Supporting Information for

Poly(*N*-isopropylacrylamide) coated gold nanoparticles as colourimetric temperature and salt sensors

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Experimental Section

Materials. *N*-Isopropylacrylamide (NIPAM) was purchased from Scientific Polymer Products, INC. and was recrystallized twice in n-hexane prior to use. Sodium chloride (NaCl), sodium thiocyanate (NaSCN) and AIBN were obtained from Sigma Aldrich. AIBN was recrystallized twice from methanol before use. Methyl 2-(butylthiocarbonothioylthio)propanoate (MBTTC) chain transfer agent was synthesized from 2-(butylthiocarbonothioylthio) propanoic acid (BTTCP) as previously reported.[1,2] HPLC grade solvents *N*,*N*-dimethylacetamide (DMAc), acetone and diethyl ether were obtained from Sigma Aldrich, *N*,*N*-dimethylformamide (DMF) from Biosolve and *n*-hexane from Fischer Scientific.

Methods. *Nuclear magnetic resonance (NMR) spectroscopy.* ^{1}H NMR spectra of the polymer was recorded on a Bruker Avance 300 MHz spectrometer in deuterated chloroform ($CDCl_3$) with TMS as internal standard at room temperature.

Gas chromatography (GC). Gas chromatography was performed on 7890A from Agilent Technologies with an Agilent J&W Advanced Capillary GC column (30 m, 0.320 mm, and 0.25 mm). Injections were performed with an Agilent Technologies 7693 auto sampler. Detection was done with a FID detector. Injector and detector temperatures were kept constant at 250 and 280°C, respectively. The column was initially set at 50°C, followed by two heating stages: from 50°C to 100°C with a rate of 20°C /min and from 100°C to 300°C with a rate of 50°C /min, and then held at this temperature for 0.5 minutes. Conversion of NIPAM was determined based on the integration of monomer peaks using DMF as internal standard.

Size-exclusion chromatography (SEC). Size-exclusion chromatography (SEC) was performed on an Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler, a thermostatted column compartment, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). Analyses were performed on two Mixed-D (Agilent) 30 cm columns and a Mixed-D precolumn (Agilent) in series at 50 ^{o}C. DMA containing 50 mM of LiCl was used as eluent at a flow rate of 0.593 mL/min. The spectra were analysed using the Agilent Chemstation software with the GPC add on. Molar mass and dispersity (Đ) values were calculated against PMMA standards.

Transmission electron microscopy (TEM). TEM specimens were prepared by immersion of a carbon-support film on a Ni grid into the citrate@AuNPs solution or PNIPAM@AuNPs solution followed by careful wiping off the excess solution. Nanoparticles that had adhered to the carbon film were investigated by means of various TEM modes: conventional and high-resolution (HR) TEM and STEM. A microscope JEOL JEM2200FS-Cs-corrected, operated at 200 kV and equipped with Schottky-type FEG, EDX JEOL JED-2300D and JEOL in-column omega filter was used.

Dynamic light scattering (DLS). The size and zeta potential of the AuNPs (gold concentration of 0.09 mg/mL) were measured by DLS using a Malvern Zetasizer Nano Series operating a 4mW He−Ne laser at 633 nm. All samples were filtered through a 0.2 μm filter prior to analysis. The intensity of the scattered light was measured at an angle of 173° and at constantly changing temperatures from 20 to 35 °C, equilibrated at every temperature for 180s and at a heating rate of 2.0 ^{o}C/min. Measurements at a 90 degree scattering angle were performed in a Zetasizer Nano S90. Both methods measure the correlation function of the scattered light intensity fluctuation and the size of the particles is calculated through the Stokes−Einstein equation ($d(H)= kT/3\pi\eta D$) where d(H) is the mean hydrodynamic diameter, k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the dispersing medium, and D is the apparent diffusion coefficient.

