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Luminescent Silver Nanoclusters Acting as a Label-Free Photoswitch in Metal Ion Sensing

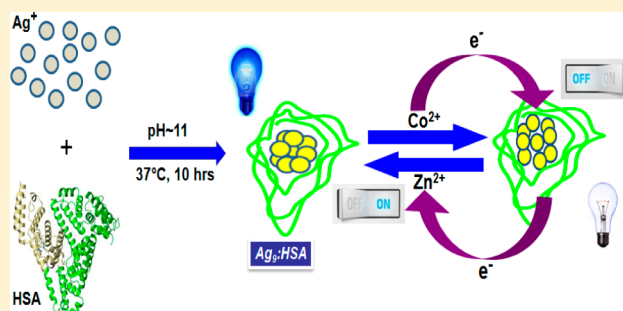
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S Supporting Information

ABSTRACT: In this work, we report the application of protein-templated Ag nanoclusters as a luminescent photoswitch for the detection of metal ions. Ag nanoclusters were synthesized using the circulatory protein human serum albumin (HSA) as a template, whose synthetic procedure can be tuned to make them toggle between blue-emitting (Ag₉:HSA) and red-emitting (Ag₁₄:HSA) nanoclusters. The photoluminescence (PL) intensity of Ag₉:HSA was quenched significantly in the presence of 1 mM Co(II) ions. However, the PL of these quenched nanoclusters was completely restored in the presence of 3 mM Zn(II) ions. This enables them to be used as dual sensors and can serve as luminescent turn “on” and “off” metal switches.

In contrast, the Ag₁₄:HSA did not exhibit any photoswitchable properties but was able to detect Hg(II) selectively and to a high detection limit (10 nM). The luminescent-based sensing properties of these Ag:NCs were further supported by our time-resolved studies. The present study exhibits a promising step toward the application of luminescent metal nanoclusters as potential metal sensors since by tuning their luminescent properties we were able to detect and quantify metal ions selectively and simultaneously switch their sensing behaviors.



Noble metal nanoclusters (NCs) possess some superior photophysical properties in terms of high photostability, photoluminescence (PL), and large Stokes shift.^{1–3} Further, these NCs are characterized by having low toxicity which enables them to play a leading role in several biological applications of late.^{4,5} These NCs (typically <1 nm) usually serve as the missing link that exists between discrete atoms and the bulk nanomaterials such that their size falls within the range of the Fermi wavelength of conduction electrons and results in size-dependent luminescence, thus exhibiting better optical, electrical, and biomedical properties compared to larger metal nanoparticles.^{1,6} On similar grounds, silver nanoclusters (Ag:NCs) have proved to be excellent fluorophores for optical biolabeling, sensing, and imaging even at single-molecule resolution.^{7,8} Metal ions usually play a big role in living organisms either in metabolic and transport activities, or for use in metalloproteins and cofactors, and to protect themselves against the toxic effects of excess metal.⁹ Out of the several transition metals, zinc (Zn) occupies a seminal position in biological materials.¹⁰ As a catalytic agent, Zn is mainly found in metallothionein, carbonic anhydrase (maintains the pH levels of the blood), alcohol dehydrogenase, and a variety of hydrolases,^{11,12} whereas in case of nucleic acid polymerases, transcription factors, and “zinc fingers”, it plays a structural role.¹³ Zn also participates in prebiotic reactions, transcribing DNA to RNA,¹⁴ and sometimes has a regulatory role, like in the case of alkaline phosphatase which catalyzes the hydrolysis of phosphoric esters.¹⁵ Free Zn ions are supposed to be a potent

killer of neurons, glia, and other cell types.¹⁶ Similarly, the other transition metal cobalt (Co) too has important biological significances and is mainly present in cobalamin, also known as vitamin B₁₂.¹⁷ Deficiency of this particular vitamin-B₁₂ leads to the severe diseases like pernicious anemia in humans,¹⁸ and Co poisoning leads to gastrointestinal distress and heart failure, thus reflecting its adverse role in living organisms.¹⁹ Excess Co ions may also cause allergic dermatitis, rhinitis, and asthma, while inhalation of dust contaminated with Co may have pathogenic infections in the lung parenchyma.²⁰ The heavy metal mercury (Hg) as such has no biological role, but it is a highly toxic metal, and several health hazards and risks are associated with it. It is volatile in nature, highly soluble at pH = 7, and gets released into the environment mostly in the form of Hg(II) via weathering of HgS.²¹ Hg is a cumulative poison since there are only a few pathways available for its excretion from the body. It generally enters the biosystems through the respiratory tract, the gastrointestinal tract, and through the skin, thereby causing maximum damage to the central nervous system.^{9,22} High exposures of the heavy metal Hg have adverse effects on humans resulting in hyperirritability, fatigue, behavioral changes, hallucinations, etc., while low doses of the

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same metal affect the normal endothelial and cardiovascular functions.²³ It also harms marine life cycle to a large extent.

