



Atomically precise cluster-based white light emitters[§]

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Abstract. Materials emitting white luminescence are receiving increasing attention due to their potential applications in electroluminescent devices, information displays and fluorescent sensors. To produce white light, one must have either three primary colors, blue, green and red or two colors, blue and orange. In this paper, we have used thiol/phosphine protected red luminescent silver nanoclusters (Ag NCs), $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (BDT = 1,3-benzenedithiol), $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ and $\text{Ag}_{29}(\text{LA})_{12}$ (LA = lipoic acid) as one of the fluorophores for white light emission. These clusters are mixed with blue luminescent silicon nanoparticles (Si NPs) and green luminescent fluorescein isothiocyanate (FITC). The mixtures show white luminescence with CIE coordinates of (0.31, 0.34), (0.33, 0.35) and (0.29, 0.31) which are in good agreement with pure white light (0.33, 0.33). The other clusters with yellow, blue, orange, etc., luminescence can also be used to make white light. This work provides a prospective pathway for white light emission based on atomically precise noble metal NCs.

Keywords. Nanocluster (NC); silicon nanoparticles (Si NPs); photoluminescence (PL); fluorescein isothiocyanate (FITC); electrospray ionization mass spectrometry (ESI MS); white light emission.

1. Introduction

White light emission is of importance from many perspectives.^{1,2} A number of emerging materials such as gels,³ quantum dots,⁴ supramolecular assemblies^{5,6} and many molecular systems⁷ have been used for white light emission. Noble metal nanoclusters (NCs) with their inherent photoluminescence (PL) make them suitable for white light emission.⁸ Over a hundred cluster systems of this kind are known and the area is expanding tremendously. Among these NCs, protein protected NCs such as $\text{Au}_{25}@\text{BSA}$, $\text{Ag}@\text{Cys}$, $\text{Ag}@\text{Lys}$, etc., are water-soluble and highly luminescent.^{9–14} Apart from protein protected clusters, glutathione (SG) protected clusters such as, $\text{Au}_{25}(\text{SG})_{18}$,^{15,16} $\text{Au}_{23}(\text{SG})_{18}$,¹⁷ $\text{Au}_{22}(\text{SG})_{18}$,¹⁸ $\text{Au}_{18}(\text{SG})_{14}$,¹⁹ $\text{Ag}_{11}(\text{SG})_7$,²⁰ $\text{Ag}_{15}(\text{SG})_{11}$,²¹ $\text{Ag}_{31}(\text{SG})_{19}$,²² $\text{Ag}_{32}(\text{SG})_{19}$,²³ etc., and some other clusters^{24–30} of water-soluble thiols such as, mercaptosuccinic acid (MSA), mercaptopropionic acid (MPA),

lipoic acid (LA), dihydrolipoic acid (DHLLA), etc., exhibit intense luminescence in aqueous medium. But, there are very few reports on the luminescent thiol/phosphine protected NCs in organic solvents and most of them are less emissive. However, their luminescence can be increased either by rigidifying their surface or by doping with another metal ions.^{31–35} For a long time, Au NCs attracted attention due to their stability and excellent luminescence but, recently Ag NCs are also beginning to gain the attention of the researchers due to their new properties and various applications. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$,³⁶ $[\text{Ag}_{62}\text{S}_{13}(\text{StBu})_{32}](\text{BF}_4)_4$,³⁷ $[\text{Ag}_{33}\text{S}_3(\text{StBu})_{16}(\text{CF}_3\text{COO})_9(\text{NO}_3)(\text{CH}_3\text{CN})_2](\text{NO}_3)_3$,³⁸ etc. NCs are known to be red luminescent while $\text{Ag}_{14}(3,4\text{-DFBT})_{12}(\text{PPh}_3)_8$ displays luminescence in the yellow region (emission maximum is at 535 nm).³⁹ The alloys of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ using Au and Pt exhibit enhanced luminescence, near about 26 times and

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2.3 times, respectively.^{31,40} Similarly, the luminescence increment for other Ag NCs is yet to be examined.

