Electronic Supplementary Material (ESI) for Nanoscale Advances.

Correlating structural changes in thermoresponsive hydrogels to the optical response of embedded plasmonic nanoparticles

Supplementary Information

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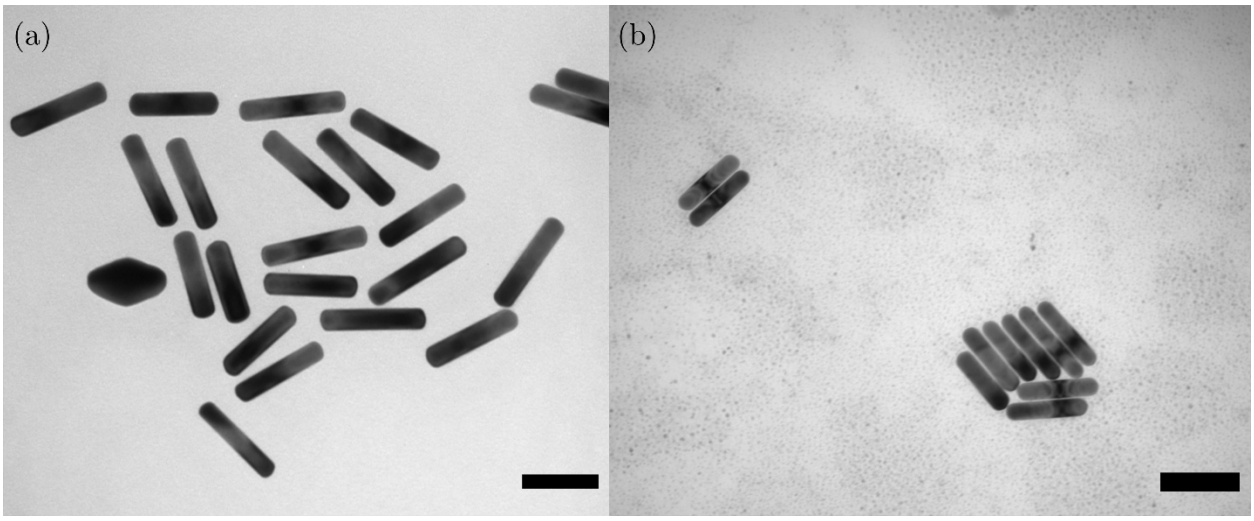


Figure S1. Transmission electron microscopy of AuNRs (a) as-synthesized and (b) after partial ligand exchange to N,N'-bis(acryloyl)cystamine. Scalebars are 100 nm.

