

Study on Working Principle, Structure, Enhancement Technology, and Applications of Organic Light-emitting Diodes

Hao Sheng¹

¹Department of Electrical & Computer Engineering, Ohio State University, Ohio, United States

Corresponding author: sheng.202@buckeyemail.osu.edu

Abstract: Nowadays OLEDs outperform normal LEDs in terms of ease-processing, flexibility, skinniness, lightweight, and manufacturing cost. However, there is still much room to improve in terms of materials, efficiency, and longevity. Improving the performance of OLEDs has become the most popular research area. In order to make full use of excitons after recombination of carriers, phosphorescent OLED has been proposed. Recently, there is a gradual trend for phosphorescent OLEDs to be replaced by TADF OLEDs, as these TADF OLEDs can not only exhibit 100% internal quantum efficiency and are cheap to produce because they do not contain precious metals. At the same time, TADF OLEDs are considered to have more room for development especially in the aspect of longevity and color. Therefore, more researches are still needed to solve the blue OLED problem because compared to other colors, such as red and green OLEDs, blue OLEDs still have a big gap in stability and efficiency. In this work, the history of OLEDs, their working principle, the technologies that have been improved, and the cross-border derivative applications were studied.

Keywords: Organic Light-emitting Diodes, lighting, structure, application.

1. Introduction

OLED is a type of LED that uses organic materials as the light-emitting layer. OLEDs have a light-emitting electro-luminescent film layer composed of organic molecules. For inorganic electronics, integrated circuits can only be fabricated in high-temperature environments on heat-resistant semiconductors. Unlike the previous inorganic electronics, OLED is not essentially a crystal but a molecule. So, OLED does not require high-temperature production environment, thus it is easier and less expensive to produce OLED. Also, because OLEDs can be made in low-temperature environments, unlike inorganic OLEDs that can only be made on heat-resistant semiconductor crystals, they can be used along with a wide variety of materials, such as glass and plastic [1]. Moreover, the characteristics of organic semiconductors can be achieved by changing the molecular structure, so organic semiconductors have much potential for development. In modern times, OLEDs is considered to be a hotspot because of their excellent performance in various aspects.

OLED materials have been studied for a long time. In 1950, André Bernanose discovered that electricity causes organic matter to glow by applying high voltage to an acridine orange in the air [2]. In 1960, Martin Pope and his colleagues depicted the minimum energy required for an electrode contact to be created when holes and electrons are injected. This electrode contact, the Omega Dark Injection Electrode, laid the foundation for developing all OLEDs. In 1963, Pop and his group discovered that a direct current under a vacuum illuminates an anthracene crystal. Two years later, double injection compound electroluminescence from a single anthracene crystal was achieved via the use of empty space and electrons injected pole. Low voltage OLEDs were discovered in the late 1980s. In 1990, a breakthrough was made in organic polymer electroluminescence. In that year, the Cavendish Laboratory at the University of Cambridge, UK, successfully developed a green light-emitting polymer device, which further improved the lifetime and stability of OLEDs [1].

Up to now, the study of OLED materials is still of great significance. Therefore, this report will discuss OLEDs from their working principle, structure, improvement technology, and application direction.

2. OLED Working Principle and Structure

Figure 1 in the following illustrates the fundamental construction of an OLED. On the substrate are all the functional layers. The substrate can be made of materials such as plastic or glass. The functional layer consists of three parts, the anode, the cathode, and the organic material wrapped between the electrodes. The upper and lower positive and negative electrodes will usually have one side that is translucent, which allows the light emitted by the instrument to come through [3].

