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4-benzyl pyrazolone functionalized gold nanoparticles for fluorescence sensing and detection of Al $^{3+}$ ion in water samples

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Abstract: A new type of gold nanoparticles was synthesized by using benzoyl pyrazolone as a capping agent. The synthesized AuNPs exhibited a spherical shape and a monodisperse and fluorescence emission characteristic peak at 650 nm. The AuNPs –BMPBP was demonstrated as sensitive and selective fluorescent chemosensor for detection of Al $^{3+}$ ion. In the presence of Al $^{3+}$ ion, the fluorescent emission of BMPBP-AuNPs at 650 nm, increased with an increasing concentration of Al $^{3+}$ ion with a low detection limit (2 μM), the proposed method provided to apply determination of Al $^{3+}$ ion of tap water with satisfactory results.

Keywords: 4-benzoyl pyrazolone; fluorescence sensing; Functionalized gold nanoparticles; detection Al $^{3+}$ ion

1. Introduction

Determination of Al $^{3+}$ ion is most important in various aspects such as in the clinical diagnosis for identification of dementia, myopathy, renal-dystrophy, Parkinson and Al-zheimer`s diseases. Al $^{3+}$ ion can be found at trace level in the drinking water because aluminum sulfate, shortly known as Alum, is normally used as the flocculating agent in water treatment process. While, aluminum phosphide is most commonly used to protect grain held in stores can be released when this compound contact with humidity and contaminate on the grain surface [1]. Aluminum is naturally found in waters and living tissues in its ionic form Al $^{3+}$. At low pH, the solubility of aluminum minerals elevates the levels of available Al $^{3+}$[2]. Aluminum ion is classified as toxic pollution considering what adverse effects it can do to the body. In addition. the evaluation and early detection of aluminum ion trace or concentration is not as comprehensive compared to other metal ions. Therefore, The formation development of or a molecular probes leading towards in-situ detection of aluminum ion is very important [3]. In the meantime, there are evident of an insufficient amount number of spectroscopic characteristics and ineffective coordination ability of Al $^{3+}$ ion. Thus, the development for the detection of Al $^{3+}$ ion still serves as a challenge; [4-5] . The development of chemosensors with low detection limit, high selective and high sensitivity has been interesting due to their essential role in medical, environmental and biological applications. The fluorescence chemosensor for determination of metal ions have attracted.

