

# Recent Progress in the Development of Organometallic Complexes, Inorganic Phosphors and Quantum Dots for White Light Emitting Devices

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**Abstract** : Recent years have brought remarkable developments in white light emitting devices (WLEDs) and white organic light-emitting devices (WOLEDs). However, their efficiency, CIE values, CRI and lifetime are still not ideal. This review covers detailed discussion about syntheses of organometallic complexes, inorganic phosphors and quantum dots used in WLEDs, WOLEDs and their electroluminescent properties until December 2007.

**Keywords** : Organometallic complexes, Inorganic phosphors, white light emitting devices, quantum dot, electroluminescence.

## 1. Introduction

Recent years have brought remarkable developments in small molecule-[1], polymer-[2], organometallic-[3], inorganic phosphor-, and quantum dots-related fields for white organic light-emitting devices (WOLEDs) and white light emitting devices (WLEDs). However, their efficiency, CIE values[4], CRI[5] and lifetime for devices are still not ideal.

Among many approaches to achieve white emission from small molecule-based WOLEDs, single component molecules is more desirable and demanding. As compared to multi-emitting materials, a single emitting

such as better stability, reproducibility and simple fabrication process. But only few single component white light emitting materials are reported, so there is a need of synthesis of new single materials for white OLED. In host-guest system, single doped material is preferred as it significantly simplifies the structure of WOLED, relative to multi-doped system. It also solves the problems associated with differential doping aging.

White polymer light-emitting diodes (WPLEDs) made by polymer blend system suffer from low efficiency and color instability, so, single polymers emitting white light are extremely desirable as it has great advantage over the polymer blend system in terms of no phase separation. Many single component white light emitting materials has been developed so far and CIE values

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obtained from WPLEDs are closer to ideal values as compared to those of obtained by WOLED.

Following subject named as "Recent Progress in the Development of Small Molecules for White Organic Light Emitting Devices", thinking about a weak and a strong points of small molecule- and polymer-emitting luminescence, I hope to discuss the topic about syntheses of organometallic compounds, inorganic phosphors, quantum dots and their electroluminescent properties until december 2007.

## 2. Organometallic complexes as white light-emitting materials

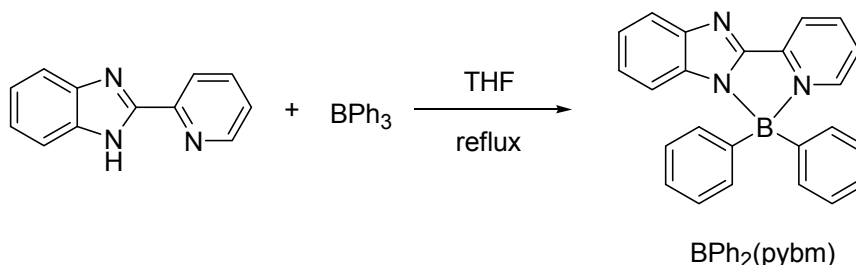
Organometallic compounds will be employed as functional materials in a variety of application fields which can be considered as part of the electronics industry[3]. Synthesis of organometallic complexes for WOLED is very important area of research as the presence of metal in white light emitting complex alters the electronic and hence luminescent properties of the complex, which sometimes gives very good results. Researchers have synthesized complexes of transition metals, main group metal and also rare earth metal. We'll here discuss complexes from all three groups.

### 2.1. Main group metal complexes

Wang *et al.* presented a new boron complex  $BPh_2(pybm)$  containing 2-(2-pyridyl)benzimidazole ligand[6]. It was synthesized using *N,N*-bidentate ligand instead of *N,O*-bidentate such as quinolinol. The reaction was performed according to Scheme 1 below.

To investigate the electroluminescent properties of  $BPh_2(pybm)$ , typical three-layer device with the configuration of ITO / NBP /  $BPh_2(pybm)$  /  $Alq_3$  / LiF / Al was fabricated by using  $BPh_2(pybm)$  as the emitter, NBP as the hole transporting layer and  $Alq_3$  as the electron transporting layer. Broader emission band from device were observed ranging from 400 nm to 750 nm, indicating the three layer LED device emitted white light covering the whole visible light region. The white light comes from exciplex emission between NBP and  $BPh_2(pybm)$  interface in addition to exciton emission from  $BPh_2(pybm)$  and  $Alq_3$ , respectively. This compound may be promising candidate for white LEDs.

Likewise, knowing the need of simple approach for making efficient white electroluminescent devices, Wang *et al.* reported on high-efficiency white electroluminescence from a double-layer device based on a luminescent boron complex of the dianion of 1,6-bis(2-hydroxy-5-methylphenyl)pyridine ((mdppy)BF) whose structure is shown below[7].



Scheme 1. The synthetic route of  $BPh_2(pybm)$ .

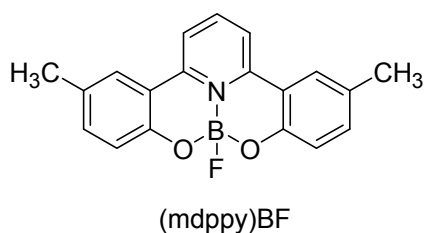


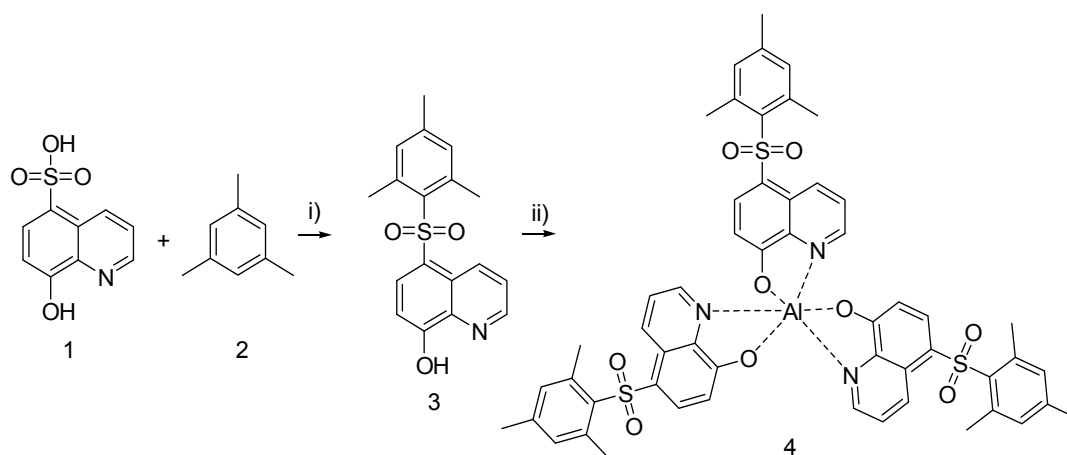
Fig. 1. Structure of (mdppy)BF.

The ligand 1,6-bis(2-hydroxy-5-methylphenyl)pyridine ( $H_2mdppy$ ) was prepared by the reaction of 2,6-dibromopyridine and Grignard reagent from 2-bromo-4-methylanisole in THF with  $[NiCl_2(dppe)]$  as catalyst ( $dppe$ ,  $Ph_2PCH_2CH_2PPh_2$ ). This was followed by demethylation in molten pyridinium chloride to give  $H_2mdppy$ . Reaction of  $H_2mdppy$  with one equivalent of  $BF_3$  in benzene gave (mdppy)BF.

To investigate the EL properties of (mdppy)BF, an organic electroluminescent device was fabricated by vacuum thermal evaporation of NPB and (mdppy)BF onto cleaned glass substrates precoated with conductive transparent indium tin oxide (ITO). The device exhibited a significantly

broader EL spectrum, ranging from 400 to 700 nm, which completely covers the total wavelength region of visible light emission, that is, high-quality white electroluminescence was obtained. The CIE  $x,y$  coordinates are (0.30, 0.36). When the driving voltage was varied from 4 to 18 V, the CIE coordinates remained almost unchanged.

