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The Introduction of Different Types of OLEDs

Zhendong Cheng [1,†], Zimeng Yan[2, *,†]

[1]Shanghai World Foreign Language Academy, Shanghai 200231, China
[2]Beijing Lu He International Academy, Beijing 101149, China

zmyan@student.wust.edu.pl
[†]These authors contributed equally to this work.

Abstract. As display technology advances, organic light emitting diodes (OLEDs) have attracted a lot of attention worldwide due to their light weight, flexibility, wide viewing angle, etc. This paper briefly introduces the history and the different historical OLEDs, including phosphorescence, thermally activated delayed fluorescence (TADF), and triplet-triplet annihilation (TTA). Then, this article mainly presents two kinds of OLEDs. The first is small-molecule OLED with typical three organic layers. The purity of the material is quite high, and it can produce high-quality films with high fluorescence quantum efficiency, which can produce a variety of colors of light. Its disadvantages are poor thermal stability and limited carrier transport capacity. The second is polymer based OLED. Compared with small molecule organic luminescence materials, polymer materials have higher physical strength, better processibility, mechanical properties, and thermal stability. In this regard, recent research progress and the comparison between these two types of OLEDs are proposed. They both are considered the most promising display technologies.

Keywords: Display technique, Small molecule OLED, Polymer OLED, Flexible display.

1. Introduction

Thirty years ago, the cathode ray tube (CRT) system was dominant, and the liquid crystal display (LCD) had just begun to appear, and the prospects of display technology had undergone considerable changes. Even today, LCD sales still account for a part of the entire display market, but the control of this ancient technology is weakening. Mobile phones and home theaters are just two examples of new markets that promote the development of display technology at both ends. LCD (active and passive matrix design) is the choice of small displays, but organic light emitting diode (OLED) technology is entering the mobile field, and mobile phones and other small and medium-sized devices (display 17 inches) are developing at an extremely fast speed. In the large-screen market, LCD and PDP displays are competing for supremacy. The final market share of these two technologies will undoubtedly be determined by many factors, including cost and power consumption [1].

The advantages of OLED are various. The organic layers of OLEDs are thinner, lighter and more flexible than the crystal layers of light emitting diode (LED) or LCD. Flexible materials can be applied in OLED substrates instead of rigid materials. Flexible OLED substrates are fabricated with plastics, while LED and LCD use glass substrates. OLED is brighter than LED, and the organic layers of OLEDs are much thinner than inorganic crystals in LED, so the charge transport and emitting layers of OLEDs

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can adopt multiple layer structure. In addition, LED and LCD need to be supported by glass, which will absorb some light. OLEDs are easier to manufacture and can be manufactured in larger sizes. OLED is plastic, so it can be made into large pieces. OLED has a wide viewing angle, up to about 170 degrees. The working principle of LCD is to block light, so there is a natural viewing barrier at some angles. OLEDs themselves emit light, so their vision is much wider [1].

OLEDs consist of anode, cathode and multiple organic layers inserted between them, comprising hole injection layer (HIL), hole transfer layer (HTL), emissive layer (EML), electron transfer layer (ETL) and electron injection layer (EIL). EML determines the OLED performances to a large extent. OLED can realize full-color display and white light emission via red, green, and blue (RGB) colour mode. The International Electrotechnical Commission coordinates (CIE) can be used to define the color of OLED devices. The efficiency of OLED, that is, the ability to convert electrons into photons, can be directly evaluated using quantum efficiency (QE), which is calculated by the ratio of photon to injected charge. QE is classified into internal QE (IQE) and external QE (EQE), which represent the numerical ratios of the total photons produced and emitted in the device to the charges, respectively. The structure as well as characteristics of the emitter will seriously affect the efficiency of OLEDs [2].

The mechanism of OLED is as follows: (1) Electrons (holes) are injected into the ETL/HTL by applying potential to the corresponding electrodes; (2) Charge transfer (redox reaction) occurs between different free radical ions; (3) Coulomb trapping of charges in luminescent materials; (4) Excitons are formed on the molecules of luminescent materials, and the excess energy generated by recombination excites the molecules; (5) Electromagnetic radiation generated when molecules return to the basic state. The emission wavelength is dependent on the EML [2,3].

