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Thermosensitive and  
Thermoreversible 1D Assemblies  
of Plasmonic Nanoparticles

2013년 2월

서울대학교 대학원  
화학부 무기화학 전공  
김 필 용

# Thermosensitive and Thermoreversible 1D Assemblies of Plasmonic Nanoparticles

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Thermosensitive and  
Thermoreversible 1D Assemblies  
of Plasmonic Nanoparticles

by Phil Yong Kim

Thesis Advisor: Prof. Jwa-Min Nam

A Thesis for M.S. Degree in Inorganic Chemistry

Graduate School

Seoul National University

## Abstract

# Thermosensitive and Thermoreversible 1D Assemblies of Plasmonic Nanoparticles

Phil Yong Kim

Department of Chemistry

The Graduate School

Seoul National University

We have studied the fine-tuning of plasmonic coupling from the charged nanoparticle(NP)s in aqueous solution and revealed the thermoreversible assembly of one-dimensional structure by the temperature-dependent surface charge variation of NPs. When the linear assemblies start developing in aqueous solution by adding salt to diminish the electrostatic force, the charged NPs evade the relatively strong electrostatic repulsions of the chain sides and prefer to the chain ends, proceeding to nanochains by end-on

attachment. The linear self-assembly process is reversible when nanoparticles are modified with adequately strong surfactants which bring the short-range steric repulsion by surfactant layer to counter the van der Waals attraction between NPs at high ionic strength. And the thermoresponsive assembly and disassembly were reversible by the temperature-dependent surface charge variation which directly affect the electrostatic repulsion of NPs. Interestingly, the specific temperature limited the average chain length of the linear nanostructures as a form of the temperature memory and thus, the hue differences based on temperature-dependent surface plasmonic coupling are easily discernible by the naked eye and the UV-vis spectra. This simple and cost-effective concept could represents a new strategy to development of novel functional devices in related fields of nanobiotechnology, nanoelectronics, and phononics.

**Keywords:** plasmonic coupling, self-assembly, thermosensitivity, thermoreversibility, fine-tuning

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# Contents

Abstract	
Introduction	1
Experimental Section	4
Results and Discussion	6
Conclusion	14
References	15
Acknowledgement	17
Schemes and Figures	18
Korean Abstract	25

## Introduction

Controlling the nanoparticle(NP)-based architecture with accurate distance and directed orientation from plasmonic metal NPs has been a great matter of concern in plasmonics.<sup>[1]</sup> Localized surface plasmon resonance(LSPR) of NP gives unique optical, magnetic and electronic properties to nanostructures when surface plasmon coupling occurs in various fashion between neighboring NPs. In that regard, NPs have been promising candidates for a wide range of applications in the fields of optoelectronics, nanomagnetism, nano-electronics and nanomedicine.<sup>[2]</sup> Accordingly, new synthetic pathways for desired structures and specific functions are main goals of plasmonic research and related areas. Various methods were developed to generate diverse dimensional nanoassemblies with biomolecules, polymers and physical confinements as linkers and templates.<sup>[3]</sup> Among these techniques, one-dimensional(1D) approach recently gained much attention to elucidate the anisotropic interactions that was

not well studied and to manufacture functional 1D device such as subwavelength optical guiding and biochemical sensor.<sup>[4]</sup>

More interestingly, It was reported that the anisotropic linear assemblies are constructed from isotropically charged sphere NPs without linkers and templates. The linear structures are formed when various interparticle forces are balanced. For examples, two main forces are the van der Waals attraction to make nanoparticle self-assemblies and electrostatic repulsion to inhibit the growth of nanoparticle structure. As the linear assemblies start developing in aqueous solution, where electrostatic interactions are ubiquitous, by adding salt to diminish the electrostatic repulsion, charged NPs evade the relatively strong electrostatic forces of the chain sides and, preferring to the chain ends, proceed to nanochains by end-on attachment to NP dimers, trimmers, tetramers and so on (Scheme 1a).<sup>[5]</sup> Also, it was discovered that the linear self-assembly process is reversible when nanoparticles are modified with adequately forceful surfactants which bring the short-range steric repulsion by

