Latest Development of Soluble OLED Materials and its Application to Mid- to Large-sized Panel Production.

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Keywords: conjugated polymer; efficiency; photo stability; ink-jet printing; high resolution panel

ABSTRACT

We present the latest status of high performance OLED material development based on conjugated polymer technologies. The material which shows high performance is very suitable for printed OLED panel fabrication. New materials for higher resolution panel fabrication have been developed and they provide wider application of IJP devices.

1 Introduction

Recently, middle- and large-sized OLED display panels are being developed intensively and the trend of panel is oriented to wide color gamut and higher resolution. In such situation, soluble light-emitting materials attract much attention from a viewpoint of low-cost mass production and/or their applicability to fabrication of higher resolution panels.

We have been developing soluble organic light-emitting materials applicable to printed electronics based on conjugated polymer technologies, and obtained materials which show very high level of OLED performance and are applicable to manufacturing of TV panels, IT monitors and other products. Furthermore, we have developed new materials which are suitable for fabrication of higher resolution panels.

2 Development and Results

2.1 Latest performance of polymer-OLED

In the recent study, we made a significant progress in efficiency, color and lifetime of our RGB OLED materials. Performance of polymer-OLED on bottom-emission (BE) device and top-emission (TE) device at the end of 2020 is shown in Table 1. Also, some latest results and discussion for further improvement in color, efficiency, image-sticking lifetime (T95) and Ink-jet printed (IJP) device performance by development of material and ink are described in below.

2.2 Polymer OLED basic material design

Our polymer-based OLED materials consist of the elements shown below[1][2][3].

Red and Green emitting materials: The emitter is a metal-centered dendritic complex with phosphorescent emission and embedded in conjugated polymer. The polymer has an adequate Triplet energy level (T1) derived from carefully designed monomers and polymer sequence control.

Blue emitting materials: The emitter is based on fluorescent material and a totally conjugated polymer consists of monomers of backbone, electron-transporting, hole-transporting and emitting units. These monomers are integrated into one polymer chain by Suzuki-polymerization.

Interlayer (hole-transporting layer) materials (IL) : The interlayer polymer has a similar design with the blue emitting polymer, but does not contain electron-transporting and emitting units. The polymer is designed to show much higher hole-mobility than RGB emitting polymers. In addition, the polymer contains thermally cross-linking units, so the deposited layer becomes insoluble after thermal annealing and this enables sub-sequential layer formation using solution on top of IL without any inter-mixing between the layers.

Table. 1 Performance of polymer-OLED (2020)

		Red	Green	Blue
Spin-BE device @1,000nit	Efficiency (cd/A)	18.0	76.1	6.4
	Color CIE-(x,y)	0.68, 0.32	0.32, 0.63	0.13, 0.10
	T95 lifetime (hrs)	11,000	26,000	1050
Spin-TE device @1,000nit	Efficiency (cd/A)	43.6	102.8	5.8
	Color CIE-(x,y)	0.68, 0.32	0.24, 0.72	0.13, 0.06
	T95 lifetime (hrs)	38,000	10,000	390

2.3 Efficiency and Lifetime

OLED efficiency consists of the factors of (1) charge balance, (2) singlet/triplet yield, (3) PLQY (Photoluminescent quantum yield), and (4) out-coupling efficiency. We have been developing high efficient blue materials by improving PLQY, singlet yield by TTA (triple-triplet annihilation)[4][5] and outcoupling efficiency using dipole orientation[6] of emitting polymer. Furthermore, we have also achieved higher efficiency on TE devices by developing a blue emitter which has a narrow PL spectrum shape and an optimal peak wavelength for better outcoupling.

For the lifetime improvement, we always pay attention to 1) material intrinsic stability (thermal, chemical, electro-chemical, and light), 2) reduction in formation of higher energy state by exciton-exciton annihilation and 3) reduction in impurities and defects. One hypothesis of material degradation is that SSA (singlet-singlet annihilation) and/or TTA (triplet-triplet annihilation) may form higher energy state (Sn and/or Tn), which causes chemical degradation. Based on these fundamental studies and screening of materials, we see significant improvement in T95 (image-sticking lifetime) for our green OLED material by suppressing Tn state formation as shown in Fig. 1. New green material showed T95 improvement by 2.4 times against standard one.

