

Photoluminescence and Electroluminescence of Organic Light Emitting Diodes Based on Tris-(8-quinolinolato) Aluminum Nanoparticles

HUA, Rui-Nian^{*a}(华瑞年) NIU, Jing-Hua^b(牛晶华) YU, Tian-Zhi^b(俞天智)
HONG, Zi-Ruo^b(洪自若) LI, Wen-Lian^b(李文连) FAN, Sheng-Di^a(范圣第)

^a College of Life Science, Dalian Nationalities University, Dalian, Liaoning 116600, China

^b Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin 130033, China

Tris-(8-quinolinolato) aluminum (AlQ₃) organic nanoparticles with an average diameter 20 nm were prepared through a reprecipitation method. The AlQ₃ nanoparticles are spherical and the average particle size does not change by varying the aging time. The photoluminescent and electroluminescent properties were investigated via the AlQ₃ nanoparticles and the device based on the AlQ₃ nanoparticles, respectively. Blue shift of both the photoluminescence and electroluminescence spectra for the AlQ₃ nanoparticles was observed. With increasing the driving bias, the maximum EL emission peak of the AlQ₃ nanoparticles was shifted to longer wavelength. The maximum luminance and luminous efficiency of the AlQ₃ nanoparticle-based device are about 600 cd/m² at driving bias 16V and 0.19 cd/A at a current density of 150 mA/cm², respectively. The obvious quantum size effect of electro-luminescence devices with the AlQ₃ nanoparticles has been proved, which will open a useful route and new studying field of organic electronic devices, and the study of the fundamental process connecting both of those more conventional classes of materials, *i.e.*, organic molecular crystals.

Keywords tris-(8-quinolinolato) aluminum, nanoparticle, photoluminescence, electroluminescence, device

Introduction

Nanometer-sized particles have attracted great interest in recent years because of their unique properties in physics and chemistry as well as their potential application to industry.¹ Many nanoparticles of different chemical compositions, shapes and size distributions have been prepared by many different kinds of methods.^{2–4} However, little attention has been paid to the fabrication of organic nanoparticles, which was probably due to lower thermal stability and weaker mechanical properties.⁵ Electrical and optical properties of organic molecular materials differed from those of inorganic metals and semiconductors fundamentally due to weak intermolecular interaction forces of the van der Waals type and the small radius of the Frenkel exciton.⁶ Up to now, the fundamental studies on the size-dependent organic nanomaterials, and the routes for controlling the size and shape of such particles are still challenging and of particular interest.

Nakanishi and his co-workers prepared microcrystals of perylene by the simple reprecipitation processes and found that their nanoparticles exhibit size-dependent photoluminescent (PL) emission because of the reduc-

tion of the barrier from S-exciton to F-exciton states in the nanoparticles.^{7,8} Yao *et al.*^{6,9–11} have synthesized a series of organic nanoparticles by the reprecipitation method and organic nanotubes by the immersing technique using porous alumina membranes as the template,¹² such as, 1,3-diphenyl-5-(2-anthryl)-2-pyrazoline (DAP),⁹ 1-phenyl-3-((dimethylamino) styryl)-5-((dimethylamino)phenyl)-2-pyrazoline (PDDP),⁶ 1,3-diphenyl-2-pyrazoline (DP),¹⁰ 1,3-diphenyl-5-pyrenyl-2-pyrazoline (DPP) nanoparticles¹¹ and *R*-di-2-naphthyl prolinol (DNP) nanotubes.¹² They suggested that the organic nanoparticles also possess significant quantum size effects resembling those of inorganic semiconductors and metals. Jang *et al.*⁵ have prepared dye-conducting polymer core-shell composite nanoparticles (pyrene-polypyrrole) using microemulsion micelles as nanoreactors. They have found that the emission colors of the nanohybrids could be controlled in the region from violet to blue by changing the amount of embedded pyrene. Lee *et al.*¹³ have synthesized 1,4-bis[2-(5-phenyloxazolyl)]benzene (POPOP) nanowires using an anodic aluminum oxide (AAO) membrane, and observed that the emission spectra from the nanowire arrays exhibited size-dependent lumines-