Recently, different methods of obtaining white emission based on singlet exciplexes[8] and triplet excimers have also been proposed, which is clearly advantageous from the perspectives of both cost and the ease of fabrication. But the chromaticities of devices constituted by photo-complexes are still far from the real and saturated white emission of the 1931 CIE  $x,y$  coordinates (0.33, 0.33). Cheng *et al.* presented experimental study of color tunable blends based on the novel blue-green metal complexes, tris(5-(mesitylsulfone-8-hydroxyquinolato)aluminum(III) ( $Al(MSq)_3$ ), synthesized by the molecular engineering of  $Alq_3$  to obtain saturated white organic light-emitting devices[9]. Synthetic route of  $Al(MSq)_3$  is shown in Scheme 2.



(i) 10%  $P_2O_5$  in methanesulfonic acid, (ii) THF, triethylaluminium.

Scheme 2. Synthesis of  $Al(MSq)_3$ .

Due to the blending of the strong electron-withdrawing character of  $\text{Al}(\text{MSq})_3$  and an electron-donating molecule of TPD, an exciplex emission of yellow-orange color was observed from  $\text{Al}(\text{MSq})_3/\text{TPD}$  interaction during excitation in the solid phase. By adjusting the ratio of  $\text{Al}(\text{MSq})_3$  and TPD, a blue-green emission, from  $\text{Al}(\text{MSq})_3$ , and a yellow orange emission, from  $\text{Al}(\text{MSq})_3/\text{TPD}$ , could be obtained simultaneously. This phenomenon was also observed in their corresponding EL processes. Devices comprised of the three components, i.e. PVK, TPD, and  $\text{Al}(\text{MSq})_3$ , as the active region were produced by a solution process. A saturated white emission with (0.35, 0.34) was observed in the EL spectra, and their 1931 CIE x,y values were closer to the saturated white light (0.33, 0.33) than those reported in the literature while an additional hole-blocking layer of BCP was inserted into the device. Although the exciplex formation decreases the quantum efficiency of the device, it was confirmed that it is a possible way for fabricating a white light EL device.

Similarly, Li *et al.* reported a very efficient white light emitting device based on aluminum complex[10]. It was shown that a bright white electroluminescence (EL) emission can be achieved using a minimum doping technique, that is, the concentration of the dopant DCJTB (4-(dicyanomethylene)-2-

*t*-butyl-6-(1,1,7,7-tetramethyljuloli-dyl-9-enyl)-4H-pyran) was controlled to be 0.5 wt% of the host BALq (bis(2-methyl-8-quinolinolato) (para-phenylphenolato) aluminium(III)). Structures of DCJTB and BALq are shown in the Fig. 2 below.

White OLEDs are fabricated with tiny amount of red dye DCJTB (0.5 wt%) and BALq as host material. Energy transfer from the host BALq to the dopant DCJTB is controlled by varying the dopant concentration. Blue band emission from the host BALq and red band emission from the DCJTB combined to lead to white light emission with high performance. The results show a maximum luminance of 21,000  $\text{cd}/\text{m}^2$  at 15V, a power efficiency of 1.10  $\text{lm}/\text{W}$  at 11V and CIE coordinates of (0.32, 0.34) at 8V to (0.30, 0.32) at 11V. The application of this single white emissive layer may simplify the fabrication process of device.

## 2.2. Transition metal complexes

WOLEDs employing phosphorescent materials have led to significant improvements in efficiency; targeting backlights for full-color active-matrix displays combined with color filters[11-13]. A number of device structural concepts have been employed to generate white electrophosphorescence. Electrophosphorescent OLEDs have been shown to have very high

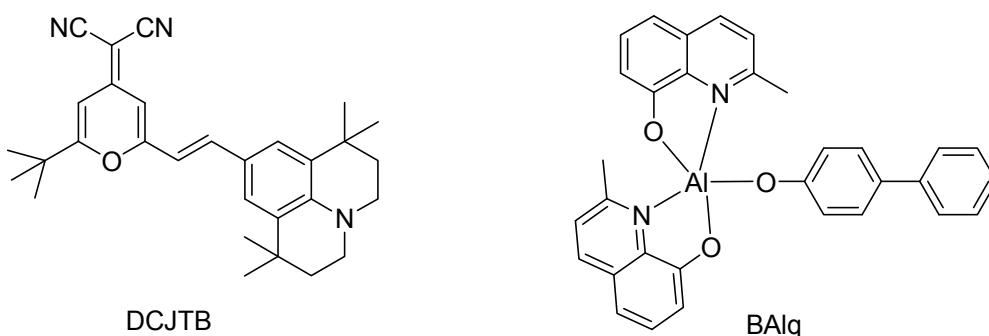


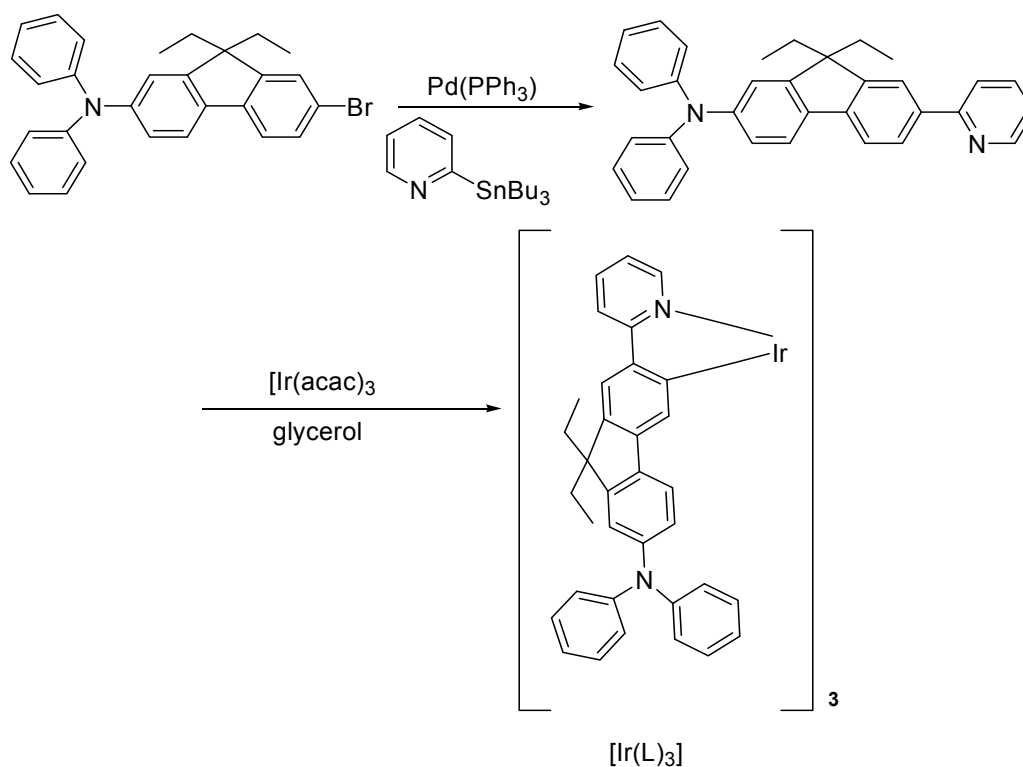
Fig. 2. Structures of red dye DCJTB and host material BALq.

external quantum efficiency when used for monochromatic light emission. Among phosphorescent heavy-metal compounds reported, cyclometalated iridium(III) complexes have emerged as the most promising materials for high-performance work because they show intense triplet emission at room temperature and significantly shorter phosphor lifetime when compared with other heavy metal compounds. The device efficiency and emission color of iridium-based OLEDs can be modified easily by tuning the structure of the organic ligand chromophore.