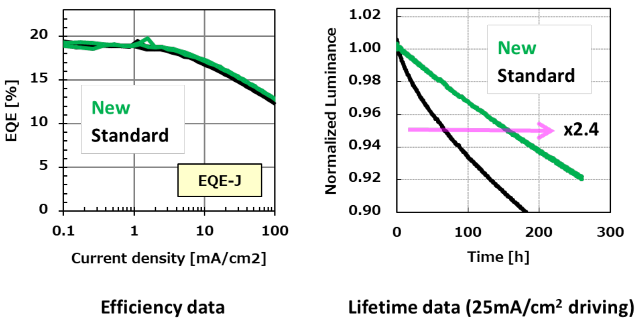


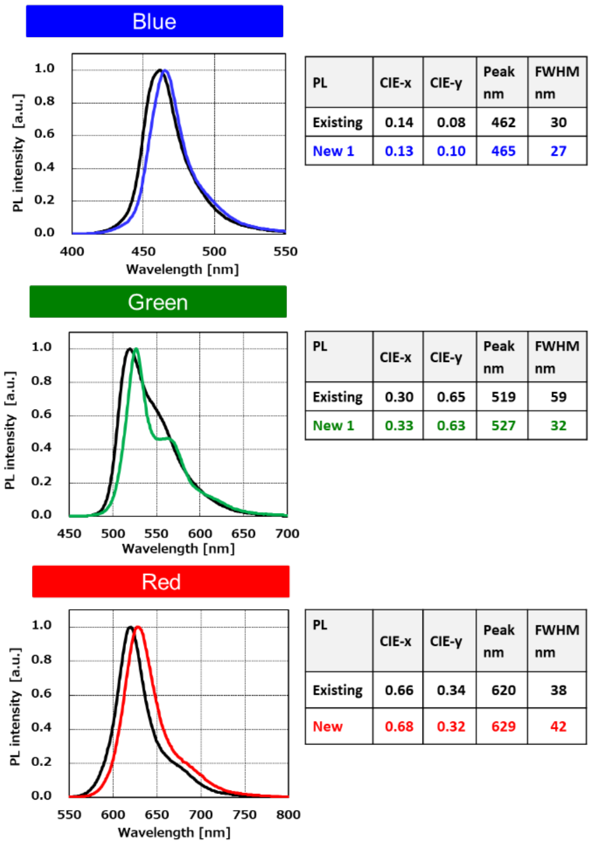
Fig. 1 Latest result of lifetime improvement of green material with exciton control (spin-coating, BE device).

2.4 Color & spectrum

The recent OLED display development is oriented to wider color gamut such as BT.2020. We are focusing on improvement in emission spectrum of emitter. We have found new emitters which show better peak position and narrow FWHM as shown in Fig. 2. Peak positions of RGB emitters are tunable for top emission micro-cavity and target color.

2.5 Ink-jet printed (IJP) device performance

IJP device sometimes shows lower efficiency and shorter lifetime than spin-coating (SC) device. Understanding and control of "Ink-jet printing parameters" are essential to achieve the best IJP device performance. Our recent study revealed the following two factors are important ; (a) film flatness and (b) contamination. Also, demand for (c) higher resolution OLED display is increasing recently and we discuss new materials for this application.



PL	CIE-x	CIE-y	Peak nm	FWHM nm
Existing	0.14	0.08	462	30
New 1	0.13	0.10	465	27

PL	CIE-x	CIE-y	Peak nm	FWHM nm
Existing	0.30	0.65	519	59
New 1	0.33	0.63	527	32

PL	CIE-x	CIE-y	Peak nm	FWHM nm
Existing	0.66	0.34	620	38
New	0.68	0.32	629	42

Fig. 2 Latest improvement of film PL spectrum by development of new emitters.

(a) Film flatness: As discussed in many papers, “Marangoni flow” arising from surface-tension gradient of ink in pixel is affected to film flatness. When surface-tension at outer area is higher than inner area, convection gives concave shape of film. On the other hand, higher surface tension at inner area than outer area gives convex shape (Fig. 3).

