Fluorescence stability of 8-hydroxyquinoline aluminum

Gui Yu [a], Dezhen Shen [b,c], Yunqi Liu [a,*], Daoben Zhu [a]

[a] *Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[b] *Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130022,*
People's Republic of China
[c] *Laboratory of excited state processes, Chinese Academy of Sciences, Changchun 130021, People's Republic of China*

Received 26 August 2000; in final form 24 October 2000

Abstract

Physical and chemical characteristics of 8-hydroxyquinoline aluminum (Alq_3) have been investigated in this work. The fluorescence stabilities of Alq_3 films were compared before and after UV irradiation. They were analyzed by using a UV-Vis absorption spectrophotometer, an in situ fluorescence spectrometer, attenuated X-ray photoelectron spectroscopy, and a nanosecond fluorescence spectrophotometer. Degradation in photoluminescence properties was significant in the presence of humid air (at an 85% relative humidity). These results indicate that water and oxygen aid the photodegradation, and the degradation mechanism of Alq_3 in the presence of H_2O and O_2 is discussed in terms of chemical reactions. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Organic/polymeric electroluminescent materials and devices have attracted much attention since the breakthrough made by Tang and Friend and their potential applications in large area and flat panel displays [1,2]. The organic/polymeric light emitting diodes (LEDs) exhibit many advantages over inorganic LEDs in being driven by low dc voltage, high luminous efficiency, high brightness and multicolor emission. Although much progress has been made in improving emission efficiencies and brightness [3,4] and in prolonging the lifetime of the devices [5–9], they still suffer from limited life due to degradation. These include the degradation of both hole and electron injecting con-
tacts [10], the deterioration of organic/polymeric layers [11], the interfacial change of two organic layers [12], and the degradation of top electrodes [13].

Most organic/polymeric LEDs under ambient atmosphere have a short operational lifetime, ranging from a few hours to several hundred hours. The lifetime of the encapsulated diodes was increased by more than two orders of magnitude over that of the unencapsulated ones [8]. These results indicate that atmospheric moisture and oxygen have a great effect on the lifetime of the diodes. It has been shown that poly(phenylene vinylene) (PPV) derivatives can be readily photooxidized by the oxygen in air and that an ester species is among the oxidation products. The formation of carbonyl species can quench luminescence from the polymer [14–16]. However, reports on the atmospheric moisture effect on luminescence of organic materials are

* Corresponding author. Fax: +86-10-62559373.
 E-mail address: liuyq@infoc3.icas.ac.cn (Y.Q. Liu).

still limited [17,18]. On the other hand, 8-hydroxyquinoline aluminum (Alq$_3$) has been used most widely as an emitting material in organic LEDs. The electroluminescence (EL) spectrum of Alq$_3$ is identical to its photoluminescence (PL) spectrum. This indicates that PL and EL of Alq$_3$ are imbued with the same carrier recombination mechanisms. Both PL and EL mechanisms in this material involve light emission via the radiative recombination of singlet exciton species. Therefore, the study of fluorescence quenching of Alq$_3$ may be useful to explain the stability of the organic LEDs using Alq$_3$ as an emitting material. Although the thermal and morphological stability of Alq$_3$ was reported [19], photophysics and photochemistry of Alq$_3$ have not received considerable attention.

In this Letter, we report the absorption spectra, PL spectra, X-ray photoemission spectra, and fluorescence decay curves during UV-lamp irradiation at 365 nm. From these experimental results, we obtained information about luminescence quenching.

