

# Development of Polymer Organic Light-Emitting Diodes



Sumitomo Chemical Co., Ltd.  
Advanced Materials Development Laboratory  
Nobuhiko AKINO  
Yoshiaki TSUBATA  
Takeshi YAMADA\*

Organic light-emitting diodes have many advantages including self-emission, thinness and light weight, and they have been the subject of much interest for next-generation display technology. Light-emitting polymers are expected to be particularly suitable for printing processes which are essential for the cost-effective production of large-sized panels. In this paper, the material design for higher efficiency and longer lifetime, and the latest progress in polymer organic light-emitting diodes (PLEDs) are discussed.

This paper is translated from R&D Report, "SUMITOMO KAGAKU", vol. 2018.

## Introduction

Organic light emitting diodes (OLEDs) have superior characteristics including self-emission, high-speed response, thinness and light weight, and active research and development on them has moved forward as the next generation of display technology. Devices with OLEDs expanded rapidly in 2017, with events such as Toshiba Corp., Sony Corp. and Panasonic Corp. bringing 4K OLED televisions to the market one after another, and Apple using an OLED display in the iPhone X in November. Furthermore, in December 2017, JOLED produced the world's first 21.6 inch 4K OLED panel by a printing process, commercialized it and began shipping it.

OLEDs are devices where organic light emitting materials emit light by injecting electrons and holes from electrodes in a layered structure of thin organic films, and they are roughly divided into the vapor deposition type formed by vacuum vapor deposition of the thin films and the soluble type formed by a solution process. In terms of the vapor deposition type, which uses small molecule materials, a high luminance and high-efficiency OLED was reported by Tang and Van Slyke<sup>1)</sup> of Eastman Kodak Co. in 1987. On the other hand, in terms of the soluble type, which uses polymer materials, light emission from polymer OLEDs was observed using conjugated polymers by Burroughes et

al.<sup>2)</sup> at Cambridge University in 1989 and also in Japan by Sumitomo Chemical Co., Ltd. at almost the same time.<sup>3)</sup> However, the external quantum efficiency was 0.1% or less, and the lifetime was only at the level of a few minutes. Thereafter, Sumitomo Chemical Co., Ltd., Covion Ltd. (currently Merck & Co.), Dow Chemical Co., Cambridge Display Technology Ltd. (CDT) and others began actively working on the development of polymer light emitting materials, and as a result of moving forward in parallel with development of device structures, it can be said that the performance has reached the level to make incorporation into OLED panels possible at present after about 30 years of development.

Polymer OLED materials have excellent solubility in a solvent, and since red, green and blue materials (RGB materials) can be easily printed, there are great expectations for the possibility of manufacturing large panels without using masks and improvements in material utilization efficiency over vapor deposition materials, which are currently the main stream for OLEDs. In this paper, we will introduce recent progress in material characteristics and the future outlook while reviewing OLED material development by Sumitomo Chemical Co., Ltd.

## Polymer OLED Materials

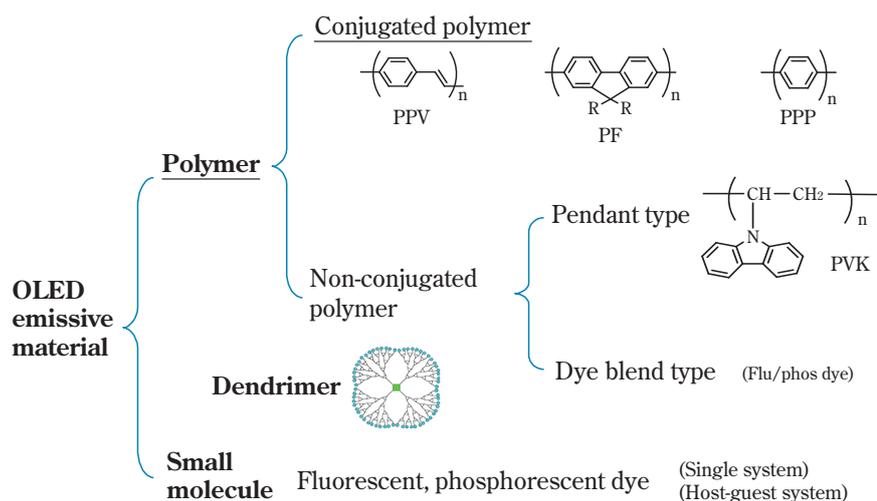
Light emitting materials for OLEDs are roughly categorized into polymer types and small molecule types as shown in Fig. 1, and the polymer types are further classified into conjugated polymers and non-conjugated

\* Currently: PLED Business Planning Office

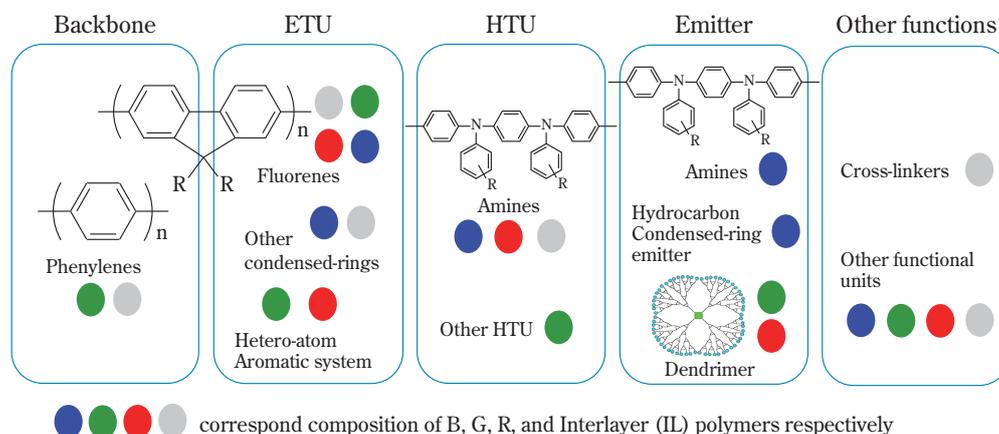
polymers.<sup>4)</sup> In addition, dendrimers (dendritic molecules) may also be used as light emitting materials intermediate between polymer and small molecule ones. **Fig. 1** shows typical polymer and dendrimer-based light emitting materials for OLEDs. In conjugated polymers, the main chain carbons have  $sp^2$  carbons, and  $\pi$  electrons delocalized in the conjugated system; therefore, there is the feature that transporting of the charge (electrons and holes) is excellent. Furthermore, there are many conjugated polymers formed from  $sp^2$  carbons that exhibit fluorescence in the visible light region, and currently conjugated polymers such as polyphenylene vinylene (PPV),<sup>2), 5)</sup> polyfluorene (PF)<sup>6)–9)</sup> and poly(p-phenylene) (PPP)<sup>10)</sup> have mainly been developed as light emitting materials and charge transport materials.

