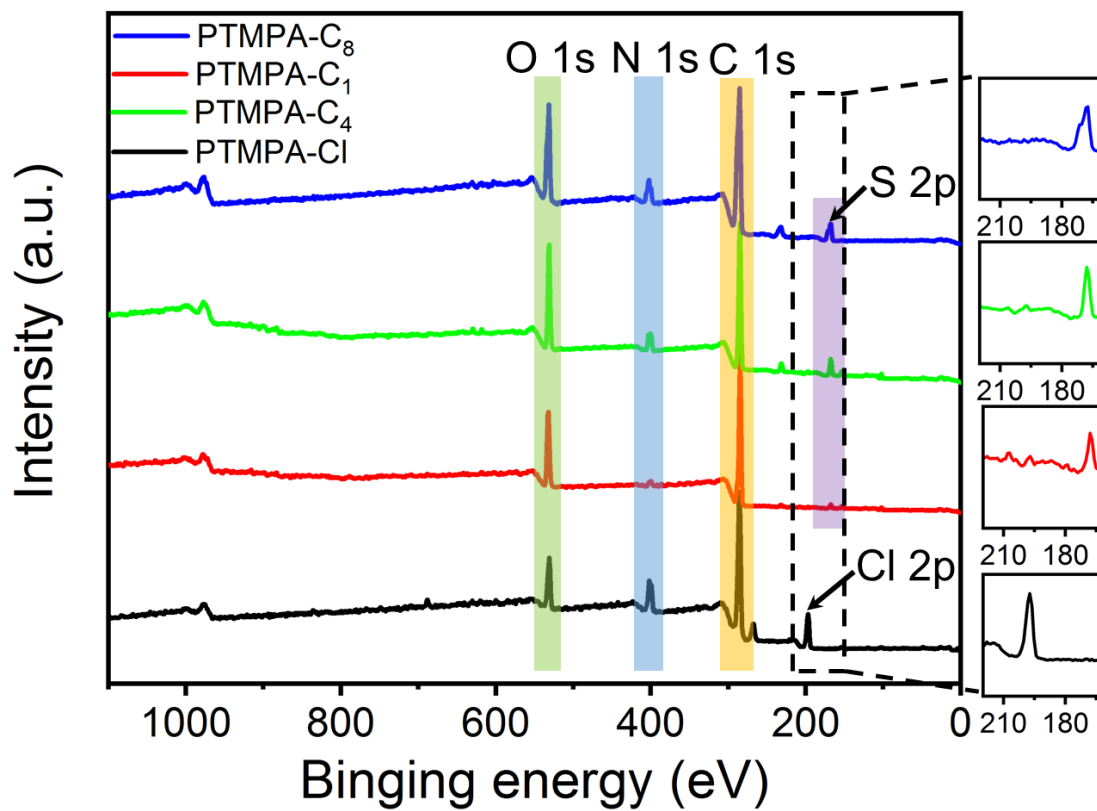
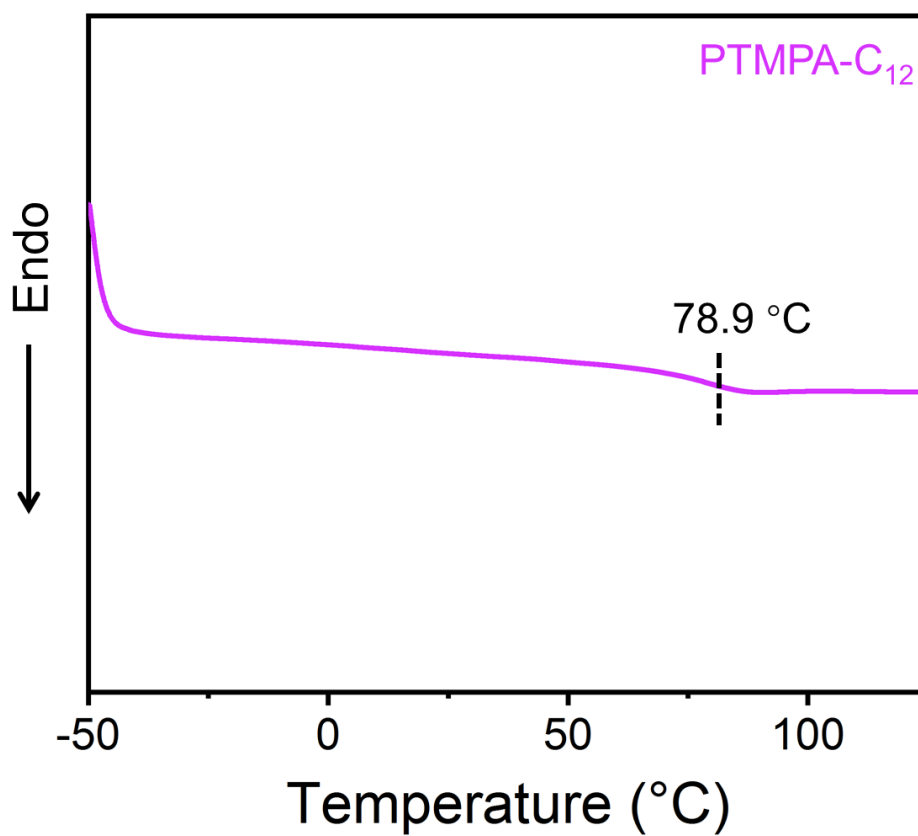


