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Observation of Photovoltaic Effects in Bright Red Organic Electroluminescent Diodes Doped with Red Dopant *

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Photovoltaic (PV) effects for red bright organic light-emitting diodes (OLEDs) in which the red light emitted from the dopant 4-(dicyanomethylene)-2-t-butyl-6- (1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) have been observed. The OLEDs show organic photovoltaic properties. At the optimum doping concentration, the main eletroluminescence parameters including the maximum brightness and the maximum luminous efficiency under current density of 20 mA/cm^2 are 3280 cd/m^2 and 1.54 cd/A, respectively. When irradiated by a 365-nm UV-light (4 mW/cm^2), the device exhibits the PV parameters of the open-circuit voltage 1.4 V, short-circuit current 2.9 μA/cm^2, fill factor 0.22, and power conversion efficiency 0.022%. Effects of every organic layer, especially the doped DCJTB on the PV performance, are also discussed. It is expected that the research for the PV property of the small molecular doping OLEDs will be of benefit for flat panel display technology in the future.

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Organic light-emitting diodes (OLEDs) constitute a rapidly developing field, which have potential applications in the future of flat panel display technology.[1,2] Some focus on conjugated organic polymers[3,4] and others focus on small molecular materials.[5−8] In an electroluminescent (EL) process, an electron and a hole recombine to form an exciton described as an electron and hole pair loosely bound to each other by their Coulomb attraction; they must release their excess energy in the form of visible light, or luminescence when they meet and then radiate. In the meantime the organic photovoltaic (OPV) cells have obtained rapid progress because OPV cells can be made lightweight and at low cost compared with inorganic PV ones. In a PV process, excitons are formed under a suitable illumination and dissociated by an inner electric field or by charge transfer to a nearby donor or acceptor at the interface between two organic layers. The field pushes the holes toward the anode, the electrons toward the cathode. Those carriers reaching the electrodes provide a voltage that could be used in photo-electric conversion applications ranging from photodetectors to solar cells. Most studies have focused on conjugated polymer.[9−11] Much attention has also been paid to small molecules recently.[12,13] Our group has first reported the OPV cell with rare earth complex,[14] which shows EL emission when driving by forward bias. Hong *et al.*[15] also reported an OPV cell made from small molecular materials, which shows EL emission when driving by forward bias. Both these studies emphasize the effect of the exciplex formation, which is a transient donor–acceptor complex between an excited state and a ground state, on PV properties. The EL emissions of their devices come from exciplex formation and thus the luminous efficiencies are too low to have practicality for flat panel display technology. PV properties of the bright doping organic small molecular EL devices which may be used for flat panel display technology have not yet been reported so far.

In this Letter, PV properties for bright red OLEDs in which the red emission results from the doped 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4 *H*-pyran (DCJTB) dye are investigated. The PV properties of the red EL device under illumination of 365 nm UV light are demonstrated to be from the interface between N,N′-diohenyl-N,N′-bis (1-naphthyl-(1,1′-biphenyl)-4,4′-diamine (NPB) and 8-hydroxyquinoline aluminium (Alq_3), and it is independent of DCJTB and copper phthalocyanine (CuPc), which plays a very important role for the EL performance.

The configuration of the diodes and the chemical structure of the materials used in this study are shown in Fig. 1. The organic materials were obtained commercially. For comparison, the EL devices doped with 3 wt.%, without DCJTB, and doped with 8 wt.% were named as device A, device B, and device C, respectively. The ITO-coated glass has a sheet resistance of 100 Ω/sq. The substrates are pre-cleaned by ultrason-

