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Colorimetric Determination of Al(III) Based on the Aggregation of Gold Nanoparticles Functionalized with Novel 4-Benzoyl Pyrazolone Derivative

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Abstract. A sensitive and selective colorimetric method has been developed for detection of Al^{3+} ion using 4-benzoyl pyrazolone-functionalized gold nanoparticles (BMPBP-AuNPs) as novel colorimetric probes. The BMPBP-AuNPs were characterized by UV-visible spectrometry and transmission electron microscopy (TEM). It was found that the addition of the Al^{3+} ions led to a rapid aggregation of the BMPBP-AuNPs, which changed the color of the mixture from red to blue. Furthermore, there was a shift in the characteristic surface plasmon resonance (SPR) peak from 524 to 650 nm of BMPBP-AuNPs, which confirmed that a good linear relation ($R^2 = 0.9935$) was present between the absorption ratio of 524 and 650 nm. Also, the assay detected the Al^{3+} ion concentrations in the linear range 0-12 ppm with the detection limit is 0.05 ppm. Finally, the synthesized BMPBP-AuNPs were successfully used as a colorimetric sensor for the selective and sensitive detection of the Al^{3+} ions in water samples.

INTRODUCTION

The gold nanoparticles (AuNPs) are essential colorimetric indicators as they have to depend on the distant optical properties and have a large surface area [1]. They are also used for the optical sensing of nanomaterials as they show a good surface plasmon resonance (SPR) absorption in the visible light region, have a simple preparatory technique, higher stability and a good biocompatibility [2]. Amongst the nanomaterials, AuNPs are very popular due to their different aspects like the imaging system analysis. While carrying out colorimetric analysis, the aggregation of the AuNPs is an important mechanism which leads to changes in their SPR (color, absorbance, and extinction). Therefore, owing to their tunable optical properties, the AuNPs are seen to be especially interesting [3].

The quantitative and qualitative detections of different heavy metal ions in various biological and environmental samples have gained a considerable importance as these metal ions can prove to be toxic to the living organisms beyond a certain concentration [4, 5]. Aluminum is one such important metal which is detected on the earth's crust. This metal is used in numerous applications like food additives, drugs, cosmetics, water treatment and purification, surgical materials etc.; however, higher concentrations of aluminum is toxic [6]. Due to vast industrialization, aluminum pollution has shown a huge increase. The Al^{3+} ions are responsible for many neurological diseases, as the Al^{3+} ions induce oxidative stress within the brain tissues, and cause Alzheimer's. Many studies have shown a close relationship between the Al^{3+} ion concentration and human health; thus, determining the concentration of Al^{3+} in the environmental samples is very important [7]. According to the World Health Organization (WHO), the permissible

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level of the Al^{3+} ions in the drinking water is 7.4 μM [8]. Moreover, the Environmental Protection Agency (EPA, USA) has non-enforceable drinking water standards for Al^{3+} ion at 50 ppm [9].

Many scientists have tried to develop chemosensors for Al^{3+} detection, as this metal ion shows characteristic poor coordination ability as compared to other ions. Hence, a lot of additional effort must be put in designing and developing new sensors for the selective and sensitive detection of Al^{3+} ions from the biological and environmental samples [10]. Over the past few years, scientists have developed several analytical techniques for detecting trace amounts of Al^{3+} ions from the environmental samples, which include inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and the atomic absorption spectrometry (AAS) [11]. However, all these techniques are time-consuming, complex and require a tedious sample preparation before detection. Due to these limitations, the nanosensors are seen as an effective device which can be used in the field and they also have a higher selectivity and sensitivity. However, the colorimetric detection based on monitoring of the color change because of aggregation is a commonly used method for heavy metal ion detection [12].