While most such clusters emit in the red or NIR region,^{2,41} there are other nanosystems such as silicon (Si) nanoparticles (NPs) which emit in the blue and green regions.^{43–48} Small-sized luminescent Si NPs are used in several applications such as solid state lighting, full-colour displays, optical sensors, and biological imaging.^{49,50} Combining these two different categories of systems (noble metal NCs and Si NPs) with other molecular emitters, it may be possible to create stable white light emission. These molecular materials could be incorporated in appropriate matrices to produce new materials with novel properties for further advanced applications.

In this paper, we have combined well-characterized red luminescent atomically precise cluster systems $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$, $[Au_xAg_{29-x}(BDT)_{12}(PPh_3)_4]^{3-}$ and $Ag_{29}(LA)_{12}$ with Si NPs and complemented their emission with that of fluorescein isothiocyanate (FITC), a well-known molecular emitter. As these clusters were stable in water and other systems too, it was possible to make a homogeneous solution with varying concentrations of all components to accomplish white light emission with CIE coordinates of (0.31, 0.34), (0.33, 0.35) and (0.29, 0.31). Although not demonstrated here, FITC could be replaced with a yellow emitting cluster to achieve white light emission and also, it was possible to replace Si NPs with clusters so that all-cluster based white light emitters could be realized.

2. Experiment

2.1 Materials and physical measurements

Sodium borohydride ($NaBH_4$, 95%), 1,3-BDT ($\geq 99\%$), FITC and aminopropyl trimethoxysilane (APTMS) were purchased from Sigma-Aldrich. LA and silver nitrate ($AgNO_3$) were purchased from Rankem chemicals. Triphenylphosphine (PPh_3 , 98%) was purchased from Spectrochem. Dichloromethane (DCM), dimethylformamide (DMF) and methanol (MeOH) were purchased from Rankem and were of HPLC grade. Sodium citrate was purchased from Sarabhai M. Chemicals. Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) was synthesized in our laboratory. All solvents and chemicals were used without further purification.

The absorption spectra were measured using a PerkinElmer Lambda 25 spectrometer. Electrospray ionization mass spectrometric (ESI MS) measurements were performed using a Waters Synapt G2-Si high-resolution mass spectrometer. PL spectra were measured in a HORIBA JOBIN YVON Nano Log instrument. The bandpass for excitation and emission was set at 3 nm. High-resolution transmission

electron microscopic (HRTEM) studies of Si NPs were performed with a JEOL 3010 instrument. The samples were prepared by drop casting Si NPs solution (H_2O) on carbon-coated copper grids and allowing it to dry under ambient conditions.

2.2 Synthesis of $[Ag_{29}(1,3-BDT)_{12}(PPh_3)_4]^{3-}$

The $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$ cluster was synthesized following a reported protocol after small modifications.³⁶ About 20 mg of $AgNO_3$ was dissolved in a mixture of 5 mL of methanol and 9 mL of DCM. Then, the solution was allowed to stir and after 5 min, 13.5 μ L of 1,3-BDT was added to the reaction mixture. Immediately, the colorless solution turned yellow which indicated the formation of silver thiolate. Then, 200 mg of PPh_3 was dissolved in 0.5 mL of DCM and added to the solution. This turned the solution colorless again, indicating the formation of Ag–S–P complexes. After 10–15 min, ~ 11 mg of $NaBH_4$ (in 0.5 mL of ice cold H_2O) was added dropwise which changed the color of the solution to dark-brown. Finally, the reaction mixture was kept at room temperature under dark conditions for 3 h. After completion of the reaction, the reddish brown precipitate was collected by centrifuging the mixture and the supernatant was discarded. Then, the precipitate was washed twice or thrice with methanol to remove the unreacted by-products. Finally, the orange colored cluster was extracted in DMF.