Cloud point temperature determination by Crystal 16. Cloud point temperatures were measured on a Crystal16^{TM} parallel crystalliser from Avantium Technologies connected to a recirculation chiller and dry compressed air. Aqueous polymer solutions (5 mg/ml) were heated from 10 to 45 ^{o}C with a heating rate of 1.0 ^{o}C/min followed by cooling to 2^{o}C at a cooling rate of 1.0 ^{o}C

/min under stirring while continuously monitoring the transmittance of the sample. This heating-cooling cycle was repeated two times. The cloud point temperatures are reported as the 50% transmittance temperature in the 2nd heating run.

UV-visible spectroscopy (UV-Vis). UV−vis spectra were measured with a Cary 100 Bio UV-Visible spectrophotometer equipped with a temperature controller. AuNPs were placed in plastic cuvettes, and spectral analysis was performed in the 300−800 nm range at 20°C. In the case of temperature-dependent measurements (gold concentration of 0.09 mg/mL), the absorbance was monitored while changing the temperatures from 20 to 45 °C. Temperatures were changed in 2 °C intervals from 25-45 °C and incubated 2 min to assure thermal equilibration. In case of isothermal salt (NaCl and NaSCN) titration at every addition of salt, incubated for 2 min to assure thermal equilibration.

Synthesis of PNIPAM. The RAFT polymerization of NIPAM was performed in a 25 mL Schlenk tube under nitrogen atmosphere. NIPAM (2 g, 17,67mmol), methyl 2-(butylthiocarbonothioylthio)propanoate (MBTTC) (44.61 mg, 0.18 mmol), 2,2′-azobisisobutyronitrile (AIBN) (14.51 mg, 0.09 mmol), and DMF (8.8 mL) were charged in the 25 mL Schlenk tube at a molar ratio of 100:1:0.5. The solution was deoxygenated by three freeze−pump−thaw cycles. Then the reaction mixture was placed in a preheated oil bath at 60 °C to initiate the polymerization. After 50 min of polymerization, the reaction vessel was removed from the oil bath and opened to the air to stop the polymerization. The resulting polymer was precipitated by dropping the polymer solution into a large amount of a 50:50 mixture of hexane and diethyl ether. After decantation of the solvent, the polymer was dissolved in tetrahydrofuran (THF) and precipitated again in diethyl ether. This precipitation procedure was repeated three times. The resulting powdery light yellow polymer was dried overnight under vacuum at 50 °C. The monomer conversion was determined by GC whereas SEC was used to determine the molecular weight and dispersity (Đ). ^{1}H was used to confirm the polymer structure as well as to calculate the degree of polymerization (DP). (Conversion = 38 %, M_{nGC} = 4.5 kg/mol; $M_{nSEC(DMA)}$ = 10.6 kg/mol and Đ = 1.1; M_{nNMR} = 5.1 kg/mol and DP = 43).

Preparation of citrate@AuNPs. Citrate stabilized AuNPs were synthesized according to the reported Turkevich method.[3] All glassware was first washed with aqua regia and then rinsed with Milli-Q water several times prior to the synthesis. Briefly, 20 mL of a 1 mM aqueous $HAuCl_4$ solution was refluxed for 30 min. Then 2 mL of 1 wt % sodium citrate in milliQ water was quickly added and the colour of the solution changed from yellow to wine red within 5 min. After cooling, the reaction solution was stored at 4 °C before further use.

Preparation of PNIPAM coated AuNPs. A total of 9 mL of a citrate stabilized gold nanoparticle solution was mixed with 200 μL of an aqueous solution containing 8 mg of PNIPAM and stirred overnight at room temperature. The resulting PNIPAM@AuNPs were three times purified by centrifugation at 4 °C with 10 000 g for 20 min followed be re-dispersion in milliQ water.

