### **Development of Printable Materials for Organic Light-Emitting Diode**

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Organic light-emitting diode (OLED) displays have been employed for several commercial applications, such as mobile phones, TVs, and so on, because of their high-speed response, thinness, and lightweight. Printable OLEDs have been given increasing attention owing to their large cost reduction potential, whereas most OLED displays are fabricated by vacuum evaporation using many vacuum chambers. At Sumitomo Chemical Co., Ltd., we have developed printable OLED materials and achieved their practical usage for the first time in the world. In this paper, we give a brief overview of existing printable OLEDs and present a feature of our materials and technologies.

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#### Introduction

There are many luminescent materials and optical devices worldwide but only a few electro-luminescence (EL) device technologies exist that emit light from the materials through which an electric current flows<sup>1)</sup>. Among these technologies, organic electro-luminescence (also known as "organic light-emitting diode", OLED), which made it possible to pass an electric current through organic material, thought to be an insulator, and make it emit light in the three primary colors of RGB, is truly an exceptional and epoch-making technology<sup>2), 3)</sup>.

OLEDs have undergone active research and development as a next-generation display technology with features such as high-speed response, thinness, and lightweight, and today, they are widely used in the market as a display for TVs and smartphones. Current products of OLED displays are similar to conventional EL device products, such as compound semiconductor LEDs, from the perspective that they are manufactured by depositing luminescent materials in vacuum chambers (the evaporation method is often used for OLEDs). Meanwhile, Sumitomo Chemical Co., Ltd. has developed solution-processable OLED materials. These materials enable printed optoelectronics, which is a revolutionary manufacturing method that upends the conventional understanding of EL device manufacturing, where coating and filming are conducted in an atmosphere like a home inkjet printer.

Our company's development of OLED materials<sup>4)</sup>, derived from research on conductive polymers that started in 1981, has reached the level of actualizing practical characteristics while promoting joint development with various companies, including display manufacturers. And it was achieved that the first display products using our materials were shipped in 2017. This is the world's first EL device product that employs the inkjet printing method to form the active layer (emission layer)<sup>5)</sup>.

Solution-processed OLEDs were an unexplored area of science and technology, but our company has paved the way for their practical application by elucidating the driving principle and degradation mechanism. Currently, we are vigorously continuing material development in order to meet the demand for advanced display performance. In this paper, we introduce the features and technologies of the polymer-type OLED materials developed and manufactured by our company while providing an overview of the material technology and device technology of solution-processed OLEDs.

# Material requirements for solution-processed OLEDs:

### 1. OLED driving principle and physical property requirements

First, we provide an overview of the OLED's driving principle and physical property requirements. The operating mechanism of the OLED can be understood by referencing an inorganic semiconductor LED, where electrons and holes are supplied from the cathode and anode, respectively, into the film; when the two meet on the molecule, an excited state is generated, which leads to luminescence (**Fig. 1**)<sup>6</sup>. The emission efficiency (external quantum efficiency (*EQE*)) of an OLED is expressed by the following Eq. (1):

$$EQE = \gamma \cdot \eta_{\rm eh} \cdot \phi_{\rm ph} \cdot (1 - Q) \cdot \eta_{\rm oc} \tag{1}$$

where  $\gamma$  is the balance factor between the electron current and hole current,  $\eta_{\rm eh}$  is the excited state generation probability due to charge recombination,  $\phi_{\rm ph}$  is the emission quantum yield from the excited state, Q is the quenching factor (electrode quenching, *etc.*) that depends on the device structure, and  $\eta_{\rm oc}$  is the extraction efficiency of the light that is generated inside the device to the outside of the device (external optical outcoupling efficiency).

Functions required in a material are the functions of (1) receiving charges (electrons, holes) from the electrodes, (2) passing electric charge as current, (3) recombining electrons and holes to generate excited states, and (4) converting the generated excited state

into light (luminescence); with (1) and (2) related to  $\gamma$ , (3) related to  $\eta_{eh}$ , and (4) related to  $\phi_{ph}$ . *Q* and  $\eta_{oc}$  are the main factors related to device design, but  $\eta_{oc}$ , in particular, depends greatly on the position of light generation within the device due to the microcavity effect described later, so the functional requirements of (1), (2), and (3) are closely related to  $\eta_{oc}$ . Thus, OLED materials are subject to various requirements for active device operation, which are interrelated and directly impact device performance.

### 2. Material requirements for device structures and manufacturing methods

Next, we provide an overview of the material requirements associated with device structures and manufacturing methods. The organic layer in OLEDs is composed of several layers, and its total thickness is several dozens to several hundreds of nanometers, with the thickness of one layer being extremely thin at 20 nm or less in some cases. Fig. 2(a) shows a schematic diagram of the layer structure and the energy bands of a typical evaporation-processed OLED. Evaporation-processed OLEDs, in which low-molecular-weight materials are deposited by the vacuum evaporation method, have been developed by dividing the above-mentioned functions (1)-(4) that are required for the OLED into respective functional layers and developing functionally specialized materials. For example, white OLEDs (WOLEDs), which are currently commercially available as display panels for TVs, consist of multilayer films composed of a dozen or so layers<sup>7</sup>).