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ication in alcohol and acetone, respectively, and then irradiated by a UV–ozone lamp in a chamber. CuPc and NPB were used as hole-injection layer and hole-transport layer, Alq_3 and red dye DCJTB were used as host and red dopant in the emitter layer, LiF and Al were used as the cathode buffer layer and the cathode layer, respectively. They were deposited by vacuum evaporation in a chamber pressure of about 10^{-6} Torr at a rate of 2 Å/s. The film thickness was monitored in vacuo with a quartz crystal monitor. The devices were encapsulated under dry nitrogen and all the performance measurements were carried out under ambient atmosphere. The active area of device is 15 mm^2. The absorption spectra were measured with a Shimadzu UV-3000 spectrophotometer. The EL spectra, the Commission Internationale de L'Eclairage coordinates (CIE) were measured with a Hitachi MPF-4 Fluorescence spectrophotometer. The current was measured by a C63-type current meter, and the brightness was measured by a 1980A spot photometer. The spectral response curves of the OLEDs were determined by illumination with different wavelengths at a constant power density of 40 $\mu W/cm^2$ (Xe lamp). The incident light for PV measurement was admitted through the glass/ITO side.

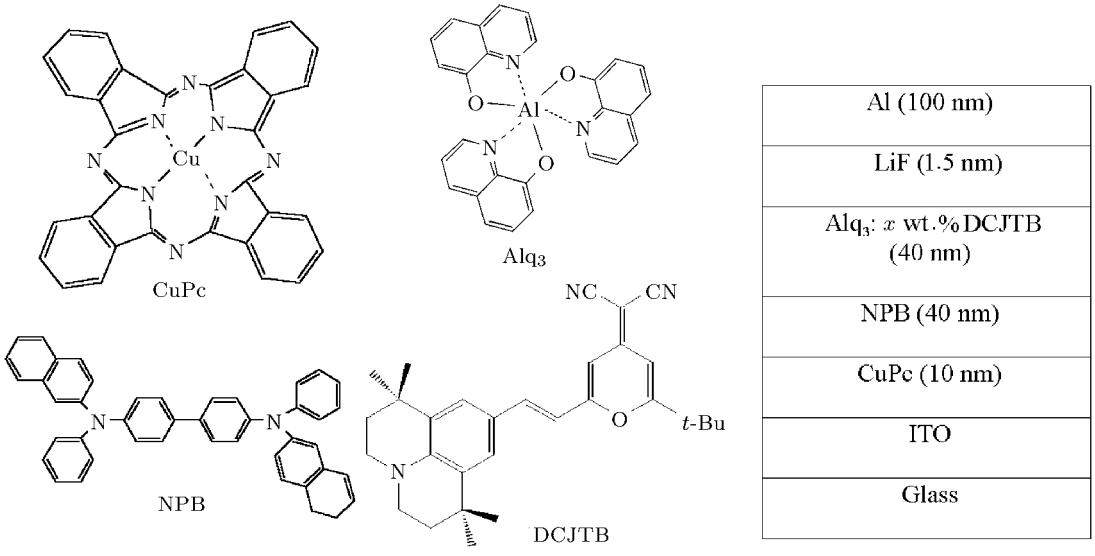

Fig. 1. Chemical structures of organic materials used and device structure.

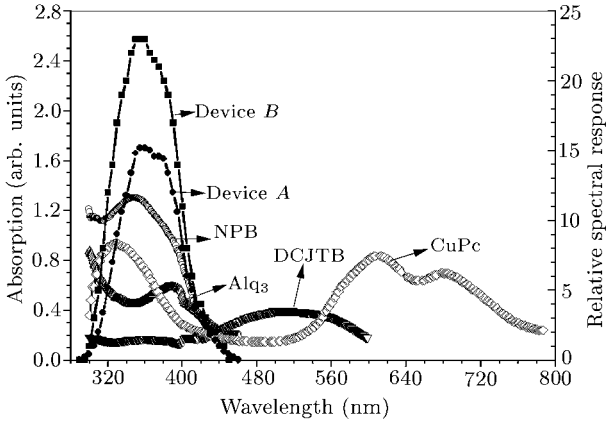

Fig. 2. Photovoltaic spectral response of device A (closed circles) and device B (closed squares), and absorption spectra of the NPB film (open circles), Alq_3 film (open up-triangles), DCJTB film (down-triangles), and CuPc film (diamonds).

