

Applications of phosphorescent organic light emitting diodes

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Abstract. Organic light-emitting diodes (OLED) materials have been widely applied in many fields, among which phosphorescent OLED materials have more and more attention due to their luminescence efficiency and performance. At present, the luminescence layer of many OLED devices adopts phosphorescent materials as the main body to achieve a better visual experience for users. The research and development of blue electrophosphorescent materials are not mature enough. The two big aspects including color purity and the service life are major problems, and many researchers are now working on research methods of conquering the blue phosphorescent OLED materials shortage. In this article, fluorescent and phosphorescent OLED materials have been mentioned. The applications and branches of phosphorescent OLED materials are described. The article also analyzes the shortcomings of phosphorescent OLED and explained the reasons, mainly thermal activation delay fluorescence (TADF). Its purpose is to reduce the expensiveness of phosphorescent OLED materials. Meanwhile, the luminescence efficiency of fluorescent materials can be greatly improved. Additionally, the basic principles of luminescent OLED materials and the applications of phosphorescent OLED materials are also illustrated, including the prospect of blue phosphorescent OLED materials.

Keywords: luminescent OLED, red phosphorescent OLED, blue phosphorescent OLED.

1. Introduction

The concept of OLED semiconductor has been around for several years, to be specific, OLED is a kind of device that produces electroluminescence using a multilayer organic film structure. It is easy to produce and only requires a low driving voltage. These main characteristics make OLED stand out for flat display applications in recent years. Compared with the previous products of LED or LCD, the organic plastic layer in OLED is sleazier, lighter, also more dexterous. OLED is brighter compared to LEDs, and its luminous efficiency is naturally higher. The organic layer of OLED is thinner than the corresponding inorganic crystal layer in LED, so the conductive layer and emission layer of OLED can be multilayered. Meanwhile, OLED does not require the backlight system used in LCD [1]. Selectively blocking certain areas of the backlight to make the image appear gives light to LCD devices, while OLEDs emit light on their own. Since OLED materials don't need a backlight system, the power uses is less than the LCD devices. This is significant in battery-powered devices just like mobile phones. Since OLED materials are manufactured of plastic, they are able made in big or small pieces [1].

OLED semiconductor is known as a current-type of OLED that give out light through the carriers' injection and recombination, with a large proportional to injected current [2]. According to the action in the electric field, the hole produced by the anode and electrons given by the cathode of OLED will shift, which injected into the hole transport layer and electron transport layer respectively, then migrate to the luminescence layer. As long as the two joints are in the luminescent layer, the energy excitons are produced, excitons exciting light-emitting molecules and eventually producing visible light. To be more precise, the mechanism and structure are both illustrated in Figure 1.

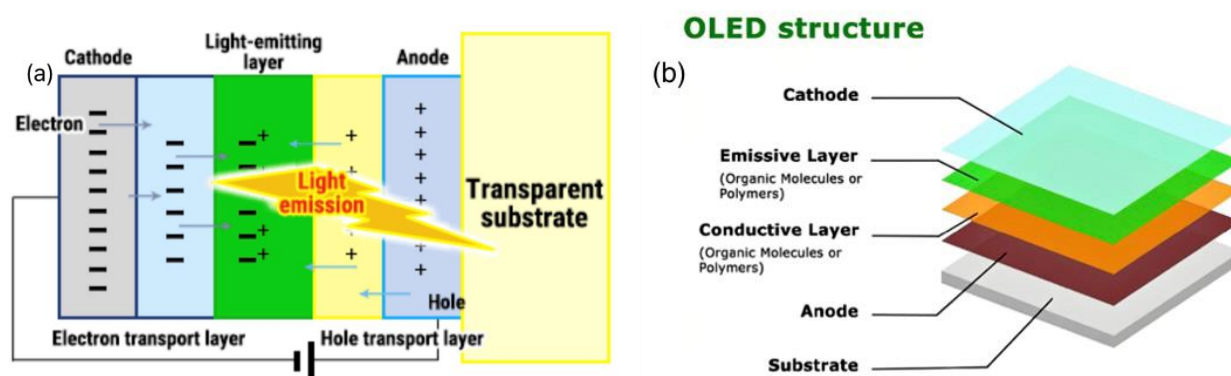


Figure 1. (a) Mechanism of light emission by OLED lighting, (b) Structure of OLED displays.