Shedding light on all these aspects of metal ions in biology, it is of utmost importance to probe these ions in minute levels in the system under study. Although different techniques such as colorimetry,²⁴ light scattering,²⁵ isothermal calorimetry,²⁶ and electrochemical methods²⁷ were used for metal sensing, however, fluorescence seems to have an edge over all the other techniques for sensing applications because it is extremely sensitive to the changes in local environment around the fluorophore, which in our case are the Ag:NCs formed within a protein (human serum albumin, HSA) scaffold. Hence, any small interaction of these Ag:NCs with metal ions will result in changes in their luminescent properties thereby leading to high limit of detection. Several groups have come up with the idea of using luminescent metal NCs as a tool for sensing metal ions.^{28–32} However, most of them reported the application of noble metal (Au or Ag) NCs as luminescent sensors for Hg or copper (Cu) ion detection,^{29–32} while very few groups have reported their use in the detection of other metal ions that have important biological roles. In our previous study,³³ we have synthesized blue- and red-emitting luminescent Ag:NCs with high quantum yield (more than 10%), excellent photostability, and high PL lifetimes. The novelty of that study stems from the fact that the Ag:HSA NCs could be interconverted (depending upon the experimental conditions) at will and as per our need.³³ On the basis of these excellent luminescent properties of our NCs, we have tried to develop a luminescent metal ion sensor which could detect different ions by tuning its luminescent properties from blue to red and vice versa. In fact our goal was successful as the two Ag:NCs indeed detected different metal ions: Ag₉:HSA NCs were able to detect Co(II) and Zn(II), whereas the Ag₁₄:HSA NCs sensed Hg(II) ions selectively to a high detection limit. However, the most surprising aspect of this study was that the Ag₉:HSA, which were able to detect both Co(II) as well as Zn(II), also showed reverse trend in their sensing behavior. While addition of Co(II) exhibited subsequent quenching of PL intensity of the Ag₉:HSA, Zn(II) on the contrary resulted in the enhancement of the emission properties of Ag₉:HSA. This further led us to the idea of using Ag₉:HSA as a photoluminescent switch whose luminescence can be turned “off” in the presence of Co(II) and similarly could be turned “on” in the presence of Zn(II). The details of the syntheses of the Ag₉:HSA and Ag₁₄:HSA NCs and their associated luminescent properties are mentioned elsewhere.³³ Previous studies based on the colorimetric approaches of noble metal nanoparticles have exhibited sensing properties for Co(II) metal ions, and the limit of detections were relatively high, but such methodologies have been used to detect only one metal ion present in any system.^{34,35} However, with the technique mentioned herein, we can exclusively detect three metal ions in solution starting from one Ag:NC by using very simple redox chemistry,³³ which makes our study unique and extremely versatile.

■ EXPERIMENTAL DETAILS

Materials. HSA, silver nitrate (AgNO₃), sodium borohydride (NaBH₄), and all the metal salts were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) was purchased from Rankem, and 30% hydrogen peroxide (H₂O₂) was purchased from Merck. All the chemicals were of analytical grade and were used without further purification. Milli-Q water

was used throughout the experiments for making the sample solutions, unless or otherwise mentioned.

Instrumentation. Steady-state luminescence measurements were recorded on a Horiba Jobin Yvon Fluorolog 3-111. The PL spectra were measured with a 10 mm path length quartz cuvette. Both the emission and the excitation slits were kept at 5 nm. For PL lifetime measurements, the Ag₉:HSA solutions were excited at 375 nm and Ag₁₄:HSA solutions at 470 nm using N-375L and N-470L picosecond diodes (IBH-NanoLED), respectively. The emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (model R-3809U-50). The time-correlated single photon counting (TCSPC) setup consist of an Ortec 9327 picotiming amplifier. The data was collected with a PCI-6602 interface card as a multichannel analyzer. Full width at half-maximum (fwhm) for the 375 and 470 nm excitations was about 150 and 140 ps, respectively. The limit of detection was calculated from the PL intensity where the change in PL intensity in the presence of metal ions was above 3 times the standard deviation for Ag:NCs in the absence of any metal ion.

