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Advances in phosphors based on organic materials for light emitting devices

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ABSTRACT

A brief overview is presented in the light emitting diodes (LEDs) based on purely organic materials. Organic LEDs are of great interest to the research community because of their outstanding properties and flexibility. Comparison between devices made using different organic materials and their derivatives with respect to synthetic protocols, characterizations, quantum efficiencies, sensitivity, specificity and their applications in various fields have been discussed. This review also discusses the essential requirement and scientific issues that arise in synthesizing cost-effective and environmental friendly organic LEDs diodes based on purely organic materials. This mini review aims to capture and convey some of the key current developments in phosphors formed by purely organic materials and highlights some possible future applications. Hence, this study comes up with a widespread discussion on the various contents in a single platform. Also, it offers avenues for new researchers for futuristic development in the area.

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1. Introduction

In the past several years, substantial development has been made in the fabrication of electroluminescent polymers and organic materials for the use of light-emitting diodes (LEDs) [1–14]. The research interests in this direction were inspired by the prospective uses of these materials in the optoelectronics industries. The potential benefits of purely organic materials based LEDs with respect to rare earth doped inorganic materials includes ease of synthesis, affordable, lightweight and hold a productive domain and versatility. These key points stimulated their applications in solid-state lighting but other disciplines of science and technology as well. So far, large numbers of review articles have been published which reflects the interest of educational and automated research in purely organic materials based phosphors and their uses in LEDs [1–14].

1.1. At a glance: scientific interest in conducting polymers

Polymers are considered as bad conductor of electricity or insulator. Irrespective of their outstanding physical and chemical characteristics, their uses in the electronics industry is still very limited. In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa discovered the chemical and physical properties of conjugated polymers (CPs). They awarded the Nobel Prize in Chemistry in 2000 for their discoveries in the field of CPs [15]. CPs is kind of polymer with the spatially extended π-bonding system, which forms the delocalized charge carrier. By monitoring the extent of doping, the polymers can be transformed from a semiconductor to a metal or stabilized at any intermediate state. The cutting-edge technologies are being established every day; there is a continual requirement for innovative materials with exceptional properties for use in a variety of fields. Currently, remarkable research efforts have been generated in the area of CPs due to their potential for the new generation of display technology [15,16]. Moreover, their synthetic methods, structure, and physical and chemical properties have been studied extensively in the past few decades [15]. The effect of aryl groups on PL efficiency and redox behavior of thiophene-based conducting polymers has been investigated [17]. It was concluded that the PL properties are not only depending upon to the substituents on the thiophene ring but also to the aromatic groups attached to the polymer chains. The literature review showed that extremely insightful review article on recent advancements in purely organic materials for light emitting devices has been recently reviewed [15].

1.2. Electroluminescence in organic materials

The first breakthrough in the generation of light by the electric excitation has been observed by Pope et al. [18] in anthracene crystals doped with 0.1 mol% tetracene. The operating voltage required to

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produce electroluminescence (EL) was of several hundred volts. Afterwards, EL in pure and doped anthracene crystals was reported by various researchers [19–21]. A very low emission intensity and efficiency was observed by different investigators in organic crystals of tetracene [22], naphthalene [23], pyrene [24], octaethylporphin [25], and p-terphenyl [26]. Regardless of the high quantum efficiency of these materials, no promising device has been invented due to the large number of shortcomings including high voltage, large crystal thickness and poor electrical contact [10]. Apart from this, fundamental physical processes involved in EL such as charge injection, charge transportation, exciton formation and light emission, etc. have not been thoroughly understood [10]. In most of the organic materials, the electrons are highly bonded to each other and, as a result, the probability of emission from triplet states is very less [27].

The most exciting development was achieved in 1987 by Tang and Van Slyke [28] when they fabricated an LED based on organic materials. They have observed electroluminescent emission efficiency, fast response, low voltage drive, and simplicity of fabrication. This discovery is considered as the real start of organic electronics and organic light emitting diode (OLED) based on polymeric materials. In the polymer filed, the LEDs of thin film poly(p-phenylene vinylene) (PVP) was first reported by Burroughs et al. [29] in 1990. They have synthesized PVP films by using a solution processable precursor via spin coating method. PVP has many advantages including ease of synthesis, excellent structural properties and emits light in the green-yellows area of the spectrum with a practically high performance of order 0.005% and lasted only a few minutes. The results indicate that the synthesized PVP films can be employed for the fabrication of large-area light-emitting displays applications. The EL of the polymer (PVK) had been described by Partridge in 1983 [30], but this work did not draw significant recognition from the scientific society. Later, EL properties of self-assembled polymer thin films have been reported by Tian et al. [31].