In connection to this concept, Wong *et al.* synthesized a novel iridium(III) cyclometalated complex  $[\text{Ir}(\text{L})_3]$  ( $\text{L} = 9,9\text{-diethyl-7-pyridinylfluoren-2-yl}$ )diphenylamine) containing a diphenylaminofluorene framework which emits very strong orange color both in steady-state emission and

electrophosphorescence and can be exploited in the realization of WOLEDs[14]. Synthetic route for the complex is shown in Scheme 3. General structures of other materials used for device fabrication are also shown below.

The WOLED device employs two emission layers in which one layer contains 5%  $[\text{Ir}(\text{L})_3]$  doped in the CBP host matrix (CBP = 4,4'-*N,N'*-dicarbazolebiphenyl) and another layer is composed of the mCP host (mCP = *N,N'*-dicarbazolyl-3,5-benzene) doped with a 8% blue-emitting phosphor, iridium-(III)bis(4,6-di-fluorophenyl)-pyridinato-*N,C*<sup>2</sup>)picolinat e (FIrPic). The threshold voltage of the device is 4.2 V, and the brightness reaches 3200  $\text{cd/m}^2$  at 10 V and 30  $\text{mA/cm}^2$ . The color of the white light corresponds to the Commission Internationale de L'Eclairage (CIE) coordinates of (0.31, 0.41) and a strong voltage dependence of the electroluminescence



Scheme 3. Synthesis of  $[\text{Ir}(\text{L})_3]$ .

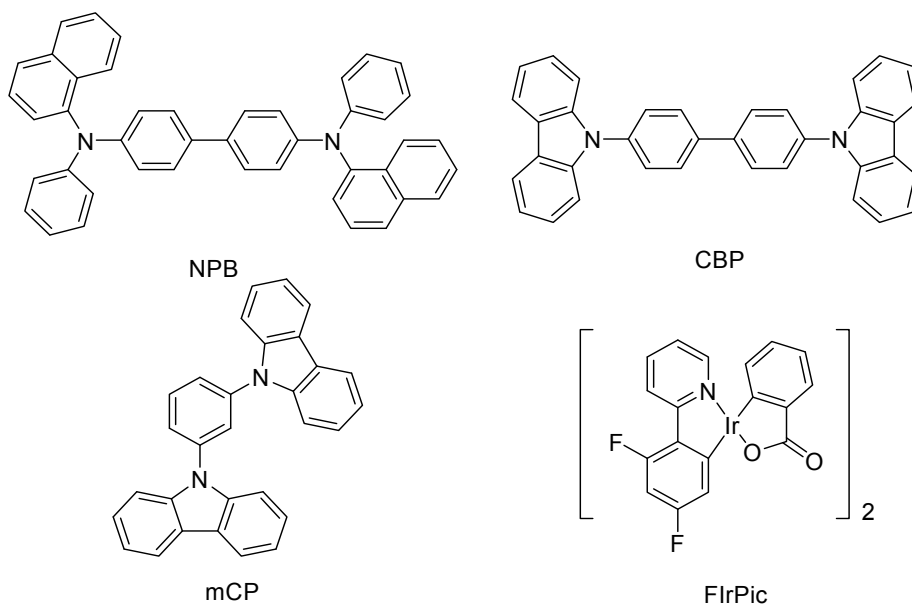


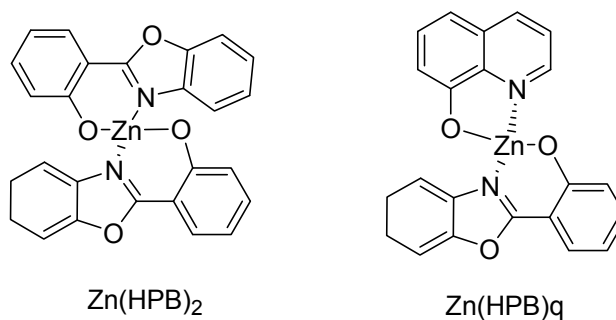
Fig. 3. Structure of compounds used in device fabrication.

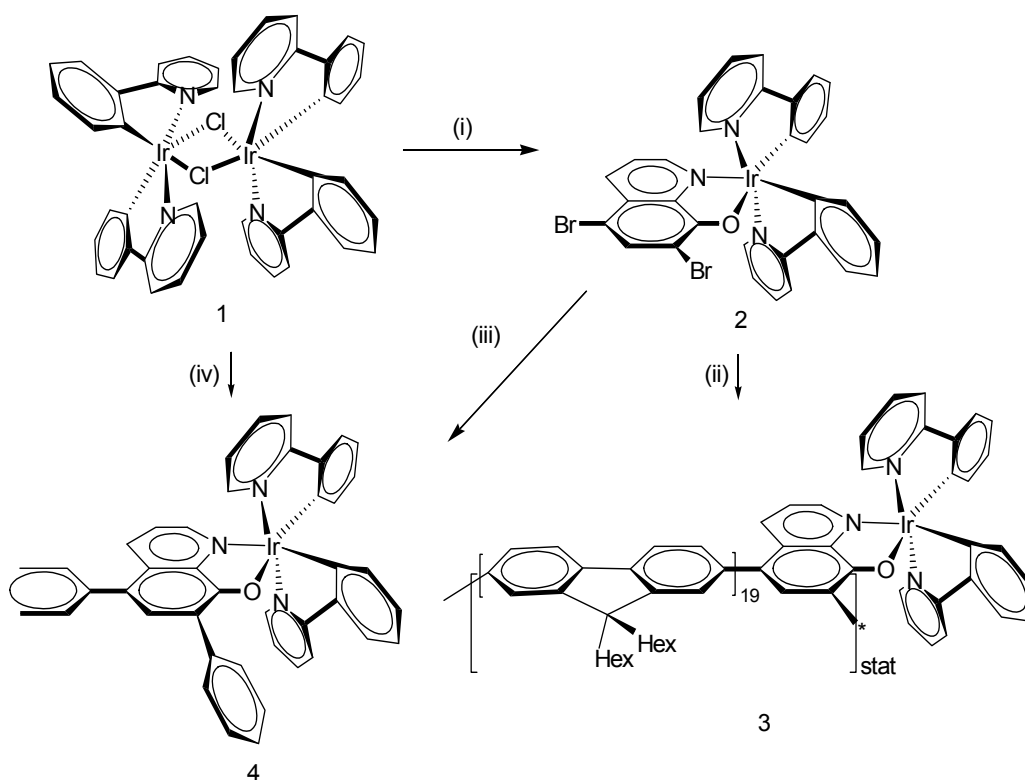
spectrum is observed, with the blue color intensity increasing relative to the orange component at increasing voltage. The maximum current efficiency of 17.8 cd/A and power efficiency of 7.6 lm/W are achieved for the WOLED device.

The design principle for the preparation of WPLEDs given by Slugovc *et al.* is based on an easy synthesis of iridium(III) compounds starting from commercially available materials and provides the possibility of simple incorporation into polymers via a standard

Suzuki procedure as shown in the Scheme 4[15].

White emission was reported from iridium compound 3 (poly(2,7-fluorendiyl)-*co*-bis( $K^2(C^2,N)$ -2-phenylpyridine)( $K^2(N,O)$ -5,7-diyl-8-quinolinolate) iridium(III)). A blend of polyfluorene with iridium compound 3 including the iridium(III) moiety and fluorene units turned out to exhibit white electroluminescence with colour coordinates of  $x = 0.30$ ,  $y = 0.35$  according to the CIE standard 1931, resulting from blue

Fig. 4. structures of the complexes Zn(HPB)<sub>2</sub> and Zn(HPB)q.