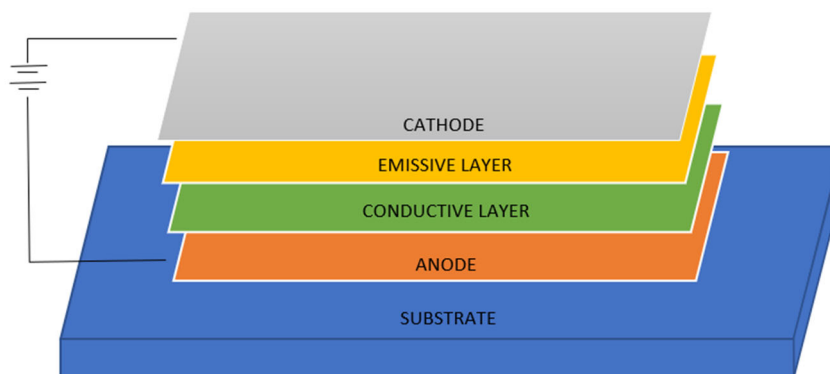


Figure 1. The basic OLED structures

OLEDs work by carrier injection and electron and hole compounding leading to light emission. The light emission goes through four parts, free electron injected, transport of conduction electrons, binding of free electrons, and luminescence [1].

First, the cathode will supply electrons to the anode. The negative electrode provides electrons to the bottom electron-free orbital of the light-emitting layer. In contrast, the positive electrode absorbs electrons thereby leaving space for the highest free orbitals of the conducting layer [4]. When injected, charge carriers pass through and reorganize in the organic semiconductor. Electrons and holes usually quiver and attract each other because of the property that positive and negative poles attract each other, which is the recombination process. The recombination process generates light energy, thus producing brightness. The whole method would be shown in Figure 2 [3]. Since holes in organic semiconductors have much higher mobility, hole-electron coupling occurs near the emissive layer.

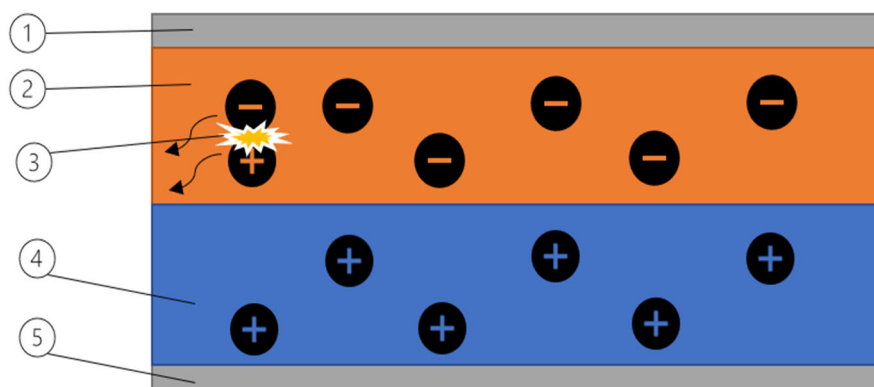


Figure 2. Working process of OLED: 1. Negative electron donor (-), 2. Emissive layer, 3. Radiations emitted, 4. A conductive layer, and 5. Positive electron acceptor (+)

3. Characteristics Parameters

Several parameters can be used to quantify various aspects of OLED performance. First, the luminance is the luminous intensity of the substance. Second, the current efficiency is the quotient of adequate electrical flow to total applied electrical discharge. Third, external quantum efficiency (ECE) represents balance among the total quantity of photons generated by machine and charge injected into machine. Fourth, power efficiency is the ratio of luminous flux to power consumption [5]. Fifth, lifetime, the length of time an OLED device can operate.

4. Enhancement Technology for Blue OLEDs

White inorganic LEDs are widely used in many areas, for example, indoor, outdoor, and auto lighting. Similarly, to inorganic LEDs, OLEDs have great potential for fabricating solid-state lighting devices. Generally, two primary methods can be used for white solid-state lighting devices: RGB and phosphor-based. For RGB systems, three basic colors, green, red, and blue, blend to produce white light. Although there have been many studies on RGB emitters in recent years, producing high-performance blue emitters is still quite tricky due to the wide band gap and the complexity of inserting charges in blue emitters. This report would focus on blue OLEDs. The electroluminescence properties and lifetime of blue emitters need to be enhanced. OLED emitters have undergone three generations: the 1st generation of fluorescent diodes, the 2st generation of phosphorescent diodes, and the 3rd generation based on the TADF effect.

4.1 blue fluorescent OLED

For the evolution of blue fluorescent OLED, outstanding researches were done by Shi et al [6].

