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Fabrication of a white organic light-emitting device with single liq:rubrence luminescent layer[*]

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A kind of white OLED with single luminescent layer was designed, in which rubrene was doped in Liq. The structure of the devices is ITO/PVK:TPD/Liq: Rubrene/Alq3/Al. The brightness of the devices comes to 3120 cd/m^2(at a driving voltage of 25 V), the CIE coordinates of the typical devices is (0.308,0.347), and the coordinates is very close to the white equi-energy point. The emitting and luminescent characteristics of the devices were discussed.

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Since the white OLED was reported in 1994 by J, kido .etc [1], the research of white OLED has attracted considerable interest due to their various advantages, such as, high brightness, wide visual angle and fast response. As a new organic semiconductor solid state lighting display device, it can be used as a backlight of LCD. Many methods such as dye codope[2], multi-layer structure[3], polymer mixer[4], quantum well structure[5], exciplex luminescence[6], cavity effect [7] and white-light-emitting materials[8] are used to fabricate OLED.

White OLED of adopting dye is a kind of device with monolayer structure. The white light in this device is formed by mixing the light of matrix and dye through energy transfer, which is different from traditional single ETM OLED. There are many advantages using this structure, such as reducing the complexity of fabrication and luminescence quenching of dye, high brightness and efficiency of the device. The Commission International De L'Eclairage(CIE) coordinate is near (0.33, 0.33). And the CIE coordinates varies little while the drive-voltage changes.

In this paper, white OLED is triumphantly fabricated using dye doping method. Liq is used as the main body of luminescence material, which is straw yellow powder small molecule complex, with the heat-stability and the characteristics of thermal resistance[9-10], film-forming, and good vacuum sublimation. So Liq is a kind of material with well blue-light emitting. The HOMO and LUMO levels of Liq are 5.8 ev and 2.8 ev[11]. White OLEDs with a single layer consisting of an orange-red dopant 5,6,11,12-tetraphenylnaphthacene (rubrene) and a blue light emitting material 8-hydroxyquinoline lithium (Liq) mixed with a certain proportion are fabricated.

The chemical structures of the organic materials in experiments such as poly(N-vinylcarbazole)(PVK), N,N'-Dipheny-N,N'-bis (3-methylphenyl)benzidine, tris-(8-hydrox-yquinoline) aluminum(Alq3),5,6,11,12-tetraphenylnaphthacene (rubrene) and 8-hydroxyquinoline lithium (Liq) are shown in Fig.1.

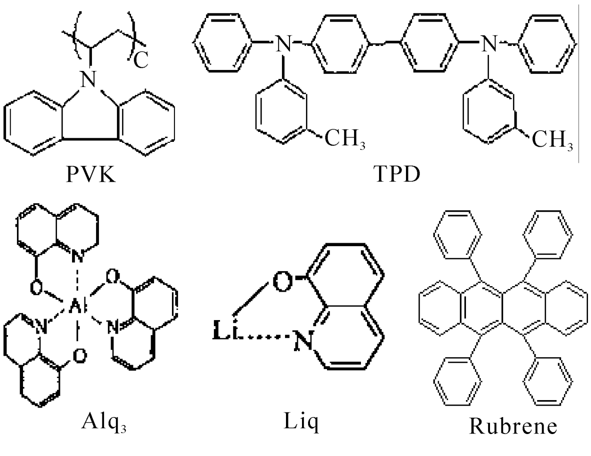

Fig.1 Chemical structures of the organic materials used

The structure of the device is ITO (150 nm)/PVK:TPD (80 nm)/Liq: Rubrene(50 nm)/Alq$_3$ (30 nm)/Al(100 nm). There are five parts. The transport material of hole is made from the mixture of PVK and TPD. The radiation layer and electronic transport layer are made from Liq:Rubrene and Alq$_3$. The anode is ITO. The cathode is Al. The process electric glass, which is daubed on the surface with ITO (interfacial resistance is about 70 Ω/□),is prepared using the methods of spin coating and evaporation coating. Also,Liq and rubrene

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with different mass concentrations is mingled. The structure of the device is showed in Fig.2.