Synthesis of Blue- and Red-Emitting Ag:HSA Nano-clusters. Synthesis of Ag₉:HSA nanoclusters was carried out under optimized conditions by adding 5 mL of aqueous solution of AgNO₃ (0.01 M) to 5 mL of HSA solution (7.5 × 10^{−4} M) under vigorous stirring. After 2 min, 0.3 mL of NaOH (1 M) was added to the reaction mixture in order to maintain the reaction pH ~ 11, thereby activating the reducing ability of HSA (rendered by the 18 tyrosine residues in HSA). The mixture was incubated at 37 °C for 10 h under constant vigorous stirring. The Ag₉:HSA formation was indicated by the change in the color of the solution from colorless to yellow (stable for months) when viewed under ordinary visible light. Addition of NaBH₄ (0.01 M) dropwise to the above solution resulted in Ag₁₄:HSA formation which was indicated by change in the color of the solution from colorless to reddish brown. The reaction takes about 5 min for completion, which is much faster compared to Ag₉:HSA NC preparation. These newly formed red-emitting Ag:NCs when treated with 15 μL (per mL of Ag₁₄:HSA) of 30% H₂O₂ yield Ag₉:HSA with almost 100% recovery. The interconversion processes are rapid and take place within 5 min.³³

Metal Ion Sensing Procedure. The salts of metal ions Ca²⁺, Cu²⁺, Cr³⁺, Co²⁺, Cd²⁺, Fe³⁺, Hg²⁺, K⁺, Mn²⁺, Mg²⁺, Na⁺, Ni²⁺, Pb²⁺, and Zn²⁺ were taken, and their aqueous solutions were prepared in Milli-Q water in higher concentrations. These solutions were further diluted, and microliter aliquots of the respected diluted solutions of the metal ions were added to 2 mL of solution of the NCs in such a way that the desired final concentration of metal ion(s) in the solution is achieved. The solutions were made homogeneous by thorough mixing and were then incubated at room temperature for 2 min. Subsequently, they were transferred into the cuvette and the corresponding PL properties were recorded.

■ RESULTS AND DISCUSSION

For sensing studies, aqueous solutions of different metal salts were used and their concentration was initially kept at 10 nM, which was gradually increased up to 1 mM. On successive addition of Co(II) ions to the Ag₉:HSA solution starting from 10 nM, there is very small change in its initial luminescence intensity, but on increasing the concentration of Co(II), the luminescence intensity was quenched by 22% at 1 μM Co(II). On further increasing the concentration of Co(II) in Ag₉:HSA

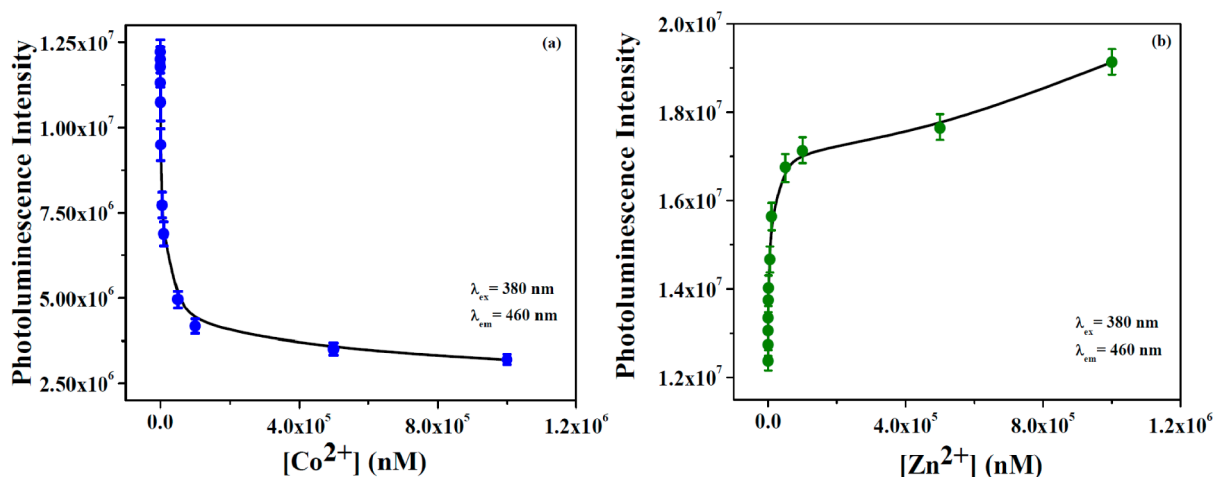


Figure 1. Variation in PL intensity of Ag₉:HSA in the presence of (a) Co (II) ions and (b) Zn (II) ions.