According to the primary colors of light (green, red, and blue), red and green phosphorescent materials have been mass-produced in OLED displays. The existing technology of green and red phosphorescent materials is relatively mature, and the color purity of deep red phosphorescent materials is extremely high, however, blue phosphorescent materials have been showing weakness in color purity and longevity. Learned, Samsung in the invention of the blue phosphor technology study, blue phosphor layer (EML) as important research difficulties are being overcome, in February 2022, it was reported that the Blu-ray device lifetime, with the LT70 reaching 1,113 hours at 1000 CD/m², 0.197 CIEy. Samsung has developed a dual-main blue phosphorescent OLED EML by introducing 3, 5-DBT to Pt(II) compound as a precursor of azacyclic carbene [3]. A similar two-subject structure that has been used in green phosphorescent OLED EML is used in this blue phosphorescent OLED EML study. If the blue phosphorescent structure layer is successfully developed and promoted, OLED technology will stride to a new height.

In this article, the properties and derivations of OLED luminescent materials and phosphorescent materials are described, and the new technologies of different phosphorescent OLED materials are introduced.

2. OLED luminescent materials

The organic luminescent materials are the organic device that can produce photons in the excited state of organic molecules under the excitation of light and then release energy back to the ground state. The photon generation process is the result of exciton transition. Excitons are divided into singlet excitons and triplet excitons, which refer to electron-hole pairs with opposite spin directions and electron-hole pairs with the same spin directions, respectively. The synthesis route of the material is simple and easy to operate, so it has a good industrial prospect. Such material can be used in organic electrical devices as the dopant layer or the main body part in the luminescent layer, or as a single luminescent layer or any layer in the transmission layer [4]. The organic devices prepared by using this OLED efficient effect material can achieve deep red light (which leads better visual experience), low voltage, and also high efficiency [4].

Luminescent OLED materials can generally be categorized into two groups according to their molecular structure of compounds, including high polymer and organic small molecule compounds. The molecular mass of a polymer is in the range of 10000 to 100000, usually electrically conjugated polymer or semiconductor conjugated polymer. Providing this kind of material is cheap and easy to operate. However, the purity of this material is hard to improve, and it is not as good as small molecule organic compounds in terms of brightness, durability, and color, the market prospect is depressed in recent years as the result [5].

Organic small molecule luminescent materials are the mainstream massive production sources, they are mainly organic dyes with strong chemical modification, wide selection, easy purification, high quantum efficiency, and the advantages of producing emission peaks of various colors (e.g., red,

green, blue, and yellow). However, most organic dyes have concentration quenching problems in the state of solid, resulting in the emission peaks becoming wider or red-shifted. So they are usually doped at low concentrations in a host that has some kind of carrier property, usually the same material as the ETM and HTM layers [5][6]. Doped organic dyes should meet the conditions that it has high fluorescence quantum efficiency, besides, there is also a good overlap in the middle of the absorption spectrum of the dye and the emission spectrum of the subject, that is, the subject and the amount of dye are adapted, and energy can be transferred effectively from the subject to the dye. The emission peak of red, green, and blue is as narrow as possible to obtain good color purity. The organic small molecule luminescent materials have high stability and could evaporate easily as well.