2. Briefly history of OLED

An OLED was manufactured by Tang et al. which was the first electroluminescent (EL) device fabricated with multi-layer organic compounds as EML [4]. The driving voltage of organic EL is too high, so it can achieve ideal optical output only when its driving voltage is more than 100V. Therefore, its energy conversion rate is very low and basically less than 0.1% W/W [5,6]. Even though some organic EL devices require extremely high fluorescence quantum yield at 100% which is appropriate to display application.

The EL diode designed by Tang et al. is composed of two layers of organic thin films between the anode and cathode, one of which can only carry out unipolar transport, while the traditional organic EL battery uses a single layer of organic material [4]. The morphology, transport, recombination and luminescent properties of organic materials were selected to enable them to be used for constructing and operating thin film EL devices [4]. Low-function alloys prepared by vapor co-deposition were also used as cathodes for effective electron injection [4]. Indium tin oxide (ITO) anode and Mg:Ag alloy cathode could effectively inject holes and electrons [4]. In the vicinity of the organic interface region, charge recombination and green EL emissions were limited. The driving voltage was lower than 10 V, the EQE was 1%, the luminous efficiency was 1.5lm/W, and the brightness of 1000cd/m2 was feasible [4].

Polymer light emitting diode (PLED) is the second kind of OLED in which the emissive material is a polymer. In 1989, Jeremy Byrd of the University of Cambridge and his colleagues first observed EL in a conjugated polymer and discovered that the conductive polymer PPV has good electrochromic optical rotation performance. They fabricated PLED devices based on PPV, and then deeply recognized the development potential of PLED [7]. Polymers are mostly composed of small organic molecules that are linked together in a chain form to form polymer OLEDs by the spin-coating method.

In 1992, Cao Yong and others from Cambridge Display Technology Co., Ltd. used polyethylene terephthalate (PET) as a flexible transparent substrate material to form a conductive film on the conductive material of polyaniline (PANI) or polyaniline mixture through solution spin-coating and prepared a flexible PLED. The most intriguing feature of an organic EL display is revealed in this research finding.

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After more than 20 years of research and development, polymer OLED has achieved a high EQE of 5-10% and a long service life of more than tens of thousands of hours. Polymer OLEDs display not only RGB emissions, but also white emissions, which is critical for various applications.

2.1. Fluorescence

The electron is first excited to the singlet state (S1), and back to the ground state (S0). This process will emit fluorescence. Under the condition of electric excitation, the probability of hole and electron combining to form S1 and triplet (T1) excitons is 25% and 75%, respectively. Fluorescent dyes can only use the formed singlet excitons through the energy transfer between singlet states. Therefore, the maximum IQE of devices made of singlet luminescent materials is 25%. In practical applications, the EQE of organic EL devices prepared with fluorescent dyes is up to 5% due to the influence of factors such as device interface refraction.

2.2. Phosphorescence

Phosphorescent OLEDs can make full use of S1 and triplet state (T1) excitons to achieve 100% IQE. When an electron in excited molecules undergo spin reversal and change the multiplicity of the molecule from singlet state to triplet state and emits light. This isoenergetic radiation-less process called intersystem crossing (ISC) which is the fundamental principle of phosphorescence. In general, most purely organic molecules prohibit ISC processes. However, the spin-orbit coupling (SOC) process generated by heavy metals can unlock them in organic complexes. Though the SOC can be prohibited by the spin-selection criterion, the radiation still decays to the ground state. Phosphorescent materials have developed rapidly in the past few decades. Until now, there were plenty of different types of phosphorescence devices have been reported, for example complexs, pure organic compounds under room-temperature phosphorescence properties [3].