After that, significant research efforts have made by various authors in this directions by developing phosphors based on purely organic materials because of their properties and versatility [32]. Organic phosphors (OPs) have been found potential applications in organic electronics [33–34], as well as chemical and biological detection [35–37]. The potential advantages of purely organic materials based phosphors with respect to rare earth doped inorganic materials includes ease of synthesis and handling, cost efficient and very high emission quantum efficiency. Research efforts are still going on this direction to synthesize environmental friendly, safer and more energy efficient organic phosphors for use in the light-emitting applications [27,38]. Various authors reported the synthesis of yellow-green phosphors based on different organic materials. Organic phosphors based on 1,9-anthrapyridone, cationic dyes, 4-amino naphthalic acid and other compounds have been utilized for daylight fluorescent pigments [39–40]. OPs based on the pyridine and their derivatives have also been documented in the literature [27,41–44].

The emission of light from polymeric materials is not a pretty natural in everyday occurrence. However, phosphors based on organic materials suffer from some limitations. They are very ineffective emitters and very low probability of emission from triplet states due to which very little discussions on modern phosphorescent applications based on these materials [45–47]. These drawbacks make OPs less studied sector and, as a result, most of the research efforts so far dedicated to luminescent materials based on inorganic or organometallic. However, most of the phosphorescence studies to date are focused on inorganic or organometallic systems [48,49]. It has been widely accepted that purely organic materials are non-phosphorescent in character. Purely organic materials based LEDs devices have a simple geometry consist of a thin film these materials which is sandwiched between two electrodes [50].

2. Factors responsible for phosphorescence

To overcome these problems, the research efforts in this direction could built-up the scope for a new generation of materials for solid-state lighting applications, exploiting the relatively low cost and tuneable chemical versatility of systems based on organic materials. In this regard, Bolton et al. [51] presented a phenomenon in the year 2011 that individually combines three important factors that are responsible for bright phosphorescence from purely organic crystals. According to them, the phosphorescence in organic materials is probably attributed to aromatic carbonyls, the heavy atom effect, and halogen bonding. They have explained these factors in a better way on the basis of existing literature. The design principle for purely organic phosphors is based on directed heavy atom effect and shown schematically in Fig. 1. They discussed it by considering chromophores in two different phases with and without halogen bonding (i) solution phase or any disordered phase and (ii) crystalline phase. Fig. 1a reveals that aromatic aldehyde chromophores are in solution phase without halogen bonding. In this case, the triplet generation is not so high, which is sufficient to produce fluorescence. As a result, the vibrational loss of triplets is dominant, making triplet emission inefficient. When the chromophore is in crystalline phase with halogen bonding, the coupling of halogen atom with aldehyde took place (Fig. 1(b)). Apart from this, it generated triplet's states effectively, which suppresses fluorescence, and at the same time promoting phosphorescence by enhanced spin-orbit to the ground state and reduced vibrational freedom of the aldehyde. They have further studied the directed heavy atoms effect more effectively by considering a mixed crystal design.

3. Devices based on organic materials

Till date, a large number of polymeric materials are studied and used for LEDs as reflected by the existing literature [15 & references within]. In these devices, the emitting layer is a thin film deposited by various methods which are sandwiched between two electrodes as shown in Fig. 2 [52]. It is well documented that single layer LEDs suffered from some drawbacks including low efficiency and a short lifetime, etc. To overcome these issues, LEDs based on multilayers has been fabricated by various authors [2]. If the multicolor emission of light is required, the number of emitting layers would be equivalent to the number of colors, with every panel capable of transmitting one particular color.

The schematic diagram showing the physical phenomena occurred in polymer Electroluminescence (EL) is represented in Fig. 3. The primary processes considered for the operation of devices includes the formation of the exciton and its decay. The formation of exciton further depends on upon (i) carrier injection, (ii) carrier transport and (iii) carrier combination, whereas the decay process includes a competition between radiative and non-radiative decay channels [53]. The detailed mechanism involved during these processes has been discussed by various authors [52,53].

Very recently, a group of researchers from United State America and Korea [54] reported temperature phosphorescence by inserting a purely organic phosphor into an amorphous glassy polymer matrix. It was noted that the reduced beta-relaxation isotactic poly (methyl methacrylate) (PMMA) effectively reduced triplet vibrational decay and promote the implanted OPs to attain a strong luminescence quantum yield of 7.5%. They fabricated a microfluidic device consisted of a polydimethylsiloxane network integrated on a

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