

# Highly Luminescent Material Based on Alq<sub>3</sub>:Ag Nanoparticles

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**Abstract** Tris (8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) is an organic semiconductor molecule, widely used as an electron transport layer, light emitting layer in organic light-emitting diodes and a host for fluorescent and phosphorescent dyes. In this work thin films of pure and silver (Ag), copper (Cu), terbium (Tb) doped Alq<sub>3</sub> nanoparticles were synthesized using the physical vapor condensation method. They were fabricated on glass substrates and characterized by X-ray diffraction, scanning electron microscope (SEM), energy dispersive spectroscopy, atomic force microscope (AFM), UV-visible absorption spectra and studied for their photoluminescence (PL) properties. SEM and AFM results show spherical nanoparticles with size around 70–80 nm. These nanoparticles have almost equal sizes and a homogeneous size distribution. The maximum absorption of Alq<sub>3</sub> nanoparticles is observed at 300 nm, while the surface plasmon resonant band of Ag doped sample appears at 450 nm. The PL emission spectra of Tb, Cu and Ag doped Alq<sub>3</sub> nanoparticles show a single broad band at around 515 nm, which is similar to that of the pure one, but with enhanced PL intensity. The sample doped with Ag at a concentration ratio of Alq<sub>3</sub>:Ag=1:0.8 is found to have the highest PL intensity, which is around 2 times stronger than that of the pure one. This enhancement could be attributed to the surface

plasmon resonance of Ag ions that might have increased the absorption and then the quantum yield. These remarkable result suggest that Alq<sub>3</sub> nanoparticles incorporated with Ag ions might be quite useful for future nano-optoelectronic devices.

**Keywords** Organic semiconductor · Alq<sub>3</sub> · Nanoparticles · Photoluminescence

## Introduction

Organic semiconductors have attracted great attention for using them in organic light-emitting devices [1–3]. Tris (8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) is an organometallic molecule widely used as an electron transport layer [4, 5] as well as a light emitting layer in organic light-emitting diodes (LEDs) [1, 3, 6–8]. It has also been used as a host for fluorescent and phosphorescent dyes [9, 10]. It was reported in 1987 by Tang and VanSlyke [1] to have strong electroluminescence.

In this era of nanotechnology, it is quite interesting to produce Alq<sub>3</sub> organic semiconductor in nanostructure form. The quantum size effect of nanostructured materials such as nanoparticles, nanowires, nanorods may induce new optical, electrical, magnetic and mechanical properties as compared with those of conventional materials [11, 12]. At the nano-scale, many properties of Alq<sub>3</sub> can be improved and utilized for nano opto-electronic devices. Recently, few papers were published on nanostructures of Alq<sub>3</sub>, despite the fact that such kind of nanostructures are of great importance for the potential application in nano-optoelectronic devices [13–16]. Researchers have also focused on improving its luminescence properties by adding different materials to Alq<sub>3</sub> [16–22], however, a limited improvement is observed in this direction.

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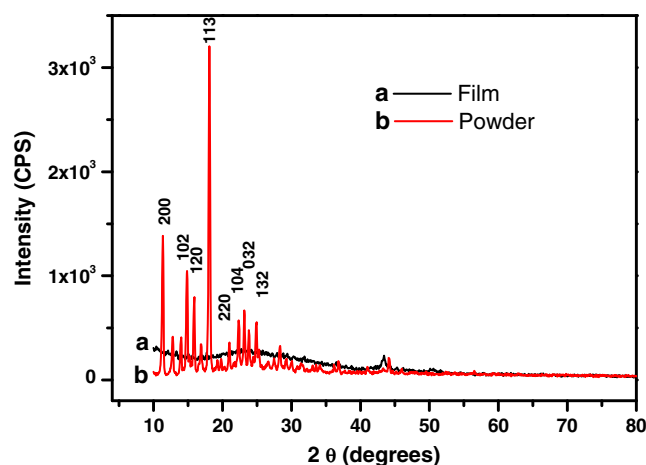
In this work, we report on producing pure and silver (Ag), copper (Cu), terbium (Tb) doped Alq<sub>3</sub> nanoparticles films using the physical vapor condensation method. They were fabricated on glass substrates and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscope (AFM), energy dispersive spectroscopy (EDS), UV-visible absorption spectra and studied for their photoluminescence (PL) properties. Incorporating Alq<sub>3</sub> with Ag ions is found to enhance its emission by a factor of 2, which might be quite useful for future nano-optoelectronic devices.

