# Key Technologies in Soluble OLED Materials

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**ABSTRACT**

*High-performance soluble OLED materials have been developed. Our wide library of platform was effective for improving device performance. For wide color gamut, new emitters with deep in color and narrow full-width at half maximum were developed. Further, solvent systems having physical properties suitable for improving film uniformity were found.*

## 1 INTRODUCTION

Mitsubishi Chemical Corporation successfully developed high performance, ink-jet printable materials for OLED display. We have already developed and mass-produced inks for OLED lighting panels.[1] Soluble OLED materials for display have been improved based on platform (PF) and light-emitting ink technology for lighting panels. We have PF libraries of a wide range of the properties such as ionization potential (IP) and hole-mobility as shown in Fig. 1, which are effective not only for lighting but also for display applications.

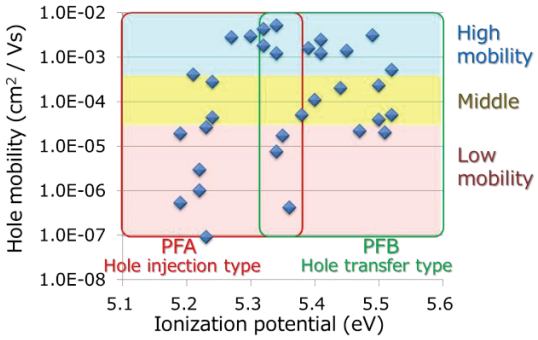


**Fig. 1** Ionization potential and hole mobility of platform libraries

PF materials have IPs around 5.2-5.3 eV, which is suitable for hole injection layer, and are called platform type A (PFA). PF materials with IPs around 5.4-5.5 eV, is suitable for hole transport layer, and are called platform type B (PFB). Fig.2 shows typical OLED structure using PFA and PFB layers.

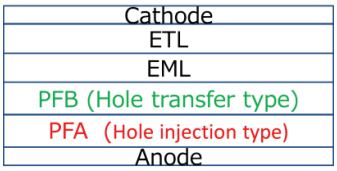


**Fig. 2** OLED structure with PFA and PFB

PFA ink contains p-dopant to help the hole injection from anode. The p-dopant system we developed has attributes like thermal and chemical stability, good solubility in organic solvents and high doping strength and is being studied by many research institutions. [2] However, in the printed OLEDs, p-dopant can be diffused to the adjacent layer unintentionally, resulting in worse device properties. In this paper, we report on the no-diffusible p-dopant.

We also have many types of small molecules that can be suitably used for the host materials of the light-emitting layer. Each small molecule type host material has ability to inject and/or transport electron or hole charge, to generate and confine exciton. And all host material has qualified high solubility, low crystallinity, and high durability for producing ink-jet printed OLEDs. By combining a plurality of such small molecule type materials, we have taken advantage of printed OLEDs compared to vaper deposited OLEDs that there is no limit on the number of materials used for the layer.

Small molecule type light-emitting ink is effective not only for improving efficiency and lifetime characteristics but also for adjusting viscosity. Fig. 3 shows viscosity vs. concentration of small molecule ink and polymer inks. In generally, it is difficult to stably jet an ink whose viscosity is too high. Therefore, there is a limit to the concentration of the polymer ink. On the other hand, small molecule inks with low dependence of viscosity on concentration can be produced at a higher concentration than polymer inks.

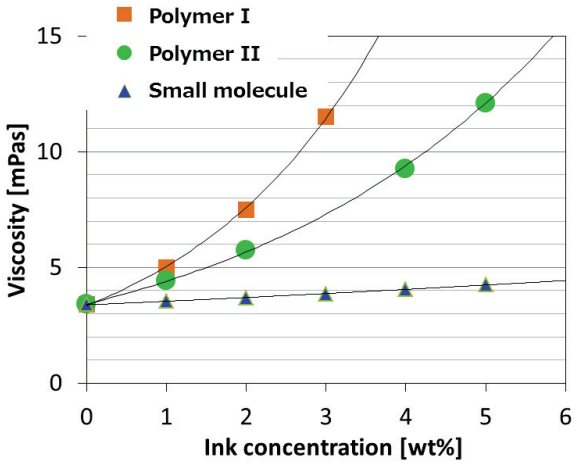


**Fig. 3** Viscosity vs. ink concentration

Besides efficiency and lifetime, several items such as i) deep color emitter for wide color gamut and ii) film uniformity in the pixel are absolutely required for display applications. In this paper, the recent progress on the above two items i) and ii) is reported and discussed.