In the past few years, there has been a huge interest in developing fluorescent sensors for different metal ions as they offer many advantages like a higher sensitivity and selectivity, a higher response time, inexpensive equipment, operational ease, instantaneous response along with a real-time detection. Many fluorescent sensors using for detection Al^{3+} are designed; however, a majority of them were prepared using organic solvents [4]. The fluorescence sensors are a type of analytical devices which can detect the target analytes with the help of some components which generate fluorescent signals that can also be used for the molecular recognition and environmental monitoring. The fluorescence properties can be associated with a ligand shell, resulting from a ligand-metal charge transfer that is induced by a selective interaction occurring between the ligand and the analyte, and they could affect the nanoparticle fluorescence [5]. Although many of the fluorescent sensors used for Al^{3+} detection show a good selectivity, certain limitations like poor water solubility and a complex synthetic process were also observed [6]. Some fluorescent sensors were operated with organic solvent or in aqueous solution of organic solvent others displayed less sensitivity to Al $^{3+}$ with poor detection limits.[8],[11]. In contrast, The Al^{3+} ion, with its relatively small radius (0.5˚A) andhigh ionic charge (r = 4.81), is a hard Lewis acid and thus prefers to form stable complexes with the nitrogen and oxygen atoms (thehard donor atoms or hard donor bases) of ligands [7]. Many optical sensors, especially fluorescent sensors, are an important analytical tool and can be used for developing economic assays without requiring costly instruments. Studies have shown that many of the fluorescent chemosensors, based on their design, are used for detecting the Al^{3+} ions, as they have Al^{3+} sensitive receptors with a high selectivity and sensitivity[8-9]. Gold nanoparticles (AuNPs) as interesting materials in numerous areas including drug delivery, organic synthesis, and sensors. Therefore, there is a need to develop a technology that can regulate gold as well as other expensive noble metal nanoparticles without losing precious metals [10]. The AuNPs are acquired through chemical reduction of gold ions. The optical absorption band at a wavelength around 530 nm is responsible for the characteristic color of gold colloids [11]. AuNPs possess distinct electronic and optical properties which make them the best colour indicating probes in the formation of analytical methods for the range of analyses sensing [12]. Studies have conclusively revealed that the synthesis of AuNP citrate stabilized on the basis of the aqueous phase reduction of tetrachloroauric acid ($HAuCl_4$) by sodium citrate. Turkevich and his workers reveal the possibility of controlling AuNPs size to 5 to 150 nm by simply varying the reaction conditions (i.e. sodium citrate at levels of gold salt, pH of the solution and the solvent [13]. The scientific resources specifically associated to the functionalized AuNPs present relative paucity and become fascinating nanomaterials for sensing heavy metal ions [14]. The major advantage of AuNPs is the possibility of surface functionalization with many ligands. The nanoparticles can be stabilized through the utilization of compatible capping agents or protective agents that prevent aggregation. The common stabilizing agents include different classes of chelating ligand, polymers, citrate and thiols. Moreover, the surface of the nanoparticle must be functionalized with functional moieties or compounds which can be enabled for specific process. The most common stabilization of nanoparticle mechanism encompasses charge stabilization and steric stabilization. Thus, with the help of surface functionalization, there is an additional improvement in the stability of AuNPs at high salt concentrations, as well as the application of AuNPs through the immobilization of several moieties with analytes [15]. Gold nanoparticles (AuNPs) as interesting materials in numerous areas including drug delivery, organic synthesis, and sensors. In this work, BMPBP-AuNPs were prepared and proposed as fluorescence probe for rapid, selective and sensitive detection of Al^{3+} ion . This leads to the development of a highly selective and sensitive method for monitoring of Al^{3+} ion by using BMPBP-AuNPs as a fluorescence probe. Furthermore, the applicability of detection system has been demonstrated by analysis of Al ion in tap water.

2. Materials and Methods

2.1 Chemicals and materials

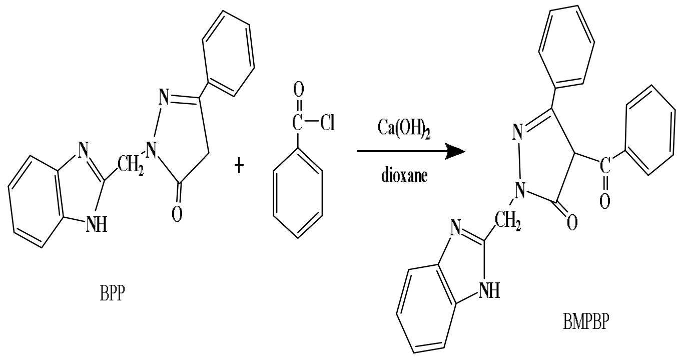
All solvent and starting materials were purchased and obtained from commercial sources. Hydrogen tetrachloroaurate ($HAuCL_4.4H_2O$) and sodium citrate were obtained from Sigma Aldrich, Aluminum (III) nitrate $Al(NO_3)_3.9H_2O$ was purchased from Aldrich. All chemicals were of analytical grade and used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

2.2 Apparatus

Transmission electron microscopy (TEM) measurement were 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 spectrum is active in the wavelength range of 200-800 nm. In this study, Lambda 750 double beam and a 500 single beam spectrophotometer (Perkin Elmer) was used and the fluorescence generated in the reactive zones was estimated using LS55 fluorescence photometer (Perkin Elmer).