2.3 Synthesis of $[Au_xAg_{29-x}(1,3-BDT)_{12}(PPh_3)_4]^{3-}$

The above-mentioned procedure after the slight modification was used for the synthesis of Au doped $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$, namely $[Au_xAg_{29-x}(BDT)_{12}(PPh_3)_4]^{3-}$. About ~ 6 mg of $HAuCl_4$ was dissolved in 5 mL of MeOH and to that solution, ~ 14 mg of $AgNO_3$ was added. Then, 9 mL of DCM was added to this mixture and kept for stirring. After 5 min, ~ 13.5 μ L of 1,3-BDT was added to this mixture followed by the addition of ~ 200 mg of PPh_3 . Then, ~ 11 mg of $NaBH_4$ dissolved in 0.5 mL of ice cold H_2O was added dropwise in the mixture. After 3 h of reaction under dark conditions, the solution was transferred to a round-bottomed flask and dried completely by rotary evaporation. The dried material was washed with MeOH repeatedly. Then the precipitate was collected by centrifugation. Finally, DMF was used to extract the orange colored product.

2.4 Synthesis of $[Ag_{29}(LA)_{12}]$

The cluster was prepared by an already reported method with slight modifications.²⁹ About 20 mg of LA was dissolved in 14 mL of water and then to this solution, 7 mg of $NaBH_4$ was added. The mixture was kept for stirring so that all LA had dissolved. Then, 4 mg of $AgNO_3$ was dissolved in 1 mL of water followed by the addition of 10 mg of $NaBH_4$ in 2 mL water. Next, the reaction was allowed to stir for 3 h under

dark condition at room temperature. The product cluster was stored at 4 °C temperature.

2.5 Synthesis of blue luminescent Si NPs

A reported procedure was followed for this synthesis with small changes.⁴³ A 20 mL aqueous solution of ~1 g sodium citrate was prepared and 1 mL of aminopropyl trimethoxysilane (APTMS) was added to this solution. This mixture was agitated homogeneously for 5 min. Then, the solution was kept at 170 °C in a hydrothermal bomb for 24 h. After the end of the reaction, it was cooled down to the room temperature and then, the transparent solution was dialyzed using a membrane of molecular weight cut off 12 kDa.

2.6 White light emission

The blue luminescent Si NPs, green luminescent FITC and red luminescent $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ / $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ / $\text{Ag}_{29}(\text{LA})_{12}$ cluster were mixed to get white light emission. The $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ and $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ clusters were soluble in organic solvents such as DMF but not in H_2O . As DMF and H_2O are miscible to each other, the DMF solutions of these clusters were added in H_2O and were stable in the DMF/ H_2O mixture. The absorption and emission spectra of these clusters in DMF/ H_2O were checked and the results are presented in the discussion section. $\text{Ag}_{29}(\text{LA})_{12}$ was soluble in water, so also FITC and Si NPs. All the solvents were miscible and the mixture was stable. The excitation wavelength chosen for white light emission was 360 nm.

3. Results and Discussion

White light emission is composed of three primary colors, blue, green and red. Here, we have used Si NPs as the blue emission source, FITC as the green emission source and NCs as the red emission source. The red luminescent $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ cluster was prepared by following a reported protocol.³⁶ The cluster is highly soluble in DMF, although it is sparingly soluble in DCM, acetonitrile, etc. The as-synthesized cluster was thoroughly characterized by optical spectroscopy and ESI MS (Figure 1). The absorption spectrum of the cluster presented in Figure 1A shows a maximum at 445 nm along with a shoulder at ~512 nm. It possesses bright red luminescence under UV light as shown in the inset of Figure 1A. At 450 nm excitation, the emission maximum is at 655 nm (see inset of Figure 1A). ESI MS was performed to confirm the cluster composition which is presented in Figure 1B. It was measured in the -ve ion mode and the mass spectrum is presented in Figure 1B in a mass range of m/z 1400–2500. The spectrum exhibits 5 peaks and the separation between two neighboring peaks is m/z 87.33. An expanded view of ESI MS is given in Figure S1 (Supplementary Information) which shows the separation between two peaks in isotopic distribution is 0.33 suggesting 3^- charge state. Thus, the separation of m/z 87.33 corresponds to one PPh_3 ligand (262). Theoretical isotopic distribution of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ species is shown in the inset of Figure 1B which matches exactly with the experimental isotopic distribution.

