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A Review of the Application of Organic Dyes Based on Naphthalimide in Optical and Electrical Devices

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ABSTRACT

The two technologies of dye-sensitized solar cells (DSSCs) and organic light-emitting devices (OLEDs) are emerging in the development of new sources of energy and lighting,

respectively. The exceptional features of these technologies, including their color, insensitivity to temperature, and high response angle, have caused their attention and development. Organic compounds play a key role in these two technologies and cause the effective response and stability of the device, so high stability, longevity, and the possibility of simple application in the structure of the structure are of great importance. Molecular engineering and the application of various substitutions to the naphthalimide core can produce promising results for the preparation of stable organic materials with diversity in properties. In this review, naphthalimides are introduced as an effective core in the preparation of light- and electricity-sensitive dyes. Its application in two technologies, DSSCs and OLED, is explained, and the different components of these technologies are briefly introduced. One of the highest efficiencies reported for dye-sensitized solar cells based on naphthalimide as photosensitizers is 10.8 %. This sensitizer has alkyl and indoline groups. Different structures of arrangement of electron donor and electron acceptor groups will be investigated and the performance efficiency of these devices will also be investigated. Studies show that the amino group is an important substitution in the preparation of naphthalimide fluorescent dyes. The presence of this group will increase the efficiency of the amplifier by up to 10 %.

Keywords: Dye-sensitized solar cells, Organic light-emitting devices, Naphthalimides, Photovoltaic, Luminescence.

1. Introduction

The issues of energy and economy are very important in human life because these two factors improve the social welfare index. The growth of energy consumption and the importance of providing new sources and forms of energy are very important for the development of technology. The development of energy resources should be done in such a way that, in addition to the ease of procurement, it avoids environmental pollution and does not reduce air quality. In other words, in order to preserve the human race, the introduction of broad, safe and environmentally friendly energy sources should be considered. All countries should invest in this issue because the development of clean energy has a direct impact on life expectancy [1]. The epidemic of Corona disease showed that health and related research are very important. In addition, during this period, energy consumption increased significantly, but due to the limitations of industrial activity, fossil energy consumption decreased. Therefore, renewable energy sources and the energy produced by them were considered and consumed. Research shows that energy production, economic growth, and life expectancy have linear and non-linear effects on each other. Factors such as the cost of living, technological development, increasing the heat of the earth, and the production of carbon dioxide gas are caused by these factors [2]. Of course, the life expectancy index varies according to countries' incomes, and countries with high incomes have a lower life expectancy than countries with lower incomes [3]. Electrical energy has increased dramatically due to the increase in electrical tools used, and alternative ways to reduce energy consumption and replace them with light-emitting devices with high efficiency should be considered. Another common method for classifying dyes is the method of their use or functional

classification. Dyes have a variety of applications in various industries, including: dyeing textiles, food and health products, medicine, coloring polymers, optics, lasers, photonics, etc. The production of energy and light is one of the emerging applications of dyes, which is very important for the development and progress of humans' lives [3]. In this article, two types of energy, including photovoltaic and electric energy, are investigated. The device of each case is introduced, and the role of dyes, especially naphthalimide dyes, is studied.

2. Photovoltaic Devices

The photovoltaic effect was discovered in 1839 by Edmond Becquerel. After that, with the development of research, photoactive and photoelectric effects were introduced. The response of silicon to light was accidentally discovered in 1953 and led to the production of the first generation of photovoltaic devices. Then, the development of this technology by preparing silicon modules and expanding its use in spacecraft was investigated. The sudden need for this technology was announced with the possibility of diminishing fossil fuel resources and oil embargoes in 1976. Until now, the commercial market for photovoltaics has been dominated by silicon-based solar cells due to their high efficiency, good stability, and low energy loss. But this technology also has weaknesses, such as: dependence on temperature, lack of response in mild and cloudy conditions, high weight of modules, and the fragile nature of the device [5]. In 1960, anthracene was introduced as an organic compound with optical conductivity, and later, with the expansion of research, compounds with conjugated systems that have electrical conductivity were also discovered. Research has shown that increasing the conjugation system helps to improve

conductivity. Therefore, the second generation of solar cells was prepared as thin-film devices. Due to its high cost and complex production methods, this technology did not receive public attention and could not develop significantly. Therefore, many efforts were made to develop new photosensitive materials and, to study layering methods and intramolecular and interlayer interactions [6]. Figure 1 shows the publication process of articles in the photovoltaic field [7]. As a result of this research, electroluminescence conjugated polymers, diodes, transistors, and organic photovoltaic devices were introduced. One of the most important technologies developed in 1991 by Gratzel and his colleagues was solar cells sensitized to dyes [8]. In the following, this technology will be introduced.

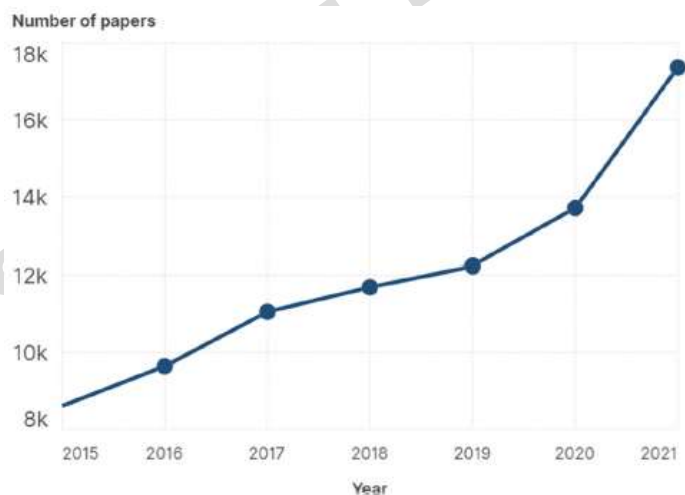


Figure 1. Published articles in the field of photovoltaics [7] (Reprinted with permission from [7]. Copyright 2023, Elsevier Publishing due to open access).

2.1. Dye-sensitized solar cells

Renewable energy sources are important for energy production, and one of the most

important of them is solar energy, which is abundant and easily available in many countries. Among the devices produced for the use of solar energy, dye-sensitized solar cells (DSSCs) are very desirable because of their low cost, colorful, and the possibility of being used in building design, ease of preparation, and insensitivity to temperature and light changes [9, 10]. As shown in Figure 1, this device (DSSCs) has several essential and important parts. Two electrodes, anode and cathode, are necessary to complete the electrical circuit. To prepare the anode electrode, a semiconductor layer is placed on a conductive substrate, the indicated layer, and then the sensitizer is placed on it. The cathode electrode, or counter electrode, is prepared from the address layer of a platinum layer on the conductor substrate. The presence of a redox couple as an electrolyte is necessary to supply the excited transition electron of a semiconductor. In this technology, an electric current is produced by stimulating the sensitizer (dye) against sunlight. By receiving sunlight, the sensitizer transfers its valence layer electron to the lowest empty molecular orbital. In a thermodynamic process, the excited electron is transferred to the conduction band of the semiconductor and enters the electric circuit. Next, the electrolyte supplies the lack of sensitizing electrons needed to create the ground state and prevent its destruction. This cycle continues until all the components do their jobs. Usually, the end of the life of the solar cell is due to leakage of the electrolyte or its evaporation. When the electrolyte is not able to supply the lost electron of the sensitizer, the return to the base state is not transferred, and the sensitizer, which is the main part of the electron production, is destroyed. DSSCs efficiency is calculated based on photocurrent (J_{sc}), photovoltage (V_{oc}), and fill factor (FF) parameters (Eq. 1) [9].

$$\eta = J_{sc} \times V_{oc} \times FF \quad (1)$$

Each of these factors can be increased by optimizing the components of the DSSCs, and as a result, the efficiency of the device increases. For example, using a suitable photosensitizer that can have a high response to light and establish a stronger connection with the semiconductor pores will increase the photocurrent. To prepare a suitable device, it is important to obtain high efficiency and low cost, and this is achieved by engineering and designing different parts of this technology. Engineering energy levels of the electrolyte, photosensitizer, and semiconductor conduction band lead to an increase in photocurrent. Calculations show that the amount of photocurrent can be increased up to 1.6 volts. Shunt and serial resistance are two important factors in determining the filling factor, which is caused by the function of electron transfer in the electrodes. As mentioned, the photosensitizer has a main and important role in the structure of the DSSCs, which will be discussed further [9].

