

P-56: Blue-green Electroluminescence from Aluminum and α -pyridoin Complex

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Abstract

A novel blue-green emitting aluminum complex was developed by employing 8-hydroxyquinoline as co-ligand for enhancement of electron transport and light emission abilities so that the electroluminescent (EL) devices do not need additional electron transport layer. The aluminum complex (PAIQ) of 8-hydroxyquinoline and α -pyridoin was synthesized. The structure of the PAIQ was elucidated by FT-IR, UV-Vis and XPS. The PAIQ complex showed thermal stability up to 350 °C under nitrogen flow by TGA. The photoluminescence (PL) was measured from solid film of the PAIQ complex on quartz substrate. The EL device was fabricated by the vacuum deposition. The device having the structure of ITO/TPD/PAIQ/Al was studied, where *N,N*-bis(3-methylphenyl)-*N,N'*-diphenyl-benzidine (TPD) was used as a hole transporting layer. The EL device emitted a blue-green light.

1. Introduction

As OLEDs have many advantages such as active emission, high brightness, low driving voltage, wide viewing angle, weight lightness and potential low cost, it is attracting much attention as a candidate for new flat panel display. These devices are injection type and the first architecture of the double-layered organic EL device was reported by VanSlyke.[1] However, there are many subjects to realize the full color displays. EL materials are divided into organic dye, metal-chelate complex and conjugated polymer.[2] The typical metal-chelate EL material is tris(8-hydroxyquinolate) aluminum (Alq₃). Many researchers have developed high performance green organic EL devices with tris(8-hydroxyquinolate) aluminum (Alq₃).[3-4] Also OLEDs have gone into the stage of practical study since Pioneer Co. reported the first commercial product of organic green EL display using small molecule.[5] However, most of the previous work on metal-chelate EL complexes have focused on the system with one kind of ligand such as Alq₃, and much less attention has been directed toward metal-chelate systems containing two different ligands.[6]

In this article, we report on a novel blue-green light emitting aluminum complex. The heterotropic organoaluminum complex synthesized from α -pyridoin and 8-hydroxyquinoline was found to show PL and EL properties. Since the Alq₃ has excellent abilities of electron transport and light emission, we have employed 8-hydroxyquinoline as co-ligand for enhancement of electron transport abilities so that the electroluminescent (EL) devices do not need additional electron transport layer. The PL and EL properties are respectively discussed from cast film and EL device which was fabricated by vacuum deposition.

2. Experimental

2.1 Materials

All the chemicals employed in synthesis were purchased from Aldrich Co. Aluminum chloride hexahydrate (AlCl₃·6H₂O), α -pyridoin and 8-hydroxyquinoline were used without further purification.

2.2 Synthesis of complexes of PAI and PAIQ

The syntheses of PAI and PAIQ were followed the procedures of closely-related literatures.[7-8] In a round bottomed flask, α -pyridoin (1.5mmol, 0.321g) was dissolved in 10ml of absolute ethanol. To the solution was added 0.4ml of pyridine. The solution was stirred at 70 °C during 20 minutes. Aqueous solution (5ml) of aluminum chloride hexahydrate (1mmol, 0.241g) was added and followed by stirring at 70 °C for 24 hour. Yellow precipitates were collected and washed by water and ethanol, and then dried in vacuum oven. PAIQ was also prepared as same procedure. The yellow precipitates were additionally washed with acetone. The complexes showed thermal stability up to 350 °C under nitrogen flow by TGA.

2.3 Instruments and measurement

UV-Vis absorption spectra were measured by a UV-VIS Spectrometer (Shimadzu UV-3100S). Fluorescence Spectrometer (HITACHI F-4500) was used for photoluminescence spectroscopy. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a DuPon 951 thermogravimetric analyzer. Differential scanning calorimetry (DSC) thermograms were taken on a DuPon 910 differential scanning calorimeter under nitrogen atmosphere at a scanning rate of 10 °C/min. FT-IR spectra were obtained with a Shimadzu 8201PC FT-IR Spectrometer using a KBr pellet. ¹H-NMR spectra were recorded on a Varian 300 MHz FT-NMR Spectrometer in methanol-d₄. X-Ray photoelectron spectroscopy (XPS) spectra were obtained on ESCALAB 250 XPS spectrometer (V.G Scientific).

