



Development of a highly selective colorimetric pyrophosphate probe based on a metal complex and gold nanoparticles: change in selectivity induced by metal ion tuning of the metal complex



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ABSTRACT

In this study, we developed a colorimetric sensing system for pyrophosphate (PPI) with a probe composed of phosphate functionalized-gold nanoparticles as the reporter unit and [Cu₃(1,3,5-tris[bis(pyridine-2-ylmethyl)aminomethyl]-2,4,6-triethylbenzene)]⁶⁺ (**2**) as the receptor unit. The proposed probe allows easy detection of PPI with the naked eye, and selectively recognizes PPI with a detection limit of 320 nM. Unlike previous AuNP based-PPI sensing systems, this probe exhibits high selectivity for PPI over various other phosphate derivatives including adenosine triphosphate (ATP) and adenosine diphosphate (ADP).

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PPI is an important anion that plays a key role in many biological processes such as being the product of adenosine triphosphate (ATP) hydrolysis, DNA polymerization, and many enzymatic reactions.¹ It is also known that abnormal PPI levels can cause calcium pyrophosphate dehydrate (CPPD) crystal deposition disease, osteoarthritis, and rheumatoid arthritis.² Therefore, a variety of sensors for the detection of PPI have been investigated over the last few years. Since Czarnik et al. reported a cationic amine-based PPI probe, other PPI probes have been developed using several approaches including metal–ligand interactions, electrostatic interactions, and hydrogen bonding.³ Utilization of metal–ligand interactions is the most popular approach to the development of PPI probes because well-designed metal complexes have a high binding affinity for PPI in aqueous solution. Many PPI probes have been developed using metal complexes. Although these probes have high sensitivities to PPI, in many cases they suffer from low selectivity for PPI over other phosphate derivatives such as ATP and adenosine diphosphate (ADP).

Colorimetric chemosensors are very practical because they have the advantage of detecting targets with only the naked eye. Despite these benefits, most PPI colorimetric probes have difficulty detecting PPI in real samples because they have low sensitivity compared to fluorescent PPI chemosensors. Recently, we developed a

competitive assay-based colorimetric PPI probe using 11-mercaptooundecylphosphoric acid functionalized gold nanoparticles (Phos-AuNPs) and a metal complex based-PPI receptor.⁴ Compared to previous organic dye-based colorimetric pyrophosphate probes, this probe had enhanced sensitivity through utilization of the unique optical properties of AuNPs of extremely high extinction coefficient and distance-dependent surface plasmon resonance, which could detect pyrophosphate with high sensitivity similar to that of fluorescent probes.⁵ However, this probe had relatively low selectivity due to interference from phosphate derivatives such as ATP and ADP. Thus, the challenge of developing a highly sensitive AuNPs based-PPI probe with high selectivity over other phosphate derivatives such as ATP and ADP remained.

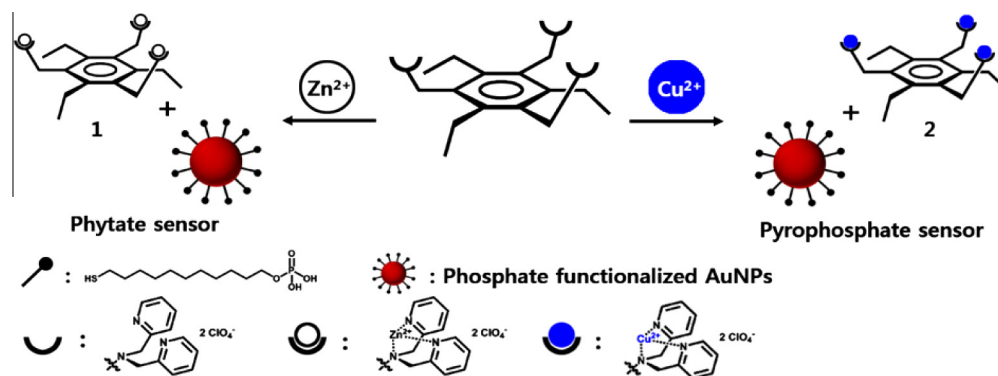
Metal ion exchange in metal complex based-anion probes is an efficient strategy for controlling the selectivity of anion probes since selectivity is strongly dependent on the particular metal ion species used.⁶ Some research groups have adapted the metal ion tuning strategy to improve the selectivity of PPI probes. For example, both Yoon et al. and Ahn et al. showed that the selectivities of metal complex based-chemosensors were enhanced upon changing from Zn²⁺ to Cu²⁺.⁷ Recently, we developed a colorimetric phytate probe using Phos-AuNPs as the signaling unit and [Zn₃(1,3,5-tris[bis(pyridine-2-ylmethyl)aminomethyl]-2,4,6-triethylbenzene)]⁶⁺ (**1**) as the receptor unit. With this probe, a phytate concentration of ~300 nM could easily be detected with the naked eye, and the sensor had high selectivity for phytate over various other phosphate derivatives.⁸