Firstly, blue host materials need to be explored. Two major compounds were compared, diary anthracenes and di(styryl)aryl anthracenes. In the diary anthracene class, the main focus was on 2-(t-butyl)-9,10-bis(2-naphthyl) anthracene (TBADN), 9,10-bis(2-naphthyl) anthracene (ADN), and 2-methyl-9,10-(2-naphthyl) anthracene (MADN). Figure 3 depicts the half-life and luminescence performance of the three mentioned compounds, with MADN excelling in the blue host talent of the diary anthracene type.

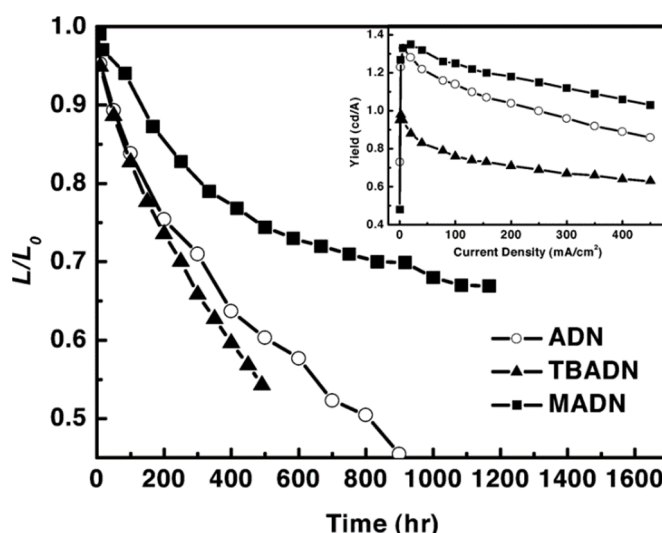


Figure 3. Comparison of device half-life and electroluminescence efficiency of ADN, TBADN, and MADN [6]

MADN has the best luminous efficiency and the lowest driving voltage. Its predicted half-life is about 7000 hours at the same initial luminance conditions, which is seven and three times longer than the lifetimes of TBADN and ADN. Within the di(styrene)aromatic class, two significant compounds, DPVBi and DVPA, were compared. The original DPVBi, 4,4'-bis(2,2'-diphenyl vinyl)-1,1'-diphenyl,

is a small molecule semiconducting material with a wide band gap (3.1 eV). However, his team found this is not a very good material because its 38% relative quantum efficiency does not effectively support the transfer of Forster energy. Therefore, a new material, DPVPA, was reported by replacing the biphenyl heart of DPVBi with diphenyl anthracene. The quantum efficiency of DPVPA is nearly three times that of DPVBi. Then, DPVPA and MADN were compared to identify a better material. Table 1 shows the details of their electroluminescence properties.

Table.1. Comparison of Electroluminescence Performance of Undoped and Doped Devices of MADN and DPVPA [6]

Host	Device	Voltage (V)	Luminous Area (cd/A)	Luminous Efficiency (lm/W)
MADN	Undoped	6.2	1.4	0.7
	TBP(0.5%)	6.3	3.4	1.7
	DSA-Ph(3%)	5.7	9.7	5.5
DPVPA	Undoped	7.3	4.0	1.7
	DSA-Ph(3%)	6.7	10.2	4.8

The external quantum efficiency of DPVPA would be better, but it emits more greenish than blue light. The driving voltage of MADN is one-fifth lower than that of DPVPA, which indicates that MADN can transport carriers more excellently. In terms of device lifetime, the MADN has a longer half-life (7000 hours) than the DPVPA's half-life (5600 hours) extrapolated at a uniform initial brightness, as shown in Figure 4 below.

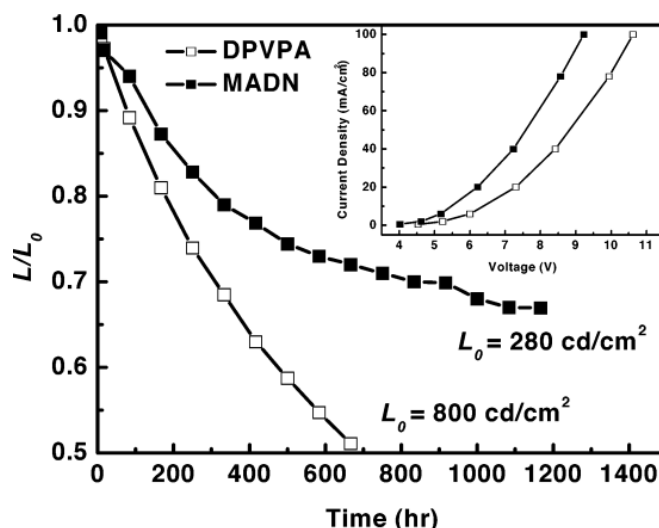


Figure 4. Device half-life and electroluminescence efficiency of DPVPA and MADN [6]

