Technical Report

Development of Phosphorescent Green Host Material for Organic Light Emitting Diode

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Abstract

The phosphorescent organic light emitting diode, OLED, which is theoretically capable of converting electrical energy into light energy with 100% conversion efficiency, was announced in the late1990s. However, to put it to practical use, significant improvements in driving voltage and lifetime were required. By studying phosphorescent green host materials based on the light-emitting mechanism of OLED, Nippon Steel Chemical & Material Co., Ltd. developed several phosphorescent green host materials that show a practical level of low driving voltage and long lifetime while maintaining the high current efficiency of the phosphorescent OLED and became the first in the world to commercialize it.

1. Introduction

1.1 Proposal of practical fluorescent OLED

When voltage is applied to an organic material, electrons and holes are injected into the organic material and recombine with each other in the organic material to emit light. This principle of the organic light emitting diode, OLED, had been known in the 1960s.[1] In 1987, Tang et al.[2] of Eastman Kodak in the United States demonstrated the commercial possibility of OLED. They announced a fluorescent OLED device using tris (8-hydroxyquinoline) aluminum complex (Alq_3), as shown in **Fig. 1**. Three technical advances occurred. The first was the adoption of a functionally separated device structure. A two-layer structure was constructed consisting of a hole transport layer made of a hole transporting material and a light emitting layer made of a light emitting material with electron transporting properties. The two-layer structure confined charges and improved the recombination probability. The second was that an amorphous organic material was selected and a thin film of several tens of nanometers was formed using a vacuum deposition method, enabling charge injection at low voltage. The third was the use of a stable metal with a small work function for the cathode and the improvement of electron injection and oxidation durability. These three techniques have succeeded in making organic materials emit light stably. OLED devices currently in practical use are also based on those ideas.

1.2 Proposal of practical phosphorescent OLED

Light emitted from organic materials can be classified into two types: fluorescence, which is emitted from a singlet excited state, and phosphorescence, which is emitted from a triplet excited state. In ordinary organic materials, the probability of light emission (phosphorescence) from the triplet excited state, which occurs with a 75% probability, is extremely low. Most of them are thermally de-

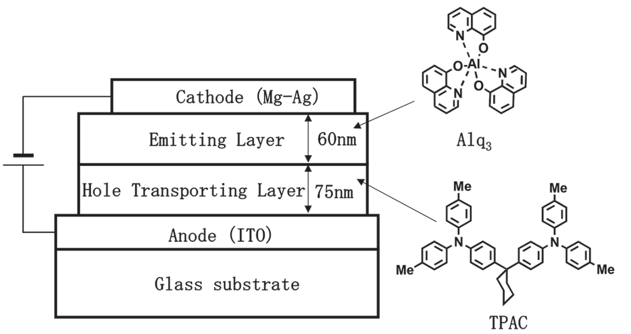

Fig. 1 Fluorescent OLED device structure proposed by Tang et al.[2]

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activated. Light emission (fluorescence) from the singlet excited state, which occurs with a 25% probability, can only be obtained. In other words, 75% of the input electrical energy is lost. In response to this situation, in 1999, Forrest et al.[3] of Princeton University in the United States reported a phosphorescent OLED device that uses an iridium complex as a light emitting material, which enables light emission (phosphorescence) from the triplet excited state at room temperature due to the heavy atom effect. Furthermore, the singlet excited state is converted to the triplet excited state by intersystem crossing, so that, theoretically, all of the input electrical energy is converted into light energy.

The phosphorescent device proposed by Forrest et al.[3] is shown in **Fig. 2**. Tris-(phenylpyridine) iridium complex $\mathrm{Ir(ppy)_3}$ was used as the light emitting material and was mixed with a host material that transports electric charges and excitation energy to form a light emitting layer. The device was configured with a hole blocking layer. It achieved an external quantum efficiency, EQE, of 8%, clearly exceeding the theoretical EQE of fluorescent devices of 5% (the product of a fluorescent internal quantum efficiency of 25% and a light extraction efficiency of 20%). Furthermore, through vigorous research by several institutions thereafter, the EQE approached the upper limit of 20% (the product of an internal quantum efficiency of 100% and a light extraction efficiency of 20%),[4–7] and an EQE even exceeding the upper limit of 20% was reported,[8] making it clear that phosphorescent devices show an EQE four times that of conventional fluorescent devices.