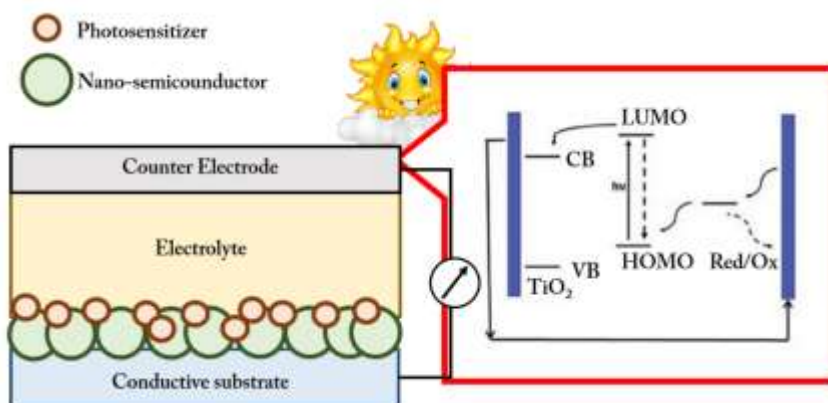


Figure 2. DSSCs and its function.

2.2. Photosensitizers

The photosensitizer (dye) in the structure of the DSSCs plays the role of producing electrons. In other words, these components absorb sunlight and convert it into electrical energy. In order for a chemical compound to be used as a sensitizer in the structure of a solar cell, it must have a number of characteristics, which include: a wide absorption range in the visible and near-infrared region, the ability to create effective bonds with semiconductors, a LUMO energy range lower than the semiconductor conduction band, the ability to receive electrons from the redox couple and high fading. Dyes used in the structure of DSSCs are divided into three categories: organometallic, organic metal-free, and natural. In this classification, organometallic dyes have the highest efficiency and technical characteristics, but the preparation process is complicated, expensive, and polluting. Organic dyes have a simpler process and high reproducibility, but on the other hand, their efficiency is lower than organometallics. Natural dyes can be obtained from various sources, such as seeds, flowers, leaves, fruits, stems, etc., and do not pollute the environment. These materials are very cheap, and widely available, and have a very simple preparation process. The most important drawback of this class is their very low yield. One of the important technologies to improve the final efficiency of the sensitizer in the solar cell is the use of quantum dots. As mentioned, organic dyes are in the middle in efficiency and ease of preparation. Many researchers have looked into this issue, and structural engineering is crucial for the efficient preparation of metal-free compounds [11, 12]. In many new technologies, such as optical compounds, sensors, and drugs, the use of naphthalimides and their derivatives has been suggested. Because naphthalimides have a cost-effective synthesis process and their optical properties can be engineered [13]. In the following, the use of naphthalimide in the preparation of highly efficient

sensitizers is described.

2.2.1. Photosensitizers based on naphthalimide

Metal-free organic compounds are one of the suitable options for use in DSSCs, which have many advantages. The strengths of these compounds are: high molar absorption coefficient, diversity in molecular structure design, many chemical structures, ease of preparation, high reproducibility, etc. [14]. One of the most important weaknesses of these compounds is the possibility of aggregation on the semiconductor surface and the lack of production and transfer of excited electrons [15]. In order to prepare a suitable photosensitizer that has minimal aggregation, chromophores and a skeleton that have high photophysical and electrochemical characteristics should be used in addition to the proper configuration. In the design of light-sensitive molecules, the electron-donating and electron-accepting groups are connected to each other with a conjugated system, which is also the main point of connection to the semiconductor surface. For each of these parts, a variety of groups and chemical structures can be used, and this choice is better to expand the conjugated system [16, 17].

1,8-Naphthalimides are one of the most effective chemical structures and skeletons in the preparation of all kinds of light-sensitive and fluorescent dyes. The most important feature of this class is their high thermal stability, high electron affinity, and oxidation stability, which has led to the development and expansion of this type of compound. Naphthalimides (Figure 3) dissolve better in water than diimine and pyridine derivatives, making them a more interesting research topic [18]. In these structures, the naphthalene ring acts as a conjugate bridge that connects electron-donating and electron-accepting

groups. Organic compounds based on naphthalimide have high thermal stability and often have good fluorescence emission power. Engineering the chemical groups at the 4-position of the naphthalimide ring can change the fluorescence intensity. The effectiveness of position 4 has also been confirmed in theoretical calculations. Therefore, naphthalimide-based structures have wide applications in molecular imaging, analytical chemistry, material chemistry, and medicine [19, 20]. In the following, an overview of the applications of naphthalimides as sensitizers in the DSSCs structure will be presented.

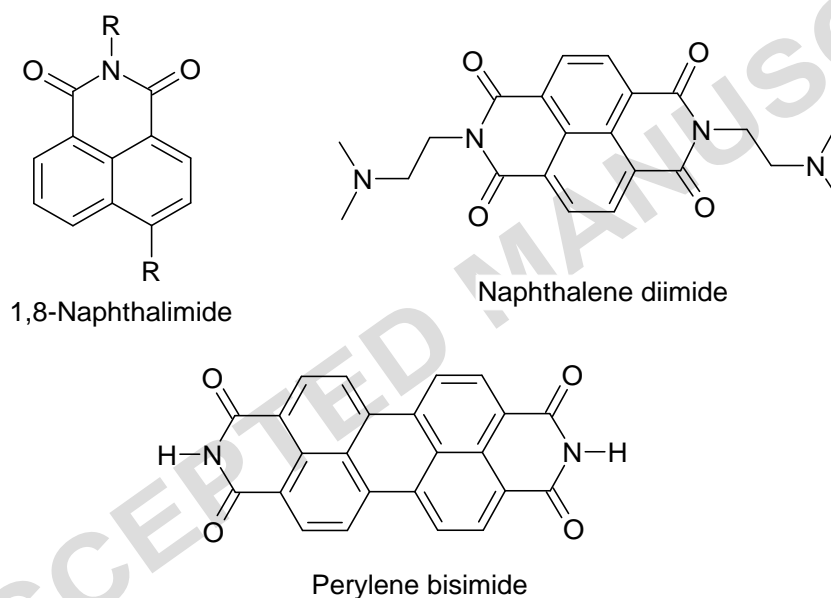


Figure 3. Naphthalimide and its derivative [18, 19].

Lin et al. prepared a naphthalimide structure containing an alkyl carboxyl chain for use in DSSCs. A carboxylic acid group was chosen to create an effective bond on the semiconductor, and finally, the prepared dye has a medium emission in the green area. The prepared dye showed 10.8 % efficiency in the DSSCs, while the efficiency doubled when combined with N719 [21]. Since indolines are great for making sensitizers, adding naphthalimides as an electron-accepting group should make this structure work better.

Saini et al. designed this approach for the preparation of light-sensitive dyes with D-A- π -A arrangements. Scientists looked at cyanoacrylic acid mixed with naphthalimide, which acts as an electron acceptor. They found that the color performance got better as the distance between these two groups got bigger. In addition, the elevation of the conjugated system causes the absorption maximum to shift to higher wavelengths and create a red hue. The highest efficiency reported in this series of compounds is around 5 % [22]. Three organic azo dyes were prepared using the naphthalimide group for use in DSSCs. In this research, the effect of different electron acceptor groups and their distance to the naphthalimide group was investigated and evaluated. The results showed that all the prepared dyes have aggregation on the semiconductor, and to prepare the DSSCs, it is necessary to use an anti-aggregation agent. The highest efficiency in the DSSCs was obtained for the dye with cyanoacrylic acid and four double bonds with the naphthalimide group, or about 4.82 % [23]. Nucleophilic and Suzuki coupling reactions were used to connect the pyrazinyl group to the nitrogen of the naphthalimide ring, and two organic dyes with intense green fluorescence were prepared. The synthesized dyes have a melting point of 300 °C and a monoclinic crystal structure. Synthesized dyes have many intermolecular interactions that cause accumulation potential in the layers. On the other hand, it has high optical and thermal stability, which makes it suitable for use in light-sensitive structures [24]. Three organic dyes (Figure 4) were prepared based on naphthalimide and using acenaphthene as the starting material. The maximum absorption of the prepared dyes was observed in the region of 427-435 nm and it was deposited on two types of semiconductors. The shift in the absorption peak revealed a slight aggregation of synthetic dyes on the semiconductors. The efficiency obtained for dyes in

the DSSCs is about 1.3 % [25].

