

유기발광다이오드 조명용 유기발광체의 최근 동향

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Recent Progress on Organic Emitters for Organic Light Emitting Diode Lightings

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초 록

유기 발광 다이오드(OLED)는 학문 및 산업분야에서 많은 관심을 받고 있다. OLED는 이미 휴대폰과 TV분야에서 상업화에 성공하고 있으며, 조명분야에서는 기존에 사용되어왔던 백열등, 형광등과는 다르게 면발광, 대면적, 초경량, 초박형, 유연성의 특징은 물론 낮은 에너지 사용 등의 차별성을 가지고 있기 때문에 최근 많은 관심을 받고 있다. 본 논문에서는 white organic light-emitting diode (WOLED)에 적용되는 대표적인 형광 및 인광 발광 재료들을 소개한다. 이렇게 선행 연구된 물질들을 이해하고 체계적으로 분류하는 것은 앞으로 새로운 발광 재료를 연구, 개발하는데 큰 도움을 줄 수 있을 것으로 기대된다.

Abstract

Organic light-emitting diode (OLED) has drawn a lot of attention in academic and industrial fields, which has been successfully commercialized in mobile phones and TV's. In the field of lighting, unlike the existing incandescent or fluorescent lighting, OLED has distinctive qualities such as surface lighting-emission, large-area, lightweight, ultrathin, flexibility in addition to low energy use. This article introduces prominent fluorescent, phosphorescent, and luminescent materials applied to white OLED (WOLED). The understanding and systematic classification of previously studied substances are expected to be greatly helpful for the development of new luminous materials in future.

Keywords: organic light-emitting diode, lighting, emitter, fluorescence, phosphorescence

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable progress in both academic and industrial interests since the pioneering work by Tang et al. in 1987[1]. OLED has recently been commercialized in the mobile phone market, and intensive application attempts are being made for commercial applications in OLED TV and lighting. Accordingly, OLED is transforming into the mainstream of next-generation displays. Importance of OLED over existing liquid crystal displays (LCDs) stands out because of many advantages like flexibility,

self-emission, full-color emission, low driving voltage, and fast response time[2-7].

However, while the development of OLED process technology is needed for OLED to gain exclusive dominance in markets like TV and lighting, the development of a red, green and blue (RGB) emitter with high electroluminescence (EL) efficiency, good thermal property, and long device lifetime as well as pure color coordinates is essential for embodiment of high performance device.

Especially in case of the lighting market, OLEDs have area emission characteristics unlike existing light sources, showing excellent energy saving effect with environment-friendly lighting characterized by large area, ultra-light weight, and ultra-thin shape. There is an increasing importance of studies on application of OLEDs as the next-generation lighting to replace existing fluorescent and incandescent lamps[6]. In terms of technology such OLED lights can be divided into three color

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Table 1. Energy Levels of Blue Phosphorescent Host

| Emitter | HOMO (eV) | LUMO (eV) | E_T^a (eV) | T_g^b (°C) | Ref. |
|---------|-----------|-----------|--------------|--------------|------------|
| 1 | 6.3 | 2.8 | 2.6 | 62 | [11,29,30] |
| 2 | 5.9~6.1 | 2.4~2.5 | 2.9 | 55 | [12,22] |
| 3 | - | - | 3.0 | - | [13] |
| 4 | 5.9 | 2.4 | 2.95 | - | [14] |
| 5 | 5.7 | 2.2 | 2.95 | - | [15] |
| 6 | 5.8 | 2.6 | 2.88 | - | [16] |
| 7 | 6.0 | 2.6 | - | 111 | [17] |
| 8 | 6.1 | 2.6 | 2.8 | 10 | [17] |
| 9 | 5.89 | 2.40 | 2.76 | 115 | [18] |
| 10 | 5.96 | 2.43 | 2.77 | 123 | [18] |
| 11 | 6.10 | - | 2.9 | 101 | [19] |
| 12 | 6.12 | 2.56 | 3.01 | 148 | [20] |
| 13 | 6.0 | 2.5 | 3.02 | 131 | [21] |
| 14 | 5.9 | 2.5 | 2.97 | 163 | [22] |
| 15 | 6.1 | 2.6 | 3.0 | - | [23] |
| 16 | 6.31 | 2.77 | 3.02 | 123 | [24] |
| 17 | 6.25 | 2.75 | 2.81 | - | [25] |
| 18 | 6.21 | 2.64 | 3.0 | - | [26] |
| 19 | 6.10 | 2.58 | 2.94 | 128 | [27] |
| 20 | 6.09 | 2.57 | 2.92 | 115 | [27] |
| 21 | 6.69 | 2.99 | 2.96 | 100 | [27] |
| 22 | 6.08 | 2.56 | 3.00 | 110 | [28] |
| 23 | 6.09 | - | - | - | [28] |
| 24 | 6.68 | - | - | - | [28] |
| 25 | 7.2 | 2.8 | 3.5 | 26 | [29,30] |
| 26 | 7.2 | 2.8 | 3.5 | - | [29,30] |
| 27 | 7.2 | 2.8 | 3.5 | 46 | [30] |

^aTriplet energy level, ^bglass transition temperature

white OLED using red, green and blue emitter and two color white OLED using sky-blue, orange or sky-blue, red emitter[7-9]. Since low cost is regarded as important in the lighting field unlike the display field, studies are more actively conducted on two color white OLEDs with relatively simple structure. In addition, as emission spectrum of organic materials generally has broader wavelength than emission spectrum of inorganic materials, it is possible to manufacture white OLEDs applicable to lighting using two color combinations of sky-blue and orange or sky-blue and red.

Emitters applied to two color white OLEDs can be classified into fluorescence materials and phosphorescence materials. Fluorescence materials are materials that consist of polycyclic aromatic hydrocarbons advantageous for manufacturing long lifetime devices because of excellent stability, but maximum quantum efficiency of these materials is only 25% since they only use singlet. Phosphorescence materials can harvest both singlet and triplet, and it is theoretically possible to achieve internal quantum efficiency of 100%. These materials are advanta-

geous for manufacture of high efficiency devices, but stability of materials is relatively low and therefore results in disadvantageous device lifetime. Studies on two color white OLEDs include studies on devices that only consist of fluorescence materials and devices that only consist of phosphorescence materials, but they are more actively focusing on fluorescence & phosphorescence white OLEDs which combine advantages of the two materials.

In order to embody white OLEDs with high efficiency and long lifetime, emitters must be studied for high EL efficiency, good thermal property, and long device lifetime. In addition, such studies must be based on independent research and development on each material. In order to provide for fundamental understanding and directivity of research on emitting materials applicable to OLED lighting, this article classifies materials into fluorescence and phosphorescence materials and introduces information on characteristics and devices of each material.

