Investigation on potential applications of thermal activated delayed fluorescence materials in organic electroluminescent devices

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Abstract. In the past few years, organic battery light emitting devices have attracted a lot of attention, showing great application potential. Fluorescence material, phosphorescence material and thermal activated delayed fluorescence (TADF) material, have attracted more and more attention. However, phosphorescent material is limited by the useage of a heavy metal, Ir. So people want to find a more efficient and environmental-friendly material:TADF. TADF polymer can be used as a new type of organic photoelectric functional materials due to its high exciton utilization. This work focuses on the working principle, advantages, applications of TADF materials and the imagination for future applications. OLED emission of different light colors is also worthy of attention, the differences and efficiency of the three colors have sparked discussion as well. On this basis, starting from the luminescence principle and device structure of TADF, the advantages and disadvantages of TADF materials are summarized. Finally, the solution to "aggregation-caused quenching" problem (ACQ) is found, so as to focus on the application of technology and envisage the future application direction.

Keywords: Thermal Activated Delayed Fluorescence (TADF), Organic Light-Emitting Diode (OLED), Principle, Application.

1. Introduction

With the development of science and technology, organic battery light-emitting devices have become more and more popular, so organic solid-state light-emitting materials have attracted more and more attention,including fluorescence, phosphorescence and TADF.But the maximum internal quantum efficiency of a fluorescent material is only 25%. Normally, the triplet state cannot move back to the ground state due to the transition confinement, but if there is a heavy metal in the molecule (such as Iridium), which may cause spin-orbit coupling, it becomes possible to move the triplet state back to the ground state,which causes the phosphorescent material. Because 75% of the energy of the triplet state is used, Therefore, phosphorescent materials can theoretically achieve 100% internal quantum efficiency.However, phosphorescent materials require the use of a heavy metal, Ir, which is not environmentally friendly and is limited, so people wanted to find a more efficient and environmentally friendly material,TADF [1].

Thermal activated delayed fluorescence (TADF) polymer has the advantages of good molecular diversity, solution treatment, high flexibility, low cost, and easy to implement large-area flexible devices. After experiencing CRT, LCD and PDP technology, display technology is developing towards these above aspects, and TADF is in line with the development direction of organic electronic light-emitting devices in the future because of its many advantages.TADF polymer can be used as a new type of organic photoelectric functional materials due to its high exciton utilization [2].

Therefore, by first introducing the unique molecular design of TADF in detail, and then explaining its luminescence principle in detail, we further expand the molecular characteristics of TADF made by its unique structure, such as higher luminescence efficiency and more diverse colors. Secondly, we will briefly introduce and compare the characteristics of TADF materials with different colors in the following part, so as to summarize and propose a specific method to improve the luminescence efficiency of different colors. In addition, through its molecular structure, summarizes its limitations, and tries to use a variety of methods to suppress this phenomenon, through further research, summarizes a better solution. Finally, through the above discussion, combined with the current market application of TADF, it gives a reasonable assumption about the application prospect of TADF. Starting from the most basic excellent properties of TADF, such as lower cost, more diverse colors, and more environmentally friendly manufacturing methods, we should target target groups, further eat up the market share of organic electronic devices, gradually phase out outdated materials, and expand the market demand for TADF.

2. TADF material

2.1. The structure of TADF

At present, the common design strategy for constructing TADF polymers is to design and synthesize TADF polymers from small molecule materials with TADF effect by conjugated or non-conjugated means. As it is shown in Figure 1 TADF polymers have five kinds of structures. The structures are Dendrimers,Alternating type, Graft Type,Self-host type, and Non-conjugated.

Although there are many organic conjugated units, the donor structures commonly used to construct TADF polymers mainly focus on the strong electron donor capacity, high triplet energy level, good stability and simple preparation process [3].