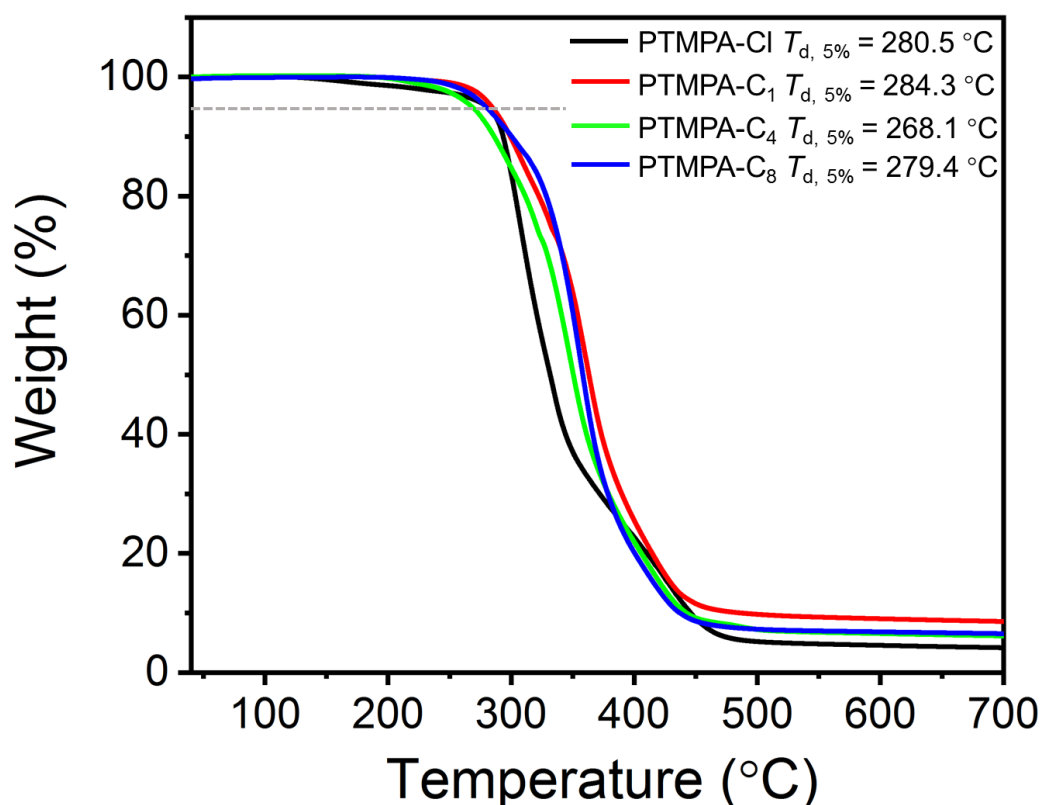
Figure S4. XPS spectra of PTMPA-Cl and PTMPAs with different counterions.

DSC curve of PTMPA-C<sub>12</sub>



**Figure S5.** DSC curve of PTMPA-C<sub>12</sub>, which was obtained by the counterion exchange of PTMPA-Cl with sodium dodecyl sulfonate.

## TGA analyses of PTMPA-Cl and PTMPAs with different sulfonate counterions



**Figure S6.** TGA curves of PTMPA-Cl exchanged with different counterions.

## Syntheses and characterization of nucleobase-containing polyelectrolytes with different counterions

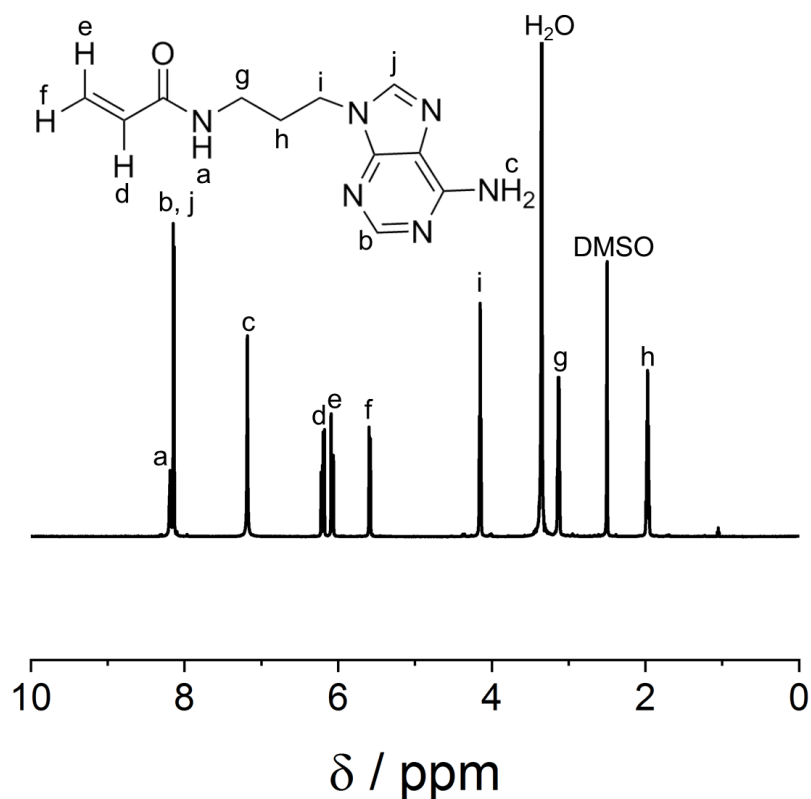
### Synthesis of 3-(adenine-9-yl)propyl acrylamide (AAm) and 3-(thymine-1-yl)propyl acrylamide (TAm)

*N*-(3-Bromopropyl) acrylamide was synthesized as follows. First, 3-bromopropylamine (20.2 g, 90 mmol), triethylamine (TEA) (24 mL, 172.7 mmol), and 4-(dimethylamino) pyridine (DMAP) (576 mg, 4.6 mmol) were added to a 500 mL round bottom flask with  $\text{CH}_2\text{Cl}_2$  (DCM, 300 mL). Then, acryloyl chloride (8.4 mL, 103.4 mmol) was added dropwise into the mixture under an ice water bath. Then the reaction solution was left at room temperature for another 5 h. After the reaction, the reaction solution was washed three times with deionized water ( $3 \times 100\text{ mL}$ ). The organic layer was



collected and dried with anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. Then, 2, 6-bis(1,1-dimethylethyl)-4-methylphenol (12.6 mg, 0.06 mmol) was added to the filtrate followed by concentrating under vacuum to give a brown oil. The brown oil (11.2 g, 65%) was used for the following reaction immediately without further purification.