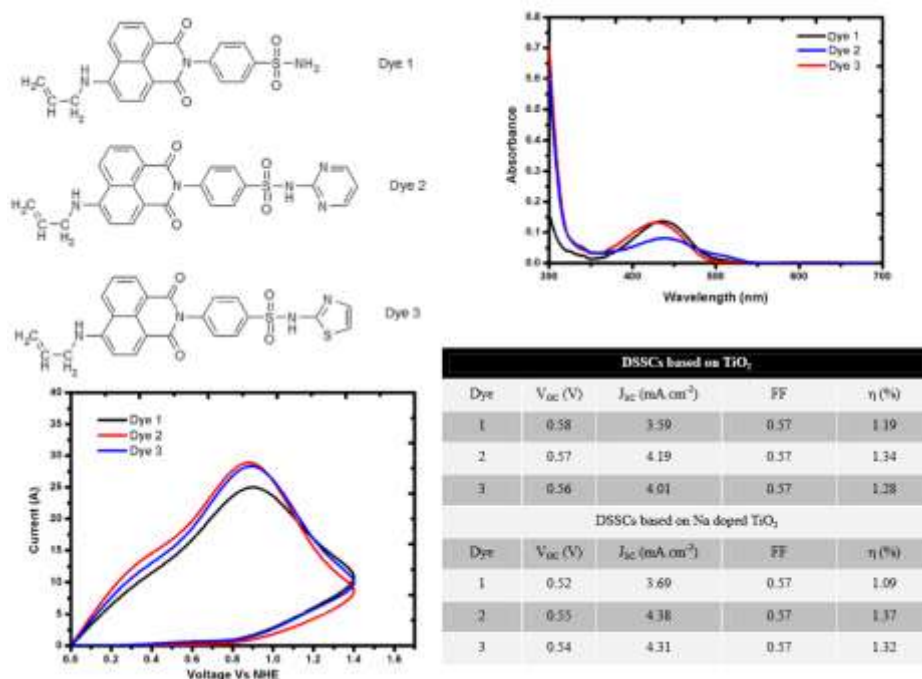


Figure 4. Chemical structure of dyes based on naphthalimide and their performance [25].

Some researchers have used computational methods to extract the optimal structure of organic dyes based on naphthalimide. In research, eight T-shaped organic dyes that had a naphthalimide conjugate bridge were investigated with DFT. Some important factors in the DSSCs, such as efficiency, light harvesting rate, electron injection current, and the return cycle of the dye to the base state, were considered effective factors in the calculations. The findings showed that the naphthalimide structure creates a structure that stops aggregation and energy levels that are good for solar cells [26]. It was looked into what happens when naphthalimide is added as an acceptor electron group to phenothiazine-based organic dyes. In these compounds, naphthalimide is placed at the 7-position of the phenothiazine ring by a triple bond. The efficiency of the DSSCs prepared using these dyes was reported at 4.9 % [27]. Recently, studies have been published on the

preparation of organometallic complexes using naphthalimide units for use in DSSCs. In particular, a heteroleptic complex was made with naphthalimide and phenanthroline as its building blocks and copper as its main metal. Studies showed that the presence of these chemical structures causes a 32 % increase in quantum efficiency and a 20 % in DSSCs conversion efficiency, and this performance improvement is due to the presence of naphthalimide groups [28]. In another study, a 4-ethynyl-naphthalimide group was selected to prepare an organometallic complex with cobalt as the central metal. The results showed that, due to the increase in the length of the conjugated system, absorption and emission are transferred to higher wavelengths. The prepared complex has a triclinic crystal structure and has two oxidation maxima in voltammetry behavior. As a result, the prepared structure can be used as a sensitizer in the solar cell structure [29].

3. OLED devices

Providing sources of energy and lighting production is important because of their widespread use in life, especially in business and advertising. Therefore, the introduction of low cost and efficient methods for the production of lighting has been considered. For example, the efficiency of ordinary lamps is 16 IM/W, fluorescent lamps are 70 IM/W, and LED lamps are 300 IM/W. As a result, LED technology replaced older energy sources. A more recent approach is to use a light-emitting organic compound (without or with doping), which is known as OLED (organic light-emitting diodes) [30]. Recently, the issue of OLED has received attention in industry and academia due to the widespread use of this technology in smartphone screens, TV screens, and lighting production panels. This technology has many advantages over liquid crystal displays and has been

significantly developed in the display industry. The advantages of this technology include: no need for background light; low thickness and weight; high contrast; high response time; high resolution; and the possibility of preparing flexible samples [31]. OLED is prepared in multi-layers, and these layers are placed on top of each other successively with different methods. Conventional methods for this purpose are: plasma with evaporation, spin coating, and thermal evaporation with vacuum. The simplest device is made of three layers, including the radiating layer and two electrodes. This device has low efficiency due to the large hole-electron gap. This problem can be solved by using a multi-layered system with organic materials with charge transfer properties. These compounds are used as electron-hole regions (Figure 5) [30].

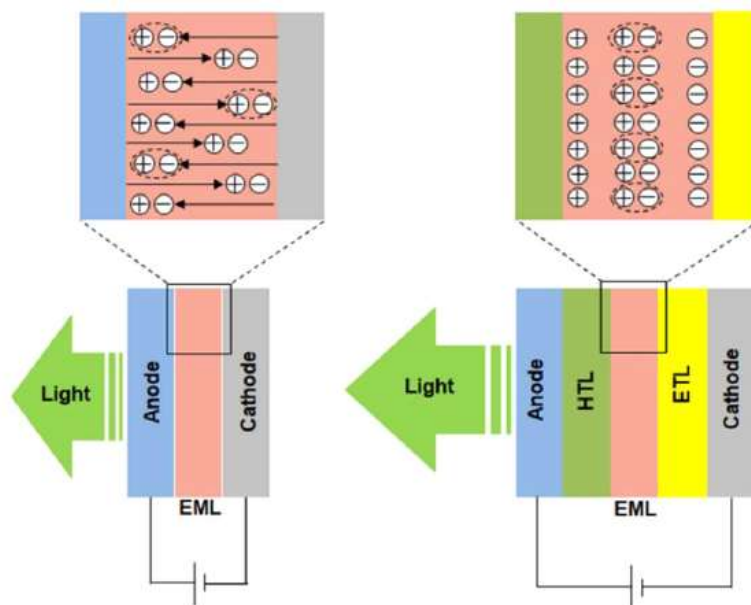


Figure 5. OLED configuration [30] Left: monolayer configuration, and right: multi-layer configuration (reprinted with permission from [30]. Copyright 2020; Elsevier publishing due to open access).

Applying an external voltage between two electrodes produces holes in the anode and electrons in the cathode. Holes move towards the highest occupied molecular orbital (HOMO), and electrons move towards the lowest unoccupied molecular orbital (LUMO). Electrons and holes produced in the recombination region come close to each other, and due to Coulomb interactions, excitons are produced. According to exciton statistics, electrons and holes can form four different exciton states, one singlet and three triplets, in a ratio of 1:3. According to the orbital conservation law, the spins remain unchanged until the molecularly excited levels are filled. Singlet and triplet excitons fill the singlet and triplet molecular levels, respectively. According to statistics, 75 % of molecules are in the T₁ state and 25% in the S₁ state. The rapid decay from S₁ to S₀ (ground state) causes fluorescence at a high rate compared to forbidden processes (intersystem crossings). Therefore, the use of fluorescent compounds in OLED causes the non-radiative decay of all triplet excitons and the quantum efficiency is limited to a maximum of 25 % (Figure 6) [30, 31].

