

Alternating current organic light emitting diodes based on polymer heterojunction

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Most alternating current (ac) polymer EL (electroluminescent) devices to date are based on symmetrical structure. Here novel alternating current EL devices with asymmetric structure are successfully fabricated by using a hole type polymer PDDOPV [poly (2,5-bis (dodecyloxy)-phenylenevinylene)] and an electron type polymer PPQ [poly (phenyl quinoxaline)]. We report that performance of polymer devices with heterojunction in ac operation is not so sensitive to thickness of the two polymer layers as in direct current (dc) operation. This new advantage of ac operation mode over dc means easy production and cheap facilities in large-scale production in the near future. Different emission spectra are obtained when our ac devices operate in ac mode, forward and reverse bias. Emission spectrum at reverse bias includes two parts: one is from PDDOPV, the other is from PPQ.

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Since the initial discovery of the electroluminescence in PPV [poly(p-phenylenevinylene)]^[1], polymer EL devices have been widely investigated owing to their potential applications in high efficiency, low drive voltage, large-area and full-color flat-panel displays^[2], especially the improvement of operational stability^[3-5]. Recently, ac LEDs (light emitting diodes) have attracted much attention because of their unique operation mode^[6,7]. All the ac LEDs have symmetrical structure.

There are at least two important advantages in ac organic LEDs. First, the transportation of charge carriers in organic semiconductor is realized by the redox reaction of organic molecule, and the redox reaction effect can be accumulated in dc organic LEDs, which leads to the failure of the devices. Secondly, the accumulation of the migration of metal atoms from electrode to organic layer in dc operation can also result in the failure of devices. Both kinds of accumulation can be retarded or reversed in ac operation, therefore devices operated in ac mode are more stable.

In this letter, we report our successful fabrication of ac light emitting devices with asymmetric structure that can also be operated under both forward and reverse bias. A new advantage of ac operation mode is found in our experiment. The structure of our ac polymer LEDs is shown in Fig. 1. PDDOPV has been proved to be an excellent hole type semiconducting polymer in our previous work^[8-10], while PPQ has been proved to be an electron transport conjugated polymer^[11].

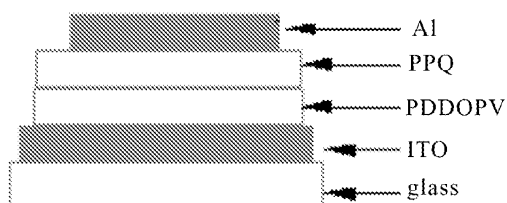


Fig. 1. Schematic diagram of the ac light-emitting device with asymmetric structure.

In the experiment, the soluble precursor of PDDOPV was dissolved in chloroform, and then the solution was spin-casted onto a piece of fully cleaned ITO glass substrate. After thermal conversion at 180 °C for 2 hours in vacuum at pressure below 5×10^{-3} Pa, the PDDOPV film was obtained and the color was red. After that, the solution of soluble PPQ dissolved in chloroform was spin-casted onto the PDDOPV film and heated at the same condition. Finally, the aluminum contact was evaporated on the PPQ layer. The thickness of PDDOPV layer and PPQ layer was measured by an ellipsometer. Since the thickness structure is very important for organic EL multilayer devices^[7,12], we made twenty bilayer devices with different thickness. We also made some single layer devices of PDDOPV and PPQ for comparison. The ac driving frequency is 50 Hz. The area of each cell device is 0.78 cm².

Here we mainly investigate four devices with following structure: Device PDD: ITO/PDDOPV(100 nm)/Al, Device PPQ: ITO/PPQ(40 nm)/Al, Device 1: ITO/PDDOPV(70 nm)/PPQ(40 nm)/Al, Device 2: ITO/PDDOPV(100 nm)/PPQ(70 nm)/Al.

Device 1 is the best in brightness, luminescent efficiency and stability, while Device 2 is poor in brightness and luminescent efficiency.

The EL and PL (photoluminescent) spectra of Device PDD and Device PPQ are shown in Fig. 2. The EL spectra and PL spectra of Device PPQ have peak at 450 nm, while the EL and PL spectra of Device PDD have peak at 584 nm. D. O'Brien *et al.*^[11] did not find light emission from device ITO/PPQ/Al under forward bias. In our experiment, we do observe Device PPQ emitting weak blue light under forward bias, but the decay rate is too fast for recording the EL spectrum. However, stable blue emission from Device PPQ is observed in ac drive. This phenomenon proves the advantage of ac drive mode in operational stability.