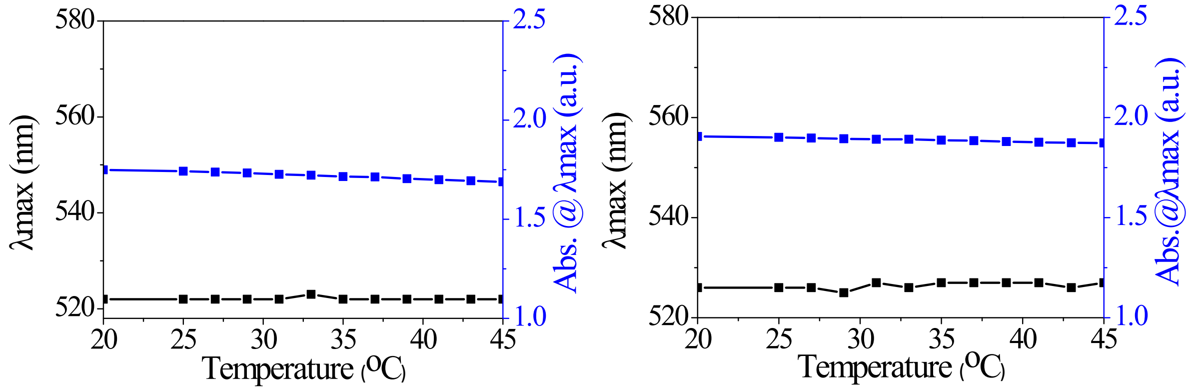


Fig. S1 Variation of maximum absorbance and maximum absorbance wavelength (λ_{max}) of SPR peak versus temperature plot of citrate@AuNPs (left) and PNIPAM@AuNPs (right) in MilliQ water in absence of salt.

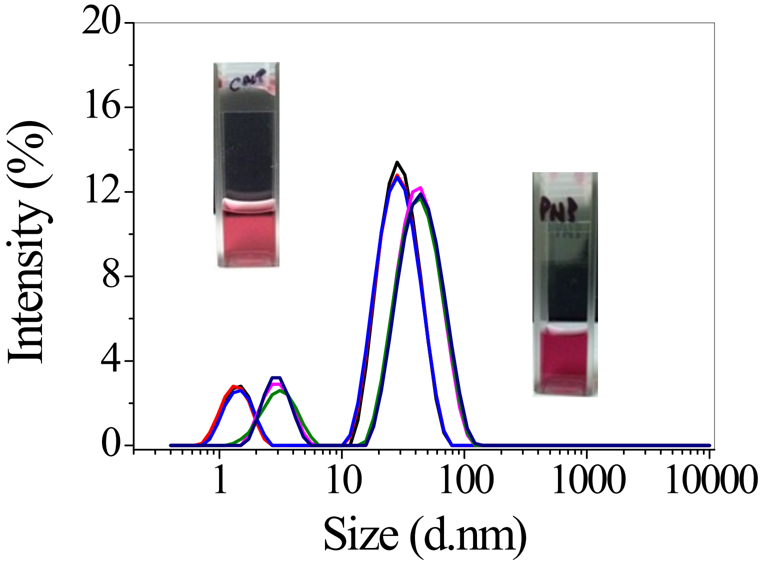


Fig. S2 Size distribution of citrate (A) and polymer coated (B) AuNPs obtained via DLS measured in 173 degree scattering angle (concentration of the AuNPs = 0.09 mg/mL in MilliQ water; temperature = 20 °C).

