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Carbazole-Bridged Triphenylamine-Bipyridine Bipolar Hosts for High-Efficiency Low Roll-off Multi-Color PhOLEDs

Tanmay Chatterjee^a, Wen-Yi Hung^{b*}, Wei-Feng Tang^b, Hsiao-Fan Chen^a and Ken-Tsung Wong^{a,c*}

^a Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan
 ^b Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 202,
 ^c Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

* Corresponding authors E-mail addresses: wenhung@mail.ntou.edu.tw (W.-Y. Hung); kenwong@ntu.edu.tw (K.-T. Wong)

ABSTRACT

Three new bipolar molecules composed of carbazole, triarylamine, and bipyridine were synthesized and utilized as host materials in multi-color phosphorescent OLEDs (PhOLEDs). These carbazole-based materials comprise a hole-transport triarylamine at C3 and an electron-transport 2,4'- or 4,4'-bipyridine at N9. The different bipyridine isomers and linking topology of the bipyridine with respect to carbazole N9 not only allows fine-tuning of physical properties but also imparts conformational change which subsequently affects molecular packing and carrier transport properties in the solid state. PhOLEDs were fabricated using green [(ppy)₂Ir(acac)], yellow [(bt)₂Ir(acac)], and red [(mpq)₂Ir(acac)] as doped emitters, which showed low driving voltage, high external quantum efficiency (EQE), and extremely low efficiency roll-off. Among these new bipolar materials, the **2Cz-44Bpy**-hosted device doping with 10% (ppy)₂Ir(acac) as green emitting layer showed a high EQE of 22% (79.8 cd A⁻¹) and power efficiency (PE) of 102.5 Im W⁻¹ at a practical brightness of 100 cd m⁻². In addition, the device showed limited efficiency roll-off (21.6% EQE) and low driving voltage (2.8 V) at a practical brightness of 1000 cd m⁻².

Key Words: bipolar host, carbazole, bipyridine, electrophosphorescence

1. Introduction

The discovery of phosphorescent organic light-emitting diodes (PhOLEDs) is a major breakthrough in display technology owing to the inherent ~100% exciton harnessing ability of the phosphorescent materials.^[1,2] To realize highly efficient PhOLEDs, homogeneous dispersion of the phosphors in a suitable host matrix is crucial for suppression of undesired excited state processes such as aggregation quenching, triplet-triplet annihilation (TTA) at high current, etc., which deteriorate the device efficiency.^[3] Moreover, the host materials also play an important role for charge transport and electron/hole balance as well as confinement of emissive exciton within the emissive layer, which are key factors responsible for highly efficient PhOLEDs. In recent years, bipolar host materials have gained immense interests both in academia and industry as they possess excellent carrier transport properties for both holes and electrons, which usually lead to high device efficiencies with simple device structures. The bipolar property can be rationally achieved by virtue of incorporating electron deficient (electron- transport, ET) and electron rich (hole-transport, HT) functionalities with a suitable spacer in a molecular framework. Carbazole has been widely-used as a HT moiety in most host materials because of its high triplet energy $(E_{\rm T})$ (~3 eV), excellent hole transport capability, and high thermal stability. For example, Lee et al. synthesized a series of carbazole/triazine hybrid bipolar hosts for efficient green phosphorescent devices. ^[4] Ma *et al.* recently reported a high $E_{\rm T}$ (3.03 eV) carbazole/benzonitrile bipolar host based on a saturated adamantane spacer, giving excellent device performance for blue PhOLED.^[5] A recent report by Cheng et al. demonstrates carbazole/quinoline based bipolar hosts ($E_T = 2.51 - 2.95 \text{ eV}$) gave an external quantum efficiency (EQE) as high as 25.6% (68.1 lm W⁻¹) in a yellow PhOLED with low efficiency roll-off. ^[6] The spacer linking ET and HT moieties is crucial for designing effective bipolar hosts. A suitable spacer can avoid efficient

