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Please cite this article as: Braveenth R, Ahn DH, Han J-H, Moon JS, Kim SW, Lee HA, Qiong W, Kwon JH, Chai KY, Utilizing triazine/pyrimid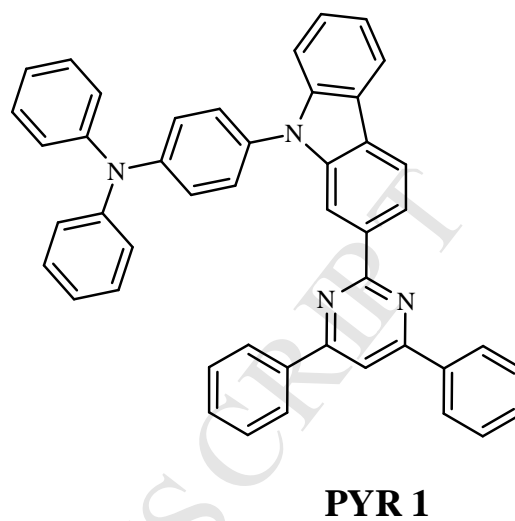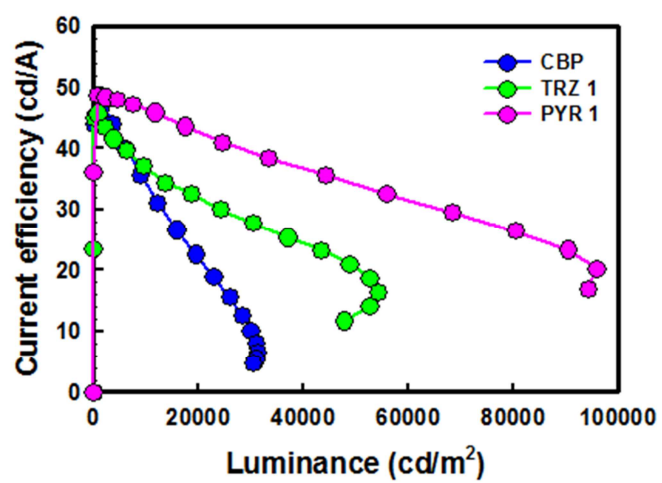ine acceptor and carbazole-triphenylamine donor based bipolar novel host materials for highly luminescent green phosphorescent OLEDs with lower efficiency roll-off, *Dyes and Pigments* (2018), doi: 10.1016/j.dyepig.2018.05.022.
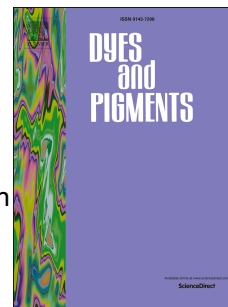
Graphical abstract

PYR 1

Utilizing triazine/pyrimidine acceptor and carbazole-triphenylamine donor based bipolar novel host materials for highly luminescent green phosphorescent OLEDs with lower efficiency roll-off

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Abstract

In this work, two novel bipolar host materials were designed, synthesized and applied in green phosphorescent based OLEDs. Both the host materials, 4-(2-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline (**TRZ 1**) and 4-(2-(4,6-diphenylpyrimidin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline (**PYR 1**) exhibited high thermal stability, with decomposition temperatures of 425 °C and 400 °C, respectively. The triplet energy of PYR 1 (2.63 eV) was higher than that of TRZ 1 (2.44 eV), and facilitated suitable energy transfer to the green dopant. The PYR 1 based green device demonstrated an excellent maximum current efficiency of 48.7 cd/A and external quantum efficiency of 16.4%. Interestingly, the green device with PYR 1 showed an outstanding brightness of 95,870 cd/m^2, which is three times greater than that of the reference CBP based device (31,370 cd/m^2). The bipolar host PYR 1 is a promising material for high luminescent and low efficiency roll off applications, especially for green PhOLEDs.

Keywords: organic light emitting diodes, bipolar host, green phosphorescent, triazine, pyrimidine.

1. Introduction

Organic light emitting diodes (OLEDs) have received great attention from both the research community and industry for their excellent potential in display technologies [1,2]. Charge recombination to produce singlet and triplet excitons is determined by spin statistics. According to the statistics, the ratio of singlet to triplet formation is 1:3, which corresponds to a theoretical internal quantum efficiency (IQE) of 25%. However, the IQE can be increased by utilizing triplet excitons. Phosphorescence-based emitters are highly efficient materials compared to fluorescence emitters [3–5]. In 1998, Forrest et al. made a key advance in the development of phosphorescent organic light emitting diodes (PhOLEDs), attaining a higher IQE by using heavy metal complexes with intersystem crossing (ISC) [6–8]. This mechanism requires the phosphorescence emitters to be doped with appropriate host materials to prevent quenching processes such as triplet-triplet annihilation (TTA) and aggregation quenching (ACQ) [3,9–13]. The design of the host material is crucial to ensure proper energy transfer from the host to the dopant in the PhOLEDs. The energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the triplet energy of host materials should be higher than those of the dopant in order to achieve effective transfer. At the same time, the frontier molecular orbital (FMO) energy levels of adjacent layers, such as the hole transporting layer (HTL) and electron transporting layer (ETL), should match [14–23].

Additionally, maintaining a proper charge balance is key to obtaining better efficiencies in PhOLEDs. Generally, the hole mobility of the HTL is higher than that of the ETL. Thus, host materials should be modified to achieve charge balance; this approach has been successfully implemented by introducing bipolar host materials. Recently, many groups have reported work on bipolar host strategies, using different electron donating and electron withdrawing groups to develop materials that exhibit steady charge balance at the emission layer (EML) [12,24–31].

