

Supporting Information

Repurposing Pinacol Esters of Boronic Acids for Tuning Viscoelastic Properties of Glucose-responsive Polymer Hydrogels: Effects on Insulin Release Kinetics

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Supporting Figures

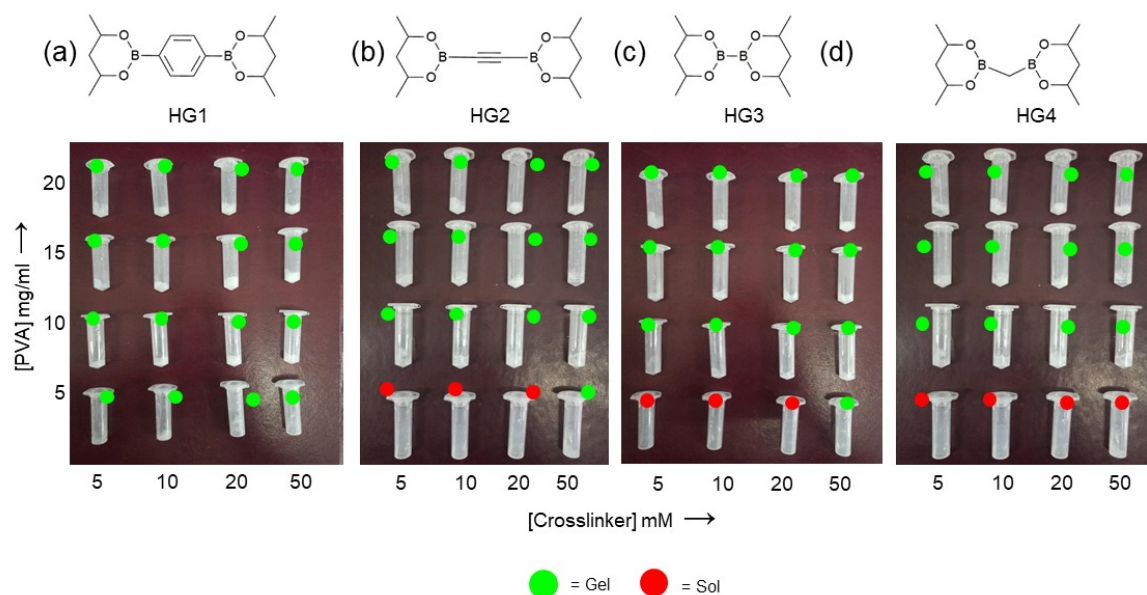


Fig. S1 Phase diagram of HG1-4. Red, and green dots correspond to solution, and gel phases, respectively.

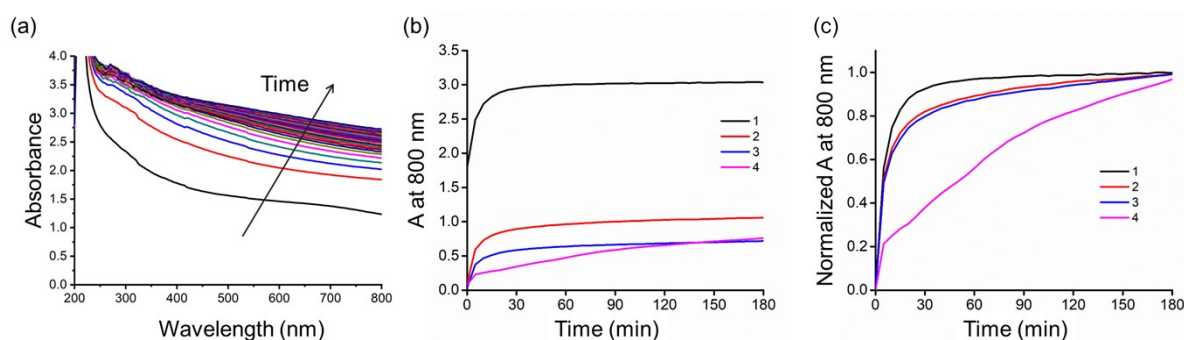


Fig. S2 Kinetics measured using turbidimetric measurements. (a) Representative absorbance spectra of HG1. Absorbance spectra is obtained every 5 minutes. (b) Absorbance at 800 nm is measured with respect to time. (c) Normalized absorbance plotted against the time. L1 show significantly faster kinetics followed by L2 and L3. L4 demonstrated the slowest kinetics.