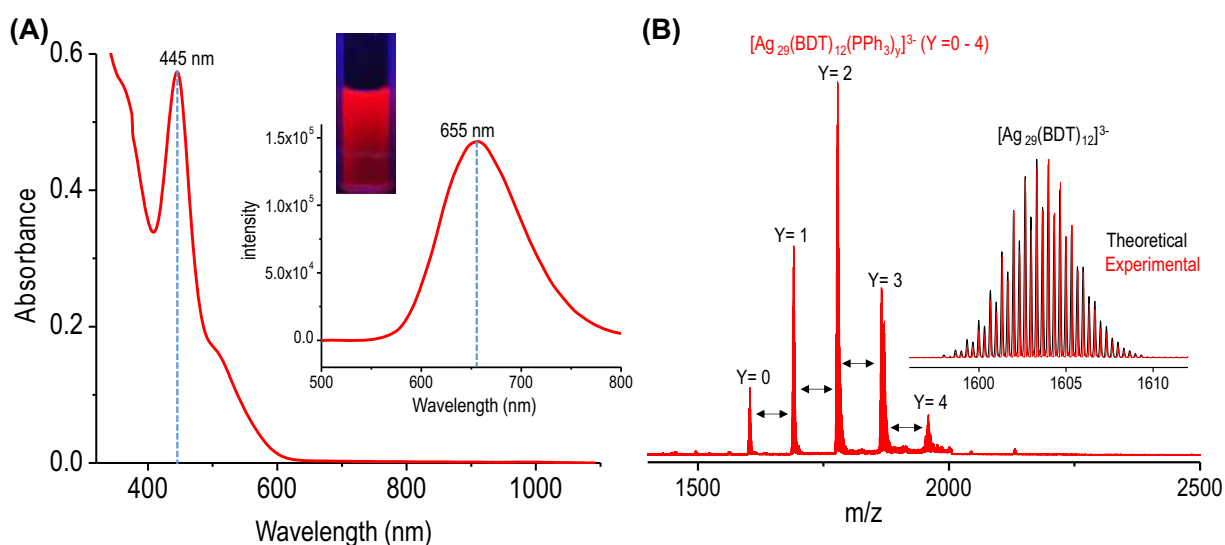


Figure 1. (A) The UV-Vis absorption spectrum of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ having an absorption maximum at 445 nm. Inset: The emission spectrum of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ at 450 nm excitation. (B) The ESI MS of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ which shows a systematic PPh_3 loss. Inset: the theoretical and the experimental isotopic distributions of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ showing perfect fitting.

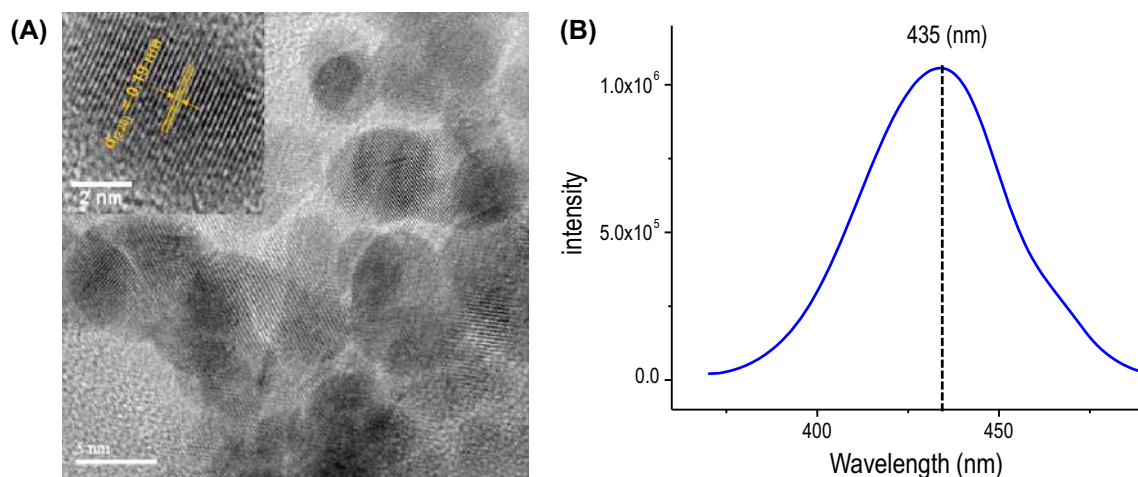


Figure 2. (A) The HRTEM images of blue emitting Si NPs. The inset shows the lattice spacing of 0.19 nm which is arising from the (220) lattice plane of silicon. (B) The emission spectrum of Si NPs shows a maximum at 435 nm at 360 nm excitation.