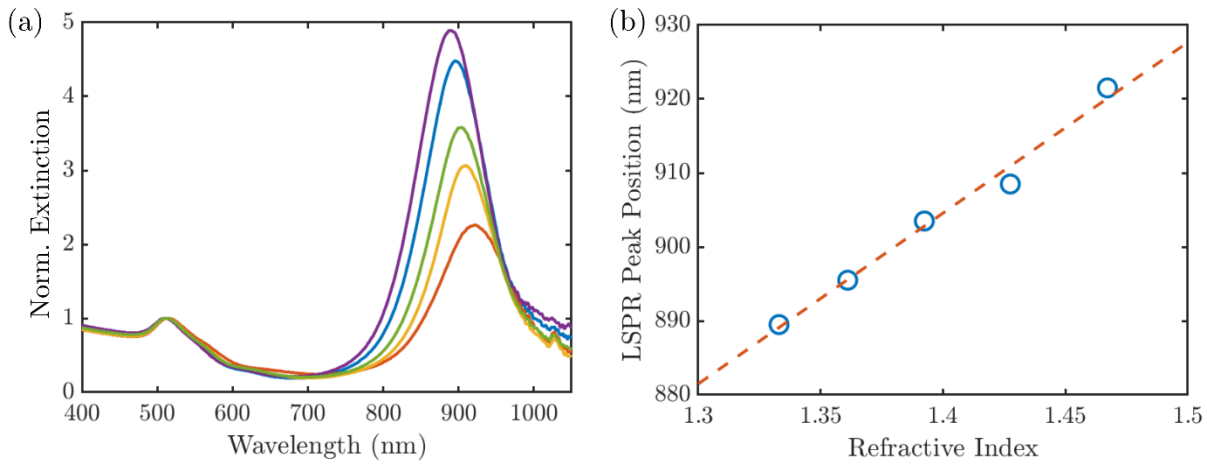


Figure S2. Characterization of the refractive index sensitivity of the AuNRs. (a) UV/Vis/NIR extinction spectra of AuNRs in varying refractive index media. The plasmon resonances red-shift as the medium changes from water (purple) to 25/75 (blue) to 50/50 (green) and 75/25 (orange) water/glycerol mixtures and finally to pure glycerol (red). (b) Peak position of the longitudinal plasmon resonance of AuNRs versus refractive index of the medium. The dashed line shows a line of best fit with a slope of 310 nm/RIU.

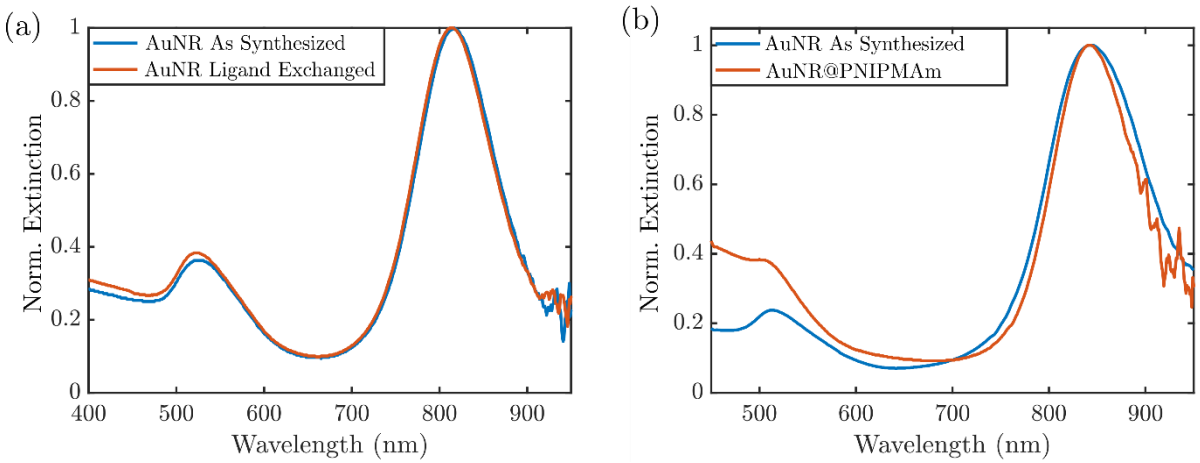


Figure S3. Extinction spectra of AuNRs. (a) Minimal change is observed upon partial ligand exchange to N,N'-bis(acryloyl)cystamine. (b) Minimal shift in the plasmon resonances are observed upon growth of the PNIPMAm shell, but an increase in scattering is evident at shorter wavelengths.

