Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplemental Information

Multi-stimuli responsive tetra-PPO_{60}-PEO_{20} ethylene diamine block copolymer enables pH, temperature, and solvent regulation of Au nanoparticle composite plasmonic response

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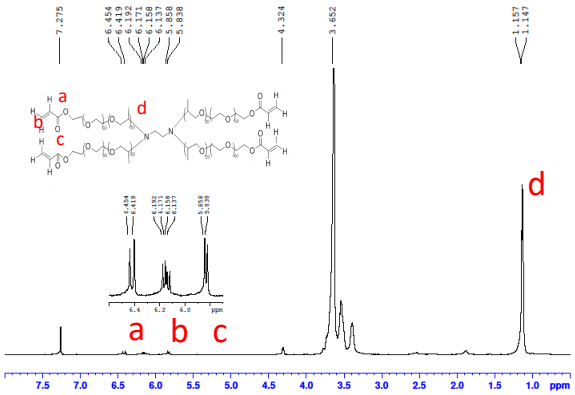
Figure S1. ^{1}H NMR spectrum of tetra-acrylated Tetronic, Tet1107(Acr)$_4$. Functionalization determined to be 95%.



$$\% \text{ function} = \frac{\text{number of repeats PPO} \times 3\ (^{1}\text{H}(-\text{CH}_3))}{\text{actual number of } ^{1}\text{H}(-\text{CH}_3)} \times 100$$

Figure S2. Comparison of ATR/FT-IR spectrum collected on solid Tetronic 1107 (black) and solid tetra-acrylated Tetronic 1107, Tet1107(Acr)$_4$ (blue). (A) High wavenumber region and (B) low wavenumber region.

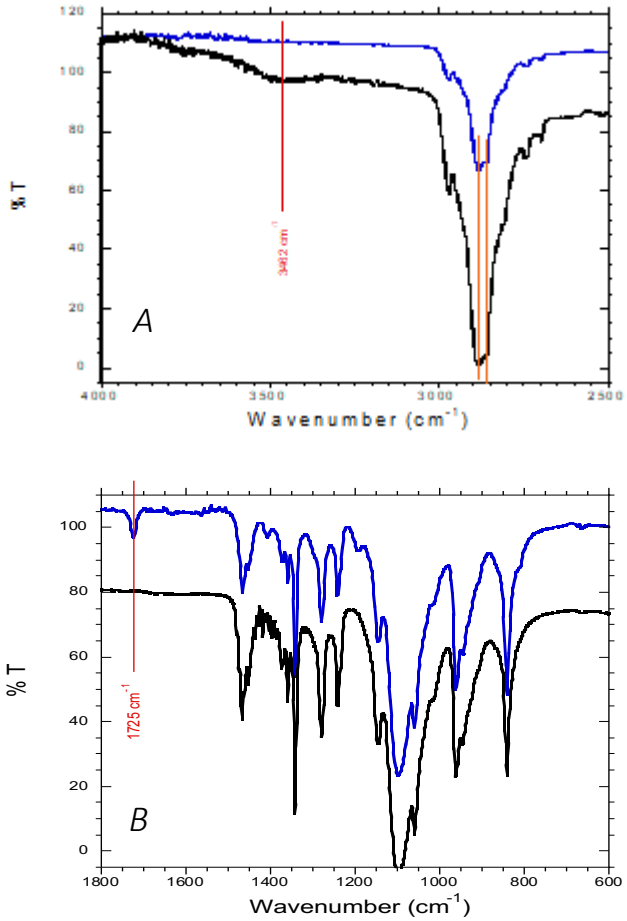


Figure S3. (A) Time-dependent Vis-NIR spectra collected on a mesophase mixture prepared with 0.733 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0371 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0852 ± 0.0005 DMPC lipid, and Φ_p = 0.114 ± 0.005 Tetronic 1107(Acr)$_4$, with Au molar concentration of 6.41mM. (B) a mesophase mixture prepared with 0.730 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0370 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0866 ± 0.0005 DMPC lipid, and Φ_p = 0.147 ± 0.005 F98(Acr)$_2$, with Au molar concentration of 7.09 mM.