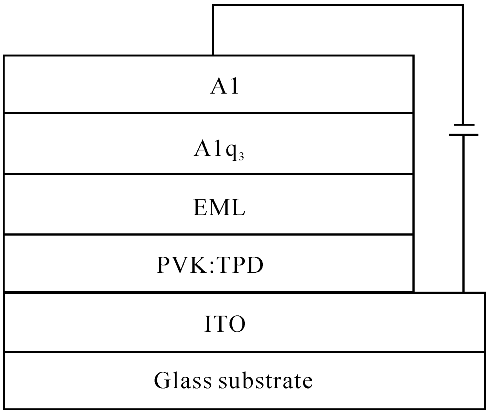

Fig.2 The structure of device

Under laboratory conditions, first, we throw the glass uropatagia covered with ITO film into deionized water with detergent added. After the water is boiling for several minutes, take out the uropatagia and make sure that the glass uropatagia is well swilled out by means of cold deionized water. Second, the ultrasonic cleaning is implemented to the uropatagia with acetone, grain alcohol and deionized water, respectively. Then, put the uropatagia into vacuum chamber after cleaning it with deionized water and drying it. Mix PVK with TPD [12], dissolve the mixture in vacuum chamber (the consistency is about 10~20 mg/ml), form a film onto the uropatagia using spin coating. In order to acquire white electroluminescence more close to ideal white color with the coordinates, we drop Rubrene into Liq with different mass percent (shown in Tab.1). It is difficult to control the proportion of mixture when we use the method of vapor deposition to form luminous layer, so we confect the mixed solvent (the consistency is about 10 mg/ml) with Liq, Rubrene and tetrahydrofuran solution, and form film with spin coating. The rate of spinning is about 1000-2000 rmin/n, the spinning-time is 20~30 s. Because Alq_3 and Al are materials with good thermal stability, evaporation coating is better way to form films. The thicknesses of all films are measured by elliptical polarization spectrograph. The degree of vacuum is lower than 2×10^{-3} Pa in experiments.

Based upon the color mixture principle, the CIE coordinates of mixed color is on the line of the two colors. White organic light emitting devices with different mass concentrations of rubrene (4%, 6%, 8%, 10%) have been successfully fabricated. The structure of these devices is ITO/PVK:TPD/Liq:Rubrene/Alq_3/Al.Fig.3 shows the electroluminescence (EL) spectra of these devices under the drive voltage of 18V. In the figure,the two peaks of devices with these doping concentrations of 4%, 6% and 8% are located at about 482 and 563 nm respectively, which correspond to the characteristic luminescence of Liq and rubrene. There is a shoulder peak of rubrene located at 613 nm. As the doping concentration of rubrene decreases from 8% to 4%, the blue color component of Liq becomes stronger in the EL spectra, which indicates that white electroluminescence can be gotten and improved through adjusting the doping concentration.

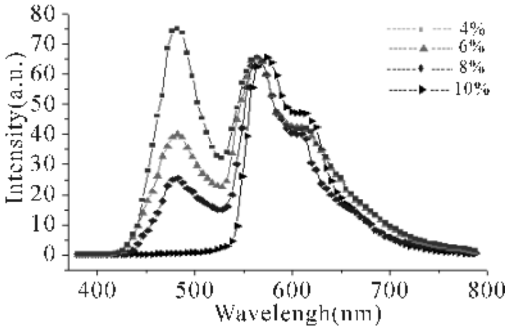

Fig.3 EL spectra of devices with different concentration

Meanwhile, it is found that there is no luminescence component of Liq when the concentration of Rubrene is 10%. The luminescence is all from rubrene molecular, of which the peak is located at 576 nm. It shows that there is a complete energy transfer between Liq and rubrene.

The relative intensity of blue emission was basically equivalent to the orange-red emission when the concentration of Rubrene is 4%, and white light is obtained if mixing the two colors. The best CIE coordinate is (0.308, 0.347), which is close to ideal white color with the coordinates of (0.33, 0.33). As shown in Fig.3, the spectra are composed of the two colors.

Tab.1 shows the CIE coordinates (1931) of devices with different mass concentrations of rubrene under the drive voltage of 18 V.

Tab.1 The CIE coordinates of devices with different concentrations

Mass concentrations	CIE (1931) coordinates	
	x	*y*
4%	0.308	0.347
6%	0.329	0.433
8%	0.359	0.497
10%	0.436	0.502

The energy level structure of device is shown in Fig.4. During the process of the electroluminescence, holes or electrons are captured by adulterant as a kind of trap. When electric current goes through device, the hole or electron is captured and exciton is formed with the contrary carrier. To form exciton, the HOMO level of the dopant must be higher than that of main material, or the LUMO level of the dopant must be below that of main material[13]. In the figure, the LUMO level of Rubrene is below the levels of Liq and Alq_3, and the HOMO levels of them are near together, so the electrons are captured by the Rubrene molecules easily.

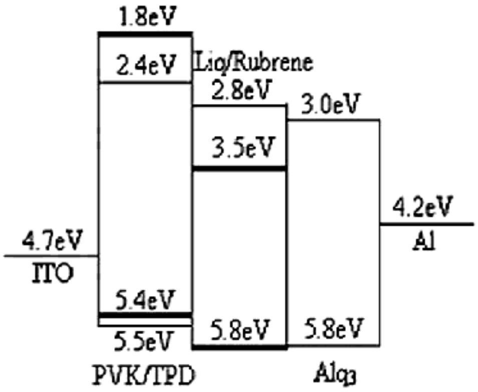

Fig.4 Energy band diagram of device

The electrons from Al cathode entering the LUMO level of Rubrene are much easier than that of Liq, which result in the electron concentration on LUMO level far higher than that of Liq. The electrons can stay a long time because of the big space between the molecules of Rubrene, and form excitons with the holes from PVK:TPD layer. The holes from anode entering the HOMO level of Rubrene is the same easy as that of Liq, and the probability of combination between holes and electrons of Rubrene is bigger that of Liq. The luminescence is all from rubrene molecule when the doping concentration is increased to a certain value (such as 10%); both Liq and Rubrene can emit light simultaneously as the mass concentration decreased below 10%. Therefore, the right doping concentration of rubrene is very important to acquire white electroluminescence more close to ideal white color with the coordinates of (0.33, 0.33).