Adenine (6.0 g, 44.4 mmol) was added to the dried DMF (200 mL), and NaH (60%, dispersion in Paraffin Liquid) (1.1 g, 46.6 mmol) was slowly added under an ice water bath. The mixture was stirred for an hour until no bubbles formed, then freshly synthesized *N*-(3-bromopropyl) acrylamide (9.3 g, 48.8 mmol) was added into the viscous mixture dropwise. After the reaction overnight, the solvent was removed under vacuum. The mixture was further purified by column chromatography using a mixture of ethyl acetate (EtOAc) and  $\text{CH}_3\text{OH}$  as eluent and a gradient from 100:0 to 100:4 (v: v) to give a white solid, AAm (5.6 g, 51%).<sup>S1</sup> Assigned  $^1\text{H}$  NMR spectrum was shown in Figure S7.

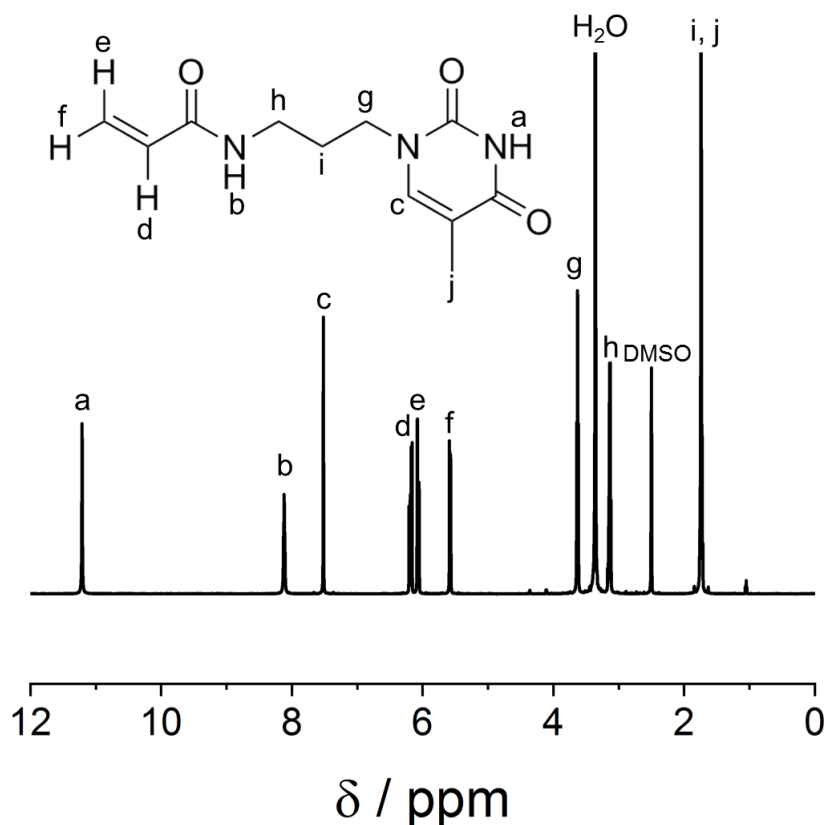


**Figure S7.** Assigned  $^1\text{H}$  NMR spectrum of 3-(adenine-9-yl) propyl acrylamide (AAm) in  $\text{DMSO}-d_6$ .

For the synthesis of TAM, benzoyl chloride (22.5 mL, 193.6 mmol) and thymine (6.0 g, 48.4 mmol) were suspended in a mixture of acetonitrile (60 mL) and pyridine (24 mL), stirred overnight at room temperature. After concentration, the resulting viscous liquid was diluted with DCM, extracted with deionized water (3 × 100 mL). The organic layer was collected and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The obtained solid was dissolved in dioxane (30 mL), then K<sub>2</sub>CO<sub>3</sub> (8.2 g) in 30 mL of water was added and the reaction mixture was stirred for 2 h. The crude product was concentrated and colourless crystals 3-benzoyl thymine (9.5 g, 85%) were recrystallized from the solution.

NaH (60%, dispersion in Paraffin Liquid) (0.8 g, 21.0 mmol) was added to a solution of 3-benzoyl thymine (4.6 g, 20.0 mmol) in a dry DMF (50 mL) slowly. The mixture was stirred for 1 hour until no gas was produced. The obtained viscous mixture was put in an ice water bath and the newly synthesized *N*-(3-bromopropyl) acrylamide (4.6 g, 24.0 mmol) was added dropwise. The yellow viscous mixture was further stirred overnight prior to concentration in vacuo. Using a mixture of EtOAc and petroleum ether (1:2, v: v) as the eluent, the mixture was further purified by column chromatography to give a viscous liquid, 3-(3-benzoylthymine-1-yl) acrylamide (4.4 g, 65%).

3-(3-Benzoylthymine-1-yl) acrylamide (4.4 g, 12.9 mmol) was dissolved in a mixture of TFA/DCM (3:1, v: v) (40 mL). The reaction solution was stirred overnight at room temperature. After the reaction was completed, the solvent was removed under vacuum. The attained residue was purified by column chromatography with EtOAc as the solvent to give a viscous liquid. Then add ethanol (40 mL) to yield a white solid (2.6 g, 70%) through recrystallization.<sup>S2, 3</sup> Assigned <sup>1</sup>H NMR spectrum was shown in Figure S8.



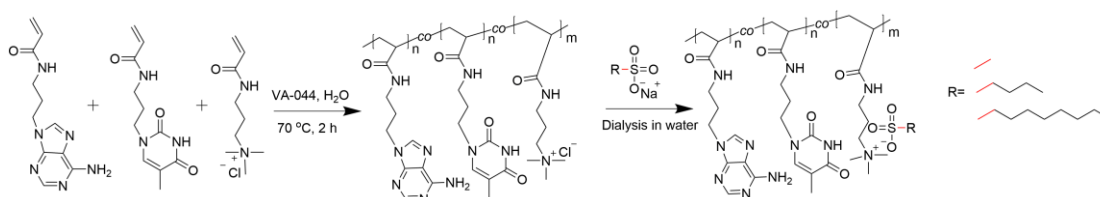
**Figure S8.** Assigned  $^1\text{H}$  NMR spectrum of 3-(thymine-1-yl) propyl acrylamide (TAm) in  $\text{DMSO-}d_6$ .