In this study, we report two novel bipolar host materials 4-(2-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline (**TRZ 1**) and 4-(2-(4,6-diphenylpyrimidin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline (**PYR 1**) containing a hole transporting carbazole-triphenyl amine derivative and an electron withdrawing triazine or pyrimidine derivative for application in green PhOLEDs. The carbazole moiety is widely used as a donating group because of its high hole mobility and triplet energy (3.0 eV) [4, 32-34]. Triazine and pyrimidine are good electron-withdrawing and hole-blocking moieties owing to

their high electron deficiencies, which makes them suitable for use in high-efficiency green PhOLEDs. Consequently, we expect that our design will result in stable physical properties such as thermal strength to enhance the lifetime of the device. We have compared the performance of our green devices with that of the well-known host material CBP based on the same device structure.

2. Materials and methods

2.1. Materials

All reagents and solvents were obtained from commercial suppliers. 3M Ph-MgBr, CYC and toluene were purchased from Sigma Aldrich (Seoul, Korea). PYR and Ph-BoA were obtained from TCI chemicals (Seoul, Korea). THF was distilled from sodium/benzophenone before use. Methanol, chloroform, n-hexane and dichloromethane were bought from SK chemicals (Gyeonggi-do, Korea). Starting material 1 was obtained from Green Guardee Technology Co., LTD (Beijing, China). Analytical thin layer chromatography (TLC) was performed using aluminum backed Merck Kieselgel 60 coated plates with both 254nm and 365nm UV visualization (Seoul, Korea). Column chromatography was carried out using Silica gel with mesh size of 200- 300. All reactions were stirred magnetically, unless otherwise mentioned and we used deionized water for all purposes related to our current study.

2.2. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded using a JEON JNM-ECP FT-NMR spectrometer (Peabody, MA, USA) operating at 500 MHz. Absorbance spectra were obtained using a SINCO S-4100 UV-Vis spectrophotometer (SINCO, Seoul, Korea). The band gap (E_g) was estimated from the onset of the UV-visible absorbance spectra. Photoluminescence (PL) spectra were measured using a JASCO FP-8500 spectrofluorimeter (JASCO, Tokyo, Japan), and tetrahydrofuran (THF) was used as the solvent. The triplet energy level (E_T) was determined from the onset wavelength of the emission spectra at 77 K in toluene (10^{-4} M). To measure the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels, cyclic voltammetry (CV) was carried out using a BioLogic SP-50 (Biologic, Paris, France). The HOMO level was calculated by subtracting the oxidation potential shift between ferrocene and the HTMs. The LUMO level was estimated by subtracting the band gap to the obtained HOMO level. The current density-voltage-luminance (*J-V-L*) characteristics of each device were measured using a luminance color meter (Konica Minolta CS-100A) and a source meter unit (Keithley 2635A, USA). The electroluminescence (EL) spectra and CIE (Commission

Internationale l'Eclairage) 1931 color coordinates were obtained using a Konica Minolta CS-2000 spectroradiometer (Japan). Molecular simulations were carried out using density function theory (DFT) calculations with the B3LYP (Beck three parameter hybrid functional and Lee-Yang-Parr correlation functional) and double numerical plus d- function (DND) atomic orbital basic set with DMol3 module implemented in material studio 8.0 software (Accelrys inc, San Diego, CA, USA). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using SDT Q600 V20.9 Build 20 and DSC Q200 V24.9 Build 121 (TA Instruments, New Castle, DE, USA) instruments with a heating rate of 10 °C/min under nitrogen atmosphere. Mass analysis was carried out using a Xevo TQ-S spectrometer (Waters, Milford, MA, USA). TOF MS data was collected using a Hybrid Tandem spectrometer (SYNAPT G2-Si-HDMS, Waters, Herts, England). Elemental analysis (EA) was recorded by a IT/flash/2000 elemental analyzer (Thermo Fisher Scientific, Loughborough, England). IR spectra was obtained by a Fourier Transform infrared spectrometer (Perkin Elmer, Boston, MA, USA).

2.3. Synthesis procedure

2.3.1. Synthesis of 2-chloro-4,6-diphenyl-1,3,5-triazine (**2Ph-TRZ**)

2,4,6-trichloro-1,3,5-triazine (**CYC**, 5 g, 27 mmol) was placed in 250 ml two neck round bottom flask under vacuum conditions for 15 min. An inert atmosphere was then introduced by using a nitrogen balloon, and 100 ml of anhydrous THF was added. The mixture was then stirred at 0 °C, and 20ml of 3M phenyl magnesium bromide **Ph-MgBr** was injected dropwise. The mixture was kept at room temperature for 12 h while stirring. After completion of the reaction, then evaporated and recrystallized using the solvent methanol (100 ml) to yield a pale white solid as the requisite product 2Ph-TRZ.

2-chloro-4,6-diphenyl-1,3,5-triazine

Yield: 89%; pale white solid; ^{1}H NMR (500 MHz, CDCl3) δ 8.61-8.63 (d, $J = 7$ Hz, 4H), 7.61-7.64 (t, $J = 7.5$ Hz, 2H), 7.53-7.56 (t, $J = 7.5$ Hz, 4H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 173.4, 172.2, 134.4, 133.6, 129.4, 128.9.

2.3.2. Synthesis of 2-chloro-4, 6-diphenylpyrimidine (**2Ph-PYR**)

A mixture of 2, 4, 6-trichloropyrimidine (**PYR**, 1.3 ml, 7 mmol), phenylboronic acid (**Ph-BoA**, 1.5 g, 12 mmol), Pd(PPh$_3$P)$_4$ (0.2 g, 0.17 mmol), 40 ml of 2M aqueous K$_2$CO$_3$ solution , 40 ml of water, 25 ml of ethanol, and 80 ml of toluene

were added in a two neck round bottom flask equipped with condenser and refluxed at 110 °C for 8 h under nitrogen atmosphere. After completion of the reaction, the mixture was worked up using ethyl acetate (60 ml) and water (50 ml). The organic layer was dried over anhydrous magnesium sulfate and then filtered and concentrated. The crude residues were separated using a silica column and an *n*-hexane: dichloromethane (4:1) solvent system to obtain the intermediate **2P-PYR** as a white solid.

2-chloro-4, 6-diphenylpyrimidine

Yield: 74%; white solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13-8.14 (m, 4H), 8.01 (s, 1H), 7.51-7.55 (m, 6H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 167.7, 162.1, 135.7, 131.7, 129.1, 127.5, 111.0.