In the past few decades, the nanosensor-based chemical and biological sensors have witnessed a huge revolution, because of the optical properties of the nanomaterials like the SPR, which help in the detection of the metal ion concentrations lower than the WHO guidelines. However, detecting the alkaline-earth, alkali and transition metal ions can be challenging, as selectivity is an important property while using nanosensors for the environmental and biological samples [13]. Thus, the colorimetric sensing is based on their SPR spectral shift, resulting in a color change, which can be noticed with naked eye [14]. After a literature survey, it was seen that there were very few reports which applied a colorimetric technique for detecting Al^{3+} and Zn^{2+} ions using the surface functionalized AuNPs [15]. Many studies have tried detecting the Al^{3+} ions in the biological and environmental samples with the help of optical sensors which used organic ligands like naphthalene, naphthalimide and coumarin [16]. Furthermore, Gupta et al. developed a fluorescence sensor using the 4-amino antipyrine for detecting Al^{3+} metal ions, and they were able to detect this metal easily with their naked eyes under a UV lamp [17]. This method was reported to be very sensitive and selective towards the Al^{3+} ions. Thus, a reporter or ligand can easily bind to the molecules or ions in the sample, and concomitantly change the system property like the color (detected using a colorimetric assay) or the fluorescence intensity (detected using a fluorescence assay) [18].

In this study, the authors have applied a colorimetric detection technique using BMPBP-AuNPs for sensitive and selective detections of the Al^{3+} ions in the spiked samples that were collected from the water bodies in USIM Campus. It was found that the BMPBP-AuNPs rapidly aggregated when the samples contained Al^{3+} ions, which resulted in a color change from red to blue and the SPR peak also showed a red shift. BMPBP-AuNPs were aggregated because of the formation of a complex between 4-benzoyl pyrazolone functionalized gold nanoparticles and the Al^{3+} ions.

EXPERIMENTAL

Chemicals

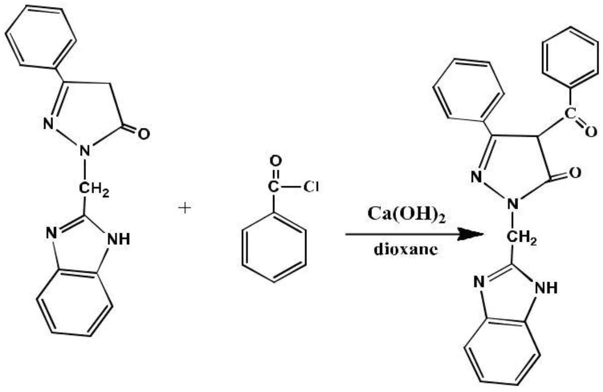
All solvent and starting materials were purchased and obtained from commercial sources. Hydrogen tetrachloroaurate ($HAuCL_4.4H_2O$) and sodium citrate were obtained from Sigma Aldrich, aluminum (III) nitrate $Al(NO_3)_3.9H_2O$ was purchased from Aldrich. All chemicals were of analytical grade and used without further purification. The ionization water was used for the preparation of aqueous solution in the whole experiment.

Instrumentation

Transmission electron microscopy (TEM) measurement was performed on (Jeol JEM 2100F field emission TEM) operated at an accelerating voltage of 80 kV. Statistical analysis of TEM data was done with image processing program (Image software). The UV-vis spectra were recorded in the wavelength range of 200 – 800 nm using Lambda 750 double beam and a 500 single beam spectrophotometer (Perkin Elmer).

Synthesis of 1-((benzoimidazol-2-ly) methyl)-3-phenyl-4-benzoyl-pyrazol-5-one (BMPBP)

The synthesized 1-[(benzimidazole-2-yl)methyl]-3-phenyl-pyrazol-5-one (0.01 mol) was dissolved in a hot 1,4-dioxane solution (10 mL) in the flask with stirrer [20]. Then, calcium hydroxide (0.02 mol) was mixed with the above solution, followed by a dropwise addition of benzoyl chloride (0.01 mol). Once all the chemicals mixed, this reaction mixture was refluxed for 3-6 hrs. Thereafter, it was poured into a dilute acidic solution of HCl (10 mL, 2 N) under vigorous stirring conditions. Then, the mixture was refrigerated till the appearance of pink crystals. These crystals were collected, washed using distilled water, and recrystallized with absolute ethanol to yield BMPBP crystals as shown in Scheme 1. These crystals were dried and stored in a desiccator. Yield recorded was ca. 91%, IR: 3006 cm^{-1} ν(CH), 3178 cm^{-1} ν(NH), 2932 cm^{-1} ν(CH_2), 1712 cm^{-1} of ν(C=O), and 1741 cm^{-1} ν(C=O); ^{1}HNMR (DMSO-d6) δ 13.15 (NH), 2.4 (CH of benzoyl pyrazolone), 7-8 (m, H aromatic), and 3.3 (CH_2 of benzimidazole ring) ppm; ^{13}C NMR (DMSO-d_6) δ 30 (CH), 76 (CH_2), 128.2, 128.30, 128.36, 128.53, 128.70, 129.16, 130.25, 130.53, 131.64, 131.91, 133.43, 134.21, 148.82, 156.69, 163.57, 167.02 (C=O) for the pyrazolone ring.