surfactant layer to resist the van der Waals attraction at high ionic strength. And the thermoresponsive assembly and disassembly were reversible by electrostatic repulsion owing to the temperature-dependent surface charge variation of NPs (Scheme 1b).<sup>[6]</sup> In this study, we report the fine-tuning of plasmonic coupling of the charged NPs by controlling the thermoreversible 1D assembly and its unique self-assembly behavior by temperature-oriented structural memory. The specific temperature limited the average chain length of the linear nanostructures as a form of the temperature memory and thus, the hue differences based on temperature-dependent surface plasmonic coupling are easily discernible by the naked eye and the UV-vis spectra.

## Experimental Section

### Materials and Instrument

All commercially available chemical reagents were used without further purification. Dithiothreitol (DTT), mineral oil, L-cysteine, glutathione, bis(*p*-sulfonatophenyl)-phenylphosphine (BSPP) were purchased from the Sigma. Methoxy-PEG-thiol (MW 5000, NPS) was purchased from Laysan Bio, Inc. Gold Nanoparticle(AuNP) (20nm) solutions were purchased from BBInternational, Inc.(Cardiff, UK) NANOpure water (>18.0 M, Milli-Q) was used for all the experiments. The formvar/carbon-coated copper grid (Ted Pella, Inc. Redding, CA, USA) and EF-TEM (JEOL, Japan) were used for the TEM image analysis. Zeta potential analyzer(Malvern, UK) was used to measure zeta potential of BSPP-AuNPs. The thermal cycle experiments were carried out with the thermocycler (SensoQuest, Germany).

## **Synthesis of BSPP modified gold nanoparticles**

BSPP modified AuNPs are synthesized by a ligand exchange process from the citrate capped AuNPs. Typically, AuNP (20nm) solution was mixed with BSPP(5mg/ml) and stirred for 12 h. Then, AuNPs were purified by centrifugation, washed 3 times with NANOpure water, dispersed in NANOpure water.

## Results and Discussion

First, charged NPs were prepared with citrate gold NPs (20nm in diameter) and BSPP ligands by a ligand exchange method and AuNPs were dispersed in an aqueous media of 50mM NaCl. We excluded 2wt% agarose in the earlier report by Y. Yin et al. to prevent the formation of a hydrogel and make advantage of 1D assembly to further applications.<sup>6</sup> To test the thermoreponsive behavior of our system, the sample was put to a cuvette which was set at 30°C and then, temperature was lowered by 2°C intervals with a holding time of 1 minute. When the sample was cooled from 24°C, temperature-dependent plasmonic characters based on NP assembly were spotted but AuNPs were disassembled in the range of 30-24°C (Fig. 1a). As soon as the cooling started from 24°C, there was a gradual reduction in intensity of the absorption peak at 525nm. Meanwhile, new shoulders begun to appear at longer wavelengths, reaching a peak around 750nm at 6°C and there was no red-shift of the

original 525nm absorption maximum. The new shoulder and peak denote the linear assembly of the charged NPs as a result of the electrostatic energy which is directly connected to the temperature-dependent zeta potential of charged NPs.<sup>[7,8]</sup>

The total interparticle interaction energy consists of van der Waals potential energy (attraction force), short-range repulsion energy and electrostatic energy (repulsion force).<sup>[5,6]</sup> Because the first two factors rely heavily on the characteristics of NPs themselves, it is possible to tune the electrostatic energy by the dielectric constant of the solvent, the surface potential of colloids, and temperature when the number and size of colloids are set. And the alterations in the diffuse double-layer(DDL) thickness is believed to the change in the zeta potential with temperature. The DDL means the two parallel layers of charge surrounding an gold colloid.<sup>9</sup> In our system, the first layer is made of the negatively charged BSPP which is directly adsorbed onto the NP. The second layer is composed of sodium ions attracted to the first layer by electric interactions and this layer is loosely