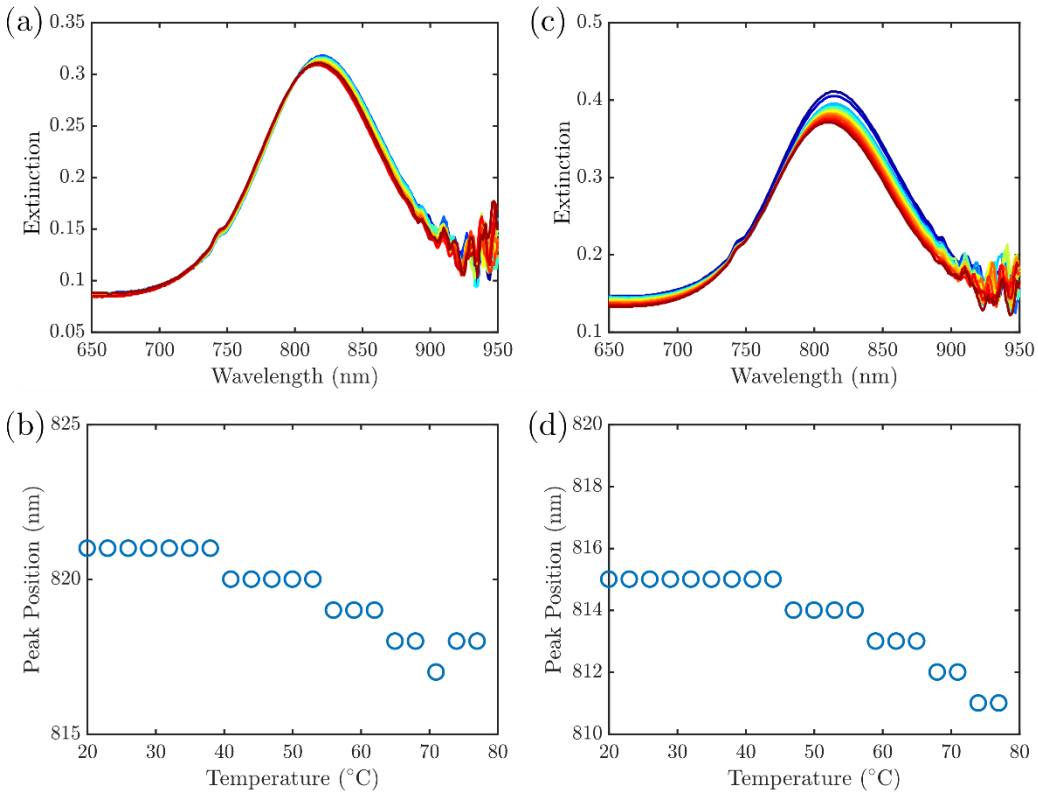


Figure S4. Temperature dependent extinction of AuNRs without PNIPMAm. (a) NIR extinction of as-synthesized AuNRs as temperature is increased from 20°C to 80 °C. (b) Longitudinal plasmon resonance peak position vs temperature shows minimal change for as-synthesized AuNRs. (c) NIR extinction of ligand-exchanged AuNRs as temperature is increased from 20°C to 80 °C. (b) Longitudinal plasmon resonance peak position vs temperature shows minimal change for ligand-exchanged AuNRs.