2. Experimental

Alq$_3$ was synthesized according to the method reported in the literature [20] and purified twice using vacuum sublimation. The Alq$_3$ thin films (~ 100 nm) were evaporated at 1 Å/s on quartz glass substrates. In order to investigate the fluorescence degradation, the Alq$_3$ thin films were irradiated using an 8 W UV-lamp at 254 and 365 nm in humid air [at 85% relative humidity (RH)]. Absorption and PL spectra were obtained using a Hitachi U-3010 spectrophotometer and a Hitachi F-4500 fluorescence spectrometer, respectively. The fluorescence decay curves were measured using a Nanosecond SP-70/80 NS Fluorescence Spectrophotometer for photoexcitation at 337 nm. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCA-LAB MKII analyzer, using a Mg k_α X-ray Source ($hv = 1253.6$ eV) in an ultrahigh vacuum (UHV) system. The pressure of the chamber was maintained in the 10^{-9} mbar range throughout the experiments.

3. Results and discussion

Fig. 1 shows the C(1s), O(1s), and Al(2p) X-ray photoemission spectra of Alq$_3$ films before and after UV irradiation at 365 nm. The C(1s) X-ray
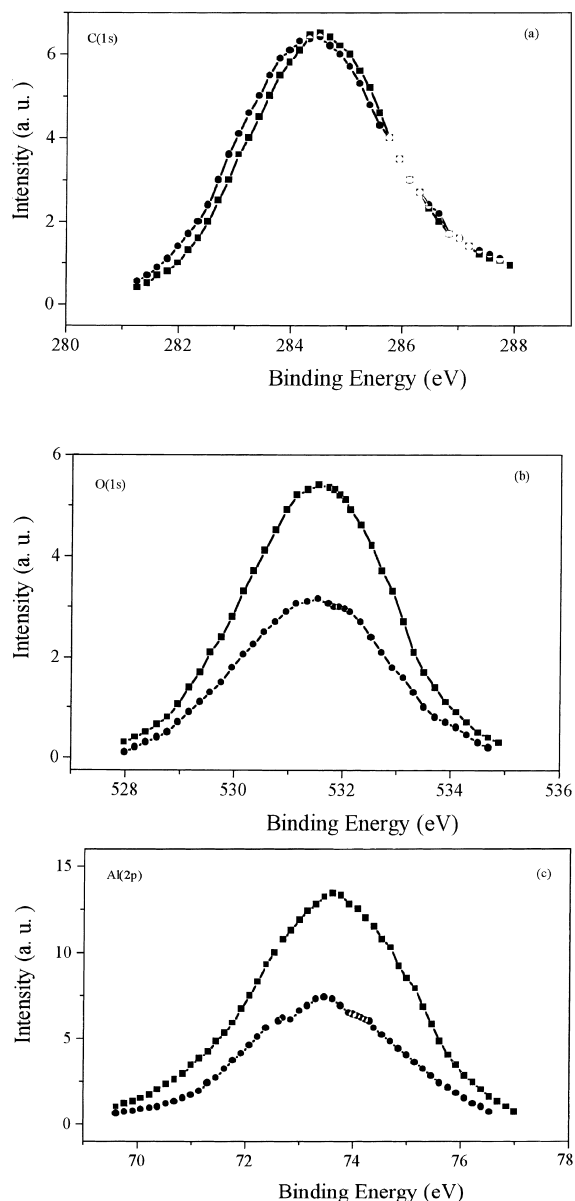

Fig. 1. X-ray photoemission spectra of Alq$_3$ films before (■) and after (●) UV irradiation at 365 nm. (a) C(1s), (b) O(1s), (c) Al(2p).

photoemission spectrum of the unirradiated Alq$_3$ thin film shows a peak at 284.6 eV. The C(1s) spectrum of the irradiated film shows a similar peak to that of the pristine Alq$_3$, but its full width at half-maximum (FWHM) is larger than that of the pristine spectrum and the peak decreases in intensity after irradiation. The decreasing peak intensity is caused by the hydrolysis of Alq$_3$. The O(1s) binding energy of as-prepared neutral Alq$_3$ thin film is at 531.6 eV. For the irradiated film, two O(1s) peaks were observed, one corresponds to the neutral Alq$_3$; the additional O(1s) peak at 531.8 eV corresponds to a charged state of the irradiated film. The peak at 531.6 eV decreases in intensity after irradiation, and the broadening of the lines occurs. The Al(2p) spectrum of the unirradiated Alq$_3$ film shows a peak at 73.8 eV, but the Al(2p) spectrum of the irradiated film shows two new shoulders around 72.9 and 74.3 eV besides the one at 73.8 eV. This result indicates that irradiated Alq$_3$ provides two new states of aluminum, corresponding to the two-photodegradation products containing Al^{3+} [21].