2.3 Synthesis of 1-((benzoimidazol-2-ly) methyl)-3-phenyl-4-benzoyl-pyrazol-5-one (BMPBP) [16]

The synthesized 1-[(Benzimidazole- 2-yl) methyl]-3- phenyl-pyrazol-5-one (BPP) (0.01mol) was dissolved in 10 mL hot 1,4-dioxane solution in the flask with the stirrer. Then, calcium hydroxide (0.02 mol) is mixed with the above solution, followed by a dropwise addition of 0.01 mol benzoyl chloride. Once all the chemicals were mixed, this reaction mixture is refluxed for 3-6 hrs. Thereafter, it was poured into a dilute acidic solution of HCl (10 mL, 2N) 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 the desiccator. Yield was at 91%, IR : 3006 ν (CH), 3178 ν (NH), 2932 $\nu(CH_2)$, 1712 of ν C=O cm-1, and 1741 ν(C=O); 1HNMR ($DMSO-d_6$) 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 (CH2), 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).

2.4 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 [17]. All glassware was 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. Thereafter, trisodium citrate (10 mL, 38.8 mM) was added to the flask and the reaction mixture was further stirred for 15 mins. The solution colour changed from pale yellowish to red, which indicated that the AuNPs were formed as shown in scheme 2. The excess amounts of sodium citrate could be removed by centrifuging (11000 rpm, 10 mins) the citrate-reduced AuNPs. The solution of the synthesized BMPBP–AuNPs were prepared by adding BMPBP (1 mM) to a 20mL 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 sample.

2.5 Fluorimetric detection of Al $^{3+}$ using BMPBP-AuNPs

Typically, 10 mL of BMPBP-AuNPs suspension was diluted with 30 mL of deionized water to give a total volume of 40 mL as a stock solution for the detection of Al $^{3+}$ into the 10 mL volumetric contained volume of 1mM Standard Al $^{3+}$ solution was diluted by deionized water. Thus, to evaluated the sensitivity toward Al $^{3+}$, different concentration (4, 10, 12, 16 and 22 µM). Then, 1000 µL of the as-prepared AuNPs was added into the diluted Al $^{3+}$ solution. The mixture was made to a final volume of 10 mL with deionized water and incubated at room temperature for 10 min before measure the fluorescence spectrum.

2.6 Selective of Metal Ions by Using BMPBP-AuNPs sensor

Into the 50 mL volumetric flask contained 1000 µM metal ions including (Na^+, Zn^{2+}, Cu^{2+}, N^{i2+}, Fe^{3+}, Cd^{2+}, Cr^{3+}, and Al^{3+}). Then 1 mL of the synthesized BMPBP functionalized AuNPs solution was added into each metal ions solution. Thus, the mixture solution was adjusted to the final volume of 10 mL with deionized water and the solution was incubated at room temperature for 10 min before recording the individual fluorescence spectrum.

2.7 Application of the sensor in real samples

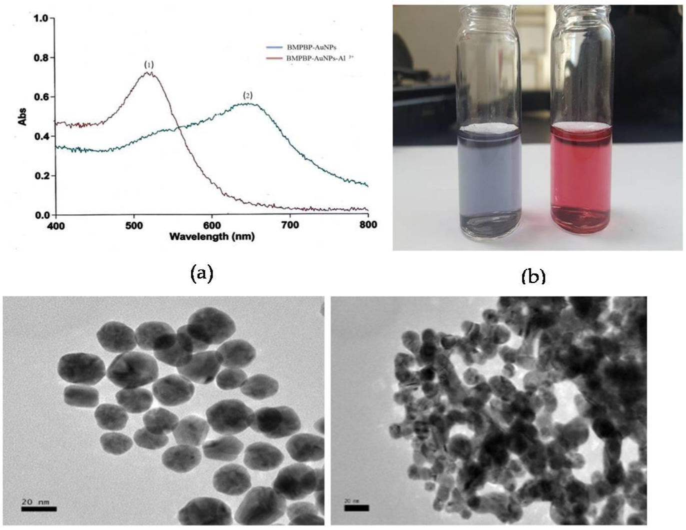
In order to demonstrate the applicability of the proposed sensor in determination of 0.1 mL, 1000 µM of standard Al^{3+} solution was spiked. Then, 1 mL of the as prepared BMPBP-AuNPs solution was added into the sample solution and mixed thoroughly and left for 15 min before recording the fluorescence spectra.