3. Result and discussion

3.1 Synthesis and structure determination

The chemical structures of PAI and PAIQ were estimated from FT-IR, UV-Vis and XPS spectra. FT-IR spectra of yellow powder products of PAI, PAIQ and α -pyridoin itself are shown together in Fig. 1. α -Pyridoin itself has the enol structure due to the strong O-H-N intramolecular hydrogen bondings (Fig. 2).

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The spectroscopic data revealed that the enol form of α -pyridoin is converted to its keto isomer when aluminum metal is complexed. Although the enolic complex was kinetically favored to the keto form, the enolic structure is rearranged later to thermodynamically stable keto isomer. The conjugated carbonyl band of ca. 1690cm^{-1} , which was not seen in FT-IR spectrum of α -pyridoin itself, appeared when the complex was formed.

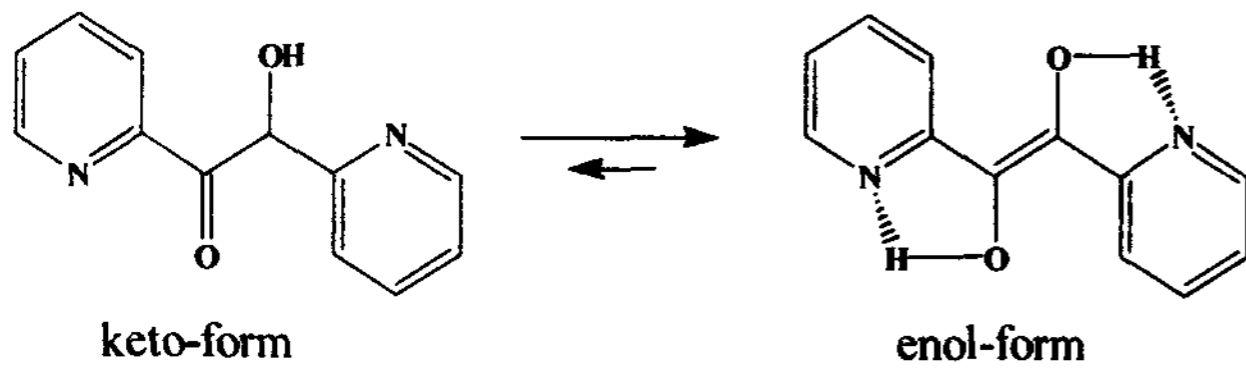


Fig. 1 Chemical structures of keto-enol tautomer of α -pyridoin

UV-Vis spectra also supported the conversion from enol to keto structure (Fig. 3). The absorption peak around 380nm , which is due to the conjugated structure of enol isomer, disappeared when the complex was formed. Al(III) reagent also has no absorption in visible region. For the quantitative analysis of the complex elements, XPS spectra were examined with considering the atomic sensitivity factor.