electronic communication between ET and HT moieties, and effectively retain a high $E_{\rm T}$ that allows blocking the backward energy transfer from the emitter to the host. ^[7] An efficient π conjugation-impede spacer can be either a saturated atom/group (*e.g.* sp^3 carbon, ^[8] Si atom ^[8c-d]) or a linkage type that can reduce effective conjugation (e.g. meta-linkage) or lead to large dihedral angles (e.g. highly twisted conformation) between aromatic rings.^[9] We previously reported three highly twisted bipolar host materials (PhczNBI, PhczCBI, and PhczDCBI) consisting of 9-phenylcarbazole (donor) and N-phenylbenzimidazole (acceptor) bridged via a 2,2'-biphenyl linker through a series of ortho-ortho connectivity. They possess good carrier transport ability ($\mu_e \approx \mu_h \approx 10^{-6}$ - 10^{-4} cm² V⁻¹ s⁻¹), high triplet energies (2.55–2.71 eV) and excellent performance as host in PhOLED devices.^[10] In addition, the ortho- and meta-linkage strategies were also successfully adapted in another report to reduce effective conjugation between carbazole and benzimidazole in host materials (o-CPhBzIm and m-CPhBzIm), in which *m*-CPhBzIm can serve as a universal host for various dopants with high η_{ext} and a three-color single-host WOLED hosted by o-CPhBzIm achieved efficiencies of 18.5%, 32.6 cd A⁻¹, and 34.1 Im W⁻¹.^[11] In addition to carbazole, triphenylamine is also a widely used HT moiety for host materials owing to its low oxidation potential and good hole transport capability.^[12] There are a good number of ET groups that have been studied and tested as a bipolar host component such as oxadiazole, ^[13] triazole, ^[14] benzimidazole, ^[15] pyridine, ^[16] triazine, ^[17] diphenylphosphineoxide ^[18] etc. However, the study of bipyridine-containing material for PhOLED is rare. Kido *et al.* reported two ET materials based on 2,2'-bipyridine which gave an efficient green PhOLED (21%) with low operating voltages (3.2 V at 1000 cd m⁻²). ^[19] The 2,2'-bipyridine not only serves as ET moiety but can also induce molecular orientation through CH…N weak hydrogen bonding in addition to π - π stacking. In this article, we report three isomeric bipolar hybrids (5Cz-24Bpy,

3Cz-44Bpy, and **2Cz-44Bpy**) based on HT triphenylamine and ET 2,4'- and 4,4'-bipyridine bridging by a carbazole core through C(3) and N(9), respectively (Scheme 1). The three compounds are differed by their connectivity of bipyridine. The central carbazole is attached to the 5-position of 2,4'-bipyridine in **5Cz-24Bpy**, whereas **3Cz-44Bpy** and **2Cz-44Bpy** have the carbazole attached to the 3- and 2-position of 4,4'-bipyridine, respectively, giving *ortho-* and *meta*-linkage with respect to the disubstituted pyridine. The different connectivity not only produces different electronic coupling between the HT and ET blocks but also alters molecular geometry due to different steric repulsion and leads to different packing motif in thin film. Therefore, the $E_{\rm T}$ and charge transport capability of these isomers were fine-tuned. PhOLED devices based on **5Cz-24Bpy**, **3Cz-44Bpy** and **2Cz-44Bpy** were fabricated for green (ppy)₂Ir(acac), yellow (bt)₂Ir(acac), and red (mpq)₂Ir(acac) phosphors. A maximum current efficiency (CE) of 79.8 cd A⁻¹ and a EQE of 22.0% were achieved for green PhOLED hosted by **2Cz-44Bpy**. Furthermore, high efficiencies of 57.3 cd A⁻¹ and 22.4 % were obtained for **3Cz-44Bpy**-based yellow device.

2. Results and Discussion

2.1. Synthesis

Scheme 1 depicts the synthesis of **5Cz-24Bpy**, **3Cz-44Bpy**, and **2Cz-44Bpy**. The carbazole donor (**1**) was obtained through a Suzuki-Miyaura coupling between 3-bromocarbazole and 4-diphenylaminophenyl boronic acid. Similarly, bipyridine derivatives (**2a** and **2c**) were synthesized by copper-catalyzed regioselective C–C coupling between dibromo substituted pyridine and 4-pyridinylboronic acid. ^[20] We prepared **2b** through a Suzuki coupling of 4-pyridinylboronic acid with 3-bromo-4-iodopyridine which was in turn synthesized by iodination of LDA deprotonated 3-bromopyridine at –95°C. ^[21] Finally, the target compounds **5Cz-24Bpy**, **3Cz-44Bpy** and **2Cz-44Bpy** were obtained by Ullmann coupling between **1** and **2a-c** at high temperature in a sealed tube using a literature protocol (Scheme 1). ^[22] Detailed synthetic procedures are summarized in the Supporting information. All these compounds were purified through column chromatography and further through vacuum sublimation and their molecular structures were unambiguously determined on the basis of various spectroscopic techniques. Single crystal structures were obtained for **5Cz-24Bpy** and **2Cz-44Bpy**.

2.2. Thermal properties

Thermal and morphological stability are important prerequisites to give OLED devices with higher operational stability. Glass transition temperature (T_g) should be sufficiently high to prevent any morphological change assisted by the Joule heating during device operation. Thermal properties of the synthesized compounds were examined by thermogravimmetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen (Table 1). All these compounds are characterized by impressive thermal stability where the 5% weight loss temperatures (T_d) are recorded as 425, 324 and 420 °C respectively for **5Cz-24Bpy**, **3Cz-44Bpy** and 2Cz-44Bpy (Table 1). The lower T_d of 3Cz-44Bpy as compared to the two other congeners is probably due to its inherent puckered structure causing weaker intermolecular forces in the solid matrix. Both 5Cz-24Bpy and 2Cz-44Bpy possess a high T_g (~110 °C) which is promising for host material in terms of morphological stability in device. No T_g was observed for 3Cz-44Bpy.