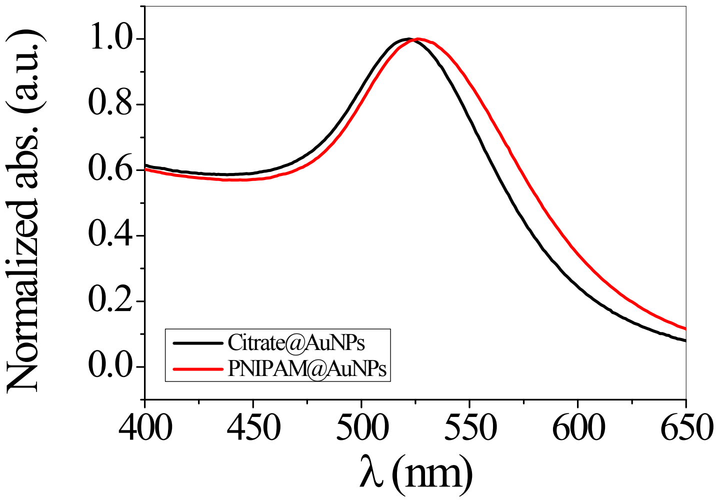


Fig. S3 Normalized UV−vis absorbance spectra of citrate and PNIPAM coated AuNPs measured at 20 °C.

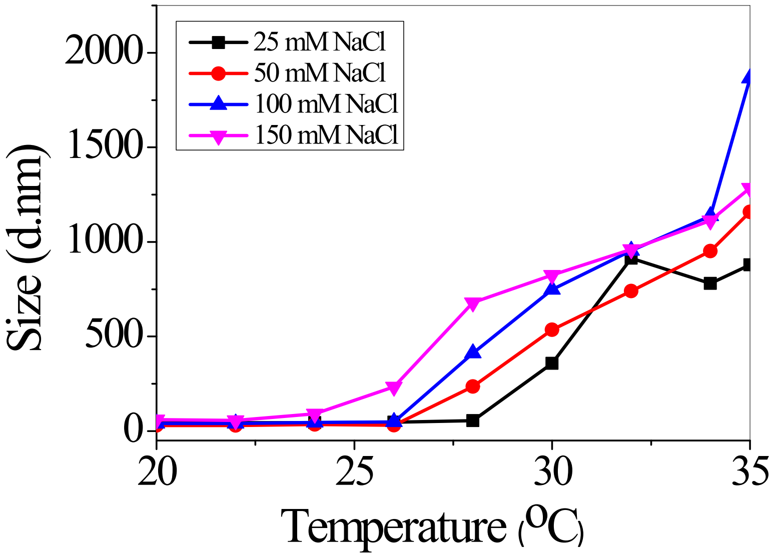


Fig. S4 $Z_{ave.}$ size of the PNIPAM@AuNPs in aqueous NaCl solutions of different NaCl concentration (25, 50, 100 and 150 mM) as a function of temperature (heating rate 2°C/min).