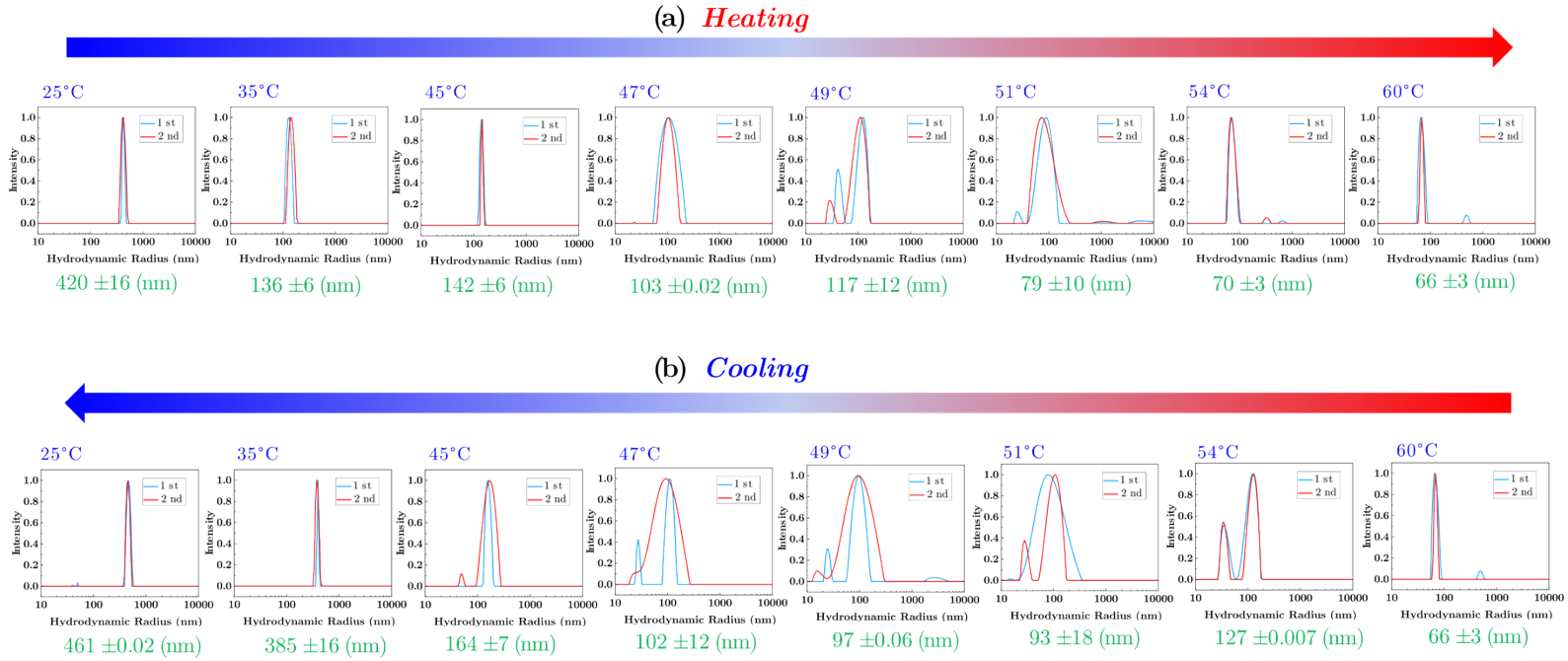


Figure S5. Dynamic light scattering data of AuNR-PNIPMam microgels while (a) heating and (b) cooling. Two independent measurements were made of each sample at each temperature.

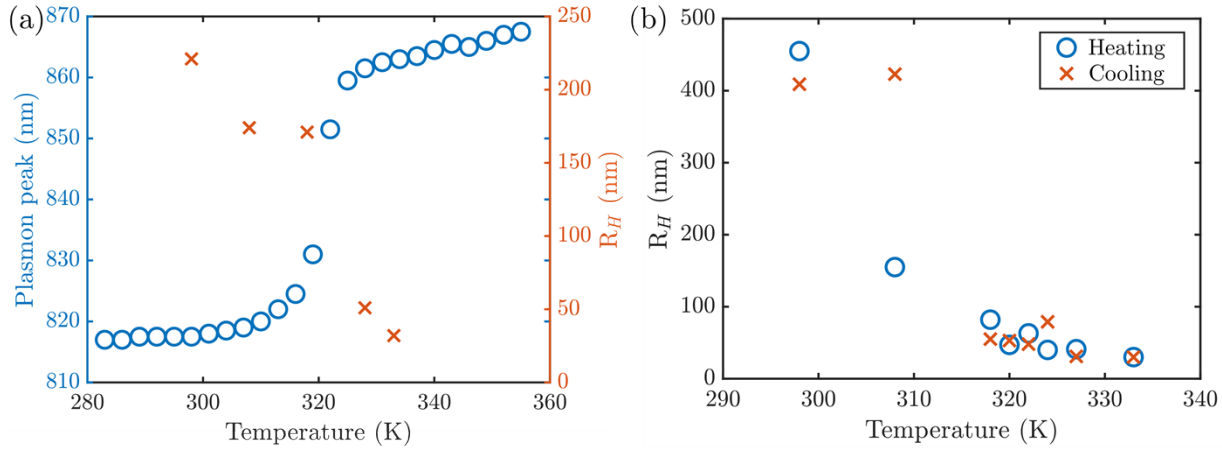


Figure S6. (a) Plasmon peak position (left y-axis) and hydrodynamic radius (right y-axis) of another sample of AuNR@PNIPMAm vs temperature. (b) Hydrodynamic radius of PNIPMAm microgel (with no AuNR) while heating and cooling.