(i) 5,7-dibromo-8-hydroxyquinoline,  $\text{CH}_2\text{Cl}_2$ -EtOH,  $\text{Et}_3\text{N}$ ,  $80^\circ\text{C}$ , 20 h, (ii) 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 2,7-dibromo-9,9-dihexylfluorene, toluene-EtOH- $\text{H}_2\text{O}$ ,  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{Na}_2\text{CO}_3$ ,  $90^\circ\text{C}$ , 24 h, (iii) phenylboronic acid, toluene-EtOH- $\text{H}_2\text{O}$ ,  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{Na}_2\text{CO}_3$ ,  $90^\circ\text{C}$ , 24 h, (iv) 5,7-diphenyl-8-hydroxyquinoline,  $\text{CH}_2\text{Cl}_2$ -EtOH,  $\text{Et}_3\text{N}$ ,  $80^\circ\text{C}$ , 20 h.

Scheme 4. Synthesis of Iridium Compound.

polyfluorene emission, green emission of the keto-defect and red emission of the iridium compound.

Jang *et al.* synthesized new electroluminescence materials such as [2-(2-hydroxyphenyl)benzoxazole] ( $\text{Zn}(\text{HPB})_2$ ) and [(2-(2-hydroxyphenyl)benzoxazole) (8-hydroxyquinoline)] ( $\text{Zn}(\text{HPB})\text{q}$ ) whose structure are shown in the Fig. 4 below[16].

A white OLED with the structure ITO / PEDOT : PSS (23 nm) / NPB (40 nm)/ $\text{Zn}(\text{HPB})_2$  (40 nm) /  $\text{Zn}(\text{HPB})\text{q}$  (20 nm) /  $\text{Alq}_3$ (10 nm) / LiAl (120 nm) was fabricated based on  $\text{Zn}(\text{HPB})_2$  and  $\text{Zn}(\text{HPB})\text{q}$ . As a result, they obtained a maximum luminance of  $15171 \text{ cd/m}^2$  at a current density of  $955$

$\text{mA/cm}^2$ . The maximum external quantum efficiency and luminous efficiency are 0.7% and  $1.65 \text{ cd/A}$ , respectively. The CIE coordinates are (0.28, 0.35) at an applied voltage of 9.75 V.

Similarly, complexes of gold also exhibit white luminescence. Luminescence is a prominent property of Au(I) compounds in the solid state, as well as in rigid media at low temperatures. For these systems, understanding their emission and tuning their excited state properties are essential for their eventual use as luminescent sensors and dopant emitters in OLED applications. As a consequence of aurophilic interactions, Au(I) dimers are often found to have solid-state

structural arrangements possessing one dimensional A–Au chains, but the luminescence from these systems often shows a poor correlation between  $\lambda_{em}$  and intra- and intermolecular Au–Au separations. In connection to this, Eisenberg *et al.* reported the structures of several Au(I) dimmers and their luminescence properties that include multiple emissions, bright white solid-state luminescence, and, as seen for the diaminocarbene complex, brilliant emissions of different color from different frozen glasses[17].

### 2.3. Rare earth metal complexes

The rare earth metal complexes exhibit extremely sharp emission bands in photoluminescent (PL) and electroluminescent (EL) spectra[18].

Cremona *et al.* reported the fabrication and the characterization of a white triple-layer OLED using a  $\beta$ -diketone binuclear complex,  $\text{Eu}(\text{btfa})_3\text{phen} \text{ Tb}(\text{acac})_3$  as the emitting layer[14]. The electroluminescent (EL) spectra of fabricated devices show a wide emission band from 400 to 700 nm with a  $100 \text{ cd/m}^2$  of luminance. The structure of the complex synthesized is shown in Fig. 5.

Devices of three layers using  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  binuclear complexes as emitting layer have been developed to achieve white light. The white emission results from a combined action between the binuclear complex, acting as hole blocking and emitting layer. It was found that the device color depends on the EL emission of the  $\text{Re}^{3+}$  ions via an intramolecular energy transfer, from the ligand electrophosphorescence and from the NPB. The ratio between these emissions can be controlled by using the bias voltage and the thickness of the different layers.

Cola *et al.* observed partial transfer of excited-state energy from the Ir(III) center to the Eu(III) center in a d-f bimetallic assembly which leads to the emission of white light[20]. Structure of the complex is shown in the Fig. 6.

Similarly Li *et al.* reported a series of  $\text{Eu}_x\text{Tb}_{1-x}(\text{aca})_3\text{phen}$  dinuclear complexes which were employed as the emitting layer in OLEDs from which the white emission was observed at an appropriate DC voltage[21]. Structure of the complex synthesized is shown in the Fig. 7.

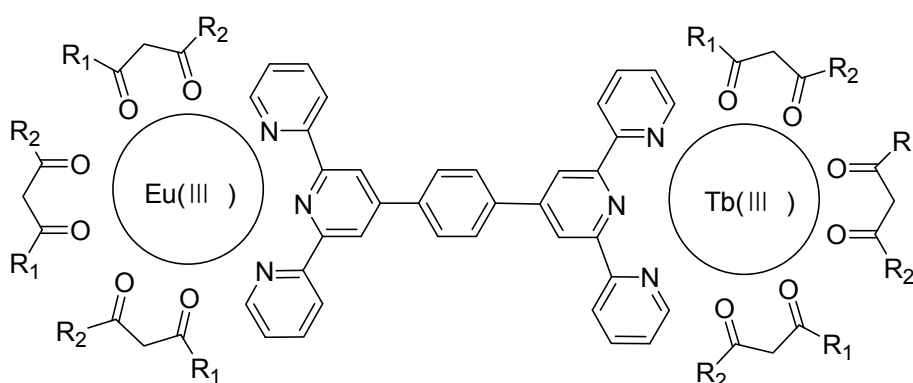


Fig. 5. Structure of  $\beta$ -diketones binuclear complex  $[\text{Eu}(\text{btfa})_3\text{phen}]\text{Tb}(\text{acac})_3$ .



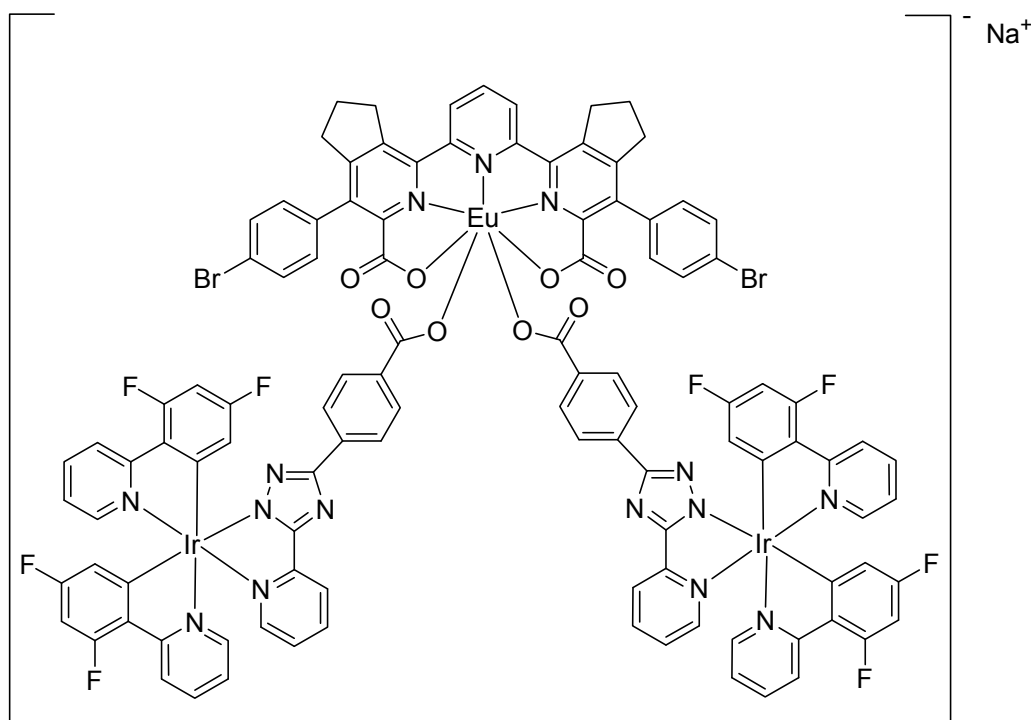
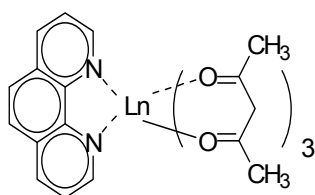


Fig. 6. Structure of the Eu (III) complex.