* E-mail: rnhua@dlnu.edu.cn; Tel.: 0086-0411-87633470

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cent properties. Recently, Wang *et al.*^{14,15} prepared nanoparticles, nanowires and nanobelts of tris-(8-quinolinolato) aluminum (AlQ₃) by a vapor condensation method. Due to the strong electroluminescence (EL) of AlQ₃-based organic light emitting diodes (OLEDs) at driving bias, AlQ₃ has become one of the most attractive electron transporter and emitting materials. To the best of our knowledge, a number of papers have reported the PL absorption and emission properties of different organic molecular nanoparticles, however, the electroluminescent properties of organic molecular nanoparticles have not yet been reported. In this work, AlQ₃ nanoparticles with an average diameter of 20 nm were synthesized by the reprecipitation method and the PL and EL properties of the AlQ₃ nanoparticles were studied.

Experimental

Chemicals and instrumentation

All solvents and chemicals were spectrographically pure and used without further purification.

Nanoparticle size and morphology were measured using a field emission scanning electron microscope (FESEM, XL30 ESEM FEG). Photoluminescent spectra were measured using a Hitachi F-4500 fluorescence spectrometer. Electroluminescent spectra were collected by a fiber optic apparatus and dispersed onto a CCD Si-detector.

Synthesis of AlQ₃ nanoparticles

The organic nanoparticles of AlQ₃ were prepared through the reprecipitation technique. As a typical preparation process, 100 μ L of AlQ₃-saturated *N,N*-dimethyl formamide (DMF) stock solution (*ca.* 1.0×10^{-3} mol/L) were rapidly injected (<2 s) into a 5.0 mL chloroform solvent at room temperature (25 $^{\circ}$ C), and

finally AlQ₃ nanoparticles with an average diameter of about 20 nm were formed.

Fabrication of EL device

The EL device consisting of ITO/PEDOT-PSS (70 nm)/poly(vinylcarbazole) (PVK) (100 nm)/AlQ₃ nanoparticle (100 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (30 nm)/LiF (1 nm)/Al (100 nm) was constructed as follows. The 70 nm thick PEDOT-PSS layer was spin-deposited onto the cleaned ITO coated. The 100 nm thick PVK layer was spin deposited on the PEDOT-PSS layer, followed by the deposition of chloroform-dispersed AlQ₃ nanoparticles. The AlQ₃ nanoparticle layer was dried using a vacuum oven at 80 $^{\circ}$ C, resulting in a layer of 100 nm thickness. The 30 nm thick BCP layer was vacuum-evaporated onto the AlQ₃ nanoparticle layer, and then the 1 nm thick LiF layer and 100 nm thick Al cathode were also vacuum-evaporated without breaking the vacuum to complete the device. To operate the device, positive and negative voltages were applied to the ITO and Al electrodes, respectively.

Results and discussion

The sizes and shapes of the AlQ₃ nanoparticles were observed on a field emission scanning electron microscope. Figure 1 shows the morphology of the AlQ₃ nanoparticles with the average diameter of about 20 nm. No change of the average particle size by varying the aging time was observed. As the aging reaction time was increased from 24 to 48 h, the individual particles became slightly bigger than others in diameter. This was probably aggregation of the AlQ₃ nanoparticles due to a long time placement and no ultrasonic treatment after the AlQ₃ nanoparticle formation.