The $B-V$ and η_L-V curves (η_L stands for luminescent efficiency) for Device 1 under forward bias and ac drive are shown in Figs. 3(a) and (b), respectively. We can

see that the brightness of both devices increase monotonically with applied voltage. While each η_L - V curve has an obvious peak. We attribute it to light emitting saturation. For both devices, the peak η_L in ac drive is higher than the peak η_L under forward bias.

For Device 1, when the voltage is low, both the current and brightness in ac drive are higher than that under forward bias with the same voltage value. As the drive voltage increases, the increasing speeds of the current and brightness in ac operation slow down due to the saturation of light emission and then the current and brightness under forward bias gradually catch up with the current and brightness in ac operation. The highest brightness of Device 1 in ac operation and dc forward bias operation has the same magnitude order.

The EL spectra of Device 1 shown in Fig. 4 indicate that the spectra in both forward bias and ac drive have only one peak which is obviously from PDDOPV, but the spectra under reverse bias have two or three peaks, one of them is from PDDOPV and the other one or two from PPQ. It should be pointed out that multi-peak structure is existed in emission spectra from PPQ^[13].

From Fig. 3, we can also find that the highest brightness and the highest luminescent efficiency of Device 2 in ac operation are about two-order magnitude lower than that of Device 1, but three-order magnitude in dc forward bias operation. The luminescent efficiency at ac operation is about one order higher than that under forward bias, that is to say, devices with poor performance can be compensated in ac operation. The performance difference of devices in ac operation with different thickness is lower than that in dc forward bias drive. Namely, the performance of our devices in ac operation is not so sensitive to thickness structure as in dc forward bias operation. This character of ac drive mode is an advantage in commercial production of organic thin film EL devices because this character leads to the permission of small thickness difference in organic layer in large-scaled production, which means easy and cheap production.

In order to understand the difference between ac operation mode and dc forward bias operation mode, the energy diagram of the bilayer device is shown in Fig. 5. When the device operates at forward bias, holes accumulate at the PDDOPV side of PDDOPV/PPQ interface and electrons accumulate at the PPQ side of PDDOPV/PPQ interface. The accumulation results in space-charges at the interface. In the reverse bias, the holes left from the pervious forward-biased half cycle at the PDDOPV side of the interface will lower barrier for electrons and enhance electron injection. On one hand, injected electrons from ITO electrode will recombine with holes of space-charges to form PDDOPV excitons and yield light emission during the reverse-bias half-cycle of ac operation. On the other hand, injected holes from Al electrode will recombine with electrons of space-charges to form PPQ excitons. Some of the PPQ excitons may yield light emission directly, and some other excitons may transfer their energy to PDDOPV layer and form PDDOPV excitons. In another word, there are two parts of light emission during the reverse-bias half-cycle of ac operation. One is similar to dc reverse bias, and the other is from space-charges. For device 2, because the thickness structure is not optimized and the light

emission under forward bias is rather weak, the part from the space-charges is stronger than the recombination light emission under dc bias, so light emission in ac drive mode is stronger than that of dc forward bias

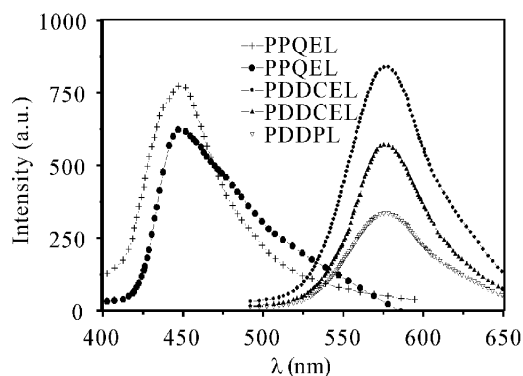


Fig. 2. PL spectra and EL spectra of Device ITO/PPQ/Al and Device ITO/PDDOPV/Al.