1.3 Development issues of phosphorescent green host materials

The phosphorescent devices mentioned above had a great impact on the industry in terms of their usefulness and practical feasibility. However, major improvements were required in terms of driving voltage and lifetime to bring them to practical levels. Among the various physical properties required for phosphorescent green host materials, a high triplet excitation energy (T1 energy) was necessary, as described later. This requirement was a major difference from conventional fluorescent device materials and from the phosphorescent red host materials that Nippon Steel Chemical & Material Co., Ltd. had already developed. In 2004, when Nippon Steel Chemical & Material started developing phosphorescent green host materials, there were no known materials that had the T1 energy required to achieve an efficiency approaching the upper limit of EQE also showed low driving voltage and long lifetime. New green host materials had to be found.

2. Main Subject

2.1 Light emission mechanism of OLED and guidelines for improving characteristics of OLED devices

The device structure of a typical OLED is shown in **Fig. 3**. Its light emission mechanism is as follows: (1) holes and electrons are injected from both electrodes into the light emitting layer via the charge transporting layer and charge blocking layer, respectively. Next, (2) both charges (holes and electrons) injected into the light emitting layer move over the host material or light emitting material and recombine and become excited on the light emitting material (direct recombination type), or recombine on the host material and the light emitting material becomes excited by the energy transfer to the light emitting material (energy transfer type). Finally, (3) the light emitting material in the excited state emits light.

Considering the above discussion, we now focus on the function of the host material. The device characteristics can be improved by efficiently conducting the steps of charge injection into the light emitting layer, charge transport within the light emitting layer, and energy transfer from the host material to the light emitting material. In other words, the current efficiency can be improved by suppressing losses in the respective processes. The driving voltage can be reduced by reducing the resistance. Also, the driving lifetime can be improved by using a host material with such a molecular structure that high durability is ensured in the active states, such as the charged and excited states.

2.2 Development of electron injecting and transporting host materials with low driving voltage and long lifetime

In order to efficiently transfer energy from the host material to the light emitting material and to suppress reverse energy transfer from the light emitting material to the host material, it is important to set the T1 energy of the host material to a certain value or higher. On the other hand, in order to reduce the resistance in the charge injection and transport processes in the light emitting layer, it is important to optimize the highest occupied molecular orbital, HOMO, levels and lowest unoccupied molecular orbital, LUMO, levels as well as the mobility of holes and electrons. Since the iridium complex-based light emitting material has a higher HOMO level than the hole transporting material and electron blocking material, the

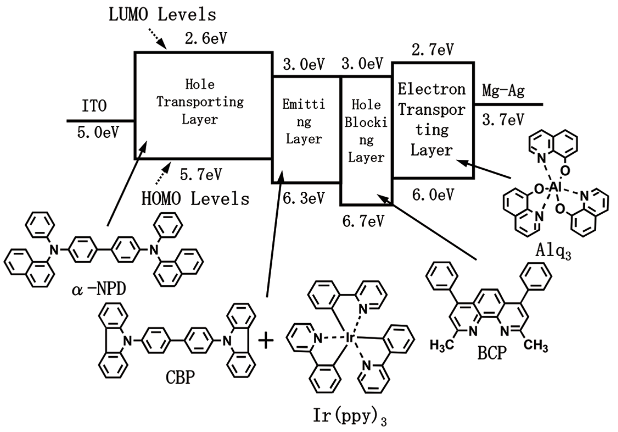


Fig. 2 Phosphorescent OLED device structure proposed by Forrest et al.[3]

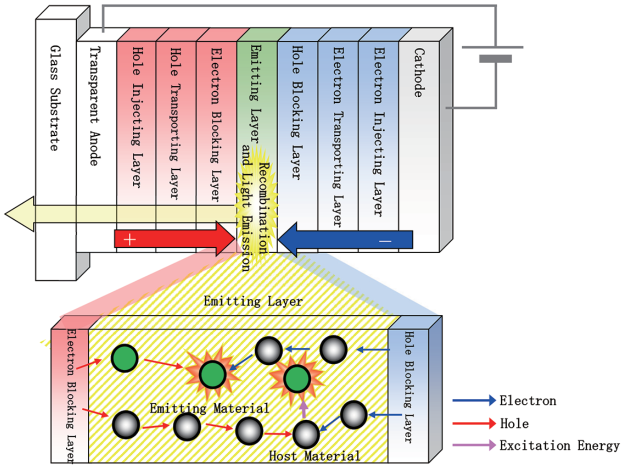


Fig. 3 Device structure of OLED and light emitting mechanisms

holes can be injected into the light emitting material and then move in the light emitting layer through hopping conduction. On the other hand, in terms of electron injection, the iridium complex-based light emitting material has a high LUMO level relative to the electron transporting material and hole blocking material. It makes it difficult for the electrons to be injected into the light emitting material. Therefore, it was thought that applying a host material with a high electron injection property, i.e., a low LUMO level, would be effective in reducing the driving voltage. Based on the above idea, in order to achieve low driving voltage and long lifetime while maintaining the high current efficiency that is characteristic of phosphorescent materials, the key to the material design was to have a high T1 energy and a low LUMO level and to realize this objective with a highly durable molecular structure.