Fig. 2 shows fluorescence decay curves of Alq$_3$ at several different exposure times under air and UV-light (365 nm). The initial PL decay is non-exponential. The PL decay of the irradiated films is more rapid for longer exposure times. These results again indicated that a chemical reaction occurred in the Alq$_3$ layer and that quenchers formed during UV-light irradiation. Photoexcitation of Alq$_3$ creates an exciton, which diffuses to the quenching centers and is non-radiatively captured by quench centers. The concentration of the quenchers increases with increasing irradiation time. Therefore, the result that the fluorescence decays with increasing irradiation time was obtained.

Alq$_3$ is a chelate-complex, and exhibits strong fluorescence. The absorption and PL spectra of Alq$_3$ are influenced by the ligand – 8-hydroxyquinoline (8-Hq). Uniform Alq$_3$ thin films could be easily formed by conventional vacuum deposition and no crystallization was found in our films. Fig. 3 shows absorption spectra of Alq$_3$ films before and after UV irradiation at 365 nm. The absorption spectrum of the unirradiated film has a maximum at 392.5 nm [17], which is caused by the π–π* transition of the ligand. The absorption maximum and the shapes for the absorption spectra of irradiated Alq$_3$ films are almost the same as that of the pristine Alq$_3$ thin film, however, the absorbance decreases with increasing irradiation time. These results indicate that the numbers of Alq$_3$ molecules are reduced with increasing irradiation time, and the chemical structure of Alq$_3$ is changed during irradiation under ambient conditions in humid air.

Al^{3+} is an oxidizing state of the aluminum atom, and has no occupied valence electron orbitals. Therefore, Al^{3+} does not exhibit fluorescence. The ligand under the influence of Al^{3+} forms a rigid
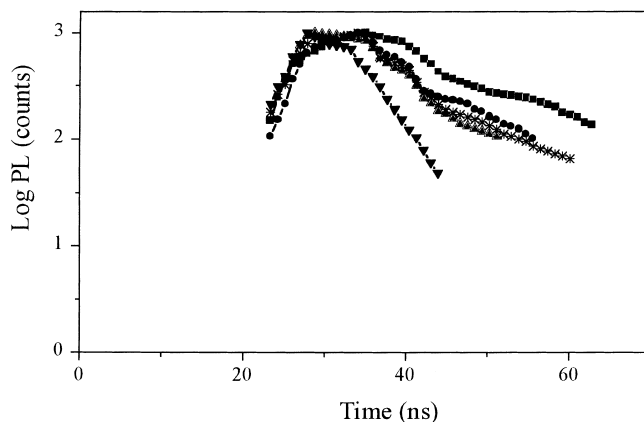

Fig. 2. Fluorescence decay curves of Alq$_3$ films at several different exposure times under air and UV-light (365 nm) [0 h (■), 10 h (●), 20 h (∗), 30 h (▲), 40 h (▼)].
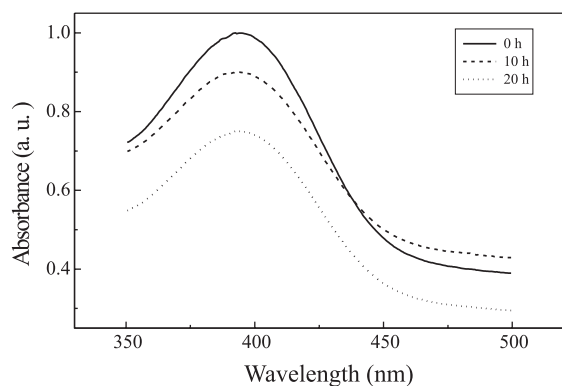
Fig. 3. Absorption spectra of Alq$_3$ films before and after UV irradiation at 365 nm.