There are many kinds of OLED luminescent materials, they can generally be divided into fluorescent luminescent materials and phosphorescent luminescent materials according to the luminescent method. From the perspective of the luminescence mechanism of materials, four types of exciton group transition distribution states can be generated according to all combinations of atomic group transition possibilities. One asymmetric singlet exciton rotation mode corresponds to the luminescent mechanism of fluorescent luminescent materials, and three symmetric triplet exciton rotation modes, corresponding to the luminescent mechanism of phosphorescent luminescent materials [5][6]. For the fluorescent luminescent OLED materials, singlet excitons are much more efficient than triplet excitons in most cases, since their rapid recombination rate, as a result, the injected vectors will be concentrated and can only emit light through a single exciton, rather go through the other three triplet excitons. Furthermore, fluorescent materials are less costly but less efficient in emitting light. Over the electricity generated by loading voltage, only 25% of the light can be used to emit light. The remaining 75% is converted into heat and released, all in all, it has both drawbacks and advantages in the application of OLED Semiconductor. By contrast, phosphorescent materials are re-injected with heavy metals (e.g. Ir, Pt, Eu, Os) atoms, as a result of the spin orbits of heavy metal atoms, the recombinant rate of singlet excitons and triplet excitons is close [7]. The injected vector can be uniformly distributed in four exciton rotation distribution states, the luminescence can be achieved in all four distribution states. Phosphorescent materials can produce full use of singlet and triplet excitons energy during the procedure of luminescence, consequently, the quantum efficiency of phosphorescent materials can reach 100% theoretically, and 75% of the energy wasted by fluorescent materials that are converted into thermal energy can be converted into light energy. This kind of material effectively promotes the luminescence efficiency of OLED products, which are widely used in the industry at present [7].

3. Phosphorescent organic light-emitting materials

The light still emitted after excitation has stopped is generally known as phosphorescence. A material that emits phosphorescence when excited by electromagnetic radiation and ion rays is called phosphorescent material. As same as other types of OLED materials, phosphorescent OLED materials produce light by electroluminescence in an organic semiconductor layer that occurs in the electric current. The organic layer to electrodes is the place where electrons and holes are injected, and then form excitons. Fluorescent organic molecules are used in OLED materials only, the decay to triplet exciton is quantum mechanically forbidden according to the selection rules, which means triplet excitons' light-emitting time lasts longer, and phosphorescence is negatively readily shown. Thus, the only formation of singlet excitons is fluorescent OLED materials that can work in the emission of useful radiation, putting forward a theoretical limit to the internal quantum efficiency (excitons formed per emission of a photon) of 25% [7,8].

3.1. Red phosphorescent OLED materials

The luminescence of existing white phosphorescent OLED displays is composed of red phosphorescent OLED materials, green phosphorescent OLED materials, and blue phosphorescent materials. Like it is shown in Figure 2.

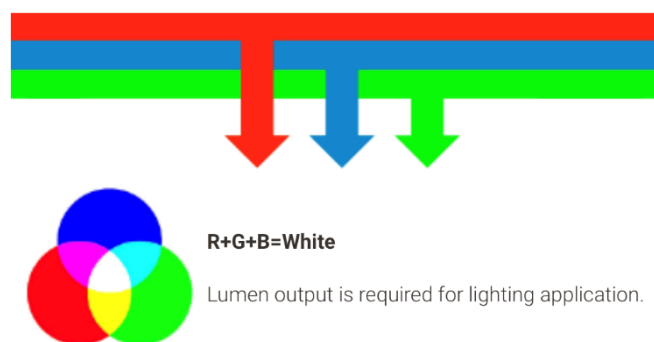


Figure 2. Optical white consists of three primary colors of light, corresponding to red, green, and blue phosphorescent materials.

The white light produced by them is closely related to their respective performance. Since the discovery of OLED organic phosphorescent materials in the late 1990s, Blue electrophosphorescent materials always lag behind the development of green or red phosphorescent materials. Blue electrophosphorescent materials development so far very few can do it like a deep red light or dark green color purity, blue phosphorescent OLED materials still shows substantive problems. Compared to the other two materials, their service life is too short, and even the high purity of dark blue color produces an unsatisfactorily effect on the OLED [9]. To produce a better performance of white OLED, red phosphorescent OLED materials have to be very high in color purity requirements, otherwise, the produced white OLED can not be close to pure white.