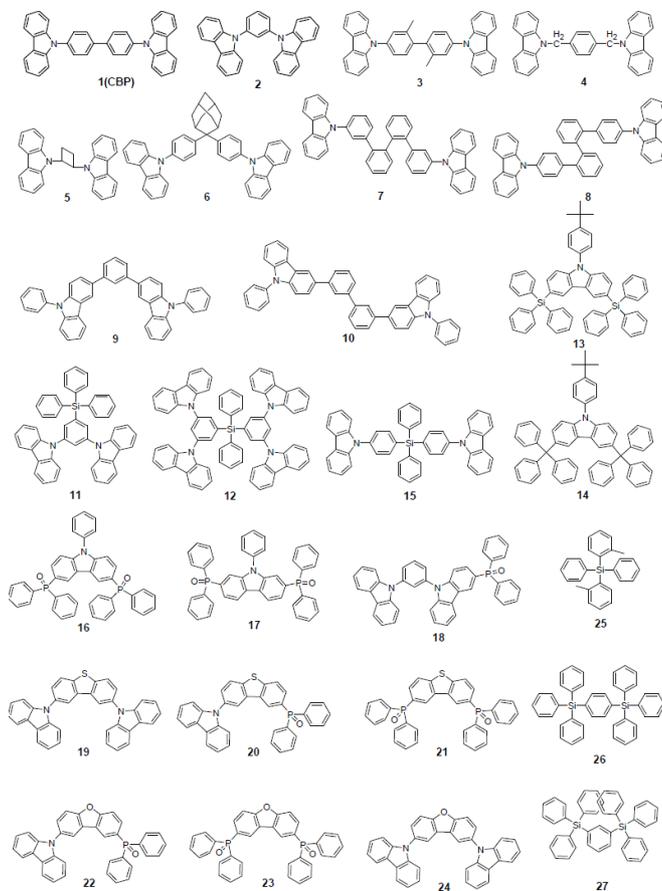


Figure 1. Chemical structures of blue phosphorescent hosts.

2. Phosphorescent Emitters

2.1. Phosphorescent blue host

Blue phosphorescent host materials are required to achieve high efficiency of lighting application of white OLEDs. Also, many studies are underway. Since triplet energy of blue phosphorescent dopant materials in general is 2.70~2.75 eV, host material should have higher triplet energy. When triplet energy of host material is lower than that of dopant material, back energy transfer can occur from the dopant to host. Such back energy transfer can consequently show disadvantages like triplet exciton quenching and low device efficiency. Therefore, blue phosphorescent host materials must have triplet energy of 2.75 eV or higher in order to prevent back energy transfer of exciton.

Representative core structures with high triplet energy include carbazole, arylsilan, dibenzofuran and dibenzothiophene. For the development of blue phosphorescent host materials with high triplet energy, it is not only necessary to have core structure but also to reduce conjugation length for wide band gap. For example, introduction of sp^3 carbon, silicon or phosphine oxide unit and introduction of sterically hindered structure can reduce the conjugation length of intramolecule. As mentioned earlier, since triplet energy is extremely important for improvement of device performance in blue phosphorescent host materials, we are going to focus on the introduction of phosphorescent host materials based on each core structure and their triplet energy.

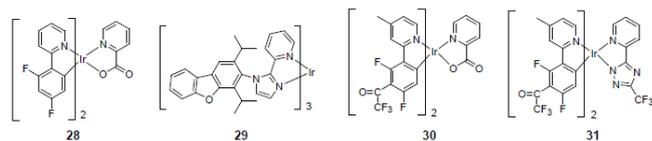


Figure 2. Chemical structures of blue phosphorescent dopants.

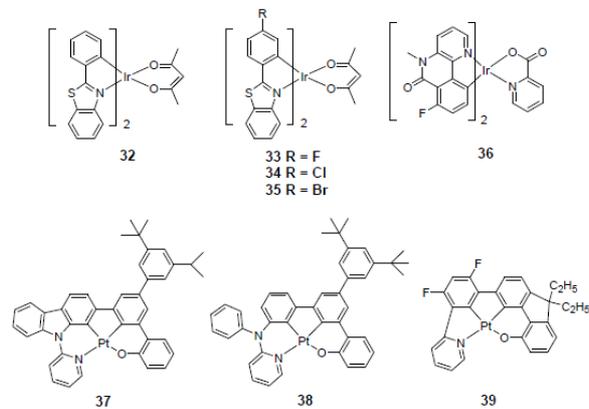


Figure 3. Chemical structures of yellow dopant materials.

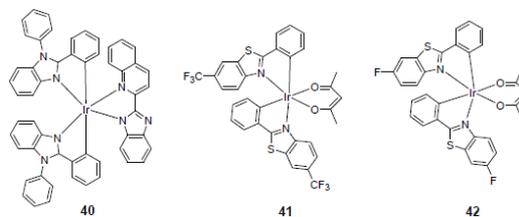


Figure 4. Chemical structures of Orange dopant materials.

Carbazole core has high triplet energy of 3.02 eV and hole transport properties, it can be used as a blue phosphorescent host materials[10]. Substitution position of carbazole or other units could affect on the triplet energy of the phosphorescent host material. Emitter 1, para-linked carbazoles with biphenyl, is the most widely used as a phosphorescent host material. However in case of emitter 1, triplet energy was smaller at 2.6 eV than 2.7 eV of emitter 28 used as the dopant. This system is hard to achieve high efficiency due to back energy transfer from emitter 28 to emitter 1[11]. In case of emitter 2, a derivative of carbazole that linked phenyl in meta position, high triplet energy of 2.9 eV was shown for wide band gap and use as blue phosphorescent host material[12]. Emitter 3, a derivative of carbazole that linked 2,2' position of biphenyl in para position, had similar chemical structure as emitter 1[13]. Triplet energy of emitter 3 was higher than emitter 1 at 3.0 eV. With the introduction of methyl group in biphenyl unit, emitter 32 was structurally distorted to maintain triplet energy of carbazole. Other phosphorescent host materials based on carbazole core such as emitter 4[14], emitter 5[15], emitter 6[16], emitter 7[17], emitter 9[18], and emitter 10[18] are summarized in Table 1.