## 2 MATERIAL DEVELOPMENT

### 2.1 Deep-Red Emitter

For the next-generation OLED displays, each emission wavelength of the red, green and blue emitters must be deeper in color and the full-width at half maximum of the spectrum must be narrower. However, in the case of the red emitter the longer emission wavelength results in a large drop of the quantum yield in accordance with the energy-gap law. To overcome this antimony, more precise relationships of the structure of the emitter to the emission wavelength and the quantum yield are must be obtained. We report the method of measurement of absolute PLQY in the solution with good duplicability and the development of new highly efficient deep-red emitter as soluble OLED material appropriate for the manufacture of printed device.

The practical and accurate method of PLQY measurement was modified.[3] Absolute PL quantum yield spectrometer C2290-02 (Hamamatsu photonics K. K.) was used and the wavelength of excitation light is adjusted at 380 nm. 2-Methyltetrahydrofuran was used as a solvent since the difference of maximum emission wavelength of the emitter in the solution and that of printed OLED seemed to be small. The purity of the emitter is usually over 99.5% determined by the liquid chromatography. The concentration of the emitter solution was around $1x10^{-5}$ mol/l. To the top part of the 1 cm quartz cell was attached a solution reservoir and a cock. After the emitter solution was charged into the cell and the reservoir, nitrogen gas generated from the commercial liquid nitrogen introduced through a PTFE tube (0.5 mm in diameter) was bubbled at room temperature (around 20°C) for 30 minutes or longer to avoid quenching the phosphorescence emission by the dissolved oxygen. Although a certain amount of the solvent was volatilized during the bubbling, final concentration of the solution did not exceed $2x10^{-5}$ mol/l. After the bubbling, the cock of the sample cell is shut and the PLQY measurement was performed as soon as possible. By this method, the PLQY of our standard red emitter exhibited 0.70±0.01 at $\lambda_{max}$ 620 nm with excellent reproducibility.

We have already synthesized many types of red emissive tris-cyclometalated iridium complexes such as quinolines, isoquinolines, quinazolines, naphtyridines and quinoxalines as the emissive main ligands. The results of PLQY measured by our method of these red emitters are shown in Fig. 4.

The trend of almost linear relationship between PLQY and $\lambda_{max}$ is good agreement with the energy gap law.[4] To our surprise, even the highest PLQY data between 610 nm and 650 nm also show the linear relationship (dotted line in Fig. 4) despite of the data of iridium complexes having different types of ligands.

To exceed the highest PLQY line and to develop more efficient deep-red emitter, the relationship between the ligand structure and PLQY of Fig. 4 was carefully investigated especially in terms of the kind and the position of substituents of the main ligand. As a result, further slight rigidification of the main ligand and/or enhancement of the MLCT character by substitution of an electron-withdrawing group would be required for higher PLQY besides appropriate choice of the type of the main ligand. Former ligand rigidification tends to make the complex poor soluble, so the introduction of more flexible solubilizing substituent is necessary.