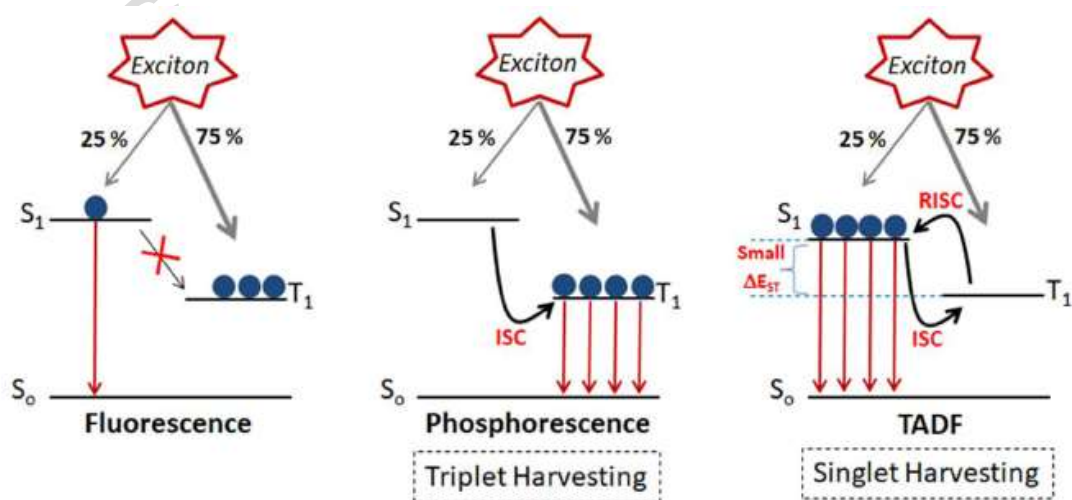


Figure 6. Emission mechanism in OLEDs [30]; (Reprinted with permission from [30]).

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The preparation of new compounds with the possibility of phosphorylating is the subject of much research in the field of materials used in OLED. For this purpose, increasing the spin-orbit coupling (SOC) is used. Theoretically, such devices are able to provide 100% efficiency. Organometallic complexes have such properties, and compounds based on Ir (III) and Pt (II) are known as the most efficient green and red emitters. But blue emitters can hardly be produced by this method, and for this purpose, the first-generation method with low efficiency must be used [30]. A lot of research is being done to improve the performance and efficiency of fluorescent devices in industry and universities. Areas such as the preparation of blue and red luminescent materials need more attention and research. Research published in this field in the years 2000-2020 is shown in Figure 7, which shows that the progress of water technology requires unique materials and products [31].

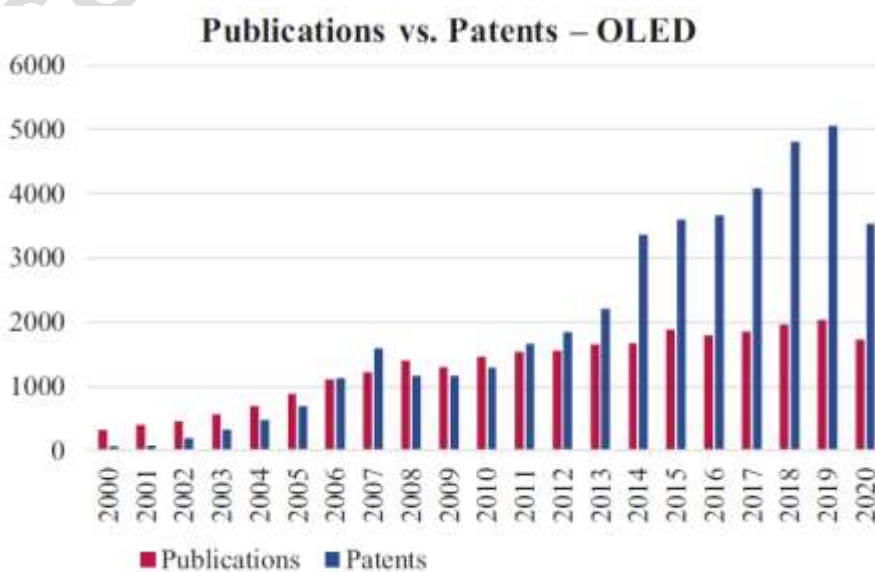


Figure 7. The number of articles and patents published in the field of water [31]; (reprinted with permission from [31]. Copyright 2021; Wiley Publishing due to open access).

3.1. Emitters for application in OLEDs

Much research has been done to prepare highly efficient phosphors to be used as emitters in OLED devices. One approach to classifying these compounds is based on their chemical structure, which includes: small molecules, dendritic, and polymeric phosphorescent emitter. Small molecule phosphors are proposed as dopant emitters due to their good solubility in processing solvents such as toluene, chlorobenzene, and tetrahydrofuran (THF). To get around interactions within and between molecules, twisted and non-planar structures are often suggested to make sure high phosphorescence efficiency. In some cases, the low solubility of these compounds limits the performance of electroluminescence. On the other hand, heterogeneous morphology causes phase separation between the host matrix and the radiating component. To overcome the dissolution limitation, it is possible to substitute aliphatic chains in molecules. One way to make it easier to dissolve is to add an alkoxy group to the para-nitrogen position of the difluorophenylpyridine group. Many small-molecule complexes with Ir, Au, and Pt as central metals have been developed for fluorescence in the green-red region. In addition, iridium-based complexes have the ability to provide orange phosphorescence, but their electroluminescence efficiency is relatively low. The prepared complexes, with platinum central metal and carbazole ligands or functionalized acetylides, show red fluorescence in the green region with high intensity. Recently, the effect of CN groups on the

fluorescence of platinum complexes was evaluated, and the results showed that these compounds have high fluorescence efficiency in the yellow and green regions [32].

There are metal complexes with dendritic networks that are often used as dendritic phosphorescence materials. By changing the dendron metal, these materials can improve the light emission. Biphenyl dendrons on the iridium metal core, which have an anchoring position, have a high fluorescence efficiency. The prepared film with these compounds has a higher efficiency than the fluorescence compound solution. Triphenylaminatedendrons with iridium as the central metal have a red emission and a quantum efficiency of 11.7%. The use of triarylamines can increase the intensity of fluorescence. A class of fluorescent dendrimers was prepared using iridium and conjugated carbazoles to provide green fluorescence with an efficiency of about 10 %. In addition to the preparation of new fluorescent materials, the way they are used also affects their performance and final yield. For example, encapsulation of dendritic materials (especially in the presence of iridium metal) it reduces the possibility of fluorescence quenching due to unwanted aggregations, and on the other hand, it increases the ease of making successive layers in the presence of various solvents. On the other hand, these compounds are able to provide fluorescence with a specific color, which is obtained through the combination of several dendritic fluorescence materials with different emissions. In addition, by carefully adjusting the dendron, unwanted impurities can be eliminated [32, 33].

Some polymers that have an organometallic complex have been prepared as emitters. There are different arrangements for preparing these compounds, including: a conjugated system with a repeating complex unit, an unconjugated system with a repeating complex

unit, and an organic polymer attached to a metal complex. A vinyl-type polynorbornene copolymer containing iridium and biphenyl complexes as side groups was prepared, which had a red emission with a yield of 5.1%. A similar structure was prepared in the presence of conjugated polycarbazole, which showed intense green emission with a yield of 9.6 % [34]. The advantages of polymer light-emitting materials are: low production cost, homogeneous emission, no phase separation, and very high spectral stability. Studies show that molecular design has a direct effect on emission efficiency, and thermal and photophysical properties. Issues that are effective in the design and synthesis of light-emitting polymers are: appropriate host compositions, an appropriate energy gap between the HOMO and LUMO layers; and charge current balance.

In luminescent polymers, it is important to control the interactions between and within molecules so that steric effects don't cause interactions that stop the emission. Studies show that iridium has the best performance in the preparation of light-emitting polymers, and its emission efficiency is higher compared to other central metals with the same structure [35].

3.2. Naphthalimide in OLEDs

Naphthalimides have a planar conjugated system that has unique optical, electrochemical, and photoelectric properties. Naphthalimides are very suitable for preparing light-emitting compounds, which are used in light-emitting sensors, ion probes, and optical and electrical devices. Naphthalimide-based organic molecules have an electron-deficient nucleus that has carbonyl groups. This arrangement can cause a low reduction potential and a high energy gap, so it is excellent for preparing N-type organic semiconductors.