attached to the first layer because sodium ions migrate in the fluid under the influential factors such as electric attraction and thermal motion. Accordingly, at higher temperature, relatively high thermal energy make the DDL thickness diminish by breaking the interactions between the first and second layers and, thus, zeta potential on AuNPs increase (Fig. 1b). In control experiments where no sodium ions are present, there was no thermoresponsiveness in the optical property and zeta potential because of not forming the second layers on NPs (data not shown). When the more salt concentration, the assembly begun at higher temperature and the chain length was longer as previously reported (Fig. S1). Transmission electron microscopy (TEM) images of the 1D self-assembly of charged NPs suggested that the chain length relates to the electrostatic energy governed by temperature variation (Fig. 1c).

Next, we tested the reversibility and tunability of the linear assembly of charged NPs. The sample of 70mM NaCl was under thermal cycle conditions with 1°C intervals and a holding time of

1 minute and colour changes were observed by the increment of temperature (Fig. 2a). The interesting feature of this test is the clearness and memory of the color generation in temperature transition and the narrow temperature scope for the color change. During 25 cycles, the AuNP solution demonstrated the faultless thermoresponsive reversibility and optical shifting. From  $-1^{\circ}\text{C}$  to  $18^{\circ}\text{C}$ , The  $2^{\circ}\text{C}$  difference made the discernible color changes visualized with the naked eye and the greenish blue color was tuned into the multiple colour series: blue, violet, pink and red. In addition, after 22 thermal cycles, the same sample was set to  $16^{\circ}\text{C}$ ,  $4^{\circ}\text{C}$  and  $12^{\circ}\text{C}$  to evaluate the ability of color generation for the specific heat. After repeated thermal cycles at  $16^{\circ}\text{C}$ ,  $4^{\circ}\text{C}$ ,  $12^{\circ}\text{C}$ , this system produced the same results as previously obtained.

The AuNP solution of 90mM NaCl was monitored and recorded from  $6^{\circ}\text{C}$  to  $26^{\circ}\text{C}$  with  $1^{\circ}\text{C}$  intervals and a holding time of 1 minute to verify the ionic strength effect on the linear assembly of the charged NPs (Fig. 2b). The impeccable thermoreversible construction and plasmonic coupling was the

same as before while the sample was tuned in to a particular temperature by 2 degree Celsius. The different sized 1D structures remembered the temperature where they had been assembled (at 7°C, 15°C and 9°C). These results support that it takes higher energy to peel off the layers of sodium ions from the AuNP bounded BSPP-layers if the ionic strength arises.

To identify the colour temperature codes with the thermoresponsive fine-tuning property of the negative-charged NPs, four solutions of different ionic strengths (in 60, 70, 80 and 90 mM NaCl) in a strip PCR tube were investigated using the same protocol (Fig. 2c). As expected, by four degree Celsius and 10mM NaCl, the regular expression pattern with the hue variation were recorded with the temperature switching. With combination of aligned samples, plasmonic coupling based color coding for temperature was made and, although the system was unoptimized, four samples illustrated a digitized interpretation of the temperature by 2 degree Celsius from 0°C to 16°C. This concept can be broadened to show a colour code reading of wide

temperature range by simply adding more samples in a strip (Fig. 2d).

The system we presented was simple but it seemed undecided whether temperature sensitive 1D nanostructure or temperature memory of that. To clarify the temperature dependent 1D assembly fashion, two different reaction pathway was applied to reveal its assembly mechanism. First, the solution of 50mM NaCl was cooled from 24 degree Celsius with 2°C difference and a holding time of 1 minute and this process was monitored by UV-vis spectra (Fig. 3a). At 16°C, a shoulder started to appear accompanying the decrement of intensity of the original peak at 525nm. Along with lowering the temperature, shoulders at longer wavelengths evolved into a new peak at 750nm while the solution color was shifted from reddish to bluish demonstrating the fine-tuning of 1D plasmonic coupling of the linear self-assembly. In contrast, a extraordinary outcome was resulted from the cooling the sample with a holding time of 10minutes (Fig. 3b). At 20°C, self-assembly started to begin but

this assembly process was not able to create a new peak at longer wavelengths eventually. Moreover, the rate of the intensity loss about 525nm was much faster and quite regular. As a result, the scheduled colour change did not take place as the evidence of uncontrolled self-assembly or random aggregation from the charged NPs with the intensity loss of the red colour. In both cases, the end products were back to the disassembled states when the temperature arose.