(Ln = Eu, Tb)

Fig. 7. Structure of  $-x(\text{aca})_3\text{phen}$  dinuclear complex.

The mole ratios of the  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  are 8 : 2, 5 : 5, 2 : 8, 1 : 9, respectively. The  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions are just in one molecule. These complexes can easily evaporate into film and two kinds of devices were obtained based on them. Device I : ITO/PVK : NPB /  $\text{Eu}_{0.5}\text{Tb}_{0.5}(\text{aca})_3\text{phen}$  / Al, and device II : ITO / PVK : TPD /  $\text{Eu}_{0.5}\text{Tb}_{0.5}(\text{aca})_3\text{phen}$  / Al. Although white light can be obtained from both types of devices, the voltage values at

which the white emission begins to appear are very different. The performance of device I is better than that of device II, because the white light can be seen at lower voltage. This work indicates that use of binuclear complexes with  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  in EL device will be interesting for design of new organic EL materials and a new type EL device configuration.

Pyo *et al.* synthesized several lanthanide complexes such as  $\text{Eu}(\text{TTA})_3(\text{Phen})$ ,  $\text{Tb}(\text{ACAC})_3(\text{Cl-Phen})$ [22], where the devices have structures of anode / TPD[ $\text{Tb}(\text{ACAC})_3(\text{Cl-Phen})$ ] /  $\text{Eu}(\text{TTA})_3(\text{Phen})$  /  $\text{Alq}_3$  or  $\text{Bebq}_2$  / cathode and the low work function metal alloy such as Li : Al was used as the electron injecting electrode (cathode). Structures of the metal complexes are shown in the Fig. 8.

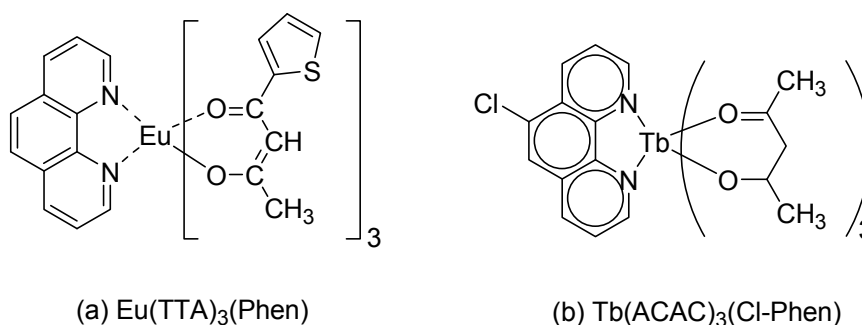


Fig. 8. Structure of the complexes as Eu(TTA)<sub>3</sub>(Phen) and Tb(ACAC)<sub>3</sub>(Cl-Phen).

It was found that the turn-on voltage of the device using Beq<sub>2</sub> were lower than that of the devices using Alq<sub>3</sub> as an electron transporting material. On the other hand, the blue light emitting intensity in the TPD layer of the device using Beq<sub>2</sub> were lower than that of the devices using Alq<sub>3</sub> as an electron transporting material.

### 3. White Luminescence from LED

#### 3.1. Phosphor-based LEDs

Most white LEDs in production today are based on an InGaN-GaN structure, and emit blue light of wavelengths between 450 nm - 470 nm blue GaN. These GaN-based, InGaN-active-layer LEDs are covered by a yellowish phosphor coating usually made of cerium-doped yttrium aluminum garnet (Ce<sup>3+</sup> : YAG) crystals which have been powdered and bound in a type of viscous adhesive. The LED chip emits blue light, part of which is efficiently converted to a broad spectrum centered at about 580 nm (yellow) by the Ce<sup>3+</sup> : YAG. The single crystal form of Ce<sup>3+</sup> : YAG is actually considered a scintillator rather than a phosphor. Since yellow light stimulates the red and green receptors of the eye, the resulting mix of blue and yellow light gives the appearance of white, the resulting shade often called "lunar white". This approach was developed by Nichia and

was used by them for manufacturing of white LEDs from 1996[23].

The pale yellow emission of the Ce<sup>3+</sup> : YAG can be tuned by substituting the cerium with other rare earth elements such as terbium and gadolinium and can even be further adjusted by substituting some or all of the aluminum in the YAG with gallium. Due to the spectral characteristics of the diode, the red and green colors of objects in its blue yellow light are not as vivid as in broad spectrum light. Manufacturing variations and varying thicknesses in the phosphor make the LEDs produce light with different color temperatures, from warm yellowish to cold bluish; the LEDs have to be sorted during manufacturing by their actual characteristics.

White LEDs can also be made by coating near ultraviolet (NUV) emitting LEDs with a mixture of high efficiency europium-based red and blue emitting phosphors plus green emitting copper and aluminum-doped zinc sulfide (ZnS : Cu, Al). This is a method analogous to the way fluorescent lamps work. However the ultraviolet light causes photodegradation to the epoxy resin and many other materials used in LED packaging, causing manufacturing challenges and shorter lifetimes. This method is less efficient than the blue LED with YAG : Ce phosphor, as the Stokes shift is larger and more energy is therefore converted to heat, but yields light

with better spectral characteristics, which render color better. Due to the higher radiative output of the ultraviolet LEDs than of the blue ones, both approaches offer comparable brightness. The newest method used to produce white light LEDs uses no phosphors at all and is based on homoepitaxially grown zinc selenide (ZnSe) on a ZnSe substrate which simultaneously emits blue light from its active region and yellow light from the substrate.

### 3.2. Phosphor and white luminescence

When phosphor is exposed to some kind of excitement e.g. electrons, photons, current, *etc.*, they reemit the absorbed energy in form of light, usually in the longer wavelength region. This effect is known as luminescence. As LEDs are monochromatic by nature, phosphors are also used in most white LEDs to achieve white light in a simple and efficient manner. In order to get sufficient brightness, a high intensity LED is needed to excite the phosphor to emit the desired color which will combine with other colors to light that is perceived as white by the human eye. Phosphors are usually made of zinc sulfide or yttrium oxides-doped with certain transition metals (Ag, Mn, Zn *etc.*) or rare earth metals (Ce, Eu, Tb and *etc.*) to obtain certain colors. The dopants have also an important role in inserting point defects into the crystal. They provide the intermediate energy states for electrons in order to emit light in the visible spectrum after they fall back from the conduction band to the valence band. The mechanism for fluorescence, the luminescence that terminates after the causing effect depletes, depends also on temperature-related energy fluctuation of the lattice. The oscillation causes the displaced electron to escape from the potential traps created by the imperfections and fall back their initial state to emit light. The effect is prominent in rare earth and transition metals. Generally there are three approaches in which phosphor

can be used to achieve white emission from LEDs. These are UV-LED with triple-wavelength RGB phosphors, blue LED with a YAG yellow phosphor or blue LED with different phosphors.

### 3.3. Blue LED & yellow phosphor

The use of a blue-emitting chip in combination with a yellow phosphor is currently the most widely used approach for producing white light with LEDs and considered the least expensive method for producing white light. Since blue LEDs emit light with a shorter wavelength than red ones, it is possible to develop a suitable and intense yellow light-emitting phosphor that can complement the blue emission to yield ideal white light[24]. Out of all the phosphor LEDs described, cerium-doped yttrium aluminate garnet YAG : Ce phosphor was found to be the most suitable phosphor satisfactorily tested on GaN LEDs for the production of white light[25,26].