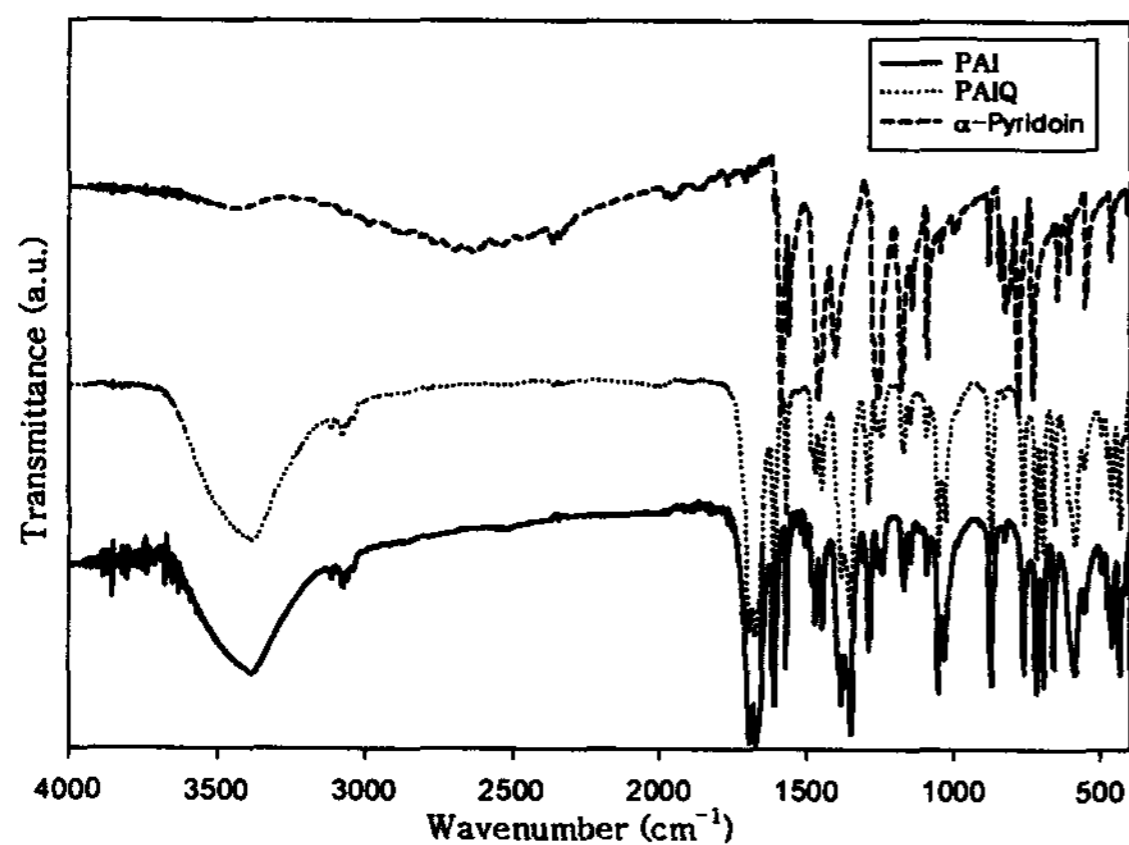


Fig. 2 FT-IR spectra of α -pyridoin, PAI and PAIQ

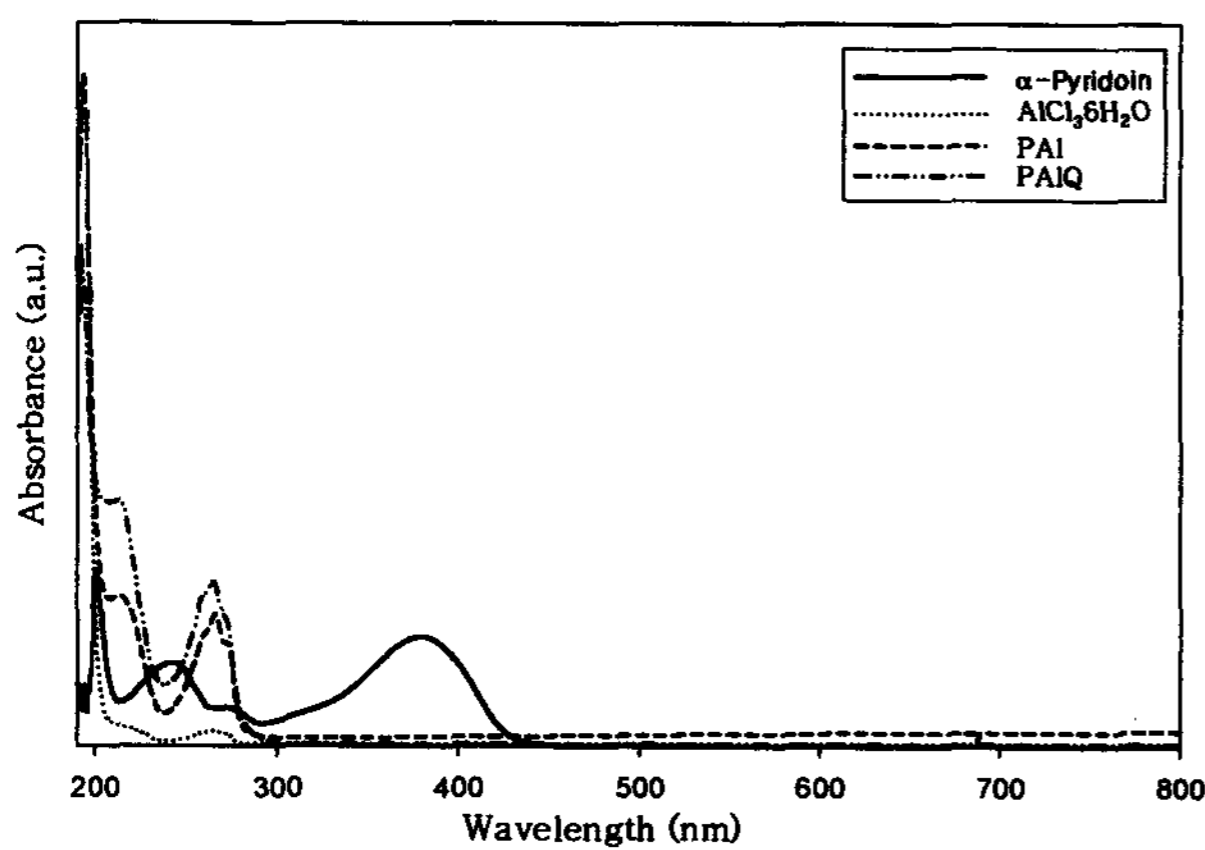


Fig. 3 UV-Vis spectra of PAI and PAIQ

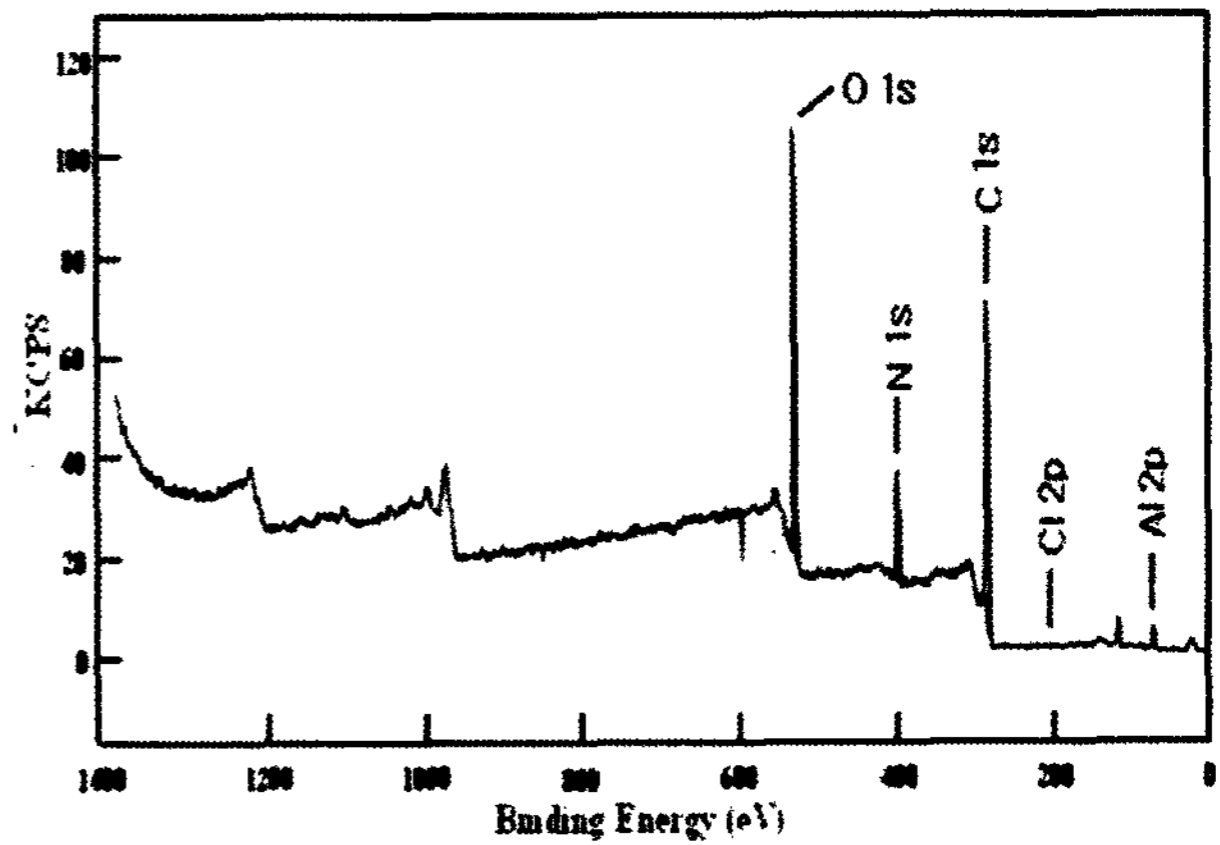


Fig. 4 XPS spectrum of PAIQ

The XPS spectra revealed the kinds of elements and also the relatively quantitative amount of the elements incorporated in the complex PAI and PAIQ. The structure determination was mainly based on the XPS data, PAI was estimated as $\text{Al}_3(\alpha\text{-pyridoin})_3(\text{H}_2\text{O})_8$. Fig. 4 shows the XPS spectrum indicating the kinds of elements C, N, O, and Al composing of PAI. From the binding energies of Al and O in each XPS spectrum, we could also confirm that there exists coordination bond between aluminum and oxygen atoms.