Triphenylsilyl unit was introduced to the carbazole core and thermal stability could be improved without decreasing triplet energy of the materials. While glass transition temperature of emitter 2 was 55 °C, temperature of emitter 11 which substituted triphenylsilyl group into emitter 2 was increased to 101 °C[19]. Emitter 12 also showed high

Table 2. The Summary of the PL and EL Performance for the Emitters

| Emitter | CIE (x, y) | LE ^a (cd/A) | PE ^b (lm/W) | EQE ^c (%) | Reference |
|---------|--------------|------------------------|------------------------|----------------------|-----------|
| 50 | (0.15, 0.09) | 2.63 | 1.96 | 5.17 | [44] |
| 51 | (0.15, 0.12) | 5.60 | 5.70 | 5.10 | [45] |
| 52 | (0.15, 0.30) | 7.90 | 6.80 | - | [46] |
| 53 | (0.15, 0.17) | 8.44 ^d | 4.67 ^d | 6.83 ^d | [47] |
| 54 | (0.15, 0.20) | 10.90 ^d | 5.42 ^d | 7.72 ^d | [47] |
| 55 | (0.15, 0.25) | 11.20 ^d | 4.87 ^d | 7.34 ^d | [48] |
| 56 | (0.15, 0.19) | 9.45 ^d | 4.69 ^d | 7.15 ^d | [48] |
| 57 | (0.15, 0.20) | 9.79 ^d | 4.86 ^d | 7.35 ^d | [48] |
| 58 | (0.15, 0.22) | 9.12 ^d | 4.23 ^d | 6.34 ^d | [48] |
| 59 | (0.15, 0.24) | 10.10 ^d | 4.66 ^d | 6.66 ^d | [48] |
| 60 | (0.14, 0.18) | 7.79 | 4.33 | 6.54 | [49] |
| 61 | (0.13, 0.17) | 8.56 | 4.61 | 7.32 | [49] |
| 62 | (0.14, 0.16) | 9.11 | 6.13 | 8.16 | [49] |
| 63 | (0.14, 0.15) | 8.11 | 5.12 | 7.45 | [49] |
| 64 | (0.17, 0.08) | 4.90 | - | 6.10 | [50] |
| 65 | (0.16, 0.08) | 5.30 | - | 6.70 | [50] |
| 66 | (0.16, 0.07) | 5.40 | - | 6.80 | [50] |
| 67 | (0.15, 0.11) | 5.20 | 1.90 | 5.20 | [51] |
| 68 | (0.15, 0.24) | 10.50 | 4.00 | 6.40 | [52] |
| 69 | (0.16, 0.11) | 4.90 | - | 8.60 | [53] |
| 70 | (0.16, 0.11) | 4.90 | - | 8.60 | [53] |
| 71 | (0.15, 0.14) | 7.47 | 7.30 | 6.31 | [54] |
| 72 | (0.15, 0.15) | 6.40 | 3.84 | 5.26 | [54] |
| 73 | (0.15, 0.10) | 5.76 | 2.19 | 5.98 | [54] |
| 74 | (0.15, 0.07) | 1.72 | 0.65 | 5.10 | [55] |
| 75 | (0.13, 0.21) | 10.01 | 4.90 | 6.90 | [56] |
| 76 | (0.15, 0.11) | 5.66 | 6.13 | 5.02 | [57] |
| 77 | (0.14, 0.09) | - | 4.20 | 5.40 | [58] |
| 78 | - | - | 12.0 | 3.10 | [62] |

^aLuminance efficiency. ^bPower efficiency. ^cExternal quantum efficiency. ^dValues collected at 20 mA cm⁻².

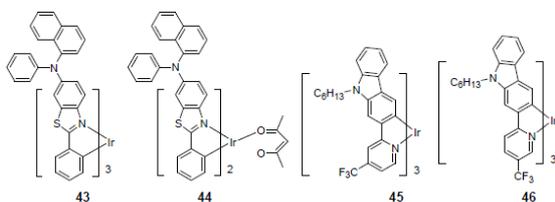


Figure 5. Chemical structures of red dopant materials.

glass transition temperature of 148 °C[20]. The triplet energy of emitter **11** was 2.90 eV and the triplet energy of emitter **12** was 3.01 eV. Emitter **13**[21], emitter **14**[22] and emitter **15**[23] were also developed by adopting phenyl carbazole with triphenylsilyl or diphenylsilane. Those materials showed high triplet energy and high glass transition temperature.

Host materials with high triplet energy and charge transport characteristics were developed by introducing moieties such as dibenzothio-

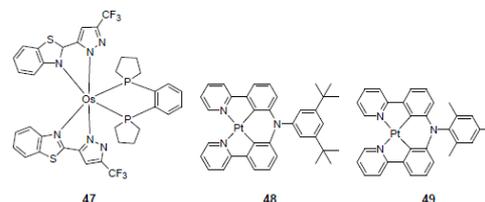


Figure 6. Chemical structures of red dopant materials.

phene core and dibenzofuran core in addition to phosphine oxide unit. Phosphine oxide unit could enhance electron transport properties without decreasing triplet energy of core structure. Emitter **16** including two diphenylphosphine oxide units at 3,6 position of phenyl carbazole showed high triplet energy of 3.02 eV and balanced charge transport properties[24]. Emitter **17** which substituted diphenylphosphine oxide units in 2,7 position of phenyl carbazole showed lower triplet energy and band gap than emitter **16**[25]. Emitter **18** which substituted diphe-

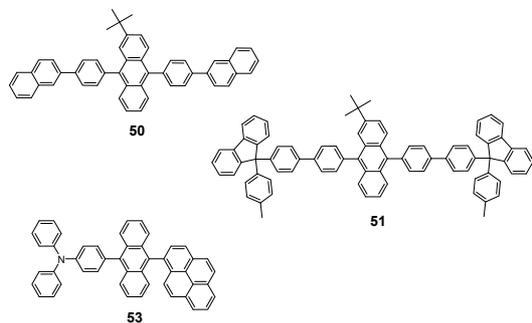


Figure 7. Chemical structures of symmetric or asymmetric DPA derivatives.

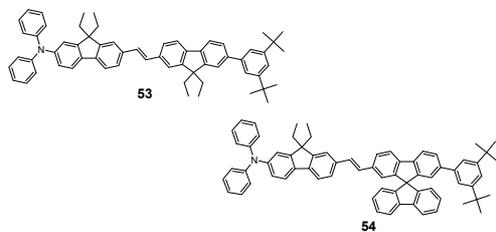


Figure 8. Chemical structures of fluorene derivatives including bulky tert-butyl group.