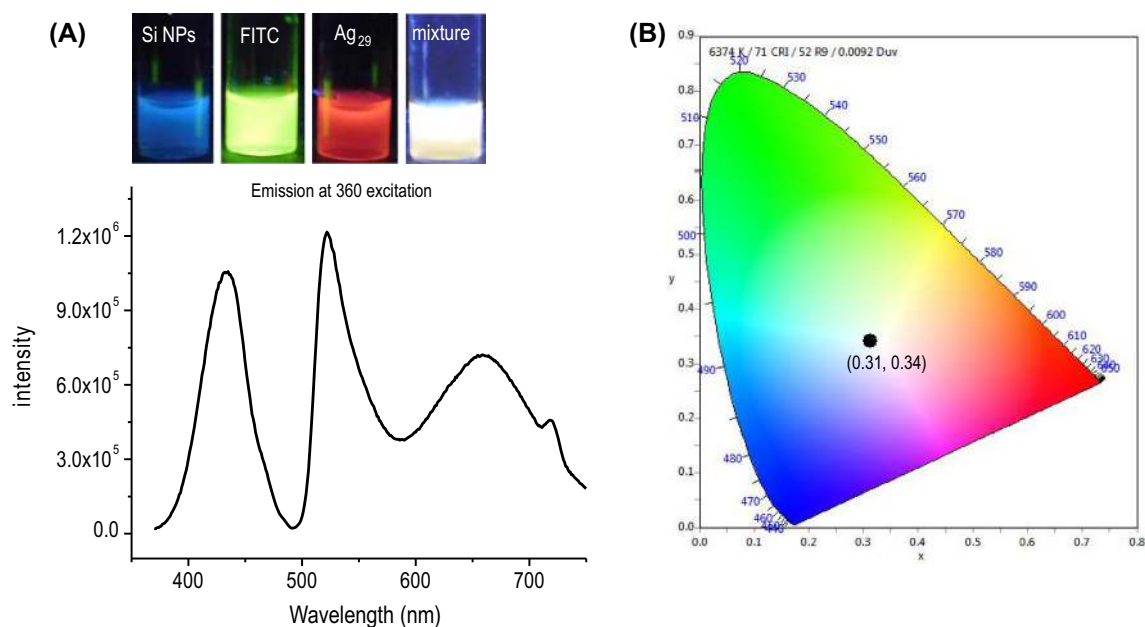


Figure 3. (A) White light emission from a mixture of blue luminescent Si NPs, green luminescent FITC dye and red luminescent $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ cluster. Inset: photographs under UV light. (B) Chromaticity diagram which shows the coordinates of the white light emitted (0.31, 0.34) from a mixture of blue, green and red fluorophores.

The Si NPs were prepared by a reported method using APTMS and sodium citrate as mentioned in the experimental section. The as-synthesized Si NPs were characterized using HRTEM and PL spectroscopy and the data are presented in Figure 2. The HRTEM image in Figure 2A suggests the formation of NPs which are ~ 5 nm in size. The NPs are showing a lattice spacing of 0.19 nm, matching with the (220) plane of silicon. It is known that the smaller sized Si NPs undergo a transition from indirect to direct bandgap semiconductor.⁵¹ In this case, as the synthesized Si NPs are smaller in size, they

show luminescence. The emission spectrum is shown in Figure 2B which manifests a peak at 435 nm at 360 nm excitation.