From the UV-vis spectra attained, we drew the explanations to two synthetic processes from the same starting materials (Fig. 3c). It is obvious that the assembled state is energetically favored more than the disassembled state when the van der Waals attraction wins electrostatic repulsion. Thus, provided that the linear assembly from the charged colloids is the spontaneous process, the final products from both cases should be analogous to one another with minor alterations, which is not matching with the our system. But rather, when the rate of the temperature shifting is relatively high, kinetically controlled

products are formed. In kinetic control, the product K1 through K4 is less stable but required the lower activation than the product T. As a result, in kinetic pathway, differently sized 1D nanostructure are easily and fast constructed depending on the specific temperature. On the other hand, If the slow process, the system is under the thermodynamic reaction control, which result in the most stable end product T. As holding the particular temperature for 10 minutes, the van der Waals forces on the neighboring preformed small nanochains dominate the electrostatic repulsion between the chain sides, proceeding to the 2D and 3D growth with the charged NPs and little nanochains. Taken together, if not the temperature-dependent structural memory of the linear nanostructure, there are no explanations on both phenomena.

## Conclusion

This is the first time that colloids are employed to produce the thermoreversible fine-tuning assembly and plasmonic coupling of 1D nanostructure where the assembly process originated in the temperature-dependent structural memory starting from the charged NPs. This simple and cost-effective concept could represent a new strategy to development of novel optical devices in related fields of nanobiotechnology, nanoelectronics, and phononics. Particularly, the system opens up a new strategy in 1D colorimetric biosensor, based on active tuning of the distance of NPs, which differs from conventional ones in this respect.

