Molecular Design and Device Design to Improve Stabilities of Organic Light-Emitting Diodes

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Although organic light-emitting diodes (OLEDs) with internal quantum efficiencies of approximately 100% have been demonstrated using phosphorescent or thermally activated delayed fluorescent (TADF) emitters, the lifetimes of OLEDs have seldom been discussed owing to the complicated degradation mechanism. To realize OLEDs for practical applications, it is essential to extend their lifetimes. In recent years, attempts to improve the stability of OLEDs have been increasingly reported. One approach is to prevent the decrease in brightness resulting from OLED operation, so-called improvement of the operational stability. Another approach is to prevent the decrease in light-emitting area caused by oxygen/moisture, so-called improvement of the air-stability. In this review, molecular design and device design to improve the stability of OLEDs are introduced.

Keywords: Organic light-emitting diodes, Operational stability, Air-stability, Inverted structure

1. Introduction

Organic light-emitting diodes (OLEDs) have been intensively studied as a key technology for next-generation displays and light sources [1,2]. In recent years, several devices using OLEDs have started to be commercialized, such as smartphones. In the future, the characteristic features of organic semiconductor materials will enable the low-cost fabrication of such devices on flexible substrates. To reduce the power consumption of devices using OLEDs, the emission mechanism along with new luminescence materials have been intensively studied over the last 30 years with the goal of harvesting all excitons for emission. The internal quantum efficiency (IQE), defined as the number of photons generated per injected carrier, was typically limited to 25% in first-generation fluorescent OLEDs. Phosphorescent OLEDs (PHOLEDs), so-called second-generation OLEDs, containing iridium complexes were first proposed in 1999, and IQEs of nearly 100% were reported in the following year [3-7]. In 2015, the IQEs of third-generation OLEDs employing thermally activated delayed fluorescence (TADF) materials have reached nearly 100% [5]. IQEs of approximately 100% are now common for OLEDs employing phosphorescent or TADF emitters [8-11].

There have been much fewer reports on the stability of OLEDs than on their efficiency even though stability is one of the most important parameters for the practical application of OLEDs. However, in recent years, the stability of OLEDs has begun to be intensively discussed from two viewpoints: operational stability and air-stability. Since high operational stability is essential for almost all OLEDs used for practical applications, there have been many reports on materials suitable for achieving operationally stable OLEDs [12-23]. Some OLEDs employing flexible substrates or simple encapsulation structures have been applied for optoelectronic sensors and biophotonics in recent years [24-26]. The most important issue remaining for the practical application of these flexible devices is to improve the air-stability of their OLEDs. It was proposed that the light-emitting area of OLEDs decreases rapidly when oxygen and moisture react with alkali metals, which are typically used as the electron injection layer in conventional OLEDs [27,28].

Inverted OLEDs (iOLEDs) with a bottom cathode have been intensively studied as an ideal...
structure for improving the air-stability of OLEDs [28-33].

In this review, the recent progress in improving the stability of OLEDs is introduced. The first topic discussed is molecular design for realizing operationally stable OLEDs. Not only some emitting layers but also carrier-transporting materials suitable for realizing operationally stable OLEDs are introduced. The second topic is device design for realizing air-stable OLEDs. An inverted structure with a bottom cathode is effective for eliminating reactive materials such as alkali metals. Some electron injection materials that can be used as alternatives to alkali metals are introduced in addition to the basic concept of iOLEDs.