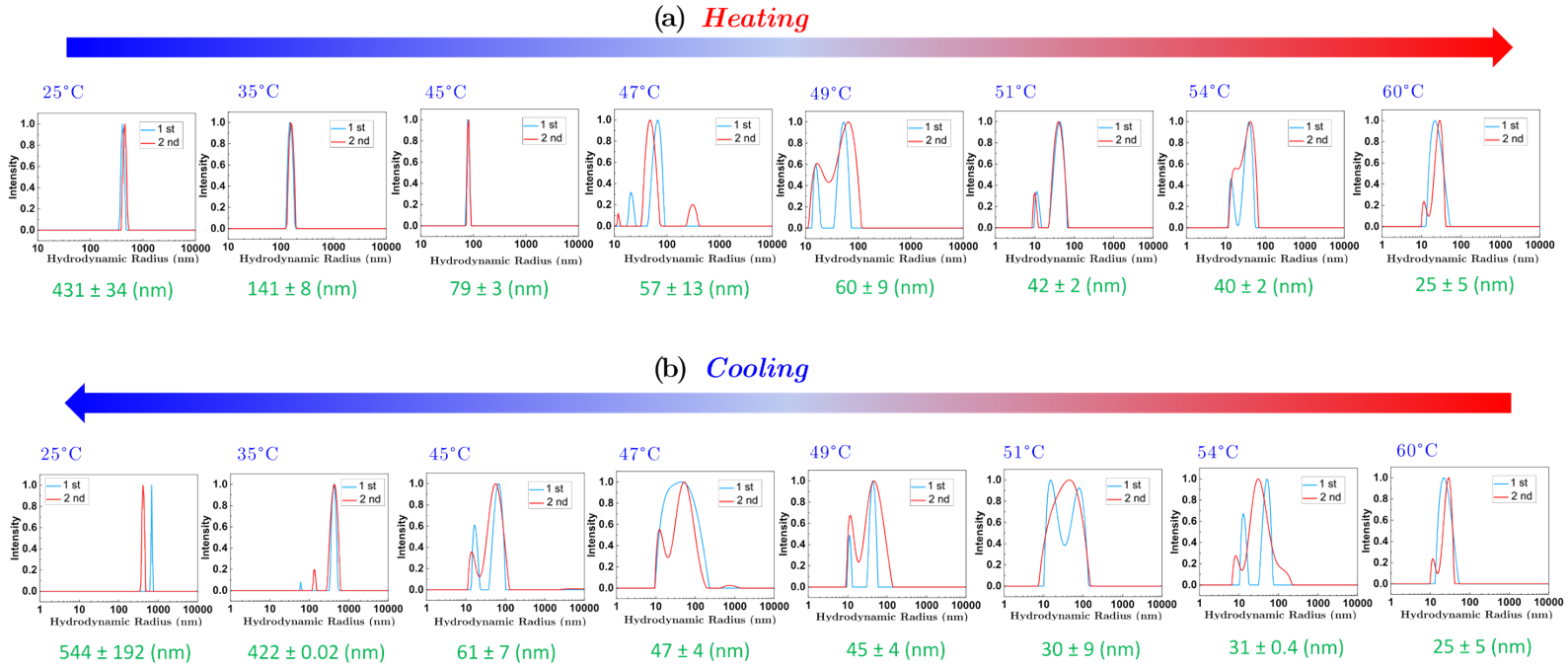
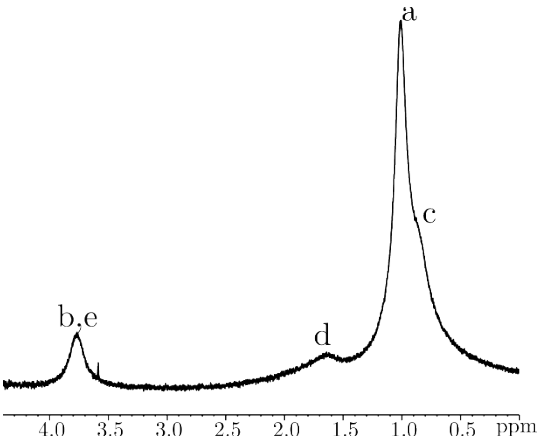


Figure S7. Dynamic light scattering data of PNIPMam while (a) heating and (b) cooling. Two independent measurements were made of each sample at each temperature.