Secondly, MADN as a host material is superior to DPVPA in many aspects, despite the decrease in its luminescence efficiency. However, this improvement in luminescence efficiency can be achieved by the judicious selection of matched dopants for efficient energy transfer. Diphenyl amino-di(styryl)aromatic (DSA-Ph) is a good light blue dopant. As shown in Figure 5, compared to DPVPA, giving MADN doping with DSA-Ph limits the loss of fluorescence intensity caused by the current. According to the experiments, the lifetime of the 3% DSA-Ph doped MADN device will be very long, up to 46000 hours.

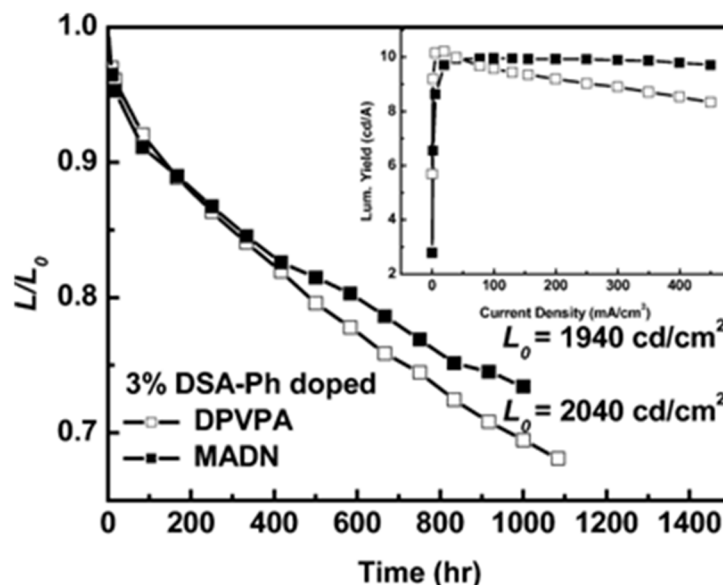


Figure 5. Device Lifetime and Electroluminescence Efficiency Comparison of DPVPA and MADN with 3% DSA-Ph Dopant [6]

The dark blue emitter is more worthy of discussion than the light blue emitter. The simplest solution is that the conjugation length (chromophore) of the di(styryl)phenyl dopant with the monoaryl core can be reduced appropriately. By changing the substituents of nitrogen (R1 and R2) and styrene (R3 and R4), the dark blue emitter is achieved by optimizing the structure, as shown in Figure 6. Also, at 3% reference conditions, the emitter can be effectively emitted by using a modified DSA-Ph.

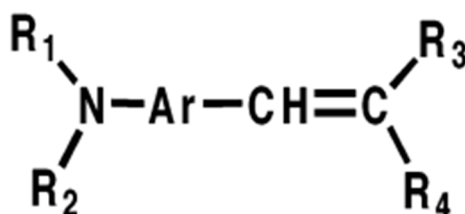


Figure 6. The General Structure of DSA-Ph for Deep Blue Emission [6]

Moreover, by adding 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole-blocking layer interspersed between the emitting layer and Alq3, the devices containing a hole-blocking layer can ultimately convert electrical energy into light energy compared to conventional devices. The maximum external electron efficiency can reach 4.2%, nearly reaching the limit of fluorescent OLED.