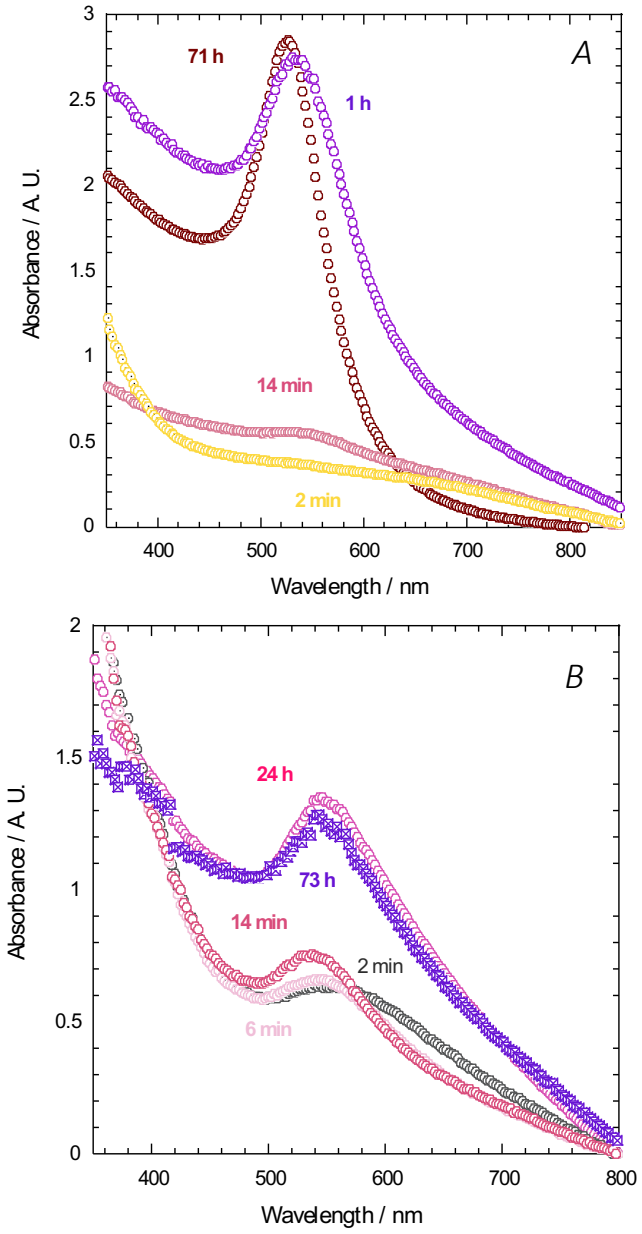


Figure S4. Time-dependent ratio of absorbance post addition of DPPH to complex fluid during Au NP network polymer composite formation. Red curve is time course for a composition prepared with 0.733 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0371 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0852 ± 0.0005 DMPC lipid, and Φ_p = 0.114 ± 0.005 Tetronic 1107(Acr)$_4$, with Au molar concentration of 6.41mM. Purple curve is composition prepared with 0.730 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0370 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0862 ± 0.0005 DMPC lipid, and Φ_p = 0.147 ± 0.005 F98(Acr)$_2$, with Au molar concentration of 7.09 mM