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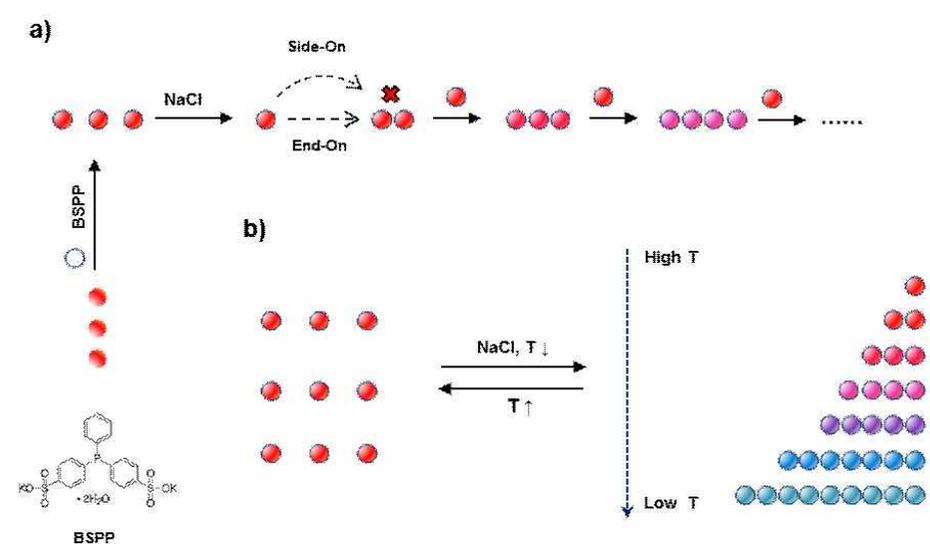
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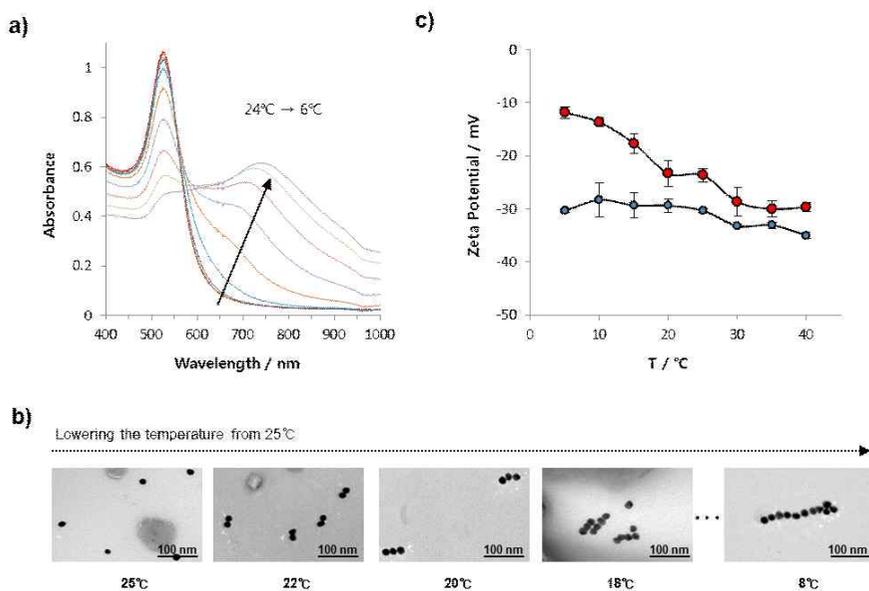
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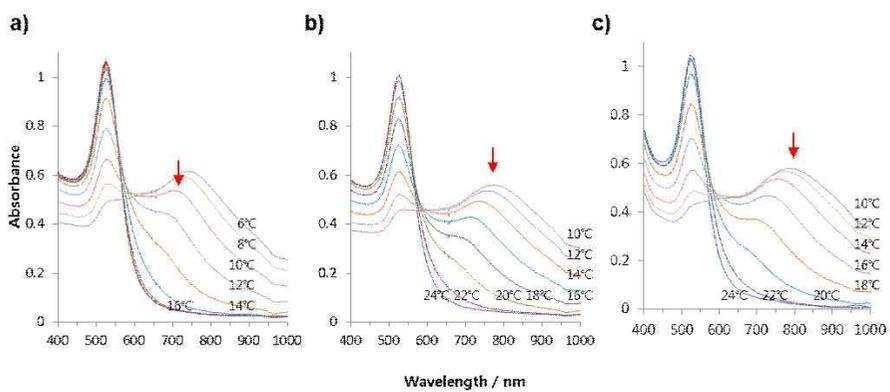
## Schemes and Figures



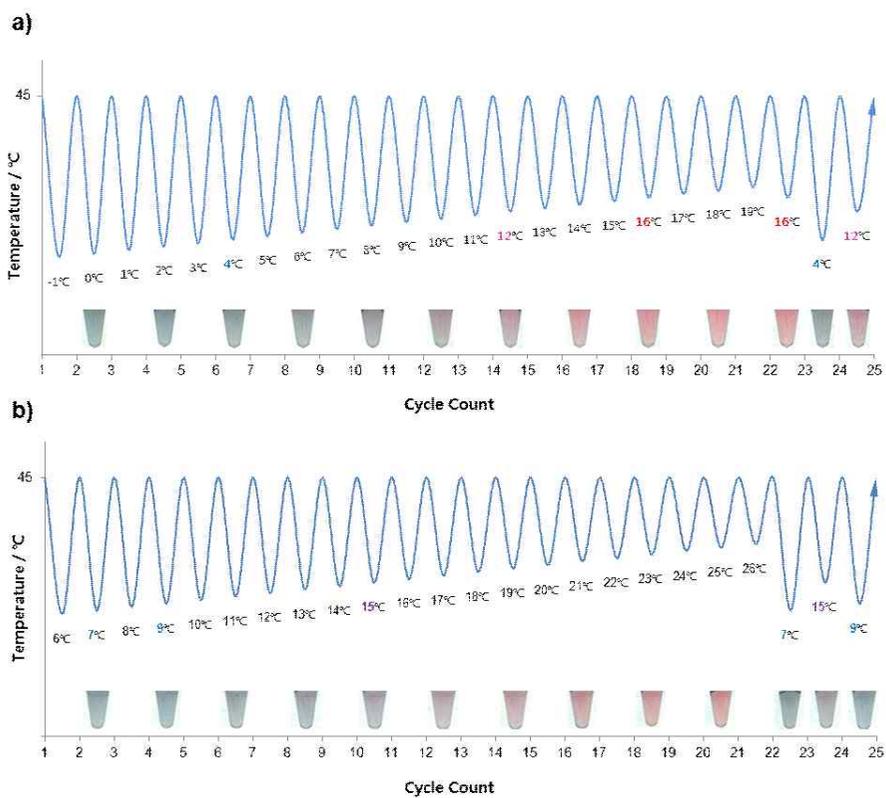
**Scheme 1.** a) linear self-assembly of charged colloids when balanced between electrostatic repulsion and van der Waals attraction with the chain side electrostatic repulsions are bigger than the chain end electrostatic repulsions. b) the thermoresponsive 1D chain growth by electrostatic repulsion owing to the temperature-dependent surface charge variation of charged nanoparticles.