Another feature of polymer OLED materials is the ability to incorporate various functions into the molecule by polymerization as is shown in **Fig. 2** and as a result

being able to have simple device structures. Polymers having the desired features can be designed by polymerization using light emission (emitters), electron transport properties (ET) and hole transport properties (HT) in the units making up the conjugated polymer. Thus, the emission color and the charge injection as well as the charge transport balance can be controlled; therefore, it is possible to greatly improve the performance. For example, in adjusting the emission color, a unit having the desired spectrum may be introduced into the polymer. Polyfluorene based<sup>11)–14)</sup> and polycarbazole (PVK) based<sup>15)</sup> polymers are not only suitable for their own blue light emission but also can be used for obtaining light emission other than blue by copolymerization with thiophene, amines, acenes, etc.<sup>16), 17)</sup> For example, anthracene (blue), naphthacene (green), pentacene (red), etc. can be cited for acenes. In addition, even with non-conjugated polymers, similar functions



**Fig. 1** Schematic classification of organic emissive materials



**Fig. 2** Schematic classification and typical structures of functional units in a light emitting polymer. ETU and HTU represent electron transporting unit and hole transporting unit, respectively.

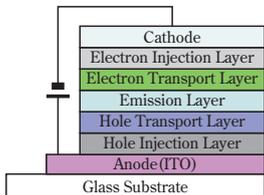
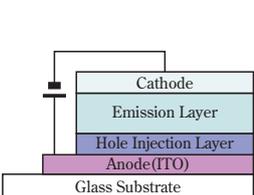
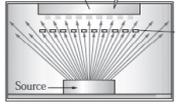
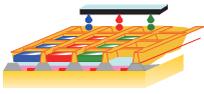
can be achieved by polymerization of monomers having charge transport properties and light emission in side chains.<sup>18)</sup>

While polymers are normally a linear chain of monomers, dendrimers have a shape in which units are joined such that branches are formed one after another as shown in **Fig. 1**. Furthermore, dendrimers are high molecular weight substances, but since they are single molecules, they are characterized by the molecular weight being uniquely determined and by not having a molecular weight dispersion. As an example, a light emitting group is used for a core, in particular, a metal complex exhibiting phosphorescent light emission, and aromatic groups are used in the surrounding branched parts (called dendrons) to form a structure having soluble groups in the outer shell, thereby being able to obtain a dendrimer with superior charge transport properties and solubility.

## Polymer OLED Devices

The features of polymer OLED devices (PLED, P-OLED) include, as with small molecule OLED devices, (1) high contrast, (2) wide viewing angle, (3) vivid color, (4) thinness, (5) high-speed response because of self emission and (6) low power consumption, which is an important in mobile devices. The most important merits of polymer-based devices over small molecule-based devices are device structure and processes as well as the possibility for cost reductions from the aspect of material utilization efficiency. As is shown in

**Table 1** Comparison between small molecule and polymer OLEDs

	Small Molecule	Polymer
		
Process	Dry process (Vacuum evaporation) 	Solution process 
Patterning	Shadow mask	Printing (IJ etc.)
Structure	Complex layer structure (5-6) → Complex process	Simple layer structure (2-3) → Simple process, scalable
Material	Separated function	Integrated function
Issue	Layer structure complexity Difficulty in mask patterning	Performance (esp. lifetime) Patterning technology

**Table 1**, the structure of small molecule OLED devices is a complicated multilayer structure, and vacuum vapor deposition is primarily used for manufacturing. On the other hand, the structures for polymer OLED devices are comparatively simple and are 2 to 3 layer structures, and printing processes such as inkjet methods and dye coating methods can be used in the main for film formation of the organic layers. This is because polymer OLED materials can comparatively easily be given solubility to solvents. Since it is possible to easily print RGB material on large substrates, there are great expectations for polymer materials compared with vapor deposition materials, which are currently the main stream for the current OLEDs, because of the ability to manufacture large panels without a mask and improvements in material utilization efficiency.

To form the uniform organic layer films in OLED devices, it is preferable that the polymer material have a high molecular weight. Therefore, ingenuity such as purity of monomers, conditions for polymerization and methods for post-processing refinement is necessary. At Sumitomo Chemical Co., Ltd. we have synthesized polymers using the Yamamoto reaction or Suzuki reaction, and technology for precise molecular weight control of molecules with which the weight average molecular weight in a polystyrene conversion is approximately 10,000 – 1,000,000 has been established.