Since 1998, M.A. Baaldo has produced red phosphorescent materials. The main phosphorescent doped materials are 2, 3, 7, 8, 12, 13, 17, 18-octaethyl-21H, 23H-phorine platinum (PtOE) complexes [10]. Since then, the phosphorescent organic light-emitting diode ushered in a period of rapid development. The commonly used central metal atoms of phosphorescent materials include Pt, Os, Ir, Ru, and Eu [11]. The recombinant rate according to singlet and triplet excitons is similar due to the special combination of spin orbits of heavy metal atoms. Iridium complex consistently being the hotspot of phosphorescent materials studies. The quantum efficiency is theoretically 100%, and the wavelength (color gamut) of iridium complexes can be easily adjusted by changes in molecular structure. This kind of material has the advantages of good thermal stability, short phosphorescence lifetime, high luminescence efficiency, and light color adjustment, and its regular octahedral structure will not form molecular stacking, which will affect the physical characteristics of light.

Recently, a team led by Yang et al from Shenzhen university designed and synthesized a novel binuclear platinum complex to achieve high-performance red and near-infrared OLEDs independent of intermolecular stacking by reinforcing intramolecular metal-metal interactions through rigid molecular Bridges [12]. According to the strong intramolecular Pt-Pt and π - π molecular attractions, the material system has good thermal stability, and its red light and NIR emission efficiencies exceed 60% and 40%, respectively, and its luminescence lifetime is about 1 microsecond. The external quantum efficiencies of near-infrared OLED and red OLED devices are 15% and 23% respectively, and the efficiency roll drop is small [11,12]. In particular, the research on device life shows that this kind of material has good stability. The existing red OLED phosphorescent materials can reach 100,000 hours under 200LUX, which is no longer a problem [13]. It is expected to replace the current industrial iridium complex materials and has great application potential.

3.2. Blue phosphorescent OLED materials

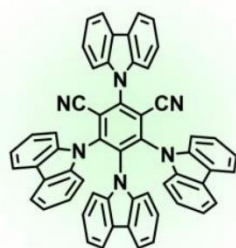
Blue light, another one of the three primary colors of light, is the core component of solid-state lighting and full-color display, and also shows broad application prospects in biomedicine, optical communication, and other fields. Compared to red phosphorescent OLED materials, the previous blue phosphorescent OLED materials own a certain gap in terms of several types and color purity. The research and development of blue phosphorescence materials will be the key in the field of organic phosphorescence technology [14].

The short service time has been a major bottleneck towards the blue phosphorescent materials in previous research [15]. Recently, Samsung reported that it is currently developing blue phosphorescent OLED materials, which will be used in QD OLED (quantum dot organic light emitting display, which has a wide spectrum, low energy consumption, high brightness, and long lifespan) panels, to better improve the luminescence efficiency and extend the lifespan of OLED panels [16]. Samsung Display reported that they produced a Blu-ray device that has a lifetime with the LT70 reaching 1,113 hours at 1000 CD/m², 0.197 CIEy. The company has developed a dual-main blue phosphorescent OLED EML by introducing 3, 5-DBT to Pt (II) compound as a precursor of azacyclic carbene [16]. At present, Firpic is the blue phosphorescent material with good effect. Its luminous peak is 470nm and CIE coordinate is (x=0.16; Y =0.29), the external quantum efficiency of the device is 5.5% when it is doped in CBP, but 14.4% when it is doped in the matrix material SimCP [16,17]. Other blue phosphorescent materials also achieve blue shift by fluorination of 2-phenylpyridine at different positions and changing the auxiliary ligands. Trifluoromethyl substituted triazole and tetrazolium ligands were used as auxiliary ligands to prepare FIrTaz and FIrN4 complexes. FirN4 was doped in mCP to produce a device with a large emission peak of 462 nm, which is currently reported to be a bluer device with a large luminance of 11000Cd /m, but its efficiency of 5.8% is lower than that of FIr6 and other blue light materials [18].

There are a variety of ways to improve and commercialize blue phosphorescent OLED materials. If the blue phosphorescent OLED material is successfully developed, the blue phosphorescent OLED material, which is stacked in three layers, will be replaced by the blue phosphorescent OLED material. It could reduce the number of stacked layers by one layer, and increase the luminescence efficiency and service life [19].

About its benefits, the usual OLED, which uses the principle of fluorescence luminescence, uses the phenomenon of a single excited state transition of the material. According to the theoretical analysis and experimental estimation results, the maximum limit efficiency of OLED doped with fluorescent materials is about 25%. If electrophosphorescent materials are used as dopants, both single-excited and three-excited states can be used, and the limit of luminescence efficiency ceases to exist. The blue phosphorescent material can greatly improve the luminescence efficiency of OLED and create conditions for providing better full-color OLED displays.