SCHEME 1. Synthesis of the 1-((benzoimidazol-2-ly)methyl)-3-phenyl-4-benzoyl-pyrazol-5-one (BMPBP)

Synthesis of the 1-((benzoimidazol-2-ly) methyl)-3-phenyl-4-benzoyl-1,4-dihydropyrazol-5-one capped AuNPs (BMPBP–AuNPs)

The citrate-capped AuNPs have been prepared using the method described by Frens [20]. All glassware were cleaned before used. In brief, $HAuCl_4$ solution (100 mL, 10 mM) was added to a 250-mL round bottom flask and boiled under constant stirring for 20 mins. Then, trisodium citrate (10 mL, 38.8 mM) was added to the flask and the reaction mixture was further stirred for 15 mins. The solution color changed from pale yellowish to red, which indicated that the AuNPs were formed. The excess amount of sodium citrate was removed by centrifuging (11000 rpm, 10 mins) the citrate-reduced AuNPs. The solution of the synthesized BMPBP–AuNPs were prepared by adding BMPBP (100 µl, 1 mM) to a 20 mL solution of Au NPs and constantly stirred. The resultant BMPBP-AuNPs mixture was used for carrying out the colorimetric assay for Al^{3+} detection in the water samples.

Colorimetric detection of Al^{3+} ion using BMPBP-AuNPs Sensing

Aluminum nitrate was dissolved in deionized water to prepare a stock solution of aluminum nitrate (1 mM) for additional use. BMPBP-AuNPs were used to detect Al^{3+}, where 1.5 mL of aqueous solution was mixed (spiked) with 0.2 mL Al^{3+} solution to make the final concentration reached the range of 0.375–188 ppm and an aqueous solution was employed for color sensing at room temperature. Then, the mixture was agitated for a while and then left for 1 minute at room temperature. The TEM microscopy and UV-vis spectrophotometer were employed to determine the resultant color change, which was done by evaluating the absorbance values.

Selective Detection of Al^{3+} Ion

For verifying the selective detection of Al^{3+} using the synthesized BMPBP-AuNPs, several metal ions were tested i.e. Na^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+} and Al^{3+} after dissolving $Al(NO_3)_3.9H_2O$ and the other metal salts (7.5 ppm) to be tested. The metal analysis showed the effect of the metal ions against the synthesized nanoparticles. The results obtained indicated that the nanoparticles were more selective against the Al^{3+} ions. This was detected using the UV-visible spectrophotometric analysis.

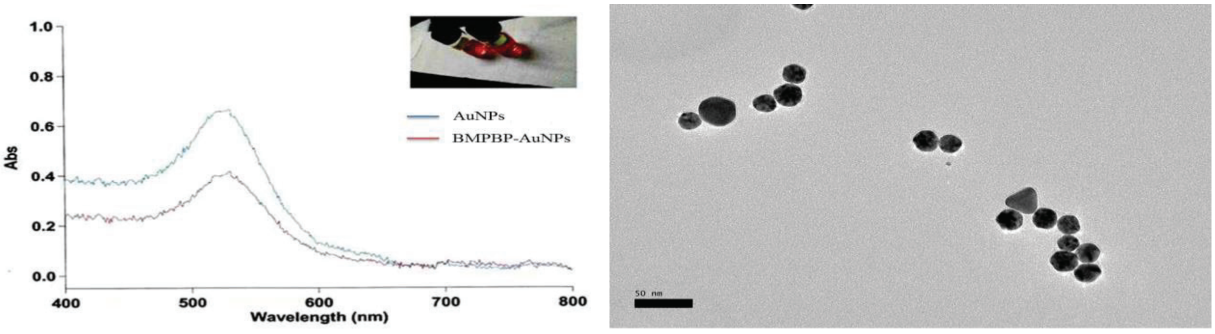
Detection of Al^{3+} in Real Sample

BMPBP-AuNPs was used as a probe for Al^{3+} ion detection in drinking water sample (tap water) to confirm the method's practical applicability. From USIM Campus, the water samples were taken and then filtered using a 0.22 μm membrane. The water was spiked with various concentrations of Al^{3+} (0.375, 0.75, 1.5, 3, and 12 ppm) and the mentioned procedure was used for analysis.