2.3. Thermally activated delayed fluorescence (TADF)

TADF utilizes thermal energy to convert triplet excitons into singlet excitons through RISC to achieve 100% IQE. The electroluminescent process of TADF molecules is significant to improve the IQE of OLEDs: (1) Electrons and holes (with a ratio of 1:3) are combined to generate S1 and T1 excitons; (2) High excitonic states pass through vibrational relaxation and internal conversion ;(3) The original S1 excitons return to S0 by fast fluorescence emission, or degenerate to triplet state excitons by ISC; (4) Triplet excited state can be partially converted to late singlet excited state by RISC, and by The delayed fluorescence emission decays further to the ground state. Among these processes, triplet to singlet is the critical process for increasing fluorescence emission. Therefore, TADF molecules should be in S1 and T1 states to guarantee RISC by creating molecules with a small overlap of ΔE_{ST} [3].

2.4. Triplet-triplet annihilation (TTA)

TTA refers to the process that two T1 excitons fuse into S1, so the maximum utilization efficiency of excitons will be promoted to 62.5%. It is regarded as an effective three-trap method for fabricating high-efficiency OLED devices, particularly for blue light. The TTA molecule should restrict the energy gap state to satisfy this condition. In the application of TTA materials, OLEDs can display more efficient rolling due to high driving voltage or sensitizer concentration, which is crucial to facilitate the TTA process [3].

3. OLED and PLED

Organic light-emitting diodes can be divided into small molecule OLED and PLED according to the molecular size of light-emitting materials. The manufacturing process of OLED is mature and PLED is the hot direction of display technology development at present.

3.1. Small molecule OLED

There are three organic layers sandwiched between the electrodes, forming a representative small

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molecule OLED with double heterostructure. EML usually contains a luminescent dye or dopant dispersed in a suitable host material (usually HTL or ETL material). PLED structure is relatively simple. Its single solution treatment layer combines the luminescent polymer (LEP) layer with the main body, emitter and charge transfer function. The basic structure is shown in Figure 1.

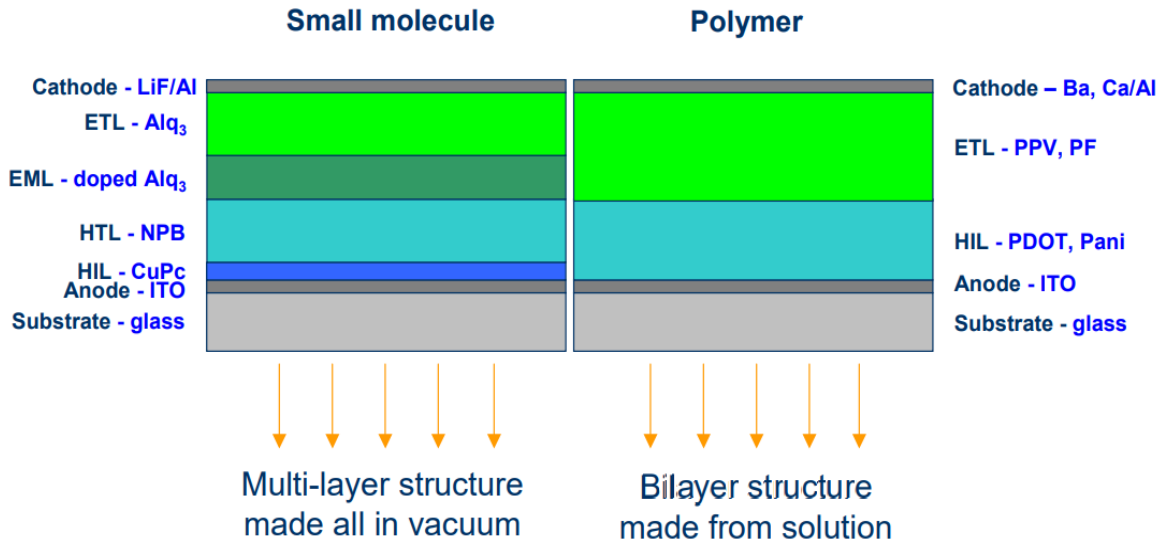


Figure 1. the structure of small molecule OLED and polymer OLED [8].