4.2 Blue Phosphorescent OLED

Only the radiative transition from S1 to S0 is permitted for fluorescent OLEDs, as intersystem crossover (ISC) between states of different multiplicity is not conceivable according to fundamental physics principles. Only 25% of the exciton produced after an electrical stimulation has singlet multiplicity and is emissive (Figure 7, first generation). The remaining 75% are triplet multiplicities and do not contribute to light emission. Therefore, fluorescent OLEDs have an IQE limit of 25% and an EQE limit of a few percent. Metal-organic compounds have been found to use the remaining 75% of excitons. Because of the extremely high spin-orbit coupling caused by rare metals like iridium and platinum, the T1 → S0 leap becomes radiative, and an ISC process occurs between S1 and T1 in the phosphorescent emitter (Figure 7, second generation). Theoretically, this method permits the usage of up to 100% of internal electron efficiency and up to 100% of generated excitons to produce light. For blue phosphorescent OLEDs, the main issue is a suitable and efficient material, and there have

been many studies in recent years[7]. In 2018, T.J. et al. developed a core structure of a carbazole-dibenzothiophene molecule as a hole-transporting high-triplet energy host to achieve high external electron efficiency in blue phosphorescent OLEDs. The CzThTh host with a carbazole-dibenzothiophene core and dibenzothiophene functional group efficiently harvested triplet excitons from Ir(dbi)₃ triplet emitters and exhibited high EQE (22.8%) through carrier balancing [8].

4.3 Blue Thermally Activated Delayed Fluorescence (TADF) OLED

Although the great performance and application potential of phosphorescent emitters in OLED technology, the presence of expensive and toxic rare earth metals and noble metals such as Ir and Pt in complex structures has led to recycling and price issues, limiting their application on an industrial scale. As a result, inefficient first-generation fluorescent blue light emitters are still widely used in commerce. The solution to this problem is third-generation emitters. They shift from phosphorescent to fluorescent emitters and exhibit TADF. A simplified description of the TADF mechanism is as follows. In the assumptions of previous techniques, ΔE among S1 and T1 energy levels normally should about 0.5 to 1.0 eV to enable efficient energy exchange between the different energy levels. Nevertheless, in TADF, ΔE between S1 and T1 is designed to be very small. The energy level difference in an efficient TADF would be less than 100 meV [7] so that the reverse intersystem crossover could be allowed to occur, and the exciton of T1 is converted to S1 during thermal activation (Figure 7, third generation).

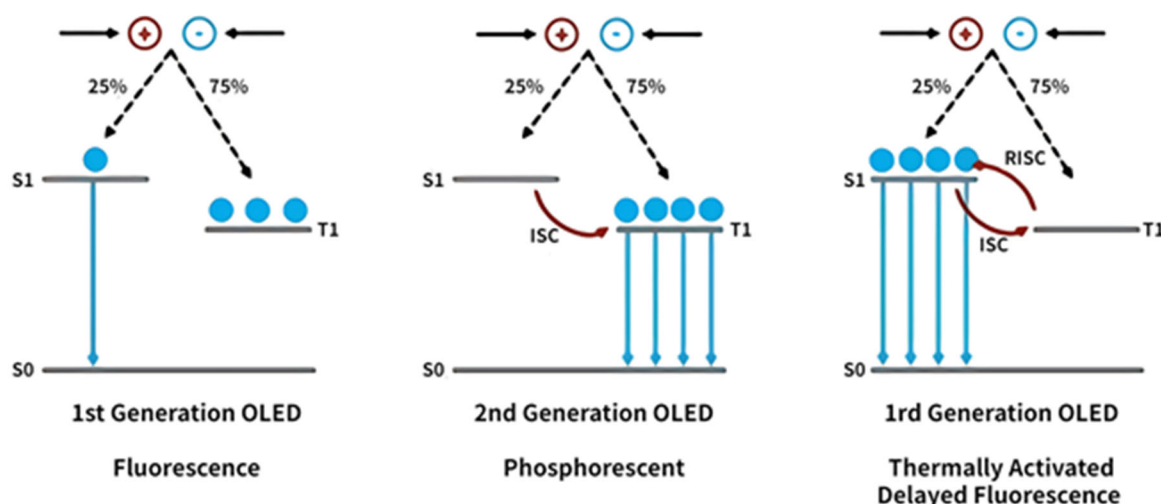


Figure 7. The operating principle of 1st, 2nd, and 3rd generation of OLEDs

Because of the very small energy polarity difference, the exciton can decay from the S1 state to the S0 state by fluorescence decay. Since reverse intersystem crossover is a slow process, the fluorescence of the three-state exciton evades the fluorescence of the exciton produced directly in the S1 state by delayed generation; therefore, it is called TADF.