Difficulties emerge when forming such a multilayer







**Fig. 2** Comparison of the OLED structure and energy band diagram (a) Device made by vacuum evaporation (small molecule) (b) Device made by solution process (polymer)

film with a coating process. This is because there is a need to incorporate a function to prevent the lower layer from being dissolved when the solution of the upper layer is dropped onto the lower layer. One method to prevent the dissolution of the lower layer film is to crosslink and cure the lower layer film; another method involves using a solvent that does not dissolve the lower layer film in the solution for the upper layer film<sup>8</sup>. With the former method, a curing process is added each time the number of layers increases, and the lower layer material is required to withstand multiple curing processes. With the latter method, the higher the layer, the fewer the solvent options, and the more layers there are, the greater the difficulty.

In our company's development of solution-processable OLED materials, we solved this problem by using the features of polymers to create functionally integrated materials. In other words, as shown in **Fig. 2**(b), we put into practical application a solution-processed OLED by developing a material that can satisfy the required functions (1)-(4) even in a device structure with a very small number of layers.

Here, we would also like to touch on the cost advantages for the structure of devices with a small number of layers and the inkjet printing method. **Table 1** shows a comparison of manufacturing technologies for various OLED displays. Currently, there are three types of vacuum evaporation methods. The evaporation method



#### Table 1 Comparison between OLED display manufacturing technologies

(a) that is used for manufacturing small displays such as smartphones requires a large number of vacuum evaporation equipment and high-definition shadow masks for each color (referred to as fine metal masks (FMMs)) and has problems such as difficulties in increasing the size of FMM and low material usage efficiency. The evaporation method (b) is used for manufacturing large displays and does not require FMMs but has a very large number of layers and requires even more vacuum chambers. In addition to the fact that pixels are white light-emitting structures and require color filters, there is also the problem of high power consumption due to low external optical outcoupling efficiency due to device structure requirements. Using the recently developed evaporation method (c) to form only the blue OLEDs should be done to resolve this problem, but it is said that there are still problems with the quantum dot color conversion film. In contrast to these evaporation-processed OLEDs, the inkjet printing method for solution-processed OLEDs eliminates material waste because each RGB color is applied only where necessary. The inkjet printing display has a three-primary-color emittable pixel, so it is possible to design a display that does not use a color filter. Furthermore, FMMs are not required, so it is easy to increase the screen size, and there is a high degree of freedom in terms of size, such as the ability to build displays of different sizes on the same substrate. Given these features of the manufacturing method, the inkjet printing method has many opportunities for reducing display manufacturing costs, and it is a technology that enables the inexpensive manufacturing of large-screen and high-performance displays<sup>9)</sup>.

Selection of the solvent used for the ink is imperative in the inkjet printing method, and not all solvents can be used without limitation<sup>10)</sup>. Stabilizing ink ejection requires selecting a solvent with the appropriate viscosity and boiling point; solvents that damage the inkjet head must be avoided. Furthermore, as mentioned above, the film thickness of the functional film in OLEDs is extremely thin, and obtaining a flat film in the pixel with the ejected ink requires precise control of the film formation behavior during drying. For these problems with inkjet printing methods, the polymer OLED materials developed by our company have the advantage of the ink viscosity and film formation properties being easy to control, as described later. Therefore, we accomplished commercialization by systematically addressing the issues associated with inkjet printing processes one at a time.

### 3. Polymer OLED materials of Sumitomo Chemical Co., Ltd.

As mentioned above, we have developed function-integrated OLED materials that can be applied to the inkjet printing method and its device structure. **Fig. 3** illustrates an overview of the material developed by our company. Our company has developed, manufactured, and sold fluorescent blue light-emitting layer materials, phosphorescent green light-emitting layer materials, and interlayer materials.

Our company's OLED material is a copolymer that introduces multiple functional units based on fluorene. The diagram on the right in **Fig. 3** shows an overview of the compound as an example of the blue light-emitting



Portfolio of Sumitomo's solution-processable polymer OLED materials

Fig. 3

layer material. Here, fluorene is the major building block of the backbone and is responsible for electron transport, and the copolymerized amine units are responsible for hole transport, charge recombination, and luminescence. As shown in the figure, the fluorene unit chain forms a conjugated system, thus forming an excited state with the amine unit. A solubilizing group is introduced into the substituent R to impart solubility in the inkjet solvent. The interlayer material (IL) is used between the hole injection layer (HiL) and emission layer (EML), simultaneously is a hole transport layer (HTL), and has an electron-blocking function. The IL is positioned below the EML, so the unit with the thermally cross-linkable substituent is copolymerized to impart resistance to the device manufacturing process so that dissolution does not occur when the upper layer ink is applied. Thus, our company's polymer OLED material is an extremely advanced function-integrated material that integrates various functions into a single polymer chain, and all these technologies, including the synthesis and purification methods, are unique to our company.