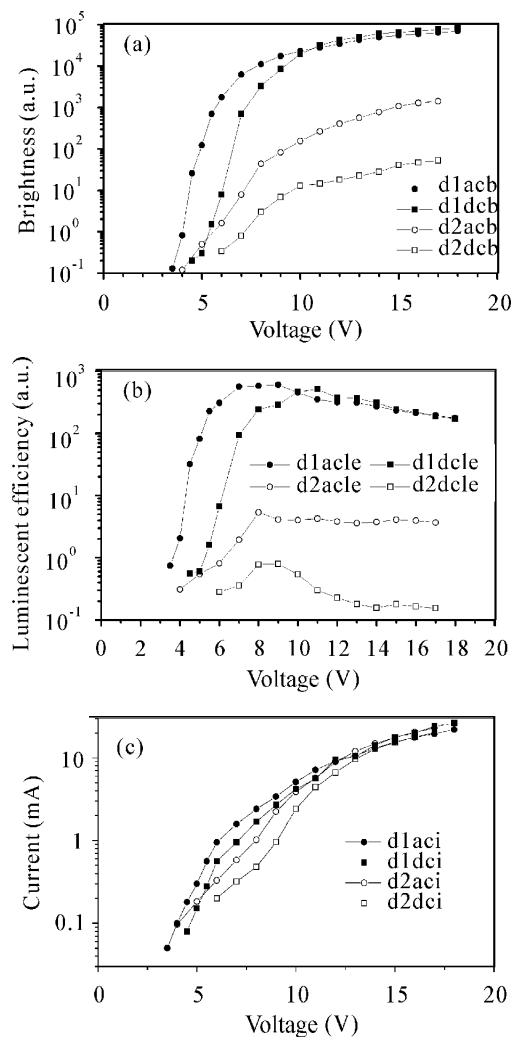


Fig. 3. B - V curves (a), η_L - V curves (b) and I - V curves (c) of Device 1 and Device 2 in ac operation and dc forward bias operation. Here d1 and d2 stand for Device 1 and Device 2, b for brightness, le for luminescent efficiency, and i for current. (x -coordinates are dc forward bias voltage value in dc operation, and virtual value in ac operation).

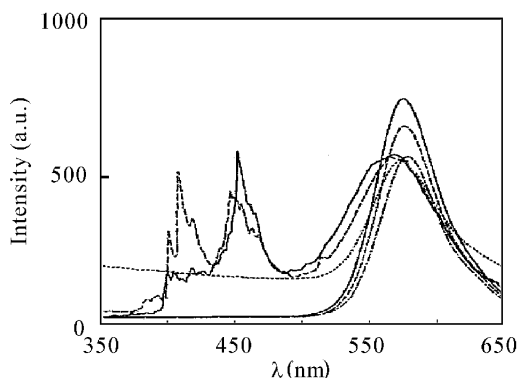


Fig. 4. EL spectra of Device 1, dc forward bias 10 (dash) and 18 V (solid); and dc reverse bias 21 (dash) and 24 V (solid); ac drive 10 and 18 V (dot).

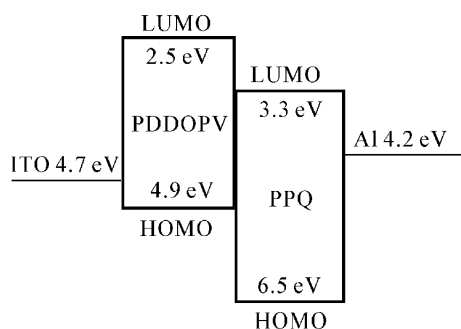


Fig. 5. Energy diagram of device ITO/PDDOPV/PPQ/Al.

drive mode.

In conclusion, we have successfully made ac polymer light emitting diodes with asymmetric structure that can also be operated in both forward bias and reverse bias. Emission in both dc forward bias and ac drive is from PDDOPV but emission in dc reverse bias drive includes two parts, one is originated from PDDOPV, the other from PPQ. The performance at ac operation of devices based on polymer heterojunction is not so sensitive to thickness structure as in dc forward bias operation. This character makes production of ac light emitting devices much easier than the production of dc light emitting devices. EL from single layer devices of PPQ under ac

operation is much more stable than that under dc operation. This verifies the advantage of ac drive mode in operational stability over dc drive mode.

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