For TADF OLED, Komatsu et al. based the molecular manipulation of the electronically excited state energy of the TADF emitter of pyrimidines to achieve dark blue emission. The novel pyrimidine emitters, produced by using distorted molecular structures induced by spatial site blocking of methyl groups, contain different numbers of large methyl substituents in the acceptor part, leading to an increase the excited singlet and triplet state energies. The result of performance is really good, with an EQE calculation of 25% [9]. In 2021, Chan et al. looked for ways to overcome most of the problems of blue OLEDs, including efficiency, lifetime, and color purity. The new blue OLED of this design has a high-efficiency pure OLED (EQE of 32%), narrow emission (full half-peak width of 19 nm) and good stability (brightness at 1,000 cd m⁻² for 18 hours of 95%). This is a super fluorescent

OLED that connects two cells in series with improved single excited state energy transfer from a light blue assistant dopant (called anisotropic donor type TADF (HDT-1)) that displays TADF to a pure blue emitter [10].

5. Different applications for OLED

5.1 Health Care

OLEDs can greatly lower the cost of these biosensor devices since they are straightforward to fabricate utilizing a low-cost solution treatment technique. Furthermore, due to the high moldability of OLEDs, biosensors may be made on unusual materials such as paper, plastic, and fabric. In 2019, Negi et al. designed an OLED-based sensor application to diagnose "ovarian cancer." Because ovarian cancer can be diagnosed achieved through the detection of the difference in wavelength when light physically affects the body's urothelium, the detection light and light supply for the cancer detection sensor are two types of OLEDs, multilayer OLEDs and three-hole blocking layer OLEDs. In the meantime, the three-hole block layer is driven by the dual-gate organic TFT. When compared to single-gate TFTs, the DG-OTFT performs eighteen percent better. At 440 and 420 nm incident wavelengths, the cathode currents of multilayer organic LEDs were summarized as 13 and 29 mA [11].

5.2 Sensor

The sensor mentioned in section 5.1 about health care is a light sensor. In addition, Kim et al., in 2011, capacitive touch sensing characteristics of fragile ultra-thin active-matrix OLED devices were reported. At just 1.2 mm thick, the touch sensor platform is the thinnest OLED platform on the market, and it can work at temperatures lower than 200°C. Electrostatic simulation is used to examine the capacitance fluctuation and inner E-field distribution built on the Q3D extractor model in order to produce the optimal noise-free capacitive touch sensor construction and validate the fault-free signal of a 4-inch diagonal capacitive touch sensor [12].

5.3 Military

The military requires the unique ruggedness of OLEDs because of the specific needs of the military to perform its mission, such as visor-type displays as well as intelligent goggles. The wide field of view properties of OLEDs is also used, for example, in windshield displays for aircraft. In the future, OLEDs will be used in military operations as visors, camouflage systems, and intelligent light-emitting windows [13].

5.4 Fashion

Photonic textile generation is a promising emerging industry. The creation of photonic textiles is a promising new industry. The lightweight, transparent, and even foldable nature of organic diode devices perfectly fits the requirements of photonic textile products. Because of the wide-angle light-emitting qualities of OLEDs, they can emit light uniformly over a larger surface. And organic light-emitting diode production environment restrictions are less, and can be made in a variety of textile materials as a base. But life is still a huge challenge.

5.5 Displays

Non-organic led, liquid crystal display (LCD), and even vacuum fluorescent display (VFD) have been widely used in life, so why has the research on organic light-emitting diode been commonly discussed today? Table.2. shows the advantages and disadvantages of each display in widespread daily use.

Table.2. Comparison of OLED, LCD, VFD, and LED

	OLED	LCD	VFD	LED
Resolution	higher	highest	lower	lowest
Contrast	highest	worst	high	normal
Brightness	Highest	worst	normal	highest
Chromaticity	Best	normal	worst	Good
Response speed	Good	Bad	Good	Bad

OLED is outstanding in all aspects. OLED displays are thinner, lighter, and more flexible (such as foldable OLED display screens), have more extensive screen views, more power saving, and can also do transparent displays.