*2.3.3. Synthesis of 4-(2-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline (**TRZ 1**)*

A mixture of 2-chloro-4,6-diphenyl-1,3,5-triazine (**2Ph-TRZ**, 1 g, 3.7 mmol), (9-(4-(diphenylamino)phenyl)-9H-carbazol-2-yl)boronic acid (**1**, 2.2 g, 4.9 mmol), Pd(PPh$_3$P)$_4$ (0.01 g, 0.01 mmol), 40 ml of 2M aqueous K$_2$CO$_3$ solution, 40 ml of water, 30 ml of THF, and 80 ml of toluene were added in a two neck round bottom flask equipped with condenser. The mixture was then stirred at 110 °C for 12 h under nitrogen atmosphere. The residues were extracted with dichloromethane (3 * 30 ml) and deionized water (80 ml). The organic layer was collected and dried over anhydrous magnesium sulfate. Finally, the crude was separated using a silica column with an *n*-hexane: dichloromethane (6:1 to 4:1) gradient-based mobile phase to achieve the pure **TRZ 1** target molecule.

4-(2-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline

Yield: 86%; Greenish yellow solid; FT-IR (KBr pellet): $υ_{max}$ 3057, 1622, 1588, 1522, 1510, 1472, 1444, 1372, 1358, 1337, 1311, 1279, 1226, 1174, 1154, 1100, 1069, 1024, 1001 and 931 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.87 (s, 1H), 8.73-8.78 (m, 5H), 8.28-8.30 (d, *J* = 10 Hz, 1H), 8.21-8.23 (d, *J* = 10 Hz, 1H), 7.56-7.64 (m, 6H), 7.48-7.52 (m, 4H), 7.31-7.37 (m, 7H), 7.26-7.28 (m, 4H), 7.09-7.21 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 172.2, 171.6, 147.6, 140.3, 136.4, 132.5, 129.6, 128.1, 127.1, 124.8, 124.2, 123.5, 121.1, 120.7, 120.2, 110.9, 110.3, 100.0; MS (APCI) *m/z*: 641.83 for C$_{45}$H$_{31}$N$_5$ [(M+H)$^+$]. TOF MS (ES+) *m/z*: cal. for C$_{45}$H$_{31}$N$_5$ 641.25, found 641.26; Anal.

Calcd for $C_{45}H_{31}N_5$ (%): C, 84.22; H, 4.87; N, 10.91.Found: C, 83.64; H, 4.82; N, 11.11.

2.3.4. Synthesis of 4-(2-(4,6-diphenylpyrimidin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline (**PYR 1**)

A mixture of 2-chloro-4,6-diphenylpyrimidine (**2Ph-PYR**, 1 g, 3.7 mmol), (9-(4-(diphenylamino)phenyl)-9H-carbazol-2-yl)boronic acid (**1**, 2.2 g, 4.9 mmol), $Pd(PPh_3P)_4$ (0.01 g, 0.01 mmol), 40 ml of 2M aqueous K_2CO_3 solution , 40 ml of water, 30 ml of THF, and 80 ml of toluene were added in a two neck round bottom flask equipped with condenser. The mixture was then stirred at 110 °C for 12 h under nitrogen atmosphere. The residues were extracted with dichloromethane (2 * 30 ml) and deionized water (40 ml). The organic layer was collected and dried over anhydrous magnesium sulfate. Finally, the crude was separated using a silica column and an *n*-hexane: dichloromethane (8:1 to 3:1) gradient-based mobile phase to achieve the pure **PYR 1** target molecule.