3.3 Photoluminescence Property of PAIQ

The PL spectra of the complexes PAI and PAIQ are shown in Fig. 5. The PL spectra are measured on solid films deposited on a quartz substrate. The PAI and PAIQ film strongly emitted blue-green light around 490nm when excited by UV light of 260nm (Fig. 5). The broad emitting band of PAI seems to be composed of three kinds of different peaks. Although the broad band should be explained by complexity of PAI structure, the characterization of each band could not be done at this point. Both PAIQ and PAI complexes indicated same maximum peak at 490nm . But the PAIQ showed much narrow and simplified emission peak. The emission pattern of PAI and PAIQ together with the spectroscopic analysis on the chemical structures led to the suggestion of the coordination structures. The pyridyl N and the nearest O are thought to become the ligands to Al^{3+} . The strong fluorescence seems due to the formation of stable bonds together with the N and O ligands as demonstrated in Alq_3 .

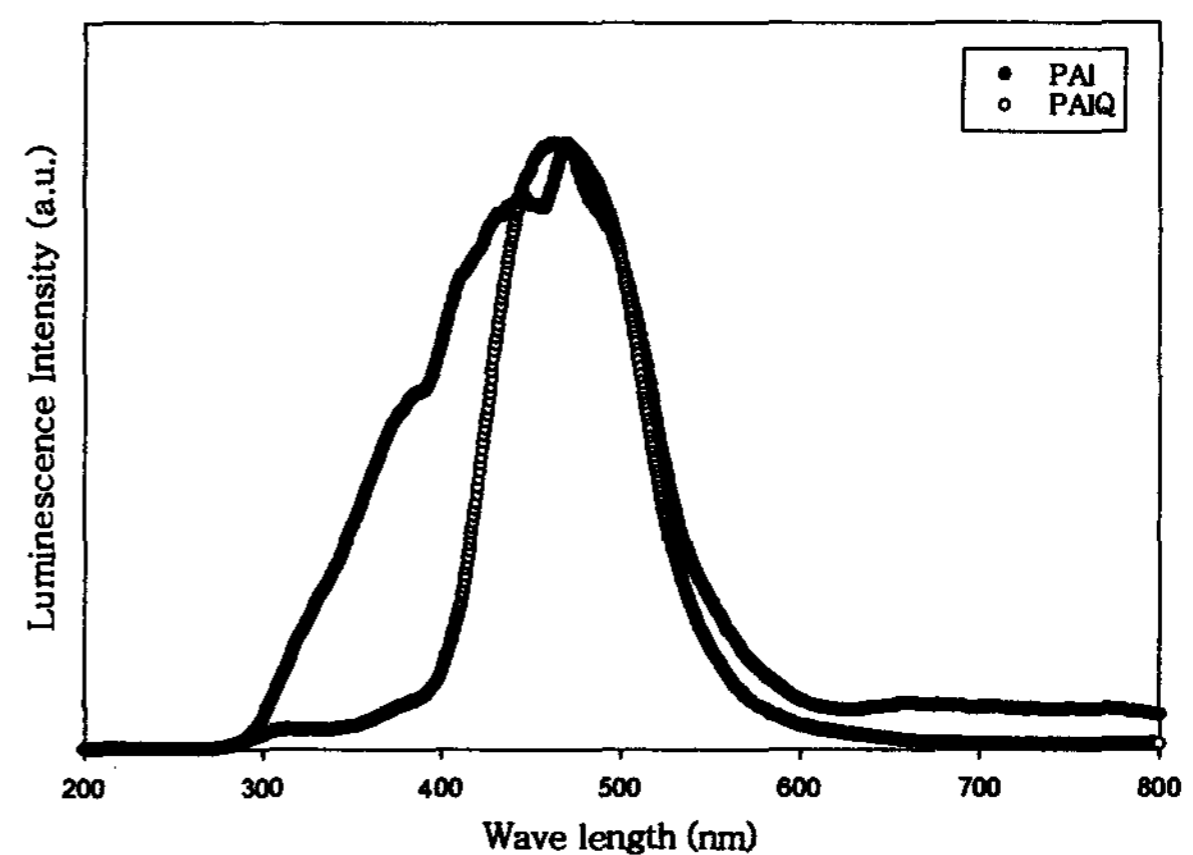


Fig. 5 PL spectra of PAI and PAIQ in solid film excited by 260nm UV-light

3.4 Electroluminescence property of PAIQ

Electroluminescent (EL) devices having the structure of ITO/TPD/PAI/Al were fabricated by vacuum deposition, where *N,N*-bis(3-methylphenyl)-*N,N*-diphenylbenzidine (TPD) was used as a hole transporting layer. Simple two-layer structure consisting of TPD hole transport layer (40nm) and PAI emitting layer (60nm) was used in this study. In order to improve hole injection efficiency a hole transporting layer was needed.[9] TPD has LUMO and HOMO values of -2.2V and -5.4eV , respectively. All layers were continuously deposited under a vacuum of 1×10^{-7} torr without vacuum interruption.

The EL spectra were plotted in Fig. 6. PAI and PAIQ showed maximum intensities at different positions. The PAI device indicated blue-green emission at 475nm. When compared to the PL spectra, the maximum wavelength was red-shifted about 5nm in EL spectra. And PAIQ EL device indicated blue-green emission at 504nm, in this case, about 34nm was red-shifted compared to the PL spectra.