3. Results and discussion

3.1 The mechanism for determination of Al^{3+} ion

Figure 1. shows UV-vis absorption spectra of the BMPBP-AuNPs as a colorimetric sensor using Al^{3+} ion and determined the corresponding UV-Vis spectra under the optimized conditions as-prepared BMPBP-AuNPs exhibited a surface plasma resonance (SPR) absorption band peaked at 524 nm and the color of the solution appeared red as shown in Figure. 1(b) (left). After addition of an appropriate amount of Al^{3+}, the SPR peak at shifting from 524 nm to 650 nm appeared as shown in

Figure 1(a) . Meanwhile, the solution color change from red to blue was distinguishable and perceivable by the naked eye as shown in Figure 1(b) (left). The wavelength red shift and the solution color exhibited the aggregation of BMPBP-AuNPs which was furtherly confirmed by TEM characterized Figure1(c) and Figure 1 (d). Thus, the BMPBP-AuNPs could be monitored by observing a gradual color change after adding the Al^{3+} ions.



(a) (b)

(c) (d)

Figure 1. Absorption spectra (a), Optical photographs (b) of BMPBP-AuNPs without and with Al $^{3+}$ (5.7Mm). TEM image (c) BMBPBP-AuNPs (d) TEM image of BMPBP-AuNPs-Al^{3+}.

3.2 Sensitivity of BMPBP-AuNPs as Fluorescent Sensor for Detection of Al^{3+} Ion

A study was carried out on the fluorescence emission characteristics of BMPBP-Au NPs that exhibited sensitivity to the varying concentration of Al^{3+} ion, (4, 10, 12, 16 and 22 μM). This behaviour is depicted in Figure 2 (a). which demonstrates the change in the intensity of emission of BMPBP-Au NPs on increasing the concentration of Al^{3+} ions. There was a gradual rise in the emission fluorescence intensity of BMPBP-Au NPs as the addition of Al^{3+} increased. The rise in fluorescence implies that BMPBP-Au NPs most probably form stable fluorescence complexes in the presence of Al^{3+}. The addition of Al^{3+} causes a significant augmentation of both the emission of BMPBP-Au NPs and the excitation band. This indicates that Al^{3+} prompts the aggregation of acyl pyrazolone-gold nanoparticles and the same was also verified by the resonance of Al^{3+} ions. Moreover, the aggregation of BMPBP-Au NPs induced by Al^{3+} ions is primarily accredited to the coordination between Al^{3+} carbonyl group [18] and hydroxyl of pyrazolone ring, and the high affinity of electrostatic. It can be concluded that the negatively charged surface of BMPBP-Au NPs was neutralized by Al^{3+}, implying the electrostatic interaction between Al^{3+} and BMPBP-Au NPs. the linear relationship between the BMPBP-AuNPs and Al^{3+} concentration and the fluorescence intensity, For quantification, a practically usable range from 6 to 22 μM (R^2 = 0.99) was determined and shown in inset: the relationship between fluorescence intensity and Al^{3+} concentration as shown in Figure 2(b). The detection limit was determined to be at 2 μM, which is less than the toxicity level of Al^{3+} in drinking water that was defined as 7.4 μM by the Word Health Organization (WHO). The outcome shows that this fluorescent sensor could be used for determining Al^{3+} sensitivity in aqueous solutions.