Figure 2 indicates the PV spectral response curves of devices A and B together with the absorption spectra of CuPc-, NPB-, Alq_3-, and DCJTB-film, respectively. The PV response curve of device C is not shown in Fig. 2 but the shape of the PV response curve for device C is the same as that of device A though the relative intensity is different. It can be seen from Fig. 2 that the PV responses of these devices are mainly in the UV region, so a 365 nm UV light (4 mW/cm^2) was introduced for the study of PV properties of these OLEDs. Comparing the spectral response curve with absorptions of the NPB film and the Alq_3 film and the difference between the absorptions, it is noticed that the PV responses correspond to both the films and the contribution of the NPB layer to the PV effects is larger than that of the Alq_3 layer due to the fact that the NPB layer has absorption stronger than that of the Alq_3 layer.

The EL parameters including the maximum EL emitting peak, luminous efficiency, CIE, and maximum brightness, and the typical PV parameters including the opencircuit voltage V_{oc}, short-circuit current I_{sc}, fill factor (FF), and power conversion efficiency η of the devices are listed in Table 1. It is obvious that the device with 3-wt.% DCJTB displays a high luminous efficiency (1.54 cd/A under current

density of 20 mA/cm^2) and the maximum brightness 3280 cd/m^2 along with a better colour purity (x = 0.612, y = 0.381). The diode can also show the previous PV effects when illuminated with the UV light. The device exhibits V_{oc} = 1.4 V of, I_{sc} = 2.9 μA/cm^2, and I_{sc} = 0.022%, under illumination of 365 nm UV light (4 mW/cm^2). From Table 1 it is also noticed that as DCJTB content increases up to 8 wt.%, the device exhibits lower EL performance and PV properties are comparable with the 3-wt.% DCJTB doping diode. The maximum EL brightness and luminous efficiency of device C decrease to about 10% compared to those of device A. The lower EL performance of device C compared with device A should be attributed to the concentration quenching mechanism of DCJTB. For the PV performances of device C, I_{sc} and η decrease to half of those of device A, whereas V_{oc} increases slightly. For the undoped DCTTB, the device shows relatively high PV properties, and I_{sc} increases about twice and η increases about 1.7 times of those of device A. This indicates that DCJTB is an important factor on PV properties of the OLEDs. The reason will be discussed in the following.

Table 1. The main parameters in comparison of EL and PV among devices A–C.

Parameters	Device A	Device B	Device C
EL[a] peak (nm)	621	521	641
CIE[a] (x, y)	(0.612, 0.381)	(0.295, 0.537)	(0.657, 0.537)
Maximum brightness (cd/m^2)	3280	> 6000	230
Luminescence Efficiency[b] (cd/A)	1.54	2.56	0.19
V_{oc}^{c} (V)	1.4	1.2	1.7
I_{sc}^{c} (μA/cm^2)	2.9	8.7	1.3
FF[c]	0.22	0.23	0.20
η^{c}	0.022%	0.060 %	0.011%

[a]Driving voltage: 8 V
[b]At current density of 20 mA/cm^2
[c]Simulated 365 nm UV-light illumination: 4 mW/cm^2

In our EL devices, the thin layer of CuPc inserted between the NPB and ITO layers acts as a hole injection layer so that it can balance the injected electrons and holes better, and thus increase the EL efficiency. In order to observe the contribution of the CuPc layer to the PV effects in either the undoped device or the DCJTB-doped devices, the PV spectral responses in the range of λ = 200–750 nm of the three devices were measured. Although the relative spectral responses of the three devices in λ = 200–750 nm were tested, the PV response in λ = 550–750 nm of the three devices, which corresponds to the absorption of CuPc, was not observed, Even though the thickness of CuPc increases to 40 nm and the thicknesses of the other function layers are kept constant, no PV response in λ = 550–750 nm was observed too, implying that the CuPc layer has no PV contribution to the devices. It may be reasonable that, although the photo-generated excitons can be generated in both the CuPc layer and the NPB layer by absorbing UV light, the excitons could not be dissociated at the CuPc/NPB interface because the interface is not taken as the location of active site due to the electron-donor function of both the CuPc layer and the NPB layer. Thus excitons generated from the CuPc layer were only decayed among the CuPc layer, so excitons created in the NPB layer can only be diffused to the interface between the NPB- and DCJTB-doped (or no-doped) Alq_3 layer where the NPB excitons were dissociated because NPB and Alq_3 acted as the electron donor and the electron accepter, respectively. Thus in our three-layer devices A–C, contribution of the CuPc layer to the PV effects should not be observed though the CuPc layer has played an important role in the two-layer PV device [16] and the three-layer PV device.[13]

