Electronic Supplementary Information for

Synthesis of end-functionalized boronic acid containing (co)polymers and their bioconjugates with rodlike viruses for multiple responsive hydrogels

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Synthesis of phenylboronic acid containing monomer.

The synthesis of phenylboronic acid containing monomer, 4-(1,6-dioxo-2,5-diaza-7-oxamyl) phenylboronic acid (DDOPBA, **1** in Scheme 1), was based on the procedure devised by Kataoka.[1] A two-neck round-bottom flask containing 10 g (60.3 mmol) 4-carboxyphenylboronic acid (CPBA) was dried in vacuum for 1 day. N_2 was charged into the flask and 150 mL (2.1 mol) thionyl chloride was added. The resulted mixture was stirred under N_2 atmosphere at 90℃ for 24 hrs. The excess amount of thionyl chloride was distilled away, resulting in 4-(chloroformyl) phenylboronic acid as white solids. To the same flask immerged in an ice-water bath, 120 mL dried THF was added and stirred to obtain the 4-(chloroformyl) phenylboronic acid solution. Under N_2 atmosphere, the solution wad added slowly into a mixture of 10 mL ethylenediamine (71.9 mmol) and 10 mL triethylamine (71.9mmol) which was pre-

cooled in another ice-water bath. The reaction was performed for 20h. Excess of ethylenediamine was distilled away. The residual was dissolved in 100 mL unltrapure water. The pH of the solution was adjusted to 4 by adding 5mol L^{-1} HCl solution, resulting in white precipitates which was confirmed by ^{1}H NMR as the byproduct, 4,4'-(ethylenedicarbamoyl) phenylboronic acid. After filtering away the byproduct , the filtrate was concentrated and kept at 4 ^{o}C overnight， resulting in white production, 4-[(2-aminoethyl)carbamoyl) phenylboronic acid (AECPBA) with a yield of 46%. ^{1}H NMR(400 MHz, D_2O) δ: 3.3ppm [NH_2-CH_2-CH_2-, 2H], 3.7 ppm [NH_2-CH_2-CH_2-, 2H], 7.8 ppm [-NH-COC_6H_4-$B(OH)_2$, 4H]. To 150 mL freshly prepared 1mol L^{-1} NaOH solution in an ice-water bath, AECPBA (4 g, 19.2 mmol) was added under N_2 atmosphere and stirred for 30 min. Acryloyl chloride (5.2 mL, 57.6 mmol) was added dropwise into the solution. The reaction was allowed to proceed at room temperature for 24 h. The reaction mixture was then concentrated and the pH was adjusted to 4 by adding 1mol L^{-1} HCl solution. The white product, 4-(1,6-Dioxo-2,5-diaza-7-oxamyl) phenylboronic acid (DDOPBA), was collected after storing at 4℃ for one night. The raw product was further purified by twice recrystallization. The final yield based on AECPBA was 65%. ^{1}H NMR(400 MHz, D_2O) (δ, ppm): 3.5 [-$NHCH_2$-CH_2-NH-, 4H], 5.8 ppm [CH2=CH-CO-NH-, 1H], 6.1-6.3 ppm [CH_2dCH-CO-NH-, 2H], 7.6 ppm [-NH-C_6H_4-$B(OH)_2$, 4H].