These compounds are very efficient illuminants that have very good efficiency. This good performance is due to the high chemical and optical stability, the possibility of setting the value of the emission range, and the ability to form a film. The electronic properties of naphthalimide-based luminescent materials have a direct effect on the color emitted in OLED devices. The nature and placement of substituents on the naphthalimide core have a direct effect on chemical and physical behaviors and sensitivity to light and electricity. All kinds of amines are suggested for the reaction and preparation of emitter naphthalimide derivatives. These groups can be placed on the nitrogen ring or in the free positions of the aromatic ring. Another effective strategy is to increase the conjugated system. The positions 3 and 4 of the naphthalimide ring are very suitable for replacing halogen, nitro, and amino groups. The addition of amino and alkoxy substituents as electron-donating groups in positions 3, 4, 5 or 6 of the aromatic ring can improve the emission efficiency due to the creation of an excited surface of polar charge. Placing the right substituents in good places can control and engineer the emission range from blue to green or yellow. The emission range will be red-shifted if aromatic groups are attached to the nitrogen of the naphthalimide unit. The electron mobility and affinity of naphthalimide derivatives are about 3.1 and 0.16 eV, respectively. This makes them perfect for making stable materials that give off a lot of light. The image of naphthalimides with different illumination is shown in Figure 8 [36]. In the following, an overview of the applications of naphthalimides as sensitizers in the OLED structure will be presented.

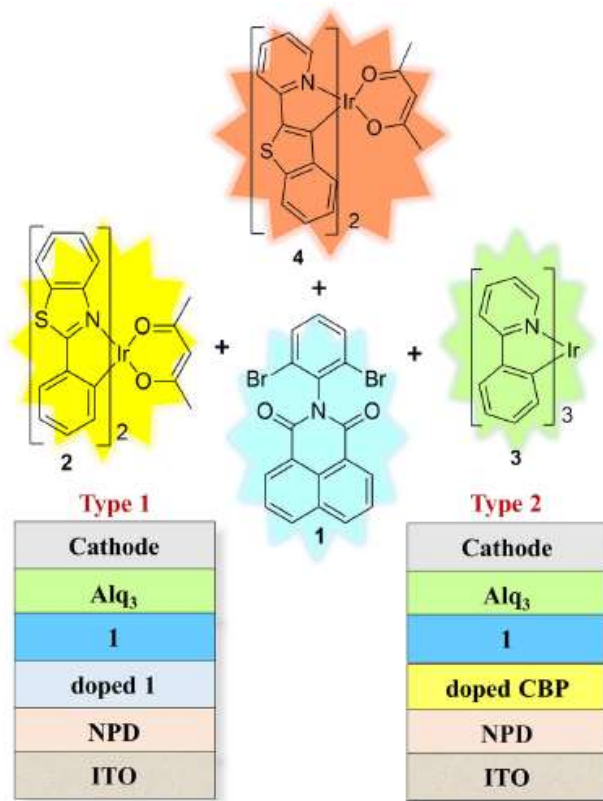


Figure 8. Schematic illustration of naphthalimides as emitter in OLED [36]; (Reprinted with permission from [36]. Copyright 2022; Springer Publishing due to open access).

The naphthalimide ring was made brighter by adding carbazole to positions 2 and 9 of the naphthalimide ring (through a click reaction) and then polymerizing it. The results showed that the oxidation and reaction of the substituted compound in position 2 are easier than in position 9. This difference is due to the participation of oxygen and nitrogen electrons in the conjugated structure in substitution at position 2 [37]. An organic dye was synthesized based on naphthalimide with a D- π -A configuration. CV studies showed that the transfer process involves a single electron. The effect of the solvent on the synthesized compounds was investigated, and the results showed that with an increase in the polarity of the solvent, the red hue created is due to the stabilization of

the more polar state in the presence of polar solvents. These compounds have intramolecular rotations and show stronger diffusion in polar solvents or their mixtures. If you add an extra phenyl group to the chromophore, it has better optical properties because it makes the electron flow process easier [38]. We made 12 kinds of light-emitting molecules (Figure 9) by putting phenoxy groups with aldehyde and nitrile in the fourth position of the naphthalimide ring. These dyes were prepared from acenaphthene as a raw material using reactions such as bromination, imidation, and oxidation. These compounds are stable up to 260–280 °C and have a band gap in the 2.83–3.02 eV range with deep blue fluorescence. The highest quantum efficiency reported for these materials is about 1.4 % [36].

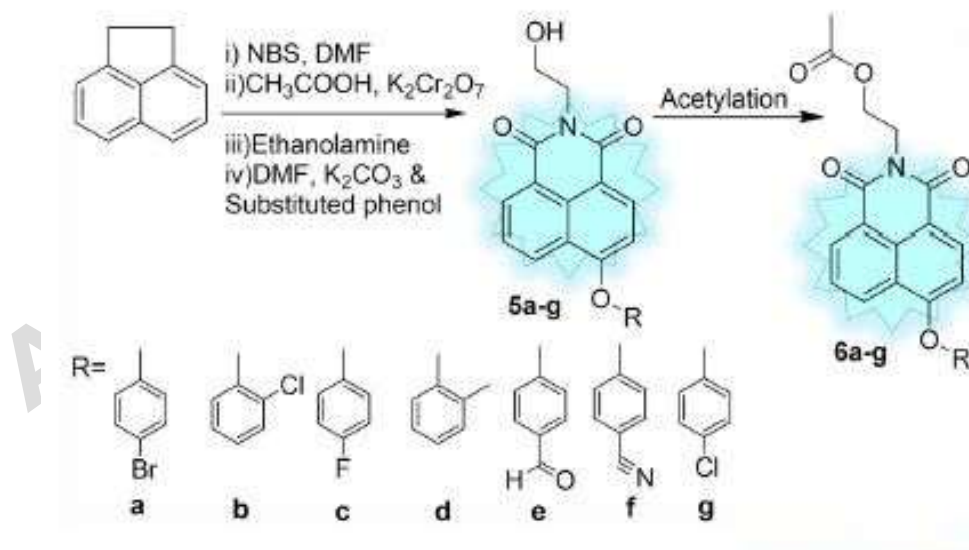


Figure 9. Fluorescence chromophores based on naphthalimide with blue emission[36]; (Reprinted with permission from [36]. Copyright 2022; Springer Publishing due to open access).

In a new approach, benzo and naphthodioxane are fused together and added to the naphthalimide structure. For the preparation of these compounds, the most important reaction is bromination, which places three different bromines in the naphthalimide core. The prepared dyes were stable up to 400 degrees and showed a green emission in the OLED structure and a yield of 6.9% [39]. In another study, the effect of the presence of imine and beta-ketoanamine units at the 3-position of the naphthalimide nucleus was investigated. The effect of substitution group, bond type, and substitution site in naphthalene ring on thermal, electrochemical, optical and electrical properties was investigated. The results showed that imines are more prone to hydrolysis and ketoanamine has unwanted accumulations in the excited state. Therefore, based on the conditions and the final application, the type of substitution chosen is different [40, 41]. A chiral molecule based on naphthalimide with red emission and high thermal stability (405 °C) was prepared. The synthesized compounds have a strong red emission in the region of 592 nm, and a quantum efficiency of 12.4 % and show high electrochemical properties [42]. The presence of an imine substituent in the conjugated system, which connects the phenyl group to the naphthalimide body, provides a wide range of emitting hues. Gan et al. prepared two series of naphthalimides with hydrazone substituents (Figure 10). By adding different amino acids to these compounds, the conjugated system grew, which caused the emission wavelength to shift by a bathochromic amount. These compounds did not show quenching effects with red emission at any concentration. Studies showed that the use of the CN group increased the life of fluorescence. Naphthalimides have different hues, from white to water (Table 1). Molecular engineering and the placement of suitable substitutions are two methods for achieving

this diversity [36].