## Experimental Details

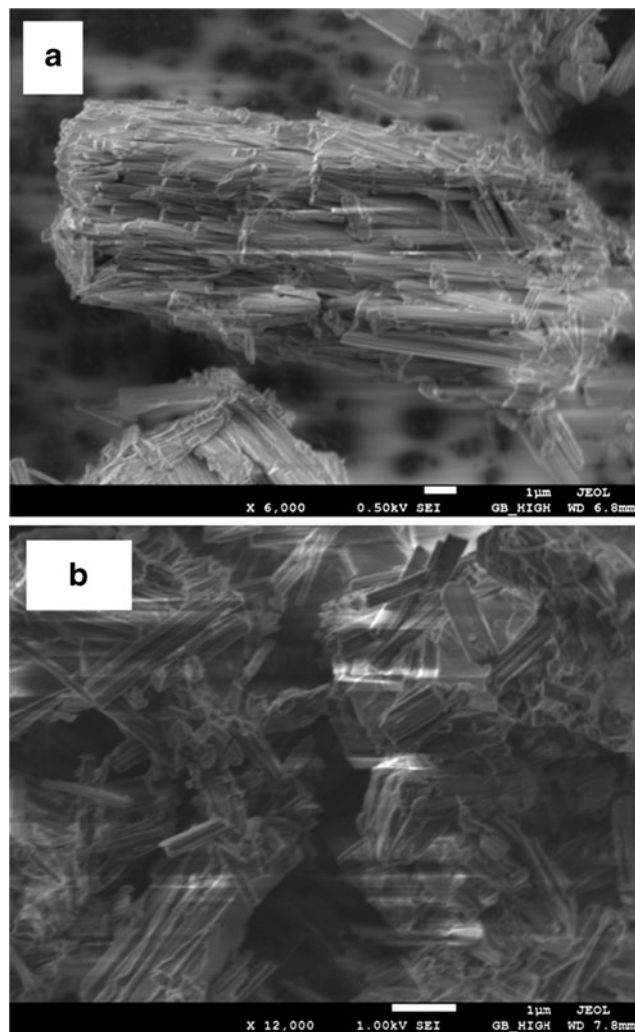
Thin films of Alq<sub>3</sub> nanoparticles were fabricated using the physical vapor condensation method. In this method 0.1 g of highly pure Alq<sub>3</sub> powder, obtained from Sigma Aldrich is kept in a molybdenum boat. Glass substrates were used to deposit the nanomaterials. The substrate was placed above the boat at a distance of around 10 cm. The chamber of the system was evacuated to a vacuum in the order of 10<sup>-6</sup> Torr, then the source material is heated up to 650 °C, with a heating rate of 3 °C/min.

For the Ag doped samples, silver ions were incorporated at different concentrations. The used concentration ratios by weight of Alq<sub>3</sub>:Ag are 1:0.2, 1:0.4, 1:0.6, 1:0.8 and 1:1. Silver ions are obtained from highly pure AgNO<sub>3</sub> powder. In a typical case (For a ratio of 1:0.2) 100 mg of AgNO<sub>3</sub> was dissolved in around 20 ml of double distilled water, and then 0.5 g of Alq<sub>3</sub> was added to this solution. The baker containing this solution is kept in a sonicator bath and sonicated for 4 h to incorporate Ag ions in the Alq<sub>3</sub> matrix. Finally, the material was dried at about 50 °C for 8 h to get powder form of Alq<sub>3</sub> doped with Ag ions. This powder then is used to grow the nanoparticles as mentioned above. Similarly Tb and Cu doped samples at a typical concentration of 1:0.2 for Alq<sub>3</sub>:dopant were prepared by the same method and included in this study. These dopants were used in their chloride forms.

The as-synthesized films of Alq<sub>3</sub> nanoparticles were characterized by X-ray diffraction with an Ultima-IV (Rigaku, Japan) diffractometer (Cu K $\alpha$  radiation  $\lambda=1.5418$  Å wavelength at 40 kV accelerating voltage and 30 mA current), using parallel beam geometry and a multi-purpose thin film attachment. The morphology of the films was analyzed with a field emission scanning electron microscopy (FESEM), JSM-7500 F (JEOL – Japan) operated at 13–20 kV. The chemical composition of a typical film was measured by the energy dispersive spectroscopy technique using Oxford EDS system. The morphology of the films was also analyzed by tapping-mode atomic force microscopy (AFM) with scanning area of (500×500) nm. The used system is a variable temperature UHV AFM/STM model XA 50/500, Omicron, Germany.



