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A Compact History of the OLEDs

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Abstract. People's demand for lighting and display is gradually increasing as society and technology progress. Therefore, the scientific community has been eager to find a new kind of luminescent material suitable for industrial society. The effort paid off, as scientists discovered light conversion and its efficient Organic Light Emitting Diode materials through experiments. These materials can be divided into three distinct generations as a result of continuous updating and iteration: the first-gen (first generation) of fluorescent materials, the second- gen of phosphorescent materials, and the third-gen of TADF. In order to let the public better understand the development history of OLED materials, this paper will focus on the mechanism of different materials to discuss the schemes and introduce some of the latest applications of these materials. At the end of this review, it will illustrate why TADF the third generation of OLED light emitting material is the most promising in terms of practical applications compared with other materials and the vision of the future of OLED.

Keywords: OLED, TADF, Fluorescence, Phosphorescence.

1. Introduction

The display device market has changed dramatically due to the pursuit of display color and practicality. Display technology has surpassed printing technology as the primary means of knowledge and information dissemination over the last century. With the rapid development of communication technology and people's pursuit of color and the practicality of display equipment, display equipment has been forced into a multifunction and digital direction, particularly in recent years. Modern display devices, in particular, are evolving in the direction of high density, high resolution, energy efficiency, high luminescence, colorfulness, and huge screen.

Karl Ferdinand Braun, a Nobel Prize-winning physicist, and inventor designed the first Cathode Ray Tube in 1897. High-speed electrons are emitted by the electron gun, and their deflection angle is controlled by vertical and horizontal deflection coils [1]. The high-speed electrons finally strike the screen, causing it to glow. The power of the electron beam is controlled by voltage, and different light and dark spots on the screen form various patterns and texts.

In the nineteenth century, Austrian botanists discovered liquid crystals, which means that a substance has both the fluidity of a liquid and the arrangement of a crystal. The electro-optical effect occurs when the arrangement of liquid crystal molecules changes in an electric field, affecting their optical properties. British scientists developed the first liquid crystal display- LCD in the last century by utilizing the electro-optical effect of liquid crystals [2].

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The plasma display screen first appeared between 2000 and 2014. The plasma screen is made up of several plasma tubes, each one representing a pixel [3]. The plasma tube is similar to the fluorescent lamp, which is a miniature ultraviolet fluorescent lamp. When high pressure is applied inside the plasma tube, electric energy is released, causing the inert gas in the tube to emit ultraviolet light, which then excites the red, green, and blue phosphorescent material coated on the glass, producing the primary colors red, green, and blue. After the three colors are combined, images of various colors can be displayed.

Despite the indelible contribution of these materials in the history of human display technology, their shortcomings such as low display efficiency are increasingly exposed. The emergence of OLED seems to be the key to solving these problems. OLED has a lightweight and small thickness, high brightness, and high light efficiency; rich luminous materials, easy to-realize color display, fast response speed, high-quality dynamic picture, a wide range of temperatures; flexibility, simple processability, low cost; Strong seismic ability and a series of other advantages, so it is called the ideal display in the future, in the field of lighting light source also shows amazing application potential. However, due to the relative lack of publicity of OLED in various countries, it is necessary to summarize the existing relevant material mechanism and introduce it in combination with the latest application, to raise people's attention to OLED, and provide a relatively detailed analysis of different OLED material mechanism for future researchers. It is hoped that this paper will contribute to developing OLED materials and make it more convenient for people to study new materials, to create cross-era high conversion rate OLED materials. To build a sustainable development of the goal of society, continuous efforts to improve the energy conversion rate, to achieve efficient energy and electricity saving. To provide more feasible and effective solutions to energy shortage in the world's energy-scarce countries or regions, and to contribute to the cause of human equality. This paper will introduce the mechanism of the third-generation OLED material, combined with the details of the example to explain the mystery.