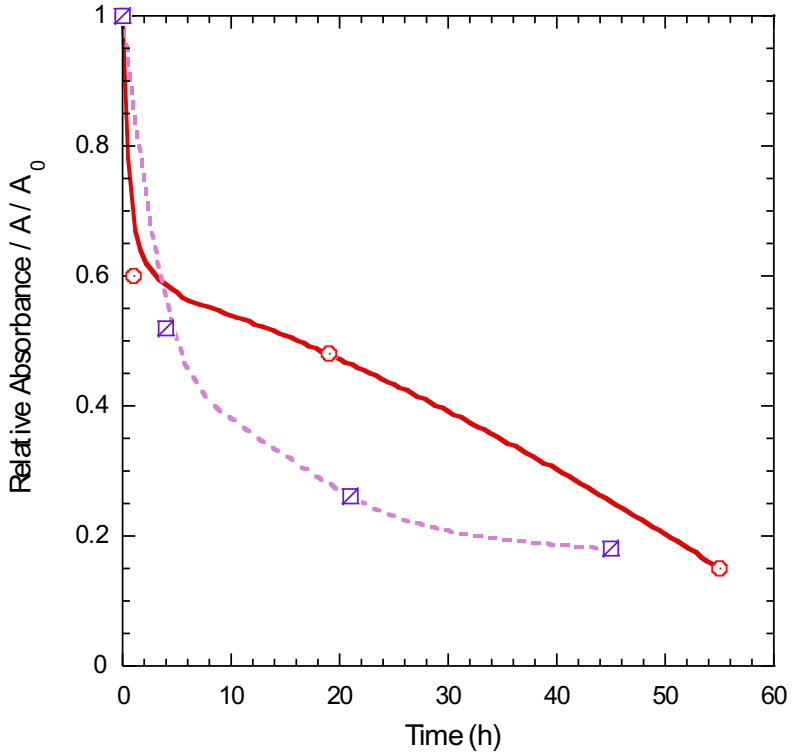


Figure S5. (A) Fast scan (10 °C min^{-1}) N_2 atmosphere TGA collected on a photo-crosslinked complex fluid. Weight % (black) and derivative weight loss (blue). (B) Differential scanning calorimetry (DSC) taken on the photo-crosslinked network polymer.