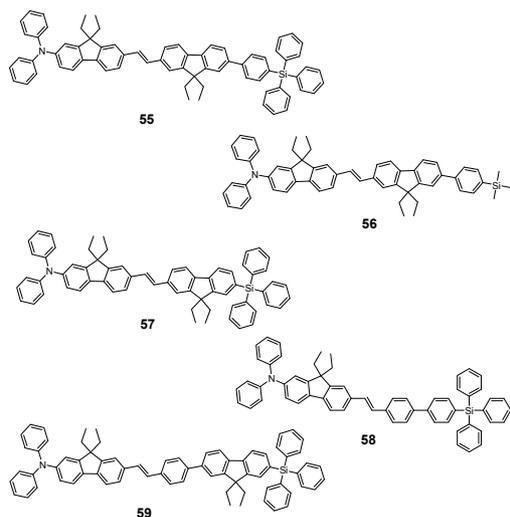


Figure 9. Chemical structures of fluorene derivatives including bulky silicon group.

nylphosphine oxide unit into emitter **2** had similar triplet energy as emitter **2** with improved electron transport properties[26]. Host materials with high triplet energy and bipolar charge transport ability were developed by substituting carbazole and diphenylphosphine oxide moiety into dibenzothiophene core or dibenzofuran core. High triplet energy host materials of emitter **19**, emitter **20**, and emitter **21** were synthesized and charge transport properties were compared[27]. Emitter **20** having one carbazole and diphenylphosphine oxide unit in dibenzothiophene core showed bipolar charge transport properties. Dibenzofuran derivatives of emitter **22**, emitter **23**, and emitter **24** were studied by manufacturing devices with single or mixed host structure[28].

Host materials of tetraphenylsilane core were synthesized to get high triplet energy. Host materials that use Si atom to disconnect con-

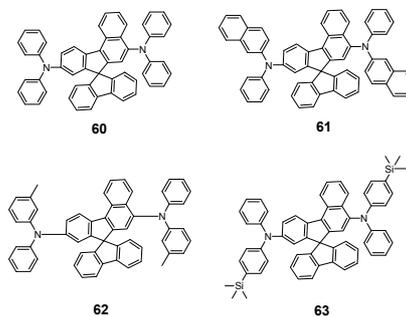


Figure 10. Chemical structures of spirofluorene derivatives.

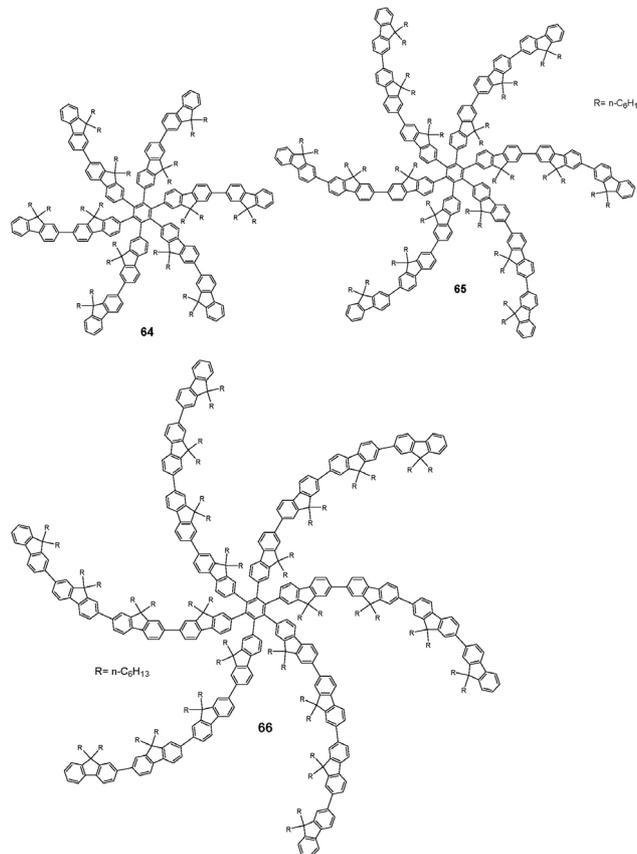


Figure 11. Chemical structures of oligofluorene derivatives with propeller-like core.

jugation of phenyl units could increase band gap and triplet energy. Emitter **25**[29,30], emitter **26**[29,30] and emitter **27**[30] were developed by changing substitution positions and showed high triplet energy. But, deep HOMO level of emitter **25**, emitter **26** and emitter **27** limits hole injection from hole transport layer to emitting layer and causes increase of driving voltage.

2.2. Phosphorescent blue dopant

Emitter **28** is a blue phosphorescent dopant very well known as Firpic. However, many efforts for improvement were made as emitter **28** has greenish blue wavelength and short lifetime. Zhou's group developed emitter **29**, a homoleptic tricyclic metalated iridium(III) complex in which ligand is substituted as a type, to compare its EL perfor-

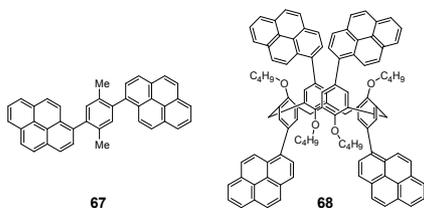


Figure 12. Chemical structures of pyrene derivatives.

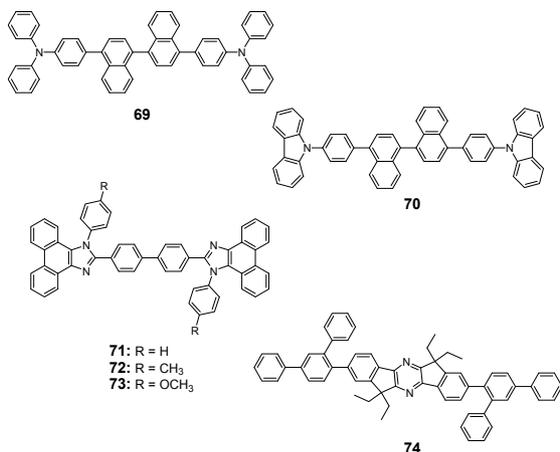


Figure 13. Chemical structures of other categorized blue fluorescent emitters.

mance with emitter **28**[31]. While properties of a device that used emitter **28** were LE (luminance efficiency) of 30.5 cd/A, PE (power efficiency) of 20.7 lm/W and EQE (external quantum efficiency) of 13.5%, a device that used emitter **29** showed improved efficiency with LE of 61.5 cd/A, PE of 43.7 lm/W and EQE of 23.1%. In addition, lifetime of the device that used emitter **29** was 5.8 h, which is relatively longer than 0.1 h of the emitter **28** device. Nonetheless, the device that used emitter **29** had Commission Internationale de L'Eclairage coordinates (CIE) value of (0.19, 0.44), which is more greenish blue compared to (0.16, 0.36) of the device that used emitter **28**. Kim's group developed emitter **30** and emitter **31** as perfluoro carbonyl-substituted iridium complex for the development of phosphorescence blue dopants with high efficiency and deep blue emission[32]. The device that used emitter **59** had LE of 21.7 cd/A, PE of 19 lm/W and high EQE of 17.1%, as well as CIE value of (0.141, 0.158) showing deeper blue emission compared to emitter **57**. Also, emitter **60** had CIE value of (0.147, 0.116) in the deeper blue region.