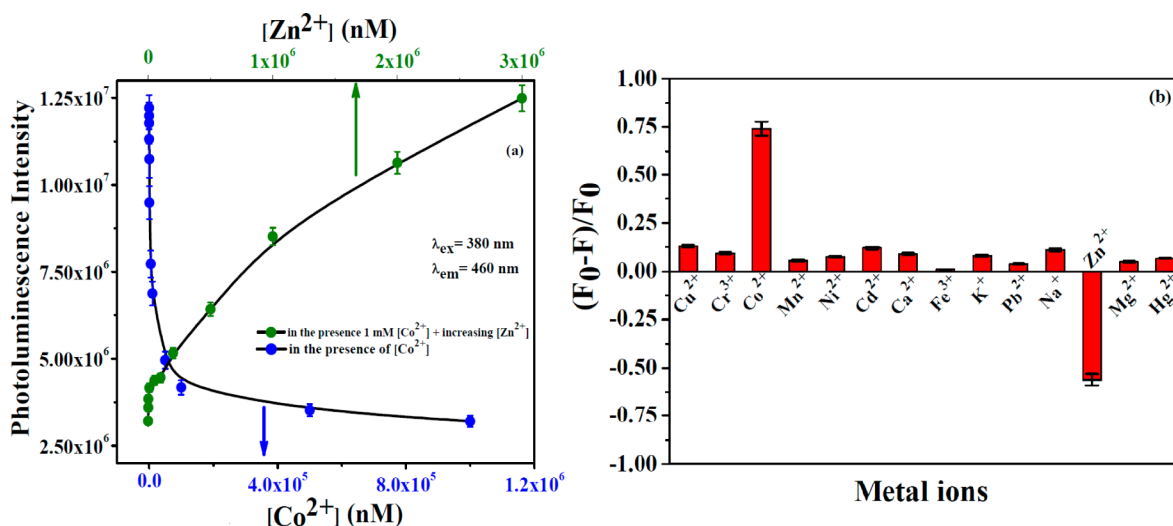


Figure 2. Turn “on” and “off” behavior in PL intensity of Ag₉:HSA in the presence of (a) Co (II) ions and subsequent addition of Zn (II) ions as marked in the figure. The upper and the lower abscissas represent the concentrations of Zn(II) and Co(II) ions, respectively. (b) Representative plot showing the extent of PL quenching of Ag₉:HSA in the presence of 1 mM aqueous solution of different metals ions. F_0 and F are the PL intensities of Ag₉:HSA in the absence and presence of 1 mM metal ions, respectively.

solution, the luminescence intensity finally gets reduced to 74% at 1 mM Co(II). The limit of detection for Co(II) ions was found to be 100 nM (please refer to the Instrumentation section for details). This stepwise decrement in luminescence intensity of the Ag₉:HSA NCs is depicted in Figure 1a and Supporting Information Figure S1.

Similarly, when Zn(II) ions were added to the Ag₉:HSA, the luminescence intensity followed a two-step incremental behavior with a gradual increment (nearly 14%) for concentration up to 1 μ M, while further addition of Zn(II) ions until 1 mM resulted in rapid enhancement in emission intensity; the intensity increased by 56% as compared to its initial value in the absence of Zn(II) (Figure 1b, Supporting Information Figure S2). The limit of detection for Zn(II) ions was found to be 50 nM. These two opposing trends in the sensing behavior of Ag₉:HSA in the presence of Co(II) and Zn(II) ions prompted us to check whether the PL of the quenched NCs in the presence of 1 mM Co(II) can be restored by subsequent addition of Zn(II). Interestingly, addition of 3 mM Zn(II) indeed switched on the emission properties of the quenched Ag₉:HSA NCs (Figure 2a).

Although almost a total recovery of PL intensity could be achieved, the emission peak maximum was significantly blue-shifted by about 7 nm in the presence of 3 mM Zn(II) (Supporting Information Figure S3). To check whether this photoluminescent sensor can detect any other metal ions, we have also carried out studies under exactly similar conditions as applied for Zn(II) and Co(II). However, none of these metal ions could show quenching or enhancement up to an extent comparable to what was observed for Co(II) or Zn(II) (Figure 2b). To validate the exclusive and selective sensing capabilities of Ag₉:HSA, we have carried out PL experiments in the simultaneous presence of Co(II) [or Zn(II)] and other metal ions in solution. We have also studied the effect of anions keeping the cation fixed and found that, for both the cases, the PL intensities did not show any observable deviations, thereby establishing the fact that the performances of our sensors are not affected in any way. Thus, we were able to design selective on and off metal sensor using the blue-emitting Ag₉:HSA NCs. Hence, our synthesized blue-emitting Ag₉:HSA NCs can serve as a dual sensor; the presence of Zn(II) ions can also be detected selectively and quantitatively even in the presence of