Although there is a stronger absorption of DCTTB at about 515 nm compared to that in the UV region λ = 300–450 nm, the PV effects of devices A and C at about 515 nm have not yet observed. Thus, we believe that the generated excitions of DCJTB in devices A and C can be decayed and cannot be dissociated at the NPB/(Alq_3:DCJTB) interface and thus have no contribution on the PV performance. In order to investigate further the effect of the DCJTB excitons on the PV properties, the device with the structure of ITO/CuPc(10 nm)/NPB(40 nm)/DCJTB(40 nm)/LiF (1.5 nm)/Al(100 nm) was fabricated, that is to say, the whole layer near NPB is DCJTB. The device did not show either PV performance or EL emission when illuminated by UV light or driven by a forward bias, respectively. Therefore, we believe that DCJTB possesses bad electron mobility and is a poor electron-accepter.

When devices A and C were illuminated by UV light, only the excitons generated from NPB and Alq_3 can diffuse to the NPB/(Alq_3:DCJTB) interface, where is a region of active site for dissociation of the excitons, thus the photon-generated electrons are transported from the Alq_3:DCJTB layer and collected by the LiF/Al electrode, and photon-generated holes are transported from the NPB layer and the CuPc layer towards the ITO electrode. Thus it is implied that the contacting interface of NPB molecules with Alq_3 molecules mainly contributes to the PV performance. The excitons of both CuPc and DCJTB did not give any contribution to the PV performance. From the EL mechanism of devices A and C we know that the doped DCJTB molecules in Alq_3 host can absorb energies from the Alq_3 excitons and emit red light, so the energies of the Alq_3 excitons which were excited by UV light can also be adsorbed by DCJTB molecules, and DCJTB molecules and Alq_3 molecules at the same layer, so the doped DCJTB molecules in devices A and C can quench the Alq_3 excitons and thus reduce the dissociated quantities of

the Alq_3 excitons in the Alq_3:DCJTB layer. Because of poor electron mobility of DCJTB molecules, when the doped concentration of DCJTB was increased, the transporting rate of photon-generated electrons in the Alq_3:DCJTB layer was also reduced and thus induced the photocurrent decreasing obviously; meantime the resistance of the device increases remarkably. Therefore, device C shows remarkably relatively lower I_{sc} and slightly higher V_{oc} than those of device A.

In summary, red EL devices which DCJTB acted as dopant have been fabricated, with suitable concentration of 3-wt.% DCJTB. The EL peak, the maximum luminance and the luminous efficiency under current density of $20\,mA/cm^2$ of the device are 621 nm, $3280\,cd/m^2$, and 1.54 cd/A, respectively. Under illumination of 365 UV light ($4\,mW/cm^2$), the device shows the PV properties of the open-circuit voltage 1.4 V, short-circuit current $2.9\,\mu A/cm^2$, and power conversion efficiency 0.022%. It was found that the CuPc layer where the generating excitons can dissociate and thus directly contribute to PV performance in the previous PV devices can play only a role for the hole-transporting layer on PV performance in our EL diodes. In the future, it will be possible to benefit from the PV properties of the EL devices. When the EL devices are used as displays, they can be charged by solar energy by adscititious apparatus in chitchat for the driving of the EL display.

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