The advantage of OLEDs with small molecules is that the purity of the materials is quite high and can produce high-quality films. QE fluorescence based OLEDs is high and they can produce various colours of luminescence. The disadvantages are poor thermal stability and limited carrier transport capacity. In device preparation, lower concentration doping is generally used in the main material. This necessitates a high degree of overlap between the absorption spectrum of organic small molecules and the emission spectrum of the main material, to realize the effective transfer of energy from the main to the small molecules.

Several different small-molecule OLED blue-emitting materials will be introduced, such as phosphorescent metal arylpyridine-type Ir(III) complexes and cyano-type intra-molecular donor-acceptor (D-A) TADF materials. The most commonly investigated blue phosphorescent polypicolinate-(4,6-fluorophenyl)pyridine-C2,N](picolinate)iridium (Firpic), is a representative arylpyridine-type blue phosphorescent emission body. With up to 100% IQE and up to 30.3% EQE. This emitter exhibits excellent electrophosphorescence efficiency in OLED devices [9]. The device's electroluminescence (ELmax) peak is typically at 475 nm and emitted light is typically blue-green in color [10-12]. To make the color of Firpic more pure, Lee and colleagues developed bis((3,5 -difluoro-4-cyanophenyl) pyridine) iridium(III) picolinate with cyano-group as A unit [13,14]. Using this compound, deep-blue phosphorescent OLEDs with high efficiency were fabricated. The EQE_{max} reached 23.9% with CIE of (0.14, 0.21) [13,14]. The electron acceptor cyano units enabled the construction of very efficient blue emitters from weak donors. Furthermore, cyano-type emitters usually exhibit long lifetimes in applications due to the triple bond C≡N and aromatic ring with high stability [15]. Adachi and coworkers described the first CN-based blue TADF OLED, 4,5-di(9-H-carbazol-9-yl)phthalonitrile (2CzPN), with a tiny ΔE_{ST} of 0.09 eV. The maximum EQE that can be used to create sky-blue OLED devices is 8.0%, with an ELmax of 480 nm, and a sigglet-host EQE of 13.6% is even greater for doped OLEDs [16,17].

Several different green light-emitting materials for small-molecule OLEDs are listed below. Many studies have focused on generating heteroleptic compounds by substituting novel ancillary ligands for phenylpyridine ligands [18]. Kim et al. Very efficient green OLED devices were created using Ir(ppy)2acac (I) and Ir(ppy)2tmd (II) as well as Ir(ppy)3 (III). The EQEs of I and II are 30.51% and

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32.01%, respectively, which are higher than the EQE of 25.91% of III, which is due to their larger horizontal dipoles that are affected by the phosphorescent properties. The effect of ancillary ligands is greater [19]. These derivatives are often used to make green TADF emitters because they generally have stronger accepting properties than sulfones. To create the D-A-D molecule 9-[2,8]-9-carbazole-[dibenzothiophene-S,S-dioxide]-carbazole (DTC-DBT) with a ΔE_{ST} of 0.35 eV, Jankus and co-workers used Dibenzothiophene produced the electron acceptor - S,S-sulfur dioxide [20]. Using these materials, OLEDs with an EQE_{max} of 14.0% can be created [20].

Compared with green and blue luminescent materials, red luminescent materials have been rarely reported due to their deficiencies in molecular design and efficiency. Jeon and colleagues fabricated high performance OLED devices with an EQE_{max} of 21% and a CIE of (0.62, 0.37) [21]. Bis(2-phenylquinoline)(acetylacetonate)iridium [Ir(phq)2(acac)] was used as the doping material [21]. The emitter contains an extensive π-conjugated structure, which is crucial to achieve red emission [3]. Jiang and co-workers created red D-A type asymmetric emitters 2-carbazol-9-ylanthraquinone (Cz-AQ) and 2-(4- Diphenylamine-phenyl)anthraquinone (TPA-AQ) [22]. Cz-AQ and TPA-AQ have orange and red emission peaks at 572 and 612 nm, respectively, and their solution-processed OLED devices showed 5.8% and 7.8% high external quantum efficiency [22].