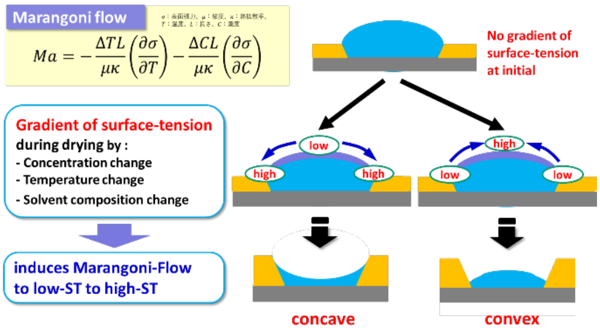


Fig. 3 Marangoni flow and shape of film in pixel.

Viscosity increase of ink during drying can act as a resistance against Marangoni flow. To obtain the flat film, control of viscosity increase is extremely important. Pining point is also important parameter which is related to contact angle and surface tension of ink/bank. Our recent study found that viscosity increase of ink came from aggregation of conjugated polymer chains. Also, we have been able to identify aggregation parts in polymer chains and can control viscosity increase by changing the amount of aggregation parts (Fig. 4). By control of viscosity increase, flat film by IJP can be achieved such as Polymer B in Fig. 4. This is the unique behavior in polymer system, not in small molecule system, and an effective tool to control film flatness.

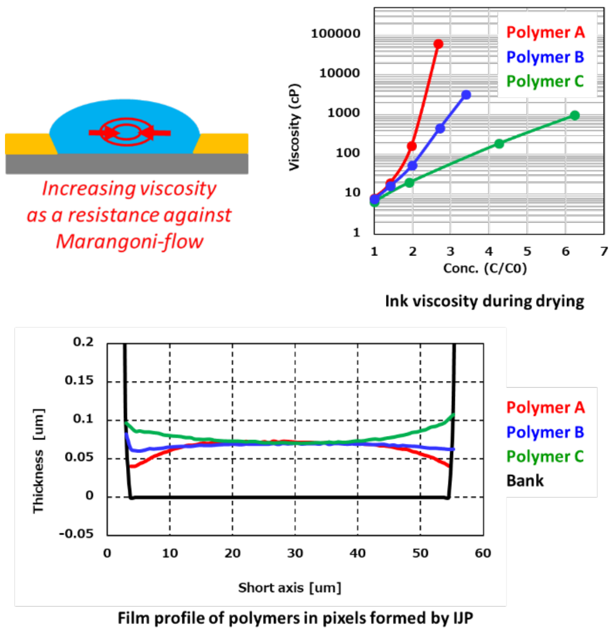


Fig. 4 Viscosity increase of ink during drying and profile of film formed by IJP

(b) Contamination: There are much higher possibilities of contamination in IJP device than spin (flat) coating device. The major factors of contaminations are 1) dissolution of non-cross-linked part of interlayer to EML (cross-contamination), 2) residual solvent in EML film and 3) contamination from bank chemicals. To prevent cross-contamination between interlayer and EML, high cross-linking yield of interlayer was achieved by a new cross-linking unit and effective polymer process to reduce dissolution part of interlayer. Ink solvent design and suitable drying condition of EML are effective to remove the influence of residual solvent.

As a result of controlling key IJP parameters, we have achieved flat film profile on IJP-BE device (Fig. 5) and the same performance of IJP-BE device as SC-BE device (Fig. 6).

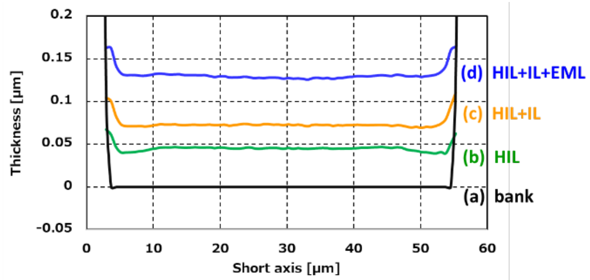


Fig. 5 Film profile on IJP-BE device. (a) Bank, (b) Film of HIL only, (c) Film of IL on HIL, (d) Film of EML on IL/HIL.