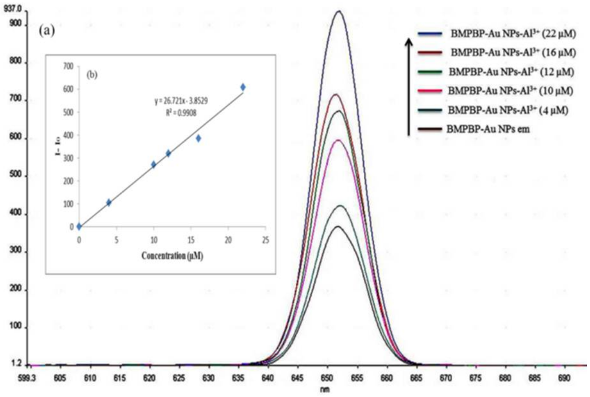


Figure 2 . (a) Fluorescence emission spectra of BMPBP-AuNPs after adding various concentration of Al^{3+} from 4 to 22 μM. (b) inset: the relationship between fluorescence intensity and Al^{3+} concentration.

3.3 Selectivity of BMPBP-AuNPs as Fluorescent Sensor for The detection of Al^{3+} Ion

To evaluate the practical applicability of BMPBP-AuNPs 100 μL as Al^{3+} selective fluorescence nanosensor, an investigation was carried out on a number of environmentally relevant metal ions including (Na^{+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Cr^{3+}, and Al^{3+}). At first, it was analyzed if these metals, when used on their own, can weaken or augment the BMPBP-AuNPs sensors. As depicted in Figure 2, the fluorescence emission at 650 nm is represented as a function of different ions that interact with BMPBP-AuNPs. It was observed that all the metal ions showed only an insignificant effect on the fluorescence of BMPBP-AuNPs, implying that the sensing discussed herein displays high specificity for Al^{3+} ions. The BMPBP-AuNPs exhibited significant enhancement in fluorescence with Al^{3+} ions. Thus, the suggesting the occurrence of chelation between the carbonyl group or –OH group is crucial for Al^{3+} sensing as it can selectively chelate to Al^{3+} over other metal ions [19] as shown in Figure 3.

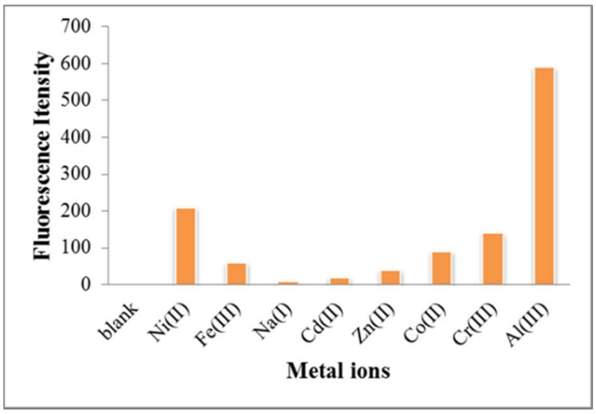


Figure 3. Fluorescence intensity histograms of BMPBP-AuNPs in the presence of different metal ions.

3.4 Effect of pH

The impact of pH on the fluorescence emission is studied for the fluorescence spectra of BMPBP-AuNPs with Al^{3+} exposed to various pH ranging from 4 to 11. As presented in Figure 4, the fluorescence intensity of BMPBP-AuNPs-Al^{3+} was seen to increase when set at weak acidic conditions ($pH \leq 5$) which suggests that the sensor is optimum to be used as Al^{3+} fluorescence sensor for weak acid aqueous medium. The sensor design is focused on chelating metal ions through its carbonyl of acyl and hydroxyl of the pyrazolone ring. Significant changes could be observed in the fluorescence as the BMPBP-AuNPs remained in the keto form, while coordination with Al^{3+} ion was in the enol form, contributing to proper fluorescence emission.