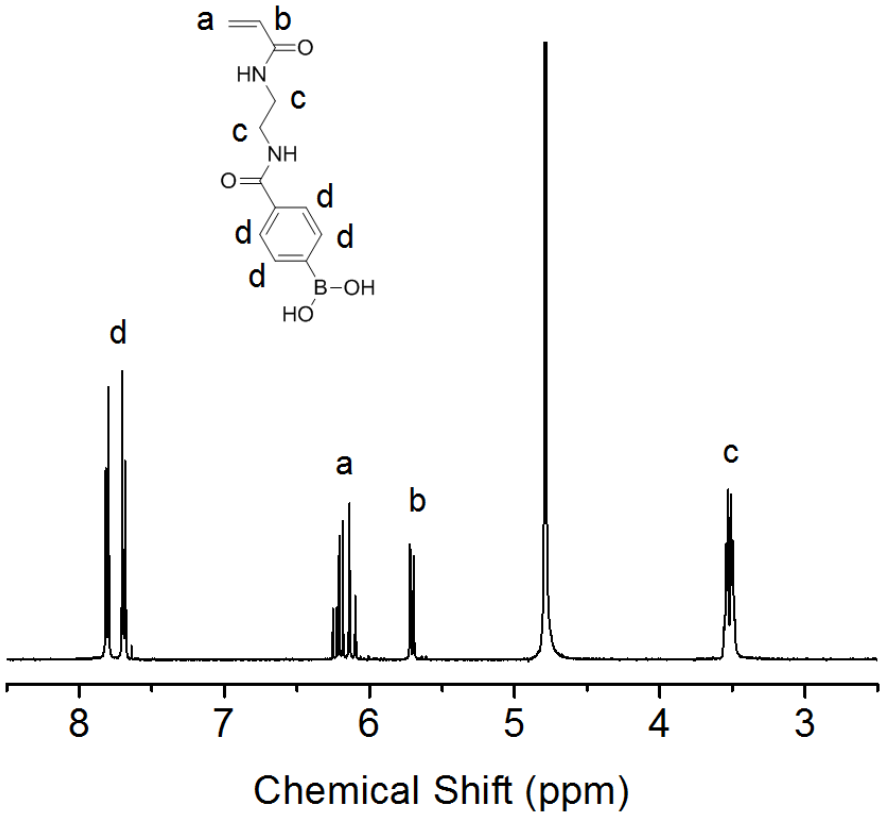

Figure S1. ^{1}H NMR spectrum of DDOPBA(compound 1 in Scheme 1)