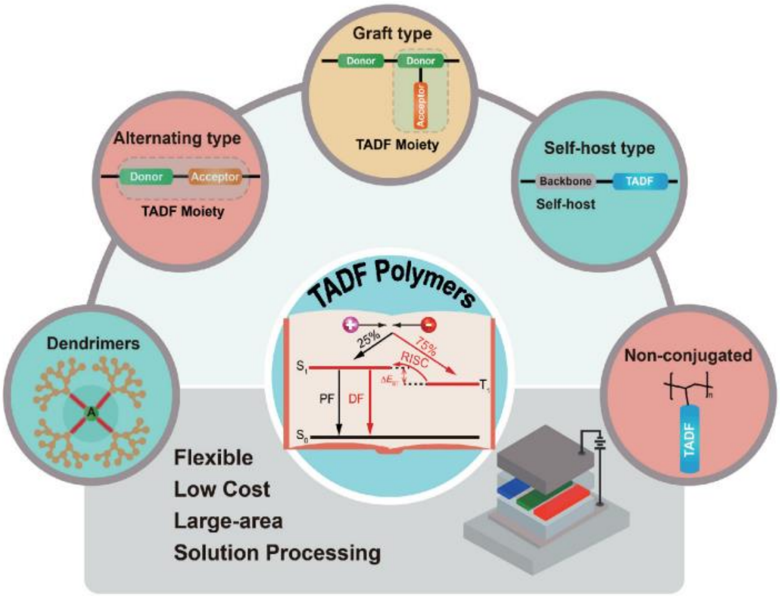

Figure 1.TADF structure conclusion [3]

2.2. The determination of the number of network layers

Generally speaking,as shown in Figure 2, the electroluminescence of TADF polymer OLED devices has the following four processes :

(1)Excitons are created when electrons and holes combine in the presence of an external electric field; The ratio of singlet and triplet excitons generated is 1:3, in accordance with the spin selection rule;

(2) By means of vibrational relaxation, internal transformation, or interseries crossover, the singlet and triplet excitons in the highly excited state are converted into the lowest singlet (S1) or triplet (T1) excitons;

(3) T1 exciton formed by electric field excitation and ISC process is upconverted to S1 exciton by RISC process under the action of heat activation;

(4) S1 excitons directly formed by electric field excitation and S1 excitons formed by RISC process radiate down to the ground state (S0) with immediate fluorescence with nanosecond luminescence lifetime and DF with subtle or even millisecond lifetime theoretically achieving 100% IQE.

In the above process, the RISC process from T1 to S1 is the key to improve the utilization of T1 exciton. It is worth noting that in TADF polymer, the energy level of S1 state is slightly higher than that of T1 state, so ISC process is more effective than RISC process, so most excitons generated by electric field are in T1 state with low energy level. Therefore, the T1 state exciton must have a slow non-radiative decay rate, which is expected to obtain high DF efficiency, and then significantly improve the comprehensive performance of the device [4].

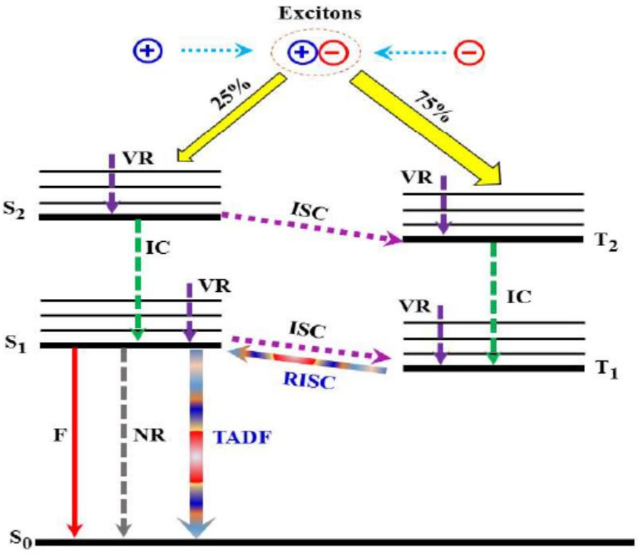

Figure 2. Principle of TADF [4]

3. Different Colors of TADF

3.1. Theory of OLED emission of different light colors

The large data prediction model for the user's electricity consumption is implemented in the Clementine software.