As is shown in **Table 1**, the simplest polymer OLED devices consist of an anode, a hole injection layer (HIL), an emission layer (EML) and a cathode, but the device light emission efficiency can be greatly improved by introducing a layer, interlayer (IL), between the hole injection layer and the emission layer.<sup>19)</sup> The IL layer not only has hole transport properties, but also has a function as a blocking layer for electrons and excitons. It has been observed that quenching of the light emitting excitons by the hole injection layer can be suppressed by insertion an IL layer of Poly[9,9-dioctylfluorene-*co*-N-(4-*sec*-butylphenyl)-diphenylamine] (50:50) (F8-TFB) with a thickness only about 10 nm between a hole injection layer formed from a thiophene based polymer conductor (PEDOT, PSS) and an emission layer formed from Poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8-BT).<sup>19)</sup> Furthermore, by introducing cross-linkable units into the IL layer, it is possible to fabricate the emission layer by a wet process on top of that layer. The interlayer can be considered to be a revolutionary technical innovation in the development of OLED devices.

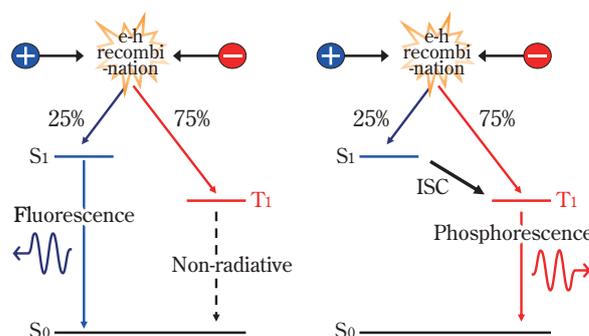
## Improvements to Polymer OLED Material Characteristics (1): Efficiency

The external Quantum efficiency (*EQE*) for OLED devices is expressed by the following formula (1).

$$EQE = \gamma \cdot \eta_{e-h} \cdot \phi_{ph} \cdot (1-Q) \cdot \eta_{OC} \quad (1)$$

Here,  $\gamma$  indicates the balance factor between electrons and holes,  $\eta_{e-h}$  the electron and hole recombination probability,  $\phi_{ph}$  the quantum yield,  $Q$  the extinction factor due to electrodes and  $\eta_{OC}$  the outcoupling efficiency. Based on this formula, it is possible to improve light emission efficiency by improving the balance in the quantity of charges injected by the electrodes, improving the electron and hole recombination probability and exciton generation probability in the emission layer, improving the quantum yield of the material, designing recombination locations that are not quenched by the electrodes, and designing film thickness and optical characteristics advantageous for outcoupling. Up to now, improvements have moved forward by means of theoretical designs for materials giving high emission intensity with the aid of quantum chemistry calculations, the selection of electrode types and materials for hole injection for the electron and hole balance factor<sup>20, 21</sup>, and hole trapping designs for resolving electrode quench, along with the development of IL layers having a high energy level and device structure designs in which a recombination region is trapped in the vicinity of the emission layer and IL layer boundary.

From the standpoint of material development, improvement of emissive exciton generation probability is an important factor for further *EQE* improvements. Excitons, which are generated by the recombination of electrons and holes include singlet excitons and triplet excitons, and the probabilities of their being generated are 25% for singlet excitons and 75% for triplet excitons according to the rules of spin statistics. Normally, light emission in organic compounds is only from the fluorescence from the singlet exciton state, and the remaining 75% in the triplet exciton state do not emit light and are heat dissipated. In other words, of the excitons obtained by recombination, only 25% contribute to light emission (Fig. 3). If phosphorescence could be obtained from the triplet exciton states, the 75% of the excitons generated by recombination could be utilized as emission. In 1999, Forrest at Princeton University and Thompson at the University of Southern



**Fig. 3** Schematic illustrations of fluorescence (left) and phosphorescence (right) mechanisms

California, et al.<sup>22)–24)</sup> found that they could take advantage of phosphorescence from the triplet exciton state, which had originally been a forbidden transition, with iridium complexes and platinum complexes. This is caused by the strong spin-orbit interaction (heavy atom effect) of iridium, etc. In iridium complexes, etc., inter-system crossing (ISC) also occurs due to spin-orbit interaction, and since singlet excitons are converted into triplet excitons, it turns out that 100% of the excitons generated can be extracted as phosphorescence (Fig. 3). Generally, the light outcoupling efficiency is thought to be 20%; therefore, the upper limit for *EQE* is 20% in formula (1). OLED devices have been realized 20% *EQE* by using phosphorescent materials,<sup>25, 26)</sup> and the internal quantum efficiency (*IQE*) has just about reached 100%. Use of phosphorescent materials is one important means for increasing efficiency.

There has come to be a large amount of research on dispersed polymer OLED materials which combine small molecule phosphorescent materials and polymers.<sup>26), 27)</sup> In this research there are many examples of the use of polymers in which the main chain is not conjugated and carrier transport units are incorporated into the main chain and side chains. Changing composition and parameters is comparatively easy, and it can be assumed that the level of singlets and triplets is easily controlled. Polymers in which the triplet level of blue phosphorescent materials can be handled even though the main chains are conjugated have been proposed using a meta-bonded polyphenylene backbone.<sup>28)</sup> Conjugated polymers can essentially be expected to have superior low-voltage drive for charge transport since their electrons are delocalized; therefore, practical material designs are expected from this approach of “proper control of conjugation.” On the other hand, Burn et al. at Oxford University