### Syntheses of random copolymers of TMPA, AAm, and TAm with different molar ratios

Poly((3-acrylamidopropyltrimethylammoniumchloride)-*co*-(3-(adenine-9-yl) propyl acrylamide)-*co*-(3-(thymine-1-yl) propyl acrylamide)) P(TMPA-*co*-AAm-*co*-TAm) copolymers were prepared by using conventional free radical polymerization with VA-044 as the initiator (Scheme S2). A typical synthetic procedure is as follows. For P(TMPA<sub>0.7</sub>-*co*-AAm<sub>0.15</sub>-*co*-TAm<sub>0.15</sub>) (P<sub>70-15-15</sub>), a dried ampoule was charged with TMPA (784.5 mg, 2.85 mmol), AAm (150.0 mg, 0.61 mmol), TAm (144.5 mg, 0.61 mmol), VA-044 (13.1 mg, 0.04 mmol), and deionized water (3.5 mL). The reaction mixture was degassed through 3 freeze-pump-thaw cycles, then put in an oil bath at 70 °C for 2 h with constant stirring. After polymerization, an aliquot of the reaction

mixture was taken and analyzed by  $^1\text{H}$  NMR spectroscopy to calculate the monomer conversion. The residual solution was precipitated three times from cold isopropanol. The purified polymer was dried in a vacuum oven overnight at room temperature and further characterized by  $^1\text{H}$  NMR spectroscopy, SEC, FT-IR, DSC, and TGA, respectively.

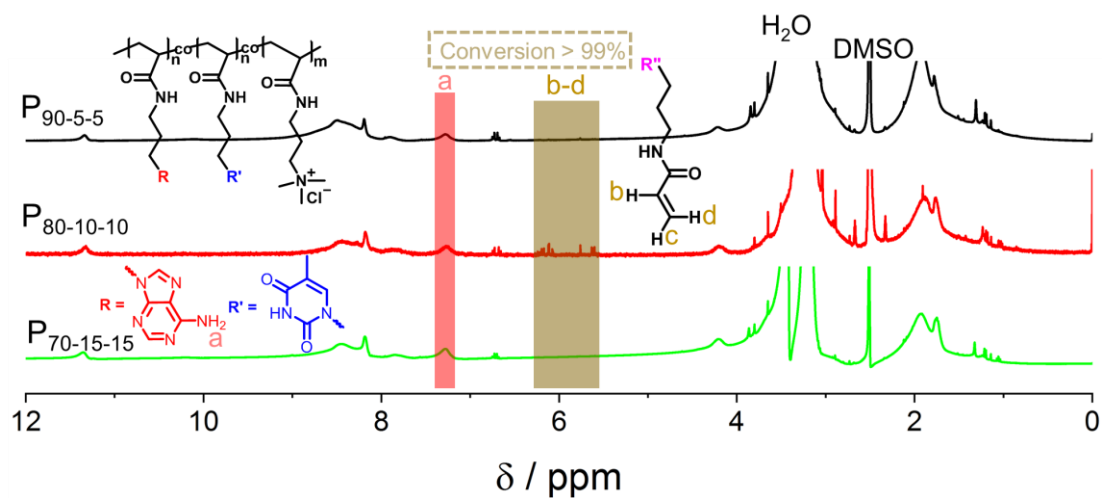
**Scheme S2.** Preparation of nucleobase-containing copolymers of TMPA, AAm and TAm with different molar ratios and the counterion exchange of obtained copolymers.



### Counterion exchange of nucleobase-containing cationic polyelectrolyte copolymers

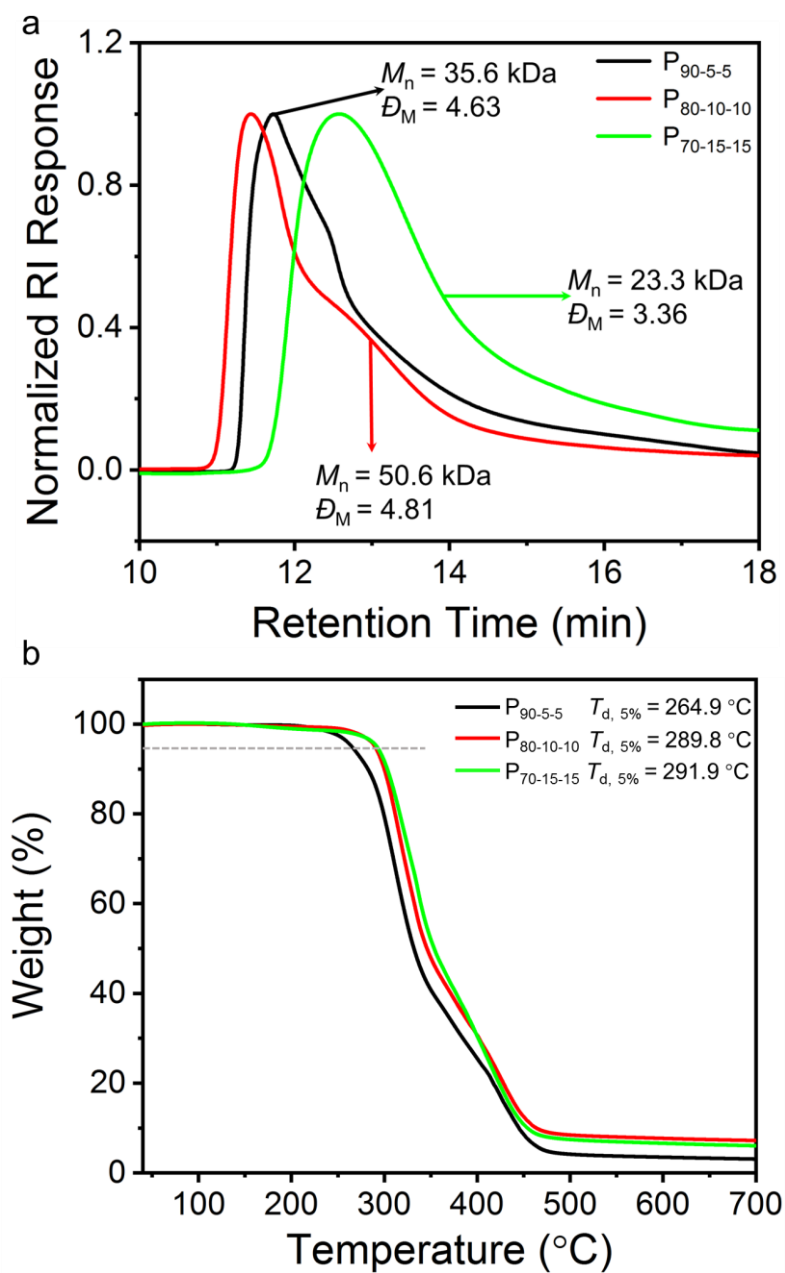
The counterion exchange of nucleobase-containing cationic polyelectrolyte copolymers was shown in Scheme S2. Take  $\text{P}_{70-15-15-\text{C}_8}$  as the example and the typical process is as follows.  $\text{P}_{70-15-15}$  (100.0 mg, 0.32 mmol) was first added to deionized water to dissolve (20 mL) and sodium 1-octane sulfonate (349.0 mg, 1.61 mmol) was dissolved in deionized water (1 mL) at the same time. Then the 1-octane sulfonate solution was added to the  $\text{P}_{70-15-15}$  solution drop-by-drop under stirring. Owing to the long alkyl chain of sodium 1-octane sulfonate, the counterion exchange of  $\text{P}_{70-15-15}$  results in the occurrence of phase separation directly. The obtained white solid  $\text{P}_{70-15-15-\text{C}_8}$  was further rinsed three times with deionized water.