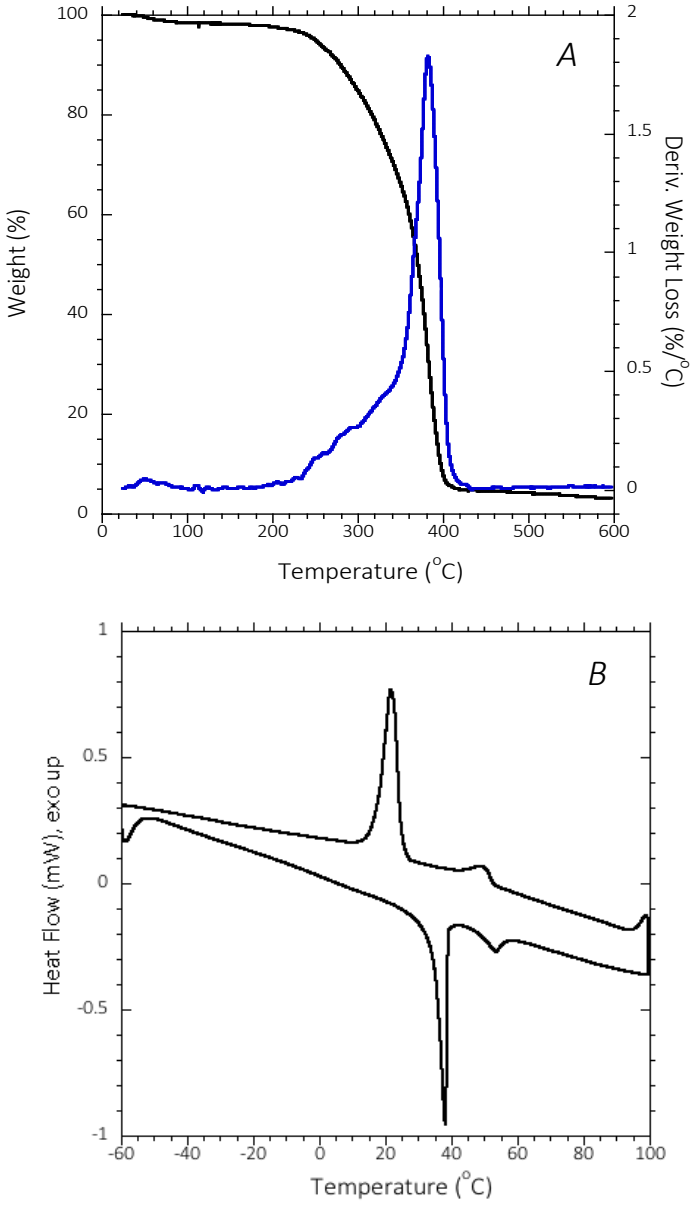


Figure S6. (A) Representative STEM image collected on grid cast particles released from a network composite using a 17 (v/v) % aqueous hydrazine solution. (B) Histogram of nanoparticle size distribution. (C), (D) Representative STEM images collected on Au NP Tet(Acr)$_4$-based polymer composites directly formed on the TEM grid. The bright contrast of Au NP in comparison with the dark background of the polymeric matrix is related to the Z-contrast of the HAADF image in which the intensity escalates with the atomic number I ~ Z (1.8-2). The size distribution histogram in Figure E was calculated for N=200 particles and fitted with a Gaussian distribution to obtain the mean± 1-sigma diameter. Elemental analysis of the sample is shown in Figure F where the characteristic peaks for Au are present. Additional peaks for C and O are related to the polymer; a small Cl peak can be associated with residual materials from $HAuCl_4$ precursor, and Cu from the copper support grid. (G) Representative STEM images collected on Au NP F98(Acr)$_2$-based polymer composites directly formed on the TEM grid. (H) The size distribution histogram N=200 particles.