The simulation technology Nippon Steel Chemical & Material established jointly with the Advanced Technology Research Laboratories of Nippon Steel Corporation was used to estimate material properties such as the T1 energy and LUMO level. This technology, which enables the estimation of material properties accurately and quickly, was used to clarify the relationships between device characteristics and material properties with molecular structures and was also used as a primary screening method to narrow down molecular structures with appropriate properties, thereby improving efficiency and voltage. On the other hand, to improve device lifetime, we studied molecular frameworks that show high durability against charged and excited states. Through these efforts, we found host A, which has a new molecular structure that had not been applied to OLED devices until then. Host A showed a high electron injection property compared to 4,4'-bis (9H-carbazol-9-yl) biphenyl (CBP), which was used in the report by Forrest et al.[3] and was then used as the standard material for green phosphorescent hosts at the time. Host A also had high T1 energy that allowed efficient energy transfer to the light emitting material and excellent durability. In addition, its high electron injection and transport properties make it possible to omit the hole blocking layer, which was previously considered essential for phosphorescent devices, thereby simplifying the device structure.

The device evaluation results of Host A are shown in **Table 1**. Host A was confirmed to show low driving voltage and long lifetime characteristics compared to CBP. By further optimization of the device structure, it also achieved an EQE of 18%, approaching the theoretical limit, and a luminance half-life of 60 000 h (both at 1 000 cd/m^2). In this way, host A accomplished a breakthrough.[9] Host A, with these excellent characteristics, was adopted for passive matrix-type OLED displays and lighting devices and Nippon Steel Chemical & Material achieved the practical application of a green phosphorescent host material ahead of the rest of the world.

2.3 Development of mixed host materials with low driving voltage and long lifetime

Host A showed lower driving voltage and longer lifetime characteristics compared to the green host materials available at that time. But further improvement of the lifetime was required for application to active matrix-type OLED displays like smartphones, etc. In OLED devices using host A, the high electron injection and transport properties of host A cause a bias in the charge balance in the emitting layer, and the emitting region is localized in a narrow region near the electron blocking layer. Therefore, it was thought that the deterioration of the emitting layer material due to the concentration of local load on some of the emitting layer materials, or the deterioration of the adjacent layer materials due to the leakage of electrons or excitons to the adjacent layers, was the cause of the decrease in lifetime characteristics (**Fig. 4**(1)).

Thereupon, we considered that by mixing a hole injecting and transporting host (P-type host) with an electron injecting and transporting host (N-type host), we could suppress the electron injection and transport property in the light-emitting layer and improve the hole injection and transport property, and by adjusting the injection and transport balance of holes and electrons, we could expand the light-emitting region and eliminate the local material degradation in the light-emitting layer and the degradation of materials in adjacent layers (Fig. 4(2)). To realize this concept, we set a design guideline for the P-type host by focusing on the HOMO level and hole mobility that affect the hole injection and transport properties. In addition, to widely put the mixed host to practical use, it was necessary to have a mixed host material prepared by premixing two types of host materials with the same vapor deposition rate so that their film fabrication could be performed by using manufacturing equipment and technology for single hosts. As described above, we conducted our material study on the basis of the development concept of expanding the light emitting region by applying a P-type host and adjusting the vapor deposition rate of two host materials. We eventually discovered the mixed host B.

The device evaluation results of the mixed host B are shown in **Table 2**. Although the mixed host B showed a 0.3 V voltage increase compared to host A, it achieved a three-fold improvement in lifetime. It also achieved a low driving voltage and long lifetime characteristics applicable to active matrix-type OLED displays. **Figure 5** shows the evaluation results of the mixing ratio stability during the vapor deposition process of the mixed host B. It can be seen that the mixing ratio in the vapor deposited film was maintained constant from the early to late stages of vapor deposition.