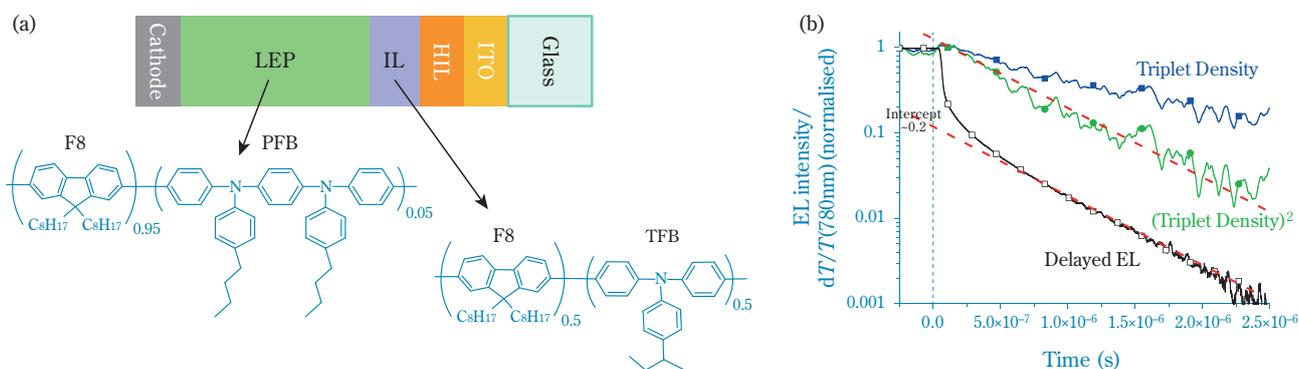
have found that dendrimers in which dendrons have been introduced into an iridium complex, etc., are useful as phosphorescent materials with which devices can be created by the wet process.<sup>29)–31)</sup> Polymer OLED devices that make use of conjugated polymers and dendrimers have been observed to exhibit a high level of performance.<sup>32)</sup> Combinations of phosphorescent materials and polymer materials are extremely important work for increasing efficiency, and it is thought that a large amount of research will be moved forward in the future, leading to improved characteristics.

On the other hand, OLED devices with fluorescent materials can only contribute to a maximum of 25% of light emission out of the excitons generated as described above. However, since 2000, there have been reports of high-efficiency light emission where the generation probability of singlet excitons may exceed the 25% of the spin statistics rules.<sup>33)–36)</sup> There has been very interesting research that might show that the probability of singlet exciton generation may be greater than 25% for conjugated polymers, but on the other hand, it has been reported that in small molecule OLED devices, one singlet exciton can be generated from two triplet excitons by triplet-triplet annihilation (TTA).<sup>37), 38)</sup>

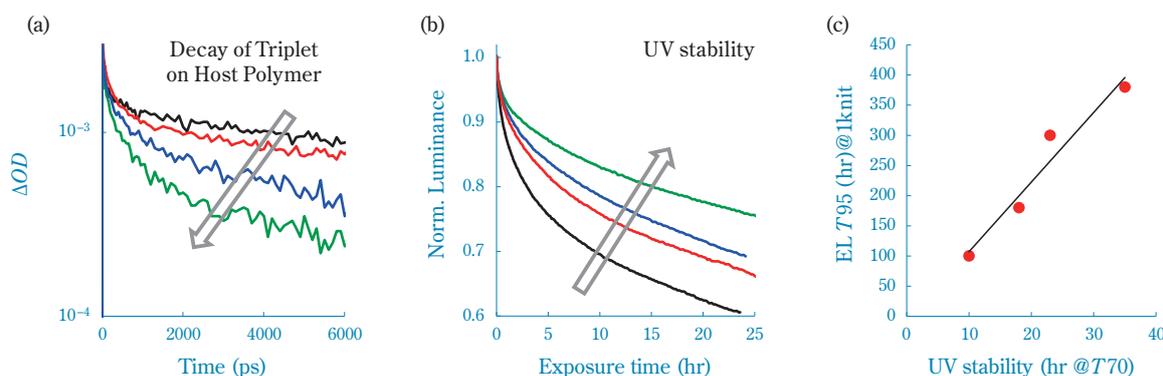
A polymer OLED device in which F8TFB is used in the IL layer and Ppoly[9,9-dioctylfluorene-*co*-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine] (95:5) (F8-PFB) is used in the emission layer is shown in Fig. 4 (a).<sup>39)</sup> As a result of the delayed fluorescent analysis by time resolved electroluminescence measurements on this device, it was clear that the delayed fluorescent components were approximately 20% of the light emission (intercept of delayed electroluminescence at time zero in Fig. 4 (b)). Comparing decay behavior (black line) for delayed fluorescence with the

behavior of the triplet exciton density (blue line) on F8-PFB measured by a transient absorption technique in Fig. 4 (b), it was found that the time scale for both decay was approximately the same ( $O(\mu\text{s})$ ). In another important point, compared with the decay curve (green line) for the square of the triplet exciton density, the delayed fluorescence has the same slope (red dashed line), and this suggests that two triplet excitons contribute to the generation of delayed fluorescence. These can be assumed to be results that strongly support that TTA is the origin of the delayed fluorescence. By making use of this TTA, in the generation probability for singlet excitons, the generation by TTA is added to the 25% of the spin statistics rule.<sup>39)–42)</sup> A high-efficiency light emitting device having *EQE* of 10% or more in a blue fluorescent material has already been reported.<sup>41)</sup> Several theories of singlet exciton generation probability (how many singlet excitons  $S_1$  are generated from two triplet excitons  $T_1$ ) due to TTA have been conceived ranging from 5% to 50%,<sup>38), 43), 44)</sup> and no conclusion has been reached. The maximum case is the addition of half of 75%, 37.5%, because one singlet exciton is generated from two triplet excitons, and the total probability of generation of singlet excitons turns out to be  $25\% + 37.5\% = 62.5\%$ .<sup>38)</sup>

As a result of continuing investigations for improvement, we developed a triplet control polymer (TCP) that gives rise to TTA with excellent efficiency. By blending this TCP with a blue light emitting polymer, it became clear that the triplet excitons affected not only the light emission efficiency, but also the luminance lifetime in OLED devices. The changes in optical density (*OD*),  $\Delta OD$ , which correspond to the triplet exciton density present on the host polymer as measured using transient absorption spectroscopy, are shown in Fig. 5 (a)