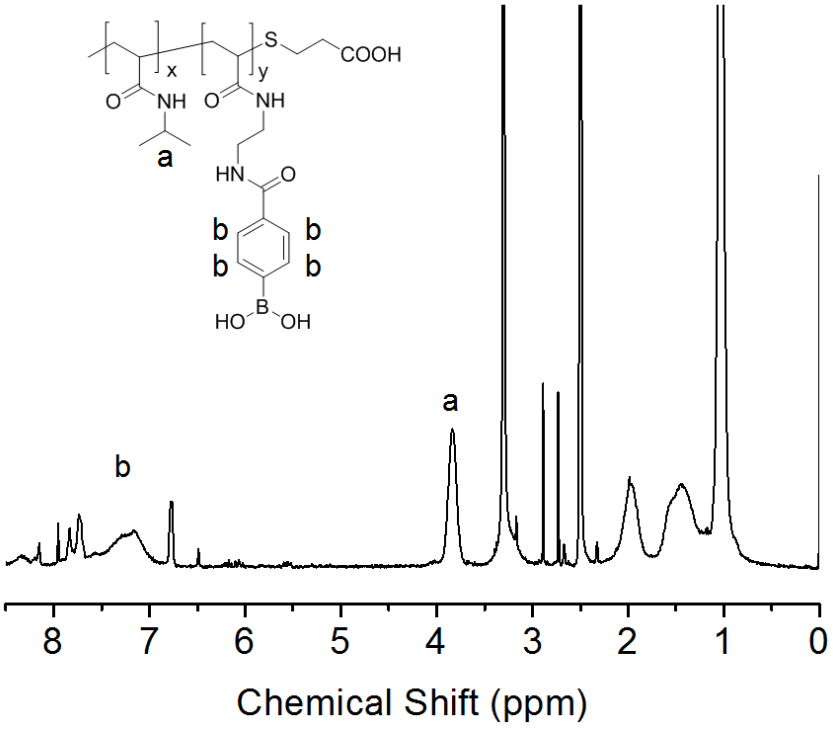

Figure S2. ^{1}H NMR spectrum of poly(NIPAM-*co*-PBA)-COOH

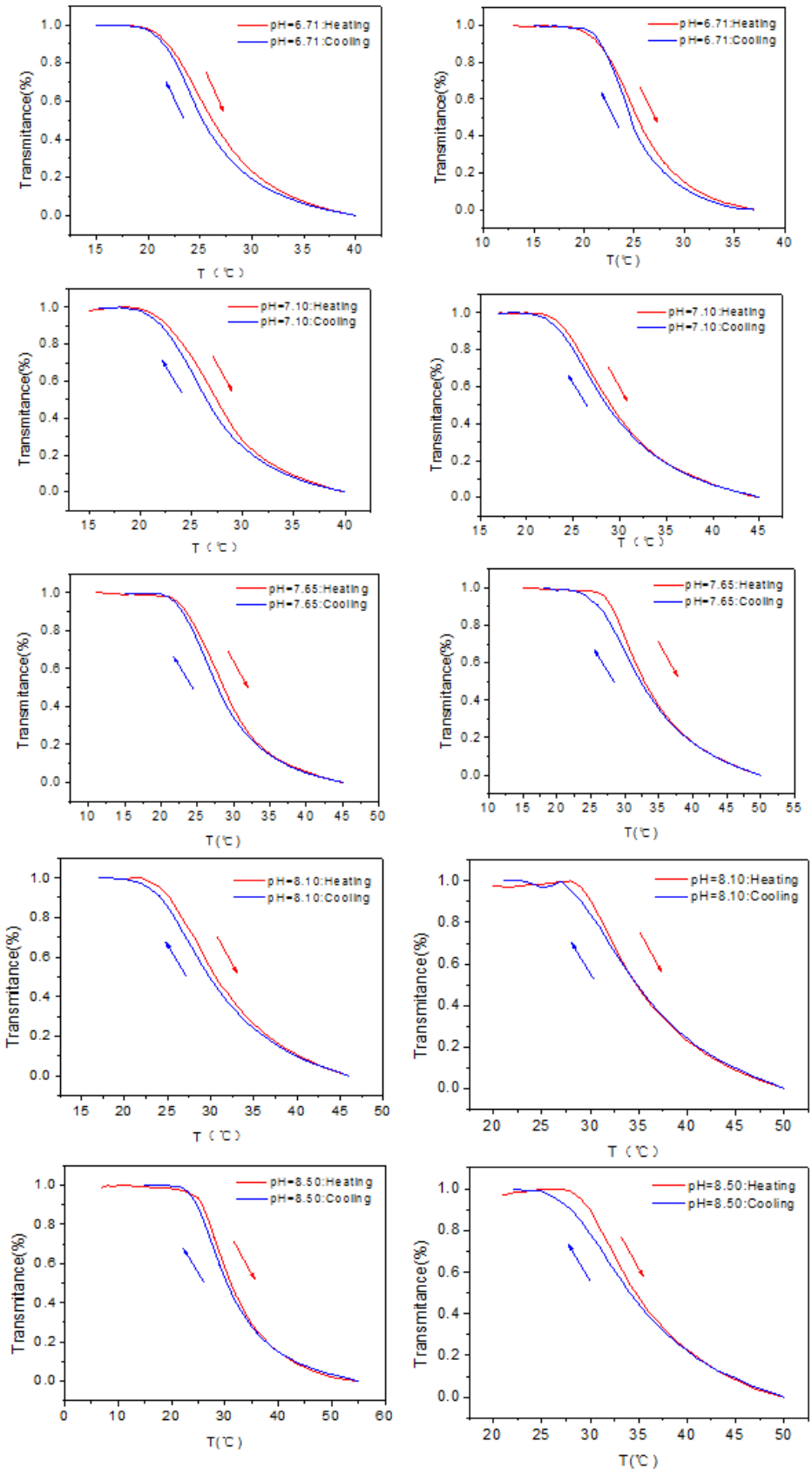

Figure S3. Transmittance versus temperature of end-functionalized phenylboronic acid containing PNIPAM random copolymers in the absence (Left panels) or presence of 25 mM glucose (Right panels). Red curves: heating; Blue curves: cooling.