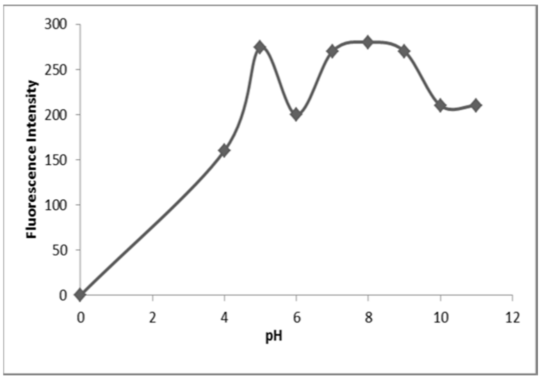


Figure 4. Effect of pH on intensity of BMPBP-AuNPs in presence of Al^{3+} ion

4. Reversible Sensing Nature

A key characteristic of the molecular sensor is its reversible sensing behaviour. Fluorescence was observed with chemosensors that were enhanced with Al^{3+} in the solution phase. Reconverting and reusing of free chemosensor for sensing application was easy and simple. It's characteristic to reversibly bind Al^{3+} to BMPBP in aqueous solution is considered crucial for many applications. The reversibility was assessed for BMPBP with Al^{3+} as shown in Figure 5. When Al^{3+} ion was added to the solution, the fluorescence intensity could be recovered back to its original intensity of BMPBP-Al^{3+} complexe. These results specify that a reversible chemosensor for Al^{3+} could have been sensor BMPBP. On the other hand, the acyl pyrazolone (BMPBP) in nanomaterials possess surface-related properties that are significant to the AuNPs-related colorimetric assays. Here, a colour change from red to blue could be observed during the analyte-ligand binding that also induces aggregation of AuNPs, which is also optimum for fluorescent. These approaches and principles have been employed to differentiate and detect between ligand functionalized gold nanoparticles and ligand with Al^{3+}.

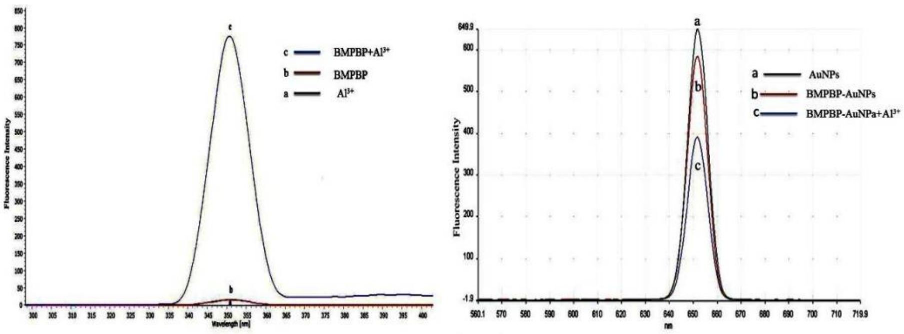


Figure 5. A Fluorescence emission spectra (a) Al^{3+} (b) BMPBP and (c) BMPBP in the presence of Al^{3+} ion. B Fluorescence emission spectra (a) AuNPs (b) BMPBP-AuNPs (c) BMPBP-AuNPs-Al^{3+}.

5. Application of BMPBP-Au NPs for the analysis of Al^{3+} ion in water sample using fluorescence spectrophotometry

In order to further demonstrate the feasibility of the sensor developed in determination of Al^{+3}. The standard addition method was performed and calculated based on the standard curve 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+} (91 to 111 %), with RSD values lower than 2.7 %. 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 using fluorescence spectrophotometry

Real Sample	Added (µM)	Found (µM)	Recovery %	RSD % (n =3)
A	2	1.9	96	2.7
B	8	7.3	91	1.9
C	12	13.4	111	1.3

6. Conclusion

In this study, cost-effective, selective and novel BMPBP-AuNPs based on fluorescence method has been developed for the detection of Al^{3+} ion in the water sample. A red shift in SPR peak 650 nm and the Al^{3+}. The sensing of Al^{3+} ion can be also detected by the naked eye and, with the spectrophotometric method, it has the linear range within 4 to 22 µM with the detection limit (LOD) was 2 µM. 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 fluorescence sensor for the selective and real-time detection of the Al^{3+} ions in environmental samples.

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Conflicts of Interest: The authors declare no conflict of interest.

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