**The final conversion of nucleobase-containing polyelectrolytes with different molar ratios by  $^1\text{H}$  NMR spectroscopy**



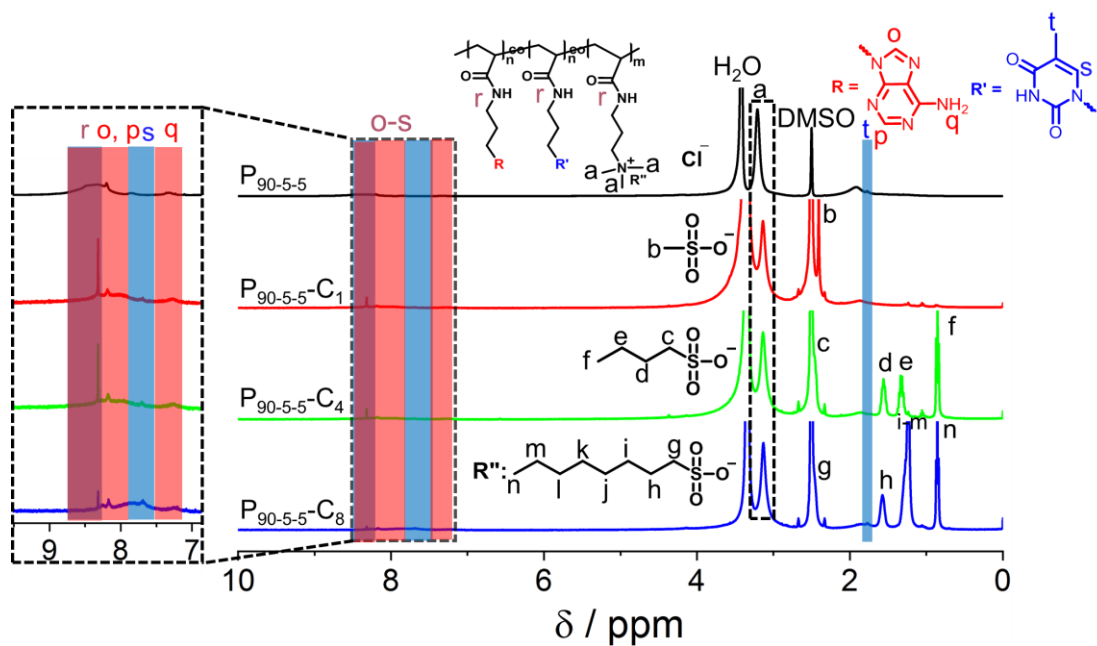
**Figure S9.**  $^1\text{H}$  NMR spectra for  $\text{P}_{90-5-5}$ ,  $\text{P}_{80-10-10}$ , and  $\text{P}_{70-15-15}$  after polymerization without purification, showing high monomer conversions.