In the doped device, the energy transfer is occurred during the excition of guest molecules. The theory of Förster exciton energy transfer is used to explain luminescence of doping molecule in the host transport material. The characteristic parameter of this theory is Förster critical transfer radius Ro. There is a larger value of Ro when the overlap of the EL spectrum of doper and the absorption spectrum is broader, so the efficiency of Förster energy transfer is higher. The EL spectrum of Liq and absorption spectrum of Rubrene are shown in Fig.5. From the figure, it is found that Rubrene is a good energy accepter for Liq because of the broad overlap between the Liq emission spectrum and Rubrene absorption spectrum. Consequently, it is easy for energy transfer. Many electrons from Alq_3 layer get across the potential barrier and enter the LUMO level of Liq, at the same time some electrons from the Rubrene enter the LUMO level of Liq under the acceleration of electric field. These electrons form excitons with holes on HOMO level of Liq from HTL. Most energy transfers from excited Liq molecules to Rubrene through interacting resonante of dipole-dipole, and Rubrene excitons are formed. The Rubrene molecular emission is composed of these excions and that from carriers captured. There is also a little Liq molecular emission from the Liq excitons. Consequently, the EL spectra are mainly Rubrene emission even in relatively light doping. Nevertheless, in very tiny doping, both Liq and Rubrene can emit light simultaneously, and the proportion of the corresponding spectra varied with the changing of concentration of Rubrene in Liq.

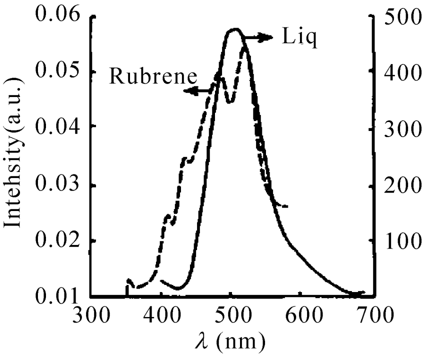

Fig.5 EL spectrum of Liq and absorption spectrum of Rubrene

The characteristics of current-voltage (*J*-*V*) and luminescence-voltage (*L*-*V*) of device with the concentration of 1.1% are analyzed below. Fig.6 shows the characteristic of current density-voltage. In the figure, the current density is increased with drive voltage, which shows a diode characteristic. The characteristic of luminescence-voltage is shown in Fig.7. From the figure, we found that the open volt-

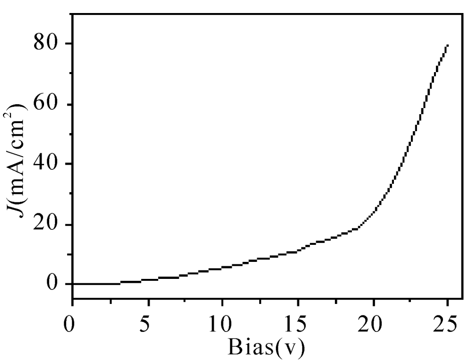

Fig.6 Current-voltage curve of device with 4% Rubrene concentration

age is 8 V, and the luminescence brightness of device is 3120 cd/m^2 when the drive voltage increases to 25 V.

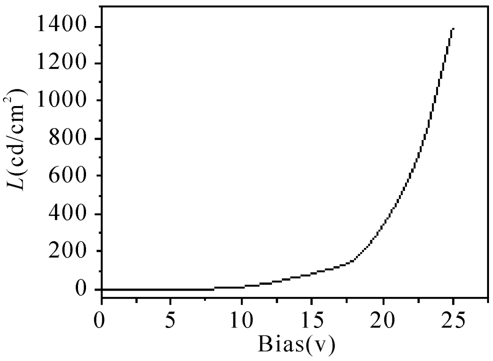

Fig.7 Brightness-voltage curve of device with 4% Rubrene concentration

Four white organic light emitting devices with different mass concentrations of rubrene (4%, 6%, 8%, 10%) have been successfully fabricated. When the mass concentration is 4% and the thickness of luminous layer is 50 nm, the white light device is obtained with the best CIE coordinate of (0.308, 0.347). The open voltage is 8 V, and the luminescence brightness of device is 3120 cd/m^2 when the drive voltage increases to 25 V. We also analyze the light characteristic of devices with different doping concentration. The structure of this device is simple. The fabrication technology of this device is also easier. The problem of self absorption in multilayer device has been avoided availably. The performance of white OLED has been improved obviously.

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