White light is an optimal composition of three primary colors, red, green and blue. Thus, we have mixed the blue emitting Si NPs, red emitting $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ and a green emitting FITC dye. Si NPs and FITC were solubilized in H₂O and $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ cluster was taken in DMF. The DMF solution of the cluster was mixed with H₂O. The absorption and emission spectra were checked which suggest that

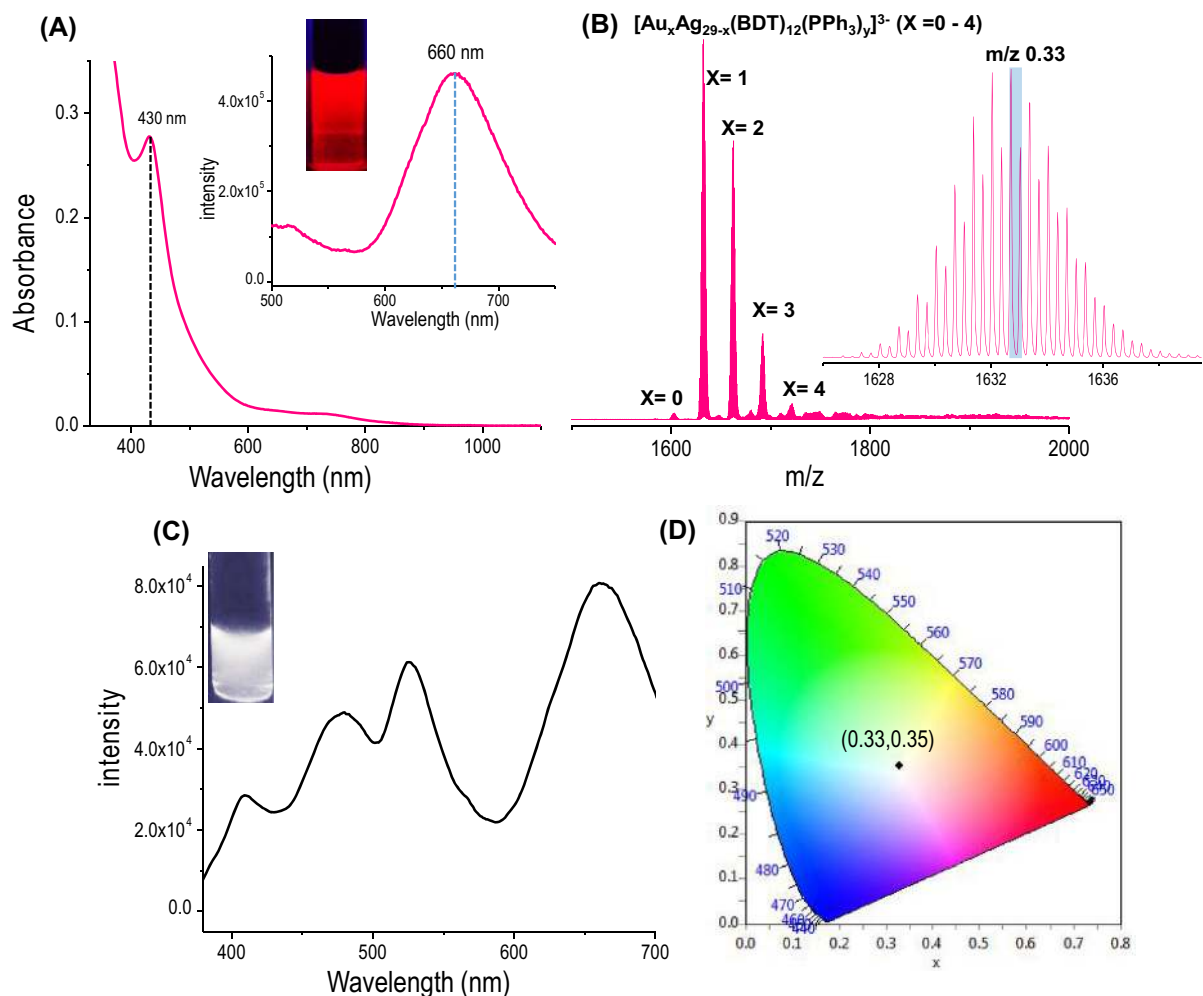


Figure 4. (A) The UV-Vis absorption spectrum of $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ having an absorption maximum at 430 nm. Inset: The emission spectrum of $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ at 450 nm excitation which shows an emission maximum at 690 nm. (B) The ESI MS of $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$, $X = 0 - 4$. The inset shows expanded ESI MS which shows a separation of 0.33 confirming the 3^- charge state. (C) The emission spectrum of white luminescence generated from a mixture of Si NPs, FITC and $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ at 360 nm excitation. Photograph of white light emission under UV light is presented in the inset. (D) The CIE chromaticity diagram of white luminescence having coordinates of (0.33, 0.35).

the cluster is stable in the DMF/ H_2O mixture (Figure S2, Supplementary Information).