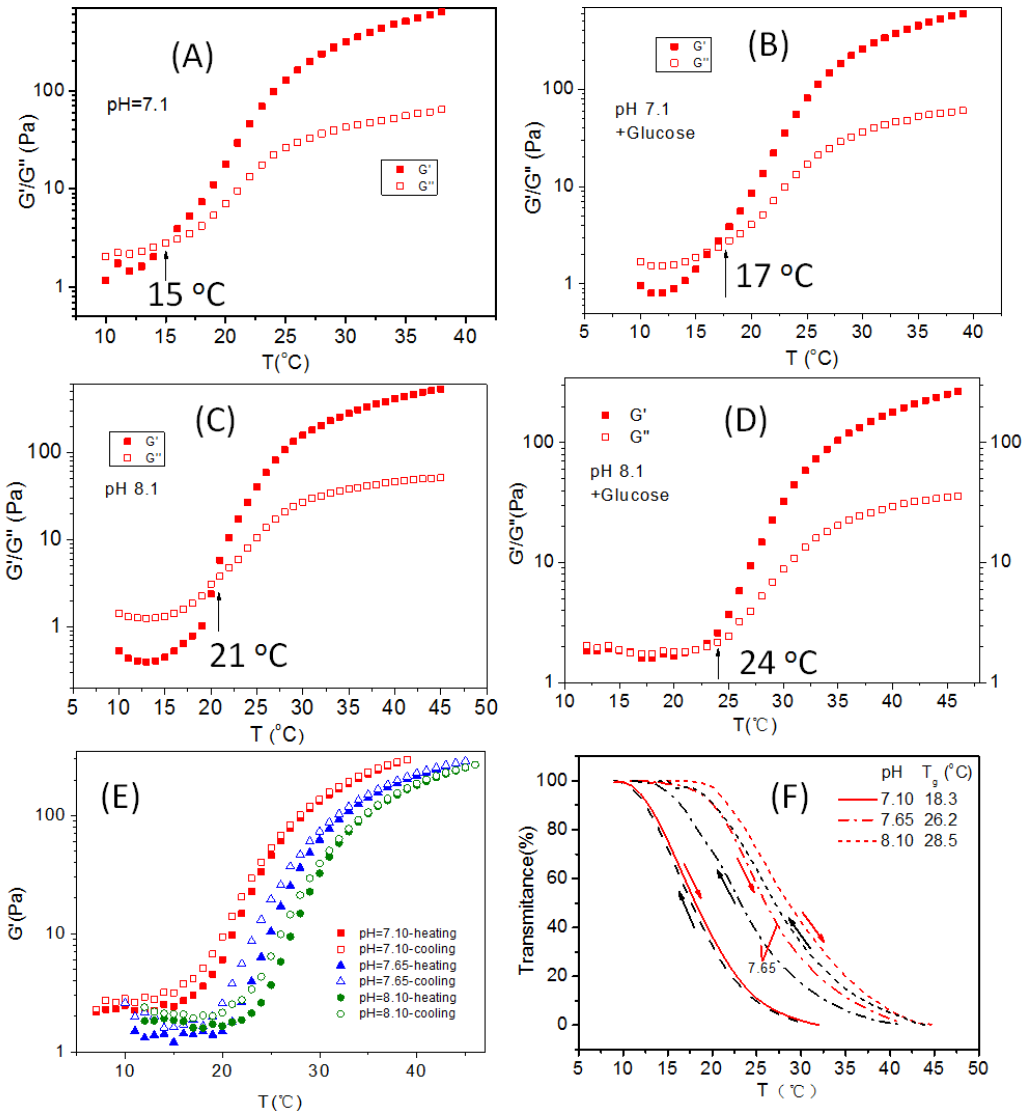

Figure S3. (A) ~ (E) Rheological analysis of the gelation behavior of the M13 virus grafted with phenylboronic acid containing PNIPAM random copolymers. The concentration of the polymer grafted virus is 7 mg mL^{-1}, the stain was 0.8% and frequency was 1 Hz. The heating/cooling rate was 4 ^{o}C min^{-1}. (A) ~ (D) Modulus G′ and G″ as a function of temperature at different pH in the absence (A and C) or presence (B and D) of glucose. The arrows indicate the transition temperature which is defined as the critical gelation temperature. (E) Storage modulus G′ as a function of temperature during heating and cooling at several pH in the presence of 25 mM glucose. (F) Transmittance versus temperature during heating/cooling cycles in the presence of 25 mM glucose. The concentration of virus is 3 mg mL^{-1} in PBS buffer. Red curves: heating; Black curves: cooling. The heating/cooling speed is 1 ^{o}C per 5 mins.

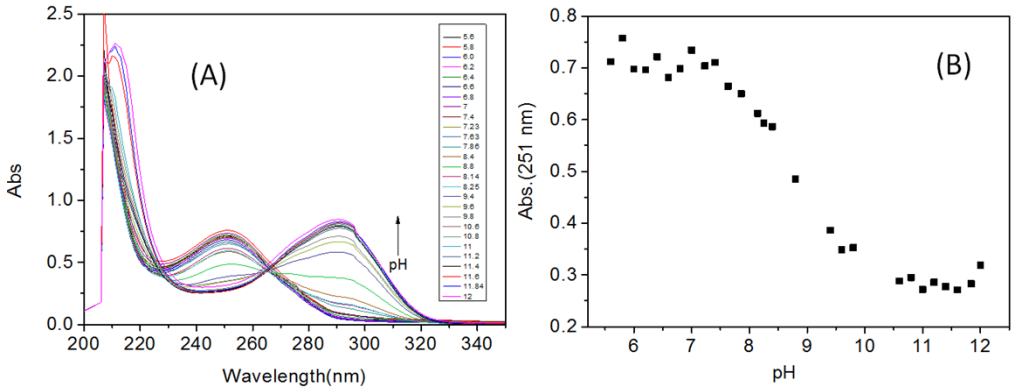

Figure S4. (A) Ultraviolet-visible spectra of end-functionalized phenylboronic acid containing PNIPAM random copolymers, poly(NIPAM-*co*-PBA)-COOH, during pH titration. The concentration of the polymer was 0.01 wt % and temperature was 10℃. The scanning range was 200-350 nm. (B) The absorption intensity at 251 nm in (A) versus temperature.

Reference

1 A. Matsumoto, S. Ikeda, A. Harada and K. Kataoka, *Biomacromolecules*, 2003, **4**, 1410-1416.