**SEC and TGA of nucleobase-containing polyelectrolytes with different molar ratios**

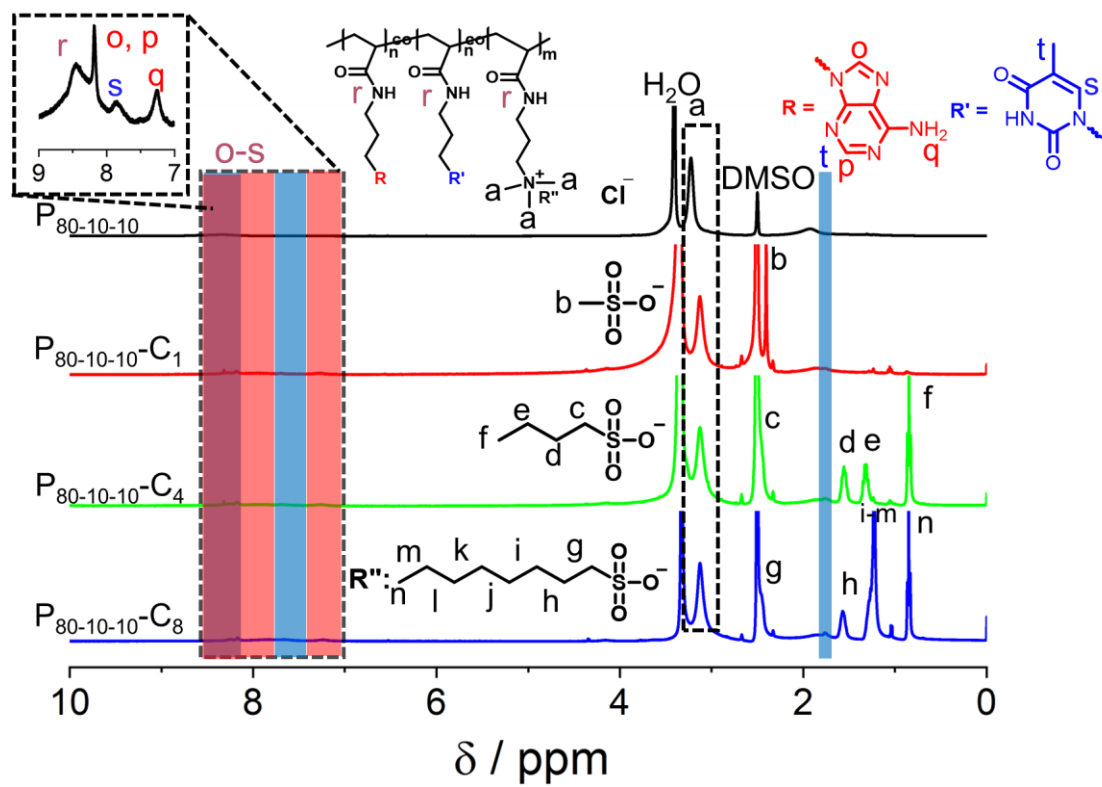


**Figure S10.** (a) SEC traces of nucleobase-containing copolymers of TMPA, AAm and TAM with different molar ratios with aqueous solution as the eluent; (b) TGA curves of nucleobase-containing copolymers of TMPA, AAm and TAM with different molar ratios.

**$^1\text{H}$  NMR spectra of nucleobase-containing polyelectrolytes with different counterions**

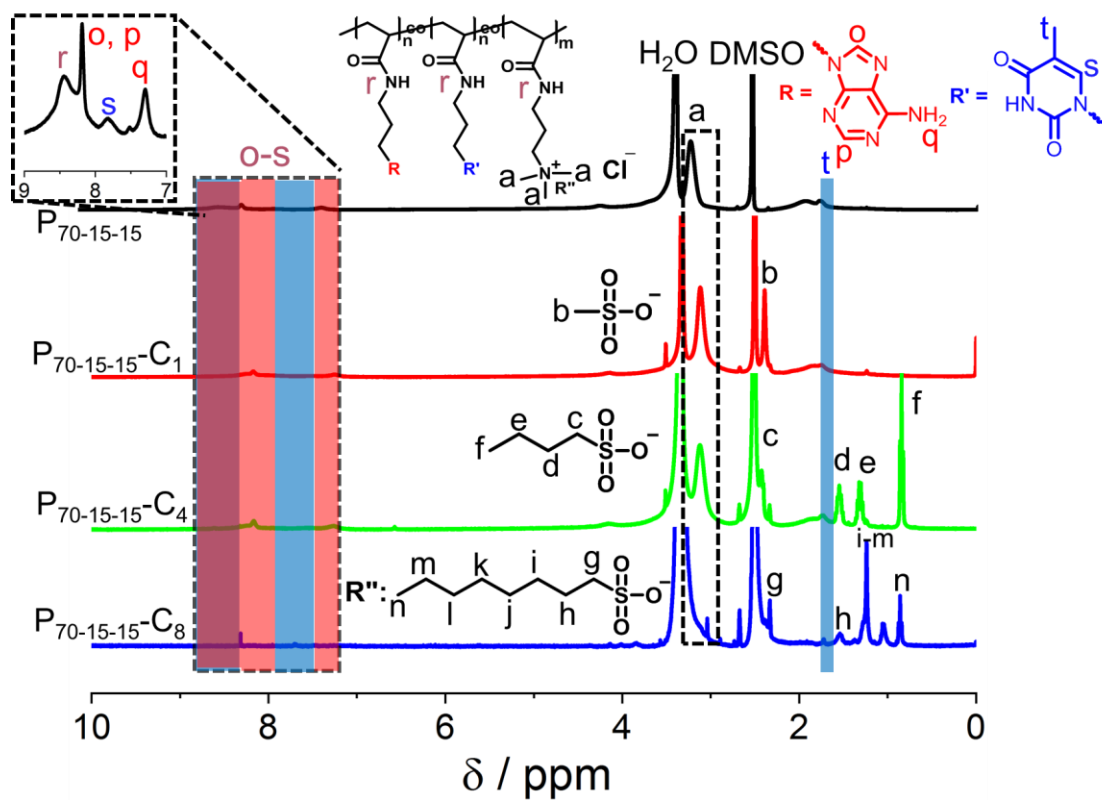


**Figure S11.** Assigned  $^1\text{H}$  NMR spectra of  $\text{P}_{90-5-5}$  with different counterions in  $\text{DMSO-}d_6$ .



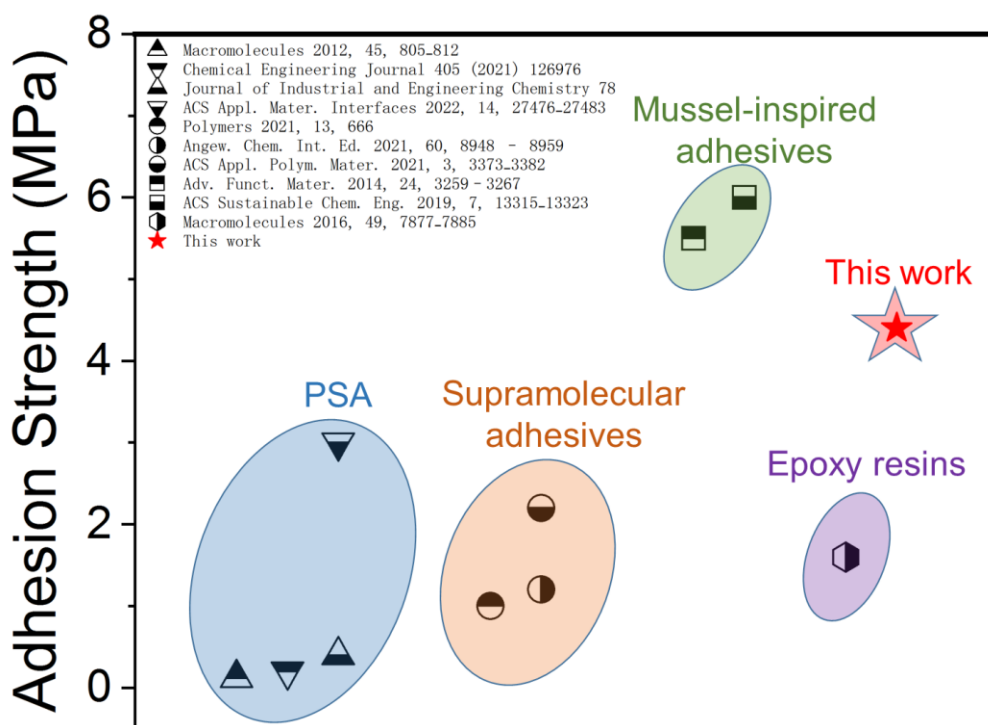
**Figure S12.** Assigned  $^1\text{H}$  NMR spectra of  $\text{P}_{80-10-10}$  with different counterions in  $\text{DMSO-}d_6$ .