The individual colors of Si NP, FITC, $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ and the color of their mixture (Si NPs: FITC: $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ is 3:1:2 v/v/v) are shown in the inset of Figure 3A. The luminescence spectrum of the mixture which emits white light emission at 360 nm excitation is shown in Figure 3A. The CIE 1931 color system is the most widely used colorimetric standard and the CIE plot can be obtained from the visible spectrum. This is represented by two color coordinates, X and Y. The CIE chromaticity diagram of the mixture is presented in Figure 3B which analyzes the color characteristics of luminescent materials. The observed white light emission exhibits CIE coordinates of (0.31,

0.34) which is in good agreement to that of pure white light (0.33, 0.33). The color of individual components and the mixture under UV light are shown in the inset of Figure 3A.

The similar kind of experiment to produce white light emission was performed using the Au doped $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ cluster with enhanced luminescence. The synthetic procedure is given in the experimental section. Characterization data of the cluster by optical spectroscopy and mass spectrometry are presented in Figure 4. The absorption spectrum of $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ looks similar to that of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (Figure 4A). It exhibits an absorption maximum at 430 nm along with a small peak at 730 nm. The cluster shows luminescence at ~ 660 nm

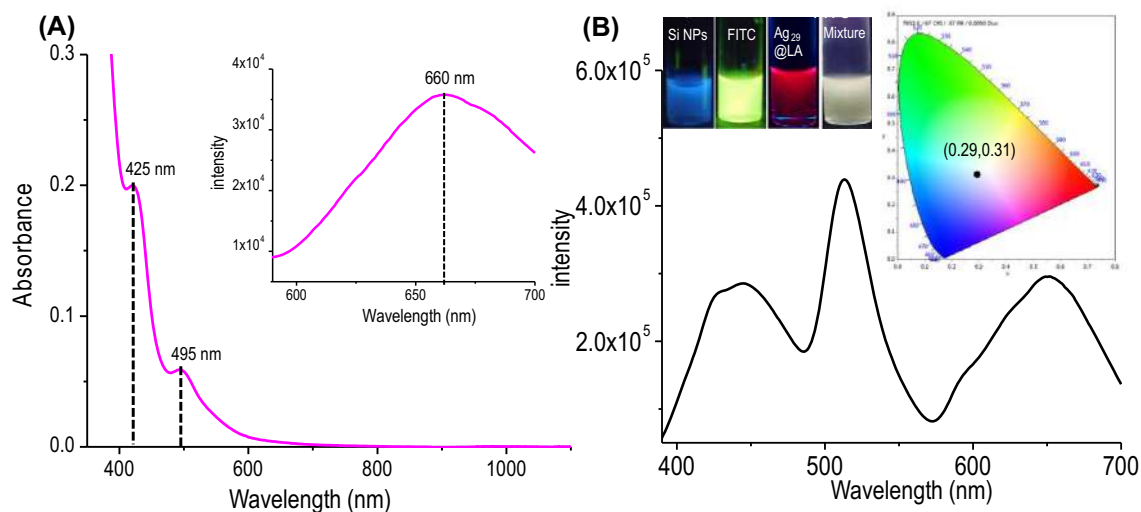


Figure 5. (A) The UV-Vis absorption spectrum of $\text{Ag}_{29}(\text{L})_{12}$ having an absorption maximum at 425 nm and a shoulder at ~ 495 nm. Inset: The emission spectrum of $\text{Ag}_{29}(\text{LA})_{12}$ at 425 nm excitation shows a maximum at 660 nm. (B) The emission spectrum of white light produced by the mixture of Si NPs, FITC and $\text{Ag}_{29}(\text{LA})_{12}$. Inset: The CIE chromaticity diagram for white light emission which shows the color coordinates, (0.29, 0.31).