RESULTS AND DISCUSSION

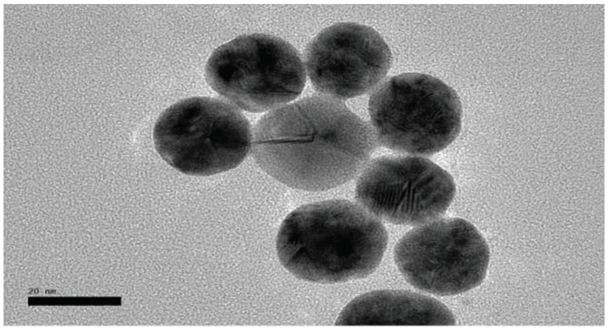
Characterization of BMPBP-AuNPs

Figure 1 shows the synthesis results as well as BMPBP-AuNPs' characterization. Within seconds after adding $HAuCl_4$ to a diluted solution of sodium citrate, the red colour became visible. Figure 1(a) shows the UV-vis spectra of BMPBP-AuNPs and AuNPs. The synthesis of gold nanoparticles was confirmed with the appearance of bright red color, which gave a peak at 520 nm in UV-vis spectrum. The BMPBP-AuNPs was also observed in Fig. 1(a) with the red color and appearance of a peak with a slight shift at 524 nm. This was further confirmed by TEM analysis. The AuNPs' TEM demonstrated that the NPs were monodispersed, and each with a mean diameter of 20 nm. However, the BMPBP compound resulted in an increase in the diameter of AuNPs to 21 nm, which showed surface modification of the AuNPs, as presented in Fig. 1(b) and (c).



(a)

(b)

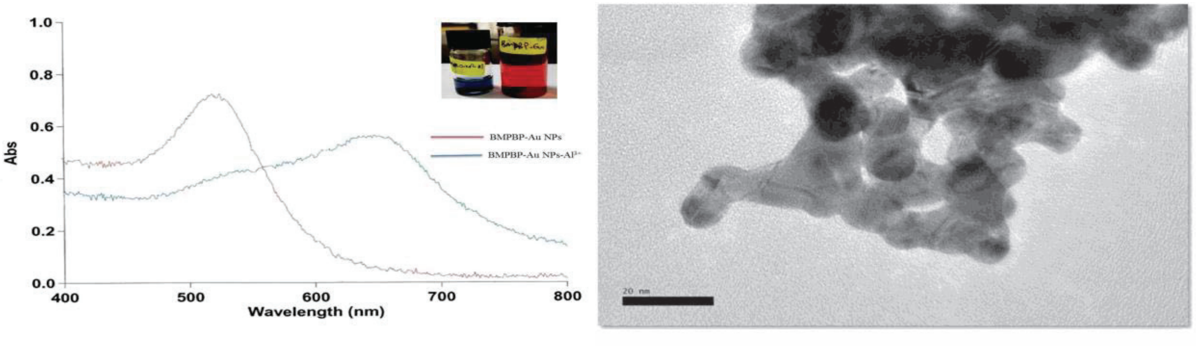


(c)

FIGURE 1. (a) UV-vis spectra shows the absorption of AuNPs and BMPBP-Au NPs .(b) TEM image of AuNPs. (c) TEM image of BMPBP-Au NPs in absence of Al^{3+}

A Sensing Mechanism for the Detection of Al^{3+} Ion using BMPBP-AuNPs

Herein, we also investigated the sensitivity of the BMPBP-AuNPs as a colorimetric sensor using Al^{3+} ion and determined the corresponding UV-Vis spectra under the optimized conditions. Figure 2(a), shows the UV-Vis spectra and the subsequent color change in the BMPBP-AuNPs with Al^{3+} ion. When the Al^{3+} solution was added to the dispersed BMPBP-AuNPs, there was a shift in the absorbance from 524 nm to 650 nm. This resulted in a color change from red to blue. All the resultant changes were attributed to the BMPBP-AuNPs-Al^{3+} aggregation and this was further confirmed by the TEM image Fig. 2(b). In addition, a gradual aggregation of the BMPBP-AuNPs could be monitored by observing a gradual color change after adding the Al^{3+} ions.