Most organic small molecule thin films are prepared by vacuum thermal evaporation. Vacuum thermal evaporation is the process of using a heating evaporation approach to evaporate the weighing film materials under vacuum setting, and the particles move onto the surface of the substrate to form a film. The advantages of vapor phase deposition are simple film forming process, high purity and dense film, and unique film structure and performance.

3.2 Polymer OLED

Compared with organic light-emitting materials with small molecules, polymer materials have higher physical strength, good processability, mechanical property, and thermal stability. In addition, because polymer materials are resistant to high temperatures, have a simple device structure, and are easy to be dissolved by common solvent, they are suitable for wet processes (printing processes) like inkjet, spin coating, and live spray printing. PLED is mostly fabricated in the form of spin-coating, and the equipment cost is low. Moreover, PLED uses inkjet technology, which is easy to achieve large sizes. However, the pixel colour positioning accuracy of inkjet technology is not easy to control, so it is difficult to achieve full colour in large sizes. Metal complexes are between organic and inorganic compounds. They have both the advantages of high fluorescence QE of organic compounds and the characteristics of inorganic stability. They are the on of most promising luminescent materials.

Polymer oleds exhibit not only RGB emission, but also white emission, which is critical for a variety of applications. Li Chensen published the first warm white OLED with TADF polymers. The combination of both fluorescence and TADF creates a polymer with tunable emission color according to aggregation-enhanced emission (AEE) properties. 2-(10h-phenothiazin-10-yl) dibenzothiophene-s,s-sulfur dioxide units (yellow TADF emitting units) and dibenzothiophene units (blue fluorescent emitting units) can be successfully fabricated with different ratios polymers that possess both TADF and AEE properties [23]. One of them is that in various THF/water mixtures, the emission color of P3 alters from blue-green to white or yellow, and it emits white in the solid state, dispersed by polymethylmethacrylate [23]. Furthermore, the EL device of P3 exhibited two-color warm white light emission with a high color rendering index (CRI) of 77, a low open circuit voltage (Von) of 2.9 V, a CEmax of 23.0 cd A^{-1}, and a luminous efficiency (PE_{max}) of 32.8 lm W^{-1}. At 5 V, the maximum EQE reached 10.4%, and the CIE was (0.37,0.38) [23]. The main luminescent materials include PPV and its derivatives, fluorene homopolymer, copolymer, polythiophene, polyquinoline, etc.

Flexible polymer OLED is a field that mobile phone manufacturers are competing to enter at present, with a bright future. Flexible OLED has a significant impact on the progress of modern technology. Its mass manufacturing is conductive to the development of next generation smartphones. In addition, flexible OLED will also significantly impact wearable device promotion because of their low power consumption as well as flexibility. With continuous penetration of personal intelligent terminals, flexible

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screens will be widely used in the future. Recently, researchers from the School of Engineering of South China University of Technology have developed a new type of substrate with good thermal performance and high transparency through nanocellulose/polyacrylate (standard number of rods) hybrid polymer [24]. Due to the nanoscale of cellulose nanofibers (CNFSs) and their effective interface interactions with the standard rods, the thermal stability of the matrix is greatly improved [24]. The maximum working temperature can reach 220 ℃ [24]. At the same time, the hybrid substrate also shows excellent mechanical strength [24]. It is worth noting that after adding CNF, the transparency of the composite substrate has no obvious loss, and maintains 85% high transmittance and 1.75% low fog at 600nm [24]. In addition, compared with traditional polyester substrate OLED devices, the photoelectric performance of hybrid substrate OLED devices has been significantly improved [24].

4. Conclusion

The common characteristic of OLED and PLED materials is that they both contain conjugated chemical structures and have a high degree of fluorescence efficiency. However, the molecular weight of the two materials is quite different. The molecular weight of small molecular materials is generally about hundreds, while the molecular weight of polymers is between tens of thousands and millions. In terms of material acquisition, the synthesis and purification of small molecular materials are simpler than those of polymers, and the requirements for mass production and purity of materials are easier to achieve. Relatively speaking, the material properties of small molecules are easier to obtain than those of polymers, but the thermal stability and mechanical properties of polymers are better. The development of both kinds of materials are promising regarding organic electroluminescence.

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