6. Conclusions

This work describes the history of OLEDs, the fundamentals of how they work, the technologies that have been improved, and the cross-border derivative applications. Although organic LEDs outperform normal LEDs in terms of ease of preparation, flexibility, skinniness, lightweight, and manufacturing cost, there is still significant space for development in terms of materials, efficiency, and longevity. In recent decades, improving the performance of OLED devices became a trend. Phosphorescent OLEDs have been proposed in order to enable the excitons after charge carrier recombination to be fully utilized. Recently, there is a gradual trend for phosphorescent OLEDs to be replaced by TADF OLEDs, as these TADF OLEDs can not only exhibit 100% internal quantum efficiency and are cheap to produce because they do not contain precious metals. However, there is certainly space to improve in terms of longevity and color. Great amount of research is still needed to solve the blue OLED problem because compared to other colors, such as red and green OLEDs, blue OLEDs still have a big gap in stability and efficiency.

References

- [1] Sugandha Yadav, Poornima Mittal, Shubham Negi. Recent advancements over a decade for OLEDs: from structural diversity, role of layers, colour emission, material classification, performance improvement, fabrication to applications [J]. Bulletin of Materials Science: Published by the Indian Academy of Sciences, 2022, 45: 109.
- [2] Nikhil Sain, Deepesh Sharma, Priya Choudhary. A review paper on: organic light-emitting diode (OLED) technology and applications [J]. Physics, International journal of engineering research and technology, 2018, 4(11): 587-591.
- [3] Anshika Srivastava, Brijesh Kumar. Organic light emitting diodes-recent advancements [J]. 2017 14th IEEE India Council International Conference (INDICON), 2017, 1-6.
- [4] Bernard Geffroy, Philippe le Roy, Christophe Prat. Organic light-emitting diode (oled) technology: materials, devices and display technologies [J]. Polymer International, 2006, 55(6): 572-582.
- [5] Shumeng Wang, Hongyang Zhang, Baohua Zhang, et. al. Towards high-power-efficiency solution-processed oleds: material and device perspectives [J]. Materials Science and Engineering, 2020, 140: 100547.
- [6] Shih-Wen Wen, Meng-Ting Lee, Chin H. Chen. The recent development of blue fluorescent OLED materials and devices [J]. Journal of Display Technology, 2005, 1(1): 90-99.
- [7] T. J. Penfold, F. B. Dias, A. P. Monkman. The theory of thermally activated delayed fluorescence for organic light emitting diodes [j]. Chemical Communications (Cambridge, England), 2018, 54(32): 3926-3935.
- [8] Louise M. Cañada, Johanna Kölling, Thomas S. Teets . Blue-phosphorescent bis-cyclometalated iridium complexes with aryl isocyanide ancillary ligands [J]. Polyhedron, 2020, 178: 114332.

- [9] Ryutaro Komatsu, Tatsuya Ohsawa, Hisahiro Sasabe, et. al. Manipulating the electronic excited state energies of pyrimidine-based thermally activated delayed fluorescence emitters to realize efficient deep-blue emission [J]. *ACS Applied Materials & Interfaces*, 2017,9(5): 4742–4749.
- [10] Chin-Yiu Chan, Masaki Tanaka, Yi-Ting Lee, et. al. Stable pure-blue hyperfluorescence organic light-emitting diodes with high-efficiency and narrow emission [J]. *Nature Photonics*, 2021,15(3): 203–207.
- [11] Shubham Negi, Poornima Mittal, Brijesh Kumar, et. al. Organic led based light sensor for detection of ovarian cancer [J]. *Microelectronic Engineering*, 2019, 218: 111154.
- [12] Sunkook Kim, Woong Choi, Woojin Rim, et.al. A highly sensitive capacitive touch sensor integrated on a thin-film-encapsulated active-matrix oled for ultrathin displays. *Ieee Transactions on Electron Devices*, 2011,58(10): 3609–3615.
- [13] Priyam Kaur Sandhu, Sanjam Singla. Oled–an imminent technology [J]. *International Journal of Engineering Research and General Science*, 2015, 3: 611-616.