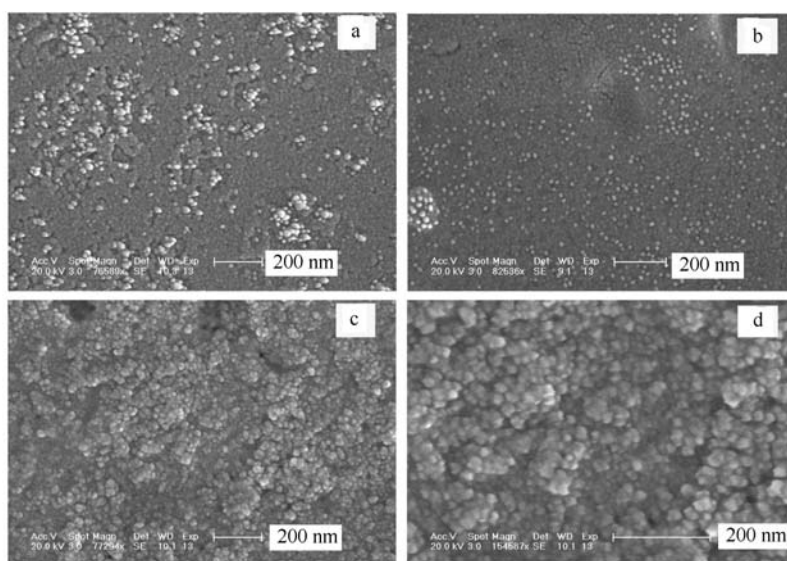


Figure 1 Field emission SEM images of AlQ₃ nanoparticles with an average diameter about 20 nm. At different aging time: (a) 10 min, (b) 60 min, (c) 24 h, (d) 48 h.

The PL spectra of the AlQ₃ nanoparticles with an average diameter of 20 nm were obtained by excitation by a He-Cd laser with a wavelength 365 nm, which are shown in Figures 2(b), 2(c), 2(d) and 2(e), respectively. In addition, PL spectra of an AlQ₃/NMF saturated solution and an AlQ₃ nanoparticle thin film with a thickness of 150 nm are also displayed in Figure 2(a) and Figure 2(f), respectively. From Figure 2(a) it is seen that there is a maximum intensity of PL emission peak at 533 nm, a broad emission band ranging from 450 to 700 nm for the AlQ₃/NMF saturated solution.

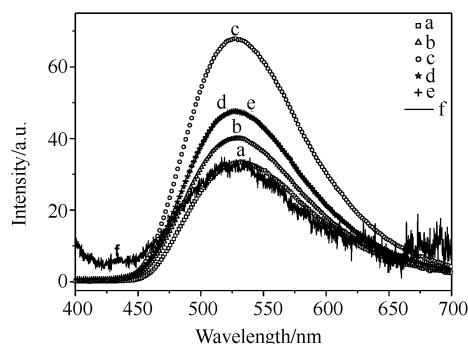


Figure 2 PL spectra of AlQ₃: (a) AlQ₃/DMF saturated solution (*ca.* 1.0×10^{-3} mol/L); (b) AlQ₃ nanoparticle dispersions in chloroform from a 10 min reaction; (c) AlQ₃ nanoparticle dispersions in chloroform from a 60 min reaction; (d) AlQ₃ nanoparticle dispersions in chloroform from a 24 h reaction; (e) AlQ₃ nanoparticle dispersions in chloroform from a 48 h reaction; (f) AlQ₃ nanoparticle thin film of a thickness 150 nm.

The PL emission spectra of both the AlQ₃ nanoparticles with an average diameter of 20 nm and the AlQ₃ nanoparticle thin film are also broad, covering the visible region from 450 to 700 nm at the same maximum intensity at about 529 nm. Blue-shifting of about 4 nm was observed in this study. A blue-shifting of the PL spectrum in nanometer-sized inorganic semiconductors whose sizes are less than 10 nm is often observed because of the quantum confinement effect.¹⁶ The size-dependence of the AlQ₃ nanoparticles with an average diameter of 20 nm is also likely due to Mie scattering, which is often observed in metal nanoparticles.⁸ Thus, it is concluded that organic nanoparticles also possess the same significant size effects like inorganic semiconductors and metals, which is an interesting phenomenon because these are a wide variety of organic molecular structures compared to the semiconductors.