2.3. Photophysical properties

Photophysical properties of 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy were investigated in dilute solution as well as in neat film (Figure 1). All photophysical data are summarized in Table 1. Absorption spectra of three isomeric chromophores in both solution and neat film are quite similar. The broad absorption band from 300 to 400 nm is contributed by both carbazoletriphenylamine and carbazole-bipyridine moieties whereas the higher energy peak at around 250 nm is mainly attributed to carbazole-bipyridine based transitions according to the absorption spectra of model molecules (Chart S1 and Figure S1). The fluorescence of these donor-acceptor chromophores is highly sensitive to the dielectric environment (Figure S2). For example, 5Cz-24Bpy shows significant solvent-dependent emission from 420 to 532 nm in solvents going from cyclohexane to THF with decrease of photoluminescence quantum yield (PLQY) from 0.25 to 0.05, respectively (Table 1). These emission properties suggest charge transfer (CT) character in the excited state which can be easily formed and accessed by photo-induced electron transfer (PET) process. Similar emission behaviour can also be found for 3Cz-44Bpy and 2Cz-44Bpy. The PET process is very efficient and fast for all three compounds as indicated by their predominant CT emission in toluene (Figure 1a). It is noted that **3Cz-44Bpy** exhibited dual emission at 387 and 518 nm (in toluene at room temperature). The higher energy emission band can be assigned to the locally (Franck-Condon) excited (LE) state which has a non-negligible

concentration in the reversible excited state $LE \leftrightarrow ICT$ reaction. The residual LE emission of **3Cz-44Bpy** indicates a less efficient PET process among the three compounds presumably due to supressed electronic coupling between the donor and the acceptor in the highly twisted conformation.

The solid-state phosphorescent spectrum is considered to better translate the $E_{\rm T}$ of the material in a PhOLED device. Therefore, the lowest $E_{\rm T}$ of **5Cz-24Bpy**, **3Cz-44Bpy** and **2Cz-44Bpy** were probed from their phosphorescent spectra in solid neat-films at 10 K instead of the solution matrix. The triplet energy, measured from the first vibronic band in the phosphorescence spectra are found to be in the range of 2.57-2.60 eV in the frozen 2-MeTHF and 2.43-2.46 eV in the neat films. These values are sufficient to host green phosphorescent dopants. The singlet-triplet energy gap ($\Delta E_{\rm ST}$) for the relevant chromophores are found to be in the range of 0.56-0.59 eV and 0.51-0.67 eV in the frozen medium and neat film, respectively. It is noted that the phosphorescence spectra of the title compounds are almost identical with that of a pure carbazole-bipyridine hybrid and triphenylamine (see Figure S3, supporting information), indicating that the triphenylamine (TPA) moiety coupled with carbazole serves as the lowest triplet energy sink.

2.4. Computational studies

The ground electronic states of the title compounds were modelled in dichloromethane solvent reaction field using the density functional theory (DFT) algorithm as implemented in the Gaussian09 program package.^[23] Relevant calculations were performed using the CAM-B3LYP/cc-pVDz functional/basis-set combination without imposing any symmetry constraint. ^[24] The various excited states and the associated oscillator strengths were calculated using the time-dependent DFT (TDDFT) code at the same level of theory. As the synthesized compounds are aimed to be used as bipolar hosts, it would be interesting to examine their frontier molecular orbitals (FMOs). Spatial disposition of the FMOs are essential for uninterrupted carrier transport using a single transporting material. Indeed, we find that in all our simulated structures, HOMOs have coefficients exclusively along the carbazole-TPA arms (π -type) and LUMOs are mostly based on the π^* orbitals of the bipyridine functionalities. As there is almost no mixing between the FMOs we assume that the n-type (bipyridine) and p-type (TPA) functionalities would function rather independently towards charge carriers and the title compounds would merit as bipolar hosts. Analysis of the TDDFT data shows that HOMO→LUMO excitation in all the structures has insignificant coefficient. This is clearly in accord to the experimental observation which determines that the low energy absorption band is primarily due to the carbazole-TPA based transitions ($\pi\pi^*$ type). The HOMO→LUMO excitation involves a charge transfer character from the donor arm to the bipyridine π^* which is ruled out for the title chromophores based on the almost polarity independent absorption spectra.