2. Fluorescent OLED

2.1. Mechanism

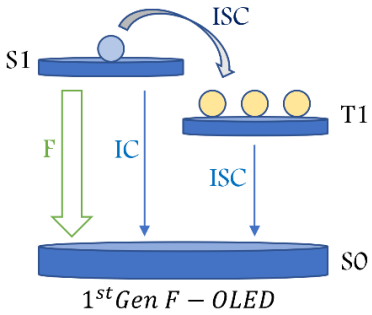

Figure 1. Schematic mechanism of fluorescence.

The first OLEDs relied on fluorescence, a type of photoluminescence known as cold light. When a material at room temperature is exposed to UV, it absorbs light energy, enters an excited state, then deexcites and emits outgoing light with a wavelength longer than the incident light's (typically in the visible light band). The glow fades as soon as the incoming light stops. Fluorescence is a property of light that emits this property. More specifically, as illustrated in Figure 1, a specific substance first transitions from the ground state to the excited state, where it absorbs radiation of a particular frequency (light), and then quantizes it to the corresponding position. According to Franck-Condon's principle, there is no time to change the configuration of the nuclei in a molecule at the moment the electron transition is complete. Before and after the transition, the configuration of the nucleus does not change, the spin of the electron does not change during the transition, the orbital of the electron before and after

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the transition has a large overlap in space, and the orbital enantiotropic changes are allowed. The transition is prohibited if the spin of the electron changes during the transition, the orbital of the electron does not overlap in space before and after the transition, or the enantiotropic of the orbital does not change. After that, electrons in the excited state are unstable and easy to return back to the ground state. When electrons go back to the ground state from S1 or S2, energy will be released in light, producing fluorescence.

Under electrical excitation, singlet excitons and triplet excitons form in a 1:3 ratio, according to spin statistics. Fluorescence devices can only utilize singlet excitons emission, so their IQE limit is 25%, and 75% of triplet excitons are wasted in the form of heat. As the external coupling efficiency of the device is about 20%~30%, the maximum "External Quantum Efficiency" of fluorescent OLED is 5%~7.5% [4].

2.2. Research progress on Fluorescence OLED

Professor Jeong-Hwan Lee and his team have produced organic light-emitting transistors which is overlapping-gate through a large number of experiments. A light-emitting transistor with two gates divided by an insulator that partly overlaps in the device 's core is the basic concept [5]. The buildup of 1transport layers. Because this structure combines the merits of fixed light emission in the core of the channel, the gapless charge transfer to the recombination region, and any desired current density. Controlling the balance of electron and hole concentrations at the edge of the emission layer. Finally, this device's high EQE of 5.7% was attained at the highest luminance of 2190 cd m^{-2}. The device topology opens up prospects for the advancement of bright thin light sources due to the high current density.

Michael R. Maciejczyk and his team find nowadays although the existing blue OLED materials with high color purity, easy processing, and high thermal stability even at high brightness, ensuring adequate device life, are still important challenges for OLED applications in displays and lighting. However, in practice, these various characteristics are usually mutually exclusive. As a result, they have developed four new green and blue light-emitting materials based on a monothiatruxene core. When compared to the previous materials, these are far superior. The decomposition temperature is 352-442°C, and the glass transition temperature is 171-336°C. At 100 cd m^{-2}, a deep-blue emitter with CIE color coordinates (0.16, 0.09) achieves a high EQE of 3.7% and a green emitter with color coordinates (0.22, 0.40) achieves a high EQE of 7% [6]. The photoluminescent quantum yields of the fluorescent materials observed are 24% and 62%, respectively. At higher luminance, performance is excellent, with only 38% and 17% efficiency rolls at 1000 cd m^{-2} respectively. The results show that using this novel molecular design to create efficient deep blue, highly stable, and soluble luminescent materials is a promising approach.

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3. Phosphorescence OLED

3.1. Mechanism

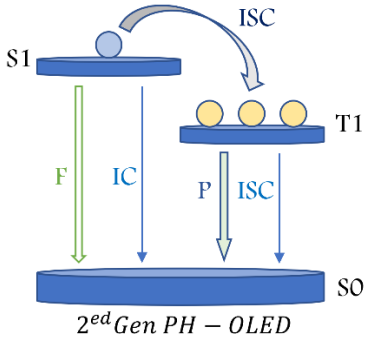

Figure 2. Schematic mechanism of phosphorescence.