Keeping this in view, Haranath *et al.* disclose a unique method of making high-brightness YAG : Ce phosphor in the nano-form by a single step auto-combustion process[27]. Ce<sup>3+</sup>-doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG : Ce) nanophosphor powders with the composition of Y<sub>(3-x)</sub>Al<sub>5</sub>O<sub>12</sub> : xCe<sup>3+</sup> (x = 0.01 - 1) were prepared from the nitrates of yttrium, aluminum and cerium dissolved in ethanol-water mixture (2:1). The methodology adapted by them results in stand-alone nanoparticles with appreciable luminescence characteristics in the yellow region, which could be due to the advantages associated with nanotechnology. Further, it is observed that the blue light from commercial LED combined with the yellow light simulated from the nanophosphor generated a white light that has colorimetric coordinates very close to the ideal white region of the chromaticity diagram. It was demonstrated that YAG : Ce nanophosphor could be simulated to produce general-purpose white

light. The methodology shown has the potential to be easily scaled up for mass production and also for duly incrementing white LED technology.

As white light emitted from blue LED using phosphor doesn't have primary red colour, lamps fabricated in this manner display poor color rendering. To solve this problem, Su *et al.* attempted to synthesize novel  $\text{Eu}^{2+}$  doped  $\text{Ba}_2\text{ZnS}_3$  phosphors for white light emitting diodes[28]. Polycrystalline samples with the general formula  $\text{Ba}_{2-x}\text{ZnS}_3 : x\text{Eu}^{2+}$  were prepared by high temperature solid-state reaction. The band gap of  $\text{Ba}_2\text{ZnS}_3$  host derived from diffuse absorption spectra is 3.35 eV. The excitation spectra of synthesized phosphors consist of three broad bands, which are consistent with the diffuse reflectance spectra. Because of its stronger broad band absorption in the range of 375-550 nm,  $\text{Ba}_2\text{ZnS}_3 : \text{Eu}^{2+}$  phosphors can be used to make GaN-based LEDs. All of the emission spectra under different light excitation ( $\lambda_{\text{ex}} = 350, 420 \text{ nm}$ ) exhibit a well-known characteristic  $4f^6 5d^1 \rightarrow 4f^7$  transition of  $\text{Eu}^{2+}$  ion, which argues that efficient energy transfer from host to  $\text{Eu}^{2+}$  ions occurs.

Park *et al.* develop a yellow phosphor that emits efficiently under the 450-470 nm excitation range[29].  $\text{Ba}^{2+} \cdot \text{Mg}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4 : \text{Eu}$  yellow phosphor and investigated its luminescent properties in an attempt to develop white LEDs by integrating the InGaN blue LED chip and the  $\text{Ba}^{2+} \cdot \text{Mg}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4 : \text{Eu}$ ; the combination of a blue LED emitting 460 nm and a broad-band yellow  $\text{Ba}^{2+} \cdot \text{Mg}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4 : \text{Eu}$  phosphor creates a white line. We feel the luminescence efficiency enhancement observed in  $\text{Ba}^{2+}$  or  $\text{Ba}^{2+} \cdot \text{Mg}^{2+}$  co-doped in  $\text{Sr}_2\text{SiO}_4 : \text{Eu}$  phosphor is substantial and is of practical significance for using the yellow phosphor for realizing white light under 450-470 nm. The white InGaN-based  $\text{Ba}^{2+} \cdot \text{Mg}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4 : \text{Eu}$  developed in this work showed a higher luminance compared with the

industrially available InGaN-based YAG : Ce.

There are many other examples of yellow phosphors for blue LED to create white light and this method is relatively easy to perform. Least expensive and the device has been commercialized. However, there exist at least three drawbacks in this combination. Firstly, the overall efficiency decreases rapidly when lowering the correlated color temperature of the device. Secondly, the white light from this combination route has an undesirable color balance and the deficiency of the red light in the visible spectra (around 600 nm) results in a low color rendering index. Thirdly, the degradation rates of LEDs and phosphor are not isochronous, thus the white light point in the color coordinates scheme shifts with working time.

### 3.4. Blue LED & red/ green phosphor

Coating green and red phosphors to a blue LED is more popular because of the higher energy conversion efficiency[30-31]. This is similar to the process involved with yellow phosphors, except that each excited phosphor re-emits a different color. Similarly, the resulting light is combined with the originating blue light to create white light. The resulting light, however, has a richer and broader wavelength spectrum and produces a higher color-quality light, albeit at an increased cost.

Presently there are many phosphor being used in WLED, but most of them do not meet the optimum requirements of white-light LEDs. For example, YAG :  $\text{Ce}^{3+}$  shows a high thermal quenching and a poor color rendition, which can be improved by sulfide-based phosphors (i.e., red,  $\text{SrS} : \text{Eu}_{12}$  and  $\text{CaS} : \text{Eu}^{2+}$ , green,  $\text{SrGa}_2\text{S}_4 : \text{Eu}^{2+}$ ). However, these sulfide materials suffer from low chemical stability in LEDs environment. Ideally the conversion phosphors for white-light LEDs must combine high quantum efficiency and absorption for

UV-blue radiation with the ability to withstand the high temperature generated by the LED without degrading and quenching the luminescence, and moreover should be chemically stable.

Attempting to solve this problem, Y. Q. Hintzen *et al.* synthesized  $\text{Eu}^{2+}$ -activated  $\text{MSi}_2\text{O}_{2-\delta}\text{N}_{2+2/3\delta}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) [32]. A new oxynitride compound  $\text{BaSi}_2\text{O}_2\text{N}_2$  was obtained in the  $\text{BaO-SiO}_2\text{-Si}_3\text{N}_4$  system. All activated  $\text{MSi}_2\text{O}_{2-\delta}\text{N}_{2+2/3\delta}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) materials can be efficiently excited in the UV to visible region (370 - 460 nm), making them attractive as conversion phosphors for LED applications. A blue-green emission at 490-500 nm is observed for  $\text{BaSi}_2\text{O}_2\text{N}_2 : \text{Eu}^{2+}$ , yellow emission at 560 nm for  $\text{CaSi}_2\text{O}_{2-\delta}\text{N}_{2+2/3\delta} : \text{Eu}^{2+}$ , and a green-yellow emission peaking from 530 to 570 nm for  $\text{SrSi}_2\text{O}_{2-\delta}\text{N}_{2+2/3\delta} : \text{Eu}^{2+}$ , the position depending on the exact value of  $\delta$ .  $\text{BaSi}_2\text{O}_2\text{N}_2 : \text{Eu}^{2+}$  is the most promising conversion phosphor for white-light LEDs due to its high conversion efficiency for blue light from InGaN-based LEDs related to its very small Stokes shift.

Although nowadays commercially applicable red emitting phosphors for white LED are divalent Eu ion activated sulfides. These sulfide phosphors are chemically unstable when exposed in the moisture environment. To tackle this problem, Wang *et al.* prepared  $\text{Eu}^{3+}$ -doped  $\text{Gd}_2\text{Mo}_3\text{O}_9$  [33].  $\text{Eu}^{3+}$  doped materials, especially in which the  $\text{Eu}^{3+}$  ions occupy a non-centro symmetric site in the host, have been widely used as the red emitting phosphors due to their intense  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission in the red spectral region. These results showed that this phosphor can be effectively excited by ultraviolet (UV) (395 nm) and blue (465 nm) light, matching the output wavelengths of ultraviolet or blue LED chips. The  $\text{Eu}^{3+}$ -doped  $\text{Gd}_2\text{Mo}_3\text{O}_9$  phosphor may be a better candidate for solid state lighting application.