**Fig. 1** XRD results of Alq<sub>3</sub> film prepared by physical vapor condensation method (curve a). The XRD pattern of the original powder is also shown (curve b)



**Fig. 2** SEM images of Alq<sub>3</sub> powder at different magnifications

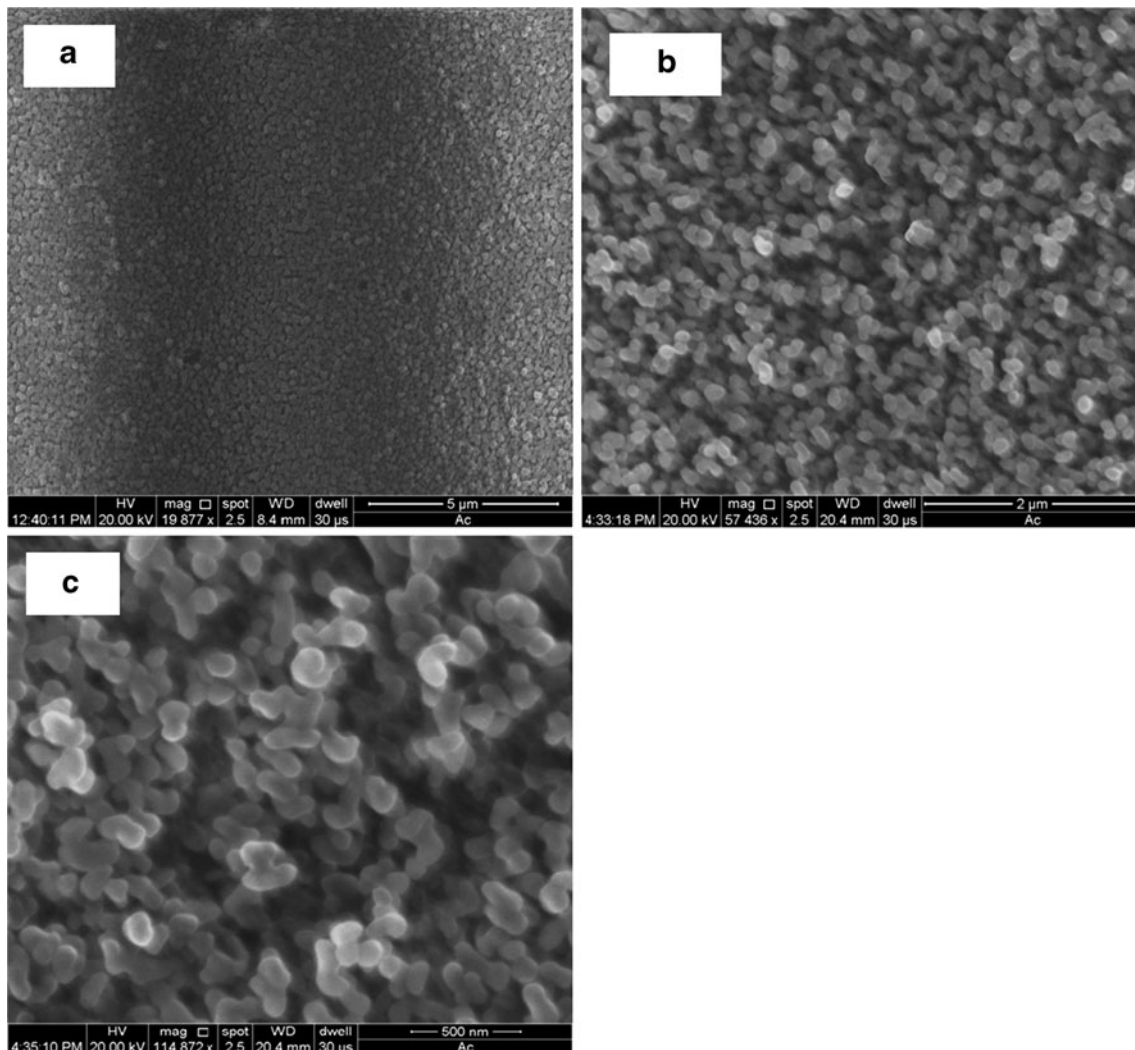
UV–visible absorption spectra of pure and Ag doped  $\text{Alq}_3$  nanoparticles films were recorded using the UV–visible spectrophotometer, model “UV-1650PC”, Shimadzu, Japan. The measurements were carried out in the range of 240–900 nm. Photoluminescence emission spectra of pure and Cu, Tb, Ag doped  $\text{Alq}_3$  nanoparticles films were recorded at room temperature using Fluorescence Spectrofluorophotometer, model RF-5301 PC, Shimadzu, Japan. The films were excited by 378 nm to record the emission spectra, while the excitation spectra were recorded by keeping the emission at 515 nm. The slit width was 3 nm.