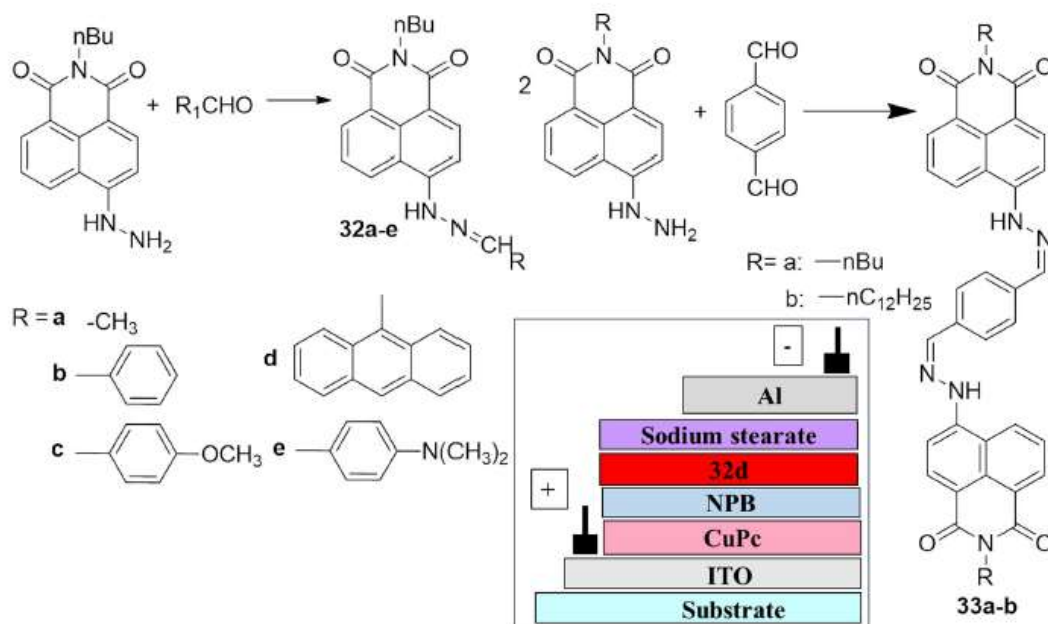
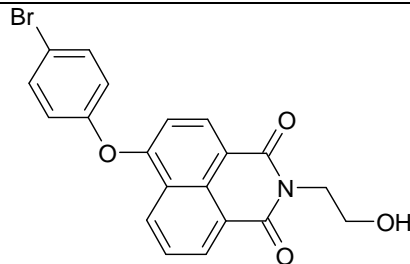
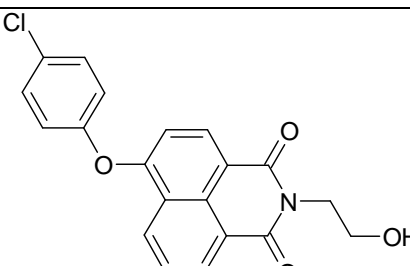
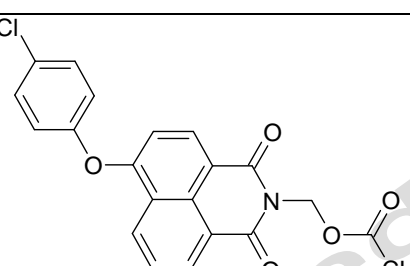
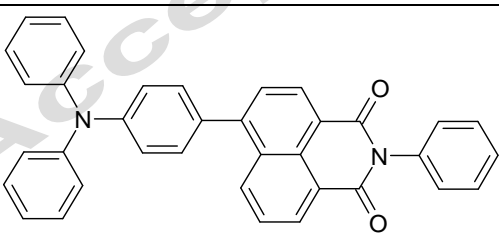
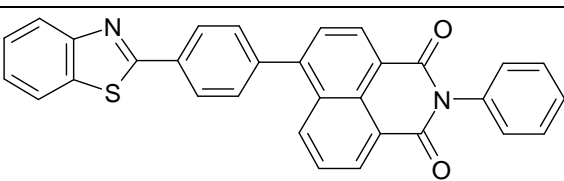
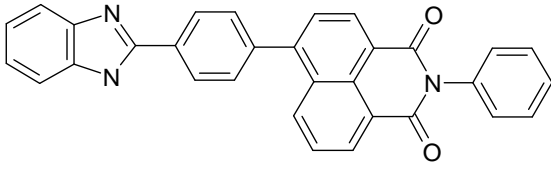
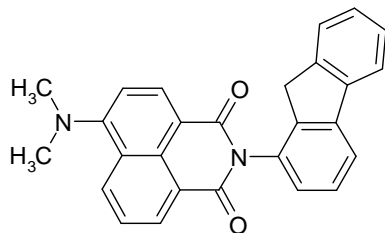
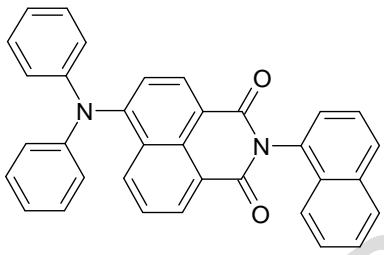
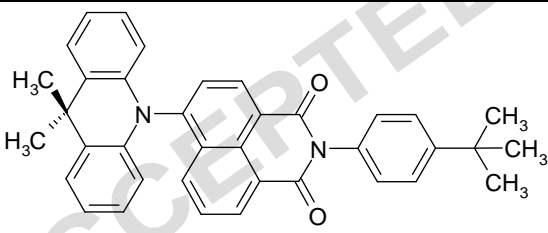
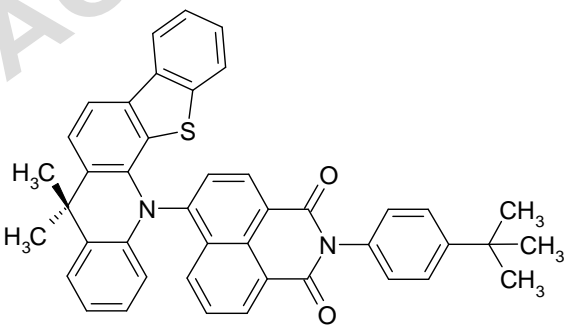


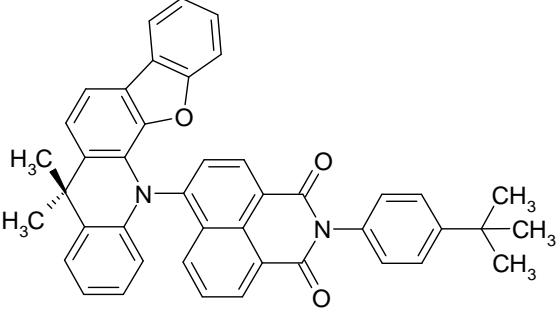
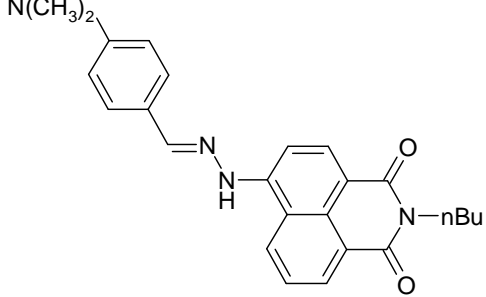
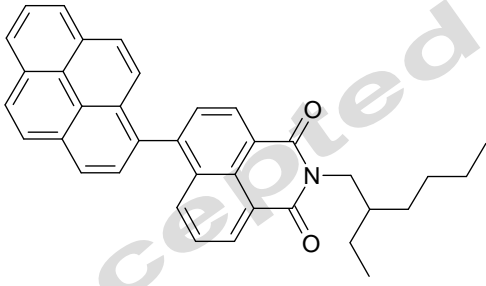
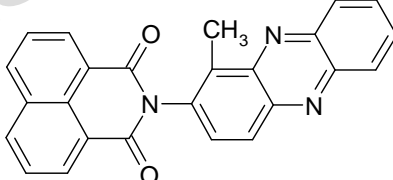
Figure 10. Naphthalimide compounds with red emission [36]; (Reprinted with permission from [36]. Copyright 2022; Springer Publishing due to open access).