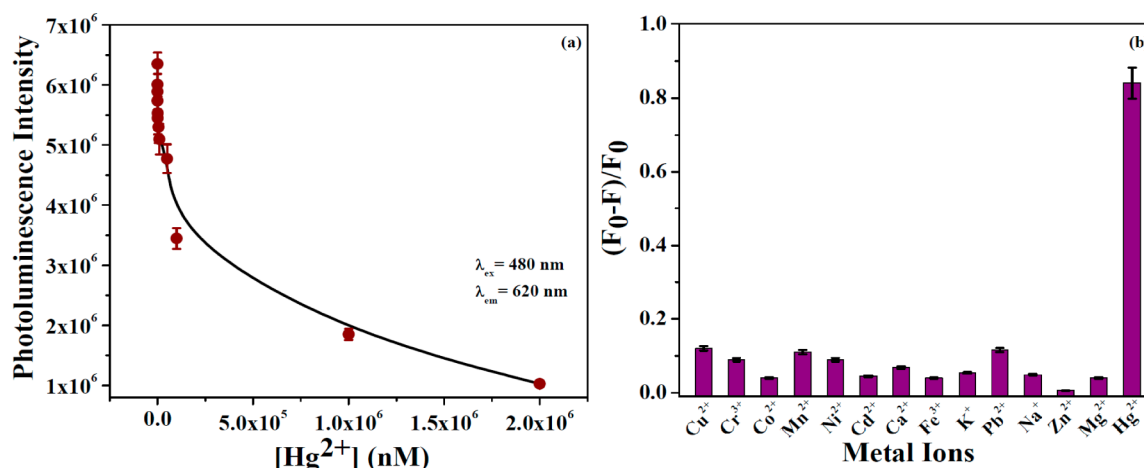


Figure 3. Variation in PL intensity of $\text{Ag}_{14}\text{:HSA}$ in the presence of (a) Hg(II) ions. (b) Representative plot showing the extent of PL quenching of $\text{Ag}_{14}\text{:HSA}$ in the presence of 2 mM aqueous solution of different metal ions. F_0 and F are the PL intensities of $\text{Ag}_{14}\text{:HSA}$ in the absence and presence of 2 mM metal ions, respectively.

Co(II) ions in solution and vice versa based on a simple fluorometric approach. In addition to that, when we tuned these blue-emitting $\text{Ag}_9\text{:HSA}$ to red-emitting $\text{Ag}_{14}\text{:HSA}$ by following the protocol as mentioned in our previous study,³³ these $\text{Ag}_{14}\text{:HSA}$ NCs could detect Hg(II) up to a limit of 10 nM, which is fairly high and exactly meets the level of detection standards (limit of Hg detection in drinking water is 10 nM) according to United States Environment Protection Agency.³⁶ Addition of 2 mM Hg(II) to $\text{Ag}_{14}\text{:HSA}$ NCs could quench the luminescence intensity almost completely (Figure 3a, Supporting Information Figure S4). This photoluminescent sensor ($\text{Ag}_{14}\text{:HSA}$) could not detect any metal ions other than Hg, and therefore it can be assigned as selective Hg(II) sensor (Figure 3b) and will surely have tremendous practical applications.

The PL of the NCs shows linear relationship with all the three metal ions detected and follows two-step models for the change in the PL intensity. The corresponding linear equations for all the three metal ions have been generated for the two different concentration ranges with very good regression coefficients (please see the Supporting Information for details).

The results obtained from the steady-state luminescent sensing of these NCs were well-supported by our time-resolved studies which showed almost the same trend in their metal ion detection capabilities. The average PL lifetime for $\text{Ag}_9\text{:HSA}$ in the absence of the metal ions was 7.43 ns. In the presence of increasing concentration of Co(II) , the values of lifetime decrease continuously until 3.85 ns (Supporting Information Figure S5). Here also, the nature of decrement follows a two-step behavior similar to what was observed in case of steady-state luminescence (Figure 4). Similarly, with the increasing concentrations of Zn(II) ions in the presence of Co(II) , the lifetime increases from 3.85 to 7.27 ns (Supporting Information Figure S6), and here also the nature of increment in lifetimes followed the steady-state results (Figure 4).

Thus, these results also prove our selective luminescence switching properties exhibited by Co(II) and Zn(II) ions. On the other hand, $\text{Ag}_{14}\text{:HSA}$ exhibited an average PL lifetime of 2.7 ns in the absence of any metal ions. However, with the gradual addition of Hg(II) , the lifetime decreases continuously to 1.1 ns at 1 mM Hg(II) as depicted by Figure 5a. In this case also, the nature of decrement in luminescence lifetime agrees well with the steady-state luminescence data (Figure 5b).

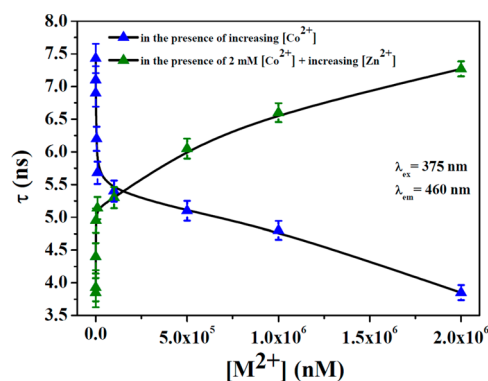


Figure 4. Turn “off” and “on” behavior in average PL lifetimes of $\text{Ag}_9\text{:HSA}$ in the presence of Co(II) ions and subsequent addition of Zn(II) ions as marked in the figure.