4-(2-(4,6-diphenylpyrimidin-2-yl)-9H-carbazol-9-yl)-N,N-diphenylaniline

Yield: 77%; yellow solid; FT-IR (KBr pellet): υ_{max} 3433, 3034, 1586, 1563, 1528, 1510, 1491, 1438, 1400, 1358, 1333, 1311, 1270, 1228, 1179, 1103, 1072, 1024 and 999 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.83 (s, 1H), 8.70-8.71 (d, J = 8.5 Hz, 1H), 8.22-8.26 (m, 5H), 8.20-8.21 (d, J = 8.5 Hz, 1H), 8.01 (s, 1H), 7.45-7.58 (m, 10H), 7.26-7.35 (m, 7H), 7.24-7.26 (m, 4H), 7.08-7.10 (t, J = 8.5 Hz, 2H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 165.1, 164.7, 147.7, 147.2, 142.2, 141.5, 137.7, 136.0, 130.8, 129.5, 129.0, 128.1, 127.3, 126.5, 125.4, 124.7, 124.4, 123.3, 120.8, 120.5, 120.1, 120.0, 110.3, 110.1, 110.1; MS (APCI) *m/z*: 640.76 for $C_{46}H_{32}N_4$ [(M+H)$^+$]. TOF MS (ES+) *m/z*: cal. for $C_{46}H_{32}N_4$ 640.26, found 640.27; Anal. Calcd for $C_{46}H_{32}N_4$ (%): C, 86.22; H, 5.03; N, 8.74.Found: C, 86.08; H, 4.95; N, 8.60.
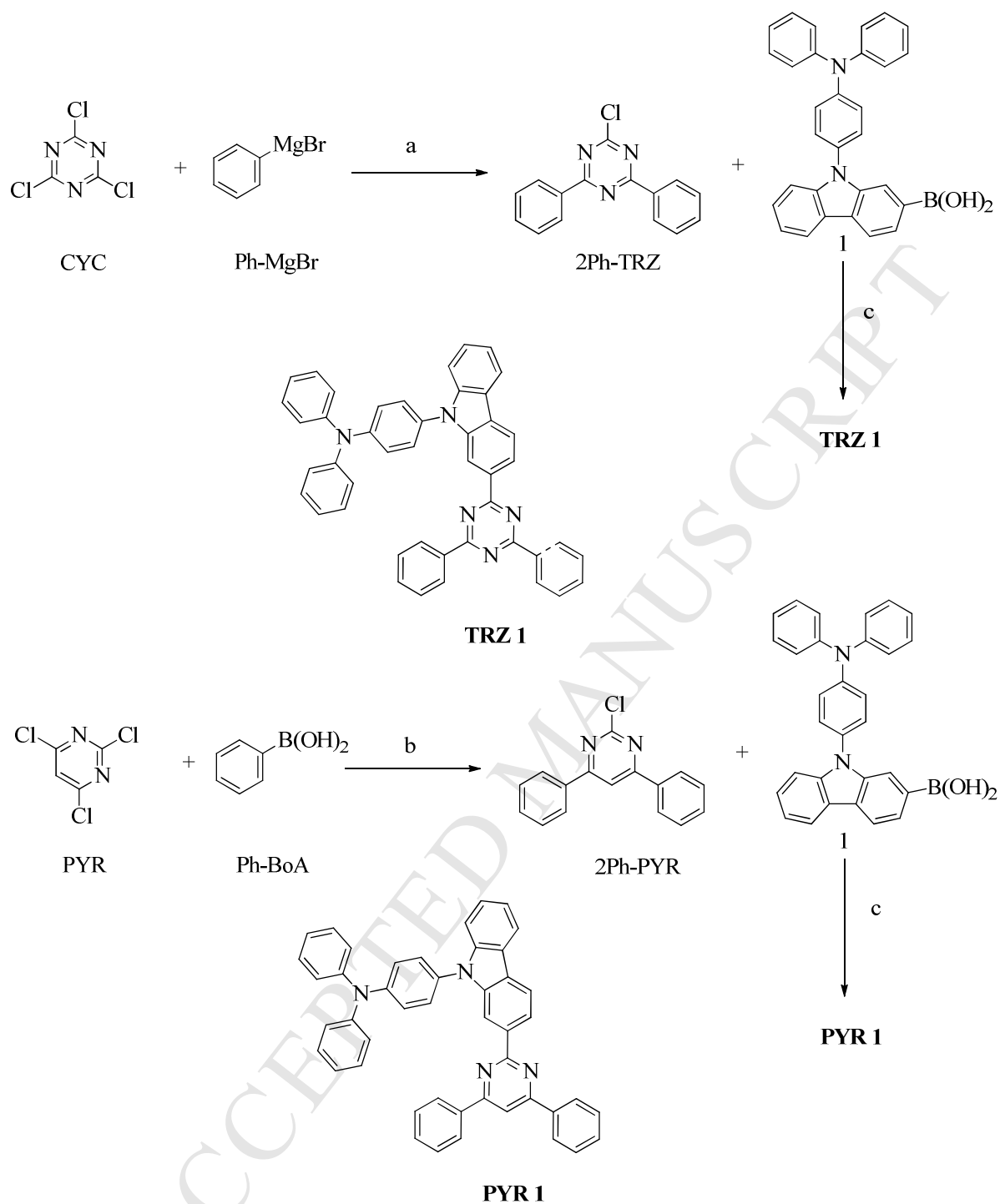
Scheme 1. Synthesis of the host materials TRZ 1 and PYR 1. (a) Anhydrous THF, 0 ℃ to room temperature, 12 h. (b) Pd(PPh₃P)₄, 2 M K₂CO₃, toluene + ethanol + water, 110 ℃, 8 h. (c) Pd(PPh₃P)₄, 2 M K₂CO₃, toluene+ THF + water, 110 ℃, 12 h.

2.4. OLED fabrication and characterization

To fabricate the OLEDs, indium-tin-oxide (ITO) coated glass substrates (50 nm, sheet resistance of 10 Ω/□) were cleaned in an ultrasonic bath with acetone and

isopropyl alcohol for 10 min and rinsed with deionized water. The substrates were then dried using nitrogen, followed by UV-ozone treatment for 10 min. All the organic layers and the metal cathode were deposited on the pre-cleaned ITO glass by vacuum evaporation under a pressure of ~1×10^{-7} Torr. The deposition rate of all the organic layers was about 0.5 Å/s. Similarly, the deposition rates of LiF and Al were maintained at 0.1 Å/s and 4.0 Å/s, respectively. Finally, all the devices were encapsulated using a glass cover and UV curable resin inside a nitrogen filled glove box. The OLED area was 4 mm^2 for all the samples studied in this work. The *J-V* and *L-V* characteristics of the fabricated OLED devices were measured using a Keithley 2635A SMU and a Konica Minolta CS-100A, respectively. The EL spectra and the Commission International de l'Eclairage (CIE) 1931 color coordinates were obtained using a Konica Minolta CS-2000 spectroradiometer.

3. Results and discussion

3.1. Synthesis

The synthetic procedures for both the host materials are depicted in Scheme 1. Both TRZ 1 and PYR 1 were synthesized using Suzuki cross coupling reactions between either 2-chloro-4,6-diphenyl-1,3,5-triazine **2Ph-(TRZ)** or 2-chloro-4,6-diphenylpyrimidine **(2Ph-PYR)** and (9-(4-(diphenylamino)phenyl)-9H-carbazol-2-yl)boronic acid (**1**) with a palladium catalyst and the base potassium carbonate. The desired bipolar host materials were achieved in good yields of 86% and 77%, respectively. The synthesized materials were purified using column chromatography, and further purification was carried out prior to device fabrication through the sublimation process. Finally, all the synthesized new materials were confirmed using NMR (^{1}H, ^{13}C), IR, elemental analysis and mass spectrometry analysis.