To produce different colors of TADF, the principle is the same properties as all the OLED devices. Which is to absorb the different wavelengths of visible light and reflect the rest of the wavelengths, then the wavelengths of colors that got reflected will catch by human eyes and become different colors that people see all the time. To achieve absorb different wavelengths, means that electrons in the devices have different requirements of energy to move to the excited state. So, the principle is to use benzonitrile as the base of organic molecules and change the carbazole group’s number, binding position, and modification group. Then the different energy requirements allowed different parts of the wavelength of visible light has been absorbed the rest of the colors will be reflected.

But there is also a problem, which the wavelength that TADF absorbed might be crossed over, which means the light that it reflects are not pure.

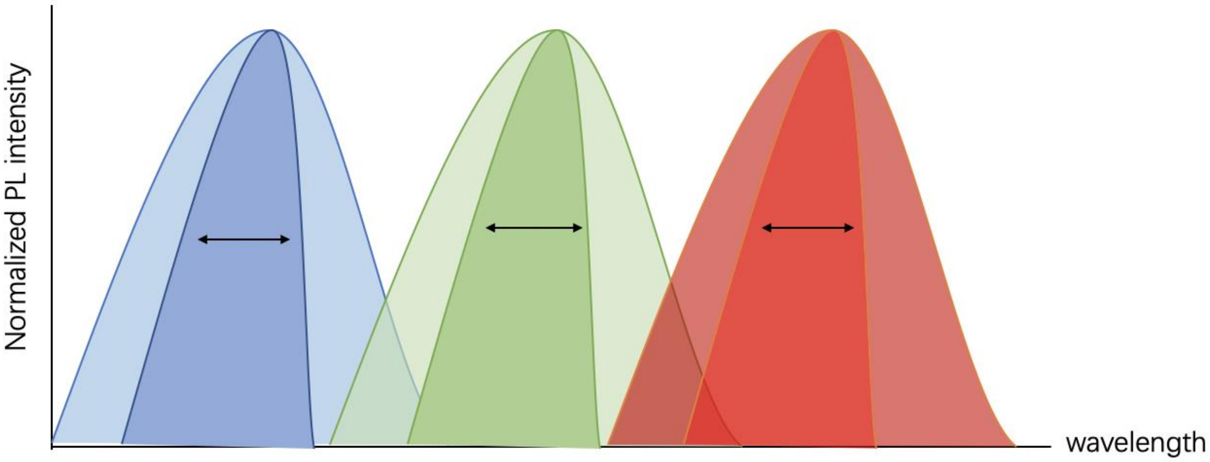

Figure 3. Cross over between the wavelength of visible light that TADF absorbed.

In the Figure, we can see that in areas with higher transparency there are crosses over between different colors, In the result, the color that reflects, or in the other words to say, the color that people see is not pure, different colors got mixed together. Therefore, professor Anda from Kyushu University has invented a technique called superfluorescence, which basically is the combination of TADF and fluorescent material, with this technique spectrum of fluorescence, got narrowed and it will also increase the efficiency of light emission.

3.2. Different ways that increase the efficiency of TADF

3.2.1 Red TADF

From the previous passage, we have known the properties of how TADF emissions different colors of light. To make red TADF the emission wavelength should be greater than 600 nm. Nowadays scientists are focusing on how to increase the emission efficiency of colored TADF to maximize its value. For red TADF first way to increase efficiency is Rational Isomer engineering [5], which is two pairs of isomers are designed and synthesized by attaching electron-donor of DPAC(9,9-diphenyl-9,10-dihydropyridine) moiety to the different position of two kinds of highly rigid planar acceptor cores. Intramolecular hydrogen bonding [6] is another way to improve emission efficiency and promote horizontal orientation, this technique is based compose of an electron-withdrawing pyrazino[2,3-f] [1,10] phenanthroline-2,3-dicarbonitrile core and various electron-donating triarylamines to make special red TADF, which in the result both of method increases the efficiency of emission of red light.