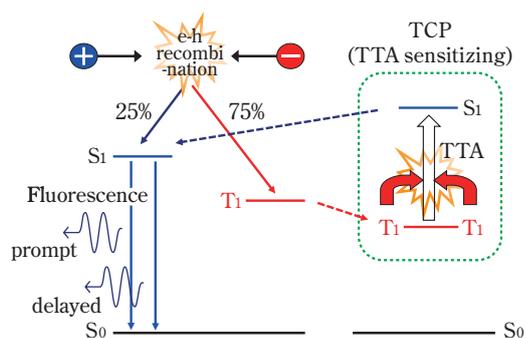
**Fig. 4** (a) Device structure and chemical structure of material used, (b) Electroluminescence turn off of the prototypical device (black) compared with the time resolved transient triplet absorption (blue) and its square (green)



**Fig. 5** (a) TCP dependence of triplet density on host polymer measured by the transient absorption of 780nm, (b) TCP dependence of UV stability, (c) Relation of device T95 with UV stability

and the TCP concentration dependence of UV stability in Fig. 5 (b). There is a trend in which the higher the UV stability is in Fig. 5 (b), the more rapid the fall of triplet excitons density on the host polymer in Fig. 5 (a) is, that is, the more rapidly the triplet excitons disappear. Furthermore, as is shown in Fig. 5 (c), it has been confirmed that UV stability has a linear relationship with OLED device lifetime.

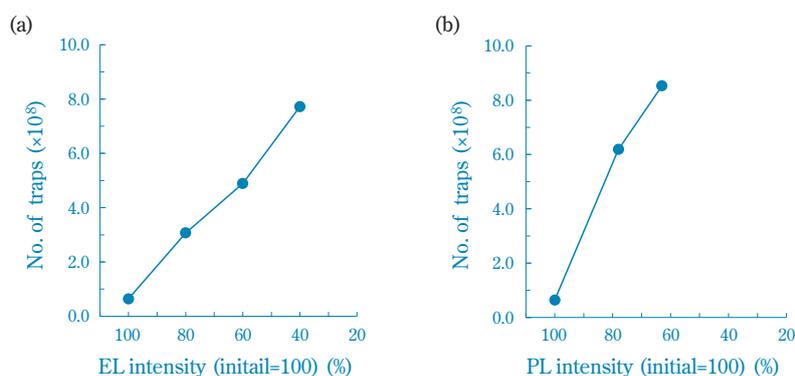
In other words, as in Fig. 6, triplet excitons  $T_1$  on the light emitting polymer are transferred to TCP, and those triplet excitons  $T_1$  undergo TTA on TCP. Furthermore, it can be assumed that it is important to run the cycle of the singlet excitons  $S_1$  generated by TTA transferring energy to the light emitting polymer and emitting light with good efficiency. It is thought that the triplets that make up 75% of the excitons generated by recombination of electrons and holes in the device are excited and are normally annihilated by a non-radiative process, but in some cases, the triplet excitons are speculated to degrade material. Their energy are rapidly annihilated by the TTA mechanism and are changed to singlet excitons for which transition is rapid, thereby improving not only efficiency but also life.



**Fig. 6** Schematic illustration of TTA process with TCP

## Improvements to Polymer OLED Material Characteristics (2): Lifetime

The gradual decrease in luminance when the devices are driven by a fixed current is called durability or lifetime. For example, the time to a reduction of 5% in luminance is sometimes used as the index of lifetime  $T_{95}$ . If devices such as OLEDs that generate light themselves have their brightness reduced by just several percent compared with surrounding pixels that are specific pixels, they are recognized as an after-image. Generally, this is called the “burn-in” phenomenon. To resolve this, it is important to suppress decreases in luminance of light emitting materials as well as have countermeasures using display driving systems. In driving polymer electroluminescent devices, there is a decrease in the intensity of photoluminescence along with a drop in electroluminescence, and they seem to be in a linear relation. The main cause of the decrease in the intensity of electroluminescence is thought to be decrease in the intensity of photoluminescence, but besides this, dispersion of impurities from electrodes and charge balance degradation because of the change in charge injection from the electrodes can also be considered. The causes of decrease in the intensity of photoluminescence are inferred to be causes such as (1) degradation of material by bond cleavage, (2) generation of trap sites, (3) impurities originating in materials and (4) external causes such as moisture, oxygen, etc. In addition, in OLED devices, impurities, such as residue of catalysts used in reactions, residual groups with polymerization activity, impurities such as metals or halogens, etc., within the light emitting material and charge transport material greatly reduce the electroluminescence properties; therefore, improvements in monomer purity, suppression of side reactions due to



**Fig. 7** (a) EL intensity vs. the number of traps generated by device driving, (b) PL intensity vs. the number of traps generated by UV irradiation

high level activation of catalysts and reduction of the amount used, terminal treatment after the polymerization and improvements in polymer purity by subsequent purification are necessary. In recent Sumitomo Chemical Co., Ltd. materials, metals such as Pd and halogen residue have been managed on the ppm level, and their effects have been minimized.

As a result of the detailed investigations on degradation of photoluminescence intensity, it has been confirmed that decreases in the photoluminescence are not found in electron major devices and hole major devices, in other words those which are driven by only electron or holes.<sup>4)</sup> In addition, it has been confirmed from the reverse engineering that there is almost no change in the intensity of fluorescence before and after driving and polymers become partially insoluble after device driving in which the polymer host and a light emitting small molecule compound are blended.<sup>4)</sup> Based on these observations, it is strongly suggested that the decrease in the intensity of photoluminescence in materials is related to the excitation state that can be formed by the hole and electron recombination and that the photoluminescence is quenched by some extinguishing factors in the polymer rather than degradation of light emitting units. Furthermore, photoluminescence intensity after driving is recovered by heating the device to  $T_g$  or higher; therefore, it has been inferred that the generation of some reversible quenching sites within the polymer is the cause of the decrease in luminance.