2. Molecular design for host

2.1. Host for phosphorescent emitters

Although there have been many reports on PHOLEDs with IQE of about 100%, the basic concept for improving both the efficiency and operational stability was first discussed as late as 2014. Operationally stable PHOLEDs have been demonstrated using two types of host: exciplexes with a small energy gap between the singlet (S$_1$) and triplet (T$_1$) excited states ($\Delta E_{ST}$) [15,18], and single TADF materials [14,16,17,20]. An emitting layer (EML) consisting of a single TADF material and a phosphorescent dopant is ideal for low-cost, high-performance PHOLEDs because strict control of the co-evaporation rate is essential when the co-evaporation of the EML involves the exciplex and the emitter [15,18]. An operationally stable PHOLED can be realized using a TADF material as the host because the electrically excited triplet excitons of the host, which are generally unstable [34], are rapidly transferred to the dopant by Förster resonance energy transfer (FRET) via reverse intersystem crossing (RISC) from the T$_1$ state to the S$_1$ state as shown in Fig. 1(a).

The host-dependent operational stability was evaluated in reference 17 using two hosts, CBP and PIC-TRZ, as shown in Figs. 1(b) and 1(c). CBP has been widely used as a host in green PHOLEDs, whereas PIC-TRZ is a TADF material [35]. The operational lifetime LT50, which is defined as the time for the luminance to decay to 50% of its initial value, strongly depends on the host material. The LT50 value was only 1,500 h for the PHOLED using CBP. In contrast, LT50 for the PHOLED using PIC-TRZ was estimated using the well-known stretched exponential decay function to be about 10,000 h [36], about seven times that of the PHOLED using
In 2017, the parameters and phenomena that mainly determine the operational stability of PHOLEDs were clarified [20]. The operational lifetimes of PHOLEDs utilizing similar TADF materials as hosts were evaluated to clarify the parameters that affect LT50. Figure 1(d) shows the TADF materials used as hosts, 2a, 2b, and 2c, which consist of several carbazoles and triazine [11]. Although the molecular structures of the hosts were similar, the PHOLEDs exhibited clear differences in LT50 as shown in Fig. 1(d). A smaller molecular weight resulted in a longer LT50. By examining the factors affecting LT50 for PHOLEDs, LT50 was found to be linearly related to the rate of FRET for PHOLEDs, which is strongly correlated with the energy transfer distance, as shown in Fig. 1e. Rapid energy transfer from the electrically excited states of the host to those of the dopant is critical for high operational stability; moreover, the FRET from the host singlet to the dopant, not the RISC process in the TADF host, mainly determines the operational stability. These findings suggest that TADF materials with small molecular radii are suitable host materials for use in operationally stable PHOLEDs.

2.2. Host for TADF emitters

In this decade, the IQEs of OLEDs employing TADF materials has reached nearly 100% without the use of heavy metals such as iridium [5]. IQEs of approximately 100% are now common for OLEDs employing TADF emitters as in the case for PHOLEDs [10]. Although LT50 for OLEDs employing TADF emitters was significantly improved by introducing interlayers of electron injection materials [19], there have been few reports on materials suitable for achieving operationally stable OLEDs employing TADF emitters.

In 2017, Cui et al. reported that electron-transferring n-type hosts, which typically include an acceptor moiety in their chemical structure, can extend the operational lifetimes of OLEDs employing TADF emitters [22]. Figure 2 shows the chemical structures of n-type hosts (SF2-TRZ, SF3-TRZ, SF4-TRZ) and the host-dependent operational stability of OLEDs employing the green TADF emitter 4CzIPN [10]. The devices with the n-type hosts exhibited long-term operational stability with device lifetime more than 30 times that of the device with the p-type host m-CBP. It was mentioned by Cui et al. that n-type hosts possess inherent advantages in balancing charge fluxes and suppressing high-energy exciton formation because of their deep HOMO levels and excellent electron transport properties. Their work offers guidelines for realizing long-lived and efficient TADF OLEDs.

3. Molecular design for hole transporters

The materials used in emitting layers, such as host materials, have been intensively studied, as pointed out in Section 2. On the other hand, carrier-transporting materials (CTMs), such as hole-transporting materials (HTMs) and electron-transporting materials (ETMs), suitable for highly efficient OLEDs have also been developed [8]. CTMs that can confine charges and excitons inside the emitting layer are essential for obtaining maximum efficiency from the emitter. In particular, triplet excitons should be confined to obtain high efficiency not only in PHOLEDs but also in OLEDs using TADF emitters [37]. However, there have been few reports on CTMs suitable for efficient and operationally stable OLEDs.