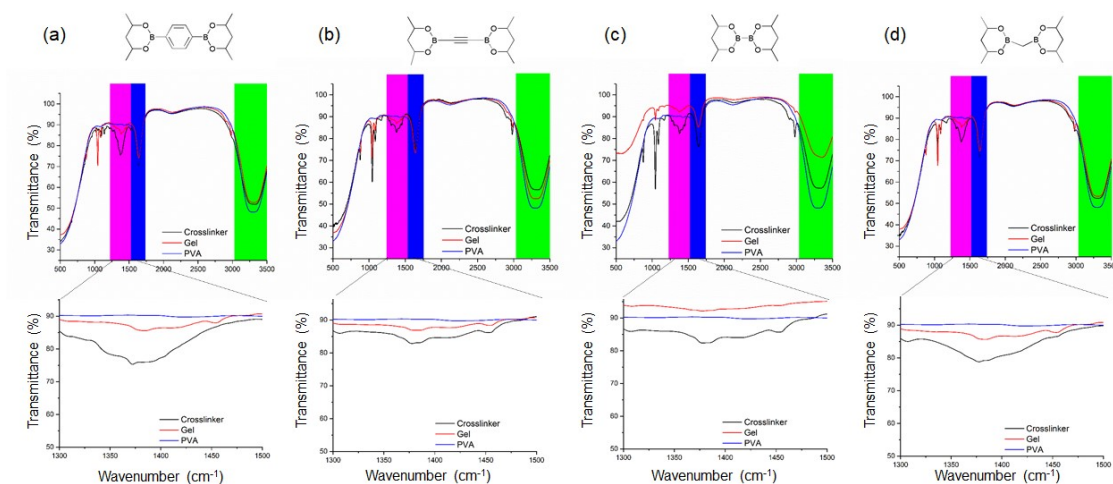


Fig. S3 FTIR spectra of HG1-4. All the hydrogels show O-H stretching (green band) and H-O-H scissoring(blue band) frequencies due to the presence of water. The B-O stretching frequency is present around 1330 -1380 cm^{-1} (magenta band) showing the the presece of boronate ester bond. 1300-1500 cm^{-1} are enlarged for clarity.

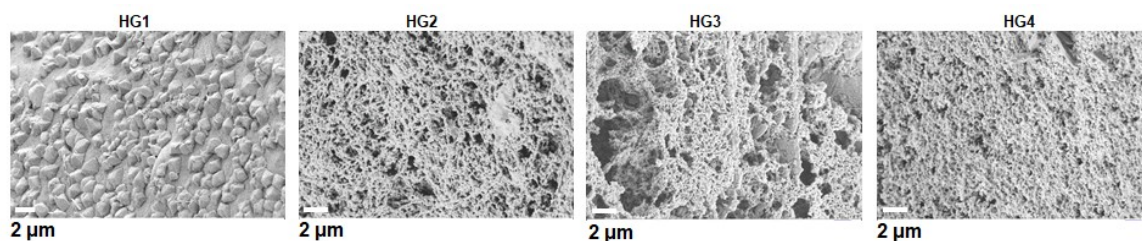


Fig. S4 SEM images of freeze dried HG1-4. While HG2-4 show microporous network, HG1 does not have such pores visible.

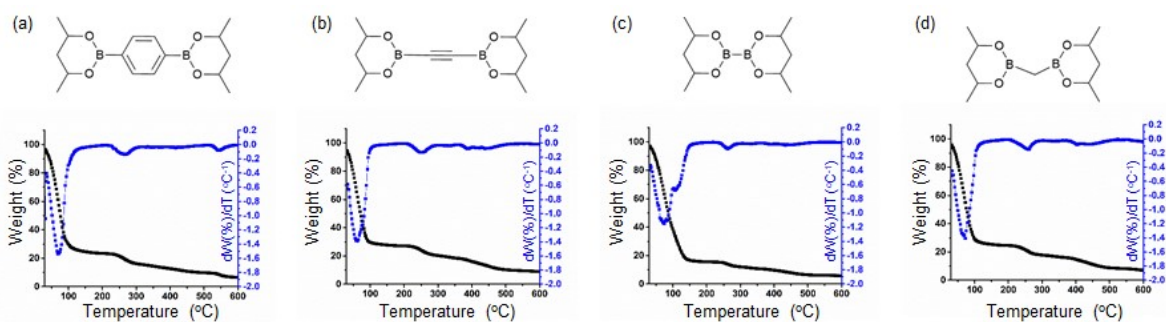


Fig. S5 TGA of HG1-4: weight (%) change curve (black) and first derivative of TGA curve (blue) plotted with respect to temperature. There is a rapid decline in the weight (%) around 80–110 $^{\circ}\text{C}$ indicating abundance of water in the HGs. The water content was measured to be 74.4%, 70.1%, 83.1%, 72.3% for HG1-4, respectively.