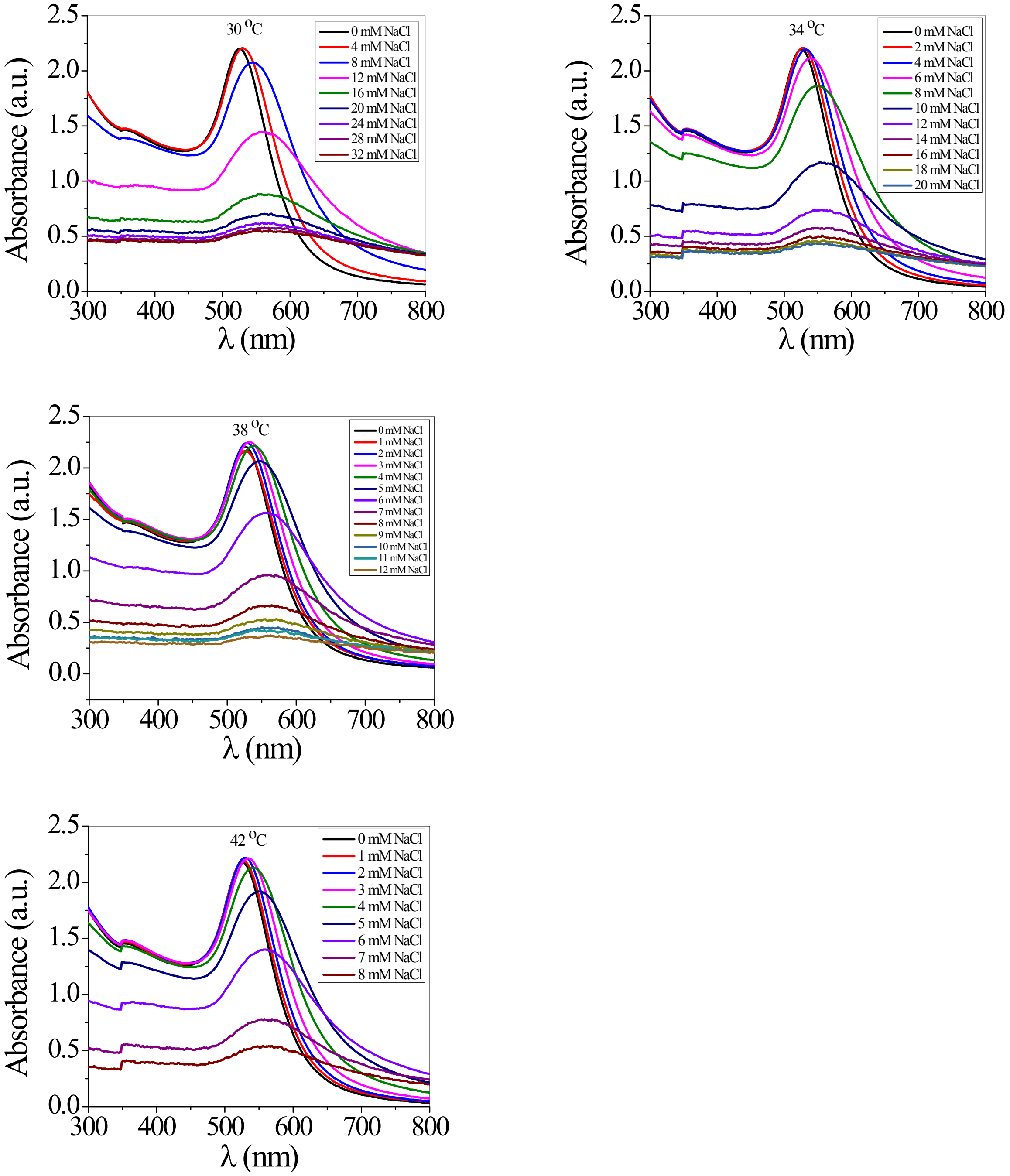
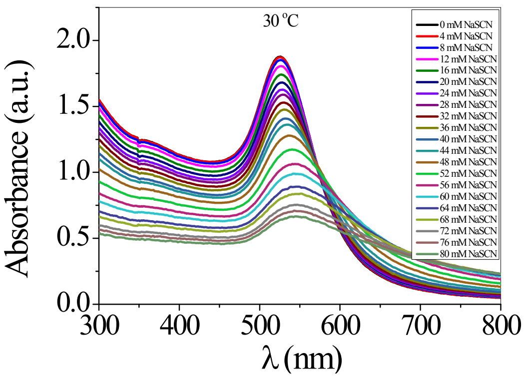
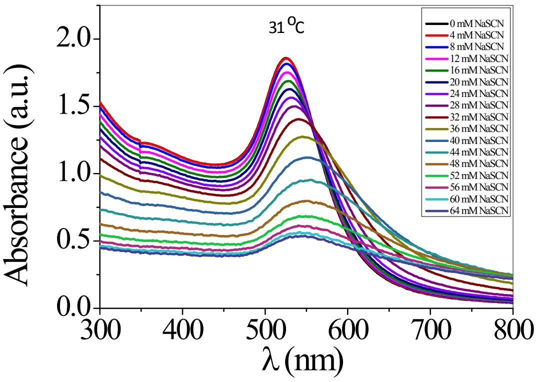
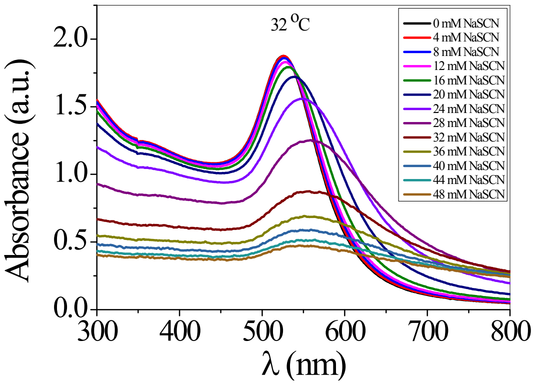
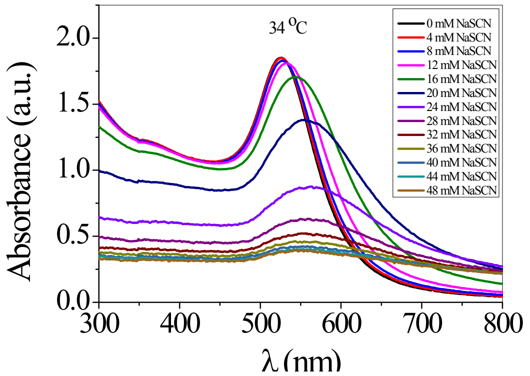


