

## Recent Progress in Polymer Light Emitting Materials

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### Abstract

The basic guidelines of material design for higher efficiency and longer lifetime, and the recent progress in polymer organic light-emitting diode (p-OLED) are reported in this invited talk.

### 1. Introduction

As self-emitting devices, OLEDs have features of fine image-quality, are ultra-thin, and are light weight. They have become familiar to general consumers as they are equipped in smart phones, tablet-PCs and TVs. Currently an evaporation process is adopted for the mass production of OLEDs. Although this process is practical when used for the mass production of small and middle size OLED displays, it is still considered that some difficulties exist in the fabrication of large TV displays from technical and cost points of view.

We have been developing organic materials applicable to printed electronics based on conjugated polymer technology, because we expect the printing process to be essential for cost-competitive mass production of large sized TVs or flexible devices.

### 2. Improvement of p-OLED performance

#### 2.1. p-OLED device

A typical polymer OLED device consists of an anode, a hole injection layer, an emissive layer, and a cathode. The introduction of an interlayer between the hole injection layer and the emissive layer has brought a big improvement in device performance [1]. The cross-linking properties of the interlayer makes it possible to stack three layers of hole injection, interlayer, and emissive layers by a printing process.

#### 2.2. Efficiency

The device efficiency can be broken-down to 4 parameters, i.g. charge-balance, singlet/triplet yield, PL quantum yield and photon out-coupling. To improve efficiency for RGBs, we investigated the impact on efficiency from these parameters independently and raised quantitative discussion for how to enhance the efficiency.

One of the fundamental limits to the efficiency of a fluorescent OLED is the ratio of emissive singlet excitons to non-emissive triplet excitons formed in the electroluminescent process. Although, from simple spin statistics, only 25% of the excitons formed are singlets, there are a number of suggested mechanisms for exhibiting greater efficiency

than the statistically expected value. In small molecule OLEDs, it was reported that triplet-triplet annihilation (TTA) increased the emission efficiency by converting triplet excitons into singlets [2,3]. It was also shown that approximately 20% of the device efficiency originated from the production of singlet excitons by TTA in the fluorescent conjugated polymer OLED using F8-PFB and an interlayer of F8-TFB. A similar phenomenon was observed in a polymer OLED with a spirofluorene derivative [4]. This mechanism yielded a very high emission efficiency of 10% EQE with  $\eta = 0.13$  in a blue-emitting device [5]. These technologies brought about remarkable progress in the performance of polymer OLEDs and became close to that of small molecule type OLEDs with a multilayer device structure.

After finding the TTA mechanism in conjugated polymer as described above, for the blue device we have improved the efficiency up to 13.4cd/A (EQE>12%) with CIE-y 0.12, which is close to theoretical limit, through the control of not only TTA yield but also emitter molecule dipole orientation and energy level of interlayer which is adjacent to emissive layer. Similar improvement was also achieved for green and red.

#### 2.3. Lifetime

For the device lifetime, we have identified that with stabilized carrier injection devices the primary mechanism of p-OLED degradation is loss of PL intensity, which is originated from excited state of polymers.

In the investigation of the PL intensity decay mechanism, we have found that PL decay was not observed in the driving of mono-polar devices (hole-major or electron-major device). These devices were fabricated with a similar procedure to the polymer OLED.

We also performed degradation analysis of the host-guest polymer OLED device by reverse engineering techniques. The polymer OLED device was fabricated with a host polymer and guest emitter compounds. After device operation the device was decomposed for chemical analysis of the host and guest materials, and the following results have been obtained:

- No change in the photoluminescence efficiency of the guest emitter.
- Formation of an insoluble layer of polymer.

These observations indicate that (1) the PL decay of emissive materials is related to the excited state by the recombination of carriers, (2) PL decay does not originate

from the degradation of the emissive unit, but from the creation of quenching sites in the host polymer.

P-OLED has high densities of triplet excited states within the emissive layer, and this leads to annihilation between triplets. We have identified that this annihilation process contributes to device efficiency as described above, and the control of triplet transfer and annihilation process also improves device lifetime significantly.

Other factor which governs device lifetime is a chemi-

cal structure dependent issues, i.e. creation of quenching site, which is related to material purity and weak-point of chemical structure. We are continuing to identify the root cause of PL instability in LEP chemical structure and improve the lifetime from the stabilization of PL intensity of molecules.

Based on these findings, we designed more robust polymer materials to reach double digit improvements of device lifetime.

Table1 Latest performance for polymer-OLED material

Spin/BE data @1000cd/m2	Non-cavity device								
	Red			Green			Blue		
Efficiency [cd/A]	31	24	18	85	72	61	12	11	7.5
Colour (C.I.E. x,y)	x=0.62 y=0.38	x=0.66 y=0.34	x=0.65 y=0.35	x=0.32 y=0.63	x=0.32 y=0.63	x=0.32 y=0.63	x=0.14 y=0.12	x=0.14 y=0.12	x=0.14 y=0.12
T50 lifetime [hrs]	350k	200k	200k	80k	350k	>300k	>10k	-	-
T95 lifetime [hrs]	-	2000	2400	1000	2600	4400	-	230	700
Vd [V]	4.2	3.3	3.2	3.9	4.7	5.0	3.7	4.0	4.0

\*Lifetime estimated from luminance acceleration test.

\*No electrical-ageing applied before lifetime test.

#### Device structure

ITO (45nm)/ spin-coated HIL (35-65nm)/ Interlayer (20nm)/ LEP (60-90nm) / low-WF cathode

### 3. Future of p-OLED materials

#### Improvement of device performance

In practical applications, the further improvement of operating lifetime is a critical issue. Regarding the lifetime, sticking image lifetime (LT95) is important in addition to half-life time in luminance (LT50). Self-emissive displays like OLEDs tend to get into a “sticking image” problem, which is the reduction of luminance in a specific area caused by continuous emission. To solve this issue, both material improvements to suppress the image sticking phenomenon and the development of operating methods are necessary. In the case of small molecule OLEDs, new materials showing LT95 of more than 500 h have been reported [6]. On the other hand, the development of polymer materials for a longer LT95 is still ongoing towards a practical level, however some investigations have been giving hints on how to solve this issue. It was observed that removal of the triplet exciton from the backbone polymer could significantly improve the stability of the device, particularly at the early stage of driving, i.e. introducing a triplet quenching additive leads to the improvement of device lifetime [7]. Careful adjustment is expected to satisfy both the need for high efficiency and a stable lifetime. Such comprehensive efforts, including material developments and detailed analysis, can bring polymer OLEDs to the goal of device performance required for practical usage.

Another trend is low power consumption as a general

environmental countermeasure. Hole injection materials and electrodes are newly developed for this purpose as well as emissive materials. These kinds of materials used in small molecule OLED devices are also being tested in polymer OLEDs.

### 4. Summary

We have significantly improved the efficiency, lifetime and hue of red, green, blue (RGB) light-emitting polymers (LEPs) through intensive studies on emission and degradation mechanism of p-OLED, as shown Table1.

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