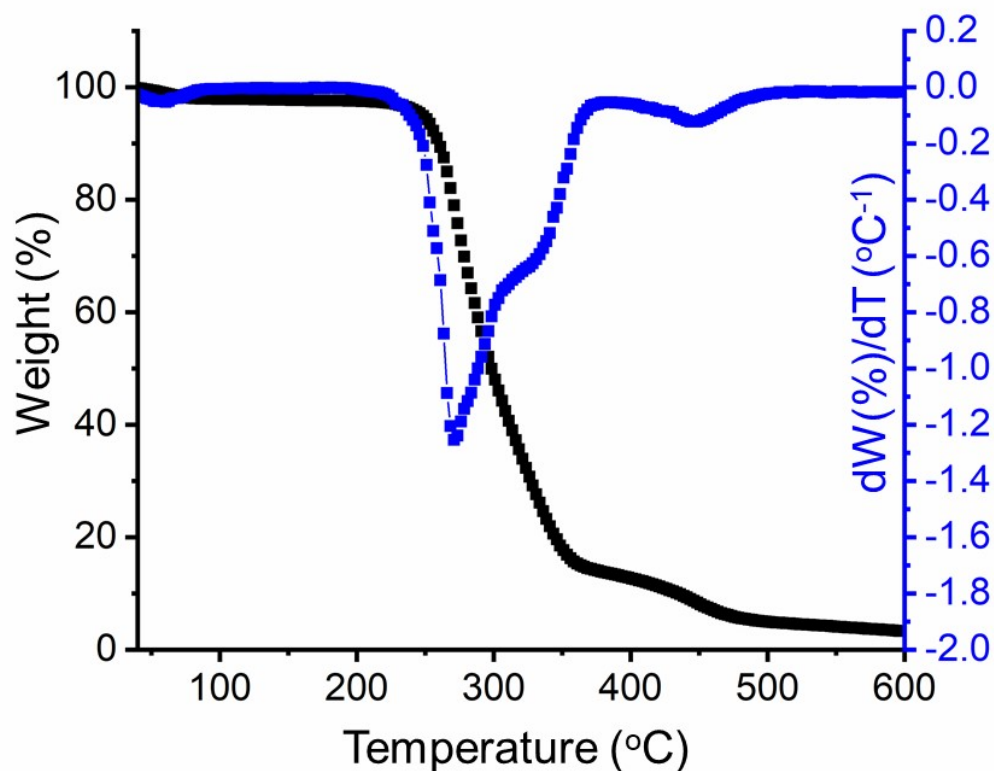


Fig. S6 TGA of pure PVA. Weight (%) change curve (black) and first derivative of TGA curve (blue) plotted with respect to temperature. A decrease in the weight (%) around 240–360 $^{\circ}\text{C}$ was observed.