From the next section onwards, we will introduce our OLED material's technologies for long operational lifetimes, high efficiency, and ink commercialization.

# Technologies for long operational lifetimes on polymer OLEDs

#### 1. Analysis of lifetime-controlling factors

One of the biggest problems with OLEDs is its lifetime. When considering the lifetime, that is, the stability of light emission intensity when the device is continuously driven (EL lifetime), a long lifetime means minimizing changes in each element (material functions (1)-(4)) in Eq. (1). For many years, we have continued to analyze the controlling factors that cause the decrease in emission intensity; here, we introduce some of the technical details.

The physical properties listed in Eq. (1) can be broadly classified into (i) components related to the emission probability of the excited state ( $\phi_{ph}$ ) and (ii) other components mainly related to the flow of current  $(\gamma, \eta_{\rm eh}, Q, \eta_{\rm oc})$ . We have developed a unique measurement method to enable an analysis that distinguishes between factors (i) and (ii). Extracting and evaluating only factor (i) requires removing the effect of current, so the stability of light emission due to photoexcitation (photo-luminescence, PL) rather than due to current excitation should be measured. We have developed a measurement system that combines a light source that can excite an emission material and a photometer to monitor the PL intensity from a measurement sample over time while continuously applying excitation light. Fig. 4(a) shows the evaluation results of PL stability. The horizontal axis is the photoexcitation time t, and the vertical axis is the PL intensity normalized at t = 0. It can be seen that a longer photoexcitation time resulted in a decreased PL intensity, and a higher excitation density (initial emission intensity) resulted in a faster decrease in PL intensity. Such a decrease in PL intensity does not occur when the electron current or hole current is applied alone<sup>11)</sup>. Additionally, the order of EL stability and PL stability was consistent among different materials<sup>11)</sup>. Based on the above, we clarified that the dominant degradation factor in polymer OLEDs is the decrease in the emission quantum yield  $\phi_{\rm ph}$ , which occurs through the excited state of the material.





(a) PL stability and (b) EL stability with different initial luminances (*i.e.*, excitation densities) (c) Dependence of PL and EL lifetime on initial luminance

Next, we consider the elementary process where the excited state causes degradation. Fig. 4(b) shows the EL stability evaluation results for the EL device using the same material as depicted in Fig. 4(a). Here, "lifetime" is defined as the time until the emission intensity decreases to a certain percentage when the excitation is continued with the same excitation density (excitation light density for PL, injection current density for EL). For example, the time for the emission intensity to drop to 80% of the initial value is expressed as the T80lifetime. Fig. 4(c) plots the PL lifetime (T85) and EL lifetime (T60) against initial emission intensity (excitation density) based on Fig. 4(a) and (b). As shown in Fig. 4(c), both PL and EL lifetimes are proportional to the square of the excitation density. This result indicates that EL degradation and PL degradation are the same degradation mode, and as mentioned above, we can also see that PL degradation is the primary cause of EL degradation. A more important fact is that degradation does not arise from a single excited state (first power of excitation density) but from a process involving multiple excited states (approximately the square of the excitation density).

As shown in **Fig. 5**, we built the degradation hypothesis from the results of **Fig. 4**(c). As shown in **Fig. 5**(a), in the organic layer there is the transport diffusion of the excited state (exciton) due to intermolecular energy transfer (*e.g.*, Förster energy transfer, FRET) and the generation of a higher-order excited state due to the meeting of two excited states (*e.g.*, singlet-singlet annihilation, SSA)<sup>12</sup>. Of these, the extremely high energy of the higher-order excited state generated by the participation of multiple excited states cuts the chemical bond of the compound, and the generated degradation product acts as a quencher for the excited state, causing a decrease in emission intensity (Fig. 5(b)). In fact, this hypothesis was confirmed by the following model experiments. If SSA arising from FRET is the cause, then if the intermolecular distance in the film can be increased to suppress FRET and reduce the probability of SSA, the durability of the film should be improved. Fig. 6 shows the results of comparing a film (model film with intermolecular separation) in which the model emission material was diluted to 5% with an optically inactive material (i.e., has no absorption at the excitation wavelength) with a 100% neat film. As shown in Fig. 6(a), the PL stability was significantly improved with the 5% diluted film. When evaluating the exciton diffusion in this film from the analysis of exciton dynamics by transient absorption spectroscopy, it was shown that exciton diffusion was greatly suppressed in the 5% diluted film (diffusion constant D is below the observation limit) compared to the 100% neat film (D = $1.5 \times 10^{-3}$  [cm<sup>2</sup>s<sup>-1</sup>]). Furthermore, as shown in Fig. 6(c), the dependence of the PL lifetime on the excitation density is equivalent (dependent on the square of excitation density). This shows that the durability was improved by decreasing the degradation probability (suppression of SSA) while keeping the degradation mode the same; thus, the degradation hypothesis in Fig. 5(b) was proven.