3.2. Thermal Analysis

The thermal stabilities of the host materials were appraised by TGA and DSC measurements; these data are shown in Table 1 and depicted in Figure 1. TRZ 1 and PYR 1 exhibited high melting point of 252 °C and 239 °C, Both of our host materials demonstrated high decomposition temperatures of over 400 °C for 5% weight reduction, which can enhance the morphological and thermal stabilities of the thin films in the devices.
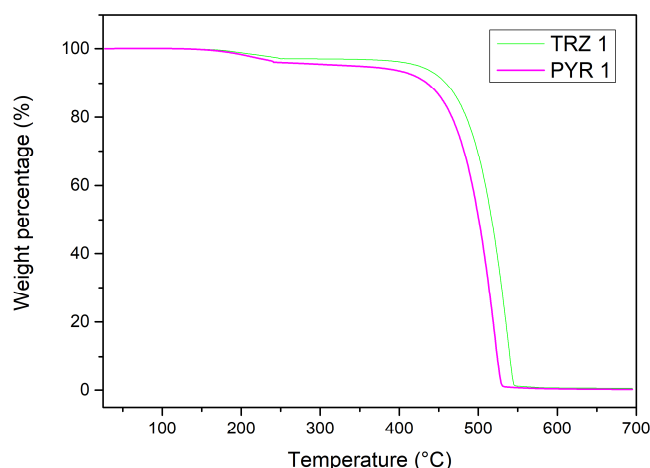
Figure 1. TGA curves of TRZ 1 and PYR 1.

3.3. *Photophysical properties*

Figure 2 shows the UV-vis absorption and photoluminescence (PL) spectra of TRZ 1 and PYR 1 at room temperature, and the results are summarized in Table 1. Both the UV-vis absorption peaks exhibited similar shapes. A sharp increase in the absorption intensity at 325 nm was observed for both TRZ 1 and PYR 1, and was attributed to a π- π^* charge transition from the electron-donating carbazole-triphenylamine moiety to the electron-withdrawing triazine or pyrimidine moiety. Band gap values of 2.89 eV and 3.06 eV were calculated for TRZ 1 and PYR 1 from their absorption edge values of 429 nm and 405 nm, respectively. The high band gap values of TRZ 1 and PYR 1 reflected the *meta* position attachment between the donor and the acceptor, which strongly reduces π-conjugation and widens the band gap by affecting the ICT process. The PL spectra at room temperature for TRZ 1 and PYR 1 exhibited maxima at 508 nm and 446 nm, respectively. The triplet energy (E_T) is the key factor in preventing energy transfer from the guest to host in host materials, and ensuring the efficiency of the resulting devices. The triplet energies of TRZ 1 and PYR 1 were estimated to be 2.44 eV and 2.63 eV from the low temperature PL spectra. The calculated values are suitable for green phosphorescence based OLEDs. The difference in the triplet energies of TRZ 1 and PYR 1 arises from the different withdrawing moieties attached to the common donor group. The triplet energy of PYR 1 was also higher than that of the reference material CBP (2.58 eV), and thus, we believed that PYR 1 based devices would show greater efficiency enhancement than TRZ 1 or CBP based devices.
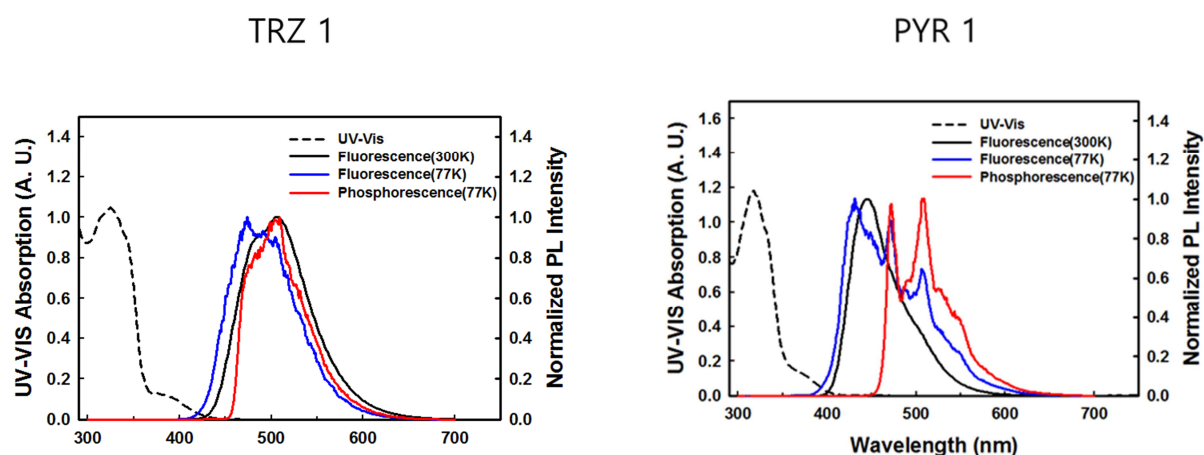
TRZ 1

PYR 1

Figure 2. UV-Vis absorption and photoluminescence spectra of the hosts TRZ 1 and PYR 1.

3.4. Electrochemical properties

The HOMO energy levels were determined from the cyclic voltammetry (CV) measurements, which are depicted in Figure 3. TRZ 1 and PYR 1 were found to have very similar HOMO levels (5.59 eV and 5.63 eV, respectively). The LUMO energy levels were calculated by adding the band gap energy to the HOMO energy, and are listed in Table 1. The LUMO energy levels of TRZ 1 and PYR 1 were 2.70 eV and 2.57 eV. PYR 1 exhibited a higher LUMO level than TRZ 1, and both host materials had higher LUMO energies than the dopant Ir(ppy)$_3$ (2.90 eV). These favorable energy levels contributed to the efficient recombination of charges at the emission layer, indicating their promise for fabricating efficient devices.
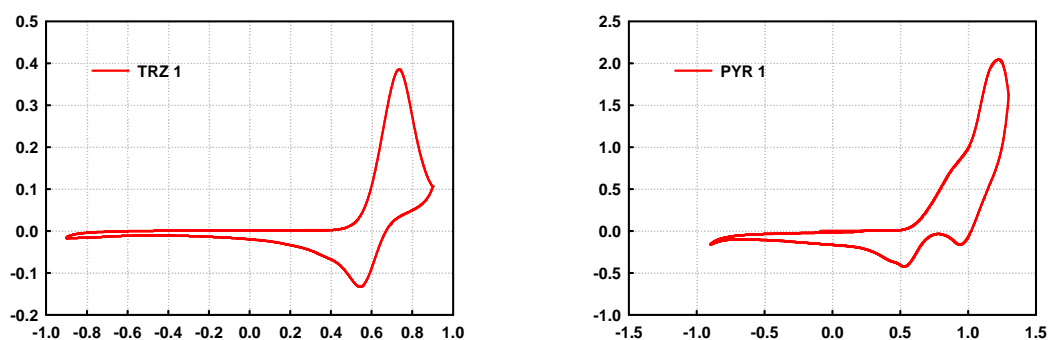

Figure 3. Cyclic voltammetry measurements of TRZ 1 and PYR 1.