## Results and Discussion

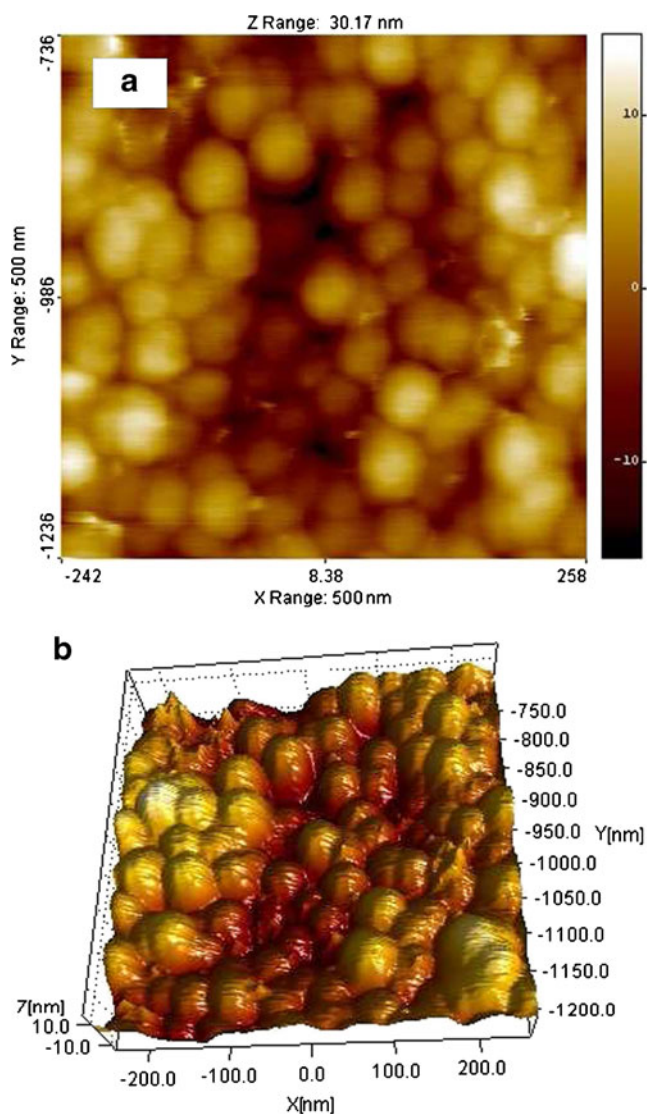
Figure 1 shows the XRD pattern with hkl values of  $\text{Alq}_3$  film prepared by the physical vapor condensation method at vacuum of  $10^{-6}$  Torr (curve a). The result shows amorphous

nature in this film. But this result is completely different than that of the original powder (curve b), where the XRD pattern displays several diffracted peaks. This indicates a presence of crystalline structure in the original powder. The observed peaks in the original powder are in agreement with those given in the JCPDS card No. 26–1550 [23] and the result on obtaining amorphous structure in  $\text{Alq}_3$  film was also reported earlier [24].

Figure 2 shows SEM images at different magnifications (a and b) for the original powder of  $\text{Alq}_3$ . Micro size rods in bundle forms can be seen in these images. These rods have diameters within the range 0.2–0.5  $\mu\text{m}$  with lengths varying from 1 to 10  $\mu\text{m}$ . Figure 3 shows SEM images at different magnifications (a, b and c) of  $\text{Alq}_3$  nanoparticles film. These nanoparticles were grown by the physical vapor condensation method at vacuum of  $10^{-6}$  Torr as mentioned above. Spherical nanoparticles with particle size around 70–80 nm can be observed in these images. These nanoparticles have