2.3. Phosphorescent yellow dopant

In 2013, Dongge Ma and Chuluo Yang's group developed a new iridium complex[33]. The synthesized material was systematically studied for optoelectronic properties according to halogen atoms (F, Cl, Br) in ligand. While the synthesized material in emitter **32** where halogen was not substituted showed LE of 69.7 cd/A and PE of 69 lm/W, Ir complex substituted with halogen atom showed PE in the range of 55.9-83.2 lm/W. In particular, emitter **33** substituted with F atom had LE of 76.8 cd/A and PE of 83.2 lm/W in yellow emission of CIE (0.45, 0.53), showing improved device efficiency compared to emitter

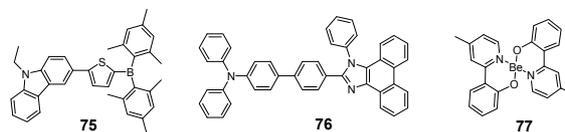


Figure 14. Chemical structures of donor/acceptor type derivatives and organometallic derivatives.

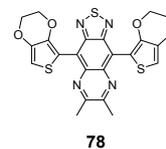


Figure 15. Chemical structures of red fluorescent emitter.

32 without halogen substitution.

In 2014, Jwo-Huei Jou's group developed a new yellow emitting iridium complex that can be manufactured by wet process and dry process[34]. As shown in Figure 12, the synthesized material showed high EQE of 71% by blocking molecular packing, the cause of self-quenching, by substituting hydrogen in 2 position with fluorine. In case of dry process using vapor deposition, high efficiency was found with EQE of 22.6% and PE of 75.1 lm/W. When the device was manufactured using wet process of spin coating method, highest efficiency was shown among yellow devices manufactured by wet process with EQE of 18.5 % and PE of 52.3 lm/W.

In 2013, Chi-Ming Che's group synthesized a new derivative of platinum(II) complex with dianionic tetradentate ligand (see Figure 12)[35]. Among the synthesized materials, emitter **37** showed high efficiency with quantum yield of 86% in solution state. When manufactured into a device, PE of 52 lm/W was shown in yellow emission of EL_{max} 568 nm and CIE (0.52, 0.47). When emitter **28** was used as a blue dopant and applied to two color white OLED, high efficiency was reported with CIE (0.34, 0.44) and PE of 61 lm/W[36]. Later on in 2014, emitters **38** and **39** in Figure 12 were synthesized by modifying Pt(II) complex presented before. In case of emitter **38**, extremely high efficiency of yellow emission was shown with PE of 118 lm/W and EQE of 26%. Also, emitter **39** was applied to white OLED as a single emitter to show CIE (0.38, 0.47) and EQE of 25.1%.

2.4. Phosphorescent orange dopant

In 2013, Wenfa Xie group synthesized emitter **40** with orange emission of 573 nm[37]. The synthesized material showed high efficiency with LE of 20.2 cd/A and PE of 23.6 ml/W for CIE (0.53, 0.46). Especially in white OLED structure of ITO/MoO₃ (3 nm)/TAPC (30 nm)/TCTA (5 nm)/POAPF : emitter **40** (7%) (6 nm)/POAPF : FIr6 (10%) (24 nm)/BmPyPhB (35 nm)/Liq (1 nm)/Mg : Ag that used a dopant called FIr6, LE of 22.1 cd/A, PE of 25.5 lm/W and color rendering index (CRI) of 80 were close to the standard white emission CIE (0.33, 0.36).

In 2011, Jiuyan Li group developed an orange emitting material as iridium complex with new 2-phenylbenzothiazole ligand[38]. Emitter **41** material showed extremely high efficiency for CIE (0.52, 0.47) with LE of 76 cd/A and PE of 45 lm/W. Moreover, two color emission

white OLED manufactured with structure of ITO/PEDOT : PSS (40 nm)/orange phosphor : emitter **1** (1 wt%, 10 nm)/ emitter **28** : emitter **1** (10 wt%, 20 nm)/TPBI (45 nm)/LiF (1 nm)/Al using emitter **28** as blue emitter showed CIE (0.35, 0.44), LE of 68.6 cd/A and high EQE of 26.2%.

2.5. Phosphorescent red dopant

In 2012, Jiuyan Li's group synthesized a new iridium complex that used 2-phenylbenzothiazole bonded with *N*-phenyl-naphthyl as ligand (emitter **43**, **44** in Figure 14)[39]. As a result of manufacturing devices with the synthesized material using emitter **1** as host and emitters **43** and **44** as dopants, emitter **43** and emitter **44** in 5% doped device respectively showed CIE (0.56, 0.44) and (0.60, 0.40), exhibiting red emission of extremely high efficiency with PE of 6.56, 7.38 lm/W and EQE of 6.49, 8.73%. In addition, as a result of manufacturing white OLED device with ITO/PEDOT : PSS (40 nm)/emitter **44** (0.5 wt%) : emitter **28** (8 wt%) : emitter **1** (60 nm)/TPBI (45 nm)/LiF (1 nm)/Al structure, PE of 5.49 lm/W and EQE of 4.9% were shown, obtaining values close to real white emission with CIE (0.33, 0.35).

In 2012, Martin R. Bryce's group synthesized many new Ir complexes based on carbazolyl pyridine ligand (see Figure 14)[40]. Among the synthesized materials, emitter **45** and **46** showed red emission with photoluminescence (PL)_{max} of 637 and 633 nm, respectively. As a result of applying these materials in a simple device of (ITO/PEDOT : PSS-HIL 1.5 (60 nm)/PVK : PBD : Ir complex (90 nm)/Ba (4 nm)/Al (100 nm)) using solution process of spin coating method, high efficiency was shown with PE of 0.6~1.1 lm/W and EQE of 4~5.8%.

Many existing red emission phosphorescence dopants having high efficiency used Ir complexes such as Ir(piq)₃ (tris[1-phenylisoquinolino-C2,N]iridium(III))[41]. However, new phosphorescence red dopants have recently been developed using heavy metals.

In 2012, Pi-Tai Chou's group developed emitter **47** with new 3-(thiazol-2-yl), 3-(benzothiazol-2-yl), 3-(imidazol-2-yl) and 3-(benzimidazol-2-yl)azole chelate[42]. Os(II) complexes exhibit green to red emissions depending on the substituted group as shown in Figure 15. Especially, emitter **47** was applied to a device of ITO/PEDOT : PSS/VB-FNPD/TCTA : emitter **47**/TPBi/CsF/Al structure and showed red emission of CIE (0.63, 0.37), yielding LE of 18.3 cd/A, high PE of 17.6 lm/W and excellent EQE of 15.6%.