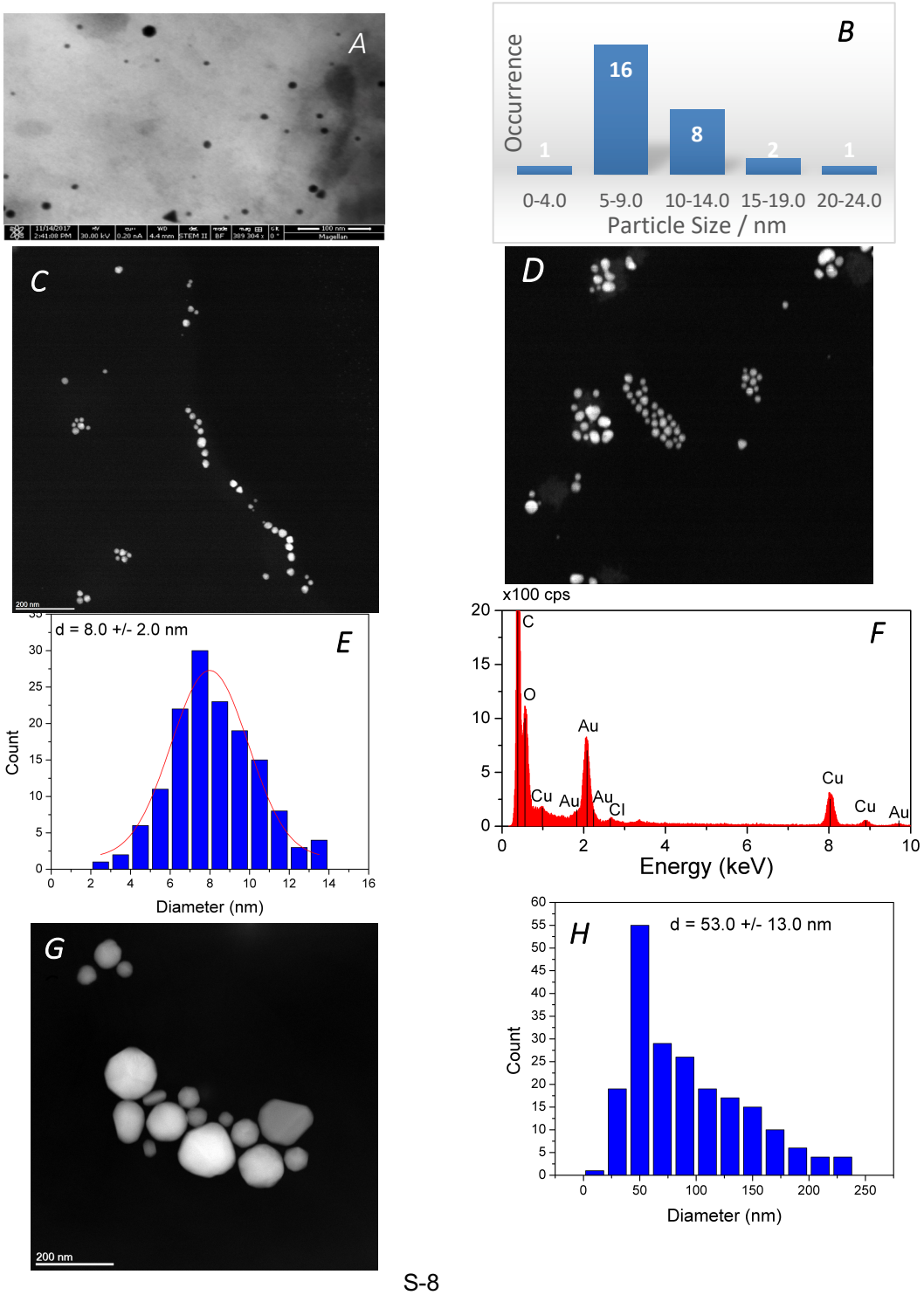


Figure S7. Temperature dependent circularly averaged small-angle X-ray scattering (SAXS) data collected on a complex fluid, lacking $[AuCl_4]^-$, (A) prepared in 100 mM acetate buffer (pH 3.66); (B) prepared in 10 mM carbonate buffer (pH 9.02).

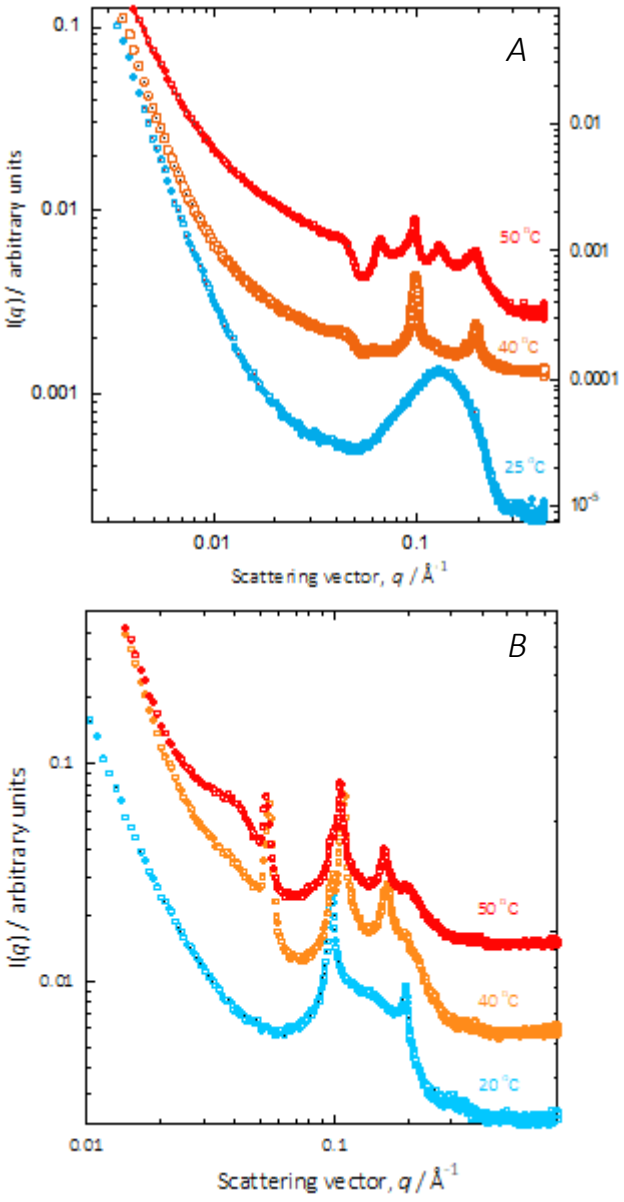
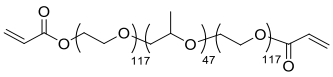
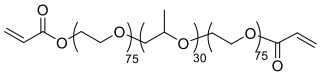


Table S1: Small angle X-ray reflections observed for a Au NP composite prepared in water at 35 °C. Reflections index to a mixture of a cubic Im3m and lamellar structure

H	K	L	$q_{(observed)}$ $Å^{-1}$	Im3m	Lamellar
1	1	0	0.116	√2	
0	0	1	0.126		1
2	0	0	0.164	√4	
2	1	1	0.200	√6	
2	2	0	0.231	√8	
3	1	0	0.254	√10	2
2	2	2	0.284	√12	
3	2	1	0.307	√14	
4	0	0	0.328	√16	
4	1	1	0.347	√18	
3	3	2	0.382	√22	3
4	3	1	0.410	√26	
4	4	0	0.468	√32	