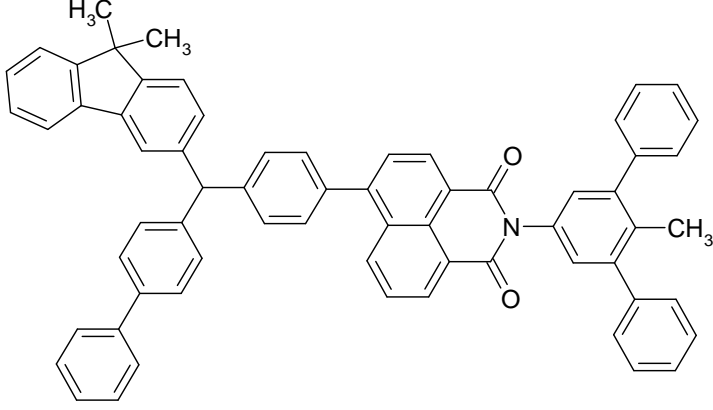
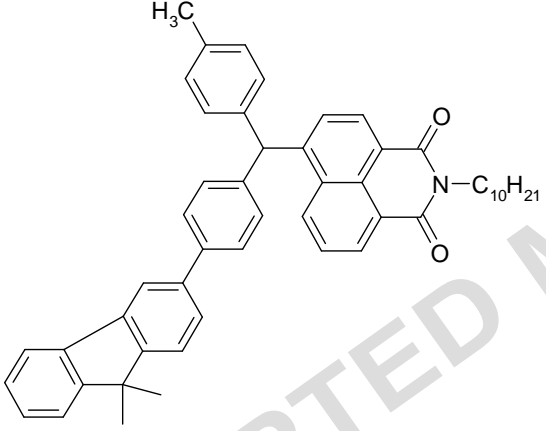
Table 1. Luminescent naphthalimides for use in OLED structure [36]; (Reprinted with permission from [36]. Copyright 2022; Springer Publishing due to open access).

Molecular Structure	$\lambda_{\text{emission}}$ (nm)	Turn-on Volt (V)	η_{EQE} (%)
Blue emitters			
	482	3	3.2

	487	7.7	0.42
	516	8.25	0.28
	516	6.92	0.47
Green emitters			
	530	5.8	1.11
	556	10	0.2

	544	7	0.22
	530	6	0.26
Orange emitters			
	562	-	0.91
	597	3	4.59
	641	4	9.2

	590	3	20.3
Red emitters			
	620	14	3.59
	657	3.7	7.0
	576	3.5	1.8

	583	2.9	7.59
White emitters			
	-	3.4	0.3

4. Conclusion

Population growth and technological development have caused a growing need for energy and lighting. A lot of research is being done in these two areas to provide new and low-risk resources. Dyes are one of the main components in the development of photovoltaic and electrical technologies. DSSCs and OLED technology are two new fields for affordable and available energy and lighting. In both of these technologies, dyes play a vital role, which produce electricity in the first (DSSCs) and light in the second (OLED). Because of its planar geometry and long conjugated system, naphthalimide is one of the most important skeletons in the preparation of materials that are sensitive to

light and electricity. Regarding this structure, it is possible to put all kinds of substitutions and electron-donating or electron-withdrawing molecular groups together to obtain the desired hue or emission. The compounds prepared with a naphthalimide core have absorption in the visible region and have yellow to violet colors. In addition, these compounds, with appropriate molecular engineering, can emit all kinds of hues, even white. The emission intensity is enhanced by increasing the length of the conjugated system and using electron donor and electron acceptor groups. Naphthalimide core can be a suitable option for preparing monomers, and as a result, luminous polymers. One of the most efficient structures in this regard is D- π -A, where the naphthalimide part plays a role as a conjugate bridge or an electron acceptor part. However, the search for the preparation of new functional materials with high efficiency and the introduction of suitable substitutes is ongoing.

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5. References

- [1]. Wang Q, Wang L, Li R. Does renewable energy help increase life expectancy? Insight from the linking renewable energy, economic growth, and life expectancy in 121 countries. *Energy Strategy Rev.* 2023; 50: 101185. <https://doi.org/10.1016/j.esr.2023.101185>.
- [2]. Huang X, Srikrishnan V, Lamontagne J, Keller K, Peng W. Effects of global climate

mitigation on regional air quality and health. *Nat Sustain.* 2023;6: 1054-1066.

<https://doi.org/10.1038/s41893-023-01133-5>.

[3] SasseJP, Trutnevte E. A low-carbon electricity sector in Europe risks sustaining regional inequalities in benefits and vulnerabilities. *NatCommun.* 2023; 14:2205.<https://doi.org/10.1038/s41467-023-37946-3>.

[4]. Ravaro LR, Zanoni KPS, Camargo ASS. Luminescent Copper(I) complexes as promising materials for the next generation of energy-saving OLED devices. *Energy Rep.* 2020; 6(4): 37-45. <https://doi.org/10.1016/j.egyr.2019.10.044>.

[5]. Sharma A, Masoumi S, Gedefew D, Oshaughnessy S, Baran D, Pakdel A. Flexible solar and thermal energy conversion devices: Organic photovoltaics (OPVs), organic thermoelectric generators (OTEGs) and hybrid PV-TEG systems. *Appl. Mater. Today.* 2022; 29: 101614. <https://doi.org/10.1016/j.apmt.2022.101614>.

[6]. Arias AC, MacKenzieJD, McCulloch I, RivnayJ, Salleo A. Materials and applications for large area electronics: solution-based approaches. *Chem Rev.* 2010; 110: 3-24. <https://doi.org/10.1021/cr900150b>.

[7]. Mahdavi A, Farhadi M, Gorji-Bandpy M, Mahmoudi A. A review of passive cooling of photovoltaic devices. *Clean Eng Technol.* 2022; 11: 100579. <https://doi.org/10.1016/j.clet.2022.100579>.

[8]. Kouhestanian E, Ranjbar M, Mozaffari SA, Salaramoli H. Investigating the effects of thickness on the performance of ZnO-based DSSC. *Prog Color Colorant Coat.* 2021; 14(2): 101-112.<https://doi.org/10.30509/pccc.2021.81685>.

[9]. Kusumawati Y, Hutama AS, Wellia DV, Subagyo R. Natural resources for dye-sensitized solar cells. *Heliyon.* 2021; 7: e08436.

- [10]. Hosseinnezhad M, Gharanjig K, Ghahari M, Nasiri S. Investigation of photo-electrode and counter electrode effect on DSSCs based on indolinedyes. *Prog Color Colorant Coat.* 2024; 17(2): 121-132.
- [11]. Shah N, Shah AA, Leung PK, Khan S, Sun K, Zhu X, Liu Q. A review of third generation solar cells. *Processes.* 2023; 11: 1852. <https://doi.org/10.3390/pr11061852>
- [12]. Hosseinnezhad M, Gharanjig K, KhodadadiYazdi M, Zarrintaj P, Moradian S, Saeb MR, Stadler FJ. Dye-sensitized solar cells based on natural photosensitizers: A green view from Iran. *J Alloy Compound.* 2020; 828: 154329. <https://doi.org/10.1016/j.jallcom.2020.154329>.
- [13]. Gopala L, Cha Y, Lee MH. Versatile naphthalimides: Their optical and biological behavior and applications from sensing to therapeutic purposes. *Dye Pigm.* 2022; 201: 110195. <https://doi.org/10.1016/j.dyepig.2022.110195>
- [14]. Hosseinnezhad M, Ranjbar Z. A review on flexible dye-sensitized solar cells as new sustainable energy resources. *Pigm Resin Technol.* 2023; 52(3): 310-320. <https://doi.org/10.1108/PRT-01-2022-0010>
- [15]. Basheer B, Mathew D, George BK, Nair CPR. An overview on the spectrum of sensitizers: The heart of dye sensitized solar cells. *Sol Energy.* 2014; 108: 479-507. <https://doi.org/10.1016/j.solener.2014.08.002>.
- [16]. Hosseinnezhad M, Ghahari M, Mobarhan G, Rouhani S, Fathi M. Towards low cost and green photovoltaic devices: Using natural photosensitizers and MoS₂/Graphene oxide composite counter electrodes. *Opt Mater.* 2023; 139: 113775. <https://doi.org/10.1016/j.optmat.2023.113775>
- [17]. Zhang F, Luo Y, Song J, Guo X, Liu Wei-li M, Chun-ping H, Yong G, Mao-fa B,

Zhishan M, Qing B. Triphenylamine-based dyes for dye-sensitized solar cells. *Dyes Pigm.* 2009; 81: 224.