Phosphorescence is a type of luminescence that occurs after the fact. When a material at normal temperature which around is exposed to incident light of UV, it gains the energy and enters an excited state (with multiple spins different from the ground state). Then, as shown in Figure 2, it deexcites slowly and emits light with a longer wavelength than the incident light. Unlike the fluorescence process, the luminous phenomenon continues after the incident light has stopped. The phosphorescent deexcitation process is prohibited by the transition selection rules of quantum mechanics, so the process is slow.

Fluorescence and phosphorescence appear to have many similarities, and the similarities and differences between the two mechanisms will be discussed. When EMR (Electromagnetic Radiation) strikes a molecule, it absorbs the energy from the environment. As a result of this absorption, an electronic transition occurs, and molecules move to higher electronic states such as the 2nd singlet state or the 1st singlet state. Electronic transitions will occur only for specific molecules and only when specific wavelengths of EMR are bombarded. This is due to the characteristic structure absorbing only radiation of a specific wavelength and energy. The absorbed wavelength of light transitions to the first electronic singlet state. The excited singlet state lasts for a short time, with the order ranging from 10^{-8} to 10^{-4}s. During this time, energy is released in the form of emissions, and this phenomenon is known as fluorescence. Because this transition requires less energy than the initial absorption, the emitted wavelength is longer.

Electrons can sometimes go to the 1st excited triplet state instead of the 1st electronic singlet state. They stay there for a while before transitioning to the ground singlet state, which causes emissions. This phenomenon is called phosphorescence. Fluorescence is immediate emissions of absorbed radiations whereas phosphorescence is delayed in the release of absorbed EMR. One reason phosphorescence can be used as the raw material for the second generation of OLED is "that phosphorescent materials can achieve 100% IQE using singlet and triplet excitons through spin-orbit coupling."

3.2. Research progress on Phosphorescence OLED

A brand-new category of Tetradentate Pt(II) complexes with ultramarine emission was described by Jin-Suk Huh and colleagues in 2021. These complexes have non-planar ligands and large-volume emery groups. The Pt(II) complex is non-planar due to the six-membered metallacycle structure. Additionally, the volume of bulky adamantyl groups lengthens the distance between molecules and lessens the emission redshift brought on by robust dipole- dipole interactions. As a result, even as the dopant concentration increases, these Pt(II) complexes' emission color remains rather stable. These new Pt(II) complexes produce deep blue (CIE y 0.15) phosphorescent OLEDs with a CIE y less than 0.13 and a maximum EQE of 22.6%, one of the highest values ever recorded for such devices. As a result, the problem of spectral redshift and extra emission peaks is thought to be resolved [7].

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Wei-Ling Chen and her team designed a dual-emission layer structure including of red- emitting Ir(piq)2acac and a deep-red Ir(fliq)2acac to generate a broad electroluminescence spectrum [8]. An efficient TCTA: CN-T2T binding system, as the emission layer's host, promotes effective energy transfer from the binding host to the red and crimson phosphors. Excimer host materials were also used in the carrier transport layers, removing the energy barrier and increasing current density. To measure borehole injection capacity and carrier balance, the injection layer structure was changed. The optimized phosphorescent OLED has a broad spectral profile with 90% coverage in the target range of 630 to 690 nm and a peak efficiency of 19.1% (10.2 cd/a and 13.8 lm/W). Because that product simply requires 5.2V to achieve a power density of 5mW/cm^2, it can be powered by two button batteries connected in series. This satisfies the requirement of OLED as the light source for phototherapy to have sufficient spectral distribution and low operating voltage in the effective wavelength range.

4. TADF

4.1. Mechanism

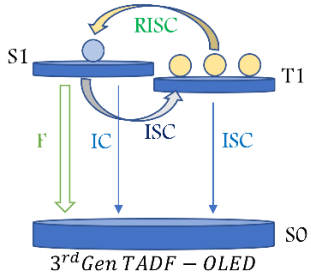

Figure 3. Schematic mechanism of TADF.