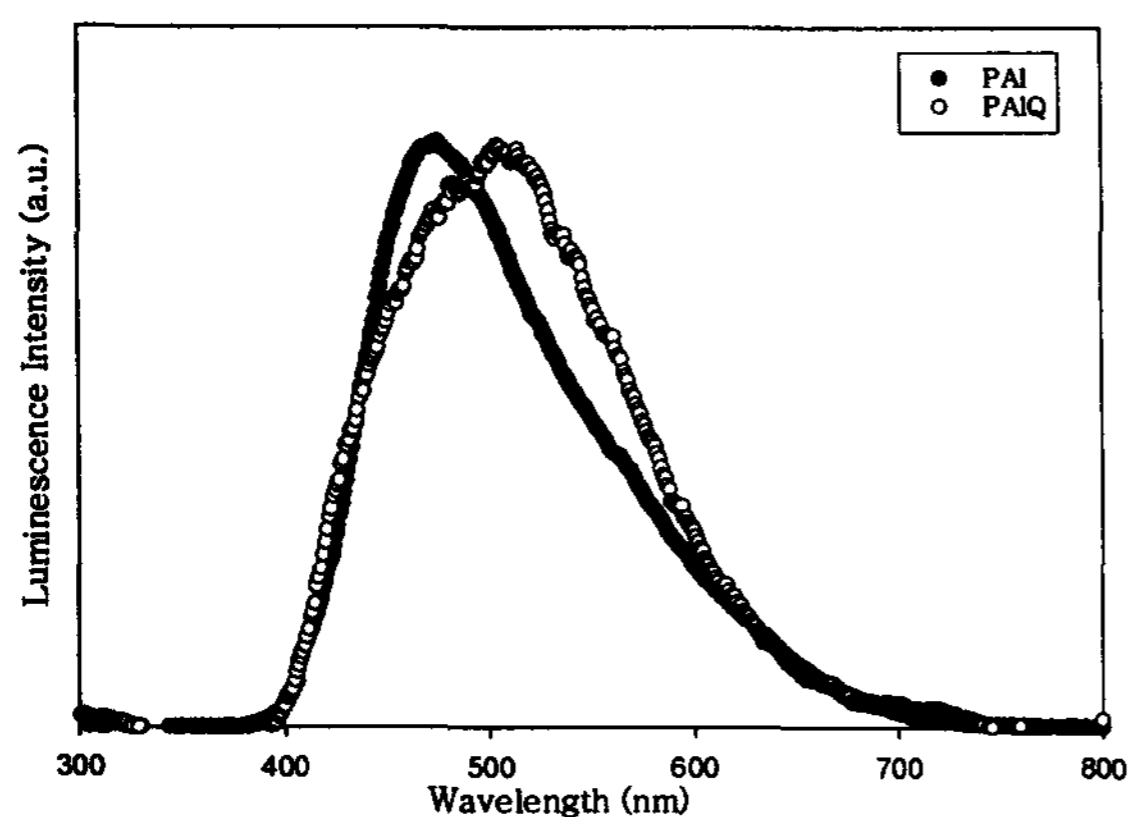


Fig. 6 EL spectra of ITO/TPD/PAI/Al and ITO/TPD/PAIQ/Al devices

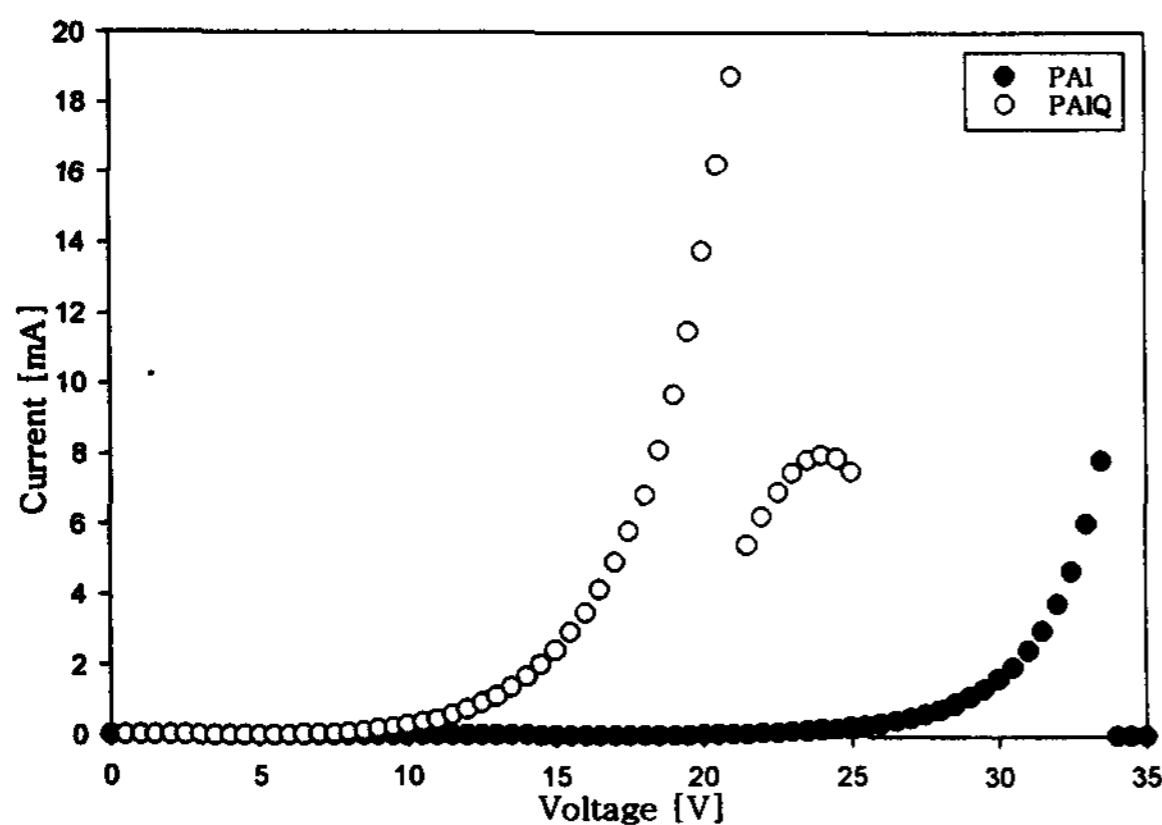


Fig. 7 Current-voltage relations in ITO/TPD/PAI/Al and ITO/TPD/PAIQ/Al devices

Fig. 7 shows the current-voltage characteristics of the PAI and PAIQ devices. In the PAI device, the turn-on voltage was about 22V. The maximum current was found to be $8\text{mA}/\text{cm}^2$ at 34V. But PAIQ device starts current flow below the turn-on voltage of PAI device. The turn-on voltage was about 8V and current intensity was $19\text{mA}/\text{m}^2$ at 21V. There are two tentative explanations on the lowered turn-on voltage. One is that there is lowered energy barrier between the electrode and charge injection layer. And the other is that the lowered energy gap

between LUMO of ITO anode HOMO of Al cathode. On the other hand, this may be caused by the difference of the charge carrier mobility in the PAI and PAIQ films. When the bias voltage exceeded the turn-on voltage, EL intensity was exponentially increased along with the bias voltage.