**Figure S13.** Assigned  $^1\text{H}$  NMR spectra of  $\text{P}_{70-15-15}$  with different counterions in  $\text{DMSO-}d_6$ .

**The comparison of adhesion strengths of the bioinspired nucleobase-containing polyelectrolytes with other common adhesives**



**Figure S14.** The comparison of adhesion strengths of the bioinspired nucleobase-containing polyelectrolytes with other common adhesives, including PSAs,<sup>S4-S7</sup> supramolecular adhesives,<sup>S8-S10</sup> mussel-inspired adhesives,<sup>S11, S12</sup> and epoxy resins.<sup>S13</sup>

FT-IR spectra of nucleobase-containing polyelectrolytes with different counterions

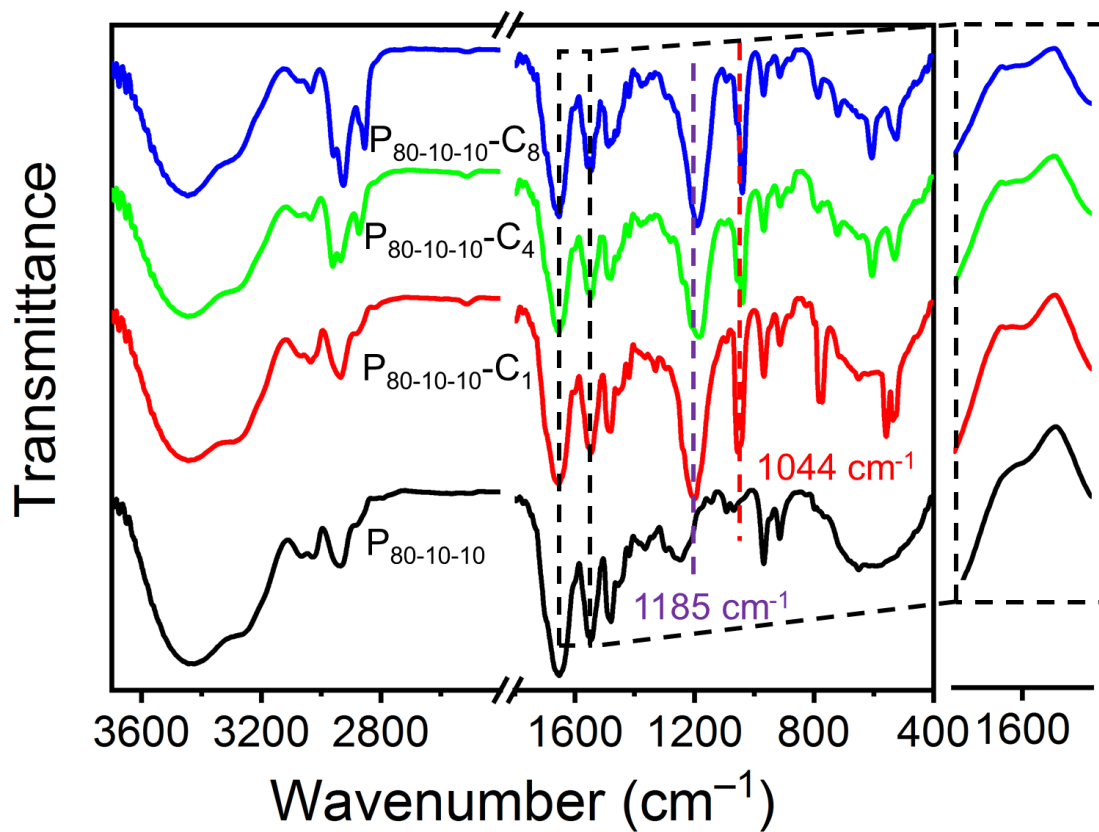


Figure S15. FT-IR spectra of P<sub>80-10-10</sub> with different counterions.

DSC analyses of nucleobase-containing polyelectrolytes with different counterions