From these studies, we can further derive a model



**Fig. 5** Schematic of (a) Photo-physical dynamics for the generation of a higher excited state via singlet-singlet annihilation(SSA) (b) Degradation products formation mechanism resulting from the generation of a higher excited state via SSA



**Fig. 6** (a) Comparison of PL stability (b) Time transience of singlet exciton density measured by transient absorption spectroscopy (c) Dependence of the PL lifetime on the initial PL intensity

equation for the EL degradation behavior (**Fig. 7**). The basis of the formulation is the assumption that the "amount of quenching degradation product generated per unit time is proportional to the square of the excited state" based on the above analysis results (Eq. (2) in **Fig. 7**). When calculating the time variation of the emission intensity (Eq. (3)) based on Eq. (2), then the degradation curve is obtained as shown in **Fig. 7**(a). Plotting the excitation density dependence of the *T*90 lifetime from this calculation result is shown in **Fig. 7**(b), and it can be seen that the model equation reproduces the experimental results like those in **Fig. 4**(c) and **Fig. 6**(c) well.

As shown by the above results, our company has developed evaluation methods, elucidated the main factors, and conducted detailed analyses such as the formulation of these methods and factors. We continue to develop materials based on the understanding of the mechanism of EL-driven degradation to this day.

#### 2. Material design technologies for long lifetimes

This section introduces recent development examples based on the above-mentioned analysis results. As mentioned above, increasing the distance between the molecules of the luminescent material to suppress the diffusion of the excited state is a powerful method for



**Fig. 7** General description of the model adopted for the simulation of the EL stability curve (a) Numerical calculation results obtained from Eq. (3) by varying  $L_0$  (b) Dependence of the calculated lifetime on  $L_0$ 



**Fig. 8** (a) Figure on the left: molecular configuration of a 9,9-dioctylfluorene decamer (40 molecules) calculated using the molecular dynamics (MD) calculation method. Table on the right: calculation results of the relative spatial density of the optically active structure of the developed material. (b) Comparison of EL device lifetime between the existing and the developed materials. These results confirm the improved lifetime performance provided by our design strategy.

achieving longer lifetimes. Fig. 8 shows a design example based on this policy and its results. Fig. 8(a) is an example of calculating the density of a model compound (9,9-Dioctylfluorene (F8) decamer) by the molecular dynamics calculation method. As mentioned above, our company's material is a fluorene-based polymer with soluble substituents, and the optically active sites that form excited state orbitals are fluorene unit chains. Therefore, if the density of the fluorene unit chain portion in the film is calculated, it can be used as an index of the intermolecular distance of the luminescent material. The table in Fig. 8(a) shows the calculation results (relative values) of the film density of the fluorene unit chains. Compared to the model compound, the conventional fluorescent blue material had a relative density of about 0.9, but the newly designed material, designed to increase the distance between molecular chains, successfully reduced the density to 0.65. Fig. 8(b) shows the EL characteristics of a top-emission OLED<sup>13)</sup> using this material. The new material has achieved a significantly longer lifetime while maintaining the same driving voltage and emission efficiency (EQE) as the conventional material.

# Technologies for high-efficiency in polymer OLEDs

#### 1. Analysis of efficiency controlling factors

Next, we discuss high-efficiency technologies. First, we review the principle that determines emission efficiency. As mentioned above, the efficiency of the OLED is described by the physical property factor of Eq. (1). Of these,  $\phi_{\rm ph}$  is broadly classified into fluorescence emission and phosphorescence emission. The excited state that is produced by the recombination of electrons and holes has the two states of singlets and triplets; the ratio based on electron spin statistics is 1:3. In phosphorescence, the triplet excited state, which occupies 75% of the excited state, can be converted into light, so the efficiency of using the excited state is high (100% in principle if the deactivation process is ignored)<sup>14)</sup>. Our company's materials already use phosphorescent materials for the green and red materials, and they have achieved high-efficiency luminescence. Our company's blue material is a fluorescent material that emits light from the singlet excited state (25% of the excited state), but we achieved high efficiency by developing triplet control technologies, which exceed the normal efficiency from singlet emission, and we have published several reports on the topic<sup>15)</sup>. Meanwhile, blue phosphorescent materials and thermally activated delayed fluorescence (TADF) materials are being developed as technologies for using up to 100% of the excited state of blue materials<sup>14)</sup>. However, these materials have not been put to practical use as a display due to the problem of durability due to the high energy and the broad luminescence spectrum.