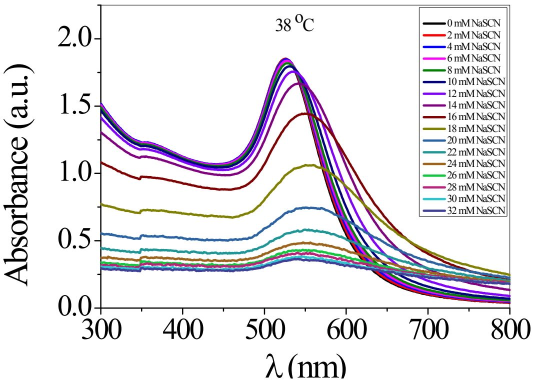
Fig. S5 UV−vis absorbance spectra of PNIPAM@AuNPs at different NaCl salt concentration and at different temperatures.

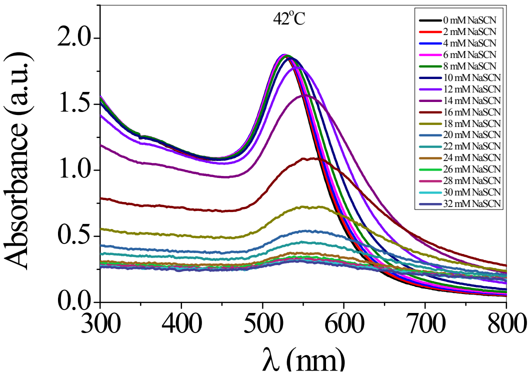

30 °C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
4 mM NaSCN
8 mM NaSCN
12 mM NaSCN
16 mM NaSCN
20 mM NaSCN
24 mM NaSCN
28 mM NaSCN
32 mM NaSCN
36 mM NaSCN
40 mM NaSCN
44 mM NaSCN
48 mM NaSCN
52 mM NaSCN
56 mM NaSCN
60 mM NaSCN
64 mM NaSCN
68 mM NaSCN
72 mM NaSCN
76 mM NaSCN
80 mM NaSCN


31 °C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
4 mM NaSCN
8 mM NaSCN
12 mM NaSCN
16 mM NaSCN
20 mM NaSCN
24 mM NaSCN
28 mM NaSCN
32 mM NaSCN
36 mM NaSCN
40 mM NaSCN
44 mM NaSCN
48 mM NaSCN
52 mM NaSCN
56 mM NaSCN
60 mM NaSCN
64 mM NaSCN


32 °C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
4 mM NaSCN
8 mM NaSCN
12 mM NaSCN
16 mM NaSCN
20 mM NaSCN
24 mM NaSCN
28 mM NaSCN
32 mM NaSCN
36 mM NaSCN
40 mM NaSCN
44 mM NaSCN
48 mM NaSCN