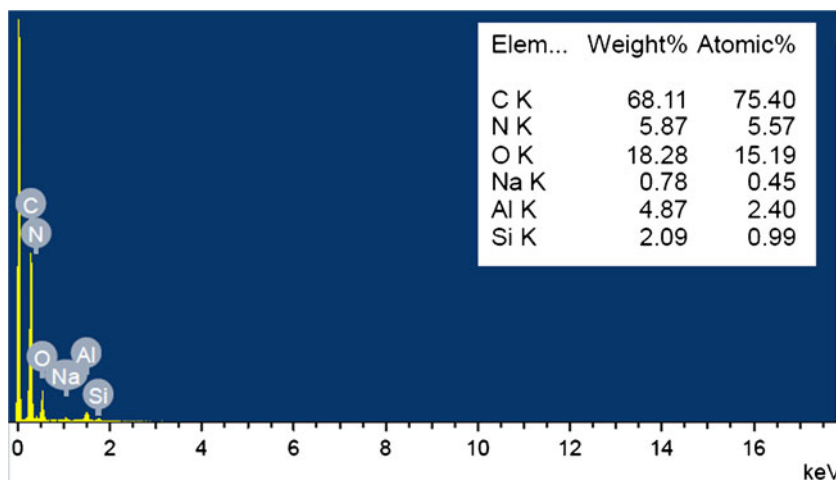


**Fig. 3** SEM mages at different magnifications of  $\text{Alq}_3$  film prepared by the physical vapor condensation method at vacuum of  $10^{-6}$  Torr



**Fig. 4** **a** Two-dimensional and **(b)** three-dimensional AFM images of Alq<sub>3</sub> film prepared by the physical vapor condensation method

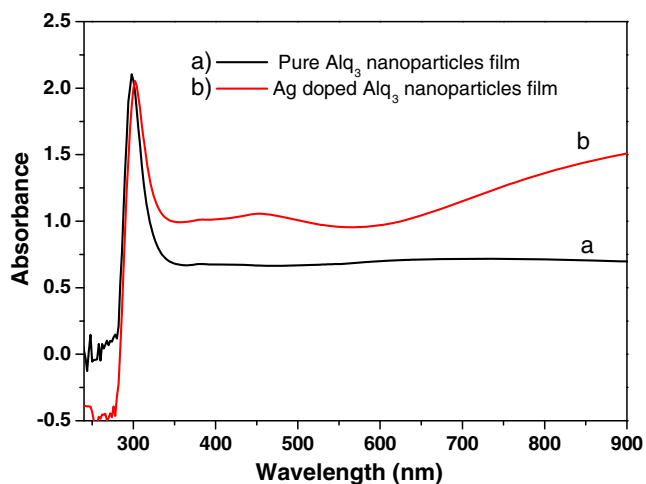
**Fig. 5** EDS quantitative and qualitative analysis of Alq<sub>3</sub> film prepared by the physical vapor condensation method



almost equal sizes with a homogeneous size distribution. Similar results were reported on Alq<sub>3</sub> nanoparticles fabricated on a silicon substrate using the vapor condensation method [16]. The particle size was reported to depend on the pressure inside the chamber, temperature of the boat, heating rate and distance between the boat and the substrate [16].

Figure 4 a and b shows two and three-dimensional AFM images of Alq<sub>3</sub> film prepared by the physical vapor condensation method at vacuum of 10<sup>-6</sup> Torr. These images show nanoparticles with sizes close to those observed by SEM. The chemical composition of pure Alq<sub>3</sub> nanoparticles film was measured by the energy dispersive spectroscopy (EDS) technique. Figure 5 shows EDS quantitative and qualitative analysis of Alq<sub>3</sub> film produced in this work. All the elements forming this compound (C<sub>27</sub>H<sub>18</sub>AlN<sub>3</sub>O<sub>3</sub>) are present in the as synthesized film.