Figure 3 shows a comparison of PL of the AlQ₃ nanoparticle solution and EL of the device based on the AlQ₃ nanoparticles. It is obvious that the EL emission was blue-shifted from 529 to 524 nm, and broader bandwidth of the EL emission spectra compared to the PL spectra was determined. These results are well-known characteristics of nanocrystal-based EL.^{16,17} Above results further indicate that the organic molecular AlQ₃ nanoparticles possess a special dependence. It was found that no EL emission was observed for the device

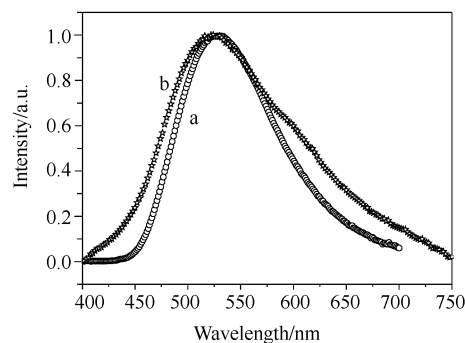


Figure 3 Comparison of PL spectra of AlQ₃ nanoparticle solution (a) and EL emission spectra of ITO/PEDOT-PSS (70 nm)/PVK (100 nm)/AlQ₃ nanoparticle (100 nm)/BCP (30 nm)/LiF (1 nm)/Al (100 nm) device at bias of 24 V (b).

without a PEDOT-PSS layer, indicating that the PEDOT-PSS either lowers the energy barrier of hole injection from the ITO electrode or enhances the hole mobility.¹⁷

Dependence of the emission spectra on the applied bias of the EL device is shown in Figure 4. We can see that the intensities and peaks of the EL emission increase with increasing the applied bias. At lower voltages, such as 10 and 12 V, both the emission spectra of the PVK and AlQ₃ nanoparticles were observed, respectively. In the meanwhile, with increasing the bias, the maximum EL peak position of the AlQ₃ nanoparticles was shifted from 500 to 517 nm. The red-shift of the EL emission peaks with increasing applied voltage was possibly attributed to local Joule heating from the large current flux and poor thermal conductivity of the emitting layer.¹⁷

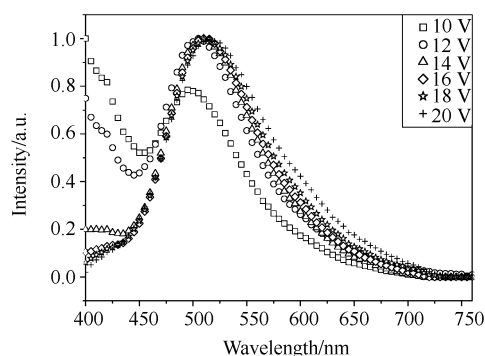


Figure 4 EL spectra of the device based on ITO/PEDOT-PSS (70 nm)/PVK (100 nm)/AlQ₃ nanoparticle (100 nm)/BCP (30 nm)/LiF (1 nm)/Al (100 nm) under different applied voltages.

Figure 5 shows the current density-voltage-luminance and luminous efficiency-current density characteristics of the ITO/PEDOT-PSS (70 nm)/PVK (100 nm)/AlQ₃ nanoparticle (100 nm)/BCP (30 nm)/LiF (1 nm)/Al (100 nm) device. It can be seen that with increasing the applied bias, the luminance and the current density increase rapidly and the threshold bias is lower than 9 V, indicating that the greater parts of the voltage

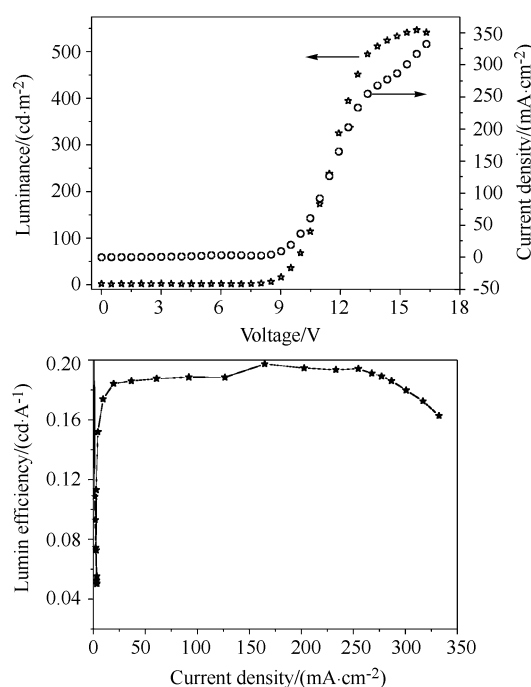


Figure 5 Current density-voltage-luminance and luminous efficiency-current density characteristics of the ITO/PEDOT-PSS (70 nm)/PVK (100 nm)/AlQ₃ nanoparticle (100 nm)/BCP (30 nm)/LiF (1 nm)/Al (100 nm) device.