In 2013, a molecular design strategy for HTMs suitable for efficient and stable green PHOLEDs was presented for the first time [12]. The typical HTMs reported until then had been phenylamine derivatives, although the HTM-dependent operational stability of OLEDs had never been discussed. In this study, the HTM-dependent device
characteristics were investigated using several HTMs consisting of a central biphenyl unit and a phenylamine as shown in Fig. 3a. The operational lifetime LT50 and EQE were found to strongly depend on the HTM. The PHOLED using α-NPD exhibited a longer LT50 than those using TPD and TPD15, whereas the EQE of the PHOLED using α-NPD was lower than that of the PHOLEDs using TPD and TPD15. The lower EQE of the PHOLED using α-NPD was caused by the quenching of the triplet excitons due to the lower triplet energy of α-NPD than that of Ir(mppy)3. In contrast to these three PHOLEDs, a PHOLED using DBTPB had both a high EQE and a long LT50. Thus, this amine derivative with dibenzothiophene was found to be a promising HTM for green PHOLEDs.

Although DBTPB with its high EQE and long LT50 is effective for achieving efficient and stable PHOLEDs, the triplet energy of DBTPB is insufficient to completely confine the triplet excitons of green emitters.

In 2015, a novel amine derivative based on dibenzothiophene was synthesized as a high-triplet-energy HTM for efficient and stable OLEDs [23]. The chemical structure of the synthesized HTM, named 4DBTP3Q, is shown in Fig. 3(b). 4DBTP3Q was designed to increase the triplet energy compared with that of DBTPB by introducing o,o’-quaterphenyl in the molecular structure of DBTPB. The triplet energy of 4DBTP3Q is much larger than that of DBTPB as shown in Figs. 3(a) and 3(b). The increased triplet energy is effective for improving both the EQE and LT50 of PHOLEDs. A PHOLED with EQE of over 20% and high operational stability has been demonstrated using 4DBTP3Q.

In 2017, another amine derivative based on dibenzothiophene was synthesized as a high-triplet-energy HTM for efficient and stable OLEDs using a TADF emitter [21]. The chemical structure of the synthesized HTM, named 4DBTHPB, is shown in Fig. 3(c). 4DBTHPB was also designed to increase the triplet energy compared with that of DBTPB by introducing hexaphenylbenzene in its molecular structure. The triplet energy of 4DBTHPB is 2.7 eV, which is larger than that of 4DBTP3Q. The optimized TADF OLED exhibited EQE of 23.2% and LT50 of approximately 10,000 h at an initial luminance of 1,000 cd/m². High operational stability has been demonstrated using 4DBTP3Q. As has been discussed, not only a suitable emitting layer but also a suitable CTM is essential for achieving efficient and stable OLEDs.
Flexible OLEDs have attracted much interest because they are expected to be widely used for displays, lighting, sensors, and biophotonics. The major issue remaining for the practical application of these flexible OLEDs is to improve their typically short lifetimes due to the poor environmental stability of conventional OLEDs. Flexible substrates such as plastic allow ambient oxygen and moisture to permeate into devices, which degrades the alkali metals used for the electron injection layer in conventional OLEDs [27]. In 2006, inverted OLEDs (iOLEDs) with a bottom cathode were proposed as an ideal structure for realizing air-stable OLEDs [29]. Figure 4(a) shows the structures of a conventional OLED and an iOLED. The advantage of employing an iOLED structure is that reactive materials such as alkali metals can be eliminated. As an alternative to alkali metals, metal oxides such as ZnO are used in most reported iOLEDs because metal oxides can reduce the surface WF of ITO.