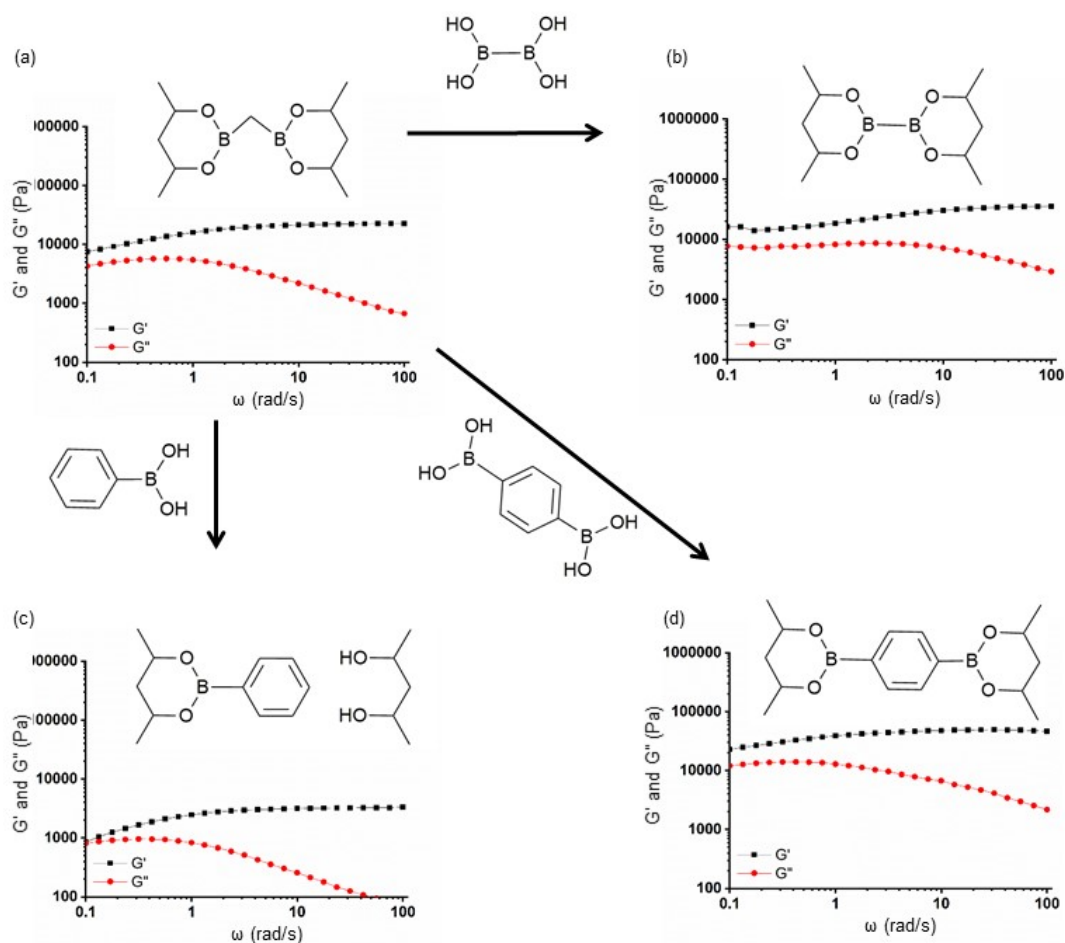


Fig. S7 In situ modulation of viscoelastic properties. Frequency sweep of storage modulus (G' , black) and loss modulus (G'' , red) of (a) HG4, (b) HG4 incubated with 100 mM tetrahydroxydiboron, (c) HG4 incubated with 100 mM benzene-1,4-diboronic acid, (d) HG4 incubated with 100 mM PBA. There is significant hardening of HG4 upon the exposure to tetrahydroxydiboron and benzene-1,4-diboronic acid. Conversely, HG4 becomes soft due to the breaking of interchain crosslinks.

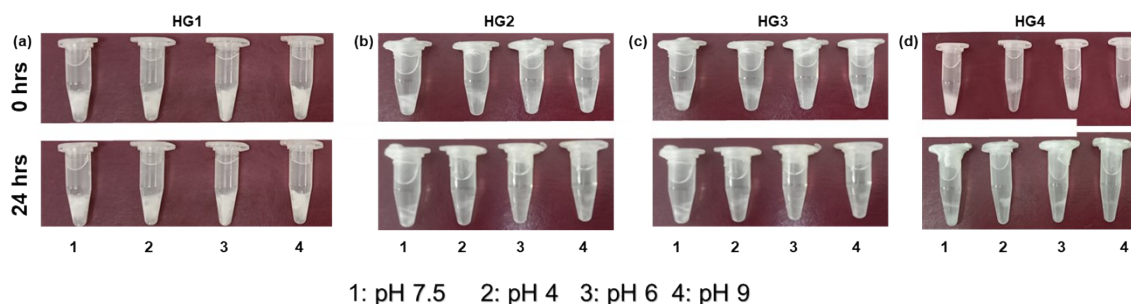


Fig. S8 Photographs of the HG1-4 at $t=0$ and $t=24$ hours under different pH conditions (7.5, 4, 6, 9) at 37 °C. HG1 show minimal degradation while HG2-4 show partial degradation in acidic pH environment.