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Based on these previous results, we expected that the selectivity of the phytate chemosensor could be changed using the metal ion tuning strategy. Indeed, we found that the phytate chemosensor could be converted to a PPI chemosensor with high sensitivity and selectivity simply by changing the metal ion in **1** from Zn^{2+} to Cu^{2+} , as

shown in [Scheme 1](#). The PPI probe consisted of Phos-AuNPs as the reporter unit and $[Cu_3(1,3,5\text{-tris[bis(pyridine-2-ylmethyl)amino-methyl]-2,4,6\text{-triethylbenzene)]}^{6+}$ (**2**) as the receptor unit. **2** binds to phosphate derivatives because the Cu^{2+} -dipicolinic amine (DPA) moiety has a high binding affinity for phosphate derivatives



Scheme 1. Schematic representation of the colorimetric pyrophosphate probe based on a metal complex and gold nanoparticles.

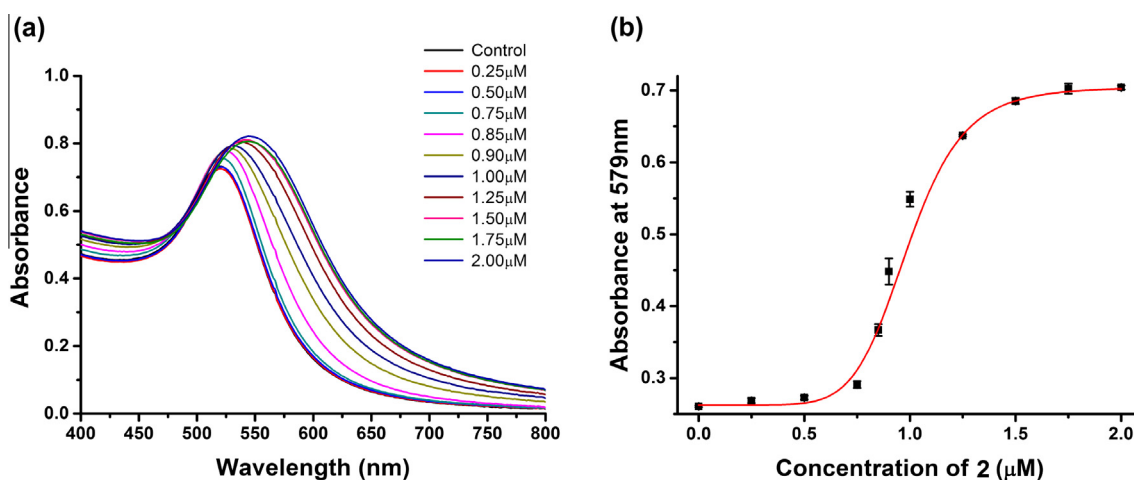


Figure 1. (a) Absorbance spectra of Phos-AuNPs (3 nM) recorded 1 min after the addition of various concentrations of **2**; (b) plot of absorbance intensities of Phos-AuNPs (3 nM) versus various concentrations of **2**.

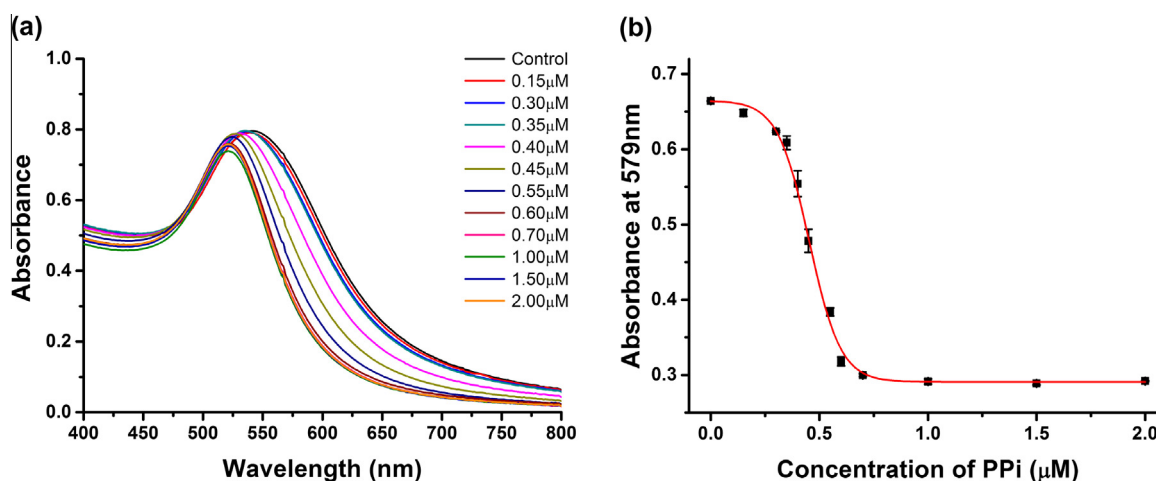


Figure 2. (a) Absorbance changes of **2** pretreated with PPI in pH 7.0 buffer solution (10 mM HEPES, 10 mM NaCl) containing Phos-AuNPs (3 nM); (b) plot of assay solution absorbance intensities at 579 nm versus PPI concentration.

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