Similarly, another  $\text{Eu}^{3+}$  activated phosphor was reported by Zhuang *et al.* which is

applicable to UV or blue LED chips [34]. The novel phosphor  $\text{CaMoO}_4 : \text{Eu}^{3+}$  was prepared by using oxides in air. The excitation and emission spectra indicate that this phosphor can be effectively excited by ultraviolet (UV) (394 nm) and blue (464 nm) light, and exhibits a satisfactory red performance (616 nm), nicely fitting with the widely applied UV or blue LED chips. The novel phosphor is much more stable and has stronger emission intensity than the sulfide red phosphors used in white LEDs.

### 3.5. Ultraviolet (UV) LED & RGB phosphor

The UV light is used to excite the different phosphors, which are doped at measured amounts. The colors are mixed resulting in a white light with the richest and broadest wavelength spectrum. The generation of white light by the UV LED/phosphor technology is very desirable like the fluorescent lamp technology. It affords the precise control over the color of the resultant white light so that it is possible to develop white LEDs with different spectra.

Many phosphors are used in UV-LED to fabricate efficient white LED. silicate-based phosphors activated with  $\text{Eu}^{2+}$  or  $\text{Mn}^{2+}$  are among the good examples of such phosphors. These phosphors show broad emission colors through the transition of  $\text{Eu}^{2+}$  or  $\text{Mn}^{2+}$  activator strongly coupled to the host lattice. The absorption and emission bands of activators are also controlled by the host lattice crystal field. The doped silicate-based phosphors with a maximum absorption of near ultraviolet give a wide range of white spectrum.

Knowing the importance of silicate-based phosphors, Kim *et al.* presented the significant combustion processing for producing white emitting  $\text{Ba}_3\text{MgSi}_2\text{O}_8 : \text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$  phosphors with fine size and narrow size distribution [35].

The integrated emission intensity is

maximized at the ratio of a mixture of citric acid and ethylene glycol to starting materials with 90%. It shows three emission colors: the blue color of 433 nm from  $\text{Eu}^{2+}$ (I) substituted by  $\text{Ba}^{2+}$  (I) site, the green color of 500 nm from  $\text{Eu}^{2+}$  (II, III) substituted by  $\text{Ba}^{2+}$  (II, III) site, the red color of 610 nm from  $\text{Mn}^{2+}$ (I, II, III). The relative intensity of the green and the blue band is significantly decreased as an increase of a fuel, suggesting that  $\text{Eu}^{2+}$  ions in our sample preferably occupy  $\text{Ba}^{2+}$ (II, III). It is due to the change in the local environment of  $\text{Eu}^{2+}$  ions resulting from organic impurities induced from the low temperature synthesis. Compared with a solid state method-prepared sample, the emission peaks of three emission bands are shifted to shorter wavelength side by 10 nm. This blue shift is described by quantum size effect. Their phosphors with maximum excitation wavelength of around 370 nm and with spherical shape can be utilized as a good phosphor layer for light-emitting diode based on ultraviolet chip/phosphor technology.

In connection to this, another silicate based phosphor activated by  $\text{Eu}^{2+}$  was reported by Su *et al*[36]. In this study novel orange phosphor of  $\text{Eu}^{2+}$  activated calcium chlorosilicate was synthesized at 1273K by conventional solid-state reactions under reductive atmosphere and investigated by means of photoluminescence excitation, diffuse reflectance and emission spectroscopies. These results show that this phosphor can be efficiently excited by the incident light of 300 – 450 nm, well matched with the emission band of 395 nm-emitting InGaN chip, and emits an intense orange light peaking at 585 nm. By combining this phosphor with a 395 nm-emitting InGaN chip, an intense orange LED was fabricated. Under 20 mA forward-bias current, its CIE chromaticity coordinates are (0.486, 0.446). The dependence of fabricated orange LED on forward-bias current indicates that it shows excellent chromaticity stability and luminance

saturation. These results show that this  $\text{Eu}^{2+}$ -activated calcium chlorosilicate is a promising orange-emitting phosphor for near-ultraviolet (UV) InGaN-based white LED.

Similarly, there are some phosphors activated by cerium. There are two major reason for which cerium-based phosphor are popular. First, among all the trivalent lanthanides,  $\text{Ce}^{3+}$  is the only one characterized by strong f-d transitions. Trivalent cerium has a  $4f^1d^0$  ground state configuration and its optical transitions in the visible region arise from  $4f^1-5d^1$  excitations. As with  $\text{Eu}^{2+}$ , cerium-based phosphor materials have broad excitation/emission bands that can be matched to the characteristics of the LED and can possibly mimic the solar spectrum. Second, the involvement of 5d levels implies that the emission wavelength can be tuned by changing the energies of the 5d levels with respect to the deeper 4f levels. For instance, by adjusting the crystal field splitting, it is possible to lower the lowest 5d level in order to decrease the 5d-5f energy band gap and shift the phosphor emission towards the red.

Keeping these facts in view, Cheetham synthesized a high temperature cubic phase in the  $\text{CaSiN}$  system with the stoichiometry  $\text{CaSiN}_2$ [37]. This phase is stabilized by cerium substitution on the calcium site.  $\text{CaSiN}_2 : \text{Ce}^{3+}$  has several important properties that make it the first of its kind and very promising for solid-state lighting applications. First, it represents the only  $\text{Ce}^{3+}$  phosphor materials showing an intense red emission with broad emission/excitation bands. The use of a red broad-band emitter will increase the CRI to as much as 90 for the setup comprising a blue LED with yellow and red phosphors. In order to achieve this target, the QE of the red phosphor must be further increased because it will be excited by the green photons from the yellow phosphor. Second,  $\text{CaSiN}_2 : \text{Ce}^{3+}$  is one of the

rare phosphor materials that can be excited in the yellow – green region. This property is of great interest for plant growth enhancement since green light is not harvested in the photosynthetic process. With  $\text{CaSiN}_2 : \text{Ce}^{3+}$ , the green photons can be down-converted into useful red photons. Thirdly, the use of chemical substitution has led to new possibilities for the  $\text{CaSiN}_2 : \text{Ce}^{3+}$  phosphor. For example, the tunable emission of this phosphor makes it very interesting as a yellow/orange phosphor to use directly in combination with a 460 nm blue LED. It is also worth mentioning that this red phosphor can be used directly in a white light setup comprising a UV LED with three red, green and blue phosphors.

#### 4. Quantum dot-based LEDs

Quantum dots are semiconductor nanocrystals that act as boxes, or three-dimensional quantum wells, to confine electrons or holes. The confinement gives rise to artificial, discrete atomic energy levels in the material, resulting in the absorption and emission of light only in certain wavelength bands. The optoelectronic properties of the semiconductor are tunable by varying the size and composition of the quantum dots. These unique abilities of quantum dots are due to their very small size (2–10 nm). Quantum dot phosphors offer the incredible and diverse advantages of tunable emission/absorption wavelength, versatile form and application, high quality white light production, low cost and high stability. Given the large share of resources and nonrenewable fuel spent on lighting each year, quantum dot phosphors represent the possibility great leaps forward in cost efficiency. The major advantage of quantum dot phosphors is the ability to produce high quality, low-cost white light relative to the standard white light producible in traditional

semiconductor systems. This can be done by intermixing red, green, and blue emitting dots homogeneously within the phosphor, a feat of great difficulty with traditional phosphors. Thus, quantum dots need only a single excitation source for multiple emission colors, even to the point of producing industry quality white light. In addition, the unique core-shell technology allows quantum dot phosphors to exhibit great stability, retaining high quantum yields and luminosities over long lifetimes, in a variety of different environments. In contrast, organic dyes and other common phosphors / fluorophores have poor photostability and short lifetimes relative to quantum dots.