Figure S8 (A) Normalized temperature dependent Vis-NIR spectra collected on Au NP F98(Acr)$_2$/LDAO/DMPC/water composite, 0.739 ± 0.01 weight fraction (Φ_w) of water, Φ_s = 0.0116 ± 0.0005 LDAO co-surfactant, and Φ_l = 0.0951 ± 0.005 DMPC lipid, and Φ_p = 0.161 ± 0.001 F98(Acr)$_2$, mM Au^{3+} and (B) Au NP F68(Acr)$_2$/LDAO/DMPC/water 0.673 ± 0.01 weight fraction (Φ_w) of water, Φ_s = 0.0110 ± 0.0005 LDAO co-surfactant, and Φ_l = 0.0951 ± 0.005 DMPC lipid, and Φ_p = 0.159 ± 0.001 F68(Acr)$_2$, 6.66 mM Au^{3+}.

F98 

F68 

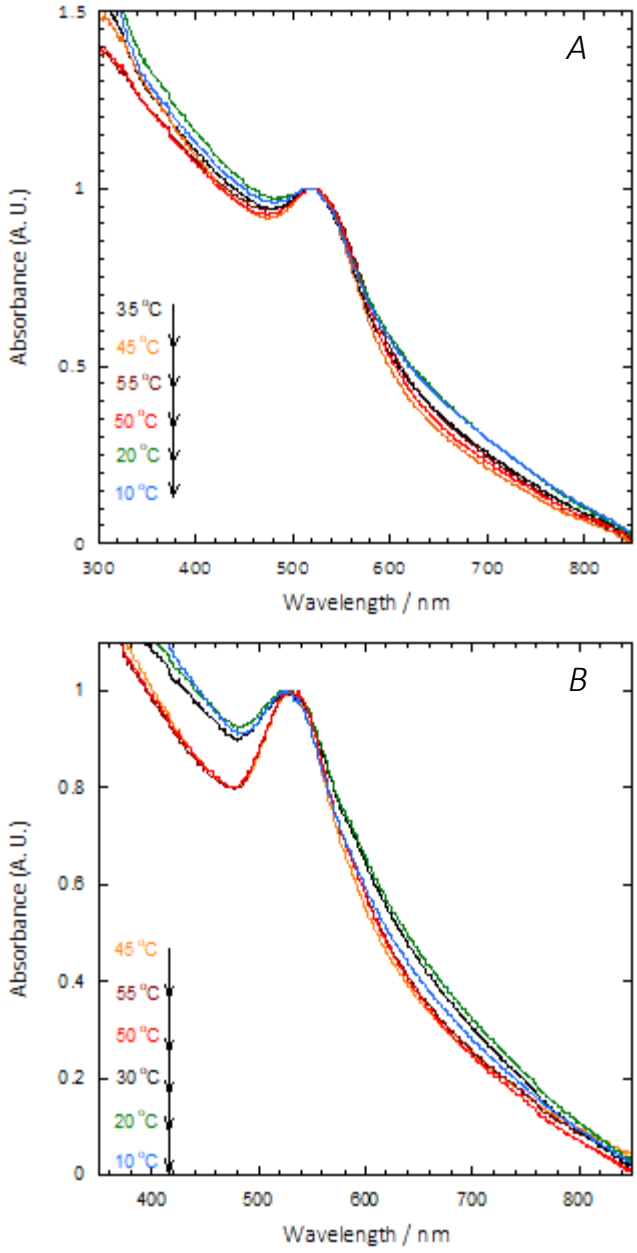


Figure S9. Temperature dependent SAXS profiles on a Au NP composite prepared with acidic (pH 3.6) buffer. The composite contains 0.733 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0371 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0852 ± 0.0005 DMPC lipid, and Φ_p = 0.114 ± 0.005 Tetronic 1107(Acr)$_4$, [Au^{3+}] = 6.41mM