Table 1. Thermal, photophysical and electrochemical properties of TRZ 1 and PYR 1.

Host	T_m [a] (°C)	T_d [b] (°C)	UV-Vis [c] (nm)	PL max [d] (nm)	HOMO [e] (eV)	LUMO [f] (eV)	E_g [g] (eV)	E_T [h] (eV)	E_s [i] (eV)
TRZ 1	253	425	429	508	5.59	2.70	2.89	2.44	2.62
PYR 1	240	400	405	446	5.63	2.57	3.06	2.63	2.88

[a] Melting point

[b] Decomposition temperature at 5% weight reduction

[c] UV absorption wavelength

[d] Photoluminescent maximum emission

[e] Highest occupied molecular orbital energy

[f] Lowest unoccupied molecular orbital energy

[g] Energy band gap

[h] Triplet energy

[i] Singlet energy

3.5. Molecular design and distribution

To study the electronic structures and molecular levels of the hosts, DFT calculations were performed with DMol3 module at double numerical plus d-functions (DND) atomic orbital basic set level. The FMO distributions are shown in Figure 4. The HOMOs of both the host materials are delocalized over the triphenylamine moiety. The LUMO of PYR 1 is clearly localized on the pyridine moiety, while that of TRZ 1 is localized on the triazine and carbazole derivatives. The host material TRZ 1 showed little extended distribution compared to the host material PYR 1. This distribution revealed that its HOMO-LUMO separation was favorable for the hole and electron transport properties of the single molecule. The only difference between TRZ 1 and PYR 1 is the withdrawing group, which was responsible for the greater distribution of the LUMO over TRZ. PYR 1 showed clearer HOMO-LUMO separation, which can enhance device efficiency by providing proper charge balance at the emission layer.
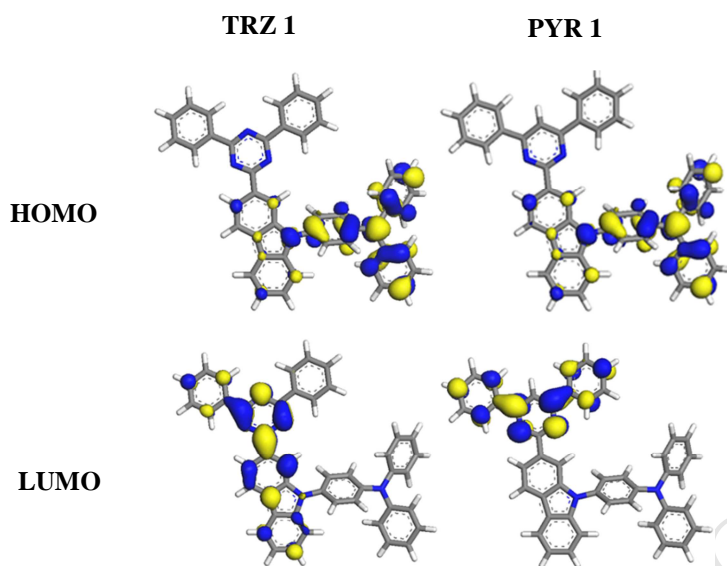
TRZ 1　　　　　　**PYR 1**

Figure 4. Spatial distribution of the HOMO and LUMO of TRZ 1 and PYR 1.

3.6. Device performances

To investigate the properties of the synthesized bipolar host materials, we fabricated green OLED based phosphorescent devices using Ir(ppy)$_3$ as a green dopant. The configuration of the device structure was ITO/ 1,4,5,8,9,11-Hexaazatriphenylenehexacarbonitrile (HATCN) (7 nm)/ 4,4′-Cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (TAPC) (43 nm)/HOST:5 wt.% Tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)3) (20 nm)/ 1,3,5-Tris(3-pyridyl-3-phenyl)benzene (TmPyPB) (35 nm)/ Lithium fluoride (LiF) (1.5 nm)/ Aluminum (Al) (100 nm), and is shown in Figure 5. In the above configuration, ITO and Al act as the anode and cathode, respectively. TAPC is used as a HTL, and TmPyPB is the ETL in the device. The triplet energies of the HTL and ETL were 2.9 eV and 2.8 eV, respectively, which were sufficiently high to block triplet exciton quenching from the green emitting EML.

The current density-voltage (*J-V*) and luminescence-voltage (*L-V*) characteristics are shown in Figure 6 and Table 2. The PYR 1 based device showed a lower turn on voltage of 2.4 V than the CBP based reference device (2.6 V). This indicates that PYR 1 has excellent bipolar characteristics to establish proper charge balance at the EML. The lower driving voltage of the PYR 1 based device (3.0 V) further enhanced the device efficiency, while the TRZ 1 based device exhibited a higher driving voltage of 3.6 V. The device based on PYR 1 demonstrated a maximum current efficiency of 48.7 cd/A, which was higher than those of the TRZ 1 (45.3 cd/A) and CBP (45.8 cd/A)

based devices. Consequently, we noted that the maximum luminescence of the TRZ 1 and PYR 1 devices were 54,170 cd/m^2 and 95,870 cd/m^2, respectively. The PYR 1 based device exhibited a maximum luminescence three times greater than that of the device based on the well-known host CBP (31,370 cd/m^2). This represents solid evidence that our PYR 1 bipolar host material has high potential for application in green PhOLEDs. The maximum external quantum efficiency (EQE) of the PYR 1 based device (16.4 %) was higher than that of the reference CBP (15.7 %) and TRZ 1 (15.3 %) based devices. As the bipolar characteristics of PYR 1 were better than those of TRZ 1, it was expected to provide superior device efficiency. We observed that the CBP based device showed rapid efficiency roll-off compared to the TRZ 1 and PYR 1 based bipolar host materials. Our synthesized host materials can be used for long term operation, which is a key factor in improving the efficiency of such devices.