chelate ring. When illuminated under an UV-lamp, the ligand absorbs light energy and this leads to a π–π* transition, then the ligand causes PL during radiative decay. The PL spectra of Alq$_3$ films before and after UV irradiation at 365 nm are shown in Fig. 4. The luminescent maximum of the unirradiated Alq$_3$ thin film is at 519 nm, the FWHM is about 80 nm, and the color is green. When the films were exposed to humid air under an UV lamp at 254 nm, after 10 h of irradiation, the PL intensities decreased to 67% of the initial value (pristine sample). However, when the films were exposed to UV irradiation under humid nitrogen, after 10 h, the PL intensities decreased only to 77%. At the same time, similar measurements were made on other Alq$_3$ films, which were illuminated
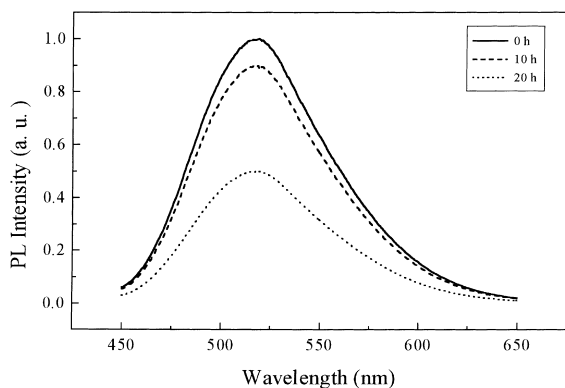

Fig. 4. PL spectra of Alq$_3$ films before and after UV irradiation at 365 nm.

under dry pure oxygen and dry pure nitrogen, respectively. After 10 h of UV irradiation, under dry pure oxygen the PL intensities decreased to about 48%, while under dry pure nitrogen the PL intensities decreased only to about 90%. These results indicate that water and oxygen have strong effects on quenching the fluorescence of Alq$_3$, and oxygen is the main fluorescence degradation agent of Alq$_3$. Priestley et al. [22] reported that water vapor did not contribute substantially to the photooxidation process of Alq$_3$, which is in contradiction to our results. We suspect that both water and oxygen may play a role in quenching the fluorescence of Alq$_3$. The PL spectra are taken at different times during the exposure to air under UV-light. The shape and emission maximum of the PL spectra for both irradiated and unirradiated Alq$_3$ films are identical, but the PL intensities decrease with increasing illumination time. This result indicates that no change was observed to the fluorescence center in the unirradiated and irradiated cases; the fluorescence center is Alq$_3$. However, there is a photoinduced quench center, which leads to the decrease in the PL intensities. In moisture and an oxygen environment, the chemical instability of this chelate was reported, and it has been shown to undergo a ligand-exchange reaction with water at elevated temperatures [15,17]. The ligand was replaced by water, forming free 8-Hq and another two chelate containing Al^{3+}. The free 8-Hq may then undergo the oxidation to produce non-emitting species that can act as the luminescence quenchers.

The environmental stability of the devices is a major problem for organic LEDs. The instability has been attributed to the deterioration of the organic as well as the electrode layers, and is highly dependent on the device configuration. Degradation in organic LEDs is attributed to cathode oxidation, cathode delaminating, anode species diffusion, the crystallization of the organic layers, especially the hole transport material, which can occur at room temperature and is believed to be accelerated by the Joule heat generated during device operation. Organic LEDs based on vapor-deposited Alq$_3$ thin films operated in inert atmospheres (low moisture level in this case) can be of very poor stability [23]. Therefore, among all

degradation factors, photodegradation of Alq_3 may not seriously affect the lifetime of EL devices and photodegradation of Alq_3 cannot be a dominant degradation mechanism.