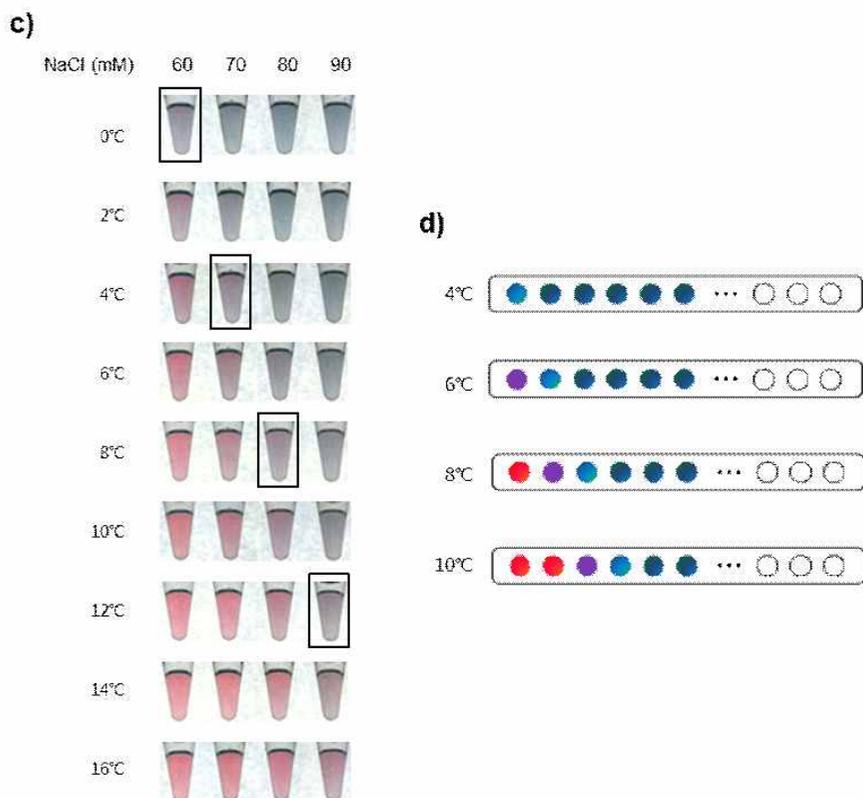
**Figure 1.** a) Temperature-dependent plasmonic optical property based on 1D nanoparticle assembly (1mM Phosphate buffer, 0-1mg/ml BSPP, 50mM NaCl, 20nm BSPP-gold nanoparticles, the temperature range from 24 °C to 6 °C). b) Zeta potential of charged nanoparticles with different ionic strength (red-50mM NaCl, Blue-no NaCl). c) TEM images of the 1D self-assembly of charged nanoparticles by temperature variation .



