## Impact of Ion Binding on Poly-L-Lysine (Un)folding Energy

## Landscape and Kinetics

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## SUPPORTING INFORMATION

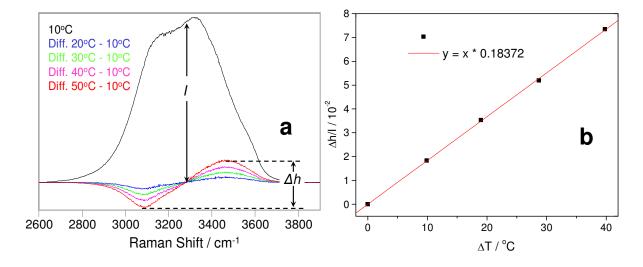


Figure S1: **a)** 204 nm excited water stretching bands at 10 °C and the difference spectra between higher temperatures and 10 °C. **b)** T-jump calibration curve which relates the magnitude of water stretching band spectral shift to the temperature change.

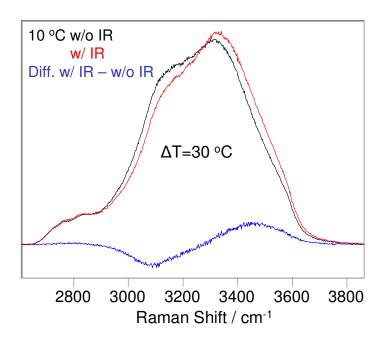


Figure S2: 204 nm excited water stretching bands of 5 mg/ml PLL in 0.5 M NaClO<sub>4</sub> (and 0.015 M NaBr) with (**red**) and without (**black**) IR pulses at 10 °C, and the difference spectrum (**blue**). The temperature jump is 30 °C.

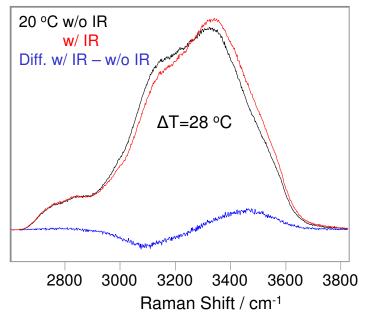


Figure S3: 204 nm excited water stretching bands of 5 mg/ml PLL in 0.5 M NaClO<sub>4</sub> (and 0.015 M NaBr) with (**red**) and without (**black**) IR pulses at 20 °C, and the difference spectrum (**blue**). The temperature jump is 28 °C.

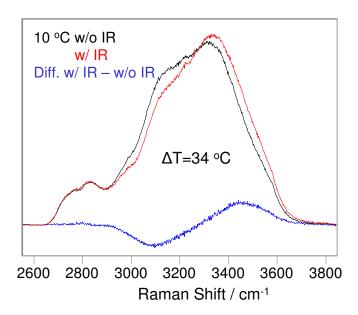


Figure S4: 204 nm excited water stretching bands of 15 mg/ml PLL in pure water with (**red**) and without (**black**) IR pulses at 10 °C, and the difference spectrum (**blue**). The temperature jump is 34 °C.

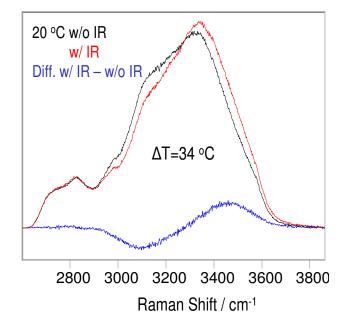


Figure S5: 204 nm excited water stretching bands of 15 mg/ml PLL in pure water with (**red**) and without (**black**) IR pulses at 20 °C, and the difference spectrum (**blue**). The temperature jump is 34 °C.

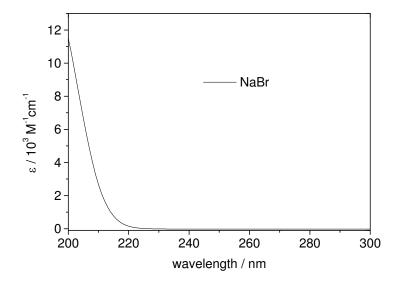


Figure S6: Molar absorptivity of NaBr in pure water.

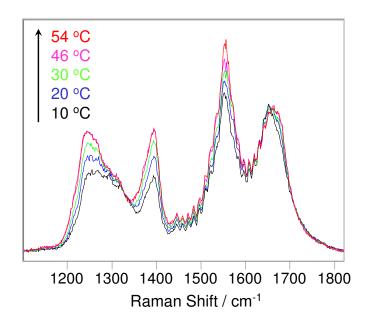


Figure S7: Temperature dependence of 204 nm excited UVRR spectra of 1 mg/ml PLL in pure water at pH 10.65. The intensities were normalized to the isosbestic point at 1335 cm<sup>-1</sup>. The  $C_{\alpha}$ -H band intensity significantly increases with increasing temperature, indicating  $\alpha$ -helix melting. The AmIII<sub>3</sub> band frequency downshifts and its intensity significantly increases, which also indicate  $\alpha$ -helix melting.

## **Reference:**

- (1) Wang, Y.; Purrello, R.; Jordan, T.; Spiro, T. G. *J Am Chem Soc* **1991**, *113*, 6359-6368.
- (2) Xiong, K.; Asciutto, E. K.; Madura, J. D.; Asher, S. A. *Biochemistry* **2009**, *48*, 10818-10826.