2.5 Electrochemical properties

The redox behaviour of the synthesized compounds was examined in dilute solution (~ 1 mM) using cyclic voltammetry with the following electrode combination: Ag|AgCl reference electrode, glassy carbon working electrode and Pt as the counter electrode. The oxidation scans were performed in dichloromethane using tetra(*n*-butylammonium) hexafluorophosphate (TBAPF₆) as the electrolyte and the reduction scans in deoxygenated dimethylformamide using tetra(*n*-butylammonium) perchlorate (TBAP) as the supporting electrolyte. Corresponding data are summarized in Table 1 and the cyclic voltammograms are presented in Figure 3. All the compounds exhibit quasi-reversible oxidation with two oxidative signals at ~0.80 V and ~1.1 V (vs Fc/Fc⁺), indicating formation of stable cation radical under the electrochemical condition. On

the other hand, the anion radicals are not stable enough under the same condition as revealed by their irreversible reductions. That the oxidation and reduction occur almost exclusively from the donor and acceptor arms of the synthesized D/A dyads are understood on the basis of the electrochemical properties of **TC56** (Chart S1) and 2,2'-bipyridine. The model compound **TC56** which is devoid of the bipyridine fragment exhibits very similar oxidation behaviour to that of 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy with two oxidative components at 0.79 V and 1.13 V (vs Fc/Fc⁺). This observation infers that oxidation occurs from an orbital which is almost similar in energy in all the compounds under investigation, the acceptor functionality has a little influence on the donor arm and both the D/A fragments are largely decoupled in the ground electronic state. Similar conclusion is also drawn on the basis of polarity insensitive absorption spectra of the relevant compounds. Both these observations are further supported by the quantum chemical simulation studies which illustrate spatial distribution of the frontier molecular orbitals as shown in Figure 2. The HOMO energies were estimated from the oxidation half-wave potentials using the formula of $-4.8 - (E_{1/2}^{ox} - 0.47)$. As we could not observe precise reduction half waves for all compounds, we estimated LUMO energy from the relationship of LUMO = HOMO + E_g where E_g is the optical band gap. These values are summarized in Table 1. However, in order to obtain the HOMO levels that are better represent the solid state environment in a PhOLED device, we have also estimated the HOMO energy levels of 24Bpy, 3Cz-44Bpy and 2Cz-44Bpy thin films by photoelectron spectroscopy (Riken AC-2) which yields very similar values to that obtained by electrochemical study (Table 1).

2.6 Crystal structure

Solid-state morphology plays a crucial role in device performance of OLEDs as the intermolecular non-covalent interactions have subtle influences on carrier mobility, migration of

excitons and importantly thin film formation ability. Single crystals suitable for X-ray diffraction structure analysis were obtained for 5Cz-24Bpy and 2Cz-44Bpy from dichloromethane-hexane mixture. Unfortunately, we were not able to get good quality 3Cz-44Bpy crystal for X-ray analysis. Relevant structures and crystal data are summarized in supporting information (Figure S4, Table S1). 5Cz-24Bpy crystallizes in C2/c space group in monoclinic system whereas molecules of 2Cz-44Bpy packs under triclinic P-1 space symmetry, both the asymmetric units containing a full molecule. Interestingly, the crystal structure of 2Cz-44Bpy is more planar than that of 5Cz-24Bpy. The dihedral angles between carbazole and phenylene ring and between carbazole and pyridine are $\sim 40^{\circ}$ and $\sim 73^{\circ}$ for **5Cz-24Bpy**, respectively, whereas these values are found to be ~10° and ~30°, respectively, for 2Cz-44Bpy. Various non-covalent interactions in the crystal structure of 5Cz-24Bpy were revealing that the molecules pack in a rather edge to face manner (Figure 4a). The inner pyridine ring (the one attached to the carbazole) of a molecule interact with the inner pyridine ring of an adjacent anti-parallel aligned molecule through weak C(32)–H(32A)····N(3) interaction ($d_{C...N} \approx 3.4$ Å, <C–H····N ≈ 152 °). A very weak C(40)–H(40A)··· π interaction (d_{C··Cg} \approx 3.7 Å, <C–H···Cg \approx 159 °) was also observed between the outer pyridine ring of a molecule and the carbazole ring of an adjacent parallel molecule. In contrast, the crystal of **2Cz-44Bpy** has a linear packing motif where two inversion symmetry related molecules forms a dimer in an anti-parallel fashion (Figure 4b) through C(10)-H(10A)····N(3) interaction between the carbazole C10 and the outer pyridine N3 ($d_{C...N} \approx 3.48$ Å, <C–H···N \approx 167 °). These dimers are further connected through C(30)–H(30A)··· π (C36=C37) interactions between triphenylamine phenylene rings ($d_{C \cdots Cg} \approx 3.6$ Å, $< C-H \cdots C_g \approx 165$ °) of two adjacent molecules to form a linear chain which then expands in three dimension through noncovalent interactions.