In 2012, Hirohiko Fukagawa's group synthesized new platinum complexes that exhibit red emission as shown in Figure 15[43]. As a result of manufacturing a device with ITO/ND-1501 (30 nm)/*a*-NPD (50 nm)/Bebq₂ : dopant (6 wt% doped, 35 nm)/ETM-143 (40 nm)/LiF (1 nm)/Al (100 nm) structure using Beq₂ as host, emitter **48** and emitter **49** respectively showed red emission of CIE (0.66, 0.33) and CIE (0.65, 0.34). Emitter **48** and emitter **49** showed higher efficiency than existing Ir complexes by respectively showing PE of 20.7 lm/W and 25.2 lm/W, and maximum EQE of 18.5% and 18.2%. High device stability was shown with device lifetime of 8,200 h and 15,000 h at 1000 cd/m².

3. Fluorescent Emitters

3.1. Blue Fluorescent Emitters

Blue emitting material is essential to the investigation of white OLED lighting. It has been difficult for blue fluorescent counterparts to achieve high-performance properties because their intrinsically wide band gaps of HOMO-LUMO energy levels make it hard to inject the hole and electron charges migrated from the adjacent hole and electron transporting layers into the emitting layers, which consequently leads to low EQEs. For this reason, up until now, more enthusiastic and comprehensive efforts have been made to develop high-performance fluorescent blue emitting materials. Among the various blue fluorescent emitting materials developed under this effort, polycyclic-, donor/acceptor- and organometallic-types of emitting materials have prominently demonstrated highly efficient EL properties with high quality of blue emission colors.

3.1.1. Polycyclic-type Emitters

Polycyclic aromatic hydrocarbons (PAHs) (or fused π -conjugated rings) such as anthracene, fluorene, pyrene, etc have been widely employed as building blocks for the design of blue fluorescent emitting materials, owing to their excellent photoluminescent and thermal properties as well as wide band-gaps. Very recently, more considerable attempts have been undertaken for sophisticated refinement of these polycyclic emitters to improve their EQEs further.

Anthracene. Among these PAH molecules, anthracene derivatives have been intensively investigated for use as the blue fluorescent emitting materials in high-performance OLEDs. In particular, 9, 10-diphenylanthracene (DPA) functionalities have been considered to be the most attractive molecular skeleton to develop high-performance blue emitting materials because the non-planar structure resulting from the end-capped phenyl rings at the 9- and 10- positions of the central anthracene unit efficiently suppresses the intermolecular interactions leading to PL quenching by concentration of emitting materials in the film state. Unfortunately, however, DPA itself tends to be crystallized during device operation, which could produce rough surfaces and grain boundaries leading to the fatal problems such as pin holes and current leakages, ultimately catastrophic device failures.

In order to improve the amorphous behaviors of DPA molecules by preventing the close molecular packing, Zhang, Lee and co-workers[44] introduced more bulky groups, *tert*-butyl units, at the C2 position of the anthracene moiety and simultaneously naphthyl units into the DPA backbone as side groups, respectively (emitter **50**, PLQY = 0.76 for solution). The non-doped emitter **50**-based OLED exhibited a saturated deep blue emission at EL maximum peak of 444 nm with a CIE (0.15, 0.09). Especially, this device exhibited the maximum EQE of 5.17% at 8.4 mA/cm² with a luminance of 221 cd/m². The high color purity and excellent EQE confirmed that the non-coplanar molecular structure of the emitter **50** can effectively prevent the intermolecular aggregations in the solid film state.

Shu and co-workers[45] have also reported that the sterically bulky aryl end-capping group, phenyl-substituted fluorene, for DPA, provides

an effective handle to prevent the close molecular packing. Furthermore, due to these bulky end groups leading to weak intermolecular interactions, the emitter **51** exhibited excellent photoluminescence quantum yield (PLQY) both in the solution and in the film state (PLQY = 0.93 and 0.84 for solution and film, respectively) without the excimer formation. Accordingly the emitter **51**-based non-doped OLEDs had high maximum values of EQEs reaching as high as 5.1% (5.6 cd/A) at 7.8 mA/cm² with CIE located at $x = 0.15$ and $y = 0.12$ which is very close to the National Television System Committee (NTSC) pure blue color.

Contrary to the symmetric DPA structure of the emitter **50** and **51**, Zhang, Lee and co-workers[46] developed the asymmetric bulky DPA derivative, the emitter **52** (PLQY = 0.48 for solution), by introducing different bulky end-groups, pyrene and triphenyl amine moieties, at the 9- and 10-positions of the anthracene core. The end-groups in the emitter **52** were expected to have an additional functionality, *i.e.*, efficient hole transportation, because the triphenylamine enables to improve the hole injection and carrier transport properties. The emitter **52**-based device showed highly efficient sky-blue emission ($x = 0.15$, $y = 0.30$) with a maximum efficiency of 7.9 cd/A (6.8 lm/W) in a non-doped device structure. In this device, the turn-on voltage (2.9 V) was also very low because the low energy barrier between hole transporting layer (HTL) and the emitter **52** (HOMO = 5.63 eV) facilitates the efficient hole injection from HTL. More interestingly, even without the layer of HTL, the emitter **52**-based non-doped device still had a high maximum efficiency of 6.1 cd/A with a CIE (0.15, 0.28).

Fluorene. Fluorene derivatives including spiro-type fluorenes have been also proven to be attractive building units for blue fluorescent emitting materials due to their high versatilities such as an excellent PL property, a good thermal and morphological stability, and a simple structural modification for tuning optical properties. The simple fluorene derivatives, however, are susceptible to produce undesirable green emissions with a PL quenching which are attributed to the excimer emission arising from aggregates in the film state or the generation of fluorene defects from oxidation.

In order to address the color purity and PL quenching problems of fluorene emitting materials even at high doping concentrations, Yoon, Lee and co-workers[47] have reported a newly designed deep-blue fluorene emitting materials, based on 2-(diphenylamino)fluoren-7-ylvinylarene derivatives (emitter **53** and **54**) where the diphenylamino fluorene core is combined with a vinylarene unit to obtain a deep-blue emission and the *tert*-butyl-based blocking group is end-capped to prevent the intermolecular interactions. From the quantum-mechanical calculations, it was revealed that the structure of the emitter **53** (PLQY = 0.81 for solution) and **54** (PLQY = 0.97 for solution) are non-planar. The calculated dihedral angles between fluorene (spirofluorene) and the end-capped substituents were found to be 37.9 and 37.4°, respectively. The OLED devices based on the emitter **53** and **54** with 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) as a host material showed a highly efficient sky blue emission ($x = 0.15$, $y = 0.17$ and 0.20 for the emitter **53** and **54**, respectively) with the EQE of 6.86 % and 7.72% at 20 mA/cm², respectively.