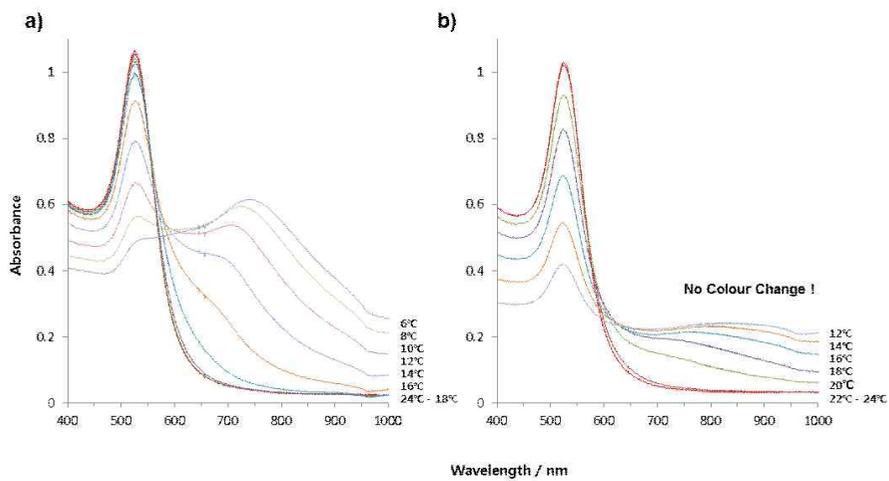
**Figure S1.** Absorption spectra of charged nanoparticle (1mM Phosphate buffer and 20 nm BSPP-gold nanoparticles, temperature range from 24 °C to 6 °C) a) 50mM NaCl. b) 60mM NaCl. c) 50mM NaCl and 5mg/ml BSPP.



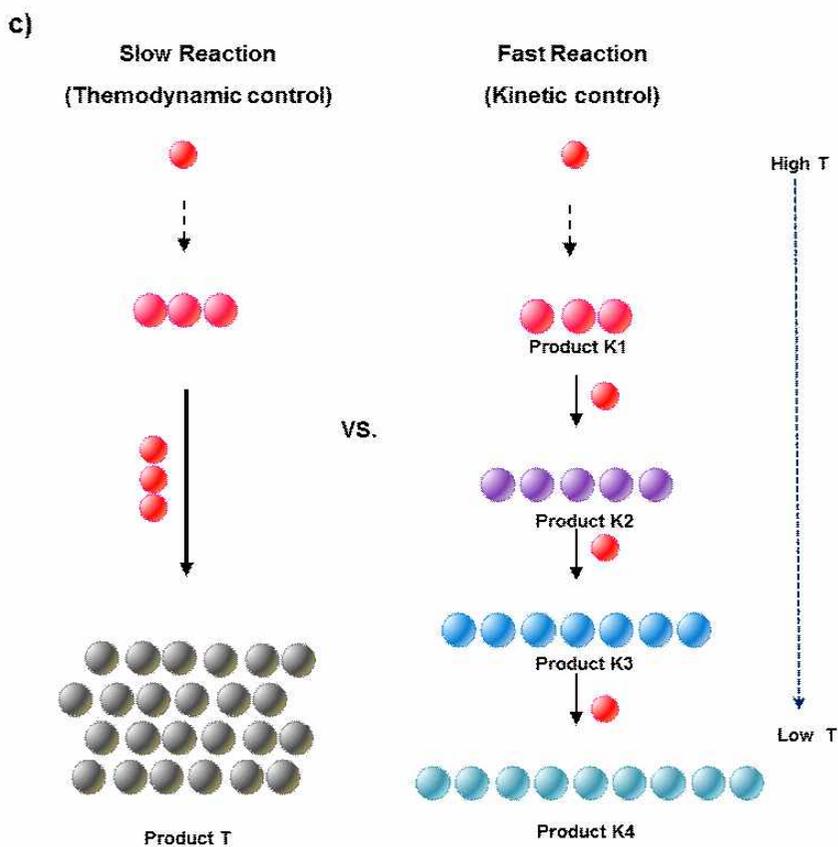
**Figure 2.** Reversibility and tunability of the linear assembly of charged NPs. a) 70mM NaCl. b) 90mM NaCl (1mM Phosphate buffer, 20 nm BSPP-gold nanoparticles, temperature range from 19 °C to -1 °C in a) and 28 °C to 6 °C in b)).