2.7 Charge carrier mobility

Carrier mobility of the title compounds were measured by time-of-flight transient photocurrent technique (TOF) ^[25] using injection blocking contacts with the common device structure of ITO/compound/Ag (200 nm) where the sample thickness for 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy were 1.37 μm, 2.85 μm and 0.91 μm, respectively, which are sufficiently thick to produce a thin sheet of charge carriers. As all the compounds have a significant absorption coefficient in the region of 300-350 nm, photo-generation of the carriers using our 337 nm laser set-up could proceed without the need of an extra charge generation layer. Typical TOF transient photocurrents for holes at room temperature are shown in supporting information (Figure S5). Figure 5 reveals that the hole mobility (μ_h) of **5Cz-24Bpy** varies from 1.8 x 10⁻⁵ to 4.1 x 10^{-5} cm² V⁻¹ s⁻¹ as the field bias sweeps from 2.2 x 10^{5} to 5.9 x 10^{5} V cm⁻¹. The same values for **3Cz-44Bpy** and **2Cz-44Bpy** are found to be 2.0 x 10^{-5} to 4.6 x 10^{-5} cm² V⁻¹ s⁻¹ (field: 5.3 x 10^5 to 10.9 x 10^5 V cm⁻¹) and 2.3 x 10^{-5} to 7.5 x 10^{-5} cm² V⁻¹ s⁻¹ (field: 4.4 x 10^5 to 9.9 x 10⁵ V cm⁻¹), respectively. Unfortunately, the transient photocurrent signal for electron was too weak for all these materials to obtain the electron mobility data using the TOF technique. Therefore, we fabricated electron-only devices to compare electron mobility of the title compounds using the common structure: ITO/BCP (30 nm)/host/TPBI (20 nm)/LiF/Al where BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) ^[26] layer with a deep HOMO (~ 6.5 eV) serves as the hole blocking layer ($\mu_e \sim 10^{-7} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and TPBI (1.3,5-tris(Nphenylbenzimidazol-2-yl)benzene) $^{[27]}$ as the electron-transport layer ($\mu_e \sim 10^{-5} \ cm^2 V^{-1} s^{-1}$). The J-V plots (Figure 5b) shows that the current density of 2Cz-44Bpy is appreciably higher than those of the two other homologues, which is possibly due to preferable electron hopping channel through its 1-D linear chain as shown in the crystal structure. Therefore, it can be realized that

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the connection topology in the title compounds plays an important role in their bipolar behavior where the hole and electron mobility for the three compounds follow the orders of 3Cz-44Bpy > 2Cz-44Bpy > 5Cz-24Bpy and $2Cz-44Bpy > 3Cz-44Bpy \approx 5Cz-24Bpy$ respectively.

2.8 Electroluminescent properties

To evaluate these new compounds as host materials for phosphorescent emitters, we selected three phosphorescent dopants: green bis(2-phenylpyridinato) iridium(III) $[(ppy)_2Ir(acac)]$,^[1a] acetylacetonate yellow bis(2-phenylbenzothiazolato) iridium(III) (acetylacetonate) [(bt)₂Ir(acac)] ^[28] and red (2-(3-methylquinolin-2-yl)phenyl) iridium(III) acetylacetonate (mpq)₂Ir(acac) ^[29] in the structure of ITO/Tris-PCz:ReO₃ (60 nm)/Tris-PCz (15 nm)/host:10 wt% dopant (25 nm)/CN-T2T (50 nm)/Lig/Al. Scheme 2 shows the schematic diagram of the device structure and the molecular structures used in the device. 9,9',9"-triphenyl-9H,9'H,9"H-3,3':6',3"-tercarbazole (Tris-PCz) with a high triplet level (E_T = 2.76 eV) and wide bandgap (Eg = 3.5 eV) can efficiently confine the triplet energy of phosphors, is selected as the HTL. ^[30] To lower hole injection barrier from ITO to 9,9',9"-triphenyl-9H,9'H,9"H-3,3':6',3"tercarbazole (Tris-PCz), we used rhenium oxides (ReO₃) as a dopant material in Tris-PCz to improves the hole injection efficiency. ^[31] A further 15 nm thick layer of Tris-PCz functions as the electron blocking layer (EBL). The emitting layer (EML, 25 nm) which consists of 10 wt% of the phosphor dopants dispersed in the host matrix (5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy) was subsequently implemented through vacuum deposition. To further confine the holes or generated excitons within the emissive region, a 50 nm thick layer of CN-T2T $^{[32]}(E_{\rm T}: 2.82 \text{ eV};$ HOMO/LUMO: 6.7/2.8 eV) is selected as the electron transport layer (ETL) to block the excitons within the EML. 8-Hydroxyquinolinolatolithium (Liq)^[33] and Al are used as electron injection layer (EIL) and cathode, respectively.