Samsung Display's current QD-OLED panel uses blue fluorescent OLED material and green phosphorescent OLED material as the emission layer. The layers, which the company calls a four-story series structure, have three blue layers and one green layer. The same goes for the 34, 55, and 65-inch panels used for monitors and TVs [18]. Using blue phosphorescent OLED material will allow the display to reduce the number of blue layers to one. Phosphorescent OLED materials can use the energy of singlet and triplet excitation, which account for 25% and 75% of the energy used by the material, respectively, allowing 100% luminance efficiency [19]. In contrast, phosphorescent OLED materials can only use the energy of singlet excitation, hence the brightness efficiency of 25%, which is why Samsung Display needs to use three layers of blue on its QD-OLED panel. The drawbacks of blue phosphorescent OLED materials are that they are hard to produce, and more importantly, the color purity of these materials is poor and extremely expensive to make [19]. To improve the color purity of blue phosphorescent materials, it could achieve an effective pure blue OLED with maximum EQE of 24.3%, CIE coordinates of 0.124 and 0.140, and FWHM of 28nm by inhibiting the intermolecular interaction [20]. Due to the inhibition of intermolecular interaction, a high doping concentration of more than 20%, Also can maintain stable color purity [21]. In addition, it can inhibit the formation of heteroplastic and obtain a higher yield of good synthetic products [21]. To solve the problem of the expansiveness of phosphorescent materials, new materials such as thermal-activated delayed fluorescence materials & superfluorescence materials are researched and developed. The basic structure of 4CzIPN (TADF) is shown in Figure 3, which was used as a thermal activated delayed fluorescence material to produce OLEDs with an internal fluorescence efficiency of over 90% and an external luminescence efficiency of about 20%, and reduces the costs of phosphorescent materials.



4CzIPN (TADF emitter)

Figure 3. The structure of 4CzIPN thermal activated delayed fluorescence(TADF) [21].

The thermal activated delayed fluorescence is characterized by a small energy gap in S1 (first single-double excited state) and T1 (first triple excited state). T1 can be up-converted to S1 by a thermally assisted reverse interseries channeling (RISC) process, followed by radioluminescence [21]. Because the RISC process is slower than the S1 radiation process, the fluorescence produced by the RISC process is often called delayed fluorescence. This is a new type of low-cost, high-efficiency organic light emitting material, known as the third generation organic light emitting material. The TADF internal quantum efficiency nears one hundred percent, which can not only reduce the phosphorescent materials' costs but also largely improve the luminescence efficiency of fluorescent materials.

4. Conclusions

To conclude, OLED has been one of the most promising materials in the field of display in recent ten years. Among them, phosphorescent materials can give singlet and triplet excitons full uses during the luminescent process. The quantum efficiency of phosphorescent materials can reach 100% of the theoretical efficiency as the consequence, this largely improves the luminescent efficiency of OLED devices that are currently widely used in the industry. This paper analyzes the phosphorescent and blue phosphorescent OLED materials and proposes and summarizes methods to improve the performance of blue phosphorescent OLED materials. The disadvantage of blue phosphorescent material is mainly reflected in low color purity and short service life. The introduction of thermal activated delayed fluorescence (TADF) materials, whose internal quantum efficiency nears 100%, effectively reduces the cost of phosphorus fluorescence materials, and can greatly improve the luminescence efficiency of fluorescence materials [21]. To improve the color purity of blue phosphorescent OLED materials, the intermolecular interaction and the structure formed by phosphorous molecules must be inhibited. The intermolecular interactions are inhibited and the color purity can be maintained at high doping concentrations of over 20%. If blue phosphorescent material is developed successfully, it could replace the previous blue fluorescent layer and emit light four times more efficiently. Then red, green and blue, all of which are phosphorescent materials, will have a more perfect visual experience, and will also create more diverse opportunities for efficient and high-performance OLED applications [15]

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