[18]. Dong HQ, Wei TB, Ma XQ, Yang QY, Zhang YF, Sun YJ, Shi BB, Yao H. 1,8-Naphthalimide-based fluorescent chemosensors: recent advances and perspectives. *J Mater Chem C.* 2020; 8: 13501-13529. <https://doi.org/10.1039/D0TC03681A>

[19]. Han DM, Song HS, Han Ch, Kim YS. Enhancement of the outdoor stability of dye-sensitized solar cells by a spectrum conversion layer with 1,8-naphthalimide derivatives. *RSC Adv.* 2015; 5: 32588-32593. <https://doi.org/10.1039/C5RA03908H>

[20]. Gauas PP, Pandurangan P, Rabiei M, Palevicius A, Vilkauskas A, Janusas G, Hosseinnzhad M, Ebrahimi-Kahrizsangi R, Nasiri S, Nunzi JM, Nutalapati V. Significance of Zn complex concentration on microstructure evolution and corrosion behavior of Al/WS₂. *Molecules.* 2023; 28: 7290. <https://doi.org/10.3390/molecules28217290>

[21]. Lin YJ, Chen JW, Hsiao PT, Tung YL, Chang C, Chen C. Efficiency improvement of dye-sensitized solar cells by in situ fluorescence resonance energy transfer. *J Mater Chem A.* 2017; 5: 9081-9089. <https://doi.org/10.1039/C7TA00638A>

[22]. Saini A, Thomas KR, Huang YJ, Ho KC. Synthesis and characterization of naphthalimide-based dyes for dye sensitized solar cells. *J Mater Sci: Mater Electron.* 2018; 29: 16565-16580. <https://doi.org/10.1007/s10854-018-9750-4>

[23]. Hosseinnzhad M, Shaki H. Investigation of photovoltaic properties of dye-sensitized solar cells based on azo dyes contain various anchoring groups. *Pigm Resin Technol.* 2019; 48(6): 481-486. <https://doi.org/10.1108/PRT-04-2019-0033>

[24]. Ren B, Yang Y, Qu Y, Cao J, Wu Y. Two fluorophore compounds based on 1, 8-

naphthalimide: Synthesis, crystal structure, and optical properties. *J MolStruct.* 2019; 1193(5): 131-140. <https://doi.org/10.1016/j.molstruc.2019.04.130>

[25]. Hosseinneshad M, Ghahari M, Shaki H, Movahedi J. Investigation of DSSCs performance: the effect of 1,8-naphthalimide dyes and Na-doped TiO₂. *Prog. Color Colrant Coat.* 2020; 13(3): 177-185. <https://doi.org/10.30509/pccc.2020.81625>

[26]. Xu Z, Li Y, Li Y, Yuan S, Hao L, Gao S, Lu X. Theoretical study of T shaped phenothiazine/carbazole based organic dyes with naphthalimide as π -spacer for DSSCs. *SpectrochimActa Part A MolBiomolSpect.* 2020; 233: 118201. <https://doi.org/10.1016/j.saa.2020.118201>

[27]. Nagarajan B, Anthrey CD, Elumalai R, ChS, Raghavachari D. Naphthalimide-phenothiazine based A'- π -D- π -A featured organic dyes for dye sensitized solar cell applications. *J PhotochemPhotobiolA Chem.* 404(1): 112820. <https://doi.org/10.1016/j.jphotochem.2020.112820>

[28]. Yang Y, Doettinger F, Kleeberg C, Frey W, Karnabl M, Tschierlei S. How the way a naphthalimide unit is implemented affects the photophysical and -catalytic properties of Cu(I) photosensitizers. *Front Chem.* 2022; 10: 1-12. <https://doi.org/10.3389/fchem.2022.936863>

[29]. Misra R M, Bijesh S, Maragani R, Reddy TS, Mobin S. Synthesis of Cpc(Dithiolene)-naphthalimide and their electronic properties. Available at SSRN: <http://dx.doi.org/10.2139/ssrn.4580609>.

[30]. Ravaro LP, Zanoni KPS, De Camargo ASS. Luminescent Copper(I) complexes as promising materials for the next generation of energy-saving OLED devices. *Energy Reports.* 2020; 6(4): 37-45. <https://doi.org/10.1016/j.egyr.2019.10.044>.

- [31]. Hong G, Gan X, Leonhardt C, Zhang Z, Seibert J, Bush JM, Brase S. A brief history of OLEDs-emitter development and industry milestones. *Ad Mater.* 2021; 3: 2005630. <https://doi.org/10.1002/adma.202005630>.
- [32]. Wang S, Zhang H, Zhang B, Xie Z, Wong W. Towards high-power-efficiency solution-processed OLEDs: Material and device perspectives. *Mater SciEng R.* 2020; 140: 100547. <https://doi.org/10.1016/j.mser.2020.100547>.
- [33]. Hosseinnzhad M, Ghahari M, Mobarhan G, Fathi M, Palevicius A, Nutalapati V, Jausas G, Nasiri S. New insights into improving the photovoltaic performance of dye-sensitized solar cells by removing platinum from the counter electrode using a graphene-MoS₂ composite or hybrid. *Micromachines,* 2023; 14: 2161. <https://doi.org/10.3390/mi14122161>.
- [34]. Jiang J, Lee JY. Degradation mechanisms and lifetime extending strategy of phosphorescent and thermally activated delayed-fluorescence organic light-emitting diodes. *Materialstodays.* 2023; 68:204-233. <https://doi.org/10.1016/j.mattod.2023.06.016>
- [35]. Xu F, Kim HU, Kim JH, Jung BJ, Grimsdale A, Hwang DH. Progress and perspective of iridium-containing phosphorescent polymers for light-emitting diodes. *ProgPolym Sci.* 2015; 47: 92-121.
- [36]. Kagatkar S, Sunil S. A systematic review on 1,8-naphthalimide derivatives as emissive materials in organic light-emitting diodes. *J Mater Sci.* 2022; 57: 105-139. <https://doi.org/10.1007/s10853-021-06602-w>
- [37]. Coban F, Ayranu R, Ak M. Naphthalimide clicked polycarbazoles: Synthesis, characterization, and investigation of their optical, electrochemical and spectroelectrochemical properties. *Synth Metal.* 2022; 285: 117031.

<https://doi.org/10.1016/j.synthmet.2022.117031>

[38]. Subiksha VS, Viswanathan T, David E, Prabu S, Palanisami N. Ferrocene appended 1,8-naphthalimide chromophores: Synthesis, theoretical, the effect of phenyl substitution on aggregation-induced enhanced emission and second-order nonlinear optical studies. *Spectrochim Acta Part A Mol Biomol Spect.* 2022; 277(5): 121282.

<https://doi.org/10.1016/j.saa.2022.121282>

[39]. Zagranjarski Y, Mutovska M, Petrova P, Tomova R, Ivanov P, Syoyannov S. Dioxin-annulated 1,8-naphthalimides – Synthesis, spectral and electrochemical properties, and application in OLED. *Dye Pigm.* 2021; 184: 108585.

<https://doi.org/10.1016/j.dyepig.2020.108585>

[40]. Korzec M, Kotowicz S, Gawecki R, Malarz K, Mrozek-Wilczkiewicz A, Siwy M, Schab-Balcerzak E, Grzelak J, Mackowski S. 1,8-Naphthalimides 3-substituted with imine or β -ketoenamine unit evaluated as compounds for organic electronics and cell imaging. *Dye Pigm.* 2021; 193: 109508. <https://doi.org/10.1016/j.dyepig.2021.109508>

[41]. Nasiri S, Rabiei M, Shaki H, Hosseinneshad M, Kalyani K, Palevicius A, Vilkauskas A, Janusas G, Nutalapati V, Kment S, Nunzi JM. What is TADF (thermally activated delayed fluorescence) compared to the mechanisms of FL (fluorescence), PH (phosphorescence), and TTA (triplet-triplet annihilation) based on a novel naphthalimide sulfonylphenyl derivative as a host?. *J Photochem Photobiol A: Chem.* 2024; 447: 115289. <https://doi.org/10.1016/j.jphotochem.2023.115289>

[42]. Wang YF, Lu HY, Chen C, Li M, Chen CF. 1,8-Naphthalimide-based circularly polarized TADF enantiomers as the emitters for efficient orange-red OLEDs. *Org Electron.* 2019; 70: 71-77. <https://doi.org/10.1016/j.orgel.2019.03.020>.