As an example of an analysis of the reversible quenching factor, we introduce trap analysis by a thermally stimulated current (TSC) technique with a thermally stimulated current measuring system (TS-FETT) manufactured by Rigaku Corporation. In normal TSC measurements, it is possible to detect a trap (shallow

trap) in the range of an energy of 0.15 eV (90 K) – 0.90 eV (400 K), but we incorporated UV irradiation in our TSC measurements and developed a unique method that was also able to detect traps (deep traps) having energies of 0.90 – 2.0 eV.<sup>45)</sup> Results of this deep trap analysis are shown in Fig. 7. It can be seen that there is a linear relationship between electroluminescent decrease and the amount of trap generation according to Fig. 7 (a). In Fig. 7 (b), the relationship between reductions in photoluminescence when material is degraded by UV irradiation and the amount of traps generated is shown. In this figure, the amount of traps was observed to increase linearly to the reduction in photoluminescence intensity. It can be assumed that these are results strongly suggesting that the traps are generated via the material being in an excited state and have a relationship to the quenching factor. This is an agreement with the results that reductions in the photoluminescence are not seen before and after driving of electron major or hole major devices.

Furthermore, the linear relationship between photoluminescence and electroluminescence intensity and the amount of traps generated has not been observed with the conventional shallow trap measurements, and this is a result specific to deep traps.

Analytical results of detailed investigations on the stability of the photoluminescence using only host systems (type case 1) and host / green phosphorescence emitter (G-em) blended systems (Case 2, Case 3) are summarized in Table 2.<sup>46)</sup> Using different excitation wavelengths, adjustments were made such that only the host was excited in Case 1, both the host and emitter excited in Case 2 and only the emitter excited in Case 3 and the intensity of photoluminescence was measured. In each case, three different hosts were used, and a comparative study of the dependency was

**Table 2** Relative stability among three hosts. Two difference combinations of host and emitter are studied.

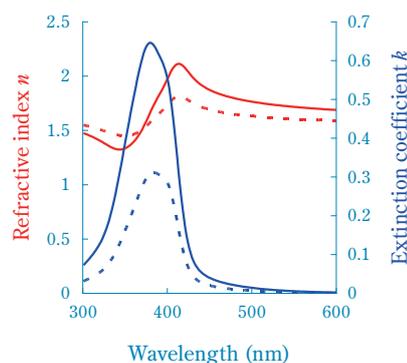
	Case 1	2	3
Scheme	325nm Ex host	365nm Ex G-em ISC	450nm Ex G-em ISC
Excited	Host	Host/G-em	G-em
Emission	Host	G-em	G-em
Normalized stability ( $T_{80}$ )			
Host 1	1	1	1
Host 2	1.0	1.6	2.7
Host 3	1.2	1.8	5.1

carried out. While in Case 1, the three types of host showed almost the same UV stability ( $T_{80}$ ), a host dependency was observed in Case 2 and Case 3. Since, from Case 1, the photoluminescence stability of the three hosts was almost the same, the host dependency observed in Case 2 and Case 3 can be thought of being related to the exciton amount (density) retained on the host as is shown in the energy level diagrams in the table. In other words, it can be assumed that (1) the excitons on the host being able to transfer energy to the emitter as efficiently as possible and/or (2) the reverse energy transfer from the emitter to the host being as small as possible are important factors in high photoluminescence stability. Effects (1) and/or (2) arising easily comes in the order of Host 1  $\rightarrow$  Host 2  $\rightarrow$  Host 3, and as a result it can be assumed that stability is improved. Since ISC occurs very quickly, the suppression of quenching site generation by retention of triplet excitons, in particular, on the host can be thought of as an important design guideline for improving stability.

## Future Outlook

We would like to describe planar alignment and the TADF mechanism, which can be thought of as important material designs from the standpoint of further improving the characteristics in future material design.

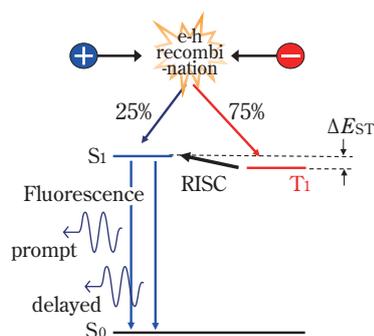
If the shape of light emitting units and its introduction into polymers are optimized, it has been found that the transition dipole moment is oriented in the direction of the plane of the substrate, and light outcoupling efficiency is improved because one can extract more light



**Fig. 8** In-plane (solid line) and out-of-plane (dashed line) refractive index (red) and Extinction coefficient (blue)

emitted from the aligned emitter parallel to the substrate, and hence,  $EQE$  is also greatly improved.<sup>47), 48)</sup> Many examples of small molecule compounds have been reported for dipole moment orientation.<sup>49)–51)</sup> The results of measurements of optical constants using spectroscopic ellipsometry for F8-PFB = 95:5 is shown in **Fig. 8** as an example of a polymer case. Differences in optical constants in an in-plane direction (solid line) and a perpendicular direction (dashed line) with respect to the substrate were observed, and even in basic polymers such as F8-PFB, it was found that planar orientation is high. In particular, with conjugated polymers, there is a tendency for the conjugation plane to be spontaneously oriented just by fabricating a layer application and formation on the substrate; therefore, this has been interpreted as the result of facilitation of planar alignment of transition dipole moment by combination of optimally designed light emitting parts. With polymers, this is an extremely interesting material design which has been conceived for “spontaneous formation of planar orientation.”