The most probable explanation for the quenching and enhancement of PL of $\text{Ag}_9\text{:HSA}$ in the presence of Co(II) and Zn(II) , respectively, is based on the electron-transfer mechanism. Co(II) ions mainly exist as a hexaaqua complex in water within the coordination sphere.³⁷ This state of Co(II) (d^7 system) possess a strong tendency to get oxidized to Co(III) state (d^6 system) and attain stable configuration.³⁷ Hence, when the Co(II) ion is added to the solution of $\text{Ag}_9\text{:HSA}$, it transfers the lone unpaired electron to the stable core of Ag atoms that forms the luminescent nanocluster, thereby destabilizing the nanocluster assembly responsible for the diminished luminescent characteristics. Since the core of these $\text{Ag}_9\text{:HSA}$ NCs is relatively stable inside the bulky scaffolds of HSA, therefore initial destabilization by electron donation has to overcome the binding forces that exist between the Ag atoms of the NC (Scheme 1).

As a result, the luminescence intensity falls significantly but in steps. Zinc is known to be a strong Lewis acid, and therefore has an affinity to accept electrons, and has identical ionic potential as Co^{2+} .⁹ Thus, initially when Zn(II) ions are slowly added to the already quenched solution of $\text{Ag}_9\text{:HSA}$ NCs, they substitute the Co(III) ions from the core shell. The electron which was already transferred in the core of the NC by the Co(II) ions is back-donated in the vacant orbital of Zn(II) leading to a strong electronic interaction and restabilizing the

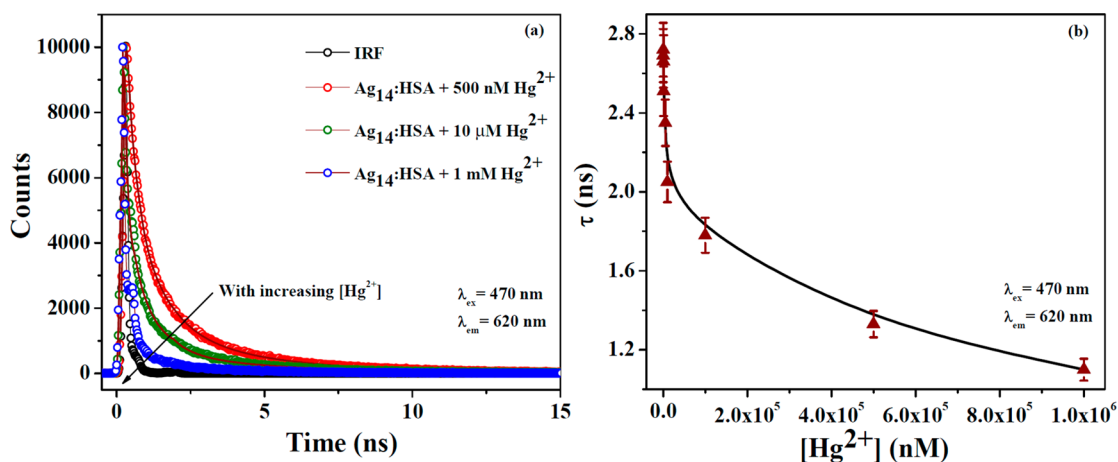
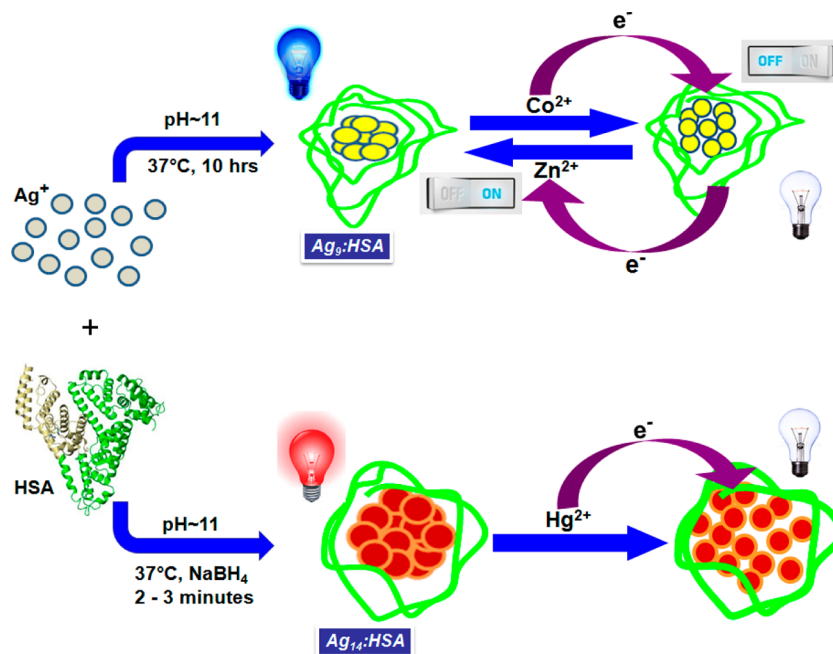


Figure 5. (a) Representative PL lifetime decay profiles of $\text{Ag}_{14}:\text{HSA}$ in the presence of increasing concentrations of $\text{Hg}(\text{II})$ ions as marked in the figure. (b) Variation in the average PL lifetimes of $\text{Ag}_{14}:\text{HSA}$ in the presence of different concentrations of $\text{Hg}(\text{II})$ ions.