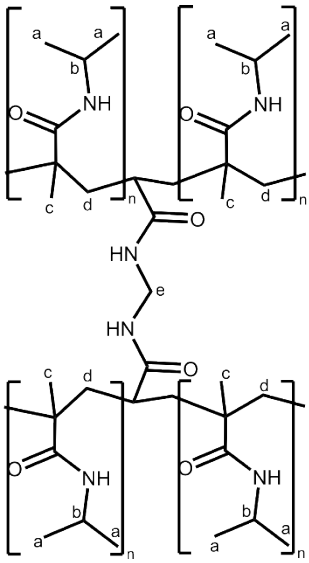


Figure S8. One-dimensional ^{1}H NMR of AuNR@PNIPMAm microgel shows four broad resonances corresponding to sidechain (a and b) and backbone (c and d) protons of the PNIPMAm as well as the crosslinker (e).

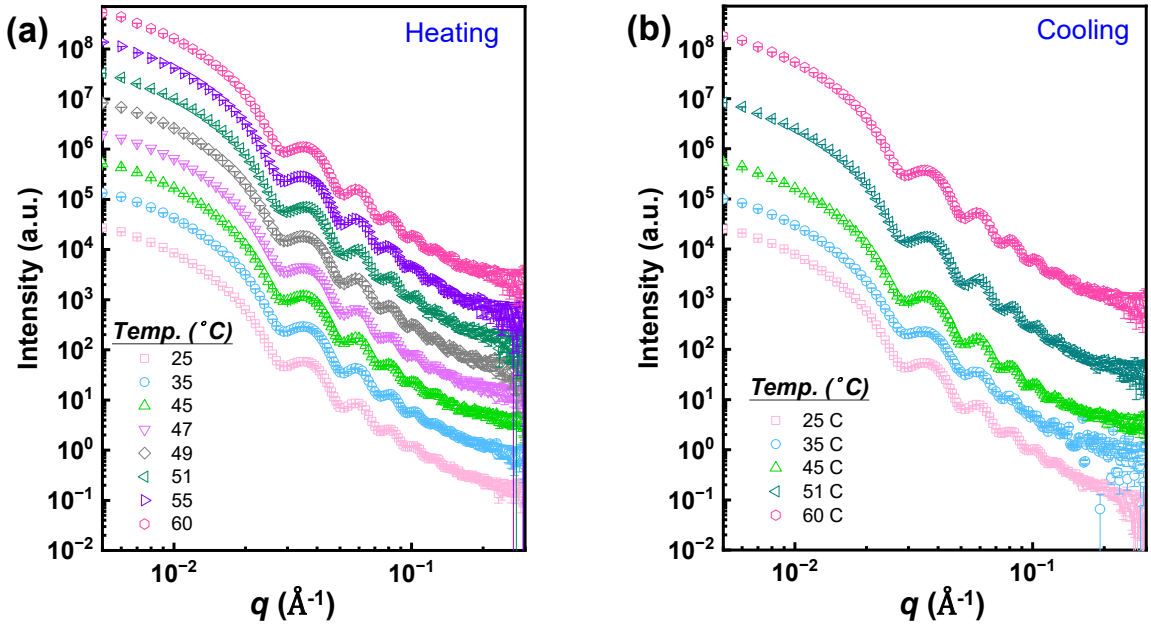


Figure S9. Small angle X-ray scattering data of AuNR@PNIPMAm upon heating and cooling. The invariance of the scattering pattern indicates that the structure of the AuNR has no temperature dependence.