Materials with thermally activated delayed fluorescence (TADF) have been attracting a great amount of attention recently as “a third generation of light emitting material” after fluorescence (1<sup>st</sup>) and phosphorescence (2<sup>nd</sup>), and are a technology for converting triplet excitons into singlet excitons without using heavy metals such as iridium and platinum. In theory, an IQE of 100%, the same as for phosphorescent materials, can be expected; therefore, a great deal of research has moved forward in recent years.<sup>52)</sup> The mechanism is that a reverse intersystem crossing (RISC) from  $T_1$  to  $S_1$  becomes thermally possible by making the difference between the excited singlet state ( $S_1$ ) and the energy for the excited triplet state ( $T_1$ ) small, and  $T_1$ , which is



**Fig. 9** Schematic illustration of TADF process

normally non-radiative, is converted to  $S_1$  and light is emitted. **Fig. 9** shows the light emission mechanism for TADF. Two types of light emission are included; prompt light emission from  $S_1$  generated direct recombination and delayed light emission from  $S_1$  converted by RISC from  $T_1$ . Both spectra match because the light emission comes from the same  $S_1$  state, but with just a delay in time via the  $T_1$  state in the delayed component. The RISC rate constant, which is important for the efficiency of TADF, is given by the following formula (2):

$$k_{\text{RISC}} \propto \exp\left(-\frac{\Delta E_{\text{ST}}}{k_{\text{B}}T}\right) \quad (2)$$

Here,  $k_{\text{B}}$  represents the Boltzmann constant and  $T$  the temperature, and RISC is more efficient when the energy difference ( $\Delta E_{\text{ST}}$ ) between  $S_1$  and  $T_1$  becomes smaller.<sup>53), 54)</sup>  $\Delta E_{\text{ST}}$  is proportional to the exchange integral; therefore, it is important that TADF materials are designed such that the overlap of HOMO and LUMO is small, and designs are made by combining donor (D) and acceptor (A) units. On the other hand, however, for high fluorescent quantum yield, overlapping of HOMO and LUMO is required; therefore, designs that “moderate adjustments” between D and A are important.<sup>55)–57)</sup>

Recently, the use of TADF materials as assisting dopant materials for fluorescent light emitting materials has been examined rather than use as light emitting materials as described above. The mechanism in which charges recombine on TADF, all singlet excitons including the singlet excitons coming via RISC are transferred to the light emitting material rapidly by Förster energy transfer and light emission obtained, is very interesting.<sup>58)</sup>

Following on the development of small molecule compounds, development based on polymer materials has also been being studied, and many reports have appeared recently. There are designs in which D and A

are arranged alternately in the main chains or side chains of polymers, designs introducing TADF units that combine D-A into the main chains or side chains of polymers and, further, dendrimer types with these designs. Please refer to the reviews for recent designs.<sup>59)</sup>

## Summary

In recent years, devices with OLEDs have increased. From the light emitting materials point of view, solution processable materials suitable for wet process in manufacturing large panels at a low cost have been getting a attention. In particular, polymer OLED materials have various characteristics such as making designs that integrate a variety of functions into one material possible, its being soluble and possible to print pixels on a large surface area by methods such as printing. While understanding the basic phenomena such as the behavior of excitons and charges in the polymers, exciton management by the TTA process, TCP blending, etc. are important for increasing efficiency and extending lifetime.

**Table 3** shows the performance of polymer OLED materials being developed by Sumitomo Chemical Co., Ltd. Here, there have been great improvements in all of efficiency, lifetime and chromaticity CIE ( $x, y$ ) in the last several years, and red, green and blue materials all have had the characteristics of high efficiency and long lifetime. Here, CIE is an abbreviation for the Commission Internationale de l’Eclairage, and CIE- $x, y$  represents the chromaticity coordinates. In terms of the performance of soluble OLED materials, we are confident that our materials possess the best performance among the materials we have known. Of course, we would like to perform further optimization of conjugated polymer OLED materials and the development of polymer

**Table 3** Latest performance of PLED

Spin coated/Bottom emission device		End/2017	
ITO/HIL/IL/EML/NaF/Al		Achieved	
Xylene ink			
R	Efficiency (cd/A)	24	
	CIE- $x,y$	0.66, 0.34	
	T95 (hr) @1knit	5800	
G	Efficiency (cd/A)	85	76
	CIE- $x,y$	0.32, 0.63	0.32, 0.63
	T95 (hr) @1knit	15000	25000
B	Efficiency (cd/A)	8.0	9.2
	CIE- $x,y$	0.14, 0.11	0.14, 0.12
	T95 (hr) @1knit	400	750

OLED materials having even better characteristics by actively bringing in new design guidelines such as planar alignment and TADF as well as having a high level of process robustness and being capable of applications in the manufacturing of large OLED displays.