drops were across the AlQ₃ nanoparticles layer, which further confirms that the AlQ₃ nanoparticle layer controls the current density-voltage characteristic of the device. The maximum luminance and luminous efficiency of the AlQ₃ nanoparticle-based device are about 600 cd/m² at 16 V bias and 0.19 cd/A at a current density of 150 mA/cm², respectively.

Conclusion

In summary, AlQ₃ nanoparticles of the average size of about 20 nm were synthesized by a reprecipitation method. The AlQ₃ nanoparticles are spherical and the average particle size does not change with varying the aging time. Blue shift of both the PL- and EL-spectra for the AlQ₃ nanoparticles was observed. These findings indicate that the organic molecular AlQ₃ nanoparticles possess special size properties. With increasing the applied bias, the maximum EL emission peak of the AlQ₃ nanoparticles was shifted to longer wavelength. The

maximum luminance and luminous efficiency of the AlQ₃ nanoparticle-based device are about 600 cd/m² at 16 V bias and 0.19 cd/A at a current density of 150 mA/cm², respectively. The obvious quantum size effect of the EL devices with the AlQ₃ nanoparticles has been proved, which will open a useful route and new studying field of organic electronic devices, such as optical modulators controlling the wavelength in organic photoconductors or EL materials, and the study of the fundamental process connecting both of those more conventional classes of materials, *i.e.*, organic molecular crystals. More detail work will be of great interest for future study.

References

- Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457.
- LaiHing, K.; Wheeler, R.; Wilson, W.; Duncan, M. *J. Chem. Phys.* **1987**, *87*, 3401.
- Wu, M.; Lin, G.; Chen, D.; Wang, G.; He, D.; Feng, S.; Xu, R. *Chem. Mater.* **2002**, *14*, 1974.
- Hua, R.; Zang, C.; Shao, C.; Xie, D.; Shi, C. *Nanotechnology* **2003**, *14*, 588.
- Jang, J.; Oh, J. H. *Adv. Mater.* **2003**, *15*, 977.
- Hu, H.; Yao, J. *J. Am. Chem. Soc.* **2001**, *123*, 1434.
- Kasai, H.; Kamatani, H.; Yoshikawa, Y.; Okada, S.; Oikawa, H.; Watanabe, A.; Itoh, O.; Nakanishi, H. *Chem. Lett.* **1997**, 1181.
- Kasai, H.; Kamatani, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1996**, *35*, L221.
- Xiao, D.; Xi, L.; Yang, W.; Fu, H.; Shuai, Z.; Fang, Y.; Yao, J. *J. Am. Chem. Soc.* **2003**, *125*, 6740.
- Fu, H.; Xiao, D.; Yao, J.; Yang, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 2883.
- Fu, H.; Loo, B. H.; Xiao, D.; Xie, R.; Ji, X.; Yao, J.; Zhang, B.; Zhang, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 962.
- Zhao, L. Y.; Yang, W. S.; Jiang, Z. W.; Yao, J. N. *Chin. J. Chem.* **2005**, *23*, 1309.
- Lee, J.; Koh, W.; Chae, W.; Kim, Y. *Chem. Commun.* **2002**, 138.
- Chiu, J.; Wang, W.; Kei, C.; Perng, T. *Appl. Phys. Lett.* **2003**, *83*, 347.
- Chiu, J.; Kei, C.; Perng, T.; Wang, W. *Adv. Mater.* **2003**, *15*, 1361.
- Schlamp, M.; Peng, X.; Alivisatos, A. *J. Appl. Phys.* **1997**, *82*, 5837.
- Yang, H.; Holloway, P. *J. Phys. Chem. B* **2003**, *107*, 9705.

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