##### 4.1. Quantum dots and white luminescence

Presently white LEDs are created by combining inorganic phosphors with UV or blue LEDs. However, several shortcomings exist in traditional phosphor technology. The first is that of untunable light emission – the color (wavelength) that each phosphor material gives off is set by nature, and is difficult to alter. This limitation is due wholly to the fixed nature of the traditional phosphors, which fixes the energy of emitted photons. A second shortcoming is inflexibility; the process for coating or doping phosphors onto the surface of LEDs is relatively costly and fairly limited, being unable to allow easily for geometric variations in the underlying LED. A third restriction is a limited absorption spectrum. Because a phosphor must absorb short wavelength to emit a longer wavelength, it is preferable that each phosphor possess a broad absorption spectrum. In reality, most phosphors absorb only within certain difficult to exploit regions of the spectrum, which are not easily changed. The final shortcoming of phosphors is their inability to produce inexpensive and high quality white light, due to the difficulty of intermixing red, green and

blue phosphors closely enough for the proper effects. This leads to low quality white light that is unsuited for many industrial uses. Moreover, there are often color differences that are easily detected with the human eye when the phosphor heats up or ages with use. Thus, restrictions on the phosphors that coat LEDs restrict the LEDs themselves.

Quantum dots which are semiconductor nanocrystals, represent a marked increase in performance over standard phosphors, because they can be tuned to absorb or emit at any visible or infrared wavelength and can be fabricated into a great variety of forms and media, eliminating completely the shortcomings of traditional phosphors. These unique abilities of quantum dots are due to their very small size (2–10 nm). At these sizes, quantum mechanics allow semiconductor materials to take on all new traits, including that of a bandgap that can be tuned with the addition or subtraction of only a few atoms to the quantum dot. The small size also allows for incredible flexibility of form, letting phosphors match whatever shape their underlying LED needs to assume. By controlling quantum dots' size, it is possible to control their color, allowing our viewer to overcome nature's limits. Quantum dots exhibit high fluorescence quantum efficiencies and large molar absorptivities[38–39]. However, they still suffer from the problem that simply mixing the traditional red, green, and blue colors to achieve white light results in a loss in total device efficiency due to self absorption for a device more than a few monolayers.

Rosenthal *et al.* at Vanderbilt University, discovered a way to make quantum dots spontaneously produce broad-spectrum white light[40]. In their report, they have shown the potential usefulness of pyrolytically grown magic-sized CdSe nanocrystals as a white-light phosphor. These ultra-small nanocrystals exhibit a strong Stokes shift and broad emission covering the entire visible

spectrum. These properties are the direct result of the extreme surface-to-volume ratio forcing the electron and hole to predominately interact at the nanocrystal surface. Consequently, these magic-sized nanocrystals provide the ideal platform to study the nanocrystal-molecule transition. Further, the combination of their intrinsic properties makes them an ideal material for solid state lighting applications. Study of the fundamental properties of this material could lead to the development of more economical and environmentally friendly materials with similar properties, eventually leading to the next generation of solid state lighting technologies. This discovery was a milestone for researcher to work in this area. Many researchers then prepared quantum dots as phosphor for White LED. Chen *et al.* synthesized CdSeZnSe quantum dots and applied it on blue InGaN chips to produce white emission[41]. They fabricated novel WLEDs, composed of CdSeZnSe QDs and InGaN chips. The binary complementary color WLED (a blue InGaN chip and yellow-emitting CdSeZnSe QDs) provides white light with a CIE 1931 coordinate of (0.32, 0.33) and color rendering index of 50. The three-band RGB WLED (a blue InGaN chip, with green-emitting, and red-emitting CdSeZnSe QDs) gives white light with a CIE-1931 coordinate of (0.33, 0.33) and color rendering index of 91.

Their major advantages are the easy tuning of the saturated color emission across the visible near-IR range and the high chemical and optical stability of the nanocrystal composites. These characteristics open the way to a new class of hybrid devices in which the low-cost, flexible technology of organic LEDs is combined with the long operating lifetime of inorganic semiconductor devices. Keeping this in view, Gigli *et al.* demonstrated the first hybrid white-LED whose emission originates only from the ternary nanocrystal composites, with



luminance performances matching the requirements of the lighting industry[42]. Bright white-light emission is obtained from homogeneous blends, without phase segregation between the active ternary QD composites and the organic matrix, exploiting the energy-transfer and charge trapping properties of the different species. The proposed approach is a new general method for the fabrication of high efficiency white-LEDs with potentially long operating lifetimes.

Recently, some IIVI semiconductor nanocrystals, such as CdSe and CdSe/CdS or CdSe/ZnS core/shell quantum dots (QDs), were used to fabricate white OLEDs by the method of doping polymers[43-46], and in some cases they were used as the sensitizer of a photorefractive polymer composite[47]. The advantages of the organic/inorganic composites may, on the one hand, utilize the stability of the inorganic nanoparticles and the tunability of emission wavelength, dependent on the size of QDs due to the quantum confinement effect, and on the other hand, merge with the flexibility and easy processing property of polymer materials; thus low cost hybrid white OLEDs with improved lifetime and colour stability can be achieved[48-53]. However, reports of hybrid white OLEDs based on QDs are rare. Knowing these facts, Ma *et al.* first time fabricated hybrid organic/inorganic white light-emitting diodes (LEDs) of semiconductor polymer poly(*N*-vinylcarbazole) (PVK) doped with CdSe/CdS coreshell semiconductor quantum dots (QDs)[54]. The collective emission of PVK and CdSe/CdS QDs due to the existence of incomplete energy transfer and charge transfer results in a fairly pure white OLED with Commission Internationale de L'Eclairage coordinates (CIE) (0.33, 0.34) at a wide range of applied voltages. It is found that the blue and red parts are originated from the emission of PVK, and the green part is then from

CdSe/CdS QDs. The maximum brightness and electroluminescence (EL) efficiency reached 180 cd/m<sup>2</sup> and 0.21 cd/A, respectively. To the best of our knowledge, this is the simplest structure and the best results so far reported for white OLEDs based on QD-doped polymer as the emitting layer with a stable Al cathode.

In connection to this, Park *et al.* obtained white emission from light-emitting diode prepared from polymer/quantum dot nanocomposites consisting of poly(9,9'-dihexyl fluorene-2,7-divinylene-*m*-phenylenevinylene-*stat-p*-phenylenevinylene) (PDHFPPV) and CdSe nanoparticles[55]. The partial energy transfer that occurs from the polymer to the quantum dots enables the quantum dots to emit red light and, in conjunction with blue light emitted from the polymer, the device generates white emission. The blue emitting matrix polymer also provides a simple device preparation process due to its high processability. This result suggests that the simple blending method can be employed to obtain polymer-based white LEDs.

## 5. Conclusion

I explained the syntheses of organometallic compounds, inorganic phosphors, quantum dots and their electroluminescent properties in this reviews. Inorganic phosphors have played a very important role to get white luminescence when used with blue and UV LEDs. Common approach is to use yellow phosphor with blue LED to get white emission. But because of one missing primary red color, the efficiency and CRI values of white emission are low. So in this approach, research should be devoted to synthesize new phosphors which simultaneously emit yellow and red light or some other color combination to solve this problem. Though getting white light from

UV-LED yields luminescence with improved spectral characteristics which renders color better, the Stokes shift is the larger and more energy is converted to heat. Therefore this approach is not efficient as well. Hence much work is needed in phosphor technology to achieve pure white emission.

The newest method to produce white light is application of quantum dots. Quantum dots phosphors offer high quality and low cost white LED relative to standard white light produced by traditional semiconductor system. The unique core-shell technology allows quantum dots phosphor to exhibit great stability and retaining high quantum yields in different environment. Organic dyes and common phosphors have poor photostability and short life time relative to quantum dots system. So, quantum dot technology for white electroluminescent devices will be a revolution in display market in near future.

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