3.2.2 Blue TADF

Blue TADF is the TADF that contains the most energy based on it have the shortest wavelength, at the same time, it is the least stable TADF. Different from red TADF, blue TADF got a 400-600nm emission wavelength, do not forget that green color is still in the between blue and red TADF, which proves again the theory that emissions between different colors overlap, so the first method is what mentioned before, it Is called Superfluorescence [7] and this technique will narrow the wavelength of TADF, based on two-unit stacked tandem hyperfluorescence OLED with an improvement on singlet-excited-state energy transfer from sky-blue assistant dopant exhibiting thermally activated delayed fluorescence (TADF) called hetero-donor-type TADF(HDT-1) to a pure-blue emitter. The second method of producing stable efficiency blue TADF is B-hetertriangulene Acceptors [8] this method is based on boron acceptors, the device based on the emitter with B-hetertriangulenes shows better performance than the device incorporating a singly bridged reference emitter over the whole luminance range.

3.2.3 Green TADF

Green TADF is the most stable compared to red and blue TADF, it is based on its emission wavelength 450-700nm, Green TADF is the most stable and efficient TADF that developed fastest and has reached the stage of commercial application, which means the firms that produce the most efficient green TADF will make the most profit, so more scientist is doing research on this most stable and profitable TADF. The first method of increasing efficiency is Ternary Boron-Oxygen-Nitrogen Embedded Polycyclic Aromatic System [9], which is A ternary B−O−N embedded multiple resonances thermally activated delayed fluorescence emitter developed based on the para B-π-B and O-π-O strategy. And another method is Simultaneously manipulating hole and electron transport [10], which is simultaneous manipulating of the hole injection and electron transport layers for (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile (4CzIPN) based green TADF organic light-emitting diodes (OLEDs).

4. Limitation of TADF material and the solution

4.1. Discovery of ACQ

As early as the middle of the 20th century, the German physical chemist Theodor Forster and others found that luminescent molecules can emit strong fluorescence when they are dispersed, for example, in a solution[11]. However, as the concentration of the solution becomes higher and higher, the fluorescence of luminescent substances will become weaker or even disappear when they reach the aggregate state. The phenomenon is shown in Figure 4.

Figure 4. A fluorescent photograph of DDPD (concentration: 0.02mol/L) taken under ultraviolet light in a mixed THF/water solvent with different water volume ratios [12]

This is a common phenomenon known as "aggregation-caused quenching" (ACQ). The ACQ phenomenon is closely related to the large π-conjugated bond structure in the molecule. For example, if two specific substances is mixed to form a solution, then a OLED material with better performance is produced. Two mixed materials are called N,N-dicyclohexy-1,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide (as Figure 5 shows) and tetrahydrofuran, which will be referred to as DDPD and THF in short respectively.

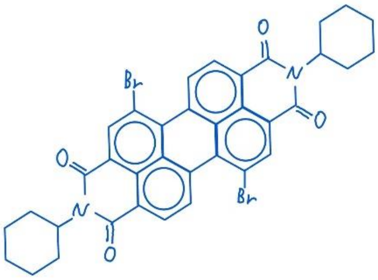

Figure 5. N,N-dicyclohexy-1,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide (DDPD)

Under the condition of high concentration of THF, DDPD can play a better fluorescence ability.However, TADF-OLED materials are usually used in a solid or aqueous state, such as when pressed into slice as a screen or placed in water to detect harmful substances.

In both states, DDPD molecules spontaneously aggregate. Because the DDPD molecule contains flat perylene rings like a disc, the perylene rings may produce strong π-π bond accumulation in the aggregate state which is formed between the π-conjugate bond structures of the benzene molecules in the perylene [13] .