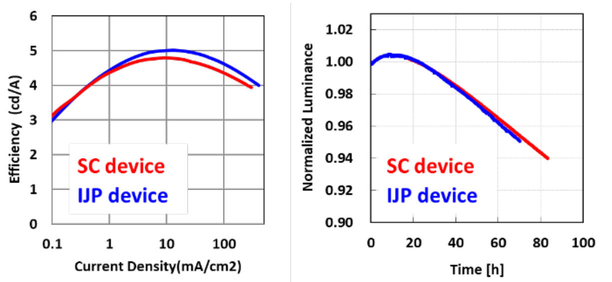


Fig. 6 Performance of blue materials on SC-BE device and IJP-BE device

(c) Higher resolution printing: The resolution of 55 inch-8K and 20 inch-4K panels are 160ppi and 200ppi, respectively. Also higher resolutions up to 300ppi are desired to widen the application of IJP OLED devices. For such higher resolution panel, higher concentration of solid content in ink is needed because ink volume in one pixel must be small as shown in Fig. 7.

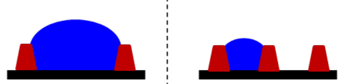
Issues	Smaller ink volume in pixel	
	100ppi	>300ppi
		
Measures by ink	**Higher concentration**	
Measures by -IJP machine -Substrate design	Larger containment of ink inside pixel (stronger hydrophobicity of bank surface)	

Fig. 7 Issues and measures for higher resolution Ink Jet printing.

We have developed materials which are suitable for fabrication of higher resolution panels by reducing Mw of polymers with keeping material performance as shown in Table 2. In some cases, reducing Mw of polymers induces a drop in device performance. Our recent study revealed that such performance drops are caused in some types of polymer sequences, and we succeeded in keeping performance with reduced Mw. As shown in

Table 2 and Fig. 8, concentration of solid content can be higher while the ink viscosity is unchanged, and these inks are suitable for fabrication of higher resolution panels.

Table. 2 Latest performance of polymer OLED materials for higher resolution panel on SC-BE device

	Red		Green		Blue	
Mw	High	Low	High	Low	High	Low
Efficiency (cd/A)	20.7	22.5	70.1	68.9	6.5	6.1
CIE-x,y	0.66, 0.34	0.66, 0.34	0.33, 0.63	0.33, 0.63	0.13, 0.10	0.13, 0.10
T95 (hrs)	140	140	620	600	550	550
Conc.(g/L) @8cP (*2)	15.4	➡ 41.0	22.2	➡ 35.0	7.9	➡ 11.6

*1 : Efficiency, CIE-x,y : @1knit, T95 : @8knit for RG @20mA/cm2 for B
*2 : Concentration of solid content in ink with 8cP viscosity.

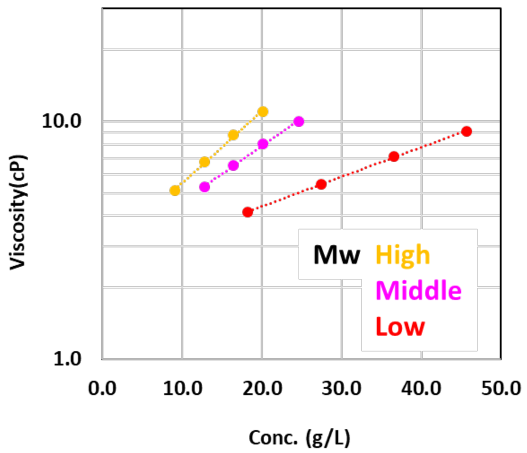


Fig. 8 Red ink viscosity against solid content concentration.

3 Summary

Our recent study has been focused on improvement of luminous efficiency and lifetime of materials. Especially, for lifetime, it is important to reduce the formation of higher energy state caused by SSA/TTA and realize higher chemical and photo stability of materials.

Optimizing PL spectrum by new emitter development achieved higher outcoupling on TE device and wider color gamut.

Key IJP parameters to improve IJP device performance, film flatness and contamination, have been identified. Factors for good film flatness of polymer OLED have been recognized.

Polymer OLED materials with low Mw which are suitable for higher resolution panel fabrication have been developed.

Our achievement in material performances, both efficiency and lifetime for RGB, are one of the best among solution-processed OLED materials as far as we know.

We will offer these materials and related information to customers to contribute OLED technology for the production of mid-to-large sized display.

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