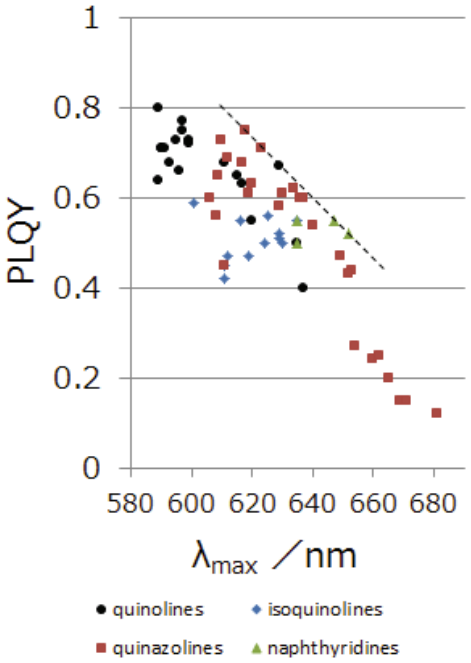


**Fig. 4** Solution PLQY vs. emission peak wavelength

Based on the consideration described above, we successfully developed the deep-red emitter showed $\lambda_{max}$ at 625nm with higher PLQY of 0.73 and slightly narrower FWHM than our standard red emitters. In addition to the relatively rigid ligand structure, the moderate shielding effect of emitter sphere by the solubilizing substituent will lead to these high performance.[5] Our new red emitter is also quite soluble in various organic solvents enough to give the stable and ink-jet printable inks for production of the red emission layer.

### 2.2 p-Dopant of PFA

In printed OLED fabrication, the diffusion of p-dopant causes some issues. The conventional p-dopant is diffused to the neighbor layers when baking at high temperature, resulting in worse device properties such as efficiency and lifetime. We have successfully

designed and developed new p-dopants that do not diffuse while maintaining high doping strength.

Fig. 5 shows the p-dopant amount of PFA/PFB/EML film elucidated by ToF-SIMS analysis, where (a) shows the amount with conventional p-dopant, (b) shows the amount with new no-diffusible p-dopant. In both devices, all layers were formed by printing process. The conventional p-dopant is diffusing to the PFB layer and even in the EML layer, but new p-dopant do not diffuse to PFB and EML layers. This no-diffusible p-dopant is useful not only to achieve higher device performance, but also to stabilize the manufacturing process.

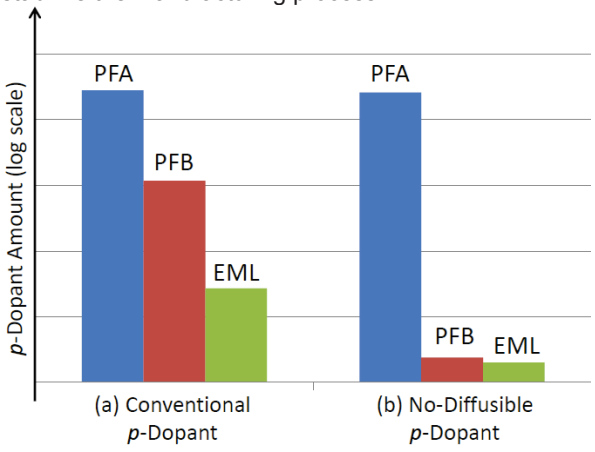


**Fig. 5** p-Dopant amount of PFA/PFB/EML film

For the performance of higher efficiency and longer lifetime, in addition to higher PLQY of emitters and no-diffusible p-dopants, optimization of several parameters including hosts and PFs are needed. For example, Ip/Ea levels and carrier mobilities of materials should be tuned for the smoother injection and transportation of carries. Delays of carriers at several surfaces induce annihilation, which reduce efficiency and lifetime. Furthermore, thicknesses of each layers have affect not only for the optical design but also for the carrier balance.

We examined optimization of hosts and PFs for the deeper-red emitter and the no-diffusible p-dopant. The bottom-emission devices showed the performance as shown in Table 1. Design strategy for the highly efficient and the no-diffusible p-dopant were also applied for green and blue devices. The typical performance of bottom-emission device is also shown in Table 1.

**Table 1.** Bottom-Emission Device Performance

| Color | Efficiency at1000 cd $m^{-2}$ [cd $A^{-1}$] | LT95 at1000 cd $m^{-2}$ [h] | CIEx,y |
|---|---|---|---|
| Red | 22 | 4000 | (0.67, 0.33) |
| Green | 80 | 11000 | (0.31, 0.64) |
| Blue | 6.8 | 300 | (0.13, 0.12) |

### 2.3 Film Uniformity in Pixels

To apply the OLED materials for displays, we need to dissolve the materials to the solvent and print it to the substrate by using an ink-jet printer or other printers. Furthermore, to separate red, green, and blue OLED finely, the substrate has pixels divided by the liquid-repelled wall, which is called bank. The OLED inks are usually printed in the pixels surrounded by the bank and dried to form the thin films. On the other hand, the device performance of OLED, such as efficiency, lifetime, and emission spectrum, is quite affected by the film thickness, since the optical cavity is constructed between two electrodes. Therefore, in-plane-uniformity of OLED film in the pixel is one of the most important parameters to determine the display performance.