To understand the electron and hole transporting abilities, a hole-only device (HOD) and an electron-only device (EOD) were fabricated. The configuration of the HOD was ITO (50 nm)/TAPC (20 nm)/HOST (50 nm)/TAPC (20 nm)/Al (100 nm) and the structure of the EOD was ITO (50 nm)/TmPyPB (20 nm)/HOST (50 nm)/TmPyPB (20 nm)/LiF (1.5 nm)/Al (100 nm); these configurations are depicted in Figure 7. The HOD results showed that the hole-transporting properties of TRZ-1 were superior to those of the PYR-1 based device, which was in agreement with the higher HOMO energy levels and also the energy barrier with TAPC layer is smaller than that of PYR 1. The higher LUMO energy value of PYR 1 resulted in greater electron transport ability than TRZ 1. The bipolar characteristics of the synthesized host materials enhanced the device properties and reduced the efficiency roll off.

The electroluminescence spectra are shown in Figure 8. The maxima of the EL peaks were observed at 513 nm, 512 nm, and 512 nm for CBP, TRZ 1, and PYR 1, respectively. All the peaks were identical and no chromic shift was observed, indicating perfect emission from the green dopant [35,36].
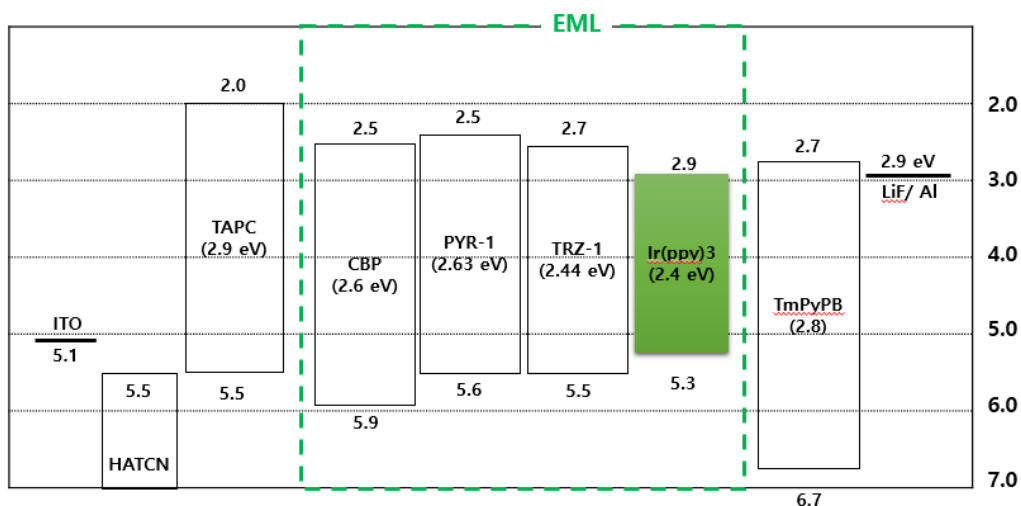
Figure 5. Device configuration of the TRZ 1, PYR 1, and CBP host material devices.
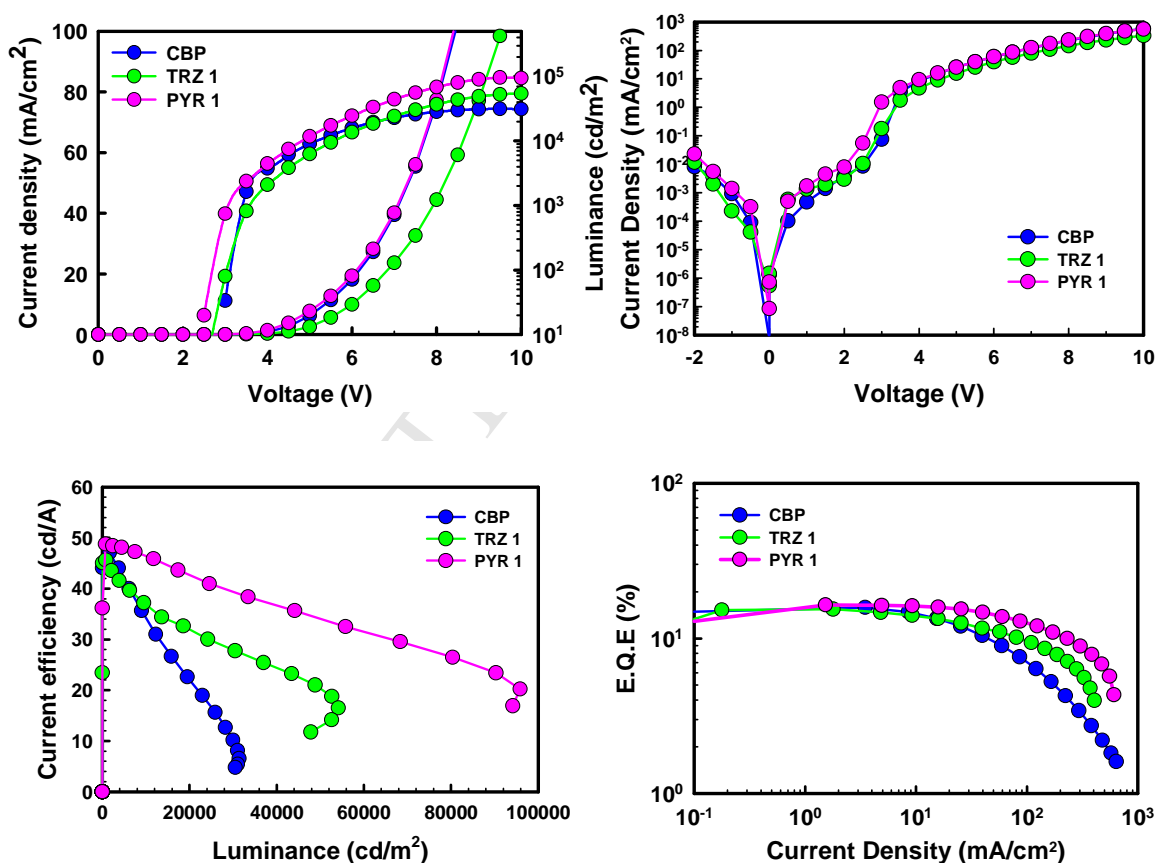