Fig. S9 Photographs of the HG1-4 with increasing concentrations of carbohydrate and glucosamine at $t=0$ and $t=24$ hours under physiological condition at pH 7.5. Red arrows indicate complete dissolution. HG1 did not show dissolution under high concentrations of molecules. However, HG2-4 show complete dissolution in more than 100 mM concentration.

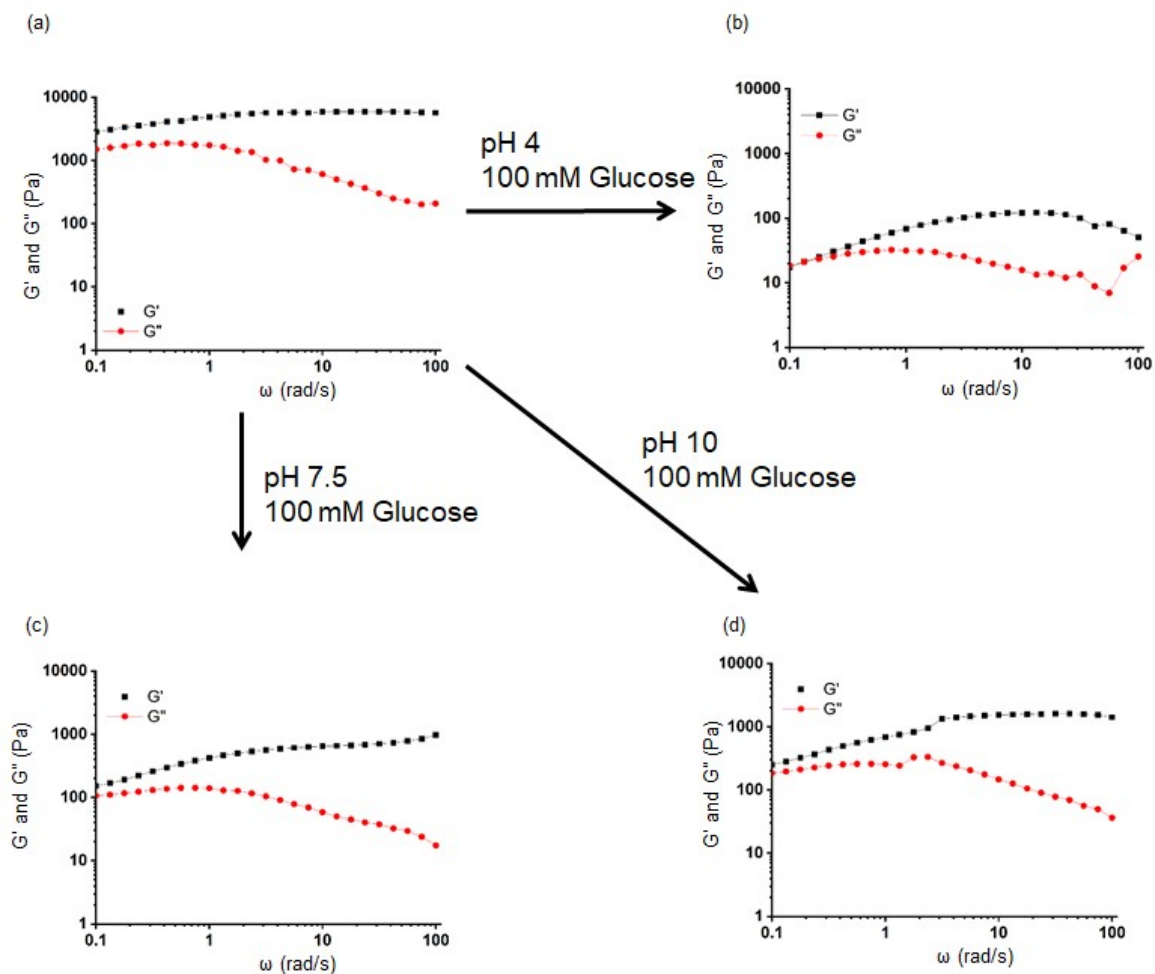


Fig. S10 In situ modulation of viscoelastic properties. Frequency sweep of storage modulus (G' , black) and loss modulus (G'' , red) of (a) HG4, (b) HG4 incubated with 100 mM glucose at pH 4, (c) HG4 incubated with 100 mM glucose at pH 7.5, (d) HG4 incubated with 100 mM glucose at pH 10 after 1 hour of exposure. Both the storage modulus (G') and loss modulus (G'') values decreased under high glucose conditions due to the breakage of crosslinks. The effect is more pronounced under pH 4 condition.