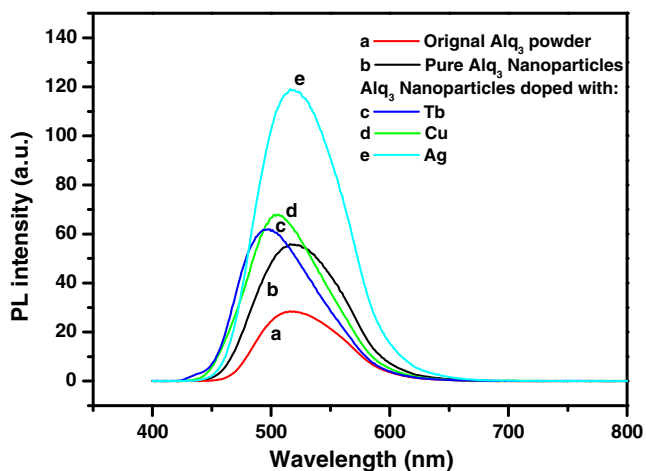
Figure 6 shows the UV–visible absorption spectra of pure (curve a) and Ag incorporated Alq<sub>3</sub> nanoparticles films (curve b). Curves a and b show maximum absorption band at around 300 nm. The Ag doped sample has one extra small band at around 450 nm, which might be the surface plasmon resonant (SPR) band of Ag [25]. Small hump is also observed in both pure and Ag doped sample at around 385 nm. It has been reported that there are two geometrical isomers for Alq<sub>3</sub> molecules: one is meridional and the other is facial [15]. It is also reported that these two isomers exist in amorphous Alq<sub>3</sub> films [26]. The absorption of meridional isomer was reported to occur at around 385 nm, while the absorption corresponding to the facial isomer supposed to be blue shifted by means to the higher energy side [15, 27]. These absorptions were attributed to the electron transfer from the highest occupied molecular orbits (HOMO) to the lowest unoccupied molecular orbits (LUMO) of Alq<sub>3</sub> [15]. In the present case the absorption band at 300 nm that observed in both pure and Ag doped Alq<sub>3</sub> nanoparticles



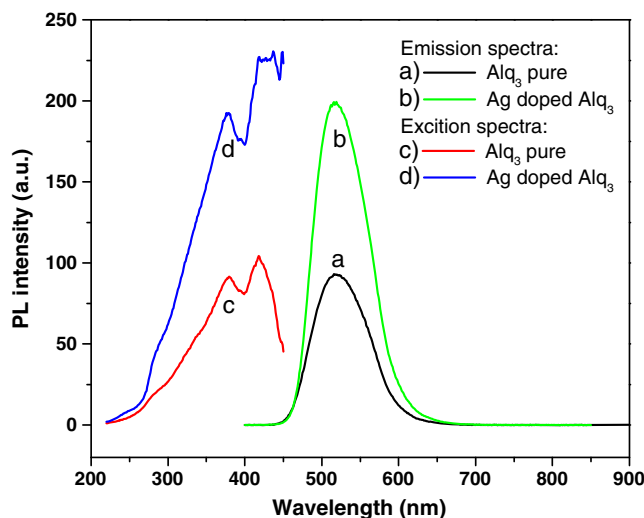
**Fig. 6** UV-visible absorption spectra of (a) un-doped and (b) Ag doped Alq<sub>3</sub> nanoparticles (at Alq<sub>3</sub>:Ag concentrations of 1:0.8)

samples might be the absorption corresponding to the transfer from HOMO to LUMO of facial isomers of Alq<sub>3</sub> molecule in amorphous form [15]. The small hump at 385 nm might be attributed to absorption of the meridinal isomer [15, 27].

Photoluminescence (PL) emission spectra of the original powder along with those of the pure and Tb, Cu, Ag doped Alq<sub>3</sub> nanoparticles films prepared by the physical vapor condensation method are shown in Fig. 7 curves a, b, c, d and e, respectively. When the powder sample was excited by 378 nm, one broad emission band is observed at around 515 nm (curve a). The pure sample in nanoparticles form shows similar band with drastic increase in the peak intensity by a factor of around 2 (curve b). The samples doped



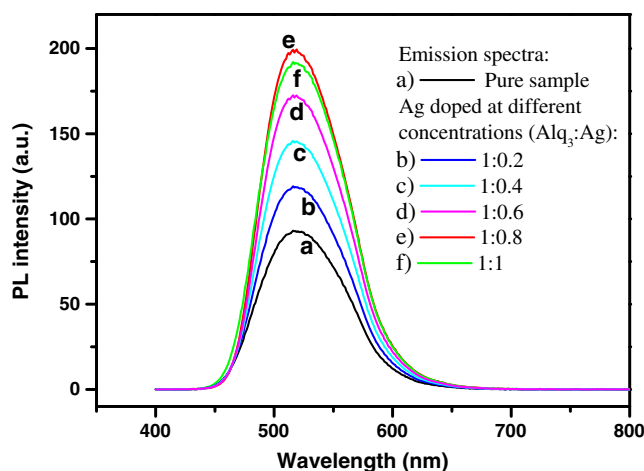
**Fig. 7** Photoluminescence emission spectra of pure and Tb, Cu, Ag doped Alq<sub>3</sub> nanoparticles films prepared by the physical vapor condensation method. The emission spectrum of the original powder is also shown