Scheme 1. Schematic Representation Showing the Mechanism of “On” and “Off” Luminescence Characteristics of $\text{Ag}_9:\text{HSA}$ and the PL Quenching of $\text{Ag}_{14}:\text{HSA}$ in the Presence of Different Metal Ions as Depicted in the Scheme



core of the NC, thereby raising its luminescence intensity. Further, $\text{Zn}(\text{II})$ ion is an acid of borderline hardness (according to the hard and soft acids and bases principle) and has strong affinity for nitrogen, oxygen, and sulfur donor atoms.³⁸ Therefore, the histidine, glutamate, aspartate, tyrosine, and cysteine residues in HSA are strongly attracted to bind to the core shell of the $\text{Zn}-\text{Ag}:\text{NC}$ assembly. Thus, the luminescence intensity increases in steps analogous to the quenching process (Scheme 1). This whole mechanism simultaneously eliminates the solvent water molecules from the near vicinity and creates a more restricted environment around the $\text{Ag}:\text{NCs}$. This fact is supported by the enhancement in luminescence intensity (due to restricted rotational freedom) and the blue shift in the emission maxima of $\text{Ag}_9:\text{HSA}$. Time-resolved study is an excited-state phenomenon unlike steady-state luminescence, but complements the latter technique in most cases, showed similar trend in ion sensing. This reveals that the excited state of the fluorophore ($\text{Ag}_9:\text{HSA}$ in this case) is slowly destabilized

with increasing $\text{Co}(\text{II})$ concentration. This destabilized system regains back its stability as $\text{Zn}(\text{II})$ ions are added, and the luminescent properties are also regenerated. Since there is significant changes in the value of lifetime, the plausible mechanism is electron transfer, and in all probabilities a complex formation between the metal ions and $\text{Ag}_9:\text{HSA}$ is not encountered. Further, the absorption spectra of the $\text{Ag}_9:\text{HSA}$ NCs exhibit a new broad peak at around 450 nm by addition of increasing concentrations of $\text{Co}(\text{II})$ ions. Subsequent additions of $\text{Zn}(\text{II})$ ions to the NC solution result in a gradual disappearance of this particular broad peak (Supporting Information Figure S7). The appearance of the new broad peak around 450 nm is due to the electron transfer from the $\text{Co}(\text{II})$ ions to the NC assembly, which resembles like a small plasmonic band due to an extra electron in the system. Similarly, a gradual disappearance of the peak by addition of $\text{Zn}(\text{II})$ ions is again caused by the electron transfer from the destabilized NC assembly to the $\text{Zn}(\text{II})$ ions. Very recently,

Table 1. Analyses of the Changes in PL Intensities in the Presence of Co(II) Ions and Zn(II) Ions in Water Samples Using Our Synthesized Ag₉:HSA NCs^a

water samples	Ag ₉ :HSA			
	% PL quenching by adding 1 mM Co(II) ions	% PL recovery by adding 3 mM Zn(II) ions	relative % detection of Co(II) ions with respect to our assay	relative % detection of Zn(II) ions with respect to our assay
Milli-Q water used in our assay	74 (1 mM)	102 (3 mM)		
distilled water	72 (0.97 mM)	102 (3 mM)	97	100.0
water supplied by municipal corporation	70 (0.95 mM)	96 (2.82 mM)	95	94.0
underground tap water	70 (0.95 mM)	99 (2.91 mM)	95	97
purified drinking water by reverse osmosis	69.5 (0.94 mM)	96 (2.82 mM)	94	94

^aRelative percentage of detection of ions in the water samples was calculated taking the values obtained in Milli-Q water as reference. The values within the parentheses indicate the corresponding concentrations of the metal ions that can be sensed in solutions prepared by using water from different sources as mentioned by PL studies using the Ag₉:HSA NCs.

using several spectroscopic techniques including absorption spectroscopy, Chong et al. reported a similar electron-transfer process for Au₂₅ clusters where it works as an electron transfer catalyst.³⁹

The mechanism of Hg(II) ion detection by Ag₁₄:HSA is rather simple as compared to the sensing behavior of Ag₉:HSA. There are several mechanisms which have been proposed for the quenching in NC luminescence by Hg(II) such as interparticle aggregation,⁴⁰ metallophilic interaction,⁴¹ and amalgam formation.⁴² The most probable mechanism of PL quenching of our synthesized Ag₁₄:HSA by Hg(II) can be ascribed to the aggregation of the NC due to amalgam formation. Mercury has a slightly higher value of reduction potential ($E^\circ_{\text{Hg}^{2+}/\text{Hg}} = 0.85$) than silver ($E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80$); therefore, there is a strong tendency of Hg(II) to form amalgam with Ag by the donation of electron density from the Ag:NCs into the vacant orbitals of Hg(II). This resulted in partial oxidation of Ag which leads to the formation of larger-sized nanoparticles which loses its discrete electronic properties thereby becoming nonluminescent in nature (Scheme 1).