This makes strong electron or energy transfer between the molecules and promoting the formation of excimer. As a result, the energy dissipation of excited molecules is severe. The way that OLED materials work is that electrons get enough energy to cross the bandgap, fill the holes and emit photons. But the formation of excimer prevents it from getting enough energy, so finally it can't emit light.

Although chemical, physical or engineering methods (such as the addition of non-aromatic ring molecules with large volume or the modification of aliphatic chain) have been used to reduce the intermolecular aggregation to inhibit the ACQ effect of organic luminaries, the results are not satisfactory. Under these methods, molecular aggregation is often only partially inhibited or temporarily inhibited; In many cases, the excellent optical properties of single molecules are greatly reduced by these methods. From the perspective of enthalpy and entropy of physical chemistry, the aggregation behavior of organic compounds in the solid state is a naturally occurring process, and deliberately inhibiting molecular aggregation can not fundamentally solve the emergence of ACQ phenomenon [13].

4.2. Solution of ACQ: AIE

ACQ phenomenon limits the application of OLED materials to a large extent.With further researches, the ACQ phenomenon can also be solved. In Figure 6, a obvious phenomenon is that the higher the percentage of water is, the brighter the solution is. It shows the opposite phenomenon and opposite rule to Figure 1. This solution is called “aggregation-induced emission” (AIE).

Figure 6. A fluorescent photograph of HPS (concentration: 0.02mol/L) taken under ultraviolet light in a mixed acetonitrile/water solvent with different water volume ratios [12].

In Figure 7 is a silole derivative, called 1,1,2,3,4, 5-hexaphenylsilole, or HPS, as the Figure 7 shows. HPS can be solved into acetonitrile. In the HPS molecule, the six benzene rings are able to rotate violently with respect to the core of silole by a single bond.

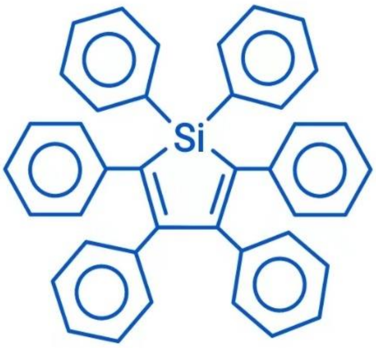

Figure 7. 1,1,2,3,4, 5-hexaphenylsilole (HPS)

When the HPS molecules are far away from each other in dilute solution, they are in an unconstrained state, and the benzene rings in the molecules can rotate or vibrate very freely, thus consuming their energy by means of these mechanical motions without the need for fluorescent radiation.

However, when these substances are in the aggregate or solid state, the molecules are stacked in random ways, which limits the rotation or vibration of the benzene ring. When molecules can't move mechanically, energy needs to find another way to get out[14]. So the electrons can gain energy to cross the bandgap, fill the hole and then emit photons.

There are three prescribed names for three different types of inter molecular motion restrictions [11,14]: Restriction of Intermolecular Rotation (RIR) and Restriction of Intermolecular Vibration (RIV) and, Restriction of Intermolecular Motion(RIM), as Figure 8 shows.

There are some AIE molecules that cannot be fully explained by RIR (e.g. 10,10,11,11, -tetrahydro-5, 5-bisdibenzo [a,d] [7] cycloene (THBA) does not have any rotating part).

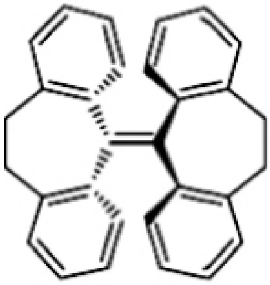

Figure 8. 10,10,11,11-tetrahydro-5, 5-bisdibenzo [a,d][7] cycloene (THBA) [14]

The THBA molecule can be viewed as consisting of two flexible parts, with two benzene rings connected by flexible bonds in each part. These two parts are not coplanar, and the whole molecule takes the trans conformation. In the solution state, the flexible and bendable bond makes the benzene ring in THBA molecule bend or vibrate dynamically, which can also be regarded as a non-radiative transition mode of excited state. In the aggregate state, the intramolecular vibration is restricted by physical obstruction due to space limitation. As a result, the non-radiative attenuation of the excited state is blocked and the radiation attenuation is turned on, thus making THBA emit light in the aggregated state[14]. The mechanism of AIE can be summarized as restriction of intermolecular motion (RIM).