Now, when considering the terms other than  $\phi_{ph}$  in Eq. (1),  $\gamma$  and  $\eta_{eh}$  are not a problem in current OLEDs, and it is thought that there is almost no waste of

injected charges in properly designed materials and devices. On the other hand, the loss in  $\eta_{oc}$  (external optical outcoupling efficiency) is large, which is a problem, particularly in displays that require color purity. In this paper, we would like to introduce an analysis of this external optical outcoupling efficiency and an example of material development.

The external optical outcoupling efficiency discussed includes the microcavity effect, waveguide mode loss, surface plasmon loss, and molecular orientation (light emission direction of molecules)<sup>14)</sup>, but here, we consider the microcavity effect. **Fig. 9** shows a schematic diagram of the microcavity effect (device structure is a bottom-emission-type). As mentioned above, the OLED is very thin, and the total film thickness is less than the emission wavelength, so this causes optical interference inside the device (**Fig. 9**(a)). As shown schematically in **Fig. 9**(b-1), the light (electromagnetic wave) generated in the EL is reflected by a reflective cathode such as Al

or an interface with a large refractive index difference (e.g., ITO/HiL interface in the figure), and the combination of multiple traveling waves and returning waves creates a standing wave, as shown in Fig. 9(b-2). Here, the distance between the reflecting interfaces (cavity length) is crucial, and the cavity length needs to be an integral multiple of  $\lambda/4$  of the emission wavelength to generate a standing wave. When the cavity length differs from the integral multiple of  $\lambda/4$ , the interference results will cancel each other out without becoming a standing wave. Additionally, if the position where the electromagnetic wave is generated in devices deviates from the position of the antinode of the standing wave, the phases of the electromagnetic wave do not match at the reflection interface, which causes the interference results to cancel out. Fig. 10 shows the result of analyzing this situation by optical calculations. Fig. 10(a) shows the light transmission spectrum from the inside of the device to the outside of the device when light is









Additionally, emission from positions d1 and d2, which are close to the antinode of the standing wave, is easily transmitted. However, transmission becomes more difficult moving away from the antinode, as shown in d3and d4, showing also that the wavelength dependence of transmission is modulated. According to the emission position dependence  $Tr(d, \lambda)$  of the optical transmission spectrum, the luminescence spectrum of the material itself also has a wavelength dependence  $PL(\lambda)$ , as shown in **Fig. 10**(b). Therefore, the external optical outcoupling efficiency Ext(d) at each emission position d is the product of  $Tr(d, \lambda)$  and  $PL(\lambda)$ , and if integrating over the wavelength range, then this is expressed as a function of d, as shown below:

$$Ext(d) = \sum_{\lambda} Tr(d, \lambda) \cdot PL(\lambda)$$
(4)

*Ext*(*d*) has an efficiency distribution in the EML, as shown in **Fig. 10**(c). It can be seen that the generation of light cannot just occur anywhere in the EML, and emission must occur at positions where the external outcoupling efficiency is high. In other words, if the light generation distribution (exciton distribution) in the EML is  $N_{\text{ex}}(d)$ , then the final external optical outcoupling efficiency is integrated over *d* and becomes:

$$OutEff = \sum_{d} Ext(d) \cdot N_{ex}(d)$$
(5)

As shown above, to improve the efficiency of OLEDs, the three factors of  $Tr(d, \lambda)$ , which is determined by the device structure design,  $N_{\text{ex}}(d)$ , which is determined by the current flow (depending on both device structure and material design), and  $PL(\lambda)$ , which is determined by the material design, need to be controlled as countermeasures for the impact of the microcavity effect.

#### 2. Material design technologies for high efficiency

Here, among the countermeasures for the impact of the microcavity effect, we would like to introduce an example of the development of  $PL(\lambda)$  control. The above Eq. (5) is transformed into the following Eq. (6), and the cavity effect spectrum  $CAVS(\lambda)$ , represented by Eq. (7), is introduced:

$$OutEff = \sum_{\lambda} PL(\lambda) \cdot CAVS(\lambda)$$
(6)

$$CAVS(\lambda) = \sum_{d} Tr(d, \lambda) \cdot N_{ex}(d)$$
(7)

The significance of Eq. (6) is to consider how to match the luminescence spectrum of the material with the spectrum *CAVS*( $\lambda$ ) determined by the device design and exciton distribution. Therefore, we considered improving the external optical outcoupling efficiency by narrowing the line width of the luminescence spectrum of the material. An example is shown in **Fig. 11**. **Fig. 11**(a) shows the optical simulation result of the cavity effect spectrum *CAVS*( $\lambda$ ) for the model of the top-emission device structure (2nd-cavity). Optical interference works more strongly in the top-emission device<sup>13</sup>), so it can be seen that almost no light is emitted in the wavelength region other than the vicinity of the designed resonance wavelength, because they cancel each other out. For such