(a)

(b)

FIGURE 2. (a) photograph shows the colors BMPBP-AuNPs and BMPBP-AuNPs-Al^{3+} and UV-Vis absorption spectra of BMPBP-AuNPs and BMPBP-AuNPs-Al^{3+}. (b) TEM shows the aggregation of BMPBP-AuNPs in present of Al^{3+} ion

Selective Sensing of the Al^{3+} Ions using the BMPBP-AuNPs

Furthermore, in this study, we investigated the selectivity of the BMPBP-AuNPs by adding a solution of different metal ions (0.1 mL, 7.5 ppm of Na^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+} and Al^{3+}) into a 2 mL solution of the BMPBP-AuNPs and then studying the corresponding UV-Vis spectra. The SPR peak of the BMPBP-Au NPs at 524 nm showed a remarkable decrease and a new peak was seen at 650 nm after the addition of the Al^{3+} ions, which confirmed that the BMPBP-AuNPs aggregated after their reaction with the Al^{3+} ions. The new peak at 650 nm was attributed to the formation of a coordinate covalent bond between the carbonyl groups of the 4-benzoyl pyrazolone – Au NPs and the Al^{3+} ions, which led to the charge transfer from the ligand to the metal. This led to the color change of the BMPBP-AuNPs solution from red to blue, which could be qualitatively detected by the naked eye. These results also indicated that the Al^{3+} ions are able to strongly interact with the C=O group present on the surface of the AuNPs and lead to their aggregation because of the electric dipole-dipole interactions. Thus, based on the results of the absorption ratio (A650/A524), it was concluded that the synthesized BMPBP-AuNPs showed a much higher selectively towards the Al^{3+} ions as compared to the other metal ions (except Cr^{3+} ion, which showed a peak at 640 nm). Furthermore, the results showed that the Al^{3+} ions led to a higher BMPBP-AuNPs aggregation and resulted in the formation of a complex as shown in Fig. 3(a) and (b).

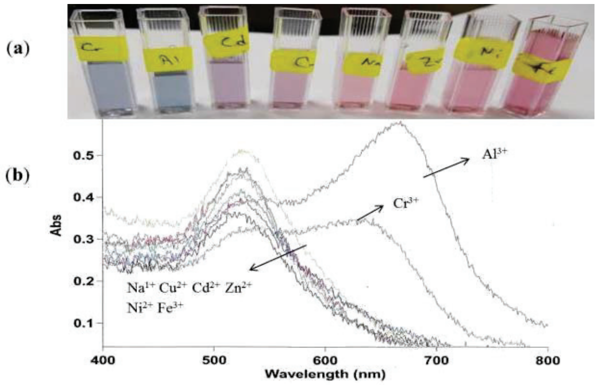
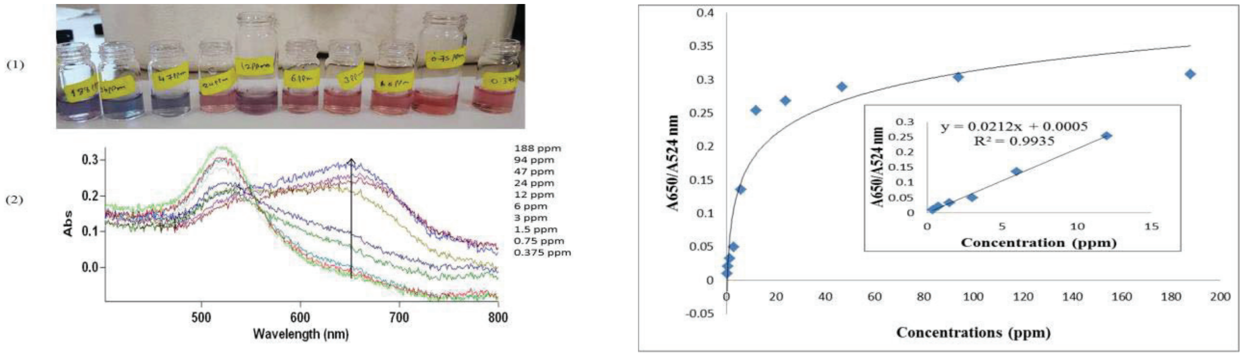