## References

- 1) C. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
- 2) J. H. Burroughes *et al.*, *Nature*, **345**, 539 (1990).
- 3) Sumitomo Chemical Co., Ltd., JP H3-244630 A (1991).
- 4) C. Sekine *et al.*, *Sci. Technol. Adv. Mater.*, **15**, 034203 (2014).
- 5) N. C. Greenham *et al.*, *Nature*, **365**, 628 (1993).
- 6) M. Bernius *et al.*, *Adv. Mater.*, **12**, 1737 (2000).
- 7) M. Bernius *et al.*, *J. Mater. Sci.: Mater. Elect.*, **11**, 111 (2000).
- 8) M. Bernius *et al.*, *Thin Solid Films*, **363**, 55 (2000).
- 9) M. Inbasekaran *et al.*, *Synth. Met.*, **111-112**, 397 (2000).
- 10) Arno Kraft *et al.*, *Angew. Chem. Int. Ed.*, **37**, 402 (1998).
- 11) C. Ego *et al.*, *Adv. Mater.*, **14**, 809 (2002).
- 12) T. Miteva *et al.*, *Adv. Mater.*, **13**, 565 (2001).
- 13) J. H. Lee and D. H. Hwang, *Chem. Comm.*, 2836 (2003).
- 14) D. Vak *et al.*, *Mater. Chem.*, **14**, 1342 (2004).
- 15) Y. Ohmori, *Oyo Butsuri*, **76**(5), 522 (2007).
- 16) W. Wu *et al.*, *Microelectronics Journal*, **35**, 343 (2004).
- 17) Q. Hou *et al.*, *Macromolecules*, **37**, 6299 (2004).
- 18) S. Tokito *et al.*, *Org. Electron.*, **4**, 105 (2003).
- 19) J. S. Kim *et al.*, *App. Phys. Lett.*, **87**, 023506 (2005).
- 20) N. Akino and Y. Zempo, *MRS Proceedings*, **846**, DD2.3 (2005).
- 21) Y. Zempo *et al.*, *J. Phys. Cond. Matt.*, **20**, 064231 (2008).
- 22) M. A. Baldo *et al.*, *Nature*, **395**, 151 (1998).
- 23) M. A. Baldo *et al.*, *Appl. Phys. Lett.*, **75**, 4 (1999).
- 24) C. Adachi *et al.*, *J. Appl. Phys.*, **90**, 5048 (2001).
- 25) S. Watanabe *et al.*, *Jpn. J. Appl. Phys.*, **46**, 1186 (2007).
- 26) J. Liu and Q. Pei, *Curr. Org. Chem.*, **14**(18), 2133 (2010).
- 27) C. Lee *et al.*, *Appl. Phys. Lett.*, **77**, 2280 (2000).
- 28) J. Liu and Q. Pei, *Macromolecules*, **43**, 9608 (2010).
- 29) M. J. Frampton *et al.*, *J. Mater. Chem.*, **14**, 2881 (2004).
- 30) S. C. Lo *et al.*, *Adv. Mater.*, **17**, 1945 (2005).
- 31) S. C. Lo *et al.*, *J. Am. Chem. Soc.*, **131**, 16681 (2009).
- 32) J. Pollow *et al.*, *SID'05 Digest*, 1071 (2005).
- 33) C. Rothe *et al.*, *Phys. Rev. Lett.*, **97**, 076602 (2006).
- 34) J. S. Wilson *et al.*, *Nature*, **413**, 828 (2001).
- 35) M. Wohlgenannt *et al.*, *Phys. Rev. Lett.*, **88**, 197401 (2002).
- 36) M. Segal *et al.*, *Phys. Rev. B*, **68**, 075211 (2003).
- 37) D. Y. Kondakov, *J. Appl. Phys.*, **102**, 114504 (2007).
- 38) D. Y. Kondakov *et al.*, *J. Appl. Phys.*, **106**, 124510 (2009).
- 39) S. M. King *et al.*, *J. Appl. Phys.*, **109**, 074502 (2011).
- 40) A. P. Monkman, *ISRN Mater. Sci.*, **19**, 670130 (2013).
- 41) M. Roberts *et al.*, *SID Sym. Digest Tech.*, **42**, 1820 (2011).
- 42) Y. Tamai *et al.*, *Chem. Mater.*, **26**, 2733 (2014).
- 43) C. E. Swenberg and N. E. Geacintov, "Organic Molecular Photophysics", John Wiley and Sons, NY (1973).
- 44) D. Y. Kondakov, *J. Soc. Inf. Disp.*, **17**, 137 (2009).
- 45) N. Hayashi and N. Akino, The 18<sup>th</sup> Yuki EL Tohronkai, 39 (2014).
- 46) T. Yamada, *SID Sym. Digest*, **47**, 487 (2016).
- 47) K. Yamamoto *et al.*, The 15<sup>th</sup> Yuki EL Tohronkai, 61 (2012).
- 48) T. Yamada *et al.*, The 15<sup>th</sup> Yuki EL Tohronkai, 59 (2012).
- 49) D. Yokoyama *et al.*, *Org. Electron.*, **10**, 127 (2009).
- 50) J. Frischeisen *et al.*, *Org. Electron.*, **12**, 809 (2011).
- 51) M. Flammich *et al.*, *Org. Electron.*, **12**, 1663 (2011).
- 52) A. Endo *et al.*, *Adv. Mater.*, **21**, 4802 (2009).
- 53) H. Uoyama *et al.*, *Nature*, **492**, 234 (2012).
- 54) A. Endo *et al.*, *Appl. Phys. Lett.*, **98**, 1 (2011).
- 55) K. Kawasumi *et al.*, *J. Am. Chem. Soc.*, **137**, 11908 (2015).
- 56) Q. Zhang *et al.*, *J. Am. Chem. Soc.*, **134**, 14706 (2012).
- 57) K. Sato *et al.*, *Phys. Rev. Lett.*, **110**, 1 (2013).
- 58) H. Nakanotani *et al.*, *Nature Commun.*, **5**, 4016 (2014).
- 59) Y. Xie and Z. Li, *J. Poly. Sci.*, **A 55**, 575 (2017).

PROFILE



*Nobuhiko AKINO*  
Sumitomo Chemical Co., Ltd.  
Advanced Materials Development Laboratory  
Group Manager, Ph.D.



*Takeshi YAMADA*  
Sumitomo Chemical Co., Ltd.  
Advanced Materials Development Laboratory  
Group Manager  
Currently: PLED Business Planning Office



*Yoshiaki TSUBATA*  
Sumitomo Chemical Co., Ltd.  
Advanced Materials Development Laboratory  
Senior Research Associate, Ph.D.