Figure 6 shows the current density–voltage–brightness (J–V–L) characteristics and efficiency versus brightness curves of the devices. The key characteristics of the devices are listed in Table 2. To make the description simple we have used the notations 1, 2 and 3 for devices hosted by **5Cz-24Bpy**, **3Cz-44Bpy** and **2Cz-44Bpy** respectively. (ppy)₂Ir(acac) was used to fabricate the green emitting devices G1-G3. Similarly, the yellow and red PHOLEDs are named as Y1-Y3 and R1-R3 respectively. Notably, all the devices exhibit a low turn-on voltage of 1.8-2.0 V indicating a barrier-free hole-injection in the device. In all the three hosts the dopants exhibit similar spectral behaviour which indicates effective confinement of the triplet excitons within the emitting layer and that the energy transfer from host to guest is complete (Figure S6).

Devices with **3Cz-44Bpy** and **2Cz-44Bpy** as hosts exhibit much higher efficiencies than the **5Cz-24Bpy** hosted device, which are consistent with the PLQY(Figure S7). The **2Cz-44Bpy** based green device G3 revealed the best device performance, with a maximum luminance (L_{max}) of 249400 cd m⁻² (at 8.4 V), a maximum forward-viewing external quantum efficiency (EQE) of 22.0 %, a peak current efficiency (CE) of 79.8 cd A⁻¹ and, a peak power efficiency (PE) of 102.5 lm W⁻¹. In addition, the roll-off of efficiency is extremely low with EQE of 21.6% at 1000 cd m⁻² (2.8 V) and 18.6% at 10000 cd m⁻² (3.5 V), respectively. For a highly efficient OLED, ideally, the operating voltage should approximately match to the photon energy (*hv*) of the emitted photons. In this study, the device G3 exhibits a turn-on voltage of as low as 1.8 V, and the operating voltage at 100 cd m⁻² is only 2.4 V, which almost equals to the emitting photon energy (2.37 eV, calculated from the (ppy)2Ir(acac) spectrum peak (522 nm)), resulting the high power efficiency (PE of 102.5 lm W⁻¹ at 100 cd m⁻²). Such high power efficiency is ascribed to the efficient electron-hole capture without additional carrier injection barrier and carrier balance in EML.

Inspiringly, a promising result was also realized in the 3Cz-44Bpy doped with (bt)₂Ir(acac) device Y2, which reveals a L_{max} of 135000 cd m⁻² at 7.8 V and relatively high EL efficiencies (22.4 %, 57.3 cd A^{-1} and 72.5 lm W^{-1}). It is clear that the EQE (22.4 %) of our present yellow OLED with the 3Cz-44Bpy host are close to the best data ever reported for (bt)₂Ir(acac)-based devices so far, especially among those with a single bipolar host. ^[34] In contrast the relevant observables for the R3 device hosted by the same host (2Cz-44Bpy) are found to be 45400 cd m^{-2} at 8.2V with EQE of 17.8 %. This observation could be explained in the following manner. The HOMO (-5.6 eV) and LUMO (-3.0) of the green emitter (ppy)₂Ir(acac) ^[1a] are perfectly aligned with the adjacent layers allowing direct formation of the excitons in the dopant. However, in case of the red dopant energy of HOMO estimated by the photoelectron spectroscopy (AC-2) is found to be -5.2 eV and that of LUMO is -3.0 eV (LUMO = HOMO+ E_g). It can thus be understood from the energy level diagram shown in Scheme 2 that the excitons in the red OLED probably form partly in the host and partly in the dopant. The excitons in the host are then transferred into the dopant which then decays radiatively. However, this process might induce some sort of nonradiative losses as compared to exciton formation directly at the dopant and this might influence the device performance.

In the PHOLEDs the triplet manifold ³MLCT is either directly formed through carrier recombination (75% probability) or through intersystem crossing from the singlet ¹MLCT excitons (25% statistical ratio). The internal quantum efficiency (η_{int}) is defined as ^{1a}:

$$\eta_{int} = \gamma \eta_{rec} \eta_{PL} = \gamma \eta_{rec} \frac{k_p}{k_p + k_{nr}} [T_1] = \gamma \eta_{rec} \frac{k_p}{k_p + k_{nr}} (0.25\phi_{ISC} + 0.75)$$

following the statistical ratio where γ is the carrier ratio, η_{rec} is the fraction of carriers that generate the excitons instead of diffusing to the opposite electrodes, η_{PL} is the photoluminescence quantum yield, k_p , k_{nr} are the radiative and nonradiative modes and ϕ_{ISC} is the intersystem crossing efficiency. The almost identical electron and hole mobility of the materials CN-T2T and Tris-PCz ^[34] infers that in our device structure $\gamma \eta_{rec}$ is at least ≥ 0.9 indicating a good carrier balance. Similarly, as we have not observed any fluorescence emission from the dopants under our experimental condition, we conclude that ϕ_{ISC} is nearly 100% in all the cases. Assuming that k_{nr} is almost temperature independent, we can conclude that the green and yellow emitting devices would achieve higher internal quantum efficiency as indicated by the PLQY data of the corresponding doped films. The red devices might possess more nonradiative modes than the green and yellow devices possibly due to the energy gap law (Table 2). Indeed, high internal quantum efficiency of above 70-80% (considering an outcoupling efficiency of 20-30%) could be realized in the **3Cz-44Bpy** and **2Cz-44Bpy** hosted devices whereas the **5Cz-24Bpy** hosted devices achieve a relatively lower value probably due to poorer PLQY.