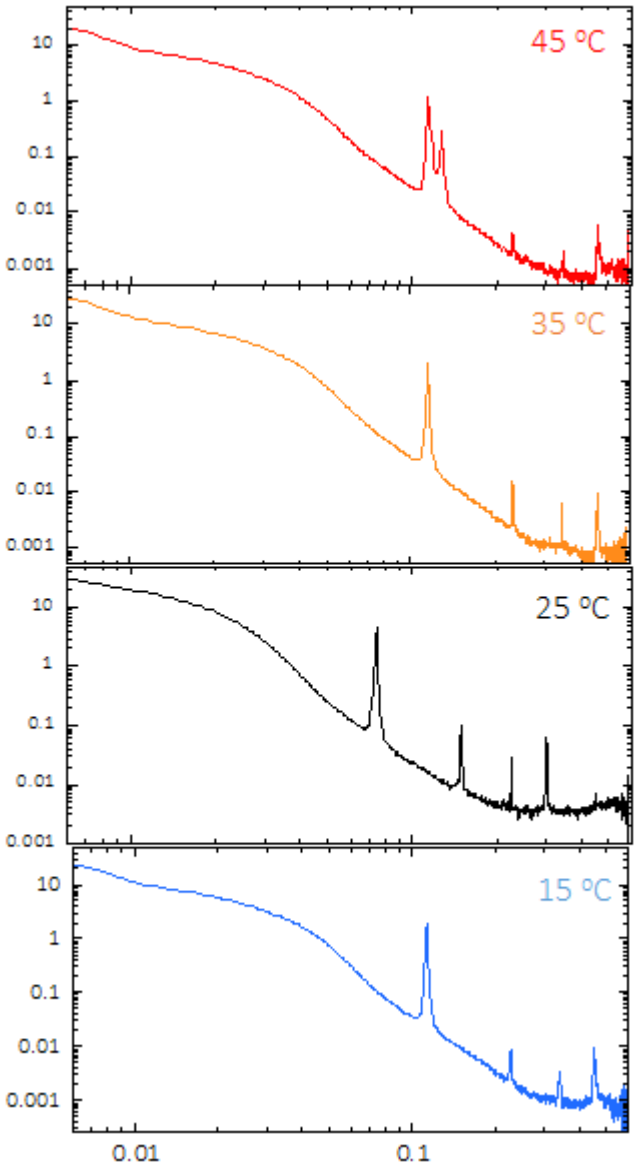


Figure S10 (A) Normalized temperature dependent Vis-NIR spectra collected on Au NP composite prepared with un-buffered water composed of 0.735 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0372 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0837 ± 0.0005 DMPC lipid, and Φ_p = 0.143 ± 0.005 Tetronic 1107(Acr)$_4$, [Au^{3+}] = 7.13 mM. (B) Normalized temperature dependent Vis-NIR collected on an acidic buffered composite. (C) Normalized temperature dependent Vis-NIR collected on a pH 9 carbonate buffered composite.