when excited at ~ 450 nm as shown in the inset of Figure 4A (photograph of the cluster under UV light is presented in the inset). ESI MS was measured and it shows a bunch of peaks as shown in Figure 4B. The first peak is at m/z 1603 and the charge state is 3^- (see inset of Figure 4B) and the spectrum can be assigned to $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$. Other peaks appear at $\sim m/z$ 1632, 1662, 1692 and 1722. The separation between the two neighboring peaks is $\sim m/z$ 30 and the charge state of all peaks is 3^- , that means the mass difference is ~ 90 which is equal to the mass of one Au atom minus that of one Ag atom (197–108). The number of Au doped in this cluster is 4 which is corroborated by Figure 4B.

This cluster was also used for white light emission after mixing the DMF solution of the cluster and aqueous solutions of Si NPs as well as FITC. The cluster stability in DMF/ H_2O mixture was checked and the data are shown in Figure S3 (Supplementary Information). The mixture (Si NPs: FITC: $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ is 2:1:4 v/v/v) shows white luminescence (emission spectrum is shown in Figure 4C) with (0.33, 0.35) CIE coordinates (Figure 4D). The value is very near to that of the pure white light (0.33, 0.33).

A water-soluble cluster $\text{Ag}_{29}(\text{LA})_{12}$ was taken, which is similar to $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$. The detailed synthetic method is presented in the experimental section. The absorption spectrum shows a maximum at 425 nm along with a shoulder at 495 nm (Figure 5A) which is matching with the previous report.²⁹ It shows emission

maximum at 660 nm when excited at 425 nm (see inset of Figure 5A). The cluster was used for white light emission after mixing with Si NPs and FITC. The mixture (Si NPs: FITC: $\text{Ag}_{29}(\text{LA})_{12}$ is 2:1:5 v/v/v) emits white light at 360 nm excitation and the PL spectrum of it is presented in Figure 5B. The CIE chromaticity diagram is given in the inset of Figure 5B showing color coordinates of (0.29, 0.31).

In the three cases above, white light generation was demonstrated using blue luminescent Si NPs, green luminescent FITC dye and three different red luminescent clusters. Mostly, in multicomponent systems, the white light emission is controlled through fluorescence resonance energy transfer (FRET) process between the different components. The excitation wavelength of white light emission was kept at 360 nm which is the excitation wavelength for Si NPs. Mixing of FITC and NCs in Si NPs solution resulted in quenching the emission intensity of Si NPs (from 1.65×10^6 to 1.05×10^6) while enhancing the emission intensity of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (from 4.43×10^5 to 7.2×10^5). The emission spectra of Si NPs, FITC and $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ at 360 nm excitation are presented in Figure S4 (Supplementary Information) and the spectrum of their mixture at the same excitation is presented in Figure 3. Note that the individual species presented have the same concentrations as in the mixture. This confirms partial energy transfer from the blue-emitting donor to the embedded energy acceptors upon excitation of Si NPs (360 nm).

4. Conclusions

In conclusion, we have presented the application of Ag NCs as an emerging fluorophore for white light emission along with blue luminescent Si NPs and the green luminescent FITC dye. The highly stable $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$, its gold doped analog $[\text{Au}_x\text{Ag}_{29-x}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ ($x = 0-4$) and $[\text{Ag}_{29}(\text{LA})_{12}]$ clusters have been synthesized and characterized. The first two clusters are soluble in DMF while the last one is soluble in water. The red, blue and green emitting materials were mixed together in appropriate composition to produce white luminescence. The mixture produced white light with emission coordinates near to that of pure white light emission (0.33, 0.33). Here, for the first time, organic soluble Ag NCs are used to produce white luminescence. An aqueous suspension of Si NPs, FITC and $\text{Ag}_{29}(\text{LA})_{12}$ has produced white light with coordinates of (0.29, 0.31).

Supplementary Information (SI)

Figures S1–S4 are available at www.ias.ac.in/chemsci.

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