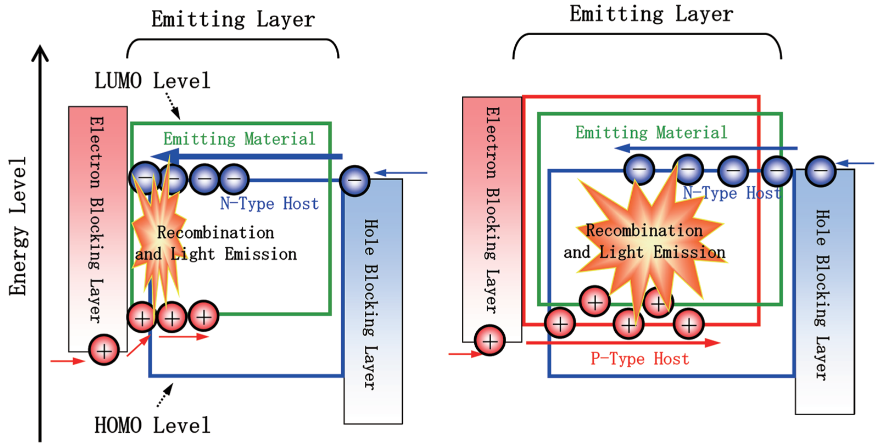
In a subsequent study, we discovered that the mixed host C helped to improve the hole injection and transport properties of the P-type host and to increase the durability of the P-type host. The

Table 1 Device evaluation results of Host A

Host	Device structure*	Current density [2.5 mA/cm^2]			Current density [12.5 mA/cm^2]
		Driving voltage (V)	Luminance (cd/m^2)	Current efficiency (cd/A)	20% luminance decay lifetime (hrs)
CBP	A	6.9	310	12.4	250
Host A	A	5.7	740	29.6	550
Host A	B	4.5	860	34.4	370

* Device Structure A: ITO(110nm) / HIL(20nm) / HTL(20nm) / Host-Green Emitter 7%(30nm) / HBL(10nm) / ETL(40nm) / EIL(1nm) / Al(100nm)

* Device Structure B: ITO(110nm) / HIL(25nm) / HTL(40nm) / Host-Green Emitter 7%(40nm) / ETL(20nm) / EIL(1nm) / Al(100nm)



(1) When N-type host is used as a single host, the light emission region is localized near the Electron Blocking Layer.

(2) When N-type host and P-type host are used as a mixed host, the light emission region is widely distributed.

Fig. 4 Relationship between charge injection/transporting properties and light emission region

Table 2 Device evaluation results of Mixed Host B and C

Host	Current density [2.5 mA/cm^2]				Current density [20 mA/cm^2]
	Driving voltage (V)	Luminance (cd/m^2)	Current efficiency (cd/A)	External quantum efficiency (%)	5% luminance decay lifetime (hrs)
Host A	2.7	1 536	61.5	16.6	63
Mixed Host B	3.0	1 550	62.0	16.2	187
Mixed Host C	3.1	1 641	65.2	17.2	375

* Device Structure : HIL(25nm) / HTL(30nm) /EBL(10nm) / Host-Green Emitter 5%(40nm) / HBL(5nm) / ETL(15nm) / EIL(1nm) / Al(70nm)

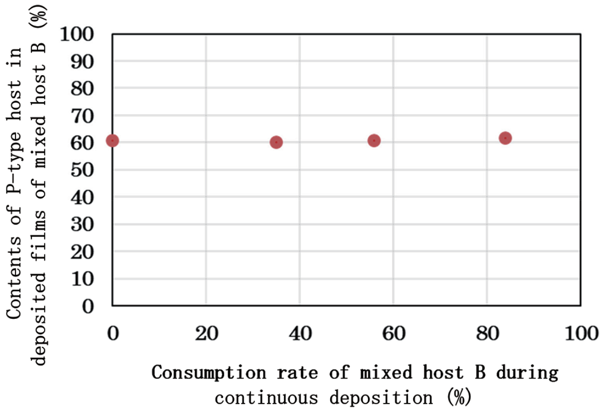


Fig. 5 Stability of mixture ratio of mixed host B during deposition process

mixed host C showed approximately twice the lifetime of the mixed host B (Table 2) and is currently used in displays of smartphones and other devices.

2.4 Commercialization of OLED materials

Nippon Steel Chemical & Material has accumulated synthesis and purification technologies for aromatic organic compound while studying the effective use and high-added value of the many aromatic compounds contained in coal tar. By making full use of these technologies, we have commercialized publicly known materials used in the charge transport layer and charge injection layer of OLED devices since 1998. Since 2000, we have commercialized our proprietary phosphorescent red and green host materials. The technologies Nippon Steel Chemical & Material have established to control and manage ppm order trace impurities that affect the characteristics of OLED devices, as well as the technologies to enable annual production at the ton level, including the final sublimation purification process, are widely recognized by OLED panel manufacturers. We continue to provide a steady supply of high-quality materials to the OLED panel manufacturers.

3. Conclusions

In this report, we described the development of phosphorescent green host materials. Nippon Steel Chemical & Materials is currently working on the development of even more highly functional green host materials, as well as highly functional blue host materials that will achieve higher efficiency than blue fluorescent materials that have not yet been put to practical use, by building on the knowledge and experience gained from these development efforts and further developing the highly functional materials we have discovered.

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