TADF which is thermally activated delayed fluorescence is a process of thermal-activated reluminescence of triplet excitons, that is, the triplet state "transforms to its higher vibrational energy level after thermal activation, and then crosses through the reverse system" to reach the vibrational energy level of the single state close to its energy level, and then radiates to produce fluorescence. The fluorescence is delayed compared with the direct luminescence of the single state, which is called E-type delayed fluorescence. Specifically, as illustrated in Figure 3, rather than fluorescence, a more efficient way to capture triplet excitons is through spin-forbidden reverse intersystem crossing (RISC) between T1 and S1, known as thermal-active delayed fluorescence (TADF). According to Hund's rule, since the repulsive force between two electrons with the same spin is less than the repulsive force between two opposite electrons, T1 is always a little lower than S1. When the energies of T1 and S1 are very close, that is, the energy level difference (ΔEst) of the singlet-triplet state is small, this RISC process can be carried out by the endothermic process of molecules. In addition, due to the prohibited transition from 1 to the ground state, the triplet state of the final radiation in the TADF molecule is transferred to singlet exciton by RISC, thus greatly improving the luminescence efficiency by delayed fluorescence (S1->SO).

4.2. Research progress on TADF-OLED

Ramanaskanda Braveenth's group designed and synthesized DBA-Bficz and DBA-Bticz, two deep blue TADF materials that bind oxygen boron-bridge (DBA) receptors with heteroatomic, oxygen, and sulfur donors, BFICz and BTICz, respectively. Both TADF materials exhibited deep blue photoluminescence at wavelengths below 450nm, indicating that the deeper HOMO level heteroatomic donor portion increased the optical band gap above 2.8 eV. Meanwhile, the photoluminescent quantum yields (PLQYs) of both TADF materials remained above 94%. The TADF product has an EQE of 33.2% based on DBA-BFICz [9]. v-DABNA is used as a fluorescent dopant to prepare hyper-fluorescent (HF) OLED devices because both of the new TADF materials have deep blue emission and great efficiency. As a TADF-sensitized host, DBA-BFICz demonstrated an EQE of 38% in HF-OLED and a narrower full width at

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half maximum (FWHM) of 19nm in bottom-emitting pure blue OLED. This solves the problem of emitting deep blue light while maintaining high efficiency in OLEDs.

Liang Chen and colleagues discovered that two types of interfacial exciplex hosts formed between a dendritic oligocarbazole donor (H2) and two pyridine-containing isomeric acceptors which are B4PyMPM and B3PyMPM of OLED excitons with TADF can be used for solution process and show tiny singlet-triplet energy splitting (90 110 meV) and the obvious TADF effect can transform triplet excitons into a singlet. They discovered that changing the structural formula of the receptor from B4PyMPM (para-pyridyl unit) to B3PyMPM (meta-pyridyl unit) significantly improves the carrier balance between the donor and acceptor layers of the interface excimer, resulting in a significant improvement in the electroluminescence efficiency of the fabricated device. The maximum PE(power efficiency) of the solution-processed TADF-OLED based on the H2/B3PyMPM exciplex host is 395.01 m W^{-1} (85.5 cd A^{-1},26.4%), which is significantly higher than previous one [10].

5. Conclusion

TADF has a high IQE of close to 100%, which can address both the issue of low luminous efficiency in first-gen fluorescent materials and the issue of high cost in second-generation phosphor materials. TADF has become the center of OLED luminous material study and development, and the industry is growing rapidly. With the continuous improvement of TADF material's overall performance, it can be widely used in the lighting period and has a promising future. OLED luminous materials have experienced three generations: the first generation is fluorescent material, the luminous rate is only about 25%, and currently is still the mainstream blue luminous material; The second generation of organic luminous materials are phosphorescent materials, whose luminous efficiency is close to 100%. They are the mainstream luminous materials of red and green, but at present, suitable blue phosphorescent materials have not been developed. Combined with the development of OLED luminous materials, blue TADF material will become a hot topic in the future.

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