Interestingly, it was also found that the introduction of the bulky silicon moieties into the backbone of 2-(diphenylamino)fluoren-7-ylvinylarene as an end-capping unit provides an additional functionality for highly efficient and deep-blue OLED devices[48], *i.e.*, these bulky silicon groups play an important role not only minimizing the intermolecular interactions but also forming thermally stable and pin-hole free amorphous thin film through steric and electronic effects (emitter **55-59**). In the optimized OLEDs using the emitter **55-59** (PLQY **55** = 0.77, **56** = 0.81, **57** = 0.84, **58** = 0.83, **59** = 0.73 for film) as a dopant, owing to the steric effect, the silicon end-capping groups efficiently prevent molecular aggregation even at high doping concentration, and thereby minimize a serious self-quenching effect of the emitting materials in the devices. Accordingly these devices exhibited excellent luminescence of 15170~35500 cd/m² and EQEs of 5.76~7.35% with CIE (0.15, 0.19~0.25). In addition, it was revealed that the devices using the emitting material with the triphenylsilyl end-capping groups show the better long-term stability than the devices with the trimethylsilyl end-capping group.

Gong and co-workers[49] designed a different series of spirofluorene derivatives bearing bulky arylamine groups as steric end-capping groups to expect to prevent effectively intermolecular interactions. The optimized geometry obtained from density functional theory (DFT) calculations indicated that the fluorene and benzofluorene in the emitter **60-63** (PLQY **60** = 0.75, **61** = 0.66, **62** = 0.74, **63** = 0.67 for solution) are significantly twisted against each other owing to the spiro centre, resulting in the non-coplanar structure which effectively prevents intermolecular interactions and, thereby, suppresses the molecular recrystallization and aggregation quenching. As a result, the OLED devices based on these emitting materials using a MADN as a host material exhibited astonishingly high maximum EQEs in the range of 6.54~8.16% with blue EL emissions (EL λ_{\max} of 462~465 nm).

Aiming to develop a highly efficient deep-blue fluorescent fluorene derivatives with a high color purity for non-doped solution-processed OLEDs, Yang, Ma and co-workers[50] designed several series of star-shaped oligofluorenes with a propeller-like core, the emitter **64-66** (PLQY **64** = 0.82 and 0.74, **65** = 0.82 and 0.81, **66** = 0.92 and 0.84 for solution and film, respectively). The author emphasized that grafting six fluorene moieties to benzene core not only constructs a star-shaped architecture, but also generates a highly twisted molecular structure, which contributes to highly efficient pure blue emissions. The good solubility and good film-forming capability enabled these emitting materials to fabricate the solution-processable highly efficient deep blue OLEDs. The simple double-layer OLEDs based on the emitter **64-66** displayed a deep-blue emission with CIE coordinates ($x = 0.16$ ~0.17, $y = 0.07$ ~0.08) and exhibited excellent maximum EQEs of up to 6.8%.

Pyrene. Despite very attractive deep blue emission colors in solution, pyrene and its analogues have a difficulty in directly utilizing as an emitting material for highly efficient blue OLEDs because they have a great propensity to aggregate and to form excimers in the film state, leading to a substantial red-shift of fluorescence emission and a decrease of the efficiency. Therefore, it is desirable to suppress the strong

tendency towards the facial π - π stacking of the pyrene moieties.

In an attempt to address this issue, Cheng and co-workers[51] designed a dipyrenyl benzene derivative, the emitter **67** (PLQY = 0.34 and 0.75 for solution and film, respectively), which adopts a twisted geometry with inter-ring torsion angles of 63.2° in the crystal state. The twisted structure is responsible for the low degree of aggregation or crystallization in the solid state leading to the highly emissive property in the solid state with good film-forming capability. The device reached the maximum efficiency of 5.2% and a very high luminance of $40,400 \text{ cd/m}^2$ with CIE (0.15, 0.11).

Chan, Sellinger and co-workers[52] explored a new type of pyrene derivative, pyrene-functionalized calix[4]arene (the emitter **68**), where pyrene units are attached to the three-dimensional 1,3-alt-calix[4]arene scaffold. The 3D scaffold played a pivotal role in forcing intramolecular pyrene units to be arranged radially orthogonal each other, thus ensuring the complete suppression of pyrene aggregation in the solid state. The device provided an excellent EQE of 6.4% at $1,460 \text{ cd/m}^2$ with CIE coordinates ($x = 0.15$, $y = 0.24$). The remarkable EL efficiency of the emitter **68** was attributed to the unique ability of the 1,3-alt-calix[4]arene scaffold at dispersing pyrene moieties that are prone to the aggregation and the concentration quenching of the excited state.

Etc. Gao and co-workers[53] have demonstrated that the binaphthyl-type PAH is also a versatile molecular backbone to generate a high-performance blue EL emission. In the emitter **69** (PLQY = 0.81 for solution) and **70** (PLQY = 0.84 for solution), the binaphthyl core units are incorporated with the arylamine groups as end-capped units. The bulky binaphthyl units made these emitting materials possess a non-coplanar configuration which decreases the tendency of crystallization and weakens intermolecular interactions in the solid state, hence leading to their pronounced morphological stability (amorphism) and high efficiency. The OLED with the emitter **69** doped in the emitter **70** as the emitting layer (EML) exhibited a pure and deep-blue EL emission (444 nm) with a CIE (0.16, 0.11), and their EQE reached 8.6% at 0.87 mA/cm^2 .

In order to realize the highly efficient non-doped blue OLEDs having both high EQEs and high power efficiencies by effectively improving the injection of charge carriers into the emissive layers from the adjacent layers, Liu and co-workers[54] employed a specific *n*-type imidazole derivative, phenanthroimidazolyl (PTI) moiety, as OLED emitting materials. By using this building block, they developed a new series of blue emitting materials, the emitter **71-73** (PLQY **71** = 0.58, **72** = 0.54, **73** = 0.48 for solution), in which the phenyl substituents attached to the PTI groups are highly twisted around the PTI groups with dihedral angles of about 85° , while the inter-ring torsion angles between the biphenyl group and two PTI groups are about 30° in the single crystal state. The non-doped OLEDs based on these emitting materials gave very high EQEs (5.26~6.31%) and pure blue emission with CIE (0.15, 0.09~0.15). In particular, among these devices, the emitter **71**-based device resulted in a very low turn-on voltage (3.0 V) and a high PE of 7.30 lm/W .