FIGURE 3. (a) Image of BMPBP-AuNPs in the presence of various metal ions (7.5 ppm), (b) UV-Vis absorption of BMPBP-Au NPs in the presence of different metal ions (7.5 ppm)

Quantification of Al^{3+} by using BMPBP-AuNPs

To quantify Al^{3+} ion in the aqueous sample, there was a need to show the potential of BMPBP-Au NPs via UV-vis spectrometric method. Under optimized conditions, to the BMPBP-AuNPs solution, variable concentrations of Al^{3+} ion (0.375, 0.75. 1.5, 3, 6, 12, 24, 47, 94 and 188 ppm) were added, after which we observed the corresponding UV-vis spectra in line with the rising concentrations of Al^{3+} ion. Gradually, the reaction mixture changed its color from red to purple to blue, which could be seen even with the naked eye as given in Fig. 4(a) (1). Also, the rise in concentration of Al^{3+} ion resulted in reduction in the SPR peak at 524 nm, and at the same time, a rise in the new absorption peak at 650 nm which is presented in Fig. 4(a) (2). From Fig. 4(b) a new calibration graph displayed the absorption ratio (A650/A524 nm), demonstrating a linear relationship of $y = 0.0212x + 0.0005$ and a correlation coefficient (R^2) of 0.9935. Furthermore, ($LOD = 3\sigma$) was employed to calculate the LOD for the Al^{3+} ions, where σ signifies the blank's standard deviation, which was (LOD = 0.05 ppm). It can be acclaimed that the BMPBP-Au NPs' UV-vis spectra amid the variable concentrations of Al^{3+} ions resulted in accumulation of BMPBP-AuNPs. Thus, it is inferred that the BMPBP-AuNPs' carbonyl group acted as a donor and thus the binding group for Al^{3+} ion, thereby causing the red shift in the SPR peak, changing from 524 nm to 650 nm, followed with subsequent changing in the solution color from red to blue.



(a) (b)

FIGURE 4. (a) (1) Visual color change of BMPBP-AuNPs with different concentrations of Al^{3+} ranging from 0.375 to 188 ppm. (2) UV-vis absorption change of BMPBP-AuNPs in the presence of different concentrations of Al^{3+}. (b) Inset: Plot of the absorbance ratios (A650/A524 nm) against Al^{3+} concentration in the range of 0.375 – 188 ppm

Application of BMPBP- AuNPs for the Analysis of Al^{3+} Ion in a Water Sample

To examine the proposed method's practical applicability and accuracy in determining Al^{3+} ion in water (tap water), which was taken from USIM Campus, the samples were spiked with certain amounts of Al^{3+} ion (1, 4, 6 and 8 ppm) that were calculated based on the analytical results as listed in Table 1. In the real sample, calculation was done for the percentage recovery and Relative Standard Deviation (RSD%) values via spiking with variable concentrations of Al^{3+} (60 – 115 %), with RSD values lower than 0.4 %. It can therefore be inferred that for the sensitive and selective detection of Al^{3+} ion, BMPBP-AuNPs can be employed as a specific colorimetric probe in environmental samples.

TABLE 1. BMPBP-AuNPs for the analysis of Al^{3+} in real samples

Sample	Added(ppm)	Found(ppm)	Recovery%	RSD% (n =3)
Water Tap	1	0.6	60	0.7
	4	4.6	115	0.4
	6	6.1	102	0.4
	8	7.7	96	0.5

CONCLUSIONS

In this study, cost-effective, selective and novel BMPBP-AuNPs based on colorimetric method has been developed for the detection of Al^{3+} ion in the water sample. Al^{3+} ion was shown to induce the aggregation of BMPBP-AuNPs due to the formation of a coordination complex between carbonyl groups and Al^{3+} ion, resulting in a visual color change from red to blue. On the other hand, a redshift in SPR peak from 524 nm to 650 nm and the Al^{3+} induced aggregation of BMPBP-AuNPs was confirmed by TEM. The sensing of Al^{3+} ion can be also be detected by the naked eye and, with the spectrophotometric method, it has the linear range within 0 – 12 ppm with the detection limit (LOD) was 0.05 ppm. This proposed method was accurate for detection of Al^{3+} ions in the water samples. Thus, the BMPBP-AuNPs could be used as a novel colorimetric sensor for the selective and real-time detection of the Al^{3+} ions in environmental samples.

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