Figure 6. Current density-voltage (J-V) and luminescence-voltage (L-V) characteristics of TRZ 1 and PYR 1, as well as those of the reference host CBP.
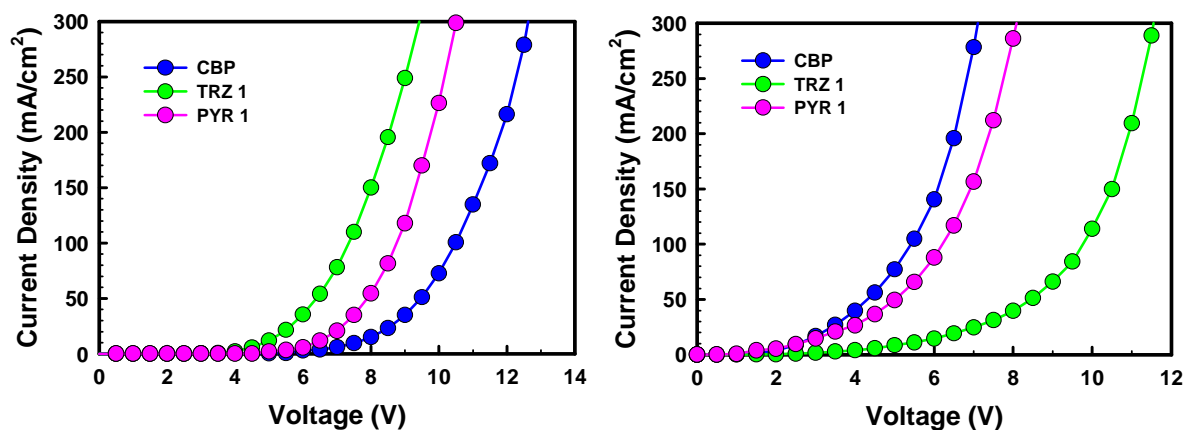
Figure 7. Efficiency of the HOD and EOD of the two bipolar host materials.

Table 2. Device performances.

Characteristic	CBP	TRZ 1	PYR 1
Turn-on Voltage	2.6 V	2.6 V	2.4 V
Driving Voltage [a]	3.3 V	3.6 V	3.0 V
Max. luminance	31,370 cd/m^2	54,170 cd/m^2	95,870 cd/m^2
Current efficiency [a] **(Max)**	47.1 / 45.8 cd/A	45.6 / 45.3 cd/A	48.7 / 48.7 cd/A
EQE [a] **(Max)**	15.8 / 15.7 %	15.4 / 15.3 %	16.4 / 16.4 %
CIE color [b]	(0.28, 0.62)	(0.28, 0.63)	(0.28, 0.63)
λ_{max} [b]	513 nm	512 nm	512 nm

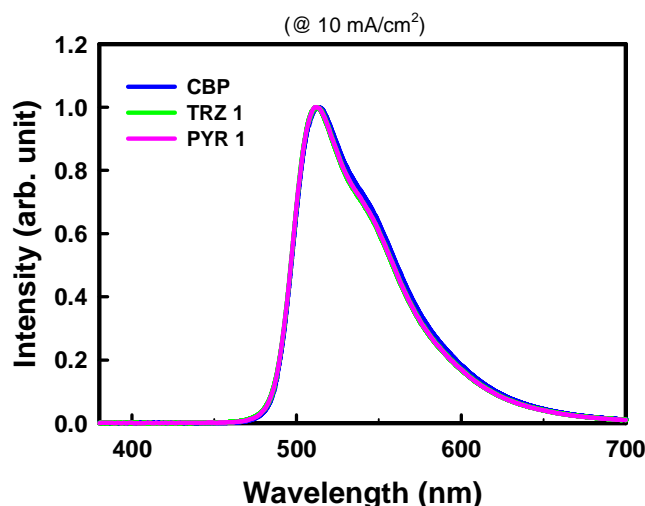[a] At 1000 cd/m^2

[b] At 10 mA/cm^2

Figure 8. Electroluminescence spectra of the green phosphorescent OLEDs.

4. Conclusion

Two novel host materials (TRZ 1 and PYR 1) were designed and synthesized using a carbazole-triphenylamine donor moiety and triazine or pyrimidine based withdrawing groups to provide bipolar characteristics. The synthesized host materials exhibited high thermal stability due to their bulky structures. The triplet energies of both the bipolar host materials were suitable to ensure effective energy flow for green phosphorescent OLEDs. The PYR 1 based green OLED device registered a lower turn on (2.4 V) and driving voltage (3.0 V). The maximum luminescence of the PYR 1 containing device (95,870 cd/m^2) was three times higher than that of the similar CBP based device. Consequently, the PYR 1 based device showed an excellent maximum current efficiency of 48.7 cd/A while exhibiting a maximum external quantum efficiency of 16.4% with lower efficiency roll off. Our new bipolar host materials can be used to enhance the efficiency of thermally stable and highly luminescent green OLED devices.

Acknowledgement

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Highlights

- Current efficiency reached 48.7 cd/A

- Lower turn on voltage of 2.4 V recorded

- Green phosphorescent OLED showed outstanding luminescence of 95,870 cd/m^2

- Both devices showed lower efficiency roll off

- Achieved EQE of 16.4%