**Fig. 11** (a) Simulation result of cavity effect spectrum  $CAVS(\lambda)$  (b) (c) Comparison between the PL spectrum of EML (black line) and the spectrum calculated by multiplying the PL spectrum by  $CAVS(\lambda)$  (green line) FWHM: Full width at half maximum



Fig. 12 Comparison of EL efficiency between the existing and the developed materials on Top-emission devices (2nd-cavity) These results confirm the improved efficiency performance provided by our design strategy.

a  $CAVS(\lambda)$ , the spectrum of our conventional luminescent material was shown by the black line in **Fig. 11**(b). Multiplying this by  $CAVS(\lambda)$  gives the spectrum, shown by the green line, and the area ratio of the light that can be extracted is reduced to 39%. This means that most of the light generated in the device was wasted with conventional materials. Conversely, we have newly developed a luminescent material with the spectrum shown by the black line in **Fig. 11**(c). With the new material, the emission half-width (FWHM) was narrowed to 37 nm, and the area ratio of the extracted light was improved to 53%. This is a 35% improvement compared to the conventional material. **Fig. 12** shows the results when manufacturing an EL device using this material in practice. The efficiency of the EL device was also improved by about 1.4 times when compared to the conventional material, and this demonstrated the effect of the material design policy of a narrow line width spectrum based on the analysis results.

# Commercialization technologies for polymer OLED materials

#### 1. Analysis of elements required for ink products

Just dissolving the synthesized compound in a solvent by itself does not immediately result in an ink product. As mentioned above, there is a need to design the ink so that it is stably ejected from the inkjet device and a flat film is formed on the substrate. Besides this, a wide variety of technologies is required for commercialization, such as storage stability of the ink. In this paper, we introduce the ink design technology for obtaining a flat film.

First, we provide an overview of the display manufacturing process using the inkjet printing method (Fig. 13). In the inkjet printing manufacturing method, partition walls of pixels called banks are formed on a substrate on which anodes are arranged, and each functional layer of an OLED is formed in these banks.



Fig. 13 Schematic of the ink-jet printing (IJP) process for OLED display production

The HiL, HTL, and EML are formed by repeatedly dropping ink from an inkjet device, drying, and baking, where HiL and HTL are cured in the baking process and the thickness of each layer differs for each RGB color. Afterward, an electron injection layer, ETL, and cathode are formed on the EML by an evaporation process. Finally, the entire substrate is sealed to complete a display panel.

Technical elements in such a printing manufacturing method require accurate and stable ejection of ink droplets from inkjet devices (uniformity of droplet volume, straightness of ejected droplets), eradication of impurities eluting from the bank, and precise control film flatness of each organic layer (HiL, HTL, EML). Above all, the flatness of the organic layers is crucial. This is because differences in the film thickness inside the bank will result in the current concentrating only in the parts where the film is thin, which causes problems such as changes in emission intensity compared to other pixels and a shorter lifetime, which results in poor image quality.

Next, we discuss the principle that determines film flatness. The film shape formed by the drying of droplets is often discussed as the coffee ring effect, and Marangoni convection generated in the droplets during drying is thought to be one of the main mechanisms<sup>16)</sup>. In the analysis of Marangoni convection, the dimensionless Marangoni number *Ma* expressed by the following equation is used:

$$Ma = -\frac{\Delta TL}{\mu k} \left(\frac{\partial \sigma}{\partial T}\right) - \frac{\Delta CL}{\mu k} \left(\frac{\partial \sigma}{\partial C}\right)$$

where  $\sigma$  is the surface tension,  $\mu$  is the viscosity, k is the thermal diffusivity, T is the temperature, L is the length (droplet size here), and *C* is the concentration. Marangoni convection is a phenomenon in which a gradient of surface tension generated in a droplet due to changes in temperature, solvent composition, and solute concentration is the driving force, which causes convection in the droplet from areas of low surface tension to areas of high surface tension. As shown in Fig. 14(a), the edge of the droplet that is dropped on the substrate dries faster because the drying rate of the solvent differs between the apex and edge of the droplet due to differences in the specific surface area. In other words, the polymer concentration on the droplet surface during drying is more likely to increase at the edges and is less likely to increase at the apex. At this time, if the relationship of [solute surface free energy] > [solvent surface tension] holds, then this means that the surface tension at the edge is higher, so convection from the apex to the edge occurs, and the solute is transported in that direction, resulting in a concave film shape. Conversely, if the relationship of



Fig. 14 Schematic of film formation based on the Marangoni convection mechanism

[solute surface free energy] < [solvent surface tension] holds, then this means that the surface tension at the edge is lower than that at the apex, so convection from the edge to the apex occurs, and the solute is transported in that direction, resulting in a convex film shape (**Fig. 14**(b))<sup>17), 18)</sup>.