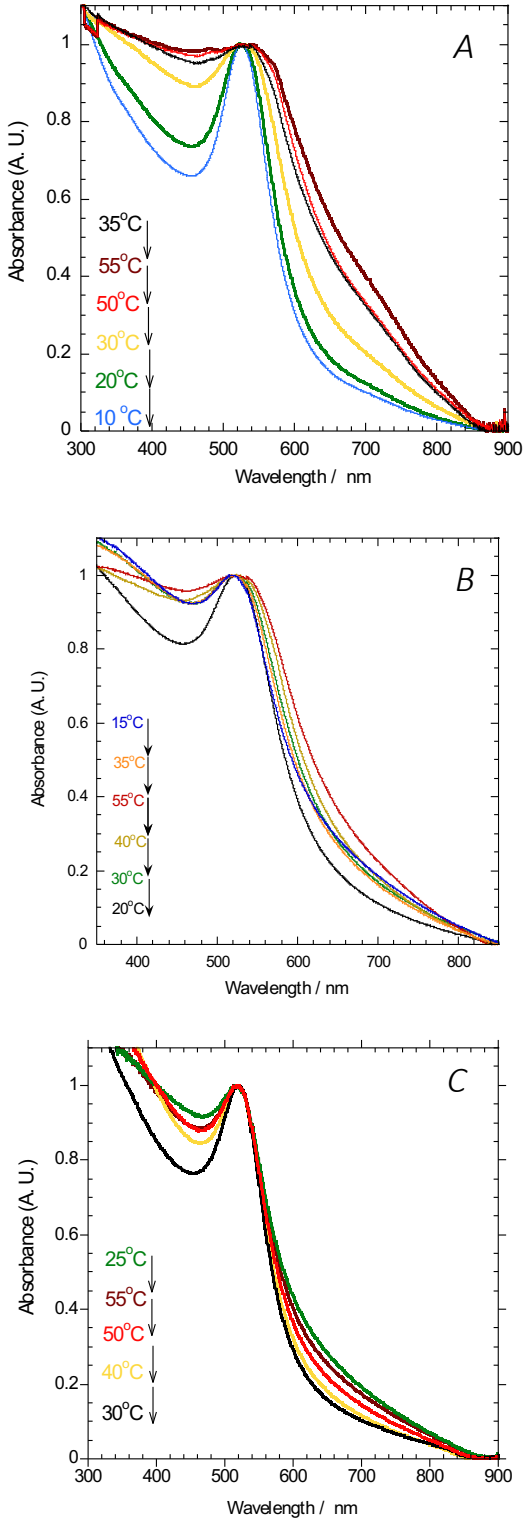


Figure S11 Temperature dependent SAXS profiles on Au NP hydrogel composite prepared in basic pH 9.03 buffer. The composite contains 0.733 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0371 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0852 ± 0.0005 DMPC lipid, and Φ_p = 0.114 ± 0.005 Tetronic 1107(Acr)$_4$, [Au^{3+}] = 6.41mM

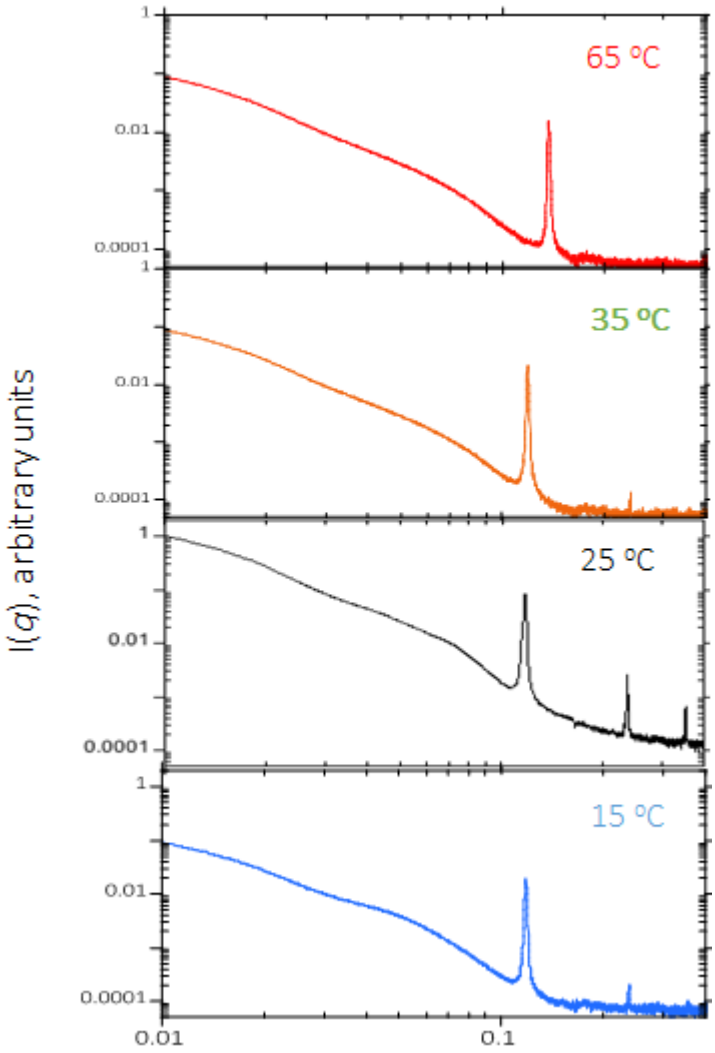


Figure S12 Diffuse reflectance optical spectrum recorded on a dehydrated (de-swollen) Au NP composite. Composite prepared with un-buffered water composed of 0.730 ± 0.001 weight fraction (Φ_w) water, Φ_s = 0.0370 ± 0.0005 Triton-X 100 co-surfactant, Φ_l = 0.0881 ± 0.0005 DMPC lipid, and Φ_p = 0.145 ± 0.005 Tetronic 1107(Acr)$_4$, [Au^{3+}] = 7.01 mM.