However, it is difficult to inject electrons from the electrode to the organic layer by employing only metal oxides. Thus, an interlayer that can reduce the electron injection barrier between the metal oxide and the organic layer is essential for realizing efficient iOLEDs.

Although there have been many reports on interlayers used in iOLEDs, amine-based molecules, typified by polyethyleneimine (PEI), have been widely used in recent years. Several iOLEDs employing PEI have been demonstrated to show similar driving voltages and efficiencies to conventional OLEDs using the same emitting material. The efficacy of electron injection from an ITO/ZnO/PEI surface has been investigated by ultraviolet photoelectron spectroscopy. The work function of ITO is about 5.0 eV, whereas by depositing ZnO, the work function was reduced to about 4.0 eV. By the physisorption of PEI on ZnO, the work function finally reached about 3.1 eV, which is comparable to that of alkali metals [38].

Fig. 4. (a) Multilayer structures of a conventional OLED and an iOLED, (b) Images of light-emitting areas of OLEDs as a function of storage time.

4. Device design for air-stable OLEDs

Flexible OLEDs have attracted much interest because they are expected to be widely used for displays, lighting, sensors, and biophotonics. The major issue remaining for the practical application of these flexible OLEDs is to improve their typically short lifetimes due to the poor environmental stability of conventional OLEDs. Flexible substrates such as plastic allow ambient oxygen and moisture to permeate into devices, which degrades the alkali metals used for the electron injection layer in conventional OLEDs [27]. In 2006, inverted OLEDs (iOLEDs) with a bottom cathode were proposed as an ideal structure for realizing air-stable OLEDs [29]. Figure 4(a) shows the structures of a conventional OLED and an iOLED. The advantage of employing an iOLED structure is that reactive materials such as alkali metals can be eliminated. As an alternative to alkali metals, metal oxides such as ZnO are used in most reported iOLEDs because metal oxides can reduce the surface WF of ITO.

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The high air-stability of an iOLED employing PEI was also demonstrated in 2014 [28]. We compared the long-term storage stability of a conventional OLED and the iOLED in air by encapsulating them using a barrier film. Figure 4(b) shows the light-emitting areas of the OLEDs as a function of storage time. Dark spot formation was observed clearly in the conventional OLED after 15 days of exposure to the atmosphere, and the emitting area had decreased by about half after 103 days. The observed shrinkage and dark spot formation may have originated from the degradation and oxidization of lithium fluoride used in the conventional OLED. In the iOLED, on the other hand, no dark spot formation or shrinkage was observed after 250 days. The iOLED was fabricated without the use of alkali metals, resulting in its high storage stability in air. Thus, it was demonstrated that iOLEDs have the potential to replace conventional OLEDs employing alkali metals in a wide variety of flexible organic optoelectronic devices.

5. Conclusion

Molecular design and device design to improve the stability of OLEDs were introduced. Highly efficient and operationally stable OLEDs are essential to reduce the power consumption of OLED-related devices. Thus, not only the design strategy of the emitting layer but also that of the CTM has been studied. It was reported that TADF materials with small molecular radii are suitable host materials for achieving efficient and stable PHOLEDs. On the other hand, n-type hosts are reported to be effective for realizing efficient and stable TADF OLEDs.

The molecular design strategies of HTMs suitable for efficient and stable OLEDs have also been discussed. Since an amine derivative with dibenzothiophene was found to act as an effective HTM, several amine derivatives with dibenzothiophene have been synthesized. Finally, efficient and stable OLEDs employing phosphorescent and TADF emitters have been demonstrated.

Inverted OLEDs, in which an alkali metal is not used as an electron injection layer, were demonstrated to have much higher air-stability than conventional OLEDs using an alkali metal. Since there is a large injection barrier between the cathode and the organic layer, interlayers that can reduce the electron injection barrier have been intensively studied. In recent years, an iOLED that exhibits similar \( J-V-L \) characteristics to a conventional OLED has been successfully demonstrated by employing ZnO/PEI as the EIL.

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