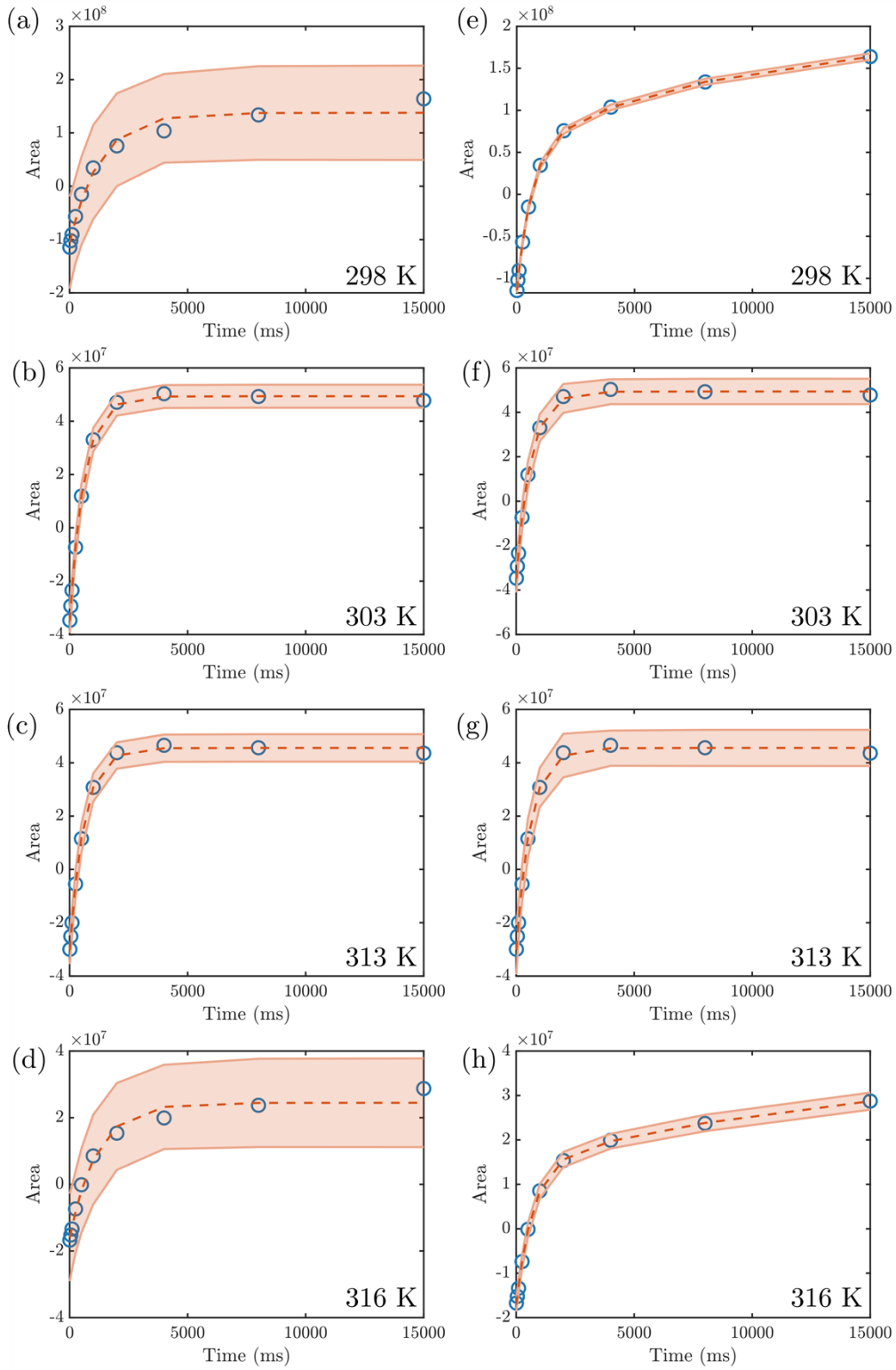


Figure S10. Inversion recovery of the backbone proton of PNIPMAm in AuNR@PNIPMAm at various temperatures, with monoexponential (a-d) or biexponential (e-f) fits. The shaded areas indicate 95% confidence intervals. At 303 K and 313 K, the relaxation is well-described by a monoexponential function, while at 298 K and 316 K, a biexponential function is required.