To establish the practical applicability of our proposed Ag:NC sensors, we have carried out some ion sensing experiments using water samples obtained from various sources. Standard solutions of Co(II) ions, Zn(II) ions, and Hg(II) ions were spiked into these water samples individually over a concentration ranging from 10 nM to 3 mM and incubated for over 10 min. The resulting solution was titrated with a 2 mL solution of Ag:NC (Ag₉:HSA or Ag₁₄:HSA, as required), and the corresponding luminescent properties were recorded. The changes in the PL spectra of Ag₉:HSA and Ag₁₄:HSA when subjected to these different water samples are shown in Supporting Information Figures S8 and S9, respectively. The corresponding analyses of the ion sensing behaviors are highlighted in Tables 1 and 2. From these results, it can be clearly stated that the unique turn “on” and “off” characteristic exhibited by our Ag₉:HSA in the presence of Co(II) and Zn(II) ions is retained even in these aqueous samples under investigation. Moreover, the high percentage of recovery of these ions in these samples under study is noteworthy (Table 1). Further, the sensing ability of Hg(II) ions by Ag₁₄:HSA is also retained in all the practical samples. The PL intensity of Ag₁₄:HSA when titrated with water samples containing Hg(II) ions was quenched to a large extent as shown in Supporting Information Figure S9. Likewise, the percentages of recovery of these ions in all the water samples are very high (Table 2).

Table 2. Analyses of the Changes in PL Intensity in the Presence of Hg(II) Ions in Water Samples Using Our Synthesized Ag₁₄:HSA NCs^a

water samples	Ag ₁₄ :HSA	
	% PL quenching by adding 2 mM Hg(II) ions	relative % detection of Hg(II) ions with respect to our assay
Milli-Q water used in our assay	84 (2 mM)	
distilled water	83 (1.98 mM)	99
water supplied by municipal corporation	79 (1.88 mM)	94
underground tap water	79 (1.88 mM)	94
purified drinking water by reverse osmosis	84 (2 mM)	100

^aRelative percentage of detection of ions in the water samples was calculated taking the values obtained in Milli-Q water as reference. The values within the parentheses indicate the corresponding concentrations of the metal ions that can be sensed in solutions prepared by using water from different sources as mentioned by PL studies using the Ag₁₄:HSA NCs.

Thus, this sensitive detection ability of our Ag:NCs demonstrate the promising applicability of our method for the quantification of Co(II), Zn(II), and Hg(II) ions up to different extents in aqueous solutions of varied purities.

CONCLUSION

We have reported the application of Ag₉:HSA NCs as metal ion sensors which selectively detected Co(II) and Zn(II) ions having significant biological roles but rarely explored to date. The limit of detection of these ions obtained in our study is fairly comparable to the international standards set for their presence in drinking water. Further the most important aspect of these blue-emitting NCs is that their sensing behavior is reversible in nature; the luminescent properties gets turned off in the presence of Co(II) while it is turned on in the presence of Zn(II), thereby opening the prospects of using these NCs as a photoswitch. This dual sensing ability of Ag₉:HSA NCs enabled us to selectively and quantitatively detect the presence of two metal ions, namely, Co(II) and Zn(II), in solution. This unique feature has potential applications in metal sensing where the concentration of such metals is really low. On tuning the Ag₉:HSA to Ag₁₄:HSA NCs by virtue of simple redox

chemistry, we were able to obtain a selective and highly sensitive Hg(II) ion sensor. Our steady-state observations were well-complemented by the time-resolved studies. Both these techniques support our explanation of the mechanism of electron transfer as the mode of interaction between the metal ions and the Ag:NCs. Besides having the advantages of extreme ease, low-cost synthetic procedures, and excellent photo-physical properties, our synthesized Ag:NCs exhibit the practicality validated by analyses of the Co(II), Zn(II), and Hg(II) ions in different water samples and hence is a clear signature of the potential applications it holds in various field investigations as label-free photoluminescent metal ion sensors.

■ ASSOCIATED CONTENT

■ Supporting Information

Linear equations for the calibration curve of detection and several spectra of the Ag:HSA NCs showing their photo-physical properties/sensing abilities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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