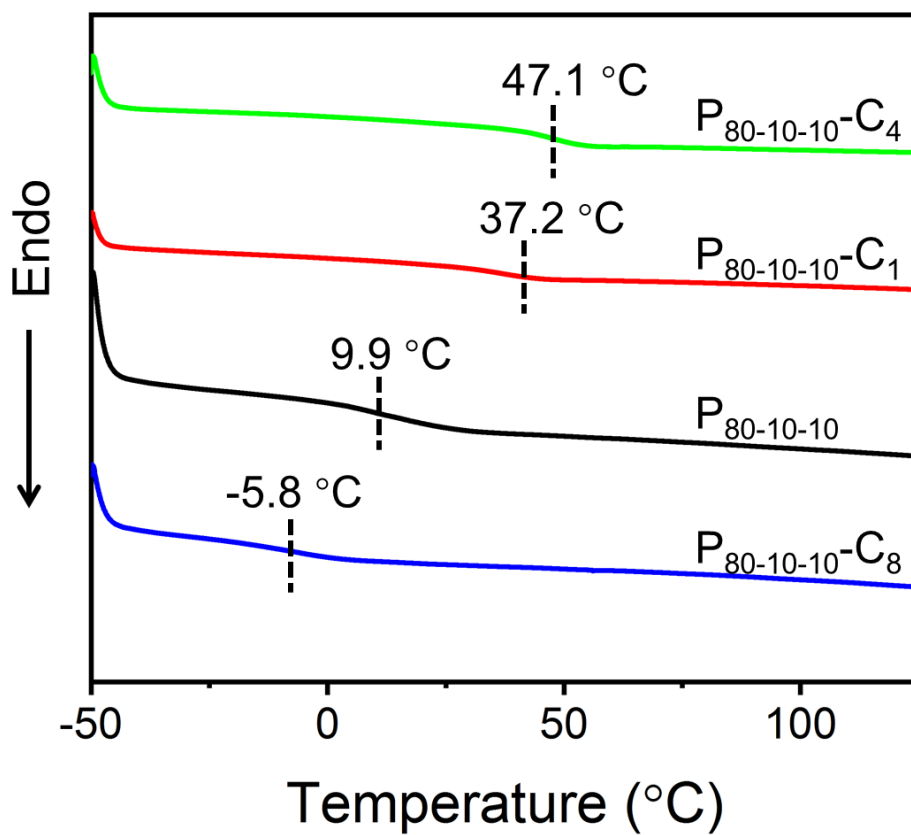
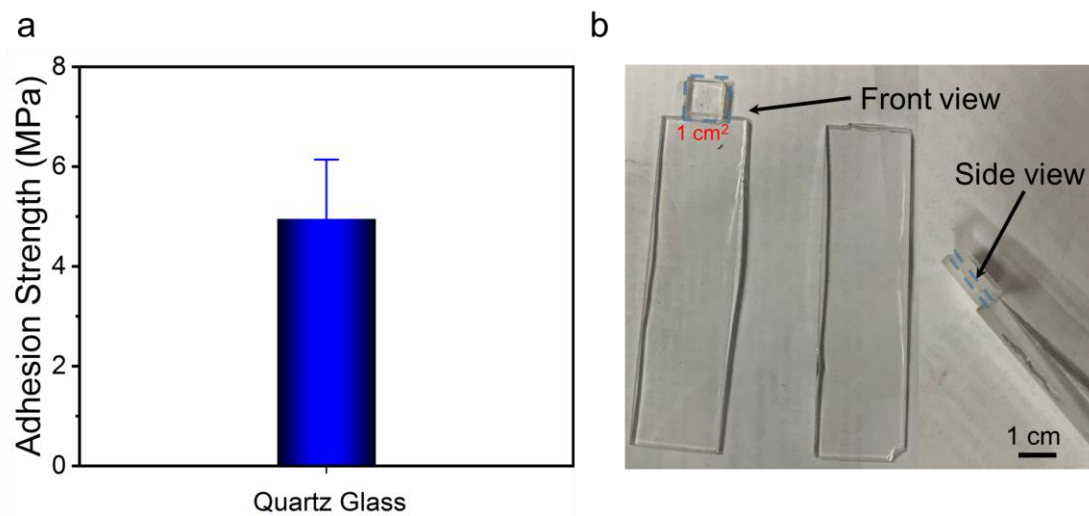
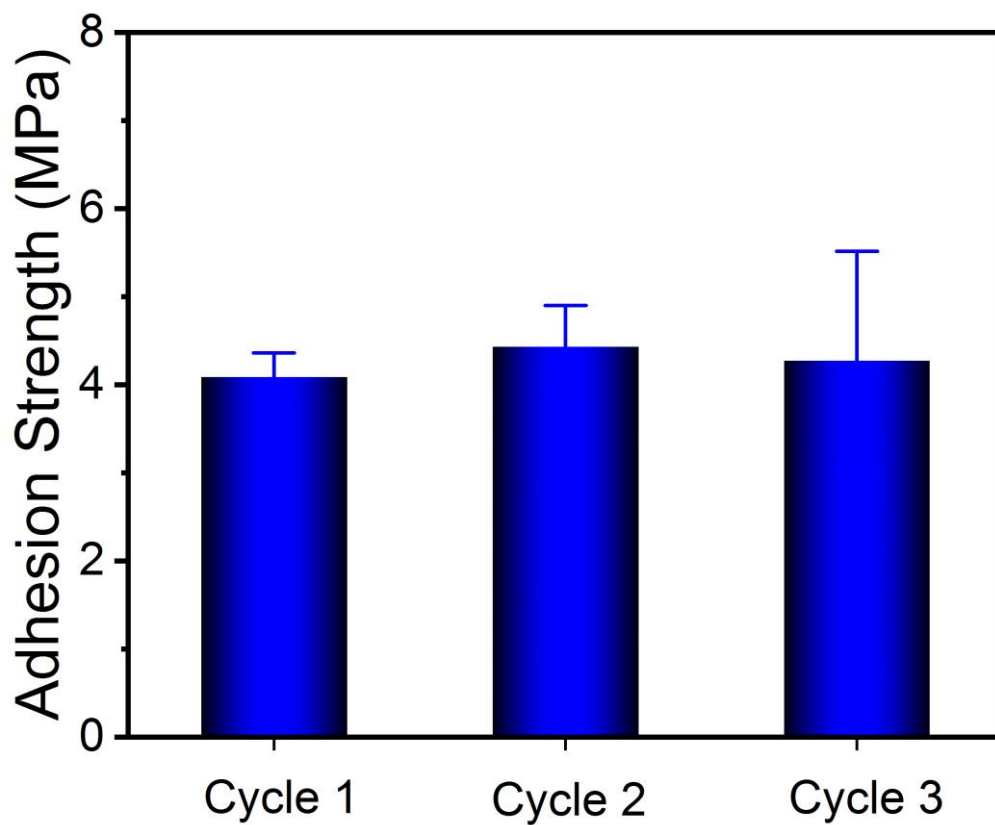


Figure S16. DSC curves of P<sub>80-10-10</sub> with different counterions.

**Adhesive properties of nucleobase-containing polyelectrolytes with different counterions**



**Figure S17.** (a) The adhesion strength of P<sub>(70-15-15)</sub>-C<sub>8</sub> on quartz glass with 0.25 cm<sup>2</sup>; (b) the digital photo shows a failed shear test on 1 cm<sup>2</sup> quartz glass.



**Figure S18.** High adhesion strengths for P<sub>70-15-15</sub>-C<sub>8</sub> between stainless steel sheets were maintained after 3 adhesion cycles without obvious damage.

## Movie

**Movie S1.** P<sub>70-15-15</sub>-C<sub>8</sub> bonded steel substrates can hold a volunteer with a weight over 70 kg.

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