Taking advantages of the characteristic optical properties of indenopyrazine units such as highly pure blue colors with a narrow full

width at half maximum (FWHM), Park and co-workers[55] developed a new indenopyrazine derivative, the emitter **74** (PLQY = 0.51 for film), with bulky aryl side groups. The emitter **74** showed a distinctive blue emission (444 nm) originating from the indenopyrazine core in the film state. The authors pointed out that the introduction of electron-accepting imine group into the core of the π -conjugated backbone stabilizes and reduces the LUMO level, and thus drastically facilitates the electron injection and electron transporting capabilities. Non-doped OLED device based on the emitter **74** exhibited a blue EL emission at 453 nm with a narrow FWHM (47 nm) (CIE (0.15, 0.07)) and highly efficient EQEs of 5.1%.

3.1.2. Donor/Acceptor Type Emitters

The incorporation of electron-donor (D) and electron-acceptor (A) moieties into the emitting materials has been considered as one of the promising molecular design strategy for enhancing EQEs of OLEDs because it endows the emitting materials with facilitating exciton formation (via stable radical cations and anions) and improving the charge balance in the emitting layers of OLEDs. However, the D-A bipolar system tends to produce the charge-transfer (CT) features from the donor unit to the acceptor unit which could cause a large bathochromic effect, and thus, impair the color purity of the blue emission. Especially, considering the intrinsic wide band gap character of the blue emitting materials, it is a great challenge to develop highly efficient blue emitting materials for OLEDs by utilizing D-A bipolar systems.

Kuo and co-workers[56] successfully explored a new D-A bipolar fluorescence chromophore, the emitter **75** (PLQY = 1.00 and 0.51 for solution and film, respectively), for highly efficient blue OLEDs by combining a carbazole donor and a dimesitylborane acceptor into one π -conjugation (electron-rich thiophene ring as a bridge unit) system. The non-doped OLEDs based on the emitter **75** showed a blue EL emission ($\lambda_{\text{max}} = 473 \text{ nm}$, CIE (0.13, 0.21)) without any exciplex formation between the emitter **75** and HTL material, and very highly efficient maximum EQEs of 6.9%. It was pointed out that all the three essential units, carbazole, dimesitylborane and thiophene, in the emitter **75** play an important role in obtaining highly efficient blue OLEDs.

Yang, Ma and coworkers[57] have reported an effective way to construct highly efficient blue OLEDs by using a twisting D-A molecule, the emitter **76** (PLQY = 0.90 and 0.90 for solution and film, respectively), comprising of two main components, triphenylamine as the donor moiety and 1,2-diphenyl-1H-phenanthro[9,10-d]imidazole (PPI) as the acceptor. In spite of CT-type molecules, very rarely, the emitter **76** showed a deep blue emission (EL_{max} of ca. 440 nm) with very high PLQYs of 90% in both the solution and the film state. In addition a non-doped OLED with the emitter **76** had not only an excellent deep-blue EL performance (CIE (0.15, 0.11)), but also a maximum EQE of 5.02%.

3.1.3. Organometallic-type Emitters

Although considerable progress has been made on the development of a variety of metal-complex phosphorescent emitting materials for

high-performance OLEDs, few metal complex-type fluorescent emitting materials, especially for blue emitting materials, have been developed and investigated so far.

Recently Liu, Wang and co-workers[58] have reported that a simple structural modification of the organometallic-type blue emitting material can dramatically improve its electroluminescent properties. They introduced sterically hindered methyl unit onto the pyridyl ring of the ligand in the original beryllium complex, bis(2-(2-hydroxyphenyl)-pyridine)beryllium (Bepp2), and therefore prepared a novel beryllium complex, the emitter **77** (PLQY = 0.55 for solution), for highly efficient non-doped blue OLEDs. In the non-doped double layered OLED device based on the emitter **77**, a high quality of blue emission (CIE (0.14, 0.09)) was achieved because the introduced methyl unit effectively prevented the possible exciplex formation with a hole transporting material. And the EQE of this device surprisingly reached 5.4% at 370 cd/m².

3.2. Red Fluorescent Emitters

Owing to the inherent low PLQYs from the red fluorescence chromophores, the red fluorescent emitter materials exceeding EQEs of 5% have been rarely found in the recent official papers.

Although it was not an academic paper, an industry report of Idemitsu Kosan in 2007 announced high efficiency red fluorescence data with efficiency of 11.4 cd/A and device lifetime of 160000 hours. However, this report will be omitted in this review as specific chemical structure of this data was not provided[59]. Nevertheless, Xue and co-workers[60] have reported a high-performance near-IR OLED based on donor-acceptor-donor conjugated oligomer, the emitter **78**, which has a narrow band gap (ca. 1.9 eV) by combining strong donors (dihydrothieno dioxin (BEDOT)) with a strong acceptor (thiadiazolo quinoxaline (TQ)). The emitter **78** had a PL maximum at 698 nm and its PLQY was measured to be 21% in solution. The emitter **78**-based OLED with 3.5 wt% doping concentration in the EML showed a maximum EQE of 1.6%. Notably, however, the EQE of device was further enhanced by almost two times (EQE = 3.1%) by incorporating a phosphorescent Ir(ppy)₃ sensitizer in the EML together with the host and the emitter, so-called the sensitized fluorescent OLED device architecture, which harvests both singlet and triplet excitons, and transfers them to the emitter **78** through Förster-type energy transfer process. Unfortunately, the maximum EQE of only 1.6% was obtained for the device with a 5 wt% doping concentration of the emitter **78** because of the inevitable aggregation-induced fluorescence quenching. Results of studies on thermally activated delayed fluorescence (TADF) have recently been presented with the Adachi's group at the center, showing active studies and results on high efficiency red fluorescent materials. As a representative case, 4,4',4''-(1,3,3a',4,6,7,9-heptaazaphenylene-2,5,8-triyl)tris(N,N-bis(4-(tert-butyl)phenyl)aniline) is a TADF material studied based on heptazine structure that showed effective TADF phenomenon using small ΔE_{st} with energy difference of 0.27 eV between S1 and T1, yielding high EL efficiency of 25.9 cd/A and EQE of 17.5%[61]. In addition, as a result of synthesizing 2,6-bis[4-(diphenylamino)phenyl]anthraquinone based on anthraquinone and applying it as a

dopant in a device, EL maximum of 624nm and CIE (0.16, 0.39) were exhibited with extremely high EQE of 12.5%. However, the results for lifetime of these materials have not yet been reported[62].

4. Conclusions

White OLED is drawing a lot of attention in industrial and academic fields. The field of lighting urgently needs the next-generation lighting with high efficiency and long service life that can replace fluorescent lighting and incandescent lighting. Recently, many research groups are conducting and presenting studies on OLED lighting. In order to actualize white OLED with high efficiency and long service life, the systematic understanding of luminous bodies is essential. This article has presented the phosphorescent and fluorescent materials that can be applied to white OLED, and summarized important blue, yellow, orange, and red luminous materials. Such systematic classification and understanding can be greatly helpful for the development of new luminous materials with high efficiency and long service life in future.

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