4. Conclusion

We described the PL stability of neat Alq_3 thin films in the presence of atmospheric moisture under UV lamp exposure. We observed that the PL intensities and absorbance decreased with increasing irradiated times, the fluorescence decays were rapid after irradiation, and the X-ray photoemission spectra of the irradiated films changed. The photodegradation reaction was the hydrolysis and oxidation process involving water and oxygen in humid air to yield the fluorescence quenchers. These results indicated that the hydrolysis reaction and photooxidation in the presence of humid air could degrade the water- and oxygen-sensitive EL materials. The photodegradation of Alq_3 may have an effect on the performance of LEDs. Therefore, encapsulation of organic LEDs to remove water and air can enhance the lifetime of LEDs.

Acknowledgements

References

[1] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913.

[2] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539.

[3] C.W. Tang, S.A. Van Slyke, J. Appl. Phys. 65 (1989) 3610.

[4] P.L. Burn, A.B. Holmes, A. Kraft, D.D.C. Bradly, A.R. Brown, R.H. Friend, J. Chem. Soc. Chem. Commun. (1992) 32.

[5] C. Hosokawa, N. Kawasaki, S. Sakamoto, T. Kusumoto, Y. Hamada, Appl. Phys. Lett. 61 (1992) 2503.

[6] J. Ittman, P. Martic, J. Appl. Phys. 72 (1992) 1957.

[7] D. Brown, A.I. Heeger, Appl. Phys. Lett. 58 (1991) 1482.

[8] P.E. Burrows, V. Bulovic, S.R. Forrest, L.S. Sapochak, D.M. McCarty, M.E. Thompson, Appl. Phys. Lett. 65 (1994) 2922.

[9] S.A. Van Slyke, C.H. Chen, C.W. Tang, Appl. Phys. Lett. 69 (1996) 2160.

[10] T.P. Nguyen, P. Jonnard, F. Vergand, P.F. Staub, J. Thirion, M. Lapkowski, V.H. Tran, Synth. Met. 75 (1995) 175.

[11] E.M. Han, L.M. Do, Y. Niidome, M. Fujihira, Chem. Lett. (1994) 969.

[12] E.M. Han, L.M. Do, N. Yamamoto, M. Fujihira, Chem. Lett. (1995) 57.

[13] L.M. Do, E.M. Han, Y. Niidome, M. Fujihira, J. Appl. Phys. 76 (1994) 5118.

[14] M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin, T.M. Miller, Phys. Rev. Lett. 73 (1994) 744.

[15] Z.T. Kim, Appl. Phys. Lett. 67 (1995) 3420.

[16] B.H. Cumpston, K.F. Jensen, Synth. Met. 73 (1995) 195.

[17] F. Papadimitrakopoulos, X.-M. Zhang, D.L. Thomsen, K.A. Higginson, Chem. Mater. 8 (1996) 1363.

[18] F. Papadimitrakopoulos, X.-M. Zhang, Synth. Met. 85 (1997) 1221.

[19] D.L. Higginson, X.-M. Zhang, F. Papadimitrakopoulos, Chem. Mater. 10 (1998) 1017.

[20] A.Y. Sonsale, S. Gopinathan, C. Gopinathan, Indian J. Chem. 14 (1975) 408.

[21] X.-M. Zhang, K.A. Higginson, F. Papadimitrakopoulos, Mat. Res. Soc. Symp. Ser. 413 (1996) 43.

[22] R. Priestley, I. Sokolik, A.D. Walser, C.W. Tang, R. Dorsinville, Synth. Met. 84 (1997) 915.

[23] Z.L. Zhang, X.Y. Jiang, S.H. Xu, T. Nagatomo, O. Omoto, J. Phys. D 31 (1998) 32.