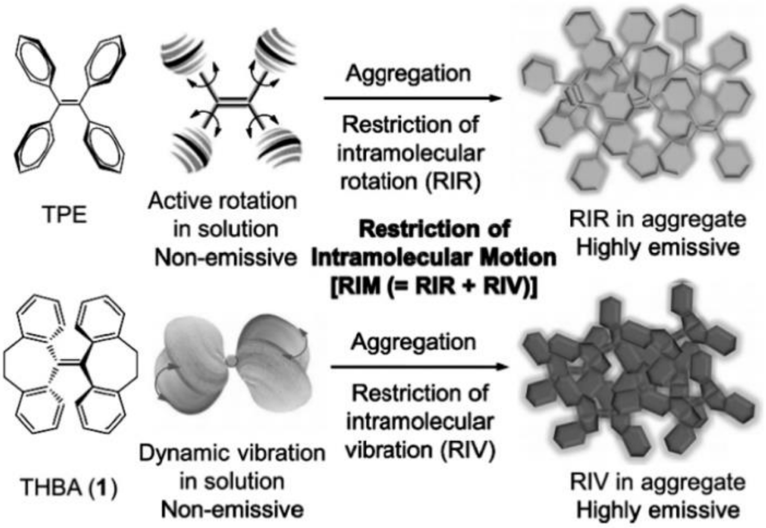

Figure 6. Schematic illustration of RIM induced fluorescence enhancement [14]

5. Applications

5.1. Current application

To date, TADF materials have made significant contributions to the development of biomedicine. TADF emitters are typical metal-free luminators, which may play a role in routine fluorescence imaging in different biological systems [15]. Meanwhile, the long-lifetime emission characteristics make TADF materials capable of fluorescence lifetime imaging (FLIM) or time-resolved luminescence imaging (TRLI), which can eliminate the interference of background signals and improve the accuracy of biological imaging.

5.2. Advantage and Defect

TADF materials, which are metal-free organic materials with distinctive photophysical properties, adaptable synthesis, and affordable production, have shown great promise in the biomedical sciences [16]:

1) TADF agents could be used as probes for conventional fluorescence imaging, LLIM, or TRLI since they have both long-lived delayed fluorescence and quick fluorescence.;

2) The fluorescence lifespan can consequently be influenced by oxygen and temperature-sensitive RISC processes, allowing the use of TADF agents in time-resolved sensing;

3) Because of the TADF molecules' short EST and subsequently efficient ISC process, they are suitable organic PSs for PDT applications. In order to increase the variety of physiological applications for intrinsically hydrophobic TADF dyes, rational design methods including molecular engineering, self-assembly, reprecipitation with polymers, and encapsulation inside different nanocarriers have been examined.

Although TADF materials have been studied somewhat in the field of biomedicine, this state-of-the-art metal-free luminescence group is still in its infancy and presents both obstacles and potential. To polymerize TADF into materials for use in medicine and other fields, a number of fundamental issues must be resolved. These include:

1) Finding more efficient methods of modification, where the targeting ability and large-scale production should be highly considered, and addressing the inherent properties of poor water solubility and undesirable bioavailability.;

2) In order to get state-of-the-art qualities like an extended luminescence duration, suppressed ACQ and O2 quenching, and better 1O2 quantum yield, greater efforts should be made to research the structure-activity connection of TADF materials in detail, allowing the development of novel

design theories and ideas of TADF materials, such as their integration with other materials like AIEgens and afterglow molecules;