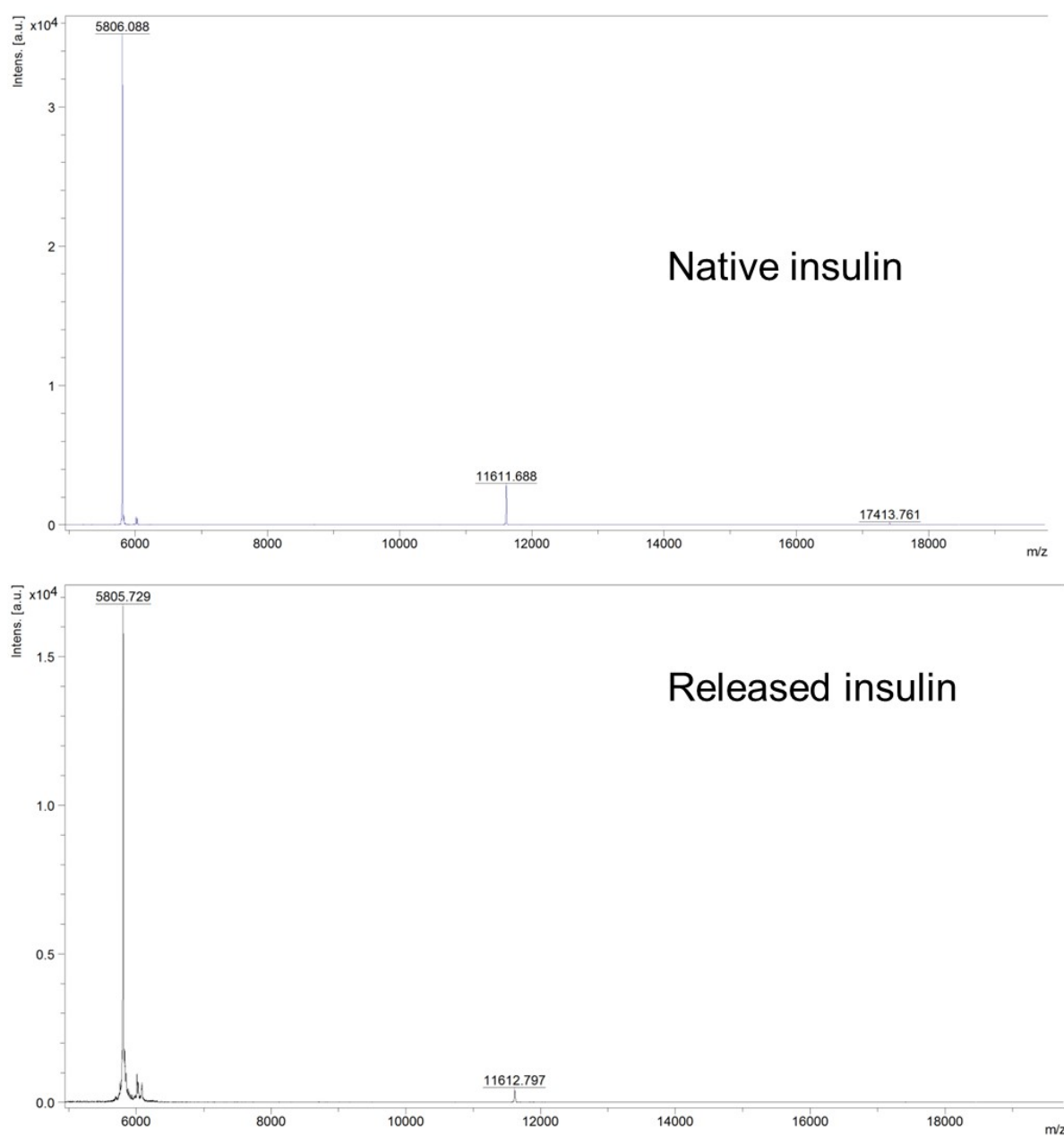


Fig. S11 MALDI-MS of the native and released insulin showing identical mass of ~ 5806 Da indicating no hydrolytic disintegration of insulin.