**Figure 2.** c) the colour temperature codes with the thermoresponsive fine-tuning property of the negative-charged NPs with four solutions of different ionic strengths. d) A digitized interpretation of the temperature by 2 degree Celsius in a strip PCR tube.



**Figure 3.** The UV-vis spectra with different holding time (1mM Phosphate buffer, 50mM NaCl and 20nm BSPP-gold nanoparticles, the temperature range from 24 °C to 6 °C), a) 1 minute. b) 10 minutes.



**Figure 3.** In the slow process, the system is under the thermodynamic reaction control and results in the most stable end product T. In the kinetic pathway, the differently sized 1D nanostructure are easily and fast constructed depending on the specific temperature. It is because of the temperature-dependent structural memory of the linear nanostructure.

## 요약(국문초록)

BSPP(bis(p-sulfonatophenyl)phenylphosphine)를 금 나노입자(20 nm)에 붙인 후, 수용액에서 온도를 변화시켜가며 UV-vis spectra, 용액의 색깔, TEM(transmission electron microscopy) 등을 관찰하였다. 기존의 연구결과에서 BSPP-금 나노입자는 5°C~40°C 사이에서 thermoreversible 하다고만 밝혔지만, 본 연구에서는 NaCl 농도와 버퍼에 따라서 thermo-reversible한 온도범위를 조절할 수 있었다. 그리고 BSPP-금 나노입자 간의 플라즈모닉 커플링(plasmonic coupling)을 온도에 따라 세밀하게 조절할 수 있는데 있는데, 이것은 기존의 polymer나 DNA를 이용한 방식이 on-off 또는 all or nothing 방식이었는데 반해서, 나노입자 1D assembly를 정밀하게 조절할 수 있다는 의미이다.

무엇보다도, thermo-reversibility의 연장선에서, BSPP-금 나노입자는 shape-memory alloy처럼 온도를 기억할 수 있다. 예를 들어, 용액이 25°C에서 붉은색을 띠도록 설정해 주고, 차가운 물에서 푸른색으로 변했다가 상온에 두면 1분 이내에 붉은색으로 돌아오는 특징을 보인다. 다른 특징은 다음과 같다. 25°C에서

붉은색을 가지는 용액의 온도를 2°C씩 내려가며 UV-vis spectra, 용액의 색깔 등을 확인했는데, 2가지 방식을 사용했다. 한 번은 dwell time을 1분으로 하고, 다른 한 번은 dwell time을 10분으로 했음. 만약 이 과정이 단순한 spontaneous reaction이라면 양쪽의 경우 유사한 결과물을 얻어야 한다. 하지만 유기화학에서 잘 알려진 ‘thermodynamic reaction control vs. kinetic reaction control’이 적용된 것처럼 최종 생산물이 반응경로에 따라서 전혀 다른 것을 확인 할 수 있었다. 비교적 빠른 속도로 온도를 낮춰준 경우는 용액색깔이 붉은색→자주→보라→남색→파랑→청파랑으로 변하면서 나노입자 1D assembly가 만들어지는 것을 확인할 수 있었지만, dwell time 10분의 경우에는 용액의 색깔이 변하지 않고 붉은색의 강도가 약해지는 것이 관찰되었다 (이 경우 온도를 올려주었을 때 상당한 양의 붉은색 침전이 바닥에 형성된 것을 확인함). 이러한 결과를 종합해 보면 온도에 따른 intermediate state가 존재한다는 것이 확인되므로 BSPP-금 나노입자는 단지 온도에 민감하게 반응하는 것이 아니라 온도에 맞는 memory를 가진다고 볼 수 있다.