We focused on the convection of ink in pixel bank during the drying process to improve the in-plane-uniformity of OLED films. Furthermore, at surface of the ink, surface tension is also inhomogeneous because of the difference of the concentration and this makes another convection, which is called “Marangoni convection”. The higher surface tension ink has, the more convection occurred.

On the other hand, viscosity of the ink also affects to the convection because it prevents the ink flow. We prepared two kinds of EML inks, which contain low viscosity solvent and high viscosity solvent, respectively. By using Dimatix Material Printer (DMP2831), these two inks were printed on the substrate with pixel bank structure, where PFA and PFB were already printed. The thickness of the bank was 1.7um. The printed inks were dried in vacuum chamber under 1 Pa, and annealed at 130 degrees Celsius for 20 minutes.

Fig. 6 shows the thickness profile of PFA/PFB/EML film, where (a) shows the profile made from the ink containing low viscosity solvent, (b) shows the profile made from the ink containing high viscosity solvent. The film uniformity was improved from 67.7% to 93.8%, where the uniformity U was calculated from formula (1),

$$U=L1/L2*100\ [\%] \qquad (1).$$

L1 represents the length of the film, whose thickness is in the range of 5% of the average thickness, and L2 represents the length of the bank opening.

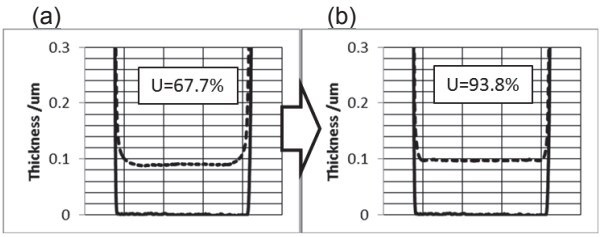


**Fig. 6** In plane uniformity of PFA/PFB/EML film

In this case, the ink convection was strong during the drying process and meniscus region became broad because the flowing direction was from the center region

to the bank wall. On the other hand, the film became very flat, since the high viscosity of the solvent prevented the ink flow. Fig. 7 shows the viscosity and surface tension of some solvents. If the ink contains the solvent which is indicated in the area enclosed with solid line, well uniformed film is obtained. But if the ink contains the solvent which is indicated in the area enclosed with dashed line, it is difficult to obtain well uniformed film. This result indicates that the higher surface tension the solvent has, the higher viscosity of the solvent is needed to make well uniformed film. In other words, it means that the ink flow induced by Marangoni convection during the drying process is prevented by high-viscosity-solvent, and became flat film.

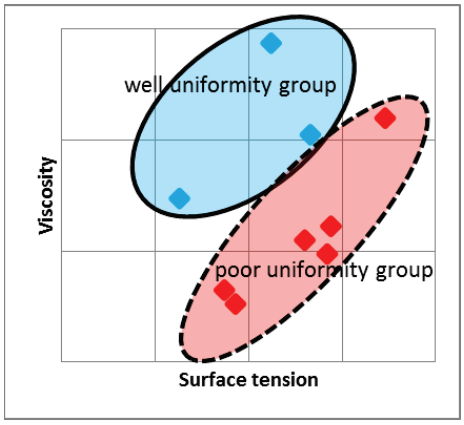


**Fig. 7** Surface tension and flow activation energy of some solvents

## 3 SUMMARY

Our PF libraries have a wide range ionization potential and hole-mobility. Many types of small molecules can be used in combination for hosts of light-emitting layers. Small molecule inks with low dependence of viscosity on concentration can be produced at a higher concentration than polymer inks.

No-diffusible p-doping system was developed as a key technology for improving OLED device performance and stabilizing manufacturing process.

Newly developed deep-red emitter shows quite high PLQY and narrow FWHM. We examined optimization of platforms and small molecule hosts for the deep-red emitter to achieve high-performance bottom-emission devices.

Besides efficiency, lifetime, and color gamut, film uniformity in pixels was also greatly improved. In order to obtain flat film, control of ink convection during the drying process was important.

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