34 °C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
4 mM NaSCN
8 mM NaSCN
12 mM NaSCN
16 mM NaSCN
20 mM NaSCN
24 mM NaSCN
28 mM NaSCN
32 mM NaSCN
36 mM NaSCN
40 mM NaSCN
44 mM NaSCN
48 mM NaSCN


38 °C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
2 mM NaSCN
4 mM NaSCN
6 mM NaSCN
8 mM NaSCN
10 mM NaSCN
12 mM NaSCN
14 mM NaSCN
16 mM NaSCN
18 mM NaSCN
20 mM NaSCN
22 mM NaSCN
24 mM NaSCN
26 mM NaSCN
28 mM NaSCN
30 mM NaSCN
32 mM NaSCN


42°C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
2 mM NaSCN
4 mM NaSCN
6 mM NaSCN
8 mM NaSCN
10 mM NaSCN
12 mM NaSCN
14 mM NaSCN
16 mM NaSCN
18 mM NaSCN
20 mM NaSCN
22 mM NaSCN
24 mM NaSCN
26 mM NaSCN
28 mM NaSCN
30 mM NaSCN
32 mM NaSCN

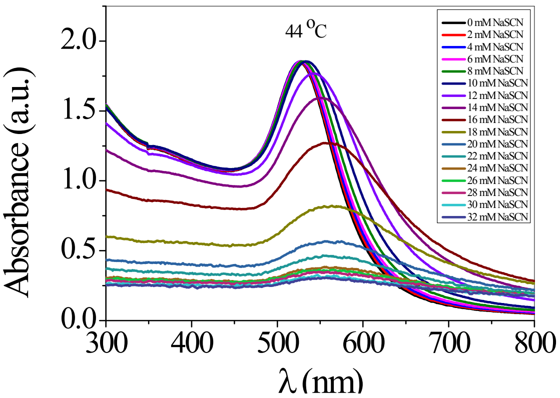

44 °C
Absorbance (a.u.)
λ (nm)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
0 mM NaSCN
2 mM NaSCN
4 mM NaSCN
6 mM NaSCN
8 mM NaSCN
10 mM NaSCN
12 mM NaSCN
14 mM NaSCN
16 mM NaSCN
18 mM NaSCN
20 mM NaSCN
22 mM NaSCN
24 mM NaSCN
26 mM NaSCN
28 mM NaSCN
30 mM NaSCN
32 mM NaSCN

Fig. S6 UV−vis absorbance spectra of PNIPAM@AuNPs at different NaSCN salt concentration and at different temperatures.

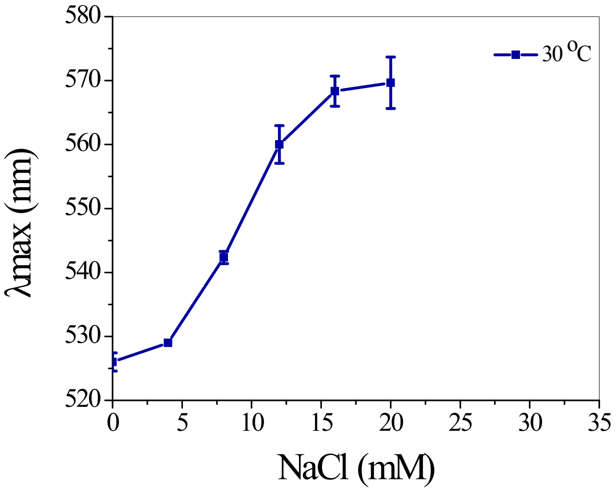


Fig. S7 The λ_{max} peak variation of the PNIPAM@AuNPs at different salt (NaCl) concentration and at 30 °C temperature (3 replicate measurements).

References

1. C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such and B. S. Hawkett, *Macromolecules,* 2005, **38,** 2191.

2. N. P. Truong, Z. Jia, M. Burgess, L. Payne, N. A. J. McMillan and M. J. Monteiro, *Biomacromolecules,* 2011, **12,** 3540.

3. J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.,* 1951, **11,** 55.