3. Conclusions

In summary, we have designed and synthesized three new bipolar molecules and evaluated their utilization as hosts in multi-color PHOLEDs. Spatial disposition of the frontier molecular orbitals are observed in all donor-acceptor hybrids, which is essential for keeping individual function of hole and electron transporting subunits. The distinct vibronic progression in the phosphorescent spectra is indicative of triphenylamine-carbazole hybrid locally excited ${}^{3}\pi\pi^{*}$ state as the triplet emitting state. Though all these compounds exhibit similar HOMO/LUMO and

triplet energy ($E_T \sim 2.6 \text{ eV}$ in frozen medium and ~ 2.5 eV in their films), the effect of structural topology on their thermal stability and carrier mobility are found to be substantially different. The observed glass transition temperature higher than 100 °C offers thin film with morphological stability. The charge carrier mobility for the relevant compounds are in the orders for hole: **3Cz-44Bpy** > **2Cz-44Bpy** > **5Cz-24Bpy** and electron: **2Cz-44Bpy** > **3Cz-44Bpy** \approx **5Cz-24Bpy**. Green, yellow and red PhOLEDs were fabricated using the newly synthesized bipolar hosts where the pertinent devices exhibit a low driving voltage (~ 2 V) and very low efficiency roll-off at high brightness. Particularly, **2Cz-44Bpy**-based green PhOLED achieved a maximum CE of 79.8 cd A⁻¹ and a EQE of 22.0% and **3Cz-44Bpy**-based yellow device also gave CE of 57.3 cd A⁻¹ and a EQE up to 22.4%. Both of **2Cz-44Bpy**- and **3Cz-44Bpy**-based devices showed rather low operating voltage and limited efficiency roll-off. In contrast, the devices hosted by **5Cz-24Bpy** are found to perform poorer than those hosted by the other two analogues, which could be due to lower carrier mobility of **5Cz-24Bpy** than others.

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List of figures

Scheme 1 Molecular structures and synthesis of the target compounds 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy.

Scheme 2 Molecular structures of the various materials used and an energy level diagram for the relevant devices.

Figure 1 Absorption, fluorescence and phosphorescence spectra of **5Cz-24Bpy**, **3Cz-44Bpy** and **2Cz-44Bpy**. (a) absorption spectra in dichloromethane at room temperature (298 K, ~ 10^{-5} M), fluorescence (broad structureless band at shorter wavelength) and phosphorescence (structured band at longer wavelength) spectra in frozen 2-methyltetrahydrofuran at 77 K. (b) absorption and fluorescence (broad structureless) spectra at room temperature (298 K) and phosphorescence spectra (structured) at 20 K in neat film.

Figure 2 HOMO (bottom) and LUMO (top) of 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy as computed in CAM-B3LYP/cc-pVDz level of theory. Hydrogen atoms are omitted for clarity. Figure 3 Cyclic voltammograms of 5CZ-24BPY (solid line), 3CZ-44BPY (dashed line) and 2CZ-44BPY (dash dotted line) (oxidation scans, vs Fc) in dichloromethane. Scan rate = 0.1 V s^{-1} .

Figure 4 Supramolecular non-covalent interactions in the crystal structure of (a) **5Cz-24Bpy** and (b) **2Cz-44Bpy**. Carbon atoms: light grey; nitrogen atoms: dark grey. Most of the hydrogen atoms are omitted for clarity.

Figure 5 (a) Hole mobility vs $E^{1/2}$ and (b) J-V characteristics of electron-only device for 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy.

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Figure 6 (a)(c)(e) Current density-voltage-luminance (*J-V-L*) characteristics. (b)(d)(f) External quantum (EQE) and power efficiencies (PE) as a function of brightness for **5Cz-24Bpy**, **3Cz-44Bpy** and **2Cz-44Bpy** hosted devices.