Our company's OLED materials generally have the relationship of [solute surface free energy] > [solvent surface tension]. Therefore, concave film shapes are more likely to form within the banks, and there is a need to introduce some form of film shape control technology. As described in the next section, our company solved this problem by discovering new factors that determine the film shape in banks, introducing a new analysis method, and establishing a methodology to control it.

### 2. Design technologies for the commercialization of ink

As described above, if Marangoni convection occurs, then solute slant will occur. Therefore, we considered suppressing the convection itself. Convection can be reduced by increasing the viscosity of the ink, but an appropriate viscosity is required for stable ejection from the inkjet head, and the viscosity of the ink cannot be excessively increased. Therefore, we focused on the ink-drying process. Even if the viscosity of the ink is low at the time of the ejection, if the viscosity increases accompanied by the increment of solute concentration during the drying process in the bank, then the Marangoni convection should be suppressed. A model experiment shown in **Fig. 15** was conducted to confirm this hypothesis. First, as shown in **Fig. 15**(a), we prepared three types of model polymers A–C with different ink viscosity dependences with respect to solid content concentration. Inks using such polymers are expected to show differences in the thickening of viscosity behavior in the process of drying the solvent in the bank. The actual shapes of the films formed by the inkjet deposition of these materials are shown in **Fig. 15**(b). Polymer C, which has a small thickening in viscosity, has a concave shape; polymer B, which has a moderate thickening in viscosity, has a flat shape; and polymer A, which has a large thickening in viscosity, has a convex shape. These results showed that we successfully found a new controlling factor of "thickened viscosity behavior during drying" that determines the film shape.

The difference in thickened viscosity behavior seen in **Fig. 15** is thought to be caused by the difference in interaction between polymer chains in the ink, and it is speculated that a stronger interaction results in easier increases in viscosity. Therefore, in ink design, it is necessary to quantitatively evaluate the strength of interaction (aggregation) between polymer chains and establish a methodology for obtaining material design guidelines.

The light scattering method is known as a method for evaluating aggregation between polymers<sup>19)</sup>. A greater molar mass of the aggregated particles in the solvent results in greater light scattering, so comparing the scattering in the THF solution, in which the polymer is thought to be completely dispersed, and the scattering in the inkjet solution, in which the polymer is thought to be aggregated, enables the acquisition of an index (molar mass ratio) of how many polymer chains are associated with each other (this



**Fig. 15** (a) Dependence of viscosity on solution concentration for three different polymers (b) Film thickness profiles formed by IJP in a bank

is defined as an "aggregation factor" in this paper). The light scattering method can estimate the extent of aggregation. However, it is difficult to know the mechanism of aggregation, and it is difficult to obtain direct information for molecular design. Therefore, we newly introduced a spin-echo method using NMR as an analysis method to directly elucidate the aggregation mechanism<sup>20)</sup>. The spin-echo method can directly observe which chemical structure in a polymer chain has what degree of molecular mobility by measuring the phase relaxation time ( $T_2$  relaxation time) of spin precession. In other words, if the mobility of a specific chemical substructure is reduced in the ink solution, then it can be judged that aggregation has occurred at that site, so the observation results could be directly reflected in molecular design. For the above-mentioned polymer A-C inks, we show the results of observing the  $T_2$  relaxation time in Fig. 16(a), where we focused on a specific common structure.

The horizontal axis is time, and the vertical axis is the NMR echo signal intensity of the common structure in each polymer. As is clear from the figure, the  $T_2$  relaxation time decreased in the order of polymers C, B, and A, and it was observed that the molecular mobility of this common structure decreased in this order. The table in **Fig. 16**(b) shows a comparison with the aggregation factor that was separately evaluated by the light scattering method. The aggregation factor increased as the molecular mobility decreased, and we found out that aggregation occurred at a specific partial structure in the polymer chain.

Adjusting the molecular structure and copolymerization ratio of the specified polymer aggregation sites enables the control of the molecular mobility as well as the thickening in viscosity properties. **Fig. 17** shows the device characteristics of the material designed based on these findings. **Fig. 17**(a) is the film profile in the bank that was inkjet printed. It can be seen that each layer



**Fig. 16** (a)  $T_2$  relaxation time of the spin-echo signal for polymer A–C inks. (b) Relationship between the film thickness profile,  $T_2$  relaxation time, and aggregation factor for the three ink samples



Fig. 17 (a) Film thickness profiles of layers stacked by IJP (b–c) EL device performance of spin-coated and inkjet printed film : (b) efficiency and (c) lifetime

is stacked extremely flatly. **Fig. 17**(b) and (c) compare the characteristics of EL devices fabricated by inkjet deposition and spin-coated deposition ((b) emission efficiency, (c) lifetime). We successfully developed a material that can exhibit device characteristics equivalent to spin-coated film formation, even in inkjet film formation.