The brightness increased with the voltage applies (Fig. 8). The maximum brightness of the PAI device was $38\text{cd}/\text{m}^2$ at threshold voltage of 34V. Compared with PAI device, the PAIQ device showed weak brightness of $9\text{cd}/\text{m}^2$. Although the PAIQ device started current flow earlier than PAI device, brightness did not go up to that of PAI device.

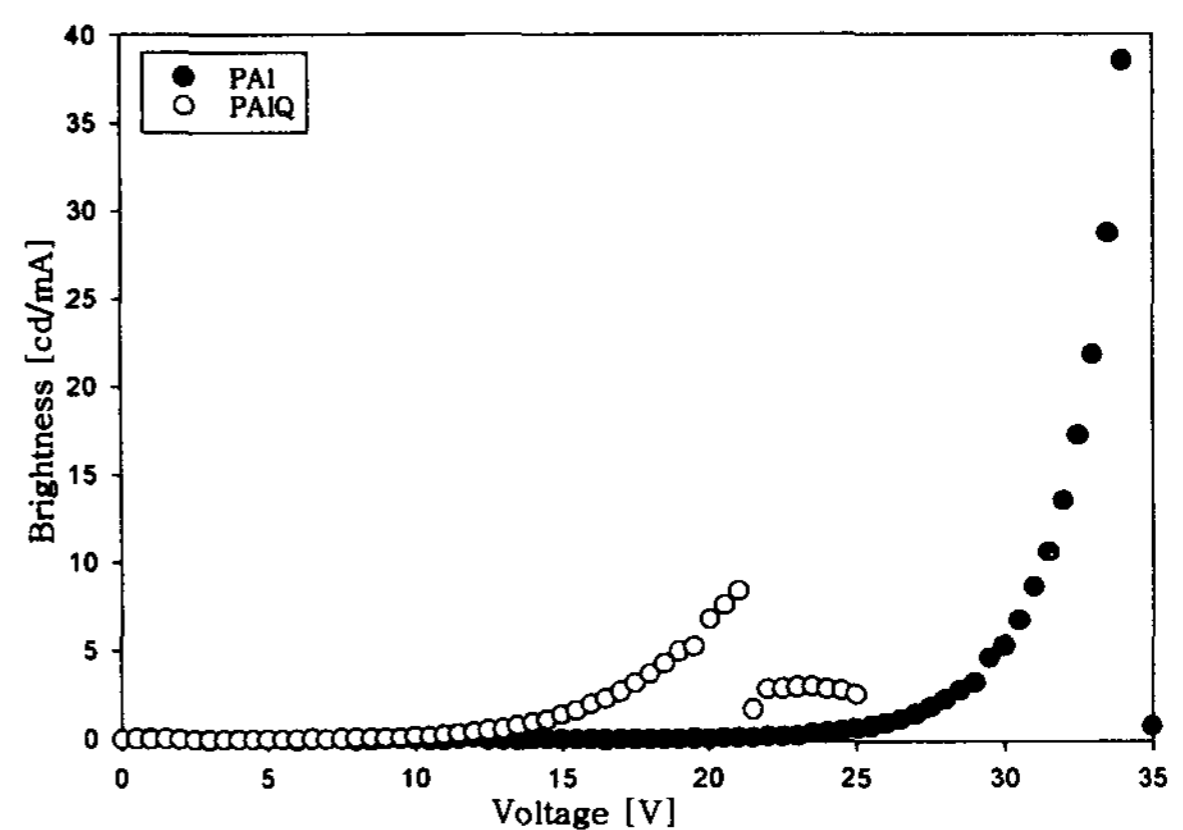


Fig. 8 Brightness-voltage relations in ITO/TPD/PAI/Al and ITO/TPD/PAIQ/Al devices

4. Conclusion

We have demonstrated the blue-green EL emission from newly synthesized aluminum complexes using α -pyridoin and 8-hydroxyquinoline as ligands. By introducing 8-hydroxyquinoline as co-ligand of α -pyridoin, the PAIQ complex showed lower turn-on voltage than the PAI complex. However, the PAIQ EL device should be improved for achievement of high brightness. The attempts to improve EL efficiencies are in progress. To facilitate hole injection from anode, PEDOT will be inserted between the hole injection electrode and TPD as the hole transport layer. And α -pyridoin complexes containing other metal ions will be investigated for EL materials.[10-12]

Acknowledgements

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