**Fig. 8** Photoluminescence emission and excitation spectra of un-doped and Ag doped Alq<sub>3</sub> nanoparticles (Alq<sub>3</sub>:Ag =1:0.8)

with Tb, Cu and Ag at a concentration ratio of 1:0.2 (Alq<sub>3</sub>: dopant) show also similar band with further enhancements in the peak intensity (curves c, d and e, respectively), particularly that of Ag. The PL intensity of Ag doped sample is around 2 times stronger than that of the pure Alq<sub>3</sub> nanoparticles. There is a slight shift to the blue region in the PL emission band of the Tb and Cu doped samples.

PL excitation and emission spectra of pure and Alq<sub>3</sub> nanoparticles incorporated with Ag ions at a concentration ratio of 1:0.8 are shown in Fig. 8. The pure material shows a single emission band at around 515 nm as mentioned above (curve a), while the excitation spectrum by keeping the emission wavelength at 515 nm shows two bands at around 378 and 420 nm (curve c). The sample incorporated with Ag ions has almost similar emission and excitation spectra



**Fig. 9** Photoluminescence emission spectra of un-doped and Ag doped Alq<sub>3</sub> nanoparticles at different concentrations

(curves b and d, respectively), but with enhanced intensity. Small band at around 450 nm in case of the excitation spectrum of Ag incorporated sample can be seen. This band might be the Ag resonance band [25]. When the samples were excited by 420 nm, same emission is observed at 515 nm. The band at 515 nm is similar to that reported in the literature [15, 16]. The emission process involved in Alq<sub>3</sub> molecule was ascribed to its 8-hydroxyquinoline ligands [15]. The enhancement in photoluminescence of Alq<sub>3</sub>:Ag in the present case might be due to the surface plasmon resonance of Ag ions. This might have increased the absorption and then the quantum yields. Enhanced photoluminescence was also found in Alq<sub>3</sub> deposited onto nanotextured silver films with porous alumina substrates [18] and Au capped Alq<sub>3</sub> films [17]. These enhancements were attributed to the increase in absorption and quantum yield. The presence of two excitation bands at 378 and 420 nm might be due to the presence of the two geometrical isomers for Alq<sub>3</sub> molecules, which are meridional and facial. Each isomer has its excitation wavelength. But these two different values of the excitation wavelengths show the same emission band at 515 nm. The UV–visible absorption spectra presented in Fig. 6 show clearly the presences of the absorption bands of these two isomers.

PL emission spectra of pure and Ag doped Alq<sub>3</sub> nanoparticles films at different concentrations are shown in Fig. 9. The pure one shows a broad emission band at 515 nm (curve a) as mentioned above. The samples incorporated with Ag ions have almost similar emission spectra, but with enhanced intensity (Curves b, c, d, e and f). The maximum intensity is found at a concentration ratio of 1:0.8 for Alq<sub>3</sub>:Ag by weight. This intensity is found to be around 2 time stronger than the that of pure Alq<sub>3</sub> nanoparticles sample. No significant enhancement in the PL intensity is observed beyond the concentration ratio of 1:1. This saturation at this concentration might be due to the PL quenching. From the application point of view incorporating Alq<sub>3</sub> with Ag ions is found to enhance its emission spectrum by a factor of 2, which might be quite useful for future nano-optoelectronic devices.

## Conclusion

Films of Alq<sub>3</sub> nanoparticles were fabricated using the physical vapor condensation method. Pure and doped samples with Tb, Cu, Ag ions were synthesized and studied for their photoluminescence properties. The PL result showed that the nanoparticles of pure Alq<sub>3</sub> have enhanced PL intensity compared with that of the original powder. The doped samples have further PL enhancements particularly that doped with Ag ions. It has the highest PL intensity, which is around 2 times stronger than that of the pure nanoparticles.

The maximum PL intensity was found at concentration ratio of Alq<sub>3</sub>:Ag equal to 1:0.8. This enhancement is attributed to the surface plasmon resonance of Ag ions that might have increased the absorption and then the quantum yield. These remarkable results suggest that Alq<sub>3</sub> nanoparticles incorporated with Ag ions might be quite useful for future nano-optoelectronic devices.

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