3) The NIR-I/II TADF emitters should be purposefully constructed in order to accomplish deep-tissue theranostics and prevent adverse effects to healthy tissues brought on by short wavelength excitation, which will also broaden the applications beyond two-photon excitation;

4) Appropriate processes to chemically or physically insert additional functional moieties into TADF materials are also required in order to develop smart or multifunctional TADF-based theranostic platforms;

5) In order to further validate the long-term biocompatibility and biosafety of TADF materials for practical transformation, complete biodegradability and body clearance functions of TADF fluorophores should be carefully explored both in vitro and in vivo, as well as additional associated pharmacokinetic parameters such as assimilation, allocation, metabolic activity, and excretion (ADME) as well as toxicity in human tumors-simulated animal models (e.g. patient-derived xenografts, humanized mouse models) should be assessed.

5.3. Potential Application

To consider the future of TADF, we should know what advantages TADF has. Based on the properties that TADF does not contain any noble metals and could realize 100% internal quantum efficiency under pure organic conditions, makes efficiency could be the main point when advertising. And based on polymer luminescent material solution processing light emitting diode (OLED) have a low cost [6]and could be produced in high quantity making the price setting for the TADF should be low, and profit will be based on the high quantity of TADF that being sell. With the good strength of TADF, some potential applications could be screens in the condition that is easy to get damaged, which the consumer is focusing on lower cost but higher quantity, for example, the outdoor screen on the side of the building, when the rocks that wind brings or any unexpected factor that damage the screen, the best choice will be OLED that using the TADF. Other applications could be children’s electronic devices, nowadays more and more children raising the demand for a phone or a computer, but most of them are extremely expensive and unaffordable, but there is demand for that device, so the potential business could be working with the company that producing the children’s electronic device, they also know the problem is the high price, so they would like to find a supplier with a lower cost and high quantity, which is exactly the benefit of TADF, so the cooperation would be perfect between TADF producer and children electronic device producer. For making more profit, TADF producers could apply the term “economy of scale” to lower the total cost, which basically with time going on the labor’s skill became expertly which increases the efficiency of production or increase the size of the factory so the total efficiency of production will increase.

5.4. Future Application

To consider the future of TADF, we should know what advantages TADF has. Based on the properties that TADF does not contain any noble metals and could realize 100% internal quantum efficiency under pure organic conditions, makes efficiency could be the main point when advertising. And based on polymer luminescent material solution processing light emitting diode (OLED) have a low cost and could be produced in high quantity making the price setting for the TADF should be low, and profit will be based on the high quantity of TADF that being sell. With the good strength of TADF, some potential applications could be screens in the condition that is easy to get damaged, which the consumer is focusing on lower cost but higher quantity, for example, the outdoor screen on the side of the building, when the rocks that wind brings or any unexpected factor that damage the screen, the best choice will be OLED that using the TADF. Other applications could be children’s electronic devices, nowadays more and more children raising the demand for a phone or a computer, but most of them are extremely expensive and unaffordable, but there is demand for that device, so the potential business could be working with the company that producing the children’s electronic device, they also know the problem is the high price, so they would like to find a supplier with a lower cost and high quantity, which is exactly the benefit of TADF, so the cooperation would be perfect between TADF producer and children electronic device producer. For making more profit, TADF producers could apply the term “economy of scale” to lower the total cost, which basically with time going on the labor’s skill became expertly which increases the efficiency of production or increase the size of the factory so the total efficiency of production will increase.

6. Conclusion

Thermal activated delayed fluorescence (TADF) materials has the advantages of good molecular diversity, good solution treatment, high flexibility, low-cost, and easy processing as flexible device. In this paper, the history and basic principles of TADF are introduced. In addition, the advantages and disadvantages of TADF polymer are summarized. This work also focuses on the applications of TADF polymer in various fields. It can be found that TADF materials still face many problems to be solved. In the future, it is a promising research direction to continue to improve the stability of TADF.

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