As described above, we discovered a new control factor of "thickened viscosity behavior during drying" that determines the shape of the inner film of the bank. Also, we introduced a spin-echo method as a new method for analyzing thickened viscosity behavior and clarified its mechanism in order to establish a film shape control technology that is essential for the commercialization of ink. These results demonstrate the superiority of the polymer OLED materials developed by our company in printing-type mass production processes in the sense that material design factors that govern film flatness can be controlled over a wide range.

#### In place of a conclusion

In the above sections, we have provided an overview of solution-processed OLEDs, the features of our company's products, and its development technologies. Finally, we would like to briefly touch on trends in the display market. Currently, the demand for higher performance continues to increase in the display market year by year. In terms of image quality, the trend has been to widen the color gamut of color reproduction and increase brightness. In particular, the standard BT.2020, which was established in 2012 by the International Telecommunication Union Radiocommunication Sector (ITU-R), has an extremely wide color gamut compared to conventional sRGB (BT.709) and DCI-P3, so there is a demand for further improvement in color purity of the three primary colors of RGB. Additionally, with respect to higher luminance, there has been a demand for an average display luminance exceeding 1000  $cd/m^2$  depending on the display applications, so there is a need for improvements in emission efficiency and lifetime. Furthermore, there is always a demand for higher resolution, so it is important to develop inks that can be used to form films on smaller pixels. Of course, there is also demand for reduced power consumption, so there is a need for improved emission efficiency as well as lower voltage. Our company is vigorously continuing to develop materials that meet these demands for advanced display performance. The high-efficiency, long-lifetime, and ink commercialization technologies described in this paper are part of these efforts, and we are confident that the solution-processed OLED becomes a *de facto* standard technology that can provide high-quality displays at a low cost.

Scientific elucidation and manufacturing technology development have progressed in parallel for OLEDs. Our company's material development is also based on many new scientific findings, as described in this paper. We would like to continue to develop new scientific horizons, share the world of solution-processed OLEDs with society, and contribute to the development of a prosperous society.

#### Reference

- Edited by Japan Society for the Promotion of Science 125th Committee, Hakko to juko no butsuri to oyo [Physics and applications of light emission and reception], BAIFUKAN (2008).
- C. Tang and S. A. VanSlyke, Appl. Phys. Lett., 51, 913 (1987).
- 3) J. H. Burroughes et al., Nature, 347, 539(1990).
- Sumitomo Chemical Co., Ltd. JP H3-244630 A (1991).
- 5) K. Noda, The 26th meeting of the Japan OLED Forum, S2-2, (2018).
- A. Mikami, The Journal of the Institute of Image Information and Television Engineers, 67(9), 800 (2013).
- C. W. Han *et al.*, "Advanced Display Technology", Springer Singapore (2021), p. 199.
- 8) S. Ho et al., J. Photonics Energy, 5(1), 057611 (2015).
- Attempts have been made to apply low-molecular-weight OLED materials for inkjet printing prototypes, but practical use has not yet been achieved. For example, refer to the following literature: S. Kim *et al.*, Dig. Tech. Pap. Soc. Inf. Disp. Int. Symp., 53(1), 391 (2022).
- M. Sakai, The Journal of the Institute of Electronics, Information and Communication Engineers, 90(7), 544 (2007).
- 11) S. Yamauchi *et al.*, The 10th meeting of the Japan OLED Forum,S-84 (2010).
- 12) F. Fennel and S. Lochbrunner, Phys. Rev. B. 92, 140301 (2015).
- S. Hofmann *et al.*, Appl. Phys. Lett., 97, 253308 (2010).

- 14) "Yuki-EL ni kansuru hakkokoritsukojo, buzaikaihatsu, atarashii yototenkai [Improvement of Luminous Efficiency, Development of Materials and New Applications Related to OLED]", Technical Information Institute Co., Ltd. (2018).
- 15) S. Yamauchi *et al.*, The 24th meeting of the Japan OLED Forum, S6-2, (2017).
- J. Fukai, J. Jpn. Soc. Colour Mater, 94(4), 112 (2021).

- 17) P. O. Babatunde *et al.*, AIChE Lett 59(3), 699 (2013).
- 18) P. O. Babatunde *et al.*, J. Chem. Eng. Japan, 45(8), 622 (2012).
- 19) T. Satou and Y. Li, Japanese Journal of Polymer Science and Technology, 75(4), 293 (2018).
- 20) S. Matsukawa *et al.*, Japanese Journal of Polymer Science and Technology, 60(6), 269 (2003).

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