	5Cz-24Bpy	3Cz-44Bpy	2Cz-44Bpy
$T_{\rm g}/T_{\rm d}/T_{\rm m}$ (°C)	110 / 425 / 170	— / 324 / 112	108 / 420 / —
$E_{1/2}^{\text{ox}}/E_{1/2}^{\text{red}}$ (V) ^[a]	0.82 / -0.71	0.81 /0.75	0.80 / —
HOMO/LUMO (eV) [b]	-5.47 / -2.38	-5.49 / -2.41	-5.48 / -2.45
HOMO/LUMO(eV) [c]	-5.41 / -2.44	-5.40 / -2.48	-5.47 / -2.37
$\epsilon (L \text{ mol}^{-1} \text{ cm}^{-1})^{[d]}$	48000	39500	54000
λ_{max}^{abs} soln./film (nm)	333 / 335	328 / 330	330 / 335
λ_{max}^{FL} (nm)/ $\Phi_{PL}^{[e]}$	420 (CH) / 0.25	460 (CH) / 0.13	460 (CH) / 0.12
	470 (Tol) / 0.23	518 (Tol) / 0.07	512 (Tol) / 0.08
	532 (THF) / 0.05	— (THF) / —	— (THF) / —
	503 (Film) / 0.47	504 (Film) / 0.27	515 (Film) / 0.09
$E_{\rm T}$ soln./film (eV) ^[f]	2.60 / 2.45	2.59 / 2.46	2.57 / 2.43
$\mu_{\rm h} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})^{[{\rm g}]}$	3.6 x 10 ⁻⁵	26.2 x 10 ⁻⁵	6.9 x 10 ⁻⁵

Table 1 Summary of the physical properties of 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy

In the initial result of the form the balf-wave and onset potential in the oxidation and reduction scan of the cyclic volummograms, respectively. [b] Calculated from the electrochemical results with respect to the FerKe⁺ redox couple. [c] HOMO was determined using bhoresettom spectroscyp (AC-2). UIMO = HOMO + E₄ where E₄ is the optical band gap (0-0 transition) in neat film. [d] molar extinction coefficient determined in THF solution, an average of five data. [e] CH = cyclohexane, ToI = tolucene. THF = terrahydrofuran. The photohuminesenee quantum yields of the samples were measured using antiracene as the shanda (in eac) 2.7). Optically matched dilute solutions (DD - 0.05) were excited under identical instrumental settings, $\Phi_{h,c}$ of the samples are reported in 10% error limit. [1] triplet energy corresponding to the first vibronic band of the phosphorescence spectra in frozen 2-methyltetrahydrofuran (77 K) and in neat film (20 K). [g] under an electric field of 4.9, 10⁵ V cm⁻¹.

Table 2. EL performances of devices

	EML	$V_{\mathrm{on}}^{\ \ b}$ [V]	$L_{\rm max}$ [cd m ⁻²]	$I_{\rm max}$ [mA cm ⁻²]	EQE [%]	$CE \\ [cd A^{-1}]$	PE [lm W ⁻¹]	$EQE^{c} \text{ at } 10^{3} \text{ cd } \text{m}^{-2}$ [%, V]	CIE [x,y]
$G1^a$	5Cz-24Bpy:10% (ppy) ₂ Ir(acac)	1.8	235700 (8.4V)	4190	14.9	53.5	76.5	14.2, 2.8	0.30,0.63
Y1	5Cz-24Bpy:10% (bt) ₂ Ir(acac)	1.8	154900 (8.2V)	3770	13.8	13.1	51.71	13.0, 2.8	0.52,0.48
R1	5Cz-24Bpy:10% (mpq) ₂ Ir(acac)	1.8	41400 (8.4V)	3880	9.0	8.6	12.3	7.5, 3.4	0.65,0.34
G2	3Cz-44Bpy:10% (ppy) ₂ Ir(acac)	1.8	223500 (8.0V)	2970	20.7	74.9	88.3	20.6, 3.0	0.31,0.63
Y2	3Cz-44Bpy:10% (bt) ₂ Ir(acac)	1.8	135000 (7.8V)	3190	22.4	57.3	72.5	21.8, 2.9	0.52,0.47
R2	3Cz-44Bpy:10% (mpq) ₂ Ir(acac)	2.0	37700 (8.4V)	3220	16.8	16.4	17.6	12.1, 3.8	0.65,0.34
G3	2Cz-44Bpy:10% (ppy) ₂ Ir(acac)	1.8	249400 (8.4V)	4240	22.0	79.8	102.5	21.6, 2.8	0.36,0.64
¥3	2Cz-44Bpy:10% (bt) ₂ Ir(acac)	1.8	155700 (8.2V)	3850	21.8	58.7	86.1	20.9, 2.8	0.51,0.48
R3	2Cz-44Bpy:10% (mpq) ₂ Ir(acac)	1.8	45400 (8.2V)	3500	17.8	17.9	22.5	15.4, 3.4	0.65,0.34

[a] The notation 1.2 and 3 indicate the devices fabricated with host materials of 5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy, respectively. [b] Turn-on voltage at which emission became detectable. c) The values of driving voltage and EQE. of device at 1000 cd m⁻³ are depicted in parentheses.

















Highlights:

- Three bipolar hosts (5Cz-24Bpy, 3Cz-44Bpy and 2Cz-44Bpy) comprising of carbazole-bridged triphenylamine-bipyridine.
- The $E_{\rm T}$ is suitable to serve as a phosphor host from green to red.
- Both of 2Cz-44Bpy- and 3Cz-44Bpy-based devices showed rather low operating voltage and limited efficiency roll-off.